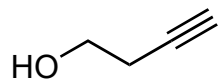


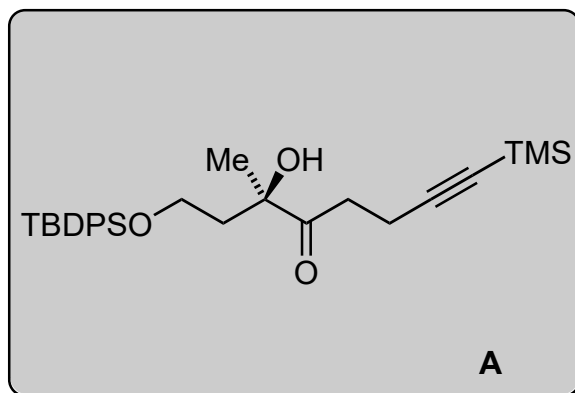
Asymmetric Total Synthesis of (-)-Phaeocaulisin A

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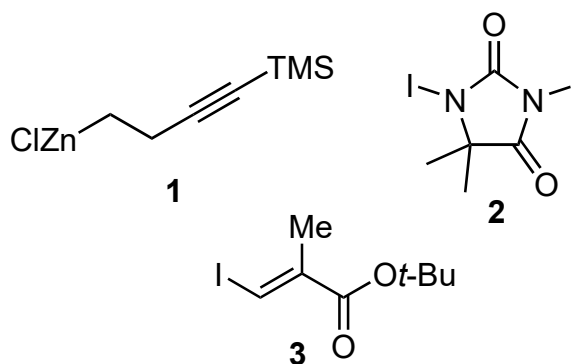


1-5



6-10

- 1) Cp_2ZrCl_2 , AlMe_3
then I_2
- 2) TBDPSCI, ImH
- 3) **1**, $\text{Pd}(\text{PPh}_3)_4$
- 4) $\text{K}_2\text{OSO}_4 \cdot 2\text{H}_2\text{O}$, (DHQD)pyr
 MeSO_2NH_2 , $\text{K}_3\text{Fe}(\text{CN})_6$, *t*-BuOH
- 5) $(\text{COCl})_2$, DMSO, Et_3N



- 6) vinylMgBr, $\text{LaCl}_3 \cdot 2\text{LiCl}$
- 7) TBAF
- 8) TEMPO, **2**
- 9) $(\text{PPh}_3\text{AuNTf}_2)_2 \cdot \text{PhMe}$, H_2O
- 10) **3**, $\text{Pd}(\text{OAc})_2$, Ag_2CO_3

please consider giving hints or intermediates, if a transformation is particularly difficult.

1) Provide a mechanism and explain the geometry of product

3) Name of the reaction?

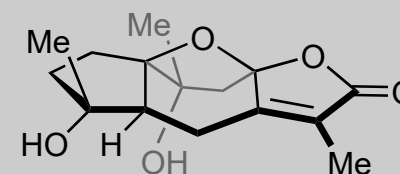
4) Name of the reaction?

5) Name of the reaction and mechanism? What could be a potential problem and how would you solve it?

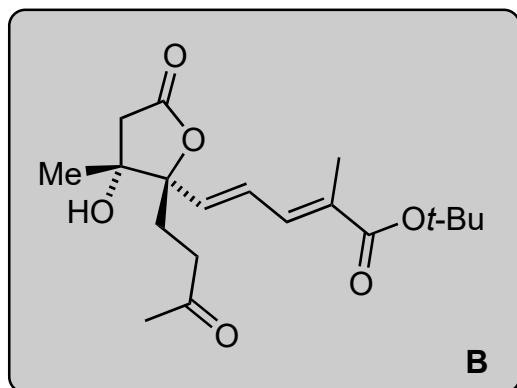
7) **Hint**: double deprotection

8) **Hint**: a lactone forms ultimately

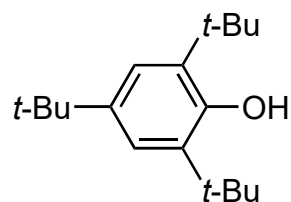
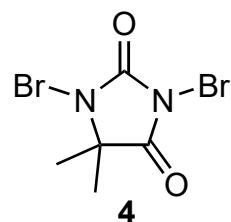
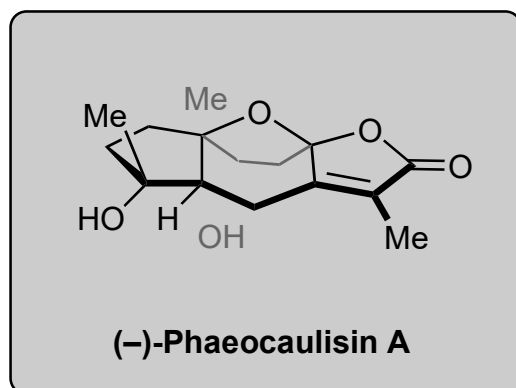
10) Name of the reaction



(-)-Phaeocaulisin A



11-17



- 11) SmI_2 , TPPA, 2,4,6-TTBP
- 12) TFA, *then* TMSCHN_2 , *then* DBU
- 13) SmI_2 (2 equiv.), TPPA, *t*-BuOH
- 14) TMSOTf, Et_3N
- 15) LDA, *then* **4**
- 16) AgOAc
- 17) 1 M HCl

11) How would you classify this reaction according to Baldwin's rule?

13) Rationalize based on Baldwin's rule