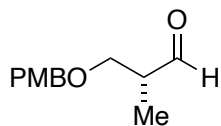


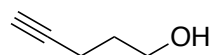
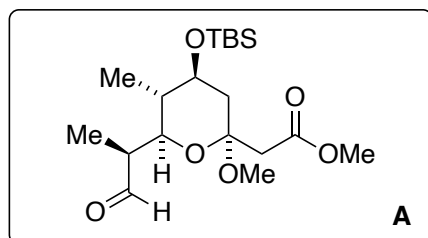
Total Synthesis and Structural Revision of Callipeltoside C

J. Carpenter, A. B. Northrup, D. Chung, J. J. M. Wiener, S.-G. Kim, D. W. C. MacMillan

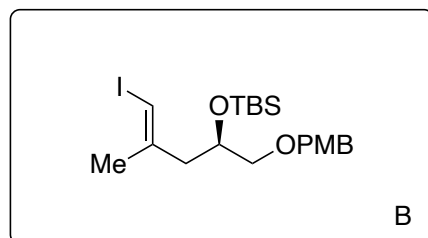
Angew. Chem. Int. Ed. **2008**, *47*, 3568.



1-6



7-13



- 1) Propionaldehyde, L-proline
- 2) Propargyl bromide, Zn
- 3) PdCl₂(CH₃CN)₂, CO, MeOH
p-benzoquinone
- 4) TBSCl, imidazole
- 5) DDQ
- 6) SO₃·py, Et₃N, DMSO

- 7) AlMe₃, [Cp₂ZrCl₂], then I₂
- 8) Oxalyl chloride, Et₃N, DMSO
- 9) PhNO, L-proline
- 10) NaBH₄
- 11) Zn, AcOH, EtOH
- 12) PMBCl, Bu₂Sn(OMe)₂, TBAI
- 13) TBSCl, imH

- 1) Explain the stereochemistry. Draw the transition state.

see below

- 3) Name of the reaction?

Semmelhack reaction

- 6) Name of the reaction?

Parikh-Doering oxidation

- 7) Name of the reaction?

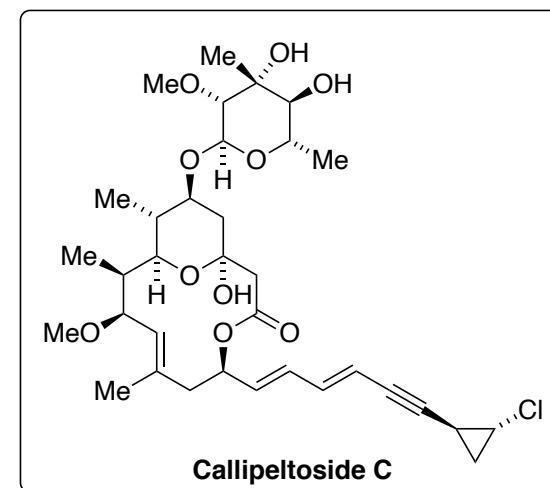
Negishi carbometalation-iodination

- 8) Name of the reaction?

Swern oxidation

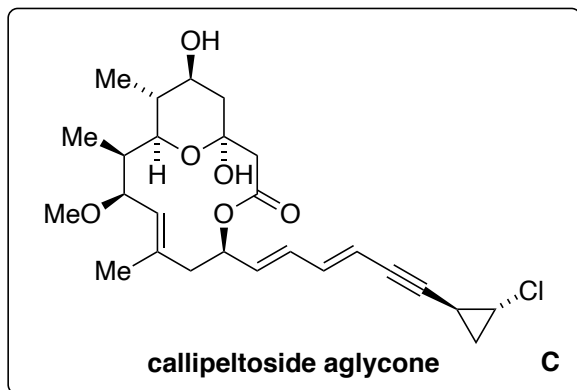
- 9) Explain the stereochemistry. Draw the transition state.

see below

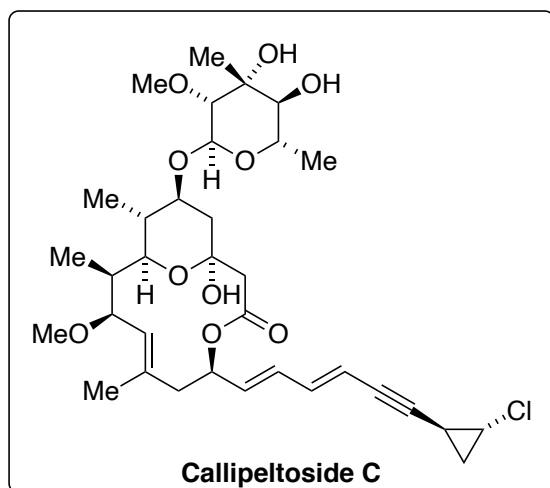


A

14-23



24-25



- 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

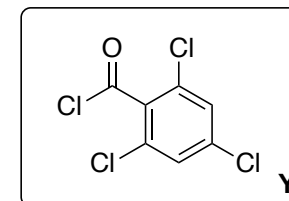
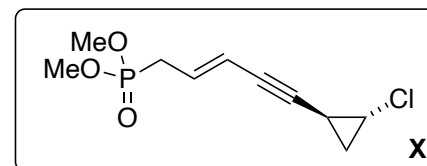
- 24) **Z**, TMSOTf
- 25) TASF

- 14) Explain the stereochemistry
see below

- 18) Name of the reaction?
Horner-Wadsworth-Emmons olefination

- 21) Name of the reaction?
Yamaguchi esterification

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



- 24) Name of the reaction?
Tietze glycosylation

