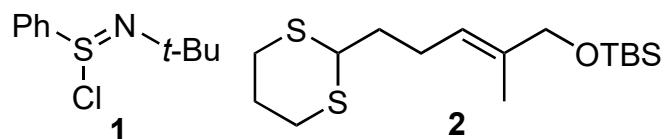
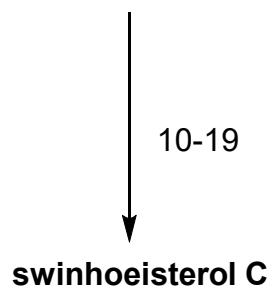
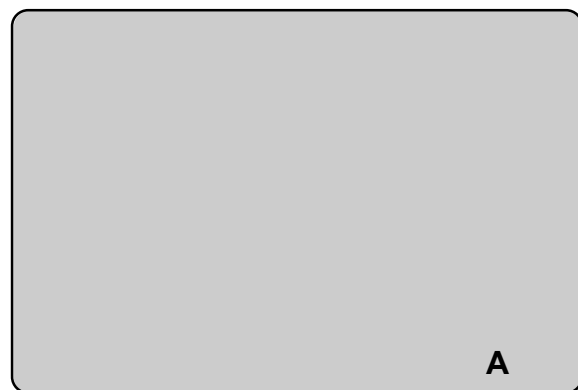
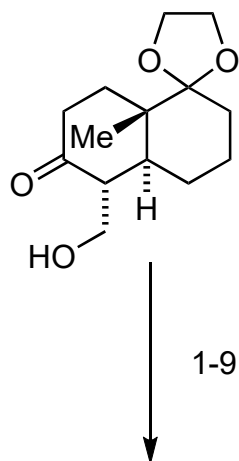


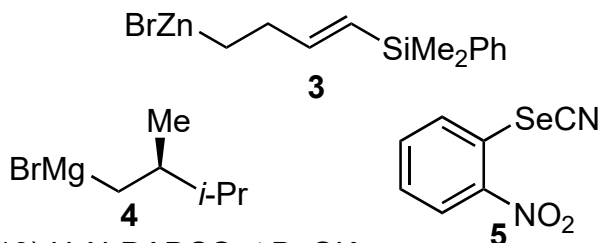
Divergent Total Syntheses of Rearranged Steroids Swinhoeisterols A-C

Huang, G.; Zhang, X.; Gu, Y.; Gui, J.

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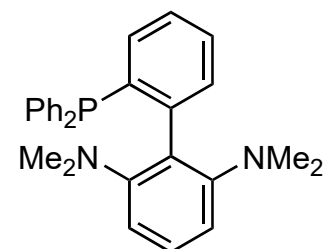
- 1) Li, *t*-BuOH, NH₃ (l)
- 2) *p*-TsOH, acetone
- 3) LiHMDS then **1**
- 4) Et₄NCl₃, NEt₃
- 5) **2**, *n*-BuLi, HMPA then substrate
- 6) KH, Comins' reagent
- 7) **3**, cat. Pd(OAc)₂, cat. PhCPhos, NMI, THF/DMA, 80 °C
- 8) TBAF·3H₂O, HMPA, 80 °C
- 9) TPAP, NMO, 4 Å MS



- 10) H₂N-DABCO, *t*-BuOK
- 11) Fe(dpm)₃, Ph(*i*-PrO)SiH₂
- 12) *t*BuOK
- 13) DIBAL-H, -40 °C then NH₄Cl (aq.)
- 14) DIBAL-H
- 15) TsCl, DMAP
- 16) **4**, CuBr·SMe₂
- 17) HgCl₂
- 18) O₃, pyr./DCM
- 19) **5**, *n*-Bu₃P then NaHCO₃, H₂O₂

1) From what famous ketone is the starting material made? Propose a reasonable route from this molecule to the starting material. Propose a stereochemical rationale for the major product of step 1.

7) Propose a reasonable mechanism. Structure of PhCPhos:



11) Who developed this type of reductive olefin coupling?

12) Epimerization

17) Swinhoeisterol A was also made in 1 step from this intermediate.

19) Swinhoeisterol B was also made in 1 step from swinhoeisterol C.

