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Construction of Acyclic Quaternary Carbon Stereocenters by Catalytic Asymmetric Hydroalkynylation of Unactivated Alkenes


Iridium-Catalyzed Asymmetric Hydroalkynylation of Unactivated Alkenes

**Significance:** The authors have developed an enantioselective iridium-catalyzed hydroalkynylation reaction. The reaction transforms trisubstituted \( \beta,\gamma \)-unsaturated amides with excellent \( \gamma \)-selectivity, forming new alkyne-substituted acyclic quaternary carbon stereocenters.

**Comment:** The kinetic isotope experiments of the alkenes resulted in an inverse KIE; suggesting that the migratory insertion of the alkene is related to the turnover-limiting step. Notably, the authors propose that the selectivity arises from both a facial preference as well as an alkene isomerization process.

**Kinetic isotope effect of alkene:**

- \( \text{Ir(cod)}_2\text{OTf} \) (10 mol%) \((R)-\text{ligand} \) (12 mol%)
- \( \sigma\text{C}_6\text{H}_4\text{F}_2, 20 \, \text{°C}, 84 \, \text{h} \)
- 23 examples up to 83% yield er up to 98.5:1.5

**Selected examples:**

- \( \text{Ir(cod)}_2\text{OTf} \) (10 mol%) \((R)-\text{ligand} \) (12 mol%)
- 1,2-dichlorobenzene
- \( \text{k}_H/\text{k}_D = 0.90 \)

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