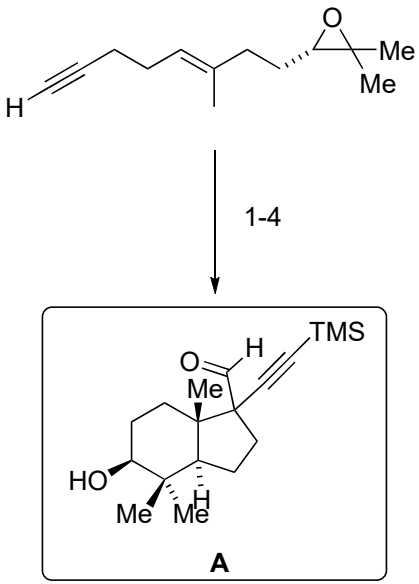
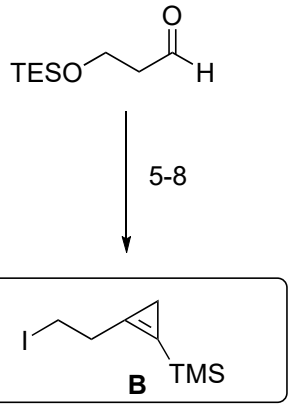
**Asymmetric Total Synthesis of (−)-Spirochensilide A**

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



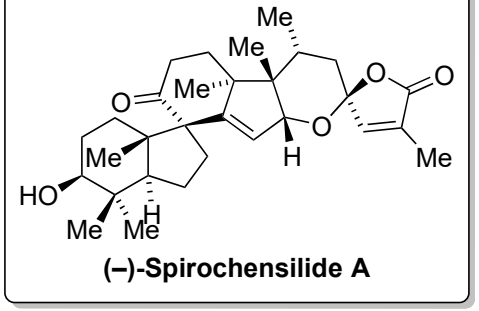

1) $TiCl_4$, $CH_2Br_2$
2) $Pd(PPh_3)_2Cl_2$, CuI, DIPA, TMS-acetylene
3) TBSCl
4) *m*-CPBA, *then* $BF_3$•$OEt_2$

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

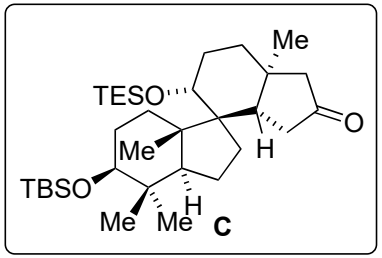
step 4: Name the reaction

semi pinacol rearrangement

step 5: Mechanism?

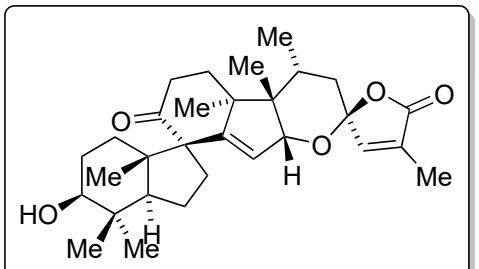


9-14



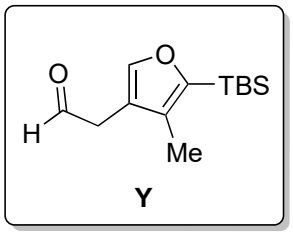

**C**

15-25

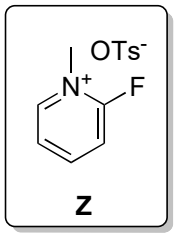



**(–)-Spirochensilide A**

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-$NH_3$




**Y**



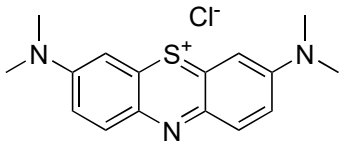

**Z**

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

step 11: Name the reaction

Pauson–Khand reaction

Structure of methylene blue?



step 5: *J. Am. Chem. Soc.* **2010**, *132*, 6640–6641.