Asymmetric [4+2] Cycloaddition of Isochromene Acetals with Boronates

Significance: The authors present the tartaric acid catalyzed asymmetric [4+2] cycloaddition of isochromene acetals with vinylboronates. A series of 1,2-dihyronaphthalene-1-carbaldehydes were prepared with excellent yields (up to 91%), diastereomeric excess (dr up to >99:1), and enantiomeric excess (er up to 98.5:1.5).

Comment: This method provides a facile access to chiral dihyronaphthalene building blocks that can be used to make important natural products and biological active compounds. Tartaric acid in combination with Ho(OTf)₃ is highly effective for the reaction.

Selected examples:

- 76% yield, er = 95.5:4.5
- 61% yield, er = 96.5:3.5
- 71% yield, er = 98.2
- 70% yield, er = 96.4
- 81% yield, er = 98.5:1.5
- 88% yield, er = 97.5:2.5
- 79% yield, er = 95.5
- 91% yield, er = 90:10
- 82% yield, er = 98.5:1.5

The reaction of α-substituted vinylboronate:

- catalyst (10 mol%), Ho(OTf)₃ (5 mol%), THF–PhMe (1:1), 4 °C, 12 h