Stereospecific Functionalization of Activated Alkylboronic Esters under Copper Catalysis

**Significance:** A copper-catalyzed method for the stereospecific functionalization of boron ‘ate’ complexes obtained from enantioenriched pinacol boronic esters and tert-butyllithium is disclosed. This protocol is operationally simple and can be carried out on gram scale.

**Comment:** The tert-butyl-activated boronate complexes undergo stereoretentive transmetalation to copper cyanide and subsequent coupling with various electrophiles such as allyl-, alkynyl-, propargyl- and acyl halides, β-haloenones and hydroxylamine esters.

**Selected examples:**

- **E–X (1.2 equiv) CuCN (20 mol%), THF 25 or 60 °C 4–12 h**
  - E–X (X = Br, Cl):
    - R1 R2
      - 31 examples up to 99% yield up to >98% es
  - E–X (X = I, Br):
    - R1 R2
      - 8 examples up to 88% yield up to >98% es
- **E–X (1.2 equiv) CuCN (20 mol%), CuF (3.0 equiv), THF 80 °C 4 h**
  - 10 examples up to 80% yield up to >98% es
- **E–X (1.2 equiv) CuCN (20 mol%), styrene (1.0 equiv), THF 60 °C 12 h**
  - 31 examples up to 99% yield up to >98% es
- **E–X (1.2 equiv) CuCN (20 mol%), CsF (3.0 equiv), THF 80 °C 4 h**
  - 8 examples up to 85% yield up to >98% es

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