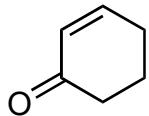
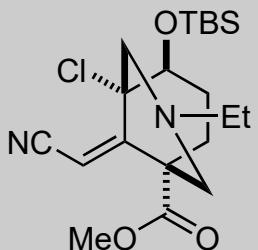


## Total Synthesis of Puberuline C

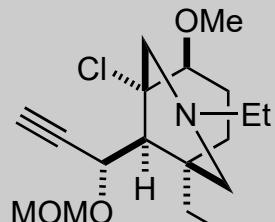
Shimakawa T.; Nakamura S.; Asai H.; Hagiwara K.; Inoue M.  
*J. Am. Chem. Soc.* **2023**, *145*, 600–609.



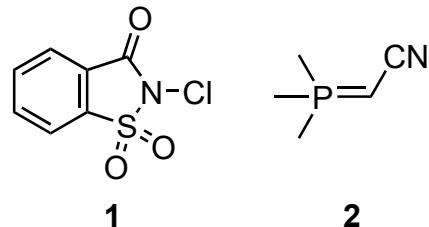
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1-9



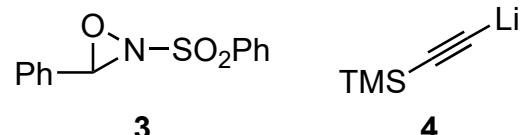
↓  
10-14



- 1) LDA, MeOCOCl
- 2)  $\text{Me}_2\text{PhSiCl}$ , Li,  $\text{Et}_2\text{Zn}$ , TMSCl
- 3) **1**
- 4) aq. HCHO, aq.  $\text{EtNH}_2$
- 5)  $\text{HBF}_4 \cdot \text{OEt}_2$
- 6)  $\text{CF}_3\text{CO}_2\text{H}$  then AcOOH
- 7) DBU,  $50^\circ\text{C}$
- 8) TBSOTf, 2,6-lutidine
- 9) **2**,  $130^\circ\text{C}$



- 10)  $\text{LiBH}_4$ ,  $\text{H}_2\text{O}$
- 11) TBAF then  $\text{MeI}$ , KOH
- 12) LDA, HMPA then **3** then  $\text{Me}_2\text{S}$ , aq.  $\text{NaHCO}_3$
- 13)  $p\text{-TsOH} \cdot \text{H}_2\text{O}$ ,  $90^\circ\text{C}$
- 14) **4**, TMEDA then  $\text{MOMBr}$  then  $\text{K}_2\text{CO}_3$ , MeOH



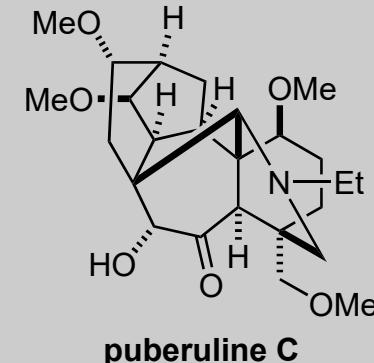
3) Name of reagent **1**?  
*N*-chlorosaccharin

6) Name of reaction?  
 Fleming-Tamao oxidation

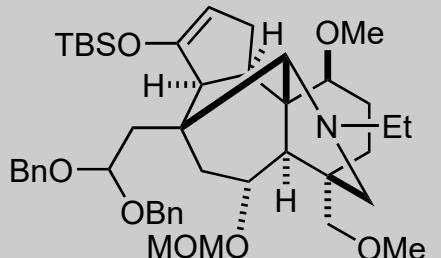
7) Hint: epimerization

12) Name of reagent **3**?  
 Davis oxaziridine

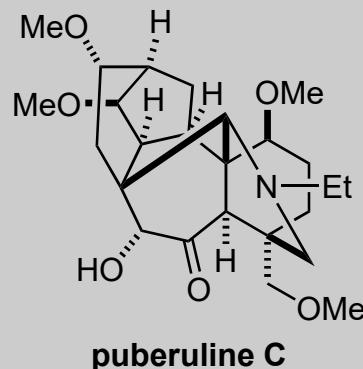
13) Hint: epimerization



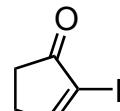
15-22



23-32



- 15) 5,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{CuI}$ ,  $i\text{-Pr}_2\text{NEt}$
- 16)  $n\text{-Bu}_3\text{SnH}$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$
- 17) allylbromide,  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ,  $\text{AsPh}_3$
- 18)  $\text{OsO}_4$ ,  $\text{NMO}$
- 19)  $\text{H}_5\text{IO}_6$
- 20)  $\text{Sc}(\text{OTf})_3$ ,  $\text{BnOH}$
- 21)  $(c\text{-Hex})_3\text{SnH}$ , V-40  
1,3-bis( $\text{CF}_3$ )benzene,  $110^\circ\text{C}$
- 22)  $\text{TBSOTf}$ ,  $\text{Et}_3\text{N}$



5

- 23)  $\text{SnCl}_4$ ,  $\text{ZnCl}_2$
- 24)  $\text{NaBH}_4$
- 25)  $\text{MeI}$ ,  $t\text{-BuOK}$
- 26)  $\text{Pd/C}$ ,  $\text{H}_2$
- 27)  $(\text{CF}_3\text{CO})_2\text{O}$ ,  $\text{DMSO}$  *then*  $\text{Et}_3\text{N}$
- 28)  $\text{SmI}_2$ ,  $\text{HMPA}$ ,  $t\text{-BuOH}$
- 29)  $\text{MeI}$ ,  $t\text{-BuOK}$
- 30)  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{Me}_2\text{S}$
- 31)  $\text{CF}_3\text{CO}_2\text{H}$  *then*  $\text{DMP}$
- 32)  $\text{LDA}$ ,  $\text{MoO}_5 \cdot \text{pyridine} \cdot \text{HMPA}$

17) Name of the reaction?

Stille coupling

18) Name of the reaction?

Upjohn dihydroxylation

21) Suggest a mechanism.

See later

23) Name of the reaction?

Mukaiyama aldol

**Radical cascade mechanism:**

