

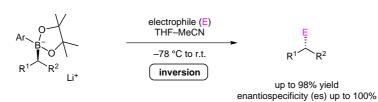
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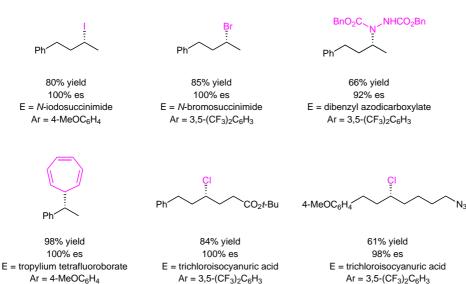
Ate Complexes of Secondary Boronic Esters as Chiral Organometallic-Type Nucleophiles for Asymmetric Synthesis *J. Am. Chem. Soc.* **2011**, *133*, 16794–16797.

Boron-Ate Complexes as Chiral Nucleophiles for Asymmetric Synthesis



 $\begin{aligned} &\text{Ar} = 4\text{-MeOC}_6 H_4, \ 3,5\text{-}(\text{CF}_3)_2 \text{C}_6 H_3 \\ &\text{R}^1 = \text{Ar}, \ \text{Ar-substituted Alk} \\ &\text{R}^2 = \text{Me}, \ \text{Et}, \ \dot{\textbf{F}} \text{Bu}, \ \text{allyl}, \ \text{substituted Alk} \\ &\text{E} = \text{various electrophiles} \end{aligned}$

Selected examples:



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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Metal-Mediated Synthesis

Key words

ate complexes

boronic esters

asymmetric synthesis



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