S. KOBAYASHI,* T. ENDO, M. UENO (THE UNIVERSITY OF TOKYO, JAPAN)
Chiral Zinc-Catalyzed Asymmetric α-Alkylallylation and α-Chloroallylation of Aldehydes
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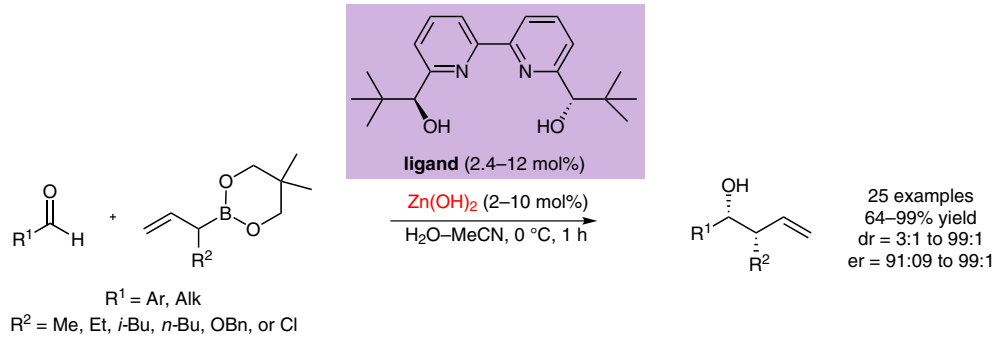
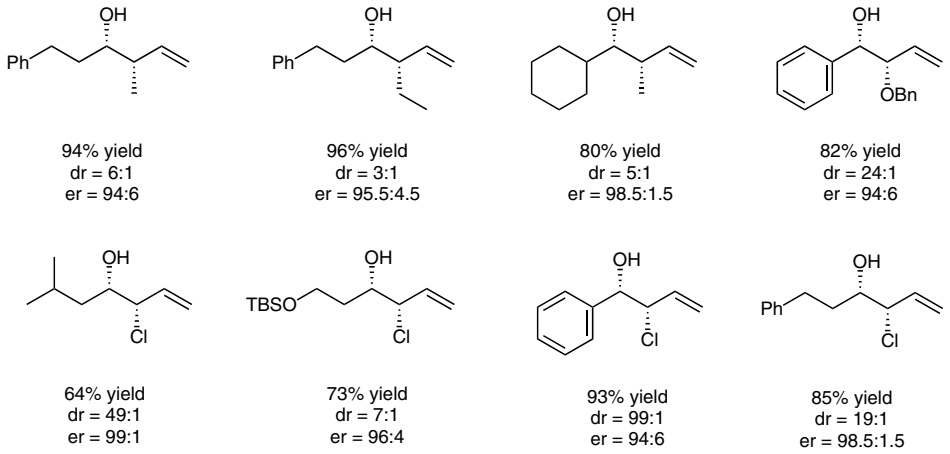
Zinc-Catalyzed Asymmetric α-Alkylallylation of Aldehydes



Selected examples:



Significance: Asymmetric allylation of aldehydes is an efficient method for the preparation of allylic alcohols, which are useful intermediates in the synthesis of complex molecules. In this report, a combination of Zn(II) and a chiral phenanthroline-diol ligand catalyzes the addition of allylboronates to aldehydes. High yields, diastereoselectivity and enantioselectivity are obtained, even in the case of α-alkylallylation and α-chloroallylation.

Comment: Based on kinetic studies, the authors propose that the rate-determining step of the reaction is transmetalation from B to Zn, leading to an active γ-substituted allylzinc species. Remarkably, this reaction takes place at 0 °C and in aqueous media. An interesting X-ray crystal structure of the ligand complexed with $ZnBr_2$ was reported, providing insight into the origin of enantioselectivity.

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Category
Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words
allylation
crotylation
boron reagents
zinc
aqueous media