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 H₂, and not i-PrOH, is the hydrogen source for the reaction.

**Equation:**

\[
\begin{align*}
\text{R} & = \text{Alk} \\
\text{R}^2 & = \text{Ph, etc.} \\
\text{FG} & = \text{Alk, Ar, F, Cl, etc.}
\end{align*}
\]

> 20 examples up to 96% yield; up to 98% ee

**Selected examples:**

- FG = Alk, Ar, F, Cl, etc.
- CoBr₂ (1 mol%) Zn (10 mol%) (S,S)-Ph-BPE (1.05 mol%) H₂ (20 atm) i-PrOH (0.2 M) 50–70 °C, 24 h

- **FG**
  - HN
  - NHCOR²

- **R¹ = Alk**
- **R² = Ph, etc.**
- **FG = Alk, Ar, F, Cl, etc.**

- 96% yield, 97% ee
- 95% yield, 98% ee
- 96% yield, 97% ee
- 95% yield, 96% ee
- 95% yield, 96% ee
- 95% yield, 97% ee
- 96% yield, 98% ee

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