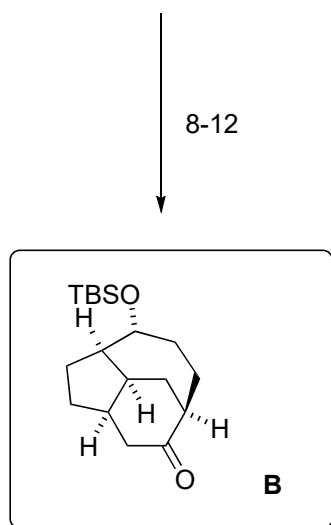
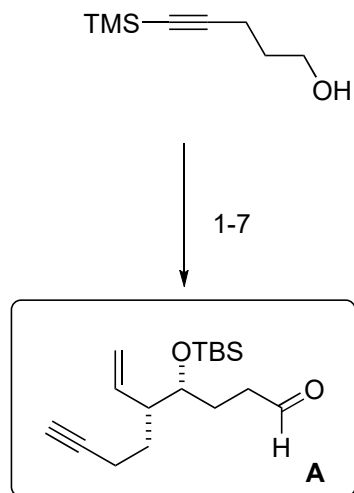


## Total Synthesis of Echinopines A and B

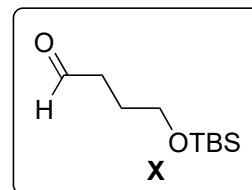
Philippe A. Peixoto, Jean-Alexandre Richard, Rene Severin and

David Y.-K. Chen

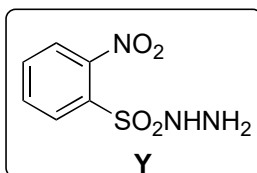
*Org. Lett.* **2011**, *13*, 5724–5727.



- 1) (COCl)<sub>2</sub>, DMSO, NEt<sub>3</sub>
- 2) Ph<sub>3</sub>PCH<sub>3</sub>I, *n*-BuLi, then TMSCH<sub>2</sub>I, then *n*-BuLi, then product of step 1
- 3) **X**, TiCl<sub>4</sub>
- 4) TBSOTf, NEt<sub>3</sub>
- 5) *p*-TsOH
- 6) K<sub>2</sub>CO<sub>3</sub>, MeOH
- 7) (COCl)<sub>2</sub>, DMSO, NEt<sub>3</sub>



- 8) nitromethane, TMG
- 9) Ac<sub>2</sub>O, pyridine
- 10) Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>
- 11) **Y**, NEt<sub>3</sub>
- 12) KO<sup>*t*</sup>-Bu, oxone, Na<sub>2</sub>HPO<sub>4</sub>



Name of step 3?

Hosomi–Sakurai reaction

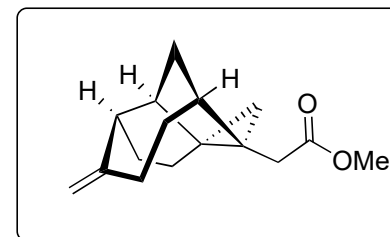
Name of step 8?

Henry reaction

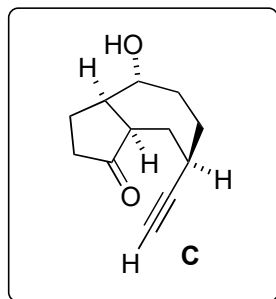
Mechanism for step 10?

Name and Mechanism for step 12?

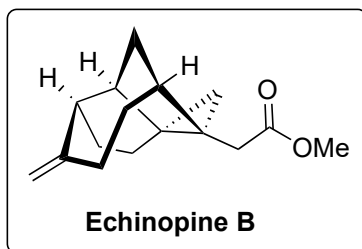
Nef-reaction



13-16



17-23

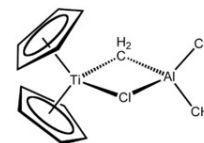


- 13) LDA, PhSeBr
- 14) H<sub>2</sub>O<sub>2</sub>
- 15) NaOH, H<sub>2</sub>O<sub>2</sub>
- 16) TsNHNH<sub>2</sub>, TFA, HCl

- 17) DMP
- 18) Ph<sub>3</sub>PCH<sub>3</sub>I, *n*-BuLi
- 19) Tebbe reagent
- 20) *n*-BuLi, (CH<sub>2</sub>O)<sub>n</sub>
- 21) CpRu(PPh<sub>3</sub>)Cl, In(OTf)<sub>3</sub>, CSA
- 22) NaClO<sub>2</sub>
- 23) TMSCHN<sub>2</sub>

Name of step 16?

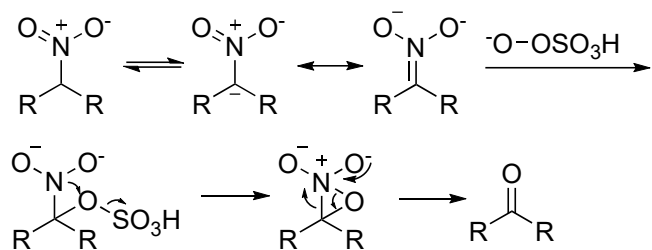
Eschenmoser fragmentation



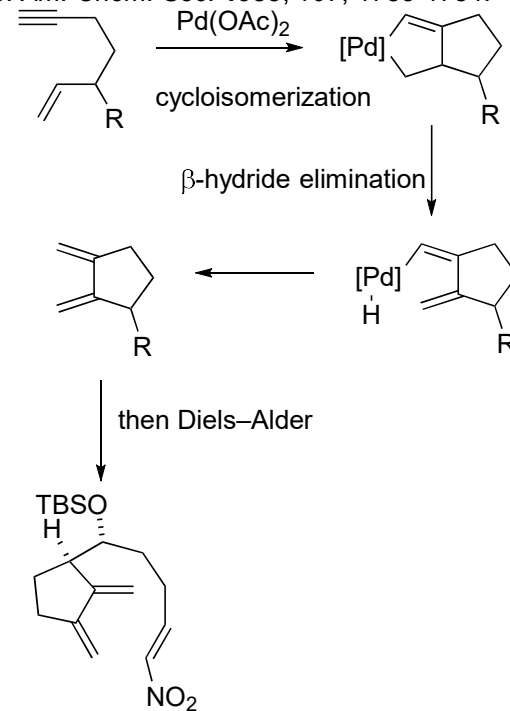
Structure of the Tebbe reagent?

Mechanism for step 21?

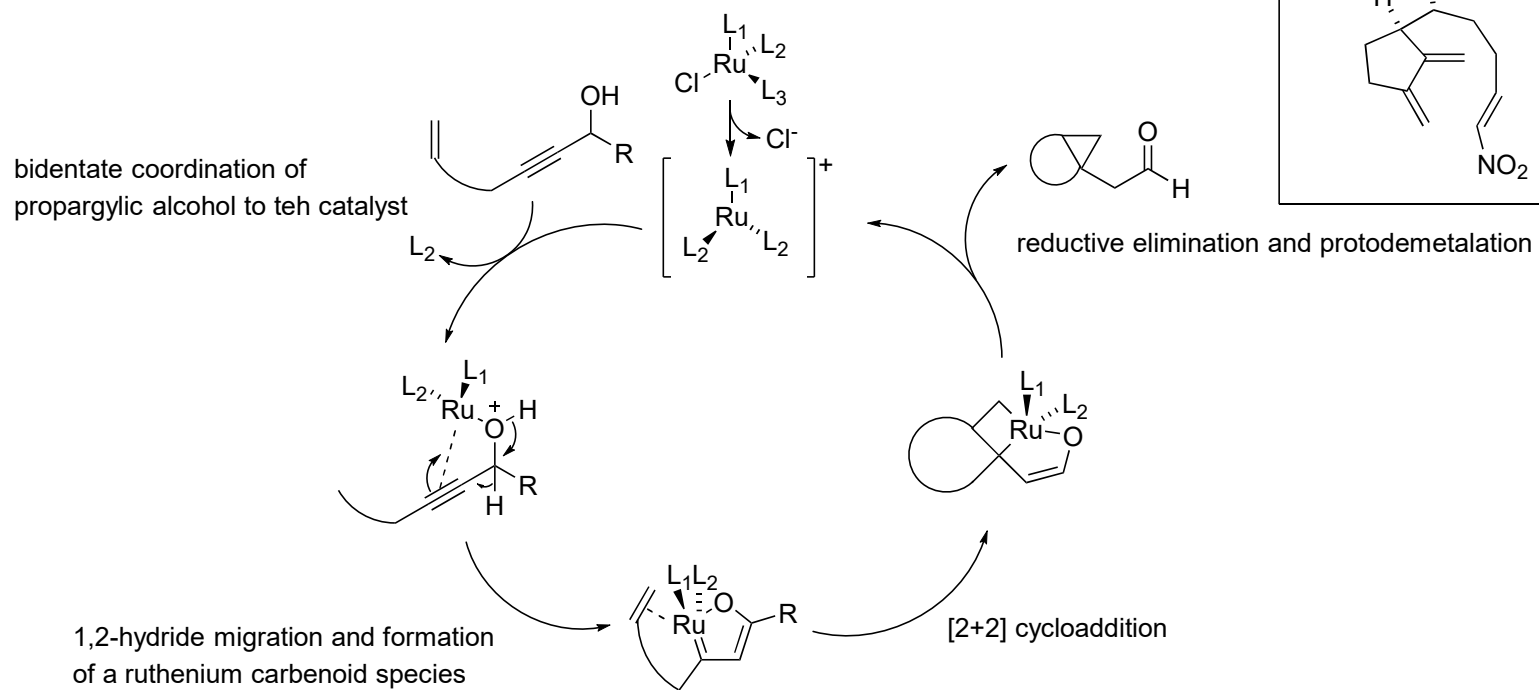
Step 12 Oxone promoted Nef-reaction:



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



Catalytic cycle of step 21 as proposed by Trost:



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