Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

1. Introduction

1. Puchot, C.; Samuel, O.; Dunach, E.; Zhao, S.; Agami, C.; Kagan, H. B., NONLINEAR EFFECTS IN ASYMMETRIC-SYNTHESIS - EXAMPLES IN ASYMMETRIC OXIDATIONS AND ALDOLIZATION REACTIONS. *J. Am. Chem. Soc.* **1986,** *108* (9), 2353-2357.

2. *Catalytic Asymmetric Synthesis*. Ojima, I. ed.; Wiley-VCH: 2000.

3. Blackmond, D. G., Kinetic aspects of nonlinear effects in asymmetric catalysis. *Acc. Chem. Res.* **2000,** *33* (6), 402-411.

4. Mikami, K.; Terada, M.; Korenaga, T.; Matsumoto, Y.; Ueki, M.; Angelaud, R., Asymmetric activation. *Angew. Chem., Int. Ed.* **2000,** *39* (20), 3532-3556.

5. Noyori, R., Asymmetric catalysis: Science and opportunities (Nobel lecture). *Angew. Chem., Int. Ed.* **2002,** *41* (12), 2008-2022.

6. Sharples, K. B., Searching for new reactivity (Nobel lecture). *Angew. Chem., Int. Ed.* **2002,** *41* (12), 2024-2032.

7. Groger, H., Catalytic enantioselective Strecker reactions and analogous syntheses. *Chem. Rev* **2003,** *103* (8), 2795-2827.

8. Sato, I.; Urabe, H.; Ishiguro, S.; Shibata, T.; Soai, K., Amplification of chirality from extremely low to greater than 99.5 % ee by asymmetric autocatalysis. *Angew. Chem., Int. Ed.* **2003,** *42* (3), 315-+.

9. Dalko, P. I.; Moisan, L., In the golden age of organocatalysis. *Angew. Chem., Int. Ed.* **2004,** *43* (39), 5138-5175.

10. Eelkema, R.; van Delden, R. A.; Feringa, B. L., Direct visual detection of the stereoselectivity of a catalytic reaction. *Angew. Chem., Int. Ed.* **2004,** *43* (38), 5013-5016.

11. Gridnev, I. D.; Serafimov, J. M.; Brown, J. M., Solution structure and reagent binding of the zinc alkoxide catalyst in the Soai asymmetric autocatalytic reaction. *Angew. Chem., Int. Ed.* **2004,** *43* (37), 4884-4887.

12. Lutz, F.; Sato, I.; Soai, K., The asymmetric power of chiral ligands determined by competitive asymmetric autocatalysis. *Org. Lett.* **2004,** *6* (10), 1613-1616.

13. Markert, C.; Pfaltz, A., Screening of chiral catalysts and catalyst mixtures by mass spectrometric monitoring of catalytic intermediates. *Angew. Chem., Int. Ed.* **2004,** *43* (19), 2498-2500.

14. Sato, I.; Sugie, R.; Matsueda, Y.; Furumura, Y.; Soai, K., Asymmetric synthesis utilizing circularly polarized light mediated by the photoequilibrium of chiral olefins in conjunction with asymmetric autocatalysis. *Angew. Chem., Int. Ed.* **2004,** *43* (34), 4490-4492.

15. Calter, M. A.; Phillips, R. M.; Flaschenriem, C., Catalytic, asymmetric, "interrupted" Feist-Benary reactions. *J. Am. Chem. Soc.* **2005,** *127* (42), 14566-14567.

16. Denmark, S. E.; Heemstra, J. R.; Beutner, G. L., Catalytic, enantioselective, vinylogous aldol reactions. *Angew. Chem., Int. Ed.* **2005,** *44* (30), 4682-4698.

17. Kawasaki, T.; Sato, M.; Ishiguro, S.; Saito, T.; Morishita, Y.; Sato, I.; Nishino, H.; Inoue, Y.; Soai, K., Enantioselective synthesis of near enantiopure compound by asymmetric autocatalysis triggered by asymmetric photolysis with circularly polarized light. *J. Am. Chem. Soc.* **2005,** *127* (10), 3274-3275.

18. Lutz, F.; Igarashi, T.; Kawasaki, T.; Soai, K., Small amounts of achiral beta-amino alcohols reverse the enantioselectivity of chiral catalysts in cooperative asymmetric autocatalysis. *J. Am. Chem. Soc.* **2005,** *127* (35), 12206-12207.

19. Oestreich, M., Strategies for catalytic asymmetric electrophilic a halogenation of carbonyl compounds. *Angew. Chem., Int. Ed.* **2005,** *44* (16), 2324-2327.

20. Podlech, J.; Gehring, T., New aspects of soai's asymmetric autocatalysis. *Angew. Chem., Int. Ed.* **2005,** *44* (36), 5776-5777.

21. Arrayas, R. G.; Adrio, J.; Carretero, J. C., Recent applications of chiral ferrocene ligands in asymmetric catalysis. *Angew. Chem., Int. Ed.* **2006,** *45* (46), 7674-7715.

22. Gawley, R. E., Do the terms "% ee" and "% de" make sense as expressions of stereoisomer composition or stereoselectivity? *J. Org. Chem.* **2006,** *71* (6), 2411-2416.

23. Guo, H. C.; Ma, J. A., Catalytic asymmetric tandem transformations triggered by conjugate additions. *Angew. Chem., Int. Ed.* **2006,** *45* (3), 354-366.

24. New Frontiers in Asymmetric Catalysis. Mikami, K.; Lautens, M., Eds. Wiley: 2007.

25. Denmark, S. E.; Beutner, G. L., Lewis base catalysis in organic synthesis. *Angew. Chem., Int. Ed.* **2008,** *47* (9), 1560-1638.

26. Gade, L. H.; Bellemin-Laponnaz, S., Exploiting threefold symmetry in asymmetric catalysis: The case of tris(oxazolinyl)ethanes ("trisox"). *Chem. Eur. J.* **2008,** *14* (14), 4142-4152.

27. Lu, Z.; Ma, S. M., Metal-catalyzed enantioselective allylation in asymmetric synthesis. *Angew. Chem., Int. Ed.* **2008,** *47* (2), 258-297.

28. Lutz, F.; Igarashi, T.; Kinoshita, T.; Asahina, M.; Tsukiyama, K.; Kawasaki, T.; Soai, K., Mechanistic insights in the reversal of enantioselectivity of chiral catalysts by achiral catalysts in asymmetric autocatalysis. *J. Am. Chem. Soc.* **2008,** *130* (10), 2956-2958.

29. Schiaffino, L.; Ercolani, G., Unraveling the mechanism of the Soai asymmetric autocatalytic reaction by first-principles calculations: Induction and amplification of chirality by self-assembly of hexamolecular complexes. *Angew. Chem., Int. Ed.* **2008,** *47* (36), 6832-6835.

30. Brown, J. M.; Deeth, R. J., Is Enantioselectivity Predictable in Asymmetric Catalysis? *Angew. Chem., Int. Ed.* **2009,** *48* (25), 4476-4479.

31. Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K., Asymmetric Autocatalysis Triggered by Carbon Isotope (C-13/C-12) Chirality. *Science* **2009,** *324* (5926), 492-495.

32. Lovering, F.; Bikker, J.; Humblet, C., Escape from Flatland: Increasing Saturation as an Approach to Improving Clinical Success. *J. Med. Chem.* **2009,** *52* (21), 6752-6756.

33. Lovering, F., Escape from Flatland 2: complexity and promiscuity. *MedChemComm* **2013,** *4* (3), 515-519.

34. Athavale, S. V.; Simon, A.; Houk, K. N.; Denmark, S. E., Structural Contributions to Autocatalysis and Asymmetric Amplification in the Soai Reaction. *J. Am. Chem. Soc.* **2020,** *142* (43), 18387-18406.

35. McVicker, R. U.; O'Boyle, N. M., Chirality of New Drug Approvals (2013–2022): Trends and Perspectives. *J. Med. Chem.* **2024,** *67* (4), 2305-2320.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

2. LUMO Activation

2.1 Lewis and Brønsted acids activation of carbonyl and imines

2.1.1 Aldol Reaction

1. Parmee, E. R.; Tempkin, O.; Masamune, S.; Abiko, A., NEW CATALYSTS FOR THE ASYMMETRIC ALDOL REACTION - CHIRAL BORANES PREPARED FROM ALPHA,ALPHA-DISUBSTITUTED GLYCINE ARENESULFONAMIDES. *J. Am. Chem. Soc.* **1991,** *113* (24), 9365-9366.
2. Corey, E. J.; Cywin, C. L.; Roper, T. D., ENANTIOSELECTIVE MUKAIYAMA-ALDOL AND ALDOL-DIHYDROPYRONE ANNULATION REACTIONS CATALYZED BY A TRYPTOPHAN-DERIVED OXAZABOROLIDINE. *Tetrahedron Lett.* **1992,** *33* (46), 6907-6910.
3. Carreira, E. M.; Singer, R. A.; Lee, W. S., CATALYTIC, ENANTIOSELECTIVE ALDOL ADDITIONS WITH METHYL AND ETHYL-ACETATE O-SILYL ENOLATES - A CHIRAL TRIDENTATE CHELATE AS A LIGAND FOR TITANIUM(IV). *J. Am. Chem. Soc.* **1994,** *116* (19), 8837-8838.
4. Carreira, E. M.; Lee, W.; Singer, R. A., CATALYTIC, ENANTIOSELECTIVE ACETONE ALDOL ADDITIONS WITH 2-METHOXYPROPENE. *J. Am. Chem. Soc.* **1995,** *117* (12), 3649-3650.
5. Singer, R. A.; Carreira, E. M., CATALYTIC, ENANTIOSELECTIVE DIENOLATE ADDITIONS TO ALDEHYDES - PREPARATION OF OPTICALLY-ACTIVE ACETOACETATE ALDOL ADDUCTS. *J. Am. Chem. Soc.* **1995,** *117* (49), 12360-12361.
6. Evans, D. A.; Burgey, C. S.; Kozlowski, M. C.; Tregay, S. W., C-2-symmetric copper(II) complexes as chiral Lewis acids. Scope and mechanism of the catalytic enantioselective aldol additions of enolsilanes to pyruvate esters. *J. Am. Chem. Soc.* **1999,** *121* (4), 686-699.
7. Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J., C-2-symmetric copper(II) complexes as chiral Lewis acids. Scope and mechanism of catalytic enantioselective aldol additions of enolsilanes to (benzyloxy)acetaldehyde. *J. Am. Chem. Soc.* **1999,** *121* (4), 669-685.
8. Denmark, S. E.; Wynn, T.; Beutner, G. L., Lewis base activation of Lewis acids. Addition of silyl ketene acetals to aldehydes. *J. Am. Chem. Soc.* **2002,** *124* (45), 13405-13407.
9. Evans, D. A.; Masse, C. E.; Wu, J., C-2-symmetric Sc(III)-complexes chiral Lewis acids. Catalytic enantioselective aldol additions glyoxylate esters. *Org. Lett.* **2002,** *4* (20), 3375-3378.
10. Evans, D. A.; Wu, J.; Masse, C. E.; MacMillan, D. W. C., A general method for the enantioselective synthesis of pantolactone derivatives. *Org. Lett.* **2002,** *4* (20), 3379-3382.
11. Yamashita, Y.; Ishitani, H.; Shimizu, H.; Kobayashi, S., Highly anti-selective asymmetric aldol reactions using chiral zirconium catalysts. Improvement of activities, structure of the novel zirconium complexes, and effect of a small amount of water for the preparation of the catalysts. *J. Am. Chem. Soc.* **2002,** *124* (13), 3292-3302.
12. De Rosa, M.; Acocella, M. R.; Villano, R.; Soriente, A.; Scettri, A., Ti(IV)/BINOL-catalyzed asymmetric aldol reaction of a masked acetoacetic ester: pronounced influence of catalyst concentration on nonlinear effects. *Tetrahedron Lett.* **2003,** *44* (32), 6087-6090.
13. Denmark, S. E.; Beutner, G. L., Lewis base activation of Lewis acids. Vinylogous aidol reactions. *J. Am. Chem. Soc.* **2003,** *125* (26), 7800-7801.
14. Denmark, S. E.; Heemstra, J. R., Lewis base activation of Lewis acids. Catalytic enantioselective addition of silyl enol ethers of achiral methyl ketones to aldehydes. *Org. Lett.* **2003,** *5* (13), 2303-2306.
15. Hamada, T.; Manabe, K.; Ishikawa, S.; Nagayama, S.; Shiro, M.; Kobayashi, S., Catalytic asymmetric aldol reactions in aqueous media using chiral bis-pyridino-18-crown-6-rare earth metal triflate complexes. *J. Am. Chem. Soc.* **2003,** *125* (10), 2989-2996.
16. Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S., Catalytic asymmetric hydroxymethylation of silicon enolates using an aqueous solution of formaldehyde with a chiral scandium complex. *J. Am. Chem. Soc.* **2004,** *126* (39), 12236-12237.
17. Kobayashi, J.; Nakamura, M.; Mori, Y.; Yamashita, Y.; Kobayashi, S., Catalytic enantio- and diastereoselective aldol reactions of glycine-derived silicon enolate with aldehydes: An efficient approach to the asymmetric synthesis of anti-beta-hydroxy- alpha-amino acid derivatives. *J. Am. Chem. Soc.* **2004,** *126* (30), 9192-9193.
18. Langner, M.; Bolm, C., C-1-symmetric sulfoximines as ligands in copper-catalyzed asymmetric Mukaiyama-type aldol reactions. *Angew. Chem., Int. Ed.* **2004,** *43* (44), 5984-5987.
19. Le, J. C. D.; Pagenkopf, B. L., A new class of substituted aryl bis(oxazoline) ligands for highly enantioselective copper-catalyzed asymmetric aldol addition of dienolsilane to pyruvate and glyoxylate esters. *Org. Lett.* **2004,** *6* (22), 4097-4099.
20. Denmark, S. E.; Beutner, G. L.; Wynn, T.; Eastgate, M. D., Lewis base activation of Lewis acids: Catalytic, enantioselective addition of silyl ketene acetals to aldehydes. *J. Am. Chem. Soc.* **2005,** *127* (11), 3774-3789.
21. Denmark, S. E.; Bui, T., Lewis base catalyzed enantioselective aldol addition of acetaldehyde-derived silyl enol ether to aldehydes. *J. Org. Chem.* **2005,** *70* (24), 10190-10193.
22. Kobayashi, S.; Ogino, T.; Shimizu, H.; Ishikawa, S.; Hamada, T.; Manabe, K., Bismuth triflate-chiral bipyridine complexes as water-compatible chiral Lewis acids. *Org. Lett.* **2005,** *7* (21), 4729-4731.
23. Moreau, X.; Bazan-Tejeda, B.; Campagne, J. M., Catalytic and asymmetric vinylogous mukaiyama reactions on aliphatic ketones: Formal asymmetric synthesis of taurospongin A. *J. Am. Chem. Soc.* **2005,** *127* (20), 7288-7289.

24. Akullian, L. C.; Snapper, M. L.; Hoveyda, A. H., A chiral Ag-based catalyst for practical, efficient, and highly enantioselective additions of enolsilanes to alpha-ketoesters. *J. Am. Chem. Soc.* **2006,** *128* (20), 6532-6533.
25. Denmark, S. E.; Wilson, T. W.; Burk, M. T.; Heemstra, J. R., Enantioselective construction of quaternary stereogenic carbons by the lewis base catalyzed additions of silyl ketene imines to aldehydes. *J. Am. Chem. Soc.* **2007,** *129* (48), 14864-+.
26. Denmark, S. E.; Chung, W. J., Lewis base activation of Lewis acids: Catalytic enantioselective glycolate aldol reactions. *Angew. Chem., Int. Ed.* **2008,** *47* (10), 1890-1892.
27. Frings, M.; Atodiresei, I.; Runsink, J.; Raabe, G.; Bolm, C., Catalyzed Vinylogous Mukaiyama Aldol Reactions with Controlled Enantio- and Diastereoselectivities. *Chem. Eur. J.* **2009,** *15* (7), 1566-1569.
28. Garcia-Garcia, P.; Lay, F.; Garcia-Garcia, P.; Rabalakos, C.; List, B., A Powerful Chiral Counteranion Motif for Asymmetric Catalysis. *Angew. Chem., Int. Ed.* **2009,** *48* (24), 4363-4366.
29. Gondi, V. B.; Hagihara, K.; Rawal, V. H., Diastereoselective and Enantioselective Synthesis of Tertiary alpha-Hydroxy Phosphonates through Hydrogen-Bond Catalysis. *Angew. Chem., Int. Ed.* **2009,** *48* (4), 776-779.
30. Liu, W. J.; Lv, B. D.; Gong, L. Z., An Asymmetric Catalytic Darzens Reaction between Diazoacetamides and Aldehydes Generates cis-Glycidic Amides with High Enantiomeric Purity. *Angew. Chem., Int. Ed.* **2009,** *48* (35), 6503-6506.
31. Senapati, B. K.; Hwang, G. S.; Lee, S.; Ryu, D. H., Enantioselective Synthesis of beta-Iodo Morita-Baylis-Hillman Esters by a Catalytic Asymmetric Three-Component Coupling Reaction. *Angew. Chem., Int. Ed.* **2009,** *48* (24), 4398-4401.
32. Yang, L.; Wang, D. X.; Huang, Z. T.; Wang, M. X., Cr(III)(salen)Cl Catalyzed Enantioselective Intramolecular Addition of Tertiary Enamides to Ketones: A General Access to Enantioenriched 1H-Pyrrol-2(3H)-one Derivatives Bearing a Hydroxylated Quaternary Carbon Atom. *J. Am. Chem. Soc.* **2009,** *131* (30), 10390-+.
33. Denmark, S. E.; Wilson, T. W., N-silyl oxyketene imines are underused yet highly versatile reagents for catalytic asymmetric synthesis. *Nature Chemistry* **2010,** *2* (11), 937-943.
34. Li, W.; Wang, J.; Hu, X. L.; Shen, K.; Wang, W. T.; Chu, Y. Y.; Lin, L. L.; Liu, X. H.; Feng, X. M., Catalytic Asymmetric Roskamp Reaction of alpha-Alkyl-alpha-diazoesters with Aromatic Aldehydes: Highly Enantioselective Synthesis of alpha-Alkyl-beta-keto Esters. *J. Am. Chem. Soc.* **2010,** *132* (25), 8532-+.
35. Mei, Y. J.; Dissanayake, P.; Allen, M. J., A New Class of Ligands for Aqueous, Lanthanide-Catalyzed, Enantioselective Mukaiyama Aldol Reactions. *J. Am. Chem. Soc.* **2010,** *132* (37), 12871-12873.
36. Ratjen, L.; Garcia-Garcia, P.; Lay, F.; Beck, M. E.; List, B., Disulfonimide-Catalyzed Asymmetric Vinylogous and Bisvinylogous Mukaiyama Aldol Reactions. *Angew. Chem., Int. Ed.* **2011,** *50* (3), 754-758.
37. Yanagisawa, A.; Kushihara, N.; Yoshida, K., Catalytic Enantioselective Synthesis of Chiral gamma-Butyrolactones. *Org. Lett.* **2011,** *13* (6), 1576-1578.
38. Zheng, K.; Yin, C. K.; Liu, X. H.; Lin, L. L.; Feng, X. M., Catalytic Asymmetric Addition of Alkyl Enol Ethers to 1,2-Dicarbonyl Compounds: Highly Enantioselective Synthesis of Substituted 3-Alkyl-3-Hydroxyoxindoles. *Angew. Chem., Int. Ed.* **2011,** *50* (11), 2573-2577.
39. Denmark, S. E.; Wilson, T. W., Lewis Base Catalyzed Enantioselective Additions of an N-Silyl Vinylketene Imine. *Angew. Chem., Int. Ed.* **2012,** *51* (13), 3236-3239.
40. Zhang, P. K.; Han, Z. B.; Wang, Z.; Ding, K. L., Spiro 4,4 -1,6-Nonadiene-Based Diphosphine Oxides in Lewis Base Catalyzed Asymmetric Double-Aldol Reactions. *Angew. Chem., Int. Ed.* **2013,** *52* (42), 11054-11058.
41. Sai, M.; Yamamoto, H., Chiral Bronsted Acid as a True Catalyst: Asymmetric Mukaiyama Aldol and Hosomi-Sakurai Allylation Reactions. *J. Am. Chem. Soc.* **2015,** *137* (22), 7091-7094.
42. Kennedy, C. R.; Lehnherr, D.; Rajapaksa, N. S.; Ford, D. D.; Park, Y.; Jacobsen, E. N., Mechanism-Guided Development of a Highly Active Bis-thiourea Catalyst for Anion-Abstraction Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (41), 13525-13528.
43. Tap, A.; Blond, A.; Wakchaure, V. N.; List, B., Chiral Allenes via Alkynylogous Mukaiyama Aldol Reaction. *Angew. Chem., Int. Ed.* **2016,** *55* (31), 8962-8965.
44. Lee, S.; Kaib, P. S. J.; List, B., Asymmetric Catalysis via Cyclic, Aliphatic Oxocarbenium Ions. *J. Am. Chem. Soc.* **2017,** *139* (6), 2156-2159.
45. Schreyer, L.; Kaib, P. S. J.; Wakchaure, V. N.; Obradors, C.; Properzi, R.; Lee, S.; List, B., Confined acids catalyze asymmetric single aldolizations of acetaldehyde enolates. *Science* **2018,** *362* (6411), 216-219.
46. Amatov, T.; Tsuji, N.; Maji, R.; Schreyer, L.; Zhou, H.; Leutzsch, M.; List, B., Confinement-Controlled, Either syn- or anti-Selective Catalytic Asymmetric Mukaiyama Aldolizations of Propionaldehyde Enolsilanes. *J. Am. Chem. Soc.* **2021,** *143* (36), 14475-14481.

2.1.2 Allylation and Ene Reactions

1. Keck, G. E.; Geraci, L. S., CATALYTIC ASYMMETRIC ALLYLATION (CAA) REACTIONS .2. A NEW ENANTIOSELECTIVE ALLYLATION PROCEDURE. *Tetrahedron Lett.* **1993,** *34* (49), 7827-7828.
2. Keck, G. E.; Krishnamurty, D.; Grier, M. C., CATALYTIC ASYMMETRIC ALLYLATION REACTIONS .3. EXTENSION TO METHALLYLSTANNANE, COMPARISON OF PROCEDURES, AND OBSERVATION OF A NONLINEAR EFFECT. *J. Org. Chem.* **1993,** *58* (24), 6543-6544.
3. Keck, G. E.; Tarbet, K. H.; Geraci, L. S., CATALYTIC ASYMMETRIC ALLYLATION OF ALDEHYDES. *J. Am. Chem. Soc.* **1993,** *115* (18), 8467-8468.
4. Evans, D. A.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T.; Tregay, S. W., C-2-symmetric copper(II) complexes as chiral Lewis acids. Enantioselective catalysis of the glyoxylate-ene reaction. *J. Am. Chem. Soc.* **1998,** *120* (23), 5824-5825.
5. Evans, D. A.; Johnson, J. S.; Burgey, C. S.; Campos, K. R., Reversal in enantioselectivity of tert-butyl versus phenyl-substituted bis(oxazoline)copper(II) catalyzed hetero Diels-Alder and ene reactions. Crystallographic and mechanistic studies. *Tetrahedron Lett.* **1999,** *40* (15), 2879-2882.
6. Evans, D. A.; Tregay, S. W.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T., C-2-symmetric copper(II) complexes as chiral Lewis acids. Catalytic enantioselective carbonyl-ene reactions with glyoxylate and pyruvate esters. *J. Am. Chem. Soc.* **2000,** *122* (33), 7936-7943.
7. Ruck, R. T.; Jacobsen, E. N., Asymmetric catalysis of hetero-ene reactions with tridentate Schiff base chromium(III) complexes. *J. Am. Chem. Soc.* **2002,** *124* (12), 2882-2883.

8. Waltz, K. M.; Gavenonis, J.; Walsh, P. J., A simple, reliable, catalytic asymmetric allylation of ketones. *Angew. Chem., Int. Ed.* **2002,** *41* (19), 3697-3699.
9. Hanawa, H.; Hashimoto, T.; Maruoka, K., Bis(((S)-binaphthoxy)(isopropoxy)titanium) oxide as a mu-oxo- type chiral Lewis acid: Application to catalytic asymmetric allylation of aldehydes. *J. Am. Chem. Soc.* **2003,** *125* (7), 1708-1709.
10. Morao, M.; McNamara, J. P.; Hillier, A. H., Carbonyl-ene reactions catalyzed by bis(oxazoline) copper(II) complexes proceed by a facile stepwise mechanism: DFT and ONIOM (DFT : PM3) studies. *J. Am. Chem. Soc.* **2003,** *125* (3), 628-629.
11. Ruck, R. T.; Jacobsen, E. N., Asymmetric hetero-ene reactions of trimethylsilyl enol ethers catalyzed by tridentate Schiff base chromium(III) complexes. *Angew. Chem., Int. Ed.* **2003,** *42* (39), 4771-4774.
12. Yuan, Y.; Zhang, X.; Ding, K. L., Quasi solvent-free enantioselective carbonyl-ene reaction with extremely low catalyst loading. *Angew. Chem., Int. Ed.* **2003,** *42* (44), 5478-5480.
13. Caplan, N. A.; Hancock, F. E.; Page, P. C. B.; Hutchings, G. J., Heterogeneous enantioselective catalyzed carbonyl- and imino- ene reactions using copper bis(oxazoline) zeolite Y. *Angew. Chem., Int. Ed.* **2004,** *43* (13), 1685-1688.
14. Kim, J. G.; Waltz, K. M.; Garcia, I. F.; Kwiatkowski, D.; Walsh, P. J., Catalytic asymmetric allylation of ketones and a tandem asymmetric allylation/diastereoselective epoxidation of cyclic enones. *J. Am. Chem. Soc.* **2004,** *126* (39), 12580-12585.
15. Matsubara, R.; Nakamura, Y.; Kobayashi, S., Highly diastereo- and enantioselective reactions of enecarbamates with ethyl glyoxylate to give optically active syn and anti alpha-alkyl-beta-hydroxy imines and ketones. *Angew. Chem., Int. Ed.* **2004,** *43* (25), 3258-3260.
16. Evans, D. A.; Wu, J., Enantioselective Syn-selective scandium-catalyzed ene reactions. *J. Am. Chem. Soc.* **2005,** *127* (22), 8006-8007.
17. Lu, J.; Ji, S. J.; Teo, Y. C.; Loh, T. P., Highly enantioselective allylation of aldehydes catalyzed by indium(III)-PYBOX complex. *Org. Lett.* **2005,** *7* (1), 159-161.
18. Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W., Asymmetric platinum group metal-catalyzed carbonyl-ene reactions: Carbon-carbon bond formation versus isomerization. *J. Org. Chem.* **2006,** *71* (26), 9751-9764.
19. Evans, D. A.; Aye, Y.; Wu, J., Asymmetric, anti-selective scandium-catalyzed Sakurai additions to glyoxyamide. Applications to the syntheses of N-Boc D-alloisoleucine and D-isoleucine. *Org. Lett.* **2006,** *8* (10), 2071-2073.
20. Matsubara, R.; Kawai, N.; Kobayashi, S., Catalytic enantioselective and diastereoselective addition of aldehyde-derived enecarbamates to alpha-oxo aldehydes. *Angew. Chem., Int. Ed.* **2006,** *45* (23), 3814-3816.
21. Matsubara, R.; Doko, T.; Uetake, R.; Kobayashi, S., Enesulfonamides as nucleophiles in catalytic asymmetric reactions. *Angew. Chem., Int. Ed.* **2007,** *46* (17), 3047-3050.
22. Mikami, K.; Kawakami, Y.; Akiyama, K.; Aikawa, K., Enantioselective catalysis of ketoester-ene reaction of silyl enol ether to construct quaternary carbons by chiral dicationic Palladium(II) complexes. *J. Am. Chem. Soc.* **2007,** *129* (43), 12950-+.
23. Grachan, M. L.; Tudge, M. T.; Jacobsen, E. N., Enantioselective catalytic carbonyl-ene cyclization reactions. *Angew. Chem., Int. Ed.* **2008,** *47* (8), 1469-1472.
24. Rueping, M.; Antonchick, A. P., Catalytic Asymmetric Aminoallylation of Aldehydes: A Catalytic Enantioselective Aza-Cope Rearrangement. *Angew. Chem., Int. Ed.* **2008,** *47* (52), 10090-10093.
25. Rueping, M.; Theissmann, T.; Kuenkel, A.; Koenigs, R. M., Highly enantioselective organocatalytic carbonyl-ene reaction with strongly acidic, chiral Bronsted acids as efficient catalysts. *Angew. Chem., Int. Ed.* **2008,** *47* (36), 6798-6801.
26. Zhao, J. F.; Tsui, H. Y.; Wu, P. J.; Lu, J.; Loh, T. P., Highly Enantioselective Carbonyl-ene Reactions Catalyzed by In(III)-PyBox Complex. *J. Am. Chem. Soc.* **2008,** *130* (49), 16492-+.
27. Zheng, K.; Shi, J.; Liu, X. H.; Feng, X. M., Asymmetric Carbonyl-Ene Reaction Catalyzed by Chiral N,N '-Dioxide-Nickel(II) Complex: Remarkably Broad Substrate Scope. *J. Am. Chem. Soc.* **2008,** *130* (47), 15770-+.
28. Brekan, J. A.; Reynolds, T. E.; Scheidt, K. A., Enantioselective Synthesis of Substituted Indanones from Silyloxyallenes. *J. Am. Chem. Soc.* **2010,** *132* (5), 1472-+.
29. Jain, P.; Antilla, J. C., Chiral Bronsted Acid-Catalyzed Allylboration of Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (34), 11884-11886.
30. Zhao, Y. J.; Li, B.; Tan, L. J. S.; Shen, Z. L.; Loh, T. P., Enantioselective Cationic Polyene Cyclization vs Enantioselective Intramolecular Carbonyl-Ene Reaction. *J. Am. Chem. Soc.* **2010,** *132* (30), 10242-10244.
31. Ren, H.; Wulff, W. D., Direct Catalytic Asymmetric Aminoallylation of Aldehydes: Synergism of Chiral and Nonchiral Bronsted Acids. *J. Am. Chem. Soc.* **2011,** *133* (15), 5656-5659.
32. Hanhan, N. V.; Ball-Jones, N. R.; Tran, N. T.; Franz, A. K., Catalytic Asymmetric 3+2 Annulation of Allylsilanes with Isatins: Synthesis of Spirooxindoles. *Angew. Chem., Int. Ed.* **2012,** *51* (4), 989-992.
33. Jain, P.; Wang, H.; Houk, K. N.; Antilla, J. C., Bronsted Acid Catalyzed Asymmetric Propargylation of Aldehydes. *Angew. Chem., Int. Ed.* **2012,** *51* (6), 1391-1394.
34. Truong, P. M.; Zavalij, P. Y.; Doyle, M. P., Highly Enantioselective Carbonyl-Ene Reactions of 2,3-Diketoesters: Efficient and Atom-Economical Process to Functionalized Chiral alpha-Hydroxy-beta-Ketoesters. *Angew. Chem., Int. Ed.* **2014,** *53* (25), 6468-6472.
35. Liu, L. P.; Leutzsch, M.; Zheng, Y. Y.; Alachraf, M. W.; Thiel, W.; List, B., Confined Acid-Catalyzed Asymmetric Carbonyl-Ene Cyclization. *J. Am. Chem. Soc.* **2015,** *137* (41), 13268-13271.
36. Lv, J.; Zhang, Q. C.; Zhong, X. R.; Luo, S. Z., Asymmetric Latent Carbocation Catalysis with Chiral Trityl Phosphate. *J. Am. Chem. Soc.* **2015,** *137* (49), 15576-15583.
37. Park, Y.; Schindler, C. S.; Jacobsen, E. N., Enantioselective Aza-Sakurai Cyclizations: Dual Role of Thiourea as H-Bond Donor and Lewis Base. *J. Am. Chem. Soc.* **2016,** *138* (45), 14848-14851.

2.1.3 Other Nucleophiles for Carbonyl Addition

1. Nelson, S. G.; Peelen, T. J.; Wan, Z. H., Catalytic asymmetric acyl halide-aldehyde cyclocondensations. A strategy for enantioselective catalyzed cross aldol reactions. *J. Am. Chem. Soc.* **1999,** *121* (41), 9742-9743.

2. Dossetter, A. G.; Jamison, T. F.; Jacobsen, E. N., Highly enantio- and diastereoselective hetero-Diels-Alder reactions catalyzed by new chiral tridentate chromium(III) catalysts. *Angew. Chem., Int. Ed.* **1999,** *38* (16), 2398-2400.

3. Suga, H.; Inoue, K.; Inoue, S.; Kakehi, A., Highly enantioselective 1,3-dipolar cycloaddition reactions of 2-benzopyrylium-4-olate catalyzed by chiral Lewis acids. *J. Am. Chem. Soc.* **2002,** *124* (50), 14836-14837.

4. Mita, T.; Ohtsuki, N.; Ikeno, T.; Yamada, T., Enantioselective 1,3-dipolar cycloaddition of nitrones catalyzed by optically active cationic cobalt(III) complexes. *Org. Lett.* **2002,** *4* (15), 2457-2460.

5. Yamashita, Y.; Saito, S.; Ishitani, H.; Kobayashi, S., Chiral hetero Diels-Alder products by enantioselective and diastereoselective zirconium catalysis. Scope, limitation, mechanism, and application to the concise synthesis of (+)- prelactone C and (+)-9-deoxygoniopypyrone. *J. Am. Chem. Soc.* **2003,** *125* (13), 3793-3798.

6. Du, H. F.; Ding, K. L., Enantioselective catalysis of hetero Diels-Alder reaction and diethylzinc addition using a single catalyst. *Org. Lett.* **2003,** *5* (7), 1091-1093.

7. Denmark, S. E.; Fan, Y., The first catalytic, asymmetric alpha-additions of isocyanides. Lewis-base-catalyzed, enantioselective Passerini-type reactions. *J. Am. Chem. Soc.* **2003,** *125* (26), 7825-7827.

8. Ryu, D. H.; Corey, E. J., Highly enantioselective cyanosilylation of aldehydes catalyzed by a chiral oxazaborolidinium ion. *J. Am. Chem. Soc.* **2004,** *126* (26), 8106-8107.

9. Yuan, Y.; Wang, X. W.; Li, X.; Ding, K. L., Highly enantioselective Friedel-Crafts reaction of aromatic amines with ethyl glyoxylate catalyzed by chiral titanium(IV) complexes: Practical synthesis of aminomandelic acid derivatives. *J. Org. Chem.* **2004,** *69* (1), 146-149.

10. Brunel, J. M.; Holmes, I. P., Chemically catalyzed asymmetric cyanohydrin syntheses. *Angew. Chem., Int. Ed.* **2004,** *43* (21), 2752-2778.

11. Anada, M.; Washio, T.; Shimada, N.; Kitagaki, S.; Nakajima, M.; Shiro, M.; Hashimoto, S., A new dirhodium(II) carboxamidate complex as a chiral lewis acid catalyst for euantioselective hetero-Diels-Alder reactions. *Angew. Chem., Int. Ed.* **2004,** *43* (20), 2665-2668.

12. Nelson, S. G.; Zhu, C.; Shen, X. Q., Catalytic asymmetric acyl halide-aldehyde cyclocondensation reactions of substituted ketenes. *J. Am. Chem. Soc.* **2004,** *126* (1), 14-15.

13. Ryu, D. H.; Corey, E. J., Enantioselective cyanosilylation of ketones catalyzed by a chiral oxazaborolidinium ion. *J. Am. Chem. Soc.* **2005,** *127* (15), 5384-5387.

14. Saito, B.; Katsuki, T., Synthesis of an optically active C-1-symmetric Al(salalen) complex and its application to the catalytic hydrophosphonylation of aldehydes. *Angew. Chem., Int. Ed.* **2005,** *44* (29), 4600-4602.

15. Gnanadesikan, V.; Corey, E. J., Enantioselective beta-lactone formation from ketene and aldehydes catalyzed by a chiral oxazaborolidine. *Org. Lett.* **2006,** *8* (21), 4943-4945.

16. Evans, D. A.; Aye, Y., Enantioselective scandium-catalyzed vinylsilane additions: A new approach to the synthesis of enantiopure beta,gamma-unsaturated alpha-hydroxy acid derivatives. *J. Am. Chem. Soc.* **2006,** *128* (34), 11034-11035.

17. Ooi, T.; Ohmatsu, K.; Maruoka, K., Catalytic asymmetric rearrangement of alpha,alpha-disubstituted alpha-siloxy aldehydes to optically active acyloins using axially chiral organoaluminum lewis acids. *J. Am. Chem. Soc.* **2007,** *129* (9), 2410-+.

18. Evans, D. A.; Aye, Y., Aluminum-catalyzed enantio- and diastereoselective carbonyl addition of propargylsilanes. A new approach to enantioenriched vinyl epoxides. *J. Am. Chem. Soc.* **2007,** *129* (31), 9606-+.

19. Jensen, K. H.; Sigman, M. S., Systematically probing the effect of catalyst acidity in a hydrogen-bond-catalyzed enantioselective reaction. *Angew. Chem., Int. Ed.* **2007,** *46* (25), 4748-4750.

20. Reynolds, T. E.; Scheidt, K. A., Catalytic enantioselective alpha-acylvinyl anion reactions of silyloxyallenes. *Angew. Chem., Int. Ed.* **2007,** *46* (41), 7806-7809.

21. Zhou, X.; Liu, X. H.; Yang, X.; Shang, D. J.; Xin, J. G.; Feng, X. M., Highly enantioselective hydrophosphonylation of aldehydes catalyzed by tridentate Schiff base aluminum(III) complexes. *Angew. Chem., Int. Ed.* **2008,** *47* (2), 392-394.

22. Wang, S. X.; Wang, M. X.; Wang, D. X.; Zhu, J. P., Catalytic enantioselective passerini three-component reaction. *Angew. Chem., Int. Ed.* **2008,** *47* (2), 388-391.

23. Yu, Z. P.; Liu, X. H.; Dong, Z. H.; Xie, M. S.; Feng, X. M., An N,N'-Dioxide/In(OTf)(3) catalyst for the asymmetric hetero-diels-alder reaction between Danishefsky's dienes and aldehydes: Application in the total synthesis of triketide. *Angew. Chem., Int. Ed.* **2008,** *47* (7), 1308-1311.

24. Yang, X. B.; Feng, J.; Zhang, J.; Wang, N.; Wang, L.; Liu, J. L.; Yu, X. Q., Highly enantioselective hetero-Diels-Alder reaction of trans-1-methoxy-2-methyl-3-trimethylsiloxybuta-1-3-diene with aromatic and aliphatic aldehydes catalyzed by 3-substituted BINOL-titanium complex. *Org. Lett.* **2008,** *10* (6), 1299-1302.

25. Terada, M.; Soga, K.; Momiyama, N., Enantioselective activation of aldehydes by chiral phosphoric acid catalysts in an aza-ene-type reaction between glyoxylate and enecarbamate. *Angew. Chem., Int. Ed.* **2008,** *47* (22), 4122-4125.

26. Reisman, S. E.; Doyle, A. G.; Jacobsen, E. N., Enantioselective thiourea-catalyzed additions to oxocarbenium ions. *J. Am. Chem. Soc.* **2008,** *130* (23), 7198-+.

27. Anderson, C. D.; Dudding, T.; Gordillo, R.; Houk, K. N., Origin of enantioselection in hetero-Diels-Alder reactions catalyzed by naphthyl-TADDOL. *Org. Lett.* **2008,** *10* (13), 2749-2752.

28. Friel, D. K.; Snapper, M. L.; Hoveyda, A. H., Aluminum-catalyzed asymmetric alkylations of pyridyl-substituted alkynyl ketones with dialkylzinc reagents. *J. Am. Chem. Soc.* **2008,** *130* (30), 9942-9951.

29. Abell, J. P.; Yamamoto, H., Catalytic enantioselective Pudovik reaction of aldehydes and aldimines with tethered bis(8-quinolinato) (TBOx) aluminum complex. *J. Am. Chem. Soc.* **2008,** *130* (32), 10521-+.

30. Kokubo, M.; Ogawa, C.; Kobayashi, S., Lewis acid catalysis in water with a hydrophilic substrate: Scandium-catalyzed hydroxymethylation with aqueous formaldehyde in water. *Angew. Chem., Int. Ed.* **2008,** *47* (36), 6909-6911.

31. Zhou, X.; Shang, D. J.; Zhang, Q.; Lin, L. L.; Liu, X. H.; Feng, X. M., Enantioselective Three-Component Kabachnik-Fields Reaction Catalyzed by Chiral Scandium(III)-N,N '-Dioxide Complexes. *Org. Lett.* **2009,** *11* (6), 1401-1404.

32. Corey, E. J., Enantioselective Catalysis Based on Cationic Oxazaborolidines. *Angew. Chem., Int. Ed.* **2009,** *48* (12), 2100-2117.

33. Terada, M.; Machioka, K.; Sorimachi, K., Activation of Hemiaminal Ethers by Chiral Bronsted Acids for Facile Access to Enantioselective Two-Carbon Homologation Using Enecarbamates. *Angew. Chem., Int. Ed.* **2009,** *48* (14), 2553-2556.

34. Sun, F. L.; Zeng, M.; Gu, Q.; You, S. L., Enantioselective Synthesis of Fluorene Derivatives by Chiral Phosphoric Acid Catalyzed Tandem Double Friedel-Crafts Reaction. *Chem. Eur. J.* **2009,** *15* (35), 8709-8712.

35. Momiyama, N.; Tabuse, H.; Terada, M., Chiral Phosphoric Acid-Governed Anti-Diastereoselective and Enantioselective Hetero-Diels-Alder Reaction of Glyoxylate. *J. Am. Chem. Soc.* **2009,** *131* (36), 12882-+.

36. Wang, X. C.; Li, Z. Y.; Doyle, M. P., Barriers to enantiocontrol in Lewis acid catalyzed hetero-Diels-Alder reactions. *Chem. Comm.* **2009,** (37), 5612-5614.

37. Yue, T.; Wang, M. X.; Wang, D. X.; Masson, G.; Zhu, J. P., Catalytic Asymmetric Passerini-Type Reaction: Chiral Aluminum-Organophosphate-Catalyzed Enantioselective alpha-Addition of Isocyanides to Aldehydes. *J. Org. Chem.* **2009,** *74* (21), 8396-8399.

38. Chaladaj, W.; Jurczak, J., Origin of the asymmetric induction in metallosalen-catalyzed reactions of aldehydes. *Chem. Comm.* **2009,** (44), 6747-6749.

39. Hanhan, N. V.; Sahin, A. H.; Chang, T. W.; Fettinger, J. C.; Franz, A. K., Catalytic Asymmetric Synthesis of Substituted 3-Hydroxy-2-Oxindoles. *Angew. Chem., Int. Ed.* **2010,** *49* (4), 744-747.

40. Seifert, A.; Scheffler, U.; Markert, M.; Mahrwald, R., Asymmetric Acid-Catalyzed Meerwein-Ponndorf-Verley-Aldol Reactions of Enolizable Aldehydes. *Org. Lett.* **2010,** *12* (8), 1660-1663.

41. Coric, I.; Vellalath, S.; List, B., Catalytic Asymmetric Transacetalization. *J. Am. Chem. Soc.* **2010,** *132* (25), 8536-+.

42. Liang, T.; Zhang, Z. J.; Antilla, J. C., Chiral Bronsted Acid Catalyzed Pinacol Rearrangement. *Angew. Chem., Int. Ed.* **2010,** *49* (50), 9734-9736.

43. Coric, I.; Muller, S.; List, B., Kinetic Resolution of Homoaldols via Catalytic Asymmetric Transacetalization. *J. Am. Chem. Soc.* **2010,** *132* (49), 17370-17373.

44. Yu, X. L.; Lu, A. D.; Wang, Y. M.; Wu, G. P.; Song, H. B.; Zhou, Z. H.; Tang, C. C., Chiral Phosphoric Acid Catalyzed Asymmetric Friedel-Crafts Alkylation of Indole with 3-Hydroxyisoindolin-1-one: Enantioselective Synthesis of 3-Indolyl-Substituted Isoindolin-1-ones. *Eur. J. Org. Chem.* **2011,** (5), 892-897.

45. Rendina, V. L.; Moebius, D. C.; Kingsbury, J. S., An Enantioselective Synthesis of 2-Aryl Cycloalkanones by Sc-Catalyzed Carbon Insertion. *Org. Lett.* **2011,** *13* (8), 2004-2007.

46. Yin, Q.; You, S. L., Chiral phosphoric acid-catalysed Friedel-Crafts alkylation reaction of indoles with racemic spiro indolin-3-ones. *Chemical Science* **2011,** *2* (7), 1344-1348.

47. Hashimoto, T.; Naganawa, Y.; Maruoka, K., Desymmetrizing Asymmetric Ring Expansion of Cyclohexanones with alpha-Diazoacetates Catalyzed by Chiral Aluminum Lewis Acid. *J. Am. Chem. Soc.* **2011,** *133* (23), 8834-8837.

48. Zhang, Z. H.; Jain, P.; Antilla, J. C., Asymmetric Reduction of Ketones by Phosphoric Acid Derived Catalysts. *Angew. Chem., Int. Ed.* **2011,** *50* (46), 10961-10964.

49. Gramigna, L.; Duce, S.; Filippini, G.; Fochi, M.; Franchini, M. C.; Bernardi, L., Organocatalytic Asymmetric Wittig Reactions: Generation of Enantioenriched Axially Chiral Olefins Breaking a Symmetry Plane. *Synlett* **2011,** (18), 2745-2749.

50. Aikawa, K.; Hioki, Y.; Shimizu, N.; Mikami, K., Catalytic Asymmetric Synthesis of Stable Oxetenes via Lewis Acid-Promoted 2+2 Cycloaddition. *J. Am. Chem. Soc.* **2011,** *133* (50), 20092-20095.

51. Handa, S.; Slaughter, L. M., Enantioselective Alkynylbenzaldehyde Cyclizations Catalyzed by Chiral Gold(I) Acyclic Diaminocarbene Complexes Containing Weak Au-Arene Interactions. *Angew. Chem., Int. Ed.* **2012,** *51* (12), 2912-2915.

52. Terada, M.; Toda, Y., Relay Catalysis Using a Rhodium Complex/Chiral Bronsted Acid Binary System: Enantioselective Reduction of a Carbonyl Ylide as the Reactive Intermediate. *Angew. Chem., Int. Ed.* **2012,** *51* (9), 2093-2097.

53. Tong, S.; Wang, D. X.; Zhao, L.; Zhu, J. P.; Wang, M. X., Enantioselective Synthesis of 4-Hydroxytetrahydropyridine Derivatives by Intramolecular Addition of Tertiary Enamides to Aldehydes. *Angew. Chem., Int. Ed.* **2012,** *51* (18), 4417-4420.

54. Sun, Z. K.; Winschel, G. A.; Borovika, A.; Nagorny, P., Chiral Phosphoric Acid-Catalyzed Enantioselective and Diastereoselective Spiroketalizations. *J. Am. Chem. Soc.* **2012,** *134* (19), 8074-8077.

55. Muratore, M. E.; Shi, L.; Pilling, A. W.; Storer, R. I.; Dixon, D. J., Exploiting a novel size exclusion phenomenon for enantioselective acid/base cascade catalysis. *Chem. Comm.* **2012,** *48* (51), 6351-6353.

56. Li, W.; Liu, X. H.; Hao, X. Y.; Cai, Y. F.; Lin, L.; Feng, X. M., A Catalytic Asymmetric Ring-Expansion Reaction of Isatins and a-Alkyl-a-Diazoesters: Highly Efficient Synthesis of Functionalized 2-Quinolone Derivatives. *Angew. Chem., Int. Ed.* **2012,** *51* (34), 8644-8647.

57. Gao, L. Z.; Kang, B. C.; Hwang, G. S.; Ryu, D. H., Enantioselective Synthesis of alpha-Alkyl-beta-ketoesters: Asymmetric Roskamp Reaction Catalyzed by an Oxazaborolidinium Ion. *Angew. Chem., Int. Ed.* **2012,** *51* (33), 8322-8325.

58. Guin, J.; Rabalakos, C.; List, B., Highly Enantioselective Hetero-Diels-Alder Reaction of 1,3-Bis(silyloxy)-1,3-dienes with Aldehydes Catalyzed by Chiral Disulfonimide. *Angew. Chem., Int. Ed.* **2012,** *51* (35), 8859-8863.

59. Rubush, D. M.; Morges, M. A.; Rose, B. J.; Thamm, D. H.; Rovis, T., An Asymmetric Synthesis of 1,2,4-Trioxane Anticancer Agents via Desymmetrization of Peroxyquinols through a Bronsted Acid Catalysis Cascade. *J. Am. Chem. Soc.* **2012,** *134* (33), 13554-13557.

60. Zhou, L.; Liu, X. H.; Ji, J.; Zhang, Y. H.; Hu, X. L.; Lin, L. L.; Feng, X. M., Enantioselective Baeyer-Villiger Oxidation: Desymmetrization of Meso Cyclic Ketones and Kinetic Resolution of Racemic 2-Arylcyclohexanones. *J. Am. Chem. Soc.* **2012,** *134* (41), 17023-17026.

61. Kim, J. H.; Coric, I.; Vellalath, S.; List, B., The Catalytic Asymmetric Acetalization. *Angew. Chem., Int. Ed.* **2013,** *52* (16), 4474-4477.

62. Gao, L.; Kang, B. C.; Ryu, D. H., Catalytic Asymmetric Insertion of Diazoesters into Aryl-CHO Bonds: Highly Enantioselective Construction of Chiral All-Carbon Quaternary Centers. *J. Am. Chem. Soc.* **2013,** *135* (39), 14556-14559.

63. Wang, P.; Tao, W. J.; Sun, X. L.; Liao, S. H.; Tang, Y., A Highly Efficient and Enantioselective Intramolecular Cannizzaro Reaction under TOX/Cu(II) Catalysis. *J. Am. Chem. Soc.* **2013,** *135* (45), 16849-16852.

64. Prevost, S.; Dupre, N.; Leutzsch, M.; Wang, Q.; Wakchaure, V.; List, B., Catalytic Asymmetric Torgov Cyclization: A Concise Total Synthesis of (+)-Estrone. *Angew. Chem., Int. Ed.* **2014,** *53* (33), 8770-8773.

65. Guin, J.; Wang, Q.; van Gemmeren, M.; List, B., The Catalytic Asymmetric Abramov Reaction. *Angew. Chem., Int. Ed.* **2015,** *54* (1), 355-358.

66. Li, W.; Tan, F.; Hao, X.; Wang, G.; Tang, Y.; Liu, X.; Lin, L.; Feng, X., Catalytic Asymmetric Intramolecular Homologation of Ketones with alpha-Diazoesters: Synthesis of Cyclic alpha-Aryl/Alkyl beta-Ketoesters. *Angew. Chem., Int. Ed.* **2015,** *54* (5), 1608-1611.

67. Yamanaka, T.; Kondoh, A.; Terada, M., Kinetic Resolution of Racemic Amino Alcohols through Intermolecular Acetalization Catalyzed by a Chiral Bronsted Acid. *J. Am. Chem. Soc.* **2015,** *137* (3), 1048-1051.

68. Kim, J. H.; Coric, I.; Palumbo, C.; List, B., Resolution of Diols via Catalytic Asymmetric Acetalization. *J. Am. Chem. Soc.* **2015,** *137* (5), 1778-1781.

69. Wang, P.; Feng, L. W.; Wang, L. J.; Li, J. F.; Liao, S. H.; Tang, Y., Asymmetric 1,2-Perfluoroalkyl Migration: Easy Access to Enantioenriched alpha-Hydroxy-alpha-perfluoroalkyl Esters. *J. Am. Chem. Soc.* **2015,** *137* (14), 4626-4629.

70. Tsui, G. C.; Liu, L. P.; List, B., The Organocatalytic Asymmetric Prins Cyclization. *Angew. Chem., Int. Ed.* **2015,** *54* (26), 7703-7706.

71. Zeng, X. P.; Cao, Z. Y.; Wang, X.; Chen, L.; Zhou, F.; Zhu, F.; Wang, C. H.; Zhou, J., Activation of Chiral (Salen)AlCl Complex by Phosphorane for Highly Enantioselective Cyanosilylation of Ketones and Enones. *J. Am. Chem. Soc.* **2016,** *138* (1), 416-425.

72. Susse, L.; Hermeke, J.; Oestreich, M., The Asymmetric Piers Hydrosilylation. *J. Am. Chem. Soc.* **2016,** *138* (22), 6940-6943.

73. Ford, D. D.; Lehnherr, D.; Kennedy, C. R.; Jacobsen, E. N., On- and Off-Cycle Catalyst Cooperativity in Anion-Binding Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (25), 7860-7863.

74. Zeng, X. P.; Zhou, J., Me-2(CH2Cl)SiCN: Bifunctional Cyanating Reagent for the Synthesis of Tertiary Alcohols with a Chloromethyl Ketone Moiety via Ketone Cyanosilylation. *J. Am. Chem. Soc.* **2016,** *138* (28), 8730-8733.

75. Das, S.; Liu, L. P.; Zheng, Y. Y.; Alachraf, M. W.; Thiel, W.; De, C. K.; List, B., Nitrated Confined Imidodiphosphates Enable a Catalytic Asymmetric Oxa-Pictet-Spengler Reaction. *J. Am. Chem. Soc.* **2016,** *138* (30), 9429-9432.

76. Liu, L. P.; Kaib, P. S. J.; Tap, A.; List, B., A General Catalytic Asymmetric Prins Cyclization. *J. Am. Chem. Soc.* **2016,** *138* (34), 10822-10825.

77. Xie, Y. W.; Cheng, G. J.; Lee, S.; Kaib, P. S. J.; Thiel, W.; List, B., Catalytic Asymmetric Vinylogous Prins Cyclization: A Highly Diastereo- and Enantioselective Entry to Tetrahydrofurans. *J. Am. Chem. Soc.* **2016,** *138* (44), 14538-14541.

78. Zheng, Y.; Tan, Y. Q.; Harms, K.; Marsch, M.; Riedel, R.; Zhang, L. L.; Meggers, E., Octahedral Ruthenium Complex with Exclusive Metal-Centered Chirality for Highly Effective Asymmetric Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (12), 4322-4325.

79. Wan, M. A.; Sun, S. T.; Li, Y. S.; Liu, L., Organocatalytic Redox Deracemization of Cyclic Benzylic Ethers Enabled by An Acetal Pool Strategy. *Angew. Chem., Int. Ed.* **2017,** *56* (18), 5116-5120.

80. Wu, H.; Wang, Q.; Zhu, J. P., Organocatalytic Enantioselective Acyloin Rearrangement of alpha-Hydroxy Acetals to alpha-Alkoxy Ketones. *Angew. Chem., Int. Ed.* **2017,** *56* (21), 5858-5861.

81. Lin, L.; Bai, X. B.; Ye, X. Y.; Zhao, X. W.; Tan, C. H.; Jiang, Z. Y., Organocatalytic Enantioselective Protonation for Photoreduction of Activated Ketones and Ketimines Induced by Visible Light. *Angew. Chem., Int. Ed.* **2017,** *56* (44), 13842-13846.

82. Wu, H.; Andres, R.; Wang, Q.; Zhu, J. P., Catalytic Enantioselective alpha-Ketol Rearrangement. *Angew. Chem., Int. Ed.* **2019,** *58* (2), 499-503.

83. Wu, H.; Wang, Q.; Zhu, J., Catalytic Enantioselective Benzilic Ester Rearrangement. *Angew. Chem., Int. Ed.* **2020,** *59* (18), 7261-7265.

84. Nam, D. G.; Shim, S. Y.; Jeong, H.-M.; Ryu, D. H., Catalytic Asymmetric Darzens-Type Epoxidation of Diazoesters: Highly Enantioselective Synthesis of Trisubstituted Epoxides. *Angew. Chem., Int. Ed.* **2021,** *60* (41), 22236-22240.

85. Díaz-Oviedo, C. D.; Maji, R.; List, B., The Catalytic Asymmetric Intermolecular Prins Reaction. *J. Am. Chem. Soc.* **2021,** *143* (49), 20598-20604.

86. Wang, X.-M.; Zhang, P.; Xu, Q.; Guo, C.-Q.; Zhang, D.-B.; Lu, C.-J.; Liu, R.-R., Enantioselective Synthesis of Nitrogen–Nitrogen Biaryl Atropisomers via Copper-Catalyzed Friedel–Crafts Alkylation Reaction. *J. Am. Chem. Soc.* **2021,** *143* (37), 15005-15010.

87. Li, S.-S.; Sun, S.; Wang, J., Catalytic Asymmetric Homologation of 4-Substituted Cyclohexanones with CF3CHN2: Enantioselective Synthesis of α-Trifluoromethyl Cycloheptanones. *Angew. Chem., Int. Ed.* **2022,** *61* (6), e202115098.

88. Tan, Z.; Zhu, S.; Liu, Y.; Feng, X., Photoinduced Chemo-, Site- and Stereoselective α-C(sp3)−H Functionalization of Sulfides. *Angew. Chem., Int. Ed.* **2022,** *61* (29), e202203374.

89. Yu, H.; Zhan, T.; Zhou, Y.; Chen, L.; Liu, X.; Feng, X., Visible-Light-Activated Asymmetric Addition of Hydrocarbons to Pyridine-Based Ketones. *ACS Catalysis* **2022,** *12* (9), 5136-5144.

90. Fan, Y.-M.; Yu, L.-J.; Gardiner, M. G.; Coote, M. L.; Sherburn, M. S., Enantioselective oxa-Diels–Alder Sequences of Dendralenes. *Angew. Chem., Int. Ed.* **2022,** *61* (39), e202204872.

91. Hou, L.; Zhou, Y.; Yu, H.; Zhan, T.; Cao, W.; Feng, X., Enantioselective Radical Addition to Ketones through Lewis Acid-Enabled Photoredox Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (48), 22140-22149.

92. Essman, J. Z.; Jacobsen, E. N., Enantioselective Potassium-Catalyzed Wittig Olefinations. *J. Am. Chem. Soc.* **2024,** *146* (11), 7165-7172.

93. Yu, X.; Zheng, C.; You, S.-L., Chiral Brønsted Acid-Catalyzed Intramolecular Asymmetric Dearomatization Reaction of Indoles with Cyclobutanones via Cascade Friedel–Crafts/Semipinacol Rearrangement. *J. Am. Chem. Soc.* **2024,** *146* (37), 25878-25887.

94. Tan, J.; Yang, L.; Su, H.; Yang, Y.; Zhong, Z.; Feng, X.; Liu, X., Visible-light-driven asymmetric aldol reaction of ketones and glycinates via synergistic Lewis acid/photoredox catalysis. *Chemical Science* **2024,** *15* (39), 16050-16058.

95. Liu, L. P.; Kim, H.; Xie, Y. W.; Fares, C.; Kaib, P. S. J.; Goddard, R.; List, B., Catalytic Asymmetric 4+2 -Cycloaddition of Dienes with Aldehydes. *J. Am. Chem. Soc.* **2017,** *139* (39), 13656-13659.

2.1.4 Mannich Reaction

1. Ishitani, H.; Ueno, M.; Kobayashi, S., Catalytic enantioselective mannich-type reactions using a novel chiral zirconium catalyst. *J. Am. Chem. Soc.* **1997,** *119* (30), 7153-7154.

2. Ferraris, D.; Young, B.; Cox, C.; Drury, W. J.; Dudding, T.; Lectka, T., Diastereo- and enantioselective alkylation of alpha-imino esters with enol silanes catalyzed by (R)-Tol-BINAP-CuClO4 center dot(MeCN)(2). *J. Org. Chem.* **1998,** *63* (18), 6090-6091.

3. Ferraris, D.; Young, B.; Dudding, T.; Lectka, T., Catalytic, enantioselective alkylation of alpha-imino esters using late transition metal phosphine complexes as catalysts. *J. Am. Chem. Soc.* **1998,** *120* (18), 4548-4549.

4. Ishitani, H.; Kitazawa, T.; Kobayashi, S., Efficient catalytic enantioselective Mannich-type reactions using a zirconium-bis(binaphthol)methane complex. *Tetrahedron Lett.* **1999,** *40* (11), 2161-2164.

5. Ishitani, H.; Ueno, M.; Kobayashi, S., Enantioselective mannich-type reactions using a novel chiral zirconium catalyst for the synthesis of optically active beta- amino acid derivatives. *J. Am. Chem. Soc.* **2000,** *122* (34), 8180-8186.

6. Xue, S.; Yu, S.; Deng, Y. H.; Wulff, W. D., Active site design in a chemzyme: Development of a highly asymmetric and remarkably temperature-independent catalyst for the imino aldol reaction. *Angew. Chem., Int. Ed.* **2001,** *40* (12), 2271-+.

7. Ferraris, D.; Young, B.; Cox, C.; Dudding, T.; Drury, W. J.; Ryzhkov, L.; Taggi, A. E.; Lectka, T., Catalytic, enantioselective alkylation of alpha-amino esters: The synthesis of nonnatural alpha-amino acid derivatives. *J. Am. Chem. Soc.* **2002,** *124* (1), 67-77.

8. Ueno, M.; Ishitani, H.; Kobayashi, S., Air-stable, storable, and highly selective chiral Lewis acid catalyst. *Org. Lett.* **2002,** *4* (20), 3395-3397.

9. Wenzel, A. G.; Jacobsen, E. N., Asymmetric catalytic Mannich reactions catalyzed by urea derivatives: Enantioselective synthesis of beta-aryl-beta-amino acids. *J. Am. Chem. Soc.* **2002,** *124* (44), 12964-12965.

10. Jaber, N.; Carree, F.; Fiaud, J. C.; Collin, J., A new enantioselective Mannich-type reaction catalyzed by bis- binaphthoxy iodo samarium. *Tetrahedron-Asymmetry* **2003,** *14* (14), 2067-2071.

11. Kobayashi, S.; Matsubara, R.; Nakamura, Y.; Kitagawa, H.; Sugiura, M., Catalytic, asymmetric Mannich-type reactions of N-acylimino esters: Reactivity, diastereo- and enantioselectivity, and application to synthesis of N-acylated amino acid derivatives. *J. Am. Chem. Soc.* **2003,** *125* (9), 2507-2515.

12. Nakamura, Y.; Matsubara, R.; Kiyohara, H.; Kobayashi, S., Catalytic, asymmetric Mannich-type reactions of alpha-imino esters bearing readily removable substituents on nitrogen. *Org. Lett.* **2003,** *5* (14), 2481-2484.

13. Taggi, A. E.; Hafez, A. M.; Lectka, T., alpha-imino esters: Versatile substrates for the catalytic, asymmetric synthesis of alpha- and beta-amino acids and beta- lactams. *Acc. Chem. Res.* **2003,** *36* (1), 10-19.

14. Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K., Enantioselective Mannich-Type Reaction Catalyzed by a Chiral Bronsted Acid. *Angew. Chem., Int. Ed.* **2004,** *43*, 1566-1568.

15. Josephsohn, N. S.; Snapper, M. L.; Hoveyda, A. H., Ag-catalyzed asymmetric Mannich reactions of enol ethers with aryl, alkyl, alkenyl, and alkynyl imines. *J. Am. Chem. Soc.* **2004,** *126* (12), 3734-3735.

16. Kobayashi, S.; Kiyohara, H.; Nakamura, Y.; Matsubara, R., Catalytic asymmetric synthesis of alpha-amino phosphonates using enantioselective carbon-carbon bond-forming reactions. *J. Am. Chem. Soc.* **2004,** *126* (21), 6558-6559.

17. Matsubara, R.; Nakamura, Y.; Kobayashi, S., Copper(II)-Catalyzed Highly Enantioselective Addition of Enamides to Imines: The Use of Enamides as Nucleophiles in Asymmetric Catalysis. *Angew. Chem., Int. Ed.* **2004,** *43*, 1679-1681.

18. Uraguchi, D.; Terada, M., Chiral Bronsted acid-catalyzed direct Mannich reactions via electrophilic activation. *J. Am. Chem. Soc.* **2004,** *126* (17), 5356-5357.

19. Josephsohn, N. S.; Carswell, E. L.; Snapper, M. L.; Hoveyda, A. H., Practical and highly enantioselective synthesis of beta-alkynyl-beta-amino esters through Ag-catalyzed asymmetric Mannich reactions of silylketene acetals and alkynyl imines. *Org. Lett.* **2005,** *7* (13), 2711-2713.

20. Kobayashi, S.; Arai, K.; Shimizu, H.; Ihori, Y.; Ishitani, H.; Yamashita, Y., A novel dinuclear chiral niobium complex for Lewis acid catalyzed enantioselective reactions: Design of a tridentate ligand and elucidation of the catalyst structure. *Angew. Chem., Int. Ed.* **2005,** *44* (5), 761-764.

21. Carswell, E. L.; Snapper, M. L.; Hoveyda, A. H., A highly efficient and practical method for catalytic asymmetric vinylogous Mannich (AVM) reactions. *Angew. Chem., Int. Ed.* **2006,** *45* (43), 7230-7233.

22. Pan, S. C.; List, B., Catalytic asymmetric three-component acyl-Strecker reaction. *Org. Lett.* **2007,** *9* (6), 1149-1151.

23. Suto, Y.; Kanai, M.; Shibasaki, M., Catalytic enantioselective Mannich-type reactions of ketoimines. *J. Am. Chem. Soc.* **2007,** *129* (3), 500-501.

24. Yamanaka, M.; Itoh, J.; Fuchibe, K.; Akiyama, T., Chiral bronsted acid catalyzed enantioselective Mannich-type reaction. *J. Am. Chem. Soc.* **2007,** *129* (21), 6756-6764.

25. Baudequin, C.; Zamfir, A.; Tsogoeva, S. B., Highly enantioselective organocatalytic formation of a quaternary carbon center via chiral Bronsted acid catalyzed self-coupling of enamides. *Chem. Comm.* **2008,** (38), 4637-4639.

26. Giera, D. S.; Sickert, M.; Schneider, C., Bronsted acid-catalyzed, enantioselective, vinylogous Mannich reaction of vinylketene silyl N,O-acetals. *Org. Lett.* **2008,** *10* (19), 4259-4262.

27. Zhang, Y.; Liu, Y. K.; Kang, T. R.; Hu, Z. K.; Chen, Y. C., Organocatalytic enantioselective Mannich-type reaction of phosphorus ylides: Synthesis of chiral N-Boc-beta-amino-alpha-methylene carboxylic esters. *J. Am. Chem. Soc.* **2008,** *130* (8), 2456-2457.

28. Dagousset, G.; Drouet, F.; Masson, G.; Zhu, J. P., Chiral Bronsted Acid-Catalyzed Enantioselective Multicomponent Mannich Reaction: Synthesis of anti-1,3-Diamines Using Enecarbamates as Nucleophiles. *Org. Lett.* **2009,** *11* (23), 5546-5549.

29. Fu, X.; Loh, W. T.; Zhang, Y.; Chen, T.; Ma, T.; Liu, H. J.; Wang, J. M.; Tan, C. H., Chiral Guanidinium Salt Catalyzed Enantioselective Phospha-Mannich Reactions. *Angew. Chem., Int. Ed.* **2009,** *48* (40), 7387-7390.

30. Desai, A. A.; Wulff, W. D., Controlled Diastereo- and Enantioselection in a Catalytic Asymmetric Aziridination. *J. Am. Chem. Soc.* **2010,** *132* (38), 13100-13103.

31. Hatano, M.; Moriyama, K.; Maki, T.; Ishihara, K., Which Is the Actual Catalyst: Chiral Phosphoric Acid or Chiral Calcium Phosphate? *Angew. Chem., Int. Ed.* **2010,** *49* (22), 3823-3826.

32. Huang, L.; Wulf, W. D., Catalytic Asymmetric Synthesis of Trisubstituted Aziridines. *J. Am. Chem. Soc.* **2011,** *133* (23), 8892-8895.

33. Larson, S. E.; Li, G. L.; Rowland, G. B.; Junge, D.; Huang, R. C.; Woodcock, H. L.; Antilla, J. C., Catalytic Asymmetric Aza-Darzens Reaction with a Vaulted Biphenanthrol Magnesium Phosphate Salt. *Org. Lett.* **2011,** *13* (9), 2188-2191.

34. Wang, Q. G.; Leutzsch, M.; van Gemmeren, M.; List, B., Disulfoninnide-Catalyzed Asymmetric Synthesis of beta(3)-Amino Esters Directly from N-Boc-Amino Sulfones. *J. Am. Chem. Soc.* **2013,** *135* (41), 15334-15337.

35. Abels, F.; Lindemann, C.; Schneider, C., A General Strategy for the Catalytic, Highly Enantio- and Diastereoselective Synthesis of Indolizidine-Based Alkaloids. *Chem. Eur. J.* **2014,** *20* (7), 1964-1979.

36. Wang, Q.; van Gemmeren, M.; List, B., Asymmetric Disulfonimide-Catalyzed Synthesis of delta-Amino-beta-Ketoester Derivatives by Vinylogous Mukaiyama-Mannich Reactions. *Angew. Chem., Int. Ed.* **2014,** *53* (49), 13592-13595.

37. Wang, Y. C.; Mo, M. J.; Zhu, K. X.; Zheng, C.; Zhang, H. B.; Wang, W.; Shao, Z. H., Asymmetric synthesis of syn-propargylamines and unsaturated beta-amino acids under Bronsted base catalysis. *Nature Communications* **2015,** *6*.

38. Zhao, J.; Fang, B.; Luo, W.; Hao, X.; Liu, X.; Lin, L.; Feng, X., Enantioselective Construction of Vicinal Tetrasubstituted Stereocenters by the Mannich Reaction of Silyl Ketene Imines with Isatin-Derived Ketimines. *Angew. Chem., Int. Ed.* **2015,** *54* (1), 241-244.

39. Gheewala, C. D.; Collins, B. E.; Lambert, T. H., An aromatic ion platform for enantioselective Bronsted acid catalysis. *Science* **2016,** *351* (6276), 961-965.

40. Zhou, F. T.; Yamamoto, H., A Powerful Chiral Phosphoric Acid Catalyst for Enantioselective Mukaiyama-Mannich Reactions. *Angew. Chem., Int. Ed.* **2016,** *55* (31), 8970-8974.

41. Grossmann, O.; Maji, R.; Aukland, M. H.; Lee, S.; List, B., Catalytic Asymmetric Additions of Enol Silanes to In Situ Generated Cyclic, Aliphatic N-Acyliminium Ions. *Angew. Chem., Int. Ed.* **2022,** *61* (9), e202115036.

2.1.5 Other Nucleophiles for Imine Addition

1. Yao, S. L.; Fang, X. M.; Jorgensen, K. A., Catalytic enantioselective ene reactions of imines: a simple approach for the formation of optically active alpha-amino acids. *Chem. Comm.* **1998,** (22), 2547-2548.
2. Sigman, M. S.; Jacobsen, E. N., Schiff base catalysts for the asymmetric Strecker reaction identified and optimized from parallel synthetic libraries. *J. Am. Chem. Soc.* **1998,** *120* (19), 4901-4902.
3. Fang, X. M.; Johannsen, M.; Yao, S. L.; Gathergood, N.; Hazell, R. G.; Jorgensen, K. A., Catalytic approach for the formation of optically active allyl alpha-amino acids by addition of allylic metal compounds to alpha-imino esters. *J. Org. Chem.* **1999,** *64* (13), 4844-4849.
4. Saaby, S.; Fang, X. M.; Gathergood, N.; Jorgensen, K. A., Formation of optically active aromatic alpha-amino acids by catalytic enantioselective addition of imines to aromatic compounds. *Angew. Chem., Int. Ed.* **2000,** *39* (22), 4114-4116.
5. Vachal, P.; Jacobsen, E. N., Enantioselective catalytic addition of HCN to ketoimines. Catalytic synthesis of quaternary amino acids. *Org. Lett.* **2000,** *2* (6), 867-870.
6. Gastner, T.; Ishitani, H.; Akiyama, R.; Kobayashi, S., Highly enantioselective allylation of imines with a chiral zirconium catalyst. *Angew. Chem., Int. Ed.* **2001,** *40* (10), 1896-1898.

7. Kagoshima, H.; Uzawa, T.; Akiyama, T., Catalytic, enantioselective propargyl- and allenylation reactions of alpha-imino ester. *Chem. Lett.* **2002,** (3), 298-299.
8. Saaby, S.; Bayon, P.; Aburel, P. S.; Jorgensen, K. A., Optically active aromatic and heteroaromatic alpha-amino acids by a one-pot catalytic enantioselective addition of aromatic and heteroaromatic C-H bonds to alpha-imino esters. *J. Org. Chem.* **2002,** *67* (12), 4352-4361.
9. Vachal, P.; Jacobsen, E. N., Structure-based analysis and optimization of a highly enantioselective catalyst for the Strecker reaction. *J. Am. Chem. Soc.* **2002,** *124* (34), 10012-10014.
10. Akiyama, T.; Daidouji, K.; Fuchibe, K., Cu(I)-catalyzed enantioselective 2+2 cycloaddition of 1- methoxyallenylsilane with alpha-imino ester: Chiral synthesis of alpha,beta-unsaturated acylsilanes. *Org. Lett.* **2003,** *5* (20), 3691-3693.
11. Timen, A. S.; Somfai, P., Investigation of Lewis acid-catalyzed asymmetric aza-Diels- Alder reactions of 2H-azirines. *J. Org. Chem.* **2003,** *68* (26), 9958-9963.
12. Mancheno, O. G.; Arrayas, R. G.; Carretero, J. C., Chiral copper complexes of phosphino sulfenyl ferrocenes as efficient catalysts for enantioselective formal Aza Diels-Alder reactions of N-sulfonyl Imines. *J. Am. Chem. Soc.* **2004,** *126* (2), 456-457.
13. Taylor, M. S.; Jacobsen, E. N., Highly enantioselective catalytic acyl-Pictet-Spengler reactions. *J. Am. Chem. Soc.* **2004,** *126* (34), 10558-10559.
14. Uraguchi, D.; Sorimachi, K.; Terada, M., Organocatalytic asymmetric aza-Friedel-Crafts alkylation of furan. *J. Am. Chem. Soc.* **2004,** *126* (38), 11804-11805.
15. Joly, G. D.; Jacobsen, E. N., Thiourea-catalyzed enantioselective hydrophosphonylation of imines: Practical access to enantiomerically enriched alpha-amino phosphonic acids. *J. Am. Chem. Soc.* **2004,** *126* (13), 4102-4103.
16. Adolfsson, H., Organocatalytic hydride transfers: A new concept in asymmetric hydrogenations. *Angew. Chem., Int. Ed.* **2005,** *44* (22), 3340-3342.
17. Akiyama, T.; Morita, H.; Itoh, J.; Fuchibe, K., Chiral Bronsted acid catalyzed enantioselective hydrophosphonylation of imines: Asymmetric synthesis of alpha-amino phosphonates. *Org. Lett.* **2005,** *7* (13), 2583-2585.
18. Hoffmann, S.; Seayad, A. M.; List, B., A powerful bronsted acid catalyst for the organocatalytic asymmetric transfer hydrogenation of imines. *Angew. Chem., Int. Ed.* **2005,** *44* (45), 7424-7427.
19. Huang, Y. J.; Yang, F. Y.; Zhu, C. J., Highly enantioseletive biginelli reaction using a new chiral ytterbium catalyst: Asymmetric synthesis of dihydropyrimidines. *J. Am. Chem. Soc.* **2005,** *127* (47), 16386-16387.
20. Itoh, T.; Miyazaki, M.; Fukuoka, H.; Nagata, K.; Ohsawa, A., Formal total synthesis of (-)-emetine using catalytic asymmetric allylation of cyclic imines as a key step. *Org. Lett.* **2006,** *8* (7), 1295-1297.
21. Kiyohara, H.; Nakamura, Y.; Matsubara, R.; Kobayashi, S., Enantiomerically enriched allylglycine derivatives through the catalytic asymmetric allylation of iminoesters and iminophosphonates with allylsilanes. *Angew. Chem., Int. Ed.* **2006,** *45* (10), 1615-1617.
22. Hoffmann, S.; Nicoletti, M.; List, B., Catalytic asymmetric reductive amination of aldehydes via dynamic kinetic resolution. *J. Am. Chem. Soc.* **2006,** *128* (40), 13074-13075.
23. Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C., Enantioselective organocatalytic reductive amination. *J. Am. Chem. Soc.* **2006,** *128* (1), 84-86.
24. Terada, M.; Machioka, K.; Sorimachi, K., Chiral bronsted acid-catalyzed tandem aza-ene type reaction/cyclization cascade for a one-pot entry to enantioenriched piperidines. *J. Am. Chem. Soc.* **2007,** *129* (34), 10336-+.
25. Li, G. L.; Liang, Y. X.; Antilla, J. C., A vaulted biaryl phosphoric acid-catalyzed reduction of alpha-imino esters: The highly enantioselective preparation of alpha-amino esters. *J. Am. Chem. Soc.* **2007,** *129* (18), 5830-+.
26. Malkov, A. V.; Stoncius, S.; Kocovsky, P., Enantioselective synthesis of 1,2-diarylaziridines by the organocatalytic reductive amination of alpha-chloroketones. *Angew. Chem., Int. Ed.* **2007,** *46* (20), 3722-3724.
27. Newman, C. A.; Antilla, J. C.; Chen, P.; Predeus, A. V.; Fielding, L.; Wulff, W. D., Regulation of orthogonal functions in a dual catalyst system. Subservient role of a nonchiral lewis acid in an asymmetric catalytic heteroatom diels-alder reaction. *J. Am. Chem. Soc.* **2007,** *129* (23), 7216-+.
28. Wanner, M. J.; van der Haas, R. N. S.; de Cuba, K. R.; van Maarseveen, J. H.; Hiemstra, H., Catalytic asymmetric Pictet-Spengler reactions via sulfenyliminium ions. *Angew. Chem., Int. Ed.* **2007,** *46* (39), 7485-7487.
29. Negru, M.; Schollmeyer, D.; Kunz, H., Enantioselective Strecker reaction catalyzed by an organocatalyst lacking a hydrogen-bond-donor function. *Angew. Chem., Int. Ed.* **2007,** *46* (48), 9339-9341.
30. Raheem, I. T.; Thiara, P. S.; Peterson, E. A.; Jacobsen, E. N., Enantioselective pictet-spengler-type cyclizations of hydroxylactams: H-bond donor catalysis by anion binding. *J. Am. Chem. Soc.* **2007,** *129* (44), 13404-+.
31. Shang, D. J.; Xin, J. G.; Liu, Y. L.; Zhou, X.; Liu, X. H.; Feng, X. M., Enantioselective aza-Diels-Alder reaction of aldimines with "Danishefsky-Type Diene" catalyzed by chiral scandium(III)-N,N '-dioxide complexes. *J. Org. Chem.* **2008,** *73* (2), 630-637.
32. Kang, Q.; Zheng, X. H.; You, S. L., Highly enantioselective Friedel-Crafts reaction of 4,7-dihydroindoles with imines by chiral phosphoric acids: Facile access to 2-indolyl methanamine derivatives. *Chem. Eur. J.* **2008,** *14* (12), 3539-3542.
33. Raheem, I. T.; Thiara, P. S.; Jacobsen, E. N., Regio- and enantioselective catalytic cyclization of pyrroles onto N-acyliminium ions. *Org. Lett.* **2008,** *10* (8), 1577-1580.
34. Sickert, M.; Schneider, C., The enantioselective, Bronsted acid catalyzed, vinylogous Mannich reaction. *Angew. Chem., Int. Ed.* **2008,** *47* (19), 3631-3634.
35. Rueping, M.; Antonchick, A. P., Bronsted-acid-catalyzed activation of nitroalkanes: A direct enantioselective aza-Henry reaction. *Org. Lett.* **2008,** *10* (9), 1731-1734.
36. Hashimoto, T.; Hirose, M.; Maruoka, K., Asymmetric imino aza-enamine reaction catalyzed by axially chiral dicarboxylic acid: Use of arylaldehyde N,N-dialkylhydrazones as acyl anion equivalent. *J. Am. Chem. Soc.* **2008,** *130* (24), 7556-+.
37. Rueping, M.; Antonchick, A. P., A highly enantioselective Bronsted acid catalyzed reaction cascade. *Angew. Chem., Int. Ed.* **2008,** *47* (31), 5836-5838.
38. Enders, D.; Narine, A. A.; Toulgoat, F.; Bisschops, T., Asymmetric Bronsted acid catalyzed isoindoline synthesis: Enhancement of enantiomeric ratio by stereoablative kinetic resolution. *Angew. Chem., Int. Ed.* **2008,** *47* (30), 5661-5665.
39. Cheng, X.; Goddard, R.; Buth, G.; List, B., Direct catalytic asymmetric three-component Kabachnik-Fields reaction. *Angew. Chem., Int. Ed.* **2008,** *47* (27), 5079-5081.
40. Simon, L.; Goodman, J. M., Theoretical study of the mechanism of Hantzsch ester hydrogenation of imines catalyzed by chiral BINOL-phosphoric acids. *J. Am. Chem. Soc.* **2008,** *130* (27), 8741-8747.

41. Alonso, I.; Esquivias, J.; Gomez-Arrayas, R.; Carretero, J. C., Understanding the behavior of N-tosyl and N-2-pyridylsulfonyl Imines in Cu-II-Catalyzed aza-friedel-crafts reactions. *J. Org. Chem.* **2008,** *73* (16), 6401-6404.
42. Li, G. L.; Fronczek, F. R.; Antilla, J. C., Catalytic asymmetric addition of alcohols to imines: Enantioselective preparation of chiral N,O-aminals. *J. Am. Chem. Soc.* **2008,** *130* (37), 12216-+.
43. Cheng, X.; Vellalath, S.; Goddard, R.; List, B., Direct Catalytic Asymmetric Synthesis of Cyclic Aminals from Aldehydes. *J. Am. Chem. Soc.* **2008,** *130* (47), 15786-+.
44. Zhang, Y.; Lu, Z. J.; Desai, A.; Wulff, W. D., Mapping the Active Site in a Chemzyme: Diversity in the N-Substituent in the Catalytic Asymmetric Aziridination of Imines. *Org. Lett.* **2008,** *10* (23), 5429-5432.
45. Rueping, M.; Antonchick, A. P.; Sugiono, E.; Grenader, K., Asymmetric Bronsted Acid Catalysis: Catalytic Enantioselective Synthesis of Highly Biologically Active Dihydroquinazolinones. *Angew. Chem., Int. Ed.* **2009,** *48* (5), 908-910.
46. Schrader, W.; Handayani, P. P.; Zhou, J.; List, B., Characterization of Key Intermediates in a Complex Organocatalytic Cascade Reaction Using Mass Spectrometry. *Angew. Chem., Int. Ed.* **2009,** *48* (8), 1463-1466.
47. Klausen, R. S.; Jacobsen, E. N., Weak Bronsted Acid-Thiourea Co-catalysis: Enantioselective, Catalytic Protio-Pictet-Spengler Reactions. *Org. Lett.* **2009,** *11* (4), 887-890.
48. Marcelli, T.; Hammar, P.; Himo, F., Origin of Enantioselectivity in the Organocatalytic Reductive Amination of alpha-Branched Aldehydes. *Adv. Synth. Catal.* **2009,** *351* (4), 525-529.
49. Terada, M.; Toda, Y., Double Bond Isomerization/Enantioselective Aza-Petasis-Ferrier Rearrangement Sequence as an Efficient Entry to Anti- and Enantioenriched beta-Amino Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (18), 6354-+.
50. Akiyama, T.; Suzuki, T.; Mori, K., Enantioselective Aza-Darzens Reaction Catalyzed by A Chiral Phosphoric Acid. *Org. Lett.* **2009,** *11* (11), 2445-2447.
51. Han, Z. Y.; Xiao, H.; Chen, X. H.; Gong, L. Z., Consecutive Intramolecular Hydroamination/Asymmetric Transfer Hydrogenation under Relay Catalysis of an Achiral Gold Complex/Chiral Bronsted Acid Binary System. *J. Am. Chem. Soc.* **2009,** *131* (26), 9182-+.
52. Peterson, E. A.; Jacobsen, E. N., Enantioselective, Thiourea-Catalyzed Intermolecular Addition of Indoles to Cyclic N-Acyl Iminium Ions. *Angew. Chem., Int. Ed.* **2009,** *48* (34), 6328-6331.
53. Muratore, M. E.; Holloway, C. A.; Pilling, A. W.; Storer, R. I.; Trevitt, G.; Dixon, D. J., Enantioselective Bronsted Acid-Catalyzed N-Acyliminium Cyclization Cascades. *J. Am. Chem. Soc.* **2009,** *131* (31), 10796-+.
54. Yue, T.; Wang, M. X.; Wang, D. X.; Masson, G.; Zhu, J. P., Bronsted Acid Catalyzed Enantioselective Three-Component Reaction Involving the alpha Addition of Isocyanides to Imines. *Angew. Chem., Int. Ed.* **2009,** *48* (36), 6717-6721.
55. Liu, X. Y.; Che, C. M., Highly Enantioselective Synthesis of Chiral Secondary Amines by Gold(I)/Chiral Bronsted Acid Catalyzed Tandem Intermolecular Hydroamination and Transfer Hydrogenation Reactions. *Org. Lett.* **2009,** *11* (18), 4204-4207.
56. Zhu, C.; Akiyama, T., Benzothiazoline: Highly Efficient Reducing Agent for the Enantioselective Organocatalytic Transfer Hydrogenation of Ketimines. *Org. Lett.* **2009,** *11* (18), 4180-4183.
57. Jones, C. R.; Pantos, G. D.; Morrison, A. J.; Smith, M. D., Plagiarizing Proteins: Enhancing Efficiency in Asymmetric Hydrogen-Bonding Catalysis through Positive Cooperativity. *Angew. Chem., Int. Ed.* **2009,** *48* (40), 7391-7394.
58. Li, N.; Chen, X. H.; Song, J.; Luo, S. W.; Fan, W.; Gong, L. Z., Highly Enantioselective Organocatalytic Biginelli and Biginelli-Like Condensations: Reversal of the Stereochemistry by Tuning the 3,3 '-Disubstituents of Phosphoric Acids. *J. Am. Chem. Soc.* **2009,** *131* (42), 15301-15310.
59. Hu, G.; Huang, L.; Huang, R. H.; Wulff, W. D., Evidence for a Boroxinate Based Bronsted Acid Derivative of VAPOL as the Active Catalyst in the Catalytic Asymmetric Aziridination Reaction. *J. Am. Chem. Soc.* **2009,** *131* (43), 15615-+.
60. Rueping, M.; Sugiono, E.; Schoepke, F. R., Thieme Chemistry Journal Awardees - Where Are They Now? Asymmetric Bronsted Acid Catalyzed Transfer Hydrogenations. *Synlett* **2010,** (6), 852-865.
61. Li, G. L.; Kaplan, M. J.; Wojtas, L.; Antilla, J. C., Chiral Phosphoric Acid Catalyzed Addition of Dihydropyrans to N-Acyl Imines: Stereocontrolled Access to Enantioenriched Spirocyclic Oxazoletetrahydropyrans with Three Contiguous Stereocenters. *Org. Lett.* **2010,** *12* (9), 1960-1963.
62. Wakchaure, V. N.; Zhou, J. A.; Hoffmann, S.; List, B., Catalytic Asymmetric Reductive Amination of alpha-Branched Ketones. *Angew. Chem., Int. Ed.* **2010,** *49* (27), 4612-4614.
63. Rueping, M.; Stoeckel, M.; Sugiono, E.; Theissmann, T., Asymmetric metal-free synthesis of fluoroquinolones by organocatalytic hydrogenation. *Tetrahedron* **2010,** *66* (33), 6565-6568.
64. Rueping, M.; Theissmann, T., Asymmetric Bronsted acid catalysis in aqueous solution. *Chemical Science* **2010,** *1* (4), 473-476.
65. Rueping, M.; Brinkmann, C.; Antonchick, A. P.; Atodiresei, I., Asymmetric Synthesis of Indolines by Catalytic Enantioselective Reduction of 3H-Indoles. *Org. Lett.* **2010,** *12* (20), 4604-4607.
66. Holloway, C. A.; Muratore, M. E.; Storer, R. I.; Dixon, D. J., Direct Enantioselective Bronsted Acid Catalyzed N-Acyliminium Cyclization Cascades of Tryptamines and Ketoacids. *Org. Lett.* **2010,** *12* (21), 4720-4723.
67. Rueping, M.; Raja, S.; Nunez, A., Asymmetric Bronsted Acid-Catalyzed Friedel-Crafts Reactions of Indoles with Cyclic Imines - Efficient Generation of Nitrogen-Substituted Quaternary Carbon Centers. *Adv. Synth. Catal.* **2011,** *353* (4), 563-568.
68. Terada, M.; Kanomata, K., Metal-Free Chiral Phosphoric Acid or Chiral Metal Phosphate as Active Catalyst in the Activation of N-Acyl Aldimines. *Synlett* **2011,** (9), 1255-1258.
69. Fleischmann, M.; Drettwan, D.; Sugiono, E.; Rueping, M.; Gschwind, R. M., Bronsted Acid Catalysis: Hydrogen Bonding versus Ion Pairing in Imine Activation. *Angew. Chem., Int. Ed.* **2011,** *50* (28), 6364-6369.
70. Hashimoto, T.; Nakatsu, H.; Yamamoto, K.; Maruoka, K., Chiral Bronsted Acid-Catalyzed Asymmetric Trisubstituted Aziridine Synthesis Using alpha-Diazoacyl Oxazolidinones. *J. Am. Chem. Soc.* **2011,** *133* (25), 9730-9733.
71. Henseler, A.; Kato, M.; Mori, K.; Akiyama, T., Chiral Phosphoric Acid Catalyzed Transfer Hydrogenation: Facile Synthetic Access to Highly Optically Active Trifluoromethylated Amines. *Angew. Chem., Int. Ed.* **2011,** *50* (35), 8180-8183.
72. Lee, Y.; Klausen, R. S.; Jacobsen, E. N., Thiourea-Catalyzed Enantioselective Iso-Pictet-Spengler Reactions. *Org. Lett.* **2011,** *13* (20), 5564-5567.
73. Ren, L.; Lei, T.; Ye, J. X.; Gong, L. Z., Step-Economical Synthesis of Tetrahydroquinolines by Asymmetric Relay Catalytic Friedlander Condensation/Transfer Hydrogenation. *Angew. Chem., Int. Ed.* **2012,** *51* (3), 771-774.
74. Dagousset, G.; Retailleau, P.; Masson, G.; Zhu, J. P., Chiral Phosphoric Acid-Catalyzed Enantioselective Three-Component Povarov Reaction Using Cyclic Enethioureas as Dienophiles: Stereocontrolled Access to Enantioenriched Hexahydropyrroloquinolines. *Chem. Eur. J.* **2012,** *18* (19), 5869-5873.

75. Hashimoto, T.; Kimura, H.; Kawamata, Y.; Maruoka, K., A Catalytic Asymmetric Ugi-type Reaction With Acyclic Azomethine Imines. *Angew. Chem., Int. Ed.* **2012,** *51* (29), 7279-7281.
76. Su, Y. P.; Bouma, M. J.; Alcaraz, L.; Stocks, M.; Furber, M.; Masson, G.; Zhu, J. P., Organocatalytic Enantioselective One-Pot Four-Component Ugi-Type Multicomponent Reaction for the Synthesis of Epoxy-tetrahydropyrrolo 3,4-b pyridin-5-ones. *Chem. Eur. J.* **2012,** *18* (40), 12624-12627.
77. Gandhi, S.; List, B., Catalytic Asymmetric Three-Component Synthesis of Homoallylic Amines. *Angew. Chem., Int. Ed.* **2013,** *52* (9), 2573-2576.
78. Zhao, J. N.; Liu, X. H.; Luo, W. W.; Xie, M. S.; Lin, L. L.; Feng, X. M., Asymmetric Synthesis of beta-Amino Nitriles through a Sc-III-Catalyzed Three-Component Mannich Reaction of Silyl Ketene Imines. *Angew. Chem., Int. Ed.* **2013,** *52* (12), 3473-3477.
79. Schafer, A. G.; Wieting, J. M.; Fisher, T. J.; Mattson, A. E., Chiral Silanediols in Anion-Binding Catalysis. *Angew. Chem., Int. Ed.* **2013,** *52* (43), 11321-11324.
80. Neel, A. J.; Hehn, J. P.; Tripet, P. F.; Toste, F. D., Asymmetric Cross-Dehydrogenative Coupling Enabled by the Design and Application of Chiral Triazole-Containing Phosphoric Acids. *J. Am. Chem. Soc.* **2013,** *135* (38), 14044-14047.
81. Bergonzini, G.; Schindler, C. S.; Wallentin, C. J.; Jacobsen, E. N.; Stephenson, C. R. J., Photoredox activation and anion binding catalysis in the dual catalytic enantioselective synthesis of bamino esters. *Chemical Science* **2014,** *5* (1), 112-116.
82. Zhao, W.; Huang, L.; Guan, Y.; Wulff, W. D., Three- Component Asymmetric Catalytic Ugi Reaction- Concinnity from Diversity by Substrate- Mediated Catalyst Assembly. *Angew. Chem., Int. Ed.* **2014,** *53* (13), 3436-3441.
83. Cheng, D.-J.; Yan, L.; Tian, S.-K.; Wu, M.-Y.; Wang, L.-X.; Fan, Z.-L.; Zheng, S.-C.; Liu, X.-Y.; Tan, B., Highly Enantioselective Kinetic Resolution of Axially Chiral BINAM Derivatives Catalyzed by a Bronsted Acid. *Angew. Chem., Int. Ed.* **2014,** *53* (14), 3684-3687.
84. Yu, P.; Lin, J.-S.; Li, L.; Zheng, S.-C.; Xiong, Y.-P.; Zhao, L.-J.; Tan, B.; Liu, X.-Y., Enantioselective C-H Bond Functionalization Triggered by Radical Trifluoromethylation of Unactivated Alkene. *Angew. Chem., Int. Ed.* **2014,** *53* (44), 11890-11894.
85. Zheng, H. F.; Liu, X. H.; Xu, C. R.; Xia, Y.; Lin, L. L.; Feng, X. M., Regio- and Enantioselective Aza-Diels-Alder Reactions of 3-Vinylindoles: A Concise Synthesis of the Antimalarial Spiroindolone NITD609. *Angew. Chem., Int. Ed.* **2015,** *54* (37), 10958-10962.
86. Liu, R. R.; Ye, S. C.; Lu, C. J.; Zhuang, G. L.; Gao, J. R.; Jia, Y. X., Dual Catalysis for the Redox Annulation of Nitroalkynes with Indoles: Enantioselective Construction of Indolin-3-ones Bearing Quaternary Stereocenters. *Angew. Chem., Int. Ed.* **2015,** *54* (38), 11205-11208.
87. Yu, J.; Jiang, H. J.; Zhou, Y.; Luo, S. W.; Gong, L. Z., Sodium Salts of Anionic Chiral Cobalt(III) Complexes as Catalysts of the Enantioselective Povarov Reaction. *Angew. Chem., Int. Ed.* **2015,** *54* (38), 11209-11213.
88. Xu, X. M.; Zhao, L.; Zhu, J. P.; Wang, M. X., Catalytic Asymmetric Tandem Reaction of Tertiary Enamides: Expeditious Synthesis of Pyrrolo 2,1-a isoquinoline Alkaloid Derivatives. *Angew. Chem., Int. Ed.* **2016,** *55* (11), 3799-3803.
89. Wakchaure, V. N.; List, B., Catalytic Asymmetric Reductive Condensation of N-H Imines: Synthesis of C-2-Symmetric Secondary Amines. *Angew. Chem., Int. Ed.* **2016,** *55* (51), 15775-15778.
90. Liu, R. R.; Hu, J. P.; Hong, J. J.; Lu, C. J.; Gao, J. R.; Jia, Y. X., Enantioselective 2+2 cycloaddition of N-allenamides with cyclic N-sulfonylketimines: access to polysubstituted azetidines bearing quaternary stereocenters. *Chemical Science* **2017,** *8* (4), 2811-2815.
91. Wang, S. G.; Xia, Z. L.; Xu, R. Q.; Liu, X. J.; Zheng, C.; You, S. L., Construction of Chiral Tetrahydro-beta-Carbolines: Asymmetric Pictet-Spengler Reaction of Indolyl Dihydropyridines. *Angew. Chem., Int. Ed.* **2017,** *56* (26), 7440-7443.
92. Yu, Y. Y.; Li, J. W.; Jiang, L.; Zhang, J. R.; Zu, L. S., Catalytic Enantioselective Aza-pinacol Rearrangement. *Angew. Chem., Int. Ed.* **2017,** *56* (31), 9217-9221.
93. Hu, G.; Gupta, A. K.; Huang, L.; Zhao, W. J.; Yin, X. P.; Osminski, W. E. G.; Huang, R. H.; Wulif, W. D.; Izzo, J. A.; Vetticatt, M. J., Pyro-Borates, Spiro-Borates, and Boroxinates of BINOL-Assembly, Structures, and Reactivity. *J. Am. Chem. Soc.* **2017,** *139* (30), 10267-10285.
94. Adams, M. R.; Tien, C. H.; McDonald, R.; Speed, A. W. H., Asymmetric Imine Hydroboration Catalyzed by Chiral Diazaphospholenes. *Angew. Chem., Int. Ed.* **2017,** *56* (52), 16660-16663.
95. Bendelsmith, A. J.; Kim, S. C.; Wasa, M.; Roche, S. P.; Jacobsen, E. N., Enantioselective Synthesis of alpha-Allyl Amino Esters via Hydrogen-Bond-Donor Catalysis. *J. Am. Chem. Soc.* **2019,** *141* (29), 11414-11419.
96. Lynch-Colameta, T.; Greta, S.; Snyder, S. A., Synthesis of aza-quaternary centers via Pictet–Spengler reactions of ketonitrones. *Chemical Science* **2021,** *12* (17), 6181-6187.
97. Ronchi, E.; Paradine, S. M.; Jacobsen, E. N., Enantioselective, Catalytic Multicomponent Synthesis of Homoallylic Amines Enabled by Hydrogen-Bonding and Dispersive Interactions. *J. Am. Chem. Soc.* **2021,** *143* (19), 7272-7278.
98. Das, S.; Mitschke, B.; De, C. K.; Harden, I.; Bistoni, G.; List, B., Harnessing the ambiphilicity of silyl nitronates in a catalytic asymmetric approach to aliphatic β3-amino acids. *Nature Catalysis* **2021,** *4* (12), 1043-1049.
99. Scharf, M. J.; List, B., A Catalytic Asymmetric Pictet–Spengler Platform as a Biomimetic Diversification Strategy toward Naturally Occurring Alkaloids. *J. Am. Chem. Soc.* **2022,** *144* (34), 15451-15456.
100. Wang, L.; Gao, F.; Zhang, X.; Peng, T.; Xu, Y.; Wang, R.; Yang, D., Concerted Enantioselective [2+2] Cycloaddition Reaction of Imines Mediated by a Magnesium Catalyst. *J. Am. Chem. Soc.* **2023,** *145* (1), 610-625.
101. Zhong, Z.; Wu, H.; Chen, X.; Luo, Y.; Yang, L.; Feng, X.; Liu, X., Visible-Light-Promoted Enantioselective Acylation and Alkylation of Aldimines Enabled by 9-Fluorenone Electron-Shuttle Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (29), 20401-20413.
102. Scharf, M. J.; Tsuji, N.; Lindner, M. M.; Leutzsch, M.; Lõkov, M.; Parman, E.; Leito, I.; List, B., Highly Acidic Electron-Rich Brønsted Acids Accelerate Asymmetric Pictet–Spengler Reactions by Virtue of Stabilizing Cation–π Interactions. *J. Am. Chem. Soc.* **2024,** *146* (41), 28339-28349.
103. Guillén, M.; Leutzsch, M.; List, B., Catalytic Asymmetric Cycloaddition of Olefins with In Situ Generated N-Boc-Formaldimine. *J. Am. Chem. Soc.* **2024,** *146* (47), 32292-32297.

2.1.6 Others

1. Enders, D.; Reinhold, U., Asymmetric synthesis of amines by nucleophilic 1,2-addition of organometallic reagents to the CN-double bond. *Tetrahedron-Asymmetry* **1997,** *8* (12), 1895-1946.

2. Kobayashi, S.; Ishitani, H., Catalytic enantioselective addition to imines. *Chem. Rev* **1999,** *99* (5), 1069-1094.

3. Kobayashi, S.; Hamada, T.; Manabe, K., The catalytic asymmetric Mannich-type reactions in aqueous media. *J. Am. Chem. Soc.* **2002,** *124* (20), 5640-5641.

4. Murahashi, S.; Imada, Y.; Kawakami, T.; Harada, K.; Yonemushi, Y.; Tomita, N., Enantioselective addition of ketene silyl acetals to nitrones catalyzed by chiral titanium complexes. Synthesis of optically active beta-amino acids. *J. Am. Chem. Soc.* **2002,** *124* (12), 2888-2889.

5. Doherty, S.; Newman, C. R.; Rath, R. K.; Luo, H. K.; Nieuwenhuyzen, M.; Knight, J. G., Highly efficient asymmetric lewis acid catalysis with platinum group complexes of conformationally flexible 1,3-butadiene- bridged diphosphines, NUPHOS. *Org. Lett.* **2003,** *5* (21), 3863-3866.

6. McDougal, N. T.; Schaus, S. E., Asymmetric Morita-Baylis-Hillman reactions catalyzed by chiral Bronsted acids. *J. Am. Chem. Soc.* **2003,** *125* (40), 12094-12095.

7. Alezra, V.; Bernardinelli, G.; Corminboeuf, C.; Frey, U.; Kundig, E. P.; Merbach, A. E.; Saudan, C. M.; Viton, F.; Weber, J., CpRu((R)-Binop-F)(H2O) SbF6 , a new fluxional chiral lewis acid catalyst: Synthesis, dynamic NMR, asymmetric catalysis, and theoretical studies. *J. Am. Chem. Soc.* **2004,** *126* (15), 4843-4853.

8. Hamada, T.; Manabe, K.; Kodayashi, S., Enantio- and diastereoselective, stereospecific Mannich-type reactions in water. *J. Am. Chem. Soc.* **2004,** *126* (25), 7768-7769.

9. Keith, J. M.; Jacobsen, E. N., Asymmetric hydrocyanation of hydrazones catalyzed by lanthanide-PYBOX complexes. *Org. Lett.* **2004,** *6* (2), 153-155.

10. Pihko, P. M., Activation of carbonyl compounds by double hydrogen bonding: An emerging tool in asymmetric catalysis. *Angew. Chem., Int. Ed.* **2004,** *43* (16), 2062-2064.

11. Bolm, C.; Rantanen, T.; Schiffers, I.; Zani, L., Protonated chiral catalysts: Versatile tools for asymmetric synthesis. *Angew. Chem., Int. Ed.* **2005,** *44* (12), 1758-1763.

12. Yamamoto, H.; Futatsugi, K., "Designer acids": Combined acid catalysis for asymmetric synthesis. *Angew. Chem., Int. Ed.* **2005,** *44* (13), 1924-1942.

13. Jang, D. O.; Kim, S. Y., Highly Enantioselective Radical Addition to N-Benzoyl Hydrazones Using Chiral Ammonium Salts. *J. Am. Chem. Soc.* **2008,** *130* (48), 16152-+.

14. Minato, D.; Nagasue, Y.; Demizu, Y.; Onomura, S., Effecient Kinetic Resolution of Racemic Amino Aldehydes by Oxidation with N-Iodosuccinimide. *Angew. Chem., Int. Ed.* **2008,** *47* (49), 9458-9461.

15. Terada, M., Binaphthol-derived phosphoric acid as a versatile catalyst for enantioselective carbon-carbon bond forming reactions. *Chem. Comm.* **2008,** (35), 4097-4112.

16. Xu, S.; Wang, Z.; Zhang, X.; Zhang, X.; Ding, K., Chiral Bronsted acid catalyzed asymmetric Baeyer-Villiger reaction of 3-substituted cyclobutanones by using aqueous H2O2. *Angew. Chem., Int. Ed.* **2008,** *47* (15), 2840-2843.

17. Chen, J. H.; Liao, S. H.; Sun, X. L.; Shen, Q.; Tang, Y., Tris(oxazoline)/copper-catalyzed coupling of alkynes with nitrones: a highly enantioselective access to beta-lactams. *Tetrahedron* **2012,** *68* (25), 5042-5045.

18. Zhou, H.; Bae, H. Y.; Leutzsch, M.; Kennemur, J. L.; Bécart, D.; List, B., The Silicon–Hydrogen Exchange Reaction: A Catalytic σ-Bond Metathesis Approach to the Enantioselective Synthesis of Enol Silanes. *J. Am. Chem. Soc.* **2020,** *142* (32), 13695-13700.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

2. LUMO Activaiton

2.2 Lewis and Brønsted acids activation of extended p- systems of carbonyl and imines

2.2.1 Conjugate (Michael) Addition

1. Sibi, M. P.; Ji, J. G.; Wu, J. H.; Gurtler, S.; Porter, N. A., Chiral Lewis acid catalysis in radical reactions: Enantioselective conjugate radical additions. *J. Am. Chem. Soc.* **1996,** *118* (38), 9200-9201.

2. Sibi, M. P.; Shay, J. J.; Liu, M.; Jasperse, C. P., Chiral Lewis acid catalysis in conjugate additions of O-benzylhydroxylamine to unsaturated amides. Enantioselective synthesis of beta-amino acid precursors. *J. Am. Chem. Soc.* **1998,** *120* (26), 6615-6616.

3. Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Tedrow, J. S., C-2-symmetric Cu(II) complexes as chiral Lewis acids. Catalytic enantioselective Michael addition of silylketene acetals to alkylidene malonates. *J. Am. Chem. Soc.* **1999,** *121* (9), 1994-1995.

4. Kanemasa, S.; Oderaotoshi, Y.; Wada, E., Asymmetric conjugate addition of thiols to a 3-(2-alkenoyl)-2-oxazolidinone catalyzed by the DBFOX/Ph aqua complex of nickel(II) perchlorate. *J. Am. Chem. Soc.* **1999,** *121* (37), 8675-8676.

5. Myers, J. K.; Jacobsen, E. N., Asymmetric synthesis of beta-amino acid derivatives via catalytic conjugate addition of hydrazoic acid to unsaturated imides. *J. Am. Chem. Soc.* **1999,** *121* (38), 8959-8960.

6. Johnson, J. S.; Evans, D. A., Chiral bis(oxazoline) copper(II) complexes: Versatile catalysts for enantioselective cycloaddition, aldol, Michael, and carbonyl ene reactions. *Acc. Chem. Res.* **2000,** *33* (6), 325-335.

7. Sibi, M. P.; Asano, Y., Enantioselective conjugate addition of organomagnesium amides to enamidomalonates: Synthesis of either enantiomer of beta-amino acid derivatives. *J. Am. Chem. Soc.* **2001,** *123* (39), 9708-9709.

8. Sibi, M. P.; Manyem, S., Lanthanide Lewis acid-mediated enantioselective conjugate radical additions. *Org. Lett.* **2002,** *4* (17), 2929-2932.

9. Zhou, J.; Tang, Y., Sidearm effect: Improvement of the enantiomeric excess in the asymmetric Michael addition of indoles to alkylidene malonates. *J. Am. Chem. Soc.* **2002,** *124* (31), 9030-9031.

10. Annamalai, V.; DiMauro, E. F.; Carroll, P. J.; Kozlowski, M. C., Catalysis of the Michael addition reaction by late transition metal complexes of BINOL-derived salens. *J. Org. Chem.* **2003,** *68* (5), 1973-1981.

11. Bandini, M.; Fagioli, M.; Melchiorre, P.; Melloni, A.; Umani-Ronchi, A., Catalytic enantioselective conjugate addition of indoles to simple alpha,beta-unsaturated ketones. *Tetrahedron Lett.* **2003,** *44* (31), 5843-5846.

12. Evans, D. A.; Scheidt, K. A.; Fandrick, K. R.; Lam, H. W.; Wu, J., Enantioselective indole Friedel-Crafts alkylations catalyzed by bis(oxazolinyl)pyridine-scandium(III) triflate complexes. *J. Am. Chem. Soc.* **2003,** *125* (36), 10780-10781.

13. Sammis, G. M.; Jacobsen, E. N., Highly enantioselective, catalytic conjugate addition of cyanide to alpha,beta-unsaturated Imides. *J. Am. Chem. Soc.* **2003,** *125* (15), 4442-4443.

14. Sibi, M. P.; Prabagaran, N.; Ghorpade, S. G.; Jasperse, C. P., Enantioselective synthesis of alpha,beta-disubstituted-beta- amino acids. *J. Am. Chem. Soc.* **2003,** *125* (39), 11796-11797.

15. Sibi, M. P.; Zimmerman, J.; Rheault, T., Enantioselective conjugate radical addition to beta-acyloxy acrylate acceptors: An approach to acetate aldol-type products. *Angew. Chem., Int. Ed.* **2003,** *42* (37), 4521-4523.

16. Taylor, M. S.; Jacobsen, E. N., Enantioselective Michael additions to alpha,beta-unsaturated imides catalyzed by a Salen-Al complex. *J. Am. Chem. Soc.* **2003,** *125* (37), 11204-11205.

17. Bandini, M.; Melloni, A.; Umani-Ronchi, A., New catalytic approaches in the stereoselective Friedel-Crafts alkylation reaction. *Angew. Chem., Int. Ed.* **2004,** *43* (5), 550-556.

18. Sadow, A. D.; Haller, I.; Fadini, L.; Togni, A., Nickel(II)-catalyzed highly enantioselective hydrophosphination of methacrylonitrile. *J. Am. Chem. Soc.* **2004,** *126* (45), 14704-14705.

19. Vanderwall, C. D.; Jacobsen, E. N., Enantioselective formal hydration of alpha,beta-unsaturated imides by Al-catalyzed conjugate addition of oxime nucleophiles. *J. Am. Chem. Soc.* **2004,** *126* (45), 14724-14725.

20. Zhou, J.; Ye, M. C.; Huang, Z. Z.; Tang, Y., Controllable enantioselective Friedel-Crafts reaction between indoles and alkylidene malonates catalyzed by pseudo-C-3- symmetric trisoxazoline copper(II) complexes. *J. Org. Chem.* **2004,** *69* (4), 1309-1320.

21. Evans, D. A.; Fandrick, K. R.; Song, H. J., Enantioselective Friedel-Crafts alkylations of alpha-beta-unsaturated 2-acyl imidazoles catalyzed by bis(oxazolinyl)pyridine-scandium(III) triflate complexes. *J. Am. Chem. Soc.* **2005,** *127* (25), 8942-8943.

22. Evans, D. A.; Thomson, R. J.; Franco, F., Ni(II) Tol-BINAP-catalyzed enantioselective Michael reactions of beta-ketoesters and unsaturated N-acylthiazolidinethiones. *J. Am. Chem. Soc.* **2005,** *127* (31), 10816-10817.

23. Gandelman, M.; Jacobsen, E. N., Highly enantioselective catalytic conjugate addition of N-heterocycles to alpha,beta-unsaturated ketones and imides. *Angew. Chem., Int. Ed.* **2005,** *44* (16), 2393-2397.

24. Lyle, M. P. A.; Draper, N. D.; Wilson, P. D., Enantioselective Friedel-Crafts alkylation reactions catalyzed by a chiral nonracemic C-2-symmetric 2,2 '-bipyridyl copper(II) complex. *Org. Lett.* **2005,** *7* (5), 901-904.

25. Palomo, C.; Oiarbide, M.; Kardak, B. G.; Garcia, J. M.; Linden, A., Highly enantioselective Friedel-Crafts alkylations of pyrroles and indoles with alpha-hydroxy enones under Cu(II)-simple bis(oxazoline) catalysis. *J. Am. Chem. Soc.* **2005,** *127* (12), 4154-4155.

26. Sadow, A. D.; Togni, A., Enantioselective addition of secondary phosphines to methacrylonitrile: Catalysis and mechanism. *J. Am. Chem. Soc.* **2005,** *127* (48), 17012-17024.

27. Sibi, M. P.; Petrovic, G.; Zimmerman, J., Enantioselective radical addition/trapping reactions with alpha,beta-disubstituted unsaturated imides. Synthesis of anti-propionate aldols. *J. Am. Chem. Soc.* **2005,** *127* (8), 2390-2391.

28. Sibl, M. P.; Patil, K., Enantioselective H-atom transfer reaction: A strategy to synthesize formaldehyde aldol products. *Org. Lett.* **2005,** *7* (8), 1453-1456.

29. Taylor, M. S.; Zalatan, D. N.; Lerchner, A. M.; Jacobsen, E. N., Highly enantioselective conjugate additions to alpha,beta-unsaturated ketones catalyzed by a (Salen)Al complex. *J. Am. Chem. Soc.* **2005,** *127* (4), 1313-1317.

30. Evans, D. A.; Fandrick, K. R., Catalytic enantioselective pyrrole alkylations of alpha,beta-unsaturated 2-acyl imidazoles. *Org. Lett.* **2006,** *8* (11), 2249-2252.

31. Lee, S.; Lim, C. J.; Kim, S.; Subramaniam, R.; Zimmerman, J.; Sibi, M. P., Enantioselective conjugate radical addition to alpha '-hydroxy enones. *Org. Lett.* **2006,** *8* (19), 4311-4313.

32. Liu, D.; Hong, S. W.; Corey, E. J., Enantioselective synthesis of bridged- or fused-ring bicyclic ketones by a catalytic asymmetric Michael addition pathway. *J. Am. Chem. Soc.* **2006,** *128* (25), 8160-8161.

33. Monge, D.; Martin-Zamora, E.; Vazquez, J.; Alcarazo, M.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M., Enantioselective conjugate addition of N,N-dialkylhydrazones to alpha-hydroxy enones. *Org. Lett.* **2007,** *9* (15), 2867-2870.

34. Sibi, M. P.; Nad, S., Enantioselective radical reactions: Stereoselective aldol synthesis from cyclic ketones. *Angew. Chem., Int. Ed.* **2007,** *46* (48), 9231-9234.

35. Sibi, M. P.; Soeta, T., Enantioselective conjugate addition of hydrazines to alpha,beta-unsaturated imides. Synthesis of chiral pyrazolidinones. *J. Am. Chem. Soc.* **2007,** *129* (15), 4522-+.

36. Takenaka, N.; Abell, J. P.; Yamamoto, H., Asymmetric conjugate addition of silyl enol ethers catalyzed by tethered bis(8-quinolinolato) aluminum complexes. *J. Am. Chem. Soc.* **2007,** *129* (4), 742-743.

37. Arai, T.; Yokoyama, N., Tandem catalytic asymmetric Friedel-Crafts/Henry reaction: Control of three contiguous acyclic stereocenters. *Angew. Chem., Int. Ed.* **2008,** *47* (27), 4989-4992.

38. Itoh, J.; Fuchibe, K.; Akiyama, T., Chiral phosphoric acid catalyzed enantioselective Friedel-Crafts alkylation of indoles with nitroalkenes: Cooperative effect of 3 angstrom molecular sieves. *Angew. Chem., Int. Ed.* **2008,** *47* (21), 4016-4018.

39. Li, P. F.; Wang, Y. C.; Liang, X. M.; Ye, J. X., Asymmetric multifunctional organocatalytic Michael addition of nitroalkanes to alpha,beta-unsaturated ketones. *Chem. Comm.* **2008,** (28), 3302-3304.

40. Martin, N. J. A.; Cheng, X.; List, B., Organocatalytic asymmetric transferhydrogenation of beta-nitroacrylates: Accessing beta(2)-amino acids. *J. Am. Chem. Soc.* **2008,** *130* (42), 13862-13863.

41. Shi, M.; Liu, X. G., Asymmetric Morita-Baylis-Hillman reaction of arylaldehydes with 2-cyclohexen-1-one catalyzed by chiral bis(thio)urea and DABCO. *Org. Lett.* **2008,** *10* (6), 1043-1046.

42. Sibi, M. P.; Coulomb, J.; Stanley, L. M., Enantioselective Enolate Protonations: Friedel-Crafts Reactions with alpha-Substituted Acrylates. *Angew. Chem., Int. Ed.* **2008,** *47* (51), 9913-9915.

43. Wang, L. J.; Liu, X. H.; Dong, Z. H.; Fu, X.; Feng, X. M., Asymmetric Intramolecular Oxa-Michael Addition of Activated alpha,beta-Unsaturated Ketones Catalyzed by a Chiral N,N '-Dioxide Nickel(II) Complex: Highly Enantioselective Synthesis of Flavanones. *Angew. Chem., Int. Ed.* **2008,** *47* (45), 8670-8673.

44. Boersma, A. J.; Feringa, B. L.; Roelfes, G., Enantioselective Friedel-Crafts Reactions in Water Using a DNA-Based Catalyst. *Angew. Chem., Int. Ed.* **2009,** *48* (18), 3346-3348.

45. Cai, Q.; Zhao, Z. A.; You, S. L., Asymmetric Construction of Polycyclic Indoles through Olefin Cross-Metathesis/Intramolecular Friedel-Crafts Alkylation under Sequential Catalysis. *Angew. Chem., Int. Ed.* **2009,** *48* (40), 7428-7431.

46. Murarka, S.; Deb, I.; Zhang, C.; Seidel, D., Catalytic Enantioselective Intramolecular Redox Reactions: Ring-Fused Tetrahydroquinolines. *J. Am. Chem. Soc.* **2009,** *131* (37), 13226-+.

47. Sheng, Y. F.; Li, G. Q.; Kang, Q.; Zhang, A. J.; You, S. L., Asymmetric Friedel-Crafts Reaction of 4,7-Dihydroindoles with Nitroolefins by Chiral Bronsted Acids under Low Catalyst Loading. *Chem. Eur. J.* **2009,** *15* (14), 3351-3354.

48. Smith, S. W.; Fu, G. C., Asymmetric Carbon-Carbon Bond Formation gamma to a Carbonyl Group: Phosphine-Catalyzed Addition of Nitromethane to Allenes. *J. Am. Chem. Soc.* **2009,** *131* (40), 14231-+.

49. Uraguchi, D.; Nakashima, D.; Ooi, T., Chiral Arylaminophosphonium Barfates as a New Class of Charged Bronsted Acid for the Enantioselective Activation of Nonionic Lewis Bases. *J. Am. Chem. Soc.* **2009,** *131* (21), 7242-+.

50. Cai, Q. A.; Zheng, C.; You, S. L., Enantioselective Intramolecular Aza-Michael Additions of Indoles Catalyzed by Chiral Phosphoric Acids. *Angew. Chem., Int. Ed.* **2010,** *49* (46), 8666-8669.

51. Takenaka, N.; Chen, J. S.; Captain, B.; Sarangthem, R. S.; Chandrakumar, A., Helical Chiral 2-Aminopyridinium Ions: A New Class of Hydrogen Bond Donor Catalysts. *J. Am. Chem. Soc.* **2010,** *132* (13), 4536-+.

52. Wang, X. F.; Chen, J. R.; Cao, Y. J.; Cheng, H. G.; Xiao, W. J., An Enantioselective Approach to Highly Substituted Tetrahydrocarbazoles through Hydrogen Bonding-Catalyzed Cascade Reactions. *Org. Lett.* **2010,** *12* (5), 1140-1143.

53. Marques-Lopez, E.; Alcaine, A.; Tejero, T.; Herrera, R. P., Enhanced Efficiency of Thiourea Catalysts by External Bronsted Acids in the Friedel-Crafts Alkylation of Indoles. *Eur. J. Org. Chem.* **2011,** (20-21), 3700-3705.

54. Sparr, C.; Gilmour, R., Cyclopropyl Iminium Activation: Reactivity Umpolung in Enantioselective Organocatalytic Reaction Design. *Angew. Chem., Int. Ed.* **2011,** *50* (36), 8391-8395.

55. Wang, W. T.; Lian, X. J.; Chen, D. H.; Liu, X. H.; Lin, L. L.; Feng, X. M., Highly enantioselective yttrium(III)-catalyzed Friedel-Crafts alkylation of beta-trichloro(trifluoro)methyl aryl enones with indoles. *Chem. Comm.* **2011,** *47* (27), 7821-7823.

56. Wang, Z.; Yang, Z. G.; Chen, D. H.; Liu, X. H.; Lin, L. L.; Feng, X. M., Highly Enantioselective Michael Addition of Pyrazolin-5-ones Catalyzed by Chiral Metal/N,N '-Dioxide Complexes: Metal-Directed Switch in Enantioselectivity. *Angew. Chem., Int. Ed.* **2011,** *50* (21), 4928-4932.

57. Xu, X. F.; Hu, W. H.; Doyle, M. P., Highly Enantioselective Catalytic Synthesis of Functionalized Chiral Diazoacetoacetates. *Angew. Chem., Int. Ed.* **2011,** *50* (28), 6392-6395.

58. Kieffer, M. E.; Repka, L. M.; Reisman, S. E., Enantioselective Synthesis of Tryptophan Derivatives by a Tandem Friedel-Crafts Conjugate Addition/Asymmetric Protonation Reaction. *J. Am. Chem. Soc.* **2012,** *134* (11), 5131-5137.

59. Liu, L.; Ma, H. L.; Xiao, Y. M.; Du, F. P.; Qin, Z. H.; Li, N.; Fu, B., Highly enantioselective Friedel-Crafts alkylation of indoles and pyrrole with beta,gamma-unsaturated alpha-ketoesters catalyzed by heteroarylidene-tethered bis(oxazoline) copper complexes. *Chem. Comm.* **2012,** *48* (74), 9281-9283.

60. Arai, T.; Yamamoto, Y.; Awata, A.; Kamiya, K.; Ishibashi, M.; Arai, M. A., Catalytic Asymmetric Synthesis of Mixed 3,3 '-Bisindoles and Their Evaluation as Wnt Signaling Inhibitors. *Angew. Chem., Int. Ed.* **2013,** *52* (9), 2486-2490.

61. Cheng, H. G.; Lu, L. Q.; Wang, T.; Yang, Q. Q.; Liu, X. P.; Li, Y.; Deng, Q. H.; Chen, J. R.; Xiao, W. J., Highly Enantioselective Friedel-Crafts Alkylation/N-Hemiacetalization Cascade Reaction with Indoles. *Angew. Chem., Int. Ed.* **2013,** *52* (11), 3250-3254.

62. Gao, J. R.; Wu, H.; Xiang, B.; Yu, W. B.; Han, L.; Jia, Y. X., Highly Enantioselective Construction of Trifluoromethylated All-Carbon Quaternary Stereocenters via Nickel-Catalyzed Friedel-Crafts Alkylation Reaction. *J. Am. Chem. Soc.* **2013,** *135* (8), 2983-2986.

63. Hashimoto, T.; Nakatsu, H.; Takiguchi, Y.; Maruoka, K., Axially Chiral Dicarboxylic Acid Catalyzed Activation of Quinone Imine Ketals: Enantioselective Arylation of Enecarbamates. *J. Am. Chem. Soc.* **2013,** *135* (43), 16010-16013.

64. Lee, S. I.; Hwang, G. S.; Ryu, D. H., Catalytic Enantioselective Carbon Insertion into the beta-Vinyl C-H Bond of Cyclic Enones. *J. Am. Chem. Soc.* **2013,** *135* (19), 7126-7129.

65. Mao, H. B.; Lin, A. J.; Shi, Y.; Mao, Z. J.; Zhu, X. B.; Li, W. P.; Hu, H. W.; Cheng, Y. X.; Zhu, C. J., Construction of Enantiomerically Enriched Diazo Compounds Using Diazo Esters as Nucleophiles: Chiral Lewis Base Catalysis. *Angew. Chem., Int. Ed.* **2013,** *52* (24), 6288-6292.

66. Bera, S.; Samanta, R. C.; Daniliuc, C. G.; Studer, A., Asymmetric Synthesis of Highly Substituted beta-Lactones through Oxidative Carbene Catalysis with LiCl as Cooperative Lewis Acid. *Angew. Chem., Int. Ed.* **2014,** *53* (36), 9622-9626.

67. Candish, L.; Levens, A.; Lupton, D. W., Enantioselective All-Carbon (4+2) Annulation by N-Heterocyclic Carbene Catalysis. *J. Am. Chem. Soc.* **2014,** *136* (41), 14397-14400.

68. Chen, X.-Y.; Gao, Z.-H.; Song, C.-Y.; Zhang, C.-L.; Wang, Z.-X.; Ye, S., N-Heterocyclic Carbene Catalyzed Cyclocondensation of alpha,beta-Unsaturated Carboxylic Acids: Enantioselective Synthesis of Pyrrolidinone and Dihydropyridinone Derivatives. *Angew. Chem., Int. Ed.* **2014,** *53* (43), 11611-11615.

69. Huo, H. H.; Fu, C.; Harms, K.; Meggers, E., Asymmetric Catalysis with Substitutionally Labile yet Stereochemically Stable Chiral-at-Metal Iridium(III) Complex. *J. Am. Chem. Soc.* **2014,** *136* (8), 2990-2993.

70. Espelt, L. R.; McPherson, I. S.; Wiensch, E. M.; Yoon, T. P., Enantioselective Conjugate Additions of alpha-Amino Radicals via Cooperative Photoredox and Lewis Acid Catalysis. *J. Am. Chem. Soc.* **2015,** *137* (7), 2452-2455.

71. Hashimoto, T.; Galvez, A. O.; Maruoka, K., Boronic Acid-Catalyzed, Highly Enantioselective Aza-Michael Additions of Hydroxamic Acid to Quinone Imine Ketals. *J. Am. Chem. Soc.* **2015,** *137* (51), 16016-16019.

72. Li, J.; Huang, R.; Xing, Y. K.; Qiu, G. F.; Tao, H. Y.; Wang, C. J., Catalytic Asymmetric Cascade Vinylogous Mukaiyama 1,6-Michael/Michael Addition of 2-Silyloxyfurans with Azoalkenes: Direct Approach to Fused Butyrolactones. *J. Am. Chem. Soc.* **2015,** *137* (32), 10124-10127.

73. Wang, C.; Chen, L.-A.; Huo, H.; Shen, X.; Harms, K.; Gong, L.; Meggers, E., Asymmetric Lewis acid catalysis directed by octahedral rhodium centrochirality. *Chemical Science* **2015,** *6* (2), 1094-1100.

74. Yang, D. X.; Wang, L. Q.; Kai, M.; Li, D.; Yao, X. J.; Wang, R., Application of a C-C Bond-Forming Conjugate Addition Reaction in Asymmetric Dearomatization of beta-Naphthols. *Angew. Chem., Int. Ed.* **2015,** *54* (33), 9523-9527.

75. Zhao, X.; Liu, X.; Mei, H.; Guo, J.; Lin, L.; Feng, X., Asymmetric Dearomatization of Indoles through a Michael/Friedel-Crafts-Type Cascade To Construct Polycyclic Spiroindolines. *Angew. Chem., Int. Ed.* **2015,** *54* (13), 4032-4035.

76. Daniels, B. E.; Ni, J.; Reisman, S. E., Synthesis of Enantioenriched Indolines by a Conjugate Addition/Asymmetric Protonation/Aza-Prins Cascade Reaction. *Angew. Chem., Int. Ed.* **2016,** *55* (10), 3398-3402.

77. Ghosh, S. K.; Ganzmann, C.; Bhuvanesh, N.; Gladysz, J. A., Werner Complexes with -Dimethylaminoalkyl Substituted Ethylenediamine Ligands: Bifunctional Hydrogen-Bond-Donor Catalysts for Highly Enantioselective Michael Additions. *Angew. Chem., Int. Ed.* **2016,** *55* (13), 4356-4360.

78. Huo, H.; Harms, K.; Meggers, E., Catalytic, Enantioselective Addition of Alkyl Radicals to Alkenes via Visible-Light-Activated Photoredox Catalysis with a Chiral Rhodium Complex. *J. Am. Chem. Soc.* **2016,** *138* (22), 6936-6939.

79. Luo, W. W.; Yuan, X.; Lin, L. L.; Zhou, P. F.; Liu, X. H.; Feng, X. M., A N,N '-dioxide/Mg(OTf)(2) complex catalyzed enantioselective alpha-addition of isocyanides to alkylidene malonates. *Chemical Science* **2016,** *7* (7), 4736-4740.

80. Vellalath, S.; Romo, D., Asymmetric Organocatalysis: The Emerging Utility of ,-Unsaturated Acylammonium Salts. *Angew. Chem., Int. Ed.* **2016,** *55* (45), 13934-13943.

81. Wang, C. Y.; Harms, K.; Meggers, E., Catalytic Asymmetric C-sp3-H Functionalization under Photoredox Conditions by Radical Translocation and Stereocontrolled Alkene Addition. *Angew. Chem., Int. Ed.* **2016,** *55* (43), 13495-13498.

82. Yetra, S. R.; Mondal, S.; Mukherjee, S.; Gonnade, R. G.; Biju, A. T., Enantioselective Synthesis of Spirocyclohexadienones by NHC-Catalyzed Formal 3+3 Annulation Reaction of Enals. *Angew. Chem., Int. Ed.* **2016,** *55* (1), 268-272.

83. Matviitsuk, A.; Greenhalgh, M. D.; Antunez, D. J. B.; Slawin, A. M. Z.; Smith, A. D., Aryloxide-Facilitated Catalyst Turnover in Enantioselective ,-Unsaturated Acyl Ammonium Catalysis. *Angew. Chem., Int. Ed.* **2017,** *56* (40), 12282-12287.

84. Yuan, W.; Zhou, Z. J.; Gong, L.; Meggers, E., Asymmetric alkylation of remote C(sp(3))-H bonds by combining proton-coupled electron transfer with chiral Lewis acid catalysis. *Chem. Comm.* **2017,** *53* (64), 8964-8967.

85. Zheng, J. F.; Lin, L. L.; Dai, L.; Tang, Q.; Liu, X. H.; Feng, X. M., Nickel-Catalyzed Conjugate Addition of Silyl Ketene Imines to In Situ Generated Indol-2-ones: Highly Enantioselective Construction of Vicinal All-Carbon Quaternary Stereocenters. *Angew. Chem., Int. Ed.* **2017,** *56* (42), 13107-13111.

86. Zhou, P. F.; Lin, L. L.; Chen, L.; Zhong, X.; Liu, X. H.; Feng, X. M., Iron-Catalyzed Asymmetric Haloazidation of alpha,/beta-Unsaturated Ketones: Construction of Organic Azides with Two Vicinal Stereocenters. *J. Am. Chem. Soc.* **2017,** *139* (38), 13414-13419.

87. Zhou, Z. J.; Li, Y. J.; Han, B. W.; Gong, L.; Meggers, E., Enantioselective catalytic beta-amination through proton-coupled electron transfer followed by stereocontrolled radical-radical coupling. *Chemical Science* **2017,** *8* (8), 5757-5763.

88. He, W. G.; Hu, J. D.; Wang, P. Y.; Chen, L.; Ji, K.; Yang, S. Y.; Li, Y.; Xie, Z. L.; Xie, W. Q., Highly Enantioselective Tandem Michael Addition of Tryptamine-Derived Oxindoles to Alkynones: Concise Synthesis of Strychnos Alkaloids. *Angew. Chem., Int. Ed.* **2018,** *57* (14), 3806-3809.

89. Liu, Q. J.; Zhu, J.; Song, X. Y.; Wang, L. J.; Wang, S. W. R.; Tang, Y., Highly Enantioselective 3+2 Annulation of Indoles with Quinones to Access Structurally Diverse Benzofuroindolines. *Angew. Chem., Int. Ed.* **2018,** *57* (14), 3810-3814.

90. Lu, S. C.; Ong, J. Y.; Poh, S. B.; Tsang, T.; Zhao, Y., Transition-Metal-Free Decarboxylative Propargylic Substitution/Cyclization with either Azolium Enolates or Acyl Anions. *Angew. Chem., Int. Ed.* **2018,** *57* (20), 5714-5719.

91. Ma, J. J.; Lin, J. H.; Zhao, L. F.; Harms, K.; Marsch, M.; Xie, X. L.; Meggers, E., Synthesis of beta-Substituted gamma-Aminobutyric Acid Derivatives through Enantioselective Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2018,** *57* (35), 11193-11197.

92. Shen, X.; Li, Y. J.; Wen, Z. R.; Cao, S.; Hou, X. Y.; Gong, L., A chiral nickel DBFOX complex as a bifunctional catalyst for visible-light-promoted asymmetric photoredox reactions. *Chemical Science* **2018,** *9* (20), 4562-4568.

93. Yin, Y. L.; Dai, Y. T.; Jia, H. S.; Li, J. T.; Bu, L. W.; Qiao, B. K.; Zhao, X. W.; Jiang, Z. Y., Conjugate Addition-Enantioselective Protonation of N-Aryl Glycines to alpha-Branched 2-Vinylazaarenes via Cooperative Photoredox and Asymmetric Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (19), 6083-6087.

94. Kuang, Y. L.; Wang, K.; Shi, X. C.; Huang, X. Q.; Meggers, E.; Wu, J., Asymmetric Synthesis of 1,4-Dicarbonyl Compounds from Aldehydes by Hydrogen Atom Transfer Photocatalysis and Chiral Lewis Acid Catalysis. *Angew. Chem., Int. Ed.* **2019,** *58* (47), 16859-16863.

95. Wonner, P.; Dreger, A.; Vogel, L.; Engelage, E.; Huber, S. M., Chalcogen Bonding Catalysis of a Nitro-Michael Reaction. *Angew. Chem., Int. Ed.* **2019,** *58* (47), 16923-16927.

96. Zhang, K.; Lu, L. Q.; Jia, Y.; Wang, Y.; Lu, F. D.; Pan, F. F.; Xiao, W. J., Exploration of a Chiral Cobalt Catalyst for Visible-Light-Induced Enantioselective Radical Conjugate Addition. *Angew. Chem., Int. Ed.* **2019,** *58* (38), 13375-13379.

97. Horibe, T.; Sakakibara, M.; Hiramatsu, R.; Takeda, K.; Ishihara, K., One-Pot Tandem Michael Addition/Enantioselective Conia-Ene Cyclization Mediated by Chiral Iron(III)/Silver(I) Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2020,** *59* (38), 16470-16474.

98. Kim, J. Y.; Lee, Y. S.; Choi, Y.; Ryu, D. H., Enantioselective 1,2-Addition of α-Aminoalkyl Radical to Aldehydes via Visible-Light Photoredox Initiated Chiral Oxazaborolidinium Ion Catalysis. *ACS Catalysis* **2020,** *10* (18), 10585-10591.

99. Ye, C.-X.; Chen, S.; Han, F.; Xie, X.; Ivlev, S.; Houk, K. N.; Meggers, E., Atroposelective Synthesis of Axially Chiral N-Arylpyrroles by Chiral-at-Rhodium Catalysis. *Angew. Chem., Int. Ed.* **2020,** *59* (32), 13552-13556.

100. Zhong, Z.; Xiao, Z.; Liu, X.; Cao, W.; Feng, X., Catalytic asymmetric synthesis of 3,2′-pyrrolinyl spirooxindoles via conjugate addition/Schmidt-type rearrangement of vinyl azides and (E)-alkenyloxindoles. *Chemical Science* **2020,** *11* (42), 11492-11497.

101. Dong, X.; Li, Q. Y.; Yoon, T. P., Enantioselective Synthesis of γ-Oxycarbonyl Motifs by Conjugate Addition of Photogenerated α-Alkoxy Radicals. *Org. Lett.* **2021,** *23* (15), 5703-5708.

102. Xu, Y.-Y.; Gao, Z.-H.; Li, C.-B.; Ye, S., Enantioselective N-Heterocyclic Carbene Catalyzed α-Oxidative Coupling of Enals with Carboxylic Acids Using an Iodine(III) Reagent. *Angew. Chem., Int. Ed.* **2023,** *62* (11), e202218362.

103. Zhang, D.; Pu, M.; Liu, Z.; Zhou, Y.; Yang, Z.; Liu, X.; Wu, Y.-D.; Feng, X., Enantioselective anti-Dihalogenation of Electron-Deficient Olefin: A Triplet Halo-Radical Pylon Intermediate. *J. Am. Chem. Soc.* **2023,** *145* (8), 4808-4818.

104. Zhu, T. S.; Mou, C. L.; Li, B. S.; Smetankova, M.; Song, B. A.; Chi, Y. R., N-Heterocyclic Carbene-Catalyzed delta-Carbon LUMO Activation of Unsaturated Aldehydes. *J. Am. Chem. Soc.* **2015,** *137* (17), 5658-5661.

2.2.2 Diels Alder reaction

1. Narasaka, K.; Inoue, M.; Okada, N., ASYMMETRIC DIELS-ALDER REACTION PROMOTED BY A CHIRAL TITANIUM REAGENT. *Chem. Lett.* **1986,** (7), 1109-1112.

2. Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A., CHIRAL ALKOXYTITANIUM(IV) COMPLEXES FOR ENANTIOSELECTIVE NUCLEOPHILIC ADDITIONS TO ALDEHYDES AND AS LEWIS-ACIDS IN DIELS-ALDER REACTIONS. *Helv. Chim. Acta* **1987,** *70* (4), 954-974.

3. Furuta, K.; Kanematsu, A.; Yamamoto, H.; Takaoka, S., ASYMMETRIC INTRAMOLECULAR DIELS-ALDER REACTION CATALYZED BY CHIRAL ACYLOXYBORANE COMPLEX. *Tetrahedron Lett.* **1989,** *30* (51), 7231-7232.

4. Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H., CHIRAL (ACYLOXY)BORANE (CAB) - A POWERFUL AND PRACTICAL CATALYST FOR ASYMMETRIC DIELS-ALDER REACTIONS. *J. Org. Chem.* **1989,** *54* (7), 1481-1483.

5. Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J., ASYMMETRIC DIELS-ALDER REACTION CATALYZED BY A CHIRAL TITANIUM REAGENT. *J. Am. Chem. Soc.* **1989,** *111* (14), 5340-5345.

6. Takasu, M.; Yamamoto, H., NEW CHIRAL LEWIS ACID CATALYSTS PREPARED FROM SIMPLE AMINO-ACIDS AND THEIR USE IN ASYMMETRIC DIELS-ALDER REACTIONS. *Synlett* **1990,** (4), 194-196.

7. Corey, E. J.; Loh, T. P., 1ST APPLICATION OF ATTRACTIVE INTRAMOLECULAR INTERACTIONS TO THE DESIGN OF CHIRAL CATALYSTS FOR HIGHLY ENANTIOSELECTIVE DIELS-ALDER REACTIONS. *J. Am. Chem. Soc.* **1991,** *113* (23), 8966-8967.

8. Gao, Q. Z.; Maruyama, T.; Mouri, M.; Yamamoto, H., ASYMMETRIC HETERO-DIELS-ALDER REACTION CATALYZED BY STABLE AND EASILY PREPARED CAB CATALYSTS. *J. Org. Chem.* **1992,** *57* (7), 1951-1952.

9. Hattori, K.; Yamamoto, H., ASYMMETRIC AZA-DIELS-ALDER REACTION CATALYZED BY BORON REAGENT - EFFECT OF BIPHENOL AND BINAPHTHOL LIGAND. *Synlett* **1993,** (2), 129-130.

10. Ishihara, K.; Gao, Q. Z.; Yamamoto, H., ENANTIOSELECTIVE DIELS-ALDER REACTION OF ALPHA-BROMO ALPHA,BETA-ENALS WITH DIENES UNDER CATALYSIS BY CAB. *J. Org. Chem.* **1993,** *58* (24), 6917-6919.

11. Ishihara, K.; Gao, Q. Z.; Yamamoto, H., MECHANISTIC STUDIES OF A CAB-CATALYZED ASYMMETRIC DIELS-ALDER REACTION. *J. Am. Chem. Soc.* **1993,** *115* (22), 10412-10413.

12. Corey, E. J.; Sarshar, S.; Lee, D. H., FIRST EXAMPLE OF A HIGHLY ENANTIOSELECTIVE CATALYTIC DIELS-ALDER REACTION OF AN ACHIRAL C-2-NU-SYMMETRICAL DIENOPHILE AND AN ACHIRAL DIENE. *J. Am. Chem. Soc.* **1994,** *116* (26), 12089-12090.

13. Corey, E. J.; Guzmanperez, A.; Loh, T. P., DEMONSTRATION OF THE SYNTHETIC POWER OF OXAZABOROLIDINE-CATALYZED ENANTIOSELECTIVE DIELS-ALDER REACTIONS BY VERY EFFICIENT ROUTES TO CASSIOL AND GIBBERELLIC-ACID. *J. Am. Chem. Soc.* **1994,** *116* (8), 3611-3612.

14. Ichiyanagi, T.; Shimizu, M.; Fujisawa, T., Enantioselective Diels-Alder reaction using chiral Mg complexes derived from chiral 2- 2-(alkyl- or 2 2- (arylsulfonyl)amino phenyl -4-phenyl-1,3-oxazoline. *J. Org. Chem.* **1997,** *62* (23), 7937-7941.

15. Evans, D. A.; Olhava, E. J.; Johnson, J. S.; Janey, J. M., Chiral C-2-symmetric Cu-II complexes as catalysts for enantioselective hetero-Diels-Alder reactions. *Angew. Chem., Int. Ed.* **1998,** *37* (24), 3372-3375.

16. Evans, D. A.; Barnes, D. M.; Johnson, J. S.; Lectka, R.; von Matt, P.; Miller, S. J.; Murry, J. A.; Norcross, R. D.; Shaughnessy, E. A.; Campos, K. R., Bis(oxazoline) and bis(oxazolinyl)pyridine copper complexes as enantioselective Diels-Alder catalysts: Reaction scope and synthetic applications. *J. Am. Chem. Soc.* **1999,** *121* (33), 7582-7594.

17. Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt, P., Chiral bis(oxazoline)copper(II) complexes as Lewis acid catalysts for the enantioselective Diels-Alder reaction. *J. Am. Chem. Soc.* **1999,** *121* (33), 7559-7573.

18. Evans, D. A.; Johnson, J. S.; Olhava, E. J., Enantioselective synthesis of dihydropyrans. Catalysis of hetero Diels-Alder reactions by bis(oxazoline) copper(II) complexes. *J. Am. Chem. Soc.* **2000,** *122* (8), 1635-1649.

19. Sibi, M. P.; Venkatraman, L.; Liu, M.; Jasperse, C. P., A new approach to enantiocontrol and enantioselectivity amplification: Chiral relay in Diels-Alder reactions. *J. Am. Chem. Soc.* **2001,** *123* (34), 8444-8445.

20. Corey, E. J.; Shibata, T.; Lee, T. W., Asymmetric Diels-Alder reactions catalyzed by a triflic acid activated chiral oxazaborolidine. *J. Am. Chem. Soc.* **2002,** *124* (15), 3808-3809.

21. Ryu, D. H.; Lee, T. W.; Corey, E. J., Broad-spectrum enantioselective Diels-Alder catalysis by chiral, cationic oxazaborolidines. *J. Am. Chem. Soc.* **2002,** *124* (34), 9992-9993.

22. Huang, Y.; Iwama, T.; Rawal, V. H., Design and development of highly effective lewis acid catalysts for enantioselective Diels-Alder reactions. *J. Am. Chem. Soc.* **2002,** *124* (21), 5950-5951.

23. Kozmin, S. A.; Iwama, T.; Huang, Y.; Rawal, V. H., An efficient approach to Aspidosperma alkaloids via [4+2] cycloadditions of aminosiloxydienes: Stereocontrolled total synthesis of (+/-)-tabersonine. Gram-scale catalytic asymmetric syntheses of (+)-tabersonine and (+)-16-methoxytabersonine. Asymmetric syntheses of (+)-aspidospermidine and (-)-quebrachamine. *J. Am. Chem. Soc.* **2002,** *124* (17), 4628-4641.

24. Gademann, K.; Chavez, D. E.; Jacobsen, E. N., Highly enantioselective inverse-electron-demand hetero-Diels- Alder reactions of alpha,beta-unsaturated aldehydes. *Angew. Chem., Int. Ed.* **2002,** *41* (16), 3059-3061.

25. Gao, X.; Hall, D. G., 3-boronoacrolein as an exceptional heterodiene in the highly enantio- and diastereoselective Cr(III)-catalyzed three- component 4+2 /allylboration. *J. Am. Chem. Soc.* **2003,** *125* (31), 9308-9309.

26. Ryu, D. H.; Corey, E. J., Triflimide activation of a chiral oxazaborolidine leads to a more general catalytic system for enantioselective Diels-Alder addition. *J. Am. Chem. Soc.* **2003,** *125* (21), 6388-6390.

27. Sprott, K. T.; Corey, E. J., A new cationic, chiral catalyst for highly enantioselective Diels-Alder reactions. *Org. Lett.* **2003,** *5* (14), 2465-2467.

28. Asao, N.; Kasahara, T.; Yamamoto, Y., Functionalized 1,2-dihydronaphthalenes from the Cu(OTf)(2)- catalyzed 4+2 cycloaddition of o-alkynyl(oxo)benzenes with alkenes. *Angew. Chem., Int. Ed.* **2003,** *42* (30), 3504-3506.

29. Owens, T. D.; Souers, A. J.; Ellman, J. A., The preparation and utility of bis(sulfinyl)imidoamidine ligands for the copper-catalyzed Diels-Alder reaction. *J. Org. Chem.* **2003,** *68* (1), 3-10.

30. Palomo, C.; Oiarbide, M.; Garcia, J. M.; Gonzalez, A.; Arceo, E., alpha '-hydroxy enones as achiral templates for Lewis acid-catalyzed enantioselective Diels-Alder reactions. *J. Am. Chem. Soc.* **2003,** *125* (46), 13942-13943.

31. Evans, D. A.; Wu, J., Enantioselective rare-earth catalyzed quinone Diels-Alder reactions. *J. Am. Chem. Soc.* **2003,** *125* (34), 10162-10163.

32. Fukuzawa, S.; Komuro, Y.; Nakano, N.; Obara, S., New chiral scandium(III)/bisimine and diol complexes catalyzed asymmetric Diels-Alder reaction. *Tetrahedron Lett.* **2003,** *44* (18), 3671-3674.

33. Chavez, D. E.; Jacobsen, E. N., Catalyst-controlled inverse-electron-demand hetero-Diels-Alder reactions in the enantio- and diastereloselective synthesis of iridoid natural products. *Org. Lett.* **2003,** *5* (14), 2563-2565.

34. Hu, Q. Y.; Zhou, G.; Corey, E. J., Application of chiral cationic catalysts to several classical syntheses of racemic natural products transforms them into highly enantioselective pathways. *J. Am. Chem. Soc.* **2004,** *126* (42), 13708-13713.

35. Ryu, D. H.; Zhou, G.; Corey, E. J., Enantioselective and structure-selective Diels-Alder reactions of unsymmetrical quinones catalyzed by a chiral oxazaborolidinium cation. Predictive selection rules. *J. Am. Chem. Soc.* **2004,** *126* (15), 4800-4802.

36. Jarvo, E. R.; Lawrence, B. M.; Jacobsen, E. N., Highly enantio- and regioselective quinone Diels-Alder reactions catalyzed by a tridentate (Schiff base)Cr-III complex. *Angew. Chem., Int. Ed.* **2005,** *44* (37), 6043-6046.

37. Futatsugi, K.; Yamamoto, H., Oxazaborolidine-derived Lewis acid assisted Lewis acid as a moisture-tolerant catalyst for enantioselective Diels-Alder reactions. *Angew. Chem., Int. Ed.* **2005,** *44* (10), 1484-1487.

38. Ryu, D. H.; Zhou, G.; Corey, E. J., Nonparallelism between reaction rate and dienophile-catalyst affinity in catalytic enantioselective Diels-Alder reactions. *Org. Lett.* **2005,** *7* (8), 1633-1636.

39. Rajaram, S.; Sigman, M. S., Design of hydrogen bond catalysts based on a modular oxazoline template: Application to an enantioselective hetero Diels-Alder reaction. *Org. Lett.* **2005,** *7* (24), 5473-5475.

40. Sibi, M. P.; Stanley, L. M.; Nie, X. P.; Venkatraman, L.; Liu, M.; Jasperse, C. P., The role of achiral pyrazolidinone templates in enantioselective Diels-Alder reactions: Scope, limitations, and conformational insights. *J. Am. Chem. Soc.* **2007,** *129* (2), 395-405.

41. Liu, D.; Canales, E.; Corey, E. J., Chiral oxazaborolidine-aluminum bromide complexes are unusually powerful and effective catalysts for enantioselective Diels-Alder reactions. *J. Am. Chem. Soc.* **2007,** *129* (6), 1498-+.

42. Payette, J. N.; Yamamoto, H., Regioselective and asymmetric Diels-Alder reaction of 1-and 2-substituted cyclopentadienes catalyzed by a bronsted acid activated chiral oxazaborolidine. *J. Am. Chem. Soc.* **2007,** *129* (31), 9536-+.

43. Esquivias, J.; Arrayas, R. G.; Carretero, J. C., Catalytic asymmetric inverse-electron-demand Diels-Alder reaction of N-sulfonyl-1-aza-1,3-dienes. *J. Am. Chem. Soc.* **2007,** *129* (6), 1480-+.

44. Wang, Y.; Wolf, J.; Zavalij, P.; Doyle, M. R., Cationic chiral dirhodium carboxamidates are activated for Lewis acid catalysis. *Angew. Chem., Int. Ed.* **2008,** *47* (8), 1439-1442.

45. Teichert, A.; Pfaltz, A., Mass spectrometric screening of enantioselective Diels-Alder reactions. *Angew. Chem., Int. Ed.* **2008,** *47* (18), 3360-3362.

46. Ishihara, K.; Fushimi, M., Catalytic enantioselective [2+4] and [2+2] cycloaddition reactions with propiolamides. *J. Am. Chem. Soc.* **2008,** *130* (24), 7532-+.

47. Canales, E.; Corey, E. J., Highly enantioselective [4+2]cycloaddition reactions catalyzed by a chiral N-methyl-oxazaborolidinium cation. *Org. Lett.* **2008,** *10* (15), 3271-3273.

48. Sudo, Y.; Shirasaki, D.; Harada, S.; Nishida, A., Highly enantioselective Diels-Alder reactions of Danishefsky type dienes with electron-deficient alkenes catalyzed by Yb(III)-BINAMIDE complexes. *J. Am. Chem. Soc.* **2008,** *130* (38), 12588-+.

49. Reymond, S.; Cossy, J., Copper-Catalyzed Diels-Alder Reactions. *Chem. Rev* **2008,** *108* (12), 5359-5406.

50. Paddon-Row, M. N.; Anderson, C. D.; Houk, K. N., Computational Evaluation of Enantioselective Diels-Alder Reactions Mediated by Corey's Cationic Oxazaborolidine Catalysts. *J. Org. Chem.* **2009,** *74* (2), 861-868.

51. Payette, J. N.; Yamamoto, H., Cationic-Oxazaborolidine-Catalyzed Enantioselective Diels-Alder Reaction of alpha,beta-Unsaturated Acetylenic Ketones. *Angew. Chem., Int. Ed.* **2009,** *48* (43), 8060-8062.

52. Li, P. F.; Yamamoto, H., Lewis Acid Catalyzed Inverse-Electron-Demand Diels-Alder Reaction of Tropones. *J. Am. Chem. Soc.* **2009,** *131* (46), 16628-+.

53. Sakakura, A.; Kondo, R.; Matsumura, Y.; Akakura, M.; Ishihara, K., Rational Design of Highly Effective Asymmetric Diels-Alder Catalysts Bearing 4,4 '-Sulfonamidomethyl Groups. *J. Am. Chem. Soc.* **2009,** *131* (49), 17762-17764.

54. Schotes, C.; Mezzetti, A., Asymmetric Diels-Alder Reactions of Unsaturated beta-Ketoesters Catalyzed by Chiral Ruthenium PNNP Complexes. *J. Am. Chem. Soc.* **2010,** *132* (11), 3652-+.

55. Mukherjee, S.; Corey, E. J., 4+2 Cycloaddition Reactions Catalyzed by a Chiral Oxazaborolidinium Cation. Reaction Rates and Diastereo-, Regio-, and Enantioselectivity Depend on Whether Both Bonds Are Formed Simultaneously. *Org. Lett.* **2010,** *12* (5), 1024-1027.

56. Xie, M. S.; Chen, X. H.; Zhu, Y.; Gao, B.; Lin, L. L.; Liu, X. H.; Feng, X. M., Asymmetric Three-Component Inverse Electron-Demand Aza-Diels-Alder Reaction: Efficient Synthesis of Ring-Fused Tetrahydroquinolines. *Angew. Chem., Int. Ed.* **2010,** *49* (22), 3799-3802.

57. Shibatomi, K.; Futatsugi, K.; Kobayashi, F.; Iwasa, S.; Yamamoto, H., Stereoselective Construction of Halogenated Quaternary Stereogenic Centers via Catalytic Asymmetric Diels-Alder Reaction. *J. Am. Chem. Soc.* **2010,** *132* (16), 5625-+.

58. Wang, C.; Han, Z. Y.; Luo, H. W.; Gong, L. Z., Highly Enantioselective Relay Catalysis in the Three-Component Reaction for Direct Construction of Structurally Complex Heterocycles. *Org. Lett.* **2010,** *12* (10), 2266-2269.

59. Livieri, A.; Boiocchi, M.; Desimoni, G.; Faita, G., Enantioselective Cycloadditions of 2-Alkenoylpyridine-N-oxides Catalysed by a Bis(oxazoline)/Cu(II) Complex: Structure of the Reactive Intermediate. *Chem. Eur. J.* **2011,** *17* (2), 516-520.

60. Zhu, Y.; Xie, M. S.; Dong, S. X.; Zhao, X. H.; Lin, L. L.; Liu, X. H.; Feng, X. M., Asymmetric Cycloaddition of beta,gamma-Unsaturated alpha-Ketoesters with Electron-Rich Alkenes Catalyzed by a Chiral Er(OTf)(3)/N,N '-Dioxide Complex: Highly Enantioselective Synthesis of 3,4-Dihydro-2H-pyrans. *Chem. Eur. J.* **2011,** *17* (29), 8202-8208.

61. Xie, H.; Sammis, G. M.; Flamme, E. M.; Kraml, C. M.; Sorensen, E. J., The Catalytic Asymmetric Diels-Alder Reactions and Post-cycloaddition Reductive Transpositions of 1-Hydrazinodienes. *Chem. Eur. J.* **2011,** *17* (40), 11131-11134.

62. Hatano, M.; Mizuno, T.; Izumiseki, A.; Usami, R.; Asai, T.; Akakura, M.; Ishihara, K., Enantioselective Diels-Alder Reactions with Anomalous endo/exo Selectivities Using Conformationally Flexible Chiral Supramolecular Catalysts. *Angew. Chem., Int. Ed.* **2011,** *50* (51), 12189-12192.

63. Momiyama, N.; Konno, T.; Furiya, Y.; Iwamoto, T.; Terada, M., Design of Chiral Bis-phosphoric Acid Catalyst Derived from (R)-3,3 '-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels-Alder Reaction of alpha,beta-Unsaturated Aldehydes with Amidodienes. *J. Am. Chem. Soc.* **2011,** *133* (48), 19294-19297.

64. Schotes, C.; Althaus, M.; Aardoom, R.; Mezzetti, A., Asymmetric Diels-Alder and Ficini Reactions with Alkylidene beta-Ketoesters Catalyzed by Chiral Ruthenium PNNP Complexes: Mechanistic Insight. *J. Am. Chem. Soc.* **2012,** *134* (2), 1331-1343.

65. Han, Z. Y.; Chen, D. F.; Wang, Y. Y.; Guo, R.; Wang, P. S.; Wang, C.; Gong, L. Z., Hybrid Metal/Organo Relay Catalysis Enables Enynes To Be Latent Dienes for Asymmetric Diels-Alder Reaction. *J. Am. Chem. Soc.* **2012,** *134* (15), 6532-6535.

66. Sakata, K.; Fujimoto, H., Quantum Chemical Study of Diels-Alder Reactions Catalyzed by Lewis Acid Activated Oxazaborolidines. *J. Org. Chem.* **2013,** *78* (7), 3095-3103.

67. Li, G. L.; Liang, T.; Wojtas, L.; Antilla, J. C., An Asymmetric DielsAlder Reaction Catalyzed by Chiral Phosphate Magnesium Complexes: Highly Enantioselective Synthesis of Chiral Spirooxindoles. *Angew. Chem., Int. Ed.* **2013,** *52* (17), 4628-4632.

68. Abbasov, M. E.; Hudson, B. M.; Tantillo, D. J.; Romo, D., Acylammonium Salts as Dienophiles in Diels-Alder/Lactonization Organocascades. *J. Am. Chem. Soc.* **2014,** *136* (12), 4492-4495.

69. Tong, M.-C.; Chen, X.; Li, J.; Huang, R.; Tao, H.; Wang, C.-J., Catalytic Asymmetric Synthesis of 2,3 - Fused Indoline Heterocycles through Inverse- Electron- Demand Aza- Diels- Alder Reaction of Indoles with Azoalkenes. *Angew. Chem., Int. Ed.* **2014,** *53* (18), 4680-4684.

70. Matsumura, Y.; Suzuki, T.; Sakakura, A.; Ishihara, K., Catalytic Enantioselective Inverse Electron Demand Hetero-Diels-Alder Reaction with Allylsilanes. *Angew. Chem., Int. Ed.* **2014,** *53* (24), 6131-6134.

71. Luan, Y.; Barbato, K. S.; Moquist, P. N.; Kodama, T.; Schaus, S. E., Enantioselective Synthesis of 1,2-Dihydronaphthalene-1-carbaldehydes by Addition of Boronates to Isochromene Acetals Catalyzed by Tartaric Acid. *J. Am. Chem. Soc.* **2015,** *137* (9), 3233-3236.

72. Chu, J. C. K.; Dalton, D. M.; Rovis, T., Zn-Catalyzed Enantio- and Diastereoselective Formal 4+2 Cycloaddition Involving Two Electron-Deficient Partners: Asymmetric Synthesis of Piperidines from 1-Azadienes and Nitro-Alkenes. *J. Am. Chem. Soc.* **2015,** *137* (13), 4445-4452.

73. Hatano, M.; Goto, Y.; Izumiseki, A.; Akakura, M.; Ishihara, K., Boron Tribromide-Assisted Chiral Phosphoric Acid Catalyst for a Highly Enantioselective Diels-Alder Reaction of 1,2-Dihydropyridines. *J. Am. Chem. Soc.* **2015,** *137* (42), 13472-13475.

74. Hsiao, C. C.; Raja, S.; Liao, H. H.; Atodiresei, I.; Rueping, M., Ortho-Quinone Methides as Reactive Intermediates in Asymmetric Bronsted Acid Catalyzed Cycloadditions with Unactivated Alkenes by Exclusive Activation of the Electrophile. *Angew. Chem., Int. Ed.* **2015,** *54* (19), 5762-5765.

75. Reddy, K. M.; Bhimireddy, E.; Thirupathi, B.; Breitler, S.; Yu, S. M.; Corey, E. J., Cationic Chiral Fluorinated Oxazaborolidines. More Potent, Second-Generation Catalysts for Highly Enantioselective Cycloaddition Reactions. *J. Am. Chem. Soc.* **2016,** *138* (7), 2443-2453.

76. Gatzenmeier, T.; van Gemmeren, M.; Xie, Y. W.; Hofler, D.; Leutzsch, M.; List, B., Asymmetric Lewis acid organocatalysis of the Diels-Alder reaction by a silylated C-H acid. *Science* **2016,** *351* (6276), 949-952.

77. Li, J.; Lin, L. L.; Hu, B. W.; Lian, X. J.; Wang, G.; Liu, X. H.; Feng, X. M., Bimetallic Gold(I)/Chiral N,N-Dioxide Nickel(II) Asymmetric Relay Catalysis: Chemo- and Enantioselective Synthesis of Spiroketals and Spiroaminals. *Angew. Chem., Int. Ed.* **2016,** *55* (20), 6075-6078.

78. Liu, Q. J.; Wang, L. J.; Kang, Q. K.; Zhang, X. P.; Tang, Y., Cy-SaBOX/Copper(II)-Catalyzed Highly Diastereo- and Enantioselective Synthesis of Bicyclic N,O Acetals. *Angew. Chem., Int. Ed.* **2016,** *55* (32), 9220-9223.

79. Thirupathi, B.; Breitler, S.; Reddy, K. M.; Corey, E. J., Acceleration of Enantioselective Cycloadditions Catalyzed by Second-Generation Chiral Oxazaborolidinium Triflimidates by Biscoordinating Lewis Acids. *J. Am. Chem. Soc.* **2016,** *138* (34), 10842-10845.

80. Xie, Y. W.; List, B., Catalytic Asymmetric Intramolecular 4+2 Cycloaddition of In Situ Generated ortho-Quinone Methides. *Angew. Chem., Int. Ed.* **2017,** *56* (18), 4936-4940.

81. Wang, L.; Lv, J.; Zhang, L.; Luo, S. Z., Catalytic Regio- and Enantioselective 4+2 Annulation Reactions of Non-activated Allenes by a Chiral Cationic Indium Complex. *Angew. Chem., Int. Ed.* **2017,** *56* (36), 10867-10871.

82. Jayakumar, S.; Louven, K.; Strohmann, C.; Kumar, K., A Tunable and Enantioselective Hetero-Diels-Alder Reaction Provides Access to Distinct Piperidinoyl Spirooxindoles. *Angew. Chem., Int. Ed.* **2017,** *56* (50), 15945-15949.

83. Kretzschmar, M.; Hofmann, F.; Moock, D.; Schneider, C., Intramolecular Aza-Diels-Alder Reactions of ortho-Quinone Methide Imines: Rapid, Catalytic, and Enantioselective Assembly of Benzannulated Quinolizidines. *Angew. Chem., Int. Ed.* **2018,** *57* (17), 4774-4778.

84. Gillard, R. M.; Fernando, J. E. M.; Lupton, D. W., Enantioselective N-Heterocyclic Carbene Catalysis via the Dienyl Acyl Azolium. *Angew. Chem., Int. Ed.* **2018,** *57* (17), 4712-4716.

85. Thirupathi, N.; Wei, F.; Tung, C. H.; Xu, Z. H., Divergent synthesis of chiral cyclic azides via asymmetric cycloaddition reactions of vinyl azides. *Nature Communications* **2019,** *10*.

86. Shen, B.; He, Q.; Dong, S.; Liu, X.; Feng, X., A chiral cobalt(ii) complex catalyzed enantioselective aza-Piancatelli rearrangement/Diels–Alder cascade reaction. *Chemical Science* **2020,** *11* (15), 3862-3867.

87. Si, X.-G.; Zhang, Z.-M.; Zheng, C.-G.; Li, Z.-T.; Cai, Q., Enantioselective Synthesis of cis-Decalin Derivatives by the Inverse-Electron-Demand Diels–Alder Reaction of 2-Pyrones. *Angew. Chem., Int. Ed.* **2020,** *59* (42), 18412-18417.

88. Yan, P.; Zhong, C.; Zhang, J.; Liu, Y.; Fang, H.; Lu, P., 3-(Methoxycarbonyl)Cyclobutenone as a Reactive Dienophile in Enantioselective Diels–Alder Reactions Catalyzed by Chiral Oxazaborolidinium Ions. *Angew. Chem., Int. Ed.* **2021,** *60* (9), 4609-4613.

89. Xu, M.-M.; You, X.-Y.; Zhang, Y.-Z.; Lu, Y.; Tan, K.; Yang, L.; Cai, Q., Enantioselective Synthesis of Axially Chiral Biaryls by Diels–Alder/Retro-Diels–Alder Reaction of 2-Pyrones with Alkynes. *J. Am. Chem. Soc.* **2021,** *143* (24), 8993-9001.

90. Lu, Y.; Xu, M.-M.; Zhang, Z.-M.; Zhang, J.; Cai, Q., Catalytic Asymmetric Inverse-Electron-Demand Diels–Alder Reactions of 2-Pyrones with Indenes: Total Syntheses of Cephanolides A and B. *Angew. Chem., Int. Ed.* **2021,** *60* (51), 26610-26615.

91. Xu, M.-M.; Yang, L.; Tan, K.; Chen, X.; Lu, Q.-T.; Houk, K. N.; Cai, Q., An enantioselective ambimodal cross-Diels–Alder reaction and applications in synthesis. *Nature Catalysis* **2021,** *4* (10), 892-900.

92. Ghosh, S.; Erchinger, J. E.; Maji, R.; List, B., Catalytic Asymmetric Spirocyclizing Diels–Alder Reactions of Enones: Stereoselective Total and Formal Syntheses of α-Chamigrene, β-Chamigrene, Laurencenone C, Colletoic Acid, and Omphalic Acid. *J. Am. Chem. Soc.* **2022,** *144* (15), 6703-6708.

93. Yesilcimen, A.; Jiang, N.-C.; Gottlieb, F. H.; Wasa, M., Enantioselective Organocopper-Catalyzed Hetero Diels–Alder Reaction through in Situ Oxidation of Ethers into Enol Ethers. *J. Am. Chem. Soc.* **2022,** *144* (14), 6173-6179.

94. Zhang, F.; Ren, B.-T.; Zhou, Y.; Liu, Y.; Feng, X., Enantioselective construction of cis-hydroindole scaffolds via an asymmetric inverse-electron-demand Diels–Alder reaction: application to the formal total synthesis of (+)-minovincine. *Chemical Science* **2022,** *13* (19), 5562-5567.

95. Huang, G.; Guillot, R.; Kouklovsky, C.; Maryasin, B.; de la Torre, A., Diastereo- and Enantioselective Inverse-Electron-Demand Diels–Alder Cycloaddition between 2-Pyrones and Acyclic Enol Ethers. *Angew. Chem., Int. Ed.* **2022,** *61* (42), e202208185.

96. Si, X.-G.; Feng, S.-X.; Wang, Z.-Y.; Chen, X.; Xu, M.-M.; Zhang, Y.-Z.; He, J.-X.; Yang, L.; Cai, Q., Enantioselective Synthesis of cis-Decalins by Merging the Birch Reduction and Inverse-Electron-Demand Diels–Alder Reaction. *Angew. Chem., Int. Ed.* **2023,** *62* (32), e202303876.

97. Li, M.; Huang, X.-L.; Zhang, Z.-Y.; Wang, Z.; Wu, Z.; Yang, H.; Shen, W.-J.; Cheng, Y.-Z.; You, S.-L., Gd(III)-Catalyzed Regio-, Diastereo-, and Enantioselective [4 + 2] Photocycloaddition of Naphthalene Derivatives. *J. Am. Chem. Soc.* **2024,** *146* (25), 16982-16989.

2.2.3 [3+2] Cycloaddition

1. Ukaji, Y.; Sada, K.; Inomata, K., Enantioselective Synthesis of 2-Isoxazolines Via Asymmetric 1,3-Dipolar Cycloaddition of Nitrile Oxide to Achiral Allyl Alcohol. *Chem. Lett.* **1993,** (11), 1847-1850.

2. Viton, F.; Bernardinelli, G.; Kundig, E. P., Iron and ruthenium Lewis acid catalyzed asymmetric 1,3-dipolar cycloaddition reactions between nitrones and enals. *J. Am. Chem. Soc.* **2002,** *124* (18), 4968-4969.

3. Kobayashi, S.; Shimizu, H.; Yamashita, Y.; Ishitani, H.; Kobayashi, J., Asymmetric intramolecular 3+2 cycloaddition reactions of acylhydrazones/olefins using a chiral zirconium catalyst. *J. Am. Chem. Soc.* **2002,** *124* (46), 13678-13679.

4. Sibi, M. P.; Ma, Z. H.; Jasperse, C. P., Exo selective enantioselective nitrone cycloadditions. *J. Am. Chem. Soc.* **2004,** *126* (3), 718-719.

5. Sibi, M. P.; Itoh, K.; Jasperse, C. P., Chiral Lewis acid catalysis in nitrile oxide cycloadditions. *J. Am. Chem. Soc.* **2004,** *126* (17), 5366-5367.

6. Shirahase, M.; Kanemasa, S.; Oderaotoshi, Y., Chiral DBFOX/Ph complex catalyzed enantioselective nitrone cycloadditions to alpha,beta-unsaturated aldehydes. *Org. Lett.* **2004,** *6* (5), 675-678.

7. Carmona, D.; Lamata, M. P.; Viguri, F.; Rodriguez, R.; Oro, L. A.; Balana, A. I.; Lahoz, F. J.; Tejero, T.; Merino, P.; Franco, S.; Montesa, I., The complete characterization of a rhodium Lewis acid- dipolarophile complex as an intermediate for the enantioselective catalytic 1,3-dipolar cycloaddition of C,N- diphenylnitrone to methacrolein. *J. Am. Chem. Soc.* **2004,** *126* (9), 2716-2717.

8. Shirahase, M.; Kanemasa, S.; Hasegawa, M., Improved catalysis of nitrone 1,3-dipolar cycloadditions by solving the aggregation issue of the DBFOX/Ph-transition metal complexes. *Tetrahedron Lett.* **2004,** *45* (21), 4061-4063.

9. Palomo, C.; Oiarbide, M.; Arceo, E.; Garcia, J. M.; Lopez, R.; Gonzalez, A.; Linden, A., Lewis acid catalyzed asymmetric cycloadditions of nitrones: alpha '-Hydroxy enones as efficient reaction partners. *Angew. Chem., Int. Ed.* **2005,** *44* (38), 6187-6190.

10. Carmona, D.; Lamata, M. P.; Viguri, F.; Rodriguez, R.; Oro, L. A.; Lahoz, F. J.; Balana, A. I.; Tejero, T.; Merino, P., Enantioselective 1,3-dipolar cycloaddition of nitrones to methacrolein catalyzed by (eta(5)-C5Me5)M{(R)-Prophos} containing complexes (M = Rh, Ir; (R)-Prophos=1,2-bis(diphenylphosphino)propane): On the origin of the enantioselectivity. *J. Am. Chem. Soc.* **2005,** *127* (38), 13386-13398.

11. Sibi, M. P.; Ma, Z. H.; Itoh, K.; Prabagaran, N.; Jasperse, C. P., Enantioselective cycloadditions with alpha,beta-disubstituted acrylimides. *Org. Lett.* **2005,** *7* (12), 2349-2352.

12. Sibi, M. P.; Stanley, L. M.; Jasperse, C. P., An entry to a chiral dihydropyrazole scaffold: Enantioselective 3+2 cycloaddition of nitrile imines. *J. Am. Chem. Soc.* **2005,** *127* (23), 8276-8277.

13. Sibi, M. P.; Ma, Z. H.; Jasperse, C. P., Enantioselective addition of nitrones to activated cyclopropanes. *J. Am. Chem. Soc.* **2005,** *127* (16), 5764-5765.

14. Kano, T.; Hashimoto, T.; Maruoka, K., Asymmetric 1,3-dipolar cycloaddition reaction of nitrones and acrolein with a bis-titanium catalyst as chiral lewis acid. *J. Am. Chem. Soc.* **2005,** *127* (34), 11926-11927.

15. Evans, D. A.; Song, H. J.; Fandrick, K. R., Enantioselective nitrone cycloadditions of alpha,beta-unsaturated 2-acyl imidazoles catalyzed by bis(oxazolinyl)pyridine-cerium(IV) triflate complexes. *Org. Lett.* **2006,** *8* (15), 3351-3354.

16. Kano, T.; Hashimoto, T.; Maruoka, K., Enantioselective 1,3-dipolar cycloaddition reaction between diazoacetates and alpha-substituted acroleins: Total synthesis of manzacidin A. *J. Am. Chem. Soc.* **2006,** *128* (7), 2174-2175.

17. Kang, Y. B.; Sun, X. L.; Tang, Y., Highly enantioselective and diastereoselective cycloaddition of cyclopropanes with nitrones and its application in the kinetic resolution of 2-substituted cyclopropane-1,1-dicarboxylates. *Angew. Chem., Int. Ed.* **2007,** *46* (21), 3918-3921.

18. Repka, L. M.; Ni, J.; Reisman, S. E., Enantioselective Synthesis of Pyrroloindolines by a Formal 3+2 Cycloaddition Reaction. *J. Am. Chem. Soc.* **2010,** *132* (41), 14418-14420.

19. Sakakura, A.; Hori, M.; Fushimi, M.; Ishihara, K., Catalytic Enantioselective 1,3-Dipolar Cycloadditions of Nitrones with Propioloylpyrazoles and Acryloylpyrazoles Induced by Chiral pi-Cation Catalysts. *J. Am. Chem. Soc.* **2010,** *132* (44), 15550-15552.

20. Wang, X. C.; Weigl, C.; Doyle, M. P., Solvent Enhancement of Reaction Selectivity: A Unique Property of Cationic Chiral Dirhodium Carboxamidates. *J. Am. Chem. Soc.* **2011,** *133* (24), 9572-9579.

21. Rueping, M.; Maji, M. S.; Kucuk, H. B.; Atodiresei, I., Asymmetric Bronsted Acid Catalyzed CycloadditionsEfficient Enantioselective Synthesis of Pyrazolidines, Pyrazolines, and 1,3-Diamines from N-Acyl Hyrazones and Alkenes. *Angew. Chem., Int. Ed.* **2012,** *51* (51), 12864-12868.

22. Lykke, L.; Carlsen, B. D.; Rambo, R. S.; Jorgensen, K. A., Catalytic Asymmetric Synthesis of 4-Nitropyrazolidines: An Access to Optically Active 1,2,3-Triamines. *J. Am. Chem. Soc.* **2014,** *136* (32), 11296-11299.

23. Hong, X.; Kucuk, H. B.; Maji, M. S.; Yang, Y.-F.; Rueping, M.; Houk, K. N., Mechanism and Selectivity of N-Triflylphosphoramide Catalyzed (3(+)+2) Cycloaddition between Hydrazones and Alkenes. *J. Am. Chem. Soc.* **2014,** *136* (39), 13769-13780.

24. Hori, M.; Sakakura, A.; Ishihara, K., Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Imines with Propioloylpyrazoles Induced by Chiral pi-Cation Catalysts. *J. Am. Chem. Soc.* **2014,** *136* (38), 13198-13201.

25. Wu, M. Y.; He, W. W.; Liu, X. Y.; Tan, B., Asymmetric Construction of Spirooxindoles by Organocatalytic Multicomponent Reactions Using Diazooxindoles. *Angew. Chem., Int. Ed.* **2015,** *54* (32), 9409-9413.

26. Yang, X.; Cheng, F.; Kou, Y. D.; Pang, S.; Shen, Y. C.; Huang, Y. Y.; Shibata, N., Catalytic Asymmetric 1,3-Dipolar Cycloaddition of beta-Fluoroalkylated alpha,beta-Unsaturated 2-Pyridylsulfones with Nitrones for Chiral Fluoroalkylated Isoxazolidines and gamma-Amino Alcohols. *Angew. Chem., Int. Ed.* **2017,** *56* (6), 1510-1514.

27. Jia, Z. J.; Shan, G.; Daniliuc, C. G.; Antonchick, A. P.; Waldmann, H., Enantioselective Synthesis of the Spirotropanyl Oxindole Scaffold through Bimetallic Relay Catalysis. *Angew. Chem., Int. Ed.* **2018,** *57* (44), 14493-14497.

28. Liu, E. C.; Topczewski, J. J., Enantioselective Copper Catalyzed Alkyne - Azide Cycloaddition by Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2019,** *141* (13), 5135-5138.

29. Casado-Sanchez, A.; Domingo-Legarda, P.; Cabrera, S.; Aleman, J., Visible light photocatalytic asymmetric synthesis of pyrrolo 1,2-a indoles via intermolecular 3+2 cycloaddition. *Chem. Comm.* **2019,** *55* (75), 11303-11306.

30. Zhang, D.; Su, Z.; He, Q.; Wu, Z.; Zhou, Y.; Pan, C.; Liu, X.; Feng, X., Diversified Transformations of Tetrahydroindolizines to Construct Chiral 3-Arylindolizines and Dicarbofunctionalized 1,5-Diketones. *J. Am. Chem. Soc.* **2020,** *142* (37), 15975-15985.

2.2.4 Other Reactions

1. Aggarwal, V. K.; Beffield, A. J., Catalytic asymmetric nazarov reactions promoted by chiral Lewis acid complexes. *Org. Lett.* **2003,** *5* (26), 5075-5078.

2. Liang, G. X.; Trauner, D., Enantioselective Nazarov reactions through catalytic asymmetric proton transfer. *J. Am. Chem. Soc.* **2004,** *126* (31), 9544-9545.

3. Rueping, M.; Ieawsuwan, W.; Antonchick, A. P.; Nachtsheim, B. J., Chiral Bronsted acids in the catalytic asymmetric Nazarov cyclization - The first enantioselective organocatalytic electrocyclic reaction. *Angew. Chem., Int. Ed.* **2007,** *46* (12), 2097-2100.

4. Rueping, M.; Antonchick, A. P., Organocatalytic enantioselective reduction of Pyridines. *Angew. Chem., Int. Ed.* **2007,** *46* (24), 4562-4565.

5. Canales, E.; Corey, E. J., Highly enantioselective [2+2]-cycloaddition reactions catalyzed by a chiral aluminum bromide complex. *J. Am. Chem. Soc.* **2007,** *129* (42), 12686-+.

6. Uyeda, C.; Jacobsen, E. N., Enantioselective Claisen rearrangements with a hydrogen-bond donor catalyst. *J. Am. Chem. Soc.* **2008,** *130* (29), 9228-+.

7. Walz, I.; Togni, A., Ni(II)-catalyzed enantioselective Nazarov cyclizations. *Chem. Comm.* **2008,** (36), 4315-4317.

8. Parsons, A. T.; Johnson, J. S., Catalytic Enantioselective Synthesis of Tetrahydrofurans: A Dynamic Kinetic Asymmetric [3+2] Cycloaddition of Racemic Cyclopropanes and Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (9), 3122-+.

9. Muller, C.; Bauer, A.; Bach, T., Light-Driven Enantioselective Organocatalysis. *Angew. Chem., Int. Ed.* **2009,** *48* (36), 6640-6642.

10. Maciver, E. E.; Thompson, S.; Smith, M. D., Catalytic Asymmetric 6 pi Electrocyclization: Enantioselective Synthesis of Functionalized Indolines. *Angew. Chem., Int. Ed.* **2009,** *48* (52), 9979-9982.

11. Muller, S.; List, B., A Catalytic Asymmetric 6 pi Electrocyclization: Enantioselective Synthesis of 2-Pyrazolines. *Angew. Chem., Int. Ed.* **2009,** *48* (52), 9975-9978.

12. Albrecht, D.; Vogt, F.; Bach, T., Diastereo- and Enantioselective Intramolecular 2+2 Photocycloaddition Reactions of 3-(omega '-Alkenyl)- and 3-(omega '-Alkenyloxy)-Substituted 5,6-Dihydro-1H-pyridin-2-ones. *Chem. Eur. J.* **2010,** *16* (14), 4284-4296.

13. Cao, P.; Deng, C.; Zhou, Y. Y.; Sun, X. L.; Zheng, J. C.; Xie, Z. W.; Tang, Y., Asymmetric Nazarov Reaction Catalyzed by Chiral Tris(oxazoline)/Copper(II). *Angew. Chem., Int. Ed.* **2010,** *49* (26), 4463-4466.

14. Muller, S.; List, B., Catalytic Asymmetric 6 pi-Electrocyclization: Accessing Highly Substituted Optically Active 2-Pyrazolines via Diastereoselective Alkylations. *Synthesis* **2010,** (13), 2171-2178.

15. Parsons, A. T.; Smith, A. G.; Neel, A. J.; Johnson, J. S., Dynamic Kinetic Asymmetric Synthesis of Substituted Pyrrolidines from Racemic Cyclopropanes and Aldimines: Reaction Development and Mechanistic Insights. *J. Am. Chem. Soc.* **2010,** *132* (28), 9688-9692.

16. Guo, H.; Herdtweck, E.; Bach, T., Enantioselective Lewis Acid Catalysis in Intramolecular 2+2 Photocycloaddition Reactions of Coumarins. *Angew. Chem., Int. Ed.* **2010,** *49* (42), 7782-7785.

17. Uyeda, C.; Rotheli, A. R.; Jacobsen, E. N., Catalytic Enantioselective Claisen Rearrangements of O-Allyl beta-Ketoesters. *Angew. Chem., Int. Ed.* **2010,** *49* (50), 9753-9756.

18. Campbell, M. J.; Johnson, J. S.; Parsons, A. T.; Pohlhaus, P. D.; Sanders, S. D., Complexity-Building Annulations of Strained Cycloalkanes and C=O pi Bonds. *J. Org. Chem.* **2010,** *75* (19), 6317-6325.

19. Schotes, C.; Mezzetti, A., Enantioselective Ficini Reaction: Ruthenium/PNNP-Catalyzed 2+2 Cycloaddition of Ynamides with Cyclic Enones. *Angew. Chem., Int. Ed.* **2011,** *50* (13), 3072-3074.

20. Uyeda, C.; Jacobsen, E. N., Transition-State Charge Stabilization through Multiple Non-covalent Interactions in the Guanidinium-Catalyzed Enantioselective Claisen Rearrangement. *J. Am. Chem. Soc.* **2011,** *133* (13), 5062-5075.

21. Mori, K.; Ehara, K.; Kurihara, K.; Akiyama, T., Selective Activation of Enantiotopic C(sp(3))-Hydrogen by Means of Chiral Phosphoric Acid: Asymmetric Synthesis of Tetrahydroquinoline Derivatives. *J. Am. Chem. Soc.* **2011,** *133* (16), 6166-6169.

22. Rueping, M.; Ieawsuwan, W., Asymmetric Bronsted acid catalyzed carbonyl activation - organocatalytic domino electrocyclization-halogenation reaction. *Chem. Comm.* **2011,** *47* (41), 11450-11452.

23. Troendlin, J.; Rehbein, J.; Hiersemann, M.; Trapp, O., Integration of Catalysis and Analysis is the Key: Rapid and Precise Investigation of the Catalytic Asymmetric Gosteli-Claisen Rearrangement. *J. Am. Chem. Soc.* **2011,** *133* (41), 16444-16450.

24. Muller, C.; Bauer, A.; Maturi, M. M.; Cuquerella, M. C.; Miranda, M. A.; Bach, T., Enantioselective Intramolecular 2+2 -Photocycloaddition Reactions of 4-Substituted Quinolones Catalyzed by a Chiral Sensitizer with a Hydrogen-Bonding Motif. *J. Am. Chem. Soc.* **2011,** *133* (41), 16689-16697.

25. Leboeuf, D.; Huang, J.; Gandon, V.; Frontier, A. J., Using Nazarov Electrocyclization to Stage Chemoselective 1,2 -Migrations: Stereoselective Synthesis of Functionalized Cyclopentenones. *Angew. Chem., Int. Ed.* **2011,** *50* (46), 10981-10985.

26. Gao, L.; Hwang, G.-S.; Ryu, D. H., Oxazaborolidinium Ion-Catalyzed Cyclopropanation of alpha-Substituted Acroleins: Enantioselective Synthesis of Cyclopropanes Bearing Two Chiral Quaternary Centers. *J. Am. Chem. Soc.* **2011,** *133* (51), 20708-20711.

27. Muller, S.; Webber, M. J.; List, B., The Catalytic Asymmetric Fischer Indolization. *J. Am. Chem. Soc.* **2011,** *133* (46), 18534-18537.

28. Austin, K. A. B.; Herdtweck, E.; Bach, T., Intramolecular 2+2 Photocycloaddition of Substituted Isoquinolones: Enantioselectivity and Kinetic Resolution Induced by a Chiral Template. *Angew. Chem., Int. Ed.* **2011,** *50* (36), 8416-8419.

29. Eitel, S. H.; Bauer, M.; Schweinfurth, D.; Deibel, N.; Sarkar, B.; Kelm, H.; Kruger, H. J.; Frey, W.; Peters, R., Paramagnetic Palladacycles with Pd-III Centers Are Highly Active Catalysts for Asymmetric Aza-Claisen Rearrangements. *J. Am. Chem. Soc.* **2012,** *134* (10), 4683-4693.

30. Zhang, Y. Q.; Zhang, J. L., Kinetic resolution of 1-(1-alkynyl)cyclopropyl ketones by gold(I)-catalyzed asymmetric 4+3 cycloaddition with nitrones: scope, mechanism and applications. *Chem. Comm.* **2012,** *48* (39), 4710-4712.

31. Biswas, A.; De Sarkar, S.; Tebben, L.; Studer, A., Enantioselective cyclopropanation of enals by oxidative N-heterocyclic carbene catalysis. *Chem. Comm.* **2012,** *48* (42), 5190-5192.

32. Chen, J. R.; Dong, W. R.; Candy, M.; Pan, F. F.; Jorres, M.; Bolm, C., Enantioselective Synthesis of Dihydropyrazoles by Formal 4+1 Cycloaddition of in Situ-Derived Azoalkenes and Sulfur Ylides. *J. Am. Chem. Soc.* **2012,** *134* (16), 6924-6927.

33. Brimioulle, R.; Guo, H.; Bach, T., Enantioselective Intramolecular 2+2 Photocycloaddition Reactions of 4-Substituted Coumarins Catalyzed by a Chiral Lewis Acid. *Chem. Eur. J.* **2012,** *18* (24), 7552-7560.

34. Zhou, Y. Y.; Wang, L. J.; Li, J.; Sun, X. L.; Tang, Y., Side-Arm-Promoted Highly Enantioselective Ring-Opening Reactions and Kinetic Resolution of Donor-Acceptor Cyclopropanes with Amines. *J. Am. Chem. Soc.* **2012,** *134* (22), 9066-9069.

35. Tan, J. J.; Cheon, C. H.; Yamamoto, H., Catalytic Asymmetric Claisen Rearrangement of Enolphosphonates: Construction of Vicinal Tertiary and All-Carbon Quaternary Centers. *Angew. Chem., Int. Ed.* **2012,** *51* (33), 8264-8267.

36. Wiegand, C.; Herdtweck, E.; Bach, T., Enantioselectivity in visible light-induced, singlet oxygen 2+4 cycloaddition reactions (type II photooxygenations) of 2-pyridones. *Chem. Comm.* **2012,** *48* (82), 10195-10197.

37. Zhou, Y. Y.; Li, J.; Ling, L.; Liao, S. H.; Sun, X. L.; Li, Y. X.; Wang, L. J.; Tang, Y., Highly Enantioselective 3+3 Cycloaddition of Aromatic Azomethine Imines with Cyclopropanes Directed by pi-pi Stacking Interactions. *Angew. Chem., Int. Ed.* **2013,** *52* (5), 1452-1456.

38. MacDonald, M. J.; Hesp, C. R.; Schipper, D. J.; Pesant, M.; Beauchemin, A. M., Highly Enantioselective Intermolecular Hydroamination of Allylic Amines with Chiral Aldehydes as Tethering Catalysts. *Chem. Eur. J.* **2013,** *19* (8), 2597-2601.

39. Xu, H.; Qu, J. P.; Liao, S. H.; Xiong, H.; Tang, Y., Highly Enantioselective 3+2 Annulation of Cyclic Enol Silyl Ethers with DonorAcceptor Cyclopropanes: Accessing 3a-Hydroxy n.3.0 Carbobicycles. *Angew. Chem., Int. Ed.* **2013,** *52* (14), 4004-4007.

40. Hutson, G. E.; Turkmen, Y. E.; Rawal, V. H., Salen Promoted Enantioselective Nazarov Cyclizations of Activated and Unactivated Dienones. *J. Am. Chem. Soc.* **2013,** *135* (13), 4988-4991.

41. Xie, M. S.; Liu, X. H.; Wu, X. X.; Cai, Y. F.; Lin, L. L.; Feng, X. M., Catalytic Asymmetric 8+2 Cycloaddition: Synthesis of Cycloheptatriene-Fused Pyrrole Derivatives. *Angew. Chem., Int. Ed.* **2013,** *52* (21), 5604-5607.

42. Martinez, A.; Webber, M. J.; Muller, S.; List, B., Versatile Access to Chiral Indolines by Catalytic Asymmetric Fischer Indolization. *Angew. Chem., Int. Ed.* **2013,** *52* (36), 9486-9490.

43. Xiong, H.; Xu, H.; Liao, S. H.; Xie, Z. W.; Tang, Y., Copper-Catalyzed Highly Enantioselective Cyclopentannulation of Indoles with Donor-Acceptor Cyclopropanes. *J. Am. Chem. Soc.* **2013,** *135* (21), 7851-7854.

44. Das, A.; Volla, C. M. R.; Atodiresei, I.; Bettray, W.; Rueping, M., Asymmetric Ion Pair Catalysis of 6Electrocyclizations: BrOnsted Acid Catalyzed Enantioselective Synthesis of Optically Active 1,4-Dihydropyridazines. *Angew. Chem., Int. Ed.* **2013,** *52* (31), 8008-8011.

45. De, C. K.; Pesciaioli, F.; List, B., Catalytic Asymmetric Benzidine Rearrangement. *Angew. Chem., Int. Ed.* **2013,** *52* (35), 9293-9295.

46. Coote, S. C.; Bach, T., Enantioselective Intermolecular 2+2 Photocycloadditions of Isoquinolone Mediated by a Chiral Hydrogen-Bonding Template. *J. Am. Chem. Soc.* **2013,** *135* (40), 14948-14951.

47. Maity, P.; Pemberton, R. P.; Tantillo, D. J.; Tambar, U. K., Bronsted Acid Catalyzed Enantioselective Indole Aza-Claisen Rearrangement Mediated by an Arene CH-O Interaction. *J. Am. Chem. Soc.* **2013,** *135* (44), 16380-16383.

48. Brimioulle, R.; Bach, T., Enantioselective Lewis Acid Catalysis of Intramolecular Enone 2+2 Photocycloaddition Reactions. *Science* **2013,** *342* (6160), 840-843.

49. Chen, W.; Lin, L.; Cai, Y.; Xia, Y.; Cao, W.; Liu, X.; Feng, X., Catalytic asymmetric 3+2 cycloaddition of aromatic aldehydes with oxiranes by C-C bond cleavage of epoxides: highly efficient synthesis of chiral 1,3-dioxolanes. *Chem. Comm.* **2014,** *50* (17), 2161-2163.

50. Alonso, R.; Bach, T., A Chiral Thioxanthone as an Organocatalyst for Enantioselective 2+2 Photocycloaddition Reactions Induced by Visible Light**. *Angew. Chem., Int. Ed.* **2014,** *53* (17), 4368-4371.

51. Vallavoju, N.; Selvakumar, S.; Jockusch, S.; Sibi, M. P.; Sivaguru, J., Enantioselective Organo-Photocatalysis Mediated by Atropisomeric Thiourea Derivatives. *Angew. Chem., Int. Ed.* **2014,** *53* (22), 5604-5608.

52. Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P., A Dual-Catalysis Approach to Enantioselective 2+2 Photocycloadditions Using Visible Light. *Science* **2014,** *344* (6182), 392-396.

53. Zhu, J.; Liang, Y.; Wang, L.; Zheng, Z.-B.; Houk, K. N.; Tang, Y., Remote Ester Groups Switch Selectivity: Diastereodivergent Synthesis of Tetracyclic Spiroindolines. *J. Am. Chem. Soc.* **2014,** *136* (19), 6900-6903.

54. Jolit, A.; Walleser, P. M.; Yap, G. P. A.; Tius, M. A., Catalytic Enantioselective Nazarov Cyclization: Construction of Vicinal All-Carbon-Atom Quaternary Stereocenters. *Angew. Chem., Int. Ed.* **2014,** *53* (24), 6180-6183.

55. Maturi, M. M.; Bach, T., Enantioselective Catalysis of the Intermolecular 2+2 Photocycloaddition between 2-Pyridones and Acetylenedicarboxylates. *Angew. Chem., Int. Ed.* **2014,** *53* (29), 7661-7664.

56. Ball-Jones, N. R.; Badillo, J. J.; Tran, N. T.; Franz, A. K., Catalytic Enantioselective Carboannulation with Allylsilanes. *Angew. Chem., Int. Ed.* **2014,** *53* (36), 9462-9465.

57. Chen, W. L.; Fu, X.; Lin, L. L.; Yuan, X.; Luo, W. W.; Feng, J. H.; Liu, X. H.; Feng, X. M., An asymmetric 3+2 cycloaddition of alkynes with oxiranes by selective C-C bond cleavage of epoxides: highly efficient synthesis of chiral furan derivatives. *Chem. Comm.* **2014,** *50* (78), 11480-11483.

58. Liu, Y.; Hu, H.; Zheng, H.; Xia, Y.; Liu, X.; Lin, L.; Feng, X., Nickel(II)-Catalyzed Asymmetric Propargyl and Allyl Claisen Rearrangements to Allenyl-and Allyl-Substituted beta-Ketoesters. *Angew. Chem., Int. Ed.* **2014,** *53* (43), 11579-11582.

59. Brimioulle, R.; Bach, T., 2+2 Photocycloaddition of 3-Alkenyloxy-2-cycloalkenones: Enantioselective Lewis Acid Catalysis and Ring Expansion. *Angew. Chem., Int. Ed.* **2014,** *53* (47), 12921-12924.

60. Xia, Y.; Liu, X.; Zheng, H.; Lin, L.; Feng, X., Asymmetric Synthesis of 2,3-Dihydropyrroles by Ring-Opening/Cyclization of Cyclopropyl Ketones Using Primary Amines. *Angew. Chem., Int. Ed.* **2015,** *54* (1), 227-230.

61. Raja, S.; Nakajima, M.; Rueping, M., Experimental and Computational Study of the Catalytic Asymmetric 4 pi-Electrocyclization of N-Heterocycles. *Angew. Chem., Int. Ed.* **2015,** *54* (9), 2762-2765.

62. Enomoto, K.; Oyama, H.; Nakada, M., Highly Enantioselective Catalytic Asymmetric 2+2 Cycloadditions of Cyclic alpha-Alkylidene beta-Oxo Imides with Ynamides. *Chem. Eur. J.* **2015,** *21* (7), 2798-2802.

63. Conner, M. L.; Xu, Y.; Brown, M. K., Catalytic Enantioselective Allenoate-Alkene 2+2 Cycloadditions. *J. Am. Chem. Soc.* **2015,** *137* (10), 3482-3485.

64. Kitamura, K.; Shimada, N.; Stewart, C.; Atesin, A. C.; Atesin, T. A.; Tius, M. A., Enantioselective Palladium(0)-Catalyzed Nazarov-Type Cyclization. *Angew. Chem., Int. Ed.* **2015,** *54* (21), 6288-6291.

65. Brimioulle, R.; Bauer, A.; Bach, T., Enantioselective Lewis Acid Catalysis in Intramolecular 2+2 Photocycloaddition Reactions: A Mechanistic Comparison between Representative Coumarin and Enone Substrates. *J. Am. Chem. Soc.* **2015,** *137* (15), 5170-5176.

66. Hu, J. L.; Wang, L. J.; Xu, H.; Xie, Z. W.; Tang, Y., Highly Diastereoselective and Enantioselective Formal 4+3 Cycloaddition of Donor-Acceptor Cyclobutanes with Nitrones. *Org. Lett.* **2015,** *17* (11), 2680-2683.

67. Xu, H.; Hu, J. L.; Wang, L. J.; Liao, S. H.; Tang, Y., Asymmetric Annulation of Donor-Acceptor Cyclopropanes with Dienes. *J. Am. Chem. Soc.* **2015,** *137* (25), 8006-8009.

68. Yang, B. M.; Cai, P. J.; Tu, Y. Q.; Yu, Z. X.; Chen, Z. M.; Wang, S. H.; Wang, S. H.; Zhang, F. M., Organocatalytic Asymmetric Tandem Nazarov Cyclization/Semipinacol Rearrangement: Rapid Construction of Chiral Spiro 4.4 nonane-1,6-diones. *J. Am. Chem. Soc.* **2015,** *137* (26), 8344-8347.

69. Liu, Q. J.; Yan, W. G.; Wang, L. J.; Zhang, X. P.; Tang, Y., One-Pot Catalytic Asymmetric Synthesis of Tetrahydrocarbazoles. *Org. Lett.* **2015,** *17* (16), 4014-4017.

70. Xia, Y.; Lin, L. L.; Chang, F. Z.; Fu, X.; Liu, X. H.; Feng, X. M., Asymmetric Ring-Opening of Cyclopropyl Ketones with Thiol, Alcohol, and Carboxylic Acid Nucleophiles Catalyzed by a Chiral N,N '-Dioxide-Scandium(III) Complex. *Angew. Chem., Int. Ed.* **2015,** *54* (46), 13748-13752.

71. Asari, A. H.; Lam, Y. H.; Tius, M. A.; Houk, K. N., Origins of the Stereoselectivity in a Thiourea-Primary Amine-Catalyzed Nazarov Cyclization. *J. Am. Chem. Soc.* **2015,** *137* (40), 13191-13199.

72. Liao, H. H.; Chatupheeraphat, A.; Hsiao, C. C.; Atodiresei, I.; Rueping, M., Asymmetric Bronsted Acid Catalyzed Synthesis of Triarylmethanes-Construction of Communesin and Spiroindoline Scaffolds. *Angew. Chem., Int. Ed.* **2015,** *54* (51), 15540-15544.

73. Goodman, C. G.; Johnson, J. S., Asymmetric Synthesis of beta-Amino Amides by Catalytic Enantioconvergent 2-Aza-Cope Rearrangement. *J. Am. Chem. Soc.* **2015,** *137* (46), 14574-14577.

74. Kang, Q. K.; Wang, L. J.; Liu, Q. J.; Li, J. F.; Tang, Y., Asymmetric H2O-Nucleophilic Ring Opening of D-A Cyclopropanes: Catalyst Serves as a Source of Water. *J. Am. Chem. Soc.* **2015,** *137* (46), 14594-14597.

75. Guo, J.; Liu, Y. B.; Li, X. Q.; Liu, X. H.; Lin, L. L.; Feng, X. M., Nickel(II)-catalyzed enantioselective cyclopropanation of 3-alkenyl-oxindoles with phenyliodonium ylide via free carbene. *Chemical Science* **2016,** *7* (4), 2717-2721.

76. Liu, Y. B.; Liu, X. H.; Hu, H. P.; Guo, J.; Xia, Y.; Lin, L. L.; Feng, X. M., Synergistic Kinetic Resolution and Asymmetric Propargyl Claisen Rearrangement for the Synthesis of Chiral Allenes. *Angew. Chem., Int. Ed.* **2016,** *55* (12), 4054-4058.

77. Liao, Y. T.; Liu, X. H.; Zhang, Y.; Xu, Y. L.; Xia, Y.; Lin, L. L.; Feng, X. M., Asymmetric 3+2 cycloaddition of donor-acceptor aziridines with aldehydes via carbon-carbon bond cleavage. *Chemical Science* **2016,** *7* (6), 3775-3779.

78. Huang, R.; Chang, X.; Li, J.; Wang, C. J., Cu(I)-Catalyzed Asymmetric Multicomponent Cascade Inverse Electron-Demand Aza-Diels Alder/Nucleophilic Addition/Ring-Opening Reaction Involving 2-Methoxyfurans as Efficient Dienophiles. *J. Am. Chem. Soc.* **2016,** *138* (12), 3998-4001.

79. Amador, A. G.; Sherbrook, E. M.; Yoon, T. P., Enantioselective Photocatalytic 3+2 Cycloadditions of Aryl Cyclopropyl Ketones. *J. Am. Chem. Soc.* **2016,** *138* (14), 4722-4725.

80. Kang, T. F.; Ge, S. L.; Lin, L. L.; Lu, Y.; Liu, X. H.; Feng, X. M., A Chiral N,N '-Dioxide-Zn-II Complex Catalyzes the Enantioselective 2+2 Cycloaddition of Alkynones with Cyclic Enol Silyl Ethers. *Angew. Chem., Int. Ed.* **2016,** *55* (18), 5541-5544.

81. Troster, A.; Alonso, R.; Bauer, A.; Bach, T., Enantioselective Intermolecular 2+2 Photocycloaddition Reactions of 2(1H)-Quinolones Induced by Visible Light Irradiation. *J. Am. Chem. Soc.* **2016,** *138* (25), 7808-7811.

82. Xia, Y.; Lin, L. L.; Chang, F. Z.; Liao, Y. T.; Liu, X. H.; Feng, X. M., Asymmetric Ring Opening/Cyclization/Retro-Mannich Reaction of Cyclopropyl Ketones with Aryl 1,2-Diamines for the Synthesis of Benzimidazole Derivatives. *Angew. Chem., Int. Ed.* **2016,** *55* (40), 12228-12232.

83. Hu, J. L.; Feng, L. W.; Wang, L. J.; Xie, Z. W.; Tang, Y.; Li, X. G., Enantioselective Construction of Cyclobutanes: A New and Concise Approach to the Total Synthesis of (+)-Piperarborenine B. *J. Am. Chem. Soc.* **2016,** *138* (40), 13151-13154.

84. Wang, D. C.; Xie, M. S.; Guo, H. M.; Qu, G. R.; Zhang, M. C.; You, S. L., Enantioselective Dearomative 3+2 Cycloaddition Reactions of Benzothiazoles. *Angew. Chem., Int. Ed.* **2016,** *55* (45), 14111-14115.

85. Levens, A.; Ametovski, A.; Lupton, D. W., Enantioselective (4+2) Annulation of Donor-Acceptor Cyclobutanes by N-Heterocyclic Carbene Catalysis. *Angew. Chem., Int. Ed.* **2016,** *55* (52), 16136-16140.

86. Wu, X. X.; Liu, B.; Zhang, Y. X.; Jeret, M.; Wang, H. L.; Zheng, P. C.; Yang, S.; Song, B. A.; Chi, Y. R., Enantioselective Nucleophilic beta-Carbon-Atom Amination of Enals: Carbene-Catalyzed Formal 3+2 Reactions. *Angew. Chem., Int. Ed.* **2016,** *55* (40), 12280-12284.

87. Li, J.; Lin, L. L.; Hu, B. W.; Zhou, P. F.; Huang, T. Y.; Liu, X. H.; Feng, X. M., Gold(I)/Chiral N,N '-Dioxide-Nickel(II) Relay Catalysis for Asymmetric Tandem Intermolecular Hydroalkoxylation/Claisen Rearrangement. *Angew. Chem., Int. Ed.* **2017,** *56* (3), 885-888.

88. Feng, L. W.; Ren, H.; Xiong, H.; Wang, P.; Wang, L. J.; Tang, Y., Reaction of Donor-Acceptor Cyclobutanes with Indoles: A General Protocol for the Formal Total Synthesis of (+/-)-Strychnine and the Total Synthesis of (+/-)-Akuammicine. *Angew. Chem., Int. Ed.* **2017,** *56* (11), 3055-3058.

89. Wu, X. X.; Hao, L.; Zhang, Y. X.; Rakesh, M.; Reddi, R. N.; Yang, S.; Song, B. A.; Chi, Y. R., Construction of Fused Pyrrolidines and beta-Lactones by Carbene-Catalyzed C-N, C-C, and C-O Bond Formations. *Angew. Chem., Int. Ed.* **2017,** *56* (15), 4201-4205.

90. Chen, H.; Wang, L. J.; Wang, F.; Zhao, L. P.; Wang, P.; Tang, Y., Access to Hexahydrocarbazoles: The Thorpe-Ingold Effects of the Ligand on Enantioselectivity. *Angew. Chem., Int. Ed.* **2017,** *56* (24), 6942-6945.

91. Liao, Y. T.; Zhou, B. X.; Xia, Y.; Liu, X. H.; Lin, L. L.; Feng, X. M., Asymmetric 3+2 Cycloaddition of 2,2 '-Diester Aziridines To Synthesize Pyrrolidine Derivatives. *Acs Catalysis* **2017,** *7* (6), 3934-3939.

92. Huang, X. Q.; Quinn, T. R.; Harms, K.; Webster, R. D.; Zhang, L. L.; Wiest, O.; Meggers, E., Direct Visible-Light-Excited Asymmetric Lewis Acid Catalysis of Intermolecular 2+2 Photocycloadditions. *J. Am. Chem. Soc.* **2017,** *139* (27), 9120-9123.

93. Miller, Z. D.; Lee, B. J.; Yoon, T. P., Enantioselective Crossed Photocycloadditions of Styrenic Olefins by Lewis Acid Catalyzed Triplet Sensitization. *Angew. Chem., Int. Ed.* **2017,** *56* (39), 11891-11895.

94. Perrotta, D.; Wang, M.-M.; Waser, J., Lewis Acid Catalyzed Enantioselective Desymmetrization of Donor–Acceptor meso-Diaminocyclopropanes. *Angew. Chem., Int. Ed.* **2018,** *57* (18), 5120-5123.

95. Poplata, S.; Bach, T., Enantioselective Intermolecular 2+2 Photocycloaddition Reaction of Cyclic Enones and Its Application in a Synthesis of (-)-Grandisol. *J. Am. Chem. Soc.* **2018,** *140* (9), 3228-3231.

96. Huang, X. Q.; Lin, J. H.; Shen, T. Q.; Harms, K.; Marchini, M.; Ceroni, P.; Meggers, E., Asymmetric 3+2 Photocycloadditions of Cyclopropanes with Alkenes or Alkynes through Visible-Light Excitation of Catalyst-Bound Substrates. *Angew. Chem., Int. Ed.* **2018,** *57* (19), 5454-5458.

97. Hu, N. F.; Jung, H.; Zheng, Y.; Lee, J.; Zhang, L. L.; Ullah, Z.; Xie, X. L.; Harms, K.; Baik, M. H.; Meggers, E., Catalytic Asymmetric Dearomatization by Visible-Light-Activated 2+2 Photocycloaddition. *Angew. Chem., Int. Ed.* **2018,** *57* (21), 6242-6246.

98. Xu, X.; Zhang, J. L.; Dong, S. X.; Lin, L. L.; Lin, X. B.; Liu, X. H.; Feng, X. M., Nickel(II)-Catalyzed Asymmetric Propargyl 2,3 Wittig Rearrangement of Oxindole Derivatives: A Chiral Amplification Effect. *Angew. Chem., Int. Ed.* **2018,** *57* (28), 8734-8738.

99. Zhu, M.; Wang, D. C.; Xie, M. S.; Qu, G. R.; Guo, H. M., Enantioselective Friedel-Crafts Alkylation Reactions of beta-Naphthols with Donor-Acceptor Aminocyclopropanes. *Chem. Eur. J.* **2018,** *24* (58), 15512-15516.

100. Holzl-Hobmeier, A.; Bauer, A.; Silva, A. V.; Huber, S. M.; Bannwarth, C.; Bach, T., Catalytic deracemization of chiral allenes by sensitized excitation with visible light. *Nature* **2018,** *564* (7735), 240-+.

101. Chen, K. Q.; Gao, Z. H.; Ye, S., (Dynamic) Kinetic Resolution of Enamines/Imines: Enantioselective N-Heterocyclic Carbene Catalyzed 3+3 Annulation of Bromoenals and Enamines/Imines. *Angew. Chem., Int. Ed.* **2019,** *58* (4), 1183-1187.

102. Troster, A.; Bauer, A.; Jandl, C.; Bach, T., Enantioselective Visible-Light-Mediated Formation of 3-Cyclopropylquinolones by Triplet-Sensitized Deracemization. *Angew. Chem., Int. Ed.* **2019,** *58* (11), 3538-3541.

103. Hao, E. J.; Fu, D. D.; Wang, D. C.; Zhang, T.; Qu, G. R.; Li, G. X.; Lan, Y.; Guo, H. M., Chemoselective asymmetric dearomative 3+2 cycloaddition reactions of purines with aminocyclopropanes. *Organic Chemistry Frontiers* **2019,** *6* (6), 863-867.

104. Ouyang, J.; Kennemur, J. L.; Kanta, D.; Fares, C.; List, B., Strong and Confined Acids Enable a Catalytic Asymmetric Nazarov Cyclization of Simple Divinyl Ketones. *J. Am. Chem. Soc.* **2019,** *141* (8), 3414-3418.

105. Hong, Y. B.; Jarrige, L.; Harms, K.; Meggers, E., Chiral-at-Iron Catalyst: Expanding the Chemical Space for Asymmetric Earth-Abundant Metal Catalysis. *J. Am. Chem. Soc.* **2019,** *141* (11), 4569-4572.

106. Daub, M. E.; Jung, H.; Lee, B. J.; Won, J.; Baik, M. H.; Yoon, T. P., Enantioselective 2+2 Cycloadditions of Cinnamate Esters: Generalizing Lewis Acid Catalysis of Triplet Energy Transfer. *J. Am. Chem. Soc.* **2019,** *141* (24), 9543-9547.

107. Pandit, R. P.; Kim, S. T.; Ryu, D. H., Asymmetric Synthesis of Enantioenriched 2-Aryl-2,3-Dihydrobenzofurans by a Lewis Acid Catalyzed Cyclopropanation/Intramolecular Rearrangement Sequence. *Angew. Chem., Int. Ed.* **2019,** *58* (38), 13427-13432.

108. Zheng, J.; Swords, W. B.; Jung, H.; Skubi, K. L.; Kidd, J. B.; Meyer, G. J.; Baik, M. H.; Yoon, T. P., Enantioselective Intermolecular Excited-State Photoreactions Using a Chiral Ir Triplet Sensitizer: Separating Association from Energy Transfer in Asymmetric Photocatalysis. *J. Am. Chem. Soc.* **2019,** *141* (34), 13625-13634.

109. Zhang, C. H.; Chen, S. M.; Ye, C. X.; Harms, K.; Zhang, L. L.; Houk, K. N.; Meggers, E., Asymmetric Photocatalysis by Intramolecular Hydrogen-Atom Transfer in Photoexcited Catalyst-Substrate Complex. *Angew. Chem., Int. Ed.* **2019,** *58* (41), 14462-14466.

110. Leverenz, M.; Merten, C.; Dreuw, A.; Bach, T., Lewis Acid Catalyzed Enantioselective Photochemical Rearrangements on the Singlet Potential Energy Surface. *J. Am. Chem. Soc.* **2019,** *141* (51), 20053-20057.

111. Miró, J.; Gensch, T.; Ellwart, M.; Han, S.-J.; Lin, H.-H.; Sigman, M. S.; Toste, F. D., Enantioselective Allenoate-Claisen Rearrangement Using Chiral Phosphate Catalysts. *J. Am. Chem. Soc.* **2020,** *142* (13), 6390-6399.

112. Plaza, M.; Jandl, C.; Bach, T., Photochemical Deracemization of Allenes and Subsequent Chirality Transfer. *Angew. Chem., Int. Ed.* **2020,** *59* (31), 12785-12788.

113. Li, X.; Kutta, R. J.; Jandl, C.; Bauer, A.; Nuernberger, P.; Bach, T., Photochemically Induced Ring Opening of Spirocyclopropyl Oxindoles: Evidence for a Triplet 1,3-Diradical Intermediate and Deracemization by a Chiral Sensitizer. *Angew. Chem., Int. Ed.* **2020,** *59* (48), 21640-21647.

114. Zeng, L.; Xu, J.; Zhang, D.; Yan, Z.; Cheng, G.; Rao, W.; Gao, L., Catalytic Enantioselective [2+2] Cycloaddition of α-Halo Acroleins: Construction of Cyclobutanes Containing Two Tetrasubstituted Stereocenters. *Angew. Chem., Int. Ed.* **2020,** *59* (49), 21890-21894.

115. Schwinger, D. P.; Bach, T., Chiral 1,3,2-Oxazaborolidine Catalysts for Enantioselective Photochemical Reactions. *Acc. Chem. Res.* **2020,** *53* (9), 1933-1943.

116. Li, X.; Großkopf, J.; Jandl, C.; Bach, T., Enantioselective, Visible Light Mediated Aza Paternò–Büchi Reactions of Quinoxalinones. *Angew. Chem., Int. Ed.* **2021,** *60* (5), 2684-2688.

117. Pecho, F.; Sempere, Y.; Gramüller, J.; Hörmann, F. M.; Gschwind, R. M.; Bach, T., Enantioselective [2 + 2] Photocycloaddition via Iminium Ions: Catalysis by a Sensitizing Chiral Brønsted Acid. *J. Am. Chem. Soc.* **2021,** *143* (25), 9350-9354.

118. Plaza, M.; Großkopf, J.; Breitenlechner, S.; Bannwarth, C.; Bach, T., Photochemical Deracemization of Primary Allene Amides by Triplet Energy Transfer: A Combined Synthetic and Theoretical Study. *J. Am. Chem. Soc.* **2021,** *143* (29), 11209-11217.

119. Zhang, M.; Wang, X.-C., Bifunctional Borane Catalysis of a Hydride Transfer/Enantioselective [2+2] Cycloaddition Cascade. *Angew. Chem., Int. Ed.* **2021,** *60* (31), 17185-17190.

120. Rigotti, T.; Schwinger, D. P.; Graßl, R.; Jandl, C.; Bach, T., Enantioselective crossed intramolecular [2+2] photocycloaddition reactions mediated by a chiral chelating Lewis acid. *Chemical Science* **2022,** *13* (8), 2378-2384.

121. Wu, X.; Sparr, C., Stereoselective Synthesis of Atropisomeric Acridinium Salts by the Catalyst-Controlled Cyclization of ortho-Quinone Methide Iminiums. *Angew. Chem., Int. Ed.* **2022,** *61* (19), e202201424.

122. Zhang, F.; Sang, X.; Zhou, Y.; Cao, W.; Feng, X., Enantioselective Synthesis of Azetidines through [3 + 1]-Cycloaddition of Donor–Acceptor Aziridines with Isocyanides. *Org. Lett.* **2022,** *24* (7), 1513-1517.

123. Ouyang, J.; Maji, R.; Leutzsch, M.; Mitschke, B.; List, B., Design of an Organocatalytic Asymmetric (4 + 3) Cycloaddition of 2-Indolylalcohols with Dienolsilanes. *J. Am. Chem. Soc.* **2022,** *144* (19), 8460-8466.

124. Kratz, T.; Steinbach, P.; Breitenlechner, S.; Storch, G.; Bannwarth, C.; Bach, T., Photochemical Deracemization of Chiral Alkenes via Triplet Energy Transfer. *J. Am. Chem. Soc.* **2022,** *144* (23), 10133-10138.

125. Zhong, X.; Huang, M.; Xiong, H.; Liang, Y.; Zhou, W.; Cai, Q., Asymmetric Synthesis of Spiro[Azetidine-3,3′-Indoline]-2,2′-Diones via Copper(I)-Catalyzed Kinugasa/C−C Coupling Cascade Reaction. *Angew. Chem., Int. Ed.* **2022,** *61* (42), e202208323.

126. Xiao, W.; Ning, L.; Xin, S.; Dong, S.; Liu, X.; Feng, X., Enantioselective [2+2] Cycloaddition of Allenyl Imide with Mono- or Disubstituted Alkenes. *Angew. Chem., Int. Ed.* **2022,** *61* (44), e202211596.

127. Stegbauer, S.; Jandl, C.; Bach, T., Chiral Lewis acid catalysis in a visible light-triggered cycloaddition/rearrangement cascade. *Chemical Science* **2022,** *13* (40), 11856-11862.

128. Jones, B. A.; Solon, P.; Popescu, M. V.; Du, J.-Y.; Paton, R.; Smith, M. D., Catalytic Enantioselective 6π Photocyclization of Acrylanilides. *J. Am. Chem. Soc.* **2023,** *145* (1), 171-178.

129. Das, S.; Zhu, C.; Demirbas, D.; Bill, E.; De, C. K.; List, B., Asymmetric counteranion-directed photoredox catalysis. *Science* **2023,** *379* (6631), 494-499.

130. Yao, L.; Takeda, K.; Ando, K.; Ishihara, K., Enantioselective aromatic Claisen rearrangement of allyl 2-naphthyl ethers catalyzed by π–Cu(ii) complexes. *Chemical Science* **2023,** *14* (9), 2441-2446.

131. Leverenz, M.; Brockmann, H.; Dreuw, A.; Bach, T.; Storch, G., Enantiodivergent Photochemical Rearrangements Due to Different Coordination Modes at an Oxazaborolidine Lewis Acid Catalyst. *ACS Catalysis* **2023,** *13* (9), 5896-5905.

132. Yang, L.; He, J.; Wang, H.; Xu, W.; Zhang, X.; Lang, M.; Wang, J.; Peng, S., Asymmetric (5 + 3) Annulation of Donor–Acceptor Cyclopropanes with Imidazolidines: Access to Saturated 1,4-Diazocanes. *ACS Catalysis* **2023,** *13* (8), 5752-5758.

133. Ohmura, S.; Katagiri, K.; Kato, H.; Horibe, T.; Miyakawa, S.; Hasegawa, J.-y.; Ishihara, K., Highly Enantioselective Radical Cation [2 + 2] and [4 + 2] Cycloadditions by Chiral Iron(III) Photoredox Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (28), 15054-15060.

134. Onneken, C.; Morack, T.; Soika, J.; Sokolova, O.; Niemeyer, N.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Neugebauer, J.; Gilmour, R., Light-enabled deracemization of cyclopropanes by Al-salen photocatalysis. *Nature* **2023,** *621* (7980), 753-759.

135. de Robichon, M.; Kratz, T.; Beyer, F.; Zuber, J.; Merten, C.; Bach, T., Enantioselective, Intermolecular [π2+σ2] Photocycloaddition Reactions of 2(1H)-Quinolones and Bicyclo[1.1.0]butanes. *J. Am. Chem. Soc.* **2023,** *145* (45), 24466-24470.

136. Yan, P.; Stegbauer, S.; Wu, Q.; Kolodzeiski, E.; Stein, C. J.; Lu, P.; Bach, T., Enantioselective Intramolecular ortho Photocycloaddition Reactions of 2-Acetonaphthones. *Angew. Chem., Int. Ed.* **2024,** *63* (13), e202318126.

137. Kidd, J. B.; Fiala, T. A.; Swords, W. B.; Park, Y.; Meyer, K. A.; Sanders, K. M.; Guzei, I. A.; Wright, J. C.; Yoon, T. P., Enantioselective Paternò–Büchi Reactions: Strategic Application of a Triplet Rebound Mechanism for Asymmetric Photocatalysis. *J. Am. Chem. Soc.* **2024,** *146* (22), 15293-15300.

138. Wu, F.; Wu, W.-B.; Xiao, Y.; Li, Z.; Tang, L.; He, H.-X.; Yang, X.-C.; Wang, J.-J.; Cai, Y.; Xu, T.-T.; Tao, J.-H.; Wang, G.; Feng, J.-J., Zinc-Catalyzed Enantioselective Formal (3+2) Cycloadditions of Bicyclobutanes with Imines: Catalytic Asymmetric Synthesis of Azabicyclo[2.1.1]hexanes. *Angew. Chem., Int. Ed.* **2024,** *63* (48), e202406548.

139. Zhang, X.-G.; Zhou, Z.-Y.; Li, J.-X.; Chen, J.-J.; Zhou, Q.-L., Copper-Catalyzed Enantioselective [4π + 2σ] Cycloaddition of Bicyclobutanes with Nitrones. *J. Am. Chem. Soc.* **2024,** *146* (40), 27274-27281.

140. Yang, X.-C.; Wu, F.; Wu, W.-B.; Zhang, X.; Feng, J.-J., Enantioselective dearomative formal (3+3) cycloadditions of bicyclobutanes with aromatic azomethine imines: access to fused 2,3-diazabicyclo[3.1.1]heptanes. *Chemical Science* **2024,** *15* (46), 19488-19495.

141. Li, Y.-J.; Wu, Z.-L.; Gu, Q.-S.; Fan, T.; Duan, M.-H.; Wu, L.; Wang, Y.-T.; Wu, J.-P.; Fu, F.-L.; Sang, F.; Peng, A.-T.; Jiang, Y.; Liu, X.-Y.; Lin, J.-S., Catalytic Intermolecular Asymmetric [2π + 2σ] Cycloadditions of Bicyclo[1.1.0]butanes: Practical Synthesis of Enantioenriched Highly Substituted Bicyclo[2.1.1]hexanes. *J. Am. Chem. Soc.* **2024,** *146* (50), 34427-34441.

142. Qiao, X.; Xu, J.; He, H.; Gao, S., Enantioselective Excited-State Nazarov Reaction: A Relay Strategy of Electrocyclization and Parallel Kinetic Resolution. *Org. Lett.* **2024,** *26* (50), 11005-11010.

2.3 Iminium Catalysis

1. Ahrendt, K. A.; Borths, C. J.; MacMillan, D. W. C., New strategies for organic catalysis: The first highly enantioselective organocatalytic Diels-Alder reaction. *J. Am. Chem. Soc.* **2000,** *122* (17), 4243-4244.

2. Jen, W. S.; Wiener, J. J. M.; MacMillan, D. W. C., New strategies for organic catalysis: The first enantioselective organocatalytic 1,3-dipolar cycloaddition. *J. Am. Chem. Soc.* **2000,** *122* (40), 9874-9875.

3. Paras, N. A.; MacMillan, D. W. C., New strategies in organic catalysis: The first enantioselective organocatalytic Friedel-Crafts alkylation. *J. Am. Chem. Soc.* **2001,** *123* (18), 4370-4371.

4. Austin, J. F.; MacMillan, D. W. C., Enantioselective organocatalytic indole alkylations. Design of a new and highly effective chiral amine for iminium catalysis. *J. Am. Chem. Soc.* **2002,** *124* (7), 1172-1173.

5. Northrup, A. B.; MacMillan, D. W. C., The first general enantioselective catalytic Diels-Alder reaction with simple alpha,beta-unsaturated ketones. *J. Am. Chem. Soc.* **2002,** *124* (11), 2458-2460.

6. Paras, N. A.; MacMillan, D. W. C., The enantioselective organocatalytic 1,4-addition of electron-rich benzenes to alpha,beta-unsaturated aldehydes. *J. Am. Chem. Soc.* **2002,** *124* (27), 7894-7895.

7. Halland, N.; Hazell, R. G.; Jorgensen, K. A., Organocatalytic asymmetric conjugate addition of nitroalkanes to alpha,beta-unsaturated enones using novel imidazoline catalysts. *J. Org. Chem.* **2002,** *67* (24), 8331-8338.

8. Halland, N.; Hansen, T.; Jorgensen, K. A., Organocatalytic asymmetric Michael reaction of cyclic 1,3- dicarbonyl compounds and alpha,beta-unsaturated ketones - A highly atom-economic catalytic one-step formation of optically active warfarin anticoagulant. *Angew. Chem., Int. Ed.* **2003,** *42* (40), 4955-4957.

9. Halland, N.; Aburel, P. S.; Jorgensen, K. A., Highly enantioselective organocatalytic conjugate addition of malonates to acyclic alpha,beta-unsaturated enones. *Angew. Chem., Int. Ed.* **2003,** *42* (6), 661-665.

10. Brown, S. P.; Goodwin, N. C.; MacMillan, D. W. C., The first enantioselective organocatalytic Mukaiyama- Michael reaction: A direct method for the synthesis of enantioenriched gamma-butenolide architecture. *J. Am. Chem. Soc.* **2003,** *125* (5), 1192-1194.

11. Prieto, A.; Halland, N.; Jorgensen, K. A., Novel imidazolidine-tetrazole organocatalyst for asymmetric conjugate addition of nitroalkanes. *Org. Lett.* **2005,** *7* (18), 3897-3900.

12. Ouellet, S. G.; Tuttle, J. B.; MacMillan, D. W. C., Enantioselective organocatalytic hydride reduction. *J. Am. Chem. Soc.* **2005,** *127* (1), 32-33.

13. Lemay, M.; Ogilvie, W. W., Aqueous enantioselective organocatalytic Diels-Alder reactions employing hydrazide catalysts. A new scaffold for organic acceleration. *Org. Lett.* **2005,** *7* (19), 4141-4144.

14. Ishihara, K.; Nakano, K., Design of an organocatalyst for the enantioselective Diels-Alder reaction with alpha-acyloxyacroleins. *J. Am. Chem. Soc.* **2005,** *127* (30), 10504-10505.

15. Reyes, E.; Jiang, H.; Milelli, A.; Elsner, P.; Hazell, R. G.; Jorgensen, K. A., How to make five contiguous stereocenters in one reaction: Asymmetric organocatalytic synthesis of pentasubstituted cyclohexanes. *Angew. Chem., Int. Ed.* **2007,** *46* (48), 9202-9205.

16. Lee, S.; MacMillan, D. W. C., Organocatalytic vinyl and Friedel-Crafts alkylations with trifluoroborate salts. *J. Am. Chem. Soc.* **2007,** *129* (50), 15438-+.

17. Zhou, J.; List, B., Organocatalytic asymmetric reaction cascade to substituted cyclohexylamines. *J. Am. Chem. Soc.* **2007,** *129* (24), 7498-+.

18. Vicario, J. L.; Reboredo, S.; Badia, D.; Carrillo, L., Organocatalytic enantioselective [3+2]cycloaddition of azomethine ylides and alpha,beta-unsaturated aldehydes. *Angew. Chem., Int. Ed.* **2007,** *46* (27), 5168-5170.

19. Bertelsen, S.; Diner, P.; Johansen, R. L.; Jorgensen, K. A., Asymmetric organocatalytic beta-hydroxylation of alpha,beta-unsaturated aldehydes. *J. Am. Chem. Soc.* **2007,** *129* (6), 1536-+.

20. Pesciaioli, F.; De Vincentiis, F.; Galzerano, P.; Bencivenni, G.; Bartoli, G.; Mazzanti, A.; Melchiorre, P., Organocatalytic Asymmetric Aziridination of Enones. *Angew. Chem., Int. Ed.* **2008,** *47* (45), 8703-8706.

21. Reisinger, C. M.; Wang, X. W.; List, B., Catalytic Asymmetric Hydroperoxidation of alpha,beta-Unsaturated Ketones: An Approach to Enantiopure Peroxyhemiketals, Epoxides, and Aldols. *Angew. Chem., Int. Ed.* **2008,** *47* (42), 8112-8115.

22. Cabrera, S.; Reyes, E.; Aleman, J.; Milelli, A.; Kobbelgaard, S.; Jorgensen, K. A., Organocatalytic asymmetric synthesis of alpha,alpha-disubstituted alpha-amino acids and derivatives. *J. Am. Chem. Soc.* **2008,** *130* (36), 12031-12037.

23. Hayashi, Y.; Samanta, S.; Gotoh, H.; Ishikawa, H., Asymmetric Diels-Alder reactions of alpha,beta-unsaturated aldehydes catalyzed by a diarylprolinol silyl ether salt in the presence of water. *Angew. Chem., Int. Ed.* **2008,** *47* (35), 6634-6637.

24. Zu, L. S.; Xie, H. X.; Li, H.; Wang, J.; Yu, X. H.; Wang, W., Chiral amine-catalyzed enantioselective cascade aza-ene-type cyclization reactions. *Chem. Eur. J.* **2008,** *14* (21), 6333-6335.

25. Bertelsen, S.; Johansen, R. L.; Jorgensen, K. A., Controlling the formation of 1 out of 64 stereoisomers using organocatalysis. *Chem. Comm.* **2008,** (26), 3016-3018.

26. Rueping, M.; Sugiono, E.; Merino, E., Asymmetric organocatalysis: An efficient enantioselective access to benzopyranes and chromenes. *Chem. Eur. J.* **2008,** *14* (21), 6329-6332.

27. He, H.; Pei, B. J.; Chou, H. H.; Tian, T.; Chan, W. H.; Lee, A. W. M., Camphor sulfonyl hydrazines (CaSH) as organocatalysts in enantioselective Diels-Alder reactions. *Org. Lett.* **2008,** *10* (12), 2421-2424.

28. Hong, B. C.; Nimje, R. Y.; Sadani, A. A.; Liao, J. H., Organocatalytic enantioselective domino Michael-aldol condensation of 5-oxoalkanal and alpha,beta-unsaturated aldehydes. Efficient assembly of densely functionalized cyclohexenes. *Org. Lett.* **2008,** *10* (12), 2345-2348.

29. Hayashi, Y.; Gotoh, H.; Masui, R.; Ishikawa, H., Diphenylprolinol silyl ether as a catalyst in an enantioselective, catalytic, formal aza [3+3] cycloaddition reaction for the formation of enantioenriched piperidines. *Angew. Chem., Int. Ed.* **2008,** *47* (21), 4012-4015.

30. Chi, Y. G.; Scroggins, S. T.; Frechet, J. M. J., One-pot multi-component asymmetric cascade reactions catalyzed by soluble star polymers with highly branched non-interpenetrating catalytic cores. *J. Am. Chem. Soc.* **2008,** *130* (20), 6322-+.

31. Rueping, M.; Sugiono, E.; Merino, E., Asymmetric iminium ion catalysis: An efficient enantioselective synthesis of pyranonaphthoquinones and beta-lapachones. *Angew. Chem., Int. Ed.* **2008,** *47* (16), 3046-3049.

32. Evans, G.; Gibbs, T. J. K.; Jenkins, R. L.; Coles, S. J.; Hursthouse, M. B.; Platts, J. A.; Tomkinson, N. C. O., Kinetics of iminium ion catalysis. *Angew. Chem., Int. Ed.* **2008,** *47* (15), 2820-2823.

33. Jiang, J.; Yu, J.; Sun, X. X.; Rao, Q. Q.; Gong, L. Z., Organocatalytic asymmetric three-component cyclization of cinnamaldehydes and primary amines with 1,3-dicarbonyl compounds: Straightforward access to enantiomerically enriched dihydropyridines. *Angew. Chem., Int. Ed.* **2008,** *47* (13), 2458-2462.

34. Hong, B. C.; Jan, R. H.; Tsai, C. W.; Nimje, R. Y.; Liao, J. H.; Lee, G. H., Organocatalytic Enantioselective Cascade Michael-Michael-Wittig Reactions of Phosphorus Ylides: One-Pot Synthesis of the all-cis Trisubstituted Cyclohexenecarboxylates via the [1+2+3] Annulation. *Org. Lett.* **2009,** *11* (22), 5246-5249.

35. Zhang, E.; Fan, C. A.; Tu, Y. Q.; Zhang, F. M.; Song, Y. L., Organocatalytic Asymmetric Vinylogous alpha-Ketol Rearrangement: Enantioselective Construction of Chiral All-Carbon Quaternary Stereocenters in Spirocyclic Diketones via Semipinacol-Type 1,2-Carbon Migration. *J. Am. Chem. Soc.* **2009,** *131* (41), 14626-+.

36. Galzerano, P.; Pesciaioli, F.; Mazzanti, A.; Bartoli, G.; Melchiorre, P., Asymmetric Organocatalytic Cascade Reactions with alpha-Substituted alpha,beta-Unsaturated Aldehydes. *Angew. Chem., Int. Ed.* **2009,** *48* (42), 7892-7894.

37. Gutierrez, O.; Iafe, R. G.; Houk, K. N., Origin of Stereoselectivity in the Imidazolidinone-Catalyzed Reductions of Cyclic alpha,beta-Unsaturated Ketones. *Org. Lett.* **2009,** *11* (19), 4298-4301.

38. Jiang, H.; Holub, N.; Paixao, M. W.; Tiberi, C.; Falcicchio, A.; Jorgensen, K. A., Iminium-Ion Activation as an Efficient Strategy for Divergent Synthesis of Optically Active Propargylic, Homopropargylic, and Allenic Compounds. *Chem. Eur. J.* **2009,** *15* (38), 9638-9641.

39. Nielsen, M.; Jacobsen, C. B.; Paixao, M. W.; Holub, N.; Jorgensen, K. A., Asymmetric Organocatalytic Formal Alkynylation and Alkenylation of alpha,beta-Unsaturated Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (30), 10581-10586.

40. Reyes, E.; Talavera, G.; Vicario, J. L.; Badia, D.; Carrillo, L., Enantioselective Organocatalytic Domino Oxa-Michael/Aldol/Hemiacetalization: Synthesis of Polysubstituted Furofuranes Containing Four Stereocenters. *Angew. Chem., Int. Ed.* **2009,** *48* (31), 5701-5704.

41. Liu, Y. K.; Ma, C.; Jiang, K.; Liu, T. Y.; Chen, Y. C., Asymmetric Tandem Michael Addition-Wittig Reaction to Cyclohexenone Annulation. *Org. Lett.* **2009,** *11* (13), 2848-2851.

42. Jiang, H.; Elsner, P.; Jensen, K. L.; Falcicchio, A.; Marcos, V.; Jorgensen, K. A., Achieving Molecular Complexity by Organocatalytic One-Pot Strategies-A Fast Entry for Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated alpha-Amino Acids. *Angew. Chem., Int. Ed.* **2009,** *48* (37), 6844-6848.

43. Sparr, C.; Schweizer, W. B.; Senn, H. M.; Gilmour, R., The Fluorine-Iminium Ion Gauche Effect: Proof of Principle and Application to Asymmetric Organocatalysis. *Angew. Chem., Int. Ed.* **2009,** *48* (17), 3065-3068.

44. Pohjakallio, A.; Pihko, P. M., Enantioselective Synthesis of 2-Isoxazolines by a One-Flask Conjugate Addition/Oxime-Transfer Process. *Chem. Eur. J.* **2009,** *15* (16), 3960-3964.

45. Lattanzi, A., alpha,alpha-Diarylprolinols: bifunctional organocatalysts for asymmetric synthesis. *Chem. Comm.* **2009,** (12), 1452-1463.

46. Albrecht, L.; Richter, B.; Vila, C.; Krawczyk, H.; Jorgensen, K. A., Organocatalytic Domino Michael-Knoevenagel Condensation Reaction for the Synthesis of Optically Active 3-Diethoxyphosphoryl-2-oxocyclohex-3-enecarboxylates. *Chem. Eur. J.* **2009,** *15* (13), 3093-3102.

47. Franzen, J.; Fisher, A., Asymmetric Alkaloid Synthesis: A One-Pot Organocatalytic Reaction to Quinolizidine Derivatives. *Angew. Chem., Int. Ed.* **2009,** *48* (4), 787-791.

48. Brazier, J. B.; Evans, G.; Gibbs, T. J. K.; Coles, S. J.; Hursthouse, M. B.; Platts, J. A.; Tomkinson, N. C. O., Solution Phase, Solid State, and Theoretical Investigations on the MacMillan Imidazolidinone. *Org. Lett.* **2009,** *11* (1), 133-136.

49. Pohjakallio, A.; Pihko, P. M.; Laitinen, U. M., Synthesis of 2-Isoxazolines: Enantioselective and Racemic Methods Based on Conjugate Additions of Oximes. *Chem. Eur. J.* **2010,** *16* (37), 11325-11339.

50. Kang, Y. K.; Kim, S. M.; Kim, D. Y., Enantioselective Organocatalytic C-H Bond Functionalization via Tandem 1,5-Hydride Transfer/Ring Closure: Asymmetric Synthesis of Tetrahydroquinolines. *J. Am. Chem. Soc.* **2010,** *132* (34), 11847-11849.

51. Feng, X.; Cui, H. L.; Xu, S.; Wu, L.; Chen, Y. C., Organocatalytic Direct Vinylogous Michael Addition of alpha,beta-Unsaturated gamma-Butyrolactam to alpha,beta-Unsaturated Aldehydes and an Illustration to Scaffold Diversity Synthesis. *Chem. Eur. J.* **2010,** *16* (34), 10309-10312.

52. Lifchits, O.; Reisinger, C. M.; List, B., Catalytic Asymmetric Epoxidation of alpha-Branched Enals. *J. Am. Chem. Soc.* **2010,** *132* (30), 10227-10229.

53. Albrecht, L.; Jiang, H.; Dickmeiss, G.; Gschwend, B.; Hansen, S. G.; Jorgensen, K. A., Asymmetric Formal trans-Dihydroxylation and trans-Aminohydroxylation of alpha,beta-Unsaturated Aldehydes via an Organocatalytic Reaction Cascade. *J. Am. Chem. Soc.* **2010,** *132* (26), 9188-9196.

54. Gotoh, H.; Ogino, H.; Ishikawa, H.; Hayashi, Y., One-pot synthesis of chiral bicyclo 3.3.0 octatrienes using diphenylprolinol silyl ether-mediated ene-type reaction. *Tetrahedron* **2010,** *66* (26), 4894-4899.

55. Terrasson, V.; van der Lee, A.; de Figueiredo, R. M.; Campagne, J. M., Organocatalyzed Cyclopropanation of alpha-Substituted alpha,beta-Unsaturated Aldehydes: Enantioselective Synthesis of Cyclopropanes Bearing a Chiral Quaternary Center. *Chem. Eur. J.* **2010,** *16* (26), 7875-7880.

56. Nakano, H.; Osone, K.; Takeshita, M.; Kwon, E.; Seki, C.; Matsuyama, H.; Takano, N.; Kohari, Y., A novel chiral oxazolidine organocatalyst for the synthesis of an oseltamivir intermediate using a highly enantioselective Diels-Alder reaction of 1,2-dihydropyridine. *Chem. Comm.* **2010,** *46* (26), 4827-4829.

57. Jiang, K.; Jia, Z. J.; Yin, X. A.; Wu, L.; Chen, Y. C., Asymmetric Quadruple Aminocatalytic Domino Reactions to Fused Carbocycles Incorporating a Spirooxindole Motif. *Org. Lett.* **2010,** *12* (12), 2766-2769.

58. Holub, N.; Jiang, H.; Paixao, M. W.; Tiberi, C.; Jorgensen, K. A., An Unexpected Michael Aldol Smiles Rearrangement Sequence for the Synthesis of Versatile Optically Active Bicyclic Structures by Using Asymmetric Organocatalysis. *Chem. Eur. J.* **2010,** *16* (14), 4337-4346.

59. Zhang, X. S.; Zhang, S. L.; Wang, W., Iminium-Allenamine Cascade Catalysis: One-Pot Access to Chiral 4H-Chromenes by a Highly Enantioselective Michael-Michael Sequence. *Angew. Chem., Int. Ed.* **2010,** *49* (8), 1481-1484.

60. Bow, W. F.; Basak, A. K.; Jolit, A.; Vicic, D. A.; Tius, M. A., Enamine-Iminium Ion Nazarov Cyclization of alpha-Ketolenones. *Org. Lett.* **2010,** *12* (3), 440-443.

61. Reboredo, S.; Vicario, J. L.; Badia, D.; Carrillo, L.; Reyes, E., Complete 2,5-Diastereocontrol in the Organocatalytic Enantioselective 3+2 Cycloaddition of Enals with Azomethine Ylides Derived from a-Iminocyanoacetates: Asymmetric Synthesis of Pyrrolidines with Four Stereocentres. *Adv. Synth. Catal.* **2011,** *353* (18), 3307-3312.

62. Albrecht, L.; Ransborg, L. K.; Lauridsen, V.; Overgaard, M.; Zweifel, T.; Jorgensen, K. A., Taming the Friedel-Crafts Reaction: Organocatalytic Approach to Optically Active 2,3-Dihydrobenzofurans. *Angew. Chem., Int. Ed.* **2011,** *50* (52), 12496-12500.

63. Wu, X. Y.; Dai, X. Y.; Fang, H. H.; Nie, L. L.; Chen, J.; Cao, W. G.; Zhao, G., One-Pot Three-Component Syntheses of Indoloquinolizidine Derivatives Using an Organocatalytic Michael Addition and Subsequent Pictet-Spengler Cyclization. *Chem. Eur. J.* **2011,** *17* (38), 10509-10513.

64. Jones, S. B.; Simmons, B.; Mastracchio, A.; MacMillan, D. W. C., Collective synthesis of natural products by means of organocascade catalysis. *Nature* **2011,** *475* (7355), 183-188.

65. Alonso, B.; Reyes, E.; Carrillo, L.; Vicario, J. L.; Badia, D., Organocatalytic Enantioselective Formal Conjugate Addition of a Hydroxymoyl Anion to alpha,beta-Unsaturated Aldehydes. *Chem. Eur. J.* **2011,** *17* (22), 6048-6051.

66. Jacobsen, C. B.; Nielsen, M.; Worgull, D.; Zweifel, T.; Fisker, E.; Jorgensen, K. A., Asymmetric Organocatalytic Monofluorovinylations. *J. Am. Chem. Soc.* **2011,** *133* (19), 7398-7404.

67. Albrecht, L.; Albrecht, A.; Ransborg, L. K.; Jorgensen, K. A., Asymmetric organocatalytic 3+2 -annulation strategy for the synthesis of N-fused heteroaromatic compounds. *Chemical Science* **2011,** *2* (7), 1273-1277.

68. Hayashi, Y.; Itoh, T.; Ishikawa, H., Oxidative and Enantioselective Cross-Coupling of Aldehydes and Nitromethane Catalyzed by Diphenylprolinol Silyl Ether. *Angew. Chem., Int. Ed.* **2011,** *50* (17), 3920-3924.

69. Worgull, D.; Dickmeiss, G.; Jensen, K. L.; Franke, P. T.; Holub, N.; Jorgensen, K. A., Optically Active Bicyclic N-Heterocycles by Organocatalytic Asymmetric Michael Addition/Cyclization Sequences. *Chem. Eur. J.* **2011,** *17* (15), 4076-4080.

70. Lee, A.; Michrowska, A.; Sulzer-Mosse, S.; List, B., The Catalytic Asymmetric Knoevenagel Condensation. *Angew. Chem., Int. Ed.* **2011,** *50* (7), 1707-1710.

71. Dickmeiss, G.; Jensen, K. L.; Worgull, D.; Franke, P. T.; Jorgensen, K. A., An Asymmetric Organocatalytic One-Pot Strategy to Octahydroacridines. *Angew. Chem., Int. Ed.* **2011,** *50* (7), 1580-1583.

72. Brazier, J. B.; Jones, K. M.; Platts, J. A.; Tomkinson, N. C. O., On the Roles of Protic Solvents in Imidazolidinone-Catalyzed Transformations. *Angew. Chem., Int. Ed.* **2011,** *50* (7), 1613-1616.

73. Gupta, V.; Sudhir, V. S.; Mandal, T.; Schneider, C., Organocatalytic, Highly Enantioselective Vinylogous Mukaiyama-Michael Reaction of Acyclic Dienol Silyl Ethers. *Angew. Chem., Int. Ed.* **2012,** *51* (50), 12609-12612.

74. Fernandez, M.; Uria, U.; Vicario, J. L.; Reyes, E.; Carrillo, L., Enantioselective Conjugate Addition of Donor-Acceptor Hydrazones to alpha,beta-Unsaturated Aldehydes through Formal Diaza-Ene Reaction: Access to 1,4-Dicarbonyl Compounds. *J. Am. Chem. Soc.* **2012,** *134* (29), 11872-11875.

75. Rueping, M.; Sunden, H.; Sugiono, E., Unifying Metal- and Organocatalysis for Asymmetric Oxidative Iminium Activation: A Relay Catalytic System Enabling the Combined Allylic Oxidation of Alcohols and Prolinol Ether Catalyzed Iminium Reactions. *Chem. Eur. J.* **2012,** *18* (12), 3649-3653.

76. Rueping, M.; Sunden, H.; Hubener, L.; Sugiono, E., Asymmetric oxidative Lewis base catalysis-unifying iminium and enamine organocatalysis with oxidations. *Chem. Comm.* **2012,** *48* (16), 2201-2203.

77. Bergonzini, G.; Melchiorre, P., Dioxindole in Asymmetric Catalytic Synthesis: Routes to Enantioenriched 3-Substituted 3-Hydroxyoxindoles and the Preparation of Maremycin A. *Angew. Chem., Int. Ed.* **2012,** *51* (4), 971-974.

78. Silvi, M.; Chatterjee, I.; Liu, Y. K.; Melchiorre, P., Controlling the Molecular Topology of Vinylogous Iminium Ions by Logical Substrate Design: Highly Regio- and Stereoselective Aminocatalytic 1,6-Addition to Linear 2,4-Dienals. *Angew. Chem., Int. Ed.* **2013,** *52* (41), 10780-10783.

79. Moran, A.; Hamilton, A.; Bo, C.; Melchiorre, P., A Mechanistic Rationale for the 9-Amino(9-deoxy)epi Cinchona Alkaloids Catalyzed Asymmetric Reactions via Iminium Ion Activation of Enones. *J. Am. Chem. Soc.* **2013,** *135* (24), 9091-9098.

80. Dell'Amico, L.; Albrecht, L.; Naicker, T.; Poulsen, P. H.; Jorgensen, K. A., Beyond Classical Reactivity Patterns: Shifting from 1,4-to 1,6-Additions in Regio- and Enantioselective Organocatalyzed Vinylogous Reactions of Olefinic Lactones with Enals and 2,4-Dienals. *J. Am. Chem. Soc.* **2013,** *135* (21), 8063-8070.

81. Duan, G. J.; Ling, J. B.; Wang, W. P.; Luo, Y. C.; Xu, P. F., Organocatalytic formal 2+2 cycloaddition initiated by vinylogous Friedel-Crafts alkylation: enantioselective synthesis of substituted cyclobutane derivatives. *Chem. Comm.* **2013,** *49* (41), 4625-4627.

82. Moberg, C., Mechanism of Diphenylprolinol Silyl Ether Catalyzed Michael Addition Revisitedbut Still Controversial. *Angew. Chem., Int. Ed.* **2013,** *52* (8), 2160-2162.

83. Wu, W. B.; Li, X.; Huang, H. C.; Yuan, X. Q.; Lu, J. Z.; Zhu, K. L.; Ye, J. X., Asymmetric Intramolecular Oxa-Michael Reactions of Cyclohexadienones Catalyzed by a Primary Amine Salt. *Angew. Chem., Int. Ed.* **2013,** *52* (6), 1743-1747.

84. Wallbaum, J.; Garve, L. K. B.; Jones, P. G.; Werz, D. B., Ring-Opening Regio-, Diastereo-, and Enantioselective 1,3 Chlorochalcoge nation of Cyclopropyl Carbaldehydes. *Chem. Eur. J.* **2016,** *22* (52), 18756-18759.

85. Liu, Y. E.; Lu, Z. L.; Li, B.; Tian, J. X.; Liu, F.; Zhao, J. Y.; Hou, C. K.; Li, Y. K.; Niu, L. L.; Zhao, B. G., Enzyme-Inspired Axially Chiral Pyridoxamines Armed with a Cooperative Lateral Amine Chain for Enantioselective Biomimetic Transamination. *J. Am. Chem. Soc.* **2016,** *138* (34), 10730-10733.

86. Sanchez-Diez, E.; Vesga, D. L.; Reyes, E.; Uria, U.; Carrillo, L.; Vicario, J. L., Organocatalytically Generated Donor Acceptor Cyclopropanes in Domino Reactions. One-Step Enantioselective Synthesis of Pyrrolo 1,2-a quinolines. *Org. Lett.* **2016,** *18* (6), 1270-1273.

87. Claraz, A.; Sahoo, G.; Berta, D.; Madarasz, A.; Papai, I.; Pihko, P. M., A Catalyst Designed for the Enantioselective Construction of Methyland Alkyl-Substituted Tertiary Stereocenters. *Angew. Chem., Int. Ed.* **2016,** *55* (2), 669-673.

88. Zheng, S. C.; Wu, S.; Zhou, Q. H.; Chung, L. W.; Ye, L.; Tan, B., Organocatalytic atroposelective synthesis of axially chiral styrenes. *Nature Communications* **2017,** *8*.

89. Bahamonde, A.; Murphy, J. J.; Savarese, M.; Bremond, E.; Cavalli, A.; Melchiorre, P., Studies on the Enantioselective Iminium Ion Trapping of Radicals Triggered by an Electron-Relay Mechanism. *J. Am. Chem. Soc.* **2017,** *139* (12), 4559-4567.

90. Dell'Amico, L.; Fernandez-Alvarez, V. M.; Maseras, F.; Melchiorre, P., Light-Driven Enantioselective Organocatalytic beta-Benzylation of Enals. *Angew. Chem., Int. Ed.* **2017,** *56* (12), 3304-3308.

91. Diaz, E.; Reyes, E.; Uria, U.; Carrillo, L.; Tejero, T.; Merino, P.; Vicario, J. L., Carboxylates as Nucleophiles in the Enantioselective Ring-Opening of Formylcyclopropanes under Iminium Ion Catalysis. *Chem. Eur. J.* **2018,** *24* (35), 8764-8768.

92. Zhao, C.-G.; Feng, Z.-T.; Xu, G.-Q.; Gao, A.; Chen, J.-W.; Wang, Z.-Y.; Xu, P.-F., Highly Enantioselective Construction of Strained Spiro[2,3]hexanes through a Michael Addition/Ring Expansion/Cyclization Cascade. *Angew. Chem., Int. Ed.* **2020,** *59* (8), 3058-3062.

93. Jessen, N. I.; Bura, M.; Bertuzzi, G.; Jørgensen, K. A., Aminocatalytic [8+2] Cycloaddition Reactions toward Chiral Cyclazines. *Angew. Chem., Int. Ed.* **2021,** *60* (34), 18527-18531.

94. Wong, T. H.-F.; Ma, D.; Di Sanza, R.; Melchiorre, P., Photoredox Organocatalysis for the Enantioselective Synthesis of 1,7-Dicarbonyl Compounds. *Org. Lett.* **2022,** *24* (8), 1695-1699.

95. Rodríguez, R. I.; Sicignano, M.; Alemán, J., Fluorinated Sulfinates as Source of Alkyl Radicals in the Photo-Enantiocontrolled β-Functionalization of Enals. *Angew. Chem., Int. Ed.* **2022,** *61* (9), e202112632.

96. Barløse, C. D.; Bitsch, R. S.; Faghtmann, J.; Escobar, C. D.; Casacchia, M. E.; Kristensen, A.; Jørgensen, K. A., Mechanistic Investigation of the Pseudo-Halogen Effect in Enantioselective Aminocatalyzed [6 + 4] and [10 + 6] Cycloadditions: Enabling Unique Favorskii-Like Rearrangements. *J. Am. Chem. Soc.* **2024,** *146* (49), 34231-34251.

97. Goti, G.; Bieszczad, B.; Vega-Penaloza, A.; Melchiorre, P., Stereocontrolled Synthesis of 1,4-Dicarbonyl Compounds by Photochemical Organocatalytic Acyl Radical Addition to Enals. *Angew. Chem., Int. Ed.* **2019,** *58* (4), 1213-1217.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

2.4. Activation of electrophiles other than carbonyl/imines

2.4.1 Epoxidation

1. Nishinaga, A.; Yamato, H.; Abe, T.; Maruyama, K.; Matsuura, T., Asymmetric Induction in Oxygenation of Styrene Catalyzed by Cobalt Schiff-Base Complex. *Tetrahedron Letters* **1988,** *29* (48), 6309-6312.

2. Ozaki, S.; Mimura, H.; Yasuhara, N.; Masui, M.; Yamagata, Y.; Tomita, K.; Collins, T. J., Synthesis of Chiral Square-Planar Cobalt(Iii) Complexes and Catalytic Asymmetric Epoxidations with These Complexes. *Journal of the Chemical Society-Perkin Transactions 2* **1990,** (3), 353-360.

3. Halterman, R. L.; Jan, S. T., Catalytic Asymmetric Epoxidation of Unfunctionalized Alkenes Using the 1st D4-Symmetrical Metallotetraphenylporphyrin. *J. Org. Chem.* **1991,** *56* (18), 5253-5254.

4. Jacobsen, E. N.; Zhang, W.; Guler, M. L., ELECTRONIC TUNING OF ASYMMETRIC CATALYSTS. *J. Am. Chem. Soc.* **1991,** *113* (17), 6703-6704.

5. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L., HIGHLY ENANTIOSELECTIVE EPOXIDATION CATALYSTS DERIVED FROM 1,2-DIAMINOCYCLOHEXANE. *J. Am. Chem. Soc.* **1991,** *113* (18), 7063-7064.

6. Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T., Optically-Active Beta-Ketoiminato Manganese(Iii) Complexes as Efficient Catalysts in Enantioselective Aerobic Epoxidation of Unfunctionalized Olefins. *Inorganica Chimica Acta* **1994,** *220* (1-2), 283-287.

7. Nishiyama, H.; Park, S. B.; Haga, M.; Aoki, K.; Itoh, K., Ruthenium(Ii)Cl-2-Bis(Oxazolinyl)Bipyridine Complex - Its Structure and Reactivity. *Chemistry Letters* **1994,** (6), 1111-1114.

8. Nishiyama, H.; Shimada, T.; Itoh, H.; Sugiyama, H.; Motoyama, Y., Novel ruthenium-pyridinedicarboxylate complexes of terpyridine and chiral bis(oxazolinyl)pyridine: a new catalytic system for alkene epoxidation with bis(acetoxy)iodo benzene as an oxygen donor. *Chem. Commun.* **1997,** (19), 1863-1864.

9. Wang, Z. X.; Tu, Y.; Frohn, M.; Zhang, J. R.; Shi, Y., An efficient catalytic asymmetric epoxidation method. *J. Am. Chem. Soc.* **1997,** *119* (46), 11224-11235.

10. End, N.; Pfaltz, A., Enantioselective epoxidation catalysed by ruthenium complexes with chiral tetradentate bisamide ligands. *Chem. Commun.* **1998,** (5), 589-590.

11. Lai, T. S.; Zhang, R.; Cheung, K. K.; Kwong, H. L.; Che, C. M., Aerobic enantioselective alkene epoxidation by a chiral trans-dioxo(D-4-porphyrinato) ruthenium(VI) complex. *Chem. Commun.* **1998,** (15), 1583-1584.

12. Palucki, M.; Finney, N. S.; Pospisil, P. J.; Guler, M. L.; Ishida, T.; Jacobsen, E. N., The mechanistic basis for electronic effects on enantioselectivity in the (salen)Mn(III)-catalyzed epoxidation reaction. *J. Am. Chem. Soc.* **1998,** *120* (5), 948-954.

13. Francis, M. B.; Jacobsen, E. N., Discovery of novel catalysts for alkene epoxidation from metal-binding combinatorial libraries. *Angew. Chem.-Int. Edit.* **1999,** *38* (7), 937-941.

14. Gross, Z.; Ini, S., Asymmetric catalysis by a chiral ruthenium porphyrin: Epoxidation, hydroxylation, and partial kinetic resolution of hydrocarbons. *Org. Lett.* **1999,** *1* (13), 2077-2080.

15. Katsuki, T., The catalytic enantioselective synthesis of optically active epoxides and tetrahydrofurans. Asymmetric epoxidation, the desymmetrization of meso-tetrahydrofurans, and enantiospecific ring-enlargement. *Current Organic Chemistry* **2001,** *5* (6), 663-678.

16. Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T., Asymmetric epoxidation with a photoactivated Ru(salen) complex. *Chemistry-a European Journal* **2001,** *7* (17), 3776-3782.

17. Aggarwal, V. K.; Lopin, C.; Sandrinelli, F., New insights in the mechanism of amine catalyzed epoxidation: Dual role of protonated ammonium salts as both phase transfer catalysts and activators of Oxone. *J. Am. Chem. Soc.* **2003,** *125* (25), 7596-7601.

18. Bolm, C., Vanadium-catalyzed asymmetric oxidations. *Coordination Chemistry Reviews* **2003,** *237* (1-2), 245-256.

19. Cavallo, L.; Jacobsen, H., Electronic effects in (salen)Mn-based epoxidation catalysts. *J. Org. Chem.* **2003,** *68* (16), 6202-6207.

20. Page, P. C. B.; Buckley, B. R.; Blacker, A. J., Iminium salt catalysts for asymmetric epoxidation: The first high enantioselectivities. *Org. Lett.* **2004,** *6* (10), 1543-1546.

21. Shi, Y., Organocatalytic asymmetric epoxidation of olefins by chiral ketones. *Accounts of Chemical Research* **2004,** *37* (8), 488-496.

22. Tse, M. K.; Dobler, C.; Bhor, S.; Klawonn, M.; Magerlein, W.; Hugl, H.; Beller, M., Development of a ruthenium-catalyzed asymmetric epoxidation procedure with hydrogen peroxide as the oxidant. *Angew. Chem.-Int. Edit.* **2004,** *43* (39), 5255-5260.

23. Page, P. C. B.; Buckley, B. R.; Heaney, H.; Blacker, A. J., Asymmetric epoxidation of cis-alkenes mediated by iminium salts: Highly enantioselective synthesis of levcromakalim. *Org. Lett.* **2005,** *7* (3), 375-377.

24. Barlan, A. U.; Basak, A.; Yamamoto, H., Enantioselective oxidation of olefins catalyzed by a chiral bishydroxamic acid complex of molybdenum. *Angew. Chem.-Int. Edit.* **2006,** *45* (35), 5849-5852.

25. Burke, C. P.; Shi, Y., Regio- and enantioselective epoxidation of dienes by a chiral dioxirane: Synthesis of optically active vinyl cis-epoxides. *Angew. Chem.-Int. Edit.* **2006,** *45* (27), 4475-4478.

26. Colladon, M.; Scarso, A.; Sgarbossa, P.; Michelin, R. A.; Strukul, G., Asymmetric epoxidation of terminal alkenes with hydrogen peroxide catalyzed by pentafluorophenyl Pt-II complexes. *J. Am. Chem. Soc.* **2006,** *128* (43), 14006-14007.

27. Sawada, Y.; Matsumoto, K.; Kondo, S.; Watanabe, H.; Ozawa, T.; Suzuki, K.; Saito, B.; Katsuki, T., Titanium-salan-catalyzed asymmetric epoxidation with aqueous hydrogen peroxide as the oxidant. *Angew. Chem.-Int. Edit.* **2006,** *45* (21), 3478-3480.

28. Shen, Y. M.; Wang, B.; Shi, Y., Enantioselective synthesis of 2-aryl cyclopentanones by asymmetric epoxidation and epoxide rearrangement. *Angew. Chem.-Int. Edit.* **2006,** *45* (9), 1429-1432.

29. Page, P. C. B.; Farah, M. M.; Buckley, B. R.; Blacker, A. J., New chiral binaphthalene-derived iminium salt organocatalysts for asymmetric epoxidation of alkenes. *J. Org. Chem.* **2007,** *72* (12), 4424-4430.

30. Kurti, L.; Blewett, M. M.; Corey, E. J., Origin of Enantioselectivity in the Jacobsen Epoxidation of Olefins. *Org. Lett.* **2009,** *11* (20), 4592-4595.

31. Lim, S. M.; Hill, N.; Myers, A. G., A Method for the Preparation of Differentiated trans-1,2-Diol Derivatives with Enantio- and Diastereocontrol. *J. Am. Chem. Soc.* **2009,** *131* (16), 5763-+.

32. Matsumoto, K.; Oguma, T.; Katsuki, T., Highly Enantioselective Epoxidation of Styrenes Catalyzed by Proline-Derived C-1-Symmetric Titanium(Salan) Complexes. *Angew. Chem.-Int. Edit.* **2009,** *48* (40), 7432-7435.

33. Novikov, R.; Bernardinelli, G.; Lacour, J., Highly Enantioselective Biphasic Iminium-Catalyzed Epoxidation of Alkenes. On the Importance of the Counterion and of N(sp(2))-C(sp(3)) Rotamers. *Adv. Synth. Catal.* **2009,** *351* (4), 596-606.

34. Egami, H.; Oguma, T.; Katsuki, T., Oxidation Catalysis of Nb(salan) Complexes: Asymmetric Epoxidation of Allylic Alcohols Using Aqueous Hydrogen Peroxide as an Oxidant. *J. Am. Chem. Soc.* **2010,** *132* (16), 5886-5895.

35. Li, Z.; Yamamoto, H., Zirconium(IV)- and Hafnium(IV)-Catalyzed Highly Enantioselective Epoxidation of Homoallylic and Bishomoallylic Alcohols. *J. Am. Chem. Soc.* **2010,** *132* (23), 7878-+.

36. Liao, S. H.; List, B., Asymmetric Counteranion-Directed Transition-Metal Catalysis: Enantioselective Epoxidation of Alkenes with Manganese(III) Salen Phosphate Complexes. *Angew. Chem.-Int. Edit.* **2010,** *49* (3), 628-631.

37. Kolundzic, F.; Noshi, M. N.; Tjandra, M.; Movassaghi, M.; Miller, S. J., Chemoselective and Enantioselective Oxidation of Indoles Employing Aspartyl Peptide Catalysts. *J. Am. Chem. Soc.* **2011,** *133* (23), 9104-9111.

38. Lichtor, P. A.; Miller, S. J., Combinatorial evolution of site- and enantioselective catalysts for polyene epoxidation. *Nat. Chem.* **2012,** *4* (12), 990-995.

39. Niwa, T.; Nakada, M., A Non-Heme Iron(III) Complex with Porphyrin-like Properties That Catalyzes Asymmetric Epoxidation. *J. Am. Chem. Soc.* **2012,** *134* (33), 13538-13541.

40. Page, P. C. B.; Bartlett, C. J.; Chan, Y. H.; Day, D.; Parker, P.; Buckley, B. R.; Rassias, G. A.; Slawin, A. M. Z.; Allin, S. M.; Lacour, J.; Pinto, A., Asymmetric Epoxidation Using Iminium Salt Organocatalysts Featuring Dynamically Controlled Atropoisomerism. *J. Org. Chem.* **2012,** *77* (14), 6128-6138.

41. Cusso, O.; Garcia-Bosch, I.; Ribas, X.; Lloret-Fillol, J.; Costas, M., Asymmetric Epoxidation with H2O2 by Manipulating the Electronic Properties of Non-heme Iron Catalysts. *J. Am. Chem. Soc.* **2013,** *135* (39), 14871-14878.

42. Uraguchi, D.; Tsutsumi, R.; Ooi, T., Catalytic Asymmetric Oxidation of N-Sulfonyl Imines with Hydrogen Peroxide-Trichloroacetonitrile System. *J. Am. Chem. Soc.* **2013,** *135* (22), 8161-8164.

43. Abascal, N. C.; Lichtor, P. A.; Giuliano, M. W.; Miller, S. J., Function-oriented investigations of a peptide-based catalyst that mediates enantioselective allylic alcohol epoxidation. *Chem. Sci.* **2014,** *5* (11), 4504-4511.

44. Lichtor, P. A.; Miller, S. J., Experimental Lineage and Functional Analysis of a Remotely Directed Peptide Epoxidation Catalyst. *J. Am. Chem. Soc.* **2014,** *136* (14), 5301-5308.

45. Cusso, O.; Ribas, X.; Lloret-Fillol, J.; Costas, M., Synergistic Interplay of a Non-Heme Iron Catalyst and Amino Acid Coligands in H2O2 Activation for Asymmetric Epoxidation of alpha-Ayl-Substituted Styrenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (9), 2729-2733.

46. Cusso, O.; Cianfanelli, M.; Ribas, X.; Gebbink, R.; Costas, M., Iron Catalyzed Highly Enantioselective Epoxidation of Cyclic Aliphatic Enones with Aqueous H2O2. *J. Am. Chem. Soc.* **2016,** *138* (8), 2732-2738.

47. Miao, C. X.; Wang, B.; Wang, Y.; Xia, C. G.; Lee, Y. M.; Nam, W. W.; Sun, W., Proton-Promoted and Anion-Enhanced Epoxidation of Olefins by Hydrogen Peroxide in the Presence of Nonheme Manganese Catalysts. *J. Am. Chem. Soc.* **2016,** *138* (3), 936-943.

2.4.2 Aziridination

1. Evans, D. A.; Faul, M. M.; Bilodeau, M. T., Copper-Catalyzed Aziridination of Olefins by (N-(Para-Toluenesulfonyl)Imino)Phenyliodinane. *J. Org. Chem.* **1991,** *56* (24), 6744-6746.

2. Oconnor, K. J.; Wey, S. J.; Burrows, C. J., Alkene Aziridination and Epoxidation Catalyzed by Chiral Metal Salen Complexes. *Tetrahedron Letters* **1992,** *33* (8), 1001-1004.

3. Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M., Bis(Oxazoline) Copper-Complexes as Chiral Catalysts for the Enantioselective Aziridination of Olefins. *J. Am. Chem. Soc.* **1993,** *115* (12), 5328-5329.

4. Li, Z.; Conser, K. R.; Jacobsen, E. N., Asymmetric Alkene Aziridination with Readily Available Chiral Diimine-Based Catalysts. *J. Am. Chem. Soc.* **1993,** *115* (12), 5326-5327.

5. Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T., Asymmetric Aziridination by Using Optically-Active (Salen)Manganese(Iii) Complexes. *Synlett* **1993,** (7), 469-471.

6. Evens, D. A.; Faul, M. M.; Bilodeau, M. T., Development of the Copper-Catalyzed Olefin Aziridination Reaction. *J. Am. Chem. Soc.* **1994,** *116* (7), 2742-2753.

7. Li, Z.; Quan, R. W.; Jacobsen, E. N., Mechanism of the (Diimine)Copper-Catalyzed Asymmetric Aziridination of Alkenes - Nitrene Transfer Via Ligand- Accelerated Catalysis. *J. Am. Chem. Soc.* **1995,** *117* (21), 5889-5890.

8. Muller, P.; Baud, C.; Jacquier, Y., A method for rhodium(II)-catalyzed aziridination of olefins. *Tetrahedron* **1996,** *52* (5), 1543-1548.

9. Albone, D. P.; Aujla, P. S.; Taylor, P. C.; Challenger, S.; Derrick, A. M., A simple copper catalyst for both aziridination of alkenes and amination of activated hydrocarbons with chloramine-T trihydrate. *J. Org. Chem.* **1998,** *63* (25), 9569-9571.

10. Dauban, P.; Dodd, R. H., PhI=NSes: A new iminoiodinane reagent for the copper-catalyzed aziridination of olefins. *J. Org. Chem.* **1999,** *64* (14), 5304-5307.

11. Brandt, P.; Sodergren, M. J.; Andersson, P. G.; Norrby, P. O., Mechanistic studies of copper-catalyzed alkene aziridination. *J. Am. Chem. Soc.* **2000,** *122* (33), 8013-8020.

12. Sanders, C. J.; Gillespie, K. M.; Bell, D.; Scott, P., Structural origins of a dramatic variation in catalyst efficiency in enantioselective alkene aziridination: Implications for design of ligands based on chiral biaryldiamines. *J. Am. Chem. Soc.* **2000,** *122* (29), 7132-7133.

13. Dauban, P.; Saniere, L.; Tarrade, A.; Dodd, R. H., Copper-catalyzed nitrogen transfer mediated by iodosylbenzene PhI=O. *J. Am. Chem. Soc.* **2001,** *123* (31), 7707-7708.

14. Gillespie, K. M.; Crust, E. J.; Deeth, R. J.; Scott, P., Mechanism of alkene aziridination in the (biaryldiimine)Cu-I catalyst system; precise substrate orientation via two-centre binding. *Chem. Commun.* **2001,** (8), 785-786.

15. Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P.; Westmoreland, I.; Thickitt, C. P.; Scott, P., Enantioselective aziridination using copper complexes of biaryl Schiff bases. *J. Org. Chem.* **2002,** *67* (10), 3450-3458.

16. Krumper, J. R.; Gerisch, M.; Suh, J. M.; Bergman, R. G.; Tilley, T. D., Monomeric rhodium(II) catalysts for the preparation of aziridines and enantioselective formation of cyclopropanes from ethyl diazoacetate at room temperature. *J. Org. Chem.* **2003,** *68* (25), 9705-9710.

17. Liang, J. L.; Yuan, S. X.; Chan, P. W. H.; Che, C. M., Chiral rhodium(II,II) dimers catalyzed enantioselective intramolecular aziridination of sulfonamides and carbamates. *Tetrahedron Letters* **2003,** *44* (31), 5917-5920.

18. Cui, Y.; He, C., Efficient aziridination of olefins catalyzed by a unique disilver(I) compound. *J. Am. Chem. Soc.* **2003,** *125* (52), 16202-16203.

19. Ranocchiari, M.; Mezzetti, A., Ru/PNNP-Catalyzed Asymmetric Imine Aziridination by Diazo Ester Activation. *Organometallics* **2009,** *28* (13), 3611-3613.

20. Jin, L. M.; Xu, X.; Lu, H. J.; Cui, X.; Wojtas, L.; Zhang, X. P., Effective Synthesis of Chiral N-Fluoroaryl Aziridines through Enantioselective Aziridination of Alkenes with Fluoroaryl Azides. *Angew. Chem.-Int. Edit.* **2013,** *52* (20), 5309-5313.

21. Liu, C.; Yi, J. C.; Zheng, Z. B.; Tang, Y.; Dai, L. X.; You, S. L., Enantioselective Synthesis of 3a-Amino-Pyrroloindolines by CopperCatalyzed Direct Asymmetric Dearomative Amination of Tryptamines. *Angew. Chem.-Int. Edit.* **2016,** *55* (2), 751-754.

22. Jiang, H. L.; Lang, K.; Lu, H. J.; Wojtas, L.; Zhang, X. P., Asymmetric Radical Bicyclization of Allyl Azidoformates via Cobalt(II)-Based Metalloradical Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (27), 9164-9167.

23. Tan, Y.; Han, F.; Hemming, M.; Wang, J.; Harms, K.; Xie, X.; Meggers, E., Asymmetric Ring-Closing Aminooxygenation of Alkenes en Route to 2-Amino-1,3-Diols with Vicinal Stereocenters. *Org. Lett.* **2020,** *22* (16), 6653-6656.

24. Han, X.; Shan, L.-X.; Zhu, J.-X.; Zhang, C.-S.; Zhang, X.-M.; Zhang, F.-M.; Wang, H.; Tu, Y.-Q.; Yang, M.; Zhang, W.-S., Copper-Nitrene-Catalyzed Desymmetric Oxaziridination/1,2-Alkyl Rearrangement of 1,3-Diketones toward Bicyclic Lactams. *Angewandte Chemie International Edition* **2021,** *60* (42), 22688-22692.

25. Boquet, V.; Nasrallah, A.; Dana, A. L.; Brunard, E.; Di Chenna, P. H.; Duran, F. J.; Retailleau, P.; Darses, B.; Sircoglou, M.; Dauban, P., Rhodium(II)-Catalyzed Enantioselective Intermolecular Aziridination of Alkenes. *J. Am. Chem. Soc.* **2022,** *144* (37), 17156-17164.

26. Wang, J.; Luo, M.-P.; Gu, Y.-J.; Liu, Y.-Y.; Yin, Q.; Wang, S.-G., Chiral CpxRhodium(III)-Catalyzed Enantioselective Aziridination of Unactivated Terminal Alkenes. *Angewandte Chemie International Edition* **2024,** *63* (12), e202400502.

2.4.3 Cyclopropanation

1. Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R., HOMOGENEOUS CATALYSIS IN DECOMPOSITION OF DIAZO COMPOUNDS BY COPPER CHELATES. *Tetrahedron* **1968,** *24* (9), 3655-&.

2. Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S., Highly Enantioselective Synthesis of Cyclopropane Derivatives through Chiral Cobalt(Ii) Complex Catalyzed Carbenoid Reaction - General Scope and Factors Determining Enantioselectivity. *J. Am. Chem. Soc.* **1978,** *100* (11), 3443-3448.

3. Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S., Enantioselective Carbenoid Cyclopropanation Catalyzed by Chiral Vic-Dioximatocobalt(Ii) Complexes Prepared from Natural Camphor and Beta-Pinene - Mechanism and Stereochemistry. *J. Am. Chem. Soc.* **1978,** *100* (11), 3449-3461.

4. Fritschi, H.; Leutenegger, U.; Pfaltz, A., Chiral Copper Semicorrin Complexes as Enantioselective Catalysts for the Cyclopropanation of Olefins by Diazo- Compounds. *Angewandte Chemie-International Edition in English* **1986,** *25* (11), 1005-1006.

5. Fritschi, H.; Leutenegger, U.; Siegmann, K.; Pfaltz, A.; Keller, W.; Kratky, C., SEMICORRIN METAL-COMPLEXES AS ENANTIOSELECTIVE CATALYSTS .1. SYNTHESIS OF CHIRAL SEMICORRIN LIGANDS AND GENERAL CONCEPTS. *Helvetica Chimica Acta* **1988,** *71* (6), 1541-1552.

6. Fritschi, H.; Leutenegger, U.; Pfaltz, A., SEMICORRIN METAL-COMPLEXES AS ENANTIOSELECTIVE CATALYSTS .2. ENANTIOSELECTIVE CYCLOPROPANE FORMATION FROM OLEFINS WITH DIAZO-COMPOUNDS CATALYZED BY CHIRAL (SEMICORRINATO)COPPER COMPLEXES. *Helvetica Chimica Acta* **1988,** *71* (6), 1553-1565.

7. Lowenthal, R. E.; Masamune, S., Asymmetric Copper-Catalyzed Cyclopropanation of Trisubstituted and Unsymmetrical Cis-1,2-Disubstituted Olefins - Modified Bis- Oxazoline Ligands. *Tetrahedron Letters* **1991,** *32* (50), 7373-7376.

8. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M., Bis(Oxazolines) as Chiral Ligands in Metal-Catalyzed Asymmetric Reactions - Catalytic, Asymmetric Cyclopropanation of Olefins. *J. Am. Chem. Soc.* **1991,** *113* (2), 726-728.

9. Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S. B.; Itoh, K., New Chiral Ruthenium Bis(Oxazolinyl)Pyridine Catalyst - Efficient Asymmetric Cyclopropanation of Olefins with Diazoacetates. *J. Am. Chem. Soc.* **1994,** *116* (5), 2223-2224.

10. Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K., Chiral Ruthenium(Ii)-Bis(2-Oxazolin-2-Yl) Pyridine Complexes - Asymmetric Catalytic Cyclopropanation of Olefins and Diazoacetates. *Bulletin of the Chemical Society of Japan* **1995,** *68* (5), 1247-1262.

11. Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalmann, C. J.; Pieters, R. J.; Protopopova, M. N.; Raab, C. E.; Roos, G. H. P.; Zhou, Q. L.; Martin, S. F., ENANTIOSELECTIVE INTRAMOLECULAR CYCLOPROPANATIONS OF ALLYLIC AND HOMOALLYLIC DIAZOACETATES AND DIAZOACETAMIDES USING CHIRAL DIRHODIUM(II) CARBOXAMIDE CATALYSTS. *J. Am. Chem. Soc.* **1995,** *117* (21), 5763-5775.

12. Ichiyanagi, T.; Shimizu, M.; Fujisawa, T., Asymmetric cyclopropanation of olefins with diazoacetate using chiral copper catalysts. *Tetrahedron* **1997,** *53* (28), 9599-9610.

13. Calter, M. A., Transition metal-catalyzed, asymmetric reactions of diazo compounds. *Current Organic Chemistry* **1997,** *1* (1), 37-70.

14. Fukuda, T.; Katsuki, T., Highly enantioselective cyclopropanation of styrene derivatives using Co(III)-salen complex as a catalyst. *Tetrahedron* **1997,** *53* (21), 7201-7208.

15. Wu, X. Y.; Li, X. H.; Zhou, Q. L., Chiral quinolinyl-oxazolines as ligands for copper(I)-catalyzed asymmetric cyclopropanation. *Tetrahedron-Asymmetry* **1998,** *9* (23), 4143-4150.

16. Nishiyama, H.; Soeda, N.; Naito, T.; Motoyama, Y., Single-chiral bis(oxazolinyl)pyridine (pybox). Efficiency in asymmetric catalytic cyclopropanation. *Tetrahedron-Asymmetry* **1998,** *9* (16), 2865-2869.

17. Uchida, T.; Irie, R.; Katsuki, T., Chiral (ON)Ru-salen catalyzed cyclopropanation: High cis- and enantioselectivity. *Synlett* **1999,** (7), 1163-1165.

18. Braunstein, P.; Naud, F.; Pfaltz, A.; Rettig, S. J., Ruthenium complexes with novel tridentate N,P,N ligands containing a phosphonite bridge between two chiral oxazolines. Catalytic activity in cyclopropanation of olefins and transfer hydrogenation of acetophenone. *Organometallics* **2000,** *19* (14), 2676-2683.

19. Sanders, C. J.; Gillespie, K. M.; Scott, P., Catalyst structure and the enantioselective cyclopropanation of alkenes by copper complexes of biaryldiimines: the importance of ligand acceleration. *Tetrahedron-Asymmetry* **2001,** *12* (7), 1055-1061.

20. Forbes, D. C.; McMills, M. C., Catalytic asymmetric metal carbene transformations. *Current Organic Chemistry* **2001,** *5* (11), 1091-1105.

21. Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H., Asymmetric cyclopropanation in protic media conducted by chiral bis(hydroxymethyl-dihydrooxazolyl)pyridine-ruthenium catalysts. *Chem. Commun.* **2001,** (01), 59-60.

22. Yao, X. Q.; Qiu, M.; Lu, W. R.; Chen, H. L.; Zheng, Z., Substituted salen-Ru(II) complexes as catalysts in the asymmetric cyclopropanation of styrene by ethyl diazoacetate: the influence of substituents and achiral additives on activity and enantioselectivity. *Tetrahedron-Asymmetry* **2001,** *12* (2), 197-204.

23. Clariana, J.; Comelles, J.; Moreno-Manas, M.; Vallribera, A., 2,2 '-isopropylidenebis (4R)-(1-adamantyl)-2-oxazoline (Adam- Box). A new enantiopure C-2-symmetrical ligand: enantioselective cyclopropanations, Diels-Alder reactions, and allylic oxidations. *Tetrahedron-Asymmetry* **2002,** *13* (14), 1551-1554.

24. Miller, J. A.; Jin, W. C.; Nguyen, S. T., An efficient and highly enantio- and diastereoselective cyclopropanation of olefins catalyzed by Schiff-base ruthenium(II) complexes. *Angew. Chem.-Int. Edit.* **2002,** *41* (16), 2953-2956.

25. Nagashima, T.; Davies, H. M. L., Catalytic asymmetric cyclopropanation using bridged dirhodium tetraprolinates on solid support. *Org. Lett.* **2002,** *4* (12), 1989-1992.

26. Honma, M.; Sawada, T.; Fujisawa, Y.; Utsugi, M.; Watanabe, H.; Umino, A.; Matsumura, T.; Hagihara, T.; Takano, M.; Nakada, M., Asymmetric catalysis on the intramolecular cyclopropanation of alpha-diazo-beta-keto sulfones. *J. Am. Chem. Soc.* **2003,** *125* (10), 2860-2861.

27. Davies, H. M. L.; Venkataramani, C., Dirhodium tetraprolinate-catalyzed asymmetric cycloproplanations with high turnover numbers. *Org. Lett.* **2003,** *5* (9), 1403-1406.

28. Chen, Y.; Zhang, X. P., Vitamin B-12 derivatives as natural asymmetric catalysts: Enantioselective cyclopropanation of alkenes. *J. Org. Chem.* **2004,** *69* (7), 2431-2435.

29. Davies, H. M. L.; Lee, G. H., Dirhodium(II) tetra(N-(dodecyl benzenesulfonyl)prolinate) catalyzed enantioselective cyclopropenation of alkynes. *Org. Lett.* **2004,** *6* (8), 1233-1236.

30. Davies, H. M. L.; Lee, G. H., Enantioselective synthesis of cyclopropylphosphonates containing quaternary stereocenters using a D-2-symmetric chiral catalyst Rh-2(S-biTISP)(2). *Org. Lett.* **2004,** *6* (13), 2117-2120.

31. Lou, Y.; Horikawa, M.; Kloster, R. A.; Hawryluk, N. A.; Corey, E. J., A new chiral Rh(II) catalyst for enantioselective 2+1 -cycloaddition. Mechanistic implications and applications. *J. Am. Chem. Soc.* **2004,** *126* (29), 8916-8918.

32. Muller, P.; Ghanem, A., Rh(II)-catalyzed enantioselective cyclopropanation of olefins with dimethyl malonate via in situ generated phenyliodonium ylide. *Org. Lett.* **2004,** *6* (23), 4347-4350.

33. Moreau, B.; Charette, A. B., Expedient synthesis of cyclopropane alpha-amino acids by the catalytic asymmetric cyclopropanation of alkenes using iodonium ylides derived from methyl nitroacetate. *J. Am. Chem. Soc.* **2005,** *127* (51), 18014-18015.

34. Deng, L.; Giessert, A. J.; Gerlitz, O. O.; Dai, X.; Diver, S. T.; Davies, H. M. L., Metal carbene-promoted sequential transformations for the enantioselective synthesis of highly functionalized cycloheptadienes. *J. Am. Chem. Soc.* **2005,** *127* (5), 1342-1343.

35. Lou, Y.; Remarchuk, T. P.; Corey, E. J., Catalysis of enantioselective [2+1]-cycloaddition reactions of ethyl diazoacetate and terminal acetylenes using mixed-ligand complexes of the series Rh-2(RCO2)(n) (L-4-n(star)). Stereochemical heuristics for ligand exchange and catalyst synthesis. *J. Am. Chem. Soc.* **2005,** *127* (41), 14223-14230.

36. Nowlan, D. T.; Singleton, D. A., Mechanism and origin of enantioselectivity in the Rh-2(OAc)(DPTI)(3)-catalyzed cyclopropenation of alkynes. *J. Am. Chem. Soc.* **2005,** *127* (17), 6190-6191.

37. Bonaccorsi, C.; Mezzetti, A., Optimization or breakthrough? The first highly cis- and enantioselective asymmetric cyclopropanation of 1-octene by "electronic and counterion" tuning of RuCl(PNNP) (+) catalysts. *Organometallics* **2005,** *24* (21), 4953-4960.

38. Cornejo, A.; Fraile, J. M.; Garcia, J. I.; Gil, M. J.; Martinez-Merino, V.; Mayoral, J. A.; Salvatella, L., Asymmetric versus C-2-symmetric ligands: Origin of the enantioselectivity in ruthenium-pybox-catalyzed cyclopropanation reactions. *Angew. Chem.-Int. Edit.* **2005,** *44* (3), 458-461.

39. Miller, J. A.; Gross, B. A.; Zhuravel, M. A.; Jin, W. C.; Nguyen, S. T., Axial ligand effects: Utilization of chiral sulfoxide additives for the induction of asymmetry in (salen)ruthenium(II) olefin cyclopropanation catalysts. *Angew. Chem.-Int. Edit.* **2005,** *44* (25), 3885-3889.

40. Kim, H. Y.; Lurain, A. E.; Garcia-Garcia, P.; Carroll, P. J.; Walsh, P. J., Highly enantio- and diastereoselective tandem generation of cyclopropyl alcohols with up to four contiguous stereocenters. *J. Am. Chem. Soc.* **2005,** *127* (38), 13138-13139.

41. Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D., Gold(I)-catalyzed stereoselective olefin cyclopropanation. *J. Am. Chem. Soc.* **2005,** *127* (51), 18002-18003.

42. Denton, J. R.; Sukumaran, D.; Davies, H. M. L., Enantioselective synthesis of trifluoromethyl-substituted cyclopropanes. *Org. Lett.* **2007,** *9* (14), 2625-2628.

43. Kanchiku, S.; Suematsu, H.; Matsumoto, K.; Uchida, T.; Katsuki, T., Construction of an aryliridium-salen complex for highly cis- and enantioselective cyclopropanations. *Angew. Chem.-Int. Edit.* **2007,** *46* (21), 3889-3891.

44. Lu, Z. J.; Zhang, Y.; Wulff, W. D., Direct access to N-H-aziridines from asymmetric catalytic aziridination with borate catalysts derived from vaulted binaphthol and vaulted biphenanthrol ligands. *J. Am. Chem. Soc.* **2007,** *129* (22), 7185-7194.

45. Shitama, H.; Katsuki, T., Asymmetric Simmons-Smith reaction of allylic alcohols with al Lewis acid/N Lewis base bifunctional Al(Salalen) catalyst. *Angew. Chem.-Int. Edit.* **2008,** *47* (13), 2450-2453.

46. Zhu, S. F.; Ruppel, J. V.; Lu, H. J.; Wojtas, L.; Zhang, X. P., Cobalt-catalyzed, asymmetric cyclopropanation with diazosulfones: Rigidification and polarization of ligand chiral environment via hydrogen bonding and cyclization. *J. Am. Chem. Soc.* **2008,** *130* (15), 5042-+.

47. Suematsu, H.; Kanchiku, S.; Uchida, T.; Katsuki, T., Construction of aryliridium-salen complexes: Enantio- and cis-selective cyclopropanation of conjugated and nonconjugated olefins. *J. Am. Chem. Soc.* **2008,** *130* (31), 10327-10337.

48. Shimada, N.; Anada, M.; Nakamura, S.; Nambu, H.; Tsutsui, H.; Hashimoto, S., Catalytic enantioselective intermolecular cycloaddition of 2-diazo-3,6-diketoester-derived carbonyl ylides with alkynes and styrenes using chiral dirhodium(II) carboxylates. *Org. Lett.* **2008,** *10* (16), 3603-3606.

49. Zhu, S.; Perman, J. A.; Zhang, X. P., Acceptor/Acceptor-Substituted Diazo Reagents for Carbene Transfers: Cobalt-Catalyzed Asymmetric Z-Cyclopropanation of Alkenes with alpha-Nitrodiazoacetates. *Angew. Chem.-Int. Edit.* **2008,** *47* (44), 8460-8463.

50. Marcoux, D.; Charette, A. B., trans-Directing Ability of Amide Groups in Cyclopropanation: Application to the Asymmetric Cyclopropanation of Alkenes with Diazo Reagents Bearing Two Carboxy Groups. *Angew. Chem.-Int. Edit.* **2008,** *47* (52), 10155-10158.

51. Doyle, M. P., Exceptional Selectivity in Cyclopropanation Reactions Catalyzed by Chiral Cobalt(II)-Porphyrin Catalysts. *Angew. Chem.-Int. Edit.* **2009,** *48* (5), 850-852.

52. Miller, L. C.; Ndungu, J. M.; Sarpong, R., Parallel Kinetic Resolution Approach to the Cyathane and Cyanthiwigin Diterpenes Using a Cyclopropanation/Cope Rearrangement. *Angew. Chem.-Int. Edit.* **2009,** *48* (13), 2398-2402.

53. Xu, Z. J.; Fang, R.; Zhao, C.; Huang, J. S.; Li, G. Y.; Zhu, N.; Che, C. M., cis-beta-Bis(carbonyl) Ruthenium-Salen Complexes: X-ray Crystal Structures and Remarkable Catalytic Properties toward Asymmetric Intramolecular Alkene Cyclopropanation. *J. Am. Chem. Soc.* **2009,** *131* (12), 4405-4417.

54. Ichinose, M.; Suematsu, H.; Katsuki, T., Efficient Construction of alpha-Spirocyclopropyl Lactones: Iridium-Salen-Catalyzed Asymmetric Cyclopropanation. *Angew. Chem.-Int. Edit.* **2009,** *48* (17), 3121-3123.

55. Marcoux, D.; Azzi, S.; Charette, A. B., TfNH2 as Achiral Hydrogen-Bond Donor Additive to Enhance the Selectivity of a Transition Metal Catalyzed Reaction. Highly Enantio- and Diastereoselective Rhodium-Catalyzed Cyclopropanation of Alkenes Using alpha-Cyano Diazoacetamide. *J. Am. Chem. Soc.* **2009,** *131* (20), 6970-+.

56. DeAngelis, A.; Dmitrenko, O.; Yap, G. P. A.; Fox, J. M., Chiral Crown Conformation of Rh-2(S-PTTL)(4): Enantioselective Cyclopropa nation with alpha-Alkyl-alpha-diazoesters. *J. Am. Chem. Soc.* **2009,** *131* (21), 7230-+.

57. Gregg, T. M.; Farrugia, M. K.; Frost, J. R., Rhodium-Mediated Enantioselective Cycloproplanation of Allenes. *Org. Lett.* **2009,** *11* (19), 4434-4436.

58. Lindsay, V. N. G.; Lin, W.; Charette, A. B., Experimental Evidence for the All-Up Reactive Conformation of Chiral Rhodium(II) Carboxylate Catalysts: Enantioselective Synthesis of cis-Cyclopropane alpha-Amino Acids. *J. Am. Chem. Soc.* **2009,** *131* (45), 16383-+.

59. Marcoux, D.; Goudreau, S. R.; Charette, A. B., trans-Directing Ability of the Amide Group: Enabling the Enantiocontrol in the Synthesis of 1,1-Dicarboxy Cyclopropanes. Reaction Development, Scope, and Synthetic Applications. *J. Org. Chem.* **2009,** *74* (23), 8939-8955.

60. Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V., Rhodium-Catalyzed Enantioselective Cyclopropanation of Olefins with N-Sulfonyl 1,2,3-Triazoles. *J. Am. Chem. Soc.* **2009,** *131* (50), 18034-+.

61. Grimster, N.; Zhang, L.; Fokin, V. V., Synthesis and Reactivity of Rhodium(II) N-Triflyl Azavinyl Carbenes. *J. Am. Chem. Soc.* **2010,** *132* (8), 2510-+.

62. Nishimura, T.; Maeda, Y.; Hayashi, T., Asymmetric Cyclopropanation of Alkenes with Dimethyl Diazomalonate Catalyzed by Chiral Diene-Rhodium Complexes. *Angew. Chem.-Int. Edit.* **2010,** *49* (40), 7324-7327.

63. Zhu, S. F.; Xu, X.; Perman, J. A.; Zhang, X. P., A General and Efficient Cobalt(II)-Based Catalytic System for Highly Stereoselective Cyclopropanation of Alkenes with alpha-Cyanodiazoacetates. *J. Am. Chem. Soc.* **2010,** *132* (37), 12796-12799.

64. Briones, J. F.; Hansen, J.; Hardcastle, K. I.; Autschbach, J.; Davies, H. M. L., Highly Enantioselective Rh(2)(S-DOSP)(4)-Catalyzed Cyclopropenation of Alkynes with Styryldiazoacetates. *J. Am. Chem. Soc.* **2010,** *132* (48), 17211-17215.

65. Uehara, M.; Suematsu, H.; Yasutomi, Y.; Katsuki, T., Enantioenriched Synthesis of Cyclopropenes with a Quaternary Stereocenter, Versatile Building Blocks. *J. Am. Chem. Soc.* **2011,** *133* (2), 170-171.

66. Morandi, B.; Mariampillai, B.; Carreira, E. M., Enantioselective Cobalt-Catalyzed Preparation of Trifluoromethyl-Substituted Cyclopropanes. *Angew. Chem.-Int. Edit.* **2011,** *50* (5), 1101-1104.

67. Hayakawa, I.; Miyazawa, Y.; Ohyoshi, T.; Asuma, Y.; Aoki, K.; Kigoshi, H., Synthetic Studies towards Optically Active 13-Oxyingenol via Asymmetric Cyclopropanation. *Synthesis* **2011,** (5), 769-777.

68. Xu, X.; Lu, H. J.; Ruppel, J. V.; Cui, X.; de Mesa, S. L.; Wojtas, L.; Zhang, X. P., Highly Asymmetric Intramolecular Cyclopropanation of Acceptor-Substituted Diazoacetates by Co(II)-Based Metalloradical Catalysis: Iterative Approach for Development of New-Generation Catalysts. *J. Am. Chem. Soc.* **2011,** *133* (39), 15292-15295.

69. Qin, C. M.; Boyarskikh, V.; Hansen, J. H.; Hardcastle, K. I.; Musaev, D. G.; Davies, H. M. L., D-2-Symmetric Dirhodium Catalyst Derived from a 1,2,2-Triarylcyclopropanecarboxylate Ligand: Design, Synthesis and Application. *J. Am. Chem. Soc.* **2011,** *133* (47), 19198-19204.

70. Gu, P. M.; Su, Y.; Wu, X. P.; Sun, J.; Liu, W. Y.; Xue, P.; Li, R., Enantioselective Preparation of cis-beta-Azidocyclopropane Esters by Cyclopropanation of Azido Alkenes Using a Chiral Dirhodium Catalyst. *Org. Lett.* **2012,** *14* (9), 2246-2249.

71. Chanthamath, S.; Phomkeona, K.; Shibatomi, K.; Iwasa, S., Highly stereoselective Ru(II)-Pheox catalyzed asymmetric cyclopropanation of terminal olefins with succinimidyl diazoacetate. *Chem. Commun.* **2012,** *48* (62), 7750-7752.

72. Briones, J. F.; Davies, H. M. L., Gold(I)-Catalyzed Asymmetric Cyclopropenation of Internal Alkynes. *J. Am. Chem. Soc.* **2012,** *134* (29), 11916-11919.

73. Li, J.; Liao, S. H.; Xiong, H.; Zhou, Y. Y.; Sun, X. L.; Zhang, Y.; Zhou, X. G.; Tang, Y., Highly Diastereo- and Enantioselective Cyclopropanation of 1,2-Disubstituted Alkenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (35), 8838-8841.

74. Deng, C.; Wang, L. J.; Zhu, J.; Tang, Y., A Chiral Cagelike Copper(I) Catalyst for the Highly Enantioselective Synthesis of 1,1-Cyclopropane Diesters. *Angew. Chem.-Int. Edit.* **2012,** *51* (46), 11620-11623.

75. Ozuduru, G.; Schubach, T.; Boysen, M. M. K., Enantioselective Cyclopropanation of Indoles: Construction of All-Carbon Quaternary Stereocenters. *Org. Lett.* **2012,** *14* (19), 4990-4993.

76. Cao, Z. Y.; Zhou, F.; Yu, Y. H.; Zhou, J., A Highly Diastereo- and Enantioselective Hg(II)-Catalyzed Cyclopropanation of Diazooxindoles and Alkenes. *Org. Lett.* **2013,** *15* (1), 42-45.

77. Qin, C. M.; Davies, H. M. L., Enantioselective Synthesis of 2-Arylbicyclo 1.1.0 butane Carboxylates. *Org. Lett.* **2013,** *15* (2), 310-313.

78. Lindsay, V. N. G.; Fiset, D.; Gritsch, P. J.; Azzi, S.; Charette, A. B., Stereoselective Rh-2(S-IBAZ)(4)-Catalyzed Cyclopropanation of Alkenes, Alkynes, and Allenes: Asymmetric Synthesis of Diacceptor Cyclopropylphosphonates and Alkylidenecyclopropanes. *J. Am. Chem. Soc.* **2013,** *135* (4), 1463-1470.

79. Chanthamath, S.; Nguyen, D. T.; Shibatomi, K.; Iwasa, S., Highly Enantioselective Synthesis of Cyclopropylamine Derivatives via Ru(II)-Pheox-Catalyzed Direct Asymmetric Cyclopropanation of Vinylcarbamates. *Org. Lett.* **2013,** *15* (4), 772-775.

80. Wang, H. B.; Guptill, D. M.; Varela-Alvarez, A.; Musaev, D. G.; Davies, H. M. L., Rhodium-catalyzed enantioselective cyclopropanation of electron-deficient alkenes. *Chem. Sci.* **2013,** *4* (7), 2844-2850.

81. Chanthamath, S.; Takaki, S.; Shibatomi, K.; Iwasa, S., Highly Stereoselective Cyclopropanation of alpha,beta-Unsaturated Carbonyl Compounds with Methyl (Diazoacetoxy) acetate Catalyzed by a Chiral Ruthenium(II) Complex. *Angew. Chem.-Int. Edit.* **2013,** *52* (22), 5818-5821.

82. Cao, Z. Y.; Wang, X. M.; Tan, C.; Zhao, X. L.; Zhou, J.; Ding, K. L., Highly Stereoselective Olefin Cyclopropanation of Diazooxindoles Catalyzed by a C-2-Symmetric Spiroketal Bisphosphine/Au(I) Complex. *J. Am. Chem. Soc.* **2013,** *135* (22), 8197-8200.

83. Chepiga, K. M.; Qin, C. M.; Alford, J. S.; Chennamadhavuni, S.; Gregg, T. M.; Olson, J. P.; Davies, H. M. L., Guide to enantioselective dirhodium(II)-catalyzed cyclopropanation with aryldiazoacetates. *Tetrahedron* **2013,** *69* (27-28), 5765-5771.

84. Panish, R.; Chintala, S. R.; Boruta, D. T.; Fang, Y. Z.; Taylor, M. T.; Fox, J. M., Enantioselective Synthesis of Cyclobutanes via Sequential Rh-catalyzed Bicyclobutanation/Cu-catalyzed Homoconjugate Addition. *J. Am. Chem. Soc.* **2013,** *135* (25), 9283-9286.

85. Xu, X.; Zhu, S. F.; Cui, X.; Wojtas, L.; Zhang, X. P., Cobalt(II)-Catalyzed Asymmetric Olefin Cyclopropanation with alpha-Ketodiazoacetates. *Angew. Chem.-Int. Edit.* **2013,** *52* (45), 11857-11861.

86. Chanthamath, S.; Ozaki, S.; Shibatomi, K.; Iwasa, S., Highly Stereoselective Synthesis of Cyclopropylphosphonates Catalyzed by Chiral Ru(II)-Pheox Complex. *Org. Lett.* **2014,** *16* (11), 3012-3015.

87. Shen, J.-J.; Zhu, S.-F.; Cai, Y.; Xu, H.; Xie, X.-L.; Zhou, Q.-L., Enantioselective Iron-Catalyzed Intramolecular Cyclopropanation Reactions. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13188-13191.

88. Miura, T.; Nakamuro, T.; Liang, C.-J.; Murakami, M., Synthesis of trans-Cycloalkenes via Enantioselective Cyclopropanation and Skeletal Rearrangement. *J. Am. Chem. Soc.* **2014,** *136* (45), 15905-15908.

89. Pons, A.; Ivashkin, P.; Poisson, T.; Charette, A. B.; Pannecoucke, X.; Jubault, P., Catalytic Enantioselective Synthesis of Halocyclopropanes. *Chemistry-a European Journal* **2016,** *22* (18), 6239-6242.

90. Su, Y.; Li, Q. F.; Zhao, Y. M.; Gu, P. M., Preparation of Optically Active cis-Cyclopropane Carboxylates: Cyclopropanation of alpha-Silyl Stryenes with Aryldiazoacetates and Desilylation of the Resulting Silyl Cyclopropanes. *Org. Lett.* **2016,** *18* (17), 4356-4359.

91. Xie, M. S.; Zhou, P.; Niu, H. Y.; Qu, G. R.; Guo, H. M., Enantioselective Intermolecular Cyclopropanations for the Synthesis of Chiral Pyrimidine Carbocyclic Nucleosides. *Org. Lett.* **2016,** *18* (17), 4344-4347.

92. Huang, K. X.; Xie, M. S.; Zhao, G. F.; Qu, G. R.; Guo, H. M., Synthesis of Chiral Cyclopropyl Carbocyclic Purine Nucleosides via Asymmetric Intramolecular Cyclopropanations Catalyzed by a Chiral Ruthenium(II) Complex. *Adv. Synth. Catal.* **2016,** *358* (22), 3627-3632.

93. Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P., Asymmetric Radical Cyclopropanation of Alkenes with In Situ Generated Donor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (3), 1049-1052.

94. Xu, X.; Wang, Y.; Cui, X.; Wojtas, L.; Zhang, X. P., Metalloradical activation of alpha-formyldiazoacetates for the catalytic asymmetric radical cyclopropanation of alkenes. *Chem. Sci.* **2017,** *8* (6), 4347-4351.

95. Pilsl, L. K. A.; Ertl, T.; Reiser, O., Enantioselective Three-Step Synthesis of Homo-beta-proline: A Donor-Acceptor Cyclopropane as Key Intermediate. *Org. Lett.* **2017,** *19* (10), 2754-2757.

96. Xu, H.; Li, Y. P.; Cai, Y.; Wang, G. P.; Zhu, S. F.; Zhou, Q. L., Highly Enantioselective Copper- and Iron-Catalyzed Intramolecular Cyclopropanation of Indoles. *J. Am. Chem. Soc.* **2017,** *139* (23), 7697-7700.

97. Bos, M.; Huang, W. S.; Poisson, T.; Pannecoucke, X.; Charette, A. B.; Jubault, P., Catalytic Enantioselective Synthesis of Highly Functionalized Difluoromethylated Cyclopropanes. *Angew. Chem.-Int. Edit.* **2017,** *56* (43), 13319-13323.

98. Kotozaki, M.; Chanthamath, S.; Fujisawa, I.; Shibatomi, K.; Iwasa, S., Highly stereoselective cyclopropanation of various olefins with diazosulfones catalyzed by Ru(II)-Pheox complexes. *Chem. Commun.* **2017,** *53* (90), 12193-12196.

99. Deng, C.; Liu, H. K.; Zheng, Z. B.; Wang, L. J.; Yu, X.; Zhang, W. H.; Tang, Y., Copper-Catalyzed Enantioselective Cyclopropanation of Internal Olefins with Diazomalonates. *Org. Lett.* **2017,** *19* (21), 5717-5719.

100. Carreras, J.; Caballero, A.; Perez, P. J., Enantio- and Diastereoselective Cyclopropanation of 1-Alkenylboronates: Synthesis of 1-Boryl-2,3-Disubstituted Cyclopropanes. *Angew. Chem.-Int. Edit.* **2018,** *57* (9), 2334-+.

101. Pirovano, V.; Brambilla, E.; Tseberlidis, G., Copper(I)(Pyridine-Containing Ligand) Catalyzed Regio- and Steroselective Synthesis of 2-Vinylcyclopropa b indolines from 2-Vinylindoles. *Org. Lett.* **2018,** *20* (2), 405-408.

102. Huang, W. S.; Schlinquer, C.; Poisson, T.; Pannecoucke, X.; Charette, A. B.; Jubault, P., General Catalytic Enantioselective Access to Monohalomethyl and Trifluoromethyl Cyclopropanes. *Chemistry-a European Journal* **2018,** *24* (41), 10339-10343.

103. Zhu, D.; Chen, L.; Zhang, H.; Ma, Z.; Jiang, H.; Zhu, S., Highly Chemo- and Stereoselective Catalyst-Controlled Allylic C−H Insertion and Cyclopropanation Using Donor/Donor Carbenes. *Angewandte Chemie International Edition* **2018,** *57* (38), 12405-12409.

104. Shim, S. Y.; Choi, Y.; Ryu, D. H., Asymmetric Synthesis of Cyclobutanone via Lewis Acid Catalyzed Tandem Cyclopropanation/Semipinacol Rearrangement. *J. Am. Chem. Soc.* **2018,** *140* (36), 11184-11188.

105. Montesinos-Magraner, M.; Costantini, M.; Ramírez-Contreras, R.; Muratore, M. E.; Johansson, M. J.; Mendoza, A., General Cyclopropane Assembly by Enantioselective Transfer of a Redox-Active Carbene to Aliphatic Olefins. *Angewandte Chemie* **2019,** *131* (18), 5991-5996.

106. Fu, J. T.; Wurzer, N.; Lehner, V.; Reiser, O.; Davies, H. M. L., Rh(II)-Catalyzed Monocyclopropanation of Pyrroles and Its Application to the Synthesis Pharmaceutically Relevant Compounds. *Org. Lett.* **2019,** *21* (15), 6102-6106.

107. Shao, X. X.; Malcolmson, S. J., Catalytic Enantio- and Diastereoselective Cyclopropanation of 2-Azadienes for the Synthesis of Aminocyclopropanes Bearing Quaternary Carbon Stereogenic Centers. *Org. Lett.* **2019,** *21* (18), 7380-7385.

108. Da Ho, L.; Otog, N.; Fujisawa, I.; Iwasa, S., Catalytic Asymmetric Carbene Transfer Reactions of Diazo Oxime Ethers with Olefins and Their Synthetic Applications. *Org. Lett.* **2019,** *21* (18), 7470-7474.

109. Chu, Z. W.; Tang, Z. Q.; Zhang, K. N.; Wang, L.; Li, W. B.; Wu, H. H.; Zhang, J. L., Gold(I)-Catalyzed Enantioselective Cyclopropanation of alpha-Aryl Diazoacetates with Enamides. *Organometallics* **2019,** *38* (20), 4036-4042.

110. Zhang, Z.-Q.; Zheng, M.-M.; Xue, X.-S.; Marek, I.; Zhang, F.-G.; Ma, J.-A., Catalytic Enantioselective Cyclopropenation of Internal Alkynes: Access to Difluoromethylated Three-Membered Carbocycles. *Angewandte Chemie International Edition* **2019,** *58* (50), 18191-18196.

111. Tran, U. P. N.; Hommelsheim, R.; Yang, Z.; Empel, C.; Hock, K. J.; Nguyen, T. V.; Koenigs, R. M., Catalytic Synthesis of Trifluoromethyl Cyclopropenes and Oligo-Cyclopropenes. *Chemistry-a European Journal* **2020,** *26* (6), 1254-1257.

112. Smith, K. L.; Padgett, C. L.; Mackay, W. D.; Johnson, J. S., Catalytic, Asymmetric Dearomative Synthesis of Complex Cyclohexanes via a Highly Regio- and Stereoselective Arene Cyclopropanation Using α-Cyanodiazoacetates. *J. Am. Chem. Soc.* **2020,** *142* (14), 6449-6455.

113. Caló, F. P.; Fürstner, A., A Heteroleptic Dirhodium Catalyst for Asymmetric Cyclopropanation with α-Stannyl α-Diazoacetate. "Stereoretentive" Stille Coupling with Formation of Chiral Quarternary Carbon Centers. *Angewandte Chemie International Edition* **2020,** *59* (33), 13900-13907.

114. Liu, X.; Wang, Z.-S.; Zhai, T.-Y.; Luo, C.; Zhang, Y.-P.; Chen, Y.-B.; Deng, C.; Liu, R.-S.; Ye, L.-W., Copper-Catalyzed Azide–Ynamide Cyclization to Generate α-Imino Copper Carbenes: Divergent and Enantioselective Access to Polycyclic N-Heterocycles. *Angewandte Chemie International Edition* **2020,** *59* (41), 17984-17990.

115. Zhou, L.; Yan, W.-G.; Sun, X.-L.; Wang, L.; Tang, Y., A Versatile Enantioselective Catalytic Cyclopropanation-Rearrangement Approach to the Divergent Construction of Chiral Spiroaminals and Fused Bicyclic Acetals. *Angewandte Chemie International Edition* **2020,** *59* (43), 18964-18969.

116. Wertz, B.; Ren, Z.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., Comparison of 1,2-Diarylcyclopropanecarboxylates with 1,2,2-Triarylcyclopropanecarboxylates as Chiral Ligands for Dirhodium-Catalyzed Cyclopropanation and C–H Functionalization. *The Journal of Organic Chemistry* **2020,** *85* (19), 12199-12211.

117. Singha, S.; Buchsteiner, M.; Bistoni, G.; Goddard, R.; Fürstner, A., A New Ligand Design Based on London Dispersion Empowers Chiral Bismuth–Rhodium Paddlewheel Catalysts. *J. Am. Chem. Soc.* **2021,** *143* (15), 5666-5673.

118. Lee, W.-C. C.; Wang, D.-S.; Zhang, C.; Xie, J.; Li, B.; Zhang, X. P., Asymmetric radical cyclopropanation of dehydroaminocarboxylates: Stereoselective synthesis of cyclopropyl α-amino acids. *Chem* **2021,** *7* (6), 1588-1601.

119. Zhang, C.; Wang, D.-S.; Lee, W.-C. C.; McKillop, A. M.; Zhang, X. P., Controlling Enantioselectivity and Diastereoselectivity in Radical Cascade Cyclization for Construction of Bicyclic Structures. *J. Am. Chem. Soc.* **2021,** *143* (29), 11130-11140.

120. Wang, X.; Ke, J.; Zhu, Y.; Deb, A.; Xu, Y.; Zhang, X. P., Asymmetric Radical Process for General Synthesis of Chiral Heteroaryl Cyclopropanes. *J. Am. Chem. Soc.* **2021,** *143* (29), 11121-11129.

121. Altarejos, J.; Sucunza, D.; Vaquero, J. J.; Carreras, J., Enantioselective Copper-Catalyzed Synthesis of Trifluoromethyl-Cyclopropylboronates. *Org. Lett.* **2021,** *23* (15), 6174-6178.

122. Sharland, J. C.; Wei, B.; Hardee, D. J.; Hodges, T. R.; Gong, W.; Voight, E. A.; Davies, H. M. L., Asymmetric synthesis of pharmaceutically relevant 1-aryl-2-heteroaryl- and 1,2-diheteroarylcyclopropane-1-carboxylates. *Chem. Sci.* **2021,** *12* (33), 11181-11190.

123. Schmidt, T. A.; Sparr, C., Catalyst-Controlled Stereoselective Barton–Kellogg Olefination. *Angewandte Chemie International Edition* **2021,** *60* (44), 23911-23916.

124. Zhu, D.; Cao, T.; Chen, K.; Zhu, S., Rh2(ii)-catalyzed enantioselective intramolecular Büchner reaction and aromatic substitution of donor–donor carbenes. *Chem. Sci.* **2022,** *13* (7), 1992-2000.

125. Ke, J.; Lee, W.-C. C.; Wang, X.; Wang, Y.; Wen, X.; Zhang, X. P., Metalloradical Activation of In Situ-Generated α-Alkynyldiazomethanes for Asymmetric Radical Cyclopropanation of Alkenes. *J. Am. Chem. Soc.* **2022,** *144* (5), 2368-2378.

126. Su, J.; Li, Q.; Shao, Y.; Sun, J., Catalytic Transformations of 2-Pyridones by Rhodium-Mediated Carbene Transfer. *Org. Lett.* **2022,** *24* (8), 1637-1641.

127. Caló, F. P.; Zimmer, A.; Bistoni, G.; Fürstner, A., From Serendipity to Rational Design: Heteroleptic Dirhodium Amidate Complexes for Diastereodivergent Asymmetric Cyclopropanation. *J. Am. Chem. Soc.* **2022,** *144* (16), 7465-7478.

128. Guan, F.; Zhou, R.; Ren, X.; Guo, Z.; Wang, C.; Zhou, C.-Y., Asymmetric dearomative cyclopropanation of naphthalenes to construct polycyclic compounds. *Chem. Sci.* **2022,** *13* (44), 13015-13019.

129. Zhang, J.; Xu, W.; Xu, M.-H., Low Coordination State RhI-Complex as High Performance Catalyst for Asymmetric Intramolecular Cyclopropanation: Construction of penta-Substituted Cyclopropanes. *Angewandte Chemie International Edition* **2023,** *62* (10), e202216799.

130. Cao, L.-Y.; Wang, J.-L.; Wang, K.; Wu, J.-B.; Wang, D.-K.; Peng, J.-M.; Bai, J.; Zhuo, C.-X., Catalytic Asymmetric Deoxygenative Cyclopropanation Reactions by a Chiral Salen-Mo Catalyst. *J. Am. Chem. Soc.* **2023,** *145* (5), 2765-2772.

131. Lee, W.-C. C.; Wang, J.; Zhu, Y.; Zhang, X. P., Asymmetric Radical Bicyclization for Stereoselective Construction of Tricyclic Chromanones and Chromanes with Fused Cyclopropanes. *J. Am. Chem. Soc.* **2023,** *145* (21), 11622-11632.

132. Berger, K. E.; Martinez, R. J.; Zhou, J.; Uyeda, C., Catalytic Asymmetric Cyclopropanations with Nonstabilized Carbenes. *J. Am. Chem. Soc.* **2023,** *145* (17), 9441-9447.

133. Liu, H.-L.; Wang, X.; Gao, K.; Wang, Z., Catalytic Diastereo- and Enantioselective Cyclopropanation of gem-Dihaloalkanes and Terminal Olefins. *Angewandte Chemie International Edition* **2023,** *62* (28), e202305987.

134. Peeters, M.; Decaens, J.; Fürstner, A., Taming of Furfurylidenes by Chiral Bismuth-Rhodium Paddlewheel Catalysts. Preparation and Functionalization of Optically Active 1,1-Disubstituted (Trifluoromethyl)cyclopropanes. *Angewandte Chemie International Edition* **2023,** *62* (44), e202311598.

135. Zhang, J.; Ma, Z.; Xu, W.; Wang, Z.; Chung, L. W.; Xu, M.-H., Asymmetric Cyclopropanation of Primary N-Vinylamides via Carbene Transfer Catalyzed by Cationic Rh(I)/Diene Complexes: An Unexpected Outer-Sphere Mechanism. *ACS Catalysis* **2024,** *14* (12), 9385-9396.

136. Zhang, X.; Song, Q.; Liu, S.; Sivaguru, P.; Liu, Z.; Yang, Y.; Ning, Y.; Anderson, E. A.; de Ruiter, G.; Bi, X., Asymmetric dearomative single-atom skeletal editing of indoles and pyrroles. *Nat. Chem.* **2025,** *17* (2), 215-225.

137. Lowenthal, R. E.; Abiko, A.; Masamune, S., Asymmetric Catalytic Cyclopropanation of Olefins - Bis- Oxazoline Copper-Complexes. *Tetrahedron Letters* **1990,** *31* (42), 6005-6008.

2.4.4 Dihydroxylation

1. Wai, J. S. M.; Marko, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B., A MECHANISTIC INSIGHT LEADS TO A GREATLY IMPROVED OSMIUM-CATALYZED ASYMMETRIC DIHYDROXYLATION PROCESS. *J. Am. Chem. Soc.* **1989,** *111* (3), 1123-1125.

2. Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K. S.; Kwong, H. L.; Morikawa, K.; Wang, Z. M.; Xu, D. Q.; Zhang, X. L., THE OSMIUM-CATALYZED ASYMMETRIC DIHYDROXYLATION - A NEW LIGAND CLASS AND A PROCESS IMPROVEMENT. *J. Org. Chem.* **1992,** *57* (10), 2768-2771.

3. Wang, L.; Sharpless, K. B., CATALYTIC ASYMMETRIC DIHYDROXYLATION OF CIS-DISUBSTITUTED OLEFINS. *J. Am. Chem. Soc.* **1992,** *114* (19), 7568-7570.

4. Xu, D. Q.; Crispino, G. A.; Sharpless, K. B., SELECTIVE ASYMMETRIC DIHYDROXYLATION OF DIENES. *J. Am. Chem. Soc.* **1992,** *114* (19), 7570-7571.

5. Kolb, H. C.; Vannieuwenhze, M. S.; Sharpless, K. B., Catalytic Asymmetric Dihydroxylation. *Chemical Reviews* **1994,** *94* (8), 2483-2547.

6. Corey, E. J.; Guzmanperez, A.; Noe, M. C., THE APPLICATION OF A MECHANISTIC MODEL LEADS TO THE EXTENSION OF THE SHARPLESS ASYMMETRIC DIHYDROXYLATION TO ALLYLIC 4-METHOXYBENZOATES AND CONFORMATIONALLY RELATED AMINE AND HOMOALLYLIC ALCOHOL DERIVATIVES. *J. Am. Chem. Soc.* **1995,** *117* (44), 10805-10816.

7. Corey, E. J.; Noe, M. C.; Guzmanperez, A., KINETIC RESOLUTION BY ENANTIOSELECTIVE DIHYDROXYLATION OF SECONDARY ALLYLIC 4-METHOXYBENZOATE ESTERS USING A MECHANISTICALLY DESIGNED CINCHONA ALKALOID CATALYST. *J. Am. Chem. Soc.* **1995,** *117* (44), 10817-10824.

8. Li, G. G.; Angert, H. H.; Sharpless, K. B., N-halocarbamate salts lead to more efficient catalytic asymmetric aminohydroxylation. *Angew. Chem.-Int. Edit.* **1996,** *35* (23-24), 2813-2817.

9. Li, G. G.; Chang, H. T.; Sharpless, K. B., Catalytic asymmetric aminohydroxylation (AA) of olefins. *Angew. Chem.-Int. Edit.* **1996,** *35* (4), 451-454.

10. Norrby, P. O.; Becker, H.; Sharpless, K. B., Toward an understanding of the high enantioselectivity in the osmium-catalyzed asymmetric dihydroxylation .3. New insights into isomeric forms of the putative osmaoxetane intermediate. *J. Am. Chem. Soc.* **1996,** *118* (1), 35-42.

11. Bruncko, M.; Schlingloff, G.; Sharpless, K. B., N-bromoacetamide - A new nitrogen source for the catalytic asymmetric aminohydroxylation of olefins. *Angew. Chem.-Int. Edit.* **1997,** *36* (13-14), 1483-1486.

12. Rubin, A. E.; Sharpless, K. B., A highly efficient aminohydroxylation process. *Angew. Chem.-Int. Edit.* **1997,** *36* (23), 2637-2640.

13. Bodkin, J. A.; McLeod, M. D., The Sharpless asymmetric aminohydroxylation. *Journal of the Chemical Society-Perkin Transactions 1* **2002,** (24), 2733-2746.

14. Nesterenko, V.; Byers, J. T.; Hergenrother, P. J., The use of pH to influence regio- and chemoselectivity in the asymmetric aminohydroxylation of styrenes. *Org. Lett.* **2003,** *5* (3), 281-284.

15. Liu, Z. S.; Ma, N. C.; Jia, Y. X.; Bois-Choussy, M.; Malabarba, A.; Zhu, J. P., Synthesis of beta-amino-alpha-hydroxy esters and beta-amino-alpha-azido ester by sharpless asymmetric aminohydroxylation, byproducts analysis. *J. Org. Chem.* **2005,** *70* (7), 2847-2850.

16. Suzuki, K.; Oldenburg, P. D.; Que, L., Iron-catalyzed asymmetric olefin cis-dihydroxylation with 97 % enantiomeric excess. *Angew. Chem.-Int. Edit.* **2008,** *47* (10), 1887-1889.

17. Junttila, M. H.; Hormi, O. O. E., Methanesulfonamide: a Cosolvent and a General Acid Catalyst in Sharpless Asymmetric Dihydroxylations. *J. Org. Chem.* **2009,** *74* (8), 3038-3047.

18. Nakanishi, M.; Minard, C.; Retailleau, P.; Cariou, K.; Dodd, R. H., Copper(I) Catalyzed Regioselective Asymmetric Alkoxyamination of Aryl Enamide Derivatives. *Org. Lett.* **2011,** *13* (21), 5792-5795.

19. Williamson, K. S.; Yoon, T. P., Iron Catalyzed Asymmetric Oxyamination of Olefins. *J. Am. Chem. Soc.* **2012,** *134* (30), 12370-12373.

20. Ott, A. A.; Goshey, C. S.; Topczewski, J. J., Dynamic Kinetic Resolution of Allylic Azides via Asymmetric Dihydroxylation. *J. Am. Chem. Soc.* **2017,** *139* (23), 7737-7740.

2.4.5 CH/XH Functionalization

1. Doyle, M. P.; Vanoeveren, A.; Westrum, L. J.; Protopopova, M. N.; Clayton, T. W., ASYMMETRIC-SYNTHESIS OF LACTONES WITH HIGH ENANTIOSELECTIVITY BY INTRAMOLECULAR CARBON HYDROGEN INSERTION REACTIONS OF ALKYL DIAZOACETATES CATALYZED BY CHIRAL RHODIUM(II) CARBOXAMIDES. *J. Am. Chem. Soc.* **1991,** *113* (23), 8982-8984.

2. Yang, H.; Khan, M. A.; Nicholas, K. M., Chiral Pd-Chelates, Cu-Chelates and Ni-Chelates and Their Utilities as Catalysts in Allylic Acetoxylation of Alkenes. *Journal of Molecular Catalysis* **1994,** *91* (3), 319-334.

3. Andrus, M. B.; Argade, A. B.; Chen, X.; Pamment, M. G., The Asymmetric Kharasch Reaction - Catalytic Enantioselective Allylic Acyloxylation of Olefins with Chiral Copper(I) Complexes and Tert-Butyl Perbenzoate. *Tetrahedron Letters* **1995,** *36* (17), 2945-2948.

4. Gokhale, A. S.; Minidis, A. B. E.; Pfaltz, A., Enantioselective Allylic Oxidation Catalyzed by Chiral Bisoxazoline-Copper Complexes. *Tetrahedron Letters* **1995,** *36* (11), 1831-1834.

5. Kawasaki, K.; Tsumura, S.; Katsuki, T., Enantioselective Allylic Oxidation Using Biomimetic Tris(Oxazolines)-Copper(Ii) Complex. *Synlett* **1995,** (12), 1245-&.

6. Levina, A.; Muzart, J., Enantioselective Allylic Oxidation in the Presence of the Cu(I)/Cu(Ii)-Proline Catalytic-System. *Tetrahedron-Asymmetry* **1995,** *6* (1), 147-156.

7. Rispens, M. T.; Zondervan, C.; Feringa, B. L., Catalytic Enantioselective Allylic Oxidation. *Tetrahedron-Asymmetry* **1995,** *6* (3), 661-664.

8. Sodergren, M. J.; Andersson, P. G., Chiral, bicyclic proline derivatives and their application as ligands for copper in the catalytic asymmetric allylic oxidation of olefins. *Tetrahedron Letters* **1996,** *37* (42), 7577-7580.

9. Zondervan, C.; Feringa, B. L., Remarkable reversal of the non-linear effect in the catalytic enantioselective allylic oxidation of cyclohexene using copper proline complexes and t-butyl hydroperoxide. *Tetrahedron-Asymmetry* **1996,** *7* (7), 1895-1898.

10. Clark, J. S.; Tolhurst, K. F.; Taylor, M.; Swallow, S., Enantioselective allylic acyloxylation catalysed by copper- oxazoline complexes. *Journal of the Chemical Society-Perkin Transactions 1* **1998,** (7), 1167-1169.

11. Fahrni, C. J., Allylic oxidation catalyzed by chiral dinuclear copper complexes. *Tetrahedron* **1998,** *54* (21), 5465-5470.

12. Sekar, G.; DattaGupta, A.; Singh, V. K., Asymmetric kharasch reaction: Catalytic enantioselective allylic oxidation of olefins using chiral pyridine bis(diphenyloxazoline) copper complexes and tert-butyl perbenzoate. *J. Org. Chem.* **1998,** *63* (9), 2961-2967.

13. Miyafuji, A.; Katsuki, T., Asymmetric desymmetrization of meso-tetrahydrofuran derivatives by highly enantiotopic selective C-H oxidation. *Tetrahedron* **1998,** *54* (35), 10339-10348.

14. Anada, M.; Watanabe, N.; Hashimoto, S., Highly enantioselective construction of the key azetidin-2-ones for the synthesis of carbapenem antibiotics via intramolecular C-H insertion reactions of alpha-methoxycarbonyl-alpha-diazoacetamides catalysed by chiral dirhodium(II) carboxylates. *Chem. Commun.* **1998,** (15), 1517-1518.

15. Davies, H. M. L.; Hansen, T.; Hopper, D. W.; Panaro, S. A., Highly regio-, diastereo-, and enantioselective C-H insertions of methyl aryldiazoacetates into cyclic N-BOC-protected amines. Asymmetric synthesis of novel C-2-symmetric amines and threo-methylphenidate. *J. Am. Chem. Soc.* **1999,** *121* (27), 6509-6510.

16. Andrus, M. B.; Asgari, D., Asymmetric allylic oxidation with biarylbisoxazoline-copper(I) catalysis. *Tetrahedron* **2000,** *56* (32), 5775-5780.

17. Malkov, A. V.; Bella, M.; Langer, V.; Kocovsky, P., PINDY: A novel, pinene-derived bipyridine ligand and its application in asymmetric, copper(I)-catalyzed allylic oxidation. *Org. Lett.* **2000,** *2* (20), 3047-3049.

18. Davies, H. M. L.; Hansen, T.; Churchill, M. R., Catalytic asymmetric C-H activation of alkanes and tetrahydrofuran. *J. Am. Chem. Soc.* **2000,** *122* (13), 3063-3070.

19. Eames, J.; Watkinson, M., Catalytic allylic oxidation of alkenes using an asymmetric Kharasch-Sosnovsky reaction. *Angew. Chem.-Int. Edit.* **2001,** *40* (19), 3567-+.

20. Davies, H. M. L.; Ren, P. D., Catalytic asymmetric C-H activation of silyl enol ethers as an equivalent of an asymmetric Michael reaction. *J. Am. Chem. Soc.* **2001,** *123* (9), 2070-2071.

21. Andrus, M. B.; Zhou, Z. N., Highly enantioselective copper-bisoxazoline-catalyzed allylic oxidation of cyclic olefins with tert-butyl p-nitroperbenzoate. *J. Am. Chem. Soc.* **2002,** *124* (30), 8806-8807.

22. Chelucci, G.; Loriga, G.; Murineddu, G.; Pinna, G. A., Synthesis and application in asymmetric copper(I)-catalyzed allylic oxidation of a new chiral 1,10-phenanthroline derived from pinene. *Tetrahedron Letters* **2002,** *43* (19), 3601-3604.

23. Zhang, X. M.; Qu, Z. H.; Ma, Z. H.; Shi, W. F.; Jin, X. L.; Wang, J. B., Catalytic asymmetric 2,3 -sigmatropic rearrangement of sulfur ylides generated from copper(I) carbenoids and allyl sulfides. *J. Org. Chem.* **2002,** *67* (16), 5621-5625.

24. Davies, H. M. L.; Venkataramani, C., Catalytic enantioselective synthesis of beta(2)-amino acids. *Angew. Chem.-Int. Edit.* **2002,** *41* (12), 2197-2199.

25. Saito, H.; Oishi, H.; Kitagaki, S.; Nakamura, S.; Anada, M.; Hashimoto, S., Enantio- and diastereoselective synthesis of cis-2-aryl-3-methoxycarbonyl-2,3-dihydrobenzofurans via the Rh(II)-catalyzed C-H insertion process. *Org. Lett.* **2002,** *4* (22), 3887-3890.

26. Davies, H. M. L.; Beckwith, R. E. J.; Antoulinakis, E. G.; Jin, Q. H., New strategic reactions for organic synthesis: Catalytic asymmetric C-H activation alpha to oxygen as a surrogate to the aldol reaction. *J. Org. Chem.* **2003,** *68* (16), 6126-6132.

27. Davies, H. M. L.; Venkataramani, C.; Hansen, T.; Hopper, D. W., New strategic reactions for organic synthesis: Catalytic asymmetric C-H activation alpha to nitrogen as a surrogate for the Mannich reaction. *J. Am. Chem. Soc.* **2003,** *125* (21), 6462-6468.

28. Davies, H. M. L.; Walji, A. M., Asymmetric intermolecular C-H activation, using immobilized dirhodium tetrakis((S)-N-(dodecylbenzenesulfonyl)-prolinate) as a recoverable catalyst. *Org. Lett.* **2003,** *5* (4), 479-482.

29. Davies, H. M. L.; Beckwith, R. E. J., Catalytic enantioselective C-H activation by means of metal-carbenoid-induced C-H insertion. *Chemical Reviews* **2003,** *103* (8), 2861-2903.

30. Davies, H. M. L.; Jin, Q. H., Double C-H activation strategy for the asymmetric synthesis of C-2-Symmetric anilines. *Org. Lett.* **2004,** *6* (11), 1769-1772.

31. Davies, H. M. L.; Jin, Q. H., Highly diastereoselective and enantioselective C-H functionalization of 1,2-dihydronaphthalenes: A combined C-H activation/cope rearrangement followed by a retro-cope rearrangement. *J. Am. Chem. Soc.* **2004,** *126* (35), 10862-10863.

32. Davis, F. A.; Wu, Y. Z.; Xu, H.; Zhang, J. Y., Asymmetric synthesis of cis-5-substituted pyrrolidine 2-phosphonates using metal carbenoid NH insertion and beta-amino beta-ketophosphonates. *Org. Lett.* **2004,** *6* (24), 4523-4525.

33. Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J., Expanding the scope of C-H amination through catalyst design. *J. Am. Chem. Soc.* **2004,** *126* (47), 15378-15379.

34. Davies, H. M. L.; Hedley, S. J.; Bohall, B. R., Asymmetric intermolecular C-H functionalization of benzyl silyl ethers mediated by chiral auxiliary-based aryldiazoacetates and chiral dirhodium catalysts. *J. Org. Chem.* **2005,** *70* (26), 10737-10742.

35. Davies, H. M. L.; Jin, Q. H., Enantioselective double C-H activation of dihydronaphthalenes. *Org. Lett.* **2005,** *7* (12), 2293-2296.

36. Davies, H. M. L.; Walji, A. M., Direct synthesis of (+)-erogorgiaene through a kinetic enantiodifferentiating step. *Angew. Chem.-Int. Edit.* **2005,** *44* (11), 1733-1735.

37. Maier, T. C.; Fu, G. C., Catalytic enantioselective O-H insertion reactions. *J. Am. Chem. Soc.* **2006,** *128* (14), 4594-4595.

38. Davies, H. M. L., Recent advances in catalytic enantioselective intermolecular C-H functionalization. *Angew. Chem.-Int. Edit.* **2006,** *45* (39), 6422-6425.

39. Davies, H. M. L.; Dal, X.; Long, M. S., Combined C-H activation/cope rearrangement as a strategic reaction in organic synthesis: Total synthesis of (-)-colombiasin A and (-)-elisapterosin B. *J. Am. Chem. Soc.* **2006,** *128* (7), 2485-2490.

40. Son, S.; Fu, G. C., Copper-catalyzed asymmetric [4+1] cycloadditions of enones with diazo compounds to form dihydrofurans. *J. Am. Chem. Soc.* **2007,** *129* (5), 1046-1047.

41. Li, C. Y.; Wang, X. B.; Sun, X. L.; Tang, Y.; Zheng, J. C.; Xu, Z. H.; Zhou, Y. G.; Dai, L. X., Iron porphyrin-catalyzed olefination of ketenes with diazoacetate for the enantioselective synthesis of allenes. *J. Am. Chem. Soc.* **2007,** *129* (6), 1494-+.

42. Reddy, R. P.; Davies, H. M. L., Asymmetric synthesis of tropanes by rhodium-catalyzed [4+3] cycloaddition. *J. Am. Chem. Soc.* **2007,** *129* (34), 10312-+.

43. Liu, B.; Zhu, S. F.; Zhang, W.; Chen, C.; Zhou, Q. L., Highly enantioselective insertion of carbenoids into N-H bonds catalyzed by copper complexes of chiral spiro bisoxazolines. *J. Am. Chem. Soc.* **2007,** *129* (18), 5834-+.

44. Nechab, M.; Kumar, D. N.; Philouze, C.; Einhorn, C.; Einhorn, J., Variable C-2-symmetric analogues of N-hydroxyphthalimide as enantioselective catalysts for aerobic oxidation: Kinetic resolution of oxazolidines. *Angew. Chem.-Int. Edit.* **2007,** *46* (17), 3080-3083.

45. Chen, C.; Zhu, S. F.; Liu, B.; Wang, L. X.; Zhou, Q. L., Highly enantioselective insertion of carbenoids into o-h bonds of phenols: An efficient approach to chiral alpha-aryloxycarboxylic esters. *J. Am. Chem. Soc.* **2007,** *129* (42), 12616-+.

46. Davies, H. M. L.; Manning, J. R., Catalytic C-H functionalization by metal carbenoid and nitrenoid insertion. *Nature* **2008,** *451* (7177), 417-424.

47. Liang, C. G.; Collet, F.; Robert-Peillard, F.; Muller, P.; Dodd, R. H.; Dauban, P., Toward a synthetically useful stereoselective C-H amination of hydrocarbons. *J. Am. Chem. Soc.* **2008,** *130* (1), 343-350.

48. Zhu, S. T.; Chen, C.; Cai, Y.; Zhou, Q. L., Catalytic asymmetric reaction with water: Enantioselective synthesis of alpha-Hydroxyesters by a copper-carbenoid O-H insertion reaction. *Angew. Chem.-Int. Edit.* **2008,** *47* (5), 932-934.

49. Zalatan, D. N.; Du Bois, J., A chiral rhodium carboxamidate catalyst for enantioselective C-H amination. *J. Am. Chem. Soc.* **2008,** *130* (29), 9220-+.

50. Milczek, E.; Boudet, N.; Blakey, S., Enantioselective C-H amination using cationic ruthenium(II)-pybox catalysts. *Angew. Chem.-Int. Edit.* **2008,** *47* (36), 6825-6828.

51. Zhang, Y. Z.; Zhu, S. F.; Wang, L. X.; Zhou, Q. L., Copper-Catalyzed Highly Enantioselective Carbenoid Insertion into Si-H Bonds. *Angew. Chem.-Int. Edit.* **2008,** *47* (44), 8496-8498.

52. Thu, H. Y.; Tong, G. S. M.; Huang, J. S.; Chan, S. L. F.; Deng, Q. H.; Che, C. M., Highly Selective Metal Catalysts for Intermolecular Carbenoid Insertion into Primary C-H Bonds and Enantioselective C-C Bond Formation. *Angew. Chem.-Int. Edit.* **2008,** *47* (50), 9747-9751.

53. Liang, C. G.; Collet, F.; Robert-Peillard, F.; Muller, P.; Dodd, R. H.; Dauban, P., Toward a synthetically useful stereoselective C-H amination of hydrocarbons. *J. Am. Chem. Soc.* **2008,** *130* (1), 343-350.

54. Alamsetti, S. K.; Mannam, S.; Mutupandi, P.; Sekar, G., Galactose Oxidase Model: Biomimetic Enantiomer-Differentiating Oxidation of Alcohols by a Chiral Copper Complex. *Chemistry-a European Journal* **2009,** *15* (5), 1086-1090.

55. Suematsu, H.; Katsuki, T., Iridium(III) Catalyzed Diastereo- and Enantioselective C-H Bond Functionalization. *J. Am. Chem. Soc.* **2009,** *131* (40), 14218-+.

56. Guan, X. Y.; Yang, L. P.; Hu, W. H., Cooperative Catalysis in Multicomponent Reactions: Highly Enantioselective Synthesis of gamma-Hydroxyketones with a Quaternary Carbon Stereocenter. *Angew. Chem.-Int. Edit.* **2010,** *49* (12), 2190-2192.

57. Weickgenannt, A.; Mewald, M.; Muesmann, T. W. T.; Oestreich, M., Catalytic Asymmetric Si-O Coupling of Simple Achiral Silanes and Chiral Donor-Functionalized Alcohols. *Angew. Chem.-Int. Edit.* **2010,** *49* (12), 2223-2226.

58. Flynn, C. J.; Elcoate, C. J.; Lawrence, S. E.; Maguire, A. R., Highly Enantioselective Intramolecular Copper Catalyzed C-H Insertion Reactions of alpha-Diazosulfones. *J. Am. Chem. Soc.* **2010,** *132* (4), 1184-+.

59. Zhu, S. F.; Cai, Y.; Mao, H. X.; Xie, J. H.; Zhou, Q. L., Enantioselective iron-catalysed O-H bond insertions. *Nat. Chem.* **2010,** *2* (7), 546-551.

60. Hou, Z. R.; Wang, J.; He, P.; Qin, B.; Liu, X. H.; Lin, L. L.; Feng, X. M., Highly Enantioselective Insertion of Carbenoids into N-H Bonds Catalyzed by Copper(I) Complexes of Binol Derivatives. *Angew. Chem.-Int. Edit.* **2010,** *49* (28), 4763-4766.

61. Slattery, C. N.; Ford, A.; Maguire, A. R., Catalytic asymmetric C-H insertion reactions of alpha-diazocarbonyl compounds. *Tetrahedron* **2010,** *66* (34), 6681-6705.

62. Zhu, S. F.; Song, X. G.; Li, Y.; Cai, Y.; Zhou, Q. L., Enantioselective Copper-Catalyzed Intramolecular O-H Insertion: An Efficient Approach to Chiral 2-Carboxy Cyclic Ethers. *J. Am. Chem. Soc.* **2010,** *132* (46), 16374-16376.

63. DeAngelis, A.; Shurtleff, V. W.; Dmitrenko, O.; Fox, J. M., Rhodium(II)-Catalyzed Enantioselective C-H Functionalization of Indoles. *J. Am. Chem. Soc.* **2011,** *133* (6), 1650-1653.

64. Hansen, J. H.; Gregg, T. M.; Ovalles, S. R.; Lian, Y. J.; Autschbach, J.; Davies, H. M. L., On the Mechanism and Selectivity of the Combined C-H Activation/Cope Rearrangement. *J. Am. Chem. Soc.* **2011,** *133* (13), 5076-5085.

65. Wu, J.; Becerril, J.; Lian, Y. J.; Davies, H. M. L.; Porco, J. A.; Panek, J. S., Sequential Transformations to Access Polycyclic Chemotypes: Asymmetric Crotylation and Metal Carbenoid Reactions. *Angew. Chem.-Int. Edit.* **2011,** *50* (26), 5938-5942.

66. Chuprakov, S.; Malik, J. A.; Zibinsky, M.; Fokin, V. V., Catalytic Asymmetric C-H Insertions of Rhodium(II) Azavinyl Carbenes. *J. Am. Chem. Soc.* **2011,** *133* (27), 10352-10355.

67. Lian, Y. J.; Davies, H. M. L., Combined C-H Functionalization/Cope Rearrangement with Vinyl Ethers as a Surrogate for the Vinylogous Mukaiyama Aldol Reaction. *J. Am. Chem. Soc.* **2011,** *133* (31), 11940-11943.

68. Lian, Y. J.; Hardcastle, K. I.; Davies, H. M. L., Computationally Guided Stereocontrol of the Combined C-H Functionalization/Cope Rearrangement. *Angew. Chem.-Int. Edit.* **2011,** *50* (40), 9370-9373.

69. Zhu, S. F.; Xu, B.; Wang, G. P.; Zhou, Q. L., Well-Defined Binuclear Chiral Spiro Copper Catalysts for Enantioselective N-H Insertion. *J. Am. Chem. Soc.* **2012,** *134* (1), 436-442.

70. Nishioka, Y.; Uchida, T.; Katsuki, T., Enantio- and Regioselective Intermolecular Benzylic and Allylic C-H Bond Amination. *Angew. Chem.-Int. Edit.* **2013,** *52* (6), 1739-1742.

71. Song, X. G.; Zhu, S. F.; Xie, X. L.; Zhou, Q. L., Enantioselective Copper-Catalyzed Intramolecular Phenolic O-H Bond Insertion: Synthesis of Chiral 2-Carboxy Dihydrobenzofurans, Dihydrobenzopyrans, and Tetrahydrobenzooxepines. *Angew. Chem.-Int. Edit.* **2013,** *52* (9), 2555-2558.

72. Wang, H. B.; Li, G.; Engle, K. M.; Yu, J. Q.; Dayies, H. M. L., Sequential C-H Functionalization Reactions for the Enantioselective Synthesis of Highly Functionalized 2,3-Dihydrobenzofurans. *J. Am. Chem. Soc.* **2013,** *135* (18), 6774-6777.

73. Cheng, Q. Q.; Zhu, S. F.; Zhang, Y. Z.; Xie, X. L.; Zhou, Q. L., Copper-Catalyzed B-H Bond Insertion Reaction: A Highly Efficient and Enantioselective C-B Bond-Forming Reaction with Amine-Borane and Phosphine-Borane Adducts. *J. Am. Chem. Soc.* **2013,** *135* (38), 14094-14097.

74. Ma, X.; Jiang, J.; Lv, S.; Yao, W.; Yang, Y.; Liu, S.; Xia, F.; Hu, W., An Ylide Transformation of Rhodium(I) Carbene: Enantioselective Three-Component Reaction through Trapping of Rhodium(I)-Associated Ammonium Ylides by beta-Nitroacrylates. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13136-13139.

75. Reddy, A. R.; Zhou, C.-Y.; Guo, Z.; Wei, J.; Che, C.-M., Ruthenium-Porphyrin-Catalyzed Diastereoselective Intramolecular Alkyl Carbene Insertion into C-H Bonds of Alkyl Diazomethanes Generated In Situ from N-Tosylhydrazones. *Angew. Chem.-Int. Edit.* **2014,** *53* (51), 14175-14180.

76. Soldi, C.; Lamb, K. N.; Squitieri, R. A.; Gonzalez-Lopez, M.; Di Maso, M. J.; Shaw, J. T., Enantioselective Intramolecular C-H Insertion Reactions of Donor Donor Metal Carbenoids. *J. Am. Chem. Soc.* **2014,** *136* (43), 15142-15145.

77. Guptill, D. M.; Davies, H. M. L., 2,2,2-Trichloroethyl Aryldiazoacetates as Robust Reagents for the Enantioselective C-H Functionalization of Methyl Ethers. *J. Am. Chem. Soc.* **2014,** *136* (51), 17718-17721.

78. Xu, X.; Deng, Y.; Yim, D. N.; Zavalij, P. Y.; Doyle, M. P., Enantioselective cis-beta-lactam synthesis by intramolecular C-H functionalization from enoldiazoacetamides and derivative donor-acceptor cyclopropenes. *Chem. Sci.* **2015,** *6* (4), 2196-2201.

79. Chen, D.; Zhang, X.; Qi, W. Y.; Xu, B.; Xu, M. H., Rhodium(I)-Catalyzed Asymmetric Carbene Insertion into B-H Bonds: Highly Enantioselective Access to Functionalized Organoboranes. *J. Am. Chem. Soc.* **2015,** *137* (16), 5268-5271.

80. Tang, Y.; Chen, Q. G.; Liu, X. H.; Wang, G.; Lin, L. L.; Feng, X. M., Direct Synthesis of Chiral Allenoates from the Asymmetric C-H Insertion of alpha-Diazoesters into Terminal Alkynes. *Angew. Chem.-Int. Edit.* **2015,** *54* (33), 9512-9516.

81. Gao, X.; Wu, B.; Huang, W. X.; Chen, M. W.; Zhou, Y. G., Enantioselective Palladium-Catalyzed C-H Functionalization of Indoles Using an Axially Chiral 2,2 '-Bipyridine Ligand. *Angew. Chem.-Int. Edit.* **2015,** *54* (41), 11956-11960.

82. Weldy, N. M.; Schafer, A. G.; Owens, C. P.; Herting, C. J.; Varela-Alvarez, A.; Chen, S.; Niemeyer, Z.; Musaev, D. G.; Sigman, M. S.; Davies, H. M. L.; Blakey, S. B., Iridium(III)-bis(imidazolinyl)phenyl catalysts for enantioselective C-H functionalization with ethyl diazoacetate. *Chem. Sci.* **2016,** *7* (5), 3142-3146.

83. Tokumasu, K.; Yazaki, R.; Ohshima, T., Direct Catalytic Chemoselective alpha-Amination of Acylpyrazoles: A Concise Route to Unnatural alpha-Amino Acid Derivatives. *J. Am. Chem. Soc.* **2016,** *138* (8), 2664-2669.

84. Zhu, D.; Ma, J.; Luo, K.; Fu, H. G.; Zhang, L.; Zhu, S. F., Enantioselective Intramolecular C-H Insertion of Donor and Donor/Donor Carbenes by a Nondiazo Approach. *Angew. Chem.-Int. Edit.* **2016,** *55* (29), 8452-8456.

85. Gray, E. E.; Nielsen, M. K.; Choquette, K. A.; Kalow, J. A.; Graham, T. J. A.; Doyle, A. G., Nucleophilic (Radio)Fluorination of alpha-Diazocarbonyl Compounds Enabled by Copper-Catalyzed H-F Insertion. *J. Am. Chem. Soc.* **2016,** *138* (34), 10802-10805.

86. Poh, J. S.; Makai, S.; von Keutz, T.; Tran, D. N.; Battilocchio, C.; Pasau, P.; Ley, S. V., Rapid Asymmetric Synthesis of Disubstituted Allenes by Coupling of Flow-Generated Diazo Compounds and Propargylated Amines. *Angew. Chem.-Int. Edit.* **2017,** *56* (7), 1864-1868.

87. Milan, M.; Bietti, M.; Costas, M., Highly Enantioselective Oxidation of Nonactivated Aliphatic C-H Bonds with Hydrogen Peroxide Catalyzed by Manganese Complexes. *Acs Central Science* **2017,** *3* (3), 196-204.

88. Zhao, F.; Li, N.; Zhang, T.; Han, Z. Y.; Luo, S. W.; Gong, L. Z., Enantioselective Aza-Ene-type Reactions of Enamides with Gold Carbenes Generated from alpha-Diazoesters. *Angew. Chem.-Int. Edit.* **2017,** *56* (12), 3247-3251.

89. Yang, J. M.; Li, Z. Q.; Li, M. L.; He, Q.; Zhu, S. F.; Zhou, Q. L., Catalytic B-H Bond Insertion Reactions Using Alkynes as Carbene Precursors. *J. Am. Chem. Soc.* **2017,** *139* (10), 3784-3789.

90. Kang, K. T.; Kim, S. T.; Hwang, G. S.; Ryu, D. H., Catalytic Enantioselective Protonation/Nucleophilic Addition of Diazoesters with Chiral Oxazaborolidinium Ion Activated Carboxylic Acids. *Angew. Chem.-Int. Edit.* **2017,** *56* (14), 3977-3981.

91. Arredondo, V.; Hiew, S. C.; Gutman, E. S.; Premachandra, I.; Van Vranken, D. L., Enantioselective Palladium-Catalyzed Carbene Insertion into the N-H Bonds of Aromatic Heterocycles. *Angew. Chem.-Int. Edit.* **2017,** *56* (15), 4156-4159.

92. Liu, S. Y.; Jiang, J.; Chen, J. H.; Wei, Q. H.; Yao, W. F.; Xia, F.; Hu, W. H., A DFT calculation-inspired Rh(I)-catalyzed reaction via suppression of alpha-H shift in alpha-alkyldiazoacetates. *Chem. Sci.* **2017,** *8* (6), 4312-4317.

93. Hari, D. P.; Waser, J., Enantioselective Copper-Catalyzed Oxy-Alkynylation of Diazo Compounds. *J. Am. Chem. Soc.* **2017,** *139* (25), 8420-8423.

94. Qu, B.; Xu, D. Q.; Sun, Q. S.; Miao, C. X.; Lee, Y. M.; Li, X. X.; Nam, W.; Sun, W., Highly Enantioselective Oxidation of Spirocyclic Hydrocarbons by Bioinspired Manganese Catalysts and Hydrogen Peroxide. *Acs Catalysis* **2018,** *8* (3), 2479-2487.

95. Wen, X.; Wang, Y.; Zhang, X. P., Enantioselective radical process for synthesis of chiral indolines by metalloradical alkylation of diverse C(sp(3))-H bonds. *Chem. Sci.* **2018,** *9* (22), 5082-5086.

96. Liao, K. B.; Yang, Y. F.; Lie, Y. Z.; Sanders, J. N.; Houk, K. N.; Musaev, D. G.; Davies, H. M. L., Design of catalysts for site-selective and enantioselective functionalization of non-activated primary C-H bonds. *Nat. Chem.* **2018,** *10* (10), 1048-1055.

97. Pang, Y.; He, Q.; Li, Z. Q.; Yang, J. M.; Yu, J. H.; Zhu, S. F.; Zhou, Q. L., Rhodium-Catalyzed B-H Bond Insertion Reactions of Unstabilized Diazo Compounds Generated in Situ from Tosylhydrazones. *J. Am. Chem. Soc.* **2018,** *140* (34), 10663-10668.

98. Souza, L. W.; Squitieri, R. A.; Dimirjian, C. A.; Hodur, B. M.; Nickerson, L. A.; Penrod, C. N.; Cordova, J.; Fettinger, J. C.; Shaw, J. T., Enantioselective Synthesis of Indolines, Benzodihydrothiophenes, and Indanes by C-H Insertion of Donor/Donor Carbenes. *Angew. Chem.-Int. Edit.* **2018,** *57* (46), 15213-15216.

99. Li, C. Q.; Lang, K.; Lu, H. J.; Hu, Y.; Cui, X.; Wojtas, L.; Zhang, X. P., Catalytic Radical Process for Enantioselective Amination of C(sp(3))-H Bonds. *Angew. Chem.-Int. Edit.* **2018,** *57* (51), 16837-16841.

100. Xu, G. Y.; Chen, P.; Liu, P.; Tang, S. B.; Zhang, X. H.; Sun, J. T., Access to N-Substituted 2-Pyridones by Catalytic Intermolecular Dearomatization and 1,4-Acyl Transfer. *Angew. Chem.-Int. Edit.* **2019,** *58* (7), 1980-1984.

101. Qin, J.; Zhou, Z. J.; Cui, T. J.; Hemming, M.; Meggers, E., Enantioselective intramolecular C-H amination of aliphatic azides by dual ruthenium and phosphine catalysis. *Chem. Sci.* **2019,** *10* (11), 3202-3207.

102. Nasrallah, A.; Boquet, V.; Hecker, A.; Retailleau, P.; Darses, B.; Dauban, P., Catalytic Enantioselective Intermolecular Benzylic C(sp(3))-H Amination. *Angew. Chem.-Int. Edit.* **2019,** *58* (24), 8192-8196.

103. Liang, X. S.; Li, R. D.; Wang, X. C., Copper-Catalyzed Asymmetric Annulation Reactions of Carbenes with 2-Iminyl- or 2-Acyl-Substituted Phenols: Convenient Access to Enantioenriched 2,3-Dihydrobenzofurans. *Angew. Chem.-Int. Edit.* **2019,** *58* (39), 13885-13889.

104. Yang, J.; Ruan, P. R.; Yang, W.; Feng, X. M.; Liu, X. H., Enantioselective carbene insertion into the N-H bond of benzophenone imine. *Chem. Sci.* **2019,** *10* (44), 10305-10309.

105. Carreras, V.; Besnard, C.; Gandon, V.; Ollevier, T., Asymmetric Cu-I-Catalyzed Insertion Reaction of 1-Aryl-2,2,2-trifluoro-1-diazoethanes into Si-H Bonds. *Org. Lett.* **2019,** *21* (22), 9094-9098.

106. Zhou, Z. J.; Chen, S. M.; Hong, Y. B.; Winterling, E.; Tan, Y. Q.; Hemming, M.; Harms, K.; Houk, K. N.; Meggers, E., Non-C-2-Symmetric Chiral-at-Ruthenium Catalyst for Highly Efficient Enantioselective Intramolecular C(sp(3))-H Amidation. *J. Am. Chem. Soc.* **2019,** *141* (48), 19048-19057.

107. Wang, H.-X.; Richard, Y.; Wan, Q.; Zhou, C.-Y.; Che, C.-M., Iridium(III)-Catalyzed Intermolecular C(sp3)−H Insertion Reaction of Quinoid Carbene: A Radical Mechanism. *Angewandte Chemie International Edition* **2020,** *59* (5), 1845-1850.

108. Kong, L.; Han, X.; Liu, S.; Zou, Y.; Lan, Y.; Li, X., Rhodium(III)-Catalyzed Asymmetric Access to Spirocycles through C−H Activation and Axial-to-Central Chirality Transfer. *Angewandte Chemie International Edition* **2020,** *59* (18), 7188-7192.

109. Yang, L.-L.; Evans, D.; Xu, B.; Li, W.-T.; Li, M.-L.; Zhu, S.-F.; Houk, K. N.; Zhou, Q.-L., Enantioselective Diarylcarbene Insertion into Si–H Bonds Induced by Electronic Properties of the Carbenes. *J. Am. Chem. Soc.* **2020,** *142* (28), 12394-12399.

110. Ju, M.; Zerull, E. E.; Roberts, J. M.; Huang, M.; Guzei, I. A.; Schomaker, J. M., Silver-Catalyzed Enantioselective Propargylic C–H Bond Amination through Rational Ligand Design. *J. Am. Chem. Soc.* **2020,** *142* (30), 12930-12936.

111. Sun, S.; Yang, Y.; Zhao, R.; Zhang, D.; Liu, L., Site- and Enantiodifferentiating C(sp3)–H Oxidation Enables Asymmetric Access to Structurally and Stereochemically Diverse Saturated Cyclic Ethers. *J. Am. Chem. Soc.* **2020,** *142* (45), 19346-19353.

112. Jin, L.-M.; Xu, P.; Xie, J.; Zhang, X. P., Enantioselective Intermolecular Radical C–H Amination. *J. Am. Chem. Soc.* **2020,** *142* (49), 20828-20836.

113. Lang, K.; Li, C.; Kim, I.; Zhang, X. P., Enantioconvergent Amination of Racemic Tertiary C–H Bonds. *J. Am. Chem. Soc.* **2020,** *142* (49), 20902-20911.

114. Liu, B.; Xie, P.; Zhao, J.; Wang, J.; Wang, M.; Jiang, Y.; Chang, J.; Li, X., Rhodium-Catalyzed Enantioselective Synthesis of β-Amino Alcohols via Desymmetrization of gem-Dimethyl Groups. *Angewandte Chemie International Edition* **2021,** *60* (15), 8396-8400.

115. Dong, Y.; Lund, C. J.; Porter, G. J.; Clarke, R. M.; Zheng, S.-L.; Cundari, T. R.; Betley, T. A., Enantioselective C–H Amination Catalyzed by Nickel Iminyl Complexes Supported by Anionic Bisoxazoline (BOX) Ligands. *J. Am. Chem. Soc.* **2021,** *143* (2), 817-829.

116. Zhu, D.-X.; Xia, H.; Liu, J.-G.; Chung, L. W.; Xu, M.-H., Regiospecific and Enantioselective Arylvinylcarbene Insertion of a C–H Bond of Aniline Derivatives Enabled by a Rh(I)-Diene Catalyst. *J. Am. Chem. Soc.* **2021,** *143* (6), 2608-2619.

117. Lee, E.; Hwang, Y.; Kim, Y. B.; Kim, D.; Chang, S., Enantioselective Access to Spirolactams via Nitrenoid Transfer Enabled by Enhanced Noncovalent Interactions. *J. Am. Chem. Soc.* **2021,** *143* (17), 6363-6369.

118. Ankudinov, N. M.; Chusov, D. A.; Nelyubina, Y. V.; Perekalin, D. S., Synthesis of Rhodium Complexes with Chiral Diene Ligands via Diastereoselective Coordination and Their Application in the Asymmetric Insertion of Diazo Compounds into E−H Bonds. *Angewandte Chemie International Edition* **2021,** *60* (34), 18712-18720.

119. Zhu, D.-X.; Liu, J.-G.; Xu, M.-H., Stereodivergent Synthesis of Enantioenriched 2,3-Disubstituted Dihydrobenzofurans via a One-Pot C–H Functionalization/Oxa-Michael Addition Cascade. *J. Am. Chem. Soc.* **2021,** *143* (23), 8583-8589.

120. Yang, W.; Pu, M.; Lin, X.; Chen, M.; Song, Y.; Liu, X.; Wu, Y.-D.; Feng, X., Enantioselective Formal Vinylogous N–H Insertion of Secondary Aliphatic Amines Catalyzed by a High-Spin Cobalt(II) Complex. *J. Am. Chem. Soc.* **2021,** *143* (25), 9648-9656.

121. Wei, B.; Hatridge, T. A.; Jones, C. W.; Davies, H. M. L., Copper(II) Acetate-Induced Oxidation of Hydrazones to Diazo Compounds under Flow Conditions Followed by Dirhodium-Catalyzed Enantioselective Cyclopropanation Reactions. *Org. Lett.* **2021,** *23* (14), 5363-5367.

122. Xie, J.; Xu, P.; Zhu, Y.; Wang, J.; Lee, W.-C. C.; Zhang, X. P., New Catalytic Radical Process Involving 1,4-Hydrogen Atom Abstraction: Asymmetric Construction of Cyclobutanones. *J. Am. Chem. Soc.* **2021,** *143* (30), 11670-11678.

123. Lazib, Y.; Retailleau, P.; Saget, T.; Darses, B.; Dauban, P., Asymmetric Synthesis of Enantiopure Pyrrolidines by C(sp3)−H Amination of Hydrocarbons. *Angewandte Chemie International Edition* **2021,** *60* (40), 21708-21712.

124. Li, Z.; Chen, Y.; Wang, C.; Xu, G.; Shao, Y.; Zhang, X.; Tang, S.; Sun, J., Construction of C−C Axial Chirality via Asymmetric Carbene Insertion into Arene C−H Bonds. *Angewandte Chemie International Edition* **2021,** *60* (49), 25714-25718.

125. Fanourakis, A.; Williams, B. D.; Paterson, K. J.; Phipps, R. J., Enantioselective Intermolecular C–H Amination Directed by a Chiral Cation. *J. Am. Chem. Soc.* **2021,** *143* (27), 10070-10076.

126. Huang, M.-Y.; Zhao, Y.-T.; Zhang, C.-D.; Zhu, S.-F., Highly Regio-, Stereo-, and Enantioselective Copper-Catalyzed B−H Bond Insertion of α-Silylcarbenes: Efficient Access to Chiral Allylic gem-Silylboranes. *Angewandte Chemie International Edition* **2022,** *61* (26), e202203343.

127. Nie, X.; Ye, C.-X.; Ivlev, S. I.; Meggers, E., Nitrene-Mediated C−H Oxygenation: Catalytic Enantioselective Formation of Five-Membered Cyclic Organic Carbonates. *Angewandte Chemie International Edition* **2022,** *61* (48), e202211971.

128. Wu, K.; Zhang, X.; Wu, L.-L.; Huang, J.-S.; Che, C.-M., A Convergent, Modular Approach to Trifluoromethyl-Bearing 5-Membered Rings via Catalytic C(sp3)−H Activation. *Angewandte Chemie International Edition* **2023,** *62* (9), e202215891.

129. Xu, P.; Xie, J.; Wang, D.-S.; Zhang, X. P., Metalloradical approach for concurrent control in intermolecular radical allylic C−H amination. *Nat. Chem.* **2023,** *15* (4), 498-507.

130. Naeem, Y.; Matsuo, B. T.; Davies, H. M. L., Enantioselective Intermolecular C–H Functionalization of Primary Benzylic C–H Bonds Using ((Aryl)(diazo)methyl)phosphonates. *ACS Catalysis* **2024,** *14* (1), 124-130.

131. Paterson, K. J.; Dahiya, A.; Williams, B. D.; Phipps, R. J., Tertiary Amides as Directing Groups for Enantioselective C−H Amination using Ion-Paired Rhodium Complexes. *Angewandte Chemie International Edition* **2024,** *63* (14), e202317489.

132. Nguyen, T.-T. H.; Bosse, A. T.; Ly, D.; Suarez, C. A.; Fu, J.; Shimabukuro, K.; Musaev, D. G.; Davies, H. M. L., Diaryldiazoketones as Effective Carbene Sources for Highly Selective Rh(II)-Catalyzed Intermolecular C–H Functionalization. *J. Am. Chem. Soc.* **2024,** *146* (12), 8447-8455.

133. Chen, Z.; Shimabukuro, K.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., D4-Symmetric Dirhodium Tetrakis(binaphthylphosphate) Catalysts for Enantioselective Functionalization of Unactivated C–H Bonds. *J. Am. Chem. Soc.* **2024,** *146* (28), 19460-19473.

134. Hodson, N. J.; Takano, S.; Fanourakis, A.; Phipps, R. J., Enantioselective Nitrene Transfer to Hydrocinnamyl Alcohols and Allylic Alcohols Enabled by Systematic Exploration of the Structure of Ion-Paired Rhodium Catalysts. *J. Am. Chem. Soc.* **2024,** *146* (32), 22629-22641.

135. Demirel, N.; Dawor, M.; Nadler, G.; Ivlev, S. I.; Meggers, E., Stereogenic-at-iron mesoionic carbene complex for enantioselective C–H amidation. *Chem. Sci.* **2024,** *15* (38), 15625-15631.

2.4.6 Other Reactions

1. Cogan, D. A.; Liu, G. C.; Kim, K. J.; Backes, B. J.; Ellman, J. A., Catalytic asymmetric oxidation of tert-butyl disulfide. Synthesis of tert-butanesulfinamides, tert-butyl sulfoxides, and tert-butanesulfinimines. *J. Am. Chem. Soc.* **1998,** *120* (32), 8011-8019.

2. Evans, D. A.; Johnson, D. S., Catalytic enantioselective amination of enolsilanes using C-2- symmetric copper(II) complexes as chiral Lewis acids. *Org. Lett.* **1999,** *1* (4), 595-598.

3. Yamashita, Y.; Ishitani, H.; Kobayashi, S., Silver-catalyzed asymmetric amination of silyl enol ethers. *Canadian Journal of Chemistry* **2000,** *78* (6), 666-672.

4. Momiyama, N.; Yamamoto, H., Catalytic enantioselective synthesis of alpha-aminooxy and alpha-hydroxy ketone using nitrosobenzene. *J. Am. Chem. Soc.* **2003,** *125* (20), 6038-6039.

5. Legros, J.; Bolm, C., Iron-catalyzed asymmetric sulfide oxidation with aqueous hydrogen peroxide. *Angew. Chem.-Int. Edit.* **2003,** *42* (44), 5487-5489.

6. Tamura, Y.; Uchida, T.; Katsuki, T., Highly enantioselective (OC)Ru(salen)-catalyzed sulfimidation using N-alkoxycarbonyl azide as nitrene precursor. *Tetrahedron Letters* **2003,** *44* (16), 3301-3303.

7. Uchida, T.; Tamura, Y.; Ohba, M.; Katsuki, T., Mechanism of asymmetric sulfimidation with N-alkoxycarbonyl azide in the presence of (OC)Ru(salen) complex. *Tetrahedron Letters* **2003,** *44* (43), 7965-7968.

8. Blum, S. A.; Bergman, R. G.; Ellman, J. A., Enantioselective oxidation of di-tert-butyl disulfide with a vanadium catalyst: Progress toward mechanism elucidation. *J. Org. Chem.* **2003,** *68* (1), 150-155.

9. Momiyama, N.; Yamamoto, H., Enantioselective O- and N-nitroso aldol synthesis of tin enolates. Isolation of three BINAP-silver complexes and their role in regio- and enantioselectivity. *J. Am. Chem. Soc.* **2004,** *126* (17), 5360-5361.

10. Greck, C.; Drouillat, B.; Thomassigny, C., Asymmetric electrophilic alpha-amination of carbonyl groups. *European Journal of Organic Chemistry* **2004,** (7), 1377-1385.

11. Yamamoto, Y.; Yamamoto, H., Catalytic, highly enantio, and diastereoselective nitroso Diels-Alder reaction. *J. Am. Chem. Soc.* **2004,** *126* (13), 4128-4129.

12. Peltier, H. M.; Evans, J. W.; Ellman, J. A., Catalytic enantioselective sulfinyl transfer using cinchona alkaloid catalysts. *Org. Lett.* **2005,** *7* (9), 1733-1736.

13. Balcells, D.; Maseras, F.; Ujaque, G., Computational rationalization of the dependence of the enantioselectivity on the nature of the catalyst in the vanadium-catalyzed oxidation of sulfides by hydrogen peroxide. *J. Am. Chem. Soc.* **2005,** *127* (10), 3624-3634.

14. Schoumacker, S.; Hamelin, O.; Teti, S.; Pecaut, J.; Fontecave, M., Activation of oxaziridines by Lewis acids: Application in enantioselective sulfoxidation. *J. Org. Chem.* **2005,** *70* (1), 301-308.

15. Azoulay, S.; Manabe, K.; Kobayashi, S., Catalytic asymmetric ring opening of meso-epoxides with aromatic amines in water. *Org. Lett.* **2005,** *7* (21), 4593-4595.

16. Momiyama, N.; Yamamoto, H., Bronsted acid catalysis of achiral enamine for regio- and enantioselective nitroso aldol synthesis. *J. Am. Chem. Soc.* **2005,** *127* (4), 1080-1081.

17. Yamamoto, Y.; Yamamoto, H., Catalytic asymmetric nitroso-Diels-Alder reaction with acyclic dienes. *Angew. Chem.-Int. Edit.* **2005,** *44* (43), 7082-7085.

18. Matsubara, R.; Kobayashi, S., Catalytic asymmetric amination of enecarbamates. *Angew. Chem.-Int. Edit.* **2006,** *45* (47), 7993-7995.

19. Egami, H.; Katsuki, T., Fe(salan)-catalyzed asymmetric oxidation of sulfides with hydrogen peroxide in water. *J. Am. Chem. Soc.* **2007,** *129* (29), 8940-+.

20. Gansauer, A.; Fan, C. A.; Keller, F.; Keil, J., Titanocene-catalyzed regiodivergent epoxide openings. *J. Am. Chem. Soc.* **2007,** *129* (12), 3484-+.

21. Jana, C. K.; Studer, A., Divergent reactions for racemates: Catalytic, enantioselective, and regiodivergent nitroso diels-alder reactions. *Angew. Chem.-Int. Edit.* **2007,** *46* (34), 6542-6544.

22. Rowland, E. B.; Rowland, G. B.; Rivera-Otero, E.; Antilla, J. C., Bronsted acid-catalyzed desymmetrization of meso-aziridines. *J. Am. Chem. Soc.* **2007,** *129* (40), 12084-+.

23. Kawasaki, M.; Li, P. F.; Yamamoto, H., Enantioselective O-nitroso aldol reaction of silyl enol ethers. *Angew. Chem.-Int. Edit.* **2008,** *47* (20), 3795-3797.

24. Jiao, P.; Nakashima, D.; Yamamoto, H., Enantioselective 1,3-dipolar cycloaddition of nitrones with ethyl vinyl ether: The difference between bronsted and Lewis acid catalysis. *Angew. Chem.-Int. Edit.* **2008,** *47* (13), 2411-2413.

25. Ishimaru, T.; Shibata, N.; Horikawa, T.; Yasuda, N.; Nakamura, S.; Toru, T.; Shiro, M., Cinchona alkaloid catalyzed enantioselective fluorination of allyl silanes, silyl enol ethers, and oxindoles. *Angew. Chem.-Int. Edit.* **2008,** *47* (22), 4157-4161.

26. Cheon, C. H.; Yamamoto, H., A Bronsted acid catalyst for the enantioselective protonation reaction. *J. Am. Chem. Soc.* **2008,** *130* (29), 9246-+.

27. Bao, H. L.; Zhou, J.; Wang, Z.; Guo, Y. L.; You, T. P.; Ding, K. L., Insight into the mechanism of the asymmetric ring-opening aminolysis of 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane catalyzed by titanium/BINOLate/water system: Evidence for the Ti(BINOLate)(2)-bearing active catalyst entities and the role of water. *J. Am. Chem. Soc.* **2008,** *130* (31), 10116-10127.

28. Fukamizu, K.; Miyake, Y.; Nishibayashi, Y., Ruthenium-catalyzed enantioselective carbon-carbon bond forming reaction via allenylidene-ene process: Synthetic approach to chiral heterocycles such as chromane, thiochromane, and 1,2,3,4-tetrahydroquinoline derivatives. *J. Am. Chem. Soc.* **2008,** *130* (32), 10498-+.

29. Takenaka, N.; Sarangthem, R. S.; Captain, B., Helical Chiral Pyridine N-Oxides: A New Family of Asymmetric Catalysts. *Angew. Chem.-Int. Edit.* **2008,** *47* (50), 9708-9710.

30. Hamilton, G. L.; Kanai, T.; Toste, F. D., Chiral Anion-Mediated Asymmetric Ring Opening of meso-Aziridinium and Episulfonium Ions. *J. Am. Chem. Soc.* **2008,** *130* (45), 14984-+.

31. Pu, X. T.; Qi, X. B.; Ready, J. M., Allenes in Asymmetric Catalysis: Asymmetric Ring Opening of meso-Epoxides Catalyzed by Allene-Containing Phosphine Oxides. *J. Am. Chem. Soc.* **2009,** *131* (30), 10364-+.

32. Jana, C. K.; Grimme, S.; Studer, A., Enantioselective Nitroso-Diels-Alder Reaction and Its Application for the Synthesis of (-)-Peracetylated Conduramine A-1. *Chemistry-a European Journal* **2009,** *15* (36), 9078-9084.

33. Sato, S.; Shibuya, M.; Kanoh, N.; Iwabuchi, Y., Highly enantioselective intramolecular aza-spiroannulation onto indoles using chiral rhodium catalysis: asymmetric entry to the spiro-beta-lactam core of chartellines. *Chem. Commun.* **2009,** (41), 6264-6266.

34. Li, Z. J.; Davies, H. M. L., Enantioselective C-C Bond Formation by Rhodium-Catalyzed Tandem Ylide Formation/[2,3]-Sigmatropic Rearrangement between Donor/Acceptor Carbenoids and Allylic Alcohols. *J. Am. Chem. Soc.* **2010,** *132* (1), 396-401.

35. Lian, Y. J.; Davies, H. M. L., Rhodium-Catalyzed 3+2 Annulation of Indoles. *J. Am. Chem. Soc.* **2010,** *132* (2), 440-+.

36. Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B., An Organocatalytic Asymmetric Chlorolactonization. *J. Am. Chem. Soc.* **2010,** *132* (10), 3298-+.

37. Zhang, W.; Zheng, S. Q.; Liu, N.; Werness, J. B.; Guzei, I. A.; Tang, W. P., Enantioselective Bromolactonization of Conjugated (Z)-Enynes. *J. Am. Chem. Soc.* **2010,** *132* (11), 3664-+.

38. Uyanik, M.; Yasui, T.; Ishihara, K., Enantioselective Kita Oxidative Spirolactonization Catalyzed by In Situ Generated Chiral Hypervalent Iodine(III) Species. *Angew. Chem.-Int. Edit.* **2010,** *49* (12), 2175-2177.

39. Yanagisawa, A.; Takeshita, S.; Izumi, Y.; Yoshida, K., Enantioselective Nitroso Aldol Reaction Catalyzed by QuinoxP*center dot Silver(I) Complex and Tin Methoxide. *J. Am. Chem. Soc.* **2010,** *132* (15), 5328-+.

40. Chatterjee, I.; Jana, C. K.; Steinmetz, M.; Grimme, S.; Studer, A., Copper-Catalyzed Enantioselective 2+2 Cycloadditions of 2-Nitrosopyridine with Ketenes. *Adv. Synth. Catal.* **2010,** *352* (6), 945-948.

41. Lu, M.; Lu, Y. P.; Zhu, D.; Zeng, X. F.; Li, X. S.; Zhong, G. F., Chiral Bronsted Acid Catalyzed Enantioselective alpha-Aminoxylation of Enecarbamates. *Angew. Chem.-Int. Edit.* **2010,** *49* (46), 8588-8592.

42. Tanaka, H.; Nishikawa, H.; Uchida, T.; Katsuki, T., Photopromoted Ru-Catalyzed Asymmetric Aerobic Sulfide Oxidation and Epoxidation Using Water as a Proton Transfer Mediator. *J. Am. Chem. Soc.* **2010,** *132* (34), 12034-12041.

43. Uraguchi, D.; Kinoshita, N.; Ooi, T., Catalytic Asymmetric Protonation of alpha-Amino Acid-Derived Ketene Disilyl Acetals Using P-Spiro Diaminodioxaphosphonium Barfates as Chiral Proton. *J. Am. Chem. Soc.* **2010,** *132* (35), 12240-12242.

44. Murai, K.; Matsushita, T.; Nakamura, A.; Fukushima, S.; Shimura, M.; Fujioka, H., Asymmetric Bromolactonization Catalyzed by a C(3)-Symmetric Chiral Trisimidazoline. *Angew. Chem.-Int. Edit.* **2010,** *49* (48), 9174-9177.

45. Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K., Quaternary Ammonium (Hypo)iodite Catalysis for Enantioselective Oxidative Cycloetherification. *Science* **2010,** *328* (5984), 1376-1379.

46. Fujisaki, J.; Matsumoto, K.; Katsuki, T., Catalytic Asymmetric Oxidation of Cyclic Dithioacetals: Highly Diastereo- and Enantioselective Synthesis of the S-Oxides by a Chiral Aluminum(salalen) Complex. *J. Am. Chem. Soc.* **2011,** *133* (1), 56-61.

47. Yousefi, R.; Whitehead, D. C.; Mueller, J. M.; Staples, R. J.; Borhan, B., On the Chlorenium Source in the Asymmetric Chlorolactonization Reaction. *Org. Lett.* **2011,** *13* (4), 608-611.

48. Lee, J. Y.; You, Y. S.; Kang, S. H., Asymmetric Synthesis of All-Carbon Quaternary Stereocenters via Desymmetrization of 2,2-Disubstituted 1,3-Propanediols. *J. Am. Chem. Soc.* **2011,** *133* (6), 1772-1774.

49. Hennecke, U.; Muller, C. H.; Frohlich, R., Enantioselective Haloetherification by Asymmetric Opening of meso-Halonium Ions. *Org. Lett.* **2011,** *13* (5), 860-863.

50. Jaganathan, A.; Garzan, A.; Whitehead, D. C.; Staples, R. J.; Borhan, B., A Catalytic Asymmetric Chlorocyclization of Unsaturated Amides. *Angew. Chem.-Int. Edit.* **2011,** *50* (11), 2593-2596.

51. Nicolaou, K. C.; Simmons, N. L.; Ying, Y. C.; Heretsch, P. M.; Chen, J. S., Enantioselective Dichlorination of Allylic Alcohols. *J. Am. Chem. Soc.* **2011,** *133* (21), 8134-8137.

52. Chen, Z. M.; Zhang, Q. W.; Chen, Z. H.; Li, H.; Tu, Y. Q.; Zhang, F. M.; Tian, J. M., Organocatalytic Asymmetric Halogenation/Semipinacol Rearrangement: Highly Efficient Synthesis of Chiral alpha-Oxa-Quaternary beta-Haloketones. *J. Am. Chem. Soc.* **2011,** *133* (23), 8818-8821.

53. Li, H.; Zhang, F. M.; Tu, Y. Q.; Zhang, Q. W.; Chen, Z. M.; Chen, Z. H.; Li, J., Enantioselective bromination/semipinacol rearrangement for the synthesis of beta-bromoketones containing an all-alpha-carbon quaternary center. *Chem. Sci.* **2011,** *2* (9), 1839-1841.

54. Lozano, O.; Blessley, G.; del Campo, T. M.; Thompson, A. L.; Giuffredi, G. T.; Bettati, M.; Walker, M.; Borman, R.; Gouverneur, V., Organocatalyzed Enantioselective Fluorocyclizations. *Angew. Chem.-Int. Edit.* **2011,** *50* (35), 8105-8109.

55. Cheon, C. H.; Kanno, O.; Toste, F. D., Chiral Bronsted Acid from a Cationic Gold(I) Complex: Catalytic Enantioselective Protonation of Silyl Enol Ethers of Ketones. *J. Am. Chem. Soc.* **2011,** *133* (34), 13248-13251.

56. Li, W.; Liu, X. H.; Hao, X. Y.; Hu, X. L.; Chu, Y. Y.; Cao, W. D.; Qin, S.; Hu, C. W.; Lin, L. L.; Feng, X. M., New Electrophilic Addition of alpha-Diazoesters with Ketones for Enantioselective C-N Bond Formation. *J. Am. Chem. Soc.* **2011,** *133* (39), 15268-15271.

57. Denmark, S. E.; Kornfilt, D. J. P.; Vogler, T., Catalytic Asymmetric Thiofunctionalization of Unactivated Alkenes. *J. Am. Chem. Soc.* **2011,** *133* (39), 15308-15311.

58. Wang, X. C.; Xu, X. F.; Zavalij, P. Y.; Doyle, M. P., Asymmeric Formal 3+3 -Cycloaddition Reactions of Nitrones with Electrophilic Vinylcarbene Intermediates. *J. Am. Chem. Soc.* **2011,** *133* (41), 16402-16405.

59. Chatterjee, I.; Frohlich, R.; Studer, A., Formation of Isoxazolidines by Enantioselective Copper-Catalyzed Annulation of 2-Nitrosopyridine with Allylstannanes. *Angew. Chem.-Int. Edit.* **2011,** *50* (47), 11257-11260.

60. Rauniyar, V.; Lackner, A. D.; Hamilton, G. L.; Toste, F. D., Asymmetric Electrophilic Fluorination Using an Anionic Chiral Phase-Transfer Catalyst. *Science* **2011,** *334* (6063), 1681-1684.

61. Denmark, S. E.; Burk, M. T., Enantioselective Bromocycloetherification by Lewis Base/Chiral Bronsted Acid Cooperative Catalysis. *Org. Lett.* **2012,** *14* (1), 256-259.

62. Dobish, M. C.; Johnston, J. N., Achiral Counterion Control of Enantioselectivity in a Bronsted Acid-Catalyzed Iodolactonization. *J. Am. Chem. Soc.* **2012,** *134* (14), 6068-6071.

63. Worthy, A. D.; Sun, X. X.; Tan, K. L., Site-Selective Catalysis: Toward a Regiodivergent Resolution of 1,2-Diols. *J. Am. Chem. Soc.* **2012,** *134* (17), 7321-7324.

64. Zhang, W.; Liu, N.; Schienebeck, C. M.; Decloux, K.; Zheng, S. Q.; Werness, J. B.; Tang, W. P., Catalytic Enantioselective Halolactonization of Enynes and Alkenes. *Chemistry-a European Journal* **2012,** *18* (23), 7296-7305.

65. Phipps, R. J.; Hiramatsu, K.; Toste, F. D., Asymmetric Fluorination of Enamides: Access to alpha-Fluoroimines Using an Anionic Chiral Phase-Transfer Catalyst. *J. Am. Chem. Soc.* **2012,** *134* (20), 8376-8379.

66. Ohmatsu, K.; Hamajima, Y.; Ooi, T., Catalytic Asymmetric Ring Openings of Meso and Terminal Aziridines with Halides Mediated by Chiral 1,2,3-Triazolium Silicates. *J. Am. Chem. Soc.* **2012,** *134* (21), 8794-8797.

67. Jiang, X. J.; Tan, C. K.; Zhou, L.; Yeung, Y. Y., Enantioselective Bromolactonization Using an S-Alkyl Thiocarbamate Catalyst. *Angew. Chem.-Int. Edit.* **2012,** *51* (31), 7771-7775.

68. Li, Z. J.; Parr, B. T.; Davies, H. M. L., Highly Stereoselective C-C Bond Formation by Rhodium-Catalyzed Tandem Ylide Formation/ 2,3 -Sigmatropic Rearrangement between Donor/Acceptor Carbenoids and Chiral Allylic Alcohols. *J. Am. Chem. Soc.* **2012,** *134* (26), 10942-10946.

69. Wang, Y. M.; Wu, J.; Hoong, C.; Rauniyar, V.; Toste, F. D., Enantioselective Halocyclization Using Reagents Tailored for Chiral Anion Phase-Transfer Catalysis. *J. Am. Chem. Soc.* **2012,** *134* (31), 12928-12931.

70. Honjo, T.; Phipps, R. J.; Rauniyar, V.; Toste, F. D., A Doubly Axially Chiral Phosphoric Acid Catalyst for the Asymmetric Tandem Oxyfluorination of Enamides. *Angew. Chem.-Int. Edit.* **2012,** *51* (38), 9684-9688.

71. Xu, X. F.; Zavalij, P. Y.; Doyle, M. P., Synthesis of Tetrahydropyridazines by a Metal-Carbene-Directed Enantioselective Vinylogous N-H Insertion/Lewis Acid-Catalyzed Diastereoselective Mannich Addition. *Angew. Chem.-Int. Edit.* **2012,** *51* (39), 9829-9833.

72. Li, Z. J.; Boyarskikh, V.; Hansen, J. H.; Autschbach, J.; Musaev, D. G.; Davies, H. M. L., Scope and Mechanistic Analysis of the Enantioselective Synthesis of Allenes by Rhodium-Catalyzed Tandem Ylide Formation/ 2,3 -Sigmatropic Rearrangement between Donor/Acceptor Carbenoids and Propargylic Alcohols. *J. Am. Chem. Soc.* **2012,** *134* (37), 15497-15504.

73. Lin, S.; Jacobsen, E. N., Thiourea-catalysed ring opening of episulfonium ions with indole derivatives by means of stabilizing non-covalent interactions. *Nat. Chem.* **2012,** *4* (10), 817-824.

74. Zhou, C. Y.; Wang, J. C.; Wei, J. H.; Xu, Z. J.; Guo, Z.; Low, K. H.; Che, C. M., Dirhodium Carboxylates Catalyzed Enantioselective Coupling Reactions of alpha-Diazophosphonates, Anilines, and Electron-Deficient Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (45), 11376-11380.

75. Cheng, Y. A.; Chen, T.; Tan, C. K.; Heng, J. J.; Yeung, Y. Y., Efficient Medium Ring Size Bromolactonization Using a Sulfur-Based Zwitterionic Organocatalyst. *J. Am. Chem. Soc.* **2012,** *134* (40), 16492-16495.

76. Chen, F.; Tan, C. K.; Yeung, Y. Y., C-2-Symmetric Cyclic Selenium-Catalyzed Enantioselective Bromoaminocyclization. *J. Am. Chem. Soc.* **2013,** *135* (4), 1232-1235.

77. Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y., Asymmetric Dearomatizing Spirolactonization of Naphthols Catalyzed by Spirobiindane-Based Chiral Hypervalent Iodine Species. *J. Am. Chem. Soc.* **2013,** *135* (11), 4558-4566.

78. Brindle, C. S.; Yeung, C. S.; Jacobsen, E. N., Chiral beta-iodoamines by urea-catalysed iodocyclization of trichloroacetimidates. *Chem. Sci.* **2013,** *4* (5), 2100-2104.

79. Zhang, W.; Liu, N.; Schienebeck, C. M.; Zhou, X.; Izhar, II; Guzei, I. A.; Tang, W. P., Enantioselective intermolecular bromoesterification of allylic sulfonamides. *Chem. Sci.* **2013,** *4* (6), 2652-2656.

80. Denmark, S. E.; Jaunet, A., Catalytic, Enantioselective, Intramolecular Carbosulfenylation of Olefins. *J. Am. Chem. Soc.* **2013,** *135* (17), 6419-6422.

81. Brown, A. R.; Uyeda, C.; Brotherton, C. A.; Jacobsen, E. N., Enantioselective Thiourea-CataByzed Intramolecular Cope-Type Hydroamination. *J. Am. Chem. Soc.* **2013,** *135* (18), 6747-6749.

82. Spangler, J. E.; Davies, H. M. L., Catalytic Asymmetric Synthesis of Pyrroloindolines via a Rhodium(II)-Catalyzed Annulation of Indoles. *J. Am. Chem. Soc.* **2013,** *135* (18), 6802-6805.

83. Farid, U.; Malmedy, F.; Claveau, R.; Albers, L.; Wirth, T., Stereoselective Rearrangements with Chiral Hypervalent Iodine Reagents. *Angew. Chem.-Int. Edit.* **2013,** *52* (27), 7018-7022.

84. Wang, Z. B.; Chen, Z. L.; Sun, J. W., Catalytic Enantioselective Intermolecular Desymmetrization of 3-Substituted Oxetanes. *Angew. Chem.-Int. Edit.* **2013,** *52* (26), 6685-6688.

85. Wilking, M.; Muck-Lichtenfeld, C.; Daniliuc, C. G.; Hennecke, U., Enantioselective, Desymmetrizing Bromolactonization of Alkynes. *J. Am. Chem. Soc.* **2013,** *135* (22), 8133-8136.

86. Huang, D. S.; Liu, X. Q.; Li, L. J.; Cai, Y. D.; Liu, W. G.; Shi, Y., Enantioselective Bromoaminocyclization of Allyl N-Tosylcarbamates Catalyzed by a Chiral Phosphine-Sc(OTf)(3) Complex. *J. Am. Chem. Soc.* **2013,** *135* (22), 8101-8104.

87. Shunatona, H. P.; Fruh, N.; Wang, Y. M.; Rauniyar, V.; Toste, F. D., Enantioselective Fluoroamination: 1,4-Addition to Conjugated Dienes Using Anionic Phase-Transfer Catalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (30), 7724-7727.

88. Wang, J.; Frings, M.; Bolm, C., Enantioselective Nitrene Transfer to Sulfides Catalyzed by a Chiral Iron Complex. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8661-8665.

89. Tripathi, C. B.; Mukherjee, S., Catalytic Enantioselective Iodoetherification of Oximes. *Angew. Chem.-Int. Edit.* **2013,** *52* (32), 8450-8453.

90. Uyanik, M.; Yasui, T.; Ishihara, K., Hydrogen Bonding and Alcohol Effects in Asymmetric Hypervalent Iodine Catalysis: Enantioselective Oxidative Dearomatization of Phenols. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9215-9218.

91. Briones, J. F.; Davies, H. M. L., Enantioselective Gold(I)-Catalyzed Vinylogous 3+2 Cycloaddition between Vinyldiazoacetates and Enol Ethers. *J. Am. Chem. Soc.* **2013,** *135* (36), 13314-13317.

92. Jaganathan, A.; Staples, R. J.; Borhan, B., Kinetic Resolution of Unsaturated Amides in a Chlorocyclization Reaction: Concomitant Enantiomer Differentiation and Face Selective Alkene Chlorination by a Single Catalyst. *J. Am. Chem. Soc.* **2013,** *135* (39), 14806-14813.

93. Qin, C. M.; Davies, H. M. L., Rh-2(R-TPCP)(4)-Catalyzed Enantioselective 3+2 -Cycloaddition between Nitrones and Vinyldiazoacetates. *J. Am. Chem. Soc.* **2013,** *135* (39), 14516-14519.

94. Xu, X. F.; Zavalij, P. Y.; Doyle, M. P., Highly Enantioselective Dearomatizing Formal 3+3 Cycloaddition Reactions of N-Acyliminopyridinium Ylides with Electrophilic Enol Carbene Intermediates. *Angew. Chem.-Int. Edit.* **2013,** *52* (48), 12664-12668.

95. Xie, W. Q.; Jiang, G. D.; Liu, H.; Hu, J. D.; Pan, X. X.; Zhang, H.; Wan, X. L.; Lai, Y. S.; Ma, D. W., Highly Enantioselective Bromocyclization of Tryptamines and Its Application in the Synthesis of (-)-Chimonanthine. *Angew. Chem.-Int. Edit.* **2013,** *52* (49), 12924-12927.

96. Kwok, S. W.; Zhang, L.; Grimster, N. P.; Fokin, V. V., Catalytic Asymmetric Transannulation of NH-1,2,3-Triazoles with Olefins. *Angew. Chem.-Int. Edit.* **2014,** *53* (13), 3452-3456.

97. Denmark, S. E.; Chi, H. M., Catalytic, Enantioselective, Intramolecular Carbosulfenylation of Olefins. Mechanistic Aspects: A Remarkable Case of Negative Catalysis. *J. Am. Chem. Soc.* **2014,** *136* (9), 3655-3663.

98. Yang, X.; Phipps, R. J.; Toste, F. D., Asymmetric Fluorination of alpha-Branched Cyclohexanones Enabled by a Combination of Chiral Anion Phase-Transfer Catalysis and Enamine Catalysis using Protected Amino Acids. *J. Am. Chem. Soc.* **2014,** *136* (14), 5225-5228.

99. Nelson, H. M.; Reisberg, S. H.; Shunatona, H. P.; Patel, J. S.; Toste, F. D., Chiral Anion Phase Transfer of Aryldiazonium Cations: An Enantioselective Synthesis of C3-Diazenated Pyrroloindolines. *Angew. Chem.-Int. Edit.* **2014,** *53* (22), 5600-5603.

100. Ke, Z.; Tan, C. K.; Chen, F.; Yeung, Y.-Y., Catalytic Asymmetric Bromoetherification and Desymmetrization of Olefinic 1,3-Diols with C-2-Symmetric Sulfides. *J. Am. Chem. Soc.* **2014,** *136* (15), 5627-5630.

101. Nakatsuji, H.; Sawamura, Y.; Sakakura, A.; Ishihara, K., Cooperative Activation with Chiral Nucleophilic Catalysts and N-Haloimides: Enantioselective Iodolactonization of 4-Arylmethyl-4-pentenoic Acids. *Angew. Chem.-Int. Edit.* **2014,** *53* (27), 6974-6977.

102. Denmark, S. E.; Chi, H. M., Lewis Base Catalyzed, Enantioselective, Intramolecular Sulfenoamination of Olefins. *J. Am. Chem. Soc.* **2014,** *136* (25), 8915-8918.

103. Lebel, H.; Piras, H.; Bartholomeues, J., Rhodium-Catalyzed Stereoselective Amination of Thioethers with N-Mesyloxycarbamates: DMAP and Bis(DMAP)CH2Cl2 as Key Additives. *Angew. Chem.-Int. Edit.* **2014,** *53* (28), 7300-7304.

104. Uyanik, M.; Hayashi, H.; Ishihara, K., High-turnover hypoiodite catalysis for asymmetric synthesis of tocopherols. *Science* **2014,** *345* (6194), 291-294.

105. Mizar, P.; Burrelli, A.; Guenther, E.; Soeftje, M.; Farooq, U.; Wirth, T., Organocatalytic Stereoselective Iodoamination of Alkenes. *Chemistry-a European Journal* **2014,** *20* (41), 13113-13116.

106. Zi, W.; Wang, Y.-M.; Toste, F. D., An In Situ Directing Group Strategy for Chiral Anion Phase-Transfer Fluorination of Allylic Alcohols. *J. Am. Chem. Soc.* **2014,** *136* (37), 12864-12867.

107. Denmark, S. E.; Rossi, S.; Webster, M. P.; Wang, H., Catalytic, Enantioselective Sulfenylation of Ketone-Derived Enoxysilanes. *J. Am. Chem. Soc.* **2014,** *136* (37), 13016-13028.

108. Guzman, P. E.; Lian, Y.; Davies, H. M. L., Reversal of the Regiochemistry in the Rhodium-Catalyzed 4+3 Cycloaddition between Vinyldiazoacetates and Dienes. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13083-13087.

109. Romney, D. K.; Colvin, S. M.; Miller, S. J., Catalyst Control over Regio- and Enantioselectivity in Baeyer-Villiger Oxidations of Functionalized Ketones. *J. Am. Chem. Soc.* **2014,** *136* (40), 14019-14022.

110. Toda, Y.; Pink, M.; Johnston, J. N., Bronsted Acid Catalyzed Phosphoramidic Acid Additions to Alkenes: Diastereo- and Enantioselective Halogenative Cyclizations for the Synthesis of C- and P-Chiral Phosphoramidates. *J. Am. Chem. Soc.* **2014,** *136* (42), 14734-14737.

111. Zhang, H.; Lin, S.; Jacobsen, E. N., Enantioselective Selenocyclization via Dynamic Kinetic Resolution of Seleniranium Ions by Hydrogen-Bond Donor Catalysts. *J. Am. Chem. Soc.* **2014,** *136* (47), 16485-16488.

112. Denmark, S. E.; Hartmann, E.; Kornfilt, D. J. P.; Wang, H., Mechanistic, crystallographic, and computational studies on the catalytic, enantioselective sulfenofunctionalization of alkenes. *Nat. Chem.* **2014,** *6* (12), 1056-1064.

113. Nelson, H. M.; Patel, J. S.; Shunatona, H. P.; Toste, F. D., Enantioselective alpha-amination enabled by a BINAM-derived phase-transfer catalyst. *Chem. Sci.* **2015,** *6* (1), 170-173.

114. Wang, S.-G.; Yin, Q.; Zhuo, C.-X.; You, S.-L., Asymmetric Dearomatization of beta-Naphthols through an Amination Reaction Catalyzed by a Chiral Phosphoric Acid. *Angew. Chem.-Int. Edit.* **2015,** *54* (2), 647-650.

115. Nan, J.; Liu, J.; Zheng, H.; Zuo, Z.; Hou, L.; Hu, H.; Wang, Y.; Luan, X., Direct Asymmetric Dearomatization of 2-Naphthols by Scandium-Catalyzed Electrophilic Amination. *Angew. Chem.-Int. Edit.* **2015,** *54* (8), 2356-2360.

116. Zhang, D. Y.; Xu, L.; Wu, H.; Gong, L. Z., Chiral Iodine-Catalyzed Dearomatizative Spirocyclization for the Enantioselective Construction of an All-Carbon Stereogenic Center. *Chemistry-a European Journal* **2015,** *21* (29), 10314-10317.

117. Soltanzadeh, B.; Jaganathan, A.; Staples, R. J.; Borhan, B., Highly Stereoselective Intermolecular Haloetherification and Haloesterification of Allyl Amides. *Angew. Chem.-Int. Edit.* **2015,** *54* (33), 9517-9522.

118. Egami, H.; Asada, J.; Sato, K.; Hashizume, D.; Kawato, Y.; Hamashima, Y., Asymmetric Fluorolactonization with a Bifunctional Hydroxyl Carboxylate Catalyst. *J. Am. Chem. Soc.* **2015,** *137* (32), 10132-10135.

119. Shen, Z. G.; Pan, X. X.; Lai, Y. S.; Hu, J. D.; Wan, X. L.; Li, X. G.; Zhang, H.; Xie, W. Q., Chiral ion-pair organocatalyst promotes highly enantioselective 3-exo iodo-cycloetherification of allyl alcohols. *Chem. Sci.* **2015,** *6* (12), 6986-6990.

120. Arai, T.; Watanabe, O.; Yabe, S.; Yamanaka, M., Catalytic Asymmetric Iodocyclization of N-Tosyl Alkenamides using Aminoiminophenoxy Copper Carboxylate: A Concise Synthesis of Chiral 8-Oxa-6-Azabicyclo 3.2.1 octanes. *Angew. Chem.-Int. Edit.* **2015,** *54* (43), 12767-12771.

121. Diener, M. E.; Metrano, A. J.; Kusano, S.; Miller, S. J., Enantioselective Synthesis of 3-Arylquinazolin-4(3H)-ones via Peptide-Catalyzed Atroposelective Bromination. *J. Am. Chem. Soc.* **2015,** *137* (38), 12369-12377.

122. Maji, B.; Yamamoto, H., Catalytic Enantioselective Nitroso Diels-Alder Reaction. *J. Am. Chem. Soc.* **2015,** *137* (50), 15957-15963.

123. Haubenreisser, S.; Woste, T. H.; Martinez, C.; Ishihara, K.; Muniz, K., Structurally Defined Molecular Hypervalent Iodine Catalysts for Intermolecular Enantioselective Reactions. *Angew. Chem.-Int. Edit.* **2016,** *55* (1), 413-417.

124. Liu, C.; Oblak, E. Z.; Vander Wal, M. N.; Dilger, A. K.; Almstead, D. K.; MacMillan, D. W. C., Oxy-Allyl Cation Catalysis: An Enantioselective Electrophilic Activation Mode. *J. Am. Chem. Soc.* **2016,** *138* (7), 2134-2137.

125. Neel, A. J.; Milo, A.; Sigman, M. S.; Toste, F. D., Enantiodivergent Fluorination of Allylic Alcohols: Data Set Design Reveals Structural Interplay between Achiral Directing Group and Chiral Anion. *J. Am. Chem. Soc.* **2016,** *138* (11), 3863-3875.

126. Yao, L.; Zhu, Q.; Wei, L.; Wang, Z. F.; Wang, C. J., Dysprosium(III)-Catalyzed Ring-Opening of meso-Epoxides: Desymmetrization by Remote Stereocontrol in a Thiolysis/Elimination Sequence. *Angew. Chem.-Int. Edit.* **2016,** *55* (19), 5829-5833.

127. Banik, S. M.; Medley, J. W.; Jacobsen, E. N., Catalytic, Diastereoselective 1,2-Difluorination of Alkenes. *J. Am. Chem. Soc.* **2016,** *138* (15), 5000-5003.

128. Kawamata, Y.; Hashimoto, T.; Maruoka, K., A Chiral Electrophilic Selenium Catalyst for Highly Enantioselective Oxidative Cyclization. *J. Am. Chem. Soc.* **2016,** *138* (16), 5206-5209.

129. Banik, S. M.; Medley, J. W.; Jacobsen, E. N., Catalytic, asymmetric difluorination of alkenes to generate difluoromethylated stereocenters. *Science* **2016,** *353* (6294), 51-54.

130. Deng, Y. M.; Yglesias, M. V.; Arman, H.; Doyle, M. P., Catalytic Asymmetric Synthesis of Cyclopentyl beta-Amino Esters by 3+2 Cycloaddition of Enecarbamates with Electrophilic Metalloenolcarbene Intermediates. *Angew. Chem.-Int. Edit.* **2016,** *55* (34), 10108-10112.

131. Kuroda, Y.; Harada, S.; Oonishi, A.; Kiyama, H.; Yamaoka, Y.; Yamada, K.; Takasu, K., Use of a Catalytic Chiral Leaving Group for Asymmetric Substitutions at sp(3)-Hybridized Carbon Atoms: Kinetic Resolution of beta-Amino Alcohols by p-Methoxybenzylation. *Angew. Chem.-Int. Edit.* **2016,** *55* (42), 13137-13141.

132. Woerly, E. M.; Banik, S. M.; Jacobsen, E. N., Enantioselective, Catalytic Fluorolactonization Reactions with a Nucleophilic Fluoride Source. *J. Am. Chem. Soc.* **2016,** *138* (42), 13858-13861.

133. Samanta, R. C.; Yamamoto, H., Catalytic Asymmetric Bromocyclization of Polyenes. *J. Am. Chem. Soc.* **2017,** *139* (4), 1460-1463.

134. Soltanzadeh, B.; Jaganathan, A.; Yi, Y.; Yi, H.; Staples, R. J.; Borhan, B., Highly Regio- and Enantioselective Vicinal Dihalogenation of Allyl Amides. *J. Am. Chem. Soc.* **2017,** *139* (6), 2132-2135.

135. Muniz, K.; Barreiro, L.; Romero, R. M.; Martinez, C., Catalytic Asymmetric Diamination of Styrenes. *J. Am. Chem. Soc.* **2017,** *139* (12), 4354-4357.

136. Deng, Y. M.; Massey, L. A.; Zavalij, P. Y.; Doyle, M. P., Catalytic Asymmetric 3+1 -Cycloaddition Reaction of Ylides with Electrophilic Metallo-enolcarbene Intermediates. *Angew. Chem.-Int. Edit.* **2017,** *56* (26), 7479-7483.

137. Dohi, T.; Sasa, H.; Miyazaki, K.; Fujitake, M.; Takenaga, N.; Kita, Y., Chiral Atropisomeric 8,8 '-Diiodobinaphthalene for Asymmetric Dearomatizing Spirolactonizations in Hypervalent Iodine Oxidations. *J. Org. Chem.* **2017,** *82* (22), 11954-11960.

138. Banik, S. M.; Levina, A.; Hyde, A. M.; Jacobsen, E. N., Lewis acid enhancement by hydrogen-bond donors for asymmetric catalysis. *Science* **2017,** *358* (6364), 761-764.

139. Biswas, S.; Kubota, K.; Orlandi, M.; Turberg, M.; Miles, D. H.; Sigman, M. S.; Toste, F. D., Enantioselective Synthesis of N,S-Acetals by an Oxidative Pummerer-Type Transformation using Phase-Transfer Catalysis. *Angew. Chem.-Int. Edit.* **2018,** *57* (2), 589-593.

140. Knowe, M. T.; Danneman, M. W.; Sun, S.; Pink, M.; Johnston, J. N., Biomimetic Desymmetrization of a Carboxylic Acid. *J. Am. Chem. Soc.* **2018,** *140* (6), 1998-2001.

141. Egami, H.; Niwa, T.; Sato, H.; Hotta, R.; Rouno, D.; Kawato, Y.; Hamashima, Y., Dianionic Phase-Transfer Catalyst for Asymmetric Fluoro-cyclization. *J. Am. Chem. Soc.* **2018,** *140* (8), 2785-2788.

142. Pluta, R.; Krach, P. E.; Cavallo, L.; Falivene, L.; Rueping, M., Metal-Free Catalytic Asymmetric Fluorination of Keto Esters Using a Combination of Hydrogen Fluoride (HF) and Oxidant: Experiment and Computation. *Acs Catalysis* **2018,** *8* (3), 2582-2588.

143. Lin, X. B.; Tang, Y.; Yang, W.; Tan, F.; Lin, L. L.; Liu, X. H.; Feng, X. M., Chiral Nickel(II) Complex Catalyzed Enantioselective Doyle-Kirmse Reaction of alpha-Diazo Pyrazoleamides. *J. Am. Chem. Soc.* **2018,** *140* (9), 3299-3305.

144. Rodriguez, K. X.; Pilato, T. C.; Ashfeld, B. L., An unusual stereoretentive 1,3-quaternary carbon shift resulting in an enantioselective Rh-II-catalyzed formal 4+1 -cycloaddition between diazo compounds and vinyl ketenes. *Chem. Sci.* **2018,** *9* (12), 3221-3226.

145. Tao, Z. L.; Robb, K. A.; Zhao, K.; Denmark, S. E., Enantioselective, Lewis Base-Catalyzed Sulfenocyclization of Polyenes. *J. Am. Chem. Soc.* **2018,** *140* (10), 3569-3573.

146. Nakamuro, T.; Hagiwara, K.; Miura, T.; Murakami, M., Enantioselective Denitrogenative Annulation of 1H-Tetrazoles with Styrenes Catalyzed by Rhodium. *Angew. Chem.-Int. Edit.* **2018,** *57* (19), 5497-5500.

147. Mennie, K. M.; Banik, S. M.; Reichert, E. C.; Jacobsen, E. N., Catalytic Diastereo- and Enantioselective Fluoroamination of Alkenes. *J. Am. Chem. Soc.* **2018,** *140* (14), 4797-4802.

148. Liu, X.; Lang, Y. Y.; Ji, J. Y.; Luo, J.; Zhao, X., Chiral Selenide-Catalyzed Enantioselective Allylic Reaction and Intermolecular Difunctionalization of Alkenes: Efficient Construction of C-SCF3 Stereogenic Molecules. *J. Am. Chem. Soc.* **2018,** *140* (14), 4782-4786.

149. Wang, Y.; Yuan, H.; Lu, H. F.; Zheng, W. H., Development of Planar Chiral Iodoarenes Based on 2.2 Paracyclophane and Their Application in Catalytic Enantioselective Fluorination of beta-Ketoesters. *Org. Lett.* **2018,** *20* (9), 2555-2558.

150. Hashimoto, T.; Shimazaki, Y.; Omatsu, Y.; Maruoka, K., Indanol-Based Chiral Organoiodine Catalysts for Enantioselective Hydrative Dearomatization. *Angew. Chem.-Int. Edit.* **2018,** *57* (24), 7200-7204.

151. Lu, Y. H.; Nakatsuji, H.; Okumura, Y.; Yao, L.; Ishihara, K., Enantioselective Halo-oxy- and Halo-azacyclizations Induced by Chiral Amidophosphate Catalysts and Halo-Lewis Acids. *J. Am. Chem. Soc.* **2018,** *140* (19), 6039-6043.

152. Ye, B. H.; Zhao, J.; Zhao, K.; McKenna, J. M.; Toste, F. D., Chiral Diaryliodonium Phosphate Enables Light Driven Diastereoselective alpha-C(sp(3))-H Acetalization. *J. Am. Chem. Soc.* **2018,** *140* (26), 8350-8356.

153. Scheidt, F.; Schafer, M.; Sarie, J. C.; Daniliuc, C. G.; Molloy, J. J.; Gilmour, R., Enantioselective, Catalytic Vicinal Difluorination of Alkenes. *Angew. Chem.-Int. Edit.* **2018,** *57* (50), 16431-16435.

154. Wang, H. M.; Zhang, L.; Tu, Y. S.; Xiang, R. Q.; Guo, Y. L.; Zhang, J. L., Phosphine-Catalyzed Difunctionalization of beta-Fluoroalkyl alpha,beta-Enones: A Direct Approach to beta-Amino alpha-Diazo Carbonyl Compounds. *Angew. Chem.-Int. Edit.* **2018,** *57* (48), 15787-15791.

155. Tao, Z. L.; Robb, K. A.; Panger, J. L.; Denmark, S. E., Enantioselective, Lewis Base-Catalyzed Carbosulfenylation of Alkenylboronates by 1,2-Boronate Migration. *J. Am. Chem. Soc.* **2018,** *140* (46), 15621-15625.

156. Zhou, B. Y.; Haj, M. K.; Jacobsen, E. N.; Houk, K. N.; Xue, X. S., Mechanism and Origins of Chemo- and Stereoselectivities of Aryl Iodide-Catalyzed Asymmetric Difluorinations of beta-Substituted Styrenes. *J. Am. Chem. Soc.* **2018,** *140* (45), 15206-15218.

157. Cao, Q. X.; Luo, J.; Zhao, X. D., Chiral Sulfide Catalysis for Desymmetrizing Enantioselective Chlorination. *Angew. Chem.-Int. Edit.* **2019,** *58* (5), 1315-1319.

158. Zhang, D.-Y.; Zhang, Y.; Wu, H.; Gong, L.-Z., Organoiodine-Catalyzed Enantioselective Alkoxylation/Oxidative Rearrangement of Allylic Alcohols. *Angewandte Chemie International Edition* **2019,** *58* (22), 7450-7453.

159. Haj, M. K.; Banik, S. M.; Jacobsen, E. N., Catalytic, Enantioselective 1,2-Difluorination of Cinnamamides. *Org. Lett.* **2019,** *21* (13), 4919-4923.

160. Wedek, V.; Van Lommel, R.; Daniliuc, C. G.; De Proft, F.; Hennecke, U., Organocatalytic, Enantioselective Dichlorination of Unfunctionalized Alkenes. *Angew. Chem.-Int. Edit.* **2019,** *58* (27), 9239-9243.

161. Cai, L. C.; Zhang, K.; Chen, S. M.; Lepage, R. J.; Houk, K. N.; Krenske, E. H.; Kwon, O., Catalytic Asymmetric Staudinger-aza-Wittig Reaction for the Synthesis of Heterocyclic Amines. *J. Am. Chem. Soc.* **2019,** *141* (24), 9537-9542.

162. Matviitsuk, A.; Denmark, S. E., Enantio- and Diastereoselective, Lewis Base Catalyzed, Cascade Sulfenoacetalization of Alkenyl Aldehydes. *Angew. Chem.-Int. Edit.* **2019,** *58* (36), 12486-12490.

163. Zheng, H. L.; Sang, Y. Q.; Houk, K. N.; Xue, X. S.; Cheng, J. P., Mechanism and Origins of Enantioselectivities in Spirobiindane-Based Hypervalent Iodine(III)-Induced Asymmetric Dearomatizing Spirolactonizations. *J. Am. Chem. Soc.* **2019,** *141* (40), 16046-16056.

164. Cheng, Y.-Z.; Zhao, Q.-R.; Zhang, X.; You, S.-L., Asymmetric Dearomatization of Indole Derivatives with N-Hydroxycarbamates Enabled by Photoredox Catalysis. *Angewandte Chemie International Edition* **2019,** *58* (50), 18069-18074.

165. Hsieh, S. Y.; Tang, Y.; Crotti, S.; Stone, E. A.; Miller, S. J., Catalytic Enantioselective Pyridine N-Oxidation. *J. Am. Chem. Soc.* **2019,** *141* (46), 18624-18629.

166. Tao, Z. L.; Gilbert, B. B.; Denmark, S. E., Catalytic, Enantioselective syn-Diamination of Alkenes. *J. Am. Chem. Soc.* **2019,** *141* (48), 19161-19170.

167. Abazid, A. H.; Nachtsheim, B. J., A Triazole-Substituted Aryl Iodide with Omnipotent Reactivity in Enantioselective Oxidations. *Angew. Chem.-Int. Edit.* **2020,** *59* (4), 1479-1484.

168. Liang, Y. Y.; Ji, J. Y.; Zhang, X. Y.; Jiang, Q. B.; Luo, J.; Zhao, X. D., Enantioselective Construction of Axially Chiral Amino Sulfide Vinyl Arenes by Chiral Sulfide-Catalyzed Electrophilic Carbothiolation of Alkynes. *Angew. Chem.-Int. Edit.* **2020,** *59* (12), 4959-4964.

169. Yousefi, R.; Sarkar, A.; Ashtekar, K. D.; Whitehead, D. C.; Kakeshpour, T.; Holmes, D.; Reed, P.; Jackson, J. E.; Borhan, B., Mechanistic Insights into the Origin of Stereoselectivity in an Asymmetric Chlorolactonization Catalyzed by (DHQD)2PHAL. *J. Am. Chem. Soc.* **2020,** *142* (15), 7179-7189.

170. Stone, E. A.; Cutrona, K. J.; Miller, S. J., Asymmetric Catalysis upon Helically Chiral Loratadine Analogues Unveils Enantiomer-Dependent Antihistamine Activity. *J. Am. Chem. Soc.* **2020,** *142* (29), 12690-12698.

171. Levin, M. D.; Ovian, J. M.; Read, J. A.; Sigman, M. S.; Jacobsen, E. N., Catalytic Enantioselective Synthesis of Difluorinated Alkyl Bromides. *J. Am. Chem. Soc.* **2020,** *142* (35), 14831-14837.

172. Sharma, H. A.; Mennie, K. M.; Kwan, E. E.; Jacobsen, E. N., Enantioselective Aryl-Iodide-Catalyzed Wagner–Meerwein Rearrangements. *J. Am. Chem. Soc.* **2020,** *142* (37), 16090-16096.

173. Beleh, O. M.; Miller, E.; Toste, F. D.; Miller, S. J., Catalytic Dynamic Kinetic Resolutions in Tandem to Construct Two-Axis Terphenyl Atropisomers. *J. Am. Chem. Soc.* **2020,** *142* (38), 16461-16470.

174. Uraguchi, D.; Kimura, Y.; Ueoka, F.; Ooi, T., Urea as a Redox-Active Directing Group under Asymmetric Photocatalysis of Iridium-Chiral Borate Ion Pairs. *J. Am. Chem. Soc.* **2020,** *142* (46), 19462-19467.

175. Wang, Q.; Lübcke, M.; Biosca, M.; Hedberg, M.; Eriksson, L.; Himo, F.; Szabó, K. J., Enantioselective Construction of Tertiary Fluoride Stereocenters by Organocatalytic Fluorocyclization. *J. Am. Chem. Soc.* **2020,** *142* (47), 20048-20057.

176. Wang, Y.; Yang, B.; Wu, X.-X.; Wu, Z.-G., Recent Application of Chiral Aryliodine Based on the 2-Iodoresorcinol Core in Asymmetric Catalysis. *Synthesis* **2020,** *53* (05), 889-903.

177. Steigerwald, D. C.; Soltanzadeh, B.; Sarkar, A.; Morgenstern, C. C.; Staples, R. J.; Borhan, B., Ritter-enabled catalytic asymmetric chloroamidation of olefins. *Chem. Sci.* **2021,** *12* (5), 1834-1842.

178. Meyer, S.; Häfliger, J.; Schäfer, M.; Molloy, J. J.; Daniliuc, C. G.; Gilmour, R., A Chiral Pentafluorinated Isopropyl Group via Iodine(I)/(III) Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (12), 6430-6434.

179. Kim, S.; Kim, D.; Hong, S. Y.; Chang, S., Tuning Orbital Symmetry of Iridium Nitrenoid Enables Catalytic Diastereo- and Enantioselective Alkene Difunctionalizations. *J. Am. Chem. Soc.* **2021,** *143* (10), 3993-4004.

180. Wu, S.; Xiang, S.-H.; Li, S.; Ding, W.-Y.; Zhang, L.; Jiang, P.-Y.; Zhou, Z.-A.; Tan, B., Urea group-directed organocatalytic asymmetric versatile dihalogenation of alkenes and alkynes. *Nature Catalysis* **2021,** *4* (8), 692-702.

181. Mumford, E. M.; Hemric, B. N.; Denmark, S. E., Catalytic, Enantioselective Syn-Oxyamination of Alkenes. *J. Am. Chem. Soc.* **2021,** *143* (33), 13408-13417.

182. Xu, Y.; Wang, Z.; Sun, J., Asymmetric [3 + 1]-Cycloaddition Reaction via Diazo Discrimination. *Org. Lett.* **2021,** *23* (19), 7613-7617.

183. Niwa, T.; Nishibashi, K.; Sato, H.; Ujiie, K.; Yamashita, K.; Egami, H.; Hamashima, Y., Structure Dependence in Asymmetric Deprotonative Fluorination and Fluorocyclization Reactions of Allylamine Derivatives with Linked Binaphthyl Dicarboxylate Phase-Transfer Catalyst. *J. Am. Chem. Soc.* **2021,** *143* (40), 16599-16609.

184. Ge, L.; Zhou, H.; Chiou, M.-F.; Jiang, H.; Jian, W.; Ye, C.; Li, X.; Zhu, X.; Xiong, H.; Li, Y.; Song, L.; Zhang, X.; Bao, H., Iron-catalysed asymmetric carboazidation of styrenes. *Nature Catalysis* **2021,** *4* (1), 28-35.

185. Lv, D.; Sun, Q.; Zhou, H.; Ge, L.; Qu, Y.; Li, T.; Ma, X.; Li, Y.; Bao, H., Iron-Catalyzed Radical Asymmetric Aminoazidation and Diazidation of Styrenes. *Angewandte Chemie International Edition* **2021,** *60* (22), 12455-12460.

186. Wang, K.; Li, Y.; Li, X.; Li, D.; Bao, H., Iron-Catalyzed Asymmetric Decarboxylative Azidation. *Org. Lett.* **2021,** *23* (22), 8847-8851.

187. Lin, X.; Pu, M.; Sang, X.; Li, S.; Liu, X.; Wu, Y.-D.; Feng, X., Asymmetric Catalytic (2+1) Cycloaddition of Thioketones to Synthesize Tetrasubstituted Thiiranes. *Angewandte Chemie International Edition* **2022,** *61* (19), e202201151.

188. Tanaka, H.; Ukegawa, N.; Uyanik, M.; Ishihara, K., Hypoiodite-Catalyzed Oxidative Umpolung of Indoles for Enantioselective Dearomatization. *J. Am. Chem. Soc.* **2022,** *144* (13), 5756-5761.

189. Schäfer, M.; Stünkel, T.; Daniliuc, C. G.; Gilmour, R., Regio- and Enantioselective Intermolecular Aminofluorination of Alkenes via Iodine(I)/Iodine(III) Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (32), e202205508.

190. Häfliger, J.; Sokolova, O. O.; Lenz, M.; Daniliuc, C. G.; Gilmour, R., Stereocontrolled Synthesis of Fluorinated Isochromans via Iodine(I)/Iodine(III) Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (30), e202205277.

191. Cao, M.; Wang, H.; Ma, Y.; Tung, C.-H.; Liu, L., Site- and Enantioselective Manganese-Catalyzed Benzylic C–H Azidation of Indolines. *J. Am. Chem. Soc.* **2022,** *144* (33), 15383-15390.

192. Liao, L.; Xu, X.; Ji, J.; Zhao, X., Asymmetric Intermolecular Iodinative Difunctionalization of Allylic Sulfonamides Enabled by Organosulfide Catalysis: Modular Entry to Iodinated Chiral Molecules. *J. Am. Chem. Soc.* **2022,** *144* (36), 16490-16501.

193. Greenwood, N. S.; Champlin, A. T.; Ellman, J. A., Catalytic Enantioselective Sulfur Alkylation of Sulfenamides for the Asymmetric Synthesis of Sulfoximines. *J. Am. Chem. Soc.* **2022,** *144* (39), 17808-17814.

194. Xie, C.; Kim, J.; Mai, B. K.; Cao, S.; Ye, R.; Wang, X.-Y.; Liu, P.; Kwon, O., Enantioselective Synthesis of Quaternary Oxindoles: Desymmetrizing Staudinger–Aza-Wittig Reaction Enabled by a Bespoke HypPhos Oxide Catalyst. *J. Am. Chem. Soc.* **2022,** *144* (46), 21318-21327.

195. Rose, B. T.; Timmerman, J. C.; Bawel, S. A.; Chin, S.; Zhang, H.; Denmark, S. E., High-Level Data Fusion Enables the Chemoinformatically Guided Discovery of Chiral Disulfonimide Catalysts for Atropselective Iodination of 2-Amino-6-arylpyridines. *J. Am. Chem. Soc.* **2022,** *144* (50), 22950-22964.

196. Cheng, Y.-F.; Yu, Z.-L.; Tian, Y.; Liu, J.-R.; Wen, H.-T.; Jiang, N.-C.; Bian, J.-Q.; Xu, G.-X.; Xu, D.-T.; Li, Z.-L.; Gu, Q.-S.; Hong, X.; Liu, X.-Y., Cu-catalysed enantioselective radical heteroatomic S–O cross-coupling. *Nat. Chem.* **2023,** *15* (3), 395-404.

197. Liu, X.; Liu, L.-G.; Chen, C.-M.; Li, X.; Xu, Z.; Lu, X.; Zhou, B.; Ye, L.-W., Copper-Catalyzed Enantioselective Doyle–Kirmse Reaction of Azide-Ynamides via α-Imino Copper Carbenes. *Angewandte Chemie International Edition* **2023,** *62* (10), e202216923.

198. Zhou, H.; Properzi, R.; Leutzsch, M.; Belanzoni, P.; Bistoni, G.; Tsuji, N.; Han, J. T.; Zhu, C.; List, B., Organocatalytic DYKAT of Si-Stereogenic Silanes. *J. Am. Chem. Soc.* **2023,** *145* (9), 4994-5000.

199. Zheng, H.; Cai, L.; Pan, M.; Uyanik, M.; Ishihara, K.; Xue, X.-S., Catalyst-Substrate Helical Character Matching Determines the Enantioselectivity in the Ishihara-Type Iodoarenes Catalyzed Asymmetric Kita-Dearomative Spirolactonization. *J. Am. Chem. Soc.* **2023,** *145* (13), 7301-7312.

200. Wang, G.; Chen, T.; Jia, K.; Ma, W.; Tung, C.-H.; Liu, L., Catalytic Asymmetric Oxidation of Amines to Hydroxylamines. *J. Am. Chem. Soc.* **2023,** *145* (40), 22276-22283.

201. Stünkel, T.; Siebold, K.; Okumatsu, D.; Murata, K.; Ruyet, L.; Daniliuc, C. G.; Gilmour, R., para-Selective dearomatization of phenols by I(i)/I(iii) catalysis-based fluorination. *Chem. Sci.* **2023,** *14* (46), 13574-13580.

202. Huang, N.; Luo, J.; Liao, L.; Zhao, X., Catalytic Enantioselective Aminative Difunctionalization of Alkenes. *J. Am. Chem. Soc.* **2024,** *146* (10), 7029-7038.

203. Ruyet, L.; Roblick, C.; Häfliger, J.; Wang, Z.-X.; Stoffels, T. J.; Daniliuc, C. G.; Gilmour, R., Catalytic Ring Expanding Difluorination: An Enantioselective Platform to Access β,β-Difluorinated Carbocycles. *Angewandte Chemie International Edition* **2024,** *63* (22), e202403957.

204. Yang, H.; Zhang, J.; Zhang, S.; Xue, Z.; Hu, S.; Chen, Y.; Tang, Y., Chiral Bisphosphine-Catalyzed Asymmetric Staudinger/aza-Wittig Reaction: An Enantioselective Desymmetrizing Approach to Crinine-Type Amaryllidaceae Alkaloids. *J. Am. Chem. Soc.* **2024,** *146* (20), 14136-14148.

205. Liu, Z.; Wu, H.; Zhang, H.; Wang, F.; Liu, X.; Dong, S.; Hong, X.; Feng, X., Iron-Catalyzed Asymmetric Imidation of Sulfides via Sterically Biased Nitrene Transfer. *J. Am. Chem. Soc.* **2024,** *146* (26), 18050-18060.

206. Teo, W. J.; Esteve Guasch, J.; Jiang, L.; Li, B.; Suero, M. G., Rh-Catalyzed Enantioselective Single-Carbon Insertion of Alkenes. *J. Am. Chem. Soc.* **2024,** *146* (31), 21837-21846.

207. Angle, S. R.; Sharma, H. A.; Choi, C. K.; Carlson, K. E.; Hou, Y.; Nwachukwu, J. C.; Kim, S. H.; Katzenellenbogen, B. S.; Nettles, K. W.; Katzenellenbogen, J. A.; Jacobsen, E. N., Iterative Catalyst-Controlled Diastereoselective Matteson Homologations Enable the Selective Synthesis of Benzestrol Isomers. *J. Am. Chem. Soc.* **2024,** *146* (45), 30771-30777.

208. Frank, E.; Park, S.; Harrer, E.; Flügel, J. L.; Fischer, M.; Nuernberger, P.; Rehbein, J.; Breder, A., Asymmetric Migratory Tsuji–Wacker Oxidation Enables the Enantioselective Synthesis of Hetero- and Isosteric Diarylmethanes. *J. Am. Chem. Soc.* **2024,** *146* (50), 34383-34393.

209. Xiao, Z.; Pu, M.; Li, Y.; Yang, W.; Wang, F.; Feng, X.; Liu, X., Asymmetric Catalytic Synthesis of Allylic Sulfenamides from Vinyl α-Diazo Compounds by a Rearrangement Route. *Angewandte Chemie International Edition* **2025,** *64* (2), e202414712.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

2.5. Activation of Allylic Systems

2.5.1 Asymmetric Electrophilic Allylation: Pd

1. Hayashi, T.; Kanehira, K.; Tsuchiya, H.; Kumada, M., New Chiral Ligands Designed for Palladium-Catalyzed Asymmetric Allylic Alkylation. *J. Chem. Soc.-Chem. Commun.* **1982,** (20), 1162-1164.

2. Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y., Asymmetric Allylic Amination Catalyzed by Chiral Ferrocenylphosphine-Palladium Complexes. *Tetrahedron Lett.* **1990,** *31* (12), 1743-1746.

3. Trost, B. M., Designing a receptor for molecular recognition in a catalytic synthetic reaction: Allylic Alkylation. *Accounts Chem. Res.* **1996,** *29* (8), 355-364.

4. Trost, B. M.; VanVranken, D. L., Asymmetric transition metal-catalyzed allylic alkylations. *Chem. Rev.* **1996,** *96* (1), 395-422.

5. Steinhagen, H.; Reggelin, M.; Helmchen, G., Palladium-catalyzed allylic alkylation with phosphinoaryldihydrooxazole ligands: First evidence and NMR spectroscopic structure determination of a primary olefin-Pd-o complex. *Angew. Chem.-Int. Edit. Engl.* **1997,** *36* (19), 2108-2110.

6. Kudis, S.; Helmchen, G., Enantioselective allylic substitution of cyclic substrates by catalysis with palladium complexes of P,N-chelate ligands with a cymantrene unit. *Angew. Chem.-Int. Edit.* **1998,** *37* (21), 3047-3050.

7. Trost, B. M.; Toste, F. D., Regio- and enantioselective allylic alkylation of an unsymmetrical substrate: A working model. *J. Am. Chem. Soc.* **1999,** *121* (19), 4545-4554.

8. Trost, B. M.; Surivet, J. P., Diastereo- and enantioselective allylation of substituted nitroalkanes. *J. Am. Chem. Soc.* **2000,** *122* (26), 6291-6292.

9. Helmchen, G.; Pfaltz, A., Phosphinooxazolines - A new class of versatile, modular P,N-ligands for asymmetric catalysis. *Accounts Chem. Res.* **2000,** *33* (6), 336-345.

10. El-Qisiari, A. K.; Qaseer, H. A.; Henry, P. M., An air oxidizable bimetallic palladium(II) catalyst for asymmetric allylic oxidation of olefins in acetic acid. *Tetrahedron Lett.* **2002,** *43* (23), 4229-4231.

11. Gais, H. J.; Bohme, A., Palladium(0)-catalyzed enantioselective O,S-rearrangement of racemic O-allylic thiocarbamates: A new entry to enantioenriched allylic sulfur compounds. *J. Org. Chem.* **2002,** *67* (4), 1153-1161.

12. Kitagawa, O.; Kohriyama, M.; Taguchi, T., Catalytic asymmetric synthesis of optically active atropisomeric anilides through enantioselective N-allylation with chiral Pd-tol-BINAP catalyst. *J. Org. Chem.* **2002,** *67* (24), 8682-8684.

13. Malkoch, M.; Hallman, K.; Lutsenko, S.; Hult, A.; Malmstrom, E.; Moberg, C., Dendritic oxazoline ligands in enantioselective palladium- catalyzed allylic alkylations. *J. Org. Chem.* **2002,** *67* (23), 8197-8202.

14. Trost, B. M.; Krische, M. J.; Berl, V.; Grenzer, E. M., Chemo-, regio-, and enantioselective Pd-catalyzed allylic alkylation of indolocarbazole pro-aglycons. *Org. Lett.* **2002,** *4* (12), 2005-2008.

15. Trost, B. M.; Machacek, M. R., An Efficient one-pot enantio- and diastereoselective synthesis of heterocycles. *Angew. Chem.-Int. Edit.* **2002,** *41* (24), 4693-4697.

16. Trost, B. M.; Pan, Z. Y.; Zambrano, J.; Kujat, C., Polymer-supported C-2-symmetric ligands for palladium-catalyzed asymmetric allylic alkylation reactions. *Angew. Chem.-Int. Edit.* **2002,** *41* (24), 4691-4693.

17. Trost, B. M.; Sacchi, K. L.; Schroeder, G. M.; Asakawa, N., Intramolecular palladium-catalyzed allylic alkylation: Enantio- and diastereoselective synthesis of 2.2.2 bicycles. *Org. Lett.* **2002,** *4* (20), 3427-3430.

18. Trost, B. M.; Schroeder, G. M.; Kristensen, J., Palladium-catalyzed asymmetric allylic alkylation of alpha-aryl ketones. *Angew. Chem.-Int. Edit.* **2002,** *41* (18), 3492-3495.

19. Graening, T.; Schmalz, H. G., Pd-catalyzed enantioselective allylic substitution: New strategic options for the total synthesis of natural products. *Angew. Chem.-Int. Edit.* **2003,** *42* (23), 2580-2584.

20. Lee, E. K.; Kim, S. H.; Jung, B. H.; Ahn, W. S.; Kim, G. J., New enantioselective chiral imidazolidine ligands for Pd- catalyzed asymmetric allylic alkylation. *Tetrahedron Lett.* **2003,** *44* (9), 1971-1974.

21. Lussem, B. J.; Gais, H. J., Palladium-catalyzed deracemization of allylic carbonates in water with formation of allylic alcohols: Hydrogen carbonate ion as nucleophile in the palladium-catalyzed allylic substitution and kinetic resolution. *J. Am. Chem. Soc.* **2003,** *125* (20), 6066-6067.

22. Trost, B. M.; Fandrick, D. R., Dynamic kinetic asymmetric cycloadditions of isocyanates to vinylaziridines. *J. Am. Chem. Soc.* **2003,** *125* (39), 11836-11837.

23. Trost, B. M.; Jakel, C.; Plietker, B., Palladium-catalyzed asymmetric addition of pronucleophiles to allenes. *J. Am. Chem. Soc.* **2003,** *125* (15), 4438-4439.

24. Trost, B. M.; Jiang, C. H., Pd-catalyzed asymmetric allylic alkylation. A short route to the cyclopentyl core of viridenomycin. *Org. Lett.* **2003,** *5* (9), 1563-1565.

25. Trost, B. M.; Shen, H. C.; Dong, L.; Surivet, J. P., Unusual effects in the Pd-catalyzed asymmetric allylic alkylations: Synthesis of chiral chromans. *J. Am. Chem. Soc.* **2003,** *125* (31), 9276-9277.

26. Trost, B. M.; Toste, F. D., Palladium catalyzed kinetic and dynamic kinetic asymmetric transformations of gamma-acyloxybutenolides. Enantioselective total synthesis of (+)-aflatoxin B-1 and B-2a. *J. Am. Chem. Soc.* **2003,** *125* (10), 3090-3100.

27. Trost, B. M.; Crawley, M. L., Asymmetric transition-metal-catalyzed allylic alkylations: Applications in total synthesis. *Chem. Rev.* **2003,** *103* (8), 2921-2943.

28. Behenna, D. C.; Stoltz, B. M., The enantioselective Tsuji allylation. *J. Am. Chem. Soc.* **2004,** *126* (46), 15044-15045.

29. Jansat, S.; Gomez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillon, S.; Chaudret, B., A case for enantioselective allylic alkylation catalyzed by palladium nanoparticles. *J. Am. Chem. Soc.* **2004,** *126* (6), 1592-1593.

30. Molander, G. A.; Burke, J. P.; Carroll, P. J., Synthesis and application of chiral cyclopropane-based ligands in palladium-catalyzed allylic alkylation. *J. Org. Chem.* **2004,** *69* (23), 8062-8069.

31. Trost, B. M.; Shen, H. C.; Dong, L.; Surivet, J. P.; Sylvain, C., Synthesis of chiral chromans by the Pd-catalyzed asymmetric allylic alkylation (AAA): Scope, mechanism, and applications. *J. Am. Chem. Soc.* **2004,** *126* (38), 11966-11983.

32. Watson, I. D. G.; Styler, S. A.; Yudin, A. K., Unusual selectivity of unprotected aziridines in palladium- catalyzed allylic amination enables facile preparation of branched aziridines. *J. Am. Chem. Soc.* **2004,** *126* (16), 5086-5087.

33. Trost, B. M., Asymmetric allylic alkylation, an enabling methodology. *J. Org. Chem.* **2004,** *69* (18), 5813-5837.

34. Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C., Serial ligand catalysis: A highly selective allylic C-H oxidation. *J. Am. Chem. Soc.* **2005,** *127* (19), 6970-6971.

35. Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M., Deracemization of quaternary stereocenters by Pd-catalyzed enantioconvergent decarboxylative allylation of racemic beta-ketoesters. *Angew. Chem.-Int. Edit.* **2005,** *44* (42), 6924-6927.

36. Nemoto, T.; Masuda, T.; Akimoto, Y.; Fukuyama, T.; Hamada, Y., Pd-catalyzed asymmetric allylic amination using aspartic acid derived P-chirogenic diaminophosphine oxides: DIAPHOXs. *Org. Lett.* **2005,** *7* (20), 4447-4450.

37. Trost, B. M.; Fandrick, D. R., DYKAT of vinyl aziridines: total synthesis of (+)-pseudodistomin D. *Org. Lett.* **2005,** *7* (5), 823-826.

38. Trost, B. M.; Fandrick, D. R.; Dinh, D. C., Dynamic kinetic asymmetric allylic alkylations of allenes. *J. Am. Chem. Soc.* **2005,** *127* (41), 14186-14187.

39. Trost, B. M.; Frederiksen, M. U., Palladium-catalyzed asymmetric allylation of prochiral nucleophiles: Synthesis of 3-allyl-3-aryl oxindoles. *Angew. Chem.-Int. Edit.* **2005,** *44* (2), 308-310.

40. Trost, B. M.; Machacek, M. R.; Tsui, H. C., Development of aliphatic alcohols as nucleophiles for palladium-catalyzed DYKAT reactions: Total synthesis of (+)-hippospongic acid A. *J. Am. Chem. Soc.* **2005,** *127* (19), 7014-7024.

41. Trost, B. M.; Xu, J. Y., Regio- and enantioselective Pd-catalyzed allylic alkylation of ketones through allyl enol carbonates. *J. Am. Chem. Soc.* **2005,** *127* (9), 2846-2847.

42. Trost, B. M.; Xu, J. Y., Palladium-catalyzed asymmetric allylic alpha-alkylation of acyclic ketones. *J. Am. Chem. Soc.* **2005,** *127* (49), 17180-17181.

43. Watson, L. D. G.; Yudin, A. K., New insights into the mechanism of palladium-catalyzed allylic amination. *J. Am. Chem. Soc.* **2005,** *127* (49), 17516-17529.

44. Yan, X. X.; Liang, C. G.; Zhang, Y.; Hong, W.; Cao, B. X.; Dai, L. X.; Hou, X. L., Highly enantioselective Pd-catalyzed allylic alkylations of acyclic ketones. *Angew. Chem.-Int. Edit.* **2005,** *44* (40), 6544-6546.

45. Zhu, S. F.; Yang, Y.; Wang, L. X.; Liu, B.; Zhou, Q. L., Synthesis and application of chiral spiro phospholane ligand in Pd-catalyzed asymmetric allylation of aldehydes with allylic alcohols. *Org. Lett.* **2005,** *7* (12), 2333-2335.

46. Kirsch, S. F.; Overman, L. E., Catalytic asymmetric synthesis of chiral allylic esters. *J. Am. Chem. Soc.* **2005,** *127* (9), 2866-2867.

47. Nakamura, M.; Hajra, L.; Endo, K.; Nakamura, E., Synthesis of chiral alpha-fluoroketones through catalytic entantioselective decarboxylation. *Angew. Chem.-Int. Edit.* **2005,** *44* (44), 7248-7251.

48. Braun, M.; Meier, T., Tsuji-Trost allylic alkylation with ketone enolates. *Angew. Chem.-Int. Edit.* **2006,** *45* (42), 6952-6955.

49. Trost, B. M.; Aponick, A., Palladium-catalyzed asymmetric allylic alkylation of meso- and dl-1,2-divinylethylene carbonate. *J. Am. Chem. Soc.* **2006,** *128* (12), 3931-3933.

50. Trost, B. M.; Bream, R. N.; Xu, J., Asymmetric allylic alkylation of cyclic vinylogous esters and thioesters by Pd-catalyzed decarboxylation of enol carbonate and beta-ketoester substrates. *Angew. Chem.-Int. Edit.* **2006,** *45* (19), 3109-3112.

51. Trost, B. M.; Quancard, J., Palladium-catalyzed enantioselective C-3 allylation of 3-substituted-1H-indoles using trialkylboranes. *J. Am. Chem. Soc.* **2006,** *128* (19), 6314-6315.

52. Trost, B. M.; Zhang, T., Asymmetric synthesis of alpha-substituted aldehydes by Pd-catalyzed asymmetric allylic alkylation-alkene isomerization-Claisen rearrangement. *Org. Lett.* **2006,** *8* (26), 6007-6010.

53. You, S. L.; Dai, L. X., Enantioselective palladium-catalyzed decarboxylative allylic alkylations. *Angew. Chem.-Int. Edit.* **2006,** *45* (32), 5246-5248.

54. Trost, B. M.; Machacek, M. R.; Aponick, A., Predicting the stereochemistry of diphenylphosphino benzoic acid (DPPBA)-based palladium-catalyzed asymmetric allylic alkylation reactions: A working model. *Accounts Chem. Res.* **2006,** *39* (10), 747-760.

55. Belanger, E.; Cantin, K.; Messe, O.; Tremblay, M.; Paquin, J. F., Enantioselective Pd-catalyzed allylation reaction of fluorinated silyl enol ethers. *J. Am. Chem. Soc.* **2007,** *129* (5), 1034-1035.

56. Trost, B. M.; Xu, J. Y.; Reichle, M., Enantioselective synthesis of alpha-tertiary hydroxyaldehydes by palladium-catalyzed asymmetric allylic alkylation of enolates. *J. Am. Chem. Soc.* **2007,** *129* (2), 282-283.

57. Zheng, W. H.; Zheng, B. H.; Zhang, Y.; Hou, X. L., Highly regio-, diastereo-, and enantioselective Pd-catalyzed allylic alkylation of acyclic ketone enolates with monosubstituted allyl substrates. *J. Am. Chem. Soc.* **2007,** *129* (25), 7718-+.

58. Lam, F. L.; Au-Yeung, T. T. L.; Kwong, F. Y.; Zhou, Z.; Wong, K. Y.; Chan, A. S. C., Palladium-(S,R-p)-ferro NPS-catalyzed asymmetric allylic etherification: Electronic effect of nonconjugated substituents on benzylic alcohols on enantioselectivity. *Angew. Chem.-Int. Edit.* **2008,** *47* (7), 1280-1283.

59. Zhang, K.; Peng, Q.; Hou, X. L.; Wu, Y. D., Highly enantioselective palladium-catalyzed alkylation of acyclic amides. *Angew. Chem.-Int. Edit.* **2008,** *47* (9), 1741-1744.

60. Overman, L. E.; Roberts, S. W.; Sneddon, H. F., Catalytic asymmetric synthesis of allylic thiol derivatives. *Org. Lett.* **2008,** *10* (7), 1485-1488.

61. Trost, B. M.; Me, J., Palladium-catalyzed diastereo- and enantioselective Wagner-Meerwein shift: Control of absolute stereochemistry in the C-C bond migration event. *J. Am. Chem. Soc.* **2008,** *130* (19), 6231-6242.

62. Butti, P.; Rochat, R.; Sadow, A. D.; Togni, A., Palladium-catalyzed enantioselective allylic phosphination. *Angew. Chem.-Int. Edit.* **2008,** *47* (26), 4878-4881.

63. Wang, C.; Tunge, J. A., Asymmetric cycloadditions of palladium-polarized aza-o-xylylenes. *J. Am. Chem. Soc.* **2008,** *130* (26), 8118-+.

64. Belanger, E.; Houze, C.; Guimond, N.; Cantin, K.; Paquin, J. F., Unexpected effect of the fluorine atom on the optimal ligand-to-palladium ratio in the enantioselective Pd-catalyzed allylation reaction of fluorinated enol carbonates. *Chem. Commun.* **2008,** (28), 3251-3253.

65. Seto, M.; Roizen, J. L.; Stoltz, B. M., Catalytic enantioselective alkylation of substituted dioxanone enol ethers: Ready access to C(alpha)-tetrasubstituted hydroxyketones, acids, and esters. *Angew. Chem.-Int. Edit.* **2008,** *47* (36), 6873-6876.

66. Trost, B. M.; Xu, J. Y.; Schmidt, T., Ligand controlled highly regio- and enantioselective synthesis of alpha-acyloxyketones by palladium-catalyzed allylic alkylation of 1,2-enediol carbonates. *J. Am. Chem. Soc.* **2008,** *130* (36), 11852-11853.

67. Trost, B. M.; Thaisrivongs, D. A., Strategy for Employing Unstabilized Nucleophiles in Palladium-Catalyzed Asymmetric Allylic Alkylations. *J. Am. Chem. Soc.* **2008,** *130* (43), 14092-+.

68. Evans, L. A.; Fey, N.; Harvey, J. N.; Hose, D.; Lloyd-Jones, G. C.; Murray, P.; Orpen, A. G.; Osborne, R.; Owen-Smith, G. J. J.; Purdie, M., Counterintuitive Kinetics in Tsuji-Trost Allylation: Ion-Pair Partitioning and Implications for Asymmetric Catalysis. *J. Am. Chem. Soc.* **2008,** *130* (44), 14471-+.

69. Movassaghi, M.; Ahmad, O. K., A Stereospecific Palladium-Catalyzed Route to Monoalkyl Diazenes for Mild Allylic Reduction. *Angew. Chem.-Int. Edit.* **2008,** *47* (46), 8909-8912.

70. Linton, E. C.; Kozlowski, M. C., Catalytic Enantioselective Meerwein-Eschenmoser Claisen Rearrangement: Asymmetric Synthesis of Allyl Oxindoles. *J. Am. Chem. Soc.* **2008,** *130* (48), 16162-+.

71. Trost, B. M.; Malhotra, S.; Olson, D. E.; Maruniak, A.; Du Bois, J., Asymmetric Synthesis of Diamine Derivatives via Sequential Palladium and Rhodium Catalysis. *J. Am. Chem. Soc.* **2009,** *131* (12), 4190-+.

72. Butts, C. P.; Filali, E.; Lloyd-Jones, G. C.; Norrby, P. O.; Sale, D. A.; Schramm, Y., Structure-Based Rationale for Selectivity in the Asymmetric Allylic Alkylation of Cycloalkenyl Esters Employing the Trost 'Standard Ligand' (TSL): Isolation, Analysis and Alkylation of the Monomeric form of the Cationic eta(3)-Cyclohexenyl Complex [(eta(3)-c-C6H9)Pd(TSL)](+). *J. Am. Chem. Soc.* **2009,** *131* (29), 9945-9957.

73. Sherden, N. H.; Behenna, D. C.; Virgil, S. C.; Stoltz, B. M., Unusual Allylpalladium Carboxylate Complexes: Identification of the Resting State of Catalytic Enantioselective Decarboxylative Allylic Alkylation Reactions of Ketones. *Angew. Chem.-Int. Edit.* **2009,** *48* (37), 6840-6843.

74. Fischer, D. F.; Barakat, A.; Xin, Z. Q.; Weiss, M. E.; Peters, R., The Asymmetric Aza-Claisen Rearrangement: Development of Widely Applicable Pentaphenylferrocenyl Palladacycle Catalysts. *Chem.-Eur. J.* **2009,** *15* (35), 8722-8741.

75. Yoshida, M.; Higuchi, M.; Shishido, K., Stereoselective Construction of Substituted Chromans by Palladium-Catalyzed Cyclization of Propargylic Carbonates with 2-(2-Hydroxyphenyl)acetates. *Org. Lett.* **2009,** *11* (20), 4752-4755.

76. Shu, W.; Yu, Q.; Ma, S. M., Development of a New Spiro-BOX Ligand and Its Application in Highly Enantioselective Palladium-Catalyzed Cyclization of 2-Iodoanilines with Allenes. *Adv. Synth. Catal.* **2009,** *351* (17), 2807-2810.

77. Trost, B. M.; Xu, J. Y.; Schmidt, T., Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of Enol Carbonates. *J. Am. Chem. Soc.* **2009,** *131* (51), 18343-18357.

78. Lei, B. L.; Ding, C. H.; Yang, X. F.; Wan, X. L.; Hou, X. L., Kinetic Resolution of 2,3-Dihydro-2-substituted 4-Quinolones by Palladium-Catalyzed Asymmetric Allylic Alkylation. *J. Am. Chem. Soc.* **2009,** *131* (51), 18250-+.

79. Olson, A. C.; Overman, L. E.; Sneddon, H. F.; Ziller, J. W., Catalytic Asymmetric Synthesis of Branched Chiral Allylic Phenyl Ethers from (E)-Allylic Alcohols. *Adv. Synth. Catal.* **2009,** *351* (18), 3186-3192.

80. Rodrigues, A.; Lee, E. E.; Batey, R. A., Enantioselective Palladium(II)-Catalyzed Formal [3,3]-Sigmatropic Rearrangement of 2-Allyloxypyridines and Related Heterocycles. *Org. Lett.* **2010,** *12* (2), 260-263.

81. Streuff, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M., A palladium-catalysed enolate alkylation cascade for the formation of adjacent quaternary and tertiary stereocentres. *Nat. Chem.* **2010,** *2* (3), 192-196.

82. Shintani, R.; Tsuji, T.; Park, S.; Hayashi, T., Mechanistic Investigation of the Palladium-Catalyzed Decarboxylative Cyclization of gamma-Methylidene- delta-valerolactones with lsocyanates: Kinetic Studies and Origin of the Site Selectivity in the Nucleophilic Attack at a (pi-Allyl)palladium. *J. Am. Chem. Soc.* **2010,** *132* (21), 7508-7513.

83. Trost, B. M.; Lehr, K.; Michaelis, D. J.; Xu, J. Y.; Buckl, A. K., Palladium-Catalyzed Asymmetric Allylic Alkylation of 2-Acylimidazoles as Ester Enolate Equivalents. *J. Am. Chem. Soc.* **2010,** *132* (26), 8915-+.

84. Zhang, P.; Brozek, L. A.; Morken, J. P., Pd-Catalyzed Enantioselective Allyl-Allyl Cross-Coupling. *J. Am. Chem. Soc.* **2010,** *132* (31), 10686-10688.

85. Chen, J. P.; Ding, C. H.; Liu, W.; Hou, X. L.; Dai, L. X., Palladium-Catalyzed Regio-, Diastereo-, and Enantioselective Allylic Alkylation of Acylsilanes with Monosubstituted Allyl Substrates. *J. Am. Chem. Soc.* **2010,** *132* (44), 15493-15495.

86. Cannon, J. S.; Kirsch, S. F.; Overman, L. E., Catalytic Asymmetric Synthesis of Chiral Allylic Esters. *J. Am. Chem. Soc.* **2010,** *132* (43), 15185-15191.

87. Cannon, J. S.; Kirsch, S. F.; Overman, L. E.; Sneddon, H. F., Mechanism of the Cobalt Oxazoline Palladacycle (COP)-Catalyzed Asymmetric Synthesis of Allylic Esters. *J. Am. Chem. Soc.* **2010,** *132* (43), 15192-15203.

88. Trost, B. M.; Czabaniuk, L. C., Palladium-Catalyzed Asymmetric Benzylation of 3-Aryl Oxindoles. *J. Am. Chem. Soc.* **2010,** *132* (44), 15534-15536.

89. Trost, B. M.; Osipov, M.; Dong, G. B., Palladium-Catalyzed Dynamic Kinetic Asymmetric Transformations of Vinyl Aziridines with Nitrogen Heterocycles: Rapid Access to Biologically Active Pyrroles and Indoles. *J. Am. Chem. Soc.* **2010,** *132* (44), 15800-15807.

90. Katcher, M. H.; Doyle, A. G., Palladium-Catalyzed Asymmetric Synthesis of Allylic Fluorides. *J. Am. Chem. Soc.* **2010,** *132* (49), 17402-17404.

91. Trost, B. M.; Schaffner, B.; Osipov, M.; Wilton, D. A. A., Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of beta-ketoesters: An Unusual Counterion Effect. *Angew. Chem.-Int. Edit.* **2011,** *50* (15), 3548-3551.

92. Cao, Z. P.; Liu, Y. L.; Liu, Z. Q.; Feng, X. Q.; Zhuang, M. Y.; Du, H. F., Pd-Catalyzed Asymmetric Allylic Alkylation of Indoles and Pyrroles by Chiral Alkene-Phosphine Ligands. *Org. Lett.* **2011,** *13* (9), 2164-2167.

93. Trost, B. M.; Malhotra, S.; Chan, W. H., Exercising Regiocontrol in Palladium-Catalyzed Asymmetric Prenylations and Geranylation: Unifying Strategy toward Flustramines A and B. *J. Am. Chem. Soc.* **2011,** *133* (19), 7328-7331.

94. Olson, D. E.; Maruniak, A.; Malhotra, S.; Trost, B. M.; Du Bois, J., Synthesis and Reactivity of Unique Heterocyclic Structures en Route to Substituted Diamines. *Org. Lett.* **2011,** *13* (13), 3336-3339.

95. Trost, B. M.; Osipov, M.; Kaib, P. S. J.; Sorum, M. T., Acetoxy Meldrum's Acid: A Versatile Acyl Anion Equivalent in the Pd-Catalyzed Asymmetric Allylic Alkylation. *Org. Lett.* **2011,** *13* (12), 3222-3225.

96. Trost, B. M.; Morris, P. J., Palladium-Catalyzed Diastereo- and Enantioselective Synthesis of Substituted Cyclopentanes through a Dynamic Kinetic Asymmetric Formal 3+2 -Cycloaddition of Vinyl Cyclopropanes and Alkylidene Azlactones. *Angew. Chem.-Int. Edit.* **2011,** *50* (27), 6167-6170.

97. Zhang, P.; Le, H.; Kyne, R. E.; Morken, J. P., Enantioselective Construction of All-Carbon Quaternary Centers by Branch-Selective Pd-Catalyzed Allyl Allyi Cross-Coupling. *J. Am. Chem. Soc.* **2011,** *133* (25), 9716-9719.

98. Trost, B. M.; Thaisrivongs, D. A.; Hartwig, J., Palladium-Catalyzed Asymmetric Allylic Alkylations of Polynitrogen-Containing Aromatic Heterocycles. *J. Am. Chem. Soc.* **2011,** *133* (32), 12439-12441.

99. Trost, B. M.; Burns, A. C.; Tautz, T., Readily Accessible Chiral Diene Ligands for Rh-Catalyzed Enantioselective Conjugate Additions of Boronic Acids. *Org. Lett.* **2011,** *13* (17), 4566-4569.

100. Shaghafi, M. B.; Grote, R. E.; Jarvo, E. R., Oxazolidine Synthesis by Complementary Stereospecific and Stereoconvergent Methods. *Org. Lett.* **2011,** *13* (19), 5188-5191.

101. Katcher, M. H.; Sha, A.; Doyle, A. G., Palladium-Catalyzed Regio- and Enantioselective Fluorination of Acyclic Allylic Halides. *J. Am. Chem. Soc.* **2011,** *133* (40), 15902-15905.

102. Luparia, M.; Oliveira, M. T.; Audisio, D.; Frebault, F.; Goddard, R.; Maulide, N., Catalytic Asymmetric Diastereodivergent Deracemization. *Angew. Chem.-Int. Edit.* **2011,** *50* (52), 12631-12635.

103. Trost, B. M.; Xie, J.; Sieber, J. D., The Palladium Catalyzed Asymmetric Addition of Oxindoles and Allenes: An Atom-Economical Versatile Method for the Construction of Chiral Indole Alkaloids. *J. Am. Chem. Soc.* **2011,** *133* (50), 20611-20622.

104. Trost, B. M.; Michaelis, D. J.; Charpentier, J.; Xu, J. Y., Palladium-Catalyzed Allylic Alkylation of Carboxylic Acid Derivatives: N-Acyloxazolinones as Ester Enolate Equivalents. *Angew. Chem.-Int. Edit.* **2012,** *51* (1), 204-208.

105. Behenna, D. C.; Liu, Y. Y.; Yurino, T.; Kim, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M., Enantioselective construction of quaternary N-heterocycles by palladium-catalysed decarboxylative allylic alkylation of lactams. *Nat. Chem.* **2012,** *4* (2), 130-133.

106. Mao, B.; Ji, Y. N.; Fananas-Mastral, M.; Caroli, G.; Meetsma, A.; Feringa, B. L., Highly Enantioselective Synthesis of 3-Substituted Furanones by Palladium-Catalyzed Kinetic Resolution of Unsymmetrical Allyl Acetates. *Angew. Chem.-Int. Edit.* **2012,** *51* (13), 3168-3173.

107. Kim, H.; Rhee, Y. H., Stereodefined N,O-Acetals: Pd-Catalyzed Synthesis from Homopropargylic Amines and Utility in the Flexible Synthesis of 2,6-Substituted Piperidines. *J. Am. Chem. Soc.* **2012,** *134* (9), 4011-4014.

108. Trost, B. M.; Czabaniuk, L. C., Benzylic Phosphates as Electrophiles in the Palladium-Catalyzed Asymmetric Benzylation of Azlactones. *J. Am. Chem. Soc.* **2012,** *134* (13), 5778-5781.

109. Ohmatsu, K.; Ito, M.; Kunieda, T.; Ooi, T., Ion-paired chiral ligands for asymmetric palladium catalysis. *Nat. Chem.* **2012,** *4* (6), 473-477.

110. Audisio, D.; Luparia, M.; Oliveira, M. T.; Klutt, D.; Maulide, N., Diastereodivergent De-epimerization in Catalytic Asymmetric Allylic Alkylation. *Angew. Chem.-Int. Edit.* **2012,** *51* (29), 7314-7317.

111. Trost, B. M.; Koller, R.; Schaffner, B., Enantioselective Synthesis of Tertiary a-Hydroxyketones from Unfunctionalized Ketones: Palladium-Catalyzed Asymmetric Allylic Alkylation of Enolates. *Angew. Chem.-Int. Edit.* **2012,** *51* (33), 8290-8293.

112. Wang, X. M.; Meng, F. Y.; Wang, Y.; Han, Z. B.; Chen, Y. J.; Liu, L.; Wang, Z.; Ding, K. L., Aromatic Spiroketal Bisphosphine Ligands: Palladium-Catalyzed Asymmetric Allylic Amination of Racemic Morita-Baylis-Hillman Adducts. *Angew. Chem.-Int. Edit.* **2012,** *51* (37), 9276-9282.

113. Kim, H.; Lim, W.; Im, D.; Kim, D. G.; Rhee, Y. H., Synthetic Strategy for Cyclic Amines: A Stereodefined Cyclic N,O-Acetal as a Stereocontrol and Diversity-Generating Element. *Angew. Chem.-Int. Edit.* **2012,** *51* (48), 12055-12058.

114. Trost, B. M.; Morris, P. J.; Sprague, S. J., Palladium-Catalyzed Diastereo- and Enantioselective Formal 3+2 -Cycloadditions of Substituted Vinylcyclopropanes. *J. Am. Chem. Soc.* **2012,** *134* (42), 17823-17831.

115. Li, Q. K.; Fu, C. L.; Ma, S. M., Catalytic Asymmetric Allenylation of Malonates with the Generation of Central Chirality. *Angew. Chem.-Int. Edit.* **2012,** *51* (47), 11783-11786.

116. Keith, J. A.; Behenna, D. C.; Sherden, N.; Mohr, J. T.; Ma, S.; Marinescu, S. C.; Nielsen, R. J.; Oxgaard, J.; Stoltz, B. M.; Goddard, W. A., The Reaction Mechanism of the Enantioselective Tsuji Allylation: Inner-Sphere and Outer-Sphere Pathways, Internal Rearrangements, and Asymmetric C-C Bond Formation. *J. Am. Chem. Soc.* **2012,** *134* (46), 19050-19060.

117. Wan, B. Q.; Ma, S. M., Enantioselective Decarboxylative Amination: Synthesis of Axially Chiral Allenyl Amines. *Angew. Chem.-Int. Edit.* **2013,** *52* (1), 441-445.

118. Fournier, J.; Lozano, O.; Menozzi, C.; Arseniyadis, S.; Cossy, J., Palladium-Catalyzed Asymmetric Allylic Alkylation of Cyclic Dienol Carbonates: Efficient Route to Enantioenriched gamma-Butenolides Bearing an All-Carbon alpha-Quaternary Stereogenic Center. *Angew. Chem.-Int. Edit.* **2013,** *52* (4), 1257-1261.

119. Trost, B. M.; Thaisrivongs, D. A.; Donckele, E. J., Palladium-Catalyzed Enantioselective Allylic Alkylations through C-H Activation. *Angew. Chem.-Int. Edit.* **2013,** *52* (5), 1523-1526.

120. Trost, B. M.; Masters, J. T.; Burns, A. C., Palladium-Catalyzed Asymmetric Allylic Alkylation of 3-Aryloxindoles with Allylidene Dipivalate: A Useful Enol Pivalate Product. *Angew. Chem.-Int. Edit.* **2013,** *52* (8), 2260-2264.

121. Gartshore, C. J.; Lupton, D. W., Enantioselective Palladium-Catalyzed Decarboxylative Allylation of Carbazolones and Indolones: Formal Synthesis of (+)-KopsihainanineA. *Angew. Chem.-Int. Edit.* **2013,** *52* (15), 4113-4116.

122. Nahra, F.; Mace, Y.; Lambin, D.; Riant, O., Copper/Palladium-Catalyzed 1,4 Reduction and Asymmetric Allylic Alkylation of alpha,beta-Unsaturated Ketones: Enantioselective Dual Catalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (11), 3208-3212.

123. Du, L.; Cao, P.; Xing, J. W.; Lou, Y. Z.; Jiang, L. Y.; Li, L. C.; Liao, J., Hydrogen-Bond-Promoted Palladium Catalysis: Allylic Alkylation of Indoles with Unsymmetrical 1,3-Disubstituted Allyl Acetates Using Chiral Bis(sulfoxide) Phosphine Ligands. *Angew. Chem.-Int. Edit.* **2013,** *52* (15), 4207-4211.

124. Niyomchon, S.; Audisio, D.; Luparia, M.; Maulide, N., Regio- and Enantioselective Cyclobutene Allylations. *Org. Lett.* **2013,** *15* (9), 2318-2321.

125. Reeves, C. M.; Eidamshaus, C.; Kim, J.; Stoltz, B. M., Enantioselective Construction of alpha-Quaternary Cyclobutanones by Catalytic Asymmetric Allylic Alkylation. *Angew. Chem.-Int. Edit.* **2013,** *52* (26), 6718-6721.

126. Mei, L. Y.; Wei, Y.; Xu, Q.; Shi, M., Diastereo- and Enantioselective Construction of Oxindole-Fused Spirotetrahydrofuran Scaffolds through Palladium-Catalyzed Asymmetric 3+2 Cycloaddition of Vinyl Cyclopropanes and Isatins. *Organometallics* **2013,** *32* (12), 3544-3556.

127. Trost, B. M.; Osipov, M., Palladium-Catalyzed Asymmetric Construction of Vicinal All-Carbon Quaternary Stereocenters and its Application to the Synthesis of Cyclotryptamine Alkaloids. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9176-9181.

128. Wang, Y. L.; Zhang, W. L.; Ma, S. M., A Room-Temperature Catalytic Asymmetric Synthesis of Allenes with ECNU-Phos. *J. Am. Chem. Soc.* **2013,** *135* (31), 11517-11520.

129. Zhuo, C. X.; You, S. L., Palladium-Catalyzed Intermolecular Asymmetric Allylic Dearomatization Reaction of Naphthol Derivatives. *Angew. Chem.-Int. Edit.* **2013,** *52* (38), 10056-10059.

130. Trost, B. M.; Czabaniuk, L. C., Palladium-Catalyzed Asymmetric Benzylation of Azlactones. *Chem.-Eur. J.* **2013,** *19* (45), 15210-15218.

131. Sharma, A.; Hartwig, J. F., Enantioselective Functionalization of Allylic C-H Bonds Following a Strategy of Functionalization and Diversification. *J. Am. Chem. Soc.* **2013,** *135* (47), 17983-17989.

132. Wang, X.; Guo, P.; Han, Z.; Wang, X.; Wang, Z.; Ding, K., Spiroketal-Based Diphosphine Ligands in Pd-Catalyzed Asymmetric Allylic Amination of Morita-Baylis-Hillman Adducts: Exceptionally High Efficiency and New Mechanism. *J. Am. Chem. Soc.* **2014,** *136* (1), 405-411.

133. Zaed, A. M.; Grafton, M. W.; Ahmad, S.; Sutherland, A., Asymmetric Synthesis of cis-Aminocyclopentenols, Building Blocks for Medicinal Chemistry. *J. Org. Chem.* **2014,** *79* (3), 1511-1515.

134. Ohmatsu, K.; Ito, M.; Ooi, T., Ligand-controlled E/Z selectivity and enantioselectivity in palladium-catalyzed allylation of benzofuranones with 1,2-disubstituted allylic carbonates. *Chem. Commun.* **2014,** *50* (35), 4554-4557.

135. Trost, B. M.; Masters, J. T.; Lumb, J.-P.; Fateen, D., Asymmetric synthesis of chiral cycloalkenone derivatives via palladium catalysis. *Chemical Science* **2014,** *5* (4), 1354-1360.

136. Mingat, G.; MacLellan, P.; Laars, M.; Clayden, J., Tertiary Thiols from Allylic Thiocarbamates by Tandem Enantioselective 3,3 - Sigmatropic Rearrangement and Stereospecific Arylation. *Org. Lett.* **2014,** *16* (4), 1252-1255.

137. Zeng, B.-S.; Yu, X.; Siu, P. W.; Scheidt, K. A., Catalytic enantioselective synthesis of 2-aryl-chromenes. *Chemical Science* **2014,** *5* (6), 2277-2281.

138. Reeves, C. M.; Behenna, D. C.; Stoltz, B. M., Development of (Trimethylsilyl)ethyl Ester Protected Enolates and Applications in Palladium-Catalyzed Enantioselective Allylic Alkylation: Intermolecular Cross-Coupling of Functionalized Electrophiles. *Org. Lett.* **2014,** *16* (9), 2314-2317.

139. Zhuo, C.-X.; Zhou, Y.; You, S.-L., Highly Regio- and Enantioselective Synthesis of Polysubstituted 2H-Pyrroles via Pd-Catalyzed Intermolecular Asymmetric Allylic Dearomatization of Pyrroles. *J. Am. Chem. Soc.* **2014,** *136* (18), 6590-6593.

140. Li, Q.; Fu, C.; Ma, S., Palladium-Catalyzed Asymmetric Amination of Allenyl Phosphates: Enantioselective Synthesis of Allenes with an Additional Unsaturated Unit. *Angew. Chem.-Int. Edit.* **2014,** *53* (25), 6511-6514.

141. Khan, A.; Zheng, R.; Kan, Y.; Ye, J.; Xing, J.; Zhang, Y. J., Palladium-Catalyzed Decarboxylative Cycloaddition of Vinylethylene Carbonates with Formaldehyde: Enantioselective Construction of Tertiary Vinylglycols. *Angew. Chem.-Int. Edit.* **2014,** *53* (25), 6439-6442.

142. Ohmatsu, K.; Hara, Y.; Ooi, T., In situ generation of ion-paired chiral ligands: rapid identification of the optimal ligand for palladium-catalyzed asymmetric allylation. *Chemical Science* **2014,** *5* (9), 3645-3650.

143. Misale, A.; Niyomchon, S.; Luparia, M.; Maulide, N., Asymmetric Palladium-Catalyzed Allylic Alkylation Using Dialkylzinc Reagents: A Remarkable Ligand Effect. *Angew. Chem.-Int. Edit.* **2014,** *53* (27), 7068-7073.

144. Bauer, J. M.; Frey, W.; Peters, R., Asymmetric Cascade Reaction to Allylic Sulfonamides from Allylic Alcohols by Palladium(II)/Base-Catalyzed Rearrangement of Allylic Carbamates. *Angew. Chem.-Int. Edit.* **2014,** *53* (29), 7634-7638.

145. Zhao, R.; Sun, Z.; Mo, M.; Peng, F.; Shao, Z., Catalytic Asymmetric Assembly of C3-Monosubstituted Chiral Carbazolones and Concise Formal Synthesis of (-)-Aspidofractinine: Application of Enantioselective Pd-Catalyzed Decarboxylative Protonation of Carbazolones. *Org. Lett.* **2014,** *16* (16), 4178-4181.

146. Khan, A.; Yang, L.; Xu, J.; Jin, L. Y.; Zhang, Y. J., Palladium-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Michael Acceptors: Construction of Vicinal Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2014,** *53* (42), 11257-11260.

147. Qian, X.; Ji, P.; He, C.; Zirimwabagabo, J.-O.; Archibald, M. M.; Yeagley, A. A.; Chruma, J. J., Palladium-Catalyzed Decarboxylative Generation and Asymmetric Allylation of alpha-Imino Anions. *Org. Lett.* **2014,** *16* (19), 5228-5231.

148. Zheng, C.; Zhuo, C.-X.; You, S.-L., Mechanistic Insights into the Pd-Catalyzed Intermolecular Asymmetric Allylic Dearomatization of Multisubstituted Pyrroles: Understanding the Remarkable Regio- and Enantioselectivity. *J. Am. Chem. Soc.* **2014,** *136* (46), 16251-16259.

149. Korch, K. M.; Eidamshaus, C.; Behenna, D. C.; Nam, S.; Horne, D.; Stoltz, B. M., Enantioselective Synthesis of alpha-Secondary and alpha-Tertiary Piperazin-2-ones and Piperazines by Catalytic Asymmetric Allylic Alkylation. *Angew. Chem.-Int. Edit.* **2015,** *54* (1), 179-183.

150. Xu, C.-F.; Zheng, B.-H.; Suo, J.-J.; Ding, C.-H.; Hou, X.-L., Highly Diastereo- and Enantioselective Palladium-Catalyzed 3+2 Cycloaddition of Vinyl Aziridines and alpha,beta-Unsaturated Ketones. *Angew. Chem.-Int. Edit.* **2015,** *54* (5), 1604-1607.

151. Wei, F.; Ren, C.-L.; Wang, D.; Liu, L., Highly Enantioselective 3+2 Cycloaddition of Vinylcyclopropane with Nitroalkenes Catalyzed by Palladium(0) with a Chiral Bis(tert-amine) Ligand. *Chem.-Eur. J.* **2015,** *21* (6), 2335-2338.

152. Liu, Z.-S.; Li, W.-K.; Kang, T.-R.; He, L.; Liu, Q.-Z., Palladium-Catalyzed Asymmetric Cycloadditions of Vinylcyclopropanes and in Situ Formed Unsaturated lmines: Construction of Structurally and Optically Enriched Spiroindolenines. *Org. Lett.* **2015,** *17* (1), 150-153.

153. Numajiri, Y.; Pritchett, B. P.; Chiyoda, K.; Stoltz, B. M., Enantioselective Synthesis of alpha-Quaternary Mannich Adducts by Palladium-Catalyzed Allylic Alkylation: Total Synthesis of (+)-Sibirinine. *J. Am. Chem. Soc.* **2015,** *137* (3), 1040-1043.

154. Trost, B. M.; Donckele, E. J.; Thaisrivongs, D. A.; Osipov, M.; Masters, J. T., A New Class of Non-C-2-Symmetric Ligands for Oxidative and Redox-Neutral Palladium-Catalyzed Asymmetric Allylic Alkylations of 1,3-Diketones. *J. Am. Chem. Soc.* **2015,** *137* (7), 2776-2784.

155. Numajiri, Y.; Jimenez-Oses, G.; Wang, B.; Houk, K. N.; Stoltz, B. M., Enantioselective Synthesis of Dialkylated N-Heterocycles by Palladium-Catalyzed Allylic Alkylation. *Org. Lett.* **2015,** *17* (5), 1082-1085.

156. Marziale, A. N.; Duquette, D. C.; Craig, R. A.; Kim, K. E.; Liniger, M.; Numajiri, Y.; Stoltz, B. M., An Efficient Protocol for the Palladium-Catalyzed Asymmetric Decarboxylative Allylic Alkylation Using Low Palladium Concentrations and a Palladium(II) Precatalyst. *Adv. Synth. Catal.* **2015,** *357* (10), 2238-2245.

157. Suzuki, Y.; Seki, T.; Tanaka, S.; Kitamura, M., Intramolecular Tsuji-Trost-type Allylation of Carboxylic Acids: Asymmetric Synthesis of Highly pi-Allyl Donative Lactones. *J. Am. Chem. Soc.* **2015,** *137* (30), 9539-9542.

158. Craig, R. A.; Loskot, S. A.; Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M., Palladium-Catalyzed Enantioselective Decarboxylative Allylic Alkylation of Cyclopentanones. *Org. Lett.* **2015,** *17* (21), 5160-5163.

159. Yang, L.; Khan, A.; Zheng, R. F.; Jin, L. Y.; Zhang, Y. J., Pd-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Imines. *Org. Lett.* **2015,** *17* (24), 6230-6233.

160. Mao, J. Y.; Zhang, J. D.; Jiang, H.; Bellomo, A.; Zhang, M. N.; Gao, Z. D.; Dreher, S. D.; Walsh, P. J., Palladium-Catalyzed Asymmetric Allylic Alkylations with Toluene Derivatives as Pronucleophiles. *Angew. Chem.-Int. Edit.* **2016,** *55* (7), 2526-2530.

161. Cai, A. J.; Guo, W. S.; Martinez-Rodriguez, L.; Kleij, A. W., Palladium-Catalyzed Regio- and Enantioselective Synthesis of Allylic Amines Featuring Tetrasubstituted Tertiary Carbons. *J. Am. Chem. Soc.* **2016,** *138* (43), 14194-14197.

162. Liu, J. W.; Han, Z. B.; Wang, X. M.; Meng, F. Y.; Wang, Z.; Ding, K. L., Palladium-Catalyzed Asymmetric Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters by Allylation of beta-Ketocarbonyls with Morita-Baylis-Hillman Adducts. *Angew. Chem.-Int. Edit.* **2017,** *56* (18), 5050-5054.

163. Zhang, W. L.; Ma, S. M., Palladium-Catalyzed Enantioselective Alkoxycarbonylation of Propargylic Carbonates with (R)-or (S)-3,4,5-(MeO)(3)-MeOBIPHEP. *Chem.-Eur. J.* **2017,** *23* (36), 8590-8595.

164. Panda, S.; Ready, J. M., Palladium Catalyzed Asymmetric Three-Component Coupling of Boronic Esters, Indoles, and Allylic Acetates. *J. Am. Chem. Soc.* **2017,** *139* (17), 6038-6041.

165. Chen, S. S.; Wu, M. S.; Han, Z. Y., Palladium-Catalyzed Cascade sp(2) C-H Functionalization/Intramolecular Asymmetric Allylation: From Aryl Ureas and 1,3-Dienes to Chiral Indolines. *Angew. Chem.-Int. Edit.* **2017,** *56* (23), 6641-6645.

166. Adamson, N. J.; Hull, E.; Malcolmson, S. J., Enantioselective Intermolecular Addition of Aliphatic Amines to Acyclic Dienes with a Pd-PHOX Catalyst. *J. Am. Chem. Soc.* **2017,** *139* (21), 7180-7183.

167. Starkov, P.; Moore, J. T.; Duquette, D. C.; Stoltz, B. M.; Marek, I., Enantioselective Construction of Acyclic Quaternary Carbon Stereocenters: Palladium-Catalyzed Decarboxylative Allylic Alkylation of Fully Substituted Amide Enolates. *J. Am. Chem. Soc.* **2017,** *139* (28), 9615-9620.

168. Guo, W. S.; Cai, A. J.; Xie, J. N.; Kleij, A. W., Asymmetric Synthesis of ,-Disubstituted Allylic Amines through Palladium-Catalyzed Allylic Substitution. *Angew. Chem.-Int. Edit.* **2017,** *56* (39), 11797-11801.

169. Khan, A.; Khan, S.; Khan, I.; Zhao, C.; Mao, Y. X.; Chen, Y.; Zhang, Y. J., Enantioselective Construction of Tertiary C-O Bond via Allylic Substitution of Vinylethylene Carbonates with Water and Alcohols. *J. Am. Chem. Soc.* **2017,** *139* (31), 10733-10741.

170. Bernar, I.; Fiser, B.; Blanco-Ania, D.; Gomez-Bengo, E.; Rutjes, F., Pd-Catalyzed Hydroamination of Alkoxyallenes with Azole Heterocycles: Examples and Mechanistic Proposal. *Org. Lett.* **2017,** *19* (16), 4211-4214.

171. Trost, B. M.; Li, X. X., Pd-catalyzed asymmetric allylic alkylations via C-H activation of N-allyl imines with glycinates. *Chemical Science* **2017,** *8* (10), 6815-6821.

172. Li, M. M.; Wei, Y.; Liu, J.; Chen, H. W.; Lu, L. Q.; Xiao, W. J., Sequential Visible-Light Photoactivation and Palladium Catalysis Enabling Enantioselective 4+2 Cycloadditions. *J. Am. Chem. Soc.* **2017,** *139* (41), 14707-14713.

173. Wang, P.-S.; Shen, M.-L.; Wang, T.-C.; Lin, H.-C.; Gong, L.-Z., Access to Chiral Hydropyrimidines through Palladium-Catalyzed Asymmetric Allylic C−H Amination. *Angewandte Chemie International Edition* **2017,** *56* (50), 16032-16036.

174. Rong, Z. Q.; Yang, L. C.; Liu, S.; Yu, Z. Y.; Wang, Y. N.; Tan, Z. Y.; Huang, R. Z.; Lan, Y.; Zhao, Y., Nine-Membered Benzofuran-Fused Heterocycles: Enantioselective Synthesis by Pd-Catalysis and Rearrangement via Transannular Bond Formation. *J. Am. Chem. Soc.* **2017,** *139* (43), 15304-15307.

175. Cheng, Q.; Zhang, F.; Cai, Y.; Guo, Y. L.; You, S. L., Stereodivergent Synthesis of Tetrahydrofuroindoles through Pd-Catalyzed Asymmetric Dearomative Formal 3+2 Cycloaddition. *Angew. Chem.-Int. Edit.* **2018,** *57* (8), 2134-2138.

176. Huang, J. Q.; Liu, W.; Zheng, B. H.; Liu, X. Y.; Yang, Z.; Ding, C. H.; Li, H.; Peng, Q.; Hou, X. L., Pd-Catalyzed Asymmetric Cyclopropanation Reaction of Acyclic Amides with Allyl and Polyenyl Carbonates. Experimental and Computational Studies for the Origin of Cyclopropane Formation. *Acs Catalysis* **2018,** *8* (3), 1964-1972.

177. Adamson, N. J.; Wilbur, K. C. E.; Malcolmson, S. J., Enantioselective Intermolecular Pd-Catalyzed Hydroalkylation of Acyclic 1,3-Dienes with Activated Pronucleophiles. *J. Am. Chem. Soc.* **2018,** *140* (8), 2761-2764.

178. Trost, B. M.; Bai, W. J.; Hohn, C.; Bai, Y.; Cregg, J. J., Palladium-Catalyzed Asymmetric Allylic Alkylation of 3-Substituted 1H-Indoles and Tryptophan Derivatives with Vinylcyclopropanes. *J. Am. Chem. Soc.* **2018,** *140* (21), 6710-6717.

179. Murakami, R.; Sano, K.; Iwai, T.; Taniguchi, T.; Monde, K.; Sawamura, M., Palladium-Catalyzed Asymmetric C(sp(3))-H Allylation of 2-Alkylpyridines. *Angew. Chem.-Int. Edit.* **2018,** *57* (30), 9465-9469.

180. Alexy, E. J.; Zhang, H. M.; Stoltz, B. M., Catalytic Enantioselective Synthesis of Acyclic Quaternary Centers: Palladium-Catalyzed Decarboxylative Allylic Alkylation of Fully Substituted Acyclic Enol Carbonates. *J. Am. Chem. Soc.* **2018,** *140* (32), 10109-10112.

181. Liu, W.; Ali, S. Z.; Ammann, S. E.; White, M. C., Asymmetric Allylic C-H Alkylation via Palladium(II)/cis-ArSOX Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (34), 10658-10662.

182. Panda, S.; Ready, J. M., Tandem Allylation/1,2-Boronate Rearrangement for the Asymmetric Synthesis of Indolines with Adjacent Quaternary Stereocenters. *J. Am. Chem. Soc.* **2018,** *140* (41), 13242-13252.

183. Liu, J.; Mishra, S.; Aponick, A., Enol Acetates: Versatile Substrates for the Enantioselective Intermolecular Tsuji Allylation. *J. Am. Chem. Soc.* **2018,** *140* (47), 16152-16158.

184. Zhang, H. H.; Zhao, J. J.; Yu, S. Y., Enantioselective Allylic Alkylation with 4-Alkyl-1,4-dihydropyridines Enabled by Photoredox/Palladium Cocatalysis. *J. Am. Chem. Soc.* **2018,** *140* (49), 16914-16919.

185. Moon, P. J.; Wei, Z. Y.; Lundgren, R. J., Direct Catalytic Enantioselective Benzylation from Aryl Acetic Acids. *J. Am. Chem. Soc.* **2018,** *140* (50), 17418-17422.

186. Wei, Y.; Liu, S.; Li, M. M.; Li, Y.; Lan, Y.; Lu, L. Q.; Xiao, W. J., Enantioselective Trapping of Pd-Containing 1,5-Dipoles by Photogenerated Ketenes: Access to 7-Membered Lactones Bearing Chiral Quaternary Stereocenters. *J. Am. Chem. Soc.* **2019,** *141* (1), 133-137.

187. Wertjes, W. C.; Okumura, M.; Sarlah, D., Palladium-Catalyzed Dearomative syn-1,4-Diamination. *J. Am. Chem. Soc.* **2019,** *141* (1), 163-167.

188. Gao, X.; Xia, M. R.; Yuan, C. H.; Zhou, L. J.; Sun, W.; Li, C.; Wu, B.; Zhu, D. Y.; Zhang, C.; Zheng, B.; Wang, D. Q.; Guo, H. C., Enantioselective Synthesis of Chiral Medium-Sized Cyclic Compounds via Tandem Cycloaddition/Cope Rearrangement Strategy. *Acs Catalysis* **2019,** *9* (3), 1645-1654.

189. Cheng, Q.; Xie, J. H.; Weng, Y. C.; You, S. L., Pd-Catalyzed Dearomatization of Anthranils with Vinylcyclopropanes by 4+3 Cyclization Reaction. *Angew. Chem.-Int. Edit.* **2019,** *58* (17), 5739-5743.

190. Huang, X. B.; Li, X. J.; Li, T. T.; Chen, B.; Chu, W. D.; He, L.; Liu, Q. Z., Palladium-Catalyzed Highly Enantioselective Cycloaddition of Vinyl Cyclopropanes with Imines. *Org. Lett.* **2019,** *21* (6), 1713-1716.

191. Trost, B. M.; Schultz, J. E.; Chang, T. W.; Maduabum, M. R., Chemo-, Regio-, Diastereo-, and Enantioselective Palladium Allylic Alkylation of 1,3-Dioxaboroles as Synthetic Equivalents of alpha-Hydroxyketones. *J. Am. Chem. Soc.* **2019,** *141* (24), 9521-9526.

192. Trost, B. M.; Schultz, J. E.; Bai, Y., Development of Chemo- and Enantioselective Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of α-Nitroesters. *Angewandte Chemie International Edition* **2019,** *58* (34), 11820-11825.

193. Trost, B. M.; Gholami, H.; Zell, D., Palladium-Catalyzed Asymmetric Allylic Fluoroalkylation/Trifluoromethylation. *J. Am. Chem. Soc.* **2019,** *141* (29), 11446-11451.

194. Ding, W. P.; Zhang, G. P.; Jiang, Y. J.; Du, J.; Liu, X. Y.; Chen, D.; Ding, C. H.; Deng, Q. H.; Hou, X. L., Electron-Deficient Alkynes as Dipolarophile in Pd-Catalyzed Enantioselective (3+2) Cycloaddition Reaction with Vinyl Cyclopropanes. *Org. Lett.* **2019,** *21* (17), 6805-6810.

195. Trost, B. M.; Spohr, S. M.; Rolka, A. B.; Kalnmals, C. A., Desymmetrization of Phosphinic Acids via Pd-Catalyzed Asymmetric Allylic Alkylation: Rapid Access to P-Chiral Phosphinates. *J. Am. Chem. Soc.* **2019,** *141* (36), 14098-14103.

196. Tang, C. H.; Okumura, M.; Deng, H. J.; Sarlah, D., Palladium-Catalyzed Dearomative syn-1,4-Oxyamination. *Angew. Chem.-Int. Edit.* **2019,** *58* (44), 15762-15766.

197. Fan, L. F.; Luo, S. W.; Chen, S. S.; Wang, T. C.; Wang, P. S.; Gong, L. Z., Nucleophile Coordination Enabled Regioselectivity in Palladium-Catalyzed Asymmetric Allylic C-H Alkylation. *Angew. Chem.-Int. Edit.* **2019,** *58* (47), 16806-16810.

198. Trost, B. M.; Zuo, Z. J.; Schultz, J. E.; Anugula, N.; Carr, K. A., A borane-mediated palladium-catalyzed reductive allylic alkylation of alpha,beta-unsaturated carbonyl compounds. *Chemical Science* **2020,** *11* (8), 2136-2140.

199. Yu, X.; Wannenmacher, N.; Peters, R., Stereospecific Asymmetric Synthesis of Tertiary Allylic Alcohol Derivatives by Catalytic [2,3]-Meisenheimer Rearrangements. *Angewandte Chemie International Edition* **2020,** *59* (27), 10944-10948.

200. Mao, B.; Liu, H.; Yan, Z.; Xu, Y.; Xu, J.; Wang, W.; Wu, Y.; Guo, H., Palladium-Catalyzed Asymmetric [4+2] Cycloaddition of 2-Methylidenetrimethylene Carbonate with Alkenes: Access to Chiral Tetrahydropyran-Fused Spirocyclic Scaffolds. *Angewandte Chemie International Edition* **2020,** *59* (28), 11316-11320.

201. Wang, H.; Luo, H.; Zhang, Z.-M.; Zheng, W.-F.; Yin, Y.; Qian, H.; Zhang, J.; Ma, S., Pd-Catalyzed Enantioselective Syntheses of Trisubstituted Allenes via Coupling of Propargylic Benzoates with Organoboronic Acids. *J. Am. Chem. Soc.* **2020,** *142* (21), 9763-9771.

202. Li, M.-M.; Xiong, Q.; Qu, B.-L.; Xiao, Y.-Q.; Lan, Y.; Lu, L.-Q.; Xiao, W.-J., Utilizing Vinylcyclopropane Reactivity: Palladium-Catalyzed Asymmetric [5+2] Dipolar Cycloadditions. *Angewandte Chemie International Edition* **2020,** *59* (40), 17429-17434.

203. Yang, G.; Ke, Y.-M.; Zhao, Y., Stereoselective Access to Polyfunctionalized Nine-Membered Heterocycles by Sequential Gold and Palladium Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (23), 12775-12780.

204. Faltracco, M.; van de Vrande, K. N. A.; Dijkstra, M.; Saya, J. M.; Hamlin, T. A.; Ruijter, E., Palladium-Catalyzed Cascade to Benzoxepins by Using Vinyl-Substituted Donor–Acceptor Cyclopropanes. *Angewandte Chemie International Edition* **2021,** *60* (26), 14410-14414.

205. Masson-Makdissi, J.; Prieto, L.; Abel-Snape, X.; Lautens, M., Enantio- and Diastereodivergent Sequential Catalysis Featuring Two Transition-Metal-Catalyzed Asymmetric Reactions. *Angewandte Chemie International Edition* **2021,** *60* (31), 16932-16936.

206. Jang, D.-J.; Lee, S.; Lee, J.; Moon, D.; Rhee, Y. H., Palladium-Catalyzed Asymmetric Decarboxylative Addition of β-Keto Acids to Heteroatom-Substituted Allenes. *Angewandte Chemie International Edition* **2021,** *60* (41), 22166-22171.

207. Xie, J.-H.; Zheng, C.; You, S.-L., Palladium-Catalyzed Dearomative Methoxyallylation of 3-Nitroindoles with Allyl Carbonates. *Angewandte Chemie International Edition* **2021,** *60* (41), 22184-22188.

208. Zhang, H.-H.; Tang, M.; Zhao, J.-J.; Song, C.; Yu, S., Enantioselective Reductive Homocoupling of Allylic Acetates Enabled by Dual Photoredox/Palladium Catalysis: Access to C2-Symmetrical 1,5-Dienes. *J. Am. Chem. Soc.* **2021,** *143* (32), 12836-12846.

209. Kizhakkayil Mangadan, A. R.; Liu, J.; Aponick, A., Enantioselective Lactonization by π-Acid-Catalyzed Allylic Substitution: A Complement to π-Allylmetal Chemistry. *Angewandte Chemie International Edition* **2021,** *60* (41), 22224-22229.

210. Pham, Q. H.; Tague, A. J.; Richardson, C.; Hyland, C. J. T.; Pyne, S. G., The Pd-catalysed asymmetric allylic alkylation reactions of sulfamidate imines. *Chemical Science* **2021,** *12* (38), 12695-12703.

211. Doyle, M. G. J.; Gabbey, A. L.; McNutt, W.; Lundgren, R. J., Enantioselective Tertiary Electrophile (Hetero)Benzylation: Pd-Catalyzed Substitution of Isoprene Monoxide with Arylacetates**. *Angewandte Chemie International Edition* **2021,** *60* (51), 26495-26499.

212. Wang, T.-C.; Zhu, L.; Luo, S.; Nong, Z.-S.; Wang, P.-S.; Gong, L.-Z., Palladium-Catalyzed Enantioselective C(sp3)–H/C(sp3)–H Umpolung Coupling of N-Allylimine and α-Aryl Ketones. *J. Am. Chem. Soc.* **2021,** *143* (48), 20454-20461.

213. Zheng, J.; Tang, N.; Xie, H.; Breit, B., Regio-, Diastereo-, and Enantioselective Decarboxylative Hydroaminoalkylation of Dienol Ethers Enabled by Dual Palladium/Photoredox Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (20), e202200105.

214. Wang, Y.-C.; Xiao, Z.-X.; Wang, M.; Yang, S.-Q.; Liu, J.-B.; He, Z.-T., Umpolung Asymmetric 1,5-Conjugate Addition via Palladium Hydride Catalysis. *Angewandte Chemie International Edition* **2023,** *62* (2), e202215568.

215. Yang, S.-Q.; Han, A.-J.; Liu, Y.; Tang, X.-Y.; Lin, G.-Q.; He, Z.-T., Catalytic Asymmetric Hydroalkoxylation and Formal Hydration and Hydroaminoxylation of Conjugated Dienes. *J. Am. Chem. Soc.* **2023,** *145* (7), 3915-3925.

216. Nilova, A.; Mannchen, M. D.; Noel, A. N.; Semenova, E.; Grenning, A. J., Vicinal stereocenters via asymmetric allylic alkylation and Cope rearrangement: a straightforward route to functionally and stereochemically rich heterocycles. *Chemical Science* **2023,** *14* (10), 2755-2762.

217. Nong, Z.-S.; Chen, X.-R.; Wang, P.-S.; Hong, X.; Gong, L.-Z., Enantioconvergent Palladium-Catalyzed Alkylation of Tertiary Allylic C−H Bonds. *Angewandte Chemie International Edition* **2023,** *62* (46), e202312547.

218. Xie, H.; Chen, H.; Dutta, U.; Lan, Y.; Breit, B., Photochemical Asymmetric Palladium-Catalyzed Allylation Reaction: Expeditious Entry to Chiral 1,2-Amino Alcohols and 1,2-Diamines. *ACS Catalysis* **2024,** *14* (17), 13352-13361.

219. Cai, S.; Zhao, Z.; Yang, G.; Huang, H., Dynamic amine sorting enables multiselective construction of unsymmetrical chiral diamines. *Nat. Chem.* **2024,** *16* (12), 1972-1981.

2.5.2 Asymmetric Electrophilic Allylation: Ir

1. Ohmura, T.; Hartwig, J. F., Regio- and enantioselective allylic amination of achiral allylic esters catalyzed by an iridium-phosphoramidite complex. *J. Am. Chem. Soc.* **2002,** *124* (51), 15164-15165.

2. Kanayama, T.; Yoshida, K.; Miyabe, H.; Kimachi, T.; Takemoto, Y., Synthesis of beta-substituted alpha-amino acids with use of iridium-catalyzed asymmetric allylic substitution. *J. Org. Chem.* **2003,** *68* (16), 6197-6201.

3. Lopez, F.; Ohmura, T.; Hartwig, J. F., Regio- and enantioselective iridium-catalyzed intermolecular allylic etherification of achiral allylic carbonates with phenoxides. *J. Am. Chem. Soc.* **2003,** *125* (12), 3426-3427.

4. Alexakis, A.; Polet, D., Very efficient phosphoramidite ligand for asymmetric iridium- catalyzed allylic alkylation. *Org. Lett.* **2004,** *6* (20), 3529-3532.

5. Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M., Readily available 2.2.2 -bicyclooctadienes as new chiral ligands for Ir(I): Catalytic, kinetic resolution of allyl carbonates. *J. Am. Chem. Soc.* **2004,** *126* (6), 1628-1629.

6. Lipowsky, G.; Miller, N.; Helmchen, G., Regio- and enantioselective iridium-catalyzed allylic alkylation with in situ activated P,C-chelate complexes. *Angew. Chem.-Int. Edit.* **2004,** *43* (35), 4595-4597.

7. Miyabe, H.; Matsumura, A.; Moriyama, K.; Takemoto, Y., Utility of the iridium complex of the pybox ligand in regio- and enantioselective allylic substitution. *Org. Lett.* **2004,** *6* (24), 4631-4634.

8. Shu, C. T.; Hartwig, J. E., Iridium-catalyzed intermolecular allylic etherification with aliphatic alkoxides: Asymmetric synthesis of dihydropyrans and dihydrofurans. *Angew. Chem.-Int. Edit.* **2004,** *43* (36), 4794-4797.

9. Shu, C. T.; Leitner, A.; Hartwig, J. F., Enantioselective allylation of aromatic amines after in situ generation of an activated cyclometalated iridium catalyst. *Angew. Chem.-Int. Edit.* **2004,** *43* (36), 4797-4800.

10. Graening, T.; Hartwig, J. F., Iridium-catalyzed regio- and enantioselective allylation of ketone enolates. *J. Am. Chem. Soc.* **2005,** *127* (49), 17192-17193.

11. Leitner, A.; Shekhar, S.; Pouy, M. J.; Hartwig, J. F., A simple iridium catalyst with a single resolved stereocenter for enantioselective allylic amination. Catalyst selection from mechanistic analysis. *J. Am. Chem. Soc.* **2005,** *127* (44), 15506-15514.

12. Leitner, A.; Shu, C. T.; Hartwig, J. F., Effects of catalyst activation and ligand steric properties on the enantioselective allylation of amines and phenoxides. *Org. Lett.* **2005,** *7* (6), 1093-1096.

13. Polet, D.; Alexakis, A., Kinetic study of various phosphoramidite ligands in the iridium-catalyzed allylic substitution. *Org. Lett.* **2005,** *7* (8), 1621-1624.

14. Welter, C.; Dahnz, A.; Brunner, B.; Streiff, S.; Dubon, P.; Helmchen, G., Highly enantioselective syntheses of heterocycles via intramolecular Ir-catalyzed allylic amination and etherification. *Org. Lett.* **2005,** *7* (7), 1239-1242.

15. Lyothier, I.; Defieber, C.; Carreira, E. M., Iridium-catalyzed enantioselective synthesis of allylic alcohols: Silanolates as hydroxide equivalents. *Angew. Chem.-Int. Edit.* **2006,** *45* (37), 6204-6207.

16. Schelwies, M.; Dubon, P.; Helmchen, G., Enantioselective modular synthesis of 2,4-disubstituted cyclopentenones by iridium-catalyzed allylic alkylation. *Angew. Chem.-Int. Edit.* **2006,** *45* (15), 2466-2469.

17. Weihofen, R.; Tverskoy, E.; Helmchen, G., Salt-free iridium-catalyzed asymmetric allylic aminations with N,N-diacylamines and ortho-nosylamide as ammonia equivalents. *Angew. Chem.-Int. Edit.* **2006,** *45* (33), 5546-5549.

18. Shekhar, S.; Trantow, B.; Leitner, A.; Hartwig, J. F., Sequential catalytic isomerization and allylic substitution. Conversion of racemic branched allylic carbonates to enantioenriched allylic substitution products. *J. Am. Chem. Soc.* **2006,** *128* (36), 11770-11771.

19. Singh, O. V.; Han, H., Iridium(I)-catalyzed regio- and enantioselective decarboxylative allylic amidation of substituted allyl benzyl imidodicarbonates. *J. Am. Chem. Soc.* **2007,** *129* (4), 774-775.

20. Weix, D. J.; Hartwig, J. F., Regioselective and enantioselective iridium-catalyzed allylation of enamines. *J. Am. Chem. Soc.* **2007,** *129* (25), 7720-+.

21. Yamashita, Y.; Gopalarathnam, A.; Hartwig, J. F., Iridium-catalyzed, asymmetric amination of allylic alcohols activated by Lewis acids. *J. Am. Chem. Soc.* **2007,** *129* (24), 7508-+.

22. Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M., Iridium-catalyzed synthesis of primary allylic amines from allylic alcohols: Sulfamic acid as amonia equivalent. *Angew. Chem.-Int. Edit.* **2007,** *46* (17), 3139-3143.

23. Ueno, S.; Hartwig, J. F., Direct, iridium-catalyzed enantioselective and regioselective allylic etherification with aliphatic alcohols. *Angew. Chem.-Int. Edit.* **2008,** *47* (10), 1928-1931.

24. Spiess, S.; Welter, C.; Franck, G.; Taquet, J. P.; Helmchen, G., Iridium-catalyzed asymmetric allylic substitutions - Very high regioselectivity and air stability with a catalyst derived from dibenzo[a,e]cyclooctatetraene and a phosphoramidite. *Angew. Chem.-Int. Edit.* **2008,** *47* (40), 7652-7655.

25. Madrahimov, S. T.; Markovic, D.; Hartwig, J. F., The Allyl Intermediate in Regioselective and Enantioselective Iridium-Catalyzed Asymmetric Allylic Substitution Reactions. *J. Am. Chem. Soc.* **2009,** *131* (21), 7228-+.

26. Weix, D. J.; Markovic, D.; Ueda, M.; Hartwig, J. F., Direct, Intermolecular, Enantioselective, Iridium-Catalyzed Allylation of Carbamates to Form Carbamate-Protected, Branched Allylic Amines. *Org. Lett.* **2009,** *11* (13), 2944-2947.

27. Pouy, M. J.; Stanley, L. M.; Hartwig, J. F., Enantioselective, Iridium-Catalyzed Monoallylation of Ammonia. *J. Am. Chem. Soc.* **2009,** *131* (32), 11312-+.

28. Stanley, L. M.; Hartwig, J. E., Iridium-Catalyzed Regio- and Enantioselective N-Allylation of Indoles. *Angew. Chem.-Int. Edit.* **2009,** *48* (42), 7841-7844.

29. He, H.; Liu, W. B.; Dai, L. X.; You, S. L., Enantioselective Synthesis of 2,3-Dihydro-1H-benzo b azepines: Iridium-Catalyzed Tandem Allylic Vinylation/Amination Reaction. *Angew. Chem.-Int. Edit.* **2010,** *49* (8), 1496-1499.

30. Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F., Iridium-Catalyzed Kinetic Asymmetric Transformations of Racemic Allylic Benzoates. *J. Am. Chem. Soc.* **2010,** *132* (26), 8918-+.

31. Wu, Q. F.; He, H.; Liu, W. B.; You, S. L., Enantioselective Construction of Spiroindolenines by Ir-Catalyzed Allylic Alkylation Reactions. *J. Am. Chem. Soc.* **2010,** *132* (33), 11418-11419.

32. Roggen, M.; Carreira, E. M., Stereospecific Substitution of Allylic Alcohols To Give Optically Active Primary Allylic Amines: Unique Reactivity of a (P,alkene)Ir Complex Modulated by Iodide. *J. Am. Chem. Soc.* **2010,** *132* (34), 11917-11919.

33. Teichert, J. F.; Fananas-Mastral, M.; Feringa, B. L., Iridium-Catalyzed Asymmetric Intramolecular Allylic Amidation: Enantioselective Synthesis of Chiral Tetrahydroisoquinolines and Saturated Nitrogen Heterocycles. *Angew. Chem.-Int. Edit.* **2011,** *50* (3), 688-691.

34. Gartner, M.; Mader, S.; Seehafer, K.; Helmchen, G., Enantio- and Regioselective Iridium-Catalyzed Allylic Hydroxylation. *J. Am. Chem. Soc.* **2011,** *133* (7), 2072-2075.

35. Wu, Q. F.; Liu, W. B.; Zhuo, C. X.; Rong, Z. Q.; Ye, K. Y.; You, S. L., Iridium-Catalyzed Intramolecular Asymmetric Allylic Dearomatization of Phenols. *Angew. Chem.-Int. Edit.* **2011,** *50* (19), 4455-4458.

36. Gartner, M.; Jakel, M.; Achatz, M.; Sonnenschein, C.; Tverskoy, O.; Helmchen, G., Enantioselective Iridium-Catalyzed Allylic Substitutions with Hydroxamic Acid Derivatives as N-Nucleophiles. *Org. Lett.* **2011,** *13* (11), 2810-2813.

37. Roggen, M.; Carreira, E. M., Enantioselective Allylic Etherification: Selective Coupling of Two Unactivated Alcohols. *Angew. Chem.-Int. Edit.* **2011,** *50* (24), 5568-5571.

38. Touchet, S.; Carreaux, F.; Molander, G. A.; Carboni, B.; Bouillon, A., Iridium-Catalyzed Allylic Amination Route to a-Aminoboronates: Illustration of the Decisive Role of Boron Substituents. *Adv. Synth. Catal.* **2011,** *353* (18), 3391-3396.

39. Wu, Q. F.; Zheng, C.; You, S. L., Enantioselective Synthesis of Spiro Cyclopentane-1,3 '-indoles and 2,3,4,9-Tetrahydro-1H-carbazoles by Iridium-Catalyzed Allylic Dearomatization and Stereospecific Migration. *Angew. Chem.-Int. Edit.* **2012,** *51* (7), 1680-1683.

40. Lafrance, M.; Roggen, M.; Carreira, E. M., Direct, Enantioselective Iridium-Catalyzed Allylic Amination of Racemic Allylic Alcohols. *Angew. Chem.-Int. Edit.* **2012,** *51* (14), 3470-3473.

41. Liu, W. B.; Zheng, C.; Zhuo, C. X.; Dai, L. X.; You, S. L., Iridium-Catalyzed Allylic Alkylation Reaction with N-Aryl Phosphoramidite Ligands: Scope and Mechanistic Studies. *J. Am. Chem. Soc.* **2012,** *134* (10), 4812-4821.

42. Liu, W. B.; Zhang, X.; Dai, L. X.; You, S. L., Asymmetric N-Allylation of Indoles Through the Iridium-Catalyzed Allylic Alkylation/Oxidation of Indolines. *Angew. Chem.-Int. Edit.* **2012,** *51* (21), 5183-5187.

43. Madrahimov, S. T.; Hartwig, J. F., Origins of Enantioselectivity during Allylic Substitution Reactions Catalyzed by Metallacyclic Iridium Complexes. *J. Am. Chem. Soc.* **2012,** *134* (19), 8136-8147.

44. Roggen, M.; Carreira, E. M., Enantioselective Allylic Thioetherification: The Effect of Phosphoric Acid Diester on Iridium-Catalyzed Enantioconvergent Transformations. *Angew. Chem.-Int. Edit.* **2012,** *51* (34), 8652-8655.

45. Chen, W. Y.; Hartwig, J. F., Iridium-Catalyzed Regioselective and Enantioselective Allylation of Trimethylsiloxyfuran. *J. Am. Chem. Soc.* **2012,** *134* (37), 15249-15252.

46. Hu, J.; Yang, Q. J.; Xu, J. B.; Huang, C.; Fan, B. M.; Wang, J.; Lin, C. Y.; Bian, Z. X.; Chan, A. S. C., Iridium-catalyzed asymmetric hydroalkynylation reactions of oxabenzonorbornadienes. *Organic & Biomolecular Chemistry* **2013,** *11* (5), 814-820.

47. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allylic Vinylation. *J. Am. Chem. Soc.* **2013,** *135* (3), 994-997.

48. Chen, W. Y.; Hartwig, J. F., Control of Diastereoselectivity for Iridium-Catalyzed Allylation of a Prochiral Nucleophile with a Phosphate Counterion. *J. Am. Chem. Soc.* **2013,** *135* (6), 2068-2071.

49. Zhuo, C. X.; Wu, Q. F.; Zhao, Q.; Xu, Q. L.; You, S. L., Enantioselective Functionalization of Indoles and Pyrroles via an in Situ-Formed Spiro Intermediate. *J. Am. Chem. Soc.* **2013,** *135* (22), 8169-8172.

50. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allylic Alkynylation. *Angew. Chem.-Int. Edit.* **2013,** *52* (29), 7532-7535.

51. Liu, W. B.; Reeves, C. M.; Virgil, S. C.; Stoltz, B. M., Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters via Ir-Catalyzed Regio-, Diastereo-, and Enantioselective Allylic Alkylation and Applications in Sequential Pd Catalysis. *J. Am. Chem. Soc.* **2013,** *135* (29), 10626-10629.

52. Liu, W. B.; Reeves, C. M.; Stoltz, B. M., Enantio-, Diastereo-, and Regioselective Iridium-Catalyzed Asymmetric Allylic Alkylation of Acyclic beta-Ketoesters. *J. Am. Chem. Soc.* **2013,** *135* (46), 17298-17301.

53. Zhang, X.; Han, L.; You, S. L., Ir-catalyzed intermolecular asymmetric allylic dearomatization reaction of indoles. *Chemical Science* **2014,** *5* (3), 1059-1063.

54. Chen, W. Y.; Hartwig, J. F., Cation Control of Diastereoselectivity in Iridium-Catalyzed Allylic Substitutions. Formation of Enantioenriched Tertiary Alcohols and Thioethers by Allylation of 5H-Oxazol-4-ones and 5H-Thiazol-4-ones. *J. Am. Chem. Soc.* **2014,** *136* (1), 377-382.

55. Qu, J.; Rossberg, L.; Helmchen, G., Enantio- and Regioselective Iridium-Catalyzed Allylic Esterification. *J. Am. Chem. Soc.* **2014,** *136* (4), 1272-1275.

56. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allyl-Alkene Coupling. *J. Am. Chem. Soc.* **2014,** *136* (8), 3006-3009.

57. Ye, K. Y.; Dai, L. X.; You, S. L., Regio-and Enantioselective Synthesis of N-Allylindoles by Iridium-Catalyzed Allylic Amination/Transition-Metal-Catalyzed Cyclization Reactions. *Chem.-Eur. J.* **2014,** *20* (11), 3040-3044.

58. Yang, Z. P.; Wu, Q. F.; You, S. L., Direct Asymmetric Dearomatization of Pyridines and Pyrazines by Iridium-Catalyzed Allylic Amination Reactions. *Angew. Chem.-Int. Edit.* **2014,** *53* (27), 6986-6989.

59. Chen, M.; Hartwig, J. F., Iridium-Catalyzed Enantioselective Allylic Substitution of Unstabilized Enolates Derived from alpha,beta-Unsaturated Ketone. *Angew. Chem.-Int. Edit.* **2014,** *53* (33), 8691-8695.

60. Zhuo, C.-X.; Zheng, C.; You, S.-L., Transition-Metal-Catalyzed Asymmetric Allylic Dearomatization Reactions. *Accounts Chem. Res.* **2014,** *47* (8), 2558-2573.

61. Hamilton, J. Y.; Hauser, N.; Sarlah, D.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allyl-Allylsilane Cross-Coupling. *Angew. Chem.-Int. Edit.* **2014,** *53* (40), 10759-10762.

62. Chen, M.; Hartwig, J. F., Iridium-Catalyzed Regio- and Enantioselective Allylic Substitution of Silyl Dienolates Derived from Dioxinones. *Angew. Chem.-Int. Edit.* **2014,** *53* (45), 12172-12176.

63. Chen, W.; Chen, M.; Hartwig, J. F., Diastereo- and Enantioselective Iridium-Catalyzed Allylation of Cyclic Ketone Enolates: Synergetic Effect of Ligands and Barium Enolates. *J. Am. Chem. Soc.* **2014,** *136* (45), 15825-15828.

64. Grange, R. L.; Clizbe, E. A.; Counsell, E. J.; Evans, P. A., Enantioselective construction of C-chiral allylic sulfilimines via the iridium-catalyzed allylic amination with S,S-diphenylsulfilimine: asymmetric synthesis of primary allylic amines. *Chemical Science* **2015,** *6* (1), 777-781.

65. Zhang, X.; Yang, Z.-P.; Huang, L.; You, S.-L., Highly Regio- and Enantioselective Synthesis of N-Substituted 2-Pyridones: Iridium-Catalyzed Intermolecular Asymmetric Allylic Amination. *Angew. Chem.-Int. Edit.* **2015,** *54* (6), 1873-1876.

66. Breitler, S.; Carreira, E. M., Formaldehyde N,N-Dialkylhydrazones as Neutral Formyl Anion Equivalents in Iridium-Catalyzed Asymmetric Allylic Substitution. *J. Am. Chem. Soc.* **2015,** *137* (16), 5296-5299.

67. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allylic Alkylation with Functionalized Organozinc Bromides. *Angew. Chem.-Int. Edit.* **2015,** *54* (26), 7644-7647.

68. Zhang, Q.; Stockdale, D. P.; Mixdorf, J. C.; Topczewski, J. J.; Nguyen, H. M., Iridium-Catalyzed Enantioselective Fluorination of Racemic, Secondary Allylic Trichloroacetimidates. *J. Am. Chem. Soc.* **2015,** *137* (37), 11912-11915.

69. Zhuo, C. X.; Zhou, Y.; Cheng, Q.; Huang, L.; You, S. L., Enantioselective Construction of Spiroindolines with Three Contiguous Stereogenic Centers and Chiral Tryptamine Derivatives via Reactive Spiroindolenine Intermediates. *Angew. Chem.-Int. Edit.* **2015,** *54* (47), 14146-14149.

70. Chen, M.; Hartwig, J. F., Iridium-Catalyzed Enantioselective Allylic Substitution of Enol Silanes from Vinylogous Esters and Amides. *J. Am. Chem. Soc.* **2015,** *137* (43), 13972-13979.

71. Yang, Z. P.; Wu, Q. F.; Shao, W.; You, S. L., Iridium-Catalyzed Intramolecular Asymmetric Allylic Dearomatization Reaction of Pyridines, Pyrazines, Quinolines, and Isoquinolines. *J. Am. Chem. Soc.* **2015,** *137* (50), 15899-15906.

72. Cheng, Q.; Wang, Y.; You, S. L., Chemo-, Diastereo-, and Enantioselective Iridium-Catalyzed Allylic Intramolecular Dearomatization Reaction of Naphthol Derivatives. *Angew. Chem.-Int. Edit.* **2016,** *55* (10), 3496-3499.

73. Wu, Q. F.; Zheng, C.; Zhuo, C. X.; You, S. L., Highly efficient synthesis and stereoselective migration reactions of chiral five-membered aza-spiroindolenines: scope and mechanistic understanding. *Chemical Science* **2016,** *7* (7), 4453-4459.

74. Jiang, X. Y.; Chen, W. Y.; Hartwig, J. F., Iridium-Catalyzed Diastereoselective and Enantioselective Allylic Substitutions with Acyclic -Alkoxy Ketones. *Angew. Chem.-Int. Edit.* **2016,** *55* (19), 5819-5823.

75. Liu, W. B.; Okamoto, N.; Alexy, E. J.; Hong, A. Y.; Tran, K.; Stoltz, B. M., Enantioselective gamma-Alkylation of alpha,beta-Unsaturated Malonates and Ketoesters by a Sequential Ir-Catalyzed Asymmetric Allylic Alkylation/Cope Rearrangement. *J. Am. Chem. Soc.* **2016,** *138* (16), 5234-5237.

76. Huang, L.; Dai, L. X.; You, S. L., Enantioselective Synthesis of Indole-Annulated Medium-Sized Rings. *J. Am. Chem. Soc.* **2016,** *138* (18), 5793-5796.

77. Liu, J.; Cao, C. G.; Sun, H. B.; Zhang, X.; Niu, D. W., Catalytic Asymmetric Umpolung Allylation of Imines. *J. Am. Chem. Soc.* **2016,** *138* (40), 13103-13106.

78. Hethcox, J. C.; Shockley, S. E.; Stoltz, B. M., Iridium-Catalyzed Stereoselective Allylic Alkylation Reactions with Crotyl Chloride. *Angew. Chem.-Int. Edit.* **2016,** *55* (52), 16092-16095.

79. Yang, Z. P.; Zheng, C.; Huang, L.; Qian, C.; You, S. L., Iridium-Catalyzed Intramolecular Asymmetric Allylic Dearomatization Reaction of Benzoxazoles, Benzothiazoles, and Benzimidazoles. *Angew. Chem.-Int. Edit.* **2017,** *56* (6), 1530-1534.

80. Tu, H. F.; Zheng, C.; Xu, R. Q.; Liu, X. J.; You, S. L., Iridium-Catalyzed Intermolecular Asymmetric Dearomatization of beta-Naphthols with Allyl Alcohols or Allyl Ethers. *Angew. Chem.-Int. Edit.* **2017,** *56* (12), 3237-3241.

81. Liu, X. J.; You, S. L., Enantioselective Iridium-Catalyzed Allylic Substitution with 2-Methylpyridines. *Angew. Chem.-Int. Edit.* **2017,** *56* (14), 4002-4005.

82. Rossler, S. L.; Krautwald, S.; Carreira, E. M., Study of Intermediates in Iridium-(Phosphoramidite,Olefin)-Catalyzed Enantioselective Allylic Substitution. *J. Am. Chem. Soc.* **2017,** *139* (10), 3603-3606.

83. Hamilton, J. Y.; Rossler, S. L.; Carreira, E. M., Enantio- and Diastereoselective Spiroketalization Catalyzed by Chiral Iridium Complex. *J. Am. Chem. Soc.* **2017,** *139* (24), 8082-8085.

84. Huang, L.; Cai, Y.; Zheng, C.; Dai, L. X.; You, S. L., Iridium-Catalyzed Enantioselective Synthesis of Pyrrole-Annulated Medium-Sized-Ring Compounds. *Angew. Chem.-Int. Edit.* **2017,** *56* (35), 10545-10548.

85. Wang, Y.; Zheng, C.; You, S. L., Iridium-Catalyzed Asymmetric Allylic Dearomatization by a Desymmetrization Strategy. *Angew. Chem.-Int. Edit.* **2017,** *56* (47), 15093-15097.

86. Yang, Z. P.; Jiang, R.; Zheng, C.; You, S. L., Iridium-Catalyzed Intramolecular Asymmetric Allylic Alkylation of Hydroxyquinolines: Simultaneous Weakening of the Aromaticity of Two Consecutive Aromatic Rings. *J. Am. Chem. Soc.* **2018,** *140* (8), 3114-3119.

87. Petrone, D. A.; Isomura, M.; Franzoni, I.; Rossler, S. L.; Carreira, E. M., Allenylic Carbonates in Enantioselective Iridium-Catalyzed Alkylations. *J. Am. Chem. Soc.* **2018,** *140* (13), 4697-4704.

88. Hethcox, J. C.; Shockley, S. E.; Stoltz, B. M., Enantioselective Synthesis of Vicinal All-Carbon Quaternary Centers via Iridium-Catalyzed Allylic Alkylation. *Angew. Chem.-Int. Edit.* **2018,** *57* (28), 8664-8667.

89. He, Z. T.; Hartwig, J. F., Enantioselective alpha-functionalizations of ketones via allylic substitution of silyl enol ethers. *Nat. Chem.* **2019,** *11* (2), 177-183.

90. Isomura, M.; Petrone, D. A.; Carreira, E. M., Coordination-Induced Stereocontrol over Carbocations: Asymmetric Reductive Deoxygenation of Racemic Tertiary Alcohols. *J. Am. Chem. Soc.* **2019,** *141* (11), 4738-4748.

91. Sandmeier, T.; Goetzke, F. W.; Krautwald, S.; Carreira, E. M., Iridium-Catalyzed Enantioselective Allylic Substitution with Aqueous Solutions of Nucleophiles. *J. Am. Chem. Soc.* **2019,** *141* (31), 12212-12218.

92. Sorlin, A. M.; Mixdorf, J. C.; Rotella, M. E.; Martin, R. T.; Gutierrez, O.; Nguyen, H. M., The Role of Trichloroacetimidate To Enable Iridium-Catalyzed Regio-and Enantioselective Allylic Fluorination: A Combined Experimental and Computational Study. *J. Am. Chem. Soc.* **2019,** *141* (37), 14843-14852.

93. Chen, P.; Li, Y.; Chen, Z. C.; Du, W.; Chen, Y. C., Pseudo-Stereodivergent Synthesis of Enantioenriched Tetrasubstituted Alkenes by Cascade 1,3-Oxo-Allylation/Cope Rearrangement. *Angew. Chem.-Int. Edit.* **2020,** *59* (18), 7083-7088.

94. Glatz, F.; Petrone, D. A.; Carreira, E. M., Ir-Catalyzed Enantioconvergent Synthesis of Diversely Protected Allenylic Amines Employing Ammonia Surrogates. *Angewandte Chemie International Edition* **2020,** *59* (38), 16404-16408.

95. Han, M.; Yang, M.; Wu, R.; Li, Y.; Jia, T.; Gao, Y.; Ni, H.-L.; Hu, P.; Wang, B.-Q.; Cao, P., Highly Enantioselective Iridium-Catalyzed Coupling Reaction of Vinyl Azides and Racemic Allylic Carbonates. *J. Am. Chem. Soc.* **2020,** *142* (31), 13398-13405.

96. Sun, X.-S.; Wang, X.-H.; Tao, H.-Y.; Wei, L.; Wang, C.-J., Catalytic asymmetric synthesis of quaternary trifluoromethyl α- to ε-amino acid derivatives via umpolung allylation/2-aza-Cope rearrangement. *Chemical Science* **2020,** *11* (40), 10984-10990.

97. Wang, Y.; Zhang, W.-Y.; Xie, J.-H.; Yu, Z.-L.; Tan, J.-H.; Zheng, C.; Hou, X.-L.; You, S.-L., Enantioselective Desymmetrization of Bisphenol Derivatives via Ir-Catalyzed Allylic Dearomatization. *J. Am. Chem. Soc.* **2020,** *142* (45), 19354-19359.

98. Sandmeier, T.; Carreira, E. M., Enantioselective Synthesis of Cyclic Nitrones by Chemoselective Intramolecular Allylic Alkylation of Oximes. *Angewandte Chemie International Edition* **2021,** *60* (18), 9913-9918.

99. Sarkar, R.; Mukherjee, S., Iridium-catalyzed enantioselective olefinic C(sp2)–H allylic alkylation. *Chemical Science* **2021,** *12* (8), 3070-3075.

100. Isomura, M.; Petrone, D. A.; Carreira, E. M., Construction of Vicinal Quaternary Centers via Iridium-Catalyzed Asymmetric Allenylic Alkylation of Racemic Tertiary Alcohols. *J. Am. Chem. Soc.* **2021,** *143* (9), 3323-3329.

101. Davis, C. R.; Luvaga, I. K.; Ready, J. M., Enantioselective Allylation of Alkenyl Boronates Promotes a 1,2-Metalate Rearrangement with 1,3-Diastereocontrol. *J. Am. Chem. Soc.* **2021,** *143* (13), 4921-4927.

102. Crisenza, G. E. M.; Faraone, A.; Gandolfo, E.; Mazzarella, D.; Melchiorre, P., Catalytic asymmetric C–C cross-couplings enabled by photoexcitation. *Nat. Chem.* **2021,** *13* (6), 575-580.

103. Chakrabarty, A.; Mukherjee, S., Iridium-Catalyzed Enantioselective and Chemodivergent Allenylic Alkylation of Vinyl Azides for the Synthesis of α-Allenylic Amides and Ketones**. *Angewandte Chemie International Edition* **2022,** *61* (12), e202115821.

104. Liu, X.-J.; Zhang, W.-Y.; Zheng, C.; You, S.-L., Iridium-Catalyzed Asymmetric Allylic Substitution of Methyl Azaarenes. *Angewandte Chemie International Edition* **2022,** *61* (20), e202200164.

105. Zhu, J.; Wang, Y.; Charlack, A. D.; Wang, Y.-M., Enantioselective and Diastereodivergent Allylation of Propargylic C–H Bonds. *J. Am. Chem. Soc.* **2022,** *144* (34), 15480-15487.

106. Guo, J.; Ma, H.-R.; Xiong, W.-B.; Fan, L.; Zhou, Y.-Y.; Wong, H. N. C.; Cui, J.-F., Iridium-catalyzed enantioselective alkynylation and kinetic resolution of alkyl allylic alcohols. *Chemical Science* **2022,** *13* (46), 13914-13921.

107. Ghosh, S.; Changotra, A.; Petrone, D. A.; Isomura, M.; Carreira, E. M.; Sunoj, R. B., Role of Noncovalent Interactions in Inducing High Enantioselectivity in an Alcohol Reductive Deoxygenation Reaction Involving a Planar Carbocationic Intermediate. *J. Am. Chem. Soc.* **2023,** *145* (5), 2884-2900.

108. Yang, P.; Wang, R.-X.; Huang, X.-L.; Cheng, Y.-Z.; You, S.-L., Enantioselective Synthesis of Cyclobutane Derivatives via Cascade Asymmetric Allylic Etherification/[2 + 2] Photocycloaddition. *J. Am. Chem. Soc.* **2023,** *145* (40), 21752-21759.

109. Shen, H.-C.; Wang, Z.-S.; Noble, A.; Aggarwal, V. K., Simultaneous Stereoinvertive and Stereoselective C(sp3)–C(sp3) Cross-Coupling of Boronic Esters and Allylic Carbonates. *J. Am. Chem. Soc.* **2024,** *146* (20), 13719-13726.

2.5.2 Mo and Ru

Mo

1. Trost, B. M.; Lautens, M., CHEMOSELECTIVITY AND STEREOCONTROL IN MOLYBDENUM-CATALYZED ALLYLIC ALKYLATIONS. *J. Am. Chem. Soc.* **1987,** *109* (5), 1469-1478.

2. Krska, S. W.; Hughes, D. L.; Reamer, R. A.; Mathre, D. J.; Sun, Y.; Trost, B. M., The unusual role of CO transfer in molybdenum-catalyzed asymmetric alkylations. *J. Am. Chem. Soc.* **2002,** *124* (43), 12656-12657.

3. Trost, B. M.; Dogra, K., Synthesis of novel quaternary amino acids using molybdenum- catalyzed asymmetric allylic alkylation. *J. Am. Chem. Soc.* **2002,** *124* (25), 7256-7257.

4. Trost, B. M.; Dogra, K.; Hachiya, I.; Emura, T.; Hughes, D. L.; Krska, S.; Reamer, R. A.; Palucki, M.; Yasuda, N.; Reider, P. J., Designed ligands as probes for the catalytic binding mode in mo-catalyzed asymmetric allylic alkylation. *Angew. Chem.-Int. Edit.* **2002,** *41* (11), 1929-+.

5. Trost, B. M.; Zhang, Y., Molybdenum-catalyzed asymmetric allylation of 3-alkyloxindoles: Application to the formal total synthesis of (-)-physostigmine. *J. Am. Chem. Soc.* **2006,** *128* (14), 4590-4591.

6. Trost, B. M.; Zhang, Y., Mo-catalyzed regio-, diastereo-, and enantioselective allylic alkylation of 3-aryloxindoles. *J. Am. Chem. Soc.* **2007,** *129* (47), 14548-+.

7. Trost, B. M.; Zhang, Y., Catalytic Double Stereoinduction in Asymmetric Allylic Alkylation of Oxindoles. *Chem.-Eur. J.* **2010,** *16* (1), 296-303.

8. Trost, B. M.; Miller, J. R.; Hoffman, C. M., A Highly Enantio- and Diastereoselective Molybdenum-Catalyzed Asymmetric Allylic Alkylation of Cyanoesters. *J. Am. Chem. Soc.* **2011,** *133* (21), 8165-8167.

9. Trost, B. M.; Zhang, Y., Molybdenum-Catalyzed Asymmetric Allylic Alkylation of 3-Alkyloxindoles: Reaction Development and Applications. *Chem.-Eur. J.* **2011,** *17* (10), 2916-2922.

Ru

1. Onitsuka, K.; Matsushima, Y.; Takahashi, S., Kinetic resolution of allyl carbonates in asymmetric allylic alkylation catalyzed by planar-chiral cyclopentadienyl-ruthenium complexes. *Organometallics* **2005,** *24* (26), 6472-6474.

2. Constant, S.; Tortoioli, S.; Muller, J.; Lacour, J., An enantioselective CpRu-catalyzed Carroll rearrangement. *Angew. Chem.-Int. Edit.* **2007,** *46* (12), 2082-2085.

3. Constant, S.; Tortoioli, S.; Muller, J.; Linder, D.; Buron, F.; Lacour, J., Air- and microwave-stable (C5H5)Ru catalysts for improved regio and enantioselective carroll rearrangements. *Angew. Chem.-Int. Edit.* **2007,** *46* (47), 8979-8982.

4. Matsuzawa, H.; Kanao, K.; Miyake, Y.; Nishibayashi, Y., Remarkable effect of N-substituent on enantioselective ruthenium-catalyzed propargylation of indoles with propargylic alcohols. *Org. Lett.* **2007,** *9* (26), 5561-5564.

5. Linder, D.; Buron, F.; Constant, S.; Lacour, J., Enantioselective CpRu-Catalyzed Carroll Rearrangement - Ligand and Metal Source Importance. *Eur. J. Org. Chem.* **2008,** (34), 5778-5785.

6. Kanao, K.; Miyake, Y.; Nishibayashi, Y., Ruthenium-Catalyzed Enantioselective Intramolecular Propargylation of Thiophenes with Propargylic Alcohols. *Organometallics* **2009,** *28* (9), 2920-2926.

7. Tanaka, S.; Seki, T.; Kitamura, M., Asymmetric Dehydrative Cyclization of omega-Hydroxy Allyl Alcohols Catalyzed by Ruthenium Complexes. *Angew. Chem.-Int. Edit.* **2009,** *48* (47), 8948-8951.

8. Austeri, M.; Linder, D.; Lacour, J., (Cyclopentadienyl)ruthenium-Catalyzed Regio- and Enantioselective Decarboxylative Allylic Etherification of Allyl Aryl and Alkyl Carbonates. *Adv. Synth. Catal.* **2010,** *352* (18), 3339-3347.

9. Geherty, M. E.; Dura, R. D.; Nelson, S. G., Catalytic Asymmetric Claisen Rearrangement of Unactivated Allyl Vinyl Ethers. *J. Am. Chem. Soc.* **2010,** *132* (34), 11875-11877.

10. Kanbayashi, N.; Onitsuka, K., Enantioselective Synthesis of Allylic Esters via Asymmetric Allylic Substitution with Metal Carboxylates Using Planar-Chiral Cyclopentadienyl Ruthenium Catalysts. *J. Am. Chem. Soc.* **2010,** *132* (4), 1206-+.

11. Kanbayashi, N.; Onitsuka, K., Ruthenium-Catalyzed Regio- and Enantioselective Allylic Substitution with Water: Direct Synthesis of Chiral Allylic Alcohols. *Angew. Chem.-Int. Edit.* **2011,** *50* (22), 5197-5199.

12. Miyata, K.; Kutsuna, H.; Kawakami, S.; Kitamura, M., A Chiral Bidentate sp(2)-N Ligand, Naph-diPIM: Application to CpRu-Catalyzed Asymmetric Dehydrative C-, N-, and O-Allylation. *Angew. Chem.-Int. Edit.* **2011,** *50* (20), 4649-4653.

13. Kanbayashi, N.; Takenaka, K.; Okamura, T.; Onitsuka, K., Asymmetric Auto-Tandem Catalysis with a Planar-Chiral Ruthenium Complex: Sequential Allylic Amidation and Atom-Transfer Radical Cyclization. *Angew. Chem.-Int. Edit.* **2013,** *52* (18), 4897-4901.

14. Trost, B. M.; Rao, M.; Dieskau, A. P., A Chiral Sulfoxide-Ligated Ruthenium Complex for Asymmetric Catalysis: Enantio- and Regioselective Allylic Substitution. *J. Am. Chem. Soc.* **2013,** *135* (49), 18697-18704.

2.5.3 Other Metals and Reactions

1. Lautens, M.; Fagnou, K.; Yang, D. Q., Rhodium-catalyzed asymmetric ring opening reactions of oxabicyclic alkenes: Application of halide effects in the development of a general process. *J. Am. Chem. Soc.* **2003,** *125* (48), 14884-14892.
2. Lautens, M.; Yoshida, M., Rhodium-catalyzed addition of arylboronic acids to alkynyl aza- heteroaromatic compounds in water. *J. Org. Chem.* **2003,** *68* (3), 762-769.
3. Anderson, C. E.; Overman, L. E., Catalytic asymmetric rearrangement of allylic trichloroacetimidates. A practical method for preparing allylic amines and congeners of high enantiomeric purity. *J. Am. Chem. Soc.* **2003,** *125* (41), 12412-12413.
4. Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J., Catalytic asymmetric rearrangement of allylic N-aryl trifluoroacetimidates. A useful method for transforming prochiral allylic alcohols to chiral allylic amines. *Org. Lett.* **2003,** *5* (11), 1809-1812.
5. Berkowitz, D. B.; Maiti, G., Following an ISES lead: The first examples of asymmetric Ni(0)- mediated allylic amination. *Org. Lett.* **2004,** *6* (16), 2661-2664.
6. Leong, P.; Lautens, M., Rhodium-catalyzed asymmetric ring opening of oxabicyclic alkenes with sulfur nucleophiles. *J. Org. Chem.* **2004,** *69* (6), 2194-2196.
7. Kirsch, S. F.; Overman, L. E.; Watson, M. P., Monomeric cobalt oxazoline palladacycles (COP). Useful catalysts for catalytic asymmetric rearrangement of allylic trichloroacetimidates. *J. Org. Chem.* **2004,** *69* (23), 8101-8104.
8. Moyano, A.; Rosol, M.; Moreno, R. M.; Lopez, C.; Maestro, M. A., Oxazoline-mediated interannular cyclopalladation of ferrocene: Chiral palladium(II) catalysts for the enantioselective aza-claisen rearrangement. *Angew. Chem.-Int. Edit.* **2005,** *44* (12), 1865-1869.
9. Prasad, R. S.; Anderson, C. E.; Richards, C. J.; Overman, L. E., Synthesis of tert-leucine-derived cobalt oxazoline palladacycles. Reversal of palladation diastereoselectivity and application to the asymmetric rearrangement of N-aryl trifluoroacetimidates. *Organometallics* **2005,** *24* (1), 77-81.
10. Inada, Y.; Nishibayashi, Y.; Uemura, S., Ruthenium-catalyzed asymmetric propargylic substitution reactions of propargylic alcohols with acetone. *Angew. Chem.-Int. Edit.* **2005,** *44* (47), 7715-7717.
11. Weiss, M. E.; Fischer, D. F.; Xin, Z. Q.; Jautze, S.; Schweizer, W. B.; Peters, R., Practical, highly active, and enantioselective ferrocenyl-imidazoline palladacycle catalysts (FIPs) for the aza-claisen rearrangement of N-para-methoxyphenyl trifluoroacetimidates. *Angew. Chem.-Int. Edit.* **2006,** *45* (34), 5694-5698.
12. Fischer, D. E.; Xin, Z. Q.; Peters, R., Asymmetric formation of allylic amines with N-substituted quaternary stereocenters by Pd-II-catalyzed aza-Claisen rearrangements. *Angew. Chem.-Int. Edit.* **2007,** *46* (40), 7704-7707.
13. Watson, M. P.; Overman, L. E.; Bergman, R. G., Kinetic and computational analysis of the palladium(II)-catalyzed asymmetric allylic trichloroacetimidate rearrangement: Development of a model for enantioselectivity. *J. Am. Chem. Soc.* **2007,** *129* (16), 5031-5044.
14. Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y., Ruthenium-catalyzed enantioselective prolpargylation of aromatic compounds with propargylic alcohols via allenylidene intermediates. *Angew. Chem.-Int. Edit.* **2007,** *46* (34), 6488-6491.
15. Menard, F.; Lautens, M., Chemodivergence in enantioselective desymmetrization of diazabicycles: Ring-opening versus reductive arylation. *Angew. Chem.-Int. Edit.* **2008,** *47* (11), 2085-2088.
16. Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H., Enantioselective copper-catalyzed propargylic amination. *Angew. Chem.-Int. Edit.* **2008,** *47* (20), 3777-3780.
17. Hattori, G.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y., Copper-catalyzed asymmetric propargylic substitution reactions of propargylic acetates with amines. *Angew. Chem.-Int. Edit.* **2008,** *47* (20), 3781-3783.
18. Webster, R.; Boing, C.; Lautens, M., Reagent-Controlled Regiodivergent Resolution of Unsymmetrical Oxabicyclic Alkenes Using a Cationic Rhodium Catalyst. *J. Am. Chem. Soc.* **2009,** *131* (2), 444-+.
19. Cui, H. L.; Feng, X.; Peng, J.; Lei, J.; Jiang, K.; Chen, Y. C., Chemoselective Asymmetric N-Allylic Alkylation of Indoles with Morita-Baylis-Hillman Carbonates. *Angew. Chem.-Int. Edit.* **2009,** *48* (31), 5737-5740.
20. Bandini, M.; Eichholzer, A., Enantioselective Gold-Catalyzed Allylic Alkylation of Indoles with Alcohols: An Efficient Route to Functionalized Tetrahydrocarbazoles. *Angew. Chem.-Int. Edit.* **2009,** *48* (50), 9533-9537.
21. Hattori, G.; Sakata, K.; Matsuzawa, H.; Tanabe, Y.; Miyake, Y.; Nishibayashi, Y., Copper-Catalyzed Enantioselective Propargylic Amination of Propargylic Esters with Amines: Copper-Allenylidene Complexes as Key Intermediates. *J. Am. Chem. Soc.* **2010,** *132* (30), 10592-10608.
22. Yamamoto, H.; Ho, E.; Namba, K.; Imagawa, H.; Nishizawa, M., Hg(OTf)(2)-BINAPHANE-Catalyzed Enantioselective Anilino Sulfonamide Allyl Alcohol Cyclization. *Chem.-Eur. J.* **2010,** *16* (37), 11271-11274.
23. Bao, H. L.; Qi, X. B.; Tambar, U. K., Catalytic Enantioselective 2,3 -Rearrangements of Amine N-Oxides. *J. Am. Chem. Soc.* **2011,** *133* (5), 1206-1208.
24. Bandini, M., Allylic Alcohols: Sustainable Sources for Catalytic Enantioselective Alkylation Reactions. *Angew. Chem.-Int. Edit.* **2011,** *50* (5), 994-995.
25. Rueping, M.; Uria, U.; Lin, M. Y.; Atodiresei, I., Chiral Organic Contact Ion Pairs in Metal-Free Catalytic Asymmetric Allylic Substitutions. *J. Am. Chem. Soc.* **2011,** *133* (11), 3732-3735.
26. Yoshida, A.; Hattori, G.; Miyake, Y.; Nishibayashi, Y., Copper-Catalyzed Enantioselective Propargylic Amination of Nonaromatic Propargylic Esters with Amines. *Org. Lett.* **2011,** *13* (9), 2460-2463.
27. Boyer, A.; Lautens, M., Rhodium-Catalyzed Domino Enantioselective Synthesis of Bicyclo 2.2.2 lactones. *Angew. Chem.-Int. Edit.* **2011,** *50* (32), 7346-7349.
28. Koschker, P.; Lumbroso, A.; Breit, B., Enantioselective Synthesis of Branched Allylic Esters via Rhodium-Catalyzed Coupling of Allenes with Carboxylic Acids. *J. Am. Chem. Soc.* **2011,** *133* (51), 20746-20749.

29. Evans, P. A.; Clizbe, E. A.; Lawler, M. J.; Oliver, S., Enantioselective rhodium-catalyzed allylic alkylation of acyclic alpha-alkoxy substituted ketones using a chiral monodentate phosphite ligand. *Chemical Science* **2012,** *3* (6), 1835-1838.
30. Tsui, G. C.; Lautens, M., Rhodium(I)-Catalyzed Domino Asymmetric Ring Opening/Enantioselective Isomerization of Oxabicyclic Alkenes with Water. *Angew. Chem.-Int. Edit.* **2012,** *51* (22), 5400-5404.
31. Guo, B. Y.; Schwarzwalder, G.; Njardarson, J. T., Catalytic Ring Expansion of Vinyl Oxetanes: Asymmetric Synthesis of Dihydropyrans Using Chiral Counterion Catalysis. *Angew. Chem.-Int. Edit.* **2012,** *51* (23), 5675-5678.
32. Arnold, J. S.; Nguyen, H. M., Rhodium-Catalyzed Dynamic Kinetic Asymmetric Transformations of Racemic Tertiary Allylic Trichloroacetimidates with Anilines. *J. Am. Chem. Soc.* **2012,** *134* (20), 8380-8383.
33. Zhang, C.; Hu, X. H.; Wang, Y. H.; Zheng, Z.; Xu, J.; Hu, X. P., Highly Diastereo- and Enantioselective Cu-Catalyzed 3+3 Cycloaddition of Propargyl Esters with Cyclic Enamines toward Chiral Bicyclo n.3.1 Frameworks. *J. Am. Chem. Soc.* **2012,** *134* (23), 9585-9588.
34. Cooke, M. L.; Xu, K.; Breit, B., Enantioselective Rhodium-Catalyzed Synthesis of Branched Allylic Amines by Intermolecular Hydroamination of Terminal Allenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (43), 10876-10879.
35. Zhu, J. T.; Tsui, G. C.; Lautens, M., Rhodium-Catalyzed Enantioselective Nucleophilic Fluorination: Ring Opening of Oxabicyclic Alkenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (49), 12353-12356.
36. Qi, Z. S.; Li, X. W., Rhodium(III)-Catalyzed Coupling of Arenes with 7-Oxa/Azabenzonorbornadienes by CH Activation. *Angew. Chem.-Int. Edit.* **2013,** *52* (34), 8995-9000.
37. Zhang, Y.; Wu, Q. F.; Cui, S. L., Rh(III)-catalyzed C-H activation-desymmetrization of diazabicycles with arenes: facile synthesis of functionalized cyclopentenes. *Chemical Science* **2014,** *5* (1), 297-302.
38. Zhu, F. L.; Zou, Y.; Zhang, D. Y.; Wang, Y. H.; Hu, X. H.; Chen, S.; Xu, J.; Hu, X. P., Enantioselective Copper-Catalyzed Decarboxylative Propargylic Alkylation of Propargyl beta-Ketoesters with a Chiral Ketimine P,N,N-Ligand. *Angew. Chem.-Int. Edit.* **2014,** *53* (5), 1410-1414.
39. Han, F.-Z.; Zhu, F.-L.; Wang, Y.-H.; Zou, Y.; Hu, X.-H.; Chen, S.; Hu, X.-P., Highly Enantioselective Copper-Catalyzed Propargylic Substitution of Propargylic Acetates with 1,3-Dicarbonyl Compounds. *Org. Lett.* **2014,** *16* (2), 588-591.
40. Xu, K.; Thieme, N.; Breit, B., Atom-Economic, Regiodivergent, and Stereoselective Coupling of Imidazole Derivatives with Terminal Allenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (8), 2162-2165.
41. Arnold, J. S.; Mwenda, E. T.; Nguyen, H. M., Rhodium-Catalyzed Sequential Allylic Amination and Olefin Hydroacylation Reactions: Enantioselective Synthesis of Seven-Membered Nitrogen Heterocycles. *Angew. Chem.-Int. Edit.* **2014,** *53* (14), 3688-3692.
42. Zhang, L.; Le, C. M.; Lautens, M., The Use of Silyl Ketene Acetals and Enol Ethers in the Catalytic Enantioselective Alkylative Ring Opening of Oxa/Aza Bicyclic Alkenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (23), 5951-5954.
43. Zhu, F.-L.; Wang, Y.-H.; Zhang, D.-Y.; Xu, J.; Hu, X.-P., Enantioselective Synthesis of Highly Functionalized Dihydrofurans through Copper-Catalyzed Asymmetric Formal 3+2 Cycloaddition of beta-Ketoesters with Propargylic Esters. *Angew. Chem.-Int. Edit.* **2014,** *53* (38), 10223-10227.
44. Li, C.; Kaehny, M.; Breit, B., Rhodium-Catalyzed Chemo-, Regio-, and Enantioselective Addition of 2-Pyridones to Terminal Allenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13780-13784.
45. Pritzius, A. B.; Breit, B., Asymmetric Rhodium-Catalyzed Addition of Thiols to Allenes: Synthesis of Branched Allylic Thioethers and Sulfones. *Angew. Chem.-Int. Edit.* **2015,** *54* (10), 3121-3125.
46. Nakajima, K.; Shibata, M.; Nishibayashi, Y., Copper-Catalyzed Enantioselective Propargylic Etherification of Propargylic Esters with Alcohols. *J. Am. Chem. Soc.* **2015,** *137* (7), 2472-2475.
47. Haydl, A. M.; Xu, K.; Breit, B., Regio- and Enantioselective Synthesis of N-Substituted Pyrazoles by Rhodium-Catalyzed Asymmetric Addition to Allenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (24), 7149-7153.
48. Turnbull, B. W. H.; Evans, P. A., Enantioselective Rhodium-Catalyzed Allylic Substitution with a Nitrile Anion: Construction of Acyclic Quaternary Carbon Stereogenic Centers. *J. Am. Chem. Soc.* **2015,** *137* (19), 6156-6159.
49. Shao, W.; Li, H.; Liu, C.; Liu, C. J.; You, S. L., Copper-Catalyzed Intermolecular Asymmetric Propargylic Dearomatization of Indoles. *Angew. Chem.-Int. Edit.* **2015,** *54* (26), 7684-7687.
50. Pritzius, A. B.; Breit, B., Z-Selective Hydrothiolation of Racemic 1,3-Disubstituted Allenes: An Atom-Economic Rhodium-Catalyzed Dynamic Kinetic Resolution. *Angew. Chem.-Int. Edit.* **2015,** *54* (52), 15818-15822.
51. Sidera, M.; Fletcher, S. P., Rhodium-catalysed asymmetric allylic arylation of racemic halides with arylboronic acids. *Nat. Chem.* **2015,** *7* (11), 935-939.
52. Kita, Y.; Kavthe, R. D.; Oda, H.; Mashima, K., Asymmetric Allylic Alkylation of -Ketoesters with Allylic Alcohols by a Nickel/Diphosphine Catalyst. *Angew. Chem.-Int. Edit.* **2016,** *55* (3), 1098-1101.
53. Xu, K.; Wang, Y. H.; Khakyzadeh, V.; Breit, B., Asymmetric synthesis of allylic amines via hydroamination of allenes with benzophenone imine. *Chemical Science* **2016,** *7* (5), 3313-3316.
54. Shao, L.; Wang, Y. H.; Zhang, D. Y.; Xu, J.; Hu, X. P., Desilylation-Activated Propargylic Transformation: Enantioselective Copper-Catalyzed 3+2 Cycloaddition of Propargylic Esters with -Naphthol or Phenol Derivatives. *Angew. Chem.-Int. Edit.* **2016,** *55* (16), 5014-5018.
55. Loh, C. C. J.; Schmid, M.; Peters, B.; Fang, X.; Lautens, M., Exploiting Distal Reactivity of Coumarins: A Rhodium-Catalyzed Vinylogous Asymmetric Ring-Opening Reaction. *Angew. Chem.-Int. Edit.* **2016,** *55* (14), 4600-4604.
56. Liu, Z.; Breit, B., Rhodium-Catalyzed Enantioselective Intermolecular Hydroalkoxylation of Allenes and Alkynes with Alcohols: Synthesis of Branched Allylic Ethers. *Angew. Chem.-Int. Edit.* **2016,** *55* (29), 8440-8443.
57. Tsuchida, K.; Senda, Y.; Nakajima, K.; Nishibayashi, Y., Construction of Chiral Tri- and Tetra-Arylmethanes Bearing Quaternary Carbon Centers: Copper-Catalyzed Enantioselective Propargylation of Indoles with Propargylic Esters. *Angew. Chem.-Int. Edit.* **2016,** *55* (33), 9728-9732.
58. Wang, Q.; Li, T. R.; Lu, L. Q.; Li, M. M.; Zhang, K.; Xiao, W. J., Catalytic Asymmetric 4+1 Annulation of Sulfur Ylides with Copper-Allenylidene Intermediates. *J. Am. Chem. Soc.* **2016,** *138* (27), 8360-8363.
59. Loh, C. C. J.; Schmid, M.; Webster, R.; Yen, A.; Yazdi, S. K.; Franke, P. T.; Lautens, M., Rhodium-Catalyzed Asymmetric Cycloisomerization and Parallel Kinetic Resolution of Racemic Oxabicycles. *Angew. Chem.-Int. Edit.* **2016,** *55* (34), 10074-10078.
60. Huang, X.; Wu, S. Z.; Wu, W. T.; Li, P. B.; Fu, C. L.; Ma, S. M., Palladium-catalysed formation of vicinal all-carbon quaternary centres via propargylation. *Nature Communications* **2016,** *7*.
61. Wright, T. B.; Evans, P. A., Enantioselective Rhodium-Catalyzed Allylic Alkylation of Prochiral alpha,alpha-Disubstituted Aldehyde Enolates for the Construction of Acyclic Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2016,** *138* (47), 15303-15306.

62. Thieme, N.; Breit, B., Enantioselective and Regiodivergent Addition of Purines to Terminal Allenes: Synthesis of Abacavir. *Angew. Chem.-Int. Edit.* **2017,** *56* (6), 1520-1524.
63. Beck, T. M.; Breit, B., Regio- and Enantioselective Rhodium-Catalyzed Addition of 1,3-Diketones to Allenes: Construction of Asymmetric Tertiary and Quaternary All Carbon Centers. *Angew. Chem.-Int. Edit.* **2017,** *56* (7), 1903-1907.
64. Yang, X. H.; Dong, V. M., Rhodium-Catalyzed Hydrofunctionalization: Enantioselective Coupling of Indolines and 1,3-Dienes. *J. Am. Chem. Soc.* **2017,** *139* (5), 1774-1777.
65. Yen, A.; Choo, K. L.; Yazdi, S. K.; Franke, P. T.; Webster, R.; Franzoni, I.; Loh, C. C. J.; Poblador-Bahamonde, A. I.; Lautens, M., Rhodium-Catalyzed Enantioselective Isomerization of meso-Oxabenzonorbornadienes to 1,2-Naphthalene Oxides. *Angew. Chem.-Int. Edit.* **2017,** *56* (22), 6307-6311.
66. Cheng, L. J.; Brown, A. P. N.; Cordier, C. J., Enantioselective propargylic 1,3 -rearrangements: copper-catalyzed O-to-N migrations toward C-N bond formation. *Chemical Science* **2017,** *8* (6), 4299-4305.
67. Li, R. Z.; Tang, H.; Yang, K. R.; Wan, L. Q.; Zhang, X.; Liu, J.; Fu, Z. Y.; Niu, D. W., Enantioselective Propargylation of Polyols and Desymmetrization of meso 1,2-Diols by Copper/Borinic Acid Dual Catalysis. *Angew. Chem.-Int. Edit.* **2017,** *56* (25), 7213-7217.
68. Cruz, F. A.; Zhu, Y. M.; Tercenio, Q. D.; Shen, Z. M.; Doneta, V. M., Alkyne Hydroheteroarylation: Enantioselective Coupling of Indoles and Alkynes via Rh-Hydride Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (31), 10641-10644.
69. Zhang, K.; Lu, L. Q.; Yao, S.; Chen, J. R.; Shi, D. Q.; Xiao, W. J., Enantioconvergent Copper Catalysis: In Situ Generation of the Chiral Phosphorus Ylide and Its Wittig Reactions. *J. Am. Chem. Soc.* **2017,** *139* (36), 12847-12854.
70. Gomez, J. E.; Guo, W. S.; Gaspa, S.; Kleij, A. W., Copper-Catalyzed Synthesis of -Amino Acids Featuring Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2017,** *56* (47), 15035-15038.
71. Chen, Z. W.; Dong, V. M., Enantioselective semireduction of allenes. *Nature Communications* **2017,** *8*.
72. Okumura, M.; Shved, A. S.; Sarlah, D., Palladium-Catalyzed Dearomative syn-1,4-Carboamination. *J. Am. Chem. Soc.* **2017,** *139* (49), 17787-17790.
73. Grugel, C. P.; Breit, B., Rhodium-Catalyzed Enantioselective Decarboxylative Alkynylation of Allenes with Arylpropiolic Acids. *Org. Lett.* **2018,** *20* (4), 1066-1069.
74. Hernandez, L. W.; Klockner, U.; Pospech, J.; Hauss, L.; Sarlah, D., Nickel-Catalyzed Dearomative trans-1,2-Carboamination. *J. Am. Chem. Soc.* **2018,** *140* (13), 4503-4507.
75. Wendlandt, A. E.; Vangal, P.; Jacobsen, E. N., Quaternary stereocentres via an enantioconvergent catalytic S(N)1 reaction. *Nature* **2018,** *556* (7702), 447-451.
76. Steib, P.; Breit, B., Enantioselective Rhodium-Catalyzed Dimerization of omega-Allenyl Carboxylic Acids: Straightforward Synthesis of C-2-Symmetric Macrodiolides. *Angew. Chem.-Int. Edit.* **2018,** *57* (22), 6572-6576.
77. Tang, S. B.; Zhang, X.; Tu, H. F.; You, S. L., Regio- and Enantioselective Rhodium-Catalyzed Allylic Alkylation of Racemic Allylic Alcohols with 1,3-Diketones. *J. Am. Chem. Soc.* **2018,** *140* (24), 7737-7742.
78. Mistry, N.; Fletcher, S. P., Catalytic asymmetric synthesis of geminal-dicarboxylates. *Chemical Science* **2018,** *9* (29), 6307-6312.
79. Yang, X. H.; Davison, R. T.; Dong, V. M., Catalytic Hydrothiolation: Regio- and Enantioselective Coupling of Thiols and Dienes. *J. Am. Chem. Soc.* **2018,** *140* (33), 10443-10446.
80. Yang, X. F.; Zheng, G. F.; Li, X. W., Rhodium(III)-Catalyzed Enantioselective Coupling of Indoles and 7-Azabenzonorbornadienes by C-H Activation/Desymmetrization. *Angew. Chem.-Int. Edit.* **2019,** *58* (1), 322-326.
81. Wang, S. G.; Cramer, N., An Enantioselective (CpRh)-Rh-x(III)-Catalyzed C-H Functionalization/Ring-Opening Route to Chiral Cyclopentenylamines. *Angew. Chem.-Int. Edit.* **2019,** *58* (8), 2514-2518.
82. Gomez, J. E.; Cristofol, A.; Kleij, A. W., Copper-Catalyzed Enantioselective Construction of Tertiary Propargylic Sulfones. *Angew. Chem.-Int. Edit.* **2019,** *58* (12), 3903-3907.
83. Chen, T.; Gan, L. F.; Wang, R.; Deng, Y. H.; Peng, F. Z.; Lautens, M.; Shao, Z. H., Rhodium(I)/Zn(OTf)(2)-Catalyzed Asymmetric Ring Opening/Cyclopropanation of Oxabenzonorbornadienes with Phosphorus Ylides. *Angew. Chem.-Int. Edit.* **2019,** *58* (44), 15819-15823.
84. Long, J. G.; Yu, R. R.; Gao, J. H.; Fang, X. J., Access to 1,3-Dinitriles by Enantioselective Auto-tandem Catalysis: Merging Allylic Cyanation with Asymmetric Hydrocyanation. *Angew. Chem.-Int. Edit.* **2020,** *59* (17), 6785-6789.
85. Kranidiotis-Hisatomi, N.; Yi, H.; Oestreich, M., Enantio- and Regioconvergent Nickel-Catalyzed C(sp3)−C(sp3) Cross-Coupling of Allylic Electrophiles Steered by a Silyl Group. *Angewandte Chemie International Edition* **2021,** *60* (24), 13652-13655.
86. Guo, W.; Zuo, L.; Cui, M.; Yan, B.; Ni, S., Propargylic Amination Enabled the Access to Enantioenriched Acyclic α-Quaternary α-Amino Ketones. *J. Am. Chem. Soc.* **2021,** *143* (20), 7629-7634.
87. Xu, W.-B.; Sun, M.; Shu, M.; Li, C., Rhodium-Catalyzed Regio- and Enantioselective Allylic Amination of Racemic 1,2-Disubstituted Allylic Phosphates. *J. Am. Chem. Soc.* **2021,** *143* (22), 8255-8260.
88. Ng, J. S.; Hayashi, T., Asymmetric Synthesis of Fluorinated Allenes by Rhodium-Catalyzed Enantioselective Alkylation/Defluorination of Propargyl Difluorides with Alkylzincs. *Angewandte Chemie International Edition* **2021,** *60* (38), 20771-20775.
89. Liu, T.; Ni, S.; Guo, W., Practical asymmetric amine nucleophilic approach for the modular construction of protected α-quaternary amino acids. *Chemical Science* **2022,** *13* (23), 6806-6812.
90. Wang, H.; Qian, H.; Zhang, J.; Ma, S., Catalytic Asymmetric Axially Chiral Allenyl C–P Bond Formation. *J. Am. Chem. Soc.* **2022,** *144* (28), 12619-12626.
91. Jiang, Z.-T.; Chen, Z.; Zeng, Y.; Shi, J.-L.; Xia, Y., Enantioselective Formation of All-Carbon Quaternary Stereocenters in gem-Difluorinated Cyclopropanes via Rhodium-Catalyzed Stereoablative Kinetic Resolution. *Org. Lett.* **2022,** *24* (33), 6176-6181.
92. Xu, X.; Wang, M.; Peng, L.; Guo, C., Nickel-Catalyzed Asymmetric Propargylation for the Synthesis of Axially Chiral 1,3-Disubstituted Allenes. *J. Am. Chem. Soc.* **2022,** *144* (46), 21022-21029.
93. Egea-Arrebola, D.; Goetzke, F. W.; Fletcher, S. P., Rhodium-Catalyzed Asymmetric Arylation of Cyclobutenone Ketals. *Angewandte Chemie International Edition* **2023,** *62* (13), e202217381.
94. Li, Q.; Wang, Z.; Dong, V. M.; Yang, X.-H., Enantioselective Hydroalkoxylation of 1,3-Dienes via Ni-Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (7), 3909-3914.
95. Garcia-Roca, A.; Pérez-Soto, R.; Stoica, G.; Benet-Buchholz, J.; Maseras, F.; Kleij, A. W., Comprehensive Mechanistic Scenario for the Cu-Mediated Asymmetric Propargylic Sulfonylation Forging Tertiary Carbon Stereocenters. *J. Am. Chem. Soc.* **2023,** *145* (11), 6442-6452.
96. Sun, Y.-Z.; Ren, Z.-Y.; Yang, Y.-X.; Liu, Y.; Lin, G.-Q.; He, Z.-T., Asymmetric Substitution by Alkynyl Copper Driven Dearomatization and Rearomatization. *Angewandte Chemie International Edition* **2023,** *62* (47), e202314517.

97. Stojalnikova, V.; Webster, S. J.; Liu, K.; Fletcher, S. P., Chelation enables selectivity control in enantioconvergent Suzuki–Miyaura cross-couplings on acyclic allylic systems. *Nat. Chem.* **2024,** *16* (5), 791-799.
98. Zhu, J.; Xiang, H.; Chang, H.; Corcoran, J. C.; Ding, R.; Xia, Y.; Liu, P.; Wang, Y.-M., Enantioselective and Regiodivergent Synthesis of Propargyl- and Allenylsilanes through Catalytic Propargylic C−H Deprotonation. *Angewandte Chemie International Edition* **2024,** *63* (16), e202318040.
99. Zhang, Z.; Sun, Y.; Gong, Y.; Tang, D.-L.; Luo, H.; Zhao, Z.-P.; Zhou, F.; Wang, X.; Zhou, J., Enantioselective propargylic amination and related tandem sequences to α-tertiary ethynylamines and azacycles. *Nat. Chem.* **2024,** *16* (4), 521-532.
100. Brösamlen, D.; Neb, D.; Oestreich, M., Enantio- and Regioconvergent Nickel-Catalyzed Etherification of Phenols by Allylation to Access Chiral C(sp3)−O Allyl Aryl Ethers. *Angewandte Chemie International Edition* **2024,** *63* (48), e202412181.

2.6. Activation C-C Double Bonds

1. El-Qisairi, A.; Hamed, O.; Henry, P. M., A new palladium(II)-catalyzed asymmetric chlorohydrin synthesis. *Journal of Organic Chemistry* **1998,** *63* (9), 2790-2791.

2. Hamed, O.; Henry, P. M., Oxidation of olefins by palladium(II). 16. A new palladium(II)- catalyzed asymmetric chlorohydrin synthesis. *Organometallics* **1998,** *17* (23), 5184-5189.

3. El-Qisairi, A.; Henry, P. M., Oxidation of olefins by palladium(II) Part 17. An asymmetric chlorohydrin synthesis catalyzed by a bimetallic palladium(II) complex. *J. Organomet. Chem.* **2000,** *603* (1), 50-60.

4. Kang, S. H.; Kim, M., Enantioselective mercuriocyclization of gamma-hydroxy-cis- alkenes. *J. Am. Chem. Soc.* **2003,** *125* (16), 4684-4685.

5. Kang, S. H.; Kim, M. Y.; Kang, S. Y., Catalytic asymmetric mercuriocyclization of gamma-hydroxy-cis-alkenes. *Angew. Chem.-Int. Edit.* **2004,** *43* (45), 6177-6180.

6. Gorin, D. J.; Toste, F. D., Relativistic effects in homogeneous gold catalysis. *Nature* **2007,** *446* (7134), 395-403.

7. Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D., A powerful chiral counterion strategy for asymmetric transition metal catalysis. *Science* **2007,** *317* (5837), 496-499.

8. LaLonde, R. L.; Sherry, B. D.; Kang, E. J.; Toste, F. D., Gold(I)-catalyzed enantioselective intramolecular hydroamination of allenes. *J. Am. Chem. Soc.* **2007,** *129* (9), 2452-+.

9. Tarselli, M. A.; Chianese, A. R.; Lee, S. J.; Gagne, M. R., Gold(I)-catalyzed asymmetric cycloisomerization of eneallenes into vinylcyclohexenes. *Angew. Chem.-Int. Edit.* **2007,** *46* (35), 6670-6673.

10. Zhang, Y.; Sigman, M. S., Palladium(II)-catalyzed enantioselective aerobic dialkoxylation of 2-propenyl phenols: A pronounced effect of copper additives on enantioselectivity. *J. Am. Chem. Soc.* **2007,** *129* (11), 3076-+.

11. Zhang, Z. B.; Bender, C. F.; Widenhoefer, R. A., Gold(I)-catalyzed dynamic kinetic enantioselective intramolecular hydroamination of allenes. *J. Am. Chem. Soc.* **2007,** *129* (46), 14148-+.

12. Aikawa, K.; Kojima, M.; Mikami, K., Axial Chirality Control of Gold(biphep) Complexes by Chiral Anions: Application to Asymmetric Catalysis. *Angew. Chem.-Int. Edit.* **2009,** *48* (33), 6073-6077.

13. Chao, C. M.; Beltrami, D.; Toullec, P. Y.; Michelet, V., Asymmetric Au(I)-catalyzed synthesis of bicyclo[4.1.0]heptene derivatives via a cycloisomerization process of 1,6-enynes. *Chem. Commun.* **2009,** (45), 6988-6990.

14. Chao, C. M.; Vitale, M. R.; Toullec, P. Y.; Genet, J. P.; Michelet, V., Asymmetric Gold-Catalyzed Hydroarylation/Cyclization Reactions. *Chem.-Eur. J.* **2009,** *15* (6), 1319-1323.

15. Jensen, K. H.; Pathak, T. P.; Zhang, Y.; Sigman, M. S., Palladium-Catalyzed Enantioselective Addition of Two Distinct Nucleophiles across Alkenes Capable of Quinone Methide Formation. *J. Am. Chem. Soc.* **2009,** *131* (47), 17074-+.

16. Kleinbeck, F.; Toste, F. D., Gold(I)-Catalyzed Enantioselective Ring Expansion of Allenylcyclopropanols. *J. Am. Chem. Soc.* **2009,** *131* (26), 9178-+.

17. Watson, L. D. G.; Ritter, S.; Toste, F. D., Asymmetric Synthesis of Medium-Sized Rings by Intramolecular Au(I)-Catalyzed Cyclopropanation. *J. Am. Chem. Soc.* **2009,** *131* (6), 2056-+.

18. Zhang, Z. B.; Lee, S. D.; Widenhoefer, R. A., Intermolecular Hydroamination of Ethylene and 1-Alkenes with Cyclic Ureas Catalyzed by Achiral and Chiral Gold(I) Complexes. *J. Am. Chem. Soc.* **2009,** *131* (15), 5372-+.

19. Gonzalez, A. Z.; Toste, F. D., Gold(I)-Catalyzed Enantioselective [4+2]-Cycloaddition of Allene-dienes. *Org. Lett.* **2010,** *12* (1), 200-203.

20. LaLonde, R. L.; Wang, Z. J.; Mba, M.; Lackner, A. D.; Toste, F. D., Gold(I)-Catalyzed Enantioselective Synthesis of Pyrazolidines, Isoxazolidines, and Tetrahydrooxazines. *Angew. Chem.-Int. Edit.* **2010,** *49* (3), 598-601.

21. Liu, F.; Qian, D. Y.; Li, L.; Zhao, X. L.; Zhang, J. L., Diastereo- and Enantioselective Gold(I)-Catalyzed Intermolecular Tandem Cyclization/ 3+3 Cycloadditions of 2-(1-Alkynyl)-2-alken-1-ones with Nitrones. *Angew. Chem.-Int. Edit.* **2010,** *49* (37), 6669-6672.

22. Martinez, A.; Garcia-Garcia, P.; Fernandez-Rodriguez, M. A.; Rodriguez, F.; Sanz, R., Gold(I)-Catalyzed Enantioselective Synthesis of Functionalized Indenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (27), 4633-4637.

23. Sethofer, S. G.; Mayer, T.; Toste, F. D., Gold(I)-Catalyzed Enantioselective Polycyclization Reactions. *J. Am. Chem. Soc.* **2010,** *132* (24), 8276-+.

24. Teller, H.; Flugge, S.; Goddard, R.; Furstner, A., Enantioselective Gold Catalysis: Opportunities Provided by Monodentate Phosphoramidite Ligands with an Acyclic TADDOL Backbone. *Angew. Chem.-Int. Edit.* **2010,** *49* (11), 1949-1953.

25. Alonso, I.; Faustino, H.; Lopez, F.; Mascarenas, J. L., Enantioselective Gold(I)-Catalyzed Intramolecular (4+3) Cycloadditions of Allenedienes. *Angew. Chem.-Int. Edit.* **2011,** *50* (48), 11496-11500.

26. Gonzalez, A. Z.; Benitez, D.; Tkatchouk, E.; Goddard, W. A.; Toste, F. D., Phosphoramidite Gold(I)-Catalyzed Diastereo- and Enantioselective Synthesis of 3,4-Substituted Pyrrolidines. *J. Am. Chem. Soc.* **2011,** *133* (14), 5500-5507.

27. Jullien, H.; Brissy, D.; Sylvain, R.; Retailleau, P.; Naubron, J. V.; Gladiali, S.; Marinetti, A., Cyclometalated N-Heterocyclic Carbene-Platinum Catalysts for the Enantioselective Cycloisomerization of Nitrogen-Tethered 1,6-Enynes. *Adv. Synth. Catal.* **2011,** *353* (7), 1109-1124.

28. Kanno, O.; Kuriyama, W.; Wang, Z. J.; Toste, F. D., Regio- and Enantioselective Hydroamination of Dienes by Gold(I)/Menthol Cooperative Catalysis. *Angew. Chem.-Int. Edit.* **2011,** *50* (42), 9919-9922.

29. Shapiro, N. D.; Rauniyar, V.; Hamilton, G. L.; Wu, J.; Toste, F. D., Asymmetric additions to dienes catalysed by a dithiophosphoric acid. *Nature* **2011,** *470* (7333), 245-+.

30. Wang, Y. M.; Kuzniewski, C. N.; Rauniyar, V.; Hoong, C.; Toste, F. D., Chiral (Acyclic Diaminocarbene)Gold(I)-Catalyzed Dynamic Kinetic Asymmetric Transformation of Propargyl Esters. *J. Am. Chem. Soc.* **2011,** *133* (33), 12972-12975.

31. Zhou, G. H.; Liu, F.; Zhang, J. L., Enantioselective Gold-Catalyzed Functionalization of Unreactive sp(3) C-H Bonds through a Redox-Neutral Domino Reaction. *Chem.-Eur. J.* **2011,** *17* (11), 3101-3104.

32. Bandini, M.; Bottoni, A.; Chiarucci, M.; Cera, G.; Miscione, G. P., Mechanistic Insights into Enantioselective Gold-Catalyzed Allylation of Indoles with Alcohols: The Counterion Effect. *J. Am. Chem. Soc.* **2012,** *134* (51), 20690-20700.

33. Brazeau, J. F.; Zhang, S. Y.; Colomer, I.; Corkey, B. K.; Toste, F. D., Enantioselective Cyclizations of Silyloxyenynes Catalyzed by Cationic Metal Phosphine Complexes. *J. Am. Chem. Soc.* **2012,** *134* (5), 2742-2749.

34. Cera, G.; Chiarucci, M.; Mazzanti, A.; Mancinelli, M.; Bandini, M., Enantioselective Gold-Catalyzed Synthesis of Polycyclic Indolines. *Org. Lett.* **2012,** *14* (5), 1350-1353.

35. Felix, R. J.; Weber, D.; Gutierrez, O.; Tantillo, D. J.; Gagne, M. R., A gold-catalysed enantioselective Cope rearrangement of achiral 1,5-dienes. *Nature Chemistry* **2012,** *4* (5), 405-409.

36. Francos, J.; Grande-Carmona, F.; Faustino, H.; Iglesias-Siguenza, J.; Diez, E.; Alonso, I.; Fernandez, R.; Lassaletta, J. M.; Lopez, F.; Mascarenas, J. L., Axially Chiral Triazoloisoquinolin-3-ylidene Ligands in Gold(I)-Catalyzed Asymmetric Intermolecular (4+2) Cycloadditions of Allenamides and Dienes. *J. Am. Chem. Soc.* **2012,** *134* (35), 14322-14325.

37. Gawade, S. A.; Bhunia, S.; Liu, R. S., Intermolecular Gold-Catalyzed Diastereo- and Enantioselective 2+2+3 Cycloadditions of 1,6-Enynes with Nitrones. *Angew. Chem.-Int. Edit.* **2012,** *51* (31), 7835-7838.

38. Kojima, M.; Mikami, K., Enantioselective Intramolecular Hydroamination of N-Alkenyl Ureas Catalyzed by tropos BIPHEP-Gold(I) Complexes with Au-Au Interaction. *Synlett* **2012,** *23* (1), 57-61.

39. Mourad, A. K.; Leutzow, J.; Czekelius, C., Anion-Induced Enantioselective Cyclization of Diynamides to Pyrrolidines Catalyzed by Cationic Gold Complexes. *Angew. Chem.-Int. Edit.* **2012,** *51* (44), 11149-11152.

40. Mukherjee, P.; Widenhoefer, R. A., Gold(I)-Catalyzed Enantioselective Intramolecular Dehydrative Amination of Allylic Alcohols with Carbamates. *Angew. Chem.-Int. Edit.* **2012,** *51* (6), 1405-1407.

41. Rodriguez, L. I.; Roth, T.; Fillol, J. L.; Wadepohl, H.; Gade, L. H., The More GolduThe More Enantioselective: Cyclohydroaminations of ?-Allenyl Sulfonamides with Mono-, Bis-, and Trisphospholane Gold(I) Catalysts. *Chem.-Eur. J.* **2012,** *18* (12), 3721-3728.

42. Suarez-Pantiga, S.; Hernandez-Diaz, C.; Rubio, E.; Gonzalez, J. M., Intermolecular 2+2 Reaction of N-Allenylsulfonamides with Vinylarenes: Enantioselective Gold(I)-Catalyzed Synthesis of Cyclobutane Derivatives. *Angew. Chem.-Int. Edit.* **2012,** *51* (46), 11552-11555.

43. Surendra, K.; Corey, E. J., Highly Enantioselective Proton-Initiated Polycyclization of Polyenes. *J. Am. Chem. Soc.* **2012,** *134* (29), 11992-11994.

44. Teller, H.; Corbet, M.; Mantilli, L.; Gopakumar, G.; Goddard, R.; Thiel, W.; Furstner, A., One-Point Binding Ligands for Asymmetric Gold Catalysis: Phosphoramidites with a TADDOL-Related but Acyclic Backbone. *J. Am. Chem. Soc.* **2012,** *134* (37), 15331-15342.

45. Wang, Y.; Zheng, K.; Hong, R., Chiral Silver Phosphate-Catalyzed Cycloisomeric Kinetic Resolution of alpha-Allenic Alcohols. *J. Am. Chem. Soc.* **2012,** *134* (9), 4096-4099.

46. Chiarucci, M.; Mocci, R.; Syntrivanis, L. D.; Cera, G.; Mazzanti, A.; Bandini, M., Merging Synthesis and Enantioselective Functionalization of Indoles by a Gold-Catalyzed Asymmetric Cascade Reaction. *Angew. Chem.-Int. Edit.* **2013,** *52* (41), 10850-10853.

47. Cochrane, N. A.; Nguyen, H.; Gagne, M. R., Catalytic Enantioselective Cyclization and C3-Fluorination of Polyenes. *J. Am. Chem. Soc.* **2013,** *135* (2), 628-631.

48. Cox, N.; Uehling, M. R.; Haelsig, K. T.; Lalic, G., Catalytic Asymmetric Synthesis of Cyclic Ethers Containing an alpha-Tetrasubstituted Stereocenter. *Angew. Chem.-Int. Edit.* **2013,** *52* (18), 4878-4882.

49. Faustino, H.; Alonso, I.; Mascarenas, J. L.; Lopez, F., Gold(I)-Catalyzed Cascade Cycloadditions between Allenamides and Carbonyl-Tethered Alkenes: An Enantioselective Approach to Oxa-Bridged Medium-Sized Carbocycles. *Angew. Chem.-Int. Edit.* **2013,** *52* (25), 6526-6530.

50. Huang, L.; Yang, H. B.; Zhang, D. H.; Zhang, Z.; Tang, X. Y.; Xu, Q.; Shi, M., Gold-Catalyzed Intramolecular Regio- and Enantioselective Cycloisomerization of 1,1-Bis(indolyl)-5-alkynes. *Angew. Chem.-Int. Edit.* **2013,** *52* (26), 6767-6771.

51. Li, G. H.; Zhou, W.; Li, X. X.; Bi, Q. W.; Wang, Z.; Zhao, Z. G.; Hu, W. X.; Chen, Z. L., Gold catalyzed enantioselective intermolecular 3+2 dipolar cycloaddition of N-allenyl amides with nitrones. *Chem. Commun.* **2013,** *49* (42), 4770-4772.

52. Miles, D. H.; Veguillas, M.; Toste, F. D., Gold(I)-catalyzed enantioselective bromocyclization reactions of allenes. *Chemical Science* **2013,** *4* (9), 3427-3431.

53. Sakuma, M.; Sakakura, A.; Ishihara, K., Kinetic Resolution of Racemic Carboxylic Acids through Asymmetric Protolactonization Promoted by Chiral Phosphonous Acid Diester. *Org. Lett.* **2013,** *15* (11), 2838-2841.

54. Sanjuan, A. M.; Garcia-Garcia, P.; Fernandez-Rodriguez, M. A.; Sanz, R., Enantioselective Synthesis of Cyclopentadienes by Gold(I)-Catalyzed Cyclization of 1,3-Dien-5-ynes. *Adv. Synth. Catal.* **2013,** *355* (10), 1955-1962.

55. Du Lee, S.; Timmerman, J. C.; Widenhoefer, R. A., Enantioselective Intramolecular Hydroamination of Unactivated Alkenes Catalyzed by Mono- and Bis(gold) Phosphine Complexes. *Adv. Synth. Catal.* **2014,** *356* (14-15), 3187-3192.

56. Handa, S.; Lippincott, D. J.; Aue, D. H.; Lipshutz, B. H., Asymmetric Gold-Catalyzed Lactonizations in Water at Room Temperature. *Angew. Chem.-Int. Edit.* **2014,** *53* (40), 10658-10662.

57. Nakamura, K.; Furumi, S.; Takeuchi, M.; Shibuya, T.; Tanaka, K., Enantioselective Synthesis and Enhanced Circularly Polarized Luminescence of S-Shaped Double Azahelicenes. *J. Am. Chem. Soc.* **2014,** *136* (15), 5555-5558.

58. Qian, D.; Hu, H.; Liu, F.; Tang, B.; Ye, W.; Wang, Y.; Zhang, J., Gold(I)-Catalyzed Highly Diastereo- and Enantioselective Alkyne Oxidation/Cyclopropanation of 1,6-Enynes. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13751-13755.

59. Romano, C.; Jia, M.; Monari, M.; Manoni, E.; Bandini, M., Metal-Free Enantioselective Electrophilic Activation of Allenamides: Stereoselective Dearomatization of Indoles. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13854-13857.

60. Surendra, K.; Rajendar, G.; Corey, E. J., Useful Catalytic Enantioselective Cationic Double Annulation Reactions Initiated at an Internal pi-Bond: Method and Applications. *J. Am. Chem. Soc.* **2014,** *136* (2), 642-645.

61. Yavari, K.; Aillard, P.; Zhang, Y.; Nuter, F.; Retailleau, P.; Voituriez, A.; Marinetti, A., Helicenes with Embedded Phosphole Units in Enantioselective Gold Catalysis. *Angew. Chem.-Int. Edit.* **2014,** *53* (3), 861-865.

62. Zhang, Z.-M.; Chen, P.; Li, W.; Niu, Y.; Zhao, X.-L.; Zhang, J., A New Type of Chiral Sulfinamide Monophosphine Ligands: Stereodivergent Synthesis and Application in Enantioselective Gold(I)Catalyzed Cycloaddition Reactions**. *Angew. Chem.-Int. Edit.* **2014,** *53* (17), 4350-4354.

63. Ilg, M. K.; Wolf, L. M.; Mantilli, L.; Fares, C.; Thiel, W.; Furstner, A., A Striking Case of Enantioinversion in Gold Catalysis and Its Probable Origins. *Chem.-Eur. J.* **2015,** *21* (35), 12279-12284.

64. Ji, K.; Zheng, Z.; Wang, Z.; Zhang, L., Enantioselective Oxidative Gold Catalysis Enabled by a Designed Chiral P,N-Bidentate Ligand. *Angew. Chem.-Int. Edit.* **2015,** *54* (4), 1245-1249.

65. Jia, M.; Monari, M.; Yang, Q.-Q.; Bandini, M., Enantioselective gold catalyzed dearomative 2+2 -cycloaddition between indoles and allenamides. *Chem. Commun.* **2015,** *51* (12), 2320-2323.

66. Klimczyk, S.; Misale, A.; Huang, X. L.; Maulide, N., Dimeric TADDOL Phosphoramidites in Asymmetric Catalysis: Domino Deracemization and Cyclopropanation of Sulfonium Ylides. *Angew. Chem.-Int. Edit.* **2015,** *54* (35), 10365-10369.

67. Wang, Y. D.; Zhang, P. C.; Liu, Y.; Xia, F.; Zhang, J. L., Enantioselective gold-catalyzed intermolecular 2+2 versus 4+2 -cycloadditions of 3-styrylindoles with N-allenamides: observation of interesting substituent effects. *Chemical Science* **2015,** *6* (10), 5564-5570.

68. Wang, Y. D.; Zhang, P. C.; Qian, D. Y.; Zhang, J. L., Highly Regio-, Diastereo-, and Enantioselective Gold(I)-Catalyzed Intermolecular Annulations with N-Allenamides at the Proximal C=C Bond. *Angew. Chem.-Int. Edit.* **2015,** *54* (49), 14849-14852.

69. Wang, Z.; Ai, F.; Wang, Z.; Zhao, W.; Zhu, G.; Lin, Z.; Sun, J., Organocatalytic Asymmetric Synthesis of 1,1-Diarylethanes by Transfer Hydrogenation. *J. Am. Chem. Soc.* **2015,** *137* (1), 383-389.

70. Wu, H. M.; Zi, W. W.; Li, G. G.; Lu, H. J.; Toste, F. D., Gold(I)-Catalyzed Desymmetrization of 1,4-Dienes by an Enantioselective Tandem Alkoxylation/Claisen Rearrangement. *Angew. Chem.-Int. Edit.* **2015,** *54* (29), 8529-8532.

71. Zi, W.; Wu, H.; Toste, F. D., Gold(I)-Catalyzed Dearomative Rautenstrauch Rearrangement: Enantioselective Access to Cyclopenta b indoles. *J. Am. Chem. Soc.* **2015,** *137* (9), 3225-3228.

72. Zi, W. W.; Toste, F. D., Gold(I)-Catalyzed Enantioselective Desymmetrization of 1,3-Diols through Intramolecular Hydroalkoxylation of Allenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (48), 14447-14451.

73. Khrakovsky, D. A.; Tao, C. Z.; Johnson, M. W.; Thornbury, R. T.; Shevick, S. L.; Toste, F. D., Enantioselective, Stereodivergent Hydroazidation and Hydroamination of Allenes Catalyzed by Acyclic Diaminocarbene (ADC) Gold(I) Complexes. *Angew. Chem.-Int. Edit.* **2016,** *55* (20), 6079-6083.

74. Bohan, P. T.; Toste, F. D., Well-Defined Chiral Gold(III) Complex Catalyzed Direct Enantioconvergent Kinetic Resolution of 1,5-Enynes. *J. Am. Chem. Soc.* **2017,** *139* (32), 11016-11019.

75. Garcia-Morales, C.; Ranieri, B.; Escofet, I.; Lopez-Suarez, L.; Obradors, C.; Konovalov, A. I.; Echavarren, A. M., Enantioselective Synthesis of Cyclobutenes by Intermolecular 2+2 Cycloaddition with Non-C-2 Symmetric Digold Catalysts. *J. Am. Chem. Soc.* **2017,** *139* (39), 13628-13631.

76. Gonzalez-Fernandez, E.; Nicholls, L. D. M.; Schaaf, L. D.; Fares, C.; Lehmann, C. W.; Alcarazo, M., Enantioselective Synthesis of 6 Carbohelicenes. *J. Am. Chem. Soc.* **2017,** *139* (4), 1428-1431.

77. Li, Y. Y.; Li, W. B.; Zhang, J. L., Gold-Catalyzed Enantioselective Annulations. *Chem.-Eur. J.* **2017,** *23* (3), 467-512.

78. Niemeyer, Z. L.; Pindi, S.; Khrakovsky, D. A.; Kuzniewski, C. N.; Hong, C. M.; Joyce, L. A.; Sigman, M. S.; Toste, F. D., Parameterization of Acyclic Diaminocarbene Ligands Applied to a Gold(I)-Catalyzed Enantioselective Tandem Rearrangement/Cyclization. *J. Am. Chem. Soc.* **2017,** *139* (37), 12943-12946.

79. Pirovano, V.; Borri, M.; Abbiati, G.; Rizzato, S.; Rossi, E., Gold(I)-Catalyzed Enantioselective Synthesis of Tetrahydrocarbazoles through Dearomative 4+2 Cycloadditions of 3/2-Substituted 2/3-Vinylindoles. *Adv. Synth. Catal.* **2017,** *359* (11), 1912-1918.

80. Wang, Y. D.; Zhang, P. C.; Di, X. Y.; Dai, Q.; Zhang, Z. M.; Zhang, J. L., Gold-Catalyzed Asymmetric Intramolecular Cyclization of N-Allenamides for the Synthesis of Chiral Tetrahydrocarbolines. *Angew. Chem.-Int. Edit.* **2017,** *56* (50), 15905-15909.

81. Wang, Z. X.; Nicolini, C.; Hervieu, C.; Wong, Y. F.; Zanoni, G.; Zhang, L. M., Remote Cooperative Group Strategy Enables Ligands for Accelerative Asymmetric Gold Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (45), 16064-16067.

82. Zhu, Y. G.; He, W.; Wang, W.; Pitsch, C. E.; Wang, X. T.; Wang, X., Enantioselective Tandem Cyclization of Alkyne-Tethered Indoles Using Cooperative Silver(I)/Chiral Phosphoric Acid Catalysis. *Angew. Chem.-Int. Edit.* **2017,** *56* (40), 12206-12209.

83. Kim, H.; Choi, S. Y.; Shin, S., Asymmetric Synthesis of Dihydropyranones via Gold(I)-Catalyzed Intermolecular 4+2 Annulation of Propiolates and Alkenes. *Angew. Chem.-Int. Edit.* **2018,** *57* (40), 13130-13134.

84. Marcote, D. C.; Varela, I.; Fernandez-Casado, J.; Mascarenas, J. L.; Lopez, F., Gold(I)-Catalyzed Enantioselective Annulations between Allenes and Alkene-Tethered Oxime Ethers: A Straight Entry to Highly Substituted Piperidines and aza-Bridged Medium-Sized Carbocycles. *J. Am. Chem. Soc.* **2018,** *140* (48), 16821-16833.

85. Nanko, M.; Shibuya, S.; Inaba, Y.; Ono, S.; Ito, S.; Mikami, K., gem-Digold Acetylide Complexes for Catalytic Intermolecular 4+2 Cycloaddition: Having Two Gold Centers Is Better for Asymmetric Catalysis. *Org. Lett.* **2018,** *20* (23), 7353-7357.

86. Zuccarello, G.; Mayans, J. G.; Escofet, I.; Scharnagel, D.; Kirillova, M. S.; Perez-Jimeno, A. H.; Calleja, P.; Boothe, J. R.; Echavarren, A. M., Enantioselective Folding of Enynes by Gold(I) Catalysts with a Remote C-2-Chiral Element. *J. Am. Chem. Soc.* **2019,** *141* (30), 11858-11863.

87. Hartung, T.; Machleid, R.; Simon, M.; Golz, C.; Alcarazo, M., Enantioselective Synthesis of 1,12-Disubstituted 4 Helicenes. *Angew. Chem.-Int. Edit.* **2020,** *59* (14), 5660-5664.

88. Kim, H.; Jang, J.; Shin, S., Gold-Catalyzed Asymmetric Thioallylation of Propiolates via Charge-Induced Thio-Claisen Rearrangement. *J. Am. Chem. Soc.* **2020,** *142* (49), 20788-20795.

89. Hong, F.-L.; Shi, C.-Y.; Hong, P.; Zhai, T.-Y.; Zhu, X.-Q.; Lu, X.; Ye, L.-W., Copper-Catalyzed Asymmetric Diyne Cyclization via [1,2]-Stevens-Type Rearrangement for the Synthesis of Chiral Chromeno[3,4-c]pyrroles. *Angewandte Chemie International Edition* **2022,** *61* (7), e202115554.

90. Lin, B.; Yang, T.; Zhang, D.; Zhou, Y.; Wu, L.; Qiu, J.; Chen, G.-Q.; Che, C.-M.; Zhang, X., Gold-Catalyzed Desymmetric Lactonization of Alkynylmalonic Acids Enabled by Chiral Bifunctional P,N ligands. *Angewandte Chemie International Edition* **2022,** *61* (23), e202201739.

91. Pelliccioli, V.; Hartung, T.; Simon, M.; Golz, C.; Licandro, E.; Cauteruccio, S.; Alcarazo, M., Enantioselective Synthesis of Dithia[5]helicenes and their Postsynthetic Functionalization to Access Dithia[9]helicenes. *Angewandte Chemie International Edition* **2022,** *61* (6), e202114577.

92. Qi, L.-J.; Li, C.-T.; Huang, Z.-Q.; Jiang, J.-T.; Zhu, X.-Q.; Lu, X.; Ye, L.-W., Enantioselective Copper-Catalyzed Formal [2+1] and [4+1] Annulations of Diynes with Ketones via Carbonyl Ylides. *Angewandte Chemie International Edition* **2022,** *61* (43), e202210637.

93. Zhou, H.; Han, J. T.; Nöthling, N.; Lindner, M. M.; Jenniches, J.; Kühn, C.; Tsuji, N.; Zhang, L.; List, B., Organocatalytic Asymmetric Synthesis of Si-Stereogenic Silyl Ethers. *J. Am. Chem. Soc.* **2022,** *144* (23), 10156-10161.

94. Raut, R. K.; Matsutani, S.; Shi, F.; Kataoka, S.; Poje, M.; Mitschke, B.; Maeda, S.; Tsuji, N.; List, B., Catalytic asymmetric fragmentation of cyclopropanes. *Science* **2024,** *386* (6718), 225-230.

95. Wakchaure, V. N.; DeSnoo, W.; Laconsay, C. J.; Leutzsch, M.; Tsuji, N.; Tantillo, D. J.; List, B., Catalytic asymmetric cationic shifts of aliphatic hydrocarbons. *Nature* **2024,** *625* (7994), 287-292.

2.7. Chiral Acylation

1. Liang, J.; Ruble, J. C.; Fu, G. C., Dynamic kinetic resolutions catalyzed by a planar-chiral derivative of DMAP: Enantioselective synthesis of protected alpha-amino acids from racemic azlactones. *J. Org. Chem.* **1998,** *63* (10), 3154-3155.

2. Ruble, J. C.; Fu, G. C., Enantioselective construction of quaternary stereocenters: Rearrangements of O-acylated azlactones catalyzed by a planar-chiral derivative of 4-(pyrrolidino)pyridine. *J. Am. Chem. Soc.* **1998,** *120* (44), 11532-11533.

3. Ruble, J. C.; Tweddell, J.; Fu, G. C., Kinetic resolution of arylalkylcarbinols catalyzed by a planar-chiral derivative of DMAP: A new benchmark for nonenzymatic acylation. *J. Org. Chem.* **1998,** *63* (9), 2794-2795.

4. Tao, B. T.; Ruble, J. C.; Hoic, D. A.; Fu, G. C., Nonenzymatic kinetic resolution of propargylic alcohols by a planar-chiral DMAP derivative: Crystallographic characterization of the acylated catalyst. *J. Am. Chem. Soc.* **1999,** *121* (21), 5091-5092.

5. Hills, I. D.; Fu, G. C., Catalytic enantioselective synthesis of oxindoles and benzofuranones that bear a quaternary stereocenter. *Angew. Chem.-Int. Edit.* **2003,** *42* (33), 3921-3924.

6. Shaw, S. A.; Aleman, P.; Vedejs, E., Development of chiral nucleophilic pyridine catalysts: Applications in asymmetric quaternary carbon synthesis. *J. Am. Chem. Soc.* **2003,** *125* (44), 13368-13369.

7. Vedejs, E.; Daugulis, A., A highly enantioselective phosphabicyclooctane catalyst for the kinetic resolution of benzylic alcohols. *J. Am. Chem. Soc.* **2003,** *125* (14), 4166-4173.

8. Vedejs, E.; Daugulis, O.; Harper, L. A.; MacKay, J. A.; Powell, D. R., A comparison of monocyclic and bicyclic phospholanes as acyl- transfer catalysts. *J. Org. Chem.* **2003,** *68* (13), 5020-5027.

9. Birman, V. B.; Uffman, E. W.; Hui, J.; Li, X. M.; Kilbane, C. J., 2,3-dihydroimidazo 1,2-a pyridines: A new class of enantioselective acyl transfer catalysts and their use in kinetic resolution of alcohols. *J. Am. Chem. Soc.* **2004,** *126* (39), 12226-12227.

10. Evans, J. W.; Fierman, M. B.; Miller, S. J.; Ellman, J. A., Catalytic enantioselective synthesis of sulfinate esters through the dynamic resolution of tert-butanesulfinyl chloride. *J. Am. Chem. Soc.* **2004,** *126* (26), 8134-8135.

11. Ishihara, K.; Kosugi, Y.; Akakura, M., Rational design of an L-histidine-derived minimal artificial acylase for the kinetic resolution of racemic alcohols. *J. Am. Chem. Soc.* **2004,** *126* (39), 12212-12213.

12. MacKay, J. A.; Vedejs, E., Enantioselective acylation using a second-generation P-aryl-2- phosphabicyclo 3.3.0 octane catalyst. *J. Org. Chem.* **2004,** *69* (20), 6934-6937.

13. Vedejs, E.; Daugulis, O.; Tuttle, N., Desymmetrization of meso-hydrobenzoin using chiral, nucleophilic phosphine catalysts. *J. Org. Chem.* **2004,** *69* (4), 1389-1392.

14. Kano, T.; Sasaki, K.; Maruoka, K., Enantioselective acylation of secondary alcohols catalyzed by chiral N-heterocyclic carbenes. *Org. Lett.* **2005,** *7* (7), 1347-1349.

15. Mermerian, A. H.; Fu, G. C., Catalytic enantioselective construction of all-carbon quaternary stereocenters: Synthetic and mechanistic studies of the C-acylation of silyl ketene acetals. *J. Am. Chem. Soc.* **2005,** *127* (15), 5604-5607.

16. Kundig, E. P.; Garcia, A. E.; Lomberget, T.; Garcia, P. P.; Romanens, P., Truncated Cinchona alkaloids as catalysts in enantioselective monobenzoylation of meso-1,2-diols. *Chem. Commun.* **2008,** (30), 3519-3521.

17. Lewis, C. A.; Gustafson, J. L.; Chiu, A.; Balsells, J.; Pollard, D.; Murry, J.; Reamer, R. A.; Hansen, K. B.; Miller, S. J., A Case of Remote Asymmetric Induction in the Peptide-Catalyzed Desymmetrization of a Bis(phenol). *J. Am. Chem. Soc.* **2008,** *130* (48), 16358-16365.

18. Li, X. M.; Liu, P.; Houk, K. N.; Birman, V. B., Origin of enantioselectivity in CF3-PIP-catalyzed kinetic resolution of secondary benzylic alcohols. *J. Am. Chem. Soc.* **2008,** *130* (42), 13836-13837.

19. Muller, C. E.; Wanka, L.; Jewell, K.; Schreiner, P. R., Enantioselective kinetic resolution of trans-cycloalkane-1,2-diols. *Angew. Chem.-Int. Edit.* **2008,** *47* (33), 6180-6183.

20. Muller, C. E.; Wanka, L.; Jewell, K.; Schreiner, P. R., Enantioselective kinetic resolution of trans-cycloalkane-1,2-diols. *Angew. Chem.-Int. Edit.* **2008,** *47* (33), 6180-6183.

21. Shiina, I.; Nakata, K.; Onda, Y. S., Kinetic Resolution of Racemic Carboxylic Acids Using Achiral Alcohols by the Promotion of Benzoic Anhydrides and Tetramisole Derivatives: Production of Chiral Nonsteroidal Anti-Inflammatory Drugs and Their Esters. *Eur. J. Org. Chem.* **2008,** (35), 5887-5890.

22. De, C. K.; Klauber, E. G.; Seidel, D., Merging Nucleophilic and Hydrogen Bonding Catalysis: An Anion Binding Approach to the Kinetic Resolution of Amines. *J. Am. Chem. Soc.* **2009,** *131* (47), 17060-+.

23. Joannesse, C.; Johnston, C. P.; Concellon, C.; Simal, C.; Philp, D.; Smith, A. D., Isothiourea-Catalyzed Enantioselective Carboxy Group Transfer. *Angew. Chem.-Int. Edit.* **2009,** *48* (47), 8914-8918.

24. Fowler, B. S.; Mikochik, P. J.; Miller, S. J., Peptide-Catalyzed Kinetic Resolution of Formamides and Thioformamides as an Entry to Nonracemic Amines. *J. Am. Chem. Soc.* **2010,** *132* (9), 2870-+.

25. Hu, B.; Meng, M.; Wang, Z.; Du, W. T.; Fossey, J. S.; Hu, X. Q.; Deng, W. P., A Highly Selective Ferrocene-Based Planar Chiral PIP (Fc-PIP) Acyl Transfer Catalyst for the Kinetic Resolution of Alcohols. *J. Am. Chem. Soc.* **2010,** *132* (47), 17041-17044.

26. Klauber, E. G.; De, C. K.; Shah, T. K.; Seidel, D., Merging Nucleophilic and Hydrogen Bonding Catalysis: An Anion Binding Approach to the Kinetic Resolution of Propargylic Amines. *J. Am. Chem. Soc.* **2010,** *132* (39), 13624-13626.

27. Shiina, I.; Nakata, K.; Ono, K.; Onda, Y.; Itagak, M., Kinetic Resolution of Racemic alpha-Arylalkanoic Acids with Achiral Alcohols via the Asymmetric Esterification Using Carboxylic Anhydrides and Acyl-Transfer Catalysts. *J. Am. Chem. Soc.* **2010,** *132* (33), 11629-11641.

28. Zhang, Z. F.; Xie, F.; Jia, J.; Zhang, W. B., Chiral Bicycle Imidazole Nucleophilic Catalysts: Rational Design, Facile Synthesis, and Successful Application in Asymmetric Steglich Rearrangement. *J. Am. Chem. Soc.* **2010,** *132* (45), 15939-15941.

29. Binanzer, M.; Hsieh, S. Y.; Bode, J. W., Catalytic Kinetic Resolution of Cyclic Secondary Amines. *J. Am. Chem. Soc.* **2011,** *133* (49), 19698-19701.

30. Birrell, J. A.; Desrosiers, J. N.; Jacobsen, E. N., Enantioselective Acylation of Silyl Ketene Acetals through Fluoride Anion-Binding Catalysis. *J. Am. Chem. Soc.* **2011,** *133* (35), 13872-13875.

31. Bumbu, V. D.; Birman, V. B., Kinetic Resolution of N-Acyl-beta-Lactams via Benzotetramisole-Catalyzed Enantioselective Alcoholysis. *J. Am. Chem. Soc.* **2011,** *133* (35), 13902-13905.

32. De, C. K.; Seidel, D., Catalytic Enantioselective Desymmetrization of meso-Diamines: A Dual Small-Molecule Catalysis Approach. *J. Am. Chem. Soc.* **2011,** *133* (37), 14538-14541.

33. Iwahana, S.; Iida, H.; Yashima, E., Oxidative Esterification, Thioesterification, and Amidation of Aldehydes by a Two-Component Organocatalyst System Using a Chiral N-Heterocyclic Carbene and Redox-Active Riboflavin. *Chem.-Eur. J.* **2011,** *17* (29), 8009-8013.

34. Klauber, E. G.; Mittal, N.; Shah, T. K.; Seidel, D., A Dual-Catalysis/Anion-Binding Approach to the Kinetic Resolution of Allylic Amines. *Org. Lett.* **2011,** *13* (9), 2464-2467.

35. Muller, C. E.; Schreiner, P. R., Organocatalytic Enantioselective Acyl Transfer onto Racemic as well as meso Alcohols, Amines, and Thiols. *Angew. Chem.-Int. Edit.* **2011,** *50* (27), 6012-6042.

36. Nielsen, M.; Jacobsen, C. B.; Jorgensen, K. A., Asymmetric Organocatalytic Electrophilic Phosphination. *Angew. Chem.-Int. Edit.* **2011,** *50* (14), 3211-3214.

37. Rong, Z. Q.; Jia, M. Q.; You, S. L., Enantioselective N-Heterocyclic Carbene-Catalyzed Michael Addition to alpha,beta-Unsaturated Aldehydes by Redox Oxidation. *Org. Lett.* **2011,** *13* (15), 4080-4083.

38. Sakakura, A.; Umemura, S.; Ishihara, K., Desymmetrization of meso-Glycerol Derivatives Induced by L-Histidine-Derived Acylation Catalysts. *Adv. Synth. Catal.* **2011,** *353* (11-12), 1938-1942.

39. Sun, F. G.; Sun, L. H.; Ye, S., N-Heterocyclic Carbene-Catalyzed Enantioselective Annulation of Bromoenal and 1,3-Dicarbonyl Compounds. *Adv. Synth. Catal.* **2011,** *353* (17), 3134-3138.

40. Yang, X.; Birman, V. B., Nonenzymatic Dynamic Kinetic Resolution of alpha-(Arylthio)- and alpha-(Alkylthio) alkanoic Acids. *Angew. Chem.-Int. Edit.* **2011,** *50* (24), 5553-5555.

41. Hsieh, S. Y.; Binanzer, M.; Kreituss, I.; Bode, J. W., Expanded substrate scope and catalyst optimization for the catalytic kinetic resolution of N-heterocycles. *Chem. Commun.* **2012,** *48* (71), 8892-8894.

42. Kreituss, I.; Murakami, Y.; Binanzer, M.; Bode, J. W., Kinetic Resolution of Nitrogen Heterocycles with a Reusable Polymer-Supported Reagent. *Angew. Chem.-Int. Edit.* **2012,** *51* (42), 10660-10663.

43. Larionov, E.; Mahesh, M.; Spivey, A. C.; Wei, Y.; Zipse, H., Theoretical Prediction of Selectivity in Kinetic Resolution of Secondary Alcohols Catalyzed by Chiral DMAP Derivatives. *J. Am. Chem. Soc.* **2012,** *134* (22), 9390-9399.

44. Lee, S. Y.; Murphy, J. M.; Ukai, A.; Fu, G. C., Nonenzymatic Dynamic Kinetic Resolution of Secondary Alcohols via Enantioselective Acylation: Synthetic and Mechanistic Studies. *J. Am. Chem. Soc.* **2012,** *134* (36), 15149-15153.

45. Yang, X.; Bumbu, V. D.; Liu, P.; Li, X. M.; Jiang, H.; Uffman, E. W.; Guo, L.; Zhang, W.; Jiang, X. T.; Houk, K. N.; Birman, V. B., Catalytic, Enantioselective N-Acylation of Lactams and Thiolactams Using Amidine-Based Catalysts. *J. Am. Chem. Soc.* **2012,** *134* (42), 17605-17612.

46. Yang, X.; Liu, P.; Houk, K. N.; Birman, V. B., Manifestation of Felkin-Anh Control in Enantioselective Acyl Transfer Catalysis: Kinetic Resolution of Carboxylic Acids. *Angew. Chem.-Int. Edit.* **2012,** *51* (38), 9638-9642.

47. Cheng, J. J.; Huang, Z. J.; Chi, Y. R., NHC Organocatalytic Formal LUMO Activation of alpha,beta-Unsaturated Esters for Reaction with Enamides. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8592-8596.

48. Kuwano, S.; Harada, S.; Kang, B.; Oriez, R.; Yamaoka, Y.; Takasu, K.; Yamada, K., Enhanced Rate and Selectivity by Carboxylate Salt as a Basic Cocatalyst in Chiral N-Heterocyclic Carbene-Catalyzed Asymmetric Acylation of Secondary Alcohols. *J. Am. Chem. Soc.* **2013,** *135* (31), 11485-11488.

49. Manville, N.; Alite, H.; Haeffner, F.; Hoveyda, A. H.; Snapper, M. L., Enantioselective silyl protection of alcohols promoted by a combination of chiral and achiral Lewis basic catalysts. *Nature Chemistry* **2013,** *5* (9), 768-774.

50. Mo, J. M.; Shen, L.; Chi, Y. R., Direct beta-Activation of Saturated Aldehydes to Formal Michael Acceptors through Oxidative NHC Catalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8588-8591.

51. Robinson, E. R. T.; Fallan, C.; Simal, C.; Slawin, A. M. Z.; Smith, A. D., Anhydrides as alpha,beta-unsaturated acyl ammonium precursors: isothiourea-promoted catalytic asymmetric annulation processes. *Chemical Science* **2013,** *4* (5), 2193-2200.

52. Vellalath, S.; Van, K. N.; Romo, D., Direct Catalytic Asymmetric Synthesis of N-Heterocycles from Commodity Acid Chlorides by Employing alpha,beta-Unsaturated Acylammonium Salts. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13688-13693.

53. Allen, S. E.; Hsieh, S. Y.; Gutierrez, O.; Bode, J. W.; Kozlowski, M. C., Concerted Amidation of Activated Esters: Reaction Path and Origins of Selectivity in the Kinetic Resolution of Cyclic Amines via N-Heterocyclic Carbenes and Hydroxamic Acid Cocatalyzed Acyl Transfer. *J. Am. Chem. Soc.* **2014,** *136* (33), 11783-11791.

54. Lu, S.; Poh, S. B.; Zhao, Y., Kinetic Resolution of 1,1 '-Biaryl-2,2 '-Diols and Amino Alcohols through NHC-Catalyzed Atroposelective Acylation. *Angew. Chem.-Int. Edit.* **2014,** *53* (41), 11041-11045.

55. Ma, G. Y.; Deng, J.; Sibi, M. P., Fluxionally Chiral DMAP Catalysts: Kinetic Resolution of Axially Chiral Biaryl Compounds. *Angew. Chem.-Int. Edit.* **2014,** *53* (44), 11818-11821.

56. Roux, C.; Candy, M.; Pons, J. M.; Chuzel, O.; Bressy, C., Stereocontrol of All-Carbon Quaternary Centers through Enantioselective Desymmetrization of Meso Primary Diols by Organocatalyzed Acyl Transfer. *Angew. Chem.-Int. Edit.* **2014,** *53* (3), 766-770.

57. Fukata, Y.; Asano, K.; Matsubara, S., Facile Net Cycloaddition Approach to Optically Active 1,5-Benzothiazepines. *J. Am. Chem. Soc.* **2015,** *137* (16), 5320-5323.

58. Mittal, N.; Lippert, K. M.; De, C. K.; Klauber, E. G.; Emge, T. J.; Schreiner, P. R.; Seidel, D., A Dual-Catalysis Anion-Binding Approach to the Kinetic Resolution of Amines: Insights into the Mechanism via a Combined Experimental and Computational Study. *J. Am. Chem. Soc.* **2015,** *137* (17), 5748-5758.

59. Wanner, B.; Kreituss, I.; Gutierrez, O.; Kozlowski, M. C.; Bode, J. W., Catalytic Kinetic Resolution of Disubstituted Piperidines by Enantioselective Acylation: Synthetic Utility and Mechanistic Insights. *J. Am. Chem. Soc.* **2015,** *137* (35), 11491-11497.

60. Chen, X. K.; Fong, J. Z. M.; Xu, J. F.; Mou, C. L.; Lu, Y. P.; Yang, S.; Song, B. A.; Chi, Y. R., Carbene-Catalyzed Dynamic Kinetic Resolution of Carboxylic Esters. *J. Am. Chem. Soc.* **2016,** *138* (23), 7212-7215.

61. Dong, S. X.; Frings, M.; Cheng, H. C.; Wen, J.; Zhang, D.; Raabe, G.; Bolm, C., Organocatalytic Kinetic Resolution of Sulfoximines. *J. Am. Chem. Soc.* **2016,** *138* (7), 2166-2169.

62. Mandai, H.; Fujii, K.; Yasuhara, H.; Abe, K.; Mitsudo, K.; Korenaga, T.; Suga, S., Enantioselective acyl transfer catalysis by a combination of common catalytic motifs and electrostatic interactions. *Nature Communications* **2016,** *7*.

63. Piotrowski, D. W.; Kamlet, A. S.; Dechert-Schmitt, A. M. R.; Yan, J. L.; Brandt, T. A.; Xiao, J.; Wei, L. Q.; Barrila, M. T., Regio- and Enantioselective Synthesis of Azole Hemiaminal Esters by Lewis Base Catalyzed Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2016,** *138* (14), 4818-4823.

64. Chen, C. T.; Tsai, C. C.; Tsou, P. K.; Huang, G. T.; Yu, C. H., Enantiodivergent Steglich rearrangement of O-carboxylazlactones catalyzed by a chirality switchable helicene containing a 4-aminopyridine unit. *Chemical Science* **2017,** *8* (1), 524-529.

65. Murray, J. I.; Floden, N. J.; Bauer, A.; Fessner, N. D.; Dunklemann, D. L.; Bob-Egbe, O.; Rzepa, H. S.; Burgi, T.; Richardson, J.; Spivey, A. C., Kinetic Resolution of 2-Substituted Indolines by N-Sulfonylation using an Atropisomeric 4-DMAP-N-oxide Organocatalyst. *Angew. Chem.-Int. Edit.* **2017,** *56* (21), 5760-5764.

66. Greenhalgh, M. D.; Smith, S. M.; Walden, D. M.; Taylor, J. E.; Brice, Z.; Robinson, E. R. T.; Fallan, C.; Cordes, D. B.; Slawin, A. M. Z.; Richardson, H. C.; Grove, M. A.; Cheong, P. H. Y.; Smith, A. D., A C=O center dot center dot center dot Isothiouronium Interaction Dictates Enantiodiscrimination in Acylative Kinetic Resolutions of Tertiary Heterocyclic Alcohols. *Angew. Chem.-Int. Edit.* **2018,** *57* (12), 3200-3206.

67. Yang, H.; Zheng, W. H., Chiral-Organotin-Catalyzed Kinetic Resolution of Vicinal Amino Alcohols. *Angew. Chem.-Int. Edit.* **2019,** *58* (45), 16177-16180.

68. Yang, X.; Majhi, P. K.; Chai, H.; Liu, B.; Sun, J.; Liu, T.; Liu, Y.; Zhou, L.; Xu, J.; Liu, J.; Wang, D.; Zhao, Y.; Jin, Z.; Chi, Y. R., Carbene-Catalyzed Enantioselective Aldol Reaction: Post-Aldol Stereochemistry Control and Formation of Quaternary Stereogenic Centers. *Angewandte Chemie International Edition* **2021,** *60* (1), 159-165.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

3.Homo Activation

3.1 Chiral enolate generation

3.1.1 Chiral Enolates via Deprotonation

1. Ito, Y.; Sawamura, M.; Hayashi, T., CATALYTIC ASYMMETRIC ALDOL REACTION - REACTION OF ALDEHYDES WITH ISOCYANOACETATE CATALYZED BY A CHIRAL FERROCENYLPHOSPHINE-GOLD(I) COMPLEX. *J. Am. Chem. Soc.* **1986,** *108* (20), 6405-6406.

2. Togni, A.; Pastor, S. D., CHIRAL COOPERATIVITY - THE NATURE OF THE DIASTEREOSELECTIVE AND ENANTIOSELECTIVE STEP IN THE GOLD(I)-CATALYZED ALDOL REACTION UTILIZING CHIRAL FERROCENYLAMINE LIGANDS. *J. Org. Chem.* **1990,** *55* (5), 1649-1664.

3. Evans, D. A.; Nelson, S. G., Chiral magnesium bis(sulfonamide) complexes as catalysts for the merged enolization and enantioselective amination of N- acyloxazolidinones. A catalytic approach to the synthesis of arylglycines. *J. Am. Chem. Soc.* **1997,** *119* (27), 6452-6453.

4. Ji, J. G.; Barnes, D. M.; Zhang, J.; King, S. A.; Wittenberger, S. J.; Morton, H. E., Catalytic enantioselective conjugate addition of 1,3-dicarbonyl compounds to nitroalkenes. *J. Am. Chem. Soc.* **1999,** *121* (43), 10215-10216.

5. Hintermann, L.; Togni, A., Catalytic enantioselective fluorination of beta-ketoesters. *Angew. Chem.-Int. Edit.* **2000,** *39* (23), 4359-+.

6. Barnes, D. M.; Ji, J. G.; Fickes, M. G.; Fitzgerald, M. A.; King, S. A.; Morton, H. E.; Plagge, F. A.; Preskill, M.; Wagaw, S. H.; Wittenberger, S. J.; Zhang, J., Development of a catalytic enantioselective conjugate addition of 1,3-dicarbonyl compounds to nitroalkenes for the synthesis of endothelin-A antagonist ABT-546. Scope, mechanism, and further application to the synthesis of the antidepressant rolipram. *J. Am. Chem. Soc.* **2002,** *124* (44), 13097-13105.

7. Hamashima, Y.; Hotta, D.; Sodeoka, M., Direct generation of nucleophilic chiral palladium enolate from 1,3-dicarbonyl compounds: Catalytic enantioselective Michael reaction with enones. *J. Am. Chem. Soc.* **2002,** *124* (38), 11240-11241.

8. Hamashima, Y.; Yagi, K.; Takano, H.; Tamas, L.; Sodeoka, M., An efficient enantioselective fluorination of various beta- ketoesters catalyzed chiral palladium complexes. *J. Am. Chem. Soc.* **2002,** *124* (49), 14530-14531.

9. Piana, S.; Devillers, I.; Togni, A.; Rothlisberger, U., The mechanism of catalytic enantioselective fluorination: Computational and experimental studies. *Angew. Chem.-Int. Edit.* **2002,** *41* (6), 979-+.

10. Halland, N.; Velgaard, T.; Jorgensen, K. A., Direct asymmetric Michael reactions of cyclic 1,3-dicarbonyl compounds and enamines catalyzed by chiral bisoxazoline- copper(II) complexes. *J. Org. Chem.* **2003,** *68* (13), 5067-5074.

11. Marigo, M.; Juhl, K.; Jorgensen, K. A., Catalytic, highly enantioselective, direct amination of beta- ketoesters. *Angew. Chem.-Int. Edit.* **2003,** *42* (12), 1367-1369.

12. Marigo, M.; Kjaersgaard, A.; Juhl, K.; Gathergood, N.; Jorgensen, K. A., Direct catalytic asymmetric Mannich reactions of malonates and beta-keto esters. *Chem.-Eur. J.* **2003,** *9* (10), 2359-2367.

13. Hamashima, Y.; Takano, H.; Hotta, D.; Sodeoka, M., Immobilization and reuse of Pd complexes in ionic liquid: Efficient catalytic asymmetric fluorination and Michael reactions with beta-ketoesters. *Org. Lett.* **2003,** *5* (18), 3225-3228.

14. Evans, D. A.; Downey, C. W.; Hubbs, J. L., Ni(II) bis(oxazoline)-catalyzed enantioselective syn aldol reactions of N-propionylthiazolidinethiones in the presence of silyl triflates. *J. Am. Chem. Soc.* **2003,** *125* (29), 8706-8707.

15. Bernardi, L.; Gothelf, A. S.; Hazell, R. G.; Jorgensen, K. A., Catalytic asymmetric Mannich reactions of glycine derivatives with imines. A new approach to optically active alpha,beta- diamino acid derivatives. *J. Org. Chem.* **2003,** *68* (7), 2583-2591.

16. Frantz, R.; Hintermann, L.; Perseghini, M.; Broggini, D.; Togni, A., Titanium-catalyzed stereoselective geminal heterodihalogenation of beta-ketoesters. *Org. Lett.* **2003,** *5* (10), 1709-1712.

17. Tian, S. K.; Hong, R.; Deng, L., Catalytic asymmetric cyanosilylation of ketones with chiral Lewis base. *J. Am. Chem. Soc.* **2003,** *125* (33), 9900-9901.

18. Comelles, J.; Moreno-Manas, M.; Perez, E.; Roglans, A.; Sebastian, R. M.; Vallribera, A., Ionic and covalent copper(II)-based catalysts for Michael additions. The mechanism. *J. Org. Chem.* **2004,** *69* (20), 6834-6842.

19. Ma, S. M.; Jiao, N.; Zheng, Z. L.; Ma, Z. C.; Zhan, L.; Ye, L. W.; Deng, Y. Q.; Chen, G. F., Cu- and Pd-catalyzed asymmetric one-pot tandem addition- cyclization reaction of 2-(2 ',3 '-alkadienyl)-beta-keto esters, organic halides, and dibenzyl azodicarboxylate: An effective protocol for the enantioselective synthesis of pyrazolidine derivatives. *Org. Lett.* **2004,** *6* (13), 2193-2196.

20. Bella, M.; Jorgensen, K. A., Organocatalytic enantioselective conjugate addition to alkynones. *J. Am. Chem. Soc.* **2004,** *126* (18), 5672-5673.

21. Halland, N.; Aburel, P. S.; Jorgensen, K. A., Highly enantio- and diastereoselective organocatalytic asymmetric domino Michael-Aldol reaction of beta-ketoesters and alpha,beta-unsaturated ketones. *Angew. Chem.-Int. Edit.* **2004,** *43* (10), 1272-1277.

22. Saaby, S.; Bella, M.; Jorgensen, K. A., Asymmetric construction of quaternary stereocenters by direct organocatalytic amination of alpha-substituted alpha- cyanoacetates and beta-dicarbonyl compounds. *J. Am. Chem. Soc.* **2004,** *126* (26), 8120-8121.

23. Takenaka, K.; Uozumi, Y., Development of chiral pincer palladium complexes bearing a pyrroloimidazolone unit. Catalytic use for asymmetric Michael addition. *Org. Lett.* **2004,** *6* (11), 1833-1835.

24. Acocella, M. R.; Mancheno, O. G.; Bella, M.; Jorgensen, K. A., Organocatalytic asymmetric hydroxylation of beta-keto esters: Metal-free synthesis of optically active anti-diols. *J. Org. Chem.* **2004,** *69* (23), 8165-8167.

25. Suto, Y.; Tsuji, R.; Kanai, M.; Shibasaki, M., Cu(I)-catalyzed direct enantioselective cross aldol-type reaction of acetonitrile. *Org. Lett.* **2005,** *7* (17), 3757-3760.

26. Evans, D. A.; Seidel, D., Ni(II)-bis (R,R)-N,N '-dibenzylcyclohexane-1,2-diamine Br-2 catalyzed enantioselective Michael additions of 1,3-dicarbonyl compounds to conjugated nitroalkenes. *J. Am. Chem. Soc.* **2005,** *127* (28), 9958-9959.

27. Evans, D. A.; Thomson, R. J., Ni(II) Tol-BINAP-catalyzed enantioselective orthoester alkylations of N-acylthiazolidinethiones. *J. Am. Chem. Soc.* **2005,** *127* (30), 10506-10507.

28. Shibata, N.; Kohno, J.; Takai, K.; Ishimaru, T.; Nakamura, S.; Toru, T.; Kanemasa, S., Highly enantioselective catalytic fluorination and chlorination reactions of carbonyl compounds capable of two-point binding. *Angew. Chem.-Int. Edit.* **2005,** *44* (27), 4204-4207.

29. Bartoli, G.; Bosco, M.; Carlone, A.; Locatelli, M.; Melchiorre, P.; Sambri, L., Organocatalytic asymmetric alpha-halogenation of 1,3-dicarbonyl compounds. *Angew. Chem.-Int. Edit.* **2005,** *44* (38), 6219-6222.

30. Lou, S.; Taoka, B. M.; Ting, A.; Schaus, S. E., Asymmetric Mannich reactions of beta-keto esters with acyl imines catalyzed by cinchona alkaloids. *J. Am. Chem. Soc.* **2005,** *127* (32), 11256-11257.

31. Poulsen, T. B.; Alemparte, C.; Jorgensen, K. A., Enantioselective organocatalytic allylic amination. *J. Am. Chem. Soc.* **2005,** *127* (33), 11614-11615.

32. Hamashima, Y.; Sasamoto, N.; Hotta, D.; Somei, H.; Umebayashi, N.; Sodeoka, M., Catalytic asymmetric addition of beta-ketoesters to various Imines by using chiral palladium complexes. *Angew. Chem.-Int. Edit.* **2005,** *44* (10), 1525-1529.

33. Hamashima, Y.; Suzuki, T.; Takano, H.; Shimura, Y.; Sodeoka, M., Catalytic enantioselective fluorination of oxindoles. *J. Am. Chem. Soc.* **2005,** *127* (29), 10164-10165.

34. Kim, S. M.; Kim, H. R.; Kim, D. Y., Catalytic enantioselective fluorination and amination of beta-keto phosphonates catalyzed by chiral palladium complexes. *Org. Lett.* **2005,** *7* (12), 2309-2311.

35. Jereb, M.; Togni, A., Titanium(IV)-catalyzed enantioselective sulfenylation of beta-ketoesters. *Org. Lett.* **2005,** *7* (18), 4041-4043.

36. Magdziak, D.; Lalic, G.; Lee, H. M.; Fortner, K. C.; Aloise, A. D.; Shair, M. D., Catalytic enantioselective thioester aldol reactions that are compatible with protic functional groups. *J. Am. Chem. Soc.* **2005,** *127* (20), 7284-7285.

37. Willis, M. C.; Cutting, G. A.; Piccio, V. J. D.; Durbin, M. J.; John, M. P., The direct catalytic enantioselective synthesis of protected aryl beta-hydroxy-alpha-amino acids. *Angew. Chem.-Int. Edit.* **2005,** *44* (10), 1543-1545.

38. Li, H. M.; Song, J.; Liu, X. F.; Deng, L., Catalytic enantioselective C-C bond forming conjugate additions with vinyl sulfones. *J. Am. Chem. Soc.* **2005,** *127* (25), 8948-8949.

39. Poulsen, T. B.; Alemparte, C.; Saaby, S.; Bella, M.; Jorgensen, K. A., Direct organocatalytic and highly enantio- and diastereoselective Mannich reactions of alpha-substituted alpha-cyanoacetates. *Angew. Chem.-Int. Edit.* **2005,** *44* (19), 2896-2899.

40. Duguet, N.; Harrison-Marchand, A.; Maddaluno, J.; Tomioka, K., Enantioselective conjugate addition of a lithium ester enolate catalyzed by chiral lithium amides. *Org. Lett.* **2006,** *8* (25), 5745-5748.

41. Sasamoto, N.; Dubs, C.; Hamashima, Y.; Sodeoka, M., Pd(II)-catalyzed asymmetric addition of malonates to dihydroisoquinolines. *J. Am. Chem. Soc.* **2006,** *128* (43), 14010-14011.

42. Ishimaru, T.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T.; Kanemasa, S., Lewis acid-catalyzed enantioselective hydroxylation reactions of oxindoles and beta-keto esters using DBFOX ligand. *J. Am. Chem. Soc.* **2006,** *128* (51), 16488-16489.

43. Fortner, K. C.; Shair, M. D., Stereoelectronic effects dictate mechanistic dichotomy between Cu(II)-catalyzed and enzyme-catalyzed reactions of malonic acid half thioesters. *J. Am. Chem. Soc.* **2007,** *129* (5), 1032-1033.

44. Suzuki, T.; Hamashima, Y.; Sodeoka, M., Asymmetric fluorination of alpha-aryl acetic acid derivatives with the catalytic system NiCl2-binap/R3SiOTf/2,6-lutidine. *Angew. Chem.-Int. Edit.* **2007,** *46* (28), 5435-5439.

45. Cutting, G. A.; Stainforth, N. E.; John, M. P.; Kociok-Kohn, G.; Willis, M. C., Direct catalytic enantioselective mannich reactions: Synthesis of protected anti-alpha,beta-diamino acids. *J. Am. Chem. Soc.* **2007,** *129* (35), 10632-+.

46. Evans, D. A.; Mito, S.; Seidel, D., Scope and mechanism of enantioselective Michael additions of 1,3-dicarbonyl compounds to nitroalkenes catalyzed by nickel(II)-diamine complexes. *J. Am. Chem. Soc.* **2007,** *129* (37), 11583-11592.

47. Saito, S.; Tsubogo, T.; Kobayashi, S., Chiral calcium complexes as bronsted base catalysts for asymmetric addition of alpha-amino acid derivatives to alpha,beta-unsaturated carbonyl compounds. *J. Am. Chem. Soc.* **2007,** *129* (17), 5364-+.

48. Aleman, J.; Richter, B.; Jorgensen, K. A., Organocatalytic highly enantioselective alpha-arylation of beta-ketoesters. *Angew. Chem.-Int. Edit.* **2007,** *46* (29), 5515-5519.

49. Ogawa, S.; Shibata, N.; Inagaki, J.; Nakamura, S.; Toru, T.; Shiro, M., Cinchona-alkaloid-catalyzed enantioselective direct aldol-type reaction of oxindoles with ethyl trifluoropyruvate. *Angew. Chem.-Int. Edit.* **2007,** *46* (45), 8666-8669.

50. Lou, S.; Dai, P.; Schaus, S. E., Asymmetric Mannich reaction of dicarbonyl compounds with alpha-amido Sulfones catalyzed by cinchona alkaloids and synthesis of chiral dihydropyrimidones. *J. Org. Chem.* **2007,** *72* (26), 9998-10008.

51. Reddy, D. S.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T.; Kanemasa, S., Desymmetrization-like catalytic enantioselective fluorination of malonates and its application to pharmaceutically attractive molecules. *Angew. Chem.-Int. Edit.* **2008,** *47* (1), 164-168.

52. Agostinho, M.; Kobayashi, S., Strontium-catalyzed highly enantioselective Michael additions of malonates to enones. *J. Am. Chem. Soc.* **2008,** *130* (8), 2430-2431.

53. Guo, C.; Xue, M. X.; Zhu, M. K.; Gong, L. Z., Organocatalytic asymmetric formal [3+2]cycloaddition reaction of isocyanoesters to nitroolefins leading to highly optically active dihydropyrroles. *Angew. Chem.-Int. Edit.* **2008,** *47* (18), 3414-3417.

54. Umebayashi, N.; Hamashima, Y.; Hashizume, D.; Sodeoka, M., Catalytic enantioselective aldol-type reaction of beta-ketosters with Acetals. *Angew. Chem.-Int. Edit.* **2008,** *47* (22), 4196-4199.

55. Kobayashi, S.; Yazaki, R.; Seki, K.; Yamashita, Y., The fluorenone imines of glycine esters and their phosphonic acid analogues. *Angew. Chem.-Int. Edit.* **2008,** *47* (30), 5613-5615.

56. Leow, D. S.; Lin, S. S.; Chittimalla, S. K.; Fu, X.; Tan, C. H., Enantioselective protonation catalyzed by a chiral bicyclic guanidine derivative. *Angew. Chem.-Int. Edit.* **2008,** *47* (30), 5641-5645.

57. Tan, B.; Shi, Z. G.; Chua, P. J.; Zhong, G. F., Control of four stereocenters in an organocatalytic domino double Michael reaction: Efficient synthesis of multisubstituted cyclopentanes. *Org. Lett.* **2008,** *10* (16), 3425-3428.

58. Rigby, C. L.; Dixon, D. J., Enantioselective organocatalytic Michael additions to acrylic acid derivatives: generation of all-carbon quaternary stereocentres. *Chem. Commun.* **2008,** (32), 3798-3800.

59. Yazaki, R.; Nitabaru, T.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Addition of Allylic Cyanides to Ketoimines. *J. Am. Chem. Soc.* **2008,** *130* (44), 14477-+.

60. Yan, X. X.; Peng, Q.; Li, Q.; Zhang, K.; Yao, J.; Hou, X. L.; Wu, Y. D., Highly Diastereoselective Switchable Enantioselective Mannich Reaction of Glycine Derivatives with Imines. *J. Am. Chem. Soc.* **2008,** *130* (44), 14362-+.

61. Reddy, D. S.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T., A Dynamic Kinetic Asymmetric Transformation in the alpha-Hydroxylation of Racemic Malonates and Its Application to Biologically Active Molecules. *Angew. Chem.-Int. Edit.* **2009,** *48* (4), 803-806.

62. Xuan, Y. N.; Nie, S. Z.; Dong, L. T.; Zhang, J. M.; Yan, M., Highly Enantioselective Synthesis of Nitrocyclopropanes via Organocatalytic Conjugate Addition of Bromomalonate to alpha,beta-Unsaturated Nitroalkenes. *Org. Lett.* **2009,** *11* (7), 1583-1586.

63. Li, H.; Zhang, S. L.; Yu, C. G.; Song, X. X.; Wang, W., Organocatalytic asymmetric synthesis of chiral fluorinated quaternary carbon containing beta-ketoesters. *Chem. Commun.* **2009,** (16), 2136-2138.

64. Gioia, C.; Fini, F.; Mazzanti, A.; Bernardi, L.; Ricci, A., Organocatalytic Asymmetric Formal [3+2] Cycloaddition with in Situ-Generated N-Carbamoyl Nitrones. *J. Am. Chem. Soc.* **2009,** *131* (28), 9614-9615.

65. Noritake, S.; Shibata, N.; Nomura, Y.; Huang, Y. Y.; Matsnev, A.; Nakamura, S.; Toru, T.; Cahard, D., Enantioselective electrophilic trifluoromethylation of beta-keto esters with Umemoto reagents induced by chiral nonracemic guanidines. *Org. Biomol. Chem.* **2009,** *7* (17), 3599-3604.

66. Kawai, H.; Kusuda, A.; Nakamura, S.; Shiro, M.; Shibata, N., Catalytic Enantioselective Trifluoromethylation of Azomethine Imines with Trimethyl(trifluoromethyl)silane. *Angew. Chem.-Int. Edit.* **2009,** *48* (34), 6324-6327.

67. Paixao, M. W.; Holub, N.; Vila, C.; Nielsen, M.; Jorgensen, K. A., Trends in Organocatalytic Conjugate Addition to Enones: An Efficient Approach to Optically Active Alkynyl, Alkenyl, and Ketone Products. *Angew. Chem.-Int. Edit.* **2009,** *48* (40), 7338-7342.

68. Ma, S.; Han, X. Q.; Krishnan, S.; Virgil, S. C.; Stoltz, B. M., Catalytic Enantioselective Stereoablative Alkylation of 3-Halooxindoles: Facile Access to Oxindoles with C3 All-Carbon Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2009,** *48* (43), 8037-8041.

69. Tsubogo, T.; Yamashita, Y.; Kobayashi, S., Chiral Calcium Catalysts with Neutral Coordinative Ligands: Enantioselective 1,4-Addition Reactions of 1,3-Dicarbonyl Compounds to Nitroalkenes. *Angew. Chem.-Int. Edit.* **2009,** *48* (48), 9117-9120.

70. Yoshino, T.; Morimoto, H.; Lu, G.; Matsunaga, S.; Shibasaki, M., Construction of Contiguous Tetrasubstituted Chiral Carbon Stereocenters via Direct Catalytic Asymmetric Aldol Reaction of alpha-Isothlocyanato Esters with Ketones. *J. Am. Chem. Soc.* **2009,** *131* (47), 17082-+.

71. Baschieri, A.; Bernardi, L.; Ricci, A.; Suresh, S.; Adamo, M. F. A., Catalytic Asymmetric Conjugate Addition of Nitroalkanes to 4-Nitro-5-styrylisoxazoles. *Angew. Chem.-Int. Edit.* **2009,** *48* (49), 9342-9345.

72. Wang, H. F.; Cui, H. F.; Chai, Z.; Li, P.; Zheng, C. W.; Yang, Y. Q.; Zhao, G., Asymmetric Synthesis of Fluorinated Flavanone Derivatives by an Organocatalytic Tandem Intramolecular Oxa-Michael Addition/Electrophilic Fluorination Reaction by Using Bifunctional Cinchona Alkaloids. *Chem.-Eur. J.* **2009,** *15* (48), 13299-13303.

73. Terada, M.; Tsushima, D.; Nakano, M., Enantioselective Electrophilic Amination of alpha-Cyanothioacetates with Azodicarboxylates Catalyzed by an Axially Chiral Guanidine Base. *Adv. Synth. Catal.* **2009,** *351* (17), 2817-2821.

74. Poisson, T.; Yamashita, Y.; Kobayashi, S., Catalytic Asymmetric Protonation of Chiral Calcium Enolates via 1,4-Addition of Malonates. *J. Am. Chem. Soc.* **2010,** *132* (23), 7890-+.

75. Liu, Z.; Shi, M., Catalytic Enantioselective Addition of Cyclic beta-Keto Esters with Activated Olefins and N-Boc Imines Using Chiral C-2-Symmetric Cationic Pd2+ N-Heterocyclic Carbene (NHC) Diaqua Complexes. *Organometallics* **2010,** *29* (12), 2831-2834.

76. Guo, C.; Song, J.; Luo, S. W.; Gong, L. Z., Enantioselective Oxidative Cross-Coupling Reaction of 3-Indolylmethyl C-H Bonds with 1,3-Dicarbonyls Using a Chiral Lewis Acid-Bonded Nucleophile to Control Stereochemistry. *Angew. Chem.-Int. Edit.* **2010,** *49* (32), 5558-5562.

77. Pousse, G.; Le Cavelier, F.; Humphreys, L.; Rouden, J.; Blanchert, J., Bronsted Acid Catalyzed Asymmetric Aldol Reaction: A Complementary Approach to Enamine Catalysis. *Org. Lett.* **2010,** *12* (16), 3582-3585.

78. Hasegawa, Y.; Gridnev, I. D.; Ikariya, T., Enantioselective and Z/E-Selective Conjugate Addition of alpha-Substituted Cyanoacetates to Acetylenic Esters Catalyzed by Bifunctional Ruthenium and Iridium Complexes. *Angew. Chem.-Int. Edit.* **2010,** *49* (44), 8157-8160.

79. Li, J.; Chen, G.; Wang, Z.; Zhang, R. Z.; Zhang, X. M.; Ding, K. L., Spiro-2,2 '-bichroman-based bisoxazoline (SPANbox) ligands for Zn(II)-catalyzed enantioselective hydroxylation of beta-keto esters and 1,3-diester. *Chem. Sci.* **2011,** *2* (6), 1141-1144.

80. Xue, Z. Y.; Li, Q. H.; Tao, H. Y.; Wang, C. J., A Facile Cu(I)/TF-BiphamPhos-Catalyzed Asymmetric Approach to Unnatural alpha-Amino Acid Derivatives Containing gem-Bisphosphonates. *J. Am. Chem. Soc.* **2011,** *133* (30), 11757-11765.

81. Xiao, M.; Xie, Y.; Su, C. X.; Liu, M.; Shi, Y., Organocatalytic Asymmetric Biomimetic Transamination: From alpha-Keto Esters to Optically Active alpha-Amino Acid Derivatives. *J. Am. Chem. Soc.* **2011,** *133* (33), 12914-12917.

82. Zhang, G.; Zhang, Y. H.; Wang, R., Catalytic Asymmetric Activation of a C-sp3-H Bond Adjacent to a Nitrogen Atom: A Versatile Approach to Optically Active alpha-Alkyl alpha-Amino Acids and C1-Alkylated Tetrahydroisoquinoline Derivatives. *Angew. Chem.-Int. Edit.* **2011,** *50* (44), 10429-10432.

83. Strohmeier, M.; Leach, K.; Zajac, M. A., Asymmetric Conjugate Addition of Glycine Derivatives under Copper Catalysis. *Angew. Chem.-Int. Edit.* **2011,** *50* (51), 12335-12338.

84. Shi, D. J.; Xie, Y. J.; Zhou, H.; Xia, C. G.; Huang, H. M., A Highly Diastereo- and Enantioselective Reaction for Constructing Functionalized Cyclohexanes: Six Contiguous Stereocenters in One Step. *Angew. Chem.-Int. Edit.* **2012,** *51* (5), 1248-1251.

85. Deng, Q. H.; Wadepohl, H.; Gade, L. H., Highly Enantioselective Copper-Catalyzed Alkylation of beta-Ketoesters and Subsequent Cyclization to Spirolactones/Bi-spirolactones. *J. Am. Chem. Soc.* **2012,** *134* (6), 2946-2949.

86. Shi, S. L.; Kanai, M.; Shibasaki, M., Asymmetric Synthesis of Dihydropyranones from Ynones by Sequential Copper(I)-Catalyzed Direct Aldol and Silver(I)-Catalyzed Oxy-Michael Reactions. *Angew. Chem.-Int. Edit.* **2012,** *51* (16), 3932-3935.

87. Takechi, S.; Yasuda, S.; Kumagai, N.; Shibasaki, M., A Direct Catalytic Asymmetric Aldol Reaction of a-Sulfanyl Lactones: Efficient Synthesis of SPT Inhibitors. *Angew. Chem.-Int. Edit.* **2012,** *51* (17), 4218-4222.

88. Shibatomi, K.; Soga, Y.; Narayama, A.; Fujisawa, I.; Iwasa, S., Highly Enantioselective Chlorination of beta-Keto Esters and Subsequent S(N)2 Displacement of Tertiary Chlorides: A Flexible Method for the Construction of Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2012,** *134* (24), 9836-9839.

89. Deng, Q. H.; Wadepohl, H.; Gade, L. H., Highly Enantioselective Copper-Catalyzed Electrophilic Trifluoromethylation of beta-Ketoesters. *J. Am. Chem. Soc.* **2012,** *134* (26), 10769-10772.

90. Li, J.; Pan, W.; Wang, Z.; Zhang, X. M.; Ding, K. L., Access to Both Enantiomers of alpha-Chloro-beta-keto Esters with a Single Chiral Ligand: Highly Efficient Enantioselective Chlorination of Cyclic beta-Keto Esters Catalyzed by Chiral Copper(II) and Zinc(II) Complexes of a Spiro-2,2 '-bischroman-Based Bisoxazoline Ligand. *Adv. Synth. Catal.* **2012,** *354* (10), 1980-1986.

91. Shibata, M.; Ikeda, M.; Motoyama, K.; Miyake, Y.; Nishibayashi, Y., Enantioselective alkylation of beta-keto phosphonates by direct use of diaryl methanols as electrophiles. *Chem. Commun.* **2012,** *48* (76), 9528-9530.

92. Li, X.; Li, X. J.; Peng, F. Z.; Shao, Z. H., Mutually Complementary Metal- and Organocatalysis with Collective Synthesis: Asymmetric Conjugate Addition of 1,3-Carbonyl Compounds to Nitroenynes and Further Reactions of the Products. *Adv. Synth. Catal.* **2012,** *354* (14-15), 2873-2885.

93. Baidya, M.; Griffin, K. A.; Yamamoto, H., Catalytic Enantioselective O-Nitrosocarbonyl Aldol Reaction of beta-Dicarbonyl Compounds. *J. Am. Chem. Soc.* **2012,** *134* (45), 18566-18569.

94. Pericas, I.; Shafir, A.; Vallribera, A., Asymmetric Synthesis of L-Carbidopa Based on a Highly Enantioselective alpha-Ami nation. *Org. Lett.* **2013,** *15* (7), 1448-1451.

95. Cao, W. D.; Liu, X. H.; Peng, R. X.; He, P.; Lin, L. L.; Feng, X. M., Catalytic asymmetric cross-dehydrogenative coupling: activation of C-H bonds by a cooperative bimetallic catalyst system. *Chem. Commun.* **2013,** *49* (33), 3470-3472.

96. Deng, Q. H.; Bleith, T.; Wadepohl, H.; Gade, L. H., Enantioselective Iron-Catalyzed Azidation of beta-Keto Esters and Oxindoles. *J. Am. Chem. Soc.* **2013,** *135* (14), 5356-5359.

97. Yang, D. X.; Wang, L. Q.; Han, F. X.; Zhao, D. P.; Zhang, B. Z.; Wang, R., Direct Site-Specific and Highly Enantioselective gamma-Functionalization of Linear alpha,beta-Unsaturated Ketones: Bifunctional Catalytic Strategy. *Angew. Chem.-Int. Edit.* **2013,** *52* (26), 6739-6742.

98. Dong, S. X.; Liu, X. H.; Zhu, Y.; He, P.; Lin, L. L.; Peng, X. M., Organocatalytic Oxyamination of Azlactones: Kinetic Resolution of Oxaziridines and Asymmetric Synthesis of Oxazolin-4-ones. *J. Am. Chem. Soc.* **2013,** *135* (27), 10026-10029.

99. Wang, X. Q.; Yang, T.; Cheng, X. L.; Shen, Q. L., Enantioselective Electrophilic Trifluoromethylthiolation of beta-Ketoesters: A Case of Reactivity and Selectivity Bias for Organocatalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (49), 12860-12864.

100. Guo, J.; Dong, S. X.; Zhang, Y. L.; Kuang, Y. L.; Liu, X. H.; Lin, L. L.; Feng, X. M., Chiral Scandium(III)-Catalyzed Enantioselective alpha-Arylation of N-Unprotected 3-Substituted Oxindoles with Diaryliodonium Salts. *Angew. Chem.-Int. Edit.* **2013,** *52* (39), 10245-10249.

101. Takeda, T.; Terada, M., Development of a Chiral Bis(guanidino)iminophosphorane as an Uncharged Organosuperbase for the Enantioselective Amination of Ketones. *J. Am. Chem. Soc.* **2013,** *135* (41), 15306-15309.

102. Bootwicha, T.; Liu, X. Q.; Pluta, R.; Atodiresei, I.; Rueping, M., N-Trifluoromethylthiophthalimide: A Stable Electrophilic SCF3-Reagent and its Application in the Catalytic Asymmetric Trifluoromethylsulfenylation. *Angew. Chem.-Int. Edit.* **2013,** *52* (49), 12856-12859.

103. Odagi, M.; Furukori, K.; Watanabe, T.; Nagasawa, K., Asymmetric alpha-Hydroxylation of Tetralone-Derived beta-Ketoesters by Using a Guanidine-Urea Bifunctional Organocatalyst in the Presence of Cumene Hydroperoxide. *Chem.-Eur. J.* **2013,** *19* (49), 16740-16745.

104. Deng, Q. H.; Rettenmeier, C.; Wadepohl, H.; Gade, L. H., Copper-Boxmi Complexes as Highly Enantioselective Catalysts for Electrophilic Trifluoromethylthiolations. *Chem.-Eur. J.* **2014,** *20* (1), 93-97.

105. Rueping, M.; Liu, X.; Bootwicha, T.; Pluta, R.; Merkens, C., Catalytic enantioselective trifluoromethylthiolation of oxindoles using shelf-stable N-(trifluoromethylthio)-phthalimide and a cinchona alkaloid catalyst. *Chem. Commun.* **2014,** *50* (19), 2508-2511.

106. Bandar, J. S.; Sauer, G. S.; Wulff, W. D.; Lambert, T. H.; Vetticatt, M. J., Transition State Analysis of Enantioselective Bronsted Base Catalysis by Chiral Cyclopropenimines. *J. Am. Chem. Soc.* **2014,** *136* (30), 10700-10707.

107. Maji, B.; Yamamoto, H., Copper-Catalyzed Asymmetric Synthesis of Tertiary alpha-Hydroxy Phosphonic Acid Derivatives with In Situ Generated Nitrosocarbonyl Compounds as the Oxygen Source. *Angew. Chem.-Int. Edit.* **2014,** *53* (52), 14472-14475.

108. Lin, S.; Kawato, Y.; Kumagai, N.; Shibasaki, M., Catalytic Asymmetric Mannich-Type Reaction of N-Alkylidene-alpha-Aminoacetonitrile with Ketimines. *Angew. Chem.-Int. Edit.* **2015,** *54* (17), 5183-5186.

109. Weidner, K.; Sun, Z. D.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Aldol Reaction of an -Azido Amide. *Angew. Chem.-Int. Edit.* **2015,** *54* (21), 6236-6240.

110. Kondo, M.; Nishi, T.; Hatanaka, T.; Funahashi, Y.; Nakamura, S., Catalytic Enantioselective Reaction of -Aminoacetonitriles Using Chiral Bis(imidazoline) Palladium Catalysts. *Angew. Chem.-Int. Edit.* **2015,** *54* (28), 8198-8202.

111. Tan, Y. Q.; Yuan, W.; Gong, L.; Meggers, E., Aerobic Asymmetric Dehydrogenative Cross-Coupling between Two CspH Groups Catalyzed by a Chiral-at-Metal Rhodium Complex. *Angew. Chem.-Int. Edit.* **2015,** *54* (44), 13045-13048.

112. Kondoh, A.; Oishi, M.; Takeda, T.; Terada, M., Enantioselective Addition of a 2-Alkoxycarbonyl-1,3-dithiane to Imines Catalyzed by a Bis(guanidino)iminophosphorane Organosuperbase. *Angew. Chem.-Int. Edit.* **2015,** *54* (52), 15836-15839.

113. Cichowicz, N. R.; Kaplan, W.; Khomutnyk, Y.; Bhattarai, B.; Sun, Z. K.; Nagorny, P., Concise Enantioselective Synthesis of Oxygenated Steroids via Sequential Copper(II)-Catalyzed Michael Addition/Intramolecular Aldol Cyclization Reactions. *J. Am. Chem. Soc.* **2015,** *137* (45), 14341-14348.

114. Bleith, T.; Deng, Q. H.; Wadepohl, H.; Gade, L. H., Radical Changes in Lewis Acid Catalysis: Matching Metal and Substrate. *Angew. Chem.-Int. Edit.* **2016,** *55* (27), 7852-7856.

115. Huang, X. Q.; Webster, R. D.; Harms, K.; Meggers, E., Asymmetric Catalysis with Organic Azides and Diazo Compounds Initiated by Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **2016,** *138* (38), 12636-12642.

116. Zhou, X.; Wu, Y. W.; Deng, L., Cinchonium Betaines as Efficient Catalysts for Asymmetric Proton Transfer Catalysis: The Development of a Practical Enantioselective Isomerization of Trifluoromethyl Imines. *J. Am. Chem. Soc.* **2016,** *138* (37), 12297-12302.

117. Guo, J.; Lin, L. L.; Liu, Y. B.; Li, X. Q.; Liu, X. H.; Feng, X. M., Nickel(II)-Catalyzed Enantioselective alpha-Vinylation of beta-Keto Amides/Esters with Hypervalent Iodine Salts. *Org. Lett.* **2016,** *18* (21), 5540-5543.

118. Ohmatsu, K.; Ando, Y.; Nakashima, T.; Ooi, T., A Modular Strategy for the Direct Catalytic Asymmetric alpha-Amination of Carbonyl Compounds. *Chem* **2016,** *1* (5), 802-810.

119. Ding, W.; Lu, L. Q.; Zhou, Q. Q.; Wei, Y.; Chen, J. R.; Xiao, W. J., Bifunctional Photocatalysts for Enantioselective Aerobic Oxidation of beta-Ketoesters. *J. Am. Chem. Soc.* **2017,** *139* (1), 63-66.

120. Jarvis, C. L.; Hirschi, J. S.; Vetticatt, M. J.; Seidel, D., Catalytic Enantioselective Synthesis of Lactams through Formal 4+2 Cycloaddition of Imines with Homophthalic Anhydride. *Angew. Chem.-Int. Edit.* **2017,** *56* (10), 2670-2674.

121. Zhang, H. J.; Shi, C. Y.; Zhong, F.; Yin, L., Direct Asymmetric Vinylogous and Bisvinylogous Mannich-Type Reaction Catalyzed by a Copper(I) Complex. *J. Am. Chem. Soc.* **2017,** *139* (6), 2196-2199.

122. Tan, Y.; Luo, S. L.; Li, D. M.; Zhang, N.; Jia, S. Q.; Liu, Y. D.; Qin, W. L.; Song, C. E.; Yan, H. L., Enantioselective Synthesis of anti-syn-Trihalides and anti-syn-anti-Tetrahalides via Asymmetric beta-Elimination. *J. Am. Chem. Soc.* **2017,** *139* (18), 6431-6436.

123. Sun, B.; Balaji, P. V.; Kumagai, N.; Shibasakia, M., alpha-Halo Amides as Competent Latent Enolates: Direct Catalytic Asymmetric Mannich-Type Reaction. *J. Am. Chem. Soc.* **2017,** *139* (24), 8295-8301.

124. Kondo, M.; Omori, M.; Hatanaka, T.; Funahashi, Y.; Nakamura, S., Catalytic Enantioselective Reaction of Allenylnitriles with Imines Using Chiral Bis(imidazoline)s Palladium(II) Pincer Complexes. *Angew. Chem.-Int. Edit.* **2017,** *56* (30), 8677-8680.

125. Chen, J. F.; Gong, X.; Li, J. Y.; Li, Y. K.; Ma, J. G.; Hou, C. K.; Zhao, G. Q.; Yuan, W. C.; Zhao, B. G., Carbonyl catalysis enables a biomimetic asymmetric Mannich reaction. *Science* **2018,** *360* (6396), 1438-+.

126. Calvo, R.; Comas-Vives, A.; Togni, A.; Katayev, D., Taming Radical Intermediates for the Construction of Enantioenriched Trifluoromethylated Quaternary Carbon Centers. *Angew. Chem.-Int. Edit.* **2019,** *58* (5), 1447-1452.

127. Li, X.; He, S.; Song, Q., Enantio- and diastereoselective diarylmethylation of 1,3-dicarbonyl compounds. *Chem. Sci.* **2020,** *11* (23), 5969-5973.

128. Ishihara, K.; Nishimura, K.; Yamakawa, K., Enantio- and Site-Selective α-Fluorination of N-Acyl 3,5-Dimethylpyrazoles Catalyzed by Chiral π–CuII Complexes. *Angewandte Chemie International Edition* **2020,** *59* (40), 17641-17647.

129. Saito, A.; Adachi, S.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Addition of Alkylnitriles to Aldehydes with Designed Nickel–Carbene Complexes. *Angewandte Chemie International Edition* **2021,** *60* (16), 8739-8743.

130. Wittmann, S.; Martzel, T.; Pham Truong, C. T.; Toffano, M.; Oudeyer, S.; Guillot, R.; Bournaud, C.; Gandon, V.; Brière, J.-F.; Vo-Thanh, G., Alkylidene Meldrum's Acids as Platforms for the Vinylogous Synthesis of Dihydropyranones. *Angewandte Chemie International Edition* **2021,** *60* (20), 11110-11114.

131. Yamashita, Y.; Noguchi, A.; Fushimi, S.; Hatanaka, M.; Kobayashi, S., Chiral Metal Salts as Ligands for Catalytic Asymmetric Mannich Reactions with Simple Amides. *J. Am. Chem. Soc.* **2021,** *143* (15), 5598-5604.

132. Kennington, S. C. D.; Teloxa, S. F.; Mellado-Hidalgo, M.; Galeote, O.; Puddu, S.; Bellido, M.; Romea, P.; Urpí, F.; Aullón, G.; Font-Bardia, M., Direct and Enantioselective Aldol Reactions Catalyzed by Chiral Nickel(II) Complexes. *Angewandte Chemie International Edition* **2021,** *60* (28), 15307-15312.

133. Peng, L.; Wang, H.; Guo, C., Copper-Catalyzed Enantioselective Difluoromethylation of Amino Acids via Difluorocarbene. *J. Am. Chem. Soc.* **2021,** *143* (17), 6376-6381.

134. Zhang, C.; Gao, A. Z.; Nie, X.; Ye, C.-X.; Ivlev, S. I.; Chen, S.; Meggers, E., Catalytic α-Deracemization of Ketones Enabled by Photoredox Deprotonation and Enantioselective Protonation. *J. Am. Chem. Soc.* **2021,** *143* (33), 13393-13400.

135. Riehl, P. S.; Richardson, A. D.; Sakamoto, T.; Reid, J. P.; Schindler, C. S., Origin of enantioselectivity reversal in Lewis acid-catalysed Michael additions relying on the same chiral source. *Chem. Sci.* **2021,** *12* (42), 14133-14142.

136. Chen, Y.-X.; Huo, T.; Yin, Q.; Jiang, L.-F.; Cheng, X.; Ma, H.-X.; Jiang, Y.-X.; Sun, M.-Z.; Deng, Q.-H., Azidobenziodazolones as Azido Sources for the Enantioselective Copper-Catalyzed Azidation of N-Unprotected 3-Trifluoromethylated Oxindoles. *Org. Lett.* **2023,** *25* (15), 2739-2744.

3.1.2 Chiral Enolates from Enolates and Enol Ethers

1. Kruger, J.; Carreira, E. M., Apparent catalytic generation of chiral metal enolates: Enantioselective dienolate additions to aldehydes mediated by Tol-BINAP center dot Cu(II) fluoride complexes. *J. Am. Chem. Soc.* **1998,** *120* (4), 837-838.

2. Pagenkopf, B. L.; Kruger, J.; Stojanovic, A.; Carreira, E. M., Mechanistic insights into Cu-catalyzed asymmetric aldol reactions: Chemical and spectroscopic evidence for a metalloenolate intermediate. *Angew. Chem.-Int. Edit.* **1998,** *37* (22), 3124-3126.

3. Hussein, M. A.; Iida, A.; Tomioka, K., Studies aimed at enhancement of reactivity and enantioselectivity of a lithium ester enolate using a chiral tridentate lithium amide. *Tetrahedron* **1999,** *55* (37), 11219-11228.

4. Tomioka, K.; Fujieda, H.; Hayashi, S.; Hussein, M. A.; Kambara, T.; Nomura, Y.; Kanai, M.; Koga, K., Catalytic asymmetric reaction of lithium ester enolates with imines. *Chem. Commun.* **1999,** (8), 715-716.

5. Oisaki, K.; Suto, Y.; Kanai, M.; Shibasaki, M., A new method for the catalytic aldol reaction to ketones. *J. Am. Chem. Soc.* **2003,** *125* (19), 5644-5645.

6. Doyle, A. G.; Jacobsen, E. N., Enantioselective alkylations of tributyltin enolates catalyzed by Cr(salen)Cl: Access to enantiomerically enriched all-carbon quaternary centers. *J. Am. Chem. Soc.* **2005,** *127* (1), 62-63.

7. Oisaki, K.; Zhao, D.; Kanai, M.; Shibasaki, M., Catalytic enantioselective aldol reaction to ketones. *J. Am. Chem. Soc.* **2006,** *128* (22), 7164-7165.

8. Doyle, A. G.; Jacobsen, E. N., Enantioselective alkylation of acyclic alpha,alpha-disubstituted tributyltin enolates catalyzed by a {Cr(salen)) complex. *Angew. Chem.-Int. Edit.* **2007,** *46* (20), 3701-3705.

9. Claraz, A.; Landelle, G.; Oudeyer, S.; Levacher, V., Asymmetric Organocatalytic Protonation of Silyl Enolates Catalyzed by Simple and Original Betaines Derived from Cinchona Alkaloids. *Eur. J. Org. Chem.* **2013,** *2013* (34), 7693-7696.

10. Yanagisawa, A.; Sugita, T.; Yoshida, K., Enantioselective Protonation of Alkenyl Trifluoroacetates Catalyzed by Chiral Tin Methoxide. *Chem.-Eur. J.* **2013,** *19* (48), 16200-16203.

11. Morita, Y.; Yamamoto, T.; Nagai, H.; Shimizu, Y.; Kanai, M., Chemoselective Boron-Catalyzed Nucleophilic Activation of Carboxylic Acids for Mannich-Type Reactions. *J. Am. Chem. Soc.* **2015,** *137* (22), 7075-7078.

3.1.3 Other Ways to Generate Chiral Enolates

1. Wack, H.; Taggi, A. E.; Hafez, A. M.; Drury, W. J.; Lectka, T., Catalytic, asymmetric alpha-halogenation. *J. Am. Chem. Soc.* **2001,** *123* (7), 1531-1532.

2. Hodous, B. L.; Fu, G. C., Enantioselective Staudinger synthesis of beta-lactams catalyzed by a planar-chiral nucleophile. *J. Am. Chem. Soc.* **2002,** *124* (8), 1578-1579.

3. Hodous, B. L.; Fu, G. C., Enantioselective addition of amines to ketenes catalyzed by a planar-chiral derivative of PPY: Possible intervention of chiral Bronsted-acid catalysis. *J. Am. Chem. Soc.* **2002,** *124* (34), 10006-10007.

4. Dudding, T.; Hafez, A. M.; Taggi, A. E.; Wagerle, T. R.; Lectka, T., A catalyst that plays multiple roles: Asymmetric synthesis of beta-substituted aspartic acid derivatives through a four- stage, one-pot procedure. *Org. Lett.* **2002,** *4* (3), 387-390.

5. Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Ferraris, D.; Lectka, T., The development of the first catalyzed reaction of ketenes and imines: Catalytic, asymmetric synthesis of beta-lactams. *J. Am. Chem. Soc.* **2002,** *124* (23), 6626-6635.

6. Balan, D.; Adolfsson, H., Chiral quinuclidine-based amine catalysts for the asymmetric one-pot, three-component aza-Baylis-Hillman reaction. *Tetrahedron Lett.* **2003,** *44* (12), 2521-2524.

7. Calter, M. A.; Orr, R. K.; Song, W., Catalytic, asymmetric preparation of ketene dimers from acid chlorides. *Org. Lett.* **2003,** *5* (24), 4745-4748.

8. Wilson, J. E.; Fu, G. C., Asymmetric synthesis of highly substituted beta-lactones by nucleophile-catalyzed 2+2 cycloadditions of disubstituted ketenes with aldehydes. *Angew. Chem.-Int. Edit.* **2004,** *43* (46), 6358-6360.

9. Nicewicz, D. A.; Yates, C. M.; Johnson, J. S., Catalytic asymmetric acylation of (silyloxy)nitrile anions. *Angew. Chem.-Int. Edit.* **2004,** *43* (20), 2652-2655.

10. Nicewicz, D. A.; Yates, C. M.; Johnson, J. S., Enantioselective cyanation/Brook rearrangement/C-acylation reactions of acylsilanes catalyzed by chiral metal alkoxides. *J. Org. Chem.* **2004,** *69* (20), 6548-6555.

11. Tidwell, T. T., Catalytic asymmetric esterification of ketenes. *Angew. Chem.-Int. Edit.* **2005,** *44* (42), 6812-6814.

12. Lee, E. C.; Hodous, B. L.; Bergin, E.; Shih, C.; Fu, G. C., Catalytic asymmetric Staudinger reactions to form beta-lactams: An unanticipated dependence of diastereoselectivity on the choice of the nitrogen substituent. *J. Am. Chem. Soc.* **2005,** *127* (33), 11586-11587.

13. Mermerian, A. H.; Fu, G. C., Nucleophile-catalyzed asymmetric acylations of silyl ketene imines: Application to the enantioselective synthesis of verapamil. *Angew. Chem.-Int. Edit.* **2005,** *44* (6), 949-952.

14. Reynolds, N. T.; Rovis, T., Enantioselective protonation of catalytically generated chiral enolates as an approach to the synthesis of alpha-chloroesters. *J. Am. Chem. Soc.* **2005,** *127* (47), 16406-16407.

15. Liu, X. H.; Qin, B.; Zhou, X.; He, B.; Feng, X. M., Catalytic asymmetric cyanosilylation of ketones by a chiral amino acid salt. *J. Am. Chem. Soc.* **2005,** *127* (35), 12224-12225.

16. Cozzi, P. G., A catalytic, Me2Zn-mediated, enantioselective reformatsky reaction with ketones. *Angew. Chem.-Int. Edit.* **2006,** *45* (18), 2951-2954.

17. Phillips, E. M.; Wadamoto, M.; Chan, A.; Scheidt, K. A., A highly enantioselective intramolecular Michael reaction catalyzed by N-heterocyclic carbenes. *Angew. Chem.-Int. Edit.* **2007,** *46* (17), 3107-3110.

18. Zajac, M.; Peters, R., Catalytic asymmetric formation of beta-sultams. *Org. Lett.* **2007,** *9* (10), 2007-2010.

19. Zhang, Y. R.; He, L.; Wu, X.; Shao, P. L.; Ye, S., Chiral N-heterocyclic carbene catalyzed Staudinger reaction of ketenes with imines: Highly enantioselective synthesis of N-boc beta-lactams. *Org. Lett.* **2008,** *10* (2), 277-280.

20. Marinescu, S. C.; Nishimata, T.; Mohr, J. T.; Stoltz, B. M., Homogeneous Pd-catalyzed enantioselective decarboxylative protonation. *Org. Lett.* **2008,** *10* (6), 1039-1042.

21. Berlin, J. M.; Fu, G. C., Enantioselective nucleophilic catalysis: The synthesis of aza-beta-lactams through [2+2] cycloadditions of ketenes with azo compounds. *Angew. Chem.-Int. Edit.* **2008,** *47* (37), 7048-7050.

22. He, L.; Lv, H.; Zhang, Y. R.; Ye, S., Formal cycloaddition of disubstituted ketenes with 2-oxoaldehydes catalyzed by chiral N-heterocyclic carbenes. *J. Org. Chem.* **2008,** *73* (20), 8101-8103.

23. Blanchet, J.; Baudoux, J.; Amere, M.; Lasne, M. C.; Rouden, J., Asymmetric Malonic and Acetoacetic Acid Syntheses - A Century of Enantioselective Decarboxylative Protonations. *Eur. J. Org. Chem.* **2008,** (33), 5493-5506.

24. Alden-Danforth, E.; Scerba, M. T.; Lectka, T., Asymmetric Cycloadditions of o-Quinone Methides Employing Chiral Ammonium Fluoride Precatalysts. *Org. Lett.* **2008,** *10* (21), 4951-4953.

25. Wang, X. N.; Lv, H.; Huang, X. L.; Ye, S., Asymmetric esterification of ketenes catalyzed by an N-heterocyclic carbene. *Org. Biomol. Chem.* **2009,** *7* (2), 346-350.

26. Huang, X. L.; He, L.; Shao, P. L.; Ye, S., [4+2] Cycloaddition of Ketenes with N-Benzoyldiazenes Catalyzed by N-Heterocyclic Carbenes. *Angew. Chem.-Int. Edit.* **2009,** *48* (1), 192-195.

27. Sereda, O.; Blanrue, A.; Wilhelm, R., Enantiopure imidazolinium-dithiocarboxylates as highly selective novel organocatalysts. *Chem. Commun.* **2009,** (9), 1040-1042.

28. Dochnahl, M.; Fu, G. C., Catalytic Asymmetric Cycloaddition of Ketenes and Nitroso Compounds: Enantioselective Synthesis of alpha-Hydroxycarboxylic Acid Derivatives. *Angew. Chem.-Int. Edit.* **2009,** *48* (13), 2391-2393.

29. Cowen, B. J.; Saunders, L. B.; Miller, S. J., Pyridylalanine (Pal)-Peptide Catalyzed Enantioselective Allenoate Additions to N-Acyl Imines. *J. Am. Chem. Soc.* **2009,** *131* (17), 6105-+.

30. Yin, L.; Kanai, M.; Shibasaki, M., Nucleophile Generation via Decarboxylation: Asymmetric Construction of Contiguous Trisubstituted and Quaternary Stereocenters through a Cu(I)-Catalyzed Decarboxylative Mannich-Type Reaction. *J. Am. Chem. Soc.* **2009,** *131* (28), 9610-9611.

31. Paull, D. H.; Weatherwax, A.; Lectka, T., Catalytic, asymmetric reactions of ketenes and ketene enolates. *Tetrahedron* **2009,** *65* (34), 6771-6803.

32. Kobayashi, S.; Kinoshita, T.; Uehara, H.; Sudo, T.; Ryu, I., Organocatalytic Enantioselective Synthesis of Nitrogen-Substituted Dihydropyran-2-ones, a Key Synthetic Intermediate of 1 beta-Methylcarbapenems. *Org. Lett.* **2009,** *11* (17), 3934-3937.

33. Wang, X. N.; Shao, P. L.; Lv, H.; Ye, S., Enantioselective Synthesis of beta-Trifluoromethyl-beta-lactones via NHC-Catalyzed Ketene-Ketone Cycloaddition Reactions. *Org. Lett.* **2009,** *11* (18), 4029-4031.

34. Lv, H.; You, L.; Ye, S., Enantioselective Synthesis of Dihydrocoumarins via N-Heterocyclic Carbene-Catalyzed Cycloaddition of Ketenes and o-Quinone Methides. *Adv. Synth. Catal.* **2009,** *351* (17), 2822-2826.

35. Kawanaka, Y.; Phillips, E. M.; Scheidt, K. A., N-Heterocyclic Carbene-Catalyzed Enantioselective Mannich Reactions with alpha-Aryloxyacetaldehydes. *J. Am. Chem. Soc.* **2009,** *131* (50), 18028-+.

36. Abermil, N.; Masson, G.; Zhu, J. P., Enantioselective Aza-Morita-Baylis-Hillman Reaction Using Aliphatic alpha-Amidosulfones as Imine Surrogates. *Adv. Synth. Catal.* **2010,** *352* (4), 656-660.

37. Aroyan, C. E.; Dermenci, A.; Miller, S. J., Development of a Cysteine-Catalyzed Enantioselective Rauhut-Currier Reaction. *J. Org. Chem.* **2010,** *75* (17), 5784-5796.

38. Lv, H.; Chen, X. Y.; Sun, L. H.; Ye, S., Enantioselective Synthesis of Indole-Fused Dihydropyranones via Catalytic Cycloaddition of Ketenes and 3-Alkylenyloxindoles. *J. Org. Chem.* **2010,** *75* (20), 6973-6976.

39. Shao, P. L.; Chen, X. Y.; Ye, S., Formal 3+2 Cycloaddition of Ketenes and Oxaziridines Catalyzed by Chiral Lewis Bases: Enantioselective Synthesis of Oxazolin-4-ones. *Angew. Chem.-Int. Edit.* **2010,** *49* (45), 8412-8416.

40. Leverett, C. A.; Purohit, V. C.; Romo, D., Enantioselective, Organocatalyzed, Intramolecular Aldol Lactonizations with Keto Acids Leading to Bi- and Tricyclic beta-Lactones and Topology-Morphing Transformations. *Angew. Chem.-Int. Edit.* **2010,** *49* (49), 9479-9483.

41. Belmessieri, D.; Morrill, L. C.; Simal, C.; Slawin, A. M. Z.; Smith, A. D., Organocatalytic Functionalization of Carboxylic Acids: Isothiourea-Catalyzed Asymmetric Intra- and Intermolecular Michael Addition-Lactonizations. *J. Am. Chem. Soc.* **2011,** *133* (8), 2714-2720.

42. Koch, F. M.; Peters, R., Lewis Acid/Base Catalyzed 2+2 -Cycloaddition of Sulfenes and Aldehydes: AVersatile Entry to Chiral Sulfonyl and Sulfinyl Derivatives. *Chem.-Eur. J.* **2011,** *17* (13), 3679-3692.

43. Misaki, T.; Kawano, K.; Sugimura, T., Highly Z-Selective Asymmetric 1,4-Addition Reaction of 5H-Oxazol-4-ones with Alkynyl Carbonyl Compounds Catalyzed by Chiral Guanidines. *J. Am. Chem. Soc.* **2011,** *133* (15), 5695-5697.

44. Denis, J. B.; Masson, G.; Retailleau, P.; Zhu, J. P., Cinchona Alkaloid Amide Catalyzed Enantioselective Formal 2+2 Cycloadditions of Allenoates and Imines: Synthesis of 2,4-Disubstituted Azetidines. *Angew. Chem.-Int. Edit.* **2011,** *50* (23), 5356-5360.

45. Wang, X. J.; Fang, T.; Tong, X. F., Enantioselective Amine-Catalyzed 4+2 Annulations of Allenoates and Oxo-dienes: An Asymmetric Synthesis of Dihydropyrans. *Angew. Chem.-Int. Edit.* **2011,** *50* (23), 5361-5364.

46. Wang, X. N.; Shen, L. T.; Ye, S., Enantioselective 2+2+2 cycloaddition of ketenes and carbon disulfide catalyzed by N-heterocyclic carbenes. *Chem. Commun.* **2011,** *47* (29), 8388-8390.

47. Shen, L. T.; Shao, P. L.; Ye, S., N-Heterocyclic Carbene-Catalyzed Cyclization of Unsaturated Acyl Chlorides and Ketones. *Adv. Synth. Catal.* **2011,** *353* (11-12), 1943-1948.

48. Fang, X. Q.; Chen, X. K.; Chi, Y. R., Enantioselective Diels-Alder Reactions of Enals and Alkylidene Diketones Catalyzed by N-Heterocyclic Carbenes. *Org. Lett.* **2011,** *13* (17), 4708-4711.

49. Fujiwara, Y.; Sun, J. W.; Fu, G. C., Enantioselective carbon-sulfur bond formation: gamma additions of aryl thiols to allenoates catalyzed by a chiral phosphepine. *Chem. Sci.* **2011,** *2* (11), 2196-2198.

50. Shen, L. T.; Sun, L. H.; Ye, S., Highly Enantioselective gamma-Amination of alpha,beta-Unsaturated Acyl Chlorides with Azodicarboxylates: Efficient Synthesis of Chiral gamma-Amino Acid Derivatives. *J. Am. Chem. Soc.* **2011,** *133* (40), 15894-15897.

51. Wang, X. N.; Shen, L. T.; Ye, S., NHC-Catalyzed Enantioselective 2+2 and 2+2+2 Cycloadditions of Ketenes with Isothiocyanates. *Org. Lett.* **2011,** *13* (24), 6382-6385.

52. Ibrahim, A. A.; Nalla, D.; Van Raaphorst, M.; Kerrigan, N. J., Catalytic Asymmetric Heterodimerization of Ketenes. *J. Am. Chem. Soc.* **2012,** *134* (6), 2942-2945.

53. Simal, C.; Lebl, T.; Slawin, A. M. Z.; Smith, A. D., Dihydropyridones: Catalytic Asymmetric Synthesis, N- to C-Sulfonyl Transfer, and Derivatizations. *Angew. Chem.-Int. Edit.* **2012,** *51* (15), 3653-3657.

54. Morrill, L. C.; Lebl, T.; Slawin, A. M. Z.; Smith, A. D., Catalytic asymmetric alpha-amination of carboxylic acids using isothioureas. *Chem. Sci.* **2012,** *3* (6), 2088-2093.

55. Chen, S.; Salo, E. C.; Wheeler, K. A.; Kerrigan, N. J., BINAPHANE-Catalyzed Asymmetric Synthesis of trans-beta-Lactams from Disubstituted Ketenes and N-Tosyl Arylimines. *Org. Lett.* **2012,** *14* (7), 1784-1787.

56. Corbett, M. T.; Uraguchi, D.; Ooi, T.; Johnson, J. S., Base-Catalyzed Direct Aldolization of alpha-Alkyl-alpha-Hydroxy Trialkyl Phosphonoacetates. *Angew. Chem.-Int. Edit.* **2012,** *51* (19), 4685-4689.

57. Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H., Metal-Free Catalytic Enantioselective C-B Bond Formation: (Pinacolato)boron Conjugate Additions to alpha,beta-Unsaturated Ketones, Esters, Weinreb Amides, and Aldehydes Promoted by Chiral N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2012,** *134* (19), 8277-8285.

58. Zhao, X. D.; Ruhl, K. E.; Rovis, T., N-Heterocyclic-Carbene-Catalyzed Asymmetric Oxidative Hetero-Diels-Alder Reactions with Simple Aliphatic Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (49), 12330-12333.

59. Zhao, Y. M.; Cheung, M. S.; Lin, Z. Y.; Sun, J. W., Enantioselective Synthesis of beta,gamma-Unsaturated alpha-Fluoroesters Catalyzed by N-Heterocyclic Carbenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (41), 10359-10363.

60. Shen, L. T.; Jia, W. Q.; Ye, S., Catalytic 4+2 Cyclization of a,ss-Unsaturated Acyl Chlorides with 3-Alkylenyloxindoles: Highly Diastereo- and Enantioselective Synthesis of Spirocarbocyclic Oxindoles. *Angew. Chem.-Int. Edit.* **2013,** *52* (2), 585-588.

61. Pattawong, O.; Mustard, T. J. L.; Johnston, R. C.; Cheong, P. H. Y., Mechanism and Stereocontrol: Enantioselective Addition of Pyrrole to Ketenes Using Planar-Chiral Organocatalysts. *Angew. Chem.-Int. Edit.* **2013,** *52* (5), 1420-1423.

62. Wheeler, P.; Vora, H. U.; Rovis, T., Asymmetric NHC-catalyzed synthesis of alpha-fluoroamides from readily accessible alpha-fluoroenals. *Chem. Sci.* **2013,** *4* (4), 1674-1679.

63. Chen, X. Y.; Xia, F.; Cheng, J. T.; Ye, S., Highly Enantioselective gamma-Amination by N-Heterocyclic Carbene Catalyzed 4+2 Annulation of Oxidized Enals and Azodicarboxylates. *Angew. Chem.-Int. Edit.* **2013,** *52* (40), 10644-10647.

64. Takizawa, S.; Arteaga, F. A.; Yoshida, Y.; Suzuki, M.; Sasai, H., Organocatalyzed Formal 2+2 Cycloaddition of Ketimines with Allenoates: Facile Access to Azetidines with a Chiral Tetrasubstituted Carbon Stereogenic Center. *Org. Lett.* **2013,** *15* (16), 4142-4145.

65. Liu, G.; Shirley, M. E.; Van, K. N.; McFarlin, R. L.; Romo, D., Rapid assembly of complex cyclopentanes employing chiral, alpha,beta-unsaturated acylammonium intermediates. *Nature Chemistry* **2013,** *5* (12), 1050-1058.

66. Chen, X. K.; Yang, S.; Song, B. A.; Chi, Y. R., Functionalization of Benzylic C(sp(3))-H Bonds of Heteroaryl Aldehydes through N-Heterocyclic Carbene Organocatalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (42), 11134-11137.

67. Ni, Q. J.; Zhang, H.; Grossmann, A.; Loh, C. C. J.; Merkens, C.; Enders, D., Asymmetric Synthesis of Pyrroloindolones by N-Heterocyclic Carbene Catalyzed 2+3 Annulation of alpha-Chloroaldehydes with Nitrovinylindoles. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13562-13566.

68. Candish, L.; Forsyth, C. M.; Lupton, D. W., N-tert-Butyl Triazolylidenes: Catalysts for the Enantioselective (3+2) Annulation of ,-Unsaturated Acyl Azoliums. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9149-9152.

69. Wang, M.; Huang, Z.; Xu, J.; Chi, Y. R., N-Heterocyclic Carbene-Catalyzed 3+4 Cycloaddition and Kinetic Resolution of Azomethine Imines. *J. Am. Chem. Soc.* **2014,** *136* (4), 1214-1217.

70. Lee, S. Y.; Neufeind, S.; Fu, G. C., Enantioselective Nucleophile-Catalyzed Synthesis of Tertiary Alkyl Fluorides via the alpha-Fluorination of Ketenes: Synthetic and Mechanistic Studies. *J. Am. Chem. Soc.* **2014,** *136* (25), 8899-8902.

71. Lee, A.; Younai, A.; Price, C. K.; Izquierdo, J.; Mishra, R. K.; Scheidt, K. A., Enantioselective Annulations for Dihydroquinolones by in Situ Generation of Azolium Enolates. *J. Am. Chem. Soc.* **2014,** *136* (30), 10589-10592.

72. Li, F.; Wu, Z.; Wang, J., Oxidative Enantioselective alpha-Fluorination of Aliphatic Aldehydes Enabled by N-Heterocyclic Carbene Catalysis. *Angew. Chem.-Int. Edit.* **2015,** *54* (2), 656-659.

73. Dong, X.; Yang, W.; Hu, W.; Sun, J., N-Heterocyclic Carbene Catalyzed Enantioselective alpha-Fluorination of Aliphatic Aldehydes and alpha-Chloro Aldehydes: Synthesis of alpha-Fluoro Esters, Amides, and Thioesters. *Angew. Chem.-Int. Edit.* **2015,** *54* (2), 660-663.

74. Hesping, L.; Biswas, A.; Daniliuc, C. G.; Muck-Lichtenfeld, C.; Studer, A., Stereoselective Lewis base catalyzed formal 1,3-dipolar cycloaddition of azomethine imines with mixed anhydrides. *Chem. Sci.* **2015,** *6* (2), 1252-1257.

75. Qian, H.; Zhao, W.; Wang, Z.; Sun, J., Organocatalytic Enantio- and Diastereoselective Synthesis of 1,2-Dihydronaphthalenes from Isobenzopyrylium Ions. *J. Am. Chem. Soc.* **2015,** *137* (2), 560-563.

76. Li, B.-S.; Wang, Y.; Jin, Z.; Zheng, P.; Ganguly, R.; Chi, Y. R., Carbon-carbon bond activation of cyclobutenones enabled by the addition of chiral organocatalyst to ketone. *Nature Communications* **2015,** *6*.

77. Xu, J.; Chen, X.; Wang, M.; Zheng, P.; Song, B.-A.; Chi, Y. R., Aminomethylation of Enals through Carbene and Acid Cooperative Catalysis: Concise Access to beta(2)-Amino Acids. *Angew. Chem.-Int. Edit.* **2015,** *54* (17), 5161-5165.

78. Liu, X. G.; Meng, Z. L.; Li, C. K.; Lou, H. X.; Liu, L., Organocatalytic Enantioselective Oxidative C-H Alkenylation and Arylation of N-Carbamoyl Tetrahydropyridines and Tetrahydro-beta-carbolines. *Angew. Chem.-Int. Edit.* **2015,** *54* (20), 6012-6015.

79. Xie, C.; Wu, L. M.; Han, J. L.; Soloshonok, V. A.; Pan, Y., Assembly of Fluorinated Quaternary Stereogenic Centers through Catalytic Enantioselective Detrifluoroacetylative Aldol Reactions. *Angew. Chem.-Int. Edit.* **2015,** *54* (20), 6019-6023.

80. Chen, J. A.; Meng, S. X.; Wang, L. M.; Tang, H. M.; Huang, Y., Highly enantioselective sulfa-Michael addition reactions using N-heterocyclic carbene as a non-covalent organocatalyst. *Chem. Sci.* **2015,** *6* (7), 4184-4189.

81. Shih, J. L.; Nguyen, T. S.; May, J. A., Organocatalyzed Asymmetric Conjugate Addition of Heteroaryl and Aryl Trifluoroborates: a Synthetic Strategy for Discoipyrrole D. *Angew. Chem.-Int. Edit.* **2015,** *54* (34), 9931-9935.

82. Li, B. S.; Wang, Y. H.; Jina, Z. C.; Chi, Y. G. R., Cycloaddition of cyclobutenone and azomethine imine enabled by chiral isothiourea organic catalysts. *Chem. Sci.* **2015,** *6* (10), 6008-6012.

83. Wu, H.; Garcia, J. M.; Haeffner, F.; Radomkit, S.; Zhugralin, A. R.; Hoveyda, A. H., Mechanism of NHC-Catalyzed Conjugate Additions of Diboron and Borosilane Reagents to alpha,beta-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2015,** *137* (33), 10585-10602.

84. Xu, J. H.; Zheng, S. C.; Zhang, J. W.; Liu, X. Y.; Tan, B., Construction of Tropane Derivatives by the Organocatalytic Asymmetric Dearomatization of Isoquinolines. *Angew. Chem.-Int. Edit.* **2016,** *55* (39), 11834-11839.

85. Young, C. M.; Stark, D. G.; West, T. H.; Taylor, J. E.; Smith, A. D., Exploiting the Imidazolium Effect in Base-free Ammonium Enolate Generation: Synthetic and Mechanistic Studies. *Angew. Chem.-Int. Edit.* **2016,** *55* (46), 14392-14397.

86. Chen, P.; Wang, K.; Guo, W. G.; Liu, X. H.; Liu, Y.; Li, C., Enantioselective Reactions of 2-Sulfonylalkyl Phenols with Allenic Esters: Dynamic Kinetic Resolution and 4+2 Cycloaddition Involving ortho-Quinone Methide Intermediates. *Angew. Chem.-Int. Edit.* **2017,** *56* (13), 3689-3693.

87. Chen, X. Y.; Liu, Q.; Chauhan, P.; Li, S.; Peuronen, A.; Rissanen, K.; Jafari, E.; Enders, D., N-Heterocyclic Carbene Catalyzed 4+2 Annulation of Enals via a Double Vinylogous Michael Addition: Asymmetric Synthesis of 3,5-Diaryl Cyclohexenones. *Angew. Chem.-Int. Edit.* **2017,** *56* (22), 6241-6245.

88. Miaskiewicz, S.; Reed, J. H.; Donets, P. A.; Oliveira, C. C.; Cramer, N., Chiral 1,3,2-Diazaphospholenes as Catalytic Molecular Hydrides for Enantioselective Conjugate Reductions. *Angew. Chem.-Int. Edit.* **2018,** *57* (15), 4039-4042.

89. Zhang, Y. X.; Huang, J.; Guo, Y. Y.; Li, L.; Fu, Z. Q.; Huang, W., Access to Enantioenriched Organosilanes from Enals and beta-Silyl Enones: Carbene Organocatalysis. *Angew. Chem.-Int. Edit.* **2018,** *57* (17), 4594-4598.

90. Lee, A.; Betori, R. C.; Crane, E. A.; Scheidt, K. A., An Enantioselective Cross-Dehydrogenative Coupling Catalysis Approach to Substituted Tetrahydropyrans. *J. Am. Chem. Soc.* **2018,** *140* (20), 6212-6216.

91. Zhang, X.; Ren, J. Y.; Tan, S. M.; Tan, D.; Lee, R.; Tan, C. H., An enantioconvergent halogenophilic nucleophilic substitution (S(N)2X) reaction. *Science* **2019,** *363* (6425), 400-+.

92. Reed, J. H.; Donets, P. A.; Miaskiewicz, S.; Cramer, N., A 1,3,2-Diazaphospholene-Catalyzed Reductive Claisen Rearrangement. *Angew. Chem.-Int. Edit.* **2019,** *58* (26), 8893-8897.

93. Antunez, D. J. B.; Greenhalgh, M. D.; Brueckner, A. C.; Walden, D. M.; Elias-Rodriguez, P.; Roberts, P.; Young, B. G.; West, T. H.; Slawin, A. M. Z.; Cheong, P. H. Y.; Smith, A. D., Catalytic enantioselective synthesis of perfluoroalkyl-substituted b-lactones via a concerted asynchronous 2+2 cycloaddition: a synthetic and computational study. *Chem. Sci.* **2019,** *10* (24), 6162-6173.

94. Bae, S.; Zhang, C. H.; Gillard, R. M.; Lupton, D. W., Enantioselective N-Heterocyclic Carbene Catalyzed Bis(enoate) Rauhut-Currier Reaction. *Angew. Chem.-Int. Edit.* **2019,** *58* (38), 13370-13374.

95. Lundrigan, T.; Welsh, E. N.; Hynes, T.; Tien, C. H.; Adams, M. R.; Roy, K. R.; Robertson, K. N.; Speed, A. W. H., Enantioselective Imine Reduction Catalyzed by Phosphenium Ions. *J. Am. Chem. Soc.* **2019,** *141* (36), 14083-14088.

96. Wang, C. J.; Sun, J.; Zhou, W.; Xue, J.; Ren, B. T.; Zhang, G. Y.; Mei, Y. L.; Deng, Q. H., Enantioselective Copper-Catalyzed Electrophilic Dearomative Azidation of beta-Naphthols. *Org. Lett.* **2019,** *21* (18), 7315-7319.

97. Chen, Y.; Liu, Y.; Li, Z.; Dong, S.; Liu, X.; Feng, X., Tandem Insertion–[1,3]-Rearrangement: Highly Enantioselective Construction of α-Aminoketones. *Angewandte Chemie International Edition* **2020,** *59* (21), 8052-8056.

98. Ren, J.; Ban, X.; Zhang, X.; Tan, S. M.; Lee, R.; Tan, C.-H., Kinetic and Dynamic Kinetic Resolution of Racemic Tertiary Bromides by Pentanidium-Catalyzed Phase-Transfer Azidation. *Angewandte Chemie International Edition* **2020,** *59* (23), 9055-9058.

99. Estrada, C. D.; Ang, H. T.; Vetter, K.-M.; Ponich, A. A.; Hall, D. G., Enantioselective Desymmetrization of 2-Aryl-1,3-propanediols by Direct O-Alkylation with a Rationally Designed Chiral Hemiboronic Acid Catalyst That Mitigates Substrate Conformational Poisoning. *J. Am. Chem. Soc.* **2021,** *143* (11), 4162-4167.

100. McLaughlin, C.; Bitai, J.; Barber, L. J.; Slawin, Alexandra M. Z.; Smith, A. D., Catalytic enantioselective synthesis of 1,4-dihydropyridines via the addition of C(1)-ammonium enolates to pyridinium salts. *Chem. Sci.* **2021,** *12* (36), 12001-12011.

101. Ji, D.-S.; Liang, H.; Yang, K.-X.; Feng, Z.-T.; Luo, Y.-C.; Xu, G.-Q.; Gu, Y.; Xu, P.-F., Solvent directed chemically divergent synthesis of β-lactams and α-amino acid derivatives with chiral isothiourea. *Chem. Sci.* **2022,** *13* (6), 1801-1807.

102. Wang, Y.; Young, C. M.; Liu, H.; Hartley, W. C.; Wienhold, M.; Cordes, D. B.; Slawin, A. M. Z.; Smith, A. D., A Desilylative Approach to Alkyl Substituted C(1)-Ammonium Enolates: Application in Enantioselective [2+2] Cycloadditions. *Angewandte Chemie International Edition* **2022,** *61* (38), e202208800.

103. Weinzierl, D.; Piringer, M.; Zebrowski, P.; Stockhammer, L.; Waser, M., Photochemical Wolff Rearrangement Initiated Generation and Subsequent α-Chlorination of C1 Ammonium Enolates. *Org. Lett.* **2023,** *25* (17), 3126-3130.

104. Iglhaut, M.; Freund, P.; Bach, T., Photochemical Deracemization of N-Carboxyanhydrides En Route to Chiral α-Amino Acid Derivatives. *Angewandte Chemie International Edition* **2025,** *64* (6), e202418873.

3.2 Enamine Catalysis

1. Cordova, A.; Barbas, C. F., anti-selective SMP-catalyzed direct asymmetric Mannich-type reactions: synthesis of functionalized amino acid derivatives. *Tetrahedron Lett.* **2002,** *43* (43), 7749-7752.

2. Andrey, O.; Alexakis, A.; Bernardinelli, G., Asymmetric Michael addition of alpha-hydroxyketones to nitroolefins catalyzed by chiral diamine. *Org. Lett.* **2003,** *5* (14), 2559-2561.

3. Juhl, K.; Jorgensen, K. A., The first organocatalytic enantioselective inverse-electron- demand hetero-Diels-Alder reaction. *Angew. Chem.-Int. Edit.* **2003,** *42* (13), 1498-1501.

4. Melchiorre, P.; Jorgensen, K. A., Direct enantioselective Michael addition of aldehydes to vinyl ketones catalyzed by chiral amines. *J. Org. Chem.* **2003,** *68* (11), 4151-4157.

5. Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C., Direct and enantioselective organocatalytic alpha-chlorination of aldehydes. *J. Am. Chem. Soc.* **2004,** *126* (13), 4108-4109.

6. Fonseca, M. T. H.; List, B., Catalytic asymmetric intramolecular Michael reaction of aldehydes. *Angew. Chem.-Int. Edit.* **2004,** *43* (30), 3958-3960.

7. Halland, N.; Braunton, A.; Bachmann, S.; Marigo, M.; Jorgensen, K. A., Direct organocatalytic asymmetric alpha-chlorination of aldehydes. *J. Am. Chem. Soc.* **2004,** *126* (15), 4790-4791.

8. Mangion, I. K.; Northrup, A. B.; MacMillan, D. W. C., The importance of iminium geometry control in enamine catalysis: Identification of a new catalyst architecture for aldehyde-aldehyde couplings. *Angew. Chem.-Int. Edit.* **2004,** *43* (48), 6722-6724.

9. Marigo, M.; Bachmann, S.; Halland, N.; Braunton, A.; Jorgensen, K. A., Highly enantioselective direct organocatalytic alpha-chlorination of ketones. *Angew. Chem.-Int. Edit.* **2004,** *43* (41), 5507-5510.

10. Mase, N.; Thayumanavan, R.; Tanaka, F.; Barbas, C. F., Direct asymmetric organocatalytic Michael reactions of alpha,alpha-disubstituted aldehydes with beta-nitrostyrenes for the synthesis of quaternary carbon-containing products. *Org. Lett.* **2004,** *6* (15), 2527-2530.

11. Beeson, T. D.; MacMillan, D. W. C., Enantioselective organocatalytic alpha-fluorination of aldehydes. *J. Am. Chem. Soc.* **2005,** *127* (24), 8826-8828.

12. Chowdari, N. S.; Barbas, C. F., Total synthesis of LFA-1 antagonist BIRT-377 via organocatalytic asymmetric construction of a quaternary stereocenter. *Org. Lett.* **2005,** *7* (5), 867-870.

13. Franzen, J.; Marigo, M.; Fielenbach, D.; Wabnitz, T. C.; Kjaersgaard, A.; Jorgensen, K. A., A general organocatalyst for direct alpha-functionalization of aldehydes: Stereoselective C-C, C-N, C-F, C-BR, and C-S bond-forming reactions. Scope and mechanistic insights. *J. Am. Chem. Soc.* **2005,** *127* (51), 18296-18304.

14. Frisch, K.; Landa, A.; Saaby, S.; Jorgensen, K. A., Organocatalytic diastereo- and enantioselective annulation reactions - Construction of optically active 1,2-dihydroisoquinoline and 1,2-dihydrophthalazine derivatives. *Angew. Chem.-Int. Edit.* **2005,** *44* (37), 6058-6063.

15. Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M., Diphenylprolinol silyl ethers as efficient organocatalysts for the asymmetric Michael reaction of aldehydes and nitroalkenes. *Angew. Chem.-Int. Edit.* **2005,** *44* (27), 4212-4215.

16. Hayashi, Y.; Gotoh, H.; Tamura, T.; Yamaguchi, H.; Masui, R.; Shoji, M., Cysteine-derived organocatalyst in a highly enantioselective intramolecular Michael reaction. *J. Am. Chem. Soc.* **2005,** *127* (46), 16028-16029.

17. Huang, Y.; Walji, A. M.; Larsen, C. H.; MacMillan, D. W. C., Enantioselective organo-cascade catalysis. *J. Am. Chem. Soc.* **2005,** *127* (43), 15051-15053.

18. Janey, J. M., Recent advances in catalytic, enantioselective alpha aminations and alpha oxygenations of carbonyl compounds. *Angew. Chem.-Int. Edit.* **2005,** *44* (28), 4292-4300.

19. Marigo, M.; Fielenbach, D. I.; Braunton, A.; Kjoersgaard, A.; Jorgensen, K. A., Enantioselective formation of stereogenic carbon-fluorine centers by a simple catalytic method. *Angew. Chem.-Int. Edit.* **2005,** *44* (24), 3703-3706.

20. Marigo, M.; Franzen, J.; Poulsen, T. B.; Zhuang, W.; Jorgensen, K. A., Asymmetric organocatalytic epoxidation of alpha,beta-unsaturated aldehydes with hydrogen peroxide. *J. Am. Chem. Soc.* **2005,** *127* (19), 6964-6965.

21. Marigo, M.; Schulte, T.; Franzen, J.; Jorgensen, K. A., Asymmetric multicomponent domino reactions and highly enantioselective conjugated addition of thiols to alpha,beta-unsaturated aldehydes. *J. Am. Chem. Soc.* **2005,** *127* (45), 15710-15711.

22. Marigo, M.; Wabnitz, T. C.; Fielenbach, D.; Jorgensen, K. A., Enantioselective organocatalyzed a sulfenylation of aldehydes. *Angew. Chem.-Int. Edit.* **2005,** *44* (5), 794-797.

23. Mosse, S.; Alexakis, A., First organocatalyzed asymmetric Michael addition of aldehydes to vinyl sulfones. *Org. Lett.* **2005,** *7* (20), 4361-4364.

24. Peelen, T. J.; Chi, Y. G.; Gellman, S. H., Enantioselective organocatalytic Michael additions of aldehydes to enones with imidazolidinones: Cocatalyst effects and evidence for an enamine intermediate. *J. Am. Chem. Soc.* **2005,** *127* (33), 11598-11599.

25. Enders, D.; Huttl, M. R. M.; Grondal, C.; Raabe, G., Control of four stereocentres in a triple cascade organocatalytic reaction. *Nature* **2006,** *441* (7095), 861-863.

26. Aleman, J.; Cabrera, S.; Maerten, E.; Overgaard, J.; Jorgensen, K. A., Asymmetric organocatalytic alpha-arylation of aldehydes. *Angew. Chem.-Int. Edit.* **2007,** *46* (29), 5520-5523.

27. Hayashi, Y.; Okano, T.; Aratake, S.; Hazelard, D., Diphenylprolinol silyl ether as a catalyst in an enantioselective, catalytic, tandem Michael/Henry reaction for the control of four stereocenters. *Angew. Chem.-Int. Edit.* **2007,** *46* (26), 4922-4925.

28. Wang, J.; Li, H.; Xie, H.; Zu, L.; Shen, X.; Wang, W., Organocatalytic enantioselective cascade Michael-Aldol condensation reactions: Efficient assembly of densely functionalized chiral cyclopentenes. *Angew. Chem.-Int. Edit.* **2007,** *46* (47), 9050-9053.

29. Xie, H.; Zu, L.; Li, H.; Wang, J.; Wang, W., Organocatalytic enantioselective cascade Michael-alkylation reactions: Synthesis of chiral cyclopropanes and investigation of unexpected organocatalyzed stereoselective ring opening of cyclopropanes. *J. Am. Chem. Soc.* **2007,** *129* (35), 10886-10894.

30. Zu, L. S.; Li, H.; Xie, H.; Wang, J.; Jiang, W.; Tang, Y.; Wang, W., Synthesis of highly functionalized chiral cyclopentanes by catalytic enantio- and diastereoselective double Michael addition reactions. *Angew. Chem.-Int. Edit.* **2007,** *46* (20), 3732-3734.

31. Albrecht, L.; Richter, B.; Krawczyk, H.; Jorgensen, K. A., Enantioselective Organocatalytic Approach to alpha-Methylene-delta-lactones and delta-Lactams. *J. Org. Chem.* **2008,** *73* (21), 8337-8343.

32. Alonso, D. A.; Kitagaki, S.; Utsumi, N.; Barbas, C. F., Towards organocatalytic polyketide synthases with diverse electrophile scope: Trifluoroethyl thioesters as nucleophiles in organocatalytic Michael reactions and beyond. *Angew. Chem.-Int. Edit.* **2008,** *47* (24), 4588-4591.

33. Belot, S.; Massaro, A.; Tenti, A.; Mordini, A.; Alexakis, A., Enantioselective Organocatalytic Conjugate Addition of Aldehydes to Nitrodienes. *Org. Lett.* **2008,** *10* (20), 4557-4560.

34. Bonne, D.; Salat, L.; Dulcere, J. P.; Rodriguez, J., Sequential Organocatalyzed Michael Addition/[3+2]-Heterocyclization for the Stereoselective Synthesis of Fused-Isoxazoline Precursors of Enantiopure Cyclopentanoids. *Org. Lett.* **2008,** *10* (23), 5409-5412.

35. Cabrera, S.; Aleman, J.; Bolze, P.; Bertelsen, S.; Jorgensen, K. A., An unexpected organocatalytic asymmetric tandem Michael/Morita-Baylis-Hillman reaction. *Angew. Chem.-Int. Edit.* **2008,** *47* (1), 121-125.

36. Chandler, C. L.; List, B., Catalytic, asymmetric transannular aldolizations: Total synthesis of (+)-hirsutene. *J. Am. Chem. Soc.* **2008,** *130* (21), 6737-+.

37. Chi, Y.; Guo, L.; Kopf, N. A.; Gellman, S. H., Enantioselective organocatalytic Michael addition of aldehydes to nitroethylene: Efficient access to gamma(2)-amino acids. *J. Am. Chem. Soc.* **2008,** *130* (17), 5608-+.

38. de Figueiredo, R. M.; Frohlich, R.; Christmann, M., Amine-catalyzed cyclizations of tethered alpha,beta-unsaturated carbonyl compounds. *Angew. Chem.-Int. Edit.* **2008,** *47* (8), 1450-1453.

39. Enders, D.; Wang, C.; Bats, J. W., Organocatalytic asymmetric domino reactions: A cascade consisting of a Michael addition and an aldehyde alpha-alkylation. *Angew. Chem.-Int. Edit.* **2008,** *47* (39), 7539-7542.

40. Gianelli, C.; Sambri, L.; Carlone, A.; Bartoli, G.; Melchiorre, P., Aminocatalytic Enantioselective anti-Mannich Reaction of Aldehydes with In Situ Generated N-Cbz and N-Boc Imines. *Angew. Chem.-Int. Edit.* **2008,** *47* (45), 8700-8702.

41. Han, B.; Li, J. L.; Ma, C.; Zhang, S. J.; Chen, Y. C., Organocatalytic Asymmetric Inverse-Electron-Demand Aza-Diels-Alder Reaction of N-Sulfonyl-1-aza-1,3-butadienes and Aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (51), 9971-9974.

42. Han, B.; Li, J. L.; Ma, C.; Zhang, S. J.; Chen, Y. C., Organocatalytic Asymmetric Inverse-Electron-Demand Aza-Diels-Alder Reaction of N-Sulfonyl-1-aza-1,3-butadienes and Aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (51), 9971-9974.

43. Hayashi, Y.; Itoh, T.; Ohkubo, M.; Ishikawa, H., Asymmetric Michael reaction of acetaldehyde catalyzed by diphenylprolinol silyl ether. *Angew. Chem.-Int. Edit.* **2008,** *47* (25), 4722-4724.

44. Hayashi, Y.; Okano, T.; Itoh, T.; Urushima, T.; Ishikawa, H.; Uchimaru, T., Direct Organocatalytic Mannich Reaction of Acetaldehyde: An Improved Catalyst and Mechanistic Insight from a Computational Study. *Angew. Chem.-Int. Edit.* **2008,** *47* (47), 9053-9058.

45. Penon, O.; Carlone, A.; Mazzanti, A.; Locatelli, M.; Sambri, L.; Bartoli, G.; Melchiorrer, P., Quaternary stereogenic carbon atoms in complex molecules by an asymmetric, organocatalytic, triple-cascade reaction. *Chem.-Eur. J.* **2008,** *14* (16), 4788-4791.

46. Pesciaioli, F.; De Vincentiis, F.; Galzerano, P.; Bencivenni, G.; Bartoli, G.; Mazzanti, A.; Melchiorre, P., Organocatalytic Asymmetric Aziridination of Enones. *Angew. Chem.-Int. Edit.* **2008,** *47* (45), 8703-8706.

47. Shaikh, R. R.; Mazzanti, A.; Petrini, M.; Bartoli, G.; Melchiorre, P., Proline-Catalyzed Asymmetric Formal alpha-Alkylation of Aldehydes via Vinylogous Iminium Ion Intermediates Generated from Arylsulfonyl Indoles. *Angew. Chem.-Int. Edit.* **2008,** *47* (45), 8707-8710.

48. Shibatomi, K.; Yamamoto, H., Stereoselective synthesis of alpha,alpha-chlorofluoro carbonyl compounds leading to the construction of fluorinated chiral quaternary carbon centers. *Angew. Chem.-Int. Edit.* **2008,** *47* (31), 5796-5798.

49. Vo, N. T.; Pace, R. D. M.; O'Hara, F.; Gaunt, M. J., An enantioselective organocatalytic oxidative dearomatization strategy. *J. Am. Chem. Soc.* **2008,** *130* (2), 404-+.

50. Wang, X.; List, B., Asymmetric counteranion-directed catalysis for the epoxidation of enals. *Angew. Chem.-Int. Edit.* **2008,** *47* (6), 1119-1122.

51. Wang, X.; Reisinger, C. M.; List, B., Catalytic asymmetric epoxidation of cyclic enones. *J. Am. Chem. Soc.* **2008,** *130* (19), 6070-+.

52. Wiesner, M.; Revell, J. D.; Tonazzi, S.; Wennemers, H., Peptide catalyzed asymmetric conjugate addition reactions of aldehydes to nitroethylene - A convenient entry into gamma(2)-amino acids. *J. Am. Chem. Soc.* **2008,** *130* (17), 5610-+.

53. Zhao, G. L.; Rios, R.; Vesely, J.; Eriksson, L.; Cordova, A., Organocatalytic Enantioselective Aminosulfenylation of alpha,beta-Unsaturated Aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (44), 8468-8472.

54. Zhou, J.; Wakchaure, V.; Kraft, P.; List, B., Primary-amine-catalyzed enantioselective intramolecular aldolizations. *Angew. Chem.-Int. Edit.* **2008,** *47* (40), 7656-7658.

55. Zhu, S. L.; Yu, S. Y.; Ma, D. W., Highly efficient catalytic system for enantioselective Michael addition of aldehydes to nitroalkenes in water. *Angew. Chem.-Int. Edit.* **2008,** *47* (3), 545-548.

56. Belot, S.; Vogt, K. A.; Besnard, C.; Krause, N.; Alexakis, A., Enantioselective One-Pot Organocatalytic Michael Addition/Gold-Catalyzed Tandem Acetalization/Cyclization. *Angew. Chem.-Int. Edit.* **2009,** *48* (47), 8923-8926.

57. Bencivenni, G.; Wu, L. Y.; Mazzanti, A.; Giannichi, B.; Pesciaioli, F.; Song, M. P.; Bartoli, G.; Melchiorre, P., Targeting Structural and Stereochemical Complexity by Organocascade Catalysis: Construction of Spirocyclic Oxindoles Having Multiple Stereocenters. *Angew. Chem.-Int. Edit.* **2009,** *48* (39), 7200-7203.

58. Benfatti, F.; Capdevila, M. G.; Zoli, L.; Benedetto, E.; Cozzi, P. G., Catalytic stereoselective benzylic C-H functionalizations by oxidative C-H activation and organocatalysis. *Chem. Commun.* **2009,** (39), 5919-5921.

59. Cozzi, P. G.; Benfatti, F.; Zoli, L., Organocatalytic Asymmetric Alkylation of Aldehydes by S(N)1-Type Reaction of Alcohols. *Angew. Chem.-Int. Edit.* **2009,** *48* (7), 1313-1316.

60. Guo, L.; Chi, Y. G.; Almeida, A. M.; Guzei, I. A.; Parker, B. K.; Gellman, S. H., Stereospecific Synthesis of Conformationally Constrained gamma-Amino Acids: New Foldamer Building Blocks That Support Helical Secondary Structure. *J. Am. Chem. Soc.* **2009,** *131* (44), 16018-+.

61. Han, B.; He, Z. Q.; Li, J. L.; Li, R.; Jiang, K.; Liu, T. Y.; Chen, Y. C., Organocatalytic Regio- and Stereoselective Inverse-Electron-Demand Aza-Diels-Alder Reaction of alpha,beta-Unsaturated Aldehydes and N-Tosyl-1-aza-1,3-butadienes. *Angew. Chem.-Int. Edit.* **2009,** *48* (30), 5474-5477.

62. Jiang, H.; Falcicchio, A.; Jensen, K. L.; Paixao, M. W.; Bertelsen, S.; Jorgensen, K. A., Target-Directed Organocatalysis: A Direct Asymmetric Catalytic Approach to Chiral Propargylic and Allylic Fluorides. *J. Am. Chem. Soc.* **2009,** *131* (20), 7153-7157.

63. Kano, T.; Mii, H.; Maruoka, K., Direct Asymmetric Benzoyloxylation of Aldehydes Catalyzed by 2-Tritylpyrrolidine. *J. Am. Chem. Soc.* **2009,** *131* (10), 3450-+.

64. Kano, T.; Tanaka, Y.; Osawa, K.; Yurino, T.; Maruoka, K., Catalytic enantioselective construction of all-carbon quaternary stereocenters by an organocatalytic Diels-Alder reaction of alpha-substituted alpha, beta-unsaturated aldehydes. *Chem. Commun.* **2009,** (15), 1956-1958.

65. Marques-Lopez, E.; Herrera, R. P.; Marks, T.; Jacobs, W. C.; Konning, D.; de Figueiredo, R. M.; Christmann, M., Crossed Intramolecular Rauhut-Currier-Type Reactions via Dienamine Activation. *Org. Lett.* **2009,** *11* (18), 4116-4119.

66. McGarraugh, P. G.; Brenner, S. E., A New Organocatalyzed Michael-Michael Cascade Reaction Generates Highly Substituted Fused Carbocycles. *Org. Lett.* **2009,** *11* (24), 5654-5657.

67. Rueping, M.; Kuenkel, A.; Tato, F.; Bats, J. W., Asymmetric Organocatalytic Domino Michael/Aldol Reactions: Enantioselective Synthesis of Chiral Cycloheptanones, Tetrahydrochromenones, and Polyfunctionalized Bicyclo-[3.2.1]octanes. *Angew. Chem.-Int. Edit.* **2009,** *48* (20), 3699-3702.

68. Simmons, B.; Walji, A. M.; MacMillan, D. W. C., Cycle-Specific Organocascade Catalysis: Application to Olefin Hydroamination, Hydro-oxidation, and Amino-oxidation, and to Natural Product Synthesis. *Angew. Chem.-Int. Edit.* **2009,** *48* (24), 4349-4353.

69. Zhu, D.; Lu, M.; Dai, L.; Zhong, G. F., Highly Stereoselective One-Pot Synthesis of Bicyclic Isoxazolidines with Five Stereogenic Centers by an Organocatalytic Process. *Angew. Chem.-Int. Edit.* **2009,** *48* (33), 6089-6092.

70. Allen, A. E.; MacMillan, D. W. C., The Productive Merger of Iodonium Salts and Organocatalysis: A Non-photolytic Approach to the Enantioselective alpha-Trifluoromethylation of Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (14), 4986-+.

71. Ho, X. H.; Mho, S. I.; Kang, H.; Jang, H. Y., Electro-Organocatalysis: Enantioselective alpha-Alkylation of Aldehydes. *Eur. J. Org. Chem.* **2010,** (23), 4436-4441.

72. Jensen, K. L.; Franke, P. T.; Nielsen, L. T.; Daasbjerg, K.; Jorgensen, K. A., Anodic Oxidation and Organocatalysis: Direct Regio- and Stereoselective Access to meta-Substituted Anilines by alpha-Arylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2010,** *49* (1), 129-133.

73. Li, J. L.; Kang, T. R.; Zhou, S. L.; Li, R.; Wu, L.; Chen, Y. C., Organocatalytic Asymmetric Inverse-Electron-Demand Diels-Alder Reaction of Electron-Deficient Dienes and Crotonaldehyde. *Angew. Chem.-Int. Edit.* **2010,** *49* (36), 6418-6420.

74. Wiesner, M.; Upert, G.; Angelici, G.; Wennemers, H., Enamine Catalysis with Low Catalyst Loadings - High Efficiency via Kinetic Studies. *J. Am. Chem. Soc.* **2010,** *132* (1), 6-+.

75. Zheng, Z. L.; Perkins, B. L.; Ni, B. K., Diarylprolinol Silyl Ether Salts as New, Efficient, Water-Soluble, and Recyclable Organocatalysts for the Asymmetric Michael Addition on Water. *J. Am. Chem. Soc.* **2010,** *132* (1), 50-+.

76. Zhu, Q.; Lu, Y. X., Chiral primary amine mediated conjugate addition of branched aldehydes to vinyl sulfone: asymmetric generation of quaternary carbon centers. *Chem. Commun.* **2010,** *46* (13), 2235-2237.

77. Cai, Q.; Zheng, C.; Zhang, J. W.; You, S. L., Enantioselective Michael/Mannich Polycyclization Cascade of Indolyl Enones Catalyzed by Quinine-Derived Primary Amines. *Angew. Chem.-Int. Edit.* **2011,** *50* (37), 8665-8669.

78. Capitta, F.; Frongia, A.; Ollivier, J.; Piras, P. P.; Secci, F., Unexpected Formation of Optically Active 4-Substituted 5-Hydroxy-gamma-lactams by Organocatalyzed Reaction of 3-Substituted Cyclobutanones with Nitrosobenzene. *Synlett* **2011,** (1), 89-93.

79. Gualandi, A.; Emer, E.; Capdevila, M. G.; Cozzi, P. G., Highly Enantioselective alpha Alkylation of Aldehydes with 1,3-Benzodithiolylium Tetrafluoroborate: A Formal Organocatalytic alpha Alkylation of Aldehydes by the Carbenium Ion. *Angew. Chem.-Int. Edit.* **2011,** *50* (34), 7842-7846.

80. Hayashi, Y.; Gotoh, H.; Honma, M.; Sankar, K.; Kumar, I.; Ishikawa, H.; Konno, K.; Yui, H.; Tsuzuki, S.; Uchimaru, T., Organocatalytic, Enantioselective Intramolecular 6+2 Cycloaddition Reaction for the Formation of Tricyclopentanoids and Insight on Its Mechanism from a Computational Study. *J. Am. Chem. Soc.* **2011,** *133* (50), 20175-20185.

81. Ishikawa, H.; Sawano, S.; Yasui, Y.; Shibata, Y.; Hayashi, Y., Asymmetric One-Pot Four-Component Coupling Reaction: Synthesis of Substituted Tetrahydropyrans Catalyzed by Diphenylprolinol Silyl Ether. *Angew. Chem.-Int. Edit.* **2011,** *50* (16), 3774-3779.

82. Jia, Z. J.; Jiang, H.; Li, J. L.; Gschwend, B.; Li, Q. Z.; Yin, X. A.; Grouleff, J.; Chen, Y. C.; Jorgensen, K. A., Trienamines in Asymmetric Organocatalysis: Diels-Alder and Tandem Reactions. *J. Am. Chem. Soc.* **2011,** *133* (13), 5053-5061.

83. Jia, Z. J.; Zhou, Q.; Zhou, Q. Q.; Chen, P. Q.; Chen, Y. C., exo-Selective Asymmetric Diels-Alder Reaction of 2,4-Dienals and Nitroalkenes by Trienamine Catalysis. *Angew. Chem.-Int. Edit.* **2011,** *50* (37), 8638-8641.

84. Jiang, X. X.; Fu, D.; Shi, X. M.; Wang, S. L.; Wang, R., PPh(3)-catalyzed synthesis of dicyano-2-methylenebut-3-enoates as efficient dienes in catalytic asymmetric inverse-electron-demand Diels-Alder reaction. *Chem. Commun.* **2011,** *47* (29), 8289-8291.

85. Kwiatkowski, P.; Beeson, T. D.; Conrad, J. C.; MacMillan, D. W. C., Enantioselective Organocatalytic alpha-Fluorination of Cyclic Ketones. *J. Am. Chem. Soc.* **2011,** *133* (6), 1738-1741.

86. Leon, R.; Jawalekar, A.; Redert, T.; Gaunt, M. J., Catalytic enantioselective assembly of complex molecules containing embedded quaternary stereogenic centres from simple anisidine derivatives. *Chem. Sci.* **2011,** *2* (8), 1487-1490.

87. Liu, Y. K.; Nappi, M.; Arceo, E.; Vera, S.; Melchiorre, P., Asymmetric Catalysis of Diels-Alder Reactions with in Situ Generated Heterocyclic ortho-Quinodimethanes. *J. Am. Chem. Soc.* **2011,** *133* (38), 15212-15218.

88. McGarraugh, P. G.; Jones, J. H.; Brenner-Moyer, S. E., A General Organocatalyzed Michael-Michael Cascade Reaction Generates Functionalized Cyclohexenes. *J. Org. Chem.* **2011,** *76* (15), 6309-6319.

89. Murphy, J. J.; Quintard, A.; McArdle, P.; Alexakis, A.; Stephens, J. C., Asymmetric Organocatalytic 1,6-Conjugate Addition of Aldehydes to Dienic Sulfones. *Angew. Chem.-Int. Edit.* **2011,** *50* (22), 5095-5098.

90. Quintard, A.; Alexakis, A., 1,2-Sulfone rearrangement in organocatalytic reactions. *Org. Biomol. Chem.* **2011,** *9* (5), 1407-1418.

91. Schmid, M. B.; Zeitler, K.; Gschwind, R. M., Formation and Stability of Prolinol and Prolinol Ether Enamines by NMR: Delicate Selectivity and Reactivity Balances and Parasitic Equilibria. *J. Am. Chem. Soc.* **2011,** *133* (18), 7065-7074.

92. Stiller, J.; Marques-Lopez, E.; Herrera, R. P.; Frohlich, R.; Strohmann, C.; Christmann, M., Enantioselective alpha- and gamma-Alkylation of alpha,beta-Unsaturated Aldehydes Using Dienamine Activation. *Org. Lett.* **2011,** *13* (1), 70-73.

93. Zhang, B.; Xiang, S. K.; Zhang, L. H.; Cui, Y. X.; Jiao, N., Organocatalytic Asymmetric Intermolecular Dehydrogenative alpha-Alkylation of Aldehydes Using Molecular Oxygen as Oxidant. *Org. Lett.* **2011,** *13* (19), 5212-5215.

94. Zhang, S. L.; Xie, H. X.; Zhu, J.; Li, H.; Zhang, X. S.; Li, J.; Wang, W., Organocatalytic enantioselective beta-functionalization of aldehydes by oxidation of enamines and their application in cascade reactions. *Nature Communications* **2011,** *2*.

95. Enders, D.; Greb, A.; Deckers, K.; Selig, P.; Merkens, C., Quadruple Domino Organocatalysis: An Asymmetric Aza-Michael/Michael/Michael/Aldol Reaction Sequence Leading to Tetracyclic Indole Structures with Six Stereocenters. *Chem.-Eur. J.* **2012,** *18* (33), 10226-10229.

96. Halskov, K. S.; Johansen, T. K.; Davis, R. L.; Steurer, M.; Jensen, F.; Jorgensen, K. A., Cross-trienamines in Asymmetric Organocatalysis. *J. Am. Chem. Soc.* **2012,** *134* (31), 12943-12946.

97. Jiao, Z. W.; Zhang, S. Y.; He, C.; Tu, Y. Q.; Wang, S. H.; Zhang, F. M.; Zhang, Y. Q.; Li, H., Organocatalytic Asymmetric Direct C?sp?3?H Functionalization of Ethers: A Highly Efficient Approach to Chiral Spiroethers. *Angew. Chem.-Int. Edit.* **2012,** *51* (35), 8811-8815.

98. Li, J. L.; Zhou, S. L.; Chen, P. Q.; Dong, L.; Liu, T. Y.; Chen, Y. C., Asymmetric Diels-Alder reaction of beta,beta-disubstituted enals and chromone-fused dienes: construction of collections with high molecular complexity and skeletal diversity. *Chem. Sci.* **2012,** *3* (6), 1879-1882.

99. Ramachary, D. B.; Venkaiah, C.; Krishna, P. M., Discovery of 2-aminobuta-1,3-enynes in asymmetric organocascade catalysis: construction of drug-like spirocyclic cyclohexanes having five to six contiguous stereocenters. *Chem. Commun.* **2012,** *48* (16), 2252-2254.

100. Sahoo, G.; Rahaman, H.; Madarasz, A.; Papai, I.; Melarto, M.; Valkonen, A.; Pihko, P. M., Dihydrooxazine Oxides as Key Intermediates in Organocatalytic Michael Additions of Aldehydes to Nitroalkenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (52), 13144-13148.

101. Simonovich, S. P.; Van Humbeck, J. F.; MacMillan, D. W. C., A general approach to the enantioselective alpha-oxidation of aldehydes via synergistic catalysis. *Chem. Sci.* **2012,** *3* (1), 58-61.

102. Xiong, X. F.; Zhou, Q.; Gu, J.; Dong, L.; Liu, T. Y.; Chen, Y. C., Trienamine Catalysis with 2,4-Dienones: Development and Application in Asymmetric Diels-Alder Reactions. *Angew. Chem.-Int. Edit.* **2012,** *51* (18), 4401-4404.

103. Zhang, J. M.; Tiwari, B.; Xing, C.; Chen, X. K.; Chi, Y. G. R., Enantioselective Oxidative Cross-Dehydrogenative Coupling of Tertiary Amines to Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (15), 3649-3652.

104. Corbett, M. T.; Johnson, J. S., Enantioselective synthesis of hindered cyclic dialkyl ethers via catalytic oxa-Michael/Michael desymmetrization. *Chem. Sci.* **2013,** *4* (7), 2828-2832.

105. Jiang, X. X.; Tan, B.; Barbas, C. F., Core-Structure-Motivated Design of Iminium-Enolate Organocascade Reactions: Enantioselective Syntheses of 5,6-Dihydroindolizines. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9261-9265.

106. Kano, T.; Maruoka, K., Unique properties of chiral biaryl-based secondary amine catalysts for asymmetric enamine catalysis. *Chem. Sci.* **2013,** *4* (3), 907-915.

107. Kano, T.; Shirozu, F.; Maruoka, K., Metal-Free Enantioselective Hydroxyamination of Aldehydes with Nitrosocarbonyl Compounds Catalyzed by an Axially Chiral Amine. *J. Am. Chem. Soc.* **2013,** *135* (48), 18036-18039.

108. Ma, C.; Jia, Z. J.; Liu, J. X.; Zhou, Q. Q.; Dong, L.; Chen, Y. C., A Concise Assembly of Electron-Deficient 2,4-Dienes and 2,4-Dienals: Regio- and Stereoselective exo-Diels-Alder and Redox Reactions through Sequential Amine and Carbene Catalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (3), 948-951.

109. Noole, A.; Oseka, M.; Pehk, T.; Oeren, M.; Jarving, I.; Elsegood, M. R. J.; Malkov, A. V.; Lopp, M.; Kanger, T., 3-Chlorooxindoles: Versatile Starting Materials for Asymmetric Organocatalytic Synthesis of Spirooxindoles. *Advanced Synthesis & Catalysis* **2013,** *355* (5), 829-835.

110. Zeng, X. F.; Ni, Q. J.; Raabe, G.; Enders, D., A Branched Domino Reaction: Asymmetric Organocatalytic Two-Component Four-Step Synthesis of Polyfunctionalized Cyclohexene Derivatives. *Angew. Chem.-Int. Edit.* **2013,** *52* (10), 2977-2980.

111. Zhang, G.; Ma, Y. X.; Wang, S. L.; Kong, W. D.; Wang, R., Chiral organic contact ion pairs in metal-free catalytic enantioselective oxidative cross-dehydrogenative coupling of tertiary amines to ketones. *Chem. Sci.* **2013,** *4* (6), 2645-2651.

112. Bures, J.; Dingwall, P.; Armstrong, A.; Blackmond, D. G., Rationalization of an Unusual Solvent-Induced Inversion of Enantio-meric Excess in Organocatalytic Selenylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2014,** *53* (33), 8700-8704.

113. Caruana, L.; Kniep, F.; Johansen, T. K.; Poulsen, P. H.; Jorgensen, K. A., A New Organocatalytic Concept for Asymmetric alpha-Alkylation of Aldehydes. *J. Am. Chem. Soc.* **2014,** *136* (45), 15929-15932.

114. Dell'Amico, L.; Rassu, G.; Zambrano, V.; Sartori, A.; Curti, C.; Battistini, L.; Pelosi, G.; Casiraghi, G.; Zanardi, F., Exploring the Vinylogous Reactivity of Cyclohexenylidene Malononitriles: Switchable Regioselectivity in the Organocatalytic Asymmetric Addition to Enals Giving Highly Enantioenriched Carbabicyclic Structures. *J. Am. Chem. Soc.* **2014,** *136* (31), 11107-11114.

115. Halskov, K. S.; Donslund, B. S.; Barfusser, S.; Jorgensen, K. A., Organocatalytic Asymmetric Formation of Steroids. *Angew. Chem.-Int. Edit.* **2014,** *53* (16), 4137-4141.

116. Koley, D.; Krishna, Y.; Srinivas, K.; Khan, A. A.; Kant, R., Organocatalytic Asymmetric Mannich Cyclization of Hydroxylactams with Acetals: Total Syntheses of (-)-Epilupinine, (-)-Tashiromine, and (-)-Trachelanthamidine. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13196-13200.

117. Martin-Santos, C.; Jarava-Barrera, C.; del Pozo, S.; Parra, A.; Diaz-Tendero, S.; Mas-Balleste, R.; Cabrera, S.; Aleman, J., Highly Enantioselective Construction of Tricyclic Derivatives by the Desymmetrization of Cyclohexadienones. *Angew. Chem.-Int. Edit.* **2014,** *53* (31), 8184-8189.

118. Mengozzi, L.; Gualandi, A.; Cozzi, P. G., A highly enantioselective acyl-Mannich reaction of isoquinolines with aldehydes promoted by proline derivatives: an approach to 13-alkyl-tetrahydroprotoberberine alkaloids. *Chem. Sci.* **2014,** *5* (10), 3915-3921.

119. Brindani, N.; Rassu, G.; Dell'Amico, L.; Zambrano, V.; Pinna, L.; Curti, C.; Sartori, A.; Battistini, L.; Casiraghi, G.; Pelosi, G.; Greco, D.; Zanardi, F., Organocatalytic, Asymmetric Eliminative 4+2 Cycloaddition of Allylidene Malononitriles with Enals: Rapid Entry to Cyclohexadiene-Embedding Linear and Angular Polycycles. *Angew. Chem.-Int. Edit.* **2015,** *54* (25), 7386-7390.

120. Echemendia, R.; de La Torre, A. F.; Monteiro, J. L.; Pila, M.; Correa, A. G.; Westermann, B.; Rivera, D. G.; Paixao, M. W., Highly Stereoselective Synthesis of Natural-Product-Like Hybrids by an Organocatalytic/Multicomponent Reaction Sequence. *Angew. Chem.-Int. Edit.* **2015,** *54* (26), 7621-7625.

121. Halskov, K. S.; Kniep, F.; Lauridsen, V. H.; Iversen, E. H.; Donslund, B. S.; Jorgensen, K. A., Organocatalytic Enamine-Activation of Cyclopropanes for Highly Stereoselective Formation of Cyclobutanes. *J. Am. Chem. Soc.* **2015,** *137* (4), 1685-1691.

122. Kano, T.; Sugimoto, H.; Maruyama, H.; Maruoka, K., Regio- and Stereoselective Conjugate Addition of Aldehydes to beta-Tosyl Enones under the Catalysis of a Binaphthyl-Modified Chiral Amine. *Angew. Chem.-Int. Edit.* **2015,** *54* (29), 8462-8465.

123. Orue, A.; Uria, U.; Reyes, E.; Carrillo, L.; Vicario, J. L., Catalytic Enantioselective 5+2 Cycloaddition between Oxidopyrylium Ylides and Enals under Dienamine Activation. *Angew. Chem.-Int. Edit.* **2015,** *54* (10), 3043-3046.

124. Wang, S.; Li, X.; Liu, H.; Xu, L.; Zhuang, J.; Li, J.; Li, H.; Wang, W., Organocatalytic Enantioselective Direct Additions of Aldehydes to 4-Vinylpyridines and Electron-Deficient Vinylarenes and Their Synthetic Applications. *J. Am. Chem. Soc.* **2015,** *137* (6), 2303-2310.

125. Donslund, B. S.; Nielsen, R. P.; Monsted, S. M. N.; Jorgensen, K. A., Benzofulvenes in Trienamine Catalysis: Stereoselective Spiroindene Synthesis. *Angew. Chem.-Int. Edit.* **2016,** *55* (37), 11124-11128.

126. Nielsen, A. J.; Jenkins, H. A.; McNulty, J., Asymmetric Organocatalytic Stepwise 2+2 Entry to Tetra-Substituted Heterodimeric and Homochiral Cyclobutanes. *Chem.-Eur. J.* **2016,** *22* (27), 9111-9115.

127. Izzo, J. A.; Poulsen, P. H.; Intrator, J. A.; Jorgensen, K. A.; Vetticatt, M. J., Isotope Effects Reveal an Alternative Mechanism for "Iminium-lon" Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (27), 8396-8400.

128. Ponath, S.; Menger, M.; Grothues, L.; Weber, M.; Lentz, D.; Strohmann, C.; Christmann, M., Mechanistic Studies on the Organocatalytic alpha-Chlorination of Aldehydes: The Role and Nature of Off-Cycle Intermediates. *Angew. Chem.-Int. Edit.* **2018,** *57* (36), 11683-11687.

129. Rigotti, T.; Casado-Sanchez, A.; Cabrera, S.; Perez-Ruiz, R.; Liras, M.; O'Shea, V. A. D.; Aleman, J., A Bifunctional Photoaminocatalyst for the Alkylation of Aldehydes: Design, Analysis, and Mechanistic Studies. *Acs Catalysis* **2018,** *8* (7), 5928-5940.

130. Apel, C.; Hartmann, S. S.; Lentz, D.; Christmann, M., Dienamine-Induced Divinylcyclopropane-Cycloheptadiene Rearrangements. *Angew. Chem.-Int. Edit.* **2019,** *58* (15), 5075-5079.

131. Tobiesen, H. N.; Leth, L. A.; Iversen, M. V.; Næsborg, L.; Bertelsen, S.; Jørgensen, K. A., Stereoselective Oxidative Bioconjugation of Amino Acids and Oligopeptides to Aldehydes. *Angewandte Chemie International Edition* **2020,** *59* (42), 18490-18494.

132. Barløse, C. L.; Østergaard, N. L.; Bitsch, R. S.; Iversen, M. V.; Jørgensen, K. A., A Direct Organocatalytic Enantioselective Route to Functionalized trans-Diels–Alder Products Having the Norcarane Scaffold. *Angewandte Chemie International Edition* **2021,** *60* (33), 18318-18327.

133. Hutchinson, G.; Alamillo-Ferrer, C.; Burés, J., Mechanistically Guided Design of an Efficient and Enantioselective Aminocatalytic α-Chlorination of Aldehydes. *J. Am. Chem. Soc.* **2021,** *143* (18), 6805-6809.

134. Wang, Z.-H.; Gao, P.-S.; Wang, X.; Gao, J.-Q.; Xu, X.-T.; He, Z.; Ma, C.; Mei, T.-S., TEMPO-Enabled Electrochemical Enantioselective Oxidative Coupling of Secondary Acyclic Amines with Ketones. *J. Am. Chem. Soc.* **2021,** *143* (38), 15599-15605.

135. Ghosh, B.; Harariya, M. S.; Mukherjee, S., Catalytic Enantioselective de novo Construction of Chiral Arenes through Desymmetrizing Oxidative [4+2]-Cycloaddition. *Angewandte Chemie International Edition* **2022,** *61* (37), e202204523.

136. Yetra, S. R.; Schmitt, N.; Tambar, U. K., Catalytic photochemical enantioselective α-alkylation with pyridinium salts. *Chem. Sci.* **2023,** *14* (3), 586-592.

3.3 Phase-Transfer Catalysis

3.3.1 Cinchona-Based Catalysts

1. Dolling, U. H.; Davis, P.; Grabowski, E. J. J., EFFICIENT CATALYTIC ASYMMETRIC ALKYLATIONS .1. ENANTIOSELECTIVE SYNTHESIS OF (+)-INDACRINONE VIA CHIRAL PHASE-TRANSFER CATALYSIS. *J. Am. Chem. Soc.* **1984,** *106* (2), 446-447.

2. Odonnell, M. J.; Bennett, W. D.; Wu, S. D., The Stereoselective Synthesis of Alpha-Amino-Acids by Phase- Transfer Catalysis. *J. Am. Chem. Soc.* **1989,** *111* (6), 2353-2355.

3. Corey, E. J.; Xu, F.; Noe, M. C., A rational approach to catalytic enantioselective enolate alkylation using a structurally rigidified and defined chiral quaternary ammonium salt under phase transfer conditions. *J. Am. Chem. Soc.* **1997,** *119* (50), 12414-12415.

4. Corey, E. J.; Bo, Y. X.; Busch-Petersen, J., Highly enantioselective phase transfer catalyzed alkylation of a 3-oxygenated propionic ester equivalent; applications and mechanism. *J. Am. Chem. Soc.* **1998,** *120* (49), 13000-13001.

5. Park, H. G.; Jeong, B. S.; Yoo, M. S.; Lee, J. H.; Park, M. K.; Lee, Y. J.; Kim, M. J.; Jew, S. S., Highly enantioselective and practical cinchona-derived phase- transfer catalysts for the synthesis of alpha-amino acids. *Angew. Chem.-Int. Edit.* **2002,** *41* (16), 3036-3038.

6. Bhunnoo, R. A.; Hu, Y. L.; Laine, D. I.; Brown, R. C. D., An asymmetric phase-transfer dihydroxylation reaction. *Angew. Chem.-Int. Edit.* **2002,** *41* (18), 3479-3480.

7. Zhang, F. Y.; Corey, E. J., Highly enantioselective dimerization of alpha,beta-enones catalyzed by a rigid quaternary ammonium salt. *Org. Lett.* **2004,** *6* (19), 3397-3399.

8. Bella, M.; Kobbelgaard, S.; Jorgensen, K. A., Organocatalytic regio- and asymmetric C-selective SNAr reactions-stereoselective synthesis of optically active spiro-pyrrolidone-3,3 '-oxoindoles. *J. Am. Chem. Soc.* **2005,** *127* (11), 3670-3671.

9. Fini, F.; Sgarzani, V.; Pettersen, D.; Herrera, R. P.; Bernardi, L.; Ricci, A., Phase-transfer-catalyzed asymmetric aza-Henry reaction using N-carbamoyl imines generated in situ from alpha-amido sulfones. *Angew. Chem.-Int. Edit.* **2005,** *44* (48), 7975-7978.

10. Jew, S.; Lee, J. H.; Jeong, B. S.; Yoo, M. S.; Kim, M. J.; Lee, Y. J.; Lee, J.; Choi, S. H.; Lee, K.; Lah, M. S.; Park, H., Highly enantioselective epoxidation of 2.4-diarylenones by using dimeric cinchona phase-transfer catalysts: Enhancement of enantioselectivity by surfactants. *Angew. Chem.-Int. Edit.* **2005,** *44* (9), 1383-1385.

11. Palomo, C.; Oiarbide, M.; Laso, A.; Lopez, R., Catalytic enantioselective aza-Henry reaction with broad substrate scope. *J. Am. Chem. Soc.* **2005,** *127* (50), 17622-17623.

12. Ramachandran, P. V.; Madhi, S.; Bland-Berry, L.; Reddy, M. V. R.; O'Donnell, M. J., Catalytic enantioselective synthesis of glutamic acid derivatives via tandem conjugate addition-elimination of activated allylic acetates under chiral PTC conditions. *J. Am. Chem. Soc.* **2005,** *127* (39), 13450-13451.

13. Bell, M.; Poulsen, T. B.; Jorgensen, K. A., Organocatalytic enantioselective nucleophilic vinylic substitution by alpha-substituted-alpha-cyanoacetates under phase-transfer conditions. *J. Org. Chem.* **2007,** *72* (8), 3053-3056.

14. Bernardi, L.; Lopez-Cantarero, J.; Niess, B.; Jlrgensen, K. A., Organocatalytic asymmetric 1,6-additions of beta-ketoesters and glycine imine. *J. Am. Chem. Soc.* **2007,** *129* (17), 5772-5778.

15. Mizuta, S.; Shibata, N.; Goto, Y.; Furukawa, T.; Nakamura, S.; Toru, T., Cinchona alkaloid-catalyzed enantioselective monofluoromethylation reaction based on fluorobis(phenylsulfonyl)methane chemistry combined with a Mannich-type reaction. *J. Am. Chem. Soc.* **2007,** *129* (20), 6394-+.

16. Mizuta, S.; Shibata, N.; Akiti, S.; Fujimoto, H.; Nakamura, S.; Toru, T., Cinchona Alkaloids/TMAF combination-catalyzed nucleophilic enantioselective trifluoromethylation of aryl ketones. *Org. Lett.* **2007,** *9* (18), 3707-3710.

17. Poulsen, T. B.; Bernardi, L.; Aleman, J.; Overgaard, J.; Jorgensen, K. A., Organocatalytic asymmetric direct alpha-alkynylation of cyclic beta-ketoesters. *J. Am. Chem. Soc.* **2007,** *129* (2), 441-449.

18. Elsner, P.; Bernardi, L.; Dela Salla, G.; Overgaard, J.; Jorgensen, K. A., Organocatalytic asymmetric conjugate addition to allenic esters and ketones. *J. Am. Chem. Soc.* **2008,** *130* (14), 4897-4905.

19. Bandini, M.; Eichholzer, A.; Tragni, M.; Umani-Ronchi, A., Enantioselective phase-transfer-catalyzed intramolecular Aza-Michael reaction: Effective route to pyrazino-indole compounds. *Angew. Chem.-Int. Edit.* **2008,** *47* (17), 3238-3241.

20. Sano, D.; Nagata, K.; Itoh, T., Catalytic asymmetric hydroxylation of oxindoles by molecular oxygen using a phase-transfer catalyst. *Org. Lett.* **2008,** *10* (8), 1593-1595.

21. Poulsen, T. B.; Dickmeiss, G.; Overgaard, J.; Jorgensen, K. A., Organocatalytic asymmetric synthesis of versatile gamma-lactams. *Angew. Chem.-Int. Edit.* **2008,** *47* (25), 4687-4690.

22. Gomez-Bengoa, E.; Linden, A.; Lopez, R.; Mugica-Mendiola, I.; Oiarbide, M.; Palomo, C., Asymmetric aza-henry reaction under phase transfer catalysis: An experimental and theoretical study. *J. Am. Chem. Soc.* **2008,** *130* (25), 7955-7966.

23. Moss, T. A.; Fenwick, D. R.; Dixon, D. J., Enantio- and diastereoselective catalytic alkylation reactions with aziridines. *J. Am. Chem. Soc.* **2008,** *130* (31), 10076-+.

24. Fini, F.; Micheletti, G.; Bernardi, L.; Pettersen, D.; Fochi, M.; Ricci, A., An easy entry to optically active alpha-amino phosphonic acid derivatives using phase-transfer catalysis (PTC). *Chem. Commun.* **2008,** (36), 4345-4347.

25. Paixao, M. W.; Nielsen, M.; Jacobsen, C. B.; Jorgensen, K. A., Organocatalytic asymmetric ring-opening of aziridines. *Org. Biomol. Chem.* **2008,** *6* (19), 3467-3470.

26. Arakawa, Y.; Haraguchi, N.; Itsuno, S., An Immobilization Method of Chiral Quaternary Ammonium Salts onto Polymer Supports. *Angew. Chem.-Int. Edit.* **2008,** *47* (43), 8232-8235.

27. Furukawa, T.; Shibata, N.; Mizuta, S.; Nakamura, S.; Toru, T.; Shiro, M., Catalytic Enantioselective Michael Addition of 1-Fluoro-bis(phenylsulfonyl)methane to alpha,beta-Unsaturated Ketones Catalyzed by Cinchona Alkaloids. *Angew. Chem.-Int. Edit.* **2008,** *47* (42), 8051-8054.

28. Minakata, S.; Murakami, Y.; Tsuruoka, R.; Kitanaka, S.; Komatsu, M., Catalytic aziridination of electron-deficient olefins with an N-chloro-N-sodio carbamate and application of this novel method to asymmetric synthesis. *Chem. Commun.* **2008,** (47), 6363-6365.

29. Cassani, C.; Bernardi, L.; Fini, F.; Ricci, A., Catalytic Asymmetric Mannich Reactions of Sulfonylacetates. *Angew. Chem.-Int. Edit.* **2009,** *48* (31), 5694-5697.

30. Puglisi, A.; Raimondi, L.; Benaglia, M.; Bonsignore, M.; Rossi, S., Enantioselective catalytic addition of nitroesters to N-carboalkyloxy imines: a route to quaternary stereocenters. *Tetrahedron Lett.* **2009,** *50* (30), 4340-4342.

31. Nibbs, A. E.; Baize, A. L.; Herter, R. M.; Scheidt, K. A., Catalytic Asymmetric Alkylation of Substituted Isoflavanones. *Org. Lett.* **2009,** *11* (17), 4010-4013.

32. Moss, T. A.; Alonso, B.; Fenwick, D. R.; Dixon, D. J., Catalytic Enantio- and Diastereoselective Alkylations with Cyclic Sulfamidates. *Angew. Chem.-Int. Edit.* **2010,** *49* (3), 568-571.

33. Chen, Y. J.; Seki, K.; Yamashita, Y.; Kobayashi, S., Catalytic Carbon-Carbon Bond-Forming Reactions of Aminoalkane Derivatives with Imines. *J. Am. Chem. Soc.* **2010,** *132* (10), 3244-+.

34. Tomooka, K.; Uehara, K.; Nishikawa, R.; Suzuki, M.; Igawa, K., Enantioselective Synthesis of Planar Chiral Organonitrogen Cycles. *J. Am. Chem. Soc.* **2010,** *132* (27), 9232-9233.

35. Mahe, O.; Dez, I.; Levacher, V.; Briere, J. F., Enantioselective Phase-Transfer Catalysis: Synthesis of Pyrazolines. *Angew. Chem.-Int. Edit.* **2010,** *49* (39), 7072-7075.

36. Liu, Y.; Provencher, B. A.; Bartelson, K. J.; Deng, L., Highly enantioselective asymmetric Darzens reactions with a phase transfer catalyst. *Chem. Sci.* **2011,** *2* (7), 1301-1304.

37. Respondek, T.; Cueny, E.; Kodanko, J. J., Cumyl Ester as the C-Terminal Protecting Group in the Enantioselective Alkylation of Glycine Benzophenone Imine. *Org. Lett.* **2012,** *14* (1), 150-153.

38. Wei, Y.; He, W.; Liu, Y. L.; Liu, P.; Zhang, S. Y., Highly Enantioseiective Nitro-Mannich Reaction Catalyzed by Cinchona Alkaloids and N-Benzotriazole Derived Ammonium Salts. *Org. Lett.* **2012,** *14* (3), 704-707.

39. Moss, T. A.; Barber, D. M.; Kyle, A. F.; Dixon, D. J., Catalytic Asymmetric Alkylation Reactions for the Construction of Protected Ethylene-Amino and Propylene-Amino Motifs Attached to Quaternary Stereocentres. *Chemistry-a European Journal* **2013,** *19* (9), 3071-3081.

40. Kawai, H.; Okusu, S.; Yuan, Z.; Tokunaga, E.; Yamano, A.; Shiro, M.; Shibata, N., Enantioselective Synthesis of Epoxides Having a Tetrasubstituted Trifluoromethylated Carbon Center: Methylhydrazine-Induced Aerobic Epoxidation of beta,beta-Disubstituted Enones. *Angew. Chem.-Int. Edit.* **2013,** *52* (8), 2221-2225.

41. Claraz, A.; Oudeyer, S.; Levacher, V., Chiral Quaternary Ammonium Aryloxide/N,O-Bis(trimethyl- silyl)acetamide Combination as Efficient Organocatalytic System for the Direct Vinylogous Aldol Reaction of (5H)-Furan-2-one Derivatives. *Adv. Synth. Catal.* **2013,** *355* (5), 841-846.

42. Lykke, L.; Halskov, K. S.; Carlsen, B. D.; Chen, V. X.; Jorgensen, K. A., Catalytic Asymmetric Diaziridination. *J. Am. Chem. Soc.* **2013,** *135* (12), 4692-4695.

43. Xie, J. W.; Xu, M. L.; Zhang, R. Z.; Pan, J. Y.; Zhu, W. D., Organocatalytic Domino Reaction of Electron-Deficient 2,4-Dienes with 2-Halo-1,3-Dicarbonyl Compounds: A Highly Regio- and Stereoselective Approach to Functionalized Five-Membered Carbocycles. *Adv. Synth. Catal.* **2014,** *356* (2-3), 395-400.

44. Armstrong, R. J.; Smith, M. D., Catalytic Enantioselective Synthesis of Atropisomeric Biaryls: A Cation-Directed Nucleophilic Aromatic Substitution Reaction. *Angew. Chem.-Int. Edit.* **2014,** *53* (47), 12822-12826.

45. Denmark, S. E.; Henle, J. J., Redefining q: quaternary ammonium cross sectional area (XSA) as a general descriptor for transport-limiting PTC rate approximations. *Chem. Sci.* **2015,** *6* (4), 2211-2218.

46. Schwieter, K. E.; Johnston, J. N., Enantioselective synthesis of D-alpha-amino amides from aliphatic aldehydes. *Chem. Sci.* **2015,** *6* (4), 2590-2595.

47. Sharma, K.; Wolstenhulme, J. R.; Painter, P. P.; Yeo, D.; Grande-Carmona, F.; Johnston, C. P.; Tantillo, D. J.; Smith, M. D., Cation-Controlled Enantioselective and Diastereoselective Synthesis of Indolines: An Autoinductive Phase-Transfer Initiated 5-endo-trig Process. *J. Am. Chem. Soc.* **2015,** *137* (41), 13414-13424.

48. Wu, Y. W.; Hu, L.; Li, Z.; Deng, L., Catalytic asymmetric umpolung reactions of imines. *Nature* **2015,** *523* (7561), 445-450.

49. Rahemtulla, B. F.; Clark, H. F.; Smith, M. D., Catalytic Enantioselective Synthesis of C-1- and C-2-Symmetric Spirobiindanones through Counterion-Directed Enolate C-Acylation. *Angew. Chem.-Int. Edit.* **2016,** *55* (42), 13180-13183.

50. Hu, L.; Wu, Y. W.; Li, Z.; Deng, L., Catalytic Asymmetric Synthesis of Chiral gamma-Amino Ketones via Umpolung Reactions of Imines. *J. Am. Chem. Soc.* **2016,** *138* (49), 15817-15820.

51. Jolliffe, J. D.; Armstrong, R. J.; Smith, M. D., Catalytic enantioselective synthesis of atropisomeric biaryls by a cation-directed O-alkylation. *Nature Chemistry* **2017,** *9* (6), 558-562.

52. Hu, B.; Bezpalko, M. W.; Fei, C.; Dickie, D. A.; Foxman, B. M.; Deng, L., Origin of and a Solution for Uneven Efficiency by Cinchona Alkaloid-Derived, Pseudoenantiomeric Catalysts for Asymmetric Reactions. *J. Am. Chem. Soc.* **2018,** *140* (42), 13913-13920.

53. McLaughlin, M. F.; Massolo, E.; Liu, S. B.; Johnson, J. S., Enantioselective Phenolic alpha-Oxidation Using H2O2 via an Unusual Double Dearomatization Mechanism. *J. Am. Chem. Soc.* **2019,** *141* (6), 2645-2651.

54. Gomes, R. D.; Corey, E. J., A Method for the Catalytic Enantioselective Synthesis of Chiral alpha-Azido and alpha-Amino Ketones from Racemic alpha-Bromo Ketones, and Its Generalization to the Formation of Bonds to C, O, and S. *J. Am. Chem. Soc.* **2019,** *141* (51), 20058-20061.

55. Gao, M.; Luo, Y.; Xu, Q.; Zhao, Y.; Gong, X.; Xia, Y.; Hu, L., A Unified Catalytic Asymmetric (4+1) and (5+1) Annulation Strategy to Access Chiral Spirooxindole-Fused Oxacycles. *Angewandte Chemie International Edition* **2021,** *60* (36), 19813-19820.

56. Moser, D.; Sparr, C., Synthesis of Atropisomeric Two-Axis Systems by the Catalyst-Controlled syn- and anti-Selective Arene-Forming Aldol Condensation. *Angewandte Chemie International Edition* **2022,** *61* (24), e202202548.

57. Du, J.-Y.; Balan, T.; Claridge, T. D. W.; Smith, M. D., Counterion-Mediated Enantioconvergent Synthesis of Axially Chiral Medium Rings. *J. Am. Chem. Soc.* **2022,** *144* (32), 14790-14797.

58. Han, X.-L.; Hu, B.; Fei, C.; Li, Z.; Yu, Y.; Cheng, C.; Foxman, B.; Luo, J.; Deng, L., Catalytic Asymmetric Imine Cross-Coupling Reaction. *J. Am. Chem. Soc.* **2023,** *145* (8), 4400-4407.

59. Yin, S.; Liu, J.; Weeks, K. N.; Aponick, A., Catalytic Enantioselective Synthesis of Axially Chiral Imidazoles by Cation-Directed Desymmetrization. *J. Am. Chem. Soc.* **2023,** *145* (51), 28176-28183.

60. Cheng, C.; Yu, Y.; Gao, Y.; Li, Y.-P.; Han, X.-L.; Luo, J.; Deng, L., Catalytic Asymmetric Construction of Chiral Amines with Three Nonadjacent Stereocenters via Trifunctional Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (13), 9356-9364.

3.3.2 Other Catalysts

1. Ooi, T.; Kameda, M.; Maruoka, K., Molecular design of a C-2-symmetric chiral phase-transfer catalyst for practical asymmetric synthesis of alpha-amino acids. *J. Am. Chem. Soc.* **1999,** *121* (27), 6519-6520.
2. Kita, T.; Georgieva, A.; Hashimoto, Y.; Nakata, T.; Nagasawa, K., C-2-symmetric chiral pentacyclic guanidine: A phase-transfer catalyst for the asymmetric alkylation of tert-butyl glycinate Schiff base. *Angew. Chem.-Int. Edit.* **2002,** *41* (15), 2832-+.
3. Hashimoto, T.; Maruoka, K., Substituent effect of binaphthyl-modified spiro-type chiral phase-transfer catalysts. *Tetrahedron Lett.* **2003,** *44* (16), 3313-3316.
4. Lygo, B.; Allbutt, B.; James, S. R., Identification of a highly effective asymmetric phase-transfer catalyst derived from alpha-methylnaphthylamine. *Tetrahedron Lett.* **2003,** *44* (30), 5629-5632.

5. Mase, N.; Ohno, T.; Hoshikawa, N.; Ohishi, K.; Morimoto, H.; Yoda, H.; Takabe, K., Enantioselective alkylation using a new C-3 symmetric amine- based chiral phase-transfer catalyst. *Tetrahedron Lett.* **2003,** *44* (21), 4073-4075.
6. Ooi, T.; Doda, K.; Maruoka, K., Highly enantioselective Michael addition of silyl nitronates to alpha,beta-unsaturated aldehydes catalyzed by designer chiral ammonium bifluorides: Efficient access to optically active gamma-nitro aldehydes and their enol silyl ethers. *J. Am. Chem. Soc.* **2003,** *125* (30), 9022-9023.
7. Ooi, T.; Kameda, M.; Maruoka, K., Design of N-spiro C-2-symmetric chiral quaternary ammonium bromides as novel chiral phase-transfer catalysts: Synthesis and application to practical asymmetric synthesis of alpha- amino acids. *J. Am. Chem. Soc.* **2003,** *125* (17), 5139-5151.
8. Ooi, T.; Miki, T.; Taniguchi, M.; Shiraishi, M.; Takeuchi, M.; Maruoka, K., Highly enantioselective construction of quaternary stereocenters on beta-keto esters by phase-transfer catalytic asymmetric alkylation and Michael reaction. *Angew. Chem.-Int. Edit.* **2003,** *42* (32), 3796-3798.
9. Ooi, T.; Sakai, D.; Takeuchi, M.; Tayama, E.; Maruoka, K., Practical asymmetric synthesis of vicinal diamines through the catalytic highly enantioselective alkylation of glycine amide derivatives. *Angew. Chem.-Int. Edit.* **2003,** *42* (47), 5868-5870.
10. Jew, S. S.; Lee, Y. J.; Lee, J. H.; Myoung, J. K.; Jeong, B. S.; Yoo, M. S.; Kim, M. J.; Choi, S. H.; Ku, J. M.; Park, H. G., Highly enantioselective phase-transfer-catalytic alkylation of 2-phenyl-2-oxazoline-4-carboxylic acid tert-butyl ester for the asymmetric synthesis of alpha-alkyl serines. *Angew. Chem.-Int. Edit.* **2004,** *43* (18), 2382-2385.
11. Ooi, T.; Fujioka, S.; Maruoka, K., Highly enantioselective conjugate addition of nitroalkanes to alkylidenernalonates using efficient phase-transfer catalysis of N-spiro chiral ammonium bromides. *J. Am. Chem. Soc.* **2004,** *126* (38), 11790-11791.
12. Ooi, T.; Kameda, M.; Fujii, J.; Maruoka, K., Catalytic asymmetric synthesis of a nitrogen analogue of dialkyl tartrate by direct Mannich reaction under phase- transfer conditions. *Org. Lett.* **2004,** *6* (14), 2397-2399.
13. Ooi, T.; Kameda, M.; Taniguchi, M.; Maruoka, K., Development of highly diastereo- and enantioselective direct asymmetric aldol reaction of a glycinate Schiff base with aldehydes catalyzed by chiral quaternary ammonium salts. *J. Am. Chem. Soc.* **2004,** *126* (31), 9685-9694.
14. Shirakawa, S.; Tanaka, Y.; Maruoka, K., Development of a recyclable fluorous chiral phase-transfer catalyst: Application to the catalytic asymmetric synthesis of alpha-amino acids. *Org. Lett.* **2004,** *6* (9), 1429-1431.
15. Kitamra, M.; Shirakawa, S.; Maruoka, K., Powerful chiral phase-transfer catalysts for the asymmetric synthesis of alpha-alkyl- and alpha,alpha,-dialkyl-alpha-amino acids. *Angew. Chem.-Int. Edit.* **2005,** *44* (10), 1549-1551.
16. Okada, A.; Shibuguchi, T.; Ohshima, T.; Masu, H.; Yamaguchi, K.; Shibasaki, M., Enantio- and diastereoselective catalytic Mannich-type reaction of a glycine Schiff base using a chiral two-center phase-transfer catalyst. *Angew. Chem.-Int. Edit.* **2005,** *44* (29), 4564-4567.
17. Ooi, T.; Miki, T.; Maruoka, K., Asymmetric synthesis of functionalized aza-cyclic amino acids with quaternary stereocenters by a phase-transfer-catalyzed alkylation strategy. *Org. Lett.* **2005,** *7* (2), 191-193.
18. Ooi, T.; Ohara, D.; Fukumoto, K.; Maruoka, K., Importance of chiral phase-transfer catalysts with dual functions in obtaining high enantioselectivity in the Michael reaction of malonates and chalcone derivatives. *Org. Lett.* **2005,** *7* (15), 3195-3197.
19. Ooi, T.; Takada, S.; Fujioka, S.; Maruoka, K., N-spiro chiral quaternary ammonium bromide catalyzed diastereo- and enantioselective conjugate addition of nitroalkanes to cyclic alpha,beta-unsaturated ketones under phase-transfer conditions. *Org. Lett.* **2005,** *7* (23), 5143-5146.
20. Ooi, T.; Takeuchi, M.; Kato, D.; Uematsu, Y.; Tayama, E.; Sakai, D.; Maruoka, K., Highly enantioselective phase-transfer-catalyzed alkylation of protected alpha-amino acid amides toward practical asymmetric synthesis of vicinal diamines, alpha-amino ketones, and alpha-amino alcohols. *J. Am. Chem. Soc.* **2005,** *127* (14), 5073-5083.
21. Ooi, T.; Kato, D.; Inamura, K.; Ohmatsu, K.; Maruoka, K., Practical stereloselective synthesis of beta-branched alpha-amino acids through efficient kinetic resolution in the phase-transfer-catalyzed asymmetric alkylations. *Org. Lett.* **2007,** *9* (20), 3945-3948.
22. Uraguchi, D.; Sakaki, S.; Ooi, T., Chiral tetraaminophosphonium salt-mediated asymmetric direct henry reaction. *J. Am. Chem. Soc.* **2007,** *129* (41), 12392-+.
23. Uraguchi, D.; Ueki, Y.; Ooi, T., Chiral Tetraaminophosphonium Carboxylate-Catalyzed Direct Mannich-Type Reaction. *J. Am. Chem. Soc.* **2008,** *130* (43), 14088-+.
24. He, R. J.; Wang, X. S.; Hashimoto, T.; Maruoka, K., Binaphthyl-Modiried Quaternary Phosphonium Salts as Chiral Phase-Transfer Catalysts: Asymmetric Amination of beta-Keto Esters. *Angew. Chem.-Int. Edit.* **2008,** *47* (49), 9466-9468.
25. Uraguchi, D.; Asai, Y.; Ooi, T., Site-Directed Asymmetric Quaternization of a Peptide Backbone at a C-Terminal Azlactone. *Angew. Chem.-Int. Edit.* **2009,** *48* (4), 733-737.
26. Kim, M. H.; Choi, S. H.; Lee, Y. J.; Lee, J.; Nahm, K.; Jeong, B. S.; Park, H. G.; Jew, S. S., The highly enantioselective phase-transfer catalytic mono-alkylation of malonamic esters. *Chem. Commun.* **2009,** (7), 782-784.
27. Uraguchi, D.; Ito, T.; Ooi, T., Generation of Chiral Phosphonium Dialkyl Phosphite as a Highly Reactive P-Nucleophile: Application to Asymmetric Hydrophosphonylation of Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (11), 3836-+.
28. Wang, Y. G.; Kumano, T.; Kano, T.; Maruoka, K., Organocatalytic Approach to Enantioselective One-Pot Synthesis of Pyrrolidine, Hexahydropyrrolizine, and Octahydroindolizine Core Structures. *Org. Lett.* **2009,** *11* (9), 2027-2029.
29. He, R. J.; Ding, C. H.; Maruoka, K., Phosphonium Salts as Chiral Phase-Transfer Catalysts: Asymmetric Michael and Mannich Reactions of 3-Aryloxindoles. *Angew. Chem.-Int. Edit.* **2009,** *48* (25), 4559-4561.
30. Hashimoto, T.; Sakata, K.; Maruoka, K., alpha-Chiral Acetylenes Having an All-Carbon Quaternary Center: Phase Transfer Catalyzed Enantioselective alpha Alkylation of alpha-Alkyl-alpha-alkynyl Esters. *Angew. Chem.-Int. Edit.* **2009,** *48* (27), 5014-5017.
31. He, R. J.; Shirakawa, S.; Maruoka, K., Enantioselective Base-Free Phase-Transfer Reaction in Water-Rich Solvent. *J. Am. Chem. Soc.* **2009,** *131* (46), 16620-+.
32. Hua, M. Q.; Cui, H. F.; Wang, L.; Nie, J.; Ma, J. A., Reversal of Enantioselectivity by Tuning the Conformational Flexibility of Phase-Transfer Catalysts. *Angew. Chem.-Int. Edit.* **2010,** *49* (15), 2772-2776.
33. Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K., Quaternary Ammonium (Hypo)iodite Catalysis for Enantioselective Oxidative Cycloetherification. *Science* **2010,** *328* (5984), 1376-1379.
34. Hashimoto, T.; Sakata, K.; Maruoka, K., Phase-Transfer-Catalyzed Olefin Isomerization/alpha-Alkylation of alpha-Alkynylcrotonates as a Route for 1,4-Enynes. *Adv. Synth. Catal.* **2010,** *352* (10), 1653-1656.
35. Uraguchi, D.; Nakamura, S.; Ooi, T., Catalytic Asymmetric Direct Henry Reaction of Ynals: Short Syntheses of (2S,3R)-(+)-Xestoaminol C and (-)-Codonopsinines. *Angew. Chem.-Int. Edit.* **2010,** *49* (41), 7562-7565.
36. Hashimoto, T.; Fukumoto, K.; Abe, N.; Sakata, K.; Maruoka, K., Development of 5-silylethynyl-1,3-dioxolan-4-one as a new prochiral template for asymmetric phase-transfer catalysis. *Chem. Commun.* **2010,** *46* (40), 7593-7595.

37. Yan, H.; Bin Jang, H.; Lee, J. W.; Kim, H. K.; Lee, S. W.; Yang, J. W.; Song, C. E., A Chiral-Anion Generator: Application to Catalytic Desilylative Kinetic Resolution of Silyl-Protected Secondary Alcohols. *Angew. Chem.-Int. Edit.* **2010,** *49* (47), 8915-8917.
38. Kano, T.; Yamamoto, A.; Song, S.; Maruoka, K., Catalytic asymmetric syntheses of isoxazoline-N-oxides under phase-transfer conditions. *Chem. Commun.* **2011,** *47* (15), 4358-4360.
39. Ma, T.; Fu, X. A.; Kee, C. W.; Zong, L. L.; Pan, Y. H.; Huang, K. W.; Tan, C. H., Pentanidium-Catalyzed Enantioselective Phase-Transfer Conjugate Addition Reactions. *J. Am. Chem. Soc.* **2011,** *133* (9), 2828-2831.
40. Hong, S.; Lee, J.; Kim, M.; Park, Y.; Park, C.; Kim, M. H.; Jew, S. S.; Park, H. G., Highly Enantioselective Synthesis of alpha,alpha-Dialkylmalonates by Phase-Transfer Catalytic Desynnmetrization. *J. Am. Chem. Soc.* **2011,** *133* (13), 4924-4929.
41. Wang, L. J.; Shirakawa, S.; Maruoka, K., Asymmetric Neutral Amination of Nitroolefins Catalyzed by Chiral Bifunctional Ammonium Salts in Water-Rich Biphasic Solvent. *Angew. Chem.-Int. Edit.* **2011,** *50* (23), 5327-5330.
42. Denmark, S. E.; Gould, N. D.; Wolf, L. M., A Systematic Investigation of Quaternary Ammonium Ions as Asymmetric Phase-Transfer Catalysts. Synthesis of Catalyst Libraries and Evaluation of Catalyst Activity. *J. Org. Chem.* **2011,** *76* (11), 4260-4336.
43. Zhu, C. L.; Zhang, F. G.; Meng, W.; Nie, J.; Cahard, D.; Ma, J. A., Enantioselective Base-Free Electrophilic Amination of Benzofuran-2(3H)-ones: Catalysis by Binol-Derived P-Spiro Quaternary Phosphonium Salts. *Angew. Chem.-Int. Edit.* **2011,** *50* (26), 5869-5872.
44. Maity, P.; Lepore, S. D., Catalytic Synthesis of Nonracemic Azaproline Derivatives by Cyclization of beta-Alkynyl Hydrazines under Kinetic Resolution Conditions. *Angew. Chem.-Int. Edit.* **2011,** *50* (36), 8338-8341.
45. Shirakawa, S.; Terao, S. J.; He, R. J.; Maruoka, K., Diastereo- and enantioselective conjugate addition of alpha-substituted nitroacetates to maleimides under base-free neutral phase-transfer conditions. *Chem. Commun.* **2011,** *47* (38), 10557-10559.
46. Shirakawa, S.; Liu, K.; Ito, H.; Le, T. N.; Maruoka, K., Phase-Transfer-Catalyzed Asymmetric Synthesis of 1,1-Disubstituted Tetrahydroisoquinolines. *Adv. Synth. Catal.* **2011,** *353* (14-15), 2614-2618.
47. Park, Y.; Lee, Y. J.; Hong, S.; Kim, M.-h.; Lee, M.; Kim, T.-S.; Lee, J. K.; Jew, S.-s.; Park, H.-g., Highly Enantioselective Phase-Transfer Catalytic alpha-Alkylation of alpha-tert-Butoxycarbonyllactams: Construction of beta-Quaternary Chiral Pyrrolidine and Piperidine Systems. *Adv. Synth. Catal.* **2011,** *353* (18), 3313-3318.
48. Waser, M.; Gratzer, K.; Herchl, R.; Muller, N., Design, synthesis, and application of tartaric acid derived N-spiro quaternary ammonium salts as chiral phase-transfer catalysts. *Org. Biomol. Chem.* **2012,** *10* (2), 251-254.
49. Uraguchi, D.; Ueki, Y.; Ooi, T., Highly stereoselective catalytic conjugate addition of acyl anion equivalent to nitroolefins. *Chem. Sci.* **2012,** *3* (3), 842-845.
50. Shirakawa, S.; Liu, K.; Maruoka, K., Catalytic Asymmetric Synthesis of Axially Chiral o-Iodoanilides by Phase-Transfer Catalyzed Alkylations. *J. Am. Chem. Soc.* **2012,** *134* (2), 916-919.
51. Shirakawa, S.; Ota, K.; Terao, S. J.; Maruoka, K., The direct catalytic asymmetric aldol reaction of alpha-substituted nitroacetates with aqueous formaldehyde under base-free neutral phase-transfer conditions. *Org. Biomol. Chem.* **2012,** *10* (30), 5753-5755.
52. Johnson, K. M.; Rattley, M. S.; Sladojevich, F.; Barber, D. M.; Nunez, M. G.; Goldys, A. M.; Dixon, D. J., A New Family of Cinchona-Derived Bifunctional Asymmetric Phase-Transfer Catalysts: Application to the Enantio- and Diastereoselective Nitro-Mannich Reaction of Amidosulfones. *Org. Lett.* **2012,** *14* (10), 2492-2495.
53. Uraguchi, D.; Kinoshita, N.; Nakashima, D.; Ooi, T., Chiral ionic Bronsted acid-achiral Bronsted base synergistic catalysis for asymmetric sulfa-Michael addition to nitroolefins. *Chem. Sci.* **2012,** *3* (11), 3161-3164.
54. Uraguchi, D.; Yoshioka, K.; Ueki, Y.; Ooi, T., Highly Regio-, Diastereo-, and Enantioselective 1,6-and 1,8-Additions of Azlactones to Di- and Trienyl N-Acylpyrroles. *J. Am. Chem. Soc.* **2012,** *134* (47), 19370-19373.
55. Yang, Y. Y.; Moinodeen, F.; Chin, W.; Ma, T.; Jiang, Z. Y.; Tan, C. H., Pentanidium-Catalyzed Enantioselective alpha-Hydroxylation of Oxindoles Using Molecular Oxygen. *Org. Lett.* **2012,** *14* (18), 4762-4765.
56. Uraguchi, D.; Ueki, Y.; Sugiyama, A.; Ooi, T., Highly stereoselective Michael addition of azlactones to electron-deficient triple bonds under P-spiro chiral iminophosphorane catalysis: importance of protonation pathway. *Chem. Sci.* **2013,** *4* (3), 1308-1311.
57. Phipps, R. J.; Toste, F. D., Chiral Anion Phase-Transfer Catalysis Applied to the Direct Enantioselective Fluorinative Dearomatization of Phenols. *J. Am. Chem. Soc.* **2013,** *135* (4), 1268-1271.
58. Shirakawa, S.; Kasai, A.; Tokuda, T.; Maruoka, K., Efficient approach for the design of effective chiral quaternary phosphonium salts in asymmetric conjugate additions. *Chem. Sci.* **2013,** *4* (5), 2248-2252.
59. Shirakawa, S.; Maruoka, K., Recent Developments in Asymmetric Phase-Transfer Reactions. *Angew. Chem.-Int. Edit.* **2013,** *52* (16), 4312-4348.
60. Ha, M. W.; Lee, H.; Yi, H. Y.; Park, Y.; Kim, S.; Hong, S.; Lee, M.; Kim, M. H.; Kim, T. S.; Park, H. G., Enantioselective Phase-Transfer Catalytic -Benzylation and -Allylation of -tert-Butoxycarbonyllactones. *Adv. Synth. Catal.* **2013,** *355* (4), 637-642.
61. Kano, T.; Hayashi, Y.; Maruoka, K., Construction of a Chiral Quaternary Carbon Center by Catalytic Asymmetric Alkylation of 2-Arylcyclohexanones under Phase-Transfer Conditions. *J. Am. Chem. Soc.* **2013,** *135* (19), 7134-7137.
62. Sheshenev, A. E.; Boltukhina, E. V.; White, A. J. P.; Hii, K. K., Methylene-Bridged Bis(imidazoline)-Derived 2-Oxopyrimidinium Salts as Catalysts for Asymmetric Michael Reactions. *Angew. Chem.-Int. Edit.* **2013,** *52* (27), 6988-6991.
63. Shirakawa, S.; Tokuda, T.; Kasai, A.; Maruoka, K., Design of Chiral Bifunctional Quaternary Phosphonium Bromide Catalysts Possessing an Amide Moiety. *Org. Lett.* **2013,** *15* (13), 3350-3353.
64. Chu, W. D.; Zhang, L. F.; Bao, X.; Zhao, X. H.; Zeng, C.; Du, J. Y.; Zhang, G. B.; Wang, F. X.; Ma, X. Y.; Fan, C. A., Asymmetric Catalytic 1,6-Conjugate Addition/Aromatization of para-Quinone Methides: Enantioselective Introduction of Functionalized Diarylmethine Stereogenic Centers. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9229-9233.
65. Chen, W. C.; Yang, W. G.; Yan, L.; Tan, C. H.; Jiang, Z. Y., Bicyclic guanidinium-catalyzed enantioselective phase-transfer alkylation: direct access to pyrroloindolines and furoindolines. *Chem. Commun.* **2013,** *49* (84), 9854-9856.
66. Wu, X. Y.; Liu, Q.; Liu, Y.; Wang, Q.; Zhang, Y.; Chen, J.; Cao, W. G.; Zhao, G., Amino Acid-Derived Phosphonium Salts-Catalyzed Michael Addition of 3-Substituted Oxindoles. *Adv. Synth. Catal.* **2013,** *355* (13), 2701-2706.
67. Shirakawa, S.; Wu, X. F.; Maruoka, K., Kinetic Resolution of Axially Chiral 2-Amino-1,1 '-Biaryls by Phase-Transfer-Catalyzed N-Allylation. *Angew. Chem.-Int. Edit.* **2013,** *52* (52), 14200-14203.
68. Shirakawa, S.; Koga, K.; Tokuda, T.; Yamamoto, K.; Maruoka, K., Catalytic Asymmetric Synthesis of 3,3 '-Diaryloxindoles as Triarylmethanes with a Chiral All-Carbon Quaternary Center: Phase-Transfer-Catalyzed SNAr Reaction. *Angew. Chem.-Int. Edit.* **2014,** *53* (24), 6220-6223.
69. Wu, X.; Shirakawa, S.; Maruoka, K., Efficient asymmetric synthesis of spiro-2(3H)-furanones via phase-transfer-catalyzed alkynylation. *Org. Biomol. Chem.* **2014,** *12* (29), 5388-5392.

70. Zong, L.; Ban, X.; Kee, C. W.; Tan, C.-H., Catalytic Enantioselective Alkylation of Sulfenate Anions to Chiral Heterocyclic Sulfoxides Using Halogenated Pentanidium Salts. *Angew. Chem.-Int. Edit.* **2014,** *53* (44), 11849-11853.
71. Shirakawa, S.; Yamamoto, K.; Maruoka, K., Phase-Transfer-Catalyzed Asymmetric SNAr Reaction of alpha-Amino Acid Derivatives with Arene Chromium Complexes. *Angew. Chem.-Int. Edit.* **2015,** *54* (3), 838-840.
72. Johnston, C. P.; Kothari, A.; Sergeieva, T.; Okovytyy, S. I.; Jackson, K. E.; Paton, R. S.; Smith, M. D., Catalytic enantioselective synthesis of indanes by a cation-directed 5-endo-trig cyclization. *Nature Chemistry* **2015,** *7* (2), 171-177.
73. Suzuki, H.; Sato, I.; Yamashita, Y.; Kobayashi, S., Catalytic Asymmetric Direct-Type 1,4-Addition Reactions of Simple Amides. *J. Am. Chem. Soc.* **2015,** *137* (13), 4336-4339.
74. Kano, T.; Kobayashi, R.; Maruoka, K., Versatile In Situ Generated N-Boc-Imines: Application to Phase-Transfer-Catalyzed Asymmetric Mannich-Type Reactions. *Angew. Chem.-Int. Edit.* **2015,** *54* (29), 8471-8474.
75. Uraguchi, D.; Yamada, K.; Ooi, T., Highly E-Selective and Enantioselective Michael Addition to Electron-Deficient Internal Alkynes Under Chiral Iminophosphorane Catalysis. *Angew. Chem.-Int. Edit.* **2015,** *54* (34), 9954-9957.
76. Zong, L. L.; Du, S. B.; Chin, K. F.; Wang, C.; Tan, C. H., Enantioselective Synthesis of Quaternary Carbon Stereocenters: Addition of 3-Substituted Oxindoles to Vinyl Sulfone Catalyzed by Pentanidiums. *Angew. Chem.-Int. Edit.* **2015,** *54* (32), 9390-9393.
77. Horwitz, M. A.; Tanaka, N.; Yokosaka, T.; Uraguchi, D.; Johnson, J. S.; Ooi, T., Enantioselective reductive multicomponent coupling reactions between isatins and aldehydes. *Chem. Sci.* **2015,** *6* (11), 6086-6090.
78. Wang, C.; Zong, L. L.; Tan, C. H., Enantioselective Oxidation of Alkenes with Potassium Permanganate Catalyzed by Chiral Dicationic Bisguanidinium. *J. Am. Chem. Soc.* **2015,** *137* (33), 10677-10682.
79. Li, L.; Liu, Y. D.; Peng, Y.; Yu, L.; Wu, X. Y.; Yan, H. L., Kinetic Resolution of beta-Sulfonyl Ketones through Enantioselective beta-Elimination using a Cation-Binding Polyether Catalyst. *Angew. Chem.-Int. Edit.* **2016,** *55* (1), 331-335.
80. Teng, B.; Chen, W. C.; Dong, S.; Kee, C. W.; Gandamana, D. A.; Zong, L. L.; Tan, C. H., Pentanidium- and Bisguanidinium-Catalyzed Enantioselective Alkylations Using Silylamide as Bronsted Probase. *J. Am. Chem. Soc.* **2016,** *138* (31), 9935-9940.
81. Park, S. Y.; Liu, Y. D.; Oh, J. S.; Kweon, Y. K.; Jeong, Y. B.; Duan, M. Y.; Tan, Y.; Lee, J. W.; Yan, H. L.; Song, C. E., Asymmetric Aminalization via Cation-Binding Catalysis. *Chemistry-a European Journal* **2018,** *24* (5), 1020-1025.
82. Pawliczek, M.; Hashimoto, T.; Maruoka, K., Alkylative kinetic resolution of vicinal diols under phase-transfer conditions: a chiral ammonium borinate catalysis. *Chem. Sci.* **2018,** *9* (5), 1231-1235.
83. Cao, W. D.; Tan, D.; Lee, R.; Tan, C. H., Enantioselective 1,2-Anionotropic Rearrangement of Acylsilane through a Bisguanidinium Silicate Ion Pair. *J. Am. Chem. Soc.* **2018,** *140* (5), 1952-1955.
84. Pupo, G.; Ibba, F.; Ascough, D. M. H.; Vicini, A. C.; Ricci, P.; Christensen, K. E.; Pfeifer, L.; Morphy, J. R.; Brown, J. M.; Paton, R. S.; Gouverneur, V., Asymmetric nucleophilic fluorination under hydrogen bonding phase-transfer catalysis. *Science* **2018,** *360* (6389), 638-+.
85. Liu, Y. D.; Liu, S.; Li, D. M.; Zhang, N.; Peng, L.; Ao, J.; Song, C. E.; Lan, Y.; Yan, H. L., Kinetic Resolution of Allylic Alcohol with Chiral BINOL-Based Alkoxides: A Combination of Experimental and Theoretical Studies. *J. Am. Chem. Soc.* **2019,** *141* (2), 1150-1159.
86. Pupo, G.; Vicini, A. C.; Ascough, D. M. H.; Ibba, F.; Christensen, K. E.; Thompson, A. L.; Brown, J. M.; Paton, R. S.; Gouverneur, V., Hydrogen Bonding Phase-Transfer Catalysis with Potassium Fluoride: Enantioselective Synthesis of beta-Fluoroamines. *J. Am. Chem. Soc.* **2019,** *141* (7), 2878-2883.
87. Inukai, T.; Kano, T.; Maruoka, K., Construction of Quaternary Carbon Center by Catalytic Asymmetric Alkylation of 3-Arylpiperidin-2-ones Under Phase-Transfer Conditions. *Angewandte Chemie International Edition* **2020,** *59* (6), 2211-2214.
88. Uraguchi, D.; Ueoka, F.; Tanaka, N.; Kizu, T.; Takahashi, W.; Ooi, T., A Structurally Robust Chiral Borate Ion: Molecular Design, Synthesis, and Asymmetric Catalysis. *Angewandte Chemie International Edition* **2020,** *59* (28), 11456-11461.
89. Roagna, G.; Ascough, D. M. H.; Ibba, F.; Vicini, A. C.; Fontana, A.; Christensen, K. E.; Peschiulli, A.; Oehlrich, D.; Misale, A.; Trabanco, A. A.; Paton, R. S.; Pupo, G.; Gouverneur, V., Hydrogen Bonding Phase-Transfer Catalysis with Ionic Reactants: Enantioselective Synthesis of γ-Fluoroamines. *J. Am. Chem. Soc.* **2020,** *142* (33), 14045-14051.
90. Ohmatsu, K.; Morita, Y.; Kiyokawa, M.; Ooi, T., Catalytic Asymmetric Cyanoalkylation of Electron-Deficient Olefins with Potassium Cyanide and Alkyl Halides. *J. Am. Chem. Soc.* **2021,** *143* (29), 11218-11224.
91. Yang, J.-S.; Lu, K.; Li, C.-X.; Zhao, Z.-H.; Zhang, X.-M.; Zhang, F.-M.; Tu, Y.-Q., Chiral 1,2,3-Triazolium Salt Catalyzed Asymmetric Mono- and Dialkylation of 2,5-Diketopiperazines with the Construction of Tetrasubstituted Carbon Centers. *Angewandte Chemie International Edition* **2022,** *61* (9), e202114129.
92. Zhang, X.; Ang, E. C. X.; Yang, Z.; Kee, C. W.; Tan, C.-H., Synthesis of chiral sulfinate esters by asymmetric condensation. *Nature* **2022,** *604* (7905), 298-303.
93. Pupo, G.; Gouverneur, V., Hydrogen Bonding Phase-Transfer Catalysis with Alkali Metal Fluorides and Beyond. *J. Am. Chem. Soc.* **2022,** *144* (12), 5200-5213.
94. Odagi, M.; Mori, I.; Sugimoto, K.; Nagasawa, K., Enantioselective Oxidative Enolate Coupling of Oxindoles Catalyzed by Chiral Guanidinium Hypoiodite. *ACS Catalysis* **2023,** *13* (4), 2295-2301.
95. Pan, G.; Pu, M.; Wang, H.; Ying, M.; Li, Y.; Dong, S.; Feng, X.; Liu, X., Catalytic Enantioselective Nucleophilic Addition to Arynes by a New Quaternary Guanidinium Salt-Based Phase-Transfer Catalyst. *J. Am. Chem. Soc.* **2023,** *145* (48), 26318-26327..

.

3.4 Chiral Ylides Generation

1. Aggarwal, V. K.; Alonso, E.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Porcelloni, M.; Studley, J. R., Catalytic asymmetric synthesis of epoxides from aldehydes using sulfur ylides with in situ generation of diazocompounds. *Angew. Chem.-Int. Edit.* **2001,** *40* (8), 1430-+.

2. Longmire, J. M.; Wang, B.; Zhang, X. M., Highly enantioselective Ag(I)-catalyzed 3+2 cycloaddition of azomethine ylides. *J. Am. Chem. Soc.* **2002,** *124* (45), 13400-13401.

3. Gothelf, A. S.; Gothelf, K. V.; Hazell, R. G.; Jorgensen, K. A., Catalytic asymmetric 1,3-dipolar cycloaddition reactions of azomethine ylides - A simple approach to optically active highly functionalized proline derivatives. *Angew. Chem.-Int. Edit.* **2002,** *41* (22), 4236-4238.

4. Aggarwal, V. K.; Bae, I.; Lee, H. Y.; Richardson, J.; Williams, D. T., Sulfur-ylide-mediated synthesis of functionalized and trisubstituted epoxides with high enantioselectivity; Application to the synthesis of CDP-840. *Angew. Chem.-Int. Edit.* **2003,** *42* (28), 3274-3278.

5. Chen, C.; Li, X. D.; Schreiber, S. L., Catalytic asymmetric 3+2 cycloaddition of azomethine ylides. Development of a versatile stepwise, three-component reaction for diversity-oriented synthesis. *J. Am. Chem. Soc.* **2003,** *125* (34), 10174-10175.

6. Papageorgiou, C. D.; de Dios, M. A. C.; Ley, S. V.; Gaunt, M. J., Enantioselective organocatalytic cyclopropanation via ammonium ylides. *Angew. Chem.-Int. Edit.* **2004,** *43* (35), 4641-4644.

7. Alemparte, C.; Blay, G.; Jorgensen, K. A., A convenient procedure for the catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides and alkenes. *Org. Lett.* **2005,** *7* (21), 4569-4572.

8. Cabrera, S.; Arrayas, R. G.; Carretero, J. C., Highly enantioselective copper(I)-fesulphos-catalyzed 1,3-dipolar cycloaddition of azomethine ylides. *J. Am. Chem. Soc.* **2005,** *127* (47), 16394-16395.

9. Najera, C.; Sansano, J. M., Catalytic enantioselective 1,3-dipolar cycloaddition reaction of azomethine ylides and alkenes: The direct strategy to prepare enantioenriched highly substituted proline derivatives. *Angew. Chem.-Int. Edit.* **2005,** *44* (39), 6272-6276.

10. Huang, J.; Hsung, R. P., Chiral Lewis acid-catalyzed highly enantioselective 4+3 cycloaddition reactions of nitrogen-stabilized oxyallyl cations derived from allenamides. *J. Am. Chem. Soc.* **2005,** *127* (1), 50-51.

11. Yan, X. X.; Peng, Q.; Zhang, Y.; Zhang, K.; Hong, W.; Hou, X. L.; Wu, Y. D., A highly enantio- and diastereoselective Cu-catalyzed 1,3-dipolar cycloaddition of azomethine ylides with nitroalkenes. *Angew. Chem.-Int. Edit.* **2006,** *45* (12), 1979-1983.

12. Johansson, C. C. C.; Bremeyer, N.; Ley, S. V.; Owen, D. R.; Smith, S. C.; Gaunt, M. J., Enantioselective catalytic intramolecular cyclopropanation using modified cinchona alkaloid organocatalysts. *Angew. Chem.-Int. Edit.* **2006,** *45* (36), 6024-6028.

13. Trost, B. M.; Stambuli, J. P.; Silverman, S. M.; Schworer, U., Palladium-catalyzed asymmetric [3+2] trimethylenemethane cycloaddition reactions. *J. Am. Chem. Soc.* **2006,** *128* (41), 13328-13329.

14. Zeng, W.; Chen, G. Y.; Zhou, Y. G.; Li, Y. X., Hydrogen-bonding directed reversal of enantioselectivity. *J. Am. Chem. Soc.* **2007,** *129* (4), 750-751.

15. Cowen, B. J.; Miller, S. J., Enantioselective [3+2]-cycloadditions catalyzed by a protected, multifunctional phosphine-containing alpha-amino acid. *J. Am. Chem. Soc.* **2007,** *129* (36), 10988-+.

16. Trost, B. M.; Cramer, N.; Silverman, S. M., Enantioselective construction of spirocyclic oxindolic Cyclopentanes by palladium-catalyzed trimethylenemethane-[3+2]-cycloaddition. *J. Am. Chem. Soc.* **2007,** *129* (41), 12396-+.

17. Trost, B. M.; Silverman, S. M.; Stambuli, J. P., Palladium-catalyzed asymmetric [3+2] cycloaddition of trimethylenemethane with Imines. *J. Am. Chem. Soc.* **2007,** *129* (41), 12398-+.

18. Shintani, R.; Park, S.; Duan, W. L.; Hayashi, T., Palladium-catalyzed asymmetric [3+3] cycloaddition of trimethylenemethane derivatives with nitrones. *Angew. Chem.-Int. Edit.* **2007,** *46* (31), 5901-5903.

19. Shintani, R.; Murakami, M.; Hayashi, T., gamma-methylidene-delta-valerolactones as a coupling partner for cycloaddition: Palladium-catalyzed [4+3] cycloaddition with nitrones. *J. Am. Chem. Soc.* **2007,** *129* (41), 12356-+.

20. Melhado, A. D.; Luparia, M.; Toste, F. D., Au(I)-catalyzed enantioselective 1,3-dipolar cycloadditions of Munchnones with electron-deficient Alkenes. *J. Am. Chem. Soc.* **2007,** *129* (42), 12638-+.

21. Le Marquand, P.; Tam, W., Enantioselective palladium-catalyzed trimethylenemethane [3+2] cycloadditions. *Angew. Chem.-Int. Edit.* **2008,** *47* (16), 2926-2928.

22. Chen, X. H.; Zhang, W. Q.; Gong, L. Z., Asymmetric organocatalytic three-component 1,3-dipolar cycloaddition: Control of stereochemistry via a chiral bronsted acid activated dipole. *J. Am. Chem. Soc.* **2008,** *130* (17), 5652-+.

23. Vesely, J.; Zhao, G. L.; Bartoszewicz, A.; Cordova, A., Organocatalytic asymmetric nitrocyclopropanation of alpha,beta-unsaturated aldehydes. *Tetrahedron Lett.* **2008,** *49* (27), 4209-4212.

24. Lopez-Perez, A.; Adrio, J.; Carretero, J. C., Bis-sulfonyl ethylene as masked acetylene equivalent in catalytic asymmetric [3+2] cycloaddition of azomethine ylides. *J. Am. Chem. Soc.* **2008,** *130* (31), 10084-+.

25. Tsubogo, T.; Saito, S.; Seki, K.; Yamashita, Y.; Kobayashi, S., Development of catalytic asymmetric 1,4-addition and [3+2] cycloaddition reactions using chiral calcium complexes. *J. Am. Chem. Soc.* **2008,** *130* (40), 13321-13332.

26. Voituriez, A.; Panossian, A.; Fleury-Bregeot, N.; Retailleau, P.; Marinetti, A., 2-Phospha[3]ferrocenophanes with Planar Chirality: Synthesis and Use in Enantioselective Organocatalytic [3+2] Cyclizations. *J. Am. Chem. Soc.* **2008,** *130* (43), 14030-+.

27. Trost, B. M.; McDougall, P. J.; Hartmann, O.; Wathen, P. T., Asymmetric Synthesis of Bicyclo[4.3.1]decadienes and Bicyclo[3.3.2]decadienes via [6+3] Trimethylenemethane Cycloaddition with Tropones. *J. Am. Chem. Soc.* **2008,** *130* (45), 14960-+.

28. Shintani, R.; Park, S.; Shirozu, F.; Murakami, M.; Hayashi, T., Palladium-Catalyzed Asymmetric Decarboxylative Lactamization of gamma-Methylidene-delta-valerolactones with Isocyanates: Conversion of Racemic Lactones to Enantioenriched Lactams. *J. Am. Chem. Soc.* **2008,** *130* (48), 16174-+.

29. Liu, W. J.; Chen, X. H.; Gong, L. Z., Direct Assembly of Aldehydes, Amino Esters, and Anilines into Chiral Imidazolidines via Bronsted Acid Catalyzed Asymmetric 1,3-Dipolar Cycloadditions. *Org. Lett.* **2008,** *10* (23), 5357-5360.

30. Wang, C. J.; Liang, G.; Xue, Z. Y.; Gao, F., Highly Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylides Catalyzed by Copper(I)/TF-BiphamPhos Complexes. *J. Am. Chem. Soc.* **2008,** *130* (51), 17250-+.

31. Lopez-Perez, A.; Adrio, J.; Carretero, A. C., The Phenylsulfonyl Group as a Temporal Regiochemical Controller in the Catalytic Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides. *Angew. Chem.-Int. Edit.* **2009,** *48* (2), 340-343.

32. Companyo, X.; Alba, A. N.; Cardenas, F.; Moyano, A.; Rios, R., Asymmetric Organocatalytic Cyclopropanation - Highly Stereocontrolled Synthesis of Chiral Cyclopropanes with Quaternary Stereocenters. *Eur. J. Org. Chem.* **2009,** (18), 3075-3080.

33. Kim, H. Y.; Shih, H. J.; Knabe, W. E.; Oh, K., Reversal of Enantioselectivity between the Copper(I)- and Silver(I)-Catalyzed 1,3-Dipolar Cycloaddition Reactions Using a Brucine-Derived Amino Alcohol Ligand. *Angew. Chem.-Int. Edit.* **2009,** *48* (40), 7420-7423.

34. Chen, X. H.; Wei, Q.; Luo, S. W.; Xiao, H.; Gong, L. Z., Organocatalytic Synthesis of Spiro[pyrrolidin-3,3 '-oxindoles] with High Enantiopurity and Structural Diversity. *J. Am. Chem. Soc.* **2009,** *131* (38), 13819-13825.

35. Lee, K. S.; Zhugralin, A. R.; Hoveyda, A. H., Efficient C-B Bond Formation Promoted by N-Heterocyclic Carbenes: Synthesis of Tertiary and Quaternary B-Substituted Carbons through Metal-Free Catalytic Boron Conjugate Additions to Cyclic and Acyclic alpha,beta-Unsaturated Carbonyls. *J. Am. Chem. Soc.* **2009,** *131* (21), 7253-+.

36. Yamashita, Y.; Guo, X. X.; Takashita, R.; Kobayashi, S., Chiral Silver Amide-Catalyzed Enantioselective 3+2 Cycloaddition of alpha-Aminophosphonates with Olefins. *J. Am. Chem. Soc.* **2010,** *132* (10), 3262-+.

37. Hashimoto, T.; Maeda, Y.; Omote, M.; Nakatsu, H.; Maruoka, K., Catalytic Enantioselective 1,3-Dipolar Cycloaddition of C,N-Cyclic Azomethine Imines with alpha,beta-Unsaturated Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (12), 4076-+.

38. Arai, T.; Yokoyama, N.; Mishiro, A.; Sato, H., Catalytic Asymmetric exo'-Selective 3+2 Cycloaddition of Iminoesters with Nitroalkenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (43), 7895-7898.

39. Xiao, H.; Chai, Z.; Zheng, C. W.; Yang, Y. Q.; Liu, W.; Zhang, J. K.; Zhao, G., Asymmetric 3+2 Cycloadditions of Allenoates and Dual Activated Olefins Catalyzed by Simple Bifunctional N-Acyl Aminophosphines. *Angew. Chem.-Int. Edit.* **2010,** *49* (26), 4467-4470.

40. Riches, S. L.; Saha, C.; Filgueira, N. F.; Grange, E.; McGarrigle, E. M.; Aggarwal, V. K., On the Mechanism of Ylide-Mediated Cyclopropanations: Evidence for a Proton-Transfer Step and Its Effect on Stereoselectivity. *J. Am. Chem. Soc.* **2010,** *132* (22), 7626-7630.

41. Trost, B. M.; Silverman, S. M., Enantioselective Construction of Highly Substituted Pyrrolidines by Palladium-Catalyzed Asymmetric 3+2 Cycloaddition of Trimethylenemethane with Ketimines. *J. Am. Chem. Soc.* **2010,** *132* (24), 8238-+.

42. Bonet, A.; Gulyas, H.; Fernandez, E., Metal-Free Catalytic Boration at the beta-Position of alpha,beta-Unsaturated Compounds: A Challenging Asymmetric Induction. *Angew. Chem.-Int. Edit.* **2010,** *49* (30), 5130-5134.

43. Ishida, K.; Kusama, H.; Iwasawa, N., Enantioselective Preparation of 8-Oxabicyclo 3.2.1 octane Derivatives via Asymmetric 3+2 -Cycloaddition of Platinum-Containing Carbonyl Ylides with Vinyl Ethers. *J. Am. Chem. Soc.* **2010,** *132* (26), 8842-+.

44. Wang, Q. G.; Zhu, S. F.; Ye, L. W.; Zhou, C. Y.; Sun, X. L.; Tang, Y.; Zhou, Q. L., Catalytic Asymmetric Intramolecular Cascade Reaction for the Construction of Functionalized Benzobicyclo 4.3.0 Skeletons. Remote Control of Enantioselectivity. *Adv. Synth. Catal.* **2010,** *352* (11-12), 1914-1919.

45. Sampath, M.; Loh, T. P., Highly enantio-, regio- and diastereo-selective one-pot 2+3 -cycloaddition reaction via isomerization of 3-butynoates to allenoates. *Chem. Sci.* **2010,** *1* (6), 739-742.

46. Arai, T.; Yokoyama, N.; Mishiro, A.; Sato, H., Catalytic Asymmetric exo'-Selective 3+2 Cycloaddition of Iminoesters with Nitroalkenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (43), 7895-7898.

47. Han, X. Y.; Wang, Y. Q.; Zhong, F. R.; Lu, Y. X., Enantioselective 3+2 Cycloaddition of Allenes to Acrylates Catalyzed by Dipeptide-Derived Phosphines: Facile Creation of Functionalized Cyclopentenes Containing Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2011,** *133* (6), 1726-1729.

48. Liu, T. L.; He, Z. L.; Tao, H. Y.; Cai, Y. P.; Wang, C. J., Stereoselective construction of a 5-aza-spiro 2,4 heptane motif via catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides and ethyl cyclopropylidene acetate. *Chem. Commun.* **2011,** *47* (9), 2616-2618.

49. Melhado, A. D.; Amarante, G. W.; Wang, Z. J.; Luparia, M.; Toste, F. D., Gold(I)-Catalyzed Diastereo- and Enantioselective 1,3-Dipolar Cycloaddition and Mannich Reactions of Azlactones. *J. Am. Chem. Soc.* **2011,** *133* (10), 3517-3527.

50. Tan, B.; Candeias, N. R.; Barbas, C. F., Core-Structure-Motivated Design of a Phosphine-Catalyzed 3+2 Cycloaddition Reaction: Enantioselective Syntheses of Spirocyclopenteneoxindoles. *J. Am. Chem. Soc.* **2011,** *133* (13), 4672-4675.

51. Yamashita, Y.; Imaizumi, T.; Kobayashi, S., Chiral Silver Amide Catalyst for the 3+2 Cycloaddition of alpha-Amino Esters to Olefins. *Angew. Chem.-Int. Edit.* **2011,** *50* (21), 4893-4896.

52. Wang, M.; Wang, Z.; Shi, Y. H.; Shi, X. X.; Fossey, J. S.; Deng, W. P., An exo- and Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylides with Alkylidene Malonates Catalyzed by a N,O-Ligand/Cu(OAc)(2)-Derived Chiral Complex. *Angew. Chem.-Int. Edit.* **2011,** *50* (21), 4897-4900.

53. Trost, B. M.; Bringley, D. A.; Silverman, S. M., Asymmetric Synthesis of Methylenetetrahydrofurans by Palladium-Catalyzed 3+2 Cycloaddition of Trimethylenemethane with Aldehydes - A Novel Ligand Design. *J. Am. Chem. Soc.* **2011,** *133* (20), 7664-7667.

54. Fujiwara, Y.; Fu, G. C., Application of a New Chiral Phosphepine to the Catalytic Asymmetric Synthesis of Highly Functionalized Cyclopentenes That Bear an Array of Heteroatom-Substituted Quaternary Stereocenters. *J. Am. Chem. Soc.* **2011,** *133* (31), 12293-12297.

55. Peng, J.; Huang, X.; Jiang, L.; Cui, H. L.; Chen, Y. C., Tertiary Amine-Catalyzed Chemoselective and Asymmetric 3+2 Annulation of Morita-Baylis-Hillman Carbonates of Isatins with Propargyl Sulfones. *Org. Lett.* **2011,** *13* (17), 4584-4587.

56. Trost, B. M.; Silverman, S. M.; Stambuli, J. P., Development of an Asymmetric Trimethylenemethane Cycloaddition Reaction: Application in the Enantioselective Synthesis of Highly Substituted Carbocycles. *J. Am. Chem. Soc.* **2011,** *133* (48), 19483-19497.

57. Shimada, N.; Oohara, T.; Krishnamurthi, J.; Nambu, H.; Hashimoto, S., Catalytic Enantioselective Intermolecular Cycloaddition of Diazodiketoester-Derived Carbonyl Ylides with Indoles Using Chiral Dirhodium(II) Carboxylates. *Org. Lett.* **2011,** *13* (23), 6284-6287.

58. Steurer, M.; Jensen, K. L.; Worgull, D.; Jorgensen, K. A., Enantioselective One-Pot Synthesis of alpha-Amino Esters by a Phosphine-Catalyzed 3+2 -Cycloaddition Reaction. *Chemistry-a European Journal* **2012,** *18* (1), 76-79.

59. Trost, B. M.; Bringley, D. A.; Seng, P. S., Enantioselective Palladium-Catalyzed 3+2 Cycloadditions of Trimethylenemethane with Nitroalkenes. *Org. Lett.* **2012,** *14* (1), 234-237.

60. Trost, B. M.; Silverman, S. M., Enantioselective Construction of Pyrrolidines by Palladium-Catalyzed Asymmetric 3+2 Cycloaddition of Trimethylenemethane with Imines. *J. Am. Chem. Soc.* **2012,** *134* (10), 4941-4954.

61. Deng, H. P.; Wei, Y.; Shi, M., Enatioselective Synthesis of Highly Functionalized Trifluoromethyl-Bearing Cyclopentenes: Asymmetric 3+2 Annulation of Morita-Baylis-Hillman Carbonates with Trifluoroethylidenemalonates Catalyzed by Multifunctional Thiourea-Phosphines. *Adv. Synth. Catal.* **2012,** *354* (5), 783-789.

62. Potowski, M.; Schurmann, M.; Preut, H.; Antonchick, A. P.; Waldmann, H., Programmable enantioselective one-pot synthesis of molecules with eight stereocenters. *Nature Chemical Biology* **2012,** *8* (5), 428-430.

63. Piccinini, A.; Kavanagh, S. A.; Connon, S. J., Highly enantioselective ylide-mediated synthesis of terminal epoxides. *Chem. Commun.* **2012,** *48* (63), 7814-7816.

64. Trost, B. M.; Lam, T. M., Development of Diamidophosphite Ligands and Their Application to the Palladlium-Catalyzed Vinyl-Substituted Trimethylenemethane Asymmetric 3+2 Cycloaddition. *J. Am. Chem. Soc.* **2012,** *134* (28), 11319-11321.

65. Hernandez-Toribio, J.; Padilla, S.; Adrio, J.; Carretero, J. C., Catalytic Asymmetric Synthesis of a-Quaternary Proline Derivatives by 1,3-Dipolar Cycloaddition of a-Silylimines. *Angew. Chem.-Int. Edit.* **2012,** *51* (35), 8854-8858.

66. Potowski, M.; Bauer, J. O.; Strohmann, C.; Antonchick, A. P.; Waldmann, H., Highly Enantioselective Catalytic 6+3 Cycloadditions of Azomethine Ylides. *Angew. Chem.-Int. Edit.* **2012,** *51* (38), 9512-9516.

67. Cano, I.; Gomez-Bengoa, E.; Landa, A.; Maestro, M.; Mielgo, A.; Olaizola, I.; Oiarbide, M.; Palomo, C., N-(Diazoacetyl)oxazolidin-2-thiones as Sulfur-Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (43), 10856-10860.

68. Lim, A. D.; Codelli, J. A.; Reisman, S. E., Catalytic asymmetric synthesis of highly substituted pyrrolizidines. *Chem. Sci.* **2013,** *4* (2), 650-654.

69. Lundgren, R. J.; Wilsily, A.; Marion, N.; Ma, C.; Chung, Y. K.; Fu, G. C., Catalytic Asymmetric CN Bond Formation: Phosphine-Catalyzed Intra- and Intermolecular gamma-Addition of Nitrogen Nucleophiles to Allenoates and Alkynoates. *Angew. Chem.-Int. Edit.* **2013,** *52* (9), 2525-2528.

70. He, Z. L.; Teng, H. L.; Wang, C. J., Fulvenes as Effective Dipolarophiles in Copper(I)-Catalyzed 6+3 Cycloaddition of Azomethine Ylides: Asymmetric Construction of Piperidine Derivatives. *Angew. Chem.-Int. Edit.* **2013,** *52* (10), 2934-2938.

71. Trost, B. M.; Lam, T. M.; Herbage, M. A., Regio- and Enantioselective Synthesis of Pyrrolidines Bearing a Quaternary Center by Palladium-Catalyzed Asymmetric 3+2 Cycloaddition of Trimethylenemethanes. *J. Am. Chem. Soc.* **2013,** *135* (7), 2459-2461.

72. Trost, B. M.; Bringley, D. A., Enantioselective Synthesis of 2,2-Disubstituted Tetrahydrofurans: Palladium-Catalyzed 3+2 Cycloadditions of Trimethylenemethane with Ketones. *Angew. Chem.-Int. Edit.* **2013,** *52* (16), 4466-4469.

73. Wang, Z.; Luo, S.; Zhang, S. D.; Yang, W. L.; Liu, Y. Z.; Li, H. L.; Luo, X. Y.; Deng, W. P., Catalytic Asymmetric Construction of Quaternary -Amino Acid Containing Pyrrolidines through 1,3-Dipolar Cycloaddition of Azomethine Ylides to -Aminoacrylates. *Chemistry-a European Journal* **2013,** *19* (21), 6739-6745.

74. Trost, B. M.; Maruniak, A., Enantioselective Construction of Highly Substituted Vinylidenecylopentanes by Palladium-Catalyzed Asymmetric 3+2 Cycloaddition Reaction. *Angew. Chem.-Int. Edit.* **2013,** *52* (24), 6262-6264.

75. Hashimoto, T.; Takiguchi, Y.; Maruoka, K., Catalytic Asymmetric Three-Component 1,3-Dipolar Cycloaddition of Aldehydes, Hydrazides, and Alkynes. *J. Am. Chem. Soc.* **2013,** *135* (31), 11473-11476.

76. Xu, X. F.; Zavalij, P. J.; Doyle, M. P., A donor-acceptor cyclopropene as a dipole source for a silver(I) catalyzed asymmetric catalytic 3+3 -cycloaddition with nitrones. *Chem. Commun.* **2013,** *49* (87), 10287-10289.

77. Narayan, R.; Bauer, J. O.; Strohmann, C.; Antonchick, A. P.; Waldmann, H., Catalytic Enantioselective Synthesis of Functionalized Tropanes Reveals Novel Inhibitors of Hedgehog Signaling. *Angew. Chem.-Int. Edit.* **2013,** *52* (49), 12892-12896.

78. Trost, B. M.; Bringley, D. A.; Zhang, T.; Cramer, N., Rapid Access to Spirocyclic Oxindole Alkaloids: Application of the Asymmetric Palladium-Catalyzed 3+2 Trimethylenemethane Cycloaddition. *J. Am. Chem. Soc.* **2013,** *135* (44), 16720-16735.

79. Liu, Y. L.; Wang, X.; Zhao, Y. L.; Zhu, F.; Zeng, X. P.; Chen, L.; Wang, C. H.; Zhao, X. L.; Zhou, J., One-Pot Tandem Approach to Spirocyclic Oxindoles Featuring Adjacent Spiro-Stereocenters. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13735-13739.

80. Liu, H. L.; Wu, Y.; Zhao, Y.; Li, Z.; Zhang, L.; Yang, W. J.; Jiang, H.; Jing, C. L.; Yu, H.; Wang, B.; Xiao, Y. M.; Guo, H. C., Metal-Catalyzed 6+3 Cycloaddition of Tropone with Azomethine Ylides: A Practical Access to Piperidine-Fused Bicyclic Heterocycles. *J. Am. Chem. Soc.* **2014,** *136* (6), 2625-2629.

81. Ohmatsu, K.; Imagawa, N.; Ooi, T., Ligand-enabled multiple absolute stereocontrol in metal-catalysed cycloaddition for construction of contiguous all-carbon quaternary stereocentres. *Nature Chemistry* **2014,** *6* (1), 47-51.

82. Teng, H.-L.; Yao, L.; Wang, C.-J., Cu(I)-Catalyzed Regio- and Stereoselective 6+3 Cycloaddition of Azomethine Ylides with Tropone: An Efficient Asymmetric Access to Bridged Azabicyclo 4.3.1 decadienes. *J. Am. Chem. Soc.* **2014,** *136* (10), 4075-4080.

83. West, T. H.; Daniels, D. S. B.; Slawin, A. M. Z.; Smith, A. D., An Isothiourea-Catalyzed Asymmetric 2,3 -Rearrangement of Allylic Ammonium Ylides. *J. Am. Chem. Soc.* **2014,** *136* (12), 4476-4479.

84. Han, X. Y.; Yao, W. J.; Wang, T. L.; Tan, Y. R.; Yan, Z. Y.; Kwiatkowski, J.; Lu, Y. X., Asymmetric Synthesis of Spiropyrazolones through Phosphine-Catalyzed 4+1 Annulation. *Angew. Chem.-Int. Edit.* **2014,** *53* (22), 5643-5647.

85. Shao, P.-L.; Liao, J.-Y.; Ho, Y. A.; Zhao, Y., Highly Diastereo-and Enantioselective Silver-Catalyzed Double 3+2 Cyclization of a-Imino Esters with Isocyanoacetate**. *Angew. Chem.-Int. Edit.* **2014,** *53* (21), 5435-5439.

86. Trost, B. M.; Ehmke, V., An Approach for Rapid Increase in Molecular Complexity: Atom Economic Routes to Fused Polycyclic Ring Systems. *Org. Lett.* **2014,** *16* (10), 2708-2711.

87. Trost, B. M.; Ehmke, V.; O'Keefe, B. M.; Bringley, D. A., Palladium-Catalyzed Dearomative Trimethylenemethane Cycloaddition Reactions. *J. Am. Chem. Soc.* **2014,** *136* (23), 8213-8216.

88. Li, Q. H.; Wei, L.; Wang, C. J., Catalytic Asymmetric 1,3-Dipolar 3+6 Cycloaddition of Azomethine Ylides with 2-Acyl Cycloheptatrienes: Efficient Construction of Bridged Heterocycles Bearing Piperidine Moiety. *J. Am. Chem. Soc.* **2014,** *136* (24), 8685-8692.

89. Awata, A.; Arai, T., PyBidine/Copper Catalyst: Asymmetric exo '-Selective 3+2 Cycloaddition using Imino Ester and Electrophilic Indole. *Angew. Chem.-Int. Edit.* **2014,** *53* (39), 10462-10465.

90. Henry, C. E.; Xu, Q. H.; Fan, Y. C.; Martin, T. J.; Belding, L.; Dudding, T.; Kwon, O., Hydroxyproline-Derived Pseudoenantiomeric 2.2.1 Bicyclic Phosphines: Asymmetric Synthesis of (+)- and (-)-Pyrrolines. *J. Am. Chem. Soc.* **2014,** *136* (34), 11890-11893.

91. Ziegler, D. T.; Riesgo, L.; Ikeda, T.; Fujiwara, Y.; Fu, G. C., Biphenyl-Derived Phosphepines as Chiral Nucleophilic Catalysts: Enantioselective 4+1 Annulations To Form Functionalized Cyclopentenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13183-13187.

92. Yang, Q.-L.; Xie, M.-S.; Xia, C.; Sun, H.-L.; Zhang, D.-J.; Huang, K.-X.; Guo, Z.; Qu, G.-R.; Guo, H.-M., A rapid and divergent access to chiral azacyclic nucleoside analogues via highly enantioselective 1,3-dipolar cycloaddition of beta-nucleobase substituted acrylates. *Chem. Commun.* **2014,** *50* (94), 14809-14812.

93. Zhang, X.-N.; Chen, G.-Q.; Tang, X.-Y.; Wei, Y.; Shi, M., Phosphine-Catalyzed Annulations of 4,4-Dicyano-2-Methylenebut-3-enoates with Maleimides and Maleic Anhydride. *Angew. Chem.-Int. Edit.* **2014,** *53* (40), 10768-10773.

94. Vidadala, S. R.; Golz, C.; Strohmann, C.; Daniliuc, C.-G.; Waldmann, H., Highly Enantioselective Intramolecular 1,3-Dipolar Cycloaddition: A Route to Piperidino-Pyrrolizidines. *Angew. Chem.-Int. Edit.* **2015,** *54* (2), 651-655.

95. Arai, T.; Ogawa, H.; Awata, A.; Sato, M.; Watabe, M.; Yamanaka, M., PyBidine-Cu(OTf)(2)-Catalyzed Asymmetric 3+2 Cycloaddition with Imino Esters: Harmony of Cu-Lewis Acid and Imidazolidine-NH Hydrogen Bonding in Concerto Catalysis. *Angew. Chem.-Int. Edit.* **2015,** *54* (5), 1595-1599.

96. Yao, W.; Dou, X.; Lu, Y., Highly Enantioselective Synthesis of 3,4-Dihydropyrans through a Phosphine-Catalyzed 4+2 Annulation of Allenones and beta,gamma-Unsaturated alpha-Keto Esters. *J. Am. Chem. Soc.* **2015,** *137* (1), 54-57.

97. Potowski, M.; Merten, C.; Antonchick, A. P.; Waldmann, H., Catalytic Aerobic Oxidation and Tandem Enantioselective Cycloaddition in Cascade Multicomponent Synthesis. *Chemistry-a European Journal* **2015,** *21* (13), 4913-4917.

98. Gicquel, M.; Zhang, Y.; Aillard, P.; Retailleau, P.; Voituriez, A.; Marinetti, A., Phosphahelicenes in Asymmetric Organocatalysis: 3+2 Cyclizations of gamma-Substituted Allenes and Electron- Poor Olefins. *Angew. Chem.-Int. Edit.* **2015,** *54* (18), 5470-5473.

99. Bai, X.-F.; Song, T.; Xu, Z.; Xia, C.-G.; Huang, W.-S.; Xu, L.-W., Aromatic Amide-Derived Non-Biaryl Atropisomers as Highly Efficient Ligands in Silver-Catalyzed Asymmetric Cycloaddition Reactions. *Angew. Chem.-Int. Edit.* **2015,** *54* (17), 5255-5259.

100. Kramer, S.; Fu, G. C., Use of a New Spirophosphine To Achieve Catalytic Enantioselective 4+1 Annulations of Amines with Allenes To Generate Dihydropyrroles. *J. Am. Chem. Soc.* **2015,** *137* (11), 3803-3806.

101. Lee, S. Y.; Fujiwara, Y.; Nishiguchi, A.; Kalek, M.; Fu, G. C., Phosphine-Catalyzed Enantioselective Intramolecular 3+2 Annulations To Generate Fused Ring Systems. *J. Am. Chem. Soc.* **2015,** *137* (13), 4587-4591.

102. Murarka, S.; Jia, Z. J.; Merten, C.; Daniliuc, C. G.; Antonchick, A. P.; Waldmann, H., Rhodium(II)-Catalyzed Enantioselective Synthesis of Troponoids. *Angew. Chem.-Int. Edit.* **2015,** *54* (26), 7653-7656.

103. Kalek, M.; Fu, G. C., Phosphine-Catalyzed Doubly Stereoconvergent gamma-Additions of Racemic Heterocycles to Racemic Allenoates: The Catalytic Enantioselective Synthesis of Protected alpha,alpha-Disubstituted alpha-Amino Acid Derivatives. *J. Am. Chem. Soc.* **2015,** *137* (29), 9438-9442.

104. Trost, B. M.; Debien, L., Palladium-Catalyzed Trimethylenemethane Cycloaddition of Olefins Activated by the sigma-Electron-Withdrawing Trifluoromethyl Group. *J. Am. Chem. Soc.* **2015,** *137* (36), 11606-11609.

105. Takizawa, S.; Kishi, K.; Yoshida, Y.; Mader, S.; Arteaga, F. A.; Lee, S.; Hoshino, M.; Rueping, M.; Fujita, M.; Sasai, H., Phosphine-Catalyzed beta,gamma-Umpolung Domino Reaction of Allenic Esters: Facile Synthesis of Tetrahydrobenzofuranones Bearing a Chiral Tetrasubstituted Stereogenic Carbon Center. *Angew. Chem.-Int. Edit.* **2015,** *54* (51), 15511-15515.

106. Wang, T. L.; Yu, Z. Y.; Hoon, D. L.; Phee, C. Y.; Lan, Y.; Lu, Y. X., Regiodivergent Enantioselective gamma-Additions of Oxazolones to 2,3-Butadienoates Catalyzed by Phosphines: Synthesis of alpha,alpha-Disubstituted alpha-Amino Acids and N,O-Acetal Derivatives. *J. Am. Chem. Soc.* **2016,** *138* (1), 265-271.

107. Sankar, M. G.; Garcia-Castro, M.; Golz, C.; Strohmann, C.; Kumar, K., Engaging Allene-Derived Zwitterions in an Unprecedented Mode of Asymmetric 3+2 -Annulation Reaction. *Angew. Chem.-Int. Edit.* **2016,** *55* (33), 9709-9713.

108. Li, E. Q.; Jin, H. X.; Jia, P. H.; Dong, X. L.; Huang, Y., Bifunctional-Phosphine-Catalyzed Sequential Annulations of Allenoates and Ketimines: Construction of Functionalized Poly-heterocycle Rings. *Angew. Chem.-Int. Edit.* **2016,** *55* (38), 11591-11594.

109. Ziegler, D. T.; Fu, G. C., Catalytic Enantioselective Carbon-Oxygen Bond Formation: Phosphine-Catalyzed Synthesis of Benzylic Ethers via the Oxidation of Benzylic C-H Bonds. *J. Am. Chem. Soc.* **2016,** *138* (37), 12069-12072.

110. Pascual-Escudero, A.; de Cozar, A.; Cossio, F. P.; Adrio, J.; Carretero, J. C., Alkenyl Arenes as Dipolarophiles in Catalytic Asymmetric 1,3-Dipolar Cycloaddition Reactions of Azomethine Ylides. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15334-15338.

111. Cheng, Q. Q.; Yedoyan, J.; Arman, H.; Doyle, M. P., Copper-Catalyzed Divergent Addition Reactions of Enoldiazoacetamides with Nitrones. *J. Am. Chem. Soc.* **2016,** *138* (1), 44-47.

112. Wei, Y.; Lu, L. Q.; Li, T. R.; Feng, B.; Wang, Q.; Xiao, W. J.; Alper, H., P,SLigands for the Asymmetric Construction of Quaternary Stereocenters in Palladium-Catalyzed Decarboxylative 4+2 Cycloadditions. *Angew. Chem.-Int. Edit.* **2016,** *55* (6), 2200-2204.

113. West, T. H.; Walden, D. M.; Taylor, J. E.; Brueckner, A. C.; Johnston, R. C.; Cheong, P. H. Y.; Lloyd-Jones, G. C.; Smith, A. D., Catalytic Enantioselective 2,3 -Rearrangements of Allylic Ammonium Ylides: A Mechanistic and Computational Study. *J. Am. Chem. Soc.* **2017,** *139* (12), 4366-4375.

114. Xu, B.; Tambar, U. K., Copper-Catalyzed Enantio-, Diastereo-, and Regioselective 2,3 -Rearrangements of Iodonium Ylides. *Angew. Chem.-Int. Edit.* **2017,** *56* (33), 9868-9871.

115. Zhang, Z. K.; Sheng, Z.; Yu, W. Z.; Wu, G. J.; Zhang, R.; Chu, W. D.; Zhang, Y.; Wang, J. B., Catalytic asymmetric trifluoromethylthiolation via enantioselective 2,3 -sigmatropic rearrangement of sulfonium ylides. *Nature Chemistry* **2017,** *9* (10), 970-976.

116. Trost, B. M.; Wang, Y. L., A Deprotonation Approach to the Unprecedented Amino-Trimethylenemethane Chemistry: Regio-, Diastereo-, and Enantioselective Synthesis of Complex Amino Cycles. *Angew. Chem.-Int. Edit.* **2018,** *57* (34), 11025-11029.

117. Deng, H.; Yang, W. L.; Tian, F.; Tang, W.; Deng, W. P., Asymmetric Construction of 3-Azabicyclo 3.1.0 hexane Skeleton with Five Contiguous Stereogenic Centers by Cu-Catalyzed 1,3-Dipolar Cycloaddition of Trisubstituted Cyclopropenes. *Org. Lett.* **2018,** *20* (13), 4121-4125.

118. Yuan, Y.; Zheng, Z. J.; Ye, F.; Ma, J. H.; Xu, Z.; Bai, X. F.; Li, L.; Xu, L. W., Highly efficient desymmetrization of cyclopropenes to azabicyclo 3.1.0 hexanes with five continuous stereogenic centers by copper-catalyzed 3+2 cycloadditions. *Organic Chemistry Frontiers* **2018,** *5* (18), 2759-2764.

119. Trost, B. M.; Zell, D.; Hohn, C.; Mata, G.; Maruniak, A., Enantio- and Diastereoselective Synthesis of Chiral Allenes by Palladium-Catalyzed Asymmetric 3+2 Cycloaddition Reactions. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12916-12920.

120. Trost, B. M.; Mata, G., Enantioselective Palladium-Catalyzed 3+2 Cycloaddition of Trimethylenemethane and Fluorinated Ketones. *Angew. Chem.-Int. Edit.* **2018,** *57* (38), 12333-12337.

121. Wang, H. M.; Zhang, J. Y.; Tu, Y. S.; Zhang, J. L., Phosphine-Catalyzed Enantioselective Dearomative 3+2 -Cycloaddition of 3-Nitroindoles and 2-Nitrobenzofurans. *Angew. Chem.-Int. Edit.* **2019,** *58* (16), 5422-5426.

122. Lorton, C.; Castanheiro, T.; Voituriez, A., Catalytic and Asymmetric Process via P-III/P-V=0 Redox Cycling: Access to (Trifluoromethyl)cyclobutenes via a Michael Addition/Wittig Olefination Reaction. *J. Am. Chem. Soc.* **2019,** *141* (26), 10142-10147.

123. Motaleb, A.; Rani, S.; Das, T.; Gonnade, R. G.; Maity, P., Phosphite-Catalyzed C-H Allylation of Azaarenes via an Enantioselective 2,3 -Aza-Wittig Rearrangement. *Angew. Chem.-Int. Edit.* **2019,** *58* (40), 14104-14109.

124. Trost, B. M.; Jiao, Z. W.; Hung, C. I., Elaborating Complex Heteroaryl-Containing Cycles via Enantioselective Palladium-Catalyzed Cycloadditions. *Angew. Chem.-Int. Edit.* **2019,** *58* (42), 15154-15158.

125. Marichev, K. O.; Wang, K.; Dong, K. Y.; Greco, N.; Massey, L. A.; Deng, Y. M.; Arman, H.; Doyle, M. P., Synthesis of Chiral Tetrasubstituted Azetidines from Donor-Acceptor Azetines via Asymmetric Copper(I)-Catalyzed Imido-Ylide 3+1 -Cycloaddition with Metallo-Enolcarbenes. *Angew. Chem.-Int. Edit.* **2019,** *58* (45), 16188-16192.

126. Wu, M. Y.; Han, Z. B.; Li, K. Z.; Wu, J. E.; Ding, K. L.; Lu, Y. X., Cyclohexyl-Fused, Spirobiindane-Derived, Phosphine-Catalyzed Synthesis of Tricyclic gamma-Lactams and Kinetic Resolution of gamma-Substituted Allenoates. *J. Am. Chem. Soc.* **2019,** *141* (41), 16362-16373.

127. Trost, B. M.; Zuo, Z., Highly Regio-, Diastereo-, and Enantioselective Synthesis of Tetrahydroazepines and Benzo[b]oxepines through Palladium-Catalyzed [4+3] Cycloaddition Reactions. *Angewandte Chemie International Edition* **2020,** *59* (3), 1243-1247.

128. Trost, B. M.; Wang, Y. L.; Hung, C. I., Use of alpha-trifluoromethyl carbanions for palladium-catalysed asymmetric cycloadditions. *Nature Chemistry* **2020,** *12* (3), 294-+.

129. Lin, Q.; Hu, B.; Xu, X.; Dong, S.; Liu, X.; Feng, X., Chiral N,N′-dioxide/Mg(OTf)2 complex-catalyzed asymmetric [2,3]-rearrangement of in situ generated ammonium salts. *Chem. Sci.* **2020,** *11* (11), 3068-3073.

130. Trost, B. M.; Mata, G., Forging Odd-Membered Rings: Palladium-Catalyzed Asymmetric Cycloadditions of Trimethylenemethane. *Accounts of Chemical Research* **2020,** *53* (7), 1293-1305.

131. Li, L.; Chen, B.; Chen, J.; Huang, Y., Enantioselective Intramolecular [2,3]-Sigmatropic Rearrangement of Aldehydes via a Sulfonium Enamine Intermediate. *Angewandte Chemie International Edition* **2020,** *59* (47), 20904-20908.

132. Trost, B. M.; Jiao, Z.; Liu, Y.; Min, C.; Hung, C.-I. J., Palladium-Catalyzed Enantioselective Cycloadditions of Aliphatic 1,4-Dipoles: Access to Chiral Cyclohexanes and Spiro [2.4] heptanes. *J. Am. Chem. Soc.* **2020,** *142* (43), 18628-18636.

133. Trost, B. M.; Jiao, Z., Palladium-Catalyzed Enantioselective Cycloaddition of Carbonylogous 1,4-Dipoles: Efficient Access to Chiral Cyclohexanones. *J. Am. Chem. Soc.* **2020,** *142* (52), 21645-21650.

134. Trost, B. M.; Zuo, Z., Regiodivergent Synthesis of Spirocyclic Compounds through Pd-Catalyzed Regio- and Enantioselective [3+2] Spiroannulation. *Angewandte Chemie International Edition* **2021,** *60* (11), 5806-5810.

135. Yildirim, O.; Grigalunas, M.; Brieger, L.; Strohmann, C.; Antonchick, A. P.; Waldmann, H., Dynamic Catalytic Highly Enantioselective 1,3-Dipolar Cycloadditions. *Angewandte Chemie International Edition* **2021,** *60* (36), 20012-20020.

136. Liu, J.; Yu, L.; Zheng, C.; Zhao, G., Asymmetric Synthesis of 2,2-Difluorotetrahydrofurans through Palladium-Catalyzed Formal [3+2] Cycloaddition. *Angewandte Chemie International Edition* **2021,** *60* (44), 23641-23645.

137. Morita, T.; Murakami, H.; Asawa, Y.; Nakamura, H., Enantioselective Synthesis of Oxazaborolidines by Palladium-Catalyzed N−H/B−H Double Activation of 1,2-Azaborines. *Angewandte Chemie International Edition* **2022,** *61* (7), e202113558.

138. Xu, X.; Bao, L.; Ran, L.; Yang, Z.; Yan, D.; Wang, C.-J.; Teng, H., Synthesis of bioactive fluoropyrrolidines via copper(i)-catalysed asymmetric 1,3-dipolar cycloaddition of azomethine ylides. *Chem. Sci.* **2022,** *13* (5), 1398-1407.

139. Zhang, F.; Dai, X.; Dai, L.; Zheng, W.; Chan, W.-L.; Tang, X.; Zhang, X.; Lu, Y., Phosphine-Catalyzed Enantioselective (3+2) Annulation of Vinylcyclopropanes with Imines for the Synthesis of Chiral Pyrrolidines. *Angewandte Chemie International Edition* **2022,** *61* (24), e202203212.

140. Uno, H.; Kawai, K.; Araki, T.; Shiro, M.; Shibata, N., Enantio-, Diastereo- and Regioselective Synthesis of Chiral Cyclic and Acyclic gem-Difluoromethylenes by Palladium-Catalyzed [4+2] Cycloaddition. *Angewandte Chemie International Edition* **2022,** *61* (24), e202117635.

141. Shen, L.; Zheng, Y.; Lin, Z.; Qin, T.; Huang, Z.; Zi, W., Copper-Catalyzed Enantioselective C1,N-Dipolar (3+2) Cycloadditions of 2-Aminoallyl Cations with Indoles. *Angewandte Chemie International Edition* **2023,** *62* (8), e202217051.

142. Li, K.; Zhen, S.; Wang, W.; Du, J.; Yu, S.; Wu, Y.; Guo, H., Fungicide-inspired precursors of π-allylpalladium intermediates for palladium-catalyzed decarboxylative cycloadditions. *Chem. Sci.* **2023,** *14* (11), 3024-3029.

143. Xiao, Y.-Q.; Li, M.-M.; Zhou, Z.-X.; Li, Y.-J.; Cao, M.-Y.; Liu, X.-P.; Lu, H.-H.; Rao, L.; Lu, L.-Q.; Beauchemin, A. M.; Xiao, W.-J., Taming Chiral Quaternary Stereocenters via Remote H-Bonding Stereoinduction in Palladium-Catalyzed (3+2) Cycloadditions. *Angewandte Chemie International Edition* **2023,** *62* (3), e202212444.

144. Xu, Q.; Lu, C.-J.; Guo, C.-Q.; Feng, J.; Liu, R.-R., Palladium-catalyzed enantioselective rearrangement of dienyl cyclopropanes. *Chem. Sci.* **2023,** *14* (12), 3346-3351.

145. Pham, Q. H.; Tague, A. J.; Richardson, C.; Gardiner, M. G.; Pyne, S. G.; Hyland, C. J. T., Palladium-catalysed enantio- and regioselective (3 + 2) cycloaddition reactions of sulfamidate imine-derived 1-azadienes towards spirocyclic cyclopentanes. *Chem. Sci.* **2023,** *14* (18), 4893-4900.

146. Moser, D.; Jana, K.; Sparr, C., Atroposelective PIII/PV=O Redox Catalysis for the Isoquinoline-Forming Staudinger–aza-Wittig Reaction. *Angewandte Chemie International Edition* **2023,** *62* (39), e202309053.

147. Wang, B.-C.; Hu, F.; Bai, J.; Xiong, F.-Y.; Chen, P.; Li, J.; Tan, Y.; Guo, Y.-L.; Xiao, W.-J.; Lu, L.-Q., Synthesis of S(IV)-Stereogenic Chiral Thio-Oxazolidinones via Palladium-Catalyzed Asymmetric [3+2] Annulations. *Angewandte Chemie International Edition* **2024,** *63* (13), e202319728.

148. Jana, K.; Zhao, Z.; Musies, J.; Sparr, C., Atroposelective Arene-Forming Wittig Reaction by Phosphorus PIII/PV=O Redox Catalysis. *Angewandte Chemie International Edition* **2024,** *63* (37), e202408159.

149. Wang, X.; Gao, R.; Li, X., Catalytic Asymmetric Construction of Chiral Polysubstituted 3-Azabicyclo[3.1.1]heptanes by Copper-Catalyzed Stereoselective Formal [4π+2σ] Cycloaddition. *J. Am. Chem. Soc.* **2024,** *146* (30), 21069-21077.

150. Zhang, J.; Su, J.-Y.; Zheng, H.; Li, H.; Deng, W.-P., In(OTf)3-Catalyzed (3 + 3) Dipolar Cyclization of Bicyclo[1.1.0]butanes with N-Nucleophilic 1,3-Dipoles: Access to 2,3-Diazabicyclo[3.1.1]heptanes, 2,3-Diazabicyclo[3.1.1]heptenes, and Enantiopure 2-Azabicyclo[3.1.1]heptanes. *ACS Catalysis* **2024,** *14* (23), 17837-17849.

151. Qin, T.; He, M.; Zi, W., Palladium-catalysed [2σ + 2π] cycloaddition reactions of bicyclo[1.1.0]butanes with aldehydes. *Nature Synthesis* **2025,** *4* (1), 124-133.

152. He, Y.; Yan, B.; Ma, C.; Ni, S.; Guo, W., Ni-catalyzed asymmetric decarboxylation for the construction of carbocycles with contiguous quaternary carbon stereocenters. *Chem. Sci.* **2025,** *16* (2), 834-839.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

4.Dual Activation

4.1 BrØnsted acid / base dual activation

4.1.1Addition to Carbonyl and Imines

1. Iyer, M. S.; Gigstad, K. M.; Namdev, N. D.; Lipton, M., Asymmetric catalysis of the Strecker amino acid synthesis by a cyclic dipeptide. *J. Am. Chem. Soc.* **1996,** *118* (20), 4910-4911.

2. Corey, E. J.; Grogan, M. J., Enantioselective synthesis of alpha-amino nitriles from N- benzhydryl imines and HCN with a chiral bicyclic guanidine as catalyst. *Org. Lett.* **1999,** *1* (1), 157-160.

3. Mermerian, A. H.; Fu, G. C., Catalytic enantioselective synthesis of quaternary stereocenters via intermolecular C-acylation of silyl ketene acetals: Dual activation of the electrophile and the nucleophile. *J. Am. Chem. Soc.* **2003,** *125* (14), 4050-4051.

4. Kawahara, S.; Nakano, A.; Esumi, T.; Iwabuchi, Y.; Hatakeyama, S., beta-isocupreidine-catalyzed asymmetric Baylis-Hillman reaction of imines. *Org. Lett.* **2003,** *5* (17), 3103-3105.

5. Westermann, B., Asymmetric catalytic aza-Henry reactions leading to 1,2- diamines and 1-,2-diaminocarboxylic acids. *Angew. Chem.-Int. Edit.* **2003,** *42* (2), 151-153.

6. Mizuta, S.; Sadamori, M.; Fujimoto, T.; Yamamoto, I., Asymmetric desymmetrization of meso-1,2-diols by phosphinite derivatives of cinchona alkaloids. *Angew. Chem.-Int. Edit.* **2003,** *42* (29), 3383-3385.

7. Ma, J. A.; Cahard, D., Towards perfect catalytic asymmetric synthesis: Dual activation of the electrophile and the nucleophile. *Angew. Chem.-Int. Edit.* **2004,** *43* (35), 4566-4583.

8. Huang, J. K.; Corey, E. J., A new chiral catalyst for the enantioselective Strecker synthesis of alpha-amino acids. *Org. Lett.* **2004,** *6* (26), 5027-5029.

9. Okino, T.; Nakamura, S.; Furukawa, T.; Takemoto, Y., Enantioselective Aza-Henry reaction catalyzed by a bifunctional organocatalyst. *Org. Lett.* **2004,** *6* (4), 625-627.

10. Nugent, B. M.; Yoder, R. A.; Johnston, J. N., Chiral Proton Catalysis: A Catalytic Enantioselective Aza-Henry Reaction. *J. Am. Chem. Soc.* **2004,** *126*, 3418-3419.

11. Fierman, M. B.; O'Leary, D. J.; Steinmetz, W. E.; Miller, S. J., Structure-selectivity relationships and structure for a peptide-based enantioselective acylation catalyst. *J. Am. Chem. Soc.* **2004,** *126* (22), 6967-6971.

12. Berkessel, A.; Cleemann, F.; Mukherjee, S.; Muller, T. N.; Lex, J., Highly efficient dynamic kinetic resolution of azlactones by urea-based bifunctional organocatalysts. *Angew. Chem.-Int. Edit.* **2005,** *44* (5), 807-811.

13. Buskens, P.; Klankermayer, J.; Leitner, W., Bifunctional activation and racemization in the catalytic asymmetric aza-Baylis-Hillman reaction. *J. Am. Chem. Soc.* **2005,** *127* (48), 16762-16763.

14. Matsui, K.; Takizawa, S.; Sasai, H., Bifunctional organocatalysts for enantioselective aza-Morita-Baylis-Hillman reaction. *J. Am. Chem. Soc.* **2005,** *127* (11), 3680-3681.

15. Fuerst, D. E.; Jacobsen, E. N., Thiourea-catalyzed enantioselective cyanosilylation of ketones. *J. Am. Chem. Soc.* **2005,** *127* (25), 8964-8965.

16. Berkessel, A.; Cleemann, F.; Mukherjee, S., Kinetic resolution of oxazinones: An organocatalytic approach to enantiomerically pure beta-amino acids. *Angew. Chem.-Int. Edit.* **2005,** *44* (45), 7466-7469.

17. Honjo, T.; Sano, S.; Shiro, M.; Nagao, Y., Highly enantioselective catalytic thiolysis of prochiral cyclic dicarboxylic anhydrides utilizing a bifunctional chiral sulfonamide. *Angew. Chem.-Int. Edit.* **2005,** *44* (36), 5838-5841.

18. Singh, A.; Yoder, R. A.; Shen, B.; Johnston, J. N., Chiral proton catalysis: Enantioselective bronsted acid catalyzed additions of nitroacetic acid derivatives as glycine equivalents. *J. Am. Chem. Soc.* **2007,** *129* (12), 3466-+.

19. Qin, B.; Liu, X. H.; Shi, J.; Zheng, K.; Zhao, H. T.; Feng, X. M., Enantioselective cyanosilylation of alpha,alpha-dialkoxy ketones catalyzed by proline-derived in-situ-prepared N-oxide as bifunctional organocatalyst. *J. Org. Chem.* **2007,** *72* (7), 2374-2378.

20. Yamaoka, Y.; Miyabe, H.; Takemoto, Y., Catalytic enantioselective petasis-type reaction of quinolines catalyzed by a newly designed thiourea catalyst. *J. Am. Chem. Soc.* **2007,** *129* (21), 6686-+.

21. Robak, M. T.; Trincado, M.; Ellman, J. A., Enantioselective aza-Henry reaction with an N-sulfinyl urea organocatalyst. *J. Am. Chem. Soc.* **2007,** *129* (49), 15110-+.

22. Shi, M.; Ma, G. N.; Gaol, J., Chiral bifunctional organocatalysts in asymmetric aza-Morita-Baylis-Hillman reactions of ethyl (Arylimino)acetates with methyl vinyl ketone and ethyl vinyl ketone. *J. Org. Chem.* **2007,** *72* (25), 9779-9781.

23. Zuend, S. J.; Jacobsen, E. N., Cooperative catalysis by tertiary amino-thioureas: Mechanism and basis for enantioselectivity of ketone cyanosilylation. *J. Am. Chem. Soc.* **2007,** *129* (51), 15872-15883.

24. Wang, C.; Zhou, Z.; Tang, C., Novel bifunctional chiral thiourea catalyzed highly enantioselective aza-Henry reaction. *Org. Lett.* **2008,** *10* (9), 1707-1710.

25. Singh, A.; Johnston, J. N., A diastereo- and enantioselective synthesis of alpha-substituted syn-alpha,beta-diamino acids. *J. Am. Chem. Soc.* **2008,** *130* (18), 5866-+.

26. Connon, S. J., Asymmetric catalysis with bifunctional cinchona alkaloid-based urea and thiourea organocatalysts. *Chem. Commun.* **2008,** (22), 2499-2510.

27. Wang, C. J.; Dong, X. Q.; Zhang, Z. H.; Xue, Z. Y.; Teng, H. L., Highly anti-selective asymmetric nitro-Mannich reactions catalyzed by bifunctional amine-thiourea-bearing multiple hydrogen-bonding donors. *J. Am. Chem. Soc.* **2008,** *130* (27), 8606-+.

28. Yalalov, D. A.; Tsogoeva, S. B.; Shubina, T. E.; Martynova, I. M.; Clark, T., Evidence for an enol mechanism in a highly enantioselective Mannich-Type reaction catalyzed by primary amine-thiourea. *Angew. Chem.-Int. Edit.* **2008,** *47* (35), 6624-6628.

29. Uraguchi, D.; Koshimoto, K.; Ooi, T., Chiral ammonium betaines: A bifunctional organic base catalyst for asymmetric Mannich-type reaction of alpha-nitrocarboxylates. *J. Am. Chem. Soc.* **2008,** *130* (33), 10878-+.

30. Wilt, J. C.; Pink, M.; Johnston, J. N., A diastereo- and enantioselective synthesis of alpha-substituted anti-alpha,beta-diaminophosphonic acid derivatives. *Chem. Commun.* **2008,** (35), 4177-4179.

31. Abermil, N.; Masson, G.; Zhu, J. P., Highly enantioselective aza Morita-Baylis-Hillman reaction catalyzed by bifunctional beta-isocupreidine derivatives. *J. Am. Chem. Soc.* **2008,** *130* (38), 12596-+.

32. Li, L.; Klauber, E. G.; Seidel, D., Catalytic enantioselective aldol additions of alpha-isothiocyanato imides to aldehydes. *J. Am. Chem. Soc.* **2008,** *130* (37), 12248-+.

33. Wang, C.; Wu, X.; Zhou, L.; Sun, J., A Highly Enantioselective Organocatalytic Method for Reduction of Aromatic N-Alkyl Ketimines. *Chem.-Eur. J.* **2008,** *14* (29), 8789-8792.

34. Hatano, M.; Maki, T.; Moriyama, K.; Arinobe, M.; Ishihara, K., Pyridinium 1,1 '-Binaphthyl-2,2 '-disulfonates as Highly Effective Chiral Bronsted Acid-Base Combined Salt Catalysts for Enantioselective Mannich-Type Reaction. *J. Am. Chem. Soc.* **2008,** *130* (50), 16858-+.

35. Shen, B.; Johnston, J. N., A Formal Enantioselective Acetate Mannich Reaction: The Nitro Functional Group as a Traceless Agent for Activation and Enantiocontrol in the Synthesis of beta-Amino Acids. *Org. Lett.* **2008,** *10* (20), 4397-4400.

36. Lovick, H. M.; Michael, F. E., Reversal of enantioselectivity using tethered bisguanidine catalysts in the aza-Henry reaction. *Tetrahedron Lett.* **2009,** *50* (9), 1016-1019.

37. Garnier, J. M.; Liu, F., Trifunctional organocatalyst-promoted counterion catalysis for fast and enantioselective aza-Morita-Baylis-Hillman reactions at ambient temperature. *Org. Biomol. Chem.* **2009,** *7* (7), 1272-1275.

38. Liu, H.; Dagousset, G.; Masson, G.; Retailleau, P.; Zhu, J. P., Chiral Bronsted Acid-Catalyzed Enantioselective Three-Component Povarov Reaction. *J. Am. Chem. Soc.* **2009,** *131* (13), 4598-+.

39. Bishop, J. A.; Lou, S.; Schaus, S. E., Enantioselective Addition of Boronates to Acyl Imines Catalyzed by Chiral Biphenols. *Angew. Chem.-Int. Edit.* **2009,** *48* (24), 4337-4340.

40. Liu, H. J.; Leow, D.; Huang, K. W.; Tan, C. H., Enantioselective Synthesis of Chiral Allenoates by Guanidine-Catalyzed Isomerization of 3-Alkynoates. *J. Am. Chem. Soc.* **2009,** *131* (21), 7212-+.

41. Cucinotta, C. S.; Kosa, M.; Melchiorre, P.; Cavalli, A.; Gervasio, F. L., Bifunctional Catalysis by Natural Cinchona Alkaloids: A Mechanism Explained. *Chem.-Eur. J.* **2009,** *15* (32), 7913-7921.

42. Li, L.; Ganesh, M.; Seidel, D., Catalytic Enantioselective Synthesis of alpha,beta-Diamino Acid Derivatives. *J. Am. Chem. Soc.* **2009,** *131* (33), 11648-+.

43. Han, X.; Kwiatkowski, J.; Xue, F.; Huang, K. W.; Lu, Y. X., Asymmetric Mannich Reaction of Fluorinated Ketoesters with a Tryptophan-Derived Bifunctional Thiourea Catalyst. *Angew. Chem.-Int. Edit.* **2009,** *48* (41), 7604-7607.

44. Zuend, S. J.; Jacobsen, E. N., Mechanism of Amido-Thiourea Catalyzed Enantioselective Imine Hydrocyanation: Transition State Stabilization via Multiple Non-Covalent Interactions. *J. Am. Chem. Soc.* **2009,** *131* (42), 15358-15374.

45. Abermil, N.; Masson, G.; Zhu, J. P., Invertible Enantioselectivity in 6 '-Deoxy-6 '-acylamino-beta-isocupreidine-Catalyzed Asymmetric Aza-Morita-Baylis-Hillman Reaction: Key Role of Achiral Additive. *Org. Lett.* **2009,** *11* (20), 4648-4651.

46. Amarante, G. W.; Benassi, M.; Milagre, H. M. S.; Braga, A. A. C.; Maseras, F.; Eberlin, M. N.; Coelho, F., Bronsted Acid Catalyzed Morita-Baylis-Hillman Reaction: A New Mechanistic View for Thioureas Revealed by ESI-MS(/MS) Monitoring and DFT Calculations. *Chem.-Eur. J.* **2009,** *15* (45), 12460-12469.

47. Zuend, S. J.; Coughlin, M. P.; Lalonde, M. P.; Jacobsen, E. N., Scaleable catalytic asymmetric Strecker syntheses of unnatural alpha-amino acids. *Nature* **2009,** *461* (7266), 968-U223.

48. Li, P.; Chai, Z.; Zhao, S. L.; Yang, Y. Q.; Wang, H. F.; Zheng, C. W.; Cai, Y. P.; Zhao, G.; Zhu, S. Z., Highly enantio- and diastereoselective synthesis of alpha-trifluoromethyldihydropyrans using a novel bifunctional piperazine-thiourea catalyst. *Chem. Commun.* **2009,** (47), 7369-7371.

49. Nakamura, S.; Hayashi, M.; Hiramatsu, Y.; Shibata, N.; Funahashi, Y.; Toru, T., Catalytic Enantioselective Hydrophosphonylation of Ketimines Using Cinchona Alkaloids. *J. Am. Chem. Soc.* **2009,** *131* (51), 18240-+.

50. El-Hamdouni, N.; Companyo, X.; Rios, R.; Moyano, A., Substrate-Dependent Nonlinear Effects in Proline-Thiourea-Catalyzed Aldol Reactions: Unraveling the Role of the Thiourea Co-Catalyst. *Chem.-Eur. J.* **2010,** *16* (4), 1142-1148.

51. Xu, S. M.; Wang, Z.; Li, Y. X.; Zhang, X. M.; Wang, H. M.; Ding, K. L., Mechanistic Investigation of Chiral Phosphoric Acid Catalyzed Asymmetric Baeyer-Villiger Reaction of 3-Substituted Cyclobutanones with H2O2 as the Oxidant. *Chem.-Eur. J.* **2010,** *16* (10), 3021-3035.

52. Ube, H.; Shimada, N.; Terada, M., Asymmetric Direct Vinylogous Aldol Reaction of Furanone Derivatives Catalyzed by an Axially Chiral Guanidine Base. *Angew. Chem.-Int. Edit.* **2010,** *49* (10), 1858-1861.

53. Davis, T. A.; Wilt, J. C.; Johnston, J. N., Bifunctional Asymmetric Catalysis: Amplification of Bronsted Basicity Can Orthogonally Increase the Reactivity of a Chiral Bronsted Acid. *J. Am. Chem. Soc.* **2010,** *132* (9), 2880-+.

54. Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N., Asymmetric Cooperative Catalysis of Strong Bronsted Acid-Promoted Reactions Using Chiral Ureas. *Science* **2010,** *327* (5968), 986-990.

55. Misaki, T.; Takimoto, G.; Sugimura, T., Direct Asymmetric Aldol Reaction of 5H-Oxazol-4-ones with Aldehydes Catalyzed by Chiral Guanidines. *J. Am. Chem. Soc.* **2010,** *132* (18), 6286-+.

56. Peschiulli, A.; Procuranti, B.; O' Connor, C. J.; Connon, S. J., Synergistic organocatalysis in the kinetic resolution of secondary thiols with concomitant desymmetrization of an anhydride. *Nat. Chem.* **2010,** *2* (5), 380-384.

57. Wakchaure, V. N.; List, B., A New Structural Motif for Bifunctional Bronsted Acid/Base Organocatalysis. *Angew. Chem.-Int. Edit.* **2010,** *49* (24), 4136-4139.

58. Singh, R. P.; Foxman, B. M.; Deng, L., Asymmetric Vinylogous Aldol Reaction of Silyloxy Furans with a Chiral Organic Salt. *J. Am. Chem. Soc.* **2010,** *132* (28), 9558-9560.

59. Dong, S. X.; Liu, X. H.; Chen, X. H.; Mei, F.; Zhang, Y. L.; Gao, B.; Lin, L. L.; Feng, X. M., Chiral Bisguanidine-Catalyzed Inverse-Electron-Demand Hetero-Diels-Alder Reaction of Chalcones with Azlactones. *J. Am. Chem. Soc.* **2010,** *132* (31), 10650-10651.

60. Hashimoto, T.; Kimura, H.; Maruoka, K., Enantioselective Formal Alkenylations of Imines Catalyzed by Axially Chiral Dicarboxylic Acid Using Vinylogous Aza-Enamines. *Angew. Chem.-Int. Edit.* **2010,** *49* (38), 6844-6847.

61. Jiang, X. X.; Cao, Y. M.; Wang, Y. Q.; Liu, L. P.; Shen, F. F.; Wang, R., A Unique Approach to the Concise Synthesis of Highly Optically Active Spirooxazolines and the Discovery of a More Potent Oxindole-Type Phytoalexin Analogue. *J. Am. Chem. Soc.* **2010,** *132* (43), 15328-15333.

62. Guo, Q. S.; Bhanushali, M.; Zhao, C. G., Quinidine Thiourea-Catalyzed Aldol Reaction of Unactivated Ketones: Highly Enantioselective Synthesis of 3-Alkyl-3-hydroxy-indolin-2-ones. *Angew. Chem.-Int. Edit.* **2010,** *49* (49), 9460-9464.

63. Takizawa, S.; Inoue, N.; Hirata, S.; Sasai, H., Enantioselective Synthesis of Isoindolines: An Organocatalyzed Domino Process Based On the aza-Morita-Baylis-Hillman Reaction. *Angew. Chem.-Int. Edit.* **2010,** *49* (50), 9725-9729.

64. Vellalath, S.; Coric, I.; List, B., N-Phosphinyl Phosphoramide-A Chiral Bronsted Acid Motif for the Direct Asymmetric N,O-Acetalization of Aldehydes. *Angew. Chem.-Int. Edit.* **2010,** *49* (50), 9749-9752.

65. Luo, J.; Wang, H. F.; Han, X. A.; Xu, L. W.; Kwiatkowski, J.; Huang, K. W.; Lu, Y. X., The Direct Asymmetric Vinylogous Aldol Reaction of Furanones with alpha-Ketoesters: Access to Chiral gamma-Butenolides and Glycerol Derivatives. *Angew. Chem.-Int. Edit.* **2011,** *50* (8), 1861-1864.

66. Davis, T. A.; Johnston, J. N., Catalytic, enantioselective synthesis of stilbene cis-diamines: A concise preparation of (-)-Nutlin-3, a potent p53/MDM2 inhibitor. *Chem. Sci.* **2011,** *2* (6), 1076-1079.

67. Zhao, D. P.; Yang, D. X.; Wang, Y. J.; Wang, Y.; Wang, L. Q.; Mao, L. J.; Wang, R., Enantioselective Mannich reaction of a highly reactive Horner-Wadsworth-Emmons reagent with imines catalyzed by a bifunctional thiourea. *Chem. Sci.* **2011,** *2* (10), 1918-1921.

68. Takizawa, S.; Kiriyama, K.; Ieki, K.; Sasai, H., A bifunctional spiro-type organocatalyst with high enantiocontrol: application to the aza-Morita-Baylis-Hillman reactions. *Chem. Commun.* **2011,** *47* (32), 9227-9229.

69. Dagousset, G.; Zhu, J. P.; Masson, G., Chiral Phosphoric Acid-Catalyzed Enantioselective Three-Component Povarov Reaction Using Enecarbamates as Dienophiles: Highly Diastereo- and Enantioselective Synthesis of Substituted 4-Aminotetrahydroquinolines. *J. Am. Chem. Soc.* **2011,** *133* (37), 14804-14813.

70. Lykke, L.; Rodriguez-Escrich, C.; Jorgensen, K. A., Catalytic Enantioselective Oxaziridination. *J. Am. Chem. Soc.* **2011,** *133* (38), 14932-14935.

71. De, C. K.; Mittal, N.; Seidel, D., A Dual-Catalysis Approach to the Asymmetric Steglich Rearrangement and Catalytic Enantioselective Addition of O-Acylated Azlactones to Isoquinolines. *J. Am. Chem. Soc.* **2011,** *133* (42), 16802-16805.

72. Sakamoto, S.; Inokuma, T.; Takemoto, Y., Organocatalytic Asymmetric Neber Reaction for the Synthesis of 2H-Azirine Carboxylic Esters. *Org. Lett.* **2011,** *13* (24), 6374-6377.

73. Zhang, W. Q.; Cheng, L. F.; Yu, J.; Gong, L. Z., A Chiral Bis(betaine) Catalyst for the Mannich Reaction of Azlactones and Aliphatic Imines. *Angew. Chem.-Int. Edit.* **2012,** *51* (17), 4085-4088.

74. Cornaggia, C.; Manoni, F.; Torrente, E.; Tallon, S.; Connon, S. J., A Catalytic Asymmetric Reaction Involving Enolizable Anhydrides. *Org. Lett.* **2012,** *14* (7), 1850-1853.

75. Uraguchi, D.; Koshimoto, K.; Ooi, T., Ionic Nucleophilic Catalysis of Chiral Ammonium Betaines for Highly Stereoselective Aldol Reaction from Oxindole-Derived Vinylic Carbonates. *J. Am. Chem. Soc.* **2012,** *134* (16), 6972-6975.

76. Chen, M.; Roush, W. R., Enantioselective Synthesis of anti- and syn-Homopropargyl Alcohols via Chiral Bronsted Acid Catalyzed Asymmetric Allenylboration Reactions. *J. Am. Chem. Soc.* **2012,** *134* (26), 10947-10952.

77. Crespo-Pelna, A.; Monge, D.; Martin-Zamora, E.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M., Asymmetric Formal Carbonyl-Ene Reactions of Formaldehyde tert-Butyl Hydrazone with alpha-Keto Esters: Dual Activation by Bis-urea Catalysts. *J. Am. Chem. Soc.* **2012,** *134* (31), 12912-12915.

78. Kong, S. S.; Fan, W. D.; Wu, G. P.; Miao, Z. W., Enantioselective Synthesis of Tertiary a-Hydroxy Phosphonates Catalyzed by Carbohydrate/Cinchona Alkaloid Thiourea Organocatalysts. *Angew. Chem.-Int. Edit.* **2012,** *51* (35), 8864-8867.

79. Chen, Z. L.; Wang, B. L.; Wang, Z. B.; Zhu, G. Y.; Sun, J. W., Complex Bioactive Alkaloid-Type Polycycles through Efficient Catalytic Asymmetric Multicomponent Aza-Diels-Alder Reaction of Indoles with Oxetane as Directing Group. *Angew. Chem.-Int. Edit.* **2013,** *52* (7), 2027-2031.

80. Yuan, H. N.; Wang, S.; Nie, J.; Meng, W.; Yao, Q. W.; Ma, J. A., Hydrogen-Bond-Directed Enantioselective Decarboxylative Mannich Reaction of -Ketoacids with Ketimines: Application to the Synthesis of Anti-HIV Drug DPC083. *Angew. Chem.-Int. Edit.* **2013,** *52* (14), 3869-3873.

81. Zhu, B.; Zhang, W.; Lee, R.; Han, Z. Q.; Yang, W. G.; Tan, D.; Huang, K. W.; Jiang, Z. Y., Direct Asymmetric Vinylogous Aldol Reaction of Allyl Ketones with Isatins: Divergent Synthesis of 3-Hydroxy-2-Oxindole Derivatives. *Angew. Chem.-Int. Edit.* **2013,** *52* (26), 6666-6670.

82. Luo, C. S.; Huang, Y., A Highly Diastereo- and Enantioselective Synthesis of Tetrahydroquinolines: Quaternary Stereogenic Center Inversion and Functionalization. *J. Am. Chem. Soc.* **2013,** *135* (22), 8193-8196.

83. Saito, K.; Shibata, Y.; Yamanaka, M.; Akiyama, T., Chiral Phosphoric Acid-Catalyzed Oxidative Kinetic Resolution of Indolines Based on Transfer Hydrogenation to Imines. *J. Am. Chem. Soc.* **2013,** *135* (32), 11740-11743.

84. Takizawa, S.; Remond, E.; Arteaga, F. A.; Yoshida, Y.; Sridharan, V.; Bayardon, J.; Juge, S.; Sasai, H., P-chirogenic organocatalysts: application to the aza-Morita-Baylis-Hillman (aza-MBH) reaction of ketimines. *Chem. Commun.* **2013,** *49* (75), 8392-8394.

85. Bandar, J. S.; Lambert, T. H., Cyclopropenimine-Catalyzed Enantioselective Mannich Reactions of tert-Butyl Glycinates with N-Boc-Imines. *J. Am. Chem. Soc.* **2013,** *135* (32), 11799-11802.

86. Kano, T.; Yurino, T.; Maruoka, K., Organocatalytic Asymmetric Synthesis of Propargylamines with Two Adjacent Stereocenters: Mannich-Type Reactions of In Situ Generated C-Alkynyl Imines with beta-Keto Esters. *Angew. Chem.-Int. Edit.* **2013,** *52* (44), 11509-11512.

87. Bae, H. Y.; Sim, J. H.; Lee, J. W.; List, B.; Song, C. E., Organocatalytic Enantioselective Decarboxylative Aldol Reaction of Malonic Acid Half Thioesters with Aldehydes. *Angew. Chem.-Int. Edit.* **2013,** *52* (46), 12143-12147.

88. Nunez, M. G.; Farley, A. J. M.; Dixon, D. J., Bifunctional Iminophosphorane Organocatalysts for Enantioselective Synthesis: Application to the Ketimine Nitro-Mannich Reaction. *J. Am. Chem. Soc.* **2013,** *135* (44), 16348-16351.

89. Corbett, M. T.; Johnson, J. S., Dynamic Kinetic Asymmetric Transformations of beta-Stereogenic alpha-Ketoesters by Direct Aldolization. *Angew. Chem.-Int. Edit.* **2014,** *53* (1), 255-259.

90. Cao, Y.-M.; Shen, F.-F.; Zhang, F.-T.; Zhang, J.-L.; Wang, R., Catalytic Asymmetric 1,2-Addition of alpha-Isothiocyanato Phosphonates: Synthesis of Chiral beta-Hydroxy- or beta-Amino-Substituted alpha-Amino Phosphonic Acid Derivatives. *Angew. Chem.-Int. Edit.* **2014,** *53* (7), 1862-1866.

91. Ortin, I.; Dixon, D. J., Direct Catalytic Enantio- and Diastereoselective Mannich Reaction of Isocyanoacetates and Ketimines. *Angew. Chem.-Int. Edit.* **2014,** *53* (13), 3462-3465.

92. Bahlinger, A.; Fritz, S. P.; Wennemers, H., Stereoselective Metal-Free Synthesis of beta-Amino Thioesters with Tertiary and Quaternary Stereogenic Centers. *Angew. Chem.-Int. Edit.* **2014,** *53* (33), 8779-8783.

93. Brioche, J.; Courant, T.; Alcaraz, L.; Stocks, M.; Furber, M.; Zhu, J.; Masson, G., Chiral Phosphoric Acid-Catalyzed Enantioselective Three- Component Aza-Diels-Alder Reactions of Aminopyrroles and Aminopyrazoles. *Adv. Synth. Catal.* **2014,** *356* (8), 1719-1724.

94. Dagousset, G.; Erb, W.; Zhu, J.; Masson, G., Phosphoric Acid Catalyzed Diastereo- and Enantioselective Synthesis of Substituted 1,3-Diaminotetralins. *Org. Lett.* **2014,** *16* (9), 2554-2557.

95. Terada, M.; Komuro, T.; Toda, Y.; Korenaga, T., Mechanistic Studies of Highly Enantio- and Diastereoselective Aza-Petasis-Ferrier Rearrangement Catalyzed by Chiral Phosphoric Acid. *J. Am. Chem. Soc.* **2014,** *136* (19), 7044-7057.

96. Wasa, M.; Liu, R. Y.; Roche, S. P.; Jacobsen, E. N., Asymmetric Mannich Synthesis of a-Amino Esters by Anion-Binding Catalysis. *J. Am. Chem. Soc.* **2014,** *136* (37), 12872-12875.

97. Yang, K. S.; Rawal, V. H., Synthesis of alpha-Amino Acid Derivatives and Peptides via Enantioselective Addition of Masked Acyl Cyanides to Imines. *J. Am. Chem. Soc.* **2014,** *136* (46), 16148-16151.

98. Wang, H.-Y.; Zhang, K.; Zheng, C.-W.; Chai, Z.; Cao, D.-D.; Zhang, J.-X.; Zhao, G., Asymmetric Dual-Reagent Catalysis: Mannich-type Reactions Catalyzed by Ion Pair. *Angew. Chem.-Int. Edit.* **2015,** *54* (6), 1775-1779.

99. Montesinos-Magraner, M.; Vila, C.; Canton, R.; Blay, G.; Fernandez, I.; Munoz, M. C.; Pedro, J. R., Organocatalytic Asymmetric Addition of Naphthols and Electron-Rich Phenols to Isatin-Derived Ketimines: Highly Enantioselective Construction of Tetrasubstituted Stereocenters. *Angew. Chem.-Int. Edit.* **2015,** *54* (21), 6320-6324.

100. Huang, Y. Y.; Yang, X.; Lv, Z. C.; Cai, C.; Kai, C.; Pei, Y.; Feng, Y., Asymmetric Synthesis of 1,3-Butadienyl-2-carbinols by the Homoallenylboration of Aldehydes with a Chiral Phosphoric Acid Catalyst. *Angew. Chem.-Int. Edit.* **2015,** *54* (25), 7299-7302.

101. Zheng, Y.; Deng, L., Catalytic asymmetric direct aldol reaction of alpha-alkyl azlactones and aliphatic aldehydes. *Chem. Sci.* **2015,** *6* (11), 6510-6514.

102. Wakchaure, V. N.; Kaib, P. S. J.; Leutzsch, M.; List, B., Disulfonimide-Catalyzed Asymmetric Reduction of N-Alkyl Imines. *Angew. Chem.-Int. Edit.* **2015,** *54* (40), 11852-11856.

103. Yoneda, N.; Fukata, Y.; Asano, K.; Matsubara, S., Asymmetric Synthesis of Spiroketals with Aminothiourea Catalysts. *Angew. Chem.-Int. Edit.* **2015,** *54* (51), 15497-15500.

104. Zhang, J.; Lin, S. X.; Cheng, D. J.; Liu, X. Y.; Tan, B., Phosphoric Acid-Catalyzed Asymmetric Classic Passerini Reaction. *J. Am. Chem. Soc.* **2015,** *137* (44), 14039-14042.

105. Bongers, A.; Moon, P. J.; Beauchemin, A. M., Kinetic Resolution of Azomethine Imines by Bronsted Acid Catalyzed Enantioselective Reduction. *Angew. Chem.-Int. Edit.* **2015,** *54* (51), 15516-15519.

106. Saadi, J.; Wennemers, H., Enantioselective aldol reactions with masked fluoroacetates. *Nat. Chem.* **2016,** *8* (3), 276-280.

107. Saito, K.; Akiyama, T., Chiral Phosphoric Acid Catalyzed Kinetic Resolution of Indolines Based on a Self-Redox Reaction. *Angew. Chem.-Int. Edit.* **2016,** *55* (9), 3148-3152.

108. Galvan, A.; Gonzalez-Perez, A. B.; Alvarez, R.; de Lera, A. R.; Fananas, F. J.; Rodriguez, F., Exploiting the Multidentate Nature of Chiral Disulfonimides in a Multicomponent Reaction for the Asymmetric Synthesis of Pyrrolo 1,2-a indoles: A Remarkable Case of Enantioinversion. *Angew. Chem.-Int. Edit.* **2016,** *55* (10), 3428-3432.

109. Takeda, T.; Kondoh, A.; Terada, M., Construction of Vicinal Quaternary Stereogenic Centers by Enantioselective Direct Mannich-Type Reaction Using a Chiral Bis(guanidino)iminophosphorane Catalyst. *Angew. Chem.-Int. Edit.* **2016,** *55* (15), 4734-4737.

110. Zhang, Y.; Ao, Y. F.; Huang, Z. T.; Wang, D. X.; Wang, M. X.; Zhu, J. P., Chiral Phosphoric Acid Catalyzed Asymmetric Ugi Reaction by Dynamic Kinetic Resolution of the Primary Multicomponent Adduct. *Angew. Chem.-Int. Edit.* **2016,** *55* (17), 5282-5285.

111. Yu, C. G.; Huang, H.; Li, X. M.; Zhang, Y. T.; Wang, W., Dynamic Kinetic Resolution of Biaryl Lactones via a Chiral Bifunctional Amine Thiourea-Catalyzed Highly Atropoenantioselective Transesterification. *J. Am. Chem. Soc.* **2016,** *138* (22), 6956-6959.

112. Bae, H. Y.; Kim, M. J.; Sim, J. H.; Song, C. E., Direct Catalytic Asymmetric Mannich Reaction with Dithiomalonates as Excellent Mannich Donors: Organocatalytic Synthesis of (R)-Sitagliptin. *Angew. Chem.-Int. Edit.* **2016,** *55* (36), 10825-10829.

113. Cosimi, E.; Engl, O. D.; Saadi, J.; Ebert, M. O.; Wennemers, H., Stereoselective Organocatalyzed Synthesis of alpha-Fluorinated beta-Amino Thioesters and Their Application in Peptide Synthesis. *Angew. Chem.-Int. Edit.* **2016,** *55* (42), 13127-13131.

114. Vara, B. A.; Johnston, J. N., Enantioselective Synthesis of beta-Fluoro Amines via beta-Amino alpha-Fluoro Nitroalkanes and a Traceless Activating Group Strategy. *J. Am. Chem. Soc.* **2016,** *138* (42), 13794-13797.

115. Wang, Y. C.; Jiang, L.; Li, L.; Dai, J.; Xiong, D.; Shao, Z. H., An Arylation Strategy to Propargylamines: Catalytic Asymmetric Friedel-Crafts-type Arylation Reactions of C-Alkynyl Imines. *Angew. Chem.-Int. Edit.* **2016,** *55* (48), 15142-15146.

116. Li, S. Y.; Zhang, J. W.; Li, X. L.; Cheng, D. J.; Tan, B., Phosphoric Acid-Catalyzed Asymmetric Synthesis of SPINOL Derivatives. *J. Am. Chem. Soc.* **2016,** *138* (50), 16561-16566.

117. Nimmagadda, S. K.; Mallojjala, S. C.; Woztas, L.; Wheeler, S. E.; Antilla, J. C., Enantioselective Synthesis of Chiral Oxime Ethers: Desymmetrization and Dynamic Kinetic Resolution of Substituted Cyclohexanones. *Angew. Chem.-Int. Edit.* **2017,** *56* (9), 2454-2458.

118. Bai, X. B.; Zeng, G. K.; Shao, T. J.; Jiang, Z. Y., Catalytic Enantioselective gamma-Selective Additions of 2-Allylazaarenes to Activated Ketones. *Angew. Chem.-Int. Edit.* **2017,** *56* (13), 3684-3688.

119. Wang, Y.; Wang, Q.; Zhu, J. P., Organocatalytic Nucleophilic Addition of Hydrazones to Imines: Synthesis of Enantioenriched Vicinal Diamines. *Angew. Chem.-Int. Edit.* **2017,** *56* (20), 5612-5615.

120. Bew, S. P.; Liddle, J.; Hughes, D. L.; Pesce, P.; Thurston, S. M., Chiral BrOnsted Acid-Catalyzed Asymmetric Synthesis of N-Aryl-cis-aziridine Carboxylate Esters. *Angew. Chem.-Int. Edit.* **2017,** *56* (19), 5322-5326.

121. Miura, T.; Nakahashi, J.; Murakami, M., Enantioselective Synthesis of (E)-delta-Boryl-Substituted anti-Homoallylic Alcohols Using Palladium and a Chiral Phosphoric Acid. *Angew. Chem.-Int. Edit.* **2017,** *56* (24), 6989-6993.

122. Shimoda, Y.; Yamamoto, H., Chiral Phosphoric Acid-Catalyzed Kinetic Resolution via Amide Bond Formation. *J. Am. Chem. Soc.* **2017,** *139* (20), 6855-6858.

123. Cuadros, S.; Dell'Amico, L.; Melchiorre, P., Forging Fluorine-Containing Quaternary Stereocenters by a Light-Driven Organocatalytic Aldol Desymmetrization Process. *Angew. Chem.-Int. Edit.* **2017,** *56* (39), 11875-11879.

124. Miura, T.; Nakahashi, J.; Zhou, W.; Shiratori, Y.; Stewart, S. G.; Murakami, M., Enantioselective Synthesis of anti-1,2-Oxaborinan-3-enes from Aldehydes and 1,1-Di(boryl)alk-3-enes Using Ruthenium and Chiral Phosphoric Acid Catalysts. *J. Am. Chem. Soc.* **2017,** *139* (31), 10903-10908.

125. Klausen, R. S.; Kennedy, C. R.; Hyde, A. M.; Jacobsen, E. N., Chiral Thioureas Promote Enantioselective Pictet-Spengler Cyclization by Stabilizing Every Intermediate and Transition State in the Carboxylic Acid-Catalyzed Reaction. *J. Am. Chem. Soc.* **2017,** *139* (35), 12299-12309.

126. You, Y.; Zhang, L.; Cui, L. F.; Mi, X. L.; Luo, S. Z., Catalytic Asymmetric Mannich Reaction with N-Carbamoyl Imine Surrogates of Formaldehyde and Glyoxylate. *Angew. Chem.-Int. Edit.* **2017,** *56* (44), 13814-13818.

127. Min, C.; Lin, Y.; Seidel, D., Catalytic Enantioselective Synthesis of Mariline A and Related Isoindolinones through a Biomimetic Approach. *Angewandte Chemie International Edition* **2017,** *56* (48), 15353-15357.

128. Jiang, Y.; Thomson, R. J.; Schaus, S. E., Asymmetric Traceless Petasis Borono-Mannich Reactions of Enals: Reductive Transposition of Allylic Diazenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (52), 16631-16635.

129. Xia, Z. L.; Zheng, C.; Wang, S. G.; You, S. L., Catalytic Asymmetric Dearomatization of Indolyl Dihydropyridines through an Enamine Isomerization/Spirocyclization/Transfer Hydrogenation Sequence. *Angew. Chem.-Int. Edit.* **2018,** *57* (10), 2653-2656.

130. Uraguchi, D.; Yamada, K.; Sato, M.; Ooi, T., Catalyst-Directed Guidance of Sulfur-Substituted Enediolates to Stereoselective Carbon-Carbon Bond Formation with Aldehydes. *J. Am. Chem. Soc.* **2018,** *140* (15), 5110-5117.

131. Unhale, R. A.; Sadhu, M. M.; Ray, S. K.; Biswas, R. G.; Singh, V. K., A chiral Bronsted acid-catalyzed highly enantioselective Mannich-type reaction of -diazo esters with in situ generated N-acyl ketimines. *Chem. Commun.* **2018,** *54* (28), 3516-3519.

132. Hu, Q. P.; Kondoh, A.; Terada, M., Enantioselective direct Mannich-type reactions of 2-benzylpyridine N-oxides catalyzed by chiral bis(guanidino) iminophosphorane organosuperbase. *Chem. Sci.* **2018,** *9* (18), 4348-4351.

133. Liu, X. Y.; Liu, Y.; Chai, G. B.; Qiao, B. K.; Zhao, X. W.; Jiang, Z. Y., Organocatalytic Enantioselective Addition of alpha-Aminoalkyl Radicals to Isoquinolines. *Org. Lett.* **2018,** *20* (19), 6298-6301.

134. Chen, Z. C.; Chen, P.; Chen, Z.; Ouyang, Q.; Liang, H. P.; Du, W.; Chen, Y. C., Organocatalytic Enantioselective 1,3-Difunctionalizations of Morita-Baylis-Hillman Carbonates. *Org. Lett.* **2018,** *20* (19), 6279-6283.

135. Jarrige, L.; Glavac, D.; Levitre, G.; Retailleau, P.; Bernadat, G.; Neuville, L.; Masson, G., Chiral phosphoric acid-catalyzed enantioselective construction of structurally diverse benzothiazolopyrimidines. *Chem. Sci.* **2019,** *10* (13), 3765-3769.

136. Shen, M. L.; Shen, Y.; Wang, P. S., Merging Visible-Light Photoredox and Chiral Phosphate Catalysis for Asymmetric Friedel-Crafts Reaction with in Situ Generation of N-Acyl lmines. *Org. Lett.* **2019,** *21* (9), 2993-2997.

137. Feng, F. F.; Li, S.; Cheung, C. W.; Ma, J. A., Chiral beta-Keto Propargylamine Synthesis via Enantioselective Mannich Reaction of Enamides with C-Alkynyl N-Boc N,O-Acetals. *Org. Lett.* **2019,** *21* (20), 8419-8423.

138. Zhu, Z.; Odagi, M.; Zhao, C.; Abboud, K. A.; Kirm, H. U.; Saame, J.; Lõkov, M.; Leito, I.; Seidel, D., Highly Acidic Conjugate-Base-Stabilized Carboxylic Acids Catalyze Enantioselective oxa-Pictet–Spengler Reactions with Ketals. *Angewandte Chemie International Edition* **2020,** *59* (5), 2028-2032.

139. Thomson, C. J.; Barber, D. M.; Dixon, D. J., Catalytic Enantioselective Direct Aldol Addition of Aryl Ketones to α-Fluorinated Ketones. *Angewandte Chemie International Edition* **2020,** *59* (13), 5359-5364.

140. Shen, Y.; Shen, M.-L.; Wang, P.-S., Light-Mediated Chiral Phosphate Catalysis for Asymmetric Dicarbofunctionalization of Enamides. *ACS Catalysis* **2020,** *10* (15), 8247-8253.

141. Maskeri, M. A.; Brueckner, A. C.; Feoktistova, T.; O'Connor, M. J.; Walden, D. M.; Cheong, P. H.-Y.; Scheidt, K. A., Mechanism and origins of selectivity in the enantioselective oxa-Pictet–Spengler reaction: a cooperative catalytic complex from a hydrogen bond donor and chiral phosphoric acid. *Chem. Sci.* **2020,** *11* (33), 8736-8743.

142. Ma, C.; Sheng, F.-T.; Wang, H.-Q.; Deng, S.; Zhang, Y.-C.; Jiao, Y.; Tan, W.; Shi, F., Atroposelective Access to Oxindole-Based Axially Chiral Styrenes via the Strategy of Catalytic Kinetic Resolution. *J. Am. Chem. Soc.* **2020,** *142* (37), 15686-15696.

143. Zhang, L.; Zhu, R.; Feng, A.; Zhao, C.; Chen, L.; Feng, G.; Liu, L., Redox deracemization of β,γ-alkynyl α-amino esters. *Chem. Sci.* **2020,** *11* (17), 4444-4449.

144. Che, C.; Li, Y.-N.; Cheng, X.; Lu, Y.-N.; Wang, C.-J., Visible-Light-Enabled Enantioconvergent Synthesis of α-Amino Acid Derivatives via Synergistic Brønsted Acid/Photoredox Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (9), 4698-4704.

145. Zhao, F.; Shu, C.; Young, C. M.; Carpenter-Warren, C.; Slawin, A. M. Z.; Smith, A. D., Enantioselective Synthesis of α-Aryl-β2-Amino-Esters by Cooperative Isothiourea and Brønsted Acid Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (21), 11892-11900.

146. Kim, A.; Kim, A.; Park, S.; Kim, S.; Jo, H.; Ok, K. M.; Lee, S. K.; Song, J.; Kwon, Y., Catalytic and Enantioselective Control of the C–N Stereogenic Axis via the Pictet–Spengler Reaction. *Angewandte Chemie International Edition* **2021,** *60* (22), 12279-12283.

147. Zhu, C.; Mandrelli, F.; Zhou, H.; Maji, R.; List, B., Catalytic Asymmetric Synthesis of Unprotected β2-Amino Acids. *J. Am. Chem. Soc.* **2021,** *143* (9), 3312-3317.

148. He, Y.-P.; Wu, H.; Wang, Q.; Zhu, J., Catalytic Enantioselective Synthesis of Morpholinones Enabled by Aza-Benzilic Ester Rearrangement. *J. Am. Chem. Soc.* **2021,** *143* (19), 7320-7325.

149. Corti, V.; Riccioli, R.; Martinelli, A.; Sandri, S.; Fochi, M.; Bernardi, L., Stereodivergent entry to β-branched β-trifluoromethyl α-amino acid derivatives by sequential catalytic asymmetric reactions. *Chem. Sci.* **2021,** *12* (30), 10233-10241.

150. Kutateladze, D. A.; Jacobsen, E. N., Cooperative Hydrogen-Bond-Donor Catalysis with Hydrogen Chloride Enables Highly Enantioselective Prins Cyclization Reactions. *J. Am. Chem. Soc.* **2021,** *143* (48), 20077-20083.

151. Liang, H.; Ji, D.-S.; Xu, G.-Q.; Luo, Y.-C.; Zheng, H.; Xu, P.-F., Metal-free, visible-light induced enantioselective three-component dicarbofunctionalization and oxytrifluoromethylation of enamines via chiral phosphoric acid catalysis. *Chem. Sci.* **2022,** *13* (4), 1088-1094.

152. Chen, K.-W.; Chen, Z.-H.; Yang, S.; Wu, S.-F.; Zhang, Y.-C.; Shi, F., Organocatalytic Atroposelective Synthesis of N−N Axially Chiral Indoles and Pyrroles by De Novo Ring Formation. *Angewandte Chemie International Edition* **2022,** *61* (17), e202116829.

153. Andres, R.; Wang, Q.; Zhu, J., Catalytic Enantioselective Pictet–Spengler Reaction of α-Ketoamides Catalyzed by a Single H-Bond Donor Organocatalyst. *Angewandte Chemie International Edition* **2022,** *61* (19), e202201788.

154. Tokuhiro, Y.; Yoshikawa, K.; Murayama, S.; Nanjo, T.; Takemoto, Y., Highly Stereoselective, Organocatalytic Mannich-type Addition of Glyoxylate Cyanohydrin: A Versatile Building Block for the Asymmetric Synthesis of β-Amino-α-ketoacids. *ACS Catalysis* **2022,** *12* (9), 5292-5304.

155. Kutateladze, D. A.; Wagen, C. C.; Jacobsen, E. N., Chloride-Mediated Alkene Activation Drives Enantioselective Thiourea and Hydrogen Chloride Co-Catalyzed Prins Cyclizations. *J. Am. Chem. Soc.* **2022,** *144* (34), 15812-15824.

156. Dašková, V.; Padín, D.; Feringa, B. L., Turning Enantiomeric Relationships into Diastereomeric Ones: Self-Resolving α-Ureidophosphonates and Their Organocatalytic Enantioselective Synthesis. *J. Am. Chem. Soc.* **2022,** *144* (51), 23603-23613.

157. Che, C.; Lu, Y.-N.; Wang, C.-J., Enantio- and Diastereoselective De Novo Synthesis of 3-Substituted Proline Derivatives via Cooperative Photoredox/Brønsted Acid Catalysis and Epimerization. *J. Am. Chem. Soc.* **2023,** *145* (5), 2779-2786.

158. He, Y.-P.; Quan, R.; Li, X.-Z.; Zhu, J.; Wu, H., Asymmetric Construction of α,α-Disubstituted Piperazinones Enabled by Benzilic Amide Rearrangement. *Angewandte Chemie International Edition* **2023,** *62* (18), e202217954.

159. Obregón, E. B.; Rost, L. G.; Kocemba, I. R.; Kristensen, A.; McLeod, D. A.; Jørgensen, K. A., Enantioselective (3+2) Annulation of Donor-Acceptor Cyclopropanes with Aldehydes and Ketones Catalyzed by Brønsted Bases. *Angewandte Chemie International Edition* **2024,** *63* (42), e202410524.

4.1.2 Conjugate Addition

1. Horstmann, T. E.; Guerin, D. J.; Miller, S. J., Asymmetric conjugate addition of azide to alpha,beta-unsaturated carbonyl compounds catalyzed by simple peptides. *Angew. Chem.-Int. Edit.* **2000,** *39* (20), 3635-3638.

2. Guerin, D. J.; Miller, S. J., Asymmetric azidation-cycloaddition with open-chain peptide-based catalysts. A sequential enantioselective route to triazoles. *J. Am. Chem. Soc.* **2002,** *124* (10), 2134-2136.

3. Okino, T.; Hoashi, Y.; Takemoto, Y., Enantioselective Michael reaction of malonates to nitroolefins catalyzed by bifunctional organocatalysts. *J. Am. Chem. Soc.* **2003,** *125* (42), 12672-12673.

4. Li, H. M.; Wang, Y.; Tang, L.; Deng, L., Highly enantioselective conjugate addition of malonate and beta-ketoester to nitroalkenes: Asymmetric C-C bond formation with new bifunctional organic catalysts based on cinchona alkaloids. *J. Am. Chem. Soc.* **2004,** *126* (32), 9906-9907.

5. Ooi, T.; Ohara, D.; Tamura, M.; Maruoka, K., Design of new chiral phase-transfer catalysts with dual functions for highly enantioselective epoxidation of alpha,beta-unsaturated ketones. *J. Am. Chem. Soc.* **2004,** *126* (22), 6844-6845.

6. Hoashi, Y.; Okino, T.; Takemoto, Y., Enantioselective Michael addition to alpha,beta-unsaturated imides catalyzed by a bifunctional organocatalyst. *Angew. Chem.-Int. Edit.* **2005,** *44* (26), 4032-4035.

7. Li, H. M.; Wang, Y.; Tang, L.; Wu, F. H.; Liu, X. F.; Guo, C. Y.; Foxman, B. M.; Deng, L., Stereocontrolled creation of adjacent quaternary and tertiary stereocenters by a catalytic conjugate addition. *Angew. Chem.-Int. Edit.* **2005,** *44* (1), 105-108.

8. McCooey, S. H.; Connon, S. J., Urea- and thiourea-substituted cinchona alkaloid derivatives as highly efficient bifunctional organocatalysts for the asymmetric addition of malonate to nitroalkenes: Inversion of configuration at C9 dramatically improves catalyst performance. *Angew. Chem.-Int. Edit.* **2005,** *44* (39), 6367-6370.

9. Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X. N.; Takemoto, Y., Enantio- and diastereoselective Michael reaction of 1,3-dicarbonyl compounds to nitroolefins catalyzed by a bifunctional thiourea. *J. Am. Chem. Soc.* **2005,** *127* (1), 119-125.

10. Herrera, R. P.; Sgarzani, V.; Bernardi, L.; Ricci, A., Catalytic enantioselective Friedel-Crafts alkylation of indoles with nitroalkenes by using a simple thiourea organocatalyst. *Angew. Chem.-Int. Edit.* **2005,** *44* (40), 6576-6579.

11. Lubkoll, J.; Wennemers, H., Mimicry of polyketide synthases - Enantioselective 1,4-addition reactions of malonic acid half-thioesters to nitroolefins. *Angew. Chem.-Int. Edit.* **2007,** *46* (36), 6841-6844.

12. Perdicchia, D.; Jorgensen, K. A., Asymmetric aza-michael reactions catalyzed by cinchona alkaloids. *J. Org. Chem.* **2007,** *72* (9), 3565-3568.

13. Sibi, M. P.; Itoh, K., Organocatalysis in conjugate amine additions. Synthesis of beta-amino acid derivatives. *J. Am. Chem. Soc.* **2007,** *129* (26), 8064-+.

14. Li, D. R.; Murugan, A.; Falck, J. R., Enantioselective, organocatalytic oxy-michael addition to gamma/delta-hydroxy-alpha,beta-enones: Boronate-amine complexes as chiral hydroxide synthons. *J. Am. Chem. Soc.* **2008,** *130* (1), 46-+.

15. Wang, J.; Xie, H. X.; Li, H.; Zu, L. S.; Wang, W., A highly stereoselective hydrogen-bond-mediated Michael-Michael cascade process through dynamic kinetic resolution. *Angew. Chem.-Int. Edit.* **2008,** *47* (22), 4177-4179.

16. Peng, F. Z.; Shao, Z. H.; Fan, B. M.; Song, H.; Li, G. P.; Zhang, H. B., Organocatalytic enantioselective Michael addition of 2,4-pentandione to nitroalkenes promoted by bifunctional thioureas with central and axial chiral elements. *J. Org. Chem.* **2008,** *73* (13), 5202-5205.

17. Li, P. F.; Wang, Y. C.; Liang, X. M.; Ye, J. X., Asymmetric multifunctional organocatalytic Michael addition of nitroalkanes to alpha,beta-unsaturated ketones. *Chem. Commun.* **2008,** (28), 3302-3304.

18. Rabalakos, C.; Wulff, W. D., Enantioselective organocatalytic direct Michael addition of nitroalkanes to nitroalkenes promoted by a unique bifunctional DMAP-thiourea. *J. Am. Chem. Soc.* **2008,** *130* (41), 13524-+.

19. Malerich, J. P.; Hagihara, K.; Rawal, V. H., Chiral Squaramide Derivatives are Excellent Hydrogen Bond Donor Catalysts. *J. Am. Chem. Soc.* **2008,** *130* (44), 14416-+.

20. Gioia, C.; Hauville, A.; Bernardi, L.; Fini, F.; Ricci, A. In *Organocatalytic Asymmetric Diels-Alder Reactions of 3-Vinylindoles*, International Sympsium on Creation and Control of Advanced Selective Catalysis, Kyoto, JAPAN, 2008; Kyoto, JAPAN, 2008; pp 9236-9239.

21. Ganesh, M.; Seidel, D., Catalytic Enantioselective Additions of Indoles to Nitroalkenes. *J. Am. Chem. Soc.* **2008,** *130* (49), 16464-+.

22. Simon, L.; Goodman, J. M., What is the mechanism of amine conjugate additions to pyrazole crotonate catalyzed by thiourea catalysts? *Org. Biomol. Chem.* **2009,** *7* (3), 483-487.

23. Luo, J.; Xu, L. W.; Hay, R. A. S.; Lu, Y. X., Asymmetric Michael Addition Mediated by Novel Cinchona Alkaloid-Derived Bifunctional Catalysts Containing Sulfonamides. *Org. Lett.* **2009,** *11* (2), 437-440.

24. Liu, Y.; Sun, B. F.; Wang, B. M.; Wakem, M.; Deng, L., Catalytic Asymmetric Conjugate Addition of Simple Alkyl Thiols to alpha,beta-Unsaturated N-Acylated Oxazolidin-2-ones with Bifunctional Catalysts. *J. Am. Chem. Soc.* **2009,** *131* (2), 418-+.

25. Li, P. F.; Wen, S. G.; Yu, F.; Liu, Q. X.; Li, W. J.; Wang, Y. C.; Liang, X. M.; Ye, J. X., Enantioselective Organocatalytic Michael Addition of Malonates to alpha,beta-Unsaturated Ketones. *Org. Lett.* **2009,** *11* (3), 753-756.

26. Zhong, C.; Chen, Y. F.; Petersen, J. L.; Akhmedov, N. G.; Shi, X. D., Enantioselective Intermolecular Crossed-Conjugate Additions between Nitroalkenes and alpha,beta-Enals through a Dual Activation Strategy. *Angew. Chem.-Int. Edit.* **2009,** *48* (7), 1279-1282.

27. Dong, X. Q.; Teng, H. L.; Wang, C. J., Highly Enantioselective Direct Michael Addition of Nitroalkanes to Nitroalkenes Catalyzed by Amine-Thiourea Bearing Multiple Hydrogen-Bonding Donors. *Org. Lett.* **2009,** *11* (6), 1265-1268.

28. Tan, B.; Zeng, X. F.; Lu, Y. P.; Chua, P. J.; Zhong, G. F., Rational Design of Organocatalyst: Highly Stereoselective Michael Addition of Cyclic Ketones to Nitroolefins. *Org. Lett.* **2009,** *11* (9), 1927-1930.

29. Jiang, Z. Y.; Pan, Y. H.; Zhao, Y. J.; Ma, T.; Lee, R.; Yang, Y. Y.; Huang, K. W.; Wong, M. W.; Tan, C. H., Synthesis of a Chiral Quaternary Carbon Center Bearing a Fluorine Atom: Enantio- and Diastereoselective Guanidine-Catalyzed Addition of Fluorocarbon Nucleophiles. *Angew. Chem.-Int. Edit.* **2009,** *48* (20), 3627-3631.

30. Akiyanza, T.; Katoh, T.; Mori, K., Enantioselective Robinson-Type Annulation Reaction Catalyzed by Chiral Phosphoric Acids. *Angew. Chem.-Int. Edit.* **2009,** *48* (23), 4226-4228.

31. Inokuma, T.; Takasu, K.; Sakaeda, T.; Takemoto, Y., Hydroxyl Group-Directed Organocatalytic Asymmetric Michael Addition of alpha,beta-Unsaturated Ketones with Alkenylboronic Acids. *Org. Lett.* **2009,** *11* (11), 2425-2428.

32. Soh, J. Y. T.; Tan, C. H., Amino-Indanol Catalyzed Enantioselective Reactions of 3-Hydroxy-2-Pyridones. *J. Am. Chem. Soc.* **2009,** *131* (20), 6904-+.

33. Yu, Z. P.; Liu, X. H.; Zhou, L.; Lin, L. L.; Feng, X. M., Bifunctional Guanidine via an Amino Amide Skeleton for Asymmetric Michael Reactions of beta-Ketoesters with Nitroolefins: A Concise Synthesis of Bicyclic beta-Amino Acids. *Angew. Chem.-Int. Edit.* **2009,** *48* (28), 5195-5198.

34. Bui, T.; Syed, S.; Barbas, C. F., Thiourea-Catalyzed Highly Enantio- and Diastereoselective Additions of Oxindoles to Nitroolefins: Application to the Formal Synthesis of (+)-Physostigmine. *J. Am. Chem. Soc.* **2009,** *131* (25), 8758-+.

35. Kimmel, K. L.; Robak, M. T.; Ellman, J. A., Enantioselective Addition of Thioacetic Acid to Nitroalkenes via N-Sulfinyl Urea Organocatalysis. *J. Am. Chem. Soc.* **2009,** *131* (25), 8754-+.

36. Dickmeiss, G.; De Sio, V.; Udmark, J.; Poulsen, T. B.; Marcos, V.; Jorgensen, K. A., Organocatalytic Asymmetric Desymmetrization-Fragmentation of Cyclic Ketones. *Angew. Chem.-Int. Edit.* **2009,** *48* (36), 6650-6653.

37. Lu, H. H.; Zhang, F. G.; Meng, X. G.; Duan, S. W.; Xiao, W. J., Enantioselective Michael Reactions of beta,beta-Disubstituted Nitroalkenes: A New Approach to beta(2,2)-Amino Acids with Hetero-Quaternary Stereocenters. *Org. Lett.* **2009,** *11* (17), 3946-3949.

38. Nodes, W. J.; Nutt, D. R.; Chippindale, A. M.; Cobb, A. J. A., Enantioselective Intramolecular Michael Addition of Nitronates onto Conjugated Esters: Access to Cyclic gamma-Amino Acids with up to Three Stereocenters. *J. Am. Chem. Soc.* **2009,** *131* (44), 16016-+.

39. Yang, Y. Q.; Chai, Z.; Wang, H. F.; Chen, X. K.; Cui, H. F.; Zheng, C. W.; Xiao, H.; Li, P.; Zhao, G., Chiral Primary-Secondary Diamines Catalyzed Michael-Aldol-Dehydration Reaction between Benzoylacetates and alpha,beta-Unsaturated Ketones: Highly Enantioselective Synthesis of Functionalized Chiral Cyclohexenones. *Chem.-Eur. J.* **2009,** *15* (48), 13295-13298.

40. Mori, K.; Katoh, T.; Suzuki, T.; Noji, T.; Yamanaka, M.; Akiyama, T., Chiral Phosphoric Acid Catalyzed Desymmetrization of meso-1,3-Diones: Asymmetric Synthesis of Chiral Cyclohexenones. *Angew. Chem.-Int. Edit.* **2009,** *48* (51), 9652-9654.

41. Wang, Y.; Han, R. G.; Zhao, Y. L.; Yang, S.; Xu, P. F.; Dixon, D. J., Asymmetric Organocatalytic Relay Cascades: Catalyst-Controlled Stereoisomer Selection in the Synthesis of Functionalized Cyclohexanes. *Angew. Chem.-Int. Edit.* **2009,** *48* (52), 9834-9838.

42. Li, X.; Deng, H.; Zhang, B.; Li, J. Y.; Zhang, L.; Luo, S. Z.; Cheng, J. P., Physical Organic Study of Structure-Activity-Enantioselectivity Relationships in Asymmetric Bifunctional Thiourea Catalysis: Hints for the Design of New Organocatalysts. *Chem.-Eur. J.* **2010,** *16* (2), 450-455.

43. Zhu, Y.; Malerich, J. P.; Rawal, V. H., Squaramide-Catalyzed Enantioselective Michael Addition of Diphenyl Phosphite to Nitroalkenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (1), 153-156.

44. Wei, Q.; Gong, L. Z., Organocatalytic Asymmetric Formal 4+2 Cycloaddition for the Synthesis of Spiro 4-cyclohexanone-1,3 '-oxindoline Derivatives in High Optical Purity. *Org. Lett.* **2010,** *12* (5), 1008-1011.

45. Murai, K.; Fukushima, S.; Hayashi, S.; Takahara, Y.; Fujioka, H., C-3-Symmetric Chiral Trisimidazoline: Design and Application to Organocatalyst. *Org. Lett.* **2010,** *12* (5), 964-966.

46. Liu, C.; Lu, Y. X., Primary Amine/(+)-CSA Salt-Promoted Organocatalytic Conjugate Addition of Nitro Esters to Enones. *Org. Lett.* **2010,** *12* (10), 2278-2281.

47. Tan, B.; Lu, Y. P.; Zeng, X. F.; Chua, P. J.; Zhong, G. F., Facile Domino Access to Chiral Bicyclo 3.2.1 octanes and Discovery of a New Catalytic Activation Mode. *Org. Lett.* **2010,** *12* (12), 2682-2685.

48. Gu, Q.; Rong, Z. Q.; Zheng, C.; You, S. L., Desymmetrization of Cyclohexadienones via Bronsted Acid-Catalyzed Enantioselective Oxo-Michael Reaction. *J. Am. Chem. Soc.* **2010,** *132* (12), 4056-+.

49. Matoba, K.; Kawai, H.; Furukawa, T.; Kusuda, A.; Tokunaga, E.; Nakamura, S.; Shiro, M.; Shibata, N., Enantioselective Synthesis of Trifluoromethyl-Substituted 2-Isoxazolines: Asymmetric Hydroxylamine/Enone Cascade Reaction. *Angew. Chem.-Int. Edit.* **2010,** *49* (33), 5762-5766.

50. Sohtome, Y.; Shin, B.; Horitsugi, N.; Takagi, R.; Noguchi, K.; Nagasawa, K., Entropy-Controlled Catalytic Asymmetric 1,4-Type Friedel-Crafts Reaction of Phenols Using Conformationally Flexible Guanidine/Bisthiourea Organocatalyst. *Angew. Chem.-Int. Edit.* **2010,** *49* (40), 7299-7303.

51. Zhu, Q. A.; Lu, Y. X., Stereocontrolled Creation of All-Carbon Quaternary Stereocenters by Organocatalytic Conjugate Addition of Oxindoles to Vinyl Sulfone. *Angew. Chem.-Int. Edit.* **2010,** *49* (42), 7753-7756.

52. Wang, X. F.; Hua, Q. L.; Cheng, Y.; An, X. L.; Yang, Q. Q.; Chen, J. R.; Xiao, W. J., Organocatalytic Asymmetric Sulfa-Michael/Michael Addition Reactions: A Strategy for the Synthesis of Highly Substituted Chromans with a Quaternary Stereocenter. *Angew. Chem.-Int. Edit.* **2010,** *49* (45), 8379-8383.

53. He, P.; Liu, X. H.; Shi, J. A.; Lin, L. L.; Feng, X. M., Organocatalytic Sequential Michael Reactions: Stereoselective Synthesis of Multifunctionalized Tetrahydroindan Derivatives. *Org. Lett.* **2011,** *13* (5), 936-939.

54. Pesciaioli, F.; Righi, P.; Mazzanti, A.; Bartoli, G.; Bencivenni, G., Organocatalytic Michael-Alkylation Cascade: The Enantioselective Nitrocyclopropanation of Oxindoles. *Chem.-Eur. J.* **2011,** *17* (10), 2842-2845.

55. Tan, B.; Candeias, N. R.; Barbas, C. F., Construction of bispirooxindoles containing three quaternary stereocentres in a cascade using a single multifunctional organocatalyst. *Nat. Chem.* **2011,** *3* (6), 473-477.

56. Moccia, M.; Fini, F.; Scagnetti, M.; Adamo, M. F. A., Catalytic Enantioselective Addition of Sodium Bisulfite to Chalcones. *Angew. Chem.-Int. Edit.* **2011,** *50* (30), 6893-6895.

57. Zhao, Q. Y.; Pei, C. K.; Guan, X. Y.; Shi, M., Enantioselective Intermolecular Rauhut-Currier Reaction of Electron-Deficient Allenes with Maleimides. *Adv. Synth. Catal.* **2011,** *353* (11-12), 1973-1979.

58. Hatcher, J. M.; Kohler, M. C.; Coltart, D. M., Catalytic Asymmetric Addition of Thiols to Nitrosoalkenes Leading to Chiral Non-Racemic alpha-Sulfenyl Ketones. *Org. Lett.* **2011,** *13* (15), 3810-3813.

59. Liao, Y. H.; Liu, X. L.; Wu, Z. J.; Du, X. L.; Zhang, X. M.; Yuan, W. C., Thiourea-Catalyzed Highly Diastereo- and Enantioselective Conjugate Additions of alpha-Substituted Cyanoacetates to Maleimides: Efficient Construction of Vicinal Quaternary-Tertiary Stereocenters. *Adv. Synth. Catal.* **2011,** *353* (10), 1720-1728.

60. Gu, Q.; You, S. L., Desymmetrization of cyclohexadienones via cinchonine derived thiourea-catalyzed enantioselective aza-Michael reaction and total synthesis of (-)-Mesembrine. *Chem. Sci.* **2011,** *2* (8), 1519-1522.

61. Bartelson, K. J.; Singh, R. P.; Foxman, B. M.; Deng, L., Catalytic asymmetric 4+2 additions with aliphatic nitroalkenes. *Chem. Sci.* **2011,** *2* (10), 1940-1944.

62. Tan, B.; Hernandez-Torres, G.; Barbas, C. F., Highly Efficient Hydrogen-Bonding Catalysis of the Diels-Alder Reaction of 3-Vinylindoles and Methyleneindolinones Provides Carbazolespirooxindole Skeletons. *J. Am. Chem. Soc.* **2011,** *133* (32), 12354-12357.

63. Inokuma, T.; Furukawa, M.; Uno, T.; Suzuki, Y.; Yoshida, K.; Yano, Y.; Matsuzaki, K.; Takemoto, Y., Bifunctional Hydrogen-Bond Donors That Bear a Quinazoline or Benzothiadiazine Skeleton for Asymmetric Organocatalysis. *Chem.-Eur. J.* **2011,** *17* (37), 10470-10477.

64. He, L.; Chen, X. H.; Wang, D. N.; Luo, S. W.; Zhang, W. Q.; Yu, J.; Ren, L.; Gong, L. Z., Binaphthol-Derived Bisphosphoric Acids Serve as Efficient Organocatalysts for Highly Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylides to Electron-Deficient Olefins. *J. Am. Chem. Soc.* **2011,** *133* (34), 13504-13518.

65. Sternativo, S.; Calandriello, A.; Costantino, F.; Testaferri, L.; Tiecco, M.; Marini, F., A Highly Enantioselective One-Pot Synthesis of Spirolactones by an Organocatalyzed Michael Addition/Cyclization Sequence. *Angew. Chem.-Int. Edit.* **2011,** *50* (40), 9382-9385.

66. Provencher, B. A.; Bartelson, K. J.; Liu, Y.; Foxman, B. M.; Deng, L., Structural Study-Guided Development of Versatile Phase-Transfer Catalysts for Asymmetric Conjugate Additions of Cyanide. *Angew. Chem.-Int. Edit.* **2011,** *50* (45), 10565-10569.

67. Terada, M.; Moriya, K.; Kanomata, K.; Sorimachi, K., Chiral Bronsted Acid Catalyzed Stereoselective Addition of Azlactones to 3-Vinylindoles for Facile Access to Enantioenriched Tryptophan Derivatives. *Angew. Chem.-Int. Edit.* **2011,** *50* (52), 12586-12590.

68. Kimmel, K. L.; Weaver, J. D.; Ellman, J. A., Enantio- and diastereoselective addition of cyclohexyl Meldrum's acid to beta- and alpha,beta-disubstituted nitroalkenes via N-sulfinyl urea catalysis. *Chem. Sci.* **2012,** *3* (1), 121-125.

69. Lattanzi, A.; De Fusco, C.; Russo, A.; Poater, A.; Cavallo, L., Hexafluorobenzene: a powerful solvent for a noncovalent stereoselective organocatalytic Michael addition reaction. *Chem. Commun.* **2012,** *48* (11), 1650-1652.

70. Ling, J. B.; Su, Y.; Zhu, H. L.; Wang, G. Y.; Xu, P. F., Hydrogen-Bond-Mediated Cascade Reaction Involving Chalcones: Facile Synthesis of Enantioenriched Trisubstituted Tetrahydrothiophenes. *Org. Lett.* **2012,** *14* (4), 1090-1093.

71. Li, X.; Zhang, Y. Y.; Xue, X. S.; Jin, J. L.; Tan, B. X.; Liu, C.; Dong, N.; Cheng, J. P., Asymmetric Michael Addition Reactions between 3-Substituted Benzofuran-2(3H)-ones and 1,1-Bis(phenylsulfonyl)ethylene Catalyzed by Bifunctional Catalysts Containing Tertiary Amine and Thiourea Groups. *European Journal of Organic Chemistry* **2012,** (9), 1774-1782.

72. Palacio, C.; Connon, S. J., A novel C-5 ' substituted cinchona alkaloid-derived catalyst promotes additions of alkyl thiols to nitroolefins with excellent enantioselectivity. *Chem. Commun.* **2012,** *48* (23), 2849-2851.

73. Bandar, J. S.; Lambert, T. H., Enantioselective Bronsted Base Catalysis with Chiral Cyclopropenimines. *J. Am. Chem. Soc.* **2012,** *134* (12), 5552-5555.

74. Takizawa, S.; Tue, M. N. N.; Grossmann, A.; Enders, D.; Sasai, H., Enantioselective Synthesis of alpha-Alkylidene-gamma-Butyrolactones: Intramolecular Rauhut-Currier Reaction Promoted by Acid/Base Organocatalysts. *Angew. Chem.-Int. Edit.* **2012,** *51* (22), 5423-5426.

75. Curti, C.; Rassu, G.; Zambrano, V.; Pinna, L.; Pelosi, G.; Sartori, A.; Battistini, L.; Zanardi, F.; Casiraghi, G., Bifunctional Cinchona Alkaloid/Thiourea Catalyzes Direct and Enantioselective Vinylogous Michael Addition of 3-Alkylidene Oxindoles to Nitroolefins. *Angew. Chem.-Int. Edit.* **2012,** *51* (25), 6200-6204.

76. Kimmel, K. L.; Weaver, J. D.; Lee, M.; Ellman, J. A., Catalytic Enantioselective Protonation of Nitronates Utilizing an Organocatalyst Chiral Only at Sulfur. *J. Am. Chem. Soc.* **2012,** *134* (22), 9058-9061.

77. Dou, X. W.; Lu, Y. X., Diastereodivergent Synthesis of 3-Spirocyclopropyl-2-oxindoles through Direct Enantioselective Cyclopropanation of Oxindoles. *Chem.-Eur. J.* **2012,** *18* (27), 8315-8319.

78. Tripathi, C. B.; Kayal, S.; Mukherjee, S., Catalytic Asymmetric Synthesis of alpha,beta-Disubstituted alpha,gamma-Diaminophosphonic Acid Precursors by Michael Addition of alpha-Substituted Nitrophosphonates to Nitroolefins. *Org. Lett.* **2012,** *14* (13), 3296-3299.

79. Zhong, F. R.; Luo, J.; Chen, G. Y.; Dou, X. W.; Lu, Y. X., Highly Enantioselective Regiodivergent Allylic Alkylations of MBH Carbonates with Phthalides. *J. Am. Chem. Soc.* **2012,** *134* (24), 10222-10227.

80. Liu, X. W.; Yan, Y.; Wang, Y. Q.; Wang, C.; Sun, J., Highly Enantioselective Reduction of beta-Amino Nitroolefins with a Simple N-Sulfinyl Urea as Bifunctional Catalyst. *Chem.-Eur. J.* **2012,** *18* (30), 9204-9207.

81. Zhang, W.; Tan, D.; Lee, R.; Tong, G. H.; Chen, W. C.; Qi, B. J.; Huang, K. W.; Tan, C. H.; Jiang, Z. Y., Highly Enantio- and Diastereoselective Reactions of gamma-Substituted Butenolides Through Direct Vinylogous Conjugate Additions. *Angew. Chem.-Int. Edit.* **2012,** *51* (40), 10069-10073.

82. Loh, C. C. J.; Raabe, G.; Enders, D., Enantioselective Synthesis of Tetrahydrocarbazoles through a Michael Addition/Ciamician-Plancher Rearrangement Sequence: Asymmetric Synthesis of a Potent Constrained Analogue of MS-245. *Chem.-Eur. J.* **2012,** *18* (42), 13250-13254.

83. Pei, C. K.; Jiang, Y.; Wei, Y.; Shi, M., Enantioselective Synthesis of Highly Functionalized Phosphonate-Substituted Pyrans or Dihydropyrans Through Asymmetric 4+2 Cycloaddition of beta,gamma-Unsaturated alpha-Ketophosphonates with Allenic Esters. *Angew. Chem.-Int. Edit.* **2012,** *51* (45), 11328-11332.

84. Noole, A.; Sucman, N. S.; Kabeshov, M. A.; Kanger, T.; Macaev, F. Z.; Malkov, A. V., Highly Enantio- and Diastereoselective Generation of Two Quaternary Centers in Spirocyclopropanation of Oxindole Derivatives. *Chem.-Eur. J.* **2012,** *18* (47), 14929-14933.

85. Akagawa, K.; Kudo, K., Construction of an All-Carbon Quaternary Stereocenter by the Peptide-Catalyzed Asymmetric Michael Addition of Nitromethane to beta-Disubstituted alpha,beta-Unsaturated Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (51), 12786-12789.

86. Xiao, X.; Liu, X. H.; Dong, S. X.; Cai, Y. F.; Lin, L. L.; Feng, X. M., Asymmetric Synthesis of 2,3-Dihydroquinolin-4-one Derivatives Catalyzed by a Chiral Bisguanidium Salt. *Chem.-Eur. J.* **2012,** *18* (50), 15922-15926.

87. Zhang, Z. H.; Antilla, J. C., Enantioselective Construction of Pyrroloindolines Catalyzed by Chiral Phosphoric Acids: Total Synthesis of (-)-Debromoflustramine B. *Angew. Chem.-Int. Edit.* **2012,** *51* (47), 11778-11782.

88. Das, U.; Tsai, Y. L.; Lin, W. W., An efficient organocatalytic enantioselective synthesis of spironitrocyclopropanes. *Org. Biomol. Chem.* **2013,** *11* (1), 44-47.

89. Zhong, F. R.; Dou, X. W.; Han, X. Y.; Yao, W. J.; Zhu, Q.; Meng, Y. Z.; Lu, Y. X., Chiral Phosphine Catalyzed Asymmetric Michael Addition of Oxindoles. *Angew. Chem.-Int. Edit.* **2013,** *52* (3), 943-947.

90. Hintermann, L.; Ackerstaff, J.; Boeck, F., Inner Workings of a Cinchona Alkaloid Catalyzed Oxa-Michael Cyclization: Evidence for a Concerted Hydrogen-Bond-Network Mechanism. *Chem.-Eur. J.* **2013,** *19* (7), 2311-2321.

91. Chen, L. A.; Xu, W. C.; Huang, B.; Ma, J. J.; Wang, L.; Xi, J. W.; Harms, K.; Gong, L.; Meggers, E., Asymmetric Catalysis with an Inert Chiral-at-Metal Iridium Complex. *J. Am. Chem. Soc.* **2013,** *135* (29), 10598-10601.

92. Dou, X. W.; Yao, W. J.; Zhou, B.; Lu, Y. X., Asymmetric synthesis of 3-spirocyclopropyl-2-oxindoles via intramolecular trapping of chiral aza-ortho-xylylene. *Chem. Commun.* **2013,** *49* (80), 9224-9226.

93. Jiang, X. X.; Liu, L. P.; Zhang, P. P.; Zhong, Y.; Wang, R., Catalytic Asymmetric beta,gamma Activation of alpha,beta-Unsaturated gamma-Butyrolactams: Direct Approach to beta,gamma-Functionalized Dihydropyranopyrrolidin-2-ones. *Angew. Chem.-Int. Edit.* **2013,** *52* (43), 11329-11333.

94. Fukata, Y.; Asano, K.; Matsubara, S., Procedure-Controlled Enantioselectivity Switch in Organocatalytic 2-Oxazolidinone Synthesis. *J. Am. Chem. Soc.* **2013,** *135* (33), 12160-12163.

95. He, L.; Laurent, G.; Retailleau, P.; Folleas, B.; Brayer, J. L.; Masson, G., Highly Enantioselective Aza-Diels-Alder Reaction of 1-Azadienes with Enecarbamates Catalyzed by Chiral Phosphoric Acids. *Angew. Chem.-Int. Edit.* **2013,** *52* (42), 11088-11091.

96. Kobayashi, Y.; Taniguchi, Y.; Hayama, N.; Inokuma, T.; Takemoto, Y., A Powerful Hydrogen-Bond-Donating Organocatalyst for the Enantioselective Intramolecular Oxa-Michael Reaction of alpha,beta-Unsaturated Amides and Esters. *Angew. Chem.-Int. Edit.* **2013,** *52* (42), 11114-11118.

97. Jin, Z. C.; Xu, J. F.; Yang, S.; Song, B. A.; Chi, Y. R., Enantioselective Sulfonation of Enones with Sulfonyl Imines by Cooperative N-Heterocyclic-Carbene/Thiourea/Tertiary-Amine Multicatalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (47), 12354-12358.

98. Buyck, T.; Wang, Q.; Zhu, J. P., Catalytic Enantioselective Michael Addition of alpha-Aryl-alpha-Isocyanoacetates to Vinyl Selenone: Synthesis of alpha,alpha-Disubstituted alpha-Amino Acids and (+)- and (-)-Trigonoliimine A. *Angew. Chem.-Int. Edit.* **2013,** *52* (48), 12714-12718.

99. Yang, K. S.; Nibbs, A. E.; Turkmen, Y. E.; Rawal, V. H., Squaramide-Catalyzed Enantioselective Michael Addition of Masked Acyl Cyanides to Substituted Enones. *J. Am. Chem. Soc.* **2013,** *135* (43), 16050-16053.

100. Diosdado, S.; Etxabe, J.; Izquierdo, J.; Landa, A.; Mielgo, A.; Olaizola, I.; Lopez, R.; Palomo, C., Catalytic Enantioselective Synthesis of Tertiary Thiols From 5H-Thiazol-4-ones and Nitroolefins: Bifunctional Ureidopeptide-Based Bronsted Base Catalysis. *Angew. Chem.-Int. Edit.* **2013,** *52* (45), 11846-11851.

101. Min, C.; Mittal, N.; Sun, D. X.; Seidel, D., Conjugate-Base-Stabilized Bronsted Acids as Asymmetric Catalysts: Enantioselective Povarov Reactions with Secondary Aromatic Amines. *Angew. Chem.-Int. Edit.* **2013,** *52* (52), 14084-14088.

102. Qian, H.; Yu, X. Z.; Zhang, J. L.; Sun, J. W., Organocatalytic Enantioselective Synthesis of 2,3-Allenoates by Intermolecular Addition of Nitroalkanes to Activated Enynes. *J. Am. Chem. Soc.* **2013,** *135* (48), 18020-18023.

103. Duque, M. D. S.; Basle, O.; Genisson, Y.; Plaquevent, J. C.; Bugaut, X.; Constantieux, T.; Rodriguez, J., Enantioselective Organocatalytic Multicomponent Synthesis of 2,6-Diazabicyclo 2.2.2 octanones. *Angew. Chem.-Int. Edit.* **2013,** *52* (52), 14143-14146.

104. Manna, M. S.; Mukherjee, S., Remarkable influence of secondary catalyst site on enantioselective desymmetrization of cyclopentenedione. *Chem. Sci.* **2014,** *5* (4), 1627-1633.

105. Tian, X.; Hofmann, N.; Melchiorre, P., Asymmetric Vinylogous Diels-Alder Reactions Catalyzed by a Chiral Phosphoric Acid. *Angew. Chem.-Int. Edit.* **2014,** *53* (11), 2997-3000.

106. Manoni, F.; Connon, S. J., Catalytic Asymmetric Tamura Cycloadditions. *Angew. Chem.-Int. Edit.* **2014,** *53* (10), 2628-2632.

107. McNulty, J.; Zepeda-Velazquez, C., Enantioselective Organocatalytic Michael/Aldol Sequence: Anticancer Natural Product (+)-trans-Dihydrolycoricidine. *Angew. Chem.-Int. Edit.* **2014,** *53* (32), 8450-8454.

108. Liao, L.; Shu, C.; Zhang, M.; Liao, Y.; Hu, X.; Zhang, Y.; Wu, Z.; Yuan, W.; Zhang, X., Highly Enantioselective 3+2 Coupling of Indoles with Quinone Monoimines Promoted by a Chiral Phosphoric Acid. *Angew. Chem.-Int. Edit.* **2014,** *53* (39), 10471-10475.

109. Ma, J.; Ding, X.; Hu, Y.; Huang, Y.; Gong, L.; Meggers, E., Metal-templated chiral Bronsted base organocatalysis. *Nature Communications* **2014,** *5*.

110. Phelan, J. P.; Patel, E. J.; Ellman, J. A., Catalytic Enantioselective Addition of Thioacids to Trisubstituted Nitroalkenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (42), 11329-11332.

111. Sun, Z.; Winschel, G. A.; Zimmerman, P. M.; Nagorny, P., Enantioselective Synthesis of Piperidines through the Formation of Chiral Mixed Phosphoric Acid Acetals: Experimental and Theoretical Studies. *Angew. Chem.-Int. Edit.* **2014,** *53* (42), 11194-11198.

112. Yeung, C. S.; Ziegler, R. E.; Porco, J. A., Jr.; Jacobsen, E. N., Thiourea-Catalyzed Enantioselective Addition of Indoles to Pyrones: Alkaloid Cores with Quaternary Carbons. *J. Am. Chem. Soc.* **2014,** *136* (39), 13614-13617.

113. Zhang, Y.-C.; Zhao, J.-J.; Jiang, F.; Sun, S.-B.; Shi, F., Organocatalytic Asymmetric Arylative Dearomatization of 2,3-Disubstituted Indoles Enabled by Tandem Reactions. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13912-13915.

114. Hsiao, C.-C.; Liao, H.-H.; Rueping, M., Enantio- and Diastereoselective Access to Distant Stereocenters Embedded within Tetrahydroxanthenes: Utilizing ortho-Quinone Methides as Reactive Intermediates in Asymmetric Bronsted Acid Catalysis. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13258-13263.

115. Badiola, E.; Fiser, B.; Gomez-Bengoa, E.; Mielgo, A.; Olaizola, I.; Urruzuno, I.; Garcia, J. M.; Odriozola, J. M.; Razkin, J.; Oiarbide, M.; Palomo, C., Enantioselective Construction of Tetrasubstituted Stereogenic Carbons through Bronsted Base Catalyzed Michael Reactions: alpha '-Hydroxy Enones as Key Enoate Equivalent. *J. Am. Chem. Soc.* **2014,** *136* (51), 17869-17881.

116. Zhao, W.; Wang, Z.; Chu, B.; Sun, J., Enantioselective Formation of All-Carbon Quaternary Stereocenters from Indoles and Tertiary Alcohols Bearing A Directing Group. *Angew. Chem.-Int. Edit.* **2015,** *54* (6), 1910-1913.

117. Dong, X.; Liang, L.; Li, E.; Huang, Y., Highly Enantioselective Intermolecular Cross Rauhut-Currier Reaction Catalyzed by a Multifunctional Lewis Base Catalyst. *Angew. Chem.-Int. Edit.* **2015,** *54* (5), 1621-1624.

118. Manna, M. S.; Mukherjee, S., Organocatalytic Enantioselective Formal C(sp(2))-H Alkylation. *J. Am. Chem. Soc.* **2015,** *137* (1), 130-133.

119. Li, Y.; Su, X.; Zhou, W.; Li, W.; Zhang, J., Amino Acid Derived Phosphine-Catalyzed Enantioselective 1,4-Dipolar Spiroannulation of Cyclobutenones and Isatylidenemalononitrile. *Chem.-Eur. J.* **2015,** *21* (11), 4224-4228.

120. Zhao, J.-J.; Sun, S.-B.; He, S.-H.; Wu, Q.; Shi, F., Catalytic Asymmetric Inverse-Electron-Demand Oxa-Diels-Alder Reaction of In Situ Generated ortho-Quinone Methides with 3-Methyl-2-Vinylindoles. *Angew. Chem.-Int. Edit.* **2015,** *54* (18), 5460-5464.

121. Guo, W.; Wu, B.; Zhou, X.; Chen, P.; Wang, X.; Zhou, Y.-G.; Liu, Y.; Li, C., Formal Asymmetric Catalytic Thiolation witha Bifunctional Catalyst at a Water-Oil Interface: Synthesis of Benzyl Thiols. *Angew. Chem.-Int. Edit.* **2015,** *54* (15), 4522-4526.

122. Etxabe, J.; Izquierdo, J.; Landa, A.; Oiarbide, M.; Palomo, C., Catalytic Enantioselective Synthesis of N,C,C-Trisubstituted -Amino Acid Derivatives Using 1H-Imidazol-4(5H)-ones as Key Templates. *Angew. Chem.-Int. Edit.* **2015,** *54* (23), 6883-6886.

123. Su, X.; Zhou, W.; Li, Y. Y.; Zhang, J. L., Design, Synthesis, and Application of a Chiral Sulfinamide Phosphine Catalyst for the Enantioselective Intramolecular Rauhut-Currier Reaction. *Angew. Chem.-Int. Edit.* **2015,** *54* (23), 6874-6877.

124. Burns, A. R.; Madec, A. G. E.; Low, D. W.; Roy, I. D.; Lam, H. W., Enantioselective synthesis of bicyclo 3.n.1 alkanes by chiral phosphoric acid-catalyzed desymmetrizing Michael cyclizations. *Chem. Sci.* **2015,** *6* (6), 3550-3555.

125. Yu, J. S.; Liao, F. M.; Gao, W. M.; Liao, K.; Zuo, R. L.; Zhou, J., Michael Addition Catalyzed by Chiral Secondary Amine Phosphoramide Using Fluorinated Silyl Enol Ethers: Formation of Quaternary Carbon Stereocenters. *Angew. Chem.-Int. Edit.* **2015,** *54* (25), 7381-7385.

126. Engl, O. D.; Fritz, S. P.; Wennemers, H., Stereoselective Organocatalytic Synthesis of Oxindoles with Adjacent Tetrasubstituted Stereocenters. *Angew. Chem.-Int. Edit.* **2015,** *54* (28), 8193-8197.

127. Miles, D. H.; Guasch, J.; Toste, F. D., A Nucleophilic Strategy for Enantioselective Intermolecular alpha-Amination: Access to Enantioenriched alpha-Arylamino Ketones. *J. Am. Chem. Soc.* **2015,** *137* (24), 7632-7635.

128. Wang, Z. B.; Wong, Y. F.; Sun, J. W., Catalytic Asymmetric 1,6-Conjugate Addition of para-Quinone Methides: Formation of All-Carbon Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2015,** *54* (46), 13711-13714.

129. Wang, S. G.; Liu, X. J.; Zhao, Q. C.; Zheng, C.; Wang, S. B.; You, S. L., Asymmetric Dearomatization of beta-Naphthols through a Bifunctional-Thiourea-Catalyzed Michael Reaction. *Angew. Chem.-Int. Edit.* **2015,** *54* (49), 14929-14932.

130. Farley, A. J. M.; Sandford, C.; Dixon, D. J., Bifunctional Iminophosphorane Catalyzed Enantioselective Sulfa-Michael Addition to Unactivated alpha-Substituted Acrylate Esters. *J. Am. Chem. Soc.* **2015,** *137* (51), 15992-15995.

131. Nishimine, T.; Taira, H.; Tokunaga, E.; Shiro, M.; Shibata, N., Enantioselective Trichloromethylation of MBH-Fluorides with Chloroform Based on Silicon-assisted C-F Activation and Carbanion Exchange Induced by a Ruppert-Prakash Reagent. *Angew. Chem.-Int. Edit.* **2016,** *55* (1), 359-363.

132. Zhu, B.; Lee, R.; Li, J. T.; Ye, X. Y.; Hong, S. N.; Qiu, S.; Coote, M. L.; Jiang, Z. Y., Chemoselective Switch in the Asymmetric Organocatalysis of 5H-Oxazol-4-ones and N-Itaconimides: Addition-Protonation or 4+2 Cycloaddition. *Angew. Chem.-Int. Edit.* **2016,** *55* (4), 1299-1303.

133. Hack, D.; Durr, A. B.; Deckers, K.; Chauhan, P.; Seling, N.; Rubenach, L.; Mertens, L.; Raabe, G.; Schoenebeck, F.; Enders, D., Asymmetric Synthesis of Spiropyrazolones by Sequential Organo- and Silver Catalysis. *Angew. Chem.-Int. Edit.* **2016,** *55* (5), 1797-1800.

134. Quinonero, O.; Jean, M.; Vanthuyne, N.; Roussel, C.; Bonne, D.; Constantieux, T.; Bressy, C.; Bugaut, X.; Rodriguez, J., Combining Organocatalysis with Central-to-Axial Chirality Conversion: Atroposelective Hantzsch-Type Synthesis of 4-Arylpyridines. *Angew. Chem.-Int. Edit.* **2016,** *55* (4), 1401-1405.

135. Dell'Amico, L.; Vega-Penaloza, A.; Cuadros, S.; Melchiorre, P., Enantioselective Organocatalytic Diels-Alder Trapping of Photochemically Generated Hydroxy-o-Quinodimethanes. *Angew. Chem.-Int. Edit.* **2016,** *55* (10), 3313-3317.

136. Izquierdo, J.; Landa, A.; Bastida, I.; Lopez, R.; Oiarbide, M.; Palomo, C., Base-Catalyzed Asymmetric alpha-Functionalization of 2-(Cyanomethyl)azaarene N-Oxides Leading to Quaternary Stereocenters. *J. Am. Chem. Soc.* **2016,** *138* (10), 3282-3285.

137. Yang, C.; Zhang, E. G.; Li, X.; Cheng, J. P., Asymmetric Conjugate Addition of Benzofuran-2-ones to Alkyl 2-Phthalimidoacrylates: Modeling Structure-Stereoselectivity Relationships with Steric and Electronic Parameters. *Angew. Chem.-Int. Edit.* **2016,** *55* (22), 6506-6510.

138. Moliterno, M.; Cari, R.; Puglisi, A.; Antenucci, A.; Sperandio, C.; Moretti, E.; Di Sabato, A.; Salvio, R.; Bella, M., Quinine-Catalyzed Asymmetric Synthesis of 2,2 '-Binaphthol-Type Biaryls under Mild Reaction Conditions. *Angew. Chem.-Int. Edit.* **2016,** *55* (22), 6525-6529.

139. Okusu, S.; Okazaki, H.; Tokunaga, E.; Soloshonok, V. A.; Shibata, N., Organocatalytic Enantioselective Nucleophilic Alkynylation of Allyl Fluorides Affording Chiral Skipped Ene-ynes. *Angew. Chem.-Int. Edit.* **2016,** *55* (23), 6744-6748.

140. Zhu, B.; Qiu, S.; Li, J. T.; Coote, M. L.; Lee, R.; Jiang, Z. Y., Asymmetric 4+2 annulation of 5H-thiazol-4-ones with a chiral dipeptide-based Bronsted base catalyst. *Chem. Sci.* **2016,** *7* (9), 6060-6067.

141. Ni, C. J.; Tong, X. F., Amine-Catalyzed Asymmetric (3+3) Annulations of beta '-Acetoxy Allenoates: Enantioselective Synthesis of 4H-Pyrans. *J. Am. Chem. Soc.* **2016,** *138* (25), 7872-7875.

142. Yang, Z. Y.; He, Y.; Toste, F. D., Biomimetic Approach to the Catalytic Enantioselective Synthesis of Flavonoids. *J. Am. Chem. Soc.* **2016,** *138* (31), 9775-9778.

143. Berkes, B.; Ozsvath, K.; Molnar, L.; Gati, T.; Holczbauer, T.; Kardos, G.; Soos, T., Expedient and Diastereodivergent Assembly of Terpenoid Decalin Subunits having Quaternary Stereocenters through Organocatalytic Robinson Annulation of Nazarov Reagent. *Chem.-Eur. J.* **2016,** *22* (50), 18101-18106.

144. Liu, Y. D.; Ao, J.; Paladhi, S.; Song, C. E.; Yan, H. L., Organocatalytic Asymmetric Synthesis of Chiral Dioxazinanes and Dioxazepanes with in Situ Generated Nitrones via a Tandem Reaction Pathway Using a Cooperative Cation Binding Catalyst. *J. Am. Chem. Soc.* **2016,** *138* (50), 16486-16492.

145. Zhao, Y. L.; Lou, Q. X.; Wang, L. S.; Hu, W. H.; Zhao, J. L., Organocatalytic Friedel-Crafts Alkylation/Lactonization Reaction of Naphthols with 3-Trifluoroethylidene Oxindoles: The Asymmetric Synthesis of Dihydrocoumarins. *Angew. Chem.-Int. Edit.* **2017,** *56* (1), 338-342.

146. Frias, M.; Mas-Balleste, R.; Arias, S.; Alvarado, C.; Aleman, J., Asymmetric Synthesis of Rauhut-Currier type Products by a Regioselective Mukaiyama Reaction under Bifunctional Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (2), 672-679.

147. Raut, V. S.; Jean, M.; Vanthuyne, N.; Roussel, C.; Constantieux, T.; Bressy, C.; Bugaut, X.; Bonne, D.; Rodriguez, J., Enantioselective Syntheses of Furan Atropisomers by an Oxidative Central-to-Axial Chirality Conversion Strategy. *J. Am. Chem. Soc.* **2017,** *139* (6), 2140-2143.

148. Chen, M.; Sun, J. W., Catalytic Asymmetric N-Alkylation of Indoles and Carbazoles through 1,6-Conjugate Addition of Aza-para-quinone Methides. *Angew. Chem.-Int. Edit.* **2017,** *56* (16), 4583-4587.

149. Liu, S. Y.; Maruoka, K.; Shirakawa, S., Chiral Tertiary Sulfonium Salts as Effective Catalysts for Asymmetric Base-Free Neutral Phase-Transfer Reactions. *Angew. Chem.-Int. Edit.* **2017,** *56* (17), 4819-4823.

150. Chen, M.; Sun, J. W., How Understanding the Role of an Additive Can Lead to an Improved Synthetic Protocol without an Additive: Organocatalytic Synthesis of Chiral Diarylmethyl Alkynes. *Angew. Chem.-Int. Edit.* **2017,** *56* (39), 11966-11970.

151. Blom, J.; Vidal-Albalat, A.; Jorgensen, J.; Barlose, C. L.; Jessen, K. S.; Iversen, M. V.; Jorgensen, K. A., Directing the Activation of Donor-Acceptor Cyclopropanes Towards Stereoselective 1,3-Dipolar Cycloaddition Reactions by BrOnsted Base Catalysis. *Angew. Chem.-Int. Edit.* **2017,** *56* (39), 11831-11835.

152. Choudhury, A. R.; Manna, M. S.; Mukherjee, S., Nitro-enabled catalytic enantioselective formal umpolung alkenylation of beta-ketoesters. *Chem. Sci.* **2017,** *8* (9), 6686-6690.

153. del Pozo, S.; Vera, S.; Oiarbide, M.; Palomo, C., Catalytic Asymmetric Synthesis of Quaternary Barbituric Acids. *J. Am. Chem. Soc.* **2017,** *139* (43), 15308-15311.

154. Guerrero-Corella, A.; Esteban, F.; Iniesta, M.; Martin-Somer, A.; Parra, M.; Diaz-Tendero, S.; Fraile, A.; Aleman, J., 2-Hydroxybenzophenone as a Chemical Auxiliary for the Activation of Ketiminoesters for Highly Enantioselective Addition to Nitroalkenes under Bifunctional Catalysis. *Angew. Chem.-Int. Edit.* **2018,** *57* (19), 5350-5354.

155. Jia, S. Q.; Chen, Z. L.; Zhang, N.; Tan, Y.; Liu, Y. D.; Deng, J.; Yan, H. L., Organocatalytic Enantioselective Construction of Axially Chiral Sulfone-Containing Styrenes. *J. Am. Chem. Soc.* **2018,** *140* (23), 7056-7060.

156. Formica, M.; Sorin, G.; Farley, A. J. M.; Diaz, J.; Paton, R. S.; Dixon, D. J., Bifunctional iminophosphorane catalysed enantioselective sulfa-Michael addition of alkyl thiols to alkenyl benzimidazoles. *Chem. Sci.* **2018,** *9* (34), 6969-6974.

157. Vishe, M.; Johnston, J. N., The inverted ketene synthon: a double umpolung approach to enantioselective beta(2,3)-amino amide synthesis. *Chem. Sci.* **2019,** *10* (4), 1138-1143.

158. Thomson, C. J.; Barber, D. M.; Dixon, D. J., One-Pot Catalytic Enantioselective Synthesis of 2-Pyrazolines. *Angew. Chem.-Int. Edit.* **2019,** *58* (8), 2469-2473.

159. Kondoh, A.; Ishikawa, S.; Terada, M., Development of Chiral Ureates as Chiral Strong Brønsted Base Catalysts. *J. Am. Chem. Soc.* **2020,** *142* (8), 3724-3728.

160. Varlet, T.; Gelis, C.; Retailleau, P.; Bernadat, G.; Neuville, L.; Masson, G., Enantioselective Redox-Divergent Chiral Phosphoric Acid Catalyzed Quinone Diels–Alder Reactions. *Angewandte Chemie International Edition* **2020,** *59* (22), 8491-8496.

161. Ghosh, S.; Das, S.; De, C. K.; Yepes, D.; Neese, F.; Bistoni, G.; Leutzsch, M.; List, B., Strong and Confined Acids Control Five Stereogenic Centers in Catalytic Asymmetric Diels–Alder Reactions of Cyclohexadienones with Cyclopentadiene. *Angewandte Chemie International Edition* **2020,** *59* (30), 12347-12351.

162. Lin, Y.; Hirschi, W. J.; Kunadia, A.; Paul, A.; Ghiviriga, I.; Abboud, K. A.; Karugu, R. W.; Vetticatt, M. J.; Hirschi, J. S.; Seidel, D., A Selenourea-Thiourea Brønsted Acid Catalyst Facilitates Asymmetric Conjugate Additions of Amines to α,β-Unsaturated Esters. *J. Am. Chem. Soc.* **2020,** *142* (12), 5627-5635.

163. Li, X.; Sun, J., Organocatalytic Enantioselective Synthesis of Chiral Allenes: Remote Asymmetric 1,8-Addition of Indole Imine Methides. *Angewandte Chemie International Edition* **2020,** *59* (39), 17049-17054.

164. Zhu, Z.; Odagi, M.; Supantanapong, N.; Xu, W.; Saame, J.; Kirm, H.-U.; Abboud, K. A.; Leito, I.; Seidel, D., Modular Design of Chiral Conjugate-Base-Stabilized Carboxylic Acids: Catalytic Enantioselective [4 + 2] Cycloadditions of Acetals. *J. Am. Chem. Soc.* **2020,** *142* (36), 15252-15258.

165. Li, X.; Duan, M.; Deng, Z.; Shao, Q.; Chen, M.; Zhu, G.; Houk, K. N.; Sun, J., Catalytic enantioselective synthesis of chiral tetraarylmethanes. *Nature Catalysis* **2020,** *3* (12), 1010-1019.

166. Kong, M.; Tan, Y.; Zhao, X.; Qiao, B.; Tan, C.-H.; Cao, S.; Jiang, Z., Catalytic Reductive Cross Coupling and Enantioselective Protonation of Olefins to Construct Remote Stereocenters for Azaarenes. *J. Am. Chem. Soc.* **2021,** *143* (10), 4024-4031.

167. Dai, Z.-Y.; Nong, Z.-S.; Song, S.; Wang, P.-S., Asymmetric Photocatalytic C(sp3)–H Bond Addition to α-Substituted Acrylates. *Org. Lett.* **2021,** *23* (8), 3157-3161.

168. Zhang, H.; He, J.; Chen, Y.; Zhuang, C.; Jiang, C.; Xiao, K.; Su, Z.; Ren, X.; Wang, T., Regio- and Stereoselective Cascade of β,γ-Unsaturated Ketones by Dipeptided Phosphonium Salt Catalysis: Stereospecific Construction of Dihydrofuro-Fused [2,3-b] Skeletons. *Angewandte Chemie International Edition* **2021,** *60* (36), 19860-19870.

169. Varlet, T.; Matišić, M.; Van Elslande, E.; Neuville, L.; Gandon, V.; Masson, G., Enantioselective and Diastereodivergent Synthesis of Spiroindolenines via Chiral Phosphoric Acid-Catalyzed Cycloaddition. *J. Am. Chem. Soc.* **2021,** *143* (30), 11611-11619.

170. Li, Z.; Li, Y.; Li, X.; Wu, M.; He, M.-L.; Sun, J., Organocatalytic asymmetric formal oxidative coupling for the construction of all-aryl quaternary stereocenters. *Chem. Sci.* **2021,** *12* (35), 11793-11798.

171. Liu, S.-J.; Chen, Z.-H.; Chen, J.-Y.; Ni, S.-F.; Zhang, Y.-C.; Shi, F., Rational Design of Axially Chiral Styrene-Based Organocatalysts and Their Application in Catalytic Asymmetric (2+4) Cyclizations. *Angewandte Chemie International Edition* **2022,** *61* (7), e202112226.

172. Rozsar, D.; Formica, M.; Yamazaki, K.; Hamlin, T. A.; Dixon, D. J., Bifunctional Iminophosphorane-Catalyzed Enantioselective Sulfa-Michael Addition to Unactivated α,β-Unsaturated Amides. *J. Am. Chem. Soc.* **2022,** *144* (2), 1006-1015.

173. Ma, J.; Gao, B.; Song, G.; Zhang, R.; Wang, Q.; Ye, Z.; Chen, W.-W.; Zhao, B., Asymmetric α-Allylation of Glycinate with Switched Chemoselectivity Enabled by Customized Bifunctional Pyridoxal Catalysts. *Angewandte Chemie International Edition* **2022,** *61* (17), e202200850.

174. McLeod, D. A.; Thøgersen, M. K.; Barløse, C. L.; Skipper, M. L.; Obregón, E. B.; Jørgensen, K. A., Enantioselective (8+3) Cycloadditions by Activation of Donor–Acceptor Cyclopropanes Employing Chiral Brønsted Base Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (29), e202206096.

175. Qin, J.; Zhou, T.; Zhou, T.-P.; Tang, L.; Zuo, H.; Yu, H.; Wu, G.; Wu, Y.; Liao, R.-Z.; Zhong, F., Catalytic Atroposelective Electrophilic Amination of Indoles. *Angewandte Chemie International Edition* **2022,** *61* (31), e202205159.

176. Girvin, Z. C.; Cotter, L. F.; Yoon, H.; Chapman, S. J.; Mayer, J. M.; Yoon, T. P.; Miller, S. J., Asymmetric Photochemical [2 + 2]-Cycloaddition of Acyclic Vinylpyridines through Ternary Complex Formation and an Uncontrolled Sensitization Mechanism. *J. Am. Chem. Soc.* **2022,** *144* (43), 20109-20117.

177. Chai, X.; Hu, X.; Zhao, X.; Yin, Y.; Cao, S.; Jiang, Z., Asymmetric Hydroaminoalkylation of Alkenylazaarenes via Cooperative Photoredox and Chiral Hydrogen-Bonding Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (10), e202115110.

178. Zhu, X.-Q.; Wang, Q.; Zhu, J., Organocatalytic Enantioselective Diels–Alder Reaction of 2-Trifluoroacetamido-1,3-dienes with α,β-Unsaturated Ketones. *Angewandte Chemie International Edition* **2023,** *62* (1), e202214925.

179. Rozsar, D.; Farley, A. J. M.; McLauchlan, I.; Shennan, B. D. A.; Yamazaki, K.; Dixon, D. J., Bifunctional Iminophosphorane-Catalyzed Enantioselective Nitroalkane Addition to Unactivated α,β-Unsaturated Esters. *Angewandte Chemie International Edition* **2023,** *62* (21), e202303391.

180. Giordano, M. T.; Kitzinger, K. M.; de Jesús Cruz, P.; Liu, S.; Johnson, J. S., Catalytic, Asymmetric Michael-Aldol Annulations via a Stereodivergent/Stereoconvergent Path Operating under Curtin–Hammett Control. *J. Am. Chem. Soc.* **2023,** *145* (22), 12370-12376.

181. Su, G.; Formica, M.; Yamazaki, K.; Hamlin, T. A.; Dixon, D. J., Catalytic Enantioselective Intramolecular Oxa-Michael Reaction to α,β-Unsaturated Esters and Amides. *J. Am. Chem. Soc.* **2023,** *145* (23), 12771-12782.

182. Dai, Y.; Huang, H.; Liang, S.; Yin, Y.; Ban, X.; Zhao, X.; Jiang, Z., Catalytic Asymmetric Intermolecular [3 + 2] Photocycloaddition of Cyclopropylamines with Electron-Deficient Olefins. *Org. Lett.* **2023,** *25* (24), 4551-4555.

183. Zhou, X.; Huang, Q.; Guo, J.; Dai, L.; Lu, Y., Enantioselective De Novo Synthesis of α,α-Diaryl Ketones from Alkynes. *Angewandte Chemie International Edition* **2023,** *62* (45), e202310078.

184. Poh, C. Y. X.; Rozsar, D.; Yang, J.; Christensen, K. E.; Dixon, D. J., Bifunctional Iminophosphorane Catalyzed Amide Enolization for Enantioselective Cyclohexadienone Desymmetrization. *Angewandte Chemie International Edition* **2024,** *63* (5), e202315401.

185. Deng, Z.; Padalino, M. A.; Jan, J. E. L.; Park, S.; Danneman, M. W.; Johnston, J. N., Generality-Driven Catalyst Development: A Universal Catalyst for Enantioselective Nitroalkene Reduction. *J. Am. Chem. Soc.* **2024,** *146* (2), 1269-1275.

186. Lee, H.; Nam, H.; Lee, S. Y., Enantio- and Diastereoselective Variations on α-Iminonitriles: Harnessing Chiral Cyclopropenimine-Thiourea Organocatalysts. *J. Am. Chem. Soc.* **2024,** *146* (5), 3065-3074.

187. Fu, Q.; Cao, S.; Wang, J.; Lv, X.; Wang, H.; Zhao, X.; Jiang, Z., Enantioselective [2π + 2σ] Cycloadditions of Bicyclo[1.1.0]butanes with Vinylazaarenes through Asymmetric Photoredox Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (12), 8372-8380.

188. Lu, Y.-N.; Che, C.; Zhen, G.; Chang, X.; Dong, X.-Q.; Wang, C.-J., Visible-light-enabled stereoselective synthesis of functionalized cyclohexylamine derivatives via [4 + 2] cycloadditions. *Chem. Sci.* **2024,** *15* (17), 6507-6514.

189. Vastakaite, G.; Budinská, A.; Bögli, C. L.; Boll, L. B.; Wennemers, H., Kinetic Resolution of β-Branched Aldehydes through Peptide-Catalyzed Conjugate Addition Reactions. *J. Am. Chem. Soc.* **2024,** *146* (28), 19101-19107.

190. Yamanishi, K.; Ashihara, G.; Shiomi, S.; Harada, S.; Kitajima, M.; Takayama, H.; Ishikawa, H., New Entries in Organocatalysts from an Alkaloid Library; Development of Aminal Catalysis for a Michael Reaction Based on Calycanthine. *J. Am. Chem. Soc.* **2024,** *146* (39), 27152-27160.

191. Plachinski, E. F.; Qian, R. Z.; Villanueva, R.; Poole, D. L.; Rosenthal, T.; Yoon, T. P., Enantioselective [2π + 2σ] Photocycloaddition Enabled by Brønsted Acid Catalyzed Chromophore Activation. *J. Am. Chem. Soc.* **2024,** *146* (46), 31400-31404.

4.1.3 Other Reactions

1. Liu, X. F.; Li, H. M.; Deng, L., Highly enantioselective amination of alpha-substituted alpha-cyanoacetates with chiral catalysts accessible from both quinine and quinidine. *Org. Lett.* **2005,** *7* (2), 167-169.

2. Dai, X.; Nakai, T.; Romero, J. A. C.; Fu, G. C., Enantioselective synthesis of protected amines by the catalytic asymmetric addition of hydrazoic acid to ketenes. *Angew. Chem.-Int. Edit.* **2007,** *46* (23), 4367-4369.

3. Wang, Y.; Li, H. M.; Wang, Y. Q.; Liu, Y.; Foxman, B. M.; Deng, L., Asymmetric Diels-Alder reactions of 2-pyrones with a bifunctional organic catalyst. *J. Am. Chem. Soc.* **2007,** *129* (20), 6364-+.

4. Poisson, T.; Dalla, V.; Marsais, F.; Dupas, G.; Oudeyer, S.; Levacher, V., Organocatalytic enantioselective protonation of silyl enolates mediated by cinchona alkaloids and a latent source of HF. *Angew. Chem.-Int. Edit.* **2007,** *46* (37), 7090-7093.

5. Peschiulli, A.; Gun'ko, Y.; Connon, S. J., Highly enantioselective desymmetrization of meso anhydrides by a bifunctional thiourea-based organocatalyst at low catalyst loadings and room temperature. *J. Org. Chem.* **2008,** *73* (6), 2454-2457.

6. Fang, Y. Q.; Jacobsen, E. N., Cooperative, highly enantioselective phosphinothiourea catalysis of imine-allene [3+2] cycloadditions. *J. Am. Chem. Soc.* **2008,** *130* (17), 5660-+.

7. Oh, S. H.; Rho, H. S.; Lee, J. W.; Lee, J. E.; Youk, S. H.; Chin, J.; Song, C. E., A highly reactive and enantioselective bifunctional organocatalyst for the methanolytic desymmetrization of cyclic anhydrides: Prevention of catalyst aggregation. *Angew. Chem.-Int. Edit.* **2008,** *47* (41), 7872-7875.

8. Hashimoto, T.; Uchiyama, N.; Maruoka, K., Trans-Selective Asymmetric Aziridination of Diazoacetamides and N-Boc Imines Catalyzed by Axially Chiral Dicarboxylic Acid. *J. Am. Chem. Soc.* **2008,** *130* (44), 14380-+.

9. Jiang, Y. Q.; Shi, Y. L.; Shi, M., Chiral phosphine-catalyzed enantioselective construction of gamma-butenolides through substitution of Morita-Baylis-Hillman acetates with 2-trimethylsilyloxy furan. *J. Am. Chem. Soc.* **2008,** *130* (23), 7202-+.

10. Wang, S. X.; Chen, F. E., A Novel Cost-Effective Thiourea Bifunctional Organocatalyst for Highly Enantioselective Alcoholysis of meso-Cyclic Anhydrides: Enhanced Enantioselectivity by Configuration Inversion. *Adv. Synth. Catal.* **2009,** *351* (4), 547-552.

11. Lu, M.; Zhu, D.; Lu, Y. P.; Zeng, X. F.; Tan, B.; Xu, Z. J.; Zhong, G. F., Chiral Bronsted Acid-Catalyzed Enantioselective alpha-Hydroxylation of beta-Dicarbonyl Compounds. *J. Am. Chem. Soc.* **2009,** *131* (13), 4562-+.

12. Guo, Q. X.; Peng, Y. G.; Zhang, J. W.; Song, L.; Feng, Z.; Gong, L. Z., Highly Enantioselective Alkylation Reaction of Enamides by Bronsted-Acid Catalysis. *Org. Lett.* **2009,** *11* (20), 4620-4623.

13. Wang, X. S.; Lan, Q.; Shirakawa, S.; Maruoka, K., Chiral bifunctional phase transfer catalysts for asymmetric fluorination of beta-keto esters. *Chem. Commun.* **2010,** *46* (2), 321-323.

14. Uraguchi, D.; Koshimoto, K.; Ooi, T., Flexible synthesis, structural determination, and synthetic application of a new C-1-symmetric chiral ammonium betaine. *Chem. Commun.* **2010,** *46* (2), 300-302.

15. Bui, T.; Candeias, N. R.; Barbas, C. F., Dimeric Quinidine-Catalyzed Enantioselective Aminooxygenation of Oxindoles: An Organocatalytic Approach to 3-Hydroxyoxindole Derivatives. *J. Am. Chem. Soc.* **2010,** *132* (16), 5574-+.

16. Basak, A. K.; Shimada, N.; Bow, W. F.; Vicic, D. A.; Tius, M. A., An Organocatalytic Asymmetric Nazarov Cyclization. *J. Am. Chem. Soc.* **2010,** *132* (24), 8266-+.

17. Gustafson, J. L.; Lim, D.; Miller, S. J., Dynamic Kinetic Resolution of Biaryl Atropisomers via Peptide-Catalyzed Asymmetric Bromination. *Science* **2010,** *328* (5983), 1251-1255.

18. Liu, F.; Qian, D. Y.; Li, L.; Zhao, X. L.; Zhang, J. L., Diastereo- and Enantioselective Gold(I)-Catalyzed Intermolecular Tandem Cyclization/ 3+3 Cycloadditions of 2-(1-Alkynyl)-2-alken-1-ones with Nitrones. *Angew. Chem.-Int. Edit.* **2010,** *49* (37), 6669-6672.

19. Veitch, G. E.; Jacobsen, E. N., Tertiary Aminourea-Catalyzed Enantioselective Iodolactonization. *Angew. Chem.-Int. Edit.* **2010,** *49* (40), 7332-7335.

20. Zhou, L.; Tan, C. K.; Jiang, X. J.; Chen, F.; Yeung, Y. Y., Asymmetric Bromolactonization Using Amino-thiocarbamate Catalyst. *J. Am. Chem. Soc.* **2010,** *132* (44), 15474-15476.

21. Uraguchi, D.; Koshimoto, K.; Miyake, S.; Ooi, T., Chiral Ammonium Betaines as Ionic Nucleophilic Catalysts. *Angew. Chem.-Int. Edit.* **2010,** *49* (32), 5567-5569.

22. Ohmatsu, K.; Kiyokawa, M.; Ooi, T., Chiral 1,2,3-Triazoliums as New Cationic Organic Catalysts with Anion-Recognition Ability: Application to Asymmetric Alkylation of Oxindoles. *J. Am. Chem. Soc.* **2011,** *133* (5), 1307-1309.

23. Hayashi, M.; Nakamura, S., Catalytic Enantioselective Protonation of alpha-Oxygenated Ester Enolates Prepared through Phospha-Brook Rearrangement. *Angew. Chem.-Int. Edit.* **2011,** *50* (10), 2249-2252.

24. Hashimoto, T.; Omote, M.; Maruoka, K., Asymmetric Inverse-Electron-Demand 1,3-Dipolar Cycloaddition of C,N-Cyclic Azomethine Imines: An Umpolung Strategy. *Angew. Chem.-Int. Edit.* **2011,** *50* (15), 3489-3492.

25. Huang, J. R.; Cui, H. L.; Lei, J.; Sun, X. H.; Chen, Y. C., Organocatalytic chemoselective asymmetric N-allylic alkylation of enamides. *Chem. Commun.* **2011,** *47* (16), 4784-4786.

26. Tan, C. K.; Zhou, L.; Yeung, Y. Y., Aminothiocarbamate-Catalyzed Asymmetric Bromolactonization of 1,2-Disubstituted Olefinic Acids. *Org. Lett.* **2011,** *13* (10), 2738-2741.

27. Zhou, L.; Chen, J.; Tan, C. K.; Yeung, Y. Y., Enantioselective Bromoaminocyclization Using Amino-Thiocarbamate Catalysts. *J. Am. Chem. Soc.* **2011,** *133* (24), 9164-9167.

28. Zhong, F. R.; Han, X. Y.; Wang, Y. Q.; Lu, Y. X., Highly Enantioselective 3+2 Annulation of Morita-Baylis-Hillman Adducts Mediated by L-Threonine-Derived Phosphines: Synthesis of 3-Spirocyclopentene-2-oxindoles having Two Contiguous Quaternary Centers. *Angew. Chem.-Int. Edit.* **2011,** *50* (34), 7837-7841.

29. Beck, E. M.; Hyde, A. M.; Jacobsen, E. N., Chiral Sulfinamide/Achiral Sulfonic Acid Cocatalyzed Enantioselective Protonation of Enol Silanes. *Org. Lett.* **2011,** *13* (16), 4260-4263.

30. Wu, Y. W.; Singh, R. P.; Deng, L., Asymmetric Olefin Isomerization of Butenolides via Proton Transfer Catalysis by an Organic Molecule. *J. Am. Chem. Soc.* **2011,** *133* (32), 12458-12461.

31. Xiao, H.; Chai, Z.; Wang, H. F.; Wang, X. W.; Cao, D. D.; Liu, W.; Lu, Y. P.; Yang, Y. Q.; Zhao, G., Bifunctional N-Acyl-Aminophosphine-Catalyzed Asymmetric 4+2 Cycloadditions of Allenoates and Imines. *Chem.-Eur. J.* **2011,** *17* (38), 10561-10564.

32. Han, X.; Zhong, F.; Wang, Y.; Lu, Y., Versatile Enantioselective 3+2 Cyclization between Imines and Allenoates Catalyzed by Dipeptide-Based Phosphines. *Angew. Chem.-Int. Edit.* **2012,** *51* (3), 767-770.

33. Guo, C.; Song, J.; Huang, J.-Z.; Chen, P.-H.; Luo, S.-W.; Gong, L.-Z., Core-Structure-Oriented Asymmetric Organocatalytic Substitution of 3-Hydroxyoxindoles: Application in the Enantioselective Total Synthesis of (+)-Folicanthine. *Angew. Chem.-Int. Edit.* **2012,** *51* (4), 1046-1050.

34. Song, L.; Guo, Q. X.; Li, X. C.; Tian, J.; Peng, Y. G., The Direct Asymmetric a Alkylation of Ketones by Bronsted Acid Catalysis. *Angew. Chem.-Int. Edit.* **2012,** *51* (8), 1899-1902.

35. Xu, J. X.; Hu, Y. L.; Huang, D. F.; Wang, K. H.; Xu, C. M.; Niu, T., Thiourea-Catalyzed Enantioselective Fluorination of ss-Keto Esters. *Adv. Synth. Catal.* **2012,** *354* (2-3), 515-526.

36. Coric, I.; List, B., Asymmetric spiroacetalization catalysed by confined Bronsted acids. *Nature* **2012,** *483* (7389), 315-319.

37. Paull, D. H.; Fang, C.; Donald, J. R.; Pansick, A. D.; Martin, S. F., Bifunctional Catalyst Promotes Highly Enantioselective Bromolactonizations To Generate Stereogenic C-Br Bonds. *J. Am. Chem. Soc.* **2012,** *134* (27), 11128-11131.

38. Wu, Y. W.; Deng, L., Asymmetric Synthesis of Trifluoromethylated Amines via Catalytic Enantioselective Isomerization of Imines. *J. Am. Chem. Soc.* **2012,** *134* (35), 14334-14337.

39. Simon, L.; Goodman, J. M., Mechanism of Amination of beta-Keto Esters by Azadicarboxylates Catalyzed by an Axially Chiral Guanidine: Acyclic Keto Esters React through an E Enolate. *J. Am. Chem. Soc.* **2012,** *134* (40), 16869-16876.

40. Guin, J.; Varseev, G.; List, B., Catalytic Asymmetric Protonation of Silyl Ketene Imines. *J. Am. Chem. Soc.* **2013,** *135* (6), 2100-2103.

41. Coric, I.; Kim, J. H.; Vlaar, T.; Patil, M.; Thiel, W.; List, B., Bronsted Acid Catalyzed Asymmetric S(N)2-Type O-Alkylations. *Angew. Chem.-Int. Edit.* **2013,** *52* (12), 3490-3493.

42. Mori, K.; Ichikawa, Y.; Kobayashi, M.; Shibata, Y.; Yamanaka, M.; Akiyama, T., Enantioselective Synthesis of Multisubstituted Biaryl Skeleton by Chiral Phosphoric Acid Catalyzed Desymmetrization/Kinetic Resolution Sequence. *J. Am. Chem. Soc.* **2013,** *135* (10), 3964-3970.

43. Li, M. L.; Woods, P. A.; Smith, M. D., Cation-directed enantioselective synthesis of quaternary-substituted indolenines. *Chem. Sci.* **2013,** *4* (7), 2907-2911.

44. Li, G. Q.; Gao, H.; Keene, C.; Devonas, M.; Ess, D. H.; Kurti, L., Organocatalytic Aryl-Aryl Bond Formation: An Atroposelective 3,3 -Rearrangement Approach to BINAM Derivatives. *J. Am. Chem. Soc.* **2013,** *135* (20), 7414-7417.

45. Xue, X. S.; Li, X.; Yu, A.; Yang, C.; Song, C.; Cheng, J. P., Mechanism and Selectivity of Bioinspired Cinchona Alkaloid Derivatives Catalyzed Asymmetric Olefin Isomerization: A Computational Study. *J. Am. Chem. Soc.* **2013,** *135* (20), 7462-7473.

46. Barrett, K. T.; Miller, S. J., Enantioselective Synthesis of Atropisomeric Benzamides through Peptide-Catalyzed Bromination. *J. Am. Chem. Soc.* **2013,** *135* (8), 2963-2966.

47. Romanov-Michailidis, F.; Guenee, L.; Alexakis, A., Enantioselective Organocatalytic Fluorination-Induced Wagner-Meerwein Rearrangement. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9266-9270.

48. Zhao, Y.; Jiang, X. J.; Yeung, Y. Y., Catalytic, Enantioselective, and Highly Chemoselective Bromocyclization of Olefinic Dicarbonyl Compounds. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8597-8601.

49. Chen, Z. L.; Sun, J. W., Enantio- and Diastereoselective Assembly of Tetrahydrofuran and Tetrahydropyran Skeletons with All-Carbon-Substituted Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13593-13596.

50. Ohmatsu, K.; Ando, Y.; Ooi, T., Asymmetric Substitution at the Tetrasubstituted Chiral Carbon: Catalytic Ring-Opening Alkylation of Racemic 2,2-Disubstituted Aziridines with 3-Substituted Oxindoles. *J. Am. Chem. Soc.* **2013,** *135* (50), 18706-18709.

51. Nishimine, T.; Fukushi, K.; Shibata, N.; Taira, H.; Tokunaga, E.; Yamano, A.; Shiro, M.; Shibata, N., Kinetic Resolution of Allyl Fluorides by Enantioselective Allylic Trifluoromethylation Based on Silicon-Assisted C-F Bond Cleavage. *Angew. Chem.-Int. Edit.* **2014,** *53* (2), 517-520.

52. Mbofana, C. T.; Miller, S. J., Diastereo- and Enantioselective Addition of Anilide-Functionalized Allenoates to N-Acylimines Catalyzed by a Pyridylalanine-Based Peptide. *J. Am. Chem. Soc.* **2014,** *136* (8), 3285-3292.

53. Wang, T.; Yao, W.; Zhong, F.; Pang, G. H.; Lu, Y., Phosphine-Catalyzed Enantioselective gamma-Addition of 3-Substituted Oxindoles to 2,3-Butadienoates and 2-Butynoates: Use of Prochiral Nucleophiles. *Angew. Chem.-Int. Edit.* **2014,** *53* (11), 2964-2968.

54. Monaco, M. R.; Poladura, B.; de Los Bernardos, M. D.; Leutzsch, M.; Goddard, R.; List, B., Activation of Carboxylic Acids in Asymmetric Organocatalysis. *Angew. Chem.-Int. Edit.* **2014,** *53* (27), 7063-7067.

55. Monaco, M. R.; Prevost, S.; List, B., Organocatalytic Asymmetric Hydrolysis of Epoxides. *Angew. Chem.-Int. Edit.* **2014,** *53* (31), 8142-8145.

56. Meng, S.-S.; Liang, Y.; Cao, K.-S.; Zou, L.; Lin, X.-B.; Yang, H.; Houk, K. N.; Zheng, W.-H., Chiral Phosphoric Acid Catalyzed Highly Enantioselective Desymmetrization of 2-Substituted and 2,2-Disubstituted 1,3-Diols via Oxidative Cleavage of Benzylidene Acetals. *J. Am. Chem. Soc.* **2014,** *136* (35), 12249-12252.

57. Yin, X.-P.; Zeng, X.-P.; Liu, Y.-L.; Liao, F.-M.; Yu, J.-S.; Zhou, F.; Zhou, J., Asymmetric Triple Relay Catalysis: Enantioselective Synthesis of Spirocyclic Indolines through a One-Pot Process Featuring an Asymmetric 6 pi Electrocyclization. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13740-13745.

58. Fang, Y.-Q.; Tadross, P. M.; Jacobsen, E. N., Highly Enantioselective, Intermolecular Hydroamination of Allenyl Esters Catalyzed by Bifunctional Phosphinothioureas. *J. Am. Chem. Soc.* **2014,** *136* (52), 17966-17968.

59. Monaco, M. R.; Prevost, S.; List, B., Catalytic Asymmetric Synthesis of Thiols. *J. Am. Chem. Soc.* **2014,** *136* (49), 16982-16985.

60. Tallon, S.; Manoni, F.; Connon, S. J., A Practical Aryl Unit for Azlactone Dynamic Kinetic Resolution: Orthogonally Protected Products and A Ligation-Inspired Coupling Process. *Angew. Chem.-Int. Edit.* **2015,** *54* (3), 813-817.

61. Odagi, M.; Furukori, K.; Yamamoto, Y.; Sato, M.; Iida, K.; Yamanaka, M.; Nagasawa, K., Origin of Stereocontrol in Guanidine-Bisurea Bifunctional Organocatalyst That Promotes alpha-Hydroxylation of Tetralone-Derived beta-Ketoesters: Asymmetric Synthesis of beta- and gamma-Substituted Tetralone Derivatives via Organocatalytic Oxidative Kinetic Resolution. *J. Am. Chem. Soc.* **2015,** *137* (5), 1909-1915.

62. Romanov-Michailidis, F.; Romanova-Michaelides, M.; Pupier, M.; Alexakis, A., Enantioselective Halogenative Semi-Pinacol Rearrangement: Extension of Substrate Scope and Mechanistic Investigations. *Chem.-Eur. J.* **2015,** *21* (14), 5561-5583.

63. Yang, X.; Toste, F. D., Direct Asymmetric Amination of alpha-Branched Cyclic Ketones Catalyzed by a Chiral Phosphoric Acid. *J. Am. Chem. Soc.* **2015,** *137* (9), 3205-3208.

64. Huang, S.; Koetzner, L.; De, C. K.; List, B., Catalytic Asymmetric Dearomatizing Redox Cross Coupling of Ketones with Aryl Hydrazines Giving 1,4-Diketones. *J. Am. Chem. Soc.* **2015,** *137* (10), 3446-3449.

65. Min, C.; Lin, C. T.; Seidel, D., Catalytic Enantioselective Intramolecular Aza-Diels-Alder Reactions. *Angew. Chem.-Int. Edit.* **2015,** *54* (22), 6608-6612.

66. Wang, Z. B.; Sheong, F. K.; Sung, H. H. Y.; Williams, I. D.; Lin, Z. Y.; Sun, J. W., Catalytic Enantioselective Intermolecular Desymmetrization of Azetidines. *J. Am. Chem. Soc.* **2015,** *137* (18), 5895-5898.

67. Yin, Q.; Wang, S. G.; Liang, X. W.; Gao, D. W.; Zheng, J.; You, S. L., Organocatalytic asymmetric chlorinative dearomatization of naphthols. *Chem. Sci.* **2015,** *6* (7), 4179-4183.

68. Miyaji, R.; Asano, K.; Matsubara, S., Bifunctional Organocatalysts for the Enantioselective Synthesis of Axially Chiral Isoquinoline N-Oxides. *J. Am. Chem. Soc.* **2015,** *137* (21), 6766-6769.

69. Kuroda, Y.; Harada, S.; Oonishi, A.; Yamaoka, Y.; Yamada, K.; Takasu, K., Organocatalytic Activation of the Leaving Group in the Intramolecular Asymmetric S(N)2 ' Reaction. *Angew. Chem.-Int. Edit.* **2015,** *54* (28), 8263-8266.

70. Lin, J. S.; Yu, P.; Huang, L.; Zhang, P.; Tan, B.; Liu, X. Y., BrOnsted Acid Catalyzed Asymmetric Hydroamination of Alkenes: Synthesis of Pyrrolidines Bearing a Tetrasubstituted Carbon Stereocenter. *Angew. Chem.-Int. Edit.* **2015,** *54* (27), 7847-7851.

71. Vara, B. A.; Struble, T. J.; Wang, W. W.; Dobish, M. C.; Johnston, J. N., Enantioselective Small Molecule Synthesis by Carbon Dioxide Fixation using a Dual Bronsted Acid/Base Organocatalyst. *J. Am. Chem. Soc.* **2015,** *137* (23), 7302-7305.

72. Zheng, P. F.; Ouyang, Q.; Niu, S. L.; Shuai, L.; Yuan, Y.; Jiang, K.; Liu, T. Y.; Chen, Y. C., Enantioselective 4+1 Annulation Reactions of alpha-Substituted Ammonium Ylides To Construct Spirocyclic Oxindoles. *J. Am. Chem. Soc.* **2015,** *137* (29), 9390-9399.

73. Shugrue, C. R.; Miller, S. J., Phosphothreonine as a Catalytic Residue in Peptide-Mediated Asymmetric Transfer Hydrogenations of 8-Aminoquinolines. *Angew. Chem.-Int. Edit.* **2015,** *54* (38), 11173-11176.

74. Pous, J.; Courant, T.; Bernadat, G.; Iorga, B. I.; Blanchard, F.; Masson, G., Regio-, Diastereo-, and Enantioselective Nitroso-Diels-Alder Reaction of 1,3-Diene-1-carbamates Catalyzed by Chiral Phosphoric Acids. *J. Am. Chem. Soc.* **2015,** *137* (37), 11950-11953.

75. Chen, Y. H.; Cheng, D. J.; Zhang, J.; Wang, Y.; Liu, X. Y.; Tan, B., Atroposelective Synthesis of Axially Chiral Biaryldiols via Organocatalytic Arylation of 2-Naphthols. *J. Am. Chem. Soc.* **2015,** *137* (48), 15062-15065.

76. Yang, W.; Sun, J. W., Organocatalytic Enantioselective Synthesis of 1,4-Dioxanes and Other Oxa-Heterocycles by Oxetane Desymmetrization. *Angew. Chem.-Int. Edit.* **2016,** *55* (5), 1868-1871.

77. Yang, X. Y.; Toste, F. D., Asymmetric addition of alpha-branched cyclic ketones to allenamides catalyzed by a chiral phosphoric acid. *Chem. Sci.* **2016,** *7* (4), 2653-2656.

78. Wende, R. C.; Seitz, A.; Niedek, D.; Schuler, S. M. M.; Hofmann, C.; Becker, J.; Schreiner, P. R., The Enantioselective Dakin-West Reaction. *Angew. Chem.-Int. Edit.* **2016,** *55* (8), 2719-2723.

79. Liu, X.; An, R.; Zhang, X. L.; Luo, J.; Zhao, X. D., Enantioselective Trifluoromethylthiolating Lactonization Catalyzed by an Indane-Based Chiral Sulfide. *Angew. Chem.-Int. Edit.* **2016,** *55* (19), 5846-5850.

80. Wang, J. Z.; Zhou, J.; Xu, C.; Sun, H. B.; Kurti, L.; Xu, Q. L., Symmetry in Cascade Chirality-Transfer Processes: A Catalytic Atroposelective Direct Arylation Approach to BINOL Derivatives. *J. Am. Chem. Soc.* **2016,** *138* (16), 5202-5205.

81. Liao, S. H.; Leutzsch, M.; Monaco, M. R.; List, B., Catalytic Enantioselective Conversion of Epoxides to Thiiranes. *J. Am. Chem. Soc.* **2016,** *138* (16), 5230-5233.

82. Yang, W.; Wang, Z. B.; Sun, J. W., Enantioselective Oxetane Ring Opening with Chloride: Unusual Use of Wet Molecular Sieves for the Controlled Release of HCl. *Angew. Chem.-Int. Edit.* **2016,** *55* (24), 6954-6958.

83. Kotzner, L.; Leutzsch, M.; Sievers, S.; Patil, S.; Waldmann, H.; Zheng, Y. Y.; Thiel, W.; List, B., The Organocatalytic Approach to Enantiopure 2H- and 3H-Pyrroles: Inhibitors of the Hedgehog Signaling Pathway. *Angew. Chem.-Int. Edit.* **2016,** *55* (27), 7693-7697.

84. Tanaka, J.; Suzuki, S.; Tokunaga, E.; Haufe, G.; Shibata, N., Asymmetric Desymmetrization via Metal-Free C-F Bond Activation: Synthesis of 3,5-Diaryl-5-fluoromethyloxazolidin-2-ones with Quaternary Carbon Centers. *Angew. Chem.-Int. Edit.* **2016,** *55* (32), 9432-9436.

85. Momiyama, N.; Tabuse, H.; Noda, H.; Yamanaka, M.; Fujinami, T.; Yamanishi, K.; Izumiseki, A.; Funayama, K.; Egawa, F.; Okada, S.; Adachi, H.; Terada, M., Molecular Design of a Chiral Bronsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels Alder Reaction of Azopyridinecarboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid Monophosphoric Acid. *J. Am. Chem. Soc.* **2016,** *138* (35), 11353-11359.

86. Cai, Y. F.; Tang, Y. R.; Atodiresei, I.; Rueping, M., Catalytic Asymmetric Piancatelli Rearrangement: BrOnsted Acid Catalyzed 4Electrocyclization for the Synthesis of Multisubstituted Cyclopentenones. *Angew. Chem.-Int. Edit.* **2016,** *55* (45), 14126-14130.

87. Li, H. L.; Tong, R. B.; Sun, J. W., Catalytic Enantioselective Aza-Piancatelli Rearrangement. *Angew. Chem.-Int. Edit.* **2016,** *55* (48), 15125-15128.

88. Monaco, M. R.; Fazzi, D.; Tsuji, N.; Leutzsch, M.; Liao, S.; Thiel, W.; List, B., The Activation of Carboxylic Acids via Self-Assembly Asymmetric Organocatalysis: A Combined Experimental and Computational Investigation. *J. Am. Chem. Soc.* **2016,** *138* (44), 14740-14749.

89. Wu, H.; Wang, Q.; Zhu, J. P., Organocatalytic Enantioselective Vinylogous Pinacol Rearrangement Enabled by Chiral Ion Pairing. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15411-15414.

90. Zhang, H. H.; Wang, C. S.; Li, C.; Mei, G. J.; Li, Y. X.; Shi, F., Design and Enantioselective Construction of Axially Chiral Naphthyl-Indole Skeletons. *Angew. Chem.-Int. Edit.* **2017,** *56* (1), 116-121.

91. Zhang, L.; Zhang, J.; Ma, J.; Cheng, D. J.; Tan, B., Highly Atroposelective Synthesis of Arylpyrroles by Catalytic Asymmetric Paal-Knorr Reaction. *J. Am. Chem. Soc.* **2017,** *139* (5), 1714-1717.

92. Zhu, G. M.; Bao, G. J.; Li, Y. P.; Sun, W. S.; Li, J.; Hong, L.; Wang, R., Efficient Catalytic Kinetic Resolution of Spiro-epoxyoxindoles with Concomitant Asymmetric Friedel-Crafts Alkylation of Indoles. *Angew. Chem.-Int. Edit.* **2017,** *56* (19), 5332-5335.

93. Jarrige, L.; Blanchard, F.; Masson, G., Enantioselective Organocatalytic Intramolecular Aza-Diels-Alder Reaction. *Angew. Chem.-Int. Edit.* **2017,** *56* (35), 10573-10576.

94. Villar, L.; Uria, U.; Martinez, J. I.; Prieto, L.; Reyes, E.; Carrillo, L.; Vicario, J. L., Enantioselective Oxidative (4+3) Cycloadditions between Allenamides and Furans through Bifunctional Hydrogen-Bonding/Ion-Pairing Interactions. *Angew. Chem.-Int. Edit.* **2017,** *56* (35), 10535-10538.

95. Qi, L. W.; Mao, J. H.; Zhang, J.; Tan, B., Organocatalytic asymmetric arylation of indoles enabled by azo groups. *Nat. Chem.* **2018,** *10* (1), 58-64.

96. Fan, L. W.; Han, C. Y.; Li, X. R.; Yao, J. S.; Wang, Z. N.; Yao, C. C.; Chen, W. H.; Wang, T.; Zhao, J. F., Enantioselective Polyene Cyclization Catalyzed by a Chiral Bronsted Acid. *Angew. Chem.-Int. Edit.* **2018,** *57* (8), 2115-2119.

97. Crawford, J. M.; Stone, E. A.; Metrano, A. J.; Miller, S. J.; Sigman, M. S., Parameterization and Analysis of Peptide-Based Catalysts for the Atroposelective Bromination of 3-Arylquinazolin-4(3H)-ones. *J. Am. Chem. Soc.* **2018,** *140* (3), 868-871.

98. Li, F.; Korenaga, T.; Nakanishi, T.; Kikuchi, J.; Terada, M., Chiral Phosphoric Acid Catalyzed Enantioselective Ring Expansion Reaction of 1,3-Dithiane Derivatives: Case Study of the Nature of Ion-Pairing Interaction. *J. Am. Chem. Soc.* **2018,** *140* (7), 2629-2642.

99. Qian, D. Y.; Chen, M.; Bissember, A. C.; Sun, J. W., Counterion-Induced Asymmetric Control in Ring-Opening of Azetidiniums: Facile Access to Chiral Amines. *Angew. Chem.-Int. Edit.* **2018,** *57* (14), 3763-3766.

100. Zhang, M.; Yu, C. J.; Xie, J. Q.; Xun, X. D.; Sun, W. S.; Hong, L.; Wang, R., Phosphoric Acid Catalyzed Asymmetric 2+2 Cyclization/Penicillin-Penillonic Acid Rearrangement. *Angew. Chem.-Int. Edit.* **2018,** *57* (18), 4921-4925.

101. Ma, C.; Zhou, J. Y.; Zhang, Y. Z.; Mei, G. J.; Shi, F., Catalytic Asymmetric 2+3 Cyclizations of Azlactones with Azonaphthalenes. *Angew. Chem.-Int. Edit.* **2018,** *57* (19), 5398-5402.

102. Jin, J. W.; Zhao, Y. C.; Gouranourimi, A.; Ariafard, A.; Chan, P. W. H., Chiral Bronsted Acid Catalyzed Enantioselective Dehydrative Nazarov-Type Electrocyclization of Aryl and 2-Thienyl Vinyl Alcohols. *J. Am. Chem. Soc.* **2018,** *140* (17), 5834-5841.

103. Kondoh, A.; Akahira, S.; Oishi, M.; Terada, M., Enantioselective Formal 3+2 Cycloaddition of Epoxides with Imines under BrOnsted Base Catalysis: Synthesis of 1,3-Oxazolidines with Quaternary Stereogenic Center. *Angew. Chem.-Int. Edit.* **2018,** *57* (21), 6299-6303.

104. Ortega, A.; Manzano, R. N.; Uria, U.; Carrillo, L.; Reyes, E.; Tejero, T.; Merino, P.; Vicario, J. L., Catalytic Enantioselective Cloke-Wilson Rearrangement. *Angew. Chem.-Int. Edit.* **2018,** *57* (27), 8225-8229.

105. Proctor, R. S. J.; Davis, H. J.; Phipps, R. J., Catalytic enantioselective Minisci-type addition to heteroarenes. *Science* **2018,** *360* (6387), 419-422.

106. Coelho, J. A. S.; Matsumoto, A.; Orlandi, M.; Hilton, M. J.; Sigman, M. S.; Toste, F. D., Enantioselective fluorination of homoallylic alcohols enabled by the tuning of non-covalent interactions. *Chem. Sci.* **2018,** *9* (35), 7153-7158.

107. Gelis, C.; Levitre, G.; Merad, J.; Retailleau, P.; Neuville, L.; Masson, G., Highly Diastereo- and Enantioselective Synthesis of Cyclohepta b -indoles by Chiral-Phosphoric-Acid-Catalyzed (4+3) Cycloaddition. *Angew. Chem.-Int. Edit.* **2018,** *57* (37), 12121-12125.

108. Cao, Y. M.; Lentz, D.; Christmann, M., Synthesis of Enantioenriched Bromohydrins via Divergent Reactions of Racemic Intermediates from Anchimeric Oxygen Borrowing. *J. Am. Chem. Soc.* **2018,** *140* (34), 10677-10681.

109. Rajkumar, S.; Wang, J. W.; Zheng, S. J.; Wang, D. L.; Ye, X. Q.; Li, X. J.; Peng, Q.; Yang, X. Y., Regioselective and Enantioselective Synthesis of beta-Indolyl Cyclopentenamides by Chiral Anion Catalysis. *Angew. Chem.-Int. Edit.* **2018,** *57* (41), 13489-13494.

110. Saputra, M. A.; Nepal, B.; Dange, N. S.; Du, P.; Fronczek, F. R.; Kumar, R.; Kartika, R., Enantioselective Functionalization of Enamides at the beta-Carbon Center with Indoles. *Angew. Chem.-Int. Edit.* **2018,** *57* (47), 15558-15562.

111. Yousefi, R.; Struble, T. J.; Payne, J. L.; Vishe, M.; Schley, N. D.; Johnston, J. N., Catalytic, Enantioselective Synthesis of Cyclic Carbamates from Dialkyl Amines by CO2-Capture: Discovery, Development, and Mechanism. *J. Am. Chem. Soc.* **2019,** *141* (1), 618-625.

112. Cao, K. N.; Tan, S. M.; Lee, R.; Yang, S. W.; Jia, H. S.; Zhao, X. W.; Qiao, B. K.; Jiang, Z. Y., Catalytic Enantioselective Addition of Prochiral Radicals to Vinylpyridines. *J. Am. Chem. Soc.* **2019,** *141* (13), 5437-5443.

113. Kwon, Y.; Li, J. Q.; Reid, J. P.; Crawford, J. M.; Jacob, R.; Sigman, M. S.; Toste, F. D.; Miller, S. J., Disparate Catalytic Scaffolds for Atroposelective Cyclodehydration. *J. Am. Chem. Soc.* **2019,** *141* (16), 6698-6705.

114. Zheng, S. C.; Wang, Q.; Zhu, J. P., Catalytic Kinetic Resolution by Enantioselective Aromatization: Conversion of Racemic Intermediates of the Barton-Zard Reaction into Enantioenriched 3-Arylpyrroles. *Angew. Chem.-Int. Edit.* **2019,** *58* (27), 9215-9219.

115. Bai, J. F.; Yasumoto, K.; Kano, T.; Maruoka, K., Asymmetric Synthesis of Chiral 1,4-Enynes through Organocatalytic Alkenylation of Propargyl Alcohols with Trialkenylboroxines. *Angew. Chem.-Int. Edit.* **2019,** *58* (26), 8898-8901.

116. Wu, H.; Wang, Q.; Zhu, J. P., Catalytic Enantioselective Pinacol and Meinwald Rearrangements for the Construction of Quaternary Stereocenters. *J. Am. Chem. Soc.* **2019,** *141* (29), 11372-11377.

117. Zeng, G. K.; Li, Y. Q.; Qiao, B. K.; Zhao, X. W.; Jiang, Z. Y., Photoredox asymmetric catalytic enantioconvergent substitution of 3-chlorooxindoles. *Chem. Commun.* **2019,** *55* (76), 11362-11365.

118. Zheng, D.; Studer, A., Asymmetric Synthesis of Heterocyclic γ-Amino-Acid and Diamine Derivatives by Three-Component Radical Cascade Reactions. *Angewandte Chemie International Edition* **2019,** *58* (44), 15803-15807.

119. Peng, L.; Li, K.; Xie, C.; Li, S.; Xu, D.; Qin, W.; Yan, H., Organocatalytic Asymmetric Annulation of ortho-Alkynylanilines: Synthesis of Axially Chiral Naphthyl-C2-indoles. *Angewandte Chemie International Edition* **2019,** *58* (48), 17199-17204.

120. Shin, N. Y.; Ryss, J. M.; Zhang, X.; Miller, S. J.; Knowles, R. R., Light-driven deracemization enabled by excited-state electron transfer. *Science* **2019,** *366* (6463), 364-+.

121. Reid, J. P.; Proctor, R. S. J.; Sigman, M. S.; Phipps, R. J., Predictive Multivariate Linear Regression Analysis Guides Successful Catalytic Enantioselective Minisci Reactions of Diazines. *J. Am. Chem. Soc.* **2019,** *141* (48), 19178-19185.

122. Yang, J.; Wang, Z.; He, Z.; Li, G.; Hong, L.; Sun, W.; Wang, R., Organocatalytic Enantioselective Synthesis of Tetrasubstituted α-Amino Allenoates by Dearomative γ-Addition of 2,3-Disubstituted Indoles to β,γ-Alkynyl-α-imino Esters. *Angewandte Chemie International Edition* **2020,** *59* (2), 642-647.

123. Yang, K.; Lou, Y.; Wang, C.; Qi, L.-W.; Fang, T.; Zhang, F.; Xu, H.; Zhou, L.; Li, W.; Zhang, G.; Yu, P.; Song, Q., Chiral Brønsted Acid from Chiral Phosphoric Acid Boron Complex and Water: Asymmetric Reduction of Indoles. *Angewandte Chemie International Edition* **2020,** *59* (8), 3294-3299.

124. Coombs, G.; Sak, M. H.; Miller, S. J., Peptide-Catalyzed Fragment Couplings that Form Axially Chiral Non-C2-Symmetric Biaryls. *Angewandte Chemie International Edition* **2020,** *59* (7), 2875-2880.

125. Vaidya, S. D.; Toenjes, S. T.; Yamamoto, N.; Maddox, S. M.; Gustafson, J. L., Catalytic Atroposelective Synthesis of N-Aryl Quinoid Compounds. *J. Am. Chem. Soc.* **2020,** *142* (5), 2198-2203.

126. Pan, X. G.; Wang, Z. H.; Kan, L. L.; Mao, Y.; Zhu, Y. S.; Liu, L., Cross-dehydrogenative coupling enables enantioselective access to CF3-substituted all-carbon quaternary stereocenters. *Chem. Sci.* **2020,** *11* (9), 2414-2419.

127. Rodriguez, S.; Uria, U.; Reyes, E.; Carrillo, L.; Tejero, T.; Merino, P.; Vicario, J. L., Enantioselective Synthesis of Tropanes: Brønsted Acid Catalyzed Pseudotransannular Desymmetrization. *Angewandte Chemie International Edition* **2020,** *59* (17), 6780-6784.

128. Roos, C. B.; Demaerel, J.; Graff, D. E.; Knowles, R. R., Enantioselective Hydroamination of Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.* **2020,** *142* (13), 5974-5979.

129. Kutateladze, D. A.; Strassfeld, D. A.; Jacobsen, E. N., Enantioselective Tail-to-Head Cyclizations Catalyzed by Dual-Hydrogen-Bond Donors. *J. Am. Chem. Soc.* **2020,** *142* (15), 6951-6956.

130. Miller, E.; Kim, S.; Gibson, K.; Derrick, J. S.; Toste, F. D., Regio- and Enantioselective Bromocyclization of Difluoroalkenes as a Strategy to Access Tetrasubstituted Difluoromethylene-Containing Stereocenters. *J. Am. Chem. Soc.* **2020,** *142* (19), 8946-8952.

131. Yu, Z.-L.; Cheng, Y.-F.; Jiang, N.-C.; Wang, J.; Fan, L.-W.; Yuan, Y.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Desymmetrization of unactivated bis-alkenes via chiral Brønsted acid-catalysed hydroamination. *Chem. Sci.* **2020,** *11* (23), 5987-5993.

132. Guo, W.; Luo, Y.; Sung, H. H. Y.; Williams, I. D.; Li, P.; Sun, J., Chiral Phosphoric Acid Catalyzed Enantioselective Synthesis of α-Tertiary Amino Ketones from Sulfonium Ylides. *J. Am. Chem. Soc.* **2020,** *142* (33), 14384-14390.

133. Liu, P.; Bao, X.; Naubron, J.-V.; Chentouf, S.; Humbel, S.; Vanthuyne, N.; Jean, M.; Giordano, L.; Rodriguez, J.; Bonne, D., Simultaneous Control of Central and Helical Chiralities: Expedient Helicoselective Synthesis of Dioxa[6]helicenes. *J. Am. Chem. Soc.* **2020,** *142* (38), 16199-16204.

134. Yin, Y.; Li, Y.; Gonçalves, T. P.; Zhan, Q.; Wang, G.; Zhao, X.; Qiao, B.; Huang, K.-W.; Jiang, Z., All-Carbon Quaternary Stereocenters α to Azaarenes via Radical-Based Asymmetric Olefin Difunctionalization. *J. Am. Chem. Soc.* **2020,** *142* (46), 19451-19456.

135. Ermanis, K.; Colgan, A. C.; Proctor, R. S. J.; Hadrys, B. W.; Phipps, R. J.; Goodman, J. M., A Computational and Experimental Investigation of the Origin of Selectivity in the Chiral Phosphoric Acid Catalyzed Enantioselective Minisci Reaction. *J. Am. Chem. Soc.* **2020,** *142* (50), 21091-21101.

136. Gómez-Martínez, M.; del Carmen Pérez-Aguilar, M.; Piekarski, D. G.; Daniliuc, C. G.; García Mancheño, O., N,N-Dialkylhydrazones as Versatile Umpolung Reagents in Enantioselective Anion-Binding Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (10), 5102-5107.

137. Zhang, P.; Tsuji, N.; Ouyang, J.; List, B., Strong and Confined Acids Catalyze Asymmetric Intramolecular Hydroarylations of Unactivated Olefins with Indoles. *J. Am. Chem. Soc.* **2021,** *143* (2), 675-680.

138. Featherston, A. L.; Kwon, Y.; Pompeo, M. M.; Engl, O. D.; Leahy, D. K.; Miller, S. J., Catalytic asymmetric and stereodivergent oligonucleotide synthesis. *Science* **2021,** *371* (6530), 702-707.

139. Proctor, R. S. J.; Chuentragool, P.; Colgan, A. C.; Phipps, R. J., Hydrogen Atom Transfer-Driven Enantioselective Minisci Reaction of Amides. *J. Am. Chem. Soc.* **2021,** *143* (13), 4928-4934.

140. Tang, Y.; Miller, S. J., Catalytic Enantioselective Synthesis of Pyridyl Sulfoximines. *J. Am. Chem. Soc.* **2021,** *143* (24), 9230-9235.

141. Chan, Y.-C.; Wang, X.; Lam, Y.-P.; Wong, J.; Tse, Y.-L. S.; Yeung, Y.-Y., A Catalyst-Controlled Enantiodivergent Bromolactonization. *J. Am. Chem. Soc.* **2021,** *143* (32), 12745-12754.

142. Mao, J.-H.; Wang, Y.-B.; Yang, L.; Xiang, S.-H.; Wu, Q.-H.; Cui, Y.; Lu, Q.; Lv, J.; Li, S.; Tan, B., Organocatalyst-controlled site-selective arene C–H functionalization. *Nat. Chem.* **2021,** *13* (10), 982-991.

143. Zhang, Y.-Q.; Chen, Y.-B.; Liu, J.-R.; Wu, S.-Q.; Fan, X.-Y.; Zhang, Z.-X.; Hong, X.; Ye, L.-W., Asymmetric dearomatization catalysed by chiral Brønsted acids via activation of ynamides. *Nat. Chem.* **2021,** *13* (11), 1093-1100.

144. Dai, Y.; Liang, S.; Zeng, G.; Huang, H.; Zhao, X.; Cao, S.; Jiang, Z., Asymmetric [3 + 2] photocycloadditions of cyclopropylamines with electron-rich and electron-neutral olefins. *Chem. Sci.* **2022,** *13* (13), 3787-3795.

145. Wang, D.; Shao, Y.-B.; Chen, Y.; Xue, X.-S.; Yang, X., Enantioselective Synthesis of Planar-Chiral Macrocycles through Asymmetric Electrophilic Aromatic Amination. *Angewandte Chemie International Edition* **2022,** *61* (22), e202201064.

146. Liang, D.; Chen, J.-R.; Tan, L.-P.; He, Z.-W.; Xiao, W.-J., Catalytic Asymmetric Construction of Axially and Centrally Chiral Heterobiaryls by Minisci Reaction. *J. Am. Chem. Soc.* **2022,** *144* (13), 6040-6049.

147. Colgan, A. C.; Proctor, R. S. J.; Gibson, D. C.; Chuentragool, P.; Lahdenperä, A. S. K.; Ermanis, K.; Phipps, R. J., Hydrogen Atom Transfer Driven Enantioselective Minisci Reaction of Alcohols. *Angewandte Chemie International Edition* **2022,** *61* (25), e202200266.

148. Li, K.; Huang, S.; Liu, T.; Jia, S.; Yan, H., Organocatalytic Asymmetric Dearomatizing Hetero-Diels–Alder Reaction of Nonactivated Arenes. *J. Am. Chem. Soc.* **2022,** *144* (16), 7374-7381.

149. Payne, J. L.; Deng, Z.; Flach, A. L.; Johnston, J. N., Enantioselective iodolactonization to prepare ε-lactone rings using hypervalent iodine. *Chem. Sci.* **2022,** *13* (24), 7318-7324.

150. Guo, W.; Jiang, F.; Li, S.; Sun, J., Organocatalytic asymmetric azidation of sulfoxonium ylides: mild synthesis of enantioenriched α-azido ketones bearing a labile tertiary stereocenter. *Chem. Sci.* **2022,** *13* (39), 11648-11655.

151. Xu, E. Y.; Werth, J.; Roos, C. B.; Bendelsmith, A. J.; Sigman, M. S.; Knowles, R. R., Noncovalent Stabilization of Radical Intermediates in the Enantioselective Hydroamination of Alkenes with Sulfonamides. *J. Am. Chem. Soc.* **2022,** *144* (41), 18948-18958.

152. Lahdenperä, A. S. K.; Bacoş, P. D.; Phipps, R. J., Enantioselective Giese Additions of Prochiral α-Amino Radicals. *J. Am. Chem. Soc.* **2022,** *144* (49), 22451-22457.

153. Luo, M.-P.; Gu, Y.-J.; Wang, S.-G., Photocatalytic enantioselective Minisci reaction of β-carbolines and application to natural product synthesis. *Chem. Sci.* **2023,** *14* (2), 251-256.

154. Guo, W.; Zhou, Y.; Xie, H.; Yue, X.; Jiang, F.; Huang, H.; Han, Z.; Sun, J., Visible-light-induced organocatalytic enantioselective N–H insertion of α-diazoesters enabled by indirect free carbene capture. *Chem. Sci.* **2023,** *14* (4), 843-848.

155. Huang, S.; Zeng, Z.; Zhang, N.; Qin, W.; Lan, Y.; Yan, H., Organocatalytic asymmetric deoxygenation of sulfones to access chiral sulfinyl compounds. *Nat. Chem.* **2023,** *15* (2), 185-193.

156. Kutta, R. J.; Großkopf, J.; van Staalduinen, N.; Seitz, A.; Pracht, P.; Breitenlechner, S.; Bannwarth, C.; Nuernberger, P.; Bach, T., Multifaceted View on the Mechanism of a Photochemical Deracemization Reaction. *J. Am. Chem. Soc.* **2023,** *145* (4), 2354-2363.

157. Pan, J.-B.; Zhang, X.-G.; Shi, Y.-F.; Han, A.-C.; Chen, Y.-J.; Ouyang, J.; Li, M.-L.; Zhou, Q.-L., A Spiro Phosphamide Catalyzed Enantioselective Proton Transfer of Ylides in a Free Carbene Insertion into N−H Bonds. *Angewandte Chemie International Edition* **2023,** *62* (15), e202300691.

158. Xu, D.; Chang, Y.; Liu, Y.; Qin, W.; Yan, H., Mechanistic Features of Asymmetric Vinylidene ortho-Quinone Methide Construction and Subsequent Transformations. *ACS Catalysis* **2023,** *13* (5), 2957-2967.

159. Maji, R.; Ghosh, S.; Grossmann, O.; Zhang, P.; Leutzsch, M.; Tsuji, N.; List, B., A Catalytic Asymmetric Hydrolactonization. *J. Am. Chem. Soc.* **2023,** *145* (16), 8788-8793.

160. Formica, M.; Rogova, T.; Shi, H.; Sahara, N.; Ferko, B.; Farley, A. J. M.; Christensen, K. E.; Duarte, F.; Yamazaki, K.; Dixon, D. J., Catalytic enantioselective nucleophilic desymmetrization of phosphonate esters. *Nat. Chem.* **2023,** *15* (5), 714-721.

161. Wei, J.; Zhang, J.; Cheng, J. K.; Xiang, S.-H.; Tan, B., Modular enantioselective access to β-amino amides by Brønsted acid-catalysed multicomponent reactions. *Nat. Chem.* **2023,** *15* (5), 647-657.

162. Lin, S.-L.; Chen, Y.-H.; Liu, H.-H.; Xiang, S.-H.; Tan, B., Enantioselective Synthesis of Chiral Cyclobutenes Enabled by Brønsted Acid-Catalyzed Isomerization of BCBs. *J. Am. Chem. Soc.* **2023,** *145* (39), 21152-21158.

163. Zheng, W.-F.; Chen, J.; Qi, X.; Huang, Z., Modular and diverse synthesis of amino acids via asymmetric decarboxylative protonation of aminomalonic acids. *Nat. Chem.* **2023,** *15* (12), 1672-1682.

164. Naulin, E.; Lombard, M.; Gandon, V.; Retailleau, P.; Elslande, E. V.; Neuville, L.; Masson, G., Enantioselective and Regiodivergent Synthesis of Dihydro-1,2-oxazines from Triene-Carbamates via Chiral Phosphoric Acid-Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (48), 26504-26515.

165. Großkopf, J.; Heidecker, A. A.; Bach, T., Photochemical Deracemization of 3-Substituted Oxindoles. *Angewandte Chemie International Edition* **2023,** *62* (30), e202305274.

166. Chen, Y.-H.; Duan, M.; Lin, S.-L.; Liu, Y.-W.; Cheng, J. K.; Xiang, S.-H.; Yu, P.; Houk, K. N.; Tan, B., Organocatalytic aromatization-promoted umpolung reaction of imines. *Nat. Chem.* **2024,** *16* (3), 408-416.

167. Formica, M.; Ferko, B.; Marsh, T.; Davidson, T. A.; Yamazaki, K.; Dixon, D. J., Second Generation Catalytic Enantioselective Nucleophilic Desymmetrization at Phosphorus (V): Improved Generality, Efficiency and Modularity. *Angewandte Chemie International Edition* **2024,** *63* (18), e202400673.

168. Haas, B. C.; Lim, N.-K.; Jermaks, J.; Gaster, E.; Guo, M. C.; Malig, T. C.; Werth, J.; Zhang, H.; Toste, F. D.; Gosselin, F.; Miller, S. J.; Sigman, M. S., Enantioselective Sulfonimidamide Acylation via a Cinchona Alkaloid-Catalyzed Desymmetrization: Scope, Data Science, and Mechanistic Investigation. *J. Am. Chem. Soc.* **2024,** *146* (12), 8536-8546.

169. Sun, X.; Liu, Y.; Yin, Y.; Ban, X.; Zhao, X.; Jiang, Z., Asymmetric photoredox catalytic formal de Mayo reaction enabled by sensitization-initiated electron transfer. *Nat. Chem.* **2024,** *16* (7), 1169-1176.

170. Guria, S.; Volkov, A. N.; Khudaverdyan, R.; Van Lommel, R.; Pan, R.; Daniliuc, C. G.; De Proft, F.; Hennecke, U., Enantioselective, Brønsted Acid-Catalyzed Anti-selective Hydroamination of Alkenes. *J. Am. Chem. Soc.* **2024,** *146* (25), 17180-17188.

171. Wang, X.; Wang, S.-J.; Xin, X.; An, H.; Tu, Z.; Yang, H.; Wong, M. W.; Lu, S., Enantioconvergent and diastereoselective synthesis of atropisomeric hydrazides bearing a cyclic quaternary stereocenter through ternary catalysis. *Chem. Sci.* **2024,** *15* (33), 13240-13249.

172. Wang, J.; Fu, Q.; Cao, S.; Lv, X.; Yin, Y.; Ban, X.; Zhao, X.; Jiang, Z., Enantioselective [2 + 2] Photocycloreversion Enables De Novo Deracemization Synthesis of Cyclobutanes. *J. Am. Chem. Soc.* **2024,** *146* (32), 22840-22849.

173. Liu, S.; Zhang, C.; Han, Z.; Huang, H.; Sun, J., Organocatalytic enantio- and diastereoselective assembly of cyclopropane-incorporated polycyclic molecules via isobenzopyrylium ions. *Chem. Sci.* **2024,** *15* (37), 15274-15279.

174. Yan, X.; Pang, Y.; Zhou, Y.; Chang, R.; Ye, J., Photochemical Deracemization of Lactams with Deuteration Enabled by Dual Hydrogen Atom Transfer. *J. Am. Chem. Soc.* **2025,** *147* (1), 1186-1196.

4.2 Enamide-Acid Dual Activation

4.2.1 Proline

1. Eder, U.; Sauer, G.; Weichert, R., TOTAL SYNTHESIS OF OPTICALLY ACTIVE STEROIDS .6. NEW TYPE OF ASYMMETRIC CYCLIZATION TO OPTICALLY ACTIVE STEROID CD PARTIAL STRUCTURES. *Angew. Chem., Int. Ed.* **1971,** *10* (7), 496-&.

2. Hajos, Z. G.; Parrish, D. R., ASYMMETRIC SYNTHESIS OF BICYCLIC INTERMEDIATES OF NATURAL PRODUCT CHEMISTRY. *J. Org. Chem.* **1974,** *39* (12), 1615-1621.

3. List, B., The direct catalytic asymmetric three-component Mannich reaction. *J. Am. Chem. Soc.* **2000,** *122* (38), 9336-9337.

4. List, B.; Lerner, R. A.; Barbas, C. F., Proline-catalyzed direct asymmetric aldol reactions. *J. Am. Chem. Soc.* **2000,** *122* (10), 2395-2396.

5. Sakthivel, K.; Notz, W.; Bui, T.; Barbas, C. F., Amino acid catalyzed direct asymmetric aldol reactions: A bioorganic approach to catalytic asymmetric carbon-carbon bond-forming reactions. *J. Am. Chem. Soc.* **2001,** *123* (22), 5260-5267.

6. Bogevig, A.; Juhl, K.; Kumaragurubaran, N.; Zhuang, W.; Jorgensen, K. A., Direct organo-catalytic asymmetric alpha-amination of aldehydes - A simple approach to optically active alpha-amino aldehydes, alpha-amino alcohols, and alpha-amino acids. *Angew. Chem., Int. Ed.* **2002,** *41* (10), 1790-+.

7. Cordova, A.; Notz, W.; Zhong, G. F.; Betancort, J. M.; Barbas, C. F., A highly enantioselective amino acid-catalyzed route to functionalized alpha-amino acids. *J. Am. Chem. Soc.* **2002,** *124* (9), 1842-1843.

8. Cordova, A.; Watanabe, S.; Tanaka, F.; Notz, W.; Barbas, C. F., A highly enantioselective route to either enantiomer of both alpha- and beta-amino acid derivatives. *J. Am. Chem. Soc.* **2002,** *124* (9), 1866-1867.

9. Kumaragurubaran, N.; Juhl, K.; Zhuang, W.; Bogevig, A.; Jorgensen, K. A., Direct L-proline-catalyzed asymmetric alpha-amination of ketones. *J. Am. Chem. Soc.* **2002,** *124* (22), 6254-6255.

10. List, B., Direct catalytic asymmetric alpha-amination of aldehydes. *J. Am. Chem. Soc.* **2002,** *124* (20), 5656-5657.

11. List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J., The proline-catalyzed direct asymmetric three-component Mannich reaction: Scope, optimization, and application to the highly enantioselective synthesis of 1,2-amino alcohols. *J. Am. Chem. Soc.* **2002,** *124* (5), 827-833.

12. Northrup, A. B.; MacMillan, D. W. C., The first direct and enantioselective cross-aldol reaction of aldehydes. *J. Am. Chem. Soc.* **2002,** *124* (24), 6798-6799.

13. Alcaide, B.; Almendros, P., The direct catalytic asymmetric cross-aldol reaction of aldehydes. *Angew. Chem., Int. Ed.* **2003,** *42* (8), 858-860.

14. Bahmanyar, S.; Houk, K. N., Origins of opposite absolute stereloselectivities in proline- catalyzed direct Mannich and aldol reactions. *Org. Lett.* **2003,** *5* (8), 1249-1251.

15. Brown, S. P.; Brochu, M. P.; Sinz, C. J.; MacMillan, D. W. C., The direct and enantioselective organocatalytic alpha-oxidation of aldehydes. *J. Am. Chem. Soc.* **2003,** *125* (36), 10808-10809.

16. Cordova, A., One-pot organocatalytic direct asymmetric synthesis of gamma- amino alcohol derivatives. *Synlett* **2003,** (11), 1651-1654.

17. Cordova, A.; Barbas, C. F., Direct organocatalytic asymmetric Mannich-type reactions in aqueous media: one-pot Mannich-allylation reactions. *Tetrahedron Lett.* **2003,** *44* (9), 1923-1926.

18. Duthaler, R. O., Proline-catalyzed asymmetric alpha-amination of aldehydes and ketones - An astonishingly simple access to optically active alpha-hydrazino carbonyl compounds. *Angew. Chem., Int. Ed.* **2003,** *42* (9), 975-978.

19. Hayashi, Y.; Tsuboi, W.; Ashimine, I.; Urushima, T.; Shoji, M.; Sakai, K., The direct and enantioselective, one-pot, three-component, cross-Mannich reaction of aldehydes. *Angew. Chem., Int. Ed.* **2003,** *42* (31), 3677-3680.

20. Hayashi, Y.; Yamaguchi, J.; Hibino, K.; Shoji, M., Direct proline catalyzed asymmetric alpha-aminooxylation of aldehydes. *Tetrahedron Lett.* **2003,** *44* (45), 8293-8296.

21. Hoang, L.; Bahmanyar, S.; Houk, K. N.; List, B., Kinetic and stereochemical evidence for the involvement of only one proline molecule in the transition states of proline- catalyzed intra- and intermolecular aldol reactions. *J. Am. Chem. Soc.* **2003,** *125* (1), 16-17.

22. Pidathala, C.; Hoang, L.; Vignola, N.; List, B., Direct catalytic asymmetric enolexo aldolizations. *Angew. Chem., Int. Ed.* **2003,** *42* (24), 2785-2788.

23. Ramachary, D. B.; Chowdari, N. S.; Barbas, C. F., Organocatalytic asymmetric domino Knoevenagel/Diels-Alder reactions: A bioorganic approach to the diastereospecific and enantioselective construction of highly substituted spiro 5,5 undecane-1,5,9-triones. *Angew. Chem., Int. Ed.* **2003,** *42* (35), 4233-4237.

24. Vogt, H.; Vanderheiden, S.; Brase, S., Proline-catalysed asymmetric amination of alpha,alpha- disubstituted aldehydes: synthesis of configurationally stable enantioenriched alpha-aminoaldehydes. *Chem. Comm.* **2003,** (19), 2448-2449.

25. Zhong, G. F., A facile and rapid route to highly enantiopure 1,2-diols by novel catalytic asymmetric alpha-aminoxylation of aldehydes. *Angew. Chem., Int. Ed.* **2003,** *42* (35), 4247-4250.

26. Bogevig, A.; Sunden, H.; Cordova, A., Direct catalytic enantioselective alpha-aminoxylation of ketones: A stereoselective synthesis of alpha-hydroxy and alpha,alpha '-dihydroxy ketones. *Angew. Chem., Int. Ed.* **2004,** *43* (9), 1109-1112.

27. Cheong, P. H. Y.; Houk, K. N., Origins of selectivities in proline-catalyzed alpha-aminoxylations. *J. Am. Chem. Soc.* **2004,** *126* (43), 13912-13913.

28. Clemente, F. R.; Houk, K. N., Computational evidence foir the enamine mechanism of intramolecular Aldol reactions catalyzed by proline. *Angew. Chem., Int. Ed.* **2004,** *43* (43), 5766-5768.

29. Cordova, A.; Sunden, H.; Bogevig, A.; Johansson, M.; Himo, F., The direct catalytic asymmetric alpha-aminooxylation reaction: Development of stereoselective routes to 1,2-diols and 1,2- amino alcohols and density functional calculations. *Chem. Eur. J.* **2004,** *10* (15), 3673-3684.

30. Cordova, A.; Sunden, H.; Engqvist, M.; Ibrahem, I.; Casas, J., The direct amino acid-catalyzed asymmetric incorporation of molecular oxygen to organic compounds. *J. Am. Chem. Soc.* **2004,** *126* (29), 8914-8915.

31. Hayashi, Y.; Yamaguchi, J.; Sumiya, T.; Shoji, M., Direct proline-catalyzed asymmetric alpha-aminoxylation of ketones. *Angew. Chem., Int. Ed.* **2004,** *43* (9), 1112-1115.

32. Ibrahem, I.; Casas, J.; Cordova, A., Direct catalytic enantioselective alpha-aminomethylation of ketones. *Angew. Chem., Int. Ed.* **2004,** *43* (47), 6528-6531.

33. Iwamura, H.; Mathew, S. P.; Blackmond, D. G., In situ catalyst improvement in the proline-mediated alpha- amination of aldehydes. *J. Am. Chem. Soc.* **2004,** *126* (38), 11770-11771.

34. Iwamura, H.; Wells, D. H.; Mathew, S. P.; Klussmann, M.; Armstrong, A.; Blackmond, D. G., Probing the active catalyst in product-accelerated proline-mediated reactions. *J. Am. Chem. Soc.* **2004,** *126* (50), 16312-16313.

35. Merino, P.; Tejero, T., Organocatalyzed asymmetric alpha-aminoxylation of aldehydes and ketones - An efficient access to enantiomerically pure alpha- hydroxycarbonyl compounds, diols, and even amino alcohols. *Angew. Chem., Int. Ed.* **2004,** *43* (23), 2995-2997.

36. Northrup, A. B.; MacMillan, D. W. C., Two-step synthesis of carbohydrates by selective aldol reactions. *Science* **2004,** *305* (5691), 1752-1755.

37. Northrup, A. B.; Mangion, I. K.; Hettche, F.; MacMillan, D. W. C., Enantioselective organocatalytic direct aldol reactions of alpha-oxyaldehydes: Step one in a two-step synthesis of carbohydrates. *Angew. Chem., Int. Ed.* **2004,** *43* (16), 2152-2154.

38. Sunden, H.; Engqvist, M.; Casas, J.; Ibrahem, I.; Cordova, A., Direct amino acid catalyzed asymmetric alpha oxidation of ketones with molecular oxygen. *Angew. Chem., Int. Ed.* **2004,** *43* (47), 6532-6535.

39. Vignola, N.; List, B., Catalytic asymmetric intramolecular alpha-alkylation of aldehydes. *J. Am. Chem. Soc.* **2004,** *126* (2), 450-451.

40. Zhuang, W.; Saaby, S.; Jorgensen, K. A., Direct organocatalytic enantioselective Mannich reactions of ketimines: An approach to optically active quaternary alpha- amino acid derivatives. *Angew. Chem., Int. Ed.* **2004,** *43* (34), 4476-4478.

41. Casas, J.; Engqvist, M.; Ibrahem, I.; Kaynak, B.; Cordova, A., Direct amino acid catalyzed asymmetric synthesis of polyketide sugars. *Angew. Chem., Int. Ed.* **2005,** *44* (9), 1343-1345.

42. Enders, D.; Grondal, C., Direct organocatalytic de novo synthesis of carbohydrates. *Angew. Chem., Int. Ed.* **2005,** *44* (8), 1210-1212.

43. Enders, D.; Grondal, C.; Vrettou, M.; Raabe, G., Asymmetric synthesis of selectively protected amino sugars and derivatives by a direct organocatalytic Mannich reaction. *Angew. Chem., Int. Ed.* **2005,** *44* (26), 4079-4083.

44. Ramachary, D. B.; Barbas, C. F., Direct amino acid-catalyzed asymmetric desymmetrization of meso-compounds: Tandem aminoxylation/O-N bond heterolysis reactions. *Org. Lett.* **2005,** *7* (8), 1577-1580.

45. Marques, M. M. B., Catalytic enantioselective cross-Mannich reaction of aldehydes. *Angew. Chem., Int. Ed.* **2006,** *45* (3), 348-352.

46. Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B., Asymmetric enamine catalysis. *Chem. Rev* **2007,** *107* (12), 5471-5569.

47. Seebach, D.; Beck, A. K.; Badine, D. M.; Limbach, M.; Eschenmoser, A.; Treasurywala, A. M.; Hobi, R.; Prikoszovich, W.; Linder, B., Are Oxazolidinones Really Unproductive, Parasitic Species in Proline Catalysis? – Thoughts and Experiments Pointing to an Alternative View. *Helv. Chim. Acta* **2007,** *90* (3), 425-471.

48. Zotova, N.; Franzke, A.; Armstrong, A.; Blackmond, D. G., Clarification of the role of water in proline-mediated aldol reactions. *J. Am. Chem. Soc.* **2007,** *129* (49), 15100-+.

49. Hahn, B. T.; Frohlich, R.; Harms, K.; Glorius, F., Proline-Catalyzed Highly Enantioselective and anti-Selective Mannich Reaction of Unactivated Ketones: Synthesis of Chiral alpha-Amino Acids. *Angew. Chem., Int. Ed.* **2008,** *47* (51), 9985-9988.

50. Isart, C.; Bures, J.; Vilarrasa, J., Seebach's oxazolidinone is a good catalyst for aldol reactions. *Tetrahedron Lett.* **2008,** *49* (37), 5414-5418.

51. Mandal, T.; Zhao, C. G., Modularly designed organocatalytic assemblies for direct nitro-michael addition reactions. *Angew. Chem., Int. Ed.* **2008,** *47* (40), 7714-7717.

52. Yang, J. W.; Chandler, C.; Stadler, M.; Kampen, D.; List, B., Proline-catalysed Mannich reactions of acetaldehyde. *Nature* **2008,** *452* (7186), 453-455.

53. Chandler, C.; Galzerano, P.; Michrowska, A.; List, B., The Proline-Catalyzed Double Mannich Reaction of Acetaldehyde with N-Boc Imines. *Angew. Chem., Int. Ed.* **2009,** *48* (11), 1978-1980.

54. Poe, S. L.; Bogdan, A. R.; Mason, B. P.; Steinbacher, J. L.; Opalka, S. M.; McQuade, D. T., Use of Bifunctional Ureas to Increase the Rate of Proline-Catalyzed alpha-Aminoxylations. *J. Org. Chem.* **2009,** *74* (4), 1574-1580.

55. Zhu, H.; Clemente, F. R.; Houk, K. N.; Meyer, M. P., Rate Limiting Step Precedes C-C Bond Formation in the Archetypical Proline-Catalyzed Intramolecular Aldol Reaction. *J. Am. Chem. Soc.* **2009,** *131* (5), 1632-+.

56. Blackmond, D. G.; Moran, A.; Hughes, M.; Armstrong, A., Unusual Reversal of Enantioselectivity in the Proline-Mediated alpha-Amination of Aldehydes Induced by Tertiary Amine Additives. *J. Am. Chem. Soc.* **2010,** *132* (22), 7598-+.

57. Kanzian, T.; Lakhdar, S.; Mayr, H., Kinetic Evidence for the Formation of Oxazolidinones in the Stereogenic Step of Proline-Catalyzed Reactions. *Angew. Chem., Int. Ed.* **2010,** *49* (49), 9526-9529.

58. Millet, R.; Traff, A. M.; Petrus, M. L.; Backvall, J. E., Enantioselective Synthesis of syn- and anti-1,3-Aminoalcohols via beta-Aminoketones and Subsequent Reduction/Dynamic Kinetic Asymmetric Transformation. *J. Am. Chem. Soc.* **2010,** *132* (43), 15182-15184.

59. Schmid, M. B.; Zeitler, K.; Gschwind, R. M., The Elusive Enamine Intermediate in Proline-Catalyzed Aldol Reactions: NMR Detection, Formation Pathway, and Stabilization Trends. *Angew. Chem., Int. Ed.* **2010,** *49* (29), 4997-5003.

60. Lin, S. Z.; Deiana, L.; Zhao, G. L.; Sun, J. L.; Cordova, A., Dynamic One-Pot Three-Component Catalytic Asymmetric Transformation by Combination of Hydrogen-Bond-Donating and Amine Catalysts. *Angew. Chem., Int. Ed.* **2011,** *50* (33), 7624-7630.

61. Armstrong, A.; Boto, R. A.; Dingwall, P.; Contreras-Garcia, J.; Harvey, M. J.; Mason, N. J.; Rzepa, H. S., The Houk-List transition states for organocatalytic mechanisms revisited. *Chemical Science* **2014,** *5* (5), 2057-2071.

62. Orlandi, M.; Ceotto, M.; Benaglia, M., Kinetics versus thermodynamics in the proline catalyzed aldol reaction. *Chemical Science* **2016,** *7* (8), 5421-5427.

4.2.2 Other Amine Catalysts

1. Christoffers, J.; Baro, A., Construction of quaternary stereocenters: New perspectives through enantioselective Michael reactions. *Angew. Chem., Int. Ed.* **2003,** *42* (15), 1688-1690.

2. Imbriglio, J. E.; Vasbinder, M. M.; Miller, S. J., Dual catalyst control in the amino acid-peptide-catalyzed enantioselective Baylis-Hillman reaction. *Org. Lett.* **2003,** *5* (20), 3741-3743.

3. Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H., A new class of chiral pyrrolidine-pyridine conjugate base catalysts for use in asymmetric Michael addition reactions. *J. Am. Chem. Soc.* **2004,** *126* (31), 9558-9559.

4. Mase, N.; Tanaka, F.; Barbas, C. F., Synthesis of beta-hydroxyaldehydes with stereogenic quaternary carbon centers by direct organocatalytic asymmetric aldol reactions. *Angew. Chem., Int. Ed.* **2004,** *43* (18), 2420-2423.

5. Torii, H.; Nakadai, M.; Ishihara, K.; Saito, S.; Yamamoto, H., Asymmetric direct aldol reaction assisted by water and a proline-derived tetrazole catalyst. *Angew. Chem., Int. Ed.* **2004,** *43* (15), 1983-1986.

6. Yamamoto, Y.; Momiyama, N.; Yamamoto, H., Enantioselective tandem O-nitroso aldol/Michael reaction. *J. Am. Chem. Soc.* **2004,** *126* (19), 5962-5963.

7. Aroyan, C. E.; Vasbinder, M. M.; Miller, S. J., Dual catalyst control in the enantioselective intramolecular Morita-Baylis-Hillman reaction. *Org. Lett.* **2005,** *7* (18), 3849-3851.

8. Bassan, A.; Zou, W. B.; Reyes, E.; Himo, F.; Cordova, A., The origin of stereoselectivity in primary amino acid catalyzed intermolecular Aldol reactions. *Angew. Chem., Int. Ed.* **2005,** *44* (43), 7028-7032.

9. Chen, J. R.; Lu, H. H.; Li, X. Y.; Cheng, L.; Wan, J.; Xiao, W. J., Readily tunable and bifunctional L-prolinamide derivatives: Design and application in the direct enantioselective aldol reactions. *Org. Lett.* **2005,** *7* (20), 4543-4545.

10. Kano, T.; Takai, J.; Tokuda, O.; Maruoka, K., Design of an axially chiral amino acid with a binaphthyl backbone as an organocatalyst for a direct asymmetric aldol reaction. *Angew. Chem., Int. Ed.* **2005,** *44* (20), 3055-3057.

11. Kano, T.; Yamaguchi, Y.; Tokuda, O.; Maruoka, K., anti-Selective direct asymmetric Mannich reactions catalyzed by axially chiral amino sulfonamide as an organocatalyst. *J. Am. Chem. Soc.* **2005,** *127* (47), 16408-16409.

12. Krattiger, P.; Kovasy, R.; Revell, J. D.; Ivan, S.; Wennemers, H., Increased structural complexity leads to higher activity: Peptides as efficient and versatile catalysts for asymmetric aldol reactions. *Org. Lett.* **2005,** *7* (6), 1101-1103.

13. Kunz, R. K.; MacMillan, D. W. C., Enantioselective organocatalytic cyclopropanations. The identification of a new class of iminium catalyst based upon directed electrostatic activation. *J. Am. Chem. Soc.* **2005,** *127* (10), 3240-3241.

14. Cao, C. L.; Sun, X. L.; Kang, Y. B.; Tang, Y., Enantioselective formal [3+3] annulation for the direct construction of bicyclic skeletons with four stereogenic Centers. *Org. Lett.* **2007,** *9* (21), 4151-4154.

15. Kano, T.; Yamaguchi, Y.; Tanaka, Y.; Maruoka, K., syn-selective and enantioselective direct cross-aldol reactions between aldehydes catalyzed by an axially chiral amino sulfonamide. *Angew. Chem., Int. Ed.* **2007,** *46* (10), 1738-1740.

16. Luo, S. Z.; Xu, H.; Li, J. Y.; Zhang, L.; Cheng, J. P., A simple primary-tertiary diamine-Bronsted acid catalyst for asymmetric direct Aldol reactions of linear aliphatic ketones. *J. Am. Chem. Soc.* **2007,** *129* (11), 3074-+.

17. Malkov, A. V.; Kabeshov, M. A.; Bella, M.; Kysilka, O.; Malyshev, D. A.; Pluhackova, K.; Kocovsky, P., Vicinal amino alcohols as organocatalysts in asymmetric cross-aldol reaction of ketones: Application in the synthesis of convolutamydine a. *Org. Lett.* **2007,** *9* (26), 5473-5476.

18. Momiyama, N.; Yamamoto, Y.; Yamamoto, H., Diastereo- and enantioselective synthesis of nitroso Diels-Alder-type bicycloketones using dienamine: Mechanistic insight into sequential nitroso aldol/Michael reaction and application for optically pure 1-amino-3,4-diol synthesis. *J. Am. Chem. Soc.* **2007,** *129* (5), 1190-1195.

19. Vishnumaya; Singh, V. K., Highly enantioselective water-compatible organocatalyst for Michael reaction of ketones to nitroolefins. *Org. Lett.* **2007,** *9* (6), 1117-1119.

20. Alcaide, B.; Almendros, P., Organocatalytic reactions with acetaldehyde. *Angew. Chem., Int. Ed.* **2008,** *47* (25), 4632-4634.

21. Arnold, K.; Batsanov, A. S.; Davies, B.; Grosjean, C.; Schutz, T.; Whiting, A.; Zawatzky, K., The first example of enamine - Lewis acid cooperative bifunctional catalysis: application to the asymmetric aldol reaction. *Chem. Comm.* **2008,** (33), 3879-3881.

22. Chen, J. R.; An, X. L.; Zhu, X. Y.; Wang, X. F.; Xiao, W. J., Rational combination of two privileged chiral backbones: Highly efficient organocatalysts for asymmetric direct aldol reactions between aromatic aldehydes and acylic ketones. *J. Org. Chem.* **2008,** *73* (15), 6006-6009.

23. Hayashi, Y.; Itoh, T.; Aratake, S.; Ishikawa, H., A diarylprolinol in an asymmetric, catalytic, and direct crossed-aldol reaction of acetaldehyde. *Angew. Chem., Int. Ed.* **2008,** *47* (11), 2082-2084.

24. Kano, T.; Maruoka, K., Design of chiral bifunctional secondary amine catalysts for asymmetric enamine catalysis. *Chem. Comm.* **2008,** (43), 5465-5473.

25. Kano, T.; Ueda, M.; Maruoka, K., Direct asymmetric iodination of aldehydes using an axially chiral bifunctional amino alcohol catalyst. *J. Am. Chem. Soc.* **2008,** *130* (12), 3728-+.

26. Liu, J.; Yang, Z. G.; Wang, Z.; Wang, F.; Chen, X. H.; Liu, X. H.; Feng, X. M.; Su, Z. S.; Hu, C. W., Asymmetric direct aldol reaction of functionalized ketones catalyzed by amine organocatalysts based on bispidine. *J. Am. Chem. Soc.* **2008,** *130* (17), 5654-+.

27. Lu, M.; Zhu, D.; Lu, Y. P.; Hou, Y. X.; Tan, B.; Zhong, G. F., Organocatalytic Asymmetric alpha-Aminoxylation/Aza-Michael Reactions for the Synthesis of Functionalized Tetrahydro-1,2-oxazines. *Angew. Chem., Int. Ed.* **2008,** *47* (52), 10187-10191.

28. Lu, X. J.; Deng, L., Asymmetric aza-Michael reactions of alpha,beta-unsaturated ketones with bifunctional organic catalysts. *Angew. Chem., Int. Ed.* **2008,** *47* (40), 7710-7713.

29. Lu, X. J.; Liu, Y.; Sun, B. F.; Cindric, B.; Deng, L., Catalytic enantioselective peroxidation of alpha,beta-usaturated ketones. *J. Am. Chem. Soc.* **2008,** *130* (26), 8134-+.

30. Nakamura, S.; Hara, N.; Nakashima, H.; Kubo, K.; Shibata, N.; Toru, T., Enantioselective Synthesis of (R)-Convolutamydine A with New N-Heteroarylsulfonylprolinamides. *Chem. Eur. J.* **2008,** *14* (27), 8079-8081.

31. Nakayama, K.; Maruoka, K., Complete Switch of Product Selectivity in Asymmetric Direct Aldol Reaction with Two Different Chiral Organocatalysts from a Common Chiral Source. *J. Am. Chem. Soc.* **2008,** *130* (52), 17666-+.

32. Pouliquen, M.; Blanchet, J.; Lasne, M. C.; Rouden, J., 3-trifluoromethanesulfonamido-pyrrolidine: A general organocatalyst for anti-selective Mannich reactions. *Org. Lett.* **2008,** *10* (5), 1029-1032.

33. Quintard, A.; Bournaud, C.; Alexakis, A., Diversity-oriented synthesis towards conceptually new highly modular aminal-pyrrolidine organocatalysts. *Chem. Eur. J.* **2008,** *14* (25), 7504-7507.

34. Ramasastry, S. S. V.; Albertshofer, K.; Utsumi, N.; Barbas, C. F., Water-compatible organocatalysts for direct asymmetric syn-aldol reactions of dihydroxyacetone and aldehydes. *Org. Lett.* **2008,** *10* (8), 1621-1624.

35. Singh, R. P.; Bartelson, K.; Wang, Y.; Su, H.; Lu, X.; Deng, L., Enantioselective Diels-Alder reaction of simple alpha,beta-unsaturated ketones with a cinchona alkaloid catalyst. *J. Am. Chem. Soc.* **2008,** *130* (8), 2422-2423.

36. Zhang, H. L.; Mitsumori, S.; Utsumi, N.; Imai, M.; Garcia-Delgado, N.; Mifsud, M.; Albertshofer, K.; Cheong, P. H. Y.; Houk, K. N.; Tanaka, F.; Barbas, C. F., Catalysis of 3-pyrrolidinecarboxylic acid and related pyrrolidine derivatives in enantioselective anti-Mannich-type reactions: Importance of the 3-acid group on pyrrolidine for stereocontrol. *J. Am. Chem. Soc.* **2008,** *130* (3), 875-886.

37. Zhang, Q. Y.; Ni, B. K.; Headley, A. D., Asymmetric Michael addition reactions of aldehydes with nitrostyrenes catalyzed by functionalized chiral ionic liquids. *Tetrahedron* **2008,** *64* (22), 5091-5097.

38. Bella, M.; Schietroma, D. M. S.; Cusella, P. P.; Gasperi, T.; Visca, V., Synergic asymmetric organocatalysis (SAOc) of Cinchona alkaloids and secondary amines in the synthesis of bicyclo[2.2.2]octan-2-ones. *Chem. Comm.* **2009,** (5), 597-599.

39. Jiao, P.; Kawasaki, M.; Yamamoto, H., A Sequential O-Nitrosoaldol and Grignard Addition Process: An Enantio- and Diastereoselective Entry to Chiral 1,2-Diols. *Angew. Chem., Int. Ed.* **2009,** *48* (18), 3333-3336.

40. Kano, T.; Yamaguchi, Y.; Maruoka, K., A Designer Axially Chiral Amino Sulfonamide as an Efficient Organocatalyst for Direct Asymmetric Mannich Reactions of N-Boc-Protected Imines. *Angew. Chem., Int. Ed.* **2009,** *48* (10), 1838-1840.

41. Lakhdar, S.; Appel, R.; Mayr, H., How Does Electrostatic Activation Control Iminium-Catalyzed Cyclopropanations? *Angew. Chem., Int. Ed.* **2009,** *48* (27), 5034-5037.

42. Li, P. F.; Yamamoto, H., Amino acid salt catalyzed intramolecular Robinson annulation. *Chem. Comm.* **2009,** (36), 5412-5414.

43. Lv, J.; Zhang, J. M.; Lin, Z.; Wang, Y. M., Enantioselective Synthesis of Functionalized Nitrocyclopropanes by Organocatalytic Conjugate Addition of Bromonitroalkanes to alpha,beta-Unsaturated Enones. *Chem. Eur. J.* **2009,** *15* (4), 972-979.

44. Markert, M.; Scheffler, U.; Mahrwald, R., Asymmetric Histidine-Catalyzed Cross-Aldol Reactions of Enolizable Aldehydes: Access to Defined Configured Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2009,** *131* (46), 16642-+.

45. Rasappan, R.; Reiser, O., Cyclohexane-1,2-diamines: Efficient Catalysts for the Enantioselective Conjugate Addition of Ketones to Nitro Olefins. *Eur. J. Org. Chem.* **2009,** (9), 1305-1308.

46. Uehara, H.; Barbas, C. F., anti-Selective Asymmetric Michael Reactions of Aldehydes and Nitroolefins Catalyzed by a Primary Amine/Thiourea. *Angew. Chem., Int. Ed.* **2009,** *48* (52), 9848-9852.

47. Wiesner, M.; Neuburger, M.; Wennemers, H., Tripeptides of the Type H-D-Pro-Pro-Xaa-NH2 as Catalysts for Asymmetric 1,4-Addition Reactions: Structural Requirements for High Catalytic Efficiency. *Chem. Eur. J.* **2009,** *15* (39), 10103-10109.

48. Wu, L. Y.; Bencivenni, G.; Mancinelli, M.; Mazzanti, A.; Bartoli, G.; Melchiorre, P., Organocascade Reactions of Enones Catalyzed by a Chiral Primary Amine. *Angew. Chem., Int. Ed.* **2009,** *48* (39), 7196-7199.

49. Xu, D. Q.; Xia, A. B.; Luo, S. P.; Tang, J.; Zhang, S.; Jiang, J. R.; Xu, Z. Y., In Situ Enamine Activation in Aqueous Salt Solutions: Highly Efficient Asymmetric Organocatalytic Diels-Alder Reaction of Cyclohexenones with Nitroolefins. *Angew. Chem., Int. Ed.* **2009,** *48* (21), 3821-3824.

50. Bergonzini, G.; Vera, S.; Melchiorre, P., Cooperative Organocatalysis for the Asymmetric gamma Alkylation of alpha-Branched Enals. *Angew. Chem., Int. Ed.* **2010,** *49* (50), 9685-9688.

51. Brown, A. R.; Kuo, W. H.; Jacobsen, E. N., Enantioselective Catalytic alpha-Alkylation of Aldehydes via an S(N)1 Pathway. *J. Am. Chem. Soc.* **2010,** *132* (27), 9286-9288.

52. Jensen, K. L.; Franke, P. T.; Arroniz, C.; Kobbelgaard, S.; Jorgensen, K. A., Enantioselective Synthesis of Cyclopentene Carbaldehydes by a Direct Multicatalytic Cascade Sequence: Carbocyclization of Aldehydes with Alkynes. *Chem. Eur. J.* **2010,** *16* (6), 1750-1753.

53. Lu, A. D.; Wu, R. H.; Wang, Y. M.; Zhou, Z. H.; Wu, G. P.; Fang, J. X.; Tang, C. C., Chiral Thiophosphoramidate-Catalyzed Asymmetric Michael Addition of Ketones to Nitro Olefins. *Eur. J. Org. Chem.* **2010,** (11), 2057-2061.

54. Moteki, S. A.; Xu, S. M.; Arimitsu, S.; Maruoka, K., Design of Structurally Rigid trans-Diamine-Based Tf-Amide Organocatalysts with a Dihydroanthracene Framework for Asymmetric Conjugate Additions of Heterosubstituted Aldehydes to Vinyl Sulfones. *J. Am. Chem. Soc.* **2010,** *132* (48), 17074-17076.

55. Wen, S. G.; Li, P. F.; Wu, H. B.; Yu, F.; Liang, X. M.; Ye, J. X., Enantioselective organocatalytic phospha-Michael reaction of alpha,beta-unsaturated ketones. *Chem. Comm.* **2010,** *46* (26), 4806-4808.

56. Xiao, J.; Xu, F. X.; Lu, Y. P.; Loh, T. P., Chemzymes: A New Class of Structurally Rigid Tricyclic Amphibian Organocatalyst Inspired by Natural Product. *Org. Lett.* **2010,** *12* (6), 1220-1223.

57. Zhang, L.; Cui, L. Y.; Li, X.; Li, J. Y.; Luo, S. Z.; Cheng, J. P., Asymmetric S(N)1 alpha-Alkylation of Cyclic Ketones Catalyzed by Functionalized Chiral Ionic Liquid (FCIL) Organocatalysts. *Chem. Eur. J.* **2010,** *16* (7), 2045-2049.

58. Burns, N. Z.; Witten, M. R.; Jacobsen, E. N., Dual Catalysis in Enantioselective Oxidopyrylium-Based 5+2 Cycloadditions. *J. Am. Chem. Soc.* **2011,** *133* (37), 14578-14581.

59. Fu, N. K.; Zhang, L.; Li, J. Y.; Luo, S. Z.; Cheng, J. P., Chiral Primary Amine Catalyzed Enantioselective Protonation via an Enamine Intermediate. *Angew. Chem., Int. Ed.* **2011,** *50* (48), 11451-11455.

60. Hayashi, Y.; Yasui, Y.; Kawamura, T.; Kojima, M.; Ishikawa, H., One-Pot Synthesis of Chiral alpha-Substituted beta,gamma-Epoxy Aldehyde Derivatives through an Asymmetric Aldol Reaction of Chloroacetaldehyde. *Angew. Chem., Int. Ed.* **2011,** *50* (12), 2804-2807.

61. Huang, H. C.; Jin, Z. C.; Zhu, K. L.; Liang, X. M.; Ye, J. X., Highly Diastereo- and Enantioselective Synthesis of 5-Substituted 3-Pyrrolidin-2-ones: Vinylogous Michael Addition under Multifunctional Catalysis. *Angew. Chem., Int. Ed.* **2011,** *50* (14), 3232-3235.

62. Kano, T.; Shirozu, F.; Tatsumi, K.; Kubota, Y.; Maruoka, K., The first example of the direct asymmetric conjugate addition of aldehydes to a methylenemalonate promoted by an axially chiral amino diol catalyst. *Chemical Science* **2011,** *2* (12), 2311-2313.

63. Kano, T.; Sugimoto, H.; Maruoka, K., Efficient Organocatalytic Cross-Aldol Reaction between Aliphatic Aldehydes through Their Functional Differentiation. *J. Am. Chem. Soc.* **2011,** *133* (45), 18130-18133.

64. Lifchits, O.; Demoulin, N.; List, B., Direct Asymmetric alpha Benzoyloxylation of Cyclic Ketones. *Angew. Chem., Int. Ed.* **2011,** *50* (41), 9680-9683.

65. Rahaman, H.; Madarasz, A.; Papai, I.; Pihko, P. M., Dual Hydrogen-Bond/Enamine Catalysis Enables a Direct Enantioselective Three-Component Domino Reaction. *Angew. Chem., Int. Ed.* **2011,** *50* (27), 6123-6127.

66. Sinisi, R.; Vita, M. V.; Gualandi, A.; Emer, E.; Cozzi, P. G., S(N)1-Type Reactions in the Presence of Water: Indium(III)-Promoted Highly Enantioselective Organocatalytic Propargylation of Aldehydes. *Chem. Eur. J.* **2011,** *17* (27), 7404-7408.

67. Tian, X.; Cassani, C.; Liu, Y. K.; Moran, A.; Urakawa, A.; Galzerano, P.; Arceo, E.; Melchiorre, P., Diastereodivergent Asymmetric Sulfa-Michael Additions of alpha-Branched Enones using a Single Chiral Organic Catalyst. *J. Am. Chem. Soc.* **2011,** *133* (44), 17934-17941.

68. Albrecht, L.; Acosta, F. C.; Fraile, A.; Albrecht, A.; Christensen, J.; Jorgensen, K. A., Enantioselective H-Bond-Directing Approach for Trienamine-mediated Reactions in Asymmetric Synthesis. *Angew. Chem., Int. Ed.* **2012,** *51* (36), 9088-9092.

69. Albrecht, L.; Dickmeiss, G.; Acosta, F. C.; Rodriguez-Escrich, C.; Davis, R. L.; Jorgensen, K. A., Asymmetric Organocatalytic Formal 2+2 -Cycloadditions via Bifunctional H-Bond Directing Dienamine Catalysis. *J. Am. Chem. Soc.* **2012,** *134* (5), 2543-2546.

70. Albrecht, L.; Dickmeiss, G.; Weise, C. F.; Rodriguez-Escrich, C.; Jorgensen, K. A., Dienamine-Mediated Inverse-Electron-Demand Hetero-Diels-Alder Reaction by Using an Enantioselective H-Bond-Directing Strategy. *Angew. Chem., Int. Ed.* **2012,** *51* (52), 13109-13113.

71. Duangdee, N.; Harnying, W.; Rulli, G.; Neudorfl, J. M.; Groger, H.; Berkessel, A., Highly Enantioselective Organocatalytic Trifluoromethyl Carbinol Synthesis-A Caveat on Reaction Times and Product Isolation. *J. Am. Chem. Soc.* **2012,** *134* (27), 11196-11205.

72. Feng, X.; Zhou, Z.; Zhou, R.; Zhou, Q. Q.; Dong, L.; Chen, Y. C., Stereodivergence in Amine-Catalyzed Regioselective 4+2 Cycloadditions of beta-Substituted Cyclic Enones and Polyconjugated Malononitriles. *J. Am. Chem. Soc.* **2012,** *134* (48), 19942-19947.

73. Jiang, H.; Rodriguez-Escrich, C.; Johansen, T. K.; Davis, R. L.; Jorgensen, K. A., Organocatalytic Activation of Polycyclic Aromatic Compounds for Asymmetric Diels-Alder Reactions. *Angew. Chem., Int. Ed.* **2012,** *51* (41), 10271-10274.

74. Jiang, X. X.; Shi, X. M.; Wang, S. L.; Sun, T.; Cao, Y. M.; Wang, R., Bifunctional Organocatalytic Strategy for Inverse-Electron-Demand Diels-Alder Reactions: Highly Efficient In Situ Substrate Generation and Activation to Construct Azaspirocyclic Skeletons. *Angew. Chem., Int. Ed.* **2012,** *51* (9), 2084-2087.

75. Kang, J. Y.; Carter, R. G., Primary Amine, Thiourea-Based Dual Catalysis Motif for Synthesis of Stereogenic, All-Carbon Quaternary Center-Containing Cycloalkanones. *Org. Lett.* **2012,** *14* (12), 3178-3181.

76. Kano, T.; Sakamoto, R.; Akakura, M.; Maruoka, K., Stereocontrolled Synthesis of Vicinal Diamines by Organocatalytic Asymmetric Mannich Reaction of N-Protected Aminoacetaldehydes: Formal Synthesis of (-)-Agelastatin A. *J. Am. Chem. Soc.* **2012,** *134* (17), 7516-7520.

77. Kano, T.; Song, S.; Kubota, Y.; Maruoka, K., Highly Diastereo- and Enantioselective Mannich Reactions of Synthetically Flexible Ketimines with Secondary Amine Organocatalysts. *Angew. Chem., Int. Ed.* **2012,** *51* (5), 1191-1194.

78. Lee, J. H.; Deng, L., Asymmetric Approach toward Chiral Cyclohex-2-enones from Anisoles via an Enantioselective Isomerization by a New Chiral Diamine Catalyst. *J. Am. Chem. Soc.* **2012,** *134* (44), 18209-18212.

79. Moteki, S. A.; Han, J. W.; Arimitsu, S.; Akakura, M.; Nakayama, K.; Maruoka, K., An Achiral-Acid-Induced Switch in the Enantioselectivity of a Chiral cis-Diamine-Based Organocatalyst for Asymmetric Aldol and Mannich Reactions. *Angew. Chem., Int. Ed.* **2012,** *51* (5), 1187-1190.

80. Pierce, M. D.; Johnston, R. C.; Mahapatra, S.; Yang, H.; Carter, R. G.; Cheong, P. H. Y., Mechanism and Stereoselectivity of a Dual Amino-Catalyzed Robinson Annulation: Rare Duumvirate Stereocontrol. *J. Am. Chem. Soc.* **2012,** *134* (33), 13624-13631.

81. Talavera, G.; Reyes, E.; Vicario, J. L.; Carrillo, L., Cooperative Dienamine/Hydrogen-Bonding Catalysis: Enantioselective Formal 2+2 Cycloaddition of Enals with Nitroalkenes. *Angew. Chem., Int. Ed.* **2012,** *51* (17), 4104-4107.

82. Tsakos, M.; Kokotos, C. G.; Kokotos, G., Primary Amine-Thioureas with Improved Catalytic Properties for "Difficult" Michael Reactions: Efficient Organocatalytic Syntheses of (S)-Baclofen, (R)-Baclofen and (S)-Phenibut. *Adv. Synth. Catal.* **2012,** *354* (4), 740-746.

83. Wang, Y.; Yu, T. Y.; Zhang, H. B.; Luo, Y. C.; Xu, P. F., Hydrogen-Bond-Mediated Supramolecular Iminium Ion Catalysis. *Angew. Chem., Int. Ed.* **2012,** *51* (49), 12339-12342.

84. Bachle, F.; Duschmale, J.; Ebner, C.; Pfaltz, A.; Wennemers, H., Organocatalytic Asymmetric Conjugate Addition of Aldehydes to Nitroolefins: Identification of Catalytic Intermediates and the Stereoselectivity-Determining Step by ESI-MS. *Angew. Chem., Int. Ed.* **2013,** *52* (48), 12619-12623.

85. Kastl, R.; Wennemers, H., Peptide-Catalyzed Stereoselective Conjugate Addition Reactions Generating All-Carbon Quaternary Stereogenic Centers. *Angew. Chem., Int. Ed.* **2013,** *52* (28), 7228-7232.

86. Lalonde, M. P.; McGowan, M. A.; Rajapaksa, N. S.; Jacobsen, E. N., Enantioselective Formal Aza-Diels-Alder Reactions of Enones with Cyclic Imines Catalyzed by Primary Aminothioureas. *J. Am. Chem. Soc.* **2013,** *135* (5), 1891-1894.

87. Lifchits, O.; Mahlau, M.; Reisinger, C. M.; Lee, A.; Fares, C.; Polyak, I.; Gopakumar, G.; Thiel, W.; List, B., The Cinchona Primary Amine-Catalyzed Asymmetric Epoxidation and Hydroperoxidation of alpha,beta-Unsaturated Carbonyl Compounds with Hydrogen Peroxide. *J. Am. Chem. Soc.* **2013,** *135* (17), 6677-6693.

88. Tian, X.; Melchiorre, P., Control of Remote Stereochemistry in the Synthesis of Spirocyclic Oxindoles: Vinylogous Organocascade Catalysis. *Angew. Chem., Int. Ed.* **2013,** *52* (20), 5360-5363.

89. Di Iorio, N.; Righi, P.; Mazzanti, A.; Mancinelli, M.; Ciogli, A.; Bencivenni, G., Remote Control of Axial Chirality: Aminocatalytic Desymmetrization of N-Arylmaleimides via Vinylogous Michael Addition. *J. Am. Chem. Soc.* **2014,** *136* (29), 10250-10253.

90. Lam, Y.-h.; Houk, K. N., How Cinchona Alkaloid-Derived Primary Amines Control Asymmetric Electrophilic Fluorination of Cyclic Ketones. *J. Am. Chem. Soc.* **2014,** *136* (27), 9556-9559.

91. Li, J.-L.; Yue, C.-Z.; Chen, P.-Q.; Xiao, Y.-C.; Chen, Y.-C., Remote Enantioselective Friedel-Crafts Alkylations of Furans through HOMO Activation**. *Angew. Chem., Int. Ed.* **2014,** *53* (21), 5449-5452.

92. Link, A.; Sparr, C., Organocatalytic Atroposelective Aldol Condensation: Synthesis of Axially Chiral Biaryls by Arene Formation**. *Angew. Chem., Int. Ed.* **2014,** *53* (21), 5458-5461.

93. List, B.; Coric, I.; Grygorenko, O. O.; Kaib, P. S. J.; Komarov, I.; Lee, A.; Leutzsch, M.; Pan, S. C.; Tymtsunik, A. V.; van Gemmeren, M., The Catalytic Asymmetric alpha-Benzylation of Aldehydes. *Angew. Chem., Int. Ed.* **2014,** *53* (1), 282-285.

94. Maji, B.; Yamamoto, H., Proline-Tetrazole-Catalyzed Enantioselective N-Nitroso Aldol Reaction of Aldehydes with In Situ Generated Nitrosocarbonyl Compounds. *Angew. Chem., Int. Ed.* **2014,** *53* (33), 8714-8717.

95. Witten, M. R.; Jacobsen, E. N., Catalytic Asymmetric Synthesis of 8-Oxabicyclooctanes by Intermolecular 5+2 Pyrylium Cycloadditions. *Angew. Chem., Int. Ed.* **2014,** *53* (23), 5912-5916.

96. Xu, B.; Shi, L. L.; Zhang, Y. Z.; Wu, Z. J.; Fu, L. N.; Luo, C. Q.; Zhang, L. X.; Peng, Y. G.; Guo, Q. X., Catalytic asymmetric direct alpha-alkylation of amino esters by aldehydes via imine activation. *Chemical Science* **2014,** *5* (5), 1988-1991.

97. Xu, C. M.; Zhang, L.; Luo, S. Z., Merging Aerobic Oxidation and Enamine Catalysis in the Asymmetric alpha-Amination of beta-Ketocarbonyls Using N-Hydroxycarbamates as Nitrogen Sources. *Angew. Chem., Int. Ed.* **2014,** *53* (16), 4149-4153.

98. Yin, X.; Zheng, Y.; Feng, X.; Jiang, K.; Wei, X.-Z.; Gao, N.; Chen, Y.-C., Asymmetric 5+3 Formal Cycloadditions with Cyclic Enones through Cascade Dienamine-Dienamine Catalysis. *Angew. Chem., Int. Ed.* **2014,** *53* (24), 6245-6248.

99. Lam, Y.-h.; Houk, K. N., Origins of Stereoselectivity in Intramolecular Aldol Reactions Catalyzed by Cinchona Amines. *J. Am. Chem. Soc.* **2015,** *137* (5), 2116-2127.

100. Mose, R.; Jensen, M. E.; Preegel, G.; Jorgensen, K. A., Direct Access to Multifunctionalized Norcamphor Scaffolds by Asymmetric Organocatalytic Diels-Alder Reactions. *Angew. Chem., Int. Ed.* **2015,** *54* (46), 13630-13634.

101. Yamagata, A. D. G.; Datta, S.; Jackson, K. E.; Stegbauer, L.; Paton, R. S.; Dixon, D. J., Enantioselective Desymmetrization of Prochiral Cyclohexanones by Organocatalytic Intramolecular Michael Additions to alpha,beta-Unsaturated Esters. *Angew. Chem., Int. Ed.* **2015,** *54* (16), 4899-4903.

102. Faseke, V. C.; Sparr, C., Stereoselective Arene-Forming Aldol Condensation: Synthesis of Axially Chiral Aromatic Amides. *Angew. Chem., Int. Ed.* **2016,** *55* (25), 7261-7264.

103. Grunenfelder, C. E.; Kisunzu, J. K.; Wennemers, H., Peptide-Catalyzed Stereoselective Conjugate Addition Reactions of Aldehydes to Maleimide. *Angew. Chem., Int. Ed.* **2016,** *55* (30), 8571-8574.

104. Lagoutte, R.; Besnard, C.; Alexakis, A., Direct Organocatalysed Double Michael Addition of alpha-Angelica Lactone to Enones. *Eur. J. Org. Chem.* **2016,** (25), 4372-4381.

105. Li, Y.; Tur, F.; Nielsen, R. P.; Jiang, H.; Jensen, F.; Jorgensen, K. A., Enantioselective Formal 4+2 Cycloadditions to 3-Nitroindoles by Trienamine Catalysis: Synthesis of Chiral Dihydrocarbazoles. *Angew. Chem., Int. Ed.* **2016,** *55* (3), 1020-1024.

106. Lotter, D.; Neuburger, M.; Rickhaus, M.; Haussinger, D.; Sparr, C., Stereoselective Arene-Forming Aldol Condensation: Synthesis of Configurationally Stable Oligo-1,2-naphthylenes. *Angew. Chem., Int. Ed.* **2016,** *55* (8), 2930-2933.

107. Monleon, A.; Glaus, F.; Vergura, S.; Jorgensen, K. A., Organocatalytic Strategy for the Enantioselective Cycloaddition to Trisubstituted Nitroolefins to Create Spirocyclohexene-Oxetane Scaffolds. *Angew. Chem., Int. Ed.* **2016,** *55* (7), 2478-2482.

108. Simon, A.; Lam, Y. H.; Houk, K. N., Transition States of Vicinal Diamine-Catalyzed Aldol Reactions. *J. Am. Chem. Soc.* **2016,** *138* (2), 503-506.

109. Yoshida, K.; Itatsu, Y.; Fujino, Y.; Inoue, H.; Takao, K., Enantioselective Organocatalytic Construction of Spiroindane Derivatives by Intramolecular Friedel-Crafts-Type 1,4-Addition. *Angew. Chem., Int. Ed.* **2016,** *55* (23), 6734-6738.

110. Zhu, Y. B.; Zhang, L.; Luo, S. Z., Asymmetric Retro-Claisen Reaction by Chiral Primary Amine Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (12), 3978-3981.

111. Mose, R.; Preegel, G.; Larsen, J.; Jakobsen, S.; Iversen, E. H.; Jorgensen, K. A., Organocatalytic stereoselective 8+2 and 6+4 cycloadditions. *Nature Chemistry* **2017,** *9* (5), 487-492.

112. You, Y. E.; Zhang, L.; Luo, S. Z., Reagent-controlled enantioselectivity switch for the asymmetric fluorination of beta-ketocarbonyls by chiral primary amine catalysis. *Chemical Science* **2017,** *8* (1), 621-626.

113. Zhou, Z.; Wang, Z. X.; Zhou, Y. C.; Xiao, W.; Ouyang, Q.; Du, W.; Chen, Y. C., Switchable regioselectivity in amine-catalysed asymmetric cycloadditions. *Nature Chemistry* **2017,** *9* (6), 590-594.

114. Nacsa, E. D.; MacMillan, D. W. C., Spin-Center Shift-Enabled Direct Enantioselective alpha-Benzylation of Aldehydes with Alcohols. *J. Am. Chem. Soc.* **2018,** *140* (9), 3322-3330.

115. Wen, W.; Chen, L.; Luo, M. J.; Zhang, Y.; Chen, Y. C.; Ouyang, Q.; Guo, Q. X., Chiral Aldehyde Catalysis for the Catalytic Asymmetric Activation of Glycine Esters. *J. Am. Chem. Soc.* **2018,** *140* (30), 9774-9780.

116. Zhu, L. H.; Zhang, L.; Luo, S. Z., Catalytic Desymmetrizing Dehydrogenation of 4-Substituted Cyclohexanones through Enamine Oxidation. *Angew. Chem., Int. Ed.* **2018,** *57* (8), 2253-2258.

117. Cheng, A.; Zhang, L.; Zhou, Q.; Liu, T.; Cao, J.; Zhao, G.; Zhang, K.; Song, G.; Zhao, B., Efficient Asymmetric Biomimetic Aldol Reaction of Glycinates and Trifluoromethyl Ketones by Carbonyl Catalysis. *Angew. Chem., Int. Ed.* **2021,** *60* (37), 20166-20172.

118. Kim, B.; Kim, Y.; Lee, S. Y., Stereodivergent Carbon–Carbon Bond Formation between Iminium and Enolate Intermediates by Synergistic Organocatalysis. *J. Am. Chem. Soc.* **2021,** *143* (1), 73-79.

119. Rezayee, N. M.; Enemærke, V. J.; Linde, S. T.; Lamhauge, J. N.; Reyes-Rodríguez, G. J.; Jørgensen, K. A.; Lu, C.; Houk, K. N., An Asymmetric SN2 Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2021,** *143* (19), 7509-7520.

120. Huang, M.; Zhang, L.; Pan, T.; Luo, S., Deracemization through photochemical E/Z isomerization of enamines. *Science* **2022,** *375* (6583), 869-874.

121. Shi, M.; Zhang, Q.; Gao, J.; Mi, X.; Luo, S., Catalytic Asymmetric α-Alkylsulfenylation with a Disulfide Reagent. *Angew. Chem., Int. Ed.* **2022,** *61* (39), e202209044.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

4.3 Metal-Ligand Dual Activation

4.3.1 Reaction with Carbonyls and Imines

1. Corey, E. J.; Wang, Z., ENANTIOSELECTIVE CONVERSION OF ALDEHYDES TO CYANOHYDRINS BY A CATALYTIC-SYSTEM WITH SEPARATE CHIRAL BINDING-SITES FOR ALDEHYDE AND CYANIDE COMPONENTS. *Tetrahedron Lett.* **1993,** *34* (25), 4001-4004.

2. Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R., Asymmetric transfer hydrogenation of imines. *J. Am. Chem. Soc.* **1996,** *118* (20), 4916-4917.

3. Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R., trans-[RuCl2(phosphane)(2)(1,2-diamine)] and chiral trans-[RuCl2(diphosphane)(1,2-diamine]): Shelf-stable precatalysts for the rapid, productive, and stereoselective hydrogenation of ketones. *Angew. Chem., Int. Ed.* **1998,** *37* (12), 1703-1707.

4. Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R., Asymmetric hydrogenation of alkenyl, cyclopropyl, and aryl ketones. RuCl2(xylbinap)(1,2-diamine) as a precatalyst exhibiting a wide scope. *J. Am. Chem. Soc.* **1998,** *120* (51), 13529-13530.

5. Krueger, C. A.; Kuntz, K. W.; Dzierba, C. D.; Wirschun, W. G.; Gleason, J. D.; Snapper, M. L.; Hoveyda, A. H., Ti-catalyzed enantioselective addition of cyanide to imines. A practical synthesis of optically pure alpha-amino acids. *J. Am. Chem. Soc.* **1999,** *121* (17), 4284-4285.

6. Byrne, J. J.; Chavarot, M.; Chavant, P. Y.; Vallee, Y., Asymmetric Strecker reactions of ketimines catalysed by titanium-based complexes. *Tetrahedron Lett.* **2000,** *41* (6), 873-876.

7. Hamashima, Y.; Kanai, M.; Shibasaki, M., Catalytic enantioselective cyanosilylation of ketones. *J. Am. Chem. Soc.* **2000,** *122* (30), 7412-7413.

8. Ishitani, H.; Komiyama, S.; Hasegawa, Y.; Kobayashi, S., Catalytic asymmetric Strecker synthesis. Preparation of enantiomerically pure alpha-amino acid derivatives from aldimines and tributyltin cyanide or achiral aldehydes, amines, and hydrogen cyanide using a chiral zirconium catalyst. *J. Am. Chem. Soc.* **2000,** *122* (5), 762-766.

9. Kanai, M.; Hamashima, Y.; Shibasaki, M., Design of a new bifunctional asymmetric catalyst from carbohydrates: application to catalytic asymmetric cyanosilylation of aldehydes and acetophenone. *Tetrahedron Lett.* **2000,** *41* (14), 2405-2409.

10. Kobayashi, S.; Ishitani, H., Novel binuclear chiral zirconium catalysts used in enantioselective Strecker reactions. *Chirality* **2000,** *12* (5-6), 540-543.

11. Ohkuma, T.; Ishii, D.; Takeno, H.; Noyori, R., Asymmetric hydrogenation of amino ketones using chiral RuCl2(diphophine)(1,2-diamine) complexes. *J. Am. Chem. Soc.* **2000,** *122* (27), 6510-6511.

12. Porter, J. R.; Wirschun, W. G.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H., Ti-catalyzed regio- and enantioselective synthesis of unsaturated alpha-amino nitriles, amides, and acids. Catalyst identification through screening of parallel libraries. *J. Am. Chem. Soc.* **2000,** *122* (11), 2657-2658.

13. Takamura, M.; Funabashi, K.; Kanai, M.; Shibasaki, M., Asymmetric Reissert-type reaction promoted by bifunctional catalyst. *J. Am. Chem. Soc.* **2000,** *122* (26), 6327-6328.

14. Takamura, M.; Funabashi, K.; Kanai, M.; Shibasaki, M., Asymmetric Reissert-type reaction promoted by bifunctional catalyst. *J. Am. Chem. Soc.* **2000,** *122* (26), 6327-6328.

15. Takamura, M.; Hamashima, Y.; Usuda, H.; Kanai, M.; Shibasaki, M., A catalytic asymmetric strecker-type reaction: Interesting reactivity difference between TMSCN and HCN. *Angew. Chem., Int. Ed.* **2000,** *39* (9), 1650-+.

16. Yamakawa, M.; Ito, H.; Noyori, R., The metal-ligand bifunctional catalysis: A theoretical study on the ruthenium(II)-catalyzed hydrogen transfer between alcohols and carbonyl compounds. *J. Am. Chem. Soc.* **2000,** *122* (7), 1466-1478.

17. Funabashi, K.; Ratni, H.; Kanai, M.; Shibasaki, M., Enantioselective construction of quaternary stereocenter through a reissert-type reaction catalyzed by an electronically tuned bifunctional catalyst: Efficient synthesis of various biologically significant compounds. *J. Am. Chem. Soc.* **2001,** *123* (43), 10784-10785.

18. Josephsohn, N. S.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H., Mechanism of enantioselective Ti-catalyzed strecker reaction: Peptide-based metal complexes as bifunctional catalysts. *J. Am. Chem. Soc.* **2001,** *123* (47), 11594-11599.

19. Noyori, R.; Ohkuma, T., Asymmetric catalysis by architectural and functional molecular engineering: Practical chemo- and stereoselective hydrogenation of ketones. *Angew. Chem., Int. Ed.* **2001,** *40* (1), 40-73.

20. Yet, L., Recent developments in catalytic asymmetric Strecker-type reactions. *Angew. Chem., Int. Ed.* **2001,** *40* (5), 875-877.

21. Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H., Mechanism of the hydrogenation of ketones catalyzed by trans- dihydrido(diamine)ruthenium(II) complexes. *J. Am. Chem. Soc.* **2002,** *124* (50), 15104-15118.

22. Casas, J.; Najera, C.; Sansano, J. M.; Saa, J. M., BINOLAM, a recoverable chiral ligand for bifunctional enantioselective catalysis: The asymmetric synthesis of cyanohydrins. *Org. Lett.* **2002,** *4* (15), 2589-2592.

23. France, S.; Wack, H.; Hafez, A. M.; Taggi, A. E.; Witsil, D. R.; Lectka, T., Bifunctional asymmetric catalysis: A tandem nucleophile/Lewis acid promoted synthesis of beta-lactams. *Org. Lett.* **2002,** *4* (9), 1603-1605.

24. Mikami, K.; Terada, M.; Matsuzawa, H., "Asymmetric" catalysis by lanthanide complexes. *Angew. Chem., Int. Ed.* **2002,** *41* (19), 3555-3571.

25. Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R., trans-RuH(eta(1)-BH4)(binap)(1,2-diamine): a catalyst for asymmetric hydrogenation of simple ketones under base-free conditions. *J. Am. Chem. Soc.* **2002,** *124* (23), 6508-6509.

26. Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M., An asymmetric cyanation reaction and sequential asymmetric cyanation-nitroaldol reaction using a YLi3{tris(binaphthoxide)} single catalyst component: Catalyst tuning with achiral additives. *Angew. Chem., Int. Ed.* **2002,** *41* (19), 3636-3638.

27. Aikawa, K.; Mikami, K., Atropos but achiral tris(phosphanyl)biphenyl ligands for RU- catalyzed asymmetric hydrogenation. *Angew. Chem., Int. Ed.* **2003,** *42* (44), 5455-5458.

28. Baeza, A.; Casas, J.; Najera, C.; Sansano, J. M.; Saa, J. M., Enantioselective synthesis of cyanohydrin O-phosphates mediated by the bifunctional catalyst binolam-AlCl. *Angew. Chem., Int. Ed.* **2003,** *42* (27), 3143-3146.

29. Belokon, Y. N.; Blacker, A. J.; Clutterbuck, L. A.; North, M., Catalytic, asymmetric synthesis of cyanohydrin ethyl carbonates. *Org. Lett.* **2003,** *5* (23), 4505-4507.

30. Chen, F. X.; Feng, X. M.; Qin, B.; Zhang, G. L.; Jiang, Y. Z., Enantioselective cyanosilylation of ketones by a catalytic double-activation method employing chiral Lewis acid and achiral N-oxide catalysts. *Org. Lett.* **2003,** *5* (6), 949-952.

31. Groger, H., Catalytic enantioselective Strecker reactions and analogous syntheses. *Chem. Rev* **2003,** *103* (8), 2795-2827.

32. Ma, Y. P.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J. E., Asymmetric transfer hydrogenation of prochiral ketones in aqueous media with new water-soluble chiral vicinal diamine as ligand. *Org. Lett.* **2003,** *5* (12), 2103-2106.

33. Mansawat, W.; Bhanthumnavin, W.; Vilaivan, T., N-Salicyl-beta-aminoalcohols as a new class of ligand for catalytic asymmetric Strecker reactions. *Tetrahedron Lett.* **2003,** *44* (19), 3805-3808.

34. Masumoto, S.; Usuda, H.; Suzuki, M.; Kanai, M.; Shibasaki, M., Catalytic enantioselective Strecker reaction of ketoimines. *J. Am. Chem. Soc.* **2003,** *125* (19), 5634-5635.

35. Sandoval, C. A.; Ohkuma, T.; Muniz, K.; Noyori, R., Mechanism of asymmetric hydrogenation of ketones catalyzed by BINAP/1,2-diamine-ruthenium(II) complexes. *J. Am. Chem. Soc.* **2003,** *125* (44), 13490-13503.

36. Yang, K. S.; Lee, W. D.; Pan, J. F.; Chen, K. M., Chiral Lewis acid-catalyzed asymmetric Baylis-Hillman reactions. *J. Org. Chem.* **2003,** *68* (3), 915-919.

37. Yao, W. G.; Wang, J. B., Direct catalytic asymmetric aldol-type reaction of aldehydes with ethyl diazoacetate. *Org. Lett.* **2003,** *5* (9), 1527-1530.

38. Brunel, J. M.; Holmes, I. P., Chemically catalyzed asymmetric cyanohydrin syntheses. *Angew. Chem., Int. Ed.* **2004,** *43* (21), 2752-2778.

39. Hannedouche, J.; Clarkson, G. J.; Wills, M., A new class of "tethered" ruthenium(II) catalyst for asymmetric transfer hydrogenation reactions. *J. Am. Chem. Soc.* **2004,** *126* (4), 986-987.

40. Ichikawa, E.; Suzuki, M.; Yabu, K.; Albert, M.; Kanai, M.; Shibasaki, M., New entries in Lewis acid Lewis base bifunctional asymmetric catalyst: Catalytic enantioselective Reissert reaction of pyridine derivatives. *J. Am. Chem. Soc.* **2004,** *126* (38), 11808-11809.

41. Kogami, Y.; Nakajima, T.; Ikeno, T.; Yamada, T., Enantioselective Henry reaction catalyzed by salen-cobalt complexes. *Synthesis* **2004,** (12), 1947-1950.

42. Li, Y.; He, B.; Qin, B.; Feng, X. M.; Zhang, G. L., Highly enantioselective cyanosilylation of aldehydes catalyzed by novel beta-amino alcohol-titanium complexes. *J. Org. Chem.* **2004,** *69* (23), 7910-7913.

43. Spino, C., Recent developments in the catalytic asymmetric cyanation of ketimines. *Angew. Chem., Int. Ed.* **2004,** *43* (14), 1764-1766.

44. Zhu, C.; Shen, X. Q.; Nelson, S. G., Cinchona alkaloid-Lewis acid catalyst systems for enantioselective ketene-aldehyde cycloadditions. *J. Am. Chem. Soc.* **2004,** *126* (17), 5352-5353.

45. Calter, M. A.; Tretyak, O. A.; Flaschenriem, C., Formation of disubstituted beta-lactones using bifunctional catalysis. *Org. Lett.* **2005,** *7* (9), 1809-1812.

46. France, S.; Shah, M. H.; Weatherwax, A.; Wack, H.; Roth, J. P.; Lectka, T., Bifunctional lewis acid-nucleophile-based asymmetric catalysis: Mechanistic evidence for imine activation working in tandem with chiral enolate formation in the synthesis of beta-lactams. *J. Am. Chem. Soc.* **2005,** *127* (4), 1206-1215.

47. Hatano, M.; Ikeno, T.; Miyamoto, T.; Ishihara, K., Chiral lithium binaphtholate aqua complex as a highly effective asymmetric catalyst for cyanohydrin synthesis. *J. Am. Chem. Soc.* **2005,** *127* (31), 10776-10777.

48. Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M., A class of ruthenium(II) catalyst for asymmetric transfer hydrogenations of ketones. *J. Am. Chem. Soc.* **2005,** *127* (20), 7318-7319.

49. Lundgren, S.; Wingstrand, E.; Penhoat, M.; Moberg, C., Dual Lewis acid-Lewis base activation in enantioselective cyanation of aldehydes using acetyl cyanide and cyanoformate as cyanide sources. *J. Am. Chem. Soc.* **2005,** *127* (33), 11592-11593.

50. Muniz, K., Bifunctional metal-ligand catalysis: Hydrogenations and new reactions within the metal-(di)amine scaffold. *Angew. Chem., Int. Ed.* **2005,** *44* (41), 6622-6627.

51. Ohkuma, T.; Sandoval, C. A.; Srinivasan, R.; Lin, Q.; Wei, Y.; Muniz, K.; Noyori, R., Asymmetric hydrogenation of tert-alkyl ketones. *J. Am. Chem. Soc.* **2005,** *127* (23), 8288-8289.

52. Yamagiwa, N.; Tian, J.; Matsunaga, S.; Shibasaki, M., Catalytic asymmetric cyano-ethoxycarbonylation reaction of aldehydes using a YLi(3)Tris(binaphthoxide) (YLB) complex: Mechanism and roles of achiral additives. *J. Am. Chem. Soc.* **2005,** *127* (10), 3413-3422.

53. Koch, F. M.; Peters, R., Catalytic enantio- and diastereoselective formation of beta-sultones: Ring-strained precursors for enantioenriched beta-hydroxysulfonyl derivatives. *Angew. Chem., Int. Ed.* **2007,** *46* (15), 2685-2689.

54. Liu, S.; Xie, H. H.; Wang, L. X.; Zhou, Q. L., Dynamic kinetic resolution allows a highly enantioselective synthesis of cis-alpha-aminocycloalkanols by ruthenium-catalyzed asymmetric hydrogenation. *Angew. Chem., Int. Ed.* **2007,** *46* (39), 7506-7508.

55. Xie, J. H.; Zhou, Z. T.; Kong, W. L.; Zhou, Q. L., Ru-catalyzed asymmetric hydrogenation of racemic aldehydes via dynamic kinetic resolution: Efficient synthesis of optically active primary alcohols. *J. Am. Chem. Soc.* **2007,** *129* (7), 1868-+.

56. Zhou, H.; Peng, D.; Qin, B.; Hou, Z. R.; Liu, X. H.; Feng, X. M., Highly enantioselective aza-Henry reaction of N-tosyl imines catalyzed by N,N'-dioxide-Cu(I) complexes. *J. Org. Chem.* **2007,** *72* (26), 10302-10304.

57. Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P., Osmium(II) CNN pincer complexes as efficient catalysts for both asymmetric transfer and H-2 hydrogenation of ketones. *Angew. Chem., Int. Ed.* **2008,** *47* (23), 4362-4365.

58. Duschek, A.; Kirsch, S. F., Combining the concepts: Dual catalysis with carbophilic lewis acids. *Angew. Chem., Int. Ed.* **2008,** *47* (31), 5703-5705.

59. Hamilton, R. J.; Bergens, S. H., Direct observations of the metal-ligand bifunctional addition step in an enantioselective ketone hydrogenation. *J. Am. Chem. Soc.* **2008,** *130* (36), 11979-11987.

60. Hu, W. H.; Xu, X. F.; Zhou, J.; Liu, W. J.; Huang, H. X.; Hu, J.; Yang, L. P.; Gong, L. Z., Cooperative catalysis with chiral Bronsted acid-Rh-2(OAC)(4): Highly enantioselective three-component reactions of diazo compounds with alcohols and imines. *J. Am. Chem. Soc.* **2008,** *130* (25), 7782-+.

61. Li, C. Q.; Wang, C.; Villa-Marcos, B.; Xiao, J. L., Chiral Counteranion-Aided Asymmetric Hydrogenation of Acyclic Imines. *J. Am. Chem. Soc.* **2008,** *130* (44), 14450-+.

62. Mandai, H.; Mandai, K.; Snapper, M. L.; Hoveyda, A. H., Three-Component Ag-Catalyzed Enantioselective Vinylogous Mannich and Aza-Diels-Alder Reactions with Alkyl-Substituted Aldehydes. *J. Am. Chem. Soc.* **2008,** *130* (52), 17961-17969.

63. Morimoto, H.; Yoshino, T.; Yukawa, T.; Lu, G.; Matsunaga, S.; Shibasaki, M., Lewis Base Assisted Bronsted Base Catalysis: Bidentate Phosphine Oxides as Activators and Modulators of Bronsted Basic Lanthanum-Aryloxides. *Angew. Chem., Int. Ed.* **2008,** *47* (47), 9125-9129.

64. Nojiri, A.; Kumagai, N.; Shibasaki, M., Asymmetric catalysis via dynamic substrate/ligand/rare earth metal conglomerate. *J. Am. Chem. Soc.* **2008,** *130* (17), 5630-+.

65. Sorimachi, K.; Terada, M., Relay Catalysis by a Metal-Complex/Bronsted Acid Binary System in a Tandem Isomerization/Carbon-Carbon Bond Forming Sequence. *J. Am. Chem. Soc.* **2008,** *130* (44), 14452-+.

66. Xu, X. F.; Zhou, J.; Yang, L. P.; Hu, W. H., Selectivity control in enantioselective four-component reactions of aryl diazoacetates with alcohols, aldehydes and amines: an efficient approach to synthesizing chiral beta-amino-alpha-hydroxyesters. *Chem. Comm.* **2008,** (48), 6564-6566.

67. Yang, F.; Zhao, D. B.; Lan, J. B.; Xi, P. H.; Yang, L.; Xiang, S. H.; You, J. S., Self-assembled bifunctional catalysis induced by metal coordination interactions: An exceptionally efficient approach to enantioselective hydrophosphonylation. *Angew. Chem., Int. Ed.* **2008,** *47* (30), 5646-5649.

68. Chein, R. J.; Yeung, Y. Y.; Corey, E. J., Highly Enantioselective Oxazaborolidine-Catalyzed Reduction of 1,3-Dicarbonyl Compounds: Role of the Additive Diethylaniline. *Org. Lett.* **2009,** *11* (7), 1611-1614.

69. Li, C. Q.; Villa-Marcos, B.; Xiao, J. L., Metal-Bronsted Acid Cooperative Catalysis for Asymmetric Reductive Amination. *J. Am. Chem. Soc.* **2009,** *131* (20), 6967-+.

70. Lu, Y. D.; Johnstone, T. C.; Arndtsen, B. A., Hydrogen-Bonding Asymmetric Metal Catalysis with alpha-Amino Acids: A Simple and Tunable Approach to High Enantioinduction. *J. Am. Chem. Soc.* **2009,** *131* (32), 11284-+.

71. Wieland, L. C.; Vieira, E. M.; Snapper, M. L.; Hoveyda, A. H., Ag-Catalyzed Diastereo- and Enantioselective Vinylogous Mannich Reactions of alpha-Ketoimine Esters. Development of a Method and Investigation of its Mechanism. *J. Am. Chem. Soc.* **2009,** *131* (2), 570-576.

72. Xie, J. H.; Liu, S.; Kong, W. L.; Bai, W. J.; Wang, X. C.; Wang, L. X.; Zhou, Q. L., Highly Enantioselective and Diastereoselective Synthesis of Chiral Amino Alcohols by Ruthenium-Catalyzed Asymmetric Hydrogenation of alpha-Amino Aliphatic Ketones. *J. Am. Chem. Soc.* **2009,** *131* (12), 4222-+.

73. de Armas, P.; Tejedor, D.; Garcia-Tellado, F., Asymmetric Alkynylation of Imines by Cooperative Hydrogen Bonding and Metal Catalysis. *Angew. Chem., Int. Ed.* **2010,** *49* (6), 1013-1016.

74. Hatano, M.; Horibe, T.; Ishihara, K., Chiral Lithium(I) Binaphtholate Salts for the Enantioselective Direct Mannich-Type Reaction with a Change of Syni/Anti and Absolute Stereochemistry. *J. Am. Chem. Soc.* **2010,** *132* (1), 56-+.

75. Kim, S. J.; Jang, D. O., Indium-Mediated Catalytic Enantioselective Allylation of N-Benzoylhydrazones Using a Protonated Chiral Amine. *J. Am. Chem. Soc.* **2010,** *132* (35), 12168-12169.

76. Kull, T.; Cabrera, J.; Peters, R., Catalytic Asymmetric Synthesis of trans-Configured beta-Lactones: Cooperation of Lewis Acid and Ion Pair Catalysis. *Chem. Eur. J.* **2010,** *16* (30), 9132-9139.

77. Moquist, P. N.; Kodama, T.; Schaus, S. E., Enantioselective Addition of Boronates to Chromene Acetals Catalyzed by a Chiral Bronsted Acid/Lewis Acid System. *Angew. Chem., Int. Ed.* **2010,** *49* (39), 7096-7100.

78. Rueping, M.; Koenigs, R. M.; Atodiresei, I., Unifying Metal and Bronsted Acid Catalysis-Concepts, Mechanisms, and Classifications. *Chem. Eur. J.* **2010,** *16* (31), 9350-9365.

79. Takebayashi, S.; John, J. M.; Bergens, S. H., Desymmetrization of meso-Cyclic Imides via Enantioselective Monohydrogenation. *J. Am. Chem. Soc.* **2010,** *132* (37), 12832-12834.

80. Chen, Q. A.; Wang, D. S.; Zhou, Y. G.; Duan, Y.; Fan, H. J.; Yang, Y.; Zhang, Z., Convergent Asymmetric Disproportionation Reactions: Metal/Bronsted Acid Relay Catalysis for Enantioselective Reduction of Quinoxalines. *J. Am. Chem. Soc.* **2011,** *133* (16), 6126-6129.

81. Han, Z. Y.; Guo, R.; Wang, P. S.; Chen, D. F.; Xiao, H.; Gong, L. Z., Enantioselective concomitant creation of vicinal quaternary stereogenic centers via cyclization of alkynols triggered addition of azlactones. *Tetrahedron Lett.* **2011,** *52* (45), 5963-5967.

82. Hashimoto, T.; Omote, M.; Maruoka, K., Catalytic Asymmetric Alkynylation of C1-Substituted C,N-Cyclic Azomethine Imines by Cu(I)/Chiral Bronsted Acid Co-Catalyst. *Angew. Chem., Int. Ed.* **2011,** *50* (38), 8952-8955.

83. Huang, Y. Y.; Chakrabarti, A.; Morita, N.; Schneider, U.; Kobayashi, S., A Catalytic Asymmetric Borono Variant of Hosomi-Sakurai Reactions with N,O-Aminals. *Angew. Chem., Int. Ed.* **2011,** *50* (47), 11121-11124.

84. Lv, J.; Zhang, L.; Zhou, Y. M.; Nie, Z. X.; Luo, S. Z.; Cheng, J. P., Asymmetric Binary Acid Catalysis: A Regioselectivity Switch between Enantioselective 1,2-and 1,4-Addition through Different Counteranions of In(III). *Angew. Chem., Int. Ed.* **2011,** *50* (29), 6610-6614.

85. Matsumura, K.; Arai, N.; Hori, K.; Saito, T.; Sayo, N.; Ohkuma, T., Chiral Ruthenabicyclic Complexes: Precatalysts for Rapid, Enantioselective, and Wide-Scope Hydrogenation of Ketones. *J. Am. Chem. Soc.* **2011,** *133* (28), 10696-10699.

86. Sladojevich, F.; Trabocchi, A.; Guarna, A.; Dixon, D. J., A New Family of Cinchona-Derived Amino Phosphine Precatalysts: Application to the Highly Enantio- and Diastereoselective Silver-Catalyzed Isocyanoacetate Aldol Reaction. *J. Am. Chem. Soc.* **2011,** *133* (6), 1710-1713.

87. Song, J.; Guo, C.; Chen, P. H.; Yu, J.; Luo, S. W.; Gong, L. Z., Asymmetric Formal 3+2 Cycloaddition Reaction of Isocyanoesters to 2-Oxobutenoate Esters by a Multifunctional Chiral Silver Catalyst. *Chem. Eur. J.* **2011,** *17* (28), 7786-7790.

88. Wen, Y. Q.; Ren, W. M.; Lu, X. B., Unsymmetric salen ligands bearing a Lewis base: intramolecularly cooperative catalysis for cyanosilylation of aldehydes. *Org. Biomol. Chem.* **2011,** *9* (18), 6323-6330.

89. Xu, Z. H.; Liu, L.; Wheeler, K.; Wang, H., Asymmetric Inverse-Electron-Demand Hetero-Diels-Alder Reaction of Six-membered Cyclic Ketones: An Enamine/Metal Lewis Acid Bifunctional Approach. *Angew. Chem., Int. Ed.* **2011,** *50* (15), 3484-3488.

90. Zhang, Z. H.; Zheng, W. H.; Antilla, J. C., Highly Enantioselective Catalytic Benzoyloxylation of 3-Aryloxindoles Using Chiral VAPOL Calcium Phosphate. *Angew. Chem., Int. Ed.* **2011,** *50* (5), 1135-1138.

91. Zhou, S. L.; Fleischer, S.; Junge, K.; Beller, M., Cooperative Transition-Metal and Chiral Bronsted Acid Catalysis: Enantioselective Hydrogenation of Imines To Form Amines. *Angew. Chem., Int. Ed.* **2011,** *50* (22), 5120-5124.

92. Fleischer, S.; Werkmeister, S.; Zhou, S. L.; Junge, K.; Beller, M., Consecutive Intermolecular Reductive Hydroamination: Cooperative Transition-Metal and Chiral Bronsted Acid Catalysis. *Chem. Eur. J.* **2012,** *18* (29), 9005-9010.

93. Kato, S.; Yoshino, T.; Shibasaki, M.; Kanai, M.; Matsunaga, S., Catalytic Asymmetric Synthesis of Spirooxindoles by a Mannich-Type Reaction of Isothiocyanato Oxindoles. *Angew. Chem., Int. Ed.* **2012,** *51* (28), 7007-7010.

94. Lang, K.; Park, J.; Hong, S., Urea/Transition-Metal Cooperative Catalyst for anti-Selective Asymmetric Nitroaldol Reactions. *Angew. Chem., Int. Ed.* **2012,** *51* (7), 1620-1624.

95. Qiu, H.; Li, M.; Jiang, L. Q.; Lv, F. P.; Zan, L.; Zhai, C. W.; Doyle, M. P.; Hu, W. H., Highly enantioselective trapping of zwitterionic intermediates by imines. *Nature Chemistry* **2012,** *4* (9), 733-738.

96. Steward, K. M.; Corbett, M. T.; Goodman, C. G.; Johnson, J. S., Asymmetric Synthesis of Diverse Glycolic Acid Scaffolds via Dynamic Kinetic Resolution of alpha-Keto Esters. *J. Am. Chem. Soc.* **2012,** *134* (49), 20197-20206.

97. Zbieg, J. R.; Yamaguchi, E.; McInturff, E. L.; Krische, M. J., Enantioselective C-H Crotylation of Primary Alcohols via Hydrohydroxyalkylation of Butadiene. *Science* **2012,** *336* (6079), 324-327.

98. Corbett, M. T.; Johnson, J. S., Diametric Stereocontrol in Dynamic Catalytic Reduction of Racemic Acyl Phosphonates: Divergence from alpha-Keto Ester Congeners. *J. Am. Chem. Soc.* **2013,** *135* (2), 594-597.

99. Deng, Y. M.; Liu, L.; Sarkisian, R. G.; Wheeler, K.; Wang, H.; Xu, Z. H., Arylamine-Catalyzed Enamine Formation: Cooperative Catalysis with Arylamines and Acids. *Angew. Chem., Int. Ed.* **2013,** *52* (13), 3663-3667.

100. Hashimoto, T.; Galvez, A. O.; Maruoka, K., In Situ Assembled Boronate Ester Assisted Chiral Carboxylic Acid Catalyzed Asymmetric Trans-Aziridinations. *J. Am. Chem. Soc.* **2013,** *135* (47), 17667-17670.

101. Liu, C.; Xie, J. H.; Li, Y. L.; Chen, J. Q.; Zhou, Q. L., Asymmetric Hydrogenation of a,a'-Disubstituted Cycloketones through Dynamic Kinetic Resolution: An Efficient Construction of Chiral Diols with Three Contiguous Stereocenters. *Angew. Chem., Int. Ed.* **2013,** *52* (2), 593-596.

102. Miura, T.; Nishida, Y.; Morimoto, M.; Murakami, M., Enantioselective Synthesis of Anti Homoallylic Alcohols from Terminal Alkynes and Aldehydes Based on Concomitant Use of a Cationic Iridium Complex and a Chiral Phosphoric Acid. *J. Am. Chem. Soc.* **2013,** *135* (31), 11497-11500.

103. Murphy, S. K.; Dong, V. M., Enantioselective Ketone Hydroacylation Using Noyori's Transfer Hydrogenation Catalyst. *J. Am. Chem. Soc.* **2013,** *135* (15), 5553-5556.

104. Bergonzini, G.; Schindler, C. S.; Wallentin, C. J.; Jacobsen, E. N.; Stephenson, C. R. J., Photoredox activation and anion binding catalysis in the dual catalytic enantioselective synthesis of bamino esters. *Chemical Science* **2014,** *5* (1), 112-116.

105. Dub, P. A.; Henson, N. J.; Martin, R. L.; Gordon, J. C., Unravelling the Mechanism of the Asymmetric Hydrogenation of Acetophenone by RuX2(diphosphine)(1,2-diamine) Catalysts. *J. Am. Chem. Soc.* **2014,** *136* (9), 3505-3521.

106. Jia, S.; Xing, D.; Zhang, D.; Hu, W., Catalytic Asymmetric Functionalization of Aromatic C-H Bonds by Electrophilic Trapping of Metal-Carbene-Induced Zwitterionic Intermediates. *Angew. Chem., Int. Ed.* **2014,** *53* (48), 13098-13101.

107. Lee, A.; Scheidt, K. A., A Cooperative N-Heterocyclic Carbene/Chiral Phosphate Catalysis System for Allenolate Annulations. *Angew. Chem., Int. Ed.* **2014,** *53* (29), 7594-7598.

108. Zhang, Y.; Lim, C.-S.; Sim, D. S. B.; Pan, H.-J.; Zhao, Y., Catalytic Enantioselective Amination of Alcohols by the Use of Borrowing Hydrogen Methodology: Cooperative Catalysis by Iridium and a Chiral Phosphoric Acid. *Angew. Chem., Int. Ed.* **2014,** *53* (5), 1399-1403.

109. Zhao, Q.; Wen, J.; Tan, R.; Huang, K.; Metola, P.; Wang, R.; Anslyn, E. V.; Zhang, X., Rhodium-Catalyzed Asymmetric Hydrogenation of Unprotected NH Imines Assisted by a Thiourea. *Angew. Chem., Int. Ed.* **2014,** *53* (32), 8467-8470.

110. Bigler, R.; Huber, R.; Mezzetti, A., Highly Enantioselective Transfer Hydrogenation of Ketones with Chiral (NH)(2)P-2 Macrocyclic Iron(II) Complexes. *Angew. Chem., Int. Ed.* **2015,** *54* (17), 5171-5174.

111. de la Campa, R.; Ortin, I.; Dixon, D. J., Direct Catalytic Enantio- and Diastereoselective Ketone Aldol Reactions of Isocyanoacetates. *Angew. Chem., Int. Ed.* **2015,** *54* (16), 4895-4898.

112. Lindqvist, M.; Borre, K.; Axenov, K.; Kotai, B.; Nieger, M.; Leskela, M.; Papai, I.; Repo, T., Chiral Molecular Tweezers: Synthesis and Reactivity in Asymmetric Hydrogenation. *J. Am. Chem. Soc.* **2015,** *137* (12), 4038-4041.

113. Rong, Z. Q.; Zhang, Y.; Chua, R. H. B.; Pan, H. J.; Zhao, Y., Dynamic Kinetic Asymmetric Amination of Alcohols: From A Mixture of Four Isomers to Diastereo- and Enantiopure alpha-Branched Amines. *J. Am. Chem. Soc.* **2015,** *137* (15), 4944-4947.

114. Wu, Z.; Li, F.; Wang, J., Intermolecular Dynamic Kinetic Resolution Cooperatively Catalyzed by an N-Heterocyclic Carbene and a Lewis Acid. *Angew. Chem., Int. Ed.* **2015,** *54* (5), 1629-1633.

115. Zhang, Q.; Cui, X.; Zhang, L.; Luo, S.; Wang, H.; Wu, Y., Redox Tuning of a Direct Asymmetric Aldol Reaction. *Angew. Chem., Int. Ed.* **2015,** *54* (17), 5210-5213.

116. Touge, T.; Nara, H.; Fujiwhara, M.; Kayaki, Y.; Ikariya, T., Efficient Access to Chiral Benzhydrols via Asymmetric Transfer Hydrogenation of Unsymmetrical Benzophenones with Bifunctional Oxo-Tethered Ruthenium Catalysts. *J. Am. Chem. Soc.* **2016,** *138* (32), 10084-10087.

117. Xiao, G. L.; Ma, C. Q.; Xing, D.; Hu, W. H., Enantioselective Synthesis of alpha-Mercapto-beta-amino Esters via Rh(II)/Chiral Phosphoric Acid-Cocatalyzed Three-Component Reaction of Diazo Compounds, Thiols, and Imines. *Org. Lett.* **2016,** *18* (23), 6086-6089.

118. Brodbeck, D.; Broghammer, F.; Meisner, J.; Klepp, J.; Garnier, D.; Frey, W.; Kastner, J.; Peters, R., An Aluminum Fluoride Complex with an Appended Ammonium Salt as an Exceptionally Active Cooperative Catalyst for the Asymmetric Carboxycyanation of Aldehydes. *Angew. Chem., Int. Ed.* **2017,** *56* (14), 4056-4060.

119. Dub, P. A.; Scott, B. L.; Gordon, J. C., Why Does Alkylation of the N-H Functionality within M/NH Bifunctional Noyori-Type Catalysts Lead to Turnover? *J. Am. Chem. Soc.* **2017,** *139* (3), 1245-1260.

120. Nakamura, S.; Hayama, D., Enantioselective Reaction of 2H-Azirines with Phosphite Using Chiral Bis(imidazoline)/Zinc(II) Catalysts. *Angew. Chem., Int. Ed.* **2017,** *56* (30), 8785-8789.

121. Yang, Q.; Zhang, L.; Ye, C.; Luo, S. Z.; Wu, L. Z.; Tung, C. H., Visible-Light-Promoted Asymmetric Cross-Dehydrogenative Coupling of Tertiary Amines to Ketones by Synergistic Multiple Catalysis. *Angew. Chem., Int. Ed.* **2017,** *56* (13), 3694-3698.

122. Simon, L.; Paton, R. S., The True Catalyst Revealed: The Intervention of Chiral Ca and Mg Phosphates in Bronsted Acid Promoted Asymmetric Mannich Reactions. *J. Am. Chem. Soc.* **2018,** *140* (16), 5412-5420.

123. Kang, Z. H.; Wang, Y. H.; Zhang, D.; Wu, R. B.; Xu, X. F.; Hu, W. H., Asymmetric Counter-Anion-Directed Aminomethylation: Synthesis of Chiral beta-Amino Acids via Trapping of an Enol Intermediate. *J. Am. Chem. Soc.* **2019,** *141* (4), 1473-1478.

124. Miura, T.; Oku, N.; Murakami, M., Diastereo- and Enantioselective Synthesis of (E)-delta-Boryl-Substituted anti-Homoallylic Alcohols in Two Steps from Terminal Alkynes. *Angew. Chem., Int. Ed.* **2019,** *58* (41), 14620-14624.

125. Li, J.; Zhang, D.; Chen, J.; Ma, C.; Hu, W., Enantioselective Synthesis of Fluoroalkyl-Substituted syn-Diamines by the Asymmetric gem-Difunctionalization of 2,2,2-Trifluorodiazoethane. *ACS Catalysis* **2020,** *10* (8), 4559-4565.

126. Yang, X.; Xie, Z.; Li, Y.; Zhang, Y., Enantioselective aerobic oxidative cross-dehydrogenative coupling of glycine derivatives with ketones and aldehydes via cooperative photoredox catalysis and organocatalysis. *Chemical Science* **2020,** *11* (18), 4741-4746.

127. Zhang, L.; Yamazaki, K.; Leitch, J. A.; Manzano, R.; Atkinson, V. A. M.; Hamlin, T. A.; Dixon, D. J., Dual catalytic enantioselective desymmetrization of allene-tethered cyclohexanones. *Chemical Science* **2020,** *11* (28), 7444-7450.

128. Chen, D.-H.; Sun, W.-T.; Zhu, C.-J.; Lu, G.-S.; Wu, D.-P.; Wang, A.-E.; Huang, P.-Q., Enantioselective Reductive Cyanation and Phosphonylation of Secondary Amides by Iridium and Chiral Thiourea Sequential Catalysis. *Angew. Chem., Int. Ed.* **2021,** *60* (16), 8827-8831.

129. Dong, G.; Bao, M.; Xie, X.; Jia, S.; Hu, W.; Xu, X., Asymmetric Allylation by Chiral Organocatalyst-Promoted Formal Hetero-Ene Reactions of Alkylgold Intermediates. *Angew. Chem., Int. Ed.* **2021,** *60* (4), 1992-1999.

130. Pan, H.-J.; Lin, Y.; Gao, T.; Lau, K. K.; Feng, W.; Yang, B.; Zhao, Y., Catalytic Diastereo- and Enantioconvergent Synthesis of Vicinal Diamines from Diols through Borrowing Hydrogen. *Angew. Chem., Int. Ed.* **2021,** *60* (34), 18599-18604.

131. Qin, X.-L.; Li, A.; Han, F.-S., Desymmetric Enantioselective Reduction of Cyclic 1,3-Diketones Catalyzed by a Recyclable P-Chiral Phosphinamide Organocatalyst. *J. Am. Chem. Soc.* **2021,** *143* (7), 2994-3002.

132. Tian, J.-J.; Liu, N.; Liu, Q.-F.; Sun, W.; Wang, X.-C., Borane-Catalyzed Direct Asymmetric Vinylogous Mannich Reactions of Acyclic α,β-Unsaturated Ketones. *J. Am. Chem. Soc.* **2021,** *143* (8), 3054-3059.

133. Zhang, Z.; Hu, X., Visible-Light-Driven Catalytic Deracemization of Secondary Alcohols. *Angew. Chem., Int. Ed.* **2021,** *60* (42), 22833-22838.

134. Zhao, Q.; Li, Y.; Zhang, Q.-X.; Cheng, J.-P.; Li, X., Catalytic Asymmetric Aza-Diels–Alder Reaction of Ketimines and Unactivated Dienes. *Angew. Chem., Int. Ed.* **2021,** *60* (32), 17608-17614.

135. Zhou, S.; Li, Y.; Liu, X.; Hu, W.; Ke, Z.; Xu, X., Enantioselective Oxidative Multi-Functionalization of Terminal Alkynes with Nitrones and Alcohols for Expeditious Assembly of Chiral α-Alkoxy-β-amino-ketones. *J. Am. Chem. Soc.* **2021,** *143* (36), 14703-14711.

136. Šterman, A.; Sosič, I.; Časar, Z., Primary trifluoroborate-iminiums enable facile access to chiral α-aminoboronic acids via Ru-catalyzed asymmetric hydrogenation and simple hydrolysis of the trifluoroborate moiety. *Chemical Science* **2022,** *13* (10), 2946-2953.

137. Zhang, X.; Ma, W.; Zhang, J.; Tang, W.; Xue, D.; Xiao, J.; Sun, H.; Wang, C., Asymmetric Ruthenium-Catalyzed Hydroalkylation of Racemic Allylic Alcohols for the Synthesis of Chiral Amino Acid Derivatives. *Angew. Chem., Int. Ed.* **2022,** *61* (26), e202203244.

4.3.2 Other Reactions

1. DiMauro, E. F.; Kozlowski, M. C., BINOL-salen metal catalysts incorporating a bifunctional design. *Org. Lett.* **2001,** *3* (11), 1641-1644.

2. Itoh, K.; Kanemasa, S., Enantioselective Michael additions of nitromethane by a catalytic double activation method using chiral Lewis acid and achiral amine catalysts. *J. Am. Chem. Soc.* **2002,** *124* (45), 13394-13395.

3. Kumazawa, K.; Ishihara, K.; Yamamoto, H., Tin(IV) chloride-chiral pyrogallol derivatives as new lewis acid-assisted chiral bronsted acids for enantioselective polyene cyclization. *Org. Lett.* **2004,** *6* (15), 2551-2554.

4. Uyanik, M.; Ishibashi, H.; Ishihara, K.; Yamamoto, H., Biomimetic synthesis of acid-sensitive (-)-caparrapi oxide and (+)-8-epicaparrapi oxide induced by artif icial cyclases. *Org. Lett.* **2005,** *7* (8), 1601-1604.

5. Mashiko, T.; Hara, K.; Tanaka, D.; Fujiwara, Y.; Kumagai, N.; Shibasaki, M., En route to an efficient catalytic asymmetric synthesis of AS-3201. *J. Am. Chem. Soc.* **2007,** *129* (37), 11342-+.

6. Mukherjee, S.; List, B., Chiral counteranions in asymmetric transition-metal catalysis: Highly enantioselective Pd/Bronsted acid-catalyzed direct alpha-allylation of aldehydes. *J. Am. Chem. Soc.* **2007,** *129* (37), 11336-+.

7. Rueping, M.; Antonchick, A. R.; Brinkmann, C., Dual catalysis: A combined enantioselective bronsted acid and metal-catalyzed reaction-metal catalysis with chiral counterions. *Angew. Chem., Int. Ed.* **2007,** *46* (36), 6903-6906.

8. Tiseni, P. S.; Peters, R., Catalytic asymmetric formation of delta-lactones by [4+2] cycloaddition of zwitterionic dienolates generated from alpha,beta-unsaturated acid chlorides. *Angew. Chem., Int. Ed.* **2007,** *46* (28), 5325-5328.

9. Hasegawa, Y.; Watanabe, M.; Gridnev, I. D.; Ikariya, T., Enantioselective direct amination of alpha-cyanoacetates catalyzed by bifunctional chiral Ru and Ir amido complexes. *J. Am. Chem. Soc.* **2008,** *130* (7), 2158-+.

10. Tiseni, P. S.; Peters, R., Lewis acid-Lewis base catalyzed enantioselective hetero-Diels-Alder reaction for direct access to delta-lactones. *Org. Lett.* **2008,** *10* (10), 2019-2022.

11. Kull, T.; Peters, R., Contact ion pair directed Lewis acid catalysis: Asymmetric synthesis of trans-configured beta-lactones. *Angew. Chem., Int. Ed.* **2008,** *47* (29), 5461-5464.

12. Paull, D. H.; Scerba, M. T.; Alden-Danforth, E.; Widger, L. R.; Lectka, T., Catalytic, Asymmetric alpha-Fluorination of Acid Chlorides: Dual Metal-Ketene Enolate Activation. *J. Am. Chem. Soc.* **2008,** *130* (51), 17260-+.

13. Wu, B.; Gallucci, J. C.; Parquette, J. R.; RajanBabu, T. V., Enantioselective Desymmetrization of meso-Aziridines with TMSN3 or TMSCN Catalyzed by Discrete Yttrium Complexes. *Angew. Chem., Int. Ed.* **2009,** *48* (6), 1126-1129.

14. Yang, T.; Ferrali, A.; Sladojevich, F.; Campbell, L.; Dixon, D. J., Bronsted Base/Lewis Acid Cooperative Catalysis in the Enantioselective Conia-Ene Reaction. *J. Am. Chem. Soc.* **2009,** *131* (26), 9140-+.

15. Zajac, M.; Peters, R., Catalytic Asymmetric Synthesis of beta-Sultams as Precursors for Taurine Derivatives. *Chem. Eur. J.* **2009,** *15* (33), 8204-8222.

16. Lee, Y.; Li, B.; Hoveyda, A. H., Stereogenic-at-Metal Zn- and Al-Based N-Heterocyclic Carbene (NHC) Complexes as Bifunctional Catalysts in Cu-Free Enantioselective Allylic Alkylations. *J. Am. Chem. Soc.* **2009,** *131* (32), 11625-11633.

17. Yang, L.; Zhu, Q. M.; Guo, S. M.; Qian, B.; Xia, C. G.; Huang, H. M., Chiral Bronsted Acid Directed Iron-Catalyzed Enantioselective Friedel-Crafts Alkylation of Indoles with beta-Aryl alpha '-Hydroxy Enones. *Chem. Eur. J.* **2010,** *16* (5), 1638-1645.

18. Lv, J.; Li, X.; Zhong, L.; Luo, S. Z.; Cheng, J. P., Asymmetric Binary-Acid Catalysis with Chiral Phosphoric Acid and MgF2: Catalytic Enantioselective Friedel-Crafts Reactions of beta,gamma-Unsaturated alpha-Ketoesters. *Org. Lett.* **2010,** *12* (5), 1096-1099.

19. Tanaka, Y.; Kanai, M.; Shibasaki, M., Catalytic Enantioselective Construction of beta-Quaternary Carbons via a Conjugate Addition of Cyanide to beta,beta-Disubstituted alpha,beta-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2010,** *132* (26), 8862-+.

20. Ikeda, M.; Miyake, Y.; Nishibayashi, Y., Cooperative Catalytic Reactions Using Organocatalysts and Transition-Metal Catalysts: Enantioselective Propargylic Alkylation of Propargylic Alcohols with Aldehydes. *Angew. Chem., Int. Ed.* **2010,** *49* (40), 7289-7293.

21. Cheon, C. H.; Imahori, T.; Yamamoto, H., Development of a new Lewis base-tolerant chiral LBA and its application to catalytic asymmetric protonation reaction. *Chem. Comm.* **2010,** *46* (37), 6980-6982.

22. Drouet, F.; Lalli, C.; Liu, H.; Masson, G.; Zhu, J. P., Chiral Calcium Organophosphate-Catalyzed Enantioselective Electrophilic Amination of Enamides. *Org. Lett.* **2011,** *13* (1), 94-97.

23. Yoshida, A.; Ikeda, M.; Hattori, G.; Miyake, Y.; Nishibayashi, Y., Cooperative Catalytic Reactions Using Organocatalysts and Transition Metal Catalysts: Enantioselective Propargylic Alkylation of Propargylic Esters with Aldehydes. *Org. Lett.* **2011,** *13* (4), 592-595.

24. Zheng, W. H.; Zhang, Z. H.; Kaplan, M. J.; Antilla, J. C., Chiral Calcium VAPOL Phosphate Mediated Asymmetric Chlorination and Michael Reactions of 3-Substituted Oxindoles. *J. Am. Chem. Soc.* **2011,** *133* (10), 3339-3341.

25. Allen, A. E.; MacMillan, D. W. C., Enantioselective alpha-Arylation of Aldehydes via the Productive Merger of Iodonium Salts and Organocatalysis. *J. Am. Chem. Soc.* **2011,** *133* (12), 4260-4263.

26. Erb, J.; Paull, D. H.; Dudding, T.; Belding, L.; Lectka, T., From Bifunctional to Trifunctional (Tricomponent Nucleophile-Transition Metal-Lewis Acid) Catalysis: The Catalytic, Enantioselective alpha-Fluorination of Acid Chlorides. *J. Am. Chem. Soc.* **2011,** *133* (19), 7536-7546.

27. Rauniyar, V.; Wang, Z. J.; Burks, H. E.; Toste, F. D., Enantioselective Synthesis of Highly Substituted Furans by a Copper(II)-Catalyzed Cycloisomerization-Indole Addition Reaction. *J. Am. Chem. Soc.* **2011,** *133* (22), 8486-8489.

28. Jiang, G. X.; List, B., Enantioselective hydrovinylation via asymmetric counteranion-directed ruthenium catalysis. *Chem. Comm.* **2011,** *47* (36), 10022-10024.

29. Jiang, G. X.; Halder, R.; Fang, Y. W.; List, B., A Highly Enantioselective Overman Rearrangement through Asymmetric Counteranion-Directed Palladium Catalysis. *Angew. Chem., Int. Ed.* **2011,** *50* (41), 9752-9755.

30. Furukawa, T.; Kawazoe, J.; Zhang, W.; Nishimine, T.; Tokunaga, E.; Matsumoto, T.; Shiro, M.; Shibata, N., Asymmetric Allylic Monofluoromethylation and Methylation of Morita-Baylis-Hillman Carbonates with FBSM and BSM by Cooperative Cinchona Alkaloid/FeCl2 Catalysis. *Angew. Chem., Int. Ed.* **2011,** *50* (41), 9684-9688.

31. Jiang, G. X.; List, B., Direct Asymmetric alpha-Allylation of Aldehydes with Simple Allylic Alcohols Enabled by the Concerted Action of Three Different Catalysts. *Angew. Chem., Int. Ed.* **2011,** *50* (40), 9471-9474.

32. Xiao, Y. C.; Wang, C.; Yao, Y.; Sun, J.; Chen, Y. C., Direct Asymmetric Hydrosilylation of Indoles: Combined Lewis Base and Bronsted Acid Activation. *Angew. Chem., Int. Ed.* **2011,** *50* (45), 10661-10664.

33. Xu, B.; Zhu, S. F.; Xie, X. L.; Shen, J. J.; Zhou, Q. L., Asymmetric N-H Insertion Reaction Cooperatively Catalyzed by Rhodium and Chiral Spiro Phosphoric Acids. *Angew. Chem., Int. Ed.* **2011,** *50* (48), 11483-11486.

34. Loh, C. C. J.; Badorrek, J.; Raabe, G.; Enders, D., Merging Organocatalysis and Gold Catalysis: Enantioselective Synthesis of Tetracyclic Indole Derivatives through a Sequential Double Friedel-Crafts Type Reaction. *Chem. Eur. J.* **2011,** *17* (48), 13409-13414.

35. Sun, W. S.; Zhu, G. M.; Hong, L.; Wang, R., The Marriage of Organocatalysis with Metal Catalysis: Access to Multisubstituted Chiral 2,5-Dihydropyrroles by Cascade Iminium/Enamine-Metal Cooperative Catalysis. *Chem. Eur. J.* **2011,** *17* (50), 13958-13962.

36. Richter, C.; Ranganath, K. V. S.; Glorius, F., Enantioselective alpha-Arylation of Cyclic Ketones Catalyzed by a Combination of an Unmodified Cinchona Alkaloid and a Palladium Complex. *Adv. Synth. Catal.* **2012,** *354* (2-3), 377-382.

37. Chai, Z.; Rainey, T. J., Pd(II)/Bronsted Acid Catalyzed Enantioselective Allylic C-H Activation for the Synthesis of Spirocyclic Rings. *J. Am. Chem. Soc.* **2012,** *134* (8), 3615-3618.

38. Skucas, E.; MacMillan, D. W. C., Enantioselective alpha-Vinylation of Aldehydes via the Synergistic Combination of Copper and Amine Catalysis. *J. Am. Chem. Soc.* **2012,** *134* (22), 9090-9093.

39. Alix, A.; Lalli, C.; Retailleau, P.; Masson, G., Highly Enantioselective Electrophilic alpha-Bromination of Enecarbamates: Chiral Phosphoric Acid and Calcium Phosphate Salt Catalysts. *J. Am. Chem. Soc.* **2012,** *134* (25), 10389-10392.

40. Chiarucci, M.; di Lillo, M.; Romaniello, A.; Cozzi, P. G.; Cera, G.; Bandini, M., Gold meets enamine catalysis in the enantioselective alpha-allylic alkylation of aldehydes with alcohols. *Chemical Science* **2012,** *3* (9), 2859-2863.

41. Zhang, G.; Ma, Y. X.; Wang, S. L.; Zhang, Y. H.; Wang, R., Enantioselective Metal/Organo-Catalyzed Aerobic Oxidative sp(3) C-H Olefination of Tertiary Amines Using Molecular Oxygen as the Sole Oxidant. *J. Am. Chem. Soc.* **2012,** *134* (30), 12334-12337.

42. Fackler, P.; Huber, S. M.; Bach, T., Enantio- and Regioselective Epoxidation of Olefinic Double Bonds in Quinolones, Pyridones, and Amides Catalyzed by a Ruthenium Porphyrin Catalyst with a Hydrogen Bonding Site. *J. Am. Chem. Soc.* **2012,** *134* (30), 12869-12878.

43. Cockrell, J.; Wilhelmsen, C.; Rubin, H.; Martin, A.; Morgan, J. B., Enantioselective Synthesis and Stereoselective Ring Opening of N-Acylaziridines. *Angew. Chem., Int. Ed.* **2012,** *51* (39), 9842-9845.

44. Hyodo, K.; Nakamura, S.; Shibata, N., Enantioselective Aza-Morita-Baylis-Hillman Reactions of Acrylonitrile Catalyzed by Palladium(II) Pincer Complexes having C2-Symmetric Chiral Bis(imidazoline) Ligands. *Angew. Chem., Int. Ed.* **2012,** *51* (41), 10337-10341.

45. Zhai, H.; Borzenko, A.; Lau, Y. Y.; Ahn, S. H.; Schafer, L. L., Catalytic Asymmetric Synthesis of Substituted Morpholines and Piperazines. *Angew. Chem., Int. Ed.* **2012,** *51* (49), 12219-12223.

46. Barber, D. M.; Sanganee, H. J.; Dixon, D. J., One-Pot Catalytic Enantioselective Synthesis of Tetrahydropyridines via a Nitro-Mannich/Hydroamination Cascade. *Org. Lett.* **2012,** *14* (20), 5290-5293.

47. Hayashi, M.; Shiomi, N.; Funahashi, Y.; Nakamura, S., Cinchona Alkaloid Amides/Dialkylzinc Catalyzed Enantioselective Desymmetrization of Aziridines with Phosphites. *J. Am. Chem. Soc.* **2012,** *134* (47), 19366-19369.

48. Ibrahem, I.; Ma, G. N.; Afewerki, S.; Cordova, A., Palladium/Chiral Amine Co-catalyzed Enantioselective beta-Arylation of alpha,beta-Unsaturated Aldehydes. *Angew. Chem., Int. Ed.* **2013,** *52* (3), 878-882.

49. Ohmatsu, K.; Ito, M.; Kunieda, T.; Ooi, T., Exploiting the Modularity of Ion-Paired Chiral Ligands for Palladium-Catalyzed Enantioselective Allylation of Benzofuran-2(3H)-ones. *J. Am. Chem. Soc.* **2013,** *135* (2), 590-593.

50. Hatano, M.; Horibe, T.; Ishihara, K., Chiral Magnesium(II) Binaphtholates as Cooperative Bronsted/Lewis Acid-Base Catalysts for the Highly Enantioselective Addition of Phosphorus Nucleophiles to alpha,beta-Unsaturated Esters and Ketones. *Angew. Chem., Int. Ed.* **2013,** *52* (17), 4549-4553.

51. Ma, G. N.; Afewerki, S.; Deiana, L.; Palo-Nieto, C.; Liu, L. F.; Sun, J. L.; Ibrahem, I.; Cordova, A., A Palladium/Chiral Amine Co-catalyzed Enantioselective Dynamic Cascade Reaction: Synthesis of Polysubstituted Carbocycles with a Quaternary Carbon Stereocenter. *Angew. Chem., Int. Ed.* **2013,** *52* (23), 6050-6054.

52. Krautwald, S.; Sarlah, D.; Schafroth, M. A.; Carreira, E. M., Enantio- and Di Aereodivergent Dual Catalysis: alpha-Allylation of Branched Aldehydes. *Science* **2013,** *340* (6136), 1065-1068.

53. Yu, S. Y.; Zhang, H.; Gao, Y.; Mo, L.; Wang, S. Z.; Yao, Z. J., Asymmetric Cascade Annulation Based on Enantioselective Oxa-Diels-Alder Cycloaddition of in Situ Generated Isochrornenyliums by Cooperative Binary Catalysis of Pd(OAc)(2) and (S)-Trip. *J. Am. Chem. Soc.* **2013,** *135* (30), 11402-11407.

54. Lv, J.; Zhang, L.; Luo, S. Z.; Cheng, J. P., Switchable Diastereoselectivity in Enantioselective 4+2 Cycloadditions with Simple Olefins by Asymmetric Binary Acid Catalysis. *Angew. Chem., Int. Ed.* **2013,** *52* (37), 9786-9790.

55. Stevens, J. M.; MacMillan, D. W. C., Enantioselective alpha-Alkenylation of Aldehydes with Boronic Acids via the Synergistic Combination of Copper(II) and Amine Catalysis. *J. Am. Chem. Soc.* **2013,** *135* (32), 11756-11759.

56. Gregory, A. W.; Jakubec, P.; Turner, P.; Dixon, D. J., Gold and BINOL-Phosphoric Acid Catalyzed Enantioselective Hydroamination/N-Sulfonyliminium Cyclization Cascade. *Org. Lett.* **2013,** *15* (17), 4330-4333.

57. Sladojevich, F.; de Arriba, A. L. F.; Ortin, I.; Yang, T.; Ferrali, A.; Paton, R. S.; Dixon, D. J., Mechanistic Investigations into the Enantioselective Conia-Ene Reaction Catalyzed by Cinchona-Derived Amino Urea Pre-Catalysts and Cu-I. *Chem. Eur. J.* **2013,** *19* (42), 14286-14295.

58. Zhang, D.; Qiu, H.; Jiang, L. Q.; Lv, F. P.; Ma, C. Q.; Hu, W. H., Enantioselective Palladium(II) Phosphate Catalyzed Three-Component Reactions of Pyrrole, Diazoesters, and Imines. *Angew. Chem., Int. Ed.* **2013,** *52* (50), 13356-13360.

59. Quintard, A.; Constantieux, T.; Rodriguez, J., An Iron/Amine-Catalyzed Cascade Process for the Enantioselective Functionalization of Allylic Alcohols. *Angew. Chem., Int. Ed.* **2013,** *52* (49), 12883-12887.

60. Xu, B.; Zhu, S. F.; Zhang, Z. C.; Yu, Z. X.; Ma, Y.; Zhou, Q. L., Highly enantioselective S-H bond insertion cooperatively catalyzed by dirhodium complexes and chiral spiro phosphoric acids. *Chemical Science* **2014,** *5* (4), 1442-1448.

61. Krautwald, S.; Schafroth, M. A.; Sarlah, D.; Carreira, E. M., Stereodivergent alpha-Allylation of Linear Aldehydes with Dual Iridium and Amine Catalysis. *J. Am. Chem. Soc.* **2014,** *136* (8), 3020-3023.

62. Deiana, L.; Jiang, Y.; Palo-Nieto, C.; Afewerki, S.; Incerti-Pradillos, C. A.; Verho, O.; Tai, C. W.; Johnston, E. V.; Cordova, A., Combined Heterogeneous Metal/Chiral Amine: Multiple Relay Catalysis for Versatile Eco-Friendly Synthesis. *Angew. Chem., Int. Ed.* **2014,** *53* (13), 3447-3451.

63. Xu, B.; Zhu, S.-F.; Zuo, X.-D.; Zhang, Z.-C.; Zhou, Q.-L., Enantioselective N-H Insertion Reaction of a-Aryl a-Diazoketones: An Efficient Route to Chiral a- Aminoketones. *Angew. Chem., Int. Ed.* **2014,** *53* (15), 3913-3916.

64. Hack, D.; Loh, C. C. J.; Hartmann, J. M.; Raabe, G.; Enders, D., Merging Gold and Organocatalysis: A Facile Asymmetric Synthesis of Annulated Pyrroles. *Chem. Eur. J.* **2014,** *20* (14), 3917-3921.

65. Zhong, F.; Bach, T., Enantioselective Construction of 2,3-Dihydrofuro 2,3-b quinolines through Supramolecular Hydrogen Bonding Interactions. *Chem. Eur. J.* **2014,** *20* (42), 13522-13526.

66. Wang, P.-S.; Lin, H.-C.; Zhai, Y.-J.; Han, Z.-Y.; Gong, L.-Z., Chiral Counteranion Strategy for Asymmetric Oxidative C(sp(3))-H/C(sp(3))-H Coupling: Enantioselective alpha-Allylation of Aldehydes with Terminal Alkenes. *Angew. Chem., Int. Ed.* **2014,** *53* (45), 12218-12221.

67. Banerjee, D.; Junge, K.; Beller, M., Cooperative Catalysis by Palladium and a Chiral Phosphoric Acid: Enantioselective Amination of Racemic Allylic Alcohols. *Angew. Chem., Int. Ed.* **2014,** *53* (48), 13049-13053.

68. Frost, J. R.; Huber, S. M.; Breitenlechner, S.; Bannwarth, C.; Bach, T., Enantiotopos-Selective C-H Oxygenation Catalyzed by a Supramolecular Ruthenium Complex. *Angew. Chem., Int. Ed.* **2015,** *54* (2), 691-695.

69. Shinde, V. S.; Mane, M. V.; Vanka, K.; Mallick, A.; Patil, N. T., Gold(I)/Chiral Bronsted Acid Catalyzed Enantioselective Hydroamination-Hydroarylation of Alkynes: The Effect of a Remote Hydroxyl Group on the Reactivity and Enantioselectivity. *Chem. Eur. J.* **2015,** *21* (3), 975-979.

70. Zhang, D.; Zhou, J.; Xia, F.; Kang, Z.; Hu, W., Bond cleavage, fragment modification and reassembly in enantioselective three-component reactions. *Nature Communications* **2015,** *6*.

71. Senda, Y.; Nakajima, K.; Nishibayashi, Y., Cooperative Catalysis: Enantioselective Propargylic Alkylation of Propargylic Alcohols with Enecarbamates Using Ruthenium/Phosphoramide Hybrid Catalysts. *Angew. Chem., Int. Ed.* **2015,** *54* (13), 4060-4064.

72. Jiang, T.; Bartholomeyzik, T.; Mazuela, J.; Willersinn, J.; Backvall, J. E., Palladium(II)/Bronsted Acid-Catalyzed Enantioselective Oxidative Carbocyclization-Borylation of Enallenes. *Angew. Chem., Int. Ed.* **2015,** *54* (20), 6024-6027.

73. Xu, B.; Li, M. L.; Zuo, X. D.; Zhu, S. F.; Zhou, Q. L., Catalytic Asymmetric Arylation of alpha-Aryl-alpha-diazoacetates with Aniline Derivatives. *J. Am. Chem. Soc.* **2015,** *137* (27), 8700-8703.

74. Naesborg, L.; Halskov, K. S.; Tur, F.; Monsted, S. M. N.; Jorgensen, K. A., Asymmetric gamma-Allylation of alpha,beta-Unsaturated Aldehydes by Combined Organocatalysis and Transition-Metal Catalysis. *Angew. Chem., Int. Ed.* **2015,** *54* (35), 10193-10197.

75. Zhou, H.; Zhang, L.; Xu, C. M.; Luo, S. Z., Chiral Primary Amine/Palladium Dual Catalysis for Asymmetric Allylic Alkylation of beta-Ketocarbonyl Compounds with Allylic Alcohols. *Angew. Chem., Int. Ed.* **2015,** *54* (43), 12645-12648.

76. Sandmeier, T.; Krautwald, S.; Zipfel, H. F.; Carreira, E. M., Stereodivergent Dual Catalytic alpha-Allylation of Protected alpha-Amino- and alpha-Hydroxyacetaldehydes. *Angew. Chem., Int. Ed.* **2015,** *54* (48), 14363-14367.

77. Nelson, H. M.; Williams, B. D.; Miro, J.; Toste, F. D., Enantioselective 1,1-Arylborylation of Alkenes: Merging Chiral Anion Phase Transfer with Pd Catalysis. *J. Am. Chem. Soc.* **2015,** *137* (9), 3213-3216.

78. Meazza, M.; Light, M. E.; Mazzanti, A.; Rios, R., Synergistic catalysis: cis-cyclopropanation of benzoxazoles. *Chemical Science* **2016,** *7* (2), 984-988.

79. Guo, J. X.; Zhou, T.; Xu, B.; Zhu, S. F.; Zhou, Q. L., Enantioselective synthesis of alpha-alkenyl alpha-amino acids via N-H insertion reactions. *Chemical Science* **2016,** *7* (2), 1104-1108.

80. Cao, Z. Y.; Zhao, Y. L.; Zhou, J., Sequential Au(I)/chiral tertiary amine catalysis: a tandem C-H functionalization of anisoles or a thiophene/asymmetric Michael addition sequence to quaternary oxindoles. *Chem. Comm.* **2016,** *52* (12), 2537-2540.

81. Alamsetti, S. K.; Spanka, M.; Schneider, C., Synergistic Rhodium/Phosphoric Acid Catalysis for the Enantioselective Addition of Oxonium Ylides to ortho-Quinone Methides. *Angew. Chem., Int. Ed.* **2016,** *55* (7), 2392-2396.

82. Pupo, G.; Properzi, R.; List, B., Asymmetric Catalysis with CO2: The Direct -Allylation of Ketones. *Angew. Chem., Int. Ed.* **2016,** *55* (20), 6099-6102.

83. Yang, B.; Zhu, C.; Qiu, Y. A.; Backvall, J. E., Enzyme- and Ruthenium-Catalyzed Enantioselective Transformation of alpha-Allenic Alcohols into 2,3-Dihydrofurans. *Angew. Chem., Int. Ed.* **2016,** *55* (18), 5568-5572.

84. Liu, R. R.; Li, B. L.; Lu, J.; Shen, C.; Gao, J. R.; Jia, Y. X., Palladium/L-Proline-Catalyzed Enantioselective alpha-Arylative Desymmetrization of Cyclohexanones. *J. Am. Chem. Soc.* **2016,** *138* (16), 5198-5201.

85. Schwarz, K. J.; Amos, J. L.; Klein, J. C.; Do, D. T.; Snaddon, T. N., Uniting C1-Ammonium Enolates and Transition Metal Electrophiles via Cooperative Catalysis: The Direct Asymmetric alpha-Allylation of Aryl Acetic Acid Esters. *J. Am. Chem. Soc.* **2016,** *138* (16), 5214-5217.

86. Halskov, K. S.; Naesborg, L.; Tur, F.; Jorgensen, K. A., Asymmetric 3+2 Cycloaddition of Vinylcyclopropanes and alpha,beta-Unsaturated Aldehydes by Synergistic Palladium and Organocatalysis. *Org. Lett.* **2016,** *18* (9), 2220-2223.

87. Guo, C.; Fleige, M.; Janssen-Muller, D.; Daniliuc, C. G.; Glorius, F., Cooperative N-Heterocyclic Carbene/Palladium-Catalyzed Enantioselective Umpolung Annulations. *J. Am. Chem. Soc.* **2016,** *138* (25), 7840-7843.

88. Yuan, Z. B.; Wei, W. W.; Lin, A. J.; Yao, H. Q., Bifunctional Organo/Metal Cooperatively Catalyzed 3+2 Annulation of para-Quinone Methides with Vinylcyclopropanes: Approach to Spiro 4.5 deca-6,9-diene-8-ones. *Org. Lett.* **2016,** *18* (14), 3370-3373.

89. Lin, J. S.; Dong, X. Y.; Li, T. T.; Jiang, N. C.; Tan, B.; Liu, X. Y., A Dual-Catalytic Strategy To Direct Asymmetric Radical Aminotrifluoromethylation of Alkenes. *J. Am. Chem. Soc.* **2016,** *138* (30), 9357-9360.

90. Mo, X. B.; Hall, D. G., Dual Catalysis Using Boronic Acid and Chiral Amine: Acyclic Quaternary Carbons via Enantioselective Alkylation of Branched Aldehydes with Allylic Alcohols. *J. Am. Chem. Soc.* **2016,** *138* (34), 10762-10765.

91. Lin, H. C.; Wang, P. S.; Tao, Z. L.; Chen, Y. G.; Han, Z. Y.; Gong, L. Z., Highly Enantioselective Allylic C-H Alkylation of Terminal Olefins with Pyrazol-5-ones Enabled by Cooperative Catalysis of Palladium Complex and Bronsted Acid. *J. Am. Chem. Soc.* **2016,** *138* (43), 14354-14361.

92. Leth, L. A.; Glaus, F.; Meazza, M.; Fu, L.; Thogersen, M. K.; Bitsch, E. A.; Jorgensen, K. A., Decarboxylative 4+2 Cycloaddition by Synergistic Palladium and Organocatalysis. *Angew. Chem., Int. Ed.* **2016,** *55* (49), 15272-15276.

93. Yamamoto, E.; Hilton, M. J.; Orlandi, M.; Saini, V.; Toste, F. D.; Sigman, M. S., Development and Analysis of a Pd(0)-Catalyzed Enantioselective 1,1-Diarylation of Acrylates Enabled by Chiral Anion Phase Transfer. *J. Am. Chem. Soc.* **2016,** *138* (49), 15877-15880.

94. Laugeois, M.; Ponra, S.; Ratovelomanana-Vidal, V.; Michelet, V.; Vitale, M. R., Asymmetric preparation of polysubstituted cyclopentanes by synergistic Pd(0)/amine catalyzed formal 3+2 cycloadditions of vinyl cyclopropanes with enals. *Chem. Comm.* **2016,** *52* (30), 5332-5335.

95. Lian, X. L.; Meng, J.; Han, Z. Y., Ru(II)/Organo Relay Catalytic Three-Component Reaction of 3-Diazooxindoles, Amines, and Nitroalkene: Formal Synthesis of (-)-Psychotrimine. *Org. Lett.* **2016,** *18* (17), 4270-4273.

96. Naesborg, L.; Tur, F.; Meazza, M.; Blom, J.; Halskov, K. S.; Jorgensen, K. A., Synergistic Catalysis for the Asymmetric 3+2 Cycloaddition of Vinyl Aziridines with alpha,beta-Unsaturated Aldehydes. *Chem. Eur. J.* **2017,** *23* (2), 268-272.

97. Shang, M.; Wang, X. X.; Koo, S. M.; Youn, J.; Chan, J. Z.; Yao, W. Z.; Hastings, B. T.; Wasa, M., Frustrated Lewis Acid/Bronsted Base Catalysts for Direct Enantioselective alpha-Amination of Carbonyl Compounds. *J. Am. Chem. Soc.* **2017,** *139* (1), 95-98.

98. Jiang, X. Y.; Beiger, J. J.; Hartwig, J. F., Stereodivergent Allylic Substitutions with Aryl Acetic Acid Esters by Synergistic Iridium and Lewis Base Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (1), 87-90.

99. Zhou, Z. J.; Li, Y. J.; Gong, L.; Meggers, E., Enantioselective 2-Alkylation of 3-Substituted Indoles with Dual Chiral Lewis Acid/Hydrogen-Bond-Mediated Catalyst. *Org. Lett.* **2017,** *19* (1), 222-225.

100. Meazza, M.; Tur, F.; Hammer, N.; Jorgensen, K. A., Synergistic Diastereo- and Enantioselective Functionalization of Unactivated Alkyl Quinolines with ,-Unsaturated Aldehydes. *Angew. Chem., Int. Ed.* **2017,** *56* (6), 1634-1638.

101. Cruz, F. A.; Dong, V. M., Stereodivergent Coupling of Aldehydes and Alkynes via Synergistic Catalysis Using Rh and Jacobsen's Amine. *J. Am. Chem. Soc.* **2017,** *139* (3), 1029-1032.

102. Guo, S.; Cong, F.; Guo, R.; Wang, L.; Tang, P. P., Asymmetric silver-catalysed intermolecular bromotrifluoromethoxylation of alkenes with a new trifluoromethoxylation reagent. *Nature Chemistry* **2017,** *9* (6), 546-551.

103. Shen, D.; Chen, Q. L.; Yan, P. P.; Zeng, X. F.; Zhong, G. F., Enantioselective Dearomatization of Naphthol Derivatives with Allylic Alcohols by Cooperative Iridium and Bronsted Acid Catalysis. *Angew. Chem., Int. Ed.* **2017,** *56* (12), 3242-3246.

104. Zhou, H.; Wang, Y. N.; Zhang, L.; Cai, M.; Luo, S. Z., Enantioselective Terminal Addition to Allenes by Dual Chiral Primary Amine/Palladium Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (10), 3631-3634.

105. Guo, C.; Janssen-Muller, D.; Fleige, M.; Lerchen, A.; Daniliuc, C. G.; Glorius, F., Mechanistic Studies on a Cooperative NHC Organocatalysis/Palladium Catalysis System: Uncovering Significant Lessons for Mixed Chiral Pd(NHC)(PR3) Catalyst Design. *J. Am. Chem. Soc.* **2017,** *139* (12), 4443-4451.

106. Song, J.; Zhang, Z. J.; Gong, L. Z., Asymmetric 4+2 Annulation of C1 Ammonium Enolates with Copper-Allenylidenes. *Angew. Chem., Int. Ed.* **2017,** *56* (19), 5212-5216.

107. Manzano, R.; Datta, S.; Paton, R. S.; Dixon, D. J., Enantioselective Silver and Amine Co-catalyzed Desymmetrizing Cycloisomerization of Alkyne-Linked Cyclohexanones. *Angew. Chem., Int. Ed.* **2017,** *56* (21), 5834-5838.

108. Avila, C. M.; Patel, J. S.; Reddi, Y.; Saito, M.; Nelson, H. M.; Shunatona, H. P.; Sigman, M. S.; Sunoj, R. B.; Toste, F. D., Enantioselective Heck-Matsuda Arylations through Chiral Anion Phase-Transfer of Aryl Diazonium Salts. *Angew. Chem., Int. Ed.* **2017,** *56* (21), 5806-5811.

109. Li, M. F.; Guo, X.; Zheng, Q.; Hu, W. H.; Liu, S. Y., Enantioselective Multicomponent Reaction for Rapid Construction of 1,2,5-Triol Derivatives with Vicinal Chiral Centers. *J. Org. Chem.* **2017,** *82* (10), 5212-5221.

110. Bartlett, S. L.; Sohtome, Y.; Hashizume, D.; White, P. S.; Sawamura, M.; Johnson, J. S.; Sodeoka, M., Catalytic Enantioselective 3+2 Cycloaddition of alpha-Keto Ester Enolates and Nitrile Oxides. *J. Am. Chem. Soc.* **2017,** *139* (25), 8661-8666.

111. Jiang, H. J.; Liu, K.; Yu, J.; Zhang, L.; Gong, L. Z., Switchable Stereoselectivity in Bromoaminocyclization of Olefins: Using BrOnsted Acids of Anionic Chiral Cobalt(III) Complexes. *Angew. Chem., Int. Ed.* **2017,** *56* (39), 11931-11935.

112. Nakayama, H.; Harada, S.; Kono, M.; Nemoto, T., Chemoselective Asymmetric Intramolecular Dearomatization of Phenols with alpha-Diazoacetamides Catalyzed by Silver Phosphate. *J. Am. Chem. Soc.* **2017,** *139* (30), 10188-10191.

113. Bayeh, L.; Le, P. Q.; Tambar, U. K., Catalytic allylic oxidation of internal alkenes to a multifunctional chiral building block. *Nature* **2017,** *547* (7662), 196-+.

114. Cheng, Y. F.; Dong, X. Y.; Gu, Q. S.; Yu, Z. L.; Liu, X. Y., Achiral Pyridine Ligand-Enabled Enantioselective Radical Oxytrifluoromethylation of Alkenes with Alcohols. *Angew. Chem., Int. Ed.* **2017,** *56* (30), 8883-8886.

115. Spoehrle, S. S. M.; West, T. H.; Taylor, J. E.; Slawin, A. M. Z.; Smith, A. D., Tandem Palladium and Isothiourea Relay Catalysis: Enantioselective Synthesis of alpha-Amino Add Derivatives via Allylic Amination and 2,3 -Sigmatropic Rearrangement. *J. Am. Chem. Soc.* **2017,** *139* (34), 11895-11902.

116. Wang, G. P.; Chen, M. Q.; Zhu, S. F.; Zhou, Q. L., Enantioselective Nazarov cyclization of indole enones cooperatively catalyzed by Lewis acids and chiral Bronsted acids. *Chemical Science* **2017,** *8* (10), 7197-7202.

117. Wang, D. H.; Zhang, L.; Luo, S. Z., Enantioselective Decarboxylative alpha-Alkynylation of beta-Ketocarbonyls via a Catalytic alpha-Imino Radical Intermediate. *Org. Lett.* **2017,** *19* (18), 4924-4927.

118. Chinn, A. J.; Kim, B.; Kwon, Y.; Miller, S. J., Enantioselective Intermolecular C-O Bond Formation in the Desymmetrization of Diarylmethines Employing a Guanidinylated Peptide-Based Catalyst. *J. Am. Chem. Soc.* **2017,** *139* (49), 18107-18114.

119. Burg, F.; Gicquel, M.; Breitenlechner, S.; Pothig, A.; Bach, T., Site- and Enantioselective C-H Oxygenation Catalyzed by a Chiral Manganese Porphyrin Complex with a Remote Binding Site. *Angew. Chem., Int. Ed.* **2018,** *57* (11), 2953-2957.

120. Wang, M.; Chen, J.; Chen, Z. J.; Zhong, C. X.; Lu, P., Enantioselective Desymmetrization of Cyclobutanones Enabled by Synergistic Palladium/Enamine Catalysis. *Angew. Chem., Int. Ed.* **2018,** *57* (10), 2707-2711.

121. Song, J.; Zhang, Z. J.; Chen, S. S.; Fan, T.; Gong, L. Z., Lewis Base/Copper Cooperatively Catalyzed Asymmetric alpha-Amination of Esters with Diaziridinone. *J. Am. Chem. Soc.* **2018,** *140* (9), 3177-3180.

122. Gentry, E. C.; Rono, L. J.; Hale, M. E.; Matsuura, R.; Knowles, R. R., Enantioselective Synthesis of Pyrroloindolines via Noncovalent Stabilization of Indole Radical Cations and Applications to the Synthesis of Alkaloid Natural Products. *J. Am. Chem. Soc.* **2018,** *140* (9), 3394-3402.

123. Singha, S.; Patra, T.; Daniliuc, C. G.; Glorius, F., Highly Enantioselective 5+2 Annulations through Cooperative N-Heterocyclic Carbene (NHC) Organocatalysis and Palladium Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (10), 3551-3554.

124. Fujita, T.; Yamamoto, T.; Morita, Y.; Chen, H. Y.; Shimizu, Y.; Kanai, M., Chemo- and Enantioselective Pd/B Hybrid Catalysis for the Construction of Acyclic Quaternary Carbons: Migratory Allylation of O-Ally! Esters to alpha-C-Allyl Carboxylic Acids. *J. Am. Chem. Soc.* **2018,** *140* (18), 5899-5903.

125. Mori, K.; Isogai, R.; Kamei, Y.; Yamanaka, M.; Akiyama, T., Chiral Magnesium Bisphosphate-Catalyzed Asymmetric Double C(sp(3))-H Bond Functionalization Based on Sequential Hydride Shift/Cyclization Process. *J. Am. Chem. Soc.* **2018,** *140* (20), 6203-6207.

126. Yan, S. Y.; Han, Y. Q.; Yao, Q. J.; Nie, X. L.; Liu, L.; Shi, B. F., Palladium(II)-Catalyzed Enantioselective Arylation of Unbiased Methylene C(sp(3))-H Bonds Enabled by a 2-Pyridinylisopropyl Auxiliary and Chiral Phosphoric Acids. *Angew. Chem., Int. Ed.* **2018,** *57* (29), 9093-9097.

127. Cui, X. Y.; Ge, Y. C.; Tan, S. M.; Jiang, H.; Tan, D.; Lu, Y. P.; Lee, R.; Tan, C. H., (Guanidine)copper Complex-Catalyzed Enantioselective Dynamic Kinetic Allylic Alkynylation under Biphasic Condition. *J. Am. Chem. Soc.* **2018,** *140* (27), 8448-8455.

128. Shi, H.; Herron, A. N.; Shao, Y.; Shao, Q.; Yu, J. Q., Enantioselective remote meta-C-H arylation and alkylation via a chiral transient mediator. *Nature* **2018,** *558* (7711), 581-+.

129. Schwarz, K. J.; Yang, C.; Fyfe, J. W. B.; Snaddon, T. N., Enantioselective alpha-Benzylation of Acyclic Esters Using pi-Extended Electrophiles. *Angew. Chem., Int. Ed.* **2018,** *57* (37), 12102-12105.

130. Lin, L. Q.; Fukagawa, S.; Sekine, D.; Tomita, E.; Yoshino, T.; Matsunaga, S., Chiral Carboxylic Acid Enabled Achiral Rhodium(III)-Catalyzed Enantioselective C-H Functionalization. *Angew. Chem., Int. Ed.* **2018,** *57* (37), 12048-12052.

131. Guo, S. S.; Dong, P.; Chen, Y. S.; Feng, X. M.; Li, X. H., Chiral Guanidine/Copper Catalyzed Asymmetric Azide-Alkyne Cycloaddition/ 2+2 Cascade Reaction. *Angew. Chem., Int. Ed.* **2018,** *57* (51), 16852-16856.

132. Zheng, S. C.; Wang, Q.; Zhu, J. P., Catalytic Atropenantioselective Heteroannulation between Isocyanoacetates and Alkynyl Ketones: Synthesis of Enantioenriched Axially Chiral 3-Arylpyrroles. *Angew. Chem., Int. Ed.* **2019,** *58* (5), 1494-1498.

133. Lin, J. S.; Li, T. T.; Liu, J. R.; Jiao, G. Y.; Gu, Q. S.; Cheng, J. T.; Guo, Y. L.; Hong, X.; Liu, X. Y., Cu/Chiral Phosphoric Acid-Catalyzed Asymmetric Three-Component Radical-Initiated 1,2-Dicarbofunctionalization of Alkenes. *J. Am. Chem. Soc.* **2019,** *141* (2), 1074-1083.

134. Cheng, X. P.; Wang, Z. X.; Quintanilla, C. D.; Zhang, L. M., Chiral Bifunctional Phosphine Ligand Enabling Gold-Catalyzed Asymmetric Isomerization of Alkyne to Allene and Asymmetric Synthesis of 2,5-Dihydrofuran. *J. Am. Chem. Soc.* **2019,** *141* (9), 3787-3791.

135. Chen, L.; Luo, M. J.; Zhu, F.; Wen, W.; Guo, Q. X., Combining Chiral Aldehyde Catalysis and Transition-Metal Catalysis for Enantioselective alpha-Allylic Alkylation of Amino Acid Esters. *J. Am. Chem. Soc.* **2019,** *141* (13), 5159-5163.

136. Willig, F.; Lang, J.; Hans, A. C.; Ringenberg, M. R.; Pfeffer, D.; Frey, W.; Peters, R., Polyfunctional Imidazolium Aryloxide Betaine/Lewis Acid Catalysts as Tools for the Asymmetric Synthesis of Disfavored Diastereomers. *J. Am. Chem. Soc.* **2019,** *141* (30), 12029-12043.

137. Chen, Z. C.; Chen, Z.; Yang, Z. H.; Guo, L.; Du, W.; Chen, Y. C., Cooperative Tertiary Amine/Chiral Iridium Complex Catalyzed Asymmetric 4+3 and 3+3 Annulation Reactions. *Angew. Chem., Int. Ed.* **2019,** *58* (42), 15021-15025.

138. Falconnet, A.; Magre, M.; Maity, B.; Cavallo, L.; Rueping, M., Asymmetric Magnesium-Catalyzed Hydroboration by Metal-Ligand Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2019,** *58* (49), 17567-17571.

139. Li, M. L.; Yu, J. H.; Li, Y. H.; Zhu, S. F.; Zhou, Q. L., Highly enantioselective carbene insertion into N-H bonds of aliphatic amines. *Science* **2019,** *366* (6468), 990-+.

140. Ye, L.; Tian, Y.; Meng, X.; Gu, Q.-S.; Liu, X.-Y., Enantioselective Copper(I)/Chiral Phosphoric Acid Catalyzed Intramolecular Amination of Allylic and Benzylic C−H Bonds. *Angew. Chem., Int. Ed.* **2020,** *59* (3), 1129-1133.

141. Zhou, L.; Wu, X.; Yang, X.; Mou, C.; Song, R.; Yu, S.; Chai, H.; Pan, L.; Jin, Z.; Chi, Y. R., Gold and Carbene Relay Catalytic Enantioselective Cycloisomerization/Cyclization Reactions of Ynamides and Enals. *Angew. Chem., Int. Ed.* **2020,** *59* (4), 1557-1561.

142. Wang, Y. N.; Chai, J. L.; You, C.; Zhang, J.; Mi, X. L.; Zhang, L.; Luo, S. Z., pi-Coordinating Chiral Primary Amine/Palladium Synergistic Catalysis for Asymmetric Allylic Alkylation. *J. Am. Chem. Soc.* **2020,** *142* (6), 3184-3195.

143. Zhang, Z.; Smal, V.; Retailleau, P.; Voituriez, A.; Frison, G.; Marinetti, A.; Guinchard, X., Tethered Counterion-Directed Catalysis: Merging the Chiral Ion-Pairing and Bifunctional Ligand Strategies in Enantioselective Gold(I) Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (8), 3797-3805.

144. Annapureddy, R. R.; Jandl, C.; Bach, T., A Chiral Phenanthroline Ligand with a Hydrogen-Bonding Site: Application to the Enantioselective Amination of Methylene Groups. *J. Am. Chem. Soc.* **2020,** *142* (16), 7374-7378.

145. Tsai, C.-C.; Sandford, C.; Wu, T.; Chen, B.; Sigman, M. S.; Toste, F. D., Enantioselective Intramolecular Allylic Substitution via Synergistic Palladium/Chiral Phosphoric Acid Catalysis: Insight into Stereoinduction through Statistical Modeling. *Angew. Chem., Int. Ed.* **2020,** *59* (34), 14647-14655.

146. Li, Y.; Zhao, Y.-T.; Zhou, T.; Chen, M.-Q.; Li, Y.-P.; Huang, M.-Y.; Xu, Z.-C.; Zhu, S.-F.; Zhou, Q.-L., Highly Enantioselective O–H Bond Insertion Reaction of α-Alkyl- and α-Alkenyl-α-diazoacetates with Water. *J. Am. Chem. Soc.* **2020,** *142* (23), 10557-10566.

147. Hutchings-Goetz, L. S.; Yang, C.; Fyfe, J. W. B.; Snaddon, T. N., Enantioselective Syntheses of Strychnos and Chelidonium Alkaloids through Regio- and Stereocontrolled Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2020,** *59* (40), 17556-17564.

148. Strassfeld, D. A.; Wickens, Z. K.; Picazo, E.; Jacobsen, E. N., Highly Enantioselective, Hydrogen-Bond-Donor Catalyzed Additions to Oxetanes. *J. Am. Chem. Soc.* **2020,** *142* (20), 9175-9180.

149. Li, L.; Li, Y.; Fu, N.; Zhang, L.; Luo, S., Catalytic Asymmetric Electrochemical α-Arylation of Cyclic β-Ketocarbonyls with Anodic Benzyne Intermediates. *Angew. Chem., Int. Ed.* **2020,** *59* (34), 14347-14351.

150. Xu, L.; Yang, Q.; Zhong, S.; Li, H.; Tang, Y.; Cai, Y., Ln(III)/Chiral Brønsted Acid Catalyzed Asymmetric Cascade Ring Opening/Aza-Piancatelli Rearrangement of D–A Cyclopropanes. *Org. Lett.* **2020,** *22* (22), 9016-9021.

151. Zhang, Z.-J.; Wen, Y.-H.; Song, J.; Gong, L.-Z., Kinetic Resolution of Aziridines Enabled by N-Heterocyclic Carbene/Copper Cooperative Catalysis: Carbene Dose-Controlled Chemo-Switchability. *Angew. Chem., Int. Ed.* **2021,** *60* (6), 3268-3276.

152. Chen, C.-N.; Cheng, W.-M.; Wang, J.-K.; Chao, T.-H.; Cheng, M.-J.; Liu, R.-S., Gold-Catalyzed [3+2]-Annulations of α-Aryl Diazoketones with the Tetrasubstituted Alkenes of Cyclopentadienes: High Stereoselectivity and Enantioselectivity. *Angew. Chem., Int. Ed.* **2021,** *60* (9), 4479-4484.

153. Ito, T.; Harada, S.; Homma, H.; Takenaka, H.; Hirose, S.; Nemoto, T., Asymmetric Intramolecular Dearomatization of Nonactivated Arenes with Ynamides for Rapid Assembly of Fused Ring System under Silver Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (2), 604-611.

154. Zheng, Y.; Qin, T.; Zi, W., Enantioselective Inverse Electron Demand (3 + 2) Cycloaddition of Palladium-Oxyallyl Enabled by a Hydrogen-Bond-Donating Ligand. *J. Am. Chem. Soc.* **2021,** *143* (2), 1038-1045.

155. Annapureddy, R. R.; Burg, F.; Gramüller, J.; Golub, T. P.; Merten, C.; Huber, S. M.; Bach, T., Silver-Catalyzed Enantioselective Sulfimidation Mediated by Hydrogen Bonding Interactions. *Angew. Chem., Int. Ed.* **2021,** *60* (14), 7920-7926.

156. Wu, M.-S.; Han, Z.-Y.; Gong, L.-Z., Asymmetric α-Pentadienylation of Aldehydes with Cyclopropylacetylenes. *Org. Lett.* **2021,** *23* (3), 636-641.

157. Ma, J.; Zhou, Q.; Song, G.; Song, Y.; Zhao, G.; Ding, K.; Zhao, B., Enantioselective Synthesis of Pyroglutamic Acid Esters from Glycinate via Carbonyl Catalysis. *Angew. Chem., Int. Ed.* **2021,** *60* (19), 10588-10592.

158. Cao, J.; Hu, M.-Y.; Liu, S.-Y.; Zhang, X.-Y.; Zhu, S.-F.; Zhou, Q.-L., Enantioselective Silicon-Directed Nazarov Cyclization. *J. Am. Chem. Soc.* **2021,** *143* (18), 6962-6968.

159. Fanourakis, A.; Williams, B. D.; Paterson, K. J.; Phipps, R. J., Enantioselective Intermolecular C–H Amination Directed by a Chiral Cation. *J. Am. Chem. Soc.* **2021,** *143* (27), 10070-10076.

160. Wang, H.; Zhang, R.; Zhang, Q.; Zi, W., Synergistic Pd/Amine-Catalyzed Stereodivergent Hydroalkylation of 1,3-Dienes with Aldehydes: Reaction Development, Mechanism, and Stereochemical Origins. *J. Am. Chem. Soc.* **2021,** *143* (29), 10948-10962.

161. Cheng, X.; Li, T.; Gutman, K.; Zhang, L., Chiral Bifunctional Phosphine Ligand-Enabled Cooperative Cu Catalysis: Formation of Chiral α,β-Butenolides via Highly Enantioselective γ-Protonation. *J. Am. Chem. Soc.* **2021,** *143* (29), 10876-10881.

162. Sharma, H. A.; Essman, J. Z.; Jacobsen, E. N., Enantioselective catalytic 1,2-boronate rearrangements. *Science* **2021,** *374* (6568), 752-757.

163. Kang, Z.; Chang, W.; Tian, X.; Fu, X.; Zhao, W.; Xu, X.; Liang, Y.; Hu, W., Ternary Catalysis Enabled Three-Component Asymmetric Allylic Alkylation as a Concise Track to Chiral α,α-Disubstituted Ketones. *J. Am. Chem. Soc.* **2021,** *143* (49), 20818-20827.

164. Jiang, J.; Wang, X.; Liu, S.; Zhang, S.; Yang, B.; Zhao, Y.; Lu, S., Enantioselective Cascade Annulation of α-Amino-ynones and Enals Enabled by Gold and Oxidative NHC Relay Catalysis. *Angew. Chem., Int. Ed.* **2022,** *61* (13), e202115464.

165. Fan, T.; Song, J.; Gong, L.-Z., Asymmetric Redox Allylic Alkylation to Access 3,3′-Disubstituted Oxindoles Enabled by Ni/NHC Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2022,** *61* (22), e202201678.

166. Lin, H.-C.; Knox, G. J.; Pearson, C. M.; Yang, C.; Carta, V.; Snaddon, T. N., A Pd−H/Isothiourea Cooperative Catalysis Approach to anti-Aldol Motifs: Enantioselective α-Alkylation of Esters with Oxyallenes**. *Angew. Chem., Int. Ed.* **2022,** *61* (25), e202201753.

167. Bitai, J.; Nimmo, A. J.; Slawin, A. M. Z.; Smith, A. D., Cooperative Palladium/Isothiourea Catalyzed Enantioselective Formal (3+2) Cycloaddition of Vinylcyclopropanes and α,β-Unsaturated Esters. *Angew. Chem., Int. Ed.* **2022,** *61* (25), e202202621.

168. Kurihara, T.; Kojima, M.; Yoshino, T.; Matsunaga, S., Achiral Cp*Rh(III)/Chiral Lewis Base Cooperative Catalysis for Enantioselective Cyclization via C–H Activation. *J. Am. Chem. Soc.* **2022,** *144* (16), 7058-7065.

169. Hirata, Y.; Sekine, D.; Kato, Y.; Lin, L.; Kojima, M.; Yoshino, T.; Matsunaga, S., Cobalt(III)/Chiral Carboxylic Acid-Catalyzed Enantioselective Synthesis of Benzothiadiazine-1-oxides via C−H Activation. *Angew. Chem., Int. Ed.* **2022,** *61* (28), e202205341.

170. Chen, Y.; He, J.; Zhuang, C.; Liu, Z.; Xiao, K.; Su, Z.; Ren, X.; Wang, T., Synergistic Catalysis between a Dipeptide Phosphonium Salt and a Metal-Based Lewis Acid for Asymmetric Synthesis of N-Bridged [3.2.1] Ring Systems. *Angew. Chem., Int. Ed.* **2022,** *61* (38), e202207334.

171. Jia, Z.; Zhang, L.; Luo, S., Asymmetric C–H Dehydrogenative Allylic Alkylation by Ternary Photoredox-Cobalt-Chiral Primary Amine Catalysis under Visible Light. *J. Am. Chem. Soc.* **2022,** *144* (24), 10705-10710.

172. van den Heuvel, N.; Mason, S. M.; Mercado, B. Q.; Miller, S. J., Aspartyl β-Turn-Based Dirhodium(II) Metallopeptides for Benzylic C(sp3)–H Amination: Enantioselectivity and X-ray Structural Analysis. *J. Am. Chem. Soc.* **2023,** *145* (22), 12377-12385.

173. Wang, A.-F.; Tian, J.-M.; Zhao, X.-J.; Li, Z.-H.; Zhang, Y.; Lu, K.; Wang, H.; Zhang, S.-Y.; Tu, Y.-Q.; Ding, T.-M.; Xie, Y.-Y., Asymmetric Intramolecular Hydroalkylation of Internal Olefin with Cycloalkanone to Directly Access Polycyclic Systems. *Angew. Chem., Int. Ed.* **2023,** *62* (39), e202308858.

174. Kadarauch, M.; Whalley, D. M.; Phipps, R. J., sSPhos: A General Ligand for Enantioselective Arylative Phenol Dearomatization via Electrostatically-Directed Palladium Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (47), 25553-25558.

175. Qian, Y.; Tang, J.; Zhou, X.; Luo, J.; Yang, X.; Ke, Z.; Hu, W., Enantioselective Multifunctionalization with Rh Carbynoids. *J. Am. Chem. Soc.* **2023,** *145* (48), 26403-26411.

176. Dong, S.; Hong, K.; Zhang, Z.; Huang, J.; Xie, X.; Yuan, H.; Hu, W.; Xu, X., Construction of Chiral Quaternary Carbon Centers via Asymmetric Metal Carbene gem-Dialkylation. *Angew. Chem., Int. Ed.* **2023,** *62* (26), e202302371.

177. Zhao, K.; Yang, Z.; Yang, J.; Li, X.; Quintanilla, C. D.; Zhang, L., Desymmetrization and Parallel Kinetic Resolution of 1-Ethynylcyclobutanols via Asymmetric Cooperative Gold Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (50), 27205-27210.

178. Su, Z.; Tan, B.; He, H.; Chen, K.; Chen, S.; Lei, H.; Chen, T.-G.; Ni, S.-F.; Li, Z., Enantioselective Tsuji-Trost α-Fluoroallylation of Amino Acid Esters with Gem-Difluorinated Cyclopropanes. *Angew. Chem., Int. Ed.* **2024,** *63* (23), e202402038.

179. Xu, M.-M.; Xie, P.-P.; He, J.-X.; Zhang, Y.-Z.; Zheng, C.; Cai, Q., Enantioselective Cross-[4 + 2]-Cycloaddition/Decarboxylation of 2-Pyrones by Cooperative Catalysis of the Pd(0)/NHC Complex and Chiral Phosphoric Acid. *J. Am. Chem. Soc.* **2024,** *146* (10), 6936-6946.

180. Ahmed, H.; Ghosh, B.; Breitenlechner, S.; Feßner, M.; Merten, C.; Bach, T., Intermolecular Enantioselective Amination Reactions Mediated by Visible Light and a Chiral Iron Porphyrin Complex. *Angew. Chem., Int. Ed.* **2024,** *63* (34), e202407003.

181. Chen, K.; Zhou, S.; Li, C.; Dong, S.; Hong, K.; Xu, X., Enantioselective Construction of Quaternary Stereocenters via A Chiral Spiro Phosphoric Acid-Assisted Formal Gold Carbene gem-Dialkylation Reaction. *J. Am. Chem. Soc.* **2024,** *146* (28), 19261-19270.

182. Zhang, H.; Wen, W.; Wang, Y.-Y.; Lu, Z.-X.; Liu, J.-L.; Wu, Z.-L.; Cai, T.; Guo, Q.-X., Asymmetric bifunctionalization of allenes with aryl iodides and amino acids enabled by chiral aldehyde/palladium combined catalysis. *Chemical Science* **2024,** *15* (32), 12983-12988.

183. Hore, S.; Jeong, J.; Kim, D.; Chang, S., Visible-Light-Promoted Enantioselective α-Amidation of Aldehydes by Harnessing Organo-Iron Dual Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (32), 22172-22179.

184. Wu, X.; Zhao, K.; Quintanilla, C. D.; Zhang, L., Chiral Bifunctional Phosphine Ligand Enables Asymmetric Trapping of Catalytic Vinyl Gold Carbene Species. *J. Am. Chem. Soc.* **2024,** *146* (4), 2308-2312.

185. Gutman, K. L.; Quintanilla, C. D.; Zhang, L., Catalytic Enantioselective Protonation of Gold Enolates Enabled by Cooperative Gold(I) Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (6), 3598-3602.

186. Han, H.; Yi, W.; Ding, S.; Ren, X.; Zhao, B., Enantioselective Three-Component α-Allylic Alkylation of α-Amino Esters by Synergistic Photoinduced Pd/Carbonyl Catalysis. *Angew. Chem., Int. Ed.* **2025,** *64* (5), e202418910.

4.4 Dual Activation on Two Metal Centers

4.4.1 Addition to Carbonyl and Imines: Aldol and Mannich

1. Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C. P.; Singh, V. K., A STABLE AND EASILY PREPARED CATALYST FOR THE ENANTIOSELECTIVE REDUCTION OF KETONES - APPLICATIONS TO MULTISTEP SYNTHESES. *J. Am. Chem. Soc.* **1987,** *109* (25), 7925-7926.

2. Corey, E. J.; Cheng, X. M.; Cimprich, K. A.; Sarshar, S., REMARKABLY EFFECTIVE AND SIMPLE SYNTHESES OF ENANTIOMERICALLY PURE SECONDARY CARBINOLS FROM ACHIRAL KETONES. *Tetrahedron Lett.* **1991,** *32* (47), 6835-6838.

3. Corey, E. J.; Azimioara, M.; Sarshar, S., X-RAY CRYSTAL-STRUCTURE OF A CHIRAL OXAZABOROLIDINE CATALYST FOR ENANTIOSELECTIVE CARBONYL REDUCTION. *Tetrahedron Lett.* **1992,** *33* (24), 3429-3430.

4. Corey, E. J.; Link, J. O.; Bakshi, R. K., A MECHANISTIC AND STRUCTURAL-ANALYSIS OF THE BASIS FOR HIGH ENANTIOSELECTIVITY IN THE OXAZABOROLIDINE-CATALYZED REDUCTION OF TRIHALOMETHYL KETONES BY CATECHOLBORANE. *Tetrahedron Lett.* **1992,** *33* (47), 7107-7110.

5. Corey, E. J.; Helal, C. J., NOVEL ELECTRONIC EFFECTS OF REMOTE SUBSTITUENTS ON THE OXAZABOROLIDINE-CATALYZED ENANTIOSELECTIVE REDUCTION OF KETONES. *Tetrahedron Lett.* **1995,** *36* (50), 9153-9156.

6. Sasai, H.; Arai, S.; Tahara, Y.; Shibasaki, M., Catalytic Asymmetric-Synthesis of Alpha-Amino Phosphonates Using Lanthanoid-Potassium-Binol Complexes. *J. Org. Chem.* **1995,** *60* (21), 6656-6657.

7. Bach, J.; Berenguer, R.; Garcia, J.; Loscertales, T.; Vilarrasa, J., Highly enantioenriched propargylic alcohols by oxazaborolidine-mediated reduction of acetylenic ketones. *J. Org. Chem.* **1996,** *61* (25), 9021-9025.

8. Corey, E. J.; Helal, C. J., Aminoacrylic compounds. Part 31 - Reduction of carbonyl compounds with chiral oxazaborolidine catalysts: A new paradigm for enantioselective catalysis and a powerful new synthetic method. *Angew. Chem.-Int. Edit.* **1998,** *37* (15), 1987-2012.

9. Groger, H.; Saida, Y.; Sasai, H.; Yamaguchi, K.; Martens, J.; Shibasaki, M., A new and highly efficient asymmetric route to cyclic alpha- amino phosphonates: The first catalytic enantioselective hydrophosphonylation of cyclic imines catalyzed by chiral heterobimetallic lanthanoid complexes. *J. Am. Chem. Soc.* **1998,** *120* (13), 3089-3103.

10. Sigman, M. S.; Jacobsen, E. N., Enantioselective addition of hydrogen cyanide to imines catalyzed by a chiral (salen)Al(III) complex. *J. Am. Chem. Soc.* **1998,** *120* (21), 5315-5316.

11. Schlemminger, I.; Saida, Y.; Groger, H.; Maison, W.; Durot, N.; Sasai, H.; Shibasaki, M.; Martens, J., Concept of improved rigidity: How to make enantioselective hydrophosphonylation of cyclic imines catalyzed by chiral heterobimetallic lanthanoid complexes almost perfect. *J. Org. Chem.* **2000,** *65* (16), 4818-4825.

12. Huertas, R. E.; Corella, J. A.; Soderquist, J. A., Asymmetric oxazaborolidine-catalyzed reduction of prochiral ketones with N-tert-butyl-N-trimethylsilylamine-borane. *Tetrahedron Lett.* **2003,** *44* (24), 4435-4437.

13. Belokon, Y. N.; North, M.; Maleev, V. I.; Voskoboev, N. V.; Moskalenko, M. A.; Peregudov, A. S.; Dmitriev, A. V.; Ikonnikov, N. S.; Kagan, H. B., In situ formation of a heterobimetallic chiral (salen)Ti- IV / (salen)V-V catalyst for the asymmetric addition of TMSCN to benzaldehyde. *Angew. Chem.-Int. Edit.* **2004,** *43* (31), 4085-4089.

14. Harb, W.; Ruiz-Lopez, M. F.; Coutrot, F.; Grison, C.; Coutrot, P., A model for double asymmetric induction in the stereocontrolled reduction of glycosyl alpha-ketoesters with oxazaborolidines. *J. Am. Chem. Soc.* **2004,** *126* (22), 6996-7008.

15. Huang, X. G.; Ortiz-Marciales, M.; Huang, K.; Stepanenko, V.; Merced, F. G.; Ayala, A. M.; Correa, W.; De Jesus, M., Asymmetric synthesis of primary amines via the spiroborate-catalyzed borane reduction of oxime ethers. *Org. Lett.* **2007,** *9* (9), 1793-1795.

16. Blay, G.; Cardona, L.; Climent, E.; Pedro, J. R., Highly enantioselective zinc/binol-catalyzed alkynylation of N-sulfonyl aldimines. *Angew. Chem.-Int. Edit.* **2008,** *47* (30), 5593-5596.

17. Chen, Z. H.; Morimoto, H.; Matsunaga, S.; Shibasaki, M., A bench-stable homodinuclear Ni-2-chiff base complex for catalytic asymmetric synthesis of alpha-tetrasubstituted anti-alpha,beta-diamino acid surrogates. *J. Am. Chem. Soc.* **2008,** *130* (7), 2170-+.

18. Fu, P.; Snapper, M. L.; Hoveyda, A. H., Catalytic asymmetric alkylations of ketoimines. Enantioselective synthesis of N-Substituted quaternary carbon stereogenic centers by Zr-catalyzed additions of dialkylzinc reagents to aryl-, alkyl-, and trifluoroalkyl-substituted ketoimines. *J. Am. Chem. Soc.* **2008,** *130* (16), 5530-5541.

19. Handa, S.; Nagawa, K.; Sohtome, Y.; Matsunaga, S.; Shibasaki, M., A heterobimetallic Pd/La/Schiff base complex for anti-selective catalytic asymmetric nitroaldol reactions and applications to short syntheses of beta-adrenoceptor agonists. *Angew. Chem.-Int. Edit.* **2008,** *47* (17), 3230-3233.

20. Rauniyar, V.; Zhai, H. M.; Hall, D. G., Catalytic enantioselective allyl- and crotylboration of aldehydes using chiral diol center dot SnCl4 complexes. Optimization, substrate scope and mechanistic investigations. *J. Am. Chem. Soc.* **2008,** *130* (26), 8481-8490.

21. Yue, T.; Wang, M. X.; Wang, D. X.; Zhu, J. P., Asymmetric Synthesis of 5-(1-Hydroxyalkyl)tetrazoles by Catalytic Enantioselective Passerini-Type Reactions. *Angew. Chem.-Int. Edit.* **2008,** *47* (49), 9454-9457.

22. Zhang, X.; Huang, H. X.; Guo, X.; Guan, X. Y.; Yang, L. P.; Hu, W., Catalytic enantioselective trapping of an alcoholic oxonium ylide with aldehydes: Rh-II/Zr-IV-co-catalyzed three-component reactions of aryl diazoacetates, benzyl alcohol, and aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (35), 6647-6649.

23. Abell, J. P.; Yamamoto, H., Dual-Activation Asymmetric Strecker Reaction of Aldimines and Ketimines Catalyzed by a Tethered Bis(8-quinolinolato) Aluminum Complex. *J. Am. Chem. Soc.* **2009,** *131* (42), 15118-+.

24. Liu, X.; Henderson, J. A.; Sasaki, T.; Kishi, Y., Dramatic Improvement in Catalyst Loadings and Molar Ratios of Coupling Partners for Ni/Cr-Mediated Coupling Reactions: Heterobimetallic Catalysts. *J. Am. Chem. Soc.* **2009,** *131* (46), 16678-+.

25. Mihara, H.; Xu, Y. J.; Shepherd, N. E.; Matsunaga, S.; Shibasaki, M., A Heterobimetallic Ga/Yb-Schiff Base Complex for Catalytic Asymmetric alpha-Addition of Isocyanides to Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (24), 8384-+.

26. Sone, T.; Lu, G.; Matsunaga, S.; Shibasaki, M., Catalytic Asymmetric Synthesis of 2,2-Disubstituted Oxetanes from Ketones by Using a One-Pot Sequential Addition of Sulfur Ylide. *Angew. Chem.-Int. Edit.* **2009,** *48* (9), 1677-1680.

27. Suzuki, Y.; Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Mannich-Type Reaction of Thioamides. *Angew. Chem.-Int. Edit.* **2009,** *48* (27), 5026-5029.

28. Suyama, K.; Sakai, Y.; Matsumoto, K.; Saito, B.; Katsuki, T., Highly Enantioselective Hydrophosphonylation of Aldehydes: Base-Enhanced Aluminum-salalen Catalysis. *Angew. Chem.-Int. Edit.* **2010,** *49* (4), 797-799.

29. Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Addition of Allyl Cyanide to Ketones via Soft Lewis Acid/Hard Bronsted Base/Hard Lewis Base Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (15), 5522-5531.

30. Enders, D.; Seppelt, M., Catalytic Enantioselective Synthesis of 3-Substituted Benzosultams via Corey-Bakshi-Shibata Reduction of Cyclic N-Sulfonylimines. *Synlett* **2011,** (3), 402-404.

31. Trost, B. M.; Quintard, A., Asymmetric Catalytic Alkynylation of Acetaldehyde: Application to the Synthesis of (+)-Tetrahydropyrenophorol. *Angew. Chem.-Int. Edit.* **2012,** *51* (27), 6704-6708.

32. Cook, A. M.; Wolf, C., Efficient Access to Multifunctional Trifluoromethyl Alcohols through Base-Free Catalytic Asymmetric C-C Bond Formation with Terminal Ynamides. *Angew. Chem.-Int. Edit.* **2016,** *55* (8), 2925-2929.

33. Hatano, M.; Yamakawa, K.; Kawai, T.; Horibe, T.; Ishihara, K., Enantioselective Cyanosilylation of Ketones with Lithium(I) Dicyanotrimethylsilicate(IV) Catalyzed by a Chiral Lithium(I) Phosphoryl Phenoxide. *Angew. Chem.-Int. Edit.* **2016,** *55* (12), 4021-4025.

34. Trost, B. M.; Gnanamani, E.; Hung, C. I., Controlling Regioselectivity in the Enantioselective N-Alkylation of Indole Analogues Catalyzed by Dinuclear Zinc-ProPhenol. *Angew. Chem.-Int. Edit.* **2017,** *56* (35), 10451-10456.

35. Trost, B. M.; Saget, T.; Hung, C. I., Efficient Access to Chiral Trisubstituted Aziridines via Catalytic Enantioselective Aza-Darzens Reactions. *Angew. Chem.-Int. Edit.* **2017,** *56* (9), 2440-2444.

36. Zavesky, B. P.; Johnson, J. S., Direct Zinc(II)-Catalyzed Enantioconvergent Additions of Terminal Alkynes to alpha-Keto Esters. *Angew. Chem.-Int. Edit.* **2017,** *56* (30), 8805-8808.

37. Xiong, Y.; Zhang, G. Z., Enantioselective 1,2-Difunctionalization of 1,3-Butadiene by Sequential Alkylation and Carbonyl Allylation. *J. Am. Chem. Soc.* **2018,** *140* (8), 2735-2738.

38. Zhang, Q. L.; Yu, H. M.; Shen, L. L.; Tang, T. H.; Dong, D. F.; Chai, W. W.; Zi, W. W., Stereodivergent Coupling of 1,3-Dienes with Aldimine Esters Enabled by Synergistic Pd and Cu Catalysis. *J. Am. Chem. Soc.* **2019,** *141* (37), 14554-14559.

4.4.2 Addition to Carbonyl and Imines: Alkyl

1. Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R., CATALYTIC ASYMMETRIC INDUCTION - HIGHLY ENANTIOSELECTIVE ADDITION OF DIALKYLZINCS TO ALDEHYDES. *J. Am. Chem. Soc.* **1986,** *108* (19), 6071-6072.

2. Noyori, R.; Kitamura, M., ENANTIOSELECTIVE ADDITION OF ORGANOMETALLIC REAGENTS TO CARBONYL-COMPOUNDS - CHIRALITY TRANSFER, MULTIPLICATION, AND AMPLIFICATION. *Angew. Chem.-Int. Edit. Engl.* **1991,** *30* (1), 49-69.

3. Schmidt, B.; Seebach, D., 2,2-DIMETHYL-ALPHA,ALPHA,ALPHA'ALPHA'-TETRAKIS(BETA-NAPHTHYL)-1,3-DIOXOL AN-4,5-DIMETHANOL(DINOL) FOR THE TITANATE-MEDIATED ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ALDEHYDES. *Angew. Chem.-Int. Edit. Engl.* **1991,** *30* (10), 1321-1323.

4. Schmidt, B.; Seebach, D., CATALYTIC AND STOICHIOMETRIC ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ALDEHYDES USING A NOVEL CHIRAL SPIROTITANATE. *Angew. Chem.-Int. Edit. Engl.* **1991,** *30* (1), 99-101.

5. Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W., ON THE MECHANISMS OF ENANTIOSELECTIVE REACTIONS USING ALPHA,ALPHA,ALPHA',ALPHA'-TETRAARYL-1,3-DIOXOLANE-4,5-DIMETHANOL(TADDOL) -DERIVED TITANATES - DIFFERENCES BETWEEN C2-SYMMETRICAL AND C1-SYMMETRICAL TADDOLS FACTS, IMPLICATIONS AND GENERALIZATIONS. *Helv. Chim. Acta* **1992,** *75* (7), 2171-2209.

6. Soai, K.; Niwa, S., ENANTIOSELECTIVE ADDITION OF ORGANOZINC REAGENTS TO ALDEHYDES. *Chem. Rev.* **1992,** *92* (5), 833-856.

7. Corey, E. J.; Cimprich, K. A., HIGHLY ENANTIOSELECTIVE ALKYNYLATION OF ALDEHYDES PROMOTED BY CHIRAL OXAZABOROLIDINES. *J. Am. Chem. Soc.* **1994,** *116* (7), 3151-3152.

8. Ito, Y. N.; Ariza, X.; Beck, A. K.; Bohac, A.; Ganter, C.; Gawley, R. E.; Kuhnle, F. N. M.; Tuleja, J.; Wang, Y. M.; Seebach, D., PREPARATION AND STRUCTURAL-ANALYSIS OF SEVERAL NEW ALPHA,ALPHA,ALPHA',ALPHA'-TETRAARYL-1,3-DIOXOLANE-4,5-DIMETHANOLS (TADDOLS) AND TADDOL ANALOGS, THEIR EVALUATION AS TITANIUM LIGANDS IN THE ENANTIOSELECTIVE ADDITION OF METHYLTITANIUM AND DIETHYLZINC REAGENTS TO BENZALDEHYDE, AND REFINEMENT OF THE MECHANISTIC HYPOTHESIS. *Helv. Chim. Acta* **1994,** *77* (8), 2071-2110.

9. Dosa, P. I.; Fu, G. C., Catalytic asymmetric addition of ZnPh2 to ketones: Enantioselective formation of quaternary stereocenters. *J. Am. Chem. Soc.* **1998,** *120* (2), 445-446.

10. Guijarro, D.; Pinho, P.; Andersson, P. G., Enantioselective addition of dialkylzinc reagents to N- (diphenylphosphinoyl) imines promoted by 2- azanorbornylmethanols. *J. Org. Chem.* **1998,** *63* (8), 2530-2535.

11. Kitamura, M.; Suga, S.; Oka, H.; Noyori, R., Quantitative analysis of the chiral amplification in the amino alcohol-promoted asymmetric alkylation of aldehydes with dialkylzincs. *J. Am. Chem. Soc.* **1998,** *120* (38), 9800-9809.

12. Frantz, D. E.; Fassler, R.; Carreira, E. M., Facile enantioselective synthesis of propargylic alcohols by direct addition of terminal alkynes to aldehydes. *J. Am. Chem. Soc.* **2000,** *122* (8), 1806-1807.

13. Anand, N. K.; Carreira, E. M., A simple, mild, catalytic, enantioselective addition of terminal acetylenes to aldehydes. *J. Am. Chem. Soc.* **2001,** *123* (39), 9687-9688.

14. Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L., Enantioselective synthesis of arylamines through Zr-catalyzed addition of dialkylzincs to imines. Reaction development by screening of parallel libraries. *J. Am. Chem. Soc.* **2001,** *123* (5), 984-985.

15. Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L., Three-component catalytic asymmetric synthesis of aliphatic amines. *J. Am. Chem. Soc.* **2001,** *123* (42), 10409-10410.

16. Sato, I.; Kodaka, R.; Soai, K., Asymmetric synthesis of N-diphenylphosphinoylamines by solvent- free enantioselective addition of dialkylzincs to N- diphenylphosphinoylimines. *J. Chem. Soc.-Perkin Trans. 1* **2001,** (22), 2912-2914.

17. Seebach, D.; Beck, A. K.; Heckel, A., TADDOLs, their derivatives, and TADDOL analogues: Versatile chiral auxiliaries. *Angew. Chem.-Int. Edit.* **2001,** *40* (1), 92-138.

18. Balsells, J.; Davis, T. J.; Carroll, P.; Walsh, P. J., Insight into the mechanism of the asymmetric addition of alkyl groups to aldehydes catalyzed by titanium - BINOLate species. *J. Am. Chem. Soc.* **2002,** *124* (35), 10336-10348.

19. Bolm, C.; Rudolph, J., Catalyzed asymmetric aryl transfer reactions to aldehydes with boronic acids as aryl source. *J. Am. Chem. Soc.* **2002,** *124* (50), 14850-14851.

20. Boyall, D.; Frantz, D. E.; Carreira, E. M., Efficient enantioselective additions of terminal alkynes and aldehydes under operationally convenient conditions. *Org. Lett.* **2002,** *4* (15), 2605-2606.

21. Buono, F.; Walsh, P. J.; Blackmond, D. G., Rationalization of anomalous nonlinear effects in the alkylation of substituted benzaldehydes. *J. Am. Chem. Soc.* **2002,** *124* (46), 13652-13653.

22. Chen, Y. K.; Lurain, A. E.; Walsh, P. J., A general, highly enantioselective method for the synthesis of D and L alpha-amino acids and allylic amines. *J. Am. Chem. Soc.* **2002,** *124* (41), 12225-12231.

23. Dahmen, S.; Brase, S., The asymmetric dialkylzinc addition to imines catalyzed by 2.2 paracyclophane-based N,O-ligands. *J. Am. Chem. Soc.* **2002,** *124* (21), 5940-5941.

24. DiMauro, E. F.; Kozlowski, M. C., Development of bifunctional salen catalysts: Rapid, chemoselective alkylations of alpha-ketoesters. *J. Am. Chem. Soc.* **2002,** *124* (43), 12668-12669.

25. DiMauro, E. F.; Kozlowski, M. C., The first catalytic asymmetric addition of dialkylzincs to alpha-ketoesters. *Org. Lett.* **2002,** *4* (22), 3781-3784.

26. Gao, G.; Moore, D.; Xie, R. G.; Pu, L., Highly enantioselective phenylacetylene additions to both aliphatic and aromatic aldehydes. *Org. Lett.* **2002,** *4* (23), 4143-4146.

27. Garcia, C.; LaRochelle, L. K.; Walsh, P. J., A practical catalytic asymmetric addition of alkyl groups to ketones. *J. Am. Chem. Soc.* **2002,** *124* (37), 10970-10971.

28. Hermanns, N.; Dahmen, S.; Bolm, C.; Brase, S., Asymmetric, catalytic phenyl transfer to imines: Highly enantioselective synthesis of diarylmethylamines. *Angew. Chem.-Int. Edit.* **2002,** *41* (19), 3692-3694.

29. Li, X. S.; Lu, G.; Kwok, W. H.; Chan, A. S. C., Highly enantioselective alkynylzinc addition to aromatic aldehydes catalyzed by self-assembled titanium catalysts. *J. Am. Chem. Soc.* **2002,** *124* (43), 12636-12637.

30. Moore, D.; Pu, L., BINOL-catalyzed highly enantioselective terminal alkyne additions to aromatic aldehydes. *Org. Lett.* **2002,** *4* (11), 1855-1857.

31. Zhang, H. L.; Zhang, X. M.; Gong, L. Z.; Mi, A. Q.; Cui, X.; Jiang, Y. Z.; Choi, M. C. K.; Chan, A. S. C., Highly enantioselective diethylzinc addition to imines employing readily available N-monosubstituted amino alcohols. *Org. Lett.* **2002,** *4* (8), 1399-1402.

32. Akullian, L. C.; Snapper, M. L.; Hoveyda, A. H., Three-component enantioselective synthesis of propargylamines through Zr-catalyzed additions of alkyl zinc reagents to alkynylimines. *Angew. Chem.-Int. Edit.* **2003,** *42* (35), 4244-4247.

33. Garcia, C.; Walsh, P. J., Highly enantioselective catalytic phenylation of ketones with a constrained geometry titanium catalyst. *Org. Lett.* **2003,** *5* (20), 3641-3644.

34. Lurain, A. E.; Walsh, P. J., A catalytic asymmetric method for the synthesis of gamma- unsaturated beta-amino acid derivatives. *J. Am. Chem. Soc.* **2003,** *125* (35), 10677-10683.

35. Rasmussen, T.; Norrby, P. O., Modeling the stereoselectivity of the beta-amino alcohol-promoted addition of dialkylzinc to aldehydes. *J. Am. Chem. Soc.* **2003,** *125* (17), 5130-5138.

36. Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L., Enantioselective synthesis of propargylamines through Zr- catalyzed addition of mixed alkynylzinc reagents to arylimines. *Org. Lett.* **2003,** *5* (18), 3273-3275.

37. Xu, Z. Q.; Wang, R.; Xu, J. K.; Da, C. S.; Yan, W. J.; Chen, C., Highly enantioselective addition of phenylacetylene to aldehydes catalyzed by a beta-sulfonamide alcohol-titanium complex. *Angew. Chem.-Int. Edit.* **2003,** *42* (46), 5747-5749.

38. Dahmen, S., Enantioselective alkynylation of aldehydes catalyzed by 2.2 paracyclophane-based ligands. *Org. Lett.* **2004,** *6* (13), 2113-2116.

39. Inoue, M.; Nakada, M., Studies on catalytic asymmetric Nozaki-Hiyama propargylation. *Org. Lett.* **2004,** *6* (17), 2977-2980.

40. Li, H. M.; Walsh, P. J., Catalytic asymmetric vinylation of ketones. *J. Am. Chem. Soc.* **2004,** *126* (21), 6538-6539.

41. Jeon, S. J.; Li, H. M.; Garcia, C.; LaRochelle, L. K.; Walsh, P. J., Catalytic asymmetric addition of alkylzinc and functionalized alkylzinc reagents to ketones. *J. Org. Chem.* **2005,** *70* (2), 448-455.

42. Jeon, S. J.; Li, H. M.; Walsh, P. J., A green chemistry approach to a more efficient asymmetric catalyst: Solvent-free and highly concentrated alkyl additions to ketones. *J. Am. Chem. Soc.* **2005,** *127* (47), 16416-16425.

43. Ji, J. X.; Wu, J.; Au-Yeung, T. T. L.; Yip, C. W.; Haynes, R. K.; Chan, A. S. C., Highly enantioselective phenyl transfer to aryl aldehydes catalyzed by easily accessible chiral tertiary aminonaphthol. *J. Org. Chem.* **2005,** *70* (3), 1093-1095.

44. Li, H. M.; Walsh, P. J., Catalytic asymmetric vinylation and dienylation of ketones. *J. Am. Chem. Soc.* **2005,** *127* (23), 8355-8361.

45. Takita, R.; Yakura, K.; Ohshima, T.; Shibasaki, M., Asymmetric alkynylation of aldehydes catalyzed by an In(III)/BINOL complex. *J. Am. Chem. Soc.* **2005,** *127* (40), 13760-13761.

46. Wieland, L. C.; Deng, H. B.; Snapper, M. L.; Hoveyda, A. H., Al-catalyzed enantioselective alkylation of alpha-ketoesters by dialkylzinc reagents. Enhancement of enantioselectivity and reactivity by an achiral Lewis base additive. *J. Am. Chem. Soc.* **2005,** *127* (44), 15453-15456.

47. Yamashita, M.; Yamada, K.; Tomioka, K., Chiral amino alcohol-mediated asymmetric conjugate addition of arylalkynes to nitroolefins. *Org. Lett.* **2005,** *7* (12), 2369-2371.

48. Cozzi, P. G.; Kotrusz, P., Highly enantioselective addition of Me2Zn to aldehydes catalyzed by ClCr(Salen). *J. Am. Chem. Soc.* **2006,** *128* (15), 4940-4941.

49. Kim, J. G.; Walsh, P. J., From aryl bromides to enantioenriched benzylic alcohols in a single flask: Catalytic asymmetric arylation of aldehydes. *Angew. Chem.-Int. Edit.* **2006,** *45* (25), 4175-4178.

50. Palomo, C.; Oiarbide, M.; Halder, R.; Laso, A.; Lopez, R., Enantioselective aza-Henry reactions assisted by Zn-II and N-methylephedrine. *Angew. Chem.-Int. Edit.* **2006,** *45* (1), 117-120.

51. Trost, B. M.; Weiss, A. H.; von Wangelin, A. J., Dinuclear Zn-catalyzed asymmetric alkynylation of unsaturated aldehydes. *J. Am. Chem. Soc.* **2006,** *128* (1), 8-9.

52. Chen, C. A.; Wu, K. H.; Gau, H. M., Highly enantioselective aryl additions of [AlAr3(thf)] to ketones catalyzed by a Titanium(IV) catalyst of (S)-Binol. *Angew. Chem.-Int. Edit.* **2007,** *46* (28), 5373-5376.

53. Oisaki, K.; Zhao, D. B.; Kanai, M.; Shibasaki, M., Catalytic enantioselective alkylative aldol reaction: Efficient multicomponent assembly of dialkylzincs, allenic esters, and ketones toward highly functionalized delta-lactones with tetrasubstituted chiral centers. *J. Am. Chem. Soc.* **2007,** *129* (23), 7439-7443.

54. Salvi, L.; Jeon, S. J.; Fisher, E. L.; Carroll, P. J.; Walsh, P. J., Catalytic asymmetric generation of (Z)-disubstituted allylic alcohols. *J. Am. Chem. Soc.* **2007,** *129* (51), 16119-16125.

55. Muramatsu, Y.; Harada, T., Catalytic asymmetric alkylation of aldehydes with Grignard reagents. *Angew. Chem.-Int. Edit.* **2008,** *47* (6), 1088-1090.

56. Da, C. S.; Wang, J. R.; Yin, X. G.; Fan, X. Y.; Liu, Y.; Yu, S. L., Highly Catalytic Asymmetric Addition of Deactivated Alkyl Grignard Reagents to Aldehydes. *Org. Lett.* **2009,** *11* (24), 5578-5581.

57. Salvi, L.; Kim, J. G.; Walsh, P. J., Practical Catalytic Asymmetric Synthesis of Diaryl-, Aryl Heteroaryl-, and Diheteroarylmethanols. *J. Am. Chem. Soc.* **2009,** *131* (34), 12483-12493.

58. Endo, K.; Ogawa, M.; Shibata, T., Multinuclear Catalyst for Copper-Catalyzed Asymmetric Conjugate Addition of Organozinc Reagents. *Angew. Chem.-Int. Edit.* **2010,** *49* (13), 2410-2413.

59. Kim, H. Y.; Salvi, L.; Carroll, P. J.; Walsh, P. J., One-Pot Catalytic Enantio- and Diastereoselective Syntheses of anti-, syn-cis-Disubstituted, and syn-Vinyl Cyclopropyl Alcohols. *J. Am. Chem. Soc.* **2010,** *132* (1), 402-412.

60. Trost, B. M.; Chan, V. S.; Yamamoto, D., Enantioselective ProPhenol-Catalyzed Addition of 1,3-Diynes to Aldehydes to Generate Synthetically Versatile Building Blocks and Diyne Natural Products. *J. Am. Chem. Soc.* **2010,** *132* (14), 5186-5192.

61. Chinkov, N.; Warm, A.; Carreira, E. M., Asymmetric Autocatalysis Enables an Improved Synthesis of Efavirenz. *Angew. Chem.-Int. Edit.* **2011,** *50* (13), 2957-2961.

62. DeBerardinis, A. M.; Turlington, M.; Pu, L., Activation of Vinyl Iodides for the Highly Enantioselective Addition to Aldehydes. *Angew. Chem.-Int. Edit.* **2011,** *50* (10), 2368-2370.

4.4.3 Addition to Carbonyl and Imines: other

1. Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C. P.; Singh, V. K., A STABLE AND EASILY PREPARED CATALYST FOR THE ENANTIOSELECTIVE REDUCTION OF KETONES - APPLICATIONS TO MULTISTEP SYNTHESES. *J. Am. Chem. Soc.* **1987,** *109* (25), 7925-7926.

2. Corey, E. J.; Cheng, X. M.; Cimprich, K. A.; Sarshar, S., REMARKABLY EFFECTIVE AND SIMPLE SYNTHESES OF ENANTIOMERICALLY PURE SECONDARY CARBINOLS FROM ACHIRAL KETONES. *Tetrahedron Lett.* **1991,** *32* (47), 6835-6838.

3. Corey, E. J.; Azimioara, M.; Sarshar, S., X-RAY CRYSTAL-STRUCTURE OF A CHIRAL OXAZABOROLIDINE CATALYST FOR ENANTIOSELECTIVE CARBONYL REDUCTION. *Tetrahedron Lett.* **1992,** *33* (24), 3429-3430.

4. Corey, E. J.; Link, J. O.; Bakshi, R. K., A MECHANISTIC AND STRUCTURAL-ANALYSIS OF THE BASIS FOR HIGH ENANTIOSELECTIVITY IN THE OXAZABOROLIDINE-CATALYZED REDUCTION OF TRIHALOMETHYL KETONES BY CATECHOLBORANE. *Tetrahedron Lett.* **1992,** *33* (47), 7107-7110.

5. Corey, E. J.; Helal, C. J., NOVEL ELECTRONIC EFFECTS OF REMOTE SUBSTITUENTS ON THE OXAZABOROLIDINE-CATALYZED ENANTIOSELECTIVE REDUCTION OF KETONES. *Tetrahedron Lett.* **1995,** *36* (50), 9153-9156.

6. Sasai, H.; Arai, S.; Tahara, Y.; Shibasaki, M., Catalytic Asymmetric-Synthesis of Alpha-Amino Phosphonates Using Lanthanoid-Potassium-Binol Complexes. *J. Org. Chem.* **1995,** *60* (21), 6656-6657.

7. Bach, J.; Berenguer, R.; Garcia, J.; Loscertales, T.; Vilarrasa, J., Highly enantioenriched propargylic alcohols by oxazaborolidine-mediated reduction of acetylenic ketones. *J. Org. Chem.* **1996,** *61* (25), 9021-9025.

8. Sigman, M. S.; Jacobsen, E. N., Enantioselective addition of hydrogen cyanide to imines catalyzed by a chiral (salen)Al(III) complex. *J. Am. Chem. Soc.* **1998,** *120* (21), 5315-5316.

9. Corey, E. J.; Helal, C. J., Aminoacrylic compounds. Part 31 - Reduction of carbonyl compounds with chiral oxazaborolidine catalysts: A new paradigm for enantioselective catalysis and a powerful new synthetic method. *Angew. Chem.-Int. Edit.* **1998,** *37* (15), 1987-2012.

10. Groger, H.; Saida, Y.; Sasai, H.; Yamaguchi, K.; Martens, J.; Shibasaki, M., A new and highly efficient asymmetric route to cyclic alpha- amino phosphonates: The first catalytic enantioselective hydrophosphonylation of cyclic imines catalyzed by chiral heterobimetallic lanthanoid complexes. *J. Am. Chem. Soc.* **1998,** *120* (13), 3089-3103.

11. Schlemminger, I.; Saida, Y.; Groger, H.; Maison, W.; Durot, N.; Sasai, H.; Shibasaki, M.; Martens, J., Concept of improved rigidity: How to make enantioselective hydrophosphonylation of cyclic imines catalyzed by chiral heterobimetallic lanthanoid complexes almost perfect. *J. Org. Chem.* **2000,** *65* (16), 4818-4825.

12. Huertas, R. E.; Corella, J. A.; Soderquist, J. A., Asymmetric oxazaborolidine-catalyzed reduction of prochiral ketones with N-tert-butyl-N-trimethylsilylamine-borane. *Tetrahedron Lett.* **2003,** *44* (24), 4435-4437.

13. Harb, W.; Ruiz-Lopez, M. F.; Coutrot, F.; Grison, C.; Coutrot, P., A model for double asymmetric induction in the stereocontrolled reduction of glycosyl alpha-ketoesters with oxazaborolidines. *J. Am. Chem. Soc.* **2004,** *126* (22), 6996-7008.

14. Belokon, Y. N.; North, M.; Maleev, V. I.; Voskoboev, N. V.; Moskalenko, M. A.; Peregudov, A. S.; Dmitriev, A. V.; Ikonnikov, N. S.; Kagan, H. B., In situ formation of a heterobimetallic chiral (salen)Ti- IV / (salen)V-V catalyst for the asymmetric addition of TMSCN to benzaldehyde. *Angew. Chem.-Int. Edit.* **2004,** *43* (31), 4085-4089.

15. Huang, X. G.; Ortiz-Marciales, M.; Huang, K.; Stepanenko, V.; Merced, F. G.; Ayala, A. M.; Correa, W.; De Jesus, M., Asymmetric synthesis of primary amines via the spiroborate-catalyzed borane reduction of oxime ethers. *Org. Lett.* **2007,** *9* (9), 1793-1795.

16. Chen, Z. H.; Morimoto, H.; Matsunaga, S.; Shibasaki, M., A bench-stable homodinuclear Ni-2-chiff base complex for catalytic asymmetric synthesis of alpha-tetrasubstituted anti-alpha,beta-diamino acid surrogates. *J. Am. Chem. Soc.* **2008,** *130* (7), 2170-+.

17. Handa, S.; Nagawa, K.; Sohtome, Y.; Matsunaga, S.; Shibasaki, M., A heterobimetallic Pd/La/Schiff base complex for anti-selective catalytic asymmetric nitroaldol reactions and applications to short syntheses of beta-adrenoceptor agonists. *Angew. Chem.-Int. Edit.* **2008,** *47* (17), 3230-3233.

18. Rauniyar, V.; Zhai, H. M.; Hall, D. G., Catalytic enantioselective allyl- and crotylboration of aldehydes using chiral diol center dot SnCl4 complexes. Optimization, substrate scope and mechanistic investigations. *J. Am. Chem. Soc.* **2008,** *130* (26), 8481-8490.

19. Blay, G.; Cardona, L.; Climent, E.; Pedro, J. R., Highly enantioselective zinc/binol-catalyzed alkynylation of N-sulfonyl aldimines. *Angew. Chem.-Int. Edit.* **2008,** *47* (30), 5593-5596.

20. Zhang, X.; Huang, H. X.; Guo, X.; Guan, X. Y.; Yang, L. P.; Hu, W., Catalytic enantioselective trapping of an alcoholic oxonium ylide with aldehydes: Rh-II/Zr-IV-co-catalyzed three-component reactions of aryl diazoacetates, benzyl alcohol, and aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (35), 6647-6649.

21. Yue, T.; Wang, M. X.; Wang, D. X.; Zhu, J. P., Asymmetric Synthesis of 5-(1-Hydroxyalkyl)tetrazoles by Catalytic Enantioselective Passerini-Type Reactions. *Angew. Chem.-Int. Edit.* **2008,** *47* (49), 9454-9457.

22. Fu, P.; Snapper, M. L.; Hoveyda, A. H., Catalytic asymmetric alkylations of ketoimines. Enantioselective synthesis of N-Substituted quaternary carbon stereogenic centers by Zr-catalyzed additions of dialkylzinc reagents to aryl-, alkyl-, and trifluoroalkyl-substituted ketoimines. *J. Am. Chem. Soc.* **2008,** *130* (16), 5530-5541.

23. Sone, T.; Lu, G.; Matsunaga, S.; Shibasaki, M., Catalytic Asymmetric Synthesis of 2,2-Disubstituted Oxetanes from Ketones by Using a One-Pot Sequential Addition of Sulfur Ylide. *Angew. Chem.-Int. Edit.* **2009,** *48* (9), 1677-1680.

24. Suzuki, Y.; Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Mannich-Type Reaction of Thioamides. *Angew. Chem.-Int. Edit.* **2009,** *48* (27), 5026-5029.

25. Mihara, H.; Xu, Y. J.; Shepherd, N. E.; Matsunaga, S.; Shibasaki, M., A Heterobimetallic Ga/Yb-Schiff Base Complex for Catalytic Asymmetric alpha-Addition of Isocyanides to Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (24), 8384-+.

26. Abell, J. P.; Yamamoto, H., Dual-Activation Asymmetric Strecker Reaction of Aldimines and Ketimines Catalyzed by a Tethered Bis(8-quinolinolato) Aluminum Complex. *J. Am. Chem. Soc.* **2009,** *131* (42), 15118-+.

27. Liu, X.; Henderson, J. A.; Sasaki, T.; Kishi, Y., Dramatic Improvement in Catalyst Loadings and Molar Ratios of Coupling Partners for Ni/Cr-Mediated Coupling Reactions: Heterobimetallic Catalysts. *J. Am. Chem. Soc.* **2009,** *131* (46), 16678-+.

28. Suyama, K.; Sakai, Y.; Matsumoto, K.; Saito, B.; Katsuki, T., Highly Enantioselective Hydrophosphonylation of Aldehydes: Base-Enhanced Aluminum-salalen Catalysis. *Angew. Chem.-Int. Edit.* **2010,** *49* (4), 797-799.

29. Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Addition of Allyl Cyanide to Ketones via Soft Lewis Acid/Hard Bronsted Base/Hard Lewis Base Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (15), 5522-5531.

30. Enders, D.; Seppelt, M., Catalytic Enantioselective Synthesis of 3-Substituted Benzosultams via Corey-Bakshi-Shibata Reduction of Cyclic N-Sulfonylimines. *Synlett* **2011,** (3), 402-404.

31. Trost, B. M.; Quintard, A., Asymmetric Catalytic Alkynylation of Acetaldehyde: Application to the Synthesis of (+)-Tetrahydropyrenophorol. *Angew. Chem.-Int. Edit.* **2012,** *51* (27), 6704-6708.

32. Cook, A. M.; Wolf, C., Efficient Access to Multifunctional Trifluoromethyl Alcohols through Base-Free Catalytic Asymmetric C-C Bond Formation with Terminal Ynamides. *Angew. Chem.-Int. Edit.* **2016,** *55* (8), 2925-2929.

33. Hatano, M.; Yamakawa, K.; Kawai, T.; Horibe, T.; Ishihara, K., Enantioselective Cyanosilylation of Ketones with Lithium(I) Dicyanotrimethylsilicate(IV) Catalyzed by a Chiral Lithium(I) Phosphoryl Phenoxide. *Angew. Chem.-Int. Edit.* **2016,** *55* (12), 4021-4025.

34. Trost, B. M.; Saget, T.; Hung, C. I., Efficient Access to Chiral Trisubstituted Aziridines via Catalytic Enantioselective Aza-Darzens Reactions. *Angew. Chem.-Int. Edit.* **2017,** *56* (9), 2440-2444.

35. Zavesky, B. P.; Johnson, J. S., Direct Zinc(II)-Catalyzed Enantioconvergent Additions of Terminal Alkynes to alpha-Keto Esters. *Angew. Chem.-Int. Edit.* **2017,** *56* (30), 8805-8808.

36. Trost, B. M.; Gnanamani, E.; Hung, C. I., Controlling Regioselectivity in the Enantioselective N-Alkylation of Indole Analogues Catalyzed by Dinuclear Zinc-ProPhenol. *Angew. Chem.-Int. Edit.* **2017,** *56* (35), 10451-10456.

37. Xiong, Y.; Zhang, G. Z., Enantioselective 1,2-Difunctionalization of 1,3-Butadiene by Sequential Alkylation and Carbonyl Allylation. *J. Am. Chem. Soc.* **2018,** *140* (8), 2735-2738.

38. Zhang, Q. L.; Yu, H. M.; Shen, L. L.; Tang, T. H.; Dong, D. F.; Chai, W. W.; Zi, W. W., Stereodivergent Coupling of 1,3-Dienes with Aldimine Esters Enabled by Synergistic Pd and Cu Catalysis. *J. Am. Chem. Soc.* **2019,** *141* (37), 14554-14559.

39. Chan, J. Z.; Yesilcimen, A.; Cao, M.; Zhang, Y.; Zhang, B.; Wasa, M., Direct Conversion of N-Alkylamines to N-Propargylamines through C–H Activation Promoted by Lewis Acid/Organocopper Catalysis: Application to Late-Stage Functionalization of Bioactive Molecules. *J. Am. Chem. Soc.* **2020,** *142* (38), 16493-16505.

40. Xu, P.; Huang, Z., Catalytic reductive desymmetrization of malonic esters. *Nature Chemistry* **2021,** *13* (7), 634-642.

41. Li, Z.; Zhao, F.; Ou, W.; Huang, P.-Q.; Wang, X., Asymmetric Deoxygenative Alkynylation of Tertiary Amides Enabled by Iridium/Copper Bimetallic Relay Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (51), 26604-26609.

42. Xu, P.; Liu, S.; Huang, Z., Desymmetric Partial Reduction of Malonic Esters. *J. Am. Chem. Soc.* **2022,** *144* (15), 6918-6927.

43. Calogero, F.; Magagnano, G.; Potenti, S.; Pasca, F.; Fermi, A.; Gualandi, A.; Ceroni, P.; Bergamini, G.; Cozzi, P. G., Diastereoselective and enantioselective photoredox pinacol coupling promoted by titanium complexes with a red-absorbing organic dye. *Chemical Science* **2022,** *13* (20), 5973-5981.

44. Liu, Y.; Chen, H.; Wang, X., Synergistic Homogeneous Asymmetric Cu Catalysis with Pd Nanoparticle Catalysis in Stereoselective Coupling of Alkynes with Aldimine Esters. *J. Am. Chem. Soc.* **2024,** *146* (41), 28427-28436.

4.4.4 Conjugate Addition

1. Manickam, G.; Sundararajan, G., New C-2-symmetric heterobimetallic complex as a promoter for asymmetric Michael addition reactions. *Tetrahedron: Asymmetry* **1997,** *8* (13), 2271-2278.

2. Myers, J. K.; Jacobsen, E. N., Asymmetric synthesis of beta-amino acid derivatives via catalytic conjugate addition of hydrazoic acid to unsaturated imides. *J. Am. Chem. Soc.* **1999,** *121* (38), 8959-8960.

3. Manickam, G.; Sundararajan, G., Lithium bis (1R,5R)-3-aza-3-benzyl-1,5-diphenylpentan-1,5- diolato -aluminium - A new heterobimetallic catalyst for Michael addition reactions. *Tetrahedron* **1999,** *55* (9), 2721-2736.

4. Kim, Y. S.; Matsunaga, S.; Das, J.; Sekine, A.; Ohshima, T.; Shibasaki, M., Stable, storable, and reusable asymmetric catalyst: A novel La-linked-BINOL complex for the catalytic asymmetric Michael reaction. *J. Am. Chem. Soc.* **2000,** *122* (27), 6506-6507.

5. Prabagaran, N.; Sundararajan, G., Asymmetric Michael addition reactions using a chiral La-Na aminodiolate catalyst. *Tetrahedron: Asymmetry* **2002,** *13* (10), 1053-1058.

6. Harada, S.; Kumagai, N.; Kinoshita, T.; Matsunaga, S.; Shibasaki, M., Direct catalytic asymmetric Michael reaction of hydroxyketones: Asymmetric Zn catalysis with a Et2Zn/linked-BINOL complex. *J. Am. Chem. Soc.* **2003,** *125* (9), 2582-2590.

7. Majima, K.; Takita, R.; Okada, A.; Ohshima, T.; Shibasaki, M., Catalytic asymmetric Michael reaction of beta-keto esters: Effects of the linker heteroatom in linked-BINOL. *J. Am. Chem. Soc.* **2003,** *125* (51), 15837-15845.

8. Yamagiwa, N.; Matsunaga, S.; Shibasaki, M., Heterobimetallic catalysis in asymmetric 1,4-addition of O- alkylhydroxylamine to enones. *J. Am. Chem. Soc.* **2003,** *125* (52), 16178-16179.

9. Yamagiwa, N.; Matsunaga, S.; Shibasaki, M., Mechanistic studies of a reaction promoted by the YLi3{triS(binaphthoxide)} complex: Are three 1,1 '-Bi-2- naphthol units in a rare-earth-alkali-metal heterobimetallic complex necessary? *Angew. Chem.-Int. Edit.* **2004,** *43* (34), 4493-4497.

10. Sammis, G. M.; Danjo, H.; Jacobsen, E. N., Cooperative dual catalysis: Application to the highly enantioselective conjugate cyanation of unsaturated imides. *J. Am. Chem. Soc.* **2004,** *126* (32), 9928-9929.

11. Matsunaga, S.; Kinoshita, T.; Okada, S.; Harada, S.; Shibasaki, M., Catalytic asymmetric 1,4-addition reactions using alpha,beta-unsaturated N-acylpyrroles as highly reactive monodentate alpha,beta-unsaturated ester surrogates. *J. Am. Chem. Soc.* **2004,** *126* (24), 7559-7570.

12. Mita, T.; Sasaki, K.; Kanai, M.; Shibasaki, M., Catalytic enantioselective conjugate addition of cyanide to alpha,beta-unsaturated N-acylpyrroles. *J. Am. Chem. Soc.* **2005,** *127* (2), 514-515.

13. Yamagiwa, N.; Qin, H. B.; Matsunaga, S.; Shibasaki, M., Lewis acid-Lewis acid heterobimetallic cooperative catalysis: Mechanistic studies and application in enantioselective aza-Michael reaction. *J. Am. Chem. Soc.* **2005,** *127* (38), 13419-13427.

14. Lu, S. F.; Du, D. M.; Xu, J. X.; Zhang, S. W., Asymmetric Michael addition of nitroalkanes to nitroalkenes catalyzed by C-2-symmetric tridentate bis(oxazoline) and bis(thiazoline) zinc complexes. *J. Am. Chem. Soc.* **2006,** *128* (23), 7418-7419.

15. Trost, B. M.; Hisaindee, S., A heterodinuclear asymmetric catalyst for conjugate additions of alpha-hydroxyketones beta-substituted nitroalkenes. *Org. Lett.* **2006,** *8* (26), 6003-6005.

16. Trost, B. M.; Muller, C., Asymmetric Friedel-Crafts alkylation of pyrroles with nitroalkenes using a dinuclear zinc catalyst. *J. Am. Chem. Soc.* **2008,** *130* (8), 2438-2439.

17. Tanaka, Y.; Kanai, M.; Shibasaki, M., A catalytic enantioselective conjugate addition of cyanide to enones. *J. Am. Chem. Soc.* **2008,** *130* (19), 6072-+.

18. Jautze, S.; Peters, R. In *Enantioselective Bimetallic Catalysis of Michael Additions Forming Quaternary Stereocenters*, International Sympsium on Creation and Control of Advanced Selective Catalysis, Kyoto, JAPAN, 2008; Kyoto, JAPAN, 2008; pp 9284-9288.

19. Chen, Z.; Furutachi, M.; Kato, Y.; Matsunaga, S.; Shibasaki, M., A Stable Homodinuclear Biscobalt(III)-Schiff Base Complex for Catalytic Asymmetric 1,4-Addition Reactions of beta-Keto Esters to Alkynones. *Angew. Chem.-Int. Edit.* **2009,** *48* (12), 2218-2220.

20. Trost, B. M.; Hitce, J., Direct Asymmetric Michael Addition to Nitroalkenes: Vinylogous Nucleophilicity under Dinuclear Zinc Catalysis. *J. Am. Chem. Soc.* **2009,** *131* (13), 4572-+.

21. Cui, S.; Walker, S. D.; Woo, J. C. S.; Borths, C. J.; Mukherjee, H.; Chen, M. J.; Faul, M. M., Practical Asymmetric Conjugate Alkynylation of Meldrum's Acid-Derived Acceptors: Access to Chiral beta-Alkynyl Acids. *J. Am. Chem. Soc.* **2010,** *132* (2), 436-+.

22. Shepherd, N. E.; Tanabe, H.; Xu, Y. J.; Matsunaga, S.; Shibasaki, M., Direct Catalytic Asymmetric Vinylogous Mannich-Type and Michael Reactions of an alpha,beta-Unsaturated gamma-Butyrolactam under Dinuclear Nickel Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (11), 3666-+.

23. Yukawa, T.; Seelig, B.; Xu, Y. J.; Morimoto, H.; Matsunaga, S.; Berkessel, A.; Shibasaki, M., Catalytic Asymmetric Aza-Morita-Baylis-Hillman Reaction of Methyl Acrylate: Role of a Bifunctional La(O-iPr)(3)/Linked-BINOL Complex. *J. Am. Chem. Soc.* **2010,** *132* (34), 11988-11992.

24. Weber, M.; Jautze, S.; Frey, W.; Peters, R., Bispalladacycle-Catalyzed Bronsted Acid/Base-Promoted Asymmetric Tandem Azlactone Formation-Michael Addition. *J. Am. Chem. Soc.* **2010,** *132* (35), 12222-12225.

25. Trost, B. M.; Hirano, K., Highly Stereoselective Synthesis of a-Alkyl-a-Hydroxycarboxylic Acid Derivatives Catalyzed by a Dinuclear Zinc Complex. *Angew. Chem.-Int. Edit.* **2012,** *51* (26), 6480-6483.

26. Weber, M.; Frey, W.; Peters, R., Asymmetric Palladium(II)-Catalyzed Cascade Reaction Giving Quaternary Amino Succinimides by 1,4-Addition and a Nef-Type Reaction. *Angew. Chem.-Int. Edit.* **2013,** *52* (50), 13223-13227.

27. Chang, Y.; Cao, M.; Chan, J. Z.; Zhao, C.; Wang, Y.; Yang, R.; Wasa, M., Enantioselective Synthesis of N-Alkylamines through β-Amino C–H Functionalization Promoted by Cooperative Actions of B(C6F5)3 and a Chiral Lewis Acid Co-Catalyst. *J. Am. Chem. Soc.* **2021,** *143* (5), 2441-2455.

28. Ai, C.-R.; Liu, L.; Wang, X.-C., Borane-Catalyzed Enantioselective α-Alkylation of Unactivated 2-Alkylbenzoxazoles with Electron-Deficient Olefins. *J. Am. Chem. Soc.* **2024,** *146* (35), 24663-24669.

4.4.3 Other Reactions

1. Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y., Chiral Phosphine-Ligands Modified by Crown Ethers - an Application to Palladium-Catalyzed Asymmetric Allylation of Beta-Diketones. *J. Am. Chem. Soc.* **1992,** *114* (7), 2586-2592.

2. Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N., HIGHLY ENANTIOSELECTIVE RING-OPENING OF EPOXIDES CATALYZED BY (SALEN)CR(III) COMPLEXES. *J. Am. Chem. Soc.* **1995,** *117* (21), 5897-5898.

3. Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N., On the mechanism of asymmetric nucleophilic ring-opening of epoxides catalyzed by (salen)Cr-III complexes. *J. Am. Chem. Soc.* **1996,** *118* (44), 10924-10925.

4. Sawamura, M.; Sudoh, M.; Ito, Y., An enantioselective two-component catalyst system: Rh-Pd- catalyzed allylic alkylation of activated nitriles. *J. Am. Chem. Soc.* **1996,** *118* (13), 3309-3310.

5. Steinhagen, H.; Helmchen, G., Asymmetric two-center catalysis - Learning from nature. *Angew. Chem.-Int. Edit. Engl.* **1996,** *35* (20), 2339-2342.

6. Sawamura, M.; Nakayama, Y.; Tang, W. M.; Ito, Y., Enantioselective allylation of nitro group-stabilized carbanions catalyzed by chiral crown ether phosphine-palladium complexes. *J. Org. Chem.* **1996,** *61* (26), 9090-9096.

7. Burckhardt, U.; Baumann, M.; Trabesinger, G.; Gramlich, V.; Togni, A., In bimetallic palladium catalyst for asymmetric allylic substitution reactions. *Organometallics* **1997,** *16* (24), 5252-5259.

8. Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N., Asymmetric catalysis with water: Efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis. *Science* **1997,** *277* (5328), 936-938.

9. Konsler, R. G.; Karl, J.; Jacobsen, E. N., Cooperative asymmetric catalysis with dimeric salen complexes. *J. Am. Chem. Soc.* **1998,** *120* (41), 10780-10781.

10. Wu, M. H.; Jacobsen, E. N., Asymmetric ring opening of meso epoxides with thiols: Enantiomeric enrichment using a bifunctional nucleophile. *J. Org. Chem.* **1998,** *63* (15), 5252-5254.

11. Iida, T.; Yamamoto, N.; Matsunaga, S.; Woo, H. G.; Shibasaki, M., Enantioselective ring opening of epoxides with 4-methoxyphenol catalyzed by gallium heterobimetallic complexes: An efficient method for the synthesis of optically active 1,2-diol monoethers. *Angew. Chem.-Int. Edit.* **1998,** *37* (16), 2223-2226.

12. Quirmbach, M.; Kless, A.; Holz, J.; Tararov, V.; Borner, A., Construction of chiral Ti(IV)-Rh(I)-salenophos complexes and their application in the asymmetric hydroformylation of functionalised olefins. *Tetrahedron: Asymmetry* **1999,** *10* (9), 1803-1811.

13. Annis, D. A.; Jacobsen, E. N., Polymer-supported chiral Co(salen) complexes: Synthetic applications and mechanistic investigations in the hydrolytic kinetic resolution of terminal epoxides. *J. Am. Chem. Soc.* **1999,** *121* (17), 4147-4154.

14. Ready, J. M.; Jacobsen, E. N., Asymmetric catalytic synthesis of alpha-aryloxy alcohols: Kinetic resolution of terminal epoxides via highly enantioselective ring-opening with phenols. *J. Am. Chem. Soc.* **1999,** *121* (25), 6086-6087.

15. Wu, M. H.; Hansen, K. B.; Jacobsen, E. N., Regio- and enantioselective cyclization of epoxy alcohols catalyzed by a [Co-III(salen)] complex. *Angew. Chem.-Int. Edit.* **1999,** *38* (13-14), 2012-2014.

16. Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.; Shibasaki, M., Catalytic enantioselective meso-epoxide ring opening reaction with phenolic oxygen nucleophile promoted by gallium heterobimetallic multifunctional complexes. *J. Am. Chem. Soc.* **2000,** *122* (10), 2252-2260.

17. Ready, J. M.; Jacobsen, E. N., A practical oligomeric (salen)Co catalyst for asymmetric epoxide ring-opening reactions. *Angew. Chem.-Int. Edit.* **2002,** *41* (8), 1374-1377.

18. Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N., Highly selective hydrolytic kinetic resolution of terminal epoxides catalyzed by chiral (salen)Co-III complexes. Practical synthesis of enantioenriched terminal epoxides and 1,2-diols. *J. Am. Chem. Soc.* **2002,** *124* (7), 1307-1315.

19. Trost, B. M.; Mino, T., Desymmetrization of meso 1,3-and 1,4-diols with a dinuclear zinc asymmetric catalyst. *J. Am. Chem. Soc.* **2003,** *125* (9), 2410-2411.

20. Usuda, H.; Kuramochi, A.; Kanai, M.; Shibasaki, M., Challenge toward structural complexity using asymmetric catalysis: Target-oriented development of catalytic enantioselective Diels-Alder reaction. *Org. Lett.* **2004,** *6* (23), 4387-4390.

21. Kim, S. K.; Jacobsen, E. N., General catalytic synthesis of highly enantiomerically enriched terminal aziridines from racemic epoxides. *Angew. Chem.-Int. Edit.* **2004,** *43* (30), 3952-3954.

22. Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N., Mechanistic investigation leads to a synthetic improvement in the hydrolytic kinetic resolution of terminal epoxides. *J. Am. Chem. Soc.* **2004,** *126* (5), 1360-1362.

23. Bartoli, G.; Bosco, M.; Carlone, A.; Locatelli, M.; Melchiorre, P.; Sambri, L., Asymmetric catalytic synthesis of enantiopure N-protected 1,2-amino alcohols. *Org. Lett.* **2004,** *6* (22), 3973-3975.

24. Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A., Kinetic resolution of epoxides by a C-C bond-forming reaction: Highly enantioselective addition of indoles to cis, trans, and meso aromatic epoxides catalyzed by Cr(salen) complexes. *Angew. Chem.-Int. Edit.* **2004,** *43* (1), 84-87.

25. Schneider, C.; Sreekanth, A. R.; Mai, E., Scandium-bipyridine-catalyzed enantioselective addition of alcohols and amines to meso-epoxides. *Angew. Chem.-Int. Edit.* **2004,** *43* (42), 5691-5694.

26. Kacprzynski, M. A.; Hoveyda, A. H., Cu-catalyzed asymmetric allylic alkylations of aromatic and aliphatic phosphates with alkylzinc reagents. An effective method for enantioselective synthesis of tertiary and quaternary carbons. *J. Am. Chem. Soc.* **2004,** *126* (34), 10676-10681.

27. Mita, T.; Fujimori, L.; Wada, R.; Wen, J.; Kanai, M. L.; Shibasaki, M., Catalytic enantioselective desymmetrization of meso-N-acylaziridines with TMSCN. *J. Am. Chem. Soc.* **2005,** *127* (32), 11252-11253.

28. Corkey, B. K.; Toste, F. D., Catalytic enantioselective Conia-ene reaction. *J. Am. Chem. Soc.* **2005,** *127* (49), 17168-17169.

29. Fujimori, I.; Mita, T.; Maki, K.; Shiro, M.; Sato, A.; Furusho, S.; Kanai, M.; Shibasaki, M., Key role of the Lewis base position in asymmetric bifunctional catalysis: Design and evaluation of a new ligand for chiral polymetallic catalysts. *J. Am. Chem. Soc.* **2006,** *128* (51), 16438-16439.

30. Kakei, H.; Sone, T.; Sohtome, Y.; Matsunaga, S.; Shibasaki, M., Catalytic asymmetric cyclopropanation of enones with dimethyloxosulfonium methylide promoted by a La-Li-3-(Biphenyldiolate)(3)+NaI complex. *J. Am. Chem. Soc.* **2007,** *129* (44), 13410-13411.

31. Sone, T.; Yamaguchi, A.; Matsunaga, S.; Shibasaki, M., Catalytic asymmetric synthesis of 2,2-disubstituted terminal epoxides via dimethyloxosulfonium methylide addition to ketones. *J. Am. Chem. Soc.* **2008,** *130* (31), 10078-+.

32. Covell, D. J.; White, M. C., A chiral Lewis acid strategy for enantioselective allylic C-H oxidation. *Angew. Chem.-Int. Edit.* **2008,** *47* (34), 6448-6451.

33. Yamatsugu, K.; Yin, L.; Kamijo, S.; Kimura, Y.; Kanai, M.; Shibasaki, M., A Synthesis of Tamiflu by Using a Barium-Catalyzed Asymmetric Diels-Alder-Type Reaction. *Angew. Chem.-Int. Edit.* **2009,** *48* (6), 1070-1076.

34. Loy, R. N.; Jacobsen, E. N., Enantioselective Intramolecular Openings of Oxetanes Catalyzed by (salen)Co(III) Complexes: Access to Enantioenriched Tetrahydrofurans. *J. Am. Chem. Soc.* **2009,** *131* (8), 2786-+.

35. Meyer, M. P., Nonbonding Interactions and Stereoselection in the Corey-Bakshi-Shibata Reduction. *Org. Lett.* **2009,** *11* (19), 4338-4341.

36. Wu, B.; Parquette, J. R.; RajanBabu, T. V., Regiodivergent Ring Opening of Chiral Aziridines. *Science* **2009,** *326* (5960), 1662-1662.

37. Mouri, S.; Chen, Z. H.; Mitsunuma, H.; Furutachi, M.; Matsunaga, S.; Shibasaki, M., Catalytic Asymmetric Synthesis of 3-Aminooxindoles: Enantiofacial Selectivity Switch in Bimetallic vs Monometallic Schiff Base Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (4), 1255-+.

38. Kalow, J. A.; Doyle, A. G., Enantioselective Ring Opening of Epoxides by Fluoride Anion Promoted by a Cooperative Dual-Catalyst System. *J. Am. Chem. Soc.* **2010,** *132* (10), 3268-+.

39. Matsuzawa, A.; Mashiko, T.; Kumagai, N.; Shibasaki, M., La/Ag Heterobimetallic Cooperative Catalysis: A Catalytic Asymmetric Conia-Ene Reaction. *Angew. Chem.-Int. Edit.* **2011,** *50* (33), 7616-7619.

40. Kalow, J. A.; Doyle, A. G., Mechanistic Investigations of Cooperative Catalysis in the Enantioselective Fluorination of Epoxides. *J. Am. Chem. Soc.* **2011,** *133* (40), 16001-16012.

41. Suzuki, S.; Tokunaga, E.; Reddy, D. S.; Matsumoto, T.; Shiro, M.; Shibata, N., Enantioselective 5-endo-dig Carbocyclization of beta-Ketoesters with Internal Alkynes Employing a Four-Component Catalyst System. *Angew. Chem.-Int. Edit.* **2012,** *51* (17), 4131-4135.

42. Ford, D. D.; Nielsen, L. P. C.; Zuend, S. J.; Musgrave, C. B.; Jacobsen, E. N., Mechanistic Basis for High Stereoselectivity and Broad Substrate Scope in the (salen)Co(III)-Catalyzed Hydrolytic Kinetic Resolution. *J. Am. Chem. Soc.* **2013,** *135* (41), 15595-15608.

43. Wu, B.; Gallucci, J. C.; Parquette, J. R.; RajanBabu, T. V., Bimetatlic catalysis in the highly enantioselective ring-opening reactions of aziridines. *Chemical Science* **2014,** *5* (3), 1102-1117.

44. Xu, Y.; Kaneko, K.; Kanai, M.; Shibasaki, M.; Matsunaga, S., Regiodivergent Kinetic Resolution of Terminal and Internal rac-Aziridines with Malonates under Dinuclear Schiff Base Catalysis. *J. Am. Chem. Soc.* **2014,** *136* (25), 9190-9194.

45. Chai, Z.; Zhu, Y. M.; Yang, P. J.; Wang, S. Y.; Wang, S. W.; Liu, Z.; Yang, G. S., Copper(I)-Catalyzed Kinetic Resolution of N-Sulfonylaziridines with Indoles: Efficient Construction of Pyrroloindolines. *J. Am. Chem. Soc.* **2015,** *137* (32), 10088-10091.

46. Bhadra, S.; Akakura, M.; Yarnarnoto, H., Design of a New Bimetallic Catalyst for Asymmetric Epoxidation and Sulfoxidation. *J. Am. Chem. Soc.* **2015,** *137* (50), 15612-15615.

47. Huo, X. H.; He, R.; Zhang, X.; Zhang, W. B., An Ir/Zn Dual Catalysis for Enantio- and Diastereodivergent alpha-Allylation of alpha-Hydroxyketones. *J. Am. Chem. Soc.* **2016,** *138* (35), 11093-11096.

48. Kim, B.; Chinn, A. J.; Fandrick, D. R.; Senanayake, C. H.; Singer, R. A.; Miller, S. J., Distal Stereocontrol Using Guanidinylated Peptides as Multifunctional Ligands: Desymmetrization of Diarylmethanes via Ullman Cross-Coupling. *J. Am. Chem. Soc.* **2016,** *138* (25), 7939-7945.

49. Saito, A.; Kumagai, N.; Shibasaki, M., Cu/Pd Synergistic Dual Catalysis: Asymmetric alpha-Allylation of an alpha-CF3 Amide. *Angew. Chem.-Int. Edit.* **2017,** *56* (20), 5551-5555.

50. Yang, S.; Rui, K. H.; Tang, X. Y.; Xu, Q.; Shi, M., Rhodium/Silver Synergistic Catalysis in Highly Enantioselective Cycloisomerization/Cross Coupling of Keto-Vinylidenecyclopropanes with Terminal Alkynes. *J. Am. Chem. Soc.* **2017,** *139* (16), 5957-5964.

51. Huo, X. H.; He, R.; Fu, J. K.; Zhang, J. C.; Yang, G. Q.; Zhang, W. B., Stereoselective and Site-Specific Allylic Alkylation of Amino Acids and Small Peptides via a Pd/Cu Dual Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (29), 9819-9822.

52. Wei, L.; Xu, S. M.; Zhu, Q.; Che, C.; Wang, C. J., Synergistic Cu/Pd Catalysis for Enantioselective Allylic Alkylation of Aldimine Esters: Access to ,-Disubstituted -Amino Acids. *Angew. Chem.-Int. Edit.* **2017,** *56* (40), 12312-12316.

53. Liu, Q. S.; Wang, D. Y.; Yang, Z. J.; Luan, Y. X.; Yang, J. F.; Li, J. F.; Pu, Y. G.; Ye, M. C., Ni-Al Bimetallic Catalyzed Enantioselective Cycloaddition of Cyclopropyl Carboxamide with Alkyne. *J. Am. Chem. Soc.* **2017,** *139* (50), 18150-18153.

54. Jiang, X. Y.; Boehm, P.; Hartwig, J. F., Stereodivergent Allylation of Azaaryl Acetamides and Acetates by Synergistic Iridium and Copper Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (4), 1239-1242.

55. Huo, X. H.; Zhang, J. C.; Fu, J. K.; He, R.; Zhang, W. B., Ir/Cu Dual Catalysis: Enantio- and Diastereodivergent Access to alpha,alpha-Disubstituted alpha-Amino Acids Bearing Vicinal Stereocenters. *J. Am. Chem. Soc.* **2018,** *140* (6), 2080-2084.

56. Trost, B. M.; Tracy, J. S.; Saget, T., Direct catalytic enantioselective amination of ketones for the formation of tri- and tetrasubstituted stereocenters. *Chemical Science* **2018,** *9* (11), 2975-2980.

57. Yan, L.; Meng, Y.; Haeffner, F.; Leon, R. M.; Crockett, M. P.; Morken, J. P., Carbohydrate/DBU Cocatalyzed Alkene Diboration: Mechanistic Insight Provides Enhanced Catalytic Efficiency and Substrate Scope. *J. Am. Chem. Soc.* **2018,** *140* (10), 3663-3673.

58. Chen, Y. S.; Dong, S. X.; Xu, X.; Liu, X. H.; Feng, X. M., Bimetallic Rhodium(II)/Indium(III) Relay Catalysis for Tandem Insertion/Asymmetric Claisen Rearrangement. *Angew. Chem.-Int. Edit.* **2018,** *57* (50), 16554-16558.

59. Zhang, T.; Luan, Y.-X.; Zheng, S.-J.; Peng, Q.; Ye, M., Chiral Aluminum Complex Controls Enantioselective Nickel-Catalyzed Synthesis of Indenes: C−CN Bond Activation. *Angewandte Chemie International Edition* **2020,** *59* (19), 7439-7443.

60. He, R.; Huo, X.; Zhao, L.; Wang, F.; Jiang, L.; Liao, J.; Zhang, W., Stereodivergent Pd/Cu Catalysis for the Dynamic Kinetic Asymmetric Transformation of Racemic Unsymmetrical 1,3-Disubstituted Allyl Acetates. *J. Am. Chem. Soc.* **2020,** *142* (18), 8097-8103.

61. Changotra, A.; Bhaskararao, B.; Hadad, C. M.; Sunoj, R. B., Insights on Absolute and Relative Stereocontrol in Stereodivergent Cooperative Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (21), 9612-9624.

62. Lu, Z.; Buchwald, S. L., Enantioselective Preparation of Arenes with β-Stereogenic Centers: Confronting the 1,1-Disubstituted Olefin Problem Using CuH/Pd Cooperative Catalysis. *Angewandte Chemie International Edition* **2020,** *59* (37), 16128-16132.

63. Huang, W.-Y.; Lu, C.-H.; Ghorai, S.; Li, B.; Li, C., Regio- and Enantioselective Allylic Alkylation of Terminal Alkynes by Synergistic Rh/Cu Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (36), 15276-15281.

64. Behlen, M. J.; Uyeda, C., C2-Symmetric Dinickel Catalysts for Enantioselective [4 + 1]-Cycloadditions. *J. Am. Chem. Soc.* **2020,** *142* (41), 17294-17300.

65. Braconi, E.; Cramer, N., A Chiral Naphthyridine Diimine Ligand Enables Nickel-Catalyzed Asymmetric Alkylidenecyclopropanations. *Angewandte Chemie International Edition* **2020,** *59* (38), 16425-16429.

66. Wan, Q.; Chen, L.; Li, S.; Kang, Q.; Yuan, Y.; Du, Y., Enantioselective Synthesis of Multisubstituted Spirocyclopentane Oxindoles Enabled by Pd/Chiral Rh(III) Complex Synergistic Catalysis. *Org. Lett.* **2020,** *22* (24), 9539-9544.

67. Liao, K.; Gong, Y.; Zhu, R.-Y.; Wang, C.; Zhou, F.; Zhou, J., Highly Enantioselective CuAAC of Functional Tertiary Alcohols Featuring an Ethynyl Group and Their Kinetic Resolution. *Angewandte Chemie International Edition* **2021,** *60* (15), 8488-8493.

68. Qi, J.; Wei, F.; Tung, C.-H.; Xu, Z., Modular Synthesis of α-Quaternary Chiral β-Lactams by a Synergistic Copper/Palladium-Catalyzed Multicomponent Reaction. *Angewandte Chemie International Edition* **2021,** *60* (25), 13814-13818.

69. Yang, S.-Q.; Wang, Y.-F.; Zhao, W.-C.; Lin, G.-Q.; He, Z.-T., Stereodivergent Synthesis of Tertiary Fluoride-Tethered Allenes via Copper and Palladium Dual Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (19), 7285-7291.

70. Zhang, J.; Huo, X.; Xiao, J.; Zhao, L.; Ma, S.; Zhang, W., Enantio- and Diastereodivergent Construction of 1,3-Nonadjacent Stereocenters Bearing Axial and Central Chirality through Synergistic Pd/Cu Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (32), 12622-12632.

71. Peng, Y.; Huo, X.; Luo, Y.; Wu, L.; Zhang, W., Enantio- and Diastereodivergent Synthesis of Spirocycles through Dual-Metal-Catalyzed [3+2] Annulation of 2-Vinyloxiranes with Nucleophilic Dipoles. *Angewandte Chemie International Edition* **2021,** *60* (47), 24941-24949.

72. Xiao, L.; Wei, L.; Wang, C.-J., Stereodivergent Synthesis of Enantioenriched γ-Butyrolactones Bearing Two Vicinal Stereocenters Enabled by Synergistic Copper and Iridium Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (47), 24930-24940.

73. Wang, H.; Xu, Y.; Zhang, F.; Liu, Y.; Feng, X., Bimetallic Palladium/Cobalt Catalysis for Enantioselective Allylic C−H Alkylation via a Transient Chiral Nucleophile Strategy. *Angewandte Chemie International Edition* **2022,** *61* (12), e202115715.

74. Shi, Y.; Yang, Y.; Xu, S., Iridium-Catalyzed Enantioselective C(sp3)−H Borylation of Aminocyclopropanes. *Angewandte Chemie International Edition* **2022,** *61* (19), e202201463.

75. Yu, H.; Zhang, Q.; Zi, W., Enantioselective Three-Component Photochemical 1,4-Bisalkylation of 1,3-Butadiene with Pd/Cu Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (40), e202208411.

76. Yang, W.-L.; Shang, X.-Y.; Ni, T.; Yan, H.; Luo, X.; Zheng, H.; Li, Z.; Deng, W.-P., Diastereo- and Enantioselective Synthesis of Bisbenzannulated Spiroketals and Spiroaminals by Ir/Ag/Acid Ternary Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (42), e202210207.

77. Wang, W.; Zhang, F.; Liu, Y.; Feng, X., Diastereo- and Enantioselective Construction of Vicinal All-Carbon Quaternary Stereocenters via Iridium/Europium Bimetallic Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (39), e202208837.

78. Levi Knippel, J.; Ni, A. Z.; Schuppe, A. W.; Buchwald, S. L., A General Strategy for the Asymmetric Preparation of α-Stereogenic Allyl Silanes, Germanes, and Boronate Esters via Dual Copper Hydride- and Palladium-Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (47), e202212630.

79. Feng, S.; Dong, Y.; Buchwald, S. L., Enantioselective Hydrocarbamoylation of Alkenes. *Angewandte Chemie International Edition* **2022,** *61* (31), e202206692.

80. Zhao, L.; Luo, Y.; Xiao, J.; Huo, X.; Ma, S.; Zhang, W., Stereodivergent Synthesis of Allenes with α,β-Adjacent Central Chiralities Empowered by Synergistic Pd/Cu Catalysis. *Angewandte Chemie International Edition* **2023,** *62* (9), e202218146.

81. Kanale, V. V.; Uyeda, C., Catalytic Asymmetric Ring-Opening Reactions of Unstrained Heterocycles Using Cobalt Vinylidenes. *Angewandte Chemie International Edition* **2023,** *62* (42), e202309681.

82. Lainer, B.; Li, S.; Mammadova, F.; Dydio, P., A Merger of Relay Catalysis with Dynamic Kinetic Resolution Enables Enantioselective β-C(sp3)−H Arylation of Alcohols. *Angewandte Chemie International Edition* **2024,** *63* (35), e202408418.

83. Tang, M.-Q.; Yang, Z.-J.; Han, A.-J.; He, Z.-T., Diastereoselective and Enantioselective Hydrophosphinylations of Conjugated Enynes, Allenes and Dienes via Synergistic Pd/Co Catalysis. *Angewandte Chemie International Edition* **2025,** *64* (1), e202413428.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

4.5 Dual Activation on A Single Metal Center: Activated Systems

4.5.1 Aldol, Mannich and Allylation Reactions

1. Denmark, S. E.; Winter, S. B. D.; Su, X. P.; Wong, K. T., Chemistry of trichlorosilyl enolates .1. New reagents for catalytic, asymmetric aldol additions. *J. Am. Chem. Soc.* **1996,** *118* (31), 7404-7405.

2. Nakamura, H.; Nakamura, K.; Yamamoto, Y., Catalytic asymmetric allylation of imines via chiral bis-pi- allylpalladium complexes. *J. Am. Chem. Soc.* **1998,** *120* (17), 4242-4243.

3. Hagiwara, E.; Fujii, A.; Sodeoka, M., Enantioselective addition of enol silyl ethers to imines catalyzed by palladium complexes: A novel way to optically active acylalanine derivatives. *J. Am. Chem. Soc.* **1998,** *120* (10), 2474-2475.

4. Nakamura, K.; Nakamura, H.; Yamamoto, Y., Chiral pi-allylpalladium-catalyzed asymmetric allylation of imines: Replacement of allylstannanes by allylsilanes. *J. Org. Chem.* **1999,** *64* (8), 2614-2615.

5. Yanagisawa, A.; Kageyama, H.; Nakatsuka, Y.; Asakawa, K.; Matsumoto, Y.; Yamamoto, H., Enantioselective addition of allylic trimethoxysilanes to aldehydes catalyzed by p-Tol-BINAP center dot AgF. *Angew. Chem.-Int. Edit.* **1999,** *38* (24), 3701-3703.

6. Fujii, A.; Hagiwara, E.; Sodeoka, M., Mechanism of palladium complex-catalyzed enantioselective Mannich-type reaction: Characterization of a novel binuclear palladium enolate complex. *J. Am. Chem. Soc.* **1999,** *121* (23), 5450-5458.

7. Denmark, S. E.; Fu, J. P., On the mechanism of catalytic, enantioselective allylation of aldehydes with chlorosilanes and chiral Lewis bases. *J. Am. Chem. Soc.* **2000,** *122* (48), 12021-12022.

8. Denmark, S. E.; Stavenger, R. A., The chemistry of trichlorosilyl enolates. Aldol addition reactions of methyl ketones. *J. Am. Chem. Soc.* **2000,** *122* (37), 8837-8847.

9. Denmark, S. E.; Stavenger, R. A., Asymmetric catalysis of aldol reactions with chiral Lewis bases. *Accounts Chem. Res.* **2000,** *33* (6), 432-440.

10. Juhl, K.; Gathergood, N.; Jorgensen, K. A., Catalytic asymmetric direct Mannich reactions of carbonyl compounds with alpha-imino esters. *Angew. Chem.-Int. Edit.* **2001,** *40* (16), 2995-2997.

11. Knudsen, K. R.; Risgaard, T.; Nishiwaki, N.; Gothelf, K. V.; Jorgensen, K. A., The first catalytic asymmetric aza-Henry reaction of nitronates with imines: A novel approach to optically active beta-nitro- alpha-amino acid- and alpha,beta-diamino acid derivatives. *J. Am. Chem. Soc.* **2001,** *123* (24), 5843-5844.

12. Shimada, T.; Kina, A.; Ikeda, S.; Hayashi, T., A novel axially chiral 2,2 '-bipyridine N,N-dioxide. Its preparation and use for asymmetric allylation of aldehydes with allyl(trichloro)silane as a highly efficient catalyst. *Org. Lett.* **2002,** *4* (16), 2799-2801.

13. Denmark, S. E.; Fujimori, S., The effects of a remote stereogenic center in the Lewis base catalyzed aldol additions of chiral trichlorosilyl enolates. *Org. Lett.* **2002,** *4* (20), 3477-3480.

14. Suzuki, T.; Kinoshita, A.; Kawada, H.; Nakada, M., New asymmetric tridentate carbazole ligand: Its preparation and application to Nozaki-Hiyama allylation. *Synlett* **2003,** (4), 570-572.

15. Denmark, S. E.; Fu, J. P., Understanding the correlation of structure and selectivity in the chiral-phosphoramide-catalyzed enantioselective allylation reactions: Solution and solid-state structural studies of bisphosphoramide center dot SnCl4 complexes. *J. Am. Chem. Soc.* **2003,** *125* (8), 2208-2216.

16. Kobayashi, S.; Ogawa, C.; Konishi, H.; Sugiura, M., Chiral Sulfoxides as neutral coordinate-organocatalysts in asymmetric allylation of N-acylhydrazones using allyltrichlorosilanes. *J. Am. Chem. Soc.* **2003,** *125* (22), 6610-6611.

17. Malkov, A. V.; Bell, M.; Orsini, M.; Pernazza, D.; Massa, A.; Herrmann, P.; Meghani, P.; Kocovsky, P., New Lewis-basic N-oxides as chiral organocatalysts in asymmetric allylation of aldehydes. *J. Org. Chem.* **2003,** *68* (25), 9659-9668.

18. Malkov, A. V.; Dufkova, L.; Farrugia, L.; Kocovsky, P., Quinox, a quinoline-type N-oxide, as organocatalyst in the asymmetric allylation of aromatic aldehydes with allyltrichlorosilanes: The role of arene-arene interactions. *Angew. Chem.-Int. Edit.* **2003,** *42* (31), 3674-3677.

19. Fernandes, R. A.; Stimac, A.; Yamamoto, Y., Chiral bis-pi-allylpalladium complex catalyzed asymmetric allylation of imines: Enhancement of the enantioselectivity and chemical yield in the presence of water. *J. Am. Chem. Soc.* **2003,** *125* (46), 14133-14139.

20. Hamada, T.; Manabe, K.; Kobayashi, S., Catalytic asymmetric allylation of hydrazono esters in aqueous media by using ZnF2-chiral diamine. *Angew. Chem.-Int. Edit.* **2003,** *42* (33), 3927-3930.

21. Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W., A new copper acetate-bis(oxazoline)-catalyzed, enantioselective Henry reaction. *J. Am. Chem. Soc.* **2003,** *125* (42), 12692-12693.

22. Palomo, C.; Oiarbide, M.; Mielgo, A., Unveiling reliable catalysts for the asymmetric nitroaldol (Henry) reaction. *Angew. Chem.-Int. Edit.* **2004,** *43* (41), 5442-5444.

23. Ogawa, C.; Sugiura, M.; Kobayashi, S., Stereospecific, enantioselective allylation of alpha-hydrazono esters by using allyltrichlorosilanes with BINAP dioxides as neutral-coordinate organocatalysts. *Angew. Chem.-Int. Edit.* **2004,** *43* (47), 6491-6493.

24. Fernandes, R. A.; Yamamoto, Y., The first catalytic asymmetric allylation of imines with the tetraallylsilane-TBAF-MeOH system, using the chiral bis-pi- allylpalladium complex. *J. Org. Chem.* **2004,** *69* (3), 735-738.

25. Fernandes, R. A.; Yamamoto, Y., Catalytic asymmetric carbalkoxyallylation of Imines with the chiral bis-pi-allylpalladium complex. *J. Org. Chem.* **2004,** *69* (10), 3562-3564.

26. Zanoni, G.; Gladiali, S.; Marchetti, A.; Piccinini, P.; Tredici, I.; Vidari, G., Enantioselective catalytic allylation of carbonyl groups by Umpolung of pi-allyl palladium complexes. *Angew. Chem.-Int. Edit.* **2004,** *43* (7), 846-849.

27. Russell, A. E.; Fuller, N. O.; Taylor, S. J.; Aurriset, P.; Morken, J. P., Investigation of the Rh-catalyzed asymmetric reductive aldol reaction. Expanded scope based on reaction analysis. *Org. Lett.* **2004,** *6* (14), 2309-2312.

28. Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M., Catalytic enantioselective allylboration of ketones. *J. Am. Chem. Soc.* **2004,** *126* (29), 8910-8911.

29. Lee, J. Y.; Miller, J. J.; Hamilton, S. S.; Sigman, M. S., Stereochemical diversity in chiral ligand design: Discovery and optimization of catalysts for the enantioselective addition of allylic halides to aldehydes. *Org. Lett.* **2005,** *7* (9), 1837-1839.

30. Malkov, A. V.; Bell, M.; Castelluzzo, F.; Kocovsky, P., METHOX: A new pyridine N-oxide organocatalyst for the asymmetric allylation of aldehydes with allyltrichlorosilanes. *Org. Lett.* **2005,** *7* (15), 3219-3222.

31. Wadamoto, M.; Yamamoto, H., Silver-catalyzed asymmetric Sakurai-Hosomi allylation of ketones. *J. Am. Chem. Soc.* **2005,** *127* (42), 14556-14557.

32. Denmark, S. E.; Bui, T., Mechanistic insights into the chiral phosphoramide-catalyzed, enantioselective crossed-aldol reactions of aldehydes. *J. Org. Chem.* **2005,** *70* (25), 10393-10399.

33. Denmark, S. E.; Fan, Y.; Eastgate, M. D., Lewis base catalyzed, enantioselective aldol addition of methyl trichlorosilyl ketene acetal to ketones. *J. Org. Chem.* **2005,** *70* (13), 5235-5248.

34. Denmark, S. E.; Fujimori, S.; Pham, S. M., Lewis base catalyzed aldol additions of chiral trichlorosilyl enolates and silyl enol ethers. *J. Org. Chem.* **2005,** *70* (26), 10823-10840.

35. Nishiyama, H.; Shiomi, T.; Tsuchiya, Y.; Matsuda, I., High performance of Rh(Phebox) catalysts in asymmetric reductive aldol reaction: High anti-selectivity. *J. Am. Chem. Soc.* **2005,** *127* (19), 6972-6973.

36. Palomo, C.; Oiarbide, M.; Laso, A., Enantioselective henry reactions under dual Lewis acid/amine catalysis using chiral amino alcohol ligands. *Angew. Chem.-Int. Edit.* **2005,** *44* (25), 3881-3884.

37. Kloetzing, R. J.; Thaler, T.; Knochel, P., An improved asymmetric Reformatsky reaction mediated by (-)-N,N-dimethylaminoisoborneol. *Org. Lett.* **2006,** *8* (6), 1125-1128.

38. Zhao, D. B.; Oisaki, K.; Kanai, M.; Shibasaki, M., Dramatic ligand effect in catalytic asymmetric reductive aldol reaction of allenic esters to ketones. *J. Am. Chem. Soc.* **2006,** *128* (45), 14440-14441.

39. Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M., Catalytic enantioselective allylation of ketoimines. *J. Am. Chem. Soc.* **2006,** *128* (23), 7687-7691.

40. Kargbo, R.; Takahashi, Y.; Bhor, S.; Cook, G. R.; Lloyd-Jones, G. C.; Shepperson, I. R., Readily accessible, modular, and tuneable BINOL 3,3'-perfluoroalkylsulfones: Highly efficient catalysts for enantioselective in-mediated imine allylation. *J. Am. Chem. Soc.* **2007,** *129* (13), 3846-+.

41. Shiomi, T.; Nishiyama, H., Intermolecular asymmetric reductive aldol reaction of ketones as acceptors promoted by chiral Rh(phebox) catalyst. *Org. Lett.* **2007,** *9* (9), 1651-1654.

42. Carosi, L.; Hall, D. G., Catalytic enantioselective preparation of alpha-substituted allylboronates: One-pot addition to functionalized aldehydes and a route to chiral allylic trifluoroborate reagents. *Angew. Chem.-Int. Edit.* **2007,** *46* (31), 5913-5915.

43. Lou, S.; Moquist, P. N.; Schaus, S. E., Asymmetric allylboration of acyl imines catalyzed by chiral diols. *J. Am. Chem. Soc.* **2007,** *129* (49), 15398-15404.

44. Bee, C.; Han, S. B.; Hassan, A.; Lida, H.; Krische, M. J., Diastereo- and enantioselective hydrogenative aldol coupling of vinyl ketones: Design of effective monodentate TADDOL-Like phosphonite ligands. *J. Am. Chem. Soc.* **2008,** *130* (9), 2746-+.

45. Umeda, R.; Studer, A., Ag-catalyzed stereoselective cyclohexadienyl transfer: A novel entry into arylphenylmethanols. *Org. Lett.* **2008,** *10* (5), 993-996.

46. Fujita, M.; Nagano, T.; Schneider, U.; Hamada, T.; Ogawa, C.; Kobayashi, S., Zn-catalyzed asymmetric allylation for the synthesis of optically active allylglycine derivatives. Regio- and stereoselective formal alpha-addition of allylboronates to hydrazono esters. *J. Am. Chem. Soc.* **2008,** *130* (10), 2914-2915.

47. Malkov, A. V.; Ramirez-Lopez, P.; Biedermannova, L.; Rulisek, L.; Dufkova, L.; Kotora, M.; Zhu, F. J.; Kocovsky, P., On the mechanism of asymmetric allylation of aldehydes with allyltrichlorosi lanes catalyzed by QUINOX, a chiral lsoquinoline N-oxide. *J. Am. Chem. Soc.* **2008,** *130* (15), 5341-5348.

48. Kim, I. S.; Ngai, M. Y.; Krische, M. J., Enantioselective iridium-catalyzed carbonyl allylation from the alcohol or aldehyde oxidation level using allyl acetate as an allyl metal surrogate. *J. Am. Chem. Soc.* **2008,** *130* (20), 6340-+.

49. Yamaguchi, A.; Matsunaga, S.; Shibasaki, M., Direct catalytic asymmetric Mannich-type reactions of gamma-butenolides: Effectiveness of Bronsted acid in chiral metal catalysis. *Org. Lett.* **2008,** *10* (11), 2319-2322.

50. Dubs, C.; Hamashima, Y.; Sasamoto, N.; Seidel, T. M.; Suzuki, S.; Hashizume, D.; Sodeoka, M., Mechanistic studies on the catalytic asymmetric Mannich-type reaction with dihydroisoquinolines and development of oxidative Mannich-type reactions starting from tetrahydroisoquinolines. *J. Org. Chem.* **2008,** *73* (15), 5859-5871.

51. Lipshutz, B. H.; Amorelli, B.; Unger, J. B., CuH-Catalyzed Enantioselective Intramolecular Reductive Aldol Reactions Generating Three New Contiguous Asymmetric Stereocenters. *J. Am. Chem. Soc.* **2008,** *130* (44), 14378-+.

52. Kim, I. S.; Ngai, M. Y.; Krische, M. J., Enantioselective Iridium-Catalyzed Carbonyl Allylation from the Alcohol or Aldehyde Oxidation Level via Transfer Hydrogenative Coupling of Allyl Acetate: Departure from Chirally Modified Allyl Metal Reagents in Carbonyl Addition. *J. Am. Chem. Soc.* **2008,** *130* (44), 14891-14899.

53. Hernandez-Toribio, J.; Arrayas, R. G.; Carretero, J. C., Direct Mannich Reaction of Glycinate Schiff Bases with N-(8-Quinolyl)sulfonyl Imines: A Catalytic Asymmetric Approach to anti-alpha,beta-Diamino Esters. *J. Am. Chem. Soc.* **2008,** *130* (48), 16150-+.

54. Du, Y.; Xu, L. W.; Shimizu, Y.; Oisaki, K.; Kanai, M.; Shibasaki, M., Asymmetric Reductive Mannich Reaction to Ketimines Catalyzed by a Cu(I) Complex. *J. Am. Chem. Soc.* **2008,** *130* (48), 16146-+.

55. Zhang, G. Q.; Yashima, E.; Woggon, W. D., Versatile Supramolecular Copper(II) Complexes for Henry and Aza-Henry Reactions. *Adv. Synth. Catal.* **2009,** *351* (9), 1255-1262.

56. Denmark, S. E.; Eklov, B. M.; Yao, P. J.; Eastgate, M. D., On the Mechanism of Lewis Base Catalyzed Aldol Addition Reactions: Kinetic and Spectroscopic Investigations Using Rapid-Injection NMR. *J. Am. Chem. Soc.* **2009,** *131* (33), 11770-11787.

57. Fandrick, K. R.; Fandrick, D. R.; Reeves, J. T.; Gao, J.; Ma, S. L.; Li, W. J.; Lee, H.; Grinberg, N.; Lu, B.; Senanayake, C. H., A General Copper-BINAP-Catalyzed Asymmetric Propargylation of Ketones with Propargyl Boronates. *J. Am. Chem. Soc.* **2011,** *133* (27), 10332-10335.

58. Gao, X.; Han, H.; Krische, M. J., Direct Generation of Acyclic Polypropionate Stereopolyads via Double Diastereo- and Enantioselective Iridium-Catalyzed Crotylation of 1,3-Diols: Beyond Stepwise Carbonyl Addition in Polyketide Construction. *J. Am. Chem. Soc.* **2011,** *133* (32), 12795-12800.

59. Shimizu, H.; Igarashi, T.; Miura, T.; Murakami, M., Rhodium-Catalyzed Reaction of 1-Alkenylboronates with Aldehydes Leading to Allylation Products. *Angew. Chem.-Int. Edit.* **2011,** *50* (48), 11465-11469.

60. Xu, H. H.; Wolf, C., Asymmetric Synthesis of Chiral 1,3-Diaminopropanols: Bisoxazolidine-Catalyzed C?C Bond Formation with a-Keto Amides. *Angew. Chem.-Int. Edit.* **2011,** *50* (51), 12249-12252.

61. Grayson, M. N.; Pellegrinet, S. C.; Goodman, J. M., Mechanistic Insights into the BINOL-Derived Phosphoric Acid-Catalyzed Asymmetric Allylboration of Aldehydes. *J. Am. Chem. Soc.* **2012,** *134* (5), 2716-2722.

62. Geary, L. M.; Woo, S. K.; Leung, J. C.; Krische, M. J., Diastereo- and Enantioselective Iridium-Catalyzed Carbonyl Propargylation from the Alcohol or Aldehyde Oxidation Level: 1,3-Enynes as Allenylmetal Equivalents. *Angew. Chem.-Int. Edit.* **2012,** *51* (12), 2972-2976.

63. Vieira, E. M.; Haeffner, F.; Snapper, M. L.; Hoveyda, A. H., A Robust, Efficient, and Highly Enantioselective Method for Synthesis of Homopropargyl Amines. *Angew. Chem.-Int. Edit.* **2012,** *51* (27), 6618-6621.

64. Montgomery, T. P.; Hassan, A.; Park, B. Y.; Krische, M. J., Enantioselective Conversion of Primary Alcohols to alpha-exo-Methylene gamma-Butyrolactones via Iridium-Catalyzed C-C Bond-Forming Transfer Hydrogenation: 2-(Alkoxycarbonyl)allylation. *J. Am. Chem. Soc.* **2012,** *134* (27), 11100-11103.

65. Woo, S. K.; Geary, L. M.; Krische, M. J., Enantioselective Carbonyl Propargylation by Iridium-Catalyzed Transfer Hydrogenative Coupling of Alcohols and Propargyl Chlorides. *Angew. Chem.-Int. Edit.* **2012,** *51* (31), 7830-7834.

66. Luo, Y. F.; Hepburn, H. B.; Chotsaeng, N.; Lam, H. W., Enantioselective Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines with Allylboron Reagents. *Angew. Chem.-Int. Edit.* **2012,** *51* (33), 8309-8313.

67. Leighty, M. W.; Shen, B.; Johnston, J. N., Enantioselective Synthesis of alpha-Oxy Amides via Umpolung Amide Synthesis. *J. Am. Chem. Soc.* **2012,** *134* (37), 15233-15236.

68. Shi, S. L.; Wei, X. F.; Shimizu, Y.; Kanai, M., Copper(I)-Catalyzed Enantioselective Incorporation of Ketones to Cyclic Hemiaminals for the Synthesis of Versatile Alkaloid Precursors. *J. Am. Chem. Soc.* **2012,** *134* (41), 17019-17022.

69. Dechert-Schmitt, A. M. R.; Schmitt, D. C.; Krische, M. J., Protecting-Group-Free Diastereoselective C-C Coupling of 1,3-Glycols and Allyl Acetate through Site-Selective Primary Alcohol Dehydrogenation. *Angew. Chem.-Int. Edit.* **2013,** *52* (11), 3195-3198.

70. Shimoda, Y.; Kubo, T.; Sugiura, M.; Kotani, S.; Nakajima, M., Stereoselective Synthesis of Multiple Stereocenters by Using a Double Aldol Reaction. *Angew. Chem.-Int. Edit.* **2013,** *52* (12), 3461-3464.

71. Kohn, B. L.; Ichiishi, N.; Jarvo, E. R., Silver-Catalyzed Allenylation and Enantioselective Propargylation Reactions of Ketones. *Angew. Chem.-Int. Edit.* **2013,** *52* (16), 4414-4417.

72. Yin, L.; Takada, H.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Vinylogous Mannich-Type Reaction of gamma-Butenolides with Ketimines. *Angew. Chem.-Int. Edit.* **2013,** *52* (28), 7310-7313.

73. Kawai, J.; Chikkade, P. K.; Shimizu, Y.; Kanai, M., In situ Catalytic Generation of Allylcopper Species for Asymmetric Allylation: Toward 1H-Isochromene Skeletons. *Angew. Chem.-Int. Edit.* **2013,** *52* (28), 7177-7180.

74. Ogasawara, M.; Kotani, S.; Nakajima, H.; Furusho, H.; Miyasaka, M.; Shimoda, Y.; Wu, W. Y.; Sugiura, M.; Takahashi, T.; Nakajima, M., Atropisomeric Chiral Dienes in Asymmetric Catalysis: C-2-Symmetric (Z,Z)-2,3-Bis 1-(diphenylphosphinyl)ethylidene tetralin as a Highly Active Lewis Base Organocatalyst. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13798-13802.

75. Chikkade, P. K.; Shimizu, Y.; Kanai, M., Catalytic enantioselective synthesis of 2-(2-hydroxyethyl)indole scaffolds via consecutive intramolecular amido-cupration of allenes and asymmetric addition of carbonyl compounds. *Chem. Sci.* **2014,** *5* (4), 1585-1590.

76. Wu, H.; Haeffner, F.; Hoveyda, A. H., An Efficient, Practical, and Enantioselective Method for Synthesis of Homoallenylamides Catalyzed by an Aminoalcohol-Derived, Boron-Based Catalyst. *J. Am. Chem. Soc.* **2014,** *136* (10), 3780-3783.

77. Feng, J.; Garza, V. J.; Krische, M. J., Redox-Triggered C-C Coupling of Alcohols and Vinyl Epoxides: Diastereo- and Enantioselective Formation of All-Carbon Quaternary Centers via tert-(Hydroxy)-Prenylation. *J. Am. Chem. Soc.* **2014,** *136* (25), 8911-8914.

78. Meng, F. K.; Haeffner, F.; Hoveyda, A. H., Diastereo- and Enantioselective Reactions of Bis(pinacolato)diboron, 1,3-Enynes, and Aldehydes Catalyzed by an Easily Accessible Bisphosphine-Cu Complex. *J. Am. Chem. Soc.* **2014,** *136* (32), 11304-11307.

79. Hepburn, H. B.; Lam, H. W., The Isomerization of Allylrhodium Intermediates in the Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines. *Angew. Chem.-Int. Edit.* **2014,** *53* (43), 11605-11610.

80. Meng, F.; McGrath, K. P.; Hoveyda, A. H., Multifunctional organoboron compounds for scalable natural product synthesis. *Nature* **2014,** *513* (7518), 367-374.

81. Yin, L.; Brewitz, L.; Kumagai, N.; Shibasaki, M., Catalytic Generation of alpha-CF3 Eno late: Direct Catalytic Asymmetric Mannich-Type Reaction of alpha-CF3 Amide. *J. Am. Chem. Soc.* **2014,** *136* (52), 17958-17961.

82. Liang, T.; Nguyen, K. D.; Zhang, W. D.; Krische, M. J., Enantioselective Ruthenium-Catalyzed Carbonyl Allylation via Alkyne-Alcohol C-C Bond-Forming Transfer Hydrogenation: Allene Hydrometalation vs Oxidative Coupling. *J. Am. Chem. Soc.* **2015,** *137* (9), 3161-3164.

83. Ishida, N.; Necas, D.; Masuda, Y.; Murakami, M., Enantioselective Construction of 3-Hydroxypiperidine Scaffolds by Sequential Action of Light and Rhodium upon N-Allylglyoxylamides. *Angew. Chem.-Int. Edit.* **2015,** *54* (25), 7418-7421.

84. Wang, G.; Franke, J.; Ngo, C. Q.; Krische, M. J., Diastereo- and Enantioselective Iridium Catalyzed Coupling of Vinyl Aziridines with Alcohols: Site-Selective Modification of Unprotected Diols and Synthesis of Substituted Piperidines. *J. Am. Chem. Soc.* **2015,** *137* (24), 7915-7920.

85. Hatano, M.; Nishimura, T., Hydroxoiridium/Chiral Diene Complexes as Effective Catalysts for Asymmetric Annulation of alpha-Oxo- and Iminocarboxamides with 1,3-Dienes. *Angew. Chem.-Int. Edit.* **2015,** *54* (37), 10949-10952.

86. Bao, Y. M.; Kumagai, N.; Shibasaki, M., Managing the retro-pathway in direct catalytic asymmetric aldol reactions of thioamides. *Chem. Sci.* **2015,** *6* (11), 6124-6132.

87. Liang, T.; Zhang, W. D.; Chen, T. Y.; Nguyen, K. D.; Krische, M. J., Ruthenium Catalyzed Diastereo- and Enantioselective Coupling of Propargyl Ethers with Alcohols: Siloxy-Crotylation via Hydride Shift Enabled Conversion of Alkynes to pi-Allyls. *J. Am. Chem. Soc.* **2015,** *137* (40), 13066-13071.

88. Brewitz, L.; Arteaga, F. A.; Yin, L.; Alagiri, K.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Mannich-Type Reaction of alpha- and beta-Fluorinated Amides. *J. Am. Chem. Soc.* **2015,** *137* (50), 15929-15939.

89. Liang, T.; Zhang, W. D.; Krische, M. J., Iridium-Catalyzed C-C Coupling of a Simple Propargyl Ether with Primary Alcohols: Enantioselective Homoaldol Addition via Redox-Triggered (Z)-Siloxyallylation. *J. Am. Chem. Soc.* **2015,** *137* (51), 16024-16027.

90. Martinez, J. I.; Smith, J. J.; Hepburn, H. B.; Lam, H. W., Chain Walking of Allylrhodium Species Towards Esters During Rhodium-Catalyzed Nucleophilic Allylations of Imines. *Angew. Chem.-Int. Edit.* **2016,** *55* (3), 1108-1112.

91. Garza, V. J.; Krische, M. J., Hydroxymethylation beyond Carbonylation: Enantioselective Iridium-Catalyzed Reductive Coupling of Formaldehyde with Allylic Acetates via Enantiotopic pi-Facial Discrimination. *J. Am. Chem. Soc.* **2016,** *138* (11), 3655-3658.

92. Lee, K.; Silverio, D. L.; Torker, S.; Robbins, D. W.; Haeffner, F.; van der Mei, F. W.; Hoveyda, A. H., Catalytic enantioselective addition of organoboron reagents to fluoroketones controlled by electrostatic interactions. *Nat. Chem.* **2016,** *8* (8), 768-777.

93. Liang, T.; Woo, S. K.; Krische, M. J., C-Propargylation Overrides O-Propargylation in Reactions of Propargyl Chloride with Primary Alcohols: Rhodium-Catalyzed Transfer Hydrogenation. *Angew. Chem.-Int. Edit.* **2016,** *55* (32), 9207-9211.

94. Yeung, K.; Ruscoe, R. E.; Rae, J.; Pulis, A. P.; Procter, D. J., Enantioselective Generation of Adjacent Stereocenters in a Copper-Catalyzed Three-Component Coupling of Imines, Allenes, and Diboranes. *Angew. Chem.-Int. Edit.* **2016,** *55* (39), 11912-11916.

95. Feng, J. J.; Noack, F.; Krische, M. J., Modular Terpenoid Construction via Catalytic Enantioselective Formation of All-Carbon Quaternary Centers: Total Synthesis of Oridamycin A, Triptoquinones B and C, and Isoiresin. *J. Am. Chem. Soc.* **2016,** *138* (38), 12364-12367.

96. Alam, R.; Diner, C.; Jonker, S.; Eriksson, L.; Szabo, K. J., Catalytic Asymmetric Allylboration of Indoles and Dihydroisoquinolines with Allylboronic Acids: Stereodivergent Synthesis of up to Three Contiguous Stereocenters. *Angew. Chem.-Int. Edit.* **2016,** *55* (46), 14415-14419.

97. Liu, R. Y.; Yang, Y.; Buchwald, S. L., Regiodivergent and Diastereoselective CuH-Catalyzed Allylation of Imines with Terminal Allenes. *Angew. Chem.-Int. Edit.* **2016,** *55* (45), 14077-14080.

98. Nguyen, K. D.; Herkommer, D.; Krische, M. J., Enantioselective Formation of All-Carbon Quaternary Centers via C-H Functionalization of Methanol: Iridium-Catalyzed Diene Hydrohydroxymethylation. *J. Am. Chem. Soc.* **2016,** *138* (43), 14210-14213.

99. Jiang, Y.; Schaus, S. E., Asymmetric Petasis Borono-Mannich Allylation Reactions Catalyzed by Chiral Biphenols. *Angew. Chem.-Int. Edit.* **2017,** *56* (6), 1544-1548.

100. Noda, H.; Amemiya, F.; Weidner, K.; Kumagai, N.; Shibasaki, M., Catalytic asymmetric synthesis of CF3-substituted tertiary propargylic alcohols via direct aldol reaction of alpha-N-3 amide. *Chem. Sci.* **2017,** *8* (4), 3260-3269.

101. Meza, A. T.; Wurm, T.; Smith, L.; Kim, S. W.; Zbeig, J. R.; Stivala, C. E.; Krische, M. J., Amphiphilic pi-Allyliridium C,O-Benzoates Enable Regio- and Enantioselective Amination of Branched Allylic Acetates Bearing Linear Alkyl Groups. *J. Am. Chem. Soc.* **2018,** *140* (4), 1275-1279.

102. Tsai, E. Y.; Liu, R. Y.; Yang, Y.; Buchwald, S. L., A Regio- and Enantioselective CuH-Catalyzed Ketone Allylation with Terminal Allenes. *J. Am. Chem. Soc.* **2018,** *140* (6), 2007-2011.

103. Reddy, D. S.; Corey, E. J., Enantioselective Conversion of Oligoprenol Derivatives to Macrocycles in the Germacrene, Cembrene, and 18-Membered Cyclic Sesterterpene Series. *J. Am. Chem. Soc.* **2018,** *140* (49), 16909-16913.

104. Mitsunuma, H.; Tanabe, S.; Fuse, H.; Ohkubo, K.; Kanai, M., Catalytic asymmetric allylation of aldehydes with alkenes through allylic C(sp(3))-H functionalization mediated by organophotoredox and chiral chromium hybrid catalysis. *Chem. Sci.* **2019,** *10* (12), 3459-3465.

105. Liu, R. Y.; Zhou, Y. J.; Yang, Y.; Buchwald, S. L., Enantioselective Allylation Using Allene, a Petroleum Cracking Byproduct. *J. Am. Chem. Soc.* **2019,** *141* (6), 2251-2256.

106. Li, C. X.; Liu, R. Y.; Jesikiewicz, L. T.; Yang, Y.; Liu, P.; Buchwald, S. L., CuH-Catalyzed Enantioselective Ketone Allylation with 1,3-Dienes: Scope, Mechanism, and Applications. *J. Am. Chem. Soc.* **2019,** *141* (12), 5062-5070.

107. Brito, G. A.; Jung, W. O.; Yoo, M.; Krische, M. J., Enantioselective Iridium-Catalyzed Allylation of Acetylenic Ketones via 2-Propanol-Mediated Reductive Coupling of Allyl Acetate: C14-C23 of Pladienolide D. *Angew. Chem.-Int. Edit.* **2019,** *58* (52), 18803-18807.

108. Zhong, F.; Xue, Q.-Y.; Yin, L., Construction of Chiral 2,3-Allenols through a Copper(I)-Catalyzed Asymmetric Direct Alkynylogous Aldol Reaction. *Angewandte Chemie International Edition* **2020,** *59* (4), 1562-1566.

109. Green, J. C.; Zanghi, J. M.; Meek, S. J., Diastereo- and Enantioselective Synthesis of Homoallylic Amines Bearing Quaternary Carbon Centers. *J. Am. Chem. Soc.* **2020,** *142* (4), 1704-1709.

110. Zanghi, J. M.; Meek, S. J., Cu-Catalyzed Diastereo- and Enantioselective Reactions of γ,γ-Disubstituted Allyldiboron Compounds with Ketones. *Angewandte Chemie International Edition* **2020,** *59* (22), 8451-8455.

111. Fager, D. C.; Morrison, R. J.; Hoveyda, A. H., Regio- and Enantioselective Synthesis of Trifluoromethyl-Substituted Homoallylic α-Tertiary NH2-Amines by Reactions Facilitated by a Threonine-Based Boron-Containing Catalyst. *Angewandte Chemie International Edition* **2020,** *59* (28), 11448-11455.

112. Ye, Y.; Kevlishvili, I.; Feng, S.; Liu, P.; Buchwald, S. L., Highly Enantioselective Synthesis of Indazoles with a C3-Quaternary Chiral Center Using CuH Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (23), 10550-10556.

113. Xiang, M.; Pfaffinger, D. E.; Ortiz, E.; Brito, G. A.; Krische, M. J., Enantioselective Ruthenium-BINAP-Catalyzed Carbonyl Reductive Coupling of Alkoxyallenes: Convergent Construction of syn-sec,tert-Diols via (Z)-σ-Allylmetal Intermediates. *J. Am. Chem. Soc.* **2021,** *143* (23), 8849-8854.

114. Jung, W.-O.; Mai, B. K.; Spinello, B. J.; Dubey, Z. J.; Kim, S. W.; Stivala, C. E.; Zbieg, J. R.; Liu, P.; Krische, M. J., Enantioselective Iridium-Catalyzed Allylation of Nitroalkanes: Entry to β-Stereogenic α-Quaternary Primary Amines. *J. Am. Chem. Soc.* **2021,** *143* (25), 9343-9349.

115. Wang, L.; Wang, L.; Li, M.; Chong, Q.; Meng, F., Cobalt-Catalyzed Diastereo- and Enantioselective Reductive Allyl Additions to Aldehydes with Allylic Alcohol Derivatives via Allyl Radical Intermediates. *J. Am. Chem. Soc.* **2021,** *143* (32), 12755-12765.

116. Klake, R. K.; Edwards, M. D.; Sieber, J. D., Synthesis of 1,2-Aminoalcohols through Enantioselective Aminoallylation of Ketones by Cu-Catalyzed Reductive Coupling. *Org. Lett.* **2021,** *23* (16), 6444-6449.

117. Zhou, P.; Shao, X.; Malcolmson, S. J., A Diastereodivergent and Enantioselective Approach to syn- and anti-Diamines: Development of 2-Azatrienes for Cu-Catalyzed Reductive Couplings with Imines That Furnish Allylic Amines. *J. Am. Chem. Soc.* **2021,** *143* (34), 13999-14008.

118. Ortiz, E.; Shezaf, J. Z.; Chang, Y.-H.; Gonçalves, T. P.; Huang, K.-W.; Krische, M. J., Understanding Halide Counterion Effects in Enantioselective Ruthenium-Catalyzed Carbonyl (α-Aryl)allylation: Alkynes as Latent Allenes and Trifluoroethanol-Enhanced Turnover in The Conversion of Ethanol to Higher Alcohols via Hydrogen Auto-transfer. *J. Am. Chem. Soc.* **2021,** *143* (40), 16709-16717.

119. Calogero, F.; Potenti, S.; Bassan, E.; Fermi, A.; Gualandi, A.; Monaldi, J.; Dereli, B.; Maity, B.; Cavallo, L.; Ceroni, P.; Cozzi, P. G., Nickel-Mediated Enantioselective Photoredox Allylation of Aldehydes with Visible Light. *Angewandte Chemie International Edition* **2022,** *61* (11), e202114981.

120. Meyer, C. C.; Dubey, Z. J.; Krische, M. J., Enantioselective Iridium-Catalyzed Reductive Coupling of Dienes with Oxetanones and N-Acyl-Azetidinones Mediated by 2-Propanol. *Angewandte Chemie International Edition* **2022,** *61* (14), e202115959.

121. Deliaval, M.; Jayarajan, R.; Eriksson, L.; Szabó, K. J., Three-Component Approach to Densely Functionalized Trifluoromethyl Allenols by Asymmetric Organocatalysis. *J. Am. Chem. Soc.* **2023,** *145* (18), 10001-10006.

122. Turman, N. C.; Smith, K. L.; Crawford, E. T.; Robins, J. G.; Weber, K. M.; Liu, S.; Johnson, J. S., Rhodium-Catalyzed Asymmetric Arylation-Induced Glycolate Aldol Additions of Silyl Glyoxylates. *Angewandte Chemie International Edition* **2023,** *62* (42), e202311554.

4.5.2 Hydrogenation of Imines and Ketones

1. Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S., ASYMMETRIC HYDROGENATION OF BETA-KETO CARBOXYLIC ESTERS - A PRACTICAL, PURELY CHEMICAL ACCESS TO BETA-HYDROXY ESTERS IN HIGH ENANTIOMERIC PURITY. *J. Am. Chem. Soc.* **1987,** *109* (19), 5856-5858.

2. Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R., HOMOGENEOUS ASYMMETRIC HYDROGENATION OF FUNCTIONALIZED KETONES. *J. Am. Chem. Soc.* **1988,** *110* (2), 629-631.

3. Brunner, H.; Obermann, U., Asymmetric Catalysis .45. Enantioselective Hydrosilylation of Ketones with Rh(Cod)Cl 2/Pyridinyloxazoline Catalysts. *Chem. Berichte* **1989,** *122* (3), 499-507.

4. Chan, Y. N. C.; Osborn, J. A., Iridium(Iii) Hydride Complexes for the Catalytic Enantioselective Hydrogenation of Imines. *J. Am. Chem. Soc.* **1990,** *112* (25), 9400-9401.

5. Spindler, F.; Pugin, B.; Blaser, H. U., Novel Diphosphinoiridium Catalysts for the Enantioselective Hydrogenation of N-Arylketimines. *Angew. Chem.-Int. Edit. Engl.* **1990,** *29* (5), 558-559.

6. Burk, M. J.; Feaster, J. E., Enantioselective Hydrogenation of the C=N Group - a Catalytic Asymmetric Reductive Amination Procedure. *J. Am. Chem. Soc.* **1992,** *114* (15), 6266-6267.

7. Burk, M. J.; Martinez, J. P.; Feaster, J. E.; Cosford, N., Catalytic Asymmetric Reductive Amination of Ketones Via Highly Enantioselective Hydrogenation of the C=N Double-Bond. *Tetrahedron* **1994,** *50* (15), 4399-4428.

8. Willoughby, C. A.; Buchwald, S. L., Catalytic Asymmetric Hydrogenation of Imines with a Chiral Titanocene Catalyst - Scope and Limitations. *J. Am. Chem. Soc.* **1994,** *116* (20), 8952-8965.

9. Willoughby, C. A.; Buchwald, S. L., Catalytic Asymmetric Hydrogenation of Imines with a Chiral Titanocene Catalyst - Kinetic and Mechanistic Investigations. *J. Am. Chem. Soc.* **1994,** *116* (26), 11703-11714.

10. Nagata, T.; Yorozu, K.; Yamada, T.; Mukaiyama, T., Enantioselective Reduction of Ketones with Sodium-Borohydride, Catalyzed by Optically-Active (Beta-Oxoaldiminato)Cobalt(Ii) Complexes. *Angew. Chem.-Int. Edit. Engl.* **1995,** *34* (19), 2145-2147.

11. Nagata, T.; Sugi, K. D.; Yamada, T.; Mukaiyama, T., Effects of ligands and additive alcohols on enantioselection in highly efficient asymmetric borohydride reduction of ketones catalyzed by optically active aldiminato cobalt(II) complexes. *Synlett* **1996,** (11), 1076-&.

12. Verdaguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L., Highly enantioselective imine hydrosilylation using (S,S)-ethylenebis(eta(5)-tetrahydroindenyl)titanium difluoride. *J. Am. Chem. Soc.* **1996,** *118* (28), 6784-6785.

13. Schnider, P.; Koch, G.; Pretot, R.; Wang, G. Z.; Bohnen, F. M.; Kruger, C.; Pfaltz, A., Enantioselective hydrogenation of imines with chiral (phosphanodihydrooxazole)iridium catalysts. *Chem.-Eur. J.* **1997,** *3* (6), 887-892.

14. Sugi, K. D.; Nagata, T.; Yamada, T.; Mukaiyama, T., Enantioselective borohydride reduction of N-diphenylphosphinyl imines using optically active cobalt(II) complex catalysts. *Chem. Lett.* **1997,** (6), 493-494.

15. Verdaguer, X.; Lange, U. E. W.; Buchwald, S. L., Amine additives greatly expand the scope of asymmetric hydrosilylation of imines. *Angew. Chem.-Int. Edit.* **1998,** *37* (8), 1103-1107.

16. Burk, M. J., Modular phospholane ligands in asymmetric catalysis. *Accounts Chem. Res.* **2000,** *33* (6), 363-372.

17. Hansen, M. C.; Buchwald, S. L., A method for the asymmetric hydrosilylation of N-aryl imines. *Org. Lett.* **2000,** *2* (5), 713-715.

18. Takei, I.; Nishibayashi, Y.; Ishii, Y.; Mizobe, Y.; Uemura, S.; Hidai, M., Ruthenium-catalysed asymmetric hydrosilylation of ketoximes using chiral oxazolinylferrocenylphosphines. *Chem. Commun.* **2001,** (22), 2360-2361.

19. Xiao, D. M.; Zhang, X. M., Highly enantioselective hydrogenation of acyclic imines catalyzed by Ir-f-binaphane complexes. *Angew. Chem.-Int. Edit.* **2001,** *40* (18), 3425-+.

20. Daley, C. J. A.; Bergens, S. H., The first complete identification of a diastereomeric catalyst- substrate (alkoxide) species in an enantioselective ketone hydrogenation. Mechanistic investigations. *J. Am. Chem. Soc.* **2002,** *124* (14), 3680-3691.

21. Hamada, T.; Torii, T.; Izawa, K.; Noyori, R.; Ikariya, T., Practical synthesis of optically active styrene oxides via reductive transformation of 2-chloroacetophenones with chiral rhodium catalysts. *Org. Lett.* **2002,** *4* (24), 4373-4376.

22. Lipshutz, B. H.; Lower, A.; Noson, K., Copper(I) hydride-catalyzed asymmetric hydrosilylation of heteroaromatic ketones. *Org. Lett.* **2002,** *4* (23), 4045-4048.

23. Tao, B. T.; Fu, G. C., Application of a new family of P,N ligands to the highly enantioselective hydrosilylation of aryl alkyl and dialkyl ketones. *Angew. Chem.-Int. Edit.* **2002,** *41* (20), 3892-3894.

24. Wu, J.; Chen, H.; Kwok, W.; Guo, R. W.; Zhou, Z. Y.; Yeung, C.; Chan, A. S. C., Air-stable catalysts for highly efficient and enantioselective hydrogenation of aromatic ketones. *J. Org. Chem.* **2002,** *67* (22), 7908-7910.

25. Chi, Y. X.; Zhou, Y. G.; Zhang, X. M., Highly enantioselective reductive amination of simple aryl ketones catalyzed by Ir-f-Binaphane in the presence of titanium(IV) isopropoxide and iodine. *J. Org. Chem.* **2003,** *68* (10), 4120-4122.

26. Kadyrov, R.; Riermeier, T. H., Highly enantioselective hydrogen-transfer reductive amination: Catalytic asymmetric synthesis of primary amines. *Angew. Chem.-Int. Edit.* **2003,** *42* (44), 5472-5474.

27. Kadyrov, R.; Riermeier, T. H.; Dingerdissen, U.; Tararov, V.; Borner, A., The first highly enantioselective homogeneously catalyzed asymmetric reductive amination: Synthesis of alpha-N- benzylamino acids. *J. Org. Chem.* **2003,** *68* (10), 4067-4070.

28. Lipshutz, B. H.; Noson, K.; Chrisman, W.; Lower, A., Asymmetric hydrosilylation of aryl ketones catalyzed by copper hydride complexed by nonracemic biphenyl bis-phosphine ligands. *J. Am. Chem. Soc.* **2003,** *125* (29), 8779-8789.

29. Locatelli, M.; Cozzi, P. G., Effective modular iminooxazoline (IMOX) ligands for asymmetric catalysis: Zn(IMOX) -promoted enantioselective reduction of ketones by catecholborane. *Angew. Chem.-Int. Edit.* **2003,** *42* (40), 4928-4930.

30. Yamada, T.; Nagata, T.; Sugi, K. D.; Yorozu, K.; Ikeno, T.; Ohtsuka, Y.; Miyazaki, D.; Mukaiyama, T., Enantioselective borohydride reduction catalyzed by optically active cobalt complexes. *Chem.-Eur. J.* **2003,** *9* (18), 4485-4509.

31. Gade, L. H.; Cesar, V.; Bellemin-Laponnaz, S., A modular assembly of chiral oxazolinylcarbene-rhodium complexes: Efficient phosphane-free catalysts for the asymmetric hydrosilylation of dialkyl ketones. *Angew. Chem.-Int. Edit.* **2004,** *43* (8), 1014-1017.

32. Genov, D. G.; Ager, D. J., Asymmetric hydrogenation of ketones catalyzed by Ru-II-bicp complexes. *Angew. Chem.-Int. Edit.* **2004,** *43* (21), 2816-2819.

33. Junge, K.; Hagemann, B.; Enthaler, S.; Oehme, G.; Michalik, M.; Monsees, A.; Riermeier, T.; Dingerdissen, U.; Beller, M., Enantioselective hydrogenation of beta-ketoesters with monodentate ligands. *Angew. Chem.-Int. Edit.* **2004,** *43* (38), 5066-5069.

34. Lei, A. W.; Wu, S. L.; He, M. S.; Zhang, X. M., Highly enantioselective asymmetric hydrogenation of alpha- phthalimide ketone: An efficient entry to enantiomerically pure amino alcohols. *J. Am. Chem. Soc.* **2004,** *126* (6), 1626-1627.

35. Lipshutz, B. H.; Shimizu, H., Copper(I)-Catalyzed Asymmetric Hydrosilylations of Imines at Ambient Temperatures. *Angew. Chem.-Int. Edit.* **2004,** *in press*.

36. Ohkuma, T.; Hattori, T.; Ooka, H.; Inoue, T.; Noyori, R., BINAP/1 4-diamine-ruthenium(II) complexes for efficient asymmetric hydrogenation of 1-tetralones and analogues. *Org. Lett.* **2004,** *6* (16), 2681-2683.

37. Makino, K.; Hiroki, Y.; Hamada, Y., Dynamic kinetic resolution catalyzed by Ir axially chiral phosphine catalyst: Asymmetric synthesis of anti aromatic beta-hydroxy-alpha-amino acid esters. *J. Am. Chem. Soc.* **2005,** *127* (16), 5784-5785.

38. Nolin, K. A.; Ahn, R. W.; Toste, F. D., Enantioselective reduction of imines catalyzed by a rhenium(V)-oxo complex. *J. Am. Chem. Soc.* **2005,** *127* (36), 12462-12463.

39. Graves, C. R.; Scheidt, K. A.; Nguyen, S. T., Enantioselective MSPV reduction of ketimines using 2-propanol and (BINOL)AI(III). *Org. Lett.* **2006,** *8* (6), 1229-1232.

40. Zaitsev, A. B.; Adolfsson, H., Enantioswitchable catalysts for the asymmetric transfer hydrogenation of aryl alkyl ketones. *Org. Lett.* **2006,** *8* (22), 5129-5132.

41. Cheruku, P.; Diesen, J.; Andersson, P. G., Asymmetric hydrogenation of di and trisubstituted enol phosphinates with N,P-ligated iridium complexes. *J. Am. Chem. Soc.* **2008,** *130* (16), 5595-5599.

42. Li, S.; Zhu, S. F.; Zhang, C. M.; Song, S.; Zhou, Q. L., Iridium-catalyzed enantioselective hydrogenation of alpha,beta-unsaturated carboxylic acids. *J. Am. Chem. Soc.* **2008,** *130* (27), 8584-+.

43. Liu, S. M.; Bolm, C., Highly Enantioselective Synthesis of Optically Active Ketones by Iridium-Catalyzed Asymmetric Hydrogenation. *Angew. Chem.-Int. Edit.* **2008,** *47* (46), 8920-8923.

44. Lu, W. J.; Chen, Y. W.; Hou, X. L., Iridium-Catalyzed Highly Enantioselective Hydrogenation of the C=C Bond of alpha, beta-Unsaturated Ketones. *Angew. Chem.-Int. Edit.* **2008,** *47* (52), 10133-10136.

45. Norman, D. W.; Carraz, C. A.; Hyett, D. J.; Pringle, P. G.; Sweeney, J. B.; Orpen, A. G.; Phetmung, H.; Wingad, R. L., Bidentates versus monodentates in asymmetric hydrogenation catalysis: Synergic effects on rate and allosteric effects on enantioselectivity. *J. Am. Chem. Soc.* **2008,** *130* (21), 6840-6847.

46. Diab, L.; Smejkal, T.; Geier, J.; Breit, B., Supramolecular Catalyst for Aldehyde Hydrogenation and Tandem Hydroformylation-Hydrogenation. *Angew. Chem.-Int. Edit.* **2009,** *48* (43), 8022-8026.

47. Donoghue, P. J.; Helquist, P.; Norrby, P. O.; Wiest, O., Prediction of Enantioselectivity in Rhodium Catalyzed Hydrogenations. *J. Am. Chem. Soc.* **2009,** *131* (2), 410-+.

48. Evanno, L.; Ormala, J.; Pihko, P. M., A Highly Enantioselective Access to Tetrahydroisoquinoline and beta-Carboline Alkaloids with Simple Noyori-Type Catalysts in Aqueous Media. *Chem.-Eur. J.* **2009,** *15* (47), 12963-12967.

49. Han, Z. B.; Wang, Z.; Zhang, X. M.; Ding, K. L., Spiro[4,4]-1,6-nonadiene-Based Phosphine-Oxazoline Ligands for Iridium-Catalyzed Enantioselective Hydrogenation of Ketimines. *Angew. Chem.-Int. Edit.* **2009,** *48* (29), 5345-5349.

50. Hou, G.; Gosselin, F.; Li, W.; McWilliams, C.; Sun, Y. K.; Weisel, M.; O'Shea, P. D.; Chen, C. Y.; Davies, I. W.; Zhang, X. M., Enantioselective Hydrogenation of N-H Imines. *J. Am. Chem. Soc.* **2009,** *131* (29), 9882-+.

51. Kadyrov, R.; Koenigs, R. M.; Brinkmann, C.; Voigtlaender, D.; Rueping, M., Efficient Enantioselective Synthesis of Optically Active Diols by Asymmetric Hydrogenation with Modular Chiral Metal Catalysts. *Angew. Chem.-Int. Edit.* **2009,** *48* (41), 7556-7559.

52. Mikhailine, A.; Lough, A. J.; Morris, R. H., Efficient Asymmetric Transfer Hydrogenation of Ketones Catalyzed by an Iron Complex Containing a P-N-N-P Tetradentate Ligand Formed by Template Synthesis. *J. Am. Chem. Soc.* **2009,** *131* (4), 1394-+.

53. Steinhuebel, D.; Sun, Y. K.; Matsumura, K.; Sayo, N.; Saito, T., Direct Asymmetric Reductive Amination. *J. Am. Chem. Soc.* **2009,** *131* (32), 11316-+.

54. Zhang, B.; Xu, M. H.; Lin, G. Q., Catalytic Enantioselective Synthesis of Chiral Phthalides by Efficient Reductive Cyclization of 2-Acylarylcarboxylates under Aqueous Transfer Hydrogenation Conditions. *Org. Lett.* **2009,** *11* (20), 4712-4715.

55. Chen, D. J.; Wang, Y. T.; Klankermayer, J., Enantioselective Hydrogenation with Chiral Frustrated Lewis Pairs. *Angew. Chem.-Int. Edit.* **2010,** *49* (49), 9475-9478.

56. Inagaki, T.; Ito, A.; Ito, J.; Nishiyama, H., Asymmetric Iron-Catalyzed Hydrosilane Reduction of Ketones: Effect of Zinc Metal upon the Absolute Configuration. *Angew. Chem.-Int. Edit.* **2010,** *49* (49), 9384-9387.

57. Malkov, A. V., Change of Direction: Enantioselective CuH-Catalyzed 1,2-Reduction of alpha,beta-Unsaturated Ketones. *Angew. Chem.-Int. Edit.* **2010,** *49* (51), 9814-9815.

58. Zhou, S. L.; Fleischer, S.; Junge, K.; Das, S.; Addis, D.; Beller, M., Enantioselective Synthesis of Amines: General, Efficient Iron-Catalyzed Asymmetric Transfer Hydrogenation of Imines. *Angew. Chem.-Int. Edit.* **2010,** *49* (44), 8121-8125.

59. Berkessel, A.; Reichau, S.; von der Hoh, A.; Leconte, N.; Neudorfl, J. M., Light-Induced Enantioselective Hydrogenation Using Chiral Derivatives of Casey's Iron-Cyclopentadienone Catalyst. *Organometallics* **2011,** *30* (14), 3880-3887.

60. Steward, K. M.; Gentry, E. C.; Johnson, J. S., Dynamic Kinetic Resolution of alpha-Keto Esters via Asymmetric Transfer Hydrogenation. *J. Am. Chem. Soc.* **2012,** *134* (17), 7329-7332.

61. Zuo, W. W.; Lough, A. J.; Li, Y. F.; Morris, R. H., Amine(imine)diphosphine Iron Catalysts for Asymmetric Transfer Hydrogenation of Ketones and Imines. *Science* **2013,** *342* (6162), 1080-1083.

62. Yang, J.; Yoshikai, N., Cobalt-Catalyzed Enantioselective Intramolecular Hydroacylation of Ketones and Olefins. *J. Am. Chem. Soc.* **2014,** *136* (48), 16748-16751.

63. Yu, C.-B.; Huang, W.-X.; Shi, L.; Chen, M.-W.; Wu, B.; Zhou, Y.-G., Asymmetric Hydrogenation via Capture of Active Intermediates Generated from Aza-Pinacol Rearrangement. *J. Am. Chem. Soc.* **2014,** *136* (45), 15837-15840.

64. Bleith, T.; Wadepohl, H.; Gade, L. H., Iron Achieves Noble Metal Reactivity and Selectivity: Highly Reactive and Enantioselective Iron Complexes as Catalysts in the Hydrosilylation of Ketones. *J. Am. Chem. Soc.* **2015,** *137* (7), 2456-2459.

65. Ji, Y.; Shi, L.; Chen, M. W.; Feng, G. S.; Zhou, Y. G., Concise Redox Deracemization of Secondary and Tertiary Amines with a Tetrahydroisoquinoline Core via a Nonenzymatic Process. *J. Am. Chem. Soc.* **2015,** *137* (33), 10496-10499.

66. Chen, G. Q.; Lin, B. J.; Huang, J. M.; Zhao, L. Y.; Chen, Q. S.; Jia, S. P.; Yin, Q.; Zhang, X. M., Design and Synthesis of Chiral oxa-Spirocyclic Ligands for Ir-Catalyzed Direct Asymmetric Reduction of Bringmann's Lactones with Molecular H-2. *J. Am. Chem. Soc.* **2018,** *140* (26), 8064-8068.

67. Zhang, J. W.; Wang, J., Atropoenantioselective Redox-Neutral Amination of Biaryl Compounds through Borrowing Hydrogen and Dynamic Kinetic Resolution. *Angew. Chem.-Int. Edit.* **2018,** *57* (2), 465-469.

68. Mas-Roselló, J.; Smejkal, T.; Cramer, N., Iridium-catalyzed acid-assisted asymmetric hydrogenation of oximes to hydroxylamines. *Science* **2020,** *368* (6495), 1098-1102.

69. Xu, R.; Wang, K.; Liu, H.; Tang, W.; Sun, H.; Xue, D.; Xiao, J.; Wang, C., Anti-Markovnikov Hydroamination of Racemic Allylic Alcohols to Access Chiral γ-Amino Alcohols. *Angewandte Chemie International Edition* **2020,** *59* (49), 21959-21964.

70. Hall, C. J. J.; Goundry, W. R. F.; Donohoe, T. J., Hydrogen-Borrowing Alkylation of 1,2-Amino Alcohols in the Synthesis of Enantioenriched γ-Aminobutyric Acids. *Angewandte Chemie International Edition* **2021,** *60* (13), 6981-6985.

4.5.3 Other Addition Reactions to Carbonyls/Imines

1. Tomioka, K.; Inoue, I.; Shindo, M.; Koga, K., Catalytic Asymmetric Addition of Organolithiums to Aldimines. *Tetrahedron Lett.* **1991,** *32* (26), 3095-3098.

2. Denmark, S. E.; Nakajima, N.; Nicaise, O. J. C., Asymmetric Addition of Organolithium Reagents to Imines. *J. Am. Chem. Soc.* **1994,** *116* (19), 8797-8798.

3. Fujihara, H.; Nagai, K.; Tomioka, K., Copper-amidophosphine catalyst in asymmetric addition of organozinc to imines. *J. Am. Chem. Soc.* **2000,** *122* (48), 12055-12056.

4. Denmark, S. E.; Stiff, C. M., Effect of ligand structure in the bisoxazoline mediated asymmetric addition of methyllithium to imines. *J. Org. Chem.* **2000,** *65* (18), 5875-5878.

5. Hayashi, T.; Ishigedani, M., Rhodium-catalyzed asymmetric arylation of alpha,beta- unsaturated imines with arylstannanes. Catalytic asymmetric synthesis of allylic amines. *Tetrahedron* **2001,** *57* (13), 2589-2595.

6. Koradin, C.; Polborn, K.; Knochel, P., Enantioselective synthesis of propargylamines by copper- catalyzed addition of alkynes to enamines. *Angew. Chem.-Int. Edit.* **2002,** *41* (14), 2535-+.

7. Wei, C. M.; Li, C. J., Enantioselective direct-addition of terminal alkynes to imines catalyzed by copper(I)pybox complex in water and in toluene. *J. Am. Chem. Soc.* **2002,** *124* (20), 5638-5639.

8. Choi, H. W.; Nakajima, K.; Demeke, D.; Kang, F. A.; Jun, H. S.; Wan, Z. K.; Kishi, Y., Asymmetric Ni(II)/Cr(II)-mediated coupling reaction: Catalytic process. *Org. Lett.* **2002,** *4* (25), 4435-4438.

9. Berkessel, A.; Menche, D.; Sklorz, C. A.; Schroder, M.; Paterson, I., A highly enantioselective catalyst for the asymmetric Nozaki-Hiyama-Kishi reaction of allylic and vinylic halides. *Angew. Chem.-Int. Edit.* **2003,** *42* (9), 1032-+.

10. Boezio, A. A.; Pytkowicz, J.; Cote, A.; Charette, A. B., Asymmetric, catalytic synthesis of alpha-chiral amines using a novel bis(phosphine) monoxide chiral ligand. *J. Am. Chem. Soc.* **2003,** *125* (47), 14260-14261.

11. Gommermann, N.; Koradin, X.; Polborn, K.; Knochel, P., Enantioselective, copper(I)-catalyzed three-component reaction for the preparation of propargylamines. *Angew. Chem.-Int. Edit.* **2003,** *42* (46), 5763-5766.

12. Koradin, C.; Gommermann, N.; Polborn, K.; Knochel, P., Synthesis of enantiomerically enriched propargylamines by copper-catalyzed addition of alkynes to enamines. *Chem.-Eur. J.* **2003,** *9* (12), 2797-2811.

13. Lu, G.; Li, X. S.; Jia, X.; Chan, W. L.; Chan, A. S. C., Enantioselective alkynylation of aromatic ketones catalyzed by chiral camphorsulfonamide ligands. *Angew. Chem.-Int. Edit.* **2003,** *42* (41), 5057-5058.

14. Shi, M.; Wang, C. J., The catalytic asymmetric addition of diethylzinc to N- (diphenylphosphinoyl) imines catalyzed by Cu(OTf)(2)-chiral N- (binaphthyl-2-yl)thiophosphoramide ligands. *Adv. Synth. Catal.* **2003,** *345* (8), 971-973.

15. Soeta, T.; Nagai, K.; Fujihara, H.; Kuriyama, M.; Tomioka, K., Asymmetric alkylation of N-toluenesulfonylimines with dialkylzinc reagents catalyzed by copper-chiral amidophosphine. *J. Org. Chem.* **2003,** *68* (25), 9723-9727.

16. Wang, C. J.; Shi, M., Chiral binaphthylthiophosphoramide-Cu(I)-catalyzed asymmetric addition of diethylzinc to N-sulfonylimines. *J. Org. Chem.* **2003,** *68* (16), 6229-6237.

17. Huddleston, R. R.; Jang, H. Y.; Krische, M. J., First catalytic reductive coupling of 1,3-diynes to carbonyl partners: A new regio- and enantioselective C-C bond forming hydrogenation. *J. Am. Chem. Soc.* **2003,** *125* (38), 11488-11489.

18. Cozzi, P. G., Enantioselective alkynylation of ketones catalyzed by Zn(salen) complexes. *Angew. Chem.-Int. Edit.* **2003,** *42* (25), 2895-2898.

19. Zhang, X. M.; Zhang, H. L.; Lin, W. Q.; Gong, L. Z.; Mi, A. Q.; Cui, X.; Jiang, Y. Z.; Yu, K. B., Evaluation of chiral oxazolines for the highly enantioselective diethylzinc addition to N-(diphenylphosphinoyl) imines. *J. Org. Chem.* **2003,** *68* (11), 4322-4329.

20. Boezio, A. A.; Charette, A. B., Catalytic enantioselective addition of dialkylzinc to N- diphenylphosphinoylimines. A practical synthesis of alpha- chiral amines. *J. Am. Chem. Soc.* **2003,** *125* (7), 1692-1693.

21. Miller, K. M.; Huang, W. S.; Jamison, T. F., Catalytic asymmetric reductive coupling of alkynes and aldehydes: Enantioselective synthesis of allylic alcohols and alpha-hydroxy ketones. *J. Am. Chem. Soc.* **2003,** *125* (12), 3442-3443.

22. Inoue, M.; Nakada, M., Studies on catalytic asymmetric Nozaki-Hiyama propargylation. *Org. Lett.* **2004,** *6* (17), 2977-2980.

23. Cote, A.; Boezio, A. A.; Charette, A. B., Evidence for the structure of the enantioactive ligand in the phosphine-copper-catalyzed addition of diorganozinc reagents to imines. *Angew. Chem.-Int. Edit.* **2004,** *43* (47), 6525-6528.

24. Hayashi, T.; Kawai, M.; Tokunaga, N., Asymmetric synthesis of diarylmethyl amines by rhodium-catalyzed asymmetric addition of aryl titanium reagents to imines. *Angew. Chem.-Int. Edit.* **2004,** *43* (45), 6125-6128.

25. Kuriyama, M.; Soeta, T.; Hao, X. Y.; Chen, O.; Tomioka, K., N-BOC-L-valine-connected amidomonophosphane rhodium(I) catalyst for asymmetric arylation of N-tosylarylimines with arylboroxines. *J. Am. Chem. Soc.* **2004,** *126* (26), 8128-8129.

26. Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T., C-2-symmetric bicyclo 2.2.2 octadienes as chiral ligands: Their high performance in rhodium-catalyzed asymmetric arylation of N-tosylarylimines. *J. Am. Chem. Soc.* **2004,** *126* (42), 13584-13585.

27. Jiang, B.; Si, Y. G., Highly enantioselective construction of a chiral tertiary carbon center by alkynylation of a cyclic N-acyl ketimine: An efficient preparation of HIV therapeutics. *Angew. Chem.-Int. Edit.* **2004,** *43* (2), 216-218.

28. Ramon, D. J.; Yus, M., Chiral tertiary alcohols made by catalytic enantioselective addition of unreactive zinc reagents to poorly electrophilic ketones? *Angew. Chem.-Int. Edit.* **2004,** *43* (3), 284-287.

29. Xu, Z. Q.; Chen, C.; Xu, J. K.; Miao, M. B.; Yan, W. J.; Wang, R., Highly enantioselective addition of phenylacetylene to aldehydes catalyzed by a camphorsulfonamide ligand. *Org. Lett.* **2004,** *6* (8), 1193-1195.

30. Patel, S. J.; Jamison, T. F., Asymmetric catalytic coupling of organoboranes, alkynes, and imines with a removable (trialkylsilyloxy)ethyl group-direct access to enantiomerically pure primary allylic amines. *Angew. Chem.-Int. Edit.* **2004,** *43* (30), 3941-3944.

31. Bercot, E. A.; Rovis, T., A palladium-catalyzed enantioselective alkylative desymmetrization of meso-succinic anhydrides. *J. Am. Chem. Soc.* **2004,** *126* (33), 10248-10249.

32. Otomaru, Y.; Tokunaga, N.; Shintani, R.; Hayashi, T., C-2-symmetric bicyclo 3.3.1 nonadiene as a chiral ligand for rhodium-catalyzed asymmetric arylation of N-(4-nitrobenzenesulfonyl)arylimines. *Org. Lett.* **2005,** *7* (2), 307-310.

33. Suarez, A.; Downey, C. W.; Fu, G. C., Kinetic resolutions of azomethine imines via copper-catalyzed 3+2 cycloadditions. *J. Am. Chem. Soc.* **2005,** *127* (32), 11244-11245.

34. Miller, K. M.; Jamison, T. F., Highly regioselective, catalytic asymmetric reductive coupling of 1,3-enynes and ketones. *Org. Lett.* **2005,** *7* (14), 3077-3080.

35. Ng, S. S.; Jamison, T. F., Highly enantioselective and regioselective nickel-catalyzed coupling of allenes, aldehydes, and silanes. *J. Am. Chem. Soc.* **2005,** *127* (20), 7320-7321.

36. Tomita, D.; Wada, R.; Kanai, M.; Shibasaki, M., Enantioselective alkenylation and phenylation catalyzed by a chiral CuF complex. *J. Am. Chem. Soc.* **2005,** *127* (12), 4138-4139.

37. Shintani, R.; Okamoto, K.; Otomaru, Y.; Ueyama, K.; Hayashi, T., Catalytic asymmetric arylative cyclization of alkynals: Phosphine-free rhodium/diene complexes as efficient catalysts. *J. Am. Chem. Soc.* **2005,** *127* (1), 54-55.

38. Wu, T. R.; Chong, J. M., Asymmetric synthesis of propargylamides via 3,3 '-disubstituted binaphthol-modified alkynylboronates. *Org. Lett.* **2006,** *8* (1), 15-18.

39. Inoue, M.; Nakada, M., Studies into asymmetric catalysis of the Nozaki-Hiyama allenylation. *Angew. Chem.-Int. Edit.* **2006,** *45* (2), 252-255.

40. Bisai, A.; Singh, V. K., Enantioselective one-pot three-component synthesis of propargylamines. *Org. Lett.* **2006,** *8* (11), 2405-2408.

41. Colombo, F.; Benaglia, M.; Orlandi, S.; Usuelli, F.; Celentano, G., Very mild, enantioselective synthesis of propargylamines catalyzed by copper(I)-bisimine complexes. *J. Org. Chem.* **2006,** *71* (5), 2064-2070.

42. Taylor, A. M.; Schreiber, S. L., Enantioselective addition of terminal alkynes to isolated isoquinoline iminiums. *Org. Lett.* **2006,** *8* (1), 143-146.

43. Komanduri, V.; Krische, M. J., Enantioselective reductive coupling of 1,3-enynes to heterocyclic aromatic aldehydes and ketones via rhodium-catalyzed asymmetric hydrogenation: Mechanistic insight into the role of Bronsted acid additives. *J. Am. Chem. Soc.* **2006,** *128* (51), 16448-16449.

44. Kong, J. R.; Ngai, M. Y.; Krische, M. J., Highly enantioselective direct reductive coupling of conjugated alkynes and alpha-ketoesters via rhodium-catalyzed asymmetric hydrogenation. *J. Am. Chem. Soc.* **2006,** *128* (3), 718-719.

45. Shintani, R.; Inoue, M.; Hayashi, T., Rhodium-catalyzed asymmetric addition of aryl- and alkenylboronic acids to isatins. *Angew. Chem.-Int. Edit.* **2006,** *45* (20), 3353-3356.

46. Wolf, C.; Liu, S. L., Bisoxazolidine-catalyzed enantioselective alkynylation of aldehydes. *J. Am. Chem. Soc.* **2006,** *128* (34), 10996-10997.

47. Mazet, C.; Roseblade, S.; Kohler, V.; Pfaltz, A., Kinetic resolution of diols and pyridyl alcohols by Cu(II)(borabox)-catalyzed acylation. *Org. Lett.* **2006,** *8* (9), 1879-1882.

48. Liu, G. X.; Lu, X. Y., Cationic palladium complex catalyzed highly enantioselective intramolecular addition of arylboronic acids to ketones. A convenient synthesis of optically active cycloalkanols. *J. Am. Chem. Soc.* **2006,** *128* (51), 16504-16505.

49. Aschwanden, P.; Stephenson, C. R. J.; Carreira, E. M., Highly enantioselective access to primary propargylamines: 4-piperidinone as a convenient protecting group. *Org. Lett.* **2006,** *8* (11), 2437-2440.

50. Xia, G. Y.; Yamamoto, H., Catalytic enantioselective allenylation reactions of aldehydes with tethered bis(8-quinolinolato) (TBOx) chromium complex. *J. Am. Chem. Soc.* **2007,** *129* (3), 496-497.

51. Siewert, J.; Sandmann, R.; von Zezschwitz, P., Rhodium-catalyzed enantioselective 1,2-addition of aluminum organyl compounds to cyclic enones. *Angew. Chem.-Int. Edit.* **2007,** *46* (37), 7122-7124.

52. Hong, Y. T.; Cho, C. W.; Skucas, E.; Krische, M. J., Enantioselective reductive coupling of 1,3-enynes to glyoxalates mediated by hydrogen: Asymmetric synthesis of beta,gamma-unsaturated alpha-hydroxy esters. *Org. Lett.* **2007,** *9* (19), 3745-3748.

53. Sun, Z. K.; Yu, S. Y.; Ding, Z. D.; Ma, D. W., Enantioselective addition of activated terminal alkynes to 1-acylpyridinium salts catalyzed by Cu-bis(oxazoline) complexes. *J. Am. Chem. Soc.* **2007,** *129* (30), 9300-+.

54. Cook, M. J.; Rovis, T., Rhodium-catalyzed enantioselective desymmetrization of meso-3,5-dimethyl glutaric anhydride: A general strategy to syn-deoxypolypropionate synthons. *J. Am. Chem. Soc.* **2007,** *129* (30), 9302-+.

55. Johnson, J. B.; Bercot, E. A.; Williams, C. M.; Rovis, T., A concise synthesis of eupomatilones 4, 6, and 7 by rhodium-catalyzed enantioselective desymmetrization of cyclic meso anhydrides with organozinc reagents generated in situ. *Angew. Chem.-Int. Edit.* **2007,** *46* (24), 4514-4518.

56. Jung, B. H.; Hong, M. S.; Kang, S. H., Enantioselective synthesis of tertiary alcohols by the desynnnetrizing benzoylation of 2-substituted glycerols. *Angew. Chem.-Int. Edit.* **2007,** *46* (15), 2616-2618.

57. Chaulagain, M. R.; Sormunen, G. J.; Montgomery, J., New N-heterocyclic carbene ligand and its application in asymmetric nickel-catalyzed aldehyde/alkyne reductive couplings. *J. Am. Chem. Soc.* **2007,** *129* (31), 9568-+.

58. Skucas, E.; Kong, J. R.; Krische, M. J., Enantioselective reductive coupling of acetylene to N-arylsulfonyl imines via rhodium catalyzed C-C bond-forming hydrogenation: (Z)-Dienyl allylic amines. *J. Am. Chem. Soc.* **2007,** *129* (23), 7242-+.

59. Yang, Y.; Zhu, S. F.; Duan, H. F.; Zhou, C. Y.; Wang, L. X.; Zhou, Q. L., Asymmetric reductive coupling of dienes and aldehydes catalyzed by nickel complexes of spiro phosphoramidites: Highly enantioselective synthesis of chiral bishomoallylic alcohols. *J. Am. Chem. Soc.* **2007,** *129* (8), 2248-+.

60. Saito, B.; Egami, H.; Katsuki, T., Synthesis of an optically active Al(salalen) complex and its application to catalytic hydrophosphonylation of aldehydes and aldimines. *J. Am. Chem. Soc.* **2007,** *129* (7), 1978-1986.

61. Ngai, M. Y.; Barchuk, A.; Krische, M. J., Enantioselective lridium-catalyzed imine vinylation: Optically enriched allylic Amines via alkyne-imine reductive coupling mediated by hydrogen. *J. Am. Chem. Soc.* **2007,** *129* (42), 12644-+.

62. Pizzuti, M. G.; Minnaard, A. J.; Feringa, B. L., Catalytic enantioselective addition of organometallic reagents to N-formylimines using monodentate phosphoramidite ligands. *J. Org. Chem.* **2008,** *73* (3), 940-947.

63. Duan, H. F.; Xie, J. H.; Qiao, X. C.; Wang, L. X.; Zhou, Q. L., Enantioselective rhodium-catalyzed addition of arylboronic acids to alpha-ketoesters. *Angew. Chem.-Int. Edit.* **2008,** *47* (23), 4351-4353.

64. Lou, S.; Schaus, S. E., Asymmetric Petasis reactions catalyzed by chiral biphenols. *J. Am. Chem. Soc.* **2008,** *130* (22), 6922-+.

65. Trincado, M.; Ellman, J. A., Enantioselective synthesis of alpha-aryl alkylamines by Rh-catalyzed addition reactions of arylboronic acids to aliphatic imines. *Angew. Chem.-Int. Edit.* **2008,** *47* (30), 5623-5626.

66. Naodovic, M.; Xia, G.; Yamamoto, H., TBOxCr(III)Cl-catalyzed enantioselective synthesis of 1,3-butadien-2-ylcarbinols. *Org. Lett.* **2008,** *10* (18), 4053-4055.

67. Yang, Y.; Zhu, S. F.; Zhou, C. Y.; Zhou, Q. L., Nickel-Catalyzed Enantioselective Alkylative Coupling of Alkynes and Aldehydes: Synthesis of Chiral Allylic Alcohols with Tetrasubstituted Olefins. *J. Am. Chem. Soc.* **2008,** *130* (43), 14052-+.

68. Johnson, J. B.; Cook, M. J.; Rovis, T. In *Ligand differentiated complementary Rh-catalyst systems for the enantioselective desymmetrization of meso-cyclic anhydrides*, 9th Tetrahedron Symposium on Challenges in Organic and Bioorganic Chemistry, Berkeley, CA, Jul 22-25; Berkeley, CA, 2008; pp 3202-3210.

69. Shen, Z. M.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M., Mechanistic Insights into the Rhodium-Catalyzed Intramolecular Ketone Hydroacylation. *J. Am. Chem. Soc.* **2009,** *131* (3), 1077-1091.

70. Ma, G. N.; Zhang, T.; Shi, M., Catalytic Enantioselective Arylation of N-Tosylarylimines with Arylboronic Acids Using C-2-Symmetric Cationic N-Heterocyclic Carbene Pd2+ Diaquo Complexes. *Org. Lett.* **2009,** *11* (4), 875-878.

71. Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Addition of Allyl Cyanide to Ketones. *J. Am. Chem. Soc.* **2009,** *131* (9), 3195-+.

72. Hrdina, R.; Opekar, F.; Roithova, J.; Kotora, M., Neutral and ionic reaction mechanisms for the allylation of aldehydes by bipyridine N,N'-dioxides. *Chem. Commun.* **2009,** (17), 2314-2316.

73. Wang, W. F.; Zhang, T.; Shi, M., Chiral Bis(NHC)-Palladium(II) Complex Catalyzed and Diethylzinc-Mediated Enantioselective Umpolung Allylation of Aldehydes. *Organometallics* **2009,** *28* (8), 2640-2642.

74. Yamamoto, Y.; Kurihara, K.; Miyaura, N., Me-bipam for Enantioselective Ruthenium (II)-Catalyzed Arylation of Aldehydes with Arylboronic Acids. *Angew. Chem.-Int. Edit.* **2009,** *48* (24), 4414-4416.

75. Tomita, D.; Yamatsugu, K.; Kanai, M.; Shibasaki, M., Enantioselective Synthesis of SM-130686 Based on the Development of Asymmetric Cu(I)F Catalysis To Access 2-Oxindoles Containing a Tetrasubstituted Carbon. *J. Am. Chem. Soc.* **2009,** *131* (20), 6946-+.

76. Sugiura, M.; Kumahara, M.; Nakajima, M., Asymmetric synthesis of 4H-1,3-oxazines: enantioselective reductive cyclization of N-acylated beta-amino enones with trichlorosilane catalyzed by chiral Lewis bases. *Chem. Commun.* **2009,** (24), 3585-3587.

77. Okamoto, K.; Hayashi, T.; Rawal, V. H., Electronic and steric tuning of chiral diene ligands for rhodium-catalyzed asymmetric arylation of imines. *Chem. Commun.* **2009,** (32), 4815-4817.

78. Lu, Y.; Kim, I. S.; Hassan, A.; Del Valle, D. J.; Krische, M. J., 1,n-Glycols as Dialdehyde Equivalents in Iridium-Catalyzed Enantioselective Carbonyl Allylation and Iterative Two-Directional Assembly of 1,3-Polyols. *Angew. Chem.-Int. Edit.* **2009,** *48* (27), 5018-5021.

79. Friedman, R. K.; Rovis, T., Predictable and Regioselective Insertion of Internal Unsymmetrical Alkynes in Rhodium-Catalyzed Cycloadditions with Alkenyl Isocyanates. *J. Am. Chem. Soc.* **2009,** *131* (30), 10775-10782.

80. Itoh, J.; Han, S. B.; Krische, M. J., Enantioselective Allylation, Crotylation, and Reverse Prenylation of Substituted Isatins: Iridium-Catalyzed C-C Bond-Forming Transfer Hydrogenation. *Angew. Chem.-Int. Edit.* **2009,** *48* (34), 6313-6316.

81. Yu, R. T.; Friedman, R. K.; Rovis, T., Enantioselective Rhodium-Catalyzed [4+2+2] Cycloaddition of Dienyl Isocyanates for the Synthesis of Bicyclic Azocine Rings. *J. Am. Chem. Soc.* **2009,** *131* (37), 13250-+.

82. Shibata, Y.; Tanaka, K., Rhodium-Catalyzed Highly Enantioselective Direct Intermolecular Hydroacylation of 1,1-Disubstituted Alkenes with Unfunctionalized Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (35), 12552-+.

83. Nishimura, T.; Kumamoto, H.; Nagaosa, M.; Hayashi, T., The concise synthesis of chiral tfb ligands and their application to the rhodium-catalyzed asymmetric arylation of aldehydes. *Chem. Commun.* **2009,** (38), 5713-5715.

84. Aikawa, K.; Hioki, Y.; Mikami, K., Highly Enantioselective Alkenylation of Glyoxylate with Vinylsilane Catalyzed by Chiral Dicationic Palladium(II) Complexes. *J. Am. Chem. Soc.* **2009,** *131* (39), 13922-+.

85. Liu, S. B.; Kim, J. T.; Dong, C. G.; Kishi, Y., Catalytic Enantioselective Cr-Mediated Propargylation: Application to Halichondrin Synthesis. *Org. Lett.* **2009,** *11* (20), 4520-4523.

86. Coeffard, V.; Aylward, M.; Guiry, P. J., First Regio- and Enantioselective Chromium-Catalyzed Homoallenylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2009,** *48* (48), 9152-9155.

87. Guo, H. B.; Dong, C. G.; Kim, D. S.; Urabe, D.; Wang, J. S.; Kim, J. T.; Liu, X.; Sasaki, T.; Kishi, Y., Toolbox Approach to the Search for Effective Ligands for Catalytic Asymmetric Cr-Mediated Coupling Reactions. *J. Am. Chem. Soc.* **2009,** *131* (42), 15387-15393.

88. Han, S. B.; Kim, I. S.; Krische, M. J., Enantioselective iridium-catalyzed carbonyl allylation from the alcohol oxidation level via transfer hydrogenation: minimizing pre-activation for synthetic efficiency. *Chem. Commun.* **2009,** (47), 7278-7287.

89. Williams, V. M.; Kong, J. R.; Ko, B. J.; Mantri, Y.; Brodbelt, J. S.; Baik, M. H.; Krische, M. J., ESI-MS, DFT, and Synthetic Studies on the H-2-Mediated Coupling of Acetylene: Insertion of C=X Bonds into Rhodacyclopentadienes and Bronsted Acid Cocatalyzed Hydrogenolysis of Organorhodium Intermediates. *J. Am. Chem. Soc.* **2009,** *131* (44), 16054-16062.

90. Fernandez-Ibanez, M. A.; Macia, B.; Pizzuti, M. G.; Minnaard, A. J.; Feringa, B. L., Catalytic Enantioselective Addition of Dialkylzinc Reagents to N-Acylpyridinium Salts. *Angew. Chem.-Int. Edit.* **2009,** *48* (49), 9339-9341.

91. Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M., Desymmetrization of meso-2-Alkene-1,4-diol Derivatives through Copper(I)-Catalyzed Asymmetric Boryl Substitution and Stereoselective Allylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2010,** *49* (3), 560-563.

92. Han, S. B.; Han, H.; Krische, M. J., Diastereo- and Enantioselective anti-Alkoxyallylation Employing Allylic gem-Dicarboxylates as Allyl Donors via Iridium-Catalyzed Transfer Hydrogenation. *J. Am. Chem. Soc.* **2010,** *132* (6), 1760-+.

93. Chakrabarti, A.; Konishi, H.; Yamaguchi, M.; Schneider, U.; Kobayashi, S., Indium(I)-Catalyzed Asymmetric Allylation, Crotylation, and alpha-Chloroallylation of Hydrazones with Rare Constitutional and High Configurational Selectivities. *Angew. Chem.-Int. Edit.* **2010,** *49* (10), 1838-1841.

94. Zhang, Y. J.; Yang, J. H.; Kim, S. H.; Krische, M. J., anti-Diastereo- and Enantioselective Carbonyl (Hydroxymethyl)allylation from the Alcohol or Aldehyde Oxidation Level: Allyl Carbonates as Allylmetal Surrogates. *J. Am. Chem. Soc.* **2010,** *132* (13), 4562-+.

95. Shintani, R.; Isobe, S.; Takeda, M.; Hayashi, T., Rhodium-Catalyzed Asymmetric Synthesis of Spirocarbocycles: Arylboron Reagents as Surrogates of 1,2-Dimetalloarenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (22), 3795-3798.

96. Shi, S. L.; Xu, L. W.; Oisaki, K.; Kanai, M.; Shibasaki, M., Identification of Modular Chiral Bisphosphines Effective for Cu(I)-Catalyzed Asymmetric Allylation and Propargylation of Ketones. *J. Am. Chem. Soc.* **2010,** *132* (19), 6638-+.

97. Fandrick, D. R.; Fandrick, K. R.; Reeves, J. T.; Tan, Z. L.; Tang, W. J.; Capacci, A. G.; Rodriguez, S.; Song, J. H. J.; Lee, H.; Yee, N. K.; Senanayake, C. H., Copper Catalyzed Asymmetric Propargylation of Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (22), 7600-+.

98. Kim, H. Y.; Kim, S.; Oh, K., Orthogonal Enantioselectivity Approaches Using Homogeneous and Heterogeneous Catalyst Systems: Friedel-Crafts Alkylation of Indole. *Angew. Chem.-Int. Edit.* **2010,** *49* (26), 4476-4478.

99. Han, S. B.; Gao, X.; Krische, M. J., Iridium-Catalyzed anti-Diastereo- and Enantioselective Carbonyl (Trimethylsilyl)allylation from the Alcohol or Aldehyde Oxidation Level. *J. Am. Chem. Soc.* **2010,** *132* (26), 9153-9156.

100. Zhou, C. Y.; Zhu, S. F.; Wang, L. X.; Zhou, Q. L., Enantioselective Nickel-Catalyzed Reductive Coupling of Alkynes and Imines. *J. Am. Chem. Soc.* **2010,** *132* (32), 10955-10957.

101. Shintani, R.; Takeda, M.; Tsuji, T.; Hayashi, T., Rhodium-Catalyzed Asymmetric Arylation of N-Tosyl Ketimines. *J. Am. Chem. Soc.* **2010,** *132* (38), 13168-13169.

102. Usanov, D. L.; Yamamoto, H., Asymmetric Nozaki-Hiyama Propargylation of Aldehydes: Enhancement of Enantioselectivity by Cobalt Co-Catalysis. *Angew. Chem.-Int. Edit.* **2010,** *49* (44), 8169-8172.

103. Khan, H. A.; Kou, K. G. M.; Dong, V. M., Nitrogen-directed ketone hydroacylation: Enantioselective synthesis of benzoxazecinones. *Chem. Sci.* **2011,** *2* (3).

104. Usanov, D. L.; Yamamoto, H., Enantioselective Alkynylation of Aldehydes with 1-Haloalkynes Catalyzed by Tethered Bis(8-quinolinato) Chromium Complex. *J. Am. Chem. Soc.* **2011,** *133* (5), 1286-1289.

105. Wisniewska, H. M.; Jarvo, E. R., Enantioselective silver-catalyzed propargylation of imines. *Chem. Sci.* **2011,** *2* (4), 807-810.

106. Nadeau, C.; Aly, S.; Belyk, K., Rhodium-Catalyzed Enantioselective Addition of Boronic Acids to N-Benzylnicotinate Salts. *J. Am. Chem. Soc.* **2011,** *133* (9), 2878-2880.

107. Hassan, A.; Zbieg, J. R.; Krische, M. J., Enantioselective Iridium-Catalyzed Vinylogous Reformatsky-Aldol Reaction from the Alcohol Oxidation Level: Linear Regioselectivity by Way of Carbon-Bound Enolates. *Angew. Chem.-Int. Edit.* **2011,** *50* (15), 3493-3496.

108. Liu, P.; Krische, M. J.; Houk, K. N., Mechanism and Origins of Regio- and Enantioselectivities in Rh(I)-Catalyzed Hydrogenative Couplings of 1,3-Diynes and Activated Carbonyl Partners: Intervention of a Cumulene Intermediate. *Chem.-Eur. J.* **2011,** *17* (14), 4021-4029.

109. Zhu, S. F.; Qiao, X. C.; Zhang, Y. Z.; Wang, L. X.; Zhou, Q. L., Highly enantioselective palladium-catalyzed umpolung allylation of aldehydes. *Chem. Sci.* **2011,** *2* (6), 1135-1140.

110. Gao, X.; Zhang, Y. J.; Krische, M. J., Iridium-Catalyzed anti-Diastereo- and Enantioselective Carbonyl (alpha-Trifluoromethyl)allylation from the Alcohol or Aldehyde Oxidation Level. *Angew. Chem.-Int. Edit.* **2011,** *50* (18), 4173-4175.

111. Masuda, K.; Sakiyama, N.; Tanaka, R.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed Enantioselective Cyclizations of gamma-Alkynylaldehydes with Acyl Phosphonates: Ligand- and Substituent-Controlled C-P or C-H Bond Cleavage. *J. Am. Chem. Soc.* **2011,** *133* (18), 6918-6921.

112. Kurono, N.; Nii, N.; Sakaguchi, Y.; Uemura, M.; Ohkuma, T., Asymmetric Hydrocyanation of alpha,beta-Unsaturated Ketones into beta-Cyano Ketones with the Ru(phgly)(2)(binap) /C(6)H(5)OLi Catalyst System. *Angew. Chem.-Int. Edit.* **2011,** *50* (24), 5541-5544.

113. Campbell, M. J.; Toste, F. D., Enantioselective synthesis of cyclic carbamimidates via a three-component reaction of imines, terminal alkynes, and p-toluenesulfonylisocyanate using a monophosphine gold(I) catalyst. *Chem. Sci.* **2011,** *2* (7), 1369-1378.

114. Yin, L.; Kanai, M.; Shibasaki, M., A Facile Pathway to Enantiomerically Enriched 3-Hydroxy-2-Oxindoles: Asymmetric Intramolecular Arylation of alpha-Keto Amides Catalyzed by a Palladium-DifluorPhos Complex. *Angew. Chem.-Int. Edit.* **2011,** *50* (33), 7620-7623.

115. Zbieg, J. R.; Moran, J.; Krische, M. J., Diastereo- and Enantioselective Ruthenium-Catalyzed Hydrohydroxyalkylation of 2-Silyl-butadienes: Carbonyl syn-Crotylation from the Alcohol Oxidation Level. *J. Am. Chem. Soc.* **2011,** *133* (27), 10582-10586.

116. Cui, Z.; Yu, H. J.; Yang, R. F.; Gao, W. Y.; Feng, C. G.; Lin, G. Q., Highly Enantioselective Arylation of N-Tosylalkylaldimines Catalyzed by Rhodium-Diene Complexes. *J. Am. Chem. Soc.* **2011,** *133* (32), 12394-12397.

117. Tran, D. N.; Cramer, N., Enantioselective Rhodium(I)-Catalyzed 3+2 Annulations of Aromatic Ketimines Induced by Directed C?H Activations. *Angew. Chem.-Int. Edit.* **2011,** *50* (47), 11098-11102.

118. Cai, F.; Pu, X. T.; Qi, X. B.; Lynch, V.; Radha, A.; Ready, J. M., Chiral Allene-Containing Phosphines in Asymmetric Catalysis. *J. Am. Chem. Soc.* **2011,** *133* (45), 18066-18069.

119. Moran, J.; Smith, A. G.; Carris, R. M.; Johnson, J. S.; Krische, M. J., Polarity Inversion of Donor-Acceptor Cyclopropanes: Disubstituted delta-Lactones via Enantioselective Iridium Catalysis. *J. Am. Chem. Soc.* **2011,** *133* (46), 18618-18621.

120. Albright, A.; Gawley, R. E., Application of a C-2-Symmetric Copper Carbenoid in the Enantioselective Hydrosilylation of Dialkyl and Aryl-Alkyl Ketones. *J. Am. Chem. Soc.* **2011,** *133* (49), 19680-19683.

121. Zhu, T.-S.; Jin, S.-S.; Xu, M.-H., Rhodium-Catalyzed, Highly Enantioselective 1,2-Addition of Aryl Boronic Acids to alpha-Ketoesters and alpha-Diketones Using Simple, Chiral Sulfur-Olefin Ligands. *Angew. Chem.-Int. Edit.* **2012,** *51* (3), 780-783.

122. Madduri, A. V. R.; Harutyunyan, S. R.; Minnaard, A. J., Asymmetric Copper-Catalyzed Addition of Grignard Reagents to Aryl Alkyl Ketones. *Angew. Chem.-Int. Edit.* **2012,** *51* (13), 3164-3167.

123. Nishimura, T.; Noishiki, A.; Tsui, G. C.; Hayashi, T., Asymmetric Synthesis of (Triaryl)methylamines by Rhodium-Catalyzed Addition of Arylboroxines to Cyclic N-Sulfonyl Ketimines. *J. Am. Chem. Soc.* **2012,** *134* (11), 5056-5059.

124. Liu, X.; Li, X. Y.; Chen, Y.; Hu, Y. M.; Kishi, Y., On Ni Catalysts for Catalytic, Asymmetric Ni/Cr-Mediated Coupling Reactions. *J. Am. Chem. Soc.* **2012,** *134* (14), 6136-6139.

125. Saxena, A.; Choi, B.; Lam, H. W., Enantioselective Copper-Catalyzed Reductive Coupling of Alkenylazaarenes with Ketones. *J. Am. Chem. Soc.* **2012,** *134* (20), 8428-8431.

126. Luo, Y. F.; Carnell, A. J.; Lam, H. W., Enantioselective Rhodium-Catalyzed Addition of Potassium Alkenyltrifluoroborates to Cyclic Imines. *Angew. Chem.-Int. Edit.* **2012,** *51* (27), 6762-6766.

127. Best, D.; Kujawa, S.; Lam, H. W., Diastereo- and Enantioselective Pd(II)-Catalyzed Additions of 2-Alkylazaarenes to N-Boc Imines and Nitroalkenes. *J. Am. Chem. Soc.* **2012,** *134* (44), 18193-18196.

128. Imaizumi, T.; Yamashita, Y.; Kobayashi, S., Group 11 Metal Amide-Catalyzed Asymmetric Cycloaddition Reactions of Azomethine Imines with Terminal Alkynes. *J. Am. Chem. Soc.* **2012,** *134* (49), 20049-20052.

129. McInturff, E. L.; Yamaguchi, E.; Krische, M. J., Chiral-Anion-Dependent Inversion of Diastereo- and Enantioselectivity in Carbonyl Crotylation via Ruthenium-Catalyzed Butadiene Hydrohydroxyalkylation. *J. Am. Chem. Soc.* **2012,** *134* (51), 20628-20631.

130. Cirriez, V.; Rasson, C.; Hermant, T.; Petrignet, J.; Alvarez, J. D.; Robeyns, K.; Riant, O., Copper-Catalyzed Addition of Nucleophilic Silicon to Aldehydes. *Angew. Chem.-Int. Edit.* **2013,** *52* (6), 1785-1788.

131. Nishimura, T.; Noishiki, A.; Ebe, Y.; Hayashi, T., Hydroxorhodium/Chiral Diene Complexes as Effective Catalysts for the Asymmetric Arylation of 3-Aryl-3-hydroxyisoindolin-1-ones. *Angew. Chem.-Int. Edit.* **2013,** *52* (6), 1777-1780.

132. Wang, H.; Jiang, T.; Xu, M. H., Simple Branched Sulfur-Olefins as Chiral Ligands for Rh-Catalyzed Asymmetric Arylation of Cyclic Ketimines: Highly Enantioselective Construction of Tetrasubstituted Carbon Stereocenters. *J. Am. Chem. Soc.* **2013,** *135* (3), 971-974.

133. Nishimura, T.; Ebe, Y.; Hayashi, T., Iridium-Catalyzed 3+2 Annulation of Cyclic N-Sulfonyl Ketimines with 1,3-Dienes via C-H Activation. *J. Am. Chem. Soc.* **2013,** *135* (6), 2092-2095.

134. Harper, K. C.; Vilardi, S. C.; Sigman, M. S., Prediction of Catalyst and Substrate Performance in the Enantioselective Propargylation of Aliphatic Ketones by a Multidimensional Model of Steric Effects. *J. Am. Chem. Soc.* **2013,** *135* (7), 2482-2485.

135. Amatore, M.; Leboeuf, D.; Malacria, M.; Gandon, V.; Aubert, C., Highly Enantioselective Rhodium-Catalyzed 2+2+2 Cycloaddition of Diynes to Sulfonimines. *J. Am. Chem. Soc.* **2013,** *135* (12), 4576-4579.

136. Hong, K.; Morken, J. P., Catalytic Enantioselective One-pot Aminoborylation of Aldehydes: A Strategy for Construction of Nonracemic alpha-Amino Boronates. *J. Am. Chem. Soc.* **2013,** *135* (25), 9252-9254.

137. Johnson, T.; Lautens, M., Palladium(II)-Catalyzed Enantioselective Synthesis of alpha-(Trifluoromethyl)arylmethylamines. *Org. Lett.* **2013,** *15* (16), 4043-4045.

138. Tran, D. N.; Cramer, N., Rhodium-Catalyzed Dynamic Kinetic Asymmetric Transformations of Racemic Allenes by the 3+2 Annulation of Aryl Ketimines. *Angew. Chem.-Int. Edit.* **2013,** *52* (40), 10630-10634.

139. Zi, W. W.; Toste, F. D., Gold(I)-Catalyzed Enantioselective Carboalkoxylation of Alkynes. *J. Am. Chem. Soc.* **2013,** *135* (34), 12600-12603.

140. Cardoso, F. S. P.; Abboud, K. A.; Aponick, A., Design, Preparation, and Implementation of an Imidazole-Based Chiral Biaryl P,N-Ligand for Asymmetric Catalysis. *J. Am. Chem. Soc.* **2013,** *135* (39), 14548-14551.

141. Nishimura, T.; Nagamoto, M.; Ebe, Y.; Hayashi, T., Enantioselective 3+2 annulation via C-H activation between cyclic N-acyl ketimines and 1,3-dienes catalyzed by iridium/chiral diene complexes. *Chem. Sci.* **2013,** *4* (12), 4499-4504.

142. Lin, W. L.; Cao, T.; Fan, W.; Han, Y. L.; Kuang, J. Q.; Luo, H. W.; Miao, B. K. Y.; Tang, X. J.; Yu, Q.; Yuan, W. M.; Zhang, J. S.; Zhu, C.; Ma, S. M., Enantioselective Double Manipulation of Tetrahydroisoquinolines with Terminal Alkynes and Aldehydes under Copper(I) Catalysis. *Angew. Chem.-Int. Edit.* **2014,** *53* (1), 277-281.

143. Cook, A. M.; Wolf, C., Catalytic enantioselective nucleophilic addition of ynamides to aldehydes. *Chem. Commun.* **2014,** *50* (24), 3151-3154.

144. Shirai, T.; Ito, H.; Yamamoto, Y., Cationic Ir/Me-BIPAM-Catalyzed Asymmetric Intramolecular Direct Hydroarylation of alpha-Ketoamides. *Angew. Chem.-Int. Edit.* **2014,** *53* (10), 2658-2661.

145. Mszar, N. W.; Haeffner, F.; Hoveyda, A. H., NHC-Cu-Catalyzed Addition of Propargylboron Reagents to Phosphinoylimines. Enantioselective Synthesis of Trimethylsilyl-Substituted Homoallenylamides and Application to the Synthesis of S-(-)-Cyclooroidin. *J. Am. Chem. Soc.* **2014,** *136* (9), 3362-3365.

146. Hensel, A.; Nagura, K.; Delvos, L. B.; Oestreich, M., Enantioselective Addition of Silicon Nucleophiles to Aldimines Using a Preformed NHC- Copper(I) Complex as the Catalyst. *Angew. Chem.-Int. Edit.* **2014,** *53* (19), 4964-4967.

147. Yada, A.; Fujita, S.; Murakami, M., Enantioselective Insertion of a Carbenoid Carbon into a C-C Bond To Expand Cyclobutanols to Cyclopentanols. *J. Am. Chem. Soc.* **2014,** *136* (20), 7217-7220.

148. Kou, K. G. M.; Le, D. N.; Dong, V. M., Rh(I)-Catalyzed Intermolecular Hydroacylation: Enantioselective Cross-Coupling of Aldehydes and Ketoamides. *J. Am. Chem. Soc.* **2014,** *136* (26), 9471-9476.

149. Ebe, Y.; Nishimura, T., Iridium-Catalyzed Annulation of Salicylimines with 1,3-Dienes. *J. Am. Chem. Soc.* **2014,** *136* (26), 9284-9287.

150. Jiang, C. H.; Lu, Y. X.; Hayashi, T., High Performance of a Palladium Phosphinooxazoline Catalyst in the Asymmetric Arylation of Cyclic N-Sulfonyl Ketimines. *Angew. Chem.-Int. Edit.* **2014,** *53* (37), 9936-9939.

151. Ahlin, J. S. E.; Donets, P. A.; Cramer, N., Nickel(0)-Catalyzed Enantioselective Annulations of Alkynes and Arylenoates Enabled by a Chiral NHC Ligand: Efficient Access to Cyclopentenones. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13229-13233.

152. Bisai, V.; Suneja, A.; Singh, V. K., Asymmetric Alkynylation/Lactamization Cascade: An Expeditious Entry to Enantiomerically Enriched Isoindolinones. *Angew. Chem.-Int. Edit.* **2014,** *53* (40), 10737-10741.

153. Rong, J.; Oost, R.; Desmarchelier, A.; Minnaard, A. J.; Harutyunyan, S. R., Catalytic Asymmetric Alkylation of Acylsilanes. *Angew. Chem.-Int. Edit.* **2015,** *54* (10), 3038-3042.

154. Kubota, K.; Yamamoto, E.; Ito, H., Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aldehydes: An Efficient Route to Enantiomerically Enriched alpha-Alkoxyorganoboronate Esters. *J. Am. Chem. Soc.* **2015,** *137* (1), 420-424.

155. Ye, J.; Limouni, A.; Zaichuk, S.; Lautens, M., Synthesis of Enantioenriched 5,6-Dihydrophenanthridine Derivatives through retro-Carbopalladation of Chiral o-Bromobenzylamines. *Angew. Chem.-Int. Edit.* **2015,** *54* (10), 3116-3120.

156. Fu, W.; Nie, M.; Wang, A.; Cao, Z.; Tang, W., Highly Enantioselective Nickel-Catalyzed Intramolecular Reductive Cyclization of Alkynones. *Angew. Chem.-Int. Edit.* **2015,** *54* (8), 2520-2524.

157. Zhang, W.-Z.; Chu, J. C. K.; Oberg, K. M.; Rovis, T., Enantioselective Rhodium-Catalyzed Isomerization of 4-Iminocrotonates: Asymmetric Synthesis of a Unique Chiral Synthon. *J. Am. Chem. Soc.* **2015,** *137* (2), 553-555.

158. Chen, T.-Y.; Tsutsumi, R.; Montgomery, T. P.; Volchkov, I.; Krische, M. J., Ruthenium-Catalyzed C-C Coupling of Amino Alcohols with Dienes via Transfer Hydrogenation: Redox-Triggered Imine Addition and Related Hydroaminoalkylations. *J. Am. Chem. Soc.* **2015,** *137* (5), 1798-1801.

159. Talwar, D.; Gonzalez-de-Castro, A.; Li, H. Y.; Xiao, J. L., Regioselective Acceptorless Dehydrogenative Coupling of N-Heterocycles toward Functionalized Quinolines, Phenanthrolines, and Indoles. *Angew. Chem.-Int. Edit.* **2015,** *54* (17), 5223-5227.

160. Zhao, C. F.; Seidel, D., Enantioselective A(3) Reactions of Secondary Amines with a Cu(I)/Acid-Thiourea Catalyst Combination. *J. Am. Chem. Soc.* **2015,** *137* (14), 4650-4653.

161. Schrapel, C.; Peters, R., Exogenous-Base-Free Palladacycle-Catalyzed Highly Enantioselective Arylation of Imines with Arylboroxines. *Angew. Chem.-Int. Edit.* **2015,** *54* (35), 10289-10293.

162. Grayson, M. N.; Krische, M. J.; Houk, K. N., Ruthenium-Catalyzed Asymmetric Hydrohydroxyalkylation of Butadiene: The Role of the Formyl Hydrogen Bond in Stereochemical Control. *J. Am. Chem. Soc.* **2015,** *137* (27), 8838-8850.

163. Kumar, R.; Hoshimoto, Y.; Yabuki, H.; Ohashi, M.; Ogoshi, S., Nickel(0)-Catalyzed Enantio- and Diastereoselective Synthesis of Benzoxasiloles: Ligand-Controlled Switching from Inter- to Intramolecular Aryl-Transfer Process. *J. Am. Chem. Soc.* **2015,** *137* (36), 11838-11845.

164. Dasgupta, S.; Rivas, T.; Watson, M. P., Enantioselective Copper(I)-Catalyzed Alkynylation of Oxocarbenium Ions to Set Diaryl Tetrasubstituted Stereocenters. *Angew. Chem.-Int. Edit.* **2015,** *54* (47), 14154-14158.

165. Li, H. M.; Belyk, K. M.; Yin, J. J.; Chen, Q. H.; Hyde, A.; Ji, Y. N.; Oliver, S.; Tudge, M. T.; Campeau, L. C.; Campos, K. R., Enantioselective Synthesis of Hemiaminals via Pd-Catalyzed C-N Coupling with Chiral Bisphosphine Mono-oxides. *J. Am. Chem. Soc.* **2015,** *137* (43), 13728-13731.

166. Pappoppula, M.; Cardoso, F. S. P.; Garrett, B. O.; Aponick, A., Enantioselective Copper-Catalyzed Quinoline Alkynylation. *Angew. Chem.-Int. Edit.* **2015,** *54* (50), 15202-15206.

167. Paioti, P. H. S.; Abboud, K. A.; Aponick, A., Catalytic Enantioselective Synthesis of Amino Skipped Diynes. *J. Am. Chem. Soc.* **2016,** *138* (7), 2150-2153.

168. Lutz, J. P.; Chau, S. T.; Doyle, A. G., Nickel-catalyzed enantioselective arylation of pyridine. *Chem. Sci.* **2016,** *7* (7), 4105-4109.

169. Chen, Q. G.; Tang, Y.; Huang, T. Y.; Liu, X. H.; Lin, L. L.; Feng, X. M., Copper/Guanidine-Catalyzed Asymmetric Alkynylation of Isatins. *Angew. Chem.-Int. Edit.* **2016,** *55* (17), 5286-5289.

170. Nguyen, K. D.; Herkommer, D.; Krische, M. J., Ruthenium-BINAP Catalyzed Alcohol C-H tert-Prenylation via 1,3-Enyne Transfer Hydrogenation: Beyond Stoichiometric Carbanions in Enantioselective Carbonyl Propargylation. *J. Am. Chem. Soc.* **2016,** *138* (16), 5238-5241.

171. Huang, Y.; Huang, R. Z.; Zhao, Y., Cobalt-Catalyzed Enantioselective Vinylation of Activated Ketones and Imines. *J. Am. Chem. Soc.* **2016,** *138* (20), 6571-6576.

172. Clarke, C.; Incerti-Pradillos, C. A.; Lam, H. W., Enantioselective Nickel-Catalyzed anti-Carbometallative Cyclizations of Alkynyl Electrophiles Enabled by Reversible Alkenylnickel E/Z Isomerization. *J. Am. Chem. Soc.* **2016,** *138* (26), 8068-8071.

173. Hu, H. P.; Liu, Y. B.; Lin, L. L.; Zhang, Y. H.; Liu, X. H.; Feng, X. M., Kinetic Resolution of 2H-Azirines by Asymmetric Imine Amidation. *Angew. Chem.-Int. Edit.* **2016,** *55* (34), 10098-10101.

174. Hayashi, M.; Bachman, S.; Hashimoto, S.; Eichman, C. C.; Stoltz, B. M., Ni-Catalyzed Enantioselective C-Acylation of alpha-Substituted Lactams. *J. Am. Chem. Soc.* **2016,** *138* (29), 8997-9000.

175. Yang, Y.; Perry, I. B.; Buchwald, S. L., Copper-Catalyzed Enantioselective Addition of Styrene-Derived Nucleophiles to Imines Enabled by Ligand-Controlled Chemoselective Hydrocupration. *J. Am. Chem. Soc.* **2016,** *138* (31), 9787-9790.

176. Wu, X. S.; Chen, Z. W.; Bai, Y. B.; Dong, V. M., Diastereodivergent Construction of Bicyclic gamma-Lactones via Enantioselective Ketone Hydroacylation. *J. Am. Chem. Soc.* **2016,** *138* (37), 12013-12016.

177. Arai, T.; Kakino, J., Catalytic Asymmetric Synthesis of 3-Indolyl Methanamines Using Unprotected Indoles and N-Boc Imines under Basic Conditions. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15263-15267.

178. Bartlett, S. L.; Keiter, K. M.; Johnson, J. S., Synthesis of Complex Tertiary Glycolates by Enantioconvergent Arylation of Stereochemically Labile alpha-Keto Esters. *J. Am. Chem. Soc.* **2017,** *139* (10), 3911-3916.

179. Wei, X. F.; Xie, X. W.; Shimizu, Y.; Kanai, M., Copper(I)-Catalyzed Enantioselective Addition of Enynes to Ketones. *J. Am. Chem. Soc.* **2017,** *139* (13), 4647-4650.

180. Kubota, K.; Osaki, S.; Jin, M.; Ito, H., Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aliphatic Ketones: Synthesis of Enantioenriched Chiral Tertiary α-Hydroxyboronates. *Angewandte Chemie International Edition* **2017,** *56* (23), 6646-6650.

181. Holmes, M.; Nguyen, K. D.; Schwartz, L. A.; Luong, T.; Krische, M. J., Enantioselective Formation of CF3-Bearing All-Carbon Quaternary Stereocenters via C-H Functionalization of Methanol: Iridium Catalyzed Allene Hydrohydroxymethylation. *J. Am. Chem. Soc.* **2017,** *139* (24), 8114-8117.

182. Pulis, A. P.; Yeung, K.; Procter, D. J., Enantioselective copper catalysed, direct functionalisation of allenes via allyl copper intermediates. *Chem. Sci.* **2017,** *8* (8), 5240-5247.

183. Wang, H. B.; Lu, G.; Sormunen, G. J.; Malik, H. A.; Liu, P.; Montgomery, J., NHC Ligands Tailored for Simultaneous Regio- and Enantiocontrol in Nickel-Catalyzed Reductive Couplings. *J. Am. Chem. Soc.* **2017,** *139* (27), 9317-9324.

184. Jang, H.; Romiti, F.; Torker, S.; Hoveyda, A. H., Catalytic diastereo- and enantioselective additions of versatile allyl groups to N-H ketimines. *Nat. Chem.* **2017,** *9* (12), 1269-1275.

185. Kim, S. W.; Zhang, W. D.; Krische, M. J., Catalytic Enantioselective Carbonyl Allylation and Propargylation via Alcohol-Mediated Hydrogen Transfer: Merging the Chemistry of Grignard and Sabatier. *Accounts Chem. Res.* **2017,** *50* (9), 2371-2380.

186. Callingham, M.; Partridge, B. M.; Lewis, W.; Lam, H. W., Enantioselective Rhodium-Catalyzed Coupling of Arylboronic Acids, 1,3-Enynes, and Imines by Alkenyl-to-Allyl 1,4-Rhodium(I) Migration. *Angew. Chem.-Int. Edit.* **2017,** *56* (51), 16352-16356.

187. Nagamoto, M.; Sakamoto, K.; Nishimura, T., Iridium/Chiral Diene-Catalyzed Enantioselective (3+2) Annulation of Aromatic Ketimines with 1,3-Enynes via C-H Activation. *Adv. Synth. Catal.* **2018,** *360* (4), 791-795.

188. Li, K. N.; Shao, X. X.; Tseng, L.; Malcolmson, S. J., 2-Azadienes as Reagents for Preparing Chiral Amines: Synthesis of 1,2-Amino Tertiary Alcohols by Cu-Catalyzed Enantioselective Reductive Couplings with Ketones. *J. Am. Chem. Soc.* **2018,** *140* (2), 598-601.

189. Schwarzer, M. C.; Fujioka, A.; Ishii, T.; Ohmiya, H.; Mori, S.; Sawamura, M., Enantiocontrol by assembled attractive interactions in copper-catalyzed asymmetric direct alkynylation of alpha-ketoesters with terminal alkynes: OH center dot center dot center dot O/sp(3)-CH center dot center dot center dot O two-point hydrogen bonding combined with dispersive attractions. *Chem. Sci.* **2018,** *9* (14), 3484-3493.

190. Chen, S. M.; Zheng, Y.; Cui, T. J.; Meggers, E.; Houk, K. N., Arylketone pi-Conjugation Controls Enantioselectivity in Asymmetric Alkynylations Catalyzed by Centrochiral Ruthenium Complexes. *J. Am. Chem. Soc.* **2018,** *140* (15), 5146-5152.

191. Shao, X. X.; Li, K. N.; Malcolmson, S. J., Enantioselective Synthesis of anti-1,2-Diamines by Cu-Catalyzed Reductive Couplings of Azadienes with Aldimines and Ketimines. *J. Am. Chem. Soc.* **2018,** *140* (23), 7083-7087.

192. Karad, S. N.; Panchal, H.; Clarke, C.; Lewis, W.; Lam, H. W., Enantioselective Synthesis of Chiral Cyclopent-2-enones by Nickel-Catalyzed Desymmetrization of Malonate Esters. *Angew. Chem.-Int. Edit.* **2018,** *57* (29), 9122-9125.

193. Ambler, B. R.; Turnbull, B. W. H.; Suravarapu, S. R.; Uteuliyev, M. M.; Huynh, N. O.; Krische, M. J., Enantioselective Ruthenium-Catalyzed Benzocyclobutenone-Ketol Cycloaddition: Merging C-C Bond Activation and Transfer Hydrogenative Coupling for Type II Polyketide Construction. *J. Am. Chem. Soc.* **2018,** *140* (29), 9091-9094.

194. Cabrera, J. M.; Tauber, J.; Zhang, W. D.; Xiang, M.; Krische, M. J., Selection between Diastereomeric Kinetic vs Thermodynamic Carbonyl Binding Modes Enables Enantioselective Iridium-Catalyzed anti-(alpha-Aryl)allylation of Aqueous Fluoral Hydrate and Difluoroacetaldehyde Ethyl Hemiacetal. *J. Am. Chem. Soc.* **2018,** *140* (30), 9392-9395.

195. Choi, K.; Park, H.; Lee, C., Rhodium-Catalyzed Tandem Addition-Cyclization-Rearrangement of Alkynylhydrazones with Organoboronic Acids. *J. Am. Chem. Soc.* **2018,** *140* (33), 10407-10411.

196. Schwamb, C. B.; Fitzpatrick, K. P.; Brueckner, A. C.; Richardson, H. C.; Cheong, P. H. Y.; Scheidt, K. A., Enantioselective Synthesis of alpha-Amidoboronates Catalyzed by Planar-Chiral NHC-Cu(I) Complexes. *J. Am. Chem. Soc.* **2018,** *140* (34), 10644-10648.

197. Moskowitz, M.; Wolf, C., Catalytic Enantioselective Ynamide Additions to Isatins: Concise Access to Oxindole Alkaloids. *Angew. Chem.-Int. Edit.* **2019,** *58* (11), 3402-3406.

198. Schwartz, L. A.; Holmes, M.; Brito, G. A.; Goncalves, T. P.; Richardson, J.; Ruble, J. C.; Huang, K. W.; Krische, M. J., Cyclometalated Iridium-PhanePhos Complexes Are Active Catalysts in Enantioselective Allene-Fluoral Reductive Coupling and Related Alcohol-Mediated Carbonyl Additions That Form Acyclic Quaternary Carbon Stereocenters. *J. Am. Chem. Soc.* **2019,** *141* (5), 2087-2096.

199. Feng, J. J.; Oestreich, M., Tertiary alpha-Silyl Alcohols by Diastereoselective Coupling of 1,3-Dienes and Acylsilanes Initiated by Enantioselective Copper-Catalyzed Borylation. *Angew. Chem.-Int. Edit.* **2019,** *58* (24), 8211-8215.

200. DeRatt, L. G.; Pappoppula, M.; Aponick, A., A Facile Enantioselective Alkynylation of Chromones. *Angew. Chem.-Int. Edit.* **2019,** *58* (25), 8416-8420.

201. Spielmann, K.; Xiang, M.; Schwartz, L. A.; Krische, M. J., Direct Conversion of Primary Alcohols to 1,2-Amino Alcohols: Enantioselective Iridium-Catalyzed Carbonyl Reductive Coupling of Phthalimido-Allene via Hydrogen Auto-Transfer. *J. Am. Chem. Soc.* **2019,** *141* (36), 14136-14141.

202. Groves, A.; Sun, J. W.; Parke, H. R. I.; Callingham, M.; Argent, S. P.; Taylor, L. J.; Lam, H. W., Catalytic enantioselective arylative cyclizations of alkynyl 1,3-diketones by 1,4-rhodium(i) migration. *Chem. Sci.* **2020,** *11* (10), 2759-2764.

203. Lu, Z.; Hu, X.-D.; Zhang, H.; Zhang, X.-W.; Cai, J.; Usman, M.; Cong, H.; Liu, W.-B., Enantioselective Assembly of Cycloenones with a Nitrile-Containing All-Carbon Quaternary Center from Malononitriles Enabled by Ni Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (16), 7328-7333.

204. Gao, P.-S.; Weng, X.-J.; Wang, Z.-H.; Zheng, C.; Sun, B.; Chen, Z.-H.; You, S.-L.; Mei, T.-S., CuII/TEMPO-Catalyzed Enantioselective C(sp3)–H Alkynylation of Tertiary Cyclic Amines through Shono-Type Oxidation. *Angewandte Chemie International Edition* **2020,** *59* (35), 15254-15259.

205. Genoux, A.; González, J. A.; Merino, E.; Nevado, C., Mechanistic Insights into C(sp2)−C(sp)N Reductive Elimination from Gold(III) Cyanide Complexes. *Angewandte Chemie International Edition* **2020,** *59* (41), 17881-17886.

206. Cai, Y.; Ruan, L.-X.; Rahman, A.; Shi, S.-L., Fast Enantio- and Chemoselective Arylation of Ketones with Organoboronic Esters Enabled by Nickel/N-Heterocyclic Carbene Catalysis. *Angewandte Chemie International Edition* **2021,** *60* (10), 5262-5267.

207. Tan, F.; Pu, M.; He, J.; Li, J.; Yang, J.; Dong, S.; Liu, X.; Wu, Y.-D.; Feng, X., Catalytic Asymmetric Homologation of Ketones with α-Alkyl α-Diazo Esters. *J. Am. Chem. Soc.* **2021,** *143* (5), 2394-2402.

208. Xiang, M.; Ghosh, A.; Krische, M. J., Diastereo- and Enantioselective Ruthenium-Catalyzed C-C Coupling of 1-Arylpropynes and Alcohols: Alkynes as Chiral Allylmetal Precursors in Carbonyl anti-(α-Aryl)allylation. *J. Am. Chem. Soc.* **2021,** *143* (7), 2838-2845.

209. Li, L.; Liu, Y.-C.; Shi, H., Nickel-Catalyzed Enantioselective α-Alkenylation of N-Sulfonyl Amines: Modular Access to Chiral α-Branched Amines. *J. Am. Chem. Soc.* **2021,** *143* (11), 4154-4161.

210. Hu, X.-D.; Chen, Z.-H.; Zhao, J.; Sun, R.-Z.; Zhang, H.; Qi, X.; Liu, W.-B., Enantioselective Synthesis of α-All-Carbon Quaternary Center-Containing Carbazolones via Amino-palladation/Desymmetrizing Nitrile Addition Cascade. *J. Am. Chem. Soc.* **2021,** *143* (10), 3734-3740.

211. Xiao, B.-X.; Jiang, B.; Yan, R.-J.; Zhu, J.-X.; Xie, K.; Gao, X.-Y.; Ouyang, Q.; Du, W.; Chen, Y.-C., A Palladium Complex as an Asymmetric π-Lewis Base Catalyst for Activating 1,3-Dienes. *J. Am. Chem. Soc.* **2021,** *143* (12), 4809-4816.

212. Duan, S.; Deng, G.; Zi, Y.; Wu, X.; Tian, X.; Liu, Z.; Li, M.; Zhang, H.; Yang, X.; Walsh, P. J., Nickel-catalyzed enantioselective vinylation of aryl 2-azaallyl anions. *Chem. Sci.* **2021,** *12* (18), 6406-6412.

213. Li, Y.-L.; Zhang, S.-Q.; Chen, J.; Xia, J.-B., Highly Regio- and Enantioselective Reductive Coupling of Alkynes and Aldehydes via Photoredox Cobalt Dual Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (19), 7306-7313.

214. Cai, Y.; Shi, S.-L., Enantioconvergent Arylation of Racemic Secondary Alcohols to Chiral Tertiary Alcohols Enabled by Nickel/N-Heterocyclic Carbene Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (31), 11963-11968.

215. Davies, T. Q.; Murphy, J. J.; Dousset, M.; Fürstner, A., Nickel-Catalyzed Enantioselective Synthesis of Pre-Differentiated Homoallylic syn- or anti-1,2-Diols from Aldehydes and Dienol Ethers. *J. Am. Chem. Soc.* **2021,** *143* (34), 13489-13494.

216. Liang, L.; Zhou, S.; Zhang, W.; Tong, R., Catalytic Asymmetric Alkynylation of 3,4-Dihydro-β-carbolinium Ions Enables Collective Total Syntheses of Indole Alkaloids. *Angewandte Chemie International Edition* **2021,** *60* (47), 25135-25142.

217. De Jesús Cruz, P.; Crawford, E. T.; Liu, S.; Johnson, J. S., Stereodivergent Nucleophilic Additions to Racemic β-Oxo Acid Derivatives: Fast Addition Outcompetes Stereoconvergence in the Archetypal Configurationally Unstable Electrophile. *J. Am. Chem. Soc.* **2021,** *143* (39), 16264-16273.

218. He, Q.; Zhu, L.; Yang, Z.-H.; Zhu, B.; Ouyang, Q.; Du, W.; Chen, Y.-C., Palladium-Catalyzed Modular and Enantioselective cis-Difunctionalization of 1,3-Enynes with Imines and Boronic Reagents. *J. Am. Chem. Soc.* **2021,** *143* (43), 17989-17994.

219. Li, T.; Cheng, X.; Qian, P.; Zhang, L., Gold-catalysed asymmetric net addition of unactivated propargylic C–H bonds to tethered aldehydes. *Nature Catalysis* **2021,** *4* (2), 164-171.

220. Wu, G.; Yao, Y.; Li, G.; Zhang, X.; Qian, H.; Ma, S., Enantioselective Allenation of Terminal Alkynes Catalyzed by Copper Halides of Mixed Oxidation States and Its Application to the Total Synthesis of Scorodonin. *Angewandte Chemie International Edition* **2022,** *61* (4), e202112427.

221. Chen, Z.-H.; Sun, R.-Z.; Yao, F.; Hu, X.-D.; Xiang, L.-X.; Cong, H.; Liu, W.-B., Enantioselective Nickel-Catalyzed Reductive Aryl/Alkenyl–Cyano Cyclization Coupling to All-Carbon Quaternary Stereocenters. *J. Am. Chem. Soc.* **2022,** *144* (11), 4776-4782.

222. Wen, W.; Ai, Z.-P.; Yang, C.-L.; Li, C.-X.; Wu, Z.-L.; Cai, T.; Guo, Q.-X., Enantioselective synthesis of α-amino ketones through palladium-catalyzed asymmetric arylation of α-keto imines. *Chem. Sci.* **2022,** *13* (13), 3796-3802.

223. Dong, Y.; Schuppe, A. W.; Mai, B. K.; Liu, P.; Buchwald, S. L., Confronting the Challenging Asymmetric Carbonyl 1,2-Addition Using Vinyl Heteroarene Pronucleophiles: Ligand-Controlled Regiodivergent Processes through a Dearomatized Allyl–Cu Species. *J. Am. Chem. Soc.* **2022,** *144* (13), 5985-5995.

224. Ji, H.; Lin, D.; Tai, L.; Li, X.; Shi, Y.; Han, Q.; Chen, L.-A., Nickel-Catalyzed Enantioselective Coupling of Acid Chlorides with α-Bromobenzoates: An Asymmetric Acyloin Synthesis. *J. Am. Chem. Soc.* **2022,** *144* (50), 23019-23029.

225. Guo, X.; Shi, Z.; Zhang, F.-H.; Wang, Z., Cr-Catalyzed Regio-, Diastereo-, and Enantioselective Reductive Couplings of Ketones and Propargyl Halides. *ACS Catalysis* **2023,** *13* (5), 3170-3178.

226. Ruan, L.-X.; Sun, B.; Liu, J.-M.; Shi, S.-L., Dynamic kinetic asymmetric arylation and alkenylation of ketones. *Science* **2023,** *379* (6633), 662-670.

227. Chen, P.; Tan, S.-Z.; Zhu, L.; Ouyang, Q.; Jia, Z.-J.; Du, W.; Chen, Y.-C., Palladium-Catalyzed Inverse and Normal Dehydrogenative Aza-Morita–Baylis–Hillman Reactions with γ,δ-Unsaturated Compounds. *Angewandte Chemie International Edition* **2023,** *62* (23), e202301519.

228. Bishop, H. D.; Zhao, Q.; Uyeda, C., Catalytic Asymmetric Synthesis of Zinc Metallacycles. *J. Am. Chem. Soc.* **2023,** *145* (37), 20152-20157.

229. Pappoppula, M.; Olsen, K. L.; Ketelboeter, D. R.; Aponick, A., Enantio- and Regioselective Copper-Catalyzed 1,2-Dearomatization of Pyridines. *Angewandte Chemie International Edition* **2023,** *62* (48), e202312967.

230. Wen, L.; Ding, J.; Duan, L.; Wang, S.; An, Q.; Wang, H.; Zuo, Z., Multiplicative enhancement of stereoenrichment by a single catalyst for deracemization of alcohols. *Science* **2023,** *382* (6669), 458-464.

231. Wu, X.; Xia, H.; Gao, C.; Luan, B.; Wu, L.; Zhang, C.; Yang, D.; Hou, L.; Liu, N.; Xia, T.; Li, H.; Qu, J.; Chen, Y., Modular α-tertiary amino ester synthesis through cobalt-catalysed asymmetric aza-Barbier reaction. *Nat. Chem.* **2024,** *16* (3), 398-407.

232. Huang, C.; Tao, Y.; Cao, X.; Zhou, C.; Lu, Q., Asymmetric Paired Electrocatalysis: Enantioselective Olefin–Sulfonylimine Coupling. *J. Am. Chem. Soc.* **2024,** *146* (3), 1984-1991.

233. Cuesta-Galisteo, S.; Schörgenhumer, J.; Hervieu, C.; Nevado, C., Dual Nickel/Photoredox-Catalyzed Asymmetric Carbamoylation of Benzylic C(sp3)−H Bonds. *Angewandte Chemie International Edition* **2024,** *63* (12), e202313717.

234. Yin, S.; Weeks, K. N.; Aponick, A., Catalytic Enantioselective Alkyne Addition to Nitrones Enabled by Tunable Axially Chiral Imidazole-Based P,N-Ligands. *J. Am. Chem. Soc.* **2024,** *146* (11), 7185-7190.

235. Ketelboeter, D. R.; Pappoppula, M.; Aponick, A., Chemoselective Diazine Dearomatization: The Catalytic Enantioselective Dearomatization of Pyrazine. *J. Am. Chem. Soc.* **2024,** *146* (17), 11610-11615.

236. Chen, Z.-H.; Gu, L.-J.; Wang, B.; Xiao, L.-J.; Ye, M.; Zhou, Q.-L., Regioselective and Enantioselective Nickel-Catalyzed Intermolecular Reductive Coupling of Aliphatic Alkenes with Imines. *J. Am. Chem. Soc.* **2024,** *146* (22), 14915-14921.

237. Bender, T.; Fürstner, A., Enantioselective Synthesis of vic-Aminoalcohol Derivatives by Nickel-Catalyzed Reductive Coupling of Aldehydes with Protected Amino-pentadienoates. *J. Am. Chem. Soc.* **2024,** *146* (49), 33295-33301.

238. Ni, C.; Ramspoth, T.-F.; Reis, M. C.; Harutyunyan, S. R., Manganese(I)-Catalyzed Access to Enantioenriched Chiral Aziridine Phosphines. *Angewandte Chemie International Edition* **2025,** *64* (3), e202415623.

4.5.4 Conjugate Reduction/Hydrogenation

1. Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J., ASYMMETRIC HYDROGENATION - RHODIUM CHIRAL BISPHOSPHINE CATALYST. *J. Am. Chem. Soc.* **1977,** *99* (18), 5946-5952.

2. Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R., SYNTHESIS OF 2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL (BINAP), AN ATROPISOMERIC CHIRAL BIS(TRIARYL)PHOSPHINE, AND ITS USE IN THE RHODIUM(I)-CATALYZED ASYMMETRIC HYDROGENATION OF ALPHA-(ACYLAMINO)ACRYLIC ACIDS. *J. Am. Chem. Soc.* **1980,** *102* (27), 7932-7934.

3. Ohgo, Y.; Takeuchi, S.; Natori, Y.; Yoshimura, J., Asymmetric Reactions .10. Asymmetric Hydrogenation Catalyzed by Bis(Dimethylglyoximato)Cobalt(Ii)-Chiral Co-Catalyst (Amino Alcohol) System. *Bull. Chem. Soc. Jpn.* **1981,** *54* (7), 2124-2135.

4. Landis, C. R.; Halpern, J., ASYMMETRIC HYDROGENATION OF METHYL-(Z)-ALPHA-ACETAMIDOCINNAMATE CATALYZED BY (1,2-BIS((PHENYL-ORTHO-ANISOYL)PHOSPHINO)ETHANE)RHODIUM(I) - KINETICS, MECHANISM, AND ORIGIN OF ENANTIOSELECTION. *J. Am. Chem. Soc.* **1987,** *109* (6), 1746-1754.

5. Vonmatt, P.; Pfaltz, A., Enantioselective Conjugate Reduction of Alpha,Beta-Unsaturated Carboxamides with Semicorrin Cobalt Catalysts. *Tetrahedron: Asymmetry* **1991,** *2* (7), 691-700.

6. Misun, M.; Pfaltz, A., Enantioselective reduction of electrophilic C=C bonds with sodium tetrahydroborate and 'Semicorrin' cobalt catalysts. *Helv. Chim. Acta* **1996,** *79* (4), 961-972.

7. Appella, D. H.; Moritani, Y.; Shintani, R.; Ferreira, E. M.; Buchwald, S. L., Asymmetric conjugate reduction of alpha,beta-unsaturated esters using a chiral phosphine-copper catalyst. *J. Am. Chem. Soc.* **1999,** *121* (40), 9473-9474.

8. Hu, A. G.; Fu, Y.; Xie, J. H.; Zhou, H.; Wang, L. X.; Zhou, Q. L., Monodentate chiral spiro phosphoramidites: Efficient ligands for rhodium-catalyzed enantioselective hydrogenation of enamides. *Angew. Chem.-Int. Edit.* **2002,** *41* (13), 2348-2350.

9. Kitamura, M.; Tsukamoto, M.; Bessho, Y.; Yoshimura, M.; Kobs, U.; Widhalm, M.; Noyori, R., Mechanism of asymmetric hydrogenation of alpha- (acylamino)acrylic esters catalyzed by BINAP-ruthenium(II) diacetate. *J. Am. Chem. Soc.* **2002,** *124* (23), 6649-6667.

10. Knowles, W. S., Asymmetric hydrogenations (Nobel lecture). *Angew. Chem.-Int. Edit.* **2002,** *41* (12), 1999-2007.

11. Pena, D.; Minnaard, A. J.; de Vries, J. G.; Feringa, B. L., Highly enantioselective rhodium-catalyzed hydrogenation of beta-dehydroamino acid derivatives using monodentate phosphoramidites. *J. Am. Chem. Soc.* **2002,** *124* (49), 14552-14553.

12. Tang, W. J.; Zhang, X. M., Highly efficient synthesis of chiral beta-amino acid derivatives via asymmetric hydrogenation. *Org. Lett.* **2002,** *4* (23), 4159-4161.

13. Yue, T. Y.; Nugent, W. A., Enantioselective hydrogenation of 3-alkylidenelactams: High- throughput screening provides a surprising solution. *J. Am. Chem. Soc.* **2002,** *124* (46), 13692-13693.

14. Hua, Z. H.; Vassar, V. C.; Ojima, I., Synthesis of new chiral monodentate phosphite ligands and their use in catalytic asymmetric hydrogenation. *Org. Lett.* **2003,** *5* (21), 3831-3834.

15. Hughes, G.; Kimura, M.; Buchwald, S. L., Catalytic enantioselective conjugate reduction of lactones and lactams. *J. Am. Chem. Soc.* **2003,** *125* (37), 11253-11258.

16. Pena, D.; Minnaard, A. J.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L., Mono- versus bidentate ligands in rhodium-catalyzed asymmetric hydrogenation. A comparative rate study. *Org. Lett.* **2003,** *5* (4), 475-478.

17. Czekelius, C.; Carreira, E. M., Convenient catalytic, enantioselective conjugate reduction of nitroalkenes using CuF2. *Org. Lett.* **2004,** *6* (24), 4575-4577.

18. Fu, Y.; Guo, X. X.; Zhu, S. F.; Hu, A. G.; Xie, J. H.; Zhou, Q. L., Rhodium-catalyzed asymmetric hydrogenation of functionalized olefins using monodentate spiro phosphoramidite ligands. *J. Org. Chem.* **2004,** *69* (14), 4648-4655.

19. Hoen, R.; van den Berg, M.; Bernsmann, H.; Minnaard, A. J.; de Vries, J. G.; Feringa, B. L., Catechol-based phosphoramidites: A new class of chiral ligands for rhodium-catalyzed asymmetric hydrogenations. *Org. Lett.* **2004,** *6* (9), 1433-1436.

20. Hoge, G.; Wu, H. P.; Kissel, W. S.; Pflum, D. A.; Greene, D. J.; Bao, J., Highly selective asymmetric hydrogenation using a three hindered quadrant bisphosphine rhodium catalyst. *J. Am. Chem. Soc.* **2004,** *126* (19), 5966-5967.

21. Hu, X. P.; Zheng, Z., Unsymmetrical hybrid ferrocene-based phosphine- phosphoramidites: A new class of practical Ligands for Rh-catalyzed asymmetric hydrogenation. *Org. Lett.* **2004,** *6* (20), 3585-3588.

22. Lipshutz, B. H.; Servesko, J. M.; Petersen, T. B.; Papa, P. P.; Lover, A. A., Asymmetric 1,4-reductions of hindered beta-substituted cycloalkenones using catalytic SEGPHOS-ligated CuH. *Org. Lett.* **2004,** *6* (8), 1273-1275.

23. Lipshutz, B. H.; Servesko, J. M.; Taft, B. R., Asymmetric 1,4-hydrosilylations of alpha,beta-unsaturated esters. *J. Am. Chem. Soc.* **2004,** *126* (27), 8352-8353.

24. Wu, H. P.; Hoge, G., Highly enantioselective asymmetric hydrogenation of beta- acetamido dehydroamino acid derivatives using a three-hindered quadrant rhodium catalyst. *Org. Lett.* **2004,** *6* (20), 3645-3647.

25. Wu, S. L.; Zhang, W. C.; Zhang, Z. G.; Zhang, X. M., Synthesis of new monodentate spiro phosphoramidite ligand and its application in Rh-catalyzed asymmetric hydrogenation reactions. *Org. Lett.* **2004,** *6* (20), 3565-3567.

26. Hoen, R.; Boogers, J. A. F.; Bernsmann, H.; Minnaard, A. J.; Meetsma, A.; Tiemersma-Wegman, T. D.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L., Achiral ligands dramatically enhance rate and enantioselectivity in the Rh/phosphoramidite-catalyzed hydrogenation of alpha,beta-disubstituted unsaturated acids. *Angew. Chem.-Int. Edit.* **2005,** *44* (27), 4209-4212.

27. Hu, X. P.; Zhuo, Z., Practical Rh(I)-catalyzed asymmetric hydrogenation of beta-(acylamino)acrylates using a new unsymmetrical hybrid ferrocenylphosphine-phosphoramidite ligand: Crucial influence of an N-H proton in the ligand. *Org. Lett.* **2005,** *7* (3), 419-422.

28. Panella, L.; Feringa, B. L.; de Vries, J. G.; Minnaard, A. J., Enantioselective Rh-catalyzed hydrogenation of enol acetates and enol carbamates with monodentate phosphoramidites. *Org. Lett.* **2005,** *7* (19), 4177-4180.

29. Lee, D.; Kim, D.; Yun, J., Highly enantioselective conjugate reduction of beta,beta-disubstituted alpha,beta-unsaturated nitriles. *Angew. Chem.-Int. Edit.* **2006,** *45* (17), 2785-2787.

30. Lipshutz, B. H.; Tanaka, N.; Taft, B. R.; Lee, C. T., Chiral silanes via asymmetric hydrosilylation with catalytic CuH. *Org. Lett.* **2006,** *8* (10), 1963-1966.

31. Tsuchiya, Y.; Hamashima, Y.; Sodeoka, M., A new entry to Pd-H chemistry: Catalytic asymmetric conjugate reduction of enones with EtOH and a highly enantioselective synthesis of warfarin. *Org. Lett.* **2006,** *8* (21), 4851-4854.

32. Chen, W. P.; McCormack, P. J.; Mohammed, K.; Mbafor, W.; Roberts, S. M.; Whittall, J., Stereoselective synthesis of ferrocene-based C-2-symmetric diphosphine ligands: Application to the highly enantioselective hydrogenation of alpha-substituted cinnamic acids. *Angew. Chem.-Int. Edit.* **2007,** *46* (22), 4141-4144.

33. Desrosiers, J. N.; Charette, A. B., Catalytic enantioselective reduction of beta,beta-disubstituted vinyl phenyl Sulfones by using bisphosphine monoxide Ligands. *Angew. Chem.-Int. Edit.* **2007,** *46* (31), 5955-5957.

34. Ito, M.; Endo, Y.; Ikariya, T., Well-Defined Triflylamide-Tethered Arene-Ru(Tsdpen) Complexes for Catalytic Asymmetric Hydrogenation of Ketones. *Organometallics* **2008,** *27* (23), 6053-6055.

35. Jiang, H. Y.; Yang, C. F.; Li, C.; Fu, H. Y.; Chen, H.; Li, R. X.; Li, X. J. In *Heterogeneous Enantioselective Hydrogenation of Aromatic Ketones Catalyzed by Cinchona- and Phosphine-Modified Iridium Catalysts*, International Sympsium on Creation and Control of Advanced Selective Catalysis, Kyoto, JAPAN, 2008; Kyoto, JAPAN, 2008; pp 9240-9244.

36. Li, C. Q.; Xiao, J. L., Asymmetric hydrogenation of cyclic imines with an ionic Cp*Rh(III) catalyst. *J. Am. Chem. Soc.* **2008,** *130* (40), 13208-13209.

37. Shaikh, N. S.; Enthaler, S.; Junge, K.; Beller, M., Iron-catalyzed enantioselective hydrosilylation of ketones. *Angew. Chem.-Int. Edit.* **2008,** *47* (13), 2497-2501.

38. Breuil, P. A. R.; Patureau, F. W.; Reek, J. N. H., Singly Hydrogen Bonded Supramolecular Ligands for Highly Selective Rhodium-Catalyzed Hydrogenation Reactions. *Angew. Chem.-Int. Edit.* **2009,** *48* (12), 2162-2165.

39. Breuil, P. A. R.; Reek, J. N. H., Amino Acid Based Phosphoramidite Ligands for the Rhodium-Catalyzed Asymmetric Hydrogenation. *Eur. J. Org. Chem.* **2009,** (35), 6225-6230.

40. Rupnicki, L.; Saxena, A.; Lam, H. W., Aromatic Heterocycles as Activating Groups for Asymmetric Conjugate Addition Reactions. Enantioselective Copper-Catalyzed Reduction of 2-Alkenylheteroarenes. *J. Am. Chem. Soc.* **2009,** *131* (30), 10386-+.

41. Soltani, O.; Ariger, M. A.; Carreira, E. M., Transfer Hydrogenation in Water: Enantioselective, Catalytic Reduction of (E)-beta,beta-Disubstituted Nitroalkenes. *Org. Lett.* **2009,** *11* (18), 4196-4198.

42. Wu, H. C.; Hamid, S. A.; Yu, J. Q.; Spencer, J. B., Possible Origin of Electronic Effects in Rh(I)-Catalyzed Enantioselective Hydrogenation. *J. Am. Chem. Soc.* **2009,** *131* (28), 9604-9605.

43. Moser, R.; Boskovic, Z. V.; Crowe, C. S.; Lipshutz, B. H., CuH-Catalyzed Enantioselective 1,2-Reductions of alpha,beta-Unsaturated Ketones. *J. Am. Chem. Soc.* **2010,** *132* (23), 7852-+.

44. van Leeuwen, P.; Rivillo, D.; Raynal, M.; Freixa, Z., Enantioselective Supramolecular Catalysis Induced by Remote Chiral Diols. *J. Am. Chem. Soc.* **2011,** *133* (46), 18562-18565.

45. Zhang, J. Z.; Li, Y.; Wang, Z.; Ding, K. L., Asymmetric Hydrogenation of a- and ss-Enamido Phosphonates: Rhodium(I)/Monodentate Phosphoramidite Catalyst. *Angew. Chem.-Int. Edit.* **2011,** *50* (49), 11743-11747.

46. Wang, X. M.; Han, Z. B.; Wang, Z.; Ding, K. L., Catalytic Asymmetric Synthesis of Aromatic Spiroketals by SpinPhox/Iridium(I)-Catalyzed Hydrogenation and Spiroketalization of a,a'-Bis(2-hydroxyarylidene) Ketones. *Angew. Chem.-Int. Edit.* **2012,** *51* (4), 936-940.

47. Mueller, M.-A.; Pfaltz, A., Asymmetric Hydrogenation of alpha,beta-Unsaturated Nitriles with Base-Activated Iridium N,P Ligand Complexes. *Angew. Chem.-Int. Edit.* **2014,** *53* (33), 8668-8671.

48. Gao, M.; Meng, J.-j.; Lv, H.; Zhang, X., Highly Regio- and Enantioselective Synthesis of gamma,delta-Unsaturated Amido Esters by Catalytic Hydrogenation of Conjugated Enamides. *Angew. Chem.-Int. Edit.* **2015,** *54* (6), 1885-1887.

49. Li, W.; Schlepphorst, C.; Daniliuc, C.; Glorius, F., Asymmetric Hydrogenation of Vinylthioethers: Access to Optically Active 1,5-Benzothiazepine Derivatives. *Angew. Chem.-Int. Edit.* **2016,** *55* (10), 3300-3303.

50. Trost, B. M.; Masters, J. T.; Taft, B. R.; Lumb, J. P., Asymmetric synthesis of chiral beta-alkynyl carbonyl and sulfonyl derivatives via sequential palladium and copper catalysis. *Chem. Sci.* **2016,** *7* (9), 6217-6231.

51. Zhou, Y. J.; Bandar, J. S.; Liu, R. Y.; Buchwald, S. L., CuH-Catalyzed Asymmetric Reduction of alpha,beta-Unsaturated Carboxylic Acids to beta-Chiral Aldehydes. *J. Am. Chem. Soc.* **2018,** *140* (2), 606-609.

52. Armstrong, R. J.; Akhtar, W. M.; Young, T. A.; Duarte, F.; Donohoe, T. J., Catalytic Asymmetric Synthesis of Cyclohexanes by Hydrogen Borrowing Annulations. *Angew. Chem.-Int. Edit.* **2019,** *58* (36), 12558-12562.

53. Onneken, C.; Bussmann, K.; Gilmour, R., Inverting External Asymmetric Induction via Selective Energy Transfer Catalysis: A Strategy to β-Chiral Phosphonate Antipodes. *Angewandte Chemie International Edition* **2020,** *59* (1), 330-334.

54. Yamani, K.; Pierre, H.; Archambeau, A.; Meyer, C.; Cossy, J., Asymmetric Transfer Hydrogenation of gem-Difluorocyclopropenyl Esters: Access to Enantioenriched gem-Difluorocyclopropanes. *Angewandte Chemie International Edition* **2020,** *59* (42), 18505-18509.

55. Nishino, S.; Miura, M.; Hirano, K., An umpolung-enabled copper-catalysed regioselective hydroamination approach to α-amino acids. *Chem. Sci.* **2021,** *12* (34), 11525-11537.

56. Czekelius, C.; Carreira, E. M., Catalytic enantioselective conjugate reduction of beta,beta- disubstituted nitroalkenes. *Angew. Chem.-Int. Edit.* **2003,** *42* (39), 4793-4795.

57. Lipshutz, B. H.; Servesko, J. M., CuH-catalyzed asymmetric conjugate reductions of acyclic enones. *Angew. Chem.-Int. Edit.* **2003,** *42* (39), 4789-4792.

58. Hsiao, Y.; Rivera, N. R.; Rosner, T.; Krska, S. W.; Njolito, E.; Wang, F.; Sun, Y. K.; Armstrong, J. D.; Grabowski, E. J. J.; Tillyer, R. D.; Spindler, F.; Malan, C., Highly efficient synthesis of beta-amino acid derivatives via asymmetric hydrogenation of unprotected enamines. *J. Am. Chem. Soc.* **2004,** *126* (32), 9918-9919.

4.5.5 Conjugate Addition

1. deVries, A. H. M.; Meetsma, A.; Feringa, B. L., Enantioselective conjugate addition of dialkylzinc reagents to cyclic and acyclic enones catalyzed by chiral copper complexes of new phosphorus amidites. *Angew. Chem.-Int. Edit. Engl.* **1996,** *35* (20), 2374-2376.

2. Gomez-Bengoa, E.; Heron, N. M.; Didiuk, M. T.; Luchaco, C. A.; Hoveyda, A. H., Ni-catalyzed asymmetric addition of Grignard reagents to unsaturated cyclic acetals. The influence of added phosphine on enantioselectivity. *J. Am. Chem. Soc.* **1998,** *120* (30), 7649-7650.

3. Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N., Rhodium-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids to enones. *J. Am. Chem. Soc.* **1998,** *120* (22), 5579-5580.

4. Versleijen, J. P. G.; van Leusen, A. M.; Feringa, B. L., Copper(I) phosphoramidite catalyzed asymmetric conjugate addition of dialkylzinc reagents to alpha,beta-unsaturated nitroacetates; an enantioselective route to beta-aryl- nitroalkanes. *Tetrahedron Lett.* **1999,** *40* (31), 5803-5806.

5. Pichota, A.; Pregosin, P. S.; Valentini, M.; Worle, M.; Seebach, D., X-ray, molecular diffusion, and NOESY NMR studies of chiral, tetranuclear Cu-I catalysts based on monodentate thiol analogues of TADDOL. *Angew. Chem.-Int. Edit.* **2000,** *39* (1), 153-+.

6. Degrado, S. J.; Mizutani, H.; Hoveyda, A. H., Efficient cu-catalyzed asymmetric conjugate additions of alkylzincs to trisubstituted cyclic enones. *J. Am. Chem. Soc.* **2002,** *124* (45), 13362-13363.

7. Liang, L.; Au-Yeung, T. T. L.; Chan, A. S. C., Highly enantioselective 1,4-addition of diorganozinc reagents to cyclic enones using chiral diphosphite ligands derived from H-8-binaphthol. *Org. Lett.* **2002,** *4* (22), 3799-3801.

8. Luchaco-Cullis, C. A.; Hoveyda, A. H., Cu-catalyzed enantioselective conjugate addition of alkylzincs to cyclic nitroalkenes: Catalytic asymmetric synthesis of cyclic alpha-substituted ketones. *J. Am. Chem. Soc.* **2002,** *124* (28), 8192-8193.

9. Shintani, R.; Fu, G. C., Copper-catalyzed enantioselective conjugate addition of diethylzinc to acyclic enones in the presence of planar-chiral phosphaferrocene-oxazoline ligands. *Org. Lett.* **2002,** *4* (21), 3699-3702.

10. Zhou, H.; Wang, W. H.; Fu, Y.; Xie, J. H.; Shi, W. J.; Wang, L. X.; Zhou, Q. L., Highly enantioselective copper-catalyzed conjugate addition of diethylzinc to enones using chiral spiro phosphoramidites as ligands. *J. Org. Chem.* **2002,** *68* (4), 1582-1584.

11. Hayashi, T.; Tokunaga, N.; Yoshida, K.; Han, J. W., Rhodium-catalyzed asymmetric 1,4-addition of aryltitanium reagents generating chiral titanium enolates: Isolation as silyl enol ethers. *J. Am. Chem. Soc.* **2002,** *124* (41), 12102-12103.

12. Bertozzi, F.; Pineschi, M.; Macchia, F.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L., Copper phosphoramidite catalyzed enantioselective ring-opening of oxabicyclic alkenes: Remarkable reversal of stereocontrol. *Org. Lett.* **2002,** *4* (16), 2703-2705.

13. Duursma, A.; Minnaard, A. J.; Feringa, B. L., Highly enantioselective conjugate addition of dialkylzinc reagents to acyclic nitroalkenes: A catalytic route to beta(2)- amino acids, aldehydes, and alcohols. *J. Am. Chem. Soc.* **2003,** *125* (13), 3700-3701.

14. Hird, A. W.; Hoveyda, A. H., Cu-catalyzed enantioselective conjugate additions of alkyl zinc reagents to unsaturated N-acyloxazolidinones promoted by a chiral triamide phosphane. *Angew. Chem.-Int. Edit.* **2003,** *42* (11), 1276-1279.

15. Hu, Y. C.; Liang, X. M.; Wang, J. W.; Zheng, Z.; Hu, X. Q., Readily prepared chiral P,N Ligands and their applications in Cu-catalyzed enantioselective conjugate additions. *J. Org. Chem.* **2003,** *68* (11), 4542-4545.

16. Krauss, I. J.; Leighton, J. L., Highly practical and enantioselective Cu-catalyzed conjugate addition of alkylzinc reagents to cyclic enones at ambient temperature. *Org. Lett.* **2003,** *5* (18), 3201-3203.

17. Liang, L.; Su, L. M.; Li, X. S.; Chan, A. S. C., Highly enantioselective 1,4-conjugate addition of dialkylzinc to alpha,beta-unsaturated lactone catalyzed by diphosphite- copper complexes. *Tetrahedron Lett.* **2003,** *44* (38), 7217-7220.

18. Wan, H. H.; Hu, Y. C.; Liang, Y. X.; Gao, S.; Wang, J. W.; Zheng, Z.; Hu, X. Q., Highly enantioselective conjugate addition of diethylzinc to acyclic enones with fine-tunable phosphite-pyridine ligands. *J. Org. Chem.* **2003,** *68* (21), 8277-8280.

19. Watanabe, T.; Knopfel, T. F.; Carreira, E. M., Asymmetric conjugate addition reactions of Meldrum's acid derived acceptors employing chiral phosphoramidite ligands. *Org. Lett.* **2003,** *5* (24), 4557-4558.

20. Christoffers, J.; Baro, A., Construction of quaternary stereocenters: New perspectives through enantioselective Michael reactions. *Angew. Chem.-Int. Edit.* **2003,** *42* (15), 1688-1690.

21. Doi, H.; Sakai, T.; Iguchi, M.; Yamada, K.; Tomioka, K., Chiral ligand-controlled asymmetric conjugate addition of lithium amides to enoates. *J. Am. Chem. Soc.* **2003,** *125* (10), 2886-2887.

22. Boiteau, J. G.; Imbos, F.; Minnaard, A. J.; Feringa, B. L., Rhodium-catalyzed asymmetric conjugate additions of boronic acids using monodentate phosphoramidite ligands. *Org. Lett.* **2003,** *5* (5), 681-684.

23. Boiteau, J. G.; Minnaard, A. J.; Feringa, B. L., High efficiency and enantioselectivity in the Rh-catalyzed conjugate addition of arylboronic acids using monodentate phosphoramidites. *J. Org. Chem.* **2003,** *68* (24), 9481-9484.

24. Duursma, A.; Hoen, R.; Schuppan, J.; Hulst, R.; Minnaard, A. J.; Feringa, B. L., First examples of improved catalytic asymmetric C-C bond formation using the monodentate ligand combination approach. *Org. Lett.* **2003,** *5* (17), 3111-3113.

25. Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K., A chiral chelating diene as a new type of chiral ligand for transition metal catalysts: Its preparation and use for the rhodium-catalyzed asymmetric 1,4-addition. *J. Am. Chem. Soc.* **2003,** *125* (38), 11508-11509.

26. Oi, S.; Taira, A.; Honma, Y.; Inoue, Y., Asymmetric 1,4-addition of organosiloxanes to alpha,beta- unsaturated carbonyl compounds catalyzed by a chiral rhodium complex. *Org. Lett.* **2003,** *5* (1), 97-99.

27. Shi, Q.; Xu, L. J.; Li, X. S.; Jia, X.; Wang, R. H.; Au-Yeung, T. T. L.; Chan, A. S. C.; Hayashi, T.; Cao, R.; Hong, M. C., Bipyridyl-based diphosphine as an efficient ligand in the rhodium-catalyzed asymmetric conjugate addition of arylboronic acids to alpha,beta-unsaturated ketones. *Tetrahedron Lett.* **2003,** *44* (34), 6505-6508.

28. Yoshida, K.; Ogasawara, M.; Hayashi, T., Generation of chiral boron enolates by rhodium-catalyzed asymmetric 1,4-addition of 9-aryl-9-borabicyclo 3.3.1 nonanes (B-Ar-9BBN) to alpha,beta-unsaturated ketones. *J. Org. Chem.* **2003,** *68* (5), 1901-1905.

29. Piarulli, U.; Claverie, C.; Daubos, P.; Gennari, C.; Minnaard, A. J.; Feringa, B. L., Copper phosphoramidite-catalyzed enantioselective desymmetrization of meso-cyclic allylic bisdiethyl phosphates. *Org. Lett.* **2003,** *5* (23), 4493-4496.

30. Cauble, D. F.; Gipson, J. D.; Krische, M. J., Diastereo- and enantioselective catalytic carbometallative aldol cycloreduction: Tandem conjugate addition-aldol cyclization. *J. Am. Chem. Soc.* **2003,** *125* (5), 1110-1111.

31. Subburaj, K.; Montgomery, J., A new catalytic conjugate addition/aldol strategy that avoids preformed metalated nucleophiles. *J. Am. Chem. Soc.* **2003,** *125* (37), 11210-11211.

32. Watanabe, M.; Murata, K.; Ikariya, T., Enantioselective Michael reaction catalyzed by well-defined chiral Ru amido complexes: Isolation and characterization of the catalyst intermediate, Ru malonato complex having a metal- carbon bond. *J. Am. Chem. Soc.* **2003,** *125* (25), 7508-7509.

33. Alexakis, A.; Polet, D.; Rosset, S.; March, S., Biphenol-based phosphoramidite ligands for the enantioselective copper-catalyzed conjugate addition of diethylzine. *J. Org. Chem.* **2004,** *69* (17), 5660-5667.

34. Arink, A. M.; Braam, T. W.; Keeris, R.; Jastrzebski, J.; Benhaim, C.; Rosset, S.; Alexakis, A.; van Koten, G., Copper(I) thiolate catalysts in asymmetric conjugate addition reactions. *Org. Lett.* **2004,** *6* (12), 1959-1962.

35. Choi, H.; Hua, Z. H.; Ojima, I., Highly enantioselective copper-catalyzed conjugate addition of diethylzinc to nitroalkenes. *Org. Lett.* **2004,** *6* (16), 2689-2691.

36. Duncan, A. P.; Leighton, J. L., Enantioselective Cu-catalyzed conjugate addition of diethylzinc to acyclic aliphatic enones. *Org. Lett.* **2004,** *6* (22), 4117-4119.

37. Lopez, F.; Harutyunyan, S. R.; Minnaard, A. J.; Feringa, B. L., Copper-catalyzed enantioselective conjugate addition of Grignard reagents to acyclic enones. *J. Am. Chem. Soc.* **2004,** *126* (40), 12784-12785.

38. Mampreian, D. M.; Hoveyda, A. H., Efficient Cu-catalyzed asymmetric conjugate additions of alkylzinc reagents to aromatic and aliphatic acyclic nitroalkenes. *Org. Lett.* **2004,** *6* (16), 2829-2832.

39. Palomo, C.; Oiarbide, M.; Halder, R.; Kelso, M.; Gomez-Bengoa, E.; Garcia, J. M., Catalytic enantioselective conjugate addition of carbamates. *J. Am. Chem. Soc.* **2004,** *126* (30), 9188-9189.

40. Defieber, C.; Paquin, J. F.; Serna, S.; Carreira, E. M., Chiral 2.2.2 dienes as ligands for Rh(I) in conjugate additions of boronic acids to a wide range of acceptors. *Org. Lett.* **2004,** *6* (21), 3873-3876.

41. Duursma, A.; Boiteau, J. G.; Lefort, L.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G.; Minnaard, A. J.; Feringa, B. L., Highly enantioselective conjugate additions of potassium organotrifluoroborates to enones by use of monodentate phosphoramidite ligands. *J. Org. Chem.* **2004,** *69* (23), 8045-8052.

42. Hayashi, T.; Tokunaga, N.; Inoue, K., Rhodium-catalyzed asymmetric 1,6-addition of aryltitanates to enynones giving axially chiral allenes. *Org. Lett.* **2004,** *6* (2), 305-307.

43. Mauleon, P.; Carretero, J. C., Rhodium-catalyzed enantioselective conjugate addition of organoboronic acids to alpha,beta-unsaturated sulfones. *Org. Lett.* **2004,** *6* (18), 3195-3198.

44. Shintani, R.; Tokunaga, N.; Doi, H.; Hayashi, T., A new entry of nucleophiles in rhodium-catalyzed asymmetric 1,4-addition reactions: Addition of organozinc reagents for the synthesis of 2-aryl-4-piperidones. *J. Am. Chem. Soc.* **2004,** *126* (20), 6240-6241.

45. Shintani, R.; Ueyama, K.; Yamada, I.; Hayashi, T., Chiral norbornadienes as efficient ligands for the rhodium- catalyzed asymmetric 1,4-addition of arylboronic acids to fumaric and maleic compounds. *Org. Lett.* **2004,** *6* (19), 3425-3427.

46. Hamashima, Y.; Somei, H.; Shimura, Y.; Tamura, T.; Sodeoka, M., Amine-salt-controlled, catalytic asymmetric conjugate addition of various amines and asymmetric protonation. *Org. Lett.* **2004,** *6* (11), 1861-1864.

47. Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T., Catalytic enantioselective Michael addition of 1,3-dicarbonyl compounds to nitroalkenes catalyzed by well-defined chiral Ru amido complexes. *J. Am. Chem. Soc.* **2004,** *126* (36), 11148-11149.

48. Wu, T. R.; Chong, J. M., Ligand-catalyzed asymmetric alkynylboration of enones: A new paradigm for asymmetric synthesis using organoboranes. *J. Am. Chem. Soc.* **2005,** *127* (10), 3244-3245.

49. Brown, M. K.; Degrado, S. J.; Hoveyda, A. H., Highly enantioselective Cu-catalyzed conjugate additions of dialkylzinc reagents to unsaturated furanones and pyranones: Preparation of air-stable and catalytically active Cu-peptide complexes. *Angew. Chem.-Int. Edit.* **2005,** *44* (33), 5306-5310.

50. d'Augustin, M.; Palais, L.; Alexakis, A., Enantioselective copper-catalyzed conjugate addition to trisubstituted cyclohexenones: Construction of stereogenic quaternary centers. *Angew. Chem.-Int. Edit.* **2005,** *44* (9), 1376-1378.

51. Esquivias, J.; Arrayas, R. G.; Carretero, J. C., Copper-catalyzed enantioselective conjugate addition of dialkylzinc reagents to (2-pyridyl)sulfonyl imines of chalcones. *J. Org. Chem.* **2005,** *70* (18), 7451-7454.

52. Hird, A. W.; Hoveyda, A. H., Catalytic enantioselective alkylations of tetrasubstituted olefins. Synthesis of all-carbon quaternary stereogenic centers through Cu-catalyzed asymmetric conjugate additions of alkylzinc reagents to enones. *J. Am. Chem. Soc.* **2005,** *127* (43), 14988-14989.

53. Knopfel, T. F.; Zarotti, P.; Ichikawa, T.; Carreira, E. M., Catalytic, enantioselective, conjugate alkyne addition. *J. Am. Chem. Soc.* **2005,** *127* (27), 9682-9683.

54. Lopez, F.; Harutyunyan, S. R.; Meetsma, A.; Minnaard, A. J.; Feringa, B. L., Copper-catalyzed enantioselective conjugate addition of Grignard reagents to alpha,beta-unsaturated esters. *Angew. Chem.-Int. Edit.* **2005,** *44* (18), 2752-2756.

55. Soeta, T.; Kuriyama, M.; Tomioka, K., Catalytic asymmetric conjugate addition of dialkylzinc reagents to beta-aryl-alpha,beta-unsaturated N-2,4,6-triisopropylphenylsulfonylaldimines with use of N-Boc-L-val-connected amidophosphane-copper(I) catalyst. *J. Org. Chem.* **2005,** *70* (1), 297-300.

56. Wu, J.; Mampreian, D. M.; Hoveyda, A. H., Enantioselective synthesis of nitroalkanes bearing all-carbon quaternary stereogenic centers through Cu-catalyzed asymmetric conjugate additions. *J. Am. Chem. Soc.* **2005,** *127* (13), 4584-4585.

57. Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N., Enantioselective 1,4-addition of Ar3Bi, ArBF3 K, and ArSiF3 to enones catalyzed by a dicationic palladium(II)-chiraphos or -dipamp complex. *Organometallics* **2005,** *24* (21), 5025-5032.

58. Chen, G.; Tokunaga, N.; Hayashi, T., Rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to coumarins: Asymmetric synthesis of (R)-tolterodine. *Org. Lett.* **2005,** *7* (11), 2285-2288.

59. Chen, O.; Kuriyama, M.; Soeta, T.; Hao, X. Y.; Yamada, K. I.; Tomioka, K., Asymmetric synthesis of 5-arylcyclohexenones by rhodium(I)-catalyzed conjugate arylation of racemic 5-(trimethylsilyl)cyclohexenone with arylboronic acids. *Org. Lett.* **2005,** *7* (20), 4439-4441.

60. Hayashi, T.; Yamamoto, S.; Tokunaga, N., Rhodium-catalyzed asymmetric 1,6-addition of aryl zinc reagents to dienones. *Angew. Chem.-Int. Edit.* **2005,** *44* (27), 4224-4227.

61. Jagt, R. B. C.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J., Enantioselective synthesis of 2-aryl-4-piperidones via rhodium/phosphoramidite-catalyzed conjugate addition of arylboroxines. *Org. Lett.* **2005,** *7* (12), 2433-2435.

62. Kina, A.; Ueyama, K.; Hayashi, T., Enantiomerically pure rhodium complexes bearing 1,5-diphenyl-1,5-cyclooctadiene as a chiral diene ligand. Their use as catalysts for asymmetric 1,4-addition of phenylzinc chloride. *Org. Lett.* **2005,** *7* (26), 5889-5892.

63. Otomaru, Y.; Okamoto, K.; Shintani, R.; Hayashi, T., Preparation of C-2-symmetric bicyclo 2.2.2 octa-2,5-diene ligands and their use for rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids. *J. Org. Chem.* **2005,** *70* (7), 2503-2508.

64. Paquin, J. F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M., Asymmetric synthesis of 3,3-diarylpropanals with chiral diene-rhodium catalysts. *J. Am. Chem. Soc.* **2005,** *127* (31), 10850-10851.

65. Paquin, J. F.; Stephenson, C. R. J.; Defieber, C.; Carreira, E. M., Catalytic asymmetric synthesis with Rh-diene complexes: 1,4-addition of arylboronic acids to unsaturated esters. *Org. Lett.* **2005,** *7* (17), 3821-3824.

66. Shintani, R.; Duan, W. L.; Nagano, T.; Okada, A.; Hayashi, T., Chiral phosphine-olefin bidentate ligands in asymmetric catalysis: Rhodium-catalyzed asymmetric 1,4-addition of aryl boronic acids to maleimides. *Angew. Chem.-Int. Edit.* **2005,** *44* (29), 4611-4614.

67. Shintani, R.; Hayashi, T., Rhodium-catalyzed addition of arylzinc reagents to aryl alkynyl ketones: Synthesis of beta,beta-disubstituted indanones. *Org. Lett.* **2005,** *7* (10), 2071-2073.

68. Shintani, R.; Okamoto, K.; Hayashi, T., Carbon-carbon bond-forming enantioselective synthesis of chiral organosilicon compounds by rhodium/chiral diene-catalyzed asymmetric 1,4-addition reaction. *Org. Lett.* **2005,** *7* (21), 4757-4759.

69. Shintani, R.; Yamagami, T.; Kimura, T.; Hayashi, T., Asymmetric synthesis of 2-aryl-2,3-dihydro-4-quinolones by rhodium-catalyzed 1,4-addition of arylzinc reagents in the presence of chlorotrimethylsilane. *Org. Lett.* **2005,** *7* (23), 5317-5319.

70. Stemmler, R. T.; Bolm, C., Planar-chiral cyrhetrenes for the rhodium-catalyzed asymmetric 1,4-addition and the hydrogenation of enamides. *J. Org. Chem.* **2005,** *70* (24), 9925-9931.

71. Pineschi, M.; Del Moro, F.; Crotti, P.; Macchia, F., Catalytic asymmetric ring opening of 2,3-substituted norbornenes with organometallic reagents: A new formal aza functionalization of cyclopentadiene. *Org. Lett.* **2005,** *7* (17), 3605-3607.

72. Murphy, K. E.; Hoveyda, A. H., Catalytic enantioselective synthesis of quaternary all-carbon stereogenic centers. Preparation of alpha,alpha'-disubstituted beta,gamma-unsaturated esters through Cu-catalyzed asymmetric allylic alkylations. *Org. Lett.* **2005,** *7* (7), 1255-1258.

73. Nicolaou, K. C.; Tang, W. J.; Dagneau, P.; Faraoni, R., A catalytic asymmetric three-component 1,4-addition/aldol reaction: Enantioselective synthesis of the spirocyclic system of vannusal A. *Angew. Chem.-Int. Edit.* **2005,** *44* (25), 3874-3879.

74. Guo, R. W.; Morris, R. H.; Song, D., Enantioselective tandem Michael addition/H-2-hydrogenation catalyzed by ruthenium hydride borohydride complexes containing beta-aminophosphine ligands. *J. Am. Chem. Soc.* **2005,** *127* (2), 516-517.

75. Fillion, E.; Wilsily, A., Asymmetric synthesis of all-carbon benzylic quaternary stereocenters via Cu-catalyzed conjugate addition of dialkylzinc reagents to 5-(1-arylalkylidene) Meldrum's acids. *J. Am. Chem. Soc.* **2006,** *128* (9), 2774-2775.

76. Harutyunyan, S. R.; Lopez, F.; Browne, W. R.; Correa, A.; Pena, D.; Badorrey, R.; Meetsma, A.; Minnaard, A. J.; Feringa, B. L., On the mechanism of the copper-catalyzed enantioselective 1,4-addition of grignard reagents to alpha,beta-unsaturated carbonyl compounds. *J. Am. Chem. Soc.* **2006,** *128* (28), 9103-9118.

77. Lee, K. S.; Brown, M. K.; Hird, A. W.; Hoveyda, A. H., A practical method for enantioselective synthesis of all-carbon quaternary stereogenic centers through NHC-Cu-catalyzed conjugate additions of alkyl- and arylzinc reagents to beta-substituted cyclic enones. *J. Am. Chem. Soc.* **2006,** *128* (22), 7182-7184.

78. Li, K. Y.; Alexakis, A., Asymmetric conjugate addition to alpha-halo enones: Dramatic effect of styrene on the enantioselectivity. *Angew. Chem.-Int. Edit.* **2006,** *45* (45), 7600-7603.

79. Howell, G. P.; Fletcher, S. P.; Geurts, K.; ter Horst, B.; Feringa, B. L., Catalytic asymmetric synthesis of acyclic arrays by tandem 1,4-addition-aldol reactions. *J. Am. Chem. Soc.* **2006,** *128* (46), 14977-14985.

80. Chen, F. X.; Kina, A.; Hayashi, T., High performance of a chiral diene-rhodium catalyst for the asymmetric 1,4-addition of arylboroxines to alpha,beta-unsaturated ketones. *Org. Lett.* **2006,** *8* (2), 341-344.

81. Kina, A.; Iwamura, H.; Hayashi, T., A kinetic study on Rh/binap-catalyzed 1,4-addition of phenylboronic acid to enones: Negative nonlinear effect caused by predominant homochiral dimer contribution. *J. Am. Chem. Soc.* **2006,** *128* (12), 3904-3905.

82. Shintani, R.; Duan, W. L.; Hayashi, T., Rhodium-catalyzed asymmetric construction of quaternary carbon stereocenters: Ligand-dependent regiocontrol in the 1,4-addition to substituted maleimides. *J. Am. Chem. Soc.* **2006,** *128* (17), 5628-5629.

83. Walter, C.; Auer, G.; Oestreich, M., Rhodium-catalyzed enantioselective conjugate silyl transfer: 1,4-addition of silyl boronic esters to cyclic enones and lactones. *Angew. Chem.-Int. Edit.* **2006,** *45* (34), 5675-5677.

84. Nishimura, T.; Hirabayashi, S.; Yasuhara, Y.; Hayashi, T., Rhodium-catalyzed asymmetric hydroarylation of diphenylphosphinylallenes with arylboronic acids. *J. Am. Chem. Soc.* **2006,** *128* (8), 2556-2557.

85. Duan, W. L.; Iwamura, H.; Shintani, R.; Hayashi, T., Chiral phosphine-olefin ligands in the rhodium-catalyzed asymmetric 1,4-addition reactions. *J. Am. Chem. Soc.* **2007,** *129* (7), 2130-2138.

86. Palais, L.; Mikhel, I. S.; Bournaud, C.; Micouin, L.; Falciola, C. A.; Vuagnoux-d'Augustin, M.; Rosset, S.; Bernardinelli, G.; Alexakis, A., SimplePhos monodentate ligands: Synthesis and application in copper-catalyzed reactions. *Angew. Chem.-Int. Edit.* **2007,** *46* (39), 7462-7465.

87. Wu, T. R.; Chong, J. M., Asymmetric conjugate alkenylation of enones catalyzed by chiral diols. *J. Am. Chem. Soc.* **2007,** *129* (16), 4908-+.

88. Shintani, R.; Takatsu, K.; Hayashi, T., Rhodium-catalyzed asymmetric synthesis of 3,3-disubstituted 1-indanones. *Angew. Chem.-Int. Edit.* **2007,** *46* (20), 3735-3737.

89. Bertz, S. H.; Cope, S.; Murphy, M.; Ogle, C. A.; Taylor, B. J., Rapid injection NMR in mechanistic organocopper chemistry. Preparation of the elusive copper(III) intermediate. *J. Am. Chem. Soc.* **2007,** *129* (23), 7208-+.

90. Hu, H. P.; Snyder, J. P., Organocuprate conjugate addition: The square-planar "Cu-III" intermediate. *J. Am. Chem. Soc.* **2007,** *129* (23), 7210-+.

91. Sibi, M. P.; Soeta, T., Enantioselective conjugate addition of hydrazines to alpha,beta-unsaturated imides. Synthesis of chiral pyrazolidinones. *J. Am. Chem. Soc.* **2007,** *129* (15), 4522-+.

92. Shintani, R.; Ichikawa, Y.; Hayashi, T.; Chen, J.; Nakao, Y.; Hiyama, T., Catalytic asymmetric synthesis of allylsilanes through rhodium/chiral diene-catalyzed 1,4-addition of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes. *Org. Lett.* **2007,** *9* (22), 4643-4645.

93. Nishimura, T.; Katoh, T.; Takatsu, K.; Shintani, R.; Hayashi, T., Rhodium-catalyzed asymmetric rearrangement of alkynyl alkenyl carbinols: Synthetic equivalent to asymmetric conjugate alkynylation of enones. *J. Am. Chem. Soc.* **2007,** *129* (46), 14158-+.

94. Ruiz, B. M.; Geurts, K.; Fernandez-Ibanez, M. A.; ter Horst, B.; Minnaard, A. J.; Feringa, B. L., Highly versatile enantioselective conjugate addition of Grignard reagents to alpha,beta-unsaturated thioesters. *Org. Lett.* **2007,** *9* (24), 5123-5126.

95. Lee, J. E.; Yun, J., Catalytic asymmetric boration of acyclic alpha,beta-unsaturated esters and nitriles. *Angew. Chem.-Int. Edit.* **2008,** *47* (1), 145-147.

96. Nishimura, T.; Guo, X. X.; Uchiyama, N.; Katoh, T.; Hayashi, T., Steric tuning of silylacetylenes and chiral phosphine ligands for rhodium-catalyzed asymmetric conjugate alkynylation of enones. *J. Am. Chem. Soc.* **2008,** *130* (5), 1576-+.

97. Sieber, J. D.; Morken, J. P., Asymmetric Ni-catalyzed conjugate allylation of activated enones. *J. Am. Chem. Soc.* **2008,** *130* (14), 4978-4983.

98. Walter, C.; Oestreich, M., Catalytic asymmetric C-Si bond formation to acyclic alpha,beta-unsaturated acceptors by Rh-I-catalyzed conjugate silyl transfer using a Si-B linkage. *Angew. Chem.-Int. Edit.* **2008,** *47* (20), 3818-3820.

99. Navarre, L.; Martinez, R.; Genet, J. P.; Darses, S., Access to enantioenriched alpha-amino esters via rhodium-catalyzed 1,4-addition/enantioselective protonation. *J. Am. Chem. Soc.* **2008,** *130* (19), 6159-6169.

100. Wakabayashi, K.; Aikawa, K.; Kawauchi, S.; Mikami, K., Catalyst self-adaptation in conjugate addition to nitroalkenes and nitroacrylates: Instant chirality control in diphenylmethane-based phosphoramidite ligands. *J. Am. Chem. Soc.* **2008,** *130* (15), 5012-+.

101. Desrosiers, J. N.; Bechara, W. S.; Charette, A. B., Catalytic enantioselective addition of diorganozinc reagents to vinyl sulfones. *Org. Lett.* **2008,** *10* (11), 2315-2318.

102. Shizuka, M.; Snapper, M. L., Catalytic enantioselective Hosomi-Sakurai conjugate allylation of cyclic unsaturated ketoesters. *Angew. Chem.-Int. Edit.* **2008,** *47* (27), 5049-5051.

103. Lalic, G.; Corey, E. J., Enantioselective rhodium(I)-triethylamine catalyzed addition of potassium isopropenyl trifluoroborate to enones. *Tetrahedron Lett.* **2008,** *49* (33), 4894-4896.

104. Alexakis, A.; Backvall, J. E.; Krause, N.; Pamies, O.; Dieguez, M., Enantioselective copper-catalyzed conjugate addition and allylic substitution reactions. *Chem. Rev.* **2008,** *108* (8), 2796-2823.

105. May, T. L.; Brown, M. K.; Hoveyda, A. H., Enantioselective synthesis of all-carbon quaternary stereogenic centers by catalytic asymmetric conjugate additions of alkyl and aryl aluminum reagents to five-, six-, and seven-membered-ring beta-substituted cyclic enones. *Angew. Chem.-Int. Edit.* **2008,** *47* (38), 7358-7362.

106. Feng, C. G.; Wang, Z. Q.; Shao, C.; Xu, M. H.; Lin, G. Q., Highly practical catalytic asymmetric 1,4-addition of arylboronic acids in water using new hydrophilic chiral bicyclo[3.3.0] diene ligands. *Org. Lett.* **2008,** *10* (18), 4101-4104.

107. Robert, T.; Velder, J.; Schmalz, H. G., Enantioselective Cu-catalyzed 1,4-addition of Grignard reagents to cyclohexenone using Taddol-derived phosphine-phosphite ligands and 2-methyl-THF as a solvent. *Angew. Chem.-Int. Edit.* **2008,** *47* (40), 7718-7721.

108. Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J. P.; Darses, S., C-1-symmetric monosubstituted chiral diene ligands in asymmetric rhodium-catalyzed 1,4-addition reactions. *Angew. Chem.-Int. Edit.* **2008,** *47* (40), 7669-7672.

109. Hawner, C.; Li, K. Y.; Cirriez, V.; Alexakis, A., Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers. *Angew. Chem.-Int. Edit.* **2008,** *47* (43), 8211-8214.

110. Henon, H.; Mauduit, M.; Alexakis, A., Regiodivergent 1,4 versus 1,6 Asymmetric Copper-Catalyzed Conjugate Addition. *Angew. Chem.-Int. Edit.* **2008,** *47* (47), 9122-9124.

111. Shintani, R.; Ichikawa, Y.; Takatsu, K.; Chen, F. X.; Hayashi, T., Tuning the Chiral Environment of C-2-Symmetric Diene Ligands: Development of 3,7-Disubstituted Bicyclo[3.3.1]nona-2,6-dienes. *J. Org. Chem.* **2009,** *74* (2), 869-873.

112. Thaler, T.; Knochel, P., Copper-Catalyzed Asymmetric Michael Addition of Magnesium, Zinc, and Aluminum Organometallic Reagents: Efficient Synthesis of Chiral Molecules. *Angew. Chem.-Int. Edit.* **2009,** *48* (4), 645-648.

113. Burgi, J. J.; Mariz, R.; Gatti, M.; Drinkel, E.; Luan, X. J.; Blumentritt, S.; Linden, A.; Dorta, R., Unprecedented Selectivity via Electronic Substrate Recognition in the 1,4-Addition to Cyclic Olefins Using a Chiral Disulfoxide Rhodium Catalyst. *Angew. Chem.-Int. Edit.* **2009,** *48* (15), 2768-2771.

114. Lee, K. S.; Hoveyda, A. H., Monodentate Non-C-2-symmetric Chiral N-Heterocyclic Carbene Complexes for Enantioselective Synthesis. Cu-Catalyzed Conjugate Additions of Aryl- and Alkenylsilylfluorides to Cyclic Enones. *J. Org. Chem.* **2009,** *74* (12), 4455-4462.

115. Nishimura, T.; Tokuji, S.; Sawano, T.; Hayashi, T., Rhodium-Catalyzed Asymmetric Conjugate Alkynylation of Enones with Alkynylsilanols. *Org. Lett.* **2009,** *11* (15), 3222-3225.

116. Uchida, T.; Katsuki, T., Construction of a new type of chiral bidentate NHC ligands: copper-catalyzed asymmetric conjugate alkylation. *Tetrahedron Lett.* **2009,** *50* (33), 4741-4743.

117. Chen, I. H.; Yin, L.; Itano, W.; Kanai, M.; Shibasaki, M., Catalytic Asymmetric Synthesis of Chiral Tertiary Organoboronic Esters through Conjugate Boration of beta-Substituted Cyclic Enones. *J. Am. Chem. Soc.* **2009,** *131* (33), 11664-+.

118. Zhang, P.; Morken, J. P., Catalytic Enantioselective Allylation of Dienals through the Intermediacy of Unsaturated pi-Allyl Complexes. *J. Am. Chem. Soc.* **2009,** *131* (35), 12550-+.

119. Shintani, R.; Tsutsumi, Y.; Nagaosa, M.; Nishimura, T.; Hayashi, T., Sodium Tetraarylborates as Effective Nucleophiles in Rhodium/Diene-Catalyzed 1,4-Addition to beta,beta-Disubstituted alpha,beta-Unsaturated Ketones: Catalytic Asymmetric Construction of Quaternary Carbon Stereocenters. *J. Am. Chem. Soc.* **2009,** *131* (38), 13588-+.

120. Hu, X. C.; Zhuang, M. Y.; Cao, Z. P.; Du, H. F., Simple Chiral Chain Dienes as Ligands for Rh(I)-Catalyzed Conjugated Additions. *Org. Lett.* **2009,** *11* (20), 4744-4747.

121. Nishimura, T.; Sawano, T.; Hayashi, T., Asymmetric Synthesis of beta-Alkynyl Aldehydes by Rhodium-Catalyzed Conjugate Alkynylation. *Angew. Chem.-Int. Edit.* **2009,** *48* (43), 8057-8059.

122. Mahoney, S. J.; Dumas, A. M.; Fillion, E., Asymmetric Addition of Alkenylstannanes to Alkylidene Meldrum's Acids. *Org. Lett.* **2009,** *11* (22), 5346-5349.

123. Okamoto, M.; Yamamoto, Y.; Sakaguchi, S., A new approach to switching of enantioselectivity in NHC-Cu-catalyzed conjugate addition of alkylzincs to cyclic enones. *Chem. Commun.* **2009,** (47), 7363-7365.

124. Nishimura, T.; Wang, J.; Nagaosa, M.; Okamoto, K.; Shintani, R.; Kwong, F. Y.; Yu, W. Y.; Chan, A. S. C.; Hayashi, T., Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to beta-Phthaliminoacrylate Esters toward the Synthesis of beta-Amino Acids. *J. Am. Chem. Soc.* **2010,** *132* (2), 464-+.

125. Welker, M.; Woodward, S.; Alexakis, A., Tandem Reactions with Chiral Enolates: Preparation of Allylic Alcohols via Trapping with Vinyl Oxiranes. *Org. Lett.* **2010,** *12* (3), 576-579.

126. Hargrave, J. D.; Allen, J. C.; Kociok-Kohn, G.; Bish, G.; Frost, C. G., Catalytic Enantioselective Dieckmann-Type Annulation: Synthesis of Pyrrolidines with Quaternary Stereogenic Centers. *Angew. Chem.-Int. Edit.* **2010,** *49* (10), 1825-1829.

127. Lee, K. S.; Hoveyda, A. H., Enantioselective Conjugate Silyl Additions to Cyclic and Acyclic Unsaturated Carbonyls Catalyzed by Cu Complexes of Chiral N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2010,** *132* (9), 2898-+.

128. Nakamura, A.; Lectard, S.; Hashizume, D.; Hamashima, Y.; Sodeoka, M., Diastereo- and Enantioselective Conjugate Addition of alpha-Ketoesters to Nitroalkenes Catalyzed by a Chiral Ni(OAc)(2) Complex under Mild Conditions. *J. Am. Chem. Soc.* **2010,** *132* (12), 4036-+.

129. Guo, S. M.; Xie, Y. J.; Hu, X. Q.; Xia, C. G.; Huang, H. M., Diastereo- and Enantioselective Catalytic Tandem Michael Addition/Mannich Reaction: Access to Chiral Isoindolinones and Azetidines with Multiple Stereocenters. *Angew. Chem.-Int. Edit.* **2010,** *49* (15), 2728-2731.

130. Chen, J.; Chen, J. M.; Lang, F.; Zhang, X. Y.; Cun, L. F.; Zhu, J.; Deng, J. G.; Liao, J., A C-2-Symmetric Chiral Bis-Sulfoxide Ligand in a Rhodium-Catalyzed Reaction: Asymmetric 1,4-Addition of Sodium Tetraarylborates to Chromenones. *J. Am. Chem. Soc.* **2010,** *132* (13), 4552-+.

131. Feng, J. J.; Chen, X. F.; Shi, M.; Duan, W. L., Palladium-Catalyzed Asymmetric Addition of Diarylphosphines to Enones toward the Synthesis of Chiral Phosphines. *J. Am. Chem. Soc.* **2010,** *132* (16), 5562-+.

132. Lee, J. C. H.; Hall, D. G., Chiral Boronate Derivatives via Catalytic Enantioselective Conjugate Addition of Grignard Reagents on 3-Boronyl Unsaturated Esters and Thioesters. *J. Am. Chem. Soc.* **2010,** *132* (16), 5544-+.

133. Nishimura, T.; Yasuhara, Y.; Sawano, T.; Hayashi, T., Iridium/Chiral Diene-Catalyzed Asymmetric 1,6-Addition of Arylboroxines to alpha,beta,gamma,delta-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2010,** *132* (23), 7872-+.

134. Wang, Z. Q.; Feng, C. G.; Zhang, S. S.; Xu, M. H.; Lin, G. Q., Rhodium-Catalyzed Asymmetric Conjugate Addition of Organoboronic Acids to Nitroalkenes Using Chiral Bicyclo 3.3.0 Diene Ligands. *Angew. Chem.-Int. Edit.* **2010,** *49* (33), 5780-5783.

135. Yazaki, R.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Conjugate Addition of Terminal Alkynes to alpha,beta-Unsaturated Thioamides. *J. Am. Chem. Soc.* **2010,** *132* (30), 10275-10277.

136. Nishimura, T.; Makino, H.; Nagaosa, M.; Hayashi, T., Rhodium-Catalyzed Enantioselective 1,6-Addition of Arylboronic Acids to Enynamides: Asymmetric Synthesis of Axially Chiral Allenylsilanes. *J. Am. Chem. Soc.* **2010,** *132* (37), 12865-12867.

137. Hawner, C.; Muller, D.; Gremaud, L.; Felouat, A.; Woodward, S.; Alexakis, A., Rhodium-Catalyzed Asymmetric 1,4-Addition of Aryl Alanes to Trisubstituted Enones: Binap as an Effective Ligand in the Formation of Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2010,** *49* (42), 7769-7772.

138. den Hartog, T.; Rudolph, A.; Macia, B.; Minnaard, A. J.; Feringa, B. L., Copper-Catalyzed Enantioselective Synthesis of trans-1-Alkyl-2-substituted Cyclopropanes via Tandem Conjugate Addition-Intramolecular Enolate Trapping. *J. Am. Chem. Soc.* **2010,** *132* (41), 14349-14351.

139. Pattison, G.; Piraux, G.; Lam, H. W., Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to Alkenylheteroarenes. *J. Am. Chem. Soc.* **2010,** *132* (41), 14373-14375.

140. May, T. L.; Dabrowski, J. A.; Hoveyda, A. H., Formation of Vinyl-, Vinylhalide- or Acyl-Substituted Quaternary Carbon Stereogenic Centers through NHC-Cu-Catalyzed Enantioselective Conjugate Additions of Si-Containing Vinylaluminums to beta-Substituted Cyclic Enones. *J. Am. Chem. Soc.* **2011,** *133* (4), 736-739.

141. Yazaki, R.; Kumagai, N.; Shibasaki, M., Enantioselective Synthesis of a GPR40 Agonist AMG 837 via Catalytic Asymmetric Conjugate Addition of Terminal Alkyne to alpha,beta-Unsaturated Thioamide. *Org. Lett.* **2011,** *13* (5), 952-955.

142. Li, Q. A.; Dong, Z.; Yu, Z. X., alpha,beta-Divinyl Tetrahydropyrroles as Chiral Chain Diene Ligands in Rhodium(l)-Catalyzed Enantioselective Conjugated Additions. *Org. Lett.* **2011,** *13* (5), 1122-1125.

143. Kikushima, K.; Holder, J. C.; Gatti, M.; Stoltz, B. M., Palladium-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Five-, Six-, and Seven-Membered beta-Substituted Cyclic Enones: Enantioselective Construction of All-Carbon Quaternary Stereocenters. *J. Am. Chem. Soc.* **2011,** *133* (18), 6902-6905.

144. Wei, C. H.; Mannathan, S.; Cheng, C. H., Enantioselective Synthesis of beta-Substituted Cyclic Ketones via Cobalt-Catalyzed Asymmetric Reductive Coupling of Alkynes with Alkenes. *J. Am. Chem. Soc.* **2011,** *133* (18), 6942-6944.

145. Takatsu, K.; Shintani, R.; Hayashi, T., Copper-Catalyzed 1,4-Addition of Organoboronates to Alkylidene Cyanoacetates: Mechanistic Insight and Application to Asymmetric Catalysis. *Angew. Chem.-Int. Edit.* **2011,** *50* (24), 5548-5552.

146. Rudolph, A.; Bos, P. H.; Meetsma, A.; Minnaard, A. J.; Feringa, B. L., Catalytic Asymmetric Conjugate Addition/Oxidative Dearomatization Towards Multifunctional Spirocyclic Compounds. *Angew. Chem.-Int. Edit.* **2011,** *50* (26), 5834-5838.

147. Yazaki, R.; Kumagai, N.; Shibasaki, M., Cooperative Activation of Alkyne and Thioamide Functionalities; Direct Catalytic Asymmetric Conjugate Addition of Terminal Alkynes to alpha,beta-Unsaturated Thioamides. *Chem.-Asian J.* **2011,** *6* (7), 1778-1790.

148. Yanagida, Y.; Yazaki, R.; Kumagai, N.; Shibasaki, M., Asymmetric Synthesis of Isothiazoles through Cu Catalysis: Direct Catalytic Asymmetric Conjugate Addition of Allyl Cyanide to alpha,beta-Unsaturated Thioamides. *Angew. Chem.-Int. Edit.* **2011,** *50* (34), 7910-7914.

149. Nishimura, T.; Sawano, T.; Ou, K. Y.; Hayashi, T., Cobalt-catalyzed conjugate addition of silylacetylenes to alpha,beta-unsaturated ketones. *Chem. Commun.* **2011,** *47* (36), 10142-10144.

150. Wang, L.; Meng, W.; Zhu, C. L.; Zhen, Y.; Nie, J.; Ma, J. A., The Long-Arm Effect: Influence of Axially Chiral Phosphoramidite Ligands on the Diastereo- and Enantioselectivity of the Tandem 1,4-Addition/Fluorination. *Angew. Chem.-Int. Edit.* **2011,** *50* (40), 9442-9446.

151. Lee, J. C. H.; McDonald, R.; Hall, D. G., Enantioselective preparation and chemoselective cross-coupling of 1,1-diboron compounds. *Nat. Chem.* **2011,** *3* (11), 894-899.

152. Ibrahem, I.; Breistein, P.; Cordova, A., One-Pot Three-Component Catalytic Enantioselective Synthesis of Homoallylboronates. *Angew. Chem.-Int. Edit.* **2011,** *50* (50), 12036-12041.

153. Wang, X.; Buchwald, S. L., Rh-Catalyzed Asymmetric Hydroformylation of Functionalized 1,1-Disubstituted Olefins. *J. Am. Chem. Soc.* **2011,** *133* (47), 19080-19083.

154. Gremaud, L.; Alexakis, A., Enantioselective Copper-Catalyzed Conjugate Addition of Trimethylaluminium to beta,gamma-Unsaturated alpha-Ketoesters. *Angew. Chem.-Int. Edit.* **2012,** *51* (3), 794-797.

155. Gosiewska, S.; Raskatov, J. A.; Shintani, R.; Hayashi, T.; Brown, J. M., The Origins of Enantioselectivity in Rh-Diene Complex Catalysed Arylation of Cyclohex-2-enones. *Chem.-Eur. J.* **2012,** *18* (1), 80-84.

156. Sasaki, K.; Nishimura, T.; Shintani, R.; Kantchev, E. A. B.; Hayashi, T., Rhodium/diene-catalyzed tandem 1,4-shift/1,4-addition of (E)-1,2-diphenylethenylboronic acid to enones: density functional theory modeling and asymmetric catalysis. *Chem. Sci.* **2012,** *3* (4), 1278-1283.

157. Wang, Z.; Chen, Z. L.; Bai, S.; Li, W.; Liu, X. H.; Lin, L. L.; Feng, X. M., Highly Z-Selective Asymmetric Conjugate Addition of Alkynones with Pyrazol-5-ones Promoted by N,N'-Dioxide-Metal Complexes. *Angew. Chem.-Int. Edit.* **2012,** *51* (11), 2776-2779.

158. Shu, W.; Buchwald, S. L., Enantioselective ss-Arylation of Ketones Enabled by Lithiation/Borylation/1,4-Addition Sequence Under Flow Conditions. *Angew. Chem.-Int. Edit.* **2012,** *51* (22), 5355-5358.

159. Tsuchikawa, H.; Maekawa, Y.; Katsumura, S., Palladium-Catalyzed Asymmetric 6-Endo Cyclization of Dienamides with Substituent-Driven Activation. *Org. Lett.* **2012,** *14* (9), 2326-2329.

160. Nishimura, T.; Takiguchi, Y.; Hayashi, T., Effect of Chiral Diene Ligands in Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to alpha,beta-Unsaturated Sulfonyl Compounds. *J. Am. Chem. Soc.* **2012,** *134* (22), 9086-9089.

161. Huang, Y. H.; Pullarkat, S. A.; Teong, S.; Chew, R. J.; Li, Y. X.; Leung, P. H., Palladacycle-Catalyzed Asymmetric Intermolecular Construction of Chiral Tertiary P-Heterocycles by Stepwise Addition of H-P-H Bonds to Bis(enones). *Organometallics* **2012,** *31* (13), 4871-4875.

162. Aikawa, K.; Okamoto, T.; Mikami, K., Copper(I)-Catalyzed Asymmetric Desymmetrization: Synthesis of Five-Membered-Ring Compounds Containing All-Carbon Quaternary Stereocenters. *J. Am. Chem. Soc.* **2012,** *134* (25), 10329-10332.

163. Maksymowicz, R. M.; Roth, P. M. C.; Fletcher, S. P., Catalytic asymmetric carbon-carbon bond formation using alkenes as alkylmetal equivalents. *Nat. Chem.* **2012,** *4* (8), 649-654.

164. Yoshida, M.; Ohmiya, H.; Sawamura, M., Enantioselective Conjugate Addition of Alkylboranes Catalyzed by a Copper-N-Heterocyclic Carbene Complex. *J. Am. Chem. Soc.* **2012,** *134* (29), 11896-11899.

165. Ogawa, T.; Kumagai, N.; Shibasaki, M., Catalytic Asymmetric Conjugate Addition of Thiols to alpha,beta-Unsaturated Thioamides: Expeditious Access to Enantioenriched 1,5-Benzothiazepines. *Angew. Chem.-Int. Edit.* **2012,** *51* (34), 8551-8554.

166. Burns, A. R.; Gonzalez, J. S.; Lam, H. W., Enantioselective Copper(I)-Catalyzed Borylative Aldol Cyclizations of Enone Diones. *Angew. Chem.-Int. Edit.* **2012,** *51* (43), 10827-10831.

167. Sawano, T.; Ashouri, A.; Nishimura, T.; Hayashi, T., Cobalt-Catalyzed Asymmetric 1,6-Addition of (Triisopropylsilyl)-acetylene to alpha,beta,gamma,delta-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2012,** *134* (46), 18936-18939.

168. Kobayashi, S.; Xu, P. Y.; Endo, T.; Ueno, M.; Kitanosono, T., Chiral Copper(II)-Catalyzed Enantioselective Boron Conjugate Additions to alpha,beta-Unsaturated Carbonyl Compounds in Water. *Angew. Chem.-Int. Edit.* **2012,** *51* (51), 12763-12766.

169. Endo, K.; Hamada, D.; Yakeishi, S.; Shibata, T., Effect of Multinuclear Copper/Aluminum Complexes in Highly Asymmetric Conjugate Addition of Trimethylaluminum to Acyclic Enones. *Angew. Chem.-Int. Edit.* **2013,** *52* (2), 606-610.

170. Kantchev, E. A. B., Cooperativity between steric repulsion and crossed diene coordination governs the enantioselectivity in rhodium(I)/chiral, 1,4-and 1,5-diene-catalysed 1,4-addition reaction: a DFT study. *Chem. Sci.* **2013,** *4* (4), 1864-1875.

171. Eitel, S. H.; Jautze, S.; Frey, W.; Peters, R., Asymmetric Michael additions of alpha-cyanoacetates by soft Lewis acid/hard Bronsted acid catalysis: stereodivergency with bi- vs. monometallic catalysts. *Chem. Sci.* **2013,** *4* (5), 2218-2233.

172. Holder, J. C.; Zou, L. F.; Marziale, A. N.; Liu, P.; Lan, Y.; Gatti, M.; Kikushima, K.; Houk, K. N.; Stoltz, B. M., Mechanism and Enantioselectivity in Palladium-Catalyzed Conjugate Addition of Arylboronic Acids to beta-Substituted Cyclic Enones: Insights from Computation and Experiment. *J. Am. Chem. Soc.* **2013,** *135* (40), 14996-15007.

173. Goncalves-Contal, S.; Gremaud, L.; Alexakis, A., Enantioselective Copper-Catalyzed Conjugate Addition of Trimethylaluminum to beta,gamma-Unsaturated alpha-Ketoamides: Efficient Access to gamma-Methyl-Substituted Carbonyl Compounds. *Angew. Chem.-Int. Edit.* **2013,** *52* (48), 12701-12704.

174. McGrath, K. P.; Hoveyda, A. H., A Multicomponent Ni-, Zr-, and Cu-Catalyzed Strategy for Enantioselective Synthesis of Alkenyl-Substituted Quaternary Carbons. *Angew. Chem.-Int. Edit.* **2014,** *53* (7), 1910-1914.

175. Eschenbrenner-Lux, V.; Kuchler, P.; Ziegler, S.; Kumar, K.; Waldmann, H., An Enantioselective Inverse-Electron-Demand Imino Diels-Alder Reaction. *Angew. Chem.-Int. Edit.* **2014,** *53* (8), 2134-2137.

176. Luo, Y.; Roy, I. D.; Madec, A. G. E.; Lam, H. W., Enantioselective Synthesis of Allylboronates and Allylic Alcohols by Copper-Catalyzed 1,6-Boration. *Angew. Chem.-Int. Edit.* **2014,** *53* (16), 4186-4190.

177. Yin, L.; Takada, H.; Lin, S. Q.; Kumagai, N.; Shibasaki, M., Direct Catalytic Asymmetric Vinylogous Conjugate Addition of Unsaturated Butyrolactones to a, b-Unsaturated Thioamides**. *Angew. Chem.-Int. Edit.* **2014,** *53* (21), 5327-5331.

178. Wang, J.; Wang, M.; Cao, P.; Jiang, L.; Chen, G.; Liao, J., Rhodium-Catalyzed Asymmetric Arylation of beta,gamma-Unsaturated alpha-Ketoamides for the Construction of Nonracemic gamma,gamma-Diarylcarbonyl Compounds. *Angew. Chem.-Int. Edit.* **2014,** *53* (26), 6673-6677.

179. Zeng, X.; Gao, J. J.; Song, J. J.; Ma, S.; Desrosiers, J.-N.; Mulder, J. A.; Rodriguez, S.; Herbage, M. A.; Haddad, N.; Qu, B.; Fandrick, K. R.; Grinberg, N.; Lee, H.; Wei, X.; Yee, N. K.; Senanayake, C. H., Remarkable Enhancement of Enantioselectivity in the Asymmetric Conjugate Addition of Dimethylzinc to (Z)-Nitroalkenes with a Catalytic (MeCN)(4)Cu PF6-Hoveyda Ligand Complex. *Angew. Chem.-Int. Edit.* **2014,** *53* (45), 12153-12157.

180. Zhang, L.; Qureshi, Z.; Sonaglia, L.; Lautens, M., Sequential Rhodium/Palladium Catalysis: Enantioselective Formation of Dihydroquinolinones in the Presence of Achiral and Chiral Ligands. *Angew. Chem.-Int. Edit.* **2014,** *53* (50), 13850-13853.

181. Boeser, C. L.; Holder, J. C.; Taylor, B. L. H.; Houk, K. N.; Stoltz, B. M.; Zare, R. N., Mechanistic analysis of an asymmetric palladium-catalyzed conjugate addition of arylboronic acids to beta-substituted cyclic enones. *Chem. Sci.* **2015,** *6* (3), 1917-1922.

182. Filloux, C. M.; Rovis, T., Rh(I)-Bisphosphine-Catalyzed Asymmetric, Intermolecular Hydroheteroarylation of alpha-Substituted Acrylate Derivatives. *J. Am. Chem. Soc.* **2015,** *137* (1), 508-517.

183. Yue, G. Z.; Lei, K. N.; Hirao, H.; Zhou, J. R., Palladium-Catalyzed Asymmetric Reductive Heck Reaction of Aryl Halides. *Angew. Chem.-Int. Edit.* **2015,** *54* (22), 6531-6535.

184. Chen, Y. J.; Hu, T. J.; Feng, C. G.; Lin, G. Q., Synthesis of chiral cyclobutanes via rhodium/diene-catalyzed asymmetric 1,4-addition: a dramatic ligand effect on the diastereoselectivity. *Chem. Commun.* **2015,** *51* (42), 8773-8776.

185. Yasukawa, T.; Suzuki, A.; Miyamura, H.; Nishino, K.; Kobayashi, S., Chiral Metal Nanoparticle Systems as Heterogeneous Catalysts beyond Homogeneous Metal Complex Catalysts for Asymmetric Addition of Arylboronic Acids to alpha,beta-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2015,** *137* (20), 6616-6623.

186. Kubota, K.; Hayama, K.; Iwamoto, H.; Ito, H., Enantioselective Borylative Dearomatization of Indoles through Copper(I) Catalysis. *Angew. Chem.-Int. Edit.* **2015,** *54* (30), 8809-8813.

187. Drissi-Amraoui, S.; Morin, M. S. T.; Crevisy, C.; Basle, O.; de Figueiredo, R. M.; Mauduit, M.; Campagne, J. M., Copper-Catalyzed Asymmetric Conjugate Addition of Dimethylzinc to Acyl-N-methylimidazole Michael Acceptors: a Powerful Synthetic Platform. *Angew. Chem.-Int. Edit.* **2015,** *54* (40), 11830-11834.

188. He, Z. T.; Tang, X. Q.; Xie, L. B.; Cheng, M.; Tian, P.; Lin, G. Q., Efficient Access to Bicyclo 4.3.0 nonanes: Copper-Catalyzed Asymmetric Silylative Cyclization of Cyclohexadienone-Tethered Allenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (49), 14815-14818.

189. Kitanosono, T.; Zhu, L.; Liu, C.; Xu, P. Y.; Kobayashi, S., An Insoluble Copper(II) Acetylacetonate-Chiral Bipyridine Complex that Catalyzes Asymmetric Silyl Conjugate Addition in Water. *J. Am. Chem. Soc.* **2015,** *137* (49), 15422-15425.

190. Huang, Y. H.; Hayashi, T., Asymmetric Synthesis of Triarylmethanes by Rhodium-Catalyzed Enantioselective Arylation of Diarylmethylamines with Arylboroxines. *J. Am. Chem. Soc.* **2015,** *137* (24), 7556-7559.

191. Wang, M.; Liu, Z. L.; Zhang, X.; Tian, P. P.; Xu, Y. H.; Loh, T. P., Synthesis of Highly Substituted Racemic and Enantioenriched Allenylsilanes via Copper-Catalyzed Hydrosilylation of (Z)-2-Alken-4-ynoates with Silylboronate. *J. Am. Chem. Soc.* **2015,** *137* (47), 14830-14833.

192. Dou, X. W.; Huang, Y. H.; Hayashi, T., Asymmetric Conjugate Alkynylation of Cyclic ,-Unsaturated Carbonyl Compounds with a Chiral Diene Rhodium Catalyst. *Angew. Chem.-Int. Edit.* **2016,** *55* (3), 1133-1137.

193. Yao, Q.; Liao, Y. T.; Lin, L. L.; Lin, X. B.; Ji, J.; Liu, X. H.; Feng, X. M., Efficient Synthesis of Chiral Trisubstituted 1,2-Allenyl Ketones by Catalytic Asymmetric Conjugate Addition of Malonic Esters to Enynes. *Angew. Chem.-Int. Edit.* **2016,** *55* (5), 1859-1863.

194. Wu, C. L.; Yue, G. Z.; Nielsen, C. D. T.; Xu, K.; Hirao, H.; Zhou, J. R., Asymmetric Conjugate Addition of Organoboron Reagents to Common Enones Using Copper Catalysts. *J. Am. Chem. Soc.* **2016,** *138* (3), 742-745.

195. Dou, X. W.; Lu, Y. X.; Hayashi, T., Base-Free Conditions for Rhodium-Catalyzed Asymmetric Arylation To Produce Stereochemically Labile alpha-Aryl Ketones. *Angew. Chem.-Int. Edit.* **2016,** *55* (23), 6739-6743.

196. Meng, F. K.; Li, X. B.; Torker, S.; Shi, Y.; Shen, X.; Hoveyda, A. H., Catalytic enantioselective 1,6-conjugate additions of propargyl and allyl groups. *Nature* **2016,** *537* (7620), 387-393.

197. Wang, Z. X.; Bai, X. Y.; Yao, H. C.; Li, B. J., Synthesis of Amides with Remote Stereocenters by Catalytic Asymmetric gamma-Alkynylation of alpha,beta-Unsaturated Amides. *J. Am. Chem. Soc.* **2016,** *138* (45), 14872-14875.

198. Han, Y. X.; Breitler, S.; Zheng, S. L.; Corey, E. J., Enantioselective Conversion of Achiral Cyclohexadienones to Chiral Cyclohexenones by Desymmetrization. *Org. Lett.* **2016,** *18* (23), 6172-6175.

199. Kamikawa, K.; Tseng, Y. Y.; Jian, J. H.; Takahashi, T.; Ogasawara, M., Planar-Chiral Phosphine-Olefin Ligands Exploiting a (Cyclopentadienyl) manganese(I) Scaffold To Achieve High Robustness and High Enantioselectivity. *J. Am. Chem. Soc.* **2017,** *139* (4), 1545-1553.

200. Orlandi, M.; Hilton, M. J.; Yamamoto, E.; Toste, F. D.; Sigman, M. S., Mechanistic Investigations of the Pd(0)-Catalyzed Enantioselective 1,1-Diarylation of Benzyl Acrylates. *J. Am. Chem. Soc.* **2017,** *139* (36), 12688-12695.

201. Rodriguez-Fernandez, M.; Yan, X. C.; Collados, J. F.; White, P. B.; Harutyunyan, S. R., Lewis Acid Enabled Copper-Catalyzed Asymmetric Synthesis of Chiral beta-Substituted Amides. *J. Am. Chem. Soc.* **2017,** *139* (40), 14224-14231.

202. Wang, Z.; Hayashi, T., Rhodium-Catalyzed Enantioposition-Selective Hydroarylation of Divinylphosphine Oxides with Aryl Boroxines. *Angew. Chem.-Int. Edit.* **2018,** *57* (6), 1702-1706.

203. Zheng, X. X.; Guo, R.; Zhang, G. Z.; Zhang, D. Y., Rhodium(I)-catalyzed asymmetric 4+2 cycloaddition reactions of 2-alkylenecyclobutanols with cyclic enones through C-C bond cleavage: efficient access to trans-bicyclic compounds. *Chem. Sci.* **2018,** *9* (7), 1873-1877.

204. Shu, T.; Zhao, L.; Li, S.; Chen, X. Y.; von Essen, C.; Rissanen, K.; Enders, D., Asymmetric Synthesis of Spirocyclic-Lactams through Copper-Catalyzed Kinugasa/Michael Domino Reactions. *Angew. Chem.-Int. Edit.* **2018,** *57* (34), 10985-10988.

205. Zhang, D.; Lin, L. L.; Yang, J.; Liu, X. H.; Feng, X. M., Asymmetric Synthesis of Tetrahydroindolizines by Bimetallic Relay Catalyzed Cycloaddition of Pyridinium Ylides. *Angew. Chem.-Int. Edit.* **2018,** *57* (38), 12323-12327.

206. Wu, L. Q.; Wang, F.; Chen, P. H.; Liu, G. S., Enantioselective Construction of Quaternary All-Carbon Centers via Copper-Catalyzed Arylation of Tertiary Carbon-Centered Radicals. *J. Am. Chem. Soc.* **2019,** *141* (5), 1887-1892.

207. Mao, W. B.; Xue, W. C.; Irran, E.; Oestreich, M., Copper-Catalyzed Regio- and Enantioselective Addition of Silicon Grignard Reagents to Alkenes Activated by Azaaryl Groups. *Angew. Chem.-Int. Edit.* **2019,** *58* (31), 10723-10726.

208. Clement, H. A.; Boghi, M.; McDonald, R. M.; Bernier, L.; Coe, J. W.; Farrell, W.; Helal, C. J.; Reese, M. R.; Sach, N. W.; Lee, J. C.; Hall, D. G., High-Throughput Ligand Screening Enables the Enantioselective Conjugate Borylation of Cyclobutenones to Access Synthetically Versatile Tertiary Cyclobutylboronates. *Angewandte Chemie International Edition* **2019,** *58* (51), 18405-18409.

209. Zhong, C.; Huang, Y.; Zhang, H.; Zhou, Q.; Liu, Y.; Lu, P., Enantioselective Synthesis of 3-Substituted Cyclobutenes by Catalytic Conjugate Addition/Trapping Strategies. *Angewandte Chemie International Edition* **2020,** *59* (7), 2750-2754.

210. Larin, E. M.; Loup, J.; Polishchuk, I.; Ross, R. J.; Whyte, A.; Lautens, M., Enantio- and diastereoselective conjugate borylation/Mannich cyclization. *Chem. Sci.* **2020,** *11* (22), 5716-5723.

211. Guo, S.; Zhu, J.; Buchwald, S. L., Enantioselective Synthesis of β-Amino Acid Derivatives Enabled by Ligand-Controlled Reversal of Hydrocupration Regiochemistry. *Angewandte Chemie International Edition* **2020,** *59* (47), 20841-20845.

212. He, C.-Y.; Tan, Y.-X.; Wang, X.; Ding, R.; Wang, Y.-F.; Wang, F.; Gao, D.; Tian, P.; Lin, G.-Q., Copper(I)-catalyzed diastereo- and enantio-selective construction of optically pure exocyclic allenes. *Nature Communications* **2020,** *11* (1), 4293.

213. Guo, L.; Yuan, M.; Zhang, Y.; Wang, F.; Zhu, S.; Gutierrez, O.; Chu, L., General Method for Enantioselective Three-Component Carboarylation of Alkenes Enabled by Visible-Light Dual Photoredox/Nickel Catalysis. *J. Am. Chem. Soc.* **2020,** *142* (48), 20390-20399.

214. Shi, L.; Xing, L.-L.; Hu, W.-B.; Shu, W., Regio- and Enantioselective Ni-Catalyzed Formal Hydroalkylation, Hydrobenzylation, and Hydropropargylation of Acrylamides to α-Tertiary Amides. *Angewandte Chemie International Edition* **2021,** *60* (3), 1599-1604.

215. Ozols, K.; Onodera, S.; Woźniak, Ł.; Cramer, N., Cobalt(III)-Catalyzed Enantioselective Intermolecular Carboamination by C−H Functionalization. *Angewandte Chemie International Edition* **2021,** *60* (2), 655-659.

216. Yang, Y.; Chen, L.; Xu, S., Iridium-Catalyzed Enantioselective Unbiased Methylene C(sp3)–H Borylation of Acyclic Amides. *Angewandte Chemie International Edition* **2021,** *60* (7), 3524-3528.

217. Wang, C.; Huang, K.; Ye, J.; Duan, W.-L., Asymmetric Synthesis of P-Stereogenic Secondary Phosphine-Boranes by an Unsymmetric Bisphosphine Pincer-Nickel Complex. *J. Am. Chem. Soc.* **2021,** *143* (15), 5685-5690.

218. Cooze, C. J. C.; McNutt, W.; Schoetz, M. D.; Sosunovych, B.; Grigoryan, S.; Lundgren, R. J., Diastereo-, Enantio-, and Z-Selective α,δ-Difunctionalization of Electron-Deficient Dienes Initiated by Rh-Catalyzed Conjugate Addition. *J. Am. Chem. Soc.* **2021,** *143* (28), 10770-10777.

219. Liu, W.; Pu, M.; He, J.; Zhang, T.; Dong, S.; Liu, X.; Wu, Y.-D.; Feng, X., Iron-Catalyzed Enantioselective Radical Carboazidation and Diazidation of α,β-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc.* **2021,** *143* (30), 11856-11863.

220. Choo, K.-L.; Mirabi, B.; Demmans, K. Z.; Lautens, M., Enantioselective Synthesis of Spiro-oxiranes: An Asymmetric Addition/Aldol/Spirocyclization Domino Cascade. *Angewandte Chemie International Edition* **2021,** *60* (39), 21189-21194.

221. Wu, D.; Wu, L.; Chen, P.; Liu, G., Asymmetric Alkynylation of Tertiary Carbon-Centered Radical via Copper-Catalyzed Radical Relay. *Chinese Journal of Chemistry* **2022,** *40* (14), 1699-1704.

222. Duchemin, N.; Aubert, S.; de Souza, J. V.; Bethge, L.; Vonhoff, S.; Bronowska, A. K.; Smietana, M.; Arseniyadis, S., New Benchmark in DNA-Based Asymmetric Catalysis: Prevalence of Modified DNA/RNA Hybrid Systems. *JACS Au* **2022,** *2* (8), 1910-1917.

223. Zhang, W.-Y.; Wang, H.-C.; Wang, Y.; Zheng, C.; You, S.-L., Enantioselective Dearomatization of Indoles via SmI2-Mediated Intermolecular Reductive Coupling with Ketones. *J. Am. Chem. Soc.* **2023,** *145* (18), 10314-10321.

224. Jin, Y.; Fan, L.-F.; Ng, E. W. H.; Yu, L.; Hirao, H.; Gong, L.-Z., Atom Transfer Radical Coupling Enables Highly Enantioselective Carbo-Oxygenation of Alkenes with Hydrocarbons. *J. Am. Chem. Soc.* **2023,** *145* (40), 22031-22040.

225. Wang, Y.-Z.; Sun, B.; Zhu, X.-Y.; Gu, Y.-C.; Ma, C.; Mei, T.-S., Enantioselective Reductive Cross-Couplings of Olefins by Merging Electrochemistry with Nickel Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (44), 23910-23917.

226. Wang, S.; Zhong, C.; Huang, Y.; Lu, P., Enantioselective Hydrofunctionalization of Cyclobutenones: Total Synthesis of gem-Dimethylcyclobutane Natural Products. *Angewandte Chemie International Edition* **2024,** *63* (20), e202400515.

227. Lyu, X.; Jung, H.; Kim, D.; Chang, S., Enantioselective Access to β-Amino Carbonyls via Ni-Catalyzed Formal Olefin Hydroamidation. *J. Am. Chem. Soc.* **2024,** *146* (21), 14745-14753.

228. Ge, L.; Wang, H.; Liu, Y.; Feng, X., Asymmetric Three-Component Radical Alkene Carboazidation by Direct Activation of Aliphatic C–H Bonds. *J. Am. Chem. Soc.* **2024,** *146* (19), 13347-13355.

229. Lonardi, G.; Franco, S.; Sartorello, M.; De Faveri, C.; Stivanello, M.; Licini, G.; Orlandi, M., Enantioselective Synthesis of Cyclopropanes via CuH-Catalyzed Intramolecular Hydroalkylation. *ACS Catalysis* **2024,** *14* (11), 8730-8738.

4.5.6 Other Reactions

1. Kimmich, B. F. M.; Landis, C. R.; Powell, D. R., Synthesis and characterization of boron-containing ferrocenyl ligands for asymmetric catalysis. *Organometallics* **1996,** *15* (20), 4141-4146.

2. Sodergren, M. J.; Bertilsson, S. K.; Andersson, P. G., Allylic alcohols via catalytic asymmetric epoxide rearrangement. *J. Am. Chem. Soc.* **2000,** *122* (28), 6610-6618.

3. Ferreira, E. M.; Stoltz, B. M., The palladiuim-catalyzed oxidative kinetic resolution of secondary alcohols with molecular oxygen. *J. Am. Chem. Soc.* **2001,** *123* (31), 7725-7726.

4. Jensen, D. R.; Pugsley, J. S.; Sigman, M. S., Palladium-catalyzed enantioselective oxidations of alcohols using molecular oxygen. *J. Am. Chem. Soc.* **2001,** *123* (30), 7475-7476.

5. Magnus, A.; Bertilsson, S. K.; Andersson, P. G., Asymmetric base-mediated epoxide isomerisation. *Chem. Soc. Rev.* **2002,** *31* (4), 223-229.

6. Alexakis, A.; Croset, K., Tandem copper-catalyzed enantioselective allylation-metathesis. *Org. Lett.* **2002,** *4* (23), 4147-4149.

7. Juhl, K.; Jorgensen, K. A., Catalytic asymmetric direct alpha-amination reactions of 2-keto esters: A simple synthetic approach to optically active syn- beta-amino-alpha-hydroxy esters. *J. Am. Chem. Soc.* **2002,** *124* (11), 2420-2421.

8. Piarulli, U.; Daubos, P.; Claverie, C.; Roux, M.; Gennari, C., A catalytic and enantioselective desymmetrization of meso cyclic allylic bisdiethylphosphates with organozinc reagents. *Angew. Chem.-Int. Edit.* **2003,** *42* (2), 234-+.

9. Matsumura, Y.; Maki, T.; Murakami, S.; Onomura, O., Copper ion-induced activation and asymmetric benzoylation of 1,2-diols: Kinetic chiral molecular recognition. *J. Am. Chem. Soc.* **2003,** *125* (8), 2052-2053.

10. Bagdanoff, J. T.; Ferreira, E. M.; Stoltz, B. M., Palladium-catalyzed enantioselective oxidation of alcohols: A dramatic rate acceleration by Cs2CO3/t-BuOH. *Org. Lett.* **2003,** *5* (6), 835-837.

11. Nishibayashi, Y.; Yamauchi, A.; Onodera, G.; Uemura, S., Oxidative kinetic resolution of racemic alcohols catalyzed by chiral ferrocenyloxazolinylphosphine-ruthenium complexes. *J. Org. Chem.* **2003,** *68* (15), 5875-5880.

12. Matsumura, S.; Maeda, Y.; Nishimura, T.; Uemura, S., Palladium-catalyzed asymmetric arylation, vinylation, and allenylation of tert-cyclobutanois via enantioselective C-C bond cleavage. *J. Am. Chem. Soc.* **2003,** *125* (29), 8862-8869.

13. Larsen, A. O.; Leu, W.; Oberhuber, C. N.; Campbell, J. E.; Hoveyda, A. H., Bidentate NHC-based chiral ligands for efficient Cu-catalyzed enantioselective allylic alkylations: Structure and activity of an air-stable chiral Cu complex. *J. Am. Chem. Soc.* **2004,** *126* (36), 11130-11131.

14. Pineschi, M.; Del Moro, F.; Crotti, P.; Di Bussolo, V.; Macchia, F., Catalytic regiodivergent kinetic resolution of allylic epoxides: A new entry to allylic and homoallylic alcohols with high optical purity. *J. Org. Chem.* **2004,** *69* (6), 2099-2105.

15. Tissot-Croset, K.; Polet, D.; Alexakis, A., A highly effective phosphoramidite ligand for asymmetric allylic substitution. *Angew. Chem.-Int. Edit.* **2004,** *43* (18), 2426-2428.

16. Trend, R. M.; Stoltz, B. M., An experimentally derived model for stereoselectivity in the aerobic oxidative kinetic resolution of secondary alcohols by (Sparteine)PdCl2. *J. Am. Chem. Soc.* **2004,** *126* (14), 4482-4483.

17. Aoyama, H.; Tokunaga, M.; Kiyosu, J.; Iwasawa, T.; Obora, Y.; Tsuji, Y., Kinetic resolution of axially chiral 2,2 '-dihydroxy-1,1 '-biaryls by palladium-catalyzed alcoholysis. *J. Am. Chem. Soc.* **2005,** *127* (30), 10474-10475.

18. Goldsmith, P. J.; Teat, S. J.; Woodward, S., Enantioselective preparation of beta,beta-disubstituted alpha-methylenepropionates by MAO promotion of the zinc Schlenk equilibrium. *Angew. Chem.-Int. Edit.* **2005,** *44* (15), 2235-2237.

19. Yorimitsu, H.; Oshima, K., Recent progress in asymmetric allylic substitutions catalyzed by chiral copper complexes. *Angew. Chem.-Int. Edit.* **2005,** *44* (29), 4435-4439.

20. Dong, L.; Xu, Y. J.; Cun, L. F.; Cui, X.; Mi, A. Q.; Jiang, Y. Z.; Gong, L. Z., Asymmetric nitroallylation of arylboronic acids with nitroallyl acetates catalyzed by chiral rhodium complexes and its application in a concise total synthesis of optically pure (+)-gamma-lycorane. *Org. Lett.* **2005,** *7* (19), 4285-4288.

21. Radosevich, A. T.; Musich, C.; Toste, F. D., Vanadium-catalyzed asymmetric oxidation of alpha-hydroxy esters using molecular oxygen as stoichlometric oxidant. *J. Am. Chem. Soc.* **2005,** *127* (4), 1090-1091.

22. Falciola, C. A.; Tissot-Croset, K.; Alexakis, A., beta-disubstituted allylic chlorides: Substrates for the Cu-catalyzed asymmetric S(N)2 ' reaction. *Angew. Chem.-Int. Edit.* **2006,** *45* (36), 5995-5998.

23. Geurts, K.; Fletcher, S. P.; Feringa, B. L., Copper catalyzed asymmetric synthesis of chiral allylic esters. *J. Am. Chem. Soc.* **2006,** *128* (49), 15572-15573.

24. Umeda, R.; Studer, A., Desymmetrization of 1,4-cyclohexadienyltriisopropoxysilane using copper catalysis. *Org. Lett.* **2007,** *9* (11), 2175-2178.

25. Falciola, C. A.; Alexakis, A., 1,4-dichloro- and 1,4-dibromo-2-butenes as substrates for Cu-catalyzed asymmetric allylic substitution. *Angew. Chem.-Int. Edit.* **2007,** *46* (15), 2619-2622.

26. Chen, T.; Jiang, J. J.; Xu, Q.; Shi, M., Axially chiral NHC-Pd(II) complexes in the oxidative kinetic resolution of secondary alcohols using molecular oxygen as a terminal oxidant. *Org. Lett.* **2007,** *9* (5), 865-868.

27. Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M., Copper-catalyzed enantioselective substitution of allylic carbonates with diboron: An efficient route to optically active alpha-chiral allylboronates. *J. Am. Chem. Soc.* **2007,** *129* (48), 14856-+.

28. Miller, J. J.; Sigman, M. S., Quantitatively correlating the effect of ligand-substituent size in asymmetric catalysis using linear free energy relationships. *Angew. Chem.-Int. Edit.* **2008,** *47* (4), 771-774.

29. Lee, Y.; Akiyama, K.; Gillingham, D. G.; Brown, M. K.; Hoveyda, A. H., Highly site- and enantioselective Cu-catalyzed allylic alkylation reactions with easily accessible vinylaluminum reagents. *J. Am. Chem. Soc.* **2008,** *130* (2), 446-+.

30. Arita, S.; Koike, T.; Kayaki, Y.; Ikariya, T., Aerobic oxidative kinetic resolution of racemic secondary alcohols with chiral bifunctional amido complexes. *Angew. Chem.-Int. Edit.* **2008,** *47* (13), 2447-2449.

31. Shintani, R.; Takatsu, K.; Hayashi, T., Rhodium-catalyzed kinetic resolution of tertiary homoallyl alcohols via stereoselective carbon-carbon bond cleavage. *Org. Lett.* **2008,** *10* (6), 1191-1193.

32. Wills, M., Asymmetric catalysis using air: Clean kinetic resolution of secondary alcohols. *Angew. Chem.-Int. Edit.* **2008,** *47* (23), 4264-4267.

33. Hojo, D.; Noguchi, K.; Hirano, M.; Tanaka, K., Enantioselective synthesis of spirocyclic benzopyranones by rhodium-catalyzed intermolecular [4+2] annulation. *Angew. Chem.-Int. Edit.* **2008,** *47* (31), 5820-5822.

34. Ebner, D. C.; Trend, R. M.; Genet, C.; McGrath, M. J.; O'Brien, P.; Stoltz, B. M., Palladium-catalyzed enantioselective oxidation of chiral secondary alcohols: Access to both enantiomeric series. *Angew. Chem.-Int. Edit.* **2008,** *47* (34), 6367-6370.

35. Haak, R. M.; Berthiol, F.; Jerphagnon, T.; Gayet, A. J. A.; Tarabiono, C.; Postema, C. P.; Ritleng, V.; Pfeffer, M.; Janssen, D. B.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G., Dynamic kinetic resolution of racemic beta-haloalcohols: Direct access to enantioenriched epoxides. *J. Am. Chem. Soc.* **2008,** *130* (41), 13508-+.

36. Krishnan, S.; Bagdanoff, J. T.; Ebner, D. C.; Ramtohul, Y. K.; Tambar, U. K.; Stoltz, B. M., Pd-catalyzed enantioselective aerobic oxidation of secondary alcohols: Applications to the total synthesis of alkaloids. *J. Am. Chem. Soc.* **2008,** *130* (41), 13745-13754.

37. Seiser, T.; Cramer, N., Enantioselective C-C Bond Activation of Allenyl Cyclobutanes: Access to Cyclohexenones with Quaternary Stereogenic Centers. *Angew. Chem.-Int. Edit.* **2008**, 9294-9297.

38. Trend, R. M.; Stoltz, B. M., Structural Features and Reactivity of (Sparteine)PdCl2: A Model for Selectivity in the Oxidative Kinetic Resolution of Secondary Alcohols. *J. Am. Chem. Soc.* **2008,** *130* (47), 15957-15966.

39. Muthupandi, P.; Alamsetti, S. K.; Sekar, G., Chiral iron complex catalyzed enantioselective oxidation of racemic benzoins. *Chem. Commun.* **2009,** (22), 3288-3290.

40. Alamsetti, S. K.; Muthupandi, P.; Sekar, G., Chiral Cobalt-Catalyzed Enantiomer-Differentiating Oxidation of Racemic Benzoins by Using Molecular Oxygen as Stoichiometric Oxidant. *Chem.-Eur. J.* **2009,** *15* (22), 5424-5427.

41. Ebner, D. C.; Bagdanoff, J. T.; Ferreira, E. M.; McFadden, R. M.; Caspi, D. D.; Trend, R. M.; Stoltz, B. M., The Palladium-Catalyzed Aerobic Kinetic Resolution of Secondary Alcohols: Reaction Development, Scope, and Applications. *Chem.-Eur. J.* **2009,** *15* (47), 12978-12992.

42. Mashiko, T.; Kumagai, N.; Shibasaki, M., Managing Highly Coordinative Substrates in Asymmetric Catalysis: A Catalytic Asymmetric Amination with a Lanthanum-Based Ternary Catalyst. *J. Am. Chem. Soc.* **2009,** *131* (41), 14990-14999.

43. Langlois, J. B.; Alexakis, A., Dynamic kinetic asymmetric transformation in copper catalyzed allylic alkylation. *Chem. Commun.* **2009,** (26), 3868-3870.

44. Selim, K. B.; Matsumoto, Y.; Yamada, K.; Tomioka, K., Efficient Chiral N-Heterocyclic Carbene/Copper(I)-Catalyzed Asymmetric Allylic Arylation with Aryl Grignard Reagents. *Angew. Chem.-Int. Edit.* **2009,** *48* (46), 8733-8735.

45. Akiyama, K.; Gao, F.; Hoveyda, A. H., Stereoisomerically Pure Trisubstituted Vinylaluminum Reagents and their Utility in Copper-Catalyzed Enantioselective Synthesis of 1,4-Dienes Containing Z or E Alkenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (2), 419-423.

46. Palais, L.; Bournaud, C.; Micouin, L.; Alexakis, A., Copper-Catalysed Ring Opening of Polycyclic meso-Hydrazines with Trialkylaluminium Reagents and SimplePhos Ligands. *Chem.-Eur. J.* **2010,** *16* (8), 2567-2573.

47. Jackowski, O.; Alexakis, A., Copper-Free Asymmetric Allylic Alkylation with Grignard Reagents. *Angew. Chem.-Int. Edit.* **2010,** *49* (19), 3346-3350.

48. Seiser, T.; Cramer, N., Rhodium(I)-Catalyzed Enantioselective Activation of Cyclobutanols: Formation of Cyclohexane Derivatives with Quaternary Stereogenic Centers. *Chem.-Eur. J.* **2010,** *16* (11), 3383-3391.

49. Seiser, T.; Cramer, N., Rhodium-Catalyzed C-C Bond Cleavage: Construction of Acyclic Methyl Substituted Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2010,** *132* (15), 5340-+.

50. Brown, M. K.; Blewett, M. M.; Colombe, J. R.; Corey, E. J., Mechanism of the Enantioselective Oxidation of Racemic Secondary Alcohols Catalyzed by Chiral Mn(III)-Salen Complexes. *J. Am. Chem. Soc.* **2010,** *132* (32), 11165-11170.

51. Fananas-Mastral, M.; Feringa, B. L., Copper-Catalyzed Regio- and Enantioselective Synthesis of Chiral Enol Acetates and beta-Substituted Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (38), 13152-13153.

52. Gao, F.; McGrath, K. P.; Lee, Y.; Hoveyda, A. H., Synthesis of Quaternary Carbon Stereogenic Centers through Enantioselective Cu-Catalyzed Allylic Substitutions with Vinylaluminum Reagents. *J. Am. Chem. Soc.* **2010,** *132* (40), 14315-14320.

53. Gao, F.; Lee, Y.; Mandai, K.; Hoveyda, A. H., Quaternary Carbon Stereogenic Centers through Copper-Catalyzed Enantioselective Allylic Substitutions with Readily Accessible Aryl- or Heteroaryllithium Reagents and Aluminum Chlorides. *Angew. Chem.-Int. Edit.* **2010,** *49* (45), 8370-8374.

54. Guzman-Martinez, A.; Hoveyda, A. H., Enantioselective Synthesis of Allylboronates Bearing a Tertiary or Quaternary B-Substituted Stereogenic Carbon by NHC-Cu-Catalyzed Substitution Reactions. *J. Am. Chem. Soc.* **2010,** *132* (31), 10634-10637.

55. Waibel, M.; Cramer, N., Desymmetrizations of meso-tert-norbornenols by rhodium(I)-catalyzed enantioselective retro-allylations. *Chem. Commun.* **2011,** *47* (1), 346-348.

56. Langlois, J. B.; Alexakis, A., Identification of a Valuable Kinetic Process in Copper-Catalyzed Asymmetric Allylic Alkylation. *Angew. Chem.-Int. Edit.* **2011,** *50* (8), 1877-1881.

57. Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T., Stereoconvergent Synthesis of Chiral Allylboronates from an E/Z Mixture of Allylic Aryl Ethers Using a 6-NHC-Cu(I) Catalyst. *J. Am. Chem. Soc.* **2011,** *133* (8), 2410-2413.

58. Dabrowski, J. A.; Gao, F.; Hoveyda, A. H., Enantioselective Synthesis of Alkyne-Substituted Quaternary Carbon Stereogenic Centers through NHC-Cu-Catalyzed Allylic Substitution Reactions with (i-Bu)(2)(Alkynyl)aluminum Reagents. *J. Am. Chem. Soc.* **2011,** *133* (13), 4778-4781.

59. Huang, J. R.; Cui, H. L.; Lei, J.; Sun, X. H.; Chen, Y. C., Organocatalytic chemoselective asymmetric N-allylic alkylation of enamides. *Chem. Commun.* **2011,** *47* (16), 4784-4786.

60. Cai, Y. F.; Liu, X. H.; Jiang, J.; Chen, W. L.; Lin, L. L.; Feng, X. M., Catalytic Asymmetric Chloroamination Reaction of alpha,beta-Unsaturated gamma-Keto Esters and Chalcones. *J. Am. Chem. Soc.* **2011,** *133* (15), 5636-5639.

61. Shen, K.; Liu, X. H.; Wang, G.; Lin, L. L.; Feng, X. M., Facile and Efficient Enantioselective Hydroxyamination Reaction: Synthesis of 3-Hydroxyamino-2-Oxindoles Using Nitrosoarenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (20), 4684-4688.

62. Kumar, P.; Troast, D. M.; Cella, R.; Louie, J., Ni-Catalyzed Ketene Cycloaddition: A System That Resists the Formation of Decarbonylation Side Products. *J. Am. Chem. Soc.* **2011,** *133* (20), 7719-7721.

63. Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T., Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Aryl- and Alkenylboronates. *Angew. Chem.-Int. Edit.* **2011,** *50* (37), 8656-8659.

64. Kunisu, T.; Oguma, T.; Katsuki, T., Aerobic Oxidative Kinetic Resolution of Secondary Alcohols with Naphthoxide-Bound Iron(salan) Complex. *J. Am. Chem. Soc.* **2011,** *133* (33), 12937-12939.

65. Brozek, L. A.; Ardolino, M. J.; Morken, J. P., Diastereocontrol in Asymmetric Allyl-Allyl Cross-Coupling: Stereocontrolled Reaction of Prochiral Allylboronates with Prochiral Allyl Chlorides. *J. Am. Chem. Soc.* **2011,** *133* (42), 16778-16781.

66. Maity, P.; Srinivas, H. D.; Watson, M. P., Copper-Catalyzed Enantioselective Additions to Oxocarbenium Ions: Alkynylation of Isochroman Acetals. *J. Am. Chem. Soc.* **2011,** *133* (43), 17142-17145.

67. Langlois, J. B.; Emery, D.; Mareda, J.; Alexakis, A., Mechanistic identification and improvement of a direct enantioconvergent transformation in copper-catalyzed asymmetric allylic alkylation. *Chem. Sci.* **2012,** *3* (4), 1062-1069.

68. Jung, B.; Hoveyda, A. H., Site- and Enantioselective Formation of Allene-Bearing Tertiary or Quaternary Carbon Stereogenic Centers through NHC-Cu-Catalyzed Allylic Substitution. *J. Am. Chem. Soc.* **2012,** *134* (3), 1490-1493.

69. Fananas-Mastral, M.; Perez, M.; Bos, P. H.; Rudolph, A.; Harutyunyan, S. R.; Feringa, B. L., Enantioselective Synthesis of Tertiary and Quaternary Stereogenic Centers: Copper/Phosphoramidite-Catalyzed Allylic Alkylation with Organolithium Reagents. *Angew. Chem.-Int. Edit.* **2012,** *51* (8), 1922-1925.

70. Ye, J. T.; Li, S. H.; Chen, B.; Fan, W.; Kuang, J. Q.; Liu, J. X.; Liu, Y.; Miao, B. K. Y.; Wan, B. Q.; Wang, Y. L.; Xie, X.; Yu, Q.; Yuan, W. M.; Ma, S. M., Catalytic Asymmetric Synthesis of Optically Active Allenes from Terminal Alkynes. *Org. Lett.* **2012,** *14* (5), 1346-1349.

71. Giannerini, M.; Fananas-Mastral, M.; Feringa, B. L., Z-Selective Copper-Catalyzed Asymmetric Allylic Alkylation with Grignard Reagents. *J. Am. Chem. Soc.* **2012,** *134* (9), 4108-4111.

72. Gao, F.; Carr, J. L.; Hoveyda, A. H., Copper-Catalyzed Enantioselective Allylic Substitution with Readily Accessible Carbonyl- and Acetal-Containing Vinylboron Reagents. *Angew. Chem.-Int. Edit.* **2012,** *51* (27), 6613-6617.

73. Shido, Y.; Yoshida, M.; Tanabe, M.; Ohmiya, H.; Sawamura, M., Copper-Catalyzed Enantioselective Allylic Substitution with Alkylboranes. *J. Am. Chem. Soc.* **2012,** *134* (45), 18573-18576.

74. Li, H. L.; Muller, D.; Guenee, L.; Alexakis, A., Copper-Catalyzed Enantioselective Synthesis of Axially Chiral Allenes. *Org. Lett.* **2012,** *14* (23), 5880-5883.

75. Hornillos, V.; Perez, M.; Fananas-Mastral, M.; Feringa, B. L., Copper-Catalyzed Enantioselective Allyl-Allyl Cross-Coupling. *J. Am. Chem. Soc.* **2013,** *135* (6), 2140-2143.

76. Delvos, L. B.; Vyas, D. J.; Oestreich, M., Asymmetric Synthesis of -Chiral Allylic Silanes by Enantioconvergent -Selective Copper(I)-Catalyzed Allylic Silylation. *Angew. Chem.-Int. Edit.* **2013,** *52* (17), 4650-4653.

77. Dabrowski, J. A.; Haeffner, F.; Hoveyda, A. H., Combining NHC-Cu and BrOnsted Base Catalysis: Enantioselective Allylic Substitution/Conjugate Additions with Alkynylaluminum Reagents and Stereospecific Isomerization of the Products to Trisubstituted Allenes. *Angew. Chem.-Int. Edit.* **2013,** *52* (30), 7694-7699.

78. Chau, S. T.; Lutz, J. P.; Wu, K.; Doyle, A. G., Nickel-Catalyzed Enantioselective Arylation of Pyridinium Ions: Harnessing an Iminium Ion Activation Mode. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9153-9156.

79. Souillart, L.; Cramer, N., Exploitation of Rh(I)-Rh(III) cycles in enantioselective C-C bond cleavages: access to beta-tetralones and benzobicyclo 2.2.2 octanones. *Chem. Sci.* **2014,** *5* (2), 837-840.

80. Gao, F.; Carr, J. L.; Hoveyda, A. H., A Broadly Applicable NHC-Cu-Catalyzed Approach for Efficient, Site-, and Enantioselective Coupling of Readily Accessible (Pinacolato)alkenylboron Compounds to Allylic Phosphates and Applications to Natural Product Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (5), 2149-2161.

81. Maji, B.; Baidya, M.; Yamamoto, H., Asymmetric construction of quaternary stereocenters by magnesium catalysed direct amination of beta-ketoesters using in situ generated nitrosocarbonyl compounds as nitrogen sources. *Chem. Sci.* **2014,** *5* (10), 3941-3945.

82. Souillart, L.; Cramer, N., Highly Enantioselective Rhodium(I)-Catalyzed Carbonyl Carboacylations Initiated by C-C Bond Activation. *Angew. Chem.-Int. Edit.* **2014,** *53* (36), 9640-9644.

83. Harada, A.; Makida, Y.; Sato, T.; Ohmiya, H.; Sawamura, M., Copper-Catalyzed Enantioselective Allylic Alkylation of Terminal Alkyne Pronucleophiles. *J. Am. Chem. Soc.* **2014,** *136* (39), 13932-13939.

84. Yang, D.; Wang, L.; Han, F.; Li, D.; Zhao, D.; Cao, Y.; Ma, Y.; Kong, W.; Sun, Q.; Wang, R., Highly Enantioselective Ring-Opening Reactions of Aziridines with Indole and Its Application in the Building of C-3-Halogenated Pyrroloindolines. *Chem.-Eur. J.* **2014,** *20* (50), 16478-16483.

85. Li, H.; Grassi, D.; Guenee, L.; Buergi, T.; Alexakis, A., Copper-Catalyzed Propargylic Substitution of Dichloro Substrates: Enantioselective Synthesis of Trisubstituted Allenes and Formation of Propargylic Quaternary Stereogenic Centers. *Chem.-Eur. J.* **2014,** *20* (50), 16694-16706.

86. Yamamoto, E.; Takenouchi, Y.; Ozaki, T.; Miya, T.; Ito, H., Copper(I)-Catalyzed Enantioselective Synthesis of alpha-Chiral Linear or Carbocyclic (E)-(gamma-Alkoxyallyl)boronates. *J. Am. Chem. Soc.* **2014,** *136* (47), 16515-16521.

87. Yang, D.; Wang, L.; Han, F.; Li, D.; Zhao, D.; Wang, R., Intermolecular Enantioselective Dearomatization Reaction of beta-Naphthol Using meso-Aziridine: A Bifunctional In Situ Generated Magnesium Catalyst. *Angew. Chem.-Int. Edit.* **2015,** *54* (7), 2185-2189.

88. You, H.; Rideau, E.; Sidera, M.; Fletcher, S. P., Non-stabilized nucleophiles in Cu-catalysed dynamic kinetic asymmetric allylic alkylation. *Nature* **2015,** *517* (7534), 351-355.

89. Deng, L.; Xu, T.; Lo, H. B.; Done, G. B., Enantioselective Rh-Catalyzed Carboacylation of C=N Bonds via C-C Activation of Benzocyclobutenones. *J. Am. Chem. Soc.* **2016,** *138* (1), 369-374.

90. Shi, Y.; Hoveyda, A. H., Catalytic S(N)2-and Enantioselective Allylic Substitution with a Diborylmethane Reagent and Application in Synthesis. *Angew. Chem.-Int. Edit.* **2016,** *55* (10), 3455-3458.

91. Yasuda, Y.; Ohmiya, H.; Sawamura, M., Copper-Catalyzed Enantioselective Allyl-Allyl Coupling between Allylic Boronates and Phosphates with a Phenol/N-Heterocyclic Carbene Chiral Ligand. *Angew. Chem.-Int. Edit.* **2016,** *55* (36), 10816-10820.

92. Han, J. T.; Jang, W. J.; Kim, N.; Yun, J., Asymmetric Synthesis of Borylalkanes via Copper-Catalyzed Enantioselective Hydroallylation. *J. Am. Chem. Soc.* **2016,** *138* (46), 15146-15149.

93. Guo, R.; Zheng, X. X.; Zhang, D. Y.; Zhang, G. Z., Rhodium(I)-catalyzed stereoselective 4+2 cycloaddition of oxetanols with alkynes through C(sp(3))-C(sp(3)) bond cleavage. *Chem. Sci.* **2017,** *8* (4), 3002-3006.

94. Hojoh, K.; Ohmiya, H.; Sawamura, M., Synthesis of alpha-Quaternary Formimides and Aldehydes through Umpolung Asymmetric Copper Catalysis with Isocyanides. *J. Am. Chem. Soc.* **2017,** *139* (6), 2184-2187.

95. Rideau, E.; You, H. Z.; Sidera, M.; Claridge, T. D. W.; Fletcher, S. P., Mechanistic Studies on a Cu-Catalyzed Asymmetric Allylic Alkylation with Cyclic Racemic Starting Materials. *J. Am. Chem. Soc.* **2017,** *139* (15), 5614-5624.

96. Xu, G. X.; Zhao, H. Y.; Fu, B.; Cang, A. J.; Zhang, G.; Zhang, Q.; Xiong, T.; Zhang, Q., Ligand-Controlled Regiodivergent and Enantioselective Copper-Catalyzed Hydroallylation of Alkynes. *Angew. Chem.-Int. Edit.* **2017,** *56* (42), 13130-13134.

97. Yang, S.; Li, Q. Z.; Xu, C.; Xu, Q.; Shi, M., Rhodium-catalyzed asymmetric hydroamination and hydroindolation of keto-vinylidenecyclopropanes. *Chem. Sci.* **2018,** *9* (22), 5074-5081.

98. Cao, J.; Chen, L.; Sun, F. N.; Sun, Y. L.; Jiang, K. Z.; Yang, K. F.; Xu, Z.; Xu, L. W., Pd-Catalyzed Enantioselective Ring Opening/Cross-Coupling and Cyclopropanation of Cyclobutanones. *Angew. Chem.-Int. Edit.* **2019,** *58* (3), 897-901.

99. Sun, F. N.; Yang, W. C.; Chen, X. B.; Sun, Y. L.; Cao, J.; Xu, Z.; Xu, L. W., Enantioselective palladium/copper-catalyzed C-C sigma-bond activation synergized with Sonogashira-type C(sp(3))-C(sp) cross-coupling alkynylation. *Chem. Sci.* **2019,** *10* (32), 7579-7583.

100. Liu, Z.-L.; Yang, C.; Xue, Q.-Y.; Zhao, M.; Shan, C.-C.; Xu, Y.-H.; Loh, T.-P., Copper-Catalyzed Asymmetric Silylation of Propargyl Dichlorides: Access to Enantioenriched Functionalized Allenylsilanes. *Angewandte Chemie International Edition* **2019,** *58* (46), 16538-16542.

101. Bai, D.; Yu, Y.; Guo, H.; Chang, J.; Li, X., Nickel(0)-Catalyzed Enantioselective [3+2] Annulation of Cyclopropenones and α,β-Unsaturated Ketones/Imines. *Angewandte Chemie International Edition* **2020,** *59* (7), 2740-2744.

102. Qi, J.; Wei, F.; Huang, S.; Tung, C.-H.; Xu, Z., Copper(I)-Catalyzed Asymmetric Interrupted Kinugasa Reaction: Synthesis of α-Thiofunctional Chiral β-Lactams. *Angewandte Chemie International Edition* **2021,** *60* (9), 4561-4565.

103. Iwamoto, H.; Ozawa, Y.; Takenouchi, Y.; Imamoto, T.; Ito, H., Backbone-Modified C2-Symmetrical Chiral Bisphosphine TMS-QuinoxP*: Asymmetric Borylation of Racemic Allyl Electrophiles. *J. Am. Chem. Soc.* **2021,** *143* (17), 6413-6422.

104. Wan, Q.; Xie, J.-H.; Zheng, C.; Yuan, Y.-F.; You, S.-L., Silver-Catalyzed Asymmetric Dearomatization of Electron-Deficient Heteroarenes via Interrupted Barton–Zard Reaction. *Angewandte Chemie International Edition* **2021,** *60* (36), 19730-19734.

105. O'Connor, T. J.; Mai, B. K.; Nafie, J.; Liu, P.; Toste, F. D., Generation of Axially Chiral Fluoroallenes through a Copper-Catalyzed Enantioselective β-Fluoride Elimination. *J. Am. Chem. Soc.* **2021,** *143* (34), 13759-13768.

106. Wu, R.; Lu, J.; Cao, T.; Ma, J.; Chen, K.; Zhu, S., Enantioselective Rh(II)-Catalyzed Desymmetric Cycloisomerization of Diynes: Constructing Furan-Fused Dihydropiperidines with an Alkyne-Substituted Aza-Quaternary Stereocenter. *J. Am. Chem. Soc.* **2021,** *143* (36), 14916-14925.

107. Xu, X.; Peng, L.; Chang, X.; Guo, C., Ni/Chiral Sodium Carboxylate Dual Catalyzed Asymmetric O-Propargylation. *J. Am. Chem. Soc.* **2021,** *143* (49), 21048-21055.

108. Hou, S.-H.; Yu, X.; Zhang, R.; Wagner, C.; Dong, G., Rhodium-Catalyzed Diastereo- and Enantioselective Divergent Annulations between Cyclobutanones and 1,5-Enynes: Rapid Construction of Complex C(sp3)-Rich Scaffolds. *J. Am. Chem. Soc.* **2022,** *144* (48), 22159-22169.

109. Yu, X.; Zhang, Z.; Dong, G., Catalytic Enantioselective Synthesis of γ-Lactams with β-Quaternary Centers via Merging of C–C Activation and Sulfonyl Radical Migration. *J. Am. Chem. Soc.* **2022,** *144* (21), 9222-9228.

110. Yan, X.; Liu, M.; Pan, D.; Wang, Q.; Tang, Q.; Dai, Y.-M.; Hu, P.; Wang, B.-Q.; Huang, G.; Song, F., Diastereo- and Enantioselective Synthesis of Tetracyclic Cycloheptanols through (4+3) Annulation via C−C/C−H Activation Cascade. *Angewandte Chemie International Edition* **2024,** *63* (13), e202317433.

111. Yang, H.; Zeng, Y.; Song, X.; Che, L.; Jiang, Z.-T.; Lu, G.; Xia, Y., Rhodium-Catalyzed Enantio- and Regioselective Allylation of Indoles with gem-Difluorinated Cyclopropanes. *Angewandte Chemie International Edition* **2024,** *63* (22), e202403602.

112. Hurtado, J.; Iragorri, N.; Reyes, E.; Vicario, J. L.; Fernández, E., Cu-Catalyzed Enantioselective Borylative Desymmetrization of 1-Vinyl Cyclobutanols and Axial-to-Point Chirality Transfer in a Diastereoconvergent/Stereoretentive Allylation Scenery. *Angewandte Chemie International Edition* **2024,** *63* (43), e202411232.

113. Li, Z.-H.; Ma, J.-S.; Lu, H.-Y.; Lin, G.-Q.; He, Z.-T., Asymmetric Multicomponent Propargylations via Carbon Dioxide Shuttling and Fixation. *ACS Catalysis* **2024,** *14* (15), 11646-11656.

114. Cai, S.; Zhao, Z.; Yang, G.; Huang, H., Dynamic amine sorting enables multiselective construction of unsymmetrical chiral diamines. *Nat. Chem.* **2024,** *16* (12), 1972-1981.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

4.6 Dual Activation on A Single Metal Center: Non-Activated Systems

4.6.1 Functionalization of Non-Activated Olefins

1. Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B., CATALYTIC ASYMMETRIC EPOXIDATION AND KINETIC RESOLUTION - MODIFIED PROCEDURES INCLUDING INSITU DERIVATIZATION. *J. Am. Chem. Soc.* **1987,** *109* (19), 5765-5780.

2. Inoue, S.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R., MECHANISM OF THE ASYMMETRIC ISOMERIZATION OF ALLYLAMINES TO ENAMINES CATALYZED BY 2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL RHODIUM COMPLEXES. *J. Am. Chem. Soc.* **1990,** *112* (12), 4897-4905.

3. Woodard, S. S.; Finn, M. G.; Sharpless, K. B., MECHANISM OF ASYMMETRIC EPOXIDATION .1. KINETICS. *J. Am. Chem. Soc.* **1991,** *113* (1), 106-113.

4. Finn, M. G.; Sharpless, K. B., MECHANISM OF ASYMMETRIC EPOXIDATION .2. CATALYST STRUCTURE. *J. Am. Chem. Soc.* **1991,** *113* (1), 113-126.

5. Uozumi, Y.; Kitayama, K.; Hayashi, T., Regioselective and Enantioselective Hydrosilylation of 1- Arylalkenes by Use of Palladium-Mop Catalyst. *Tetrahedron-Asymmetry* **1993,** *4* (12), 2419-2422.

6. Casalnuovo, A. L.; Rajanbabu, T. V.; Ayers, T. A.; Warren, T. H., LIGAND ELECTRONIC EFFECTS IN ASYMMETRIC CATALYSIS - ENHANCED ENANTIOSELECTIVITY IN THE ASYMMETRIC HYDROCYANATION OF VINYLARENES. *J. Am. Chem. Soc.* **1994,** *116* (22), 9869-9882.

7. Kondakov, D. Y.; Negishi, E., ZIRCONIUM-CATALYZED ENANTIOSELECTIVE METHYLALUMINATION OF MONOSUBSTITUTED ALKENES. *J. Am. Chem. Soc.* **1995,** *117* (43), 10771-10772.

8. Visser, M. S.; Harrity, J. P. A.; Hoveyda, A. H., Zirconium-catalyzed kinetic resolution of cyclic allylic ethers. An enantioselective route to unsaturated medium ring systems. *J. Am. Chem. Soc.* **1996,** *118* (15), 3779-3780.

9. Fernandez, E.; Hooper, M. W.; Knight, F. I.; Brown, J. M., Catalytic asymmetric hydroboration-amination. *Chem. Commun.* **1997,** (2), 173-174.

10. Pioda, G.; Togni, A., Highly enantioselective palladium-catalyzed hydrosilylation of norbornene with trichlorosilane using ferrocenyl ligands. *Tetrahedron-Asymmetry* **1998,** *9* (21), 3903-3910.

11. Lightfoot, A.; Schnider, P.; Pfaltz, A., Enantioselective hydrogenation of olefins with iridium-phosphanodihydrooxazole catalysts. *Angew. Chem.-Int. Edit.* **1998,** *37* (20), 2897-2899.

12. Fernandez, E.; Maeda, K.; Hooper, M. W.; Brown, J. M., Catalytic asymmetric hydroboration/amination and alkylamination with rhodium complexes of 1,1 '-(2-diarylphosphino-1- naphthyl)isoquinoline. *Chem.-Eur. J.* **2000,** *6* (10), 1840-1846.

13. de Armas, J.; Kolis, S. P.; Hoveyda, A. H., Zr-catalyzed olefin alkylations and allylic substitution reactions with electrophiles. *J. Am. Chem. Soc.* **2000,** *122* (25), 5977-5983.

14. Kawatsura, M.; Hartwig, J. F., Palladium-catalyzed intermolecular hydroamination of vinylarenes using arylamines. *J. Am. Chem. Soc.* **2000,** *122* (39), 9546-9547.

15. Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y., Asymmetric hydrosilylation of styrenes catalyzed by palladium- MOP complexes: Ligand modification and mechanistic studies. *J. Org. Chem.* **2001,** *66* (4), 1441-1449.

16. Lober, O.; Kawatsura, M.; Hartwig, J. F., Palladium-catalyzed hydroamination of 1,3-dienes: A colorimetric assay and enantioselective additions. *J. Am. Chem. Soc.* **2001,** *123* (18), 4366-4367.

17. Luna, A. P.; Bonin, M.; Micouin, L.; Husson, H. P., Reversal of enantioselectivity in the asymmetric rhodium- versus iridium-catalyzed hydroboration of meso substrates. *J. Am. Chem. Soc.* **2002,** *124* (41), 12098-12099.

18. Menges, F.; Neuburger, M.; Pfaltz, A., Synthesis and application of chiral phosphino-imidazoline ligands: Ir-catalyzed enantioselective hydrogenation. *Org. Lett.* **2002,** *4* (26), 4713-4716.

19. Goossen, L. J., Asymmetric hydrovinylation: New perspectives through use of modular ligand systems. *Angew. Chem.-Int. Edit.* **2002,** *41* (20), 3775-3778.

20. Jensen, J. F.; Svendsen, B. Y.; la Cour, T. V.; Pedersen, H. L.; Johannsen, M., Highly enantioselective hydrosilylation of aromatic alkenes. *J. Am. Chem. Soc.* **2002,** *124* (17), 4558-4559.

21. Pedersen, H. L.; Johannsen, M., Synthesis and application of arylmonophosphinoferrocene ligands: Ultrafast asymmetric hydrosilylation of styrene. *J. Org. Chem.* **2002,** *67* (23), 7982-7994.

22. Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T., Asymmetric synthesis of 1-Aryl-1,2-ethanediols from arylacetylenes by palladium-catalyzed asymmetric hydrosilylation as a key step. *J. Am. Chem. Soc.* **2002,** *124* (8), 1584-1585.

23. Huo, S. Q.; Shi, J. C.; Negishi, E., A new protocol for the enantioselective synthesis of methyl- substituted alkanols and their derivatives through a hydroalumination/zirconium-catalyzed alkylalumination tandem process. *Angew. Chem.-Int. Edit.* **2002,** *41* (12), 2141-2143.

24. Cui, X. H.; Burgess, K., Iridium-mediated asymmetric hydrogenation of 2,3- diphenylbutadiene: A revealing kinetic study. *J. Am. Chem. Soc.* **2003,** *125* (47), 14212-14213.

25. Perry, M. C.; Cui, X. H.; Powell, M. T.; Hou, D. R.; Reibenspies, J. H.; Burgess, K., Optically active iridium imidazol-2-ylidene-oxazoline complexes: Preparation and use in asymmetric hydrogenation of arylalkenes. *J. Am. Chem. Soc.* **2003,** *125* (1), 113-123.

26. Tang, W. J.; Wang, W. M.; Zhang, X. M., Phospholane-oxazoline ligands for Ir-catalyzed asymmetric hydrogenation. *Angew. Chem.-Int. Edit.* **2003,** *42* (8), 943-+.

27. Ogasawara, M.; Ueyama, K.; Nagano, T.; Mizuhata, Y.; Hayashi, T., Palladium-catalyzed asymmetric synthesis of axially chiral (Allenylmethyl)silanes and chirality transfer to stereogenic carbon centers in S-E ' reactions. *Org. Lett.* **2003,** *5* (2), 217-219.

28. Shinohara, T.; Arai, M. A.; Wakita, K.; Arai, T.; Sasai, H., The first enantioselective intramolecular aminocarbonylation of alkenes promoted by Pd(II)-spiro bis(isoxazoline) catalyst. *Tetrahedron Lett.* **2003,** *44* (4), 711-714.

29. Suginome, M.; Ohmura, T.; Miyake, Y.; Mitani, S.; Ito, Y.; Murakami, M., Enantioface-selective palladium-catalyzed silaboration of allenes via double asymmetric induction. *J. Am. Chem. Soc.* **2003,** *125* (37), 11174-11175.

30. Morgan, J. B.; Morken, J. P., Platinum-catalyzed tandem diboration/asymmetric allylboration: Access to nonracemic functionalized 1,3-diols. *Org. Lett.* **2003,** *5* (14), 2573-2575.

31. Morgan, J. B.; Miller, S. P.; Morken, J. P., Rhodium-catalyzed enantioselective diboration of simple alkenes. *J. Am. Chem. Soc.* **2003,** *125* (29), 8702-8703.

32. Rubina, M.; Rubin, M.; Gevorgyan, V., Catalytic enantioselective hydroboration of cyclopropenes. *J. Am. Chem. Soc.* **2003,** *125* (24), 7198-7199.

33. Makita, N.; Hoshino, Y.; Yamamoto, H., Asymmetric epoxidation of homoallylic alcohols and application in a concise total synthesis of (-)-alpha-bisabolol and (-)-8- epi-alpha-bisabolol. *Angew. Chem.-Int. Edit.* **2003,** *42* (8), 941-+.

34. Okachi, T.; Murai, N.; Onaka, M., Catalytic enantioselective epoxidation of homoallylic alcohols by chiral zirconium complexes. *Org. Lett.* **2003,** *5* (1), 85-87.

35. Roesky, P. W.; Muller, T. E., Enantioselective catalytic hydroamination of alkenes. *Angew. Chem.-Int. Edit.* **2003,** *42* (24), 2708-2710.

36. Fan, Y. B.; Cui, X. H.; Burgess, K.; Hall, M. B., Electronic effects steer the mechanism of asymmetric hydrogenations of unfunctionalized aryl-substituted alkenes. *J. Am. Chem. Soc.* **2004,** *126* (51), 16688-16689.

37. Kallstrom, K.; Hedberg, C.; Brandt, P.; Bayer, A.; Andersson, P. G., Rationally designed ligands for asymmetric iridium-catalyzed hydrogenation of olefins. *J. Am. Chem. Soc.* **2004,** *126* (44), 14308-14309.

38. Liu, D.; Tang, W. J.; Zhang, X., Synthesis of a new class of conformationally rigid phosphino- oxazolines: Highly enantioselective ligands for Ir-catalyzed asymmetric hydrogenation. *Org. Lett.* **2004,** *6* (4), 513-516.

39. Schenkel, L. B.; Ellman, J. A., Application of P,N-sulfinyl imine ligands to iridium-catalyzed asymmetric hydrogenation of olefins. *J. Org. Chem.* **2004,** *69* (6), 1800-1802.

40. Smidt, S. P.; Menges, F.; Pfaltz, A., SimplePHOX, a readily available chiral ligand system for iridium-catalyzed asymmetric hydrogenation. *Org. Lett.* **2004,** *6* (12), 2023-2026.

41. Trifonova, A.; Diesen, J. S.; Chapman, C. J.; Andersson, P. G., Application of phosphine-oxazoline ligands in Ir-catalyzed asymmetric hydrogenation of acyclic aromatic N-arylimines. *Org. Lett.* **2004,** *6* (21), 3825-3827.

42. Holscher, M.; Francio, G.; Leitner, W., Origin of enantioselectivity in asymmetric hydrovinylations catalyzed by phosphoramidite nickel catalysts: An experimentally supported density functional study. *Organometallics* **2004,** *23* (23), 5606-5617.

43. Zhang, A. B.; RajanBabu, T. V., Chiral benzyl centers through asymmetric catalysis. A three- step synthesis of (R)-(-)-alpha-curcumene via asymmetric hydrovinylation. *Org. Lett.* **2004,** *6* (18), 3159-3161.

44. Zhang, A. B.; Rajanbabu, T. V., Fine-tuning monophosphine ligands for enhanced enantioselectivity. Influence of chiral hemilabile pendant groups. *Org. Lett.* **2004,** *6* (9), 1515-1517.

45. Magistrato, A.; Woo, T. K.; Togni, A.; Rothlisberger, U., Enantioselective palladium-catalyzed hydrosilylation of styrene: Detailed reaction mechanism from first-principles and hybrid QM/MM molecular dynamics simulations. *Organometallics* **2004,** *23* (13), 3218-3227.

46. Pelz, N. F.; Woodward, A. R.; Burks, H. E.; Sieber, J. D.; Morken, J. P., Palladium-catalyzed enantioselective diboration of prochiral allenes. *J. Am. Chem. Soc.* **2004,** *126* (50), 16328-16329.

47. Casey, C. P.; Martins, S. C.; Fagan, M. A., Reversal of enantioselectivity in the hydroformylation of styrene with 2S,4S-BDPP Pt(SnCl3)Cl at high temperature arises from a change in the enantioselective-determining step. *J. Am. Chem. Soc.* **2004,** *126* (17), 5585-5592.

48. Breit, B.; Breuninger, D., Desymmetrizing hydroformylation with the aid of a planar chiral catalyst-directing group. *J. Am. Chem. Soc.* **2004,** *126* (33), 10244-10245.

49. Cobley, C. J.; Gardner, K.; Klosin, J.; Praquin, C.; Hill, C.; Whiteker, G. T.; Zanotti-Gerosa, A.; Petersen, J. L.; Abboud, K. A., Synthesis and application of a new bisphosphite ligand collection for asymmetric hydroformylation of allyl cyanide. *J. Org. Chem.* **2004,** *69* (12), 4031-4040.

50. Cobley, C. J.; Klosin, J.; Qin, C.; Whiteker, G. T., Parallel ligand screening on olefin mixtures in asymmetric hydroformylation reactions. *Org. Lett.* **2004,** *6* (19), 3277-3280.

51. Crudden, C. M.; Hleba, Y. B.; Chen, A. C., Regio- and enantiocontrol in the room-temperature hydroboration of vinyl arenes with pinacol borane. *J. Am. Chem. Soc.* **2004,** *126* (30), 9200-9201.

52. Miller, S. P.; Morgan, J. B.; Nepveux, F. J.; Morken, J. P., Catalytic asymmetric carbohydroxylation of alkenes by a tandem diboration/Suzuki cross-coupling/oxidation reaction. *Org. Lett.* **2004,** *6* (1), 131-133.

53. Morgan, J. B.; Morken, J. P., Catalytic enantioselective hydrogenation of vinyl bis(boronates). *J. Am. Chem. Soc.* **2004,** *126* (47), 15338-15339.

54. Baar, C. R.; Levy, C. J.; Min, E. Y. J.; Henling, L. M.; Day, M. W.; Bercaw, J. E., Kinetic resolution of chiral alpha-olefins using optically active ansa-zirconocene polymerization catalysts. *J. Am. Chem. Soc.* **2004,** *126* (26), 8216-8231.

55. Magnin-Lachaux, M.; Tan, Z.; Liang, B.; Negishi, E., Efficient and selective synthesis of siphonarienolone and related reduced polypropionates via Zr-catalyzed asymmetric carboalumination. *Org. Lett.* **2004,** *6* (9), 1425-1427.

56. Tan, Z.; Negishi, E. I., An efficient and general method for the synthesis of alpha,omega-difunctional reduced polypropionates by Zr-catalyzed asymmetric carboalumination: synthesis of the scyphostatin side chain. *Angew. Chem.-Int. Edit.* **2004,** *43* (22), 2911-2914.

57. Grabulosa, A.; Muller, G.; Ordinas, J. I.; Mezzetti, A.; Maestro, M. A.; Font-Bardia, M.; Solans, X., Allylpalladium complexes with P-stereogenic monodentate phosphines. Application in the asymmetric hydrovinylation of styrene. *Organometallics* **2005,** *24* (21), 4961-4973.

58. Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P., Concatenated catalytic asymmetric allene diboration/allylation/functionalization. *Org. Lett.* **2005,** *7* (24), 5505-5507.

59. Novak, T.; Tan, Z.; Liang, B.; Negishi, E., All-catalytic, efficient, and asymmetric synthesis of alpha,omega-diheterofunctional reduced polypropionates via "one-pot" Zr-catalyzed asymmetric carboalumination - Pd-catalyzed cross-coupling tandem process. *J. Am. Chem. Soc.* **2005,** *127* (9), 2838-2839.

60. Axtell, A. T.; Cobley, C. J.; Klosin, J.; Whiteker, G. T.; Zanotti-Gerosa, A.; Abboud, K. A., Highly regio- and enantioselective asymmetric hydroformylation of olefins mediated by 2,5-disubstituted phospholane ligands. *Angew. Chem.-Int. Edit.* **2005,** *44* (36), 5834-5838.

61. Clark, T. P.; Landis, C. R.; Freed, S. L.; Klosin, J.; Abboud, K. A., Highly active, regioselective, and enantioselective hydroformylation with Rh catalysts ligated by bis-3,4-diazaphospholanes. *J. Am. Chem. Soc.* **2005,** *127* (14), 5040-5042.

62. Trudeau, S.; Morgan, J. B.; Shrestha, M.; Morken, J. P., Rh-catalyzed enantioselective diboration of simple alkenes: Reaction development and substrate scope. *J. Org. Chem.* **2005,** *70* (23), 9538-9544.

63. Okamoto, K.; Nishibayashi, Y.; Uemura, S.; Toshimitsu, A., Asymmetric carboselenenylation reaction of alkenes with aromatic compounds. *Angew. Chem.-Int. Edit.* **2005,** *44* (23), 3588-3591.

64. Kelly, A. R.; Lurain, A. E.; Walsh, P. J., Highly enantio- and diastereoselective one-pot synthesis of acyclic epoxy alcohols and allylic epoxy alcohols. *J. Am. Chem. Soc.* **2005,** *127* (42), 14668-14674.

65. Zhang, W.; Basak, A.; Kosugi, Y.; Hoshino, Y.; Yamamoto, H., Enantioselective epoxidation of allylic alcohols by a chiral complex of vanadium: An effective controller system and a rational mechanistic model. *Angew. Chem.-Int. Edit.* **2005,** *44* (28), 4389-4391.

66. Kim, J. Y.; Livinghouse, T., Enantioselective intramolecular alkene hydroaminations catalyzed by yttrium complexes of axially chiral bis(thiolate) ligands. *Org. Lett.* **2005,** *7* (9), 1737-1739.

67. McGrath, M. J.; O'Brien, P., Catalytic asymmetric deprotonation using a ligand exchange approach. *J. Am. Chem. Soc.* **2005,** *127* (47), 16378-16379.

68. Wilting, J.; Janssen, M.; Muller, C.; Vogt, D., The enantioselective step in the nickel-catalyzed hydrocyanation of 1,3-cyclohexadiene. *J. Am. Chem. Soc.* **2006,** *128* (35), 11374-11375.

69. Zhang, A. B.; RajanBabu, T. V., Hydrovinylation of 1,3-dienes: A new protocol, an asymmetric variation, and a potential solution to the exocyclic side chain stereochemistry problem. *J. Am. Chem. Soc.* **2006,** *128* (1), 54-55.

70. Zhang, A. B.; RajanBabu, T. V., All-carbon quaternary centers via catalytic asymmetric hydrovinylation. New approaches to the exocyclic side chain stereochemistry problem. *J. Am. Chem. Soc.* **2006,** *128* (17), 5620-5621.

71. Ohmura, T.; Taniguchi, H.; Suginome, M., Palladium-catalyzed asymmetric silaboration of allenes. *J. Am. Chem. Soc.* **2006,** *128* (42), 13682-13683.

72. Sieber, J. D.; Morken, J. P., Sequential Pd-catalyzed asymmetric allene diboration/alpha-aminoallylation. *J. Am. Chem. Soc.* **2006,** *128* (1), 74-75.

73. Trost, B. M.; Xie, J., Palladium-catalyzed asymmetric ring expansion of allenylcyclobutanols: An asymmetric Wagner-Meerwein shift. *J. Am. Chem. Soc.* **2006,** *128* (18), 6044-6045.

74. Yan, Y. J.; Zhang, X. M., A hybrid phosphorus ligand for highly enantioselective asymmetric hydroformylation. *J. Am. Chem. Soc.* **2006,** *128* (22), 7198-7202.

75. Blanc, A.; Toste, F. D., Enantioselective synthesis of cyclic ethers through a vanadium-catalyzed resolution/oxidative cyclization. *Angew. Chem.-Int. Edit.* **2006,** *45* (13), 2096-2099.

76. Bell, S.; Wustenberg, B.; Kaiser, S.; Menges, F.; Netscher, T.; Pfaltz, A., Asymmetric hydrogenation of unfunctionalized, purely alkyl-substituted olefins. *Science* **2006,** *311* (5761), 642-644.

77. Giacomina, F.; Meetsma, A.; Panella, L.; Lefort, L.; de Vries, A. H. M.; de Vries, J. G., High enantioselectivity is induced by a single monodentate phosphoramidite ligand in iridium-catalyzed asymmetric hydrogenation. *Angew. Chem.-Int. Edit.* **2007,** *46* (9), 1497-1500.

78. Burks, H. E.; Liu, S. B.; Morken, J. P., Development, mechanism, and scope of the palladium-catalyzed enantioselective allene diboration. *J. Am. Chem. Soc.* **2007,** *129* (28), 8766-8773.

79. Engman, M.; Diesen, J. S.; Paptchikhine, A.; Andersson, P. G., Iridium-catalyzed asymmetric hydrogenation of fluorinated olefins using N,P-ligands: A struggle with hydrogenolysis and selectivity. *J. Am. Chem. Soc.* **2007,** *129* (15), 4536-+.

80. Zhang, W.; Yamamoto, H., Vanadium-catalyzed asymmetric epoxidation of homoallylic alcohols. *J. Am. Chem. Soc.* **2007,** *129* (2), 286-287.

81. Schrems, M. G.; Neumann, E.; Pfaltz, A., Iridium-catalyzed asymmetric hydrogenation of unfunctionalized tetrasubstituted Olefins. *Angew. Chem.-Int. Edit.* **2007,** *46* (43), 8274-8276.

82. Du, H. F.; Yuan, W. C.; Zhao, B. G.; Shi, Y. A., Catalytic asymmetric diamination of conjugated dienes and triene. *J. Am. Chem. Soc.* **2007,** *129* (38), 11688-+.

83. Wang, A.; Wustenberg, B.; Pfaltz, A., Enantio- and diastereoselective hydrogenation of farnesol and O-protected derivatives: Stereocontrol by changing the C=C bond configuration. *Angew. Chem.-Int. Edit.* **2008,** *47* (12), 2298-2300.

84. Smith, C. R.; RajanBabu, T. V., Efficient, selective, and green: Catalyst tuning for highly enantioselective reactions of ethylene. *Org. Lett.* **2008,** *10* (8), 1657-1659.

85. Dieguez, M.; Mazuela, J.; Pamies, O.; Verendel, J. J.; Andersson, P. G., Chiral pyranoside phosphite-oxazolines: A new class of ligand for asymmetric catalytic hydrogenation of alkenes. *J. Am. Chem. Soc.* **2008,** *130* (23), 7208-+.

86. Crotti, S.; Bertolini, F.; Macchia, F.; Pineschi, M., Rhodium-catalyzed enantioselective desymmetrization of bicyclic hydrazines with alkynylboronic esters. *Chem. Commun.* **2008,** (27), 3127-3129.

87. Yasui, Y.; Kamisaki, H.; Takemoto, Y., Enantioselective synthesis of 3,3-disubstituted oxindoles through Pd-catalyzed cyanoamidation. *Org. Lett.* **2008,** *10* (15), 3303-3306.

88. Saha, B.; Smith, C. R.; RajanBabu, T. V., Ligand tuning in asymmetric hydrovinylation of 1,3-dienes: A stereoselective route to either steroid-C-20 (S) or -C-20 (R) derivatives. *J. Am. Chem. Soc.* **2008,** *130* (28), 9000-9005.

89. Lightburn, T. E.; Dombrowski, M. T.; Tan, K. L., Catalytic scaffolding ligands: An efficient strategy for directing reactions. *J. Am. Chem. Soc.* **2008,** *130* (29), 9210-+.

90. Egami, H.; Katsuki, T., Nb(salan)-catalyzed asymmetric epoxidation of allylic alcohols with hydrogen peroxide. *Angew. Chem.-Int. Edit.* **2008,** *47* (28), 5171-5174.

91. Zhu, Y.; Burgess, K., Asymmetric hydrogenation approaches to valuable, acyclic 1,3-hydroxymethyl chirons. *J. Am. Chem. Soc.* **2008,** *130* (28), 8894-+.

92. Jakobsche, C. E.; Peris, G.; Miller, S. J., Functional analysis of an aspartate-based epoxidation catalyst with amide-to-alkene peptidomimetic catalyst analogues. *Angew. Chem.-Int. Edit.* **2008,** *47* (35), 6707-6711.

93. Du, H. F.; Zhao, B. G.; Shi, Y., Catalytic asymmetric allylic and homoallylic diamination of terminal olefins via formal C-H activation. *J. Am. Chem. Soc.* **2008,** *130* (27), 8590-+.

94. Zhou, J. R.; Hartwig, J. F., Intermolecular, catalytic asymmetric hydroamination of bicyclic alkenes and dienes in high yield and enantioselectivity. *J. Am. Chem. Soc.* **2008,** *130* (37), 12220-+.

95. Nishimura, T.; Tsurumaki, E.; Kawamoto, T.; Guo, X. X.; Hayashi, T., Rhodium-catalyzed asymmetric ring-opening alkynylation of azabenzonorbornadienes. *Org. Lett.* **2008,** *10* (18), 4057-4060.

96. Li, Z.; Zhang, W.; Yamamoto, H., Vanadium-catalyzed enantioselective desymmetrization of meso secondary allylic alcohols and homoallylic alcohols. *Angew. Chem.-Int. Edit.* **2008,** *47* (39), 7520-7522.

97. Du, H. F.; Zhao, B. G.; Yuan, W. C.; Shi, Y., Cu(I)-catalyzed asymmetric diamination of conjugated dienes. *Org. Lett.* **2008,** *10* (19), 4231-4234.

98. Osborne, J. D.; Randell-Sly, H. E.; Currie, G. S.; Cowley, A. R.; Willis, M. C., Catalytic Enantioselective Intermolecular Hydroacylation: Rhodium-Catalyzed Combination of beta-S-Aldehydes and 1,3-Disubstituted Allenes. *J. Am. Chem. Soc.* **2008,** *130* (51), 17232-+.

99. Smith, S. M.; Thacker, N. C.; Takacs, J. M., Efficient amide-directed catalytic asymmetric hydroboration. *J. Am. Chem. Soc.* **2008,** *130* (12), 3734-+.

100. Hou, G. H.; Xie, J. H.; Yan, P. C.; Zhou, Q. L., Iridium-Catalyzed Asymmetric Hydrogenation of Cyclic Enamines. *J. Am. Chem. Soc.* **2009,** *131* (4), 1366-+.

101. Baeza, A.; Pfaltz, A., Iridium-Catalyzed Asymmetric Hydrogenation of Unfunctionalized Enamines. *Chem.-Eur. J.* **2009,** *15* (10), 2266-2269.

102. Najera, C.; Sansano, J. M., Asymmetric Intramolecular Carbocyanation of Alkenes by C-C Bond Activation. *Angew. Chem.-Int. Edit.* **2009,** *48* (14), 2452-2456.

103. Lee, Y. M.; Hoveyda, A. H., Efficient Boron-Copper Additions to Aryl-Substituted Alkenes Promoted by NHC-Based Catalysts. Enantioselective Cu-Catalyzed Hydroboration Reactions. *J. Am. Chem. Soc.* **2009,** *131* (9), 3160-+.

104. Kawamoto, T.; Hirabayashi, S.; Guo, X. X.; Nishimura, T.; Hayashi, T., Rhodium-catalyzed asymmetric hydroalkoxylation and hydrosulfenylation of diphenylphosphinylallenes. *Chem. Commun.* **2009,** (24), 3528-3530.

105. Michaelis, D. J.; Williamson, K. S.; Yoon, T. P., Oxaziridine-mediated enantioselective aminohydroxylation of styrenes catalyzed by copper(II) bis(oxazoline) complexes. *Tetrahedron* **2009,** *65* (26), 5118-5124.

106. Tolstoy, P.; Engman, M.; Paptchikhine, A.; Bergquist, J.; Church, T. L.; Leung, A. W. M.; Andersson, P. G., Iridium-Catalyzed Asymmetric Hydrogenation Yielding Chiral Diarylmethines with Weakly Coordinating or Noncoordinating Substituents. *J. Am. Chem. Soc.* **2009,** *131* (25), 8855-8860.

107. Burks, H. E.; Kliman, L. T.; Morken, J. P., Asymmetric 1,4-Dihydroxylation of 1,3-Dienes by Catalytic Enantioselective Diboration. *J. Am. Chem. Soc.* **2009,** *131* (26), 9134-+.

108. Mantilli, L.; Gerard, D.; Torche, S.; Besnard, C.; Mazet, C., Iridium-Catalyzed Asymmetric Isomerization of Primary Allylic Alcohols. *Angew. Chem.-Int. Edit.* **2009,** *48* (28), 5143-5147.

109. Noh, D.; Chea, H.; Ju, J.; Yun, J., Highly Regio- and Enantioselective Copper-Catalyzed Hydroboration of Styrenes. *Angew. Chem.-Int. Edit.* **2009,** *48* (33), 6062-6064.

110. Kliman, L. T.; Mlynarski, S. N.; Morken, J. P., Pt-Catalyzed Enantioselective Diboration of Terminal Alkenes with B-2(pin)(2). *J. Am. Chem. Soc.* **2009,** *131* (37), 13210-+.

111. Zhao, J.; Burgess, K., Synthesis of Vicinal Dimethyl Chirons by Asymmetric Hydrogenation of Trisubstituted Alkenes. *J. Am. Chem. Soc.* **2009,** *131* (37), 13236-+.

112. Zhao, B. G.; Du, H. F.; Shi, Y. A., Cu(I)-Catalyzed Diamination of Conjugated Olefins with Tunable Anionic Counterions. A Possible Approach to Asymmetric Diamination. *J. Org. Chem.* **2009,** *74* (21), 8392-8395.

113. Lee, Y.; Jang, H.; Hoveyda, A. H., Vicinal Diboronates in High Enantiomeric Purity through Tandem Site-Selective NHC-Cu-Catalyzed Boron-Copper Additions to Terminal Alkynes. *J. Am. Chem. Soc.* **2009,** *131* (51), 18234-+.

114. Mantilli, L.; Mazet, C., Expanded scope for the iridium-catalyzed asymmetric isomerization of primary allylic alcohols using readily accessible second-generation catalysts. *Chem. Commun.* **2010,** *46* (3), 445-447.

115. Sasaki, Y.; Zhong, C. M.; Sawamura, M.; Ito, H., Copper(I)-Catalyzed Asymmetric Monoborylation of 1,3-Dienes: Synthesis of Enantioenriched Cyclic Homoallyl- and Allylboronates. *J. Am. Chem. Soc.* **2010,** *132* (4), 1226-+.

116. Smith, S. M.; Takacs, J. M., Amide-Directed Catalytic Asymmetric Hydroboration of Trisubstituted Alkenes. *J. Am. Chem. Soc.* **2010,** *132* (6), 1740-+.

117. Reddy, V. J.; Douglas, C. J., Highly Enantioselective Intramolecular Cyanoamidation: (+)-Horsfiline, (-)-Coerulescine, and (-)-Esermethole. *Org. Lett.* **2010,** *12* (5), 952-955.

118. Sharma, R. K.; RajanBabu, T. V., Asymmetric Hydrovinylation of Unactivated Linear 1,3-Dienes. *J. Am. Chem. Soc.* **2010,** *132* (10), 3295-+.

119. Shirakura, M.; Suginome, M., Nickel-Catalyzed Asymmetric Addition of Alkyne C-H Bonds across 1,3-Dienes Using Taddol-Based Chiral Phosphoramidite Ligands. *Angew. Chem.-Int. Edit.* **2010,** *49* (22), 3827-3829.

120. Pathak, T. P.; Gligorich, K. M.; Welm, B. E.; Sigman, M. S., Synthesis and Preliminary Biological Studies of 3-Substituted Indoles Accessed by a Palladium-Catalyzed Enantioselective Alkene Difunctionalization Reaction. *J. Am. Chem. Soc.* **2010,** *132* (23), 7870-+.

121. Watkins, A. L.; Landis, C. R., Origin of Pressure Effects on Regioselectivity and Enantioselectivity in the Rhodium-Catalyzed Hydroformylation of Styrene with (S,S,S)-BisDiazaphos. *J. Am. Chem. Soc.* **2010,** *132* (30), 10306-10317.

122. Vogt, D., Cobalt-Catalyzed Asymmetric Hydrovinylation. *Angew. Chem.-Int. Edit.* **2010,** *49* (40), 7166-7168.

123. Zhong, C. M.; Kunii, S.; Kosaka, Y.; Sawamura, M.; Ito, H., Enantioselective Synthesis of trans-Aryl- and -Heteroaryl-Substituted Cyclopropylboronates by Copper(I)-Catalyzed Reactions of Allylic Phosphates with a Diboron Derivative. *J. Am. Chem. Soc.* **2010,** *132* (33), 11440-11442.

124. McDonald, R. I.; Wong, G. W.; Neupane, R. P.; Stahl, S. S.; Landis, C. R., Enantioselective Hydroformylation of N-Vinyl Carboxamides, Allyl Carbamates, and Allyl Ethers Using Chiral Diazaphospholane Ligands. *J. Am. Chem. Soc.* **2010,** *132* (40), 14027-14029.

125. Sasaki, K.; Hayashi, T., Rhodium-Catalyzed Asymmetric Conjugate Addition of Arylboroxines to Borylalkenes: Asymmetric Synthesis of beta-Arylalkylboranes. *Angew. Chem.-Int. Edit.* **2010,** *49* (44), 8145-8147.

126. Worthy, A. D.; Joe, C. L.; Lightburn, T. E.; Tan, K. L., Application of a Chiral Scaffolding Ligand in Catalytic Enantioselective Hydroformylation. *J. Am. Chem. Soc.* **2010,** *132* (42), 14757-14759.

127. Miao, L.; Haque, I.; Manzoni, M. R.; Tham, W. S.; Chemler, S. R., Diastereo- and Enantioselective Copper-Catalyzed Intramolecular Carboamination of Alkenes for the Synthesis of Hexahydro-1H-benz f indoles. *Org. Lett.* **2010,** *12* (21), 4739-4741.

128. Reznichenko, A. L.; Nguyen, H. N.; Hultzsch, K. C., Asymmetric Intermolecular Hydroamination of Unactivated Alkenes with Simple Amines. *Angew. Chem.-Int. Edit.* **2010,** *49* (47), 8984-8987.

129. Konrad, T. M.; Fuentes, J. A.; Slawin, A. M. Z.; Clarke, M. L., Highly Enantioselective Hydroxycarbonylation and Alkoxycarbonylation of Alkenes using Dipalladium Complexes as Precatalysts. *Angew. Chem.-Int. Edit.* **2010,** *49* (48), 9197-9200.

130. Coulter, M. M.; Kou, K. G. M.; Galligan, B.; Dong, V. M., Regio- and Enantioselective Intermolecular Hydroacylation: Substrate-Directed Addition of Salicylaldehydes to Homoallylic Sulfides. *J. Am. Chem. Soc.* **2010,** *132* (46), 16330-16333.

131. Phan, D. H. T.; Kou, K. G. M.; Dong, V. M., Enantioselective Desymmetrization of Cyclopropenes by Hydroacylation. *J. Am. Chem. Soc.* **2010,** *132* (46), 16354-16355.

132. Mazet, C.; Gerard, D., Highly regio- and enantioselective catalytic asymmetric hydroboration of alpha-substituted styrenyl derivatives. *Chem. Commun.* **2011,** *47* (1), 298-300.

133. Quintard, A.; Alexakis, A.; Mazet, C., Access to High Levels of Molecular Complexity by One-Pot Iridium/Enamine Asymmetric Catalysis. *Angew. Chem.-Int. Edit.* **2011,** *50* (10), 2354-2358.

134. Ramalingan, C.; Takenaka, K.; Sasai, H., Pd(II)-SPRIX catalyzed enantioselective construction of pyrrolizines/pyrroloindoles employing molecular oxygen as the sole oxidant. *Tetrahedron* **2011,** *67* (16), 2889-2894.

135. McDonald, R. I.; White, P. B.; Weinstein, A. B.; Tam, C. P.; Stahl, S. S., Enantioselective Pd(II)-Catalyzed Aerobic Oxidative Amidation of Alkenes and Insights into the Role of Electronic Asymmetry in Pyridine-Oxazoline Ligands. *Org. Lett.* **2011,** *13* (11), 2830-2833.

136. Woodmansee, D. H.; Pfaltz, A., Asymmetric hydrogenation of alkenes lacking coordinating groups. *Chem. Commun.* **2011,** *47* (28), 7912-7916.

137. Manna, K.; Xu, S. C.; Sadow, A. D., A Highly Enantioselective Zirconium Catalyst for Intramolecular Alkene Hydroamination: Significant Isotope Effects on Rate and Stereoselectivity. *Angew. Chem.-Int. Edit.* **2011,** *50* (8), 1865-1868.

138. Schuster, C. H.; Li, B.; Morken, J. P., Modular Monodentate Oxaphospholane Ligands: Utility in Highly Efficient and Enantioselective 1,4-Diboration of 1,3-Dienes. *Angew. Chem.-Int. Edit.* **2011,** *50* (34), 7906-7909.

139. Pan, S. G.; Endo, K.; Shibata, T., Ir(I)-Catalyzed Enantioselective Secondary sp(3) C-H Bond Activation of 2-(Alkylamino)pyridines with Alkenes. *Org. Lett.* **2011,** *13* (17), 4692-4695.

140. Rageot, D.; Woodmansee, D. H.; Pugin, B.; Pfaltz, A., Proline-Based P,O Ligand/Iridium Complexes as Highly Selective Catalysts: Asymmetric Hydrogenation of Trisubstituted Alkenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (41), 9598-9601.

141. Saxena, A.; Lam, H. W., Enantioselective rhodium-catalyzed arylation of electron-deficient alkenylarenes. *Chemical Science* **2011,** *2* (12), 2326-2331.

142. Zhang, X. M.; Emge, T. J.; Hultzsch, K. C., A Chiral Phenoxyamine Magnesium Catalyst for the Enantioselective Hydroamination/Cyclization of Aminoalkenes and Intermolecular Hydroamination of Vinyl Arenes. *Angew. Chem.-Int. Edit.* **2012,** *51* (2), 394-398.

143. Kliman, L. T.; Mlynarski, S. N.; Ferris, G. E.; Morken, J. P., Catalytic Enantioselective 1,2-Diboration of 1,3-Dienes: Versatile Reagents for Stereoselective Allylation. *Angew. Chem.-Int. Edit.* **2012,** *51* (2), 521-524.

144. Liwosz, T. W.; Chemler, S. R., Copper-Catalyzed Enantioselective Intramolecular Alkene Amination/Intermolecular Heck-Type Coupling Cascade. *J. Am. Chem. Soc.* **2012,** *134* (4), 2020-2023.

145. Wu, R. Q.; Beauchamps, M. G.; Laquidara, J. M.; Sowa, J. R., Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Allylic Alcohols by an Enantioselective Isomerization/Transfer Hydrogenation Mechanism. *Angew. Chem.-Int. Edit.* **2012,** *51* (9), 2106-2110.

146. Song, S.; Zhu, S. F.; Yang, S.; Li, S.; Zhou, Q. L., Enantioselective Iridium-Catalyzed Hydrogenation of ss,?-Unsaturated Carboxylic Acids: An Efficient Approach to Chiral 4-Alkyl-4-aryl Butanoic Acids. *Angew. Chem.-Int. Edit.* **2012,** *51* (11), 2708-2711.

147. Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J., Enantiopure C-1-Symmetric Bis(imino)pyridine Cobalt Complexes for Asymmetric Alkene Hydrogenation. *J. Am. Chem. Soc.* **2012,** *134* (10), 4561-4564.

148. Bovino, M. T.; Chemler, S. R., Catalytic Enantioselective Alkene Aminohalogenation/Cyclization Involving Atom Transfer. *Angew. Chem.-Int. Edit.* **2012,** *51* (16), 3923-3927.

149. Liu, W.; Lim, H. J.; RajanBabu, T. V., Asymmetric Hydrovinylation of Vinylindoles. A Facile Route to Cyclopenta g indole Natural Products (+)-cis-Trikentrin A and (+)-cis-Trikentrin B. *J. Am. Chem. Soc.* **2012,** *134* (12), 5496-5499.

150. Olivares-Romero, J. L.; Li, Z.; Yamamoto, H., Hf(IV)-Catalyzed Enantioselective Epoxidation of N-Alkenyl Sulfonamides and N-Tosyl Imines. *J. Am. Chem. Soc.* **2012,** *134* (12), 5440-5443.

151. Chikkali, S. H.; Bellini, R.; de Bruin, B.; van der Vlugt, J. I.; Reek, J. N. H., Highly Selective Asymmetric Rh-Catalyzed Hydroformylation of Heterocyclic Olefins. *J. Am. Chem. Soc.* **2012,** *134* (15), 6607-6616.

152. Sawano, T.; Ou, K.; Nishimura, T.; Hayashi, T., Cobalt-catalyzed asymmetric addition of silylacetylenes to oxa- and azabenzonorbornadienes. *Chem. Commun.* **2012,** *48* (49), 6106-6108.

153. Fan, B. M.; Yang, Q. J.; Hu, J.; Fan, C. L.; Li, S. F.; Yu, L.; Huang, C.; Tsang, W. W.; Kwong, F. Y., Asymmetric Hydroalkynylation of Norbornadienes Promoted by Chiral Iridium Catalysts. *Angew. Chem.-Int. Edit.* **2012,** *51* (31), 7821-7824.

154. Toure, M.; Chuzel, O.; Parrain, J. L., Asymmetric Rhodium-Directed anti-Markovnikov Regioselective Boracyclopentannulation. *J. Am. Chem. Soc.* **2012,** *134* (43), 17892-17895.

155. Bao, H. L.; Tambar, U. K., Catalytic Enantioselective Allylic Amination of Unactivated Terminal Olefins via an Ene Reaction/ 2,3 - Rearrangement. *J. Am. Chem. Soc.* **2012,** *134* (45), 18495-18498.

156. Igawa, K.; Yoshihiro, D.; Ichikawa, N.; Kokan, N.; Tomooka, K., Catalytic Enantioselective Synthesis of Alkenylhydrosilanes. *Angew. Chem.-Int. Edit.* **2012,** *51* (51), 12745-12748.

157. Falk, A.; Goderz, A. L.; Schmalz, H. G., Enantioselective Nickel-Catalyzed Hydrocyanation of Vinylarenes Using Chiral Phosphine-Phosphite Ligands and TMS-CN as a Source of HCN. *Angew. Chem.-Int. Edit.* **2013,** *52* (5), 1576-1580.

158. Wong, G. W.; Landis, C. R., Iterative Asymmetric Hydroformylation/Wittig Olefination Sequence. *Angew. Chem.-Int. Edit.* **2013,** *52* (5), 1564-1567.

159. Sevov, C. S.; Hartwig, J. F., Iridium-Catalyzed Intermolecular Asymmetric Hydroheteroarylation of Bicycloalkenes. *J. Am. Chem. Soc.* **2013,** *135* (6), 2116-2119.

160. Ferris, G. E.; Hong, K.; Roundtree, I. A.; Morken, J. P., A Catalytic Enantioselective Tandem Allylation Strategy for Rapid Terpene Construction: Application to the Synthesis of Pumilaside Aglycon. *J. Am. Chem. Soc.* **2013,** *135* (7), 2501-2504.

161. Olivares-Romero, J. L.; Li, Z.; Yamamoto, H., Catalytic Enantioselective Epoxidation of Tertiary Allylic and Homoallylic Alcohols. *J. Am. Chem. Soc.* **2013,** *135* (9), 3411-3413.

162. Schumacher, A.; Bernasconi, M.; Pfaltz, A., Chiral N-Heterocyclic Carbene/Pyridine Ligands for the Iridium-Catalyzed Asymmetric Hydrogenation of Olefins. *Angew. Chem.-Int. Edit.* **2013,** *52* (29), 7422-7425.

163. Arai, N.; Sato, K.; Azuma, K.; Ohkuma, T., Enantioselective Isomerization of Primary Allylic Alcohols into Chiral Aldehydes with the tol-binap/dbapen/Ruthenium(II) Catalyst. *Angew. Chem.-Int. Edit.* **2013,** *52* (29), 7500-7504.

164. Coombs, J. R.; Haeffner, F.; Kliman, L. T.; Morken, J. P., Scope and Mechanism of the Pt-Catalyzed Enantioselective Diboration of Monosubstituted Alkenes. *J. Am. Chem. Soc.* **2013,** *135* (30), 11222-11231.

165. So, C. M.; Kume, S.; Hayashi, T., Rhodium-Catalyzed Asymmetric Hydroarylation of 3-Pyrrolines Giving 3-Arylpyrrolidines: Protonation as a Key Step. *J. Am. Chem. Soc.* **2013,** *135* (30), 10990-10993.

166. Kamlet, A. S.; Preville, C.; Farley, K. A.; Piotrowski, D. W., Regioselective Hydroarylations and Parallel Kinetic Resolution of Vince Lactam. *Angew. Chem.-Int. Edit.* **2013,** *52* (40), 10607-10610.

167. Hu, D. X.; Shibuya, G. M.; Burns, N. Z., Catalytic Enantioselective Dibromination of Allylic Alcohols. *J. Am. Chem. Soc.* **2013,** *135* (35), 12960-12963.

168. Toribatake, K.; Nishiyama, H., Asymmetric Diboration of Terminal Alkenes with a Rhodium Catalyst and Subsequent Oxidation: Enantioselective Synthesis of Optically Active 1,2-Diols. *Angew. Chem.-Int. Edit.* **2013,** *52* (42), 11011-11015.

169. Sawano, T.; Ou, K. Y.; Nishimura, T.; Hayashi, T., Cobalt-Catalyzed Asymmetric Addition of Silylacetylenes to 1,1-Disubstituted Allenes. *J. Org. Chem.* **2013,** *78* (18), 8986-8993.

170. Zhu, S. L.; Niljianskul, N.; Buchwald, S. L., Enantio- and Regioselective CuH-Catalyzed Hydroamination of Alkenes. *J. Am. Chem. Soc.* **2013,** *135* (42), 15746-15749.

171. Fan, B. M.; Xu, J. B.; Yang, Q. J.; Li, S. F.; Chen, H. L.; Liu, S. S.; Yu, L.; Zhou, Y. Y.; Wang, L., Rh-Catalyzed Highly Enantioselective Hydroalkynylation Reaction of Norbornadiene Derivatives. *Org. Lett.* **2013,** *15* (23), 5956-5959.

172. Yu, C. B.; Zhou, Y. G., Palladium-Catalyzed Asymmetric Hydrogenolysis of N-Sulfonyl Aminoalcohols via Achiral Enesulfonamide Intermediates. *Angew. Chem.-Int. Edit.* **2013,** *52* (50), 13365-13368.

173. Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J., Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013,** *342* (6162), 1076-1080.

174. Dornan, P. K.; Kou, K. G. M.; Houk, K. N.; Dong, V. M., Dynamic Kinetic Resolution of Allylic Sulfoxides by Rh-Catalyzed Hydrogenation: A Combined Theoretical and Experimental Mechanistic Study. *J. Am. Chem. Soc.* **2014,** *136* (1), 291-298.

175. Mlynarski, S. N.; Schuster, C. H.; Morken, J. P., Asymmetric synthesis from terminal alkenes by cascades of diboration and cross-coupling. *Nature* **2014,** *505* (7483), 386-390.

176. Gruber, S.; Pfaltz, A., Asymmetric Hydrogenation with Iridium C,N and N,P Ligand Complexes: Characterization of Dihydride Intermediates with a Coordinated Alkene. *Angew. Chem.-Int. Edit.* **2014,** *53* (7), 1896-1900.

177. Wang, C.; Yamamoto, H., Tungsten-Catalyzed Asymmetric Epoxidation of Allylic and Homoallylic Alcohols with Hydrogen Peroxide. *J. Am. Chem. Soc.* **2014,** *136* (4), 1222-1225.

178. Talbot, E. P. A.; Fernandes, T. d. A.; McKenna, J. M.; Toste, F. D., Asymmetric Palladium-Catalyzed Directed Intermolecular Fluoroarylation of Styrenes. *J. Am. Chem. Soc.* **2014,** *136* (11), 4101-4104.

179. Xu, S.; Oda, A.; Kamada, H.; Negishi, E.-i., Highly enantioselective synthesis of gamma-, delta-, and epsilon-chiral 1-alkanols via Zr-catalyzed asymmetric carboalumination of alkenes (ZACA)-Cu- or Pd-catalyzed cross-coupling. *Proceedings of the National Academy of Sciences of the United States of America* **2014,** *111* (23), 8368-8373.

180. Van Hoveln, R. J.; Schmid, S. C.; Tretbar, M.; Buttke, C. T.; Schomaker, J. M., Formal asymmetric hydrobromination of styrenes via copper-catalyzed 1,3-halogen migration. *Chemical Science* **2014,** *5* (12), 4763-4767.

181. Abrams, M. L.; Foarta, F.; Landis, C. R., Asymmetric Hydroformylation of Z-Enamides and Enol Esters with Rhodium-Bisdiazaphos Catalysts. *J. Am. Chem. Soc.* **2014,** *136* (41), 14583-14588.

182. Zhang, L.; Zuo, Z.; Wan, X.; Huang, Z., Cobalt-Catalyzed Enantioselective Hydroboration of 1,1-Disubstituted Aryl Alkenes. *J. Am. Chem. Soc.* **2014,** *136* (44), 15501-15504.

183. Zhu, S.; Buchwald, S. L., Enantioselective CuH-Catalyzed Anti-Markovnikov Hydroamination of 1,1-Disubstituted Alkenes. *J. Am. Chem. Soc.* **2014,** *136* (45), 15913-15916.

184. Parra, A.; Amenos, L.; Guisan-Ceinos, M.; Lopez, A.; Garcia Ruano, J. L.; Tortosa, M., Copper-Catalyzed Diastereo- and Enantioselective Desymmetrization of Cyclopropenes: Synthesis of Cyclopropylboronates. *J. Am. Chem. Soc.* **2014,** *136* (45), 15833-15836.

185. Coombs, J. R.; Zhang, L.; Morken, J. P., Enantiomerically Enriched Tris(boronates): Readily Accessible Conjunctive Reagents for Asymmetric Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (46), 16140-16143.

186. Song, G.; Wylie, W. N. O.; Hou, Z., Enantioselective C-H Bond Addition of Pyridines to Alkenes Catalyzed by Chiral Half-Sandwich Rare-Earth Complexes. *J. Am. Chem. Soc.* **2014,** *136* (35), 12209-12212.

187. Sakae, R.; Hirano, K.; Satoh, T.; Miura, M., Copper-Catalyzed Stereoselective Aminoboration of Bicyclic Alkenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (2), 613-617.

188. Niljianskul, N.; Zhu, S. L.; Buchwald, S. L., Enantioselective Synthesis of alpha-Aminosilanes by Copper-Catalyzed Hydroamination of Vinylsilanes. *Angew. Chem.-Int. Edit.* **2015,** *54* (5), 1638-1641.

189. Ho, C.-Y.; Chan, C.-W.; He, L., Catalytic Asymmetric Hydroalkenylation of Vinylarenes: Electronic Effects of Substrates and Chiral N-Heterocyclic Carbene Ligands. *Angew. Chem.-Int. Edit.* **2015,** *54* (15), 4512-4516.

190. Chen, J.; Cheng, B.; Cao, M.; Lu, Z., Iron-Catalyzed Asymmetric Hydrosilylation of 1,1-Disubstituted Alkenes. *Angew. Chem.-Int. Edit.* **2015,** *54* (15), 4661-4664.

191. Lim, K. M.-H.; Hayashi, T., Rhodium-Catalyzed Asymmetric Arylation of Allyl Sulfones under the Conditions of Isomerization into Alkenyl Sulfones. *J. Am. Chem. Soc.* **2015,** *137* (9), 3201-3204.

192. Hu, D. X.; Seidl, F. J.; Bucher, C.; Burns, N. Z., Catalytic Chemo-, Regio-, and Enantioselective Bromochlorination of Allylic Alcohols. *J. Am. Chem. Soc.* **2015,** *137* (11), 3795-3798.

193. Zhu, C. L.; Tian, J. S.; Gu, Z. Y.; Xing, G. W.; Xu, H., Iron(II)-catalyzed asymmetric intramolecular olefin aminochlorination using chloride ion. *Chemical Science* **2015,** *6* (5), 3044-3050.

194. Ascic, E.; Buchwald, S. L., Highly Diastereo- and Enantioselective CuH-Catalyzed Synthesis of 2,3-Disubstituted lndolines. *J. Am. Chem. Soc.* **2015,** *137* (14), 4666-4669.

195. Timsina, Y. N.; Sharma, R. K.; RajanBabu, T. V., Cobalt-catalysed asymmetric hydrovinylation of 1,3-dienes. *Chemical Science* **2015,** *6* (7), 3994-4008.

196. Hu, N. F.; Zhao, G. Q.; Zhang, Y. Y.; Liu, X. Q.; Li, G. Y.; Tang, W. J., Synthesis of Chiral alpha-Amino Tertiary Boronic Esters by Enantioselective Hydroboration of alpha-Arylenamides. *J. Am. Chem. Soc.* **2015,** *137* (21), 6746-6749.

197. Zhu, R.; Buchwald, S. L., Versatile Enantioselective Synthesis of Functionalized Lactones via Copper-Catalyzed Radical Oxyfunctionalization of Alkenes. *J. Am. Chem. Soc.* **2015,** *137* (25), 8069-8077.

198. Chen, Q. A.; Chen, Z. W.; Dong, V. M., Rhodium-Catalyzed Enantioselective Hydroamination of Alkynes with Indolines. *J. Am. Chem. Soc.* **2015,** *137* (26), 8392-8395.

199. Wang, Y. M.; Bruno, N. C.; Placeres, A. L.; Zhu, S. L.; Buchwald, S. L., Enantioselective Synthesis of Carbo- and Heterocycles through a CuH-Catalyzed Hydroalkylation Approach. *J. Am. Chem. Soc.* **2015,** *137* (33), 10524-10527.

200. Li, H. H.; Mazet, C., Catalyst-Directed Diastereoselective Isomerization of Allylic Alcohols for the Stereoselective Construction of C(20) in Steroid Side Chains: Scope and Topological Diversification. *J. Am. Chem. Soc.* **2015,** *137* (33), 10720-10727.

201. White, D. R.; Hutt, J. T.; Wolfe, J. P., Asymmetric Pd-Catalyzed Alkene Carboamination Reactions for the Synthesis of 2-Aminoindane Derivatives. *J. Am. Chem. Soc.* **2015,** *137* (35), 11246-11249.

202. Hopkins, B. A.; Garlets, Z. J.; Wolfe, J. P., Development of Enantioselective Palladium-Catalyzed Alkene Carboalkoxylation Reactions for the Synthesis of Tetrahydrofurans. *Angew. Chem.-Int. Edit.* **2015,** *54* (45), 13390-13392.

203. Liu, J. W.; Han, Z. B.; Wang, X. M.; Wang, Z.; Ding, K. L., Highly Regio- and Enantioselective Alkoxycarbonylative Amination of Terminal Allenes Catalyzed by a Spiroketal-Based Diphosphine/Pd(II) Complex. *J. Am. Chem. Soc.* **2015,** *137* (49), 15346-15349.

204. He, Y.; Yang, Z. Y.; Thornbury, R. T.; Toste, F. D., Palladium-Catalyzed Enantioselective 1,1-Fluoroarylation of Aminoalkenes. *J. Am. Chem. Soc.* **2015,** *137* (38), 12207-12210.

205. Cahard, E.; Male, H. P. J.; Tissot, M.; Gaunt, M. J., Enantioselective and Regiodivergent Copper-Catalyzed Electrophilic Arylation of Allylic Amides with Diaryliodonium Salts. *J. Am. Chem. Soc.* **2015,** *137* (25), 7986-7989.

206. Cini, M.; Bradshaw, T. D.; Woodward, S.; Lewis, W., Asymmetric Pentafulvene Carbometalation-Access to Enantiopure Titanocene Dichlorides of Biological Relevance. *Angew. Chem.-Int. Edit.* **2015,** *54* (47), 14179-14182.

207. Wu, X.; Lin, H. C.; Li, M. L.; Li, L. L.; Han, Z. Y.; Gong, L. Z., Enantioselective 1,2-Difunctionalization of Dienes Enabled by Chiral Palladium Complex-Catalyzed Cascade Arylation/Allylic Alkylation Reaction. *J. Am. Chem. Soc.* **2015,** *137* (42), 13476-13479.

208. Jia, T.; Cao, P.; Wang, B.; Lou, Y. Z.; Yin, X. M.; Wang, M.; Liao, J., A Cu/Pd Cooperative Catalysis for Enantioselective Allylboration of Alkenes. *J. Am. Chem. Soc.* **2015,** *137* (43), 13760-13763.

209. You, W.; Brown, M. K., Catalytic Enantioselective Diarylation of Alkenes. *J. Am. Chem. Soc.* **2015,** *137* (46), 14578-14581.

210. Bandar, J. S.; Pirnot, M. T.; Buchwald, S. L., Mechanistic Studies Lead to Dramatically Improved Reaction Conditions for the Cu-Catalyzed Asymmetric Hydroamination of Olefins. *J. Am. Chem. Soc.* **2015,** *137* (46), 14812-14818.

211. Biswas, S.; Page, J. P.; Dewese, K. R.; RajanBabu, T. V., Asymmetric Catalysis with Ethylene. Synthesis of Functionalized Chiral Enolates. *J. Am. Chem. Soc.* **2015,** *137* (45), 14268-14271.

212. Muller, D. S.; Marek, I., Asymmetric Copper-Catalyzed Carbozincation of Cyclopropenes en Route to the Formation of Diastereo- and Enantiomerically Enriched Polysubstituted Cyclopropanes. *J. Am. Chem. Soc.* **2015,** *137* (49), 15414-15417.

213. Nishikawa, D.; Hirano, K.; Miura, M., Asymmetric Synthesis of alpha-Aminoboronic Acid Derivatives by Copper-Catalyzed Enantioselective Hydroamination. *J. Am. Chem. Soc.* **2015,** *137* (50), 15620-15623.

214. Kong, W. Q.; Wang, Q.; Zhu, J. P., Palladium-Catalyzed Enantioselective Domino Heck/Intermolecular C-H Bond Functionalization: Development and Application to the Synthesis of (+)-Esermethole. *J. Am. Chem. Soc.* **2015,** *137* (51), 16028-16031.

215. Xi, Y. M.; Butcher, T. W.; Zhang, J.; Hartwig, J. F., Regioselective, Asymmetric Formal Hydroamination of Unactivated Internal Alkenes. *Angew. Chem.-Int. Edit.* **2016,** *55* (2), 776-780.

216. Shoba, V. M.; Thacker, N. C.; Bochat, A. J.; Takacs, J. M., Synthesis of Chiral Tertiary Boronic Esters by Oxime-Directed Catalytic Asymmetric Hydroboration. *Angew. Chem.-Int. Edit.* **2016,** *55* (4), 1465-1469.

217. Zhu, S. L.; Niljianskul, N.; Buchwald, S. L., A direct approach to amines with remote stereocentres by enantioselective CuH-catalysed reductive relay hydroamination. *Nature Chemistry* **2016,** *8* (2), 144-150.

218. Fang, L. C.; Yan, L.; Haeffner, F.; Morken, J. P., Carbohydrate-Catalyzed Enantioselective Alkene Diboration: Enhanced Reactivity of 1,2-Bonded Diboron Complexes. *J. Am. Chem. Soc.* **2016,** *138* (8), 2508-2511.

219. Tao, Z. L.; Adili, A.; Shen, H. C.; Han, Z. Y.; Gong, L. Z., Catalytic Enantioselective Assembly of Homoallylic Alcohols from Dienes, Aryldiazonium Salts, and Aldehydes. *Angew. Chem.-Int. Edit.* **2016,** *55* (13), 4322-4326.

220. Garlets, Z. J.; Parenti, K. R.; Wolfe, J. P., Asymmetric Palladium-Catalyzed Alkene Carboamination Reactions for the Synthesis of Cyclic Sulfamides. *Chem.-Eur. J.* **2016,** *22* (17), 5919-5922.

221. Wang, Y. M.; Buchwald, S. L., Enantioselective CuH-Catalyzed Hydroallylation of Vinylarenes. *J. Am. Chem. Soc.* **2016,** *138* (15), 5024-5027.

222. You, C.; Wei, B.; Li, X. X.; Yang, Y. S.; Liu, Y.; Lv, H.; Zhang, X. M., Rhodium-Catalyzed Desymmetrization by Hydroformylation of Cyclopentenes: Synthesis of Chiral Carbocyclic Nucleosides. *Angew. Chem.-Int. Edit.* **2016,** *55* (22), 6511-6514.

223. Jumde, R. P.; Lanza, F.; Veenstra, M. J.; Harutyunyan, S. R., Catalytic asymmetric addition of Grignard reagents to alkenyl-substituted aromatic N-heterocycles. *Science* **2016,** *352* (6284), 433-437.

224. Bai, X. Y.; Wang, Z. X.; Li, B. J., Iridium-Catalyzed Enantioselective Hydroalkynylation of Enamides for the Synthesis of Homopropargyl Amides. *Angew. Chem.-Int. Edit.* **2016,** *55* (31), 9007-9011.

225. Guisan-Ceinos, M.; Parra, A.; Martin-Heras, V.; Tortosa, M., Enantioselective Synthesis of Cyclobutylboronates via a Copper-Catalyzed Desymmetrization Approach. *Angew. Chem.-Int. Edit.* **2016,** *55* (24), 6969-6972.

226. Bandar, J. S.; Ascic, E.; Buchwald, S. L., Enantioselective CuH-Catalyzed Reductive Coupling of Aryl Alkenes and Activated Carboxylic Acids. *J. Am. Chem. Soc.* **2016,** *138* (18), 5821-5824.

227. Xi, Y. M.; Hartwig, J. F., Diverse Asymmetric Hydrofunctionalization of Aliphatic Internal Alkenes through Catalytic Regioselective Hydroboration. *J. Am. Chem. Soc.* **2016,** *138* (21), 6703-6706.

228. Miro, J.; del Pozo, C.; Toste, F. D.; Fustero, S., Enantioselective Palladium-Catalyzed Oxidative beta,beta-Fluoroarylation of alpha,beta-Unsaturated Carbonyl Derivatives. *Angew. Chem.-Int. Edit.* **2016,** *55* (31), 9045-9049.

229. Chen, C. Y.; Jin, S. C.; Zhang, Z. F.; Wei, B.; Wang, H.; Zhang, K.; Lv, H.; Dong, X. Q.; Zhang, X. M., Rhodium/Yanphos-Catalyzed Asymmetric Interrupted Intramolecular Hydroaminomethylation of trans-1,2-Disubstituted Alkenes. *J. Am. Chem. Soc.* **2016,** *138* (29), 9017-9020.

230. Friis, S. D.; Pirnot, M. T.; Buchwald, S. L., Asymmetric Hydroarylation of Vinylarenes Using a Synergistic Combination of CuH and Pd Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (27), 8372-8375.

231. Chen, Z. M.; Hilton, M. J.; Sigman, M. S., Palladium-Catalyzed Enantioselective Redox-Relay Heck Arylation of 1,1-Disubstituted Homoallylic Alcohols. *J. Am. Chem. Soc.* **2016,** *138* (36), 11461-11464.

232. Huang, Y. H.; Hayashi, T., Rhodium-Catalyzed Asymmetric Arylation/Defluorination of 1-(Trifluoromethyl)alkenes Forming Enantioenriched 1,1-Difluoroalkenes. *J. Am. Chem. Soc.* **2016,** *138* (38), 12340-12343.

233. Patel, H. H.; Sigman, M. S., Enantioselective Palladium-Catalyzed Alkenylation of Trisubstituted Alkenols To Form Allylic Quaternary Centers. *J. Am. Chem. Soc.* **2016,** *138* (43), 14226-14229.

234. Teng, H. L.; Luo, Y.; Wang, B. L.; Zhang, L.; Nishiura, M.; Hou, Z. M., Synthesis of Chiral Aminocyclopropanes by Rare-Earth-Metal-Catalyzed Cyclopropene Hydroamination. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15406-15410.

235. Yang, Y.; Perry, I. B.; Lu, G.; Liu, P.; Buchwald, S. L., Copper-catalyzed asymmetric addition of olefin-derived nucleophiles to ketones. *Science* **2016,** *353* (6295), 144-150.

236. Wang, F.; Wang, D.; Wan, X.; Wu, L.; Chen, P.; Liu, G., Enantioselective Copper-Catalyzed Intermolecular Cyanotrifluoromethylation of Alkenes via Radical Process. *J. Am. Chem. Soc.* **2016,** *138* (48), 15547-15550.

237. Logan, K. M.; Brown, M. K., Catalytic Enantioselective Arylboration of Alkenylarenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (3), 851-855.

238. Zhang, C.; Tutkowski, B.; DeLuca, R. J.; Joyce, L. A.; Wiest, O.; Sigman, M. S., Palladium-catalyzed enantioselective Heck alkenylation of trisubstituted allylic alkenols: a redox-relay strategy to construct vicinal stereocenters. *Chemical Science* **2017,** *8* (3), 2277-2282.

239. Wu, Z.; Laffoon, S. D.; Nguyen, T. T.; McAlpin, J. D.; Hull, K. L., Rhodium-Catalyzed Asymmetric Synthesis of beta-Branched Amides. *Angew. Chem.-Int. Edit.* **2017,** *56* (5), 1371-1375.

240. Lovinger, G. J.; Aparece, M. D.; Morken, J. P., Pd-Catalyzed Conjunctive Cross -Coupling between Grignard-Derived Boron "Ate" Complexes and C(sp(2)) Halides or Triflates: NaOTf as a Grignard Activator and Halide Scavenger. *J. Am. Chem. Soc.* **2017,** *139* (8), 3153-3160.

241. Wu, L. Q.; Wang, F.; Wan, X. L.; Wang, D. H.; Chen, P. H.; Liu, G. S., Asymmetric Cu-Catalyzed Intermolecular Trifluoromethylarylation of Styrenes: Enantioselective Arylation of Benzylic Radicals. *J. Am. Chem. Soc.* **2017,** *139* (8), 2904-2907.

242. Liu, T. L.; Ng, T. W.; Zhao, Y., Rhodium-Catalyzed Enantioselective Isomerization of Secondary Allylic Alcohols. *J. Am. Chem. Soc.* **2017,** *139* (10), 3643-3646.

243. Ebe, Y.; Onoda, M.; Nishimura, T.; Yorimitsu, H., Iridium-Catalyzed Regio- and Enantioselective Hydroarylation of Alkenyl Ethers by Olefin Isomerization. *Angew. Chem.-Int. Edit.* **2017,** *56* (20), 5607-5611.

244. Kong, D. Y.; Han, S. N.; Wang, R.; Li, M. N.; Zi, G. F.; Hou, G. H., Kinetic resolution of racemic 2-substituted 1,2-dihydroquinolines via asymmetric Cu-catalyzed borylation. *Chemical Science* **2017,** *8* (6), 4558-4564.

245. Wang, D. H.; Wu, L. Q.; Wang, F.; Wan, X. L.; Chen, P. H.; Lin, Z. Y.; Liu, G. S., Asymmetric Copper-Catalyzed Intermolecular Aminoarylation of Styrenes: Efficient Access to Optical 2,2-Diarylethylamines. *J. Am. Chem. Soc.* **2017,** *139* (20), 6811-6814.

246. Dian, L. Y.; Muller, D. S.; Marek, I., Asymmetric Copper-Catalyzed Carbomagnesiation of Cyclopropenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (24), 6783-6787.

247. Liu, J. W.; Nie, M.; Zhou, Q. H.; Gao, S.; Jiang, W. H.; Chung, L. W.; Tang, W. J.; Ding, K. L., Enantioselective palladium-catalyzed diboration of 1,1-disubstituted allenes. *Chemical Science* **2017,** *8* (7), 5161-5165.

248. Zhou, Y. J.; Bandar, J. S.; Buchwald, S. L., Enantioselective CuH-Catalyzed Hydroacylation Employing Unsaturated Carboxylic Acids as Aldehyde Surrogates. *J. Am. Chem. Soc.* **2017,** *139* (24), 8126-8129.

249. Wang, H. X.; Yang, J. C.; Buchwald, S. L., CuH-Catalyzed Regioselective Intramolecular Hydroamination for the Synthesis of Alkyl-Substituted Chiral Aziridines. *J. Am. Chem. Soc.* **2017,** *139* (25), 8428-8431.

250. Lim, K. M. H.; Hayashi, T., Dynamic Kinetic Resolution in Rhodium-Catalyzed Asymmetric Arylation of Phospholene Oxides. *J. Am. Chem. Soc.* **2017,** *139* (24), 8122-8125.

251. Smith, J. R.; Collins, B. S. L.; Hesse, M. J.; Graham, M. A.; Myers, E. L.; Aggarwal, V. K., Enantioselective Rhodium(III)-Catalyzed Markovnikov Hydroboration of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2017,** *139* (27), 9148-9151.

252. Lukamto, D. H.; Gaunt, M. J., Enantioselective Copper-Catalyzed Arylation-Driven Semipinacol Rearrangement of Tertiary Allylic Alcohols with Diaryliodonium Salts. *J. Am. Chem. Soc.* **2017,** *139* (27), 9160-9163.

253. Cheng, B.; Lu, P.; Zhang, H. Y.; Cheng, X. P.; Lu, Z., Highly Enantioselective Cobalt-Catalyzed Hydrosilylation of Alkenes. *J. Am. Chem. Soc.* **2017,** *139* (28), 9439-9442.

254. Kim, D. K.; Riedel, J.; Kim, R. S.; Dong, V. M., Cobalt Catalysis for Enantioselective Cyclobutanone Construction. *J. Am. Chem. Soc.* **2017,** *139* (30), 10208-10211.

255. Muller, D. S.; Werner, V.; Akyol, S.; Schmalz, H. G.; Marek, I., Tandem Hydroalumination/Cu-Catalyzed Asymmetric Vinyl Metalation as a New Access to Enantioenriched Vinylcyclopropane Derivatives. *Org. Lett.* **2017,** *19* (15), 3970-3973.

256. Wu, H.; Wang, Q.; Zhu, J. P., Copper-Catalyzed Enantioselective Domino Arylation/Semipinacol Rearrangement of Allylic Alcohols with Diaryliodonium Salts. *Chem.-Eur. J.* **2017,** *23* (53), 13037-13041.

257. Li, Z. Y.; Zhao, J. B.; Sun, B. Z.; Zhou, T. T.; Liu, M. Z.; Liu, S.; Zhang, M. R.; Zhang, Q., Asymmetric Nitrone Synthesis via Ligand-Enabled Copper-Catalyzed Cope-Type Hydroamination of Cyclopropene with Oxime. *J. Am. Chem. Soc.* **2017,** *139* (34), 11702-11705.

258. Xi, Y. M.; Hartwig, J. F., Mechanistic Studies of Copper-Catalyzed Asymmetric Hydroboration of Alkenes. *J. Am. Chem. Soc.* **2017,** *139* (36), 12758-12772.

259. Loup, J.; Zell, D.; Oliveira, J. C. A.; Keil, H.; Stalke, D.; Ackermann, L., Asymmetric Iron-Catalyzed C-H Alkylation Enabled by Remote Ligand meta-Substitution. *Angew. Chem.-Int. Edit.* **2017,** *56* (45), 14197-14201.

260. Jang, W. J.; Song, S. M.; Moon, J. H.; Lee, J. Y.; Yun, J., Copper-Catalyzed Enantioselective Hydroboration of Unactivated 1,1-Disubstituted Alkenes. *J. Am. Chem. Soc.* **2017,** *139* (39), 13660-13663.

261. Yu, S. J.; Sang, H. L.; Ge, S. Z., Enantioselective Copper-Catalyzed Alkylation of Quinoline N-Oxides with Vinylarenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (50), 15896-15900.

262. Marcum, J. S.; Roberts, C. C.; Manan, R. S.; Cervarich, T. N.; Meek, S. J., Chiral Pincer Carbodicarbene Ligands for Enantioselective Rhodium-Catalyzed Hydroarylation of Terminal and Internal 1,3-Dienes with Indoles. *J. Am. Chem. Soc.* **2017,** *139* (44), 15580-15583.

263. Guo, J.; Cheng, B. A.; Shen, X. Z.; Lu, Z., Cobalt-Catalyzed Asymmetric Sequential Hydroboration/Hydrogenation of Internal Alkynes. *J. Am. Chem. Soc.* **2017,** *139* (43), 15316-15319.

264. Lovinger, G. J.; Morken, J. P., Ni-Catalyzed Enantioselective Conjunctive Coupling with C(sp(3)) Electrophiles: A Radical-Ionic Mechanistic Dichotomy. *J. Am. Chem. Soc.* **2017,** *139* (48), 17293-17296.

265. Teng, H. L.; Luo, Y.; Nishiura, M.; Hou, Z. M., Diastereodivergent Asymmetric Carboamination/Annulation of Cyclopropenes with Aminoalkenes by Chiral Lanthanum Catalysts. *J. Am. Chem. Soc.* **2017,** *139* (46), 16506-16509.

266. Lee, J.; Radomkit, S.; Torker, S.; del Pozo, J.; Hoveyda, A. H., Mechanism-based enhancement of scope and enantioselectivity for reactions involving a copper-substituted stereogenic carbon centre. *Nature Chemistry* **2018,** *10* (1), 99-108.

267. Edwards, A.; Rubina, M.; Rubin, M., Directed Rh-I-Catalyzed Asymmetric Hydroboration of Prochiral 1-Arylcycloprop-2-Ene-1-Carboxylic Acid Derivatives. *Chem.-Eur. J.* **2018,** *24* (6), 1394-1403.

268. Wu, H.; Wang, Q.; Zhu, J. P., Copper-Catalyzed Enantioselective Arylative Desymmetrization of Prochiral Cyclopentenes with Diaryliodonium Salts. *Angew. Chem.-Int. Edit.* **2018,** *57* (10), 2721-2725.

269. Simaan, M.; Marek, I., Asymmetric Catalytic Preparation of Polysubstituted Cyclopropanol and Cyclopropylamine Derivatives. *Angew. Chem.-Int. Edit.* **2018,** *57* (6), 1543-1546.

270. Shen, H. C.; Wu, Y. F.; Zhang, Y.; Fan, L. F.; Han, Z. Y.; Gong, L. Z., Palladium-Catalyzed Asymmetric Aminohydroxylation of 1,3-Dienes. *Angew. Chem.-Int. Edit.* **2018,** *57* (9), 2372-2376.

271. Huang, Y. M.; del Pozo, J.; Torker, S.; Hoveyda, A. H., Enantioselective Synthesis of Trisubstituted Allenyl B(pin) Compounds by Phosphine-Cu-Catalyzed 1,3-Enyne Hydroboration. Insights Regarding Stereochemical Integrity of Cu-Allenyl Intermediates. *J. Am. Chem. Soc.* **2018,** *140* (7), 2643-2655.

272. Wang, H.; Bai, Z.; Jiao, T. Q.; Deng, Z. Q.; Tong, H. R.; He, G.; Peng, Q.; Chen, G., Palladium-Catalyzed Amide-Directed Enantioselective Hydrocarbofunctionalization of Unactivated Alkenes Using a Chiral Monodentate Oxazoline Ligand. *J. Am. Chem. Soc.* **2018,** *140* (10), 3542-3546.

273. Cheng, B.; Liu, W. B.; Lu, Z., Iron-Catalyzed Highly Enantioselective Hydrosilylation of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2018,** *140* (15), 5014-5017.

274. Zhou, Y. J.; Engl, O. D.; Bandar, J. S.; Chant, E. D.; Buchwald, S. L., CuH-Catalyzed Asymmetric Hydroamidation of Vinylarenes. *Angew. Chem.-Int. Edit.* **2018,** *57* (22), 6672-6675.

275. Patel, H. H.; Prater, M. B.; Squire, S. O.; Sigman, M. S., Formation of Chiral Allylic Ethers via an Enantioselective Palladium Catalyzed Alkenylation of Acyclic Enol Ethers. *J. Am. Chem. Soc.* **2018,** *140* (18), 5895-5898.

276. Liu, Y. B.; Fiorito, D.; Mazet, C., Copper-catalyzed enantioselective 1,2-borylation of 1,3-dienes. *Chemical Science* **2018,** *9* (23), 5284-5288.

277. Sommer, H.; Marek, I., Diastereo- and enantioselective copper catalyzed hydroallylation of disubstituted cyclopropenes. *Chemical Science* **2018,** *9* (31), 6503-6508.

278. Grelaud, S.; Cooper, P.; Feron, L. J.; Bower, J. F., Branch-Selective and Enantioselective Iridium-Catalyzed Alkene Hydroarylation via Anilide-Directed C-H Oxidative Addition. *J. Am. Chem. Soc.* **2018,** *140* (30), 9351-9356.

279. Teo, W. J.; Ge, S. Z., Cobalt-Catalyzed Enantioselective Synthesis of Chiral gem-Bis(boryl)alkanes. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12935-12939.

280. Fu, L.; Zhou, S.; Wan, X. L.; Chen, P. H.; Liu, G. S., Enantioselective Trifluoromethylalkynylation of Alkenes via Copper-Catalyzed Radical Relay. *J. Am. Chem. Soc.* **2018,** *140* (35), 10965-10969.

281. Wang, C.; Ge, S. Z., Versatile Cobalt-Catalyzed Enantioselective Entry to Boryl-Functionalized All-Carbon Quaternary Stereogenic Centers. *J. Am. Chem. Soc.* **2018,** *140* (34), 10687-10690.

282. Wang, K.; Ding, Z. T.; Zhou, Z. J.; Kong, W. Q., Ni-Catalyzed Enantioselective Reductive Diarylation of Activated Alkenes by Domino Cyclization/Cross-Coupling. *J. Am. Chem. Soc.* **2018,** *140* (39), 12364-12368.

283. Guo, S.; Yang, J. C.; Buchwald, S. L., A Practical Electrophilic Nitrogen Source for the Synthesis of Chiral Primary Amines by Copper-Catalyzed Hydroamination. *J. Am. Chem. Soc.* **2018,** *140* (46), 15976-15984.

284. Nie, S. Z.; Davison, R. T.; Dong, V. M., Enantioselective Coupling of Dienes and Phosphine Oxides. *J. Am. Chem. Soc.* **2018,** *140* (48), 16450-16454.

285. Race, N. J.; Yuan, Q.; Sigman, M. S., Enantioselective C2-Alkylation of Indoles through a Redox-Relay Heck Reaction of 2-Indole Triflates. *Chemistry – A European Journal* **2019,** *25* (2), 512-515.

286. Xu, G. X.; Fu, B.; Zhao, H. Y.; Li, Y. F.; Zhang, G.; Wang, Y.; Xiong, T.; Zhang, Q., Enantioselective and site-specific copper-catalyzed reductive allyl-allyl cross-coupling of allenes. *Chemical Science* **2019,** *10* (6), 1802-1806.

287. Loup, J.; Muller, V.; Ghorai, D.; Ackermann, L., Enantioselective Aluminum-Free Alkene Hydroarylations through C-H Activation by a Chiral Nickel/JoSPOphos Manifold. *Angew. Chem.-Int. Edit.* **2019,** *58* (6), 1749-1753.

288. Duchemin, C.; Cramer, N., Chiral cyclopentadienyl Rh-III-catalyzed enantioselective cyclopropanation of electron-deficient olefins enable rapid access to UPF-648 and oxylipin natural products. *Chemical Science* **2019,** *10* (9), 2773-2777.

289. Dai, X. J.; Engl, O. D.; Leon, T.; Buchwald, S. L., Catalytic Asymmetric Synthesis of alpha-Arylpyrrolidines and Benzo-fused Nitrogen Heterocycles. *Angew. Chem.-Int. Edit.* **2019,** *58* (11), 3407-3411.

290. Anthony, D.; Lin, Q.; Baudet, J.; Diao, T. N., Nickel-Catalyzed Asymmetric Reductive Diarylation of Vinylarenes. *Angew. Chem.-Int. Edit.* **2019,** *58* (10), 3198-3202.

291. Nimmagadda, S. K.; Liu, M.; Karunananda, M. K.; Gao, D.-W.; Apolinar, O.; Chen, J. S.; Liu, P.; Engle, K. M., Catalytic, Enantioselective α-Alkylation of Azlactones with Nonconjugated Alkenes by Directed Nucleopalladation. *Angewandte Chemie International Edition* **2019,** *58* (12), 3923-3927.

292. Chen, Z. W.; Aota, Y.; Nguyen, H. M. H.; Dong, V. M., Dynamic Kinetic Resolution of Aldehydes by Hydroacylation. *Angew. Chem.-Int. Edit.* **2019,** *58* (14), 4705-4709.

293. Yang, Q. J.; Wang, Y. B.; Luo, S. H.; Wang, J., Kinetic Resolution and Dynamic Kinetic Resolution of Chromene by Rhodium-Catalyzed Asymmetric Hydroarylation. *Angew. Chem.-Int. Edit.* **2019,** *58* (16), 5343-5347.

294. Chen, Y. G.; Shuai, B.; Xu, X. T.; Li, Y. Q.; Yang, Q. L.; Qiu, H.; Zhang, K.; Fang, P.; Mei, T. S., Nickel-catalyzed Enantioselective Hydroarylation and Hydroalkenylation of Styrenes. *J. Am. Chem. Soc.* **2019,** *141* (8), 3395-3399.

295. Yu, L.; Somfai, P., Regio- and Enantioselective Formal Hydroamination of Enamines for the Synthesis of 1,2-Diamines. *Angew. Chem.-Int. Edit.* **2019,** *58* (25), 8551-8555.

296. Tian, Z. X.; Qiao, J. B.; Xu, G. L.; Pang, X. B.; Qi, L. L.; Ma, W. Y.; Zhao, Z. Z.; Duan, J. C.; Du, Y. F.; Su, P. F.; Liu, X. Y.; Shu, X. Z., Highly Enantioselective Cross-Electrophile Aryl-Alkenylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2019,** *141* (18), 7637-7643.

297. Bochat, A. J.; Shoba, V. M.; Takacs, J. M., Ligand-Controlled Regiodivergent Enantioselective Rhodium-Catalyzed Alkene Hydroboration. *Angew. Chem.-Int. Edit.* **2019,** *58* (28), 9434-9438.

298. Adamson, N. J.; Jeddi, H.; Malcolmson, S. J., Preparation of Chiral Allenes through Pd-Catalyzed Intermolecular Hydroamination of Conjugated Enynes: Enantioselective Synthesis Enabled by Catalyst Design. *J. Am. Chem. Soc.* **2019,** *141* (21), 8574-8583.

299. Bahamonde, A.; Al Rifaie, B.; Martin-Heras, V.; Allen, J. R.; Sigman, M. S., Enantioselective Markovnikov Addition of Carbamates to Allylic Alcohols for the Construction of alpha-Secondary and alpha-Tertiary Amines. *J. Am. Chem. Soc.* **2019,** *141* (22), 8708-8711.

300. Zhang, H. Y.; Huang, W.; Wang, T. T.; Meng, F. K., Cobalt-Catalyzed Diastereo- and Enantioselective Hydroalkenylation of Cyclopropenes with Alkenylboronic Acids. *Angew. Chem.-Int. Edit.* **2019,** *58* (32), 11049-11053.

301. Wang, Z. X.; Li, B. J., Construction of Acyclic Quaternary Carbon Stereocenters by Catalytic Asymmetric Hydroalkynylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2019,** *141* (23), 9312-9320.

302. Chen, Z. M.; Liu, J. B.; Guo, J. Y.; Loch, M.; DeLuca, R. J.; Sigman, M. S., Palladium-catalyzed enantioselective alkenylation of alkenylbenzene derivatives. *Chemical Science* **2019,** *10* (30), 7246-7250.

303. Chierchia, M.; Xu, P. L.; Lovinger, G. J.; Morken, J. P., Enantioselective Radical Addition/Cross-Coupling of Organozinc Reagents, Alkyl Iodides, and Alkenyl Boron Reagents. *Angew. Chem.-Int. Edit.* **2019,** *58* (40), 14245-14249.

304. Bayeh-Romero, L.; Buchwald, S. L., Copper Hydride Catalyzed Enantioselective Synthesis of Axially Chiral 1,3-Disubstituted Allenes. *J. Am. Chem. Soc.* **2019,** *141* (35), 13788-13794.

305. Tran, G.; Shao, W.; Mazet, C., Ni-Catalyzed Enantioselective Intermolecular Hydroamination of Branched 1,3-Dienes Using Primary Aliphatic Amines. *J. Am. Chem. Soc.* **2019,** *141* (37), 14814-14822.

306. Parsutkar, M. M.; Pagar, V. V.; RajanBabu, T. V., Catalytic Enantioselective Synthesis of Cyclobutenes from Alkynes and Alkenyl Derivatives. *J. Am. Chem. Soc.* **2019,** *141* (38), 15367-15377.

307. Fu, N. K.; Song, L.; Liu, J. J.; Shen, Y. F.; Siu, J. C.; Lin, S., New Bisoxazoline Ligands Enable Enantioselective Electrocatalytic Cyanofunctionalization of Vinylarenes. *J. Am. Chem. Soc.* **2019,** *141* (37), 14480-14485.

308. Zhang, Z. Q.; Meng, X. Y.; Sheng, J.; Lan, Q.; Wang, X. S., Enantioselective Copper-Catalyzed 1,5-Cyanotrifluoromethylation of Vinylcyclopropanes. *Org. Lett.* **2019,** *21* (20), 8256-8260.

309. Rivera-Chao, E.; Mitxelena, M.; Varela, J. A.; Fañanás-Mastral, M., Copper-Catalyzed Enantioselective Allylboration of Alkynes: Synthesis of Highly Versatile Multifunctional Building Blocks. *Angewandte Chemie International Edition* **2019,** *58* (50), 18230-18234.

310. Schuppe, A. W.; Borrajo-Calleja, G. M.; Buchwald, S. L., Enantioselective Olefin Hydrocyanation without Cyanide. *J. Am. Chem. Soc.* **2019,** *141* (47), 18668-18672.

311. Discolo, C. A.; Touney, E. E.; Pronin, S. V., Catalytic Asymmetric Radical-Polar Crossover Hydroalkoxylation. *J. Am. Chem. Soc.* **2019,** *141* (44), 17527-17532.

312. Bai, X. Y.; Zhao, W.; Sun, X.; Li, B. J., Rhodium-Catalyzed Regiodivergent and Enantioselective Hydroboration of Enamides. *J. Am. Chem. Soc.* **2019,** *141* (50), 19870-19878.

313. Liao, Y.; Yin, X.; Wang, X.; Yu, W.; Fang, D.; Hu, L.; Wang, M.; Liao, J., Enantioselective Synthesis of Multisubstituted Allenes by Cooperative Cu/Pd-Catalyzed 1,4-Arylboration of 1,3-Enynes. *Angewandte Chemie International Edition* **2020,** *59* (3), 1176-1180.

314. Hou, C.; Chen, P.; Liu, G., Enantioselective Palladium(II)-Catalyzed Oxidative Aminofluorination of Unactivated Alkenes with Et4NF·3 HF as a Fluoride Source. *Angewandte Chemie International Edition* **2020,** *59* (7), 2735-2739.

315. Zhou, L.; Li, S.; Xu, B.; Ji, D.; Wu, L.; Liu, Y.; Zhang, Z.-M.; Zhang, J., Enantioselective Difunctionalization of Alkenes by a Palladium-Catalyzed Heck/Sonogashira Sequence. *Angewandte Chemie International Edition* **2020,** *59* (7), 2769-2775.

316. He, J.; Xue, Y.; Han, B.; Zhang, C.; Wang, Y.; Zhu, S., Nickel-Catalyzed Asymmetric Reductive 1,2-Carboamination of Unactivated Alkenes. *Angewandte Chemie International Edition* **2020,** *59* (6), 2328-2332.

317. Bigler, R.; Mack, K. A.; Shen, J.; Tosatti, P.; Han, C.; Bachmann, S.; Zhang, H.; Scalone, M.; Pfaltz, A.; Denmark, S. E.; Hildbrand, S.; Gosselin, F., Asymmetric Hydrogenation of Unfunctionalized Tetrasubstituted Acyclic Olefins. *Angewandte Chemie International Edition* **2020,** *59* (7), 2844-2849.

318. Romero-Arenas, A.; Hornillos, V.; Iglesias-Siguenza, J.; Fernandez, R.; Lopez-Serrano, J.; Ros, A.; Lassaletta, J. M., Ir-Catalyzed Atroposelective Desymmetrization of Heterobiaryls: Hydroarylation of Vinyl Ethers and Bicycloalkenes. *J. Am. Chem. Soc.* **2020,** *142* (5), 2628-2639.

319. Zhang, W. W.; Zhang, S. L.; Li, B. J., Highly Enantioselective Synthesis of Propargyl Amide with Vicinal Stereocenters through Ir-Catalyzed Hydroalkynylation. *Angew. Chem.-Int. Edit.* **2020,** *59* (17), 6874-6880.

320. Fan, P.; Lan, Y.; Zhang, C.; Wang, C., Nickel/Photo-Cocatalyzed Asymmetric Acyl-Carbamoylation of Alkenes. *J. Am. Chem. Soc.* **2020,** *142* (5), 2180-2186.

321. Zhang, Y. J.; Sun, Y. W.; Chen, B.; Xu, M. C.; Li, C.; Zhang, D. Y.; Zhang, G. Z., Copper-Catalyzed Photoinduced Enantioselective Dual Carbofunctionalization of Alkenes. *Org. Lett.* **2020,** *22* (4), 1490-1494.

322. Viereck, P.; Krautwald, S.; Pabst, T. P.; Chirik, P. J., A Boron Activating Effect Enables Cobalt-Catalyzed Asymmetric Hydrogenation of Sterically Hindered Alkenes. *J. Am. Chem. Soc.* **2020,** *142* (8), 3923-3930.

323. Whyte, A.; Torelli, A.; Mirabi, B.; Prieto, L.; Rodríguez, J. F.; Lautens, M., Cobalt-Catalyzed Enantioselective Hydroarylation of 1,6-Enynes. *J. Am. Chem. Soc.* **2020,** *142* (20), 9510-9517.

324. Dong, X.-Y.; Cheng, J.-T.; Zhang, Y.-F.; Li, Z.-L.; Zhan, T.-Y.; Chen, J.-J.; Wang, F.-L.; Yang, N.-Y.; Ye, L.; Gu, Q.-S.; Liu, X.-Y., Copper-Catalyzed Asymmetric Radical 1,2-Carboalkynylation of Alkenes with Alkyl Halides and Terminal Alkynes. *J. Am. Chem. Soc.* **2020,** *142* (20), 9501-9509.

325. Duchemin, C.; Cramer, N., Enantioselective CpxRhIII-Catalyzed Carboaminations of Acrylates. *Angewandte Chemie International Edition* **2020,** *59* (33), 14129-14133.

326. Tu, H.-Y.; Wang, F.; Huo, L.; Li, Y.; Zhu, S.; Zhao, X.; Li, H.; Qing, F.-L.; Chu, L., Enantioselective Three-Component Fluoroalkylarylation of Unactivated Olefins through Nickel-Catalyzed Cross-Electrophile Coupling. *J. Am. Chem. Soc.* **2020,** *142* (21), 9604-9611.

327. Whyte, A.; Bajohr, J.; Torelli, A.; Lautens, M., Enantioselective Cobalt-Catalyzed Intermolecular Hydroacylation of 1,6-Enynes. *Angewandte Chemie International Edition* **2020,** *59* (38), 16409-16413.

328. Li, X.; Qi, X.; Hou, C.; Chen, P.; Liu, G., Palladium(II)-Catalyzed Enantioselective Azidation of Unactivated Alkenes. *Angewandte Chemie International Edition* **2020,** *59* (39), 17239-17244.

329. Ebisawa, K.; Izumi, K.; Ooka, Y.; Kato, H.; Kanazawa, S.; Komatsu, S.; Nishi, E.; Shigehisa, H., Catalyst- and Silane-Controlled Enantioselective Hydrofunctionalization of Alkenes by Cobalt-Catalyzed Hydrogen Atom Transfer and Radical-Polar Crossover. *J. Am. Chem. Soc.* **2020,** *142* (31), 13481-13490.

330. Zhang, G.; Zhou, S.; Fu, L.; Chen, P.; Li, Y.; Zou, J.; Liu, G., Asymmetric Coupling of Carbon-Centered Radicals Adjacent to Nitrogen: Copper-Catalyzed Cyanation and Etherification of Enamides. *Angewandte Chemie International Edition* **2020,** *59* (46), 20439-20444.

331. Zhou, S.; Zhang, G.; Fu, L.; Chen, P.; Li, Y.; Liu, G., Copper-Catalyzed Asymmetric Cyanation of Alkenes via Carbonyl-Assisted Coupling of Alkyl-Substituted Carbon-Centered Radicals. *Org. Lett.* **2020,** *22* (16), 6299-6303.

332. Garbo, M.; Besnard, C.; Guénée, L.; Mazet, C., Access to Optically Active 7-Membered Rings by a 2-Step Synthetic Sequence: Cu-Catalyzed Stereoselective Cyclopropanation of Branched 1,3-Dienes/Rh-Catalyzed Stereoconvergent [5 + 2] Cycloaddition. *ACS Catalysis* **2020,** *10* (16), 9604-9611.

333. He, Y.; Liu, C.; Yu, L.; Zhu, S., Enantio- and Regioselective NiH-Catalyzed Reductive Hydroarylation of Vinylarenes with Aryl Iodides. *Angewandte Chemie International Edition* **2020,** *59* (48), 21530-21534.

334. Lin, T.-Y.; Pan, Z.; Tu, Y.; Zhu, S.; Wu, H.-H.; Liu, Y.; Li, Z.; Zhang, J., Design and Synthesis of TY-Phos and Application in Palladium-Catalyzed Enantioselective Fluoroarylation of gem-Difluoroalkenes. *Angewandte Chemie International Edition* **2020,** *59* (51), 22957-22962.

335. Zhang, Q.; Dong, D.; Zi, W., Palladium-Catalyzed Regio- and Enantioselective Hydrosulfonylation of 1,3-Dienes with Sulfinic Acids: Scope, Mechanism, and Origin of Selectivity. *J. Am. Chem. Soc.* **2020,** *142* (37), 15860-15869.

336. Shao, W.; Besnard, C.; Guénée, L.; Mazet, C., Ni-Catalyzed Regiodivergent and Stereoselective Hydroalkylation of Acyclic Branched Dienes with Unstabilized C(sp3) Nucleophiles. *J. Am. Chem. Soc.* **2020,** *142* (38), 16486-16492.

337. Sakurai, S.; Matsumoto, A.; Kano, T.; Maruoka, K., Cu-Catalyzed Enantioselective Alkylarylation of Vinylarenes Enabled by Chiral Binaphthyl–BOX Hybrid Ligands. *J. Am. Chem. Soc.* **2020,** *142* (45), 19017-19022.

338. Xi, Y.; Su, B.; Qi, X.; Pedram, S.; Liu, P.; Hartwig, J. F., Application of Trimethylgermanyl-Substituted Bisphosphine Ligands with Enhanced Dispersion Interactions to Copper-Catalyzed Hydroboration of Disubstituted Alkenes. *J. Am. Chem. Soc.* **2020,** *142* (42), 18213-18222.

339. Zeng, Y.; Chiou, M.-F.; Zhu, X.; Cao, J.; Lv, D.; Jian, W.; Li, Y.; Zhang, X.; Bao, H., Copper-Catalyzed Enantioselective Radical 1,4-Difunctionalization of 1,3-Enynes. *J. Am. Chem. Soc.* **2020,** *142* (42), 18014-18021.

340. Xi, Y.; Ma, S.; Hartwig, J. F., Catalytic asymmetric addition of an amine N–H bond across internal alkenes. *Nature* **2020,** *588* (7837), 254-260.

341. Li, Y.; Zhang, F.-P.; Wang, R.-H.; Qi, S.-L.; Luan, Y.-X.; Ye, M., Carbamoyl Fluoride-Enabled Enantioselective Ni-Catalyzed Carbocarbamoylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2020,** *142* (47), 19844-19849.

342. Cuesta-Galisteo, S.; Schörgenhumer, J.; Wei, X.; Merino, E.; Nevado, C., Nickel-Catalyzed Asymmetric Synthesis of α-Arylbenzamides. *Angewandte Chemie International Edition* **2021,** *60* (3), 1605-1609.

343. Xi, Y.; Wang, C.; Zhang, Q.; Qu, J.; Chen, Y., Palladium-Catalyzed Regio-, Diastereo-, and Enantioselective 1,2-Arylfluorination of Internal Enamides. *Angewandte Chemie International Edition* **2021,** *60* (5), 2699-2703.

344. Dong, X.-Y.; Zhan, T.-Y.; Jiang, S.-P.; Liu, X.-D.; Ye, L.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Copper-Catalyzed Asymmetric Coupling of Allenyl Radicals with Terminal Alkynes to Access Tetrasubstituted Allenes. *Angewandte Chemie International Edition* **2021,** *60* (4), 2160-2164.

345. Huang, W.; Meng, F., Cobalt-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes with Cobalt Homoenolates. *Angewandte Chemie International Edition* **2021,** *60* (5), 2694-2698.

346. Liu, J.; Gong, H.; Zhu, S., Nickel-Catalyzed, Regio- and Enantioselective Benzylic Alkenylation of Olefins with Alkenyl Bromide. *Angewandte Chemie International Edition* **2021,** *60* (8), 4060-4064.

347. Teng, S.; Chi, Y. R.; Zhou, J. S., Enantioselective Three-Component Coupling of Heteroarenes, Cycloalkenes and Propargylic Acetates. *Angewandte Chemie International Edition* **2021,** *60* (9), 4491-4495.

348. Hu, Z.; Fu, L.; Chen, P.; Cao, W.; Liu, G., Enantioselective Intermolecular Aminoalkynylation of Styrenes via Copper-Catalyzed Radical Relay. *Org. Lett.* **2021,** *23* (1), 129-134.

349. He, Y.-P.; Cao, J.; Wu, H.; Wang, Q.; Zhu, J., Catalytic Enantioselective Aminopalladation–Heck Cascade. *Angewandte Chemie International Edition* **2021,** *60* (13), 7093-7097.

350. Bai, Z.; Zhang, H.; Wang, H.; Yu, H.; Chen, G.; He, G., Enantioselective Alkylamination of Unactivated Alkenes under Copper Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (2), 1195-1202.

351. Yao, Y.-H.; Yang, H.-Y.; Chen, M.; Wu, F.; Xu, X.-X.; Guan, Z.-H., Asymmetric Markovnikov Hydroaminocarbonylation of Alkenes Enabled by Palladium-Monodentate Phosphoramidite Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (1), 85-91.

352. Bera, S.; Mao, R.; Hu, X., Enantioselective C(sp3)–C(sp3) cross-coupling of non-activated alkyl electrophiles via nickel hydride catalysis. *Nature Chemistry* **2021,** *13* (3), 270-277.

353. Qian, D.; Bera, S.; Hu, X., Chiral Alkyl Amine Synthesis via Catalytic Enantioselective Hydroalkylation of Enecarbamates. *J. Am. Chem. Soc.* **2021,** *143* (4), 1959-1967.

354. Lu, F.-D.; Lu, L.-Q.; He, G.-F.; Bai, J.-C.; Xiao, W.-J., Enantioselective Radical Carbocyanation of 1,3-Dienes via Photocatalytic Generation of Allylcopper Complexes. *J. Am. Chem. Soc.* **2021,** *143* (11), 4168-4173.

355. Wang, P.-Z.; Gao, Y.; Chen, J.; Huan, X.-D.; Xiao, W.-J.; Chen, J.-R., Asymmetric three-component olefin dicarbofunctionalization enabled by photoredox and copper dual catalysis. *Nature Communications* **2021,** *12* (1), 1815.

356. Feng, S.; Buchwald, S. L., CuH-Catalyzed Regio- and Enantioselective Hydrocarboxylation of Allenes: Toward Carboxylic Acids with Acyclic Quaternary Centers. *J. Am. Chem. Soc.* **2021,** *143* (13), 4935-4941.

357. Nie, S.; Lu, A.; Kuker, E. L.; Dong, V. M., Enantioselective Hydrothiolation: Diverging Cyclopropenes through Ligand Control. *J. Am. Chem. Soc.* **2021,** *143* (16), 6176-6184.

358. Tian, B.; Li, X.; Chen, P.; Liu, G., Asymmetric Palladium-Catalyzed Oxycarbonylation of Terminal Alkenes: Efficient Access to β-Hydroxy Alkylcarboxylic Acids. *Angewandte Chemie International Edition* **2021,** *60* (27), 14881-14886.

359. Liu, Z.; Oxtoby, L. J.; Liu, M.; Li, Z.-Q.; Tran, V. T.; Gao, Y.; Engle, K. M., A Transient Directing Group Strategy Enables Enantioselective Multicomponent Organofluorine Synthesis. *J. Am. Chem. Soc.* **2021,** *143* (24), 8962-8969.

360. Ren, X.; Wang, Z.; Shen, C.; Tian, X.; Tang, L.; Ji, X.; Dong, K., Asymmetric Alkoxy- and Hydroxy-Carbonylations of Functionalized Alkenes Assisted by β-Carbonyl Groups. *Angewandte Chemie International Edition* **2021,** *60* (32), 17693-17700.

361. Jiu, A. Y.; Slocumb, H. S.; Yeung, C. S.; Yang, X.-H.; Dong, V. M., Enantioselective Addition of Pyrazoles to Dienes**. *Angewandte Chemie International Edition* **2021,** *60* (36), 19660-19664.

362. Zhang, S.-L.; Zhang, W.-W.; Li, B.-J., Ir-Catalyzed Regio- and Enantioselective Hydroalkynylation of Trisubstituted Alkene to Access All-Carbon Quaternary Stereocenters. *J. Am. Chem. Soc.* **2021,** *143* (25), 9639-9647.

363. Goetzke, F. W.; Hell, A. M. L.; van Dijk, L.; Fletcher, S. P., A catalytic asymmetric cross-coupling approach to the synthesis of cyclobutanes. *Nature Chemistry* **2021,** *13* (9), 880-886.

364. Dong, W.; Xu, X.; Ma, H.; Lei, Y.; Lin, Z.; Zhao, W., Enantioselective Rh-Catalyzed Hydroboration of Silyl Enol Ethers. *J. Am. Chem. Soc.* **2021,** *143* (29), 10902-10909.

365. Xu, L.-C.; Zhang, S.-Q.; Li, X.; Tang, M.-J.; Xie, P.-P.; Hong, X., Towards Data-Driven Design of Asymmetric Hydrogenation of Olefins: Database and Hierarchical Learning. *Angewandte Chemie International Edition* **2021,** *60* (42), 22804-22811.

366. Chang, R.; Cai, S.; Yang, G.; Yan, X.; Huang, H., Asymmetric Aminomethylative Etherification of Conjugated Dienes with Aliphatic Alcohols Facilitated by Hydrogen Bonding. *J. Am. Chem. Soc.* **2021,** *143* (32), 12467-12472.

367. Giofrè, S.; Molteni, L.; Nava, D.; Lo Presti, L.; Beccalli, E. M., Enantio- and Regioselective Palladium(II)-Catalyzed Dioxygenation of (Aza-)Alkenols. *Angewandte Chemie International Edition* **2021,** *60* (40), 21723-21727.

368. Chen, J.; Liang, Y.-J.; Wang, P.-Z.; Li, G.-Q.; Zhang, B.; Qian, H.; Huan, X.-D.; Guan, W.; Xiao, W.-J.; Chen, J.-R., Photoinduced Copper-Catalyzed Asymmetric C–O Cross-Coupling. *J. Am. Chem. Soc.* **2021,** *143* (33), 13382-13392.

369. Chen, J.; Zhu, S., Nickel-Catalyzed Multicomponent Coupling: Synthesis of α-Chiral Ketones by Reductive Hydrocarbonylation of Alkenes. *J. Am. Chem. Soc.* **2021,** *143* (35), 14089-14096.

370. Yuan, Y.; Zhao, F.; Wu, X.-F., Copper-catalyzed enantioselective carbonylation toward α-chiral secondary amides. *Chemical Science* **2021,** *12* (38), 12676-12681.

371. Ding, C.; Ren, Y.; Sun, C.; Long, J.; Yin, G., Regio- and Stereoselective Alkylboration of Endocyclic Olefins Enabled by Nickel Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (48), 20027-20034.

372. Liu, Y.-H.; Xie, P.-P.; Liu, L.; Fan, J.; Zhang, Z.-Z.; Hong, X.; Shi, B.-F., Cp*Co(III)-Catalyzed Enantioselective Hydroarylation of Unactivated Terminal Alkenes via C–H Activation. *J. Am. Chem. Soc.* **2021,** *143* (45), 19112-19120.

373. Yang, J.; Massaro, L.; Krajangsri, S.; Singh, T.; Su, H.; Silvi, E.; Ponra, S.; Eriksson, L.; Ahlquist, M. S. G.; Andersson, P. G., Combined Theoretical and Experimental Studies Unravel Multiple Pathways to Convergent Asymmetric Hydrogenation of Enamides. *J. Am. Chem. Soc.* **2021,** *143* (51), 21594-21603.

374. Schuppe, A. W.; Knippel, J. L.; Borrajo-Calleja, G. M.; Buchwald, S. L., Enantioselective Hydroalkenylation of Olefins with Enol Sulfonates Enabled by Dual Copper Hydride and Palladium Catalysis. *J. Am. Chem. Soc.* **2021,** *143* (14), 5330-5335.

375. Goetzke, F. W.; Sidera, M.; Fletcher, S. P., Catalytic asymmetric hydrometallation of cyclobutenes with salicylaldehydes. *Chemical Science* **2022,** *13* (1), 236-240.

376. Sun, S.-Z.; Cai, Y.-M.; Zhang, D.-L.; Wang, J.-B.; Yao, H.-Q.; Rui, X.-Y.; Martin, R.; Shang, M., Enantioselective Deaminative Alkylation of Amino Acid Derivatives with Unactivated Olefins. *J. Am. Chem. Soc.* **2022,** *144* (3), 1130-1137.

377. Wilhelmsen, C. A.; Zhang, X.; Myhill, J. A.; Morken, J. P., Enantioselective Synthesis of Tertiary β-Boryl Amides by Conjunctive Cross-Coupling of Alkenyl Boronates and Carbamoyl Chlorides. *Angewandte Chemie International Edition* **2022,** *61* (15), e202116784.

378. Wang, Z.-X.; Li, B.-J., Iridium-Catalyzed Regiodivergent and Enantioselective Hydroalkynylation of Unactivated 1,1-Disubstituted Alkenes. *Angewandte Chemie International Edition* **2022,** *61* (18), e202201099.

379. Zhang, Q.; Wang, S.; Yin, J.; Xiong, T.; Zhang, Q., Remote Site-Selective Asymmetric Protoboration of Unactivated Alkenes Enabled by Bimetallic Relay Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (23), e202202713.

380. Wu, X.; Luan, B.; Zhao, W.; He, F.; Wu, X.-Y.; Qu, J.; Chen, Y., Catalytic Desymmetric Dicarbofunctionalization of Unactivated Alkenes. *Angewandte Chemie International Edition* **2022,** *61* (26), e202111598.

381. Chaves-Pouso, A.; Álvarez-Constantino, A. M.; Fañanás-Mastral, M., Enantio- and Diastereoselective Copper-Catalyzed Allylboration of Alkynes with Allylic gem-Dichlorides. *Angewandte Chemie International Edition* **2022,** *61* (23), e202117696.

382. Matt, C.; Orthaber, A.; Streuff, J., Catalytic Asymmetric β-Oxygen Elimination**. *Angewandte Chemie International Edition* **2022,** *61* (22), e202114044.

383. Xu, J.-L.; Xu, Z.-Y.; Wang, Z.-L.; Ma, W.-W.; Sun, X.-Y.; Fu, Y.; Xu, Y.-H., Copper-Catalyzed Regiodivergent and Enantioselective Hydrosilylation of Allenes. *J. Am. Chem. Soc.* **2022,** *144* (12), 5535-5542.

384. Zhou, J.; Yang, Q.; Lee, C. S.; Wang, J., Enantio- and Regioselective Construction of 1,4-Diamines via Cascade Hydroamination of Methylene Cyclopropanes. *Angewandte Chemie International Edition* **2022,** *61* (24), e202202160.

385. Ji, X.; Shen, C.; Tian, X.; Zhang, H.; Ren, X.; Dong, K., Asymmetric Double Hydroxycarbonylation of Alkynes to Chiral Succinic Acids Enabled by Palladium Relay Catalysis. *Angewandte Chemie International Edition* **2022,** *61* (29), e202204156.

386. Nie, Z.; Chiou, M.-F.; Cui, J.; Qu, Y.; Zhu, X.; Jian, W.; Xiong, H.; Li, Y.; Bao, H., Copper-Catalyzed Radical Enantioselective Carbo-Esterification of Styrenes Enabled by a Perfluoroalkylated-PyBox Ligand. *Angewandte Chemie International Edition* **2022,** *61* (28), e202202077.

387. Dong, W.; Ye, Z.; Zhao, W., Enantioselective Cobalt-Catalyzed Hydroboration of Ketone-Derived Silyl Enol Ethers. *Angewandte Chemie International Edition* **2022,** *61* (29), e202117413.

388. Xi, Y.; Huang, W.; Wang, C.; Ding, H.; Xia, T.; Wu, L.; Fang, K.; Qu, J.; Chen, Y., Catalytic Asymmetric Diarylation of Internal Acyclic Styrenes and Enamides. *J. Am. Chem. Soc.* **2022,** *144* (18), 8389-8398.

389. Yang, X.; Li, X.; Chen, P.; Liu, G., Palladium(II)-Catalyzed Enantioselective Hydrooxygenation of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2022,** *144* (18), 7972-7977.

390. Iwamoto, H.; Ozawa, Y.; Hayashi, Y.; Imamoto, T.; Ito, H., Conformationally Fixed Chiral Bisphosphine Ligands by Steric Modulators on the Ligand Backbone: Selective Synthesis of Strained 1,2-Disubstituted Chiral cis-Cyclopropanes. *J. Am. Chem. Soc.* **2022,** *144* (23), 10483-10494.

391. Li, S.; Zhang, D.; Zhang, R.; Bai, S.-T.; Zhang, X., Rhodium-Catalyzed Chemo-, Regio- and Enantioselective Hydroformylation of Cyclopropyl-Functionalized Trisubstituted Alkenes. *Angewandte Chemie International Edition* **2022,** *61* (33), e202206577.

392. Zhang, H.; Huang, C.; Yuan, X.-A.; Yu, S., Photoexcited Chiral Copper Complex-Mediated Alkene E → Z Isomerization Enables Kinetic Resolution. *J. Am. Chem. Soc.* **2022,** *144* (24), 10958-10967.

393. Yu, R.; Cai, S.-Z.; Li, C.; Fang, X., Nickel-Catalyzed Asymmetric Hydroaryloxy- and Hydroalkoxycarbonylation of Cyclopropenes. *Angewandte Chemie International Edition* **2022,** *61* (36), e202200733.

394. Hu, M.; Tan, B. B.; Ge, S., Enantioselective Cobalt-Catalyzed Hydroboration of Fluoroalkyl-Substituted Alkenes to Access Chiral Fluoroalkylboronates. *J. Am. Chem. Soc.* **2022,** *144* (33), 15333-15338.

395. Dong, Y.; Shin, K.; Mai, B. K.; Liu, P.; Buchwald, S. L., Copper Hydride-Catalyzed Enantioselective Olefin Hydromethylation. *J. Am. Chem. Soc.* **2022,** *144* (36), 16303-16309.

396. Augustin, A. U.; Di Silvio, S.; Marek, I., Borylated Cyclopropanes as Spring-Loaded Entities: Access to Vicinal Tertiary and Quaternary Carbon Stereocenters in Acyclic Systems. *J. Am. Chem. Soc.* **2022,** *144* (36), 16298-16302.

397. Huang, Q.; Chen, Y.; Zhou, X.; Dai, L.; Lu, Y., Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes. *Angewandte Chemie International Edition* **2022,** *61* (46), e202210560.

398. Sun, X.; Lin, E.-Z.; Li, B.-J., Iridium-Catalyzed Branch-Selective and Enantioselective Hydroalkenylation of α-Olefins through C–H Cleavage of Enamides. *J. Am. Chem. Soc.* **2022,** *144* (38), 17351-17358.

399. Slocumb, H. S.; Nie, S.; Dong, V. M.; Yang, X.-H., Enantioselective Selenol-ene Using Rh-Hydride Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (40), 18246-18250.

400. Cheng, X.-Y.; Zhang, Y.-F.; Wang, J.-H.; Gu, Q.-S.; Li, Z.-L.; Liu, X.-Y., A Counterion/Ligand-Tuned Chemo- and Enantioselective Copper-Catalyzed Intermolecular Radical 1,2-Carboamination of Alkenes. *J. Am. Chem. Soc.* **2022,** *144* (39), 18081-18089.

401. Apolinar, O.; Kang, T.; Alturaifi, T. M.; Bedekar, P. G.; Rubel, C. Z.; Derosa, J.; Sanchez, B. B.; Wong, Q. N.; Sturgell, E. J.; Chen, J. S.; Wisniewski, S. R.; Liu, P.; Engle, K. M., Three-Component Asymmetric Ni-Catalyzed 1,2-Dicarbofunctionalization of Unactivated Alkenes via Stereoselective Migratory Insertion. *J. Am. Chem. Soc.* **2022,** *144* (42), 19337-19343.

402. Bera, S.; Fan, C.; Hu, X., Enantio- and diastereoselective construction of vicinal C(sp3) centres via nickel-catalysed hydroalkylation of alkenes. *Nature Catalysis* **2022,** *5* (12), 1180-1187.

403. Miao, H.; Guan, M.; Xiong, T.; Zhang, G.; Zhang, Q., Cobalt-Catalyzed Enantioselective Hydroamination of Arylalkenes with Secondary Amines. *Angewandte Chemie International Edition* **2023,** *62* (2), e202213913.

404. Zou, S.; Yu, B.; Huang, H., Palladium-Catalyzed Ring-Closing Aminoalkylative Amination of Unactivated Aminoenynes. *Angewandte Chemie International Edition* **2023,** *62* (3), e202215325.

405. Dong, Z.; Tang, Q.; Xu, C.; Chen, L.; Ji, H.; Zhou, S.; Song, L.; Chen, L.-A., Directed Asymmetric Nickel-Catalyzed Reductive 1,2-Diarylation of Electronically Unactivated Alkenes. *Angewandte Chemie International Edition* **2023,** *62* (13), e202218286.

406. Liang, Z.; Wang, L.; Wang, Y.; Wang, L.; Chong, Q.; Meng, F., Cobalt-Catalyzed Diastereo- and Enantioselective Carbon–Carbon Bond Forming Reactions of Cyclobutenes. *J. Am. Chem. Soc.* **2023,** *145* (6), 3588-3598.

407. Zhang, H.; He, X.; Yuan, X.-A.; Yu, S., Kinetic Resolution of 2-Cinnamylpyrrolines Enabled by Photoexcited Chiral Copper Complex-Mediated Alkene E → Z Isomerization. *ACS Catalysis* **2023,** *13* (5), 2857-2866.

408. Zhao, W.; Li, B.-J., Directing Group Repositioning Strategy Enabled Site- and Enantioselective Addition of Heteroaromatic C–H Bonds to Acyclic Internal Alkenes. *J. Am. Chem. Soc.* **2023,** *145* (12), 6861-6870.

409. Li, X.; Yang, T.; Li, J.; Li, X.; Chen, P.; Lin, Z.; Liu, G., Regio- and enantioselective remote dioxygenation of internal alkenes. *Nature Chemistry* **2023,** *15* (6), 862-871.

410. Forster, D.; Guo, W.; Wang, Q.; Zhu, J., Dual Photoredox and Copper Catalysis: Enantioselective 1,2-Amidocyanation of 1,3-Dienes. *ACS Catalysis* **2023,** *13* (11), 7523-7528.

411. Zhang, Z.-L.; Li, Z.; Xu, Y.-T.; Yu, L.; Kuang, J.; Li, Y.; Wang, J.-W.; Tian, C.; Lu, X.; Fu, Y., Cobalt-Catalyzed Facial-Selective Hydroalkylation of Cyclopropenes. *Angewandte Chemie International Edition* **2023,** *62* (30), e202306381.

412. Li, Z.; Shi, H.; Chen, X.; Peng, L.; Li, Y.; Yin, G., Nickel-Catalyzed Regio- and Enantioselective Borylative Coupling of Terminal Alkenes with Alkyl Halides Enabled by an Anionic Bisoxazoline Ligand. *J. Am. Chem. Soc.* **2023,** *145* (25), 13603-13614.

413. Du, X.; Cheng-Sánchez, I.; Nevado, C., Dual Nickel/Photoredox-Catalyzed Asymmetric Carbosulfonylation of Alkenes. *J. Am. Chem. Soc.* **2023,** *145* (23), 12532-12540.

414. Wei, Z.; Zheng, W.; Wan, X.; Hu, J., Copper-Catalyzed Enantioselective Difluoromethylation-Alkynylation of Olefins by Solving the Dilemma between Acidities and Reduction Potentials of Difluoromethylating Agents. *Angewandte Chemie International Edition* **2023,** *62* (37), e202308816.

415. Wang, M.; Simon, J. C.; Xu, M.; Corio, S. A.; Hirschi, J. S.; Dong, V. M., Copper-Catalyzed Hydroamination: Enantioselective Addition of Pyrazoles to Cyclopropenes. *J. Am. Chem. Soc.* **2023,** *145* (27), 14573-14580.

416. Fu, L.; Chen, X.; Fan, W.; Chen, P.; Liu, G., Copper-Catalyzed Asymmetric Functionalization of Vinyl Radicals for the Access to Vinylarene Atropisomers. *J. Am. Chem. Soc.* **2023,** *145* (24), 13476-13483.

417. Zhang, S.; Jiang, N.; Xiao, J.-Z.; Lin, G.-Q.; Yin, L., Copper(I)-Catalyzed Asymmetric Hydrophosphination of 3,3-Disubstituted Cyclopropenes. *Angewandte Chemie International Edition* **2023,** *62* (40), e202218798.

418. Zhan, L.-W.; Lu, C.-J.; Feng, J.; Liu, R.-R., Atroposelective Synthesis of C−N Vinylindole Atropisomers by Palladium-Catalyzed Asymmetric Hydroarylation of 1-Alkynylindoles. *Angewandte Chemie International Edition* **2023,** *62* (45), e202312930.

419. Chen, J.; Wu, L.; Zhao, Y.; Zhu, S., Enantio- and Diastereoselective NiH-Catalyzed Hydroalkylation of Enamides or Enecarbamates with Racemic α-Bromoamides. *Angewandte Chemie International Edition* **2023,** *62* (44), e202311094.

420. Jing, C.; Mao, W.; Bower, J. F., Iridium-Catalyzed Enantioselective Alkene Hydroalkylation via a Heteroaryl-Directed Enolization–Decarboxylation Sequence. *J. Am. Chem. Soc.* **2023,** *145* (44), 23918-23924.

421. Zhang, B.; Li, T.-T.; Mao, Z.-C.; Jiang, M.; Zhang, Z.; Zhao, K.; Qu, W.-Y.; Xiao, W.-J.; Chen, J.-R., Enantioselective Cyanofunctionalization of Aromatic Alkenes via Radical Anions. *J. Am. Chem. Soc.* **2024,** *146* (2), 1410-1422.

422. Zhang, S.; Li, L.; Li, D.; Zhou, Y.-Y.; Tang, Y., Catalytic Regio- and Enantioselective Boracarboxylation of Arylalkenes with CO2 and Diboron. *J. Am. Chem. Soc.* **2024,** *146* (5), 2888-2894.

423. Zheng, W.; Tan, B. B.; Ge, S.; Lu, Y., Enantioselective Copper-Catalyzed Ring-Opening Diboration of Arylidenecyclopropanes to Access Chiral Skipped 1,4- and 1,3-Diboronates. *J. Am. Chem. Soc.* **2024,** *146* (8), 5366-5374.

424. Zhou, C.; Liang, Y.; Li, Y.; Huang, M.; Luo, Z.; Yang, K.-F.; Li, Z.; Lai, G.-Q.; Zhang, P., Rapid Access to Chiral Spiro[2.3] Lactams: Stereoselective Hydroborylation and Hydrosilylation and Remote Control of Axial Chirality by Copper-Catalyzed Desymmetrization of Spirocyclopropenes. *Org. Lett.* **2024,** *26* (9), 1941-1946.

425. Hossain, A.; Anderson, R. L.; Zhang, C. S.; Chen, P.-J.; Fu, G. C., Nickel-Catalyzed Enantioconvergent and Diastereoselective Allenylation of Alkyl Electrophiles: Simultaneous Control of Central and Axial Chirality. *J. Am. Chem. Soc.* **2024,** *146* (11), 7173-7177.

426. Lee, C.; Kim, M.; Han, S.; Kim, D.; Hong, S., Nickel-Catalyzed Hydrofluorination in Unactivated Alkenes: Regio- and Enantioselective C–F Bond Formation. *J. Am. Chem. Soc.* **2024,** *146* (13), 9375-9384.

427. Wang, Z.; Zhu, J.; Wang, M.; Lu, P., Palladium-Catalyzed Divergent Enantioselective Functionalization of Cyclobutenes. *J. Am. Chem. Soc.* **2024,** *146* (18), 12691-12701.

428. Li, G.-Q.; Li, Z.-Q.; Jiang, M.; Zhang, Z.; Qian, Y.; Xiao, W.-J.; Chen, J.-R., Photoinduced Copper-Catalyzed Asymmetric Three-Component Radical 1,2-Azidooxygenation of 1,3-Dienes. *Angewandte Chemie International Edition* **2024,** *63* (32), e202405560.

429. Huang, J.; Yan, X.; Liu, X.; Chen, Z.; Jiang, T.; Zhang, L.; Ju, G.; Huang, G.; Wang, C., Enantioselective Ni-Catalyzed 1,2-Borylalkynylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2024,** *146* (25), 17140-17149.

430. Lu, L.; Chen, S.; Kong, W.; Gao, B.; Li, Y.; Zhu, L.; Yin, G., Enantioselective Synthesis of β-Aminoboronic Acids via Borylalkylation of Enamides. *J. Am. Chem. Soc.* **2024,** *146* (24), 16639-16647.

431. Huang, W.; Xi, Y.; Pan, D.; Fan, L.; Fang, K.; Huang, G.; Zhu, W.-H.; Qu, J.; Chen, Y., Palladium-Catalyzed Enantioselective Multicomponent Cross-Coupling of Trisubstituted Olefins. *J. Am. Chem. Soc.* **2024,** *146* (24), 16892-16901.

432. Zhou, L.; Li, L.; Zhang, S.; Kuang, X.-k.; Zhou, Y.-Y.; Tang, Y., Catalytic Regio- and Enantioselective Remote Hydrocarboxylation of Unactivated Alkenes with CO2. *J. Am. Chem. Soc.* **2024,** *146* (28), 18823-18830.

433. Wang, P.-Z.; Zhang, Z.; Jiang, M.; Chen, J.-R.; Xiao, W.-J., A General Copper-Box System for the Asymmetric Arylative Functionalization of Benzylic, Propargylic or Allenylic Radicals. *Angewandte Chemie International Edition* **2024,** *63* (43), e202411469.

434. Wang, J.; Xu, B.; Wang, Y.; Xia, G.; Zhang, Z.-M.; Zhang, J., Pd-Catalyzed Enantioselective Three-Component Carboamination of 1,3-Cyclohexadiene. *J. Am. Chem. Soc.* **2024,** *146* (31), 21231-21238.

435. Song, C.; Bai, X.; Li, B.; Dang, Y.; Yu, S., Photoexcited Palladium-Catalyzed Deracemization of Allenes. *J. Am. Chem. Soc.* **2024,** *146* (30), 21137-21146.

436. Dhawa, U.; Lavrencic, L.; Hu, X., Nickel-Catalyzed Enantio- and Diastereoselective Synthesis of Fluorine-Containing Vicinal Stereogenic Centers. *ACS Central Science* **2024,** *10* (8), 1657-1666.

437. Xin, S.; Liao, J.; Tang, Q.; Feng, X.; Liu, X., Photoinduced copper-catalyzed asymmetric cyanoalkylalkynylation of alkenes, terminal alkynes, and oximes. *Chemical Science* **2024,** *15* (44), 18557-18563.

438. Song, C.; Yu, S., Photoexcited Palladium-Catalyzed Synthesis of Chiral Allenes from Alkynes via Isomerization and Deracemization Sequence. *ACS Catalysis* **2024,** *14* (21), 15997-16002.

439. Du, Y.; Duan, S.; Huang, S.; Liu, T.; Zhang, H.; Walsh, P. J.; Yang, X., Enantioselective Synthesis of Aminals Via Nickel-Catalyzed Hydroamination of 2-Azadienes with Indoles and N-Heterocycles. *J. Am. Chem. Soc.* **2024,** *146* (45), 30947-30957.

440. Wang, S.-C.; Liu, L.; Duan, M.; Xie, W.; Han, J.; Xue, Y.; Wang, Y.; Wang, X.; Zhu, S., Regio- and Enantioselective Nickel-Catalyzed Ipso- and Remote Hydroamination Utilizing Organic Azides as Amino Sources for the Synthesis of Primary Amines. *J. Am. Chem. Soc.* **2024,** *146* (44), 30626-30636.

441. Li, Z.; Wang, S.; Chen, S.-C.; Zhu, X.; Lian, Z.; Xing, D., Cu-Catalyzed Asymmetric Three-Component Radical Acylarylation of Vinylarenes with Aldehydes and Aryl Boronic Acids. *J. Am. Chem. Soc.* **2024,** *146* (47), 32235-32242.

442. Yuan, F.; Qi, X.; Zhao, Y.; Jia, J.; Yan, X.; Hu, F.; Xia, Y., Diversified Synthesis of Chiral Fluorinated Cyclobutane Derivatives Enabled by Regio- and Enantioselective Hydroboration. *Angewandte Chemie International Edition* **2024,** *63* (23), e202401451.

443. Kalomenopoulos, P. G.; Emayavaramban, B.; Johnston, C. P., Enantioselective Synthesis of α-Aryl Ketones by a Cobalt-Catalyzed Semipinacol Rearrangement. *Angewandte Chemie International Edition* **2025,** *64* (2), e202414342.

444. Sun, Y.-W.; Sun, X.; Tan, H.-T.; Li, B.-J., Synthesis of γ-Amino Amides by Iridium-Catalyzed Enantioselective Hydroamination of Internal Alkenes Directed by an Amide. *Angewandte Chemie International Edition* **2025,** *64* (8), e202422944.

4.6.2 Metathesis

1. Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R., Catalytic enantioselective ring-closing metathesis by a chiral biphen-Mo complex. *J. Am. Chem. Soc.* **1998,** *120* (16), 4041-4042.

2. La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R., Mo-catalyzed asymmetric synthesis of dihydrofurans. Catalytic kinetic resolution and enantioselective desymmetrization through ring-closing metathesis. *J. Am. Chem. Soc.* **1998,** *120* (37), 9720-9721.

3. La, D. S.; Ford, J. G.; Sattely, E. S.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H., Tandem catalytic asymmetric ring-opening metathesis/cross metathesis. *J. Am. Chem. Soc.* **1999,** *121* (49), 11603-11604.

4. Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R., Chiral Mo-binol complexes: Activity, synthesis, and structure. Efficient enantioselective six-membered ring synthesis through catalytic metathesis. *J. Am. Chem. Soc.* **1999,** *121* (36), 8251-8259.

5. Weatherhead, G. S.; Ford, J. G.; Alexanian, E. J.; Schrock, R. R.; Hoveyda, A. H., Tandem catalytic asymmetric ring-opening metathesis/ring-closing metathesis. *J. Am. Chem. Soc.* **2000,** *122* (8), 1828-1829.

6. Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R., A readily available and user-friendly chiral catalyst for efficient enantioselective olefin metathesis. *Angew. Chem.-Int. Edit.* **2001,** *40* (8), 1452-+.

7. Cefalo, D. R.; Kiely, A. F.; Wuchrer, M.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H., Enantioselective synthesis of unsaturated cyclic tertiary ethers by Mo-catalyzed olefin metathesis. *J. Am. Chem. Soc.* **2001,** *123* (13), 3139-3140.

8. Hoveyda, A. H.; Schrock, R. R., Catalytic asymmetric olefin metathesis. *Chem.-Eur. J.* **2001,** *7* (5), 945-950.

9. La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H., Catalytic asymmetric ring-opening metathesis/cross metathesis (AROM/CM) reactions. Mechanism and application to enantio selective synthesis of functionalized cyclopentanes. *J. Am. Chem. Soc.* **2001,** *123* (32), 7767-7778.

10. Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H.; Schrock, R. R., Efficient catalytic enantioselective synthesis of unsaturated amines: Preparation of small- and medium-ring cyclic amines through Mo-catalyzed asymmetric ring-closing metathesis in the absence of solvent. *J. Am. Chem. Soc.* **2002,** *124* (24), 6991-6997.

11. Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R., The first polymer-supported and recyclable chiral catalyst for enantioselective olefin metathesis. *Angew. Chem.-Int. Edit.* **2002,** *41* (4), 589-+.

12. Kiely, A. F.; Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H., Enantioselective synthesis of medium-ring heterocycles, tertiary ethers, and tertiary alcohols by Mo-catalyzed ring-closing metathesis. *J. Am. Chem. Soc.* **2002,** *124* (12), 2868-2869.

13. Teng, X.; Cefalo, D. R.; Schrock, R. R.; Hoveyda, A. H., Enhancement of enantioselectivity by THF in asymmetric Mo- catalyzed olefin metathesis. catalytic enantioselective synthesis of cyclic tertiary ethers and spirocycles. *J. Am. Chem. Soc.* **2002,** *124* (36), 10779-10784.

14. Dolman, S. J.; Schrock, R. R.; Hoveyda, A. H., Enantioselective synthesis of cyclic secondary amines through Mo-catalyzed asymmetric ring-closing metathesis (ARCM). *Org. Lett.* **2003,** *5* (25), 4899-4902.

15. Tsang, W. C. P.; Jernelius, J. A.; Cortez, G. A.; Weatherhead, G. S.; Schrock, R. R.; Hoveyda, A. H., An enantiomerically pure adamantylimido molybdenum alkylidene complex. An effective new catalyst for enantioselective olefin metathesis. *J. Am. Chem. Soc.* **2003,** *125* (9), 2591-2596.

16. Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H., Chiral Ru-based complexes for asymmetric olefin metathesis: Enhancement of catalyst activity through steric and electronic modifications. *J. Am. Chem. Soc.* **2003,** *125* (41), 12502-12508.

17. Dolman, S. J.; Hultzsch, K. C.; Pezet, F.; Teng, X.; Hoveyda, A. H.; Schrock, R. R., Supported chiral Mo-based complexes as efficient catalysts for enantioselective olefin metathesis. *J. Am. Chem. Soc.* **2004,** *126* (35), 10945-10953.

18. Gillingham, D. G.; Kataoka, O.; Garber, S. B.; Hoveyda, A. H., Efficient enantioselective synthesis of functionalized tetrahydropyrans by Ru-catalyzed asymmetric ring-opening metathesis/cross-metathesis (AROM/CM). *J. Am. Chem. Soc.* **2004,** *126* (39), 12288-12290.

19. Sattely, E. S.; Cortez, G. A.; Moebius, D. C.; Schrock, R. R.; Hoveyda, A. H., Enantioselective synthesis of cyclic amides and amines through Mo-catalyzed asymmetric ring-closing metathesis. *J. Am. Chem. Soc.* **2005,** *127* (23), 8526-8533.

20. Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H., A readily available chiral Ag-based N-heterocyclic carbene complex for use in efficient and highly enantioselective Ru-catalyzed olefin metathesis and Cu-catalyzed allylic alkylation reactions. *J. Am. Chem. Soc.* **2005,** *127* (18), 6877-6882.

21. Berlin, J. M.; Goldberg, S. D.; Grubbs, R. H., Highly active chiral ruthenium catalysts for asymmetric cross- and ring-opening cross metathesis. *Angew. Chem.-Int. Edit.* **2006,** *45* (45), 7591-7595.

22. Funk, T. W.; Berlin, J. M.; Grubbs, R. H., Highly active chiral ruthenium catalysts for asymmetric ring-closing olefin metathesis. *J. Am. Chem. Soc.* **2006,** *128* (6), 1840-1846.

23. Lee, A. L.; Malcolmson, S. J.; Puglisi, A.; Schrock, R. R.; Hoveyda, A. H., Enantioselective synthesis of cyclic enol ethers and all-carbon quaternary stereogenic centers through catalytic asymmetric ring-closing metathesis. *J. Am. Chem. Soc.* **2006,** *128* (15), 5153-5157.

24. Giudici, R. E.; Hoveyda, A. H., Directed catalytic asymmetric olefin metathesis. Selectivity control by enoate and ynoate groups in Ru-catalyzed asymmetric ring-opening/cross-metathesis. *J. Am. Chem. Soc.* **2007,** *129* (13), 3824-+.

25. Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H., Highly efficient molybdenum-based catalysts for enantioselective alkene metathesis. *Nature* **2008,** *456* (7224), 933-937.

26. Harvey, J. S.; Malcolmson, S. J.; Dunne, K. S.; Meek, S. J.; Thompson, A. L.; Schrock, R. R.; Hoveyda, A. H.; Gouverneur, V., Enantioselective Synthesis of P-Stereogenic Phosphinates and Phosphine oxides by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis. *Angew. Chem.-Int. Edit.* **2009,** *48* (4), 762-766.

27. Klare, H. F. T.; Oestreich, M., Asymmetric Ring-Closing Metathesis with a Twist. *Angew. Chem.-Int. Edit.* **2009,** *48* (12), 2085-2089.

28. Meek, S. J.; Malcolmson, S. J.; Li, B.; Schrock, R. R.; Hoveyda, A. H., The Significance of Degenerate Processes to Enantioselective Olefin Metathesis Reactions Promoted by Stereogenic-at-Mo Complexes. *J. Am. Chem. Soc.* **2009,** *131* (45), 16407-+.

29. Blacquiere, J. M.; McDonald, R.; Fogg, D. E., Integrating the Schrock and Grubbs Catalysts: Ruthenium-Binaphtholate Catalysts for Olefin Metathesis. *Angew. Chem.-Int. Edit.* **2010,** *49* (22), 3807-3810.

30. Hoveyda, A. H.; Malcolmson, S. J.; Meek, S. J.; Zhugralin, A. R., Catalytic Enantioselective Olefin Metathesis in Natural Product Synthesis. Chiral Metal-Based Complexes that Deliver High Enantioselectivity and More. *Angew. Chem.-Int. Edit.* **2010,** *49* (1), 34-44.

31. Ogasawara, M.; Watanabe, S.; Nakajima, K.; Takahashi, T., Enantioselective Synthesis of Planar-Chiral Phosphaferrocenes by Molybdenum-Catalyzed Asymmetric Interannular Ring-Closing Metathesis. *J. Am. Chem. Soc.* **2010,** *132* (7), 2136-+.

32. Yu, M.; Ibrahem, I.; Hasegawa, M.; Schrock, R. R.; Hoveyda, A. H., Enol Ethers as Substrates for Efficient Z- and Enantioselective Ring-Opening/Cross-Metathesis Reactions Promoted by Stereogenic-at-Mo Complexes: Utility in Chemical Synthesis and Mechanistic Attributes. *J. Am. Chem. Soc.* **2012,** *134* (5), 2788-2799.

33. Hartung, J.; Dornan, P. K.; Grubbs, R. H., Enantioselective Olefin Metathesis with Cyclometalated Ruthenium Complexes. *J. Am. Chem. Soc.* **2014,** *136* (37), 13029-13037.

34. Hartung, J.; Grubbs, R. H., Catalytic, Enantioselective Synthesis of 1,2-anti-Diols by Asymmetric Ring-Opening/Cross- Metathesis. *Angew. Chem.-Int. Edit.* **2014,** *53* (15), 3885-3888.

35. Jončev, Z.; Sparr, C., Atroposelective Arene-Forming Alkene Metathesis. *Angewandte Chemie International Edition* **2022,** *61* (51), e202211168.

4.6.3 Cyclization and Cycloaddition Reactions

1. Lei, A. W.; He, M. S.; Wu, S. L.; Zhang, X. M., Highly enantioselective Rh-catalyzed intramolecular alder-ene reactions for the syntheses of chiral tetrahydrofurans. *Angew. Chem.-Int. Edit.* **2002,** *41* (18), 3457-3460.

2. Lei, A. W.; He, M. S.; Zhang, X. M., Highly enantioselective syntheses of functionalized (alpha- methylene-gamma-butyrolactones via Rh(I)-catalyzed intramolecular alder ene reaction: Application to formal synthesis of (+)-pilocarpine. *J. Am. Chem. Soc.* **2002,** *124* (28), 8198-8199.

3. Lei, A. W.; Waldkirch, J. P.; He, M. S.; Zhang, X. M., Highly enantioselective cycloisomerization of enynes catalyzed by rhodium for the preparation of functionalized lactams. *Angew. Chem.-Int. Edit.* **2002,** *41* (23), 4526-+.

4. Tanaka, K.; Fu, G. C., Enantioselective synthesis of cyclopentenones via rhodium- catalyzed kinetic resolution and desymmetrization of 4-alkynals. *J. Am. Chem. Soc.* **2002,** *124* (35), 10296-10297.

5. Shintani, R.; Fu, G. C., A new copper-catalyzed 3+2 cycloaddition: Enantioselective coupling of terminal alkynes with azomethine imines to generate five-membered nitrogen heterocycles. *J. Am. Chem. Soc.* **2003,** *125* (36), 10778-10779.

6. Hatano, M.; Mikami, K., Highly enantioselective quinoline synthesis via ene-type cyclization of 1,7-enynes catalyzed by a cationic BINAP- palladium(II) complex. *J. Am. Chem. Soc.* **2003,** *125* (16), 4704-4705.

7. Kato, K.; Tanaka, M.; Yamamura, S.; Yamamoto, Y.; Akita, H., Asymmetric cyclization-carbonylation of 2-propargyl-1,3-dione. *Tetrahedron Lett.* **2003,** *44* (15), 3089-3092.

8. Chakrapani, H.; Liu, C.; Widenhoefer, R. A., Enantioselective cyclization/hydrosilylation of 1,6-enynes catalyzed by a cationic rhodium bis(phosphine) complex. *Org. Lett.* **2003,** *5* (2), 157-159.

9. Lei, A. W.; He, M. S.; Zhang, X. M., Rh-catalyzed kinetic resolution of enynes and highly enantioselective formation of 4-alkenyl-2,3-disubstituted tetrahydrofurans. *J. Am. Chem. Soc.* **2003,** *125* (38), 11472-11473.

10. Tanaka, K.; Fu, G. C., Parallel kinetic resolution of 4-alkynals catalyzed by Rh(I)/Tol-BINAP: Synthesis of enantioenriched cyclobutanones and cyclopentenones. *J. Am. Chem. Soc.* **2003,** *125* (27), 8078-8079.

11. Trend, R. M.; Ramtohul, Y. K.; Ferreira, E. M.; Stoltz, B. M., Palladium-catalyzed oxidative wacker cyclizations in nonpolar organic solvents with molecular oxygen: A stepping stone to asymmetric aerobic cyclizations. *Angew. Chem.-Int. Edit.* **2003,** *42* (25), 2892-2895.

12. Shibata, T.; Fujimoto, T.; Yokota, K.; Takagi, K., Iridium complex-catalyzed highly enantio- and diastereoselective 2+2+2 cycloaddition for the synthesis of axially chiral teraryl compounds. *J. Am. Chem. Soc.* **2004,** *126* (27), 8382-8383.

13. Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M., Highly enantioselective catalytic carbon dioxide incorporation reaction: Nickel-catalyzed asymmetric carboxylative cyclization of bis-1,3-dienes. *J. Am. Chem. Soc.* **2004,** *126* (19), 5956-5957.

14. Mikami, K.; Kataoka, S.; Yusa, Y.; Aikawa, K., Racemic but Tropos (chirally flexible) BIPHEP ligands for Rh(I)-complexes: Highly enantioselective ene-type cyclization of 1,6-enynes. *Org. Lett.* **2004,** *6* (21), 3699-3701.

15. Tanaka, K.; Nishida, G.; Wada, A.; Noguchi, K., Enantioselective synthesis of axially chiral phthalides through cationic Rh-1(H-8-binap) -catalyzed cross alkyne cyclotrimerization. *Angew. Chem.-Int. Edit.* **2004,** *43* (47), 6510-6512.

16. Thalji, R. K.; Ellman, J. A.; Bergman, R. G., Highly efficient and enantioselective cyclization of aromatic imines via directed C-H bond activation. *J. Am. Chem. Soc.* **2004,** *126* (23), 7192-7193.

17. Lutete, L. M.; Kadota, I.; Yamamoto, Y., Palladium-catalyzed intramolecular asymmetric hydroamination of alkynes. *J. Am. Chem. Soc.* **2004,** *126* (6), 1622-1623.

18. Takimoto, M.; Kajima, Y.; Sato, Y.; Mori, M., Nickel-catalyzed enantioselective three-component coupling of bis-1,3-dienes, aldehydes, and dimethylzinc. *J. Org. Chem.* **2005,** *70* (21), 8605-8608.

19. Tietze, L. F.; Sommer, K. M.; Zinngrebe, J.; Stecker, F., Palladium-catalyzed enantioselective domino reaction for the efficient synthesis of vitamin E. *Angew. Chem.-Int. Edit.* **2005,** *44* (2), 257-259.

20. Evans, P. A.; Lai, K. W.; Sawyer, J. R., Regio- and enantioselective intermolecular rhodium-catalyzed 2+2+2 carbocyclization reactions of 1,6-enynes with methyl arylpropiolates. *J. Am. Chem. Soc.* **2005,** *127* (36), 12466-12467.

21. Jang, H. Y.; Hughes, F. W.; Gong, H. G.; Zhang, J. M.; Brodbelt, J. S.; Krische, M. J., Enantioselective reductive cyclization of 1,6-enynes via rhodium-catalyzed asymmetric hydrogenation: C-C bond formation precedes hydrogen activation. *J. Am. Chem. Soc.* **2005,** *127* (17), 6174-6175.

22. Mikami, K.; Kataoka, S.; Aikawa, K., Tropos or atropos nature of rhodium complexes bearing a tetrakis(phosphanyl)terphenyl ligand: Highly enantioselective catalysis of ene-type cyclization. *Org. Lett.* **2005,** *7* (26), 5777-5780.

23. Shintani, R.; Tsurusaki, A.; Okamoto, K.; Hayashi, T., Highly chemo- and enantioselective arylative cyclization of alkyne-tethered electron-deficient olefins catalyzed by rhodium complexes with chiral dienes. *Angew. Chem.-Int. Edit.* **2005,** *44* (25), 3909-3912.

24. Tanaka, K.; Hagiwara, Y.; Noguchi, K., Rhodium-catalyzed regio- and enantioselective intermolecular [4+2] carbocyclization of 4-alkynals with N,N-dialkyl acrylamides. *Angew. Chem.-Int. Edit.* **2005,** *44* (44), 7260-7263.

25. Tanaka, K.; Wada, A.; Noguchi, K., Rhodium-catalyzed chemo-, regio-, and enantioselective [2+2+2] cycloaddition of alkynes with isocyanates. *Org. Lett.* **2005,** *7* (21), 4737-4739.

26. Chow, C. P.; Shea, K. J., Dual function catalysts. Dehydrogenation and asymmetric intramolecular Diels-Alder cycloaddition of N-hydroxy formate esters and hydroxamic acids: Evidence for a ruthenium-acylnitroso intermediate. *J. Am. Chem. Soc.* **2005,** *127* (11), 3678-3679.

27. Trend, R. M.; Ramtohul, Y. K.; Stoltz, B. M., Oxidative cyclizations in a nonpolar solvent using molecular oxygen and studies on the stereochemistry of oxypalladation. *J. Am. Chem. Soc.* **2005,** *127* (50), 17778-17788.

28. Braun, I.; Rudroff, F.; Mihovilovic, M. D.; Bach, T., Synthesis of enantiomerically pure bicyclo[4.2.0] octanes by Cu-catalyzed [2+2] photocycloaddition and enantiotopos-differentiating ring opening. *Angew. Chem.-Int. Edit.* **2006,** *45* (33), 5541-5543.

29. Feducia, J. A.; Campbell, A. N.; Doherty, M. Q.; Gagne, M. R., Modular catalysts for diene cycloisomerization: Rapid and enantioselective variants for bicyclopropane synthesis. *J. Am. Chem. Soc.* **2006,** *128* (40), 13290-13297.

30. Aikawa, K.; Akutagawa, S.; Mikami, K., Asymmetric synergy between chiral dienes and diphosphines in cationic Rh(I)-catalyzed intramolecular [4+2] cycloaddition. *J. Am. Chem. Soc.* **2006,** *128* (39), 12648-12649.

31. Kinder, R. E.; Widenhoefer, R. A., Rhodium-catalyzed asymmetric cyclization/hydroboration of 1,6-enynes. *Org. Lett.* **2006,** *8* (10), 1967-1969.

32. Shibata, T.; Tahara, Y. K., Enantioselective intramolecular [2+2+2] cycloaddition of 1,4-diene-ynes: A new approach to the construction of quaternary carbon stereocenters. *J. Am. Chem. Soc.* **2006,** *128* (36), 11766-11767.

33. Tanaka, K.; Takeishi, K.; Noguchi, K., Enantioselective synthesis of axially chiral anilides through rhodium-catalyzed [2+2+2] cycloaddition of 1,6-diynes with trimethylsilylynamides. *J. Am. Chem. Soc.* **2006,** *128* (14), 4586-4587.

34. Tsuchikama, K.; Kuwata, Y.; Shibata, T., Highly enantioselective construction of a chiral spirocyclic structure by the [2+2+2] cycloaddition of diynes and exo-methylene cyclic compounds. *J. Am. Chem. Soc.* **2006,** *128* (42), 13686-13687.

35. Wender, P. A.; Haustedt, L. O.; Lim, J.; Love, J. A.; Williams, T. J.; Yoon, J. Y., Asymmetric catalysis of the [5+2] cycloaddition reaction of vinylcyclopropanes and pi-systems. *J. Am. Chem. Soc.* **2006,** *128* (19), 6302-6303.

36. Gribkov, D. V.; Hultzsch, K. C.; Hampel, F., 3,3 '-bis(trisarylsilyl)-substituted binaphtholate rare earth metal catalysts for asymmetric hydroamination. *J. Am. Chem. Soc.* **2006,** *128* (11), 3748-3759.

37. Riegert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A., Enantioselective intramolecular hydroamination catalyzed by lanthanide ate complexes coordinated by N-substituted (R)-1,1 '-binaphthyl-2,2 '-diamido ligands. *J. Org. Chem.* **2006,** *71* (6), 2514-2517.

38. Patil, N. T.; Lutete, L. M.; Wu, H. Y.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y., Palladium-catalyzed intramolecular asymmetric hydroamination, hydroalkoxylation, and hydrocarbonation of alkynes. *J. Org. Chem.* **2006,** *71* (11), 4270-4279.

39. Yip, K. T.; Yang, M.; Law, K. L.; Zhu, N. Y.; Yang, D., Pd(II)-catalyzed enantioselective oxidative tandem cyclization reactions. Synthesis of indolines through C-N and C-C bond formation. *J. Am. Chem. Soc.* **2006,** *128* (10), 3130-3131.

40. Fan, B. M.; Xie, J. H.; Li, S.; Wang, L. X.; Zhou, Q. L., Highly enantioselective hydrosilylation/cyclization of 1,6-enynes catalyzed by rhodium(I) complexes of spiro diphosphines. *Angew. Chem.-Int. Edit.* **2007,** *46* (8), 1275-1277.

41. Nishimura, T.; Kawamoto, T.; Sasaki, K.; Tsurumaki, E.; Hayashi, T., Rhodium-catalyzed asymmetric cyclodimerization of oxa- and azabicyclic alkenes. *J. Am. Chem. Soc.* **2007,** *129* (6), 1492-+.

42. Tanaka, K.; Sagae, H.; Toyoda, K.; Noguchi, K.; Hirano, M., Enantioselective synthesis of planar-chiral metacyclophanes through rhodium-catalyzed alkyne cyclotrimerization. *J. Am. Chem. Soc.* **2007,** *129* (6), 1522-+.

43. Gulfas, M.; Duran, J.; Lopez, F.; Castedo, L.; Mascarenas, J. L., Palladium-catalyzed [4+3] intramolecular cycloaddition of alkylidenecyclopropanes and dienes. *J. Am. Chem. Soc.* **2007,** *129* (36), 11026-+.

44. Shintani, R.; Sannohe, Y.; Tsuji, T.; Hayashi, T., A cationic rhodium-chiral diene complex as a high-performance catalyst for the intramolecular asymmetric [4+2] cycloaddition of alkyne-1,3-dienes. *Angew. Chem.-Int. Edit.* **2007,** *46* (38), 7277-7280.

45. Wada, A.; Noguchi, K.; Hirano, M.; Tanaka, K., Enantioselective synthesis of C-2-symmetric spirobipyridine ligands through cationic Rh(I)/modified-BINAP-catalyzed double [2+2+2] cycloaddition. *Org. Lett.* **2007,** *9* (7), 1295-1298.

46. Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L., Chiral neutral zirconium amidate complexes for the asymmetric hydroamination of alkenes. *Angew. Chem.-Int. Edit.* **2007,** *46* (3), 354-358.

47. Corkey, B. K.; Toste, F. D., Palladium-catalyzed enantioselective cyclization of silyloxy-1,6-enynes. *J. Am. Chem. Soc.* **2007,** *129* (10), 2764-+.

48. Matsuda, T.; Shigeno, M.; Murakami, M., Asymmetric synthesis of 3,4-dihydrocoumarins by rhodium-catalyzed reaction of 3-(2-hydroxyphenyl)cyclobutanones. *J. Am. Chem. Soc.* **2007,** *129* (40), 12086-+.

49. Zeng, W.; Chemler, S. R., Copper(II)-catalyzed enantioselective intramolecular carboamination of alkenes. *J. Am. Chem. Soc.* **2007,** *129* (43), 12948-+.

50. Tanaka, K.; Otake, Y.; Sagae, H.; Noguchi, K.; Hirano, M., Highly regio-, diastereo-, and enantioselective [2+2+2] cycloaddition of 1,6-enynes with electron-deficient ketones catalyzed by a cationic Rh-I/H-8-binap complex. *Angew. Chem.-Int. Edit.* **2008,** *47* (7), 1312-1316.

51. Yu, R. T.; Rovis, T., Asymmetric synthesis of bicyclic Amidines via rhodium-catalyzed [2+2+2] cycloaddition of Carbodiimides. *J. Am. Chem. Soc.* **2008,** *130* (11), 3262-+.

52. Shibata, T.; Tahara, Y. K.; Tamura, K.; Endo, K., Enantioselective syntheses of various chiral multicyclic compounds with quaternary carbon stereocenters by catalytic intramolecular cycloaddition. *J. Am. Chem. Soc.* **2008,** *130* (11), 3451-3457.

53. Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K., Enantioselective synthesis of P-stereogenic alkynylphosphine oxides by Rh-catalyzed [2+2+2] cycloaddition. *Angew. Chem.-Int. Edit.* **2008,** *47* (18), 3410-3413.

54. Shibata, Y.; Noguchi, K.; Hirano, M.; Tanaka, K., Rhodium-catalyzed highly enantio- and diastereloselective cotrimerization of alkenes and dialkyl acetylenedicarboxylates leading to furylcyclopropanes. *Org. Lett.* **2008,** *10* (13), 2825-2828.

55. Harada, H.; Thalji, R. K.; Bergman, R. G.; Ellman, J. A., Enantioselective intramolecular hydroarylation of alkenes via directed C-H bond activation. *J. Org. Chem.* **2008,** *73* (17), 6772-6779.

56. Watson, M. P.; Jacobsen, E. N., Asymmetric intramolecular arylcyanation of unactivated Olefins via C-CN bond activation. *J. Am. Chem. Soc.* **2008,** *130* (38), 12594-+.

57. Shu, W.; Yang, Q.; Jia, G. C.; Ma, S. M., Studies on palladium-catalyzed enantioselective cyclization of 3,4-allenylic hydrazines with organic halides. *Tetrahedron* **2008,** *64* (49), 11159-11166.

58. Fuller, P. H.; Kim, J. W.; Chemler, S. R., Copper Catalyzed Enantioselective Intramolecular Aminooxygenation of Alkenes. *J. Am. Chem. Soc.* **2008,** *130* (52), 17638-+.

59. Yu, R. T.; Lee, E. E.; Malik, G.; Rovis, T., Total Synthesis of Indolizidine Alkaloid (-)-209D: Overriding Substrate Bias in the Asymmetric Rhodium-Catalyzed [2+2+2] Cycloaddition. *Angew. Chem.-Int. Edit.* **2009,** *48* (13), 2379-2382.

60. Brissy, D.; Skander, M.; Jullien, H.; Retailleau, P.; Marinetti, A., Platinum(II) Catalysts for Highly Enantioselective 1,6-Enyne Cycloisomerizations. Synthetic, Structural, and Catalytic Studies. *Org. Lett.* **2009,** *11* (10), 2137-2139.

61. Scarborough, C. C.; Bergant, A.; Sazama, G. T.; Guzei, I. A.; Spencer, L. C.; Stahl, S. S., Synthesis of Pd-II complexes bearing an enantiomerically resolved seven-membered N-heterocyclic carbene ligand and initial studies of their use in asymmetric Wacker-type oxidative cyclization reactions. *Tetrahedron* **2009,** *65* (26), 5084-5092.

62. Nicolaou, K. C.; Li, A.; Ellery, S. P.; Edmonds, D. J., Rhodium-Catalyzed Asymmetric Enyne Cycloisomerization of Terminal Alkynes and Formal Total Synthesis of (-)-Platensimycin. *Angew. Chem.-Int. Edit.* **2009,** *48* (34), 6293-6295.

63. Shibata, T.; Uchiyama, T.; Endo, K., Enantioselective Synthesis of Chiral Tripodal Cage Compounds by [2+2+2] Cycloaddition of Branched Triynes. *Org. Lett.* **2009,** *11* (17), 3906-3908.

64. Shintani, R.; Nakatsu, H.; Takatsu, K.; Hayashi, T., Rhodium-Catalyzed Asymmetric [5+2] Cycloaddition of Alkyne-Vinylcyclopropanes. *Chem.-Eur. J.* **2009,** *15* (35), 8692-8694.

65. Shu, W.; Ma, S. M., Synthesis of a new spiro-BOX ligand and its application in enantioselective allylic cyclization based on carbopalladation of allenyl hydrazines. *Chem. Commun.* **2009,** (41), 6198-6200.

66. Hojo, D.; Noguchi, K.; Tanaka, K., Synthesis of Chiral Tetrasubstituted Alkenes by an Asymmetric Cascade Reaction Catalyzed Cooperatively by Cationic Rhodium(I) and Silver(I) Complexes. *Angew. Chem.-Int. Edit.* **2009,** *48* (43), 8129-8132.

67. Eisenberger, P.; Ayinla, R. O.; Lauzon, J. M. P.; Schafer, L. L., Tantalum-Amidate Complexes for the Hydroaminoalkylation of Secondary Amines: Enhanced Substrate Scope and Enantioselective Chiral Amine Synthesis. *Angew. Chem.-Int. Edit.* **2009,** *48* (44), 8361-8365.

68. He, W.; Yip, K. T.; Zhu, N. Y.; Yang, D., Pd(II)/Bu-t-quinolineoxazoline: An Air-Stable and Modular Chiral Catalyst System for Enantioselective Oxidative Cascade Cyclization. *Org. Lett.* **2009,** *11* (24), 5626-5628.

69. Tsujihara, T.; Shinohara, T.; Takenaka, K.; Takizawa, S.; Onitsuka, K.; Hatanaka, M.; Sasai, H., Enantioselective Intramolecular Oxidative Aminocarbonylation of Alkenylureas Catalyzed by Palladium-Spiro Bis(isoxazoline) Complexes. *J. Org. Chem.* **2009,** *74* (24), 9274-9279.

70. Dalton, D. M.; Oberg, K. M.; Yu, R. T.; Lee, E. E.; Perreault, S.; Oinen, M. E.; Pease, M. L.; Malik, G.; Rovis, T., Enantioselective Rhodium-Catalyzed [2+2+2] Cycloadditions of Terminal Alkynes and Alkenyl Isocyanates: Mechanistic Insights Lead to a Unified Model that Rationalizes Product Selectivity. *J. Am. Chem. Soc.* **2009,** *131* (43), 15717-15728.

71. Shen, X. Q.; Buchwald, S. L., Rhodium-Catalyzed Asymmetric Intramolecular Hydroamination of Unactivated Alkenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (3), 564-567.

72. Yamauchi, M.; Morimoto, M.; Miura, T.; Murakami, M., Enantioselective Synthesis of 3,4-Dihydroisoquinolin-1(2H)-ones by Nickel-Catalyzed Denitrogenative Annulation of 1,2,3-Benzotriazin-4(3H)-ones with Allenes. *J. Am. Chem. Soc.* **2010,** *132* (1), 54-+.

73. Fan, B. M.; Li, X. J.; Peng, F. Z.; Zhang, H. B.; Chan, A. S. C.; Shao, Z. H., Ligand-Controlled Enantioselective 2+2 Cycloaddition of Oxabicyclic Alkenes with Terminal Alkynes Using Chiral Iridium Catalysts. *Org. Lett.* **2010,** *12* (2), 304-306.

74. Tanaka, R.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed Asymmetric Reductive Cyclization of Heteroatom-Linked 5-Alkynals with Heteroatom-Substituted Acetaldehydes. *J. Am. Chem. Soc.* **2010,** *132* (4), 1238-+.

75. Nishimura, T.; Kawamoto, T.; Nagaosa, M.; Kumamoto, H.; Hayashi, T., Chiral Tetrafluorobenzobarrelene Ligands for the Rhodium-Catalyzed Asymmetric Cycloisomerization of Oxygen- and Nitrogen-Bridged 1,6-Enynes. *Angew. Chem.-Int. Edit.* **2010,** *49* (9), 1638-1641.

76. Ototake, N.; Morimoto, Y.; Mokuya, A.; Fukaya, H.; Shida, Y.; Kitagawa, O., Catalytic Enantioselective Synthesis of Atropisomeric Indoles with an N-C Chiral Axis. *Chem.-Eur. J.* **2010,** *16* (23), 6752-6755.

77. Miura, T.; Yamauchi, M.; Kosaka, A.; Murakami, M., Nickel-Catalyzed Regio- and Enantioselective Annulation Reactions of 1,2,3,4-Benzothiatriazine-1,1(2H)-dioxides with Allenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (29), 4955-4957.

78. Takenaka, K.; Mohanta, S. C.; Patil, M. L.; Rao, C. V. L.; Takizawa, S.; Suzuki, T.; Sasai, H., Enantioselective Wacker-Type Cyclization of 2-AlkenyL-1,3-diketones Promoted by Pd-SPRIX Catalyst. *Org. Lett.* **2010,** *12* (15), 3480-3483.

79. Mai, D. N.; Wolfe, J. P., Asymmetric Palladium-Catalyzed Carboamination Reactions for the Synthesis of Enantiomerically Enriched 2-(Arylmethyl)- and 2-(Alkenylmethyl)pyrrolidines. *J. Am. Chem. Soc.* **2010,** *132* (35), 12157-12159.

80. Miura, T.; Morimoto, M.; Murakami, M., Enantioselective 2+2+2 Cycloaddition Reaction of Isocyanates and Allenes Catalyzed by Nickel. *J. Am. Chem. Soc.* **2010,** *132* (45), 15836-15838.

81. Bajracharya, G. B.; Koranne, P. S.; Nadaf, R. N.; Gabr, R. K. M.; Takenaka, K.; Takizawa, S.; Sasai, H., Pd-catalyzed 5-endo-trig-type cyclization of beta, gamma-unsaturated carbonyl compounds: an efficient ring closing reaction to give gamma-butenolides and 3-pyrrolin-2-ones. *Chem. Commun.* **2010,** *46* (47), 9064-9066.

82. Kobayashi, M.; Suda, T.; Noguchi, K.; Tanaka, K., Enantioselective Construction of Bridged Multicyclic Skeletons: Intermolecular 2+2+2 Cycloaddition/Intramolecular Diels-Alder Reaction Cascade. *Angew. Chem.-Int. Edit.* **2011,** *50* (7), 1664-1667.

83. Li, Q. A.; Yu, Z. X., Enantioselective Rhodium-Catalyzed Allylic C-H Activation for the Addition to Conjugated Dienes. *Angew. Chem.-Int. Edit.* **2011,** *50* (9), 2144-2147.

84. Ochi, Y.; Kurahashi, T.; Matsubara, S., Decarbonylative Cycloaddition of Phthalic Anhydrides with Allenes. *Org. Lett.* **2011,** *13* (6), 1374-1377.

85. Oberg, K. M.; Rovis, T., Enantioselective Rhodium-Catalyzed 4+2 Cycloaddition of alpha,beta-Unsaturated Imines and Isocyanates. *J. Am. Chem. Soc.* **2011,** *133* (13), 4785-4787.

86. Shibuya, T.; Shibata, Y.; Noguchi, K.; Tanaka, K., Palladium-Catalyzed Enantioselective Intramolecular Hydroarylation of Alkynes To Form Axially Chiral 4-Aryl 2-Quinolinones. *Angew. Chem.-Int. Edit.* **2011,** *50* (17), 3963-3967.

87. Suda, T.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed Asymmetric Formal Olefination or Cycloaddition: 1,3-Dicarbonyl Compounds Reacting with 1,6-Diynes or 1,6-Enynes. *Angew. Chem.-Int. Edit.* **2011,** *50* (19), 4475-4479.

88. Takenaka, K.; Hashimoto, S.; Takizawa, S.; Sasai, H., Chlorinative Cyclization of 1,6-Enynes by Enantioselective Palladium(II)/Palladium(IV) Catalysis. *Adv. Synth. Catal.* **2011,** *353* (7), 1067-1070.

89. Brusoe, A. T.; Alexanian, E. J., Rhodium(I)-Catalyzed Ene-Allene-Allene 2+2+2 Cycloadditions: Stereoselective Synthesis of Complex trans-Fused Carbocycles. *Angew. Chem.-Int. Edit.* **2011,** *50* (29), 6596-6600.

90. Rousseaux, S.; Garcia-Fortanet, J.; Sanchez, M. A. D.; Buchwald, S. L., Palladium(0)-Catalyzed Arylative Dearomatization of Phenols. *J. Am. Chem. Soc.* **2011,** *133* (24), 9282-9285.

91. Takenaka, K.; Akita, M.; Tanigaki, Y.; Takizawa, S.; Sasai, H., Enantioselective Cyclization of 4-Alkenoic Acids via an Oxidative Allylic C-H Esterification. *Org. Lett.* **2011,** *13* (13), 3506-3509.

92. Nishimura, T.; Maeda, Y.; Hayashi, T., Chiral Diene-Phosphine Tridentate Ligands for Rhodium-Catalyzed Asymmetric Cycloisomerization of 1,6-Enynes. *Org. Lett.* **2011,** *13* (14), 3674-3677.

93. Hoffman, T. J.; Carreira, E. M., Catalytic Asymmetric Intramolecular Hydroacylation with Rhodium/Phosphoramidite-Alkene Ligand Complexes. *Angew. Chem.-Int. Edit.* **2011,** *50* (45), 10670-10674.

94. Shintani, R.; Moriya, K.; Hayashi, T., Palladium-Catalyzed Enantioselective Desymmetrization of Silacyclobutanes: Construction of Silacycles Possessing a Tetraorganosilicon Stereocenter. *J. Am. Chem. Soc.* **2011,** *133* (41), 16440-16443.

95. Barbazanges, M.; Auge, M.; Moussa, J.; Amouri, H.; Aubert, C.; Desmarets, C.; Fensterbank, L.; Gandon, V.; Malacria, M.; Ollivier, C., Enantioselective IrI-Catalyzed Carbocyclization of 1,6-Enynes by the Chiral Counterion Strategy. *Chem.-Eur. J.* **2011,** *17* (49), 13789-13794.

96. Falk, A.; Fiebig, L.; Neudoerfl, J.-M.; Adler, A.; Schmalz, H.-G., Rhodium-Catalyzed Enantioselective Intramolecular 4+2 Cycloaddition using a Chiral Phosphine-Phosphite Ligand: Importance of Microwave-Assisted Catalyst Conditioning. *Adv. Synth. Catal.* **2011,** *353* (18), 3357-3362.

97. Lin, M.; Kang, G. Y.; Guo, Y. A.; Yu, Z. X., Asymmetric Rh(I)-Catalyzed Intramolecular 3+2 Cycloaddition of 1-Yne-vinylcyclopropanes for Bicyclo 3.3.0 Compounds with a Chiral Quaternary Carbon Stereocenter and Density Functional Theory Study of the Origins of Enantioselectivity. *J. Am. Chem. Soc.* **2012,** *134* (1), 398-405.

98. Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed Enantioselective Synthesis, Crystal Structures, and Photophysical Properties of Helically Chiral 1,1 '-Bitriphenylenes. *J. Am. Chem. Soc.* **2012,** *134* (9), 4080-4083.

99. Shintani, R.; Moriya, K.; Hayashi, T., Palladium-Catalyzed Desymmetrization of Silacyclobutanes with Alkynes: Enantioselective Synthesis of Silicon-Stereogenic 1-Sila-2-cyclohexenes and Mechanistic Considerations. *Org. Lett.* **2012,** *14* (11), 2902-2905.

100. Liu, Q. C.; Wen, K.; Zhang, Z. F.; Wu, Z. X.; Zhang, Y. J.; Zhang, W. B., Pd(II)-catalyzed asymmetric Wacker-type cyclization for the preparation of 2-vinylchroman derivatives with biphenyl tetraoxazoline ligands. *Tetrahedron* **2012,** *68* (26), 5209-5215.

101. Zhu, S. L.; MacMillan, D. W. C., Enantioselective Copper-Catalyzed Construction of Aryl Pyrroloindolines via an Arylation-Cyclization Cascade. *J. Am. Chem. Soc.* **2012,** *134* (26), 10815-10818.

102. Miller, Y.; Miao, L.; Hosseini, A. S.; Chemler, S. R., Copper-Catalyzed Intramolecular Alkene Carboetherification: Synthesis of Fused-Ring and Bridged-Ring Tetrahydrofurans. *J. Am. Chem. Soc.* **2012,** *134* (29), 12149-12156.

103. Jackowski, O.; Wang, J. P.; Xie, X. M.; Ayad, T.; Zhang, Z. G.; Ratovelomanana-Vidal, V., Enantioselective Rhodium-Catalyzed Synthesis of alpha-Chloromethylene-gamma-Butyrolactams from N-Allylic Alkynamides. *Org. Lett.* **2012,** *14* (15), 4006-4009.

104. Jana, R.; Pathak, T. P.; Jensen, K. H.; Sigman, M. S., Palladium(II)-Catalyzed Enantio- and Diastereoselective Synthesis of Pyrrolidine Derivatives. *Org. Lett.* **2012,** *14* (16), 4074-4077.

105. Yang, G. Q.; Shen, C. R.; Zhang, W. B., An Asymmetric Aerobic Aza-Wacker-Type Cyclization: Synthesis of Isoindolinones Bearing Tetrasubstituted Carbon Stereocenters. *Angew. Chem.-Int. Edit.* **2012,** *51* (36), 9141-9145.

106. Hopkins, B. A.; Wolfe, J. P., Synthesis of Enantiomerically Enriched Imidazolidin-2-Ones through Asymmetric Palladium-Catalyzed Alkene Carboamination Reactions. *Angew. Chem.-Int. Edit.* **2012,** *51* (39), 9886-9890.

107. Masutomi, K.; Sakiyama, N.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed Regio-, Diastereo-, and Enantioselective 2+2+2 Cycloaddition of 1,6-Enynes with Acrylamides. *Angew. Chem.-Int. Edit.* **2012,** *51* (52), 13031-13035.

108. Xu, T.; Ko, H. M.; Savage, N. A.; Dong, G. B., Highly Enantioselective Rh-Catalyzed Carboacylation of Olefins: Efficient Syntheses of Chiral Poly-Fused Rings. *J. Am. Chem. Soc.* **2012,** *134* (49), 20005-20008.

109. Paderes, M. C.; Keister, J. B.; Chemler, S. R., Mechanistic Analysis and Optimization of the Copper-Catalyzed Enantioselective Intramolecular Alkene Aminooxygenation. *J. Org. Chem.* **2013,** *78* (2), 506-515.

110. Dalton, D. M.; Rappe, A. K.; Rovis, T., Perfluorinated Taddol phosphoramidite as an L,Z-ligand on Rh(I) and Co(-I): evidence for bidentate coordination via metal-C6F5 interaction. *Chemical Science* **2013,** *4* (5), 2062-2070.

111. Araki, T.; Noguchi, K.; Tanaka, K., Enantioselective Synthesis of Planar-Chiral Carba-Paracyclophanes: Rhodium-Catalyzed 2+2+2 Cycloaddition of Cyclic Diynes with Terminal Monoynes. *Angew. Chem.-Int. Edit.* **2013,** *52* (21), 5617-5621.

112. Manna, K.; Everett, W. C.; Schoendorff, G.; Ellern, A.; Windus, T. L.; Sadow, A. D., Highly Enantioselective Zirconium-Catalyzed Cyclization of Aminoalkenes. *J. Am. Chem. Soc.* **2013,** *135* (19), 7235-7250.

113. Ingalls, E. L.; Sibbald, P. A.; Kaminsky, W.; Michael, F. E., Enantioselective Palladium-Catalyzed Diamination of Alkenes Using N-Fluorobenzenesulfonimide. *J. Am. Chem. Soc.* **2013,** *135* (24), 8854-8856.

114. Babij, N. R.; Wolfe, J. P., Desymmetrization of meso-2,5-Diallylpyrrolidinyl Ureas through Asymmetric Palladium-Catalyzed Carboamination: Stereocontrolled Synthesis of Bicyclic Ureas. *Angew. Chem.-Int. Edit.* **2013,** *52* (35), 9247-9250.

115. Zhou, F.; Tan, C.; Tang, J.; Zhang, Y. Y.; Gao, W. M.; Wu, H. H.; Yu, Y. H.; Zhou, J., Asymmetric Copper(I)-Catalyzed Azide-Alkyne Cycloaddition to Quaternary Oxindoles. *J. Am. Chem. Soc.* **2013,** *135* (30), 10994-10997.

116. Liu, P.; Fukui, Y.; Tian, P.; He, Z. T.; Sun, C. Y.; Wu, N. Y.; Lin, G. Q., Cu-Catalyzed Asymmetric Borylative Cyclization of Cyclohexadienone-Containing 1,6-Enynes. *J. Am. Chem. Soc.* **2013,** *135* (32), 11700-11703.

117. Donets, P. A.; Cramer, N., Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamoylations of Alkenes. *J. Am. Chem. Soc.* **2013,** *135* (32), 11772-11775.

118. Takenaka, K.; Dhage, Y. D.; Sasai, H., Enantioselective Pd(II)-Pd(IV) catalysis utilizing a SPRIX ligand: efficient construction of chiral 3-oxy-tetrahydrofurans. *Chem. Commun.* **2013,** *49* (95), 11224-11226.

119. Shu, X. Z.; Schienebeck, C. M.; Song, W. Z.; Guzei, I. A.; Tang, W. P., Transfer of Chirality in the Rhodium-Catalyzed Intramolecular 5+2 Cycloaddition of 3-Acyloxy-1,4-enynes (ACEs) and Alkynes: Synthesis of Enantioenriched Bicyclo 5.3.0 decatrienes. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13601-13605.

120. Hara, J.; Ishida, M.; Kobayashi, M.; Noguchi, K.; Tanaka, K., Highly Chemo-, Regio-, and Enantioselective Rhodium-Catalyzed Cross-Cyclotrimerization of Two Different Alkynes with Alkenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (11), 2956-2959.

121. Bovino, M. T.; Liwosz, T. W.; Kendel, N. E.; Miller, Y.; Tyminska, N.; Zurek, E.; Chemler, S. R., Enantioselective Copper-Catalyzed Carboetherification of Unactivated Alkenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (25), 6383-6387.

122. Masutomi, K.; Noguchi, K.; Tanaka, K., Enantioselective Cycloisomerization of 1,6-Enynes to Bicyclo 3.1.0 hexanes Catalyzed by Rhodium and Benzoic Acid. *J. Am. Chem. Soc.* **2014,** *136* (21), 7627-7630.

123. Hopkins, B. A.; Wolfe, J. P., Enantioselective synthesis of tetrahydroquinolines, tetrahydroquinoxalines, and tetrahydroisoquinolines via Pd-Catalyzed alkene carboamination reactions. *Chemical Science* **2014,** *5* (12), 4840-4844.

124. Shaw, S.; White, J. D., A New Iron(III)-Salen Catalyst for Enantioselective Conia-ene Carbocyclization. *J. Am. Chem. Soc.* **2014,** *136* (39), 13578-13581.

125. Trost, B. M.; Ryan, M. C.; Rao, M.; Markovic, T. Z., Construction of Enantioenriched 3.1.0 Bicycles via a Ruthenium-Catalyzed Asymmetric Redox Bicycloisomerization Reaction. *J. Am. Chem. Soc.* **2014,** *136* (50), 17422-17425.

126. Shintani, R.; Takagi, C.; Ito, T.; Naito, M.; Nozaki, K., Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles by Enantioselective 2+2+2 Cycloaddition. *Angew. Chem.-Int. Edit.* **2015,** *54* (5), 1616-1620.

127. Manna, K.; Eedugurala, N.; Sadow, A. D., Zirconium-Catalyzed Desymmetrization of Aminodialkenes and Aminodialkynes through Enantioselective Hydroamination. *J. Am. Chem. Soc.* **2015,** *137* (1), 425-435.

128. Schlueter, J.; Blazejak, M.; Boeck, F.; Hintermann, L., Asymmetric Hydroalkoxylation of Non-Activated Alkenes: Titanium-Catalyzed Cycloisomerization of Allylphenols at High Temperatures. *Angew. Chem.-Int. Edit.* **2015,** *54* (13), 4014-4017.

129. Yoshida, T.; Tajima, Y.; Kobayashi, M.; Masutomi, K.; Noguchi, K.; Tanaka, K., Rhodium-Catalyzed 3+2+2 and 2+2+2 Cycloadditions of Two Alkynes with Cyclopropylideneacetamides. *Angew. Chem.-Int. Edit.* **2015,** *54* (28), 8241-8244.

130. Fang, Z. J.; Zheng, S. C.; Guo, Z.; Guo, J. Y.; Tan, B.; Liu, X. Y., Asymmetric Synthesis of Axially Chiral Isoquinolones: Nickel-Catalyzed Denitrogenative Transannulation. *Angew. Chem.-Int. Edit.* **2015,** *54* (33), 9528-9532.

131. Dieckmann, M.; Jang, Y. S.; Cramer, N., Chiral Cyclopentadienyl Iridium(III) Complexes Promote Enantioselective Cycloisomerizations Giving Fused Cyclopropanes. *Angew. Chem.-Int. Edit.* **2015,** *54* (41), 12149-12152.

132. Kossler, D.; Cramer, N., Chiral Cationic (CpRu)-Ru-x(II) Complexes for Enantioselective Yne-Enone Cyclizations. *J. Am. Chem. Soc.* **2015,** *137* (39), 12478-12481.

133. Shintani, R.; Takano, R.; Nozaki, K., Rhodium-catalyzed asymmetric synthesis of silicon-stereogenic silicon-bridged arylpyridinones. *Chemical Science* **2016,** *7* (2), 1205-1211.

134. Straker, R. N.; Peng, Q.; Mekareeya, A.; Paton, R. S.; Anderson, E. A., Computational ligand design in enantio- and diastereoselective ynamide 5+2 cycloisomerization. *Nature Communications* **2016,** *7*.

135. Tahara, Y. K.; Matsubara, R.; Mitake, A.; Sato, T.; Kanyiva, K. S.; Shibata, T., Catalytic and Enantioselective Synthesis of Chiral Multisubstituted Tribenzothiepins by Intermolecular Cycloadditions. *Angew. Chem.-Int. Edit.* **2016,** *55* (14), 4552-4556.

136. Trost, B. M.; Ryan, M. C., A Ruthenium/Phosphoramidite-Catalyzed Asymmetric Interrupted Metallo-ene Reaction. *J. Am. Chem. Soc.* **2016,** *138* (9), 2981-2984.

137. Park, J. W.; Chen, Z. W.; Dong, V. M., Rhodium-Catalyzed Enantioselective Cycloisomerization to Cyclohexenes Bearing Quaternary Carbon Centers. *J. Am. Chem. Soc.* **2016,** *138* (10), 3310-3313.

138. Hu, N. F.; Li, K.; Wang, Z.; Tang, W. J., Synthesis of Chiral 1,4-Benzodioxanes and Chromans by Enantioselective Palladium-Catalyzed Alkene Aryloxyarylation Reactions. *Angew. Chem.-Int. Edit.* **2016,** *55* (16), 5044-5048.

139. Deng, X.; Ni, S. F.; Han, Z. Y.; Guan, Y. Q.; Lv, H.; Dang, L.; Zhang, X. M., Enantioselective Rhodium-Catalyzed Cycloisomerization of (E)-1,6-Enynes. *Angew. Chem.-Int. Edit.* **2016,** *55* (21), 6295-6299.

140. Liu, C.; Yi, J. C.; Liang, X. W.; Xu, R. Q.; Dai, L. X.; You, S. L., Copper(I)-Catalyzed Asymmetric Dearomatization of Indole Acetamides with 3-Indolylphenyliodonium Salts. *Chem.-Eur. J.* **2016,** *22* (31), 10813-10816.

141. Ganss, S.; Breit, B., Enantioselective Rhodium-Catalyzed Atom-Economical Macrolactonization. *Angew. Chem.-Int. Edit.* **2016,** *55* (33), 9738-9742.

142. Masutomi, K.; Sugiyama, H.; Uekusa, H.; Shibata, Y.; Tanaka, K., Asymmetric Synthesis of Protected Cyclohexenylamines and Cyclohexenols by Rhodium-Catalyzed 2+2+2 Cycloaddition. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15373-15376.

143. Wang, F.; Wang, D. H.; Wan, X. L.; Wu, L. Q.; Chen, P. H.; Liu, G. S., Enantioselective Copper-Catalyzed Intermolecular Cyanotrifluoromethylation of Alkenes via Radical Process. *J. Am. Chem. Soc.* **2016,** *138* (48), 15547-15550.

144. Race, N. J.; Faulkner, A.; Fumagalli, G.; Yamauchi, T.; Scott, J. S.; Ryden-Landergren, M.; Sparkes, H. A.; Bower, J. F., Enantioselective Narasaka-Heck cyclizations: synthesis of tetrasubstituted nitrogen-bearing stereocenters. *Chemical Science* **2017,** *8* (3), 1981-1985.

145. Du, W.; Gu, Q. S.; Li, Y.; Lin, Z. Y.; Yang, D., Enantioselective Palladium-Catalyzed Oxidative Cascade Cyclization of Aliphatic Alkenyl Amides. *Org. Lett.* **2017,** *19* (2), 316-319.

146. Yang, B.; Qiu, Y. A.; Jiang, T.; Wulff, W. D.; Yin, X. P.; Zhu, C.; Backvall, J. E., Enantioselective Palladium-Catalyzed Carbonylative Carbocyclization of Enallenes via Cross-Dehydrogenative Coupling with Terminal Alkynes: Efficient Construction of alpha-Chirality of Ketones. *Angew. Chem.-Int. Edit.* **2017,** *56* (16), 4535-4539.

147. Zhang, W.; Chen, P. H.; Liu, G. S., Enantioselective Palladium(II)-Catalyzed Intramolecular Aminoarylation of Alkenes by Dual N-H and Aryl C-H Bond Cleavage. *Angew. Chem.-Int. Edit.* **2017,** *56* (19), 5336-5340.

148. Liu, R. R.; Wang, Y. G.; Li, Y. L.; Huang, B. B.; Liang, R. X.; Jia, Y. X., Enantioselective Dearomative Difunctionalization of Indoles by Palladium-Catalyzed Heck/Sonogashira Sequence. *Angew. Chem.-Int. Edit.* **2017,** *56* (26), 7475-7478.

149. Medina, J. M.; Moreno, J.; Racine, S.; Du, S. J.; Garg, N. K., Mizoroki-Heck Cyclizations of Amide Derivatives for the Introduction of Quaternary Centers. *Angew. Chem.-Int. Edit.* **2017,** *56* (23), 6567-6571.

150. Yu, S. J.; Wu, C. Z.; Ge, S. Z., Cobalt-Catalyzed Asymmetric Hydroboration/Cyclization of 1,6-Enynes with Pinacolborane. *J. Am. Chem. Soc.* **2017,** *139* (19), 6526-6529.

151. Kossler, D.; Perrin, F. G.; Suleymanov, A. A.; Kiefer, G.; Scopelliti, R.; Severin, K.; Cramer, N., Divergent Asymmetric Synthesis of Polycyclic Compounds via Vinyl Triazenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (38), 11490-11493.

152. Qin, X. R.; Lee, M. W. Y.; Zhou, J. S., Nickel-Catalyzed Asymmetric Reductive Heck Cyclization of Aryl Halides to Afford Indolines. *Angew. Chem.-Int. Edit.* **2017,** *56* (41), 12723-12726.

153. Tong, S.; Limouni, A.; Wang, Q.; Wang, M. X.; Zhu, J. P., Catalytic Enantioselective Double Carbopalladation/C-H Functionalization with Statistical Amplification of Product Enantiopurity: A Convertible Linker Approach. *Angew. Chem.-Int. Edit.* **2017,** *56* (45), 14192-14196.

154. Chen, J. J.; Han, X. L.; Lu, X. Y., Enantioselective Synthesis of Tetrahydropyrano 3,4-b indoles: Palladium(II)-Catalyzed Aminopalladation/1,4-Addition Sequence. *Angew. Chem.-Int. Edit.* **2017,** *56* (46), 14698-14701.

155. Torigoe, T.; Ohmura, T.; Suginome, M., Asymmetric Cycloisomerization of o-Alkenyl-N-Methylanilines to Indolines by Iridium-Catalyzed C(sp(3))-H Addition to Carbon-Carbon Double Bonds. *Angew. Chem.-Int. Edit.* **2017,** *56* (45), 14272-14276.

156. Burrows, L. C.; Jesikiewicz, L. T.; Lu, G.; Geib, S. J.; Liu, P.; Brummond, K. M., Computationally Guided Catalyst Design in the Type I Dynamic Kinetic Asymmetric Pauson-Khand Reaction of Allenyl Acetates. *J. Am. Chem. Soc.* **2017,** *139* (42), 15022-15032.

157. Luo, H. W.; Yang, Z.; Lin, W. L.; Zheng, Y. G. Y.; Ma, S. M., A catalytic highly enantioselective allene approach to oxazolines. *Chemical Science* **2018,** *9* (7), 1964-1969.

158. Wang, S. G.; Park, S. H.; Cramer, N., A Readily Accessible Class of Chiral Cp Ligands and their Application in Ru-II-Catalyzed Enantioselective Syntheses of Dihydrobenzoindoles. *Angew. Chem.-Int. Edit.* **2018,** *57* (19), 5459-5462.

159. Diesel, J.; Finogenova, A. M.; Cramer, N., Nickel-Catalyzed Enantioselective Pyridone C-H Functionalizations Enabled by a Bulky N-Heterocyclic Carbene Ligand. *J. Am. Chem. Soc.* **2018,** *140* (13), 4489-4493.

160. Wang, Y. X.; Qi, S. L.; Luan, Y. X.; Han, X. W.; Wang, S.; Chen, H.; Ye, M. C., Enantioselective Ni-Al Bimetallic Catalyzed exo-Selective C-H Cyclization of Imidazoles with Alkenes. *J. Am. Chem. Soc.* **2018,** *140* (16), 5360-5364.

161. Li, K.; Li, M. L.; Zhang, Q.; Zhu, S. F.; Zhou, Q. L., Highly Enantioselective Nickel-Catalyzed Intramolecular Hydroalkenylation of N- and O-Tethered 1,6-Dienes To Form Six-Membered Heterocycles. *J. Am. Chem. Soc.* **2018,** *140* (24), 7458-7461.

162. Kou, X. Z.; Shao, Q. H.; Ye, C. H.; Yang, G. Q.; Zhang, W. B., Asymmetric Aza-Wacker-Type Cyclization of N-Ts Hydrazine-Tethered Tetrasubstituted Olefins: Synthesis of Pyrazolines Bearing One Quaternary or Two Vicinal Stereocenters. *J. Am. Chem. Soc.* **2018,** *140* (24), 7587-7597.

163. Xue, F.; Hayashi, T., Asymmetric Synthesis of Axially Chiral 2-Aminobiaryls by Rhodium-Catalyzed Benzannulation of 1-Arylalkynes with 2-(Cyanomethyl)phenylboronates. *Angew. Chem.-Int. Edit.* **2018,** *57* (32), 10368-10372.

164. Karyakarte, S. D.; Um, C.; Berhane, I. A.; Chemler, S. R., Synthesis of Spirocyclic Ethers by Enantioselective Copper-Catalyzed Carboetherification of Alkenols. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12921-12924.

165. Shen, B.; Wan, B.; Li, X., Enantiodivergent Desymmetrization in the Rhodium(III)-Catalyzed Annulation of Sulfoximines with Diazo Compounds. *Angewandte Chemie International Edition* **2018,** *57* (47), 15534-15538.

166. Li, X.; Zhou, B.; Yang, R. Z.; Yang, F. M.; Liang, R. X.; Liu, R. R.; Jia, Y. X., Palladium-Catalyzed Enantioselective Intramolecular Dearomative Heck Reaction. *J. Am. Chem. Soc.* **2018,** *140* (42), 13945-13951.

167. Zheng, H. F.; Wang, Y.; Xu, C. R.; Xiong, Q.; Lin, L. L.; Feng, X. M., Diversified Cycloisomerization/Diels-Alder Reactions of 1,6-Enynes through Bimetallic Relay Asymmetric Catalysis. *Angew. Chem.-Int. Edit.* **2019,** *58* (16), 5327-5331.

168. Diesel, J.; Grosheva, D.; Kodama, S.; Cramer, N., A Bulky Chiral N-Heterocyclic Carbene Nickel Catalyst Enables Enantioselective C-H Functionalizations of Indoles and Pyrroles. *Angew. Chem.-Int. Edit.* **2019,** *58* (32), 11044-11048.

169. Zhang, Z. M.; Xu, B.; Wu, L. Z.; Zhou, L. J.; Ji, D. T.; Liu, Y.; Li, Z. M.; Zhang, J. L., Palladium/XuPhos-Catalyzed Enantioselective Carboiodination of Olefin-Tethered Aryl Iodides. *J. Am. Chem. Soc.* **2019,** *141* (20), 8110-8115.

170. Tian, M. M.; Bai, D. C.; Zheng, G. F.; Chang, J. B.; Li, X. W., Rh(III)-Catalyzed Asymmetric Synthesis of Axially Chiral Biindolyls by Merging C-H Activation and Nucleophilic Cyclization. *J. Am. Chem. Soc.* **2019,** *141* (24), 9527-9532.

171. Deng, L.; Fu, Y.; Lee, S. Y.; Wang, C. P.; Liu, P.; Dong, G. B., Kinetic Resolution via Rh-Catalyzed C-C Activation of Cyclobutanones at Room Temperature. *J. Am. Chem. Soc.* **2019,** *141* (41), 16260-16265.

172. Vidal, X.; Mascarenas, J. L.; Gulias, M., Palladium-Catalyzed, Enantioselective Formal Cycloaddition between Benzyltriflamides and Allenes: Straightforward Access to Enantioenriched Isoquinolines. *J. Am. Chem. Soc.* **2019,** *141* (5), 1862-1866.

173. Zhu, R. Y.; Chen, L.; Hu, X. S.; Zhou, F.; Zhou, J., Enantioselective synthesis of P-chiral tertiary phosphine oxides with an ethynyl group via Cu(i)-catalyzed azide-alkyne cycloaddition. *Chemical Science* **2020,** *11* (1), 97-106.

174. He, Y.-P.; Wu, H.; Wang, Q.; Zhu, J., Palladium-Catalyzed Enantioselective Cacchi Reaction: Asymmetric Synthesis of Axially Chiral 2,3-Disubstituted Indoles. *Angewandte Chemie International Edition* **2020,** *59* (5), 2105-2109.

175. Kinoshita, S.; Yamano, R.; Shibata, Y.; Tanaka, Y.; Hanada, K.; Matsumoto, T.; Miyamoto, K.; Muranaka, A.; Uchiyama, M.; Tanaka, K., Rhodium-Catalyzed Highly Diastereo- and Enantioselective Synthesis of a Configurationally Stable S-Shaped Double Helicene-Like Molecule. *Angewandte Chemie International Edition* **2020,** *59* (27), 11020-11027.

176. Wdowik, T.; Galster, S. L.; Carmo, R. L. L.; Chemler, S. R., Enantioselective, Aerobic Copper-Catalyzed Intramolecular Carboamination and Carboetherification of Unactivated Alkenes. *ACS Catalysis* **2020,** *10* (15), 8535-8541.

177. Yamano, M. M.; Kelleghan, A. V.; Shao, Q.; Giroud, M.; Simmons, B. J.; Li, B.; Chen, S.; Houk, K. N.; Garg, N. K., Intercepting fleeting cyclic allenes with asymmetric nickel catalysis. *Nature* **2020,** *586* (7828), 242-247.

178. Wu, X.; Qu, J.; Chen, Y., Quinim: A New Ligand Scaffold Enables Nickel-Catalyzed Enantioselective Synthesis of α-Alkylated γ-Lactam. *J. Am. Chem. Soc.* **2020,** *142* (37), 15654-15660.

179. Braconi, E.; Götzinger, A. C.; Cramer, N., Enantioselective Iron-Catalyzed Cross-[4+4]-Cycloaddition of 1,3-Dienes Provides Chiral Cyclooctadienes. *J. Am. Chem. Soc.* **2020,** *142* (47), 19819-19824.

180. Liang, R.-X.; Song, L.-J.; Lu, J.-B.; Xu, W.-Y.; Ding, C.; Jia, Y.-X., Palladium-Catalyzed Enantioselective Heteroarenyne Cycloisomerization Reaction. *Angewandte Chemie International Edition* **2021,** *60* (13), 7412-7417.

181. Da Concepción, E.; Fernández, I.; Mascareñas, J. L.; López, F., Highly Enantioselective Cobalt-Catalyzed (3+2) Cycloadditions of Alkynylidenecyclopropanes. *Angewandte Chemie International Edition* **2021,** *60* (15), 8182-8188.

182. González, J. M.; Cendón, B.; Mascareñas, J. L.; Gulías, M., Kinetic Resolution of Allyltriflamides through a Pd-Catalyzed C–H Functionalization with Allenes: Asymmetric Assembly of Tetrahydropyridines. *J. Am. Chem. Soc.* **2021,** *143* (10), 3747-3752.

183. Chen, X.-W.; Yue, J.-P.; Wang, K.; Gui, Y.-Y.; Niu, Y.-N.; Liu, J.; Ran, C.-K.; Kong, W.; Zhou, W.-J.; Yu, D.-G., Nickel-Catalyzed Asymmetric Reductive Carbo-Carboxylation of Alkenes with CO2. *Angewandte Chemie International Edition* **2021,** *60* (25), 14068-14075.

184. Liu, E.-C.; Topczewski, J. J., Enantioselective Nickel-Catalyzed Alkyne–Azide Cycloaddition by Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2021,** *143* (14), 5308-5313.

185. Dherbassy, Q.; Manna, S.; Shi, C.; Prasitwatcharakorn, W.; Crisenza, G. E. M.; Perry, G. J. P.; Procter, D. J., Enantioselective Copper-Catalyzed Borylative Cyclization for the Synthesis of Quinazolinones. *Angewandte Chemie International Edition* **2021,** *60* (26), 14355-14359.

186. Arribas, A.; Calvelo, M.; Fernández, D. F.; Rodrigues, C. A. B.; Mascareñas, J. L.; López, F., Highly Enantioselective Iridium(I)-Catalyzed Hydrocarbonation of Alkenes: A Versatile Approach to Heterocyclic Systems Bearing Quaternary Stereocenters. *Angewandte Chemie International Edition* **2021,** *60* (35), 19297-19305.

187. Hu, P.; Kong, L.; Wang, F.; Zhu, X.; Li, X., Twofold C−H Activation-Based Enantio- and Diastereoselective C−H Arylation Using Diarylacetylenes as Rare Arylating Reagents. *Angewandte Chemie International Edition* **2021,** *60* (37), 20424-20429.

188. Pan, Q.; Ping, Y.; Wang, Y.; Guo, Y.; Kong, W., Ni-Catalyzed Ligand-Controlled Regiodivergent Reductive Dicarbofunctionalization of Alkenes. *J. Am. Chem. Soc.* **2021,** *143* (27), 10282-10291.

189. Li, K.; Wei, L.; Sun, M.; Li, B.; Liu, M.; Li, C., Enantioselective Synthesis of Pyridines with All-Carbon Quaternary Carbon Centers via Cobalt-Catalyzed Desymmetric [2+2+2] Cycloaddition. *Angewandte Chemie International Edition* **2021,** *60* (37), 20204-20209.

190. Whyte, A.; Bajohr, J.; Arora, R.; Torelli, A.; Lautens, M., Sequential Pd0- and PdII-Catalyzed Cyclizations: Enantioselective Heck and Nucleopalladation Reactions. *Angewandte Chemie International Edition* **2021,** *60* (37), 20231-20236.

191. Li, Y.-L.; Zhang, P.-C.; Wu, H.-H.; Zhang, J., Palladium-Catalyzed Asymmetric Tandem Denitrogenative Heck/Tsuji–Trost of Benzotriazoles with 1,3-Dienes. *J. Am. Chem. Soc.* **2021,** *143* (33), 13010-13015.

192. Chen, X.-M.; Zhu, L.; Chen, D.-F.; Gong, L.-Z., Chiral Indoline-2-carboxylic Acid Enables Highly Enantioselective Catellani-type Annulation with 4-(Bromomethyl)cyclohexanone. *Angewandte Chemie International Edition* **2021,** *60* (47), 24844-24848.

193. Zhou, H.-Q.; Gu, X.-W.; Zhou, X.-H.; Li, L.; Ye, F.; Yin, G.-W.; Xu, Z.; Xu, L.-W., Enantioselective palladium-catalyzed C(sp2)–C(sp2) σ bond activation of cyclopropenones by merging desymmetrization and (3 + 2) spiroannulation with cyclic 1,3-diketones. *Chemical Science* **2021,** *12* (41), 13737-13743.

194. Zu, B.; Guo, Y.; He, C., Catalytic Enantioselective Construction of Chiroptical Boron-Stereogenic Compounds. *J. Am. Chem. Soc.* **2021,** *143* (39), 16302-16310.

195. Braconi, E.; Cramer, N., Crossed Regio- and Enantioselective Iron-Catalyzed [4+2]-Cycloadditions of Unactivated Dienes. *Angewandte Chemie International Edition* **2022,** *61* (7), e202112148.

196. Zhao, T.-Y.; Xiao, L.-J.; Zhou, Q.-L., Nickel-Catalyzed Desymmetric Reductive Cyclization/Coupling of 1,6-Dienes: An Enantioselective Approach to Chiral Tertiary Alcohol. *Angewandte Chemie International Edition* **2022,** *61* (11), e202115702.

197. Guo, W.-T.; Zhu, B.-H.; Chen, Y.; Yang, J.; Qian, P.-C.; Deng, C.; Ye, L.-W.; Li, L., Enantioselective Rh-Catalyzed Azide-Internal-Alkyne Cycloaddition for the Construction of Axially Chiral 1,2,3-Triazoles. *J. Am. Chem. Soc.* **2022,** *144* (15), 6981-6991.

198. Zhang, X.; Li, S.; Yu, W.; Xie, Y.; Tung, C.-H.; Xu, Z., Asymmetric Azide–Alkyne Cycloaddition with Ir(I)/Squaramide Cooperative Catalysis: Atroposelective Synthesis of Axially Chiral Aryltriazoles. *J. Am. Chem. Soc.* **2022,** *144* (14), 6200-6207.

199. Zeng, L.; Li, J.; Cui, S., Rhodium-Catalyzed Atroposelective Click Cycloaddition of Azides and Alkynes. *Angewandte Chemie International Edition* **2022,** *61* (28), e202205037.

200. Sokolova, O. O.; Bower, J. F., An endo-Directing-Group Strategy Unlocks Enantioselective (3+1+2) Carbonylative Cycloadditions of Aminocyclopropanes. *Angewandte Chemie International Edition* **2022,** *61* (32), e202205007.

201. Jia, X.-G.; Yao, Q.-W.; Shu, X.-Z., Enantioselective Reductive N-Cyclization–Alkylation Reaction of Alkene-Tethered Oxime Esters and Alkyl Iodides by Nickel Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (30), 13461-13467.

202. Han, Y.; Qin, A.; Zhang, Q.; Zhang, X.; Qian, H.; Ma, S., Rhodium-Catalyzed Dynamic Kinetic [4+2] Cycloaddition of Allene-1,3-Dienes. *Angewandte Chemie International Edition* **2022,** *61* (47), e202211635.

203. Wang, K.; Chen, J.; Liu, W.; Kong, W., Nickel-Catalyzed Defluorinative Asymmetric Cyclization of Fluoroalkyl-Substituted 1,6-Enynes for the Synthesis of Seletracetam. *Angewandte Chemie International Edition* **2022,** *61* (46), e202212664.

204. Ni, S.; Vaillant, F. L.; Mateos-Calbet, A.; Martin, R.; Cornella, J., Ni-Catalyzed Oxygen Transfer from N2O onto sp3-Hybridized Carbons. *J. Am. Chem. Soc.* **2022,** *144* (40), 18223-18228.

205. Dong, J.; Ostertag, A.; Sparr, C., o-Quinodimethane Atropisomers: Enantioselective Synthesis and Stereospecific Transformation. *Angewandte Chemie International Edition* **2022,** *61* (50), e202212627.

206. Zeng, Y.; Fang, X.-J.; Tang, R.-H.; Xie, J.-Y.; Zhang, F.-J.; Xu, Z.; Nie, Y.-X.; Xu, L.-W., Rhodium-Catalyzed Dynamic Kinetic Asymmetric Hydrosilylation to Access Silicon-Stereogenic Center. *Angewandte Chemie International Edition* **2022,** *61* (51), e202214147.

207. Chintawar, C. C.; Bhoyare, V. W.; Mane, M. V.; Patil, N. T., Enantioselective Au(I)/Au(III) Redox Catalysis Enabled by Chiral (P,N)-Ligands. *J. Am. Chem. Soc.* **2022,** *144* (16), 7089-7095.

208. Qi, L.; Dong, M.; Qian, J.; Yu, S.; Tong, X., Pd0-Catalyzed Asymmetric Carbonitratation Reaction Featuring an H-Bonding-Driven Alkyl−PdII−ONO2 Reductive Elimination. *Angewandte Chemie International Edition* **2023,** *62* (3), e202215397.

209. Singh, D.; RajanBabu, T. V., Chemodivergent, Regio- and Enantioselective Cycloaddition Reactions between 1,3-Dienes and Alkynes. *Angewandte Chemie International Edition* **2023,** *62* (8), e202216000.

210. Dong, M.; Qi, L.; Qian, J.; Yu, S.; Tong, X., Pd(0)-Catalyzed Asymmetric 7-Endo Hydroacyloxylative Cyclization of 1,6-Enyne Enabled by an Anion Ligand-Directed Strategy. *J. Am. Chem. Soc.* **2023,** *145* (3), 1973-1981.

211. Shimotsukue, R.; Fujii, K.; Sato, Y.; Nagashima, Y.; Tanaka, K., Rhodium-Catalyzed Chemo-, Regio-, Diastereo-, and Enantioselective Intermolecular [2+2+2] Cycloaddition of Three Unsymmetric 2π Components. *Angewandte Chemie International Edition* **2023,** *62* (16), e202301346.

212. Ma, Z.; Sun, L.; Zhou, J. S., Catalytic enantioselective alkenylation–heteroarylation of olefins: stereoselective syntheses of 5–7 membered azacycles and oxacycles. *Chemical Science* **2023,** *14* (11), 3010-3017.

213. Gong, Y.; Wang, C.; Zhou, F.; Liao, K.; Wang, X.-Y.; Sun, Y.; Zhang, Y.-X.; Tu, Z.; Wang, X.; Zhou, J., Sulfonyl-PYBOX Ligands Enable Kinetic Resolution of α-Tertiary Azides by CuAAC. *Angewandte Chemie International Edition* **2023,** *62* (18), e202301470.

214. Drennhaus, T.; Leifert, D.; Lammert, J.; Drennhaus, J. P.; Bergander, K.; Daniliuc, C. G.; Studer, A., Enantioselective Copper-Catalyzed Fukuyama Indole Synthesis from 2-Vinylphenyl Isocyanides. *J. Am. Chem. Soc.* **2023,** *145* (15), 8665-8676.

215. Li, Q.; Li, J.; Zhang, J.; Wu, S.; Zhang, Y.; Lin, A.; Yao, H., Enantioselective Synthesis of Bicyclo[3.2.1]octadienes via Palladium-Catalyzed Intramolecular Alkene-Alkyne Coupling Reaction. *Angewandte Chemie International Edition* **2023,** *62* (51), e202313404.

216. Wang, L.; Wang, Y.; Wu, S.; Yan, C.-G.; Zhang, C.; Zhang, J.; Han, Y., Enantioselective Synthesis of Isoindolinone by Palladium-Catalyzed Aminoalkynylation of O-Phenyl Hydroxamic Ethers with Alkynes. *J. Am. Chem. Soc.* **2024,** *146* (7), 4320-4326.

217. Cao, K.; Han, J.; Shen, H.; Yang, J.; Zhang, J.; Chen, F., Pd-Catalyzed Asymmetric Aza-Heck Cyclization/Sonogashira Reaction of Alkene-Tethered Oxime Esters and Alkynes. *ACS Catalysis* **2024,** *14* (7), 5305-5313.

218. Zhan, X.; Nie, Z.; Li, N.; Zhou, A.; Lv, H.; Liang, M.; Wu, K.; Cheng, G.-J.; Yin, Q., Catalytic Asymmetric Cascade Dearomatization of Indoles via a Photoinduced Pd-Catalyzed 1,2-Bisfunctionalization of Butadienes. *Angewandte Chemie International Edition* **2024,** *63* (26), e202404388.

219. Yang, X.; Chen, P.; Liu, G., Asymmetric 1,n-Remote Aminoacetoxylation of Unactivated Internal Alkenes Enabled by Palladium Catalysis. *Angewandte Chemie International Edition* **2024,** *63* (35), e202408305.

220. Zhang, M.; Chapman, M.; Sarode, B. R.; Xiong, B.; Liang, H.; Chen, J. K.; Weerapana, E.; Morken, J. P., Catalytic asymmetric synthesis of meta benzene isosteres. *Nature* **2024,** *633* (8028), 90-95.

221. Laohapaisan, P.; Roy, I.; Nagib, D. A., Chiral pyrrolidines via an enantioselective Hofmann-Löffler-Freytag reaction. *Chem Catalysis* **2024,** *4* (12), 101149.

222. Ju, D.; Kang, J.; Song, Z., Enantioselective Intramolecular Oxidative Aminoacetoxylation from Aryl-Substituted Alkene via Chiral Triazole-oxazoline Palladium Complexes. *Org. Lett.* **2024,** *26* (45), 9637-9642.

4.6.4 Cross-Coupling Reactions

1. Sato, Y.; Nukui, S.; Sodeoka, M.; Shibasaki, M., ASYMMETRIC HECK REACTION OF ALKENYL IODIDES IN THE PRESENCE OF SLIVER SALTS - CATALYTIC ASYMMETRIC-SYNTHESIS OF DECALIN AND FUNCTIONALIZED INDOLIZIDINE DERIVATIVES. *Tetrahedron* **1994,** *50* (2), 371-382.

2. Ashimori, A.; Bachand, B.; Overman, L. E.; Poon, D. J., Catalytic asymmetric synthesis of quaternary carbon centers. Exploratory investigations of intramolecular Heck reactions of (E)-alpha,beta-Unsaturated 2-haloanilides and analogues to form enantioenriched spirocyclic products. *J. Am. Chem. Soc.* **1998,** *120* (26), 6477-6487.

3. Ashimori, A.; Bachand, B.; Calter, M. A.; Govek, S. P.; Overman, L. E.; Poon, D. J., Catalytic asymmetric synthesis of quaternary carbon centers. Exploratory studies of intramolecular Heck reactions of (Z)-alpha,beta-unsaturated anilides and mechanistic investigations of asymmetric Heck reactions proceeding via neutral intermediates. *J. Am. Chem. Soc.* **1998,** *120* (26), 6488-6499.

4. Matsuura, T.; Overman, L. E.; Poon, D. J., Catalytic asymmetric synthesis of either enantiomer of the Calabar alkaloids physostigmine and physovenine. *J. Am. Chem. Soc.* **1998,** *120* (26), 6500-6503.

5. Shimada, T.; Cho, Y. H.; Hayashi, T., Nickel-catalyzed asymmetric Grignard cross-coupling of dinaphthothiophene giving axially chiral 1,1 '-binaphthyls. *J. Am. Chem. Soc.* **2002,** *124* (45), 13396-13397.

6. Spielvogel, D. J.; Buchwald, S. L., Nickel-BINAP catalyzed enantioselective alpha-arylation of alpha-substituted gamma-butyrolactones. *J. Am. Chem. Soc.* **2002,** *124* (14), 3500-3501.

7. Hamada, T.; Chieffi, A.; Ahman, J.; Buchwald, S. L., An improved catalyst for the asymmetric arylation of ketone enolates. *J. Am. Chem. Soc.* **2002,** *124* (7), 1261-1268.

8. Moncarz, J. R.; Laritcheva, N. F.; Glueck, D. S., Palladium-catalyzed asymmetric phosphination: Enantioselective synthesis of a P-chirogenic phosphine. *J. Am. Chem. Soc.* **2002,** *124* (45), 13356-13357.

9. Barhate, N. B.; Chen, C. T., Catalytic asymmetric oxidative couplings of 2-naphthols by tridentate N-ketopinidene-based vanadyl dicarboxylates. *Org. Lett.* **2002,** *4* (15), 2529-2532.

10. Dounay, A. B.; Hatanaka, K.; Kodanko, J. J.; Oestreich, M.; Overman, L. E.; Pfeifer, L. A.; Weiss, M. M., Catalytic asymmetric synthesis of quaternary carbons bearing two aryl substituents. Enantioselective synthesis of 3-alkyl-3- aryl oxindoles by catalytic asymmetric intramolecular Heck reactions. *J. Am. Chem. Soc.* **2003,** *125* (20), 6261-6271.

11. Nilsson, P.; Larhed, M.; Hallberg, A., A new highly asymmetric chelation-controlled heck arylation. *J. Am. Chem. Soc.* **2003,** *125* (12), 3430-3431.

12. Willis, M. C.; Powell, L. H. W.; Claverie, C. K.; Watson, S. J., Enantioselective Suzuki reactions: Catalytic asymmetric synthesis of compounds containing quaternary carbon centers. *Angew. Chem.-Int. Edit.* **2004,** *43* (10), 1249-1251.

13. Lautens, M.; Hiebert, S., Scope of palladium-catalyzed alkylative ring opening. *J. Am. Chem. Soc.* **2004,** *126* (5), 1437-1447.

14. Cabrera, S.; Arrayas, R. G.; Carretero, J. C., Cationic planar chiral palladium PS complexes as highly efficient catalysts in the enantioselective ring opening of oxa- and azabicyclic alkenes. *Angew. Chem.-Int. Edit.* **2004,** *43* (30), 3944-3947.

15. Arp, F. O.; Fu, G. C., Catalytic enantioselective Negishi reactions of racemic secondary benzylic halides. *J. Am. Chem. Soc.* **2005,** *127* (30), 10482-10483.

16. Fischer, C.; Fu, G. C., Asymmetric nickel-catalyzed negishi cross-couplings of secondary alpha-bromo amides with organozinc reagents. *J. Am. Chem. Soc.* **2005,** *127* (13), 4594-4595.

17. Kitagawa, O.; Takahashi, M.; Yoshikawa, M.; Taguchi, T., Efficient synthesis of optically active atropisomeric anilides through catalytic asymmetric N-arylation reaction. *J. Am. Chem. Soc.* **2005,** *127* (11), 3676-3677.

18. Oestreich, M.; Sempere-Culler, F.; Machotta, A. B., Catalytic desymmetrizing intramolecular Heck reaction: Evidence for an unusual hydroxy-directed migratory insertion. *Angew. Chem.-Int. Edit.* **2005,** *44* (1), 149-152.

19. Cabrera, S.; Arrayas, R. G.; Alonso, I.; Carretero, J. C., Fesulphos-palladium(II) complexes as well-defined catalysts for enantioselective ring opening of meso heterobicyclic alkenes with organozinc reagents. *J. Am. Chem. Soc.* **2005,** *127* (50), 17938-17947.

20. Kirsch, S. F.; Overman, L. E., Catalytic asymmetric intramolecular aminopalladation: Improved palladium(II) catalysts. *J. Org. Chem.* **2005,** *70* (7), 2859-2861.

21. Scriban, C.; Glueck, D. S., Platinum-catalyzed asymmetric alkylation of secondary phosphines: Enantioselective synthesis of P-stereogenic phosphines. *J. Am. Chem. Soc.* **2006,** *128* (9), 2788-2789.

22. Xie, X. A.; Chen, Y.; Ma, D. W., Enantioselective arylation of 2-methylacetoacetates catalyzed by CuI/trans-4-hydroxy-L-proline at low reaction temperatures. *J. Am. Chem. Soc.* **2006,** *128* (50), 16050-16051.

23. Mohr, J. T.; Nishimata, T.; Behenna, D. C.; Stoltz, B. M., Catalytic enantioselective decarboxylative protonation. *J. Am. Chem. Soc.* **2006,** *128* (35), 11348-11349.

24. Yoo, K. S.; Park, C. P.; Yoon, C. H.; Sakaguchi, S.; O'Neill, J.; Jung, K. W., Asymmetric intermolecular Heck-type reaction of acyclic alkenes via oxidative palladium(II) catalysis. *Org. Lett.* **2007,** *9* (20), 3933-3935.

25. Phapale, V. B.; Bunuel, E.; Garcia-Iglesias, M.; Cardenas, D. J., Ni-catalyzed cascade formation of C(sp(3))-C(sp(3)) bonds by cyclization and cross-coupling reactions of iodoalkanes with alkyl zinc halides. *Angew. Chem.-Int. Edit.* **2007,** *46* (46), 8790-8795.

26. Machotta, A. B.; Straub, B. F.; Oestreich, M., Oxygen donor-mediated equilibration of diastereomeric alkene-Palladium(II) intermediates in enantioselective desymmetrizing heck cyclizations. *J. Am. Chem. Soc.* **2007,** *129* (44), 13455-13463.

27. Kundig, E. P.; Seidel, T. M.; Jia, Y. X.; Bernardinelli, G., Bulky chiral carbene ligands and their application in the palladium-catalyzed asymmetric intramolecular alpha-arylation of amides. *Angew. Chem.-Int. Edit.* **2007,** *46* (44), 8484-8487.

28. Chan, V. S.; Bergman, R. G.; Toste, F. D., Pd-catalyzed dynamic kinetic enantioselective arylation of silylphosphines. *J. Am. Chem. Soc.* **2007,** *129* (49), 15122-+.

29. Liao, X. B.; Weng, Z. Q.; Hartwig, J. F., Enantioselective alpha-arylation of ketones with aryl triflates catalyzed by difluorphos complexes of palladium and nickel. *J. Am. Chem. Soc.* **2008,** *130* (1), 195-200.

30. Son, S.; Fu, G. C., Nickel-catalyzed asymmetric Negishi cross-couplings of secondary allylic chlorides with alkylzincs. *J. Am. Chem. Soc.* **2008,** *130* (9), 2756-+.

31. Dai, X.; Strotman, N. A.; Fu, G. C., Catalytic asymmetric Hiyama cross-couplings of racemic alpha-bromo esters. *J. Am. Chem. Soc.* **2008,** *130* (11), 3302-+.

32. Saito, B.; Fu, G. C., Enantioselective alkyl-alkyl suzuki cross-couplings of unactivated homobenzylic halides. *J. Am. Chem. Soc.* **2008,** *130* (21), 6694-+.

33. Wu, W. Q.; Peng, Q.; Dong, D. X.; Hou, X. L.; Wu, Y. D., A dramatic switch of enantioselectivity in asymmetric Heck reaction by benzylic substituents of ligands. *J. Am. Chem. Soc.* **2008,** *130* (30), 9717-9725.

34. Henriksen, S. T.; Norrby, P. O.; Kaukoranta, P.; Andersson, P. G., Combined experimental and theoretical study of the mechanism and enantioselectivity of palladium-catalyzed intermolecular Heck coupling. *J. Am. Chem. Soc.* **2008,** *130* (31), 10414-10421.

35. Jia, Y. X.; Hillgren, J. M.; Watson, E. L.; Marsden, S. P.; Kundig, E. P., Chiral N-heterocyclic carbene ligands for asymmetric catalytic oxindole synthesis. *Chem. Commun.* **2008,** (34), 4040-4042.

36. Ito, H.; Kosaka, Y.; Nonoyama, K.; Sasaki, Y.; Sawamura, M., Synthesis of optically active boron-silicon bifunctional cyclopropane derivatives through enantioselective copper(I)-catalyzed reaction of allylic carbonates with a diboron derivative. *Angew. Chem.-Int. Edit.* **2008,** *47* (39), 7424-7427.

37. Smith, S. W.; Fu, G. C., Nickel-catalyzed asymmetric cross-couplings of racemic propargylic halides with arylzinc reagents. *J. Am. Chem. Soc.* **2008,** *130* (38), 12645-+.

38. Garcia-Fortanet, J.; Buchwald, S. L., Asymmetric Palladium-Catalyzed Intramolecular alpha-Arylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2008,** *47* (42), 8108-8111.

39. Bermejo, A.; Ros, A.; Fernandez, R.; Lassaletta, J. M., C-2-Symmetric Bis-Hydrazones as Ligands in the Asymmetric Suzuki-Miyaura Cross-Coupling. *J. Am. Chem. Soc.* **2008,** *130* (47), 15798-+.

40. Rubina, M.; Sherrill, W. M.; Rubin, M., Dramatic Stereo- and Enantiodivergency in the Intermolecular Asymmetric Heck Reaction Catalyzed by Palladium Complexes with Cyclopropane-Based PHOX Ligands. *Organometallics* **2008,** *27* (24), 6393-6395.

41. Luan, X. J.; Mariz, R.; Robert, C.; Gatti, M.; Blumentritt, S.; Linden, A.; Dorta, R., Matching the Chirality of Monodentate N-Heterocyclic Carbene Ligands: A Case Study on Well-Defined Palladium Complexes for the Asymmetric alpha-Arylation of Amides. *Org. Lett.* **2008,** *10* (24), 5569-5572.

42. Lundin, P. M.; Esquivias, J.; Fu, G. C., Catalytic Asymmetric Cross-Couplings of Racemic alpha-Bromoketones with Arylzinc Reagents. *Angew. Chem.-Int. Edit.* **2009,** *48* (1), 154-156.

43. Winter, C.; Krause, N., Rhodium(I)-Catalyzed Enantioselective C-C Bond Activation. *Angew. Chem.-Int. Edit.* **2009,** *48* (14), 2460-2462.

44. Takenaka, K.; Itoh, N.; Sasai, H., Enantioselective Synthesis of C-2-Symmetric Spirobilactams via Pd-Catalyzed Intramolecular Double N-Arylation. *Org. Lett.* **2009,** *11* (7), 1483-1486.

45. Uozumi, Y.; Matsuura, Y.; Arakawa, T.; Yamada, Y. M. A., Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Palladium Catalyst Supported on an Amphiphilic Resin. *Angew. Chem.-Int. Edit.* **2009,** *48* (15), 2708-2710.

46. Kawamura, Y.; Kawano, Y.; Matsuda, T.; Ishitobi, Y.; Hosokawa, T., Palladium(II)-Catalyzed Asymmetric Coupling of Allylic Alcohols and Vinyl Ethers: Insight into the Palladium and Copper Bimetallic Catalyst. *J. Org. Chem.* **2009,** *74* (8), 3048-3053.

47. Chan, V. S.; Chiu, M.; Bergman, R. G.; Toste, F. D., Development of Ruthenium Catalysts for the Enantioselective Synthesis of P-Stereogenic Phosphines via Nucleophilic Phosphido Intermediates. *J. Am. Chem. Soc.* **2009,** *131* (16), 6021-6032.

48. Porosa, L.; Viirre, R. D., Desymmetrization of malonamides via an enantioselective intramolecular Buchwald-Hartwig reaction. *Tetrahedron Lett.* **2009,** *50* (28), 4170-4173.

49. Wurtz, S.; Lohre, C.; Frohlich, R.; Bergander, K.; Glorius, F., IBiox[(-)-menthyl]: A Sterically Demanding Chiral NHC Ligand. *J. Am. Chem. Soc.* **2009,** *131* (24), 8344-+.

50. Lessard, S.; Peng, F.; Hall, D. G., alpha-Hydroxyalkyl Heterocycles via Chiral Allylic Boronates: Pd-Catalyzed Borylation Leading to a Formal Enantioselective lsomerization of Allylic Ether and Amine. *J. Am. Chem. Soc.* **2009,** *131* (28), 9612-9613.

51. Taylor, A. M.; Altman, R. A.; Buchwald, S. L., Palladium-Catalyzed Enantioselective alpha-Arylation and alpha-Vinylation of Oxindoles Facilitated by an Axially Chiral P-Stereogenic Ligand. *J. Am. Chem. Soc.* **2009,** *131* (29), 9900-+.

52. Albicker, M. R.; Cramer, N., Enantioselective Palladium-Catalyzed Direct Arylations at Ambient Temperature: Access to Indanes with Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2009,** *48* (48), 9139-9142.

53. Schiffner, J. A.; Woste, T. H.; Oestreich, M., Enantioselective Fujiwara-Moritani Indole and Pyrrole Annulations Catalyzed by Chiral Palladium(II)-NicOx Complexes. *Eur. J. Org. Chem.* **2010,** (1), 174-182.

54. Yoo, K. S.; O'Neill, J.; Sakaguchi, S.; Giles, R.; Lee, J. H.; Jung, K. W., Asymmetric Intermolecular Boron Heck-Type Reactions via Oxidative Palladium(II) Catalysis with Chiral Tridentate NHC-Amidate-Alkoxide Ligands. *J. Org. Chem.* **2010,** *75* (1), 95-101.

55. Lou, S.; Fu, G. C., Nickel/Bis(oxazoline)-Catalyzed Asymmetric Kumada Reactions of Alkyl Electrophiles: Cross-Couplings of Racemic alpha-Bromoketones. *J. Am. Chem. Soc.* **2010,** *132* (4), 1264-+.

56. Lou, S.; Fu, G. C., Enantioselective Alkenylation via Nickel-Catalyzed Cross-Coupling with Organozirconium Reagents. *J. Am. Chem. Soc.* **2010,** *132* (14), 5010-+.

57. Luan, X. J.; Wu, L. L.; Drinkel, E.; Mariz, R.; Gatti, M.; Dorta, R., Highly Chemo- and Enantioselective Synthesis of 3-Allyl-3-aryl Oxindoles via the Direct Palladium-Catalyzed alpha-Arylation of Amides. *Org. Lett.* **2010,** *12* (9), 1912-1915.

58. Jia, Y. X.; Katayev, D.; Bernardinelli, G.; Seidel, T. M.; Kundig, E. P., New Chiral N-Heterocyclic Carbene Ligands in Palladium-Catalyzed alpha-Arylations of Amides: Conformational Locking through Allylic Strain as a Device for Stereocontrol. *Chem.-Eur. J.* **2010,** *16* (21), 6300-6309.

59. Shen, X. Q.; Jones, G. O.; Watson, D. A.; Bhayana, B.; Buchwald, S. L., Enantioselective Synthesis of Axially Chiral Biaryls by the Pd-Catalyzed Suzuki Miyaura Reaction: Substrate Scope and Quantum Mechanical Investigations. *J. Am. Chem. Soc.* **2010,** *132* (32), 11278-11287.

60. Lundin, P. M.; Fu, G. C., Asymmetric Suzuki Cross-Couplings of Activated Secondary Alkyl Electrophiles: Arylations of Racemic alpha-Chloroamides. *J. Am. Chem. Soc.* **2010,** *132* (32), 11027-11029.

61. Owston, N. A.; Fu, G. C., Asymmetric Alkyl-Alkyl Cross-Couplings of Unactivated Secondary Alkyl Electrophiles: Stereoconvergent Suzuki Reactions of Racemic Acylated Halohydrins. *J. Am. Chem. Soc.* **2010,** *132* (34), 11908-11909.

62. Zhang, S. S.; Wang, Z. Q.; Xu, M. H.; Lin, G. Q., Chiral Diene as the Ligand for the Synthesis of Axially Chiral Compounds via Palladium-Catalyzed Suzuki-Miyaura Coupling Reaction. *Org. Lett.* **2010,** *12* (23), 5546-5549.

63. Lu, Z.; Wilsily, A.; Fu, G. C., Stereoconvergent Amine-Directed Alkyl-Alkyl Suzuki Reactions of Unactivated Secondary Alkyl Chlorides. *J. Am. Chem. Soc.* **2011,** *133* (21), 8154-8157.

64. Lin, X. F.; Sun, J.; Xi, Y. Y.; Lin, D. L., How Racemic Secondary Alkyl Electrophiles Proceed to Enantioselective Products in Negishi Cross-Coupling Reactions. *Organometallics* **2011,** *30* (12), 3284-3292.

65. Nakanishi, M.; Katayev, D.; Besnard, C.; Kundig, E. P., Fused Indolines by Palladium-Catalyzed Asymmetric C-C Coupling Involving an Unactivated Methylene Group. *Angew. Chem.-Int. Edit.* **2011,** *50* (32), 7438-7441.

66. Woste, T. H.; Oestreich, M., BINAP versus BINAP(O) in Asymmetric Intermolecular Mizoroki-Heck Reactions: Substantial Effects on Selectivities. *Chem.-Eur. J.* **2011,** *17* (42), 11914-11918.

67. Zultanski, S. L.; Fu, G. C., Catalytic Asymmetric gamma-Alkylation of Carbonyl Compounds via Stereoconvergent Suzuki Cross-Couplings. *J. Am. Chem. Soc.* **2011,** *133* (39), 15362-15364.

68. Ge, S. Z.; Hartwig, J. F., Nickel-Catalyzed Asymmetric alpha-Arylation and Heteroarylation of Ketones with Chloroarenes: Effect of Halide on Selectivity, Oxidation State, and Room-Temperature Reactions. *J. Am. Chem. Soc.* **2011,** *133* (41), 16330-16333.

69. Huang, Z. Y.; Liu, Z.; Zhou, J. R., An Enantioselective, Intermolecular alpha-Arylation of Ester Enolates To Form Tertiary Stereocenters. *J. Am. Chem. Soc.* **2011,** *133* (40), 15882-15885.

70. Bigot, A.; Williamson, A. E.; Gaunt, M. J., Enantioselective alpha-Arylation of N-Acyloxazolidinones with Copper(II)-bisoxazoline Catalysts and Diaryliodonium Salts. *J. Am. Chem. Soc.* **2011,** *133* (35), 13778-13781.

71. Harvey, J. S.; Simonovich, S. P.; Jamison, C. R.; MacMillan, D. W. C., Enantioselective alpha-Arylation of Carbonyls via Cu(I)-Bisoxazoline Catalysis. *J. Am. Chem. Soc.* **2011,** *133* (35), 13782-13785.

72. Oelke, A. J.; Sun, J. W.; Fu, G. C., Nickel-Catalyzed Enantioselective Cross-Couplings of Racemic Secondary Electrophiles That Bear an Oxygen Leaving Group. *J. Am. Chem. Soc.* **2012,** *134* (6), 2966-2969.

73. Martin, N.; Pierre, C.; Davi, M.; Jazzar, R.; Baudoin, O., Diastereo- and Enantioselective Intramolecular C(sp3)?H Arylation for the Synthesis of Fused Cyclopentanes. *Chem.-Eur. J.* **2012,** *18* (15), 4480-4484.

74. Wilsily, A.; Tramutola, F.; Owston, N. A.; Fu, G. C., New Directing Groups for Metal-Catalyzed Asymmetric Carbon-Carbon Bond-Forming Processes: Stereoconvergent Alkyl-Alkyl Suzuki Cross-Couplings of Unactivated Electrophiles. *J. Am. Chem. Soc.* **2012,** *134* (13), 5794-5797.

75. Tang, W. J.; Patel, N. D.; Xu, G. Q.; Xu, X. B.; Savoie, J.; Ma, S. L.; Hao, M. H.; Keshipeddy, S.; Capacci, A. G.; Wei, X. D.; Zhang, Y. D.; Gao, J. J.; Li, W. J.; Rodriguez, S.; Lu, B. Z.; Yee, N. K.; Senanayake, C. H., Efficient Chiral Monophosphorus Ligands for Asymmetric Suzuki-Miyaura Coupling Reactions. *Org. Lett.* **2012,** *14* (9), 2258-2261.

76. Nareddy, P.; Mantilli, L.; Guenee, L.; Mazet, C., Atropoisomeric (P,N) Ligands for the Highly Enantioselective Pd-Catalyzed Intramolecular Asymmetric a-Arylation of a-Branched Aldehydes. *Angew. Chem.-Int. Edit.* **2012,** *51* (16), 3826-3831.

77. Wu, L. L.; Falivene, L.; Drinkel, E.; Grant, S.; Linden, A.; Cavallo, L.; Dorta, R., Synthesis of 3-Fluoro-3-aryl Oxindoles: Direct Enantioselective a Arylation of Amides. *Angew. Chem.-Int. Edit.* **2012,** *51* (12), 2870-2873.

78. Choi, J. W.; Fu, G. C., Catalytic Asymmetric Synthesis of Secondary Nitriles via Stereoconvergent Negishi Arylations and Alkenylations of Racemic alpha-Bromonitriles. *J. Am. Chem. Soc.* **2012,** *134* (22), 9102-9105.

79. Yang, Z. G.; Zhou, J. R., Palladium-Catalyzed, Asymmetric Mizoroki-Heck Reaction of Benzylic Electrophiles Using Phosphoramidites as Chiral Ligands. *J. Am. Chem. Soc.* **2012,** *134* (29), 11833-11835.

80. Zhou, F. T.; Guo, J. J.; Liu, J. G.; Ding, K.; Yu, S. Y.; Cai, Q., Copper-Catalyzed Desymmetric Intramolecular Ullmann C-N Coupling: An Enantioselective Preparation of Indolines. *J. Am. Chem. Soc.* **2012,** *134* (35), 14326-14329.

81. Shintani, R.; Maciver, E. E.; Tamakuni, F.; Hayashi, T., Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzooxasilines via Enantioselective Transmetalation. *J. Am. Chem. Soc.* **2012,** *134* (41), 16955-16958.

82. Binder, J. T.; Cordier, C. J.; Fu, G. C., Catalytic Enantioselective Cross-Couplings of Secondary Alkyl Electrophiles with Secondary Alkylmetal Nucleophiles: Negishi Reactions of Racemic Benzylic Bromides with Achiral Alkylzinc Reagents. *J. Am. Chem. Soc.* **2012,** *134* (41), 17003-17006.

83. McGrew, G. I.; Stanciu, C.; Zhang, J. D.; Carroll, P. J.; Dreher, S. D.; Walsh, P. J., Asymmetric Cross-Coupling of Aryl Triflates to the Benzylic Position of Benzylamines. *Angew. Chem.-Int. Edit.* **2012,** *51* (46), 11510-11513.

84. Werner, E. W.; Mei, T. S.; Burckle, A. J.; Sigman, M. S., Enantioselective Heck Arylations of Acyclic Alkenyl Alcohols Using a Redox-Relay Strategy. *Science* **2012,** *338* (6113), 1455-1458.

85. Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K., Rhodium-Catalyzed Asymmetric Synthesis of Spirosilabifluorene Derivatives. *Angew. Chem.-Int. Edit.* **2013,** *52* (5), 1520-1522.

86. Crouch, I. T.; Neff, R. K.; Frantz, D. E., Pd-Catalyzed Asymmetric beta-Hydride Elimination en Route to Chiral Allenes. *J. Am. Chem. Soc.* **2013,** *135* (13), 4970-4973.

87. Mei, T. S.; Werner, E. W.; Burckle, A. J.; Sigman, M. S., Enantioselective Redox-Relay Oxidative Heck Arylations of Acyclic Alkenyl Alcohols using Boronic Acids. *J. Am. Chem. Soc.* **2013,** *135* (18), 6830-6833.

88. Cherney, A. H.; Kadunce, N. T.; Reisman, S. E., Catalytic Asymmetric Reductive Acyl Cross-Coupling: Synthesis of Enantioenriched Acyclic alpha,alpha-Disubstituted Ketones. *J. Am. Chem. Soc.* **2013,** *135* (20), 7442-7445.

89. Saget, T.; Cramer, N., Enantioselective C-H Arylation Strategy for Functionalized Dibenzazepinones with Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2013,** *52* (30), 7865-7868.

90. Hu, J.; Hirao, H.; Li, Y. X.; Zhou, J. R., Palladium-Catalyzed Asymmetric Intermolecular Cyclization. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8676-8680.

91. Huang, Z. Y.; Lim, L. H.; Chen, Z. L.; Li, Y. X.; Zhou, F.; Su, H. B.; Zhou, J. R., Arene CH-O Hydrogen Bonding: A Stereocontrolling Tool in Palladium-Catalyzed Arylation and Vinylation of Ketones. *Angew. Chem.-Int. Edit.* **2013,** *52* (18), 4906-4911.

92. Katayev, D.; Jia, Y. X.; Sharma, A. K.; Banerjee, D.; Besnard, C.; Sunoj, R. B.; Kundig, E. P., Synthesis of 3,3-Disubstituted Oxindoles by Palladium-Catalyzed Asymmetric Intramolecular -Arylation of Amides: Reaction Development and Mechanistic Studies. *Chem.-Eur. J.* **2013,** *19* (36), 11916-11927.

93. Ros, A.; Estepa, B.; Ramirez-Lopez, P.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M., Dynamic Kinetic Cross-Coupling Strategy for the Asymmetric Synthesis of Axially Chiral Heterobiaryls. *J. Am. Chem. Soc.* **2013,** *135* (42), 15730-15733.

94. Do, H. Q.; Chandrashekar, E. R. R.; Fu, G. C., Nickel/Bis(oxazoline)-Catalyzed Asymmetric Negishi Arylations of Racemic Secondary Benzylic Electrophiles to Generate Enantioenriched 1,1-Diarylalkanes. *J. Am. Chem. Soc.* **2013,** *135* (44), 16288-16291.

95. Bhat, V.; Wang, S.; Stoltz, B. M.; Virgil, S. C., Asymmetric Synthesis of QUINAP via Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2013,** *135* (45), 16829-16832.

96. Wu, C.; Zhou, J., Asymmetric Intermolecular Heck Reaction of Aryl Halides. *J. Am. Chem. Soc.* **2014,** *136* (2), 650-652.

97. Sun, C. R.; Potter, B.; Morken, J. P., A Catalytic Enantiotopic-Group-Selective Suzuki Reaction for the Construction of Chiral Organoboronates. *J. Am. Chem. Soc.* **2014,** *136* (18), 6534-6537.

98. Cong, H.; Fu, G. C., Catalytic Enantioselective Cyclization/Cross-Coupling with Alkyl Electrophiles. *J. Am. Chem. Soc.* **2014,** *136* (10), 3788-3791.

99. Humbert, N.; Larionov, E.; Mantilli, L.; Nareddy, P.; Besnard, C.; Guenee, L.; Mazet, C., Highly Modular C-1-Symmetric Chiral (P,N) Ligands with a Stereolabile P Center: Experimental and Theoretical Studies. *Chem.-Eur. J.* **2014,** *20* (3), 745-751.

100. Zhu, Y.; Buchwald, S. L., Ligand-Controlled Asymmetric Arylation of Aliphatic alpha-Amino Anion Equivalents. *J. Am. Chem. Soc.* **2014,** *136* (12), 4500-4503.

101. Huang, Y.; Li, Y.; Leung, P.-H.; Hayashi, T., Asymmetric Synthesis of P-Stereogenic Diarylphosphinites by Palladium-Catalyzed Enantioselective Addition of Diarylphosphines to Benzoquinones. *J. Am. Chem. Soc.* **2014,** *136* (13), 4865-4868.

102. Liang, Y. F.; Fu, G. C., Catalytic Asymmetric Synthesis of Tertiary Alkyl Fluorides: Negishi Cross-Couplings of Racemic alpha,alpha-Dihaloketones. *J. Am. Chem. Soc.* **2014,** *136* (14), 5520-5524.

103. Mei, T. S.; Patel, H. H.; Sigman, M. S., Enantioselective construction of remote quaternary stereocentres. *Nature* **2014,** *508* (7496), 340-344.

104. Zhou, F.; Cheng, G.-J.; Yang, W.; Long, Y.; Zhang, S.; Wu, Y.-D.; Zhang, X.; Cai, Q., Enantioselective Formation of Cyano-Bearing All-Carbon Quaternary Stereocenters: Desymmetrization by Copper-Catalyzed N-Arylation. *Angew. Chem.-Int. Edit.* **2014,** *53* (36), 9555-9559.

105. Hilton, M. J.; Xu, L.-P.; Norrby, P.-O.; Wu, Y.-D.; Wiest, O.; Sigman, M. S., Investigating the Nature of Palladium Chain-Walking in the Enantioselective Redox-Relay Heck Reaction of Alkenyl Alcohols. *J. Org. Chem.* **2014,** *79* (24), 11841-11850.

106. Cherney, A. H.; Reisman, S. E., Nickel-Catalyzed Asymmetric Reductive Cross-Coupling Between Vinyl and Benzyl Electrophiles. *J. Am. Chem. Soc.* **2014,** *136* (41), 14365-14368.

107. Zheng, J.; You, S.-L., Construction of Axial Chirality by Rhodium-Catalyzed Asymmetric Dehydrogenative Heck Coupling of Biaryl Compounds with Alkenes. *Angew. Chem.-Int. Edit.* **2014,** *53* (48), 13244-13247.

108. Xu, R.-Q.; Gu, Q.; Wu, W.-T.; Zhao, Z.-A.; You, S.-L., Construction of Erythrinane Skeleton via Pd(0)-Catalyzed Intramolecular Dearomatization of para-Aminophenols. *J. Am. Chem. Soc.* **2014,** *136* (44), 15469-15472.

109. Mao, J.; Liu, F.; Wang, M.; Wu, L.; Zheng, B.; Liu, S.; Zhong, J.; Bian, Q.; Walsh, P. J., Cobalt-Bisoxazoline-Catalyzed Asymmetric Kumada Cross-Coupling of Racemic alpha-Bromo Esters with Aryl Grignard Reagents. *J. Am. Chem. Soc.* **2014,** *136* (50), 17662-17668.

110. Potter, B.; Szymaniak, A. A.; Edelstein, E. K.; Morken, J. P., Nonracemic Allylic Boronates through Enantiotopic-Group-Selective Cross-Coupling of Geminal Bis(boronates) and Vinyl Halides. *J. Am. Chem. Soc.* **2014,** *136* (52), 17918-17921.

111. Choi, J.; Martin-Gago, P.; Fu, G. C., Stereoconvergent Arylations and Alkenylations of Unactivated Alkyl Electrophiles: Catalytic Enantioselective Synthesis of Secondary Sulfonamides and Sulfones. *J. Am. Chem. Soc.* **2014,** *136* (34), 12161-12165.

112. Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C., Merging photoredox with nickel catalysis: Coupling of α-carboxyl sp³-carbons with aryl halides. *Science* **2014,** *345* (6195), 437-440.

113. Du, K.; Guo, P.; Chen, Y.; Cao, Z.; Wang, Z.; Tang, W., Enantioselective Palladium-Catalyzed Dearomative Cyclization for the Efficient Synthesis of Terpenes and Steroids. *Angew. Chem.-Int. Edit.* **2015,** *54* (10), 3033-3037.

114. Jiang, X.; Gandelman, M., Enantioselective Suzuki Cross-Couplings of Unactivated 1-Fluoro-1-haloalkanes: Synthesis of Chiral beta-, gamma-, delta-, and epsilon-Fluoroalkanes. *J. Am. Chem. Soc.* **2015,** *137* (7), 2542-2547.

115. Cornella, J.; Jackson, E. P.; Martin, R., Nickel-Catalyzed Enantioselective C-C Bond Formation through C-sp2-O Cleavage in Aryl Esters. *Angew. Chem.-Int. Edit.* **2015,** *54* (13), 4075-4078.

116. Zhao, Y.; Weix, D. J., Enantioselective Cross-Coupling of meso-Epoxides with Aryl Halides. *J. Am. Chem. Soc.* **2015,** *137* (9), 3237-3240.

117. Patel, H. H.; Sigman, M. S., Palladium-Catalyzed Enantioselective Heck Alkenylation of Acyclic Alkenols Using a Redox-Relay Strategy. *J. Am. Chem. Soc.* **2015,** *137* (10), 3462-3465.

118. Lin, Z. Q.; Wang, W. Z.; Yan, S. B.; Duan, W. L., Palladium-Catalyzed Enantioselective CH Arylation for the Synthesis of P-Stereogenic Compounds. *Angew. Chem.-Int. Edit.* **2015,** *54* (21), 6265-6269.

119. Yang, L.; Zheng, H. Y.; Luo, L.; Nan, J.; Liu, J. J.; Wang, Y. Y.; Luan, X. J., Palladium-Catalyzed Dynamic Kinetic Asymmetric Transformation of Racemic Biaryls: Axial-to-Central Chirality Transfer. *J. Am. Chem. Soc.* **2015,** *137* (15), 4876-4879.

120. Shen, C.; Liu, R. R.; Fan, R. J.; Li, Y. L.; Xu, T. F.; Gao, J. R.; Jia, Y. X., Enantioselective Arylative Dearomatization of Indoles via Pd-Catalyzed Intramolecular Reductive Heck Reactions. *J. Am. Chem. Soc.* **2015,** *137* (15), 4936-4939.

121. Jin, M.; Adak, L.; Nakamura, M., Iron-Catalyzed Enantioselective Cross-Coupling Reactions of alpha-Chloroesters with Aryl Grignard Reagents. *J. Am. Chem. Soc.* **2015,** *137* (22), 7128-7134.

122. Zhang, C.; Santiago, C. B.; Kou, L.; Sigman, M. S., Alkenyl Carbonyl Derivatives in Enantioselective Redox Relay Heck Reactions: Accessing alpha,beta-Unsaturated Systems. *J. Am. Chem. Soc.* **2015,** *137* (23), 7290-7293.

123. Pedroni, J.; Saget, T.; Donets, P. A.; Cramer, N., Enantioselective palladium(0)-catalyzed intramolecular cyclopropane functionalization: access to dihydroquinolones, dihydroisoquinolones and the BMS-791325 ring system. *Chemical Science* **2015,** *6* (9), 5164-5171.

124. Liu, J. G.; Tian, Y. Y.; Shi, J. L.; Zhang, S. S.; Cai, Q., An Enantioselective Synthesis of Spirobilactams through Copper-Catalyzed Intramolecular Double N-Arylation and Phase Separation. *Angew. Chem.-Int. Edit.* **2015,** *54* (37), 10917-10920.

125. Kadunce, N. T.; Reisman, S. E., Nickel-Catalyzed Asymmetric Reductive Cross-Coupling between Heteroaryl Iodides and alpha-Chloronitriles. *J. Am. Chem. Soc.* **2015,** *137* (33), 10480-10483.

126. Oliveira, C. C.; Pfaltz, A.; Correia, C. R. D., Quaternary Stereogenic Centers through Enantioselective Heck Arylation of Acyclic Olefins with Aryldiazonium Salts: Application in a Concise Synthesis of (R)-Verapamil. *Angew. Chem.-Int. Edit.* **2015,** *54* (47), 14036-14039.

127. Zhang, C.; Santiago, C. B.; Crawford, J. M.; Sigman, M. S., Enantioselective Dehydrogenative Heck Arylations of Trisubstituted Alkenes with Indoles to Construct Quaternary Stereocenters. *J. Am. Chem. Soc.* **2015,** *137* (50), 15668-15671.

128. Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P., Catalytic conjunctive cross-coupling enabled by metal-induced metallate rearrangement. *Science* **2016,** *351* (6268), 70-74.

129. Jiang, X.; Kulbitski, K.; Nisnevich, G.; Gandelman, M., Enantioselective assembly of tertiary stereocenters via multicomponent chemoselective cross-coupling of geminal chloro(iodo)alkanes. *Chemical Science* **2016,** *7* (4), 2762-2767.

130. Zuo, Z. W.; Gong, H.; Li, W.; Choi, J.; Fu, G. C.; MacMillan, D. W. C., Enantioselective Decarboxylative Arylation of alpha-Amino Acids via the Merger of Photoredox and Nickel Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (6), 1832-1835.

131. Kainz, Q. M.; Matier, C. D.; Bartoszewicz, A.; Zultanski, S. L.; Peters, J. C.; Fu, G. C., Asymmetric copper-catalyzed C-N cross-couplings induced by visible light. *Science* **2016,** *351* (6274), 681-684.

132. Oost, R.; Misale, A.; Maulide, N., Enantioconvergent Fukuyama Cross-Coupling of Racemic Benzylic Organozinc Reagents. *Angew. Chem.-Int. Edit.* **2016,** *55* (14), 4587-4590.

133. Borrajo-Calleja, G. M.; Bizet, V.; Mazet, C., Palladium-Catalyzed Enantioselective Intermolecular Carboetherification of Dihydrofurans. *J. Am. Chem. Soc.* **2016,** *138* (12), 4014-4017.

134. Shi, S. L.; Wong, Z. L.; Buchwald, S. L., Copper-catalysed enantioselective stereodivergent synthesis of amino alcohols. *Nature* **2016,** *532* (7599), 353-356.

135. Tabuchi, S.; Hirano, K.; Miura, M., Palladium-Catalyzed Asymmetric Benzylic Alkylation of Active Methylene Compounds with alpha-Naphthylbenzyl Carbonates and Pivalates. *Angew. Chem.-Int. Edit.* **2016,** *55* (24), 6973-6977.

136. Eno, M. S.; Lu, A.; Morken, J. P., Nickel-Catalyzed Asymmetric Kumada Cross-Coupling of Symmetric Cyclic Sulfates. *J. Am. Chem. Soc.* **2016,** *138* (25), 7824-7827.

137. Ramirez-Lopez, P.; Ros, A.; Romero-Arenas, A.; Iglesias-Siguenza, J.; Fernandez, R.; Lassaletta, J. M., Synthesis of IAN-type N,N-Ligands via Dynamic Kinetic Asymmetric Buchwald-Hartwig Amination. *J. Am. Chem. Soc.* **2016,** *138* (37), 12053-12056.

138. Beaud, R.; Phipps, R. J.; Gaunt, M. J., Enantioselective Cu-Catalyzed Arylation of Secondary Phosphine Oxides with Diaryliodonium Salts toward the Synthesis of P-Chiral Phosphines. *J. Am. Chem. Soc.* **2016,** *138* (40), 13183-13186.

139. Jiao, Z. W.; Beiger, J. J.; Jin, Y. S.; Ge, S. Z.; Zhou, J. S.; Hartwig, J. F., Palladium-Catalyzed Enantioselective alpha-Arylation of alpha-Fluoroketones. *J. Am. Chem. Soc.* **2016,** *138* (49), 15980-15986.

140. Jiao, Z. W.; Chee, K. W.; Zhou, J. R., Palladium-Catalyzed Asymmetric alpha-Arylation of Alkylnitriles. *J. Am. Chem. Soc.* **2016,** *138* (50), 16240-16243.

141. Feng, J.; Li, B.; He, Y.; Gu, Z. H., Enantioselective Synthesis of Atropisomeric Vinyl Arene Compounds by Palladium Catalysis: A Carbene Strategy. *Angew. Chem.-Int. Edit.* **2016,** *55* (6), 2186-2190.

142. Chu, W. D.; Zhang, L.; Zhang, Z. K.; Zhou, Q.; Mo, F. Y.; Zhang, Y.; Wang, J. B., Enantioselective Synthesis of Trisubstituted Allenes via Cu(I)-Catalyzed Coupling of Diazoalkanes with Terminal Alkynes. *J. Am. Chem. Soc.* **2016,** *138* (44), 14558-14561.

143. Jain, P.; Verma, P.; Xia, G. Q.; Yu, J. Q., Enantioselective amine alpha-functionalization via palladium-catalysed C-H arylation of thioamides. *Nature Chemistry* **2017,** *9* (2), 140-144.

144. Zhang, Q. W.; An, K.; Liu, C.; Zhang, Q.; Guo, H. F.; He, W., Construction of Chiral Tetraorganosilicons by Tandem Desymmetrization of Silacyclobutanes/Intermolecular Dehydrogenative Silylation. *Angew. Chem.-Int. Edit.* **2017,** *56* (4), 1125-1129.

145. Kattela, S.; Heerdt, G.; Correia, C. R. D., Non-Covalent Carbonyl-Directed Heck-Matsuda Desymmetrizations: Synthesis of Cyclopentene-Fused Spirooxindoles, Spirolactones, and Spirolactams. *Adv. Synth. Catal.* **2017,** *359* (2), 260-267.

146. Kong, W. Q.; Wang, Q.; Zhu, J. P., Water as a Hydride Source in Palladium-Catalyzed Enantioselective Reductive Heck Reactions. *Angew. Chem.-Int. Edit.* **2017,** *56* (14), 3987-3991.

147. Pan, C. Q.; Zhu, Z. X.; Zhang, M. K.; Gu, Z. H., Palladium-Catalyzed Enantioselective Synthesis of 2-Aryl Cyclohex-2-enone Atropisomers: Platform Molecules for the Divergent Synthesis of Axially Chiral Biaryl Compounds. *Angew. Chem.-Int. Edit.* **2017,** *56* (17), 4777-4781.

148. Mu, X.; Shibata, Y.; Makida, Y.; Fu, G. C., Control of Vicinal Stereocenters through Nickel-Catalyzed Alkyl-Alkyl Cross-Coupling. *Angew. Chem.-Int. Edit.* **2017,** *56* (21), 5821-5824.

149. Woods, B. P.; Orlandi, M.; Huang, C. Y.; Sigman, M. S.; Doylet, A. G., Nickel-Catalyzed Enantioselective Reductive Cross-Coupling of Styrenyl Aziridines. *J. Am. Chem. Soc.* **2017,** *139* (16), 5688-5691.

150. Poremba, K. E.; Kadunce, N. T.; Suzuki, N.; Cherney, A. H.; Reisman, S. E., Nickel-Catalyzed Asymmetric Reductive Cross-Coupling To Access 1,1-Diarylalkanes. *J. Am. Chem. Soc.* **2017,** *139* (16), 5684-5687.

151. Chen, Z. M.; Nervig, C. S.; DeLuca, R. J.; Sigman, M. S., Palladium-Catalyzed Enantioselective Redox-Relay Heck Alkynylation of Alkenols To Access Propargylic Stereocenters. *Angew. Chem.-Int. Edit.* **2017,** *56* (23), 6651-6654.

152. Sato, Y.; Takagi, C.; Shintani, R.; Nozaki, K., Palladium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic 5,10-Dihydrophenazasilines via Enantioselective 1,5-Palladium Migration. *Angew. Chem.-Int. Edit.* **2017,** *56* (31), 9211-9216.

153. Jia, T. Z.; Zhang, M. N.; McCollom, S. P.; Bellomo, A.; Montel, S.; Mao, J. Y.; Dreher, S. D.; Welch, C. J.; Regalado, E. L.; Williamson, R. T.; Manor, B. C.; Tomson, N. C.; Walsh, P. J., Palladium-Catalyzed Enantioselective Arylation of Aryl Sulfenate Anions: A Combined Experimental and Computational Study. *J. Am. Chem. Soc.* **2017,** *139* (24), 8337-8345.

154. Bao, X.; Wang, Q.; Zhu, J. P., Palladium-Catalyzed Enantioselective Narasaka-Heck Reaction/Direct C-H Alkylation of Arenes: Iminoarylation of Alkenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (32), 9577-9581.

155. Jang, Y. S.; Dieckmann, M.; Cramer, N., Cooperative Effects between Chiral Cp-x-Iridium(III) Catalysts and Chiral Carboxylic Acids in Enantioselective C-H Amidations of Phosphine Oxides. *Angew. Chem.-Int. Edit.* **2017,** *56* (47), 15088-15092.

156. Jiao, Z. W.; Shi, Q.; Zhou, J. S., Asymmetric Intermolecular Heck Reaction of Propargylic Acetates and Cycloalkenes to Access Fused Cyclobutenes. *Angew. Chem.-Int. Edit.* **2017,** *56* (46), 14567-14571.

157. Wang, D. H.; Zhu, N.; Chen, P. H.; Lin, Z. Y.; Liu, G. S., Enantioselective Decarboxylative Cyanation Employing Cooperative Photoredox Catalysis and Copper Catalysis. *J. Am. Chem. Soc.* **2017,** *139* (44), 15632-15635.

158. Zhu, C. D.; Wang, D. Y.; Zhao, Y.; Sun, W. Y.; Shi, Z. Z., Enantioselective Palladium-Catalyzed Intramolecular alpha-Arylative Desymmetrization of 1,3-Diketones. *J. Am. Chem. Soc.* **2017,** *139* (46), 16486-16489.

159. Hofstra, J. L.; Cherney, A. H.; Ordner, C. M.; Reisman, S. E., Synthesis of Enantioenriched Allylic Silanes via Nickel-Catalyzed Reductive Cross-Coupling. *J. Am. Chem. Soc.* **2018,** *140* (1), 139-142.

160. Bao, X.; Wang, Q.; Zhu, J. P., Palladium-Catalyzed Enantioselective Desymmetrizing Aza-Wacker Reaction: Development and Application to the Total Synthesis of (-)-Mesembrane and (+)-Crinane. *Angew. Chem.-Int. Edit.* **2018,** *57* (7), 1995-1999.

161. Cheng, R. F.; Li, B. W.; Wu, J.; Zhang, J.; Qiu, Z. Z.; Tang, W. J.; You, S. L.; Tang, Y.; Xie, Z. W., Enantioselective Synthesis of Chiral-at-Cage o-Carboranes via Pd-Catalyzed Asymmetric B-H Substitution. *J. Am. Chem. Soc.* **2018,** *140* (13), 4508-4511.

162. Yuan, Q. J.; Sigman, M. S., Palladium-Catalyzed Enantioselective Relay Heck Arylation of Enelactams: Accessing alpha,beta-Unsaturated delta-Lactams. *J. Am. Chem. Soc.* **2018,** *140* (21), 6527-6530.

163. Huang, X. L.; Oh, W.; Zhou, J. S., Palladium-Catalyzed Enantioselective Arylation of Racemic Ketones to Form Bridged Bicycles via Dynamic Kinetic Resolution. *Angew. Chem.-Int. Edit.* **2018,** *57* (26), 7673-7677.

164. Zhang, Z. M.; Xu, B.; Qian, Y. Y.; Wu, L. Z.; Wu, Y. Q.; Zhou, L. J.; Liu, Y.; Zhang, J. L., Palladium-Catalyzed Enantioselective Reductive Heck Reactions: Convenient Access to 3,3-Disubstituted 2,3-Dihydrobenzofuran. *Angew. Chem.-Int. Edit.* **2018,** *57* (32), 10373-10377.

165. Xu, S. B.; Zhao, K.; Gu, Z. H., Copper-Catalyzed Asymmetric Ring-Opening of Cyclic Diaryliodonium with Benzylic and Aliphatic Amines. *Adv. Synth. Catal.* **2018,** *360* (20), 3877-3883.

166. Carmona, R. C.; Koster, O. D.; Correia, C. R. D., Chiral N,NLigands Enabling Palladium-Catalyzed Enantioselective Intramolecular Heck-Matsuda Carbonylation Reactions by Sequential Migratory and CO Insertions. *Angew. Chem.-Int. Edit.* **2018,** *57* (37), 12067-12070.

167. Myhill, J. A.; Zhang, L.; Lovinger, G. J.; Morken, J. P., Enantioselective Construction of Tertiary Boronic Esters by Conjunctive Cross-Coupling. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12799-12803.

168. Carmona, J. A.; Hornillos, V.; Ramirez-Lopez, P.; Ros, A.; Iglesias-Siguenza, J.; Gomez-Bengoa, E.; Fernandez, R.; Lassaletta, J. M., Dynamic Kinetic Asymmetric Heck Reaction for the Simultaneous Generation of Central and Axial Chirality. *J. Am. Chem. Soc.* **2018,** *140* (35), 11067-11075.

169. Schwarzwalder, G. M.; Matier, C. D.; Fu, G. C., Enantioconvergent Cross-Couplings of Alkyl Electrophiles: The Catalytic Asymmetric Synthesis of Organosilanes. *Angew. Chem.-Int. Edit.* **2019,** *58* (11), 3571-3574.

170. Yi, H.; Mao, W. B.; Oestreich, M., Enantioselective Construction of alpha-Chiral Silanes by Nickel-Catalyzed C(sp(3))-C(sp(3)) Cross-Coupling. *Angew. Chem.-Int. Edit.* **2019,** *58* (11), 3575-3578.

171. Wu, C.; Berritt, S.; Liang, X. X.; Walsh, P. J., Palladium-Catalyzed Enantioselective Alkenylation of Sulfenate Anions. *Org. Lett.* **2019,** *21* (4), 960-964.

172. Ma, X. F.; Hazelden, I. R.; Langer, T.; Munday, R. H.; Bower, J. F., Enantioselective Aza-Heck Cyclizations of N-(Tosyloxy)carbamates: Synthesis of Pyrrolidines and Piperidines. *J. Am. Chem. Soc.* **2019,** *141* (8), 3356-3360.

173. Devannah, V.; Sharma, R.; Watson, D. A., Nickel-Catalyzed Asymmetric C-Alkylation of Nitroalkanes: Synthesis of Enantioenriched beta-Nitroamides. *J. Am. Chem. Soc.* **2019,** *141* (21), 8436-8440.

174. Li, B.; Li, T.; Aliyu, M. A.; Li, Z. H.; Tang, W., Enantioselective Palladium-Catalyzed Cross-Coupling of α-Bromo Carboxamides and Aryl Boronic Acids. *Angewandte Chemie International Edition* **2019,** *58* (33), 11355-11359.

175. Allen, J. R.; Bahamonde, A.; Furukawa, Y.; Sigman, M. S., Enantioselective N-Alkylation of Indoles via an Intermolecular Aza-Wacker-Type Reaction. *J. Am. Chem. Soc.* **2019,** *141* (22), 8670-8674.

176. Iwamoto, H.; Endo, K.; Ozawa, Y.; Watanabe, Y.; Kubota, K.; Imamoto, T.; Ito, H., Copper(I)-Catalyzed Enantioconvergent Borylation of Racemic Benzyl Chlorides Enabled by Quadrant-by-Quadrant Structure Modification of Chiral Bisphosphine Ligands. *Angew. Chem.-Int. Edit.* **2019,** *58* (32), 11112-11117.

177. Trost, B. M.; Xu, S. Y.; Sharif, E. U., New Catalytic Asymmetric Formation of Oxygen Heterocycles Bearing Nucleoside Bases at the Anomeric Carbon. *J. Am. Chem. Soc.* **2019,** *141* (26), 10199-10204.

178. Varenikov, A.; Gandelman, M., Organotitanium Nucleophiles in Asymmetric Cross-Coupling Reaction: Stereoconvergent Synthesis of Chiral alpha-CF3 Thioethers. *J. Am. Chem. Soc.* **2019,** *141* (28), 10994-10999.

179. Liu, J. B.; Yuan, Q. J.; Toste, F. D.; Sigman, M. S., Enantioselective construction of remote tertiary carbon-fluorine bonds. *Nature Chemistry* **2019,** *11* (8), 710-715.

180. Yin, H. L.; Fu, G. C., Mechanistic Investigation of Enantioconvergent Kumada Reactions of Racemic alpha-Bromoketones Catalyzed by a Nickel/Bis(oxazoline) Complex. *J. Am. Chem. Soc.* **2019,** *141* (38), 15433-15440.

181. Bartoszewicz, A.; Matier, C. D.; Fu, G. C., Enantioconvergent Alkylations of Amines by Alkyl Electrophiles: Copper-Catalyzed Nucleophilic Substitutions of Racemic alpha-Halolactams by Indoles. *J. Am. Chem. Soc.* **2019,** *141* (37), 14864-14869.

182. Dong, X. Y.; Zhang, Y. F.; Ma, C. L.; Gu, Q. S.; Wang, F. L.; Li, Z. L.; Jiang, S. P.; Liu, X. Y., A general asymmetric copper-catalysed Sonogashira C(sp(3))-C(sp) coupling. *Nature Chemistry* **2019,** *11* (12), 1158-1166.

183. Chen, J.; Wang, P. Z.; Lu, B.; Liang, D.; Yu, X. Y.; Xiao, W. J.; Chen, J. R., Enantioselective Radical Ring-Opening Cyanation of Oxime Esters by Dual Photoredox and Copper Catalysis. *Org. Lett.* **2019,** *21* (23), 9763-9768.

184. Zhu, C. H.; Chu, H. K.; Li, G.; Ma, S. M.; Zhang, J. L., Pd-Catalyzed Enantioselective Heck Reaction of Aryl Triflates and Alkynes. *J. Am. Chem. Soc.* **2019,** *141* (49), 19246-19251.

185. Bai, X.; Wu, C.; Ge, S.; Lu, Y., Pd/Cu-Catalyzed Enantioselective Sequential Heck/Sonogashira Coupling: Asymmetric Synthesis of Oxindoles Containing Trifluoromethylated Quaternary Stereogenic Centers. *Angewandte Chemie International Edition* **2020,** *59* (7), 2764-2768.

186. Teng, S.; Jiao, Z.; Chi, Y. R.; Zhou, J. S., Asymmetric Wacker-Type Oxyallenylation and Azaallenylation of Cyclic Alkenes. *Angewandte Chemie International Edition* **2020,** *59* (6), 2246-2250.

187. Zhu, D.; Jiao, Z.; Chi, Y. R.; Gonçalves, T. P.; Huang, K.-W.; Zhou, J. S., Asymmetric Three-Component Heck Arylation/Amination of Nonconjugated Cyclodienes. *Angewandte Chemie International Edition* **2020,** *59* (13), 5341-5345.

188. Meng, Y.; Kong, Z.; Morken, J. P., Catalytic Enantioselective Synthesis of anti-Vicinal Silylboronates by Conjunctive Cross-Coupling. *Angewandte Chemie International Edition* **2020,** *59* (22), 8456-8459.

189. Frey, J.; Malekafzali, A.; Delso, I.; Choppin, S.; Colobert, F.; Wencel-Delord, J., Enantioselective Synthesis of N–C Axially Chiral Compounds by Cu-Catalyzed Atroposelective Aryl Amination. *Angewandte Chemie International Edition* **2020,** *59* (23), 8844-8848.

190. Yang, Z.-P.; Fu, G. C., Convergent Catalytic Asymmetric Synthesis of Esters of Chiral Dialkyl Carbinols. *J. Am. Chem. Soc.* **2020,** *142* (12), 5870-5875.

191. Huang, X.; Nguyen, M. H.; Pu, M.; Zhang, L.; Chi, Y. R.; Wu, Y.-D.; Zhou, J. S., Asymmetric Reductive and Alkynylative Heck Bicyclization of Enynes to Access Conformationally Restricted Aza[3.1.0]bicycles. *Angewandte Chemie International Edition* **2020,** *59* (27), 10814-10818.

192. Oxtoby, L. J.; Li, Z.-Q.; Tran, V. T.; Erbay, T. G.; Deng, R.; Liu, P.; Engle, K. M., A Transient-Directing-Group Strategy Enables Enantioselective Reductive Heck Hydroarylation of Alkenes. *Angewandte Chemie International Edition* **2020,** *59* (23), 8885-8890.

193. Ding, Y.; Han, Y.-Q.; Wu, L.-S.; Zhou, T.; Yao, Q.-J.; Feng, Y.-L.; Li, Y.; Kong, K.-X.; Shi, B.-F., Pd(II)-Catalyzed Tandem Enantioselective Methylene C(sp3)−H Alkenylation–Aza-Wacker Cyclization to Access β-Stereogenic γ-Lactams. *Angewandte Chemie International Edition* **2020,** *59* (33), 14060-14064.

194. Ross, S. P.; Rahman, A. A.; Sigman, M. S., Development and Mechanistic Interrogation of Interrupted Chain-Walking in the Enantioselective Relay Heck Reaction. *J. Am. Chem. Soc.* **2020,** *142* (23), 10516-10525.

195. Xia, H.-D.; Li, Z.-L.; Gu, Q.-S.; Dong, X.-Y.; Fang, J.-H.; Du, X.-Y.; Wang, L.-L.; Liu, X.-Y., Photoinduced Copper-Catalyzed Asymmetric Decarboxylative Alkynylation with Terminal Alkynes. *Angewandte Chemie International Edition* **2020,** *59* (39), 16926-16932.

196. An, L.; Tong, F.-F.; Zhang, S.; Zhang, X., Stereoselective Functionalization of Racemic Cyclopropylzinc Reagents via Enantiodivergent Relay Coupling. *J. Am. Chem. Soc.* **2020,** *142* (27), 11884-11892.

197. Wei, X.; Shu, W.; García-Domínguez, A.; Merino, E.; Nevado, C., Asymmetric Ni-Catalyzed Radical Relayed Reductive Coupling. *J. Am. Chem. Soc.* **2020,** *142* (31), 13515-13522.

198. Zhang, X.; Zhao, K.; Li, N.; Yu, J.; Gong, L.-Z.; Gu, Z., Atroposelective Ring Opening of Cyclic Diaryliodonium Salts with Bulky Anilines Controlled by a Chiral Cobalt(III) Anion. *Angewandte Chemie International Edition* **2020,** *59* (45), 19899-19904.

199. Rosales, A. R.; Ross, S. P.; Helquist, P.; Norrby, P.-O.; Sigman, M. S.; Wiest, O., Transition State Force Field for the Asymmetric Redox-Relay Heck Reaction. *J. Am. Chem. Soc.* **2020,** *142* (21), 9700-9707.

200. Chen, M.; Wang, X.; Yang, P.; Kou, X.; Ren, Z.-H.; Guan, Z.-H., Palladium-Catalyzed Enantioselective Heck Carbonylation with a Monodentate Phosphoramidite Ligand: Asymmetric Synthesis of (+)-Physostigmine, (+)-Physovenine, and (+)-Folicanthine. *Angewandte Chemie International Edition* **2020,** *59* (29), 12199-12205.

201. Jiang, S.-P.; Dong, X.-Y.; Gu, Q.-S.; Ye, L.; Li, Z.-L.; Liu, X.-Y., Copper-Catalyzed Enantioconvergent Radical Suzuki–Miyaura C(sp3)–C(sp2) Cross-Coupling. *J. Am. Chem. Soc.* **2020,** *142* (46), 19652-19659.

202. Zhu, K.; Song, Z.; Wang, Y.; Zhang, F., Synthesis of 2,2′-Dihalobiaryls via Cu-Catalyzed Halogenation of Cyclic Diaryliodonium Salts. *Org. Lett.* **2020,** *22* (23), 9356-9359.

203. Bera, S.; Mao, R. Z.; Hu, X. L., Enantioselective C(sp(3))-C(sp(3)) cross-coupling of non-activated alkyl electrophiles via nickel hydride catalysis. *Nature Chemistry* **2021,** *13* (3), 270-+.

204. Huang, X.; Teng, S.; Chi, Y. R.; Xu, W.; Pu, M.; Wu, Y.-D.; Zhou, J. S., Enantioselective Intermolecular Heck and Reductive Heck Reactions of Aryl Triflates, Mesylates, and Tosylates Catalyzed by Nickel. *Angewandte Chemie International Edition* **2021,** *60* (6), 2828-2832.

205. Wang, Z.; Yang, Z.-P.; Fu, G. C., Quaternary stereocentres via catalytic enantioconvergent nucleophilic substitution reactions of tertiary alkyl halides. *Nature Chemistry* **2021,** *13* (3), 236-242.

206. Yang, Z.-P.; Freas, D. J.; Fu, G. C., The Asymmetric Synthesis of Amines via Nickel-Catalyzed Enantioconvergent Substitution Reactions. *J. Am. Chem. Soc.* **2021,** *143* (7), 2930-2937.

207. Sun, D.; Ma, G.; Zhao, X.; Lei, C.; Gong, H., Nickel-catalyzed asymmetric reductive arylation of α-chlorosulfones with aryl halides. *Chemical Science* **2021,** *12* (14), 5253-5258.

208. Escudero-Casao, M.; Licini, G.; Orlandi, M., Enantioselective α-Arylation of Ketones via a Novel Cu(I)–Bis(phosphine) Dioxide Catalytic System. *J. Am. Chem. Soc.* **2021,** *143* (9), 3289-3294.

209. Zheng, P.; Zhou, P.; Wang, D.; Xu, W.; Wang, H.; Xu, T., Dual Ni/photoredox-catalyzed asymmetric cross-coupling to access chiral benzylic boronic esters. *Nature Communications* **2021,** *12* (1), 1646.

210. Wang, Z.-C.; Xie, P.-P.; Xu, Y.; Hong, X.; Shi, S.-L., Low-Temperature Nickel-Catalyzed C−N Cross-Coupling via Kinetic Resolution Enabled by a Bulky and Flexible Chiral N-Heterocyclic Carbene Ligand. *Angewandte Chemie International Edition* **2021,** *60* (29), 16077-16084.

211. DeLano, T. J.; Dibrell, S. E.; Lacker, C. R.; Pancoast, A. R.; Poremba, K. E.; Cleary, L.; Sigman, M. S.; Reisman, S. E., Nickel-catalyzed asymmetric reductive cross-coupling of α-chloroesters with (hetero)aryl iodides. *Chemical Science* **2021,** *12* (22), 7758-7762.

212. Cao, J.; Wu, H.; Wang, Q.; Zhu, J., C–C bond activation enabled by dyotropic rearrangement of Pd(iv) species. *Nature Chemistry* **2021,** *13* (7), 671-676.

213. Yang, Z.-P.; Freas, D. J.; Fu, G. C., Asymmetric Synthesis of Protected Unnatural α-Amino Acids via Enantioconvergent Nickel-Catalyzed Cross-Coupling. *J. Am. Chem. Soc.* **2021,** *143* (23), 8614-8618.

214. Pan, Z.; Li, W.; Zhu, S.; Liu, F.; Wu, H.-H.; Zhang, J., Palladium/TY-Phos-Catalyzed Asymmetric Intermolecular α-Arylation of Aldehydes with Aryl Bromides. *Angewandte Chemie International Edition* **2021,** *60* (34), 18542-18546.

215. Zhou, H.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Ligand-Enabled Copper(I)-Catalyzed Asymmetric Radical C(sp3)–C Cross-Coupling Reactions. *ACS Catalysis* **2021,** *11* (13), 7978-7986.

216. Yang, K.; Mao, Y.; Xu, J.; Wang, H.; He, Y.; Li, W.; Song, Q., Construction of Axially Chiral Arylborons via Atroposelective Miyaura Borylation. *J. Am. Chem. Soc.* **2021,** *143* (27), 10048-10053.

217. Chen, C.; Peters, J. C.; Fu, G. C., Photoinduced copper-catalysed asymmetric amidation via ligand cooperativity. *Nature* **2021,** *596* (7871), 250-256.

218. Zhang, Y.-F.; Dong, X.-Y.; Cheng, J.-T.; Yang, N.-Y.; Wang, L.-L.; Wang, F.-L.; Luan, C.; Liu, J.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Enantioconvergent Cu-Catalyzed Radical C–N Coupling of Racemic Secondary Alkyl Halides to Access α-Chiral Primary Amines. *J. Am. Chem. Soc.* **2021,** *143* (37), 15413-15419.

219. Lau, S. H.; Borden, M. A.; Steiman, T. J.; Wang, L. S.; Parasram, M.; Doyle, A. G., Ni/Photoredox-Catalyzed Enantioselective Cross-Electrophile Coupling of Styrene Oxides with Aryl Iodides. *J. Am. Chem. Soc.* **2021,** *143* (38), 15873-15881.

220. Lee, H.; Ahn, J. M.; Oyala, P. H.; Citek, C.; Yin, H.; Fu, G. C.; Peters, J. C., Investigation of the C–N Bond-Forming Step in a Photoinduced, Copper-Catalyzed Enantioconvergent N–Alkylation: Characterization and Application of a Stabilized Organic Radical as a Mechanistic Probe. *J. Am. Chem. Soc.* **2022,** *144* (9), 4114-4123.

221. Wang, J.; Li, X., Asymmetric β-arylation of cyclopropanols enabled by photoredox and nickel dual catalysis. *Chemical Science* **2022,** *13* (10), 3020-3026.

222. Cho, H.; Suematsu, H.; Oyala, P. H.; Peters, J. C.; Fu, G. C., Photoinduced, Copper-Catalyzed Enantioconvergent Alkylations of Anilines by Racemic Tertiary Electrophiles: Synthesis and Mechanism. *J. Am. Chem. Soc.* **2022,** *144* (10), 4550-4558.

223. Li, S.; Chen, Q.; Yang, J.; Zhang, J., Palladium-Catalyzed Enantioselective γ-Arylation of β,γ-Unsaturated Butenolides. *Angewandte Chemie International Edition* **2022,** *61* (23), e202202046.

224. Wu, B.-B.; Xu, J.; Bian, K.-J.; Gao, Q.; Wang, X.-S., Enantioselective Synthesis of Secondary β-Trifluoromethyl Alcohols via Catalytic Asymmetric Reductive Trifluoroalkylation and Diastereoselective Reduction. *J. Am. Chem. Soc.* **2022,** *144* (14), 6543-6550.

225. Gao, Y.; Zhang, B.; Levy, L.; Zhang, H.-J.; He, C.; Baran, P. S., Ni-Catalyzed Enantioselective Dialkyl Carbinol Synthesis via Decarboxylative Cross-Coupling: Development, Scope, and Applications. *J. Am. Chem. Soc.* **2022,** *144* (24), 10992-11002.

226. Wang, F.-L.; Yang, C.-J.; Liu, J.-R.; Yang, N.-Y.; Dong, X.-Y.; Jiang, R.-Q.; Chang, X.-Y.; Li, Z.-L.; Xu, G.-X.; Yuan, D.-L.; Zhang, Y.-S.; Gu, Q.-S.; Hong, X.; Liu, X.-Y., Mechanism-based ligand design for copper-catalysed enantioconvergent C(sp3)–C(sp) cross-coupling of tertiary electrophiles with alkynes. *Nature Chemistry* **2022,** *14* (8), 949-957.

227. Tong, X.; Schneck, F.; Fu, G. C., Catalytic Enantioselective α-Alkylation of Amides by Unactivated Alkyl Electrophiles. *J. Am. Chem. Soc.* **2022,** *144* (32), 14856-14863.

228. Dong, X.-Y.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Ligand Development for Copper-Catalyzed Enantioconvergent Radical Cross-Coupling of Racemic Alkyl Halides. *J. Am. Chem. Soc.* **2022,** *144* (38), 17319-17329.

229. Lacker, C. R.; DeLano, T. J.; Chen, E. P.; Kong, J.; Belyk, K. M.; Piou, T.; Reisman, S. E., Enantioselective Synthesis of N-Benzylic Heterocycles by Ni/Photoredox Dual Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (44), 20190-20195.

230. Lai, X.-L.; Chen, M.; Wang, Y.; Song, J.; Xu, H.-C., Photoelectrochemical Asymmetric Catalysis Enables Direct and Enantioselective Decarboxylative Cyanation. *J. Am. Chem. Soc.* **2022,** *144* (44), 20201-20206.

231. Han, J.; Xiao, B.; Sun, T.-Y.; Wang, M.; Jin, L.; Yu, W.; Wang, Y.; Fang, D.-M.; Zhou, Y.; Wu, X.-F.; Wu, Y.-D.; Liao, J., Enantioselective Double Carbonylation Enabled by High-Valent Palladium Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (47), 21800-21807.

232. Yuan, Y.; Yang, J.; Zhang, J., Cu-catalyzed enantioselective decarboxylative cyanation via the synergistic merger of photocatalysis and electrochemistry. *Chemical Science* **2023,** *14* (3), 705-710.

233. Yan, M.; Zhou, Q.; Lu, P., Collective Synthesis of Chiral Tetrasubstituted Cyclobutanes Enabled by Enantioconvergent Negishi Cross-Coupling of Cyclobutenones. *Angewandte Chemie International Edition* **2023,** *62* (7), e202218008.

234. Teresa, J.; Velado, M.; Fernández de la Pradilla, R.; Viso, A.; Lozano, B.; Tortosa, M., Enantioselective Suzuki cross-coupling of 1,2-diboryl cyclopropanes. *Chemical Science* **2023,** *14* (6), 1575-1581.

235. Zuccarello, G.; Batiste, S. M.; Cho, H.; Fu, G. C., Enantioselective Synthesis of α-Aminoboronic Acid Derivatives via Copper-Catalyzed N-Alkylation. *J. Am. Chem. Soc.* **2023,** *145* (6), 3330-3334.

236. Wang, C.; Hu, X.; Xu, C.; Ge, Q.; Yang, Q.; Xiong, J.; Duan, W.-L., Synthesis of P-Stereogenic Phosphine Oxides via Nickel-Catalyzed Asymmetric Cross-Coupling of Secondary Phosphine Oxides with Alkenyl and Aryl Bromides. *Angewandte Chemie International Edition* **2023,** *62* (15), e202300011.

237. Hu, X.; Cheng-Sánchez, I.; Cuesta-Galisteo, S.; Nevado, C., Nickel-Catalyzed Enantioselective Electrochemical Reductive Cross-Coupling of Aryl Aziridines with Alkenyl Bromides. *J. Am. Chem. Soc.* **2023,** *145* (11), 6270-6279.

238. Yang, S.; Zheng, T.; Duan, L.; Xue, X.; Gu, Z., Atroposelective Three-Component Coupling of Cyclic Diaryliodoniums and Sodium Cyanate Enabled by the Dual-Role of Phenol. *Angewandte Chemie International Edition* **2023,** *62* (21), e202302749.

239. Li, Z.; Zhang, G. a.; Song, Y.; Li, M.; Li, Z.; Ding, W.; Wu, J., Copper-Catalyzed Enantioselective Decarboxylative Cyanation of Benzylic Acids Promoted by Hypervalent Iodine(III) Reagents. *Org. Lett.* **2023,** *25* (17), 3023-3028.

240. Gao, Y.; Zhang, B.; He, J.; Baran, P. S., Ni-Electrocatalytic Enantioselective Doubly Decarboxylative C(sp3)–C(sp3) Cross Coupling. *J. Am. Chem. Soc.* **2023,** *145* (21), 11518-11523.

241. Turro, R. F.; Wahlman, J. L. H.; Tong, Z. J.; Chen, X.; Yang, M.; Chen, E. P.; Hong, X.; Hadt, R. G.; Houk, K. N.; Yang, Y.-F.; Reisman, S. E., Mechanistic Investigation of Ni-Catalyzed Reductive Cross-Coupling of Alkenyl and Benzyl Electrophiles. *J. Am. Chem. Soc.* **2023,** *145* (27), 14705-14715.

242. Konowalchuk, D. J.; Hall, D. G., Divergent Synthesis of 1,2,3,4-Tetrasubstituted Cyclobutenes from a Common Scaffold: Enantioselective Desymmetrization by Dual-Catalyzed Photoredox Cross-Coupling. *Angewandte Chemie International Edition* **2023,** *62* (49), e202313503.

243. Chun, J.; Li, Y.; Xie, X.; Guo, K.; Zhao, D.; Chen, K.; Zhu, Y., Photoinduced Copper-Catalyzed Enantioconvergent Remote Alkynylation via 1,4-Heteroaryl Migration. *Org. Lett.* **2023,** *25* (42), 7739-7744.

244. Gao, Y.; Baran, P. S., Nickel-Catalyzed Enantioselective Decarboxylative Acylation: Rapid, Modular Access to α-Amino Ketones. *Angewandte Chemie International Edition* **2023,** *62* (50), e202315203.

245. Jia, Y.; Zhang, Z.; Yu, G.-M.; Jiang, X.; Lu, L.-Q.; Xiao, W.-J., Visible Light Induced Copper-Catalyzed Enantioselective Deaminative Arylation of Amino Acid Derivatives Assisted by Phenol. *Angewandte Chemie International Edition* **2023,** *62* (51), e202312102.

246. Tian, Y.; Li, X.-T.; Liu, J.-R.; Cheng, J.; Gao, A.; Yang, N.-Y.; Li, Z.; Guo, K.-X.; Zhang, W.; Wen, H.-T.; Li, Z.-L.; Gu, Q.-S.; Hong, X.; Liu, X.-Y., A general copper-catalysed enantioconvergent C(sp3)–S cross-coupling via biomimetic radical homolytic substitution. *Nature Chemistry* **2024,** *16* (3), 466-475.

247. Du, X.-Y.; Fang, J.-H.; Chen, J.-J.; Shen, B.; Liu, W.-L.; Zhang, J.-Y.; Ye, X.-M.; Yang, N.-Y.; Gu, Q.-S.; Li, Z.-L.; Yu, P.; Liu, X.-Y., Copper-Catalyzed Enantioconvergent Radical N-Alkylation of Diverse (Hetero)aromatic Amines. *J. Am. Chem. Soc.* **2024,** *146* (13), 9444-9454.

248. Guo, H.; Tan, D.; Merten, C.; Loh, C. C. J., Enantioconvergent and Site-Selective Etherification of Carbohydrate Polyols through Chiral Copper Radical Catalysis. *Angewandte Chemie International Edition* **2024,** *63* (48), e202409530.

249. Zhao, X.; Wang, C.; Yin, L.; Liu, W., Highly Enantioselective Decarboxylative Difluoromethylation. *J. Am. Chem. Soc.* **2024,** *146* (43), 29297-29304.

250. Preinfalk, A.; Oost, R.; Menger, M. F. S. J.; Simaan, M.; Lemouzy, S.; Senoner, S.; Shaaban, S.; Maryasin, B.; González, L.; Maulide, N., Enantioconvergent Negishi Cross-Couplings of Racemic Secondary Organozinc Reagents to Access Privileged Scaffolds: A Combined Experimental and Theoretical Study. *Angewandte Chemie International Edition* **2024,** *63* (50), e202414868.

251. Chen, S.; Ding, D.; Yin, L.; Wang, X.; Krause, J. A.; Liu, W., Overcoming Copper Reduction Limitation in Asymmetric Substitution: Aryl-Radical-Enabled Enantioconvergent Cyanation of Alkyl Iodides. *J. Am. Chem. Soc.* **2024,** *146* (46), 31982-31991.

4.6.5 CH Functionalization

1. Luo, Z. B.; Liu, Q. Z.; Gong, L. Z.; Cui, X.; Mi, A. Q.; Jiang, Y. Z., Novel achiral biphenol-derived diastereomeric oxovanadium(IV) complexes for highly enantioselective oxidative coupling of 2- naphthols. *Angew. Chem.-Int. Edit.* **2002,** *41* (23), 4532-+.

2. Gao, J.; Reibenspies, J. H.; Martell, A. E., Structurally defined catalysts for enantioselective oxidative coupling reactions. *Angew. Chem.-Int. Edit.* **2003,** *42* (48), 6008-6012.

3. Li, X. L.; Hewgley, J. B.; Mulrooney, C. A.; Yang, J. M.; Kozlowski, M. C., Enantioselective oxidative biaryl coupling reactions catalyzed by 1,5-diazadecalin metal complexes: Efficient formation of chiral functionalized BINOL derivatives. *J. Org. Chem.* **2003,** *68* (14), 5500-5511.

4. Mulrooney, C. A.; Li, X. L.; DiVirgilio, E. S.; Kozlowski, M. C., General approach for the synthesis of chiral perylenequinones via catalytic enantioselective oxidative biaryl coupling. *J. Am. Chem. Soc.* **2003,** *125* (23), 6856-6857.

5. Li, Z. P.; Li, C. J., Catalytic enantioselective alkynylation of prochiral sp(3) C-H bonds adjacent to a nitrogen atom. *Org. Lett.* **2004,** *6* (26), 4997-4999.

6. Guo, Q. X.; Wu, Z. J.; Luo, Z. B.; Liu, Q. Z.; Ye, J. L.; Luo, S. W.; Cun, L. F.; Gong, L. Z., Highly enantioselective oxidative couplings of 2-naphthols catalyzed by chiral bimetallic oxovanadium complexes with either oxygen or air as oxidant. *J. Am. Chem. Soc.* **2007,** *129* (45), 13927-13938.

7. Shi, B. F.; Maugel, N.; Zhang, Y. H.; Yu, J. Q., Pd-II-catalyzed enantioselective activation of C(sp(2))-H and C(sp(3))-H bonds using monoprotected amino acids as chiral ligands. *Angew. Chem.-Int. Edit.* **2008,** *47* (26), 4882-4886.

8. Hewgley, J. B.; Stahl, S. S.; Kozlowski, M. C., Mechanistic study of asymmetric oxidative biaryl coupling: Evidence for self-processing of the copper catalyst to achieve control of oxidase vs oxygenase activity. *J. Am. Chem. Soc.* **2008,** *130* (37), 12232-+.

9. Tsai, A. S.; Wilson, R. M.; Harada, H.; Bergman, R. G.; Ellman, J. A., Rhodium catalyzed enantioselective cyclization of substituted imidazoles via C-H bond activation. *Chem. Commun.* **2009,** (26), 3910-3912.

10. Tan, Q. T.; Hayashi, M., Asymmetric Desymmetrization of 4,5-Epoxycyclohex-1-ene by Enantioselective Allylic Oxidation. *Org. Lett.* **2009,** *11* (15), 3314-3317.

11. Seiser, T.; Roth, O. A.; Cramer, N., Enantioselective Synthesis of Indanols from tert-Cyclobutanols Using a Rhodium-Catalyzed C-C/C-H Activation Sequence. *Angew. Chem.-Int. Edit.* **2009,** *48* (34), 6320-6323.

12. Shi, B. F.; Zhang, Y. H.; Lam, J. K.; Wang, D. H.; Yu, J. Q., Pd(II)-Catalyzed Enantioselective C-H Olefination of Diphenylacetic Acids. *J. Am. Chem. Soc.* **2010,** *132* (2), 460-+.

13. Peng, H. M.; Dai, L. X.; You, S. L., Enantioselective Palladium-Catalyzed Direct Alkylation and Olefination Reaction of Simple Arenes. *Angew. Chem.-Int. Edit.* **2010,** *49* (34), 5826-5828.

14. Anas, S.; Cordi, A.; Kagan, H. B., Enantioselective synthesis of 2-methyl indolines by palladium catalysed asymmetric C(sp(3))-H activation/cyclisation. *Chem. Commun.* **2011,** *47* (41), 11483-11485.

15. Saget, T.; Lemouzy, S. J.; Cramer, N., Chiral Monodentate Phosphines and Bulky Carboxylic Acids: Cooperative Effects in Palladium-Catalyzed Enantioselective C(sp3)-H Functionalization. *Angew. Chem.-Int. Edit.* **2012,** *51* (9), 2238-2242.

16. Katayev, D.; Nakanishi, M.; Burgi, T.; Kundig, E. P., Asymmetric C(sp(3))-H/C(Ar) coupling reactions. Highly enantio-enriched indolines via regiodivergent reaction of a racemic mixture. *Chemical Science* **2012,** *3* (5), 1422-1425.

17. Shintani, R.; Otomo, H.; Ota, K.; Hayashi, T., Palladium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles via Enantioselective C-H Bond Functionalization. *J. Am. Chem. Soc.* **2012,** *134* (17), 7305-7308.

18. Hyster, T. K.; Knorr, L.; Ward, T. R.; Rovis, T., Biotinylated Rh(III) Complexes in Engineered Streptavidin for Accelerated Asymmetric C-H Activation. *Science* **2012,** *338* (6106), 500-503.

19. Ye, B. H.; Cramer, N., Chiral Cyclopentadienyl Ligands as Stereocontrolling Element in Asymmetric C-H Functionalization. *Science* **2012,** *338* (6106), 504-506.

20. Saget, T.; Cramer, N., Palladium(0)-Catalyzed Enantioselective C-H Arylation of Cyclopropanes: Efficient Access to Functionalized Tetrahydroquinolines. *Angew. Chem.-Int. Edit.* **2012,** *51* (51), 12842-12845.

21. Gao, D. W.; Shi, Y. C.; Gu, Q.; Zhao, Z. L.; You, S. L., Enantioselective Synthesis of Planar Chiral Ferrocenes via Palladium-Catalyzed Direct Coupling with Arylboronic Acids. *J. Am. Chem. Soc.* **2013,** *135* (1), 86-89.

22. Ye, B. H.; Cramer, N., A Tunable Class of Chiral Cp Ligands for Enantioselective Rhodium(III)-Catalyzed C-H Allylations of Benzamides. *J. Am. Chem. Soc.* **2013,** *135* (2), 636-639.

23. Cheng, X. F.; Li, Y.; Su, Y. M.; Yin, F.; Wang, J. Y.; Sheng, J.; Vora, H. U.; Wang, X. S.; Yu, J. Q., Pd(II)-Catalyzed Enantioselective C-H Activation/C-O Bond Formation: Synthesis of Chiral Benzofuranones. *J. Am. Chem. Soc.* **2013,** *135* (4), 1236-1239.

24. Larionov, E.; Nakanishi, M.; Katayev, D.; Besnard, C.; Kundig, E. P., Scope and mechanism of asymmetric C(sp(3))-H/C(Ar)-X coupling reactions: computational and experimental study. *Chemical Science* **2013,** *4* (5), 1995-2005.

25. Steffen, P.; Unkelbach, C.; Christmann, M.; Hiller, W.; Strohmann, C., Catalytic and Stereoselective ortho-Lithiation of a Ferrocene Derivative. *Angew. Chem.-Int. Edit.* **2013,** *52* (37), 9836-9840.

26. Chu, L.; Wang, X. C.; Moore, C. E.; Rheingold, A. L.; Yu, J. Q., Pd-Catalyzed Enantioselective C-H Iodination: Asymmetric Synthesis of Chiral Diarylmethylamines. *J. Am. Chem. Soc.* **2013,** *135* (44), 16344-16347.

27. Deng, R.; Huang, Y.; Ma, X.; Li, G.; Zhu, R.; Wang, B.; Kang, Y.-B.; Gu, Z., Palladium-Catalyzed Intramolecular Asymmetric C-H Functionalization/Cyclization Reaction of Metallocenes: An Efficient Approach toward the Synthesis of Planar Chiral Metallocene Compounds. *J. Am. Chem. Soc.* **2014,** *136* (12), 4472-4475.

28. Gao, D.-W.; Yin, Q.; Gu, Q.; You, S.-L., Enantioselective Synthesis of Planar Chiral Ferrocenes via Pd(0)-Catalyzed Intramolecular Direct C-H Bond Arylation. *J. Am. Chem. Soc.* **2014,** *136* (13), 4841-4844.

29. Shibata, T.; Shizuno, T., Iridium-Catalyzed Enantioselective C H Alkylation of Ferrocenes with Alkenes Using Chiral Diene Ligands**. *Angew. Chem.-Int. Edit.* **2014,** *53* (21), 5410-5413.

30. Xiao, K.-J.; Lin, D. W.; Miura, M.; Zhu, R.-Y.; Gong, W.; Wasa, M.; Yu, J.-Q., Palladium(II)-Catalyzed Enantioselective C(sp(3))-H Activation Using a Chiral Hydroxamic Acid Ligand. *J. Am. Chem. Soc.* **2014,** *136* (22), 8138-8142.

31. Ye, B.; Cramer, N., Asymmetric Synthesis of Isoindolones by Chiral Cyclopentadienyl-Rhodium(III)-Catalyzed C-H Functionalizations. *Angew. Chem.-Int. Edit.* **2014,** *53* (30), 7896-7899.

32. Pedroni, J.; Boghi, M.; Saget, T.; Cramer, N., Access to beta-Lactams by Enantioselective Palladium(0)-Catalyzed C(sp(3))-H Alkylation. *Angew. Chem.-Int. Edit.* **2014,** *53* (34), 9064-9067.

33. Du, Z.-J.; Guan, J.; Wu, G.-J.; Xu, P.; Gao, L.-X.; Han, F.-S., Pd(II)-Catalyzed Enantioselective Synthesis of P-Stereogenic Phosphinamides via Desymmetric C-H Arylation. *J. Am. Chem. Soc.* **2015,** *137* (2), 632-635.

34. Chan, K. S. L.; Fu, H.-Y.; Yu, J.-Q., Palladium(II)-Catalyzed Highly Enantioselective C-H Arylation of Cyclopropylmethylamines. *J. Am. Chem. Soc.* **2015,** *137* (5), 2042-2046.

35. Zheng, J.; Wang, S. B.; Zheng, C.; You, S. L., Asymmetric Dearomatization of Naphthols via a Rh-Catalyzed C(sp(2))-H Functionalization/Annulation Reaction. *J. Am. Chem. Soc.* **2015,** *137* (15), 4880-4883.

36. Zhang, Q. W.; An, K.; Liu, L. C.; Yue, Y.; He, W., Rhodium-Catalyzed Enantioselective Intramolecular CH Silylation for the Syntheses of Planar-Chiral Metallocene Siloles. *Angew. Chem.-Int. Edit.* **2015,** *54* (23), 6918-6921.

37. Lee, T.; Wilson, T. W.; Berg, R.; Ryberg, P.; Hartwig, J. F., Rhodium-Catalyzed Enantioselective Silylation of Arene C-H Bonds: Desymmetrization of Diarylmethanols. *J. Am. Chem. Soc.* **2015,** *137* (21), 6742-6745.

38. Chidipudi, S. R.; Burns, D. J.; Khan, I.; Lam, H. W., Enantioselective Synthesis of Spiroindenes by Enol-Directed Rhodium(III)-Catalyzed C-H Functionalization and Spiroannulation. *Angew. Chem.-Int. Edit.* **2015,** *54* (47), 13975-13979.

39. Wang, P. S.; Liu, P.; Zhai, Y. J.; Lin, H. C.; Han, Z. Y.; Gong, L. Z., Asymmetric Allylic C-H Oxidation for the Synthesis of Chromans. *J. Am. Chem. Soc.* **2015,** *137* (40), 12732-12735.

40. Xiao, K. J.; Chu, L.; Yu, J. Q., Enantioselective C-H Olefination of alpha-Hydroxy and alpha-Amino Phenylacetic Acids by Kinetic Resolution. *Angew. Chem.-Int. Edit.* **2016,** *55* (8), 2856-2860.

41. Gao, D. W.; Gu, Q.; You, S. L., An Enantioselective Oxidative C-H/C-H Cross-Coupling Reaction: Highly Efficient Method To Prepare Planar Chiral Ferrocenes. *J. Am. Chem. Soc.* **2016,** *138* (8), 2544-2547.

42. Hatano, M.; Ebe, Y.; Nishimura, T.; Yorimitsu, H., Asymmetric Alkylation of N-Sulfonylbenzamides with Vinyl Ethers via C-H Bond Activation Catalyzed by Hydroxoiridium/Chiral Diene Complexes. *J. Am. Chem. Soc.* **2016,** *138* (12), 4010-4013.

43. Zheng, J.; Cui, W. J.; Zheng, C.; You, S. L., Synthesis and Application of Chiral Spiro Cp Ligands in Rhodium-Catalyzed Asymmetric Oxidative Coupling of Biaryl Compounds with Alkenes. *J. Am. Chem. Soc.* **2016,** *138* (16), 5242-5245.

44. Lee, T.; Hartwig, J. F., Rhodium-Catalyzed Enantioselective Silylation of Cyclopropyl C-H Bonds. *Angew. Chem.-Int. Edit.* **2016,** *55* (30), 8723-8727.

45. Xiao, K. J.; Chu, L.; Chen, G.; Yu, J. Q., Kinetic Resolution of Benzylamines via Palladium(II)-Catalyzed C-H Cross-Coupling. *J. Am. Chem. Soc.* **2016,** *138* (24), 7796-7800.

46. Ammann, S. E.; Liu, W.; White, M. C., Enantioselective Allylic C-H Oxidation of Terminal Olefins to Isochromans by Palladium(II)/Chiral Sulfoxide Catalysis. *Angew. Chem.-Int. Edit.* **2016,** *55* (33), 9571-9575.

47. Chen, G.; Gong, W.; Zhuang, Z.; Andra, M. S.; Chen, Y. Q.; Hong, X.; Yang, Y. F.; Liu, T.; Houk, K. N.; Yu, J. Q., Ligand-accelerated enantioselective methylene C(sp(3))-H bond activation. *Science* **2016,** *353* (6303), 1023-1027.

48. Zhang, W.; Wang, F.; McCann, S. D.; Wang, D. H.; Chen, P. H.; Stahl, S. S.; Liu, G. S., Enantioselective cyanation of benzylic C-H bonds via copper-catalyzed radical relay. *Science* **2016,** *353* (6303), 1014-1018.

49. Wang, H.; Tong, H. R.; He, G.; Chen, G., An Enantioselective Bidentate Auxiliary Directed Palladium-Catalyzed Benzylic C-H Arylation of Amines Using a BINOL Phosphate Ligand. *Angew. Chem.-Int. Edit.* **2016,** *55* (49), 15387-15391.

50. Narute, S.; Parnes, R.; Toste, F. D.; Pappo, D., Enantioselective Oxidative Homocoupling and Cross-Coupling of 2-Naphthols Catalyzed by Chiral Iron Phosphate Complexes. *J. Am. Chem. Soc.* **2016,** *138* (50), 16553-16560.

51. Sun, Y.; Cramer, N., Rhodium(III)-Catalyzed Enantiotopic C-HActivation Enables Access to P-Chiral Cyclic Phosphinamides. *Angew. Chem.-Int. Edit.* **2017,** *56* (1), 364-367.

52. Yang, L.; Melot, R.; Neuburger, M.; Baudoin, O., Palladium(0)-catalyzed asymmetric C(sp(3))-H arylation using a chiral binol-derived phosphate and an achiral ligand. *Chemical Science* **2017,** *8* (2), 1344-1349.

53. Su, B.; Zhou, T. G.; Li, X. W.; Shao, X. R.; Xu, P. L.; Wu, W. L.; Hartwig, J. F.; Shi, Z. J., A Chiral Nitrogen Ligand for Enantioselective, Iridium-Catalyzed Silylation of Aromatic C-H Bonds. *Angew. Chem.-Int. Edit.* **2017,** *56* (4), 1092-1096.

54. Smalley, A. P.; Cuthbertson, J. D.; Gaunt, M. J., Palladium-Catalyzed Enantioselective C-H Activation of Aliphatic Amines Using Chiral Anionic BINOL-Phosphoric Acid Ligands. *J. Am. Chem. Soc.* **2017,** *139* (4), 1412-1415.

55. Wu, Q. F.; Shen, P. X.; He, J.; Wang, X. B.; Zhang, F.; Shao, Q.; Zhu, R. Y.; Mapelli, C.; Qiao, J. X.; Poss, M. A.; Yu, J. Q., Formation of alpha-chiral centers by asymmetric beta-C(sp(3))-H arylation, alkenylation, and alkynylation. *Science* **2017,** *355* (6324), 499-+.

56. He, J.; Shao, Q.; Wu, Q. F.; Yu, J. Q., Pd(II)-Catalyzed Enantioselective C(sp(3))-H Borylation. *J. Am. Chem. Soc.* **2017,** *139* (9), 3344-3347.

57. Lee, T. G.; Hartwig, J. F., Mechanistic Studies on Rhodium-Catalyzed Enantioselective Silylation of Aryl C-H Bonds. *J. Am. Chem. Soc.* **2017,** *139* (13), 4879-4886.

58. Yao, Q. J.; Zhang, S.; Zhan, B. B.; Shi, B. F., Atroposelective Synthesis of Axially Chiral Biaryls by Palladium-Catalyzed Asymmetric C-H Olefination Enabled by a Transient Chiral Auxiliary. *Angew. Chem.-Int. Edit.* **2017,** *56* (23), 6617-6621.

59. Su, B.; Zhou, T. G.; Xu, P. L.; Shi, Z. J.; Hartwig, J. F., Enantioselective Borylation of Aromatic C-H Bonds with Chiral Dinitrogen Ligands. *Angew. Chem.-Int. Edit.* **2017,** *56* (25), 7205-7208.

60. Pedroni, J.; Cramer, N., Enantioselective C-H Functionalization-Addition Sequence Delivers Densely Substituted 3-Azabicyclo 3.1.0 hexanes. *J. Am. Chem. Soc.* **2017,** *139* (36), 12398-12401.

61. Su, B.; Hartwig, J. F., Ir-Catalyzed Enantioselective, Intramolecular Silylation of Methyl C-H Bonds. *J. Am. Chem. Soc.* **2017,** *139* (35), 12137-12140.

62. Yang, L.; Neuburger, M.; Baudoin, O., Chiral Bifunctional Phosphine-Carboxylate Ligands for Palladium(0)-Catalyzed Enantioselective C-H Arylation. *Angew. Chem.-Int. Edit.* **2018,** *57* (5), 1394-1398.

63. Liao, G.; Yao, Q. J.; Zhang, Z. Z.; Wu, Y. J.; Huang, D. Y.; Shi, B. F., Scalable, Stereocontrolled Formal Syntheses of (+)-Isoschizandrin and (+)-Steganone: Development and Applications of Palladium(II)-Catalyzed Atroposelective C-H Alkynylation. *Angew. Chem.-Int. Edit.* **2018,** *57* (14), 3661-3665.

64. Sun, Y.; Cramer, N., Tailored trisubstituted chiral (CpRhIII)-Rh-x catalysts for kinetic resolutions of phosphinic amides. *Chemical Science* **2018,** *9* (11), 2981-2985.

65. Zhu, Y. C.; Li, Y.; Zhang, B. C.; Zhang, F. X.; Yang, Y. N.; Wang, X. S., Palladium-Catalyzed Enantioselective C-H Olefination of Diaryl Sulfoxides through Parallel Kinetic Resolution and Desymmetrization. *Angew. Chem.-Int. Edit.* **2018,** *57* (18), 5129-5133.

66. Wang, Y.; Wen, X.; Cui, X.; Zhang, X. P., Enantioselective Radical Cyclization for Construction of 5-Membered Ring Structures by Metalloradical C-H Alkylation. *J. Am. Chem. Soc.* **2018,** *140* (14), 4792-4796.

67. Shao, Q.; Wu, Q. F.; He, J.; Yu, J. Q., Enantioselective gamma-C(sp(3))-H Activation of Alkyl Amines via Pd(II)/Pd(0) Catalysis. *J. Am. Chem. Soc.* **2018,** *140* (16), 5322-5325.

68. Shen, P. X.; Hu, L.; Shao, Q.; Hong, K.; Yu, J. Q., Pd(II)-Catalyzed Enantioselective C(sp(3))-H Arylation of Free Carboxylic Acids. *J. Am. Chem. Soc.* **2018,** *140* (21), 6545-6549.

69. Gressies, S.; Klauck, F. J. R.; Kim, J. H.; Daniliuc, C. G.; Glorius, F., Ligand-Enabled Enantioselective C-sp3-H Activation of Tetrahydroquinolines and Saturated Aza-Heterocycles by Rh-I. *Angew. Chem.-Int. Edit.* **2018,** *57* (31), 9950-9954.

70. Jang, Y. S.; Wozniak, L.; Pedroni, J.; Cramer, N., Access to P- and Axially Chiral Biaryl Phosphine Oxides by Enantioselective (CpIrIII)-Ir-x-Catalyzed C-H Arylations. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12901-12905.

71. Grosheva, D.; Cramer, N., Enantioselective Access to 1H-Isoindoles with Quaternary Stereogenic Centers by Palladium(0)-Catalyzed C-H Functionalization. *Angew. Chem.-Int. Edit.* **2018,** *57* (41), 13644-13647.

72. Pesciaioli, F.; Dhawa, U.; Oliveira, J. C. A.; Yin, R. X.; John, M.; Ackermann, L., Enantioselective Cobalt(III)-Catalyzed C-H Activation Enabled by Chiral Carboxylic Acid Cooperation. *Angew. Chem.-Int. Edit.* **2018,** *57* (47), 15425-15429.

73. Sun, Y.; Cramer, N., Enantioselective Synthesis of Chiral-at-Sulfur 1,2-Benzothiazines by CpxRhIII-Catalyzed C−H Functionalization of Sulfoximines. *Angewandte Chemie International Edition* **2018,** *57* (47), 15539-15543.

74. Jiang, H. J.; Zhong, X. M.; Yu, J.; Zhang, Y.; Zhang, X. H.; Wu, Y. D.; Gong, L. Z., Assembling a Hybrid Pd Catalyst from a Chiral Anionic Co-III Complex and Ligand for Asymmetric C(sp(3))-H Functionalization. *Angew. Chem.-Int. Edit.* **2019,** *58* (6), 1803-1807.

75. Fukagawa, S.; Kato, Y.; Tanaka, R.; Kojima, M.; Yoshino, T.; Matsunaga, S., Enantioselective C(sp3)–H Amidation of Thioamides Catalyzed by a CobaltIII/Chiral Carboxylic Acid Hybrid System. *Angewandte Chemie International Edition* **2019,** *58* (4), 1153-1157.

76. Hu, L.; Shen, P. X.; Shao, Q.; Hong, K.; Qiao, J. X.; Yu, J. Q., Pd-II-Catalyzed Enantioselective C(sp(3))-H Activation/Cross-Coupling Reactions of Free Carboxylic Acids. *Angew. Chem.-Int. Edit.* **2019,** *58* (7), 2134-2138.

77. Li, G. Z.; Jiang, J. J.; Xie, H.; Wang, J., Introducing the Chiral Transient Directing Group Strategy to Rhodium(III)-Catalyzed Asymmetric C-H Activation. *Chem.-Eur. J.* **2019,** *25* (18), 4688-4694.

78. Han, Y. Q.; Ding, Y.; Zhou, T.; Yan, S. Y.; Song, H.; Shi, B. F., Pd(II)-Catalyzed Enantioselective Alkynylation of Unbiased Methylene C(sp(3))-H Bonds Using 3,3 '-Fluorinated-BINOL as a Chiral Ligand. *J. Am. Chem. Soc.* **2019,** *141* (11), 4558-4563.

79. Li, H. H.; Yan, X. Q.; Zhang, J. T.; Guo, W. C.; Jiang, J. J.; Wang, J., Enantioselective Synthesis of C-N Axially Chiral N-Aryloxindoles by Asymmetric Rhodium-Catalyzed Dual C-H Activation. *Angew. Chem.-Int. Edit.* **2019,** *58* (20), 6732-6736.

80. Zou, X. L.; Zhao, H. N.; Li, Y. W.; Gao, Q.; Ke, Z. F.; Xu, S. M., Chiral Bidentate Boryl Ligand Enabled Iridium-Catalyzed Asymmetric C(sp(2))-H Borylation of Diarylmethylamines. *J. Am. Chem. Soc.* **2019,** *141* (13), 5334-5342.

81. Lu, F. D.; Liu, D.; Zhu, L.; Lu, L. Q.; Yang, Q.; Zhou, Q. Q.; Wei, Y.; Lan, Y.; Xiao, W. J., Asymmetric Propargylic Radical Cyanation Enabled by Dual Organophotoredox and Copper Catalysis. *J. Am. Chem. Soc.* **2019,** *141* (15), 6167-6172.

82. Ozols, K.; Jang, Y. S.; Cramer, N., Chiral Cyclopentadienyl Cobalt(III) Complexes Enable Highly Enantioselective 3d-Metal-Catalyzed C-H Functionalizations. *J. Am. Chem. Soc.* **2019,** *141* (14), 5675-5680.

83. Reyes, R. L.; Iwai, T.; Maeda, S.; Sawamura, M., Iridium-Catalyzed Asymmetric Borylation of Unactivated Methylene C(sp(3))-H Bonds. *J. Am. Chem. Soc.* **2019,** *141* (17), 6817-6821.

84. Wang, H.; Park, Y.; Bai, Z. Q.; Chang, S.; He, G.; Chen, G., Iridium-Catalyzed Enantioselective C(sp(3))-H Amidation Controlled by Attractive Noncovalent Interactions. *J. Am. Chem. Soc.* **2019,** *141* (17), 7194-7201.

85. Brauns, M.; Cramer, N., Efficient Kinetic Resolution of Sulfur-Stereogenic Sulfoximines by Exploiting (CpRhIII)-Rh-X-Catalyzed C-H Functionalization. *Angew. Chem.-Int. Edit.* **2019,** *58* (26), 8902-8906.

86. Tian, J.-M.; Wang, A.-F.; Yang, J.-S.; Zhao, X.-J.; Tu, Y.-Q.; Zhang, S.-Y.; Chen, Z.-M., Copper-Complex-Catalyzed Asymmetric Aerobic Oxidative Cross-Coupling of 2-Naphthols: Enantioselective Synthesis of 3,3′-Substituted C1-Symmetric BINOLs. *Angewandte Chemie International Edition* **2019,** *58* (32), 11023-11027.

87. Shi, Y. J.; Gao, Q.; Xu, S. M., Chiral Bidentate Boryl Ligand Enabled Iridium-Catalyzed Enantioselective C(sp(3))-H Borylation of Cyclopropanes. *J. Am. Chem. Soc.* **2019,** *141* (27), 10599-10604.

88. Lang, K.; Torker, S.; Wojtas, L.; Zhang, X. P., Asymmetric Induction and Enantiodivergence in Catalytic Radical C-H Amination via Enantiodifferentiative H-Atom Abstraction and Stereoretentive Radical Substitution. *J. Am. Chem. Soc.* **2019,** *141* (31), 12388-12396.

89. Li, Z. Y.; Handi, H.; Lakmal, C.; Qan, X. L.; Zhu, Z. Y.; Donnadieu, B.; McClain, S. J.; Xu, X.; Cui, X., Ruthenium-Catalyzed Enantioselective C-H Functionalization: A Practical Access to Optically Active Indoline Derivatives. *J. Am. Chem. Soc.* **2019,** *141* (40), 15730-15736.

90. Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S., Catalytic Enantioselective Methylene C(sp3)−H Amidation of 8-Alkylquinolines Using a Cp*RhIII/Chiral Carboxylic Acid System. *Angewandte Chemie International Edition* **2019,** *58* (50), 18154-18158.

91. Li, J. Y.; Zhang, Z. H.; Wu, L. Q.; Zhang, W.; Chen, P. H.; Lin, Z. Y.; Liu, G. S., Site-specific allylic C-H bond functionalization with a copper-bound N-centred radical. *Nature* **2019,** *574* (7779), 516-+.

92. Gu, Q. S.; Li, Z. L.; Liu, X. Y., Copper(I)-Catalyzed Asymmetric Reactions Involving Radicals. *Accounts of Chemical Research* **2020,** *53* (1), 170-181.

93. Zheng, G.; Zhou, Z.; Zhu, G.; Zhai, S.; Xu, H.; Duan, X.; Yi, W.; Li, X., Rhodium(III)-Catalyzed Enantio- and Diastereoselective C−H Cyclopropylation of N-Phenoxylsulfonamides: Combined Experimental and Computational Studies. *Angewandte Chemie International Edition* **2020,** *59* (7), 2890-2896.

94. Nguyen, Q. H.; Guo, S. M.; Royal, T.; Baudoin, O.; Cramer, N., Intermolecular Palladium(0)-Catalyzed Atropo-enantioselective C-H Arylation of Heteroarenes. *J. Am. Chem. Soc.* **2020,** *142* (5), 2161-2167.

95. Xiao, L.-J.; Hong, K.; Luo, F.; Hu, L.; Ewing, W. R.; Yeung, K.-S.; Yu, J.-Q., PdII-Catalyzed Enantioselective C(sp3)–H Arylation of Cyclobutyl Ketones Using a Chiral Transient Directing Group. *Angewandte Chemie International Edition* **2020,** *59* (24), 9594-9600.

96. Dhawa, U.; Tian, C.; Wdowik, T.; Oliveira, J. C. A.; Hao, J.; Ackermann, L., Enantioselective Pallada-Electrocatalyzed C−H Activation by Transient Directing Groups: Expedient Access to Helicenes. *Angewandte Chemie International Edition* **2020,** *59* (32), 13451-13457.

97. Wang, F.; Qi, Z.; Zhao, Y.; Zhai, S.; Zheng, G.; Mi, R.; Huang, Z.; Zhu, X.; He, X.; Li, X., Rhodium(III)-Catalyzed Atroposelective Synthesis of Biaryls by C−H Activation and Intermolecular Coupling with Sterically Hindered Alkynes. *Angewandte Chemie International Edition* **2020,** *59* (32), 13288-13294.

98. Jiang, H.-J.; Zhong, X.-M.; Liu, Z.-Y.; Geng, R.-L.; Li, Y.-Y.; Wu, Y.-D.; Zhang, X.; Gong, L.-Z., Hybrid Palladium Catalyst Assembled from Chiral Phosphoric Acid and Thioamide for Enantioselective β-C(sp3)−H Arylation. *Angewandte Chemie International Edition* **2020,** *59* (31), 12774-12778.

99. Wang, C.-Y.; Qin, Z.-Y.; Huang, Y.-L.; Hou, Y.-M.; Jin, R.-X.; Li, C.; Wang, X.-S., Enantioselective Copper-Catalyzed Remote C(sp3)–H Alkynylation of Linear Primary Sulfonamides. *Org. Lett.* **2020,** *22* (10), 4006-4009.

100. Fu, L.; Zhang, Z.; Chen, P.; Lin, Z.; Liu, G., Enantioselective Copper-Catalyzed Alkynylation of Benzylic C–H Bonds via Radical Relay. *J. Am. Chem. Soc.* **2020,** *142* (28), 12493-12500.

101. Zhuang, Z.; Yu, J.-Q., Pd(II)-Catalyzed Enantioselective γ-C(sp3)–H Functionalizations of Free Cyclopropylmethylamines. *J. Am. Chem. Soc.* **2020,** *142* (28), 12015-12019.

102. Chen, L.; Yang, Y.; Liu, L.; Gao, Q.; Xu, S., Iridium-Catalyzed Enantioselective α-C(sp3)–H Borylation of Azacycles. *J. Am. Chem. Soc.* **2020,** *142* (28), 12062-12068.

103. Wang, S.-G.; Cramer, N., Asymmetric CpxRh(III)-Catalyzed Acrylic Acid C–H Functionalization with Allenes Provides Chiral γ-Lactones. *ACS Catalysis* **2020,** *10* (15), 8231-8236.

104. Chen, H.; Jin, W.; Yu, S., Enantioselective Remote C(sp3)–H Cyanation via Dual Photoredox and Copper Catalysis. *Org. Lett.* **2020,** *22* (15), 5910-5914.

105. Han, Y.-Q.; Yang, X.; Kong, K.-X.; Deng, Y.-T.; Wu, L.-S.; Ding, Y.; Shi, B.-F., Synthesis of Acyclic Aliphatic Amides with Contiguous Stereogenic Centers via Palladium-Catalyzed Enantio-, Chemo- and Diastereoselective Methylene C(sp3)−H arylation. *Angewandte Chemie International Edition* **2020,** *59* (46), 20455-20458.

106. Farr, C. M. B.; Kazerouni, A. M.; Park, B.; Poff, C. D.; Won, J.; Sharp, K. R.; Baik, M.-H.; Blakey, S. B., Designing a Planar Chiral Rhodium Indenyl Catalyst for Regio- and Enantioselective Allylic C–H Amidation. *J. Am. Chem. Soc.* **2020,** *142* (32), 13996-14004.

107. Reyes Ronald, L.; Sato, M.; Iwai, T.; Suzuki, K.; Maeda, S.; Sawamura, M., Asymmetric remote C–H borylation of aliphatic amides and esters with a modular iridium catalyst. *Science* **2020,** *369* (6506), 970-974.

108. Hill, D. E.; Yu, J.-Q.; Blackmond, D. G., Insights into the Role of Transient Chiral Mediators and Pyridone Ligands in Asymmetric Pd-Catalyzed C–H Functionalization. *The Journal of Organic Chemistry* **2020,** *85* (21), 13674-13679.

109. Shu, X.; Huan, L.; Huang, Q.; Huo, H., Direct Enantioselective C(sp3)–H Acylation for the Synthesis of α-Amino Ketones. *J. Am. Chem. Soc.* **2020,** *142* (45), 19058-19064.

110. Genov, G. R.; Douthwaite, J. L.; Lahdenperä, A. S. K.; Gibson, D. C.; Phipps, R. J., Enantioselective remote C–H activation directed by a chiral cation. *Science* **2020,** *367* (6483), 1246-1251.

111. Su, X.-L.; Ye, L.; Chen, J.-J.; Liu, X.-D.; Jiang, S.-P.; Wang, F.-L.; Liu, L.; Yang, C.-J.; Chang, X.-Y.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y., Copper-Catalyzed Enantioconvergent Cross-Coupling of Racemic Alkyl Bromides with Azole C(sp2)−H Bonds. *Angewandte Chemie International Edition* **2021,** *60* (1), 380-384.

112. Savary, D.; Baudoin, O., Enantioselective Pd0-Catalyzed C(sp2)–H Arylation for the Synthesis of Chiral Warped Molecules. *Angewandte Chemie International Edition* **2021,** *60* (10), 5136-5140.

113. Tian, D.; Xu, R.; Zhu, J.; Huang, J.; Dong, W.; Claverie, J.; Tang, W., Asymmetric Hydroesterification of Diarylmethyl Carbinols. *Angewandte Chemie International Edition* **2021,** *60* (12), 6305-6309.

114. Sun, L.; Chen, H.; Liu, B.; Chang, J.; Kong, L.; Wang, F.; Lan, Y.; Li, X., Rhodium-Catalyzed Atroposelective Construction of Indoles via C−H Bond Activation. *Angewandte Chemie International Edition* **2021,** *60* (15), 8391-8395.

115. Melot, R.; Zuccarello, M.; Cavalli, D.; Niggli, N.; Devereux, M.; Bürgi, T.; Baudoin, O., Palladium(0)-Catalyzed Enantioselective Intramolecular Arylation of Enantiotopic Secondary C−H Bonds. *Angewandte Chemie International Edition* **2021,** *60* (13), 7245-7250.

116. Wang, Q.; Zhang, W.-W.; Zheng, C.; Gu, Q.; You, S.-L., Enantioselective Synthesis of Azoniahelicenes by Rh-Catalyzed C–H Annulation with Alkynes. *J. Am. Chem. Soc.* **2021,** *143* (1), 114-120.

117. Chen, X.; Zhao, J.; Dong, M.; Yang, N.; Wang, J.; Zhang, Y.; Liu, K.; Tong, X., Pd(0)-Catalyzed Asymmetric Carbohalogenation: H-Bonding-Driven C(sp3)–Halogen Reductive Elimination under Mild Conditions. *J. Am. Chem. Soc.* **2021,** *143* (4), 1924-1931.

118. Lou, S.-J.; Zhuo, Q.; Nishiura, M.; Luo, G.; Hou, Z., Enantioselective C–H Alkenylation of Ferrocenes with Alkynes by Half-Sandwich Scandium Catalyst. *J. Am. Chem. Soc.* **2021,** *143* (6), 2470-2476.

119. Guo, Y.; Liu, M.-M.; Zhu, X.; Zhu, L.; He, C., Catalytic Asymmetric Synthesis of Silicon-Stereogenic Dihydrodibenzosilines: Silicon Central-to-Axial Chirality Relay. *Angewandte Chemie International Edition* **2021,** *60* (25), 13887-13891.

120. Zhou, T.; Qian, P.-F.; Li, J.-Y.; Zhou, Y.-B.; Li, H.-C.; Chen, H.-Y.; Shi, B.-F., Efficient Synthesis of Sulfur-Stereogenic Sulfoximines via Ru(II)-Catalyzed Enantioselective C–H Functionalization Enabled by Chiral Carboxylic Acid. *J. Am. Chem. Soc.* **2021,** *143* (18), 6810-6816.

121. Wu, Y.-J.; Xie, P.-P.; Zhou, G.; Yao, Q.-J.; Hong, X.; Shi, B.-F., Atroposelective synthesis of N-aryl peptoid atropisomers via a palladium(ii)-catalyzed asymmetric C–H alkynylation strategy. *Chemical Science* **2021,** *12* (27), 9391-9397.

122. Woźniak, Ł.; Cramer, N., Atropo-Enantioselective Oxidation-Enabled Iridium(III)-Catalyzed C−H Arylations with Aryl Boronic Esters. *Angewandte Chemie International Edition* **2021,** *60* (34), 18532-18536.

123. Qi, R.; Wang, C.; Huo, Y.; Chai, H.; Wang, H.; Ma, Z.; Liu, L.; Wang, R.; Xu, Z., Visible Light Induced Cu-Catalyzed Asymmetric C(sp3)–H Alkylation. *J. Am. Chem. Soc.* **2021,** *143* (32), 12777-12783.

124. Yuan, W.-K.; Shi, B.-F., Synthesis of Chiral Spirolactams via Sequential C−H Olefination/Asymmetric [4+1] Spirocyclization under a Simple CoII/Chiral Spiro Phosphoric Acid Binary System. *Angewandte Chemie International Edition* **2021,** *60* (43), 23187-23192.

125. Lu, R.; Yang, T.; Chen, X.; Fan, W.; Chen, P.; Lin, Z.; Liu, G., Enantioselective Copper-Catalyzed Radical Cyanation of Propargylic C–H Bonds: Easy Access to Chiral Allenyl Nitriles. *J. Am. Chem. Soc.* **2021,** *143* (36), 14451-14457.

126. Liu, L.; Guo, K.-X.; Tian, Y.; Yang, C.-J.; Gu, Q.-S.; Li, Z.-L.; Ye, L.; Liu, X.-Y., Copper-Catalyzed Intermolecular Enantioselective Radical Oxidative C(sp3)−H/C(sp)−H Cross-Coupling with Rationally Designed Oxazoline-Derived N,N,P(O)-Ligands. *Angewandte Chemie International Edition* **2021,** *60* (51), 26710-26717.

127. Dhawa, U.; Wdowik, T.; Hou, X.; Yuan, B.; Oliveira, J. C. A.; Ackermann, L., Enantioselective palladaelectro-catalyzed C–H olefinations and allylations for N–C axial chirality. *Chemical Science* **2021,** *12* (42), 14182-14188.

128. Mukherjee, K.; Grimblat, N.; Sau, S.; Ghosh, K.; Shankar, M.; Gandon, V.; Sahoo, A. K., Kinetic resolution of sulfur-stereogenic sulfoximines by Pd(ii)–MPAA catalyzed C–H arylation and olefination. *Chemical Science* **2021,** *12* (44), 14863-14870.

129. Jacob, N.; Zaid, Y.; Oliveira, J. C. A.; Ackermann, L.; Wencel-Delord, J., Cobalt-Catalyzed Enantioselective C–H Arylation of Indoles. *J. Am. Chem. Soc.* **2022,** *144* (2), 798-806.

130. Frey, J.; Hou, X.; Ackermann, L., Atropoenantioselective palladaelectro-catalyzed anilide C–H olefinations viable with natural sunlight as sustainable power source. *Chemical Science* **2022,** *13* (9), 2729-2734.

131. Rodrigalvarez, J.; Reeve, L. A.; Miró, J.; Gaunt, M. J., Pd(II)-Catalyzed Enantioselective C(sp3)–H Arylation of Cyclopropanes and Cyclobutanes Guided by Tertiary Alkylamines. *J. Am. Chem. Soc.* **2022,** *144* (9), 3939-3948.

132. Yao, Q.-J.; Chen, J.-H.; Song, H.; Huang, F.-R.; Shi, B.-F., Cobalt/Salox-Catalyzed Enantioselective C−H Functionalization of Arylphosphinamides. *Angewandte Chemie International Edition* **2022,** *61* (25), e202202892.

133. Ye, C.-X.; Shen, X.; Chen, S.; Meggers, E., Stereocontrolled 1,3-nitrogen migration to access chiral α-amino acids. *Nature Chemistry* **2022,** *14* (5), 566-573.

134. Liang, H.; Guo, W.; Li, J.; Jiang, J.; Wang, J., Chiral Arene Ligand as Stereocontroller for Asymmetric C−H Activation**. *Angewandte Chemie International Edition* **2022,** *61* (26), e202204926.

135. Shu, X.; Zhong, D.; Lin, Y.; Qin, X.; Huo, H., Modular Access to Chiral α-(Hetero)aryl Amines via Ni/Photoredox-Catalyzed Enantioselective Cross-Coupling. *J. Am. Chem. Soc.* **2022,** *144* (19), 8797-8806.

136. Guo, R.; Xiao, H.; Li, S.; Luo, Y.; Bai, J.; Zhang, M.; Guo, Y.; Qi, X.; Zhang, G., Photoinduced Copper-Catalyzed Asymmetric C(sp3)−H Alkynylation of Cyclic Amines by Intramolecular 1,5-Hydrogen Atom Transfer. *Angewandte Chemie International Edition* **2022,** *61* (34), e202208232.

137. Xu, P.; Fan, W.; Chen, P.; Liu, G., Enantioselective Radical Trifluoromethylation of Benzylic C–H Bonds via Cooperative Photoredox and Copper Catalysis. *J. Am. Chem. Soc.* **2022,** *144* (30), 13468-13474.

138. Chen, J.-H.; Teng, M.-Y.; Huang, F.-R.; Song, H.; Wang, Z.-K.; Zhuang, H.-L.; Wu, Y.-J.; Wu, X.; Yao, Q.-J.; Shi, B.-F., Cobalt/Salox-Catalyzed Enantioselective Dehydrogenative C−H Alkoxylation and Amination. *Angewandte Chemie International Edition* **2022,** *61* (38), e202210106.

139. Jiang, X.; Xiong, W.; Deng, S.; Lu, F.-D.; Jia, Y.; Yang, Q.; Xue, L.-Y.; Qi, X.; Tunge, J. A.; Lu, L.-Q.; Xiao, W.-J., Construction of axial chirality via asymmetric radical trapping by cobalt under visible light. *Nature Catalysis* **2022,** *5* (9), 788-797.

140. Fan, W.; Zhao, X.; Deng, Y.; Chen, P.; Wang, F.; Liu, G., Electrophotocatalytic Decoupled Radical Relay Enables Highly Efficient and Enantioselective Benzylic C–H Functionalization. *J. Am. Chem. Soc.* **2022,** *144* (47), 21674-21682.

141. González, J. M.; Vidal, X.; Ortuño, M. A.; Mascareñas, J. L.; Gulías, M., Chiral Ligands Based on Binaphthyl Scaffolds for Pd-Catalyzed Enantioselective C–H Activation/Cycloaddition Reactions. *J. Am. Chem. Soc.* **2022,** *144* (47), 21437-21442.

142. Kong, L.; Zou, Y.; Li, X.-X.; Zhang, X.-P.; Li, X., Rhodium-catalyzed enantioselective C–H alkynylation of sulfoxides in diverse patterns: desymmetrization, kinetic resolution, and parallel kinetic resolution. *Chemical Science* **2023,** *14* (2), 317-322.

143. Surgenor, R. R.; Liu, X.; Keenlyside, M. J. H.; Myers, W.; Smith, M. D., Enantioselective synthesis of atropisomeric indoles via iron-catalysed oxidative cross-coupling. *Nature Chemistry* **2023,** *15* (3), 357-365.

144. Gao, Q.; Xu, S., Site- and Stereoselective C(sp3)−H Borylation of Strained (Hetero)Cycloalkanols Enabled by Iridium Catalysis. *Angewandte Chemie International Edition* **2023,** *62* (8), e202218025.

145. Chen, X.; Lian, Z.; Kramer, S., Enantioselective Intermolecular Radical Amidation and Amination of Benzylic C−H Bonds via Dual Copper and Photocatalysis. *Angewandte Chemie International Edition* **2023,** *62* (13), e202217638.

146. Xie, T.; Chen, L.; Shen, Z.; Xu, S., Simple Ether-Directed Enantioselective C(sp3)−H Borylation of Cyclopropanes Enabled by Iridium Catalysis. *Angewandte Chemie International Edition* **2023,** *62* (14), e202300199.

147. Xu, S.; Ping, Y.; Li, W.; Guo, H.; Su, Y.; Li, Z.; Wang, M.; Kong, W., Enantioselective C(sp3)–H Functionalization of Oxacycles via Photo-HAT/Nickel Dual Catalysis. *J. Am. Chem. Soc.* **2023,** *145* (9), 5231-5241.

148. Dai, L.; Chen, Y.-Y.; Xiao, L.-J.; Zhou, Q.-L., Intermolecular Enantioselective Benzylic C(sp3)−H Amination by Cationic Copper Catalysis. *Angewandte Chemie International Edition* **2023,** *62* (24), e202304427.

149. Cheng, Z.; Yang, T.; Li, C.; Deng, Y.; Zhang, F.; Chen, P.; Lin, Z.; Ma, S.; Liu, G., Site-Selective sp2 C–H Cyanation of Allenes via Copper-Catalyzed Radical Relay. *J. Am. Chem. Soc.* **2023,** *145* (48), 25995-26002.

150. Wang, W.; Xuan, L.; Chen, Q.; Fan, R.; Zhao, F.; Dong, J.; Wang, H.; Yan, Q.; Zhou, H.; Chen, F.-E., Copper-Catalyzed Asymmetric Remote C(sp3)–H Alkylation of N-Fluorocarboxamides with Glycine Derivatives and Peptides. *J. Am. Chem. Soc.* **2024,** *146* (9), 6307-6316.

151. Zhang, Z.-J.; Simon, M. M.; Yu, S.; Li, S.-W.; Chen, X.; Cattani, S.; Hong, X.; Ackermann, L., Nickel-Catalyzed Atroposelective C–H Alkylation Enabled by Bimetallic Catalysis with Air-Stable Heteroatom-Substituted Secondary Phosphine Oxide Preligands. *J. Am. Chem. Soc.* **2024,** *146* (13), 9172-9180.

152. Teng, M.-Y.; Liu, D.-Y.; Mao, S.-Y.; Wu, X.; Chen, J.-H.; Zhong, M.-Y.; Huang, F.-R.; Yao, Q.-J.; Shi, B.-F., Asymmetric Dearomatization of Indoles through Cobalt-Catalyzed Enantioselective C−H Functionalization Enabled by Photocatalysis. *Angewandte Chemie International Edition* **2024,** *63* (40), e202407640.

153. Das, A.; Kumaran, S.; Ravi Sankar, H. S.; Premkumar, J. R.; Sundararaju, B., A Dual Cobalt-Photoredox Catalytic Approach for Asymmetric Dearomatization of Indoles with Aryl Amides via C−H Activation. *Angewandte Chemie International Edition* **2024,** *63* (40), e202406195.

154. Zhai, H.; Lv, K.; Li, J.; Wang, J.; Liu, T.; Zhao, C., Rhodium(III)-Catalyzed Atroposelective Indolization to Access Planar-Chiral Macrocycles. *J. Am. Chem. Soc.* **2024,** *146* (42), 29214-29223.

155. Pramanick, P. K.; Zhao, S.; Ji, H.-T.; Chen, X.; Yang, G., Pd(II)-Catalyzed Asymmetric [2+2] Annulation for the Construction of Chiral Benzocyclobutenes. *Angewandte Chemie International Edition* **2025,** *64* (3), e202415927.

156. Liu, X.-M.; Li, F.; Wang, T.; Dai, L.; Yang, Y.; Jiang, N.-Q.; Xue, L.-Y.; Liu, J.-Y.; Xue, X.-S.; Xiao, L.-J.; Zhou, Q.-L., Catalytic Asymmetric Oxidative Coupling between C(sp3)–H Bonds and Carboxylic Acids. *J. Am. Chem. Soc.* **2025,** *147* (1), 627-635.

4.6.5 Other Reactions

Hydrogenation of aromatic compounds

1. Legault, C. Y.; Charette, A. B., Catalytic asymmetric hydrogenation of N-iminopyridinium ylides: Expedient approach to enantioenriched substituted piperidine derivatives. *J. Am. Chem. Soc.* **2005,** *127* (25), 8966-8967.

2. Feiertag, P.; Albert, M.; Nettekoven, U.; Spindler, F., Asymmetric homogeneous hydrogenation of 2,5-disubstituted furans. *Org. Lett.* **2006,** *8* (18), 4133-4135.

3. Kaiser, S.; Smidt, S. R.; Pfaltz, A., Iridium catalysts with bicyclic pyridine-phosphinite ligands: Asymmetric hydrogenation of olefins and furan derivatives. *Angew. Chem.-Int. Edit.* **2006,** *45* (31), 5194-5197.

4. Lu, S. M.; Wang, Y. Q.; Han, X. W.; Zhou, Y. G., Asymmetric hydrogenation of quinolines and isoquinolines activated by chloroformates. *Angew. Chem.-Int. Edit.* **2006,** *45* (14), 2260-2263.

5. Kuwano, R.; Kashiwabara, M.; Ohsumi, M.; Kusano, H., Catalytic asymmetric hydrogenation of 2,3,5-trisubstituted pyrroles. *J. Am. Chem. Soc.* **2008,** *130* (3), 808-+.

6. Li, Z. W.; Wang, T. L.; He, Y. M.; Wang, Z. J.; Fan, Q. H.; Pan, J.; Xu, L. J., Air-Stable and Phosphine-Free Iridium Catalysts for Highly Enantioselective Hydrogenation of Quinoline Derivatives. *Org. Lett.* **2008,** *10* (22), 5265-5268.

7. Wang, C.; Li, C. Q.; Wu, X. F.; Pettman, A.; Xiao, J. L., pH-Regulated Asymmetric Transfer Hydrogenation of Quinolines in Water. *Angew. Chem.-Int. Edit.* **2009,** *48* (35), 6524-6528.

8. Baeza, A.; Pfaltz, A., Iridium-Catalyzed Asymmetric Hydrogenation of N-Protected Indoles. *Chem.-Eur. J.* **2010,** *16* (7), 2036-2039.

9. Wang, D. S.; Chen, Q. A.; Li, W.; Yu, C. B.; Zhou, Y. G.; Zhang, X. M., Pd-Catalyzed Asymmetric Hydrogenation of Unprotected Indoles Activated by Bronsted Acids. *J. Am. Chem. Soc.* **2010,** *132* (26), 8909-+.

10. Kuwano, R.; Kameyama, N.; Ikeda, R., Catalytic Asymmetric Hydrogenation of N-Boc-Imidazoles and Oxazoles. *J. Am. Chem. Soc.* **2011,** *133* (19), 7312-7315.

11. Ortega, N.; Urban, S.; Beiring, B.; Glorius, F., Ruthenium NHC Catalyzed Highly Asymmetric Hydrogenation of Benzofurans. *Angew. Chem.-Int. Edit.* **2012,** *51* (7), 1710-1713.

12. Urban, S.; Beiring, B.; Ortega, N.; Paul, D.; Glorius, F., Asymmetric Hydrogenation of Thiophenes and Benzothiophenes. *J. Am. Chem. Soc.* **2012,** *134* (37), 15241-15244.

13. Ortega, N.; Tang, D. T. D.; Urban, S.; Zhao, D. B.; Glorius, F., Ruthenium-NHC-Catalyzed Asymmetric Hydrogenation of Indolizines: Access to Indolizidine Alkaloids. *Angew. Chem.-Int. Edit.* **2013,** *52* (36), 9500-9503.

14. Wysocki, J.; Ortega, N.; Glorius, F., Asymmetric Hydrogenation of Disubstituted Furans. *Angew. Chem.-Int. Edit.* **2014,** *53* (33), 8751-8755.

Others

1. Schmidt, D. R.; O'Malley, S. J.; Leighton, J. L., Catalytic asymmetric silane alcoholysis: Practical access to chiral silanes. *J. Am. Chem. Soc.* **2003,** *125* (5), 1190-1191.

2. Sibi, M. P.; Tatamidani, H.; Patil, K., Enantioselective rhodium enolate protonations. A new methodology for the synthesis of beta(2)-amino acids. *Org. Lett.* **2005,** *7* (13), 2571-2573.

3. Yanagisawa, A.; Touge, T.; Arai, T., Enantioselective protonation of silyl enolates catalyzed by a binap-AgF complex. *Angew. Chem.-Int. Edit.* **2005,** *44* (10), 1546-1548.

4. Ohmura, T.; Taniguchi, H.; Kondo, Y.; Suginome, M., Palladium-catalyzed asymmetric silaborative C-C cleavage of meso-methylenecyclopropanes. *J. Am. Chem. Soc.* **2007,** *129* (12), 3518-+.

5. Garcia-Fortanet, J.; Kessler, F.; Buchwald, S. L., Palladium-Catalyzed Asymmetric Dearomatization of Naphthalene Derivatives. *J. Am. Chem. Soc.* **2009,** *131* (19), 6676-+.

6. Mercier, A.; Yeo, W. C.; Chou, J. Y.; Chaudhuri, P. D.; Bernardinelli, G.; Kundig, E. P., Synthesis of highly enantiomerically enriched planar chiral ruthenium complexes via Pd-catalysed asymmetric hydrogenolysis. *Chem. Commun.* **2009,** (35), 5227-5229.

7. Shigeno, M.; Yamamoto, T.; Murakami, M., Stereoselective Restructuring of 3-Arylcyclobutanols into 1-Indanols by Sequential Breaking and Formation of Carbon-Carbon Bonds. *Chem.-Eur. J.* **2009,** *15* (47), 12929-12931.

8. Mercier, A.; Urbaneja, X.; Yeo, W. C.; Chaudhuri, P. D.; Cumming, G. R.; House, D.; Bernardinelli, G.; Kundig, E. P., Asymmetric Catalytic Hydrogenolysis of Aryl-Halide Bonds in Fused Arene Chromium and Ruthenium Complexes. *Chem.-Eur. J.* **2010,** *16* (21), 6285-6299.

9. Waibel, M.; Cramer, N., Palladium-Catalyzed Arylative Ring-Opening Reactions of Norbornenols: Entry to Highly Substituted Cyclohexenes, Quinolines, and Tetrahydroquinolines. *Angew. Chem.-Int. Edit.* **2010,** *49* (26), 4455-4458.

10. Egami, H.; Matsumoto, K.; Oguma, T.; Kunisu, T.; Katsuki, T., Enantioenriched Synthesis of C(1)-Symmetric BINOLs: Iron-Catalyzed Cross-Coupling of 2-Naphthols and Some Mechanistic Insight. *J. Am. Chem. Soc.* **2010,** *132* (39), 13633-13635.

11. Duan, Y.; Chen, M. W.; Ye, Z. S.; Wang, D. S.; Chen, Q. A.; Zhou, Y. G., An Enantioselective Approach to 2,3-Disubstituted Indolines through Consecutive Bronsted Acid/Pd-Complex-Promoted Tandem Reactions. *Chem.-Eur. J.* **2011,** *17* (26), 7193-7197.

12. Oguma, T.; Katsuki, T. Iron-Catalyzed Dioxygen-Driven C-C Bond Formation: Oxidative Dearomatization of 2-Naphthols with Construction of a Chiral Quaternary Stereocenter. <Go to ISI>://WOS:000312351000017

http://pubs.acs.org/doi/pdfplus/10.1021/ja310203c (accessed 49).

13. Souillart, L.; Cramer, N., Exploitation of Rh(I)-Rh(III) cycles in enantioselective C-C bond cleavages: access to beta-tetralones and benzobicyclo 2.2.2 octanones. *Chemical Science* **2014,** *5* (2), 837-840.

14. Souillart, L.; Parker, E.; Cramer, N., Highly Enantioselective Rhodium(I)-Catalyzed Activation of Enantiotopic Cyclobutanone C-C Bonds. *Angew. Chem.-Int. Edit.* **2014,** *53* (11), 3001-3005.

15. Kubota, K.; Watanabe, Y.; Hayama, K.; Ito, H., Enantioselective Synthesis of Chiral Piperidines via the Stepwise Dearomatization/Borylation of Pyridines. *J. Am. Chem. Soc.* **2016,** *138* (13), 4338-4341.

16. Okamoto, K.; Nanya, A.; Eguchi, A.; Ohe, K., Asymmetric Synthesis of 2H-Azirines with a Tetrasubstituted Stereo-center by Enantioselective Ring Contraction of Isoxazoles. *Angew. Chem.-Int. Edit.* **2018,** *57* (4), 1039-1043.

17. Gribble, M. W.; Guo, S.; Buchwald, S. L., Asymmetric Cu-Catalyzed 1,4-Dearomatization of Pyridines and Pyridazines without Preactivation of the Heterocycle or Nucleophile. *J. Am. Chem. Soc.* **2018,** *140* (15), 5057-5060.

18. Wang, M. Y.; Pu, X. H.; Zhao, Y. F.; Wang, P. P.; Li, Z. X.; Zhu, C. D.; Shi, Z. Z., Enantioselective Copper-Catalyzed Defluoroalkylation Using Arylboronate-Activated Alkyl Grignard Reagents. *J. Am. Chem. Soc.* **2018,** *140* (29), 9061-9065.

19. Xu-Xu, Q. F.; Liu, Q. Q.; Zhang, X.; You, S. L., Copper-Catalyzed Ring Opening of Benzofurans and an Enantioselective Hydroamination Cascade. *Angew. Chem.-Int. Edit.* **2018,** *57* (46), 15204-15208.

20. Ye, Y. X.; Kim, S. T.; Jeong, J.; Baik, M. H.; Buchwald, S. L., CuH-Catalyzed Enantioselective Alkylation of Indole Derivatives with Ligand-Controlled Regiodivergence. *J. Am. Chem. Soc.* **2019,** *141* (9), 3901-3909.

21. Hou, S.-H.; Yu, X.; Zhang, R.; Deng, L.; Zhang, M.; Prichina, A. Y.; Dong, G., Enantioselective Type II Cycloaddition of Alkynes via C–C Activation of Cyclobutanones: Rapid and Asymmetric Construction of [3.3.1] Bridged Bicycles. *J. Am. Chem. Soc.* **2020,** *142* (30), 13180-13189.

22. Chu, H.; Cheng, J.; Yang, J.; Guo, Y.-L.; Zhang, J., Asymmetric Dearomatization of Indole by Palladium/PC-Phos-Catalyzed Dynamic Kinetic Transformation. *Angewandte Chemie International Edition* **2020,** *59* (49), 21991-21996.

23. Li, C.; Chen, B.; Ma, X.; Mo, X.; Zhang, G., Light-Promoted Copper-Catalyzed Enantioselective Alkylation of Azoles. *Angewandte Chemie International Edition* **2021,** *60* (4), 2130-2134.

24. Zhao, X.-J.; Li, Z.-H.; Ding, T.-M.; Tian, J.-M.; Tu, Y.-Q.; Wang, A.-F.; Xie, Y.-Y., Enantioselective Synthesis of 3,3′-Disubstituted 2-Amino-2′-hydroxy-1,1′-binaphthyls by Copper-Catalyzed Aerobic Oxidative Cross-Coupling. *Angewandte Chemie International Edition* **2021,** *60* (13), 7061-7065.

25. Zhu, J.; Chen, S.; He, C., Catalytic Enantioselective Dehydrogenative Si–O Coupling to Access Chiroptical Silicon-Stereogenic Siloxanes and Alkoxysilanes. *J. Am. Chem. Soc.* **2021,** *143* (14), 5301-5307.

26. Zuo, H.-D.; Zhu, S.-S.; Hao, W.-J.; Wang, S.-C.; Tu, S.-J.; Jiang, B., Copper-Catalyzed Asymmetric Deconstructive Alkynylation of Cyclic Oximes. *ACS Catalysis* **2021,** *11* (10), 6010-6019.

27. Zhang, S.; Xiao, J.-Z.; Li, Y.-B.; Shi, C.-Y.; Yin, L., Copper(I)-Catalyzed Asymmetric Alkylation of Unsymmetrical Secondary Phosphines. *J. Am. Chem. Soc.* **2021,** *143* (26), 9912-9921.

28. Huo, J.; Zhong, K.; Xue, Y.; Lyu, M.; Ping, Y.; Liu, Z.; Lan, Y.; Wang, J., Palladium-Catalyzed Enantioselective Carbene Insertion into Carbon–Silicon Bonds of Silacyclobutanes. *J. Am. Chem. Soc.* **2021,** *143* (33), 12968-12973.

29. Dai, Q.; Liu, L.; Zhang, J., Palladium/Xiao-Phos-Catalyzed Kinetic Resolution of sec-Phosphine Oxides by P-Benzylation. *Angewandte Chemie International Edition* **2021,** *60* (52), 27247-27252.

30. Kadarauch, M.; Moss, T. A.; Phipps, R. J., Intermolecular Asymmetric Arylative Dearomatization of 1-Naphthols. *J. Am. Chem. Soc.* **2024,** *146* (50), 34970-34978.

Catalytic Asymmetric Reactions in Organic Chemistry:Bibliography

! Automatically generated from web of science, mistakes possible!

5. Catalytic Umpolung

5.1 Carbene and Phosphite Catalysts

1. Enders, D.; Kallfass, U., An efficient nucleophilic carbene catalyst for the asymmetric benzoin condensation. *Angew. Chem.-Int. Edit.* **2002,** *41* (10), 1743-+.
2. Kerr, M. S.; de Alaniz, J. R.; Rovis, T., A highly enantioselective catalytic intramolecular Stetter reaction. *J. Am. Chem. Soc.* **2002,** *124* (35), 10298-10299.
3. Kerr, M. S.; Rovis, T., Enantioselective synthesis of quaternary stereocenters via a catalytic asymmetric Stetter reaction. *J. Am. Chem. Soc.* **2004,** *126* (29), 8876-8877.
4. Xin, L. H.; Potnick, J. R.; Johnson, J. S., Metallophosphites as umpolung catalysts: The enantioselective cross silyl benzoin reaction. *J. Am. Chem. Soc.* **2004,** *126* (10), 3070-3071.
5. Christmann, M., New developments in the asymmetric Stetter reaction. *Angew. Chem.-Int. Edit.* **2005,** *44* (18), 2632-2634.
6. de Alaniz, J. R.; Rovis, T., A highly enantio- and diastereoselective catalytic intramolecular stetter reaction. *J. Am. Chem. Soc.* **2005,** *127* (17), 6284-6289.
7. Mennen, S. M.; Gipson, J. D.; Kim, Y. R.; Miller, S. J., Thiazolylaianine-derived catalysts for enantioselective intermolecular aldehyde-imine cross-couplings. *J. Am. Chem. Soc.* **2005,** *127* (6), 1654-1655.
8. Amara, P.; Galvan, I. F.; Fontecilla-Camps, J. C.; Field, M. J., The enamine intermediate may not be universal to thiamine catalysis. *Angew. Chem.-Int. Edit.* **2007,** *46* (47), 9019-9022.
9. Chiang, P. C.; Kaeobamrung, J.; Bode, J. W., Enantioselective, cyclopentene-forming annulations via NHC-catalyzed benzoin-oxy-cope reactions. *J. Am. Chem. Soc.* **2007,** *129* (12), 3520-+.
10. Garrett, M. R.; Tarr, J. C.; Johnson, J. S., Enantioselective metallophosphite-catalyzed C-acylation of nitrones. *J. Am. Chem. Soc.* **2007,** *129* (43), 12944-+.
11. Cullen, S. C.; Rovis, T., Catalytic asymmetric Stetter reaction onto vinylphosphine oxides and vinylphosphonates. *Org. Lett.* **2008,** *10* (14), 3141-3144.
12. de Alaniz, J. R.; Kerr, M. S.; Moore, J. L.; Rovis, T., Scope of the asymmetric intramolecular Stetter reaction catalyzed by chiral nucleophilic triazolinylidene carbenes. *J. Org. Chem.* **2008,** *73* (6), 2033-2040.
13. Enders, D.; Han, J. W.; Henseler, A., Asymmetric intermolecular Stetter reactions catalyzed by a novel triazolium derived N-heterocyclic carbene. *Chem. Commun.* **2008,** (34), 3989-3991.
14. He, M.; Beahm, B. J.; Bode, J. W., Chiral NHC-catalyzed oxodiene Diels-Alder reactions with alpha-chloroaldehyde bisulfite salts. *Org. Lett.* **2008,** *10* (17), 3817-3820.
15. He, M.; Bode, J. W., Enantioselective, NHC-Catalyzed bicyclo-beta-lactam formation via direct annulations of enals and unsaturated N-sulfonyl ketimines. *J. Am. Chem. Soc.* **2008,** *130* (2), 418-+.
16. Li, Y.; Feng, Z.; You, S. L., D-Camphor-derived triazolium salts for catalytic intramolecular crossed aldehyde-ketone benzoin reactions. *Chem. Commun.* **2008,** (19), 2263-2265.
17. Liu, Q.; Perreault, S.; Rovis, T., Catalytic Asymmetric Intermolecular Stetter Reaction of Glyoxamides with Alkylidenemalonates. *J. Am. Chem. Soc.* **2008,** *130* (43), 14066-+.
18. Zhang, Y. R.; Lv, H.; Zhou, D.; Ye, S., Chiral N-Heterocyclic Carbene-Catalyzed Formal [4+2] Cycloaddition of Ketenes with Enones: Highly Enantioselective Synthesis of trans- and cis-delta-Lactones. *Chem.-Eur. J.* **2008,** *14* (28), 8473-8476.
19. Baragwanath, L.; Rose, C. A.; Zeitler, K.; Connon, S. J., Highly Enantioselective Benzoin Condensation Reactions Involving a Bifunctional Protic Pentafluorophenyl-Substituted Triazolium Precatalyst. *J. Org. Chem.* **2009,** *74* (23), 9214-9217.
20. DiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T., Catalytic Asymmetric Intermolecular Stetter Reaction of Heterocyclic Aldehydes with Nitroalkenes: Backbone Fluorination Improves Selectivity. *J. Am. Chem. Soc.* **2009,** *131* (31), 10872-+.
21. Ema, T.; Oue, Y.; Akihara, K.; Miyazaki, Y.; Sakai, T., Stereoselective Synthesis of Bicyclic Tertiary Alcohols with Quaternary Stereocenters via Intramolecular Crossed Benzoin Reactions Catalyzed by N-Heterocyclic Carbenes. *Org. Lett.* **2009,** *11* (21), 4866-4869.
22. Kaeobamrung, J.; Bode, J. W., Stereodivergency of Triazolium and Imidazolium-Derived NHCs for Catalytic, Enantioselective Cyclopentane Synthesis. *Org. Lett.* **2009,** *11* (3), 677-680.
23. Liu, Q.; Rovis, T., Enantio- and Diastereoselective Intermolecular Stetter Reaction of Glyoxamide and Alkylidene Ketoamides. *Org. Lett.* **2009,** *11* (13), 2856-2859.
24. Cardinal-David, B.; Raup, D. E. A.; Scheidt, K. A., Cooperative N-Heterocyclic Carbene/Lewis Acid Catalysis for Highly Stereoselective Annulation Reactions with Homoenolates. *J. Am. Chem. Soc.* **2010,** *132* (15), 5345-+.
25. Kaeobamrung, J.; Mahatthananchai, J.; Zheng, P. G.; Bode, J. W., An Enantioselective Claisen Rearrangement Catalyzed by N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2010,** *132* (26), 8810-+.
26. Cohen, D. T.; Cardinal-David, B.; Roberts, J. M.; Sarjeant, A. A.; Scheidt, K. A., NHC-Catalyzed/Titanium(IV)-Mediated Highly Diastereo- and Enantioselective Dimerization of Enals. *Org. Lett.* **2011,** *13* (5), 1068-1071.
27. Cohen, D. T.; Cardinal-David, B.; Scheidt, K. A., Lewis Acid Activated Synthesis of Highly Substituted Cyclopentanes by the N-Heterocyclic Carbene Catalyzed Addition of Homoenolate Equivalents to Unsaturated Ketoesters. *Angew. Chem.-Int. Edit.* **2011,** *50* (7), 1678-1682.
28. Fang, X. Q.; Chen, X. K.; Lv, H.; Chi, Y. R., Enantioselective Stetter Reactions of Enals and Modified Chalcones Catalyzed by N-Heterocyclic Carbenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (49), 11782-11785.

29. Fang, X. Q.; Jiang, K.; Xing, C.; Hao, L.; Chi, Y. R., A Highly Regio- and Stereoselective Cascade Annulation of Enals and Benzodi(enone)s Catalyzed by N-Heterocyclic Carbenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (8), 1910-1913.
30. Jacobsen, C. B.; Jensen, K. L.; Udmark, J.; Jorgensen, K. A., Organocatalytic Iminium Ion/Carbene Reaction Cascade for the Formation of Optically Active 2,4-Disubstituted Cyclopentenones. *Org. Lett.* **2011,** *13* (18), 4790-4793.
31. Jousseaume, T.; Wurz, N. E.; Glorius, F., Highly Enantioselective Synthesis of alpha-Amino Acid Derivatives by an NHC-Catalyzed Intermolecular Stetter Reaction. *Angew. Chem.-Int. Edit.* **2011,** *50* (6), 1410-1414.
32. Liu, F.; Bugaut, X.; Schedler, M.; Frohlich, R.; Glorius, F., Designing N-Heterocyclic Carbenes: Simultaneous Enhancement of Reactivity and Enantioselectivity in the Asymmetric Hydroacylation of Cyclopropenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (52), 12626-12630.
33. Moore, J. L.; Silvestri, A. P.; de Alaniz, J. R.; DiRocco, D. A.; Rovis, T., Mechanistic Investigation of the Enantioselective Intramolecular Stetter Reaction: Proton Transfer Is the First Irreversible Step. *Org. Lett.* **2011,** *13* (7), 1742-1745.
34. Ozboya, K. E.; Rovis, T., Enamine/carbene cascade catalysis in the diastereo- and enantioselective synthesis of functionalized cyclopentanones. *Chem. Sci.* **2011,** *2* (9), 1835-1838.
35. Piel, I.; Steinmetz, M.; Hirano, K.; Frohlich, R.; Grimme, S.; Glorius, F., Highly Asymmetric NHC-Catalyzed Hydroacylation of Unactivated Alkenes. *Angew. Chem.-Int. Edit.* **2011,** *50* (21), 4983-4987.
36. Um, J. M.; DiRocco, D. A.; Noey, E. L.; Rovis, T.; Houk, K. N., Quantum Mechanical Investigation of the Effect of Catalyst Fluorination in the Intermolecular Asymmetric Stetter Reaction. *J. Am. Chem. Soc.* **2011,** *133* (29), 11249-11254.
37. Wanner, B.; Mahatthananchai, J.; Bode, J. W., Enantioselective Synthesis of Dihydropyridinones via NHC-Catalyzed Aza-Claisen Reaction. *Org. Lett.* **2011,** *13* (19), 5378-5381.
38. Zhao, X. D.; DiRocco, D. A.; Rovis, T., N-Heterocyclic Carbene and Bronsted Acid Cooperative Catalysis: Asymmetric Synthesis of trans-gamma-Lactams. *J. Am. Chem. Soc.* **2011,** *133* (32), 12466-12469.
39. Cohen, D. T.; Eichman, C. C.; Phillips, E. M.; Zarefsky, E. R.; Scheidt, K. A., Catalytic Dynamic Kinetic Resolutions with N-Heterocyclic Carbenes: Asymmetric Synthesis of Highly Substituted beta-Lactones. *Angew. Chem.-Int. Edit.* **2012,** *51* (29), 7309-7313.
40. DiRocco, D. A.; Noey, E. L.; Houk, K. N.; Rovis, T., Catalytic Asymmetric Intermolecular Stetter Reactions of Enolizable Aldehydes with Nitrostyrenes: Computational Study Provides Insight into the Success of the Catalyst. *Angew. Chem.-Int. Edit.* **2012,** *51* (10), 2391-2394.
41. DiRocco, D. A.; Rovis, T., Catalytic Asymmetric Cross-Aza-Benzoin Reactions of Aliphatic Aldehydes with N-Boc-Protected Imines. *Angew. Chem.-Int. Edit.* **2012,** *51* (24), 5904-5906.
42. Dugal-Tessier, J.; O'Bryan, E. A.; Schroeder, T. B. H.; Cohen, D. T.; Scheidt, K. A., An N-Heterocyclic Carbene/Lewis Acid Strategy for the Stereoselective Synthesis of Spirooxindole Lactones. *Angew. Chem.-Int. Edit.* **2012,** *51* (20), 4963-4967.
43. Kravina, A. G.; Mahatthananchai, J.; Bode, J. W., Enantioselective, NHC-Catalyzed Annulations of Trisubstituted Enals and?Cyclic N-Sulfonylimines via a,ss-Unsaturated Acyl Azoliums. *Angew. Chem.-Int. Edit.* **2012,** *51* (37), 9433-9436.
44. Liu, G. S.; Wilkerson, P. D.; Toth, C. A.; Xu, H., Highly Enantioselective Cyclizations of Conjugated Trienes with Low Catalyst Loadings: A Robust Chiral N-Heterocyclic Carbene Enabled by Acetic Acid Cocatalyst. *Org. Lett.* **2012,** *14* (3), 858-861.
45. Lyngvi, E.; Bode, J. W.; Schoenebeck, F., A computational study of the origin of stereoinduction in NHC-catalyzed annulation reactions of alpha,beta-unsaturated acyl azoliums. *Chem. Sci.* **2012,** *3* (7), 2346-2350.
46. Maji, B.; Ji, L.; Wang, S. M.; Vedachalam, S.; Ganguly, R.; Liu, X. W., N-Heterocyclic Carbene Catalyzed Homoenolate-Addition Reaction of Enals and Nitroalkenes: Asymmetric Synthesis of 5-Carbon-Synthon d-Nitroesters. *Angew. Chem.-Int. Edit.* **2012,** *51* (33), 8276-8280.
47. Mo, J. M.; Chen, X. K.; Chi, Y. R., Oxidative gamma-Addition of Enals to Trifluoromethyl Ketones: Enantioselectivity Control via Lewis Acid/N-Heterocyclic Carbene Cooperative Catalysis. *J. Am. Chem. Soc.* **2012,** *134* (21), 8810-8813.
48. Wurz, N. E.; Daniliuc, C. G.; Glorius, F., Highly Enantioselective Intermolecular Stetter Reaction of Simple Acrylates: Synthesis of a-Chiral ?-Ketoesters. *Chem.-Eur. J.* **2012,** *18* (51), 16297-16301.
49. Chen, S. J.; Hao, L.; Zhang, Y. X.; Tiwari, B.; Chi, Y. R., Asymmetric Access to the Smallest Enolate Intermediate via Organocatalytic Activation of Acetic Ester. *Org. Lett.* **2013,** *15* (22), 5822-5825.
50. Fu, Z. Q.; Xu, J. F.; Zhu, T. S.; Leong, W. W. Y.; Chi, Y. R., beta-Carbon activation of saturated carboxylic esters through N-heterocyclic carbene organocatalysis. *Nature Chemistry* **2013,** *5* (10), 835-839.
51. Izquierdo, J.; Orue, A.; Scheidt, K. A., A Dual Lewis Base Activation Strategy for Enantioselective Carbene-Catalyzed Annulations. *J. Am. Chem. Soc.* **2013,** *135* (29), 10634-10637.
52. Lv, H.; Jia, W. Q.; Sun, L. H.; Ye, S., N-Heterocyclic Carbene Catalyzed 4+3 Annulation of Enals and o-Quinone Methides: Highly Enantioselective Synthesis of Benzo-epsilon-Lactones. *Angew. Chem.-Int. Edit.* **2013,** *52* (33), 8607-8610.
53. McCusker, E. O.; Scheidt, K. A., Enantioselective N-Heterocyclic Carbene Catalyzed Annulation Reactions with Imidazolidinones. *Angew. Chem.-Int. Edit.* **2013,** *52* (51), 13616-13620.
54. Sun, L. H.; Liang, Z. Q.; Jia, W. Q.; Ye, S., Enantioselective N-Heterocyclic Carbene Catalyzed Aza-Benzoin Reaction of Enals with Activated Ketimines. *Angew. Chem.-Int. Edit.* **2013,** *52* (22), 5803-5806.
55. White, N. A.; DiRocco, D. A.; Rovis, T., Asymmetric N-Heterocyclic Carbene Catalyzed Addition of Enals to Nitroalkenes: Controlling Stereochemistry via the Homoenolate Reactivity Pathway To Access delta-Lactams. *J. Am. Chem. Soc.* **2013,** *135* (23), 8504-8507.
56. Zhang, J. M.; Xing, C.; Tiwari, B.; Chi, Y. R., Catalytic Activation of Carbohydrates as Formaldehyde Equivalents for Stetter Reaction with Enones. *J. Am. Chem. Soc.* **2013,** *135* (22), 8113-8116.
57. Fu, Z.; Jiang, K.; Zhu, T.; Torres, J.; Chi, Y. R., Access to Oxoquinoline Heterocycles by N-Heterocyclic Carbene Catalyzed Ester Activation for Selective Reaction with an Enone. *Angew. Chem.-Int. Edit.* **2014,** *53* (25), 6506-6510.
58. Goodman, C. G.; Johnson, J. S., Dynamic Kinetic Asymmetric Cross-Benzoin Additions of beta-Stereogenic alpha-Keto Esters. *J. Am. Chem. Soc.* **2014,** *136* (42), 14698-14701.
59. Guo, C.; Sahoo, B.; Daniliuc, C. G.; Glorius, F., N-Heterocyclic Carbene Catalyzed Switchable Reactions of Enals with Azoalkenes: Formal 4+3 and 4+1 Annulations for the Synthesis of 1,2-Diazepines and Pyrazoles. *J. Am. Chem. Soc.* **2014,** *136* (50), 17402-17405.
60. Guo, C.; Schedler, M.; Daniliuc, C. G.; Glorius, F., N-Heterocyclic Carbene Catalyzed Formal 3+2 Annulation Reaction of Enals: An Efficient Enantioselective Access to Spiro-Heterocycles. *Angew. Chem.-Int. Edit.* **2014,** *53* (38), 10232-10236.
61. Jang, K. P.; Hutson, G. E.; Johnston, R. C.; McCusker, E. O.; Cheong, P. H. Y.; Scheidt, K. A., Asymmetric Homoenolate Additions to Acyl Phosphonates through Rational Design of a Tailored N-Heterocyclic Carbene Catalyst. *J. Am. Chem. Soc.* **2014,** *136* (1), 76-79.
62. Jin, Z.; Chen, S.; Wang, Y.; Zheng, P.; Yang, S.; Chi, Y. R., beta-Functionalization of Carboxylic Anhydrides with beta-Alkyl Substituents through Carbene Organocatalysis. *Angew. Chem.-Int. Edit.* **2014,** *53* (49), 13506-13509.

63. Li, J. L.; Sahoo, B.; Daniliuc, C. G.; Glorius, F., Conjugate Umpolung of beta,beta-Disubstituted Enals by Dual Catalysis with an N-Heterocyclic Carbene and a Bronsted Acid: Facile Construction of Contiguous Quaternary Stereocenters. *Angew. Chem.-Int. Edit.* **2014,** *53* (39), 10515-10519.
64. Goodman, C. G.; Walker, M. M.; Johnson, J. S., Enantioconvergent Synthesis of Functionalized gamma-Butyrolactones via (3+2)-Annulation. *J. Am. Chem. Soc.* **2015,** *137* (1), 122-125.
65. Guo, C.; Fleige, M.; Janssen-Muller, D.; Daniliuc, C. G.; Glorius, F., Switchable selectivity in an NHC-catalysed dearomatizing annulation reaction. *Nature Chemistry* **2015,** *7* (10), 843-848.
66. Janssen-Muller, D.; Schedler, M.; Fleige, M.; Daniliuc, C. G.; Glorius, F., Enantioselective Intramolecular Hydroacylation of Unactivated Alkenes: An NHC-Catalyzed Robust and Versatile Formation of Cyclic Chiral Ketones. *Angew. Chem.-Int. Edit.* **2015,** *54* (42), 12492-12496.
67. Wang, M. H.; Cohen, D. T.; Schwamb, C. B.; Mishra, R. K.; Scheidt, K. A., Enantioselective beta-Protonation by a Cooperative Catalysis Strategy. *J. Am. Chem. Soc.* **2015,** *137* (18), 5891-5894.
68. White, N. A.; Rovis, T., Oxidatively Initiated NHC-Catalyzed Enantioselective Synthesis of 3,4-Disubstituted Cyclopentanones from Enals. *J. Am. Chem. Soc.* **2015,** *137* (32), 10112-10115.
69. Nakano, Y.; Lupton, D. W., Enantioselective N-Heterocyclic Carbene Catalysis by the Umpolung of ,-Unsaturated Ketones. *Angew. Chem.-Int. Edit.* **2016,** *55* (9), 3135-3139.
70. Wang, L.; Li, S.; Blumel, M.; Philipps, A. R.; Wang, A.; Puttreddy, R.; Rissanen, K.; Enders, D., Asymmetric Synthesis of Spirobenzazepinones with Atroposelectivity and Spiro-1,2-Diazepinones by NHC-Catalyzed 3+4 Annulation Reactions. *Angew. Chem.-Int. Edit.* **2016,** *55* (37), 11110-11114.
71. Wu, J. C.; Zhao, C. G.; Wang, J., Enantioselective Intermolecular Enamide-Aldehyde Cross-Coupling Catalyzed by Chiral N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2016,** *138* (14), 4706-4709.
72. Zhang, G. X.; Yang, S.; Zhang, X. Y.; Lin, Q. Q.; Das, D. K.; Liu, J.; Fang, X. Q., Dynamic Kinetic Resolution Enabled by Intramolecular Benzoin Reaction: Synthetic Applications and Mechanistic Insights. *J. Am. Chem. Soc.* **2016,** *138* (25), 7932-7938.
73. Chen, X. Y.; Chen, K. Q.; Sun, D. Q.; Ye, S., N-Heterocyclic carbene-catalyzed oxidative 3+2 annulation of dioxindoles and enals: cross coupling of homoenolate and enolate. *Chem. Sci.* **2017,** *8* (3), 1936-1941.
74. Flanigan, D. M.; Rovis, T., Enantioselective N-heterocyclic carbene-catalyzed nucleophilic dearomatization of alkyl pyridiniumst. *Chem. Sci.* **2017,** *8* (9), 6566-6569.
75. Chen, X.-Y.; Xiong, J.-W.; Liu, Q.; Li, S.; Sheng, H.; von Essen, C.; Rissanen, K.; Enders, D., Control of N-Heterocyclic Carbene Catalyzed Reactions of Enals: Asymmetric Synthesis of Oxindole-γ-Amino Acid Derivatives. *Angewandte Chemie International Edition* **2018,** *57* (1), 300-304.
76. Peng, Q. P.; Guo, D. H.; Bie, J. B.; Wang, J., Catalytic Enantioselective Aza-Benzoin Reactions of Aldehydes with 2H-Azirines. *Angew. Chem.-Int. Edit.* **2018,** *57* (14), 3767-3771.
77. Scott, L.; Nakano, Y.; Zhang, C. H.; Lupton, D. W., Enantioselective N-Heterocyclic Carbene Catalyzed Cyclopentene Synthesis via the beta-Azolium Ylide. *Angew. Chem.-Int. Edit.* **2018,** *57* (32), 10299-10303.
78. Yuan, P. F.; Chen, J. A.; Zhao, J.; Huang, Y., Enantioselective Hydroamidation of Enals by Trapping of a Transient Acyl Species. *Angew. Chem.-Int. Edit.* **2018,** *57* (28), 8503-8507.
79. Zhao, C. G.; Guo, D. H.; Munkerup, K.; Huang, K. W.; Li, F. Y.; Wang, J., Enantioselective 3+3 atroposelective annulation catalyzed by N-heterocyclic carbenes. *Nature Communications* **2018,** *9*.
80. Fernando, J. E. M.; Nakano, Y.; Zhang, C. H.; Lupton, D. W., Enantioselective N-Heterocyclic Carbene Catalysis that Exploits Imine Umpolung. *Angew. Chem.-Int. Edit.* **2019,** *58* (12), 4007-4011.

5.2 SOMO Activation

1. Chatterjee, A.; Bennur, T. H.; Joshi, N. N., Truly catalytic and enantioselective pinacol coupling of aryl aldehydes mediated by chiral Ti(III) complexes. *J. Org. Chem.* **2003,** *68* (14), 5668-5671.

2. Beeson, T. D.; Mastracchio, A.; Hong, J. B.; Ashton, K.; MacMillan, D. W. C., Enantioselective organocatalysis using SOMO activation. *Science* **2007,** *316* (5824), 582-585.

3. Bertelsen, S.; Nielsen, M.; Jorgensen, K. A., Radicals in asymmetric organocatalysis. *Angew. Chem.-Int. Edit.* **2007,** *46* (39), 7356-7359.

4. Jang, H. Y.; Hong, J. B.; MacMillan, D. W. C., Enantioselective organocatalytic singly occupied molecular orbital activation: The enantioselective alpha-enolation of aldehydes. *J. Am. Chem. Soc.* **2007,** *129* (22), 7004-+.

5. Sibi, M. P.; Hasegawa, M., Organocatalysis in radical chemistry. Enantioselective alpha-oxyamination of aldehydes. *J. Am. Chem. Soc.* **2007,** *129* (14), 4124-+.

6. Kim, H.; MacMillan, D. W. C., Enantioselective organo-SOMO catalysis: The alpha-vinylation of aldehydes. *J. Am. Chem. Soc.* **2008,** *130* (2), 398-+.

7. Nicewicz, D. A.; MacMillan, D. W. C., Merging photoredox catalysis with organocatalysis: The direct asymmetric alkylation of aldehydes. *Science* **2008,** *322* (5898), 77-80.

8. Amatore, M.; Beeson, T. D.; Brown, S. P.; MacMillan, D. W. C., Enantioselective Linchpin Catalysis by SOMO Catalysis: An Approach to the Asymmetric alpha-Chlorination of Aldehydes and Terminal Epoxide Formation. *Angew. Chem.-Int. Edit.* **2009,** *48* (28), 5121-5124.

9. Conrad, J. C.; Kong, J.; Laforteza, B. N.; MacMillan, D. W. C., Enantioselective alpha-Arylation of Aldehydes via Organo-SOMO Catalysis. An Ortho-Selective Arylation Reaction Based on an Open-Shell Pathway. *J. Am. Chem. Soc.* **2009,** *131* (33), 11640-+.

10. Melchiorre, P., Light in Aminocatalysis: The Asymmetric Intermolecular alpha-Alkylation of Aldehydes. *Angew. Chem.-Int. Edit.* **2009,** *48* (8), 1360-1363.

11. Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C., Enantioselective alpha-Trifluoromethylation of Aldehydes via Photoredox Organocatalysis. *J. Am. Chem. Soc.* **2009,** *131* (31), 10875-+.

12. Nicolaou, K. C.; Reingruber, R.; Sarlah, D.; Brase, S., Enantioselective Intramolecular Friedel-Crafts-Type alpha-Arylation of Aldehydes. *J. Am. Chem. Soc.* **2009,** *131* (6), 2086-+.

13. Wilson, J. E.; Casarez, A. D.; MacMillan, D. W. C., Enantioselective Aldehyde alpha-Nitroalkylation via Oxidative Organocatalysis. *J. Am. Chem. Soc.* **2009,** *131* (32), 11332-+.

14. Devery, J. J.; Conrad, J. C.; MacMillan, D. W. C.; Flowers, R. A., Mechanistic Complexity in Organo-SOMO Activation. *Angew. Chem.-Int. Edit.* **2010,** *49* (35), 6106-6110.

15. Jui, N. T.; Lee, E. C. Y.; MacMillan, D. W. C., Enantioselective Organo-SOMO Cascade Cycloadditions: A Rapid Approach to Molecular Complexity from Simple Aldehydes and Olefins. *J. Am. Chem. Soc.* **2010,** *132* (29), 10015-10017.

16. Kano, T.; Mii, H.; Maruoka, K., Metal-Free Direct Asymmetric Aminoxylation of Aldehydes Catalyzed by a Binaphthyl-Based Chiral Amine. *Angew. Chem.-Int. Edit.* **2010,** *49* (37), 6638-6641.

17. Rendler, S.; MacMillan, D. W. C., Enantioselective Polyene Cyclization via Organo-SOMO Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (14), 5027-+.

18. Shih, H. W.; Vander Wal, M. N.; Grange, R. L.; MacMillan, D. W. C., Enantioselective alpha-Benzylation of Aldehydes via Photoredox Organocatalysis. *J. Am. Chem. Soc.* **2010,** *132* (39), 13600-13603.

19. Um, J. M.; Gutierrez, O.; Schoenebeck, F.; Houk, K. N.; MacMillan, D. W. C., Nature of Intermediates in Organo-SOMO Catalysis of alpha-Arylation of Aldehydes. *J. Am. Chem. Soc.* **2010,** *132* (17), 6001-6005.

20. Neumann, M.; Fuldner, S.; Konig, B.; Zeitler, K., Metal-Free, Cooperative Asymmetric Organophotoredox Catalysis with Visible Light. *Angew. Chem.-Int. Edit.* **2011,** *50* (4), 951-954.

21. Pham, P. V.; Ashton, K.; MacMillan, D. W. C., The intramolecular asymmetric allylation of aldehydes via organo-SOMO catalysis: A novel approach to ring construction. *Chem. Sci.* **2011,** *2* (8), 1470-1473.

22. DiRocco, D. A.; Rovis, T., Catalytic Asymmetric alpha-Acylation of Tertiary Amines Mediated by a Dual Catalysis Mode: N-Heterocyclic Carbene and Photoredox Catalysis. *J. Am. Chem. Soc.* **2012,** *134* (19), 8094-8097.

23. Jui, N. T.; Garber, J. A.; Finelli, F. G.; MacMillan, D. W. C., Enantioselective Organo-SOMO Cycloadditions: A Catalytic Approach to Complex Pyrrolidines from Olefins and Aldehydes. *J. Am. Chem. Soc.* **2012,** *134* (28), 11400-11403.

24. Streuff, J.; Feurer, M.; Bichovski, P.; Frey, G.; Gellrich, U., Enantioselective Titanium(III)-Catalyzed Reductive Cyclization of Ketonitriles. *Angew. Chem.-Int. Edit.* **2012,** *51* (34), 8661-8664.

25. Arceo, E.; Jurberg, I. D.; Alvarez-Fernandez, A.; Melchiorre, P., Photochemical activity of a key donor-acceptor complex can drive stereoselective catalytic alpha-alkylation of aldehydes. *Nature Chemistry* **2013,** *5* (9), 750-756.

26. Cecere, G.; Konig, C. M.; Alleva, J. L.; MacMillan, D. W. C., Enantioselective Direct alpha-Annination of Aldehydes via a Photoredox Mechanism: A Strategy for Asymmetric Amine Fragment Coupling. *J. Am. Chem. Soc.* **2013,** *135* (31), 11521-11524.

27. Comito, R. J.; Finelli, F. G.; MacMillan, D. W. C., Enantioselective Intramolecular Aldehyde alpha-Alkylation with Simple Olefins: Direct Access to Homo-Ene Products. *J. Am. Chem. Soc.* **2013,** *135* (25), 9358-9361.

28. Rono, L. J.; Yayla, H. G.; Wang, D. Y.; Armstrong, M. F.; Knowles, R. R., Enantioselective Photoredox Catalysis Enabled by Proton-Coupled Electron Transfer: Development of an Asymmetric Aza-Pinacol Cyclization. *J. Am. Chem. Soc.* **2013,** *135* (47), 17735-17738.

29. Arceo, E.; Bahamonde, A.; Bergonzini, G.; Melchiorre, P., Enantioselective direct alpha-alkylation of cyclic ketones by means of photo-organocatalysis. *Chem. Sci.* **2014,** *5* (6), 2438-2442.

30. Hashimoto, T.; Kawamata, Y.; Maruoka, K., An organic thiyl radical catalyst for enantioselective cyclization. *Nature Chemistry* **2014,** *6* (8), 702-705.

31. Huo, H.; Shen, X.; Wang, C.; Zhang, L.; Roese, P.; Chen, L.-A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E., Asymmetric photoredox transition-metal catalysis activated by visible light. *Nature* **2014,** *515* (7525), 100-103.

32. Riente, P.; Matas Adams, A.; Albero, J.; Palomares, E.; Pericas, M. A., Light-Driven Organocatalysis Using Inexpensive, Nontoxic Bi2O3 as the Photocatalyst. *Angew. Chem.-Int. Edit.* **2014,** *53* (36), 9613-9616.

33. White, N. A.; Rovis, T., Enantioselective N-Heterocyclic Carbene-Catalyzed beta-Hydroxylation of Enals Using Nitroarenes: An Atom Transfer Reaction That Proceeds via Single Electron Transfer. *J. Am. Chem. Soc.* **2014,** *136* (42), 14674-14677.

34. Zhu, Y.; Zhang, L.; Luo, S., Asymmetric alpha-Photoalkylation of beta-Ketocarbonyls by Primary Amine Catalysis: Facile Access to Acyclic All-Carbon Quaternary Stereocenters. *J. Am. Chem. Soc.* **2014,** *136* (42), 14642-14645.

35. Huo, H. H.; Wang, C. Y.; Harms, K.; Meggers, E., Enantioselective, Catalytic Trichloromethylation through Visible-Light-Activated Photoredox Catalysis with a Chiral Iridium Complex. *J. Am. Chem. Soc.* **2015,** *137* (30), 9551-9554.

36. Silvi, M.; Arceo, E.; Jurberg, I. D.; Cassani, C.; Melchiorre, P., Enantioselective Organocatalytic Alkylation of Aldehydes and Enals Driven by the Direct Photoexcitation of Enamines. *J. Am. Chem. Soc.* **2015,** *137* (19), 6120-6123.

37. Wang, C. Y.; Zheng, Y.; Huo, H. H.; Rose, P.; Zhang, L. L.; Harms, K.; Hilt, G.; Meggers, E., Merger of Visible Light Induced Oxidation and Enantioselective Alkylation with a Chiral Iridium Catalyst. *Chemistry-a European Journal* **2015,** *21* (20), 7355-7359.

38. Welin, E. R.; Warkentin, A. A.; Conrad, J. C.; MacMillan, D. W. C., Enantioselective alpha-Alkylation of Aldehydes by Photoredox Organocatalysis: Rapid Access to Pharmacophore Fragments from beta-Cyanoaldehydes. *Angew. Chem.-Int. Edit.* **2015,** *54* (33), 9668-9672.

39. Wozniak, L.; Murphy, J. J.; Melchiorre, P., Photo-organocatalytic Enantioselective Perfluoroalkylation of beta-Ketoesters. *J. Am. Chem. Soc.* **2015,** *137* (17), 5678-5681.

40. Zhang, Y.; Du, Y.; Huang, Z.; Xu, J.; Wu, X.; Wang, Y.; Wang, M.; Yang, S.; Webster, R. D.; Chi, Y. R., N-Heterocyclic Carbene-Catalyzed Radical Reactions for Highly Enantioselective beta-Hydroxylation of Enals. *J. Am. Chem. Soc.* **2015,** *137* (7), 2416-2419.

41. Bahamonde, A.; Melchiorre, P., Mechanism of the Stereoselective alpha-Alkylation of Aldehydes Driven by the Photochemical Activity of Enamines. *J. Am. Chem. Soc.* **2016,** *138* (25), 8019-8030.

42. Ma, J. J.; Harms, K.; Meggers, E., Enantioselective rhodium/ruthenium photoredox catalysis en route to chiral 1,2-aminoalcohols. *Chemical Communications* **2016,** *52* (66), 10183-10186.

43. Murphy, J. J.; Bastida, D.; Paria, S.; Fagnoni, M.; Melchiorre, P., Asymmetric catalytic formation of quaternary carbons by iminium ion trapping of radicals. *Nature* **2016,** *532* (7598), 218-222.

44. Wang, C. Y.; Qin, J.; Shen, X. D.; Riedel, R.; Harms, K.; Meggers, E., Asymmetric Radical-Radical Cross-Coupling through Visible-Light-Activated Iridium Catalysis. *Angew. Chem.-Int. Edit.* **2016,** *55* (2), 685-688.

45. Capacci, A. G.; Malinowski, J. T.; McAlpine, N. J.; Kuhne, J.; MacMillan, D. W. C., Direct, enantioselective alpha-alkylation of aldehydes using simple olefins. *Nature Chemistry* **2017,** *9* (11), 1073-1077.

46. Filippini, G.; Silvi, M.; Melchiorre, P., Enantioselective Formal alpha-Methylation and alpha-Benzylation of Aldehydes by Means of Photo-organocatalysis. *Angew. Chem.-Int. Edit.* **2017,** *56* (16), 4447-4451.

47. Kern, N.; Plesniak, M. P.; McDouall, J. J. W.; Procter, D. J., Enantioselective cyclizations and cyclization cascades of samarium ketyl radicals. *Nature Chemistry* **2017,** *9* (12), 1198-1204.

48. Larionov, E.; Mastandrea, M. M.; Pericas, M. A., Asymmetric Visible-Light Photoredox Cross-Dehydrogenative Coupling of Aldehydes with Xanthenes. *Acs Catalysis* **2017,** *7* (10), 7008-7013.

49. Ma, J. J.; Rosales, A. R.; Huang, X. Q.; Harms, K.; Riedel, R.; Wiest, O.; Meggers, E., Visible-Light-Activated Asymmetric beta-C-H Functionalization of Acceptor-Substituted Ketones with 1,2-Dicarbonyl Compounds. *J. Am. Chem. Soc.* **2017,** *139* (48), 17245-17248.

50. Silvi, M.; Verrier, C.; Rey, Y. P.; Buzzetti, L.; Melchiorre, P., Visible-light excitation of iminium ions enables the enantioselective catalytic beta-alkylation of enals. *Nature Chemistry* **2017,** *9* (9), 868-873.

51. Bonilla, P.; Rey, Y. P.; Holden, C. M.; Melchiorre, P., Photo-Organocatalytic Enantioselective Radical Cascade Reactions of Unactivated Olefins. *Angew. Chem.-Int. Edit.* **2018,** *57* (39), 12819-12823.

52. Leth, L. A.; Naesborg, L.; Reyes-Rodriguez, G. J.; Tobiesen, H. N.; Iversen, M. V.; Jorgensen, K. A., Enantioselective Oxidative Coupling of Carboxylic Acids to alpha-Branched Aldehydes. *J. Am. Chem. Soc.* **2018,** *140* (40), 12687-12690.

53. Mazzarella, D.; Crisenza, G. E. M.; Melchiorre, P., Asymmetric Photocatalytic C-H Functionalization of Toluene and Derivatives. *J. Am. Chem. Soc.* **2018,** *140* (27), 8439-8443.

54. Woźniak, Ł.; Magagnano, G.; Melchiorre, P., Enantioselective Photochemical Organocascade Catalysis. *Angewandte Chemie International Edition* **2018,** *57* (4), 1068-1072.

55. Blom, J.; Reyes-Rodriguez, G. J.; Tobiesen, H. N.; Lamhauge, J. N.; Iversen, M. V.; Barlose, C. L.; Hammer, N.; Rusbjerg, M.; Jorgensen, K. A., Umpolung Strategy for alpha-Functionalization of Aldehydes for the Addition of Thiols and other Nucleophiles. *Angew. Chem.-Int. Edit.* **2019,** *58* (49), 17856-17862.

56. Rezayee, N.; Lauridsen, V. H.; Naesborg, L.; Nguyen, T. V. Q.; Tobiesen, H. N.; Jorgensen, K. A., Oxidative organocatalysed enantioselective coupling of indoles with aldehydes that forms quaternary carbon stereocentres. *Chem. Sci.* **2019,** *10* (12), 3586-3591.

57. Perego, L. A.; Bonilla, P.; Melchiorre, P., Photo-Organocatalytic Enantioselective Radical Cascade Enabled by Single-Electron Transfer Activation of Allenes. *Advanced Synthesis & Catalysis* **2020,** *362* (2), 302-307.

58. Robinson, S. G.; Wu, X.; Jiang, B.; Sigman, M. S.; Lin, S., Mechanistic Studies Inform Design of Improved Ti(salen) Catalysts for Enantioselective [3 + 2] Cycloaddition. *J. Am. Chem. Soc.* **2020,** *142* (43), 18471-18482.

59. Yang, J.; Zhang, X.-M.; Zhang, F.-M.; Wang, S.-H.; Tu, Y.-Q.; Li, Z.; Wang, X.-C.; Wang, H., Enantioselective Catalytic Aldehyde α-Alkylation/Semipinacol Rearrangement: Construction of α-Quaternary-δ-Carbonyl Cycloketones and Total Synthesis of (+)-Cerapicol. *Angewandte Chemie International Edition* **2020,** *59* (22), 8471-8475.

60. Berger, M.; Carboni, D.; Melchiorre, P., Photochemical Organocatalytic Regio- and Enantioselective Conjugate Addition of Allyl Groups to Enals. *Angewandte Chemie International Edition* **2021,** *60* (50), 26373-26377.

61. Großkopf, J.; Plaza, M.; Seitz, A.; Breitenlechner, S.; Storch, G.; Bach, T., Photochemical Deracemization at sp3-Hybridized Carbon Centers via a Reversible Hydrogen Atom Transfer. *J. Am. Chem. Soc.* **2021,** *143* (50), 21241-21245.

62. Lamhauge, J. N.; Corti, V.; Liu, Y.; Jørgensen, K. A., Enantioselective α-Etherification of Branched Aldehydes via an Oxidative Umpolung Strategy. *Angewandte Chemie International Edition* **2021,** *60* (34), 18728-18733.

63. Turek, A. K.; Sak, M. H.; Miller, S. J., Kinetic Analysis of a Cysteine-Derived Thiyl-Catalyzed Asymmetric Vinylcyclopropane Cycloaddition Reflects Numerous Attractive Noncovalent Interactions. *J. Am. Chem. Soc.* **2021,** *143* (39), 16173-16183.

64. Xiong, P.; Hemming, M.; Ivlev, S. I.; Meggers, E., Electrochemical Enantioselective Nucleophilic α-C(sp3)–H Alkenylation of 2-Acyl Imidazoles. *J. Am. Chem. Soc.* **2022,** *144* (15), 6964-6971.

65. Byun, S.; Hwang, M. U.; Wise, H. R.; Bay, A. V.; Cheong, P. H. Y.; Scheidt, K. A., Light-Driven Enantioselective Carbene-Catalyzed Radical-Radical Coupling. *Angewandte Chemie International Edition* **2023,** *62* (49), e202312829.

66. Chi, Z.; Liao, J.-B.; Cheng, X.; Ye, Z.; Yuan, W.; Lin, Y.-M.; Gong, L., Asymmetric Cross-Coupling of Aldehydes with Diverse Carbonyl or Iminyl Compounds by Photoredox-Mediated Cobalt Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (15), 10857-10867.

67. Hu, H.; Shi, Z.; Guo, X.; Zhang, F.-H.; Wang, Z., A Radical Approach for Asymmetric α-C–H Addition of N-Sulfonyl Benzylamines to Aldehydes. *J. Am. Chem. Soc.* **2024,** *146* (8), 5316-5323.

68. Jana, S.; Cramer, N., Tunable Thiazolium Carbenes for Enantioselective Radical Three-Component Dicarbofunctionalizations. *J. Am. Chem. Soc.* **2024,** *146* (51), 35199-35207.

69. Lahdenperä, A. S. K.; Dhankhar, J.; Davies, D. J.; Lam, N. Y. S.; Bacoş, P. D.; de la Vega-Hernández, K.; Phipps, R. J., A chiral hydrogen atom abstraction catalyst for the enantioselective epimerization of meso-diols. *Science* **2024,** *386* (6717), 42-49.

70. Lam, N. Y. S.; Dhankhar, J.; Lahdenperä, A. S. K.; Phipps, R. J., Catalytic Enantioselective Hydrogen Atom Abstraction Enables the Asymmetric Oxidation of Meso Diols. *J. Am. Chem. Soc.* **2024,** *146* (49), 33302-33308.

71. Li, C.; Cheng, J.; Wan, X.; Li, J.; Zu, W.; Xu, Y.; Huang, Y.; Huo, H., Ni/Photoredox-Catalyzed Enantioselective Acylation of α-Bromobenzoates with Aldehydes: A Formal Approach to Aldehyde-Aldehyde Cross-Coupling. *J. Am. Chem. Soc.* **2024,** *146* (29), 19909-19918.

72. Tang, L.; Shen, C.; Hao, S.; Dong, K., A Type of Chiral C2-Symmetric Arylthiol Catalyst for Highly Enantioselective Anti-Markovnikov Hydroamination. *J. Am. Chem. Soc.* **2024,** *146* (23), 16248-16256.

73. Zhong, Z.; Wu, H.; Chen, X.; Luo, Y.; Yang, L.; Feng, X.; Liu, X., Visible-Light-Promoted Enantioselective Acylation and Alkylation of Aldimines Enabled by 9-Fluorenone Electron-Shuttle Catalysis. *J. Am. Chem. Soc.* **2024,** *146* (29), 20401-20413.