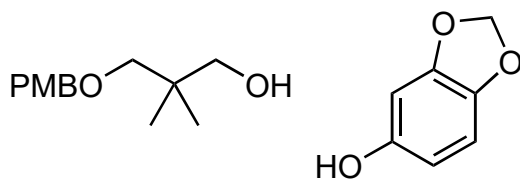


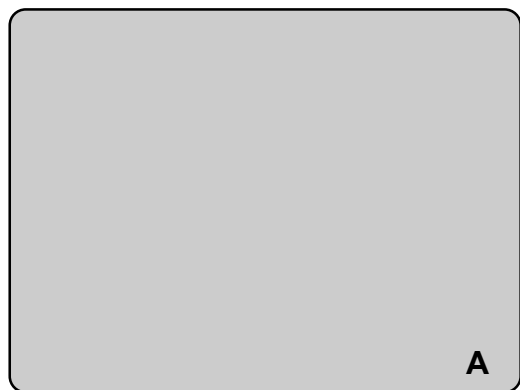
Enantioselective Synthesis of (-)-Maoecrystal V by Enantiodetermining C-H Functionalization

Lu, P.; Mailyan, A.; Gu, Z.; Guptill, D.M.; Wang, H.; Davies, H.M.L.; Zakarian, A.

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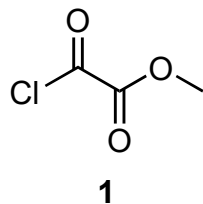
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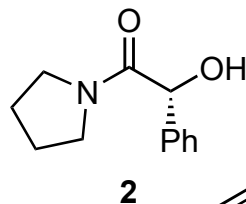
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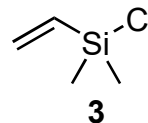
- 1) PPh_3 , DIAD
- 2) *n*-BuLi, THF; then CuI; then **1**
hint: ortho-ortho
- 3) NaOH, MeOH
- 4) BzCl, NEt_3 , PhMe;
then DMAP, **2**
- 5) TsNHNH₂, PhH, azeotropic reflux
- 6) NEt_3
- 7) $\text{Rh}_2(\text{OAc})_4$
hint: note the name of the paper;
- 8) MeOH, NaOMe



1



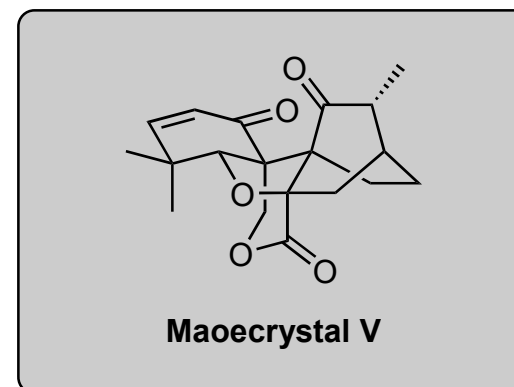
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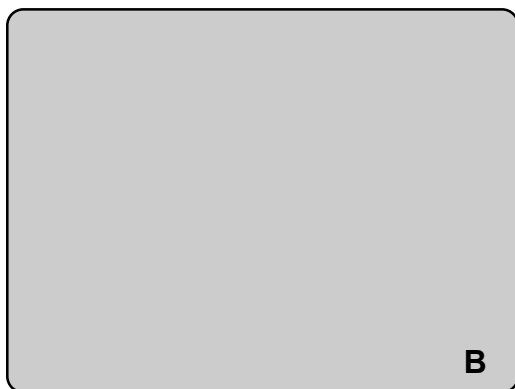
3

- 9) LDA, THF; then Et_2Zn ;
then BnOCH_2Cl , DMPU
- 10) LiAlH_4
hint: alcohol
- 11) MeMgBr (excess), PhH, reflux
- 12) PIFA, NaHCO_3 , EtOH
- 13) **3**, imidazole
- 14) PhMe, 110 °C

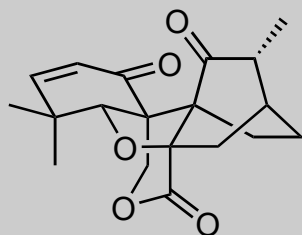
- 1) What is the name of this reaction?
- 4) What is the name of the carboxylic acid that compound **2** is the pyrrolidine amide of?
- 11) Explain the mechanism of this reaction and rationalize the regiochemical outcome of this reaction.



Maoecrystal V



15-28



Maoecrystal V

15) SmI_2 (≥ 4 eq.), THF/MeOH

16) NBu_4F

hint: two bonds are broken

17) CDI

18) $(\text{PhSe})_2$, NaBH_4

19) $(\text{Me}_3\text{Si})_3\text{SiH}$, AIBN

20) DDQ (1 eq.), rt

21) DMP

22) $\text{CH}_3\text{PPh}_3\text{Br}$, *n*-BuLi

23) LiHMDS, CH_3I

24) DDQ (10 eq.), 50 °C

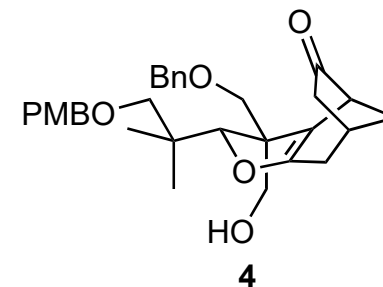
25) DMP

26) vinylmagnesium bromide

27) Hoveyda-Grubbs catalyst II

28) DMP

16) The intended product is formed in 40% yield. The major product, compound **4**, is formed in 45% yield. Propose a mechanism that accounts for this and for the unusual cleavage of a Si-C bond (leading to either products).



19) What type of reaction is this in Baldwin's classification system?

27) Draw the structure of this catalyst.