Nickel/Bis(oxazoline)-Catalyzed Asymmetric Negishi Arylations of Racemic Secondary Benzylic Electrophiles to Generate Enantioenriched 1,1-Diarylalkanes


**Arylation of Racemic Secondary Benzylic Electrophiles by Nickel Catalysis**

**Significance:** The 1,1-diarylalkane motif is found in a number of the top-selling pharmaceuticals. Therefore, the development of stereoselective methods to access this motif is a worthwhile pursuit. The authors report a two-step stereoselective synthesis of 1,1-diarylalkanes starting from racemic benzylic alcohols, which proceeds in excellent yields and with excellent enantioselectivities.

**Comment:** A previous report by the same group disclosed a nickel-catalyzed enantioconvergent Negishi arylation of propargylic carbonates that was not applicable to the use of racemic benzylic carbonates (*J. Am. Chem. Soc.* 2012, 134, 2966). The current method generates a benzylic mesylate in situ. The authors propose that the lithium iodide additive transforms the mesylate into an alkyl iodide, which can then participate in the Negishi cross-coupling.

**Selected examples:**

- **OMe**
  - 92% yield
  - 94% ee

- **OMe**
  - 87% yield
  - 93% ee

- **OMe**
  - 88% yield
  - 92% ee

- **OMe**
  - 88% yield
  - 93% ee

- **OMe**
  - 98% yield
  - 94% ee

- **CF₃**
  - 87% yield
  - 94% ee

- **BocN**
  - 77% yield
  - 93% ee

- **CO₂t-Bu**
  - 80% yield
  - 92% ee

**Key words**

- nickel
- Negishi cross-coupling
- enantioconvergency
- 1,1-diarylalkanes