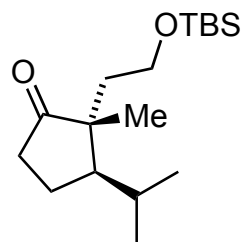


**Total Synthesis of (-)-Crinipellin A**  
 Kang, T.; Song, S. B.; Kim, W.; Kim B. G.; Lee, H.  
*J. Am. Chem. Soc.* **2014**, *136*, 10274–10276.



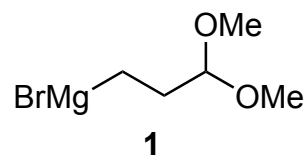
1-6



7-12

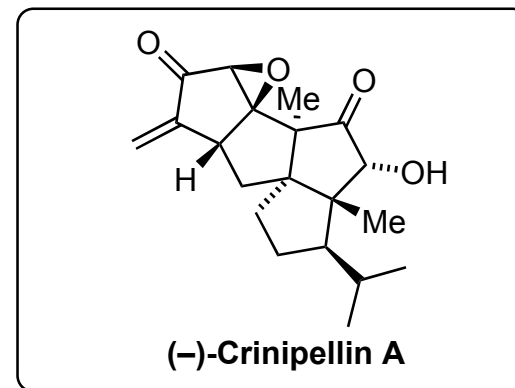
- 1)  $\text{PPh}_3\text{CH}_3\text{Br}$ , *t*-BuOK, *t*-BuOH,  $\text{Et}_2\text{O}$
- 2) TBAF, THF, 23 °C
- 3)  $(\text{COCl})_2$ , DMSO,  $\text{Et}_3\text{N}$ , THF, -78 – 23 °C
- 4)  $\text{Ph}_3\text{PCCH}_3\text{COOEt}$ , THF, reflux
- 5) LAH,  $\text{Et}_2\text{O}$ , 0 – 23 °C
- 6) (-)-DET, TBHP,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

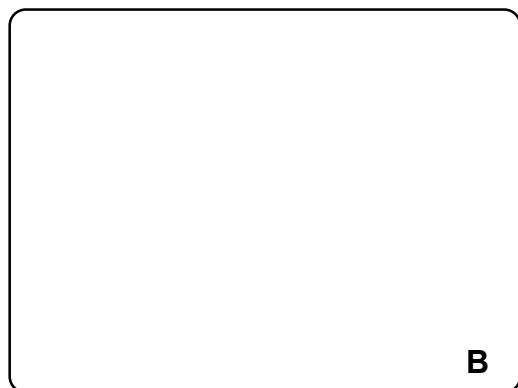
6) Name of this reaction? Do you know the stereochemical model?



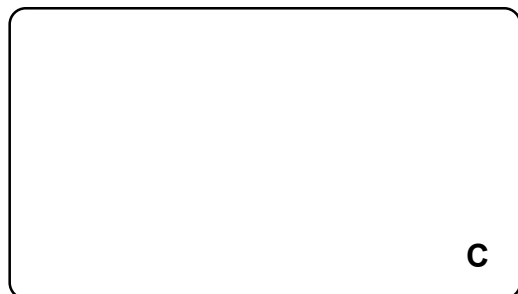
- 7)  $(\text{COCl})_2$ , DMSO,  $\text{CH}_2\text{Cl}_2$ , then  $\text{Et}_3\text{N}$ , -78 – 23 °C
- 8)  $\text{K}_2\text{CO}_3$ , Bestmann–Ohira reagent, MeOH, 23 °C
- 9)  $\text{Fe}(\text{acac})_3$ , **1**, THF, PhMe, -15 °C
- 10) TBDPSCI, Imidazole, DMAP,  $\text{CH}_2\text{Cl}_2$ , 23 °C
- 11) *p*-TsOH· $\text{H}_2\text{O}$ , HCHO, THF,  $\text{H}_2\text{O}$ , 23 °C
- 12)  $\text{H}_2\text{NNHTs}$ , MeOH, 23 °C

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

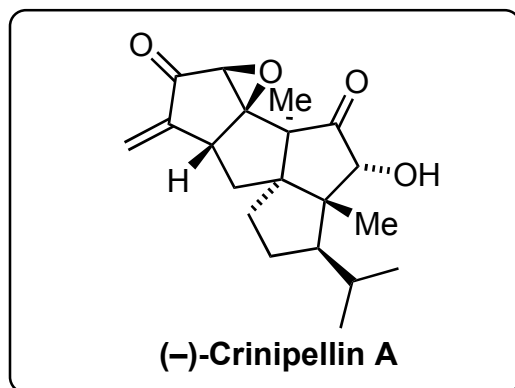




↓  
13



↓  
14-25



13) NaH, PhMe, reflux

14) TBAF, THF, 60 °C

15) PCC, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C

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

17) DMP, pyr., CH<sub>2</sub>Cl<sub>2</sub>, 23 °C

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

19) NaBH(OAc)<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C

20) 2,6-lutidine, TBSOTf, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C

21) PDC, TBHP, PhH, 23 °C

22) PhMe, 125 °C

23) H<sub>2</sub>O<sub>2</sub>, NaHCO<sub>3</sub>, THF, H<sub>2</sub>O

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?