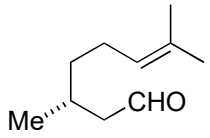
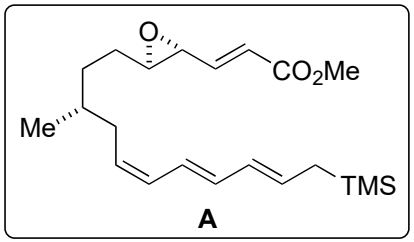
Total Synthesis of Hirsutellone B

K. C. Nicolaou, D. Sarlah, T. R. Wu, W. Zhan, *Angew. Chem. Int. Ed.* **2009**, *48*, 6870–6874.

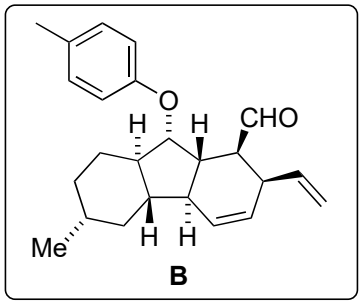


1-5



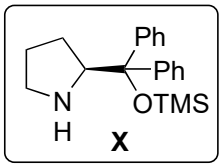
A

6-9

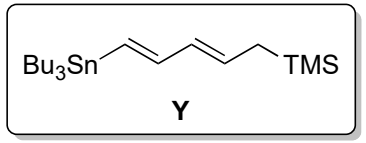


B

1) PPh_3CHI
2) O_3, Me_2S
3) $Ph_3PCHCHO$
4) **X**, H_2O_2, *then* PPh_3CHCO_2Me
5) **Y**, CuTC



X



Y

6) Et_2AlCl
7) *p*-Tol_4BiF, $Cu(OAc)_2$
8) $LiAlH_4$
9) $PhI(OAc)_2$, TEMPO

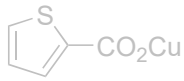
Name the starting material!

(*R*)-(+)-citronellal

Name of step 1?

Zhao–Stork olefination

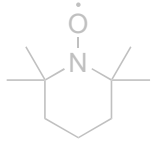
Structure of CuTC?

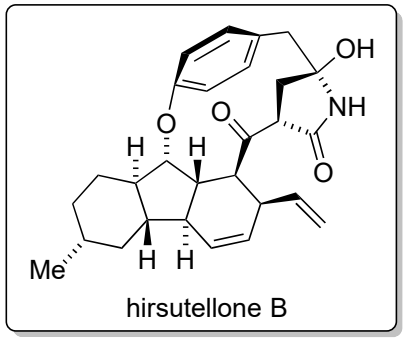


step 6: Draw a mechanism

see below

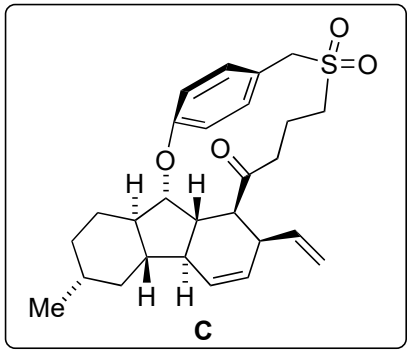
Structure of TEMPO?





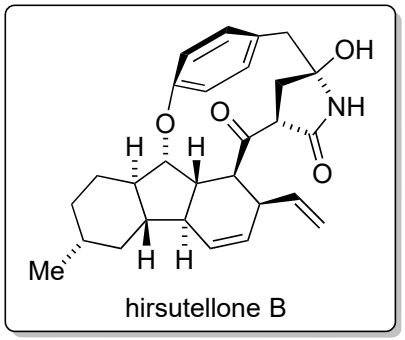
hirsutellone B

10-16



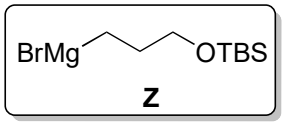
C

17-23



hirsutellone B

10) **Z**
11) DMP
12) CAN
13) $NaBH(OAc)_3$
14) ZnI_2, AcSH
15) NaOMe
16) H_2O_2, Na_2WO_4



Z

17) KOH/Al_2O_3, CF_2Br_2
18) LHMDS, $NCCO_2Me$
19) AD-mix β
20) $S{=}CCl_2$, DMAP
21) AIBN, *n*-Bu_3SnH
22) DMP
23) NH_3

step 14: Draw a mechanism

see below

Name of step 17?

Ramberg–Bäcklund reaction

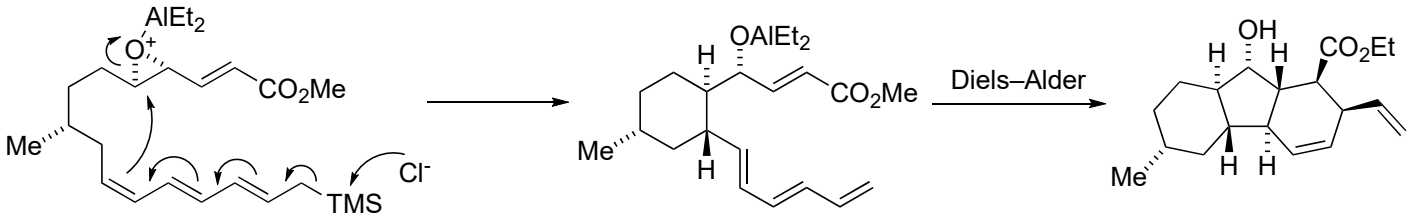
Ingredients of AD-mix β?

$(DHQD)_2PHAL$, K_2CO_3, $K_2[OsO_2(OH)_4]$, $K_3[Fe(CN)_6]$

Name of step 20 and 21?

Barton–McCombie deoxygenation

step 6:



step 14: