1. Nomenclature & Fundamentals

(a) (10 points) Draw examples of your two favorite functional groups below using skeletal structures (no other abbreviations such as R groups). Draw two separate molecules and give the name of the functional group (not the IUPAC name of the molecule).

(b) (10 points) You were introduced to many reagents in this class that are more than just letters and numbers. These friends have names that help you understand how they participate in chemical reactions. Write the full name of each chemical on the line provided:

\[
\begin{align*}
\text{NaBH}_4 & \quad \text{sodium borohydride}^2 \\
\text{H}_2\text{SO}_4 & \quad \text{sulfuric acid}^1 \\
\text{NaCN} & \quad \text{sodium cyanide}^2 \\
\text{H}_3\text{O}^+ & \quad \text{hydronium}^1 \\
\text{AC}_2\text{O} & \quad \text{acetic anhydride}^1 \\
\text{SOCl}_2 & \quad \text{thionyl chloride}^2
\end{align*}
\]

(c) (10 points) Complete the following Fischer, Haworth projections and chair conformations…

\[\alpha-\text{D-Galactopyranose}\] (the C4 epimer of D-Glucose)

(d) (10 points) The Haworth projection of a monosaccharide is given below. Indicate whether the structure below is the alpha (α) or beta (β) anomer on the small line provided. Convert this into a Fischer projection.

(e) (5 points) Galactose and gulose (above) are examples of:

\[\text{Aldopentoses} \quad \text{Ketopentoses} \quad \text{Aldohexoses} \quad \text{Ketohexoses}\]
2. Amino Acids & Peptides - The structures of L-proline, L-histidine, and L-glutamic acid at physiological pH (7.4) are provided below, along with their pKa’s. Use these to complete parts (a) through (c) below.

(a) (15 points) Titration of Glutamic Acid – Draw the structure of the dominant ionic form of glutamic acid at each indicated pH range. Indicate all charged atoms and circle those charges.

- **L-Glutamic Acid (Glu, E)**
  - pKa\(_1\) 2.1
  - pKa\(_2\) 9.2
  - pKa\(_R\) 6.0

(b) (15 points) Peptide Primary Structure - Draw the tripeptide containing L-Proline, L-Glutamic Acid, and L-Histidine at pH 1, where glutamic acid is the *N*-terminal and histidine is the *C*-terminal amino acid. Label all charged atoms where appropriate and indicate the net charge.

\[(N\text{-terminus}) - \text{Glu} – \text{Pro} – \text{His} – (C\text{-terminus})\]  @ pH 1

(c) (10 points) What is the pH range in which Glu-Pro-His tripeptide has a net charge of zero? Draw the structure of that net neutral peptide, labeling all charged atoms where appropriate.

\[4.1 \quad < \text{pH} < \quad 6.0\]
3. (40 points) **Reaction Puzzle – Multiple Choice**

Fill in the best reagent for each transformation using the choices below. **Simply put the letter in the box!** One letter per box, each letter may be used more than once, and not every letter needs to be used.

*Pro-tip: take it one reaction at a time and pay attention to the direction of the reaction arrow!*

**(A)** Br₂, HAc  
**(B)** NaCN  
**(C)** NH₃  
**(D)** 1. LiAlH₄; 2. H₃O⁺  
**(E)** 1. LiAlH₄; 2. H₂O  
**(F)** 1. NaBH₄; 2. H₃O⁺  
**(G)** NaOH  
**(H)** Excess CH₃OH, H⁺  
**(I)** SOCl₂  
**(J)** H₃O⁺  
**(K)** 1. Ethylmagnesium bromide; 2. H₃O⁺  
**(L)** 1. NH₃; 2. NaBH₄  
**(M)** 1. NaN₃, 2. LiAlH₄, 3. H₂O  
**(N)** 1. CrO₃, H₃O⁺; 2. SOCl₂
4. Mini-Puzzles. Fill in the missing molecules, paying close attention to the direction of the reaction arrow.

(a) (10 points) Show the **products** of two different reactions of α-D-allopyranose.

(b) (10 points) Show the **products** of both reactions to explain the need for N-acyl capping.

(c) (10 points) Show the **starting materials** for two different methods for making Histidine.

(d) (15 points) Draw the **triacylglycerol** product of the following reaction. You are welcome to abbreviate the hydrocarbon chain from the fatty acid.
5. Carbohydrate Puzzle

Read the following reaction descriptions carefully then draw the structures (Fischer projections) of monosaccharides A-F in the boxes provided.

Compound A is a D-aldopentose that can be oxidized to an optically inactive aldaric acid B. On Kiliani-Fischer chain extension, A is converted to C and D. Compound C can be oxidized to an optically active aldaric acid E, but D is oxidized to an optically inactive aldaric acid F. What are the structures of A-F?
6. **Mechanisms** – Draw the full arrow-pushing mechanism for **both reactions** below, including all arrows for acid-base reactions. Include all intermediates with proper charges circled for each step.

(a) **(30 points)** 1-cyclopentene carbaldehyde is made through a **base-promoted intramolecular aldol cyclization followed by E1cB reaction**. Show this full mechanism.

(b) **(20 points)** N-Acyl capping is used to decrease the reactivity of aniline to promote cleaner reactions. **Draw the full structure of Ac₂O** then draw the full arrow pushing **mechanism** of the reaction below.
7. (40 points) Multi-Step Synthesis – CHOOSE TWO
Carry out the syntheses of the indicated target molecules using the starting material provided and any other reagents or carbon sources needed. Draw the product after each synthetic step. No mechanisms.

(a)  

(b)  

(c)  

PUT A LARGE “X” OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING AND DO NOT WANT GRADED. OTHERWISE THE TOP TWO REACTIONS WILL BE GRADED, EVEN IF THEY ARE BLANK!