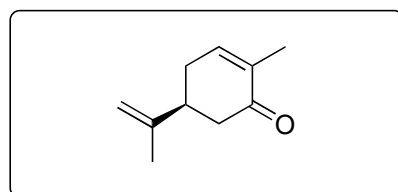


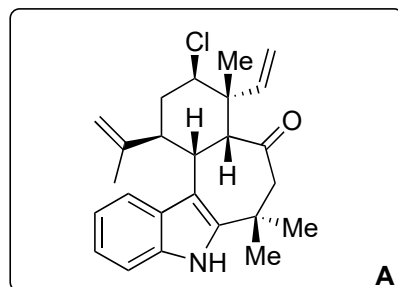
Total Synthesis of the Chlorinated Pentacyclic Indole Alkaloid (+)-Ambiguine G

Lingbowei Hu, Viresh H. Rawal

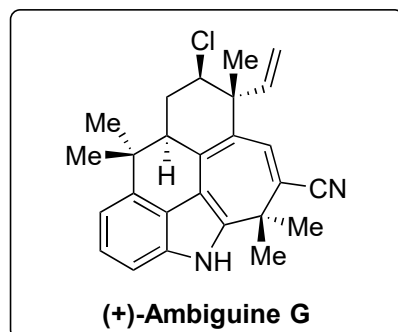
J. Am. Chem. Soc. **2021**, *143*, 10872–10875.



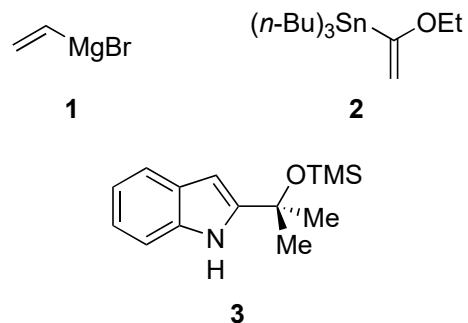
1–6



7–11

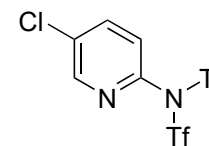


- 1) H_2O_2 , NaOH
- 2) TsNHNH₂; **1**; CuCl_2
- 3) NCS, PPh_3
- 4) NaHMDS, Comins' reagent
- 5) **2**, $\text{Pd}(\text{dppf})\text{Cl}_2$, CuI, LiCl
- 6) TMSOTf, **3**; HCl

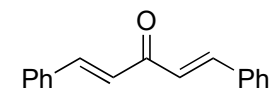


- 7) $\text{BF}_3 \cdot \text{OEt}_2$, MeOH; TBAF, DDQ
- 8) DIBAL; Et_2AlCl ; KHMDS, $\text{P}(\text{OMe})_3$, air
- 9) NBS; PPTS
- 10) $\text{Pd}(\text{dba})_2$, $\text{P}(t\text{-Bu})_3$, $\text{Zn}(\text{CN})_2$, Zn
- 11) $\text{BF}_3 \cdot \text{OEt}_2$, Et_3SiH

- 1) Name the starting material.
(*S*)-Carvone.
- 2) Propose a mechanism.
See second page.
- 3) Name the reaction.
Appel reaction.
- 4) Give the structure of Comins' reagent.



- 5) Name the reaction.
Stille cross coupling.
- 6) Classify the reaction.
(4+3) cycloaddition.
- 7) Name the reaction.
Friedel–Crafts alkylation.
- 8) Give the role of $\text{P}(\text{OMe})_3$.
Reduction of the intermediate hydroperoxide.
- 9) Give the role of PPTS.
Induces tautomerization.
- 10) Provide the structure of dba.



Mechanistic proposal for step 2:

