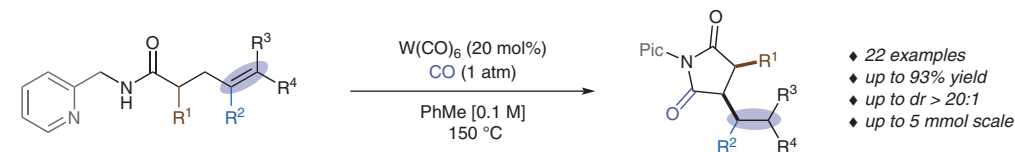


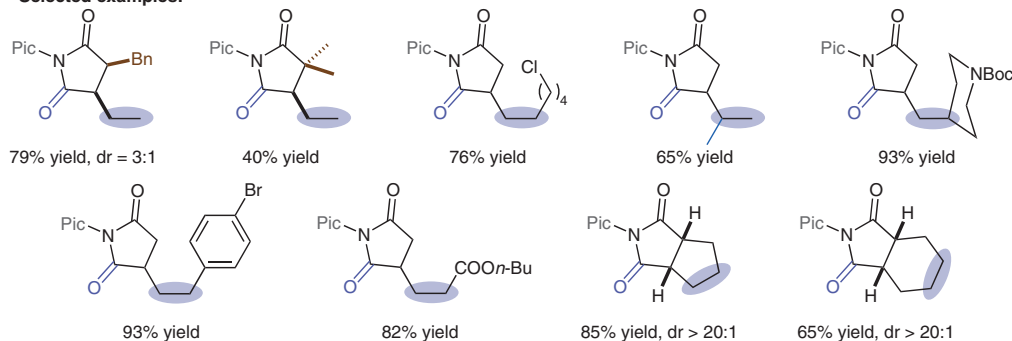
T. C. JANKINS, W. C. BELL, Y. ZHANG, Z.-Y. QIN, J. S. CHEN, M. GEMBICKY, P. LIU*, K. M. ENGLE* (UNIVERSITY OF PITTSBURGH AND THE SCRIPPS RESEARCH INSTITUTE, LA JOLLA, USA)

Low-Valent Tungsten Redox Catalysis Enables Controlled Isomerization and Carbonylative Functionalization of Alkenes
Nat. Chem. **2022**, *14*, 632–639, DOI: 10.1038/s41557-022-00951-y.

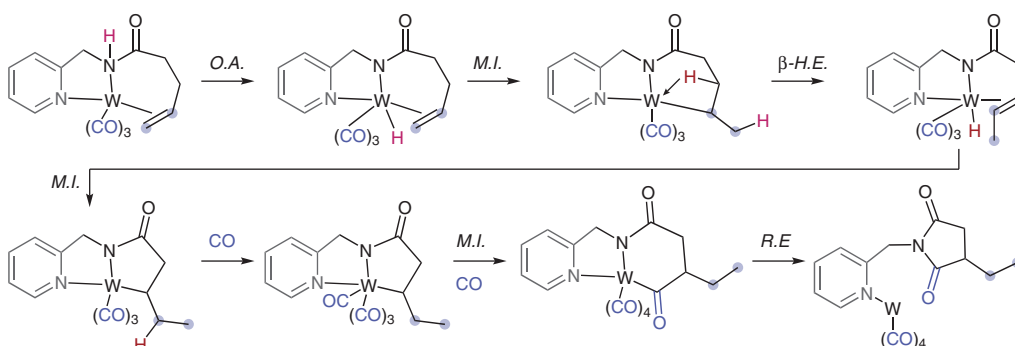
Tungsten-Catalyzed Alkene Isomerization/ Hydrocarbonylative Cyclization



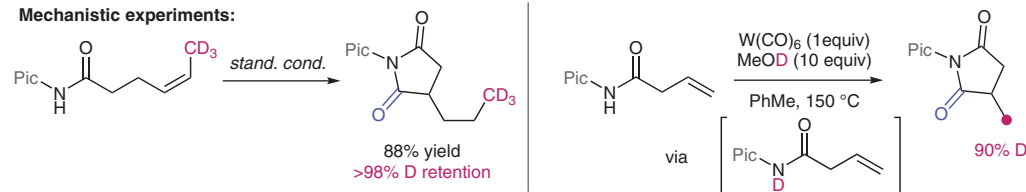
Selected examples:



Proposed reaction profile:



Mechanistic experiments:



Significance: A tungsten-catalyzed isomerization of terminal alkenes to unactivated internal positions followed by subsequent hydrocarbonylation with CO is reported. This work addresses common challenges associated with the regioselectivity of tandem alkene isomerization/functionalization reactions.

Comment: Experimental and DTF studies were carried out to elucidate the mechanism. Key to this transformation is the six- to seven-coordinate geometry changes present in the W(0)/W(II) redox cycle and the presence of a conformationally flexible directing group that allows for isomerization to take place.

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