**Significance:** Aliphatic amines are present in many pharmaceutical agents and they are often essential for activity. The potential of stereoisomers to have contrasting biological effects means that asymmetric approaches to construct amine-containing remote stereocenters has been a challenge. Buchwald and co-workers report an asymmetric copper-catalyzed hydroamination reaction that generates γ- and δ-chiral aliphatic amines.

**Comment:** The copper-catalyzed hydroamination reaction produced the desired aliphatic amines in good to excellent yields and with excellent enantio- and diastereoselectivities. The proposed mechanism starts with the formation of an alkylcopper species and subsequent β-alkoxide elimination to form the enantioenriched alkene. The hydrosilane reagent regenerates the CuH catalyst, which undergoes the anti-Markovnikov hydrocopperation to form the terminal alkylcopper species. Finally, interception with the hydroxylamine generates the product, and the hydrosilane reagent regenerates the CuH catalyst.