*This exercise sheet covers the lecture 4 about **NMR** (Nuclear magnetic resonance spectroscopy). The content is closely related to **chapter 5** of T. Sonderberg Organic Chemistry Which a Biological Emphasis.*

4.0 Overview Structure Determination

The intent of this question is to give a short overview on the analytical methods discussed in lecture 3 and 4.

Indicate for the following scenarios the method you would use and describe how you would go about solving the structure of an unknown compound using the previously methods (MS, NMR, IR, Index of Hydrogen Deficiency [IHD], Combustion Analysis, U-Vis). Use every technique **once**.

a) Determine the molar mass of the compound:

b) Find the mass percentage of each element in the compound:

c) Given the molecular formula determine how many multiple bonds and/or rings our molecule has:

d) Determine the functional groups of your compound:

e) Search for conjugated pi-bond systems:

f) Given the molecular formula determine the bonding network:

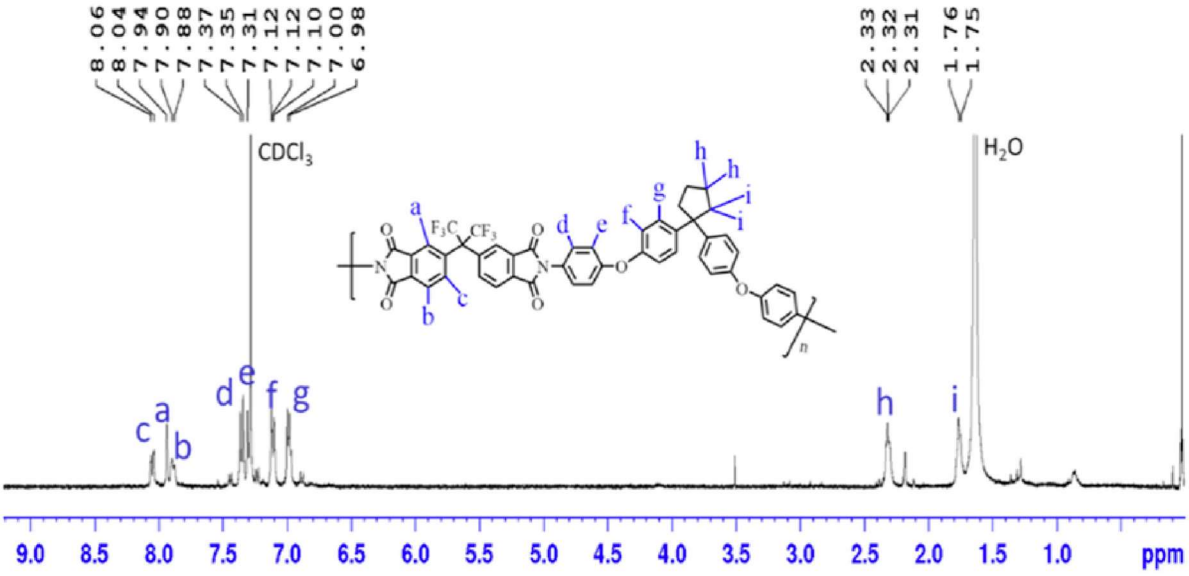
4.1 Basics of NMR

a) A student with a piercing wants to start a PhD in a NMR lab. What advice would you give this person?

b) Which of these isotopes is NMR-active? What does NMR-active mean?

- ^{1}H $I = ½$
- ^{12}C $I = 0$
- ^{13}C $I = ½$
- ^{14}N $I = 1$
- ^{16}O $I = 0$
- ^{19}F $I = ½$
- ^{31}P $I = ½$

c) Look at the ^{1}H NMR spectrum below. There is a peak located at 0 ppm, which can not be assigned to any hydrogen atom of the compound. Why is it present in the NMR spectrum? Why is the y-axis in ppm and not in Hz?



4.2 Chemical Equivalence, Shielding and Chemical Shifts

a) You are conducting a ^{1}H NMR experiment on the following molecules. Draw the molecules and indicate the chemically equivalent atoms relevant to your experiment in the structures.

Ethane

Ethanol

Phenol

2-Pentanone

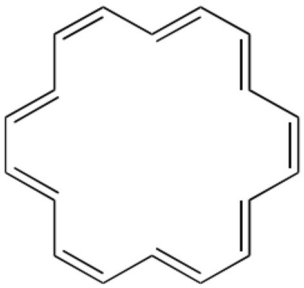
Chloroethene

1,4-Dimethylbenzene

1,2-Dichlorbenzene

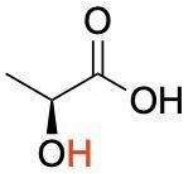
b) Explain how electrons affect the resonance frequency of a given proton. *A sketch may help you.* What does this mean to chemically non-equivalent atoms in NMR?

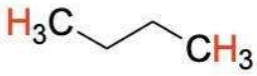
c) Below, the structure of [18]-Annulene is given. In the ^{1}H NMR experiment you observe two peaks: 8.9 ppm and -1.8 ppm in reference to TMS. Assign the two peaks to the protons in [18]-Annulene.

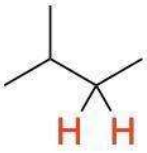


4.3 Spin-Spin Interactions: Multiplicity of NMR signals

For the protons highlighted in red in the structures below, indicate the multiplicity of the NMR signal and highlight the coupling protons.



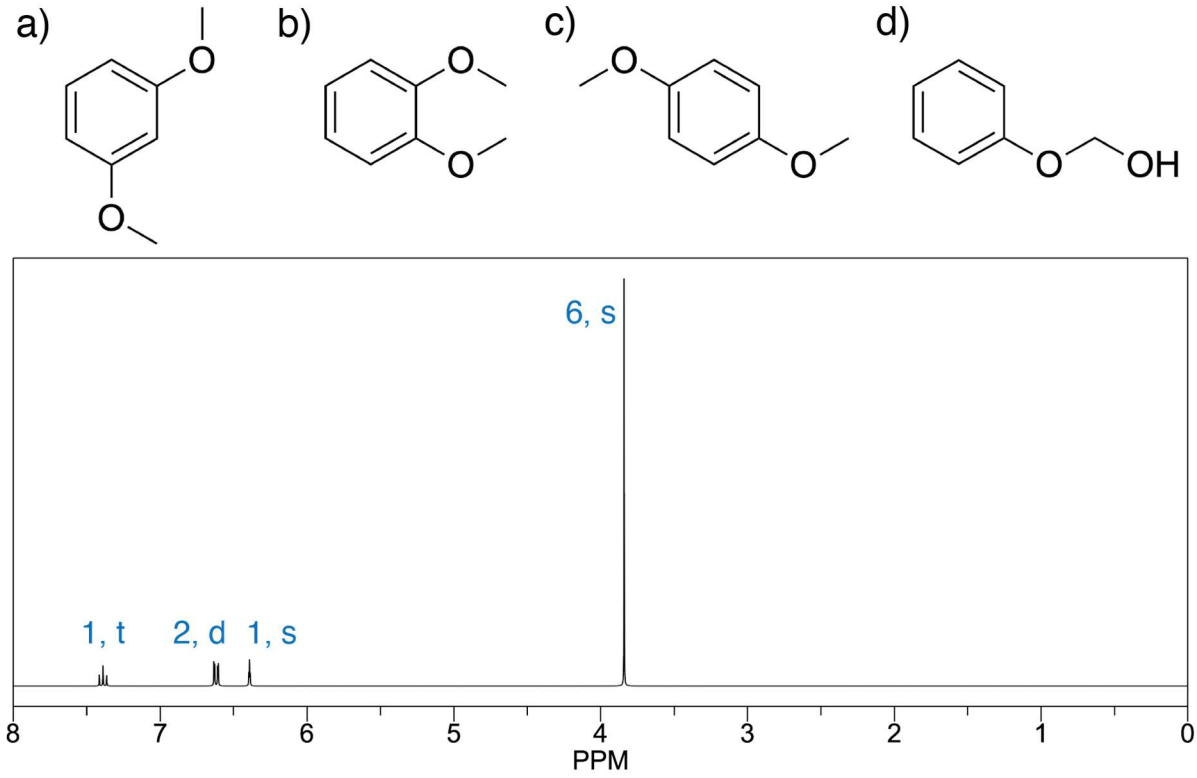




4.4 ^{1}H NMR of molecules

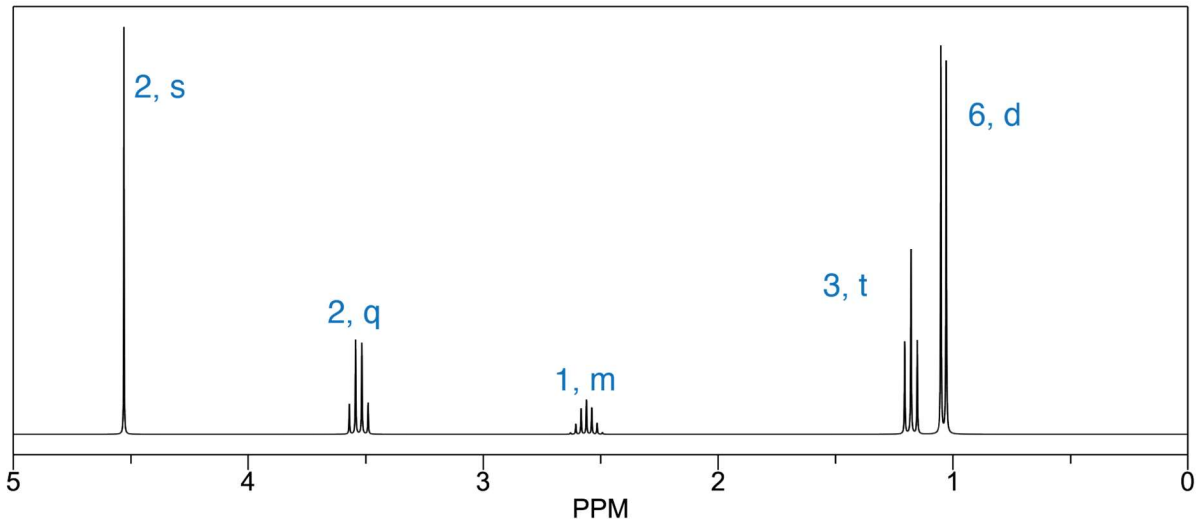
To which molecule does the following NMR spectrum belong?

I)



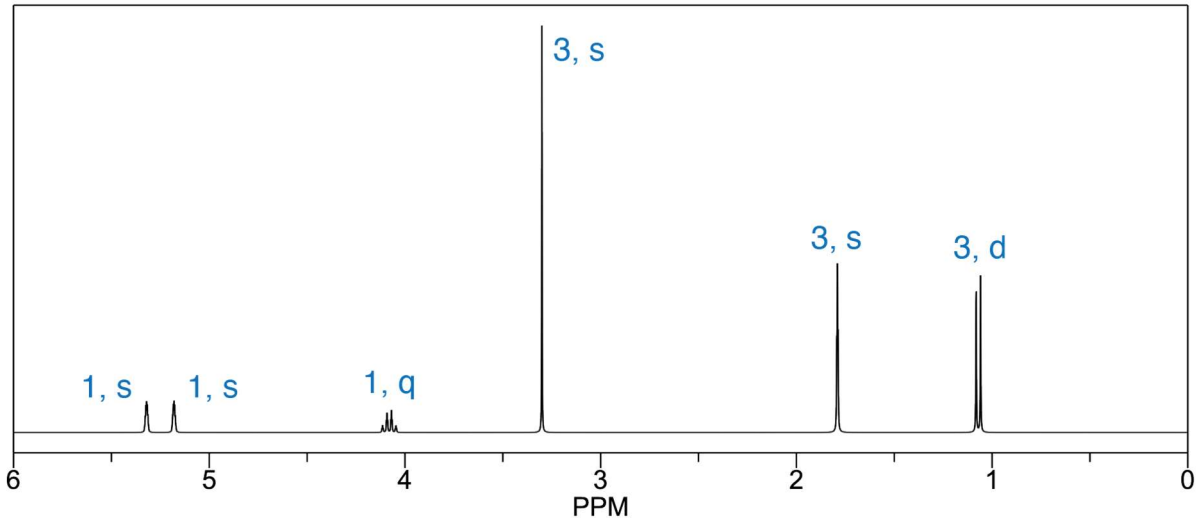
II)

a) b) c) d)



III)

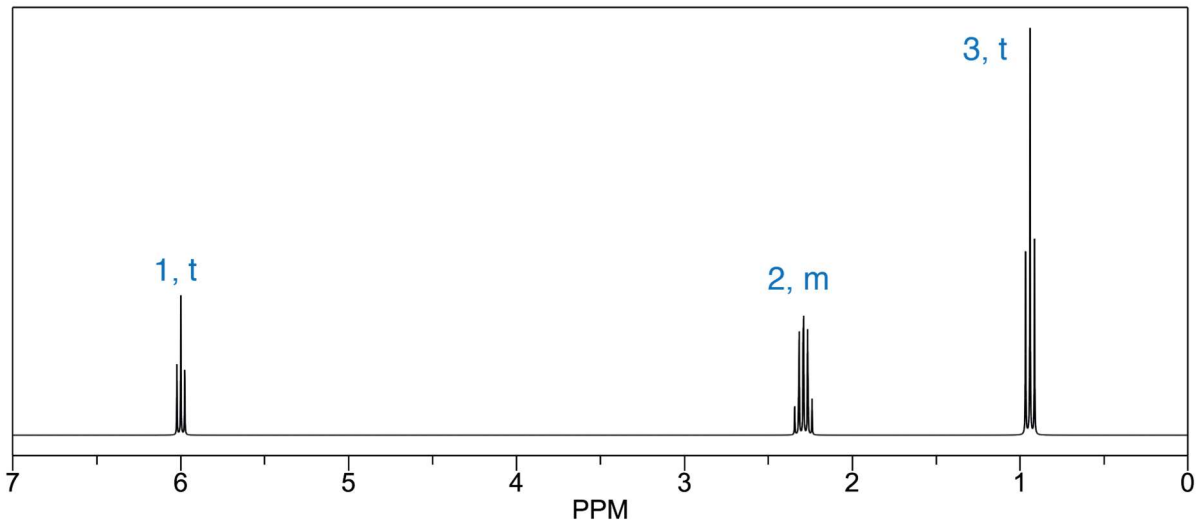
a) b) c) d)



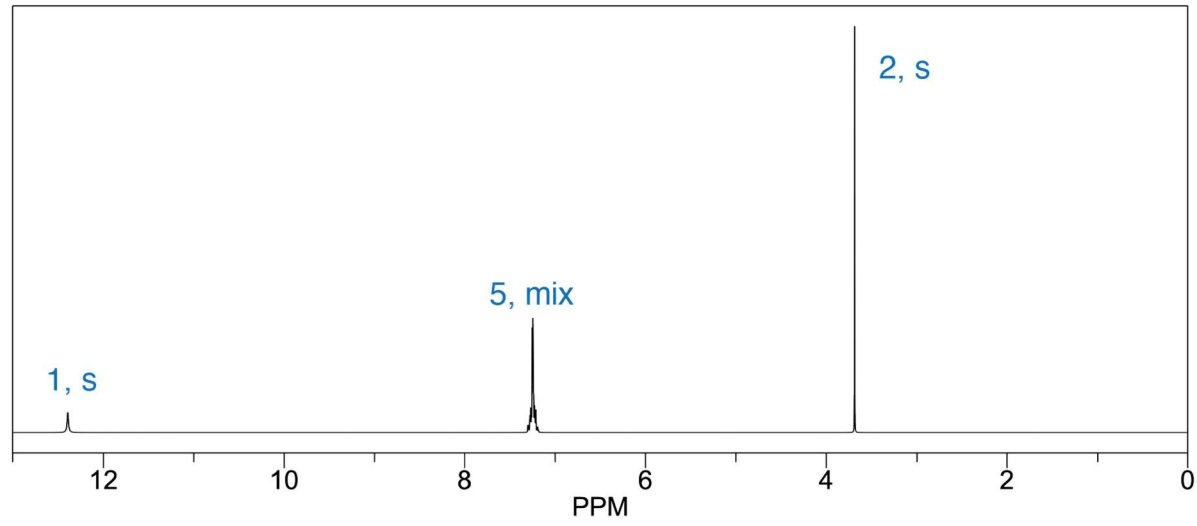
4.5 ^{1}H NMR spectra with unknown structures

Give the structures for the following chemical formulas given their respective NMR spectrum.

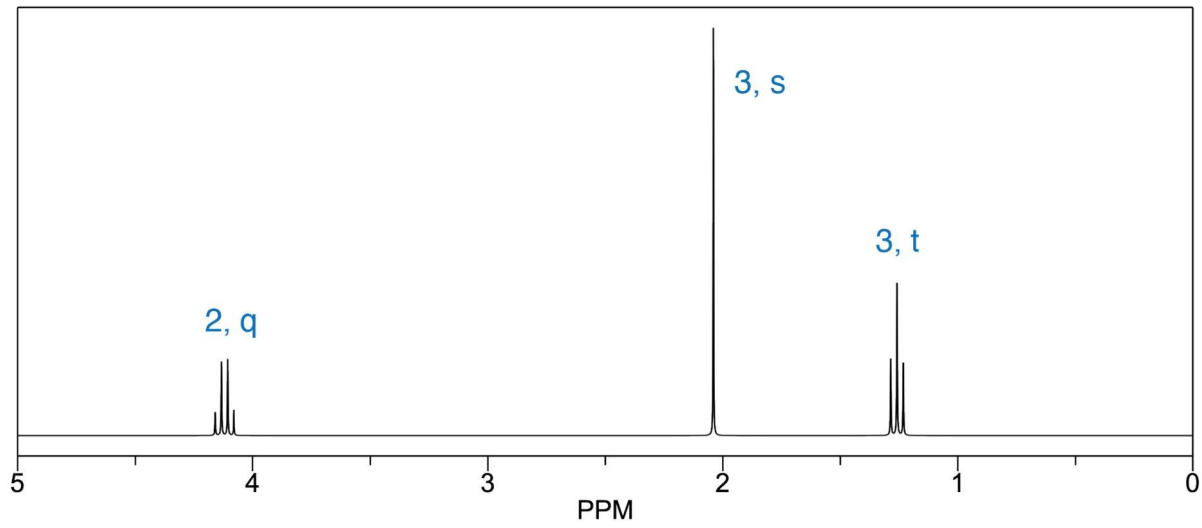
I) $C_3Br_2H_6$



II) $C_8H_8O_2$

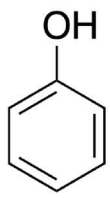


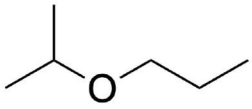
III) $C_4O_2H_8$

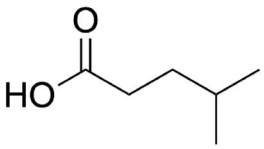


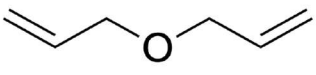
4.6 ^{13}C NMR of molecules

Match the structures below to their corresponding ^{13}C NMR spectra. Explain which peaks match with which carbon atoms.

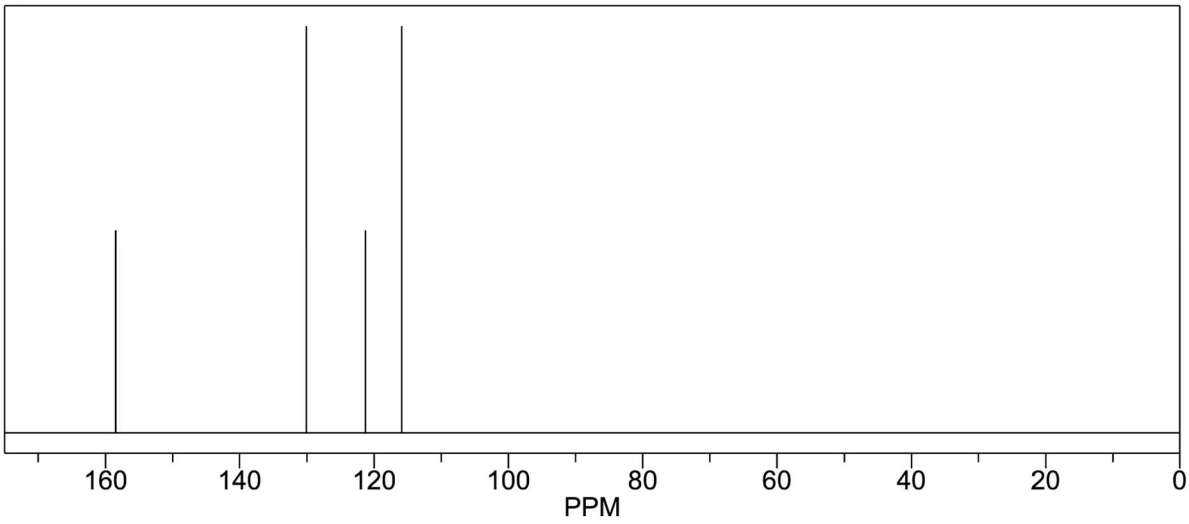
a) 

b) 

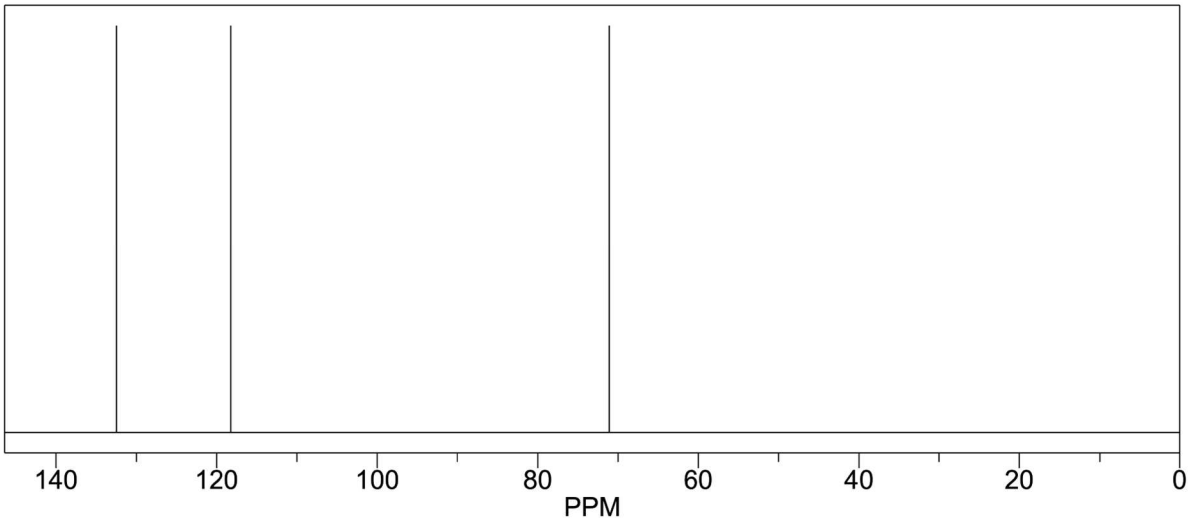
c) 

d) 

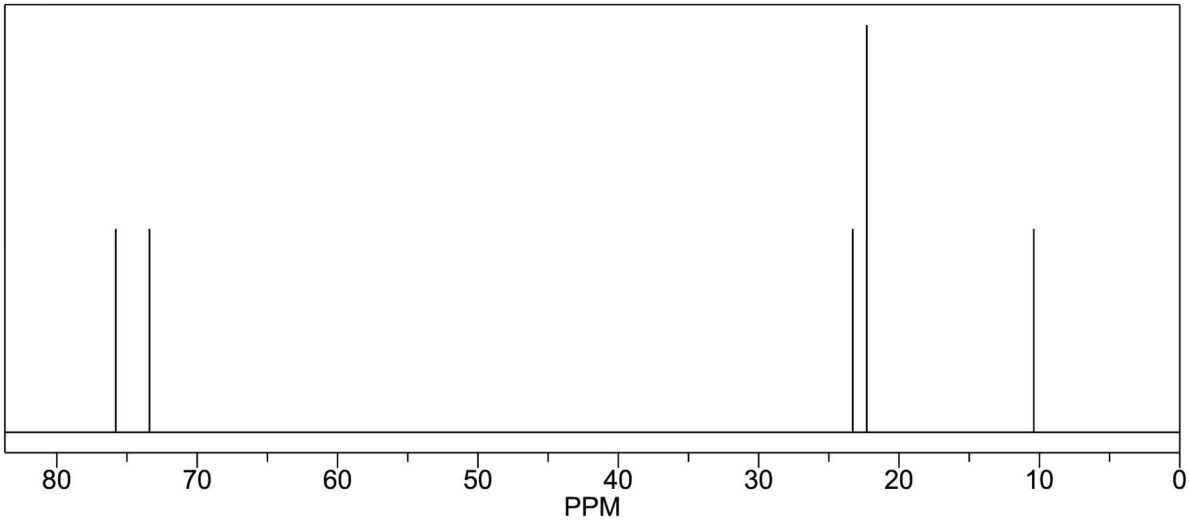
I)


160
140
120
100
80
60
40
20
0
PPM

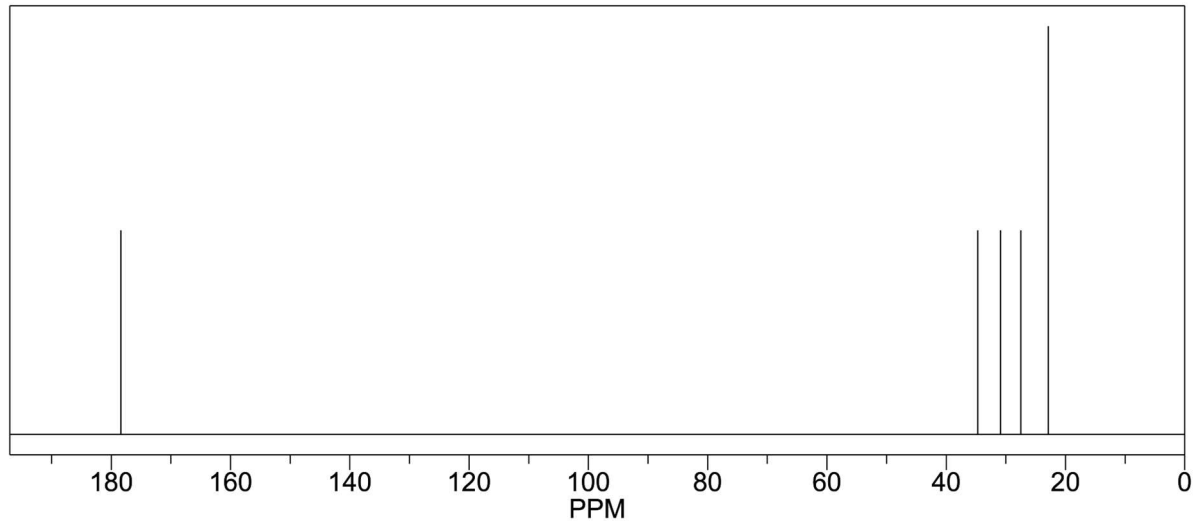
II)


140
120
100
80
60
40
20
0
PPM

III)


80
70
60
50
40
30
20
10
0
PPM

IV)



4.7 All together

Draw the compounds using the given experimental data.

a) Molecular weight: 88

Combustion analysis:
C: 68.2%
H: 13.6%

IR: ~3349 cm^-1 (broad)

^{1}H-NMR:

δ (ppm)	splitting	integration
3.38	s	2H
2.17	s	1H
0.91	s	9H

^{13}C-NMR

δ (ppm)	
73.35	CH_2
32.61	C
26.04	CH_3

b) Molecular weight 148

Combustion analysis:
C: 81.1%
H: 8.1%

IR: 1713 cm^-1 (strong)

^{1}H-NMR:

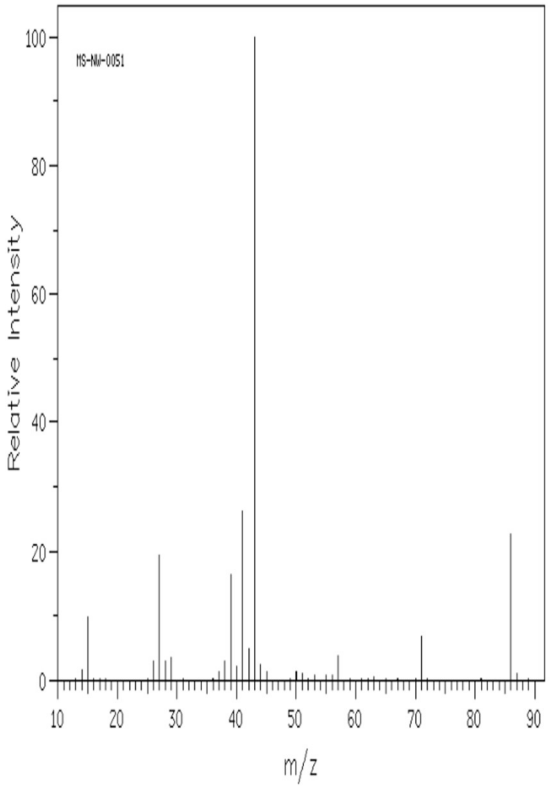
δ (ppm)	splitting	integration
7.18-7.35	m	2.5
3.66	s	1
2.44	q	1
1.01	t	1.5

^{13}C-NMR

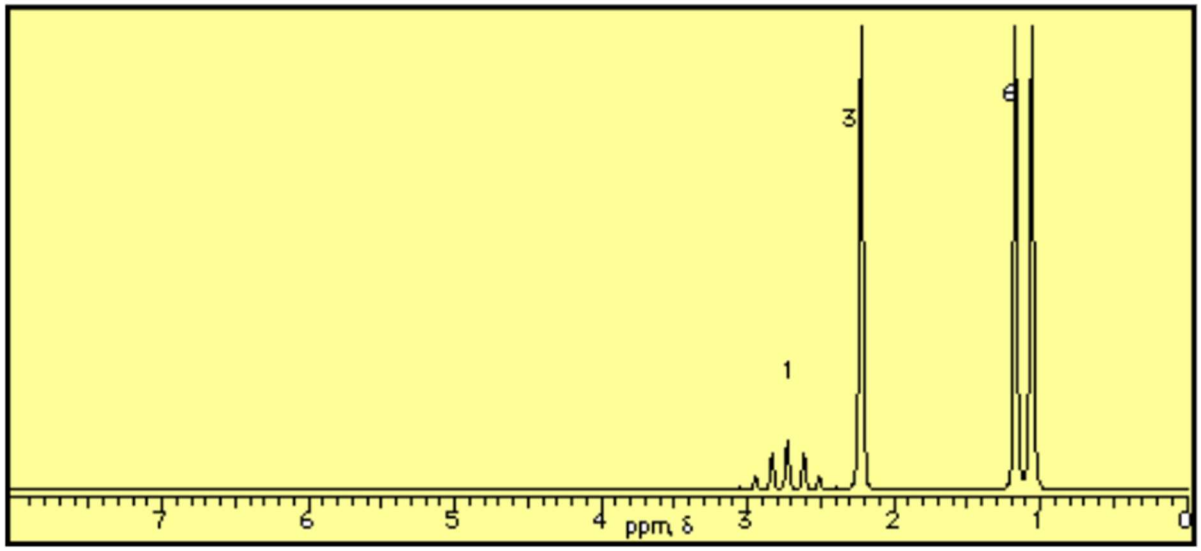
δ (ppm)	
208.79	C
134.43	C
129.31	CH
128.61	CH
126.86	CH
49.77	CH_2
35.16	CH_2
7.75	CH_3

c) Combustion analysis: C (69.7%); H (11.7%)

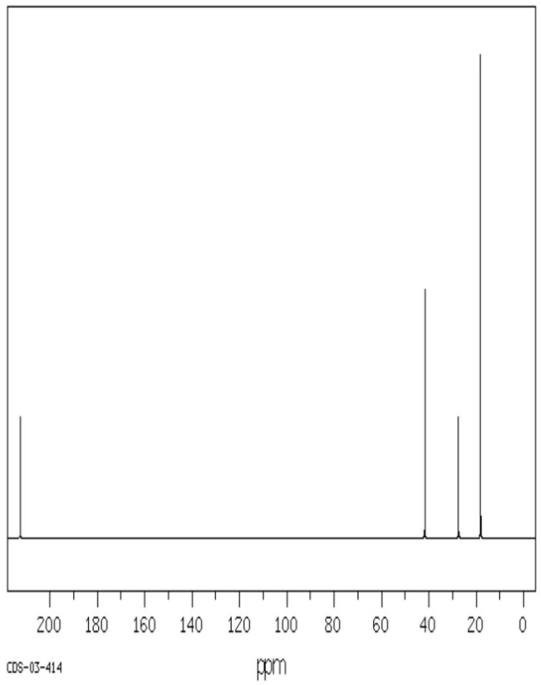
Mass Spectroscopy:



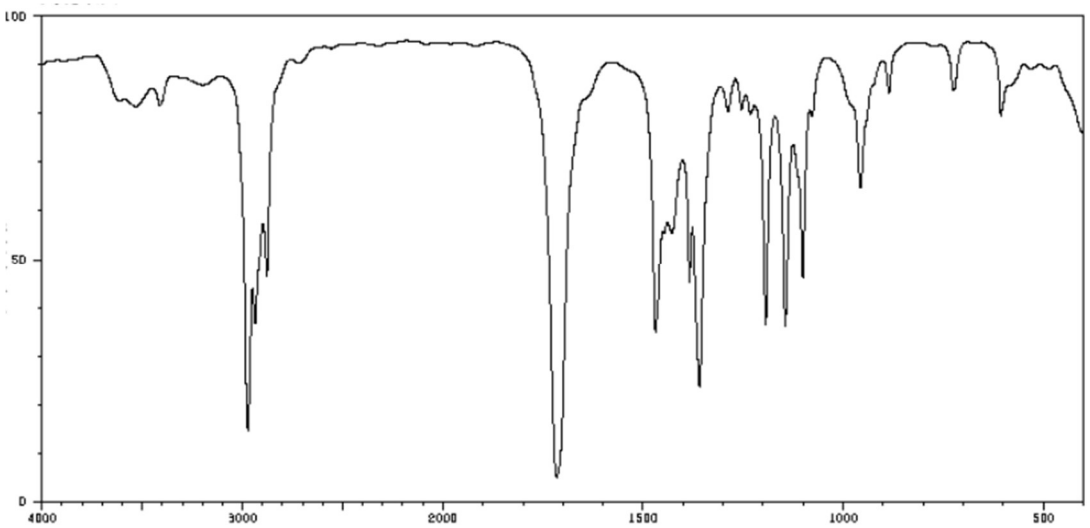
H-NMR:



C-NMR:


200 180 160 140 120 100 80 60 40 20 0
CDS-03-414
ppm

IR:


100
50
0
4000
3000
2000
1500
1000
500