Enantioselective Hydrogenation of Chloro-Substituted Alkenyl Boronates

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.

Comment: The authors present a protocol for the enantioselective iridium-catalyzed hydrogenation of chloro-substituted alkenyl boronates using a ferrocenylyphosphinimidazoline 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.