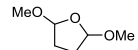
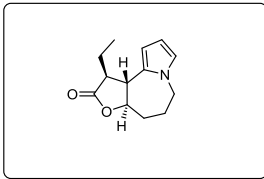


# Total Syntheses of Bisdehydroneostemoninine and Bisdehydrostemoninine

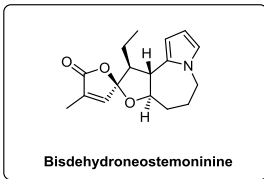
Kaiqing Ma, Xianglin Yin, Mingji Dai, *ACIE* **2018**, *57*, 15209–15212.



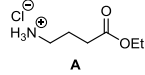
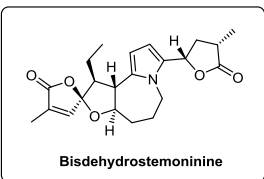
- 1) A, NaOAc, H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, reflux
- 2) MeNH(OMe)·HCl, *i*-PrMgCl, THF
- 3) VinylMgBr
- 4) NaBH<sub>4</sub>, CeCl<sub>3</sub>·7H<sub>2</sub>O, MeOH
- 5) methyl acrylate, Grubbs 2<sup>nd</sup>, PhOH/PhMe, 110 °C
- 6) BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>
- 7) LDA, ethyl iodide, HMPA, THF
- 8) K<sub>2</sub>CO<sub>3</sub>, MeOH, rt



- 9) (O*i*Pr)<sub>2</sub>TiCl, EtMgBr, THF
- 10) [Pd(neoc)(OAc)]<sub>2</sub>(OTf)<sub>2</sub>, benzoquinone, CO (1 atm), DCE
- 11) Eschenmoser's salt, LiHMDS, THF
- 12) MeI, CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, then DBU, THF
- 13) Ru<sub>3</sub>(CO)<sub>12</sub>·NEt<sub>3</sub>, dioxane, 100 °C

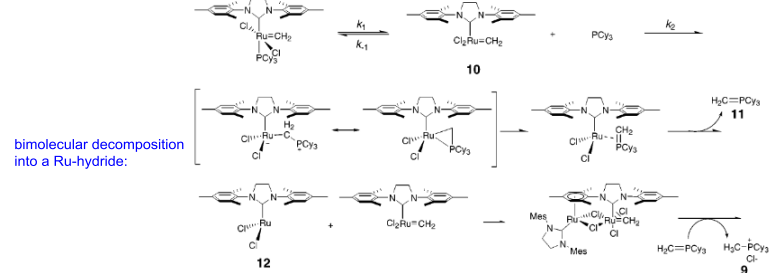


- 14) (COCl)<sub>2</sub>, DMF, AcONa, H<sub>2</sub>O
- 15) B, Zn, THF
- 16) K<sub>2</sub>CO<sub>3</sub>, *t*BuOH
- 17) Pd/C, H<sub>2</sub>, PhH/pyr



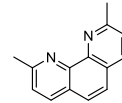
- Step 1: Name Reaction?  
Step 2: What is the role of the Grignard reagent?

- Step 5: PhOH prevents a typical side reaction for these reactants. Which side reaction is it and what exactly is the role of PhOH?



- Step 9: Name Reaction + Mechanism  
Step 10: Mechanism

neoc = Neocoproine



Presumably, phenol coordinates to the catalytically active 14-electron species, leading to a retarded catalyst decomposition

- Step 17: What is the role of pyridine?

forms a Pyridine-Pd complex->more bulky  
-> only attacks exo-methylene

