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

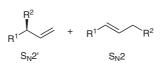
Copper-Catalyzed Asymmetric Allylic Alkylation with Organolithium Reagents

phosphoramidite Ar = Ph, 2-MeOC₆H₄

Taniaphos

$$X = CI, Br$$

 $R^1 = Ar, Alk$
 $R^2 = Alk, Ph$



25 examples $S_N2'/S_N2 = 40:60-100:0$ 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

 $S_N 2' / S_N 2 = 100:0$ 82% yield

Boc N Et

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

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

Proposed catalytic complex:

 $\label{eq:Significance: This report describes the utilization of organolithium reagents as nucleophile sources in copper-catalyzed asymmetric allylic alkylation. Using Taniaphos as the chiral ligand, various alkyllithium reagents are nicely coupled with substituted allyl bromides in SN2' manner. Using a chiral phosphoramidite ligand allows cinnamyl chloride and phenyllithium to participate in the reaction.$

SYNFACTS Contributors: Hisashi Yamamoto, Zhi Li Synfacts 2011, 8, 0855-0855 Published online: 20.07.2011 **DOI:** 10.1055/s-0030-1260817; **Reg-No.:** H08311SF

Comment: The authors proposed from ³¹P 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 regioand enantioselectivity for a very general scope of allyl halides.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

allylic alkylation

organolithium compounds

coppe

C-C bond formation

