Enantioselective Functionalization of Primary C–H Bonds

**Significance:** The authors previously described Rh-catalyzed functionalizations of secondary or tertiary C–H bonds (Liao et al. *Nature* 2016, 533, 230; Liao et al. *Nature* 2017, 551, 609). By tuning the catalyst, non-activated primary C–H bonds are functionalized with excellent site and enantioselectivities.

**Comment:** Subjecting chiral substrates to the reaction conditions allows access to either set of diastereomeric products when the appropriate catalyst enantiomer is employed. Stigmasteryl acetate could be selectively functionalized at its most sterically accessible primary C–H bond.

**Selected examples:**
- **40% yield, >99% ee**
- **83% yield, 1:1 d.r., >99% ee, 95% ee**
- **90% yield, 98% ee**
- **93% yield, 97% ee**
- **53% yield, 93% ee**
- **88% yield, >99% ee**
- **82% yield, >99% ee**
- **90% yield, 98% ee**
- **93% yield, 97% ee**
- **86% yield, >99% ee**

**Steroid C–H functionalization:**

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