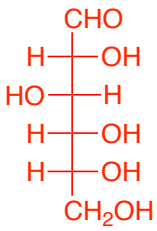
NEW MATERIAL SECTION

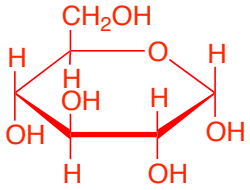
(Problems 1-4)

Problem 1. (15 points) This problem is related to carbohydrates, and the material comes from your class notes.

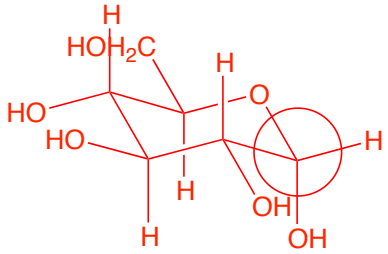
a) **Draw** the Fischer projection of D-glucose.



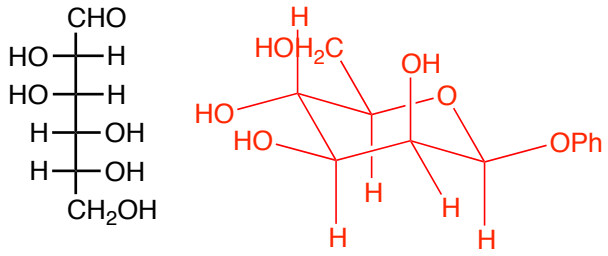
b) **Draw** the Haworth projection of α–D-glucopyranose.



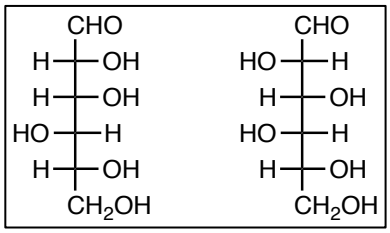
c) **Draw** the chair form of α–D-glucopyranose on the picture given. **Circle** the anomeric carbon.



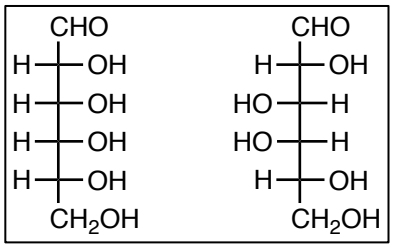
d) Here is the Fischer projection of D-mannose. Use this structure to **draw** the chair form of phenyl-β-D-mannopyranoside.



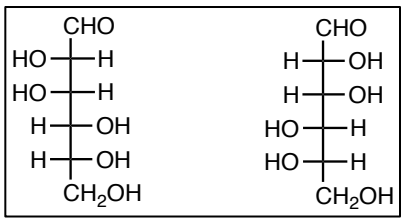
e) For each pair of sugars below, **state** whether they are enantiomers or diastereomers.



diastereomers



diastereomers

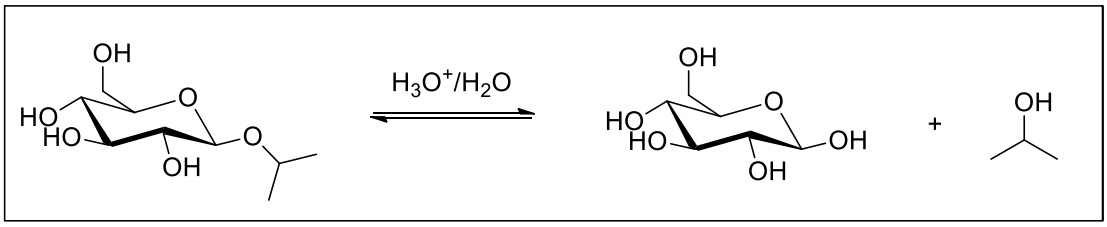


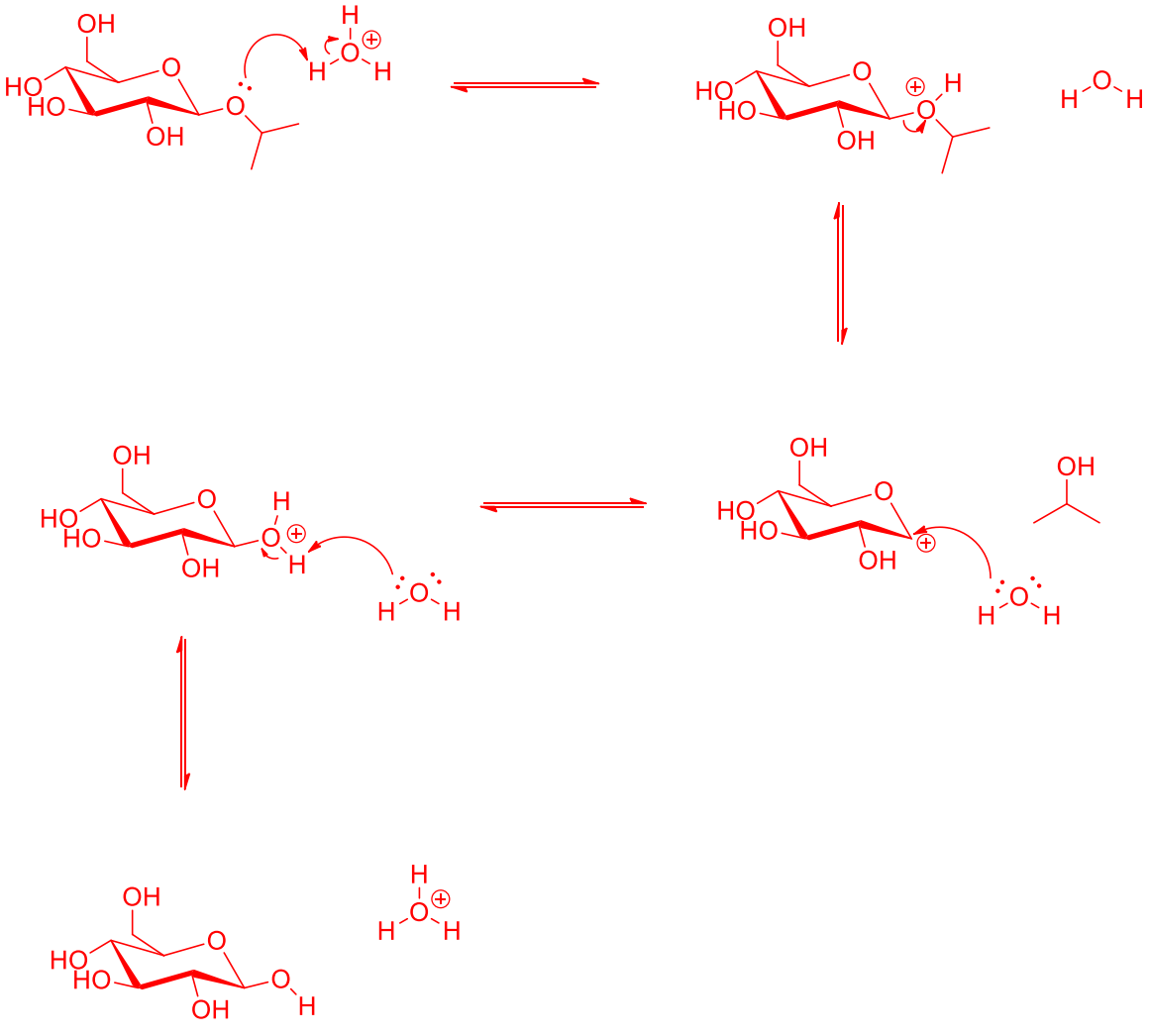
enantiomers

e) Judging by its name, can we say which direction D-ribose rotates plane-polarized light? Explain why or why not in one sentence.

No. D simply means that ribose has the same configuration as D-glyceraldehyde and does not imply that it is dextrorotatory (d).

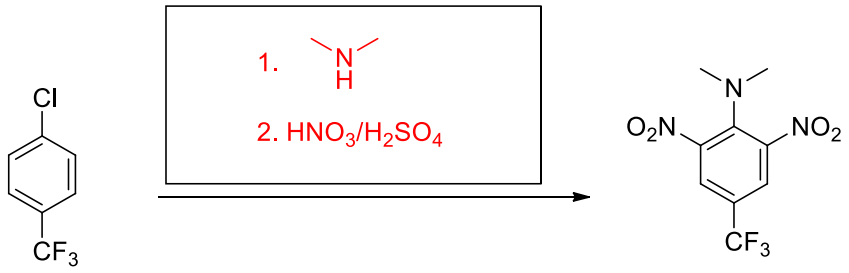
Problem 2. (15 points) Write the **mechanism** for the following pyranoside hydrolysis. Draw all arrows to indicate the movement of electrons. Write relevant lone pairs, all formal charges, and all products for each step.



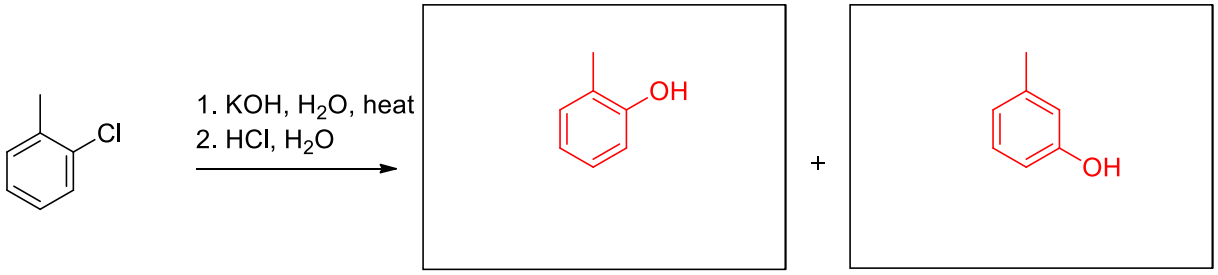


Problem 3. (15 points) Fill in the boxes with the appropriate reagents or product. Some boxes require more than one step.

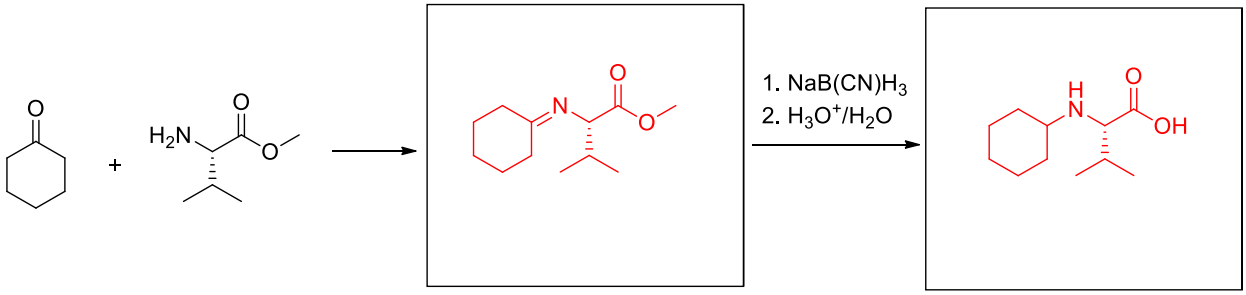
a) From HW 22.28



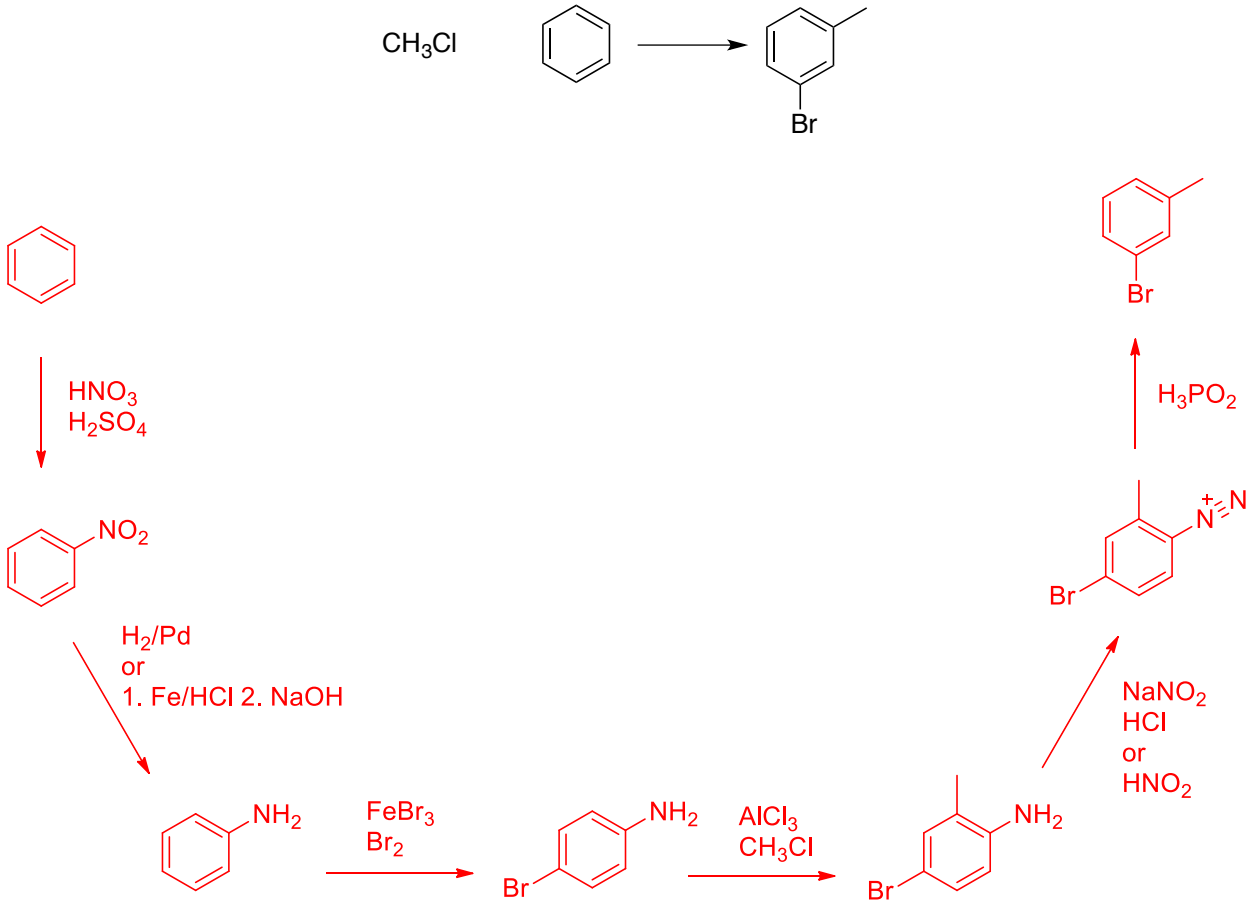
b)



c)



Problem 4. (16 points) Using the given starting materials as your only source of carbon, outline a reasonable **synthesis** for the following transformation. Show all reagents used and all intermediates created.

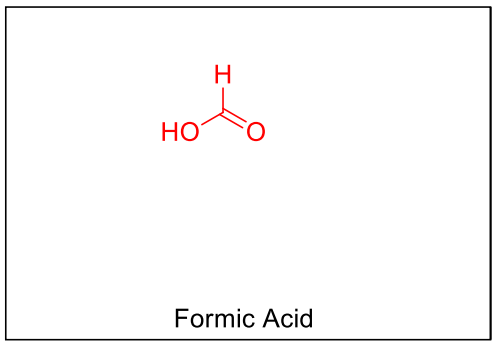


CUMULATIVE SECTION

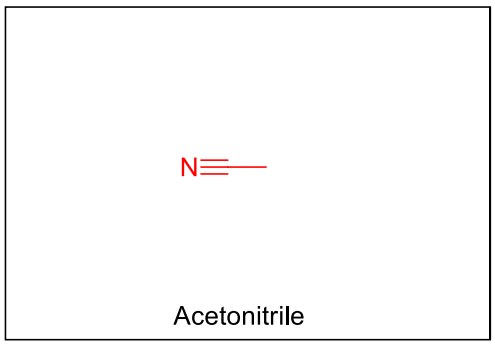
(Problems 5-19)

Problem 5. (16 points) Nomenclature

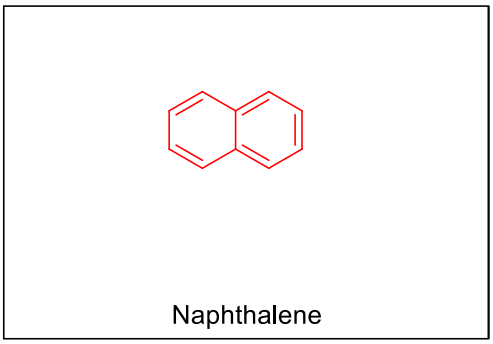
a) Draw the structures that correspond to the following IUPAC or common names.



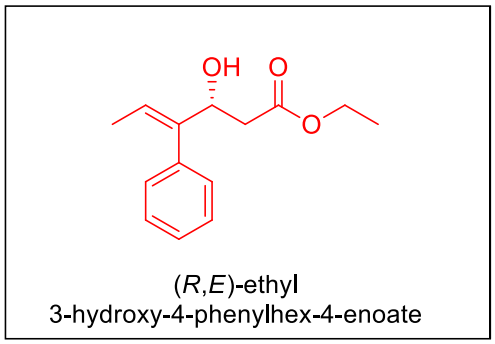
Formic Acid



Acetonitrile

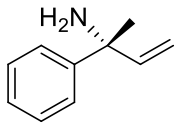


Naphthalene

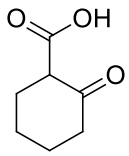


(*R*,*E*)-ethyl
3-hydroxy-4-phenylhex-4-enoate

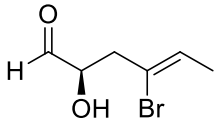
b) Provide the IUPAC name for the following molecules



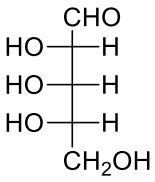
(*R*)-2-phenylbut-3-en-2-amine



2-oxocyclohexanecarboxylic acid



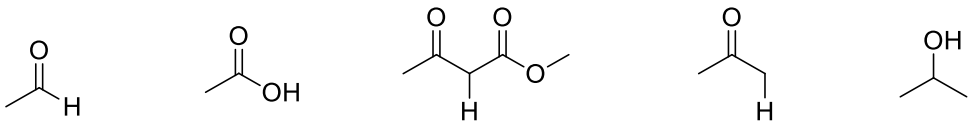
(*R*,*Z*)-4-bromo-2-hydroxyhex-4-enal



(2*S*,3*S*,4*S*)-2,3,4,5-tetrahydroxypentanal
or L-ribose

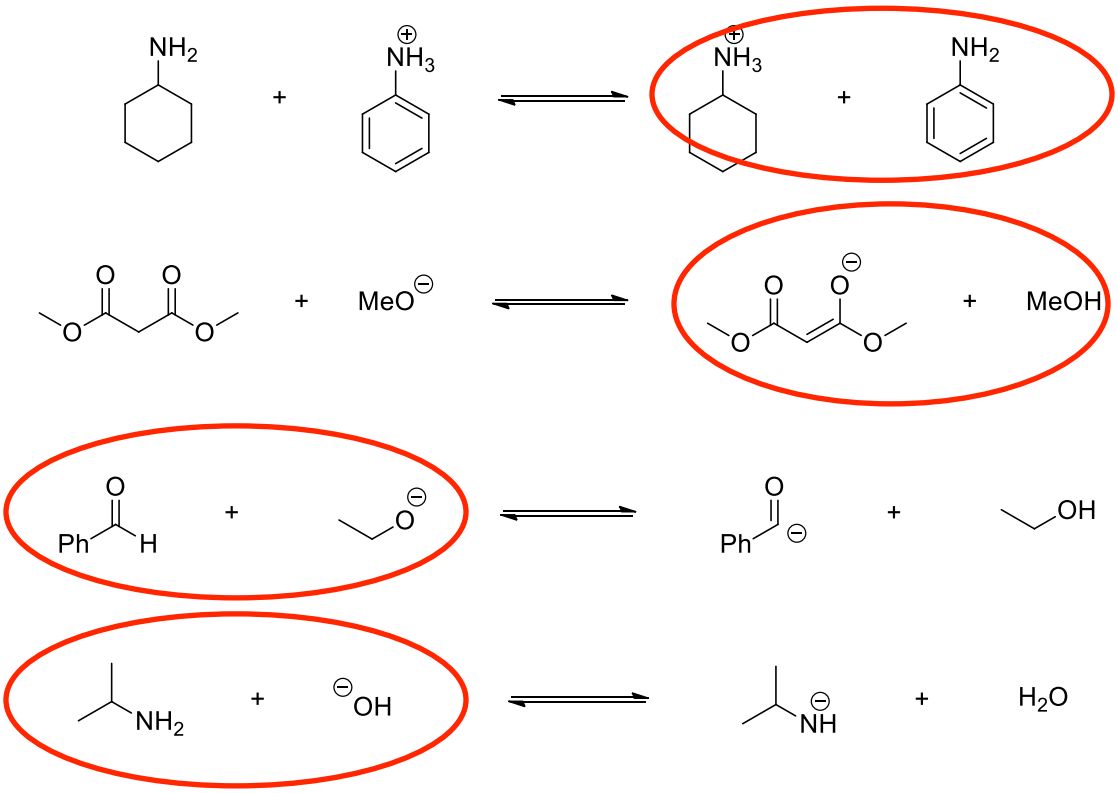
Problem 6. (13 points)

a) Rank the following protons from most acidic (1) to least acidic (5).



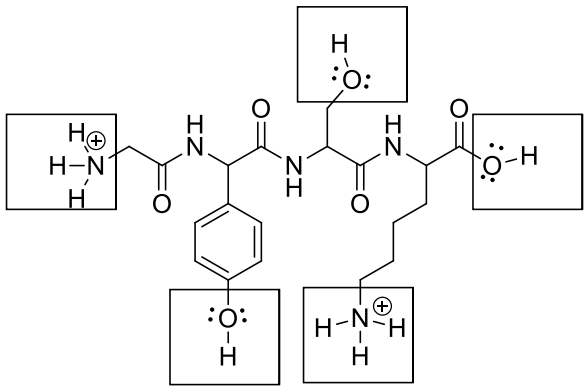
5 1 2 4 3

b) Indicate whether the right or left side of each of the following equilibria is favored.



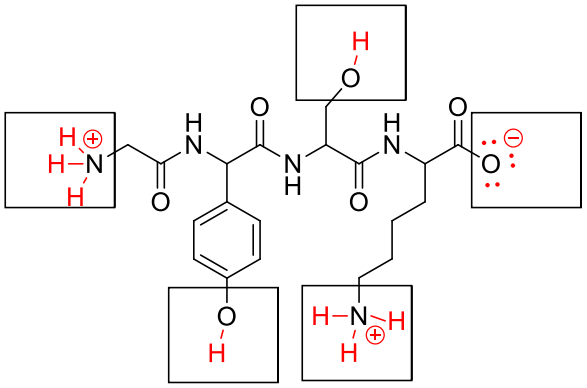
Problem 7. (12 points) For the peptide shown below, fill in the appropriate protons, lone pairs, and charges for the boxed functional groups at the indicated pHs. Also, give the overall charge of the peptide at each pH. An example is provided below.

Example: pH = 2



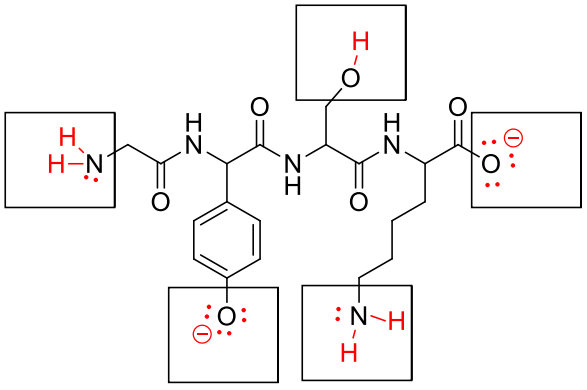
overall charge of peptide: +2

a) pH = 7



overall charge of peptide at pH 7: +1

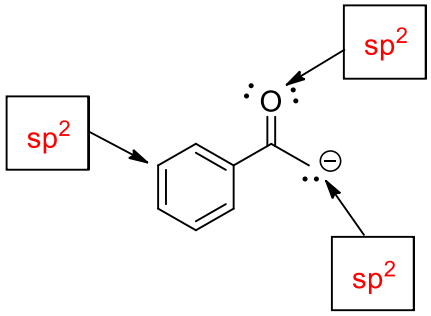
b) pH = 12

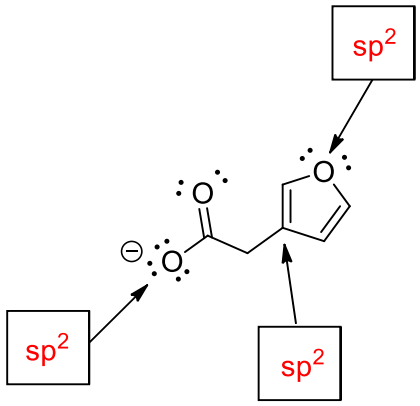


overall charge of peptide at pH 12: -2

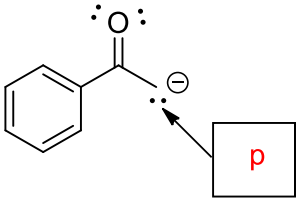
Problem 8. (9 points)

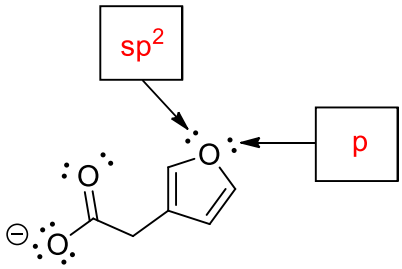
a) In the boxes provided, state the hybridization of the indicated atoms.



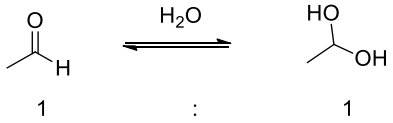


b) In the boxes provided, name the orbital in which the indicated pairs of electrons reside.

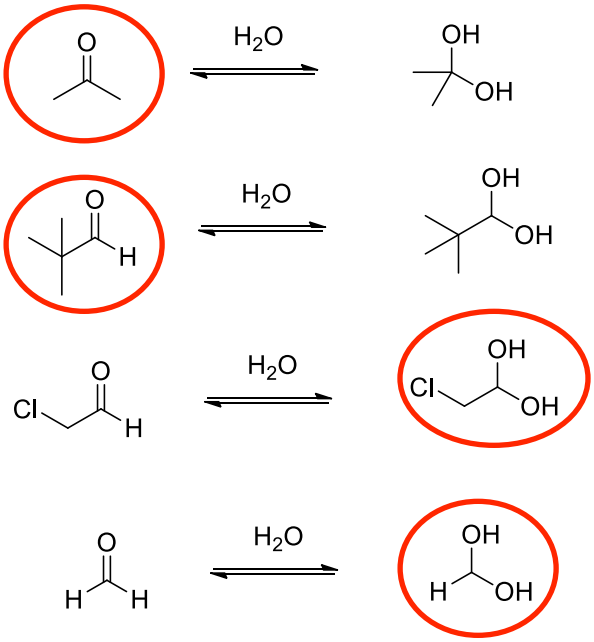




Problem 9. (6 points) In the hydration of acetaldehyde shown below, the aldehyde and geminal diol forms exist in about a 1:1 ratio.



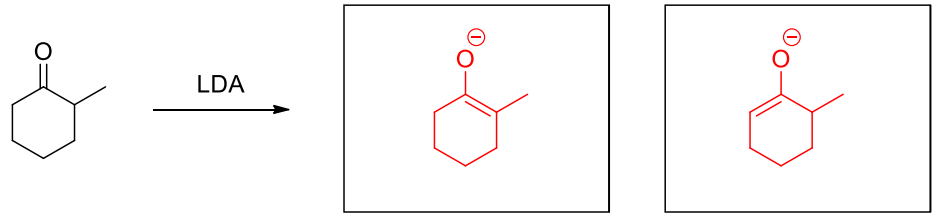
a) For the hydration of each of the carbonyl compounds below, **circle** the dominant species.



b) What happens in terms of the thermodynamics and kinetics of the reactions if you add an acid catalyst to the hydrations shown above?

A catalyst will speed up the reaction (kinetics), but it will not change which side of the equilibrium is thermodynamically favored.

Problem 10. (6 points) For the reaction below, **draw** the thermodynamic enolate and the kinetic enolate that result from deprotonation of the following ketone.

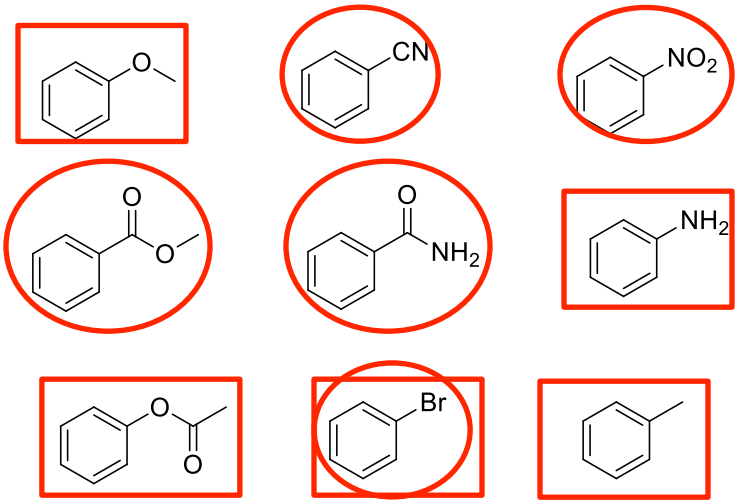


thermodynamic kinetic

Explain your answer in 1-3 sentences: The more substituted double bond is more thermodynamically stable. The alpha proton on the left side of the ketone is more accessible, and hence it is removed more quickly than one on the right side.

Problem 11. (11 points)

a) **Circle** the benzene rings with a deactivating group.
b) **Box** the benzene rings with an ortho/para directing group.



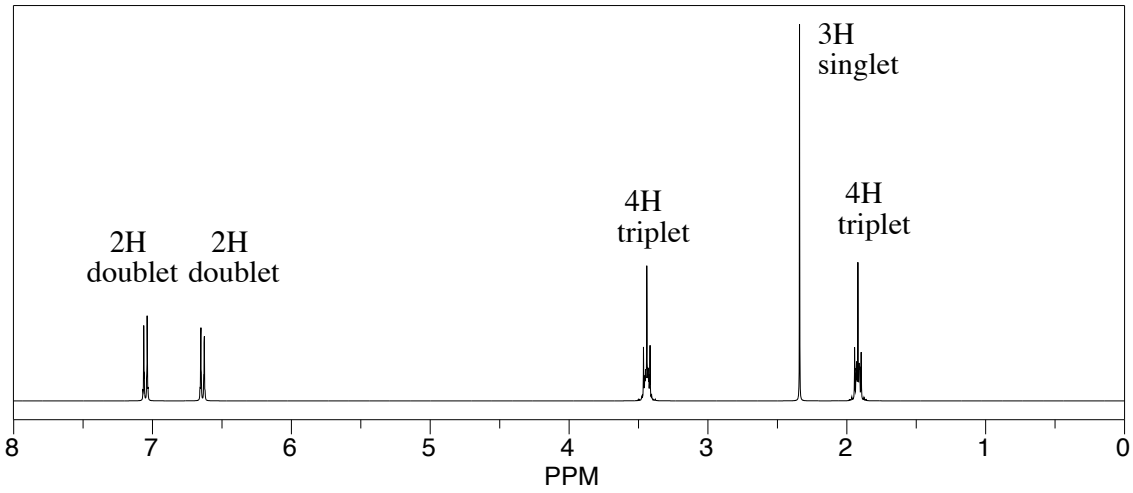
c) **Name** the two chemical phenomena that chemists use to explain how a group on a benzene ring influences the rate and regiochemistry of further substitution on that ring:

1) Induction

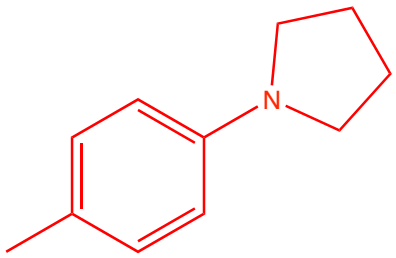
2) Resonance

Problem 12. (10 points) Propose a structure for compound A ($C_{11}H_{15}N$) consistent with the ^{1}H-NMR spectrum below. **Write your final answer in the box provided.**

Compound A ($C_{11}H_{15}N$)



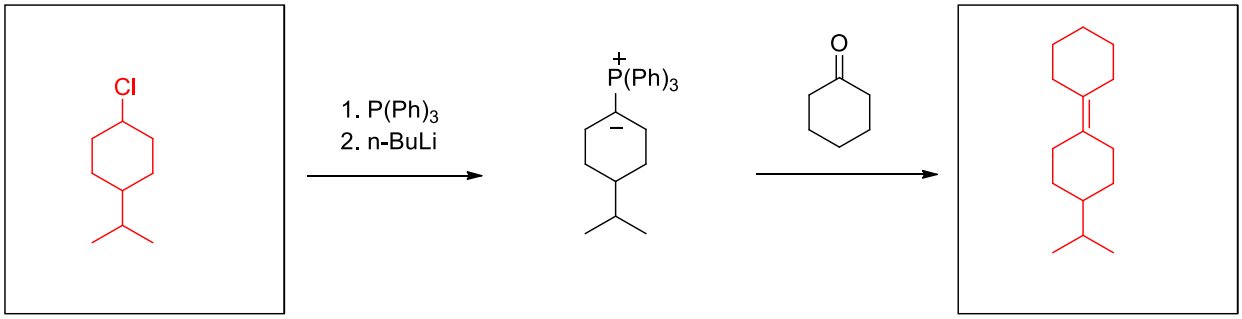
Compound C ($C_{11}H_{15}N$)



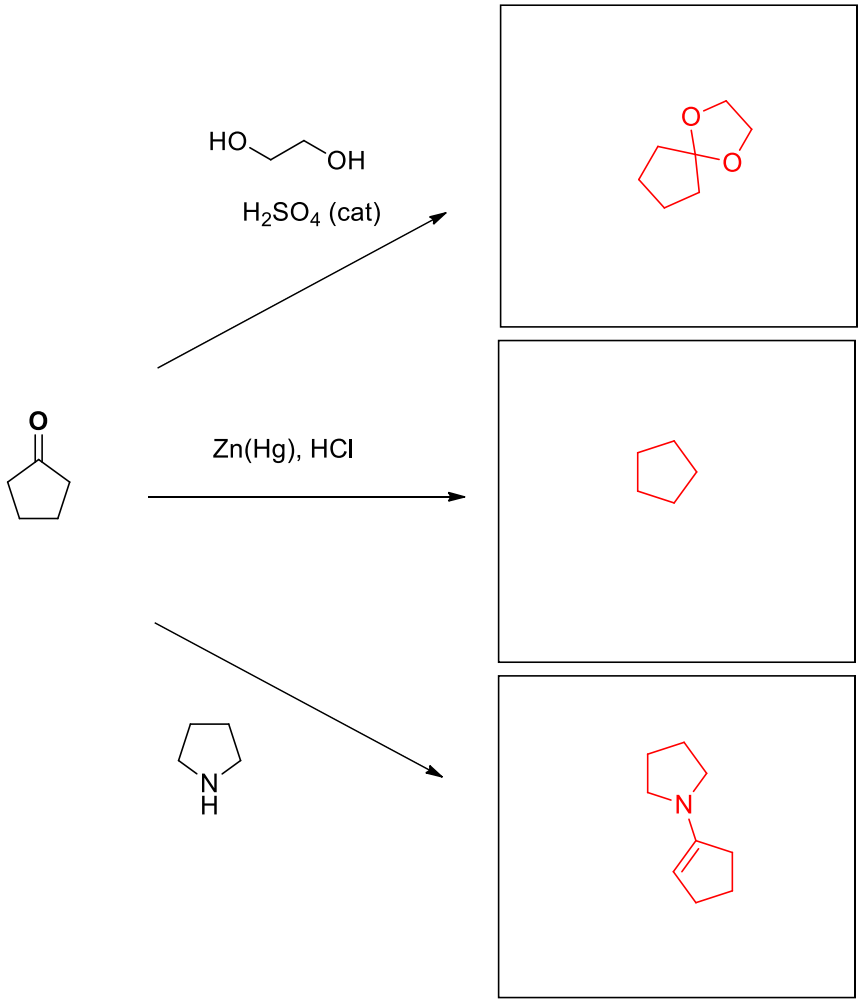
Para, methyl, aniline, N in ring, benzene

Problem 13. (38 points) Fill in the boxes with the appropriate reactant, reagents, or products. Some boxes require more than one step. If a new chiral center is created and a racemic mixture is formed, **draw both enantiomers**, and **write "racemic"** under the structure. Use wedges (▬) and dashes (·····) to indicate stereochemistry.

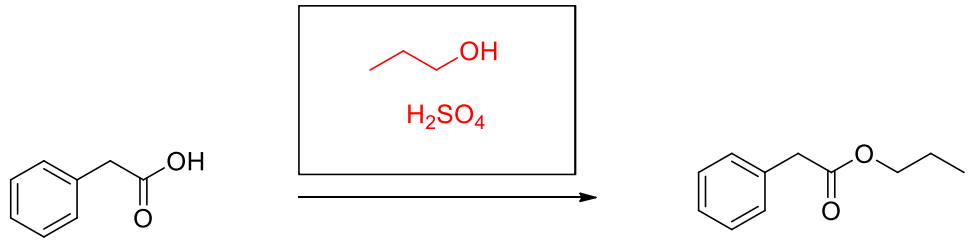
a)



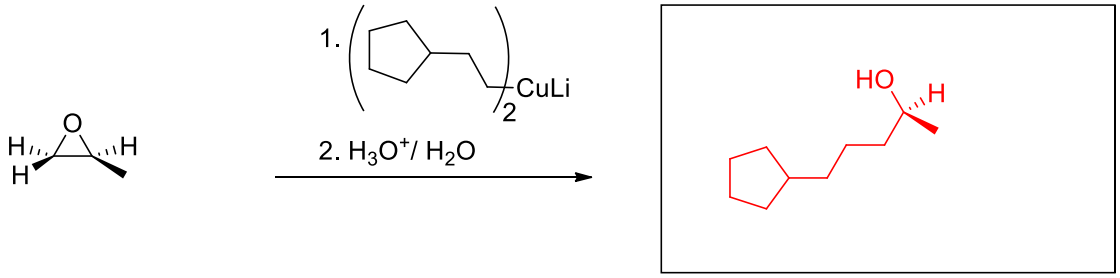
b)



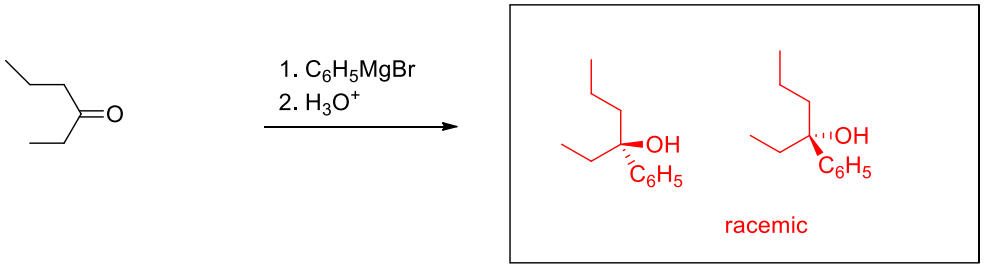
c) From HW 17.32



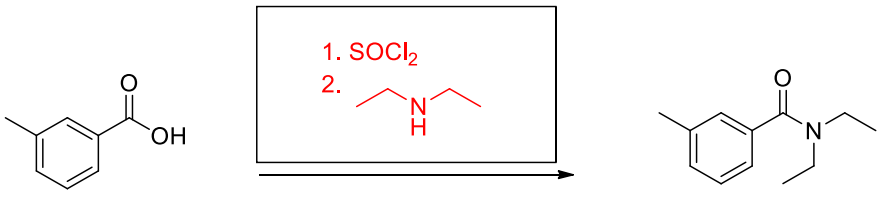
d)



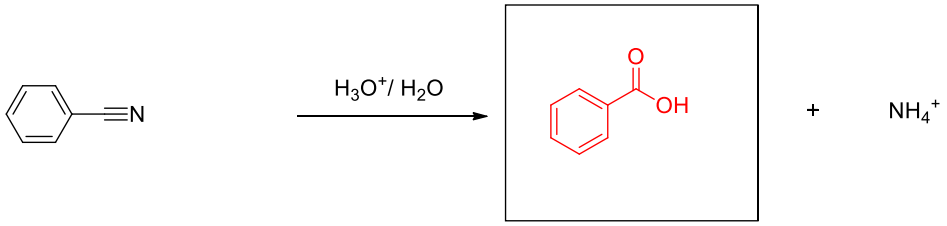
e) From HW 15.17



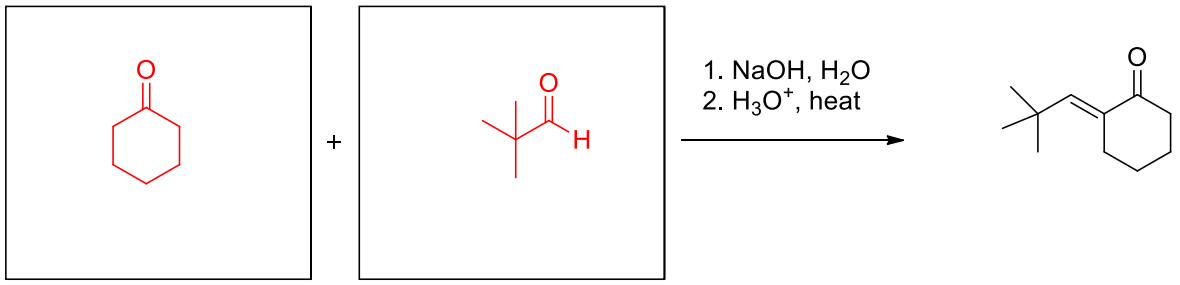
f) From HW 18.35



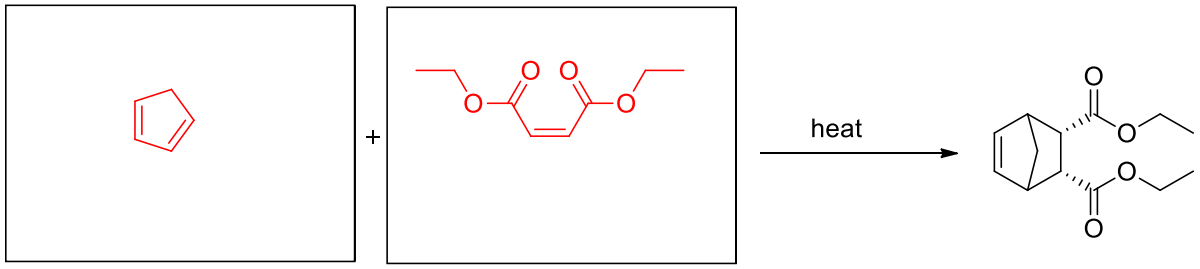
g)



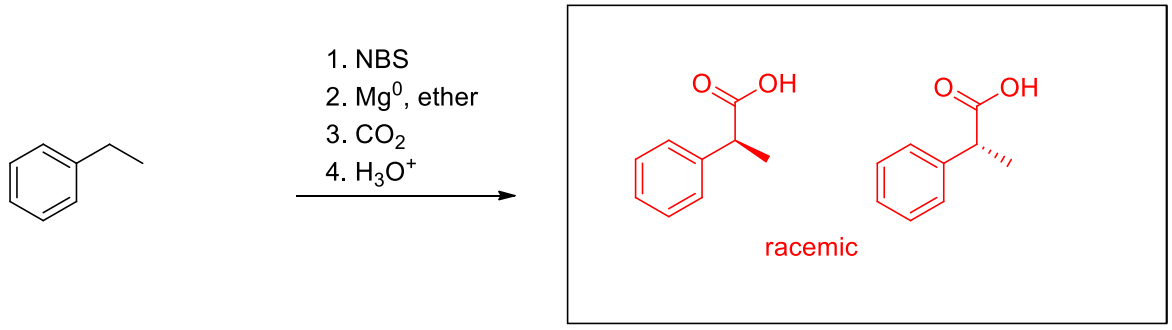
h) From HW 19.19a



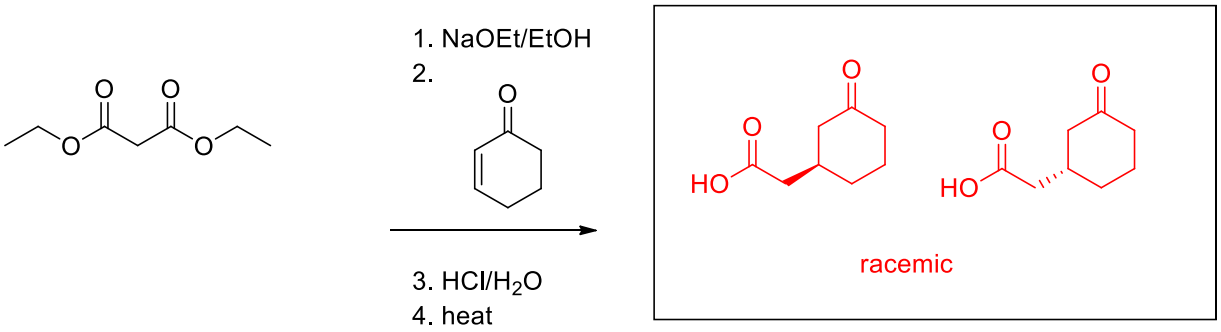
i)



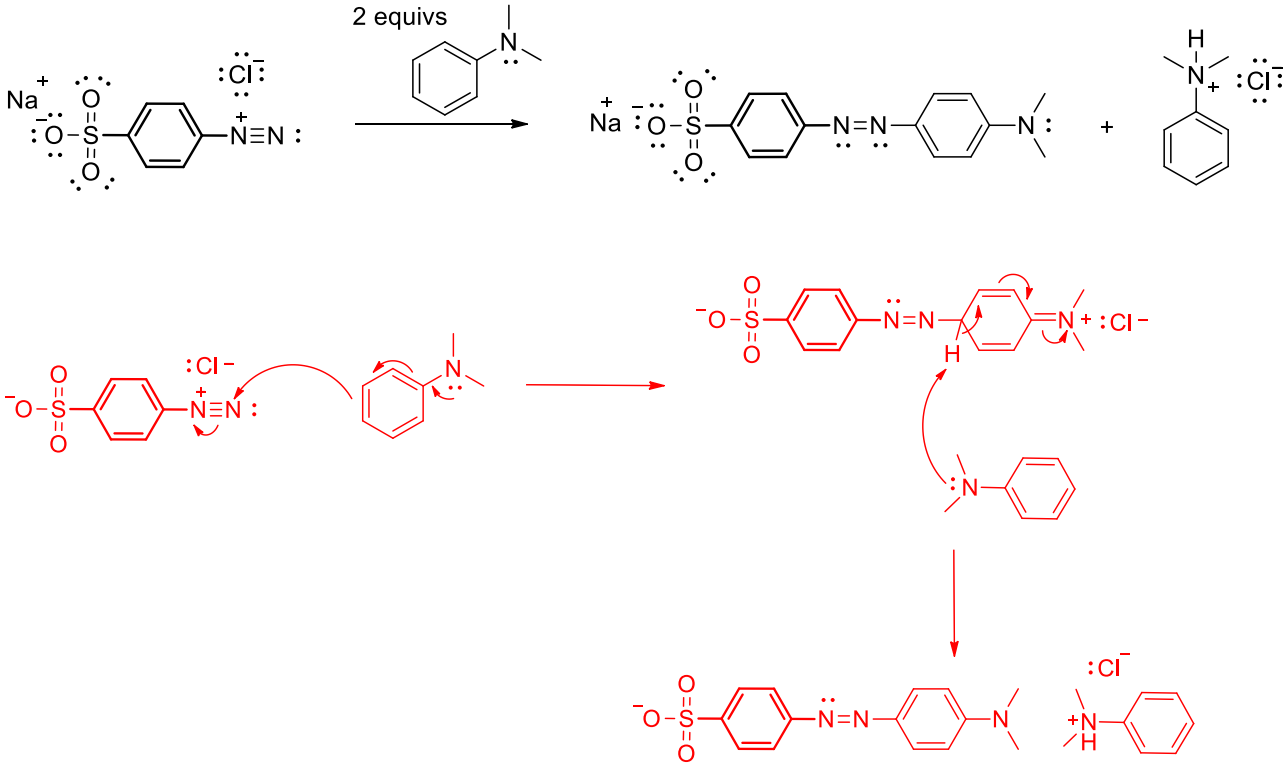
j)



k)

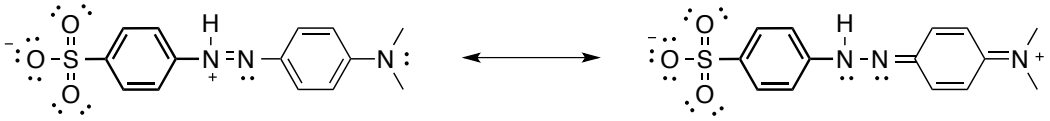


Problem 14. (12 points) Provide the ***mechanism*** for the following reaction scheme that depicts the synthesis of methyl orange. Indicate the movement of electrons using arrows. Draw relevant lone pairs, all charges, and all products at each step.



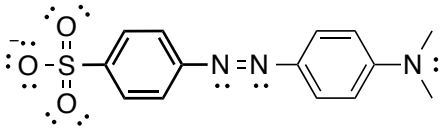
Problem 15. (8 points) Methyl orange belongs to a class of chromophores called azo dyes, which are often used to color clothing. Methyl orange is also used as a pH indicator; in acidic solution, it becomes protonated, and its color changes from yellow to red.

Protonated Methyl Orange (red):

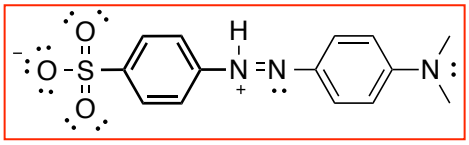


This is a zwitterion that has resonance delocalization of the newly created positive charge.

a) Circle the molecule that corresponds to the longer wavelength of *reflectance.*

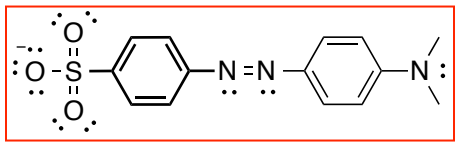


Methyl Orange (yellow)

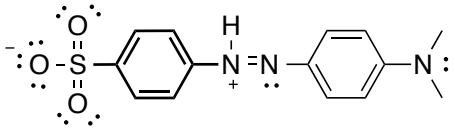


Protonated Methyl Orange (red)

b) Circle the molecule that has the higher energy *absorbance* transition.

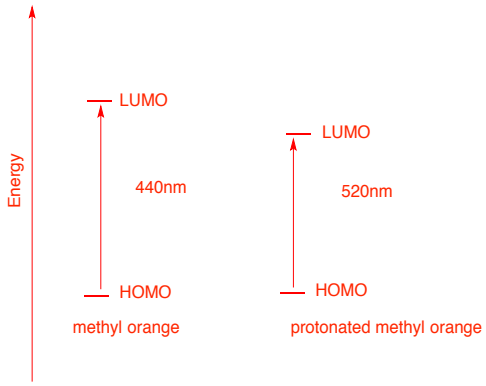


Methyl Orange (yellow – absorbs blue 440nm)

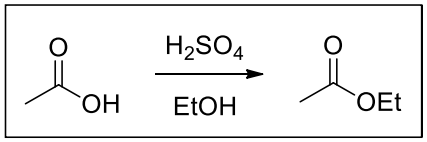


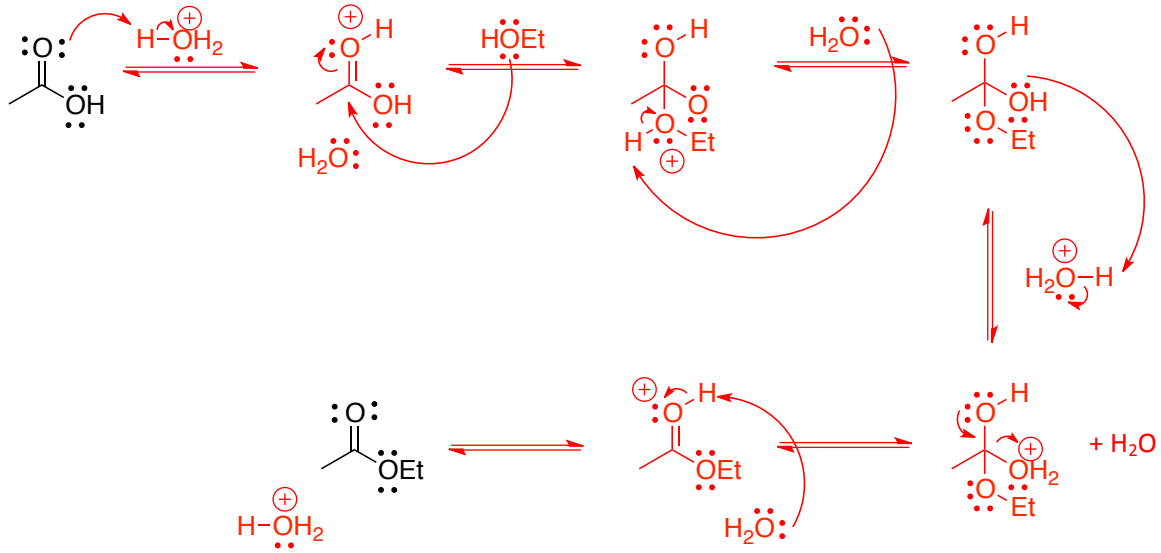
Protonated Methyl Orange (red - absorbs green 520nm)

c) Draw a diagram of the HOMO/LUMO gaps for both methyl orange and its protonated form. Label the diagram with “methyl orange” and “protonated methyl orange”.

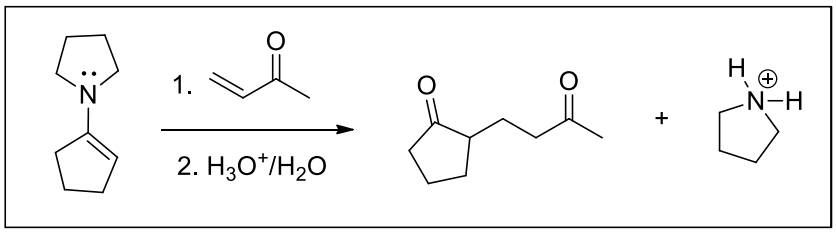


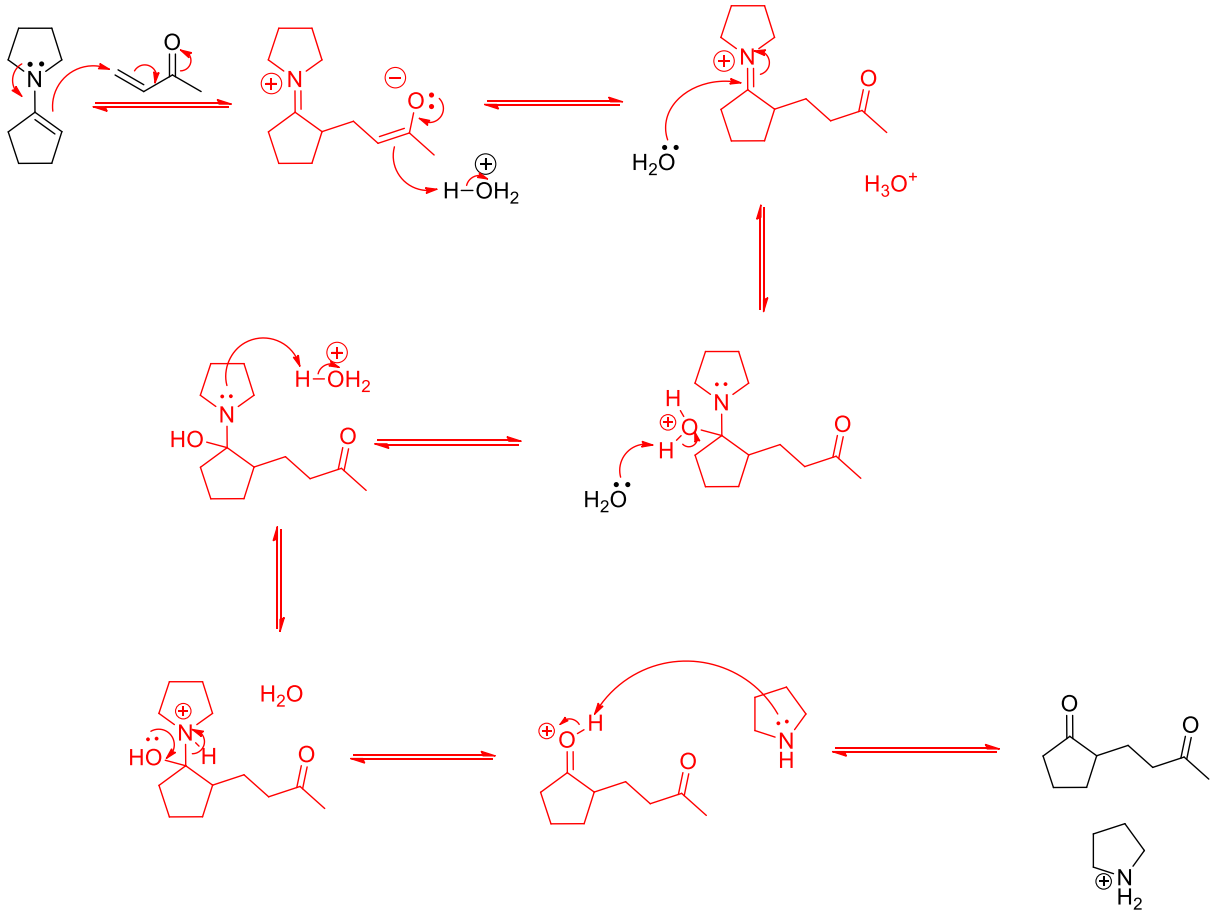
Problem 16. (27 points) Write the **mechanism** for Fischer esterification. Draw all arrows to indicate movement of all electrons. Write all lone pairs, all formal charges, and all products for each step.



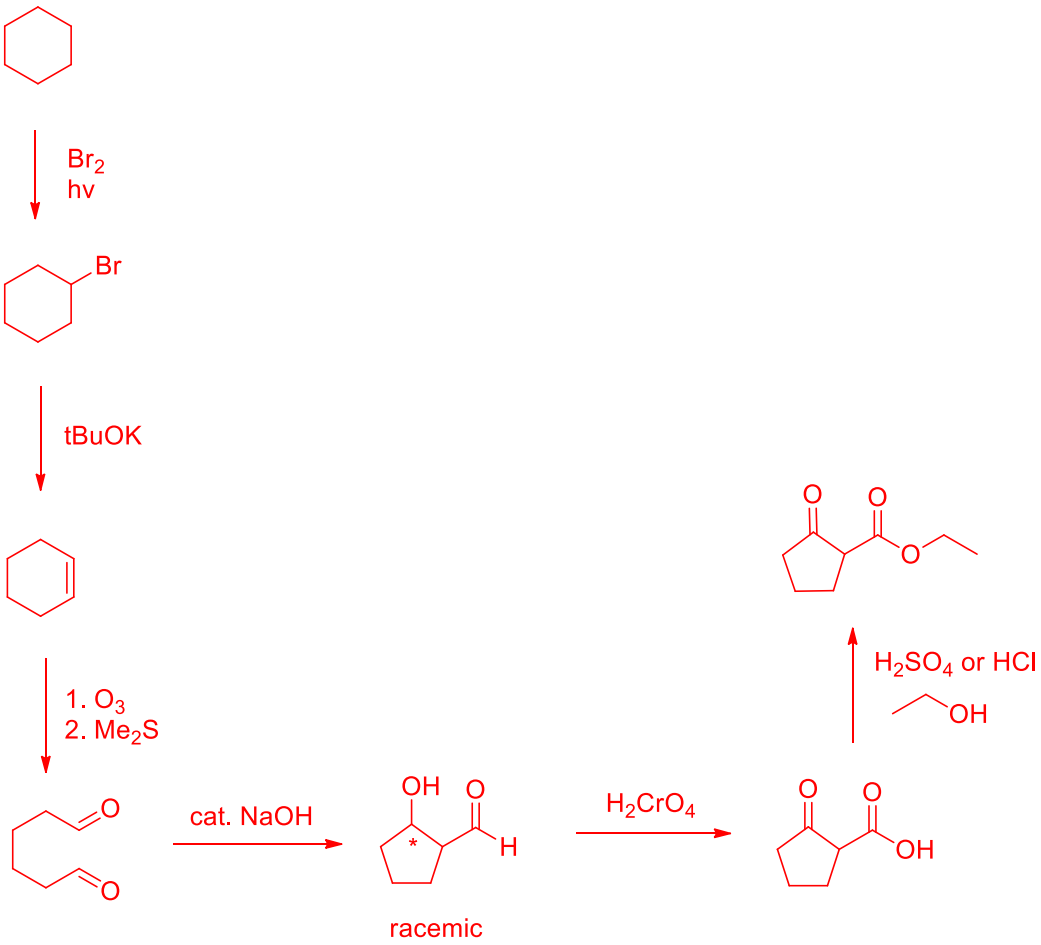


Problem 17. (34 points) Write the **mechanism** for the reaction shown below. Draw arrows to indicate movement of all electrons. Write relevant lone pairs, all formal charges, and all products for each step. (From HW 19.50)

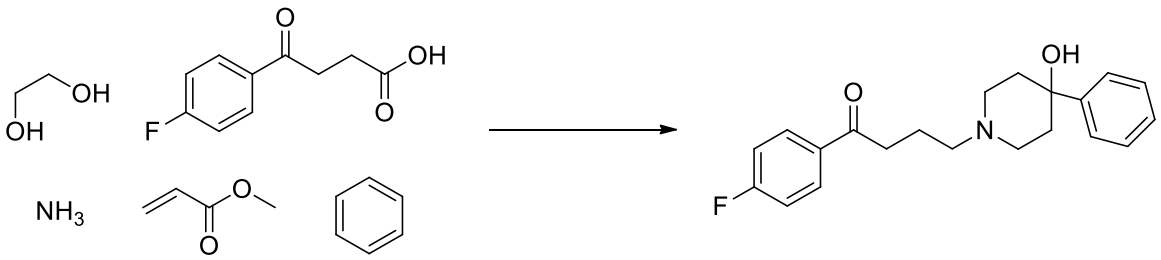




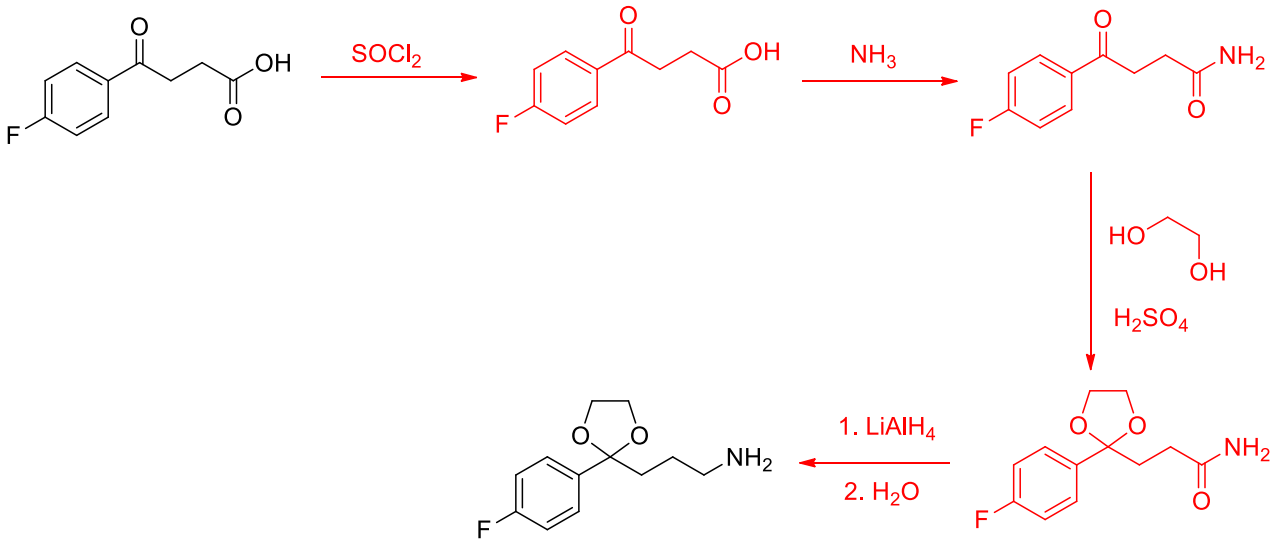
Problem 18. (16 points) Using the following starting materials as your only source of carbon, provide a **synthesis** for the following transformation. Show all reagents, steps, and intermediates. (From HW 19.77)



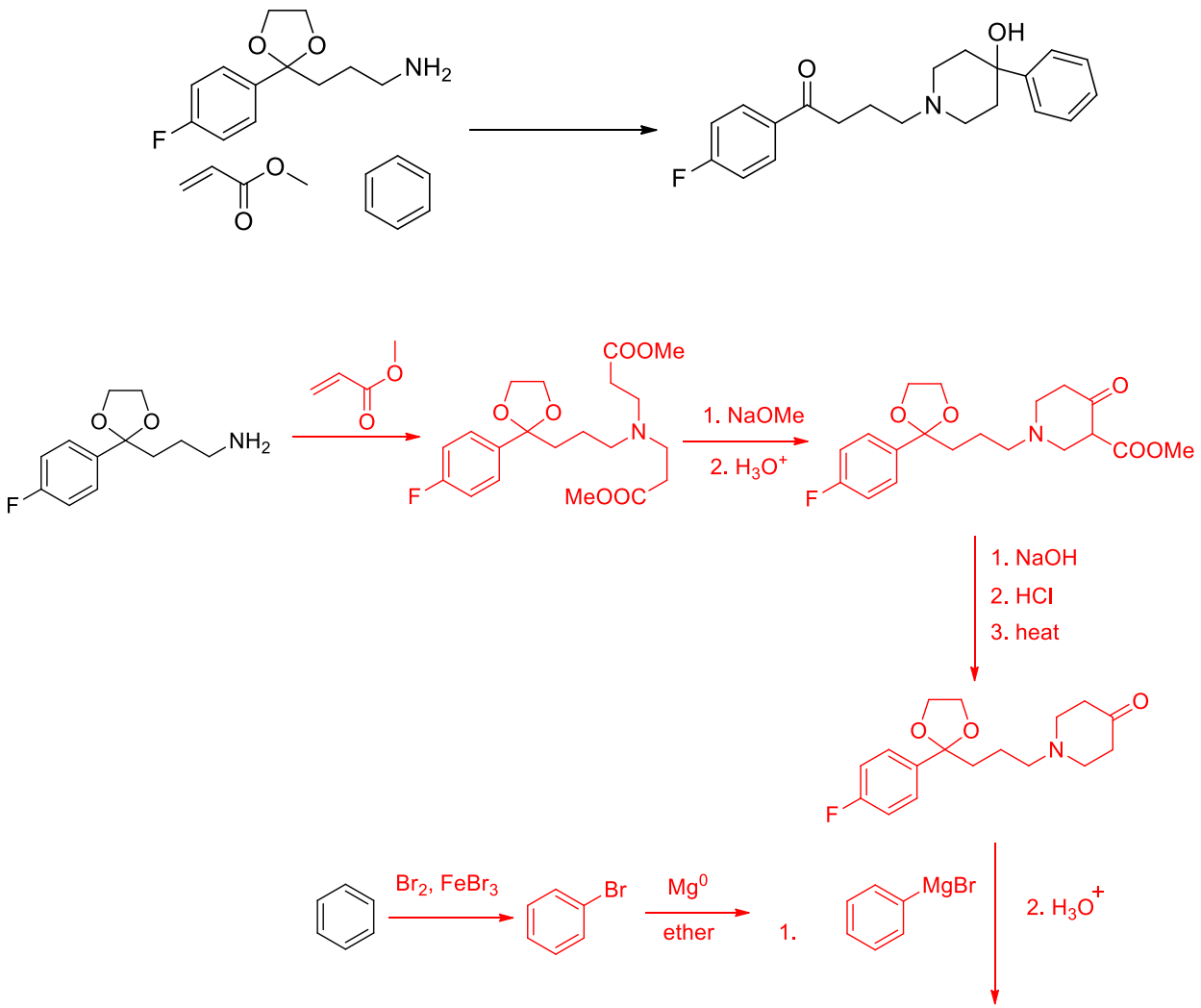
Problem 19. (26 points) Using the following starting materials as your only source of carbon, provide a **synthesis** for the following transformation. Show all reagents, steps, and intermediates. Since this is a challenging problem, we've broken it into two parts (a-b) for you that continue onto the next page (From HW 22.61)



a)



b) Hint: This sequence should include a Dieckmann reaction.



Bonus Question: (6 points) Have you been attending office hours and recitations? If so, you will likely know the names of your TAs! Write each name next to the number that corresponds to the numbered face in the picture. (Spelling must be close, but does not need to be perfect.)

1. John
2. Katharine
3. Alex
4. Brette
5. Hannah
6. Shagufta (Dr. Shabbir)