J. S. MARCUM, S. J. MEEK* (UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL, USA)
Efficient Enantio-, Diastereo-, E/Z-, and Site-Selective Nickel-Catalyzed Fragment Couplings of Aldehydes, Dienes, and Organoborons
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Nickel-Catalyzed Enantioselective Multicomponent Reaction of 1,3-Dienes, Aldehydes, and Boronic Acids

Significance: Marcum and Meek report a nickel-catalyzed multicomponent coupling reaction of aldehydes, 1,3-dienes, and arylboronic acids. The method is enantio-, diastereo-, and regioselective, affording the olefin products with extremely high E selectivity.

Comment: The authors propose that the reaction initiates via an oxidative cyclization of the 1,3-diene and the aldehyde. Subsequent transmetalation with the arylboronic acid and reductive elimination yields the product. Mechanistic studies using D₂O reveal no deuterium is incorporated.

Select examples:

- 85% yield, er = 97:3  
  rrr = 97:3, E/Z > 98:2
- 65% yield, er = 89:11  
  rr = 92:8, E/Z > 98:2
- 86% yield, er = 95:5:4:5  
  rr = 97:3, E/Z > 98:2
- 89% yield, er = 97:3  
  rr = 96:4, E/Z > 98:2

Accessing functionalized tetrahydropyrans: