UCSC, Binder Name_____

Section _____ TA _____ SID _____

CHEM 108B Organic Chemistry II
FINAL EXAM, Version B (*400 points*)

In each of the following problems, use your knowledge of organic chemistry conventions to answer the questions in the proper manner. **Be sure to read each question carefully.** You have 3 hours to complete the exam, but hopefully you won't need it! You are welcome to use pre-built models. **Complete every problem on Pages 1-8. Pages 9 & 10 (multi-step synthesis) are the only pages where you can skip problems.**

Keep your eyes on your own paper. Electronic devices of any kind are not allowed, including cell phones and calculators. Any student found using any of said devices, or found examining another student's exam, will be promptly removed from the exam room and at minimum will receive a zero on this exam. Such an incident may also be considered a form of academic dishonesty and reported to the UCSC Judiciary Affairs Committee.

1. Nomenclature (50)	
2. Lipids (40)	
3. Amino Acids (30)	
4. Peptides (40)	
5. Single Step, MC (40)	
6. Mini Puzzles (50)	
7. Reaction Puzzle (50)	
8. Mechanisms (50)	
9. Multi-Step (30)	
10. Multi-Step Challenge (20)	
Total	

Functional Group	**Suffix**
Acid chloride	-oyl chloride
Acid Anhydride	-oic anhyride
Carboxylic Acid	-oic acid
Esters	-oate or carboxylate
Amides	-amide

1. Nomenclature Edited 3/13 to remove material not covered W17

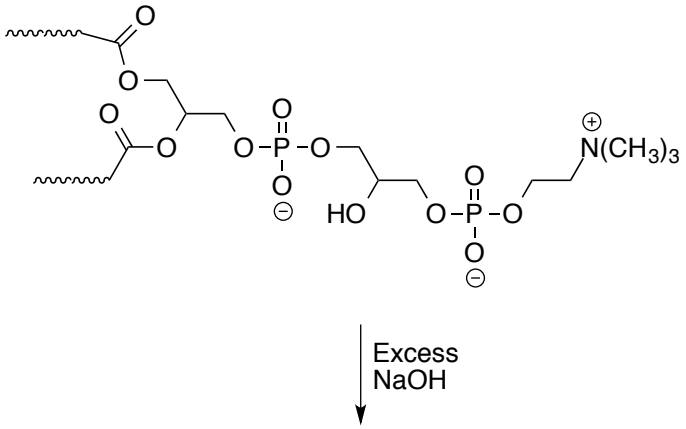
(b) (*20 points*) Complete the following Haworth projections and chair conformations…

β-D-Galactopyranose
(the C4 epimer of D-Glucose)

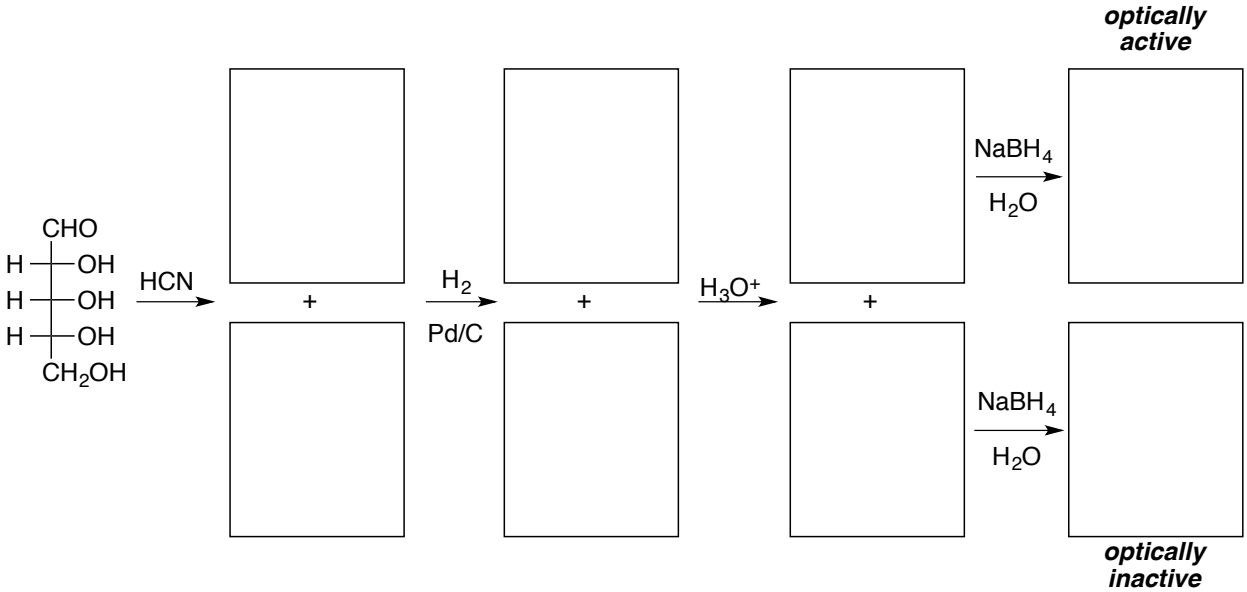
α-D-Glucopyranose

2. Biomolecules

(a) (*20 points*) The following **phospholipid** was subjected to **saponification** (basic hydrolysis). Draw the many **products of the reaction**.



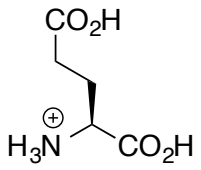
(b) (*20 points*) The D-aldopentose below was subjected to **Kiliani-Fischer synthesis** followed by **reduction** to afford two **epimers**, one of which is optically active and the other optically inactive. Fill in the boxes below to **show the structures after each step**.



3. Amino Acids

Draw the dominant ionic species of the amino acids at each of the indicated pH ranges based on the given pKa's. Indicate all charged atoms. Circle the charges as shown below.

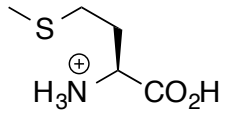
(a) (*10 points*) **Titration of Glutamic Acid** - pKa_1 2.10; pKa_2 9.47; pKa_R 4.07



L-Glutamic Acid
(fully protonated)

pH < 2.10	2.10 < pH < 4.07	4.07 < pH < 9.47	pH > 9.47
Charge:			

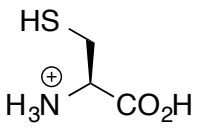
(b) (*10 points*) **Titration of Methionine** – pKa_1 2.28; pKa_2 9.21



L-Methionine
(fully protonated)

pH < 2.28	2.28 < pH < 9.21	pH > 9.21
Charge:		

(c) (*10 points*) **Titration of Cysteine** - pKa_1 2.05; pKa_2 10.25; pKa_R 8.00



D-Cysteine
(fully protonated)

pH < 2.05	2.05 < pH < 8.00	8.00 < pH < 10.25	pH > 10.25
Charge:			

4. Peptide Primary Structure

(a) (*20 points*) Draw the structure of a tripeptide containing L-Methionine, L-Glutamic Acid, and D-Cysteine at **physiological pH (7.4)** using the structures from page 3.

Met – Glu – Cys

(b) (*20 points*) Draw the structure of the **Met – Glu – Cys** tripeptide at **pH 10** using the structures from page 3.

(c) (*10 points*) Suppose Met-Glu-Cys was **hydrolyzed** into its constituent **amino acids** with HCl and subjected to two separate **electrophoresis** experiments in buffered solution. **Indicate the results (relative positions) of each amino acid on the "gels" below.**

Electrophoresis at **pH 2**

(+) (-)

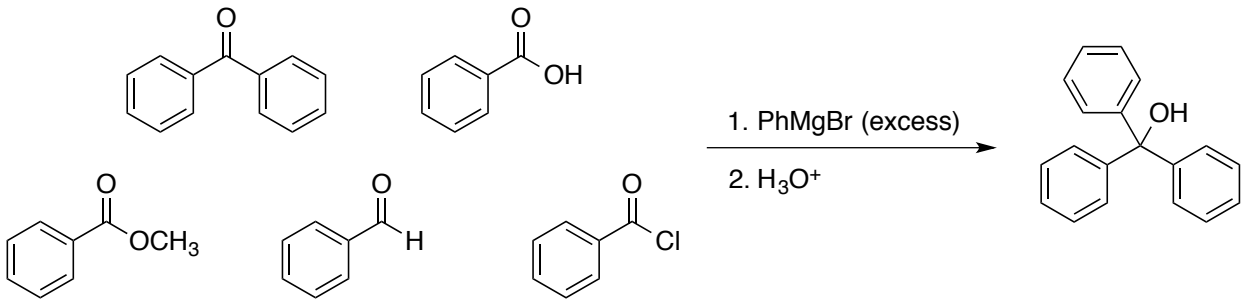
Electrophoresis at **pH 10**

(+) (-)

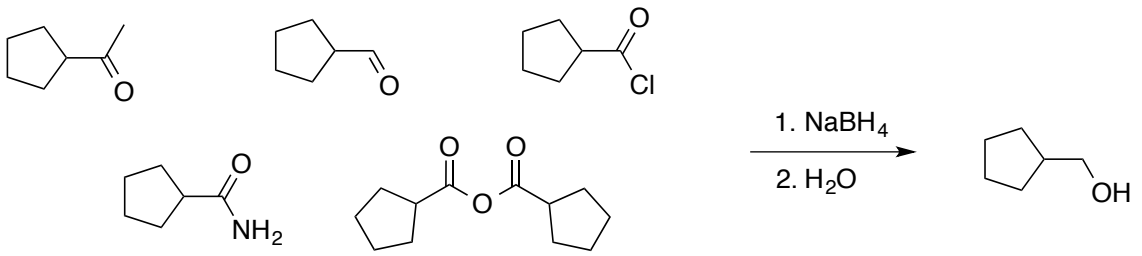
5. (*40 points*) **Single Step Reactions – <u>Multiple Choice</u>**

Circle the starting material(s) that would give the indicated product. More than one answer may be possible for each.

(a)

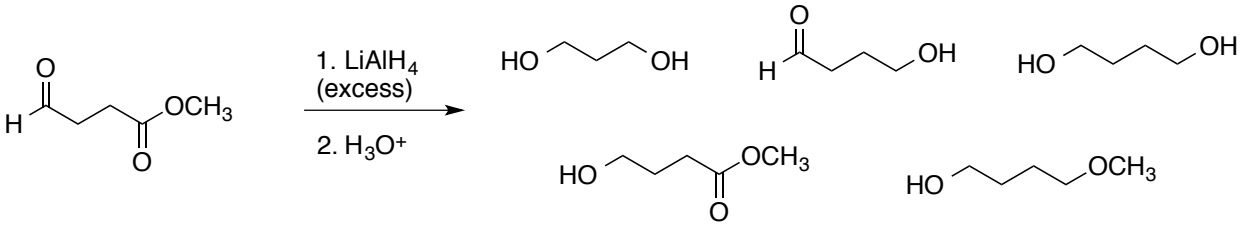


(b)



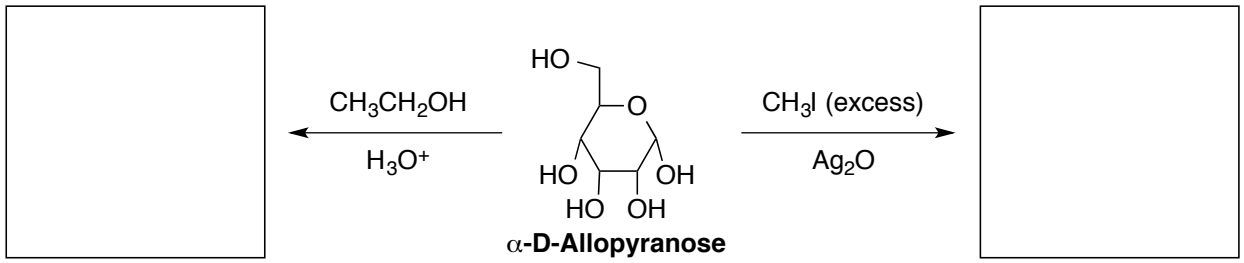
Circle the correct product in each reaction.

(c)

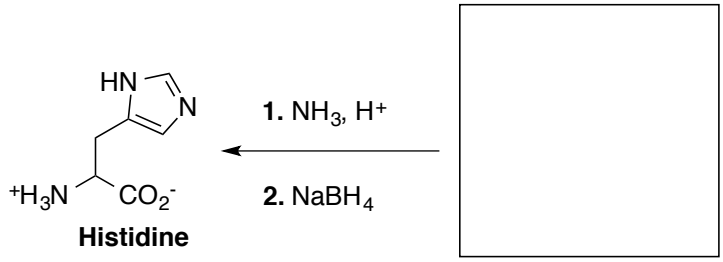


6. (*40 points*) **Mini-Puzzles**

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



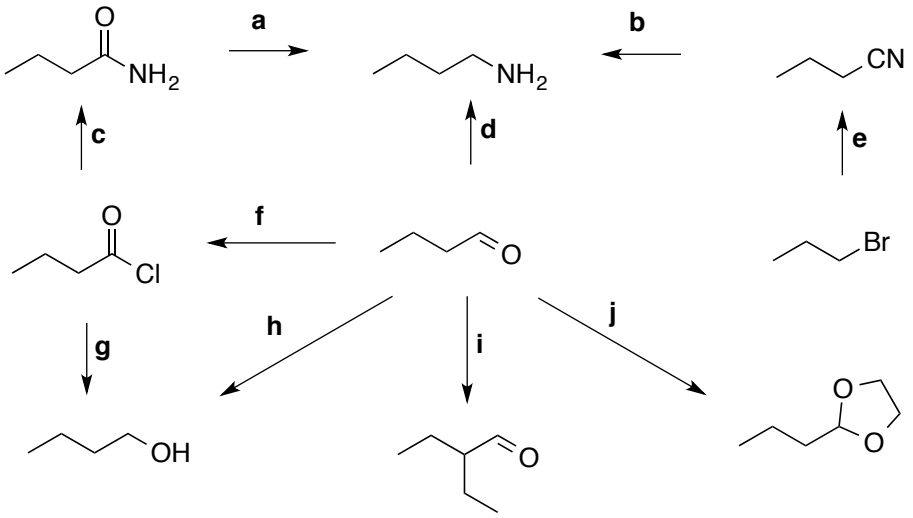
(b) Show the **starting materials** for synthesizing **Histidine.**



(c) The two reactions below give the same product. Draw that **product**.

7. (*50 points*) **Reaction Puzzle**

(a) Fill in the missing reagents. More than one set of reagents may be required in each step (letter). *Pro-tip: try not to get overwhelmed, take it one reaction at a time!*



(a) _____ **(b)** _____

(c) _____ **(d)** _____

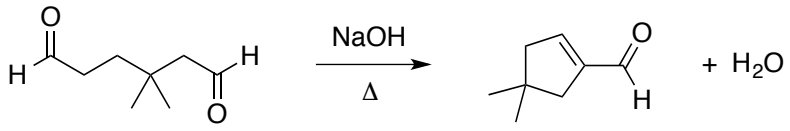
(e) _____ **(f)** _____

(g)_____ **(h)** _____

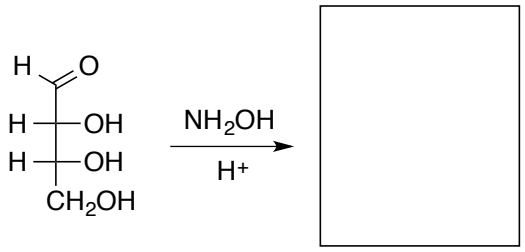
(i)_____ **(j)**_____

8. Mechanisms – Draw the full arrow-pushing mechanism for **both reactions** below, including all arrows for acid-base reactions (no "PT"). Include all intermediates with proper charges circled for each step.

(a) (*25 points*) 4,4-Dimethyl-1-cyclopentene carbaldehyde is made through a **base-promoted intramolecular aldol cyclization** of the dialdehyde below. Show this mechanism. Yes, this is the same mechanism from the second exam.
Pro tip: consistently number the carbons in the starting material & product.



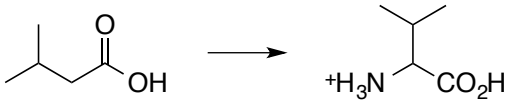
(b) (*25 points*) The first step in the **Wohl degradation** is the reaction of an aldopentose with **hydroxylamine** to form an **oxime**, which is closely related to an imine. **Draw the structure of the oxime** that would be formed in the reaction of the D-aldotetrose below. Also draw the **full arrow-pushing mechanism** for the formation of the oxime, including reaction **intermediates** and **charges** clearly indicated, in the space below.



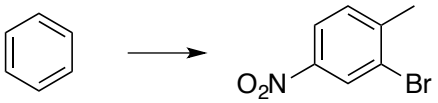
An Oxime

9. (*30 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)

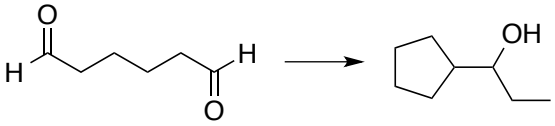


(c)

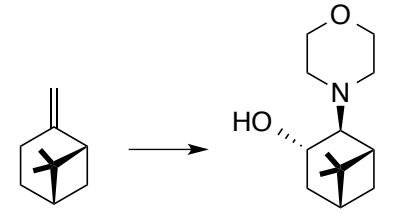
PUT A LARGE "X" OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING AND DO NOT WANT GRADED.
OTHERWISE THE TOP TWO REACTIONS WILL BE GRADED, EVEN IF THEY ARE BLANK!

10. (*20 points*) **Multi-Step Synthesis – CHOOSE ONE**
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) Show the synthesis of the following cyclopentane derivative. It would be wise to revisit page 8 for assistance!



(b) Dr. B's Ph.D. dissertation focused on the synthesis of amino alcohols for use as chiral catalysts in alkylation reactions. The synthesis of the compound below was accomplished using creative understanding of the reactions from CHEM 108A&B. Impress me with your knowledge and complete the synthesis of *trans*-2-morpholino apopinol (***trans*-2-MAP**) from ***β*-pinene**!



***β*-Pinene** ***trans*-2-MAP**

PUT A LARGE "X" OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING AND DO NOT WANT GRADED.
OTHERWISE THE FIRST REACTION WILL BE GRADED, EVEN IF IT IS BLANK!