Total Synthesis of Echinopines A and B

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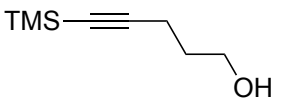
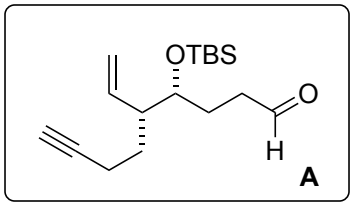
Org. Lett. **2011**, *13*, 5724–5727.

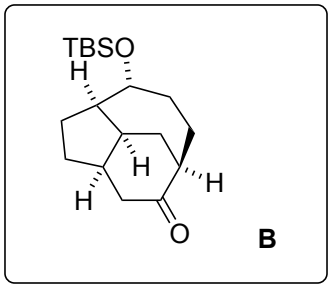


1-7



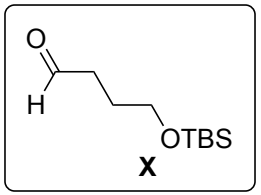
A

8-12



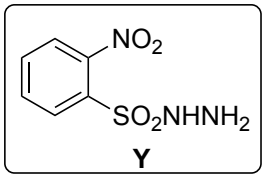
B

1) $(COCl)_2$, DMSO, NEt_3
2) Ph_3PCH_3I, *n*-BuLi, *then* $TMSCH_2I$, *then n*-BuLi, *then* product of step 1
3) **X**, $TiCl_4$
4) TBSOTf, NEt_3
5) *p*-TsOH
6) K_2CO_3, MeOH
7) $(COCl)_2$, DMSO, NEt_3



X

8) nitromethane, TMG
9) Ac_2O, pyridine
10) $Pd(OAc)_2$, PPh_3
11) **Y**, NEt_3
12) KO*t*-Bu, oxone, Na_2HPO_4



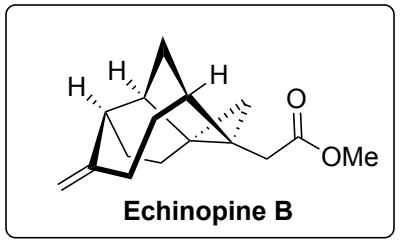
Y

Name of step 3?
Hosomi–Sakurai reaction

Name of step 8?
Henry reaction

Mechanism for step 10?

Name and Mechanism for step 12?
Nef-reaction

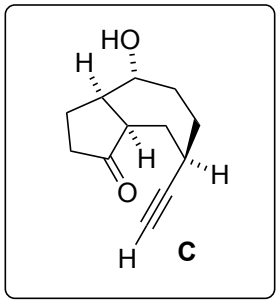


Echinopine B

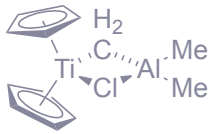
13-16

13) LDA, PhSeBr
14) H_2O_2
15) NaOH, H_2O_2
16) $TsNHNH_2$, TFA, HCl

Name of step 16?
Eschenmoser fragmentation



C

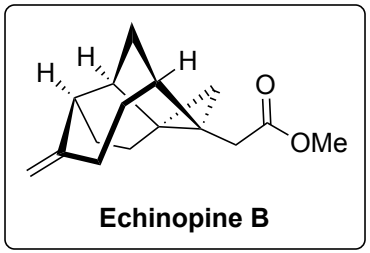


Structure of the Tebbe reagent?

17-23

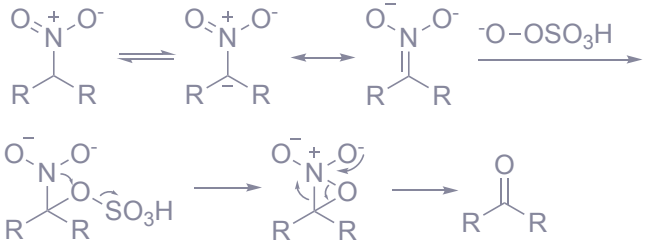
17) DMP
18) Ph_3PCH_3I, *n*-BuLi
19) Tebbe reagent
20) *n*-BuLi, $(CH_2O)_n$
21) $CpRu(PPh_3)Cl$, $In(OTf)_3$, CSA
22) $NaClO_2$
23) $TMSCHN_2$

Mechanism for step 21?

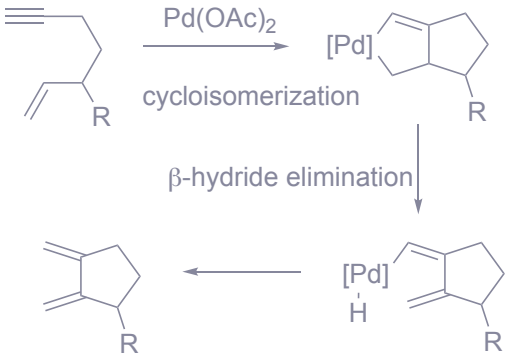


Echinopine B

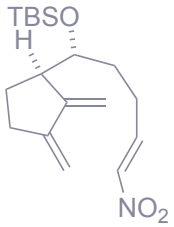
Step 12 Oxone promoted Nef-reaction:



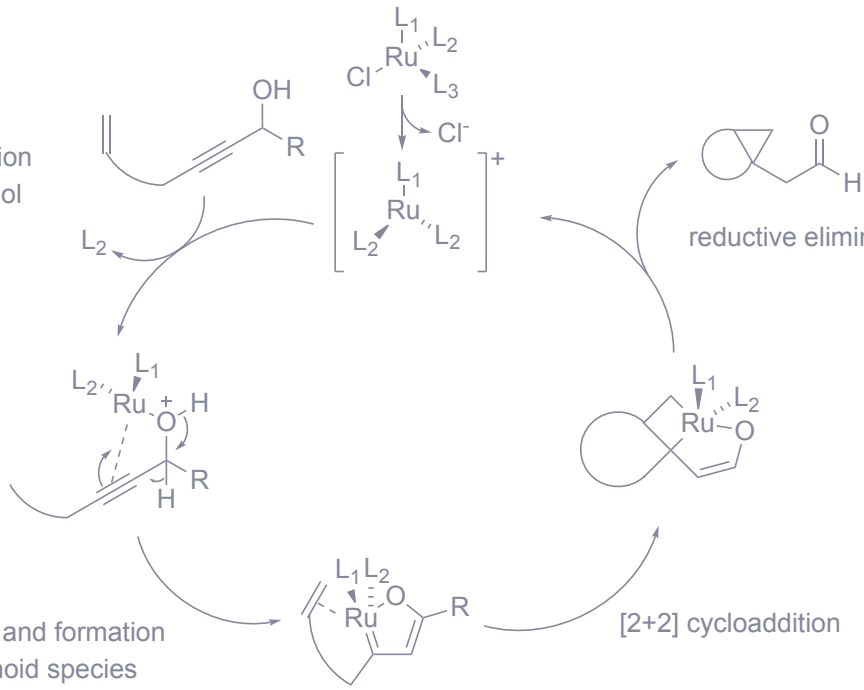
Step 10: *J. Am. Chem. Soc.* **1985**, *107*, 1783-1784.



then Diels–Alder



Catalytic cycle of step 21 as proposed by Trost:



J. Am. Chem. Soc. **2011**, *133*, 4766–4769.