Total Synthesis of Viridin and Viridiol

Y. Ji, Z. Xin, H. He, and S. Gao
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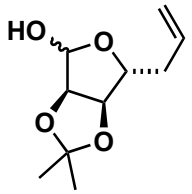
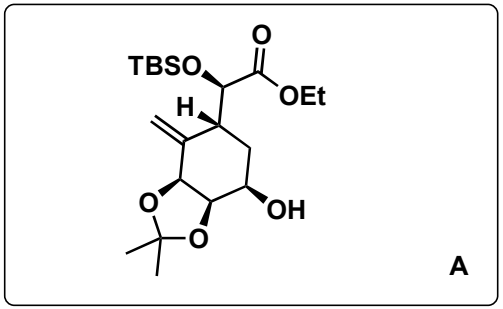


1-4



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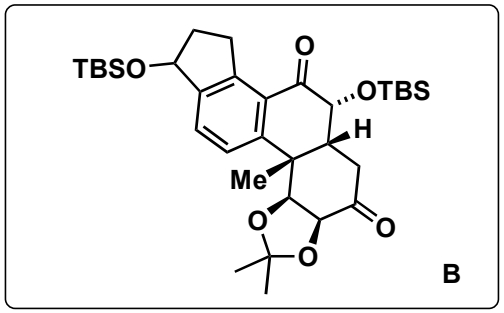
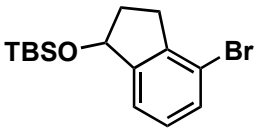


1) ethyl acrylate, Grubbs II, CuI
2) $NH_2OH{\bullet}HCl$, $NaHCO_3$, EtOH,
then Chloramine T, 0°C
3) TESOTf, NEt_3, THF, -78°C
then Raney Ni, H_2, $B(OMe)_3$, MeOH, H_2O
4) TBSOTf, then $Ph_3P{=}CH_2$, toluene



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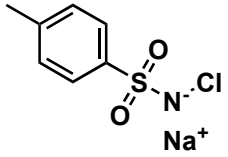
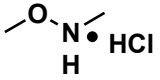
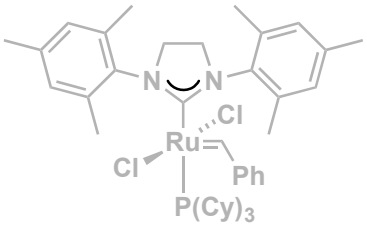


Chloramine T - strong oxidant

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



DMHH



Grubbs II

How would you make the SM in three steps?

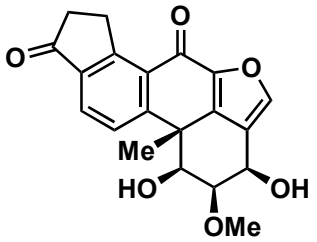
Step 1: Structure of Grubbs II?

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.

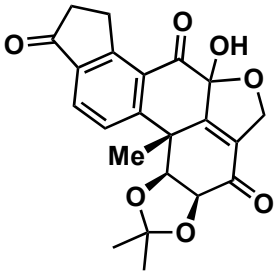
Step 7: Key step, please provide a plausible mechanism

see last page for mechanism.



viridiol

10-14



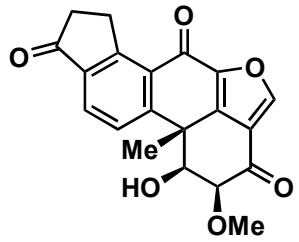
C

10) *L*-Proline, CH_2O (aq), THF, 60°C
11) HF•pyr, THF
12) TMSOTf, NEt_3
then t-BuO_2Li, THF, -10°C
13) DMP

Step 13: Please provide a mechanism

see last page for mechanism.

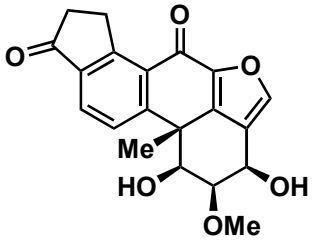
14-15



viridin

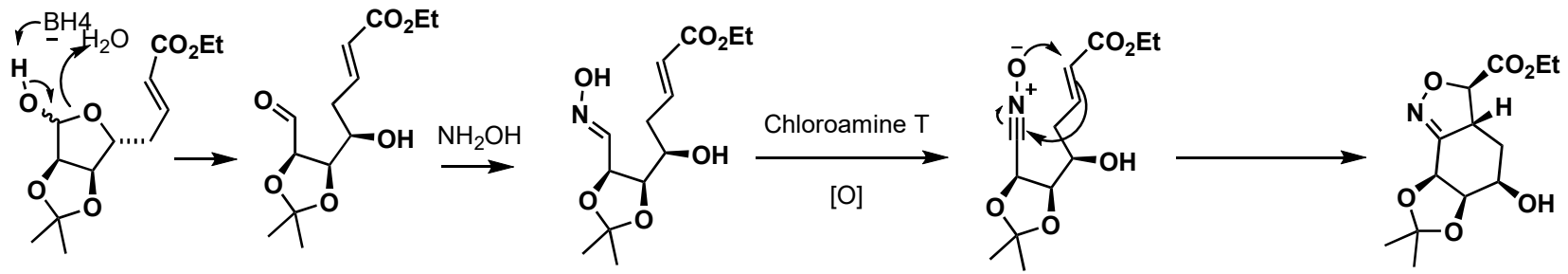
14) H_2SO_4
15) Me_3OBF_4
then H_2O, $TMSCHN_2$, 0°C

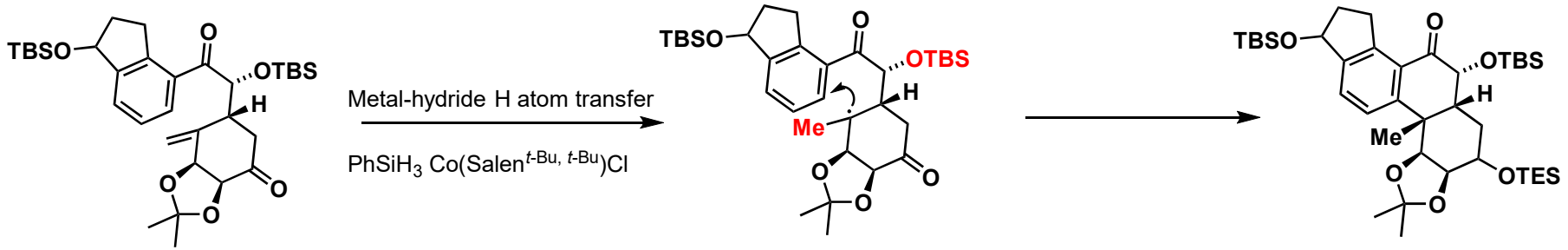
16



viridiol

16) NaBH4, EtOH/DCM, -10°C





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