

^{13}C -NMR Spectroscopy

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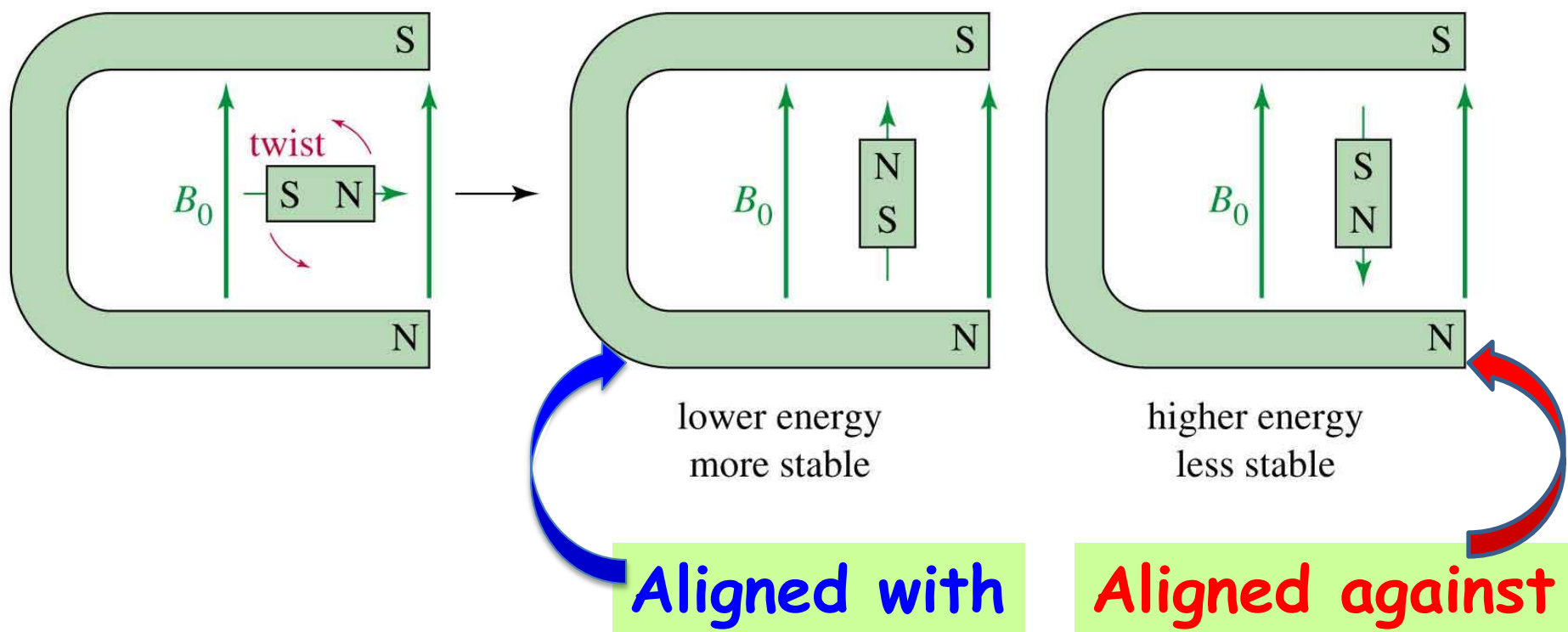
^{13}C -NMR Spectroscopy

- NMR is the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
 - ^1H
 - ^{13}C
 - ^{15}N
 - ^{19}F
 - ^{31}P
 - ^{119}Sn

^1H -NMR Spectroscopy

External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.



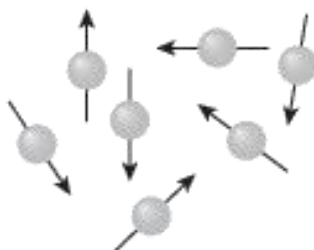
^1H -NMR Spectroscopy

- When a charged particle such as a proton spins on its axis, it creates a **magnetic field**. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0 , they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.
- The energy difference between these two states is **very small** (<0.1 cal).

A spinning proton creates a magnetic field.

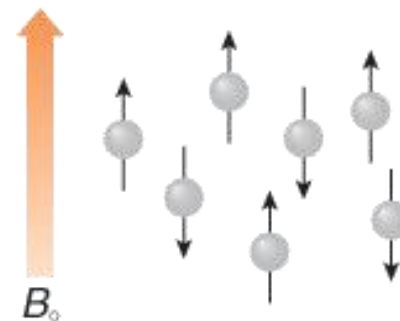


With no external magnetic field...



The nuclear magnets are randomly oriented.

In a magnetic field...



The nuclear magnets are oriented **with or against** B_0 .

^{13}C -NMR Spectroscopy

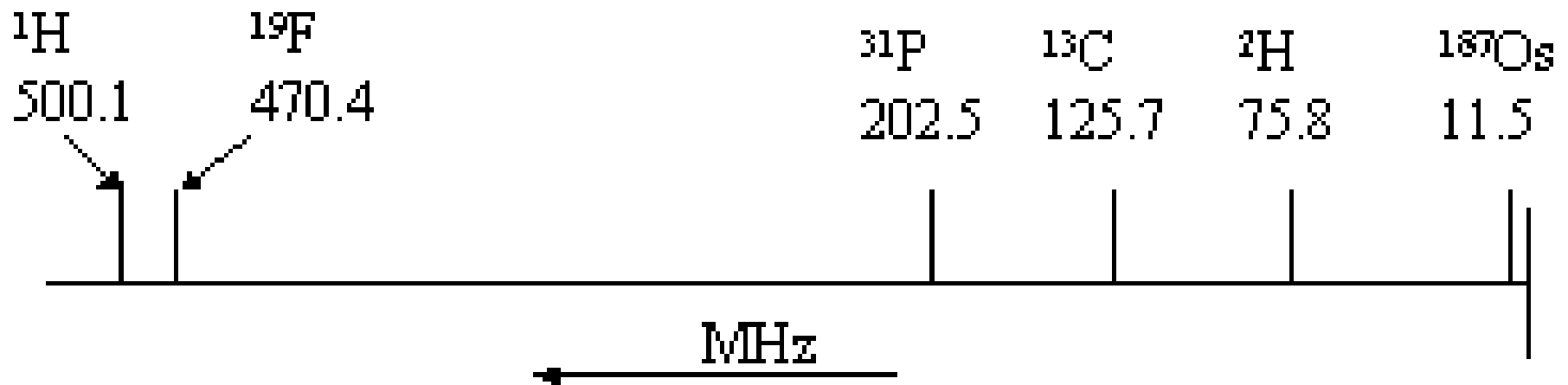
- ^{13}C Nuclei with $I=1/2$, abundance= 1.08%, and 6000 weaker than proton resonances
- Because of very low natural abundance, we actually observe a ^{13}C spectrum built up from a collection of molecules
- Gyromagnetic ratio, γ , of a ^{13}C nucleus is smaller than that of ^1H (about $1/4^{\text{th}}$)
- Energy difference is proportional to the magnetic field strength.
$$\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$$
- Therefore, ^{13}C nuclei always have resonance at lower than ^1H nuclei.
- At lower frequency, the population of excess nuclei is reduced, which in turn, reduces sensitivity in NMR measurements.

^{13}C -NMR Spectroscopy: Spin, Natural Abundance of Nuclei & γ

Isotope	Spin I	natural abundance [%]	Gyromagnetic ratio, (γ) [$10^7 \cdot \text{rad}/(\text{T} \cdot \text{s})$]	Relative sensitivity	Absolute sensitivity
^1H	1/2	99.98	26.7519	1.00	1.00
^2H	1	0.016	4.1066	$9.65 \cdot 10^{-6}$	$1.45 \cdot 10^{-6}$
^{12}C	0	98.9	--	--	--
^{13}C	1/2	1.108	6.7283	$1.59 \cdot 10^{-2}$	$1.76 \cdot 10^{-4}$
^{14}N	1	99.63	1.9338	$1.01 \cdot 10^{-3}$	$1.01 \cdot 10^{-3}$
^{15}N	1/2	0.37	-2.712	$1.04 \cdot 10^{-3}$	$3.85 \cdot 10^{-6}$
^{16}O	0	98.9	--	--	--
^{17}O	5/2	0.037	-3.6279	$2.91 \cdot 10^{-2}$	$1.08 \cdot 10^{-5}$
^{31}P	1/2	100	10.841	$6.63 \cdot 10^{-2}$	$6.63 \cdot 10^{-2}$

^{13}C -NMR Spectroscopy

^1H nuclei measured at 200 MHz frequency = about $1/4^{\text{th}}$
i.e. 50 MHz for ^{13}C nuclei



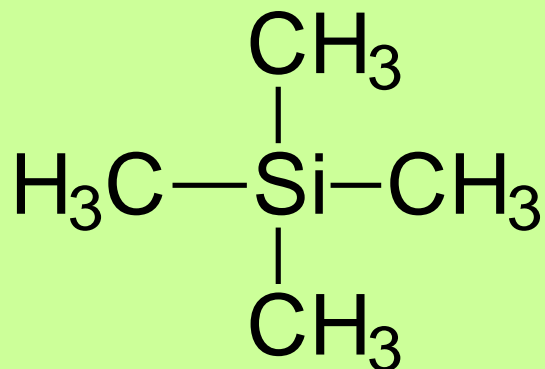
^{13}C -NMR Spectroscopy

The Chemical shift range for ^1H is usually in δ 0 - 12 ppm.

The Chemical shift range for ^{13}C is quite large and usually in δ 0 - 220 ppm.

This results is that almost all non-equivalent ^{13}C peaks appear at different Chemical shift values and rarely overlap.

Tetramethylsilane (TMS as Reference)

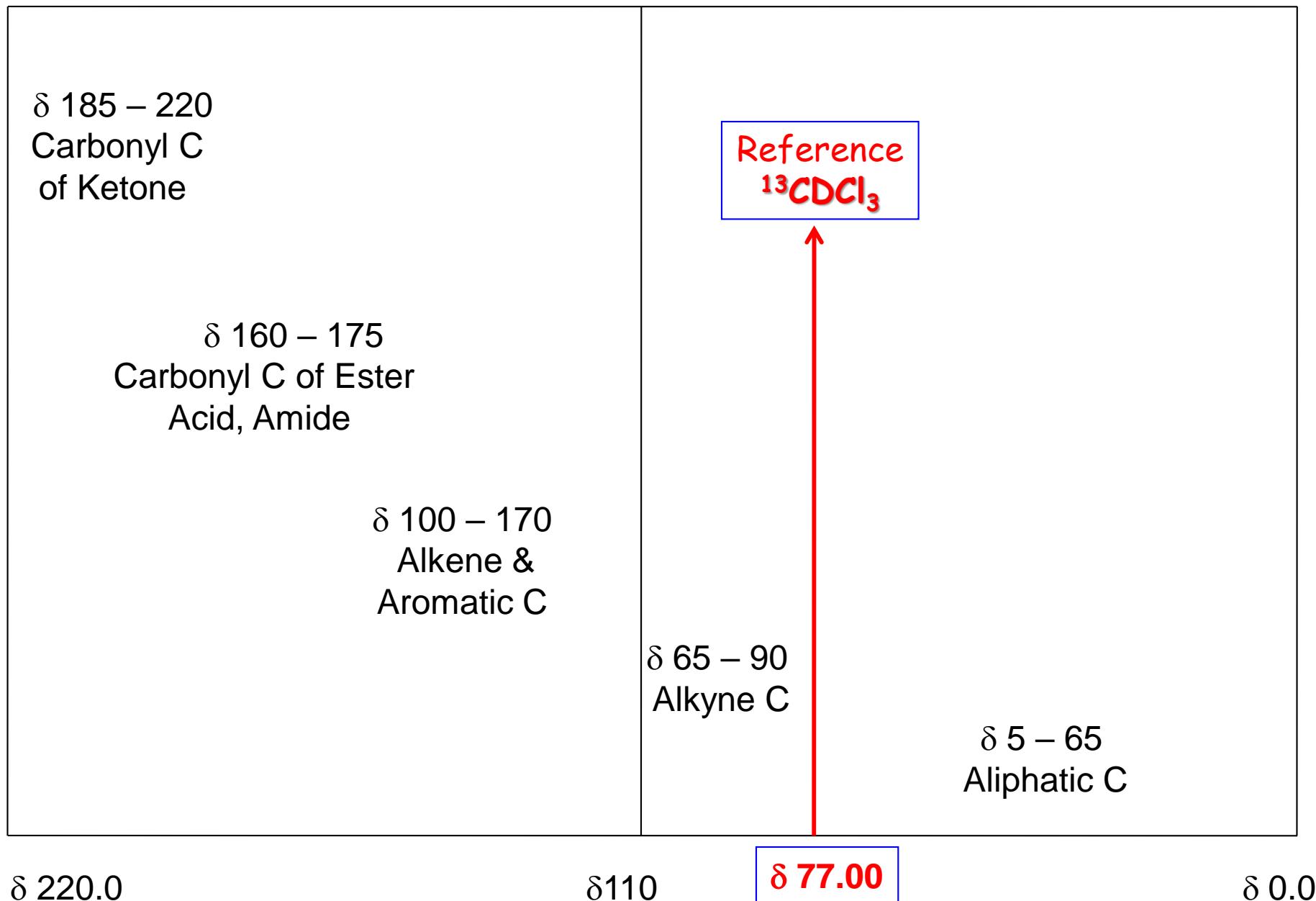


¹³C

δ = 77.00 ppm

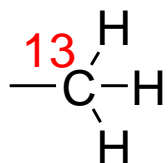
- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero (δ = 0.00)
- Organic protons absorb downfield (to the left) of the TMS signal.

^{13}C -NMR Spectroscopy



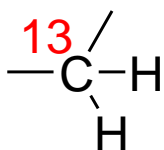
^{13}C -NMR Spectroscopy

- Shielding and Deshielding of ^{13}C Nuclei are affected on electronegativity, hybridization and anisotropy - **nearly same way as in the case of ^1H ,**
- Spin-spin coupling between non-equivalent and adjacent ^{13}C - ^{13}C (**Homonuclear**) is rarely observed since the probability of finding two ^{13}C adjacent atoms in the same molecules is even lower.
- Spin-spin couplings of adjacent ^{13}C - ^1H (Heteronuclear) is indeed observed, mostly through one bond (C - H).



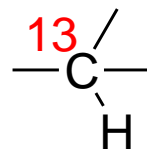
$$\begin{array}{c} n + 1 \\ 4 \end{array}$$

Methyl C



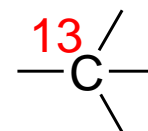
$$\begin{array}{c} n + 1 \\ 3 \end{array}$$

Methylene C



$$\begin{array}{c} n + 1 \\ 2 \end{array}$$

Methine C



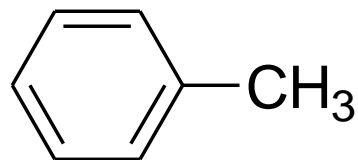
$$\begin{array}{c} n + 1 \\ 1 \end{array}$$

Quaternary C

^{13}C -NMR Spectroscopy

Since heteronuclear ^{13}C - ^1H spin-spin coupling reduces the peak intensity as well as complicates the overall ^{13}C -NMR spectrum, new technique is adopted to obtain proton-Decoupled ^{13}C -Spectrum - that shows only singlet peaks.

Proton-Decoupling is accomplished by simultaneous irradiation of all protons while measuring ^{13}C Nuclei. Modern NMR spectrometer provides a Decoupler for this purpose



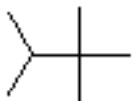
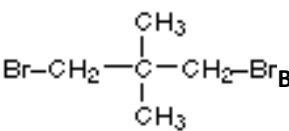

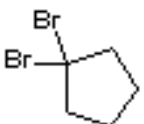

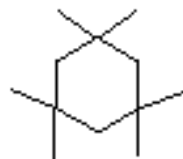
Will display **5** types of ^{13}C peaks in its NMR spectrum

CH_3 , *ipso*, *ortho*, *meta* and *para* carbons

¹³C-NMR Spectroscopy

Structurally Equivalent Atoms & Groups

For each of the compounds **A** through **F** indicate the number of structurally-distinct groups of carbon atoms, and also the number of distinct groups of equivalent hydrogens. Enter a number from 1 to 9 in each answer box.

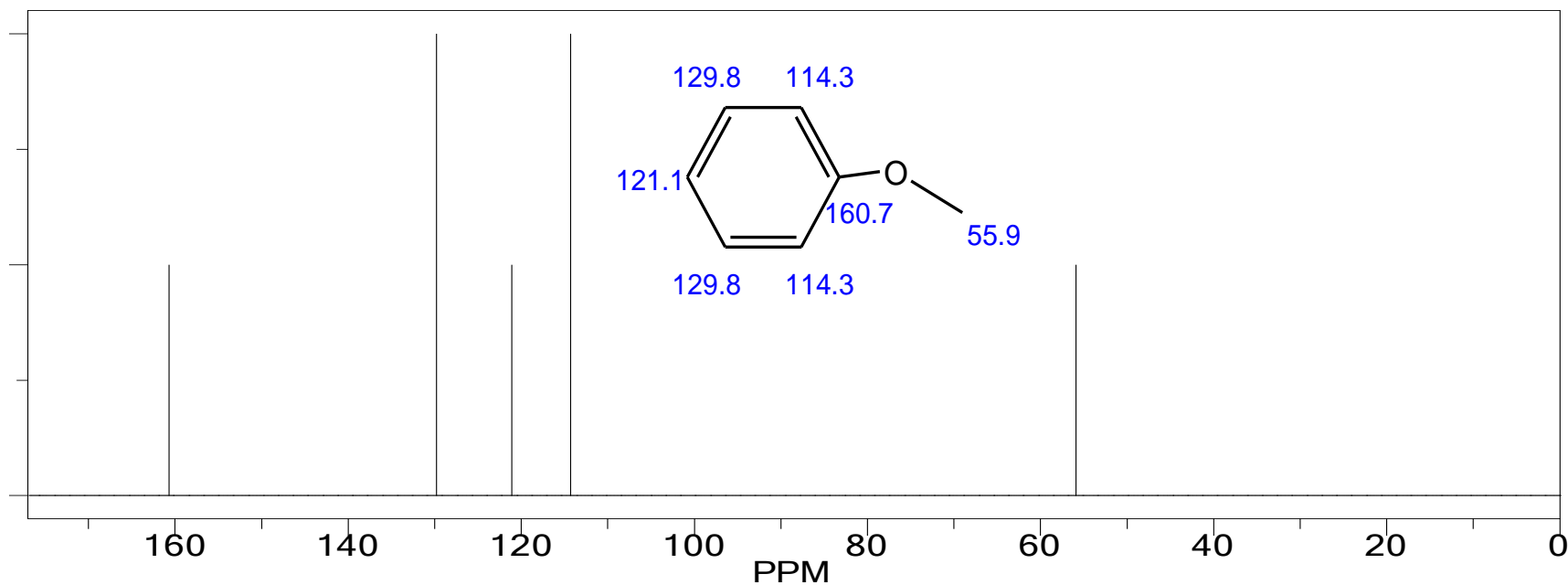
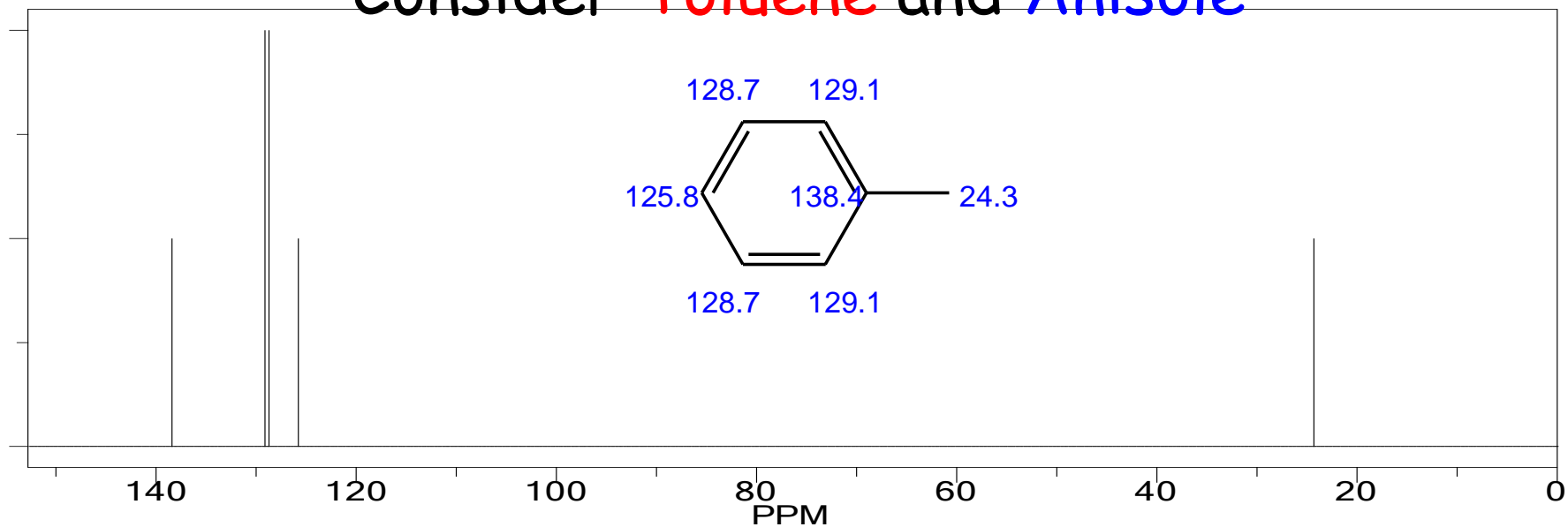
A		A	4 3	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:
B		B	3 2	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:
C		C	4 3	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:
D		D	3 2	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:
E		E	3 3	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:
F		F	3 2	Number of distinct carbon atoms: ... Number of distinct hydrogen groups:

^{13}C -NMR Spectroscopy

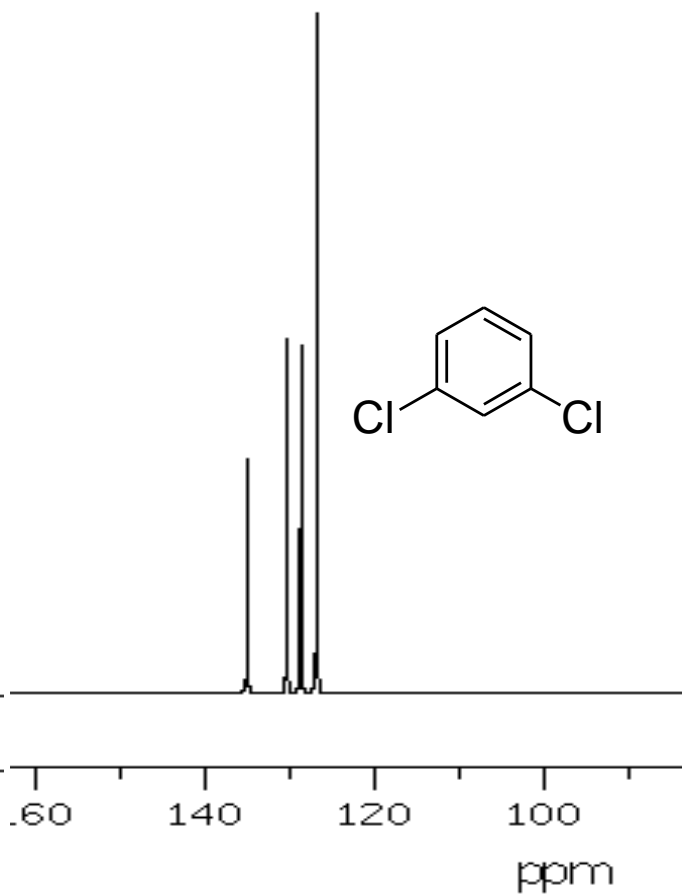
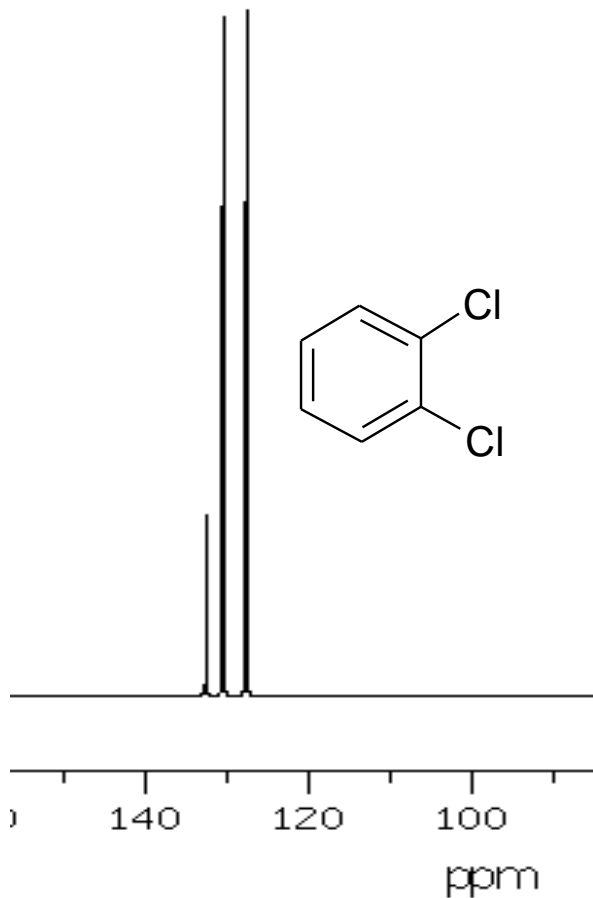
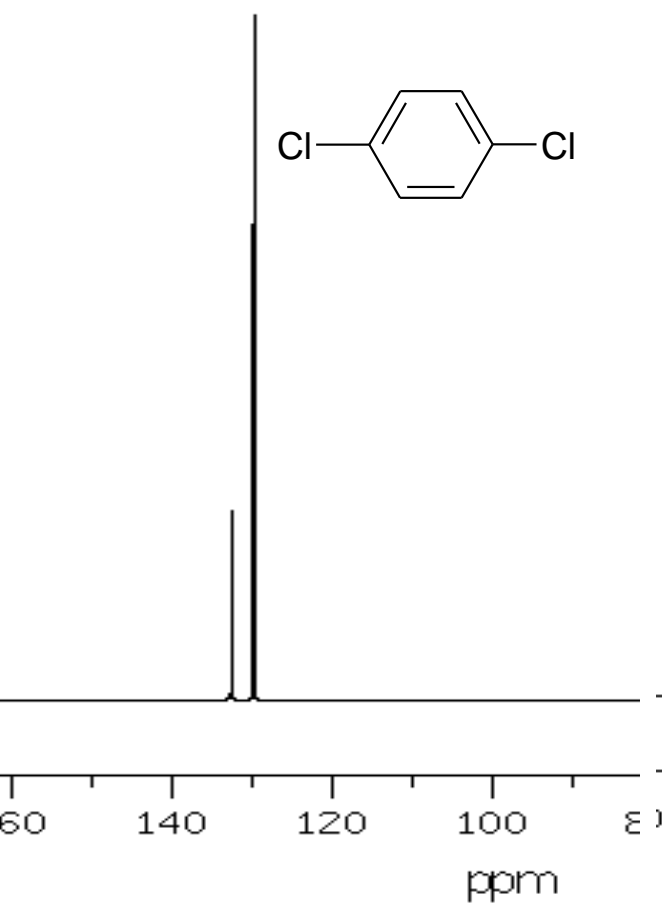
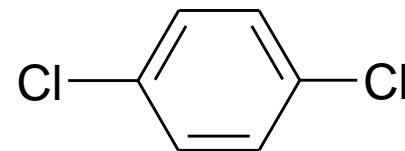
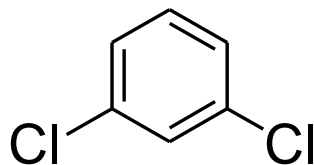
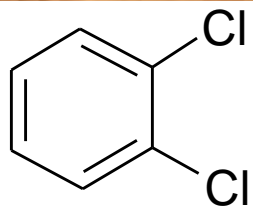
In H-Decoupled Spectrum of ^{13}C -NMR

1. Types of Carbon correspond to the Number of Peaks
- Non-equivalent Carbons
2. The Peak intensity ~~does not only indicate number of~~ equivalent Carbons, but also number of attached Hs
3. The Peak positions i.e. δ values indicate the environment

Consider Toluene and Anisole



^{13}C -NMR Spectroscopy: Types of C



^{13}C -NMR Spectroscopy: Peak intensity

In proton-decoupled ^{13}C spectrum, the peak intensities of the ^{13}C (assuming single carbon) of CH_3 , CH_2 , CH and C are usually:

$$\text{CH}_3 > \text{CH}_2 > \text{CH} > \text{C}$$

Relaxation processes

A short time after a Mag. Field is applied - a slight excess of nuclei in the lower energy (*aligned with*) state - Boltzmann equilibrium.

The method by which the excited nuclei return to lower energy state to establish Boltzmann equilibrium is called Relaxation Process.

^{13}C -NMR Spectroscopy: Peak Intensity

Relaxation process may be of two types:

Spin-Lattice relaxation (T_1) & Spin-Spin relaxation (T_2) and

Spin-Lattice relaxation -
transferring the energy to its surroundings

Spin-Spin relaxation -
transferring the energy to changing another spin

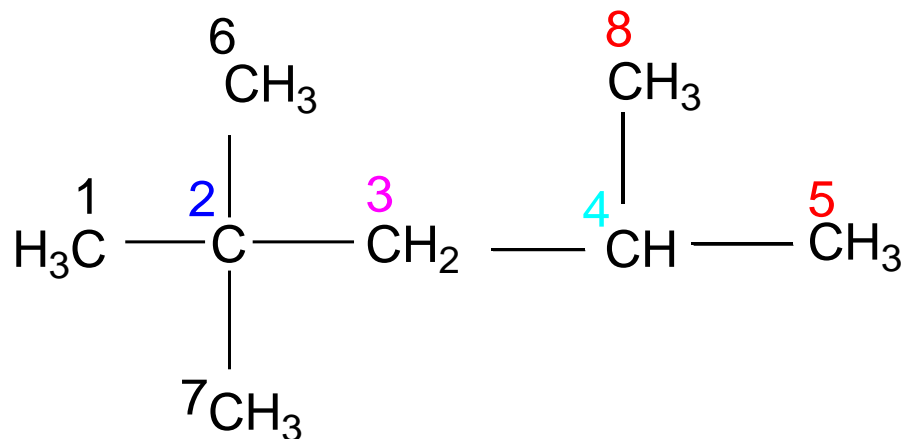
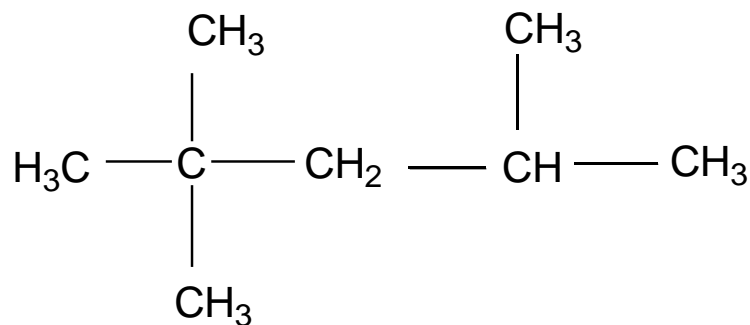
Spin-Lattice relaxation (T_1) relates to intensity of NMR signals and is quite important to ^{13}C NMR spectra because they are much longer.

The longer relaxation time - less number of transitions at a given time - makes the intensity lower.

Quaternary Carbon, not having attached any H, usually has longer T_1 and eventually with shorter peak intensity.

^{13}C -NMR Spectroscopy: T_1

For example:



2,2,4-Trimethylpentane

Carbon No	Relaxation time T_2 (Spin-Lattice)
1, 6, 7	9.3 sec
2	68 sec
3	13 sec
4	23 sec
5, 8	9.8 sec

T_2 being longest (68 sec) for:

C-2, which has no hydrogen;

C-4 is next with one H

C-3 with two H

C-1, 6, 7, 8, 5 have three H each

^{13}C -NMR Spectroscopy - NOE

Variation of ^{13}C peak intensities is also explained by **NOE**
- Nuclear Overhauser Effect or Enhancement

This effect is observed when simultaneous irradiation is operative - effect may be positive / negative

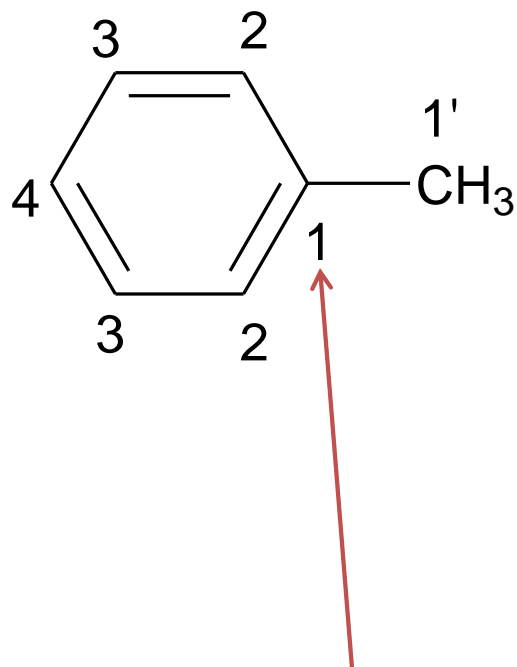
Here, it is heteronuclear i.e. operating between two dissimilar atoms - C & H - Positive Effect

Irradiating the Hs enhances (positive effect) the intensities of the attached carbon signals

Further explanation:

In proton-decoupled ^{13}C spectra, when the Hs in the molecule are irradiated, they become saturated and attain a distribution of spins very different from their equilibrium (Boltzmann) state. There are more spins than normal in the excited state. Due to the interaction of spin dipoles, the spins of the carbon nuclei "sense" the spin imbalance of the H nuclei and begin to adjust themselves to a new equilibrium state that has more spins in the lower state. This increase of population in the lower spin state of Carbon increases the intensity of the NMR signal.

^{13}C -NMR Spectroscopy - NOE & T_1



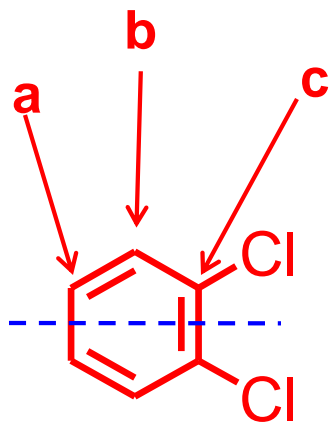
C No	T_1 (sec)	NOE
$1'$	16	0.61
1	89	0.56
2	24	1.6
3	24	1.7
4	17	1.6

The *ipso C* (**C1**), which has no hydrogen, has the longest relaxation time (T_1) and the smallest NOE.

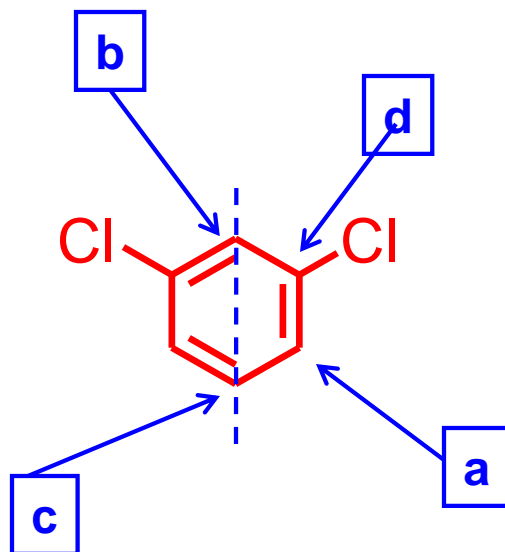
The **C1** has the lowest peak intensity.

^{13}C -NMR Spectroscopy - Peak Positions

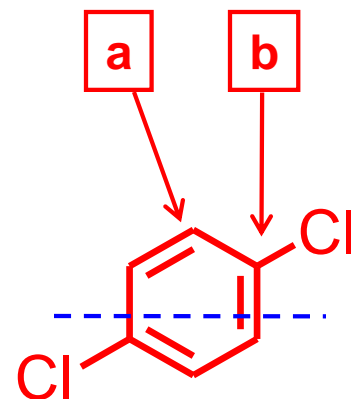
$a < b < c < d$



3 types



4 types



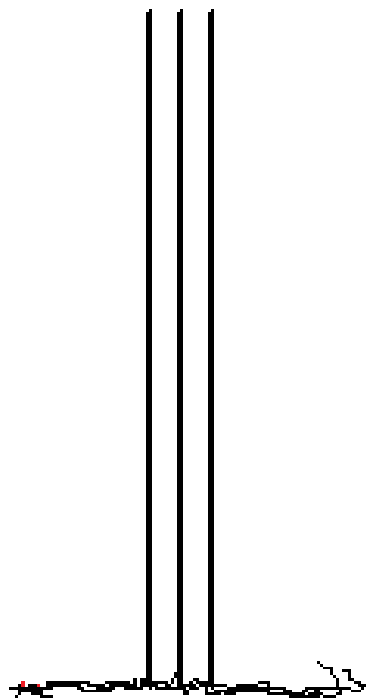
2 types

Protocol of the C-13 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	29.5	-2.3	aliphatic
	9.1	1	alpha -C
	28.2	3	beta -C
	-2.5	1	gamma -C
	-3.0		general corrections
C	35.9	-2.3	aliphatic
	36.4	4	alpha -C
	9.4	1	beta -C
	-7.6		general corrections
CH2	38.9	-2.3	aliphatic
	18.2	2	alpha -C
	28.2	3	beta -C
	-5.2		general corrections
CH3	8.8	-2.3	aliphatic
	9.1	1	alpha -C
	9.4	1	beta -C
	-7.5	3	gamma -C
	0.1		general corrections

^{13}C -NMR Spectroscopy – Solvent peaks

Chloroform-d: CDCl_3



77.00

It gives rise to a
"triplet" in ratios 1 : 1 : 1

This is because:

In contrast with H (spin = $\frac{1}{2}$), D has spin 1. A single D nucleus can adopt three different spins ($2nI + 1$), where the spins have quantum nos. -1, 0, and +1. Since all spin states are equally probable, we see different chemical shifts for the carbon atom in CDCl_3 ($2 \times 1 \times 1 + 1 = 3$) i.e. *triplet*.

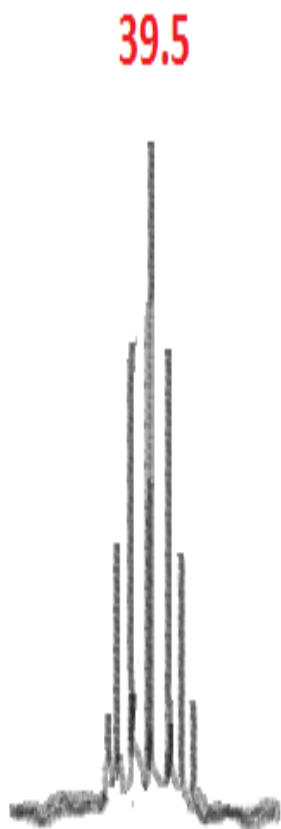
For CHCl_3

$$2 \times 1 \times \frac{1}{2} + 1 = 2$$

i.e. *doublet*

^{13}C -NMR Spectroscopy - Solvent peaks

For D-6 DMSO: $\text{CD}_3 - \text{SO} - \text{CD}_3$

$$2 n I + 1 = 2 \times 3 \times 1 + 1 = 7$$


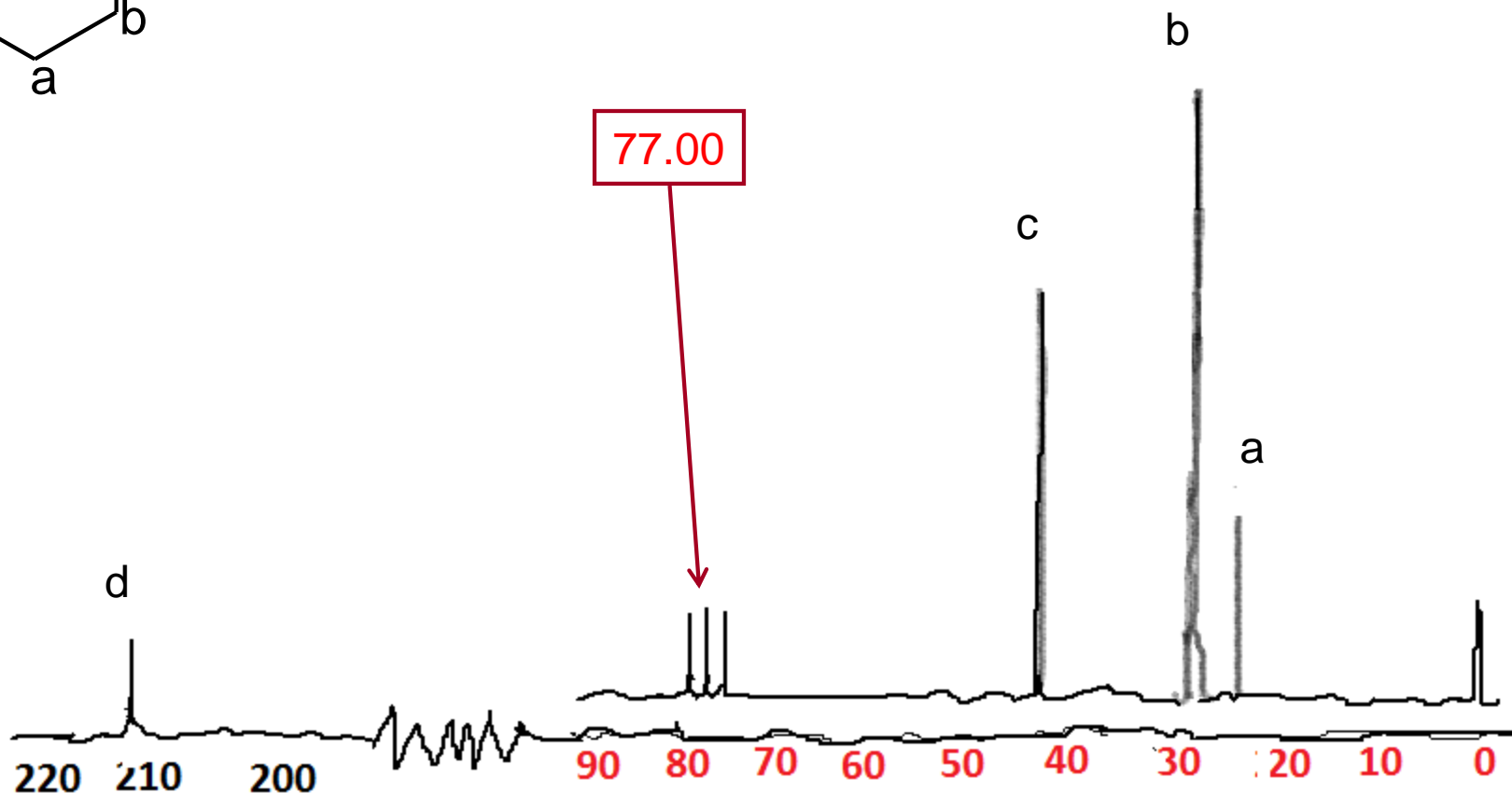
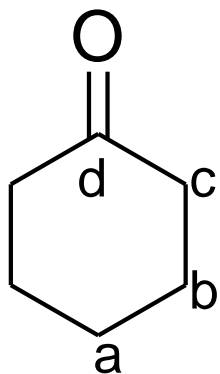
Seven peaks (septet),
centered at δ 39.5

For D-6 Acetone: $\text{CD}_3 - \text{CO} - \text{CD}_3$

$$2 n I + 1 = 2 \times 3 \times 1 + 1 = 7 \text{ (septet)}$$

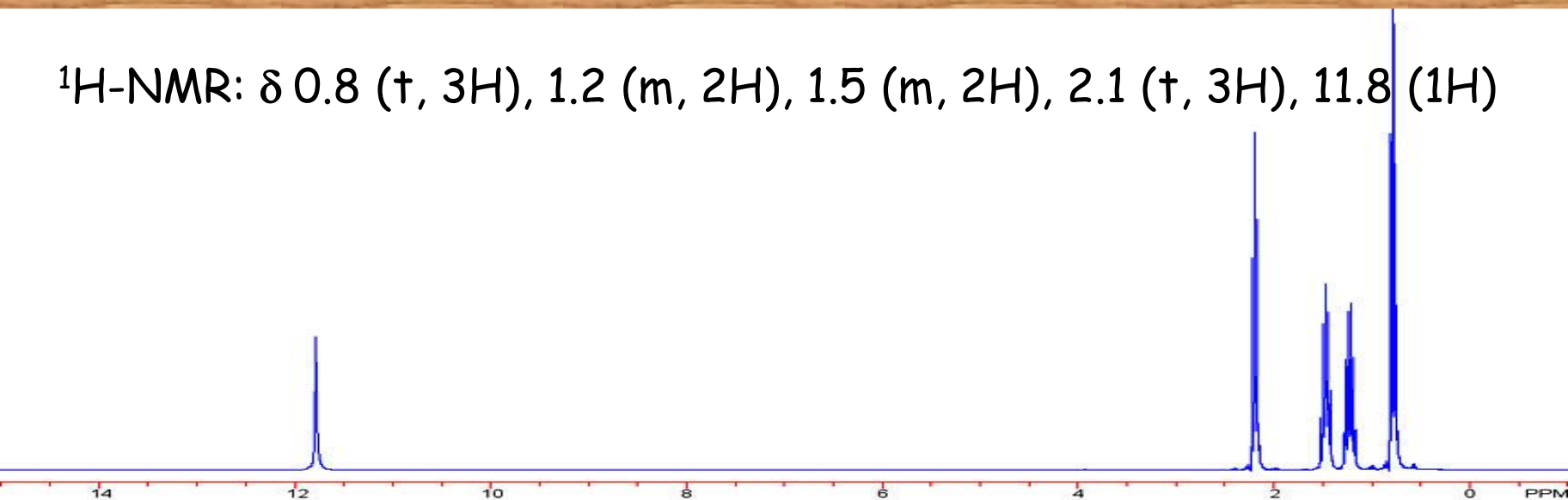
n	$2nI+1$	Relative Intensities
0	1	1
1	3	1 1 1
2	5	1 2 3 2 1
3	7	1 3 6 7 6 3 1
4	9	1 4 10 16 19 16 10 4 1

NMR Spectroscopy - Sample problem

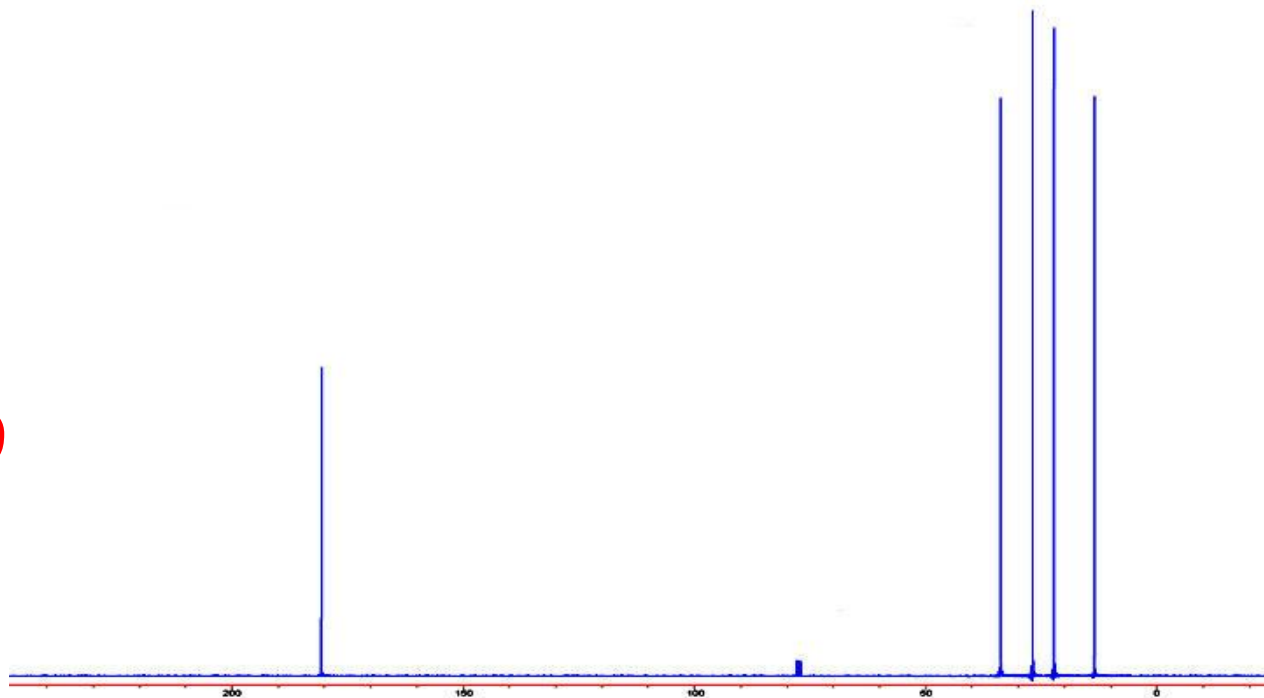
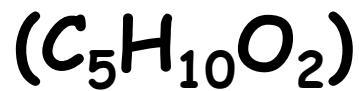


NMR Spectroscopy - Combined problem

^1H -NMR: δ 0.8 (t, 3H), 1.2 (m, 2H), 1.5 (m, 2H), 2.1 (t, 3H), 11.8 (1H)



^{13}C -NMR: δ
13, 21, 27, 33, 180



NMR Spectroscopy - Combined problem

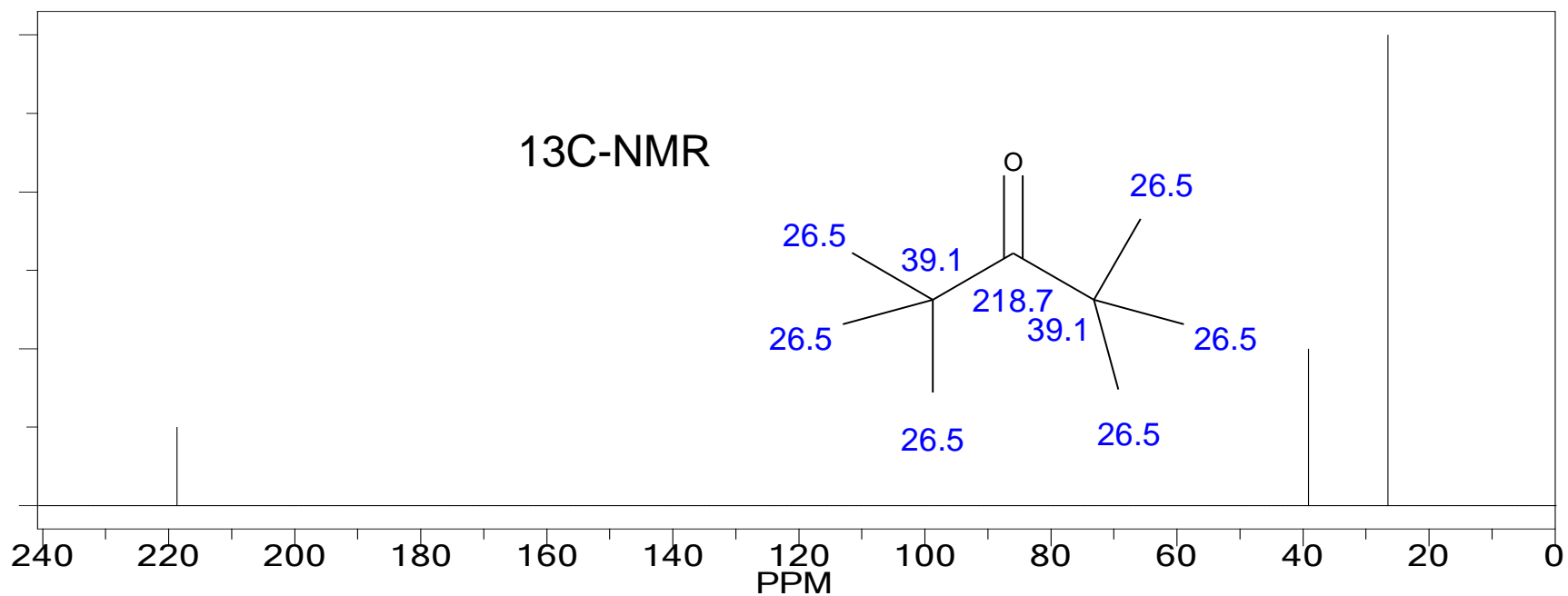
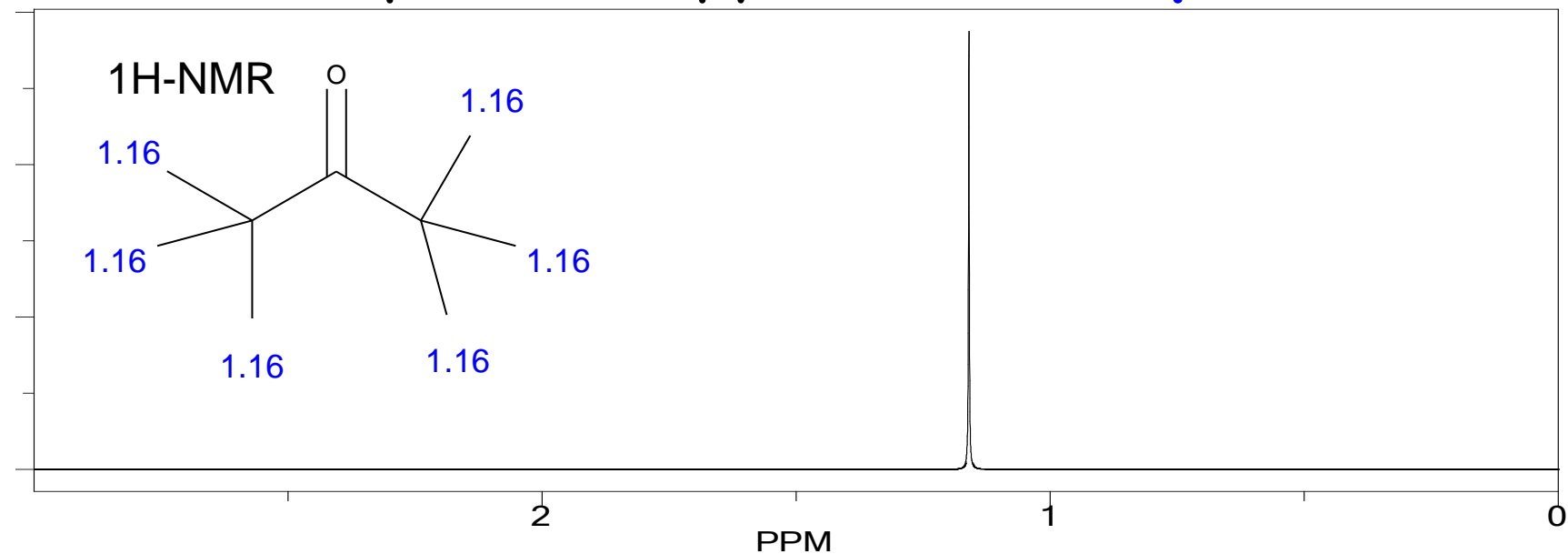
A compound of mf. $C_9H_{18}O$ shows its IR: ν_{\max} 1715 cm^{-1} ; 1H -NMR ($CDCl_3$): δ 1.16 (singlet); ^{13}C -NMR ($CDCl_3$): δ 26.5, 39.1 and 218.7. Deduce the possible structure based on the above data and interpret.

Answer:

1. The Double Bond Equivalence (DBE) is: ONE
2. It shows IR absorption max. at 1715 cm^{-1} . It may contain a carbonyl group, non-conjugated, which can account for one DBE.
3. Only one group of protons is shown in 1H -NMR. It means all 18 Hs are chemically equivalent. Thus there may be six methyl groups with same chemical environment.
4. ^{13}C -NMR shows one peak at δ 218.7 ppm, meaning that it may be a keto carbonyl carbon.
5. Considering above and placing six methyl groups on each side of a keto carbonyl Carbon, the proposed structure may be: Di *t*-Butyl ketone, which can account for all spectral data.

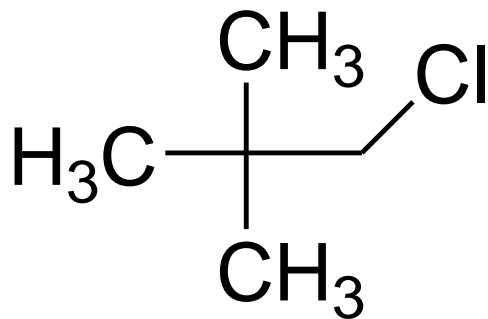
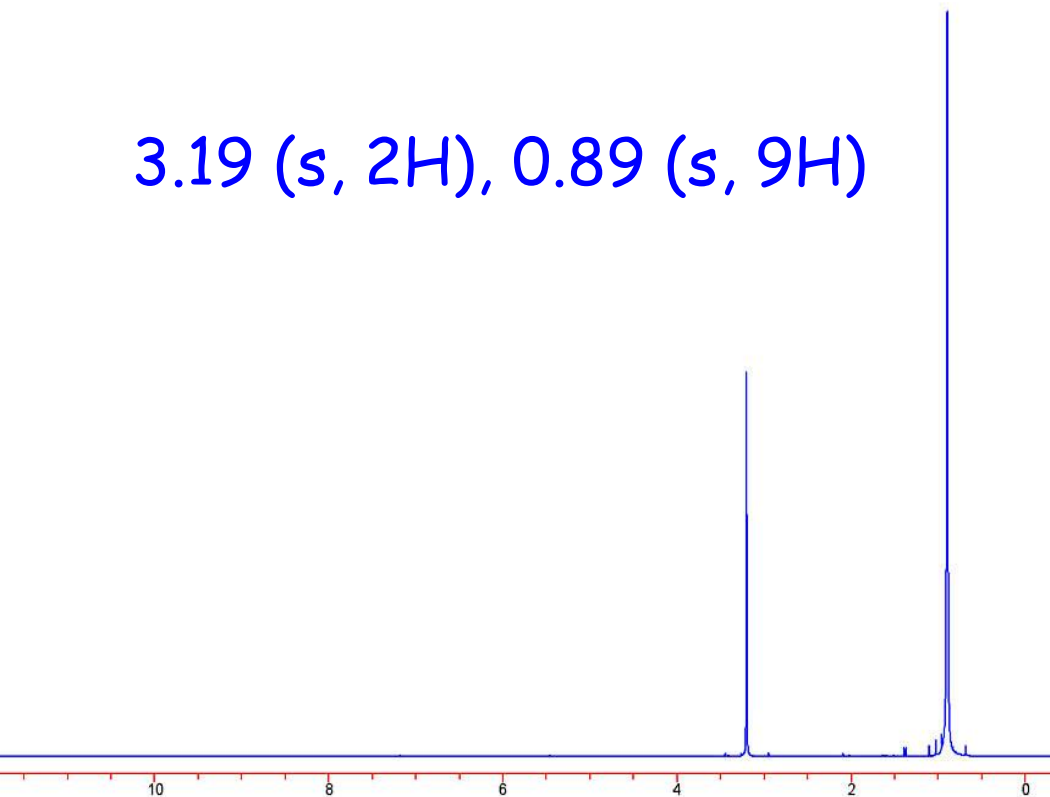
2,2,4,4-Tetramethylpentan-3-one

NMR Spectroscopy - Combined problem

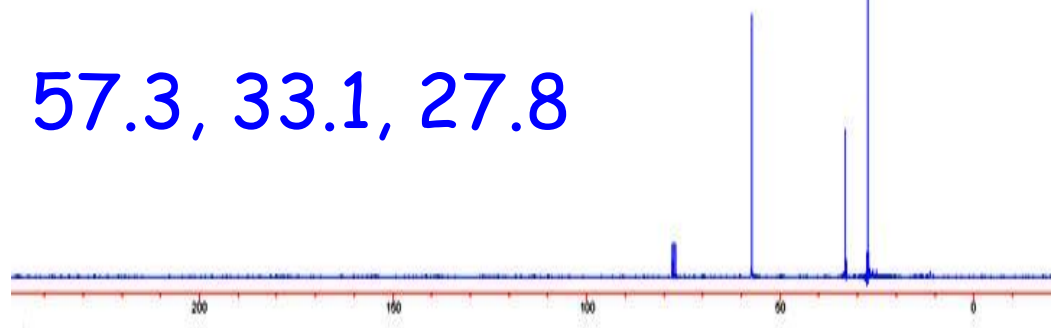


NMR Spectroscopy - Combined problem

3.19 (s, 2H), 0.89 (s, 9H)



57.3, 33.1, 27.8



(C₅H₁₁Cl)

NMR Spectroscopy - Combined problem

A liquid compound [A] of mf. C_5H_8O , exhibits IR ν_{\max} at 1740 cm^{-1} and also forms 2,4-DNP derivative. Compound [A] does not respond to haloform test. A mixture of Compound [A] and ethyl cyanoacetate is passed through pre-heated alumina ($120\text{ }^{\circ}\text{C}$) to afford a new compound [B].

The Molecular ion (m/z) for $[M+H]^+$ of the compound [B] by Mass spectrometer is found to be **180**.

IR (neat): ν_{\max} 2180, 1700, 1596 cm^{-1}

$^1\text{H-NMR}$ (CDCl_3): δ 1.12 (t, 3H, $J = 7\text{ Hz}$), 1.83 (t, 4H, $J = 5\text{ Hz}$), 2.33 (t, 4H, $J = 5\text{ Hz}$), 4.05 (q, 2H, $J = 7\text{ Hz}$)

$^{13}\text{C-NMR}$ H-Decoupled (CDCl_3): δ 14.2, 29.3, 33.1, 60.9, 101.4, 115.9, 176.5, 171.7

Identify [A] and [B]

NMR Spectroscopy - Combined problem

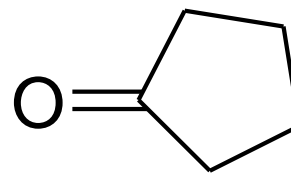
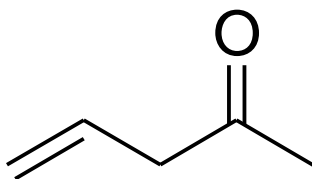
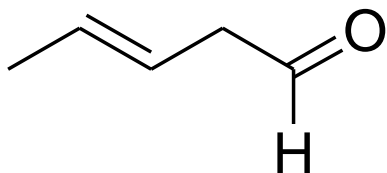
Answer

Compound [A] has DBE = 2,

IR ν_{\max} at 1740 cm^{-1} may indicate presence of carbonyl group and the other may be a double bond or a cycle,

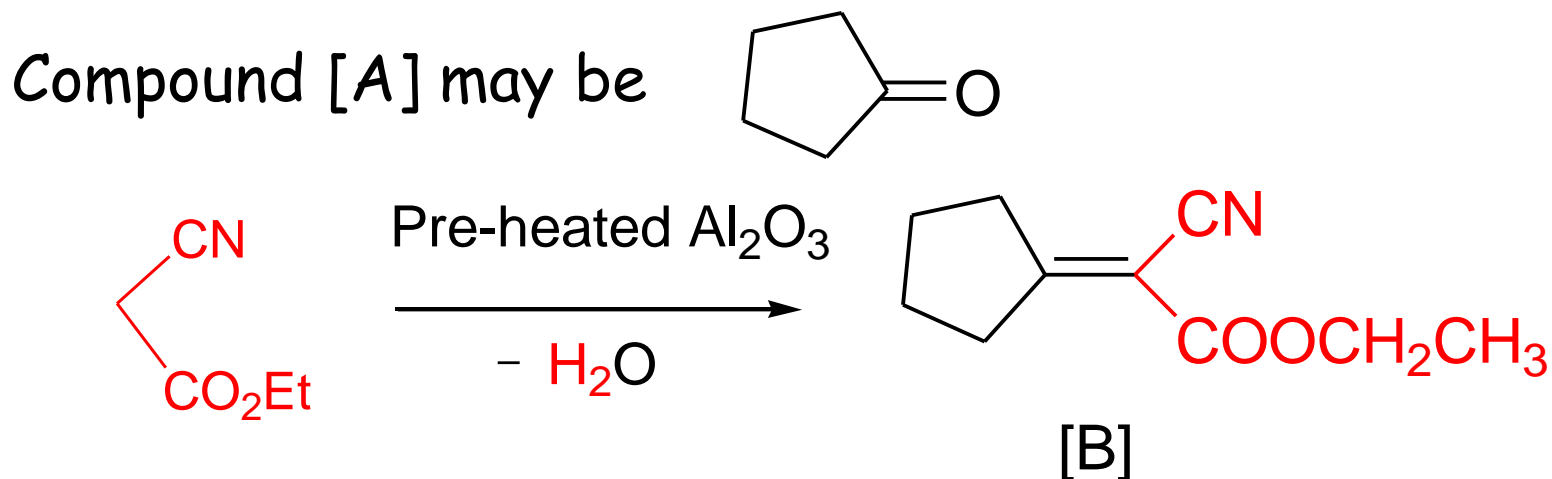
The carbonyl may be a keto or aldehyde as it gives 2,4-DNP derivatives,

If a $C = C$ is present, it may not be conjugated with the carbonyl group, and three possibilities are:



IR ν_{\max} at 1740 cm^{-1} and negative haloform test may rule out the middle ketone and aldehyde and rather favours the strained ring ketone.

NMR Spectroscopy - Combined problem



Heated Alumina may cause dehydration and condensation may occur.

Compound [B] has mf. $C_{10}H_{13}NO_2$ molecular mass is 179.

The $[M+H]^+$ at 180 thus supports for the molecular mass and hence the molecular formula as $C_{10}H_{13}NO_2$

Now, you explain all spectral data for compound [B]

^{13}C -NMR Spectroscopy - Combined problem

A stoichiometric mixture of an aldehyde [A] and an aniline [B] is heated for 4 hr to afford a compound [C], which is subjected to catalytic hydrogenation to produce a new compound [D].

The spectral and other analytical data of different compounds are as follows:

Compound [D]: mf $\text{C}_9\text{H}_{14}\text{N}_2$;

^1H -NMR (CDCl_3): δ 1.18 (d, 6H, $J = 7\text{ Hz}$), 2.97 (septet, 1H, $J = 7\text{ Hz}$), 4.01 (broad s, 3H), 6.18 (d, 2H, $J = 8\text{ Hz}$), 6.24 (d, 2H, $J = 8\text{ Hz}$)

^{13}C -NMR (CDCl_3): δ 23.4, 42.7, 114.3, 117.1, 136.8, 137.6

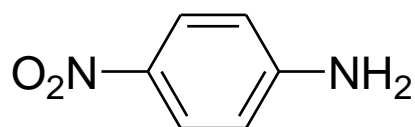
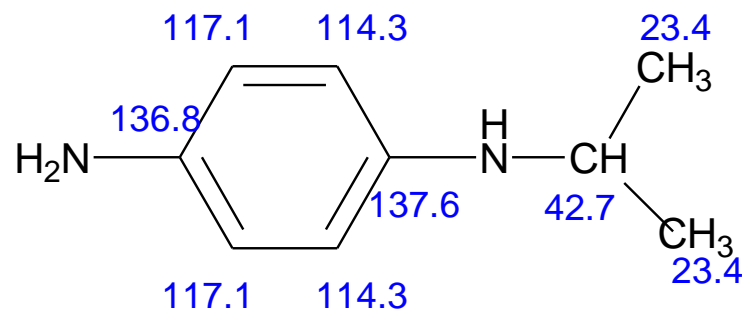
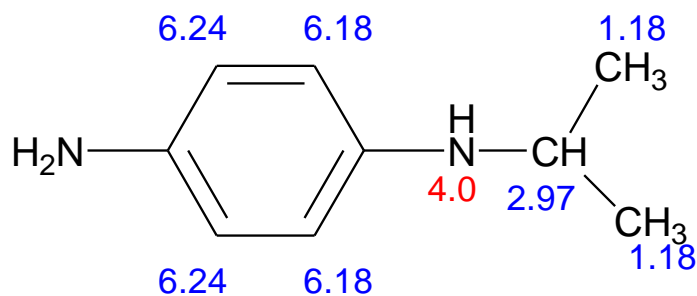
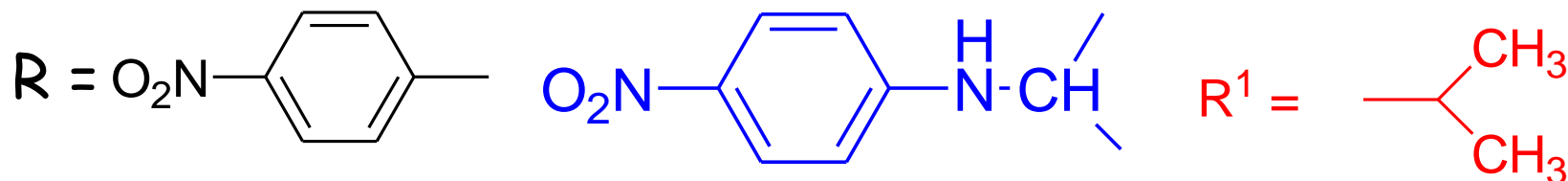
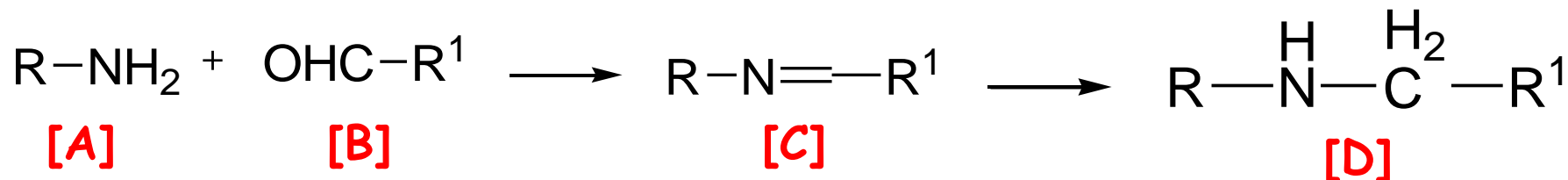
Compound [C]: IR ν_{max} (Neat): 1660, 1605, 1440, 1537, 1345 cm^{-1}

Identify compounds [A], [B], [C] and [D] and outline the reaction scheme

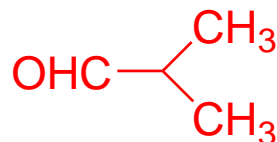
13C-NMR Spectroscopy - Combined problem

Answer

- Aldehyde and aniline on heating produces an imine (Schiff Base)
- The Schiff Base on catalytic hydrogenation will be reduced to an amine



[A]



[B]

IR data of [C]: 1605 (aromatic C=C),
 1537 & 1345 (conjugated C=N)
 1660 & 1440 cm^{-1} (conjugated NO_2)

Books Referred

1. Pavia, Lampmann and Others - NMR Spectroscopy
2. Ian Flemming - NMR Spectroscopy
3. W. Kemp - NMR Spectroscopy
4. Further reading will be supplied