

SYNFACTS Highlights in Current Synthetic Organic Chemistry

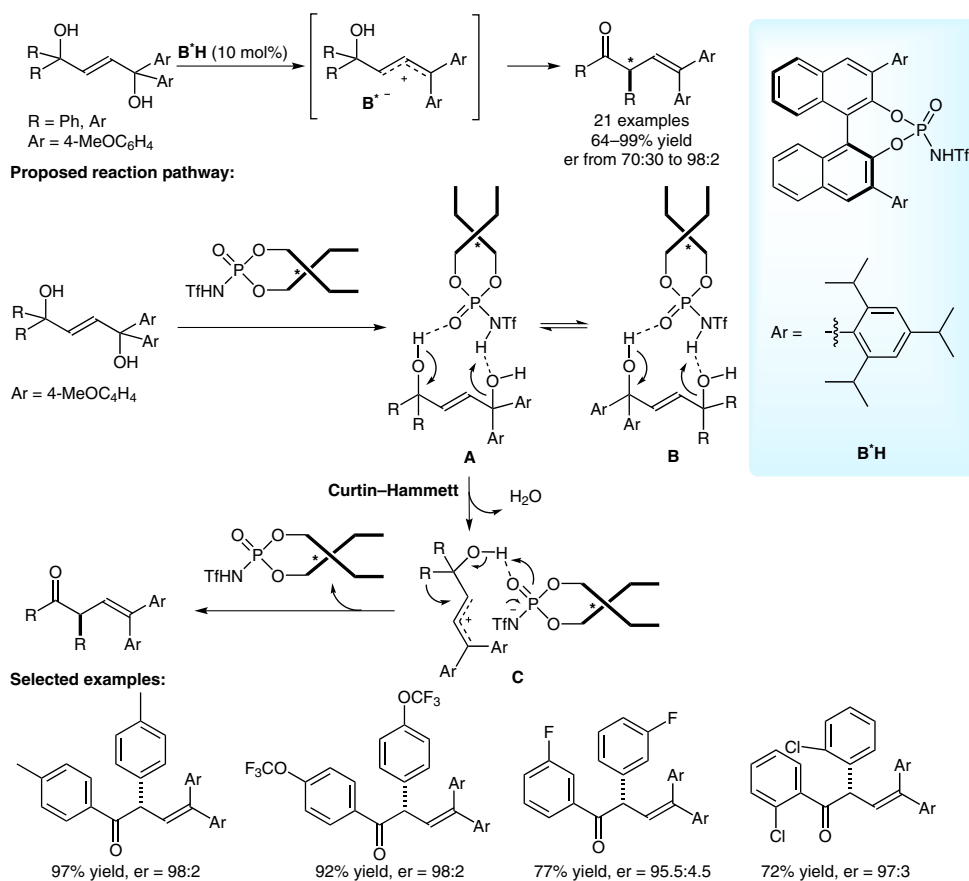
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Catalytic Enantioselective Vinylogous Pinacol Rearrangement



Significance: Zhu and co-workers report the first enantioselective vinylogous pinacol rearrangement of 1,4-diols using a chiral *N*-triflylphosphoramidate catalyst. It is proposed that ion pairing between the intermediate allylic cation and the conjugated base of the chiral Brønsted acid is the key to achieving high selectivities. Synthetic applications of this method were demonstrated by a subsequent conversion of the resulting β,γ -unsaturated ketones into enantioenriched polysubstituted tetrahydrofuran and tetrahydronaphthalene derivatives.

Comment: The vinylogous pinacol rearrangement is a well-known reaction and has been applied in the synthesis of various natural products. Here, the authors report the first catalytic asymmetric variant of this transformation, achieved by using a chiral *N*-triflylphosphoramidate catalyst and careful substrate design. However, the substrates are limited to those with diaryl substituents that can stabilize the intermediate allylic cation. This method would be even more useful if its substrate scope could be broadened.