

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

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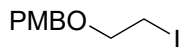
1 - 7



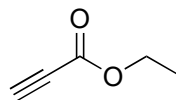
A

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

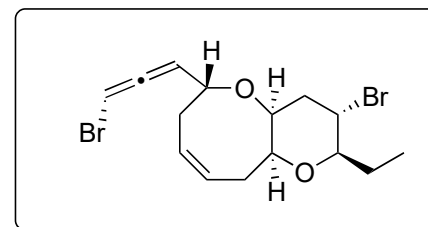


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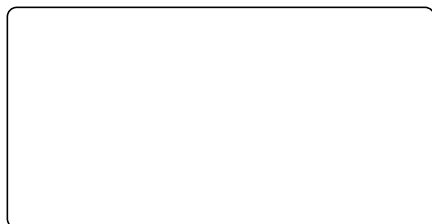
- 8) AlMe₃, MeONHMe.HCl, THF, 0 °C to 25 °C
- 9) TBSCl, imidazole, DMF, 25 °C
- 10) DIBAL-H (1.1 equiv), CH₂Cl₂, -78 °C
- 11) Br₂, NEt₃, P(OPh)₃, CH₂Cl₂, -78 °C to 25 °C
- 12) TBAF, THF, 0 °C to 25 °C
- 13) NMM, **2**, CH₂Cl₂, 25 °C
- 14) AIBN, *n*Bu₃SnH, benzene, 90 °C
- 15) LiAlH₄, THF, -78 °C
- 16)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

- 5) *Hint*: 1,2-addition
- 6) Name of the reaction?
- 7) *Hint*: two 5-membered rings are formed
Name of related reaction? Provide a mechanism

- 16) Name of the reaction?

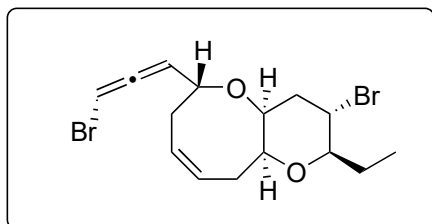


microcladallene A



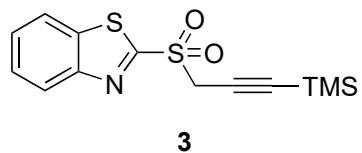
B

17 - 20

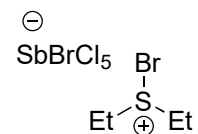


microcladallene A

- 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?
- 20) *Hint*: BDSB = brominating agent



- 20) Provide a mechanism.