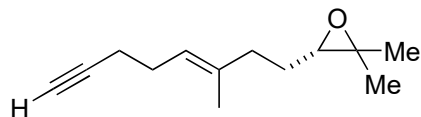
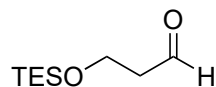
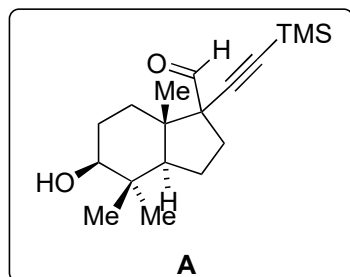


Asymmetric Total Synthesis of (-)-Spirochensilide A

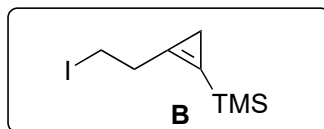
Xin-Ting Liang, Jia-Hua Chen and Zhen Yang *J. Am. Chem. Soc.* **2020**, *142*, 8116–8121.



1-4



5-8

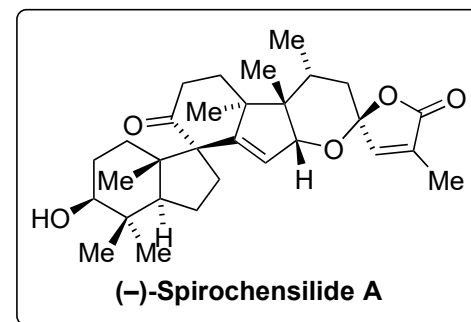


- 1) TiCl_4 , CH_2Br_2
- 2) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , DIPA , TMS-acetylene
- 3) TBSCl
- 4) *m*-CPBA, then $\text{BF}_3 \cdot \text{OEt}_2$

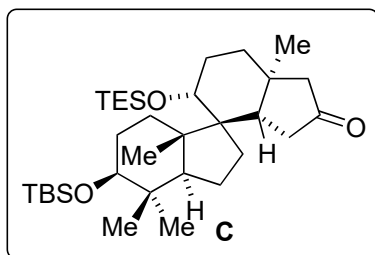
step 4: Name the reaction
semi pinacol rearrangement

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

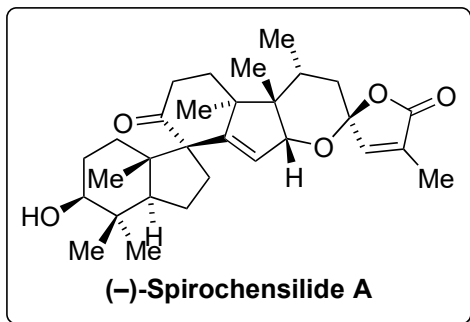
step 5: Mechanism?



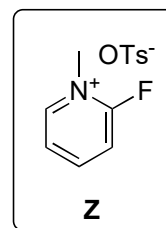
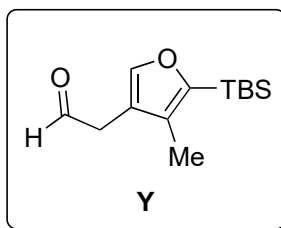
9-14



15-25



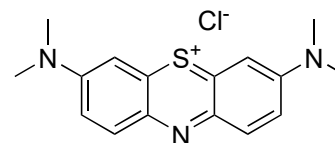
- 9) *t*-BuLi, CeCl₃, then **A**
- 10) TESOTf, NEt₃, then K₂CO₃, MeOH
- 11) W(CO)₃(MeCN)₃, EtOH, HMPA, CO
- 12) *t*-BuOK, *t*-BuOH
- 13) Pd/C, H₂
- 14) Li-NH₃



- 15) Bu₂BOTf, DIPEA, then **Y**
- 16) **Z**, then neutral Al₂O₃
- 17) Me₂CuLi
- 18) KH, MeI
- 19) LDA, PhSeCl
- 20) *m*-CPBA
- 21) DIBAL
- 22) methylene blue, O₂, hv, then ClCH₂COOH
- 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.

