Y. HU, Z. ZHANG, J. ZHANG, Y. LIU, I. D. GRIDNEV, W. ZHANG* (SHANGHAI JIAO TONG UNIVERSITY, P. R. OF CHINA)
Cobalt-Catalyzed Asymmetric Hydrogenation of C=N Bonds Enabled by Assisted Coordination and Nonbonding Interactions

Preparation of Chiral Hydrazines

\[
\text{R}^1 = \text{Alk, Ph, etc.} \\
\text{FG} = \text{Alk, Ar, F, Cl, etc.}
\]

Selected examples:

\[
\begin{align*}
\text{FG} & \text{N} \text{NCOR}^2 \\
\text{R}^1 & \text{HN} \text{NHBz} \\
\text{F} & 96\% \text{ yield, } 97\% \text{ ee} \\
\text{O} & 95\% \text{ yield, } 96\% \text{ ee} \\
\text{Cl} & 95\% \text{ yield, } 96\% \text{ ee} \\
\text{OMe} & 96\% \text{ yield, } 98\% \text{ ee}
\end{align*}
\]

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 \( \text{H}_2 \), and not \( \text{i-PrOH} \), is the hydrogen source for the reaction.