Asymmetric Total Synthesis of (–)-Phaeocaulisin A

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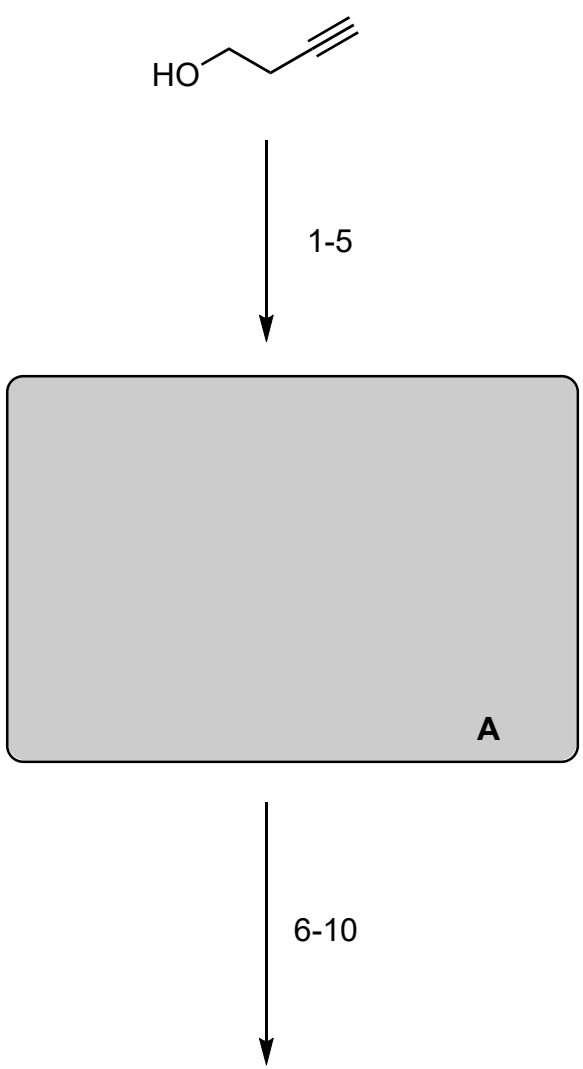
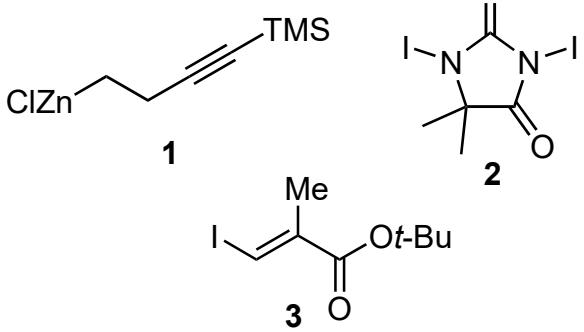


1) Cp_2ZrCl_2, $AlMe_3$
   then I_2
2) TBDPSCl, ImH
3) **1**, $Pd(PPh_3)_4$
4) $K_2OSO_4 \cdot 2H_2O$, (DHQD)pyr
   $MeSo_2NH_2$, $K_3Fe(CN)_6$, *t*-BuOH
5) $(COCl)_2$, DMSO, Et_3N



6) vinylMgBr, $LaCl_3 \cdot 2LiCl$
7) TBAF
8) TEMPO, **2**
9) $(PPh_3AuNTf_2)_2 \cdot PhMe$, H_2O
10) **3**, $Pd(OAc)_2$, Ag_2CO_3

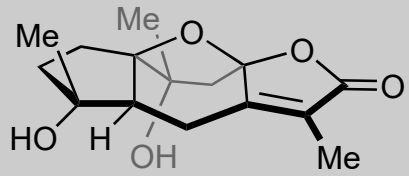
1) Provide a mechanism and explain the geometry of product

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

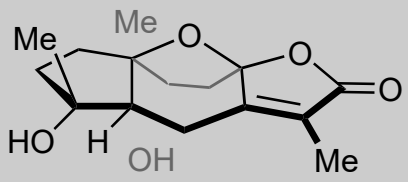
10) Name of the reaction



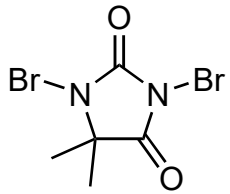
(–)-Phaeocaulisin A

B

11-17



(–)-Phaeocaulisin A



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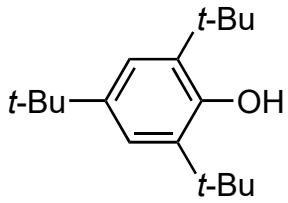

2,4,6-TTBP

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