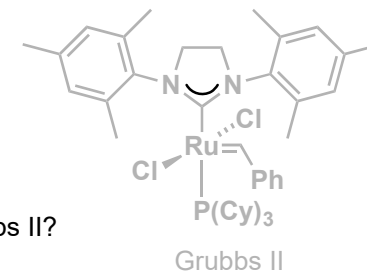


Total Synthesis of Viridin and Viridiol

Y. Ji, Z. Xin, H. He, and S. Gao
J. Am. Chem. Soc. **2019**, 141, 16208-16212

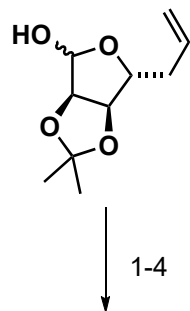
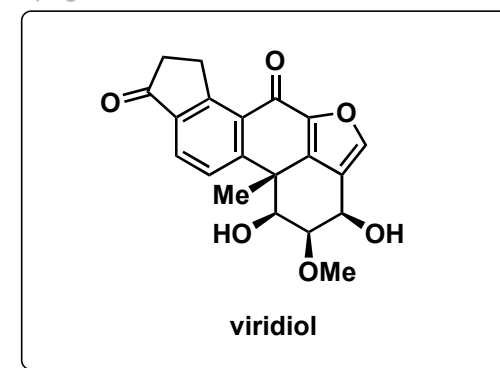


Step 1: Structure of Grubbs II?

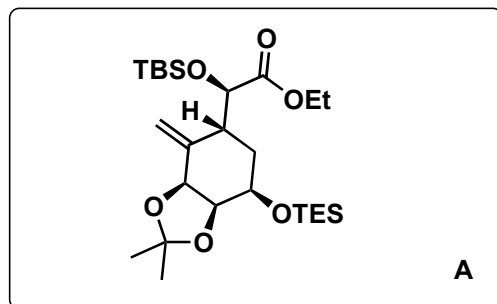
Step 2: two rings are formed, one is a heterocycle. Please provide a mechanism and the name of the newly formed heterocycle. Bonus: what other conditions could you use?

isoxazoline, see last page for mechanism, one can use sodium hypochlorite to oxidize the oxime to the nitrile oxide.

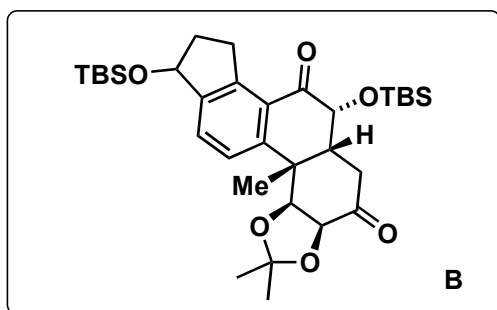
Step 7: Key step, please provide a plausible mechanism see last page for mechanism.



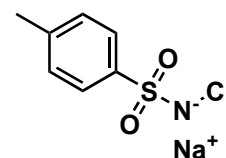
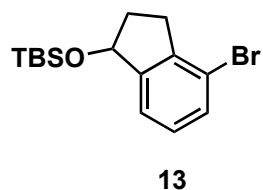
1-4



4-9

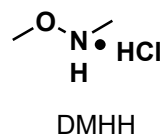


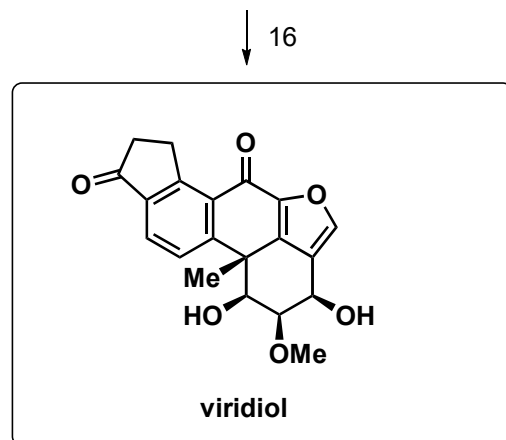
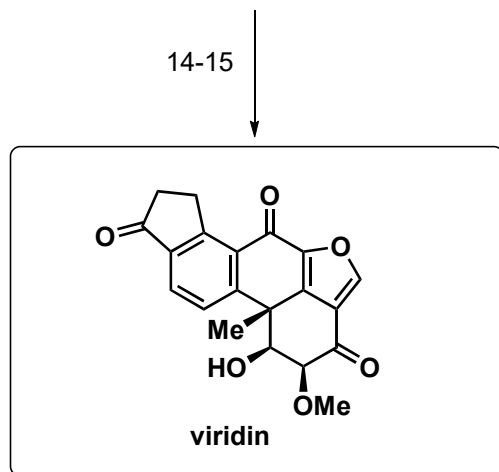
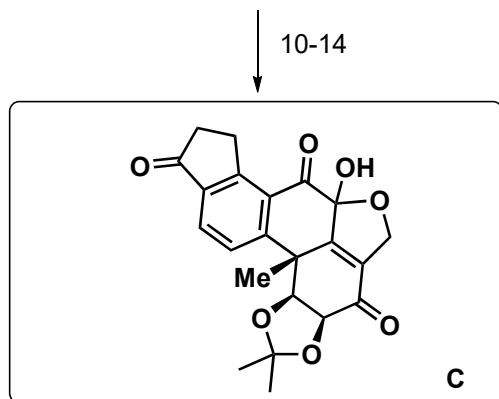
- 1) ethyl acrylate, Grubbs II, CuI
- 2) $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaHCO_3 , EtOH, then Chloramine T, 0°C
- 3) TESOTf, NEt_3 , THF, -78°C then Raney Ni, H_2 , $\text{B}(\text{OMe})_3$, MeOH, H_2O
- 4) TBSOTf, then $\text{Ph}_3\text{P}=\text{CH}_2$, toluene



Chloramine T - strong oxidant

- 5) DMHH, *i*-PrMgCl, THF
- 6) **13**, *t*-BuLi, Et_2O , -78°C
- 7) PhSiH_3 Co(Salen^{*t*-Bu}, *t*-Bu)Cl
- 8) Dowex 50W-X8
- 9) DMP





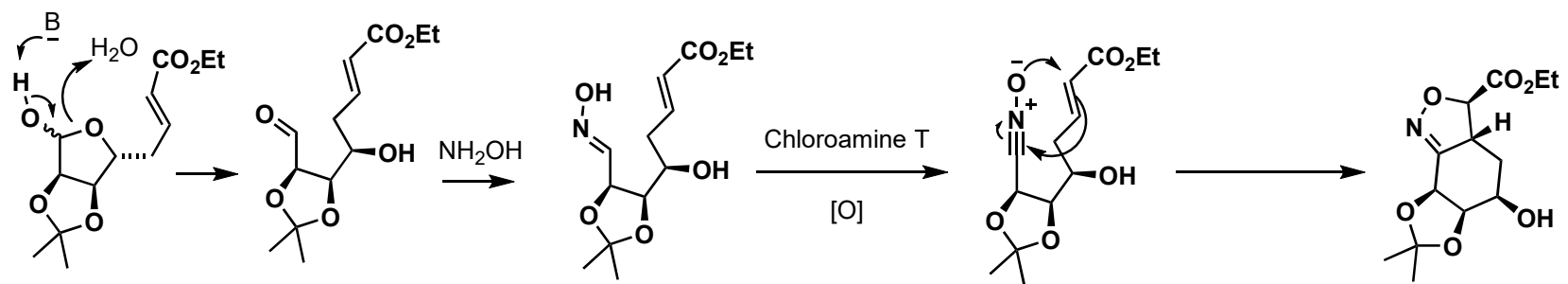
10) L-Proline, CH₂O (aq), THF, 60°C
 11) HF•pyr, THF
 12) TMSOTf, NEt₃
 then t-BuO₂Li, THF, -10°C
 13) DMP

14) H₂SO₄
 15) Me₃OBF₄
 then H₂O, TMSCHN₂, 0°C

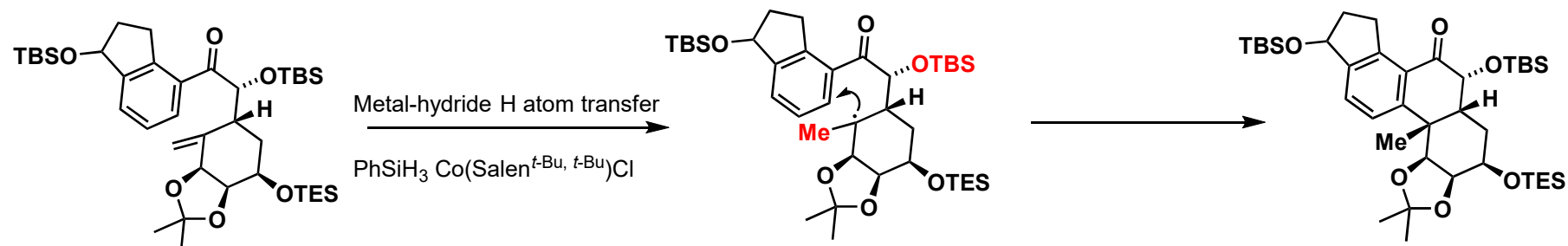
16) NaBH₄, EtOH/DCM, -10°C

Step 13: Please provide a mechanism

see last page for mechanism.



[3+2] cycloaddition



Attack from the boat conformation due to unfavorable 1,3 interactions of Me and TBS group (highlighted) when in chair conformation

