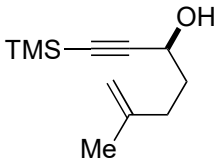
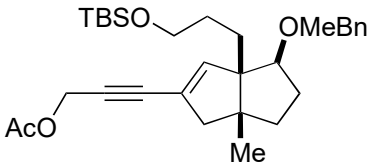
Total Synthesis of (−)-Bipolarolide D

G. A. Chesnokov, J. Friedli, F. J. Carta, K. Gademann, *JACS Au*, **2024**, DOI: https://doi.org/10.1021/jacsau.4c00680

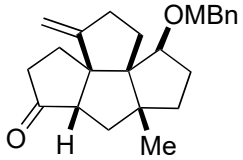


1 - 4



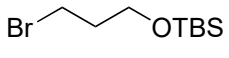
A

5 - 9



B

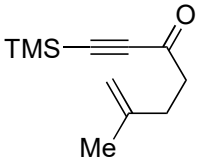
1) K_2CO_3, MeOH *then* MeBnCl
2) $Co(CO)_8$
3) *t*BuLi, CuI, **1** *then* Comins´ reag.
4) propargyl alcohol, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N *then* Ac_2O



1

5) $Au(PPh_3)Cl$, $AgNTf_2$ *then* AcCl, MeOH
6) $SO_3 \cdot Py$, DMSO
7) Ohira-Bestmann reag.
8) $HSnBu_3$, AIBN
9) CSA

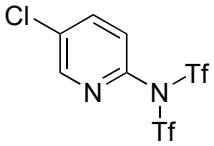
How you would prepare starting material enantioenriched?



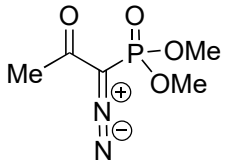
Noyori asymmetric hydrogenation → TM

Org. Lett. **2005**, *7*, 287

2) Name of the reaction?
Pauson-Khand reaction
3) Structure of the Comins´ reagent?



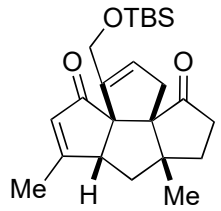
5) Name of the reaction? Mechanism of the reaction
Rautenstrauch reaction
7) Structure of Ohira-Bestmann reagent?



12-15

10) LiHMDS, TMSCl *then* O_2, $Pd(OAc)_2$
11) *m*-CBPA
12) MeLi
13) LiTMP, Et_2AlCl
14) TBSCl *then* Na, NH_3 (l)
15) PCC

10) Name of the reaction?
Saegusa-Ito dehydrogenation



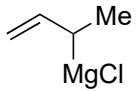
C

17-20

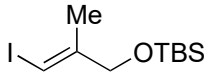
16) **2**
17) **3**, 9-BBN, 3, $Pd(PPh_3)_4$
18) $SOCl_2$
19) TBAF

Hint: In step 16 cyclization occurs

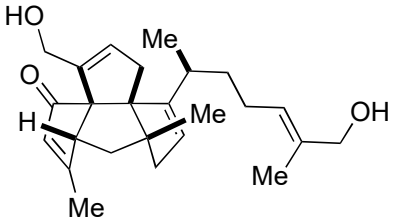
17) Name of the reaction?
Suzuki coupling



2



3



Bipolarolide D

Mechanism for step 5: