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.

**Equation:**

\[
\text{CoBr}_2 (1 \text{ mol%}) \quad \text{Zn} (10 \text{ mol%}) \\
\langle S,S \rangle \text{-Ph-BPE} (1.05 \text{ mol%}) \\
\text{H}_2 (20 \text{ atm}) \\
\text{i-PrOH} (0.2 \text{ M}) \\
50–70 \degree \text{C}, 24 \text{ h}
\]

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

**Selected examples:**

- F
  - 96% yield, 97% ee
- O
  - 95% yield, 96% ee
- Cl
  - 95% yield, 96% ee
- OMe
  - 95% yield, 98% ee
- etc.

- Ph
  - 95% yield, 97% ee
- Ar
  - 95% yield, 97% ee
- etc.

- FG
  - Alk, Ar, F, Cl, etc.