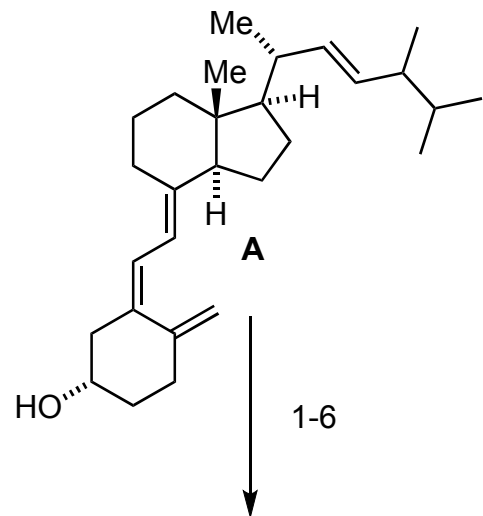


# Asymmetric Total Synthesis of Dankasterones A and B and Periconiastone A Through Radical Cyclization

Chen, P.; Wang, C.; Yang, R.; Xu, H.; Wu, J.; Jiang, H.; Chen, K.; Ma, Z.

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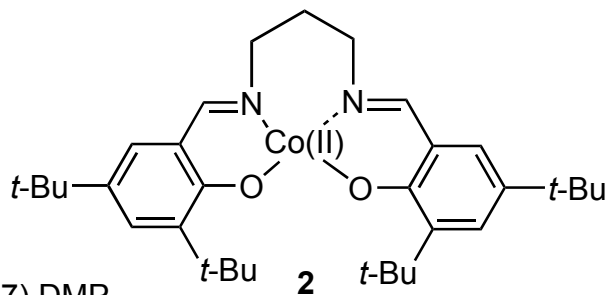
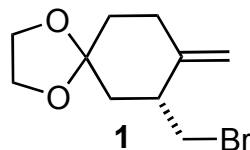


1-6



7-10

- 1) O<sub>3</sub>, MeOH, pyridine, NaBH<sub>4</sub>
- 2) BnBr (1 equiv.), NaH
- 3) DMP
- 4) NaH
- 5) LiHMDS, Comin's reagent
- 6) Pd(PPh<sub>3</sub>)<sub>4</sub>, Bu<sub>3</sub>SnCH<sub>2</sub>OH, LiCl

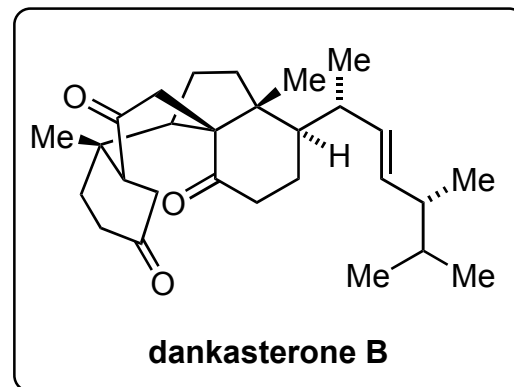


- 7) DMP
- 8) *t*-BuLi, **1**
- 9) DMP
- 10) **2**, PhI(OAc)<sub>2</sub>, TMDSO, CF<sub>3</sub>Ph, rt; then silica gel, DCM, air

name of **A**?

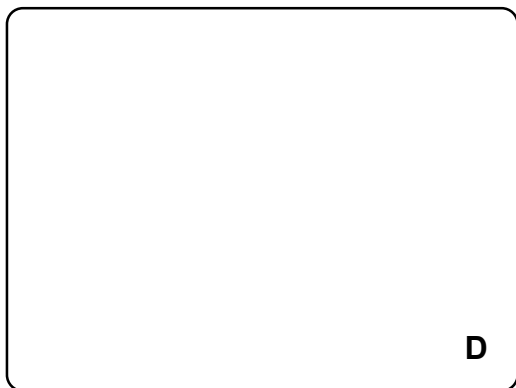
structure of Comin's reagent?

*hint 10*: silica gel/air is used to convert unknown side-products to the product.  
mechanism of 10?



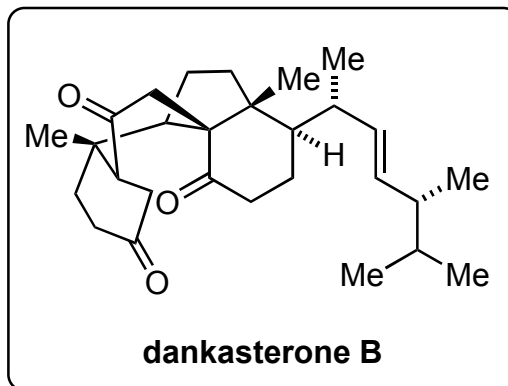


11-17



- 11) Li/NH<sub>3</sub>
- 12) LAH
- 13) Ac<sub>2</sub>O (1 equiv.), pyridine
- 14) POCl<sub>3</sub>, pyridine
- 15) *p*-TsOH, acetone, H<sub>2</sub>O
- 16) LAH
- 17) AcOH, DBAD, PPh<sub>3</sub>

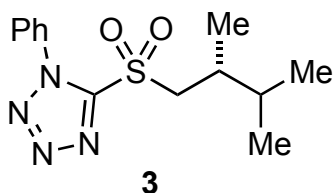
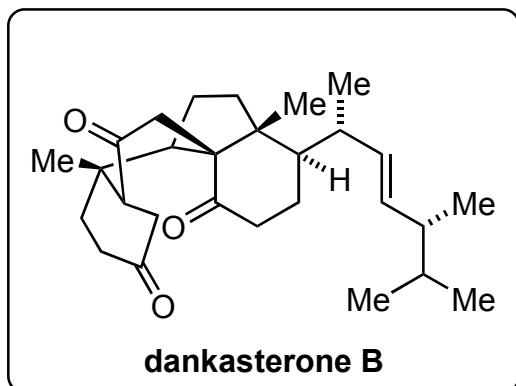
*hint 11: one deprotection occurs as well.*



18-23

- 18)  $\text{CrO}_3$ , 3,5-DMP, 4A molsieves
- 19)  $\text{HClO}_4$ , EtOAc,  $\text{O}_2$
- 20)  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ , THF,  $\text{H}_2\text{O}$
- 21)  $\text{K}_2\text{CO}_3$
- 22) DMP
- 23) LiHMDS, **3**

mechanism 19, 20?



24)  $\text{PhI}(\text{OH})(\text{OTs})$

25) DBU, TMSOTf

24

25

