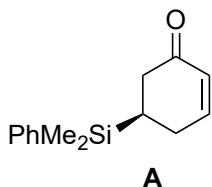
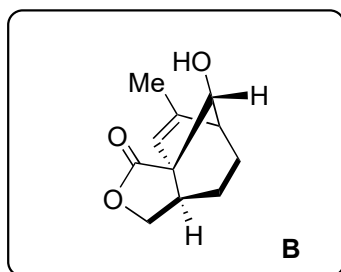


Total Synthesis of Principinol B

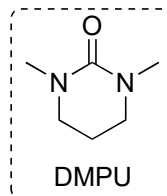
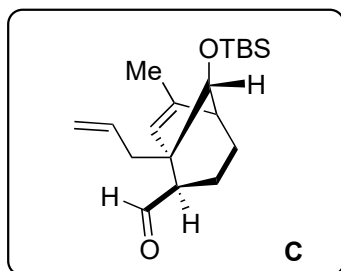
Q. Du, Z. Fan, M. Yang, *Angew. Chem. Int. Ed.* **2024**, 63, e202400956



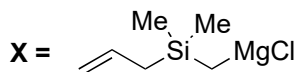
1–6



7–10



- 1) **X**, $\text{CuI} \cdot 0.75\text{Me}_2\text{S}$ then DMPU, CNCOOEt
- 2) NaH , 2,3-dibromoprop-1-ene
- 3) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ then H_2O_2
- 4) CuCl_2
- 5) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, NaBH_4
- 6) $n\text{Bu}_3\text{SnH}$, AIBN then TfOH



- 7) TBSOTf then DIBAL-H
- 8) vinylMgBr then Ac_2O
- 9) $\text{Pd}(\text{OAc})_2$, HCOOH then MeONa , MeOH
- 10) $\text{SO}_3 \cdot \text{Py}$, DIPEA, DMSO

- 3) Name of the reaction?
Hint: New ring is formed.

Tamao Fleming oxidation

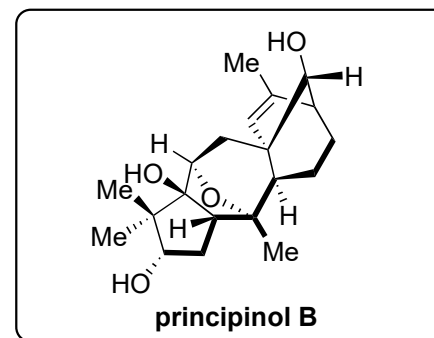
- 5) Name of the reaction?

Luche reduction

- 6) *Hint: the final product contains an **endo** double bond*

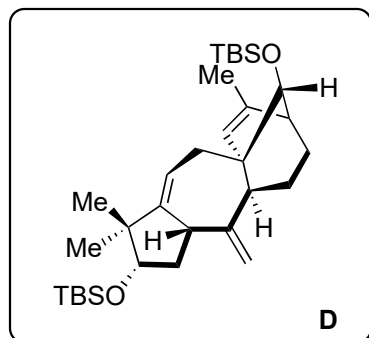
- 10) Name of the reaction?

Parikh–Doering oxidation

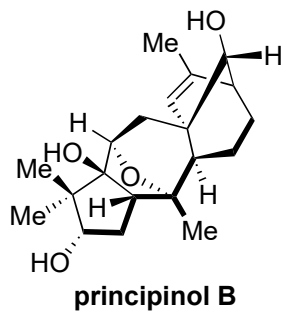


C

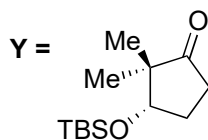
11–16



17–21



- 11) **Y**, LiHMDS
- 12) TMSOTf
- 13) Cp_2TiMe_2 100 °C *then* 0.08M HCl (aq)
- 14) DMP
- 15) MeMgBr, CeCl_3
- 16) SOCl_2 , Et_3N



- 17) *m*-CPBA, -60 °C
- 18) OsO_4
- 19) MsCl
- 20) $\text{Mn}(\text{acac})_2$, O_2 , PhSiH_3 , PPh_3
- 21) TiCl_4 , Zn, Py *then* 6M HCl (aq)

19) *Hint*: Only one hydroxy group reacted.

20) Name of the reaction?
Hint: New ring is formed

Mukaiyama hydration

