Total Synthesis of Puberuline C

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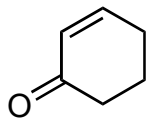
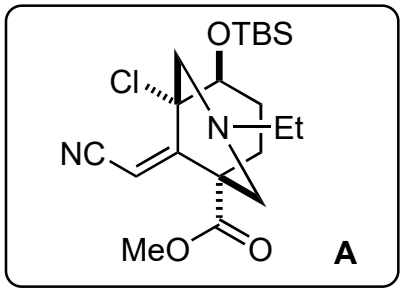


1-9



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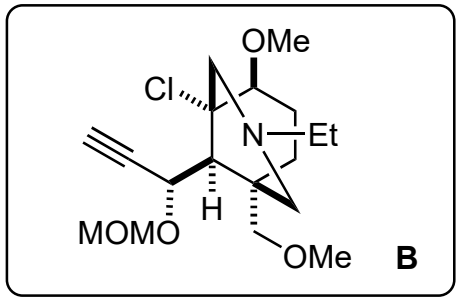
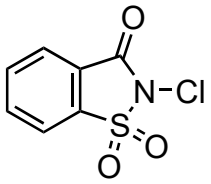


1) LDA, MeOCOCl
2) $Me_2PhSiCl$, Li, Et_2Zn, TMSCl
3) **1**
4) aq. HCHO, aq. $EtNH_2$
5) HBF_4•OEt_2
6) CF_3CO_2H *then* AcOOH
7) DBU, 50 °C
8) TBSOTf, 2,6-lutidine
9) **2**, 130 °C



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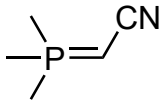
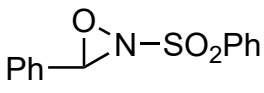


2

10) $LiBH_4$, H_2O
11) TBAF *then* MeI, KOH
12) LDA, HMPA *then* **3** *then* Me_2S, aq. $NaHCO_3$
13) *p*-TsOH•H_2O, 90 °C
14) **4**, TMEDA *then* MOMBr *then* K_2CO_3, MeOH



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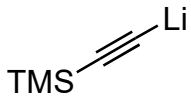


4

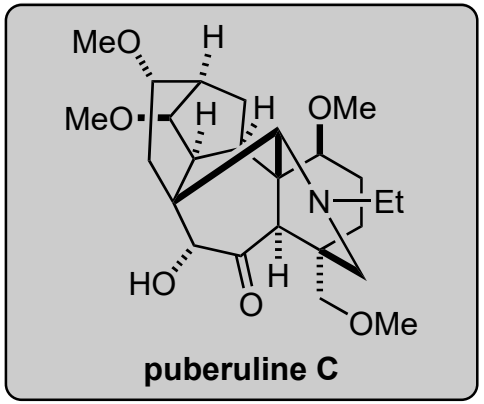
3) Name of reagent **1**?
N-chlorosaccharin

6) Name of reaction?
Fleming-Tamao oxidation

7) *Hint: epimerization*

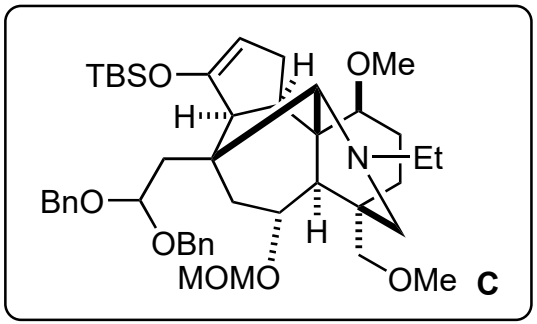
12) Name of reagent **3**?
Davis oxaziridine

13) *Hint: epimerization*



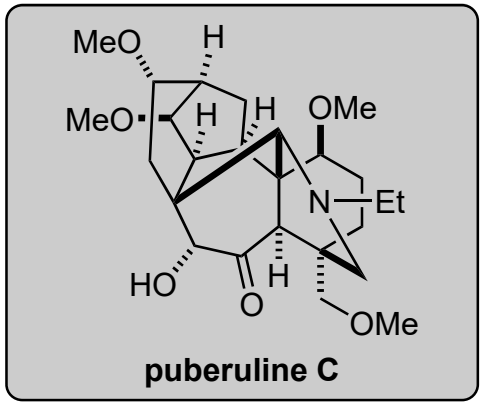
puberuline C

15-22



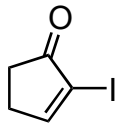
C

23-32



puberuline C

15) **5**, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NEt
16) *n*-Bu_3SnH, $PdCl_2(PPh_3)_2$
17) allylbromide, $Pd_2(dba)_3$•$CHCl_3$, $AsPh_3$
18) OsO_4, NMO
19) H_5IO_6
20) $Sc(OTf)_3$, BnOH
21) (*c*-Hex)$_3$SnH, V-40
1,3-bis(CF_3)benzene, 110 °C
22) TBSOTf, Et_3N



5

23) $SnCl_4$, $ZnCl_2$
24) $NaBH_4$
25) MeI, *t*-BuOK
26) Pd/C, H_2
27) $(CF_3CO)_2O$, DMSO *then* Et_3N
28) SmI_2, HMPA, *t*-BuOH
29) MeI, *t*-BuOK
30) BF_3•OEt_2, Me_2S
31) CF_3CO_2H *then* DMP
32) LDA, MoO_5•pyridine•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: