UCSC, Binder Name_____

Student ID # _____ Section Day/Time _____

Organic Chemistry
EXAM 2A (*250 points*)

DO NOT BEGIN THE EXAM OR TURN THE PAGE UNTIL INSTRUCTED TO DO SO.
In the meantime, please read the instructions below.

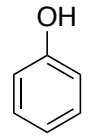
In each of the following problems, use your knowledge of organic chemistry conventions to answer the questions in the proper manner. **Be sure to read all instructions carefully. Abbreviate only when instructed to do so. You are welcome to ask questions for clarification.** You have one hour to complete this exam. Point distributions are given throughout the exam so you can use your time wisely.

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 (40)	
2 (35)	
3 (50)	
4 (50)	
5 (40)	
6 (35)	
Total	

1. Fundamentals

(a) (*5 points*) **Provide the approximate pKa's** of the following compounds on the lines provided.



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H_2O

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NH_4^+

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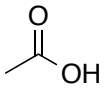

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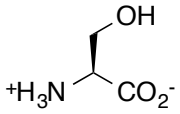
(b) (*10 points*) **Circle the most acidic proton** on each compound and **estimate its pKa**.



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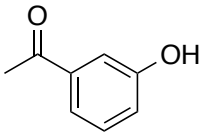

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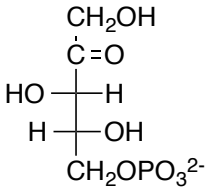
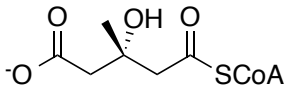
(c) (*15 points*) **Functional Groups** – Circle and name each unique functional group in the metabolic intermediate below. If a functional group appears multiple times, you can circle and name just one of them.



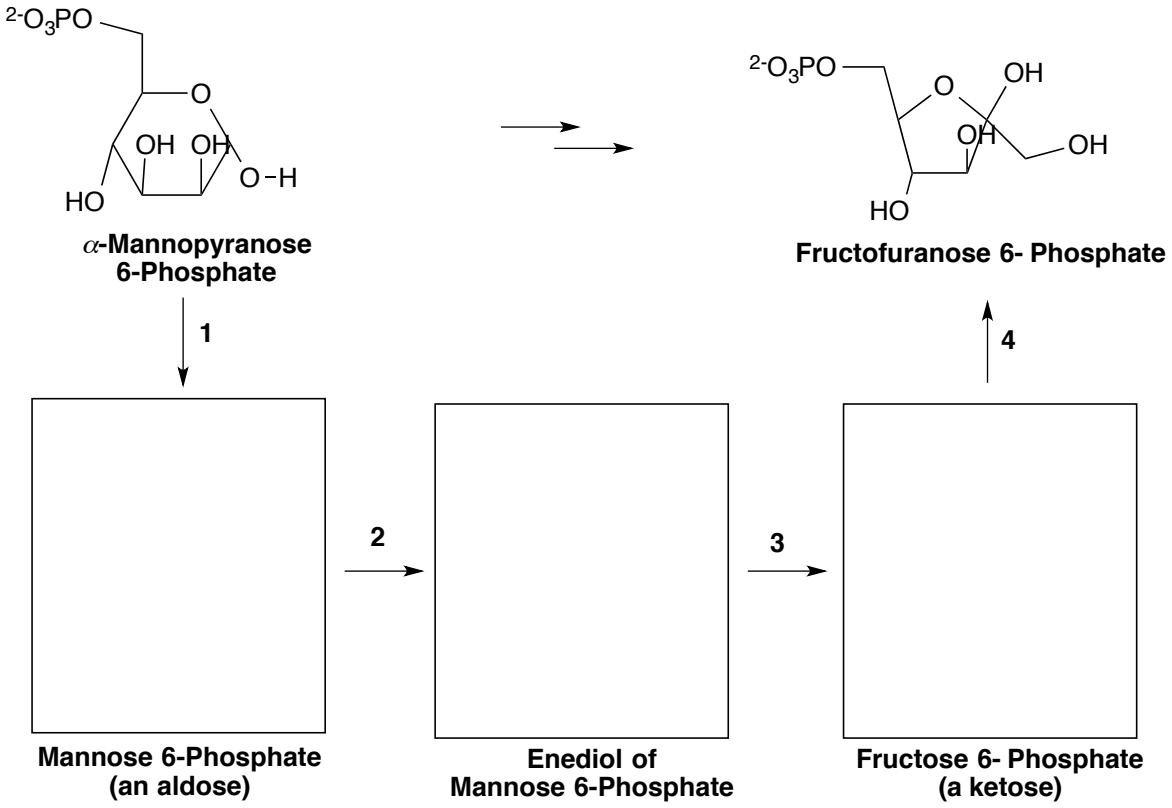


(d) (*10 points*) **Tautomers** – Draw the structure of the **enol of pyruvate** and **pyruvate**, the last step of glycolysis. No mechanisms, just structures.

Enol of Pyruvate **Pyruvate**

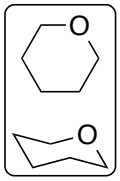
2. Carbohydrates

(a) (*15 points*) The conversion of **mannopyranose 6-phosphate** into **fructofuranose 6-phosphate** is a four-step process involving **(1)** *ring opening* of the pyranose, **(2)** *tautomerization* of the **aldose** into an **enediol**, **(3)** *tautomerization* into the **ketose**, and finally **(4)** *closing* of the furanose ring. Show the structures of these intermediates without abbreviations in the boxes provided (OK to keep the phosphate in condensed form). *No mechanisms necessary*, but you're welcome to add them if it's helpful to you. *Only the structures in the provided boxes will be graded.*



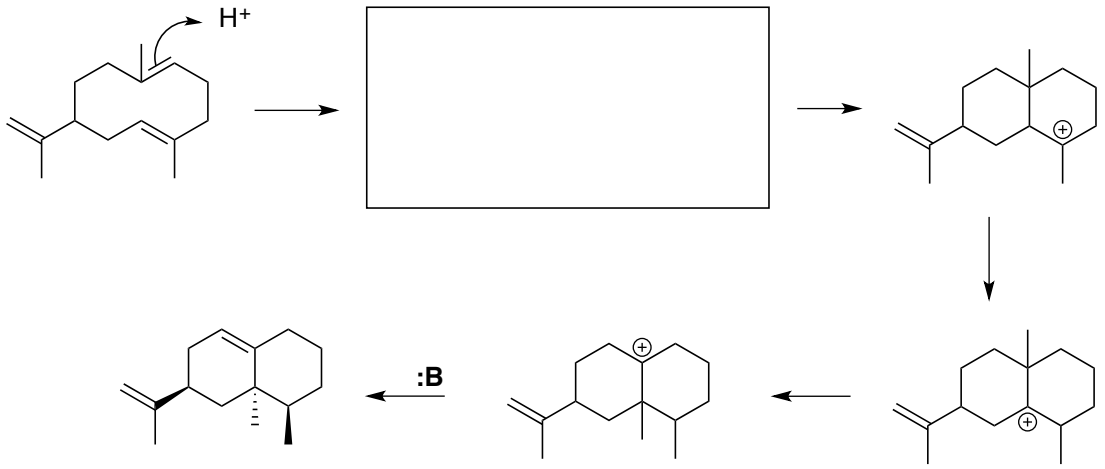
(b) (*20 points*) Draw the structure **sophorose**, the product of sugar carmelization, in **both Haworth and chair projections.** Sophorose is a disaccharide consisting of **two D-glucose units** linked by a **β-1,2-glycosidic bond**. The **free anomeric OH is in the β-form**. Use the Haworth and chair projections below as a reference for properly drawing these rings. Do not show your answer on these structures!

Sophorose (Haworth) Sophorose (Chairs)



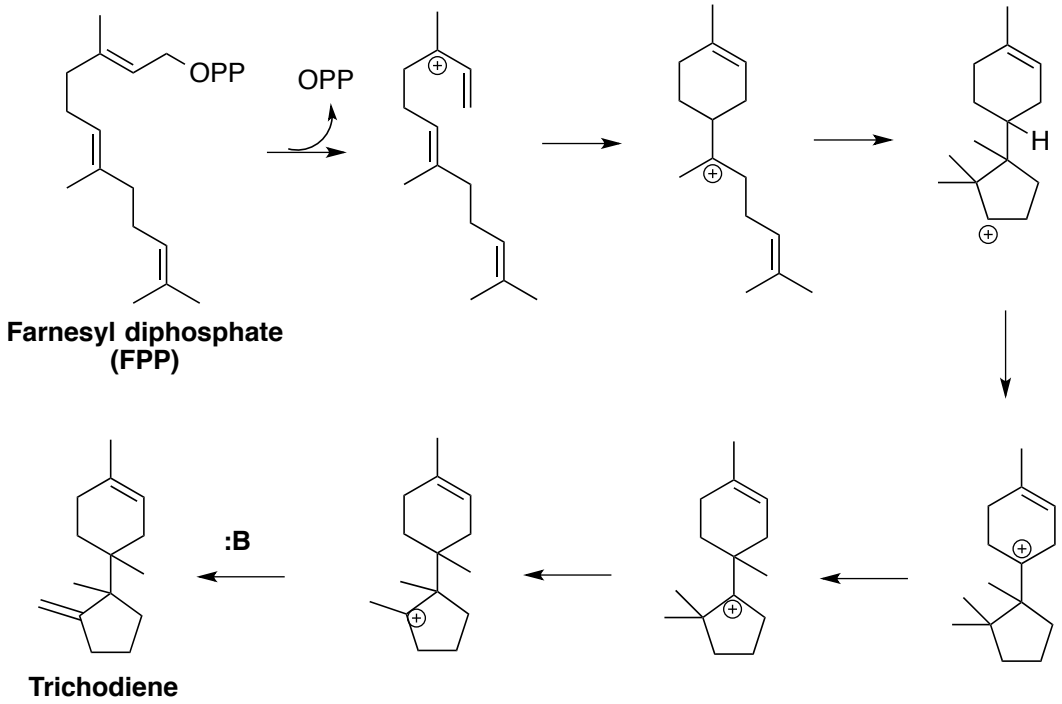
3. Mechanism Warm-up

(a) (*20 points*) The final stages in the biosynthesis of ***epi*-aristolochene** are shown below. Follow the arrow in the first step to **draw the intermediate** in the box provided. **Add arrows** to complete the mechanisms in the remaining four steps.



***epi*-Aristolochene**
(stereochem incorporated along the way, not shown until now!)

(b) (*30 points*) **Add the arrows in each step** to lead to the next product in the biosynthesis of trichodiene from FPP.

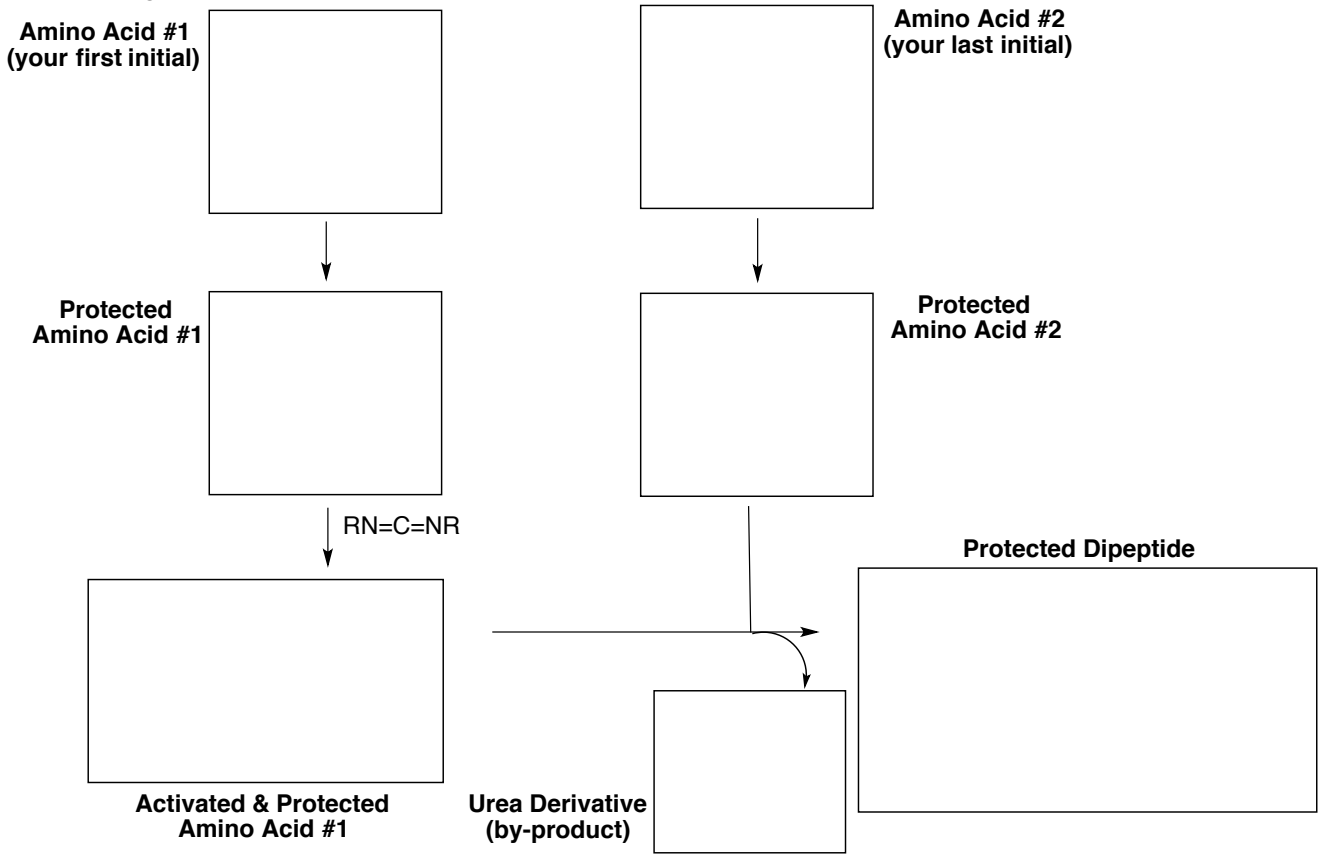


Farnesyl diphosphate (FPP)

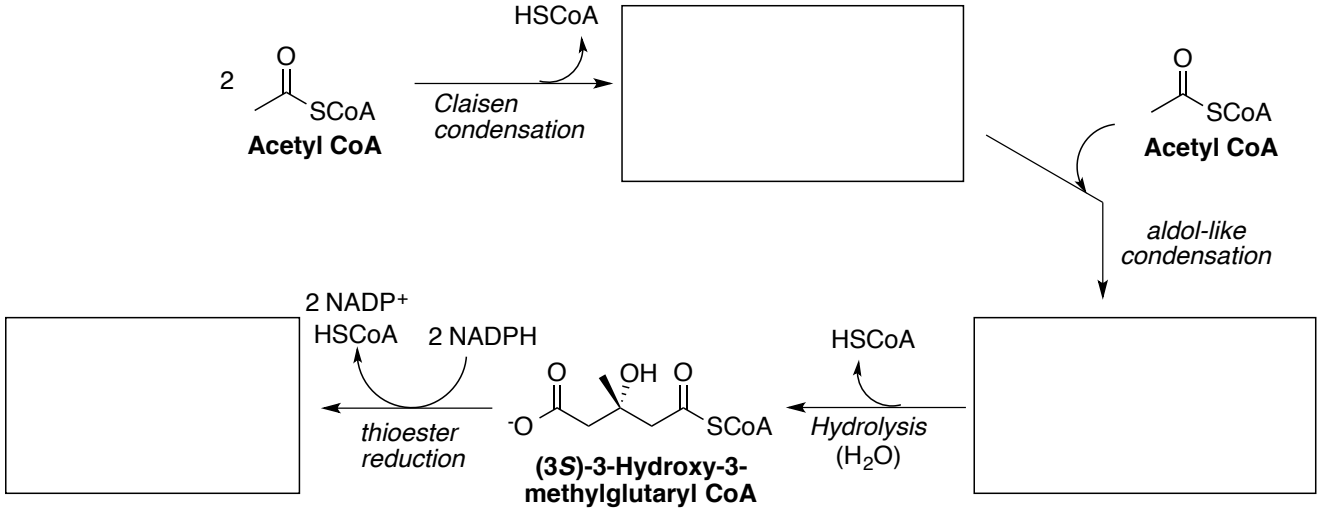
Trichodiene

4. Fill in the Boxes – No arrow-pushing necessary, only structures in boxes graded.

(a) (*35 points*) Outline the steps for the laboratory synthesis of "your" protected dipeptide. Begin by drawing the full structure of **Amino Acid #1** (with the same single letter abbreviation as your first initial) and **Amino Acid #2** (last initial). If either of your initials are one of the 6 letters without an amino acid abbreviation, move to the next letter in the alphabet. **Protect** each amino acid appropriately, then **activate the acid** of one with the carbodiimide coupling agent (**RN=C=R**). Finally, draw the structure of the **dipeptide** with protecting groups still attached as well as the by-product of the coupling reaction, a **urea derivative.**



(b) (*15 points*) Draw each intermediate in beginning stages of the synthesis of **the mavelonate pathway.**

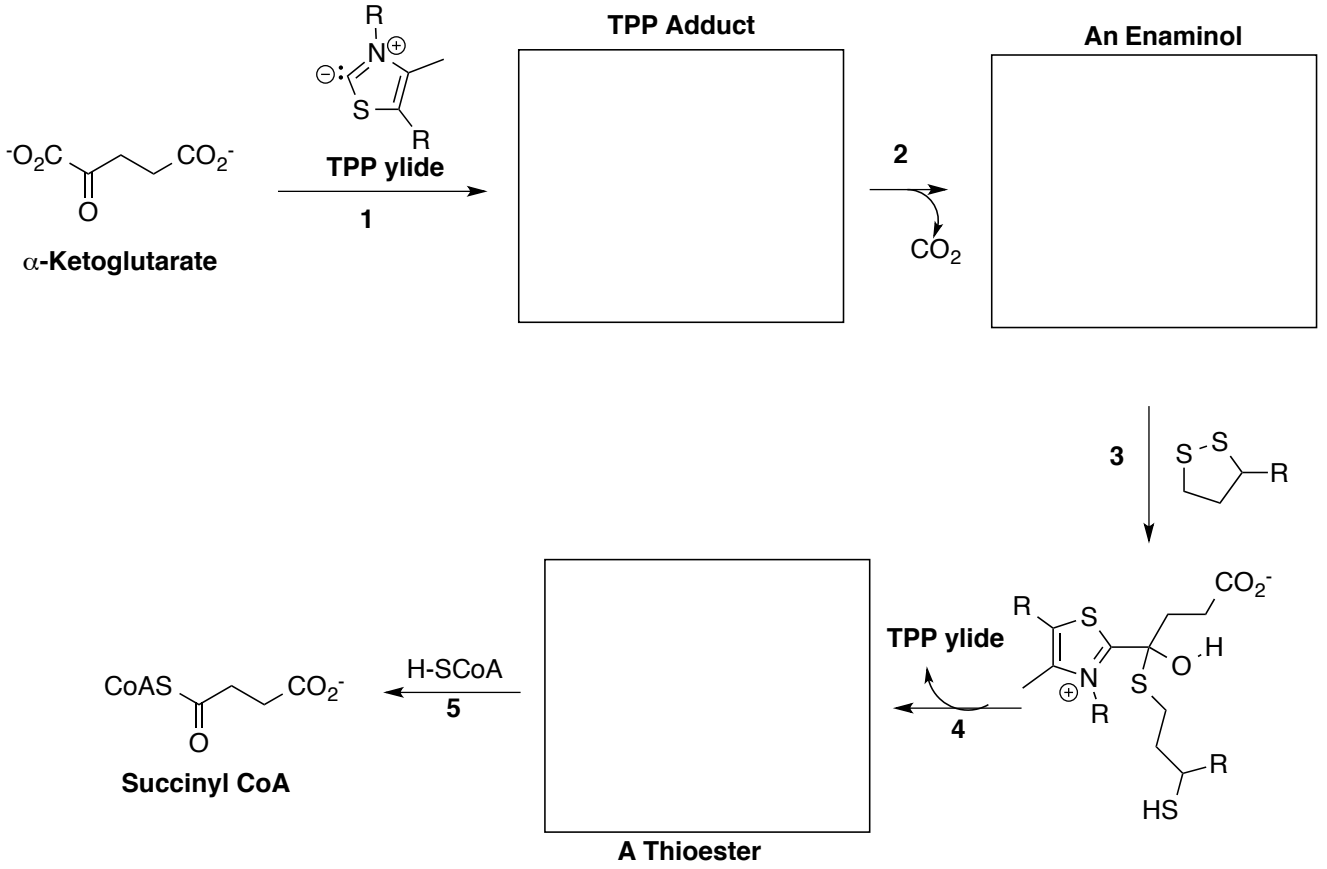


5. Reaction Mechanisms

(*40 points*) Show the mechanism for the conversion of **α–ketoglutarate** into **succinyl CoA**. The reaction involves…

(1) an initial nucleophilic addition reaction to **α–ketoglutarate** by **TPP ylid**,
(2) decarboxylation,
(3) reaction with **lipoamide**,
(4) elimination of **TPP ylid**, and finally
(5) a transesterification of the **thioester** with **coenzyme A**.

Use the structures below to complete this transformation, plus amino acid residues as acids and bases where appropriate. No additional intermediates are needed aside from the structures provided and in the boxes.

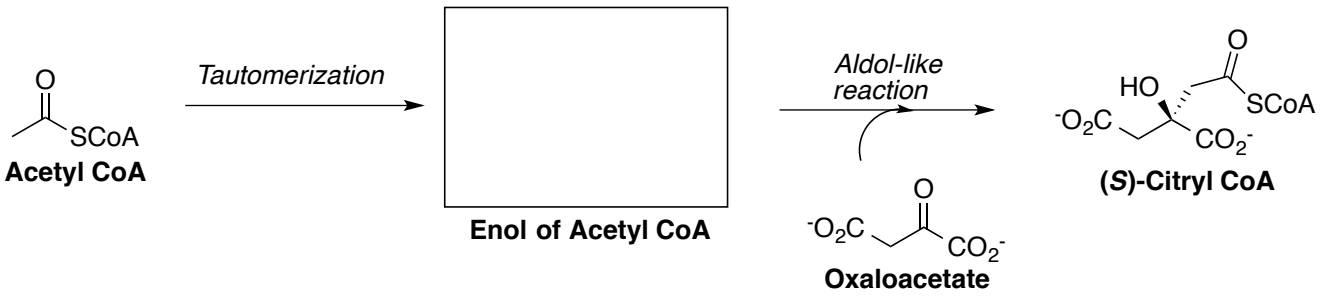


6. Active Site Design

(*35 points*) The citric acid cycle involves the attachment of an incoming **acetyl CoA** molecule to **oxaloacetate**. This occurs by an initial tautomerization of acetyl CoA followed by an aldol-like reaction of the enol of oxaloacetate. Fill in the box with the structure of the enol of acetyl CoA, then complete the mechanisms…

Design separate active sites for each step below with the following criteria in addition to standard mechanistic arrow-pushing to complete each transformation:

- Each substrate (starting material) must be held in place by **at least one H-bond to the peptide backbone**.
- **Amino acid residues must be used as acids and bases**.
  - These residues must start in their natural **physiological state**.
  - You may **use the same residues in both steps, but this is not required**.
- **Redraw the given components within the active site**. Please DO NOT draw the active sites around the structures provided or around the boxed structure.
- Complete each mechanism in one step – **no additional intermediates** aside from the enol.
- Account for **the stereochemistry** in the final product with **a few words and strategic design**.



Active site for tautomerization:

Active site for aldol-like reaction: