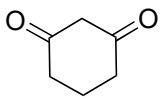
Total Synthesis of Acoapetaludine A Enabled by a Rhodium-Catalyzed Domino Cyclization

Y. Zhang, L. Wang, X. Lei, and Y. Jia. *J. Am. Chem. Soc.* **2025,** *147,* 47904–47910



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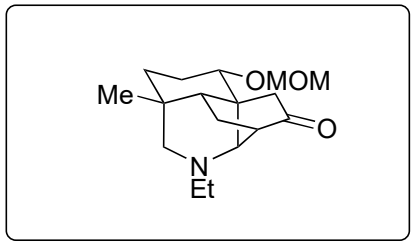
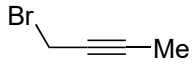


A

1) KOH, **1**
2) [η^3-($C_3H_5PdCl)_2$], **2**, **3**
3) [Rh(cod)OH]$_2$, PhB(OH)$_2$, KOH, dioxane/H_2O, 91%
4) $NaBH_4$
5) $SOCl_2$, py
6) MOMBr, TBAI, DIPEA
7) BH_3•THF *then* $NaBO_3$•$4H_2O$
8) IBX



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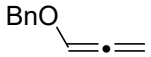

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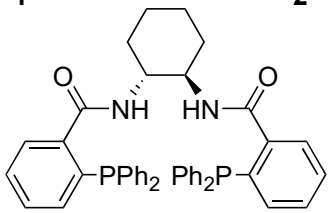

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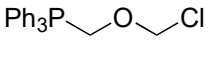
9) **4**, KHMDS
then Cl_3CCO_2H
10) *t*BuOK, MeI
11) $EtNH_2$, Ti(O*i*Pr)$_4$, $NaBH_4$
then TFAA, DMAP
12) $RuCl_3$•$3H_2O$, $NaIO_4$
13) NaOH



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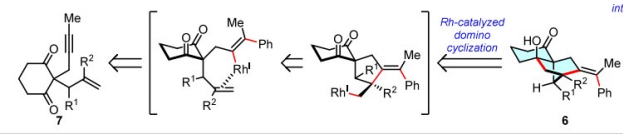
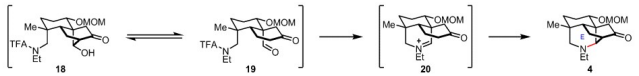
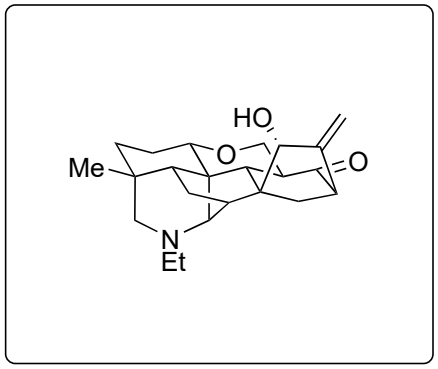
2) Who developed this reaction? *Trost*
3) Mechanism? *Hint: a tricyclic compound is formed*

5) *Hint: tertiary hydroxyl*



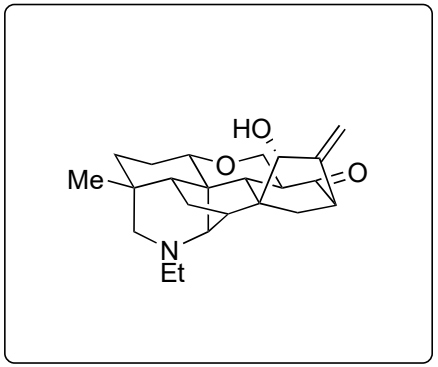
12) *Hint: a protecting group is oxidized*
13) Mechanism?





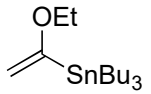
Acoapetaludine A

14-25



Acoapetaludine A

14) LiHMDS, Comins' reagent
15) I_2, $NaHCO_3$
16) HCl
17) $Pd(PPh_3)_4$, CuCl, **5**
18) NaH, **6**
19) $AlCl_3$
20) LiHMDS, $F_3CO_2CH_2CF_3$, *p*-ABSA
21) $Rh_2(OAc)_4$
22) H_2SO_4
23) Ac_2O, $CH_2(NMe_2)_2$
24) $LiAlH_4$
25) DBU, **7**



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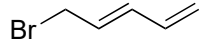

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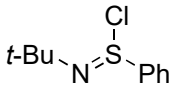

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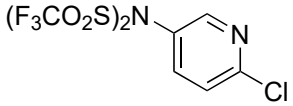
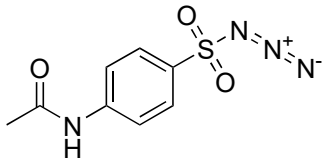
14) Structure of the Comins' reagent?



17) Name of the coupling? *Stille*

19) Name of the reaction? *Diels-Alder*
20) Structure of *p*-ABSA?



25) Who developed this reagent? *Mukaiyama*