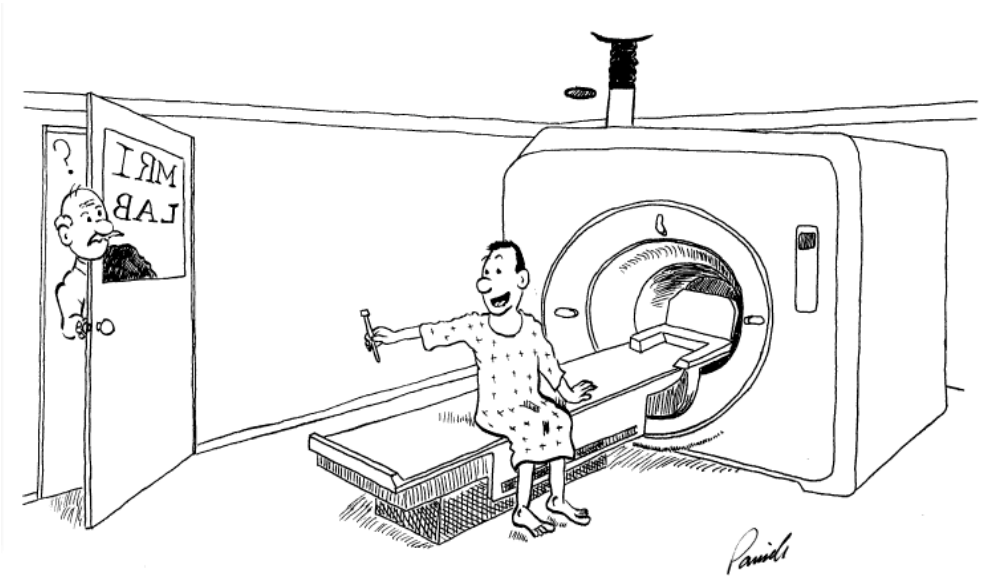
Chem 342 Organic Chem II

Midterm Exam 01

14 February 2003

NAME_____**ANSWER KEY**_____



"HEY, DOC, COULD WE RUN A QUICK PROTON WHILE WE'RE AT IT?"

Please read through each problem carefully. Enter your answers in the spaces provided.

Problem 1 18 pts _____

Problem 2 8 pts _____

Problem 3 12 pts _____

Problem 4 9 pts _____

Problem 5 9 pts _____

Problem 6 21 pts_____

Problem 7 17 pts _____

Problem 8 6 pts _____

TOTAL 100 pts_____

A note about drawing structures: you should make your drawings as clear as possible to understand. Stereochemistry should be indicated unambiguously using conventional drawing techniques (eg. bold wedges and dashes).

The most common mistake on an exam is not reading the question carefully. I suggest you go through the exam and answer the questions that come easily. Then go back and tackle the more challenging problems. Finally, check any work you have done, but remember, your first instinct is usually correct.

If you need scrap paper or more room, use the back of the test pages.

1. Indicate whether the following statements are True or False. (18 points)

F NMR Spectrsocopy gives us information about a molecule's vibrations.

T Molecules will fragment in the Mass Spectrometer to give predominantly the most stable fragment.

F Molecules that are conjugated are less stable than those that aren't.

F In the Infrared Spectrum of alcohols, the absorbance due to the OH stretch is very narrow.

T NMR Spectroscopy can tell us how many hydrogens are on a carbon.

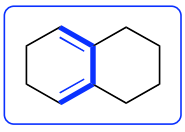
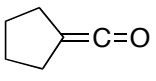
F In the proton NMR, a *tert*-Butyl group will show up as a quartet (four peaks).

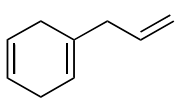
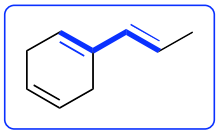
T Coupling constants are the same for protons that are splitting each other.

T The mass spectrum of benzene would be expected to show a large M^+ peak.

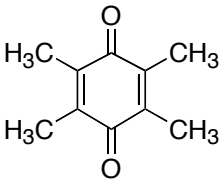
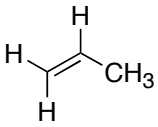
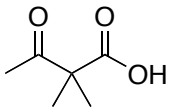
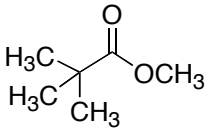
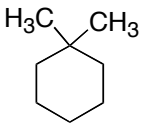
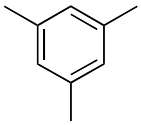
F A DEPT NMR spectra gives us information about number of carbons that correspond to each peak.

2. Circle all the following molecules that have conjugated pi-systems. (8 points)

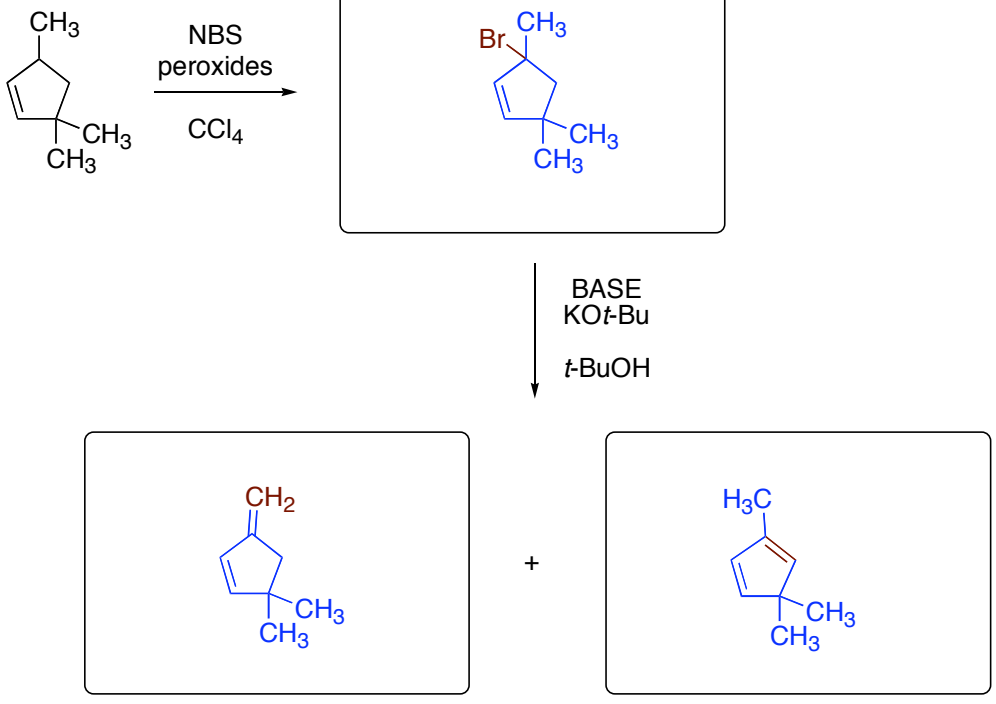



3. For the following molecules, indicate the number of different ^{1}H and ^{13}C signals you would see. (12 pts)

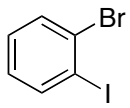
	Number of ^{1}H Resonances	Number of ^{13}C Resonances
	1	3
	4	3
	3	5
	2	4
	4	5
	2	3

4. Draw the product or products of the following reactions. (9 points)

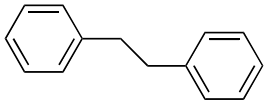


there are two possible products

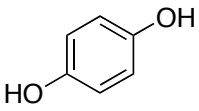
5. The three compounds shown below have very different ^{13}C NMR spectra. Match the structures with the correct spectra by placing the letter of the compound in the appropriate box. (9 points)



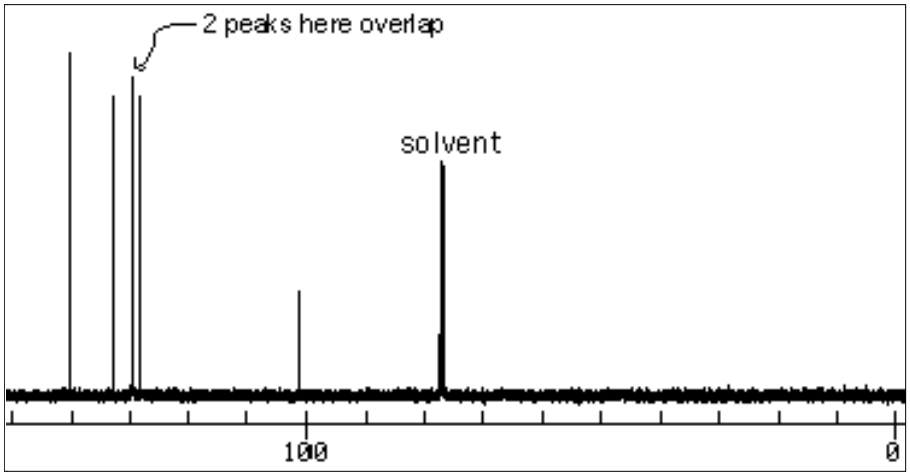
A



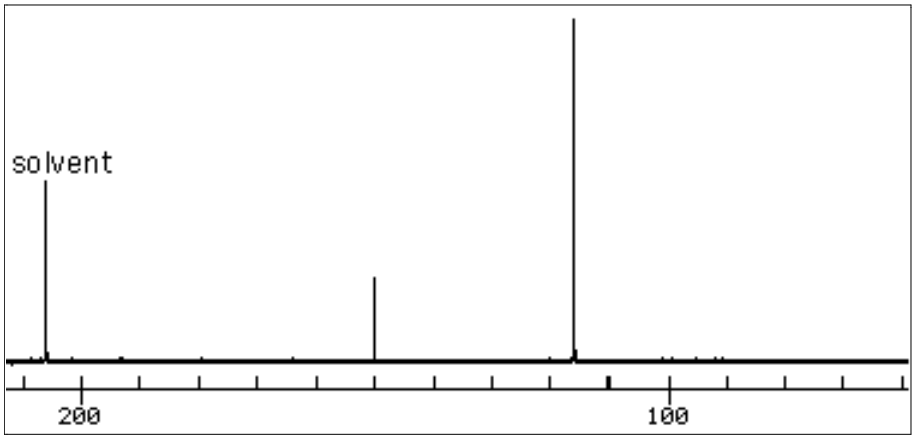
B



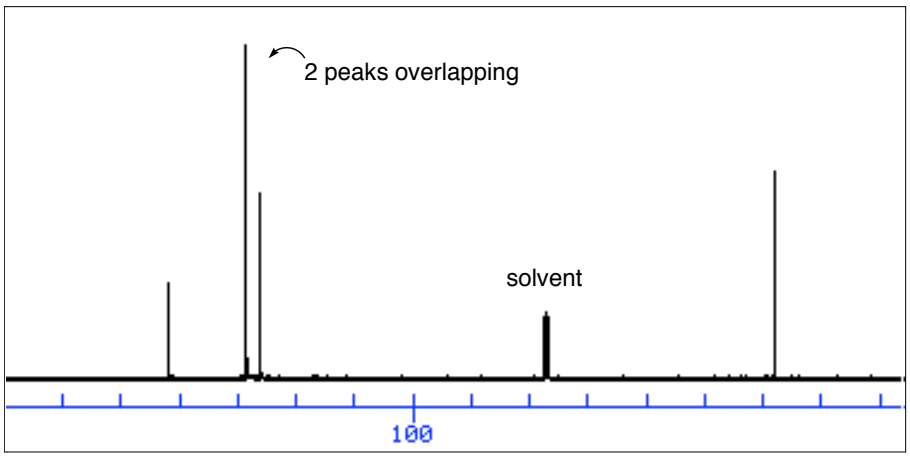
C



A



C



B

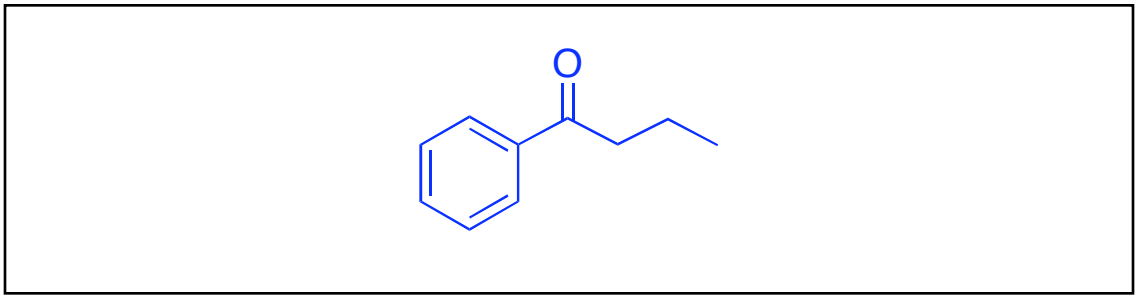
6. Answer the following questions about an unknown molecule with a molecular formula of $C_{10}H_{12}O$. The IR spectra shows a strong absorbance at 1680 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, and mass spectrum for this unknown are shown on the following page. (21 points)

How many degrees of unsaturation does the molecule possess? **5**

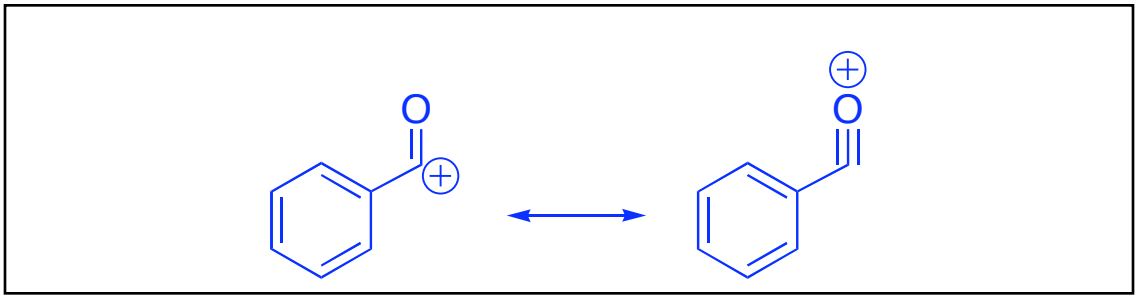
What type of functional group does the carbon resonance at 200 ppm represent - be specific?

A KETONE

What is the structure of the unknown molecule?



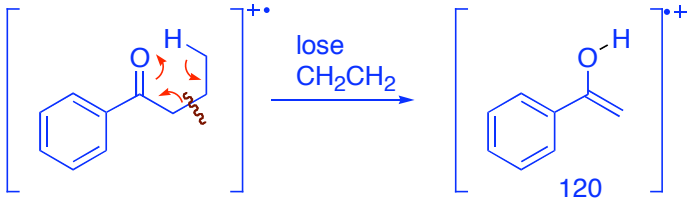
In the Mass Spectrum, what does the peak at m/z 105 correspond to (draw a structure)?

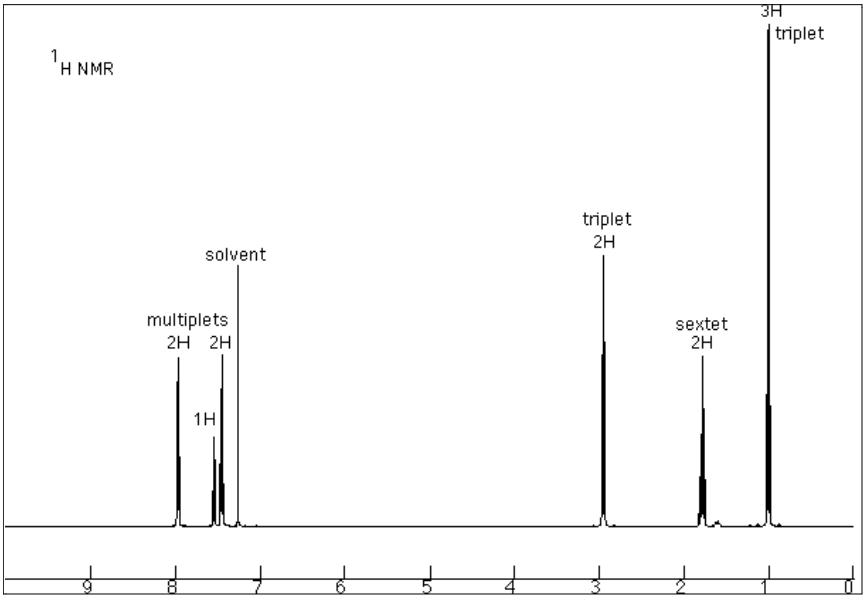


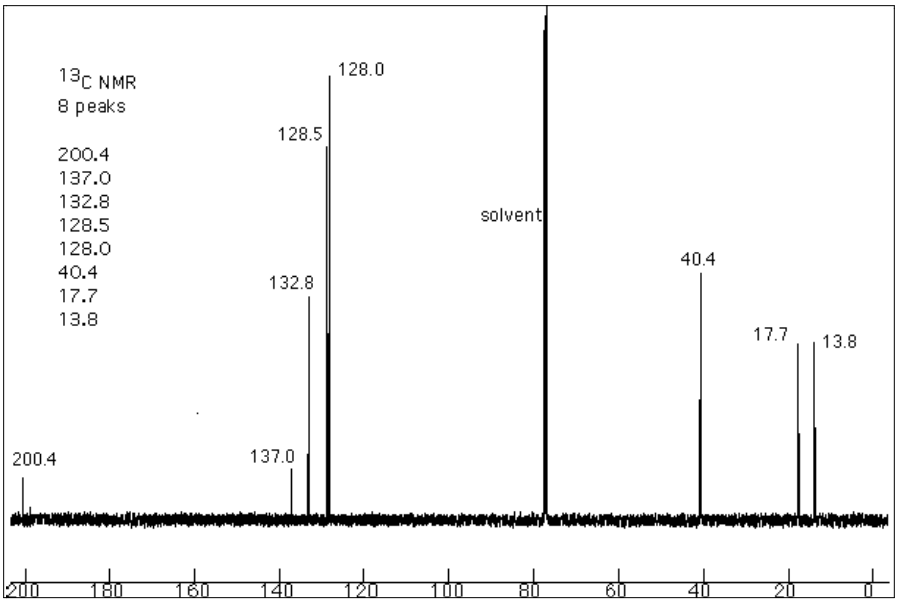
Which peak in the Mass Spectrum corresponds to the product of a McLafferty Rearrangement (beta cleavage)? I don't need a structure, only the m/z number.

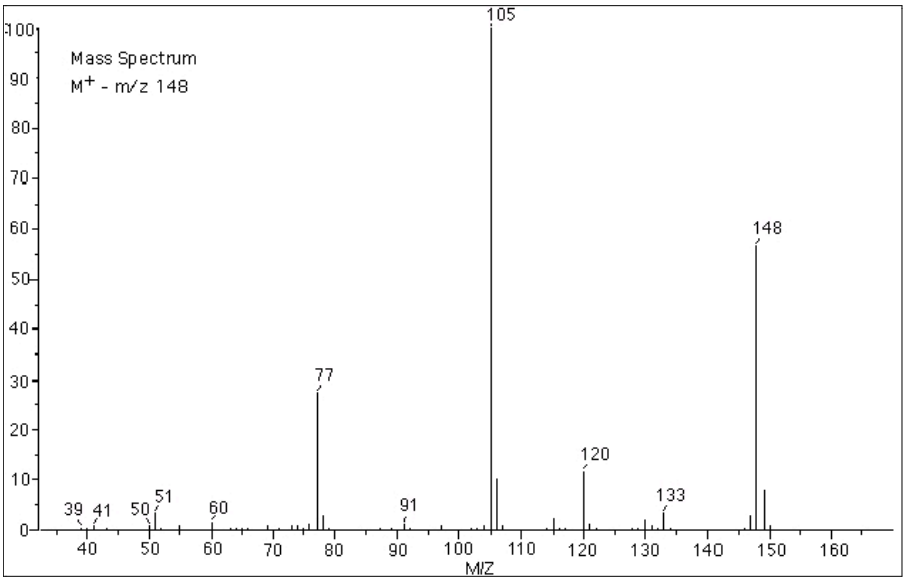
M/z =

120


H
O
lose
CH_2CH_2
O
H
120


^{1}H NMR
3H
triplet
triplet
2H
solvent
multiplets
2H
2H
1H
sextet
2H
9
8
7
6
5
4
3
2
1
0


^{13}C NMR
8 peaks
200.4
137.0
132.8
128.5
128.0
40.4
17.7
13.8
128.0
128.5
solvent
40.4
132.8
17.7
13.8
200.4
137.0
200
180
160
140
120
100
80
60
40
20
0



7. The mass spectrum of 3-bromopropanoic acid is shown on the next page. Four peaks are labeled with **A**, **B**, **C**, and **D**. Answer the following questions about this spectrum. (17 points)

Which of the peaks labeled on the spectrum is the Base Peak? **A**

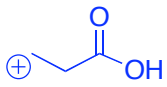
Which of the peaks labeled on the spectrum is the M^+ peak? **D**

Which of the peaks labeled on the spectrum contain bromine? **B, C, D**

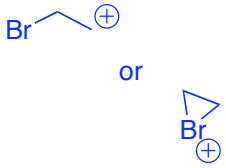
Which of the peaks labeled on the spectrum have lost bromine? **A**

Draw the structure of the fragments that are labeled?

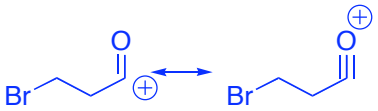
A loss of Br•

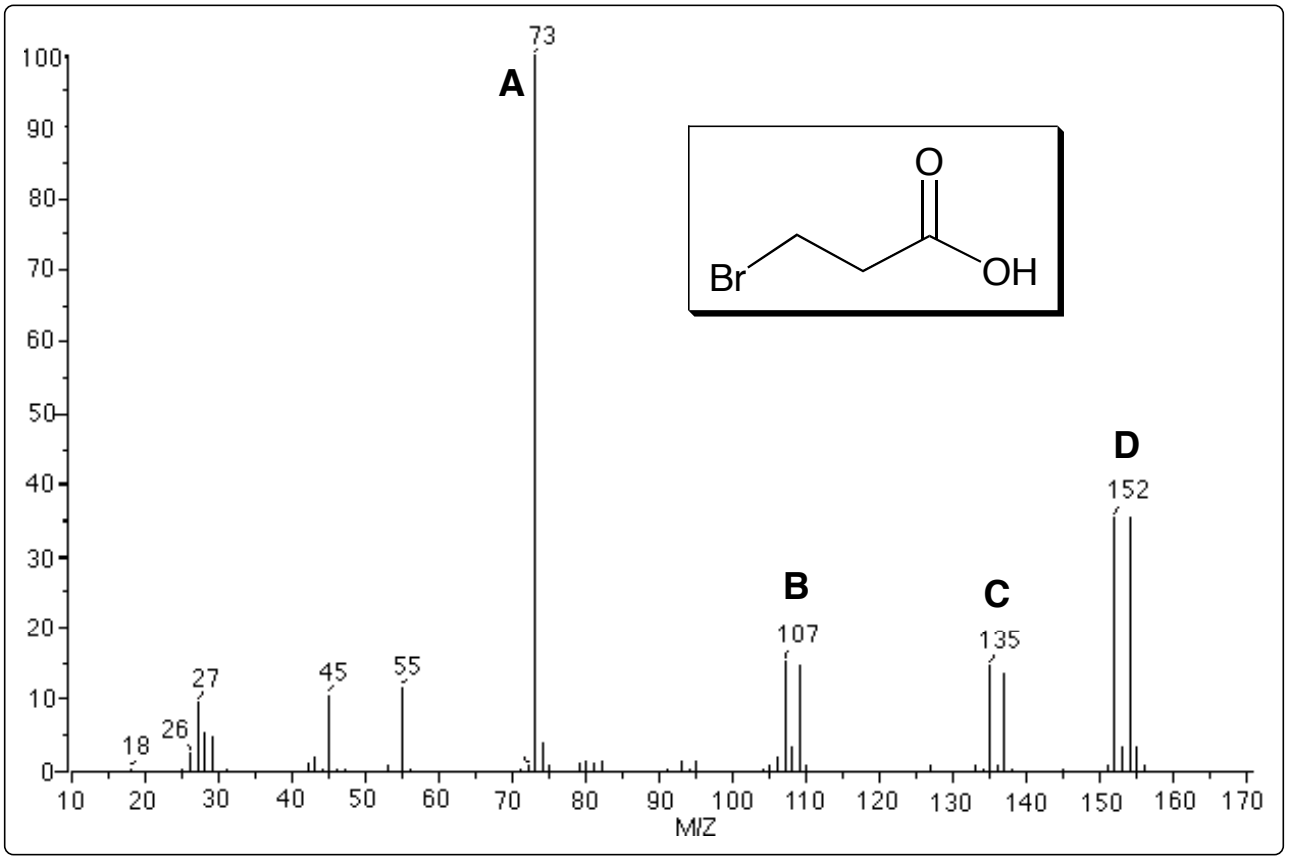


B loss of CO_2H•

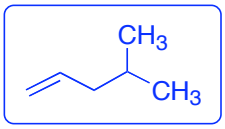


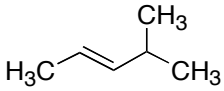
C loss of OH•

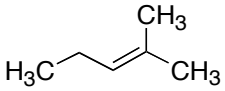


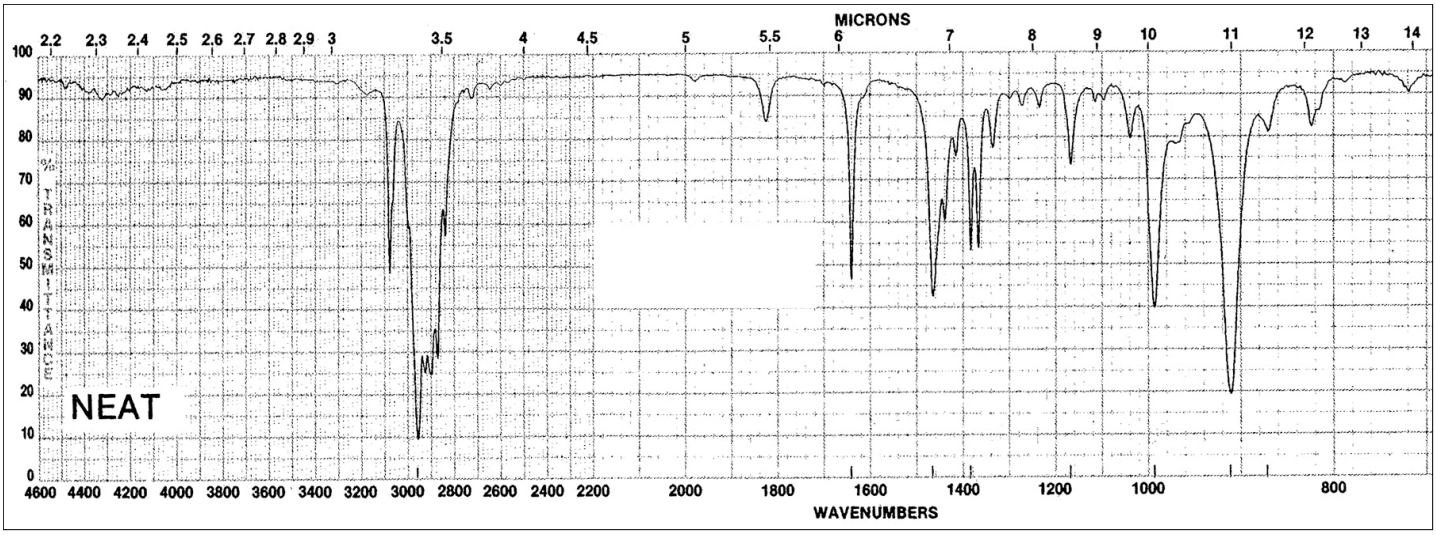


8. Circle the structure that corresponds with the following IR spectrum. (6 pts)

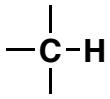
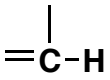
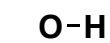
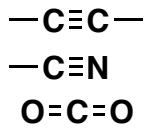
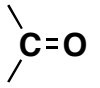
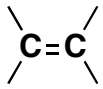




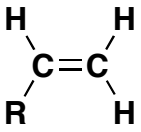
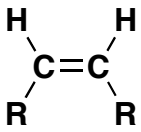
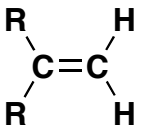
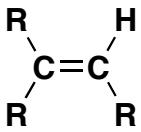
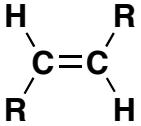



MICRONS
2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3 3.5 4 4.5 5 5.5 6 7 8 9 10 11 12 13 14
100 90 80 70 60 50 40 30 20 10 0
% TRANSMITTANCE
NEAT
4600 4400 4200 4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800
WAVENUMBERS

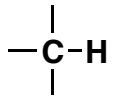
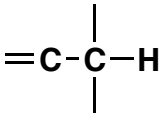
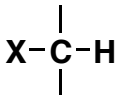
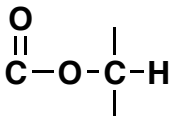
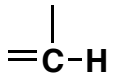
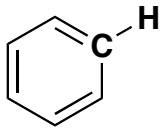
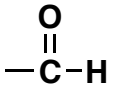
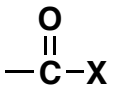
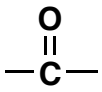
Infrared Stretching Absorptions

Functional Group	Wavenumber Range (cm^{-1})	Absorption Strength	notes
	2850-2960	medium-strong	below 3000
	3020-3100	medium	above 3000
	3300	strong	above 3000
	3400-3650	broad-strong	
	3300-3500	medium	#H's = #peaks
	2100-2260	medium	
	1680-1750	strong	
	1640-1750	medium	
C–C	800-1300	medium	
C–O	1050-1150	medium	
C–X	<1000	strong	

Alkene out of plane bending

	910 and 990	strong		700	strong
	890	strong		815	strong
	970	strong			

Typical NMR Chemical Shifts

Functional Group	Type	^{1}H Chemical Shift (ppm)	^{13}C Chemical Shift (ppm)
	Alkane	0.7 -1.8	10 - 60
	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
	next to halogen or alcohol	2.5 - 4.0	20 - 85
	next to oxygen of an ester	4.0 - 5.0	50 - 85
	vinylic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
	aldehyde	9.7 - 10.0	190 - 220
	alcohol	varies widely will exchange with D_2O	N/A
	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
	carbonyl of ketone or aldehyde	N/A	190 - 220