

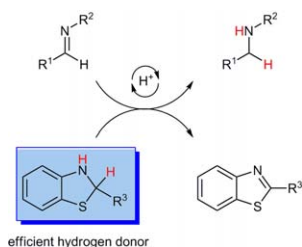
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Cluster

Brønsted acid catalysis will solve a variety of difficult problems in organic synthesis as constantly demonstrated in recent publications in the fields of asymmetric synthesis. The present Cluster provides state-of-the-art contributions from this growing field of chemical research.

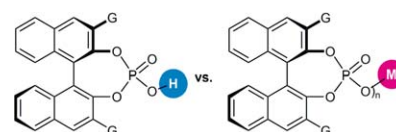
Hisashi Yamamoto and Viresh Rawal



T. Akiyama



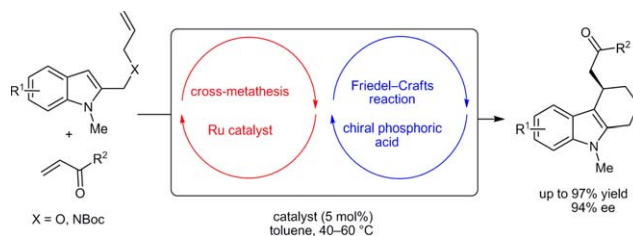
M. Terada



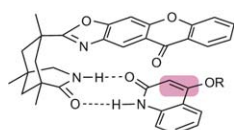
S.-L. You



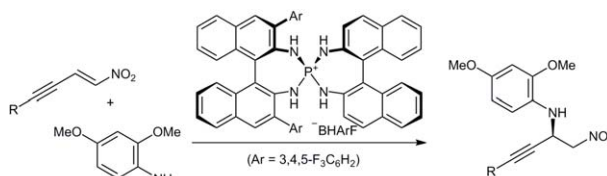
T. Bach



T. Ooi



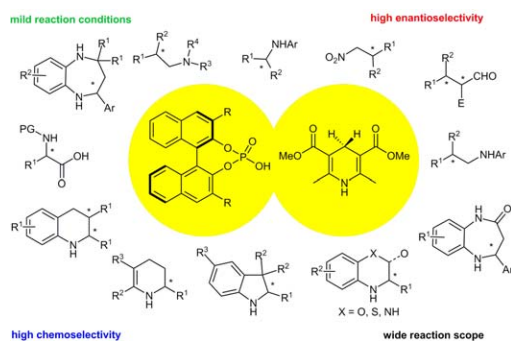
catalytic enantioselective
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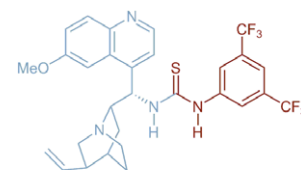
Brønsted Acid Catalysis



M. Rueping



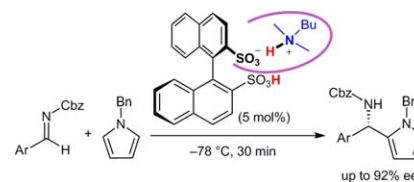
P. R. Schreiner



N. Takenaka



K. Ishihara



Brønsted Acid Catalysis

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Enantioselective catalysis had been the domain of metal-based Lewis acid complexes for decades. Hundreds of catalysts, each with a metal or metalloid atom at its center, have been developed, and these have proven effective for the promotion of a plethora of enantioselective reactions. While such catalysts continue to play a prominent role in chemical synthesis, the field of asymmetric catalysis has undergone a paradigm shift over the past ten-plus years with the advent of metal-free catalysts, dubbed organic catalysts. These new catalysts have opened up novel activation modes to accomplish a variety of enantioselective transformations. A prominent and rapidly developing subset of this field, one that shares conceptual similarities to metal-based Lewis acid catalysis, is referred to by the terms hydrogen-bonding catalysis, Brønsted acid catalysis and, occasionally, chiral proton catalysis. Analogous to metal activation, hydrogen-bond formation increases the electrophilicity of the reactant by lowering its LUMO energy, while the catalyst's chiral environment induces enantioselectivity in the reaction. The ready tunability of the donor hydrogen combined with the possibility of installing multiple hydrogen bond donor units, for greater organization and activation of the reactants, makes H-bonding catalysis a powerful modality for asymmetric reactions. Additionally, hydrogen-bonding catalysts are well suited for incorporation of Brønsted basic atoms, thereby enabling bifunctional catalysis. The ultimate value of H-bonding catalysis, however, lies not so much in its potential to supplant metal-based catalysis, but in its capacity to expand the scope of reactions that can be made asymmetric. Indeed, this potential has already been realized: H-bonding catalysis has enabled the development of entirely new enantioselective reactions, processes for which there are no equivalent metal-catalyzed reactions. This issue of *SYNLETT* includes a Cluster of papers describing some of the latest developments in hydrogen-bonding/Brønsted acid catalysis by leaders in the field.

