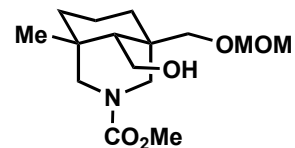


Total Synthesis of Dihydroajaconine and Gymnandine

08.02.17

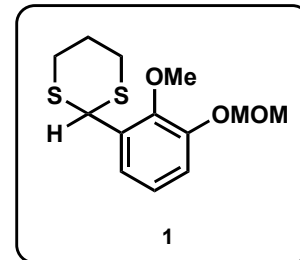


1. Ac₂O, NEt₃, DMAP
CH₂Cl₂
2. NaI, AlCl₃, MeCN/CH₂Cl₂
3. DMP, CH₂Cl₂

A

4. Ph₃PCH₃Br, KO^t-Bu, THF
5. PPh₃, I₂, im, PhH

B



6. 1, *n*-BuLi, THF
then **B**
7. HCl_{conc}, MeOH

C

8. PhI(OAc)₂, NaHCO₃
MeOH
9. Sml₂, THF/MeOH

D

10. H₂, Pd/C, EtOAc
11. Ph₃PCH₃Br, KO^t-Bu
THF

E

12. DMP
MeCN/CH₂Cl₂/H₂O

13. NaBH₄, MeOH
14. KOH, N₂H₄·H₂O
MeOH/H₂O, μW
15. **2**, DMAP, MeCN

F

16. NaNO₂, CuCl (cat.)
HCl/Et₂O, acetone, rt

G

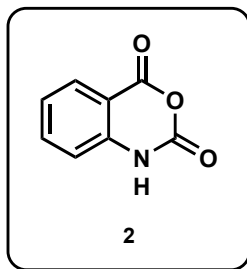
+

H

1.1

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1

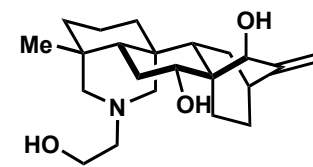


17. Et₃SiH, BF₃·OEt₂
CH₂Cl₂

18. SeO₂, *t*-BuOOH
CH₂Cl₂

I

19. [Cp₂Zr(H)Cl], THF, rt
20. Br(CH₂)₂OH, Cs₂CO₃
MeCN



dihydroajaconine

G

21. $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]$
THF, rt

J

22. AZADO, CuCl,
bpy, DMAP, O_2
 $\text{MeCN}/\text{CH}_2\text{Cl}_2$, rt

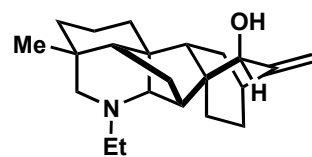
23. SmI_2 , THF, reflux
then AcCl, NaHCO_3 aq.
 CH_2Cl_2 , rt

AZADO = 2-azaadamantane *N*-oxyl
bpy = 2,2'-bipyridyl

K

24. NaH, CS_2 , MeI
THF

25. AIBN, HSnBu_3 , PhMe
26. Red-Al, THF

**gymnandine**

27. SeO_2 , *t*-BuOOH
 CH_2Cl_2

28. DMP, TFA, CH_2Cl_2

29. NaBH_4 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$
MeOH

L