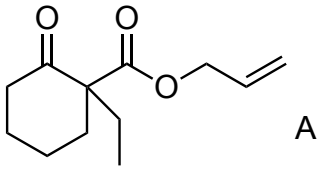
Synthesis Challenge #11 AG Wegner

Enantioselective Total Syntheses of Leuconolam–Leuconoxine–
Mersicarpine Group Monoterpene Indole Alkaloids**,** Z. Xu, Q. Wang, J. Zhu**,** *J. Am. Chem. Soc.* **2013**, *135*, 19127,àí19130

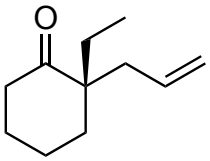
23.01.2014



A

1) $Pd_2(dba)_3$, (*S*)-*t*-BuPhox, THF, 25 °C

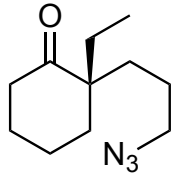
1



B

2-3

2) disiamyl borane, THF, 0 °C to rt, then NaI, NaOAc, Chloramine-T, MeOH, H_2O,
3) NaN_3, DMF, rt



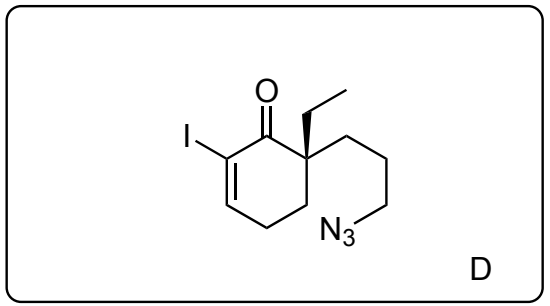
C

Please, provide a detailed mechanism for step 2).

Hydroboration-Iodonation Sequence
Kabalka, G. W.; Gooch, E. E. *J. Org. Chem.* **1981**, *46*, 2582–2584.

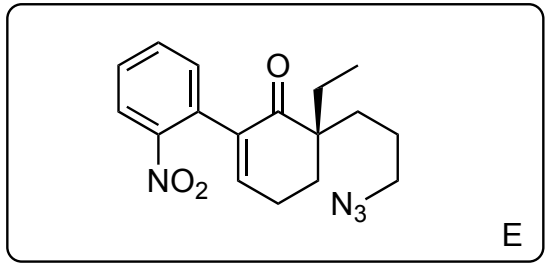
4-5

4) IBX, DMSO, 80 °C
5) I_2, DMAP, CCl_4/Py (1:1)



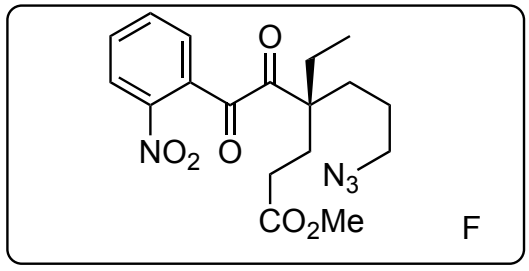
6

6) 2-$NO_2C_6H_4B(OH)_2$, $Pd_2(dba)_3$, JohnPhos, $Ba(OH)_2 \cdot 8\ H_2O$, THF, H_2O

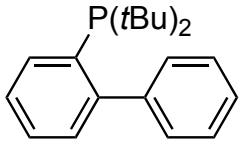


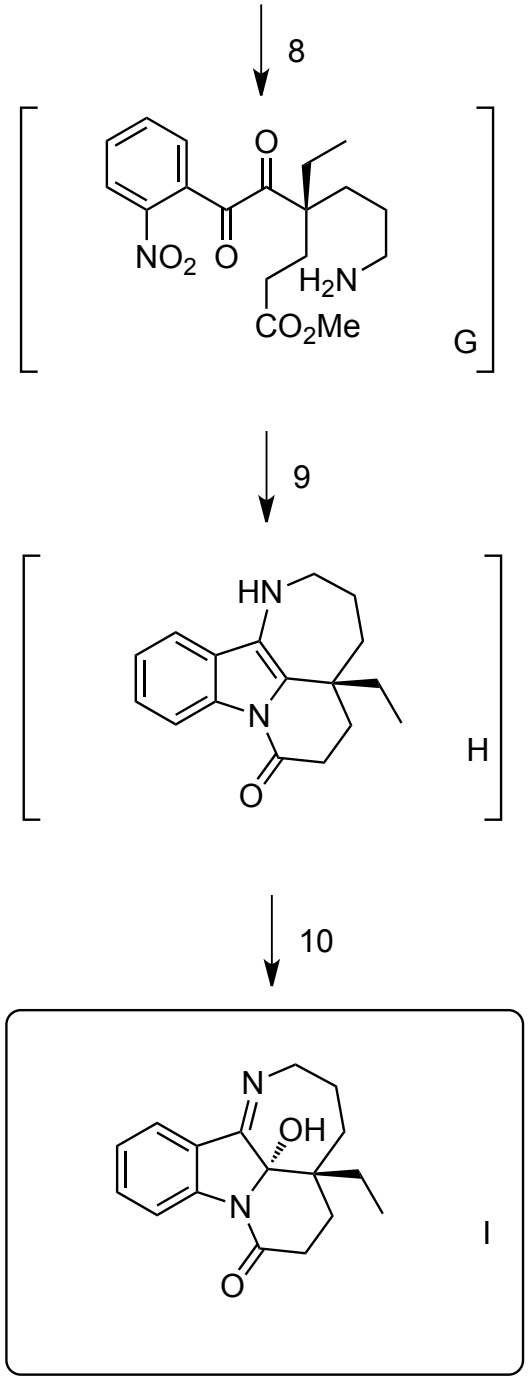
7

7) O_3, $NaHCO_3$, –78ºC, CH_2Cl_2/MeOH, then Ac_2O, Et_3N, 0ºC to RT



What is JohnPhos?



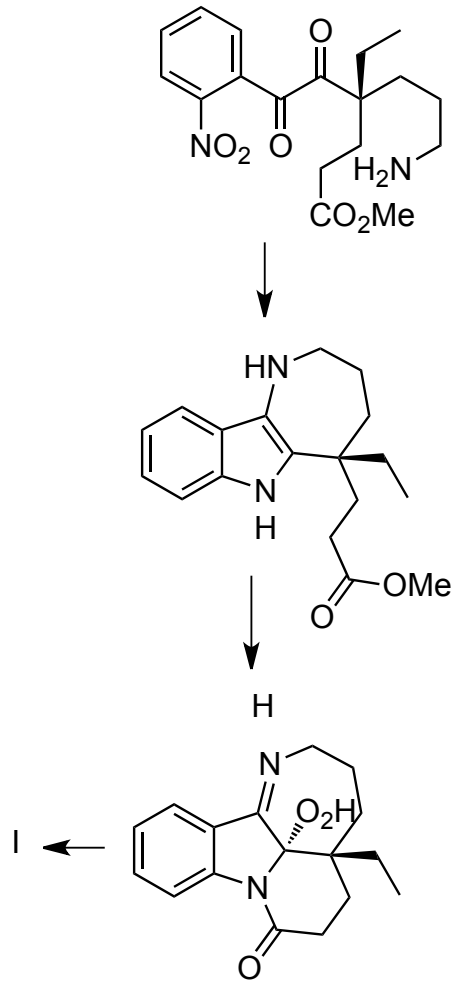


8) Pd/C H_2

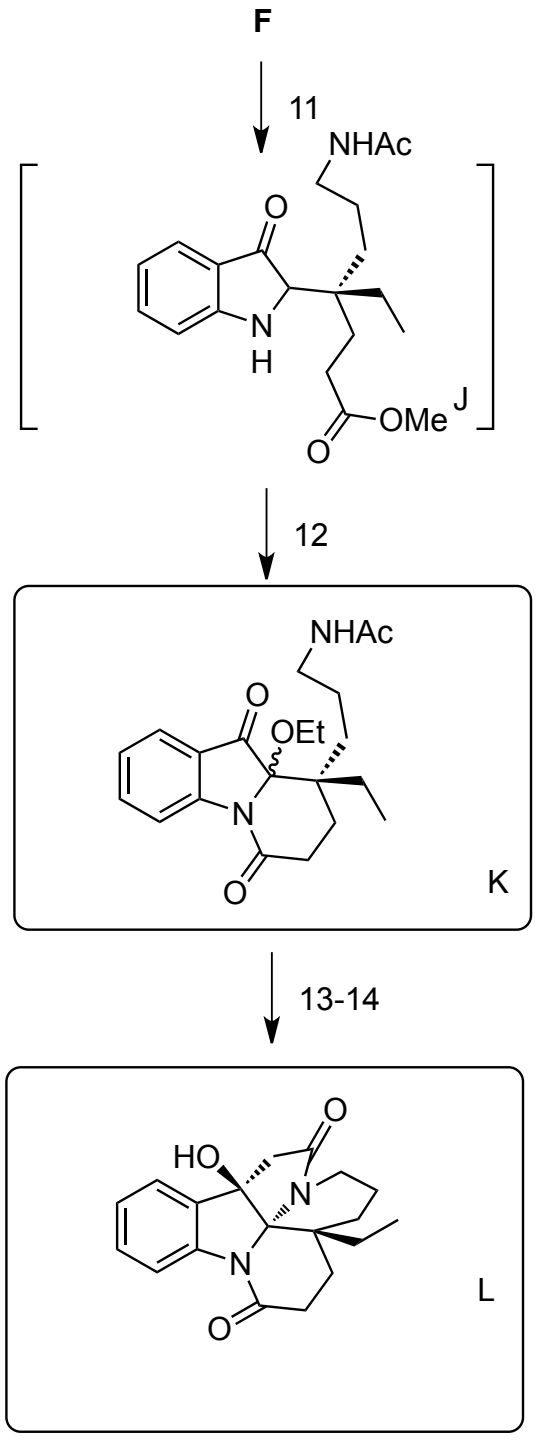
9) KOH, EtOH

10) O_2, then, Me_2S

Please, provide a detailed Mechanism for the transformation from F to I.



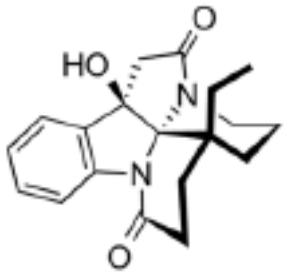
Please, draw a 3D representation of I.



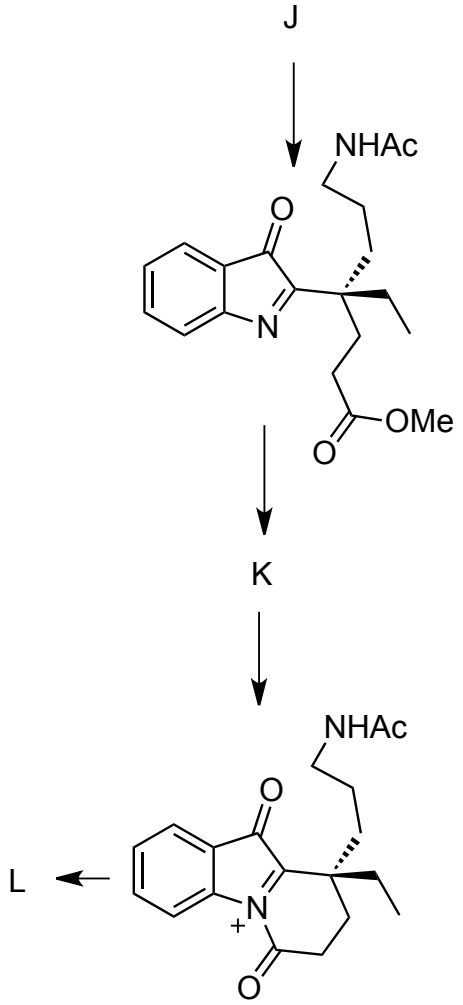
11) Pd/C, H_2, Ac_2O, EtOH

12) O_2, then KOH, EtOH

13) TFA/CH_2Cl_2
14) *t*-BuOK, THF, –50ºC, then –78ºC, HOAc



Please, provide a detailed Mechanism for the transformation from F to L.



Please, draw a 3D representation of L.