Advice and Tips for the Identification of Organic Compounds by **Modern Analytical Techniques**

- SECTION 1

  Tables of typical chemical shifts for ^{1}H and ^{13}C atoms for reference.

- SECTION 2

  There are ^{1}H and ^{13}C spectra of 4 compounds. There is also some mass spectrometry data for each compound.

1. The first page of each problem contains the **elemental analysis**, some **mass spectrometry** data and the ^{1}H and ^{13}C spectra.
2. The second page of each problem contains the same information but with lots of **hints**
3. The third page is the **answer** with the molecule drawn and the NMR peaks all assigned.

- SECTION 3

  General advice and tips on;

  a) mass spectrometry analysis
  b) ^{1}H and ^{13}C NMR analysis

Note: An examination question may also present you with **infra-red data** and some evidence for the type of **chemical reactions** and/or **tests** that the compound undergoes.

.

Typical Chemical Shifts in ^{1}H NMR Spectra

Hydrogen	Compound Type	Typical Chemical Shift δ/ppm
R-C**H**$_3$, R$_2$-C**H**$_2$, R$_3$-C**H**	Alkane	0.8-1.5
C=C**H**	Alkene	4.6-5.9
Ar-**H**	Aryl	6.5-8.5
RC**H**$_2$*Cl*, RC**H**$_2$Br	Haloalkane	3-4.3
R-C**H**$_2$O	Alcohol, ether, ester	3.4-4.3
R-O**H***	Alcohol	0.5-5*
R-N**H**$_2$*	Amine	0.5-5*
R-C**H**-CO-R	Ketone	2-3
R-C**H**O	Aldehyde	9-10
R-CONHR	Amide	5-9
R-COO**H**	Carboxylic Acid	>10
TMS	Reference	0

* -O**H** & -N**H** protons can appear almost anywhere in the spectrum. They often appear very broad. Sometimes they can be split by neighbouring protons into multiplets and sometimes not. This depends upon the conditions; especially how dry the sample is.

Typical Chemical Shifts in ^{13}C NMR Spectra

Carbon	Compound Type	Typical Chemical Shift δ/ppm
C=O	Ketone	205-220
C=O	Aldehyde	190-200
C=O	Carboxylic acids, Esters	170-185
C-C	Arene	125-150
C=C	Alkenes	115-140
R**C**H$_2$OH	Alcohols	50-65
R**C**H$_2$NH$_2$	Amines	37-45
R**C**H$_2$*Cl*	Halogenoalkanes	40-45
R$_3$**C**H	3^{o} Alkanes	25-35
CH$_3$CO-	Ketone, Aldehyde, Carb. Acid, Ester	20-30
R$_2$**C**H$_2$	2^{o} Alkanes	16-25
R**C**H$_3$	1^{o}Alkanes	10-15
TMS	Reference	0

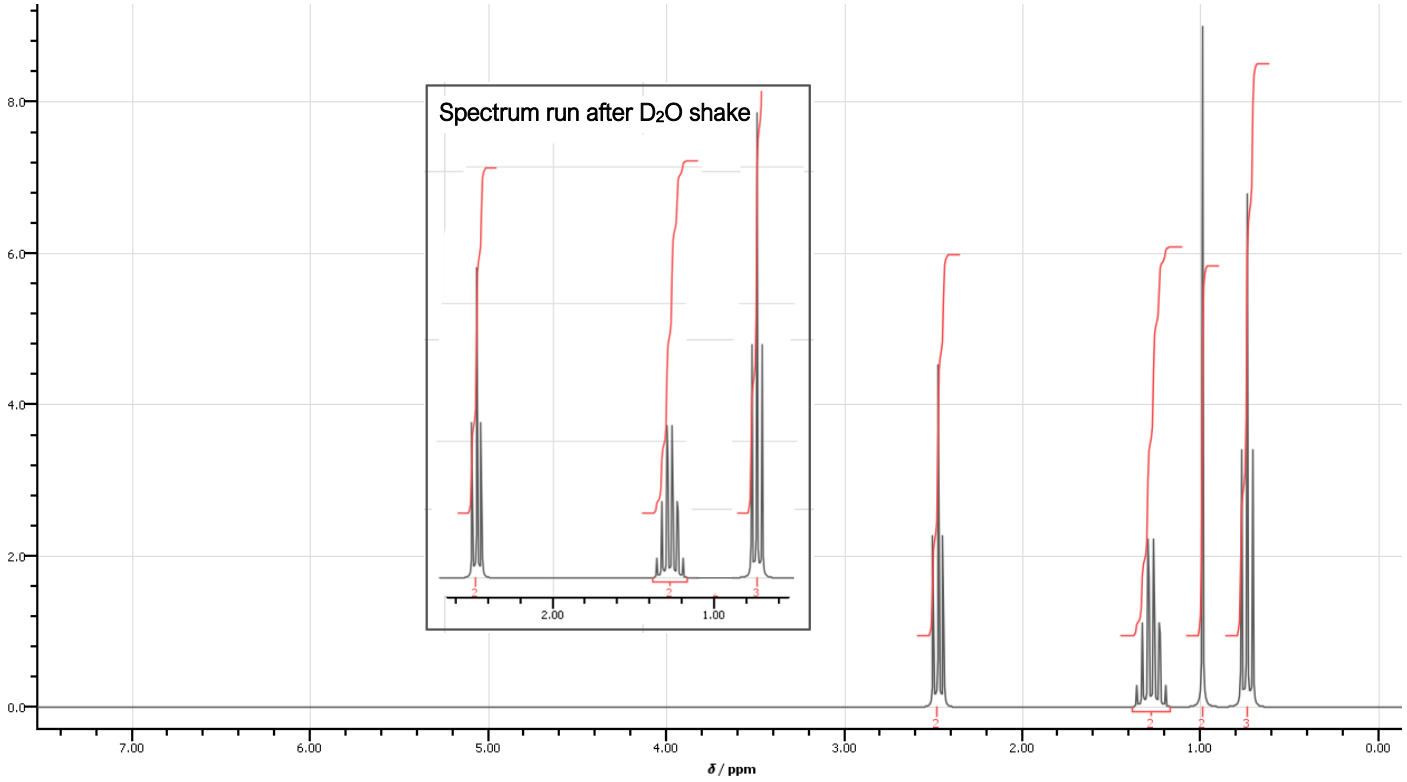
PROBLEM 1

Composition: C (60.96%), H (15.35%), N (23.70%)

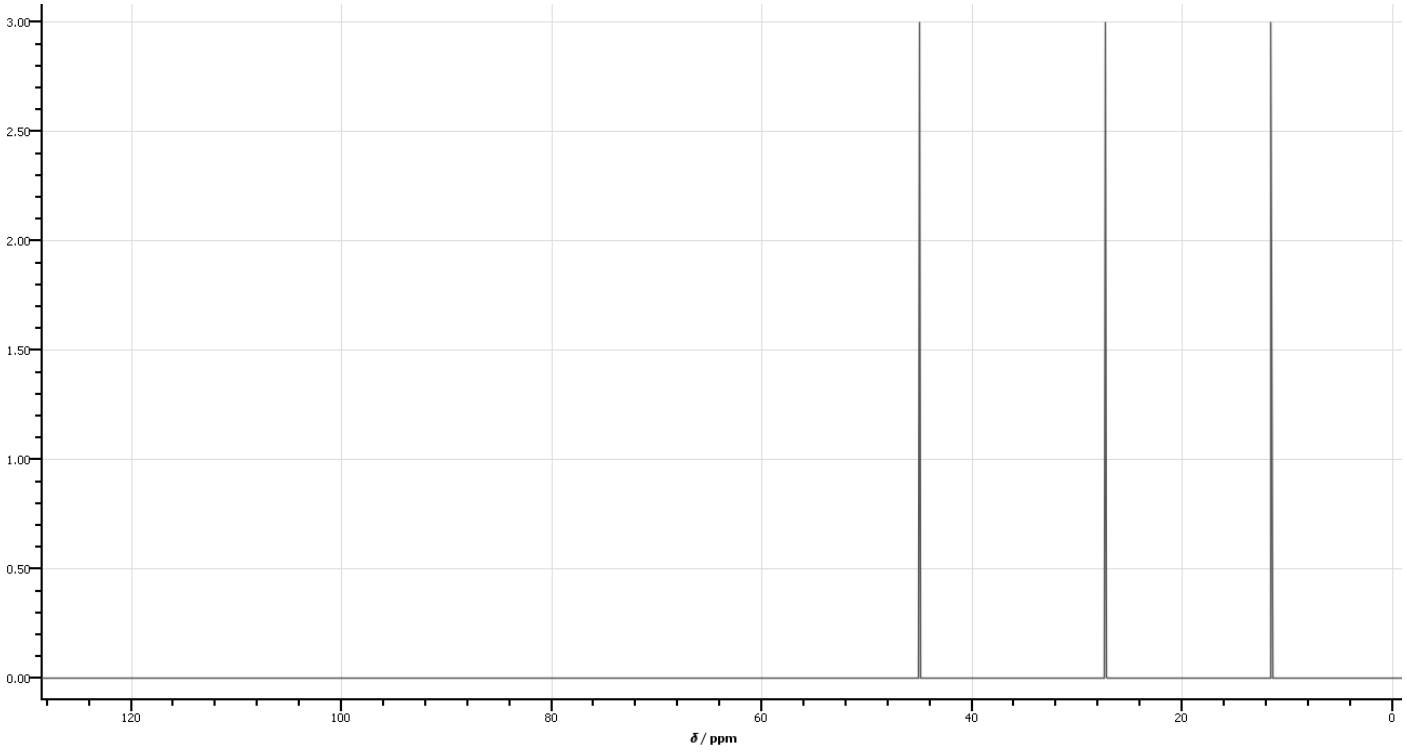
Mass spectrometry information (fragmentation pattern not very helpful!)

prominent peaks at m/z= 59, 30

^{1}H NMR



^{13}C NMR



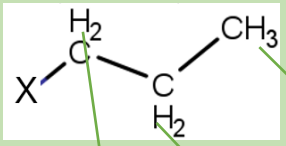
PROBLEM 1 with hints

Molecular formula: C_3H_9N This is a **saturated** small molecule. The **nitrogen** also suggests **amine** or **substituted amine.** **Simple 1°, 2° or 3° amines** (no other functional groups) have a **general formula $C_nH_{2n+3}N$.** This fits!

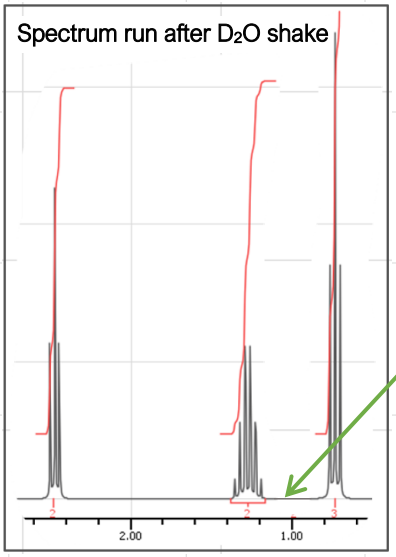
M^+ at 59 gives the molecular weight of the compound. There is a peak at **30** which could be **$H_2NCH_2^+$** 1° amines tend to fragment to give this ion! Don't worry about remembering that.

^{1}H NMR

2 x triplets (integration 2:3) and multiplet (sextet) (integration 2) grouping respectively is always a strong hint at a **propyl group**
This would account for **7 of the 9 protons** in the formula.
The remaining **2 protons** must be on the **N atom.**
This suggests a **primary amine**.



2 protons must be on the N atom.

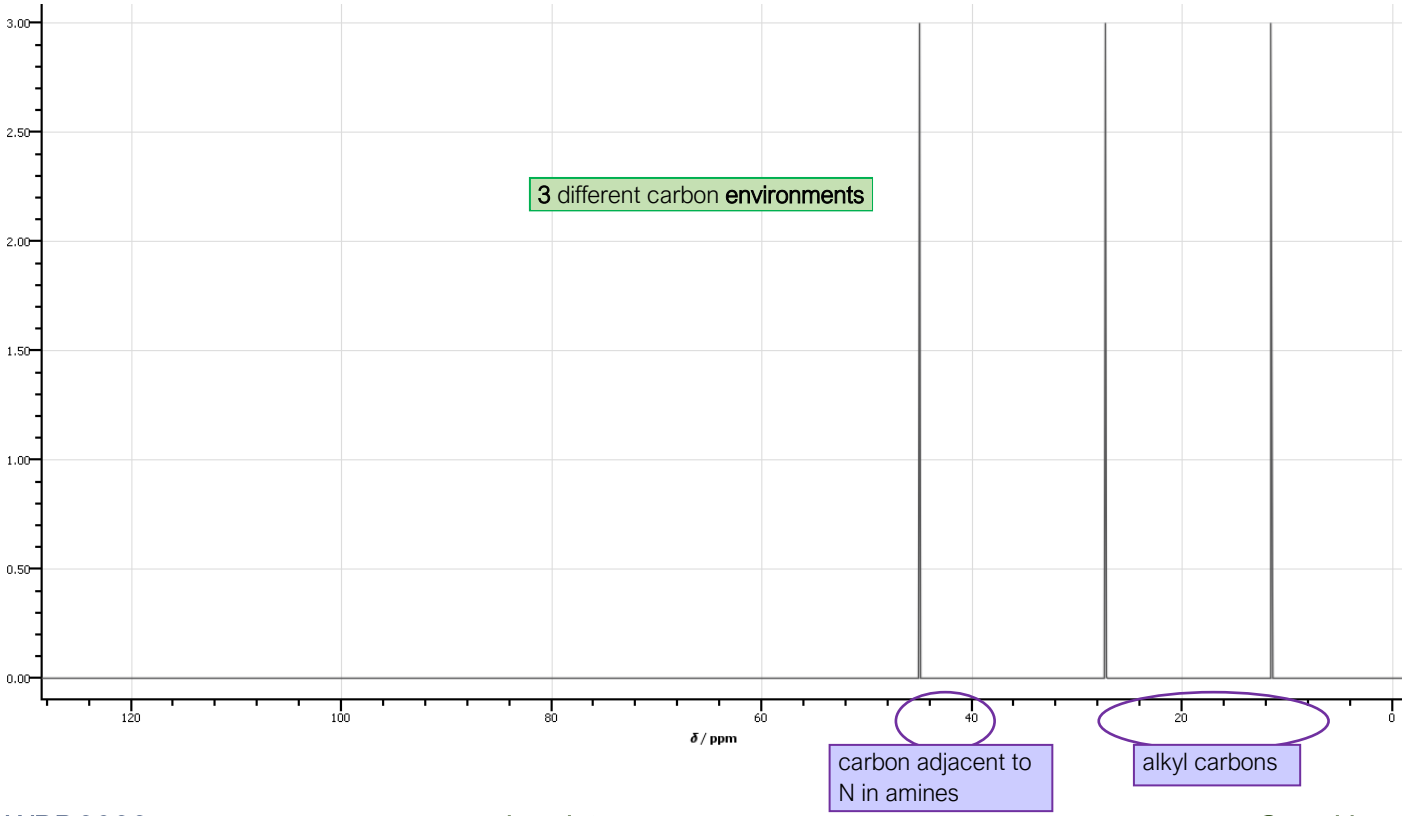


Spectrum run after **D_2O shake** shows that the N**H** has disappeared from the spectrum. The **D** (^{2}H) have **exchanged** with exchangeable (labile) ^{1}H on the Nitrogen. This occurs with N**H** and O**H** protons.

D (^{2}H) atoms are **invisible** in this typical region of the spectrum.

^{13}C NMR

3 different carbon **environments**

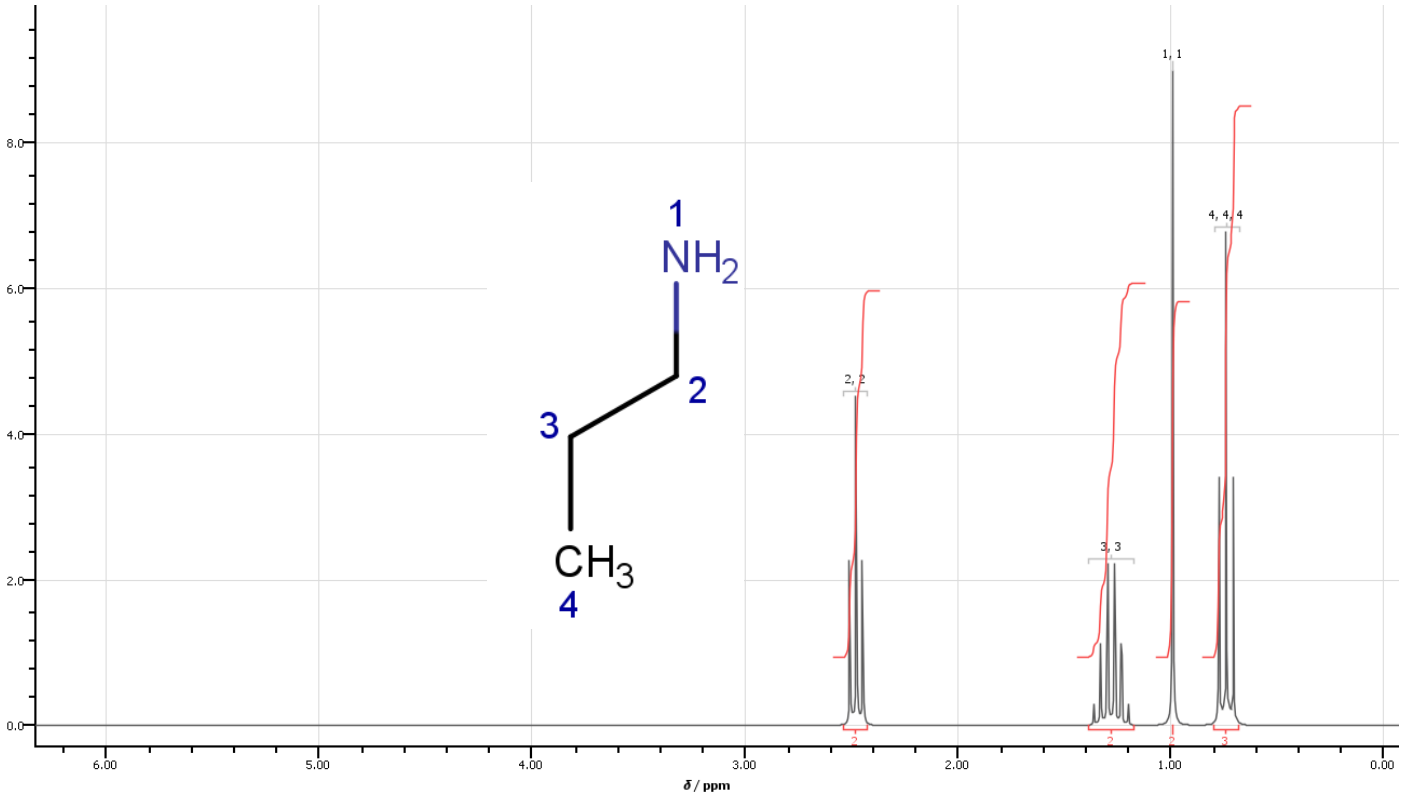


PROBLEM 1 **ANSWER**

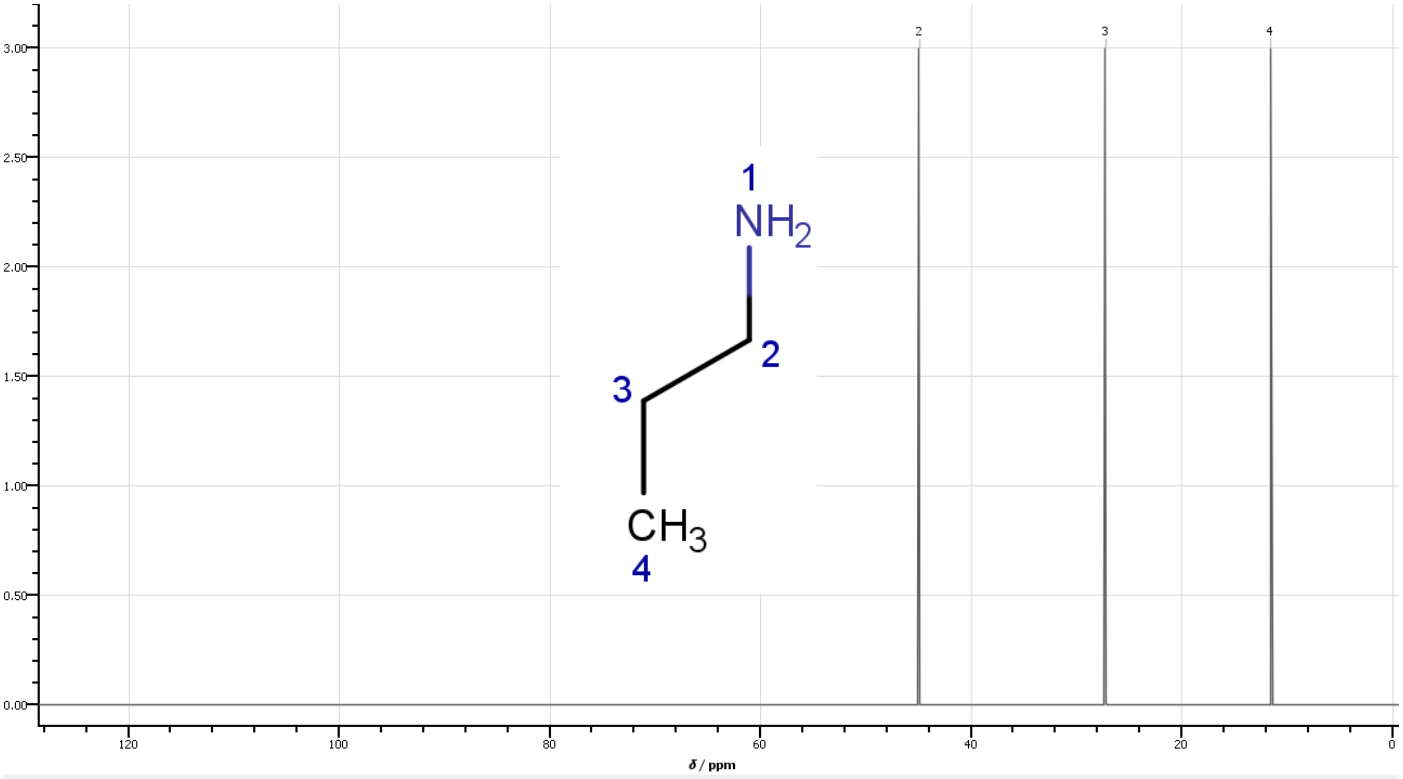
Formula: C_3H_9N

Preferred IUPAC Name = propylamine

^{1}H NMR



^{13}C NMR



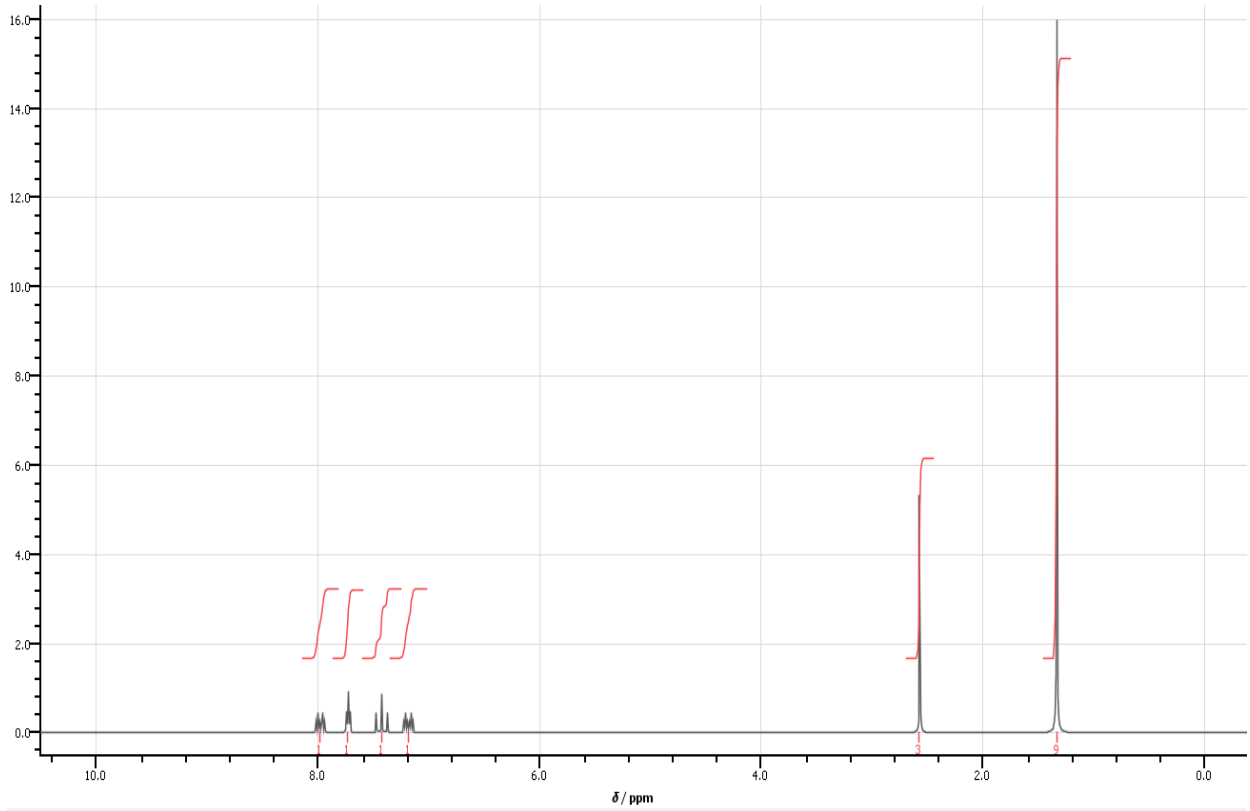
PROBLEM 2

Composition: C (81.77%), H (9.15%), O (9.08%)

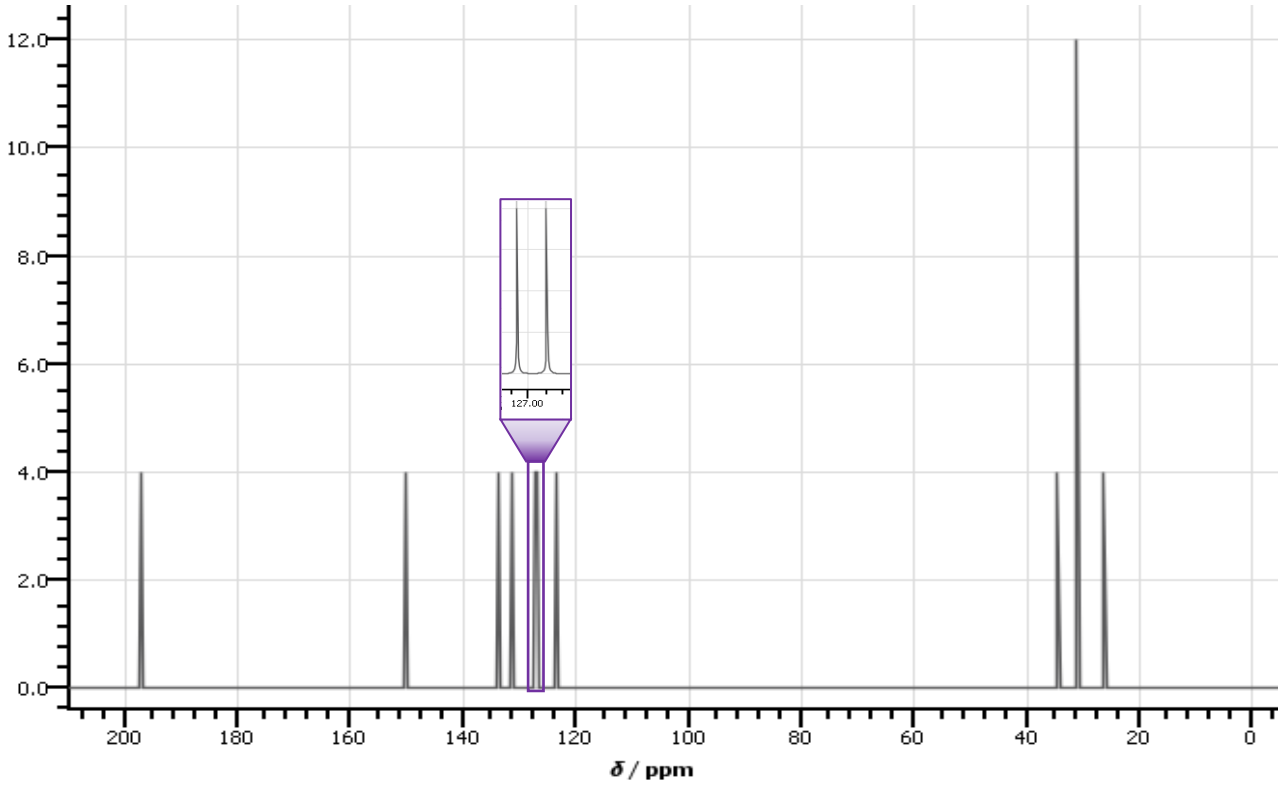
Mass spectrometry information

prominent peaks at m/z= 176, 57 and 43

^{1}H NMR



^{13}C NMR



Problem 2 with hints

Composition: C (81.77%), H (9.15%), O (9.08%)

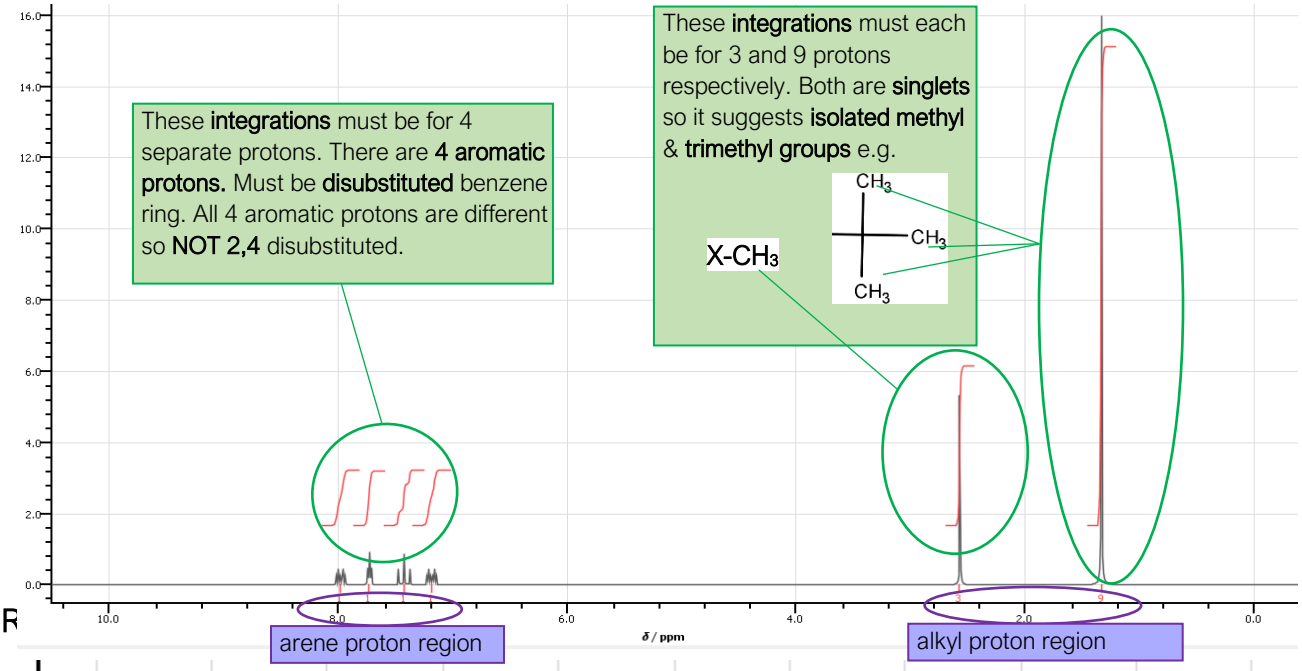
Molecular formula: $C_{12}H_{16}O$ This is **very unsaturated** and has **many carbons**. This suggests presence of a **benzene ring**. The single oxygen also suggests **aldehyde** or **ketone**.

Mass spectrometry information

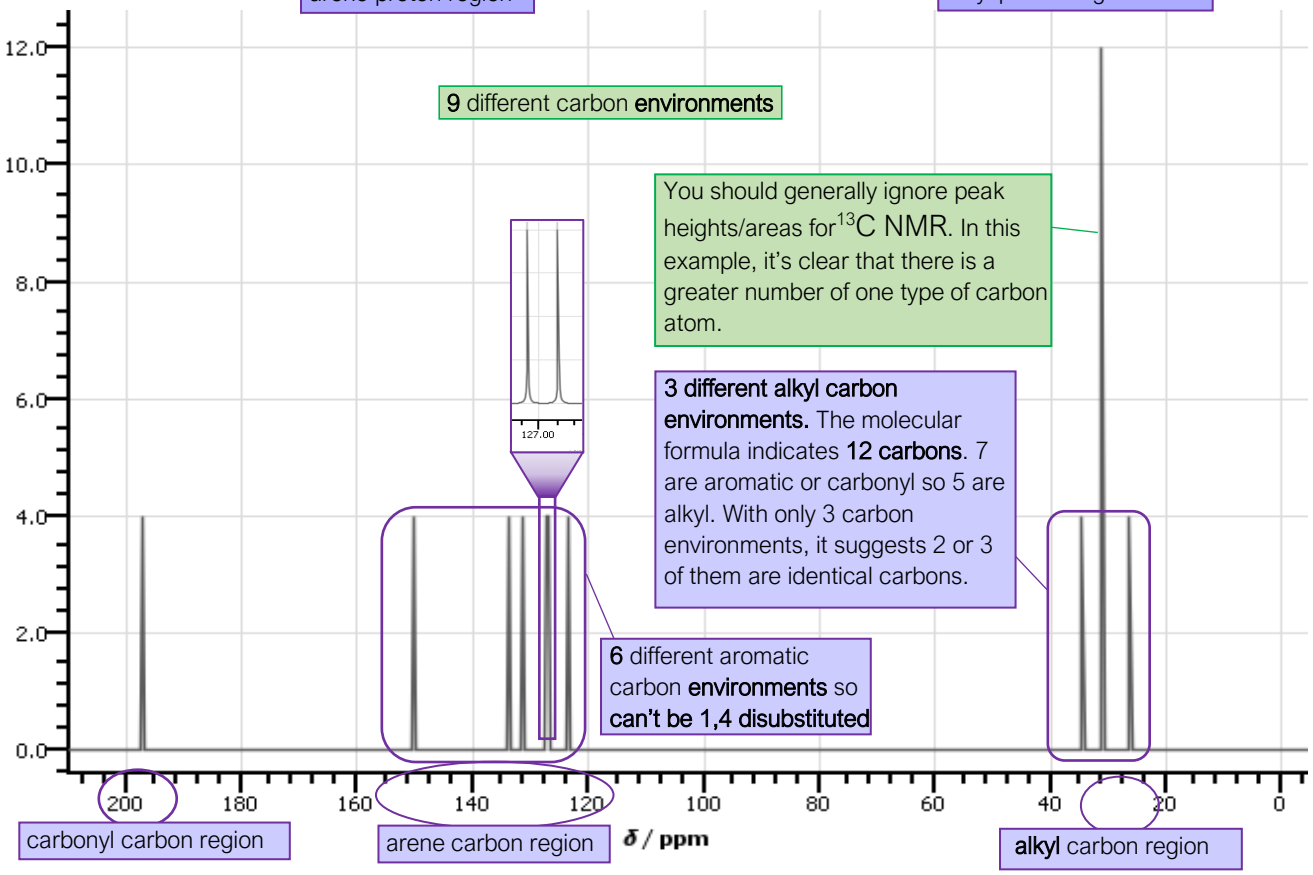
prominent peaks at m/z= 176, 57 and 43

You can assume that the M^+(parent ion) is **176** so Molecular weight: **176**
Also, there is a peak a **57** which could be a **butyl group**. This could be **1°, 2°** or **3°**
Also, there is a peak a **43** which could be a **propyl group** (1° or 2°) or an **acetyl group (CH_3CO^+)**.

^{1}H NMR



^{13}C NMR



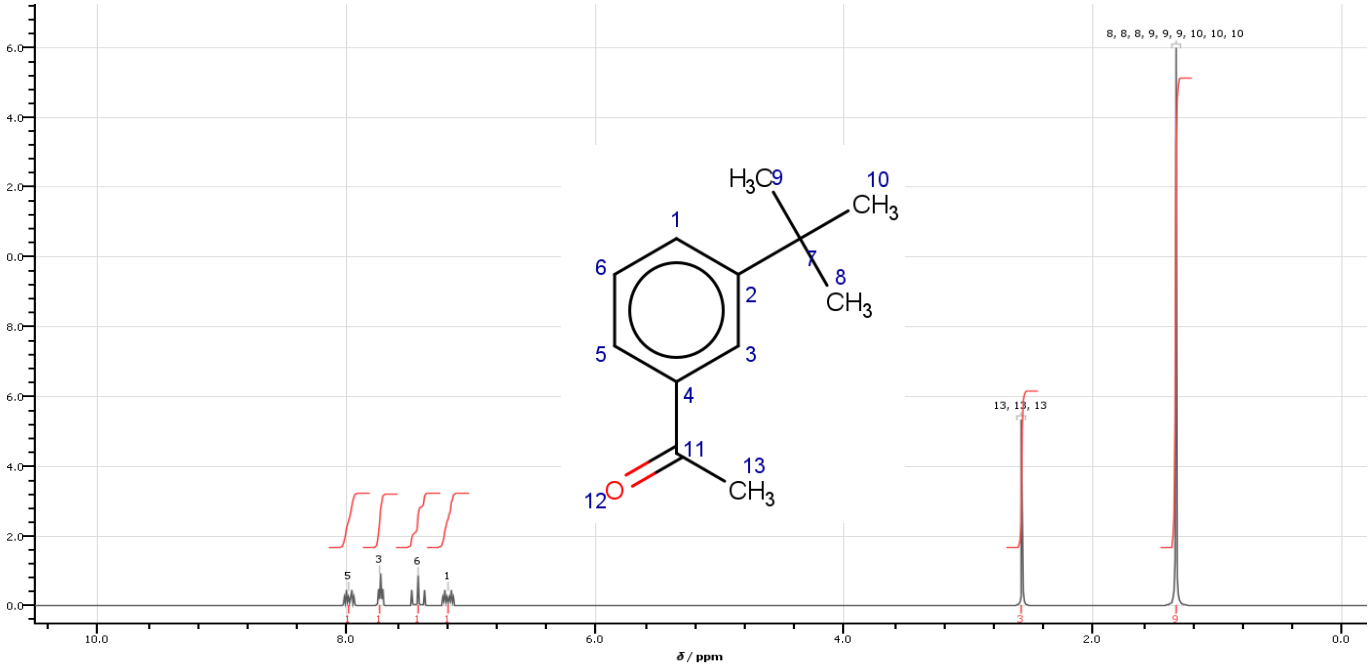
QUESTION 2 ANSWERS

Molecular formula: $C_{12}H_{16}O$

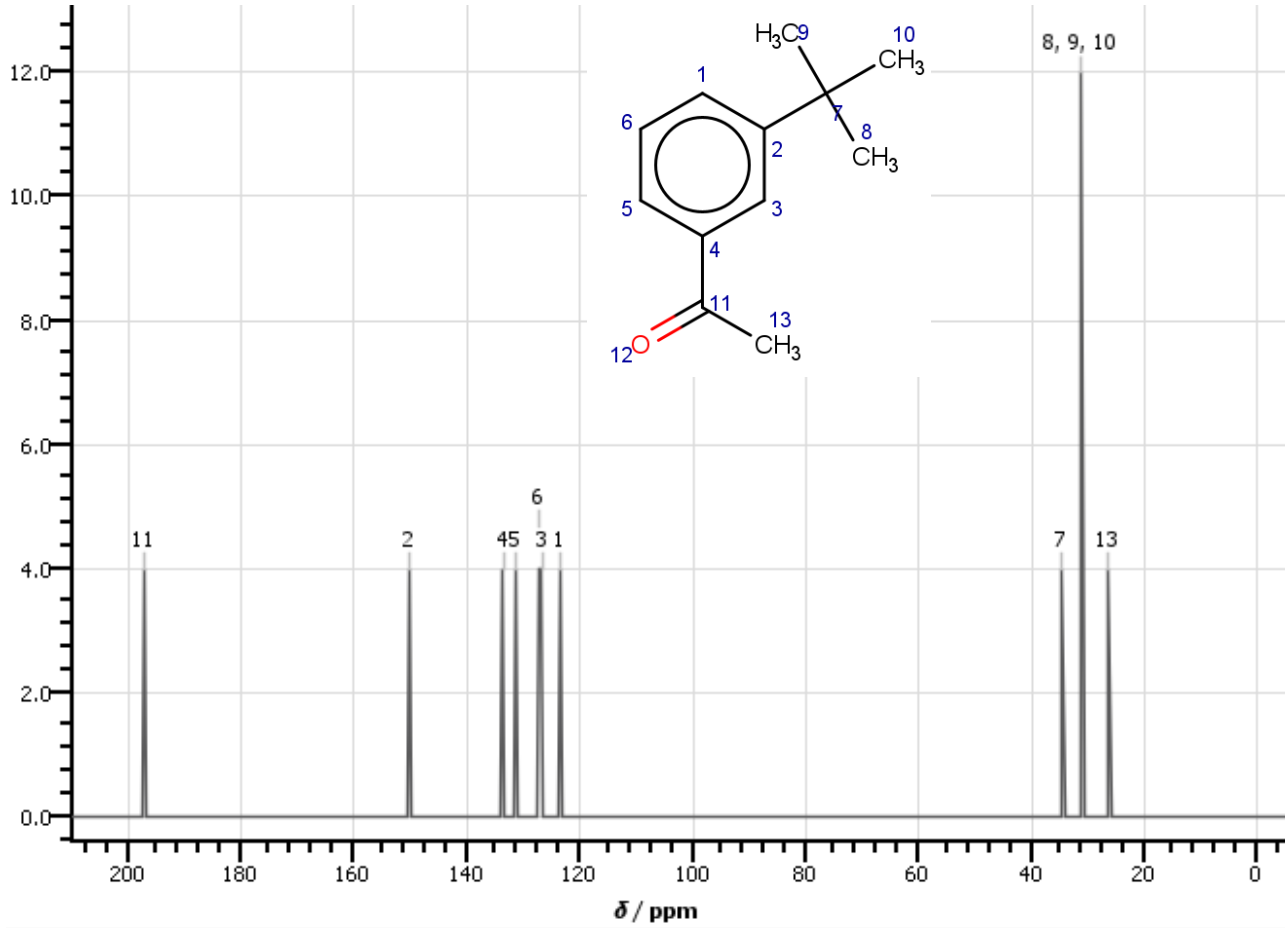
Preferred IUPAC Name = 1-(3-tert-butylphenyl)ethan-1-one (you wouldn't be expected to name this. Don't worry!)

Molecular weight: 176.3

^{1}H NMR



^{13}C NMR



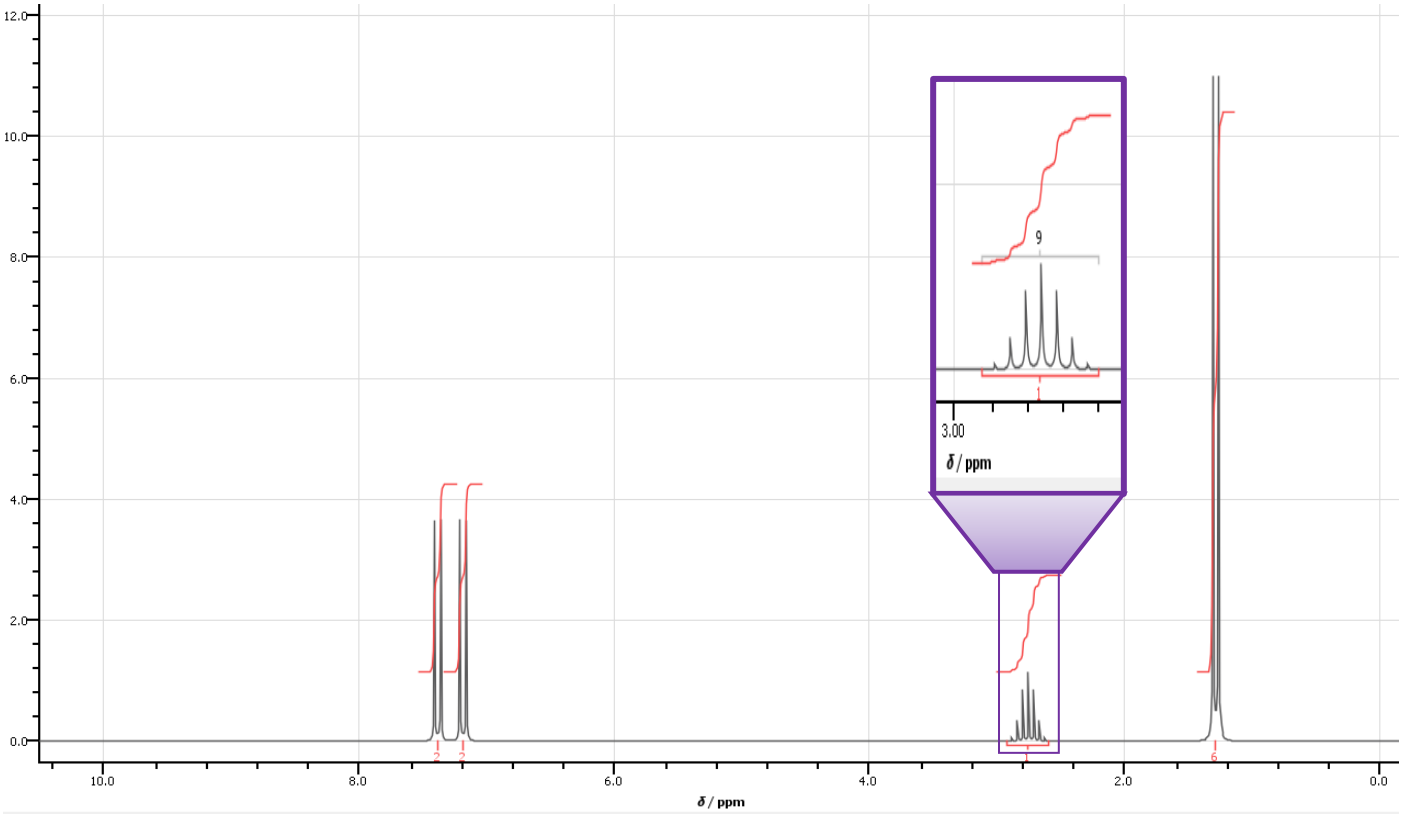
PROBLEM 3

Composition: C (60.46%), H (5.58%), Cl (17.85%), O (16.11%)

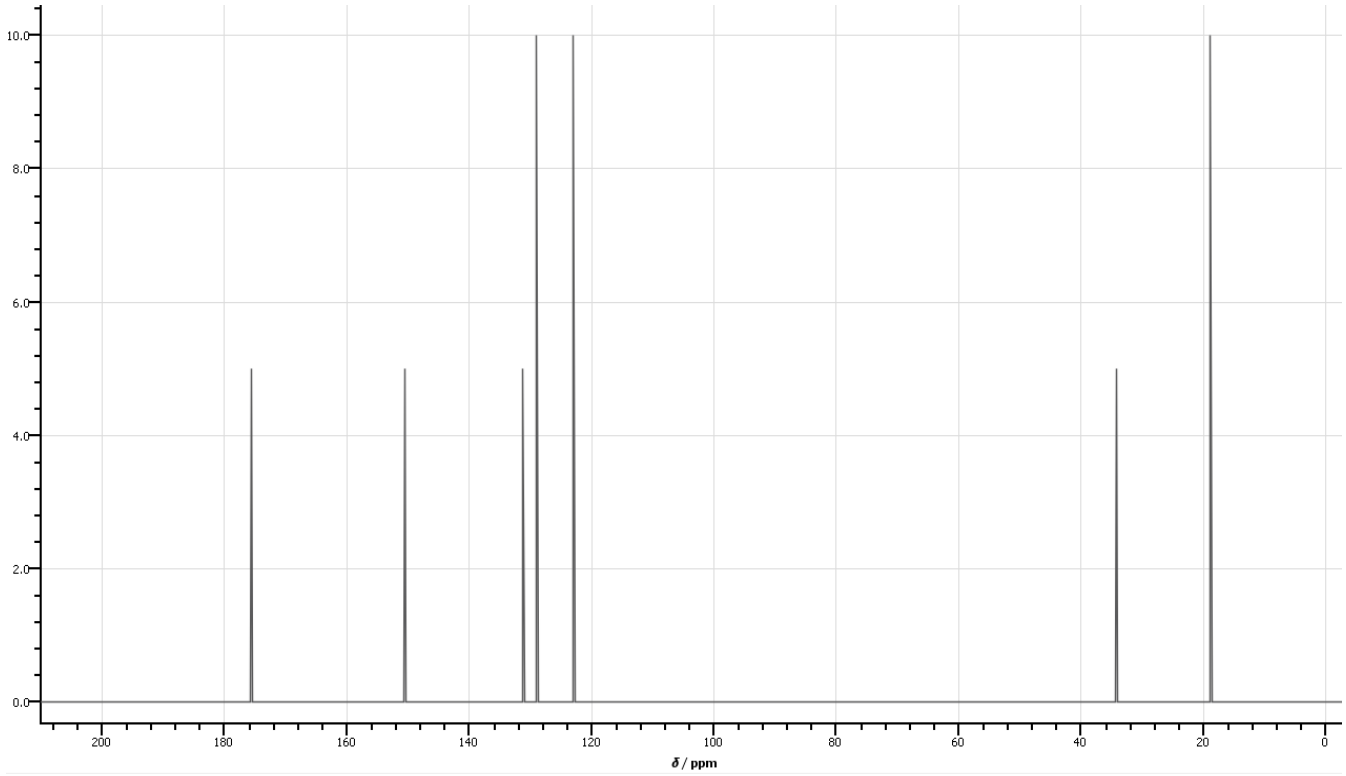
Mass spectrometry information

prominent peaks at m/z= 200 &198 (abundance ratio1:3) , 71, 43

^{1}H NMR



^{13}C NMR

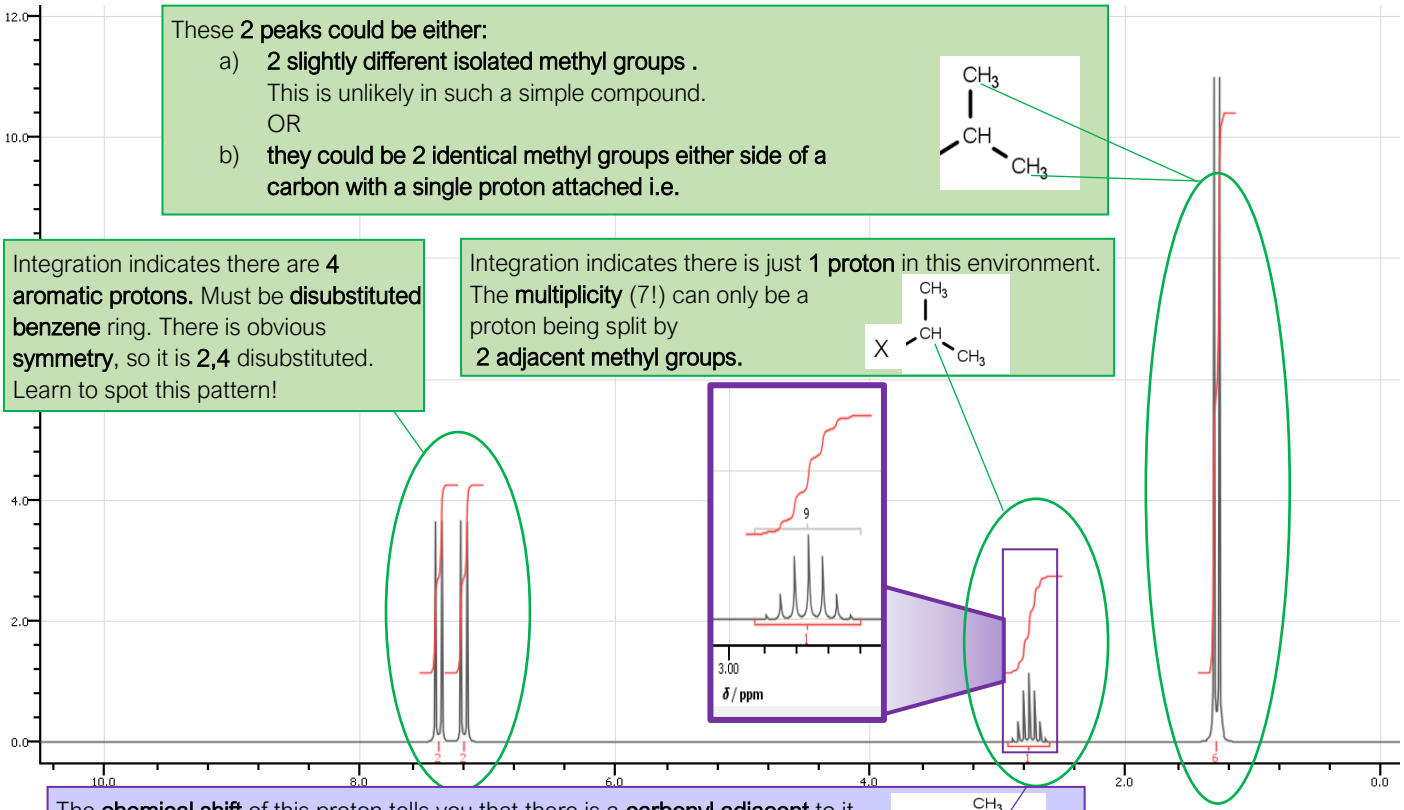


PROBLEM 3 with hints

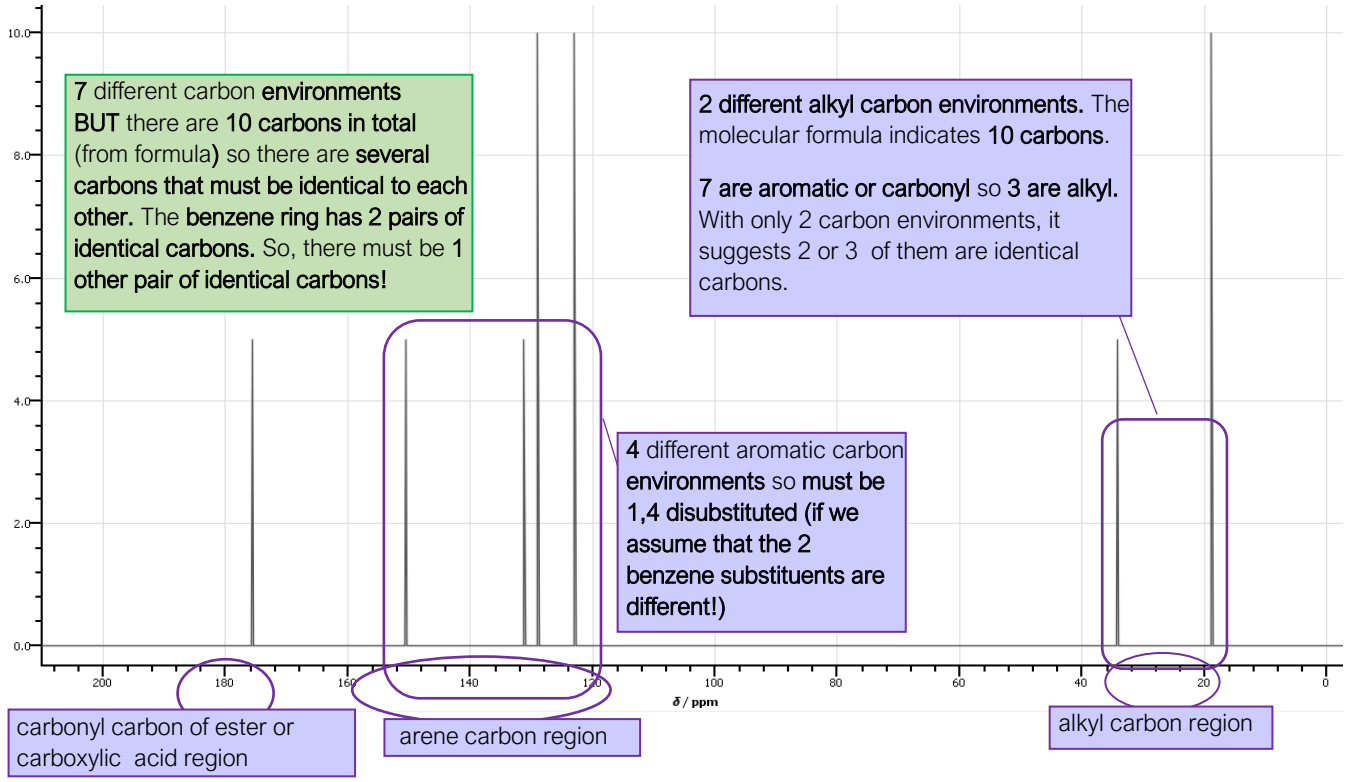
Molecular formula: $C_{10}H_{11}ClO_2$ This is **very unsaturated** and has **many carbons**. This suggests presence of a **benzene ring**. The **2 oxygens** also suggest **carb acid** or **ester**.

The **pair of peaks** at **198** and **200** with the **ratio 3:1** is a hint at a molecule containing a **Cl** atom. This is the pair of **Cl** isotopes' m/z peaks (M and M+2). This is known as the **isotope effect** (see SECTION 3). Also, there is a peak a **43** which could be a **propyl group**. This could be **1° or 2°** Also, there is a peak a **71** which could be a **propyl-C=O fragment**.

^{1}H NMR



^{13}C NMR

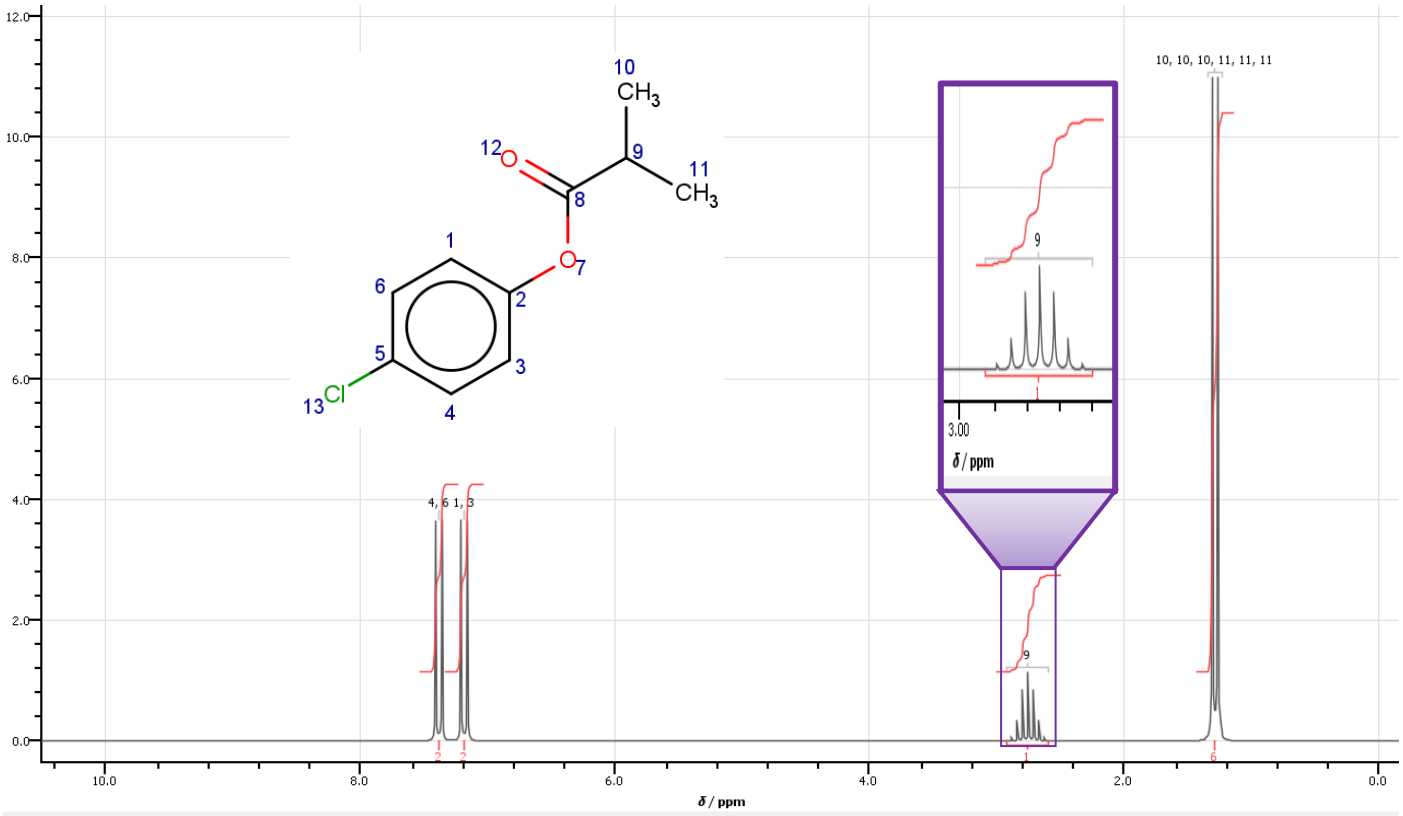


PROBLEM 3 ANSWER

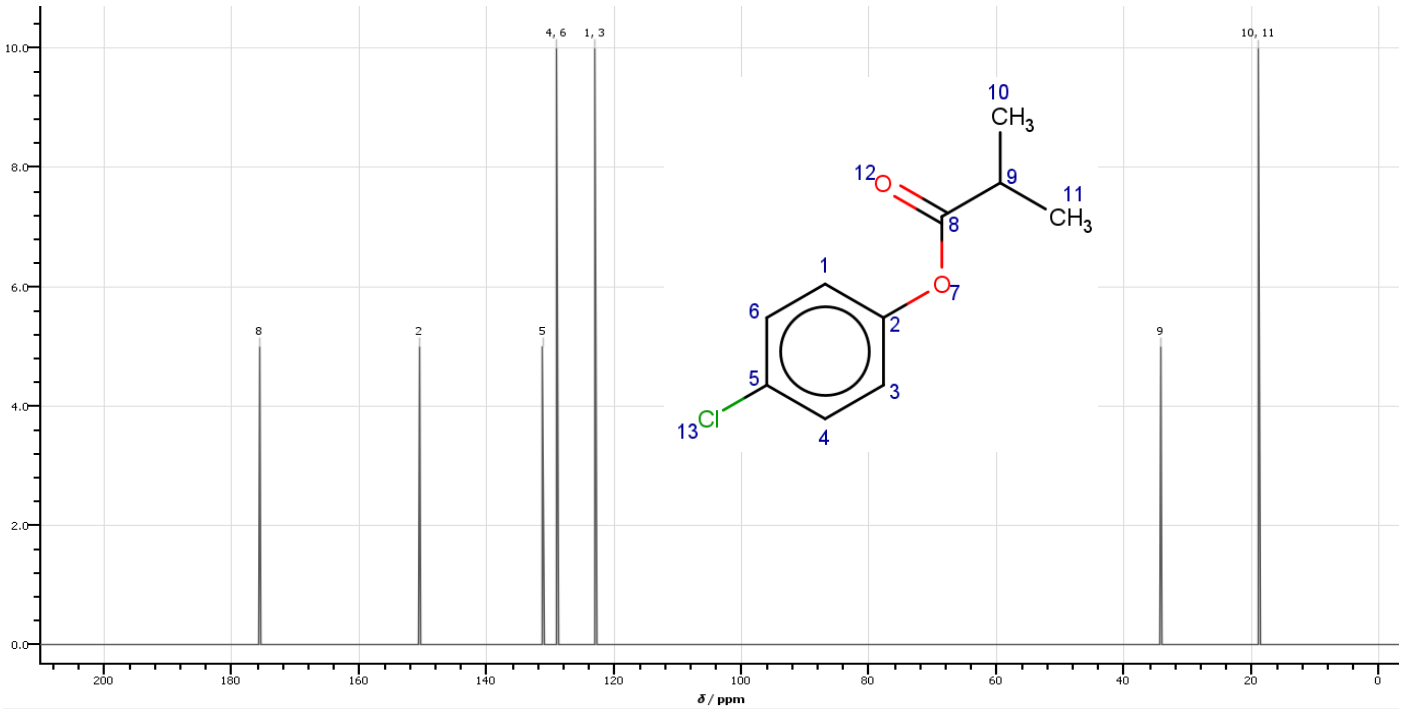
Formula: $C_{10}H_{11}Cl O_2$

Preferred IUPAC Name = 4-chlorophenyl-2-methylpropanoate

^{1}H NMR



^{13}C NMR



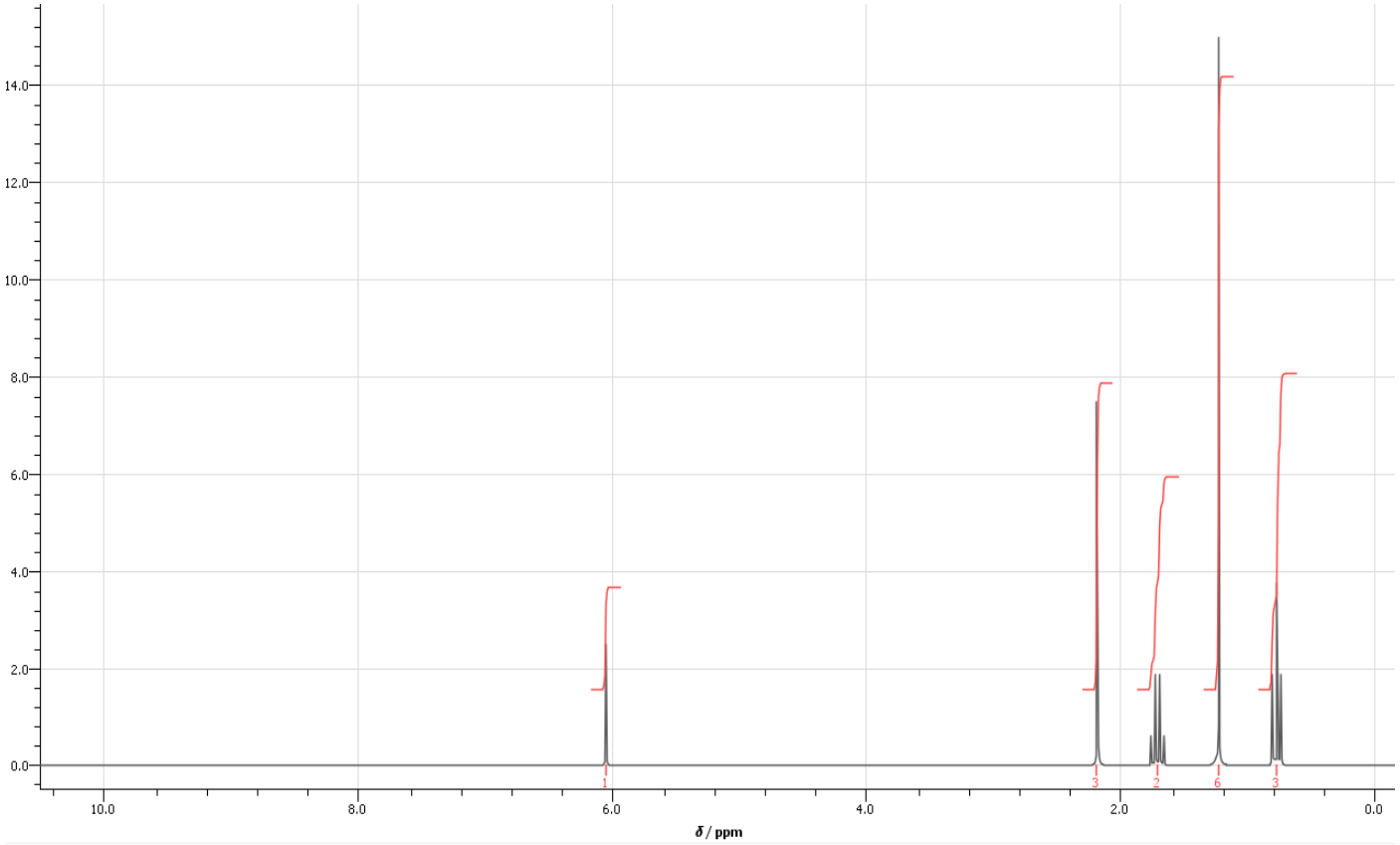
PROBLEM 4

Composition: C (65.1%), H (11.6%), N (10.9%), O (12.4%)

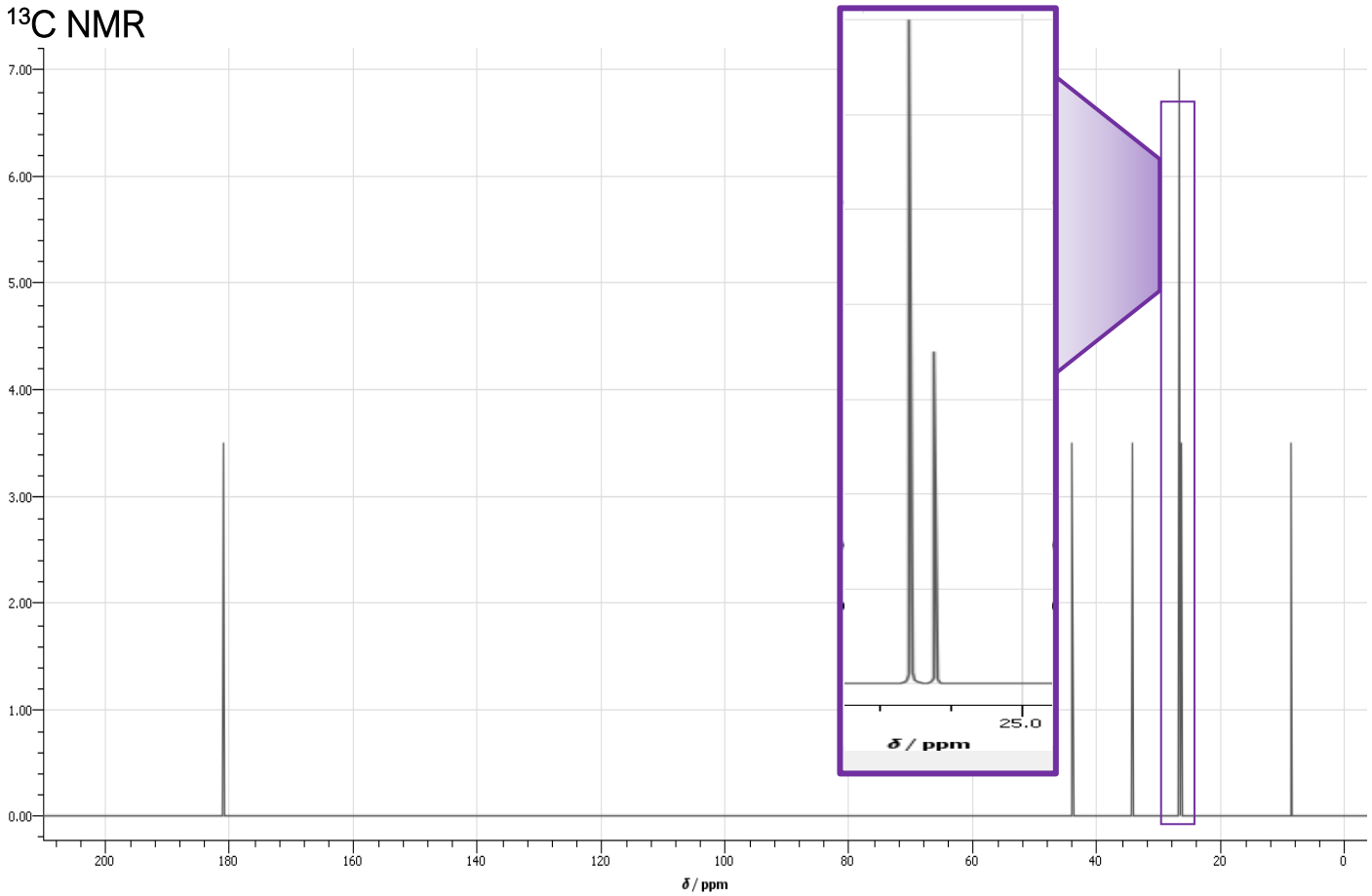
Mass spectrometry information

prominent peaks at m/z= 129, 114, 99, 71

^{1}H NMR



^{13}C NMR

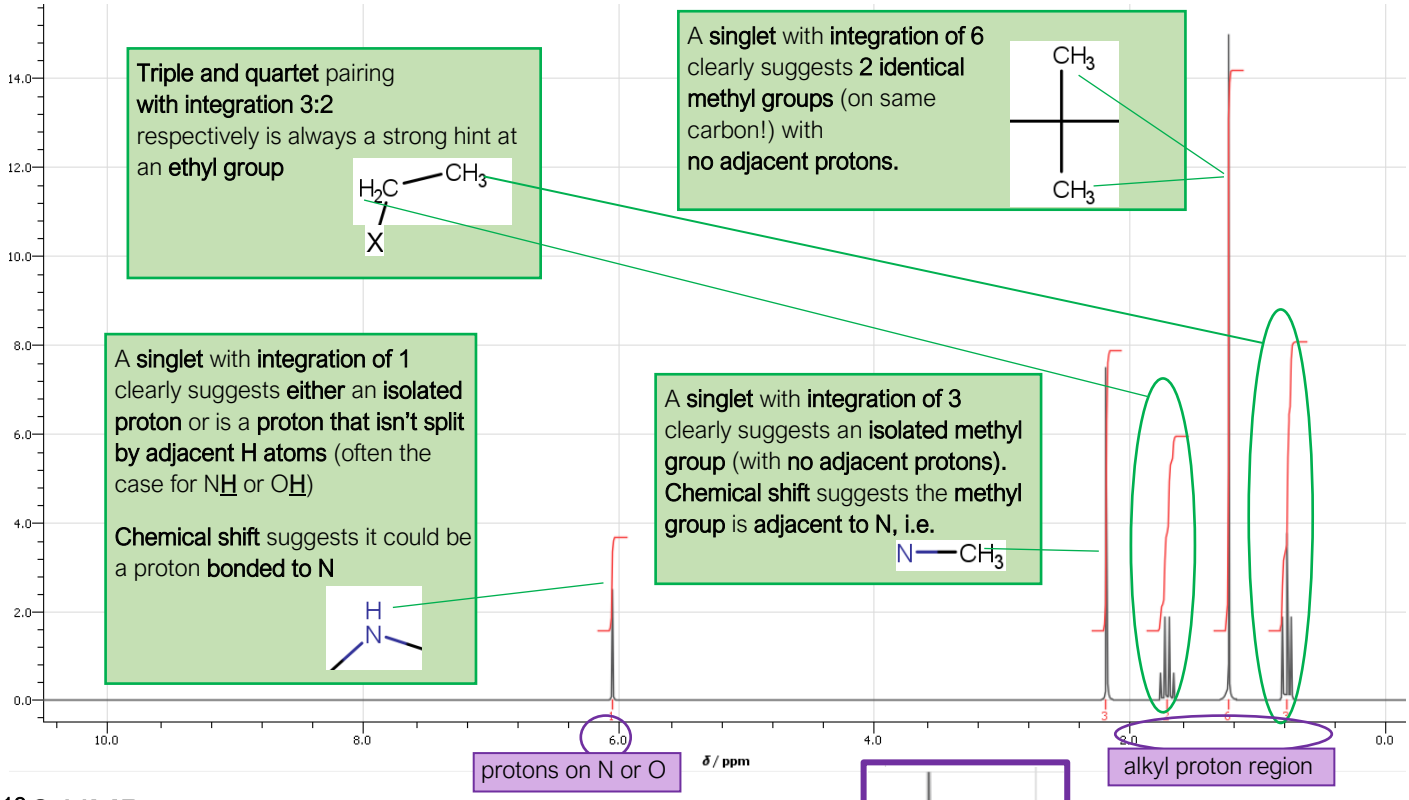


PROBLEM 4 with hints

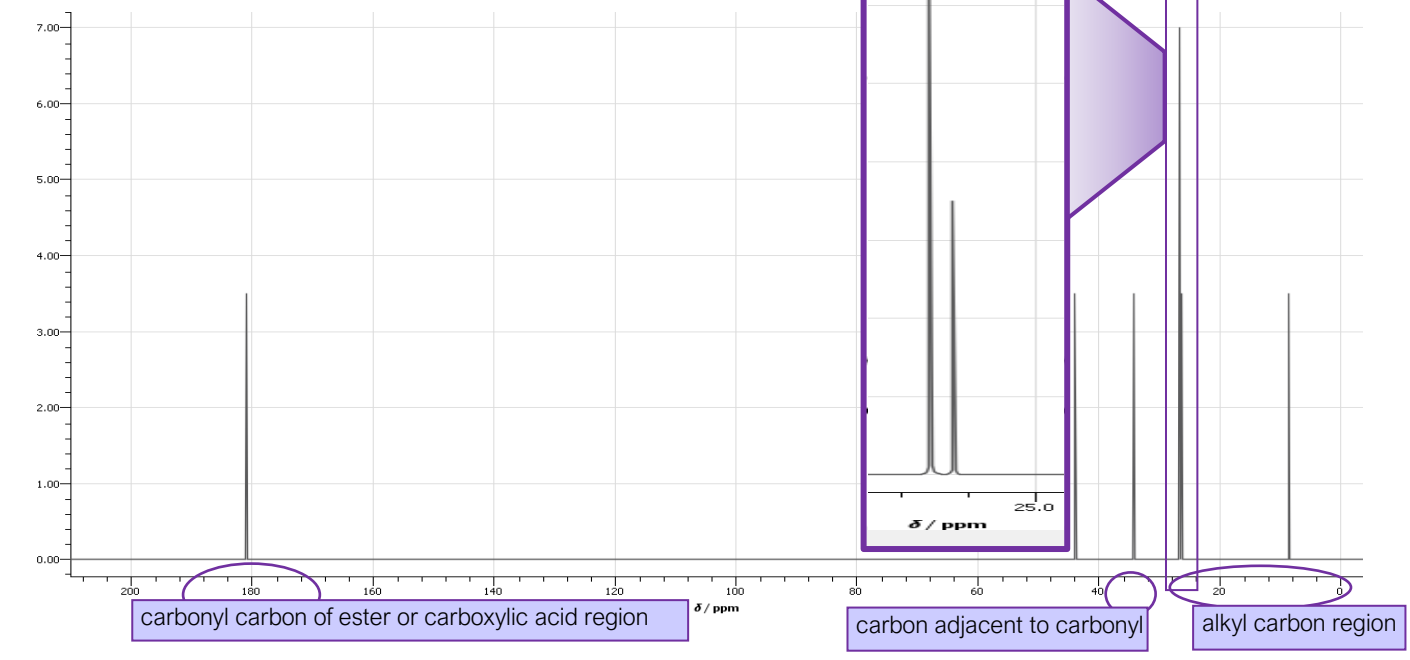
Molecular formula: $C_7H_{15}NO$ This is **pretty saturated** and has **many carbons**. **No benzene ring!** The **oxygen and nitrogen** also suggests **amide** or **substituted amide. Simple amides** (no other groups) have a **general formula $C_nH_{2n+1}NO$.** This fits!

M^+ at 129 gives the molecular weight of the compound. Peak at **114** suggests the compound has **lost of a methyl group**. Peak at **71** could suggest a **$C_5H_{11}^+$** fragment. Peak at **99** could suggest a **$C_5H_{11}CO^+$** fragment.

^{1}H NMR



^{13}C NMR

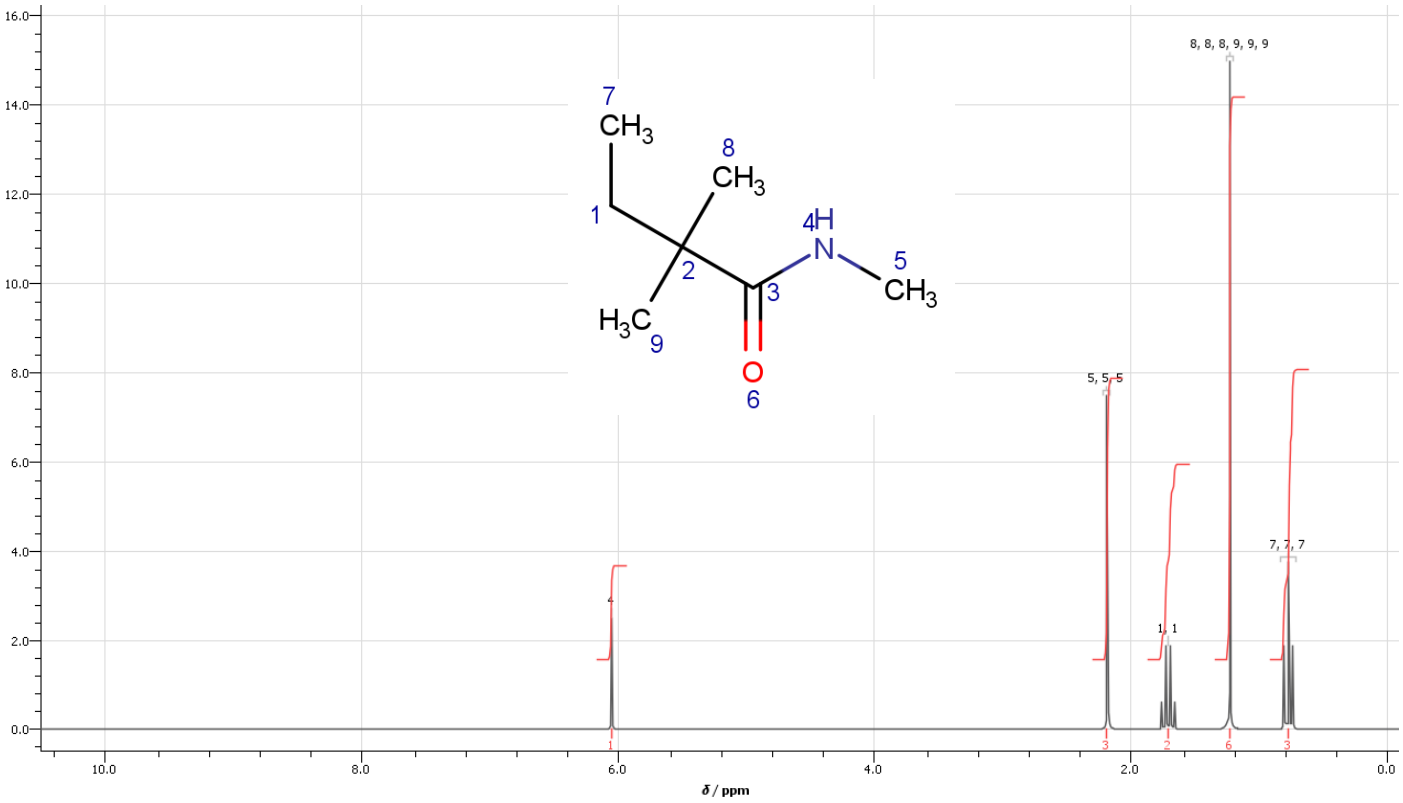


PROBLEM 4 **ANSWER**

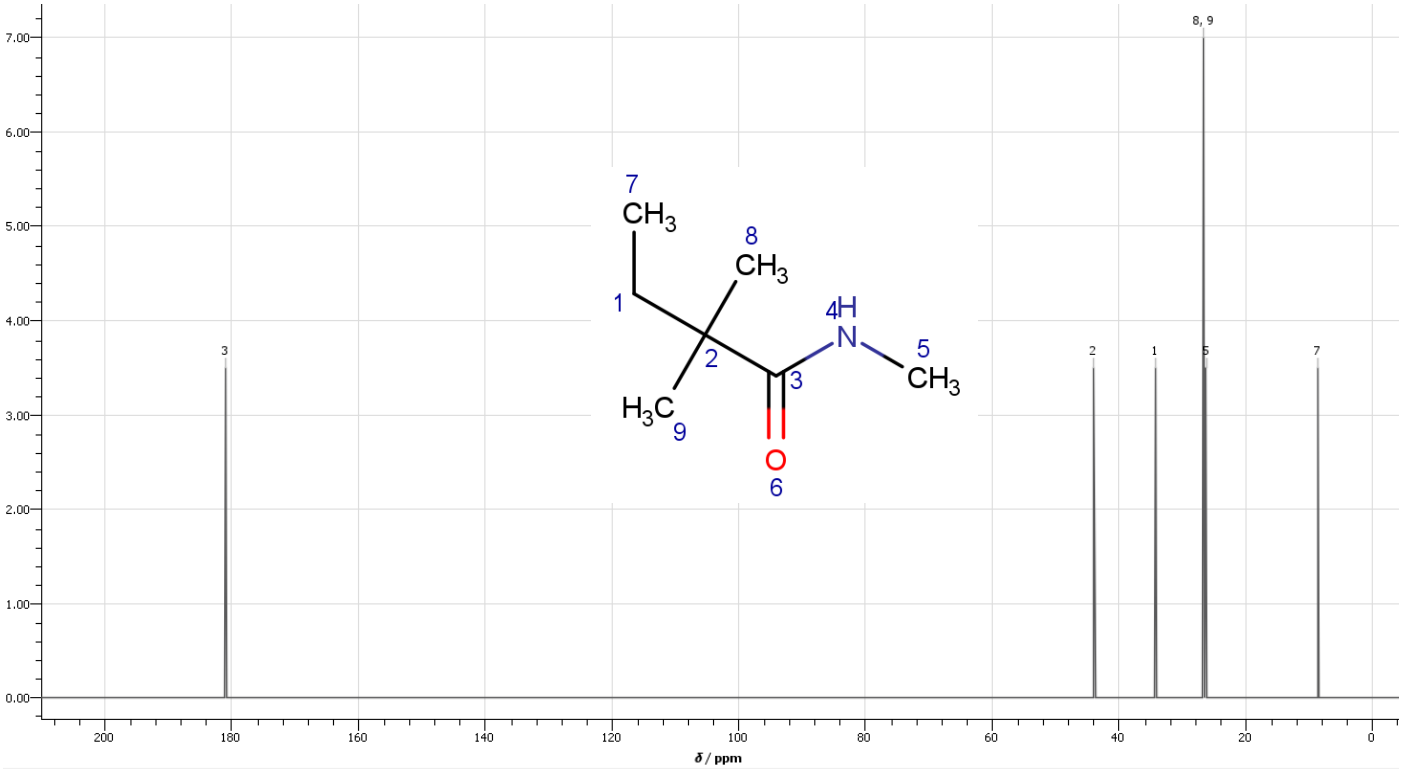
Formula: $C_7H_{15}NO$

Preferred IUPAC Name = N-methyl-2,2-dimethylbutanamide

^{1}H NMR



^{13}C NMR



❖ SECTION 3

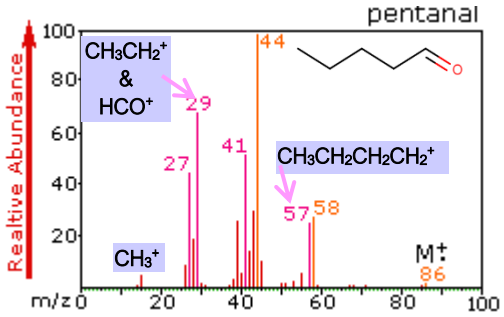
a) Mass Spectrometry; Hints from fragmentation

Below are three examples of mass spectra for the most likely 3 compounds of formula $C_5H_{10}O$

From the formula, you should quickly recognise that this is **unsaturated**. It's possible that this molecule contains both an alkene and alcohol functional group (enols exist!). But it is more **likely to be aldehyde or ketone**. These spectra are for the straight chain isomers; pentanal, pentan-2-one and pentan-3-one.

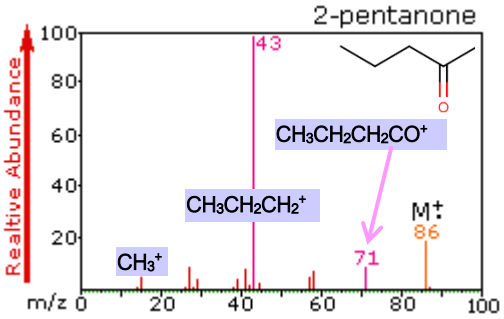
They clearly illustrate how the mass spectra of these compounds vary significantly in their fragmentation patterns. The way that they fragment is very useful in identification.

pentanal



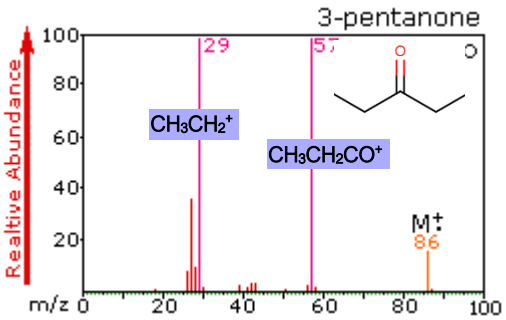
The spectrum shows a set of ions associated with the alkyl chain (e.g. m/z=57,43,29,15). Aldehydes generally show fragment ions involving **loss of groups attached to the carbonyl function**). For this reason, the m/z=29 ion is probably representing both $CH_3CH_2^+$ (a typical alkyl fragment) and HCO^+ cations.

pentan-2-one



The M^+ at m/z=86 is more abundant than in the aldehyde spectrum. Loss of carbonyl substituents include: loss of methyl (M^+-15 at m/z=71) and loss of a propyl (M^+-43 at m/z=43). These comprise the most prominent fragment ions.

pentan-3-one

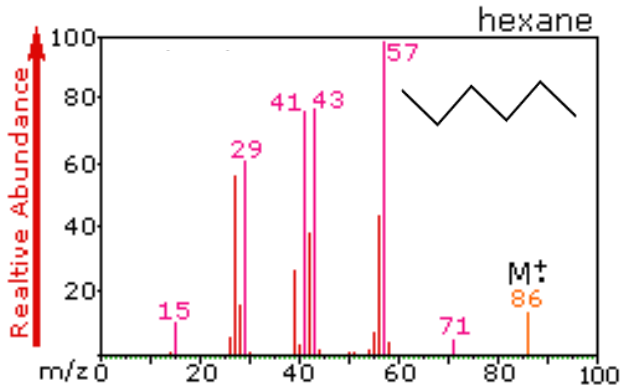


The molecular ion at m/z=86 is about as strong as in 2-pentanone. Because of the symmetry, $CH_3CH_2^+$ groups are the only carbonyl substituents that can be lost by an fragmentation. The strongest fragment ions are found at m/z=57 (from the loss of an $CH_3CH_2^+$group) and m/z=29 (the lost $CH_3CH_2^+$cation).

Fragmentation evidence for alkyl isomers.

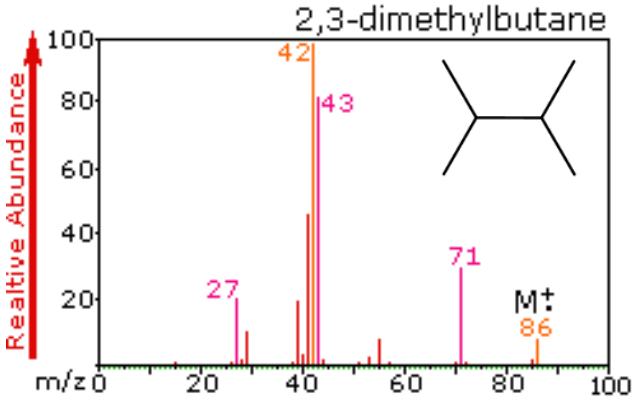
Here are a couple of spectra for **2 structural isomers of C_6H_{14} .** One is **unbranched** and the other is **branched.**

hexane



This shows the same fragmentation pattern as other unbranched alkanes. You can see the typical alkyl carbocations at m/z=15, 29, 43, 57 and 71

2,3-dimethylbutane



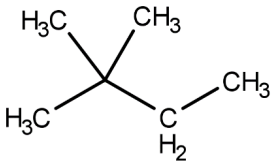
Chain branching clearly influences the fragmentation of this isomer of hexane. The molecular ion at m/z=86 There is a fragment with m/z=71 which shows loss of a methyl group. The m/z=57(butyl) ion is almost absent as there is no obvious cleavage that could produce a butyl ($C_4H_9^+$) fragment. An isopropyl cation ($CH_3CH^+CH_3$) (m/z=43) is very strong. There is almost no ethyl peak ($C_2H_5^+$) m/z=29 as this can't be easily formed from the breakup of 2,3-dimethylbutane.

Going a little further:

You may well have been introduced to the **relative stability or carbocations** when applying the rules of Markownikov addition of electrophiles to unsymmetrical alkenes. This same understanding can be applied to the predicting of the most stable fragments that will be formed and appear in a mass spectrum.

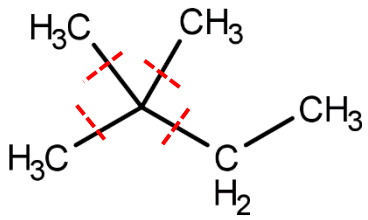
Bond cleavages that produce **fragments** which are **3º carbocations** are more likely to take place than those that give **2º or 1º,** carbocations. Likewise, bond cleavages that produce **fragments** which are **2º carbocations** are more likely to take place than those that give **1º,** carbocations.

Consider the mass spectrum of another structural isomer of hexane, **2,2-dimethylbutane**



2,2-dimethylbutane is likely to fragment in a way that should yield the most stable fragments.

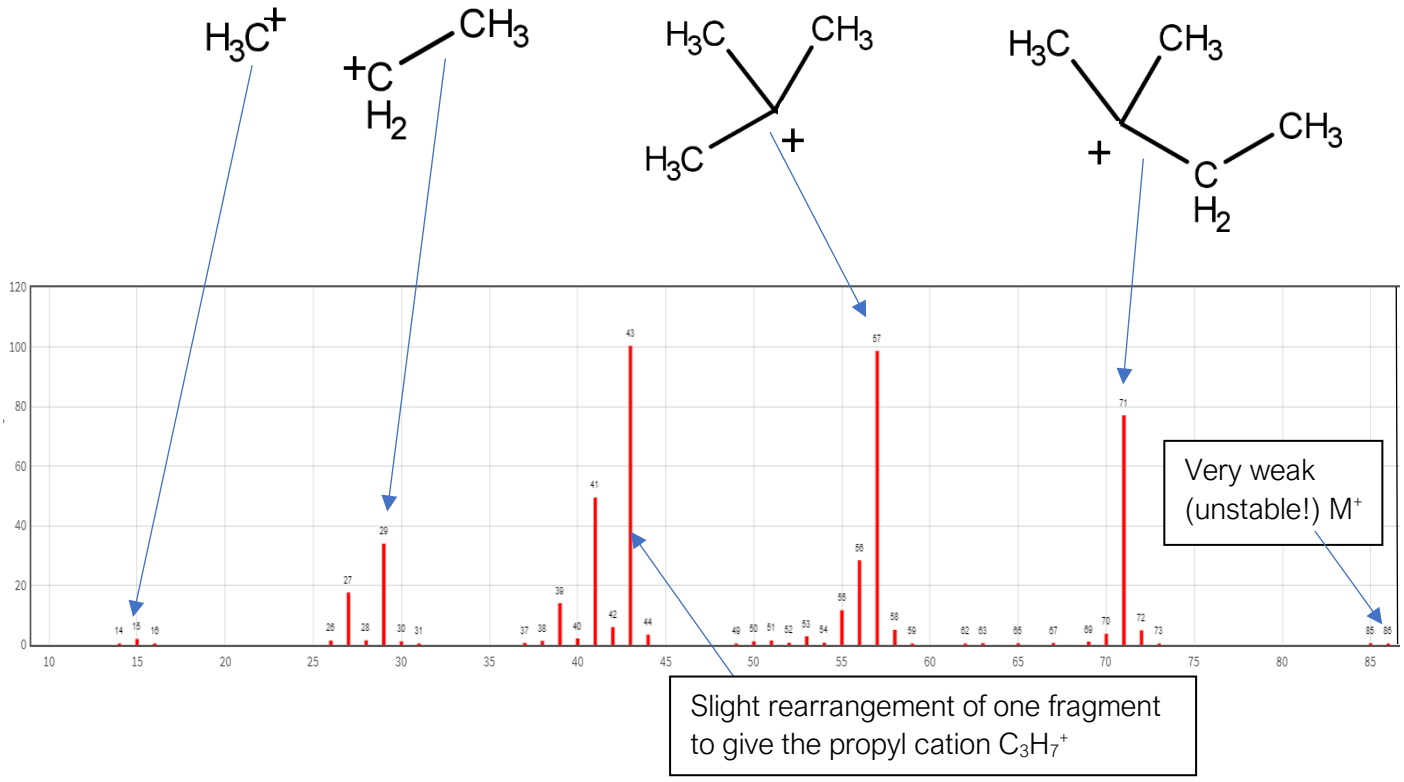
So, cleavage of the following bonds would be expected as they all produce **3º carbocations**.



m/z=86

This would produce strong peaks at:

m/z value:	15	29	57	71

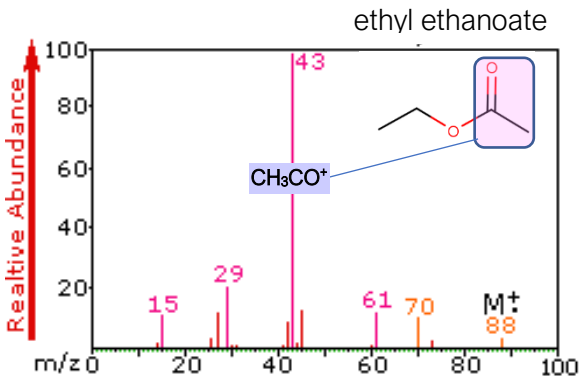


.

Fragmentation evidence for ester isomers

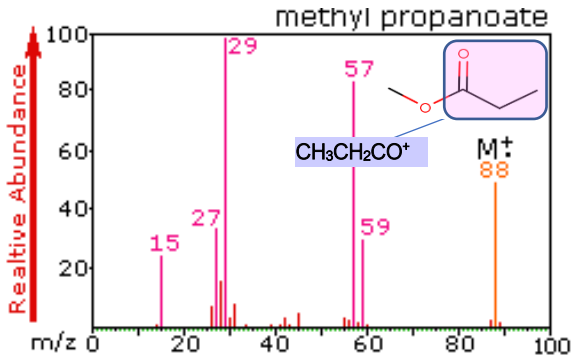
Below are 2 isomers of $C_4H_8O_2$. The fragmentation patterns help identify which is which.

ethyl ethanoate



The largest peak results from the loss of the C_2H_5O radical to leave **CH_3CO^+** fragment at m/z=43. The expected **CH_3^+** and **$CH_3CH_2^+$** ions are found at m/z=15 & 29.

methyl propanoate



Loss of the CH_3O radical to leave **$CH_3CH_2CO^+$** fragment at m/z=57. & 29. The expected methyl and ethyl ions are found at m/z=15 & 29. Interestingly, the isomeric ester, methyl propanoate, has a more abundant molecular ion than ethyl ethanoate. You shouldn't expect the parent ion M^+ to be the strongest peak.

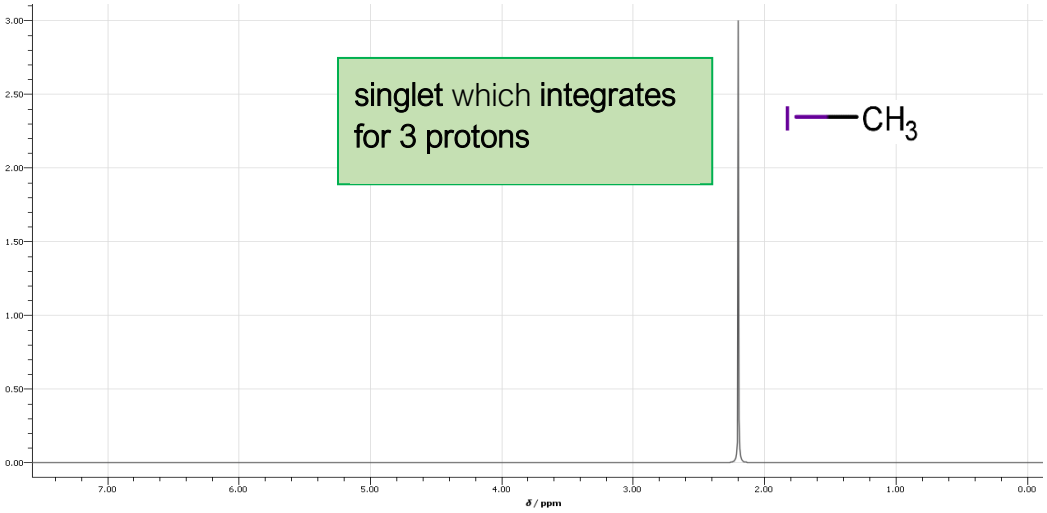
Common Fragments and their m/z values

Fragment ion	name	m/z
CH_3^+	methyl	15
$CH_3CH_2^+$	ethyl	29
$CH_3CH_2CH_2^+$	propyl	43
$CH_3CH^+CH_3$	**isopropyl** (IUPAC* propan-2-yl)	43
$CH_3CH_2CH_2CH_2^+$	butyl	57
CH_3CO^+	**acetyl** (IUPAC* is ethanoyl)	43
$CH_3CH_2CO^+$	**propionyl** (IUPAC* is propanoyl)	57

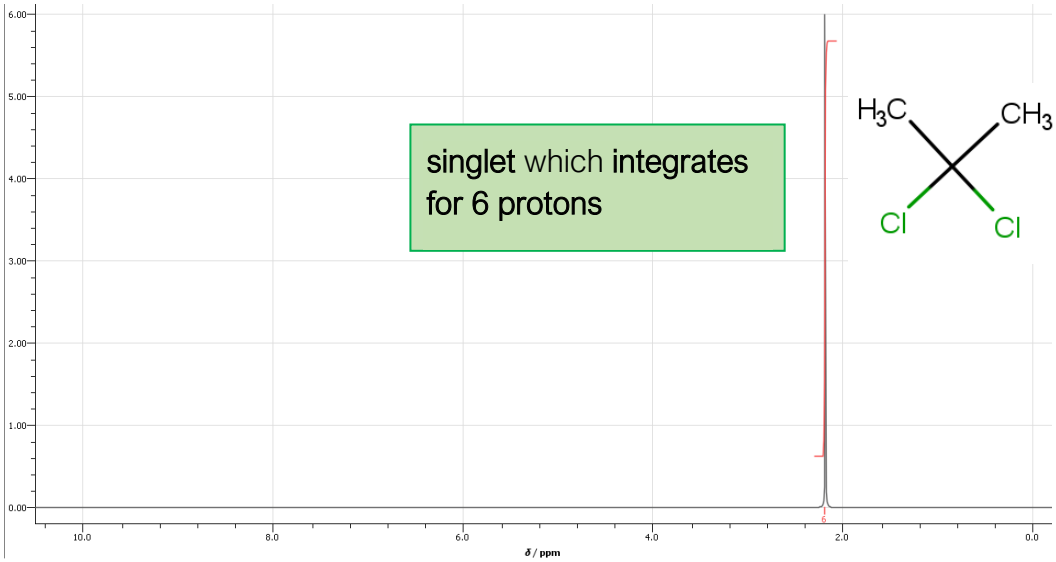
* IUPAC stands for the **International Union of Pure and Applied Chemistry**. This is an organisation that help lay down some the rules that we use in chemistry, for example in the naming of compounds (nomenclature). The organization is over 100 years old. It succeeds the previous committee which was initiated in 1860 to address the naming or organic compounds. This followed the explosion in the number of organic compounds that were being discovered or novel organic compounds that were being synthesised with new methods. **August Kekulé** (benzene!) was as the heart of its inception

b) Some NMR Common Patterns to look out for:

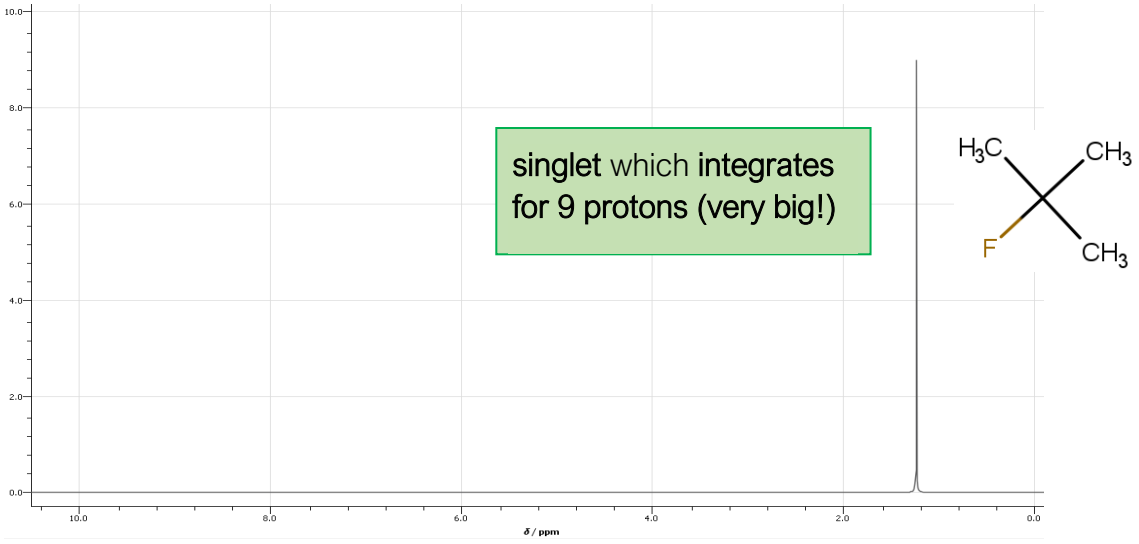
^{1}H NMR isolated methyl



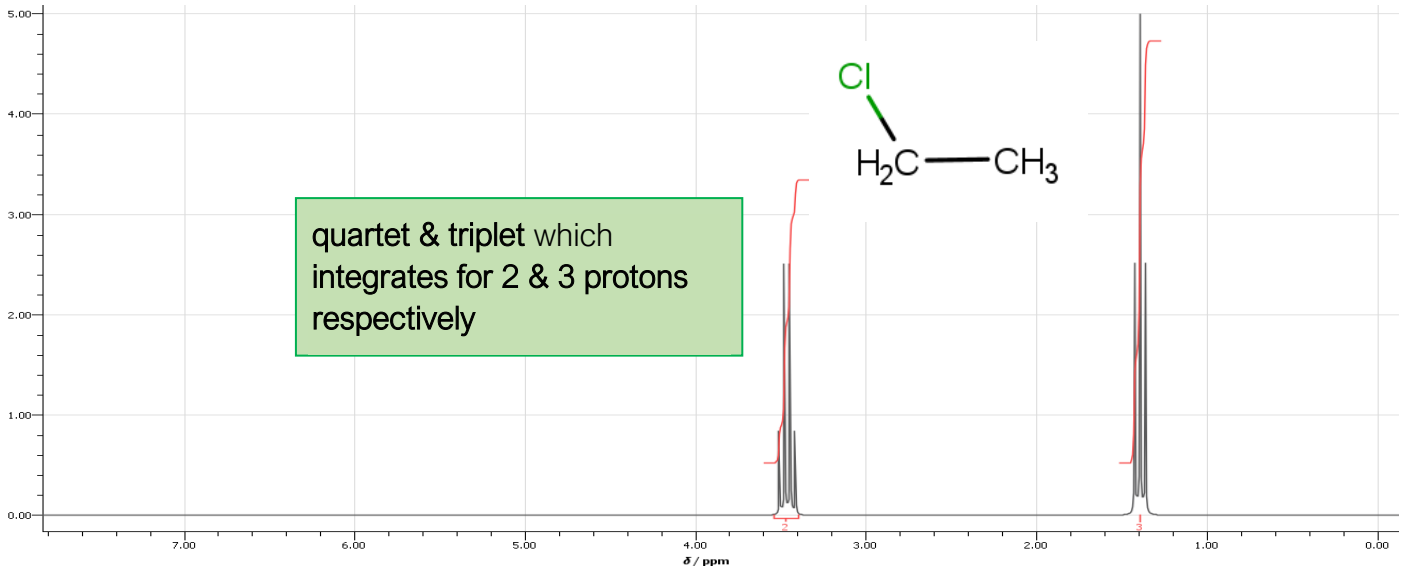
^{1}H NMR isolated dimethyl



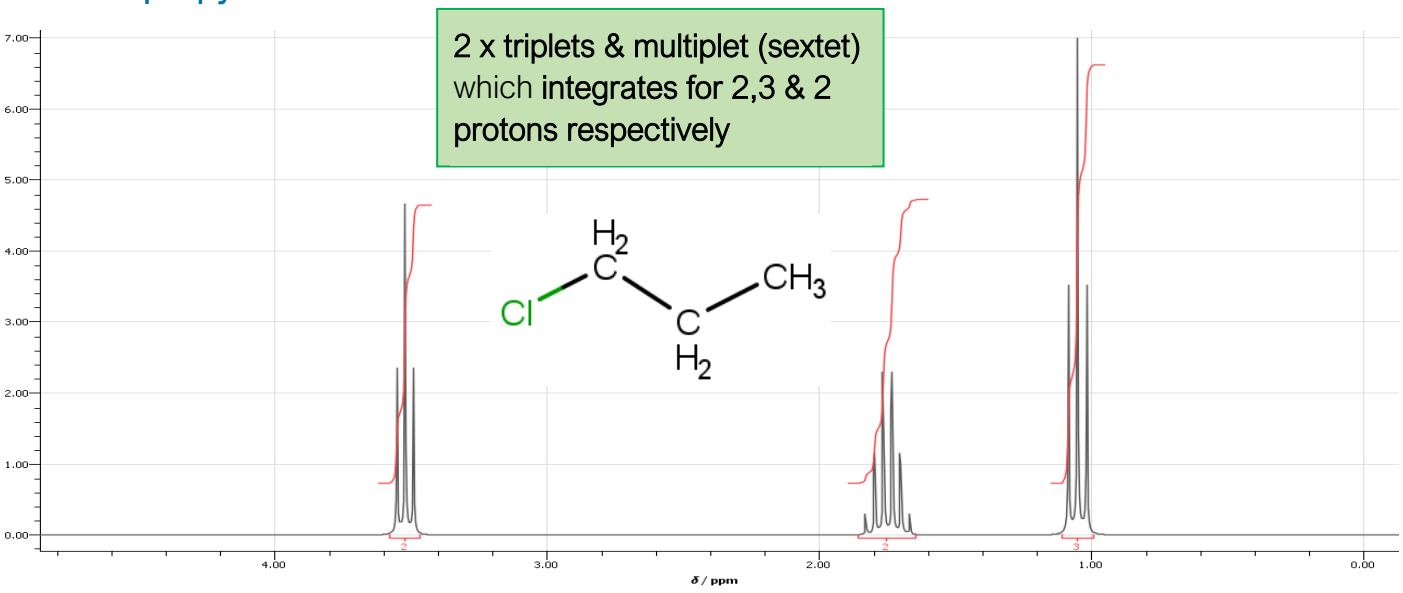
^{1}H NMR isolated trimethyl



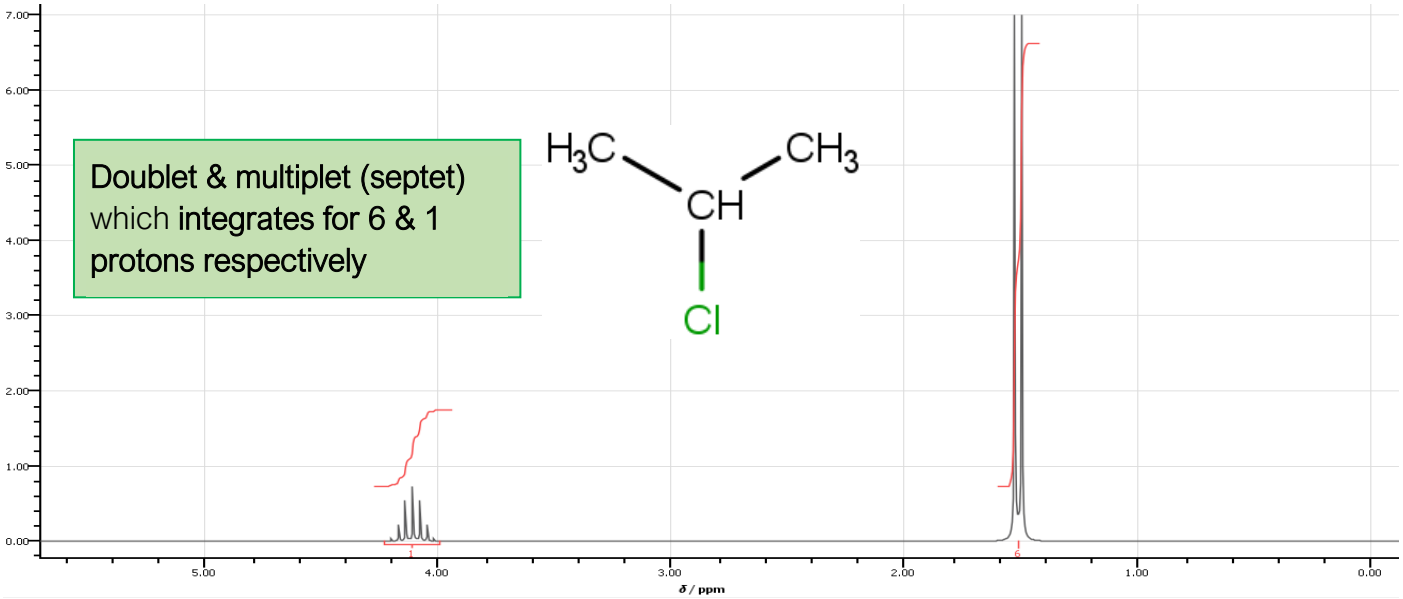
^{1}H NMR ethyl



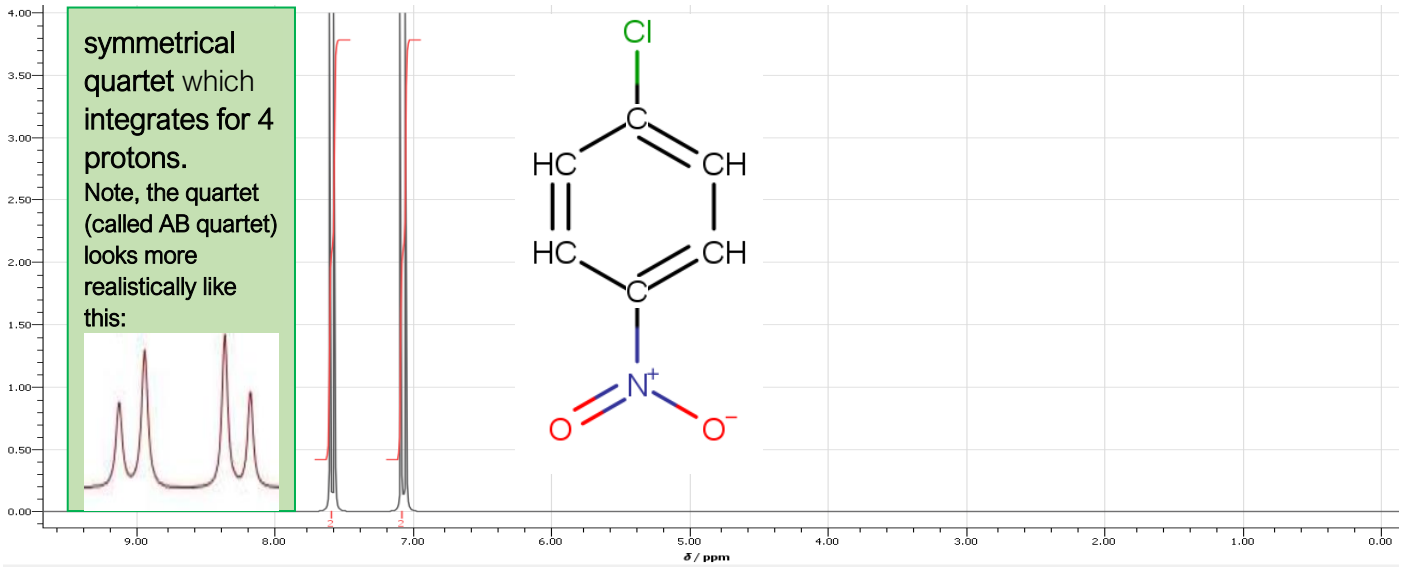
^{1}H NMR propyl



^{1}H NMR isopropyl

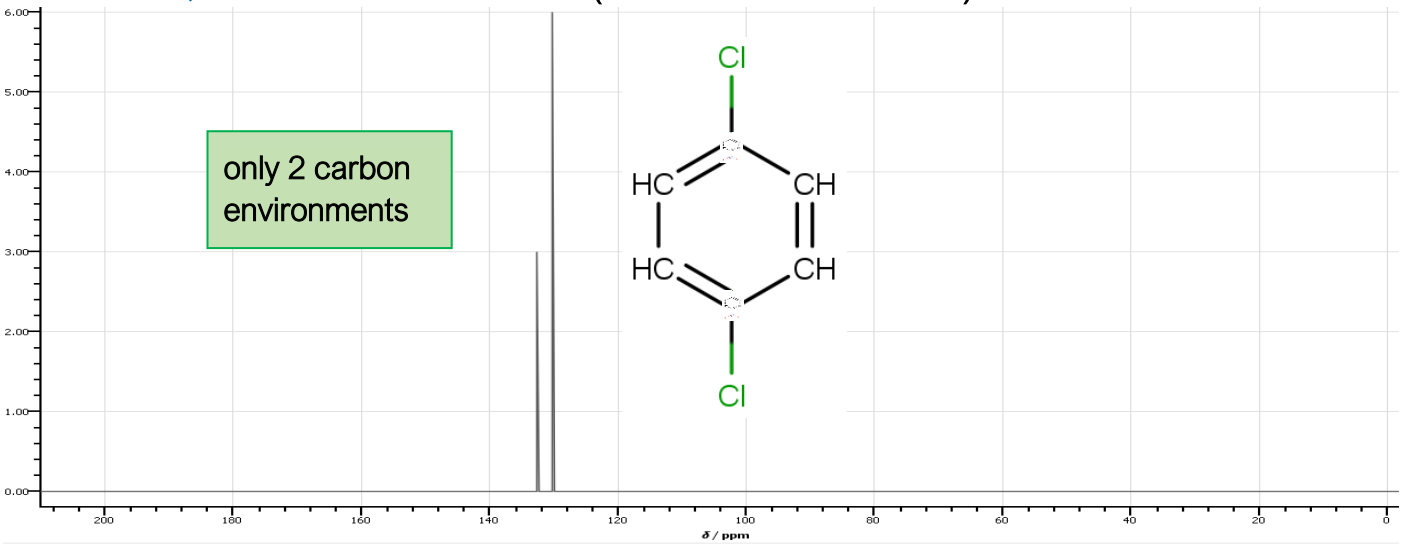


^{1}H NMR 1,4-disubstituted benzene (2 different substituents)

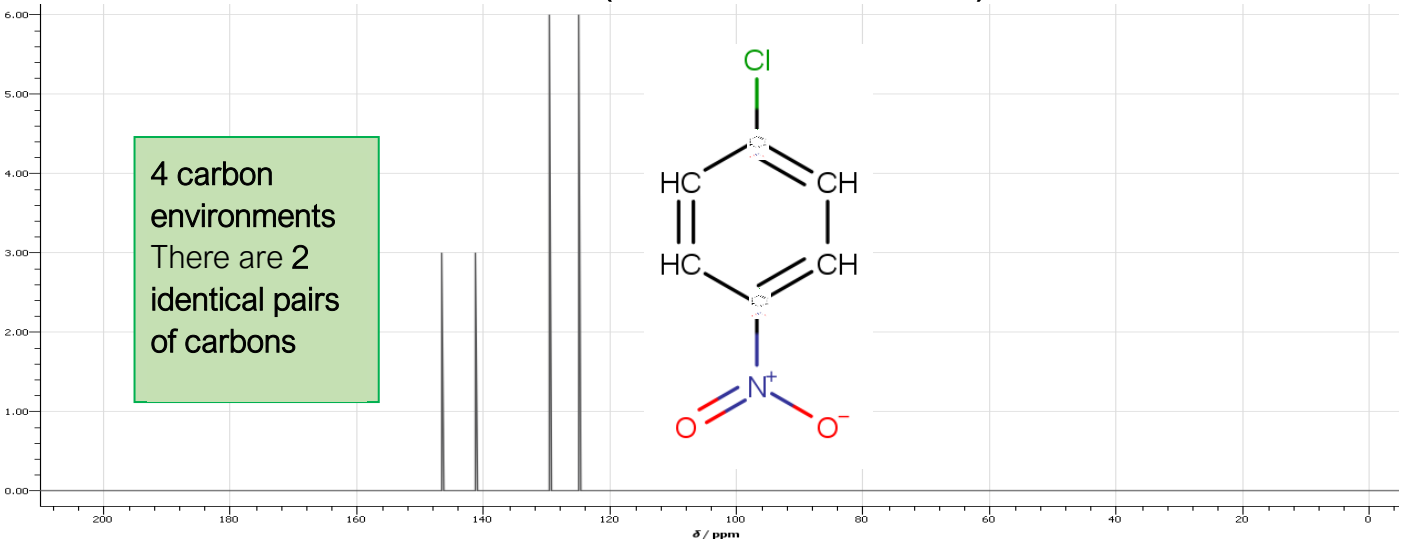


^{13}C NMR

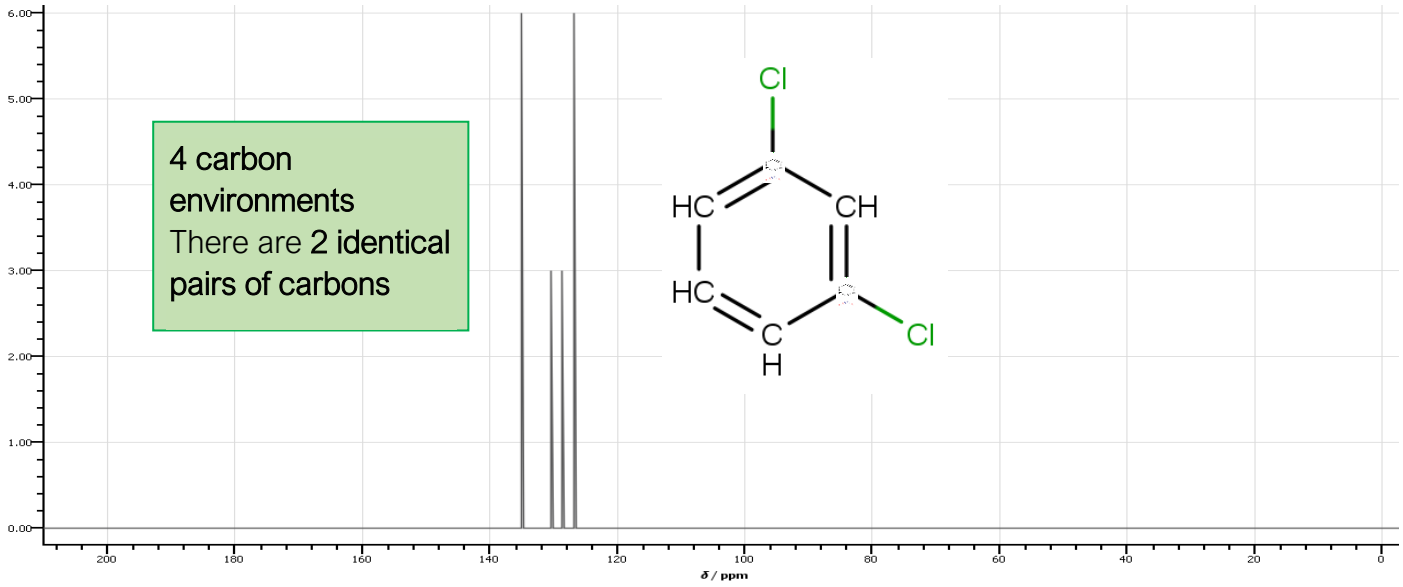
^{13}C NMR 1,4-disubstituted benzene (2 of same substituents)



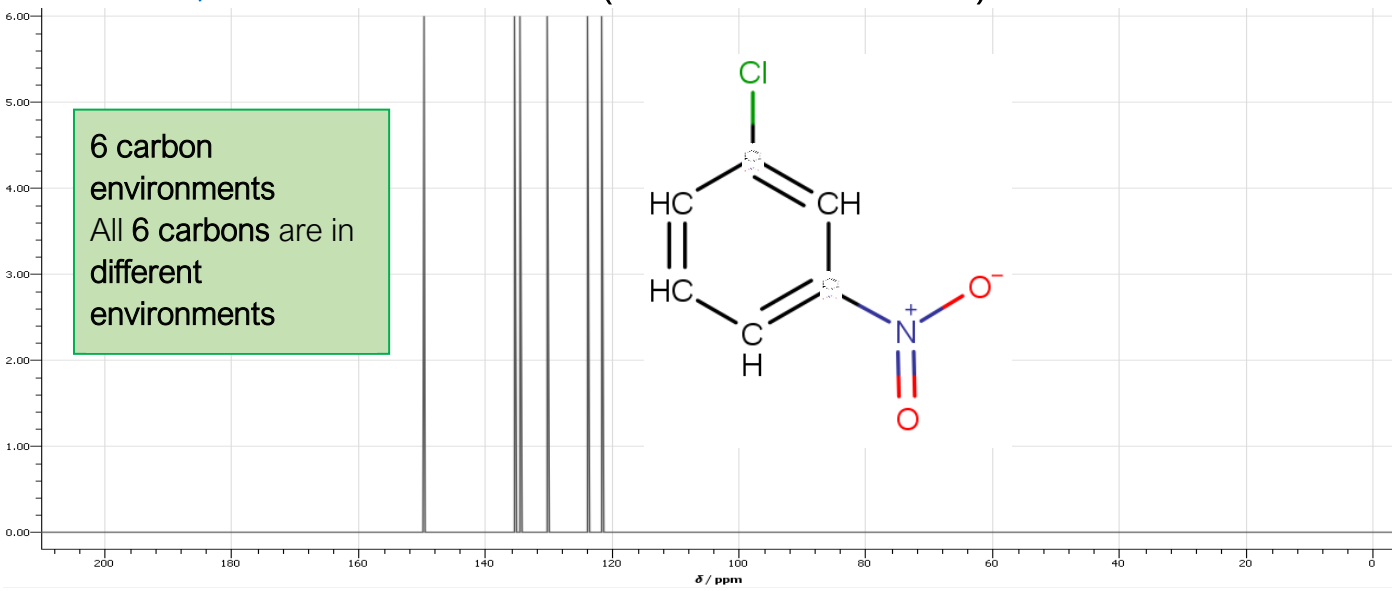
^{13}C NMR 1,4-disubstituted benzene (2 different substituents)



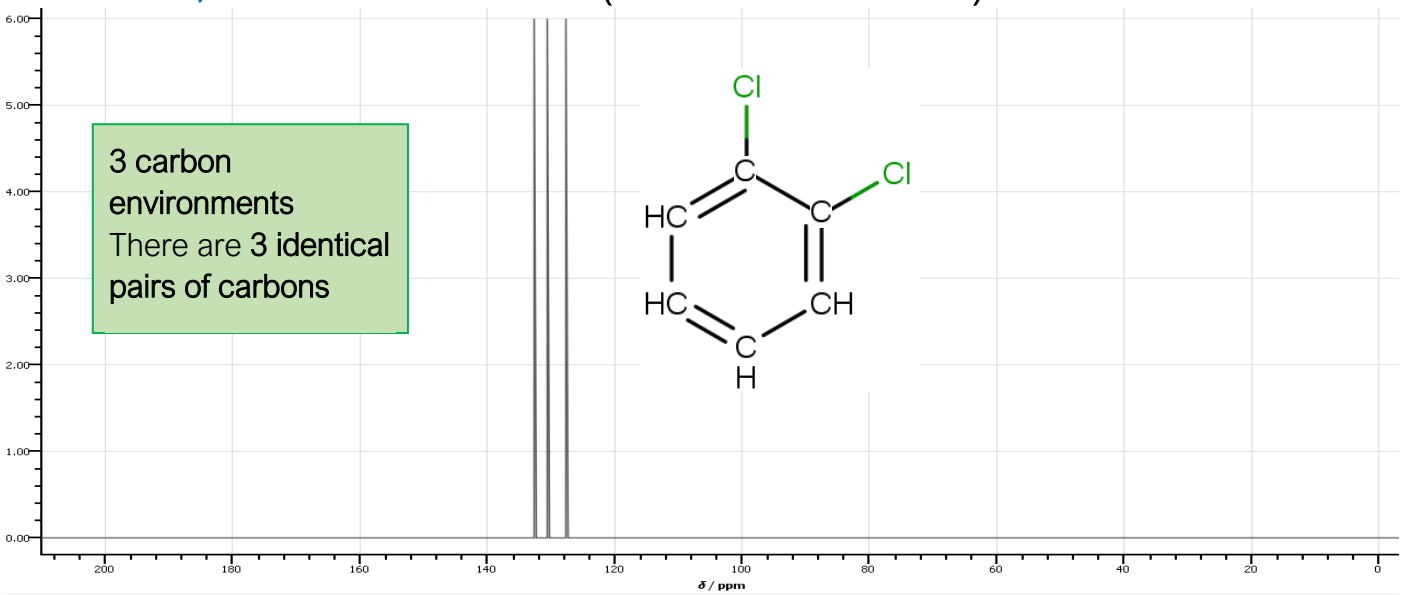
^{13}C NMR 1,3-disubstituted benzene (2 of same substituents)



^{13}C NMR 1,3-disubstituted benzene (2 different substituents)



^{13}C NMR 1,2-disubstituted benzene (2 of same substituents)



^{13}C NMR 1,2-disubstituted benzene (2 different substituents)