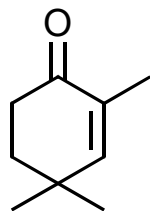


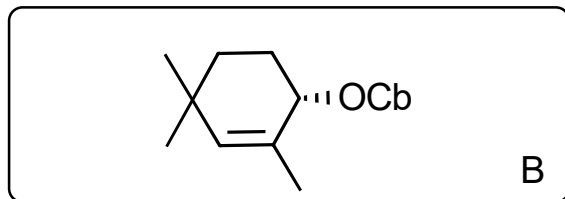
# Synthesis Challenge # 60

Convergent Route to *ent*-Kaurane Diterpenoids: Total Synthesis of Lungshengenin D and 1 $\alpha$ ,6 $\alpha$ -Diacetoxy-*ent*-kaura-9(11),16-dien-12,15-dione, X. Zhao, W. Li, J. Wang, D. Ma, *JACS*, 2017, ASAP, DOI: 10.1021/jacs.7b00140

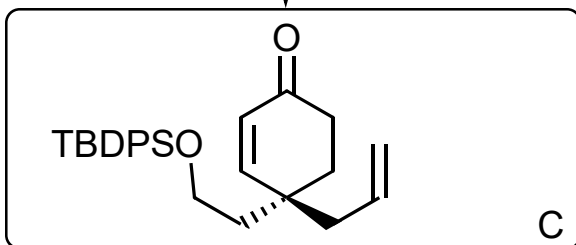
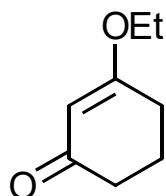
23.02.2017



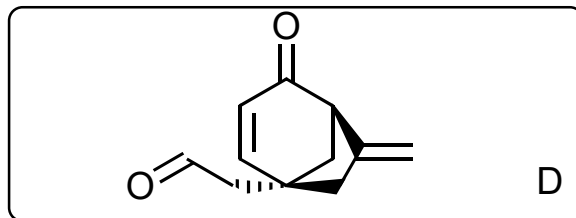
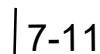
A



B



C



D

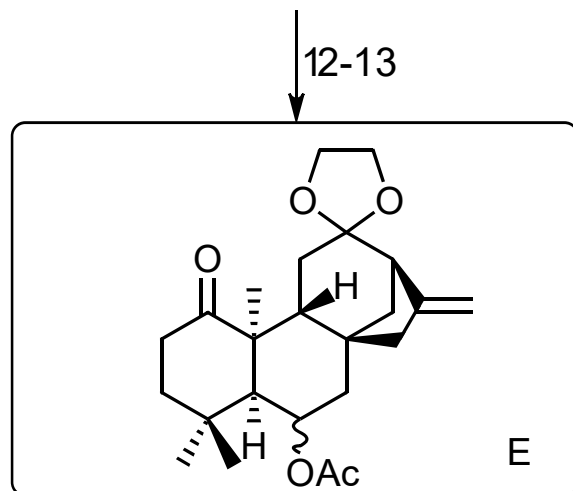
1) (*R*)-2-methyl-CBS-oxaazaborolidine  
Boran-THF complex, Toluene -40°C  
2) NaH, THF, ClCON(*i*Pr)<sub>2</sub>

3) LDA, THF, -78°C, then allyl  
chloroformate  
4) ICH<sub>2</sub>CH<sub>2</sub>OTBDPS, Cs<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN  
5) Pd<sub>2</sub>(dba)<sub>3</sub> (5mol%), (*S*)-*t*Bu-Phox  
(12.5mol%), THF, 40°C  
6) DIBAL-H, toluene, then HCl (5%),  
MeOH

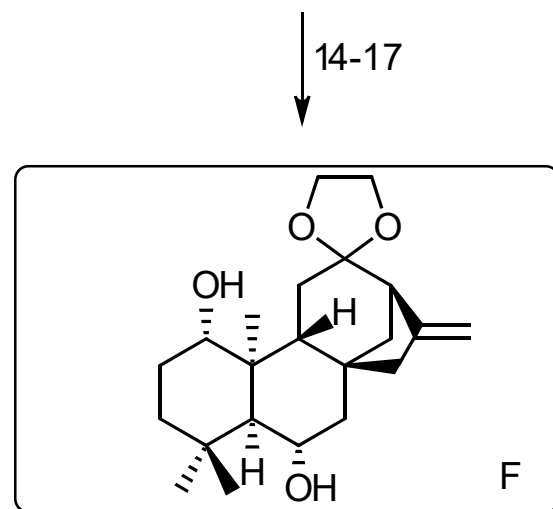
7) TBSOTf, Et<sub>3</sub>N  
8) Pd(OAc)<sub>2</sub>, O<sub>2</sub>, DMSO  
9) (CH<sub>2</sub>OH)<sub>2</sub>, PPTs, benzene, reflux  
10) TBAF, THF  
11) TPAP, NMO

12) **D** + **B**, *s*-BuLi, *rac* TMCDA,  $-78^{\circ}\text{C}$   
then,  $\text{Ac}_2\text{O}$ , DMAP  
13)  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $-20^{\circ}\text{C}$ ,  
then, aq.  $\text{NaHCO}_3$

TMCDA = *trans*-*N,N,N',N'*-tetramethyl  
1,2-diamino-cyclohexane



14)  $\text{K}_2\text{CO}_3$ , MeOH  
15) IBX, DMSO  
16) DBU, THF  
17) L-selectride, then, DIBAL-H  
in toluene,  $-78^{\circ}\text{C}$



18) NaH, AcCl, DMAP  
19) 2N HCl  
20) TMSOTf,  $-20^{\circ}\text{C}$   
21)  $\text{Pd}(\text{OAc})_2$ , MeCN  
22)  $\text{SeO}_2$ , *t*BuOOH  
23) IBX, DMSO

