Enantioselective Low-Temperature 1,4-Addition of Arylboronic Acids

Significance: Although various chiral rhodium catalysts have been developed, the rhodium-catalyzed asymmetric conjugate addition of arylboronic acids to $\alpha,\beta$-unsaturated carbonyl compounds below 0 °C has not been achieved. This paper describes the rhodium-catalyzed enantioselective 1,4-addition of arylboronic acids at low temperature. The use of the highly electron-poor (R)-MeO-F$_{12}$-BIPHEP ligand can retain the activity of the rhodium catalyst, which can serve to improve enantioselectivities.

Comment: A variety of N-substituted maleimides are applicable to this method, affording the corresponding chiral succinimides in excellent yields and enantioselectivities. Notably, the enantioselective 1,4-addition to N-H-maleimide, which has been reported as an inactive substrate for rhodium-catalyzed asymmetric 1,4-addition, is also successful. When the reaction is performed at –50 °C, the enantioselectivity is improved to up to 87% ee.