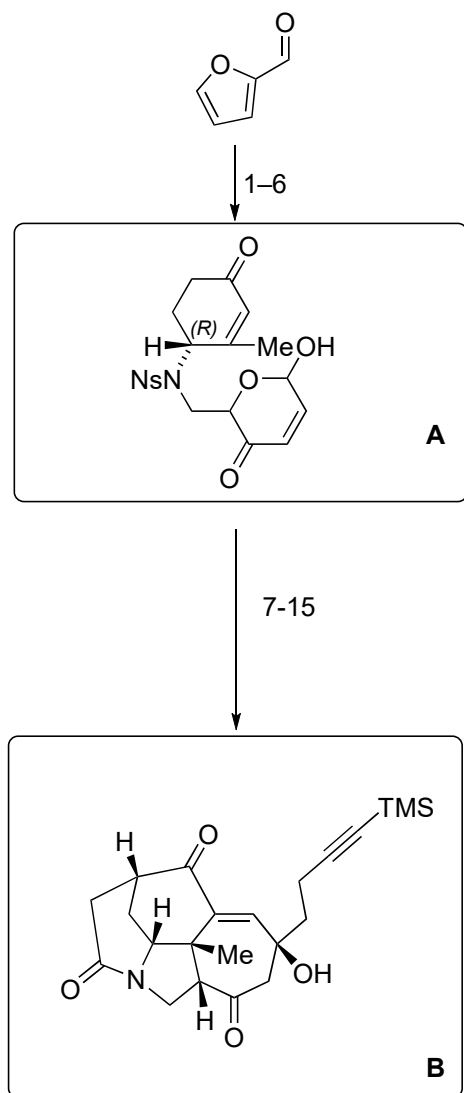
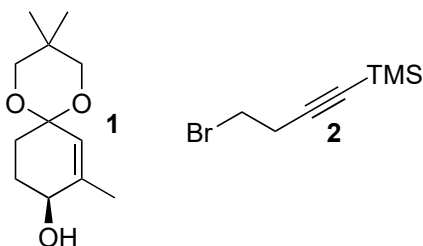


Total Synthesis of (–)-Daphnillonin B

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

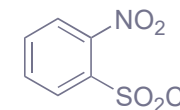


- 1) TMSCN, K_2CO_3
- 2) $LiAlH_4$
- 3) *o*-NsCl, NEt_3
- 4) TESCl, imH
- 5) **1**, PPh_3 , DIAD then TBAF
- 6) NBS, $NaHCO_3$, NaOAc, THF/ H_2O then HCl

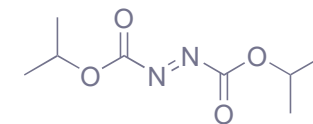


- 7) Boc_2O , DMAP, NEt_3 , 23 °C
- 8) **2**, Mg, CuCN
- 9) *p*-thiocresol, K_2CO_3
- 10) NEt_3 , $ClCOCCl_3$
- 11) *p*-TsOH, isopropenyl acetate
- 12) Grubbs II, TTMSS, AIBN, 120 °C
- 13) SmI_2 , H_2O , THF
- 14) *p*-TsOH
- 15) NEt_3 , O_2 , $P(OEt)_3$

- 1) Name of the starting material? Furfural
- 3) Structure of *o*-NsCl?



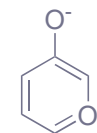
- 5) Name of the reaction? Mitsunobu
- Structure of DIAD?



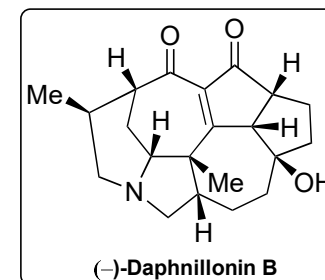
Determine the stereochemistry of the product? (R)
(SN_2 Mechanism)

- 6) Name of the reaction? Achmatowicz
- Rearrangement

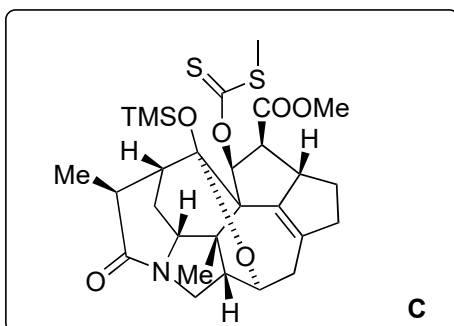
- 7) Hint: A very reactive species is formed in this step.
- What is its name? Oxidopyrylium anion



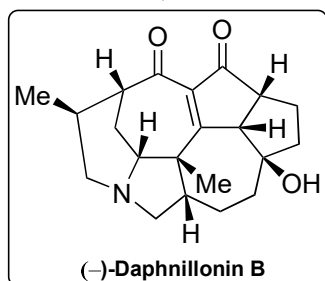
Classify the reaction. [5+2]-CA



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 the reaction? **Pauson-Khand**

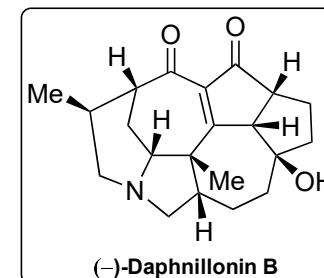
19) *Hint*: Chemo- and diastereoselective reduction of the ketone in the 7 membered ring

23) Name of the generated functional group in this reaction?
Xanthate

25) *Hint*: Draw the product natural product-like.
Name of the reaction?
Propose a Mechanism.

27) Name of the reaction?
Chugaev-Elimination

32) *Hint*: This is NOT an epoxidation
Name of this transformation?
Carboxy-Inversion Reaction



Wagner Meerwein Rearrangement

