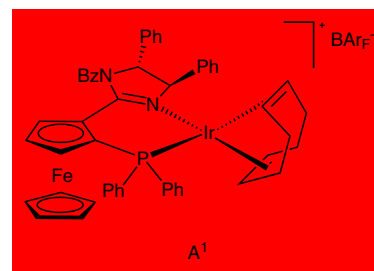
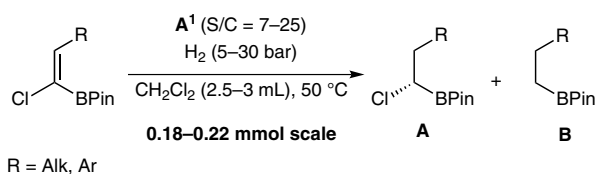


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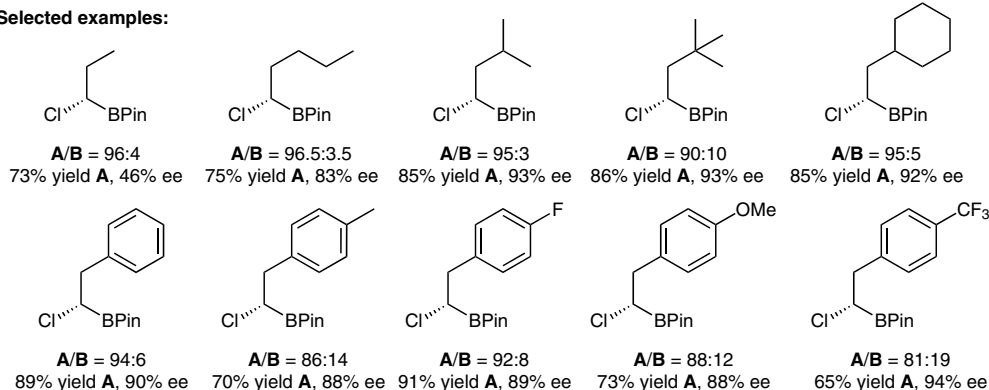
A Practical Synthetic Approach to Chiral (α -Chloroalkyl)boronic Esters via Iridium-Catalyzed Chemoselective Hydrogenation of Chloro-Substituted Alkenyl Boronates
Synthesis **2013**, 45, 2824–2831.

Enantioselective Hydrogenation of Chloro-Substituted Alkenyl Boronates

Overall transformation:



Selected examples:



Significance: Enantioenriched (α -chloroalkyl)boronic esters represent an important class of building blocks frequently used in organic synthesis. These chiral halogenated compounds are most commonly synthesized via Matteson-type rearrangements which use stoichiometric lithiated reagents, leading to stoichiometric waste streams. Transition-metal-catalyzed asymmetric hydrogenation has become the premier method for setting diversely substituted stereocenters with high enantiomeric excess under more environmentally friendly conditions. The authors report the synthesis of enantioenriched (α -chloroalkyl)boronic esters via the iridium-catalyzed asymmetric hydrogenation of chloro-substituted alkenyl boronates.

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Comment: The authors present a protocol for the enantioselective iridium-catalyzed hydrogenation of chloro-substituted alkenyl boronates using a ferrocenyl phosphinoimidazoline ligand. Good to excellent yields and enantioselectivities were obtained for both alkyl- and aryl-bearing substrates. Substrate-to-catalyst ratios (S/C) of up to 25 and hydrogen pressures as low as 5 bar are reported. This catalytic system benefits from a low amount of dechlorinated products resulting from over-reduction.