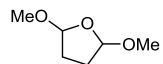


Total Syntheses of Bisdehydroneostemoninine and Bisdehydrostemoninine

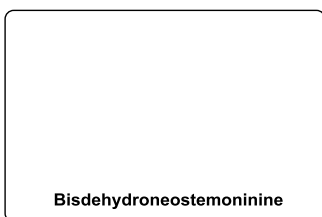
Kaiqing Ma, Xianglin Yin, Mingji Dai, *ACIE* **2018**, *57*, 15209–15212.



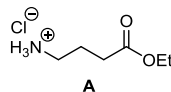
- 1) **A**, NaOAc, H₂O, CH₂Cl₂, reflux
- 2) MeNH(OMe)•HCl, *i*-PrMgCl, THF
- 3) VinylMgBr
- 4) NaBH₄, CeCl₃•7H₂O, MeOH
- 5) methyl acrylate, Grubbs 2nd, PhOH/PhMe, 110 °C
- 6) BF₃•OEt₂, CH₂Cl₂
- 7) LDA, ethyl iodide, HMPA, THF
- 8) K₂CO₃, MeOH, rt



- 9) (O*i*Pr)₃TiCl, EtMgBr, THF
- 10) [Pd(neoc)(OAc)]₂(OTf)₂, benzoquinone, CO (1 atm), DCE
- 11) Eschenmoser's salt, LiHMDS, THF
- 12) MeI, CH₂Cl₂/Et₂O, *then* DBU, THF
- 13) Ru₃(CO)₁₂, NEt₃, dioxane, 100 °C



- 14) (COCl)₂, DMF, AcONa, H₂O
- 15) **B**, Zn, THF
- 16) K₂CO₃, *t*BuOH
- 17) Pd/C, H₂, PhH/pyr



Step 1: Name Reaction?

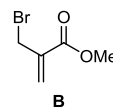
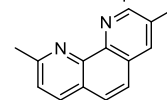
Step 2: What is the role of the Grignard reagent?

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 = Neocuproine



Step 17: What is the role of pyridine?