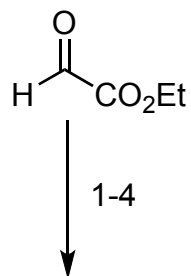
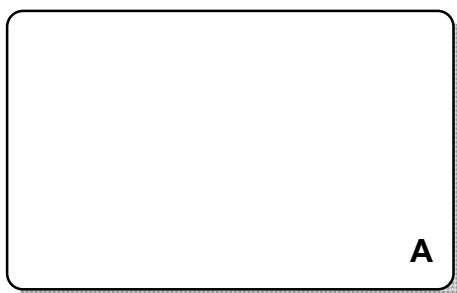


## Total Synthesis of (±)-Streptonigrin

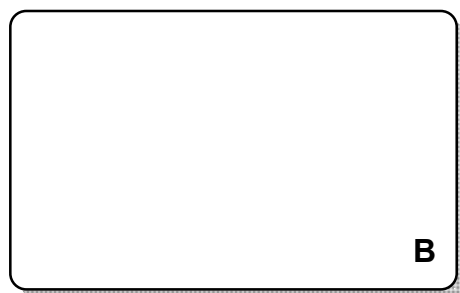
Donohoe\*, T. J.; Jones, C. R.; and Barbosa, L. C. A.  
*J. A. Chem. Soc.* **2011**, *133*, 16418–16421.



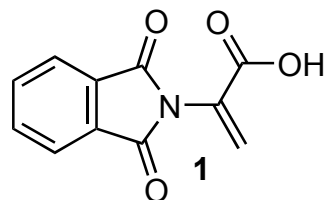
1-4



5-7

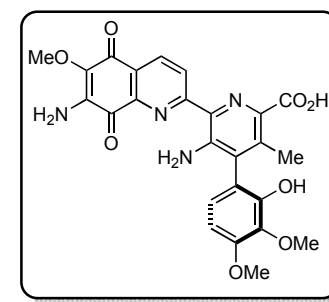


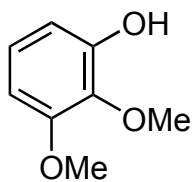
- 1)  $\text{MeONH}_2 \cdot \text{HCl}$
- 2) Crotylbromide, Zn,  $\text{NH}_4\text{Cl}$  (aq)
- 3) **1**,  $(\text{COCl})_2$  then **product of step 2**,  $\text{NEt}_3$
- 4) Grubbs-Hoyveda II (5 mol%), benzoquinone (15 mol%)



- 5) quinuclidine, MeOH then  $\text{MeNH}_2$
- 6)  $\text{Tf}_2\text{O}$ , DTBMP
- 7) NBS

4) What is the role of benzoquinone?

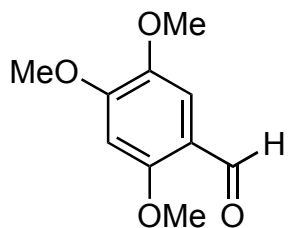




8-10



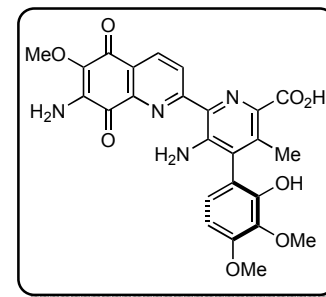
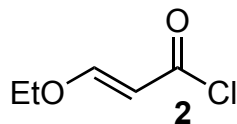
- 8) NBS (1 eq)
- 9)  $K_2CO_3$ , BnBr
- 10) *t*-BuLi then *i*-PrOB(pin)



11-16

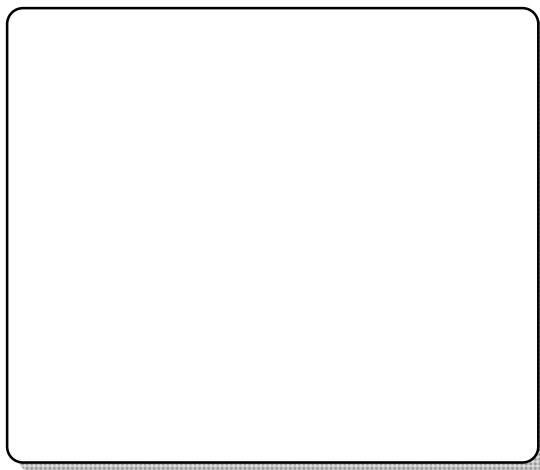


- 11)  $HNO_3$  (aq) *Hint*: Ipso
- 12)  $H_2$ , Pd/C
- 13) **2**, py
- 14)  $H_2SO_4$  *Hint*: Ring formation takes place
- 15)  $POCl_3$ , py, PhCl, DMF (cat.)
- 16)  $Me_6Sn_2$  (1.1 equiv),  $Pd[PPh_3]_4$  (5 mol%)

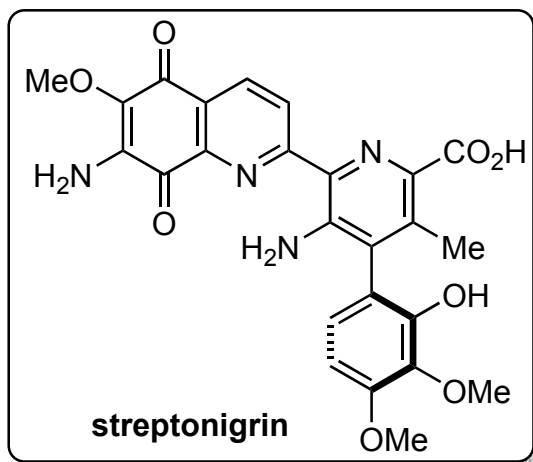


D+B

17-19



20-23



- 17)  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%),  $\text{CuI}$  (10 mol%),  $\text{CsF}$   
18) **C** (1.5 eq),  $\text{Pd}(\text{PPh}_3)_4$  (10 mol%),  $\text{K}_3\text{PO}_4$  (aq)  
19)  $\text{CAN}$  (aq)

- 20)  $\text{Br}_2$  (4 eq), py, *Hint*: double bromination  
21)  $\text{NaN}_3$   
22)  $\text{Pd/C}$  (10 wt%),  $\text{H}_2$   
23)  $\text{K}_2\text{CO}_3$  (aq)

17) Name of the reaction?

18) Name of the reaction?

19) Chemical formula  $\text{CAN}$ ?

Oxidation state of the metal?

Oxidation half reaction of the metal?

