Diastereoselective and Enantioselective Conjunctive Cross-Coupling Enabled by Boron Ligand Design


Diastereo- and Enantioselective Conjunctive Cross-Coupling via a Metallate Shift

**Significance:** The authors describe a conjunctive cross-coupling process to access products with vicinal stereogenic centers. This method avoids the generation of Suzuki–Miyaura stilbene byproducts obtained when typical boronic esters are employed.

**Comment:** Products are obtained in moderate yields and excellent enantio- and diastereoselectivities. The synthetic utility of the –B(mac) handle is demonstrated. Additionally, this methodology was used for the synthesis of (+)-obtusafuran.

**Selected examples:**
- X = OTf, 73% yield, er > 99:1
- X = OTf, 81% yield, er > 99:1
- X = Br, 58% yield, er > 99:1
- X = OTf, 64% yield, er > 99:1
- X = Br, 60% yield, er > 99:1
- X = OTf, 47% yield, er = 99:1
- X = OTf, 65% yield, er = 99:1

**Derivatizations of alkylB(mac):**

**Synthesis of (+)-obtusafuran:**

- PhLi, THF then Pd(OAc)2 (1 mol%) (mac)B Ph OMe Ph OMe 70% yield, dr > 20:1 er > 99:1 (according to oxidized product)
- NaOH, H2O2, THF, r.t., 4 h
- MeONH2, n-BuLi THF, 60 °C, 15 h then Boc2O
- BrCH2Cl, n-BuLi NaOTf, THF
- 92% yield

- PhLi, THF then Pd(OAc)2 (1 mol%) (mac)B Ph OMe Ph OMe Ph OMe 68% yield dr > 20:1 cat. Pd(OAc)2 Li2CO3, Ph(OAc)2 CsF, 100 °C, 24 h then TBAF
- Then TBAF
- (+)-obtusafuran 40% yield, er > 99:1

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