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Cobalt-Catalyzed Asymmetric Hydrogenation of C=N Bonds Enabled by Assisted Coordination and Nonbonding Interactions


Preparation of Chiral Hydrazines

Significance: Zhang and co-workers developed a cobalt-catalyzed hydrogenation of substituted hydrazones, which leads to chiral hydrazines in excellent yield and enantioselectivity. Further functionalization of the hydrazines leads to synthetically useful amines, amides, and pyrazole derivatives.

Comment: To emphasize the synthetic value of this hydrogenation, the reaction was performed on a gram scale and a TON of 2000, which is the highest TON for this cobalt-catalyzed asymmetric hydrogenation to date, was achieved. Furthermore, the authors performed deuterium labeling experiments and confirmed that H$_2$, and not i-PrOH, is the hydrogen source for the reaction.

Selected examples:

- R$_1$ = Ph, etc., FG = Alk, Ar, F, Cl, etc.
- > 20 examples
- up to 96% yield; up to 98% ee

FG-NHCOR$_2$N

CoBr$_2$ (1 mol%)  
(S,S)-Ph-BPE (1.05 mol%)  
H$_2$ (20 atm)  
i-PrOH (0.2 M)

50–70 °C, 24 h