A Unified Synthetic Approach to the Pleurotin Natural Products

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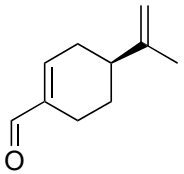
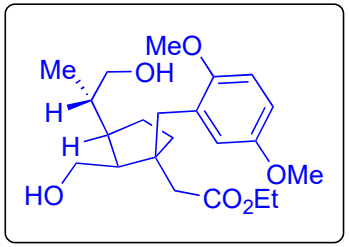


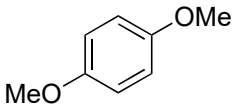
1 - 5



A

6 - 11

1) **1,** *n*BuLi, TMEDA *then* TFA, Et_3SiH
2) O_3, pyridine, isoprene *then* Me_2S
3) piperidine, AcOH *then* $NaBH_4$
4) $MeC(OEt)_3$, PivOH, 145 °C
5) 9-BBN *then* $BH_3{\cdot}Me_2S$ *then* NaOH, H_2O_2



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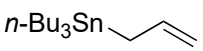


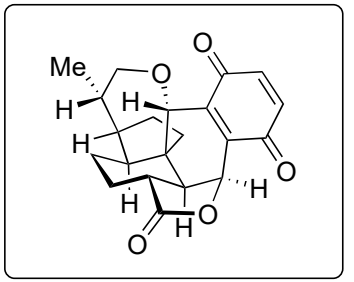
2

6) TBDPSCl, NEt_3, DMAP
7) CBr_4, PPh_3
8) DIBAL-H *then* *p*-$TsOH{\cdot}H_2O$
9) **2**, *n*-BuLi, HMPA
10) 9-BBN *then* NaOH, H_2O_2
11) DMP, $NaHCO_3$

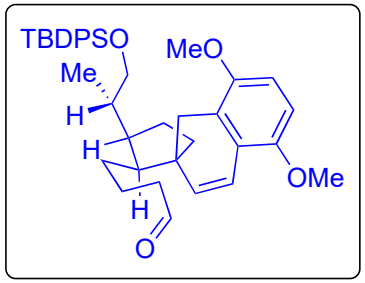
1) Name of the starting material?
(–)-perillaldehyde
2) *Hint:* regioselective ozonolysis. Role of isoprene?
Prevent overoxidative cleavage.
4) Name of the reaction?
Johnson-Claisen rearrangement.
5) *Hint:* both alkene react.

6) Hint: mono-protection.

8) Name of the reaction?
Friedel-Crafts cyclodehydration



(–)-pleurotin

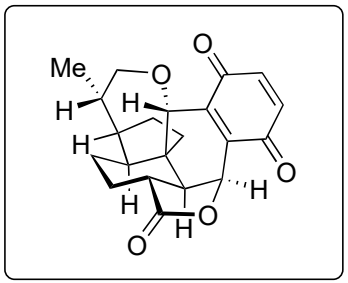


B

12 - 16

12) [Ir(dtbbpy)(ppy)$_2$][PF$_6$], piperidine, 2,4,6-triisopropylbenzenethiol, 450 nm, Blue LEDs
13) $NaClO_2$, Na_2HPO_4, 2-methyl-2-butene *then* *p*-TsOH·H_2O
14) DDQ, AcOH, 4 Å MS
15) DDQ, AcOH, 4 Å MS
16) CAN

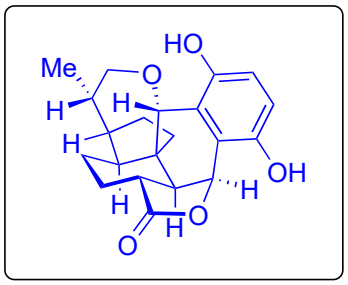
12) *Hint:* draw **B** like the natural product & a ring is closed.
13) Name of the reaction?
Pinnick oxidation



(–)-pleurotin

17

17) Zn, AcOH



(+)-leucopleurotin