Ir-Catalyzed Asymmetric Total Syntheses of Bisdehydrotuberostemonine D, Putative Bisdehydrotuberostemonine E and Structural Revision of the Latter

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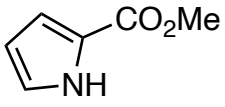
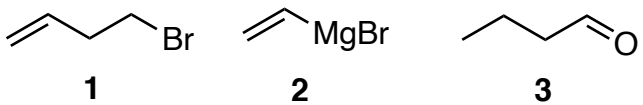


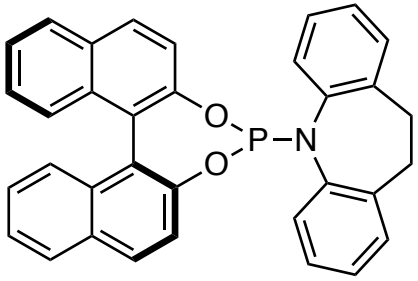
1-5

A

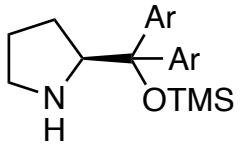


1 **2** **3**

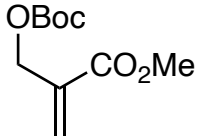
1) DMF, $POCl_3$
2) K_2CO_3, **1**; then **2**
3) **3**, $[Ir(cod)Cl]_2$, **(S)-P**, **(S)-A,** malonic acid
4) Grubbs II
5) **4**, (R)-Ir-tol-BINAP, Cs_2CO_3



(S)-P



(S)-A



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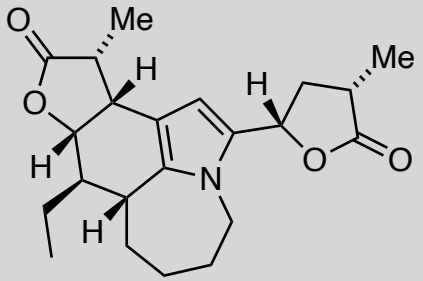
1) Name the key intermidiate, rationlize the regioselectivity

Hint:
3) α-functionlization of the aldehyde
5) one ring formed

5) classify the reaction and discribe the mechanism

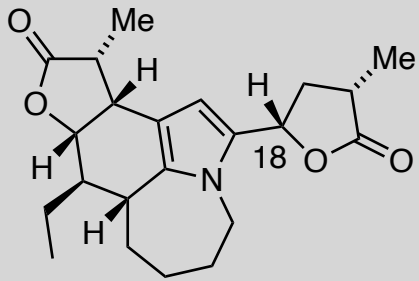


bisdehydrotuberostemonine D

6-11

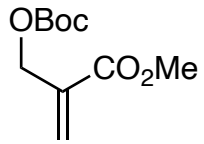
B

12-13



bisdehydrotuberostemonine D

6) $Ru_3(CO)_{12}$, Et_3N
7) NIS, $In(PTf)_2$
8) $PdCl_2(PPh_3)_2$, DIPEA
9) $Pd(OH)_2$, H_2
10) DIBAL-H
11) NMO, TPAP
12) **4**, (R)-Ir-tol-BINAP, Cs_2CO_3
13) [RuCl(R)-BINAP(BENZENE)]Cl, H_2



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7) rationlize the regioselectivity

8) name the reaction

11) name the reaction
12) Epimerization at C-18 observed, provide a mechnism
13) classify the reaction