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

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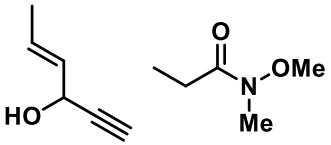
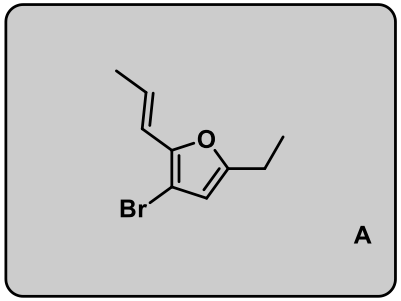
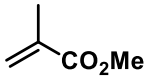


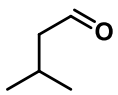
1-2

1) *i*-PrMgCl
2) HBr





1



3) CH_2O, toluene 25°C
4) $[Ph_3PCH_3]Br$, *n*-BuLi
5) PPh_3, CBr_4, DCM
6) **1**, 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, naphtalene, 2-MeTHF, 130 °C

3-9

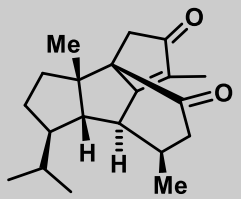
2) Hint: heterocycle

5) Name of the reaction

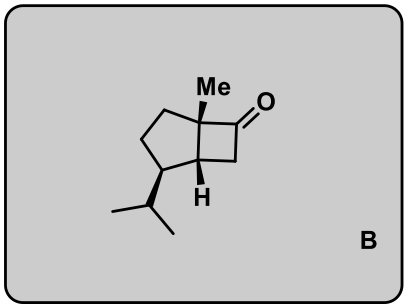
Appel reaction

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

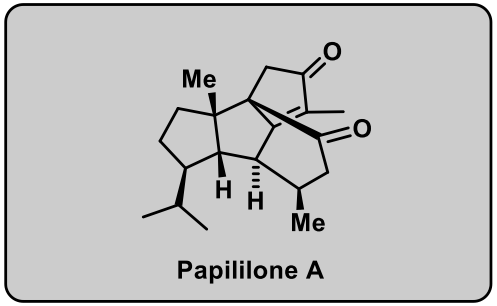
9) show a mechanism, Hint: 2 rings are formed



Papililone A



10-14



10) **A**, *n*-BuLi, *then* **B**, $LaCl_3$•2LiCl THF –78 °C
11) O_2, methylene blue, *hν*, 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) Name of the Lanthanum salt
Knochel salt

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

13) Hint: only cylopentanone reacts

14) show a mechanism

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

Scheme 3. Nitrile, Polar-Radical Crossover Cascade