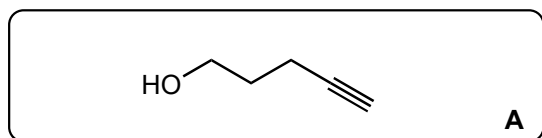


# Total Synthesis of (+)-Chinensiolide B

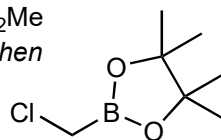
T. G. Elford, D. G. Hall *J. Am. Chem. Soc.*, **2010**, *132*, 1488–1489.



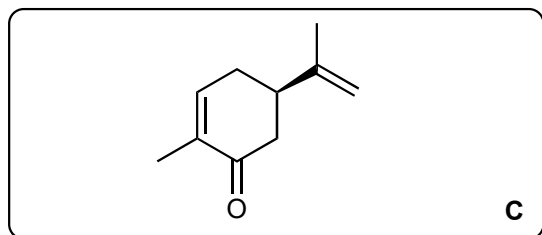
1-3



- 1) TBDPSCI
- 2) *n*-BuLi, then ClCO<sub>2</sub>Me
- 3) DIBAL-H, HMPA, then



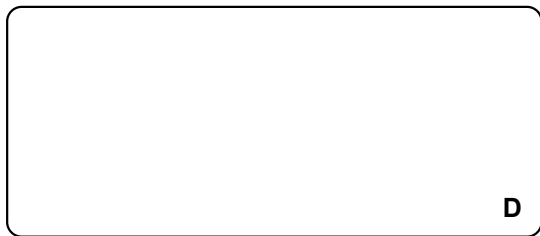
**B** is obtained as a 3.5:1 mixture of *Z/E* isomers.



4-9

- 4) H<sub>2</sub>O<sub>2</sub>, NaOH
- 5) LiCl, TFA
- 6) TBSOTf
- 7) NaOMe
- 8) LiAlH<sub>4</sub>
- 9) (COCl)<sub>2</sub>, DMSO, Et<sub>3</sub>N

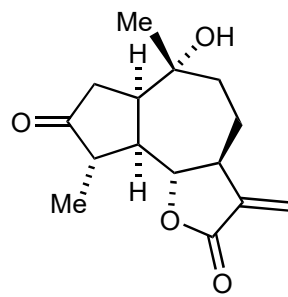
Please draw a transition state of **step 7**, that explains the regio- and stereoselectivity of this name reaction.



10–13



14–18



Only the **Z** isomer of **B** reacts. >19:1 dr

- 10) **B**, **D**,  $\text{BF}_3\text{OEt}_2$  (2.5 mol%)
- 11) TBAF
- 12)  $o\text{-NO}_2\text{-C}_6\text{H}_4\text{SeCN}$ ,  $\text{PBU}_3$
- 13)  $\text{H}_2\text{O}_2$

- 14) Grubbs II
- 15) *m*-CPBA
- 16) DIBAL-H, then  $\text{LiEt}_3\text{BH}$
- 17)  $\text{MnO}_2$
- 18) PDC

Please explain the origin of stereocontrol in **step 10** for the two newly created chiral centres.