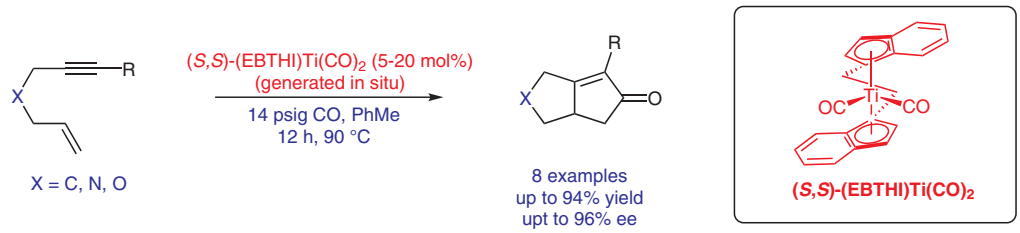
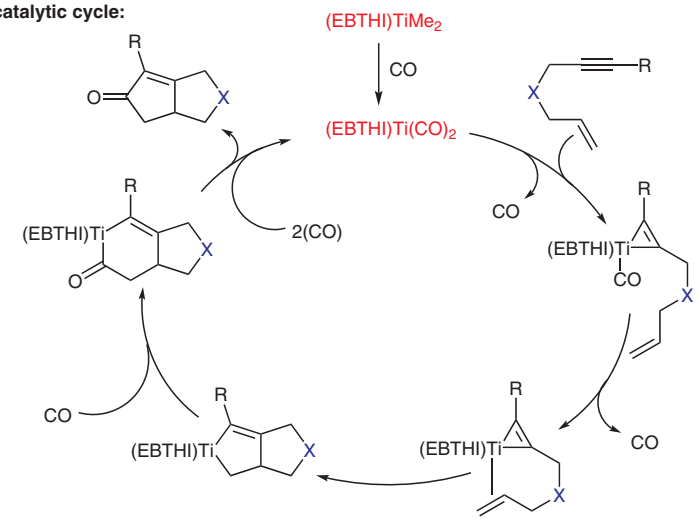
F. A. HICKS, S. L. BUCHWALD* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, USA)

Highly Enantioselective Catalytic Pauson–Khand Type Formation of Bicyclic Cyclopentenones
J. Am. Chem. Soc. **1996**, *118*, 11688–11689, DOI: 10.1021/ja9630452.

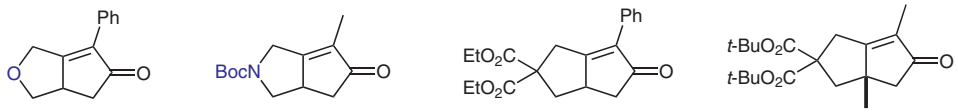
Titanium-Catalyzed Asymmetric Pauson–Khand Type Reaction



Proposed catalytic cycle:



Selected examples:



85% yield
96% ee

84% yield
74% ee

94% yield
92% ee

90% yield
74% ee

Significance: Hicks and Buchwald reported an asymmetric titanium-catalyzed Pauson–Khand type reaction to access bicyclic cyclopentenones in excellent yields and enantioselectivity. In addition to good to excellent ee values, the reaction also tolerates 1,1-disubstituted olefins amongst its wide substrate scope; a weakness in earlier Pauson–Khand systems.

Comment: The active catalyst is generated in situ, from (*S*,*S*)-(EBTHI)TiMe$_2$. Both temperature of the reaction and the pressure of CO impacted the yield; temperatures lower than 90 °C or pressures above and below 14 psig were observed to result in diminished conversions.

Review: S. E. Gibson (née Thomas), A. Stevenazzi *Angew. Chem. Int. Ed*. **2003**, *42*, 1800–1810.

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Metals in Synthesis

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asymmetric synthesis
bicyclic cyclopentenones