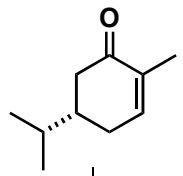
Total Synthesis of (–)-Dendrobine

C.-K. Sha, R.-T. Chiu, C.-F. Yang, N.-T. Yao, W.-H. Tseng, F.-L. Liao, S.-L. Wang.
J. Am. Chem. Soc. **1997**, *119*, 4130–4135.



1–4

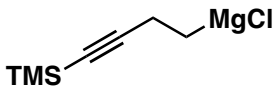
A

5–9

B

1) MeMgCl, $FeCl_3$, TMSCl, NEt_3
2) $CH(OMe)_3$, $BF_3 \cdot OEt_2$
3) LDA, TMSCl
4) *m*-CPBA, $NaHCO_3$

5) PTSA
6) **1**, CuI, *then* TMSCl, NEt_3
7) NaI, *m*-CPBA
8) Bu_3SnH, AIBN
9) TFA



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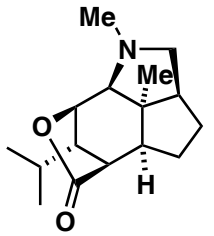
Hint step 1: No 1,2- or 1,4-addition occurs.

Step 3 and 4: Please name the reaction.
What are alternatives for this transformation?



(–)-dendrobine

10–12

10) *m*-CPBA, $BF_3 \cdot OEt_2$
11) DBU
12) $BH_3 \cdot DMS$, *then* H_2O_2, NaOH

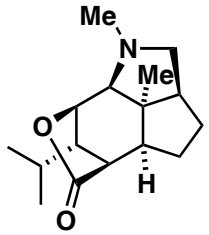
Step 11: Please name the reaction.
Step 12: Please provide a mechanism.

C

13–18

13) MsCl, NEt_3
14) NaN_3, 18-crown-6
15) CrO_3, H_2SO_4, acetone, H_2O
16) PPh_3
17) $NaBH_3CN$, HOAc
18) $(HCHO)_n$, H_2O, HCOOH

Step 15: Please name the reaction.
Step 16: Please name the reaction.



(–)-dendrobine