Asymmetric Total Synthesis of (+)-6-epi-Castanospermine by theStereoselective Formation of asyn,antiAcetylenic 2-Amino-1,3-diol Stereotriad

Louvel,J.; Botuha, C.; Chemla, F.; Demont, E.; Ferreira, Fr.; Pérez-Luna, A.

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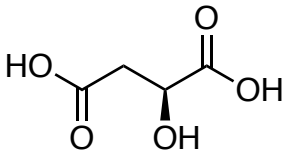
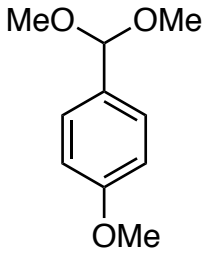


1-5

A

6-11

1) $BH_3 \cdot SMe_2$
2) **1**, CSA
3) TBDPSCl, imidazole
4) DIBAL-H, -78 °C
5) TsCl, Et_3N



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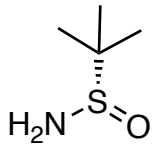

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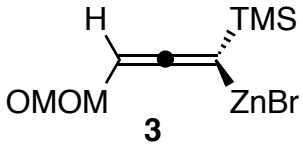
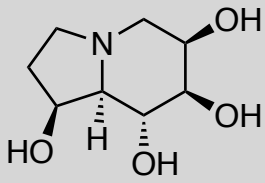


3

6) LiCl, acetone, *reflux*
7) TBAF
8) DMSO, $(COCl)_2$
9) **2**, $Ti(OEt)_4$
10) **3**, -78 °C
11) NaH, 15-crown-5

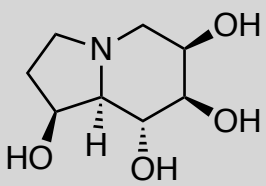
1) Name of starting material:
2) Hint: A six-membered ring is formed
8) Name the reaction:
9) Name reagent **2**:



(+)-6-*epi*-castanospermine

B

12-17



(+)-6-*epi*-castanospermine

12) H_2, Lindlar catalyst
13) HCl, MeOH, 0 °C, *then* NEt_3, allyl bromide
14) Grubbs II
15) OsO_4, NMO
16) HCl, MeOH, *reflux*
17) H_2, Pd/C

13) Hint: Chemoselective hydrolysis
15) Name the reaction: