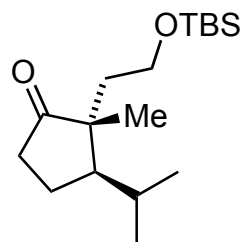
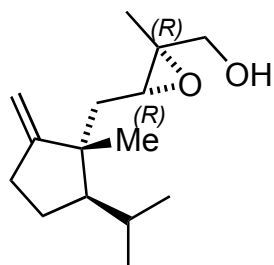


Total Synthesis of (–)-Crinipellin A
 Kang, T.; Song, S. B.; Kim, W.; Kim B. G.; Lee, H.
J. Am. Chem. Soc. **2014**, *136*, 10274–10276.



1-6



A

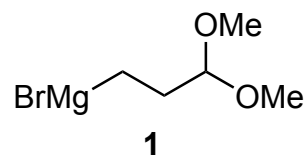
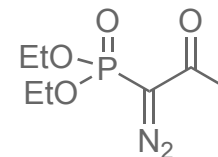
7-12

- 1) $\text{PPh}_3\text{CH}_3\text{Br}$, *t*-BuOK, *t*-BuOH, Et_2O
- 2) TBAF, THF, $23\text{ }^\circ\text{C}$
- 3) $(\text{COCl})_2$, DMSO, Et_3N , THF, $-78 - 23\text{ }^\circ\text{C}$
- 4) $\text{Ph}_3\text{PCCH}_3\text{COOEt}$, THF, reflux
- 5) LAH, Et_2O , $0 - 23\text{ }^\circ\text{C}$
- 6) (–)-DET, TBHP, $\text{Ti}(\text{O}i\text{-Pr})_4$, CH_2Cl_2 , $-30\text{ }^\circ\text{C}$

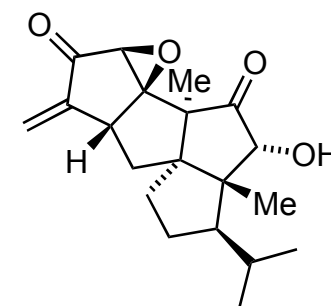
6) Name of this reaction? Do you know the stereochemical model?

Sharpless Asymmetric Epoxidation

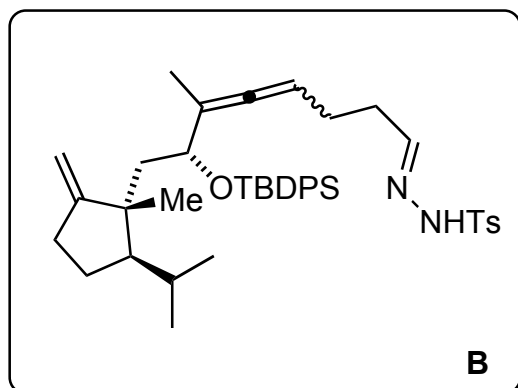
8) What is the structure of the Bestmann–Ohira reagent?



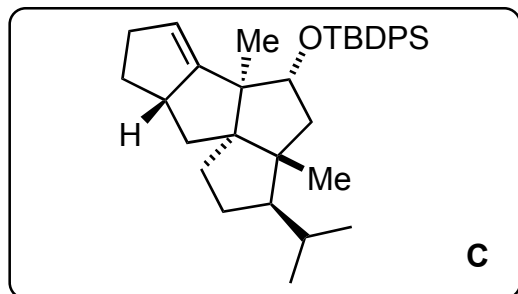
- 7) $(\text{COCl})_2$, DMSO, CH_2Cl_2 , then Et_3N , $-78 - 23\text{ }^\circ\text{C}$
- 8) K_2CO_3 , Bestmann–Ohira reagent, MeOH, $23\text{ }^\circ\text{C}$
- 9) $\text{Fe}(\text{acac})_3$, **1**, THF, PhMe, $-15\text{ }^\circ\text{C}$
- 10) TBDPSCI, Imidazole, DMAP, CH_2Cl_2 , $23\text{ }^\circ\text{C}$
- 11) *p*-TsOH· H_2O , HCHO, THF, H_2O , $23\text{ }^\circ\text{C}$
- 12) H_2NNHTs , MeOH, $23\text{ }^\circ\text{C}$



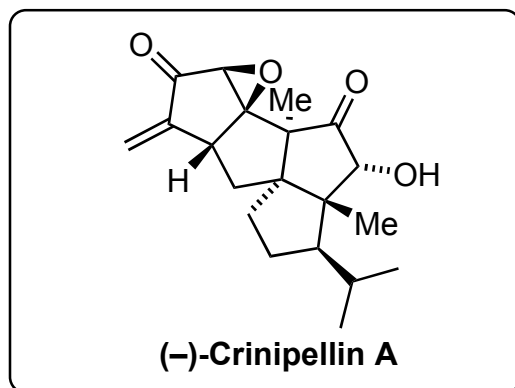
(–)-Crinipellin A



13



14-25



13) NaH, PhMe, reflux

14) TBAF, THF, 60 °C

15) PCC, CH₂Cl₂, 23 °C

16) KHMDS, Davis' oxaziridine, THF, -78 °C

17) DMP, pyr., CH₂Cl₂, 23 °C

18) *n*-BuLi, (+)-(S)-N,S-dimethyl-S-phenyl-sulfoximine (1 equiv.), -78 °C

19) NaBH(OAc)₃, CH₂Cl₂, 23 °C

20) 2,6-lutidine, TBSOTf, DCM, 23 °C

21) PDC, TBHP, PhH, 23 °C

22) PhMe, 125 °C

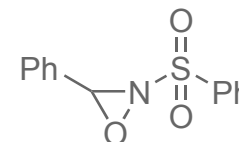
23) H₂O₂, NaHCO₃, THF, H₂O

24) LiHMDS, Eschenmoser's salt, THF, -78 °C

25) TASF, DMF, 23 °C

13) Provide a mechanism. *Hint*: 3 rings are formed.

See Below



16) What is the structure of Davis' oxaziridine?

18) *Hint*: The C8 ketone is attacked and used in the subsequent step to set the stereochemistry of the C9 hydroxyl group.

23) Name of this reaction?

Scheffer Weitz Epoxidation

Mechanism for step 13

