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

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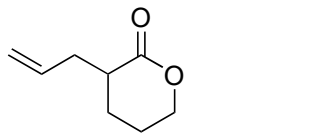
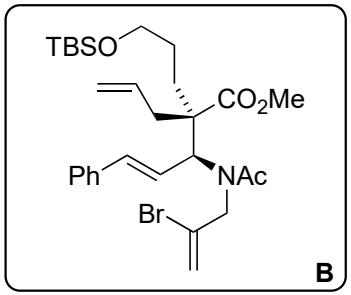
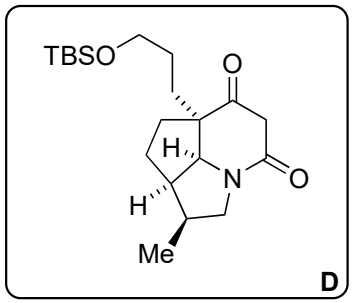


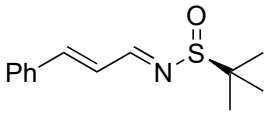
1–5




6–9




**X** =



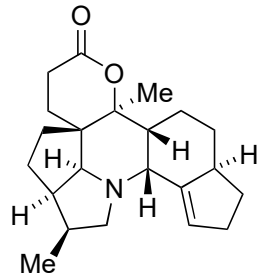

1) LDA *then* **X**
2) HCl, MeOH, Δ
3) 2,3-dibromopropene, *i*-$Pr_2NEt$, Δ
4) TBSCl, imidazole
5) $Ac_2O$, Δ

6) HG-II, Δ
7) LHMDS
8) $Bu_3SnH$, $Et_3B$, $O_2$
9) $H_2$, $Pd(OH)_2$

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

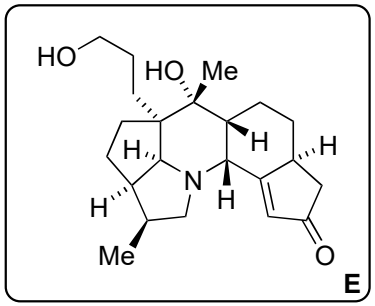
Please provide the name of the reaction in **Step 7**.

Dieckmann condensation



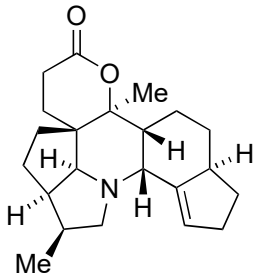

**daphlongamine H**

10–14




**E**

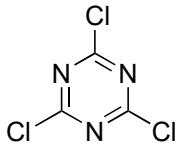
15–20




**daphlongamine H**

10) NaH, 4-iodobutene
11) TMDS, $[IrCl(CO)(PPh_3)_2]$
12) TMSOTf *then* HCCMgBr *then* 6 M HCl
13) $LaCl_3$•2LiCl *then* MeLi
14) $Co_2(CO)_8$ *then* trimethylamine *N*-oxide dihydrate

15) TFAA, pyridine *then* $SOCl_2$
16) $H_2O_2$, TFAA
17) LAH
18) $NaCNBH_3$, $BF_3$•$Et_2O$, $\Delta$
19) $CrO_3$, $H_2SO_4$, $H_2O$, acetone
20) cyanuric chloride, $NEt_3$

cyanuric chloride = 


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

Vaska's catalyst

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

Pauson–Khand reaction