Total Synthesis of Mollanol A

Yuran Wang, Rong Zhao and Ming Yang.

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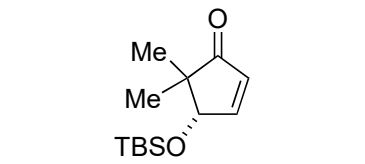
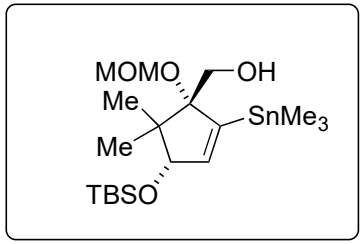
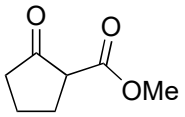


1 - 5

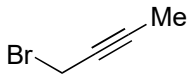


A



6 - 15

1) DMAP, I_2
2) VinylMgBr
3) MOMBr, NaI, DIPEA
4) O_3, *then* $NaBH_4$
5) Me_6Sn_2, $Pd(PPh_3)_4$



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6) NaH, *n*-BuLi, **1**
7) $InCl_3$
8) BzO_2*t*-Bu, CuBr
9) $NaBH_4$
10) MOMBr, DIPEA
11) 4.00 equiv.$TMSCH_2Li$, *then* MeOH
12) TESOTf
13) KHMDS, Comin's reagent *then* HCl
14) PDC

4) Draw mechanism, name of intermediates? *Ozonide, Criegee Intermediate*

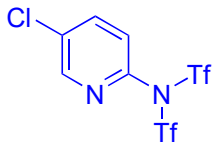
7) Name of reaction ?
Conia ene cyclization

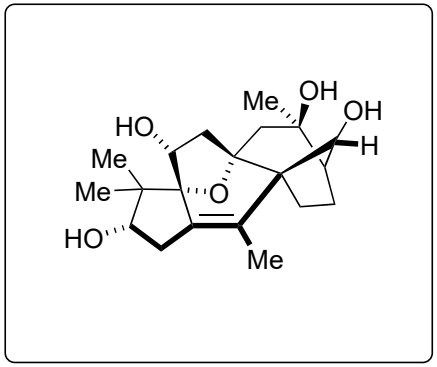
8) **Hint:** The reaction starts with the generation of an oxygen-centered radical. Explain mechanism. *Kharasch-Sosnovsky reaction mechanism. The most stable radical is the allylic tertiary one because the bridged-head radical experiences almost no stabilization through the carbonyl group.*

11) **Hint:** Two reactions are happening. One of them involves the cleavage of the BzO protecting group.

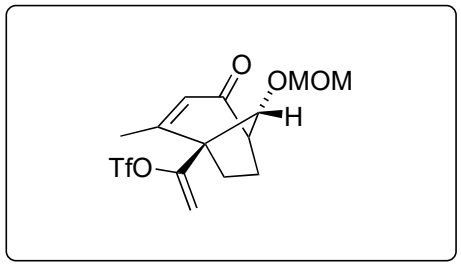
13) **Hint:** MOM stays

15) Structure of Comin's reagent?



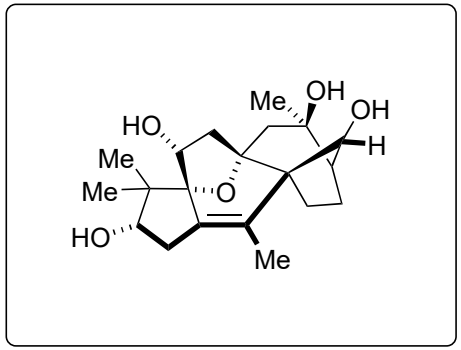


Mollanol A

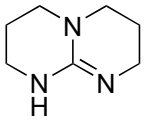


B

15 - 20



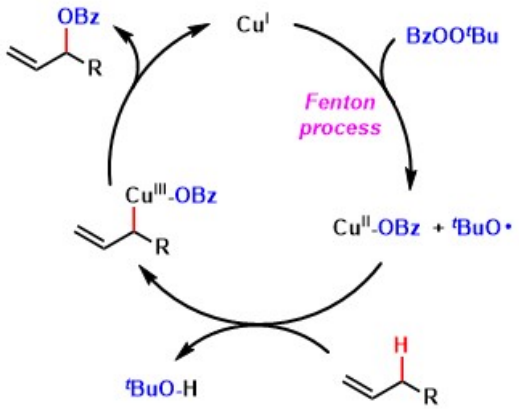
Mollanol A



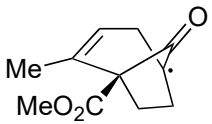
TBD

15) **A**, $Pd(PPh_3)_4$, CuCl
16) DMP
17) TBD, *then* PPTS
18) MeLi, *then* TBAF
19) Li/NH_3 (l)
20) HCl

Kharasch-Sosnovsky oxidation



16) **Hint:** Two transformations.



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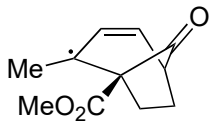

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