Enantioselective Total Synthesis of (+)-Aberrarone

W. M. Amberg, E. M. Carreira

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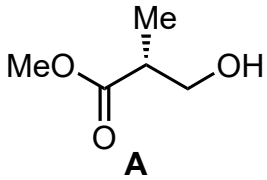
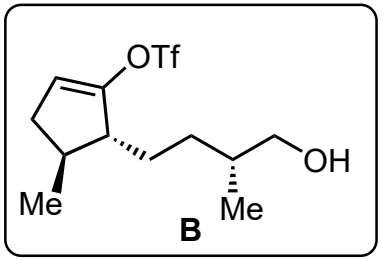


A

1-7



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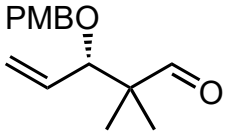
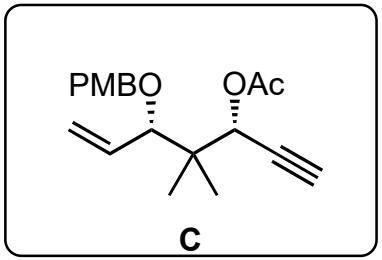
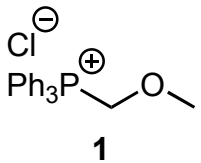


8-10



C

1. TBDPSCl, Im.
2. DIBAL-H
3. **1**, NaHMDS
   then HCl 2M
4. **2**, MeLi
   then starting material
5. NaHMDS, CS_2, MeI
6. *n*-Bu_3SnH, AIBN
7. KHMDS, Comins' reagent
   then TBAF



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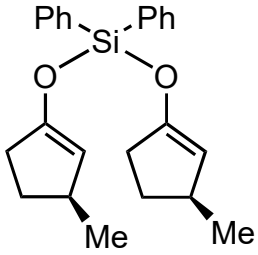

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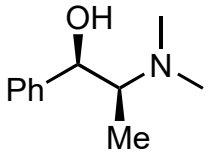
8. **3**, $Zn(OTf)_2$, Et_3N, **4**
9. TBAF
10. Et_3N, DMAP, Ac_2O



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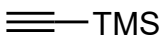

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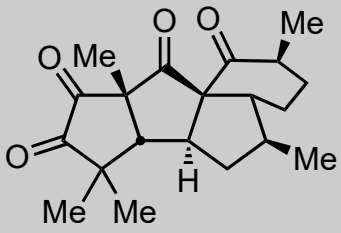
1. What is the name of starting material **A**?
   (*R*)-Roche ester

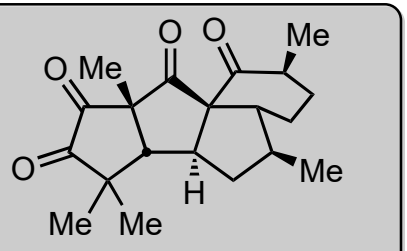
8.
i) What is the name of the chiral ligand used? N-methylephedrine

ii) What is the intermediate species?



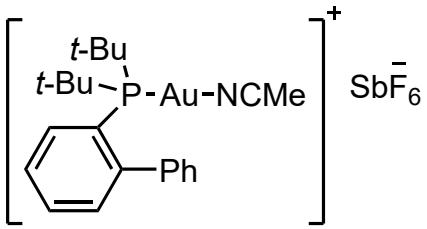
(+)-Aberrarone

11-18



(+)-Aberrarone

11. **B**, Et_3N, $PdCl_2(PPh_3)_2$, CuI
    then **C**
12. DMSO, DIPEA, SO_3•Py
13. **5**
    then, *n*-Bu_3SnOMe
14. DDQ
15. $LiAlH_4$
16. PtO_2, H_2
17. DMSO, DIPEA, SO_3•Py
18. SeO_2



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11. What is the name of the reaction?
    Sonogashira coupling
12. What is the name of the reaction?
    Parikh-Doering oxidation

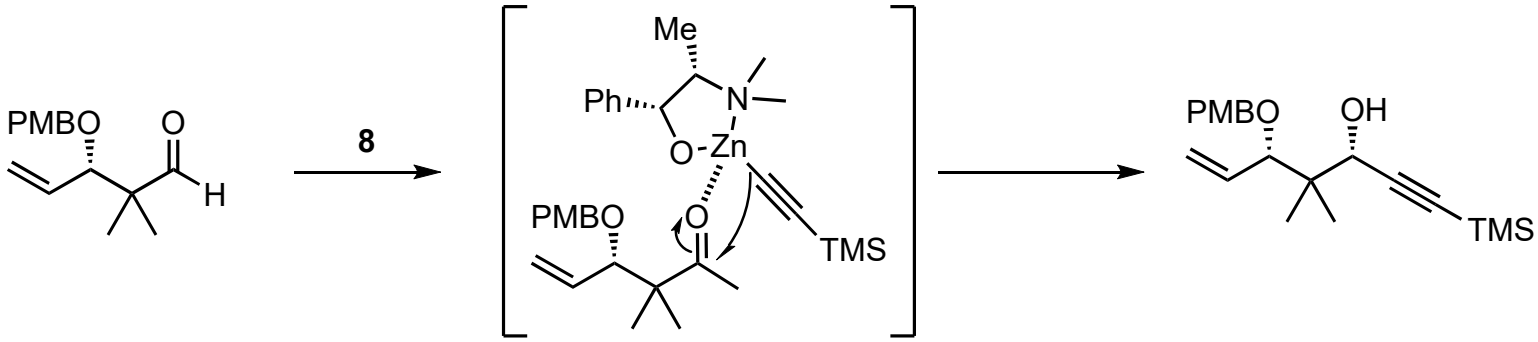
13.

i) What is the name of the gold catalyst and the phosphine ligand contained therein?
Echavarren's catalyst and JohnPhos

ii) Please draw the mechanism of the Au-cascade reaction.
see page below

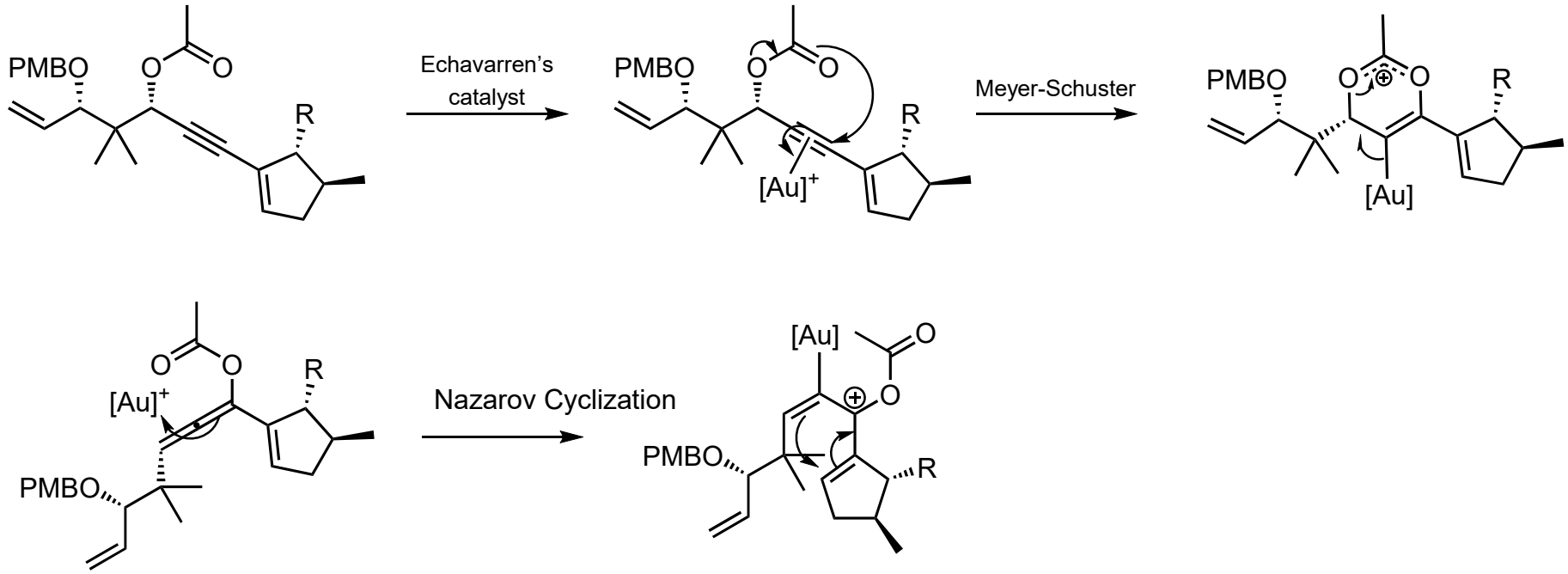
iii) What is the role of *n*-Bu_3SnOMe?
Hydrolysis of the ester followed by Sn-mediated aldol addition

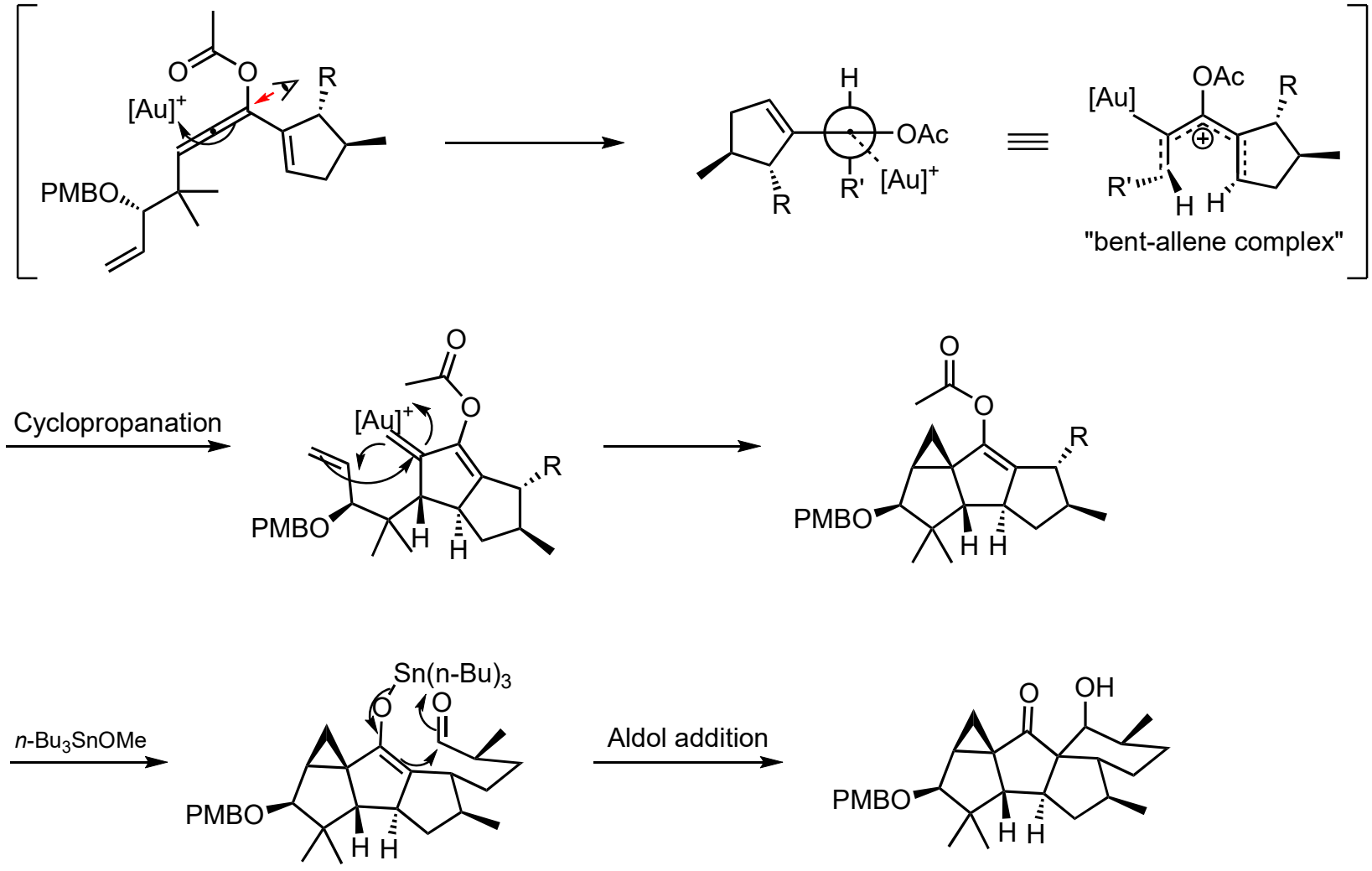
Step 8



see more: Angew. Chem. Ini. Ed. Engl. 30 (1991) 49-69.

Au-cascade reaction





See more: J. AM. CHEM. SOC. 2009, 131, 2993–3006