Diastereo- and Enantioselective Conjunctive Cross-Coupling via a Metalate 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 = OTf, 47% yield**
  - er > 99:1
- **X = OTf, 60% yield**
  - er > 99:1
- **X = OTf, 81% yield**
  - er > 99:1
- **X = OTf, 58% yield**
  - er > 99:1
- **X = OTf, 60% yield**
  - er > 99:1

**Derivatizations of alkylB(mac):**
- **PhLi, THF**
  - then
  - Pd(OCOCF3) (1 mol%) **ligand** (1.2 mol%) 4-MeOPhOTf, CsF
  - THF, 40 °C, 15 h
  - 70% yield, dr > 20:1
  - er > 99:1 (according to oxidized product)

**Synthesis of (+)-obtusafuran:**
- **cat. Pd(OCOCF3)**
  - Li2CO3, PhI(OAc)2
  - C6F6, 100 °C, 24 h
  - then TBAF
  - 68% yield
  - dr > 20:1

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