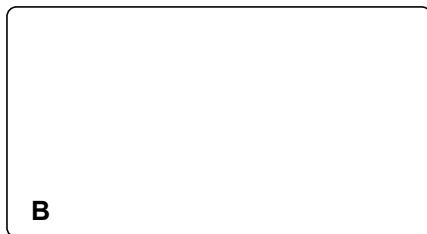
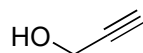


# Asymmetric Total Synthesis of Solandelactone E: Stereocontrolled Synthesis of the 1,4-diol-2-ene core via Lithiation-Borylation-Allylation Sequence

A. Robinson and V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2010**, 49, 6673–6675

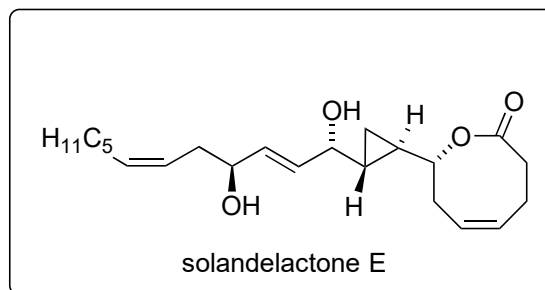


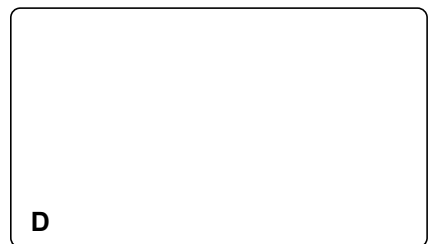
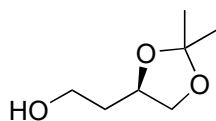
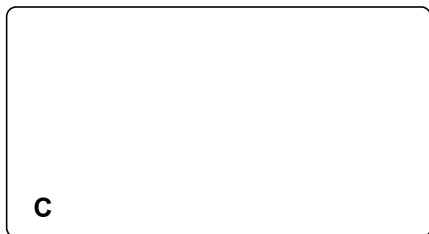
- 1) Allylbromide, In
- 2) (-)-DET, Ti(*i*OPr)<sub>4</sub>, *t*BuOOH
- 3) PhSO<sub>2</sub>Cl, Et<sub>3</sub>N, DMAP

- 4) NaHMDS, CH<sub>3</sub>CN
- 5) DHP, PPTS
- 6) K<sub>2</sub>OsO<sub>4</sub>•2H<sub>2</sub>O (cat.), NaIO<sub>4</sub>, 2,6-lutidine
- 7) HO<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>PPh<sub>3</sub>Br, NaHMDS
- 8) HCl (aq.)

How would you rationalize the outcome of step 1) ?

provide a Mechanism for step 4)

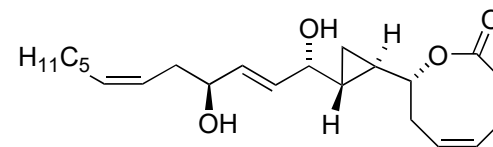




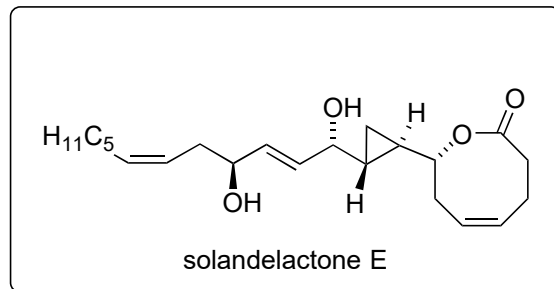
- 9) 1,3,5-trichlorobenzoyl chloride, Et<sub>3</sub>N,  
*then* DMAP, toluene 90 °C  
10) Raney-Ni, NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O

- 11) *N,N*-diisopropyl carbamoyl chloride, NaH  
12) *s*-BuLi, *then* Bu<sub>3</sub>SnCl  
13) HCl  
14) NaHCO<sub>3</sub>, NaIO<sub>4</sub>  
15) C<sub>6</sub>H<sub>13</sub>PPh<sub>3</sub>Br, NaHMDS

provide a name and mechanism for step 9)  
what alternatives to step 9) come to mind?



solandelactone E



- 16) *n*-BuLi, TMEDA, then **1**, then aldehyde **C**  
H<sub>2</sub>O<sub>2</sub>, NaOH  
17) *t*-BuOOH, Ti(*i*OPr)<sub>4</sub>  
18) AcOH, MeOH

provide a Mechanism for step 16)

