**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.