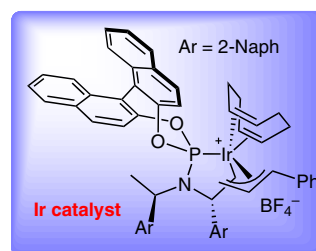
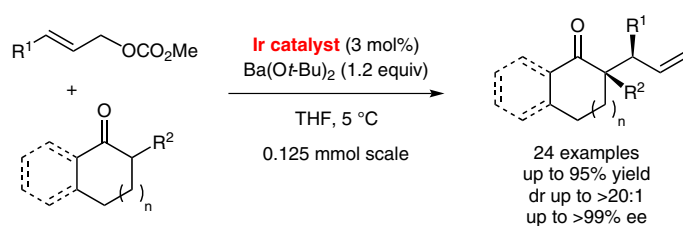


W. CHEN, M. CHEN, J. F. HARTWIG* (UNIVERSITY OF CALIFORNIA, BERKELEY, USA)
Diastereo- and Enantioselective Iridium-Catalyzed Allylation of Cyclic Ketone Enolates: Synergistic Effect of Ligands and Barium Enolates
J. Am. Chem. Soc. **2014**, *136*, 15825–15828.

Diastereo- and Enantioselective Iridium-Catalyzed Allylation of Ketone Enolates



Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

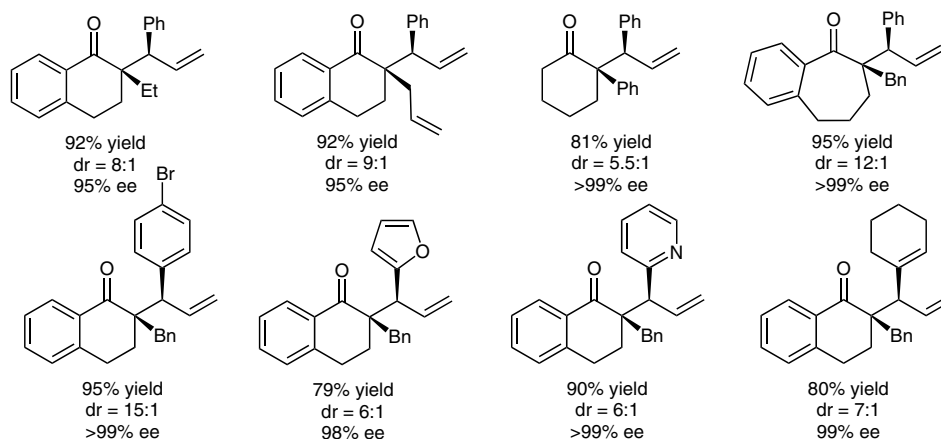
iridium

phosphoramidites

asymmetric allylic
alkylation

barium enolates

Selected examples:



Significance: The transition-metal-catalyzed asymmetric allylic alkylation (AAA) reaction is a versatile and powerful method for the construction of C–C bonds. Although palladium catalysts are routinely used in this reaction, iridium catalysts have been shown to have complementary and comparable reactivity to palladium (see Review below). Within this area of research, the diastereo- and enantioselective allylic alkylation of unstabilized ketone enolates remains a significant challenge. Herein, Hartwig and co-workers report a diastereo- and enantioselective iridium-catalyzed allylation of barium enolates derived from cyclic ketones.

Comment: The branched-selective allylic alkylation method developed by the authors provides access to products containing a vicinal quaternary and a tertiary stereogenic center – a difficult class of molecules to access using traditional Pd-catalyzed methods. The method is highly efficient and demonstrates a broad substrate scope. The authors show that good levels of diastereoselectivity can be achieved in this reaction simply through the facial selectivity of the prochiral barium enolate without necessitating coordination of the enolate directly to the metal center.

Review: J. F. Hartwig, L. M. Stanley *Acc. Chem. Res.* **2010**, *43*, 1461–1475.

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