Nickel-Catalyzed Asymmetric Reductive Coupling of Vinyl and Benzyl Halides

**Significance:** The nickel-catalyzed reductive coupling of two organic electrophiles offers a unique synthetic approach to form C–C bonds (see Review below). Reisman and co-workers report an enantioselective Ni-catalyzed reductive coupling of vinyl bromides and racemic benzylic chlorides, giving rise to substituted alkenes bearing a chiral tertiary allylic center. Although transition-metal-catalyzed allylic alkylation methods using activated organometallic reagents can provide access to similar motifs, there are few regio- and enantioselective methods for the arylation of acyclic, unsymmetrical α,γ-disubstituted allylic electrophiles (for one recent example, see: S. Son, G. C. Fu J. Am. Chem. Soc. 2008, 130, 2756).

**Comment:** Using this method, a wide range of electron-rich and electron-deficient vinyl bromides and benzylic chlorides can be employed. Both meta and para substitution on the benzyl chloride component are well tolerated. However, ortho-substituted benzylic chloride derivatives demonstrate poor reactivity and lead to lower enantioselectivities. The coupled products are obtained in good to modest yields with generally high enantioselectivity. The use of β-substituted benzyl chlorides does not lead to any erosion in enantiomeric excess. Experiments using radical inhibitors or radical clocks are inconsistent with a radical chain mechanism.