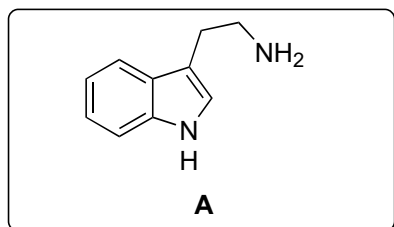


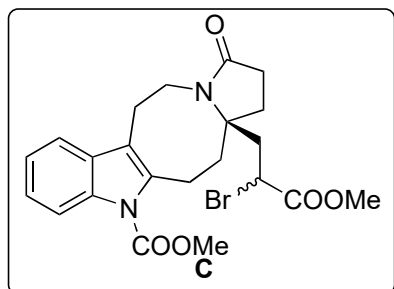
Total Synthesis of Pyrroloazocine Indole Alkaloid Grandilodine C

Fedor M. Miloserdov, Mariia S. Kirillova, Michael E. Muratore and Antonio M. Echavarren

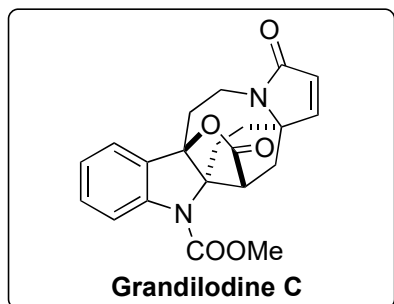
J. Am. Chem. Soc. **2018**, *140*, 5393



1-8



9-13



- 1) **B**, NEt₃, toluene, reflux, *then* HCl
- 2) Bestmann-Ohira-reagent, K₂CO₃, MeOH
- 3) AuCl, AcOH
- 4) NaHMDS, ClCO₂Me
- 5) OsO₄, NMO, *then* NaIO₄
- 6) H₂, Pd/C
- 7) SiCl₄, pyridine-*N*-oxide, *t*-BuNC, *then* MeOH
- 8) Ph₃PBr₂, NBu₄Br, imidazole

- 9) [(dppmAuCl)₂], Na₂CO₃, UV-LEDs (385 nm), MeCN
- 10) H₂SO₄ (aq), CH₂Cl₂
- 11) Lawesson's reagent
- 12) *p*-TolS(O)Cl, *i*-Pr₂NEt, *then* heat
- 13) *m*-CPBA

- 1) Name? Claisen rearrangement

- 5) Name? Lemieux-Johnson oxidation

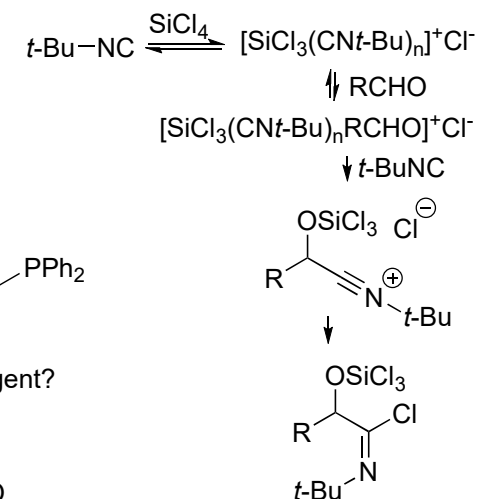
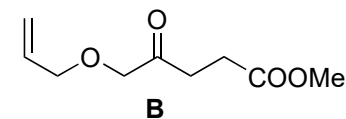
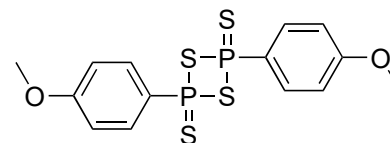
- 7) Name? Propose a mechanism! Passerini-type reaction

- 9) Mechanism? dppm: Ph₂P-CH₂-PPh₂

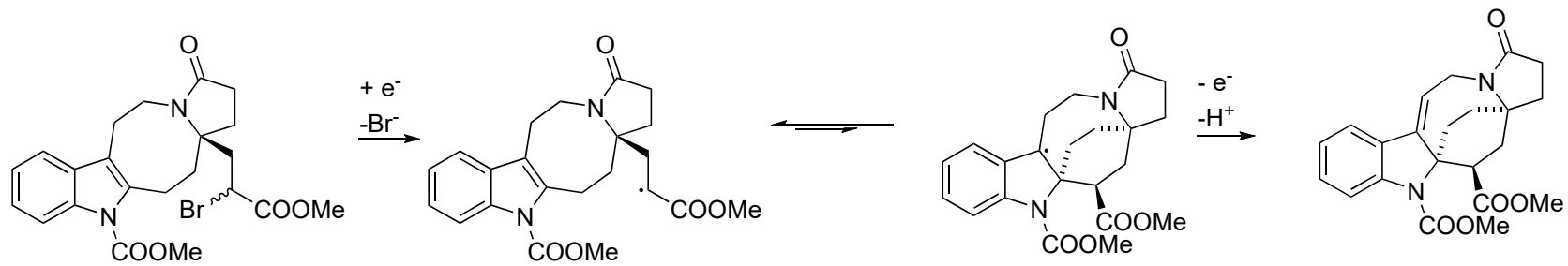
- 10) mechanism?

- 11) Structure of Lawesson's reagent?

- 12) Mechanism?



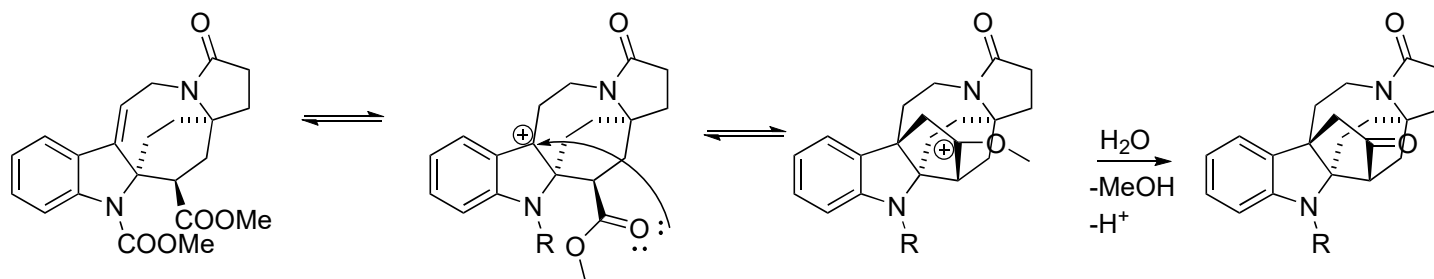
9)



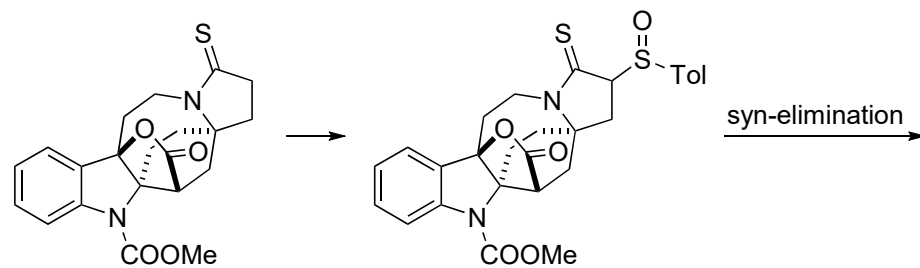
The excited gold complex acts as reducing agent

The oxidized gold complex takes up the electron

10)



12



S-sulfonylation and iminium ion participation would lead to strain