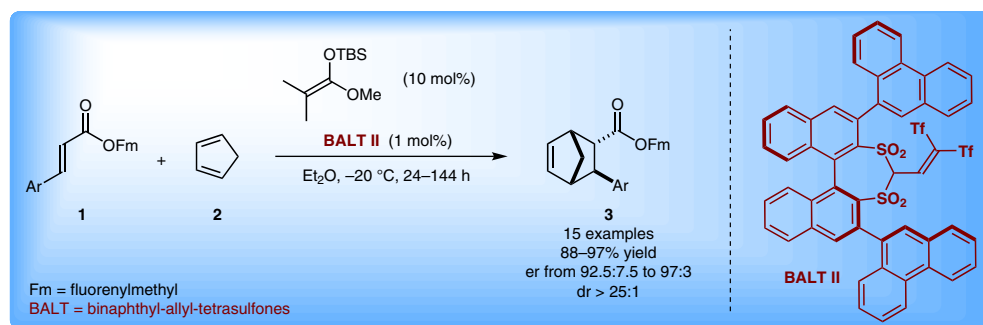
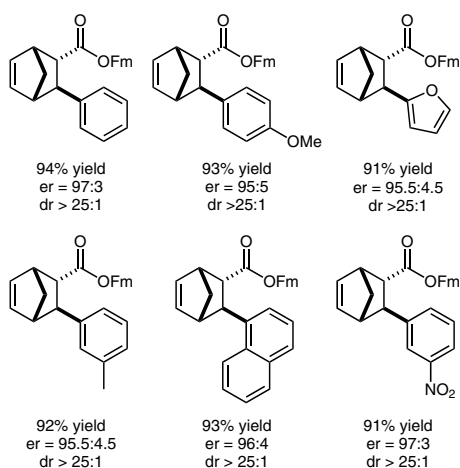


T. GATZENMEIER, M. VAN GEMMEREN, Y. XIE, D. HÖFLER, M. LEUTZSCH, B. LIST* (MAX PLANCK INSTITUT FÜR KOHLENFORSCHUNG, MÜLHEIM AN DER RUHR, GERMANY)
Asymmetric Lewis Acid Organocatalysis of the Diels–Alder Reaction by a Silylated C–H Acid
Science **2016**, *351*, 949–952.

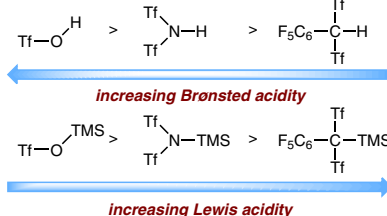
A Silylated C–H Acid Catalyst for Asymmetric Diels–Alder Reactions of Cinnamates



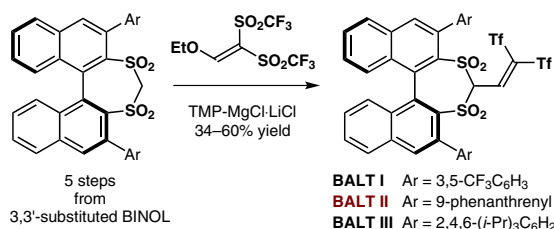
Selected examples:



Work inspiration – activity trends for achiral catalysts



Catalyst synthesis:



Significance: The List group reports the development of novel chiral C–H acids and their application as pre-Lewis acid organocatalysts in an asymmetric Diels–Alder reaction of the challenging cinnamates **1** with cyclopentadiene (**2**). In particular, the binaphthyl-allyl-tetrasulfone **BALT II** proved to be a superior precatalyst, which after activation (by silylation) afforded the desired Diels–Alder products **3** in excellent diastereo- and enantioselectivities and high yields. The substrate scope is broad and the catalyst loading is low (1 mol%).

Comment: List and co-workers disclose a novel concept in the increasingly expanding field of asymmetric counteranion directed catalysis with silylium ions. For the first time, only a catalytic amount of a silylating agent is required to generate the active silylated catalyst from an unprecedented chiral C–H acid. Control experiments indicated that no reaction occurred under Brønsted acid catalysis. The superior activity of these motifs is underlined by the only previous example of this reaction, which involved activated trifluoroethyl cinnamates (at 20 °C), and a high loading (20 mol%) of a protonated oxaborolidine catalyst (D. H. Ryu, E. J. Corey *J. Am. Chem. Soc.* **2003**, *125*, 6388).

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