A 11-Steps Total Synthesis of Magellanine through a Gold(I)-Catalyzed Dehydro Diels-Alder Reaction

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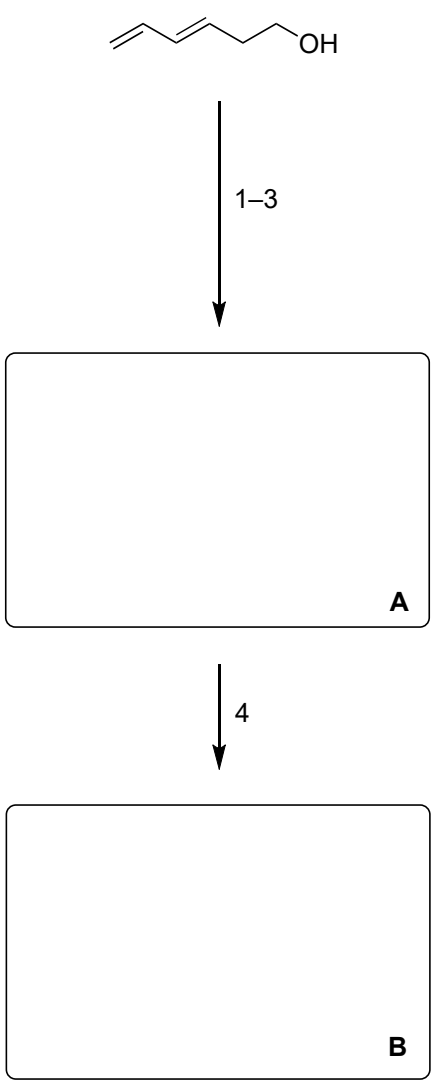
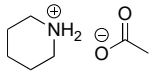
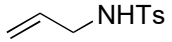
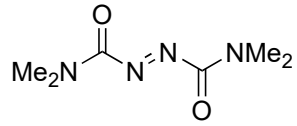


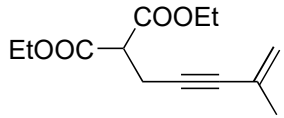
1) P^tBu_3, **W**, **X**, RT over night,
then reflux xylene
2) OsO_4, NMO,
then $NaIO_4$
3) 

, toluene reflux

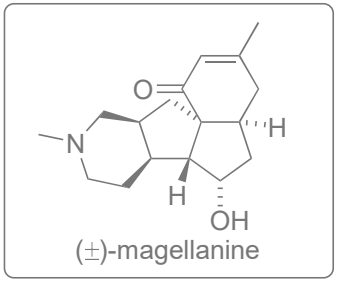
4) **A**, TIPSOTf, Me_2S
then solution of **Y** and LHMDS

W 

X 

Y 

Think of a mechanism for step 4!



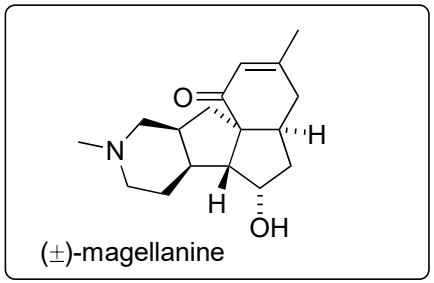
(±)-magellanine

5

C

6–11

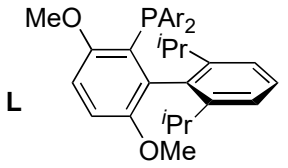
9b)



(±)-magellanine

5) [**L**AuNCMe]SbF_6
then CSA
(91%)

Think of a mechanism for step 5!



L Ar = 3,5-$(CF_3)_2C_6H_3$

6) TBAF
then LiOH (140 °C)
then HCl
7) DMP
8) PtO_2, 1 atm H_2
9) (EtO)COCl, *N*-methylmorpholine
then mercapto-4-methylthiazole 3-oxide, NEt_3,
then t-dodecylmercaptan,
O_2, 365 nm LED
then PPh_3
[9 b) DIAD, PPh_3, HCOOH,
then LiOH]
10) Na, $C_{10}H_8$,
then HOAc, $CH_2O_{(aq)}$,
then $NaBH_3CN$
11) LDA, *then* TMSCl, *then* LDA, **Z**,
then HCl, NaOH workup

Think of a mechanism for step 9!

Think of a mechanism for step 11!