Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation Reaction

Significance: In this report, ruthenium-based transfer hydrogenation catalysts are described. The catalysts exhibit impressive turnover numbers with excellent enantioselectivities for the selective reduction of CF$_3$-substituted 1,3-dicarbonyl compounds. The substrates include benzo-fused cyclic ketones which undergo reduction to furnish one stereoisomer.

Comment: Transfer hydrogenation (TH) reactions are milder and safer alternatives to metal-on-carbon-based hydrogenation reactions. Although the scope is usually limited to the reduction of carbonyls, TH avoids the use of highly pressurized systems. These reported ruthenium-based transfer hydrogenation catalysts are notable achievements in this field.

Selected examples:

L2 (S/C = 2000)
HCO$_2$H–Et$_3$N (5:2)
PhCl, 50 °C, 12 h
99.5% ee
82% yield after one recrystallization

L2 (S/C = 1000)
HCO$_2$H–Et$_3$N (3:2)
PhCl, 60 °C, 20 h
>99% ee
92% yield anti/syn > 99.9 after one recrystallization

90% yield
99.5% ee
dr > 99:1 after one recrystallization

96% yield
98% ee
dr = 96:3:1:0 after one recrystallization

51% yield
64% ee
dr = 99:1 after one recrystallization

96% yield
>99.9% ee
dr = 2:86:10:3 after one recrystallization