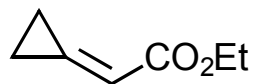


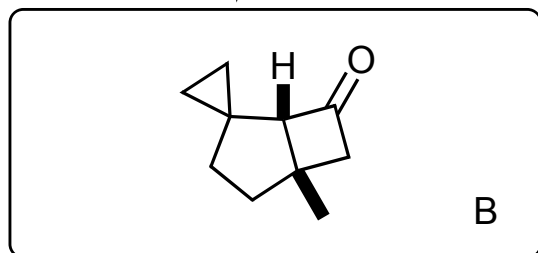
## Synthesis Challenge # 50

Total Syntheses of the Tetracyclic Cyclopropane Diterpenes Conidiogenone, Conidiogenol, and Conidiogenone B,  
 S.-H. Hou, Y.-Q. Tu, S.-H. Wang, C.-C. Xi, F.-M. Zhang, S.-H. Wang, Y.-T. Li, L. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*,  
 DOI: 10.1002/anie.201600529  
 16.06.2016

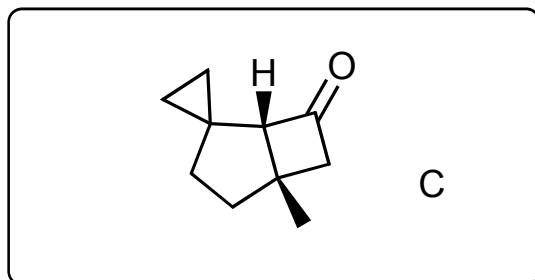


A

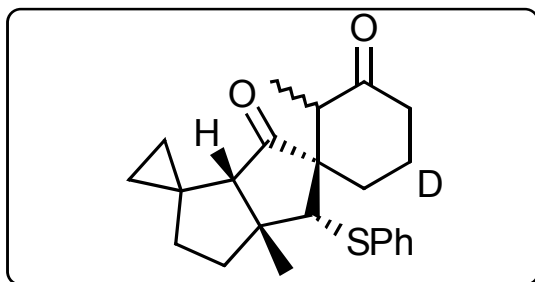
↓ 1-2



↓ 3-6



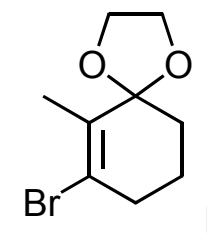
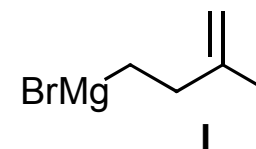
↓ 7-10



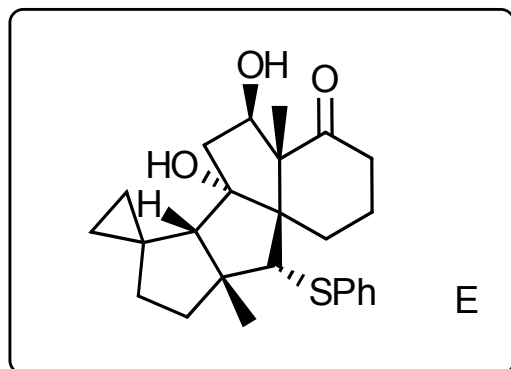
1) CuCl, TMSCl, **I**, THF, -15 °C, then  
 LiOH, THF/H<sub>2</sub>O, 25 °C  
 2) (COCl)<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, reflux, then NEt<sub>3</sub>,  
 toluene, reflux

3) L- selectride, THF, -78 °C, then  
 NaBO<sub>3</sub>·4 H<sub>2</sub>O, 0 °C  
 4) (1*S*,4*R*)- camphanoyl chloride,  
 DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C  
 5) K<sub>2</sub>CO<sub>3</sub>, MeOH, 25 °C  
 6) IBX, EtOAc, reflux

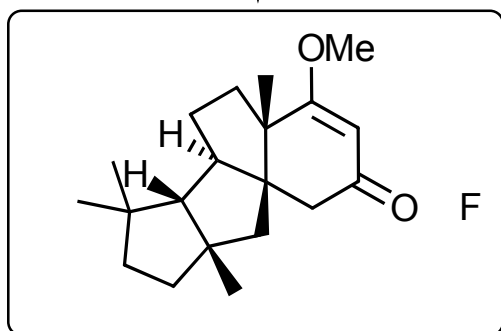
7) LDA, PhSSPh, DMPU, THF  
 8) tBuLi, **II**, THF, -78 °C, then  
 1 M HCl/H<sub>2</sub>O, 0 °C  
 9) TMSOTf, *i*Pr<sub>2</sub>NEt, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C  
 10) BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>



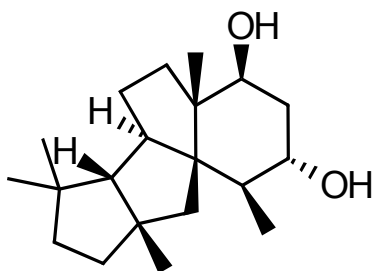
11-13



14-20



17-18



11) ethylene glycol, PTS, benzene, reflux  
12) allylmagnesium bromide, THF,  
13)  $O_3$ ,  $CH_2Cl_2$ ,  $-78\text{ }^\circ\text{C}$ , then  $PPh_3$ ,  $0\text{ }^\circ\text{C}$ , then  $2\text{ M HCl/H}_2\text{O}$ , THF,  $70\text{ }^\circ\text{C}$

14)  $MsCl$ ,  $NEt_3$ ,  $CH_2Cl_2$ ,  $0\text{ }^\circ\text{C}$   
15)  $LiBr$ ,  $Li_2CO_3$ ,  $DMF$ ,  $150\text{ }^\circ\text{C}$   
16) Raney Ni, EtOH,  $0\text{ }^\circ\text{C}$   
17) py,  $SOCl_2$ ,  $CH_2Cl_2$ ,  $0\text{ }^\circ\text{C}$   
18)  $PtO_2$ ,  $H_2$  (1 atm), HOAc, EtOAc,  $25\text{ }^\circ\text{C}$ , then DMP,  $NaHCO_3$ ,  $CH_2Cl_2$   
19)  $CH(OMe)_3$ , PTS, MeOH, reflux  
20)  $Pd(OH)_2/C$ ,  $tBuO_2H$ ,  $Cs_2CO_3$ ,

21) LDA, MeI, HMPA, THF,  $-78\text{ }^\circ\text{C}$  -  $25\text{ }^\circ\text{C}$   
22)  $LiAlH_4$ , THF,  $0\text{ }^\circ\text{C}$ , then  $1\text{ M HCl/H}_2\text{O}$ ,  $0\text{ }^\circ\text{C}$   
23) Triton B,  $tBuO_2H$ , THF,  $25\text{ }^\circ\text{C}$   
24)  $PhSe-SePh$ ,  $NaBH_4$ , HOAc, EtOH,  $0\text{ }^\circ\text{C}$   
25) L-selectride, THF,  $-78\text{ }^\circ\text{C}$

E was obtained as a mixture of diastereomers. Suggest methods for separation.