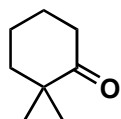


# Total Synthesis of (-)-Oridonin: An Interrupted Nazarov Approach

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



↓ 1-4

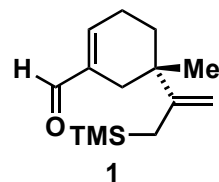


↓ 5-8



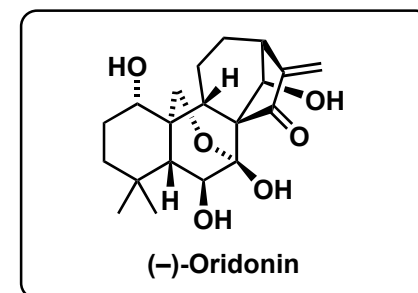
- 1) PBr<sub>3</sub>, DMF
- 2) NaH<sub>2</sub>PO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, NaClO<sub>2</sub>
- 3) K<sub>2</sub>CO<sub>3</sub>, MeI
- 4) CrO<sub>3</sub>, AcOH

- 5) (S)-CBS, BH<sub>3</sub>·SMe<sub>2</sub>
- 6) NaH, BnBr
- 7) *t*-BuLi, then **1**
- 8) PDC

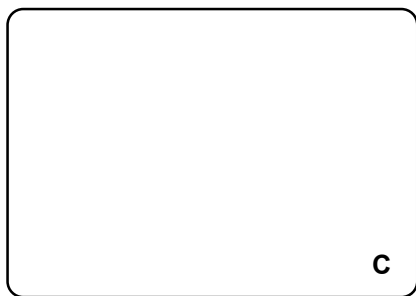


Step 1+2: Please provide the name for this transformation.

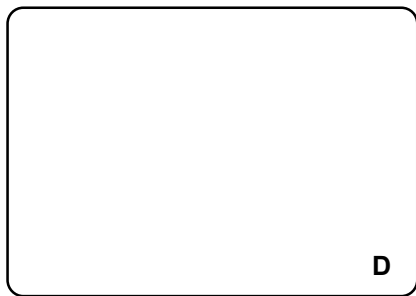
Hint for Step 6: Two Bn groups are introduced.




9–13



14–16

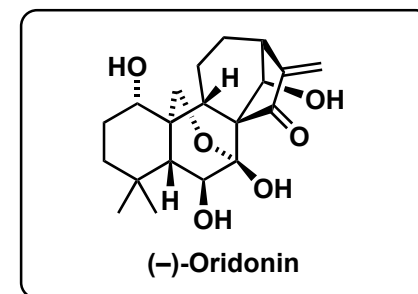


- 9)  $\text{EtAlCl}_2$   
10)  $^1\text{O}_2$  then  $\text{Ac}_2\text{O}$   
11)  $\text{RhCl}(\text{PPh}_3)_3$ , toluene, reflux  
12)   
13) *m*CPBA

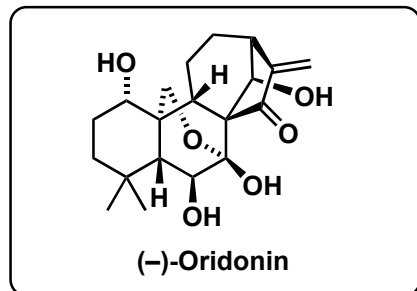
- 14) NBS  
15)  $\text{RuCl}_3$ ,  $\text{NaIO}_4$  then DBU  
16) cat.  $\text{OsO}_4$ , NMO

Step 9: Please propose a mechanism.

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



17-22



- 17)  $\text{EtAlCl}_2$
- 18)  $\text{LiAlH}_4$
- 19)  $\text{NaIO}_4$
- 20)  $p\text{TsOH}$ ,  $\text{Me}_2\text{C}(\text{OMe})_2$ , then DMP
- 21) DIBAL-H, then Red-Al, then HCl
- 22)  $^1\text{O}_2$ ,  $\text{Boc}_2\text{O}$ , then HCl

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

Hint for Step 20: Two DMP oxidations occur.