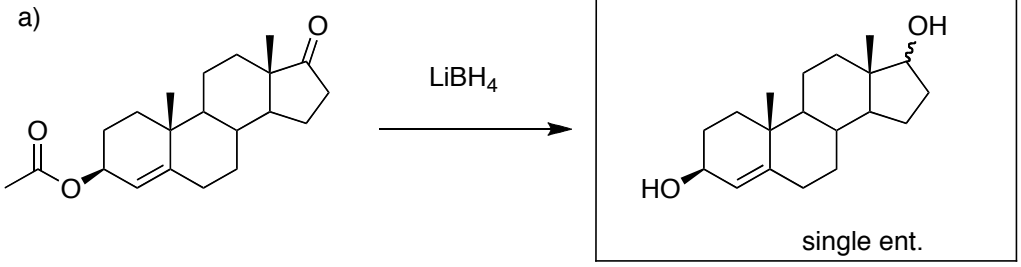
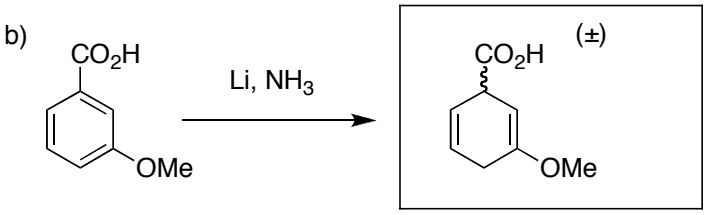
Chemistry 335 Additional Practice Final.

1. Fill in the boxes with the missing reagents, starting materials, or products **(1 mark each)**. For boxes with reaction products, show only the majo stereoisomer produced by the given reaction and *indicate whether it is achiral, racemic, or a single enantiomer* **(0.5 marks each)**.

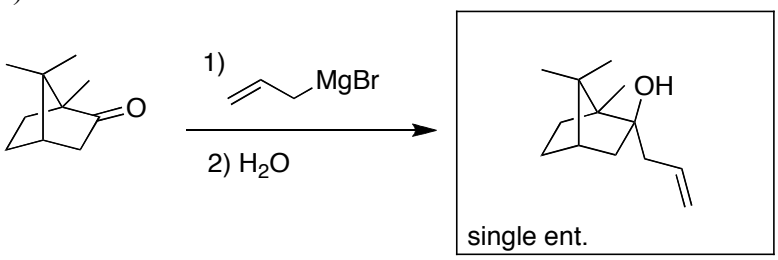
a)



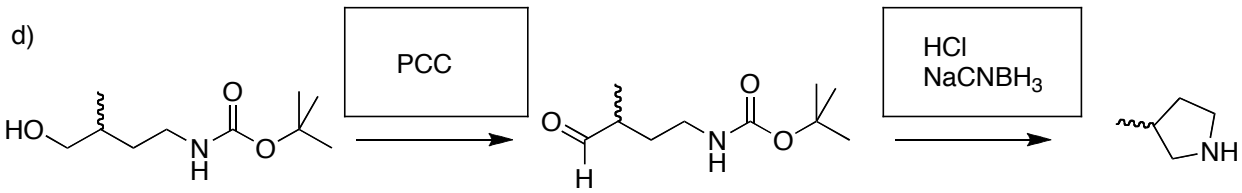
b)



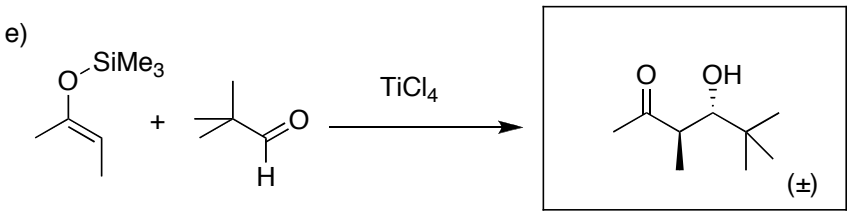
c)



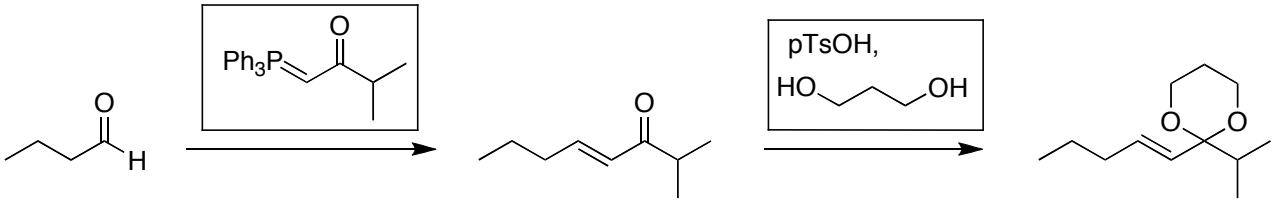
d)



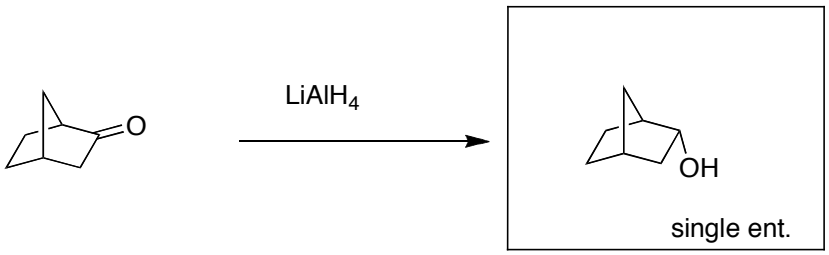
e)



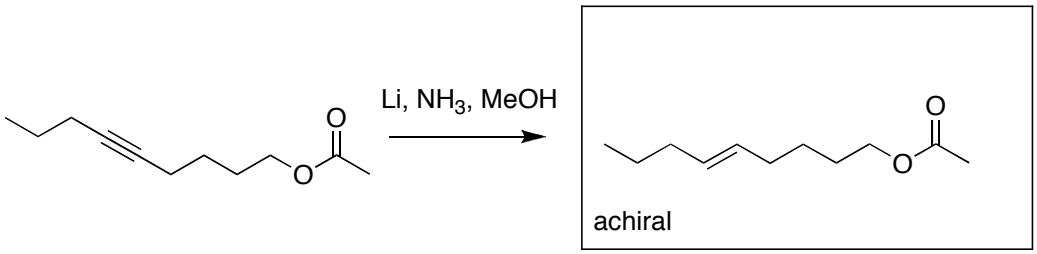
f)


O
H
Ph3P
O
O
pTsOH,
HO
OH
O
O

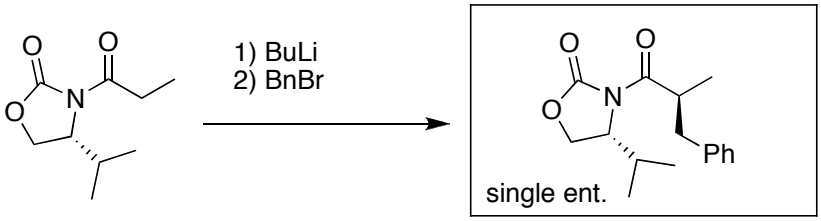
g)


O
LiAlH4
OH
single ent.

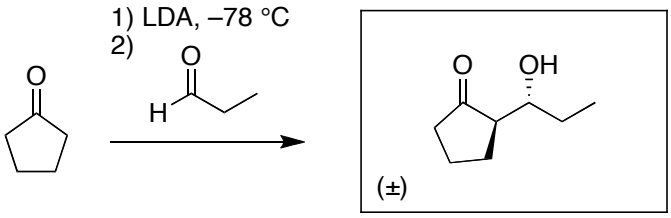
h)


O
O
Li, NH3, MeOH
O
O
achiral

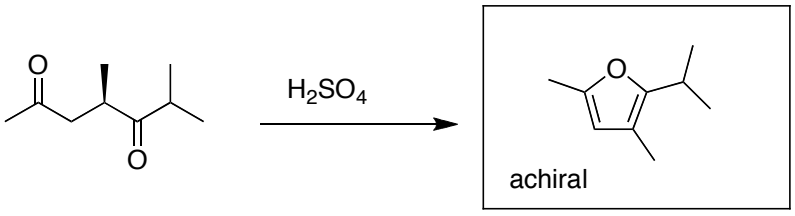
i)


O
O
O
N
1) BuLi
2) BnBr
O
O
O
N
Ph
single ent.

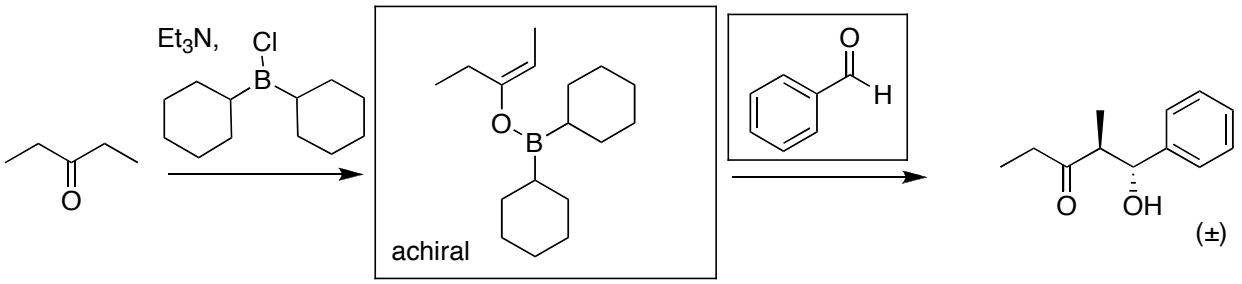
j)


1) LDA, –78 °C
2)
O
H
O
O
OH
(±)

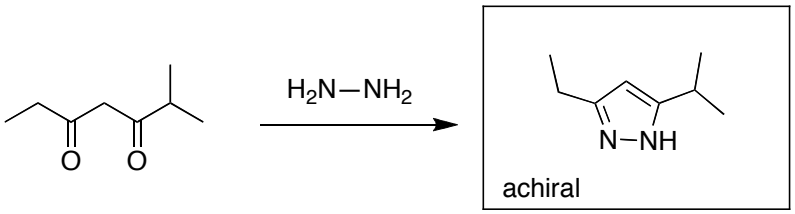
k)



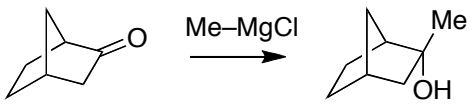
l)



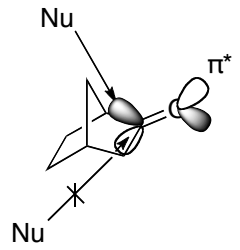
m)



2. (4 marks) Give an example of stereocontrol best explained by understanding the geometry of an antibonding orbital involved in the reaction. Include a 3D diagram of the orbitals involved.

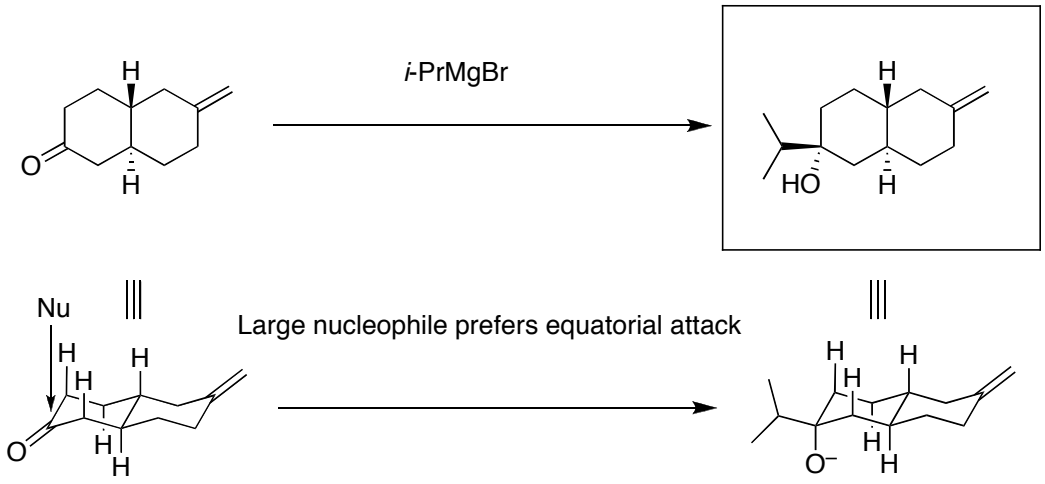


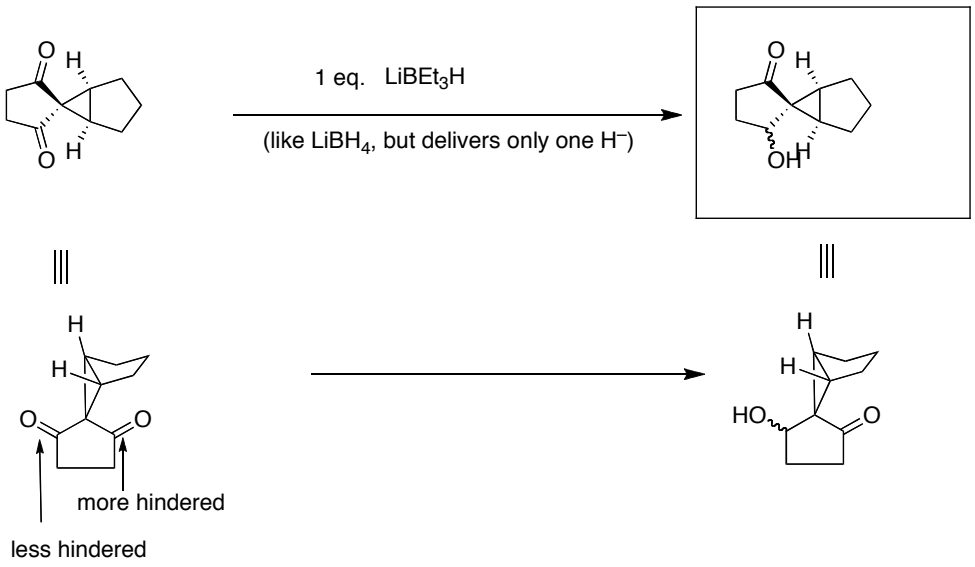
less hindered by 1-carbon bridge

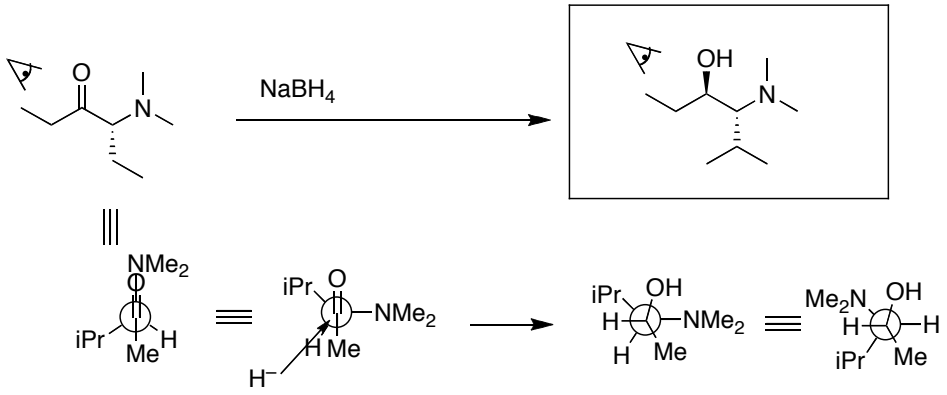


more hindered by 2-carbon bridge

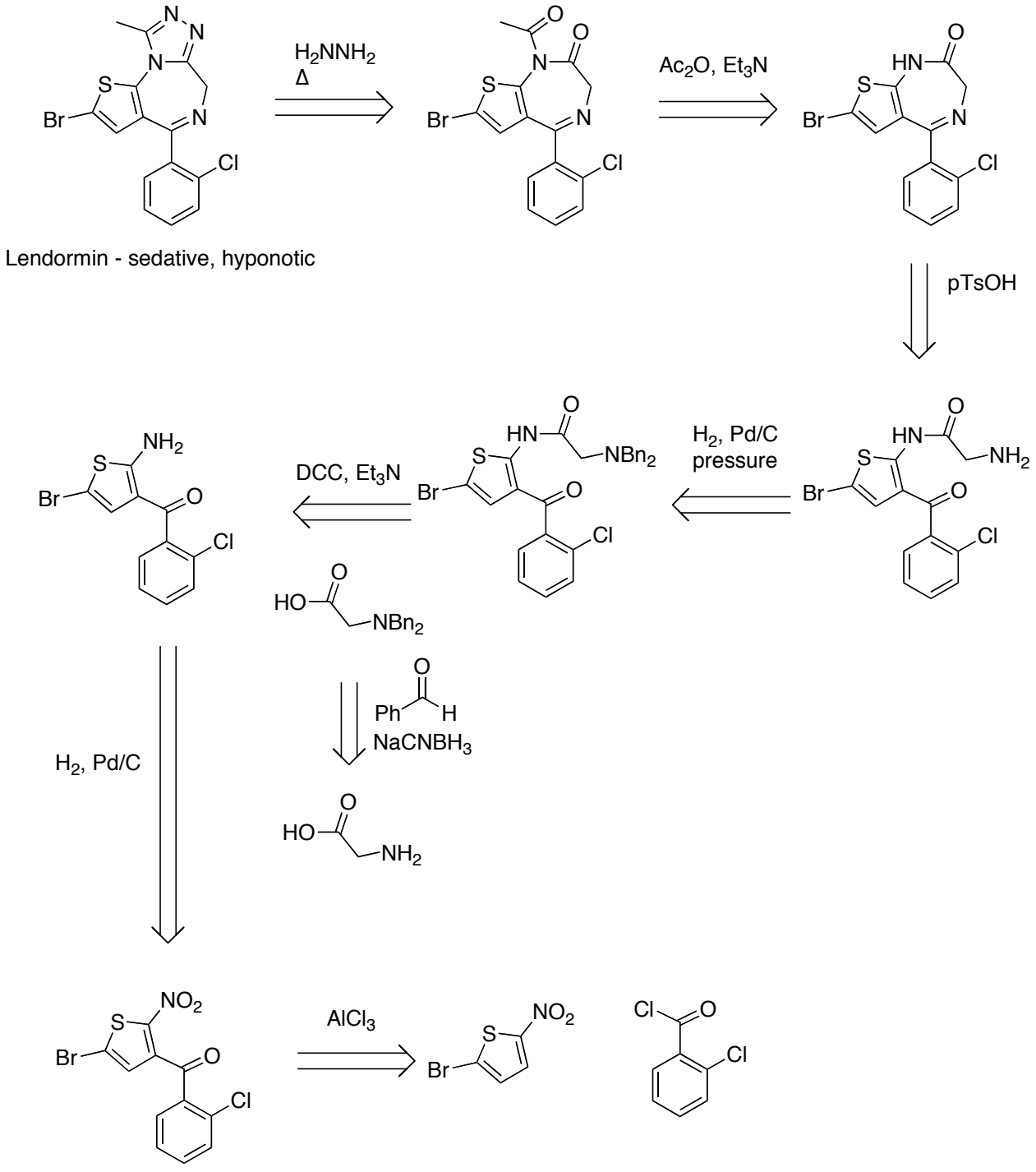
3. (4 marks each, 8 marks total) ANSWER ONLY TWO OF THE THREE PARTS. Give the product of the following reactions. Explain the origin of the observed stereoselectivity in one short phrase, and draw 3D stereochemical diagrams of starting materials and products to illustrate your point.



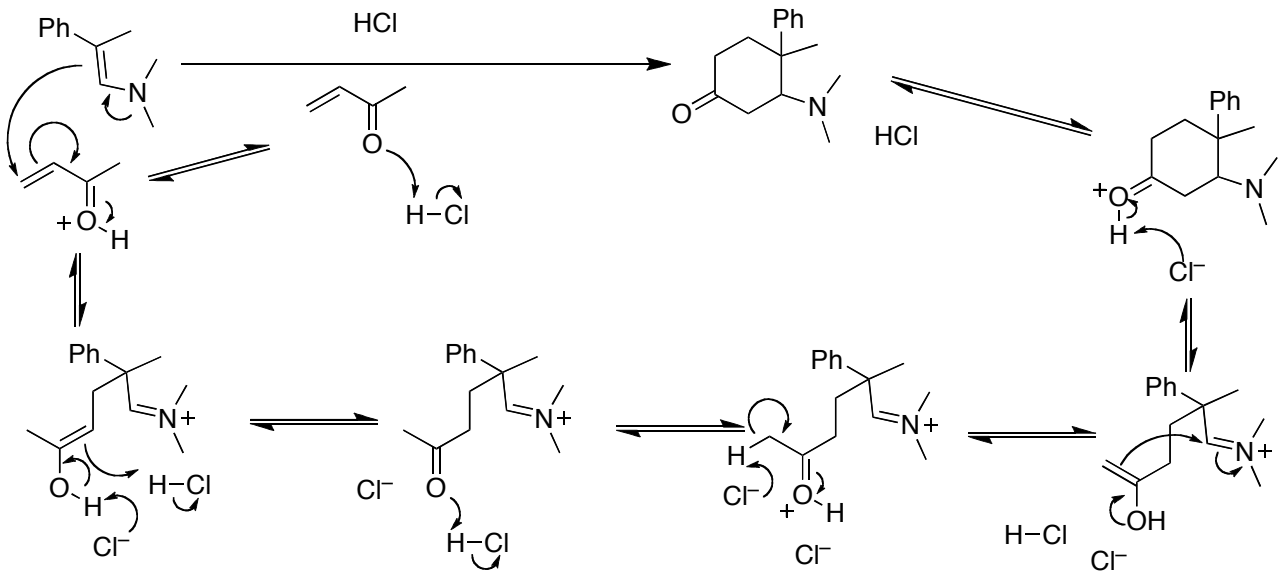




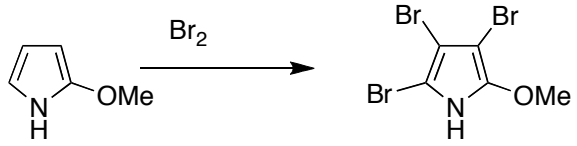
4. (8 marks) Plan the synthesis of the sedative Lendormin (below) *from materials that have a total carbon+nitrogen count of 7 or less*. Whether you go in the forward or reverse direction, clearly indicate the reagents and conditions that would be required for each reaction in the forward direction.

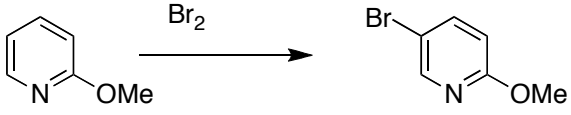


5. (8 marks) Give a detailed mechanism for the following transformation. Include all proton transfers, intermediates, and byproducts.

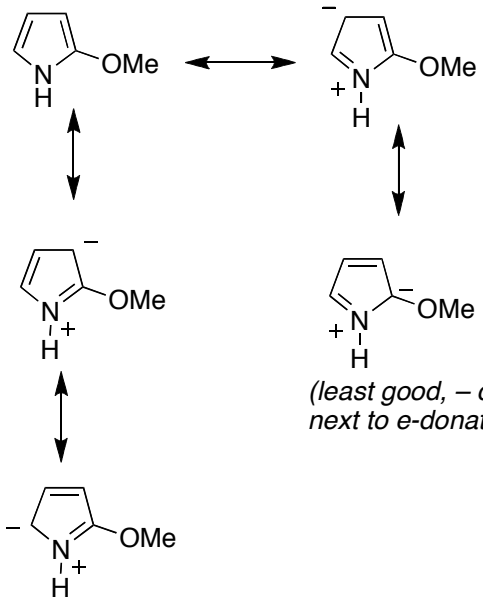


6. (6 marks) 2-methoxypyrrole is brominated exhaustively by treatment with Br_2, while 2-methoxypyridine is selectively brominated at the 5-position. Explain the differences in reactivity, and the regioselectivity of the pyridine bromination.



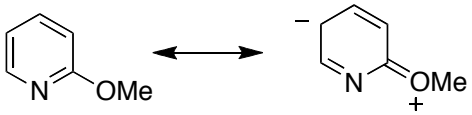


pyrrole is electron rich (enamine-type heterocycle), wth good resonance structures putting – charges at each ring carbon

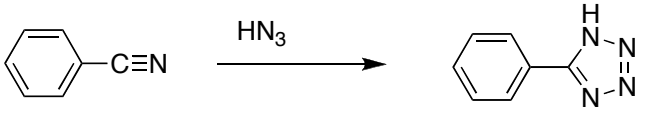


(least good, – charge is next to e-donating MeO)

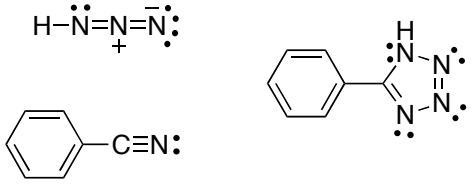
pyridine is electron poor (imine-type heterocycle), and the best resonance structure has the – charge at the 5-position (para to OMe and meta to N).



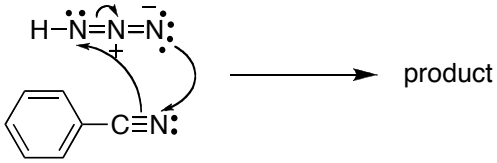
7. (4 marks) a) Show the complete Lewis structure for HN_3. Draw all lone pairs on the starting material, on HN_3, and on the product. b) Give the detailed mechanism for the reaction below, and include all proton transfers, intermediates, and byproducts. Be precise with your arrows!



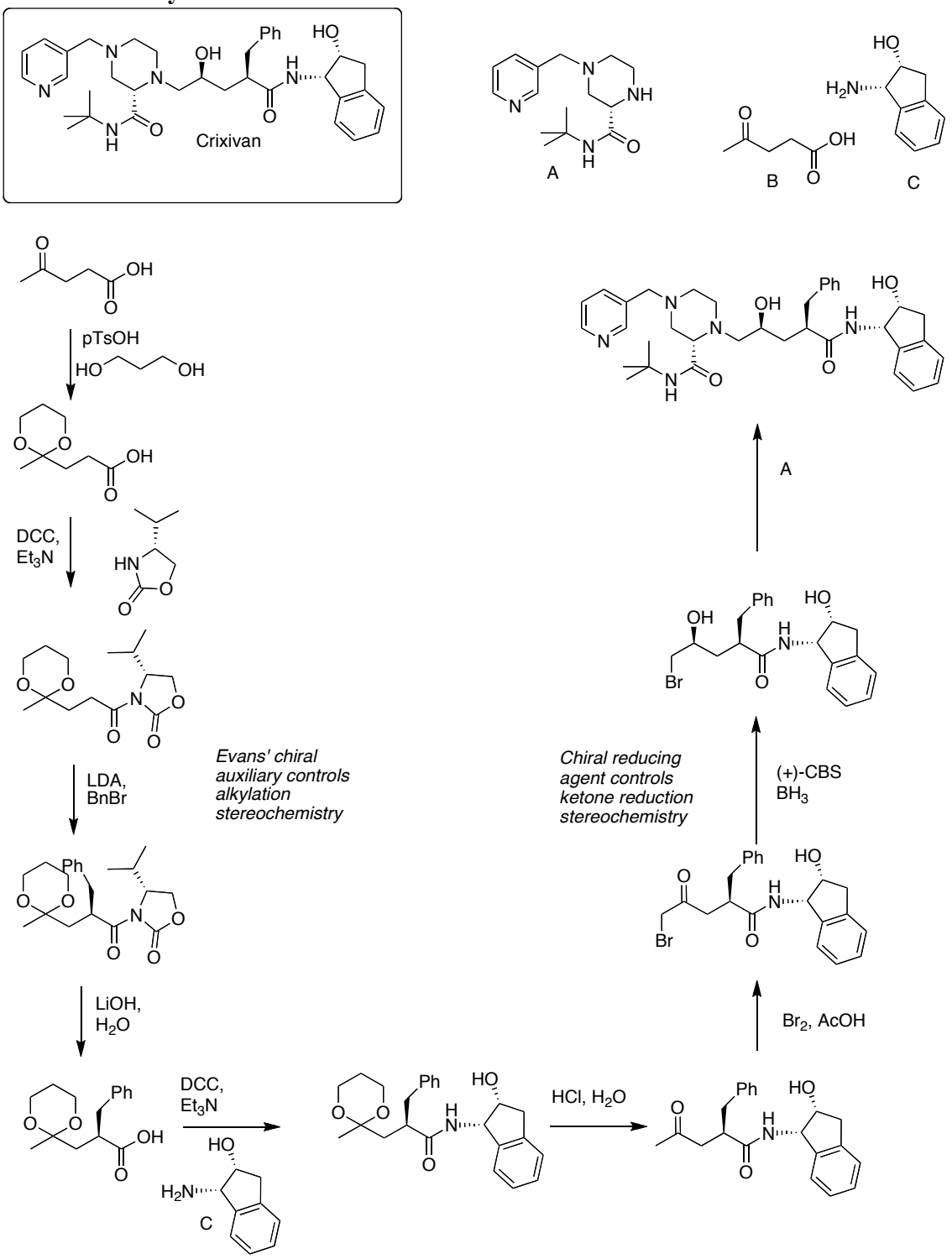
a)



b)



8. (10 marks) Plan the synthesis of the AIDS drug Crixivan (pictured below, left). You have the four key building blocks **A–C** available to you. Whether you picture the synthesis in the forward or retro direction, include reagents above each arrow. **For the creation of each of the two stereocenters not already present in the building blocks, indicate with one short phrase how you would control the stereochemistry of that center.**



END