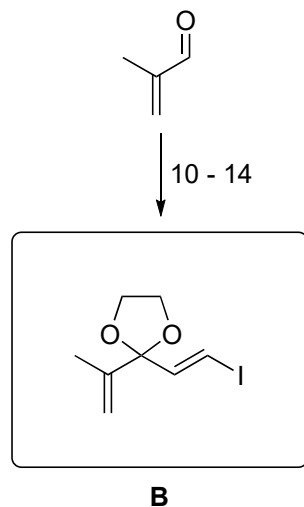
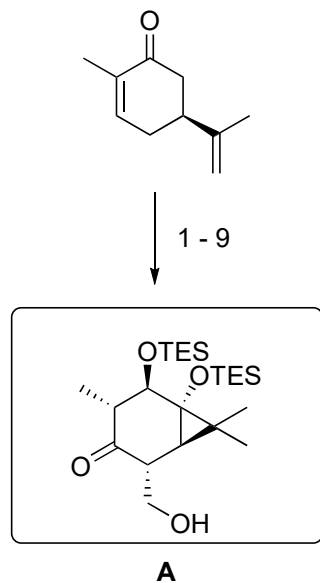


Asymmetric Total Synthesis of Euphordraculoate A and Pedrolide

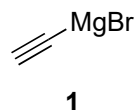
C. Tu, Y. Yang, Y. Jiang, Y. Hao, Z. Wang, S. Fu, S. Qin, and B. Liu

Angew. Chem. Int. Ed. **2024**, 63, e202409997



- 1) HBr, AcOH
- 2) NaOH, H₂O₂
- 3) LDA, HBPin, *then* NaOH, H₂O₂
- 4) TESCO (2.5 equiv), NEt₃
- 5) LiTMP, Et₂AlCl
- 6) RhCl(PPh₃)₃, H₂ then DMP
- 7) DBU (4 cycles)
- 8) LDA, TMSCl
- 9) Yb(OTf)₃, HCHO_(aq)

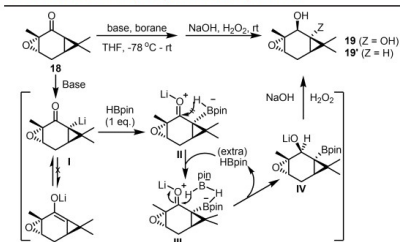
- 10) **1**, *then* TESCO
- 11) DIBAL-H, Cp₂ZrCl₂ *then* NIS
- 12) TBAF
- 13) DMP, NaHCO₃
- 14) TsOH·H₂O, (CH₂OH)₂



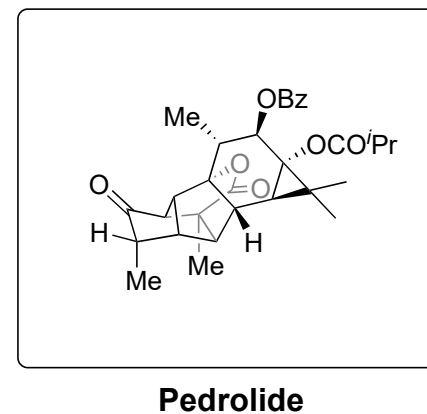
- 1) Name of starting material? (+)-*carvone*
- 2) *Hint*: 2 transformations
- 3) *Hint*: no ¹³C NMR peak above 75 ppm.

Mechanism?

Table 1: Reductive dihydroxylation of compound **18**.^[a]



- 10) Name of starting material? *Methacrolein*

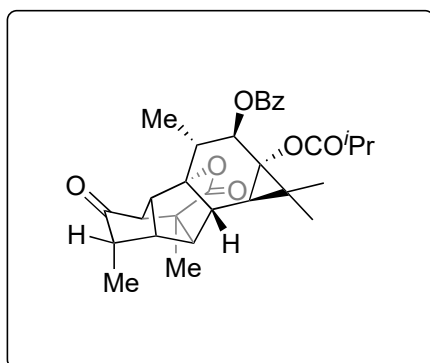


A+B

15-24

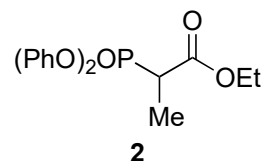
Euphordraculoate A

25



Pedrolide

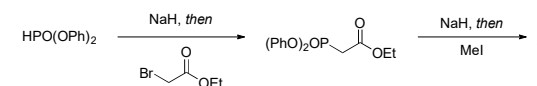
- 15) B, i PrMgCl·LiCl, then A
- 16) DMP
- 17) DBU, 2, NaI
- 18) HF·NEt₃
- 19) i PrCOCl, DIPEA, DMAP
- 20) BzCl, NEt₃
- 21) TMSOTf, (CH₂OTMS)₂



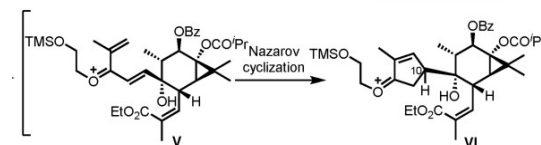
- 22) NaBH₄, CeCl₃·H₂O
- 23) NaH
- 24) TPAP, NMO, 4 Å MS

- 25) Eu(fod)₃, 150 °C

17) Name of reaction? *Ando modification of HWE olefination*
Which stereochemistry is mainly obtained?
Z(75%)/E(13%)
How would you make **2**?



- 18) *Hint*: ketone is also unmasked
- 19) *Hint*: selective of the less hindered tertiary hydroxyl
- 20) *Hint*: selective of the secondary hydroxyl
- 21) Classify this reaction & draw a mechanism. *4π-electrocyclization, Nazarov*



- 25) Mechanism? *dienyl enolization, intramolecular Diels-Alder, enol-ketone tautomerization*