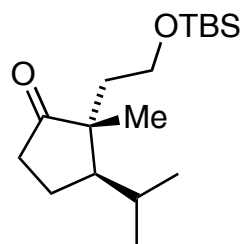
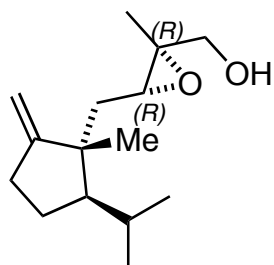


Total Synthesis of (-)-Crinipellin A
 Kang, T.; Song, S. B.; Kim, W.; Kim B. G.; Lee, H.
J. Am. Chem. Soc. 2014, *136*, 10274–10276.



1-6



A

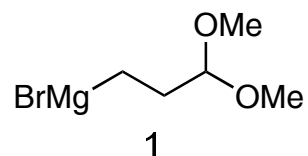
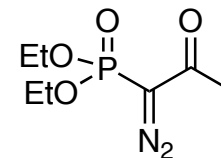
7-12

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

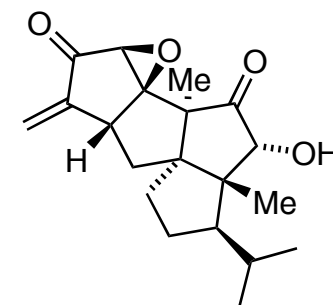
6) Name of this reaction? Do you know the stereochemical model?

Sharpless Asymmetric Epoxidation

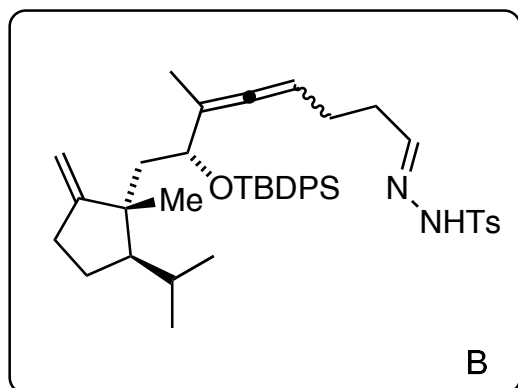
8) What is the structure of the Bestmann–Ohira reagent?



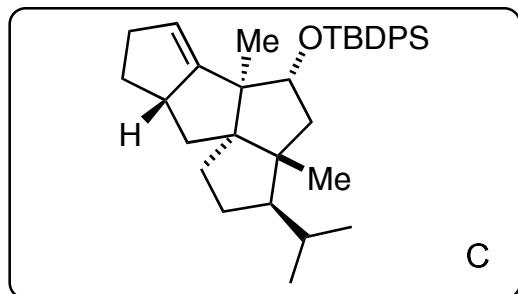
- 7) $(\text{COCl})_2$, DMSO, CH_2Cl_2 , then Et_3N , -78 – 23 °C
- 8) K_2CO_3 , Bestmann–Ohira reagent, MeOH, 23 °C
- 9) $\text{Fe}(\text{acac})_3$, 1, THF, PhMe, -15 °C
- 10) TBDPSCl, Imidazole, DMAP, DCM, 23 °C
- 11) *p*-TsOH· H_2O , HCHO, THF, H_2O , 23 °C
- 12) H_2NNHTs , MeOH, 23 °C



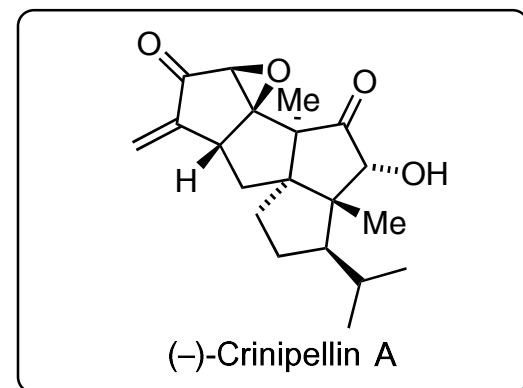
(-)-Crinipellin A



13



14-25



13) NaH, PhMe, reflux

14) TBAF, THF, 60 → C

15) PCC, DCM, 23 → C

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

17) DMP, pyr. DCM, 23 → C

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

19) NaBH(OAc)₃, DCM, 23 °C

20) 2,6-lutidine, TBSOTf, DCM, 23 °C

21) PDC, TBHP, PhH, 23 °C

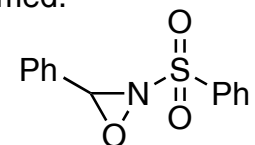
22) PhMe, 125 °C

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.



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?

→ C Schaefer Weitz Epoxidation

Mechanism for step 12

