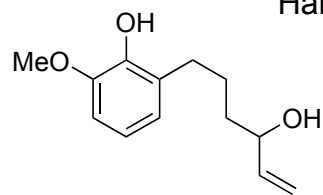
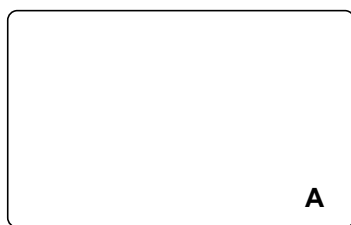


Total Synthesis of (±)-spiramilactone B

Hang Cheng, Fan-Hao Zeng, Xue Yang, Yin-Juan Meng, Liang Xu, and Feng-Peng Wang
Angew. Chem. Int. Ed. **2016**, *55*, 392–396



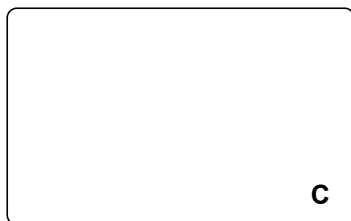
1-6



7-12

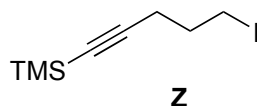


12-17



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

- 7) NaHMDS, Tf_2NPh , THF, -78°C
- 8) $\text{Pd}(\text{PPh}_3)_4$, Et_3N , CO, MeOH/DMF
- 9) LDA, DMPU, **Z**
- 10) K_2CO_3 , MeOH, rt
- 11) *n*-BuLi, ClCO_2Me
- 12) $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$, DMF, Acetone then TsOH



- 13) LiBHET_3 (1 eq.)
- 14) *m*-CPBA, NaHCO_3
- 15) MOMCl, DIPEA, DCM
- 16) $\text{Ti}(\text{O}i\text{-Pr})_2\text{Cl}_2$, DCM, 0°C
- 17) DMP, NaHCO_3

Spontaneous dimerization happens in step 1, but is reversed in 2 before the actual reaction takes place

Reaction mechanism of 3

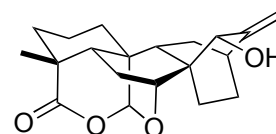
Reaction type of 8, explain mechanism

What is the role of DMPU? Comparison with HMPA?

Explain mechanism of 12

Name of reaction 14

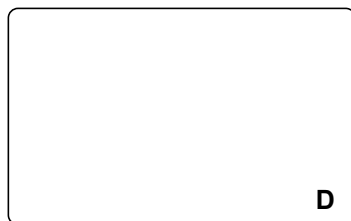
Wrong cyclisation product is obtained in 16



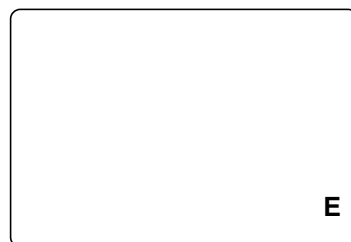
(±)-spiramilactone B

C

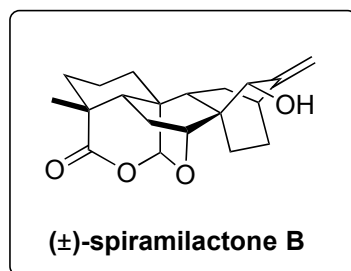
18-23



24-28



29-33



- 18) Sml_2 , THF/MeOH
- 19) NaBH_4 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, THF/MeOH
- 20) DIC, HOBt
- 21) O_3 , DCM, -78°C
- 22) PbCl_2 , Zn, TiCl_4 , CH_2Br_2
- 23) DIBAL-H

- 24) PPTS, MeOH
- 25) $\text{BH}_3 \cdot \text{Me}_2\text{S}$, 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

- 29) ZnBr_2 , *n*-PrSH
- 30) DMP, NaHCO_3
- 31) LiHMDS, $\text{CH}_2\text{N}(\text{CH}_3)_2\text{I}$, -78°C then MeI, then DBU
- 32) NaBH_4 , MeOH/DCM
- 33) PhSCl, Et_3N , 0°C , then $\text{P}(\text{OMe})_3$, MeOH, 50°C

Name of reaction 19

Name of reaction 22

Name of reaction 28

Explain the mechanism of 29

Name of reaction 33