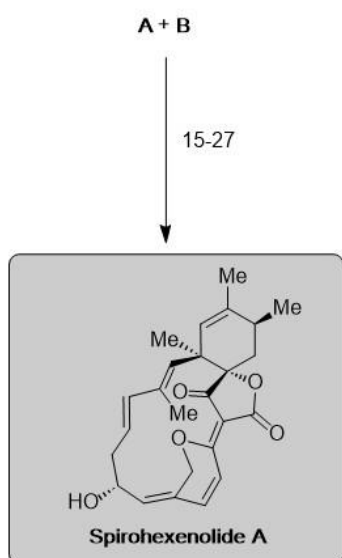
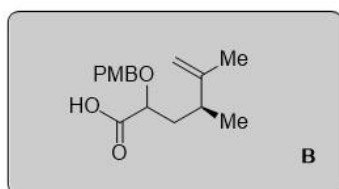
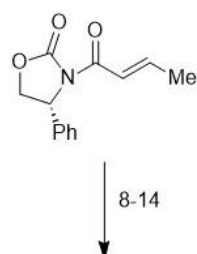
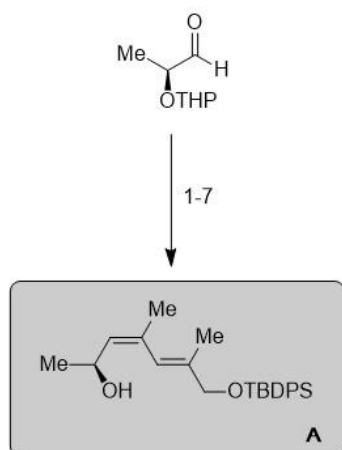


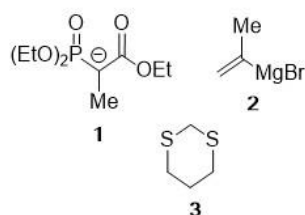
Bent π -Conjugation within a Macrocycle: Asymmetric Total Syntheses of Spirohexenolides A and B

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

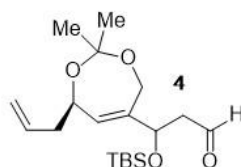
Angew. Chem. Int. Ed. **2023**, e202316259



- 1) Ando-type reagent (similar to **1**)
- 2) DIBAL-H
- 3) DMP
- 4) **1**
- 5) PTSA
- 6) DIBAL-H
- 7) TBDPSCI (1.05 equiv.)



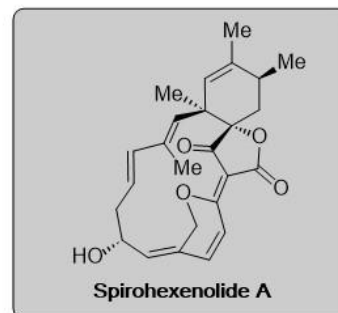
- 8) **2**, CuBr · Me₂S
- 9) AlMe₃, MeNH(OMe) · HCl
- 10) **3**, *n*-BuLi
- 11) NaBH₄
- 12) NaH, PMBCl
- 13) MeI
- 14) Pinnick



- 15) EDCI, DMPA
- 16) KHMDS, TMSCl, then TMSCHN₂
- 17) Hoveyda-Grubbs II, PhMe, 105 °C
- 18) DDQ
- 19) Ac₂O, Sc(OTf)₂
- 20) DIBAL-H
- 21) DMP
- 22) Ph₃P=CH₂
- 23) LiHMDS, then MeI
- 24) *t*-BuLi, **4**
- 25) DMP
- 26) Hoveyda-Grubbs II, PhMe, 65 °C
- 27) HCl, THF/H₂O

- 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 ¹H signal between 2.0-2.5 ppm

- 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