

SYNFACTS Highlights in Current Synthetic Organic Chemistry

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S. AICHHORN, R. BIGLER, E. L. MYERS, V. K. AGGARWAL* (UNIVERSITY OF BRISTOL, UK)
Enantioselective Synthesis of *ortho*-Substituted Benzylic Boronic Esters by a 1,2-Metalate Rearrangement/1,3-Borotropic Shift Sequence
J. Am. Chem. Soc. **2017**, *139*, 9519–9522.

Enantiospecific Couplings of Boronic Esters with *ortho*-Lithiated Benzylamines

Category

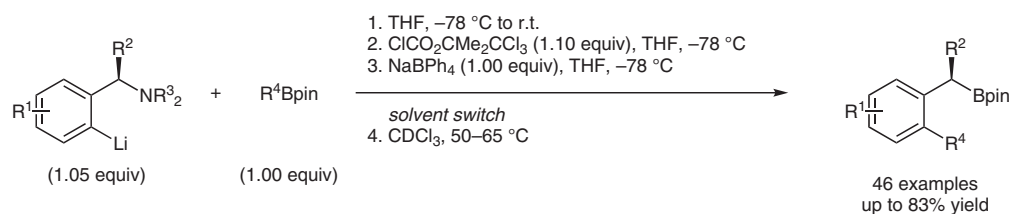
Metal-Mediated Synthesis

Key words

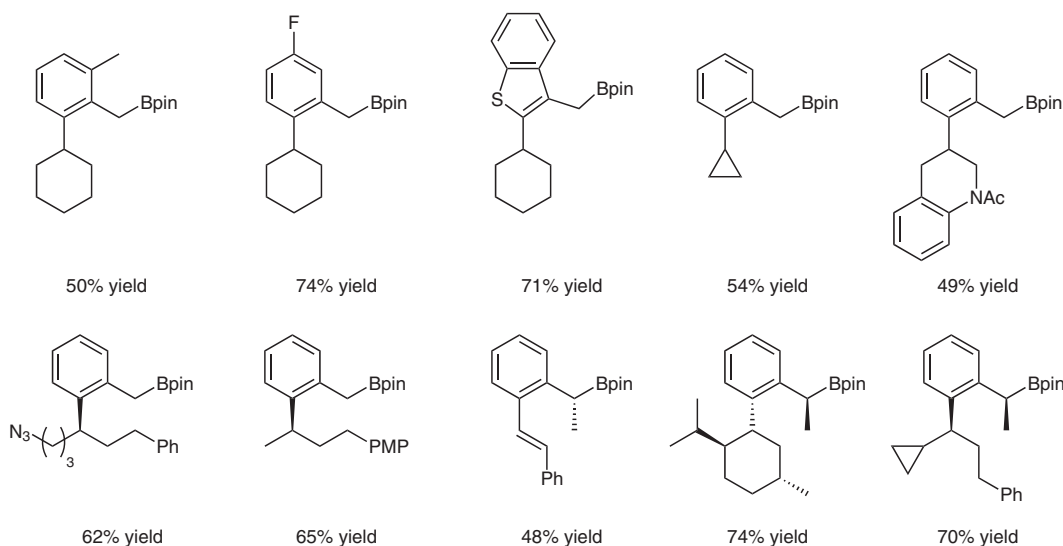
benzylic boronic esters

1,3-borotropic shift

1,2-metalate rearrangement



Selected examples:



Significance: Aggarwal and co-workers developed an enantioselective synthesis of *ortho*-substituted benzylic boronic esters, starting from *ortho*-lithiated benzylamines, boronic esters and an N-activator. The reaction proceeds through an $\text{S}_{\text{N}}2$ elimination and a 1,2-metalate rearrangement of the N-activated boronate complex to achieve a dearomatized intermediate. A subsequent Lewis acid catalyzed 1,3-borotropic shift afforded the desired products in high yields.

Comment: The authors showed that in addition to the synthetic utility of the dearomatized intermediate and the following 1,3-borotropic shift process, the intermediates can also induce allylboration of benzaldehyde or ethyl glyoxalate to afford the corresponding alcohols in excellent yield.

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