

Chemistry 232, Spring 2010  
Dr. Shaughnessy  
Final Exam  
8:00-10:30 AM, May 7<sup>th</sup>, 2010

Name: Answer Key (print)

**Honor Pledge:** I promise or affirm that I will not at any time be involved with cheating, plagiarism, fabrication, or misrepresentation while enrolled as a student at The University of Alabama. I have read the Academic Honor Code, which explains disciplinary procedures that will result from the aforementioned. I understand that violation of this code will result in penalties as severe as indefinite suspension from the University.

\_\_\_\_\_ (signature)

You will have **2 hour and 30 minutes** to complete this exam. When time is called please stop all work and turn in your exam.

Show all work. Partial credit will be given where appropriate.

This exam has **18** pages. Make sure you have all 18 pages, and that they are correctly copied, before starting the exam.

There are tables of useful data at the end of this exam.

You may use molecular models to help you answer questions on this exam.

Please turn off and put away cell phones and all other electronic equipment (iPods, calculators, etc.). You will not need a calculator for this exam.

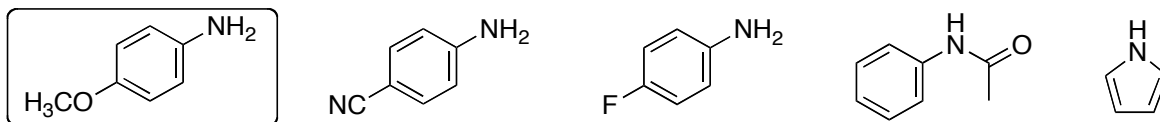
You may pick up your graded exam next week if you're still on campus.

<u>Problem</u>	<u>Score</u>
1)	_____ (20)
2)	_____ (40)
3)	_____ (16)
4)	_____ (18)
5)	_____ (16)
6)	_____ (18)
7)	_____ (15)
8)	_____ (18)
9)	_____ (20)
10)	_____ (24)
Total	_____ (205)

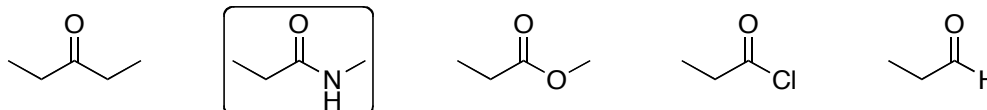
Exam is out of 200 points, with 5 extra credit points built in.

1. Circle the structure that best answers each question below. (20 points)

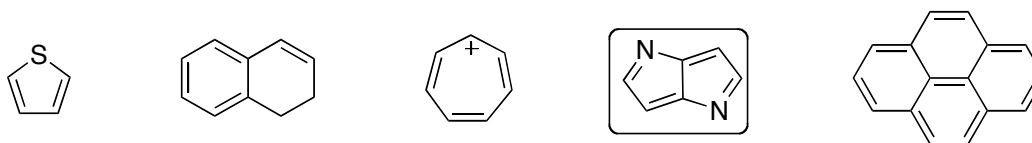
a. Which compound below would be most basic?



b. Which compound would give the lowest frequency C=O stretch in its IR spectrum?



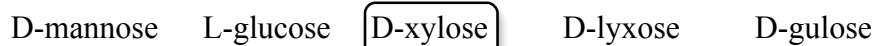
c. Which of the following compounds is anti-aromatic?



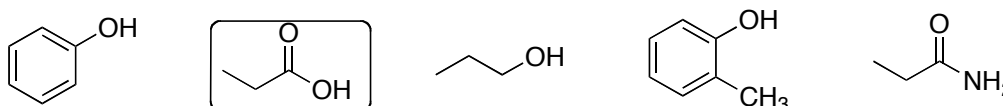
d. Which amino acid would predominately have an overall neutral charge at pH 7?



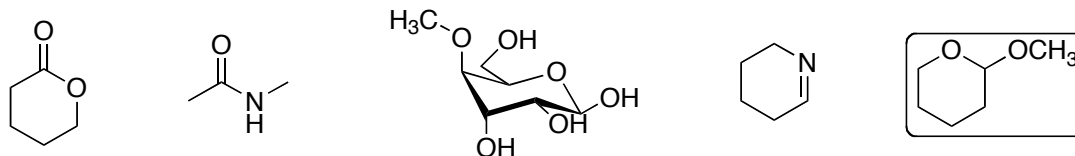
e. Which of the following sugars would give an optically inactive alditol?



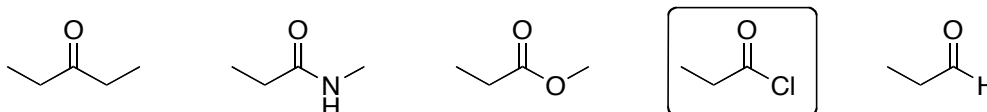
f. Which of the following would be the most acidic?



g. Which of the following compounds contains an acetal functional group?



h. Which of the following would be most electrophilic?



i. Which dipeptide would be cleaved by trypsin?

Ala•His

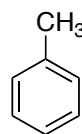
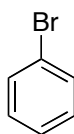
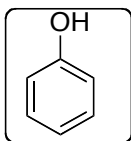
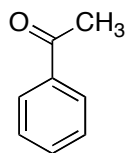
Arg•Phe

Phe•Val

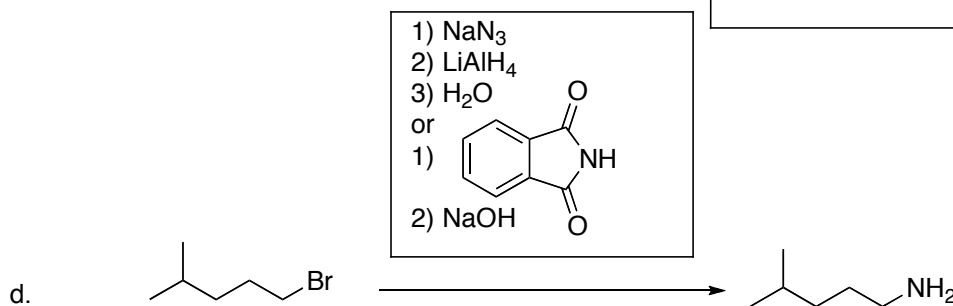
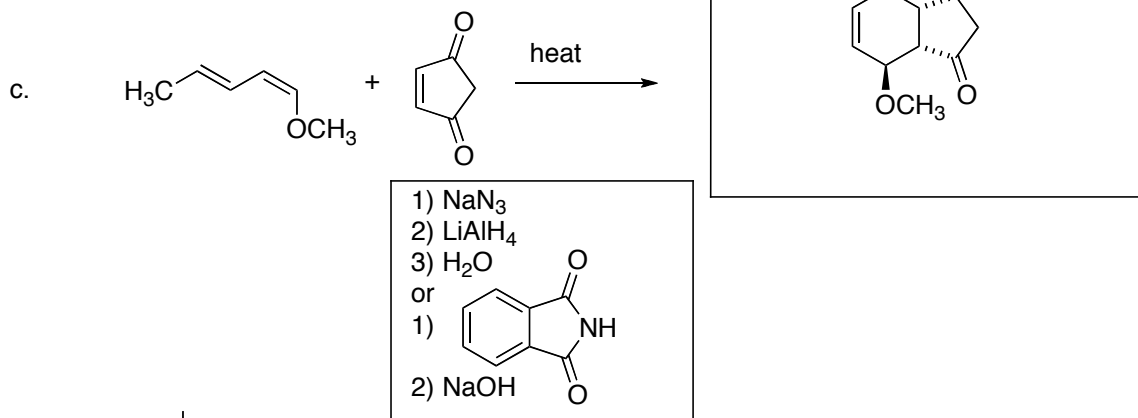
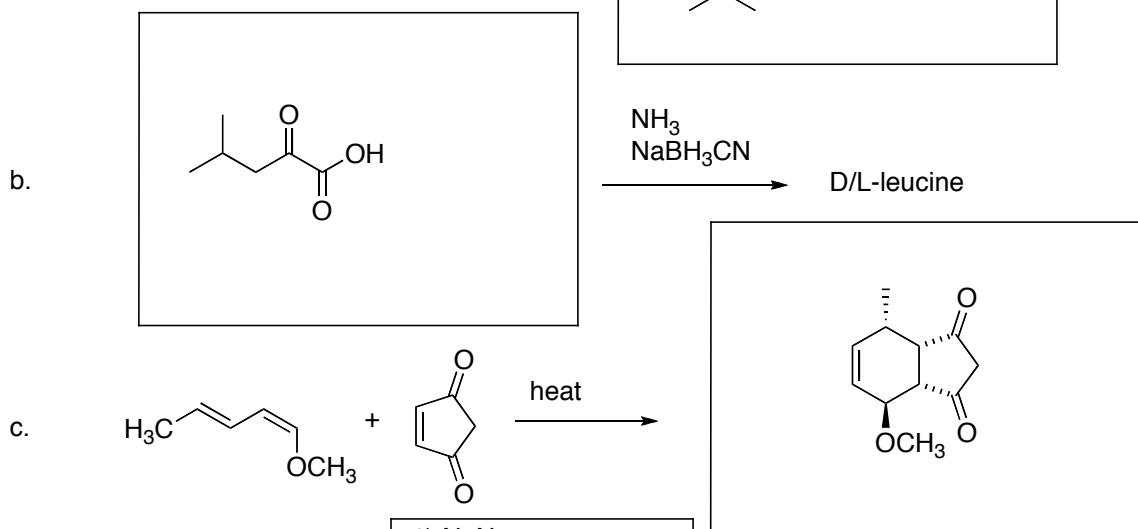
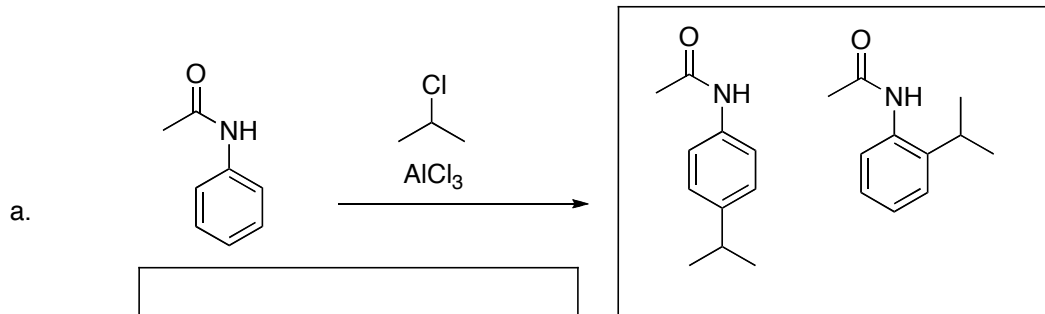
Leu•Lys

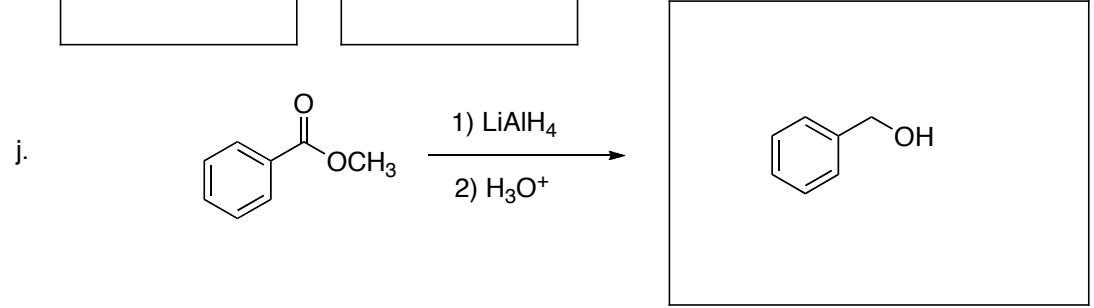
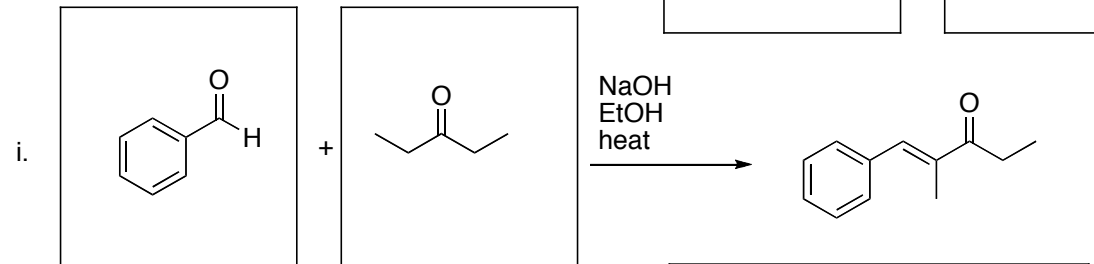
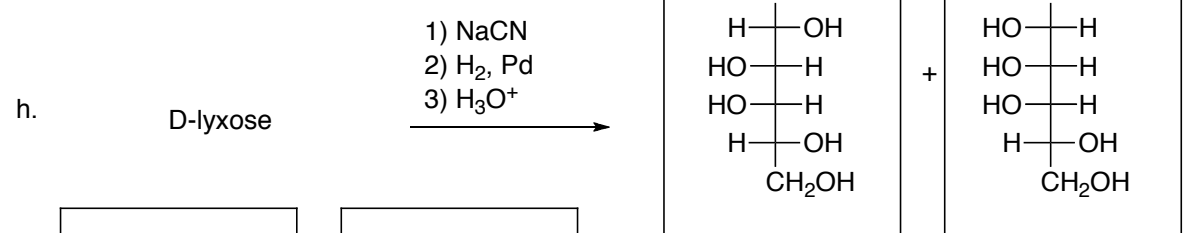
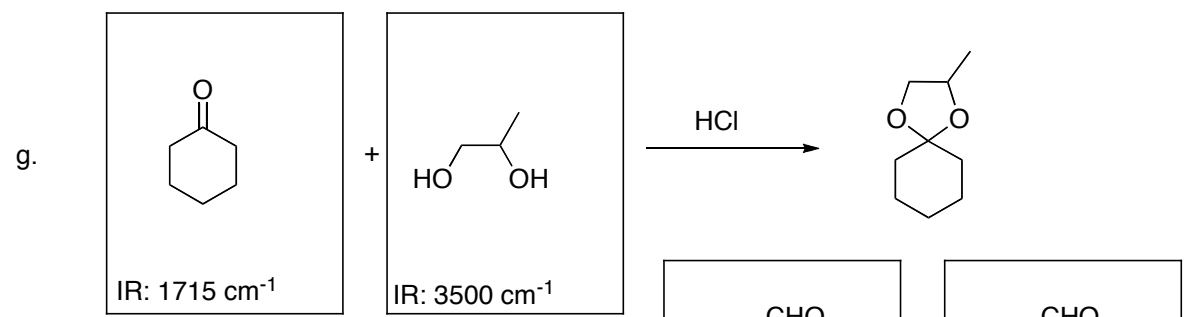
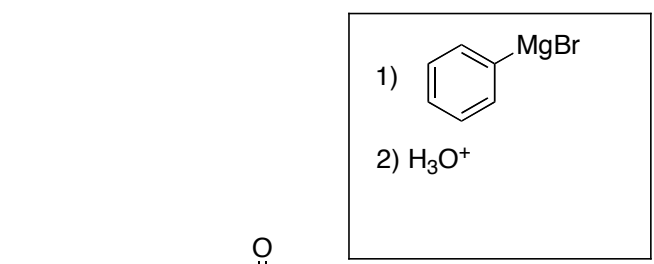
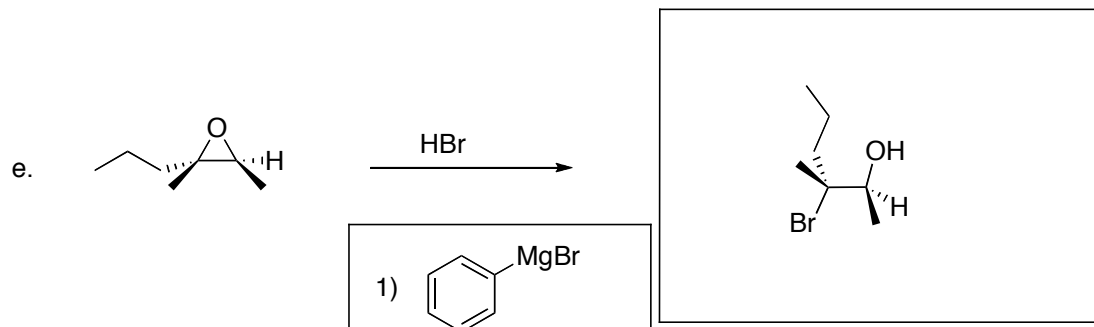
Trp•Glu

j. Which compound would be most reactive when reacted with  $\text{Br}_2$  and  $\text{FeBr}_3$ ?



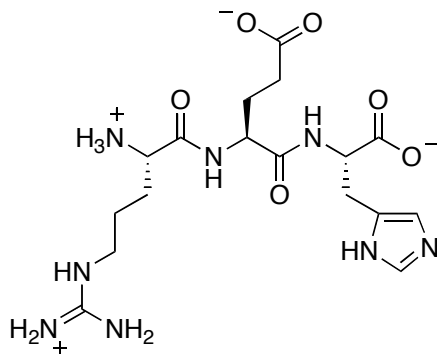
2. For each reaction below, fill in the missing starting material(s), reagent(s), or product(s). Where necessary, clearly indicate stereochemistry. There may be more than one product or reagent in each box. Where more than one product could be formed, draw only major products (40 points).





3. Answer the following questions about the tripeptide Arg-Glu-His. (16 points)

- a. Draw Arg-Glu-His as it would exist at pH 7 showing all stereochemistry and any charged atoms.



- b. Provide the overall charge on the tripeptide at the following pH values

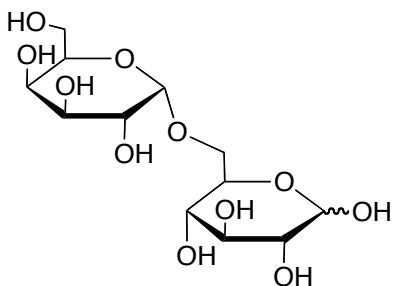
1 +3      5 +1      11 -1      14 -2

- c. Write the equation you would use to calculate the pI for this tripeptide showing which pKa values would be used. **You do not need to calculate the value of the pI.**

$$\text{pI} = \frac{6.0 + 9.2}{2} = 7.6$$

4. Melibiose is a naturally occurring disaccharide. Use the information below to draw the correct structure of melibiose as a Haworth projection. Be sure that all stereochemistry is clearly drawn. (18 points)

- Melibiose is a reducing sugar
- Hydrolysis of melibiose with dilute acid or an  $\alpha$ -glycosidase enzyme gave a 1:1 mixture of D-glucose and D-galactose.
- Oxidation of melibiose to melibionic acid using  $\text{Br}_2$  in water followed by hydrolysis with dilute acid gave D-galactose and D-gluconic acid.
- Methylation of melibionic acid with excess  $\text{CH}_3\text{I}$  and  $\text{Ag}_2\text{O}$  gave octamethylmelibionic acid. Hydrolysis gave 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,4,5-tetra-*O*-methyl-D-gluconic acid.
- Methylation of melibiose gave heptamethyl melibiose. Hydrolysis of this compound gave 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-glucose.

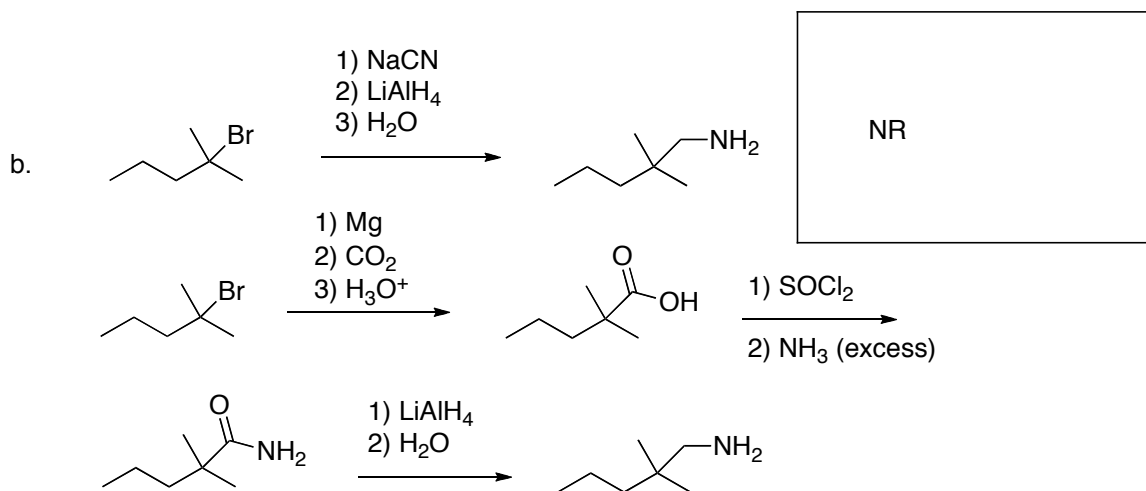
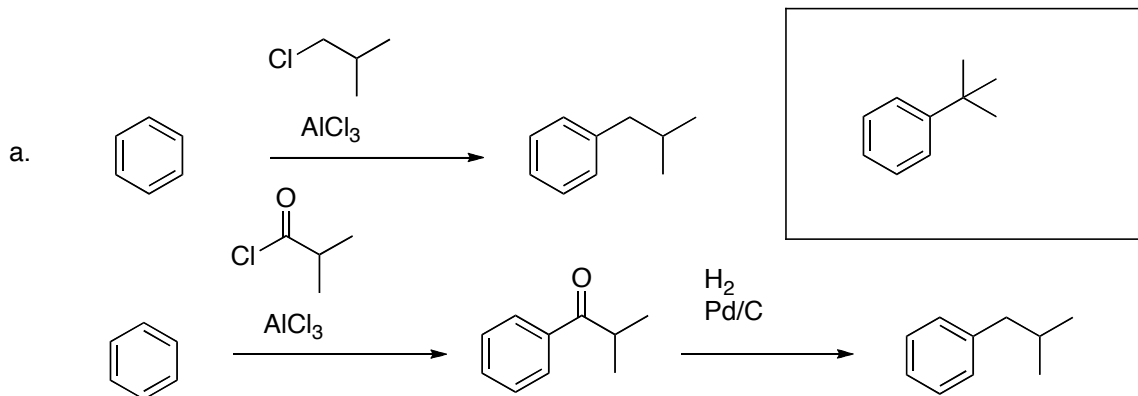


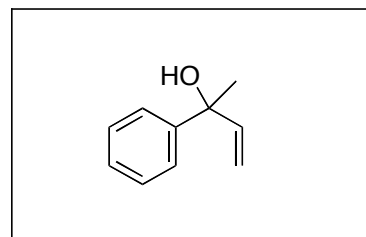
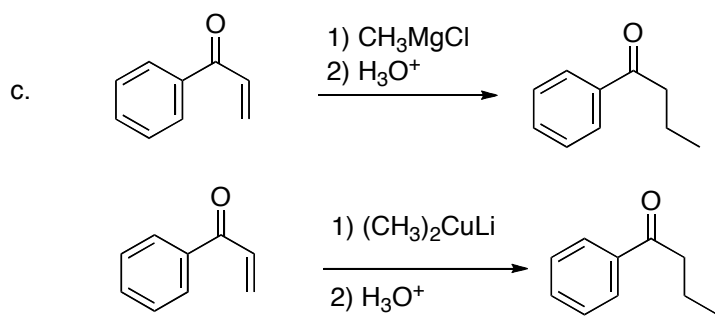
5. Angiotensin is an octapeptide that narrows blood vessels increasing blood pressure. ACE inhibitors lower blood pressure by blocking the biosynthesis of angiotensin. Use the information below to determine the aminoacid sequence for angiotensin. (16 points)

- Complete hydrolysis of angiotensin with 6M HCl gave Arg (2 equivalents), His, Ile, Phe, Pro, Tyr, and Val
- Edman degradation of angiotensin gave the PTH derivative of Arg.
- Treatment of angiotensin with carboxypeptidase gave Phe initially.
- Cleavage of angiotensin with trypsin gave 2 equivalents of Arg plus a hexapeptide (**A**).
- Cleavage of **A** with chymotrypsin gave a dipeptide **C** and a tetrapeptide **D**.
- Hydrolysis of **C** gave Tyr and Val
- Edman degradation of **D** gave the PTH derivative of Ile and a tripeptide **E**.
- Edman degradation of **E** gave the PTH derivative of His.

Arg    Arg    Val    Tyr    Ile    His    Pro    Phe

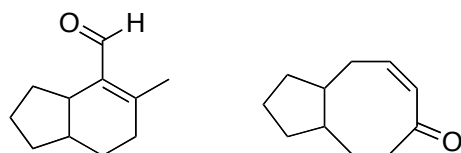
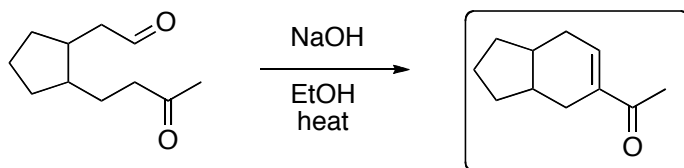
6. You are working in a synthetic lab and your labmate proposes the following reactions. Each one has a fundamental flaw that would not allow it to proceed as planned. In some cases the reaction would not work at all, while in others a different product or a mixture of products would be obtained. For each reaction, draw the product or products that would actually form under these conditions. If no product would be formed, write NR. Provide an alternate synthesis of the desired product from the same starting material. More than one step may be required. (18 points)



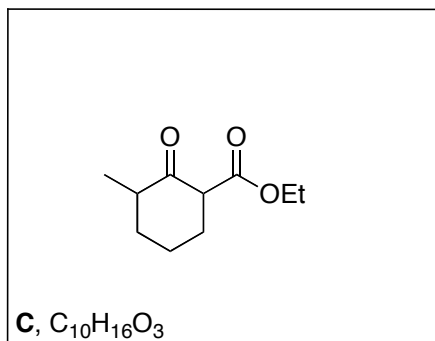
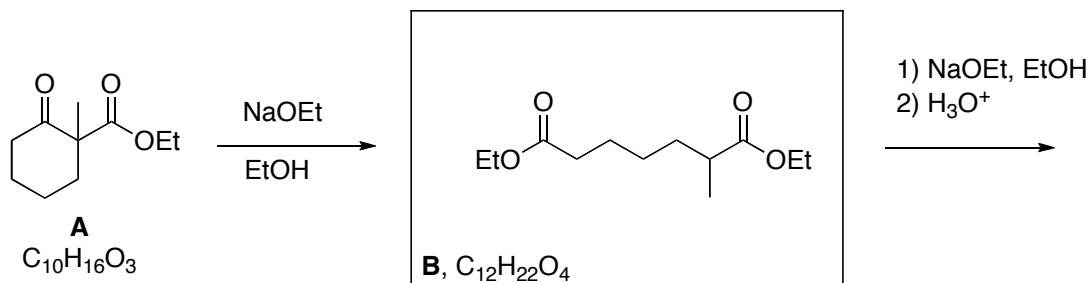


7. Provide the requested structures for each question below. (15 points)

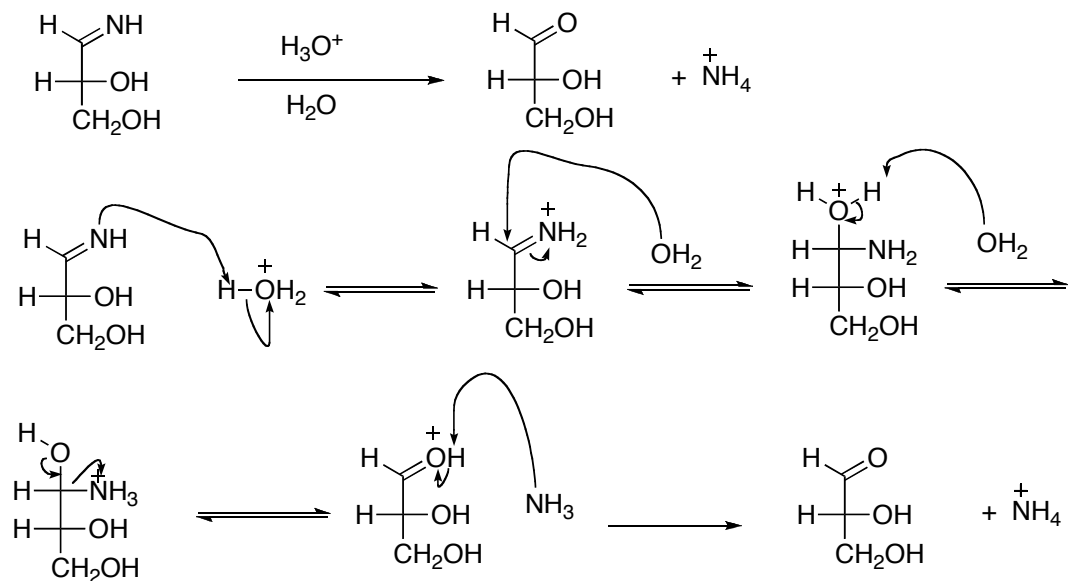
- a. Treatment of the ketoaldehyde below with base and heat results in the formation of a product with molecular formula  $C_{11}H_{16}O$ . Draw all of the possible structures with this formula that could form and circle the one that would be favored.



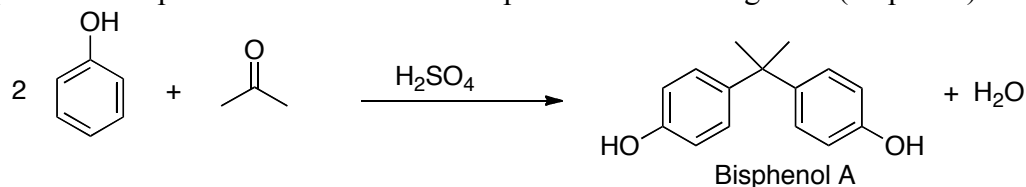
- b. When compound **A** is treated with NaOEt it undergoes a reverse Claisen reaction to give **B**. Compound **B** can react further with NaOEt to give **C** after treatment with acid. **C** has the same formula as **A**, but is a constitutional isomer (different atom connection). Propose structures for **B** and **C**.



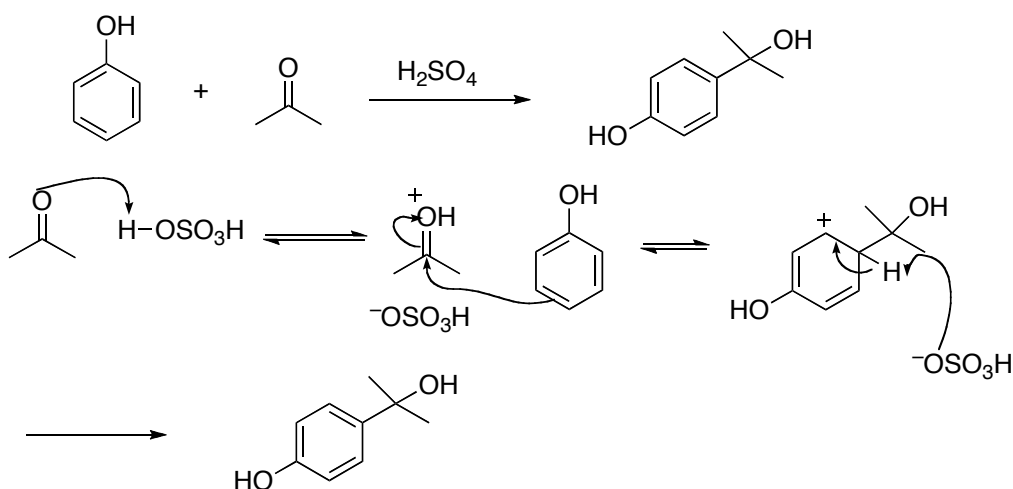
8. The last step in the Killiani-Fischer synthesis is the hydrolysis of an imine to give the aldose product. Draw a detailed electron-pushing mechanism to show how glyceraldehyde imine is converted to glyceraldehyde by reaction with aqueous acid. Show each step of the mechanism using arrows to show the motion of the electrons. Be sure to indicate any atoms with formal charges. (18 points)



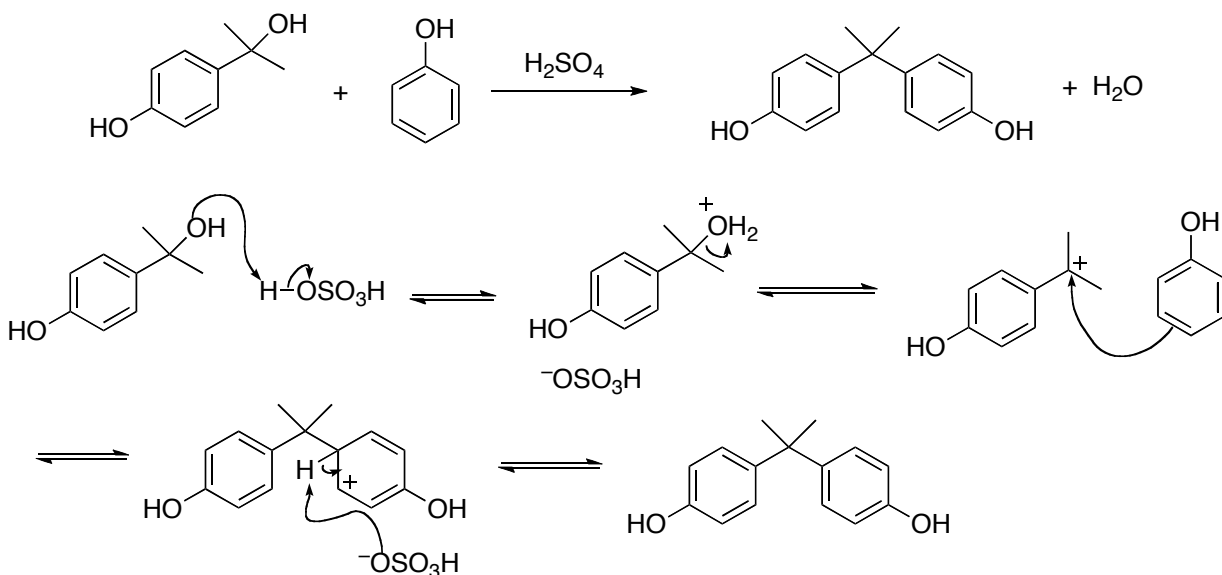
9. Bisphenol A is commonly used as a monomer for the synthesis of plastics. Although the toxicity of Bisphenol A is low, recent concerns about low-level exposure by infants has caused concern about this compound. Bisphenol A is prepared by the reaction of two equivalents of phenol with acetone in the presence of a strong acid. (20 points)



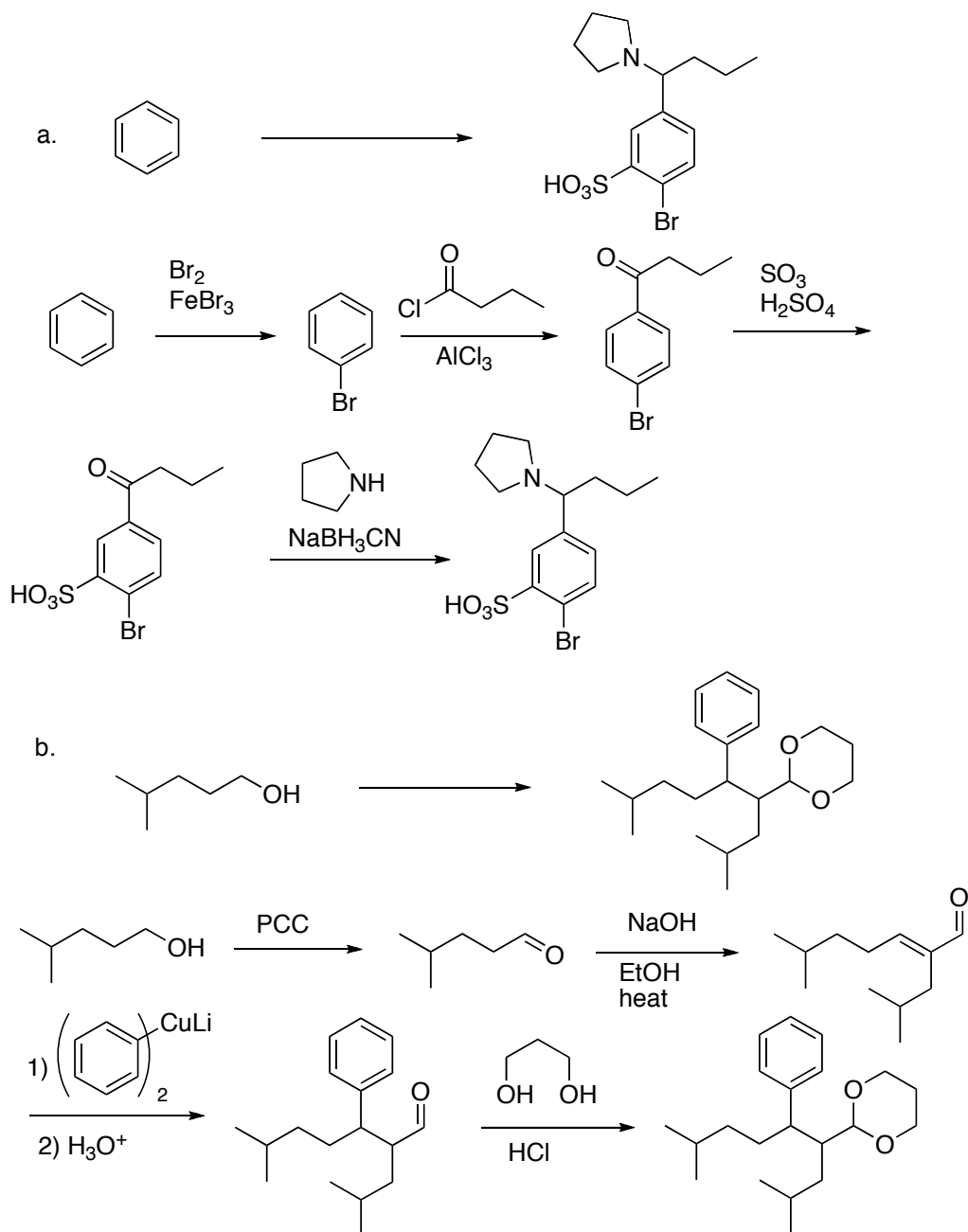
- a. The first part of the reaction is shown below. Using what you know about the reactivity, write a step-wise mechanism for the addition of the first phenol unit to acetone.

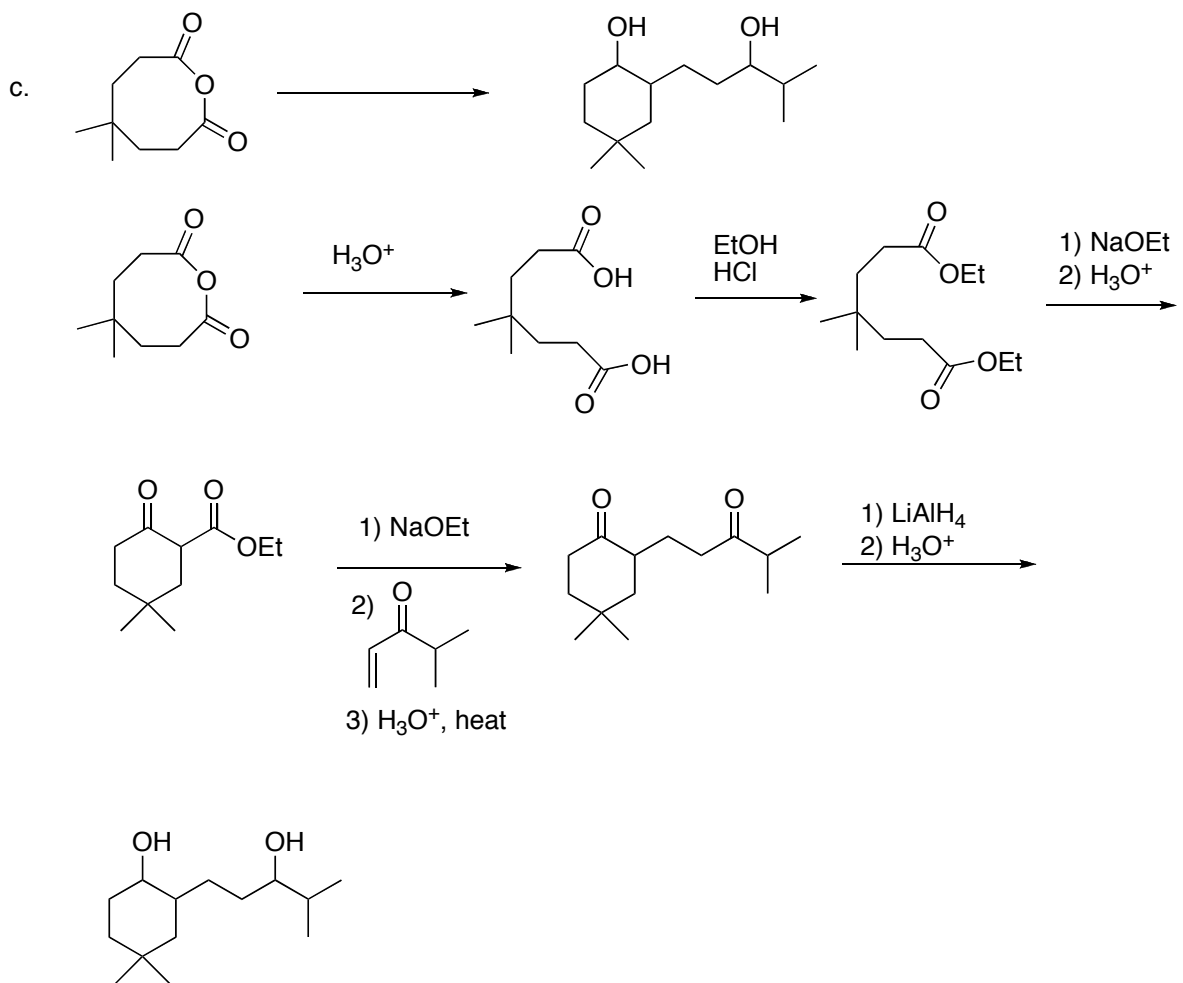


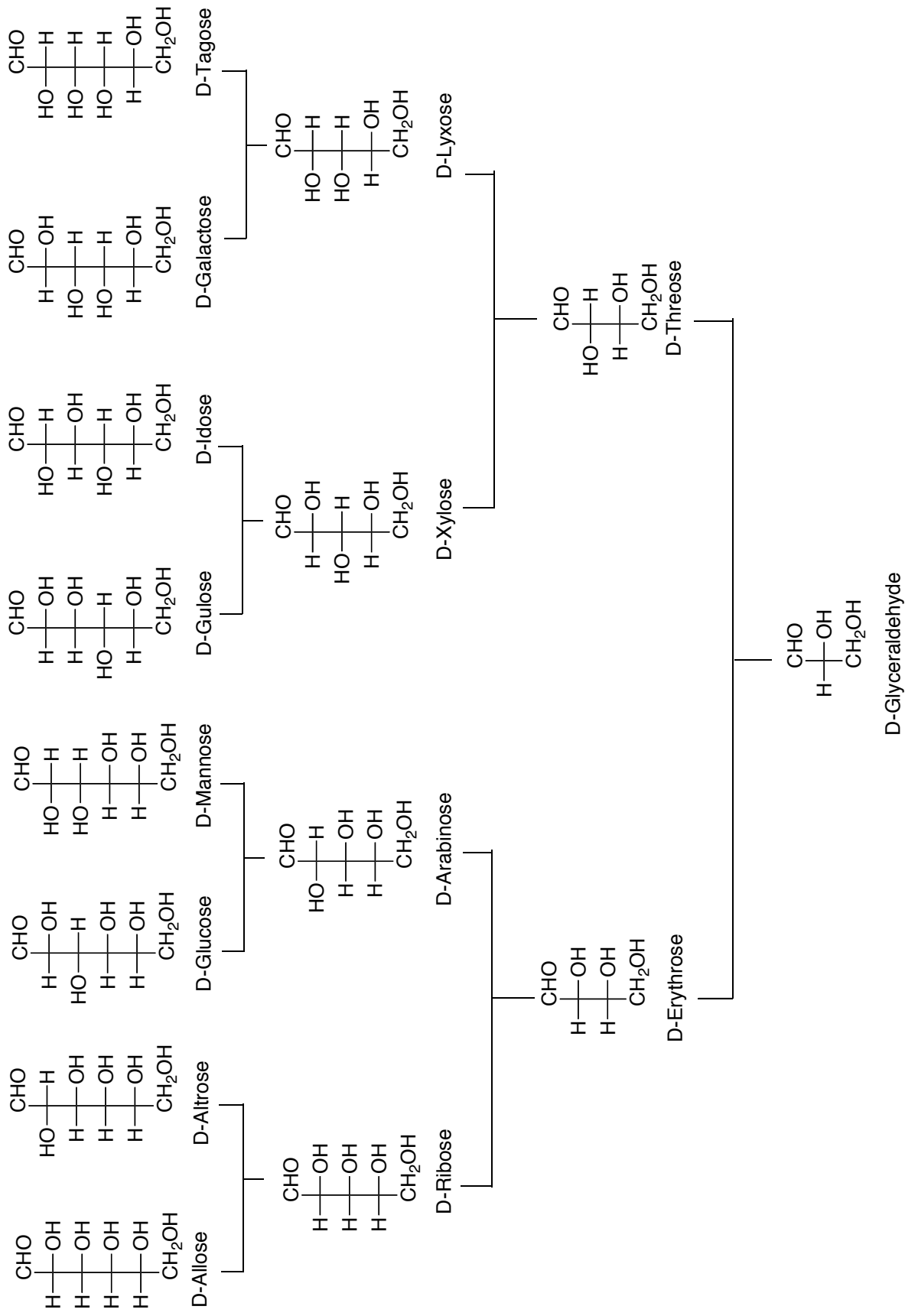
- b. The addition of the second equivalent of phenol is shown below. Provide the mechanism for this part of the reaction.

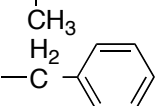
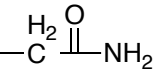
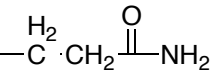
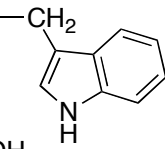
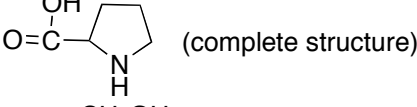
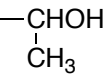
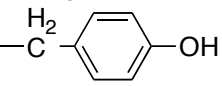
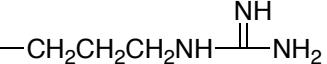
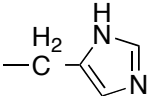


10. For the following problems, provide an efficient synthesis of the indicated compound from the starting material provided. You may use any other necessary reagents. **Organic reagents that you use in your synthesis (i.e. things that will end up in the final product) must have < 7 carbon atoms.** Your synthesis should provide the desired product as the major product in each step. (24 points).







Side Chain	Name (abbrev.)	pK <sub>a1</sub> α-CO <sub>2</sub> H	pK <sub>a2</sub> α-NH <sub>3</sub> <sup>+</sup>	pK <sub>a3</sub> sidechain
—H	Glycine (Gly)	2.3	9.6	
—CH <sub>3</sub>	Alanine (Ala)	2.3	9.7	
—CH(CH <sub>3</sub> ) <sub>2</sub>	Valine (Val)	2.3	9.6	
—CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Leucine (Leu)	2.3	9.6	
—CHCH <sub>2</sub> CH <sub>3</sub>	Isoleucine (Ile)	2.4	9.7	
	Phenylalanine (Phe)	1.8	9.1	
	Asparagine (Asn)	2.0	8.8	
	Glutamine (Gln)	2.2	9.1	
	Tryptophan (Trp)	2.4	9.4	
 (complete structure)	Proline (Pro)	2.0	10.6	
—CH <sub>2</sub> OH	Serine (Ser)	2.2	9.2	
	Threonine (Thr)	2.6	10.4	
	Tyrosine (Tyr)	2.2	9.1	10.1
—CH <sub>2</sub> SH	Cysteine (Cys)	1.7	10.8	8.3
—CH <sub>2</sub> CH <sub>2</sub> SH	Methionine (Met)	2.3	9.2	
—CH <sub>2</sub> CO <sub>2</sub> H	Aspartic Acid (Asp)	2.2	9.8	3.9
—CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	Glutamic acid (Glu)	2.2	9.7	4.3
—CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	Lysine (Lys)	2.2	9.0	10.5
	Arginine (Arg)	2.2	9.0	12.5
	Histidine (His)	1.8	9.2	6.0

All functional groups are shown in their neutral form. Depending on pH, these groups may be charged.

