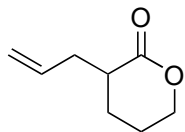


# Calyciphylline B-Type Alkaloids: Total Syntheses of (–)-Daphlongamine H and (–)-Isodaphlongamine H

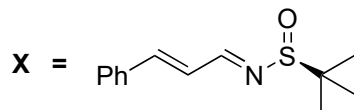
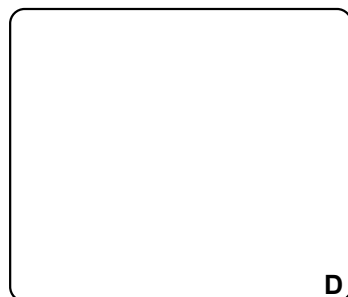
Hugelshofer, C. L.; Palani, V.; Sarpong, R.  
*J. Am. Chem. Soc.* **2019**, *141*, 8431–8435



1–5



6–9

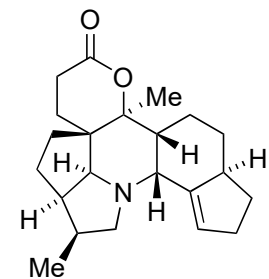


- 1) LDA *then* X
- 2) HCl, MeOH,  $\Delta$
- 3) 2,3-dibromopropene, *i*-Pr<sub>2</sub>NEt,  $\Delta$
- 4) TBSCl, imidazole
- 5) Ac<sub>2</sub>O,  $\Delta$

- 6) HG-II,  $\Delta$
- 7) LHMDS
- 8) Bu<sub>3</sub>SnH, Et<sub>3</sub>B, O<sub>2</sub>
- 9) H<sub>2</sub>, Pd(OH)<sub>2</sub>

**Step 1:** Quarternary stereocenter formed with 1:1 *dr*.  
Undesired diastereomer could be recycled.

Please provide the name of the reaction in **Step 7**.

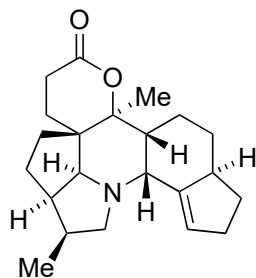


**daphlongamine H**

10–14



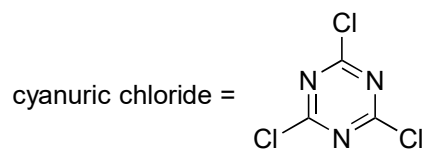
15–20



**daphlongamine H**

- 10) NaH, 4-iodobutene
- 11) TMSDS,  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$
- 12) TMSOTf *then*  $\text{HCCMgBr}$  *then* 6 M HCl
- 13)  $\text{LaCl}_3 \cdot 2\text{LiCl}$  *then* MeLi
- 14)  $\text{Co}_2(\text{CO})_8$  *then* trimethylamine *N*-oxide dihydrate

- 15) TFAA, pyridine *then*  $\text{SOCl}_2$
- 16)  $\text{H}_2\text{O}_2$ , TFAA
- 17) LAH
- 18)  $\text{NaCNBH}_3$ ,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\Delta$
- 19)  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , acetone
- 20) cyanuric chloride,  $\text{NEt}_3$



Please provide the name of the catalyst used in **Step 11**.

**Key step:** Please name the reaction in **Step 14**.