Concise Synthesis of Norzoanthamine Enabled by a Set of Photochemical Transformations

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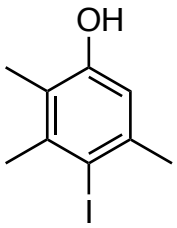
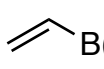


1-3

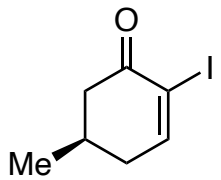
A

6-12

1) **1**, $Pd(PPh_3)_4$, NEt_3, dioxane, 120 ˚C
2) **2**, $Pd(dppf)Cl_2$, Cs_2CO_3, dioxane/H_2O, rt
3) Hg lamp, BHT, PhMe, -15 ˚C



1



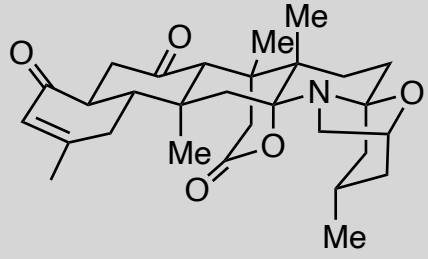
2

4) $Rh(PPh_3)_3Cl$, Et_3SiH *then* K_2CO_3, MeOH
5) Oxone, CF_3COMe, $NaHCO_3$, Na_2EDTA, MeCN
6) BF_3•OEt_2, DCM *then* 2-ethyl-2-methyl-1,3-dioxolane
7) dimethyl fumarate, Hg lamp
8) $CeCl_3$, $NaBH_4$ (1.5 eq), MeOH, -15 ˚C *then* NaOH, THF
9) NHPI, DCC, DMAP
10) $B_2(cat)_2$, hν (λ = 450 nm), DMA *then* H_2O_2 (aq.)
11) K_2CO_3, MeCN, 105 ˚C
12) DMP (2 eq)

4) *Hint*: product has a molecular formula of $C_{18}H_{24}O_2$ and the NMR in $CDCl_3$ has four ^{13}C peaks in 120-150 ppm region, one ^1H peak above 4 ppm.

6) Name the reaction for the first set of conditions.

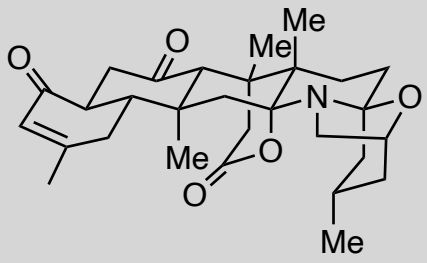
8) *Hint:* oxidation state is preserved in the B-ring.



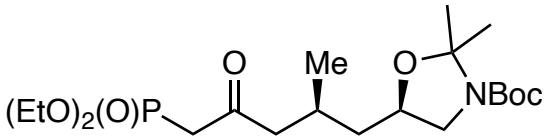
Norzoanthamine

B

13-16



Norzoanthamine



3

13) **3**, NaH
14) Pd/*C*, H_2 *then* NaOH, THF
15) AcOH (aq.), 100 ˚C
16) LiHMDS, PhS(N*t*-Bu)Cl