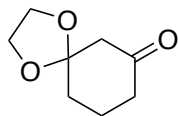


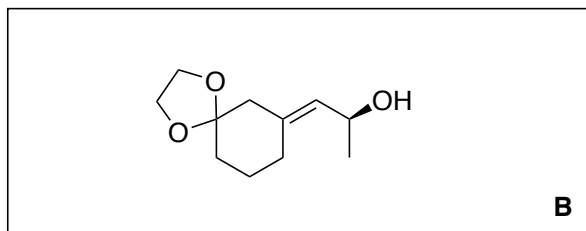
## Synthesis Challenge 104

Y. Kawamoto, N. Noguchi, T. Kobayashi, H Ito, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304132 doi.org/10.1002/anie.202304132  
20.07.2023



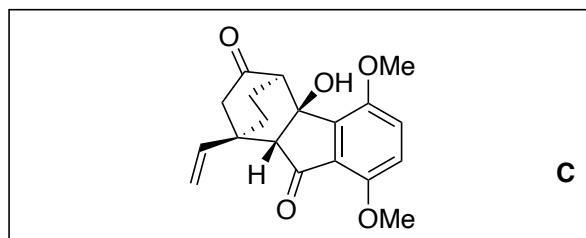
↓ ???

**A**



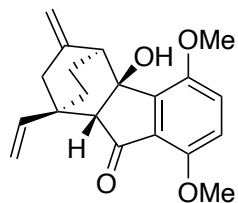
**B**

↓ 1-2



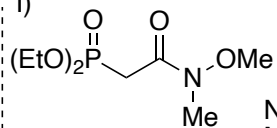
**C**

↓ 3-4



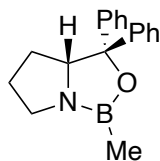
**E**

I)



NaH, THF,  $-30^{\circ}\text{C}$ , then  
MeLi,  $-78^{\circ}\text{C}$

II)



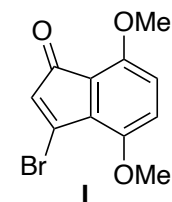
$\text{BH}_3^*\text{THF}$ , THF,  $-40^{\circ}\text{C}$

- 1) *t*BuOK toluene,  $-78^{\circ}\text{C}$ , then  $80^{\circ}\text{C}$ , **I**
- 2) 6 M HCl, *t*BuOH, rt

- 3) cat.  $\text{OsO}_4$ ,  $\text{NaIO}_4$ , 2,6-lutidine, dioxane/ $\text{H}_2\text{O}$ , rt
- 4)  $\text{Ph}_3\text{PMeBr}$ , *t*BuOK, THF, rt

Please draft a synthesis of **A**

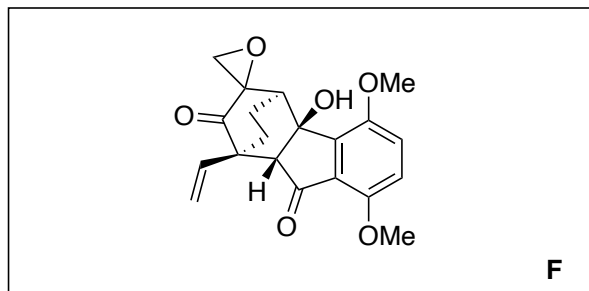
Hint: B should be obtained as a single enantiomer!



Please draft a synthesis of **I**

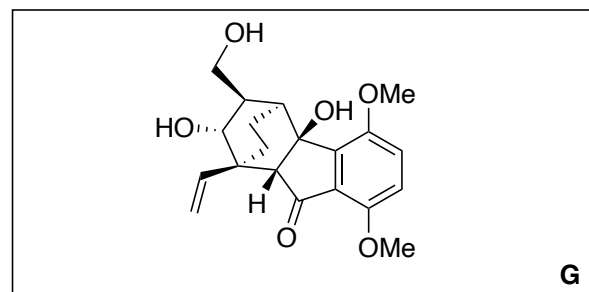
H. Tsukamoto, Y. Nomura, T. Doi, *Heterocycles* **2019**, *99*, 549–565

5-6



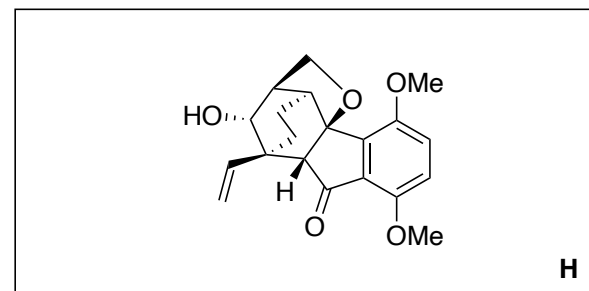
- 5)  $\text{SeO}_2$ , *t*BuOOH,  $\text{CH}_2\text{Cl}_2$ , rt, then Dess-Martin-Periodinane  
6)  $\text{H}_2\text{O}_2$ , aq.  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ , rt

7-8



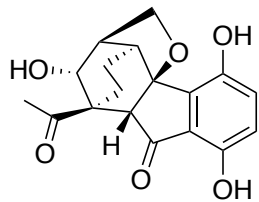
- 7)  $\text{SmI}_2$ , THF/MeOH,  $-78^\circ\text{C}$   
8)  $\text{NaBH}(\text{OAc})_3$ ,  $\text{CH}_3\text{CN}/\text{AcOH}$ , rt

9-10



- 9) TsCl,  $\text{Et}_3\text{N}$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ,  $60^\circ\text{C}$   
10) cat.  $\text{OsO}_4$ ,  $\text{NaIO}_4$ , 2,6-lutidine, dioxane/  
 $\text{H}_2\text{O}$ , rt

↓ 11-12



11) TMS-diazomethane, MgBr<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane, rt,  
then 3 M HCl, MeOH  
12) AlCl<sub>3</sub>, 1-dodecanethiol, CH<sub>2</sub>Cl<sub>2</sub>, rt

Please, provide a beautiful 3D drawing of the final product!