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 \( \alpha,\gamma \)-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 benzylic 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 \( \beta \)-substituted benzylic chlorides does not lead to any erosion in enantiomeric excess. Experiments using radical inhibitors or radical clocks are inconsistent with a radical chain mechanism.


**Key words**
- nickel
- reductive coupling
- vinyl bromides
- benzyl chlorides

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