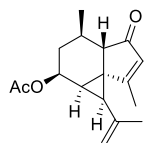


Shagene A



Shagene B

Tsukano, C.; Yagita, R.; Heike, T.; Mohammed, T. A.; Nishibayashi, K.; Irie, K.; Takemoto, Y. Asymmetric Total Synthesis of Shagenes A and B. *Angew. Chemie Int. Ed.* **2021**, 1–6

Isolated by baker and coworkers in 2014 from a soft coral in the Scotia Sea (between South America and Antarctica)

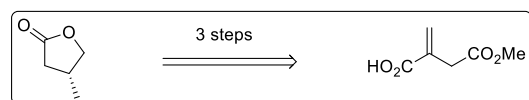
Investigation in the development of pharmaceuticals against Leishmaniasis

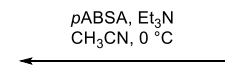
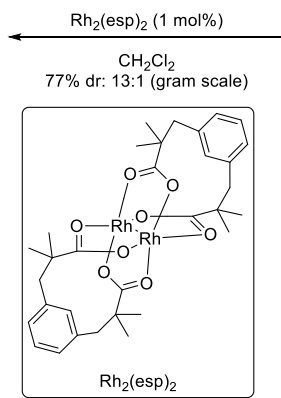
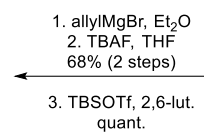
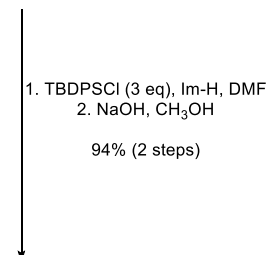
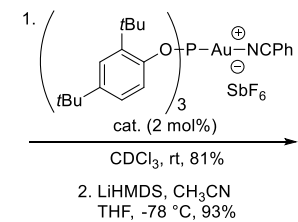
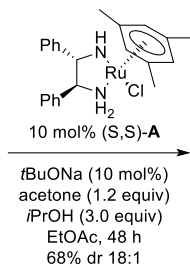
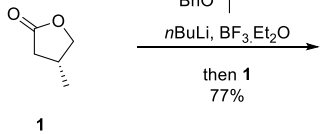
First enantioselective total synthesis

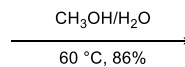
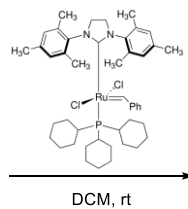
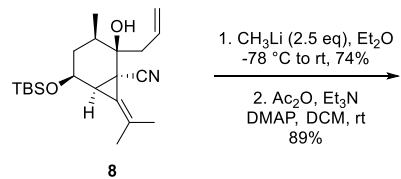
First determination of absolute configurations

Shagene A: 24 steps

Shagene B: 22 steps







9

10

11

Burgess reagent, THF
rt

Stereochemistry

[Ir(cod)(Py)(PCy₃)]BAR_F
(8 mol%)

H₂ then Argon
DCM, rt, 3 h
87%

TMSCl, LiHMDS
Et₃N, THF, -78 °C

then
1 M HCl in Et₂O
72%

1. CH₃Li, Et₂O, 0 °C
2. PDC, CH₂Cl₂, rt, 2 h
63% (2 steps)

Structure and name of PDC?

14

13

12

12'

1. DIBAL-H, DCM

1. CH₃I, NaH, THF, 50 °C
2. TBAF, THF
3. Ac₂O, Et₃N, DMAP, DCM

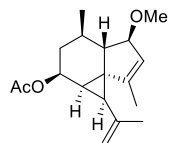
91% (3 steps)

16

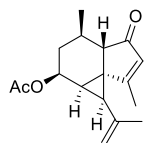
16'

A

1. HF, Pyr, THF
2. Ac₂O, Et₃N, DMAP, DCM
89% (2 steps)



Shagene A



Shagene B

Tsukano, C.; Yagita, R.; Heike, T.; Mohammed, T. A.; Nishibayashi, K.; Irie, K.; Takemoto, Y. Asymmetric Total Synthesis of Shagenes A and B. *Angew. Chemie Int. Ed.* **2021**, 1–6

Isolated by baker and coworkers in 2014 from a soft coral in the Scotia Sea (between South America and Antarctica)

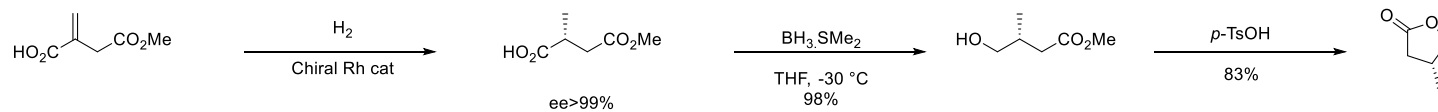
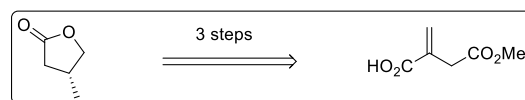
Investigation in the development of pharmaceuticals against Leishmaniasis

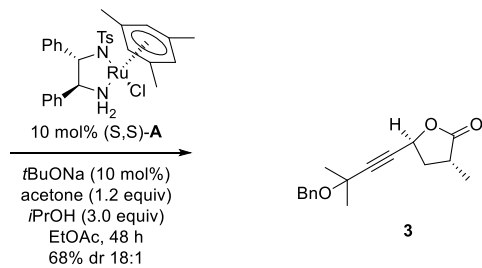
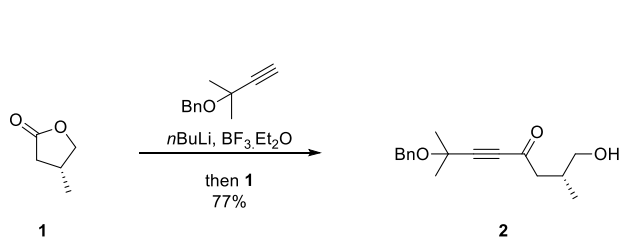
First enantioselective total synthesis

First determination of absolute configurations

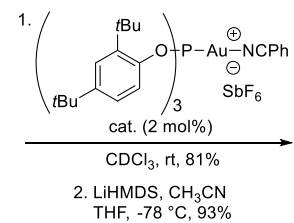
Shagene A: 24 steps

Shagene B: 22 steps

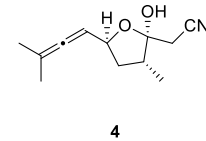




Mechanism



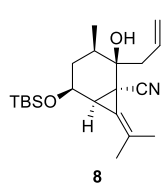
Mechanism



1. TBDPSCI (3 eq), Im-H, DMF

 2. NaOH, CH₃OH

 94% (2 steps)



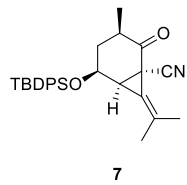
1. allylMgBr, Et₂O

 2. TBAF, THF

 68% (2 steps)

 3. TBSOTf, 2,6-lut.

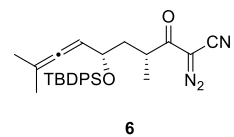
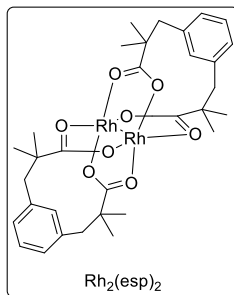
 quant.



$\text{Rh}_2(\text{esp})_2 \text{ (1 mol\%)}$

 CH_2Cl_2

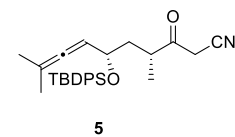
 77% dr: 13:1 (gram scale)

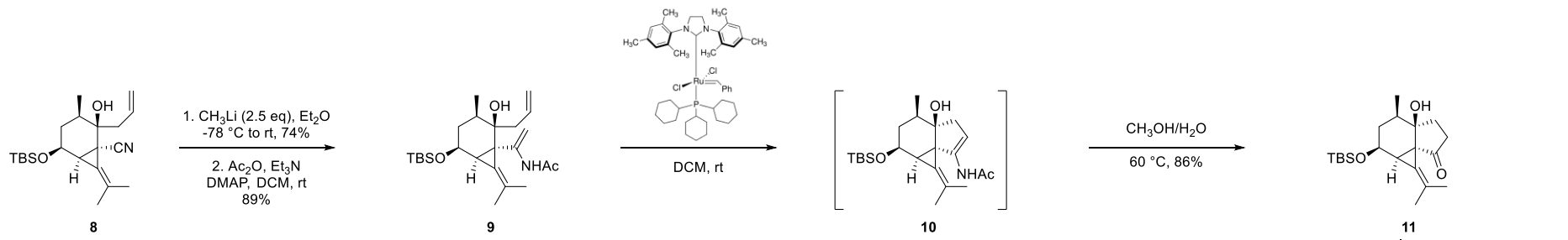


$p\text{ABSA, Et}_3\text{N}$

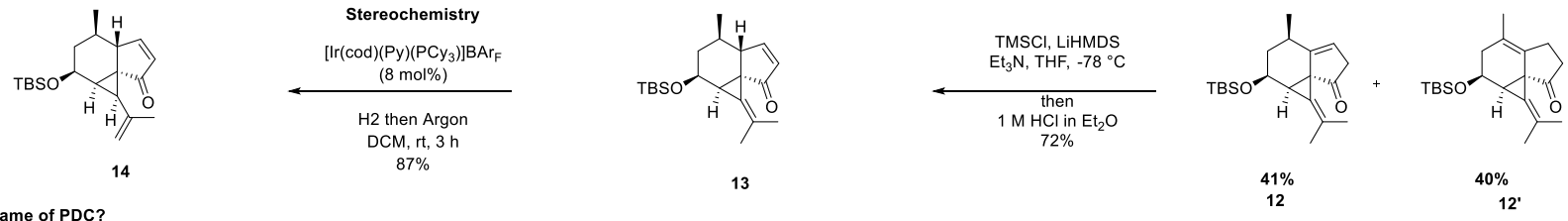
 $\text{CH}_3\text{CN, 0 }^\circ\text{C}$

Structure pABSA



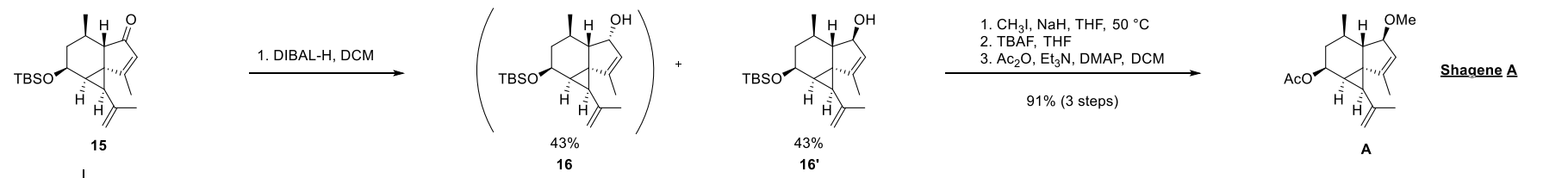


Burgess reagent, THF, rt



1. CH₃Li, Et₂O, 0 °C
2. PDC, CH₂Cl₂, rt, 2 h
63% (2 steps)

Structure and name of PDC?



1. HF, Pyr, THF
2. Ac₂O, Et₃N, DMAP, DCM
89% (2 steps)

