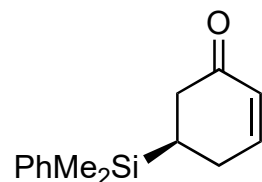
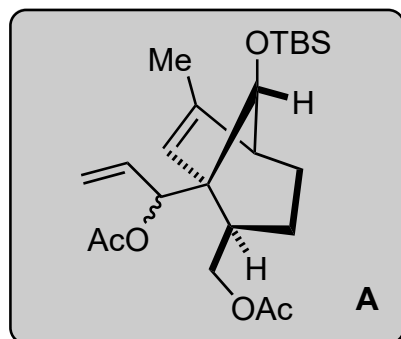


Total Synthesis of Principinol B

Qiang Du, Zhibo Fan, Ming Yang*
Angew. Chem. Int. Ed. **2024**, 63, e202400956

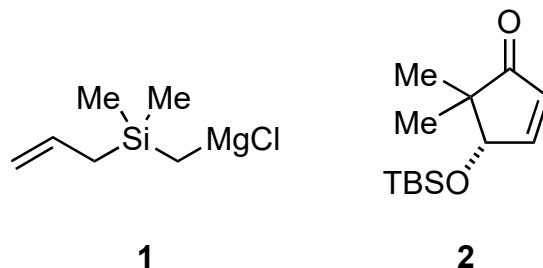


1–8



9–15

- 1) **1**, CuI, *then* DMPU, CNCOOEt
- 2) NaH, 2,3-dibromopropene
- 3) HBF₄•Et₂O, *then* H₂O₂
- 4) CuCl₂
- 5) CeCl₃•7H₂O, NaBH₄
- 6) *n*-Bu₃SnH, AIBN, *then* TfOH
- 7) TBSOTf, *then* DIBAL-H
- 8) vinylMgBr, *then* Ac₂O



- 9) Pd(OAc)₂, HCOOH, *then* MeONa, MeOH
- 10) SO₃•Py, DIPEA, DMSO
- 11) **2**, LiHMDS
- 12) TMSOTf
- 13) Cp₂TiMe₂, 100 °C, *then* aq. HCl
- 14) DMP
- 15) MeMgBr, CeCl₃

3) Name of the reaction?

Tamao-Fleming oxidation

5) Name of the reaction?

Luche reduction

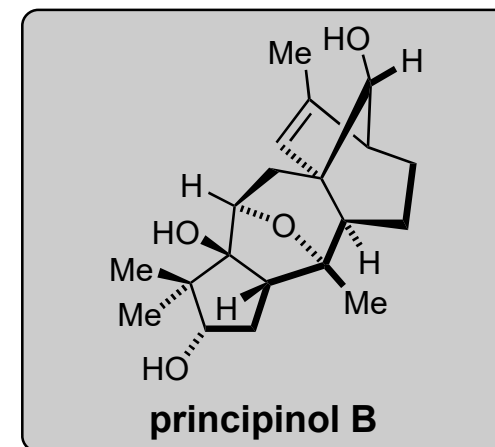
6) hint: double bond migration with TfOH

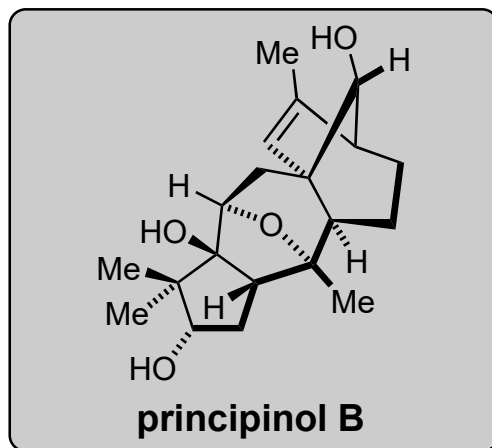
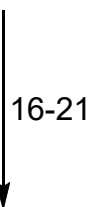
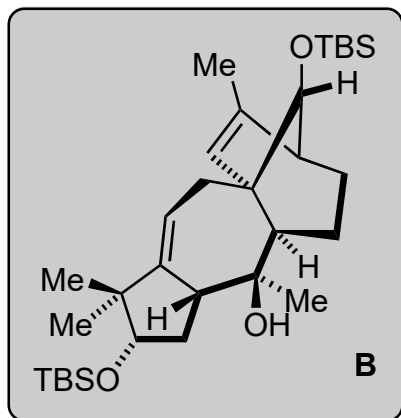
9) mechanism?

Synthesis 1986; 1986(8): 623-627

13) mechanism?

carbonyl–olefin metathesis





- 16) SOCl_2 , Et_3N
- 17) *m*-CPBA, DCM, -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* 6 M aq. HCl