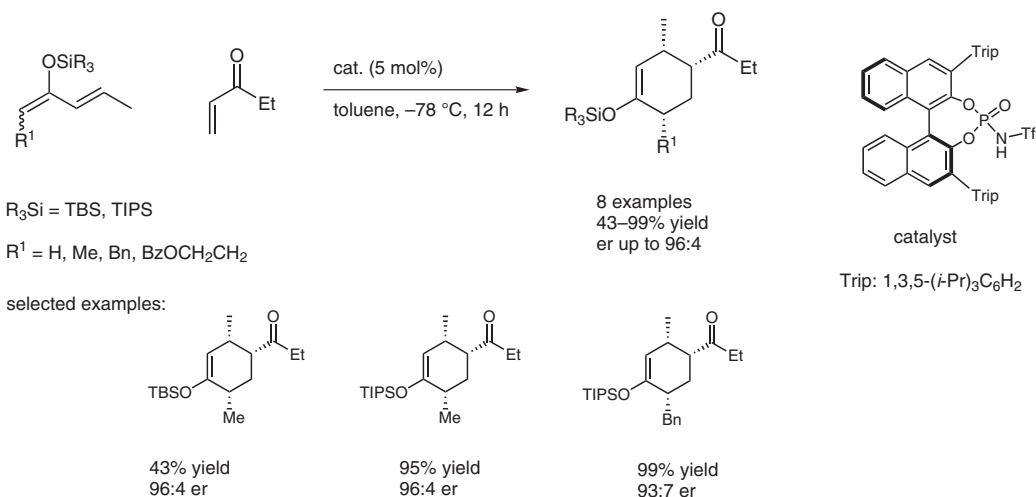


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Design of Chiral *N*-Triflyl Phosphoramidate as a Strong Chiral Brønsted Acid and Its Application to Asymmetric Diels–Alder Reaction*J. Am. Chem. Soc.* **2006**, *128*, 9626–9627.

A Phosphoramidate Catalyzed Asymmetric Diels–Alder Reaction



Significance: An organocatalyzed asymmetric Diels–Alder reaction of ethyl vinyl ketone with silyloxydiene is described. For this purpose, the authors have developed a *N*-triflyl phosphoramidate as a strong chiral Brønsted acid catalyst. This chiral catalyst allows the activation of unsaturated ketones, leading to substituted cyclohexene derivatives in moderate to good yields and good enantioselectivities.

Comment: Although metal Lewis acid catalyzed asymmetric Diels–Alder reactions are well established, reactions of α,β -unsaturated ketones are still challenging. The authors have recently shown that an achiral metal-free Brønsted acid may function as a catalyst in a non-asymmetric variant of this reaction and they now extend it to an asymmetric variant. Recently, several examples of asymmetric Brønsted acid catalysis have been reported, using chiral alcohols, thioureas, ammonium salts and phosphoric acids as appropriate catalysts. These catalysts are suitable for the activation of imines and in some cases of carbonyl compounds, although most reports are confined to reactive substrates. By modifying the well-established phosphoric acid motif, the authors overcome this limitation. The utilized *N*-triflyl catalysts are stronger Brønsted acids and are suitable catalysts for the asymmetric Diels–Alder reaction of α,β -unsaturated ketones in good enantioselectivities.

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