Enantioselective Catalytic Hydroamination of Internal Alkenes

Category

Metals in Synthesis

Key words

asymmetric
synthesis

iridium catalysis

hydroamination

Synfact
of the Month

Selected examples:

Deprotection of amine: 1. 2M HCl in dioxane (2.0 equiv), 15 min, r.t.

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-methyl-6-pyridylamine is a necessary component of the reaction. 2-Aminopyridine is not a competent ammonia surrogate and its addition inhibits the catalytic transformation.

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