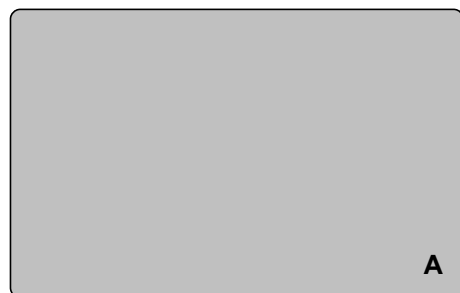
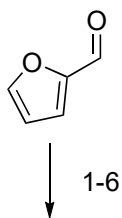
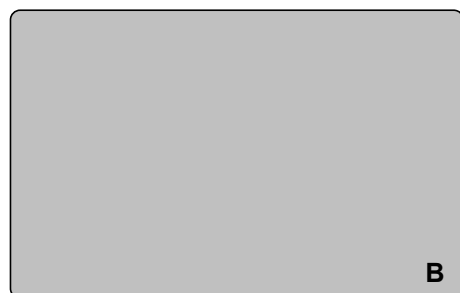


Total Synthesis of (–)-Daphnillonin B

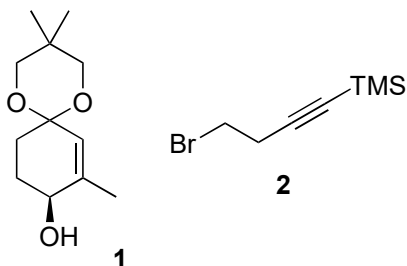
Y.-P. Zou, Z.-L. Lai, M.-W. Zhang, J. Peng, S. Ning, C.-C. Li, *J. Am. Chem. Soc.* **2023**, 145, 10998.



7-15



- 1) TMSCN, K_2CO_3
- 2) $LiAlH_4$
- 3) *o*-NsCl, NEt_3
- 4) TESCl, imH
- 5) **1**, PPh_3 , DIAD *then* TBAF
- 6) NBS, $NaHCO_3$, NaOAc, THF/ H_2O *then* HCl



- 7) Boc_2O , DMAP, NEt_3 , 23 °C
- 8) **2**, Mg, CuCN
- 9) *p*-thiocresol, K_2CO_3
- 10) NEt_3 , $ClCOCCl_3$
- 11) *p*-TsOH, isopropenyl acetate
- 12) Grubbs II, TTMSS, AIBN, 120 °C
- 13) Sml_2 , H_2O , THF
- 14) *p*-TsOH
- 15) NEt_3 , O_2 , $P(OEt)_3$

1) Name of the starting material?

3) Structure of *o*-NsCl?

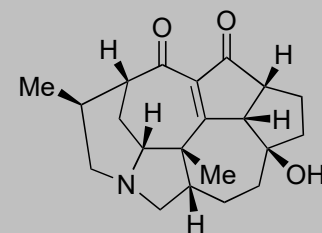
5) Name of the reaction?

What is the stereochemistry of the product?

6) Name of the reaction?

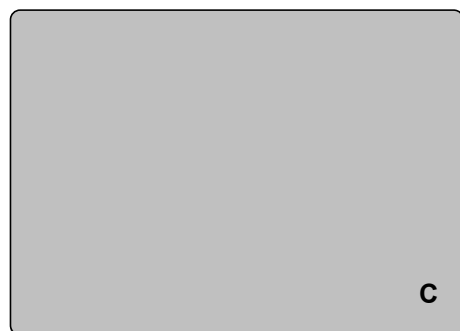
7) Classify the reaction.

7) *Hint*: A very reactive species is formed in this step.
What is its name?

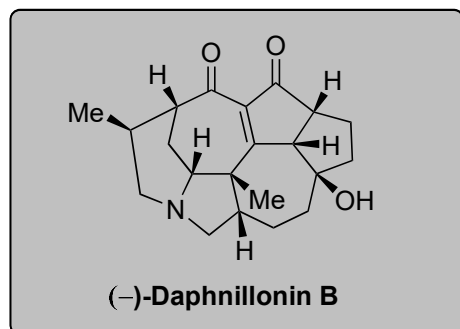


(–)-Daphnillonin B

16-24



25-35



- 16) $\text{CO}_2(\text{CO})_8$
- 17) ICl
- 18) SOCl_2 , pyr
- 19) DIBAL-H (1.3 equiv.)
- 20) NEt_3 , TMSOTf
- 21) $\text{Pd}(\text{PPh}_3)_4$, CO, NEt_3 , MeOH
- 22) LiBH_4
- 23) NaH, CS_2 , MeI
- 24) LHMDs, MeI

- 25) *o*-DCB, 180 °C
- 26) NaH, CS_2 , MeI
- 27) *o*-DCB, 180 °C
- 28) Pd/C, H_2
- 29) *m*-CPBA
- 30) SmI_2 , H_2O , THF
- 31) LiOH
- 32) *m*-CPBA, DCC
- 33) $[\text{Ir}(\text{COE})_2\text{Cl}]_2$, Et_2SiH_2
- 34) K_2CO_3
- 35) DMP

16) Name of reaction?

19) *Hint*: Chemo- and diastereoselective reduction of the ketone in the 7 membered ring

23) Name of generated functional group in this reaction?

25) Name of the reaction? Propose a Mechanism.

27) Name of the reaction?

32) *Hint*: This is NOT an epoxidation
Name of this transformation?