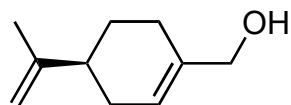
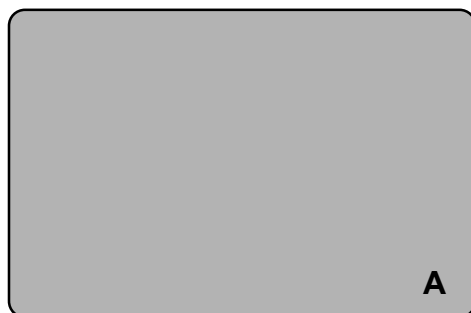


Total Synthesis of Rubriflordilactone B

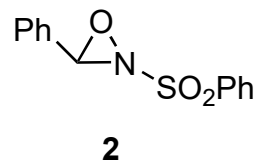
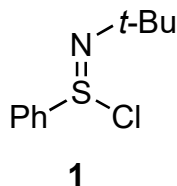
Peng Yang, Ming Yao, Jian Li, Yong Li, Ang Li*
Angew. Chem. Int. Ed. **2016**, *55*, 6964 - 6968



1-17



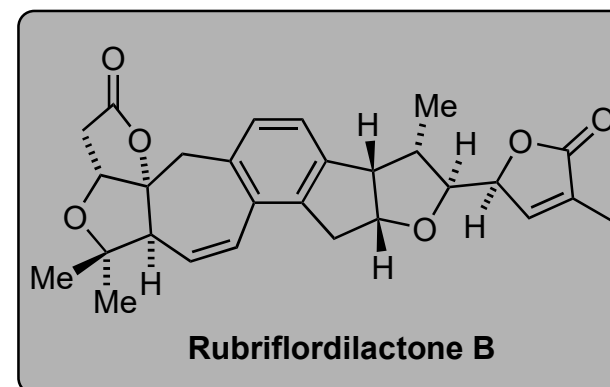
- 1) ZnI_2 , $\text{P}(\text{OEt})_3$, $140\text{ }^\circ\text{C}$
- 2) O_3 , Me_2S , $-78\text{ }^\circ\text{C}$, then aq. K_2CO_3 , r.t.
- 3) LDA, **1**, $-78\text{ }^\circ\text{C}$
- 4) L-Selectride, $-78\text{ }^\circ\text{C}$
- 5) TMSCN , AlEt_3 , r.t., then s.m., $80\text{ }^\circ\text{C}$, then aq. NaOH , r.t.
- 6) $\text{Co}(\text{acac})_2$, PhSiH_3 , O_2 , $10\text{ }^\circ\text{C}$
- 7) aq. NaOH , $80\text{ }^\circ\text{C}$
- 8) $\text{Ph}_3\text{P}=\text{CH}_2$, $-78\text{ }^\circ\text{C}$
- 9) KHMDS , **2**, then TESOTf , $-78\text{ }^\circ\text{C}$



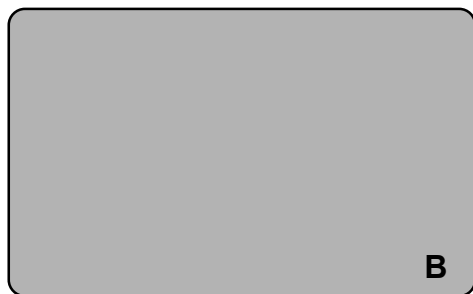
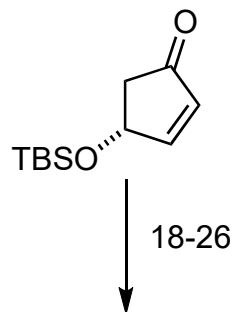
- 10) O_3 , Me_2S , $-78\text{ }^\circ\text{C}$
- 11) LiHMDS , PhNTf_2 , $-78\text{ }^\circ\text{C}$
- 12) $\text{Sc}(\text{OTf})_2$, Ac_2O , r.t.
- 13) LiHMDS , $-78\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$
- 14) Et_3SiH , $\text{BF}_3\cdot\text{OEt}_2$, $35\text{ }^\circ\text{C}$
- 15) NBS , BPO , $85\text{ }^\circ\text{C}$
- 16) NaBH_4 , $o\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$, r.t.
- 17) aq. H_2O_2 (30%), pyridine, r.t.

- 1) Name of starting material and reaction type ?
- 2) Name of the reaction ?
- 3) Name of the reaction ?
- 4) Structure of L-Selectride ?
- 6) Name of the reaction ?

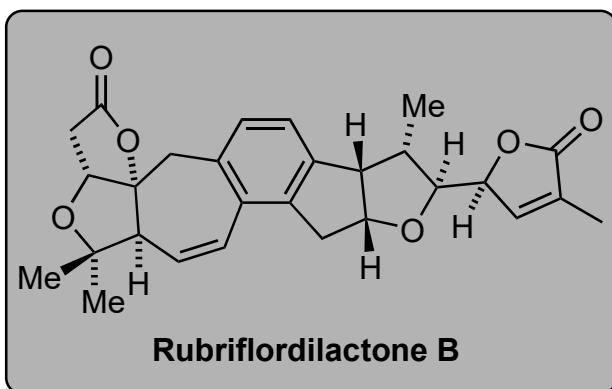
- 9) Name of the reaction ?
Name of compound **2** ?
How would you prepare it ?



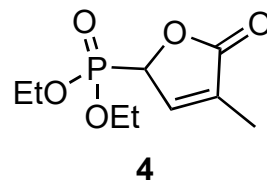
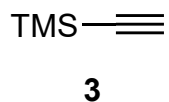
- 17) Name of the reaction ?



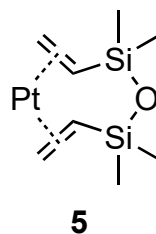
27-30



- 18) I₂, K₂CO₃, 4-DMAP, r.t.
 19) NaBH₄, CeCl₃·7 H₂O, -78 °C
 20) CuI, Et₃N, Pd(PPh₃)₂Cl₂, **3**, r.t.
 21) *o*-NO₂C₆H₄OH (cat.), EtC(OMe)₃, 180 °C
 22) TBAF, r.t.
 23) LiTMP, -78 °C
 24) DIBAL-H, -78 °C
 25) **4**, DBU, LiCl, *then* s.m., 75 °C
 26) TBSOTf, Et₃N, 0 °C,
then AcOH, TBAF, 0 °C



- 27) **A**, Pd(PPh₃)₄, CuI, LiCl, *i*Pr₂NEt, 70 °C
 28) **5**, (3-pentyl-O)SiMe₂H, r.t.
 29) 135 °C, *then* DDQ, r.t.
 30) AgF, H₂O, r.t.



- 19) Name of the reaction ?
 20) Name of the reaction ?
 21) Name and type of the reaction ?
Hint: γ,δ-unsaturated ester formed
 22) *Note*: two epimers formed

23) *Note*: conversion of undesired epimer from 22) into desired product

25) Name of the reaction conditions?
Note: two epimers formed

26) *Note*: conversion of undesired epimer from 25) into desired product

27) Name of the reaction ?
 28) Name of compound **5** ?
Note: two regioisomers formed
 Describe an alternative reaction.

29) Classify the type of the reaction.