

Circle one: I wish to have my exam  
put in the rack.

I wish to pick up  
my exam.

Printed Name Answer Key  
(Please print clearly)

Signature \_\_\_\_\_

**CHEMISTRY 262**

Final  
200 Points

May 8, 2013  
8:00-10:00 AM

This exam has 9 problems on pages 2 through 11.

**RULES**

1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam, raise your hand.

1. \_\_\_\_\_

6. \_\_\_\_\_

2. \_\_\_\_\_

7. \_\_\_\_\_

3. \_\_\_\_\_

8. \_\_\_\_\_

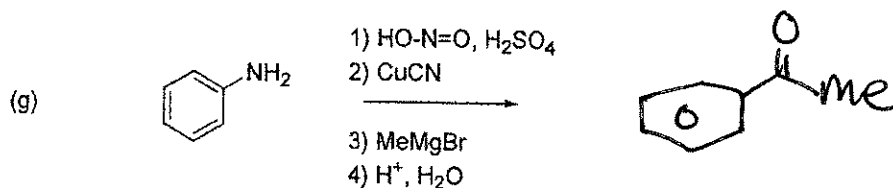
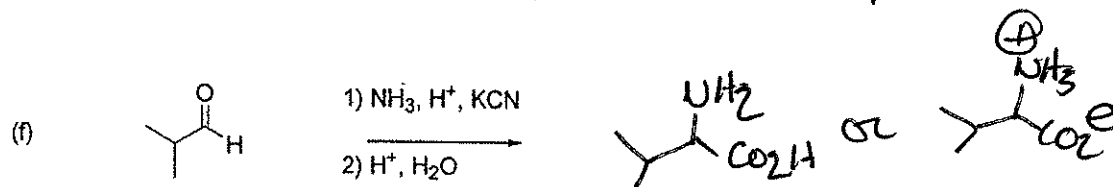
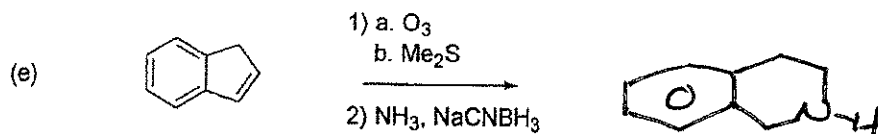
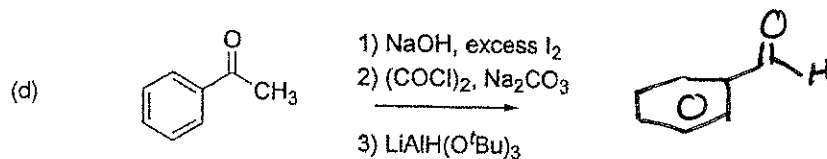
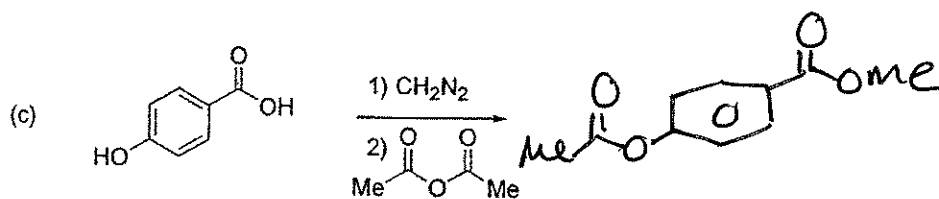
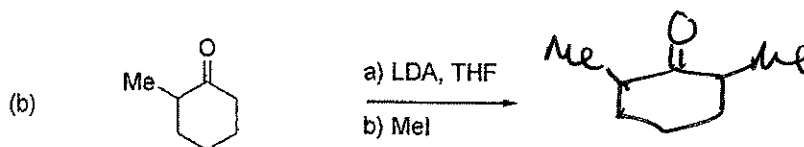
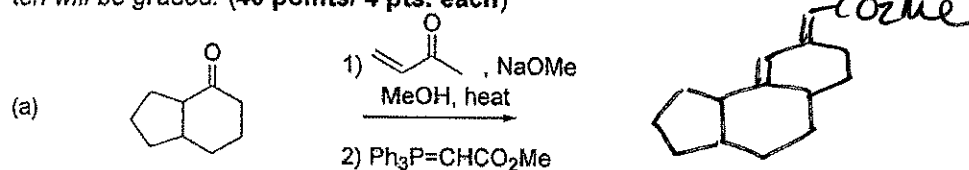
4. \_\_\_\_\_

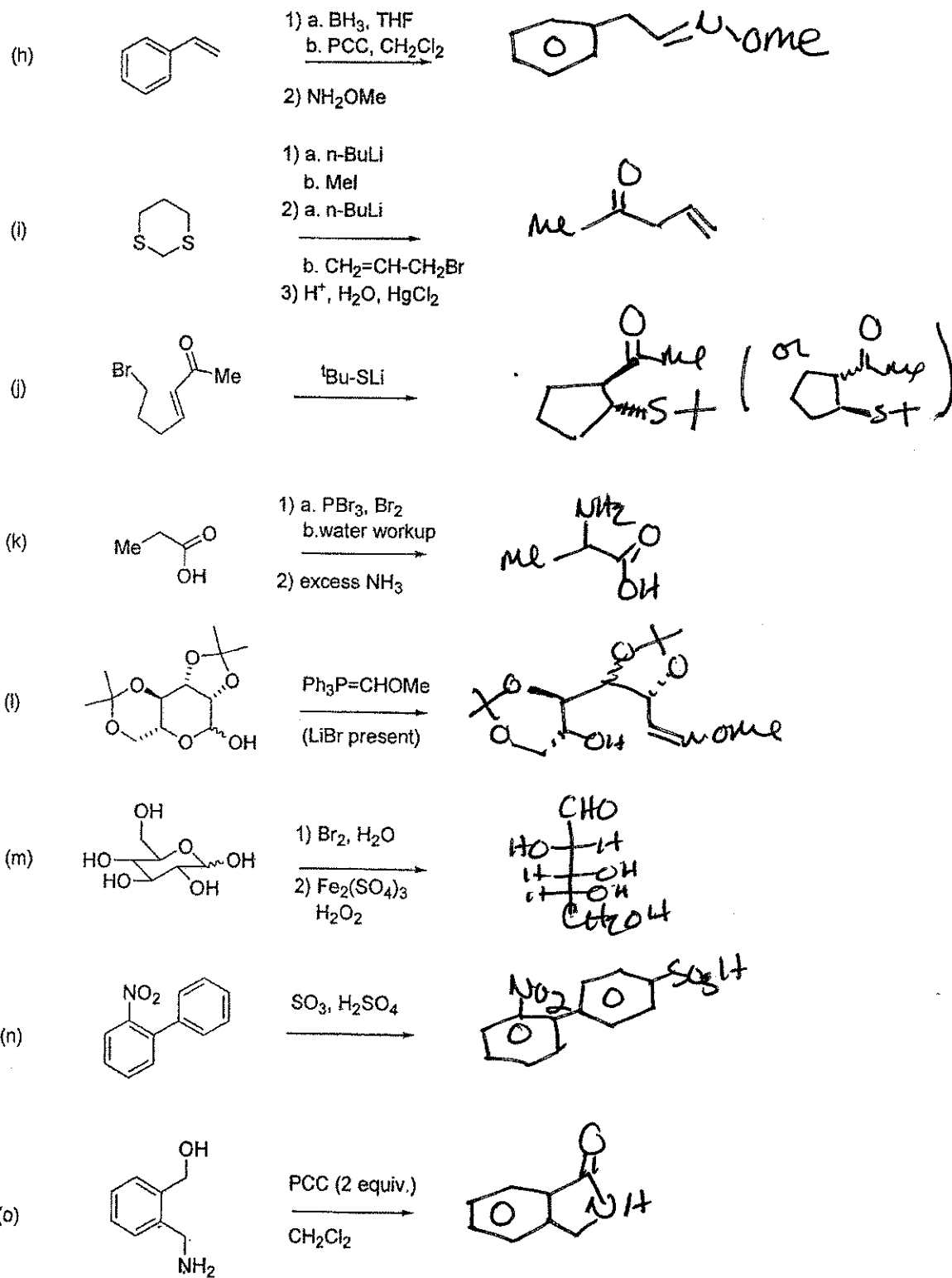
9. \_\_\_\_\_

5. \_\_\_\_\_

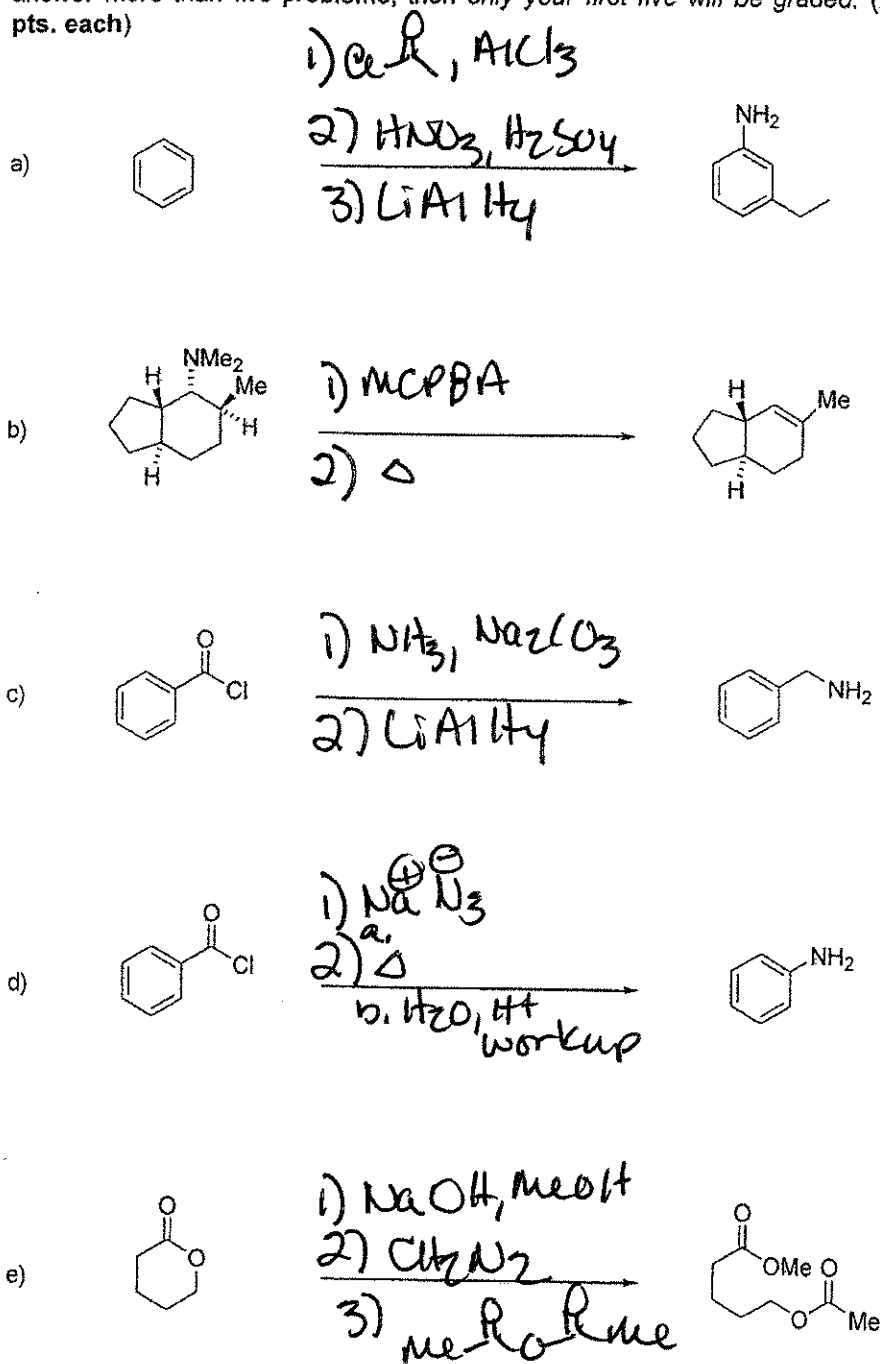
TOTAL: /200

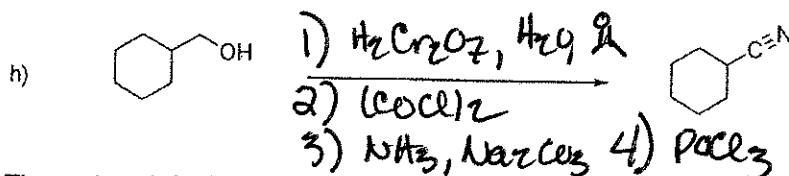
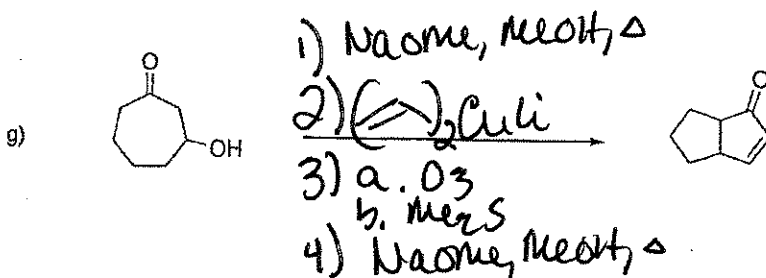
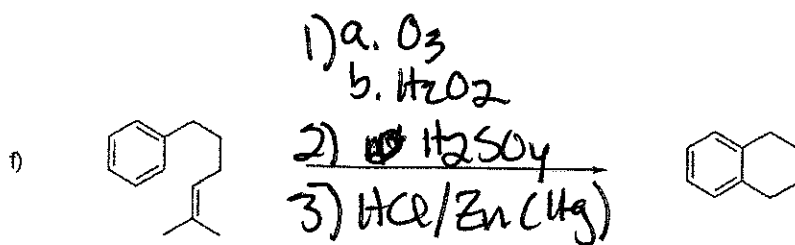
1. Predict the major product or products that you would expect to be formed in ten of the following fifteen reactions. If you feel that no reaction will occur, then answer no reaction. Be sure to answer **only** ten problems. If you answer more than ten, then *only your first ten will be graded*. (40 points/ 4 pts. each)



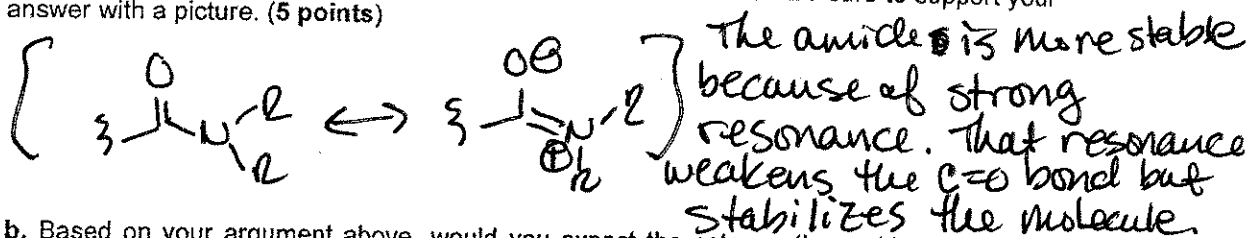


2. Fill in the reagents needed for accomplishing five of the eight following transformations. More than one step may be required. Be sure to answer **only** five problems. If you answer more than five problems, then *only your first five will be graded*. (20 points/ 4 pts. each)

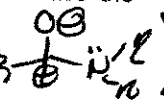




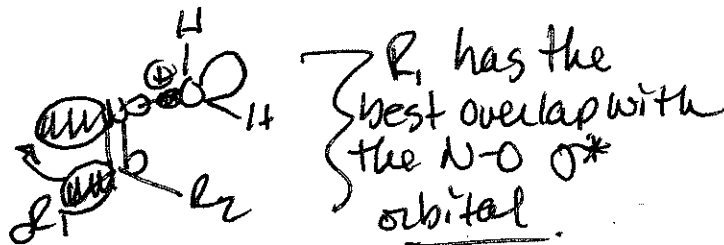
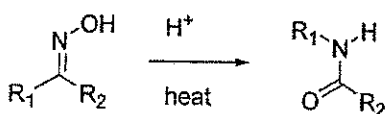
3. a. The carbonyl C=O stretch of an amide is at  $1650\text{ cm}^{-1}$  and the carbonyl C=O stretch of an ester is  $1740\text{ cm}^{-1}$ , an observation that indicates that the carbonyl of an amide is weaker than that of an ester. So why are amides more stable than esters? Be sure to support your answer with a picture. (5 points)



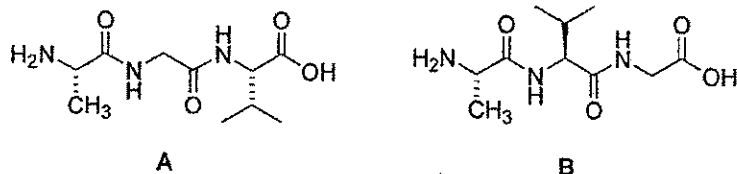
- b. Based on your argument above, would you expect the ester or the amide to have the most intense stretch in an IR? Why? (5 points)

The amide. The greater the dipole () the more the bond can couple to the IR light.

- c. Amide stability can be the driving force for reactions like the Beckmann rearrangement illustrated below. In this reaction,  $R_1$  migrates in preference to  $R_2$ . Why? Please note that you do not need to write a mechanism for the reaction. Just explain the initial migration step and support your answer with an appropriate drawing. (5 points)



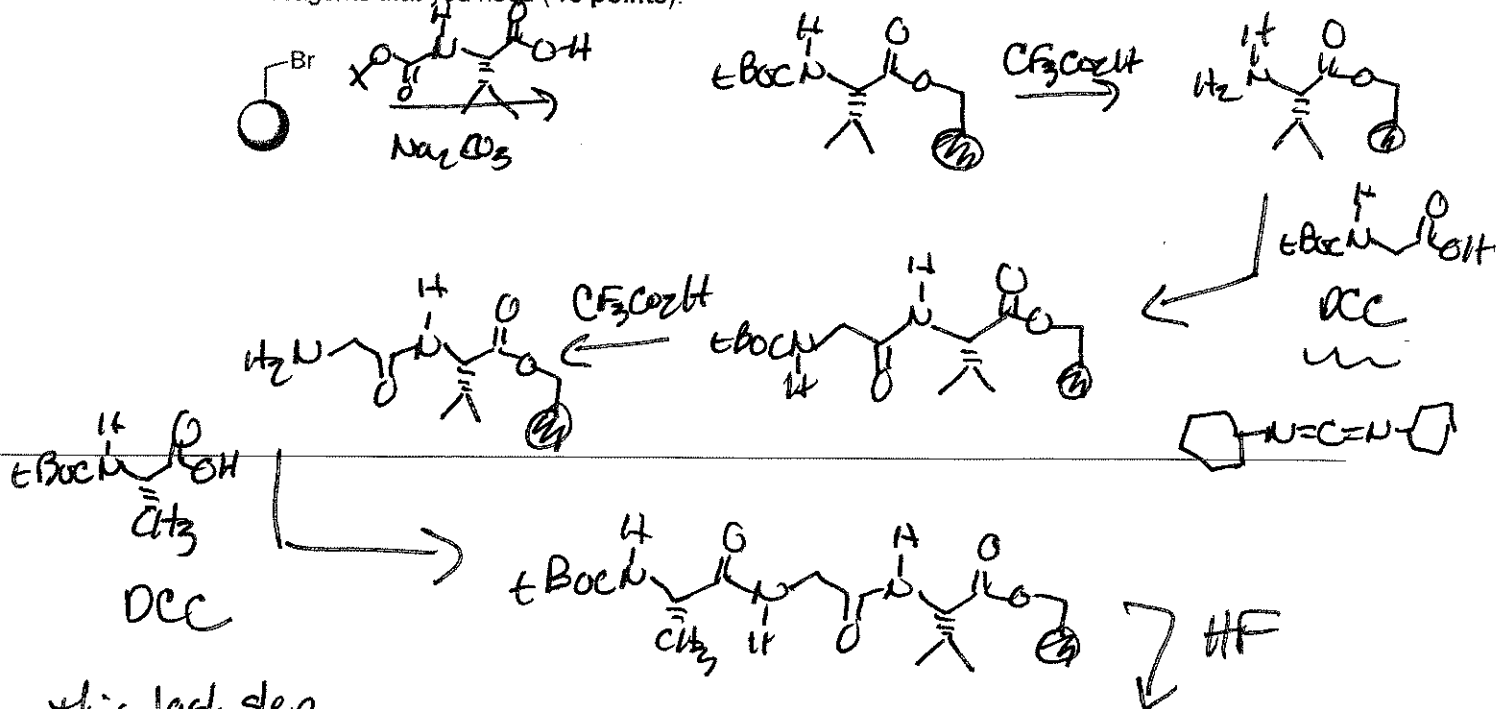
4. Several years ago a student made the pair of peptides shown below.



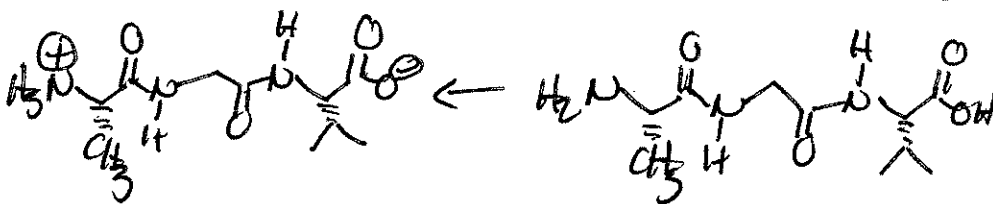
a. Unfortunately, the labels on the vials got old and fell off. How would you use a mass spectrometer to tell the difference between the two peptides? (10 points)

Look for fragments that contain the N-terminal amine. A will lead to  $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{C}^+\text{O}$  for example while B leads to  $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{C}^+\text{O}-\text{CH}(\text{CH}_2\text{CH}(\text{CH}_3)_2)$ . There are other options. You just need to show stable cations that have different masses.

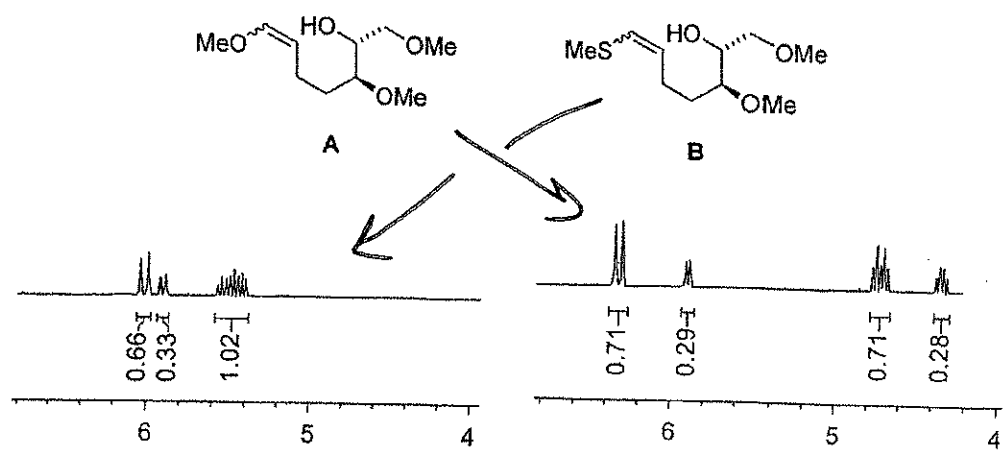
b. If you had to resynthesize peptide A, then how would you do it starting from the substrate below (the grey dot is Merrifield's resin) and any amino acid precursors and reagents that you need (15 points).



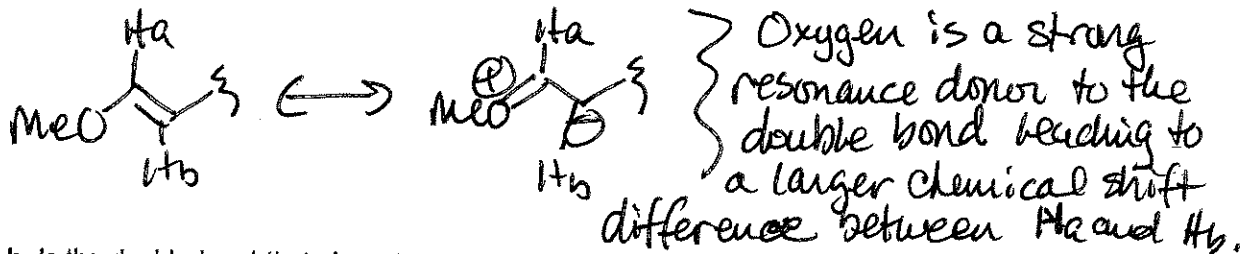
this last step is just a reminder that amino acids are zwitterions at  $\text{pH} \approx 7$ .



5. In the following scheme, an NMR spectrum is shown for each of the two molecules illustrated.



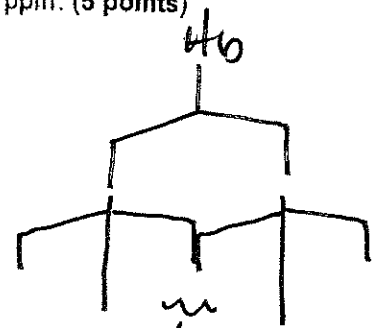
a. Draw arrows on the Scheme above that indicate which spectrum goes with which molecule. How do you know? Please support your answer with a picture. (5 points)



b. Is the double bond that gives rise to either spectrum mostly present cis or trans? Please note that for these spectra the integrations are given as numbers (0.71, 0.29, etc.). Explain how you made your assignment? (5 points)

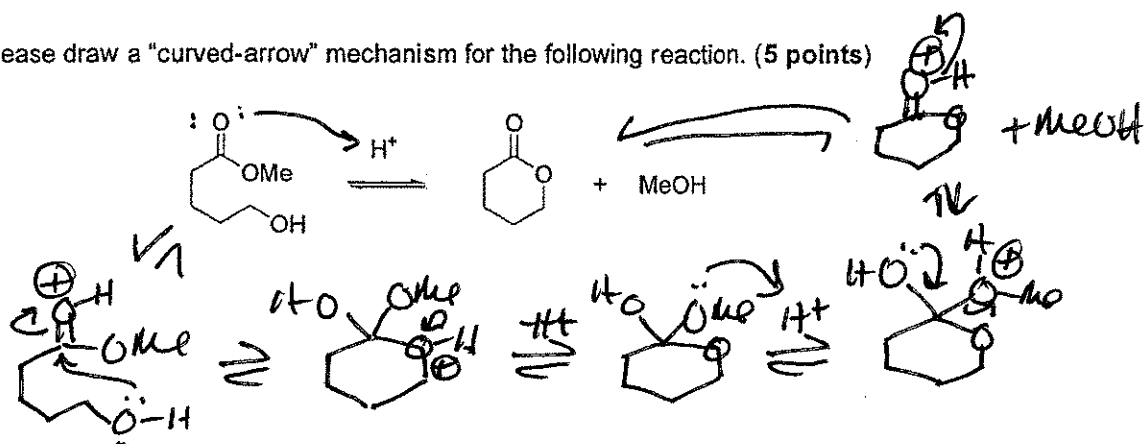
Trans. Note the larger coupling constant for the signal with the largest integration (6.4 ppm vs 5.8 ppm for example)

c. Draw a splitting tree that explains the pattern found in the NMR on the right at approximately 4.8 ppm. (5 points)

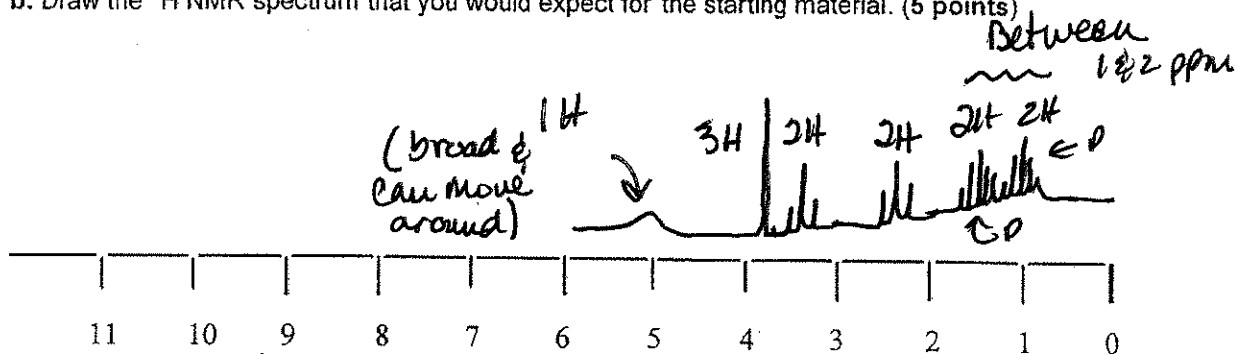


These two may overlap. It is hard to see. Either way, the pattern is a dd.

6. a. Please draw a "curved-arrow" mechanism for the following reaction. (5 points)



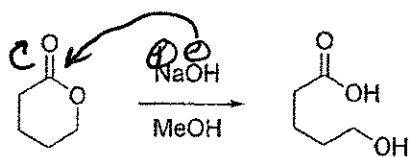
- b. Draw the  $^1H$  NMR spectrum that you would expect for the starting material. (5 points)



- c. How can you use  $^1H$  NMR to monitor the reaction in part a? Please identify one change in the spectrum that you could monitor other than the loss of the alcohol proton since OH protons in an NMR can often be difficult to assign. (5 points)

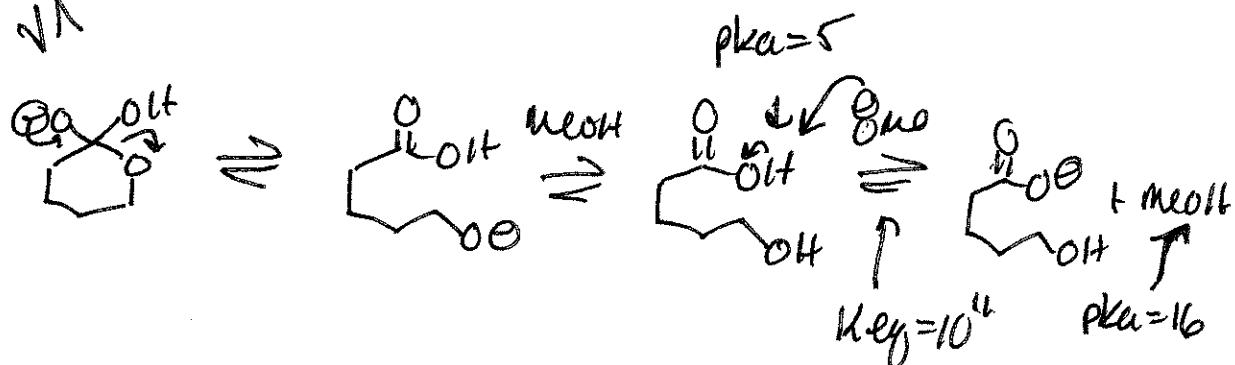
The triplet at 3.5 ppm would move downfield (greater  $\delta$ ) to approximately 4.2 ppm as the starting alcohol becomes an ester.

- d. The equilibrium shown in part a is favored thermodynamically (entropy). In spite of this observation, the reaction illustrated below does proceed nicely to the product even when MeOH is used as solvent. Why? (5 points)



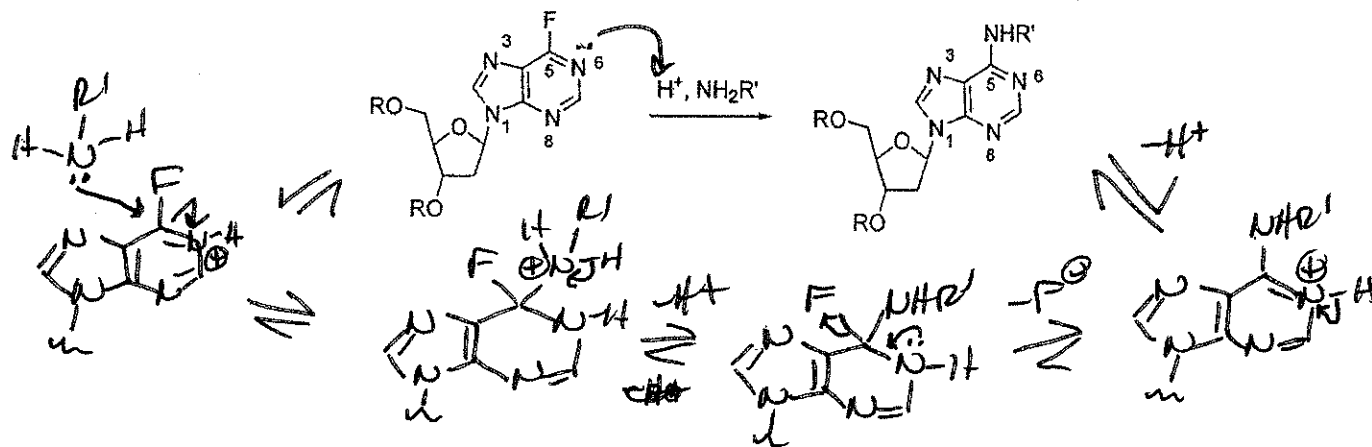
Deprotonation of the acetyl provides a strong driving force for the reaction.

V/A

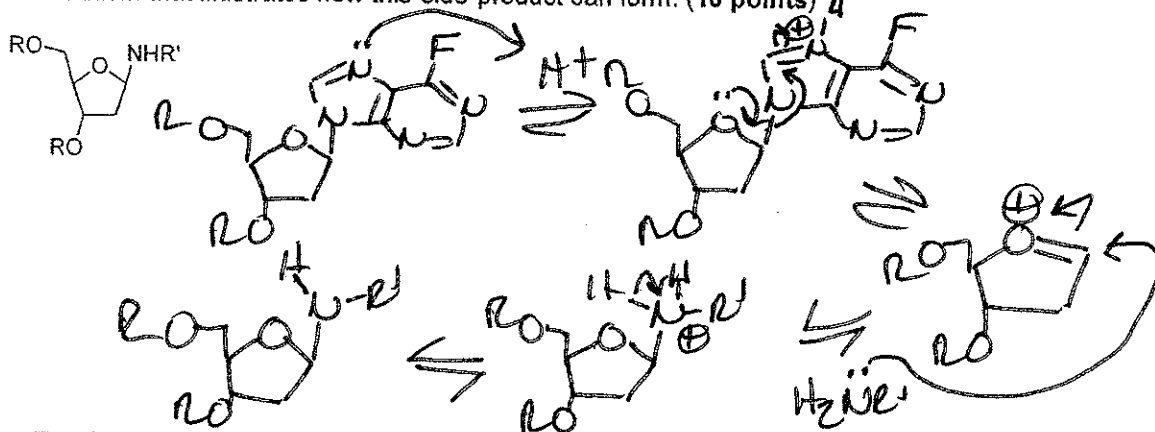




7. a. Write a "curved-arrow" mechanism for the following reaction. (10 points)



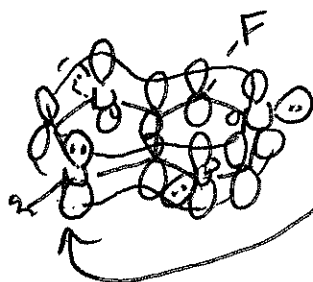
b. The reaction can lead to the side-product illustrate below. Write a "curved-arrow" mechanism that illustrates how this side-product can form. (10 points)



c. The fluoride in the starting material was in place of a potential Cl-leaving group in order to minimize the side-reaction. The idea was to use the more electronegative fluorine in order to make C5 in the starting material more electron poor and hence more susceptible to nucleophilic attack. How would you use  $^{13}\text{C}$  NMR to determine if this idea was accurate? (5 points)

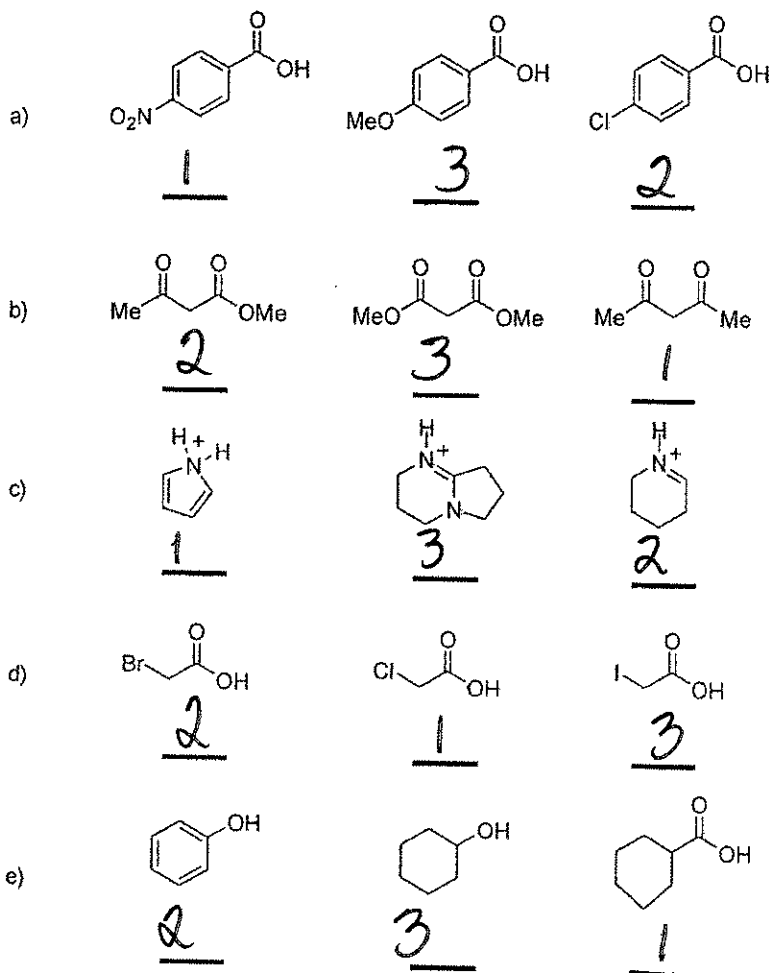
The more e $^-$ -poor C5 is the further downfield (larger  $\delta$ ) it will be in the  $^{13}\text{C}$ -NMR. If it is more downfield in the F-derivative, then the proposal is correct.

d. Protonation of the starting material can happen readily at N3, N6, and N8 but not N1. Why? (5 points)

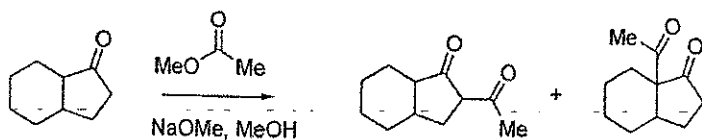


The lone-pair electrons on N1 are part of the aromatic ring.

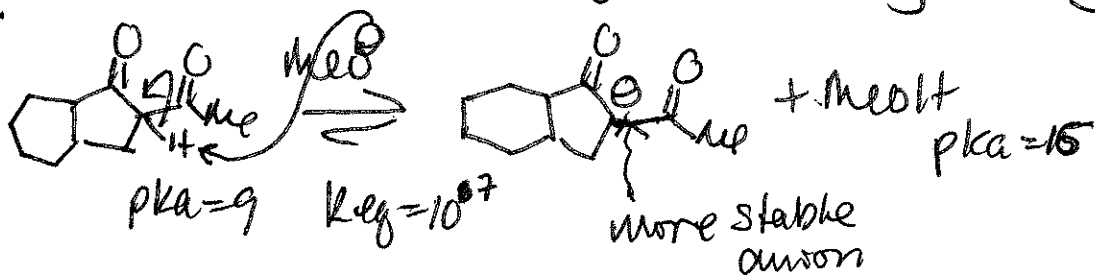
8. Rank the following molecules in terms of acidity from the most acidic (1) to the least acidic proton (3). (15 points/ 3 pts each)



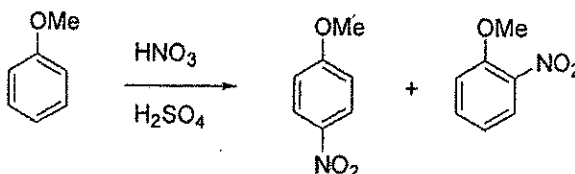
9. a. In the reaction below, product 1 is formed. Is this an example of kinetic or thermodynamic control? Explain. (5 points)



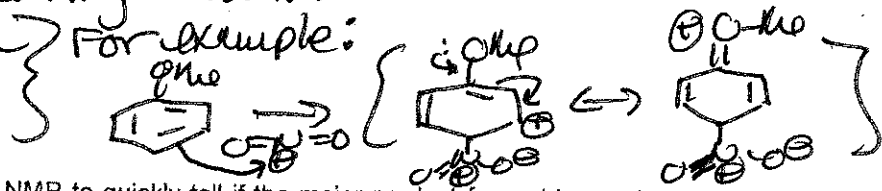
Thermodynamic. The reaction is reversible and forms product 1 because of the following driving force.



b. Why does the reaction below lead to mainly ortho and para products? (5 points)



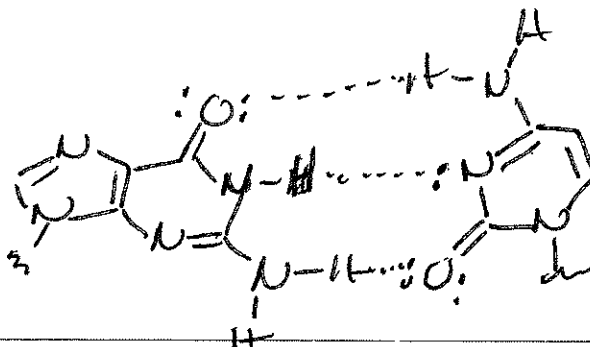
The OMe group is electron donating and stabilizes the cation in the ring when that attack occurs at either the ortho or para position. For example:



c. How could you use a  $^{13}\text{C}$  NMR to quickly tell if the major product formed in part b is the para or ortho product. (5 points)

The p-product would show 5 lines in a fully decoupled  $^{13}\text{C}$ -NMR. The m-product would show 7.

d. Since I asked you to memorize your DNA bases, please draw the structure for a GC base pair. Please show the bases and the hydrogen bonds. You do not have to show the sugars. (5 points)



# PERIODIC TABLE OF THE ELEMENTS

TABLE 11-4 Isotopic composition of some common elements															
Element	M <sup>+</sup>	M+1	M+2												
H	1.0079														
3	4														
Li	Be														
6.941	9.0122														
11	12														
Na	Mg														
22.990	24.305														
19	20														
K	Ca														
39.098	40.078														
37	38														
Rb	Sr														
85.468	87.62														
55	56														
Cs	Ba														
132.91	137.33														
87	88														
Fr	Ra														
(223)	(226)														
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.90	131.29
71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
174.97	178.49	180.95	183.85	186.21	190.2	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Lr	Unq	Unp	Unh	Uns	Uno	Une	Uun	Uuu	Uub	Uuc	Uud	Uue	Uuf	Uug	Uuh
(260)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(273)	(274)	(275)	(276)	(277)	(278)	(279)

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
138.9	140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0	180.9	183.85	186.21	190.2	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)	(223)	
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Unq	Unp	Unh	Uns	Uno	Une	Uun	Uuu	Uub	Uuc	Uud	Uue	Uuf	Uug	Uuh	
(227)	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(273)	(274)	(275)	(276)	(277)	(278)	(279)	(280)

**TABLE 11-3**  
"Exact" Masses of Common Isotopes

Isotope	Atomic Mass (amu)
<sup>12</sup> C	12.000000
<sup>1</sup> H	1.007825
<sup>16</sup> O	15.994914
<sup>14</sup> N	14.003050