**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:**

1. $\text{Ph}^+\text{I}^-$  
   - 80% yield  
   - 100% es  
   - $E = \text{N-iodosuccinimide}$  
   - $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$

2. $\text{Ph}^+\text{Br}^-$  
   - 85% yield  
   - 100% es  
   - $E = \text{N-bromosuccinimide}$  
   - $\text{Ar} = 3.5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$

3. $\text{Ph}^+\text{NHCO}_2\text{Bn}$  
   - 66% yield  
   - 92% es  
   - $E = \text{dibenzyl azodicarboxylate}$  
   - $\text{Ar} = 3.5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$

4. $\text{Ph}^+\text{CO}_2\text{t-Bu}^-$  
   - 98% yield  
   - 100% es  
   - $E = \text{tropylium tetrafluoroborate}$  
   - $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$

5. $\text{Ph}^+\text{Cl}^-$  
   - 61% yield  
   - 98% es  
   - $E = \text{trichloroisocyanuric acid}$  
   - $\text{Ar} = 3.5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$

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**Ar** = 4-MeOC$_6$H$_4$, 3.5-(CF$_3$)$_2$C$_6$H$_3$

$R^1$ = Ar, Ar-substituted Alk

$R^2$ = Me, Et, i-Bu, allyl, substituted Alk

$E$ = various electrophiles

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