

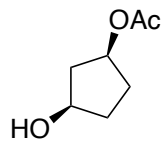
Synthesis Challenge 105

AG Wegner

Structure-Unit-Based Total Synthesis of (-)-Sinulochmodin C

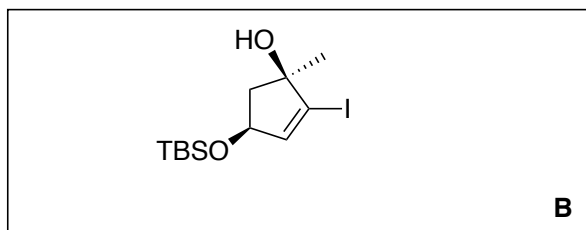
Y.-P. Zhang, S. Du, Y. Ma, W. Zhan, W. Chen, X. Yang,
H. Zhang, *Angew. Chem. Int. Ed.* **2023**, e202315481.

14.12.2023

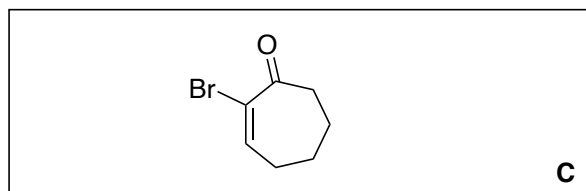


↓ ???

A

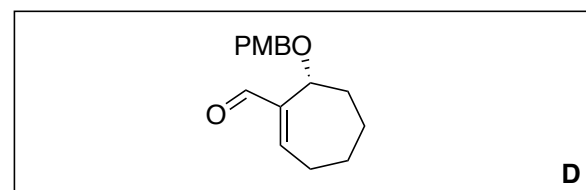


B



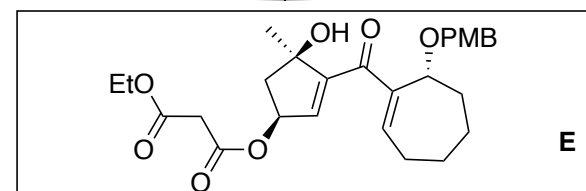
C

↓ 1-3



D

↓ 4-7



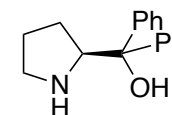
E

Please draft a synthesis of **B**

- 1) TBSCl, Et₃N
- 2) NaCO₃, EtOH
- 3) Swern or Dess-Martin Periodinane,...
- 4) Et₃N, TBSOTf, DCM, rt, then Pd(OAc)₂, DMSO, O₂
- 5) I₂, pyridine, DCM
- 6) MeMgBr, THF, rt

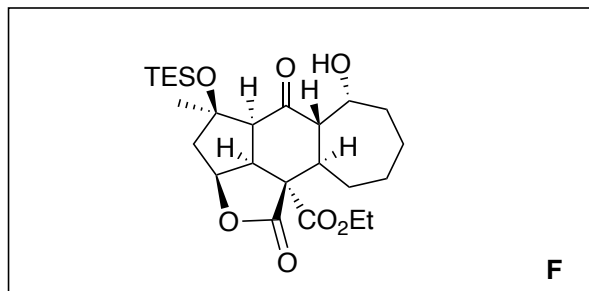
- 1) Cat **I**, B(OMe)₃ (20 mol%), BH₃*PhNEt₂, THF, rt
- 2) NaH, PMBCl, TBAI, DMF
- 3) *n*BuLi, THF, then DMF, THF -78°C

- 4) **B**, CH₃Li, *n*BuLi, THF, -78°C, then addition of **D**
- 5) IBX, DMSO
- 6) Et₃N * 3HF, THF
- 7) ClCOCH₂CO₂Et, pyridine, DCM

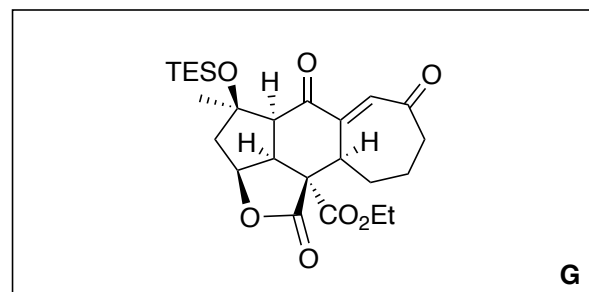


I

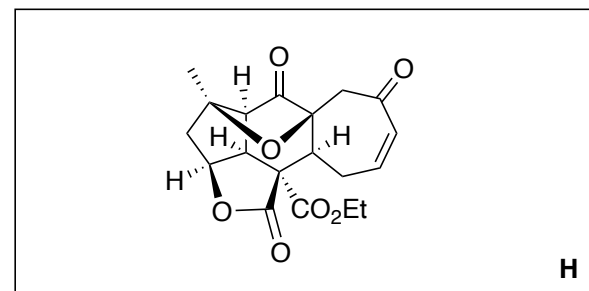
8-10



11-14



15-16



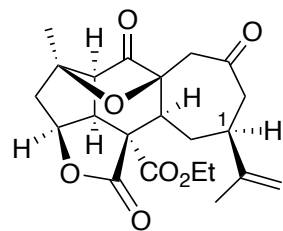
- 8) MTBD, MeCN
9) TESOTf, Et₃N, DCM
10) DDQ, DCM/H₂O

- 11) MsCl, pyridine, then MTBD, THF
12) TESOTf, Et₃N, DCM
13) NBS, acetone, then Ag₂O, acetone/H₂O
14) IBX, MeCN, reflux

- 15) InBr₃ (10mol%), Si(OEt)₄, NaHSO₄, DCM/TFE
16) Et₃N, TBSOTf, DCM, rt, then Pd(OAc)₂, DMSO, O₂

MTBD = 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene

↓ 17-18



17) *iso*-propenyl-MgBr, 2-Th(CN)CuLi, THF
18) Me₃SnOH, SCM, 80°C

2-Th(CN)CuLi = lithium 2-thienylcyanocuprate

Please, provide a beautiful 3D drawing of the final product!