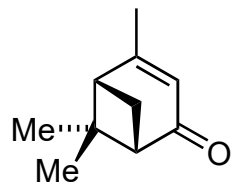


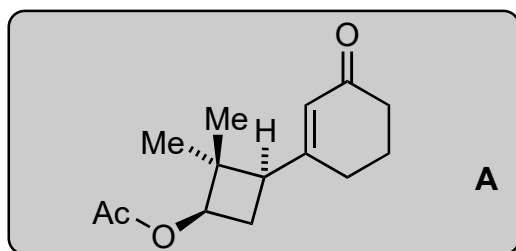
Total Synthesis of the Nominal Structure of (+)-Talaromyolide D

Qin, B.; Szypererek, A.; Tomanik, M.

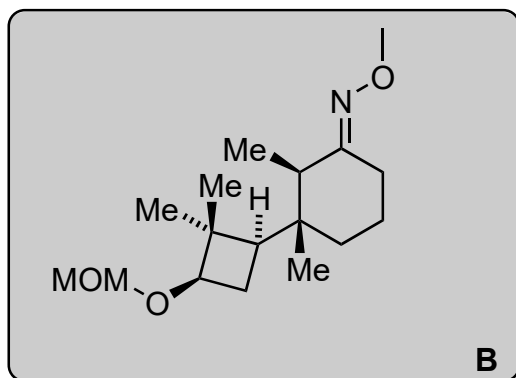
J. Am. Chem. Soc. **2025**, *147*, 31221. DOI: 10.1021/jacs.5c10325



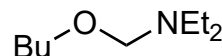
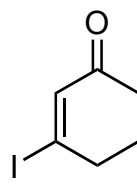
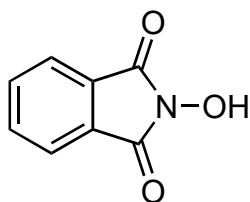
1-4



5-9



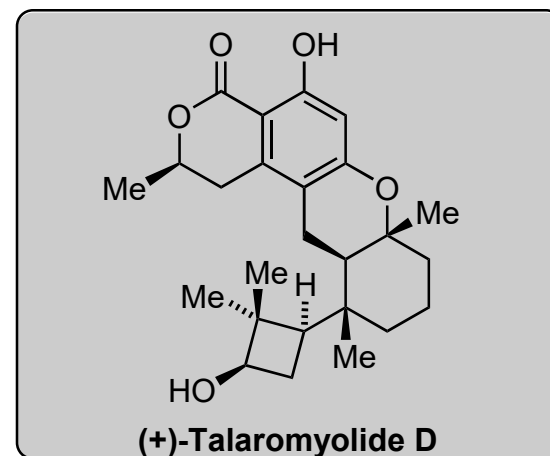
- 1) NaIO_4 , $\text{RuCl}_3 \cdot 3 \text{H}_2\text{O}$
- 2) *m*-CPBA, 50 °C
- 3) **1**, EDC, DMAP
- 4) **2**, $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, 2,2'-bpy, AgNO_3 , echem



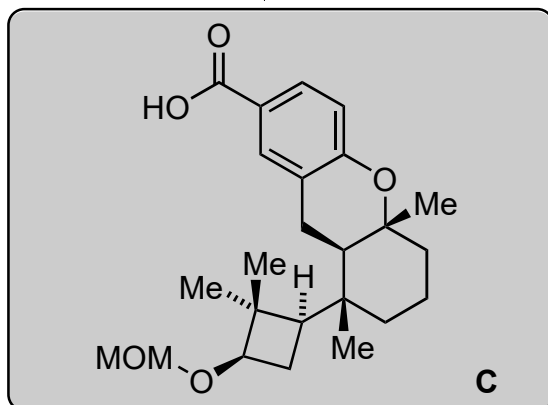
- 5) $\text{Ni}(\text{acac})_2$, AlMe_3 then **3** then *m*-CPBA
- 6) Pd/C , H_2
- 7) 4M HCl , 100 °C
- 8) $\text{NH}_2\text{OMe} \cdot \text{HCl}$
- 9) MOMCl , *i*- Pr_2NEt

- 1) HINT: Two carbonyls in product.
- 2) Name of reaction?
Baeyer-Villiger

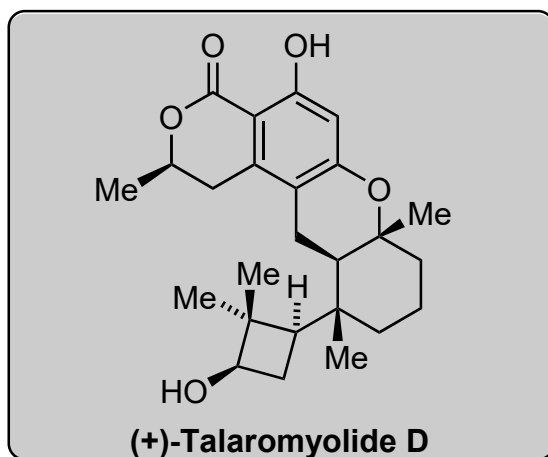
- 5) HINT: First step is 1,4-addition; intermediate has $\text{pK}_a \sim 10$. Reaction name? Cope elimination
- 7) Isomerization and deprotection



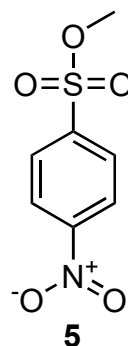
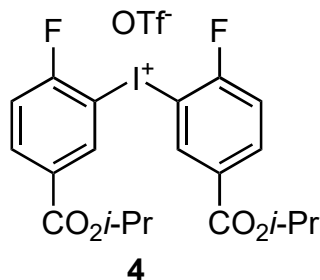
10-16



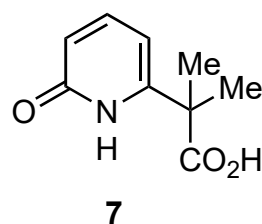
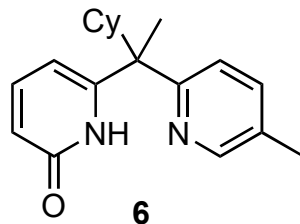
17-28



- 10) $\text{Pd}(\text{OAc})_2$, Ag_2Co_3 , PivOH , **4**
- 11) $\text{Ti}(\text{O-}i\text{Pr})_4$, EtMgBr
- 12) $\text{B}(\text{OH})_3$
- 13) Ph_3PMeBr , $t\text{-BuOK}$
- 14) $\text{Fe}(\text{acac})_3$, PhSiH_3 , **5**
- 15) NaH , DMF , 90°C
- 16) LiOH



- 17) $\text{Pd}(\text{OAc})_2$, KOAc , 1,4-benzoquinone, O_2 , **6**, 110°C
- 18) CH_2N_2
- 19) NaH , BnBr
- 20) LiOH
- 21) $\text{Pd}(\text{OAc})_2$, **7**, CsOAc , H_2O_2 , 60°C
- 22) CH_2N_2
- 23) NaH , PhNTf_2
- 24) $\text{Pd}(\text{PPh}_3)_4$, LiCl , $n\text{-Bu}_3\text{Sn-allyl}$
- 25) PdCl_2 , CuCl , O_2 , $\text{DMF}/\text{H}_2\text{O}$
- 26) BH_3 DMS , (*S*)-*n*-Bu-CBS
- 27) 6M HCl , 50°C
- 28) Pd/C , H_2



11) HINT: EtMgBr is a reductant

14) HINT: **5** behaves similarly to O_2

17) HINT: $\text{Csp}^2\text{-H}$ activation

25) Name of reaction?
Wacker oxidation