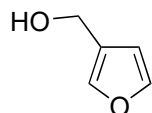


Enantioselective Total Synthesis of Bipolarolides A and B

Y. Liu, K. Sun, Q. Wei, J. Chen, S. Sun, Y. Li, Z. Feng, Y. Guo, and Z. Lu

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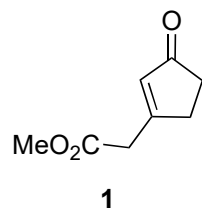
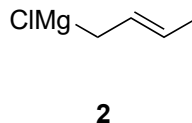
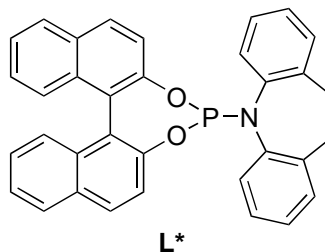
1 - 9



A

10 - 17

- 1) TIPSCl, imidazole
- 2) *n*-BuLi, HMPA
- 3) *n*-BuLi, DMF
- 4) KOH, H₂O
- 5) vinylMgBr
- 6) [Ir(cod)Cl]₂, L*, TFA, **1** then LiOH, PPh₃, 70°C
- 7) CuI, MeMgBr, BF₃•OEt₂ then MeLi, HMPA, HCHO
- 8) Tf₂O, NEt₃
- 9) LiClO₄



2 & 4) *Hint*: TIPS migration

9) Draw like then natural product
Name of the reaction?

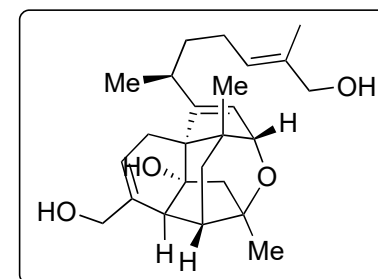
11) *Hint*: double reduction + alkene migration

13) Name of the reaction?

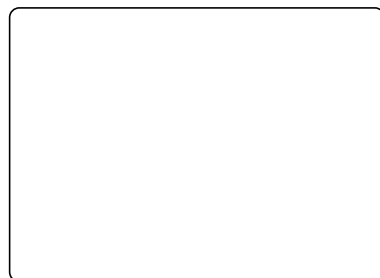
14) *Hint*: only one alcohol remains

15) Name of the reaction?

- 10) **2**
- 11) LiDBB
- 12) TMSOTf (3.0 equiv), NEt₃
- 13) PdCl₂, Cu(OAc)₂, O₂
- 14) PPTS, 100 °C
- 15) (COCl)₂, DMSO, NEt₃
- 16) Cs₂CO₃ (3 runs), 110 °C
- 17) MeLi (3 runs)

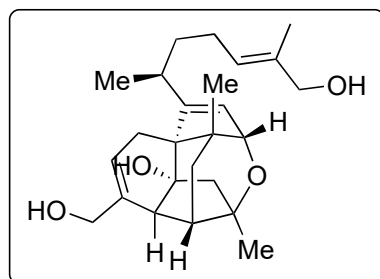


bipolarolide B

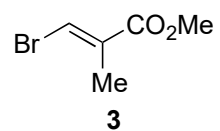
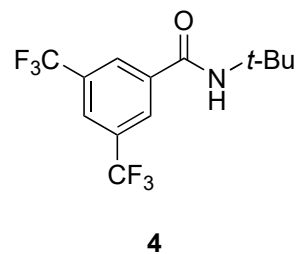


B

18 - 22



bipolarolide B



- 18) 9-BBN, NaOH, Pd(PPh₃)₄, **3**
 19) **4**, *n*-Bu₄NPF₆, *n*-Bu₄NOH, HFIP, RVC(+)-Ni(-)
 20) SeO₂
 21) DIBAL-H

- 18) Name of the reaction?
 19) *Hint*: ring formation