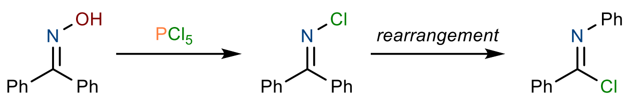
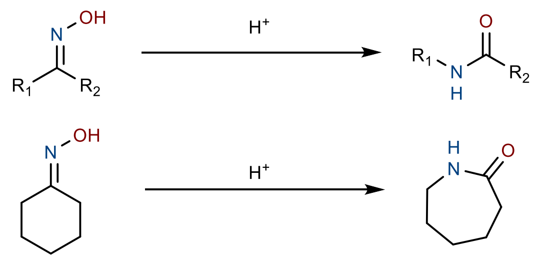
Beckmann Rearrangement

Beckmann (1886)



Beckmann, E. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 988–993. https://doi.org/10.1002/cber.188601901222.

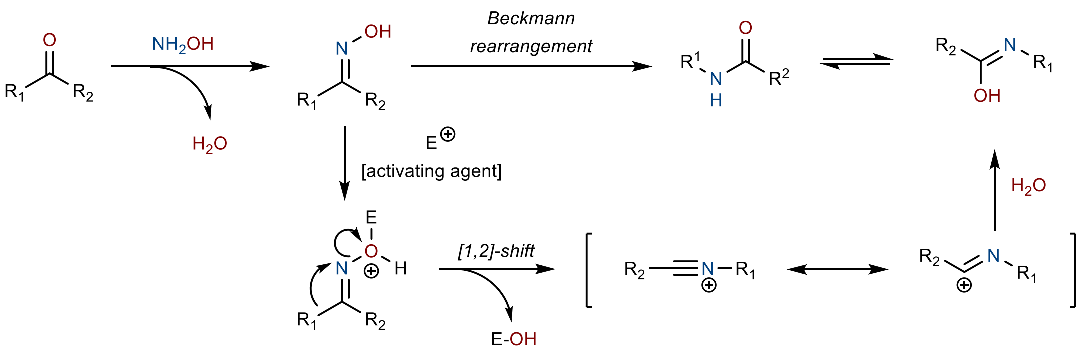
General Beckmann Rearrangement



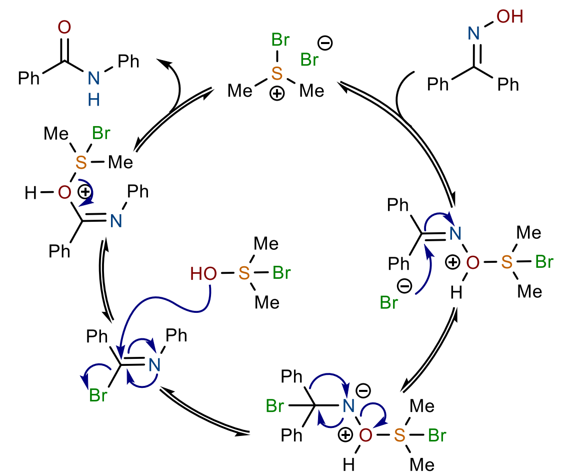
Reagent–type for Beckmann Rearrangement

- Acid catalyzed
- Transition metal catalyzed
- Microwave assisted

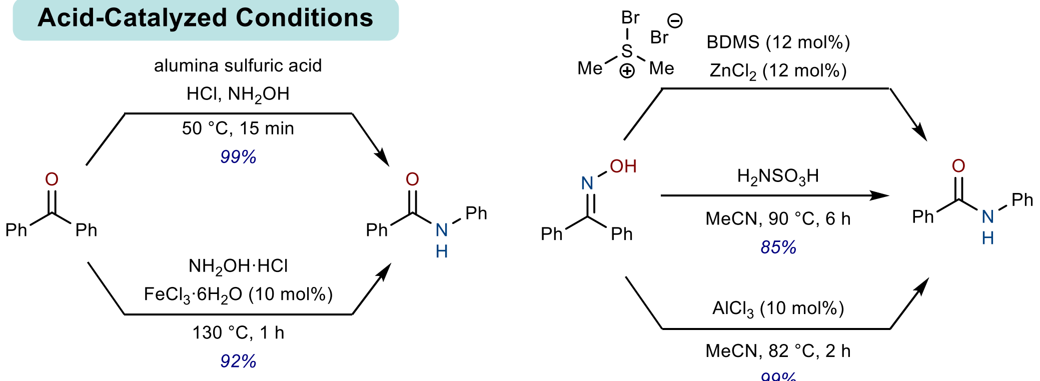
General mechanism

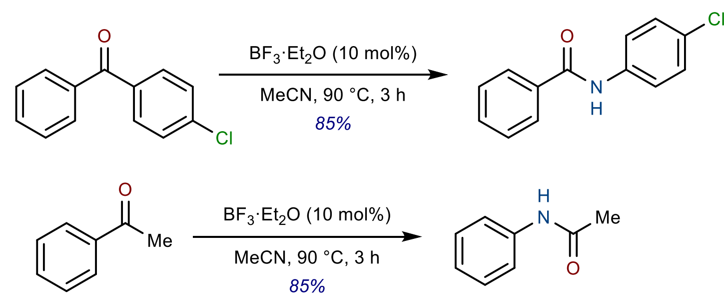


BDMS Mechanism



Acid-Catalyzed Conditions





Jain, S. *ChemistrySelect* **2024**, *9*, e202302853. https://doi.org/10.1002/slct.202302853.
Srivastava, S. *New J. Chem.* **2020**, *44*, 18530–18572. https://doi.org/10.1039/D0NJ02034F.

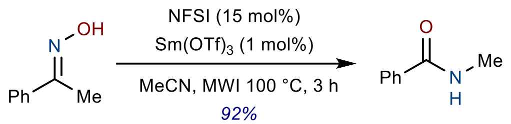
Brønsted acid sources = sulfamic acid (H_2NSO_3H), *p*-TsOH, oxalic acid, citric acid

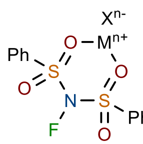
Lewis acid sources = $AlCl_3$, $BF_3{\cdot}Et_2O$, BDMS-$ZnCl_2$, Al_2O_3—HSO_3Cl, $B(OH)_3$

Beckmann Rearrangement

Microwave-Assisted

- short reaction time
- solvent free



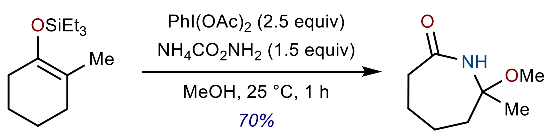


- Lewis acid assisted counterion

- Electrophile fluorine

Liu, Y. *Tetrahedron Lett.* **2016**, *57*, 5820–5824. https://doi.org/10.1016/j.tetlet.2016.11.054.

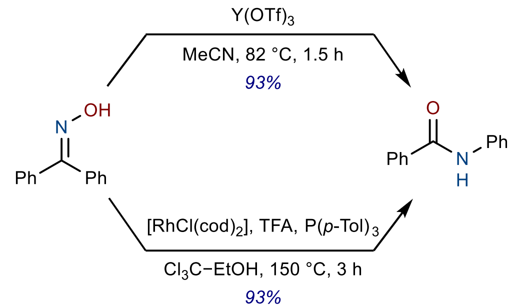
Kürti's Iodonitrene Insertion



regioselectivity of Beckmann

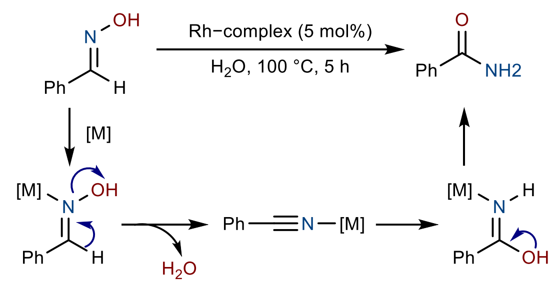
- Stereospecific & dependent on E/Z preference of oxime

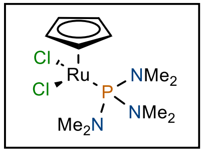
Transition Metal Catalyzed



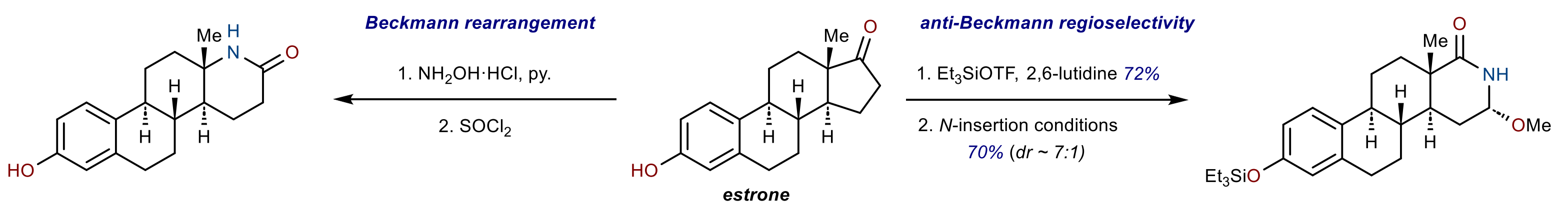
- does not require anhydrous conditions
- good selectivity

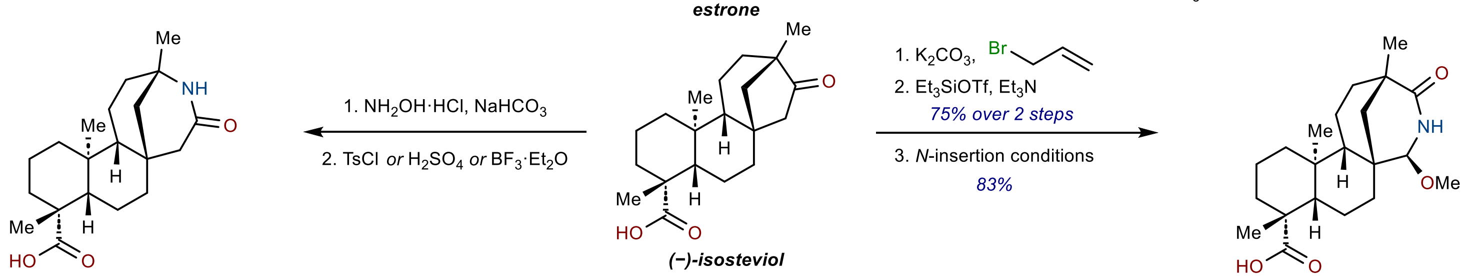
De, S. K. *Org. Prep. Proced. Int.* **2004**, *36*, 383–386. https://doi.org/10.1080/00304940409458685.





Crochet, P.; Cadierno, V. *Organometallics* **2012**, *31*, 6482–6490. https://doi.org/10.1021/om3006917.

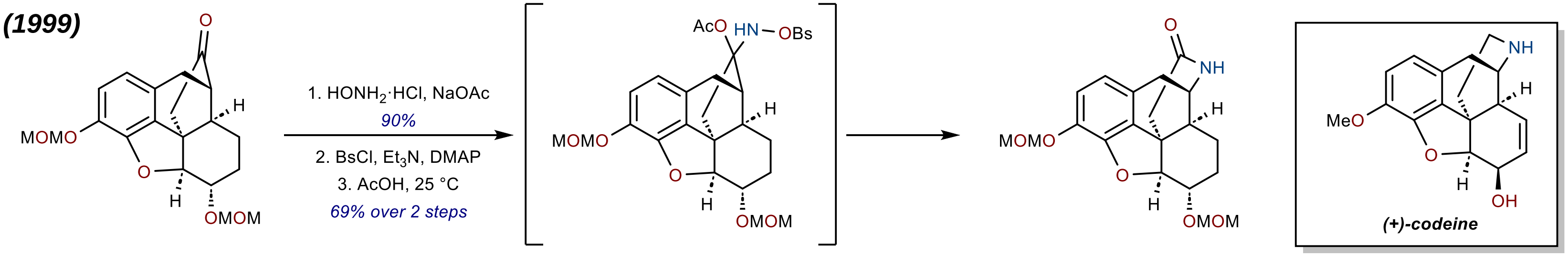




Ball, Z. T.; Kürti, L. *J. Am. Chem. Soc.* **2024**, *146*, 21129–21136. https://doi.org/10.1021/jacs.4c07111.

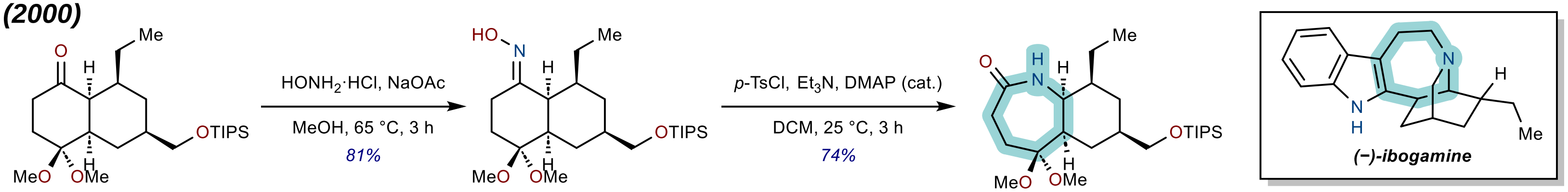
Examples in Total Synthesis

White (1999)



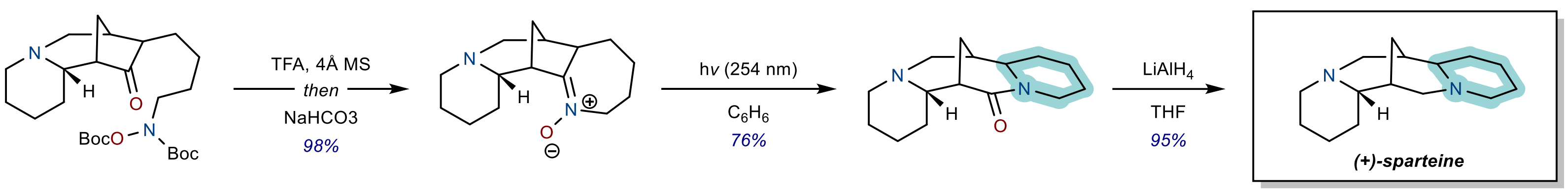
White, J. D. *J. Org. Chem.* **1999**, *64*, 7871–7884. https://doi.org/10.1021/jo990905z.

White (2000)



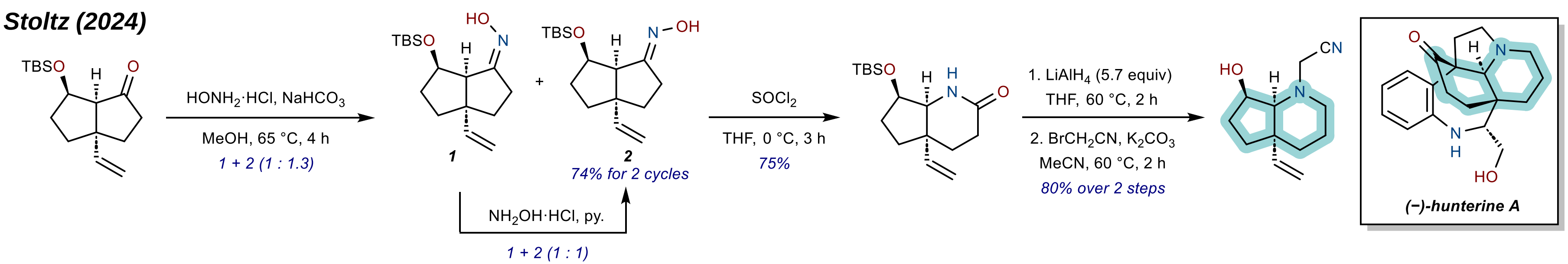
White, J. D. *Org. Lett.* **2000**, *2*, 2373–2376. https://doi.org/10.1021/ol0001463.

Aubé (2002)



Aubé, J. *Org. Lett.* **2002**, *4*, 2577–2579. https://doi.org/10.1021/ol026230v.

Stoltz (2024)



Stoltz, B. M. *J. Am. Chem. Soc.* **2024**, *146*, 4340–4345.https://doi.org/10.1021/jacs.3c13590.