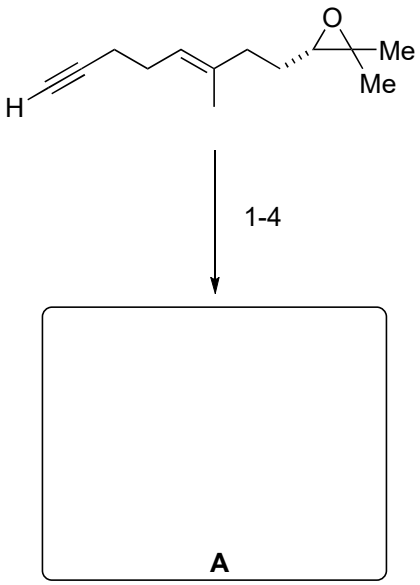
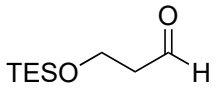
Asymmetric Total Synthesis of (−)-Spirochensilide A

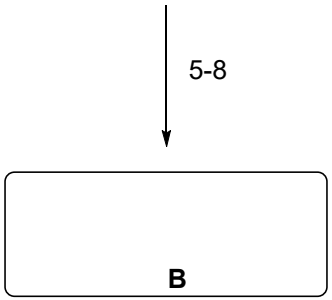
Xin-Ting Liang, Jia-Hua Chen and Zhen Yang *J. Am. Chem. Soc.* **2020**, *142*, 8116–8121.



1) $TiCl_4$, CH_2Br_2
2) $Pd(PPh_3)_2Cl_2$, CuI, DIPA, TMS-acetylene
3) TBSCl
4) *m*-CPBA, *then* BF_3•OEt_2

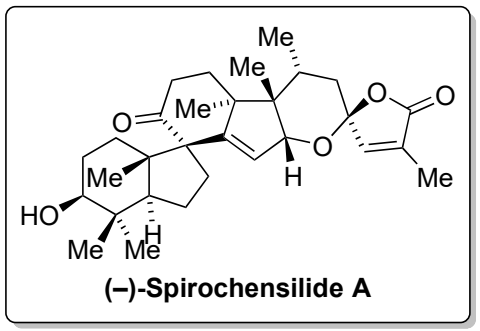
step 4: Name the reaction





5) $InCl_3$, $TMSCHN_2$, *then* $TMSCHN_2$, *n*-BuLi
6) K_2CO_3, MeOH
7) MsCl, NEt_3
8) NaI, acetone

step 5: Mechanism?



(–)-Spirochensilide A

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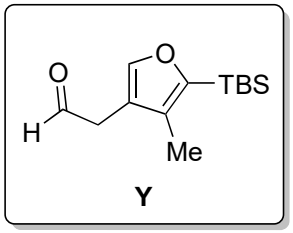
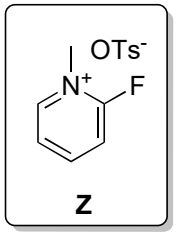
9) *t*-BuLi, $CeCl_3$, *then* **A**
10) TESOTf, NEt_3, *then* K_2CO_3, MeOH
11) $W(CO)_3(MeCN)_3$, EtOH, HMPA, CO
12) *t*-BuOK, *t*-BuOH
13) Pd/C, H_2
14) Li-NH_3

step 11: Name the reaction

C



Y

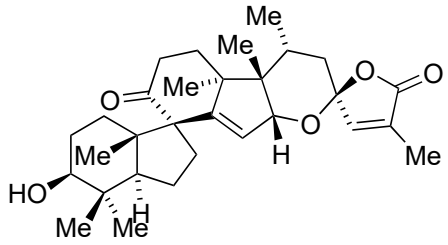


Z

15-25

15) Bu_2BOTf, DIPEA, *then* **Y**
16) **Z**, *then* neutral Al_2O_3
17) Me_2CuLi
18) KH, MeI
19) LDA, PhSeCl
20) *m*-CPBA
21) DIBAL
22) methylene blue, O_2, hν, *then* $ClCH_2COOH$
23) TBAF
24) DMP
25) aq. HF

Structure of methylene blue?



(–)-Spirochensilide A