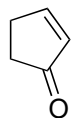


# Total Synthesis of the Meroterpenoid Manginoid A as Fueled by a Challenging Pinacol Coupling and Bicycle-forming Etherification

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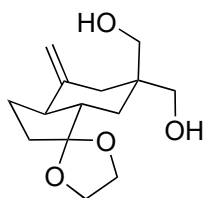
1-2

**A**

**B**

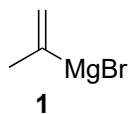
1 : 2.5

6 - 10

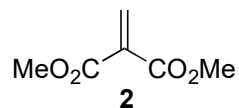


**c**

- 1) **1**, CuI, TMSCl, HMPA, -78 °C
- 2) TIPSOTf, KHMDS



- 6) **2**, SnCl<sub>4</sub>
- 7) ethylene glycol, *p*-TsOH•H<sub>2</sub>O, CH(OMe)<sub>3</sub>
- 8) TCCA
- 9) NaH
- 10) LiAlH<sub>4</sub>



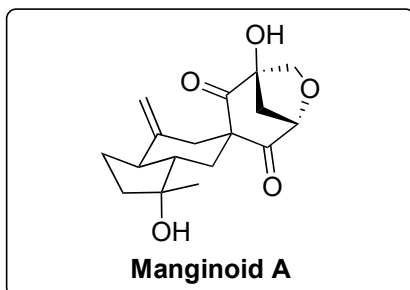
2) Tip: A and B are regioisomeric silyl enol ethers

8) What is the structure of TCCA?

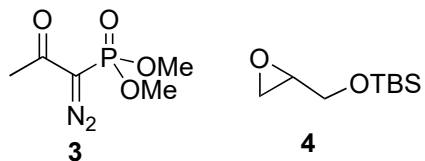
10 - 15



16-22



- 10) NIS; DMP
- 11) **3**, K<sub>2</sub>CO<sub>3</sub>, MeOH
- 12) LiHMDS, BF<sub>3</sub>•OEt, **4**
- 13) Zn, AcOH
- 14) Pd/C, H<sub>2</sub>, quinoline
- 15) DMP



- 16) Sml<sub>2</sub>, -78 °C
- 17) NBS *then* H<sub>2</sub>O *then* K<sub>2</sub>CO<sub>3</sub>, MeOH
- 18) n-BuLi, -78 °C *then* TBAF
- 19) K<sub>2</sub>CO<sub>3</sub>, MeOH
- 20) Swern
- 21) FeCl<sub>3</sub> in acetone
- 22) MeMgBr, LaCl<sub>3</sub>•2LiCl, -78 °C

11) Named reaction?

16) Named reaction? Provide a rationale on why a single diastereomer was produced.

17) Justify selectivity.

20) Tip: Double Swern.