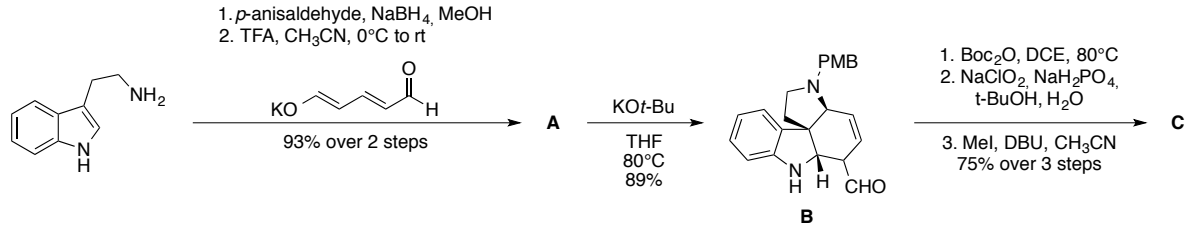
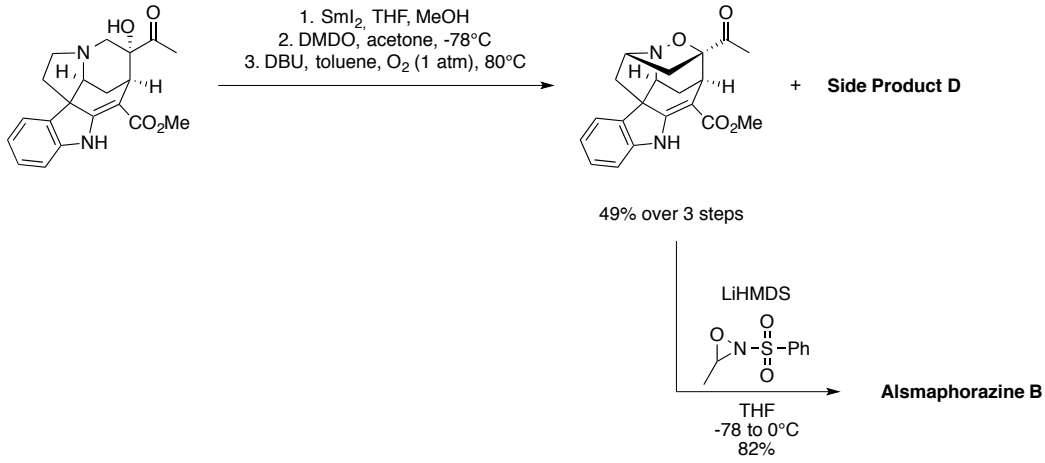
Submitted by Valentin

Total Synthesis of Alsmaphorazine



Questions :

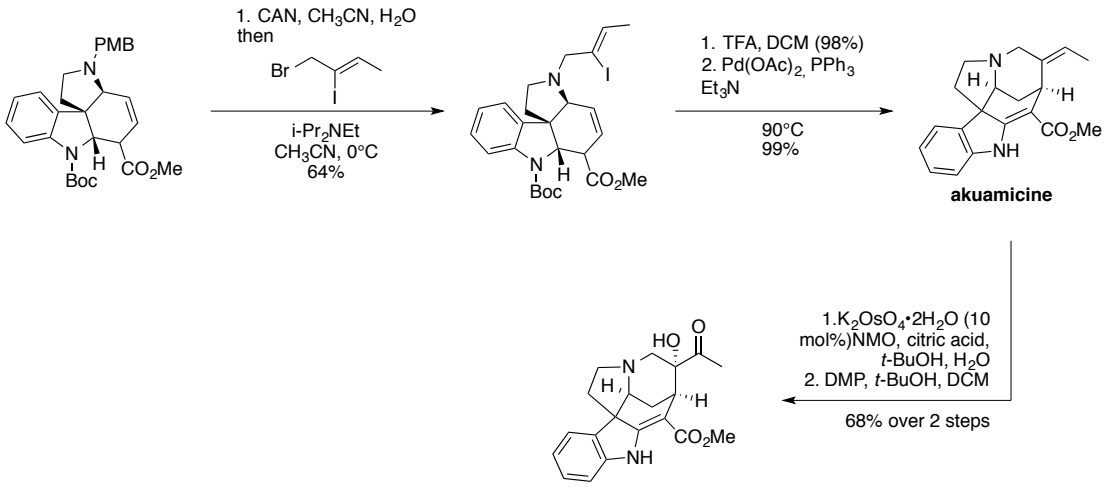
- Give the mecanism for the formation of **A** and **B**
- Give the structure of **A** and **C**



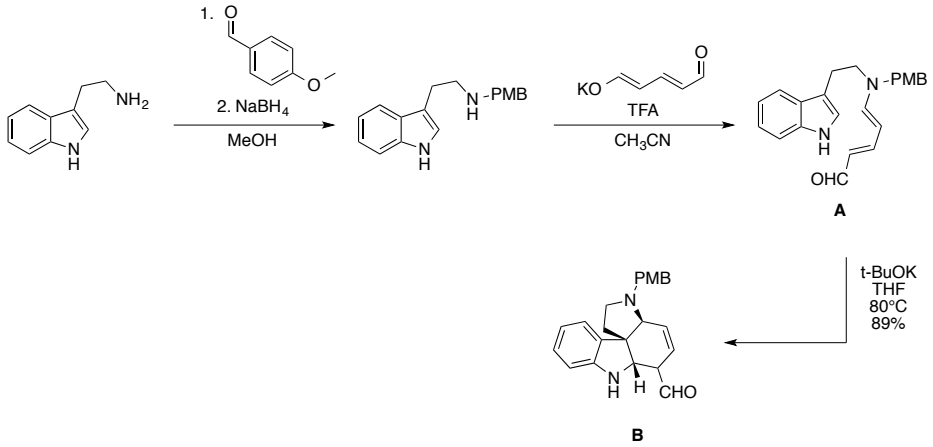
Questions :

- Give the mecanism of each reactions.
- Give the structure of the missing **side product D** and the **Alsmaphorazine B**
- Give the name of the reagent of the last step.
- How would you synthesized DMDO ?

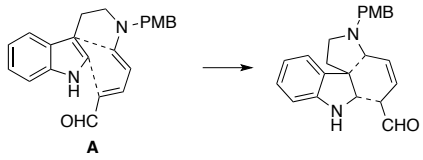
Hong, A. Y.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2015**, ASAP.


1. CAN, CH3CN, H2O
then
Br
I
i-Pr2NEt
CH3CN, 0°C
64%
1. TFA, DCM (98%)
2. Pd(OAc)2, PPh3
Et3N
90°C
99%
PMB
N
N
H
Boc
CO2Me
I
HO
O
H
CO2Me
NH
akuamicine
1.K2OsO4•2H2O (10
mol%)NMO, citric acid,
t-BuOH, H2O
2. DMP, t-BuOH, DCM
68% over 2 steps

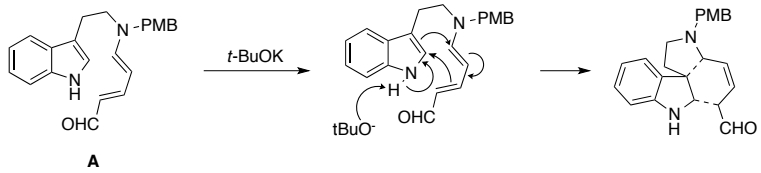
Solution



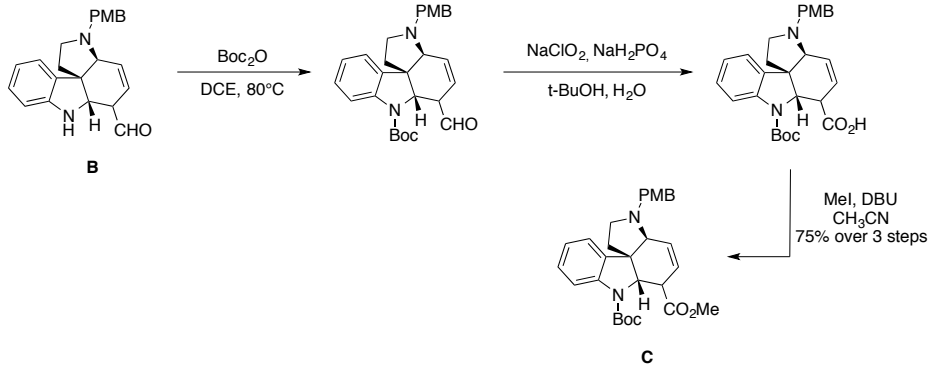
Cycloaddition for the formation of the bicycle :



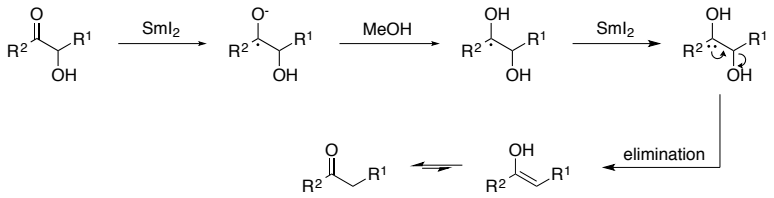
Anionic mecanism for the formation of the bicycle :



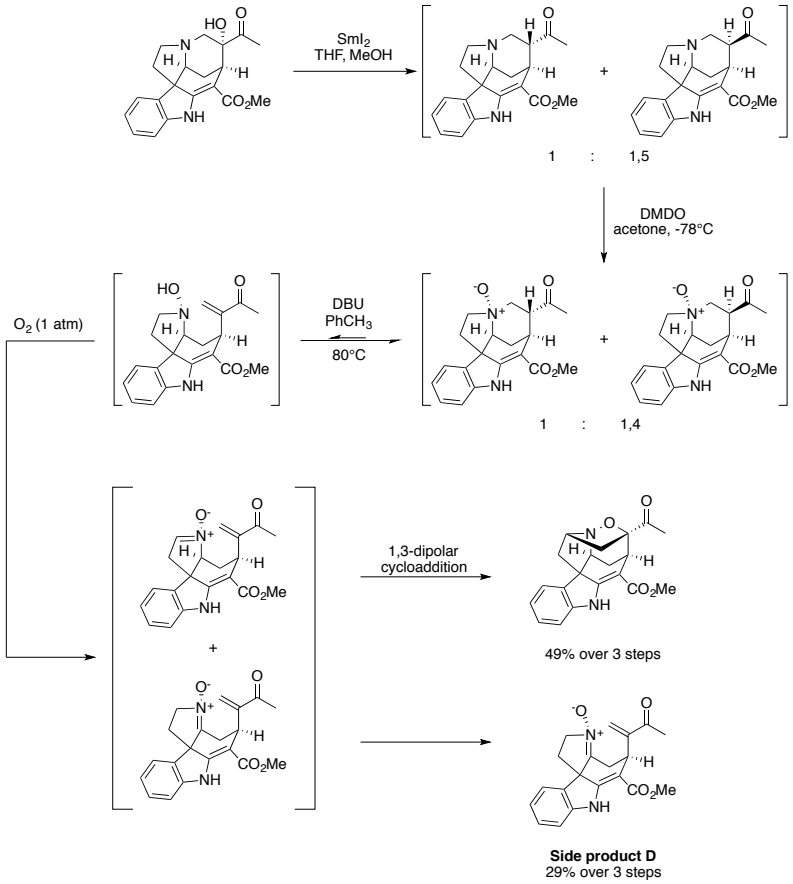
Martin, D. B. C.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2009**, *131*, 3472.



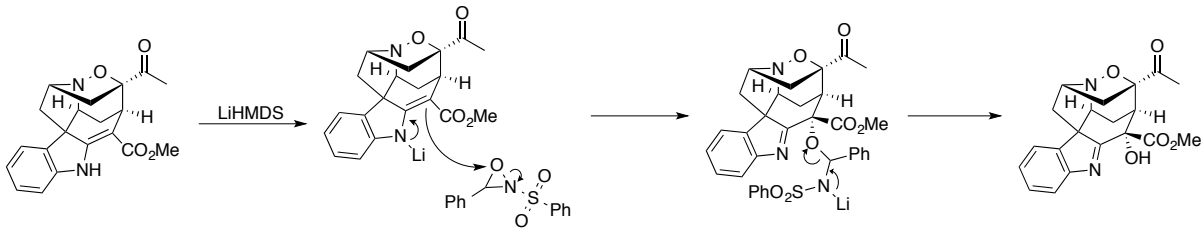
Reduction of the alcohol with SmI_2 :



Molander, G. A.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 1135.

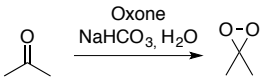


Johnson, D. H.; Rogers, M. A. T.; Trappe, G. *J. Chem. Soc.* **1956**, 1093.



Davis Oxaziridine

DMDO synthesis :



Oxone : $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$