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Effect of Chiral Diene Ligands in Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to α,β-Unsaturated Sulfonyl Compounds
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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

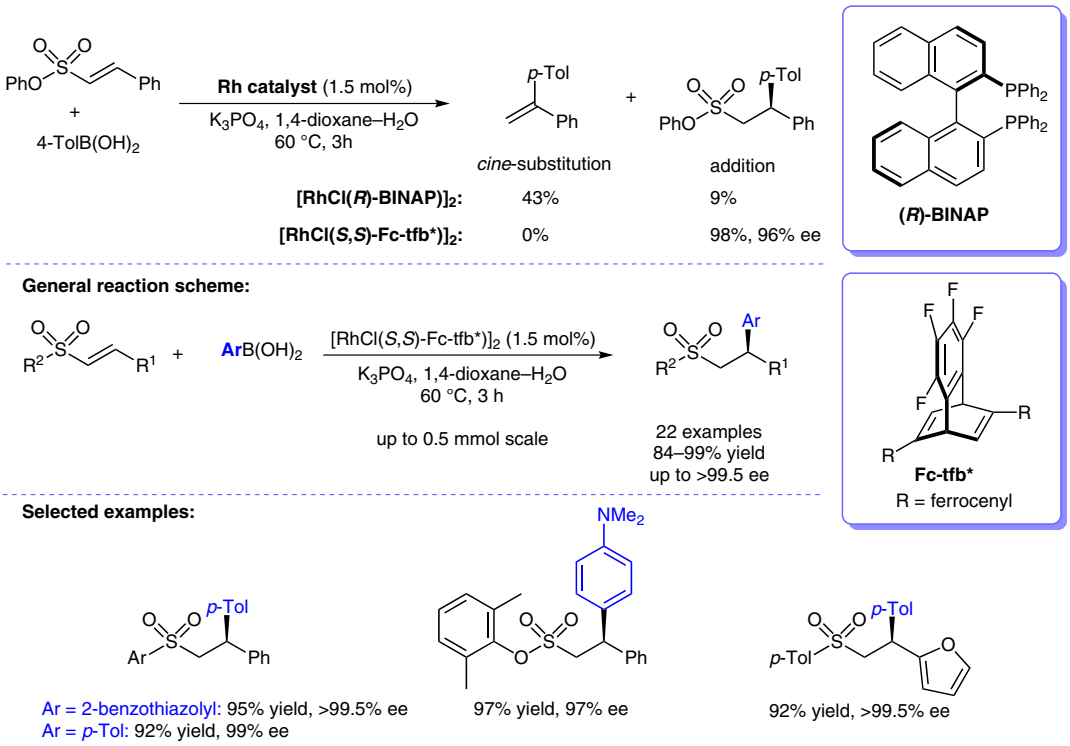
Key words

rhodium

arylboronic acids

α,β-unsaturated sulfonyls

Rh-Catalyzed Addition of Arylboronic Acids to α,β-Unsaturated Sulfonyls



Significance: Rh-catalyzed asymmetric addition of organoboron reagents to electron-deficient alkenes has become a very reliable method for the synthesis of chiral carbonyl compounds (see Review below). However, α,β-unsaturated sulfonyl compounds are prone to the competing *cine*-substitution and thus far, selective addition was only possible with 2-pyridyl sulfones. The authors report that the use of a Rh/diene catalytic system allows for the selective addition of arylboronic acids to α,β-unsaturated sulfonyls in high yields and enantioselectivities.

Review: G. Berthon, T. Hayashi, In *Catalytic Asymmetric Conjugate Reactions*; A. Córdova, Ed.; Wiley-VCH: Weinheim, **2010**, 1–70.

Comment: In this present reaction, the use of the chiral diene ligand Fc-tfb* allowed for the asymmetric addition of arylboronic acids to α,β-unsaturated sulfonyl compounds to selectively form the addition product. Though both catalysts promote the asymmetric addition of the arylboronic acid, the chiral diene ligand allowed faster protonation of the alkylrhodium intermediate, whereas with the more commonly used bisphosphine ligand BINAP, the competitive β-hydrogen elimination pathway led to mainly the *cine*-substitution product. This new catalytic system allowed the synthesis of a variety of chiral sulfonyl compounds with high yields and excellent enantioselectivity, including precursors for the modified Julia olefination (Ar = 2-benzothiazolyl).

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