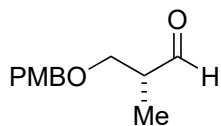
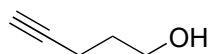
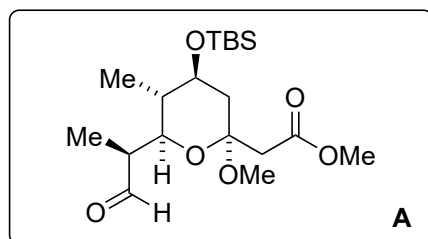


Total Synthesis and Structural Revision of Callipeltoside C

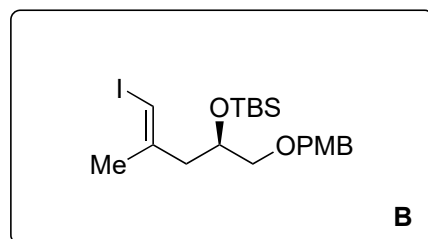
J. Carpenter, A. B. Northrup, d. Chung, J. J. M. Wiener, S.-G. Kim, D. W. C. MacMillan
Angew. Chem. Int. Ed. **2008**, 47, 3568.



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) $\text{SO}_3 \cdot \text{py}$, Et_3N , DMSO

- 7) AlMe_3 , $[\text{Cp}_2\text{ZrCl}_2]$, then I_2
- 8) Oxalyl chloride, Et_3N , DMSO
- 9) PhNO, L-proline
- 10) 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.

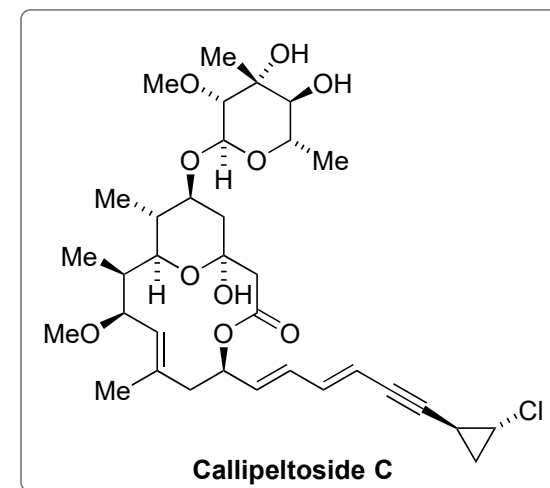
3) Name of the reaction?
 Semmelhack reaction

6) Name of the reaction?
 Parikh–Doering oxidation

7) Name of the reaction?
 Negishi carbometalation–iodination

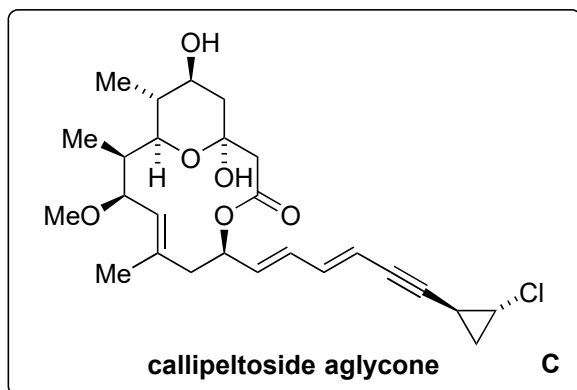
8) Name of the reaction?
 Swern oxidation

9) Explain the stereochemistry. Draw the transition state.



A

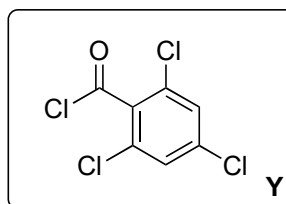
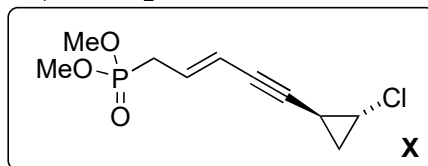
14 – 23



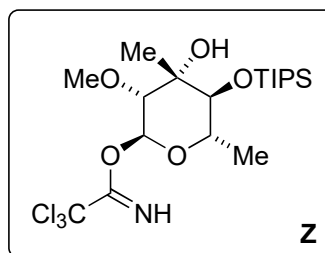
24 – 25

Callipeltoside C

- 14) $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$, then grignard of **B**
- 15) MeOTf, 2,6-DTBP
- 16) DDQ
- 17) $\text{SO}_3 \cdot \text{py}$, Et_3N , 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) $\text{PPh}_3 \cdot \text{HBr}$, H_2O
- 23) TFA, H_2O , THF



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



14) Explain the stereochemistry.

18) Name of the reaction?

Horner–Wadsworth–Emmons olefination

21) Name of the reaction?

Yamaguchi esterification

Hint: Only one TBS-deprotection happens in step 19.

In step 21 an elimination side reaction takes places.

24) Name of the reaction?

Tietze glycosylation

