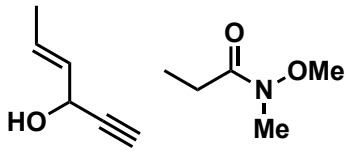
**Convergent Total Synthesis of Papililone A via Pd-Catalyzed Alkenylation/Cyclization Cascade**

Xing-Qian, ShanXiang, ZhangPeng-Fei, LianBao-Kuan, GuoYong-Qiang and TuSi-Hua Hou

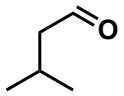
*J. Am. Chem. Soc.* **2025,** 147, 49, 44714–44719



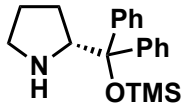

1-2

1) *i*-PrMgCl
2) HBr

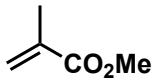
**A**




3-9




**1**




**2**

3) $CH_2O$, **1**, toluene 25°C
4) $[Ph_3PCH_3]Br$, *n*-BuLi
5) $PPh_3$, $CBr_4$, DCM
6) **2**, Mg, CuCl, TMSCl, THF, –78 °C *then* NaOH
7) $NH_4HCO_3$, $Boc_2O$, pyridine, 1,4-dioxane
8) TFAA, $NEt_3$, DCM
9) MeMgBr, $Et_2NH$, naphthalene, 2-MeTHF, 130 °C

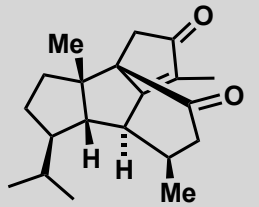
**2) Hint: heterocycle**

**3) Hint: product is (S) configured**

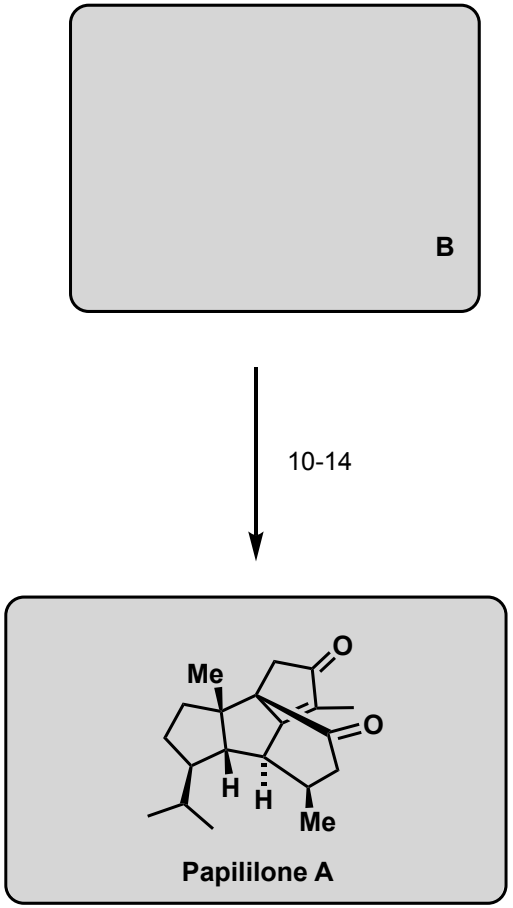
**5) Name of the reaction**

**8) Hint: all $^{13}C$ below 140 ppm**

**9) Show a mechanism, Hint: 2 rings are formed**




**Papililone A**




10) **A**, *n*-BuLi, *then* **B**, $LaCl_3$•2LiCl THF –78 °C
11) $O_2$, methylene blue, $h\nu$, DCM –80 °C *then* $Me_2S$
12) KOH, DCM/*i*PrOH
13) LiHMDS, Comin's reagent, THF –78 °C
14) $Pd(MeCN)_2Cl_2$, DPPP, $Cs_2CO_3$, toluene 140 °C

**10) Hint: Stereocenter formed is (S) configured**
**Name of the Lanthanum salt?**

**11) Role of methylene blue?**

**13) Hint: only cylopentanone reacts**

**14) Show a mechanism**