Enantioselective Hydroamination of Unactivated Internal Olefins

**Significance:** Previous hydroaminations of alkenes have been achieved with a restricted range of substrates (for example, styrenes or terminal olefins). Here, the authors succeed in asymmetric hydroamination of nonactivated internal olefins. This system provides ready access to various α-branched chiral amines with high enantioselectivities (≥96% ee).

**Comment:** Electron-rich hydroxylamines are used as aminating reagent to suppress undesired reductions of hydroxylamines. The late-stage modification of pharmaceutical compounds is also demonstrated.

**Selected examples:**

- **CF₃**
  - 81% yield
  - 97% ee
  - 80% yield
  - dr > 95:5
- **Et**
  - 78% yield
  - 97% ee
  - 76% yield
  - 97% ee

**Proposed reaction mechanism:**

- Undesired reduction pathway
- Chain walking
- Not observed