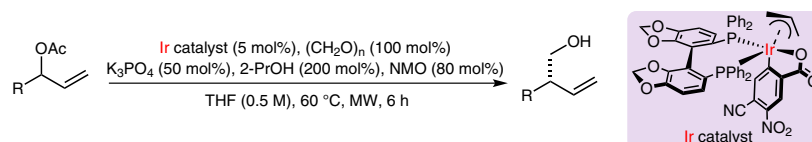
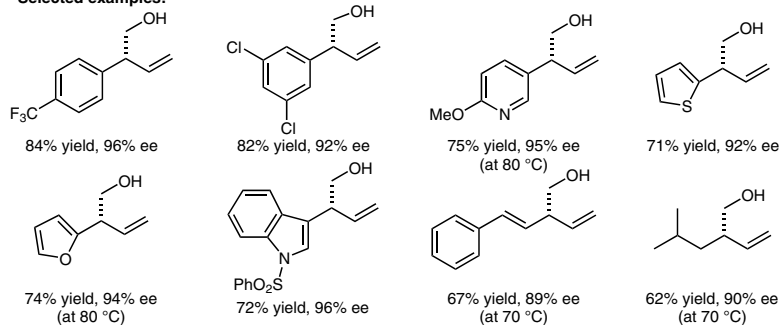


V. J. GARZA, M. J. KRISCHE\* (UNIVERSITY OF TEXAS AT AUSTIN, USA)  
Hydroxymethylation beyond Carbonylation: Enantioselective Iridium-Catalyzed Reductive Coupling of  
Formaldehyde with Allylic Acetates via Enantiotopic  $\pi$ -Facial Discrimination  
*J. Am. Chem. Soc.* **2016**, *138*, 3655–3658.

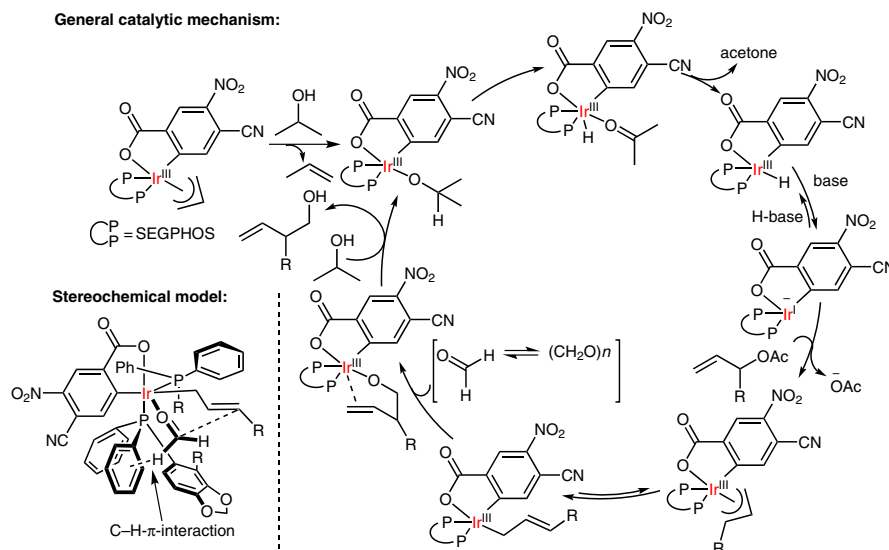
## Iridium-Catalyzed Asymmetric Hydroxymethylation



### Selected examples:



### General catalytic mechanism:



**Significance:** Existing examples of enantioselective C–C coupling reactions of formaldehyde involve asymmetric aldol reactions. Krische and Garza describe the first asymmetric nucleophilic allylation of formaldehyde in the presence of iridium catalysts to give chiral  $\beta$ -stereogenic primary homoallylic alcohols.

**Comment:** The chiral iridium complex modified by SEGPHOS permits propan-2-ol-mediated regio- and enantioselective reductive coupling of branched allylic acetates with paraformaldehyde. The reaction proceeds through formation of an iridium hydride and subsequent formation of  $\pi$ -allyl iridium intermediates.

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