Zirconium/VANOL-Catalyzed Asymmetric \( \alpha \)-Iminol Rearrangement

**Significance:** There has been no example of asymmetric \( \alpha \)-iminol rearrangement so far. Herein, the authors developed an effective catalyst system, a zirconium/VANOL complex, which works well not only with \( \alpha \)-iminols as starting material, but also with in situ generated \( \alpha \)-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-\( \text{CF}_3 \) 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 at 80 °C**
- **97% yield, 94% ee at 80 °C, 2 h**
- **91% yield, 97% ee**

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