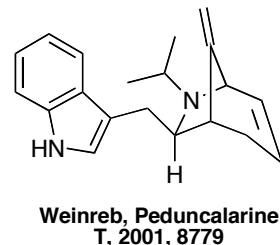
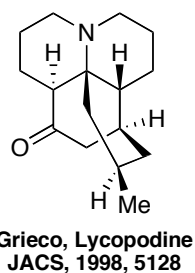
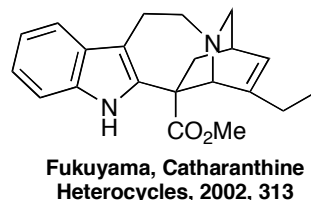
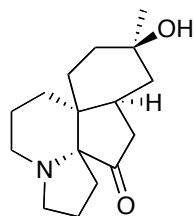
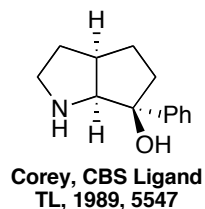


Syntheses Discussed:



Partial List of Transforms Discussed:

1. Hofmann-Löffler-Freytag Reaction
2. Ireland-Claisen Rearrangement
3. Pauson-Khand Reaction
4. Beckmann Rearrangement
5. Stieglitz Rearrangement

Relevant or Related Reviews:

1. Gansäuer, A. *Angew. Chem. Int. Ed. Eng.* **2003**, 42, 5556
2. Bowman, W.R. *J. Chem. Soc. Perkin Trans. 1.* **2002**, 2747
3. Friestad, G.K. *Tetrahedron.* **2001**, 57, 5461
4. Yet, L. *Tetrahedron.* **1999**, 55, 9349
5. Stella, L. *Angew. Chem. Int. Ed. Eng.* **1983**, 22, 337
6. Neale, R.S. *Synthesis*, **1971**, 1, 1
7. Wolff, M.E. *Chem. Rev.* **1963**, 63, 55

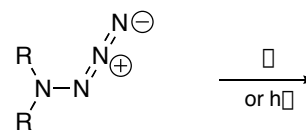
Important Note: The term nitrogen centered radical refers to a species where the initiating radical is localized on a nitrogen atom, not to transformations that terminate with a nitrogen radical. Numerous examples of the latter are known and are not discussed here.

Three types of Nitrogen Radicals:

1. Neutral Aminyl Radicals



a. Generation



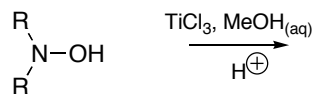
b. Reactivity

- Dimerize to form hydrazines, which disproportionate to form imines and amines
- Abstract allylic hydrogens preferably
- Can add to styrenes and arenes, if there are no allylic protons

2. Protonated Aminyl Radicals



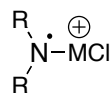
a. Generation



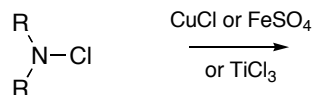
b. Reactivity

- Adds to unsaturated hydrocarbons and arenes
- Abstract protons if favorably disposed and activated

3. Aminyl Radicals Complexed to Metal Ions



a. Generation



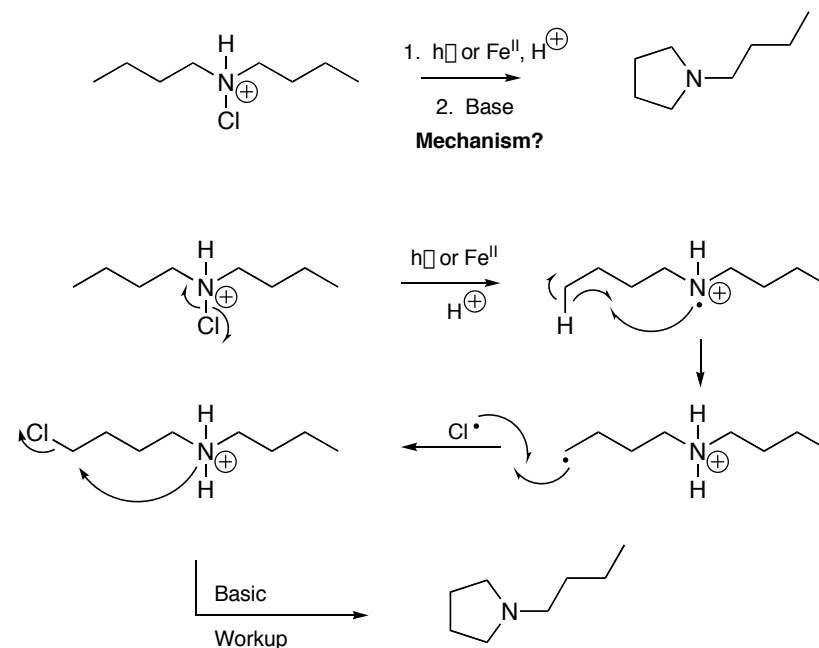
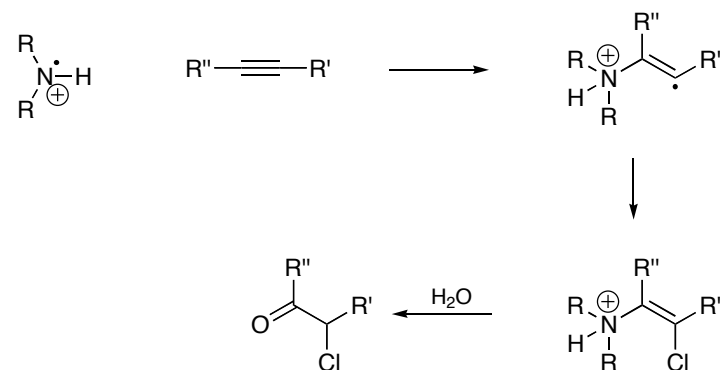
Must use neutral conditions to generate, otherwise protonated aminyl radicals are obtained

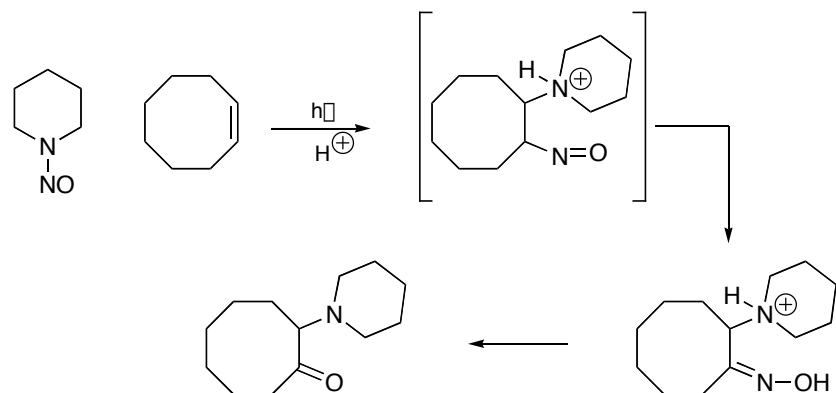
b. Reactivity

- Add to dienes, acetylenes, or alkenes
- No acid prevents electrophilic chlorination of the substrate

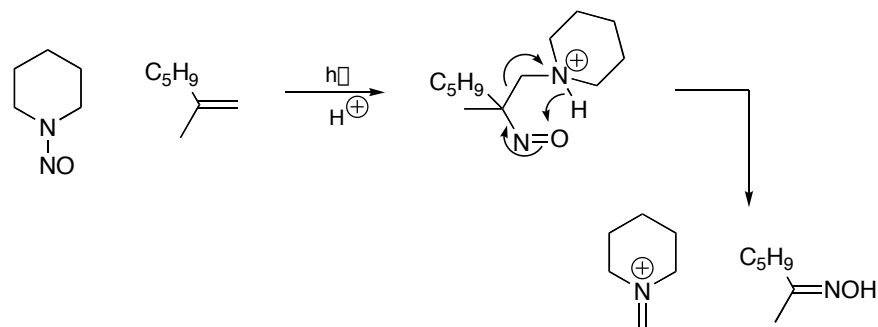
Selected Transformations:

1. Hofmann-Löffler-Freytag Reaction:

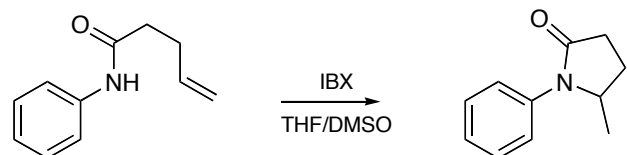
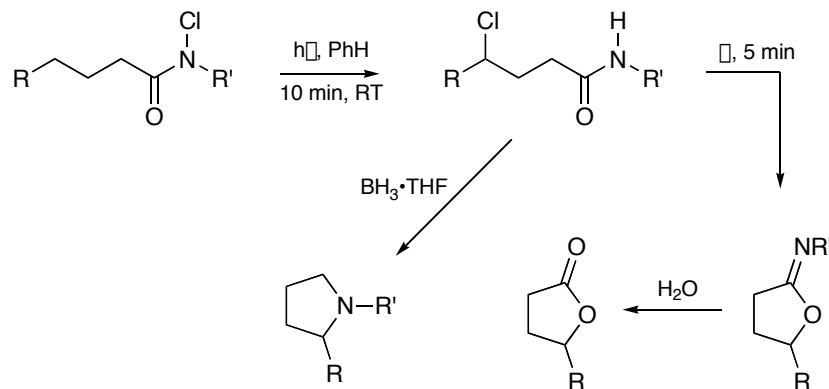
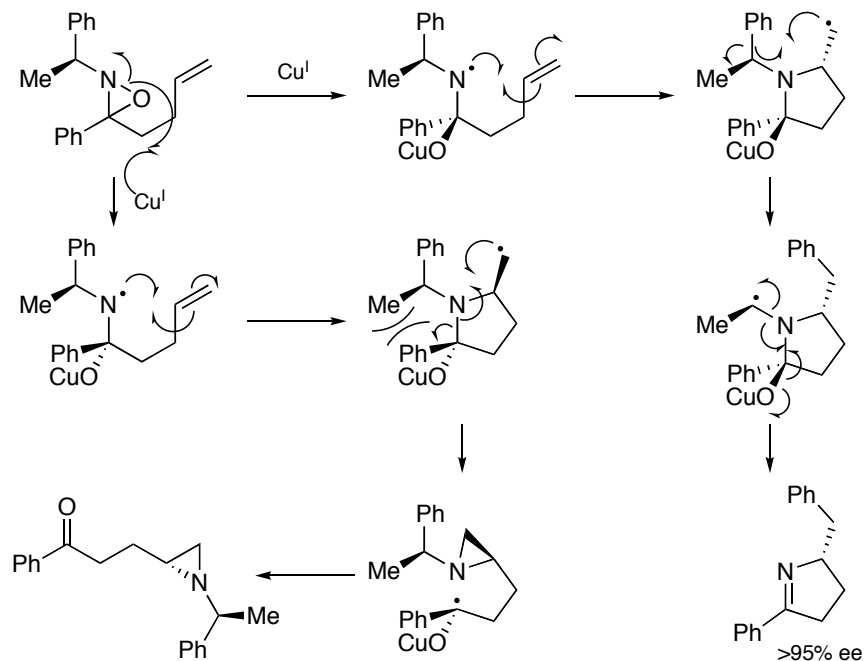
2. Synthesis of α -Chloroketones from Alkynes:

3. Synthesis of α -Amino Ketones from Alkenes:

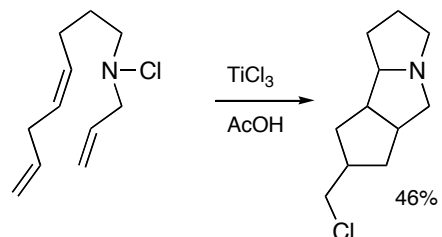
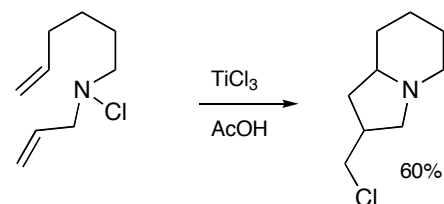
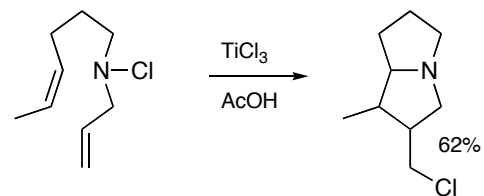
4. Synthesis of Oximes from Alkenes:



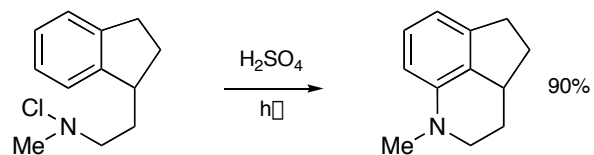
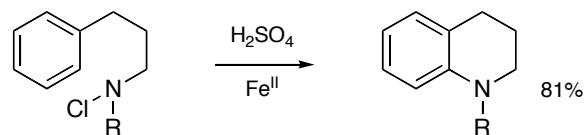
5. IBX Reactions:

6. Synthesis of α -Lactones or Pyrrolidines:7. Aubé, J. *J. Am. Chem. Soc.* 1992, 114, 5466:

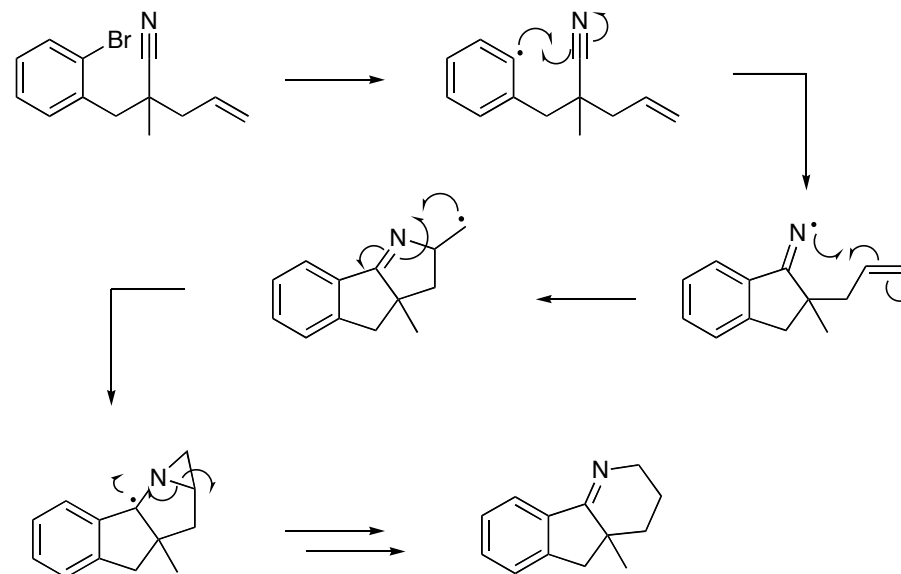
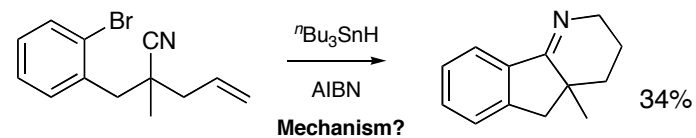
8. An Alternative to Nitrogen Stitching:



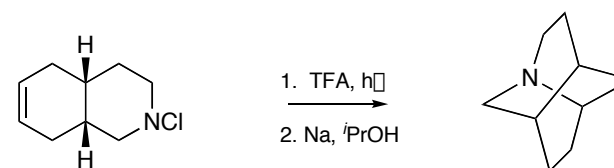
9. Aryl Amination:



10. Cyclizations involving Nitriles:

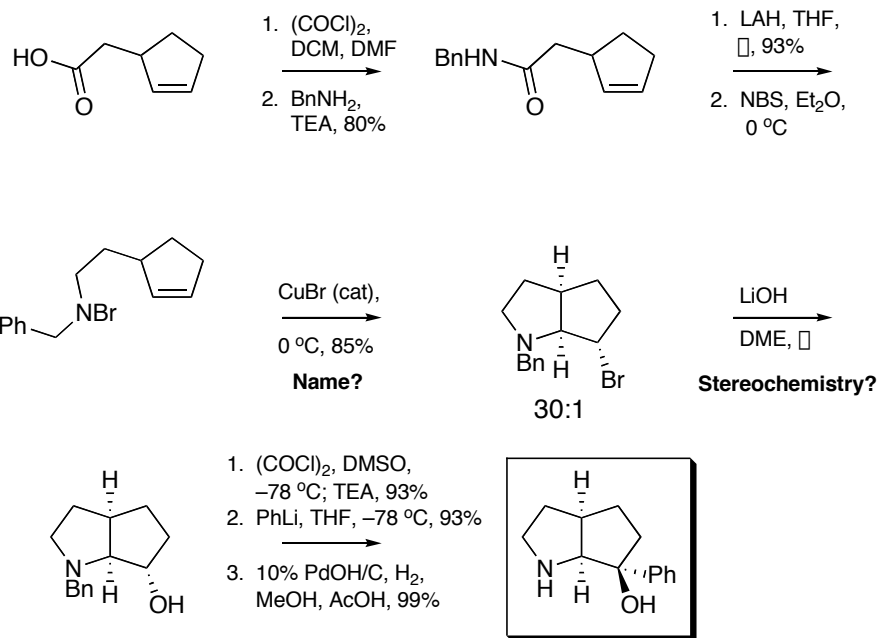


11. Synthesis of a Twistane:

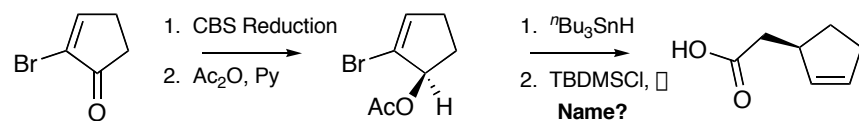


Syntheses:

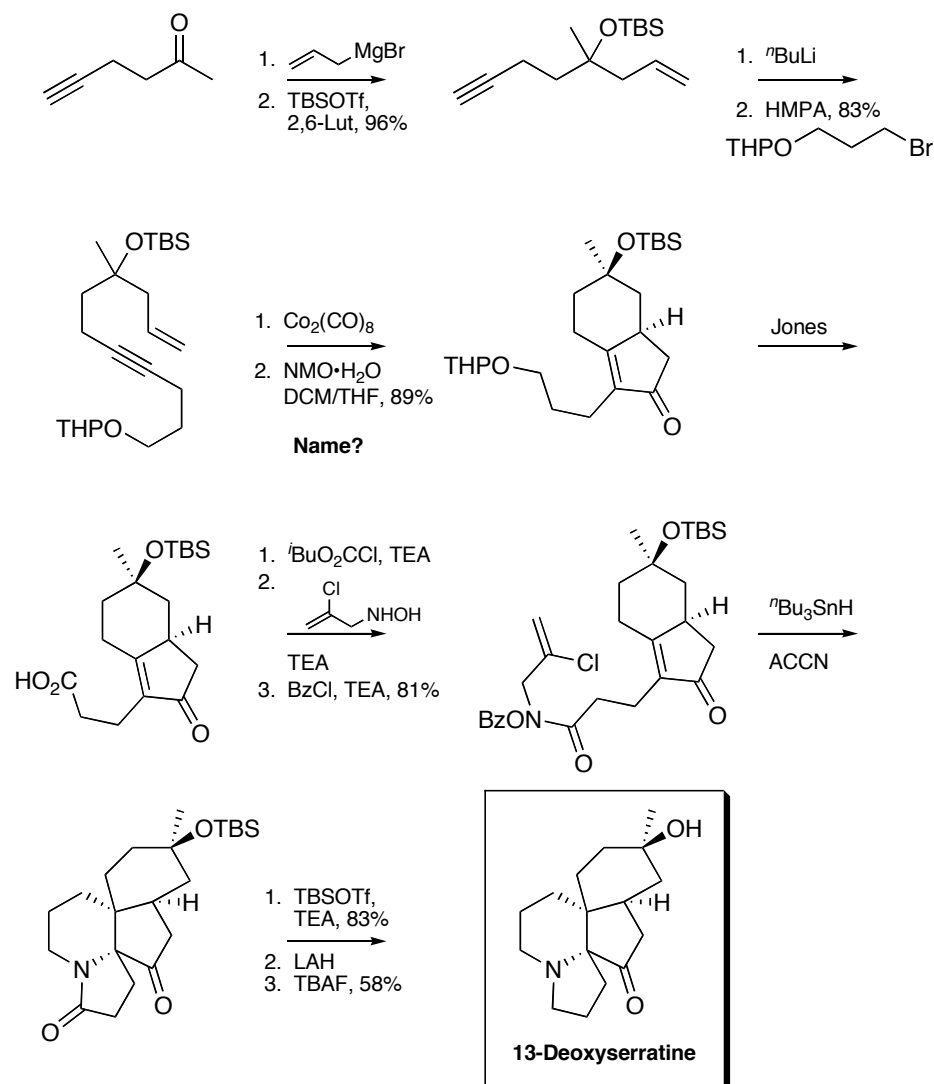
1. A Chemzymatic Ligand

Corey, E.J. *Tetrahedron Lett.* 1989, 30, 5547:

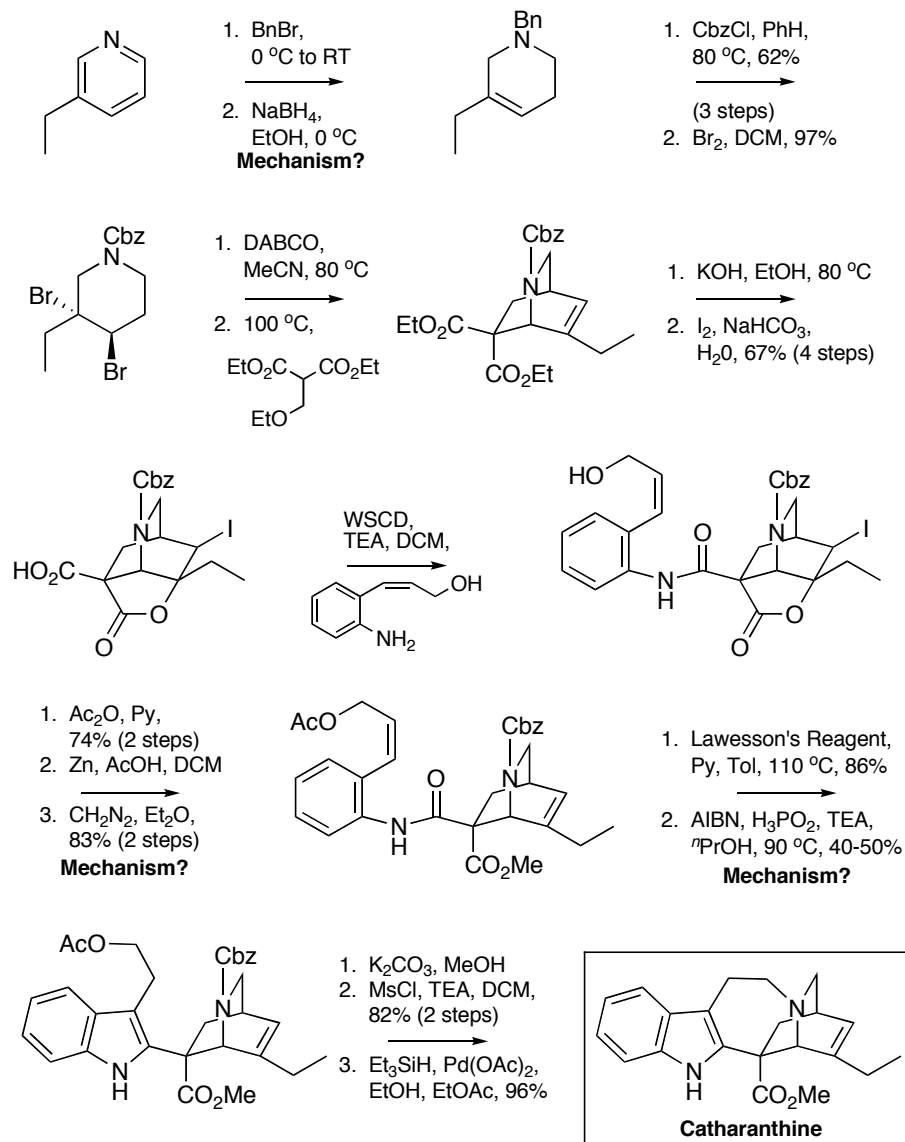
Synthesis of Chiral Starting Material Using a CBS Reduction.



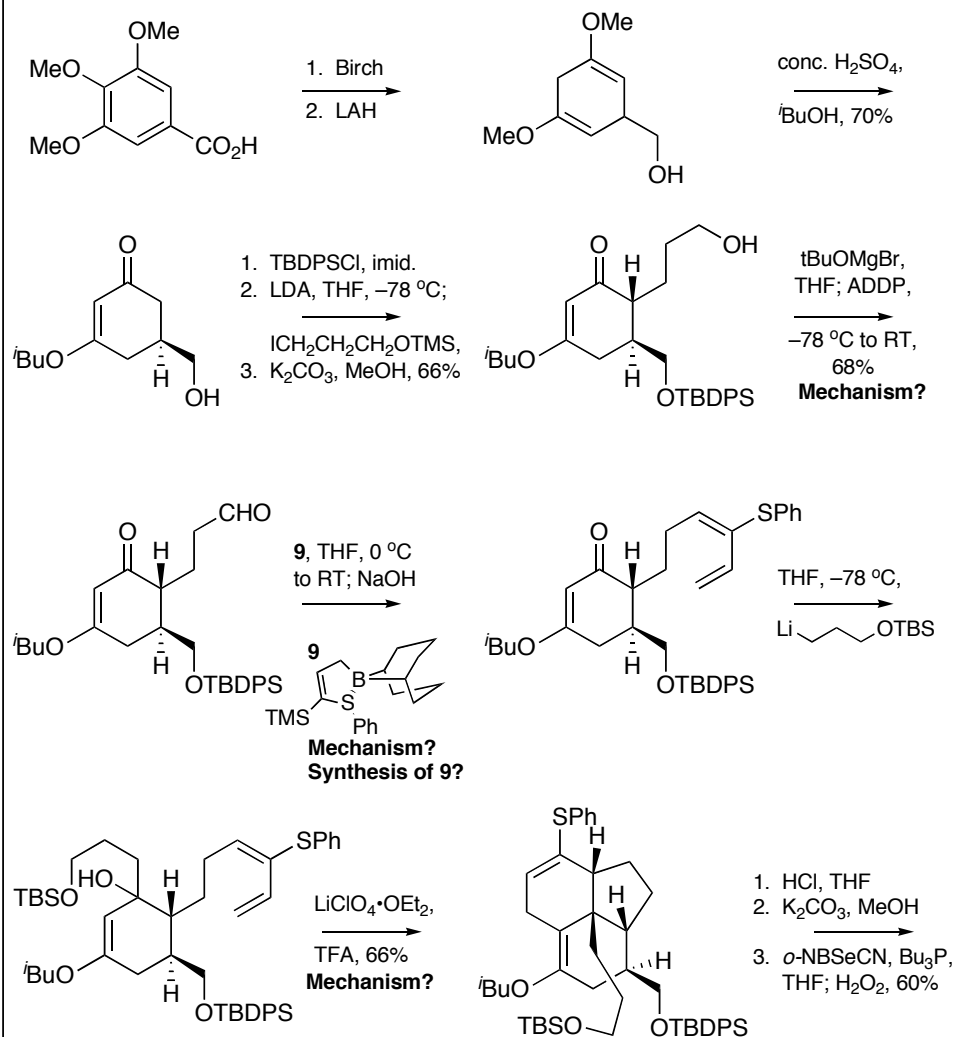
2. (±)-13-Deoxyserratine

Zard, S.Z. *Angew. Chem. Int. Ed. Eng.* 2002, 41, 1783:

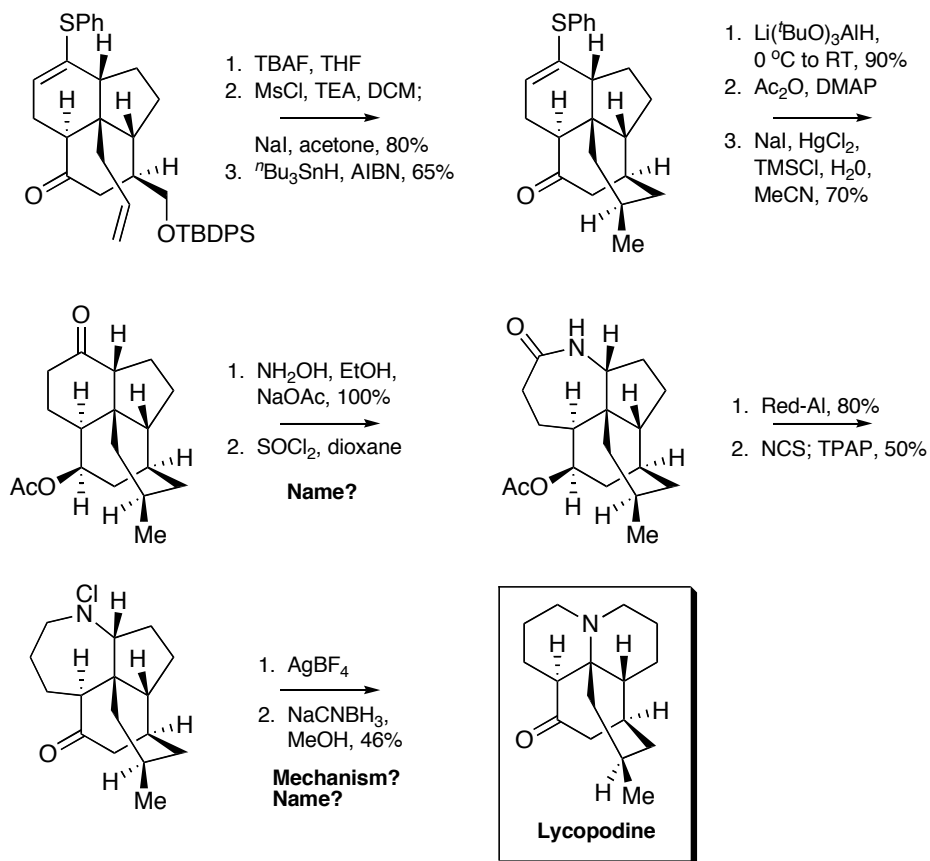
3. (±)-Catharanthine

Fukuyama, T. *Heterocycles*. 2002, 56, 313:

4. (±)-Lycopodine

Grieco, P.A. *J. Am. Chem. Soc.* 1998, 120, 5128:

4. (±)-Lycopodine (Continued)

Grieco, P.A. *J. Am. Chem. Soc.* 1998, 120, 5128:

5. Peduncularine (Formal)

Weinreb, S.M. *Tetrahedron* 2001, 57, 8779Hiemstra, H. *J. Am. Chem. Soc.* 1989, 111, 2588