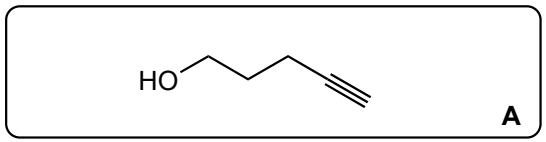
Total Synthesis of (+)-Chinensiolide B

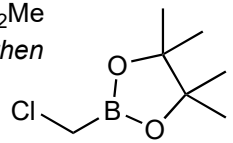
T. G. Elford, D. G. Hall *J. Am. Chem. Soc.*, **2010**, *132*, 1488–1489.

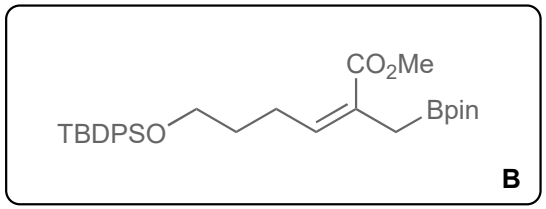


A

1-3

1) TBDPSCl
2) *n*-BuLi, *then* $ClCO_2Me$
3) DIBAL-H, HMPA, *then*

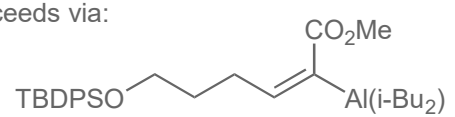


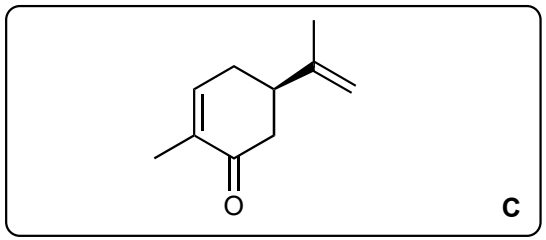


B

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

Step 3: Conjugate reduction followed by *in situ* borylation.
Reaction proceeds via:



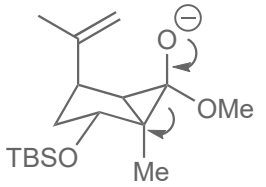


C

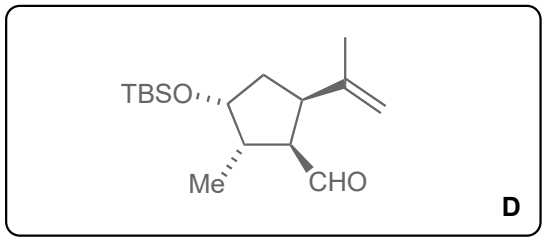
4-9

4) H_2O_2, NaOH
5) LiCl, TFA
6) TBSOTf
7) NaOMe
8) $LiAlH_4$
9) $(COCl)_2$, DMSO, Et_3N

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



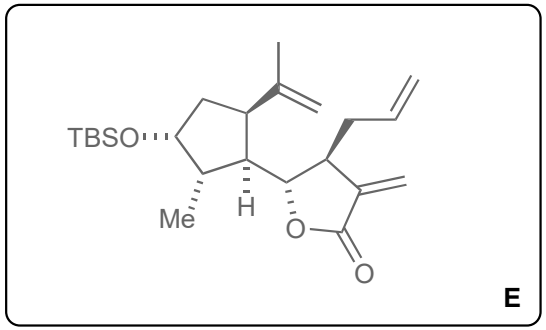
Favorskii rearrangement



10-13

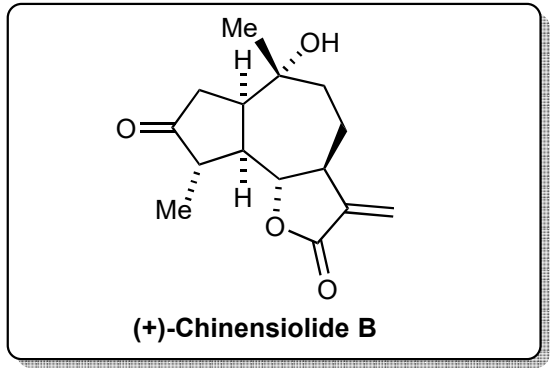
Only the *Z* isomer of **B** reacts. >19:1 dr

10) **B**, **D**, BF_3OEt_2 (2.5 mol%)
11) TBAF
12) *o*-NO_2-C_6H_4SeCN, PBu_3
13) H_2O_2



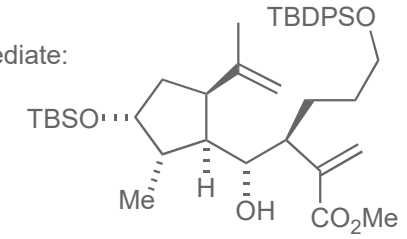
14-18

14) Grubbs II
15) *m*-CPBA
16) DIBAL-H, *then* $LiEt_3BH$
17) MnO_2
18) PDC



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

intermediate:



Tandem diastereoselective allylboration / lactonisation reaction sequence.
Trans-selectivity of addition can be explained by 6-membered chair-like transition state whereas absolute stereochemistry arises from Felkin-Anh attack on the chiral aldehyde: