Total Synthesis of (±)-Streptonigrin

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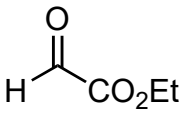


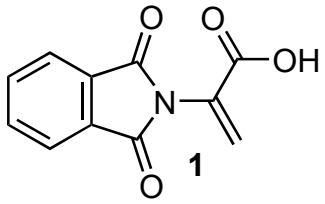
1-4

A

5-7

B

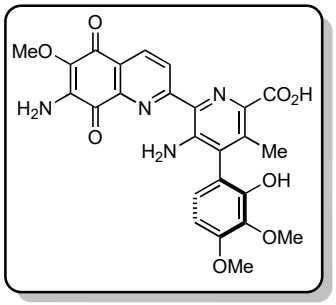
1) $MeONH_2 \cdot HCl$
2) Crotylbromide, Zn, NH_4Cl (aq)
3) **1,** $(COCl)_2$ *then* **product of step 2**, NEt_3
4) Grubbs-Hoyveda II (5 mol%), benzoquinone (15 mol%)

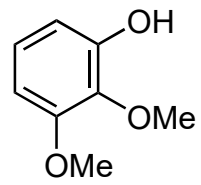


1

5) quinuclidine, MeOH then $MeNH_2$
6) Tf_2O, DTBMP
7) NBS

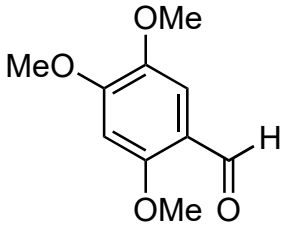
4) What is the role of benzoquinone?





8-10

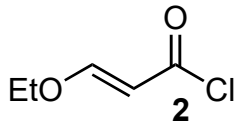
C



11-16

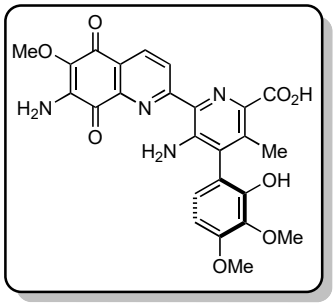
D

8) NBS (1 eq)
9) K_2CO_3, BnBr
10) *t*-BuLi then *i*-PrOB(pin)



2

11) HNO_3 (aq) *Hint:* Ipso
12) H_2, Pd/C
13) **2,** py
14) H_2SO_4 *Hint:* Ring formation takes place
15) $POCl_3$, py, PhCl, DMF (cat.)
16) Me_6Sn_2 (1.1 equiv), $Pd[PPh_3]_4$ (5 mol%)



D+B

17-19

17) $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), CsF
18) **C** (1.5 eq), $Pd(PPh_3)_4$ (10 mol%), K_3PO_4 (aq)
19) CAN (aq)

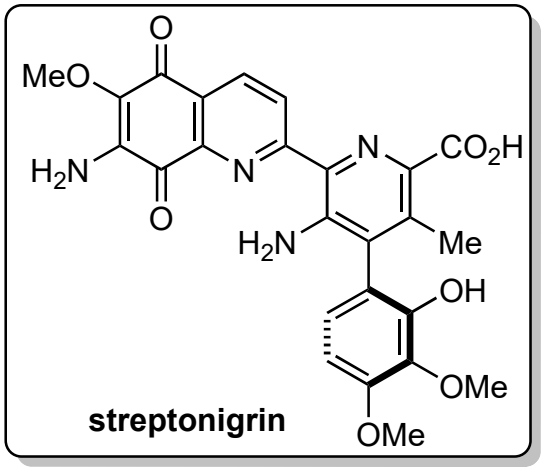
17) Name of the reaction?

18) Name of the reaction?

19) Chemical formula CAN?
Oxidation state of the metal?
Oxidation half reaction of the metal?

20-23

20) Br_2 (4 eq), py, *Hint:* double bromination
21) NaN_3
22) Pd/C (10 wt%), H_2
23) K_2CO_3 (aq)



streptonigrin