Zirconium/VANOL-Catalyzed Asymmetric α-Iminol Rearrangement

**Significance:** There has been no example of asymmetric α-iminol rearrangement so far. Herein, the authors developed an effective catalyst system, a zirconium/VANOL complex, which works well not only with α-iminols as starting material, but also with in situ generated α-iminols from an aldehyde and an aniline.

**Comment:** The zirconium/VANOL catalyst affords excellent yields and enantioselectivities for a broad range of substrates. Interestingly, N-methyl imidazole coordinated to zirconium dramatically influences the reaction. When there is a para-CF$_3$ substituent on the phenyl ring, more careful manipulations are required such as inert atmosphere and deoxygenation.

**Selected examples:**

- 94% yield, 97% ee
- 100% yield, >99% ee
- 98% yield, >99% ee
- 97% yield, 98% ee
- 95% yield, 89% ee
- 74% yield, 73% ee
- 98% yield, 98% ee, 80 °C
- 97% yield, 94% ee, 80 °C, 2 h
- 91% yield, 97% ee