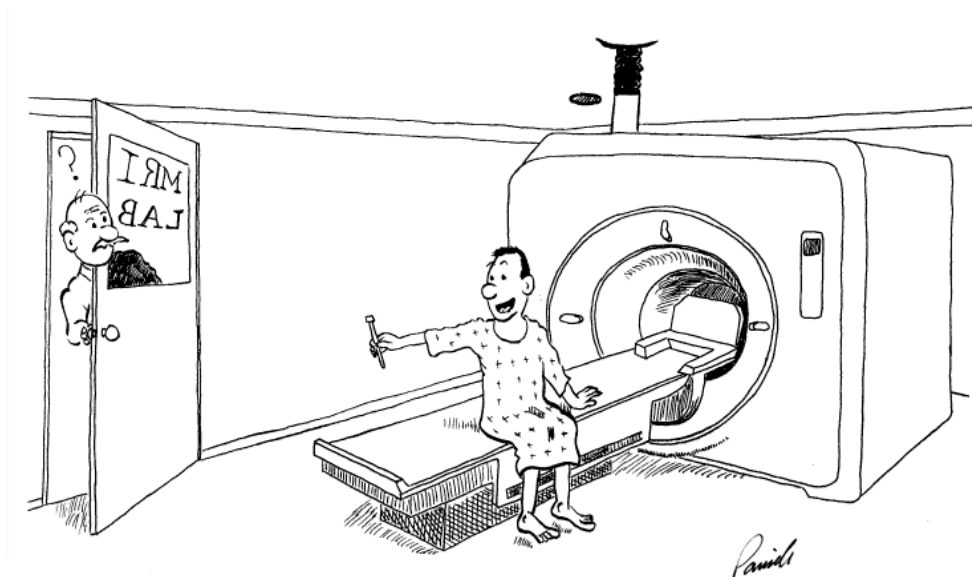


NAME _____



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

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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)

NMR Spectroscopy gives us information about a molecule's vibrations.

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

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

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

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

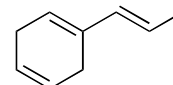
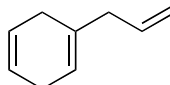
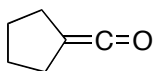
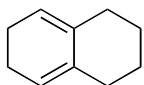
In the proton NMR, a *tert*-Butyl group will show up as a quartet (four peaks).

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

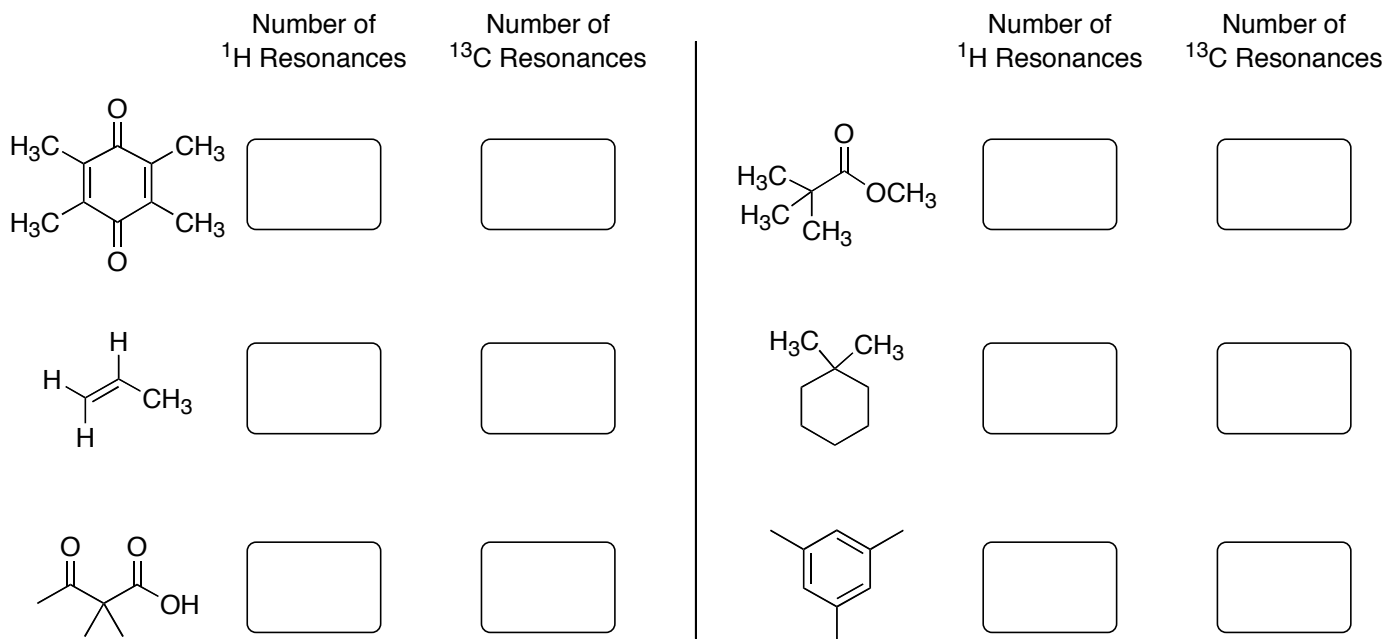
The mass spectrum of benzene would be expected to show a large M^+ peak.

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

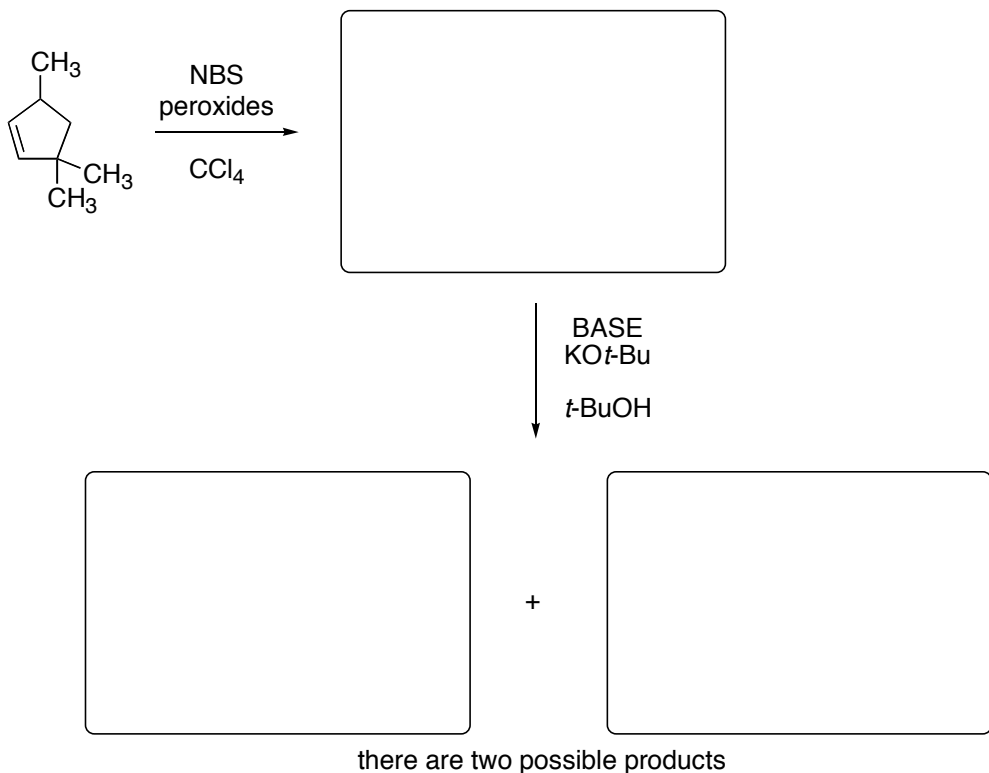
2. Circle all the following molecules that have conjugated pi-systems. (8 points)



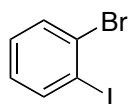
3. For the following molecules, indicate the number of different ^1H and ^{13}C signals you would see. (12 pts)



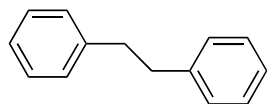
4. Draw the product or products of the following reactions. (9 points)



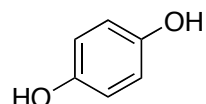
5. The three compounds shown below have very different ^{13}C NMR spectra. Match the structures with the correct spectra by placing the letter of the compound in the appropriate box. (9 points)



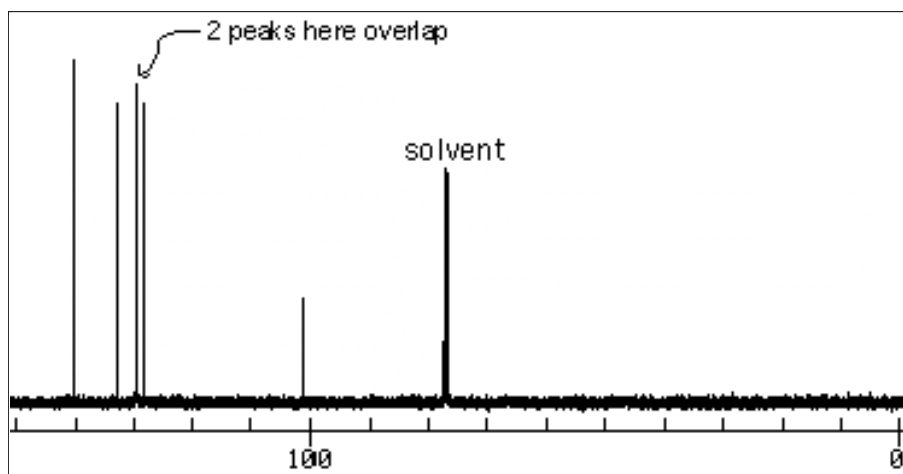
A

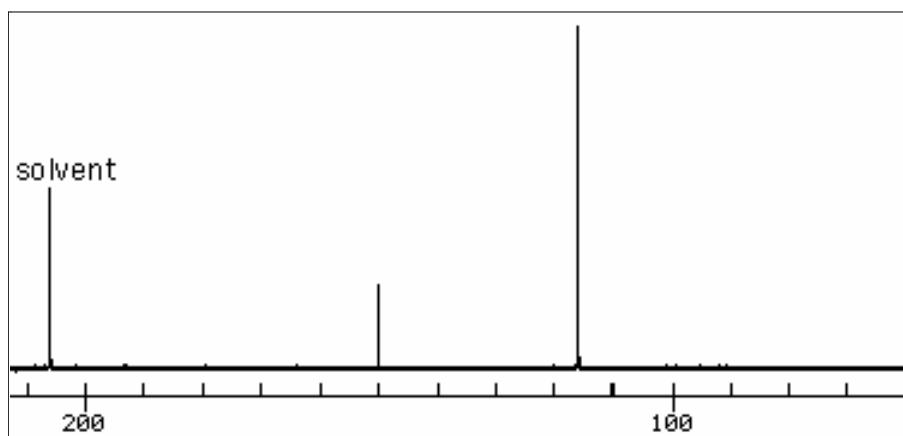


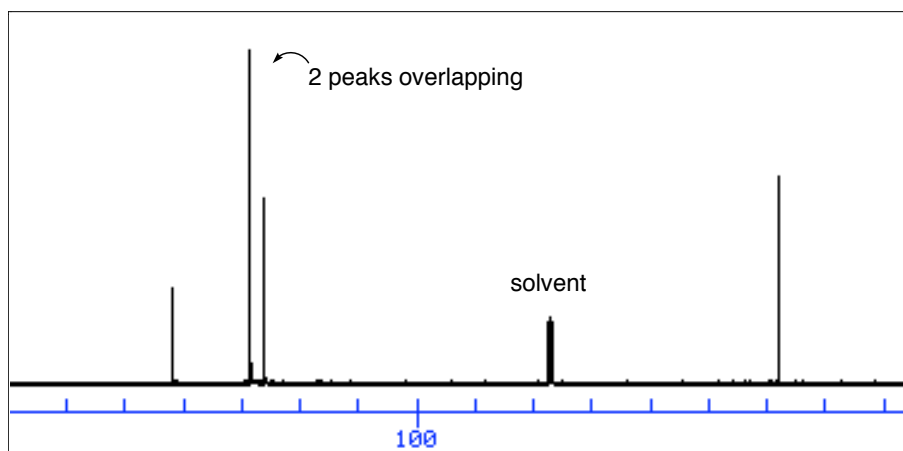
B



C







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 ^1H 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?

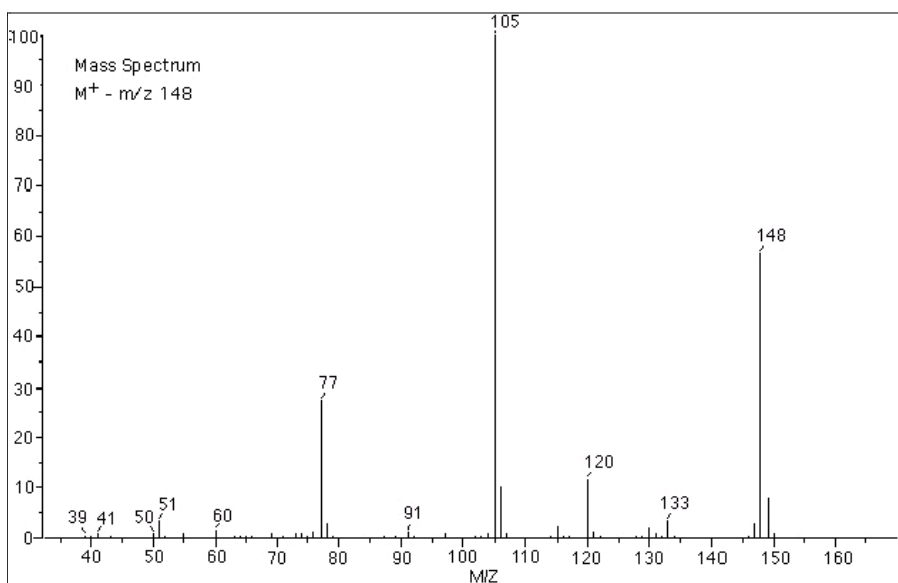
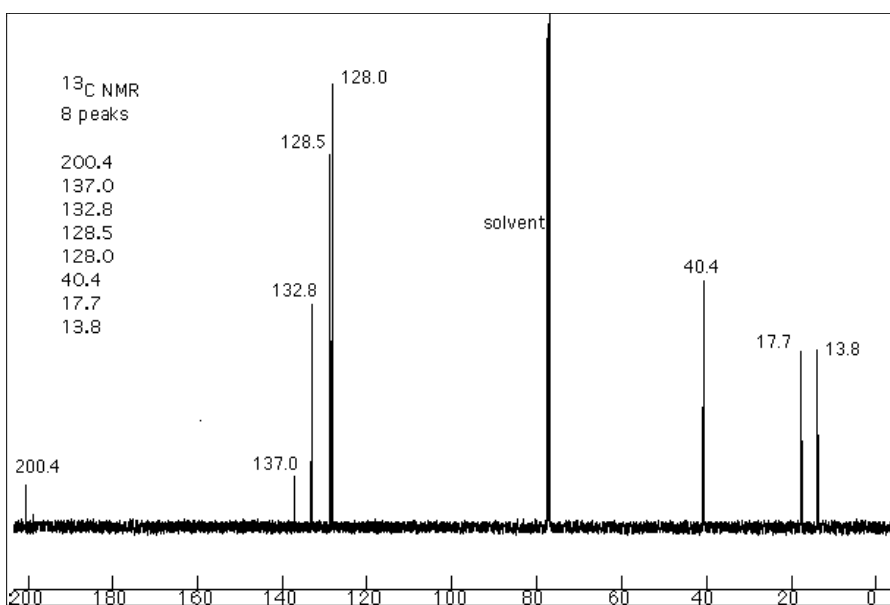
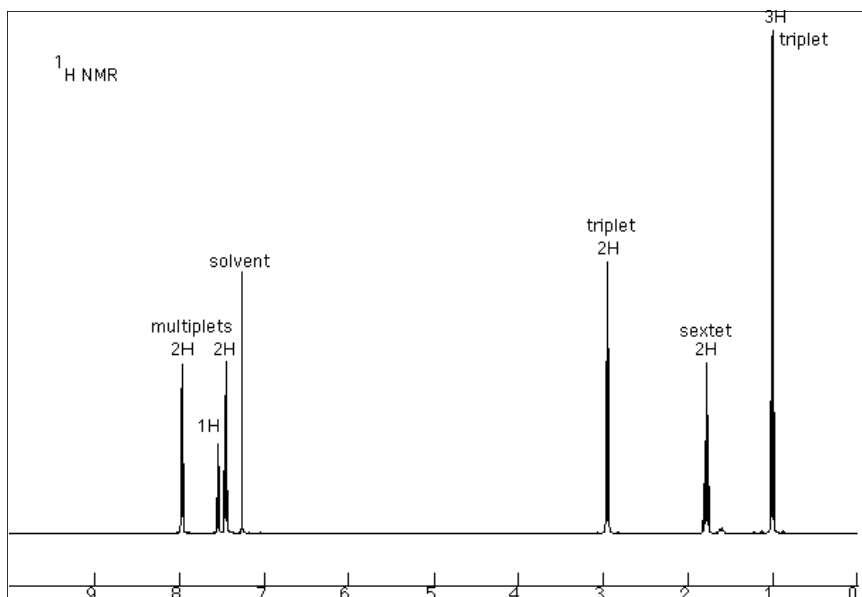
What type of functional group does the carbon resonance at 200 ppm represent - be specific?

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.

$M/z =$



-
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)

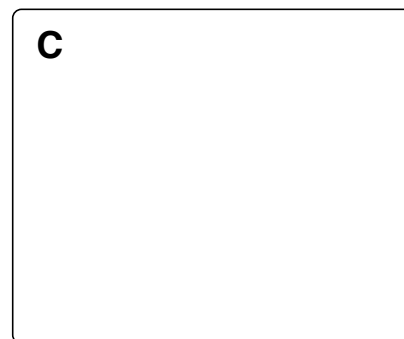
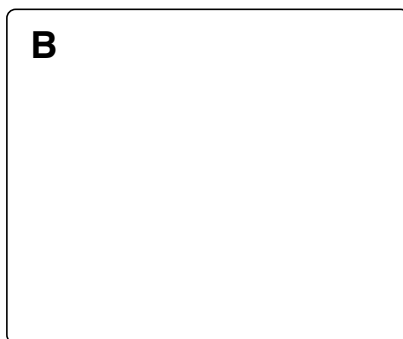
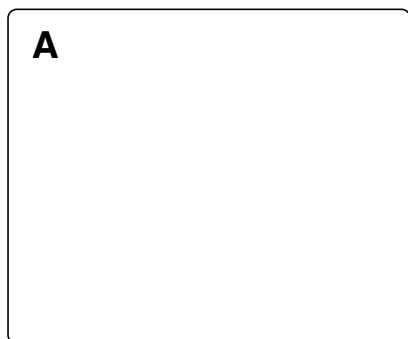
Which of the peaks labeled on the spectrum is the Base Peak?

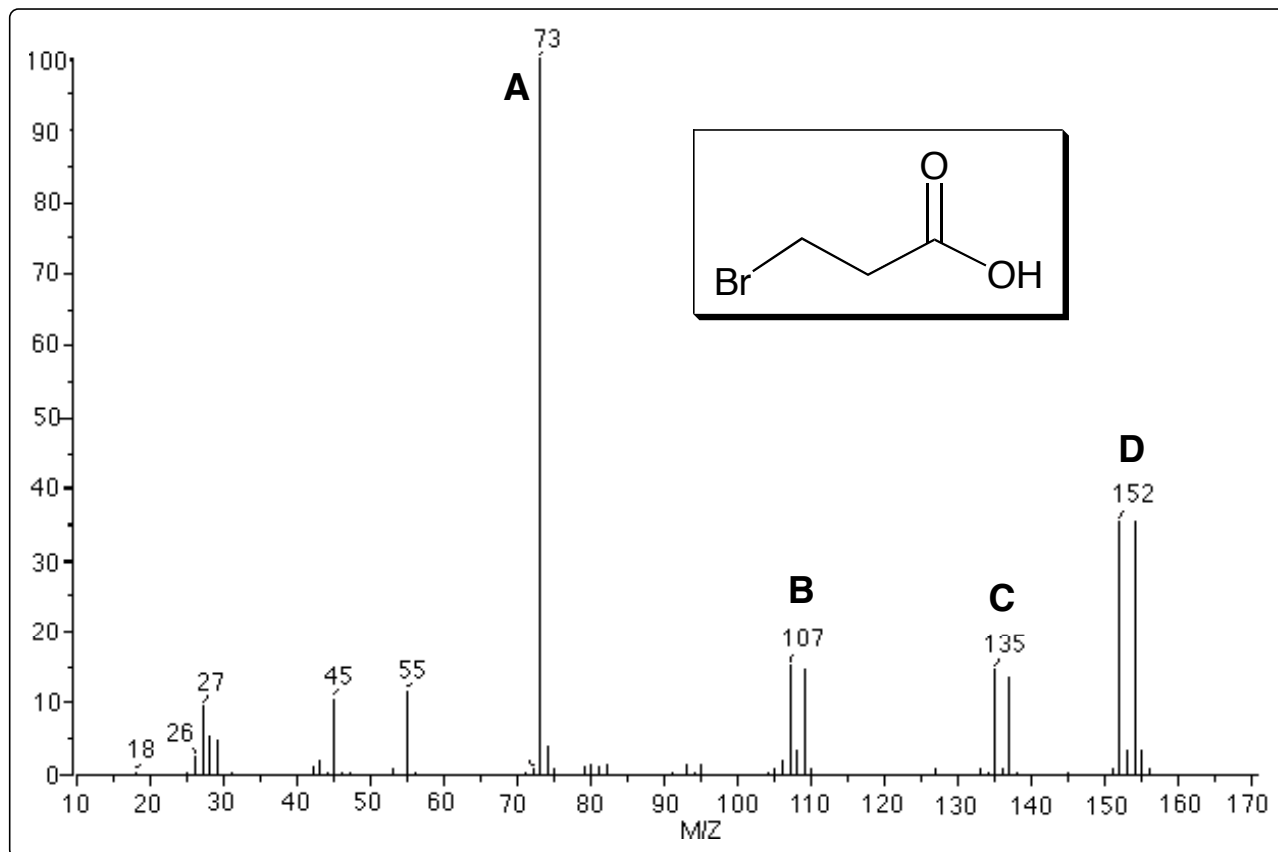
Which of the peaks labeled on the spectrum is the M^+ peak?

Which of the peaks labeled on the spectrum contain bromine?

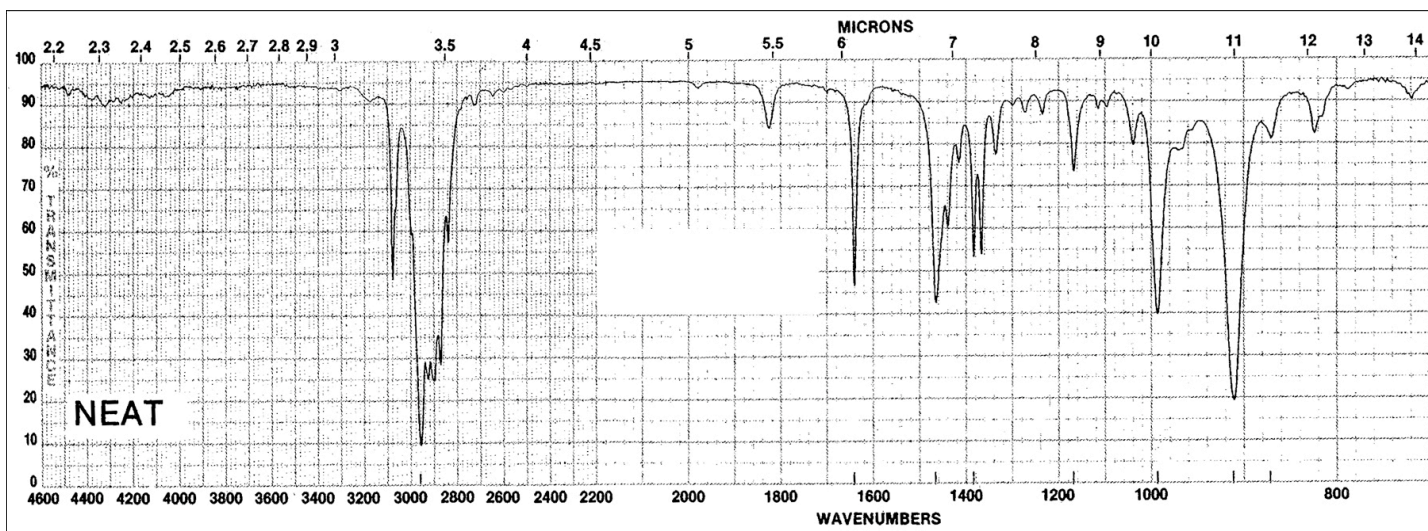
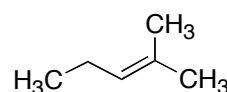
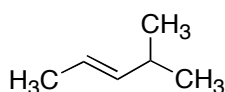
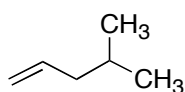
Which of the peaks labeled on the spectrum have lost bromine?

Draw the structure of the fragments that are labeled?





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



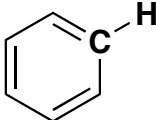
Infrared Stretching Absorptions

Functional Group	Wavenumber Range (cm ⁻¹)	Absorption Strength	notes
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	2850-2960	medium-strong	below 3000
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	3020-3100	medium	above 3000
$\equiv\text{C}-\text{H}$	3300	strong	above 3000
O-H	3400-3650	broad-strong	
N-H	3300-3500	medium	#H's = #peaks
$\begin{array}{c} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array} \quad \left. \vphantom{\begin{array}{c} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array}} \right\}$	2100-2260	medium	
$\begin{array}{c} \diagdown \\ \text{C}=\text{O} \\ \diagup \end{array}$	1680-1750	strong	
$\begin{array}{c} \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \end{array}$	1640-1750	medium	
C-C	800-1300	medium	
C-O	1050-1150	medium	
C-X	<1000	strong	

Alkene out of plane bending

$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	910 and 990	strong	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	700	strong
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	890	strong	$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	815	strong
$\begin{array}{c} \text{H} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	970	strong			

Typical NMR Chemical Shifts

Functional Group	Type	¹ H Chemical Shift (ppm)	¹³ C Chemical Shift (ppm)
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	Alkane	0.7 - 1.8	10 - 60
$\begin{array}{c} \\ =\text{C}-\text{C}-\text{H} \\ \end{array}$	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
$\begin{array}{c} \\ \text{X}-\text{C}-\text{H} \\ \end{array}$	next to halogen or alcohol	2.5 - 4.0	20 - 85
$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{O}-\text{C}-\text{H} \\ \end{array}$	next to oxygen of an ester	4.0 - 5.0	50 - 85
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	vinyllic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	aldehyde	9.7 - 10.0	190 - 220
$\text{O}-\text{H}$	alcohol	varies widely will exchange with D ₂ O	N/A
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	carbonyl of ketone or aldehyde	N/A	190 - 220