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


**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.

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**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 = Br, 60% yield, er > 99:1**

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

- **MeONH2, n-BuLi, THF, 60 °C, 15 h, then Boc2O, NaOH, H2O2, THF, rt., 4 h**
- **92% yield**
- **89% yield**
- **84% yield**

- **cat. Pd(OAc)2, L16818SF**
- **68% yield**
- **dr > 20:1**
- **(+)-obtusafuran, 40% yield, er > 99:1**