Total Synthesis Cyclopiamine B

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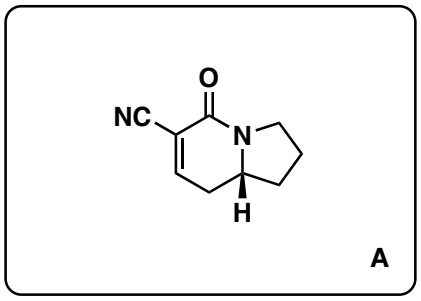
Nature **2014**, *509*, 318–324.

(*R*)-Proline

1–7



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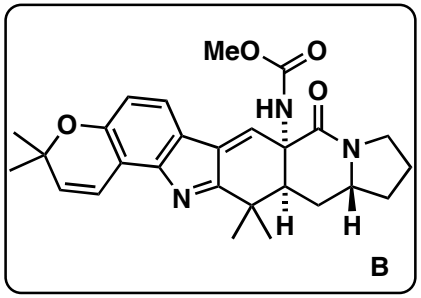
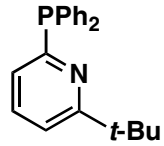
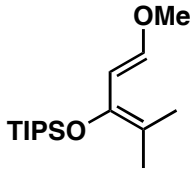


1) Boc_2O, $NaHCO_3$
2) $BF_3 \cdot THF$
3) $(COCl)_2$, DMSO, *i*-Pr_2NEt
4) $N_2CHPO(OMe)_2$, K_2CO_3
5) HCl
6) 2-cyanoacetylchloride, NEt_3
7) $[Ru(Cp)(MeCN)L_2]PF_6$, H_2O, 70 °C



L

8) **1**, $SnCl_4$
9) I_2, py, DMAP
10) **2**, EtOH, H_2O
11) PIFA, MeOH
12) **3**, $dppfPdCl_2$, K_3PO_4
13) Zn, NH_4Cl, HCO_2NH_4, *p*-TsOH



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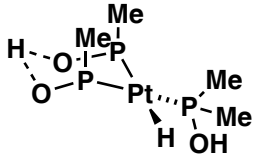

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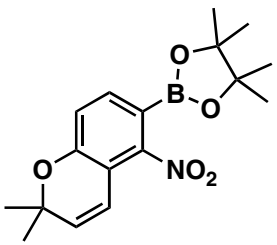

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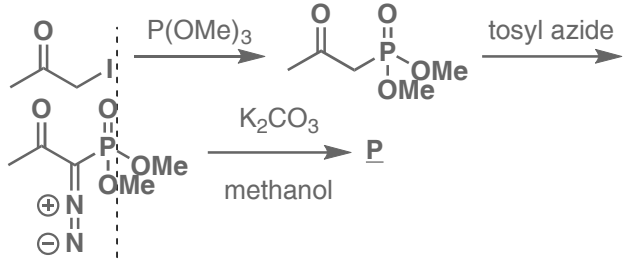
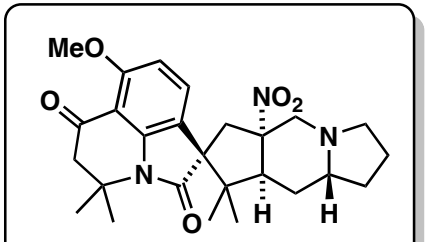
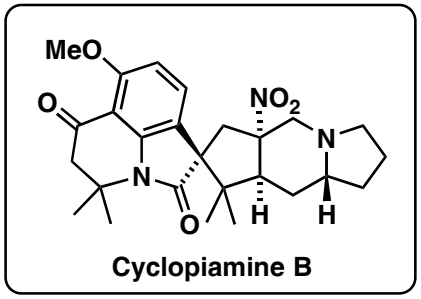


Step 4: Please name the reaction. How would you prepare this reagent?
Seyferth–Gilbert homologation
Step 7: Hint: Two reactions take place.
anti-Markownikow hydration and Knoevenagel condensation
plausible mechanism below

Step 10: What is the name of the catalyst? What is the machanism?
Ghaffar–Parkins catalyst
mechanism below



14–21

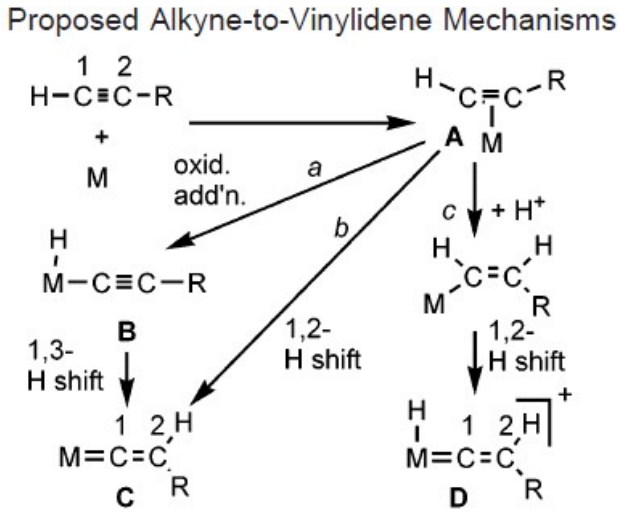


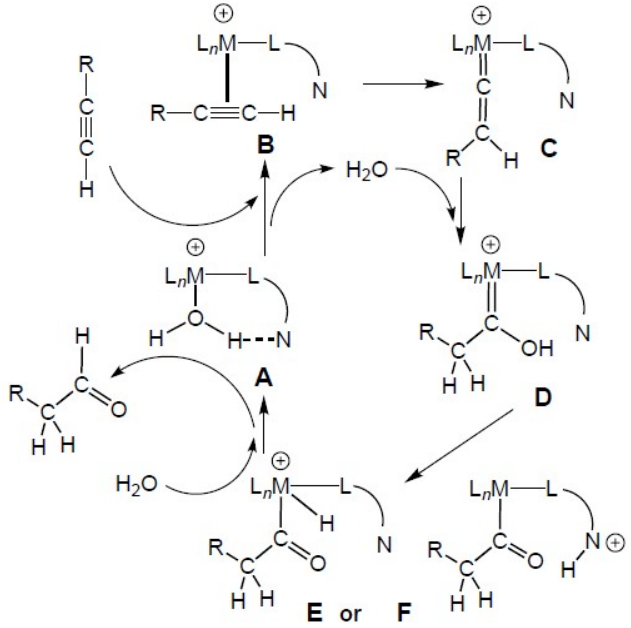
Cyclopiamine B

14) $NaCNBH_3$, HCl
15) $Pd(OAc)_2$, benzoquinone, H_2SO_4
16) Me_2S, MsOH
17) oxone, $NaHCO_3$, acetone
18) Me_3OBF_4
19) $NaCNBH_3$
20) NaH, DMF, 60 °C
21) MeI, K_2CO_3

Step 15: Please name the reaction. What is the role of benzoquinone?
Wacker oxidation; benzoquinone is used for the oxidationof Pd(0) to Pd (II)

step 7:





Scheme 2. Probable intermediates and mechanism of alkyne hydration.

step 10: