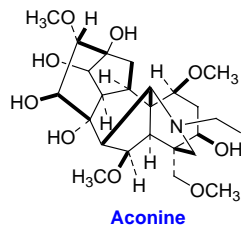
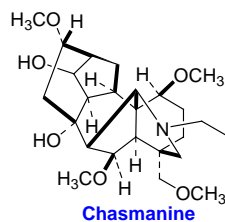
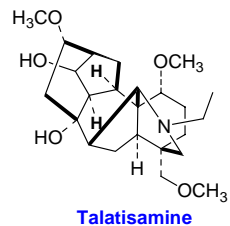


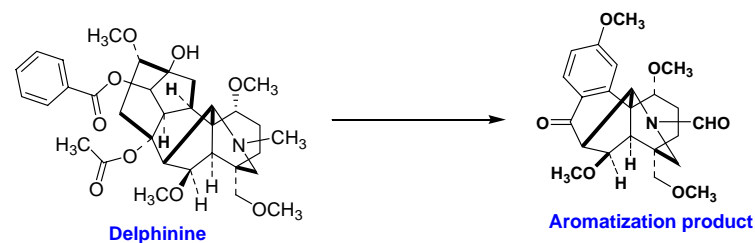
- Isolated in 1918
- Similar to another alkaloid aconine
- Medicinal property includes parasitic and insecticidal action
- Hexacyclic polybridged skeleton with seven substituents
- Structural determination and synthetic studies carried out by Karel Wiesner



Karel Frantisek Wiesner (1919-1986)

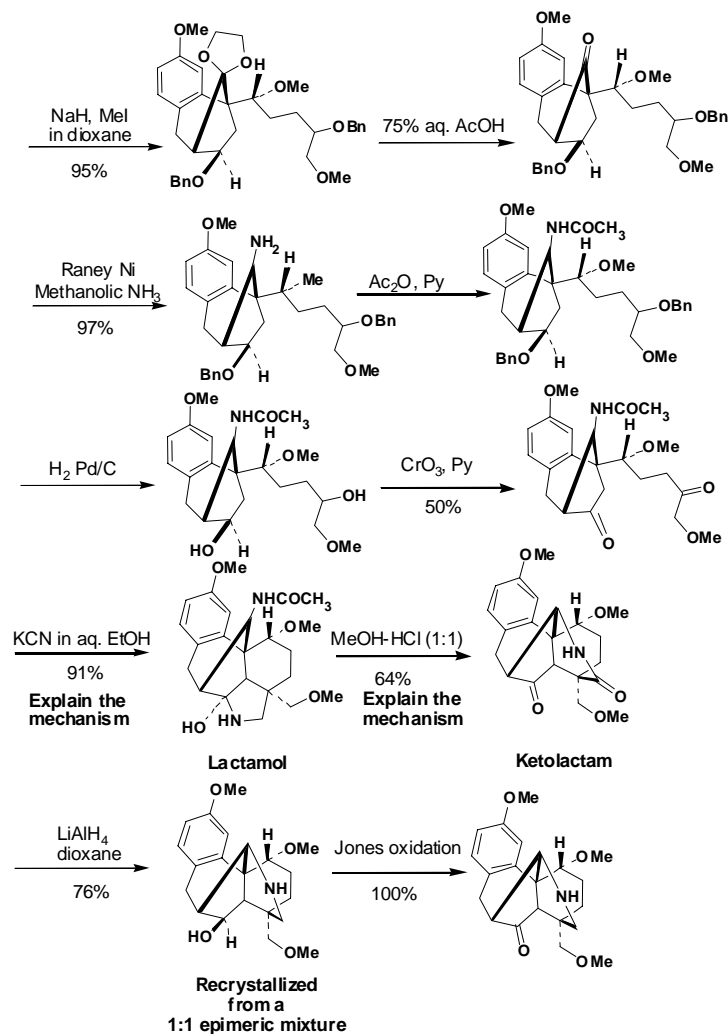
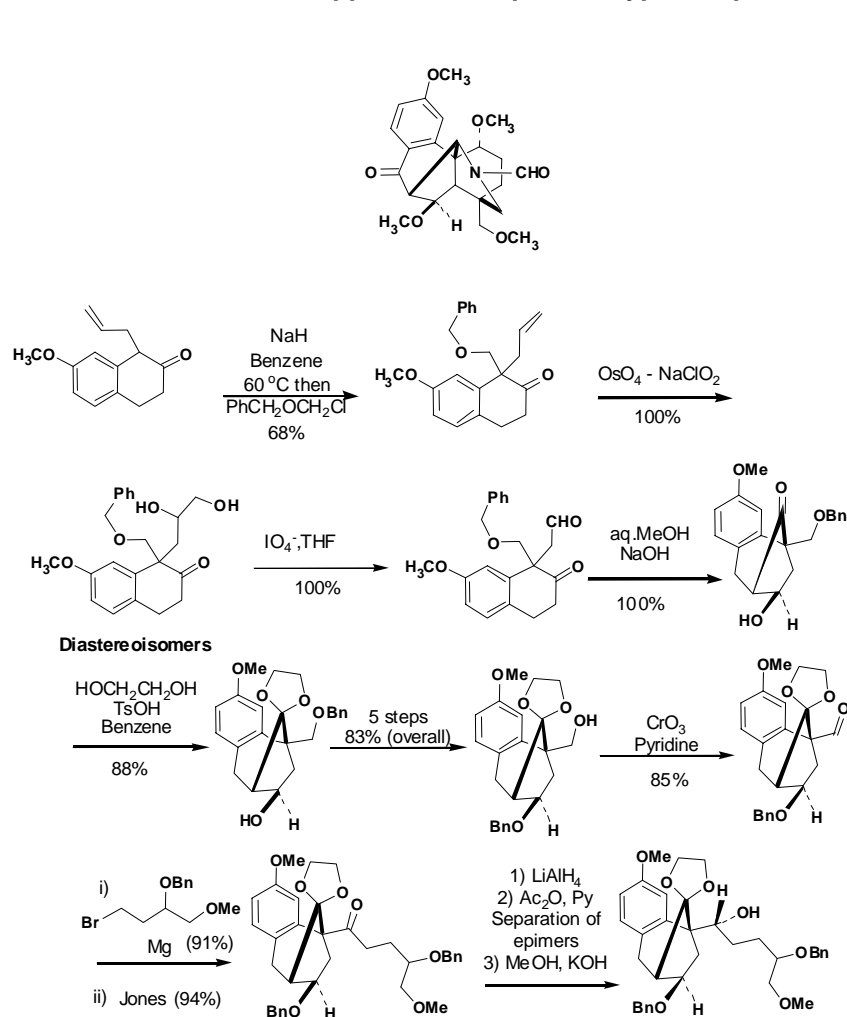
Wiesner made remarkable contributions in the area of total synthesis of complex polysubstituted polycyclic natural products. Some of his total syntheses include veatchine, atisine, annotinine, delphinine, talatisamine, chasmanine, napelline, digitoxin and other cardioactive steroids.

Degradative Studies

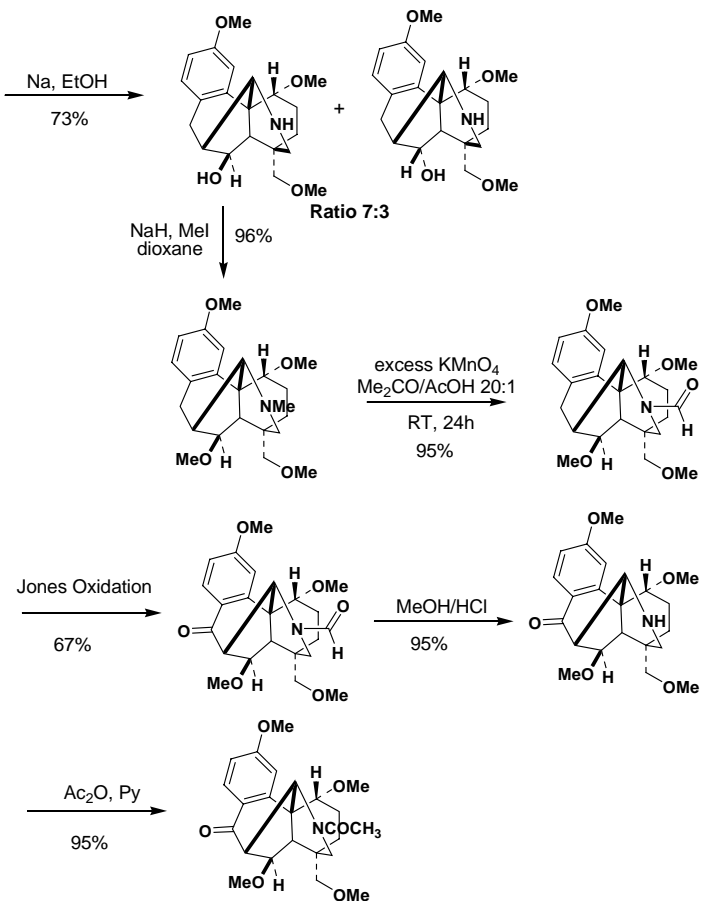


Wiesner, K.; Bickelhaupt, F.; Babin, D. R.; Gotz, M. *Tetrahedron Lett.* **1959**, 3, 11.
 Jacobs, W. A.; Pelletier, S. W. *J. Am. Chem. Soc.* **1956**, 78, 3542.
 Wiesner, K.; Bickelhaupt, F.; Babin, D. R.; Gotz, M. *Tetrahedron* **1960**, 9, 254.
 Wiesner, K. *Tetrahedron* **1985**, 41, 485.

The First Generation Approach to Delphinine Type Compounds



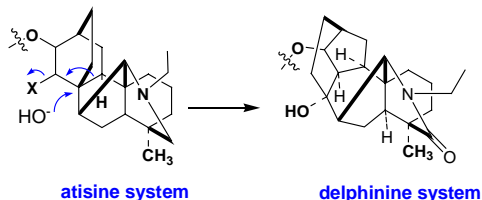
Wiesner, K.; Jay, E. W. K.; Demerson, Kanno, T.; Krepinsky, J.; Poon, L.; Tsai, T. Y. R.; Vilim, A.; Wu, C. S. *Experientia* **1970**, *26*, 1030.
Wiesner, K.; Jay, E. W. K.; Poon-Jay, L. *Experientia* **1971**, *27*, 363.



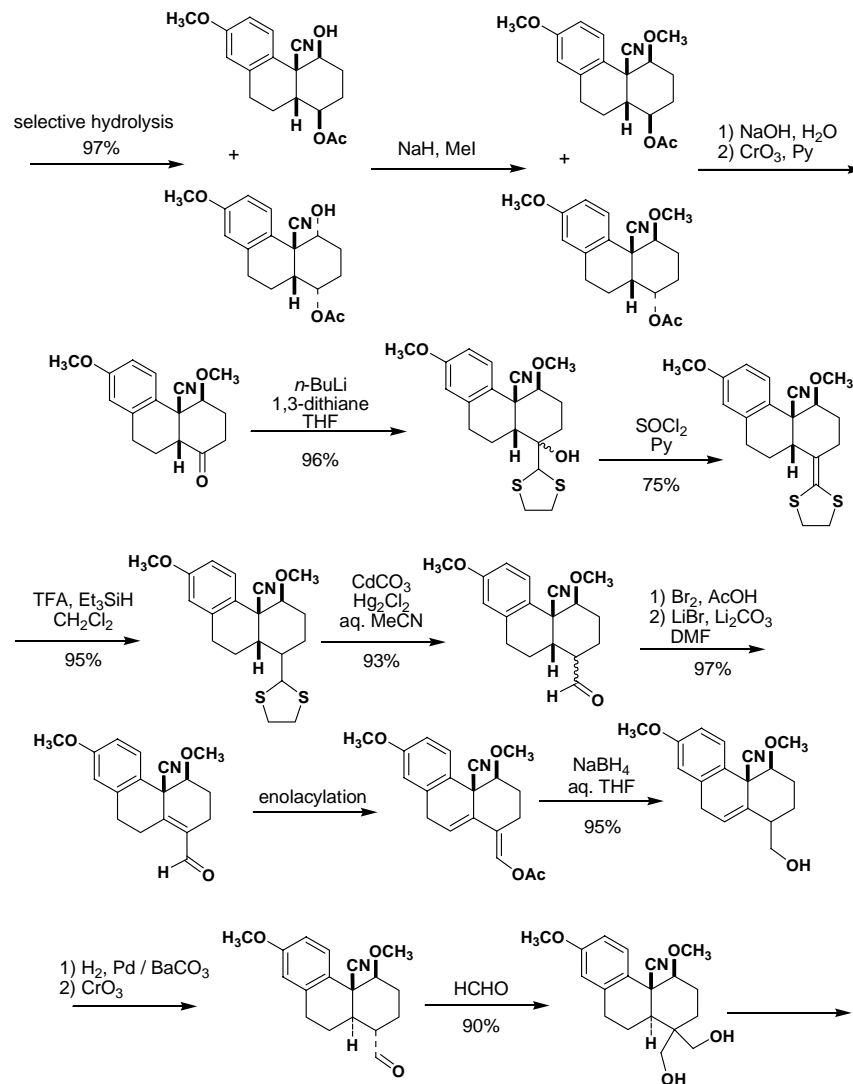
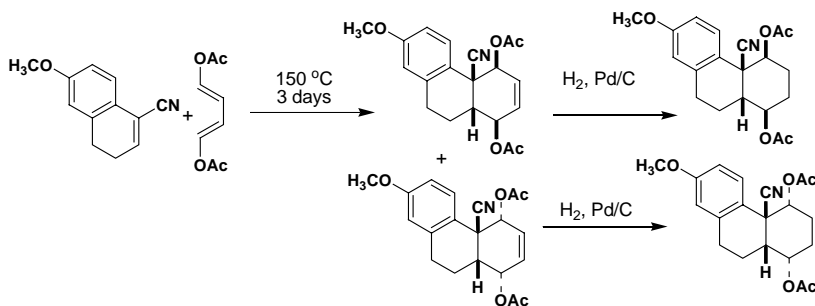
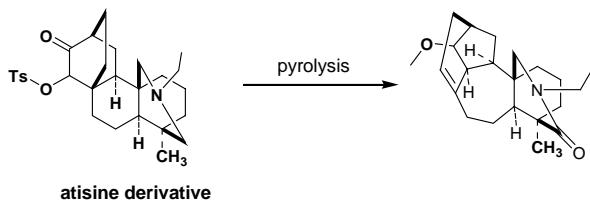
"Aromatic Intermediate" for Delphinine

Synthesis of Racemic Talatisamine: 2nd Generation Approach to Delphinine System: A possible biosynthesis of delphinine alkaloids

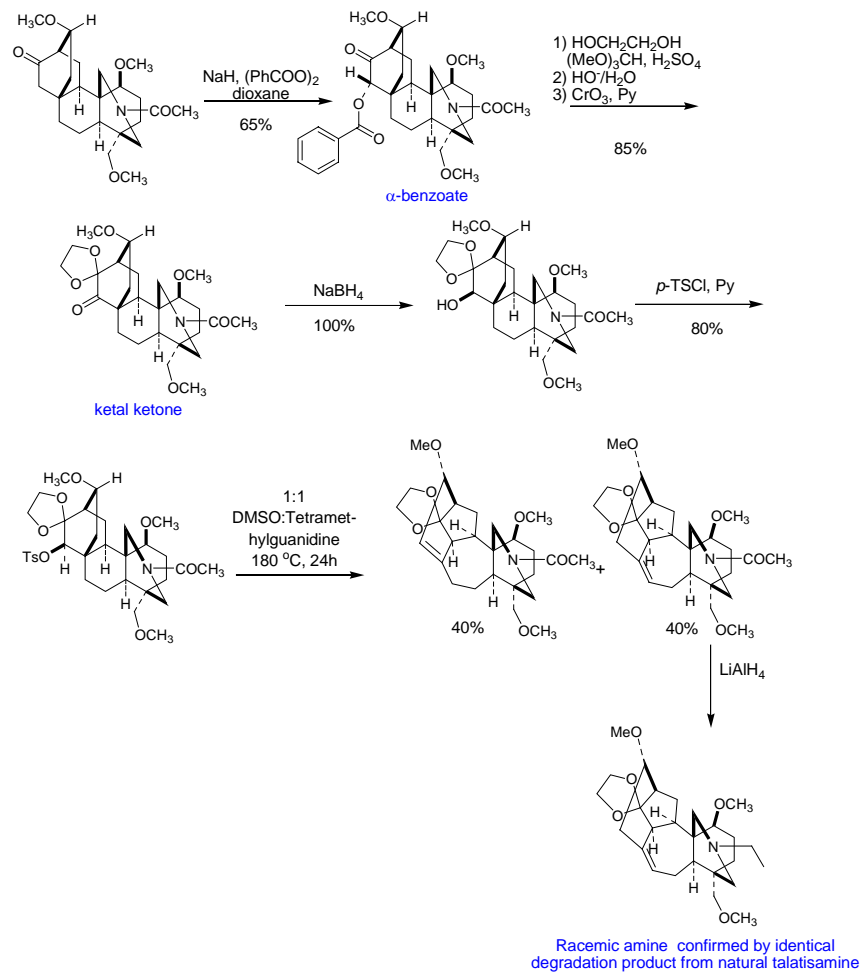
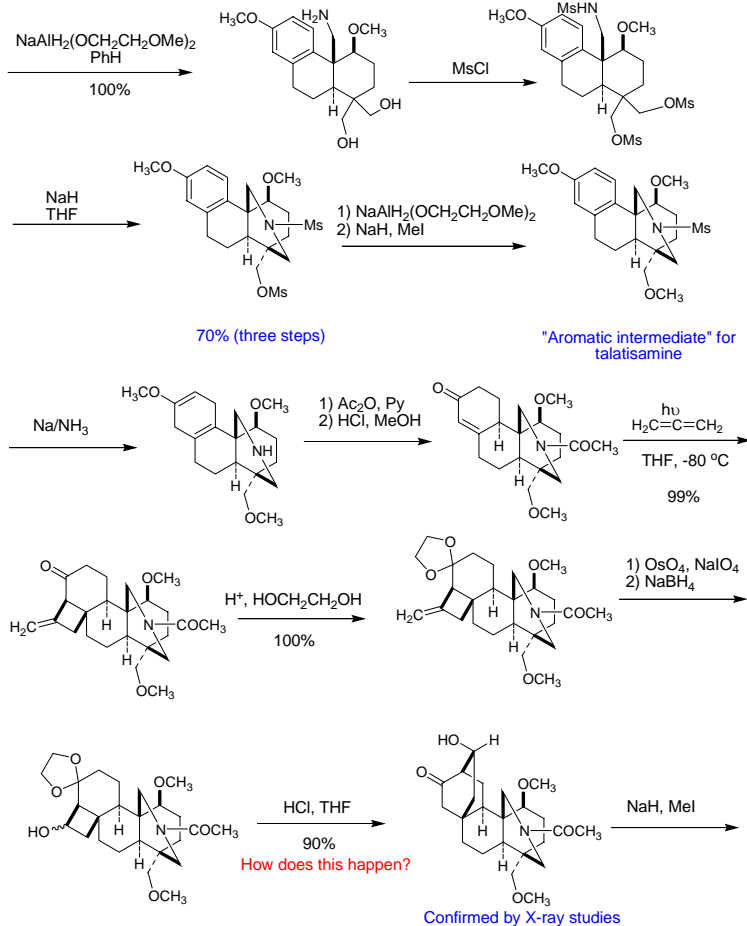
Cookson & Wiesner independently showed that the delphinine system might originate from the atisine system by loss of C-atom bridging and a rearrangement.



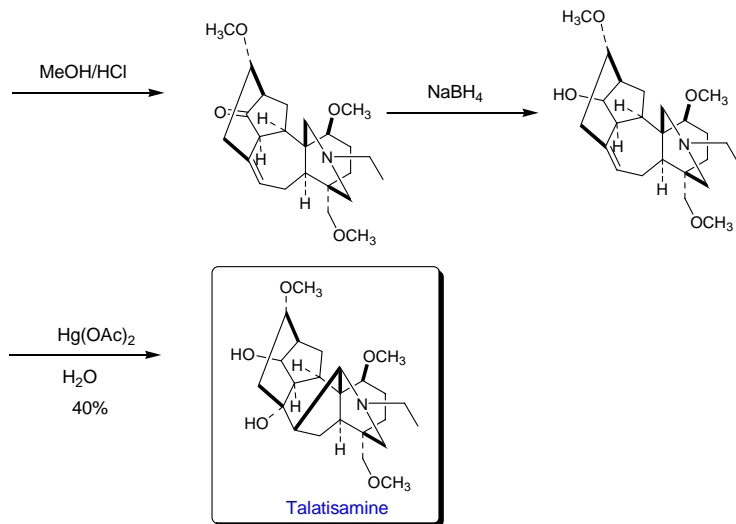
The postulated biogenetic rearrangement of the atisine skeleton was accomplished first by Johnston and Overton



Talatisamine...



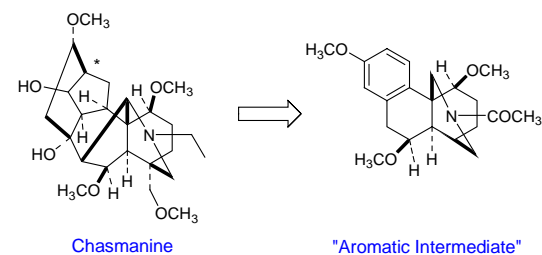
Talisamine...



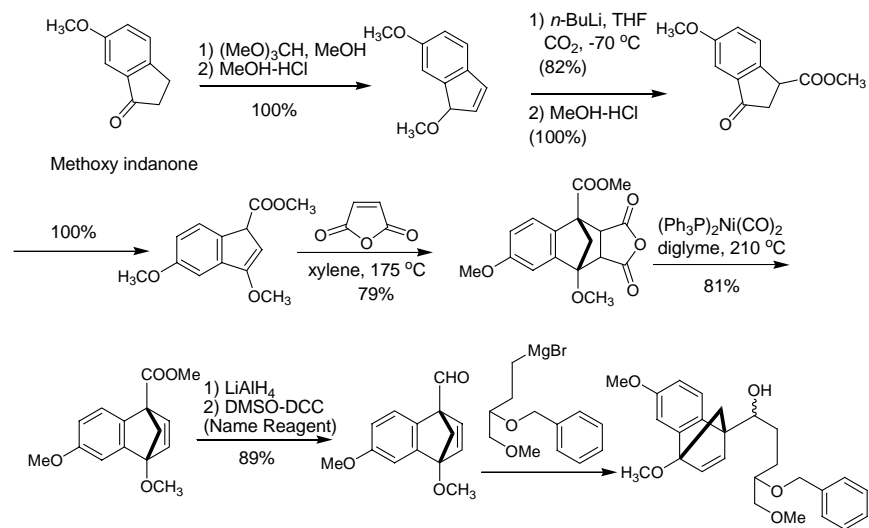
- Talisamine was the first dephinine alkaloid to be synthesized
- formation of byproducts
- non-regiospecificity of the Hg(OAc)₂ oxidation
- rather lengthy process to introduce the β-tosyloxy group
- it lacks the complete dephinine substitution

Edwards, O. E. *Chem. Comm.* **1965**, 318.

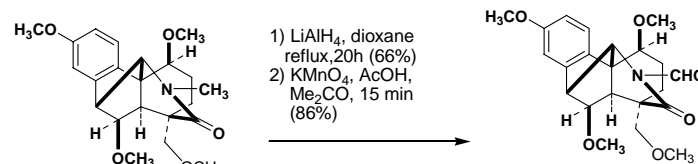
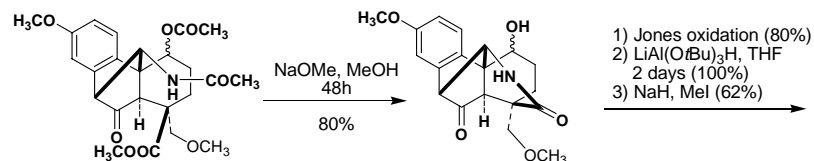
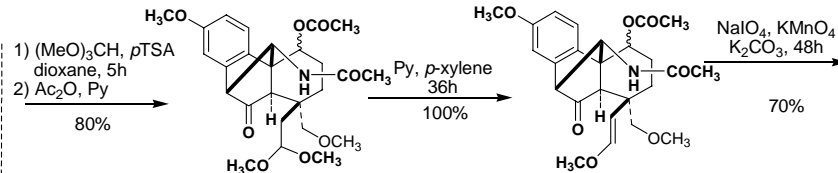
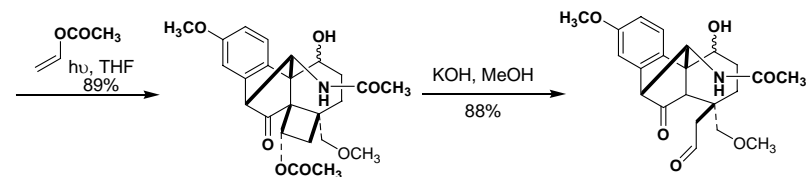
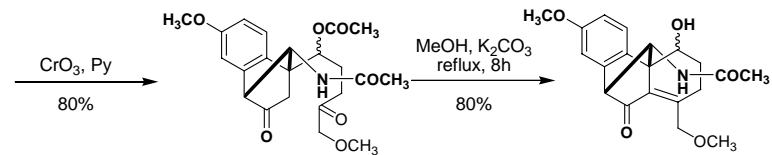
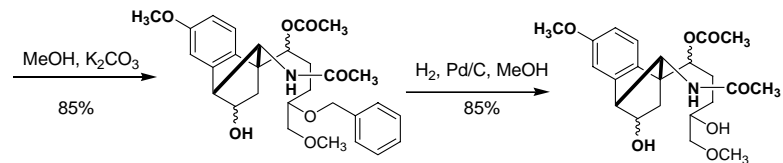
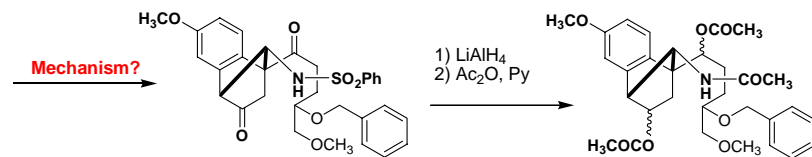
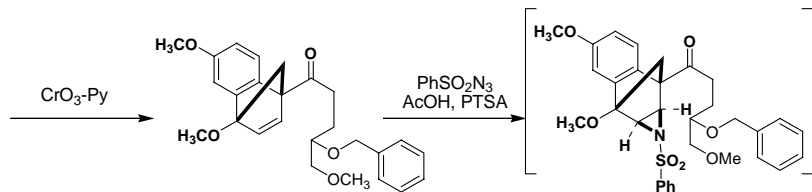
Synthesis of Chasmanine: The Third Generation Approach to the Synthesis of Dephinine System



- Chasmanine has only one substituent less than delphinine (*)

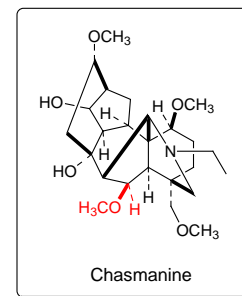


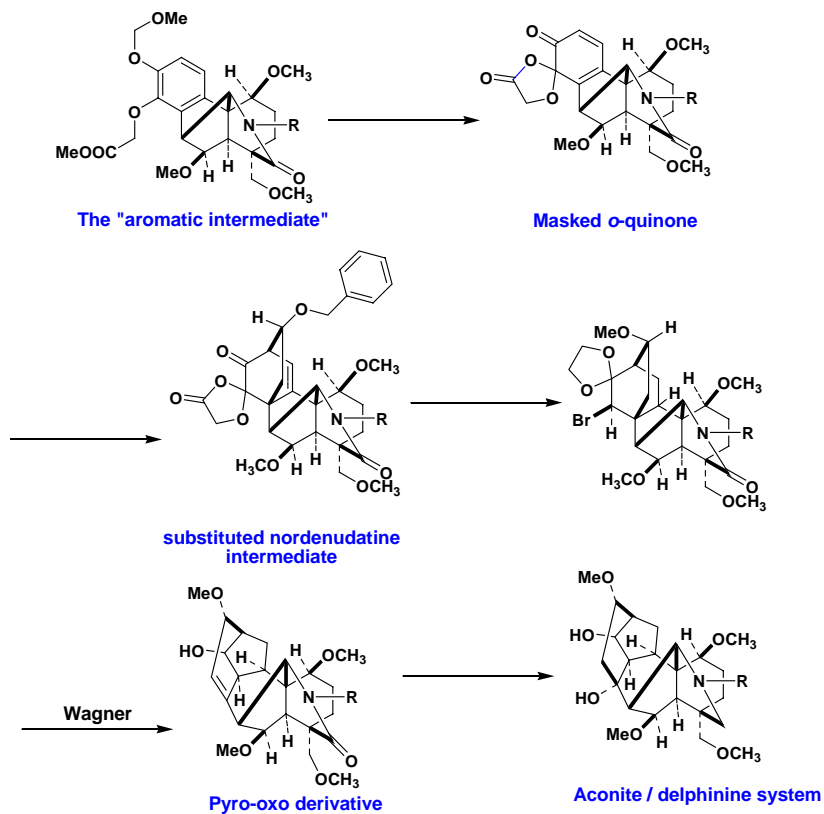
Chasmanine...



"Aromatic intermediate" for chasmanine

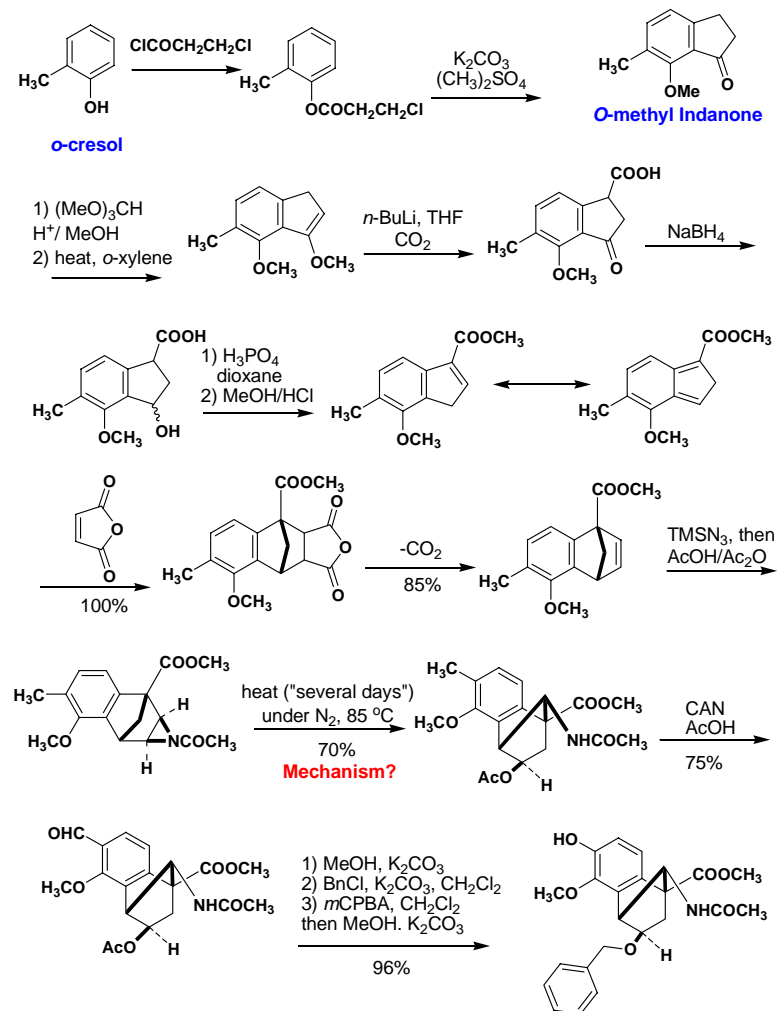
Steps →



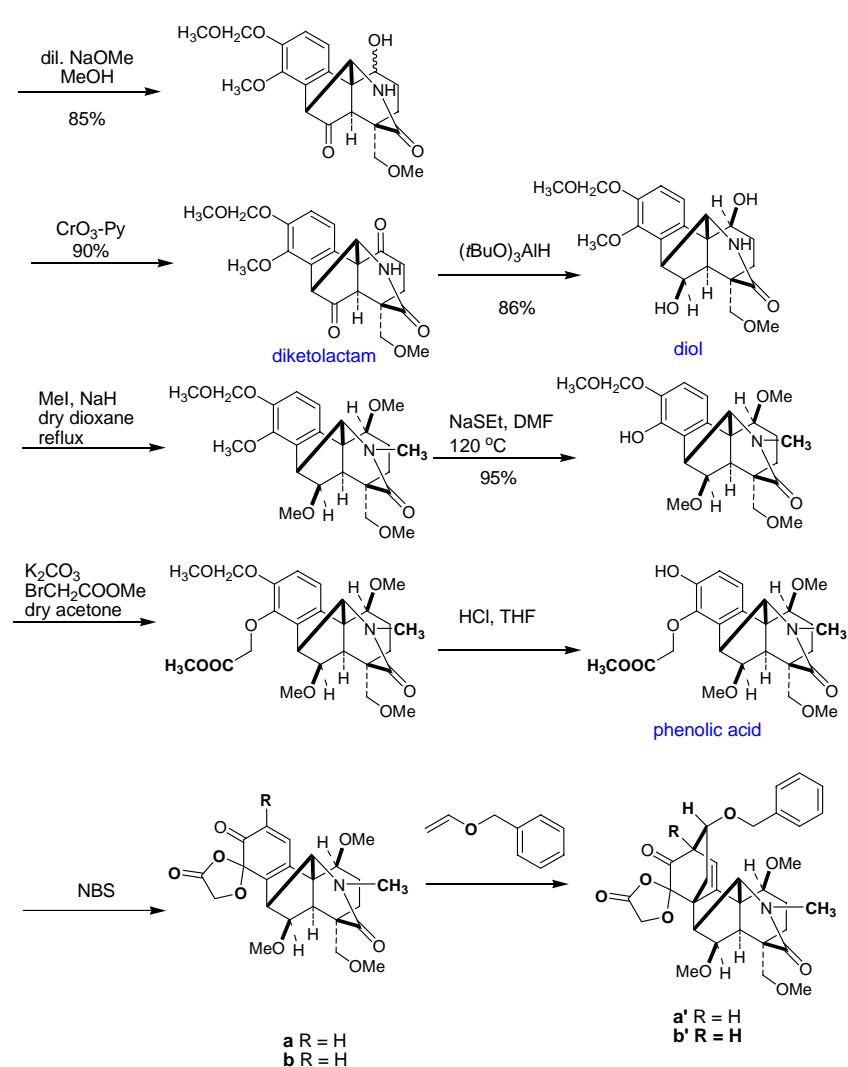
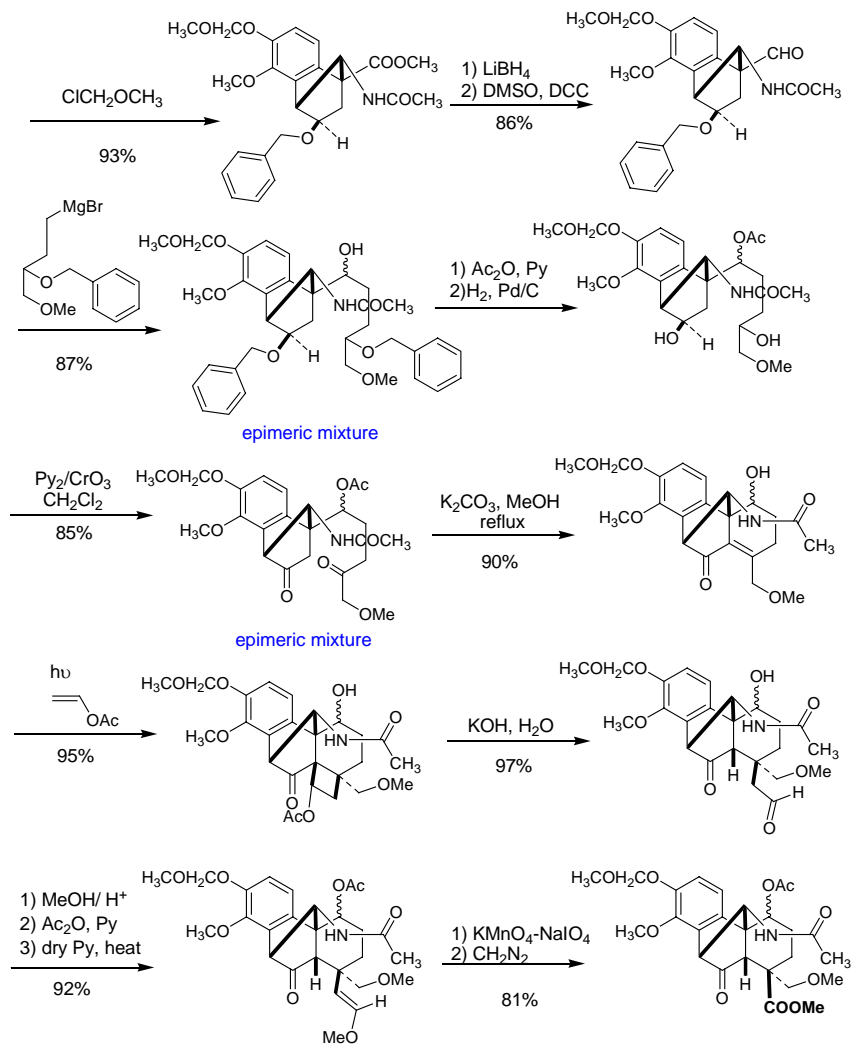
Synthesis of 13-desoxydelphinine: The Fourth Generation
Synthetic Approach to Delphinine

Wiesner, K. *Pure & Appl. Chem.* 1979, 51, 689.
Wiesner, K.; Tsai, T. Y. R.; Nambiar, K. P. *Can. J. Chem.* 1978, 56, 1451.

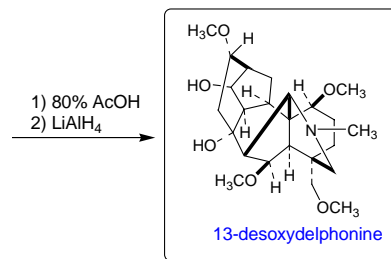
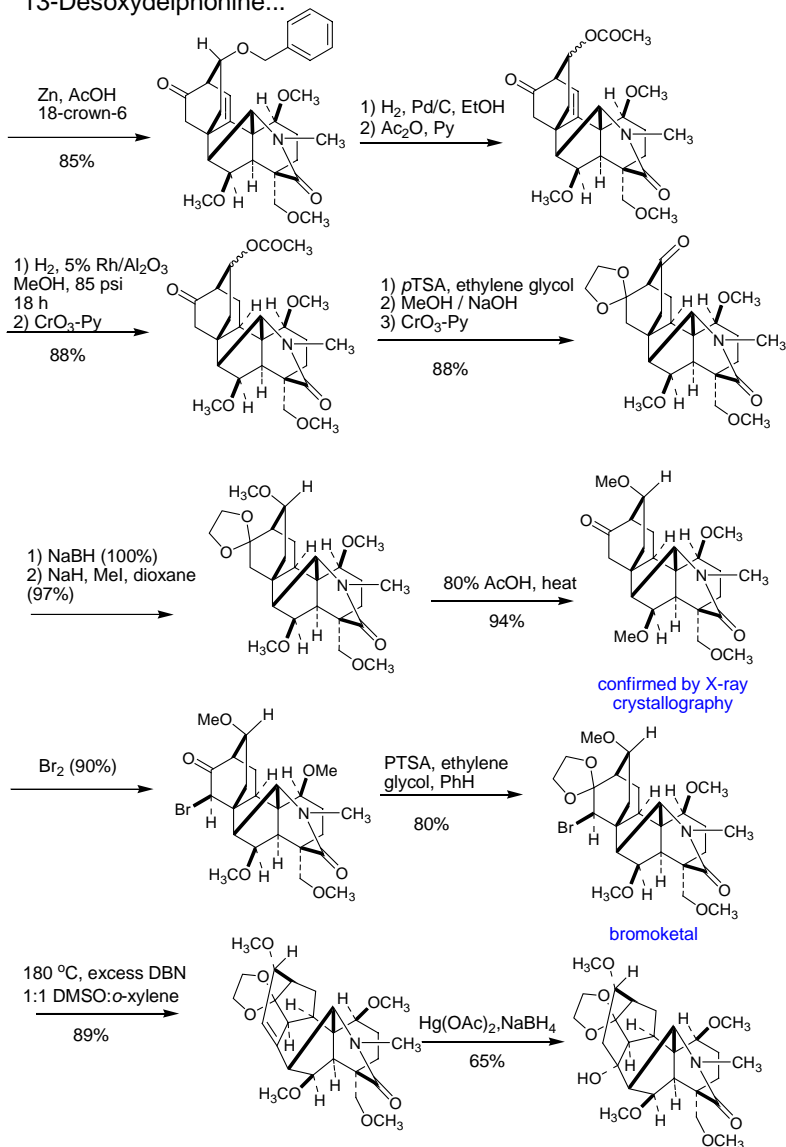
Construction of the Aromatic Intermediate



13-Desoxydelphonine...



13-Desoxydelphonine...



This route seems more efficient than the 3rd generation approach, reduces the synthesis by 10 steps