Total Synthesis of Acoapetaludine A Enabled by a Rhodium-Catalyzed Domino Cyclization

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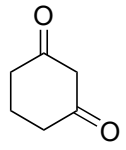

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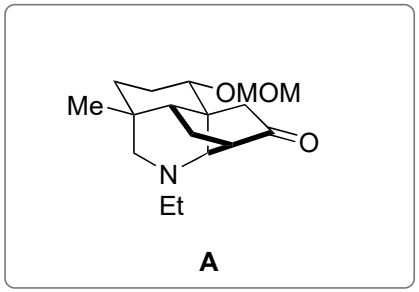
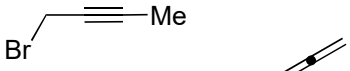


A

1) KOH, **1**
2) **2**, $(allyl)_2Pd_2Cl_2$, **3**
3) $PhB(OH)_2$, $[Rh(cod)OH]_2$
4) $NaBH_4$
5) $SOCl_2$, pyridine
6) MOMBr, DIPEA, TBAI
7) BH_3•THF then $NaBO_3$•$4H_2O$
8) IBX
9) $Ph_3PCH_2OCH_3Cl$, Cl_3CCO_2H
10) MeI, *t*-BuOK
11) $EtNH_2$, $Ti(Oi\text{-}Pr)_4$, $NaBH_4$ then TFAA, DMAP
12) $NaIO_4$, $RuCl_3$•$3H_2O$
13) NaOH



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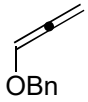

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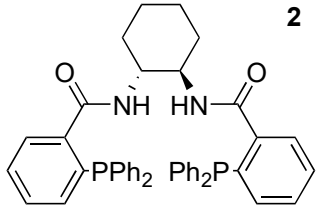

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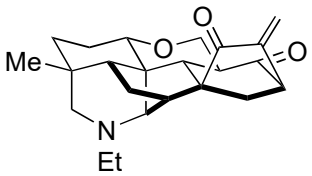
2) Name of the reaction?
Trost asymmetric allylic alkylation

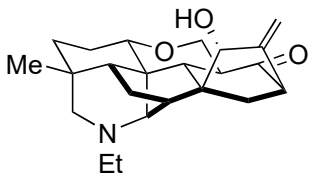
12) Hint: Oxidation in two positions
13) Hint: deprotection/retro-aldol/intramolecular Mannich reaction



Acoapetaludine A

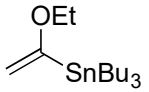
A

14-25



Acoapetaludine A

14) Comins´reagent, LiHMDS
15) I_2, $NaHCO_3$
16) HCl
17) $Pd(PPh_3)$, LiCl, CuCl, **4**
18) NaH, **5**
19) $AlCl_3$
20) LiHMDS, $F_3CCO_2CH_2CF_3$ then *p*-ABSA
21) $Rh_2(OAc)_4$
22) H_2SO_4, AcOH
23) Ac_2O, $CH_2(NMe_2)_2$
24) $LiAlH_4$
25) DBU, **6**



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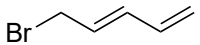

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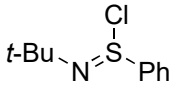

6

17) Name of the reaction?
Stille coupling