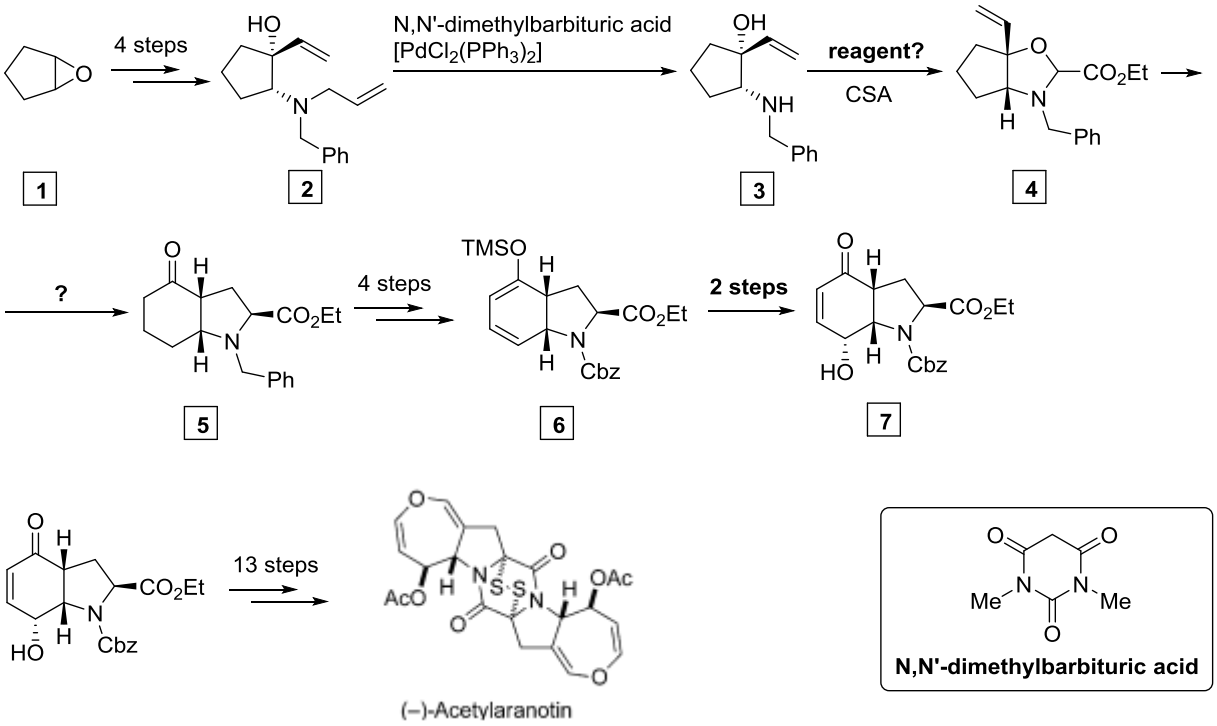
Submitted by Andrey Kuzovlev

20.03.2015

Total Synthesis of (-)-Acetylaranotin

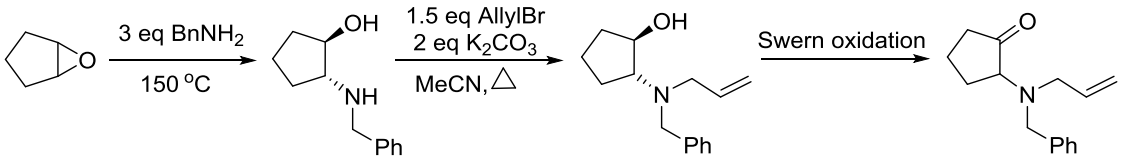
Problem:



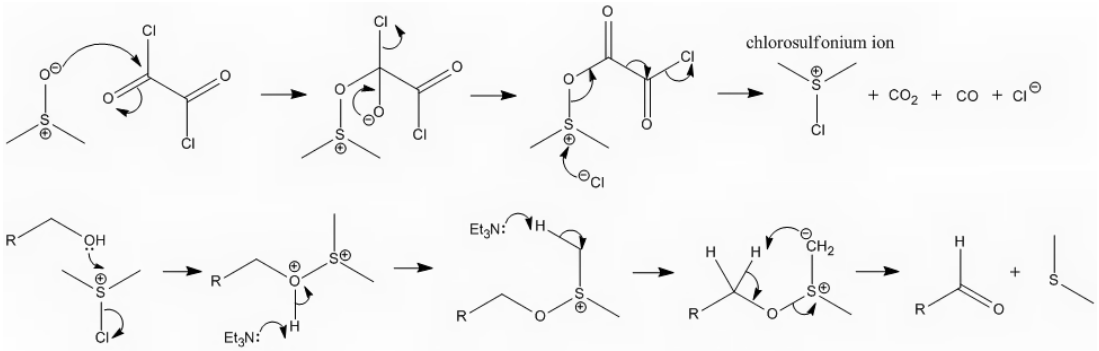
- Synthesize 2 from 1 in 4 steps, give the mechanism for the step 3 (name reaction) (Bachelors and Masters)
- Give the mechanism for the removal of the allyl group from 2.
- Which reagent will you use to get 4 from 3?
- Give a catalyst and the mechanism for the key step (4 to 5). Which name reactions do this transformation include (2 name reactions)?
- How will you make the transformation of 6 to 7 (Rubottom Oxidation)? Give the mechanism for this transformation.

Solution:

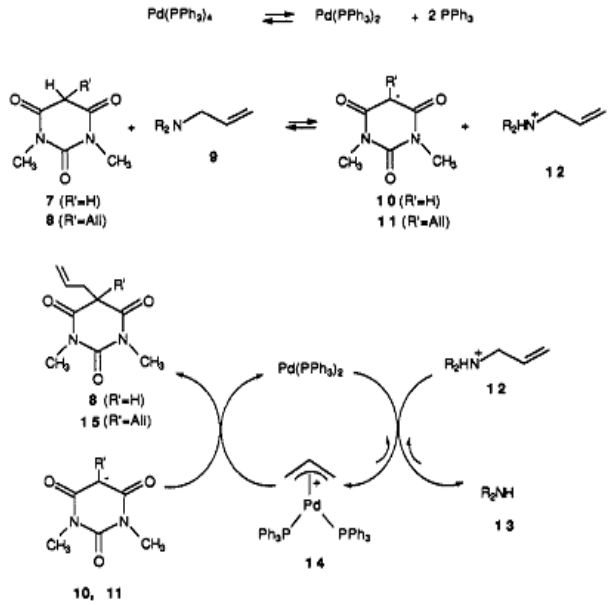
Synthesis 2 from 1 in 4 steps:[1]



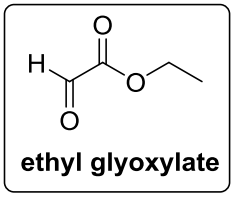
Mechanism of Swern oxidation



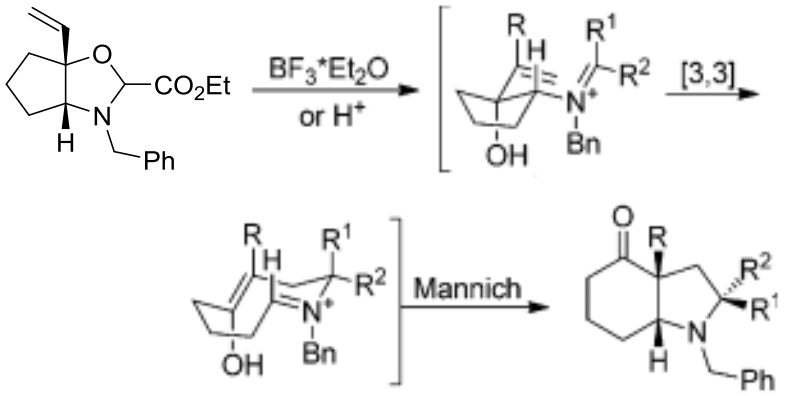
Removal of the allyl group:[2]



Reagent to get 4 from 3:

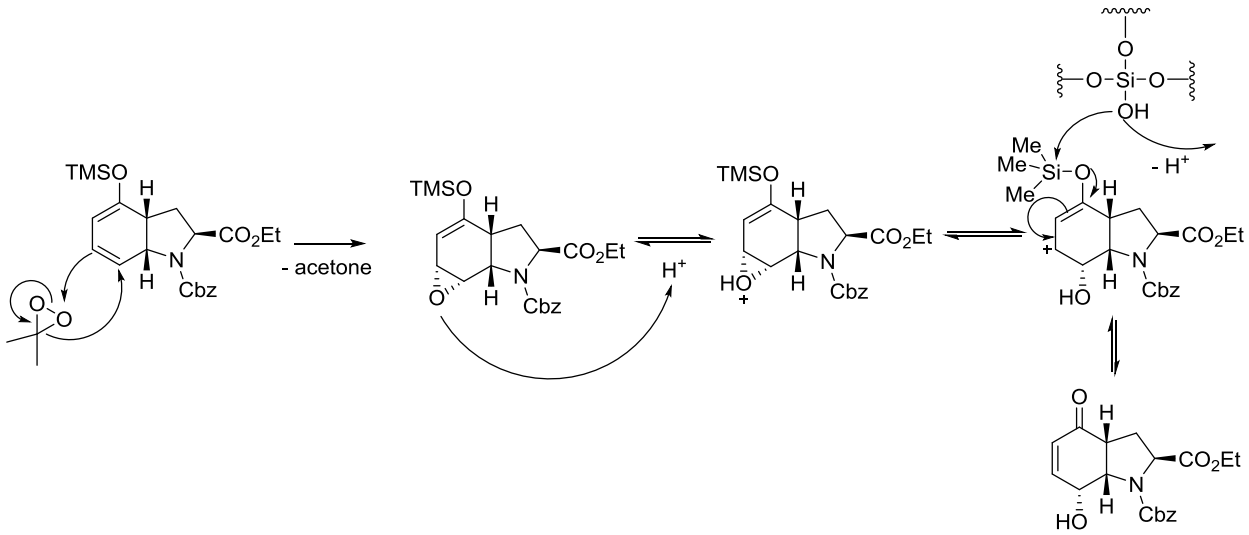


Mechanism for the key step (Aza-Cope rearrangement, Mannich cyclization):[1]



$R = H, R^2 = H, R^1 = CO_2Et$

Mechanism for the transformation of 6 to 7. Rubottom Oxidation:[3]



[1] Dmitry S. Belov, Nina K. Ratmanova, Ivan A. Andreev, and Alexander V. Kurkin *Chem. Eur. J.* **2015**, *21*, 4141-4147.

[2] Florence Garro-Helion, Ahmed Merzouk, and Francois Guibe *J. Org. Chem.* **1993**, *58*, 6109-6113.

[3] Hideto Fujiwara, Taichi Kurogi, Shun Okaya, Kentaro Okano, and Hidetoshi Tokuyama *Angew. Chem. Int. Ed.* **2012**, *51*, 13062-13065.