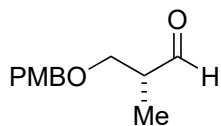
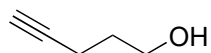


# Total Synthesis and Structural Revision of Callipeltoside C

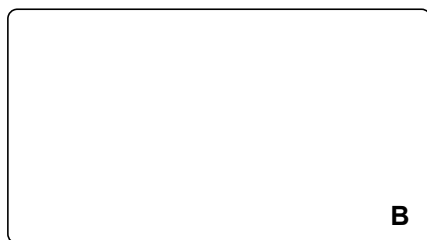
J. Carpenter, A. B. Northrup, d. Chung, J. J. M. Wiener, S.-G. Kim, D. W. C. MacMillan  
*Angew. Chem. Int. Ed.* **2008**, 47, 3568.



1 – 6



7 – 13



- 1) Propionaldehyde, L-proline
- 2) Propargyl bromide, Zn
- 3)  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ , CO, MeOH, *p*-benzoquinone
- 4) TBSCl, imH
- 5) DDQ
- 6)  $\text{SO}_3 \cdot \text{py}$ ,  $\text{Et}_3\text{N}$ , DMSO

- 7)  $\text{AlMe}_3$ ,  $[\text{Cp}_2\text{ZrCl}_2]$ , then  $\text{I}_2$
- 8) Oxalyl chloride,  $\text{Et}_3\text{N}$ , DMSO
- 9) PhNO, L-proline
- 10)  $\text{NaBH}_4$
- 11) Zn, AcOH, EtOH
- 12) PMBCl,  $\text{Bu}_2\text{Sn}(\text{OMe})_2$ , TBAI
- 13) TBSCl, imH

1) Explain the stereochemistry. Draw the transition state.

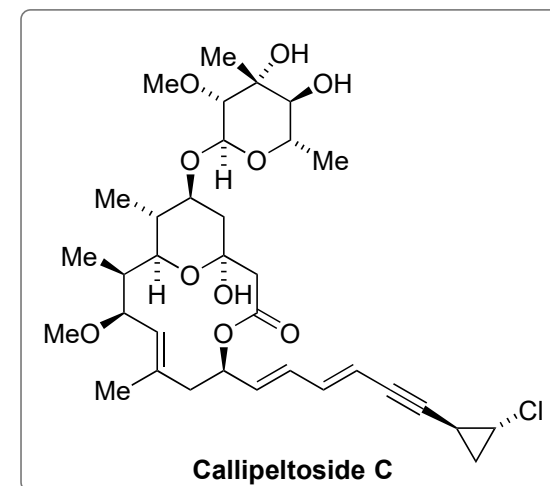
3) Name of the reaction?

6) Name of the reaction?

7) Name of the reaction?

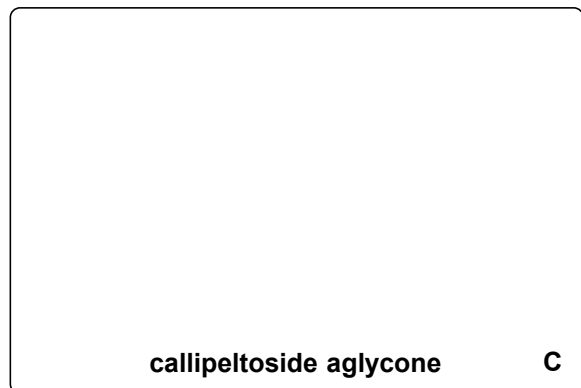
8) Name of the reaction?

9) Explain the stereochemistry. Draw the transition state.



**A**

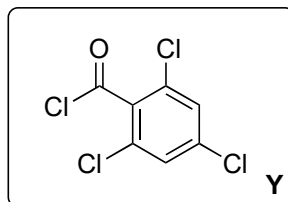
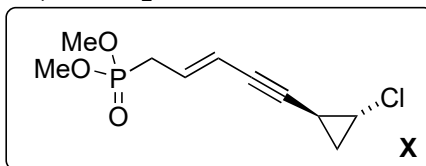
14 – 23



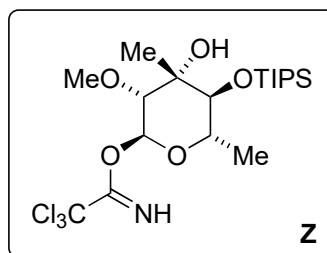
24 – 25

**Callipeltoside C**

- 14)  $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ , then grignard of **B**  
15) MeOTf, 2,6-DTBP  
16) DDQ  
17)  $\text{SO}_3 \cdot \text{py}$ ,  $\text{Et}_3\text{N}$ , DMSO  
18) LiHMDS, then **X**  
19) TBAF  
20)  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ , MeOH  
21) **Y**, DIPEA, DMAP  
22)  $\text{PPh}_3 \cdot \text{HBr}$ ,  $\text{H}_2\text{O}$   
23) TFA,  $\text{H}_2\text{O}$ , THF



- 24) **Z**, TMSOTf  
25) TASF



- 14) Explain the stereochemistry.  
18) Name of the reaction?

21) Name of the reaction?

Hint: Only one TBS-deprotection happens in step 19.  
In step 21 an elimination side reaction takes places.

24) Name of the reaction?

