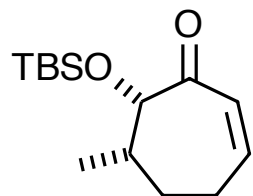


## Synthesis Challenge # 32

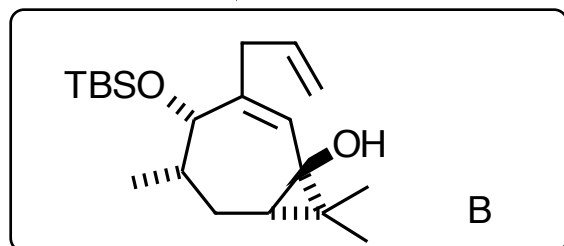
"Total Synthesis of Diterpenoid Steenkrotin A"

S. Pan, J. Xuan, B. Gao, A. Zhu, H. Ding, *Angew. Chem. Int. Ed.* **2015**, ASAP, DOI: 10.1002/anie.201502034  
23.04.2015



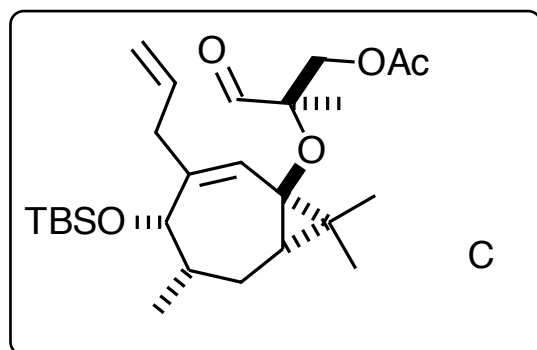
A

1-3



B

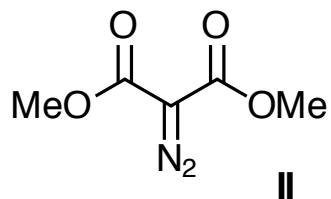
4-8



C

- 1) allyl bromide, Li, THF, 0-25°C, 2 h
- 2) PCC (2.0 equiv), SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>
- 3) TMSOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, then **I**, *n*BuLi, Et<sub>2</sub>O

- 4) [Rh<sub>2</sub>(OAc)<sub>4</sub>] (cat.), **II**, benzene
- 5) NaH, MeI, THF
- 6) LiAlH<sub>4</sub>, THF
- 7) Ac<sub>2</sub>O, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub> (10:1 d.r. at C6)
- 8) Dess–Martin periodinane, NaHCO<sub>3</sub>

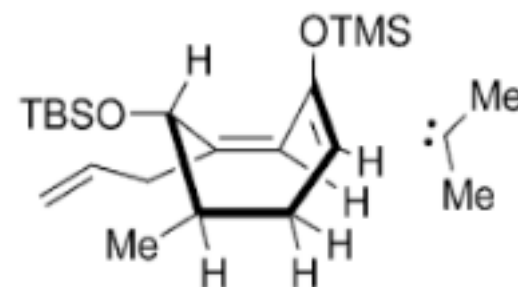


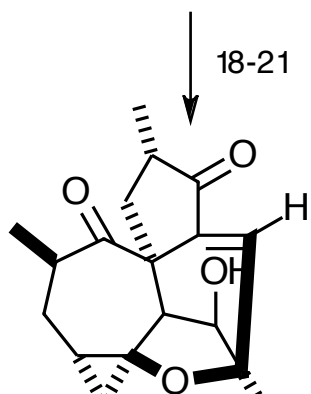
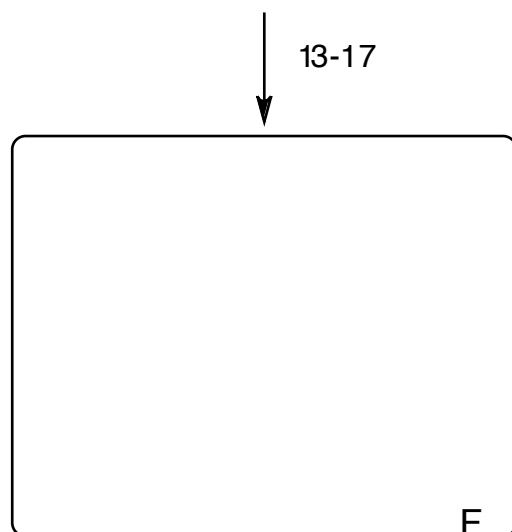
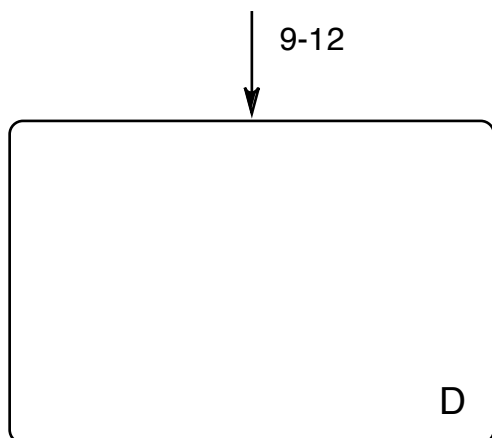
Please design a synthesis of **A** starting from a commercially available starting material.

large scale by Rubottom oxidation of the silyl dienol ether derived from commercially available 6-methyl-2-cyclohepten-1-one

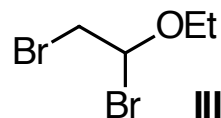


Please, provide a detailed mechanism for step 3.





- 9) HF·py (10 equiv), MeCN  
 10) **III**, PhNMe<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, (1.5:1 d.r. at C3)  
 12) Sml<sub>2</sub>, HMPA, *t*BuOH  
 13) Bz<sub>2</sub>O, Et<sub>3</sub>N, 4-DMAP, CH<sub>2</sub>Cl<sub>2</sub>



- 13) *p*-TsOH, acetone/H<sub>2</sub>O (4 :1),  
 14) Sml<sub>2</sub>, HMPA, THF  
 15) Dess–Martin periodinane, NaHCO<sub>3</sub>  
 16) KOH, benzene, then the addition  
 of MeOH, (dr = 6.3 :1)  
 17) DBU, toluene

- 18) TPAP (cat.), NMO, CH<sub>2</sub>Cl<sub>2</sub>  
 19) NaBH<sub>4</sub>, MeOH  
 20) PCC, CH<sub>2</sub>Cl<sub>2</sub>  
 21) LiOH, toluene

In step 9 is more happening, than "just" a deprotection. Please provide a mechanism. Please, provide a detailed mechanism for step 11). What is the name of the reaction in step 12)?

Please, provide a detailed mechanism for step 16).

Please provide a nice 3D drawing of G.