Chem 342 Organic Chem II

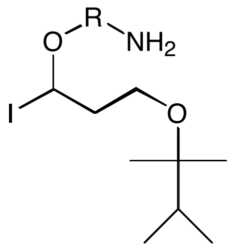
Midterm Exam 01
08 February 2002

NAME____

QUOTE OF THE DAY

It is disconcerting to reflect on the number of students we have flunked in chemistry for not knowing what we later found to be untrue.

> -- Robert L. Weber, Science With a Smile (1992)



A 1-I-1-ORN-flying-propyl-people-ether

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

Problem 1	16 pts	__________
Problem 2	8 pts	__________
Problem 3	8 pts	__________
Problem 4	9 pts	__________
Problem 5	18 pts	__________
Problem 6	20 pts	__________
Problem 7	20 pts	__________
given	1 pts	**1**
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).

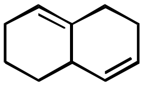
The most common mistake on an exam is not reading the question carefully. I suggest you go through the exam and answer the questions that come easily. Then go back and tackle the more challenging problems. Finally, check any work you have done, but remember, your first instinct is usually correct.

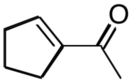
If you need scrap paper or more room, use the back of the test pages.

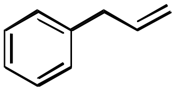
1. Indicate whether the following statements are True or False. (16 points)

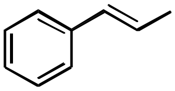
- ☐ Infrared Spectroscopy can give us information about functional groups.
- ☐ Molecules will fragment in the Mass Spectrometer to give only the most stable fragment.
- ☐ A kinetically controlled reaction gives the most stable product because the reaction is reversible.
- ☐ Conjugation lowers the energy of a molecule because the electrons are more delocalized.
- ☐ The energy required to flip a nuclear spin state aligned with a magnetic field lies in the microwave region of the electromagnetic spectrum.
- ☐ A proton signal in the NMR will be split into three peaks if it has two neighboring protons.
- ☐ Two proton resonances that are coupled to one another will each be split with different coupling constants.
- ☐ In a Diels-Alder cycloaddition reaction, all new bonds are formed in a single step.

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

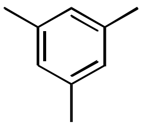


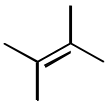


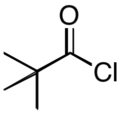


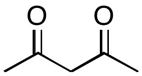


3. Circle all the following molecules that would show only a single peak in the ^{1}H NMR. (8 points)

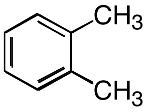






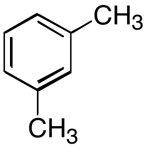


4. The three compounds shown below, ortho-, meta-, and para-xylene have very different ^{13}C NMR spectra. Match the structures with the correct spectra by placing the letter of the compound in the appropriate box. (9 points)



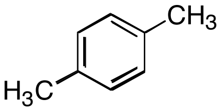
ortho-xylene

A



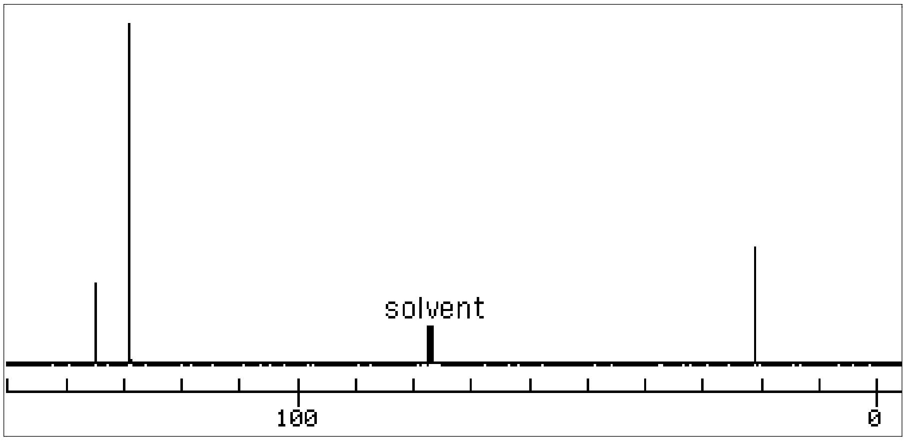
meta-xylene

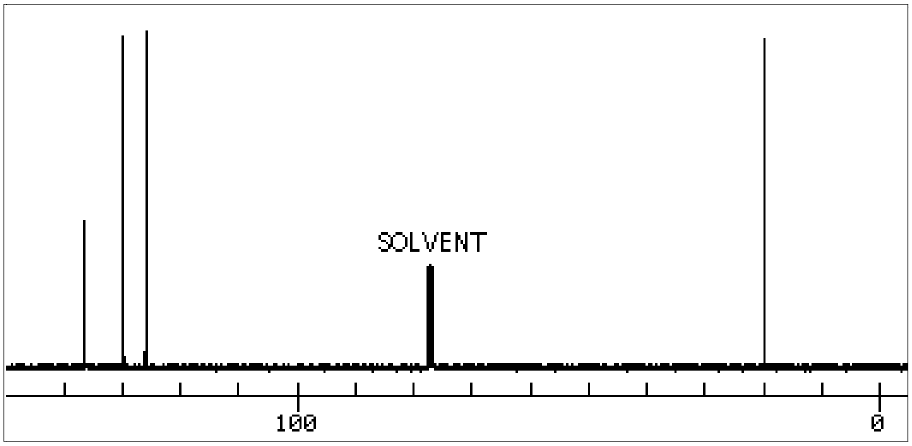
B

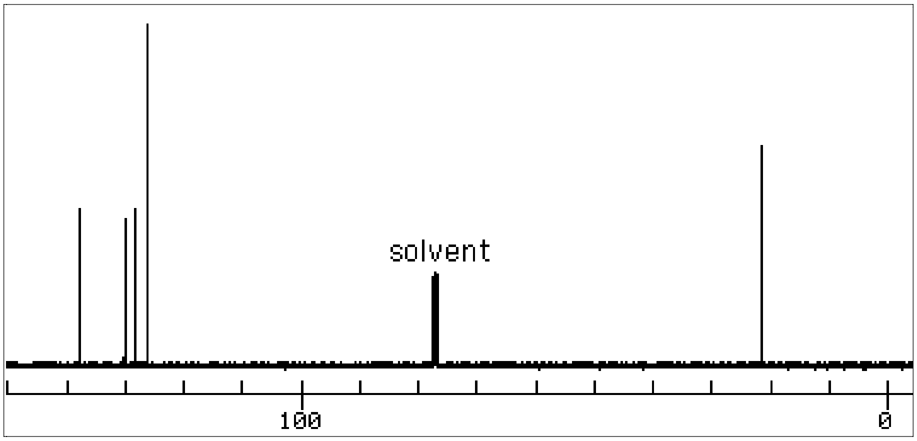


para-xylene

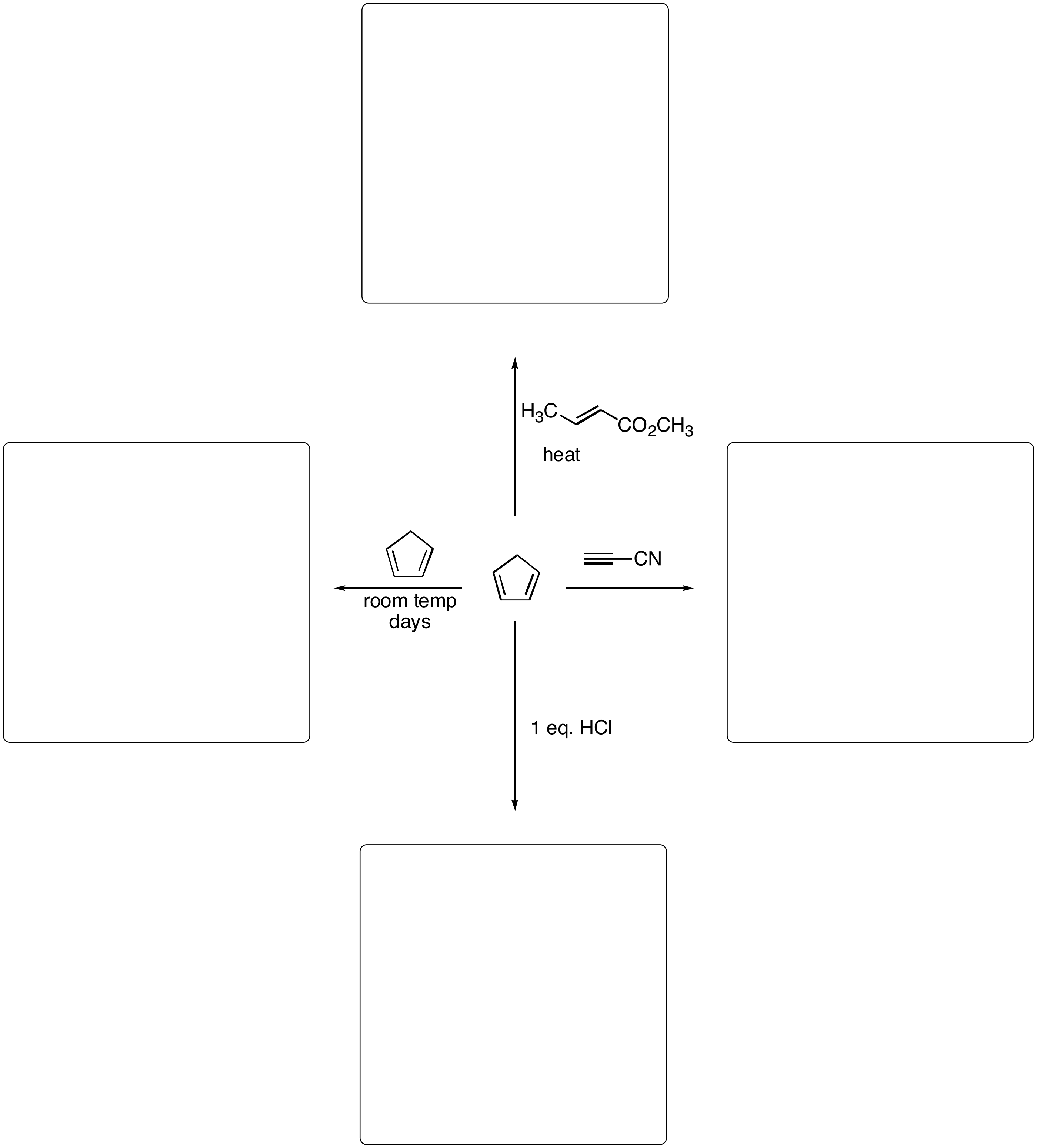
C







5. Draw the product or products of the following reactions. Show any stereochemistry clearly where appropriate. (18 points)



6. Answer the following questions about an unknown molecule with a molecular formula of C_9H_{12}. The ^{1}H NMR, ^{13}C NMR mass spectrum for this unknown compound are shown on the following page. (20 points)

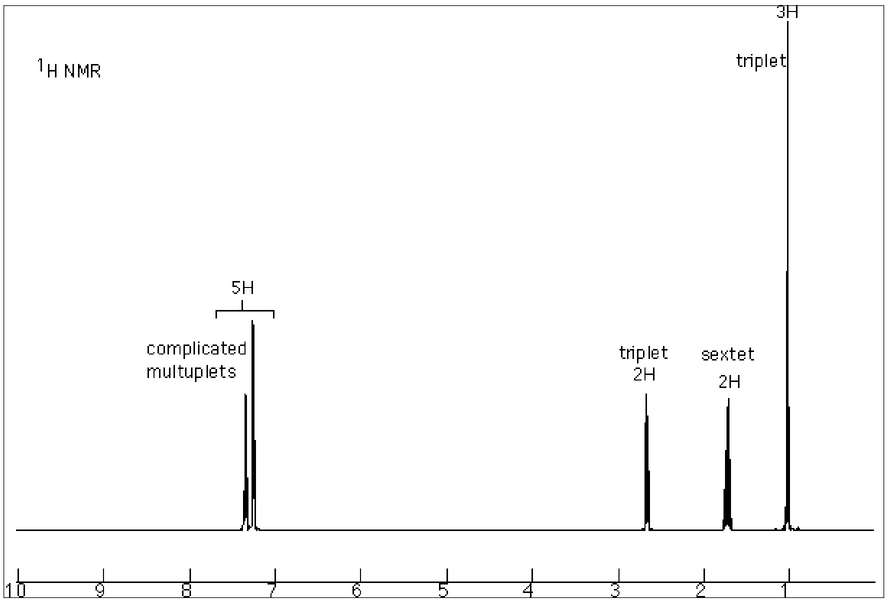
How many degrees of unsaturation does the molecule possess?

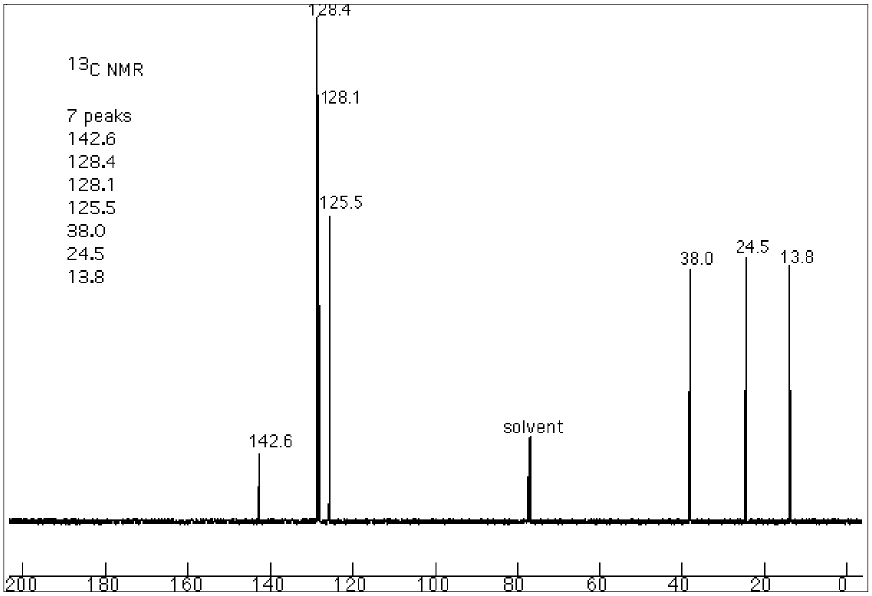
What type of functional group do the proton resonances between 7.0 and 8.0 ppm represent?

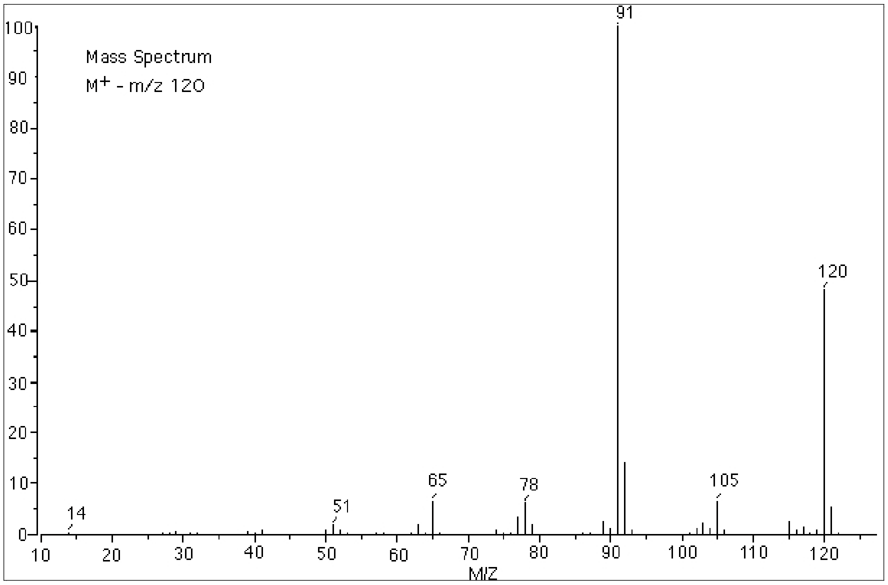
What is the structure of the unknown molecule?

In the Mass Spectrum, what does the peak at m/z 91 correspond to (draw a structure)?

Briefly explain why the MS peak at m/z 91 is the base peak.


^{1}H NMR
5H
complicated
multuplets
triplet
2H
sextet
2H
3H
triplet
10
9
8
7
6
5
4
3
2
1


^{13}C NMR
7 peaks
142.6
128.4
128.1
125.5
38.0
24.5
13.8
128.4
128.1
125.5
142.6
solvent
38.0
24.5
13.8
200
180
160
140
120
100
80
60
40
20
0


Mass Spectrum
M+ - m/z 120
100
90
80
70
60
50
40
30
20
10
0
14
51
65
78
91
105
120
10
20
30
40
50
60
70
80
90
100
110
120
M/Z

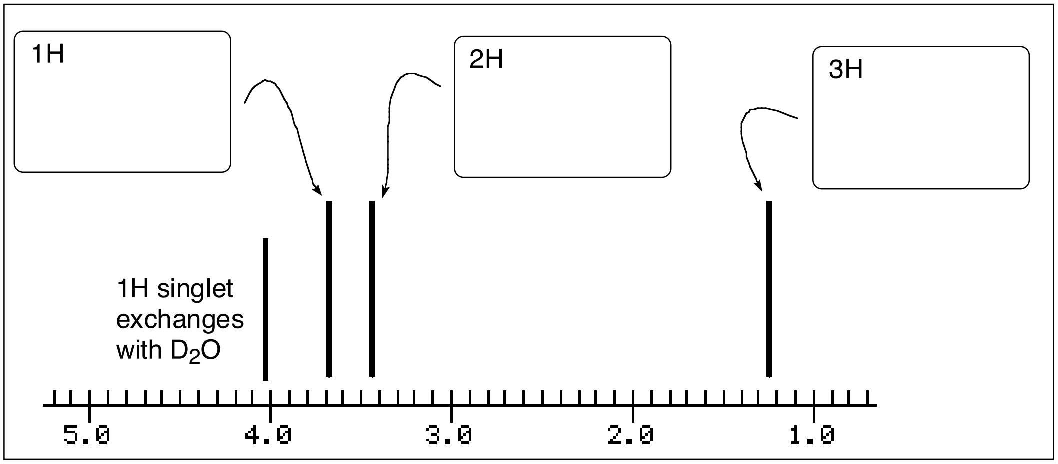
7. Answer the following questions about an unknown molecule with a molecular formula of C_3H_7ClO. A strong and broad IR absorbance is observed centered at 3500 cm^{-1}. The ^1H NMR and ^{13}C NMR spectra for this unknown compound are shown on the following page. (20 points)

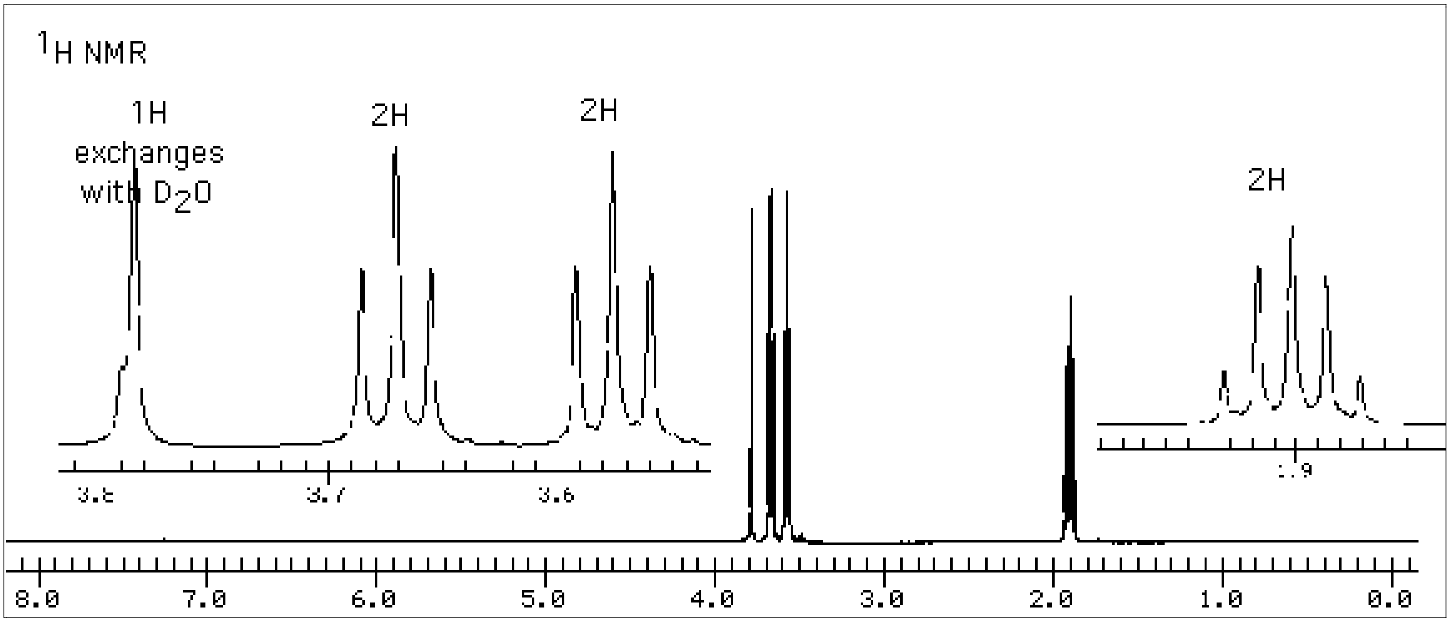
How many degrees of unsaturation does the molecule possess?

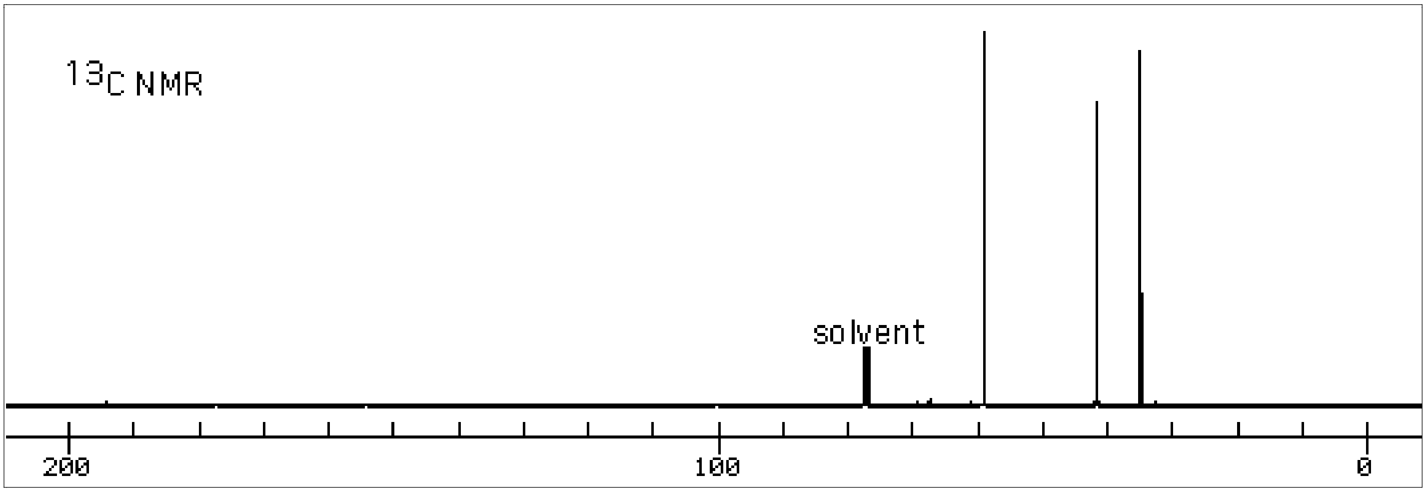
What functional group does the proton resonance at 3.8 ppm correspond to?

What is the structure of the unknown molecule?

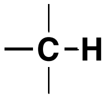
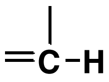
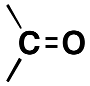
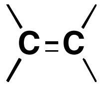
If the chlorine were moved to the middle carbon, indicate on the example spectrum below what you would expect the splitting patterns to be (eg. singlet, doublet, triplet, quartet, etc.)



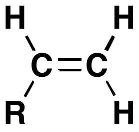
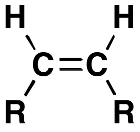
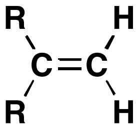
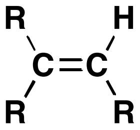
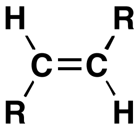

1H NMR
1H
exchanges with D2O
2H
2H
2H
3.8
3.7
3.6
1.9
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


13C NMR
solvent
200
100
0

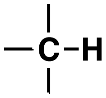
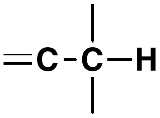
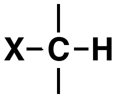
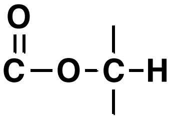
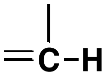
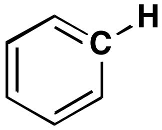
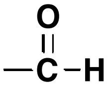
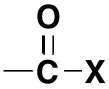
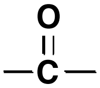
Infrared Stretching Absorptions

Functional Group	Wavenumber Range (cm^{-1})	Absorption Strength	notes
 $-\overset{\vert}{\underset{\vert}{C}}-H$	2850-2960	medium-strong	below 3000
 $=\overset{\vert}{C}-H$	3020-3100	medium	above 3000
$\equiv C-H$	3300	strong	above 3000
O–H	3400-3650	broad-strong	
N–H	3300-3500	medium	#H's = #peaks
$-C\equiv C-$ $-C\equiv N$ $O=C=O$	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)	^{1}H Chemical Shift (ppm)
 $-\overset{\vert}{\underset{\vert}{C}}-H$	Alkane	0.7 -1.8	10 - 60
 $=C-\overset{\vert}{\underset{\vert}{C}}-H$	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
 $X-\overset{\vert}{\underset{\vert}{C}}-H$	next to halogen or alcohol	2.5 - 4.0	20 - 85
 $\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-H$	next to oxygen of an ester	4.0 - 5.0	50 - 85
 $=\overset{\vert}{C}-H$	vinylic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
 $-\overset{O}{\overset{\Vert}{C}}-H$	aldehyde	9.7 - 10.0	190 - 220
O-H	alcohol	varies widely will exchange with D_2O	N/A
 $-\overset{O}{\overset{\Vert}{C}}-X$	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
 $-\overset{O}{\overset{\Vert}{C}}-$	carbonyl of ketone or aldehyde	N/A	190 - 220