UCSC, Binder Name_____

Student ID # _____ Section Day/Time _____

CHEM 109, Organic Chemistry with Biological Applications
EXAM 2B (*250 points*)

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

Page 1 (40)	
Page 2 (40)	
Page 3 (40)	
Page 4/5 (40)	
Page 6 (45)	
Page 7 (45)	
Total	

Use your knowledge of organic chemistry conventions to complete each problem in the proper manner. You have 1.5 hours to complete this exam. Point distributions are given throughout the exam so you can use your time wisely.
Be sure to read each question carefully. You are welcome to ask questions for clarification. Complete either page 4 or 5 (not both). Write your last name and first initial on the top of pages 1-7. Check your exam for 7 pages of content.

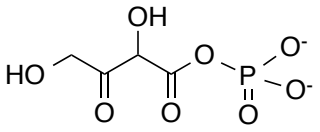
Keep your eyes on your own paper. Electronic devices of any kind are not allowed, including cell phones and calculators. Any student found using any of said devices, or found examining another student's exam, will be promptly removed from the exam room and at minimum will receive a zero on this exam.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

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

1. Fundamentals

(a) (*15 points*) **Functional Groups** – Circle and name the three functional groups in the metabolic intermediate below.



(b) (*7 points*) **Isomers** – Draw the enediol intermediate involved in the isomerization of **DHAP** to **GAP** in glycolysis. No mechanism!

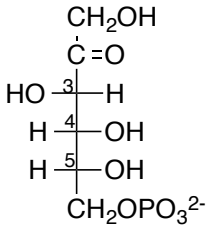
Dihydroxyacetone phosphate (DHAP) **enediol** **Glyceraldehyde-3-phosphate (GAP)**

(c) (*8 points*) **Chirality** – Assign the R/S configuration to the compounds below. Circle your answer.

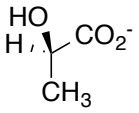
C3: R / S

C4: R / S

C5: R / S



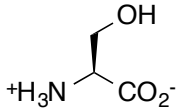
Fructose-6-phosphate (F6P)



Lactate

R / S

(e) (*10 points*) **Indicate (circle) the most acidic proton** on each compound and give the **approximate pKa** on the line provided.



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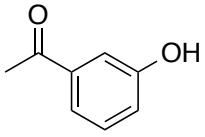

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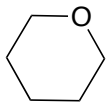
2. Carbohydrates

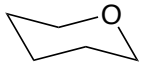
(a) (*15 points*) **Draw one example of each type of carbohydrate listed below**. There may be several correct answers possible. No abbreviations such as R groups.

L-Ketotetrose **D-Aldopentose** **L-Ketohexose**

(b) (*15 points*) Draw the structure of **D-Glucose** as a **Fischer projection** and of **β-D-Glucose** in a **Haworth projection** as well as a **chair conformation**. Stereochemistry is important!!

FISCHER HAWORTH CHAIR





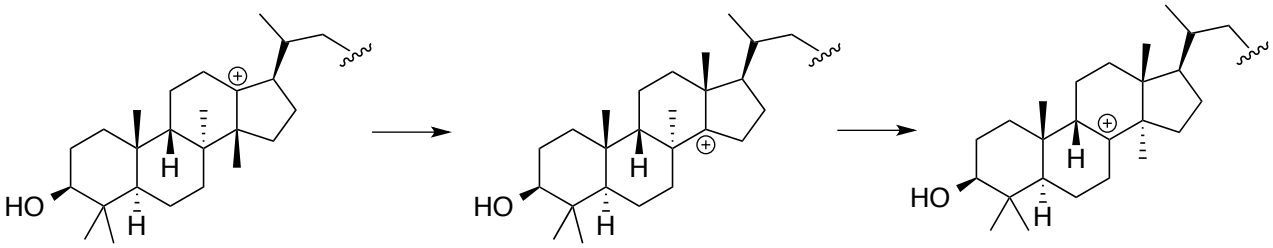
(c) (*10 points*) Draw the Haworth projection for a disaccharide composed of one D-glucopyranose unit linked through α-1,6-glycosidic bond to one β-D-mannopyranose unit (mannose has the free anomeric OH). *Mannose is the C2 epimer of glucose.*

- Draw the structure of β**–D-Mannopyranose** as a Haworth projection.
- Draw the **full structure of the disaccharide** described above using **Haworth projections**.

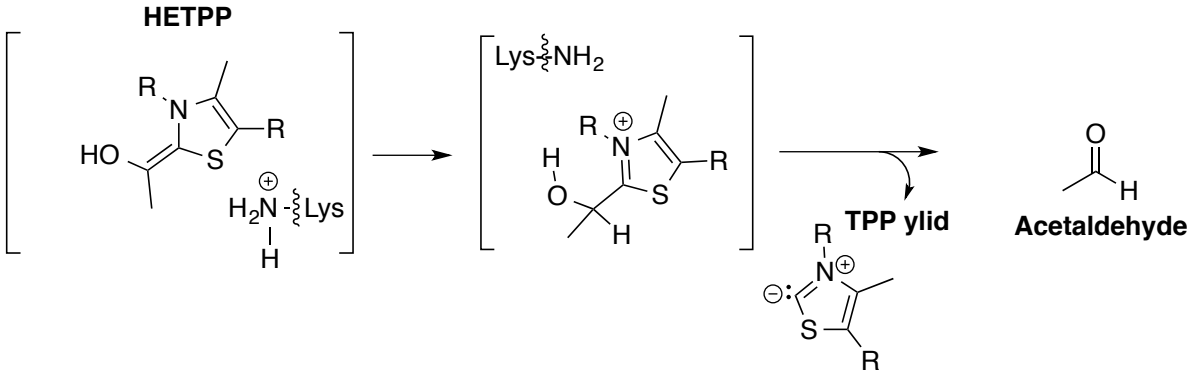
β–D-Mannopyranose Disaccharide:

3. Mechanism Warm-up – pay special attention to the start and end points of arrows

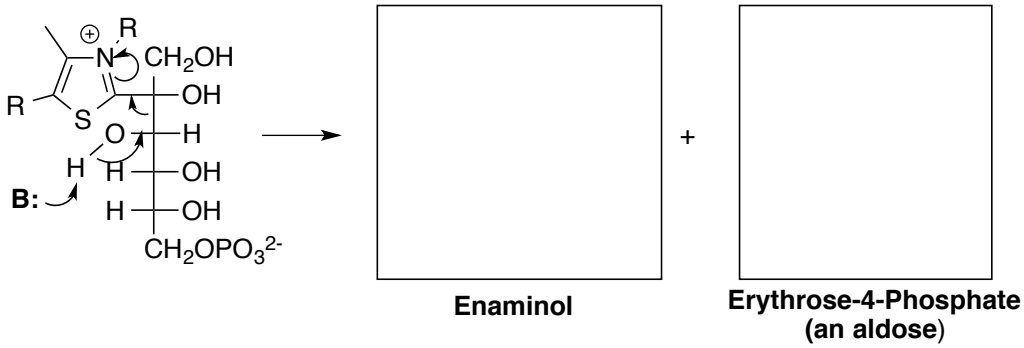
(a) (*6 points*) **Add the arrows** in each step to lead to the next product in the steps below, part of the biosynthesis of **cholesterol**.



(b) (*18 points*) **Add the arrows** to complete both steps in the mechanism below, part of the anaerobic metabolism of pyruvate**.**

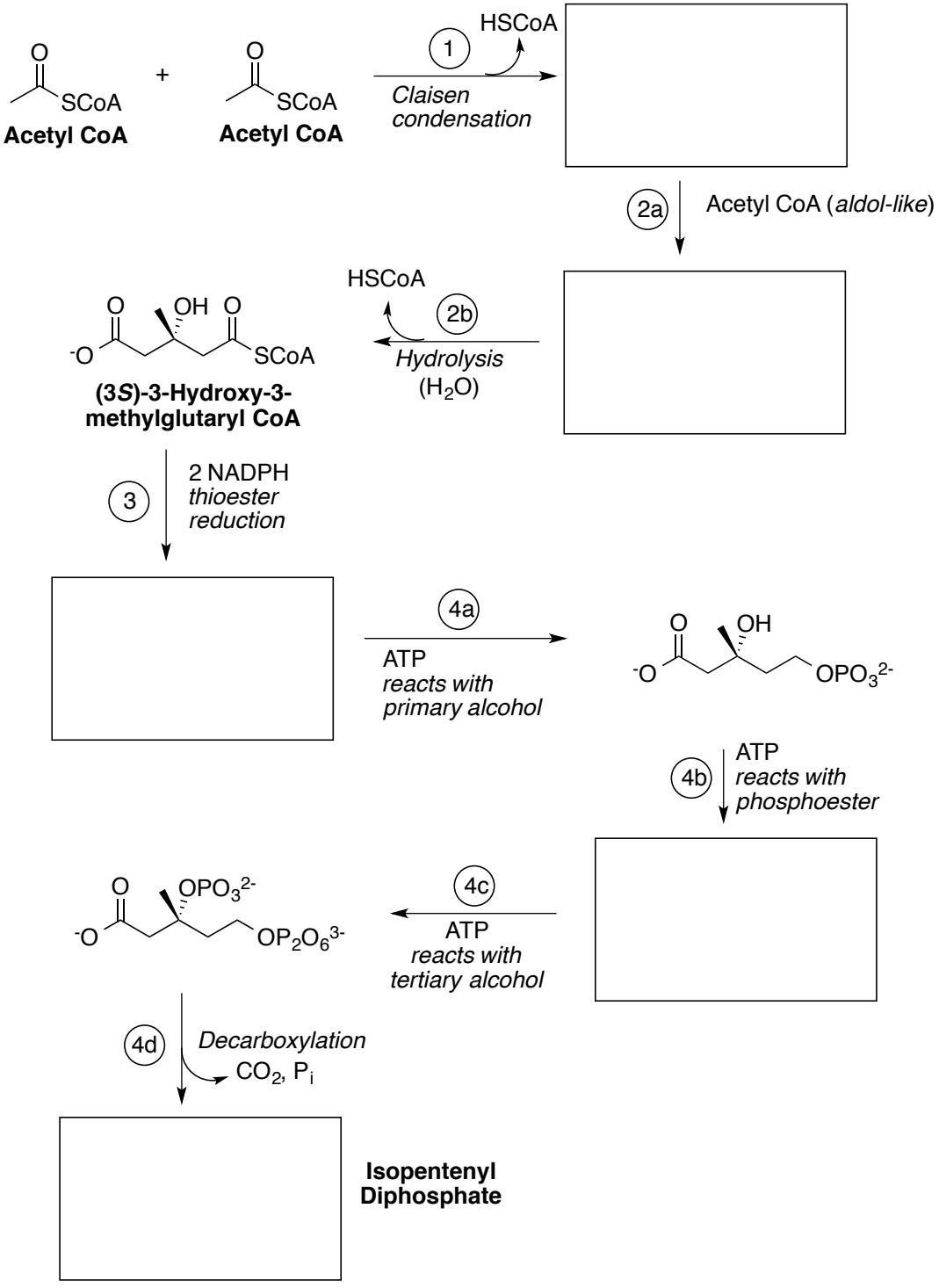


(c) (*24 points*) Follow the arrows and **draw the product**s of the retro-aldol-like reaction in gluceogenesis.



4. (*40 points*) **Fill in the Boxes on *either Page 4 or 5*. Draw a large X over the problem to skip, otherwise page 4 will be graded, even if it's blank!**

Draw each intermediate in the synthesis of **isopentenyl diphosphate (IPP)**.
No arrow pushing is necessary.

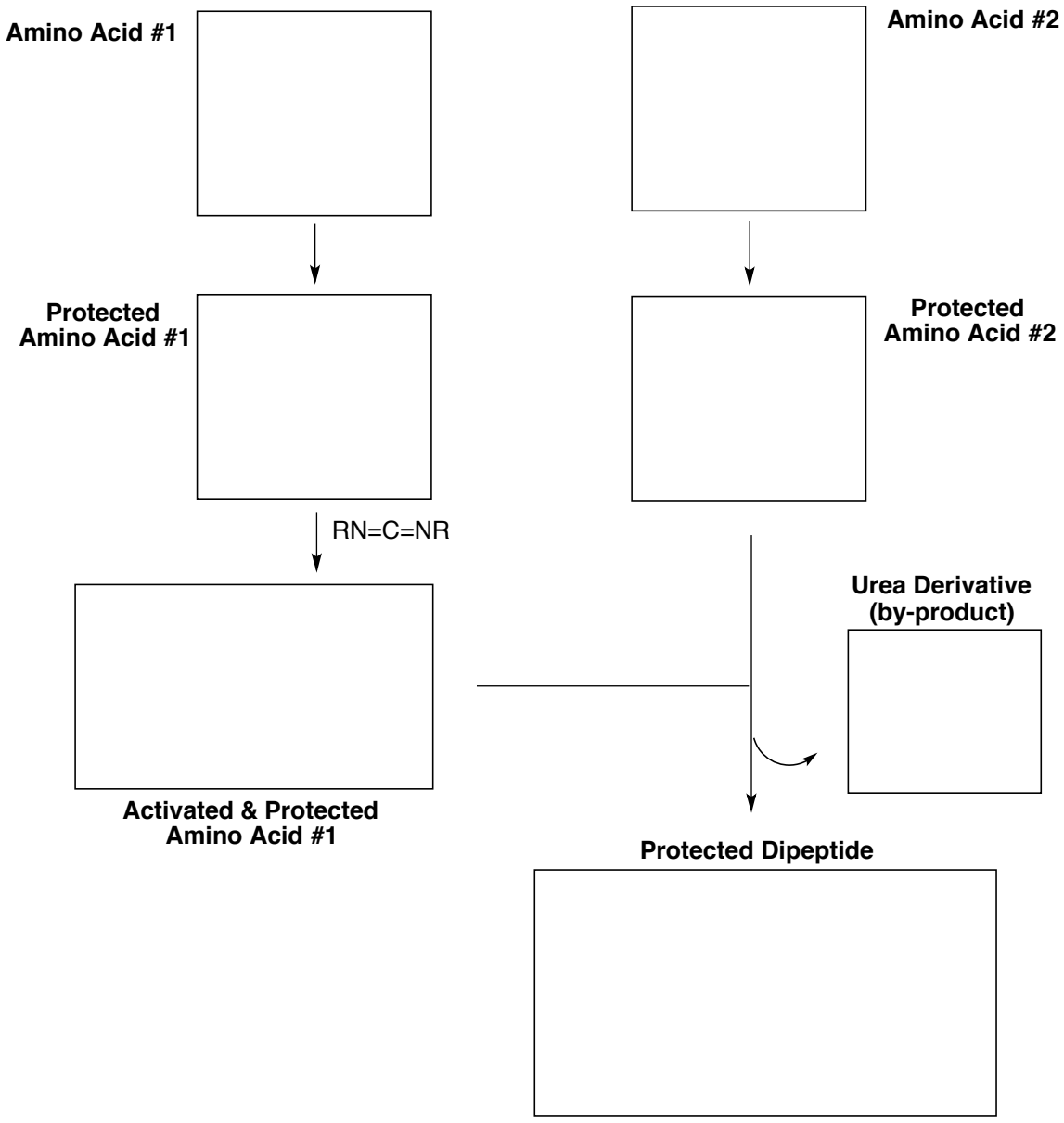


CHOOSE EITHER PAGE 4 OR 5

5. (*40 points*) **Fill in the boxes on *either Page 4 or 5*. Draw a large X over the problem to skip, otherwise page 4 will be graded, even if it's blank!** No arrow-pushing necessary, only structures in boxes graded.

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 is of the 6 letters without an amino acid abbreviation, move to the next letter in the alphabet.

Protect each amino acid appropriately (reagents not necessary), then **activate the acid** of one with the carbodiimide coupling agent (**RN=C=R**). Include stereochemistry at each step. Protect amino acid side chains with "PG" if necessary. 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.**



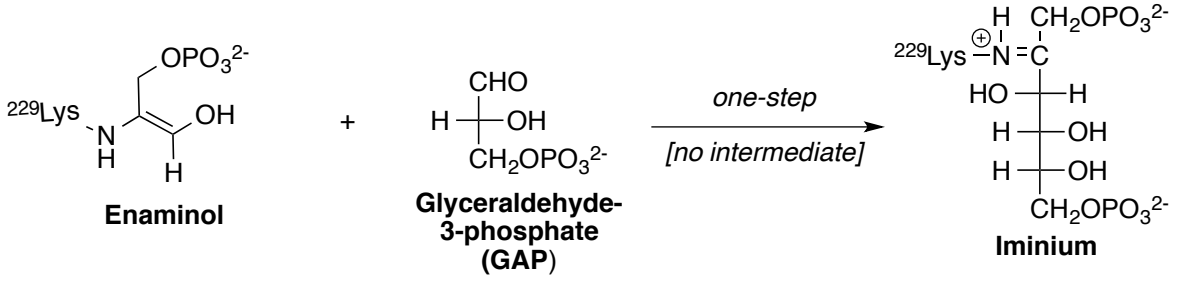
CHOOSE EITHER PAGE 4 OR 5

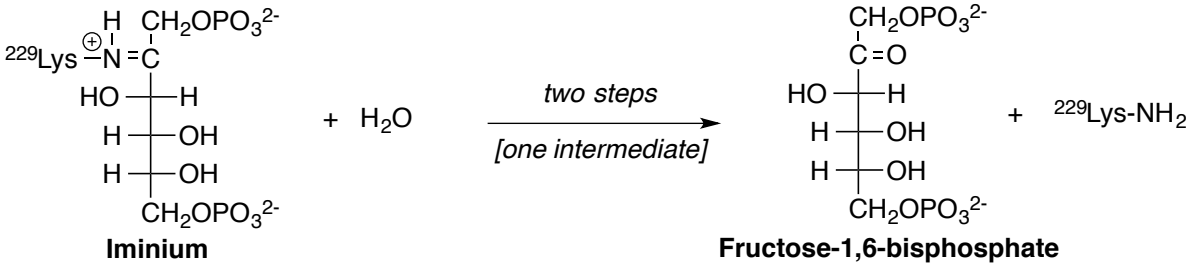
6. (*45 points*) **Reaction Mechanisms**

In gluceogenesis, the reverse of glycolysis, Dihydroxyacetone phosphate (DHAP) is covalently bound to the active site through a lysine residue to form the **enaminol** shown below. **Glyceraldehyde-3-phosphate (GAP)** joins to this **enaminol** by an aldol-like reaction to form an i**minium** intermediate followed by hydrolysis to give **fructose 1,6-bisphosphate**.

Use the materials below along with **amino acid residues as acids and bases** to propose the full arrow-pushing mechanism of the formation of the product below within the enzyme active site. **No stabilizing factors such as hydrogen bonds are necessary on this page.** Carry out each mechanism in the number of steps indicated over the arrow. Feel free to abbreviate parts of structures not directly involved in the mechanism.

Redraw the components – please do not draw any arrows to or from the structures provided!





7. (*45 points*) **Active Site Design**

The reaction of a **fatty acyl CoA** with a **2-monoacylglycerol** to give a **1,2-diacylglycerol** is catalyzed by *monoacylglycerol acyltransferase* and proceeds by two nucleophilic acyl substitution mechanisms. **Fatty acyl CoA** first undergoes a reaction with a cysteine –SH group on the enzyme to give an enzyme-bound fatty acyl intermediate, which then reacts with **2-monoacylglycerol** and the product is released by the enzyme.

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

- The substrate and intermediate must each be held in place by **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 must **re-use the same residues in both steps**.
- **Redraw the given components within the active site**. Please DO NOT draw the active sites around the structures provided!
- Complete each transformation in two steps with one intermediate.