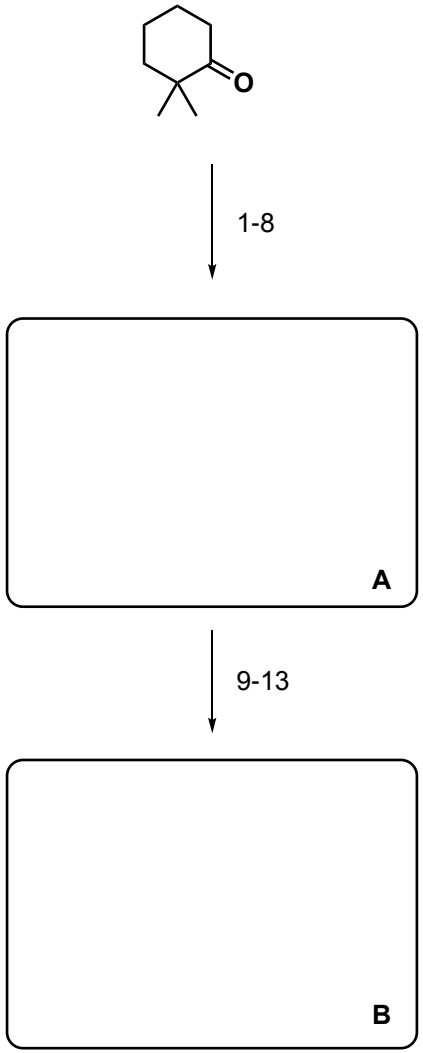
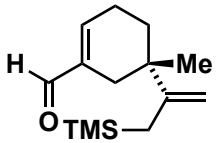
Total Synthesis of (–)-Oridonin: An Interrupted Nazarov Approach

L. Kong, F. Su, H. Yu, Z. Jiang, Y. Lu, and T. Luo, *J. Am. Chem. Soc.* **2019**, *141*, 20048–20052



1) PBr_3, DMF
2) NaH_2PO_4, H_2O_2, $NaClO_2$
3) K_2CO_3, MeI
4) CrO_3, Ac_2O, AcOH
5) (*S*)-CBS, BH_3•SMe_2
6) NaH, BnBr
7) *t*-BuLi (2 equiv.), *then* **1**
8) PDC



1

9) $EtAlCl_2$
10) O_2, TPP (cat.), Hg-lamp, *then* Ac_2O
11) $RhCl(PPh_3)_3$, toluene, reflux
12) 

13) *m*-CPBA

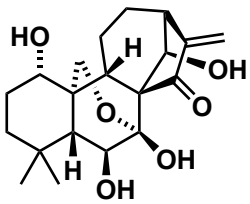
Step 1+2: Please provide the name for this transformation.

Hint for Step 6: Two Bn groups are introduced.

Step 9: Please propose a mechanism.

TPP: 5,10,15,20-tetraphenylporphyrin

Hint for Step 13: Only one functional group is selectively transformed.



(–)-oridonin

14-16

14) NBS
15) $RuCl_3$, $NaIO_4$ *then* DBU
16) OsO_4 (cat.), NMO

Hint for Step 15: first Bn protecting groups are transformed, then an elimination at another part of the molecule

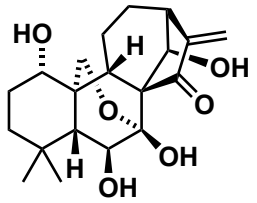
C

17-22

17) $EtAlCl_2$
18) $LiAlH_4$
19) $NaIO_4$
20) *p*-TsOH, $Me_2C(OMe)_2$, *then* DMP
21) DIBAL-H, then Red-Al, *then* HCl
22) O_2, TPP (cat.), Hg-lamp, *then* $(Boc)_2O$
DMAP, pyridine

Hint for Step 18: One carbonyl group is reduced and two protecting groups are removed.

Hint for Step 20 & 21: Two DMP oxidations occur and subsequent reductions correct the stereocenters



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