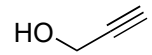
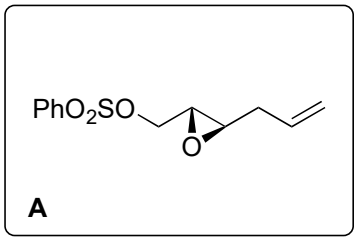
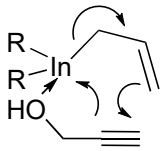
**Asymmetric Total Synthesis of Solandelactone E: Stereocontrolled Synthesis of the 1,4-diol-2-ene core via Lithiation-Borylation-Allylation Sequence**

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

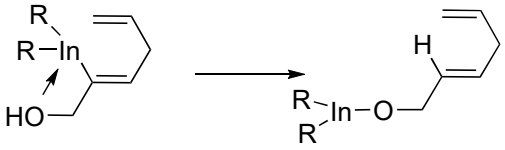





1) Allylbromide, In
2) (–)-DET, Ti(*i*OPr)$_4$, *t*-BuOOH
3) $PhSO_2Cl$, $Et_3N$, DMAP




How would you rationalize the outcome of step 1) ?

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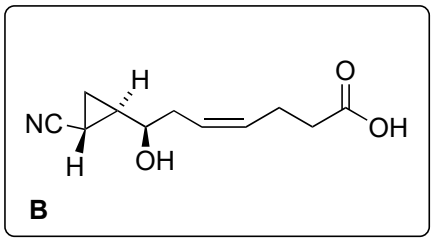
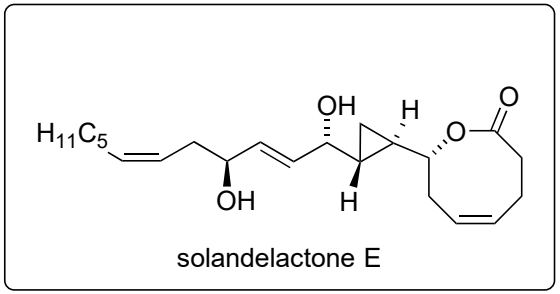
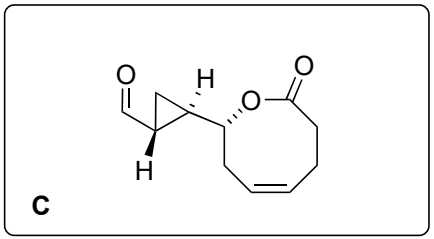
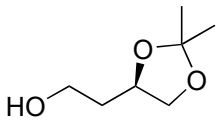
4) NaHMDS, $CH_3CN$
5) DHP, PPTS
6) $K_2OsO_4$•$2H_2O$ (cat.), $NaIO_4$, 2,6-lutidine
7) $HO_2C(CH_2)_3PPh_3Br$, NaHMDS
8) HCl (aq.)

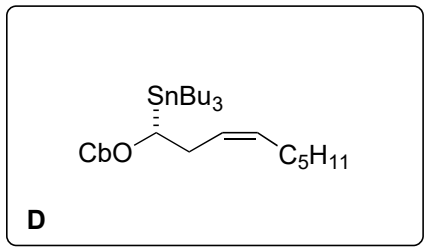
provide a Mechanism for step 4)



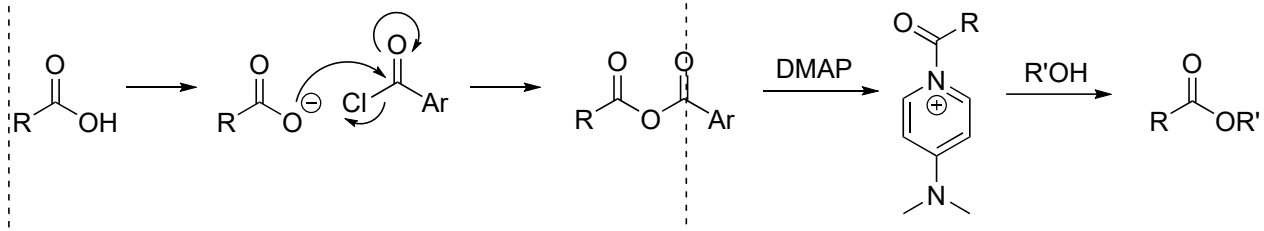





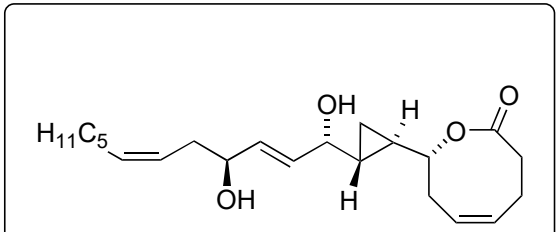

9) 1,3,5-trichlorobenzoyl chloride, $Et_3N$,
*then* DMAP, toluene 90 °C
10) Raney-Ni, $NaH_2PO_2 \bullet H_2O$




11) *N*,*N*-diisopropyl carbamoyl chloride, NaH
12) *s*-BuLi, *then* $Bu_3SnCl$
13) HCl
14) $NaHCO_3$, $NaIO_4$
15) $C_6H_{13}PPh_3Br$, NaHMDS

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

Yamaguchi lactonization

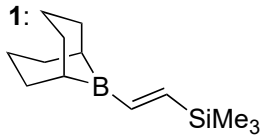


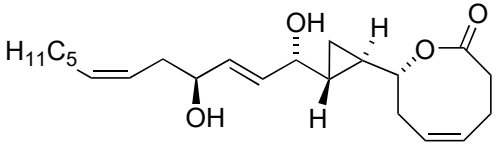

solandelactone E

16) *n*-BuLi, TMEDA, *then* **1**, *then* aldehyde **C**
$H_2O_2$, NaOH
17) *t*-BuOOH, Ti(*i*OPr)$_4$
18) AcOH, MeOH

provide a Mechanism for step 16)

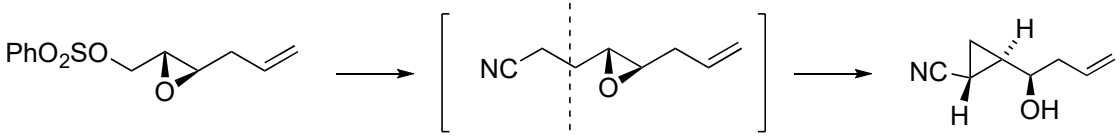
**1**:




solandelactone E

mechanism step 4):
J. Org. Chem. **2001**, *66*, 3423-3426




mechanism step 16):