Enantioselective Catalytic Hydroamination of Internal Alkenes

Significance: The authors report asymmetric hydroamination of internal alkenes. In this challenging transformation a cationic Ir-catalyst was used. Bulky SEGPHOS and SYNPHOS ligands were found to be optimal. Additional tuning of the catalyst counteranion and careful choice of the ammonia surrogate led to yields of up to 90% and enantiomeric excess of up to 98%.

Comment: Deuterium labeling studies showed that addition across the double bond occurs in syn fashion. Based on kinetic experiments, migratory insertion is likely to be the rate-limiting step of the catalytic cycle. Furthermore, 2-amino-6-methylpyridine is a necessary component of the reaction. 2-Aminopyridine is not a competent ammonia surrogate and its addition inhibits the catalytic transformation.