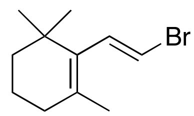
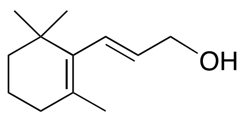
 Name _Key___________________________

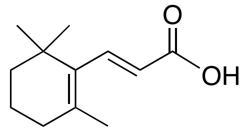
I. (4 points) Arrange the following four compounds in order of their R_f values when analyzed by thin-layer chromatography (TLC) on silica gel-coated plates using CH_2Cl_2 as the developing solvent. No partial credit is given to this question.



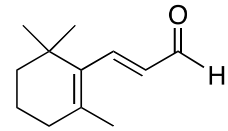
1



2



3

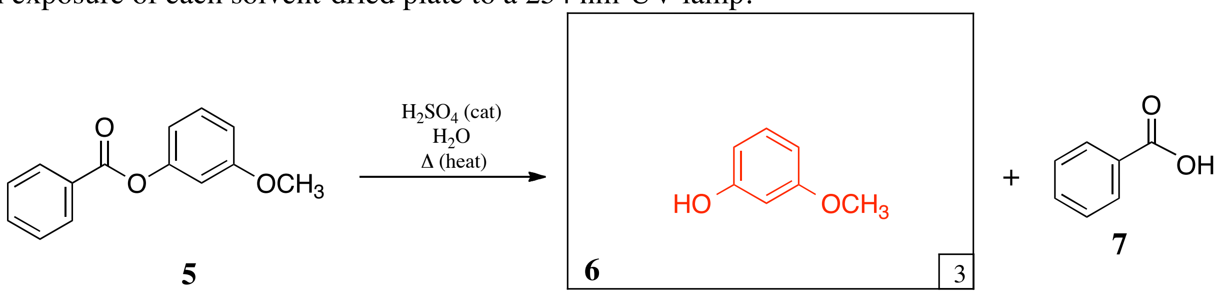


4

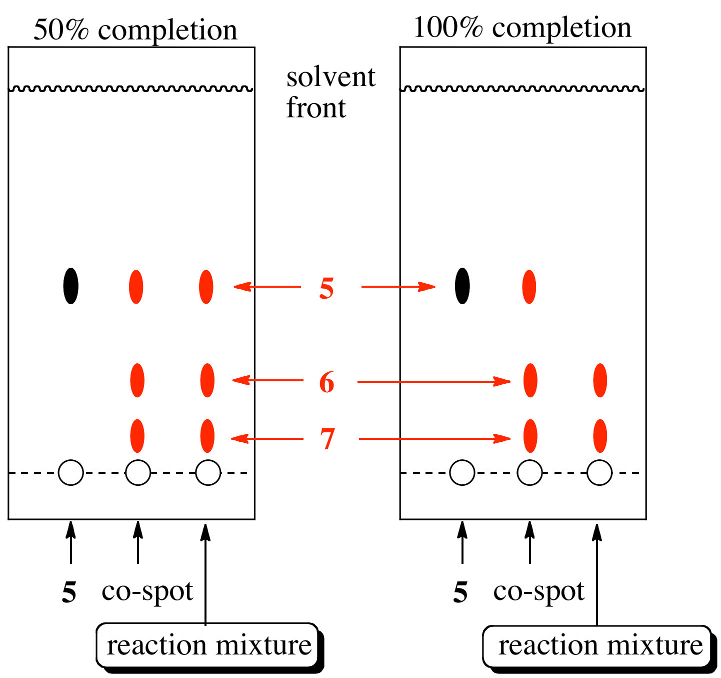
Answer: 3 < 2 < 4 < 1

lowest R_f highest R_f

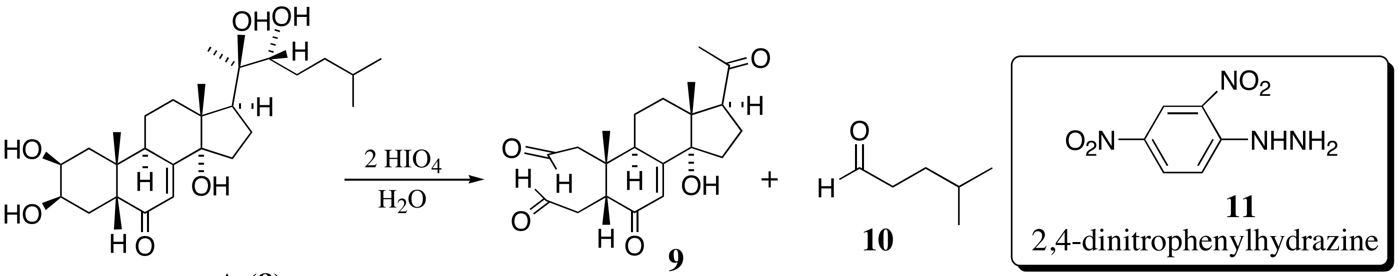
II. (9 points) Silica gel thin layer chromatography (TLC) is often used to monitor the progress of an organic reaction. For the following ester hydrolysis reaction, a solvent system is selected to give the starting material an R_f value of about 0.5. (1) Provide in the box below the structure of the expected product **6**. (2) Fill in the spots that would be expected when the reaction is 50% compete and 100% complete, each after acidic work-up. Make sure to assign each spot you draw to the corresponding compound number (**5**, **6**, or **7**). Consider only the compounds that can be visualized as a spot on TLC upon exposure of each solvent-dried plate to a 254 nm-UV lamp.



On each TLC plate, a student has placed a sample of the starting material (**5**) as a reference on the left of the plate, a spot of the reaction mixture (after acidic work-up) on the right, and a co-spot in the center of each. Co-spotting is where some of **5** and some of the reaction mixture are spotted together in order to make better comparisons.



III. (13 points) Ponasterone A (**8**) is one of the insect molting hormones. As part of my undergraduate research (last century!), I was asked to determine the structure of this hormone. To this end, 46.4 mg of ponasterone A was treated with 2 mol equivalents of HIO_4 to provide a mixture of two products, dialdehyde diketone **9** and aldehyde **10**. The crude reaction mixture was then subjected to steam distillation by which only one of these two products was distilled over together with water. This distillate mixture was dripped directly into the aqueous acidic solution containing excess 2,4-dinitrophenylhydrazine (**11**, 2,4-DNP) to immediately produce 21 mg of the yellow-colored 2,4-DNP derivative.



ponasterone A (**8**) $C_{27}H_{44}O_6$ Mw 464 | $C_{21}H_{28}O_5$ Mw 360

Provide the answer to each of the following questions in the box given.

(1) How many mgs of HIO_4 was used in this experiment? The atomic weight of iodine is 127. Show your work.

46.4 mg of **8** ≡ 46.4 mg / (464 mg/mmol) = 0.1 mmol

2 x 0.1 mmol x (formula weight of HIO_4) = 0.2 mmol x 192 mg/mmol = 38.4 mg

Answer: 38.4 mg | 3

(2) Draw the structure of the 2,4-DNP derivative formed in this experiment.

4

(3) What is the theoretical yield of the 2,4-DNP derivative? Show your work.

0.1 mmol of **8** ⟹ 0.1 mmol of the 2,4-DNP derivative of **10**

Mw of the derivative is 280 mg/mmol

0.1 mmol x 280 mg/mmol = 28 mg

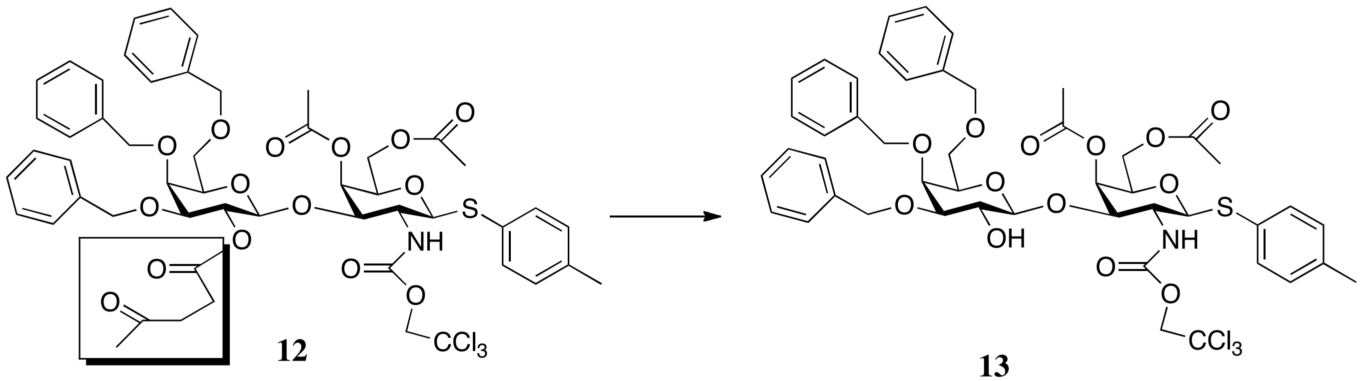
Answer: 28 mg | 3

(4) What is the percent chemical yield of the 2,4-DNP in this experiment? Show your work.

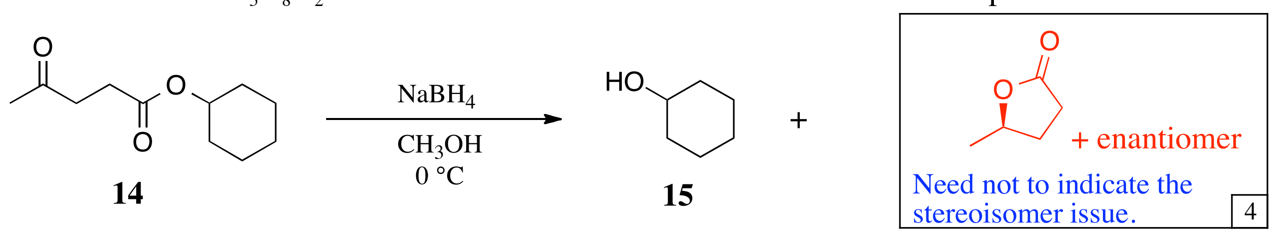
(21 mg / 28 mg) x 100 = 75%

Answer: 75% | 3

IV. (12 points) A levulinyl group [$CH_3C(=O)CH_2CH_2C(=O)$-] is an extremely versatile hydroxyl-protecting group. A team of scientists at The Scripps Research Institute in La Jolla, CA, reported that the levulinate group (indicated by a rectangular box) in differentially protected disaccharide **12** can be deprotected selectively to provide alcohol **13** in quantitative yield [*Proc. Natl. Acad. Sci., USA* **2003**, *100*, 797].

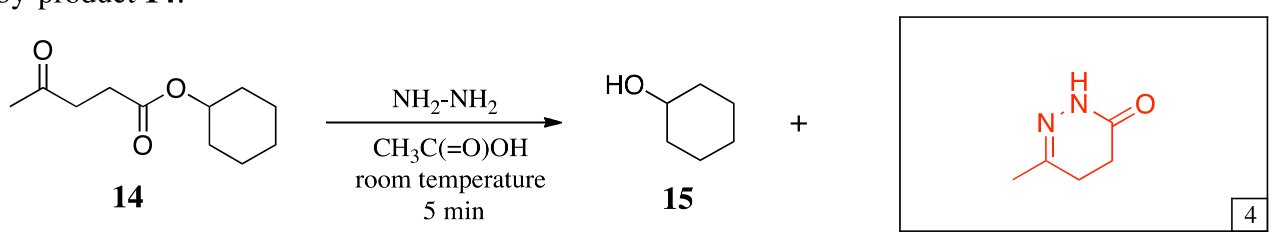


(1) The methods used to achieve this selective deprotection take advantage of the difference in electrophilicity between aldehyde/ketone and ester carbonyl groups. Among these methods known, the use of $NaBH_4$ is most convenient. In the reaction shown below, the levulinate ester of cyclohexanol, **14**, is treated with $NaBH_4$ to afford cyclohexanol (**15**). The by-product (**16**) from this reaction has the molecular formula of $C_5H_8O_2$. Provide in the box below the structure of this compound.



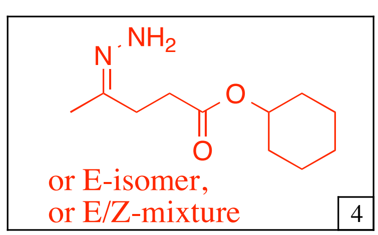
16 ($C_5H_8O_2$)

(2) When a levulinate such as **14** is treated with hydrazine (NH_2-NH_2) in acetic acid, the levulinate-protected alcohol undergoes facile deprotection (see below). Draw in the box provided the structure of the by-product **14**.



17 ($C_5H_8N_2O$)

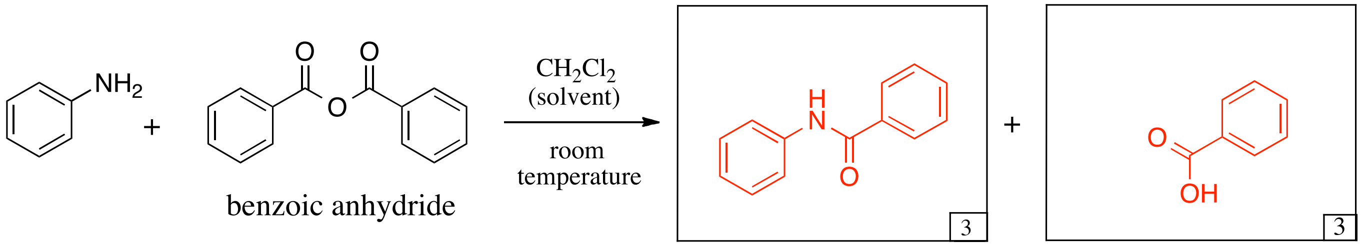
(3) The reaction of levulinate **14** with hydrazine first produces its hydrazone derivative, which further undergoes an intramolecular reaction to produce **17**. Draw in the box below the structure of this hydrazone derivative of **14**.



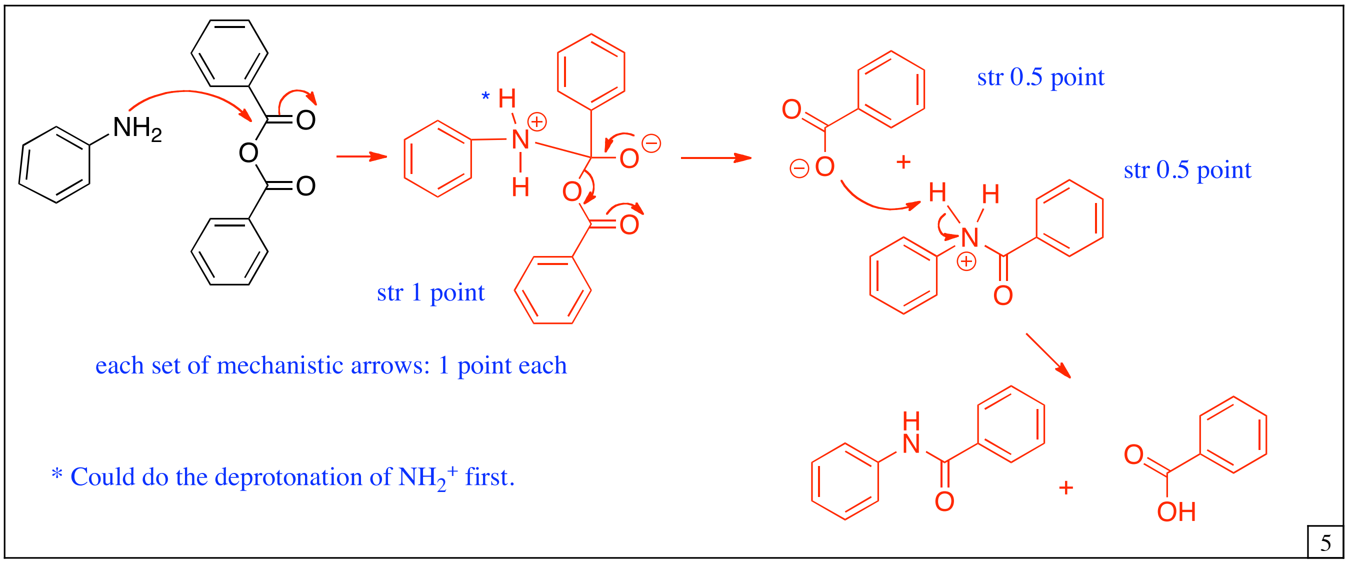
 Name _____Key________________

V. (16 points) For the following reaction, provide in the boxes below the structure of the expected product and a step by step mechanism through the use of the curved arrow convention.

(1)



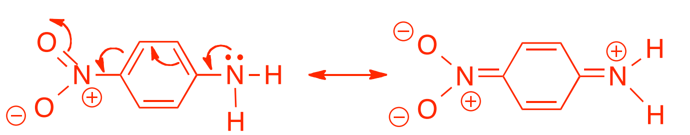
(2) Reaction mechanism:



(3) Would you expect the benzoylation reaction of 4-nitroaniline using benzoic anhydride to be faster or slower compared with that of aniline? Explain your answer. If any resonance structure(s) of 4-nitroaniline are involved in your answer, make sure to clearly draw pertinent the resonance structure.

Faster or slower (circle one that applies) (2 points)

Explanation (3 points):



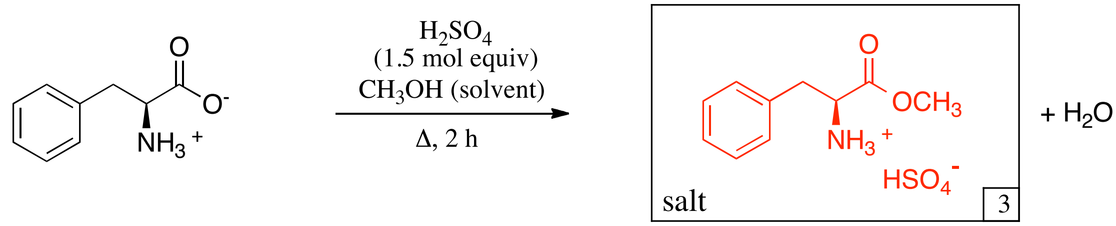
Due to a highly significant contribution of the resonance structure shown above on the right, the NH_2 lone-pair electrons are delocalized throughout the benzene ring and the nitro group, thus significantly decreasing their basicity and nucleophilicity.

5

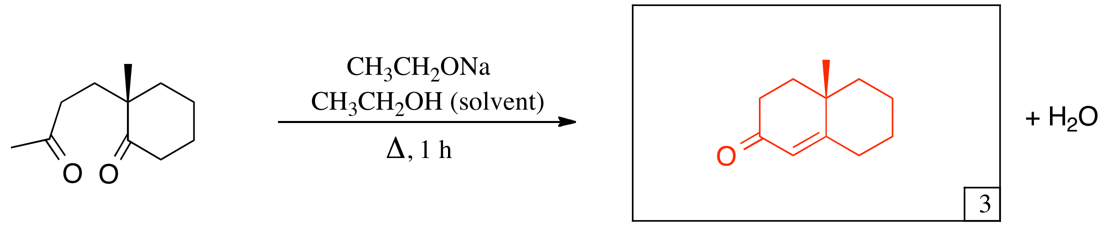
 Name______Key__________________

VI. (9 points) For each of the following synthetic reactions, draw the structure of the expected organic product in the box provided.

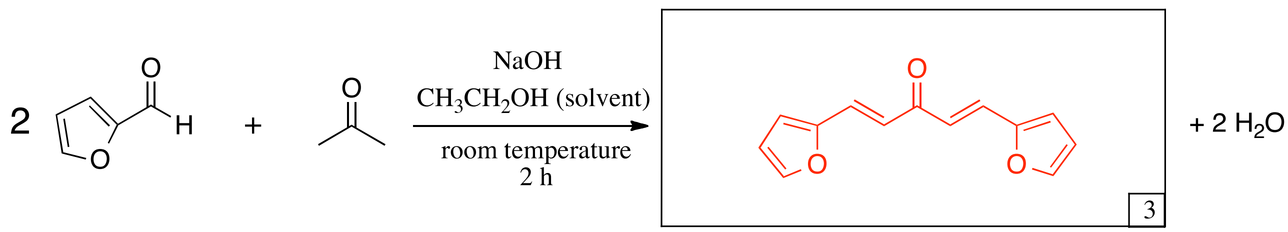
(1)



(2)

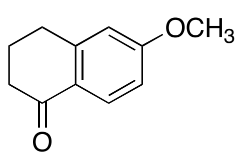


(3)

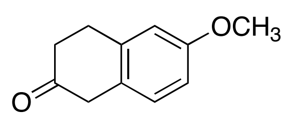


VII. (5 points) For each of the following pairs of compounds, match the expected IR frequencies for the C=O bond stretching vibration to the wavenumbers given.

(1) (2 points) 1710 or 1674 cm^{-1}

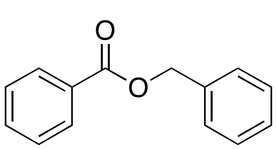


1674 cm^{-1}

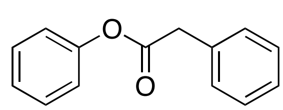


1710 cm^{-1}

(2) (3 points) 1760 or 1718 cm^{-1}



1718 cm^{-1}

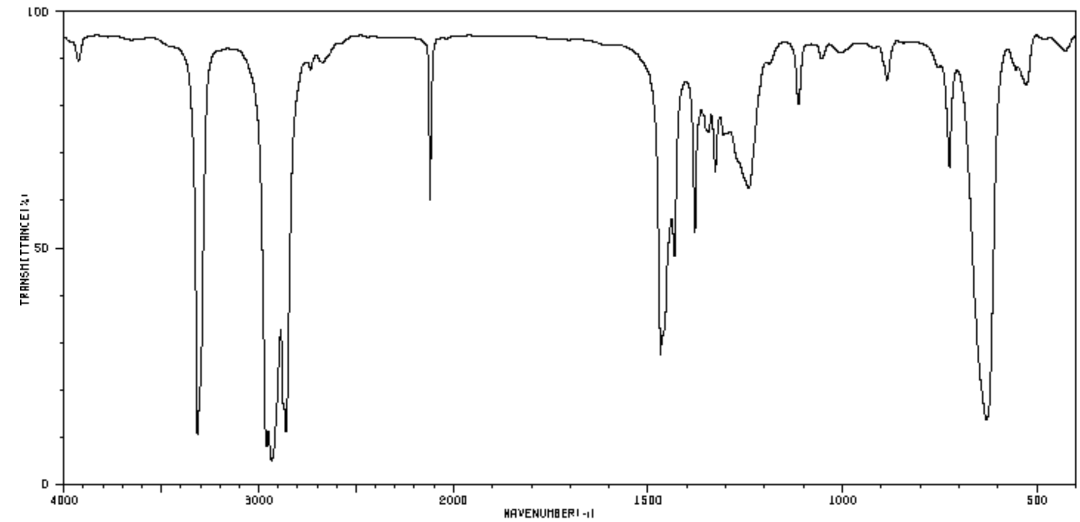


1760 cm^{-1}

VIII. (12 points). Given below are infrared (IR) spectra of four compounds. The compounds are among those structures given on page 9. Assign each spectrum to its compound by putting the letter corresponding to the compound in the answer box next to the spectrum. The tables of characteristic infrared frequencies appear on pages 10 and 11.

(1) (liquid film) Answer **D**

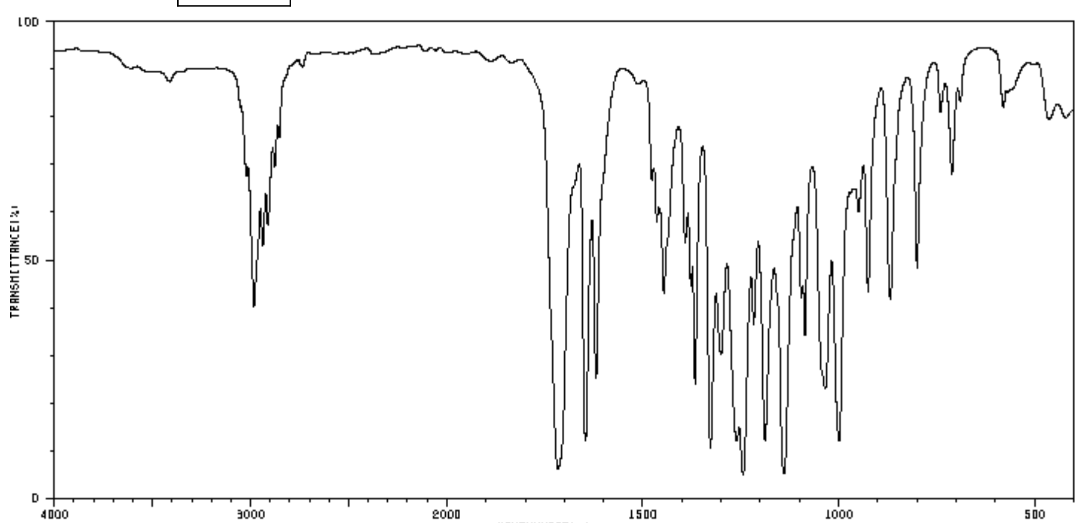
A strong, sharp peak in the 4000-3100 cm^{-1}. With the peak at 2120 cm^{-1}, this compd is likely to have an alkynic C-H. No peaks in the 1800-1500 cm^{-1} range, i.e., no C=O, no C=C!



3926	86	2673	86	1327	64
3315	10	2120	58	1242	60
2959	7	1468	26	1113	77
2933	4	1461	30	886	81
2874	15	1432	46	725	64
2861	10	1380	52	630	13
2734	84	1346	72	628	81

(2) (liquid film) Answer **G**

No peaks in the 4000-3100 cm^{-1} region -> no OH, no NH/NH_2, no νC(sp)-H. A strong νC=O peak at 1716 cm^{-1}; two νC=C peaks at 1646 & 1619 cm^{-1}. So, between F and G, this has to be G.

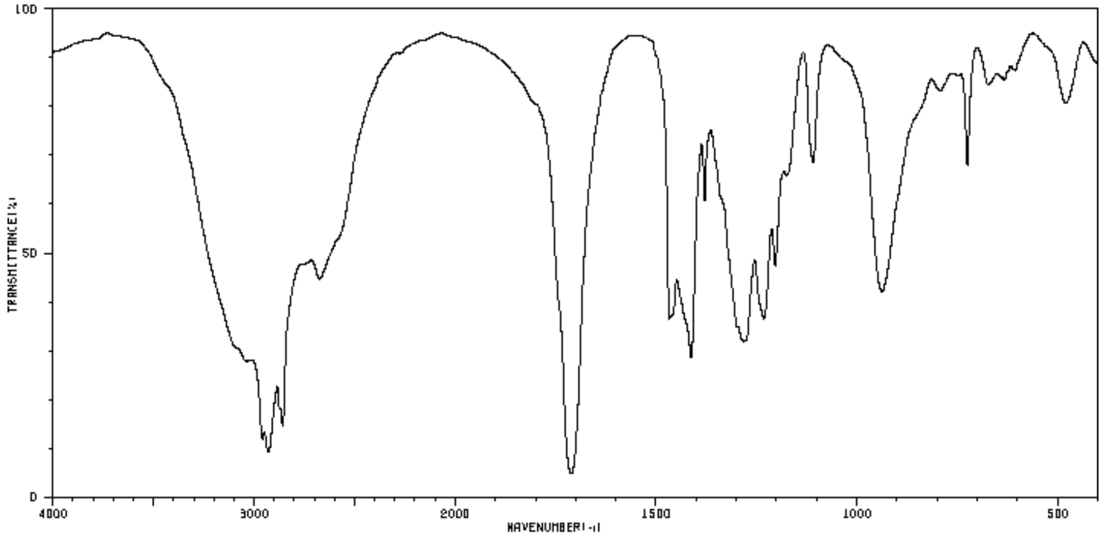


3020	64	1646	11	1367	23	1140	4
2981	38	1619	24	1328	10	1095	41
2938	50	1478	64	1301	29	1086	39
2913	66	1464	66	1261	11	1034	21
2876	66	1446	41	1244	4	1000	11
2854	72	1392	52	1217	35	949	58
1716	6	1378	42	1188	11	926	41

VIII. (continued)

(3) (liquid film) Answer **E**

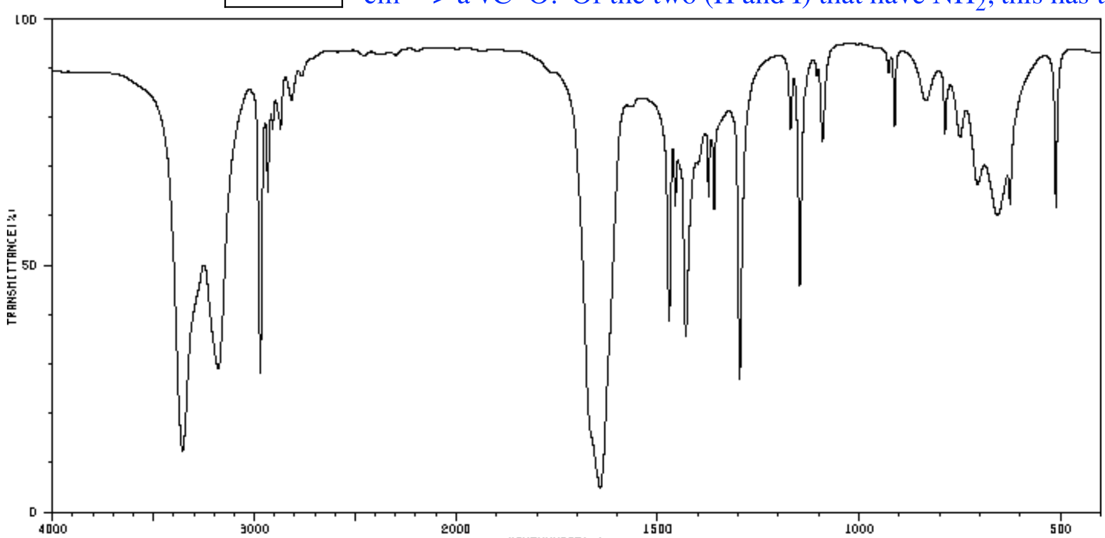
A unique pattern of νOH peaks of COOH in the 3200-2500 cm^{-1} region. No $\nu C=C$ (no peak in the 1700-1500 cm^{-1} region.



2957	11	1461	36	938	41
2930	8	1413	27	792	79
2873	17	1379	58	725	86
2869	13	1282	30	673	81
2673	43	1232	35	633	81
1711	4	1204	46	607	84
1468	36	1109	66	480	77

(4) (KBr disc) Answer **H**

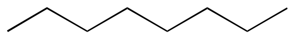
Two νNH peaks in the 4000-3100 cm^{-1} -> NH_2; a ***strong*** peak at 1642 cm^{-1} -> a $\nu C=O$. Of the two (H and I) that have NH_2, this has to be H.

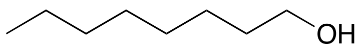


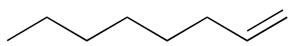
3366	12	2764	84	1297	26
3179	27	1642	4	1171	74
2972	26	1471	57	1148	44
2934	62	1466	60	1106	84
2910	74	1430	34	1091	72
2870	74	1374	62	927	86
2816	81	1360	68	912	74

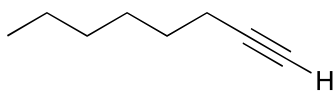
 Name ___Key_______________

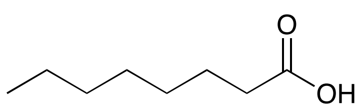
VIII. (continued)

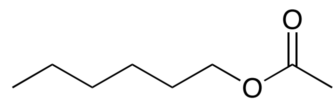
A 

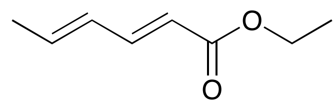
B 

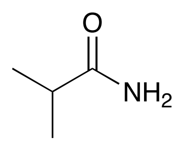
C 

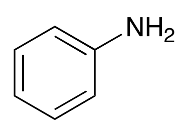
D 

E 

F 

G 

H 

I 

J