

J. T. BINDER, C. J. CORDIER, G. C. FU* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE AND CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, USA)
 Catalytic Enantioselective Cross-Couplings of Secondary Alkyl Electrophiles with Secondary Alkylmetal Nucleophiles: Negishi Reactions of Racemic Benzylic Bromides with Achiral Alkylzinc Reagents
J. Am. Chem. Soc. **2012**, *134*, 17003–17006.

Category

Metal-Catalyzed
 Asymmetric
 Synthesis and
 Stereoselective
 Reactions

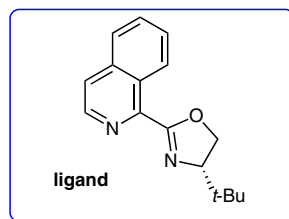
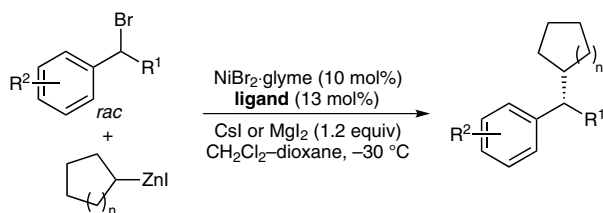
Key words

nickel

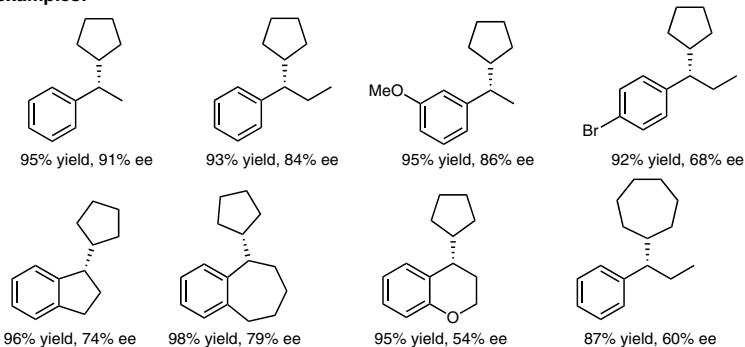
Negishi coupling

oxazoline ligands

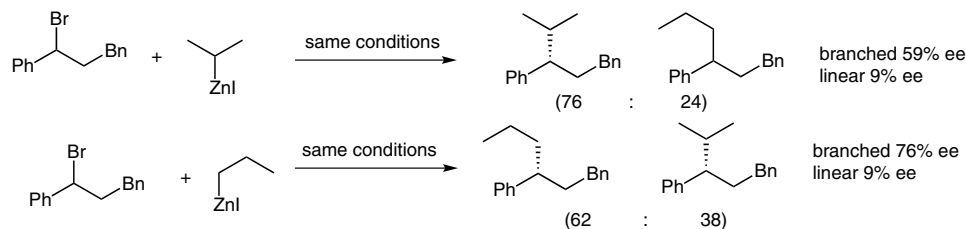
Negishi Reaction of Racemic Benzylic Bromides and Alkylzinc Reagents



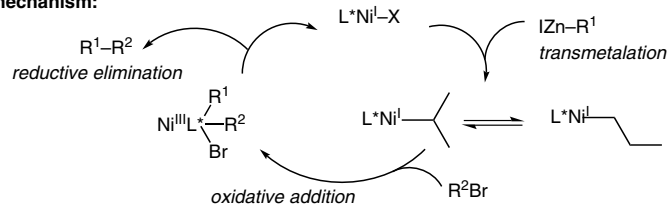
Selected examples:



For acyclic alkylzinc reagents:



Proposed mechanism:



Significance: Reported here is an enantioselective cross-coupling of racemic benzylic bromides with achiral alkylzinc reagents. A novel bidentate oxazoline-type ligand was developed, leading to the desired products in good yield and enantioselectivity.

Comment: It is surprising that both reagents are achiral. For acyclic alkylzinc reagents, an usual isomerization was observed and a substantial amount of a branched product was generated from an unbranched nucleophile.

SYNFACTS Contributors: Hisashi Yamamoto, Jiajing Tan
 Synfacts 2013, 9(1), 0073 Published online: 17.12.2012
 DOI: 10.1055/s-0032-1317780; Reg-No.: H16012SF

2013 © THIEME STUTTGART • NEW YORK