^{13}C-Nuclear Magnetic Resonance (^{13}C -NMR) Spectroscopy

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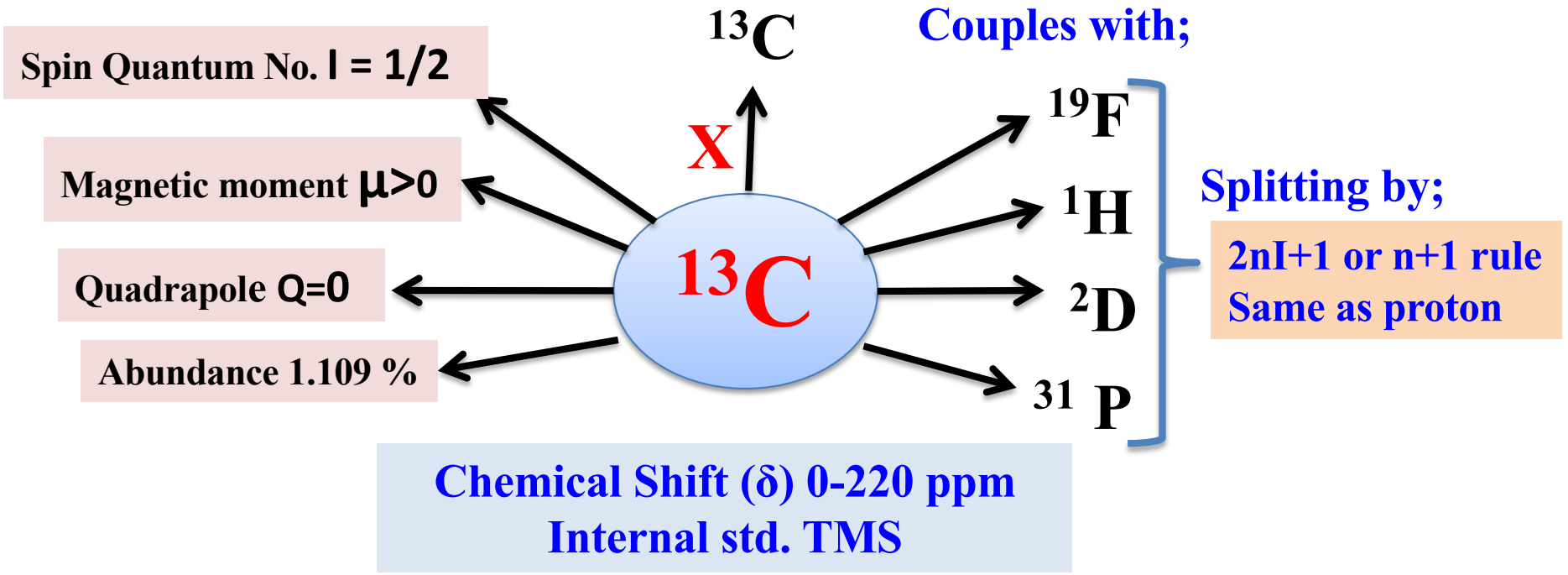
Syllabus

- **General considerations;**
- **Chemical shift [aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carbonyl compounds];**
- **Problems associated with 13C,**
- **FT- NMR,**
- **Proton decoupled off resonance.**

Carbon-13 (^{13}C)-NMR Spectroscopy

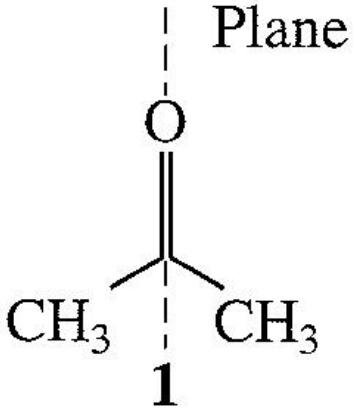


- Magnetogyric ratio of carbon (γ =68) is less than that of proton (γ =268) .
- ^{13}C nuclei resonance 6000 times weaker than ^{1}H-nuclei.
- ^{13}C-NMR resonance (25 MHz) frequency ¼ less than ^{1}H resonance (100 MHz) frequency.
- Homo-nuclear (^{13}C-^{13}C) splitting does not occur.
- Hetero-nuclear (^{13}C-^{1}H) splitting occurs through one bond coupling ($^{1}J_{C\text{-}H}$=100-250 Hz).

An important parameter derived from ^{13}C-NMR spectra is the chemical shift

Number of Signals

Using symmetry and electronic environment



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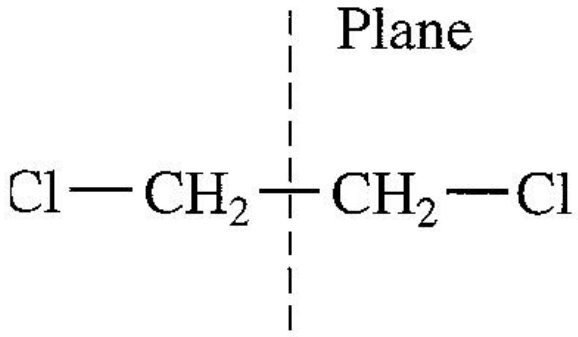

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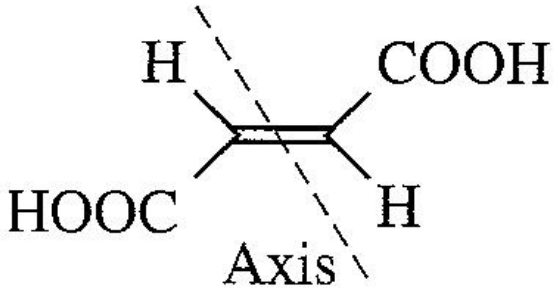

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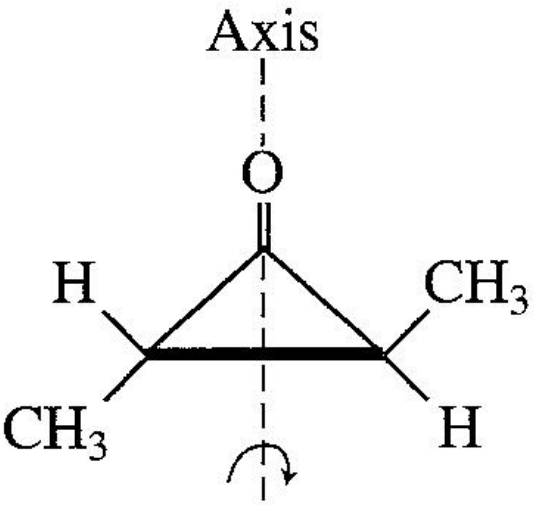

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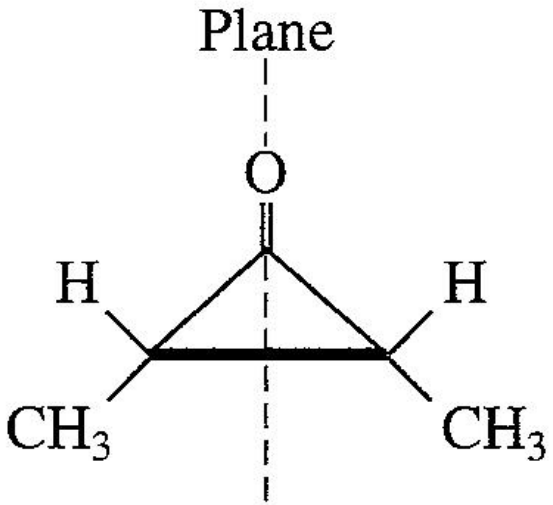
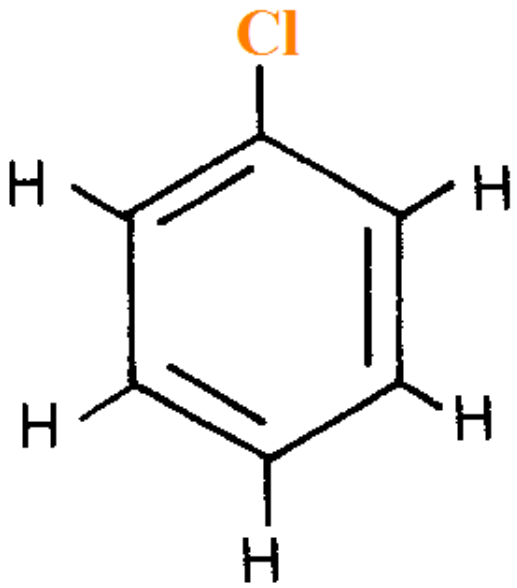
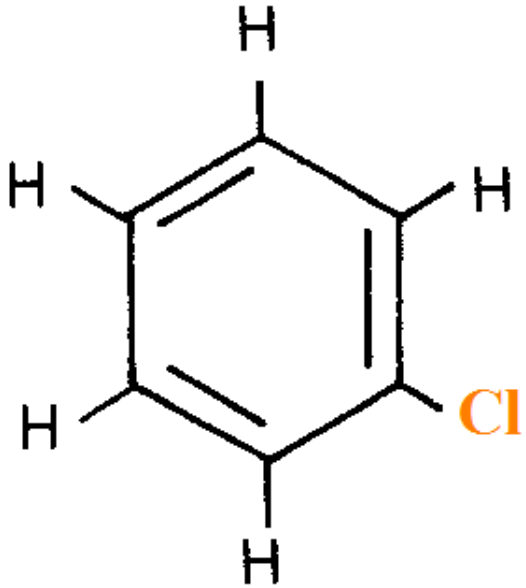
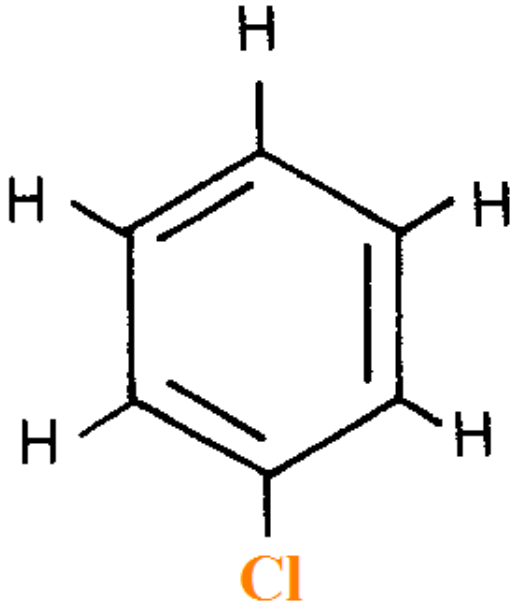


Number of Signals

Mono substituted Benzene



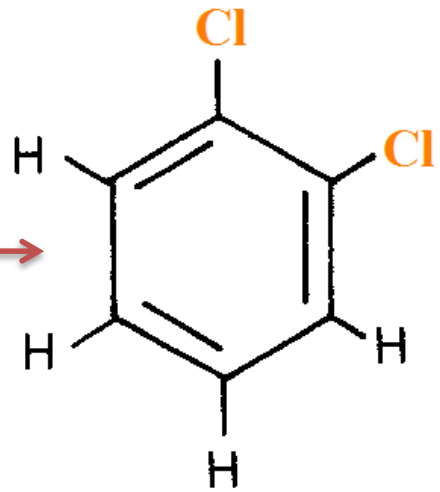


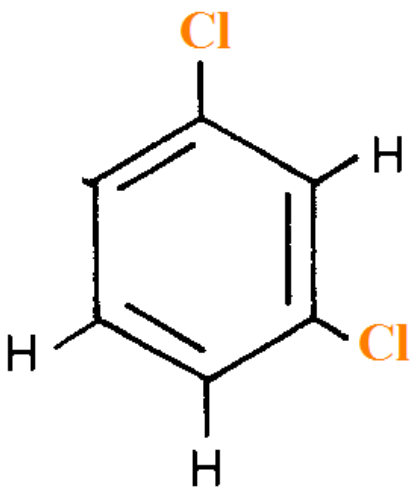


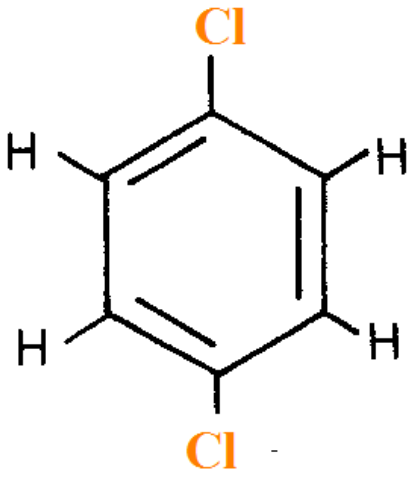
Number of Signals

Di-substituted Benzene

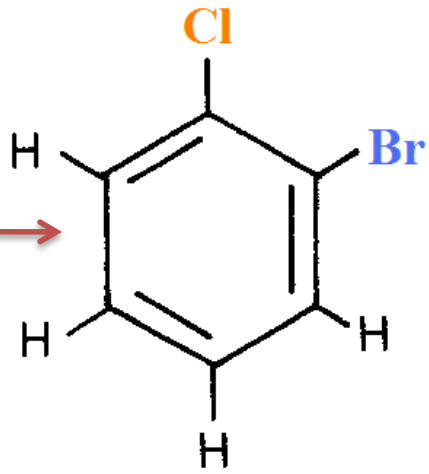
One group →

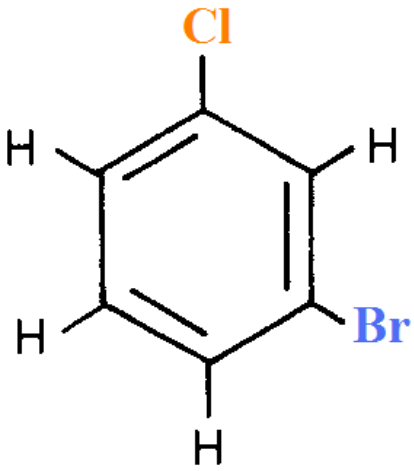


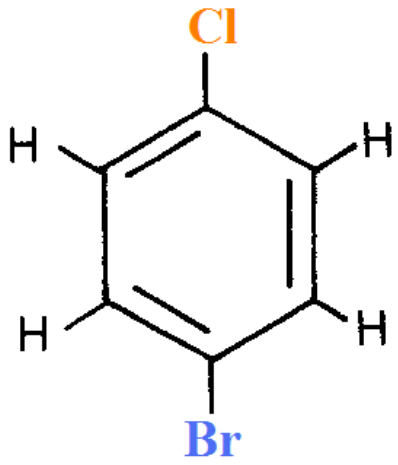




Two group →

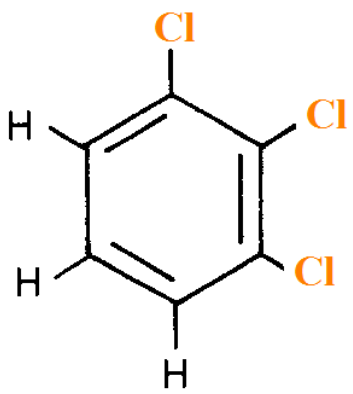


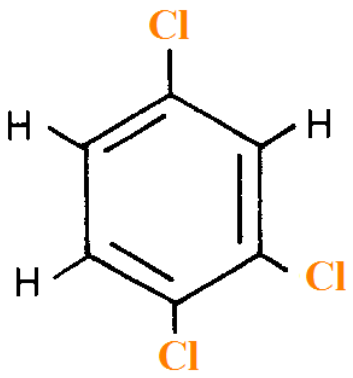


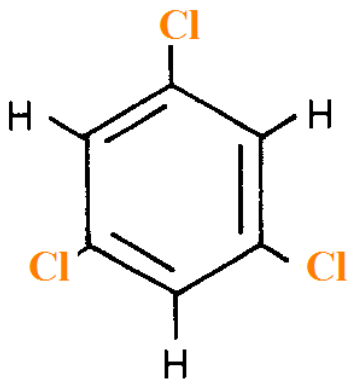


Number of Signals

Tri-substituted Benzene

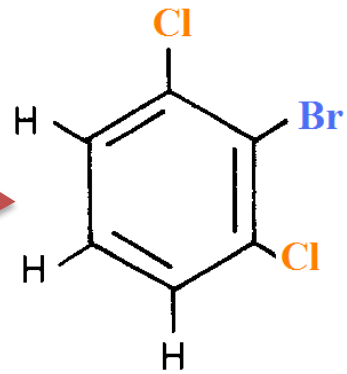


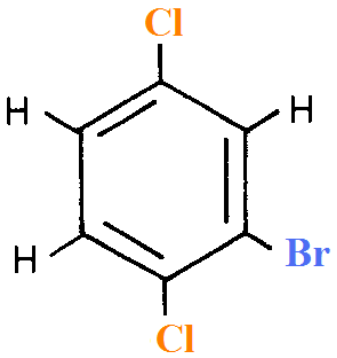


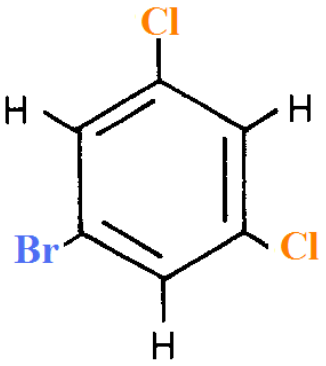


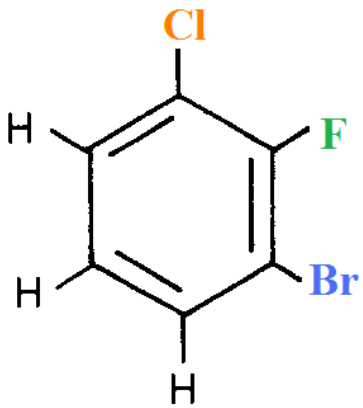
One group

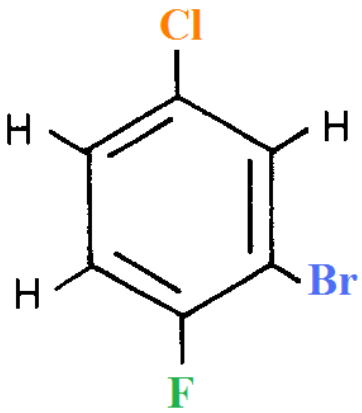
Two group

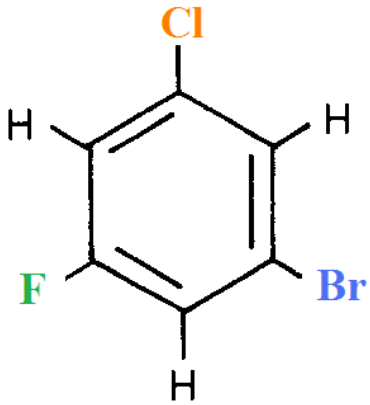








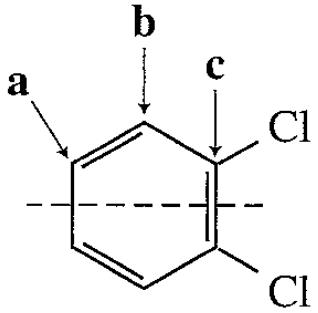




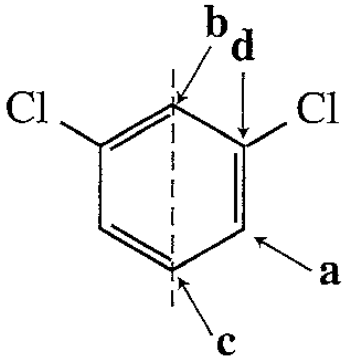
Tree group

Number of Signals

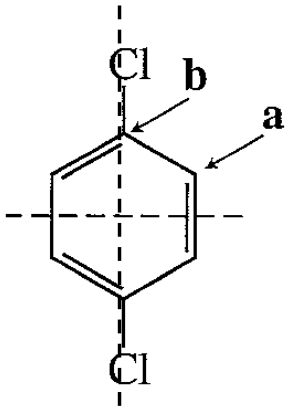
Using symmetry and electronic environment



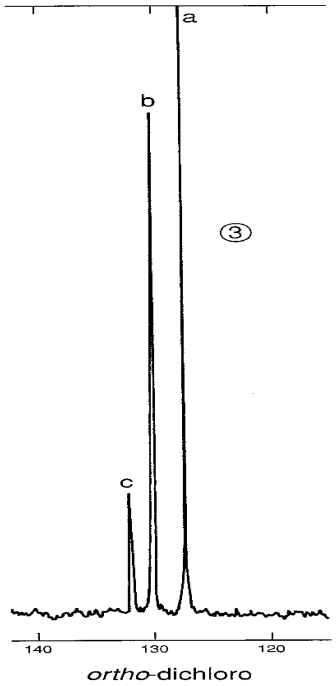
Three unique carbon atoms

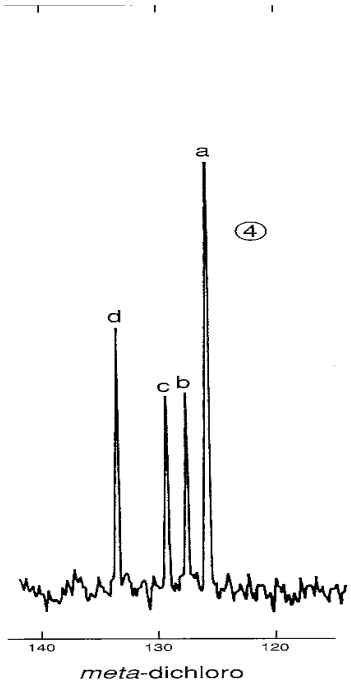


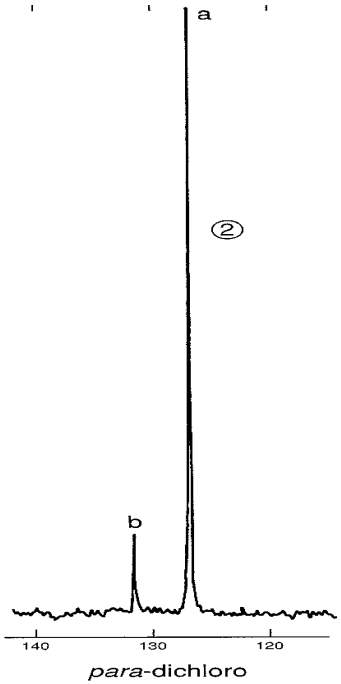
Four unique carbon atoms



Two unique carbon atoms

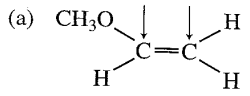


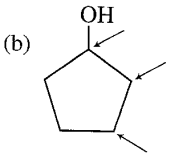


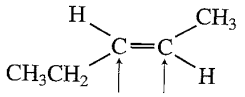


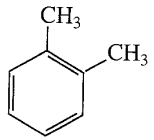
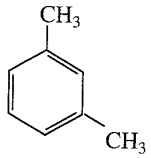
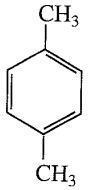
Number of Signals

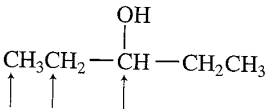
Using symmetry and electronic environment

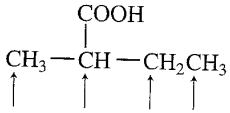
(a) 

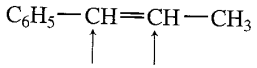
(b) 

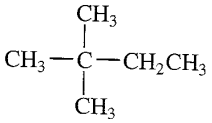
(c) 

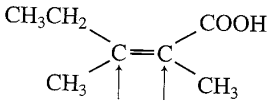
(d)  All  All  All

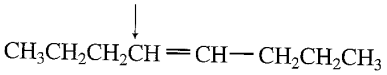
(e) 

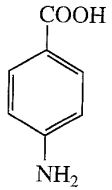
(f) 

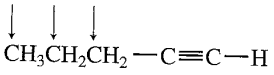
(g) 

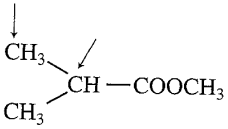
(h)  All

(i) 

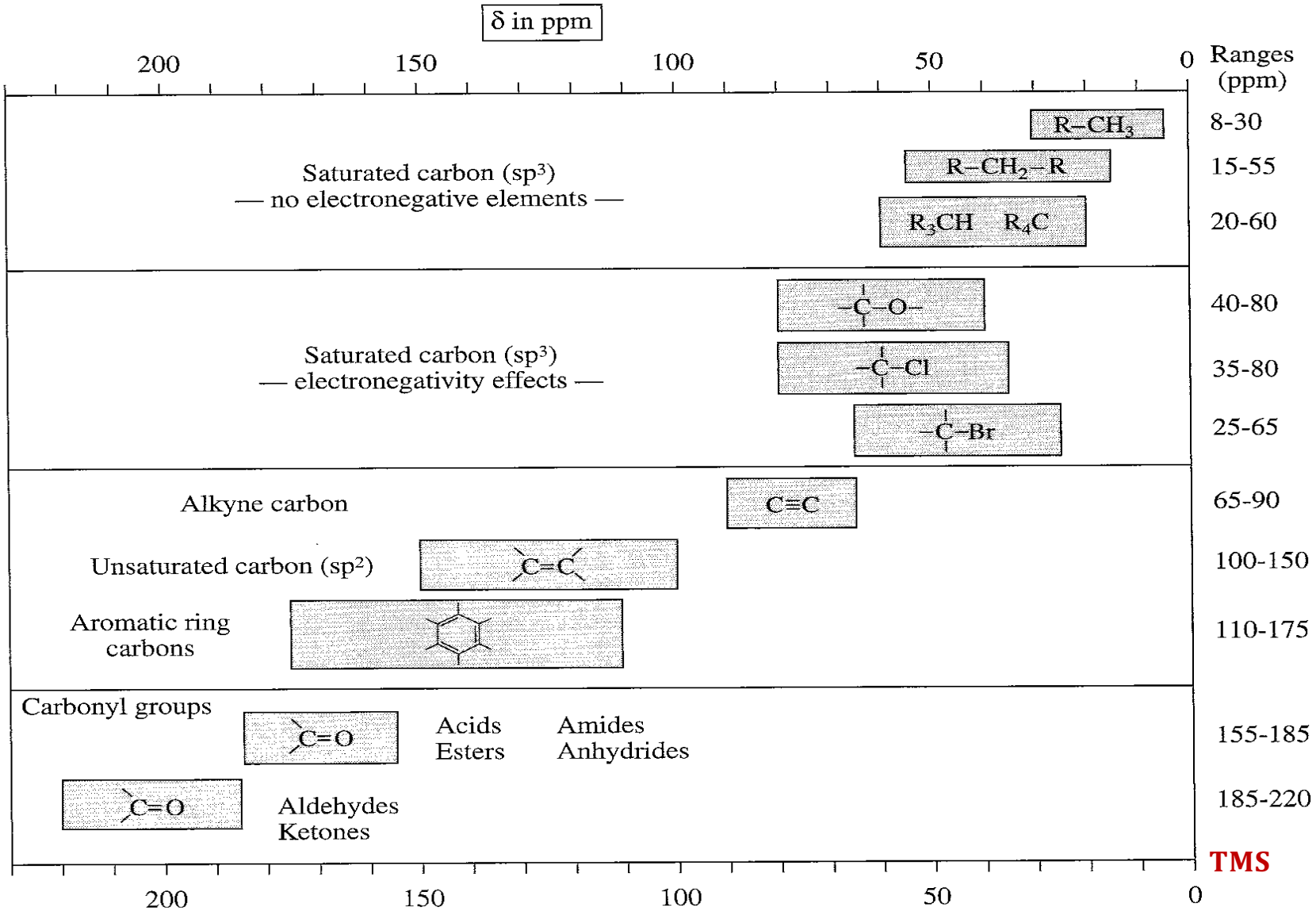
(j) 

(k)  Ring carbons

(l) 

(m) 

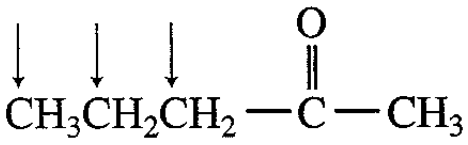
Chemical Shift (δ =0-220 ppm)



Electronegativity, hybridization and anisotropy effect same fashion as ^{1}H-NMR

Identify chemical shift

(n)



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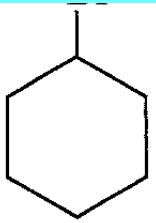

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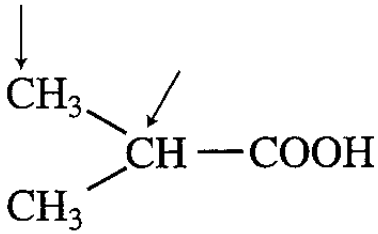

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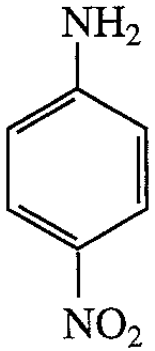

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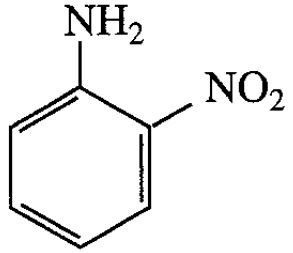

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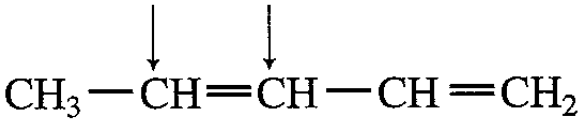

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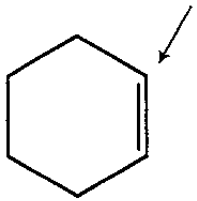

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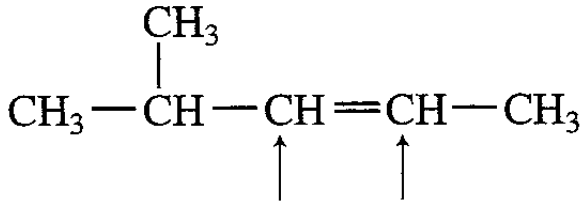
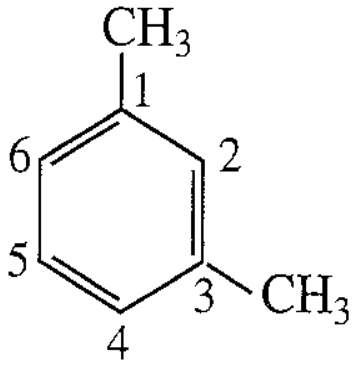


Calculation of Chemical Shift Value

Consider *m*-xylene (1,3-dimethylbenzene) as an example.

base value for the carbons in a benzene ring is 128.5 ppm.

	ipso	*ortho*	*meta*	*para*
CH_3:	9.3	0.7	−0.1	−2.9 ppm



C1 = base + *ipso* + *meta* = 128.5 + 9.3 + (−0.1) = 137.3 ppm

C2 = base + *ortho* + *ortho* = 128.5 + 0.7 + 0.7 = 129.9 ppm

C3 = C1

C4 = base + *ortho* + *para* = 128.5 + 0.7 + (−2.9) = 126.3 ppm

C5 = base + *meta* + *meta* = 128.5 + 2(−0.1) = 128.3 ppm

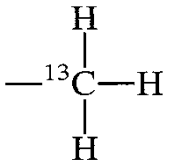
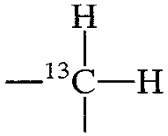
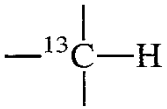
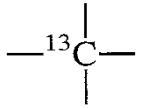
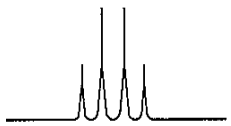
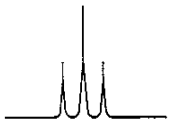
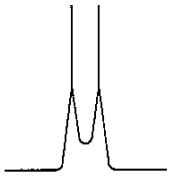
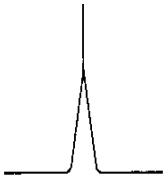
C6 = C4

Splitting of signals in ^{13}C–NMR

Homonuclear (^{13}C-^{13}C) Coupling= Not observed (low abundance)

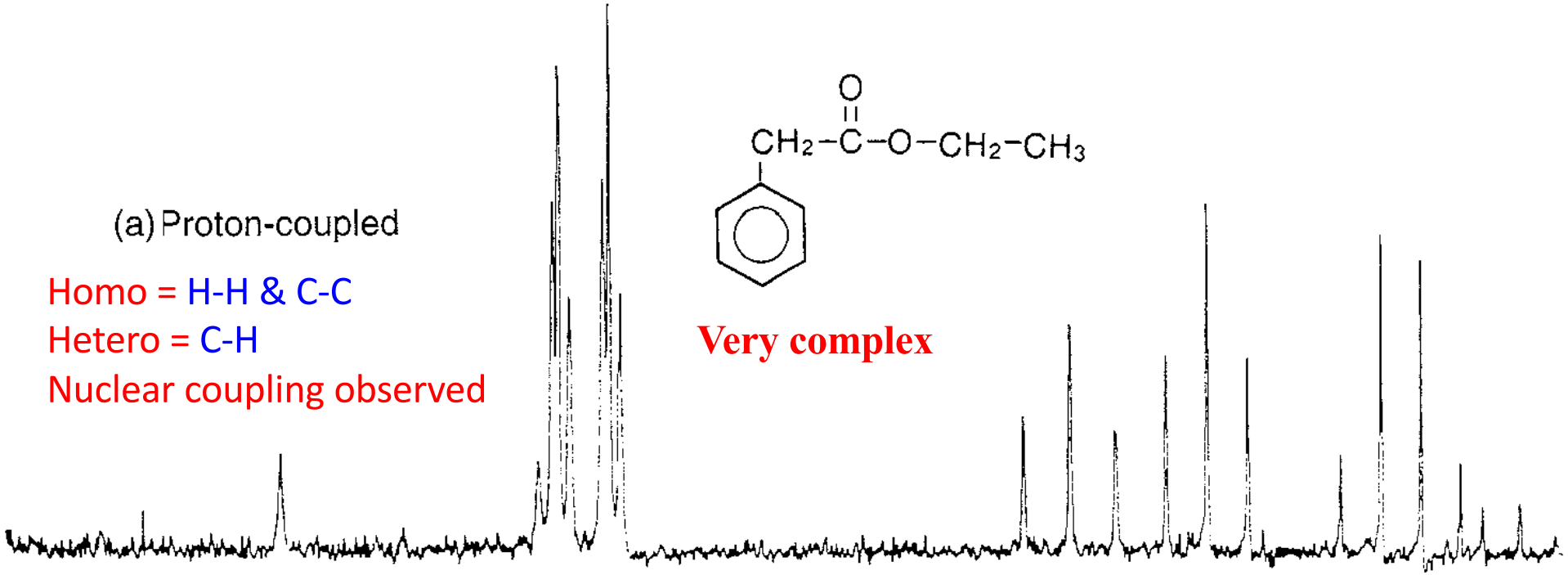
Heteronuclear (^{13}C-^{1}H) Coupling=

- Mostly observed through one bond coupling ($^{1}J_{C\text{-}H}$).
- Splitting occurs by n+1 rule
- Coupling constant ^{1}J=100 to 250 Hz (larger than H nuclei)

3 protons	2 protons	1 proton	0 protons
			
$n + 1 = 3 + 1 = 4$	$n + 1 = 3$	$n + 1 = 2$	$n + 1 = 1$
			
Methyl carbon	Methylene carbon	Methine carbon	Quaternary carbon

Proton-coupled Spectra

A spectra that show the spin-spin splitting between Carbon-13 and the proton directly attached to it are called proton coupled spectra.

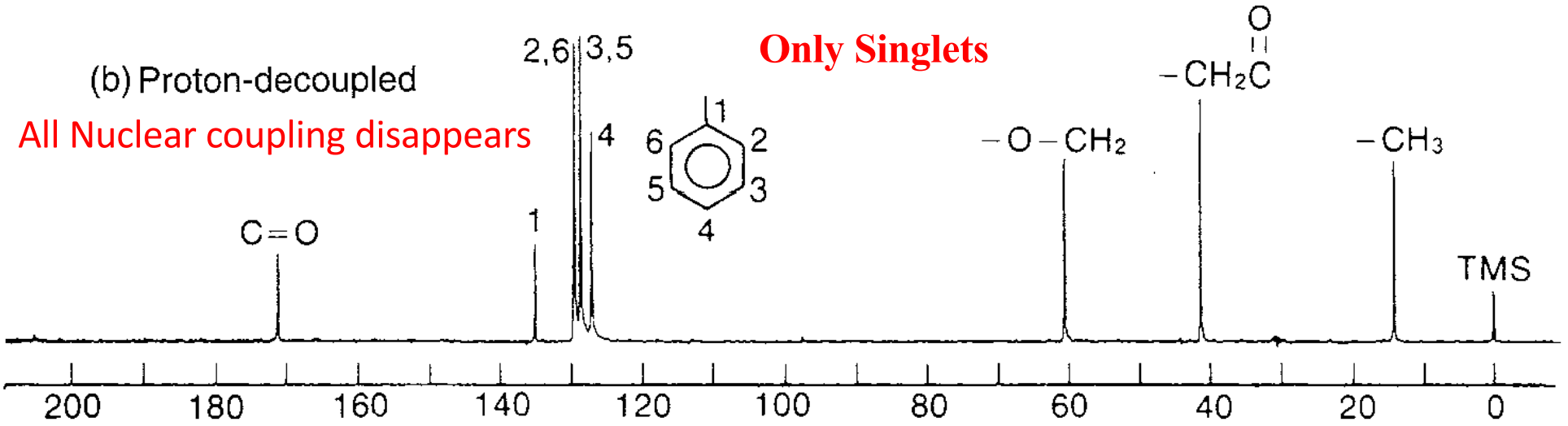


- Very complex spectra often difficult to analysis.
- The multiplets from different carbons commonly overlaps
- ^{13}C-H coupling constant are frequently larger than the chemical shift differences of the carbons in the spectrum.

Proton Decoupled Spectra

A proton decoupling is process by simultaneously irradiating all of the proton in the molecule with a broad spectrum of frequencies in the proper range (approximately 1000 MHz).

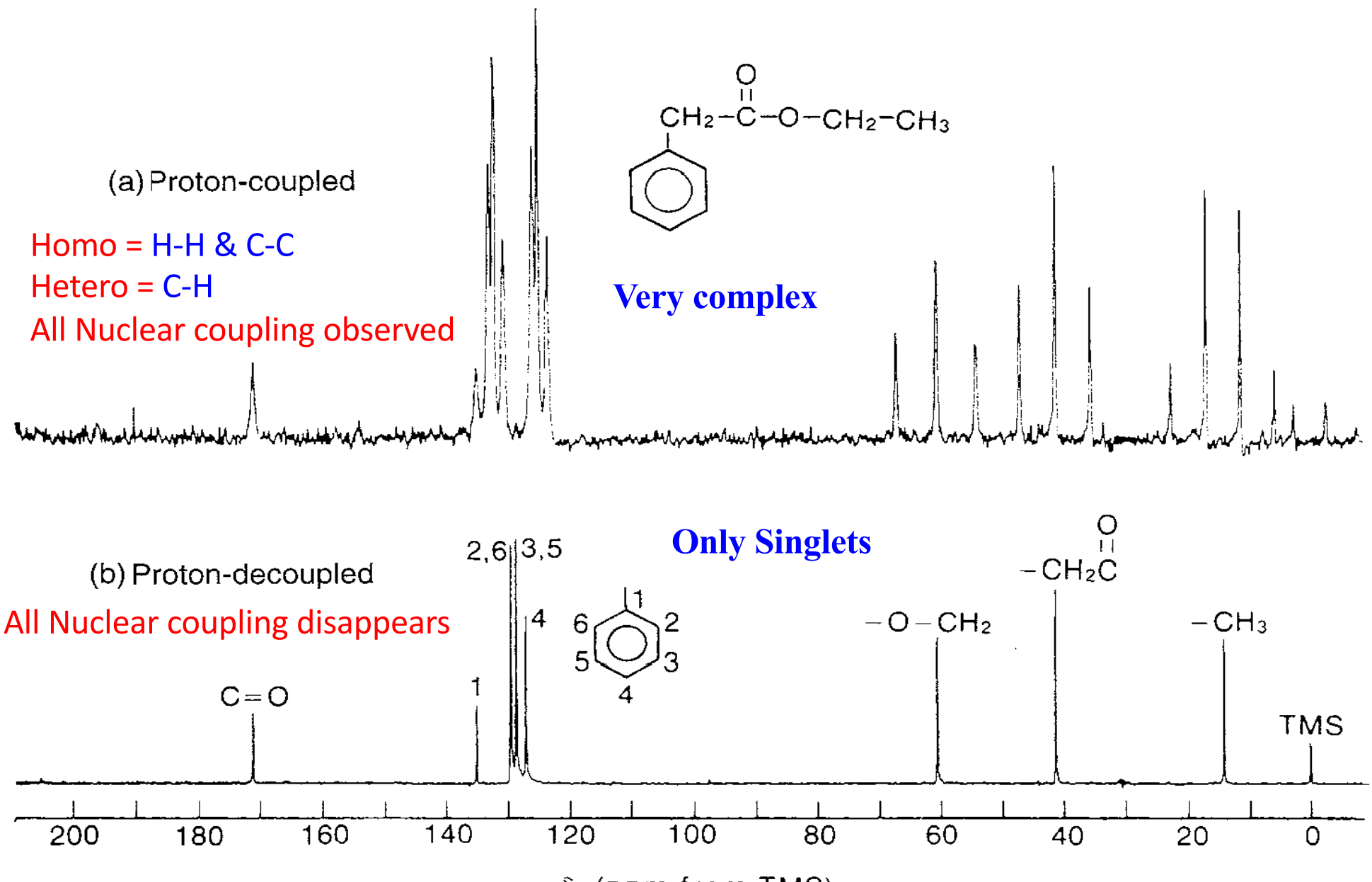
- Second frequency generator is used for decoupler.



- Avoids overlapping multiplets.
- Only Singlets are observed (All carbons become singlets).
- Advantages: Peak intensity increases due to NOE effect.

  Signal to noise ratio improve.
- Disadvantage: Information on attached hydrogen is lost.

Proton-coupled and Decoupled ^{13}C-NMR Spectra

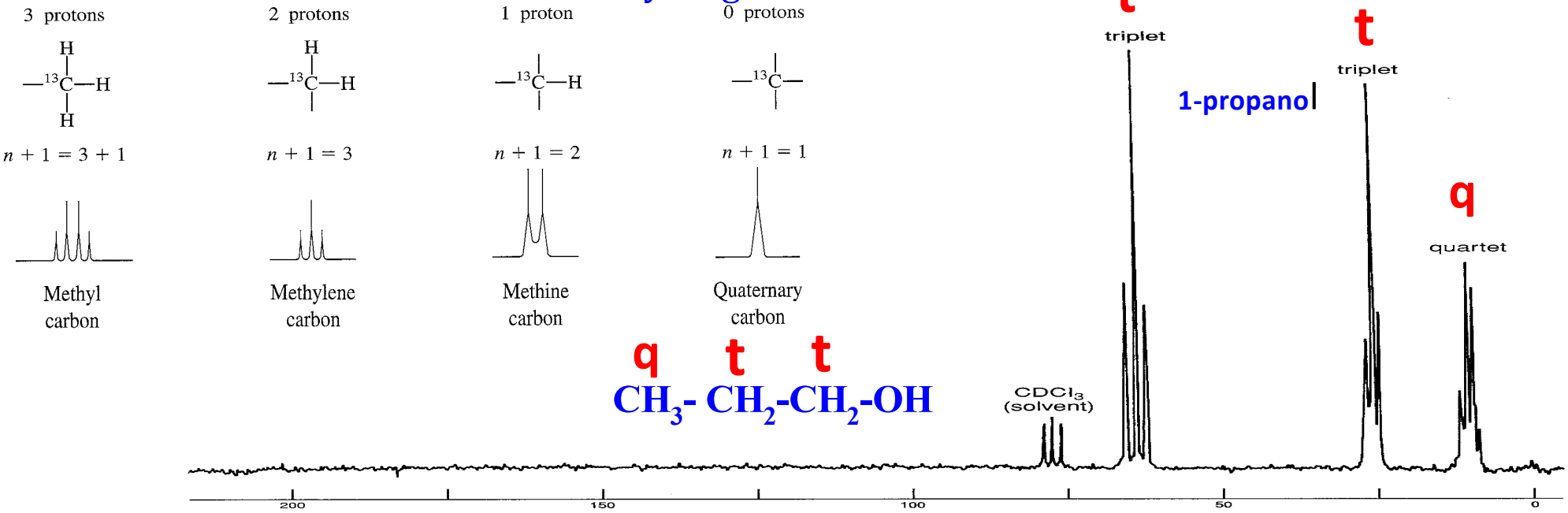


Off resonance decoupled spectra

In off resonance decoupled spectrum, the coupling between each carbon atom and each hydrogen atom attached directly (^{13}C-H) are observed by n+1 rule.

Decoupler irradiates the sample at 1000–2000 Hz upfield or 2000–3000 Hz downfield.

The n+1 rule can be used to determine whether carbon atom has three, two, one or no hydrogen attached.

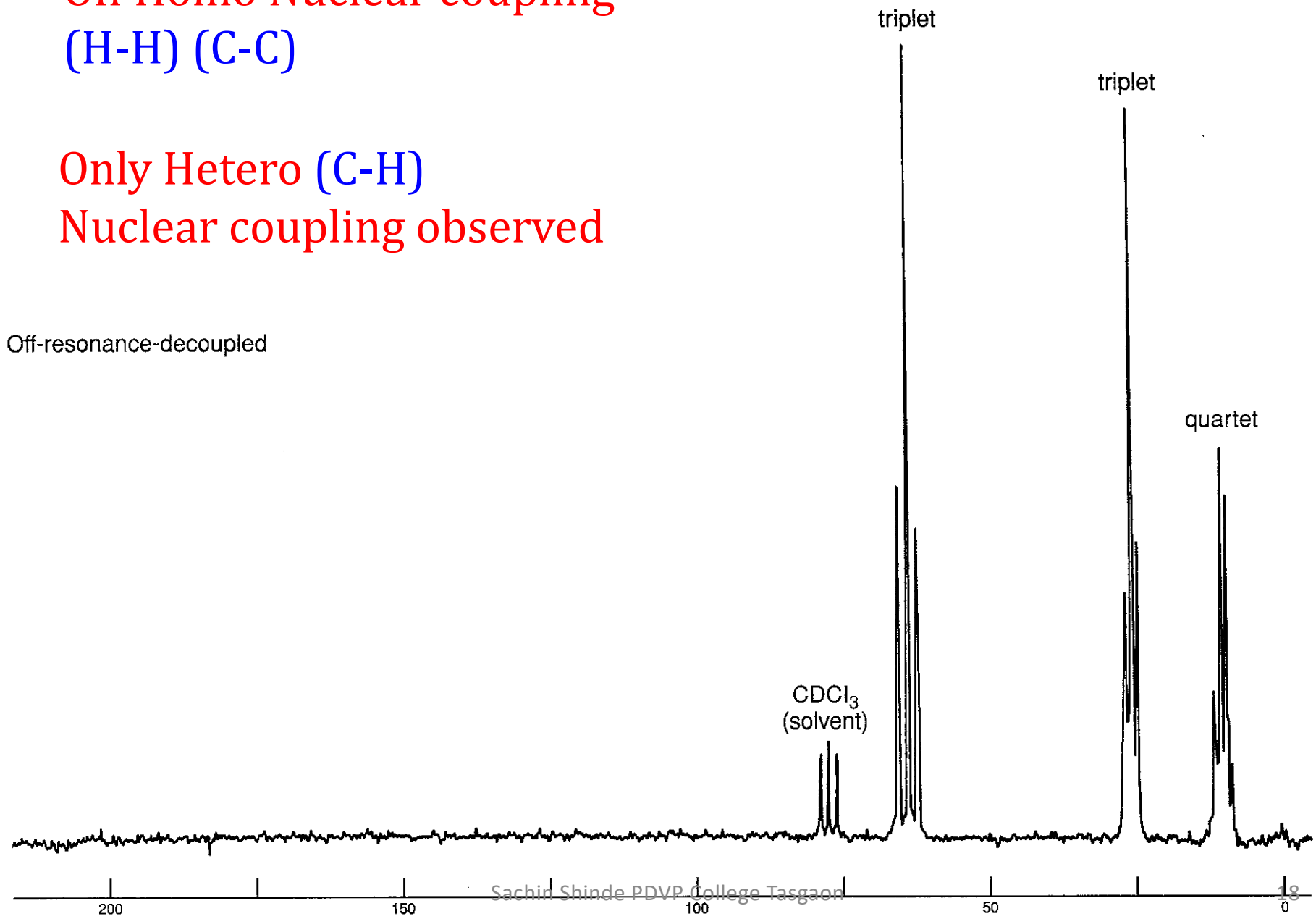


- Apparent magnitude of coupling constant is reduced. (remove overlapping of multiplets).
- Only shows one-bond hetero nuclear coupling (removes other remote carbon coupling).
- The frequency of decouple is held low to avoid complete decoupling.

Off- Resonance Spectra of 1-propanol

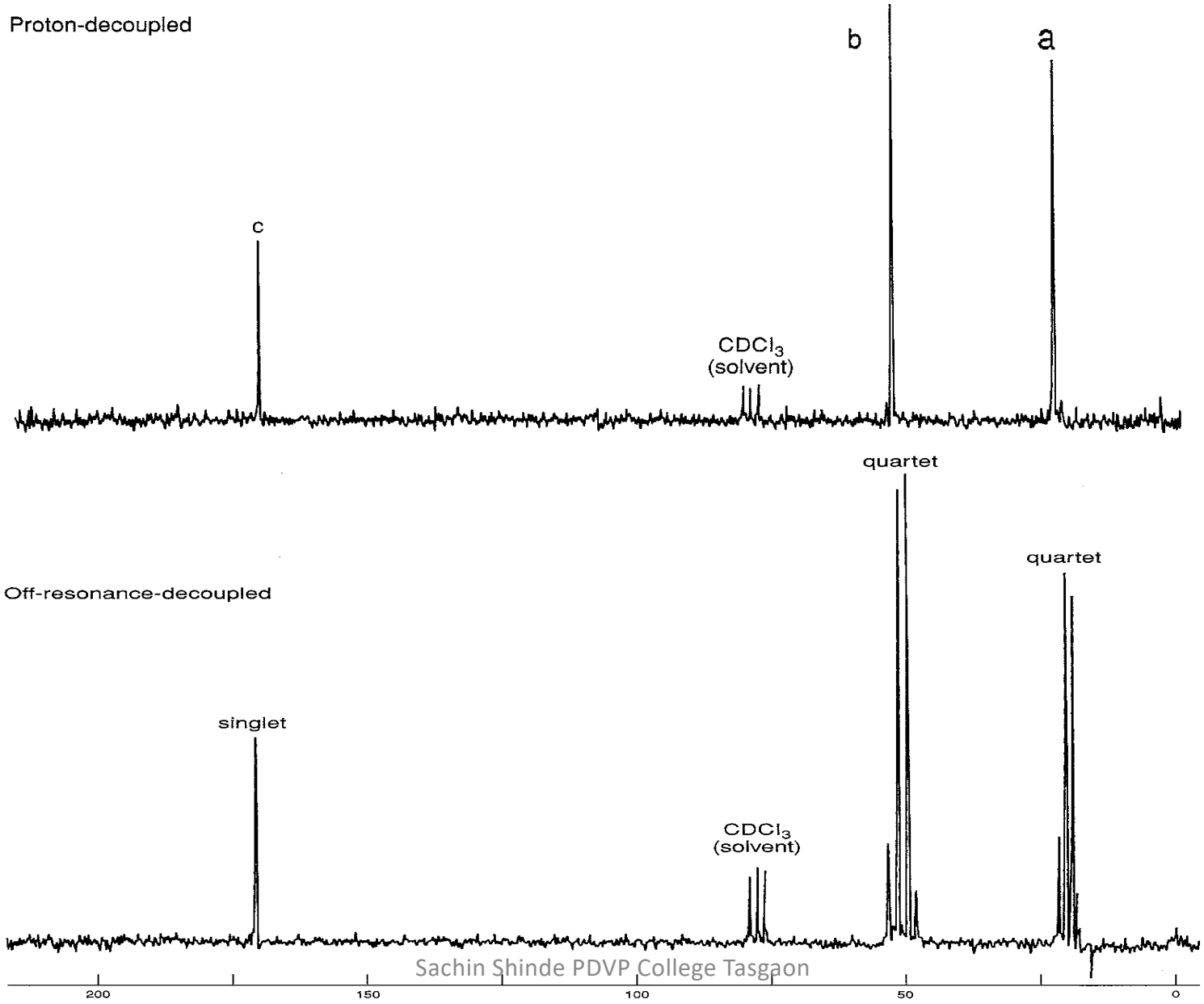
Off Homo Nuclear coupling
(H-H) (C-C)

Only Hetero (C-H)
Nuclear coupling observed



Example

A compound with the formula $C_3H_6O_2$ gives the following proton-decoupled and off-resonance-decoupled spectra. Determine the structure of the compound.



Distortionless Enhancement Polarization Transfer (DEPT)

Distortionless enhancement by polarization transfer (DEPT) is a NMR method used for determining the presence of primary (CH_3), secondary (CH_2) and tertiary (CH) carbon atoms.

The DEPT experiment differentiates between CH, CH_2 and CH_3 groups by variation of the selection angle parameter:

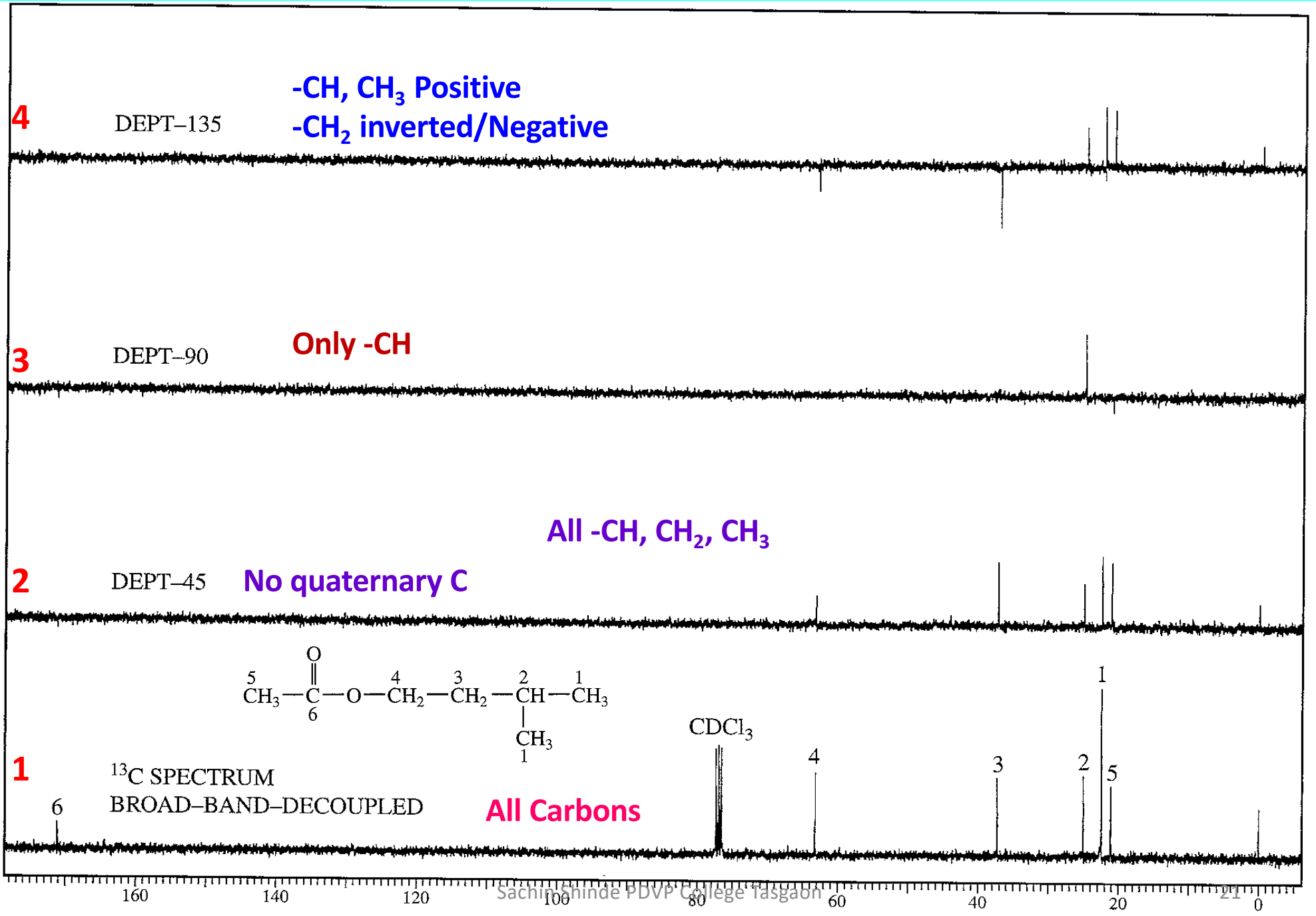
i. 135° angle gives all CH and CH_3 in a phase (+Ve) opposite to CH_2 (-Ve) **(DEPT-135)**

ii. 90° angle gives only CH groups (+Ve), the others being suppressed **(DEPT-90)**

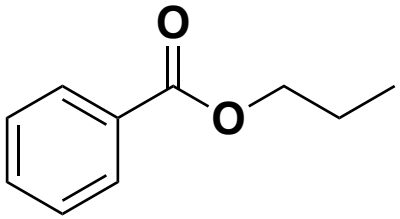
iii. 45° angle gives all carbons with attached protons in phase (+Ve): **(DEPT-45)**

- Signals from quaternary carbons and other carbons with no attached protons are always absent (due to the lack of attached protons).
- The polarization transfer from ^{1}H to ^{13}C has the secondary advantage of increasing the sensitivity over the normal ^{13}C spectrum (which has a modest enhancement from the nuclear overhauser effect (NOE) due to the ^{1}H decoupling).

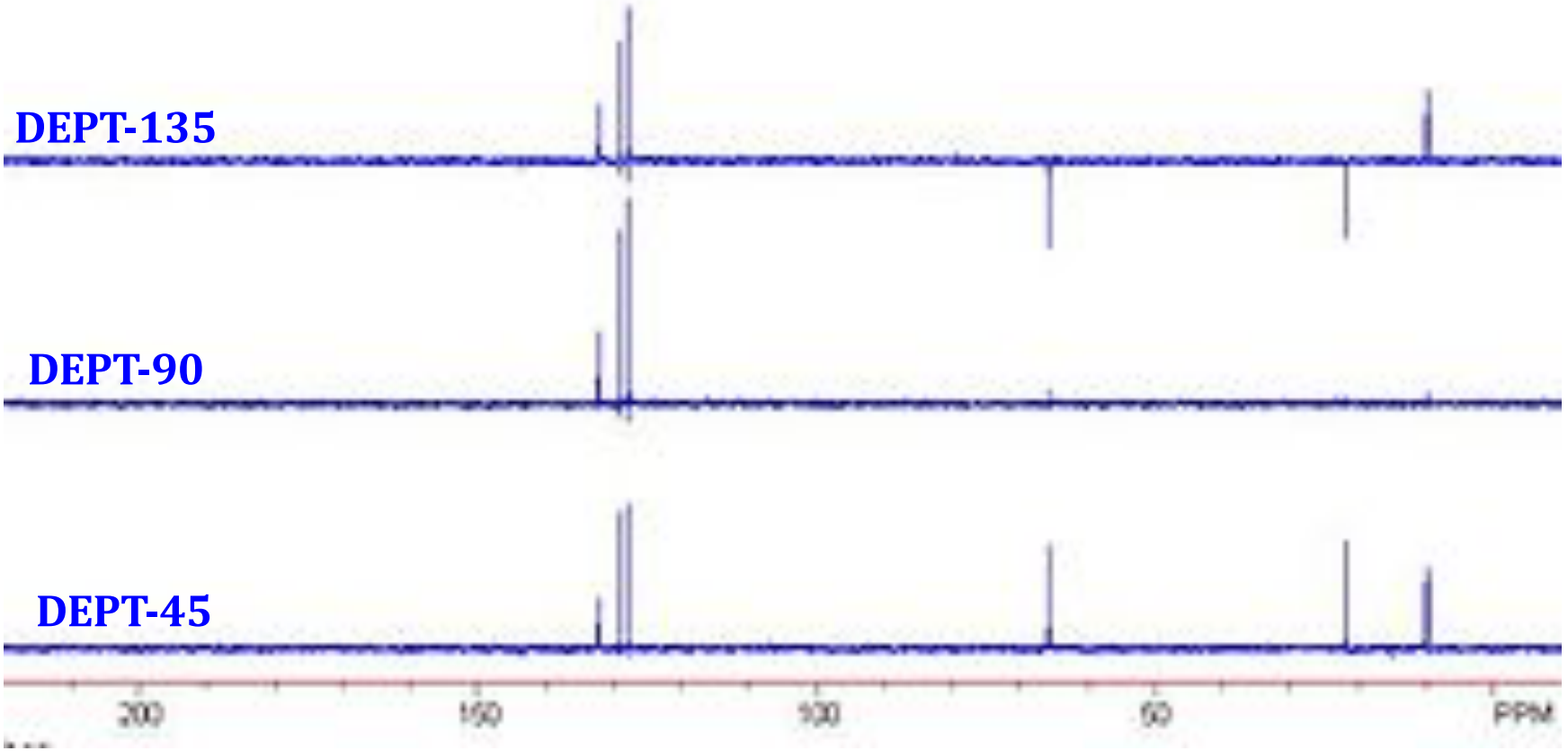
Distortionless Enhancement Polarization Transfer (DEPT)



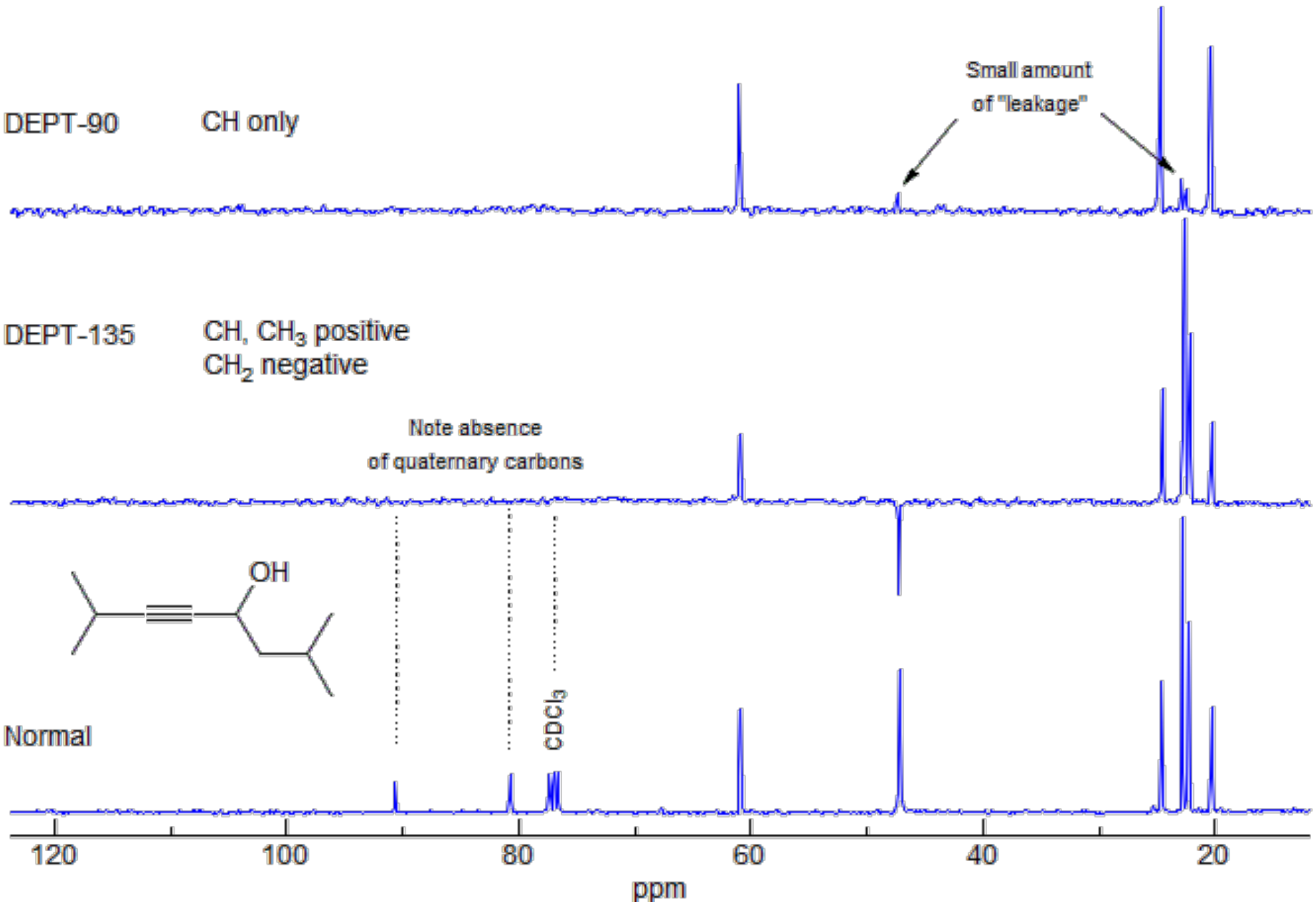
DEPT spectrum of Propyl benzoate



Propyl benzoate



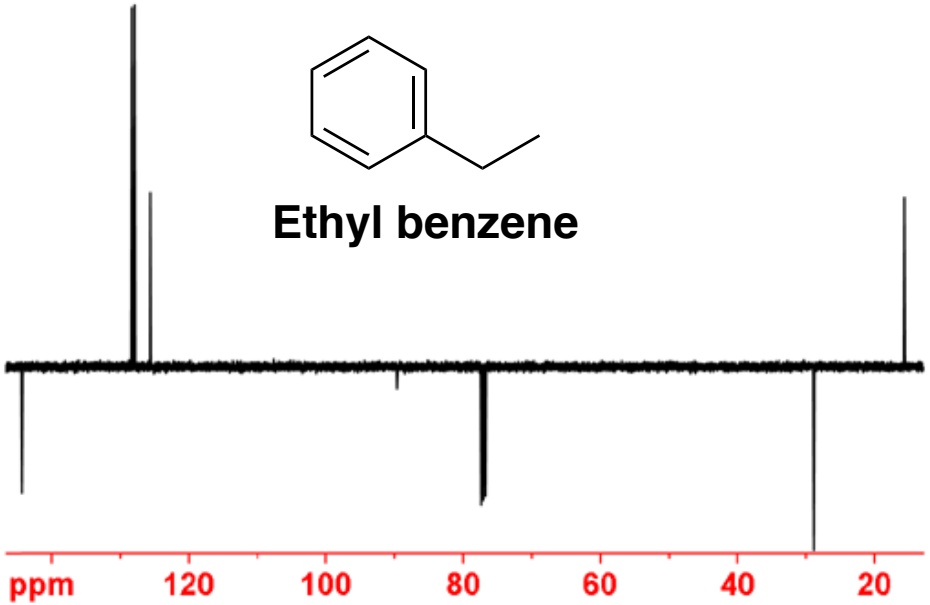
Examples of DEPT



Attached Proton Test (APT) spectra

The attached proton test (ATP) is a 1D ^{13}C-NMR experiment that is used as an aid to assignment by separating carbons unattached to protons (c) and CH_2 signals from CH and CH_3 signals.

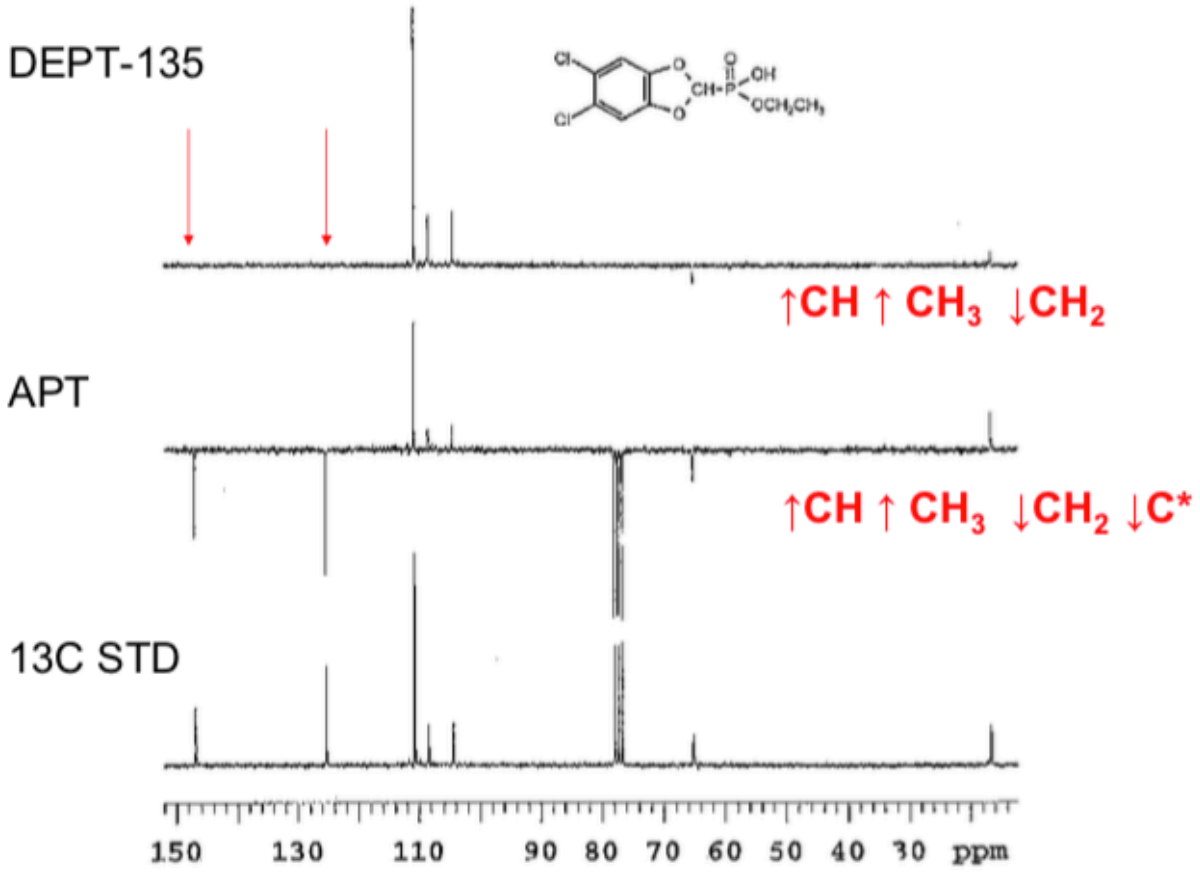
The APT experiment yields methine (CH) and methyl (CH_3) signals positive and quaternary (C) and methylene (CH_2) signals negative.



APT spectrum of ethylbenzene showing CH and CH_3 positive While $CH_2$and quaternary C are negative

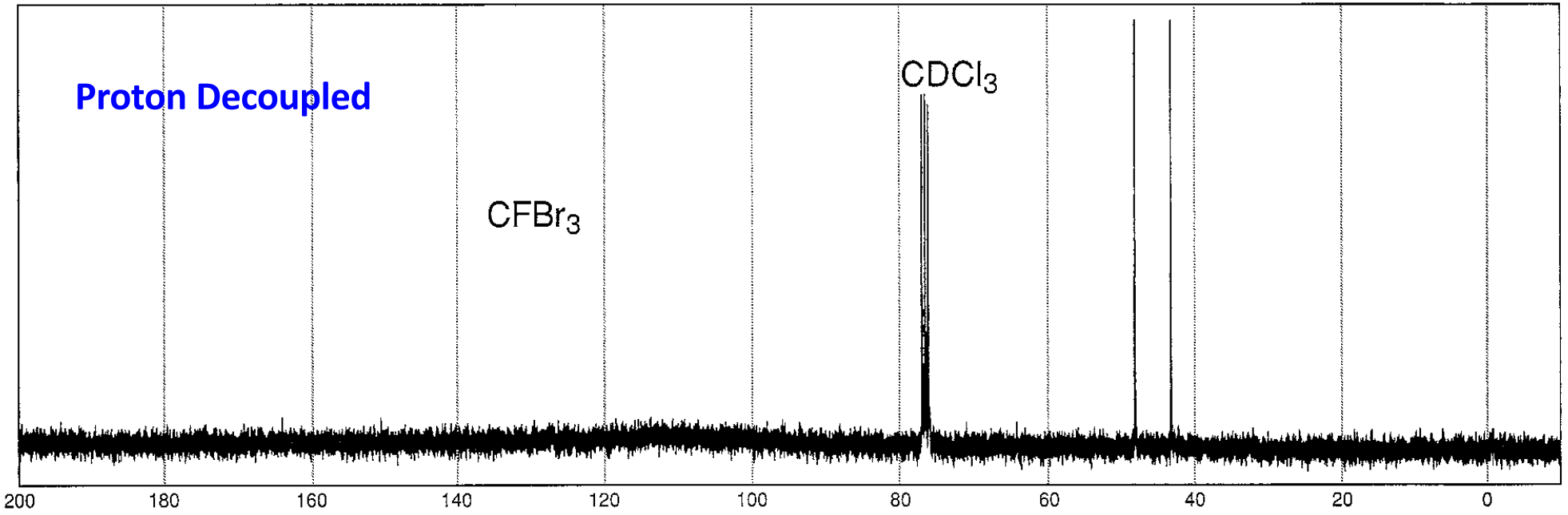
- It is slightly less sensitive than DEPT but a single experiment shows all carbon signals at once unlike DEPT that supresses quaternary carbons and requires up to three different acquisitions to yield full results.
- It is, however, sometimes possible that a CH and CH_2 signal have coincidentally equivalent chemical shifts resulting in annulment in the APT spectrum due to the opposite phases. For this reason the conventional $^{13}C\{^1H\}$ spectrum are occasionally also acquired.

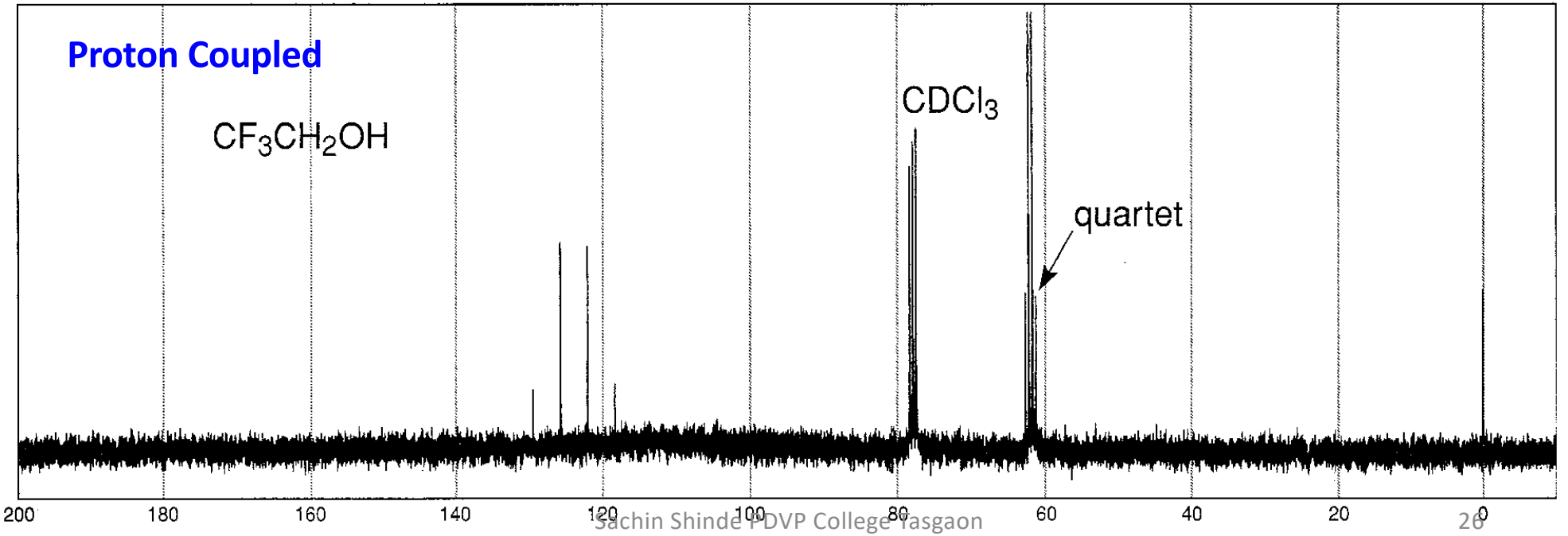
DEPT and APT spectra



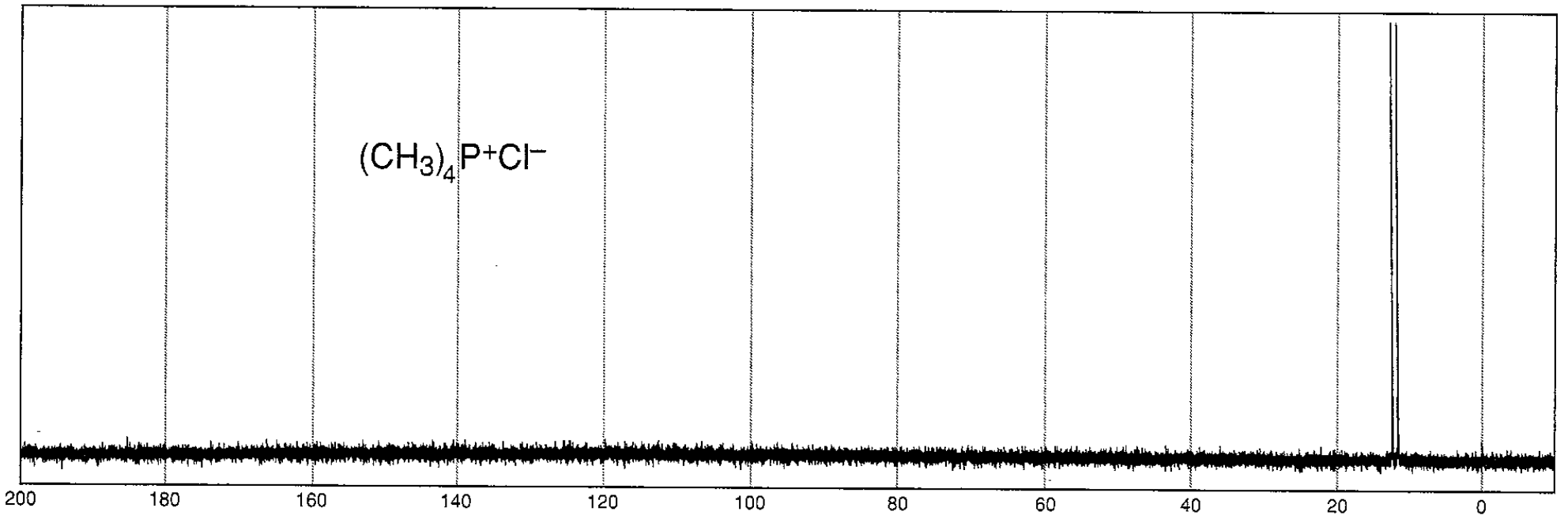
multiplicity	DEPT - 45	DEPT - 90	DEPT - 135	APT
C	No signal	No signal	No signal	-
CH	+	+	+	+
CH_2	+	No signal	-	-
CH_3	+	No signal	+	+

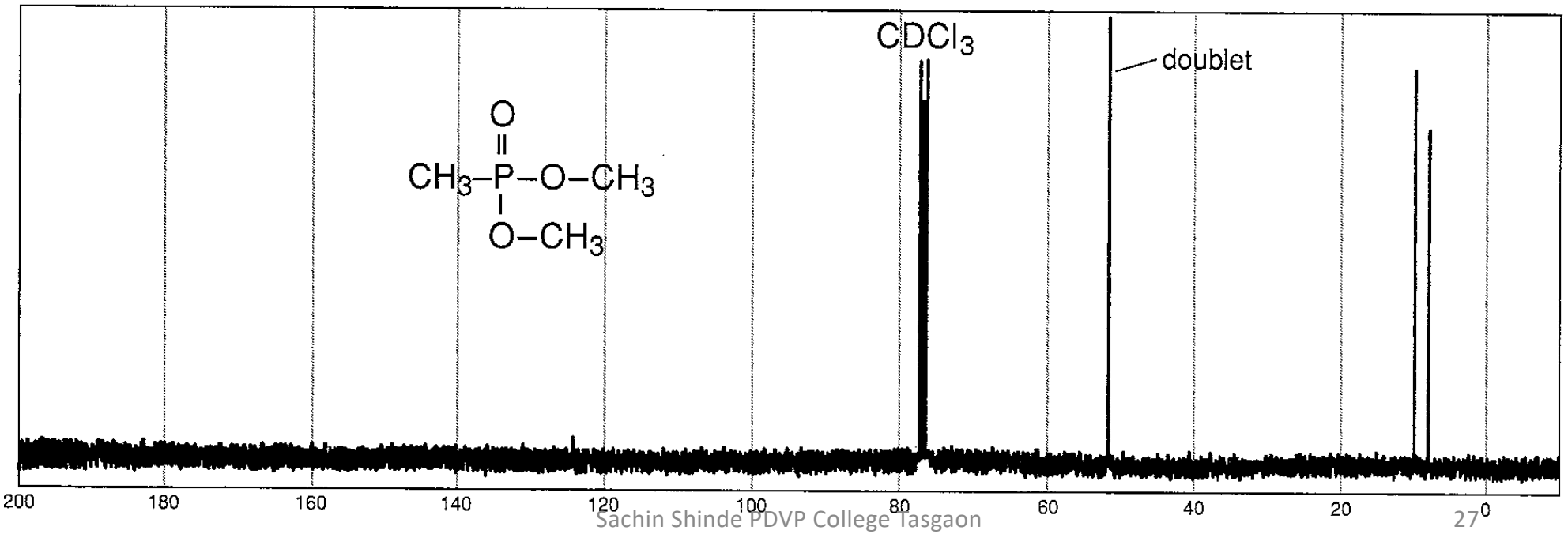
Heteronuclear coupling of carbon to fluorine-19





Heteronuclear coupling of carbon to Phosphorus-31





University Questions

Q. If operating frequency for ^{1}H-NMR is 300 MHz, what will it be for ^{13}C-NMR? (2 M)

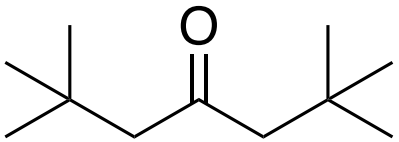
Q. In ^{13}C-NMR, signal due to d_6-DMSO appears as a group of……..peaks. (2M)

Q. In CMR, $CDCl_3$ appears as triplet, explain. (2M)

Q. Write the structure of an organic compound (MF: $C_4H_{10}O_2$) which shows only two singlet in its CMR spectrum at δ 20 and 52 ppm). (2M)

Q. Suggest the structures of three isomeric ketones having same molecular formula ($C_5H_{10}O$) and exhibits three, four and five signals in ^{1}H-decoupled ^{13}C-NMR spectrum. (2M, 3M)

Q. How many signals do you expect in broad band decoupled CMR spectrum of following compound. (2 M)



Q. Write the structures of all isomeric alcohols (MF: $C_4H_{10}O$) which exhibits three/four signals in their CMR spectrum. (4 M)

University Questions

Q. Calculate δc values for aromatic carbons in p-chlorobromo benzene. (5 M)

Given : Basic δc for aromatic ring c= 128.5 ppm

Group	:	ipso	ortho	meta	para
Cl	:	8.2	-3.4	0.8	-7.0
Br	:	8.7	-4.3	0.65	-6.0

Q. Calculate δc values for aromatic carbons in 4-aminoacetophenone. (4 M)

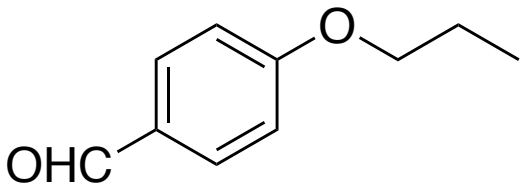
Given : Basic δc for Ar-C= 128.5 ppm

Group	:	ipso	ortho	meta	para
NH_2	:	18.2	-13.4	0.8	-10.0
$COCH_3$	:	8.9	0.1	-0.1	4.3

Q. Calculate δc values for the aromatic ring carbons in following compound. (4 M)

Given : Basic δc for Ar-C= 128.5 ppm

Group	:	ipso	ortho	meta	para
-OR	:	31.4	-14.4	1.0	-7.7
-COR	:	8.2	1.2	0.6	5.8
-R	:	9.3	0.7	-0.1	-2.9



University Questions

Q. Calculate chemical shift values for only olefinic carbons in the following compound. (2 M)

Given : Basic Value: 123.3

$COCH_3$ (α) = 15 ppm; $COCH_3$ (α') = 6 ppm; CH_3 (α') = 10.6 ppm.

Q. Write the structures of two isomeric bromides which have following spectral data. Assign the signals to various carbon atoms in the structures. (5M)

MF: C_3H_5Br

Compound A: 32.6 (t), 118.8 (t), 134.2 (d).

Compound B: 12.0 (t), 16.8 (d).

Q. Deduce the structure of an organic compound on the basis of following data. (4 M)

MF: C_5H_8O

δ (ppm)	:	22,	52,	125,	135,	168.
(Off-resonance decoupling)	:	q,	q,	t,	s,	s.

Q. Write the structures for all the isomers of a compounds (MF: C_6H_{14}) which have following data.

Isomer-I : 19.1 (q), 33.9 (d).

Isomer-II : 13.7 (q), 22.9 (t), 31.9 (t).

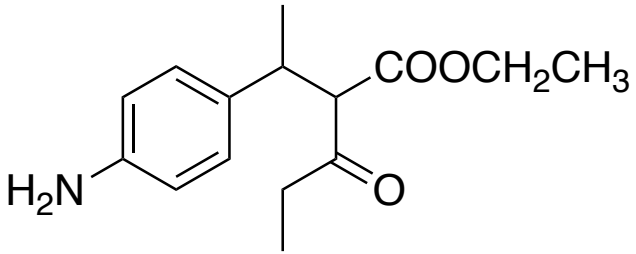
Isomer-III : 11.1 (q), 18.4 (q), 29.1 (t), 36.4 (d).

Isomer-IV : 14.0 (q), 20.5 (t), 22.4 (q), 27.6 (d), 41.6 (t).

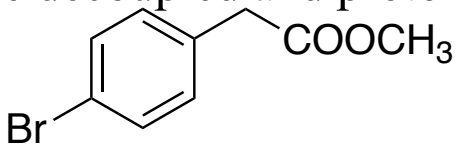
Isomer-V : 8.5 (q), 28.7 (q), 30.2 (s), 36.5 (t).

University Questions

Q. Considering following example, sketch its broad band decoupled CMR spectrum (Exact delta values not expected) and justify the use of DEPT scans in correct assignments of chemical shift values. (6 M)



Q. Sketch the off-resonance decoupled and proton decoupled ^{13}C-NMR spectrum of followings organic compound. (5 M)



(Exact δ values are not expected)

Q. Sketch the off-resonance decoupled, proton decoupled and DEPT-135 CMR spectrum of 4-methoxy benzyl cyanide (exact δ values are not expected). (4 M)

Q. Using 4-MeO-C_6H_4-$COCH_2$-CH_3 as a model compound, sketch the off-resonance decoupled and H-decoupled ^{13}C-NMR spectrum (6 M)

University Questions

Q. Sketch the proton coupled as well as proton decoupled ^{13}C-NMR spectrum of following compounds. (4 M)

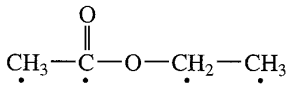
i) p-Chloropropiophenone

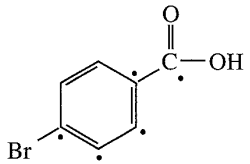
ii) Ethyl acetate

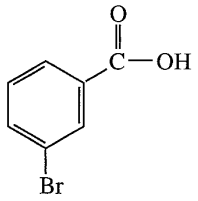
Q. In proton decoupled ^{13}C-NMR spectrum comment on the signal intensity for CH_3, H_2C-CH_2 and CH carbons. Justify your answer. (4 M).

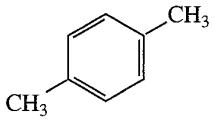
Q. Explain, how cursory examination of ^{13}C-NMR spectrum could be useful to judge the presence of alkyl, vinyl, alkyne, nitrile and amide group in the molecule. (5 M)

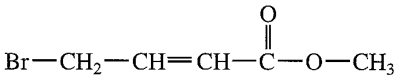
Examples:

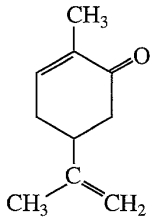
(a)  Four peaks

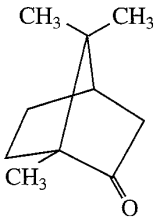
(b)  Five peaks

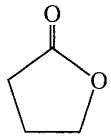
(c) 

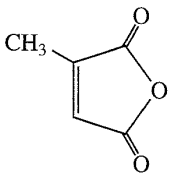
(d) 

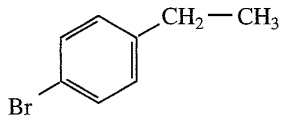
(e) 

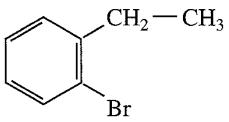
(f) 

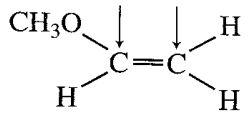
(g) 

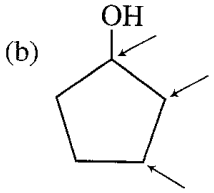
(h) 

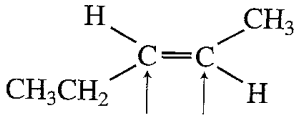
(i) 

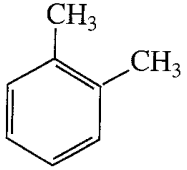
(j) 

(k) 

(a) 

(b) 

(c) 

(d) 

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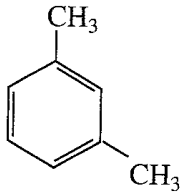

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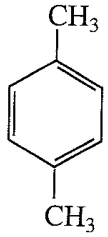

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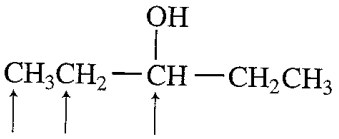
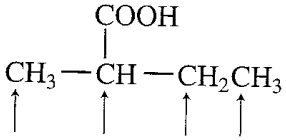
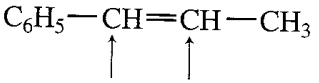
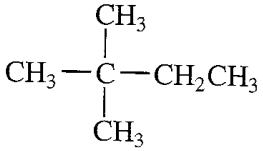
(e) 

(f) 

(g) 

(h) 

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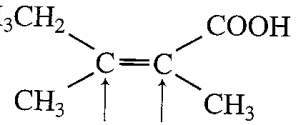
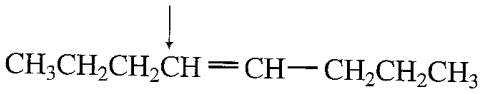
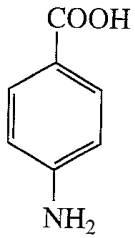
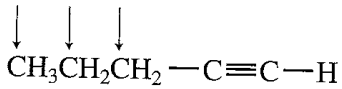
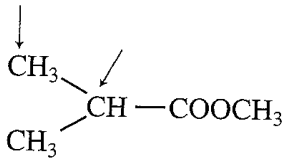
(i) 

(j) 

(k) 

Ring carbons

(l) 

(m) 

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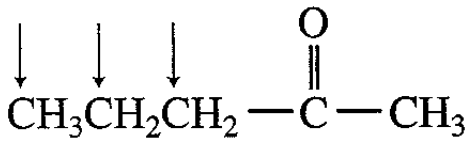
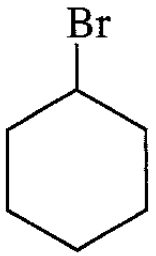
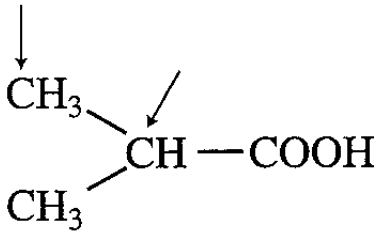


(o)



All

(p)



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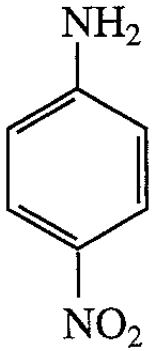

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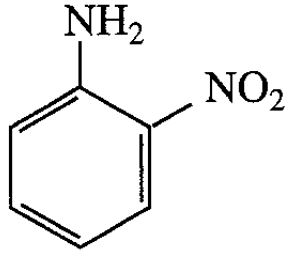

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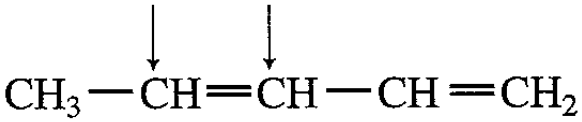

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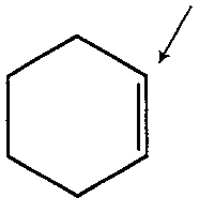

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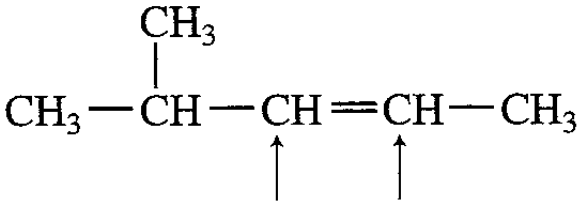
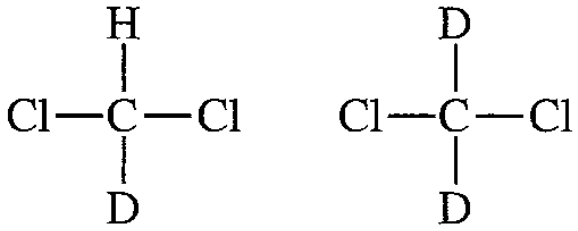
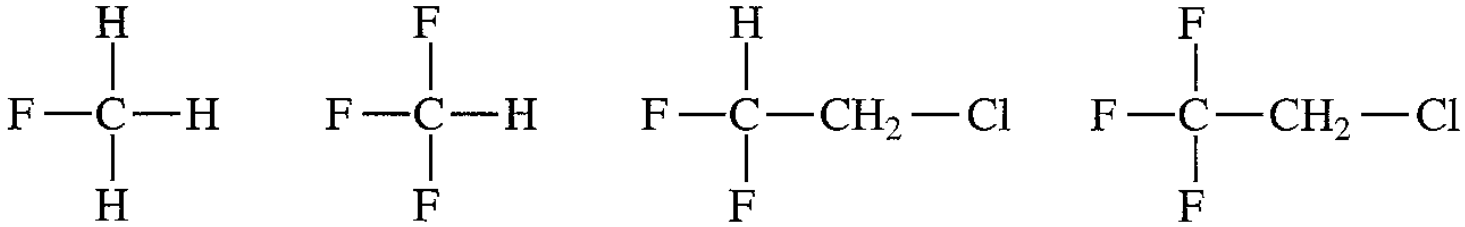


***18.** Predict the appearances of the proton-decoupled ^{13}C spectra for the following compounds.

(a) 

$I = 1$

$J_{CD} \cong 20–30$ Hz (one bond)

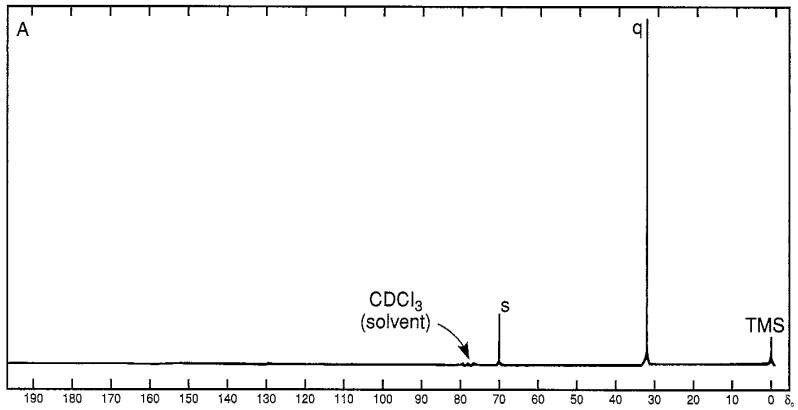
(b) 

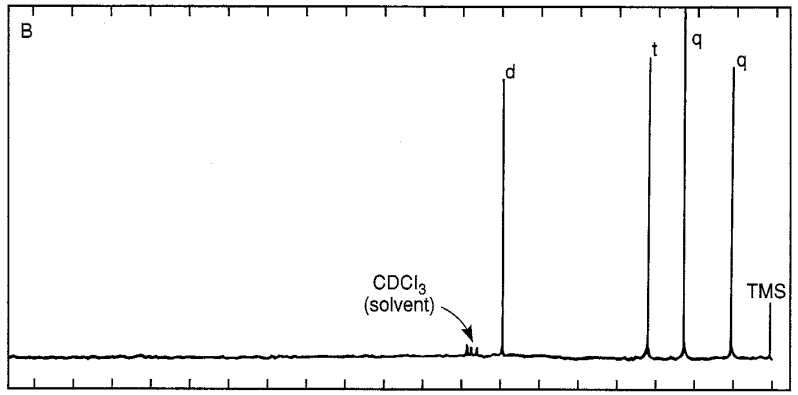
$I = \frac{1}{2}$

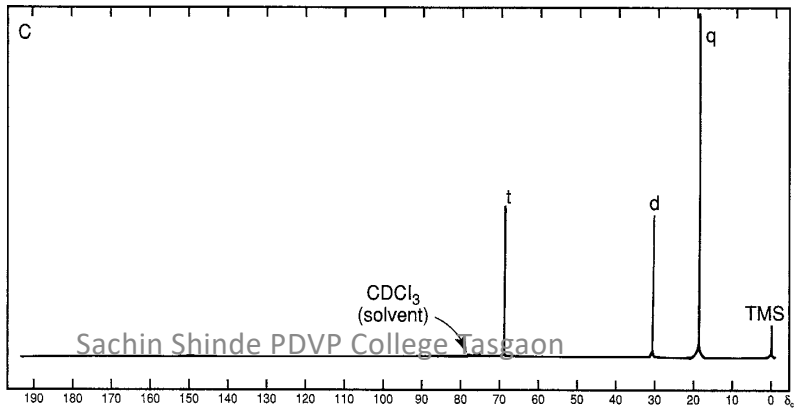
$J_{CF} > 180$ Hz (one bond)

$J_{CF} \cong 40$ Hz (two bonds)

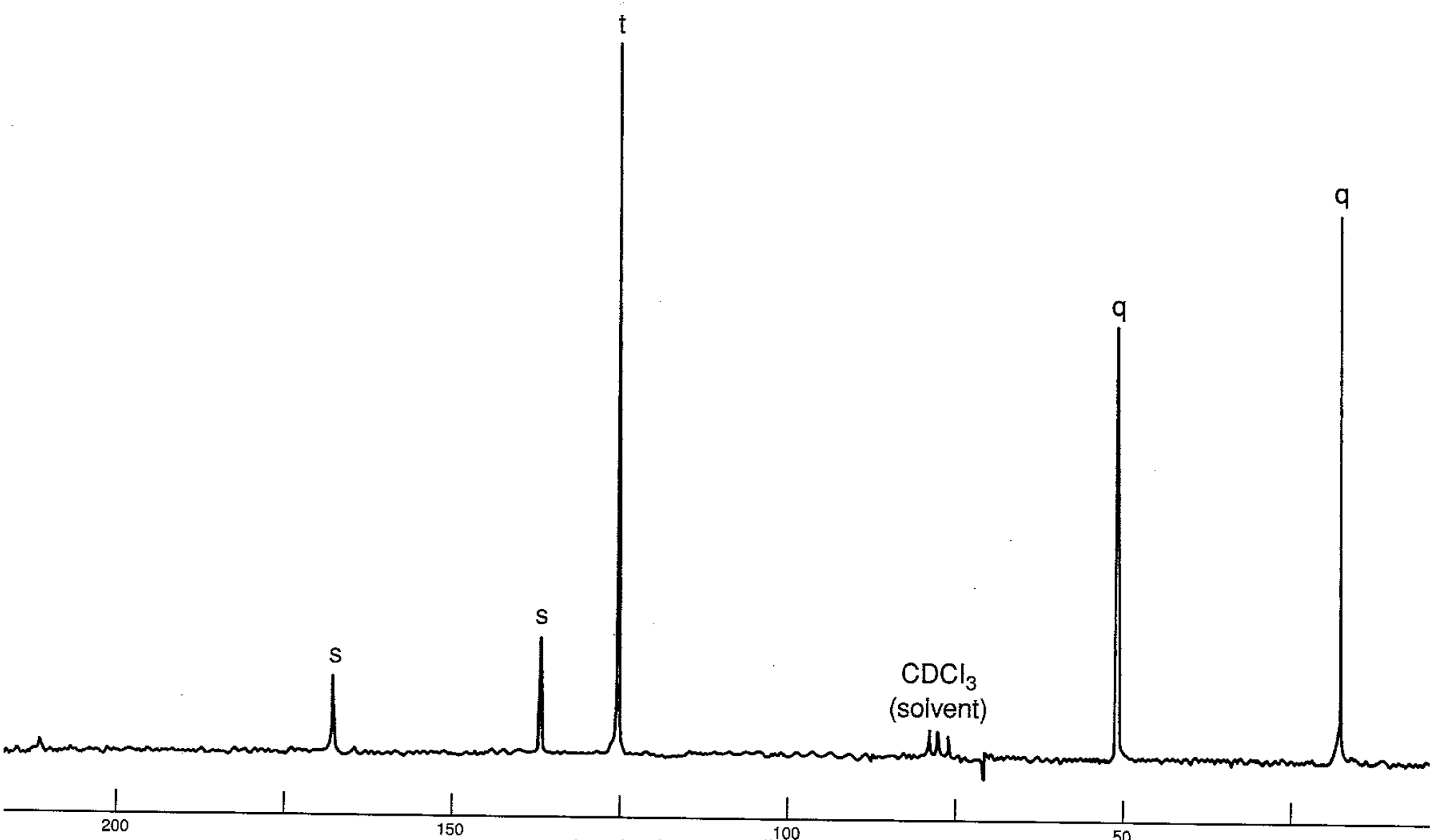
Following are proton-decoupled ^{13}C spectra for three isomeric alcohols with the formula $C_4H_{10}O$. A DEPT or an off-resonance analysis yields the multiplicities shown; **s** = singlet, **d** = doublet, **t** = triplet, and **q** = quartet. Identify the alcohol responsible for each spectrum, and assign each peak to an appropriate carbon atom or atoms.





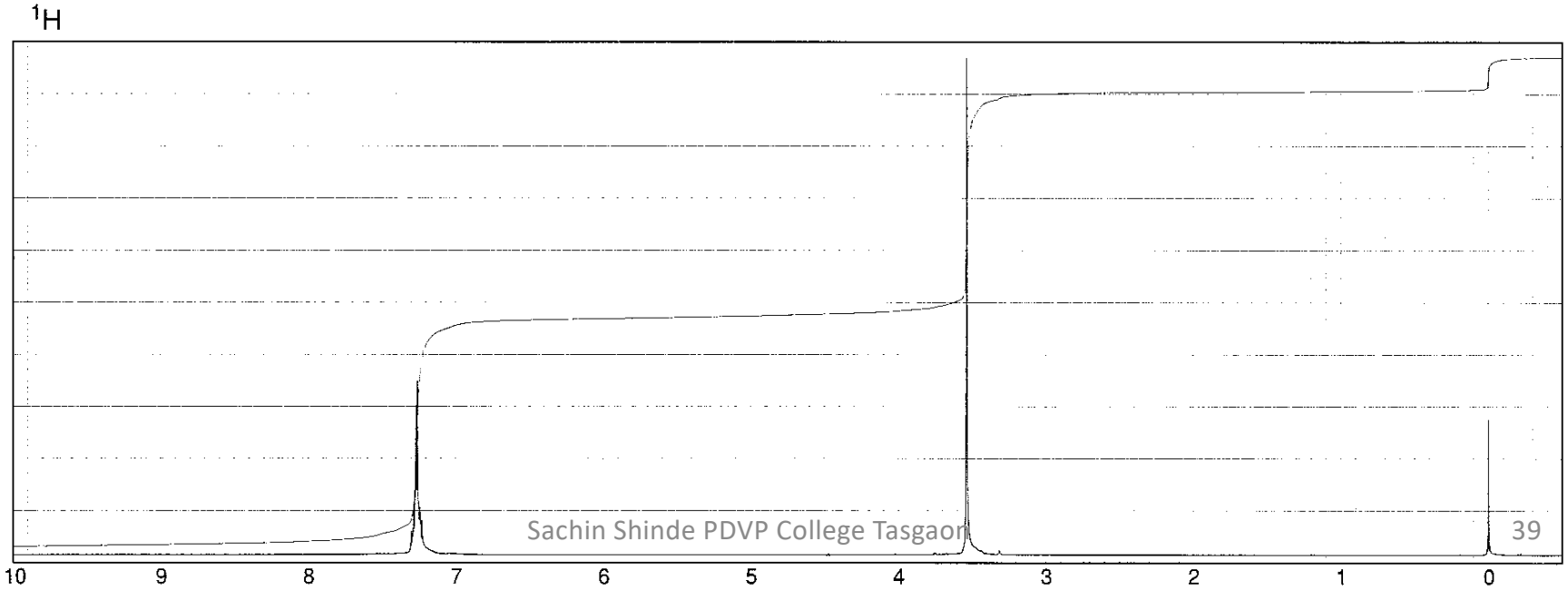


***4.** The following spectrum is of an ester with formula $C_5H_8O_2$. Multiplicities are indicated. the structure of the compound, and assign each peak.



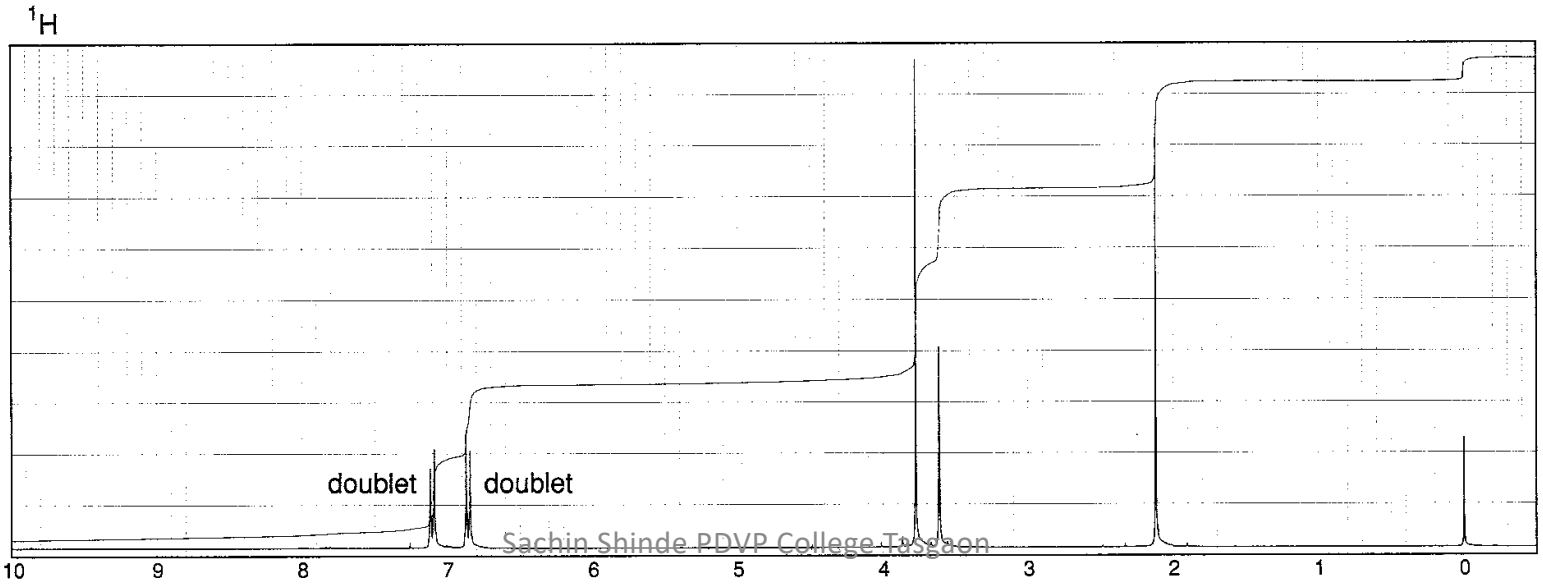
11. The proton NMR spectrum for a compound with formula C_9H_8O is shown below. The normal carbon-13 NMR spectrum has five peaks. The infrared spectrum has a strong band at 1746 cm^{-1}. The DEPT-135 and DEPT-90 spectral results are tabulated. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
44 ppm	Negative	No peak
125	Positive	Positive
127	Positive	Positive
138	No peak	No peak
215	No peak	No peak



12. The proton NMR spectrum for a compound with formula $C_{10}H_{12}O_2$ is shown below. The infrared spectrum has a strong band at 1711 cm^{-1}. The normal carbon-13 NMR spectral results are tabulated along with the DEPT-135 and DEPT-90 information. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50	Negative	No peak
55	Positive	No peak
114	Positive	Positive
126	No peak	No peak
130	Positive	Positive
159	No peak	No peak
207	No peak	No peak



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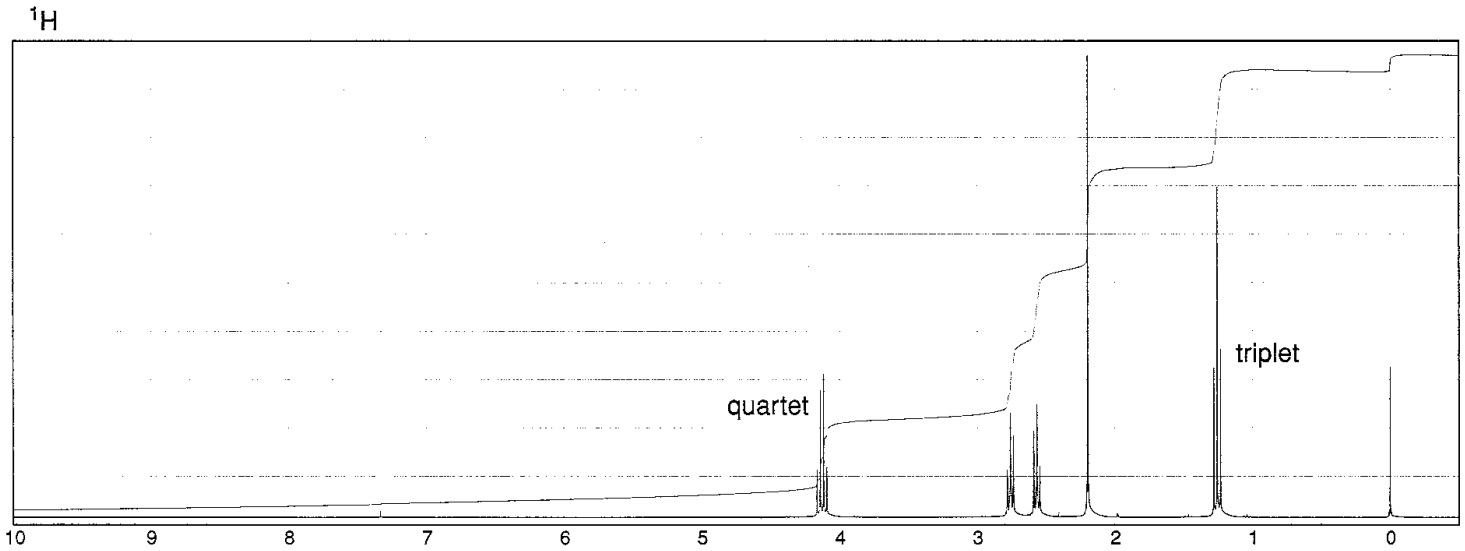
14. The proton NMR spectrum of a compound with formula $C_7H_{12}O_3$ is shown. The coupling constant for the triplet at 1.25 ppm is of the same magnitude as the one for the quartet at 4.15 ppm. The pair of distorted triplets at 2.56 and 2.75 ppm are coupled to each other. The infrared spectrum displays strong bands at 1720 and 1738 cm^{-1}. The normal carbon-13 and the DEPT experimental results are tabulated. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
28	Negative	No peak
30	Positive	No peak
38	Negative	No peak
61	Negative	No peak
173	No peak	No peak
207	No peak	No peak



16. The proton NMR spectrum is shown for a compound with formula $C_5H_9NO_4$. The infrared spectrum displays strong bands at 1750 and 1562 cm^{-1} and a medium intensity band at 1320 cm^{-1}. The normal carbon-13 and the DEPT experimental results are tabulated. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
16	Positive	No peak
63	Negative	No peak
83	Positive	Positive
165	No peak	No peak