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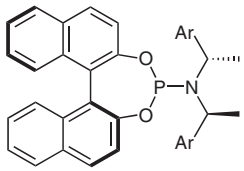
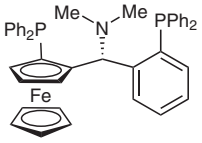
Catalytic Asymmetric Carbon–Carbon Bond Formation via Allylic Alkylations with Organolithium Compounds
Nat. Chem. **2011**, *3*, 377-381.

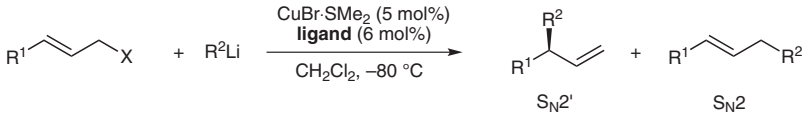
Copper-Catalyzed Asymmetric Allylic Alkylation with Organolithium Reagents



phosphoramidite
Ar = Ph, 2-MeOC$_6$H$_4$



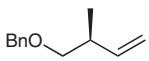
Taniaphos



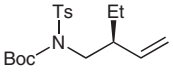
X = Cl, Br
R^1 = Ar, Alk
R^2 = Alk, Ph

25 examples
S$_N$2'/S$_N$2 = 40:60–100:0
39% to >99% yield
82% to >99% ee

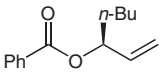
Products showing functional group tolerance:



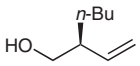
S$_N$2/S$_N$2 = 85:15
98% yield
90% ee



S$_N$2'/S$_N$2 = 84:16
72% yield
86% ee

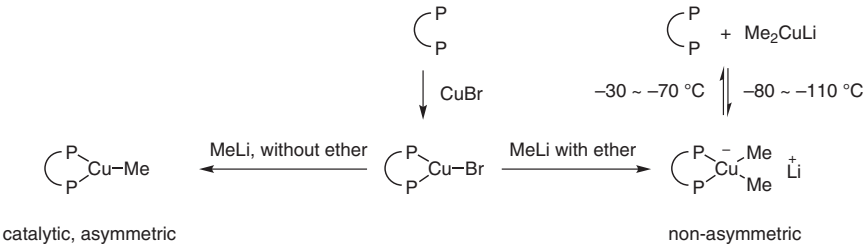


S$_N$2'/S$_N$2 = 100:0
82% yield
98% ee



S$_N$2'/S$_N$2 = 96:4
99% conversion
90% ee

Proposed catalytic complex:



catalytic, asymmetric

non-asymmetric

Significance: This report describes the utilization of organolithium reagents as nucleophile sources in copper-catalyzed asymmetric allylic alkylation. Using Taniaphos as the chiral ligand, various alkyllithium reagents are nicely coupled with substituted allyl bromides in S$_N$2′ manner. Using a chiral phosphoramidite ligand allows cinnamyl chloride and phenyllithium to participate in the reaction.

Comment: The authors proposed from ^{31}P NMR studies that the reaction passes through an intermediate state of a diphosphine copper monoalkyl species. Using ether as co-solvent stops the formation of this intermediate, therefore diminishes enantioselectivity. This method tolerates a broad range of functional groups. It provides high regio- and enantioselectivity for a very general scope of allyl halides.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

allylic alkylation

organolithium compounds

copper

C–C bond formation