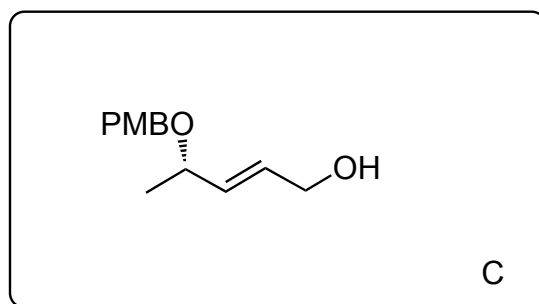
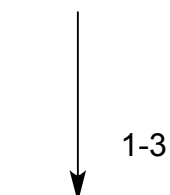
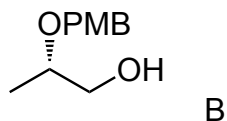
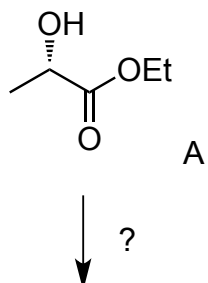


Synthesis Challenge #6 AG Wegner

The First Stereoselective Total Synthesis of (–)-Synrotolide G. Sabitha, A. Senkara Rao, A. Sandeep, J. S. Yadav, *Eur. J. Org. Chem.*, **2013**, ASAP, DOI: 10.1002/ejoc.201301215
14.11.2013

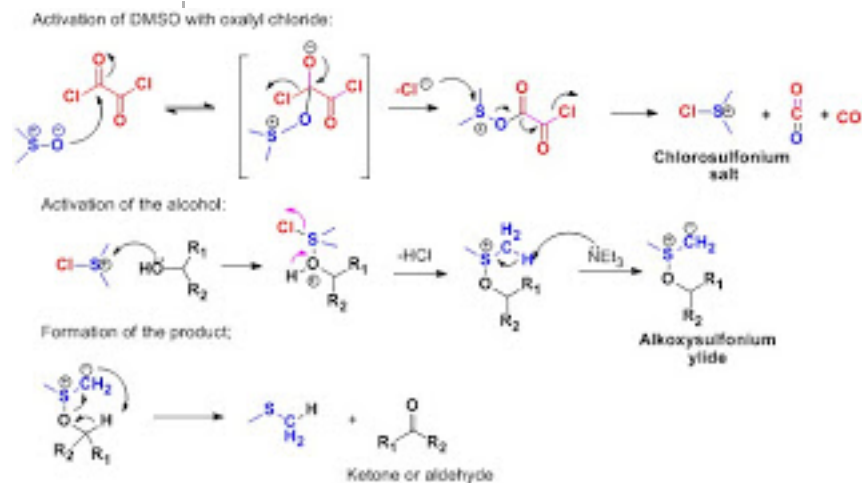


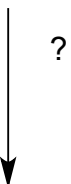
a) PMBOC(CCl₃)=NH, Sc(OTf)₃, toluene;
b) LiAlH₄, THF;

1) (COCl)₂, DMSO, Et₃N, CH₂Cl₂, –78°C
2) Ph₃P=CHCO₂Et
3) DIBAL-H, CH₂Cl₂

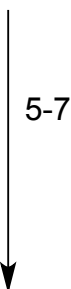
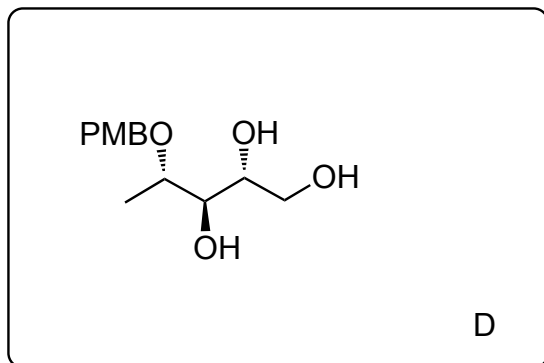
Please, provide reagents for the transformation from A to B.

Please give a detailed mechanism of step 1)?

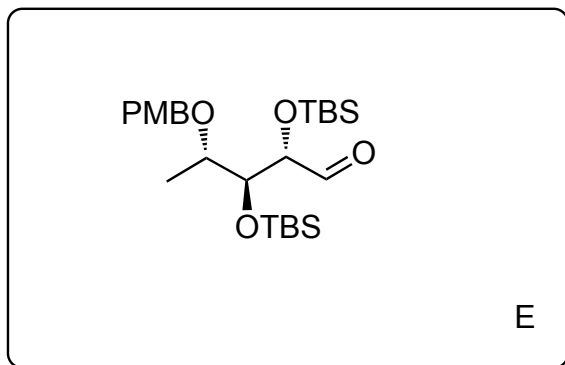




a) $\text{Ti}(\text{O}i\text{Pr})_4$, (+)-DIPT, TBHP,
 CH_2Cl_2
b) 0.5 N NaOH



5) TBS-Cl, imidazole, DMF
6) PTSA, MeOH
7) (COCl_2) , DMSO, Et_3N , CH_2Cl_2



Please, provide reagents for the transformation from C to D.

What is the oxidant in step 7)? Do you know oxidations using the same one?

Oxidant = DMSO

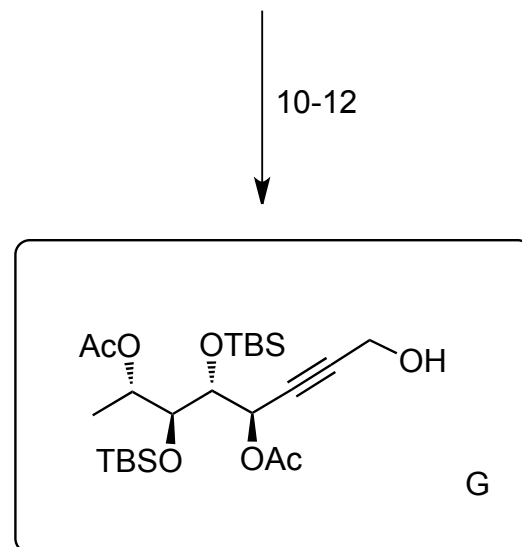
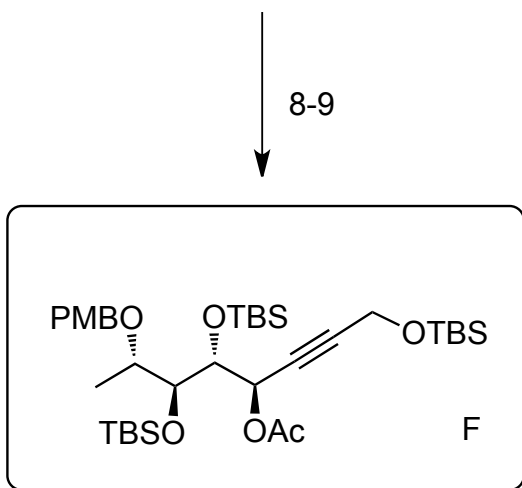
Parikh-Doering: pyridine- SO_3 /DMSO/ Et_3N

Pfitzner-Moffatt: $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ /DMSO/acid (cat.)

Albright-Goldman: Ac_2O , DMSO

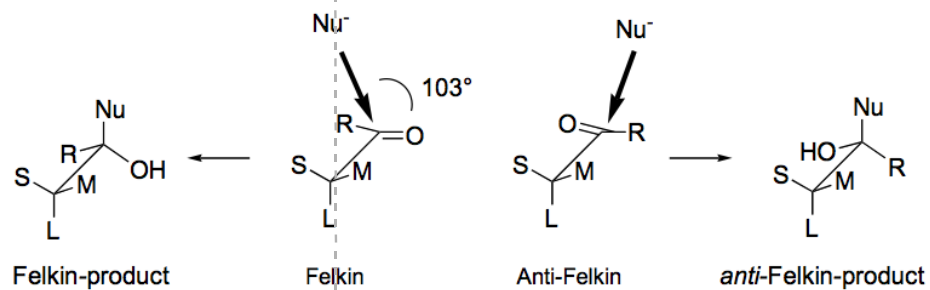
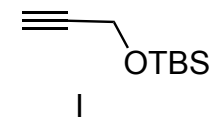
Similar:

Corey-Kim: N-succinimide, Me_2S



8) **I**, *n*BuLi, THF, -78°C
 9) Ac₂O, Et₃N, DMAP, CH₂Cl₂

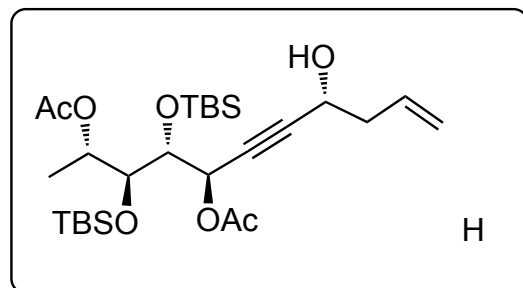
Please, rationalize the stereochemical outcome in step 8).



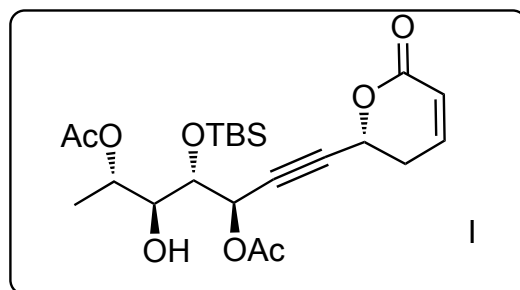
Chem. Rev. 1999, 99, 1199

10) DDQ
 11) Ac₂O, Et₃N, DMAP, CH₂Cl₂
 12) PTSA, MeOH

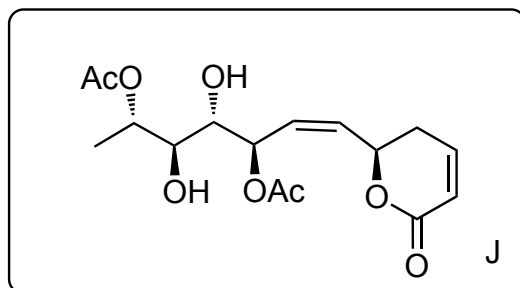
13-14



15-16

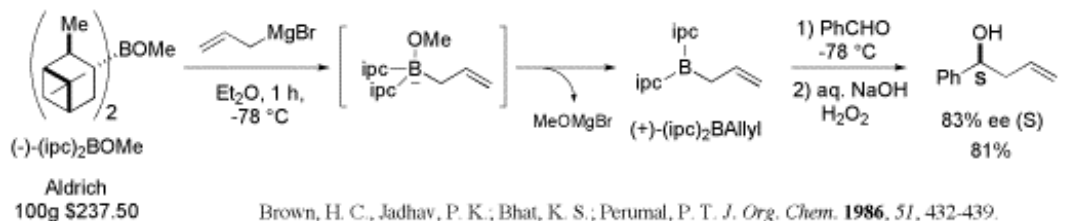


17-18



- 13) IBX, DMSO, CH₂Cl₂, 0°C
 14) (+)IPC₂Ballyl, Et₂O

Brown Asymmetric Allylation



What is (+)IPC₂Ballyl? How does it react?

- 15) acryloyl chloride, Et₃N, DMAP (cat.), CH₂Cl₂
 16) Grubbs-II, CH₂Cl₂, reflux

- 17) Pd/BaSO₄, H₂, quinoline
 18) H₂SiF₆ (20-25% in H₂O), CH₃CN