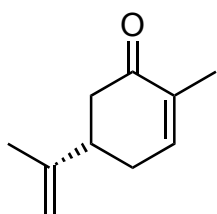


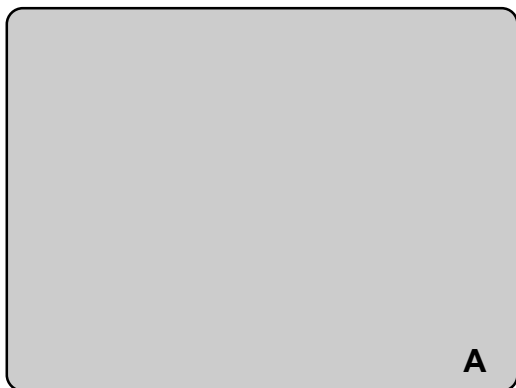
# Asymmetric Total Synthesis of Norzoanthamine

Zhengyuan Xin, Hui Wang, Haibing He, Xiaoli Zhao, Shuanhu Gao

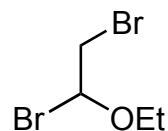
*Angew. Chem. Int. Ed.* **2021**, *60*, 12807-12812.



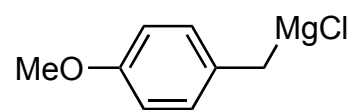
1-16



17-23



**1**



**2**

1. NaOH, H<sub>2</sub>O<sub>2</sub>, MeOH *then* *N*-acetyl-*L*-cysteine, (PhSe)<sub>2</sub>, NaOH, MeOH
2. imH, DMAP, TBSCl, DMF
3. DBU, HCHO (aq.), THF
4. O<sub>3</sub>, -78 °C, MeOH *then* Cu(BF<sub>4</sub>)<sub>2</sub>, Fe(BF<sub>4</sub>)<sub>2</sub>, -20 °C
5. TESCl, imH, DMAP, DMF
6. P(*n*-Bu)<sub>3</sub>, HCHO (aq.), CHCl<sub>3</sub>
7. TIPSCl, imH, DMAP, DCM
8. MeLi, Et<sub>2</sub>O, -78 °C
9. PDC, 4Å MS, MeCN/PhMe, 65 °C
10. PPTS, MeOH
11. PhNMe<sub>2</sub>, DCM, **1**
12. AIBN, Bu<sub>3</sub>SnH, PhMe, reflux
13. Ph<sub>3</sub>PCH<sub>3</sub>Br, *t*-BuOK, 0 °C
14. TBAF, THF
15. *p*-TSA, EtOH, CHCl<sub>3</sub>
16. DMP, DCM

17. **2**, THF, -78 °C to r.t.
18. Ac<sub>2</sub>O, Et<sub>3</sub>N, DMAP, DCM
19. **3**, PhSiH<sub>3</sub>, acetone, 38 °C *then* TBAF, NaOH (aq.)
20. Na, NH<sub>3</sub>, -78 °C
21. Ac<sub>2</sub>O, DMAP, THF *then* (CO<sub>2</sub>H) (aq.)
22. Mn(dpm)<sub>3</sub>, PhSiH<sub>3</sub>, *t*-BuOOH, *i*-PrOH *then* IBX
23. Et<sub>3</sub>N, TMSOTf, DCM, -78 °C to -20 °C *then* IBX, **4**

Step 1: Name of the SM?

Step 6: Name of the reaction?

Step 9: Name of the reaction?

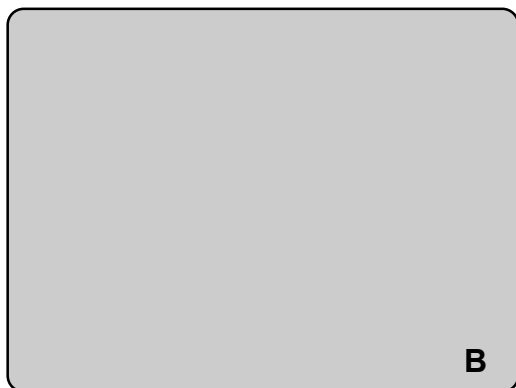
*Hint: Step 10 is a mono deprotection*

Step 12: Name of the reaction?

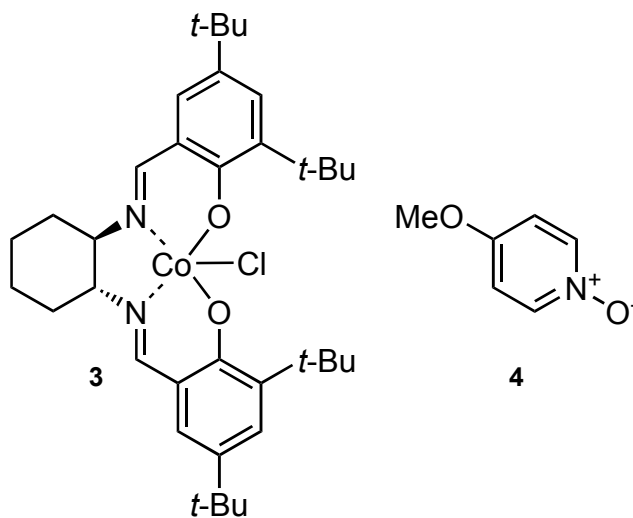
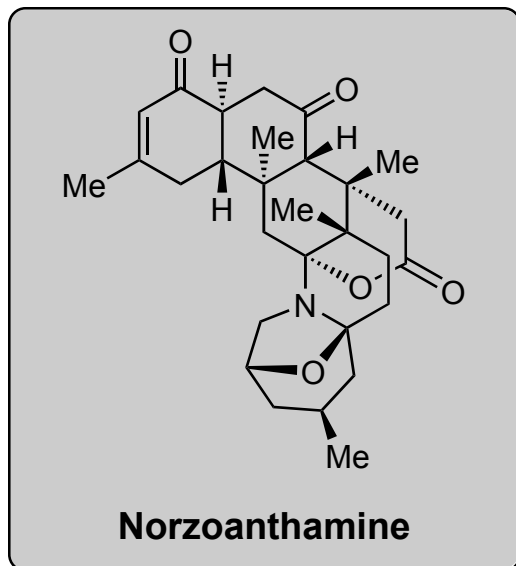
*Hint: Step 14 is a mono deprotection*

*Hint: Step 15 is an epimerization*

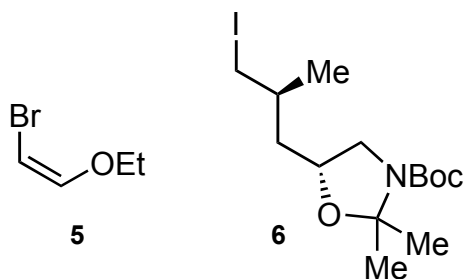
Step 20: Name of the reaction?



24-34



24. CSA, H<sub>2</sub>O, MeCN
25. MeLi, THF then LiAlH<sub>4</sub> then TIPSOTf, imH, THF/MeCN
26. TEMPO, PIDA, DCM
27. *t*-BuLi, **5**, THF then SM then (CO<sub>2</sub>H)<sub>2</sub>
28. *t*-BuLi, **6**, THF/Et<sub>2</sub>O, -78 °C then SM
29. TPAP, NMO, 4Å MS, DCM
30. Pd(PPh<sub>3</sub>)<sub>4</sub>, Bu<sub>3</sub>SnH, THF
31. TBAF, THF, 55 °C
32. PCC, NaOAc, 4Å MS, DCM
33. 2-methyl-2-butene, NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, *t*-BuOH, THF, H<sub>2</sub>O
34. AcOH, H<sub>2</sub>O, 100 °C



What is the general name of the ligand in complex **3**, how are these ligands made?

*Hint: Step 25 mono deprotection happens*

Step 29: Name of the reaction?  
*Hint: Three reactions take place*

*Hint: Two transformations occur in step 32*

Step 33: Name of the reaction?  
Why is 2-methyl-2-butene added?