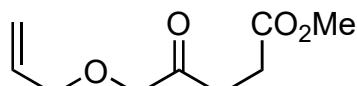


# Unified Total Synthesis of Pyrroloazocine Indole Alkaloids Sheds Light on Their Biosynthetic Relationship

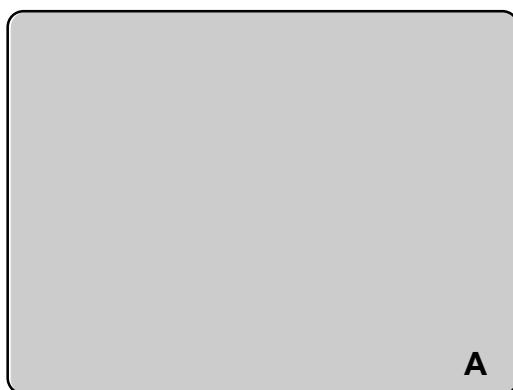
Miloserdov, F. M.; Kirillova, M. S.; Muratore, M. E.; Echavarren, A. M.

J. Am. Chem. Soc. 2018, 140, 5393–5400.

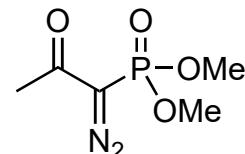


1-5

- 1) tryptamine, toluene,  $\text{NEt}_3$ , reflux *then* HCl
- 2) **1**,  $\text{K}_2\text{CO}_3$ , MeOH
- 3)  $\text{AuCl}$  (cat.), AcOH
- 4)  $\text{NaHMDS}$ ,  $\text{CICO}_2\text{Me}$
- 5)  $\text{OsO}_4$ , NMO *then*  $\text{NaIO}_4$



6-10



**1**

- 6)  $\text{H}_2$ , Pd/C
- 7)  $\text{SiCl}_4$ , pyridine *N*-oxide, t-BuNC *then* MeOH
- 8)  $\text{Ph}_3\text{PBr}$ ,  $\text{NBu}_4\text{Br}$ , imidazole
- 9)  $[(\text{dppmAuCl})_2]$  (2 mol%),  $\text{Na}_2\text{CO}_3$ , UV LEDs
- 10)  $\text{H}_2\text{SO}_4$  (50% aq)

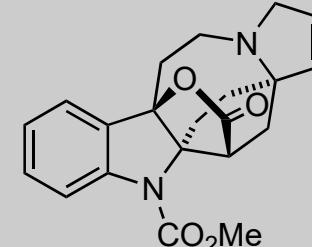
1) *hint: cyclization followed by rearrangement*  
draw out the mechanism

2) Name reaction?

3) *hint: 8-membered ring is formed*

7) *hint: product is  $\alpha$ -hydroxy ester*  
8) Name reaction?

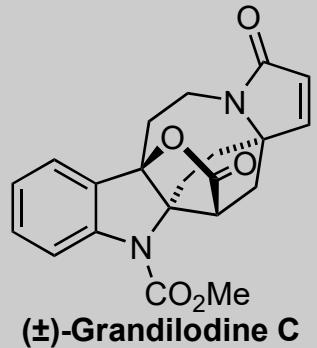
10) *hint: lactonization*



$(\pm)$ -Lapidilectine B

B

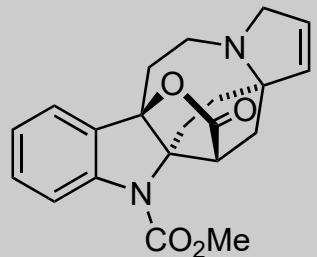
11-13



( $\pm$ )-Grandilodine C

- 11) Lawesson's reagent, toluene
- 12)  $p$ -TolSOCl,  $i$ -Pr<sub>2</sub>NEt
- 13)  $m$ -CPBA

14



( $\pm$ )-Lapidilectine B

- 14)  $\text{Me}_3\text{OBF}_4$  *then*  $\text{NaBH}_4$