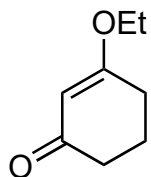
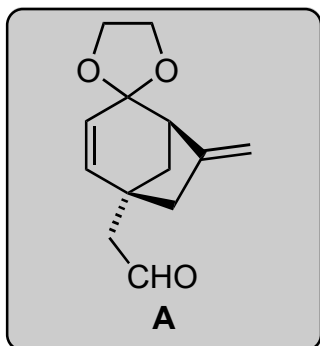


Convergent Route to ent-Kaurane Diterpenoids: Total Synthesis of Lungshenghenin D and 1 α ,6 α -Diacetoxy-ent-kaura-9(11),16-dien12,15-dione

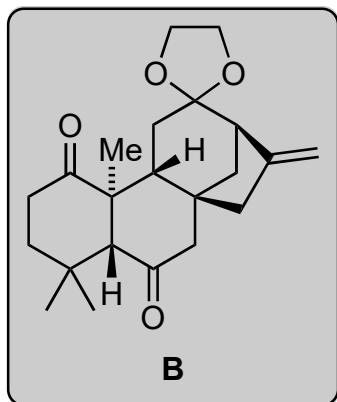
Zhao, X.; Li, W.; Wang, J.; Ma, D. *J. Am. Soc.* **2017**, *139*, 2932–2935.



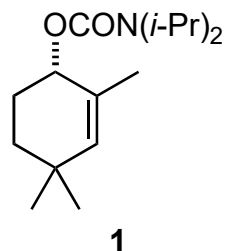
1-9



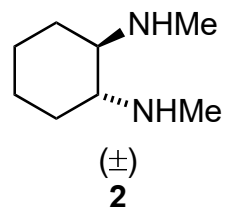
10-14



- 1) LDA *then* allyl chloroformate
- 2) ICH₂CH₂OTBDPS, CsCO₃
- 3) Pd₂(dba)₃, (S)-*t*-Bu-Phox
- 4) DIBAL-H *then* HCl, MeOH
- 5) TBSOTf
- 6) Pd(OAc)₂, O₂
- 7) (CH₂OH)₂, PPTS
- 8) TBAF
- 9) TPAP, NMO



- 10) **1**, *s*-BuLi, **2** *then* **A** *then* Ac₂O, DMAP
- 11) BF₃ · OEt₂ *then* NaHCO₃
- 12) K₂CO₃, MeOH
- 13) IBX, DMSO
- 14) DBU



3) Name of the reaction?

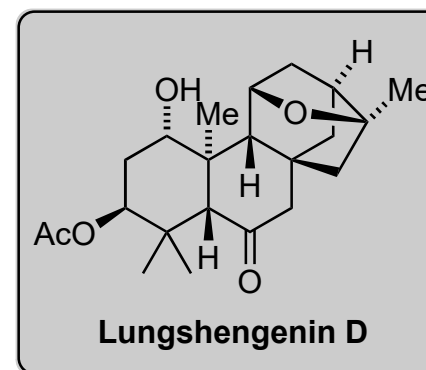
Tsuji-Trost

10) Name of the reaction?

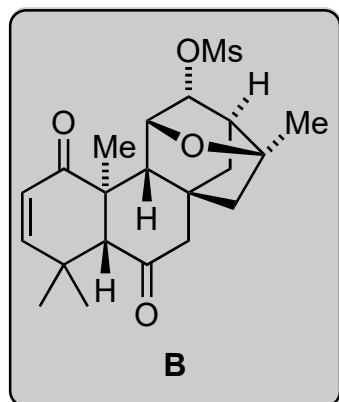
Homo-Aldol addition

11) Mechanism? Hint: product contains 5 rings

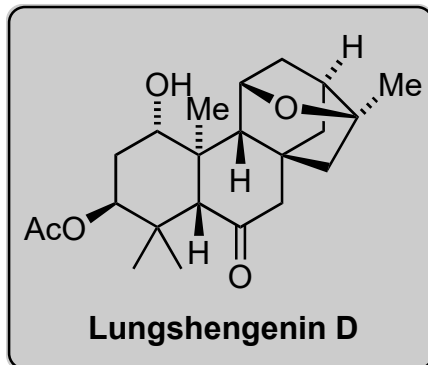
14) isomerization



15-21



22-27



- 15) KHMDS, TBSCl (4 equiv)
- 16) DDQ, DTBMP
- 17) HCl
- 18) *t*-BuOK *then* (PhSeO)₂O
- 19) HCl
- 20) NaBH₄ (1 equiv.), -10 °C
- 21) MsCl

- 22) LAH (12 equiv.)
- 23) IBX (4.6 equiv.)
- 24) *t*-BuOOH, Triton B
- 25) (PhSe)₂, NaBH₄
- 26) Me₄NBH(OAc)₃
- 27) Ac₂O, DMAP, Py

16) DTBMP: 2,6-di-tert-butyl-4-methylpyridine

19) Hint: last ring is formed

24) Triton B is a base, what is its structure?



11)

