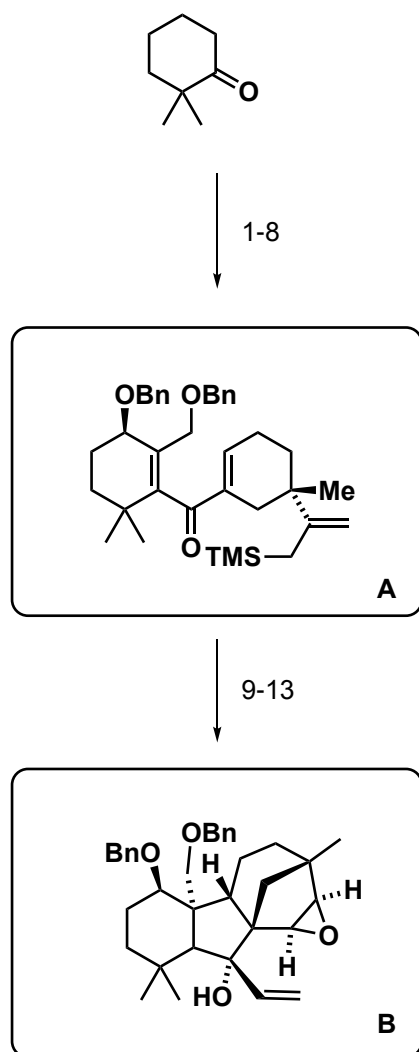
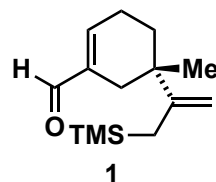



Total Synthesis of (-)-Oridonin: An Interrupted Nazarov Approach

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, $\text{BH}_3\cdot\text{SMe}_2$
- 6) NaH, BnBr
- 7) *t*-BuLi (2 equiv.), then **1**
- 8) PDC



- 9) EtAlCl_2
- 10) O_2 , TPP (cat.), Hg-lamp, then Ac_2O
- 11) $\text{RhCl}(\text{PPh}_3)_3$, toluene, reflux
- 12)  Li
- 13) *m*-CPBA

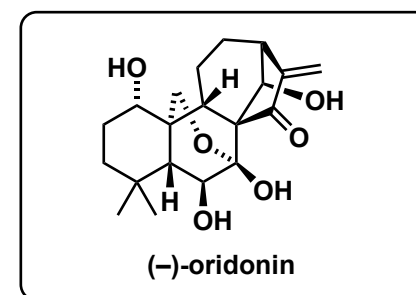
Step 1+2: Please provide the name for this transformation.
Vilsmeier reaction and Pinnick oxidation

Hint for Step 6: Two Bn groups are introduced.

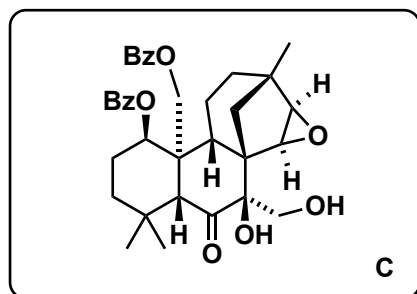
Step 9: Please propose a mechanism. *see next page*

TPP: 5,10,15,20-tetraphenylporphyrin

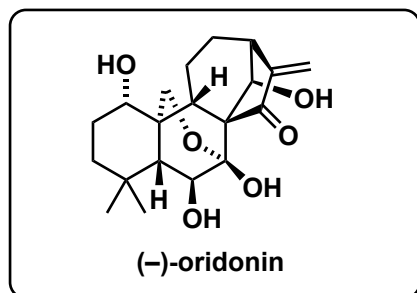
Hint for Step 13: Only one functional group is selectively transformed.



14-16



17-22

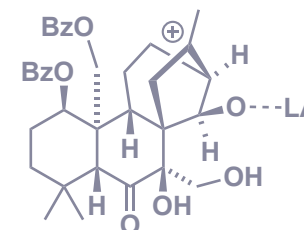


- 14) NBS
- 15) RuCl_3 , NaIO_4 then DBU
- 16) OsO_4 (cat.), NMO

- 17) EtAlCl_2
- 18) LiAlH_4
- 19) NaIO_4
- 20) *p*-TsOH, $\text{Me}_2\text{C}(\text{OMe})_2$, then DMP
- 21) DIBAL-H, then Red-Al, then HCl
- 22) O_2 , TPP (cat.), Hg-lamp, then $(\text{Boc})_2\text{O}$
DMAP, pyridine

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

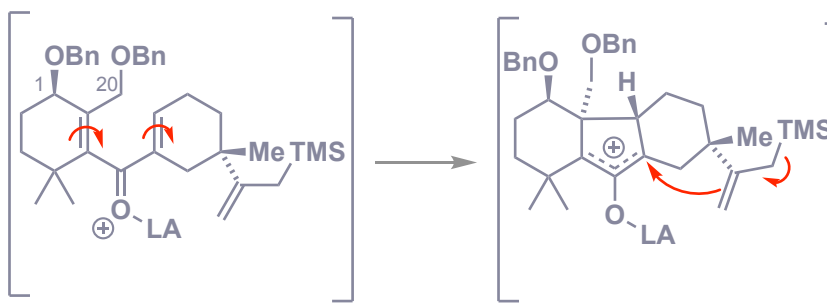
Step 17: 1,2-migration, via:



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

Step 9:



interrupted Nazarov electrocyclization or Nazarov/Hosomi-Sakurai cascade; conrotatory; substituents at C1 & C20 are proposed to control the stereoselectivity