Unified Total Synthesis of Pyrroloazocine Indole Alkaloids Sheds Light on Their Biosynthetic Relationship

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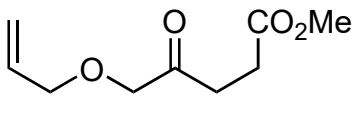

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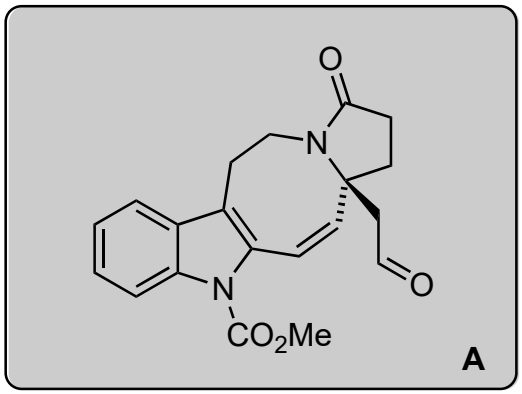
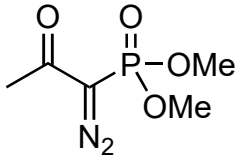


A

6-10

1) tryptamine, toluene, NEt_3, reflux *then* HCl
2) **1**, K_2CO_3, MeOH
3) AuCl (cat.), AcOH
4) NaHMDS, $ClCO_2Me$
5) OsO_4, NMO *then* $NaIO_4$



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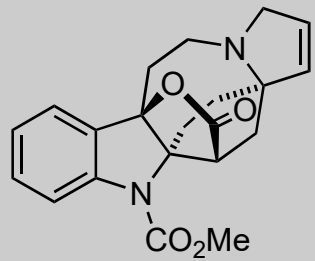
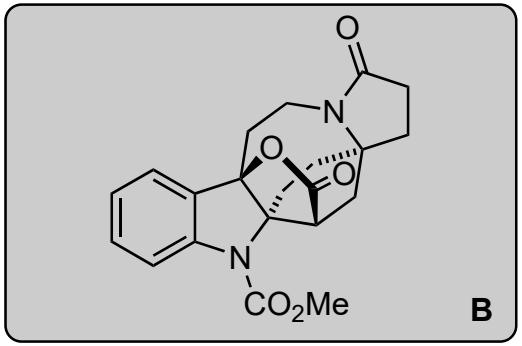
6) H_2, Pd/C
7) $SiCl_4$, pyridine *N*-oxide, t-BuNC *then* MeOH
8) Ph_3PBr, NBu_4Br, imidazole
9) $[(dppmAuCl)_2]$ (2 mol%), Na_2CO_3, UV LEDs
10) H_2SO_4 (50% aq)

1) *hint: cyclization followed by rearrangement*
draw out the mechanism
See Page 3
2) Name reaction?
Seyferth-Gilbert homologation
3) *hint: 8-membered ring is formed*

7) *hint: product is α-hydroxy ester*
8) Name reaction?
Appel reaction
10) *hint: lactonization*



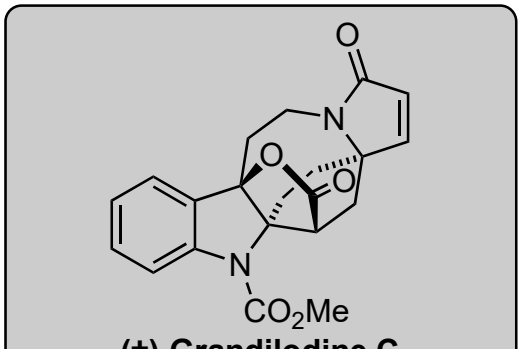
(±)-Lapidilectine B



B

11-13

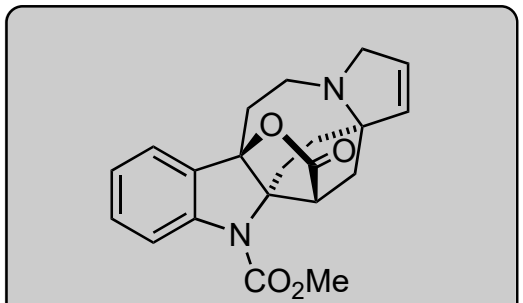
11) Lawesson's reagent, toluene
12) *p*-TolSOCl, *i*-Pr_2NEt
13) *m*-CPBA



(±)-Grandilodine C

14

14) Me_3OBF_4 *then* $NaBH_4$



(±)-Lapidilectine B

solution to step 1: ref: see *J. Am. Chem. Soc.* **2016**, *138*, 3671–3674