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:**

- 78% yield, 97% ee
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- 80% yield, dr > 95:5 with (S)-ligand
- 81% yield, dr > 95:5 with (R)-ligand

**Proposed reaction mechanism:**