Catalytic Asymmetric Total Synthesis of (−)-Garryine via anEnantioselective Heck Reaction

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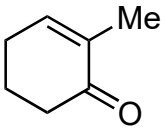
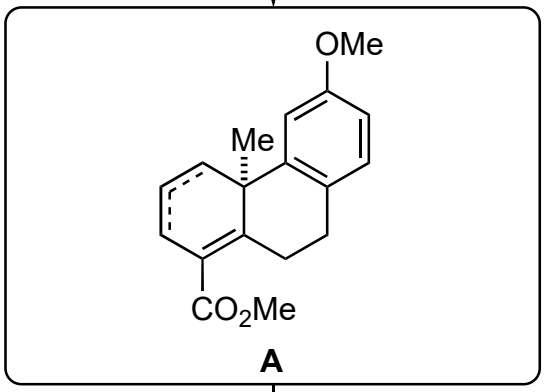
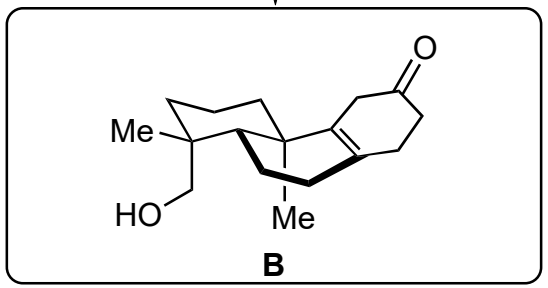


1) LiHMDS, $ClCO_2Me$;
then Tf_2O
2) **1**, 9-BBN, THF, 23 °C; *then* H_2O;
then **product of step 1**, $Pd(PPh_3)_4$,
K_3PO_4, 60 °C
3) *p*-TsOH
4) Tf_2O, Et_3N
5) $Pd_2(dba)_3$, **L**, PMP, PhF, 80 °C

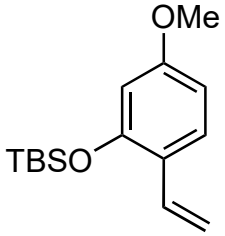


A

6) $Pd(OH)_2/C$, H_2
7) LDA, MeI
8) Li, NH_3 (liq.)



B



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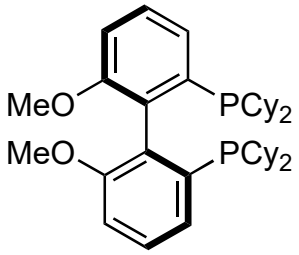


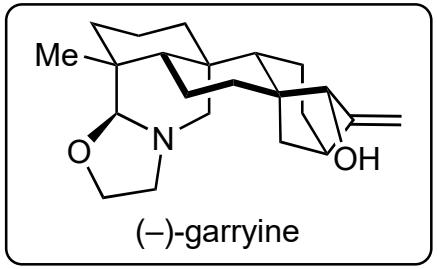
L

2) Name of the reaction?
Suzuki coupling

5) Name of the reaction?
Heck reaction

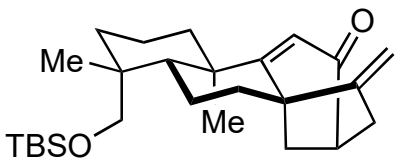
6) Name of the catalyst?
Pearlmans catalyst

8) Name of the reaction?
Birch reduction
Hint: Two reactions



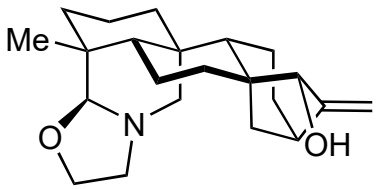
(–)-garryine

9) *m*-CPBA
10) Et_3N
11) $Sc(OTf)_3$
12) TBSCl
13) **2**, LiHMDS, HMPA
14) AIBN, *n*-Bu_3SnH

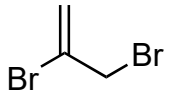


C

15) OsO_4, $NaIO_4$
16) Lawesson's reagent
17) Raney-Ni; *then* Pd/C, H_2
18) LiHMDS, MeI; *then* Comins reagent
19) $Pd(OAc)_2$, PPh_3, HCO_2H
20) TPP, O_2, *hv*; *then* Me_3P
21) Ac_2O
22) *p*-TsOH
23) PIDA, I_2, *hv*; *then* ethanolamine
24) K_2CO_3, MeOH



(–)-garryine



2

11) *Hint: Elimination*
14) *Hint: Natural product like*

15) Name of the reaction?
Lemieux–Johnson

16) *Hint: selective for the enone*

20) Name of the reaction?
Schenck ene reaction

23) Name of the reaction?
Suárez oxidation

Hint: Oxidation of the alcohol instead of ether formation after iodination