**Iridium-Catalyzed Z-Retentive Asymmetric Allylic Substitution Reactions**

**Significance:** The You group reports two unique methods for enantioselective iridium-catalyzed allylic substitution reactions, which are highly selective for the thermodynamically less stable Z-alkene products. Conventionally, metal-catalyzed asymmetric allylic substitution reactions favor the E-isomer of the products.

**Comment:** The authors rationalized their reaction design by focusing on developing a catalytic system that allowed for a slow isomerization from the initial anti-**π**-allyl complex to the more favored syn-**π**-allyl species. Subsequent capture of the chiral anti-**π**-iridium species by a nucleophile selectively generated the enantioenriched Z-alkene products.