

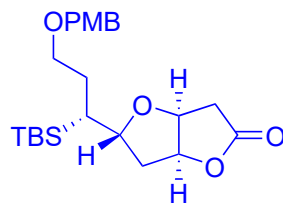
General Synthetic Approach for the *Laurencia* Family of Natural Products Empowered by a Potentially Biomimetic Ring Expansion

Yu-An Zhang, Natalie Yaw, and Scott A. Snyder.

J. Am. Chem. Soc. **2019**, *141*, 7776–7788.



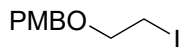
1 - 7



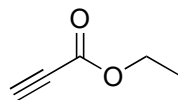
A

8 - 16

- 1) LDA, TBSCl, TBAI then *n*BuLi, **1**, THF, 0 °C to 25 °C
- 2) AcOH (1 M in H₂O), CH₂Cl₂, 25 °C
- 3) MeMgBr, THF, -78 °C
- 4) DMP, NaHCO₃, CH₂Cl₂, 25 °C
- 5) LDA, acrolein, THF, -78 °C
- 6) Et₂BOMe, LiBH₄ then H₂O₂, NaOH
- 7) PdCl₂, CuCl₂, NaOAc, CO, AcOH, 25 °C



1



2

- 8) AlMe₃, MeONHMe.HCl, THF, 0 °C to 25 °C
- 9) TBSCl, imidazole, DMF, 25 °C
- 10) DIBAL-H (1.1 equiv), CH₂Cl₂, -78 °C
- 11) Br₂, NEt₃, P(OPh)₃, CH₂Cl₂, -78 °C to 25 °C
- 12) TBAF, THF, 0 °C to 25 °C
- 13) NMM, **2**, CH₂Cl₂, 25 °C
- 14) AIBN, *n*Bu₃SnH, benzene, 90 °C
- 15) LiAlH₄, THF, -78 °C
- 16) PhSeCN, P(*n*-oct)₃, then H₂O₂, THF, 25 °C

5) *Hint*: 1,2-addition

6) Name of the reaction?

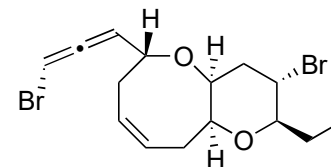
Narasaka-Prasad reduction

7) *Hint*: two 5-membered rings are formed
Name of related reaction? Provide a mechanism

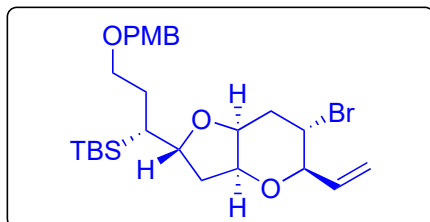
Wacker oxidation

16) Name of the reaction?

Grieco elimination

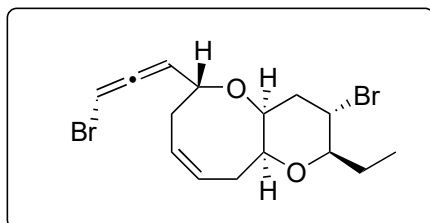


microcladallene A



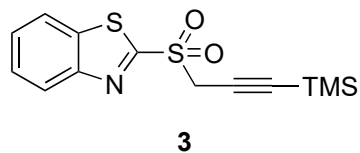
B

17 - 20



microcladallene A

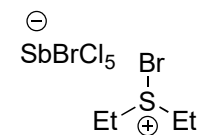
- 17) Pd/C, H₂, EtOAc, 25 °C
- 18) DMP, NaHCO₃, CH₂Cl₂, 25 °C
- 19) KHMDS, **3**, then TBAF, THF, -20 °C to 0 °C
- 20) BDSB, EtNO₂, -78 °C



19) Name of the reaction?

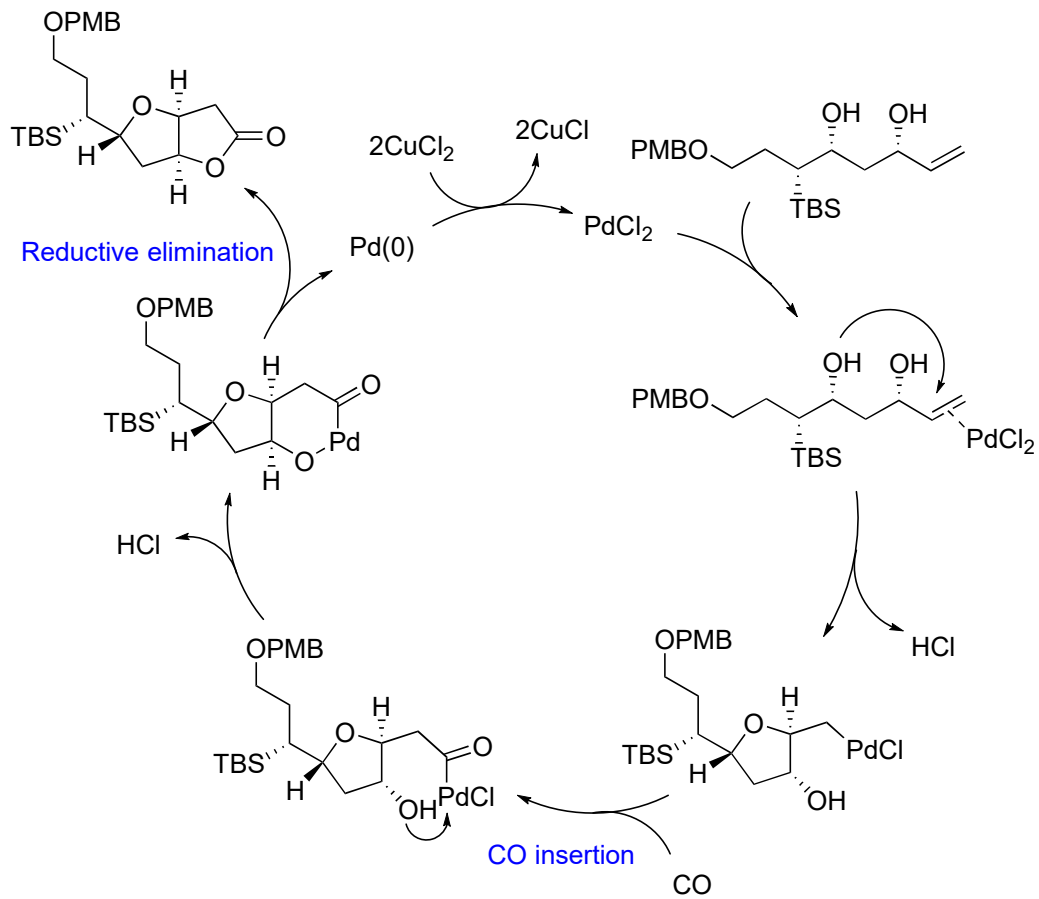
Julia-Kocienski olefination

20) *Hint*: BDSB = brominating agent



20) Provide a mechanism.

Step 7 mechanism:



Step 20 mechanism:

