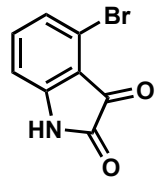
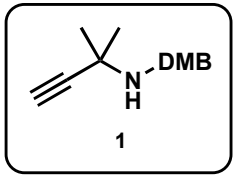
Total Synthesis of (±)-Aspergilline A



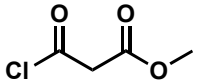
1) MeI, K_2CO_3, DMF, 80 °C

2) **1**, $Pd(PPh_3)_4$ (4 mol%), CuI (8 mol%), Cs_2CO_3, *i*-Pr_2NEt, PhMe, 85 °C

A



1



3) *i*-Pr_2NEt, DCM, -78 °C, 1 h

then **A**

B

4) 420 PSI H_2, Raney Ni, MeOH, 48 h

5) DMP, DCM

C

6) TMSOTf, Et_3N, DCM, 0-35 °C

then $TiCl_4$ (0.25 eq.), DCM, -78 °C-RT

D

7) DDQ, $CHCl_3/H_2O$, 75 °C

8) MeOTf, DCM

E

9) Cycloprop-2-en-1-one, MeCN

F + G

(2:3)

10) Oxone, MeCN/H_2O, 0 °C

11) i. PIFA, DCM, RT

ii. Degassed TFA/H_2O (3:1), 55 °C

H

12) NaSePh, 18-C-6, THF, 0 °C

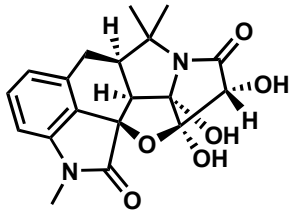
13) $Mg(ClO_4)_2$ (0.3 eq.), Ac_2O, 75 °C

14) HgO, I_2, *hv*, DCM, 115 °C

[**I**]

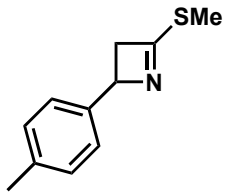
15) Bu_3SnH, AIBN, Toluene, 115 °C-RT

16) K_2CO_3, MeOH, RT



Aspergilline A

Mechanism:



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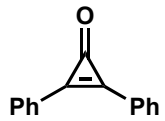

MeCN, rt

J

Toluene, reflux

K