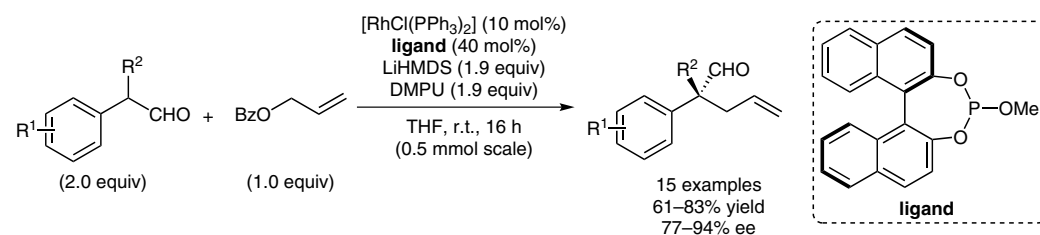


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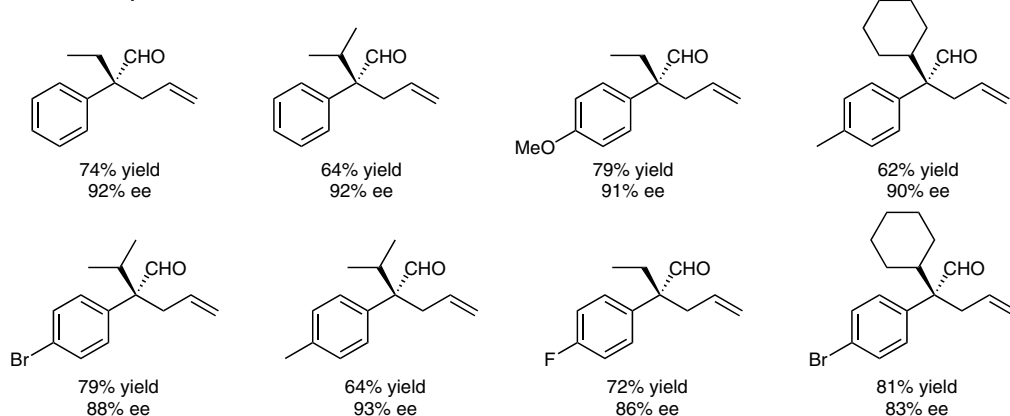
Enantioselective Rhodium-Catalyzed Allylic Alkylation of Prochiral α,α -Disubstituted Aldehyde Enolates for the Construction of Acyclic Quaternary Stereogenic Centers

J. Am. Chem. Soc. **2016**, *138*, 15303–15306.

Enantioselective Rhodium-Catalyzed α -Allylation of Aldehydes



Selected examples:



Significance: The α -functionalization of aldehydes via the formation of the corresponding enolates remains a challenge in modern synthetic chemistry. The high propensity for aldehydes to undergo competing side-reactions under basic conditions, in addition to the difficulties associated with the control of the enolate geometry in acyclic systems limit their application in stereoselective transformations. In the present work, Wright and Evans present a highly enantioselective rhodium-catalyzed allylic alkylation of α -alkyl benzylic aldehydes.

Comment: The reaction of α -alkyl benzylic aldehydes with allyl benzoate was catalyzed by a chiral rhodium-complex in the presence of LiHMDS as a base and DMPU as deaggregating reagent. The corresponding aldehydes, bearing a stereogenic quaternary center in the α -position, were obtained in moderate to good yields and enantioselectivities. The choice of the base and of the deaggregating agent was crucial for the stereochemical outcome of the reaction. Several derivatizations of the resulting products were carried out to illustrate the synthetic utility of these compounds. No examples of allylation of α,α -dialkyl aldehydes were reported.

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