**Boron–Ate Complexes as Chiral Nucleophiles for Asymmetric Synthesis**

**Significance:** The authors report that secondary chiral boronic esters can be converted into reactive nucleophiles by addition of an aryllithium reagent. These enantiomerically enriched nucleophiles react with a broad range of electrophiles with inversion of stereochemistry.

**Comment:** By changing the substituents on the aryl group on boron, a switch in mechanism from a classical 2e⁻ pathway (nucleophilic substitution) to a radical pathway was observed. Therefore, electron-poor boronic esters favor the desired nucleophilic substitution, whereas electron-rich esters give racemized products.

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**Selected examples:**

- **Ph**
  - 80% yield 100% es
  - E = N-iodosuccinimide
  - Ar = 4-MeOC₆H₄

- **Ph**
  - 85% yield 100% es
  - E = N-bromosuccinimide
  - Ar = 3,5-(CF₃)₂C₆H₃

- **Ph**
  - 66% yield 92% es
  - E = dibenzyl azodicarboxylate
  - Ar = 3,5-(CF₃)₂C₆H₃

- **Ph**
  - 98% yield 100% es
  - E = tropium tetrafluoroborate
  - Ar = 4-MeOC₆H₄

- **4-MeOC₆H₄**
  - 84% yield 100% es
  - E = trichloroisocyanuric acid
  - Ar = 3,5-(CF₃)₂C₆H₃

- **4-MeOC₆H₄**
  - 61% yield 98% es
  - E = trichloroisocyanuric acid
  - Ar = 3,5-(CF₃)₂C₆H₃