Iron-Catalyzed Asymmetric Transfer Hydrogenation of Ketimines

**Significance:** The authors report an iron-catalyzed asymmetric transfer hydrogenation under mild conditions that gives chiral amines with high enantioselectivity (94–99% ee). The system provides a solution to the challenging C=N bond reduction and proceeds with 2-propanol as the reducing agent.

**Comment:** Iron(II)–PNNP complexes that catalyze the asymmetric reduction of \(N\)-(diphenylphosphinoyl)- and \(N\)-(4-tolylsulfonyl)ketimines were developed. The \((R,R)\)-diamine catalyst produces the \((S,S)\)-amine. \((S,S)\)-3 are found to be the most active and stereoselective catalyst. The reaction outcome is influenced mainly by the steric around the imine carbon but is insensitive to its electronic character.

**Selected examples:**

- Fe(N=N)PPh\(_2\)PPh\(_2\)Br\([\text{BPh}_4]\)
  - \(R = \text{Ph}\), 92% conv., 95% ee (40 min)
  - \(R = \text{Br}\), 92% conv., 98% ee (60 min)
  - \(R = \text{OMe}\), 91% conv., 98% ee (40 min)
  - \(R = \text{SO}_2\text{Tol}\), 83% yield, 98% ee (60 min)

- \((S,S)\)-catalyst
  - 92% yield, >99% ee (30 min)
  - 26% yield, 94% ee (12 h)

- \(R = \text{Br}\), 92% conv., 98% ee (120 min)
  - 30% yield, 96% ee (60 min)

- \(R = \text{OMe}\), 91% conv., 98% ee (60 min)
  - 91% yield, >99% ee (120 min)
  - 92% conv., 95% ee (40 min)

**Category:** Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

**Key words:** iron, transfer hydrogenation, ketimines