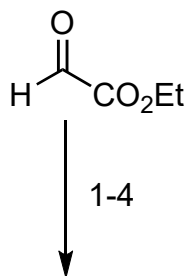
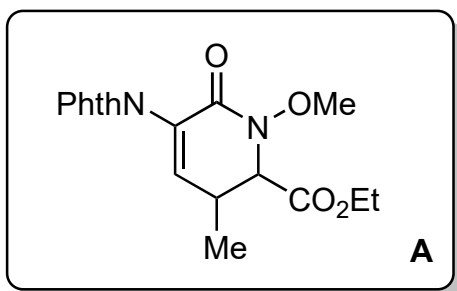


Total Synthesis of (±)-Streptonigrin

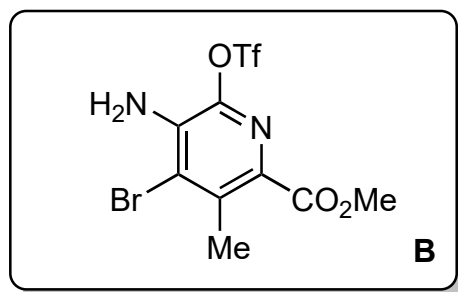
Timothy J. Donohoe*, Christopher R. Jones and Luiz C. A. Barbosa
Journal of the American Chemical Society **2011**, *133* (41), 16418–16421.
DOI: 10.1021/ja207835w



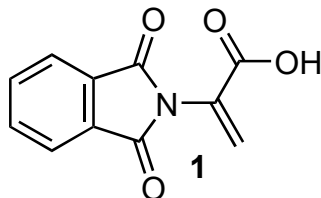
1-4



5-7



- 1) MeONH₂·HCl
- 2) Crotylbromide, Zn, NH₄Cl (aq)
- 3) **1**, (COCl)₂ then product of step 2, NEt₃
- 4) Grubbs-Hoyveda II (5 mol%), benzoquinone (15 mol%)



- 5) quinuclidine, MeOH then MeNH₂
- 6) Tf₂O, DTBMP
- 7) NBS

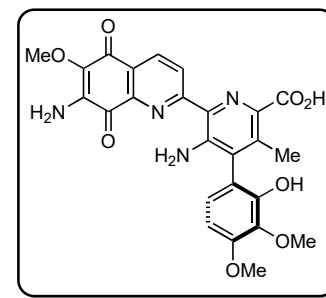
4) What is the role of benzoquinone?

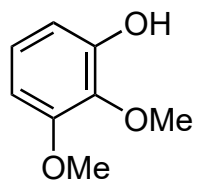
Benzoquinone is used to quench the ruthenium hydride complex. The hydride complex might be present as an impurity in the metathesis catalyst or is formed by decomposition under the reaction conditions. The ruthenium hydride complex catalyses double bond isomerisation.

sources:

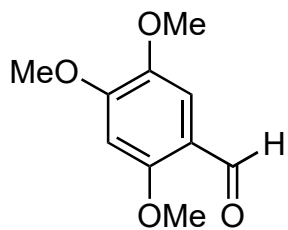
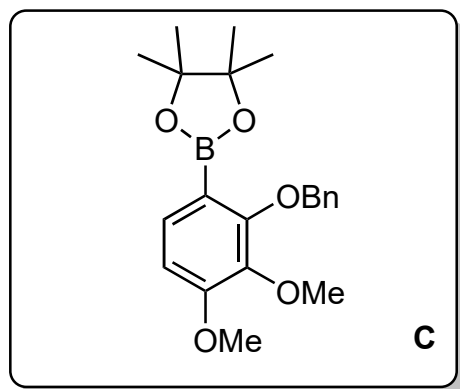
<https://doi.org/10.1002/ejoc.200300714>

<https://doi.org/10.1021/ja052939w>

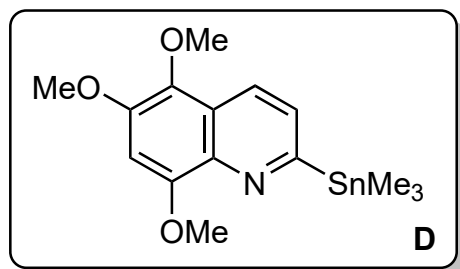




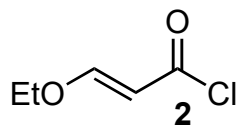
8-10



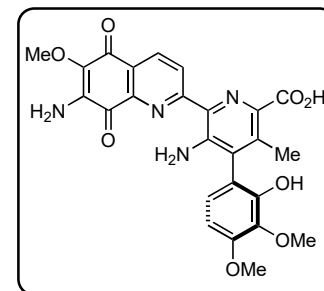
11-16



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

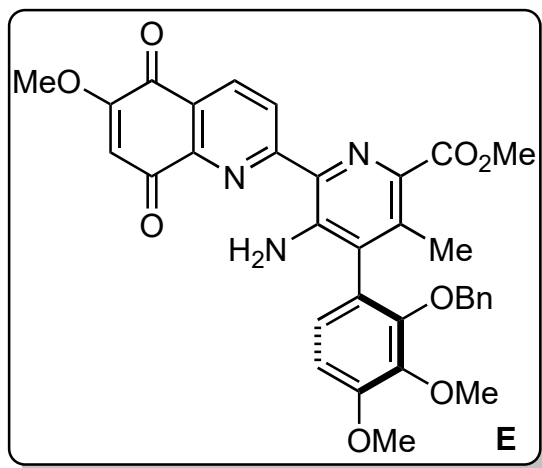


- 11) HNO_3 (aq) *Hint*: Ipso
- 12) H_2 , Pd/C
- 13) **2**, py
- 14) H_2SO_4 *Hint*: Ring formation takes place
- 15) $POCl_3$, py, PhCl, DMF (cat.)
- 16) Me_6Sn_2 (1.1 equiv), $Pd[PPh_3]_4$ (5 mol%)

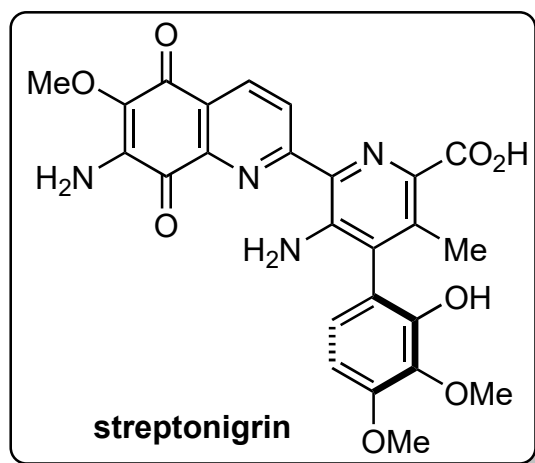


D+B

17-19



20-23



- 17) Pd(PPh₃)₄ (5 mol%), CuI (10 mol%), CsF
18) **C** (1.5 eq), Pd(PPh₃)₄ (10 mol%), K₃PO₄ (aq)
19) CAN (aq)

- 20) Br₂ (4 eq), py, *Hint*: double bromination
21) NaN₃
22) Pd/C (10 wt%), H₂
23) K₂CO₃ (aq)

17) Name of the reaction?
Stille reaction

18) Name of the reaction?
Suzuki reaction

19) Chemical formula CAN?
Oxidation state of the metal?
Half reaction of the metal?
(NH₄)₂[Ce(NO₃)₆]
Ce(IV)
Ce(IV) + e⁻ → Ce(III)

