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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.

**Selected examples:**

- **65% yield**  
  \( \text{er} = 95:5 \)

- **52% yield**  
  \( \text{er} = 98.5:1.5 \)

- **75% yield**  
  \( \text{er} = 96:4 \)

- **22% yield**  
  \( \text{er} = 93:7 \)

- **80% yield**  
  \( \text{er} = 96.5:3.5 \)

- **80% yield**  
  \( \text{er} = 95:5 \)