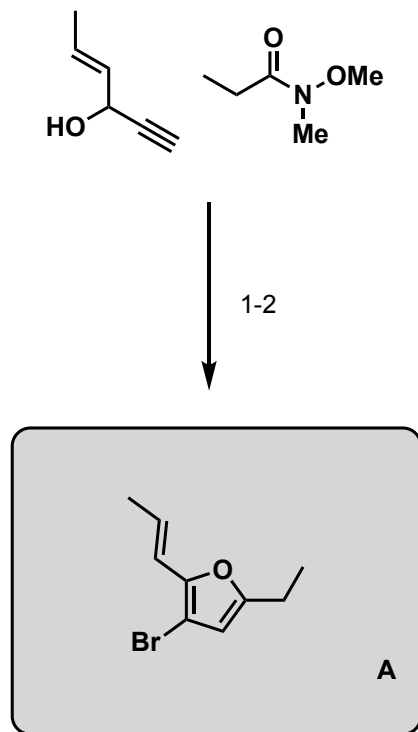


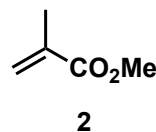
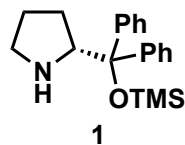
## Convergent Total Synthesis of Papililone A via Pd-Catalyzed Alkenylation/Cyclization Cascade

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

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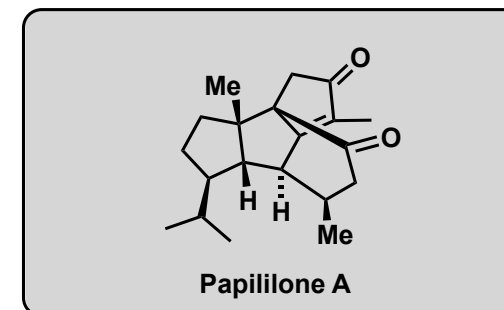


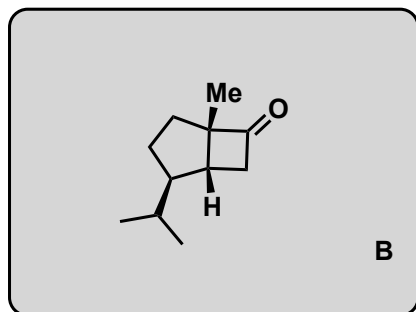
- 1) *i*-PrMgCl
- 2) HBr



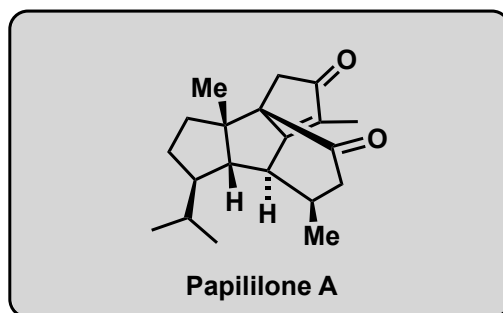
- 3)  $\text{CH}_2\text{O}$ , **1**, toluene 25 °C
- 4)  $[\text{Ph}_3\text{PCH}_3]\text{Br}$ , *n*-BuLi
- 5)  $\text{PPh}_3$ ,  $\text{CBr}_4$ , DCM
- 6) **2**, Mg, CuCl, TMSCl, THF, -78 °C then NaOH
- 7)  $\text{NH}_4\text{HCO}_3$ ,  $\text{Boc}_2\text{O}$ , pyridine, 1,4-dioxane
- 8) TFAA,  $\text{NEt}_3$ , DCM
- 9) MeMgBr,  $\text{Et}_2\text{NH}$ , naphthalene, 2-MeTHF, 130 °C

- 2) Hint: heterocycle
- 3) Hint: product is (S) configured
- 5) Name of the reaction  
Appel reaction
- 8) Hint: all  $^{13}\text{C}$  below 140 ppm
- 9) show a mechanism, Hint: 2 rings are formed





10-14



- 10) **A**, *n*-BuLi, then **B**, LaCl<sub>3</sub>•2LiCl THF -78 °C  
 11) O<sub>2</sub>, methylene blue, *hν*, DCM -80 °C then Me<sub>2</sub>S  
 12) KOH, DCM/*i*PrOH  
 13) LiHMDS, Comin's reagent, THF -78 °C  
 14) Pd(MeCN)<sub>2</sub>Cl<sub>2</sub>, DPPP, Cs<sub>2</sub>CO<sub>3</sub>, toluene 140 °C

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

**11) role of methylene blue?**  
 photosensitizer used to create singlet oxygen

**13) Hint: only cyclopentanone reacts**

**14) show a mechanism**

**9) <https://doi.org/10.1021/acs.orglett.3c01094>**

Scheme 3. Nitrile, Polar-Radical Crossover Cascade

