Total Synthesis of (±)-spiramilactone B

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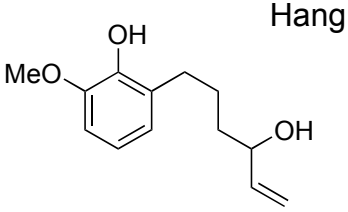
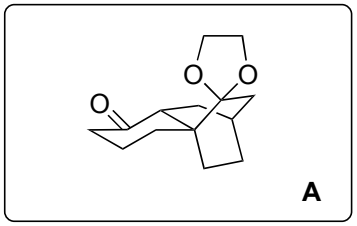
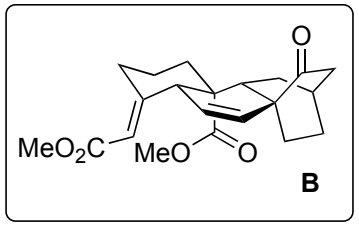


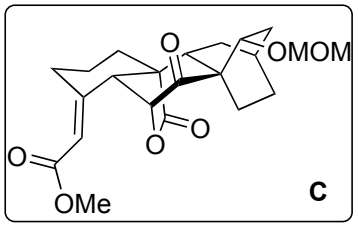
1-6



7-12

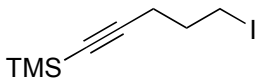


12-17



1) $PhI(OAc)_2$, MeOH
2) Mesitylene, reflux, 3h
3) SmI_2, THF/MeOH
4) Ethylene glycol, CSA, PhMe, reflux
5) DMP, Na_2CO_3
6) H_2, Pd/C

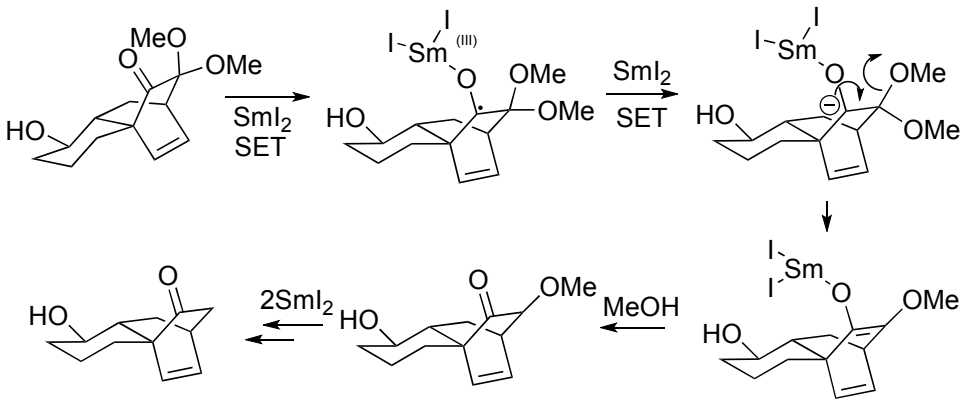
7) NaHMDS, Tf_2NPh, THF, –78ºC
8) $Pd(PPh_3)_4$, Et_3N, CO, MeOH/DMF
9) LDA, DMPU, **Z**
10) K_2CO_3, MeOH, rt
11) *n*-BuLi, $ClCO_2Me$
12) $[CpRu(CH_3CN)_3]PF_6$, DMF
then TsOH



Z

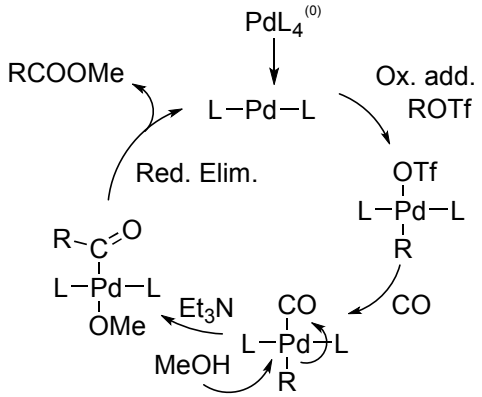
13) $LiBHEt_3$
14) *m*-CPBA, $NaHCO_3$
15) MOMCl, DIPEA, DCM
16) $Ti(O\textit{i}\text{-}Pr)_2Cl_2$, DCM, 0ºC
17) DMP, $NaHCO_3$

Reaction mechanism of 3:



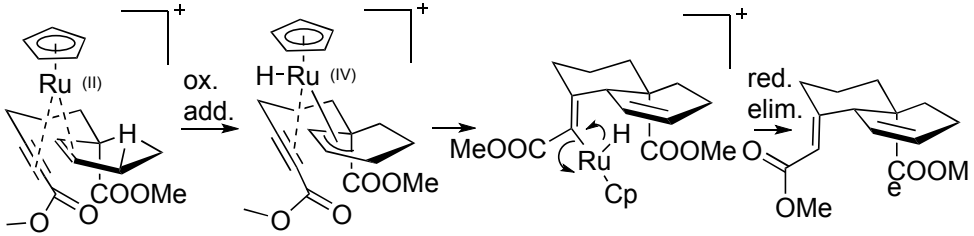
Reaction type of 8:
Heck-type
Carboalcoxylation

Explain mechanism:



Name of reaction 14:
Prilezhaev reaction

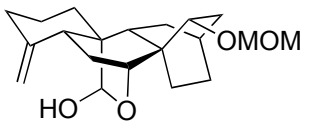
Explain mechanism of 12:



C

18-23

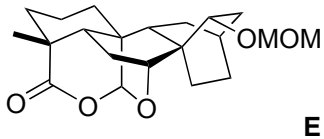
18) SmI_2, THF/MeOH
19) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, THF/MeOH
20) DIC, HOBt
21) O_3, DCM, –78ºC
22) $PbCl_2$, Zn, $TiCl_4$, CH_2Br_2
23) DIBAL-H



D

24-28

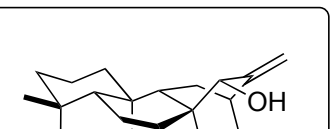
24) PPTS, MeOH
25) $BH_3 \cdot Me_2S$, then H_2O_2, 3N NaOH
26) DMP, $NaHCO_3$
27) *t*-BuOK, MeI
28) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene, *t*-BuOH/H_2O



E

29-33

29) $ZnBr_2$, *n*-PrSH
30) DMP, $NaHCO_3$
31) LiHMDS, $CH_2N(CH_3)_2I$,–78ºC then MeI, then DBU
32) $NaBH_4$, MeOH/DCM
33) PhSCl, Et_3N, 0ºC, then $P(OMe)_3$, MeOH, 50ºC



(±)-spiramilactone B

What is the role of DMPU?
Avoids nucleophilic attack of LDA

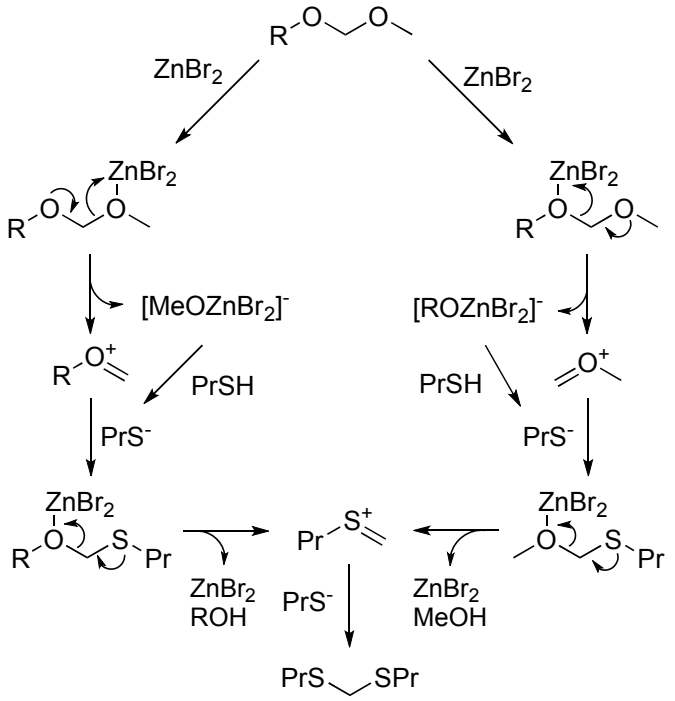
Comparison with HMPA?
DMPU is not carcinogenic, but larger amounts are usually needed

Name of reaction 19: Luche Reduction

Name of reaction 22: Takai olefination

Name of reaction 28: Pinnick oxidation

Mechanism of reaction 29:



Name of reaction 33: Mislow-Evans rearrangement