Titanium-Catalyzed Asymmetric Pauson–Khand Type Reaction

**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)TiMe₂. 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.

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**Selected examples:**

- **Ph**
  - 85% yield
  - 96% ee

- **BocN**
  - 84% yield
  - 74% ee

- **Ph**
  - 94% yield
  - 92% ee

- **t-BuO₂C**
  - 90% yield
  - 74% ee

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**Proposed catalytic cycle:**

14 psig CO, PhMe
12 h, 90 °C

(EBTHI)TiMe₂ (generated in situ)

8 examples
up to 94% yield
up to 96% ee

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**Key words**

- titanium catalysis
- Pauson–Khand type reaction
- asymmetric synthesis
- bicyclic cyclopentenones

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**Category**

- Metals in Synthesis