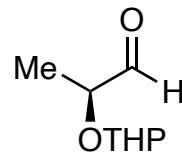


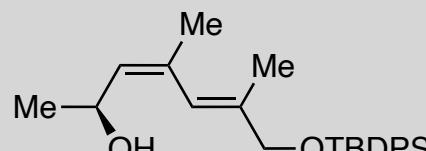
# Bent π-Conjugation within a Macrocycle: Asymmetric Total Syntheses of Spirohexenolides A and B

Guo, L.-D.; Wu, Y.; Xu, X.; Lin, Z.; Tong, R.

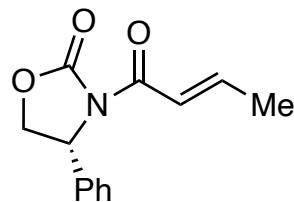
*Angew. Chem. Int. Ed.* **2023**, e202316259



1-7



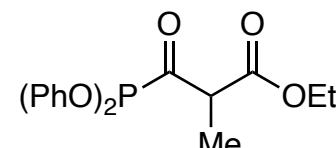
**A**



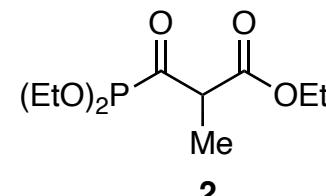
8-14



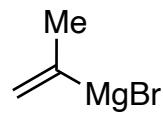
- 1) NaH, Ando-type reagent (**1**)
- 2) DIBAL-H (3.0 eq.)
- 3) DMP
- 4) NaH, **2**
- 5) PTSA · H<sub>2</sub>O
- 6) DIBAL-H (4.0 eq.)
- 7) TBDPSCl (1.05 equiv.), imidazole



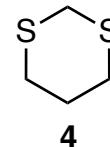
**1**



**2**



**3**

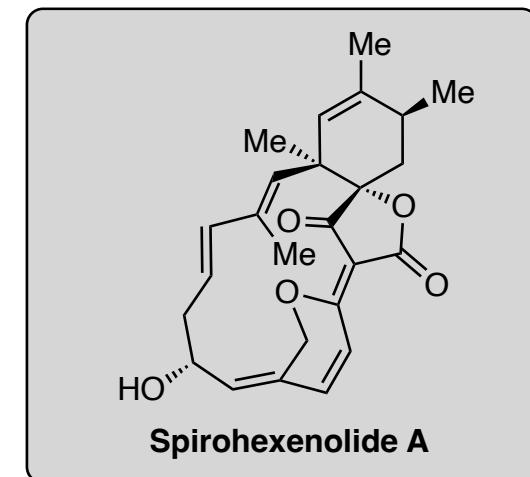


**4**

- 8) **3**, CuBr · Me<sub>2</sub>S
- 9) AlMe<sub>3</sub>, MeNH(OMe) · HCl
- 10) **4**, *n*-BuLi
- 11) NaBH<sub>4</sub>
- 12) NaH, PMBCl
- 13) Mel, NaHCO<sub>3</sub>, CH<sub>3</sub>CN/H<sub>2</sub>O
- 14) Pinnick

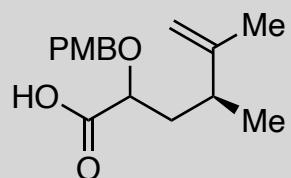
- 1) Name of the reaction?  
Horner–Wadsworth–Emmons

- 4) Name of the reaction?  
Horner–Wadsworth–Emmons



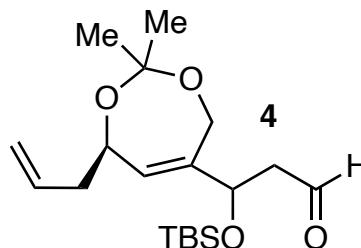
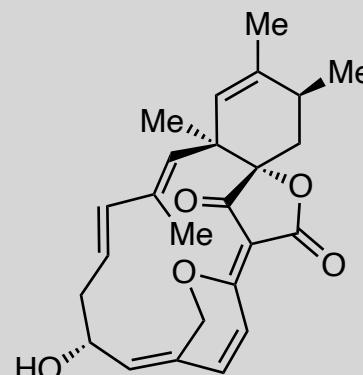
- 8) correct chiral center corresponding to C17 in the product is installed

- 13) new <sup>1</sup>H signal between 9-10 ppm



**A + B**

15-27



- 15) EDCI, DMAP
- 16) KHMDS, TMSCl, *then* TMSCHN<sub>2</sub>
- 17) Hoveyda-Grubbs II, PhMe, 105 °C
- 18) DDQ
- 19) Ac<sub>2</sub>O (10 eq.), Sc(OTf)<sub>2</sub>
- 20) DIBAL-H
- 21) DMP
- 22) Ph<sub>3</sub>P=CH<sub>2</sub>, *n*-BuLi
- 23) LiHMDS, *then* MeI
- 24) *t*-BuLi, 4
- 25) DMP
- 26) Hoveyda-Grubbs II, PhMe, 65 °C
- 27) HCl, THF/H<sub>2</sub>O

15) Name of the reaction?  
Steglich Esterification

16) Name of the reaction?  
Ireland–Claisen rearrangement

17) Type of reaction?  
Ring-closing metathesis

20) selective reduction

22) Name of reaction?  
Wittig olefination

23) Name of reaction?  
Dieckmann cyclization

27) three transformations occur;  
suggest a mechanism

