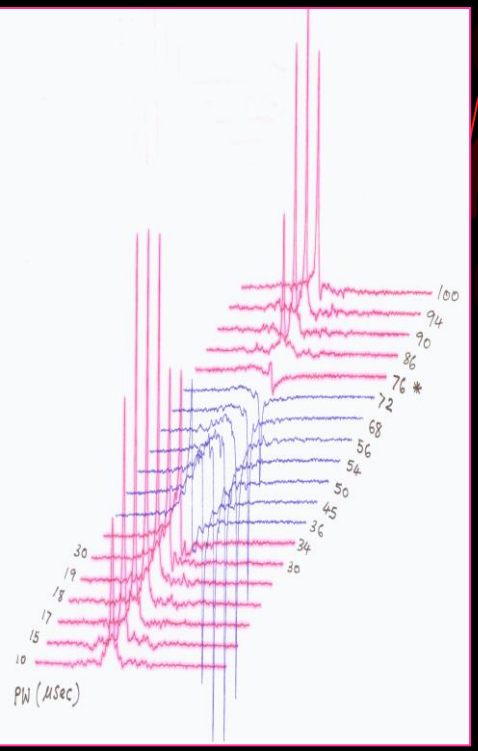
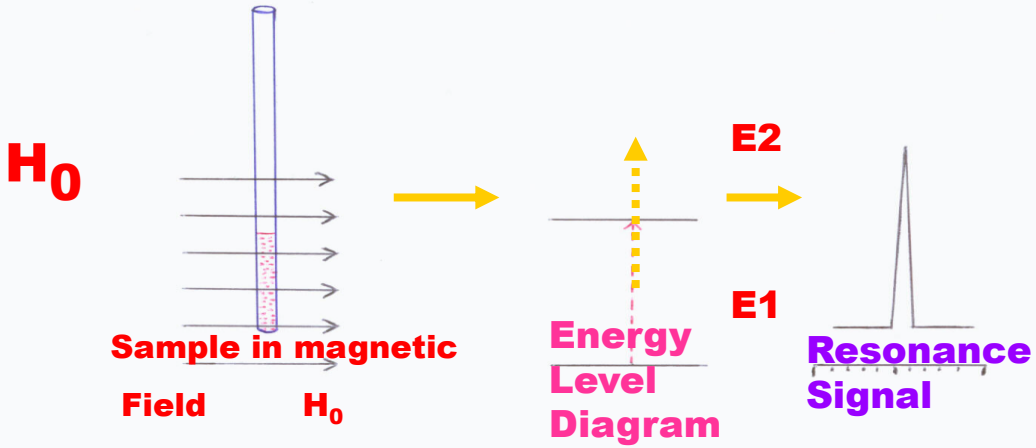
NMR SPECTROSCOPY



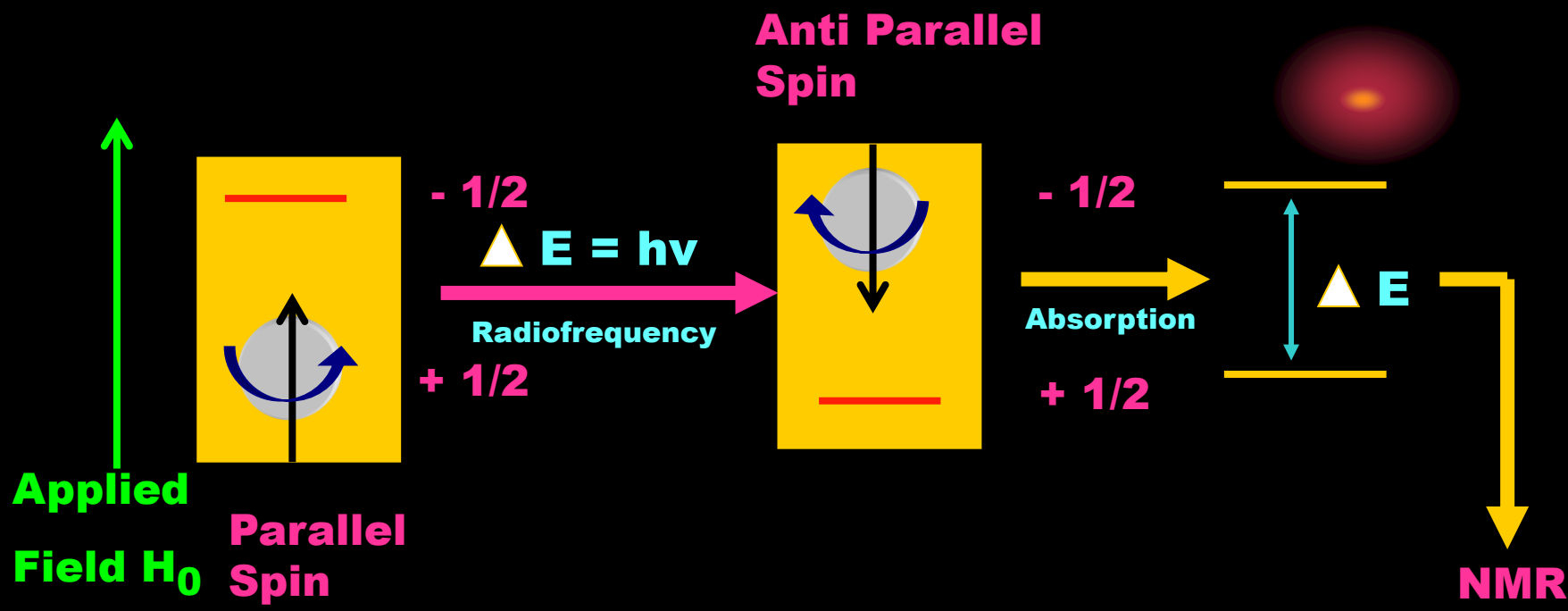
DR. M. KANJIA

When certain Nuclei are placed in a strong magnetic field, ^{1}H, ^{13}C, ^{19}F, ^{14}N, ^{15}N, ^{10}B, ^{11}B, & ^{31}P These nuclei can absorb electromagnetic radiation in the Radiofrequency (R.F.) range.

The absorption of energy can be detected, amplified and recorded as NMR signal. This phenomenon is known as NMR spectroscopy.



Absorption Of Energy



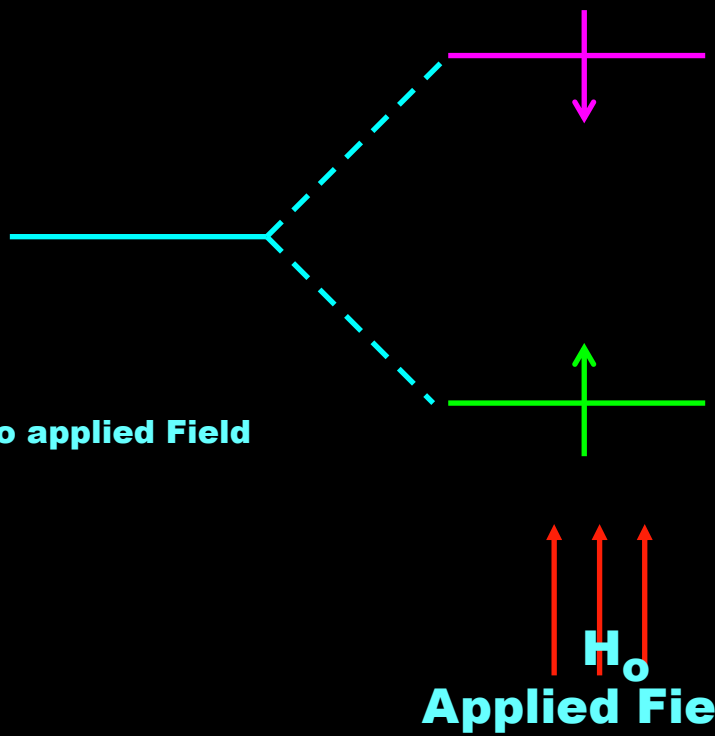
Energy Levels for Spin Active Nucleus
^{1}H, ^{13}C ^{19}F Spin Number I = ½

γ = Gyro magnetic ratio of spin active nucleus

U = Radio frequency of electromagnetic radiation μ = Magnetic moment

H_o = Applied Field

h = Planck ' s Constant



β State Higher energy Level

$\Delta E = - ½ \gamma h / 2\pi H_o$

$= 2 \mu Ho = h U$

α State Lower Energy Level

$\Delta E = + ½ \gamma h / 2 \pi H_o$

$= 2 \mu Ho = h U$

Energy Levels for Spin Active Nucleus

^{2}H, ^{7}Li & ^{14}N Spin Number I = 1

γ = Gyro magnetic ratio of spin active nucleus

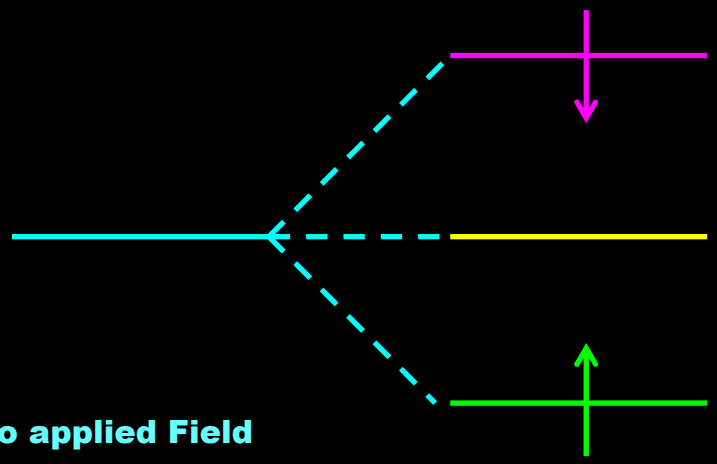
H_o = Applied Field

h = Planck ' s Constant

J_z = Z component

$$J_z = m_I \, h/2\pi$$

$$\Delta E = \gamma J_z H_0 = \gamma m_I \, h/2\pi H_0$$



β State Higher energy Level

$m_I = -1$

Ground State Energy Level

$m_I = 0$

α State Lower Energy Level

$m_I = +1$

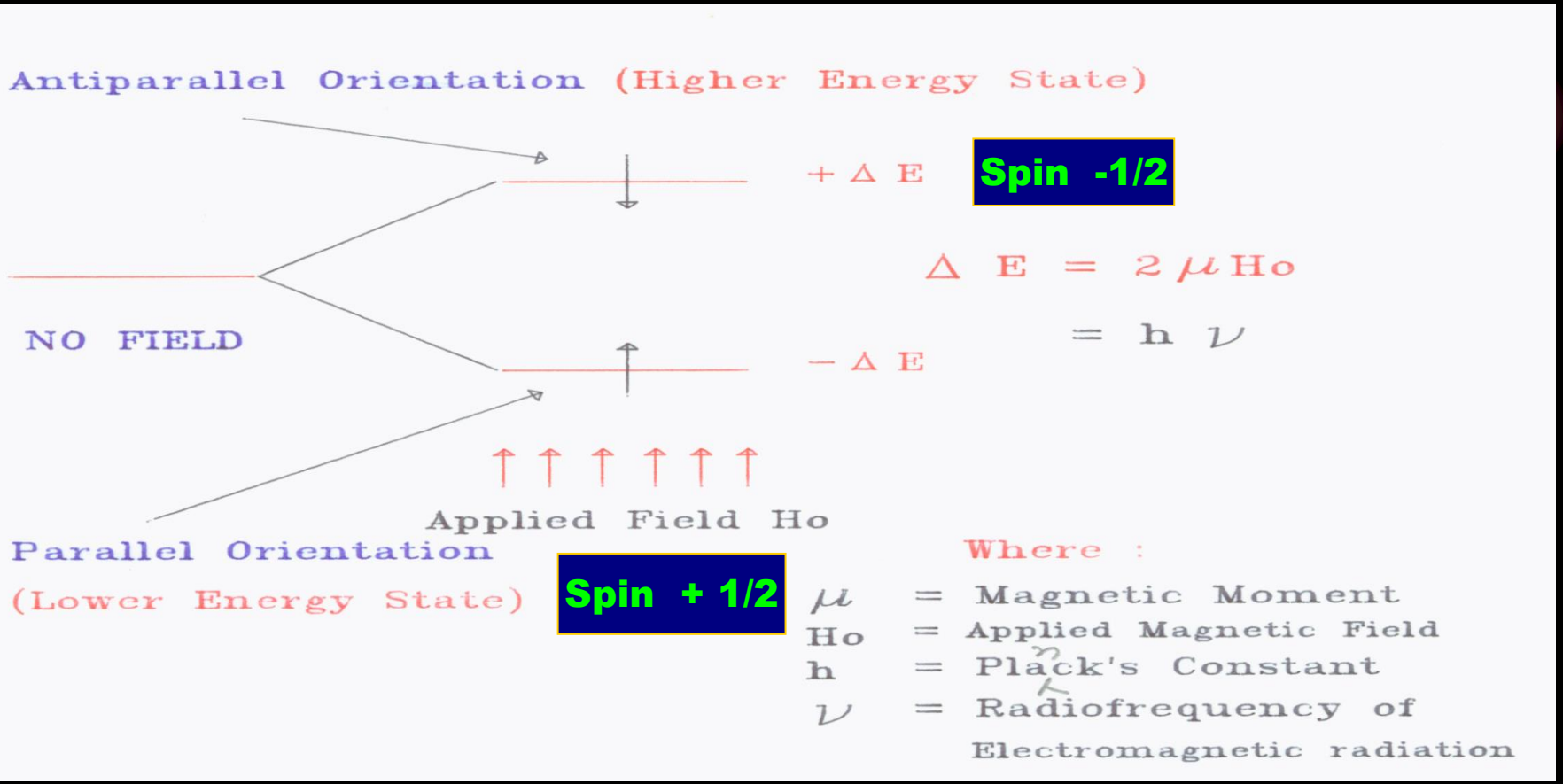
H_o

Applied Field

Radio Frequency spectrum

3.10^6 3.10^8 3.10^{10} 3.10^{12} 3.10^{14} 3.10^{16} R.F.

NMR | Microwave | Infrared | Ultraviolet



Applied field is directly proportional to radiofrequency.

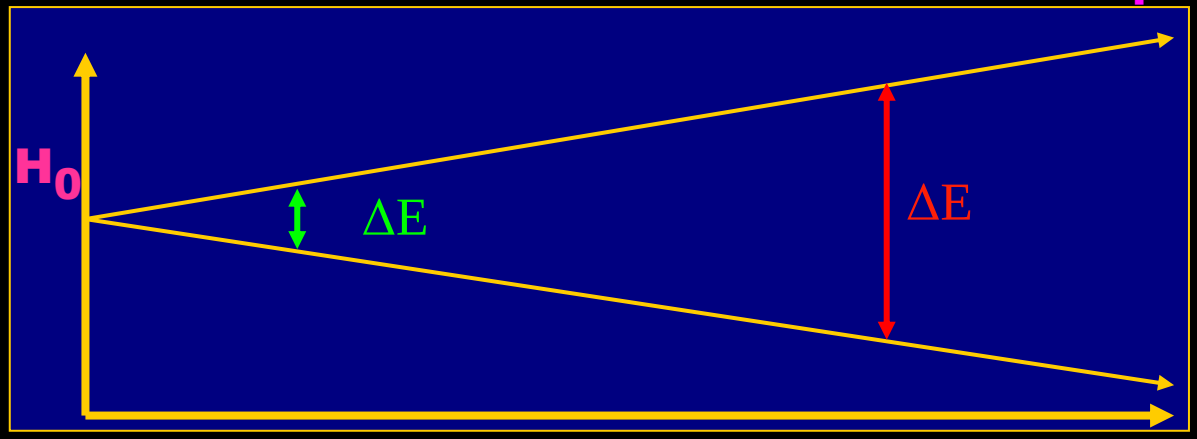
H_0 = Magnetic Field
μ = Magnetic moment
ν = Radiofrequency
h = Planck's constant

$$\Delta E = 2 \mu Ho = h \nu$$

$$Ho \alpha \nu$$

For ^{1}H ^{13}C ^{19}F ^{15}N & ^{31}P nuclei only two orientations are allowed under applied magnetic field spins are aligned parallel (in line with applied field) and anti parallel (opposite with applied field)

- The energy difference ΔE between allowed spin states increases linearly with applied field (H_0) strength.
- ^{1}H @ 7.05 T the energy difference = 0.120 J/mol = 0.286 Cal/mol
- Which corresponds to electromagnetic radiation of 300 MHz
- (300 000 000 Hz = 300 x 10^{6} Hz) .
- For ^{13}C = 0.030 J / mol = 0.00715 Cal / mol corresponds to RF of 75 MHz.

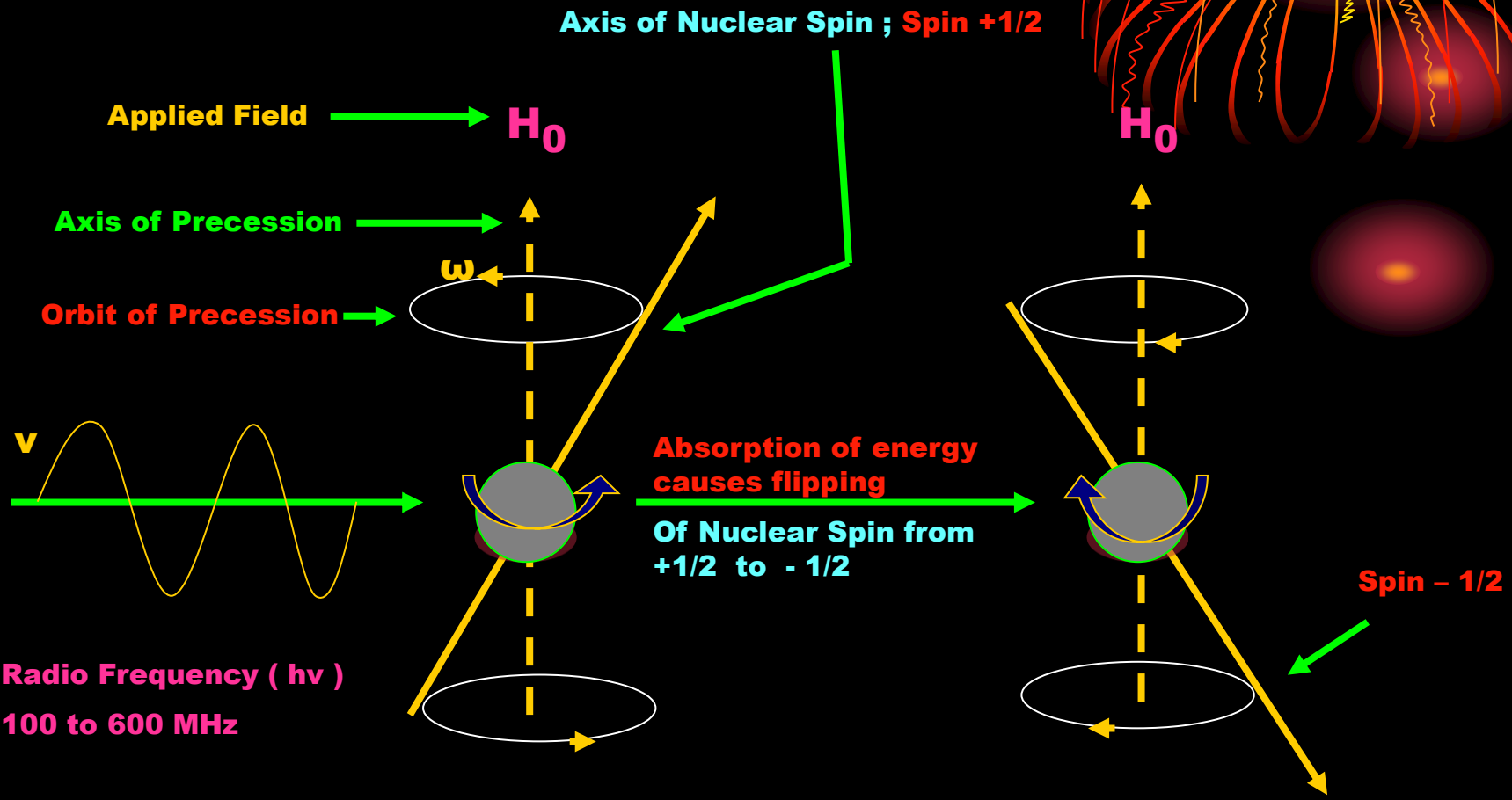


1.41 T H_0 Tesla 7.05 T

ΔE =0.0239 J / mol

ΔE = 0.120 J / mol

Nuclei precess at frequency ω when placed in a strong magnetic field.
If v = ω then energy will be absorbed and flipping of the spin will occur.
This process will give rise to NMR signal.

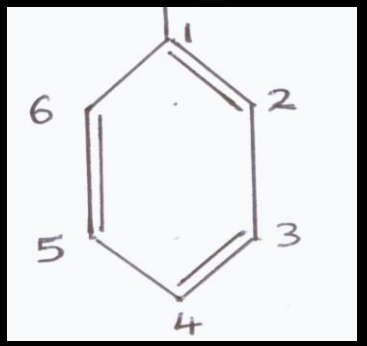


How NMR Signals are generated

- In Ethyl benzene different types of ^{1}H precess at different frequency at constant magnetic field H_0
- Radio frequency (R F) 250 MHz correspondence to 5.88 Tesla Field

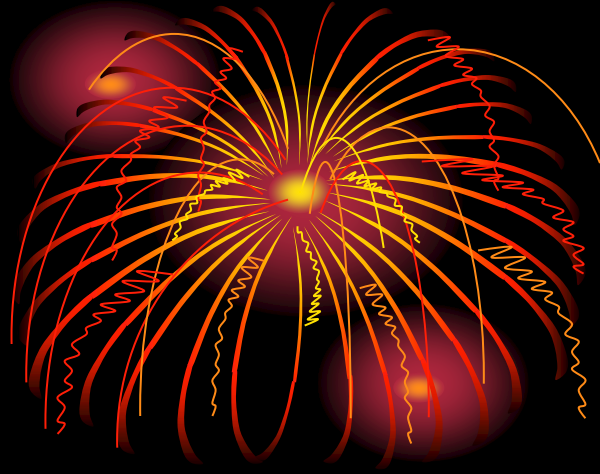
- C_6H_5-CH_2-CH_3

CH_2—CH_3



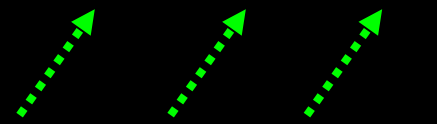
- C_6H_5 precess @ 249. 998222 MHz (1778 Hz)
- CH_2 precess @ 249. 999368 MHz (632 Hz)
- CH_3 precess @ 249. 999721 MHz (279 Hz)
- The difference is very small in the parts per million range.
- C6H5 1778 / 250 = 7.11 PPM
- CH2 632 / 250 = 2.53 PPM
- CH3 279 / 250 = 1.12 PPM

Radio Frequency Pulsed NMR



- **Broad Band**
- **RF Pulse**
- **Contains Range of**
- **Frequencies v1, v2, v3**

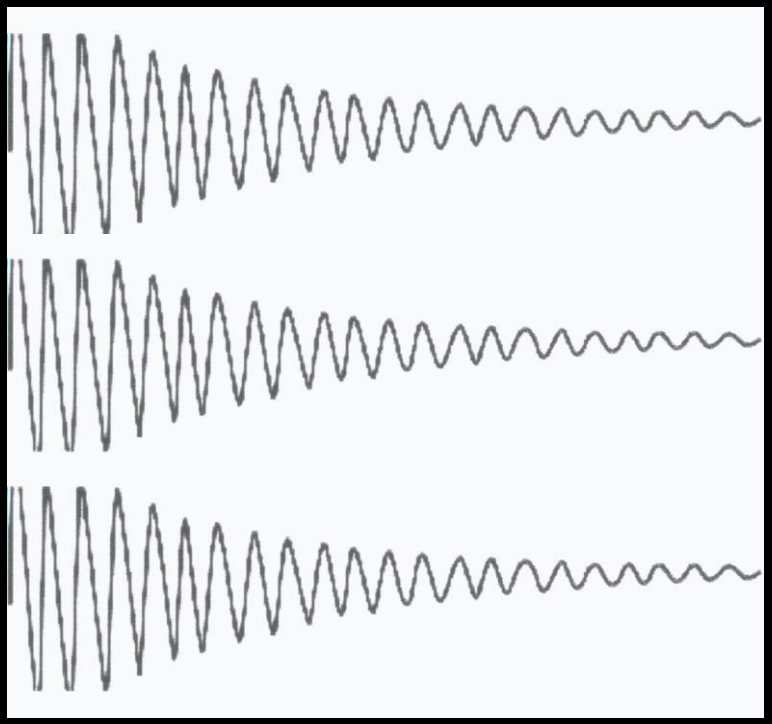
v1 v2 v3



C_6H_5-CH_2-CH_3

All kinds of ^1H are excited simultaneously with the single broad band RF pulse.

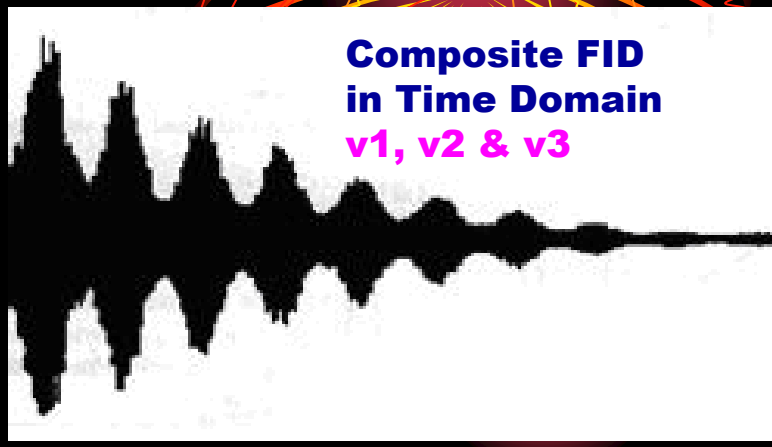
Free Induction Decay (FID)



v1

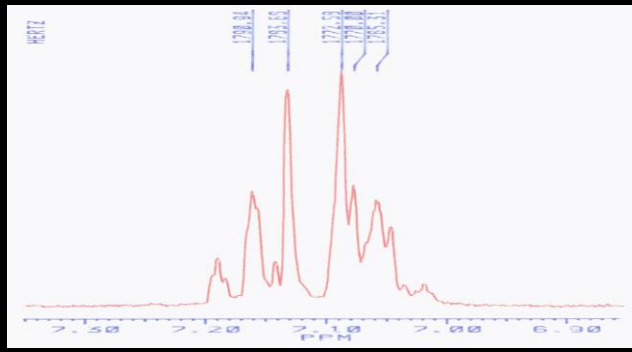
v2

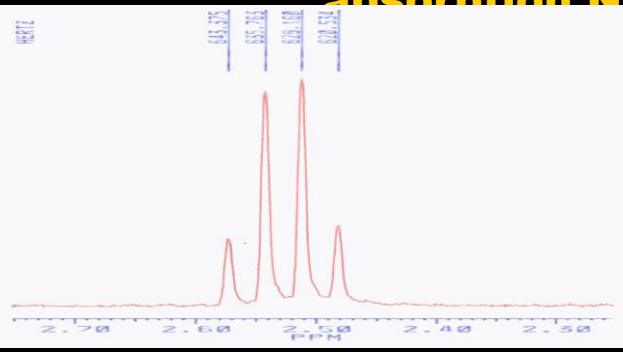
v3

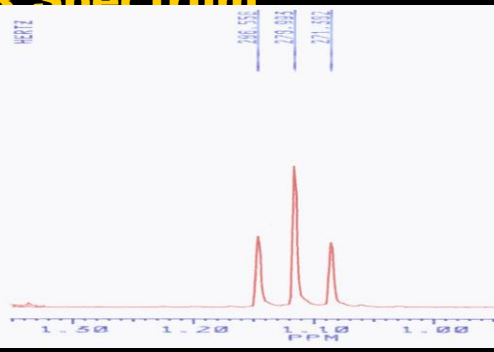


v1 , v2, & v3 have different half life.

When these FID are Fourier Transformed (FT) gives normal absorption NMR Spectrum







v1 = C_6H_5

v2 = CH_2

v3 = CH_3

NMR SIGNAL STRENGTH

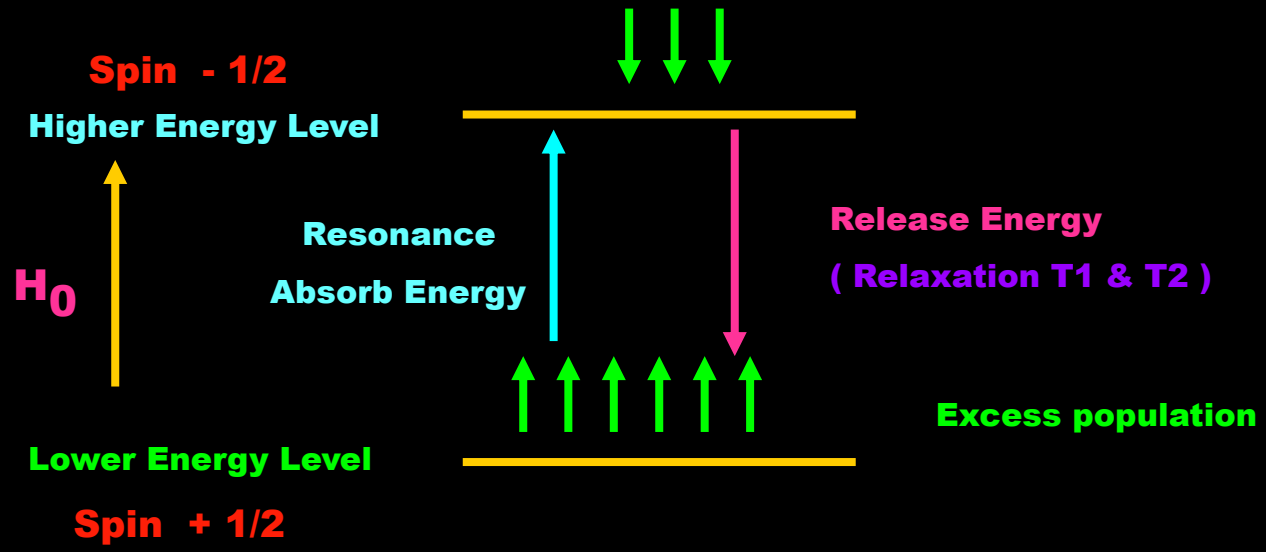
The strength of the NMR Signal depends on the Population Difference of the Parallel and Anti Parallel two spin states.

Applied Magnetic field induces both upward and downward transitions.

For NMR Signal there must be an excess of spins in the lower energy level.

Equal Populations = Saturation = No NMR Signal

Conditions for the detection of NMR Signal



Condition for NMR Signals

- 1. All the nuclei with odd mass number.
  ^{1}H, ^{11}B ^{13}C, ^{19}F, ^{29}Si & ^{31}P (I = Half Integer)

- 2. All the nuclei with even mass number
- and odd number of protons & neutrons.
  ^{2}H, ^{10}B, & ^{14}N (I = whole integer)

- 3. Those nuclei which have a non zero
- magnetic moment (u) and spin angular moment (I)
- produce NMR signals.

Typical conditions which satisfy the relationship between radiofrequencies for different nuclei at fixed magnetic field strength are given in the below table.

Nucleus	Spin No. I	% Natural Abundance	Frequency MHz	Field H0 Tesla
^{1}H	1/2	99.98	100.00	2.348
^{2}H	1	0.0115	15.35	2.348
^{10}B	3	19.00	10.74	2.348
^{11}B	3/2	81.00	32.07	2.348
^{13}C	1/2	1.10	25.14	2.348
^{14}N	1	99.60	7.22	2.348
^{15}N	1/2	0.40	10.13	2.348
^{19}F	1/2	100.00	94.05	2.348
^{29}Si	1/2	4.70	19.86	2.348
^{31}P	1/2	100.00	40.45	2.348
^{12}C	0 (zero)	98.80	NO NMR SIGNAL	
^{16}O	0 (zero)	99.80	NO NMR SIGNAL	

	No. of Peaks	Terminology	Intensity Ratio
n=0	One Peak	Singlet	1
n=1	Two Peaks	Doublet	1 1
n=2	Three Peaks	Triplet	1 2 1
n=3	Four Peaks	Quartet	1 3 3 1
n=4	Five Peaks	Quintet	1 4 6 4 1
n=5	Six Peaks	Sextet	1 5 10 10 5 1
n=6	Seven Peaks	Septet	1 6 15 20 15 6 1
n=7	Eight Peaks	Octet	1 7 21 35 35 21 7 1

$I = \frac{1}{2}$ ^{1}H , ^{13}C , ^{19}F

Pascal ' s Triangle $I = \frac{1}{2}$

The relative intensities of multiplet are given by the coefficients of the binomial expansion.

In mathematics, the binomial theorem is an important formula giving the expansion of powers of sums. Its simplest version says

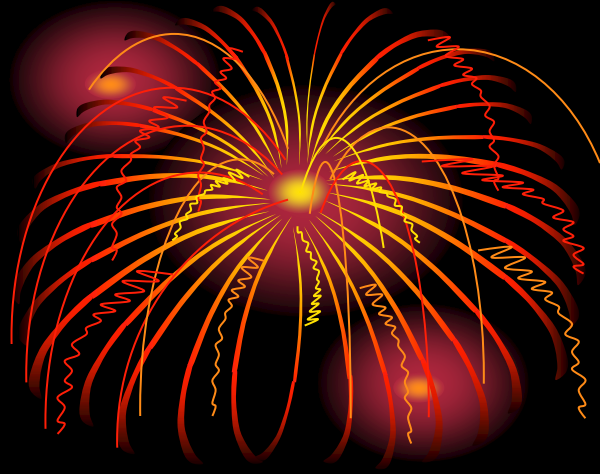
$$(x+y)^n = \sum_{k=0}^{n} \binom{n}{k} x^{n-k} y^k \qquad (1)$$

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

whenever *n* is any non-negative integer, the number is the binomial coefficient

Read the intensity ratio directly from Pascal Triangle.

Pascal Triangle and Binomial Coefficient

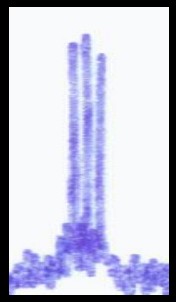


- No. Of Peaks = 2nI +1 Where n = spin active nuclei , I = Spin Number ^{1}H , I = ½
- $(X + Y)^{o}$ = 0 X + 0 Y (2nI + 1 = 2 x 0 X ½ + 1 = 1) 1
- $(X + Y)^{1}$ = 1 X + 1 Y 1 1
- $(X + Y)^{2}$ = $1X^2 + 2XY + 1Y^2$ 1 2 1
- $(X + Y)^{3}$ = $1X^3 + 3X^2Y + 3XY^2 + 1Y^3$ 1 3 3 1
- $(X + Y)^{4}$ = $1X^4 + 4X^3Y + 6X^2Y^2 + 4XY^3 + 1Y^4$ 1 4 6 4 1

	No. of Peaks	Terminology	Intensity Ratio
n=0	One Peak	Singlet	1
n=1	Three Peaks	Triplet	1 1 1
n=2	Five Peaks	Quintet	1 2 3 2 1
n=3	Seven Peaks	Septet	1 3 6 7 6 3 1
n=4	Nine Peaks	Nonet	1 4 10 17 25 17 10 4 1

Pascal ' s Triangle I = 1

I = 1 Deuterium ^{2}H (D) , ^{14}N



^{13}C NMR of $CDCl_3$

I = 1 ^{2}H to ^{13}C

Intensity ratio 1 : 1 : 1

Read the intensity ratio directly from Pascal Triangle.

- **The most common Deuterated solvents used are**

- **1. Deuterochloroform** $CDCl_3$
- **2. Deuteroacetone** CD_3COCD_3
- **3. Deuterobenzene** C_6D_6
- **4. Deuterodichloromethane** CD_2Cl_2
- **5. Deuterated water** D_2O
- **6. Deuterodimethysulphoxide** CD_3SOCD_3

Note :- The hydrogen atoms are replaced with deuterium so that no signal from solvent and also used for locking the oscillating field by the lock frequency.

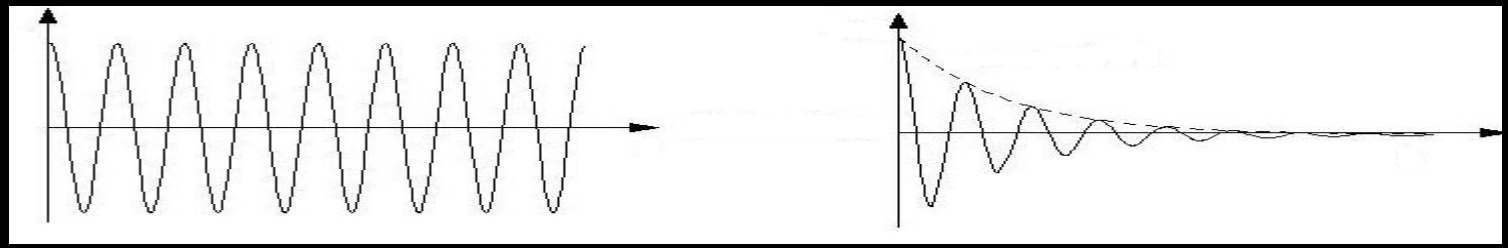
Referencing of NMR Spectra

- The reference compound should have only one absorption peak for the interested compound.
- It should also be :-
  - 1. Chemically Stable.
  - 2. Chemically Inert.
  - 3. Soluble in most common solvents.

NMR OF	Reference Compounds	
^{1}H	TMS	(TetraMethylSilane)
	TSP-D4	(3-TrimethySilyl-2,2,3,3-tetra
		DeuteroPropionic acid Sodium salt.)
^{13}C	TMS, $CDCl_3$	
^{14}N	NH_4NO_3	Acidified Saturated Solution
^{15}N	NH_2CHO	90% Formamide
	CD_3NO_2	Deuteronitromethane
^{19}F	TFA	TriFluoroAcetic Acid
	$CFCl_3$	Freon 1,1
^{31}P	H_3PO_4	85% Phosphoric Acid

Relaxation Processes T1 & T2

- **T1 is called Longitudinal Relaxation Time**
- **T2 is called Transverse Relaxation Time**
- **The magnetization does not precess indefinitely in the transverse plane but goes back to the equilibrium state. This process is called Relaxation and can be describe by two time constants T1 and T2.**
- **T1 is the Re-establishment of the equilibrium of**
- **α (Alpha) And β (beta) States.**
- **T2 is the dephasing of the transverse component**
- **The destruction of the coherent state and it is the exponential decay of the NMR signal in the detector.**



No relaxation **With relaxation**

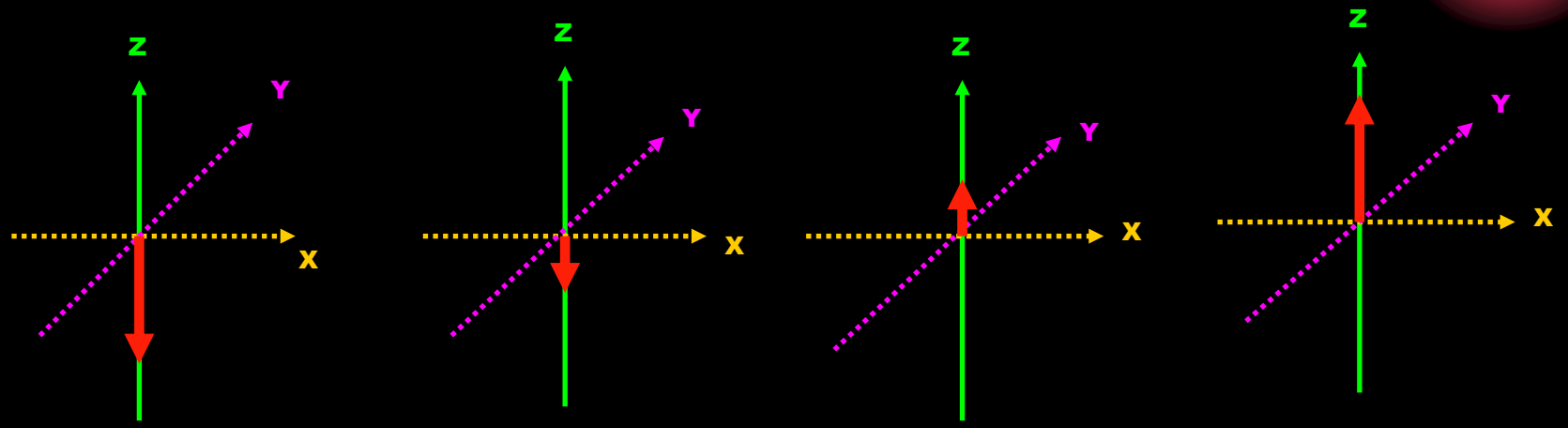
Relaxation Processes T1 & T2

- **T1 relaxation is an enthalpic process where the energy is taken from or transferred to neighbouring spins. The surrounding of the spins is called lattice hence T1 is also known as spin lattice relaxation. In this process the Z – Component of the magnetization is return back to its equilibrium state. T1 values are useful information for NMR experiment what to set up as repetition time between each NMR scan. For 1H T1 values are from 0.5 Seconds to few seconds.**

- **T2 relaxation is an entropic process and does not affect the population of spins hence there is no change in the energy. T2 is also known as spin spin relaxation. In this process the decay of the transverse (x , Y) components of the magnetization is described.**

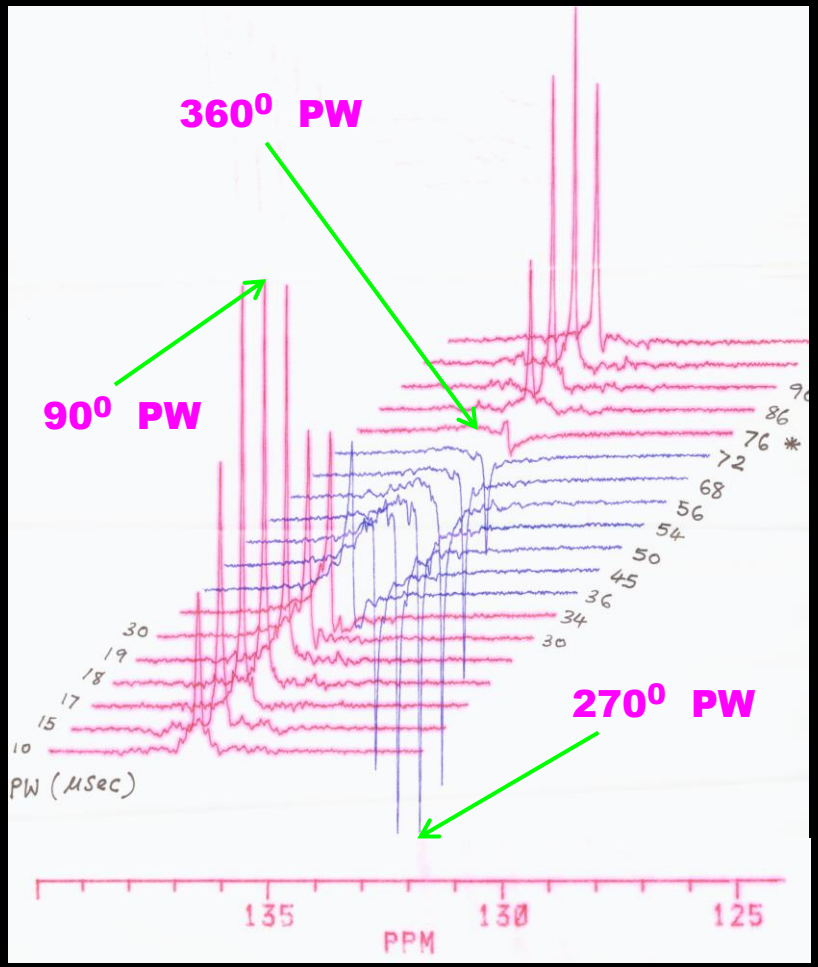
T1 Relaxation

- **T1 relaxation is an enthalpic process where the energy is taken from or transferred to neighbouring spins. The surrounding of the spins is called lattice hence T1 is also known as spin lattice relaxation. In this process the Z – Component of the magnetization is return back to its equilibrium state. T1 values are useful information for NMR experiment what to set up as repetition time between each NMR scan. For 1H T1 values are from 0.5 Seconds to few seconds.**



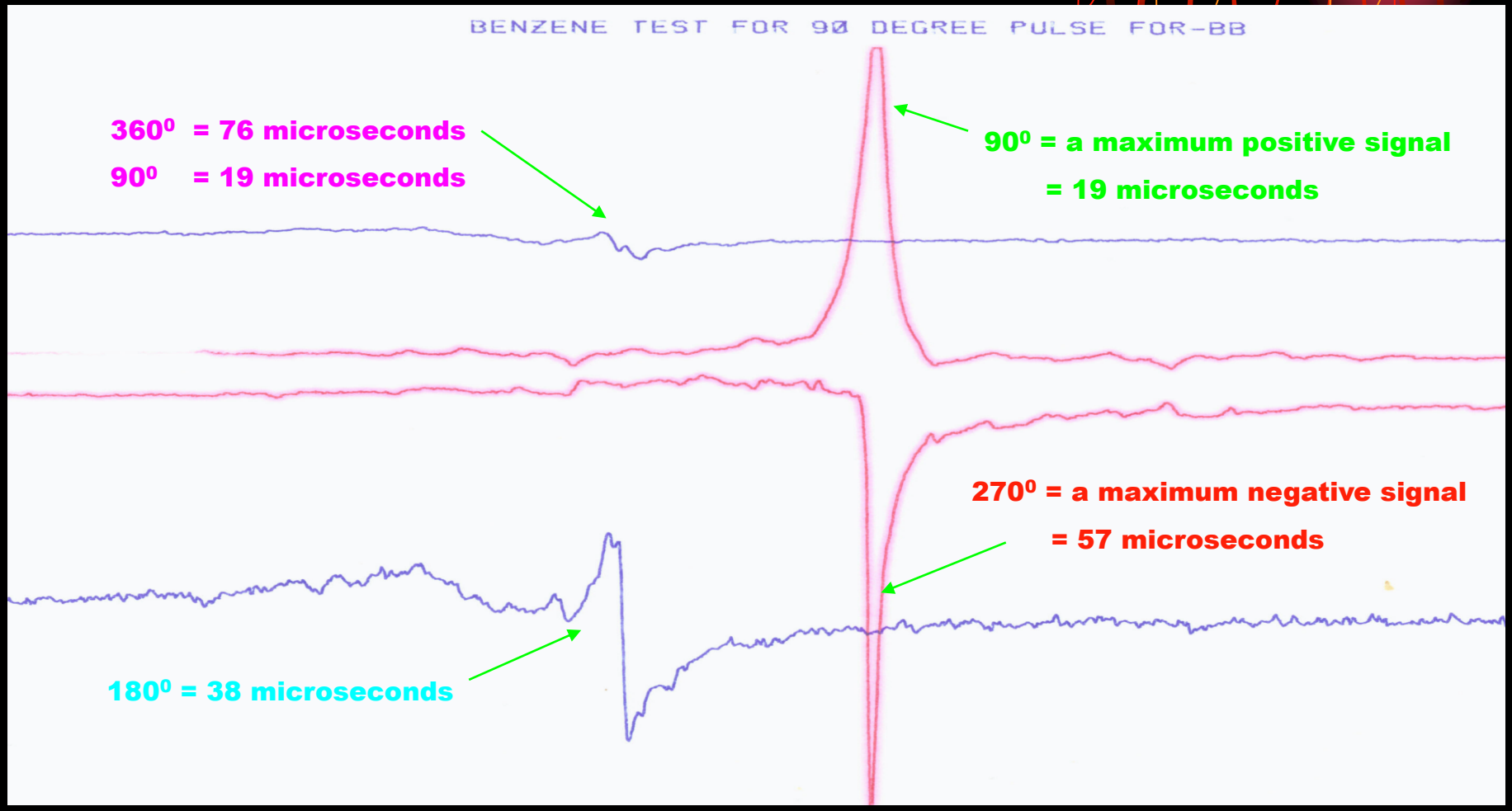
Return of the Z component of the magnetization to the equilibrium state

Spin Lattice or Longitudinal Relaxation Process T_1 And the Measurement of 90^0 & 180^0 Pulse width (PW) ^{13}C NMR Spectrum of Benzene in Acetone –D6



- when sample is placed in the magnetic field and radio frequency (RF) pulse is applied, the Boltzmann population of spins get upset and after a time delay T_1 the Boltzmann population of spins get re-established. This time delay T_1 is called the spin lattice or longitudinal relaxation time T_1
- Measurement of 90^0 and 180^0 pulses times knowledge of the 90^0 pulse time or pulse width (PW)
- for any spin active nucleus (^1H, ^{13}C, ^{19}F, ^{15}N) is required to set up all multipulses FT NMR experiments. An accurate value of 90^0 PW is crucial for T_1 value measurement. This is usually obtained using a concentrated sample to produce a strong signal after a single pulse. Record the signal intensity with various PW. All measurements must be made with the same intensity scaling and same phase corrections. The intensities should show a sinusoidal variation with pulse width PW
- 90^0 = A maximum positive signal
- 270^0 = A maximum negative signal
- 180^0 = A zero signal
- 360^0 = A zero signal
- It is easier to determine the position of null values at 180^0 and 360^0 PW The half of 180^0 or quarter of 360^0 values will be 90^0 PW

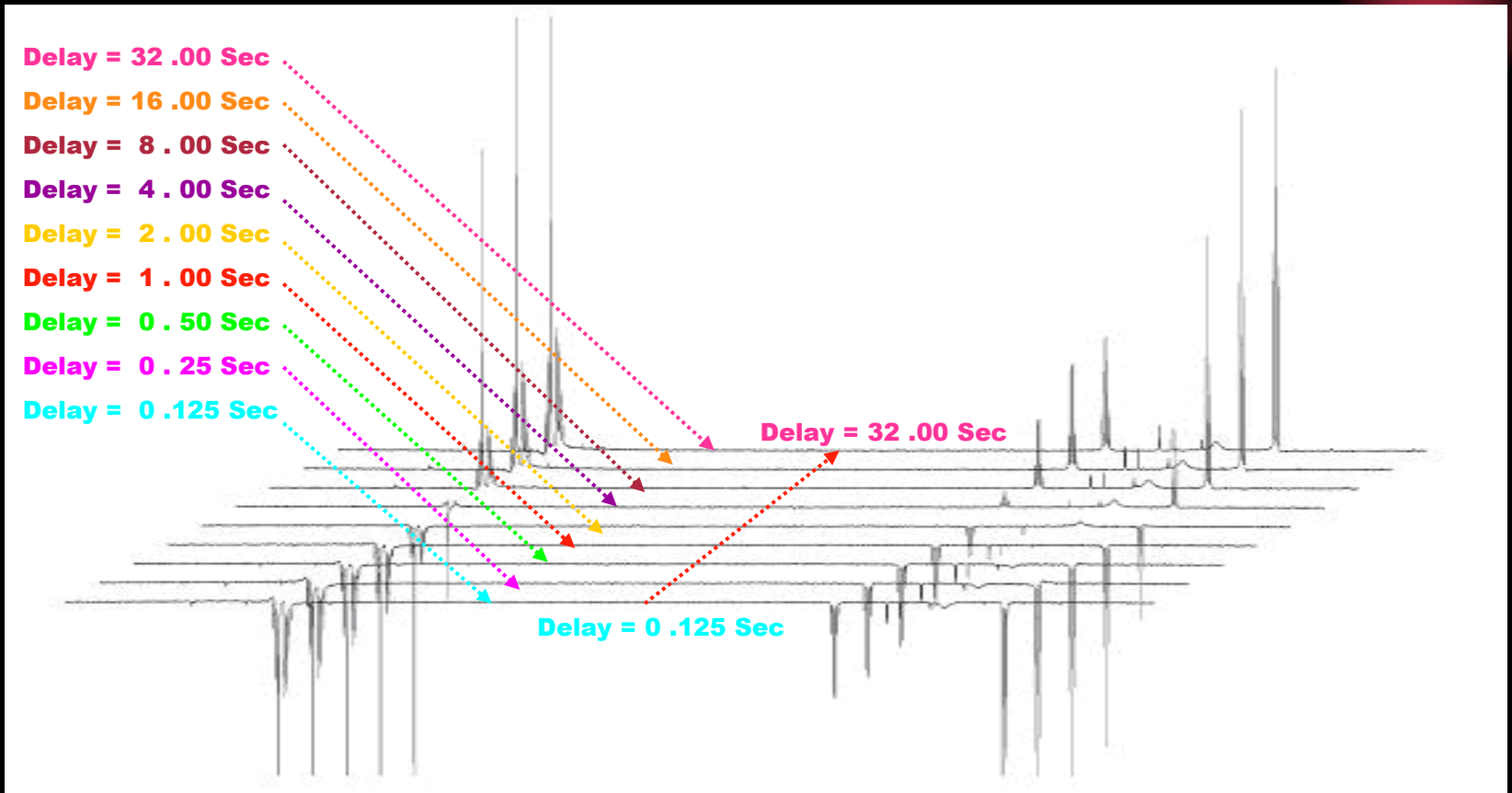
Measurement of 90^0 & 180^0 Pulse width (PW)
^{13}C NMR Spectrum of Benzene in Acetone –D6



T1 Measurement using Inversion recovery method

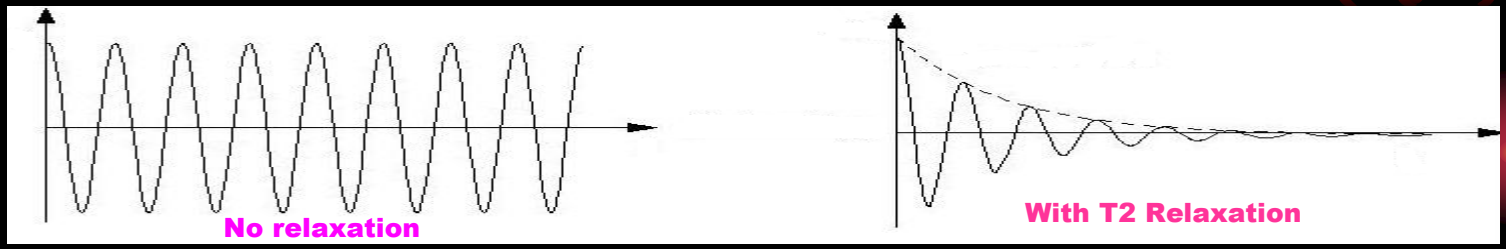
^{1}H Spectrum of Ethyl Benzene

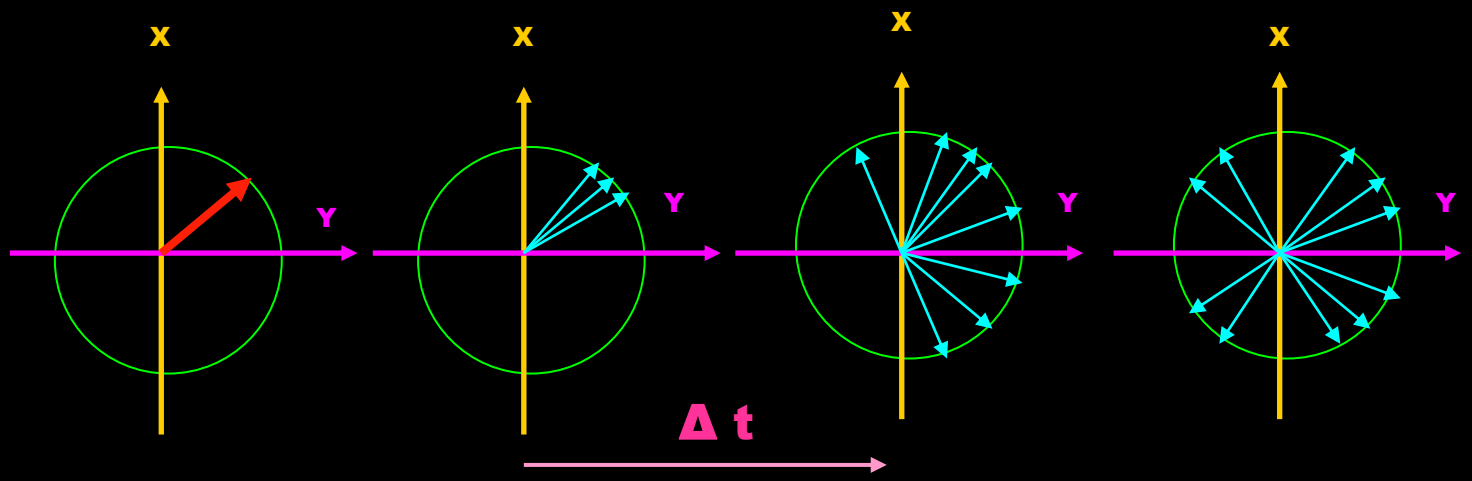
^{1}H NMR Spectrum of Ethyl Benzene



T2 Relaxation

- T2 relaxation is an entropic process and does not affect the population of spins hence there is no change in the energy. T2 is also known as spin spin relaxation. In this process the decay of the transverse (x , Y) components of the magnetization is described.



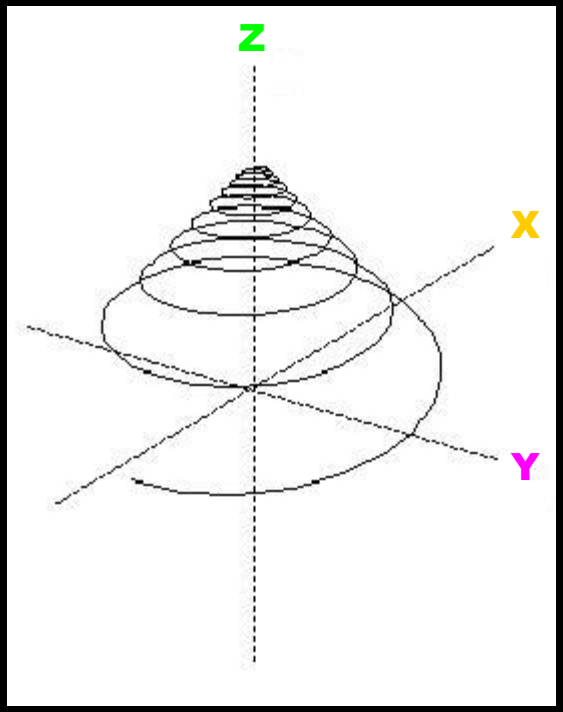


The Dephasing of the transverse coherence of (X , Y) magnetization leading to T2 relaxation

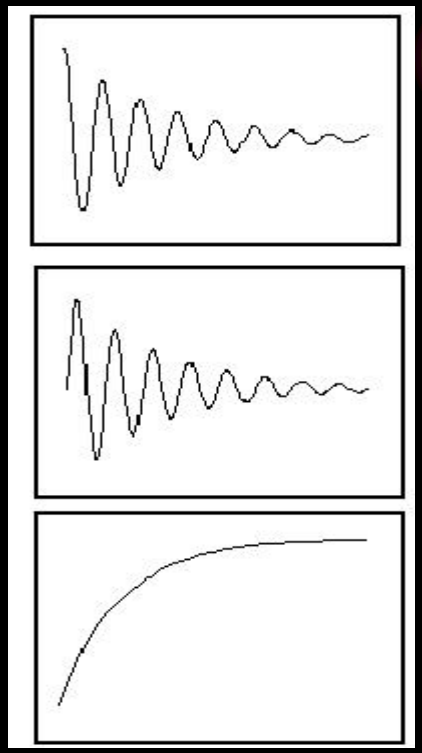
The effect of T2 on NMR signal (FID)

T2 Relaxation

- The precessing spins slowly return to the Z - axis. The movement is not circular in the transverse plane but spins follow a spiral trajectory until they have reached their initial position aligned with + / - Z - axis

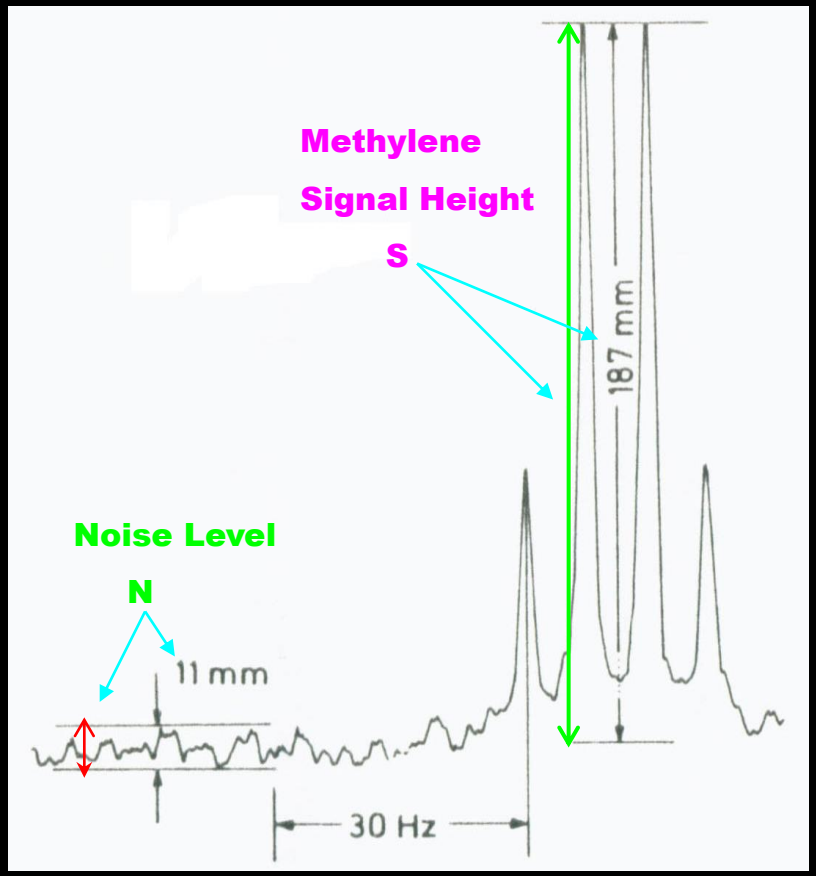


Trajectory of the magnetization



X , Y, Z , Components

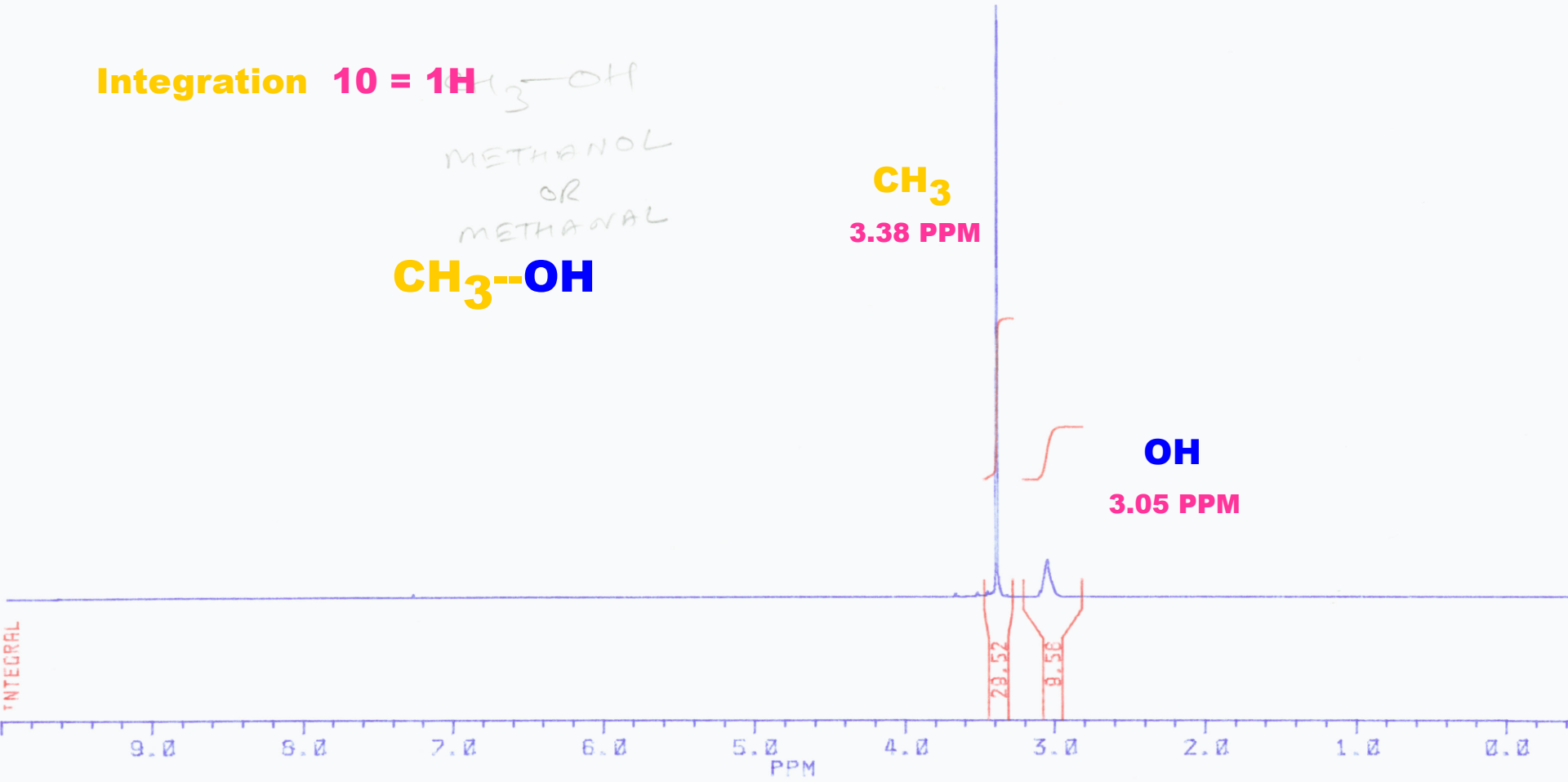
Sensitivity test with 1 % Ethyl Benzene solution in $CDCl_3$
Signal to noise ratio test S / N on methylene quartet



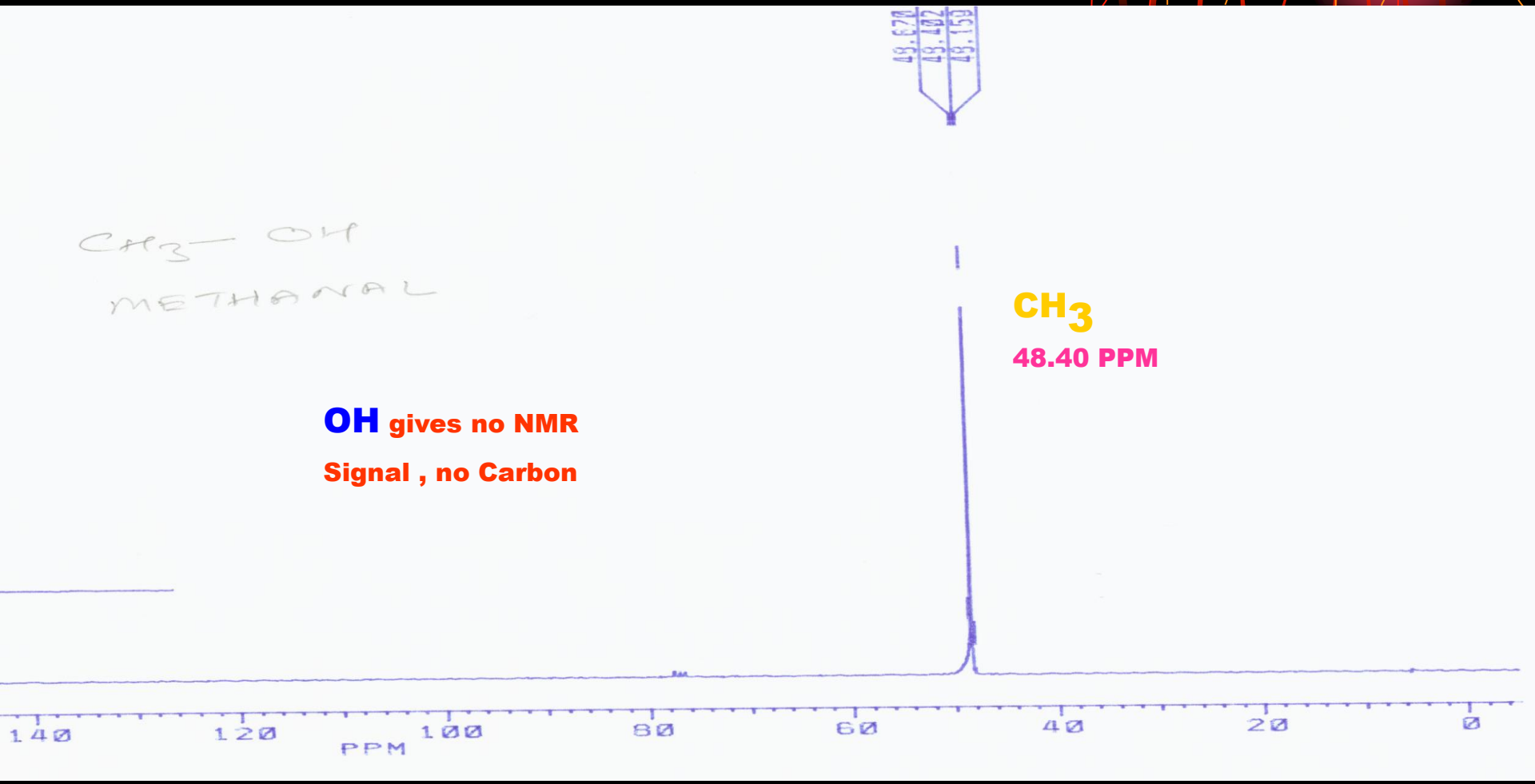
- Average Noise N = N / 2.5
- N = 11 / 2.5
- N = 4.4 mm
- The signal to noise ratio is defined as the quotient of the average signal height S and the average noise level N.
- S = 187 mm
- S / N = 187 / 4.4
- = 42.50
- Before the sensitivity test tune the Spectrometer with D_20 sample.

Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Methanal or Methanol

^{1}H NMR of CH_3--OH

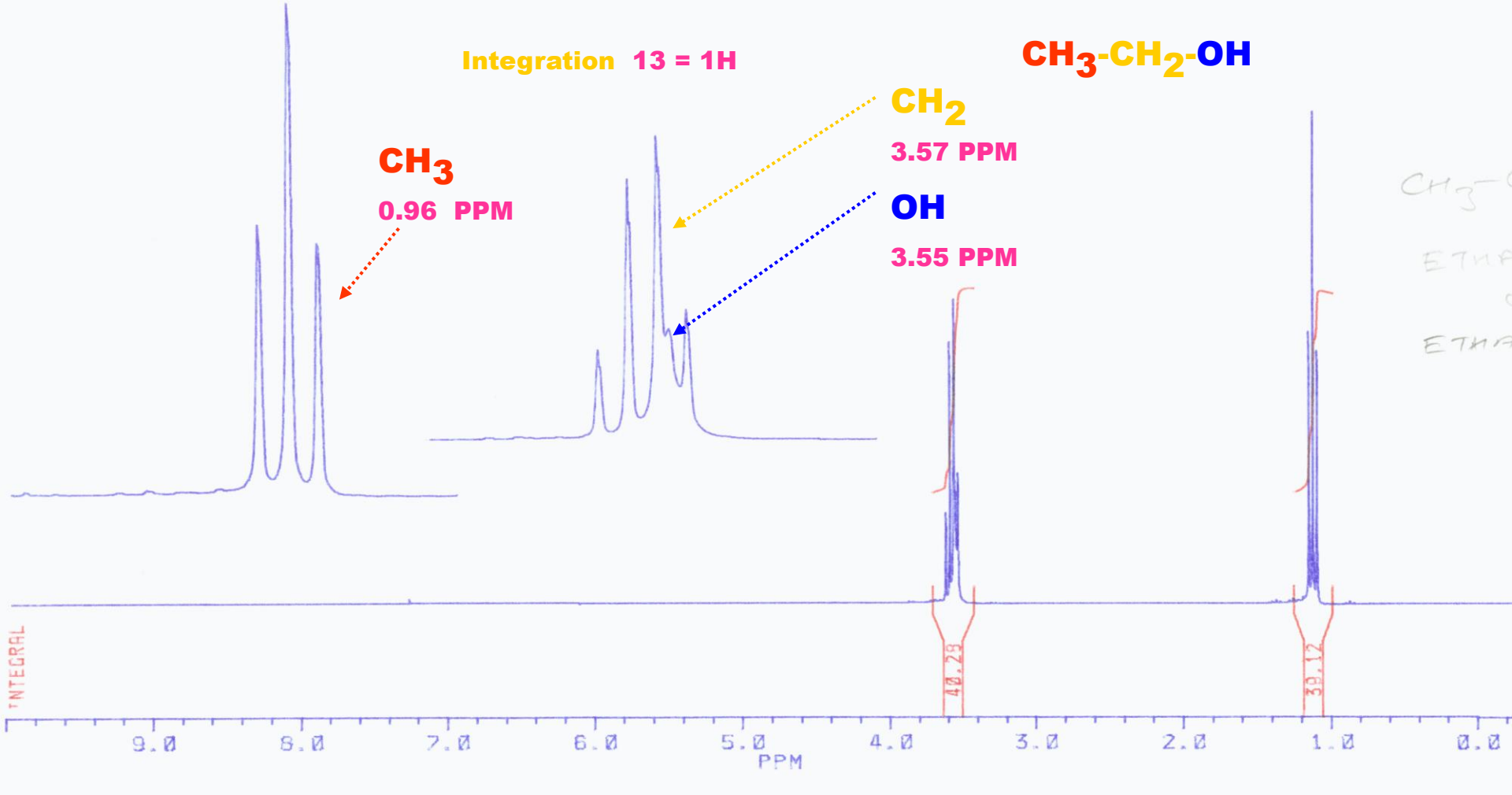


^{13}C NMR Spectrum of Methanal CH_3OH

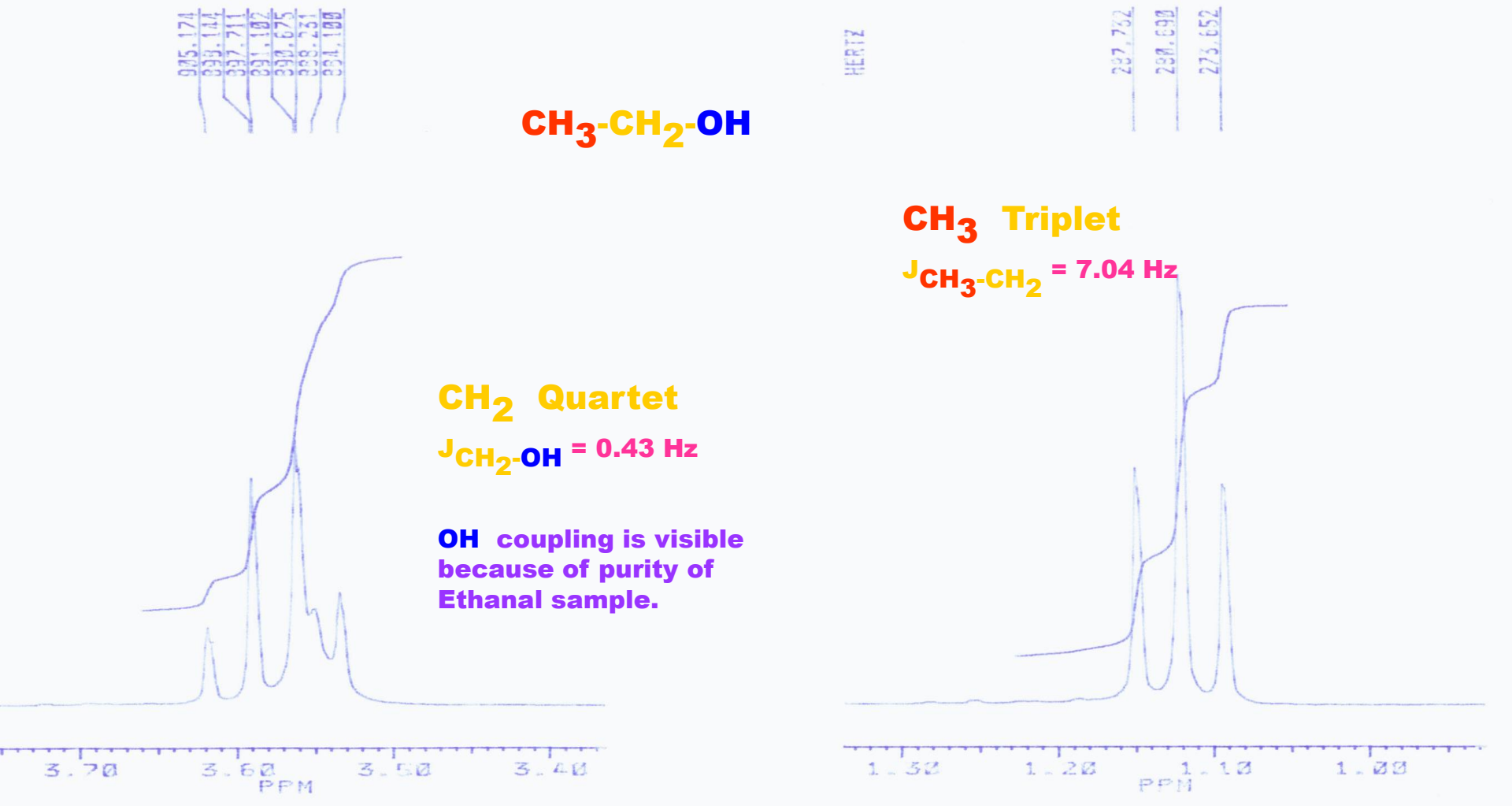


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Ethanal or Ethanol CH_3--CH_2--OH

^{1}H NMR Spectrum



Expansion of ^{1}H NMR of Ethanal $CH_3—CH_2--OH$



CH_3-CH_2-OH

CH_3 Triplet

$J_{CH_3\text{-}CH_2}$ = 7.04 Hz

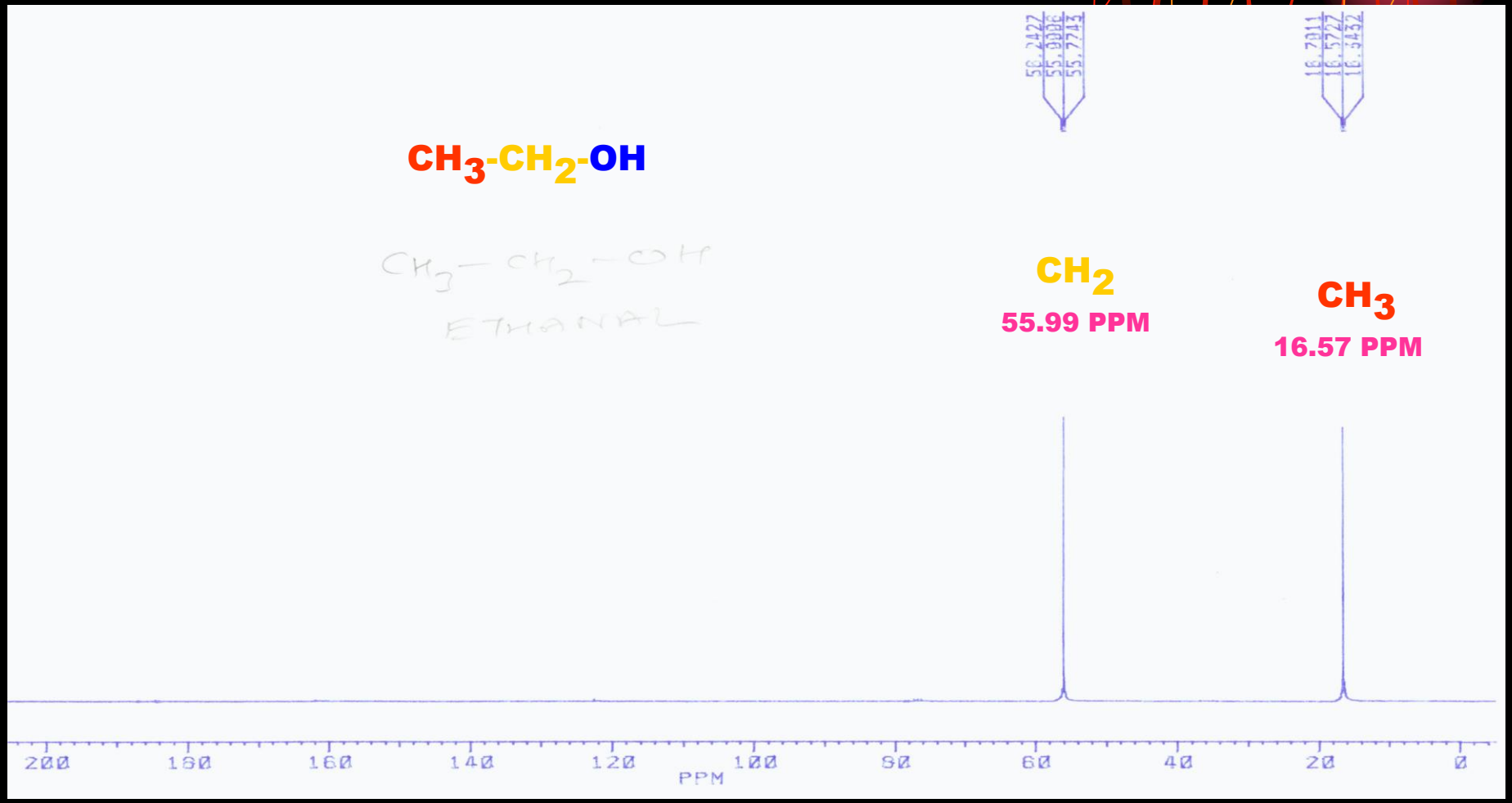
CH_2 Quartet

$J_{CH_2\text{-}OH}$ = 0.43 Hz

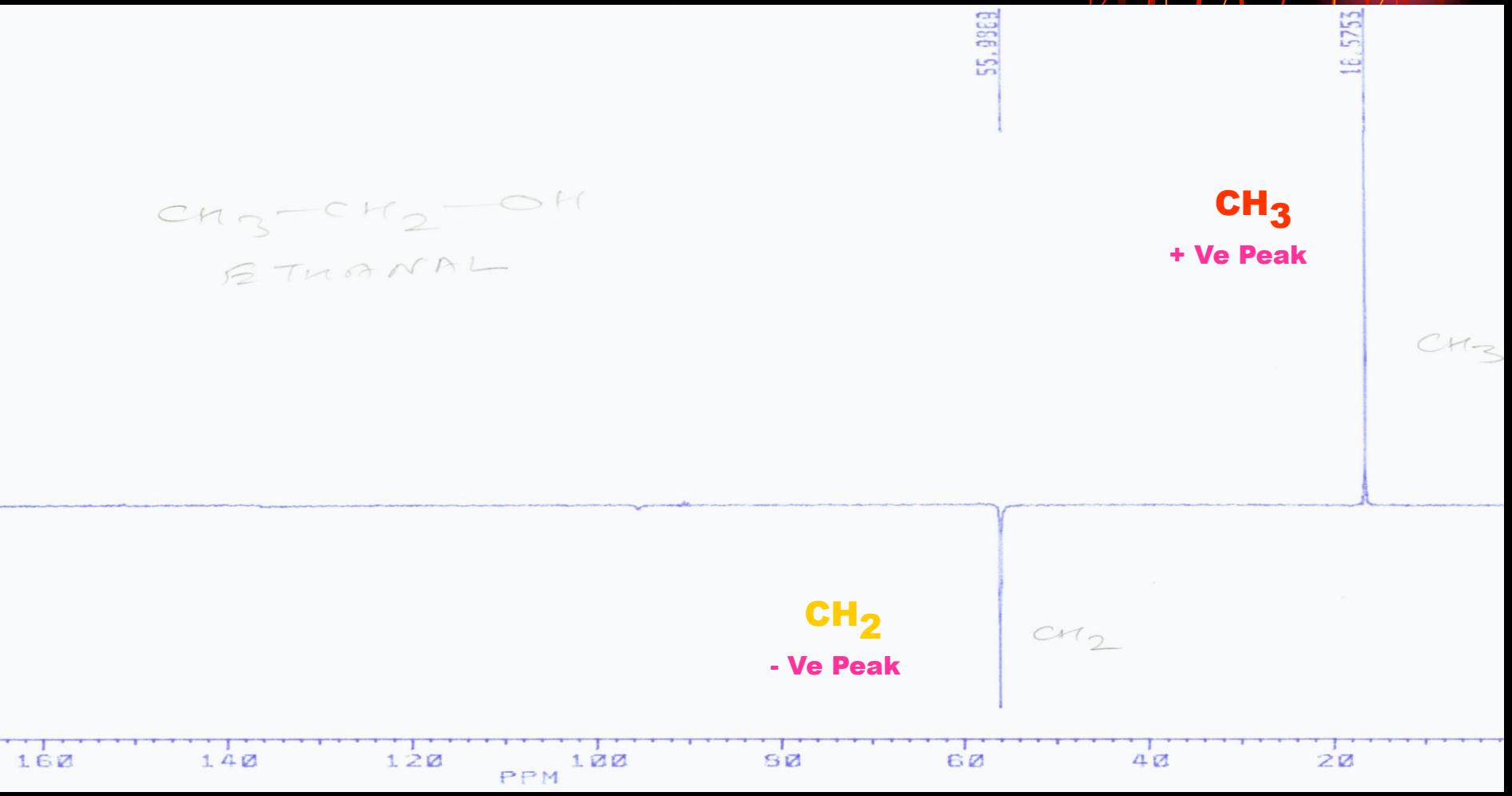
OH coupling is visible because of purity of Ethanal sample.

^{13}C NMR Spectrum of Ethanal

$CH_3—CH_2$--OH



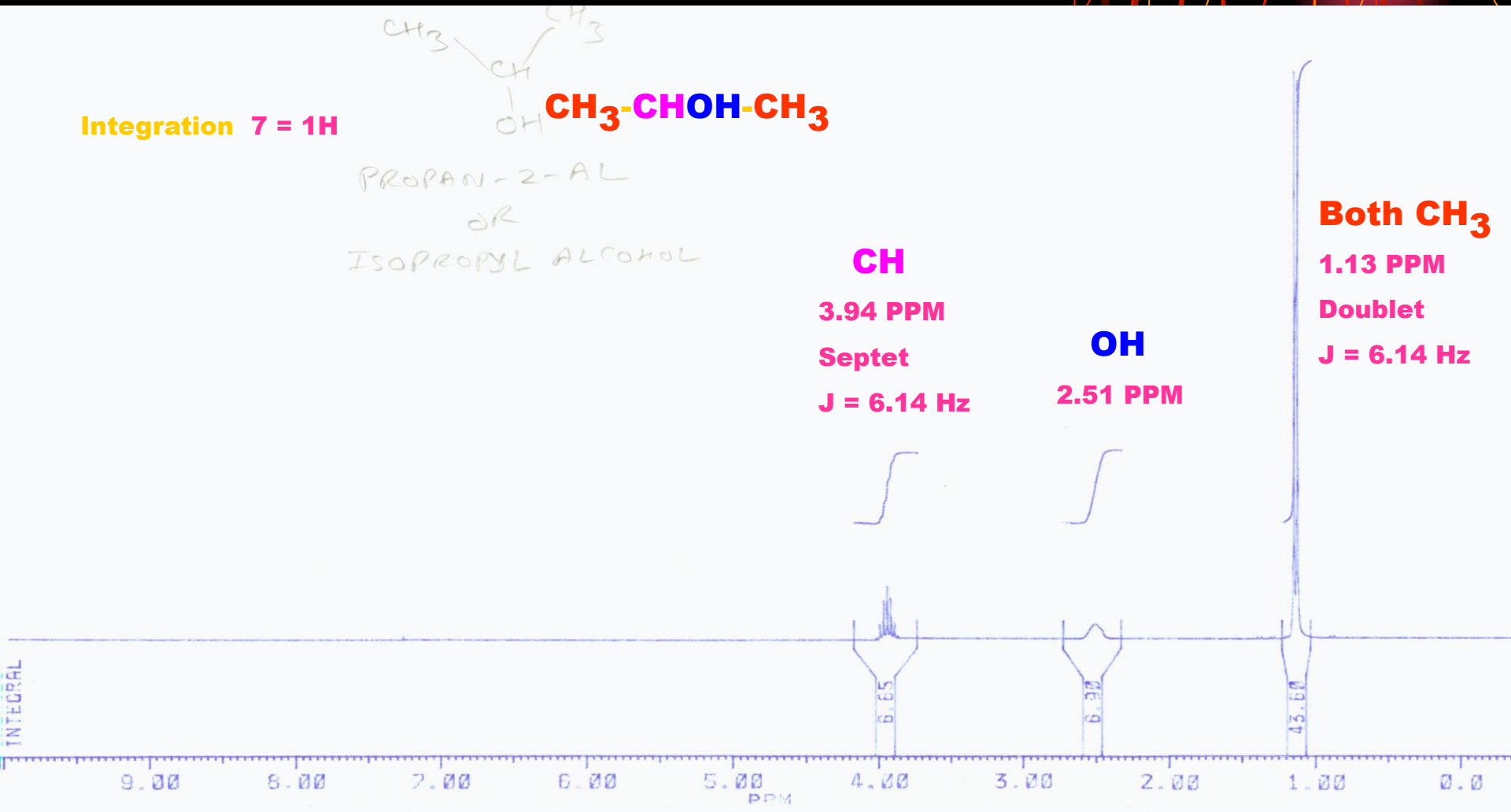
^{13}C Dept 135 NMR Spectrum of Ethanal



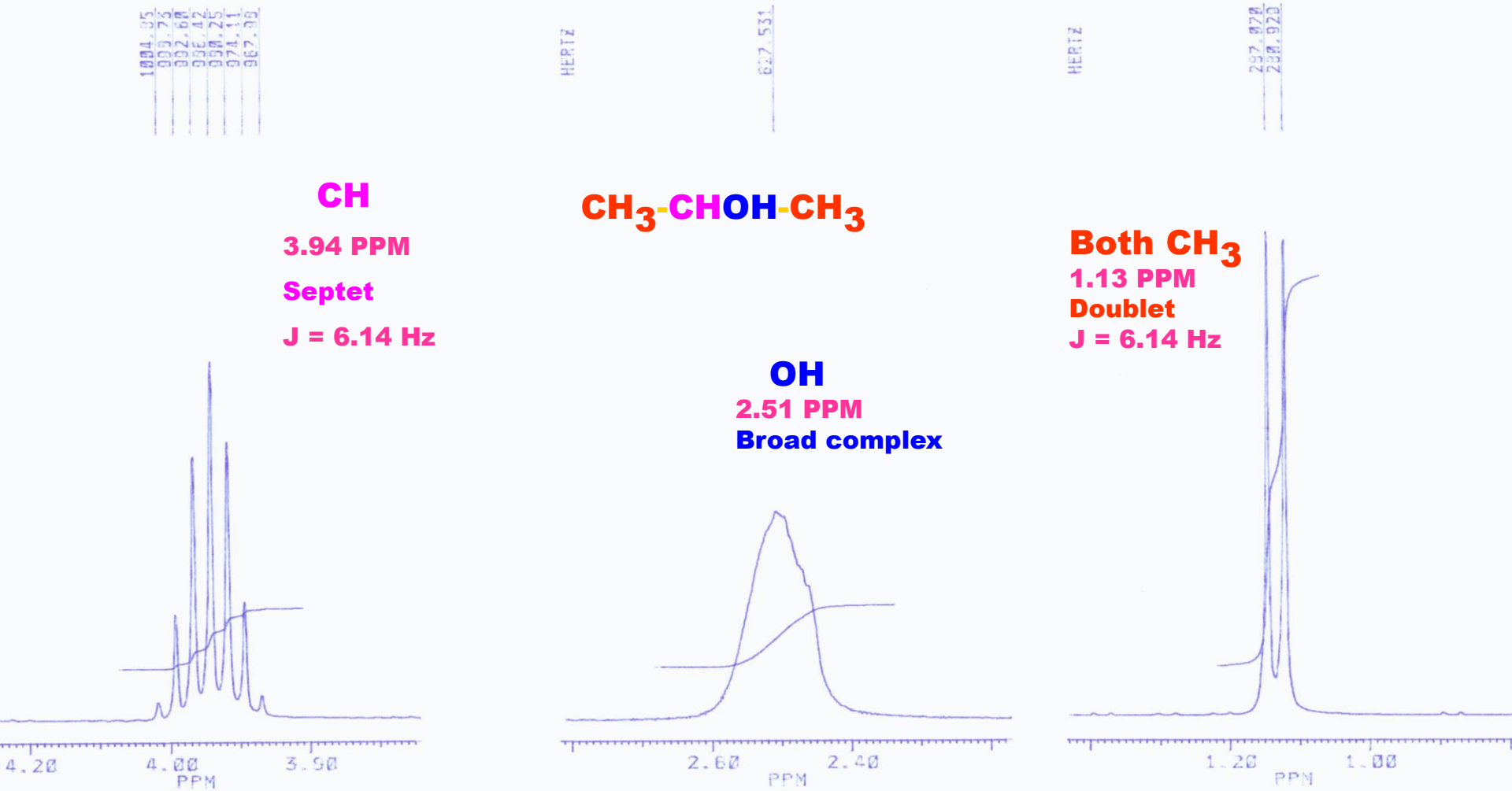
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Propan-2-al

$CH_3—CHOH—CH_3$

^{1}H NMR Spectrum



Expansion of ^{1}H NMR Spectrum of Propan-2-ol



CH

3.94 PPM

Septet

J = 6.14 Hz

CH_3-CHOH-CH_3

OH

2.51 PPM

Broad complex

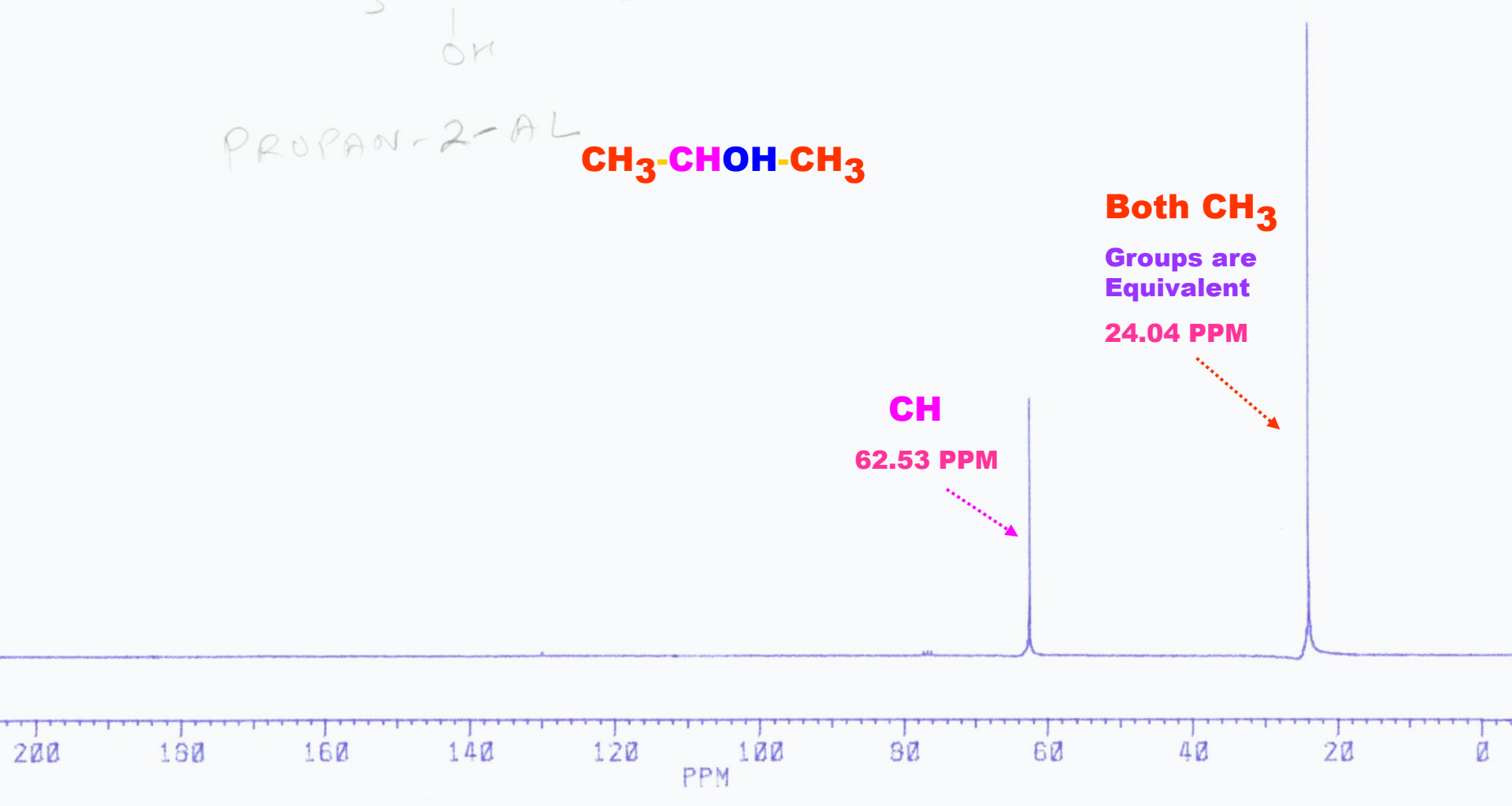
Both CH_3

1.13 PPM

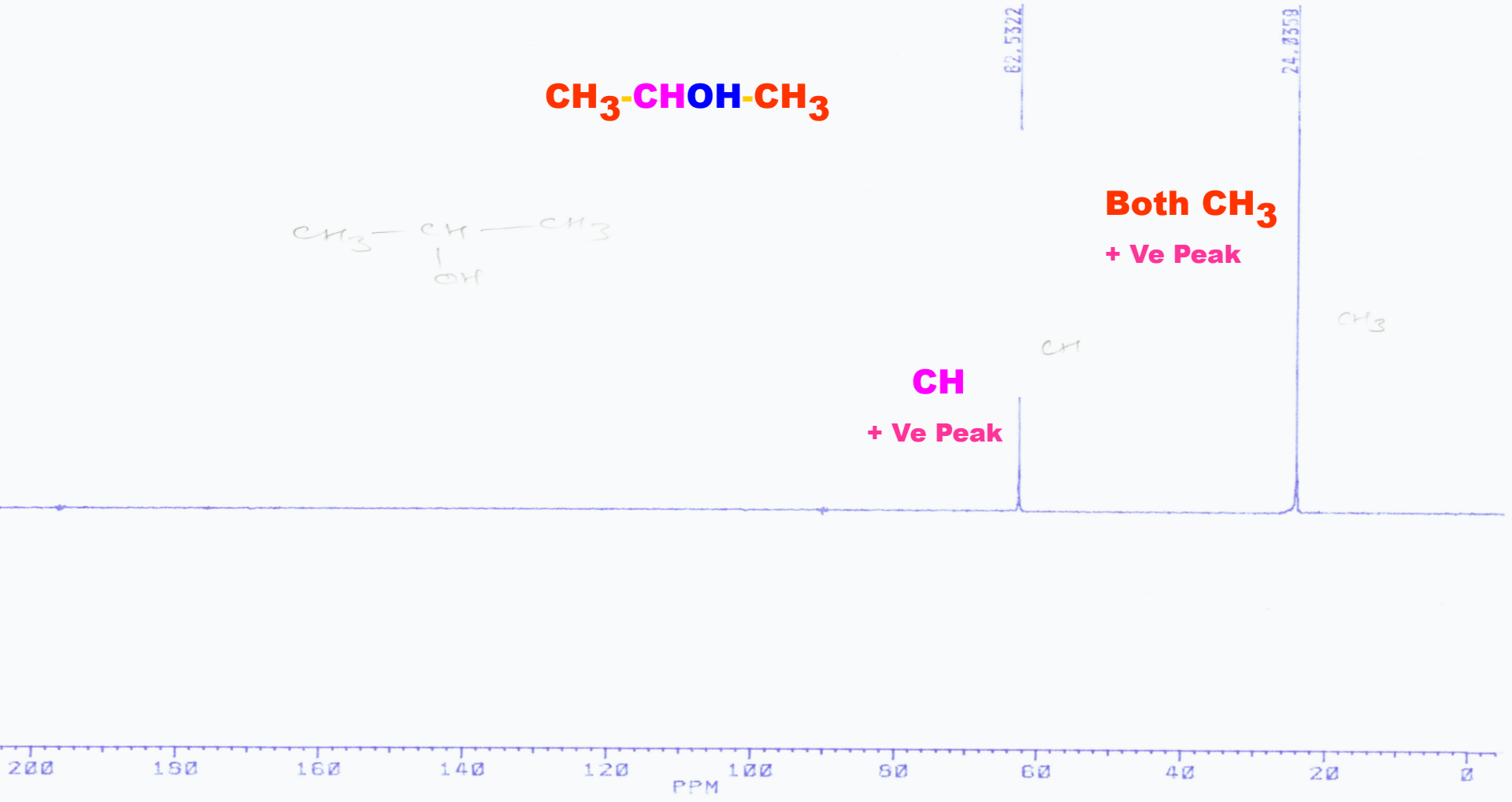
Doublet

J = 6.14 Hz

^{13}C NMR Spectrum of Propan-2-al



^{13}C Dept 135 NMR Spectrum of Propan-2-al



Analysis and interpretation of ^{1}H NMR Spectrum Of Butan-2-al

CH_3-CHOH-CH_2-CH_3
1 2 3 4

Integration 12 = 1H

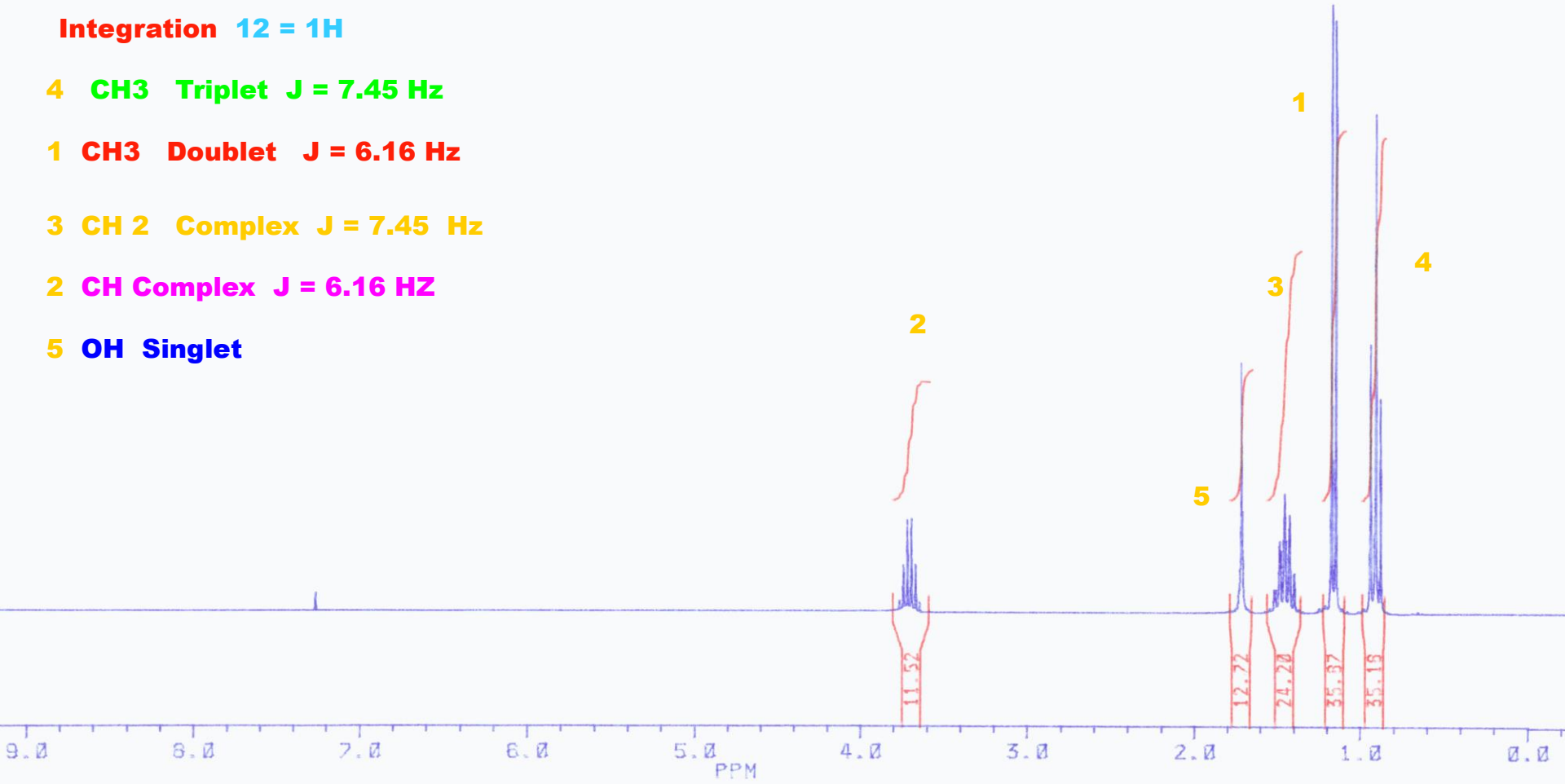
4 CH3 Triplet J = 7.45 Hz

1 CH3 Doublet J = 6.16 Hz

3 CH 2 Complex J = 7.45 Hz

2 CH Complex J = 6.16 HZ

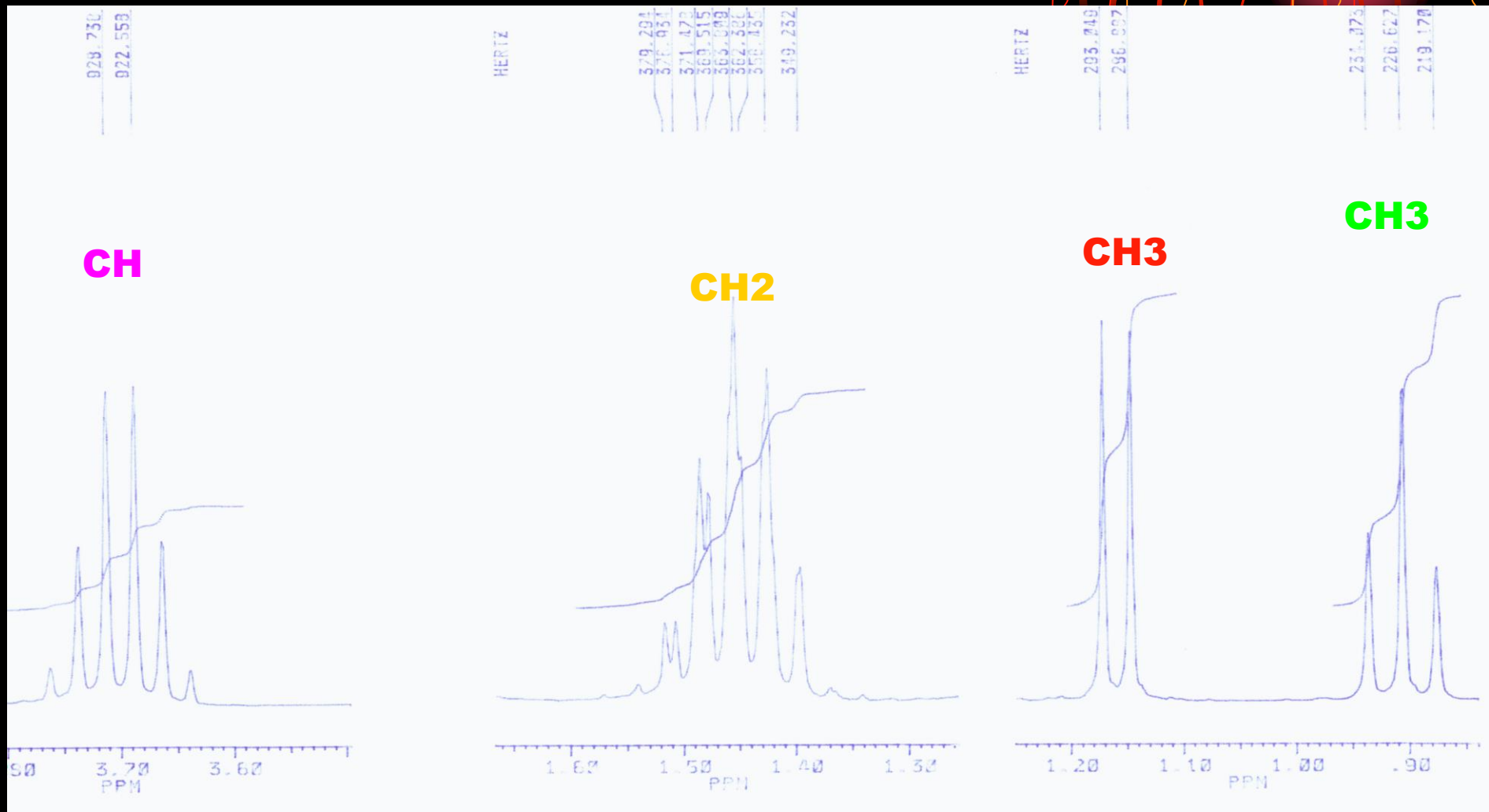
5 OH Singlet



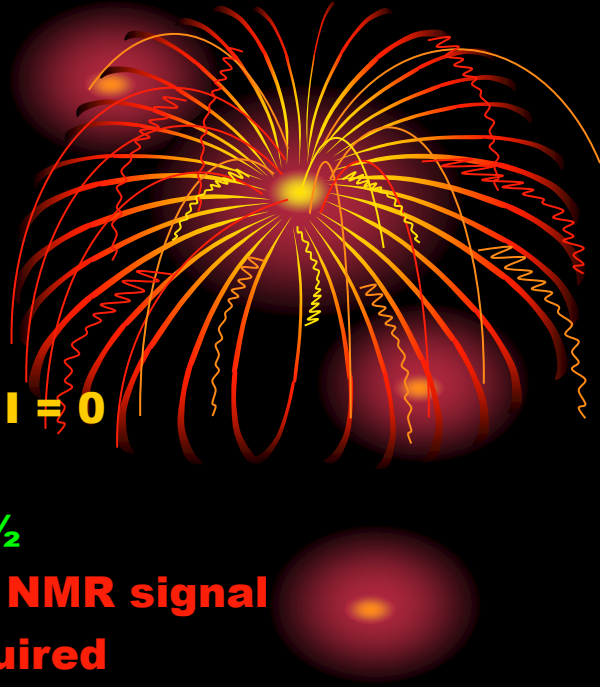
Analysis and interpretation of ^{1}H NMR Spectrum Of Butan-2-al

CH_3-CHOH-CH_2-CH_3

1 2 3 4



Facts about Carbon Atom



- Carbon ^{12}C is in most abundance 98.89 %
- Carbon ^{12}C is non NMR active as spin number I = 0
- Carbon ^{13}C is in less abundance 1.108 %
- Carbon ^{13}C is NMR active as spin number I = ½
- ^{13}C NMR signal is 6000 times weaker than ^{1}H NMR signal
- To see ^{13}C NMR signals Pulsed FT NMR is required

- Chemical Shift Range
- ^{1}H 0 to 12.00 PPM
- ^{13}C 0 to 220.00 PPM
- Resonance Frequency and Applied Field Strength

Applied Field	^{1}H RF	^{13}C
1.41 Tesla	60.00 MHz	15.10 MHz
2.35 T	100.00 MHz	25.00 MHz
5.88 T	250.00 MHz	62.90 MHz
7.05 T	300.00 MHz	75.00 MHz

Spin Spin Coupling In ^{13}C NMR Spectroscopy

^{13}C—^{13}C is not seen because the probability of two ^{13}C nuclei being in the same molecule is very small.

^{13}C—^{1}H splitting is not seen in normal ^{13}C NMR Spectra because they are measured under broad band decoupling conditions which suppress these splitting.

Normally ^{13}C NMR signal is a singlet but if ^{13}C is attached to a spin active nuclei like ^{2}H (D),^{19}F, ^{31}P then coupling are present from these nuclei. $CDCl_3$ solvent gives triplet in NMR spectrum due to ^{2}H coupling to ^{13}C.(^{2}H, I = 1)

^{13}C NMR $CDCl_3$

Distortion less Enhancement of Polarization Transfer

DEPT is useful technique to differentiate how many ^{1}H attached to ^{13}C atom.

DEPT 135 gives CH_3 & CH as positive signals

CH_2 as negative signal

C (Quaternary) as null signal

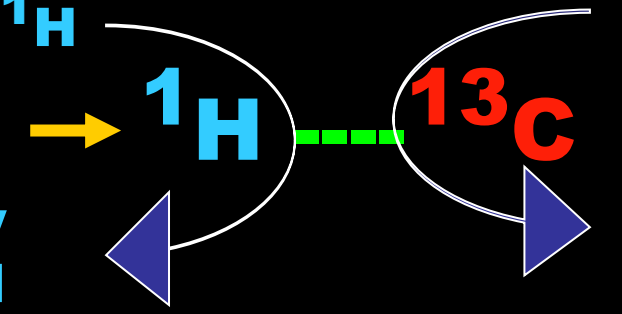
Broad Band ^{1}H Decoupled ^{13}C NMR Spectra

In this method all the ^{1}H are irradiated at certain RF and at the same time ^{13}C signals are measured at different RF.

Secondary RF source is required To decouple ^{1}H

(Decoupler)

Continuously Saturates ^{1}H



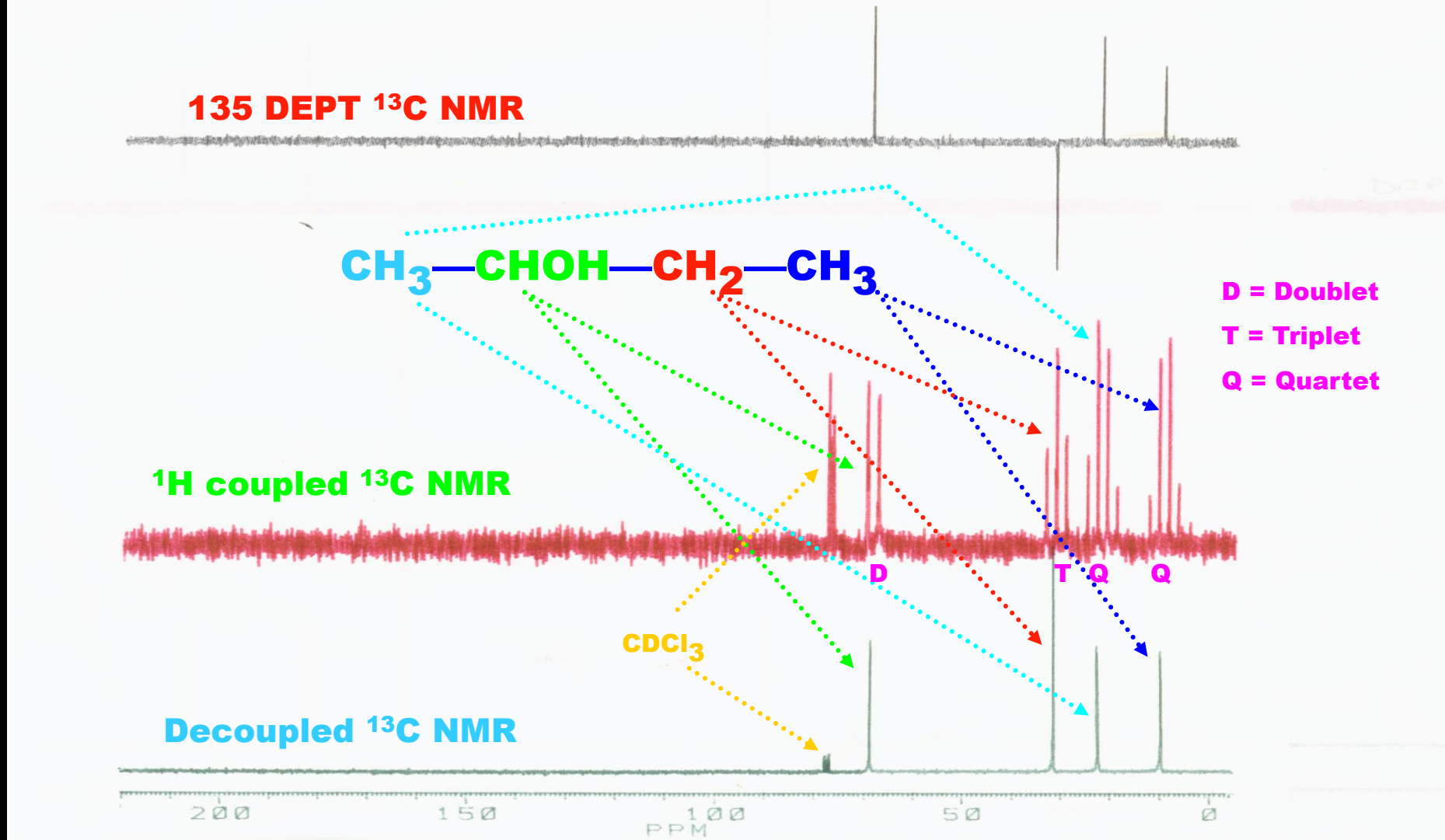
Primary RF source is tuned to measure ^{13}C NMR signals

Which gives ^{13}C FID

Saturation means there are rapid and equal transitions from upward spin state to the downward spin state. No NMR signal from ^{1}H hence ^{13}C NMR signals are all singlet.

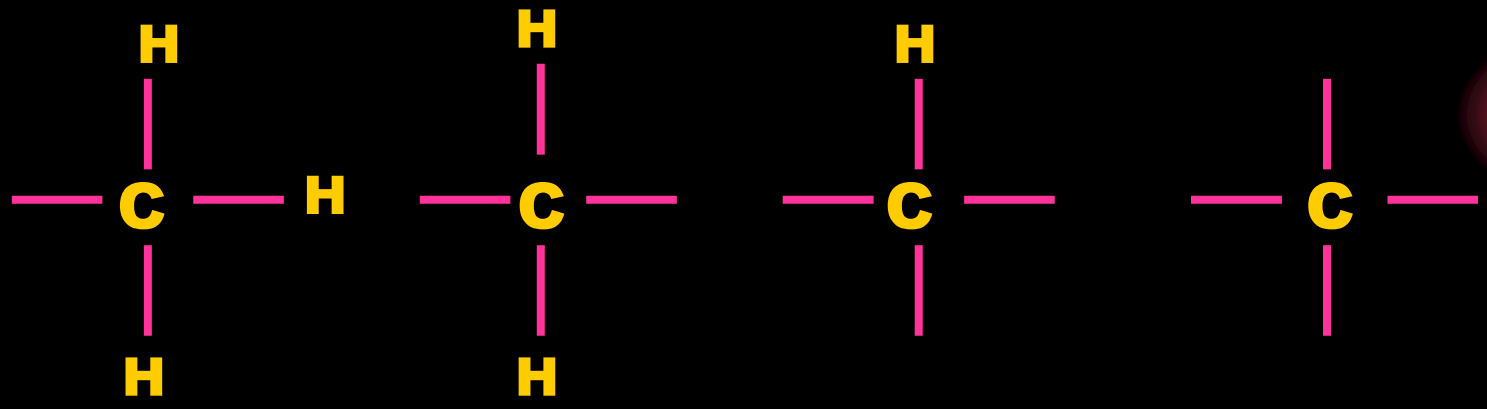
^{13}C NMR Spectra of Butan-2-ol

$CH_3—CHOH—CH_2—CH_3$



^{1}H coupling to ^{13}C in ^{13}C NMR Spectra

No. of peaks = 2nI + 1
n is No of spin active nuclei (^{1}H) [Neighbours]
I is Spin number of the active nucleus ($^{1}H = ½$)

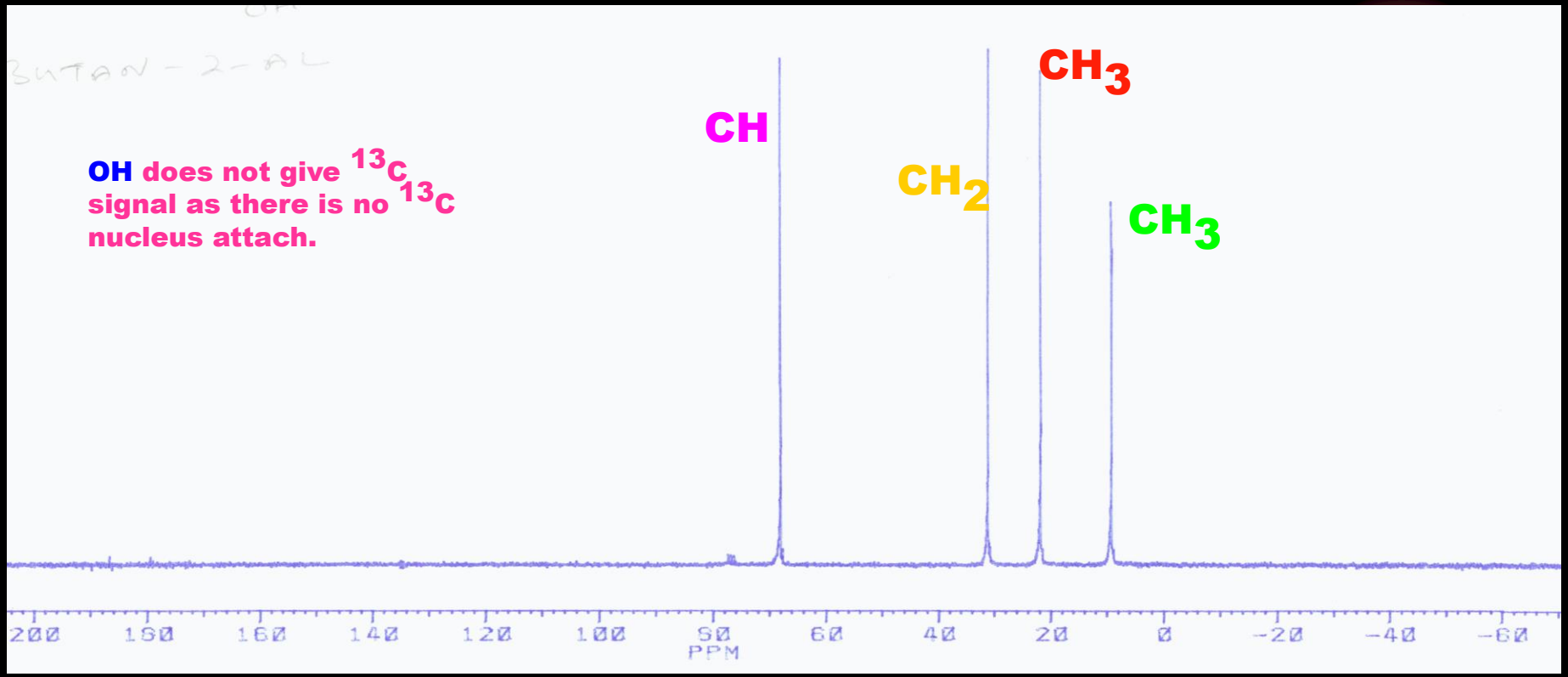


Methyl ^{13}C	Methylene ^{13}C	Methine ^{13}C	Quaternary ^{13}C
Quartet	Triplet	Doublet	Singlet

^{13}C NMR spectrum. Most of the ^{13}C NMR spectra are recorded as ^{1}H decoupled hence $CH/CH_2/CH_3$ give sharp singlet.

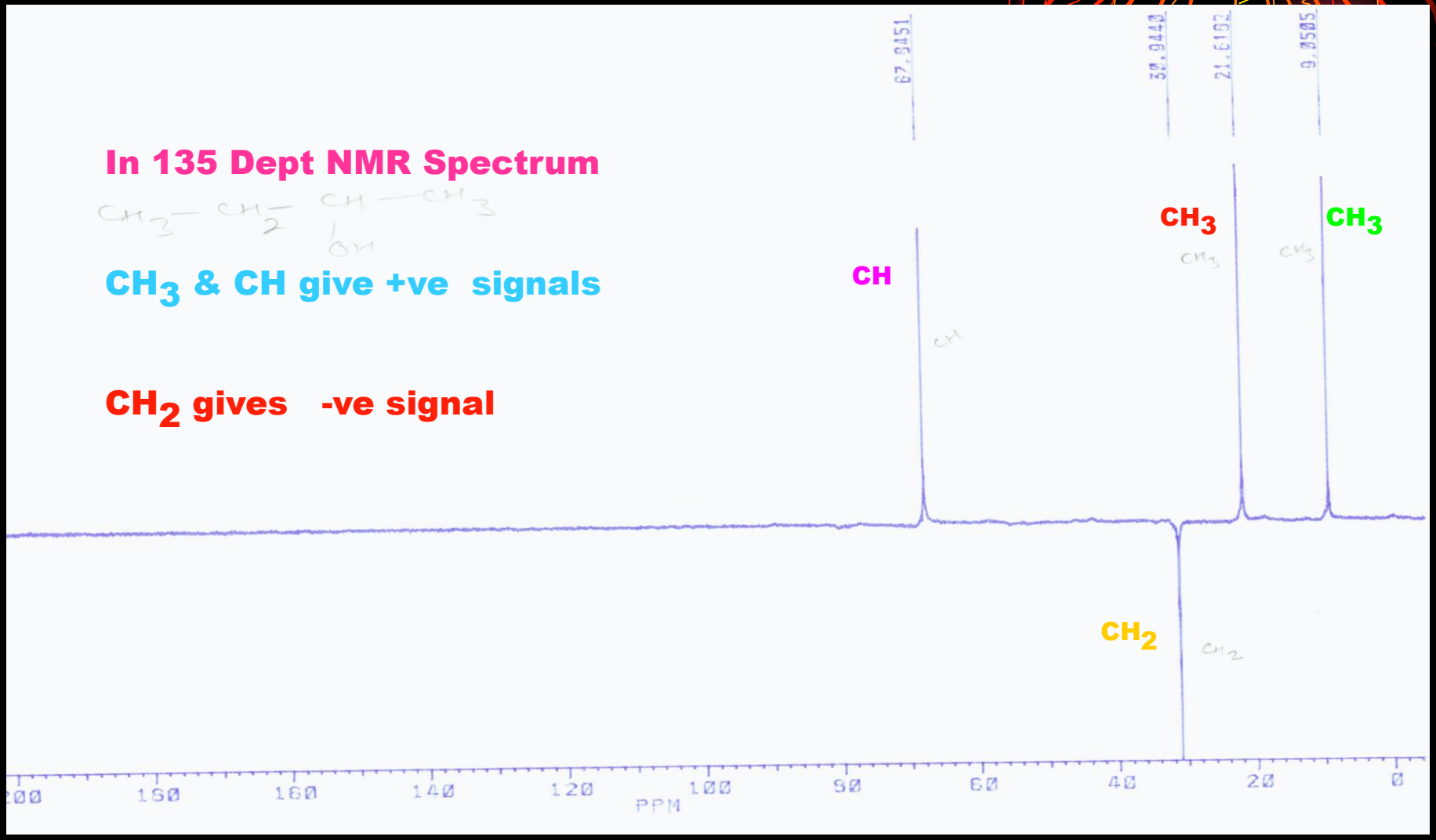
^{13}C NMR spectrum of Butan-2-al

CH_3--CHOH—CH_2—CH_3



^{13}C Dept 135 NMR spectrum of Butan-2-al

$CH_3—CHOH—CH_2—CH_3$



Analysis of ^{1}H and ^{13}C NMR Spectra Butan-2-al

CH_3-CH_2-CHOH-CH_3

CH_3	CH_3	CH_2	OH	CH	^{1}H NMR
0.91 PPM Triplet J= 7.45 Hz	1.16 Doublet J= 6.16 Hz	1.45 D of Q Complex	1.71 Singlet	3.70 T of Q Complex	D= Doublet T= Triplet Q= Quartet
CH_3	CH_3	CH_2	OH	CH	^{13}C NMR
9.03 PPM	21.63	30.96	No Signal	67.88	

Analysis and interpretation of ^{1}H NMR Spectrum

of n-Butanal CH_3-CH_2-CH_2-CH_2OH

4 3 2 1

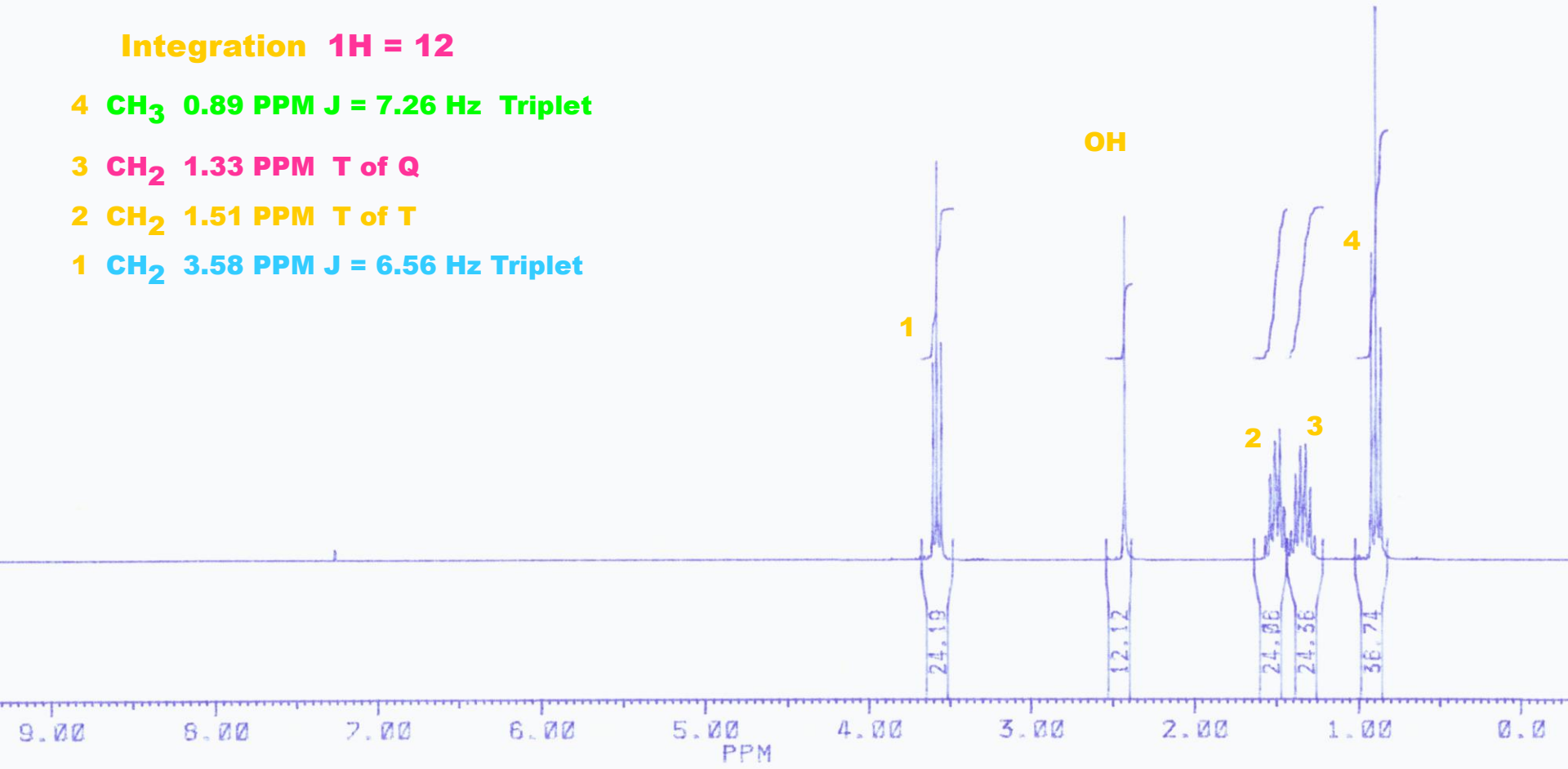
Integration 1H = 12

4 CH_3 0.89 PPM J = 7.26 Hz Triplet

3 CH_2 1.33 PPM T of Q

2 CH_2 1.51 PPM T of T

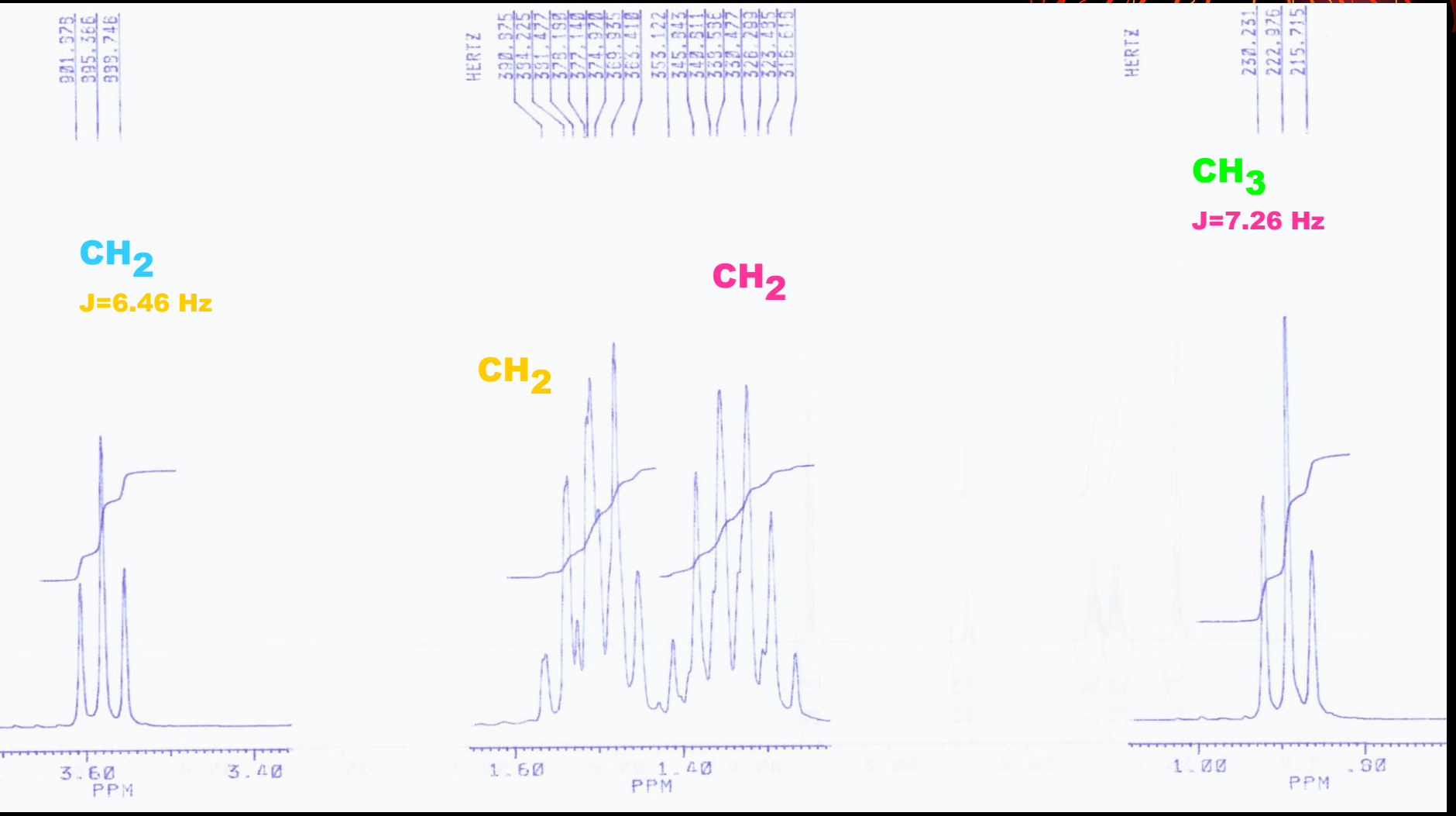
1 CH_2 3.58 PPM J = 6.56 Hz Triplet



Analysis and interpretation of ^{1}H NMR Spectrum

of n-Butanal CH_3-CH_2-CH_2-CH_2OH

4 3 2 1



^{13}C NMR Spectrum of n-Butanal

CH_3-CH_2-CH_2-CH_2OH

4 3 2 1

Chemical Shifts

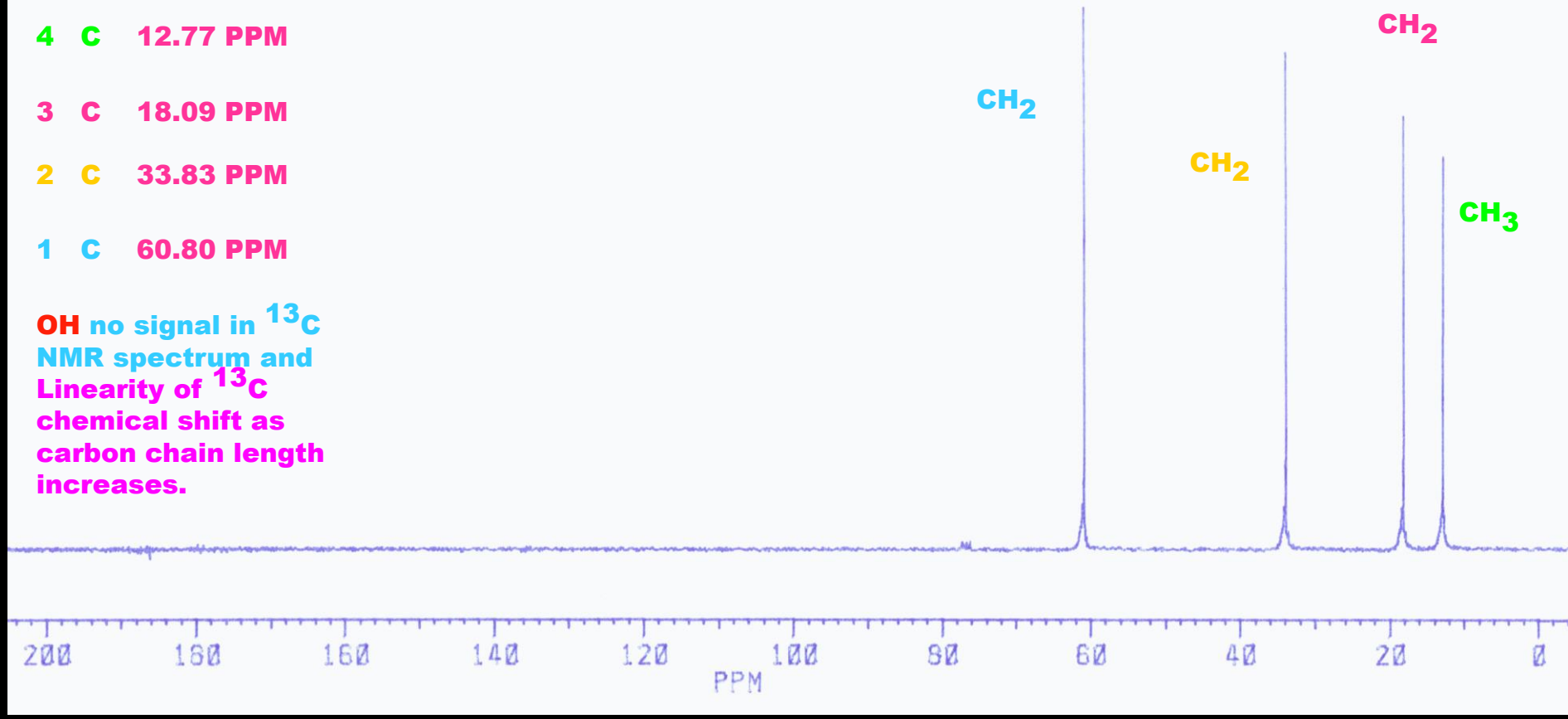
4 C 12.77 PPM

3 C 18.09 PPM

2 C 33.83 PPM

1 C 60.80 PPM

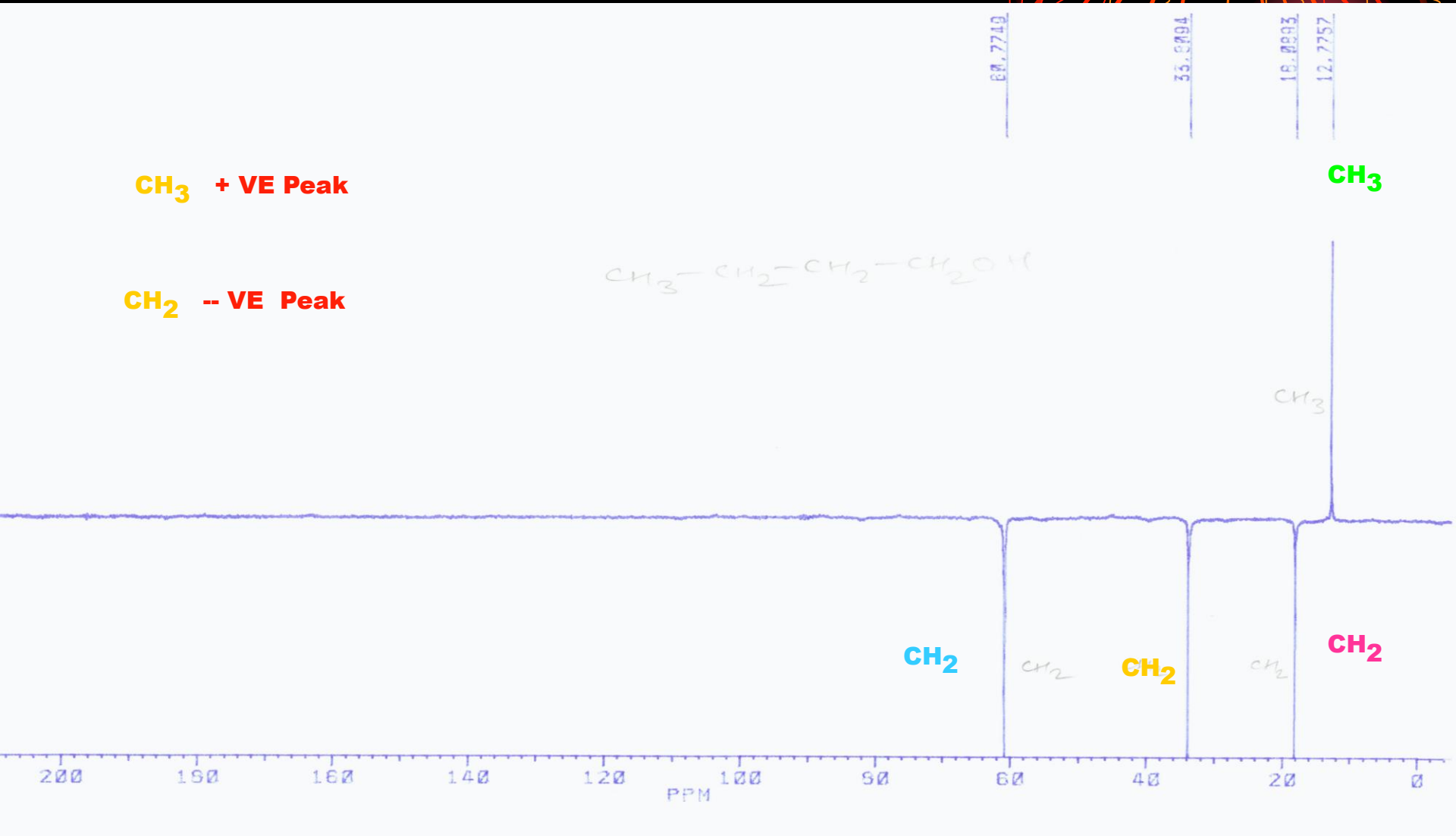
OH no signal in ^{13}C NMR spectrum and Linearity of ^{13}C chemical shift as carbon chain length increases.



^{13}C Dept 135 NMR Spectrum of n-Butanal

CH_3-CH_2-CH_2-CH_2OH

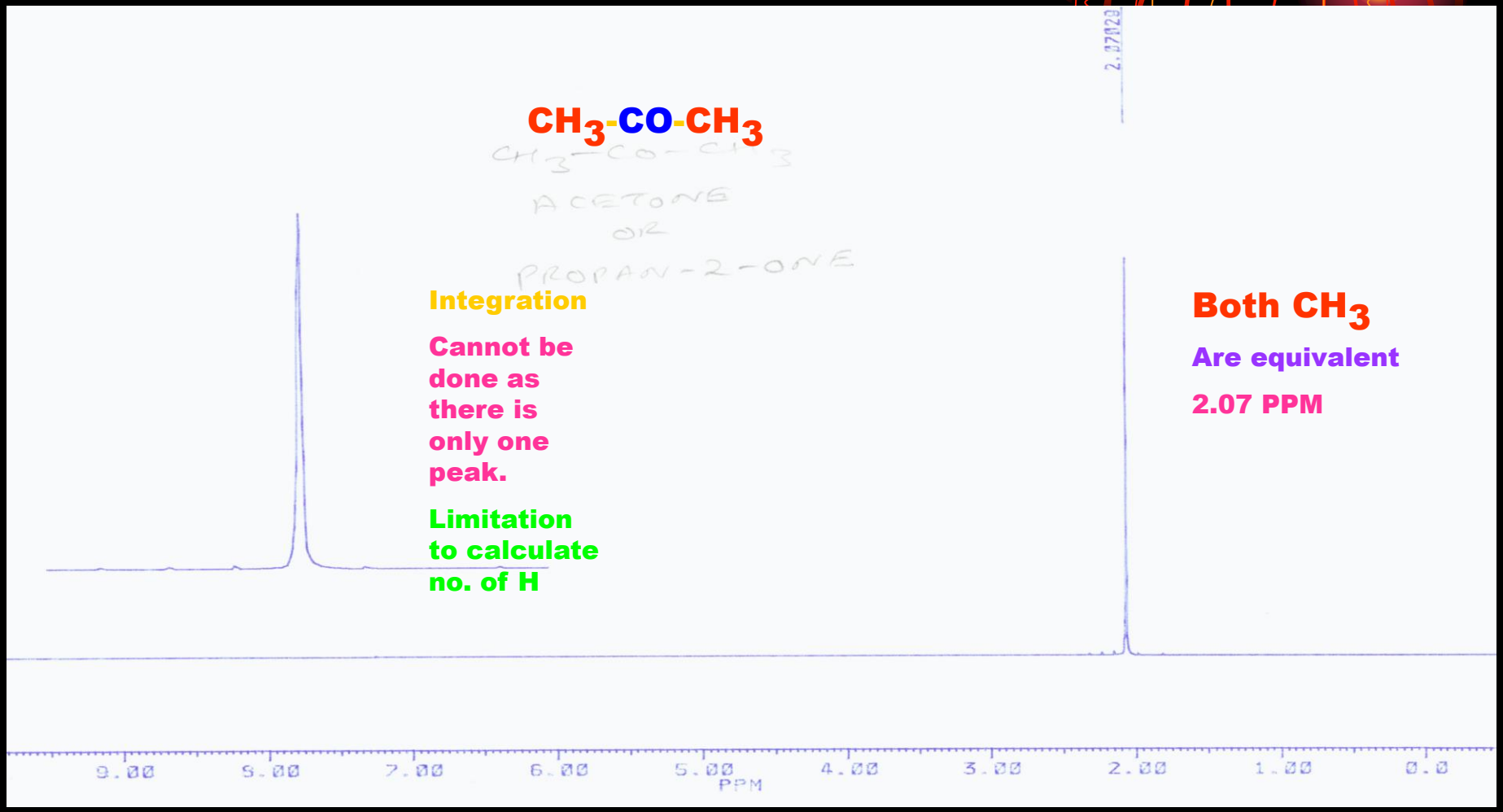
4 3 2 1



Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Propan-2-one or Acetone

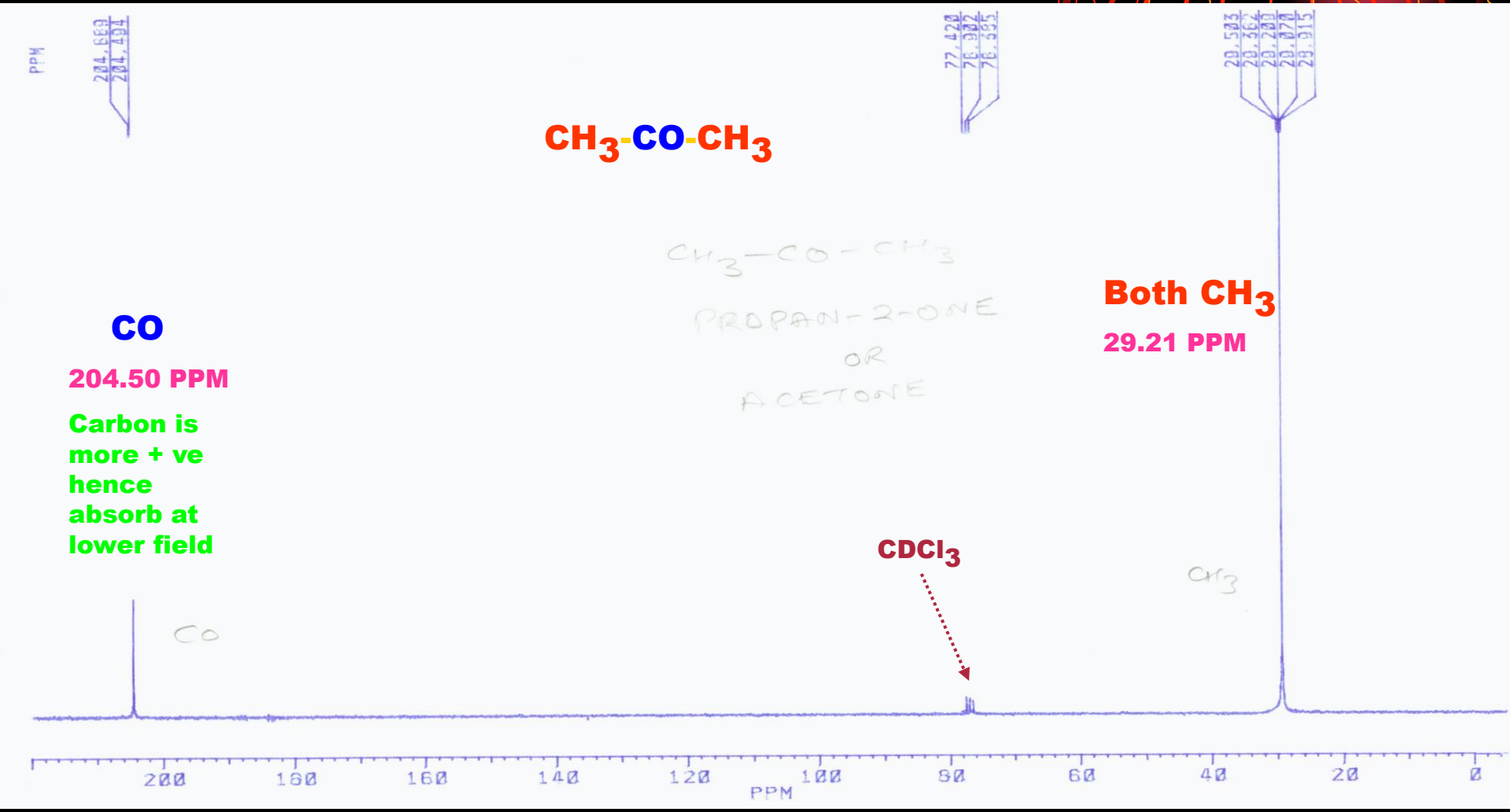
^{1}H NMR Spectrum

$CH_3—CO—CH_3$



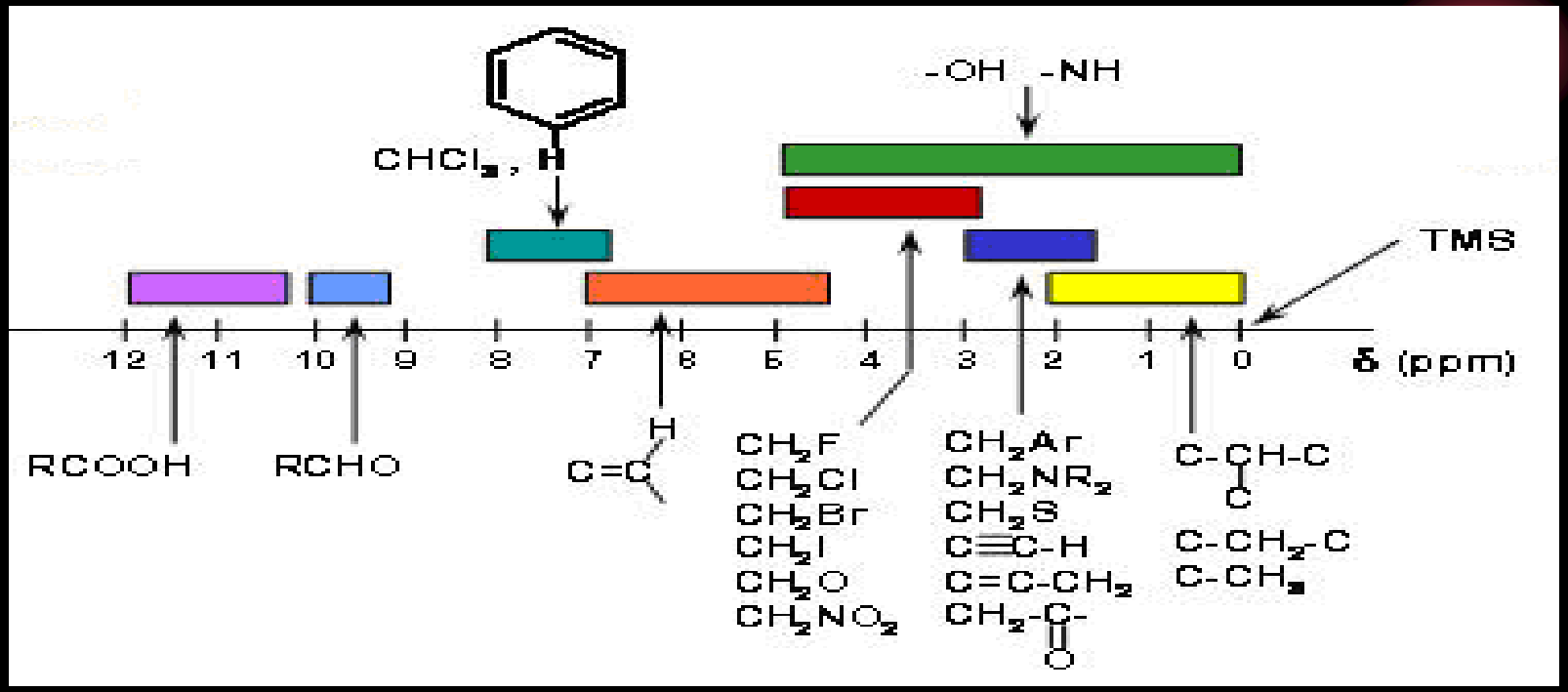
^{13}C NMR Spectrum of Propan-2one (Acetone)

$CH_3—CO—CH_3$



^{1}H Chemical Shift in PPM

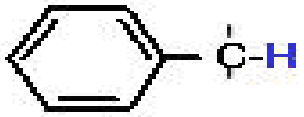
- **General Correlation Chart ^{1}H NMR Spectra**



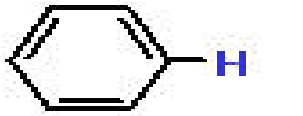
Lower Field ⟷ Higher Field

^{1}H Chemical Shift in more details

- **^{1}H Chemical Shift Range Table**

R-CH_3	0.7 - 1.3
R-CH_2-R	1.2 - 1.4
R_3CH	1.4 - 1.7
R-C=C-C-H	1.6 - 2.6
R-C(=O)-C-H	2.1 - 2.4
RO-C(=O)-C-H	2.1 - 2.5
HO-C(=O)-C-H	2.1 - 2.5
N≡C-C-H	2.1 - 3.0
R-C≡C-C-H	2.1 - 3.0
	2.3 - 2.7
R-C≡C-H	1.7 - 2.7

R-N-C-H	2.2 - 2.9
R-S-C-H	2.0 - 3.0
I-C-H	2.0 - 4.0
Br-C-H	2.7 - 4.1
Cl-C-H	3.1 - 4.1
RO-C-H	3.2 - 3.8
HO-C-H	3.2 - 3.8
R-C(=O)-O-C-H	3.5 - 4.8
O_2N-C-H	4.1 - 4.3
F-C-H	4.2 - 4.8

R-C=C-H	4.5 - 6.5
	6.5 - 8.0
R-C(=O)-N-H	5.0 - 9.0
R-C(=O)-H	9.0 - 10.0
R-C(=O)-O-H	11.0 - 12.0

R-N-H	0.5 - 4.0	Ar-N-H	3.0 - 5.0	R-S-H	1.0 - 4.0
R-O-H	0.5 - 5.0	Ar-O-H	4.0 - 7.0		

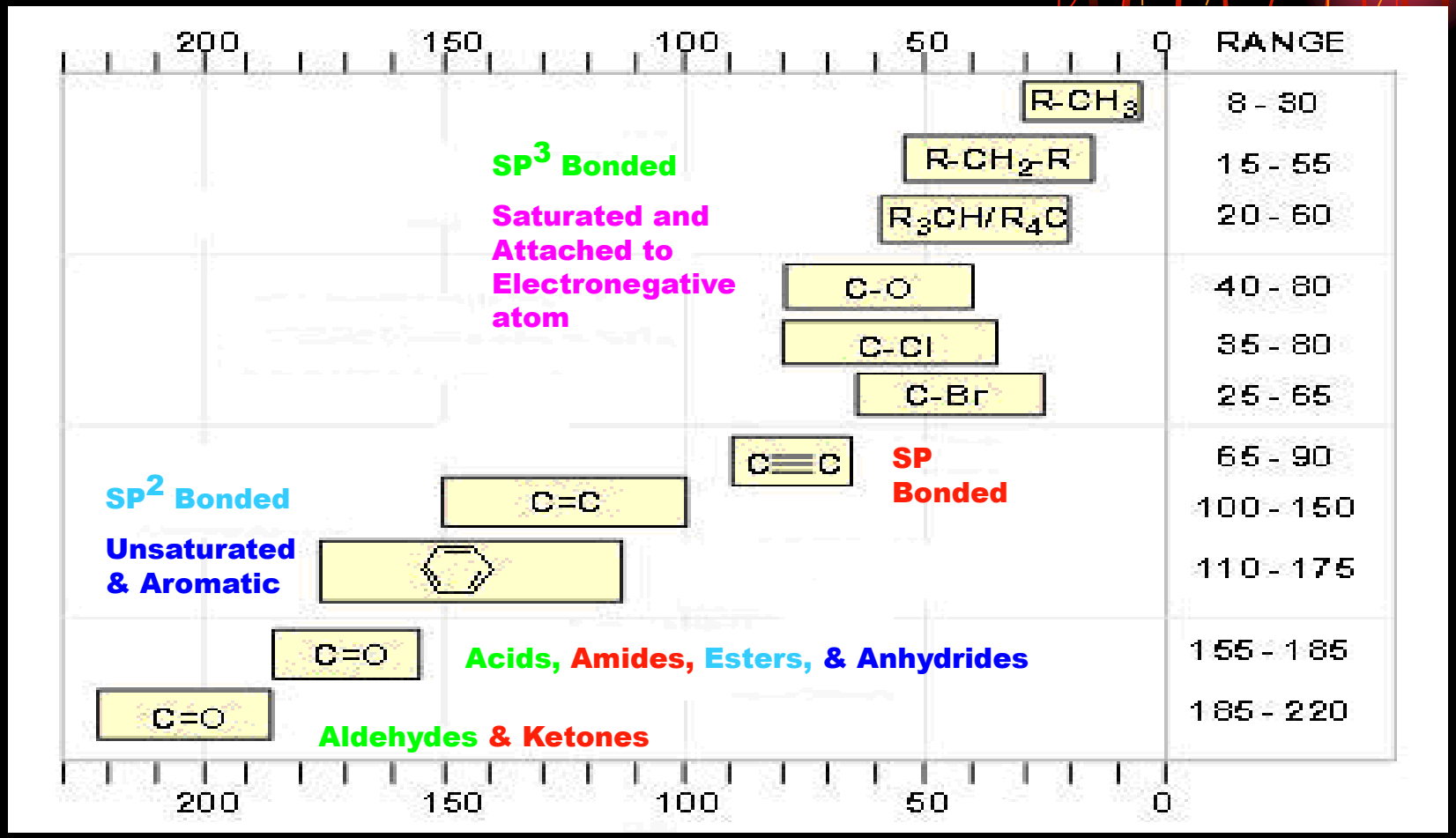
^{13}C Chemical Shift in PPM

In FT NMR Spectroscopy, the intensities of the signal get distorted hence peak heights and areas under the peak can be deceptive.

• RCH_3	0.0	to	35	PPM
• $R2CH_2$	15	to	40	PPM
• R3CH	25	to	50	PPM
• R4C	30	to	40	PPM
• RC = CR	65	to	90	PPM
• R2C ≡ CR2	100	to	150	PPM
• C_6H_6 (Aromatic)	110	to	175	PPM
• R-CO-OR	160	to	185	PPM
• R-CO-R	190	to	220	PPM
• RCH_2Br	20	to	40	PPM
• RCH_2Cl	25	to	50	PPM
• RCH_2NH_2	35	to	50	PPM
• RCH_2OH	50	to	65	PPM
• RCH_2OR	50	to	65	PPM

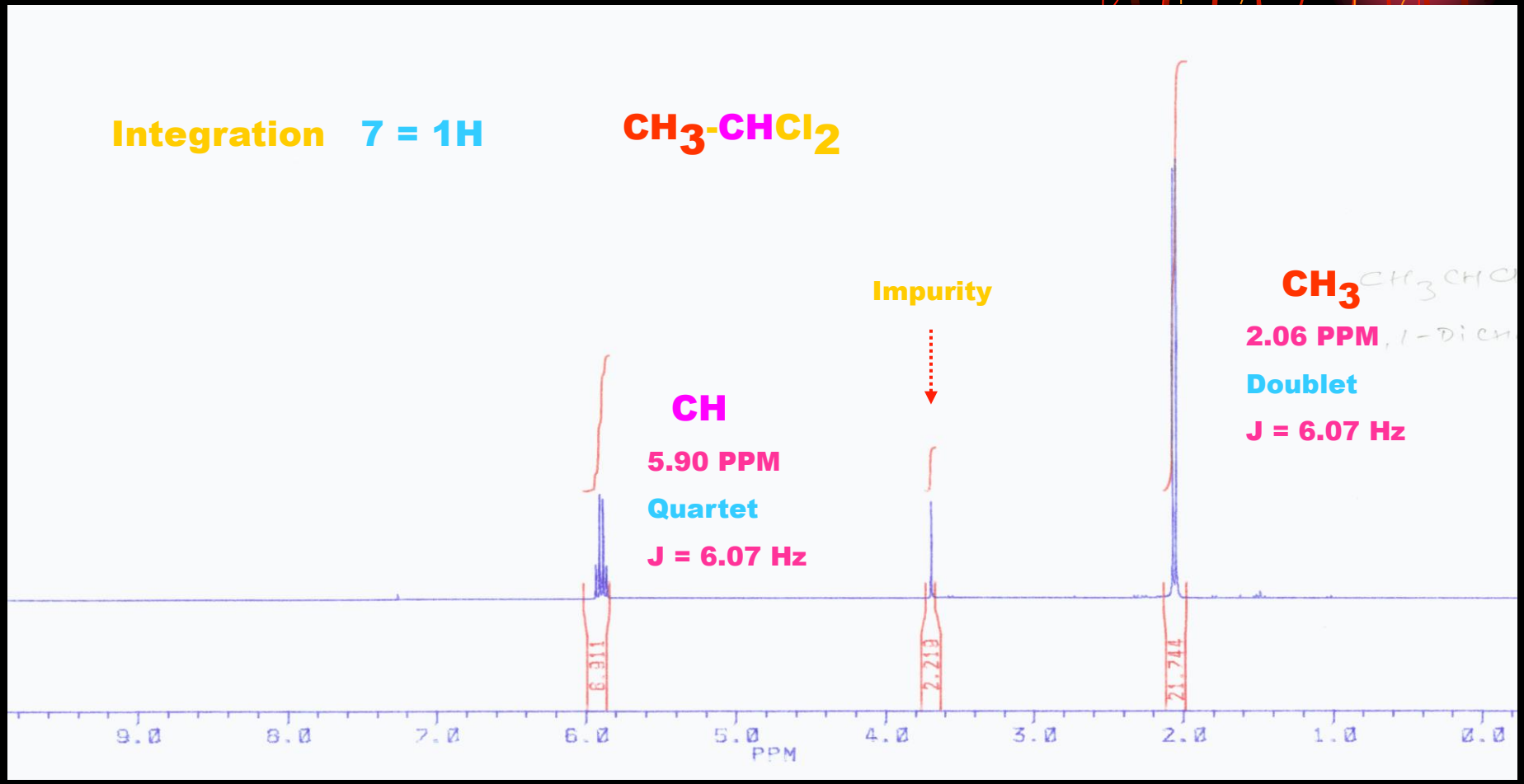
^{13}C Chemical Shift in PPM

- **^{13}C Chemical Shift Range Table**

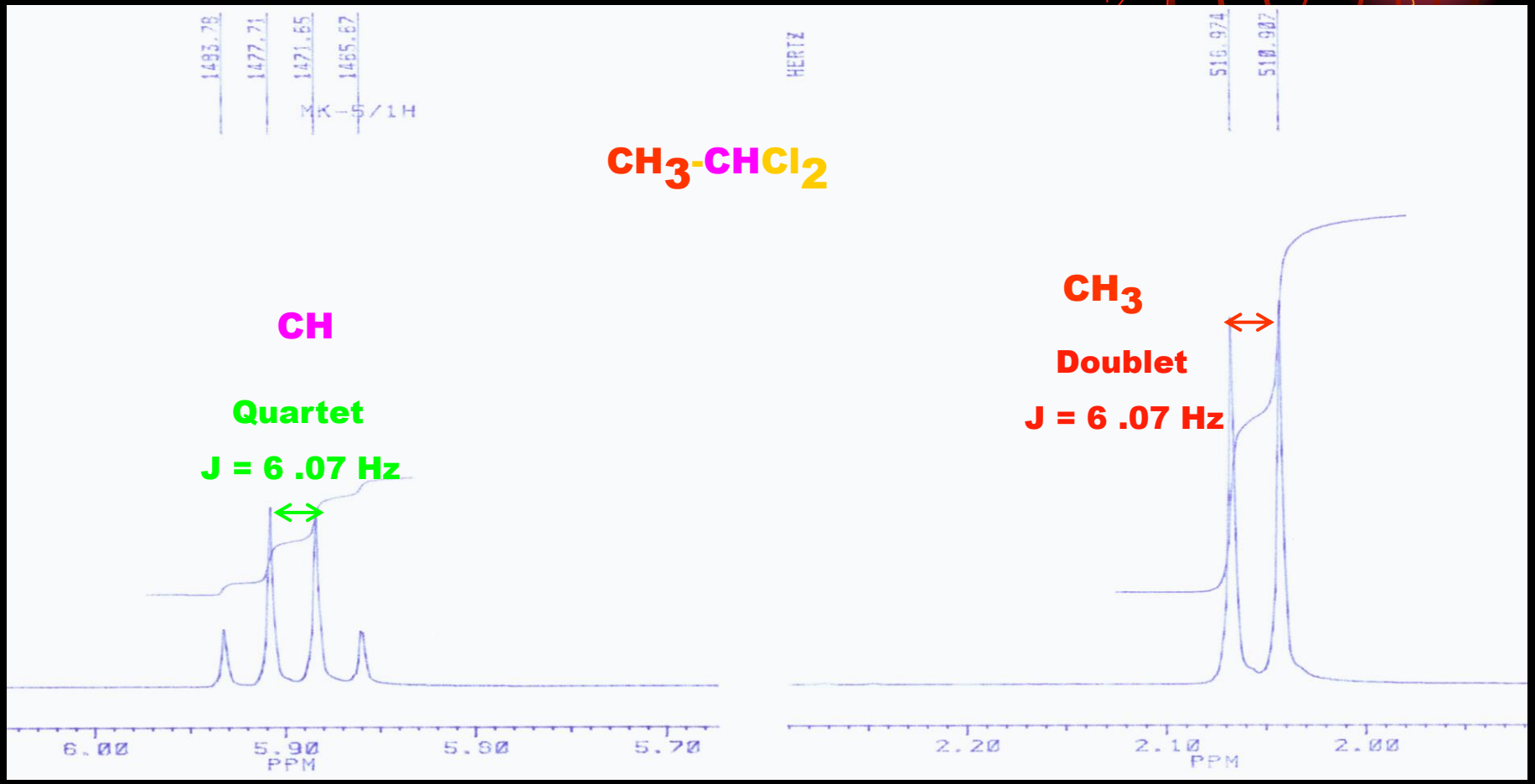


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra

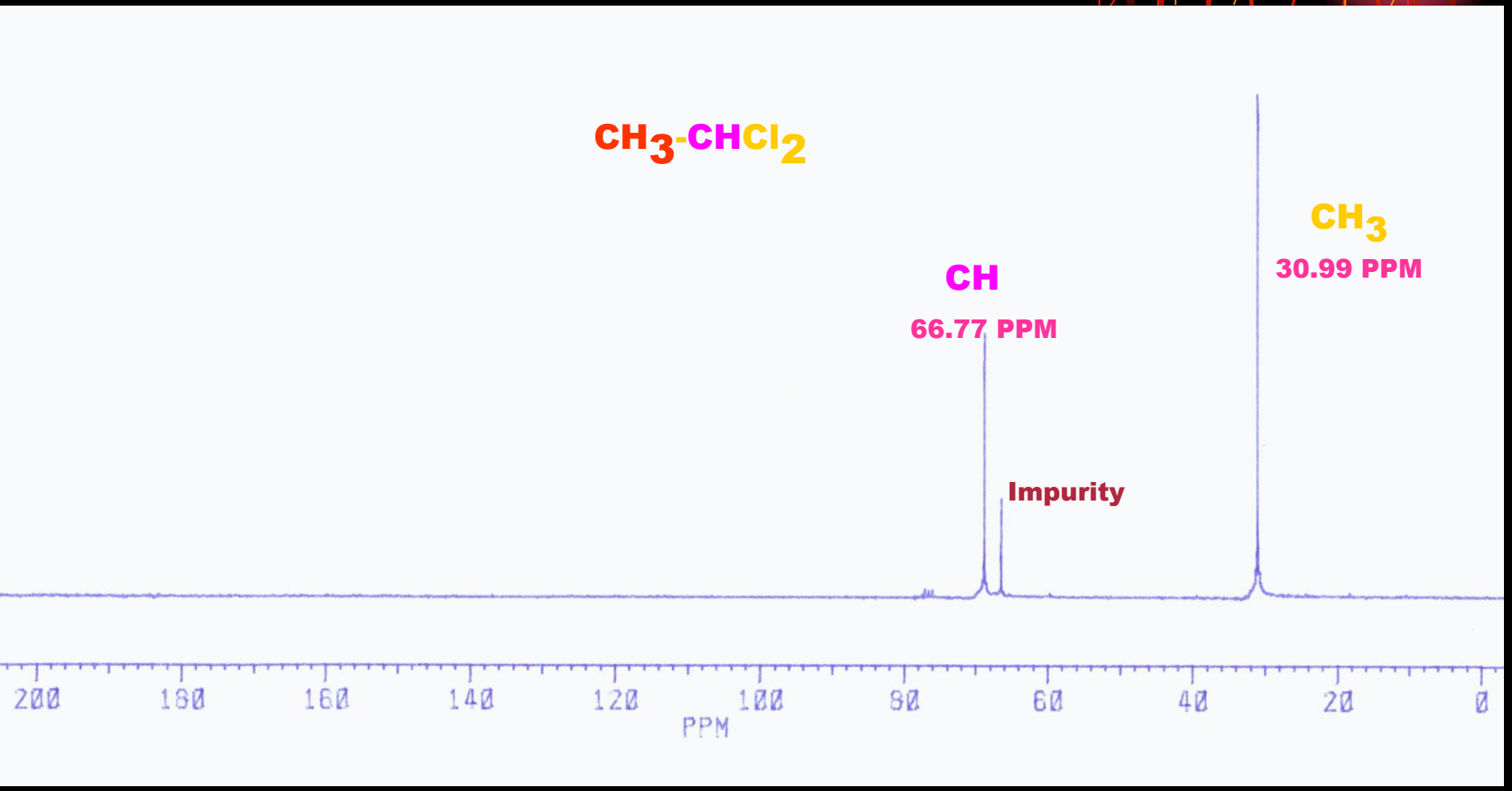
Of 1,1-Dichloroethane $\underset{2}{CH_3}—\underset{1}{CHCl_2}$



Expansion of 1H NMR of 1,1-Dichloroethane $CH_3—CHCl_2$



^{13}C NMR OF 1,1-Dichloroethane
$CH_3—CHCl_2$



Factors affecting Chemical Shifts Shielding and Deshielding effects

1. The electro negativity of the atoms within the molecule.
2. The hybridization of the adjacent atoms.
3. The diamagnetic effects from adjacent Pi bonds.

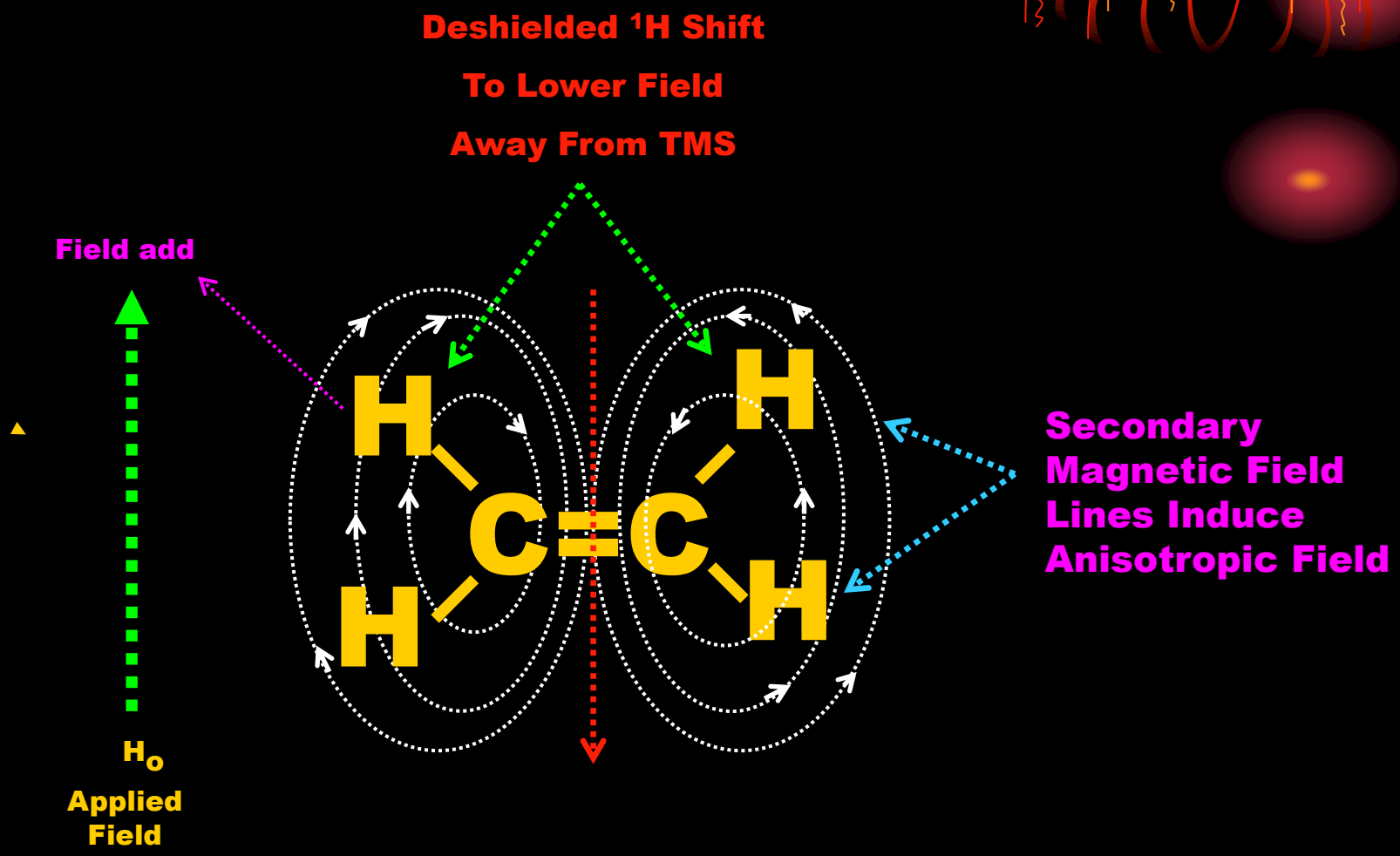
CH_3—X	Electro negativity of X	PPM
CH_3—F	4 .00	4 .26
CH_3—OH	3 .50	3 .57
CH_3—Cl	3 .10	3 .05
CH_3—Br	2 .80	2 .68
CH_3—I	2 .50	2 .16
$(CH_3)_4$—C	2 .10	0 .86
$(CH_3)_4$—Si	1 .80	0 .00

Type of ^1H R = Alkyl	Hybridization	PPM
$R\text{-}CH_3$, $R_2\text{-}CH_2$	Alkyl	0 .80 To 1 .70
$R_3\text{-}CH$		
$R_2C{=}C(R)CHR_2$	Allylic	1 .60 To 2 .60
$RC{\equiv}CH$	Acetylenic	2 .00 To 3 .00
$R_2C{=}CHR$	Vinynlic	4 .60 To 5 .70
$R_2C{=}CH_2$		
RCHO	Aldehydic	9 .50 To 10 .10

Type of ^1H	Name	PPM	Bonding (Diamagnetic effects)
RCH_3	Alkyl	0 .8 To 1 .0	SP^3
$RC{\equiv}CH$	Acetylenic	2 .0 To 3 .0	SP
$R_2C{=}CH_2$	Vinylic	4 .6 To 5 .7	SP^2

Anisotropic Field in an Alkenes (SP^2)

- **Anisotropic Field Effect**



Factors affecting Chemical Shifts
Shielding and Deshielding effects

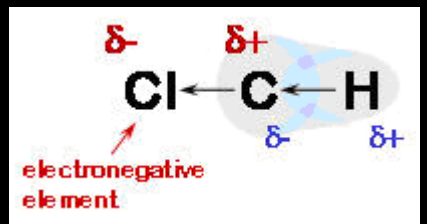
- **1. The electro negativity of the atoms within the molecule.**
- **2. The hybridization of the adjacent atoms.**
- **3. The diamagnetic effects from adjacent Pi bonds.**

CH_3-X	Electroneg-ativity of X	Chemical Shift (δ)
CH_3F	4.0	4.26
CH_3OH	3.5	3.47
CH_3Cl	3.1	3.05
CH_3Br	2.8	2.68
CH_3I	2.5	2.16
$(CH_3)_4C$	2.1	0.86
$(CH_3)_4Si$	1.8	0.00

Type of Hydrogen (R = alkyl)	Name of Hydrogen	Chemical Shift (δ)
RCH_3, R_2CH_2, R_3CH	Alkyl	0.8 - 1.7
$R_2C=C(R)CHR_2$	Allylic	1.6 - 2.6
$RC\equiv CH$	Acetylenic	2.0 - 3.0
$R_2C=CHR$, $R_2C=CH_2$	Vinylic	4.6 - 5.7
RCHO	Aldehydic	9.5-10.1

Type of H	Name	Chemical Shift (δ)	Hybridization
RCH_3	Alkyl	0.8- 1.0	SP^3
$RC\equiv CH$	Acetylenic	2.0 - 3.0	SP
$R_2C=CH_2$	Vinylic	4.6 - 5.7	SP^2

The most Deshielded atoms absorb at Lower Field (@ Higher PPM)



Chlorine takes the valence electro density away from Carbon which in turn takes more density from adjacent Hydrogen atoms causes Deshielding.

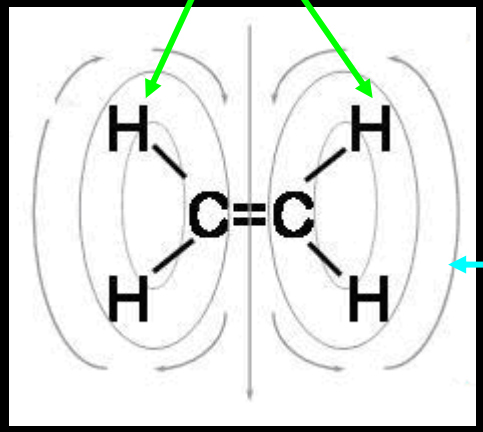
Anisotropic Field in an Alkenes (SP^2)

Anisotropic Field Effect

Deshielded ^1H

Shift To Lower Field

Fields Add



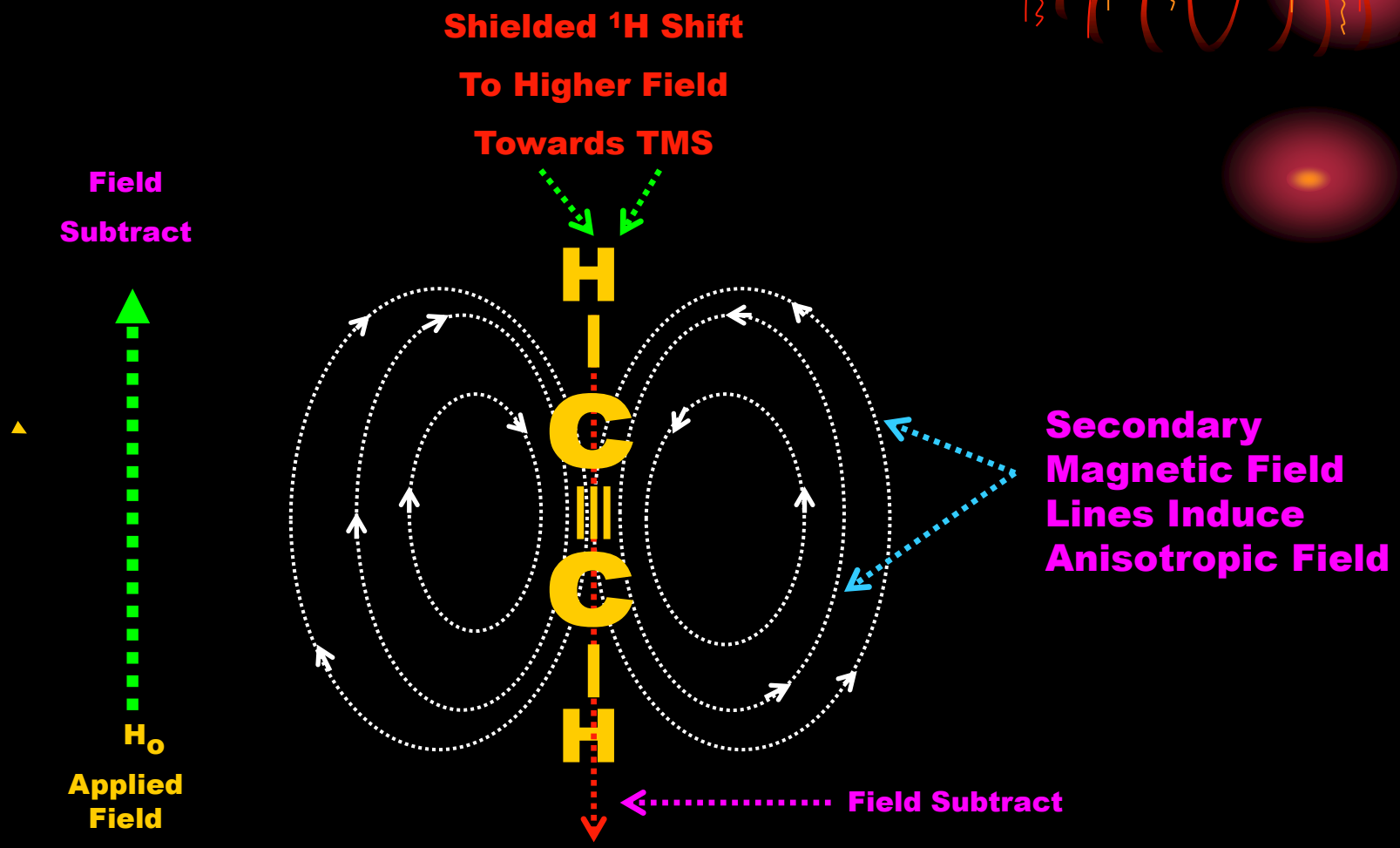
Secondary Magnetic Field Lines Induce Anisotropic Field

H_0

Applied Field

Anisotropic Field in an Alkynes (SP)

- **Anisotropic Field Effect**

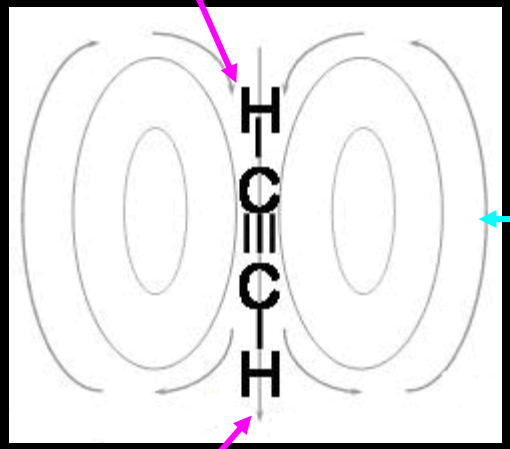


Anisotropic Field in an Alkynes (SP)

- **Anisotropic Field Effect**

Shielded ^{1}H Shift

To Higher Field



Secondary Magnetic Field Lines Induce

Anisotropic Field

H_0

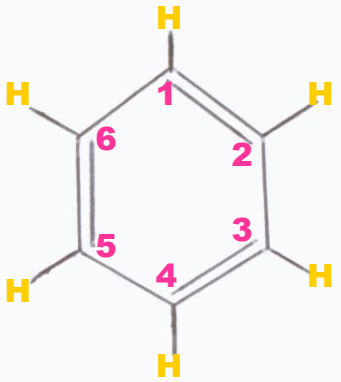
Applied Field

Fields Subtract

Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Benzene C_6H_6 ^{1}H NMR Spectrum

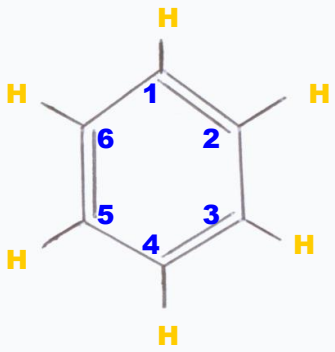
CH1 TO CH6

7 .51 PPM



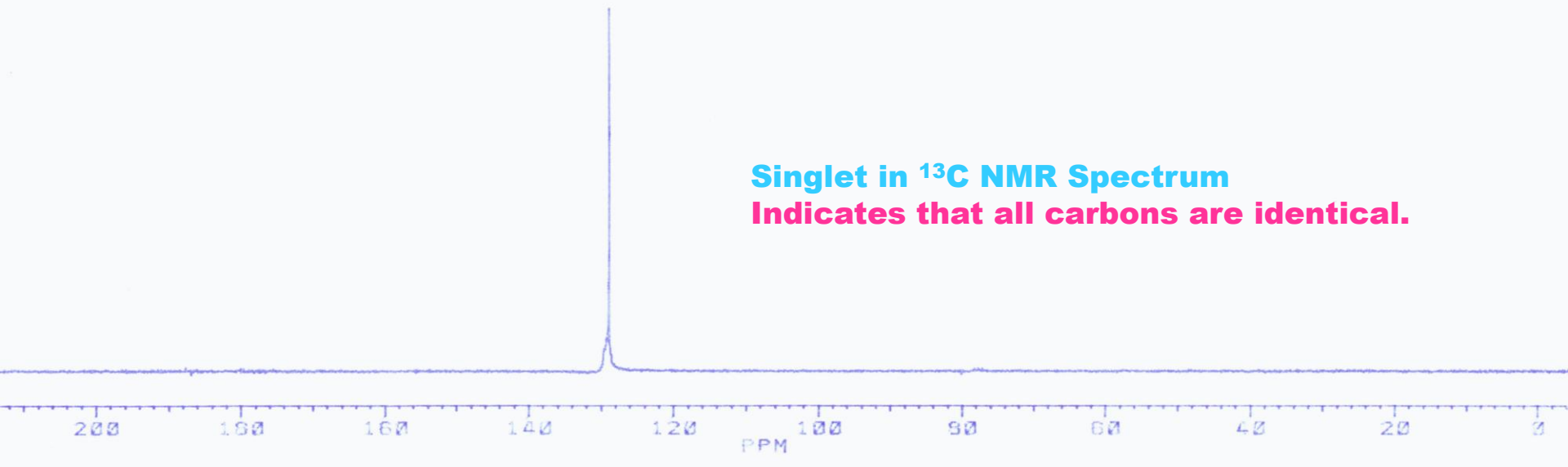
Singlet in ^{1}H NMR Spectrum indicates that all CH are Identical.

^{13}C NMR Spectrum of Benzene C_6H_6



BENZENE

C1 to C6 128 .81 PPM



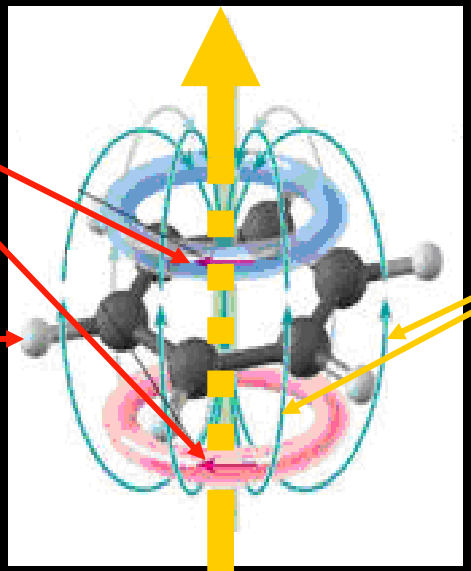
Singlet in ^{13}C NMR Spectrum
Indicates that all carbons are identical.

Magnetic Induction of the pi electrons in Aromatic Ring

- **Effect on Chemical Shift**

Induced circulation of pi electrons in the aromatic ring

^1H of Aromatic ring are Deshielded hence absorb at Lower Field.



Circulating pi electrons generate secondary field lines which reinforces the applied field

(Adding Effect)

H_0

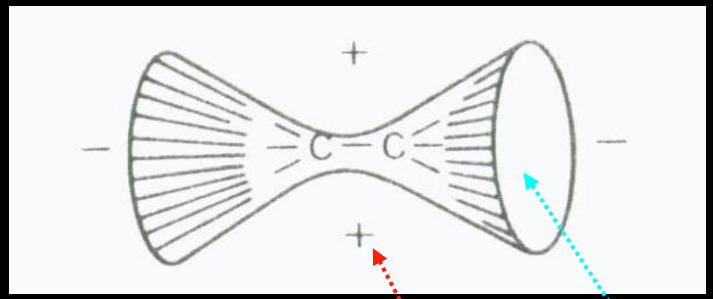
Applied Field

Anisotropic field effect of Various Bonds

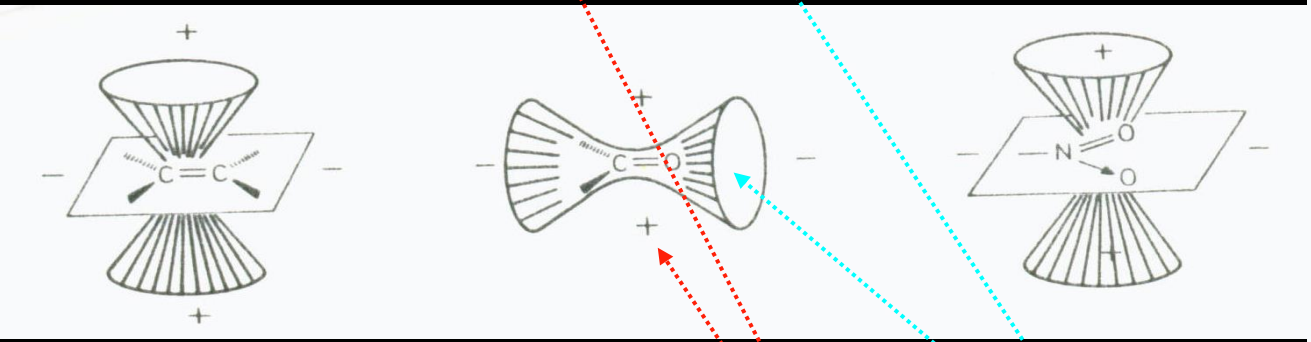
Shielded ^1H Shift to Higher Field (Towards TMS)

Deshieled ^1H Shift to Lower Field (Away from TMS)

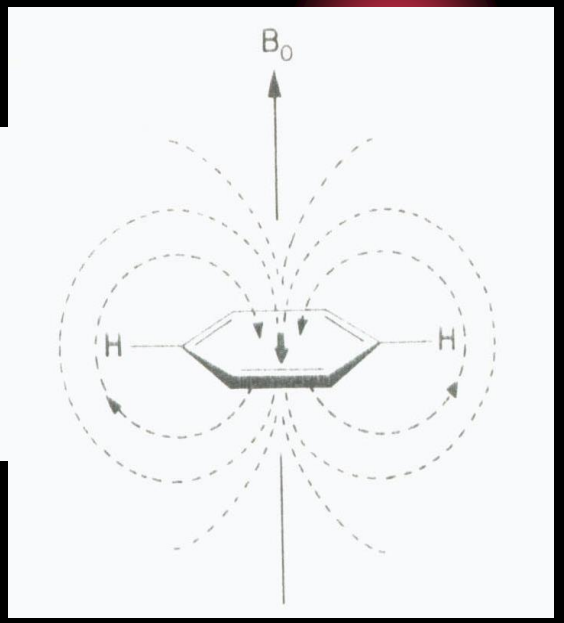
Single Bond



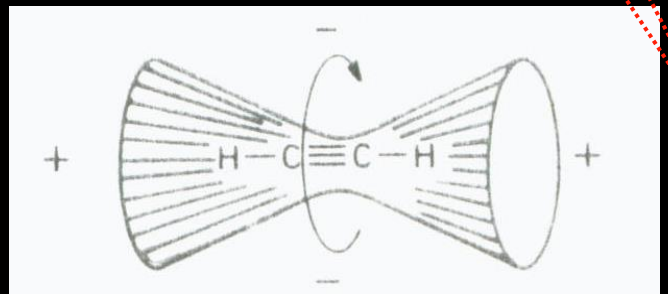
Double Bond



Aromatic Double Bond



Triple Bond



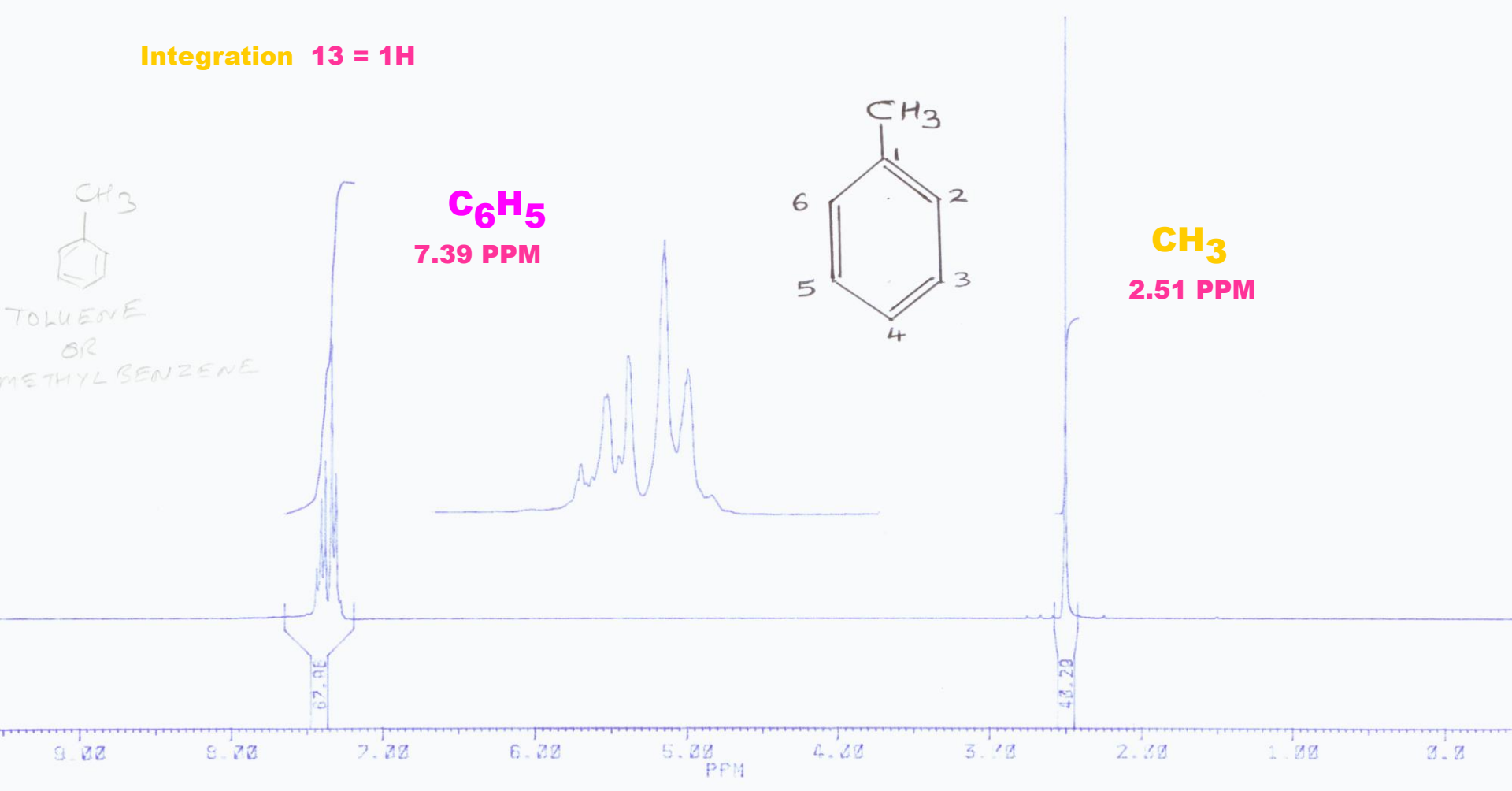
Inside the cone = Deshielded

Out side the cone = Shielded

For triple bond this is reverse

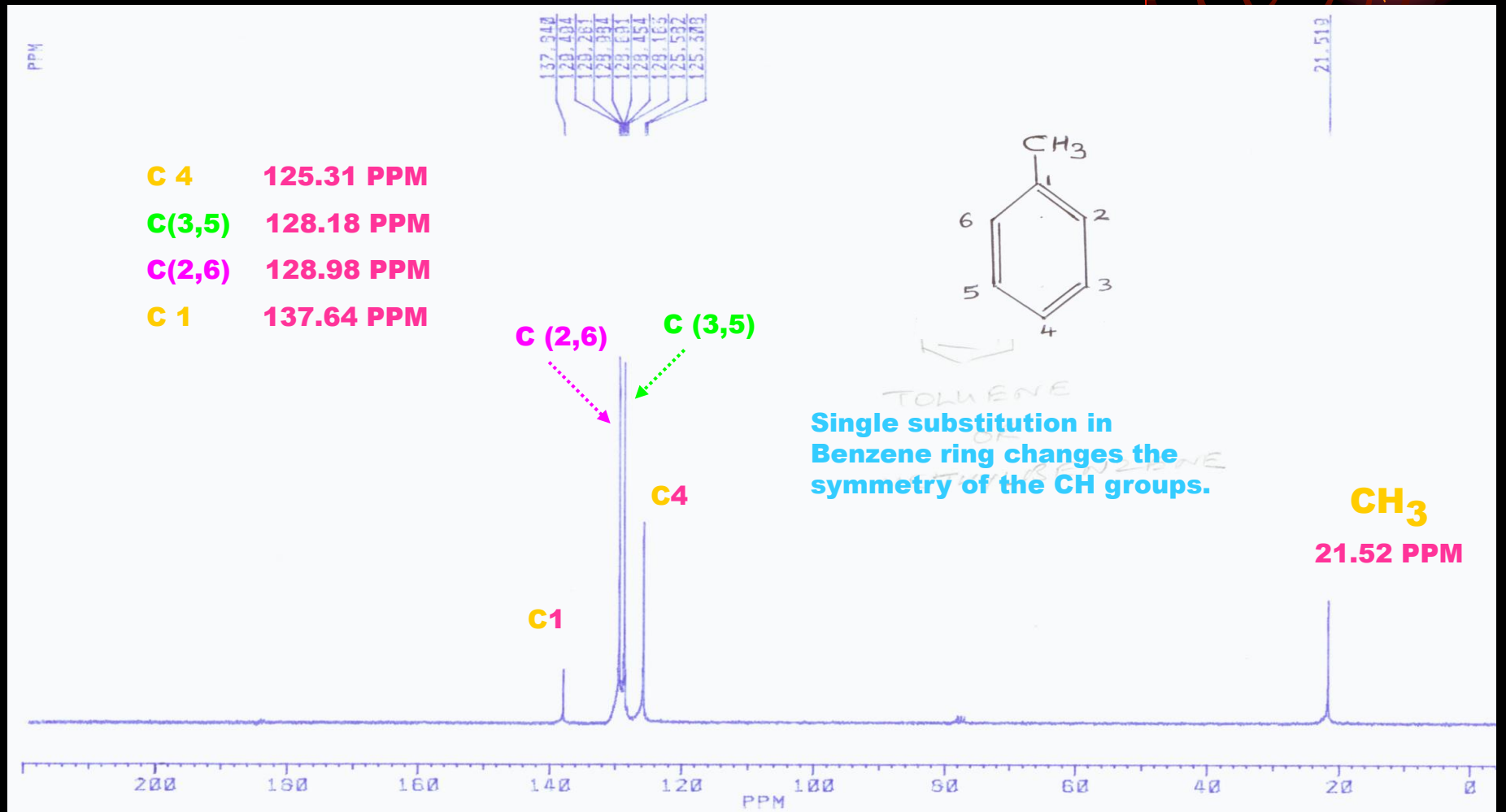
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Methyl Benzene or Toluene

^{1}H NMR Spectrum $C_6H_5—CH_3$



^{13}C NMR Spectrum of Methyl Benzene (Toluene)

$C_6H_5—CH_3$



Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Cumene (Isopropyl Benzene)

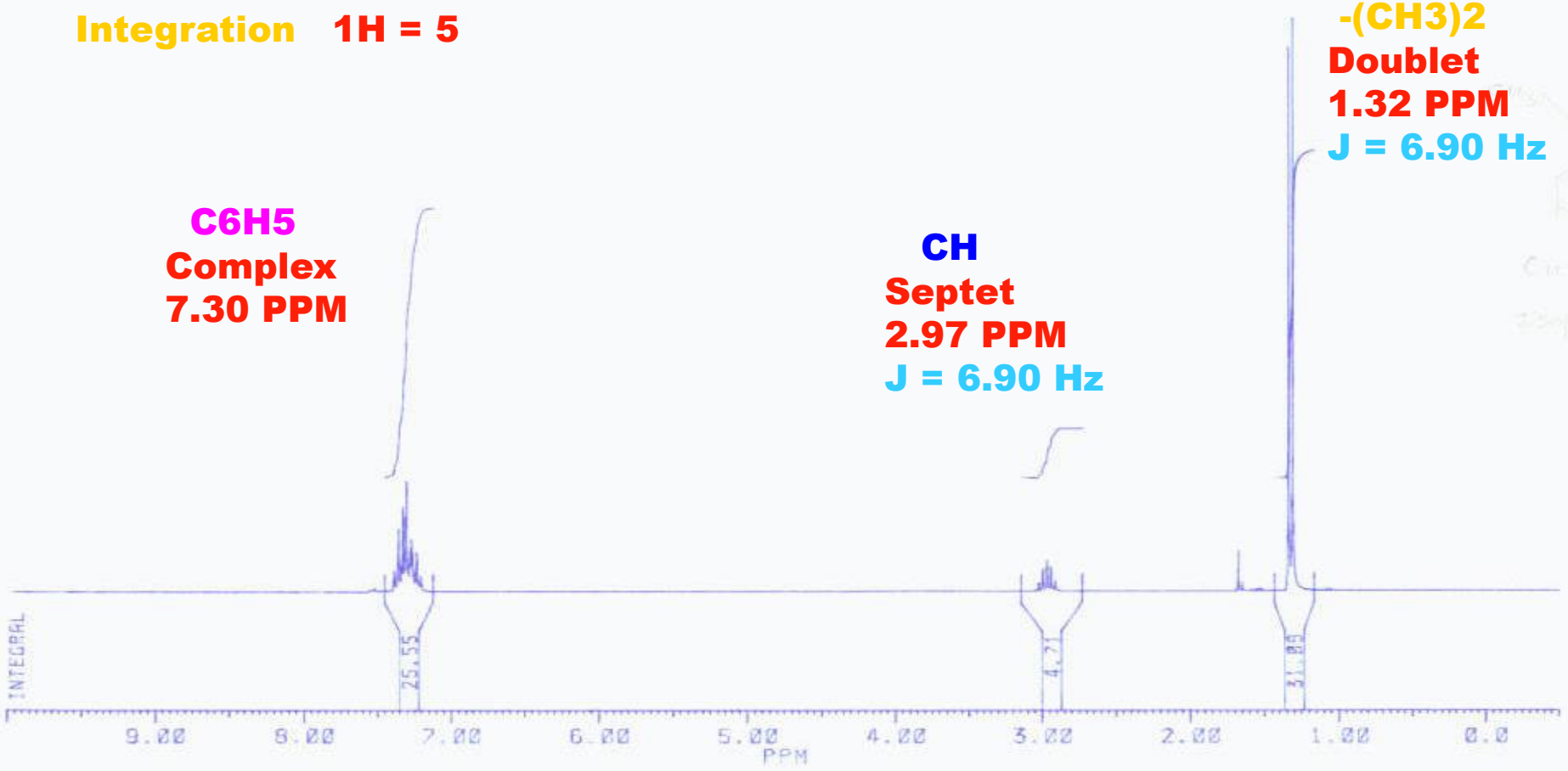
^{1}H NMR $C_6H_5—CH(CH_3)_2$

Integration 1H = 5

C6H5
Complex
7.30 PPM

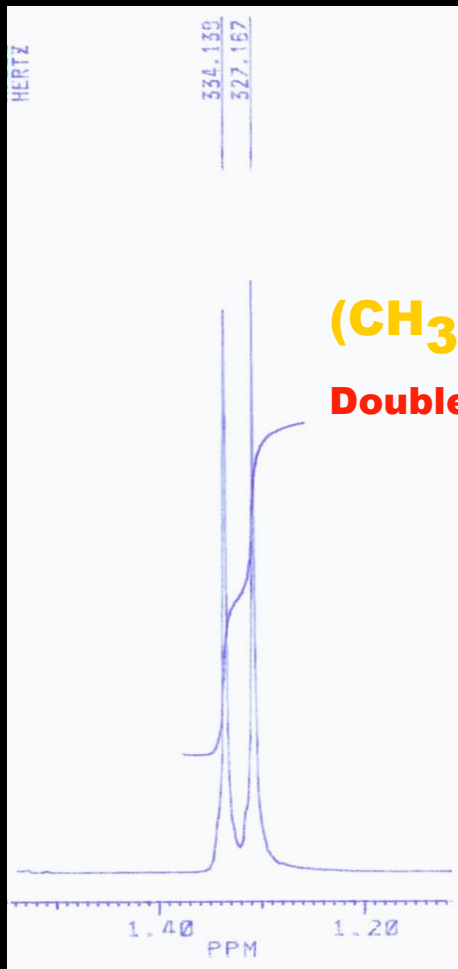
CH
Septet
2.97 PPM
J = 6.90 Hz

-(CH3)2
Doublet
1.32 PPM
J = 6.90 Hz



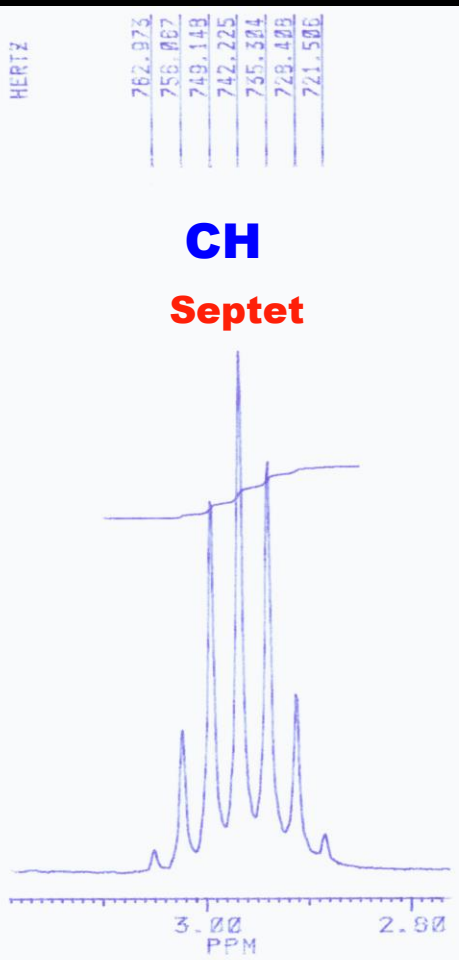
Expansion of ^{1}H NMR of Cumene (Isopropyl Benzene)

$C_6H_5—CH(\ CH_3\ )_2$



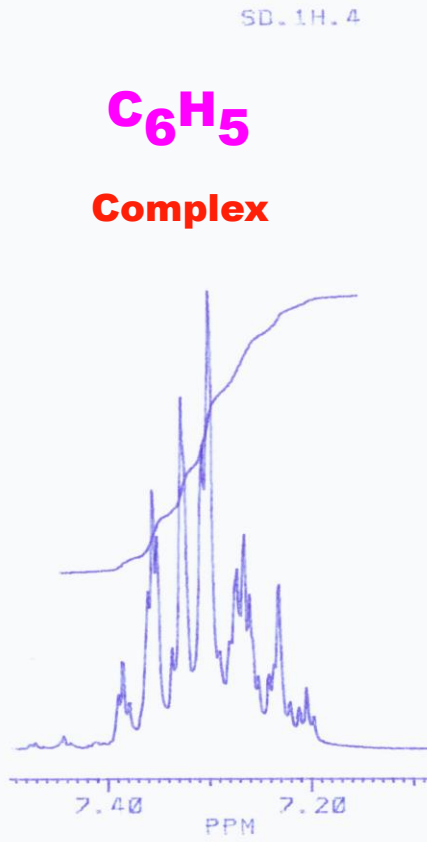
$(CH_3)_2$

Doublet



CH

Septet

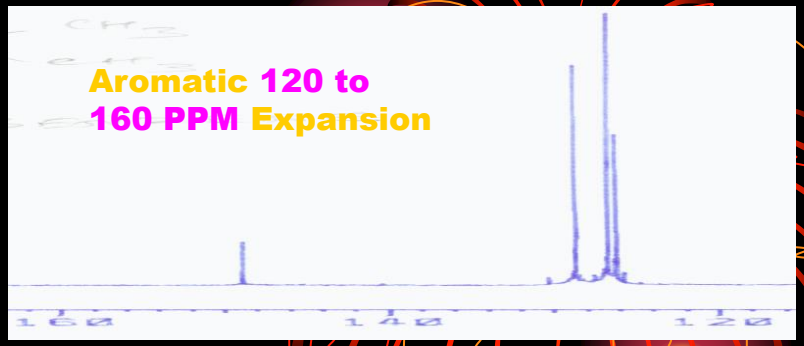


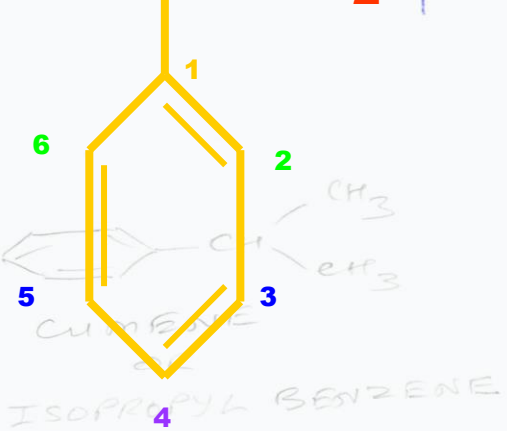
C_6H_5

Complex

^{13}C NMR Spectrum of Cumene

$C_6H_5—CH(CH_3)_2$





Aromatic Benzene

C 4 126.00 PPM

C 3 & 5 126.55 PPM

C 2 & 6 128.53 PPM

C 1 148.79 PPM

Note :- C with H Gives taller Peak (Relaxation T_1)

Height of the peak is very important for assigning the chemical shifts

C 4 has 1 H

C3 & 5 have 2 H

Height ratio 1 : 2

C 1 has no H hence smaller peak

Both CH_3

24.25 PPM

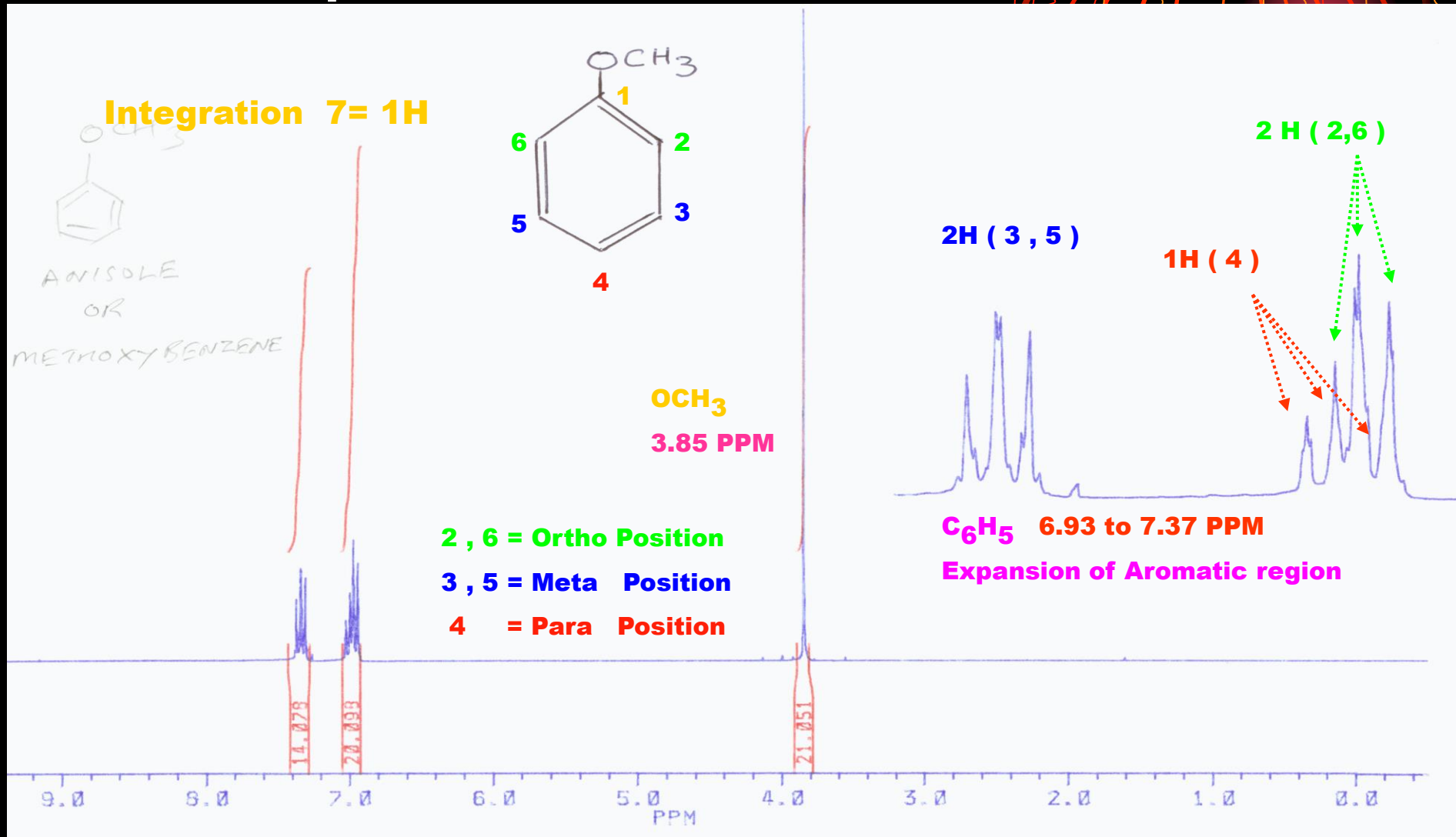
CH

34.45 PPM

C1

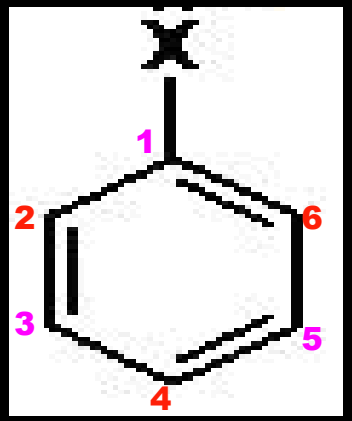
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Anisole (Methoxy Benzene) $C_6H_5—OCH_3$

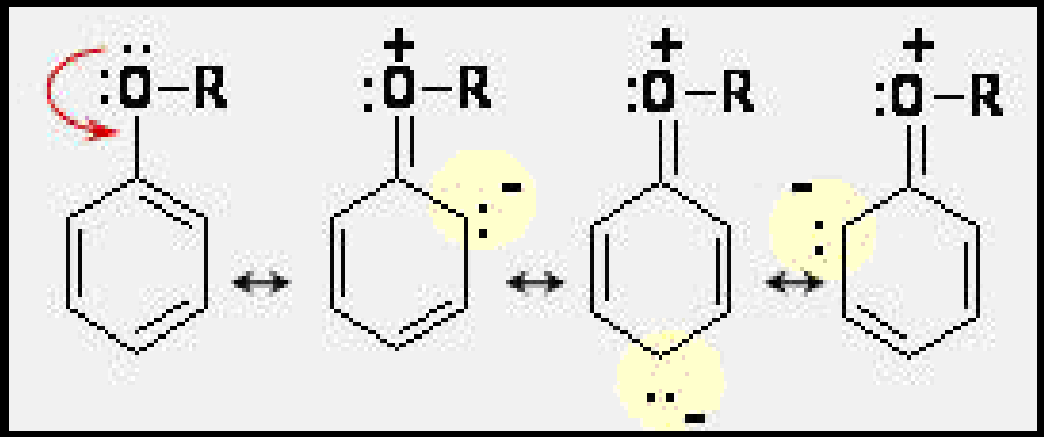
^{1}H NMR Spectrum



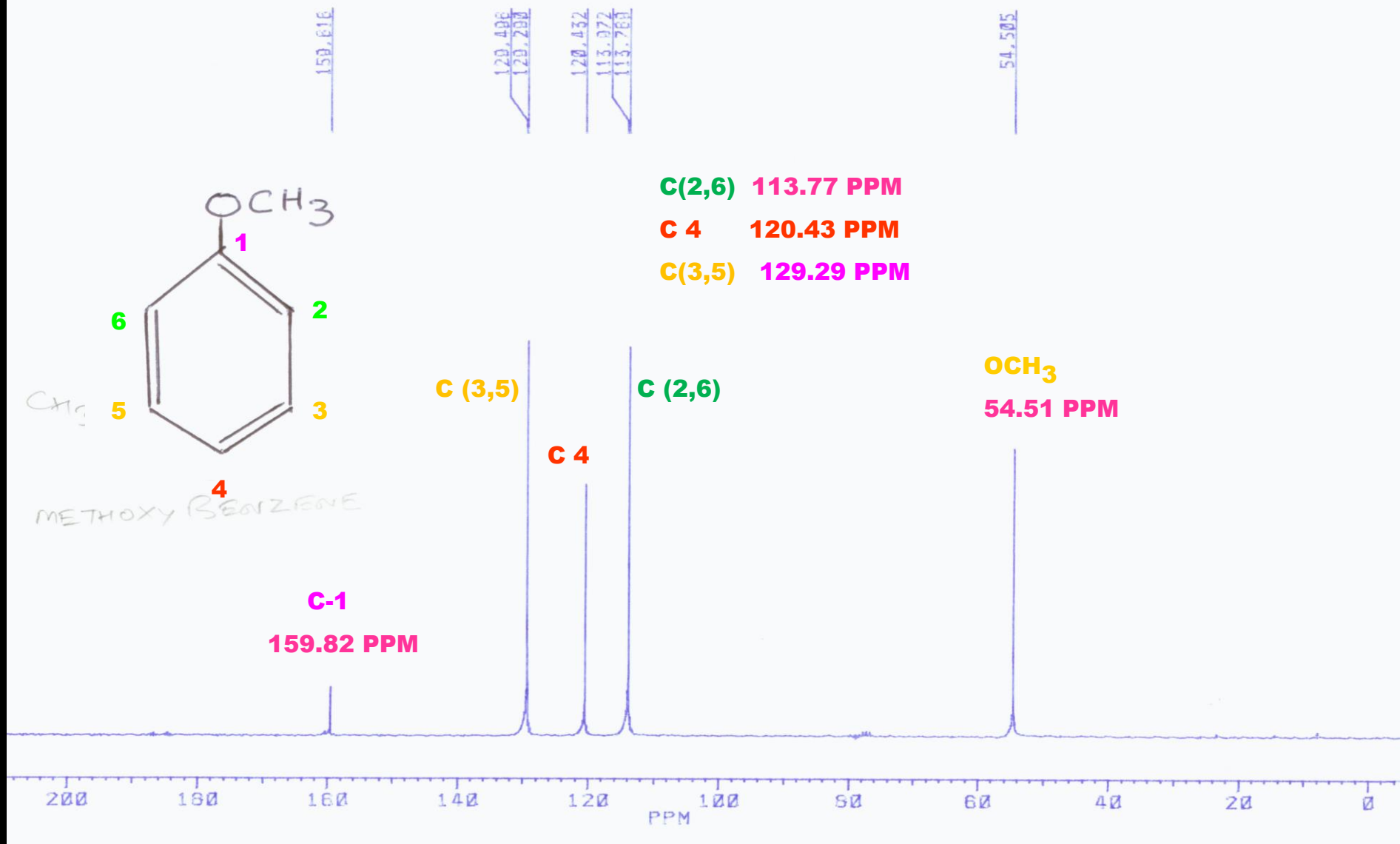
Shielding Effects on ^{1}H Ortho and Para Positions in Mono Substitution of Benzene.

- **Ortho and Para positions are shielded by mono substitution of electronegative group in benzene.**
- **X = OH, OR, NH_2, NR_2, O-CO-CH_3 Groups**
  ^{1}H attached to Positions 2 , 4 and 6 are affected.
- **Shift towards to TMS (To Right or Higher Field)**

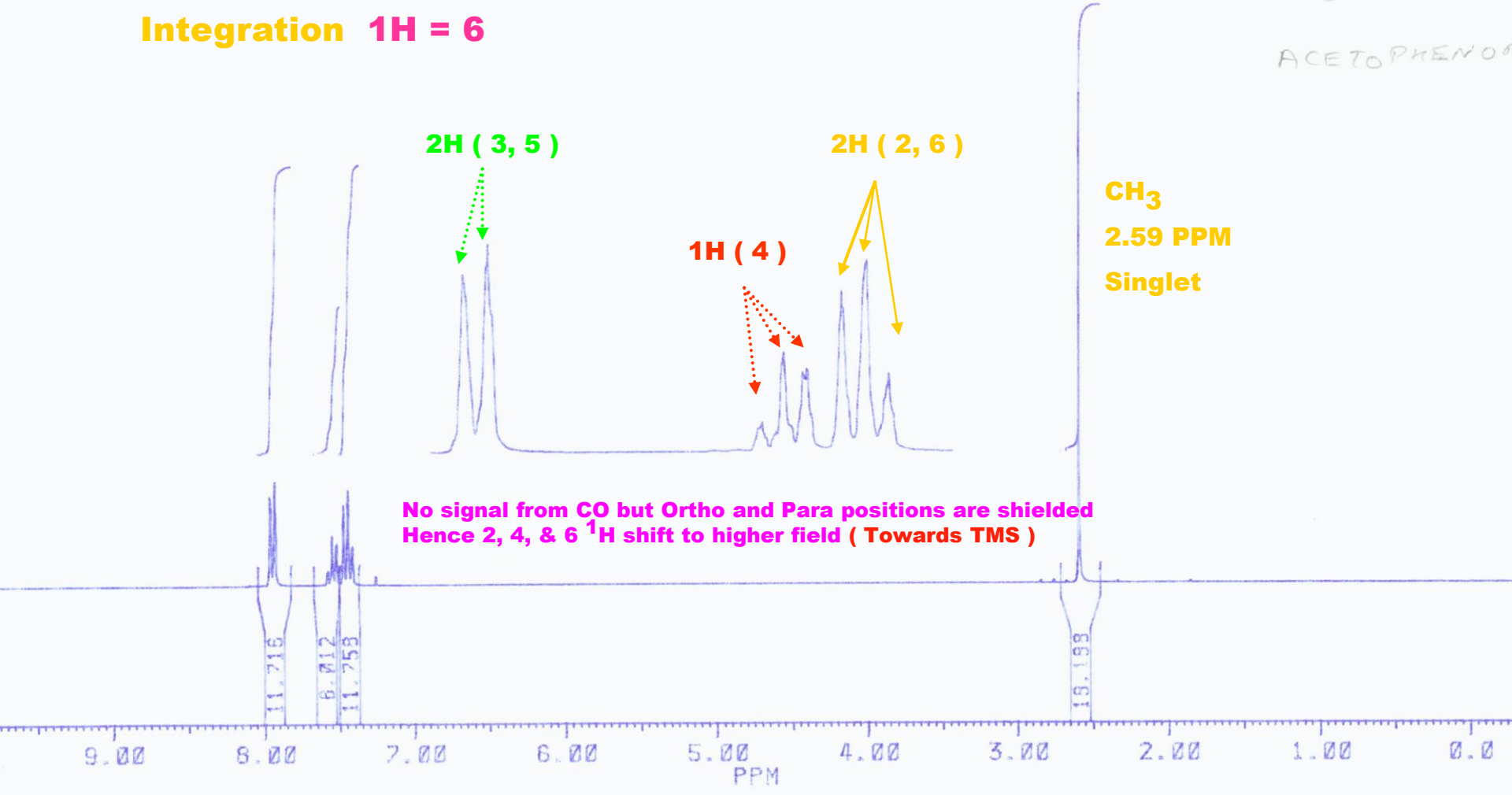




^{13}C NMR Spectrum of Anisole (Methoxy Benzene) $C_6H_5—OCH_3$

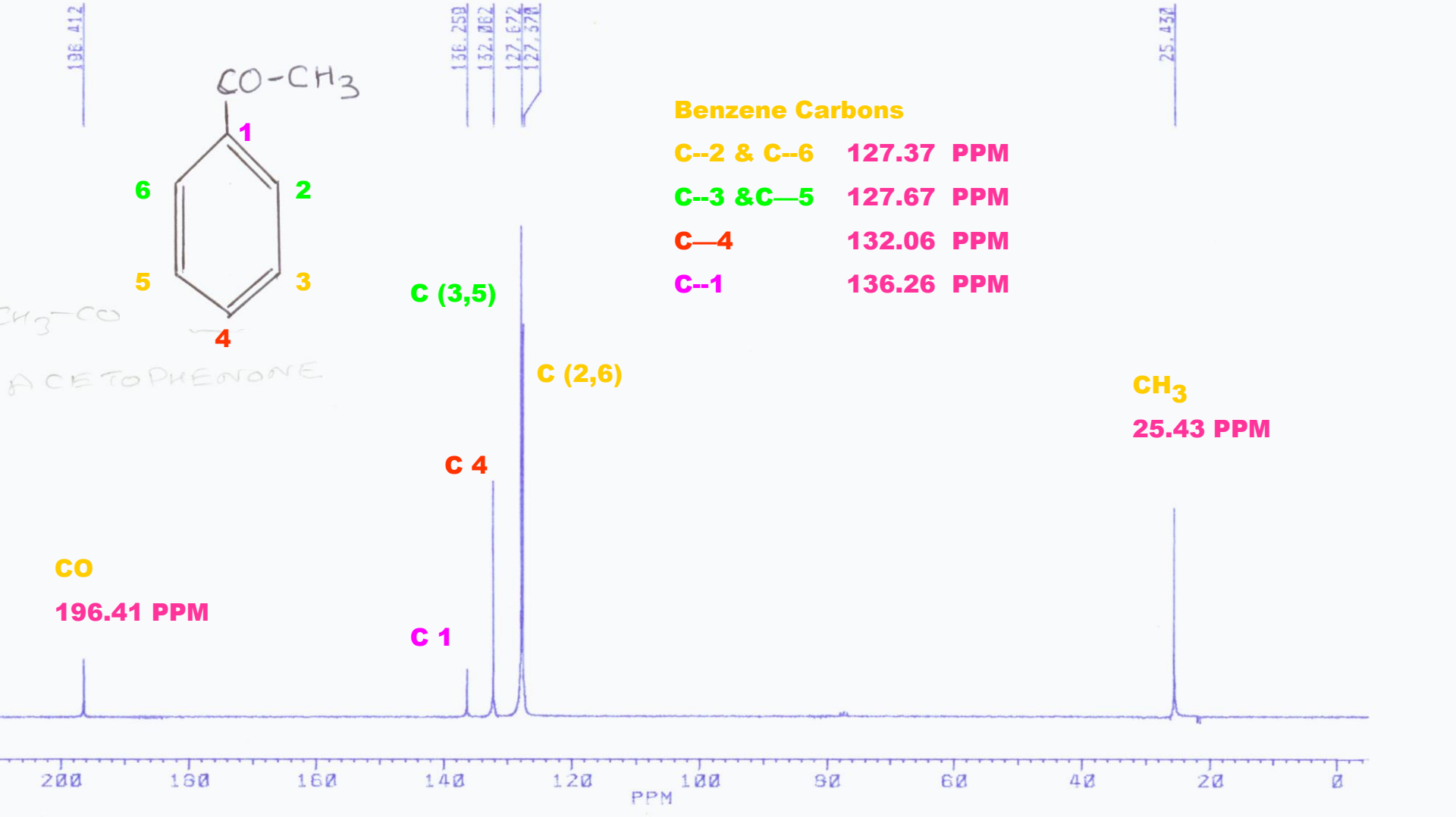


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Acetophenone $C_6H_5—CO—CH_3$



^{13}C NMR Spectrum of Acetophenone

$C_6H_5—CO—CH_3$

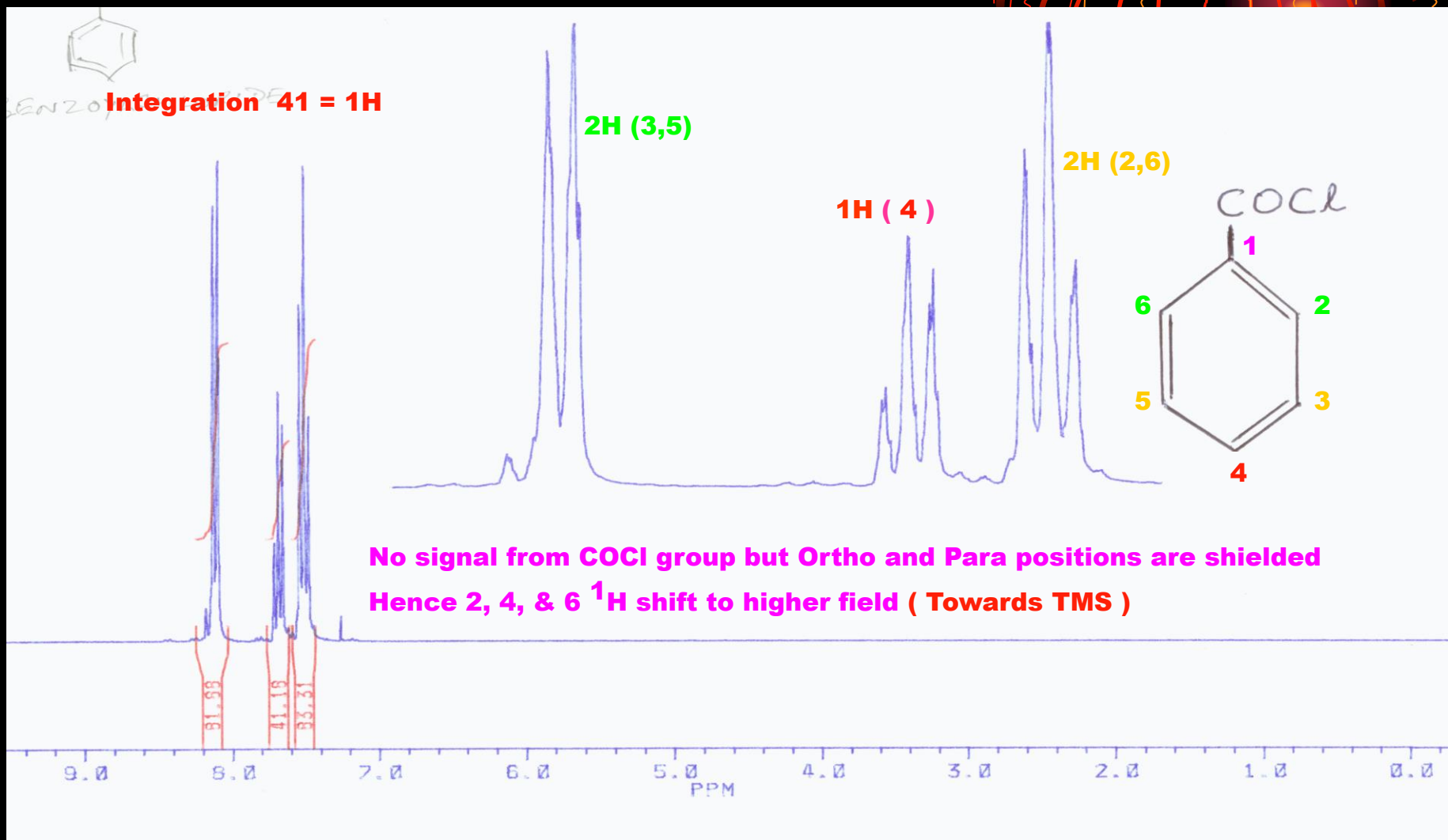


Benzene Carbons

C--2 & C--6	127.37 PPM
C--3 &C—5	127.67 PPM
C—4	132.06 PPM
C--1	136.26 PPM

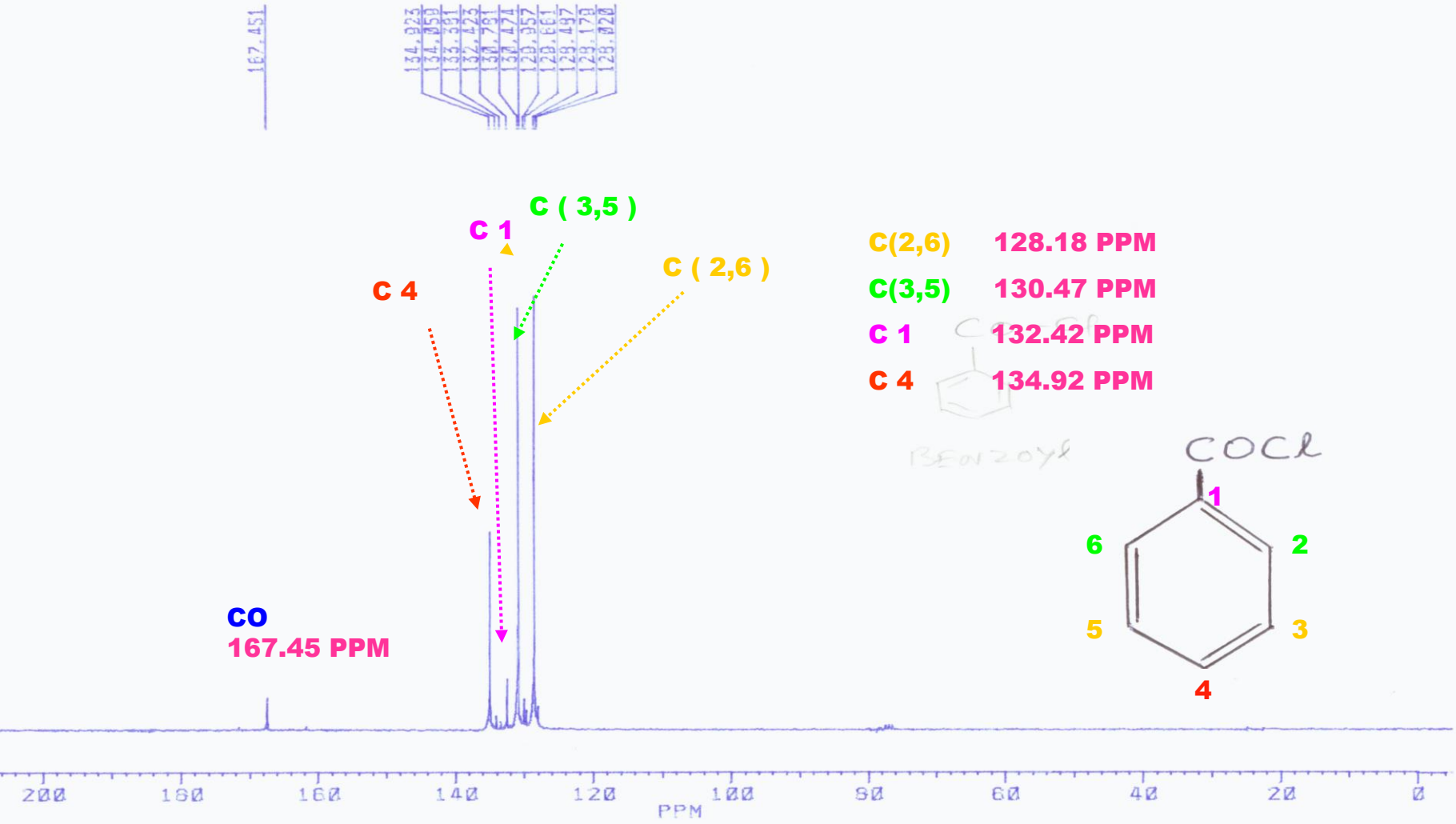
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Benzoylchloride $C_6H_5—COCl$

^{1}H NMR Spectrum



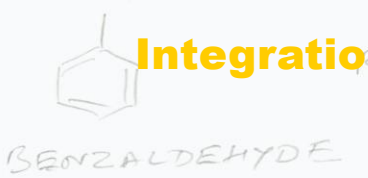
^{13}C NMR Spectrum of Benzoylchloride

C_6H_5--COCl

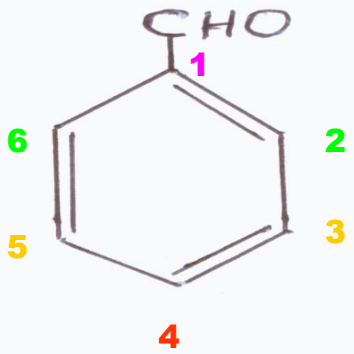


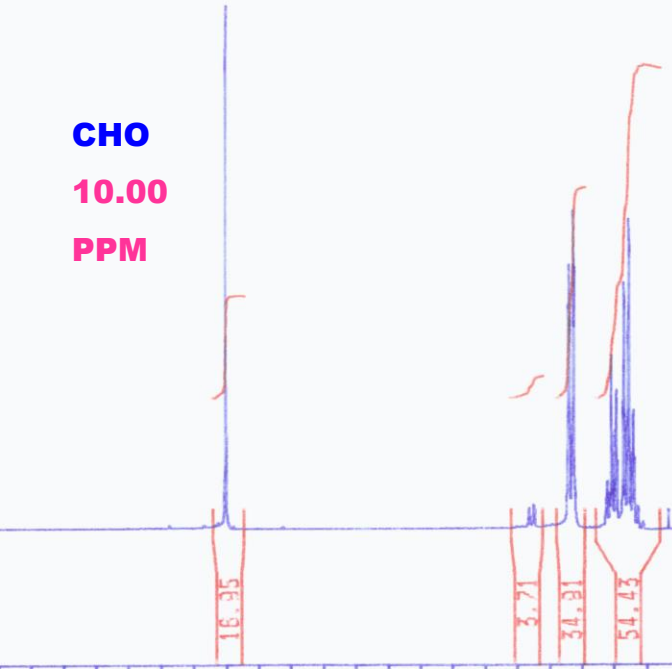
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Benzaldehyde C_6H_5—CHO

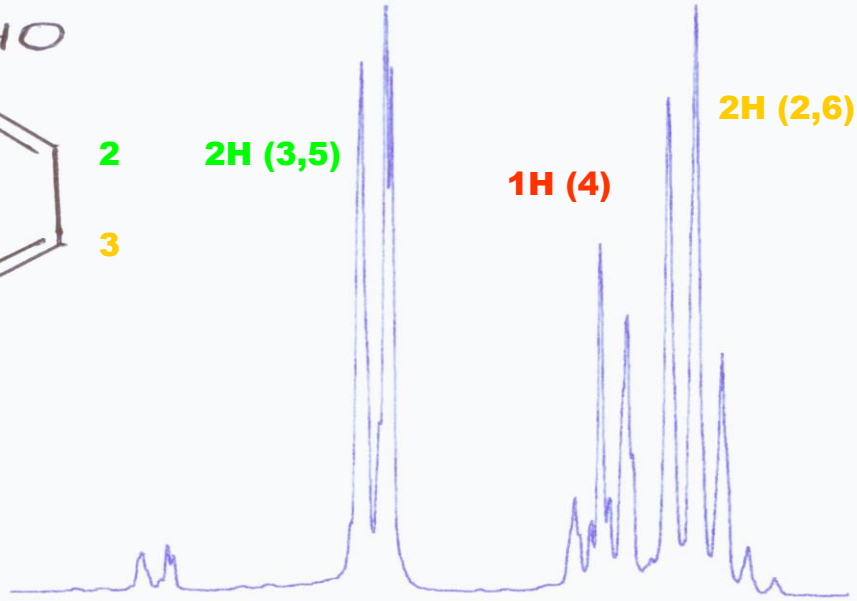
^{1}H NMR Spectrum



Integration 17 = 1H







Expansion of aromatic region

2 , 4 & 6 ^{1}H are shielded and

^{1}H of CHO group deshielded more hence shifted to very low field

^{13}C NMR Spectrum of Benzaldehyde

C_6H_5--CHO

C (2,6)

C (3,5)

C 4

C 1

CO

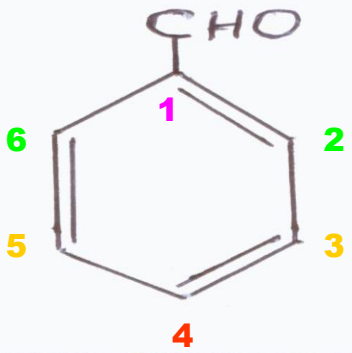
191.60 PPM

C (2,6) 128.23 PPM

C (3,5) 128.86 PPM

C 4 133.60 PPM

C 1 135.76 PPM

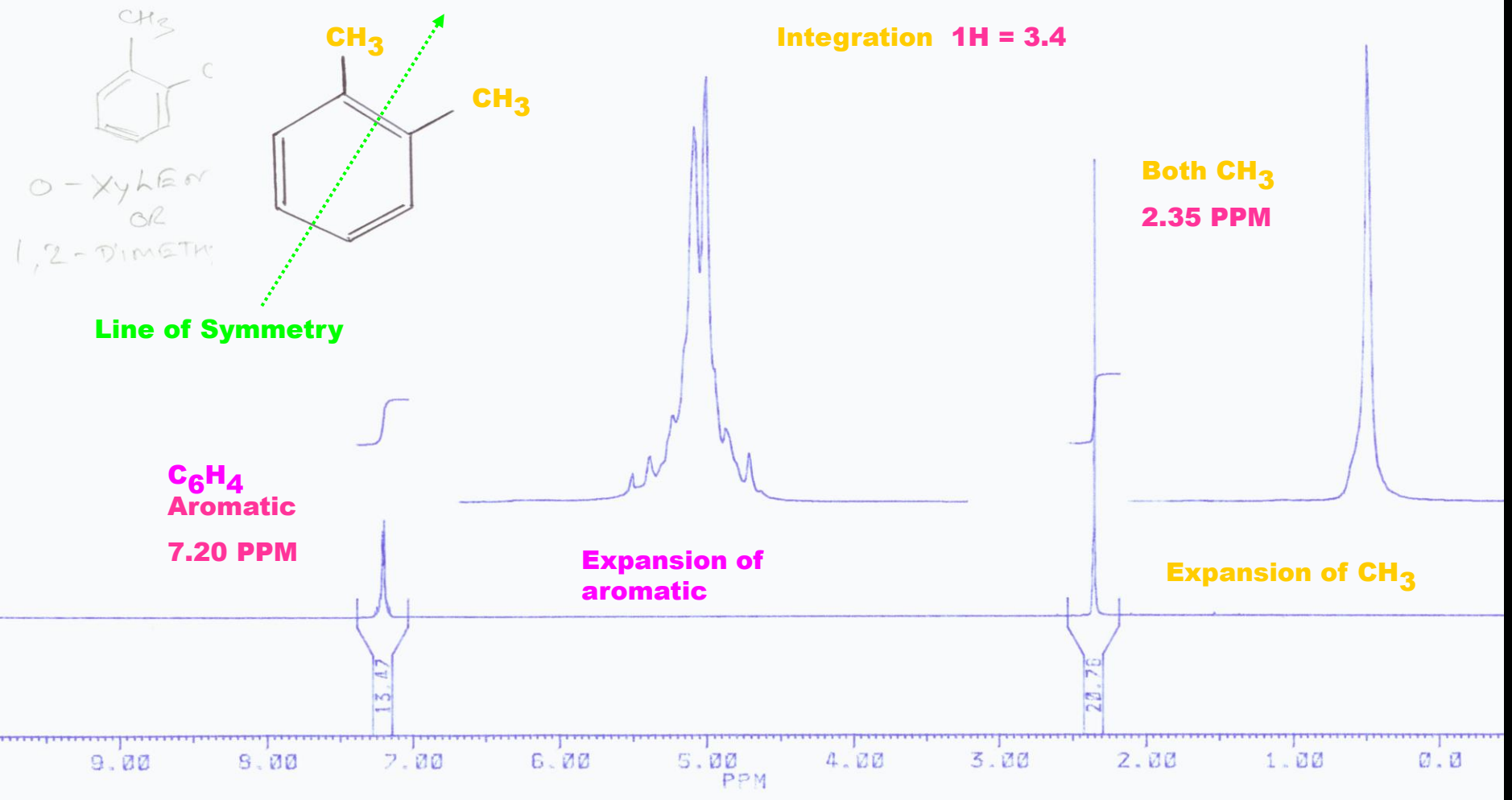


200 180 160 140 120 100 80 60 40 20 0

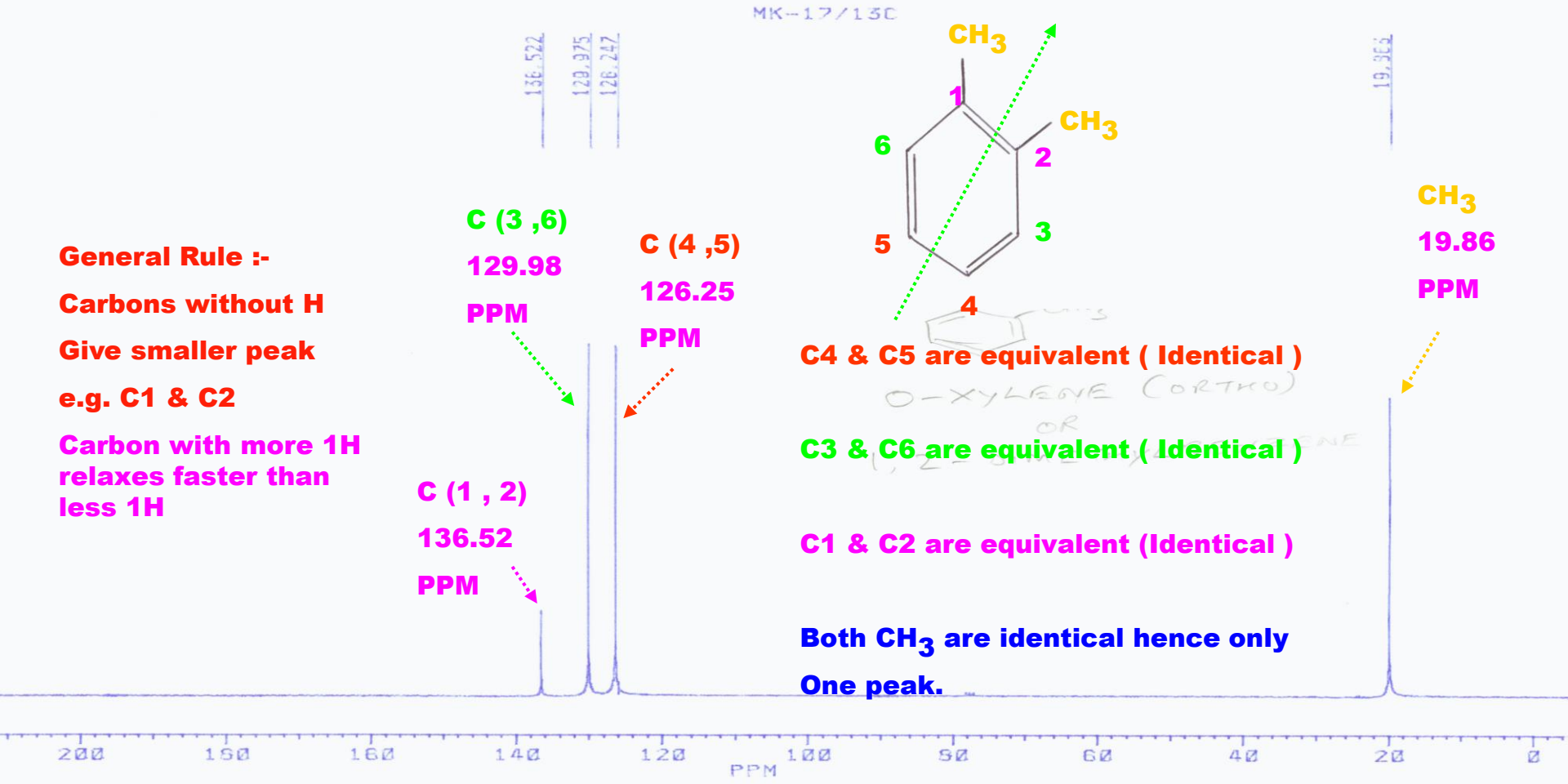
PPM

Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,2-Dimethylbenzene (O-Xylene)

C_6H_4-$(CH_3)_2$ ^{1}H NMR Spectrum



^{13}C NMR Spectrum of 1,2-Dimethylbenzene (O-Xylene)



General Rule :-

Carbons without H

Give smaller peak

e.g. C1 & C2

Carbon with more 1H relaxes faster than less 1H

C (3 ,6)

129.98

PPM

C (4 ,5)

126.25

PPM

C (1 , 2)

136.52

PPM

CH_3

19.86

PPM

C4 & C5 are equivalent (Identical)

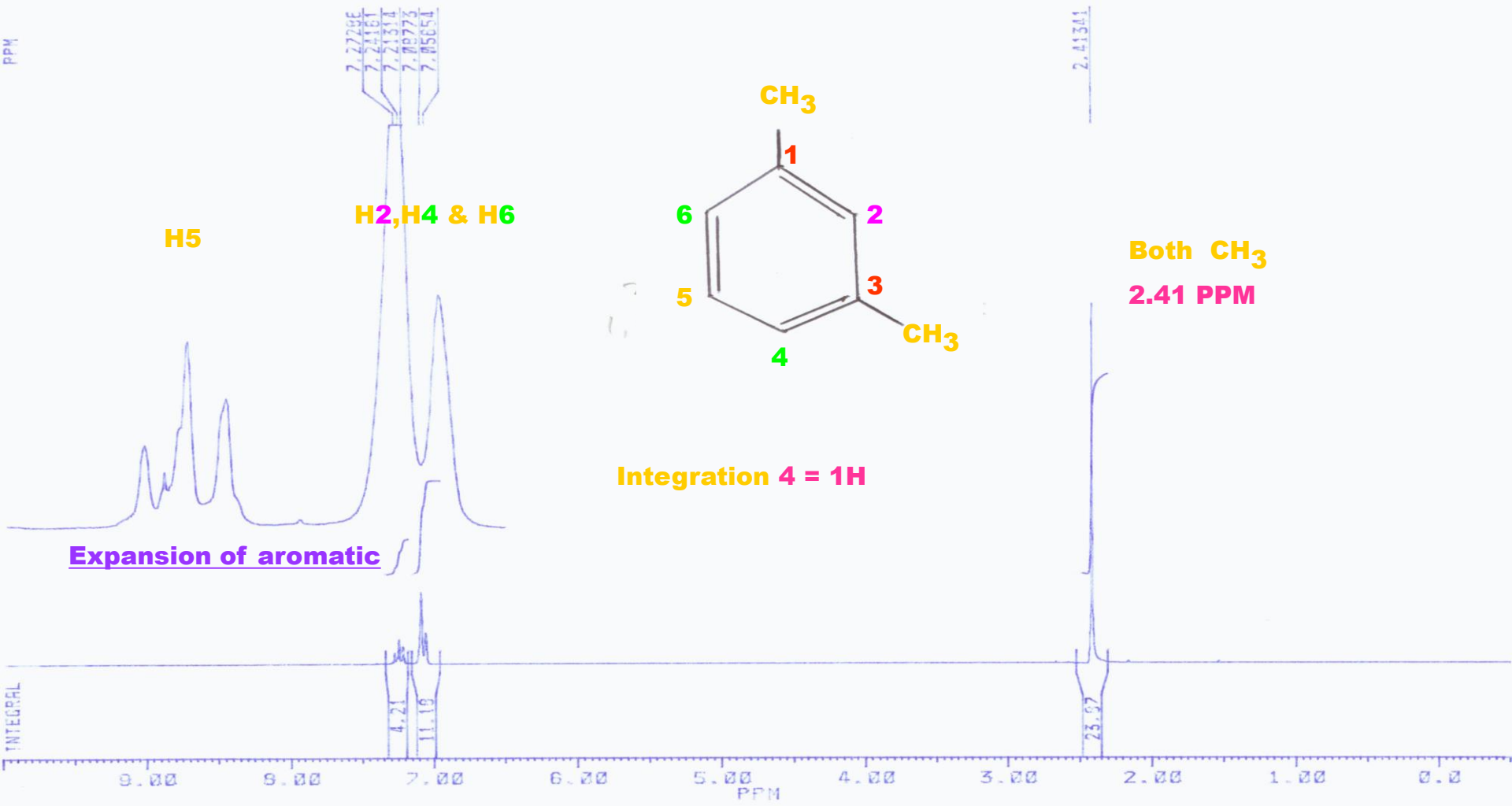
C3 & C6 are equivalent (Identical)

C1 & C2 are equivalent (Identical)

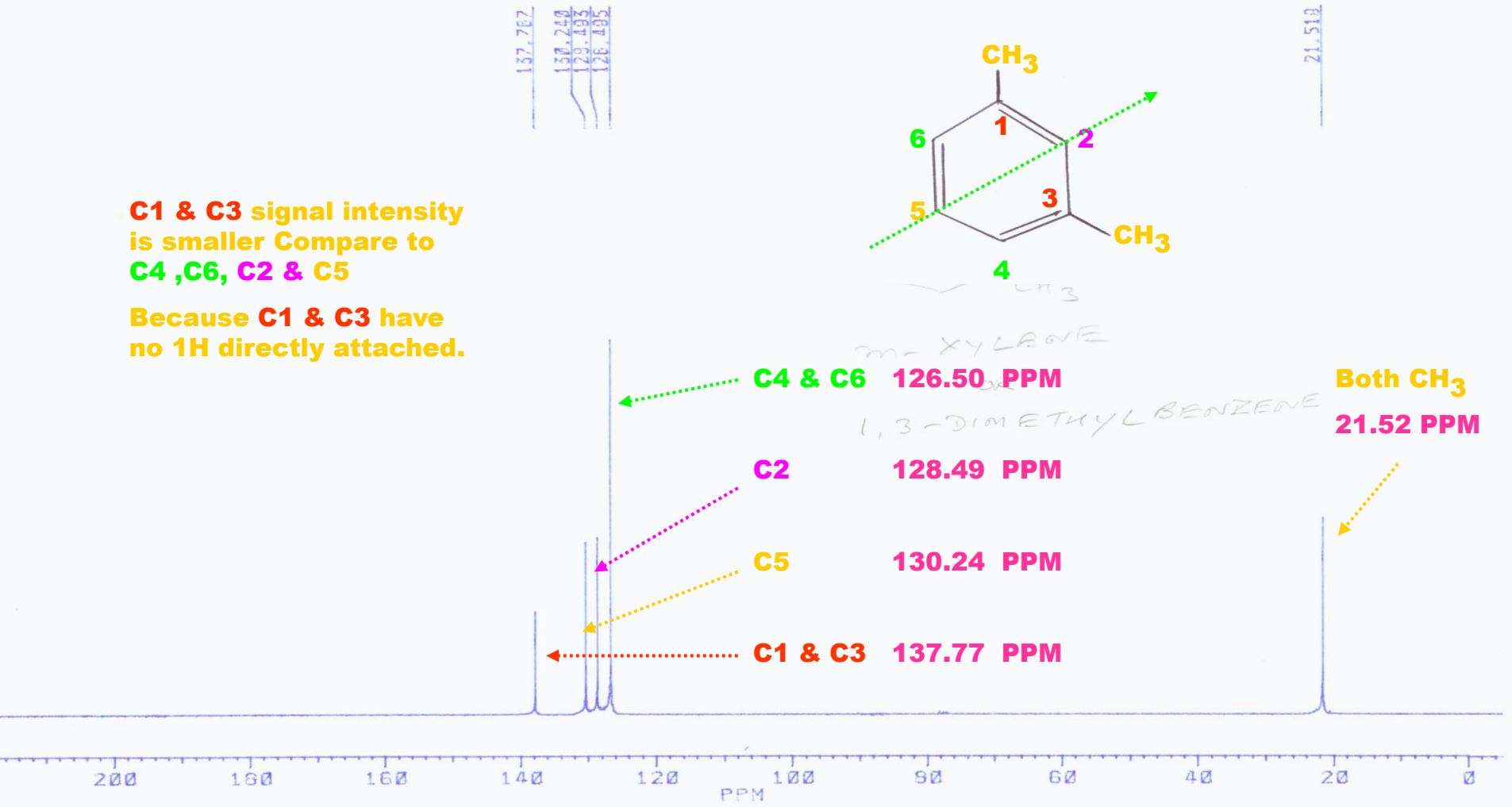
Both CH_3 are identical hence only One peak.

Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,3-Dimethylbenzene (m-Xylene)

C_6H_4-$(CH_3)_2$ ^{1}H NMR Spectrum



^{13}C NMR Spectrum of 1,3-Dimethylbenzene (m-Xylene)

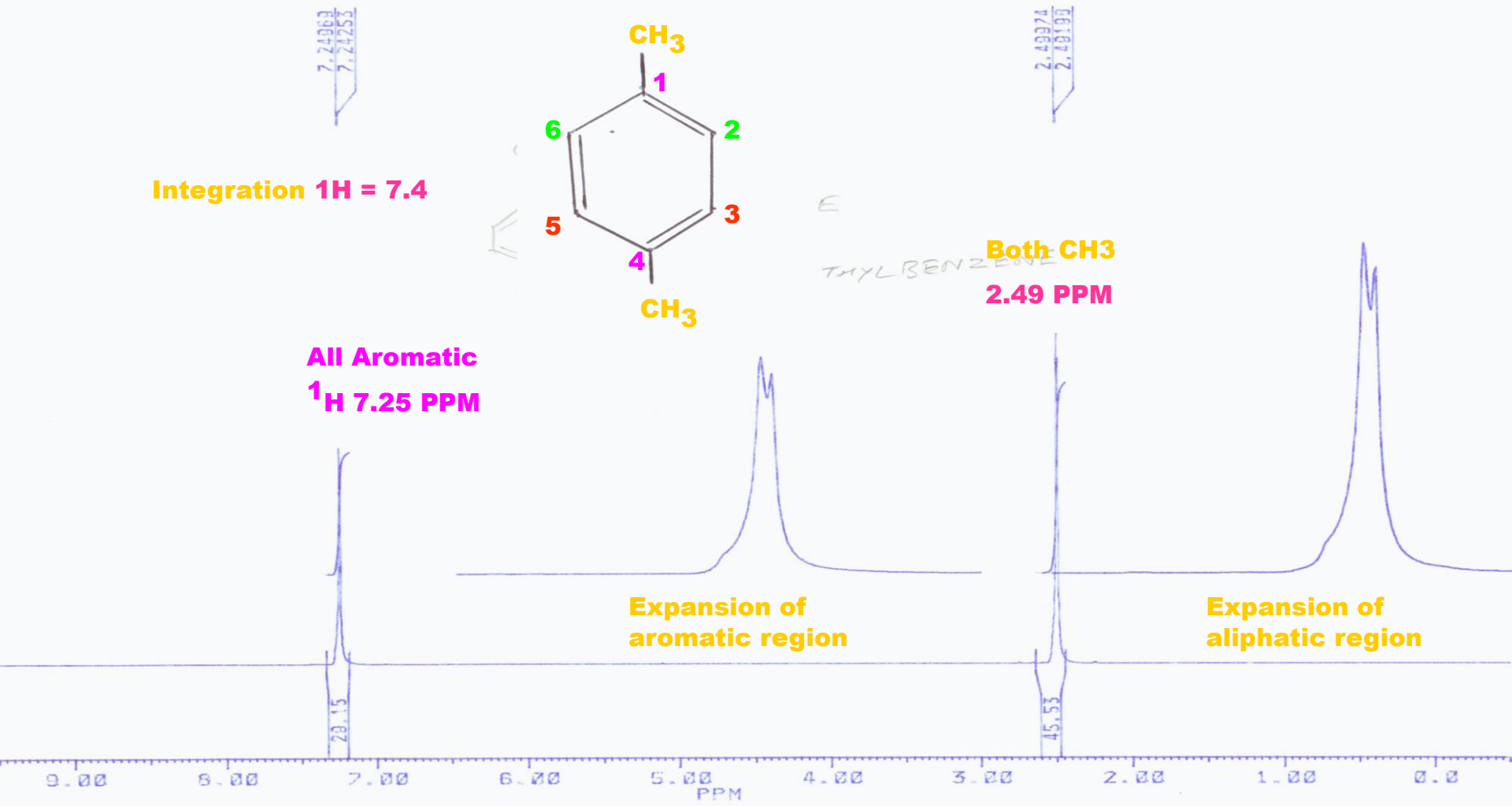


C1 & C3 signal intensity is smaller Compare to C4 ,C6, C2 & C5

Because C1 & C3 have no 1H directly attached.

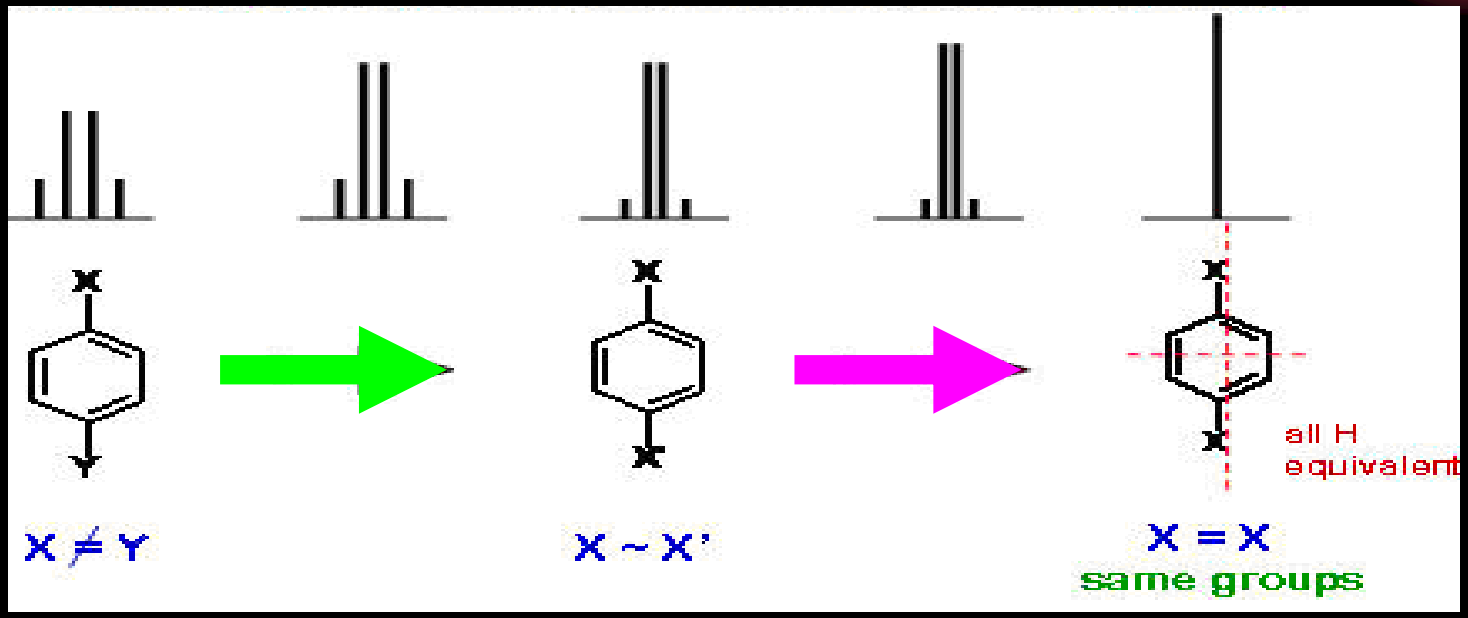
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,3-Dimethylbenzene (p-Xylene)

C_6H_4-$(CH_3)_2$ ^{1}H NMR Spectrum

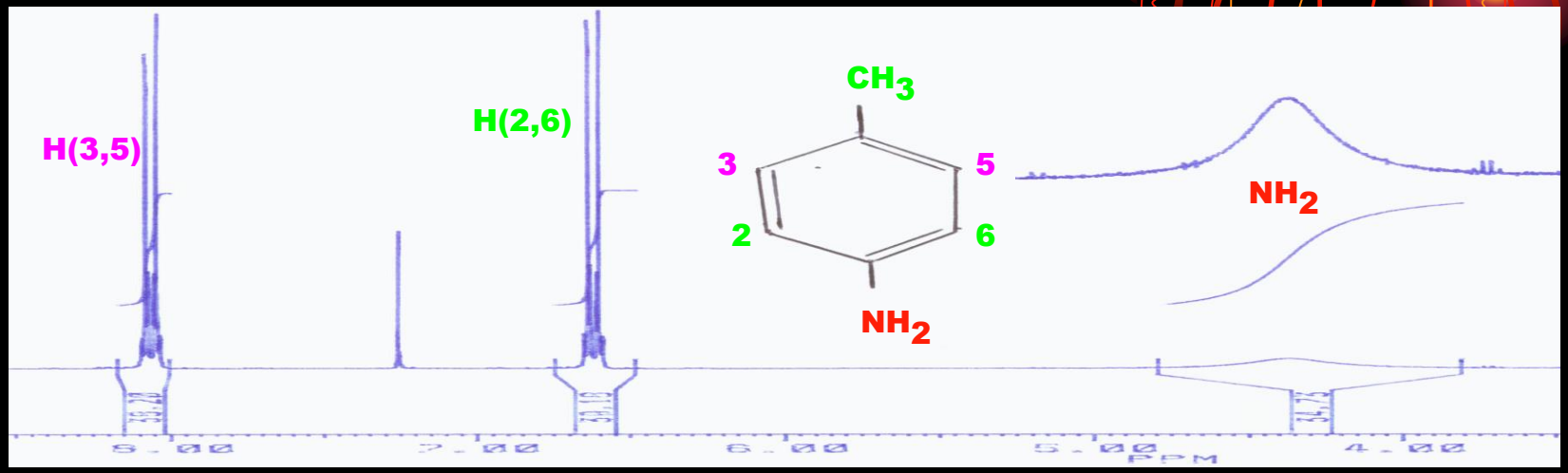


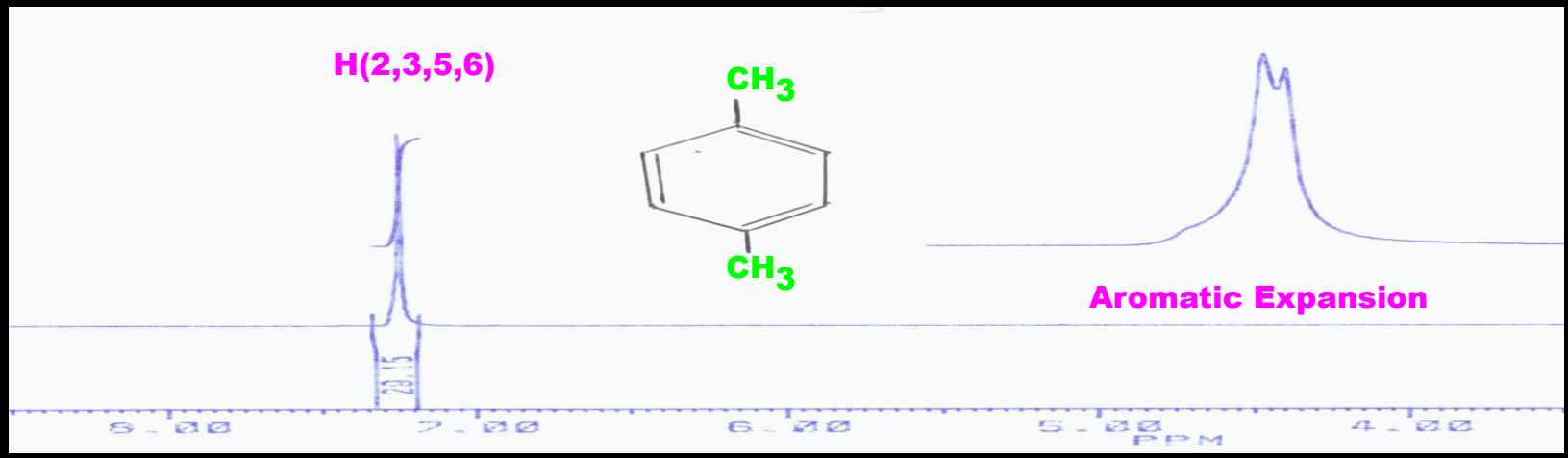
^{1}H NMR Patter of Para Disubstituted Benzene

- When two groups X & Y become more similar then
- All NMR Peaks move closer hence
- Outer peaks get smaller and finally disappear but
- Inner peaks get taller and finally merge into single peak.

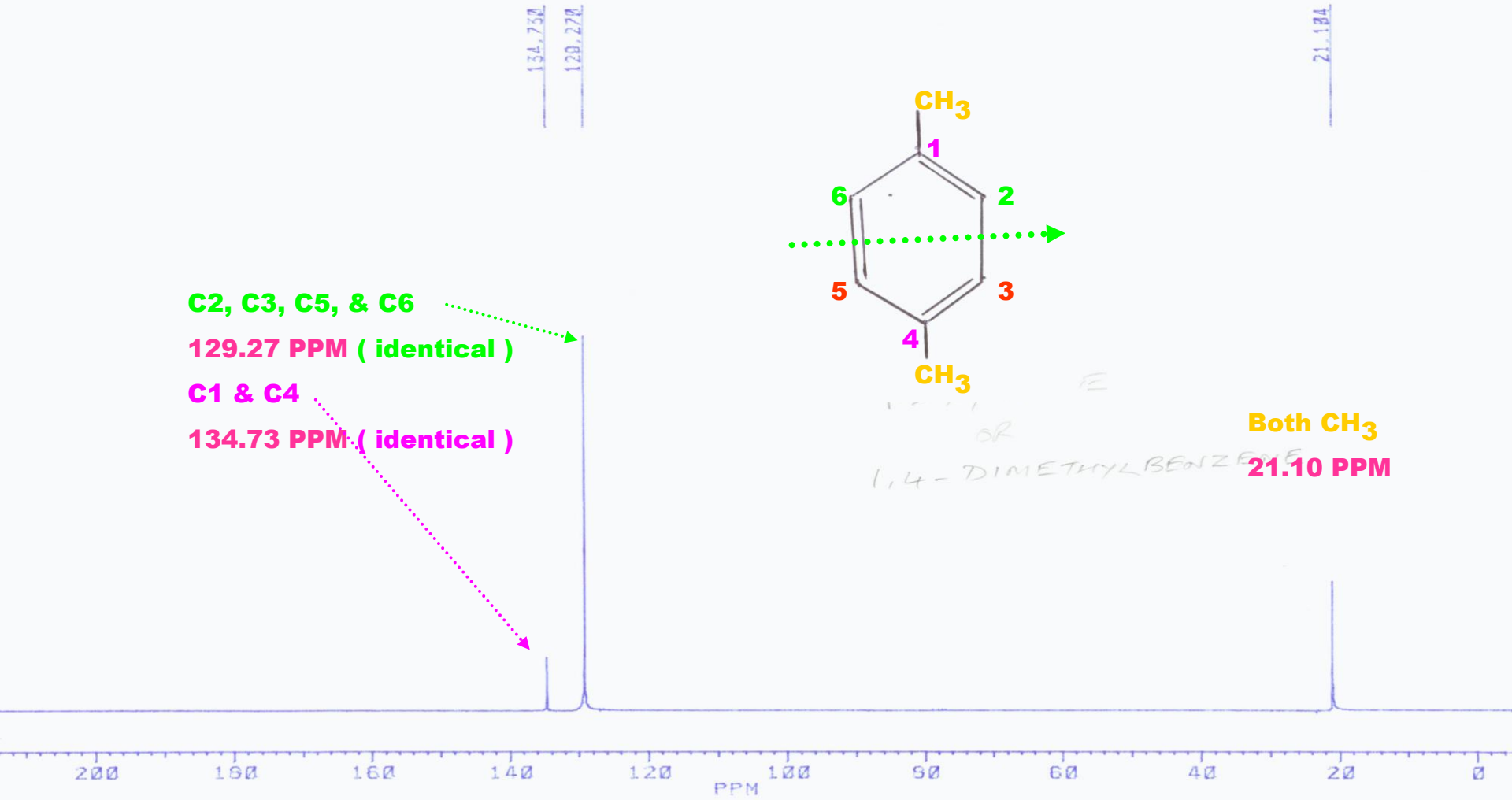


^{1}H NMR Spectra of 4-Methyl Aniline and p-Xylene only 8.5 to 4.5 PPM Region shown

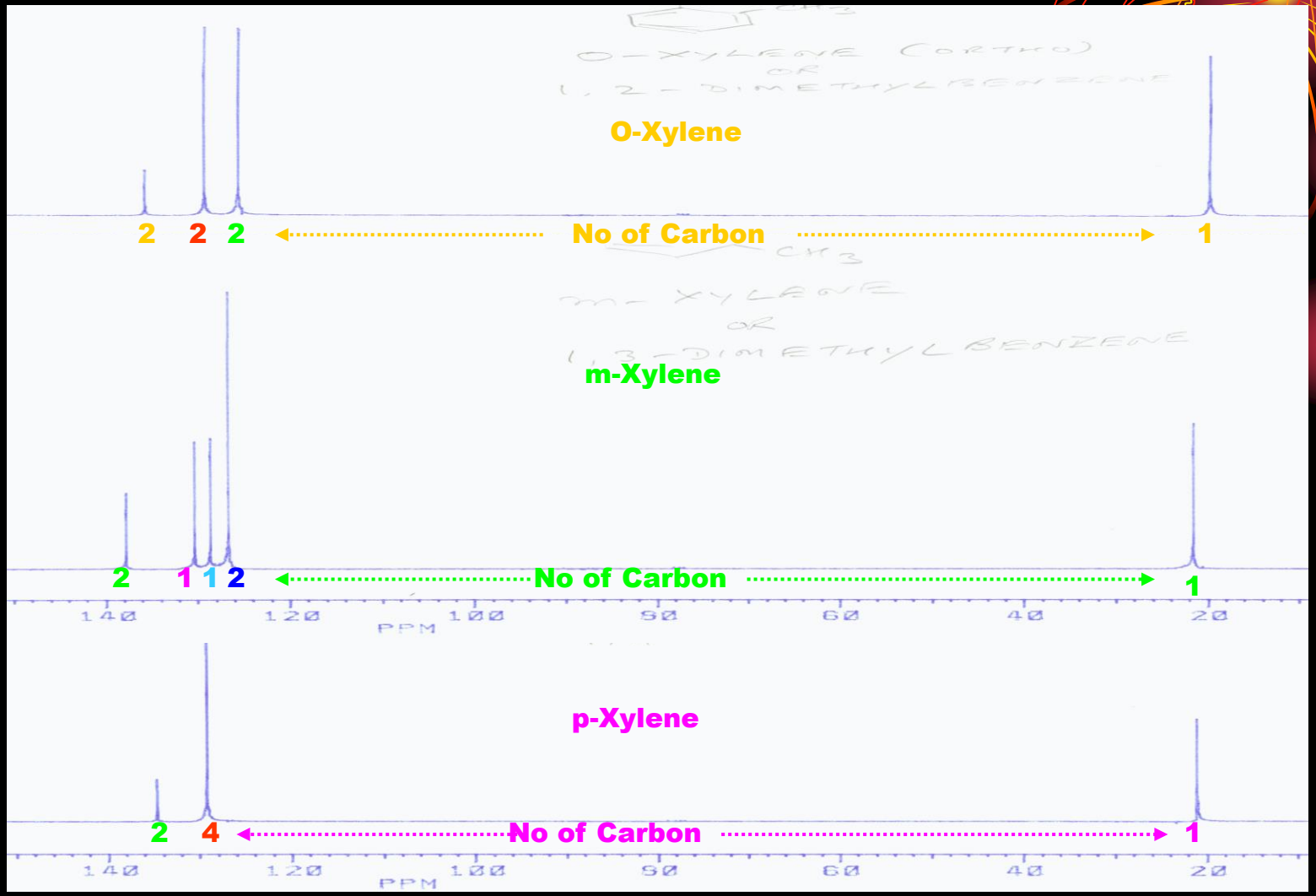




^{13}C NMR Spectrum of 1,4-Dimethylbenzene (p-Xylene)



O, M, & P- Xylene ^{13}C NMR Spectra

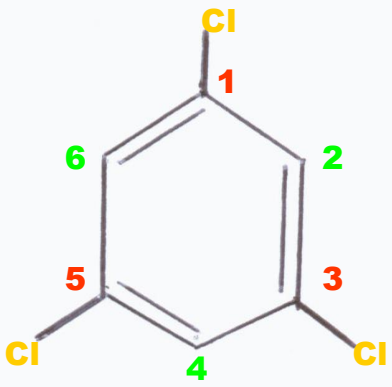


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,3,5-Trichlorobenzene

$C_6H_3Cl_3$ ^{1}H NMR Spectrum

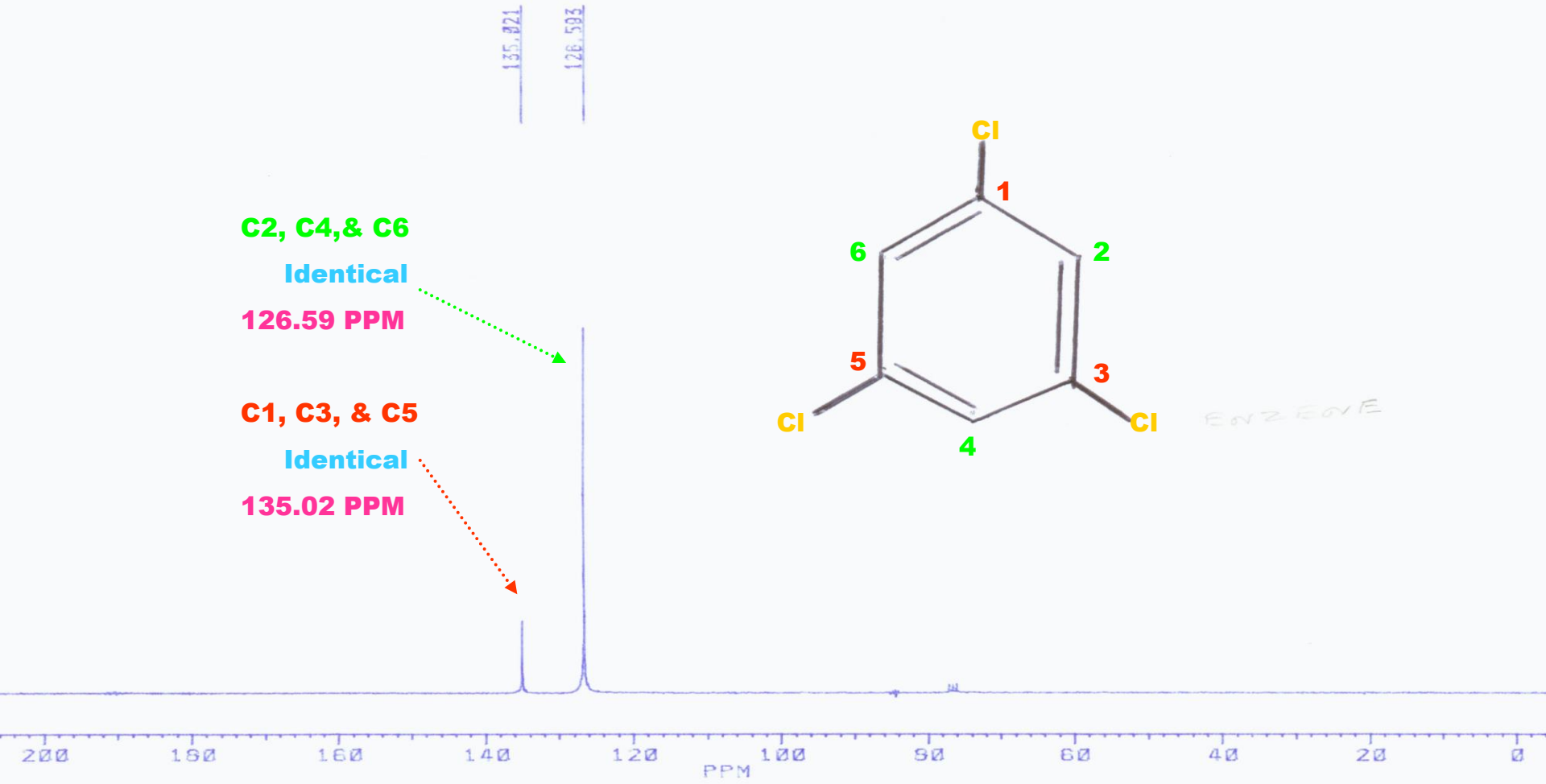
H (2, 4, 6) are Identical

7.22 PPM



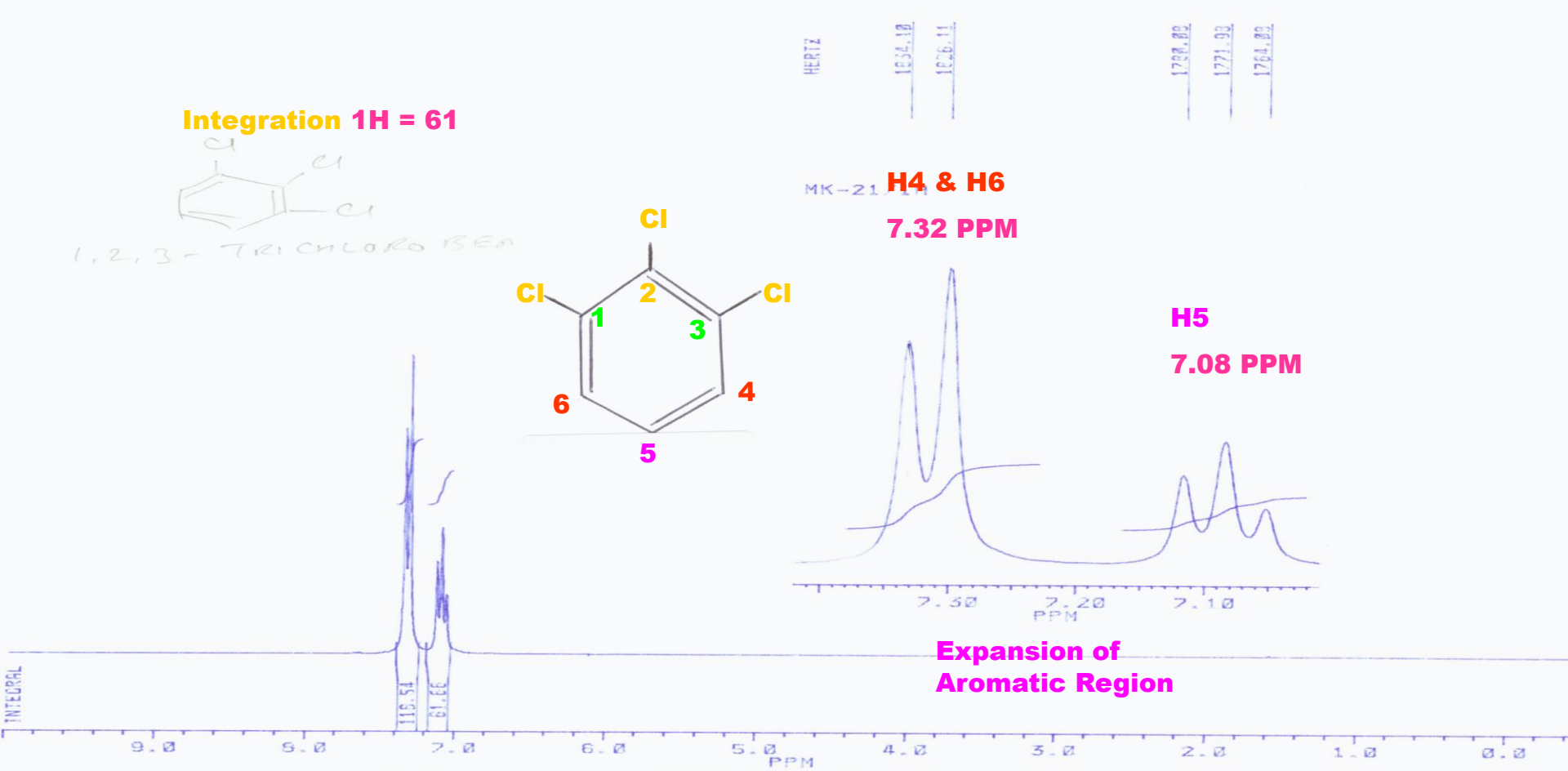
^{13}C NMR Spectrum 1,3,5-Trichlorobenzene

$C_6H_3Cl_3$



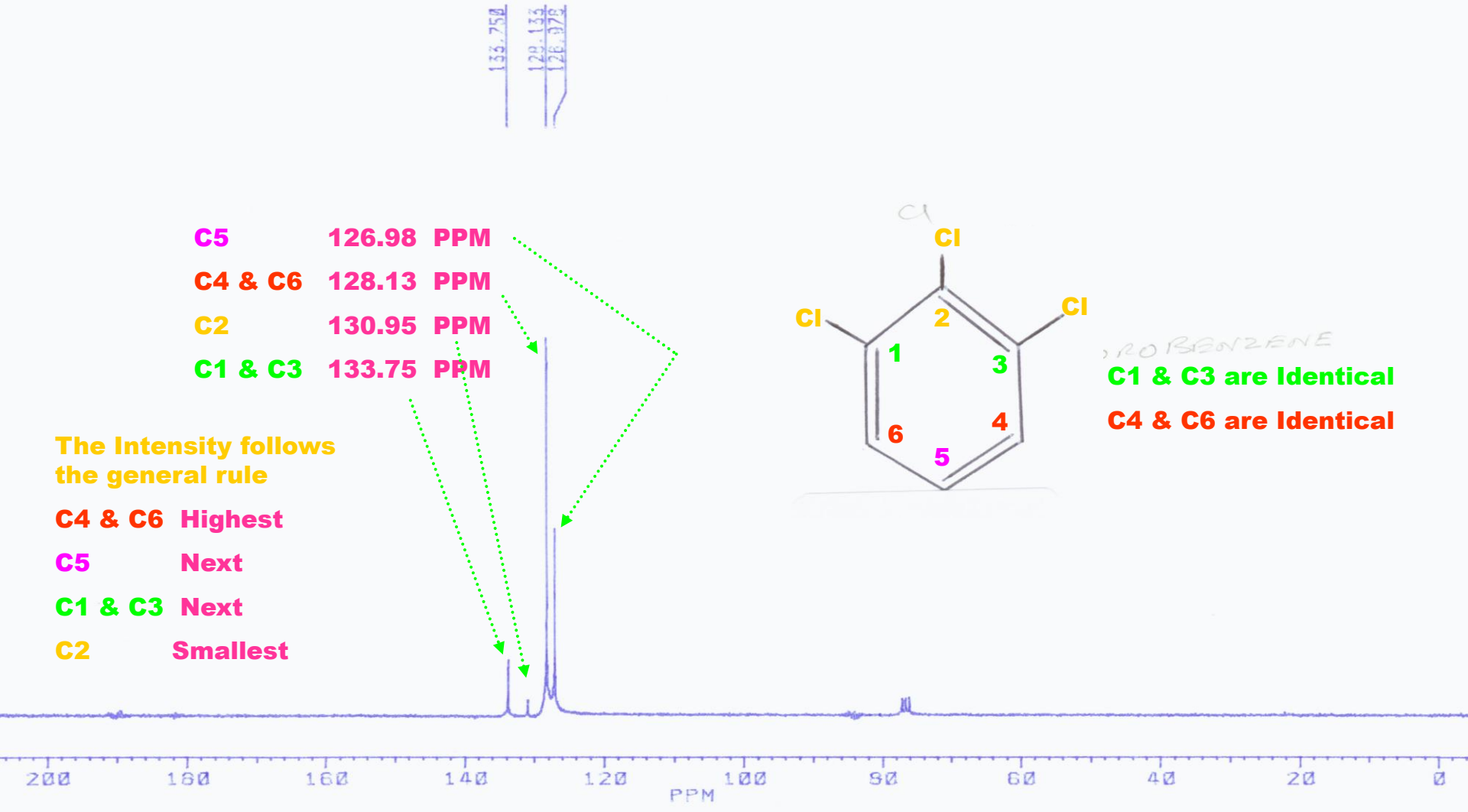
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,2,3-Trichlorobenzene

$C_6H_3Cl_3$ ^{1}H NMR Spectrum



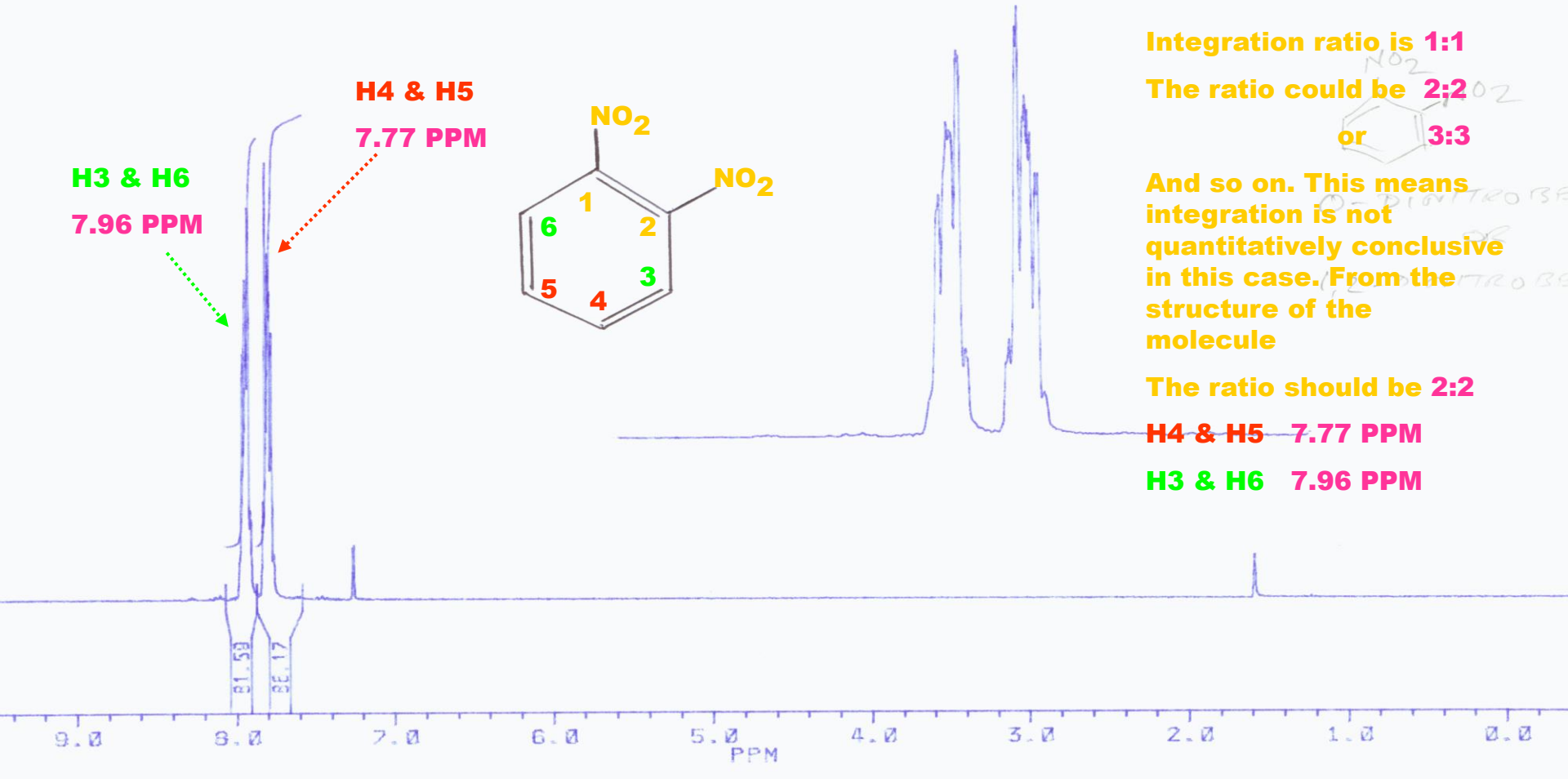
^{13}C NMR Spectrum 1,2,3-Trichlorobenzene

$C_6H_3Cl_3$



Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,2-Dinitrobenzene

$C_6H_4(NO_2)_2$ ^{1}H NMR Spectrum



Integration ratio is 1:1

The ratio could be 2:2

or 3:3

And so on. This means integration is not quantitatively conclusive in this case. From the structure of the molecule

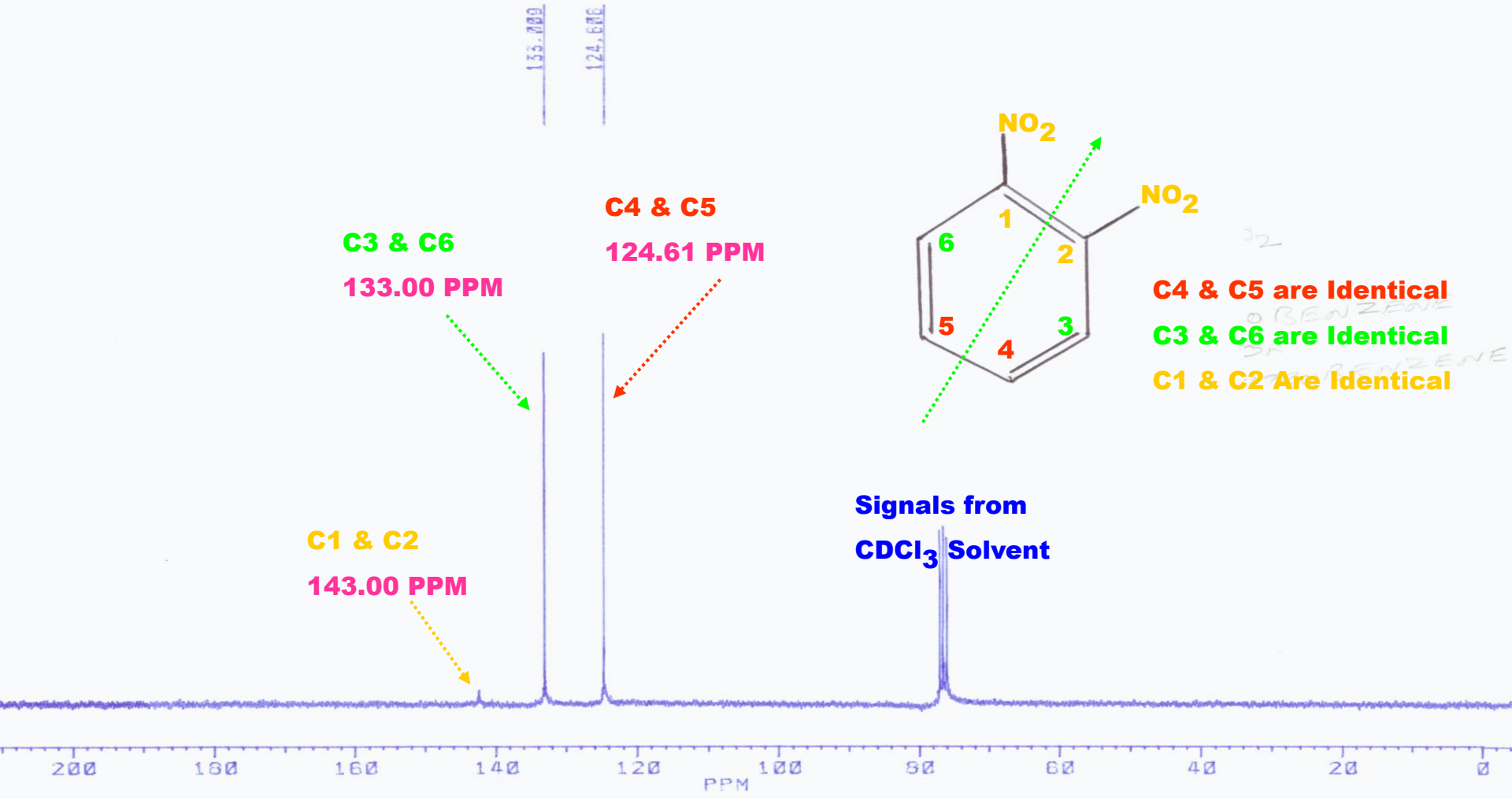
The ratio should be 2:2

H4 & H5 7.77 PPM

H3 & H6 7.96 PPM

^{13}C NMR Spectrum of 1,2-Dinitrobenzene

$C_6H_4(NO_2)_2$



Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,3-Dinitrobenzene

$C_6H_4(NO_2)_2$ ^{1}H NMR Spectrum

Integration 1H = 54

H4 & H6

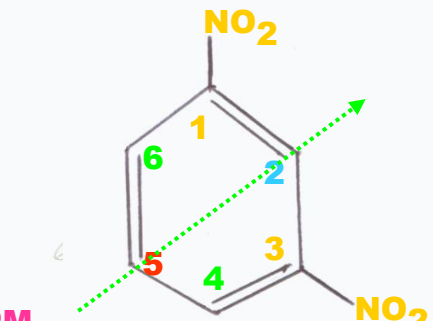
8.57 PPM

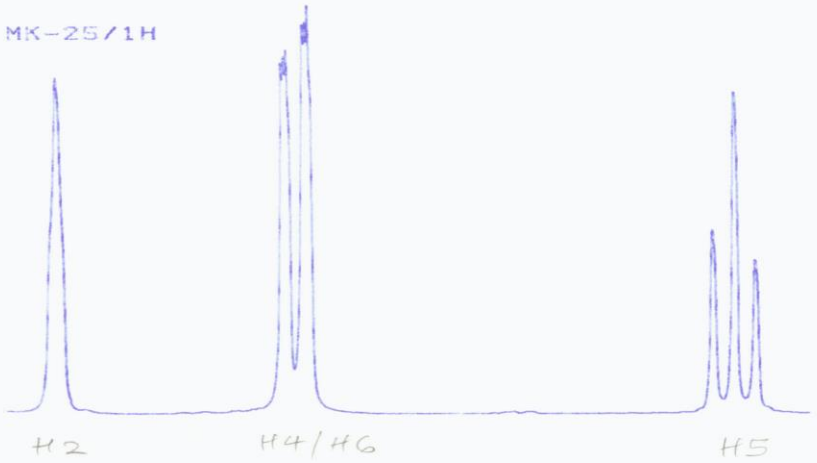
H2

8.94 PPM

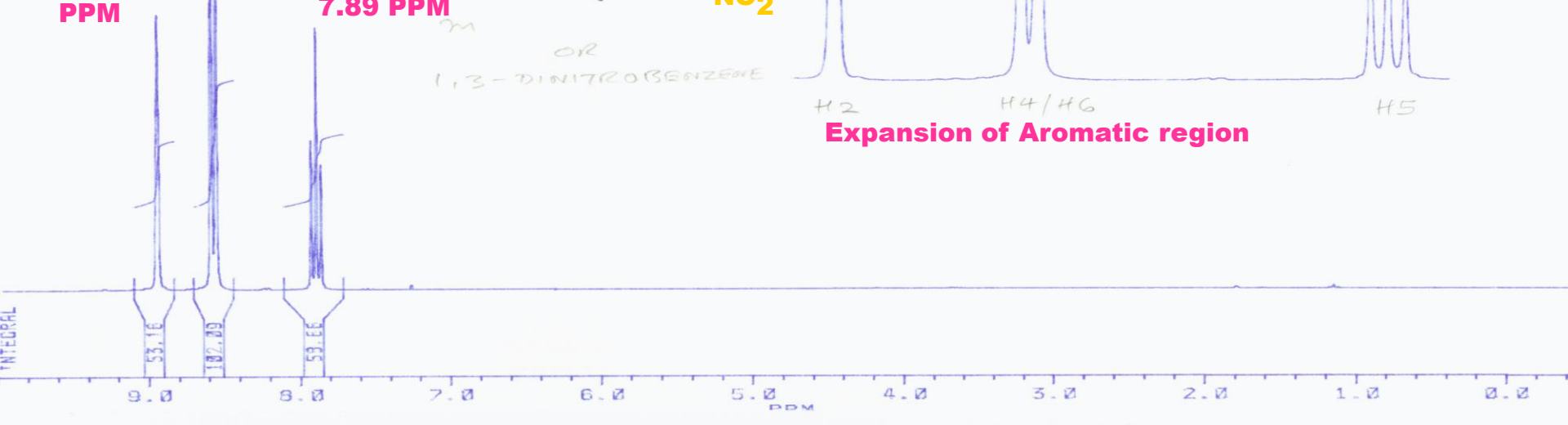
H5

7.89 PPM



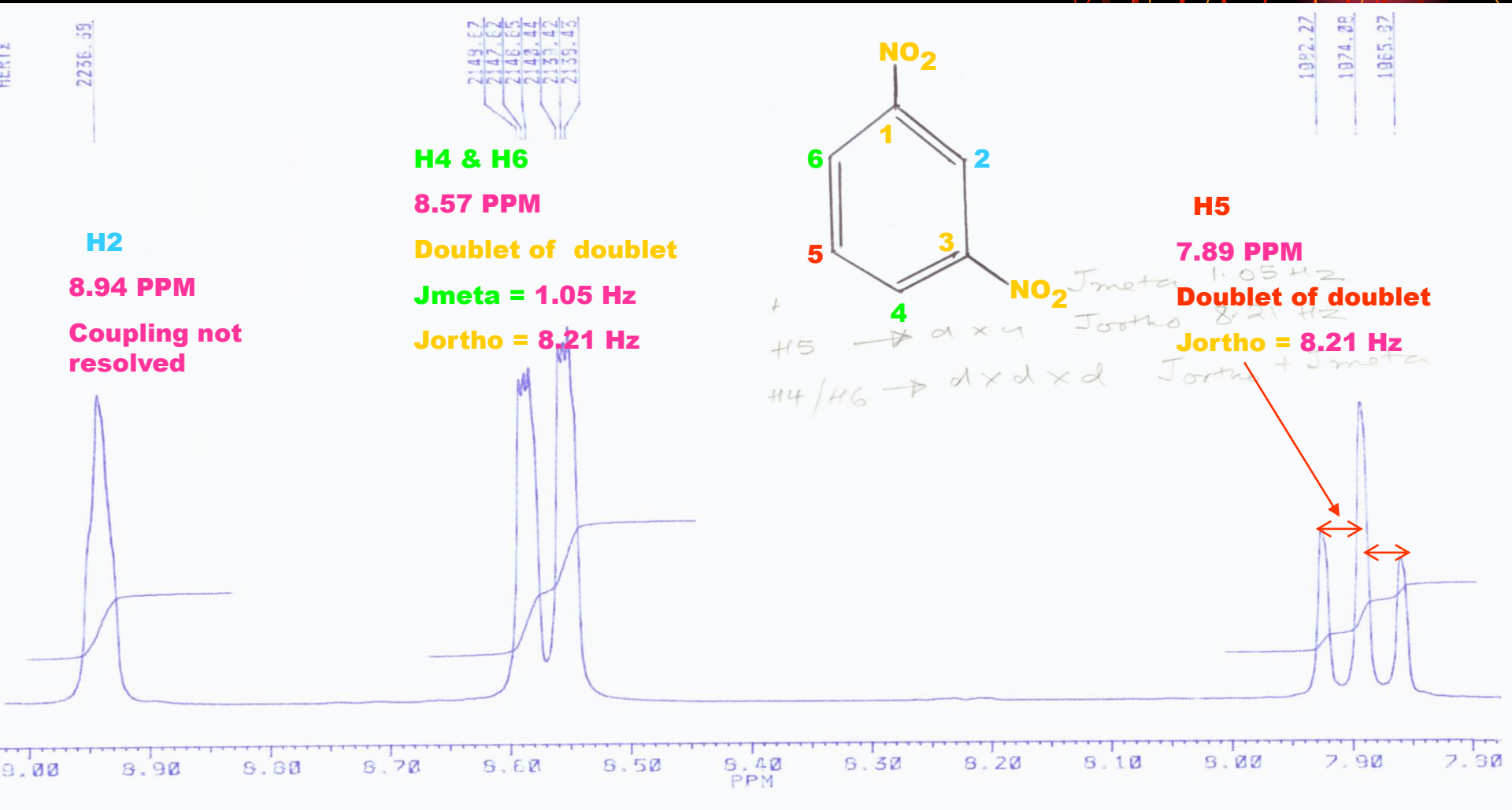


Expansion of Aromatic region



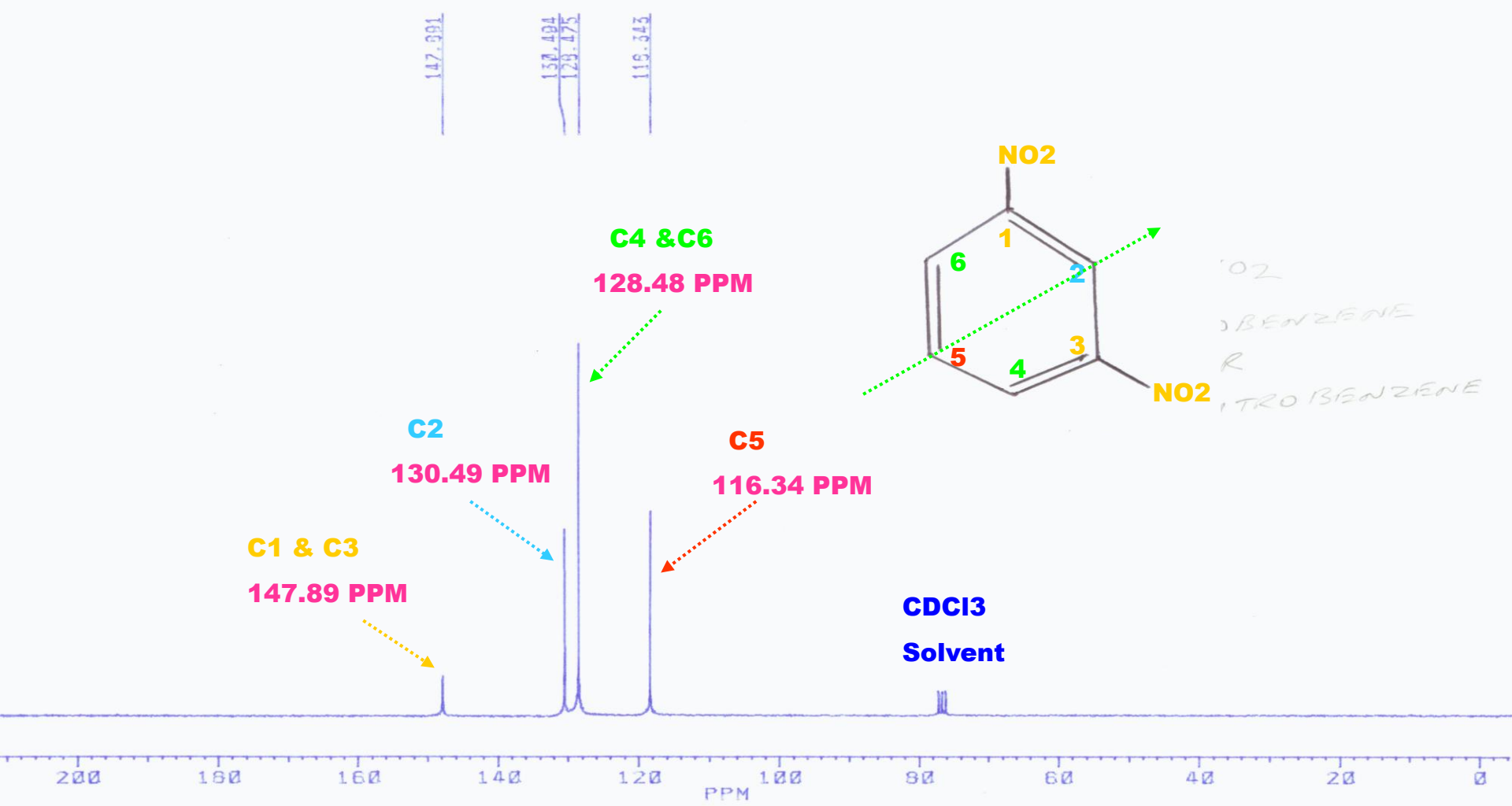
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 1,2,3-Trichlorobenzene

$C_6H_3Cl_3$ ^{1}H NMR Spectrum



^{13}C NMR Spectrum of 1,3-Dinitrobenzene

$C_6H_4(NO_2)_2$



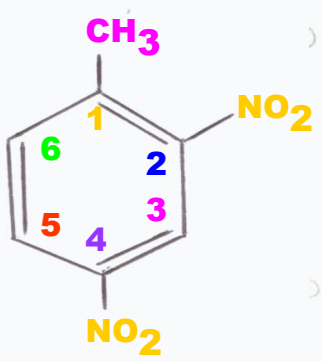
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 2,4-Dinitromethylbenzene

$C_6H_3CH_3(NO_2)_2$ ^{1}H NMR Spectrum

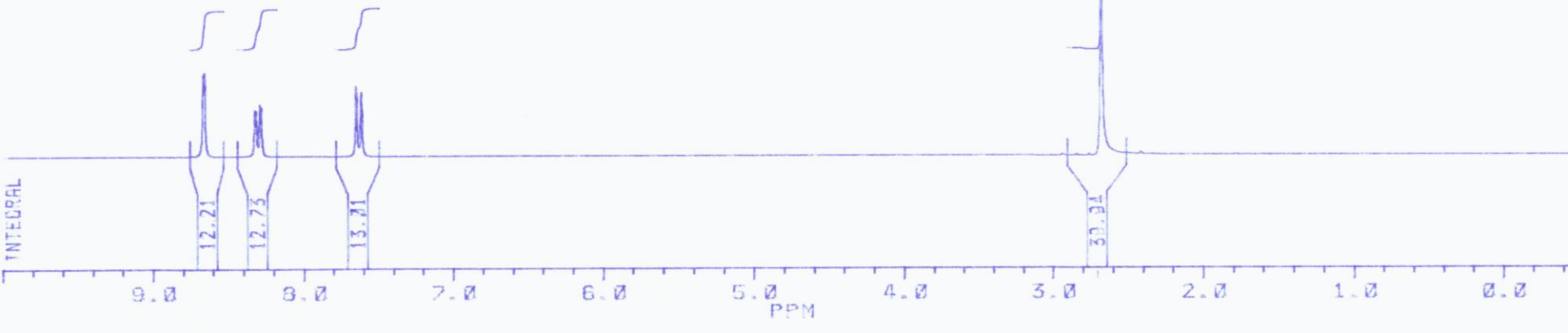
Integration 12.5 = 1H

CH_3
2.73 PPM

H3
H5
H6

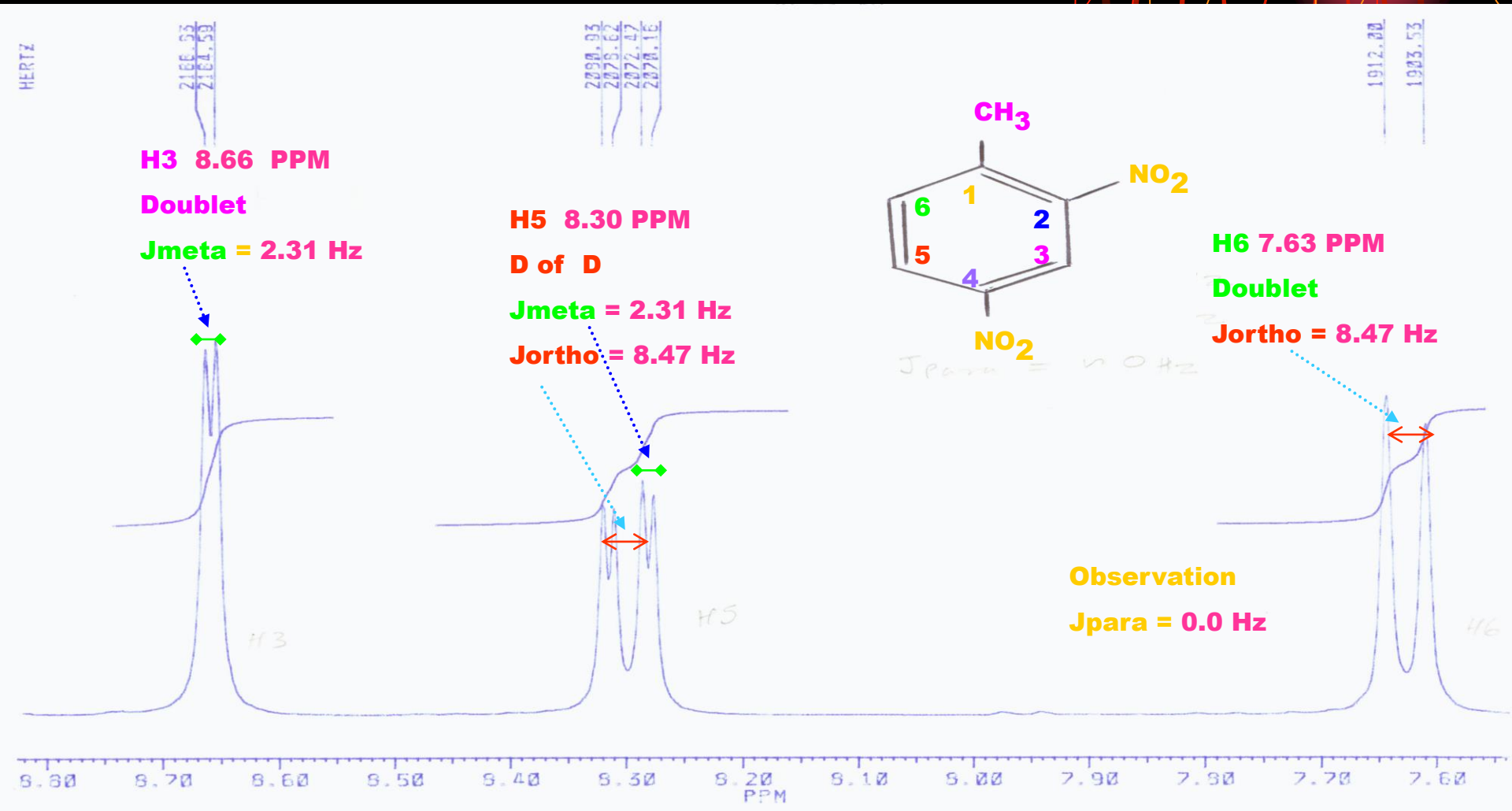


Expansion of aromatic region



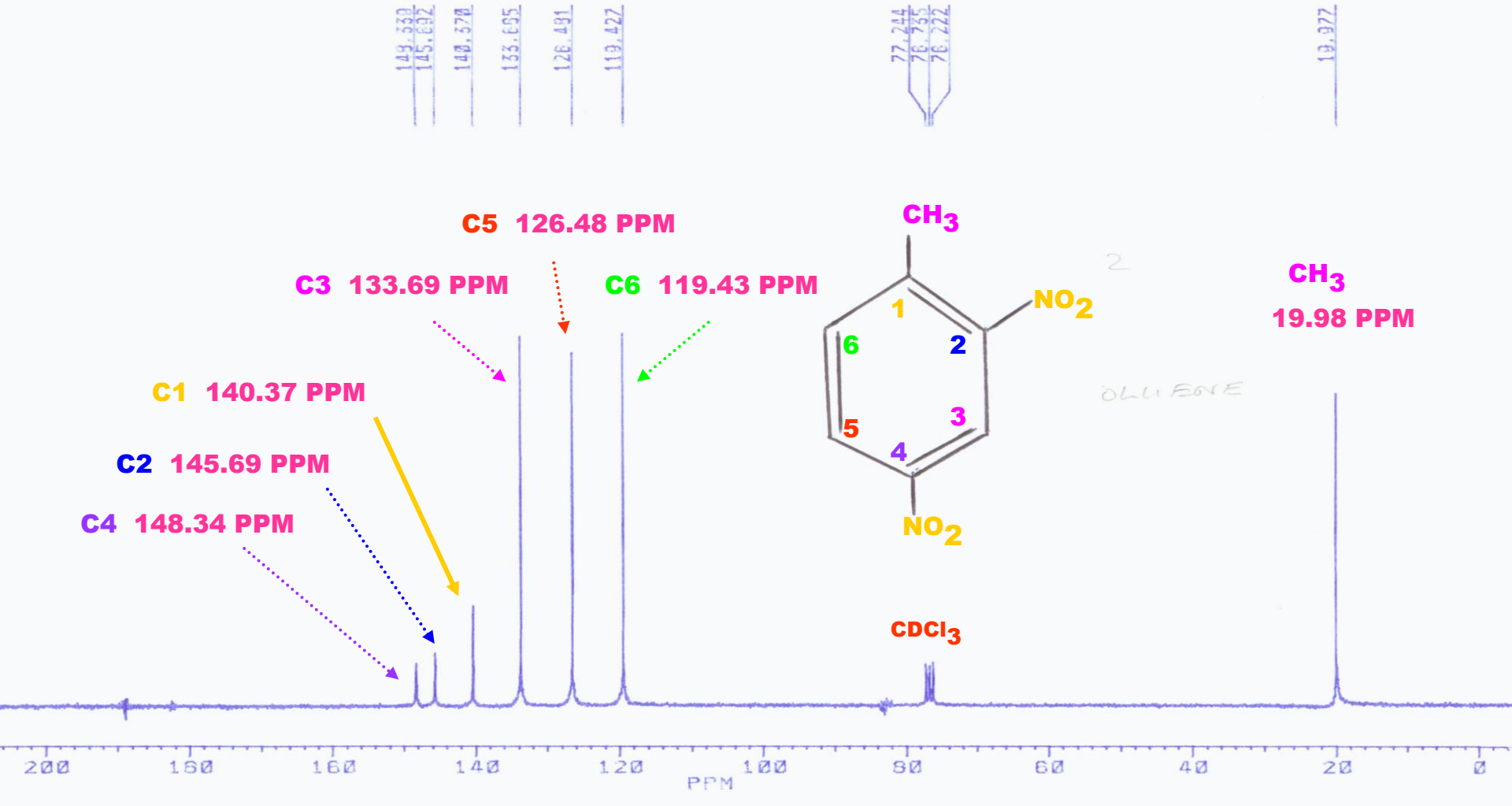
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 2,4-Dinitromethylbenzene

$C_6H_3CH_3(NO_2)_2$ ^{1}H NMR Spectrum



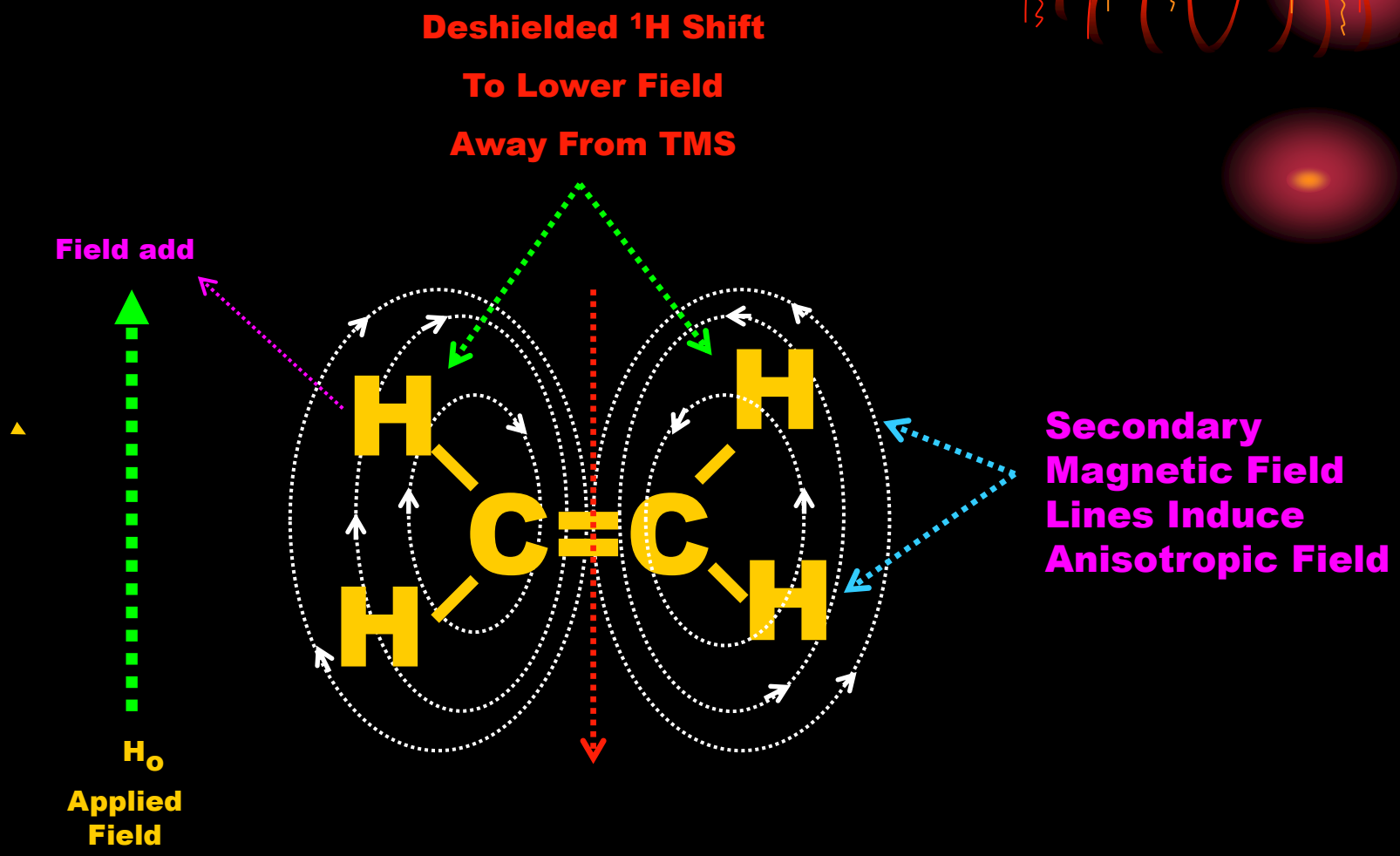
^{13}C NMR Spectra of 2,4-Dinitromethylbenzene

$C_6H_3CH_3(NO_2)_2$



Anisotropic Field in an Alkenes (SP^2)

- **Anisotropic Field Effect**

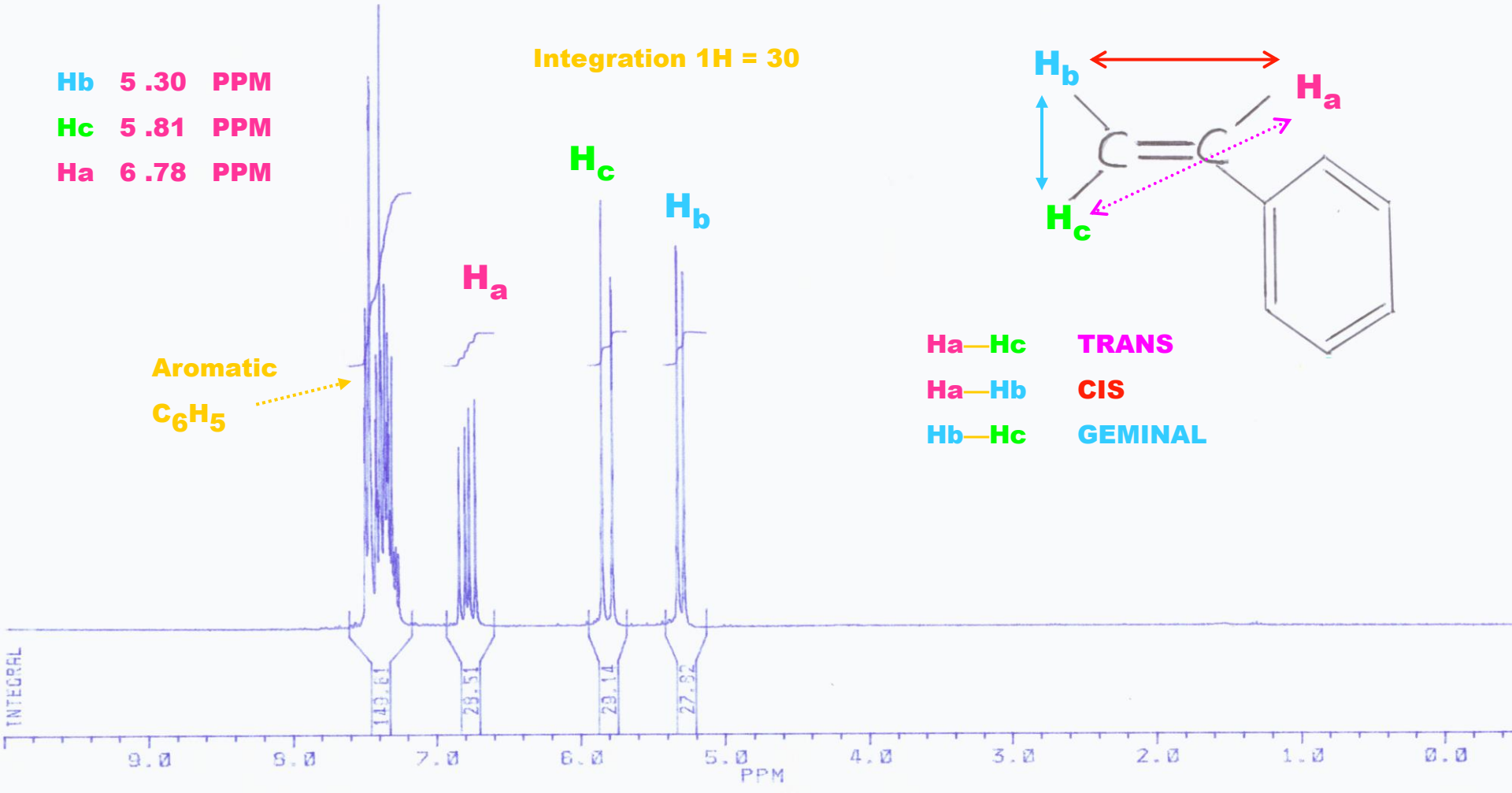


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Styrene

C_6H_5-CH=CH_2 ^{1}H NMR Spectrum

Hb 5 .30 PPM
Hc 5 .81 PPM
Ha 6 .78 PPM

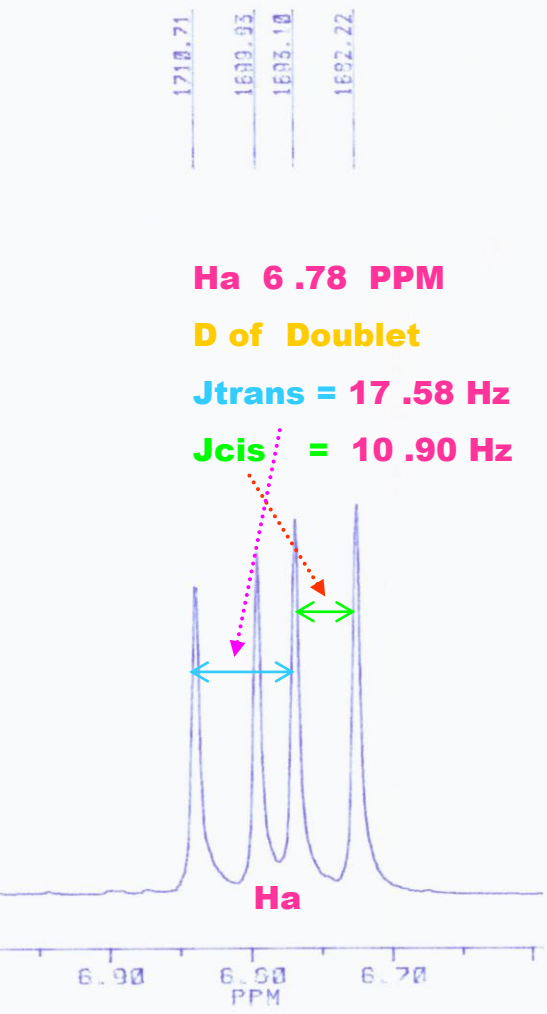
Integration 1H = 30

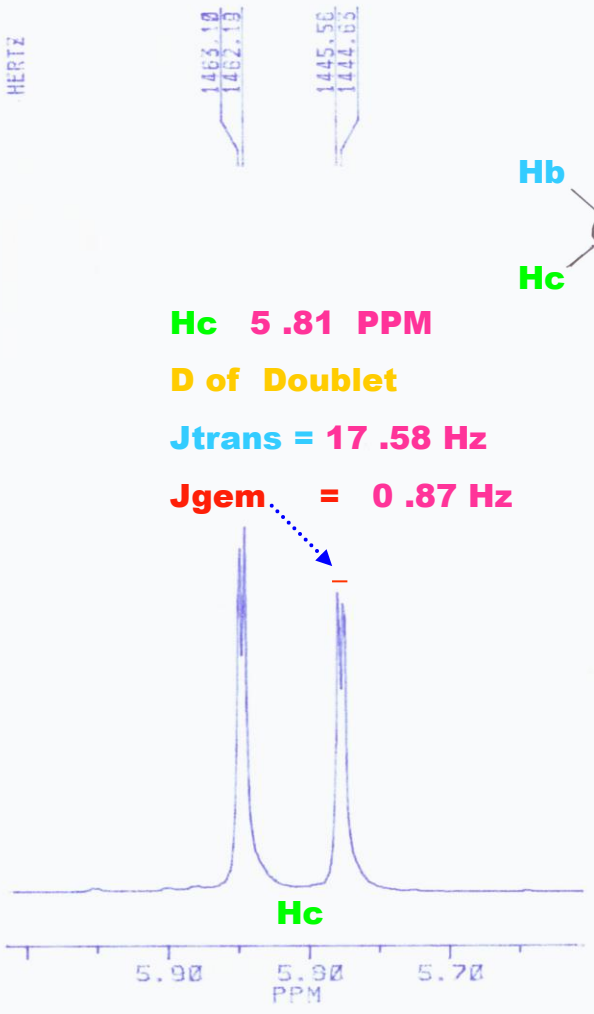


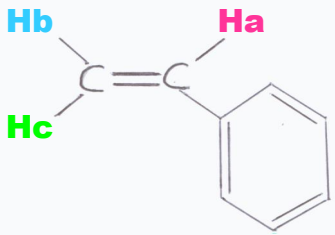
Ha—Hc TRANS
Ha—Hb CIS
Hb—Hc GEMINAL

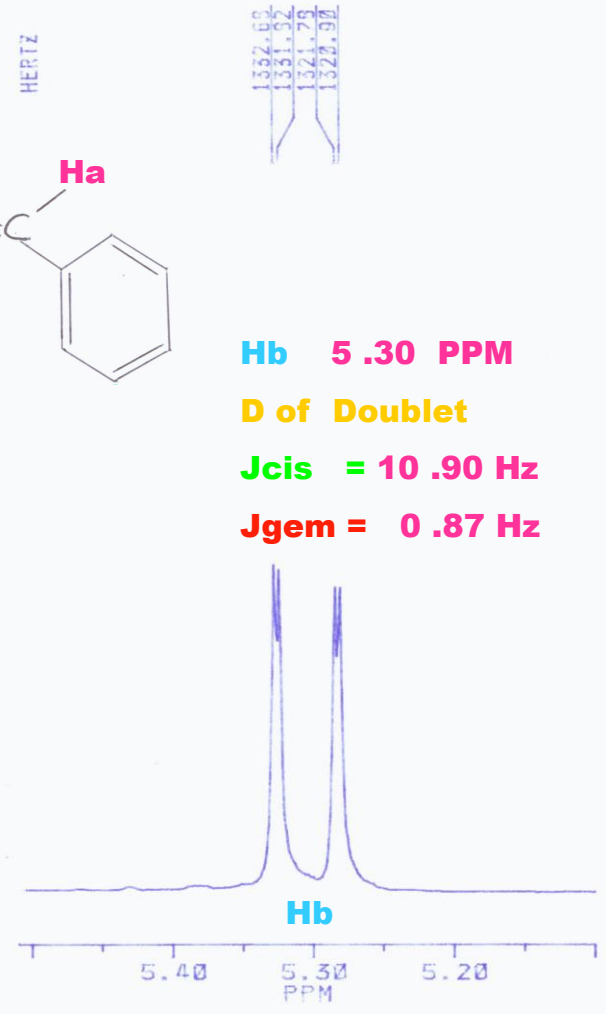
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Styrene

C_6H_5-CH=CH_2 ^{1}H NMR Spectrum



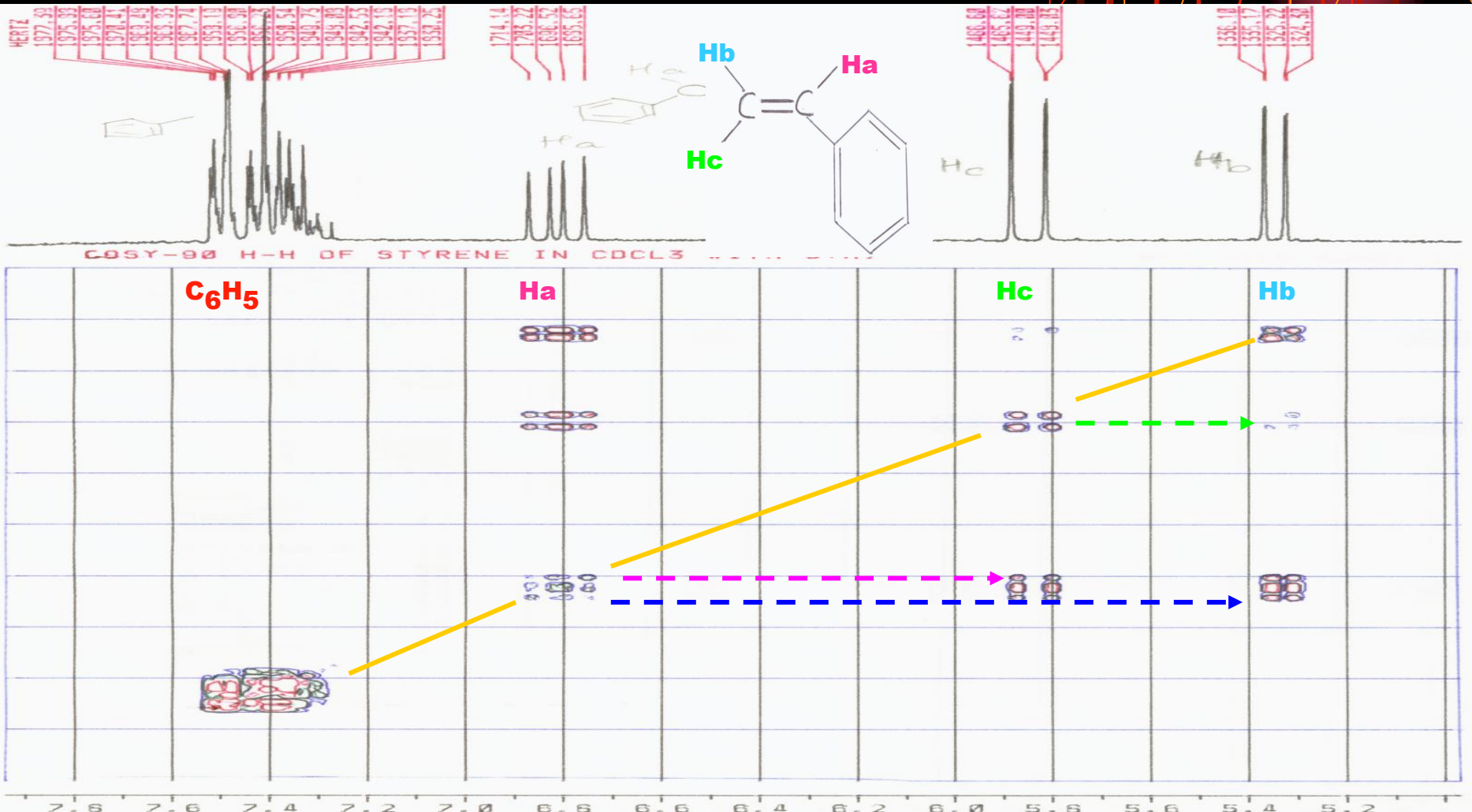


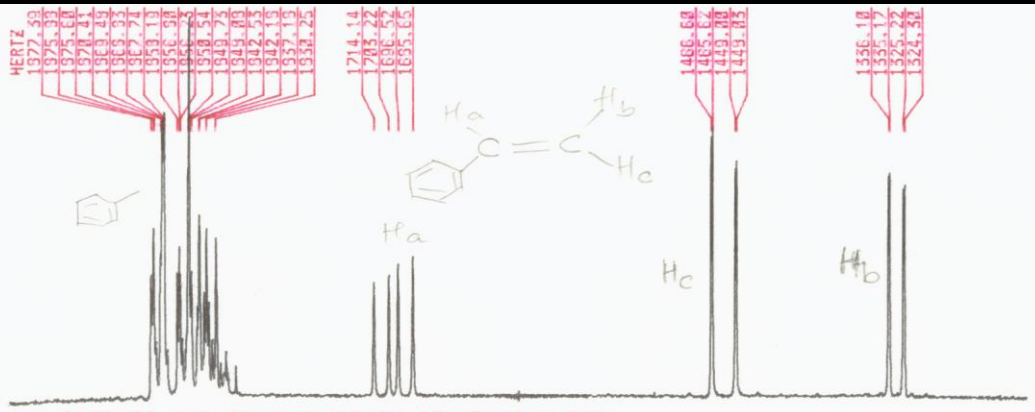


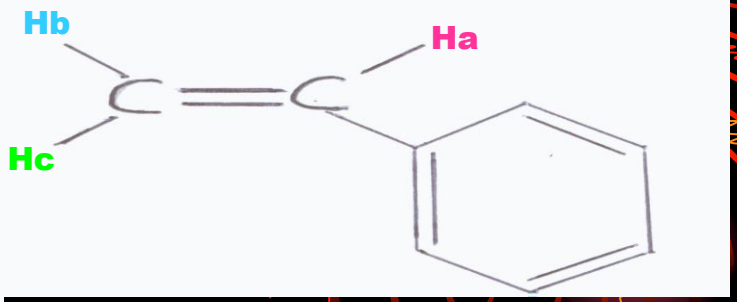


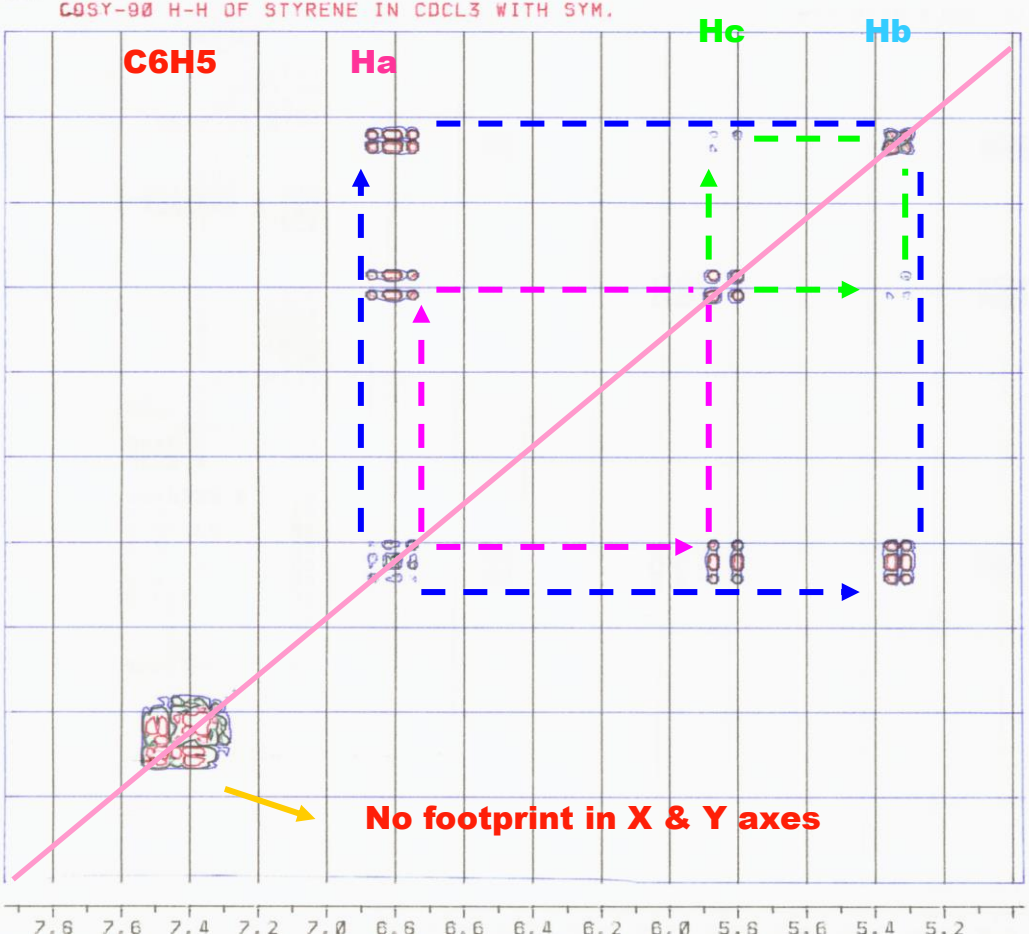
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Styrene

C_6H_5-CH=CH_2 2D COSY ^{1}H NMR Spectrum







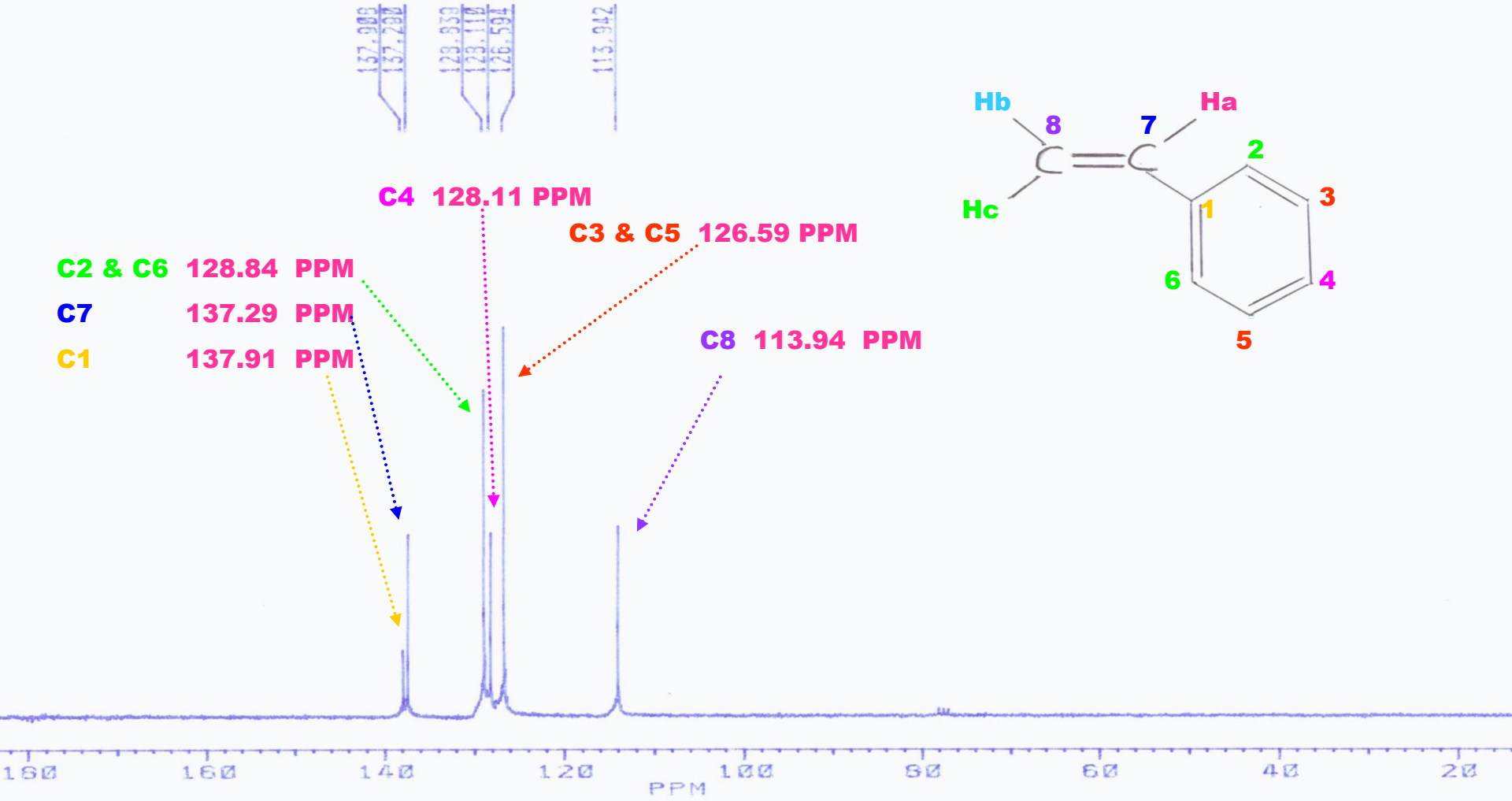


Analysis and interpretation of 2D COSY 90 1H NMR Spectrum of Styrene

C_6H_5-CH=CH_2

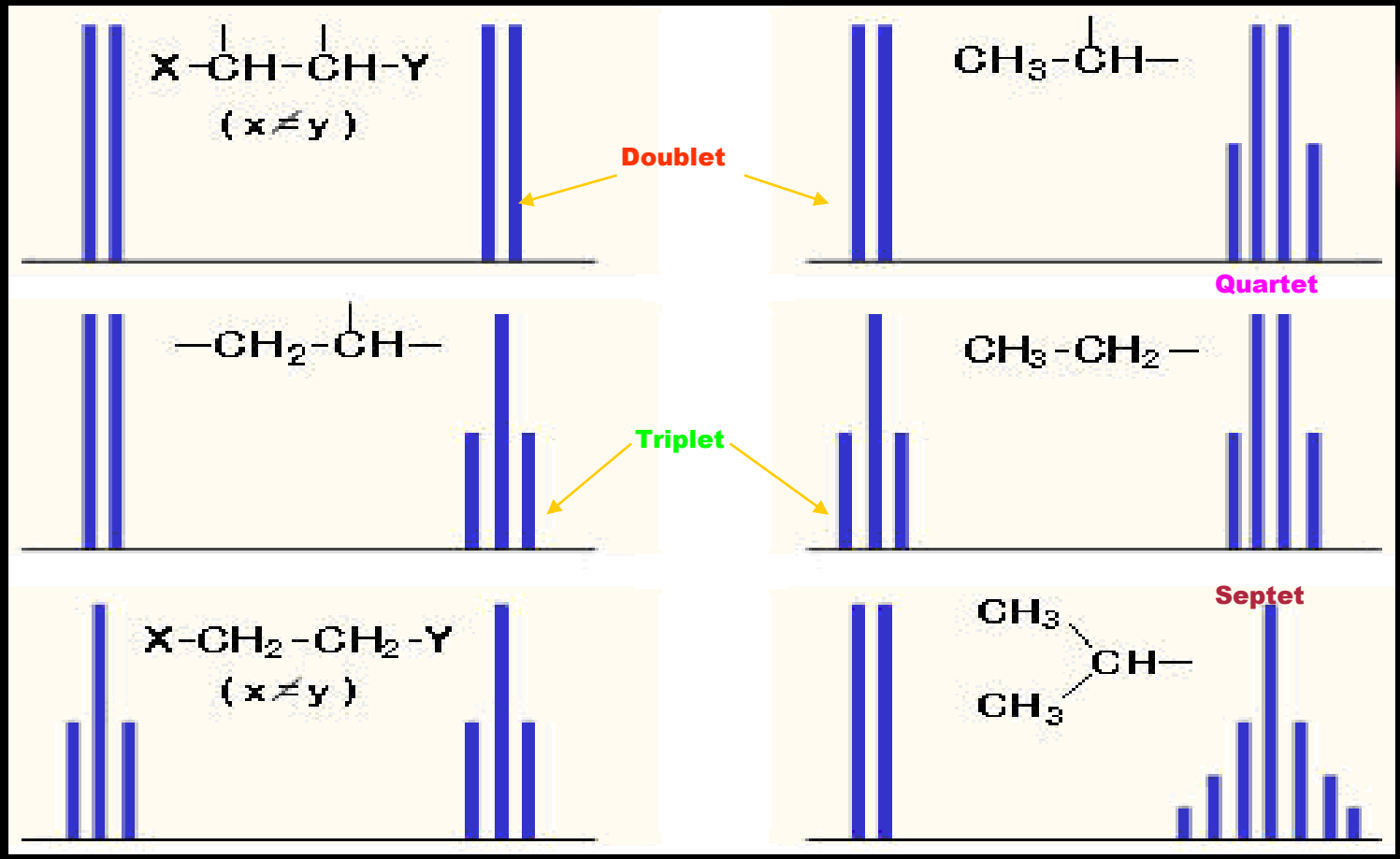
1. Every peak in spectrum gives the diagonal footprint in cosy spectrum.
2. Non coupled 1H gives only diagonal footprint and no footprint in X & Y axes.
3. Coupled 1H will give footprint in X & Y axes.
4. Number of coupling can be seen easily just by counting the number of footprints along either X or Y axis.
   In the Styrene Ha gives two footprints as shown by dashed arrows hence it is coupled to two 1H (Hb & Hc).
   Where as C6H5 give s no footprint in X & Y axes hence they are not coupled to any other 1H (Ha, Hb or Hc).
5. Aromatic region is complex to analyse.

Analysis and interpretation of ^{13}C NMR Spectrum of Styrene C_6H_5-CH=CH_2



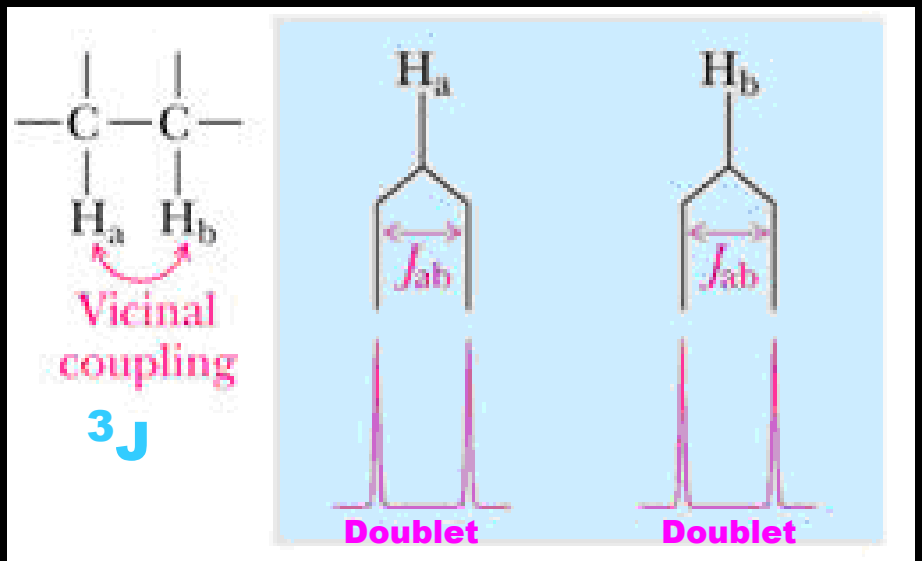
Splitting Patterns for Aliphatic ^1H

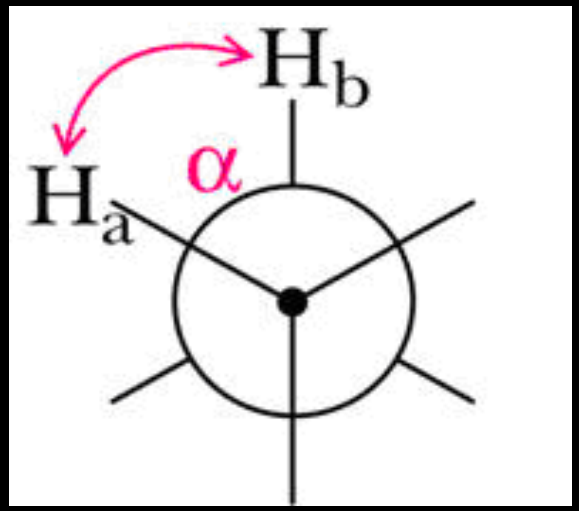
Common Patterns in ^1H NMR Spectra



Notation For Coupling Constant (^1J ^2J, ^3J, ^4J & so on)

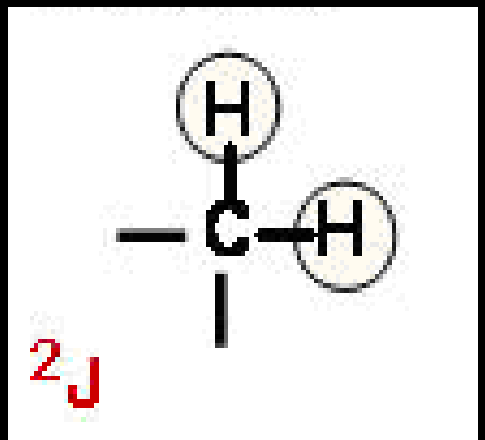
- In ^1H NMR spectra, the most common coupling constant is encountered ^1H three bonds apart ^3J. This is also called as Vicinal Coupling.
- The angle alpha factor in vicinal coupling.
- When angle alpha = 0^0 and 180^0 The coupling constant is maximum
- = 90^0 The coupling constant is minimum

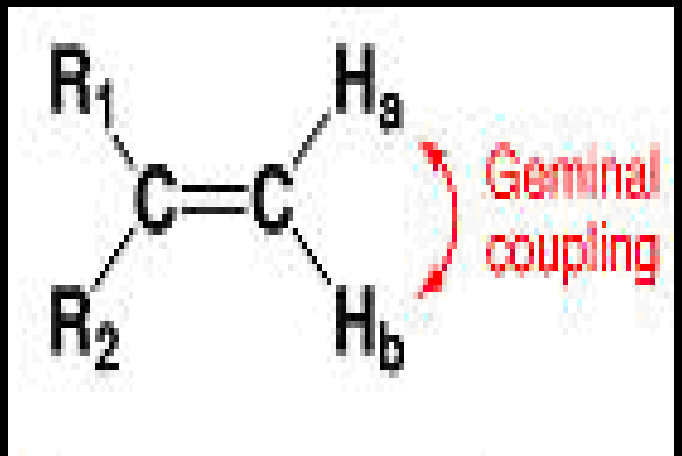




^2J coupling constant

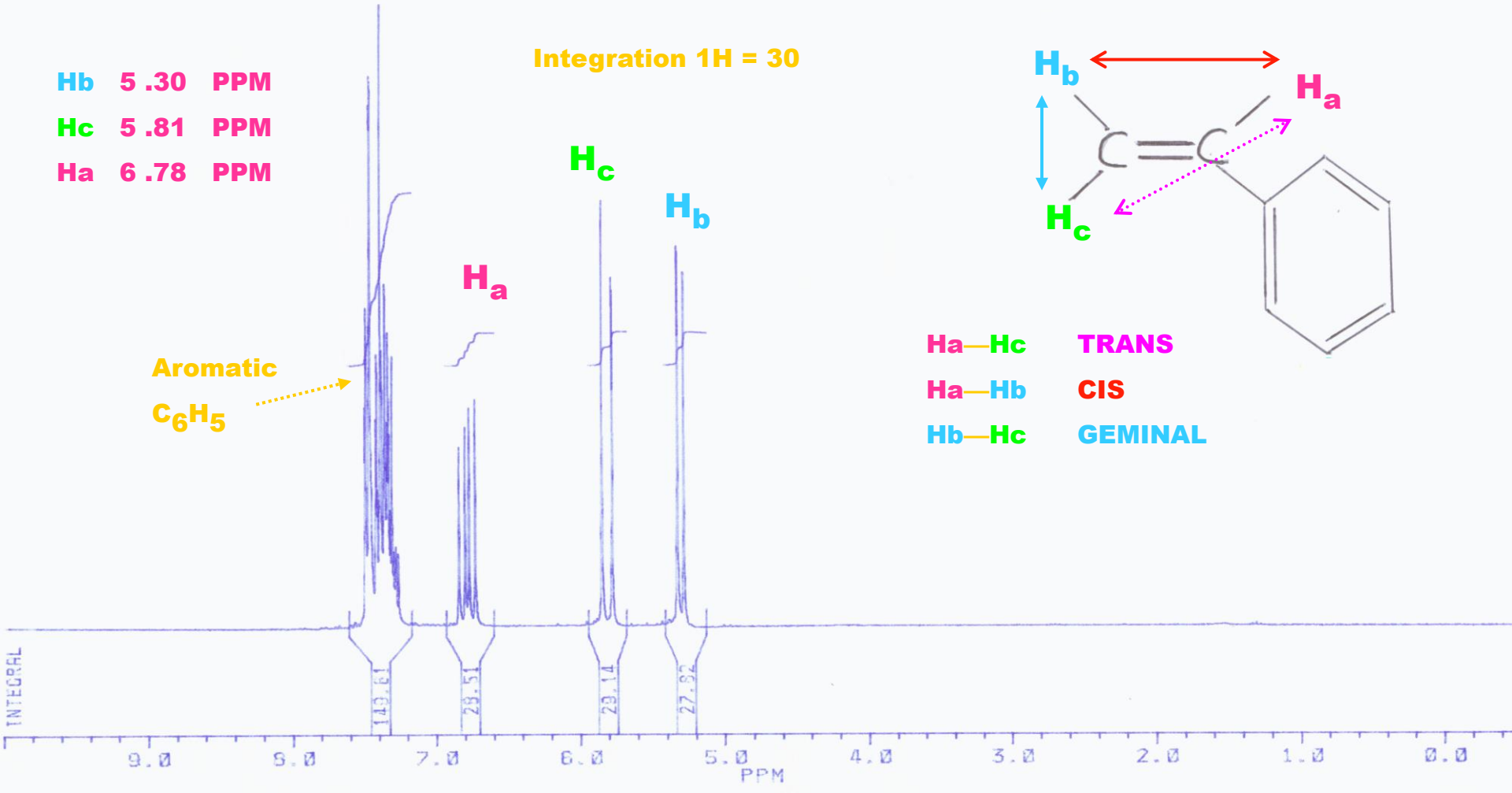
- The alpha angle H—C—C—H and the rotation round
- --C—C-- sigma bonds is also a key parameter for ^1H coupling constant.
- In Ethyl CH_3—CH_2— Group the free rotation make ^1H attached to the same carbon equivalent hence do not show coupling ^2J = 00 Hz
- In alkenes and cyclic compounds the sigma bonds rotation restricted, this may give rise the ^1H attached to the same carbon becomes non-equivalent hence couples to each other.
- This coupling is called Geminal Coupling and denoted by ^2J
- On the next slide shows the Vinylic ^1H interactions in Styrene





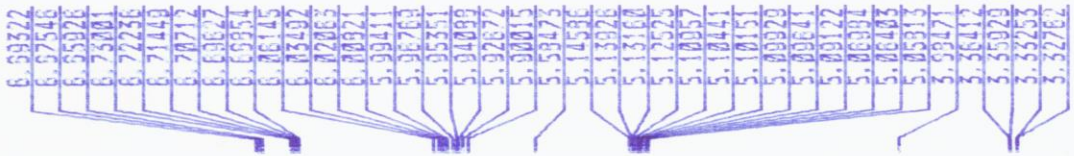
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Styrene

C_6H_5-CH=CH_2 ^{1}H NMR Spectrum

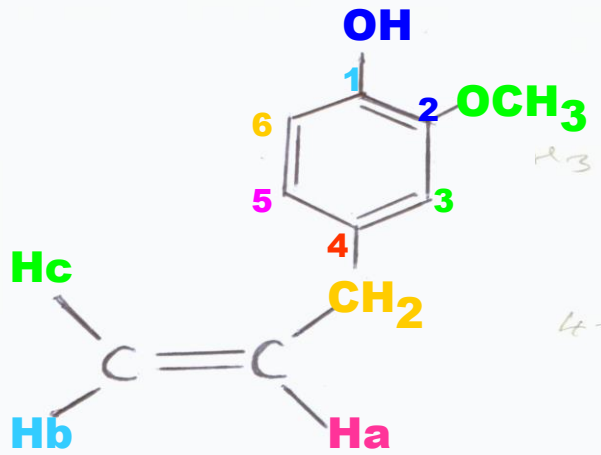


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 4-Allyl-2-MethoxyPhenol

$C_6H_3(OH)(OCH_3)(CH_2\text{-}CH{=}CH_2)$ ^{1}H NMR Spectrum



Integration 1H = 3



Hb & Hc 5.10 PPM

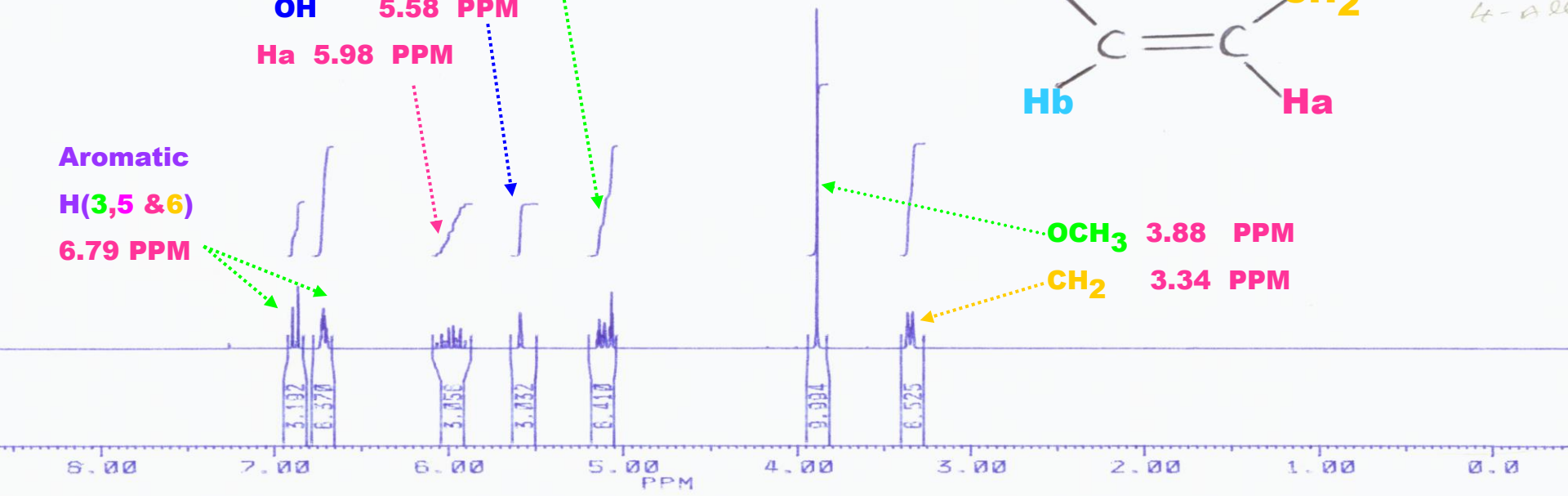
OH 5.58 PPM

Ha 5.98 PPM

Aromatic H(3,5 &6) 6.79 PPM

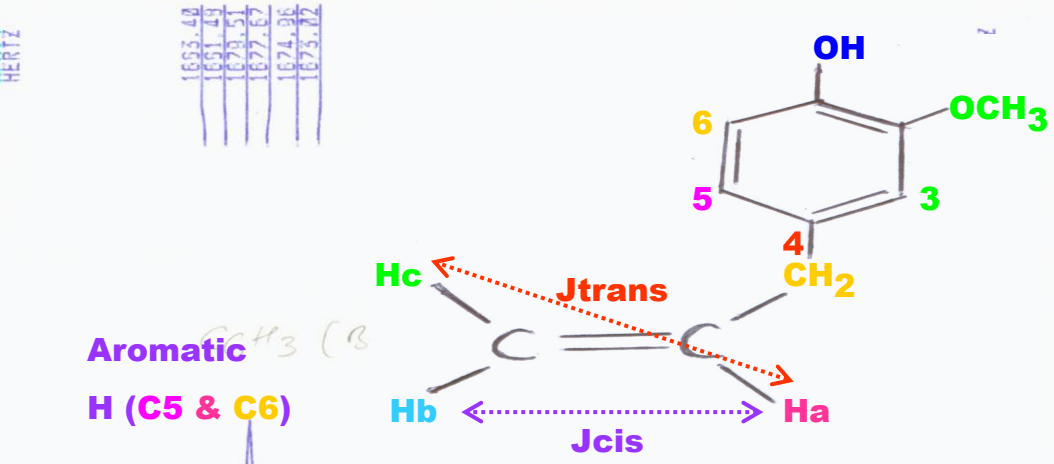
OCH_3 3.88 PPM

CH_2 3.34 PPM

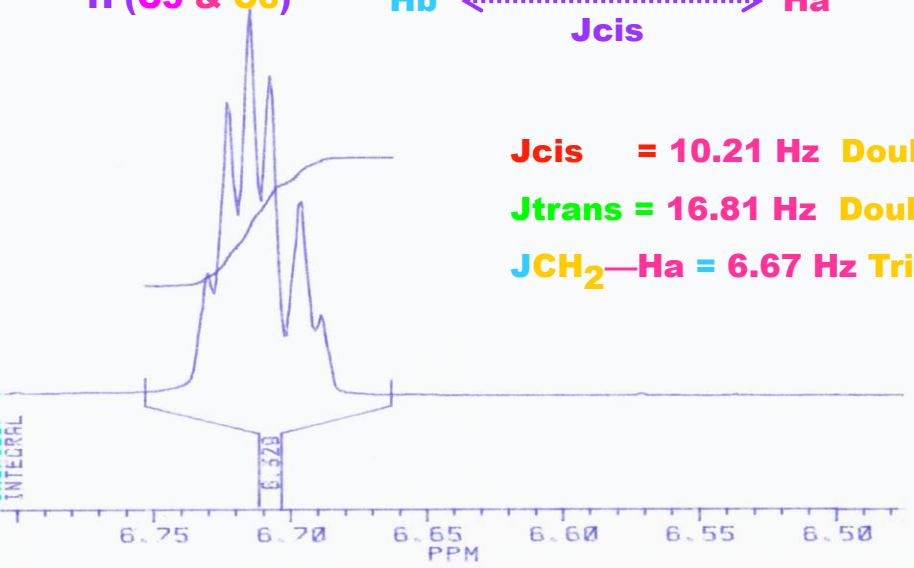


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 4-Allyl-2-MethoxyPhenol

$C_6H_3(OH)(OCH_3)(CH_2\text{-}CH{=}CH_2)$ ^{1}H NMR Spectrum



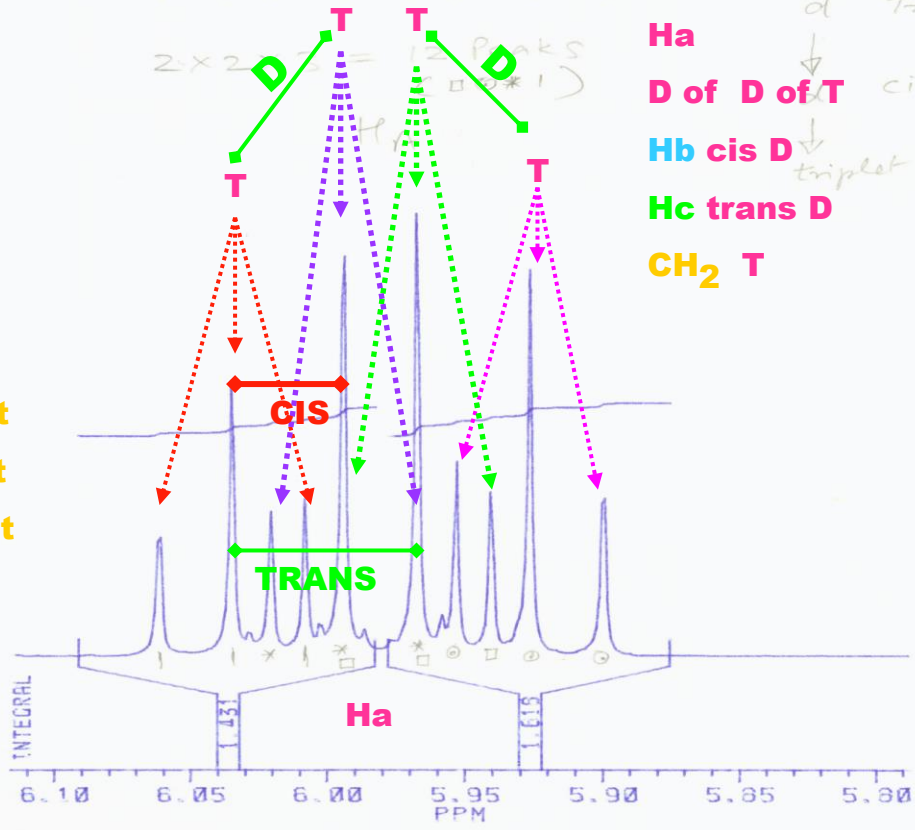
Aromatic H (C5 & C6)



Jcis = 10.21 Hz Doublet

Jtrans = 16.81 Hz Doublet

JCH_2—Ha = 6.67 Hz Triplet



Ha

D of D of T

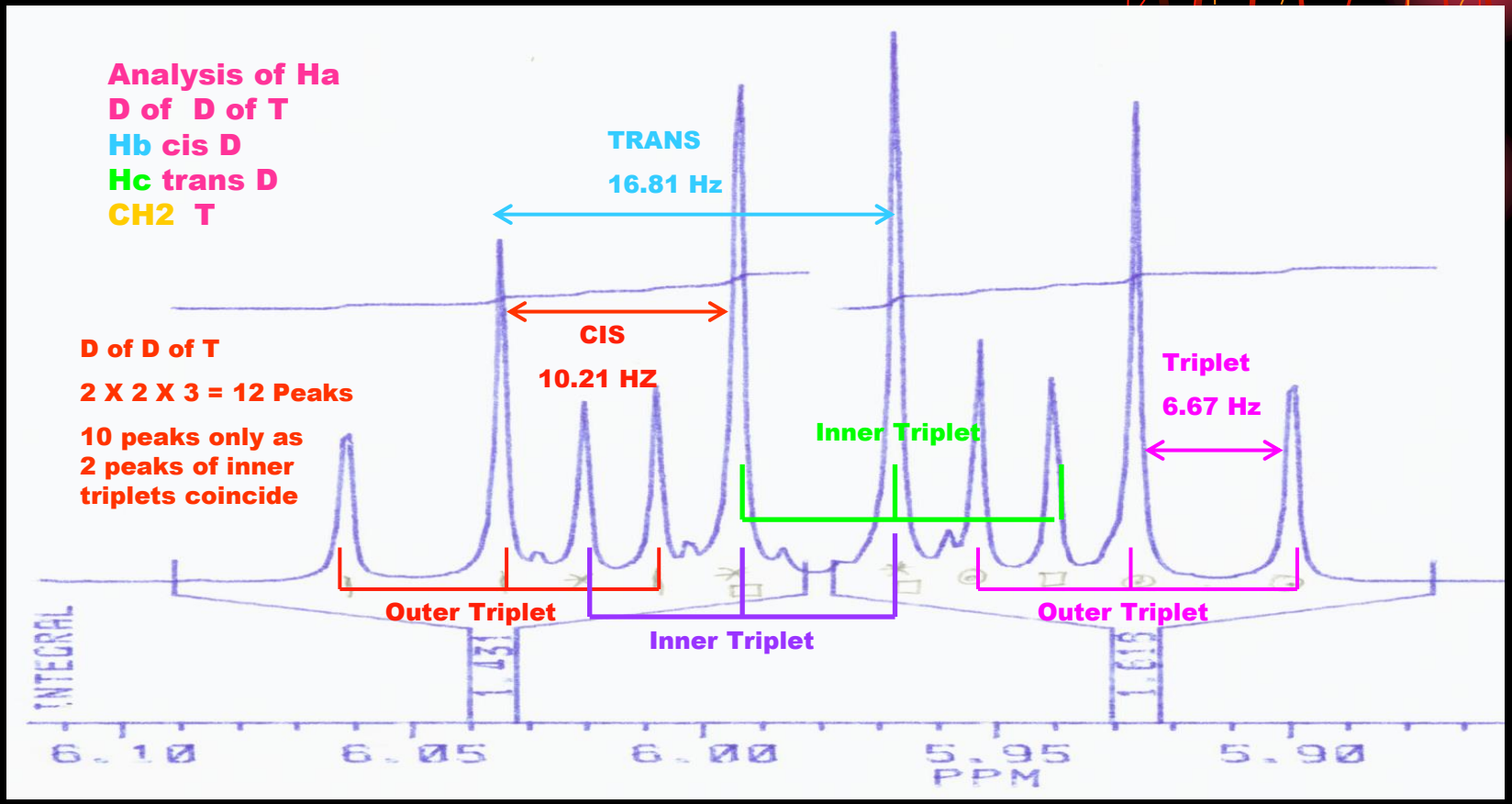
Hb cis D

Hc trans D

CH_2 T

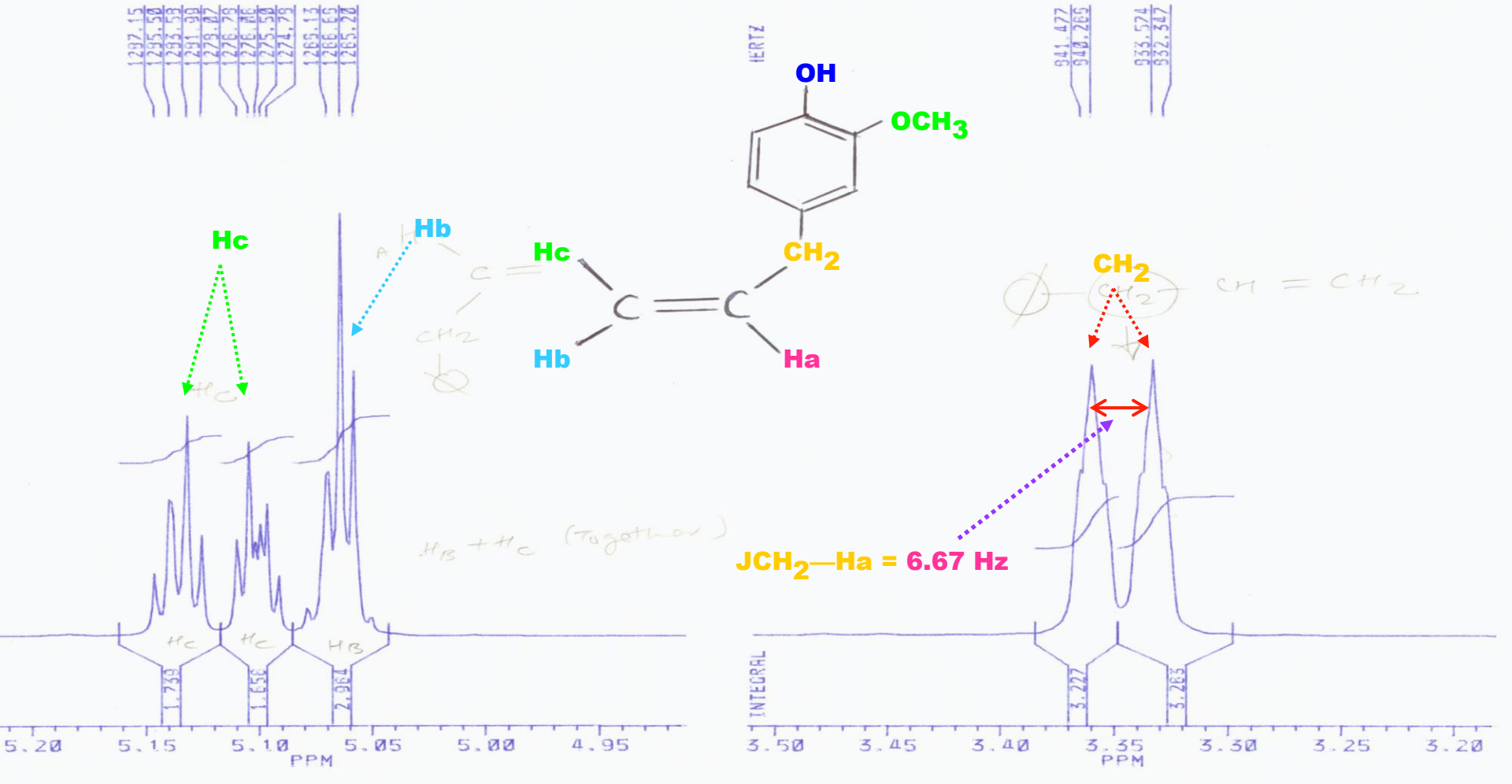
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 4-Allyl-2-MethoxyPhenol

$C_6H_3(OH)(OCH_3)(CH_2\text{-}CH{=}CH_2)$ ^{1}H NMR Spectrum



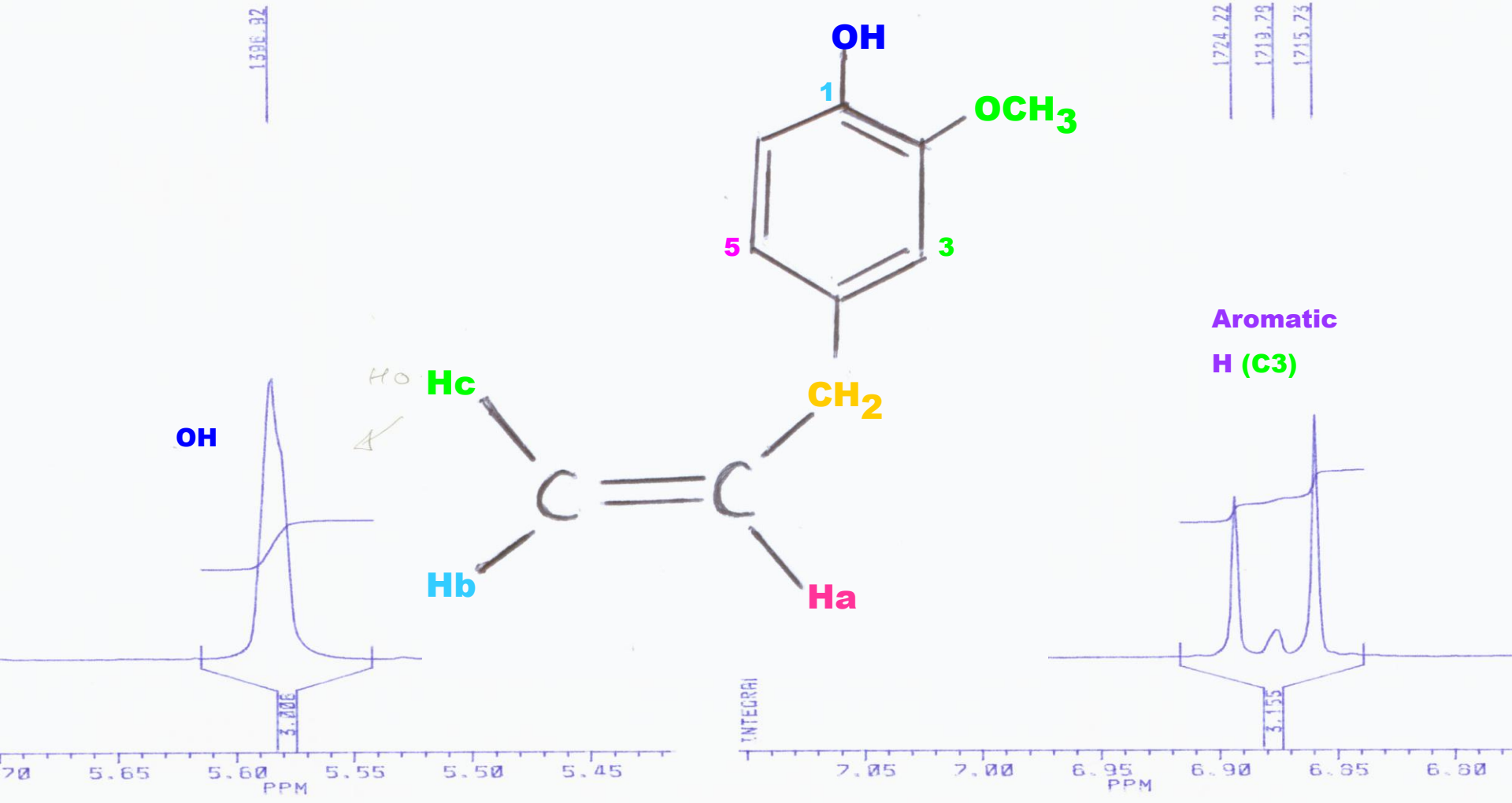
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 4-Allyl-2-MethoxyPhenol

$C_6H_3(OH)(OCH_3)(CH_2\text{-}CH{=}CH_2)$ ^{1}H NMR Spectrum



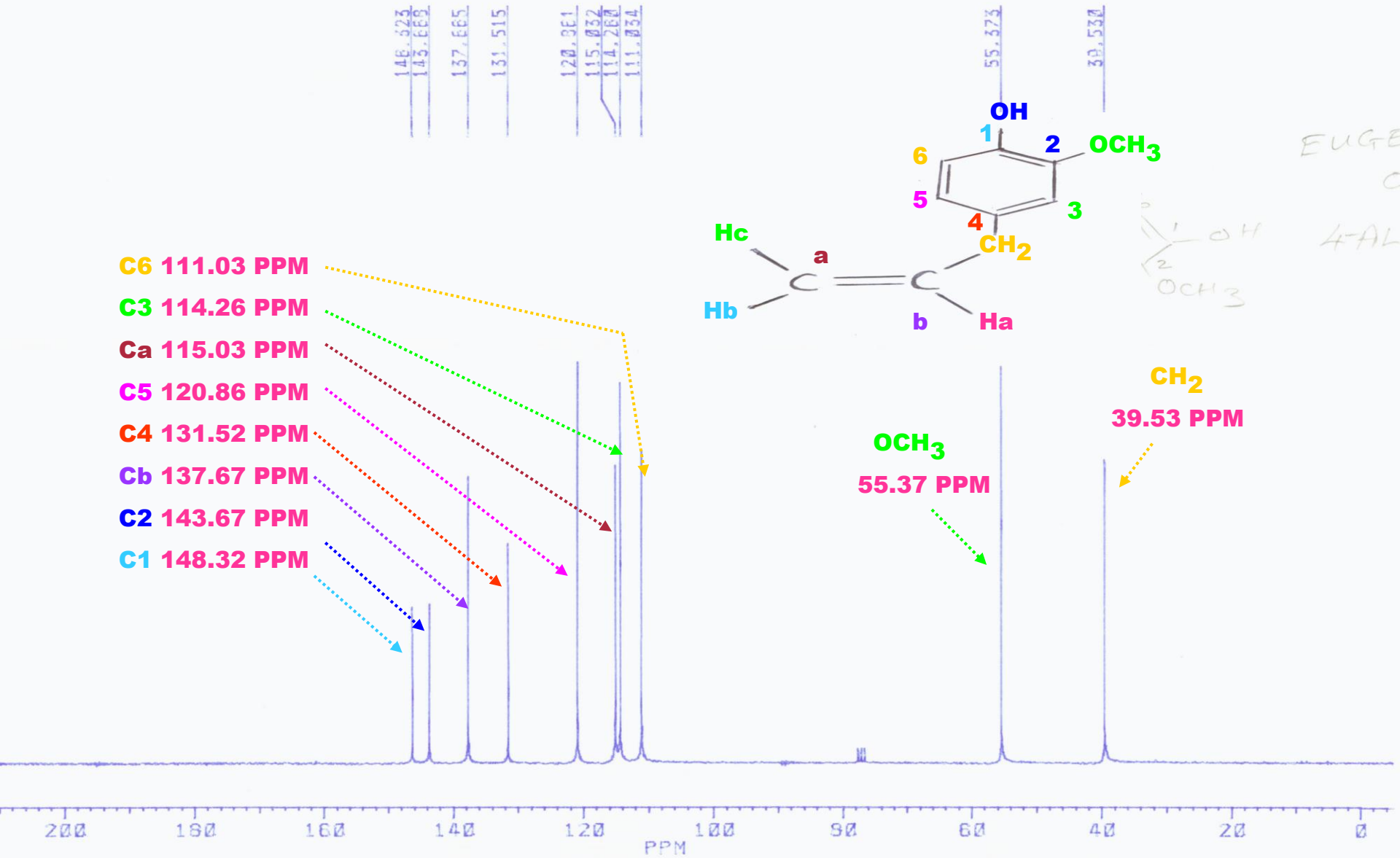
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Eugenol

^{1}H NMR Spectrum



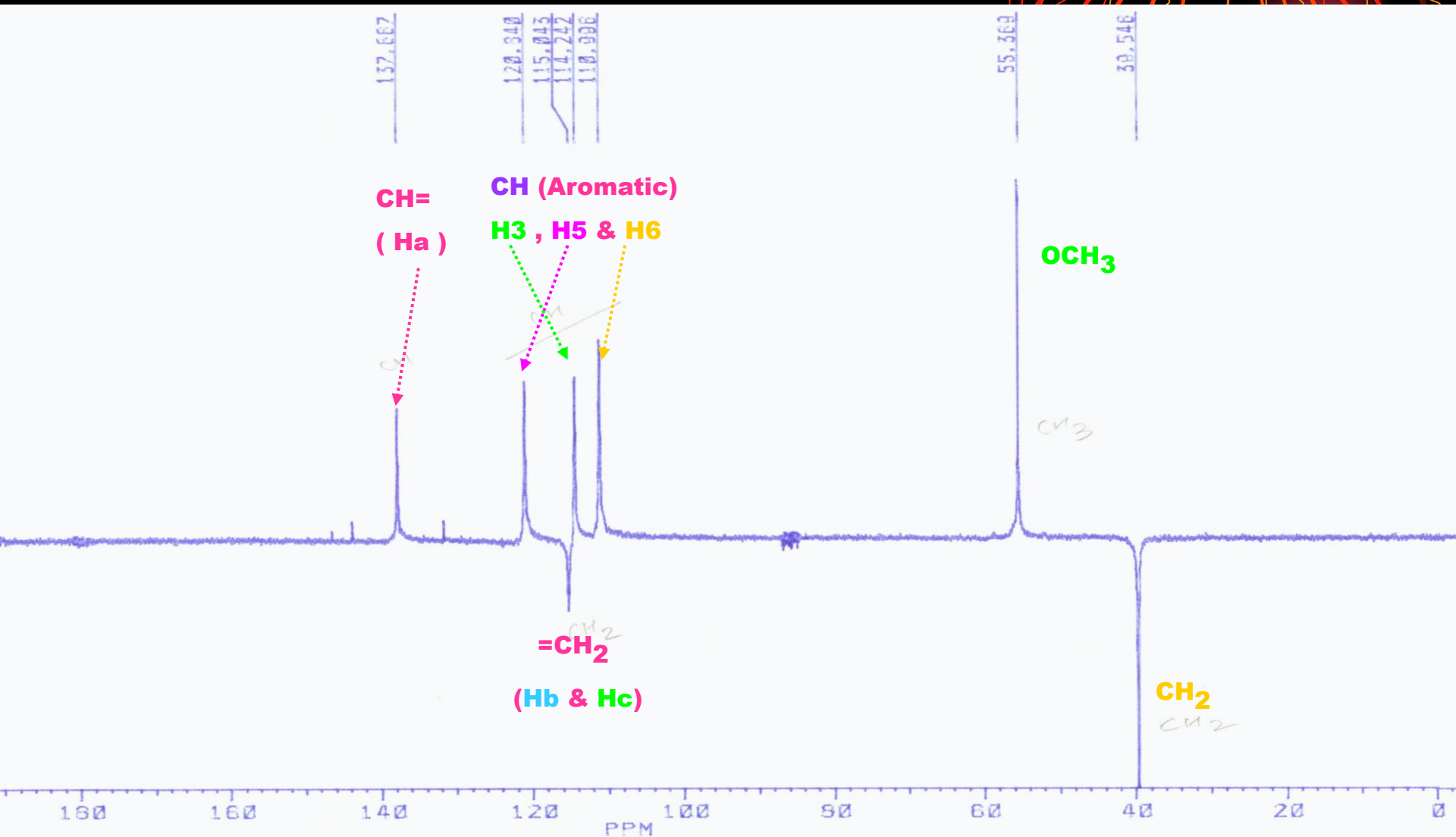
^{13}C NMR Spectrum of Eugenol.

4-Allyl-2-MethoxyPhenol



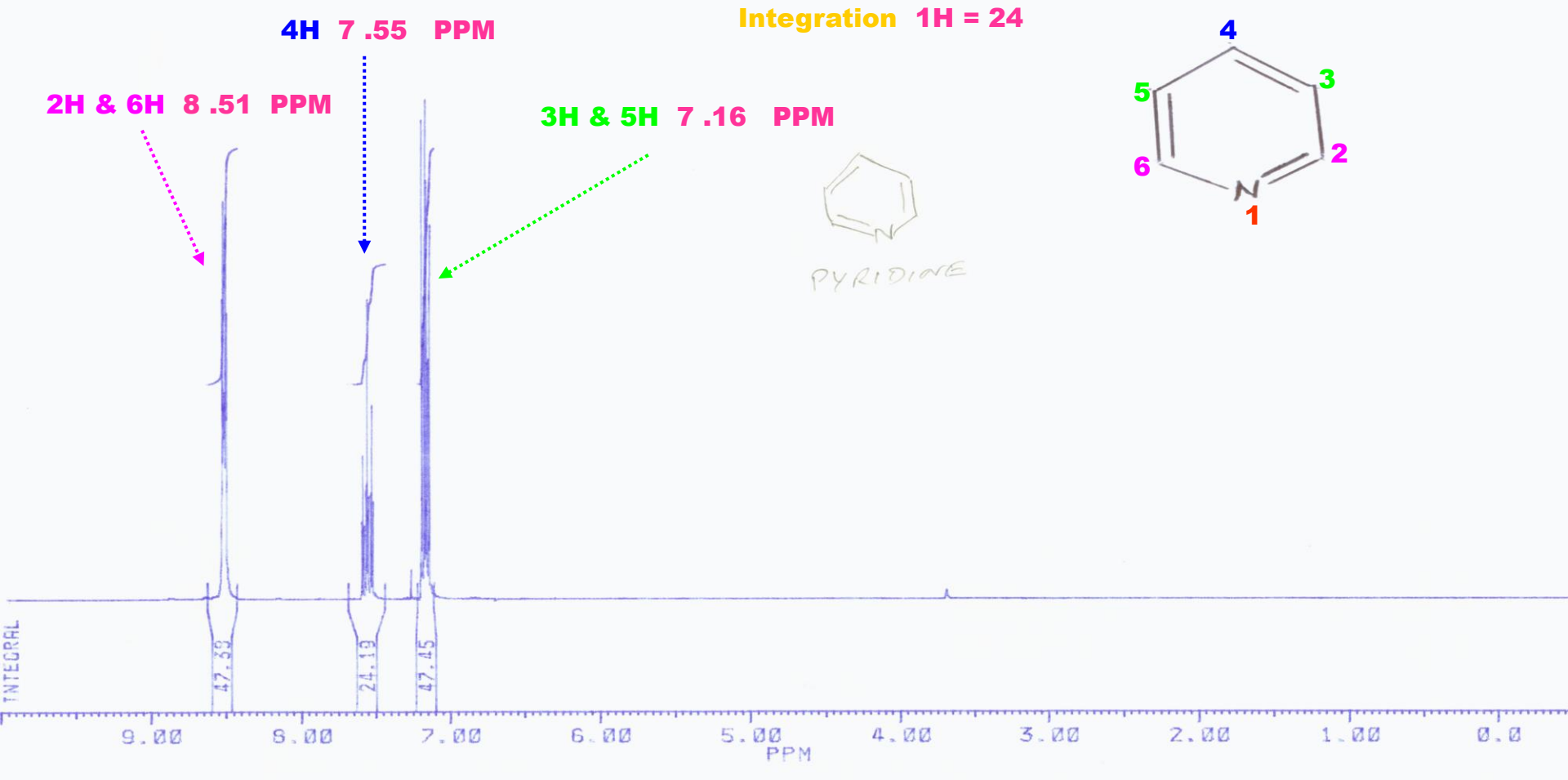
13C Dept 135 of 4-Allyl-2-MethoxyPhenol

$C_6H_3(OH)(OCH_3)(CH_2\text{-}CH{=}CH_2)$

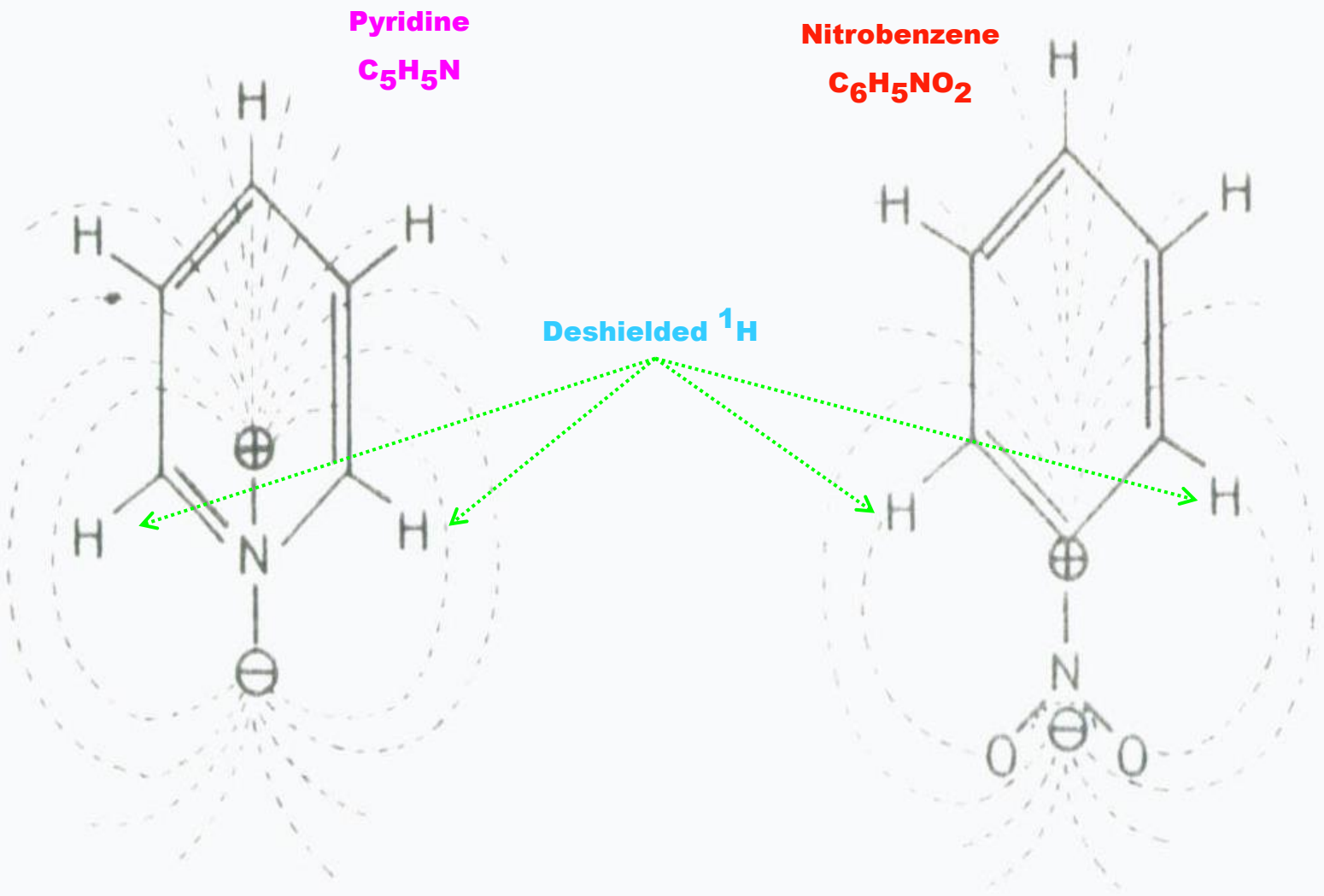


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Pyridine

C_5H_5N ^{1}H NMR Spectrum

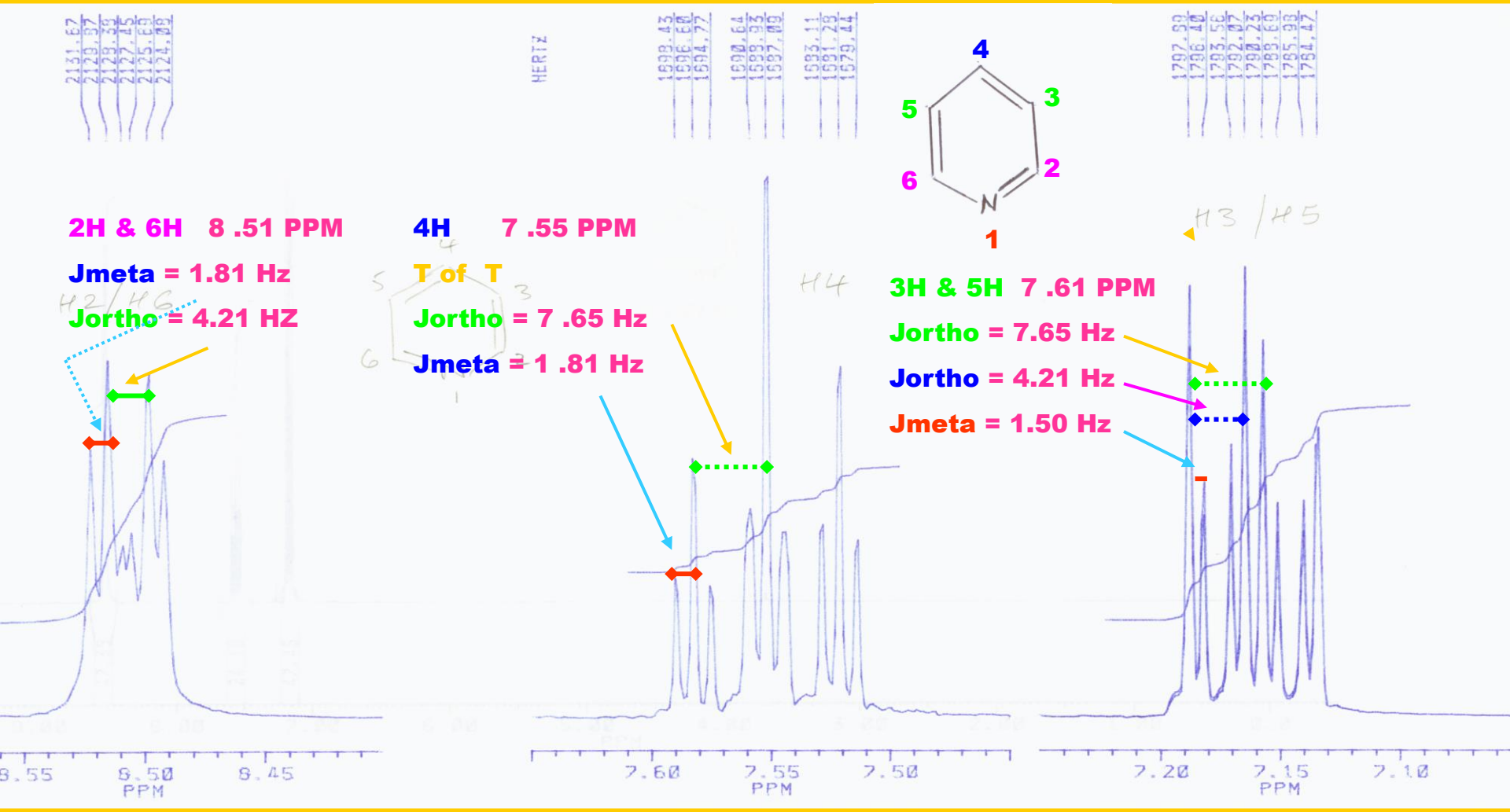


The Electric Field Effect on Pyridine & Nitrobenzene

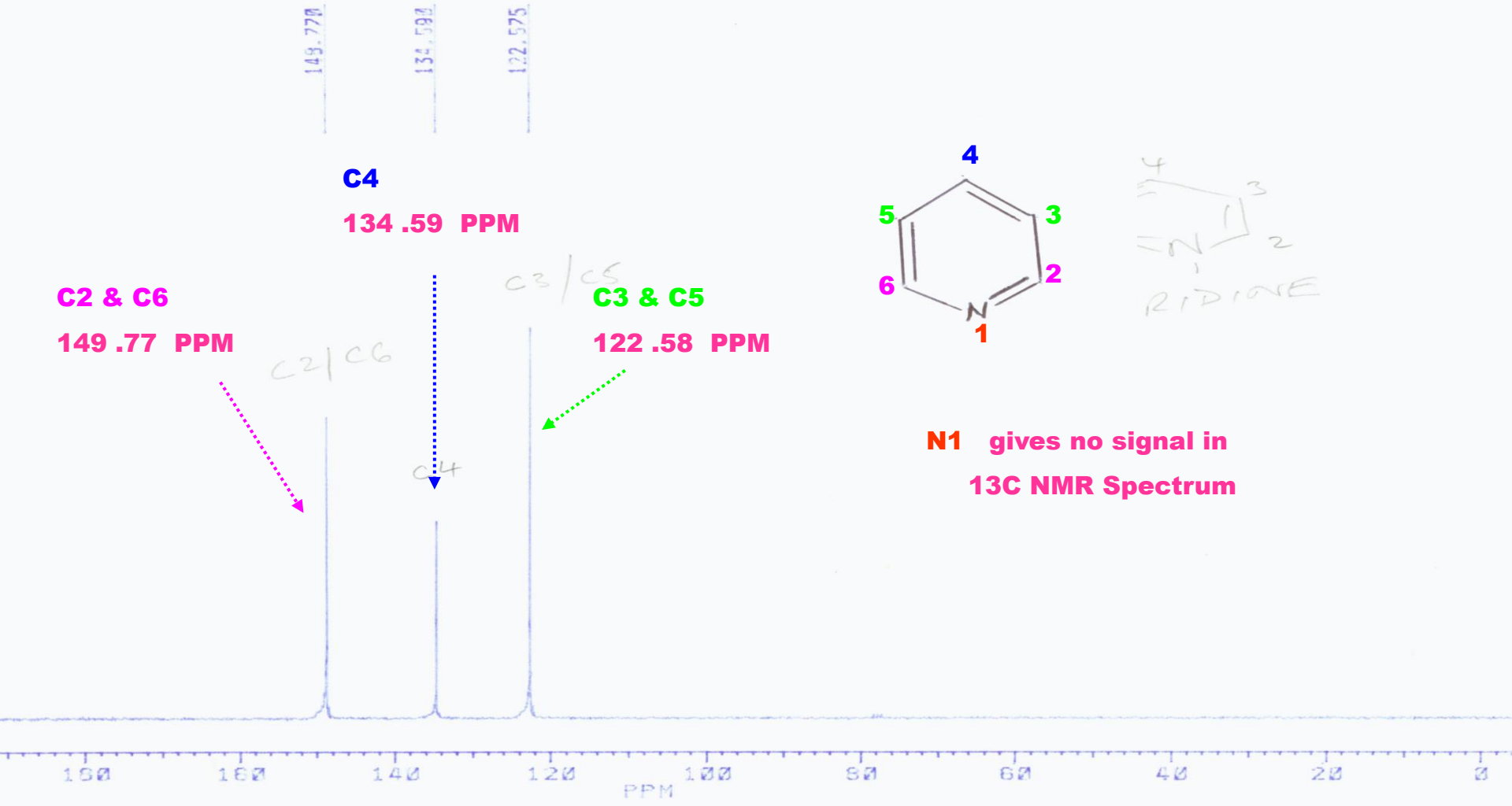


Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Pyridine

C_5H_5N ^{1}H NMR Spectrum Expansion



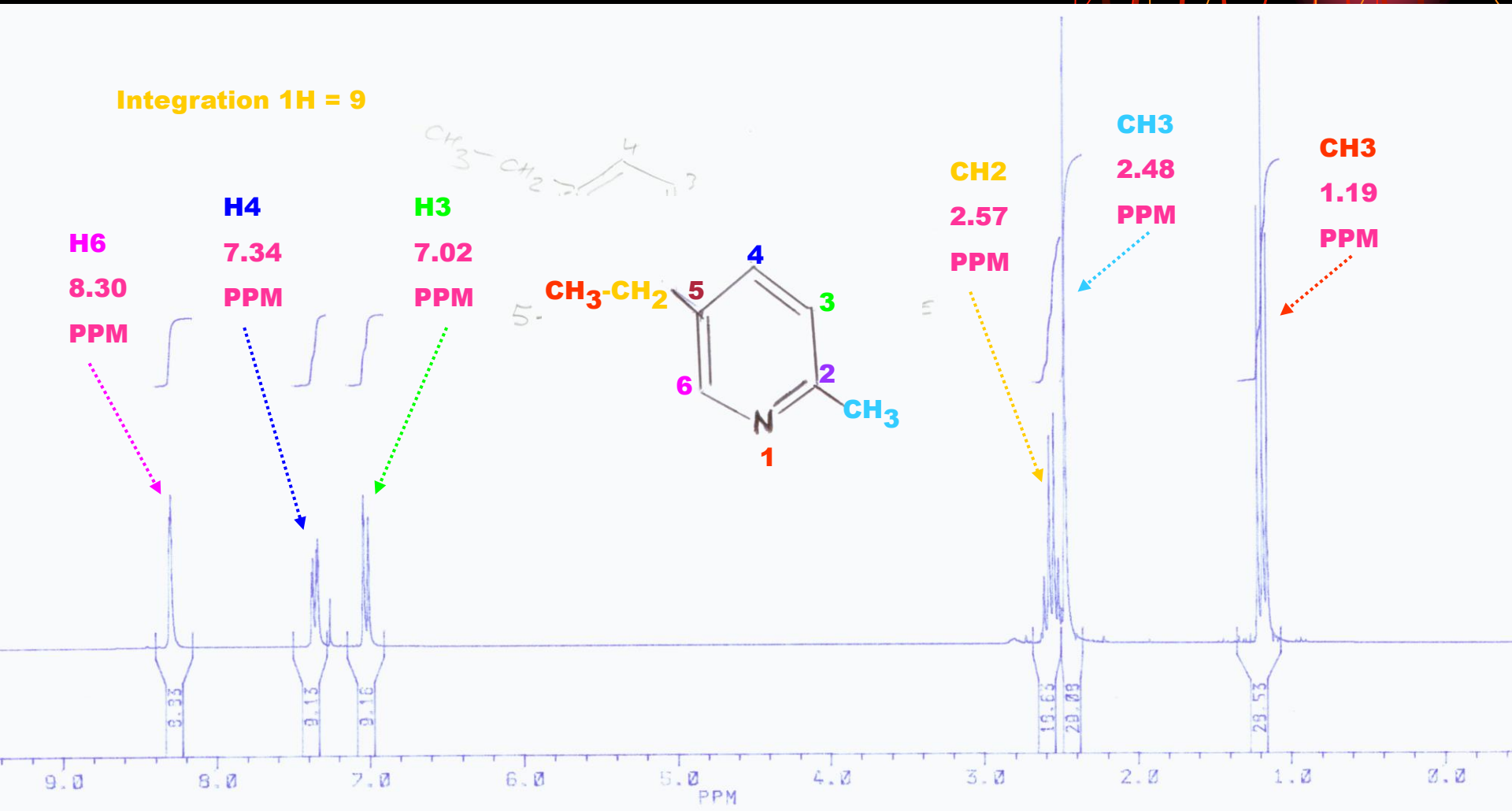
Analysis and interpretation of ^{13}C NMR Spectrum of Pyridine C_5H_5N



N1 gives no signal in 13C NMR Spectrum

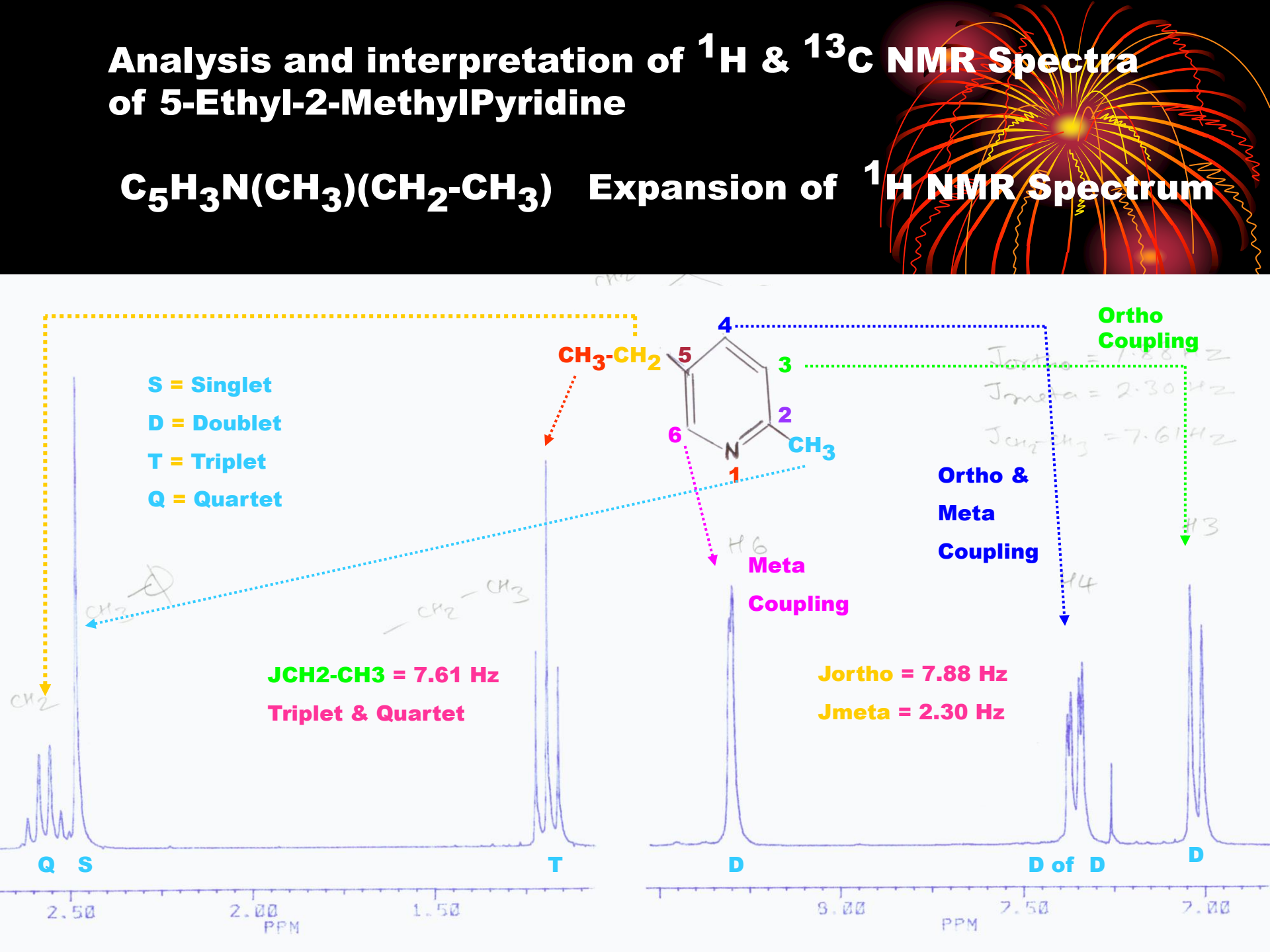
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 5-Ethyl-2-MethylPyridine

$C_5H_3N(CH_3)(CH_2\text{-}CH_3)$ ^{1}H NMR Spectrum



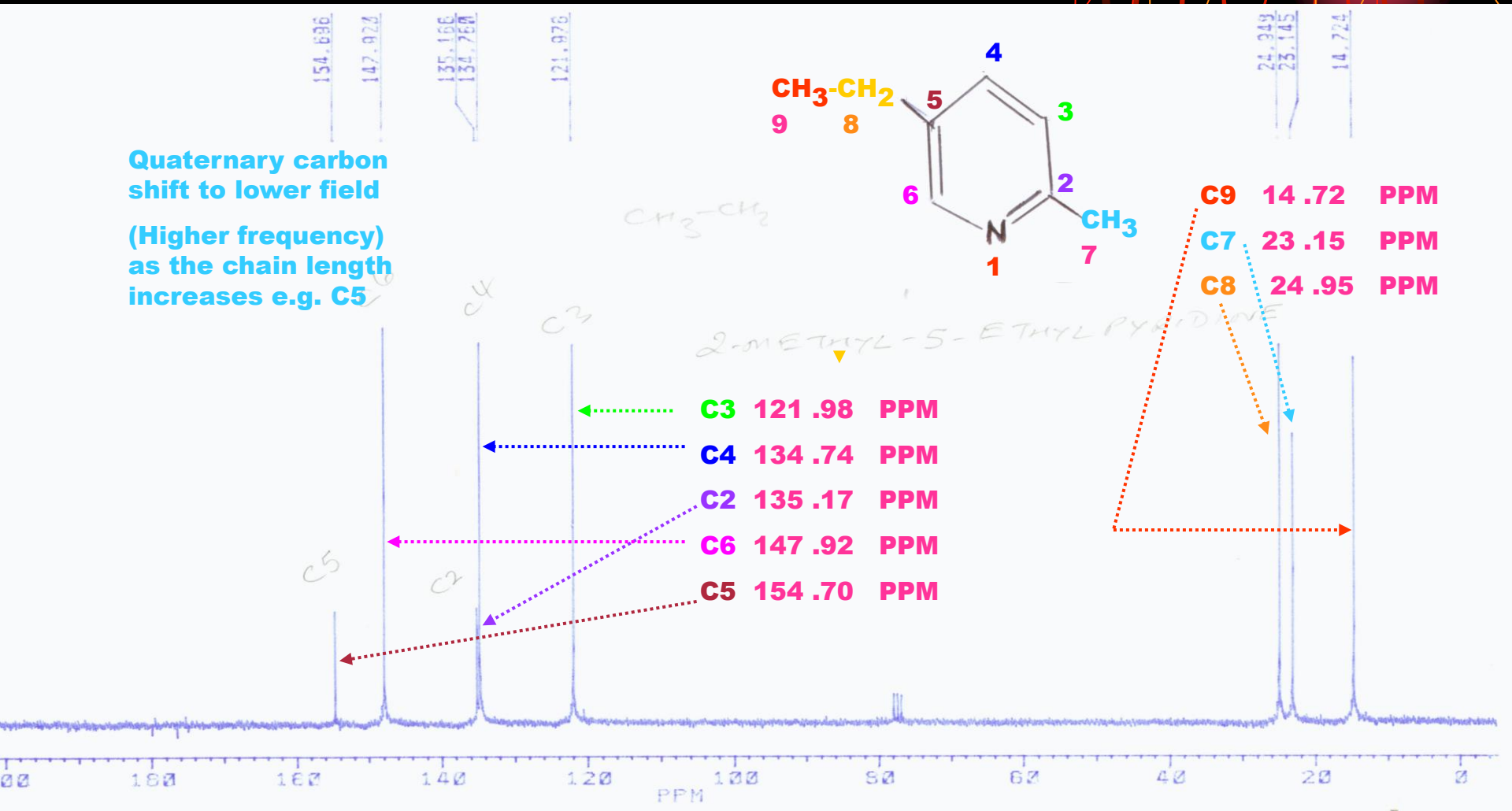
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 5-Ethyl-2-MethylPyridine

$C_5H_3N(CH_3)(CH_2\text{-}CH_3)$ Expansion of ^{1}H NMR Spectrum



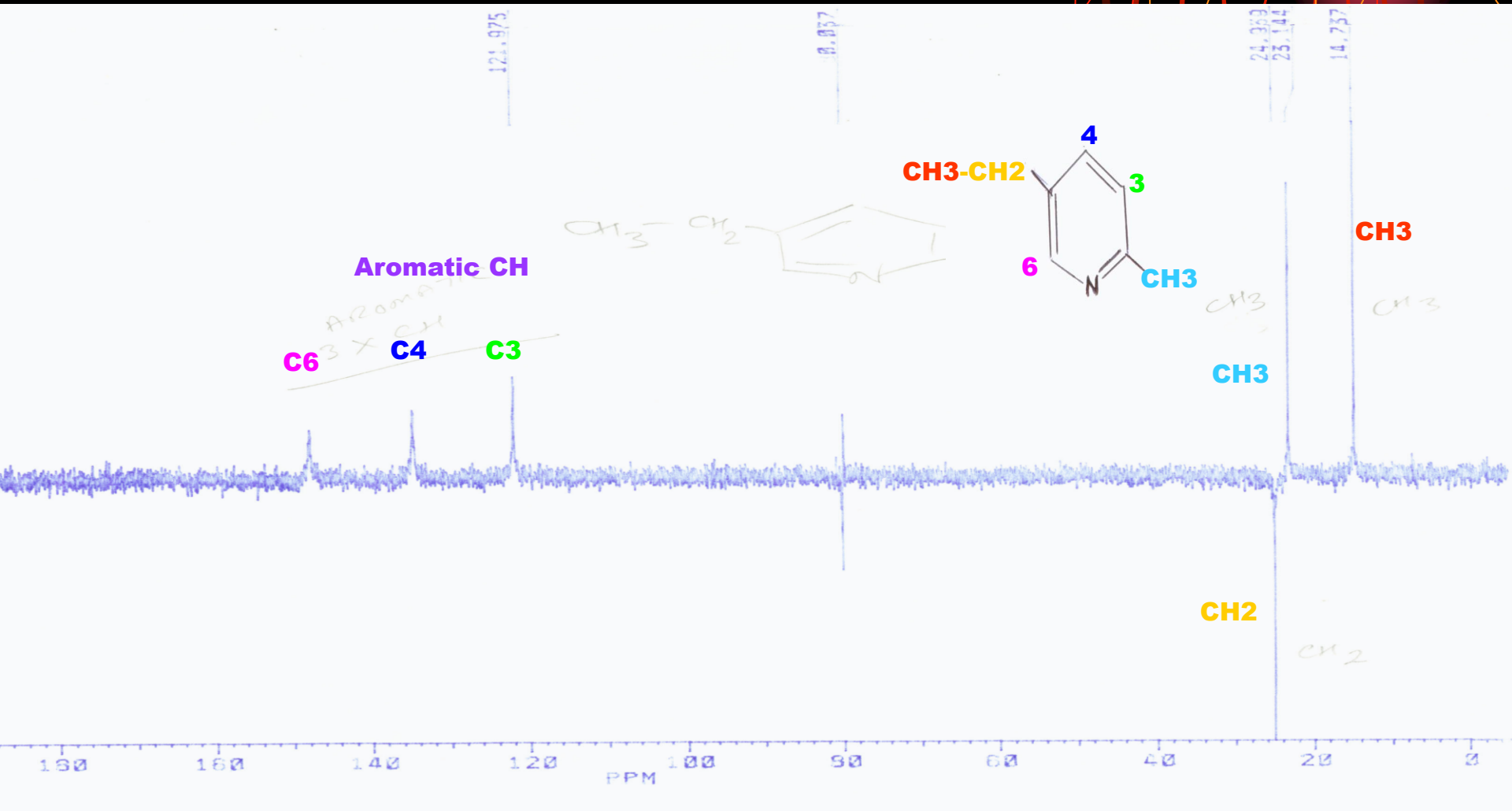
Analysis and interpretation of ^{13}C NMR Spectrum of 5-Ethyl-2-MethylPyridine

$C_5H_3N(CH_3)(CH_2\text{-}CH_3)$



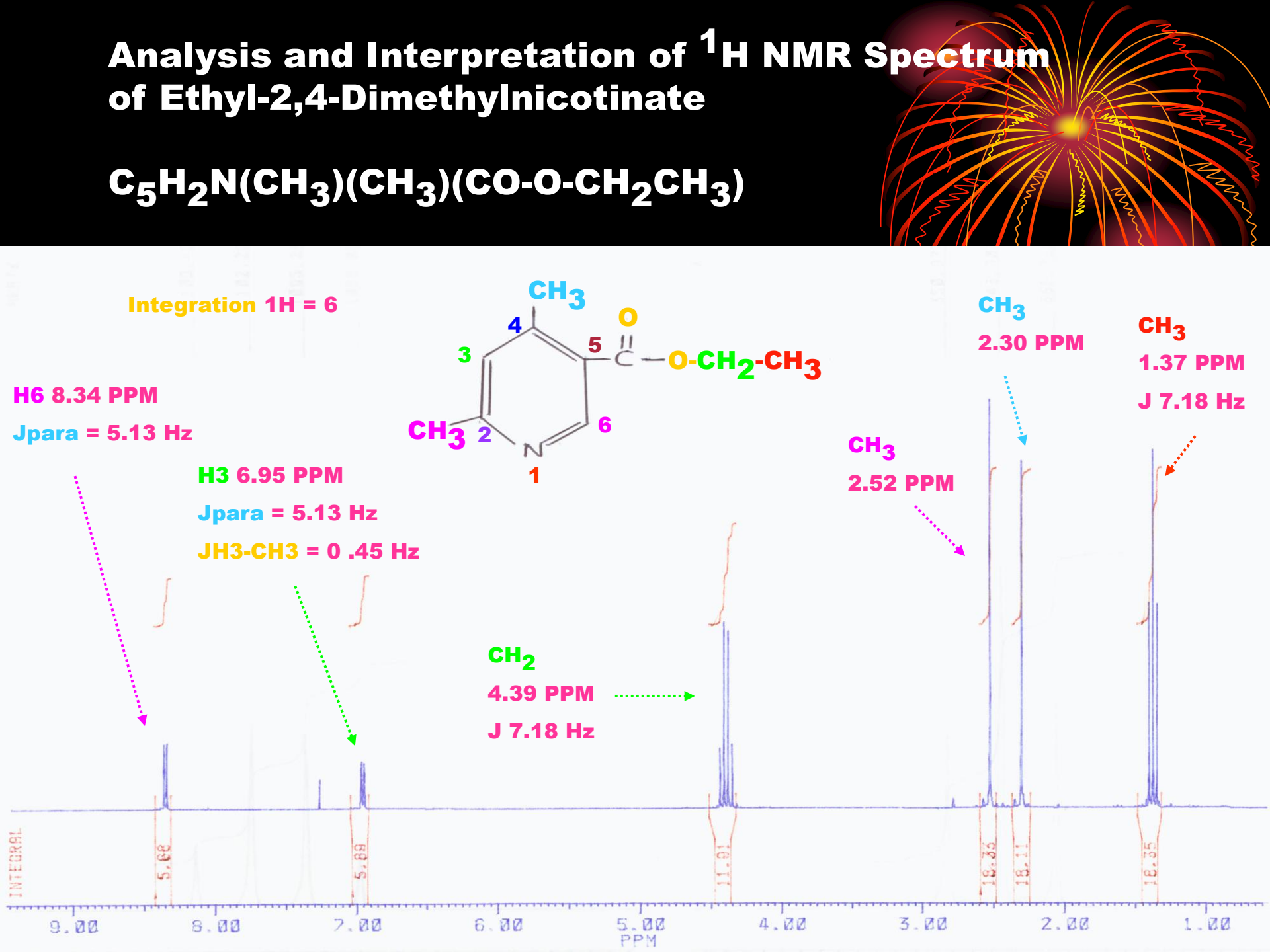
Analysis and interpretation ^{13}C DEPT 135 NMR Spectrum of 5-Ethyl-2-MethylPyridine

$C_5H_3N(CH_3)(CH_2\text{-}CH_3)$



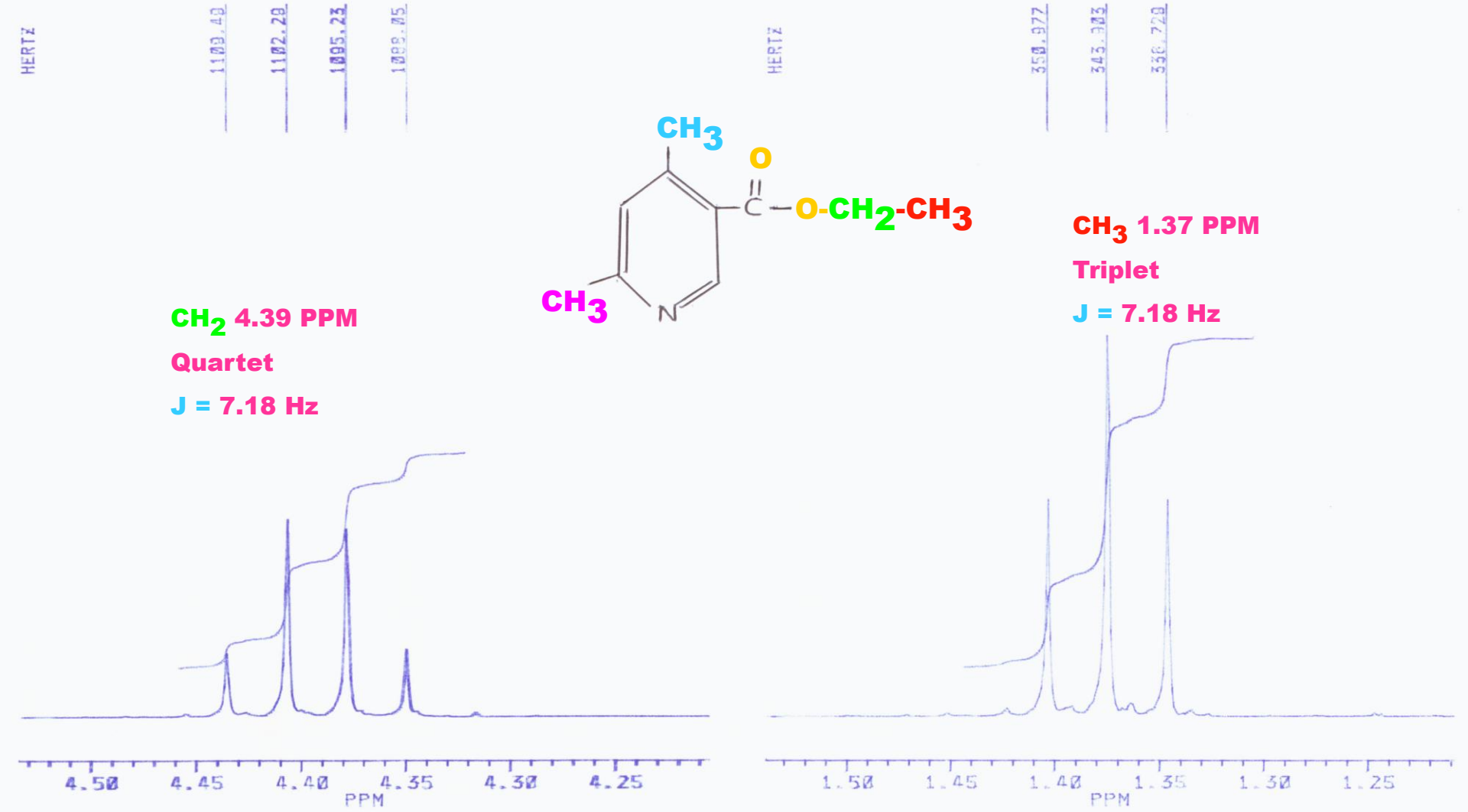
Analysis and Interpretation of ^{1}H NMR Spectrum of Ethyl-2,4-Dimethylnicotinate

$C_5H_2N(CH_3)(CH_3)(CO\text{-}O\text{-}CH_2CH_3)$



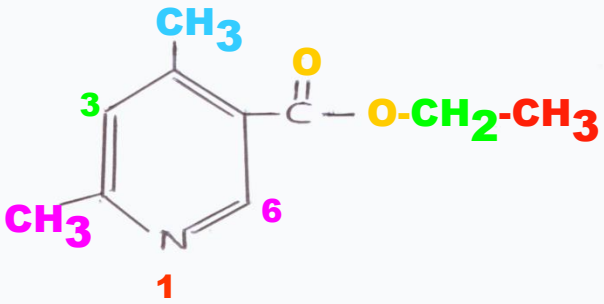
Analysis and Interpretation of ^{1}H NMR Spectrum of Ethyl-2,4-Dimethylnicotinate

$C_5H_2N(CH_3)(CH_3)(CO\text{-}O\text{-}CH_2CH_3)$



Analysis and Interpretation of ^{1}H NMR Spectrum of Ethyl-2,4-Dimethylnicotinate

$C_5H_2N(CH_3)(CH_3)(CO\text{-}O\text{-}CH_2CH_3)$



H6 8.34 PPM

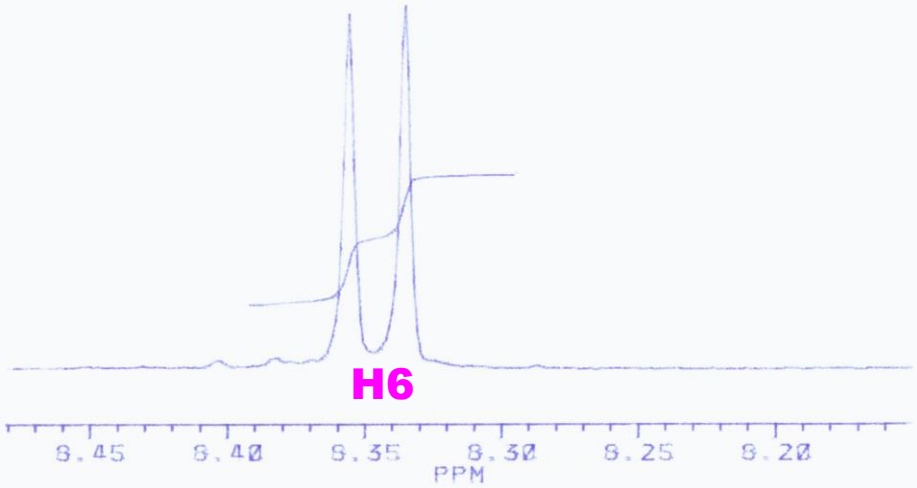
JH6-H3 = 5.13 Hz

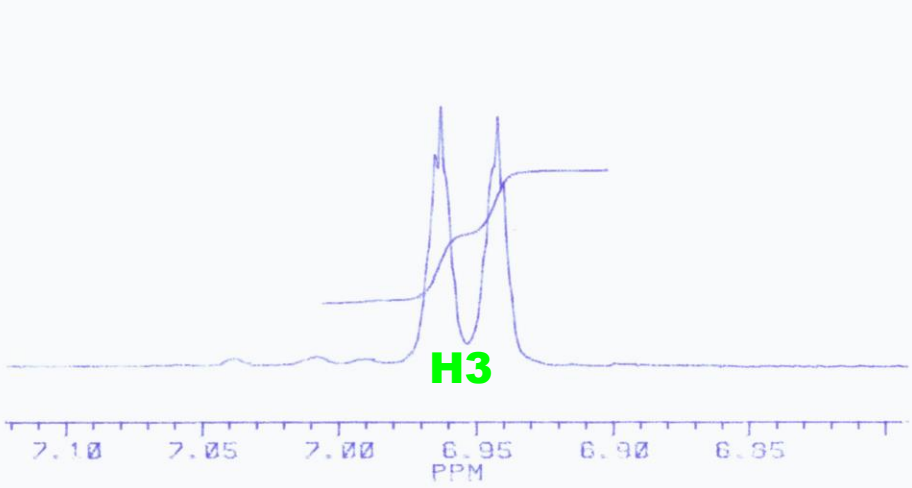
No CH3 Coupling

H3 6.95 PPM

JH3-H6 = 5.13 Hz

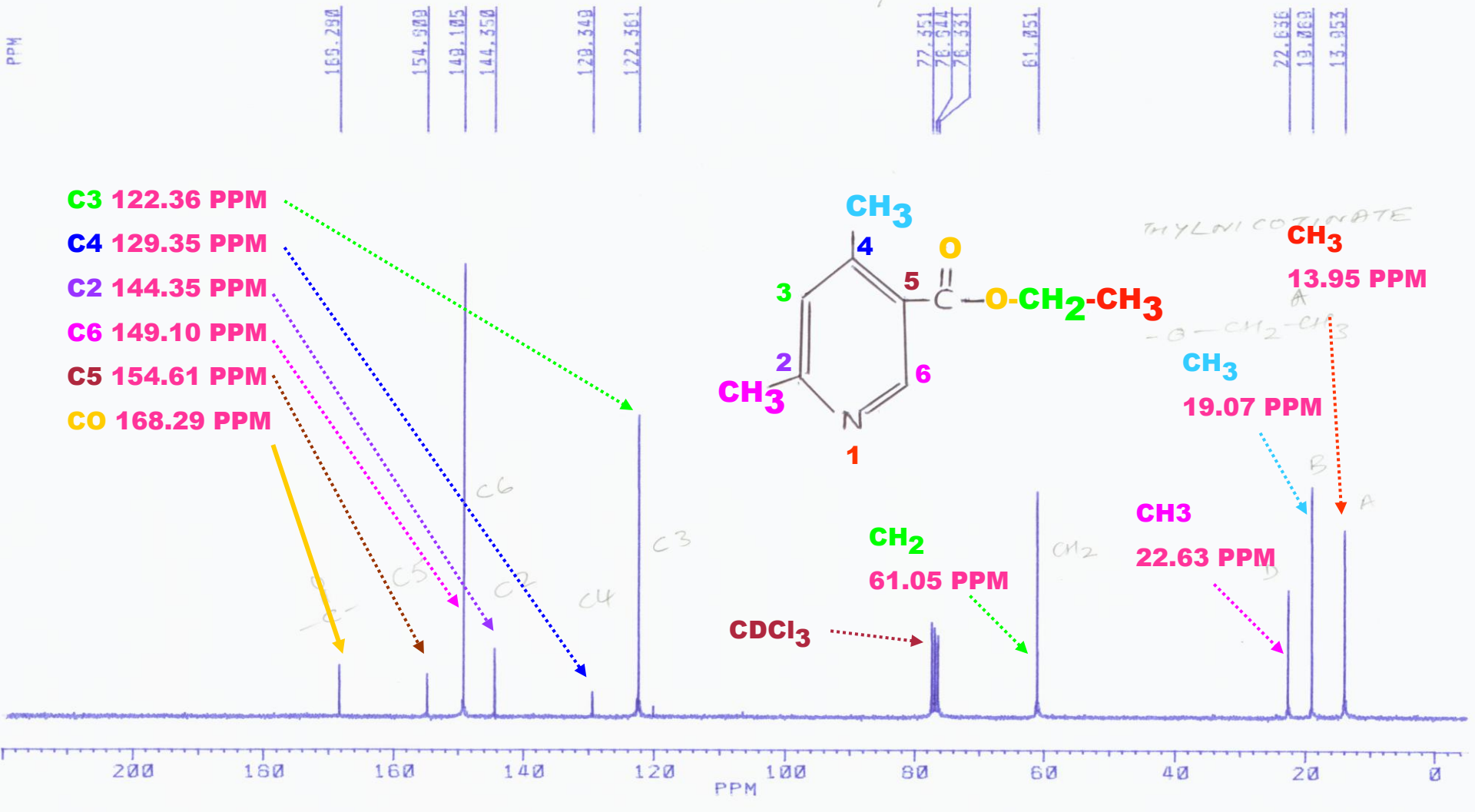
JH3-CH3 = 0.45 Hz





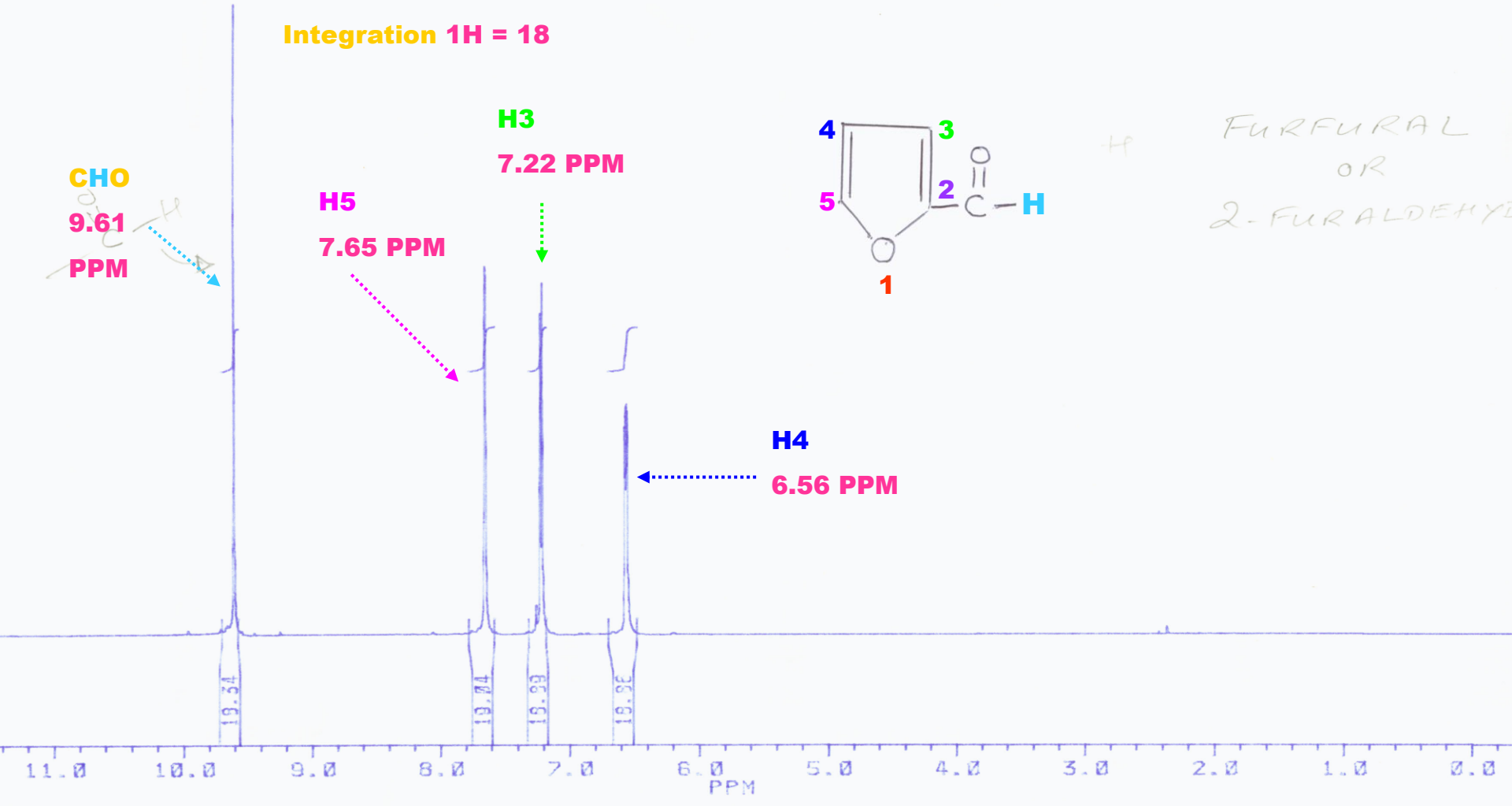
Analysis and Interpretation of ^{13}C NMR Spectrum of Ethyl-2,4-Dimethylnicotinate

$C_5H_2N(CH_3)(CH_3)(CO\text{-}O\text{-}CH_2CH_3)$



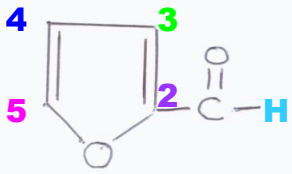
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Furfural (2-Furaldehyde)

C_4H_3O-CHO ^{1}H NMR Spectrum



Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of Furfural (2-Furaldehyde)

C_4H_3O-CHO Expansion of ^{1}H NMR Spectrum



1

H5 7.65 PPM

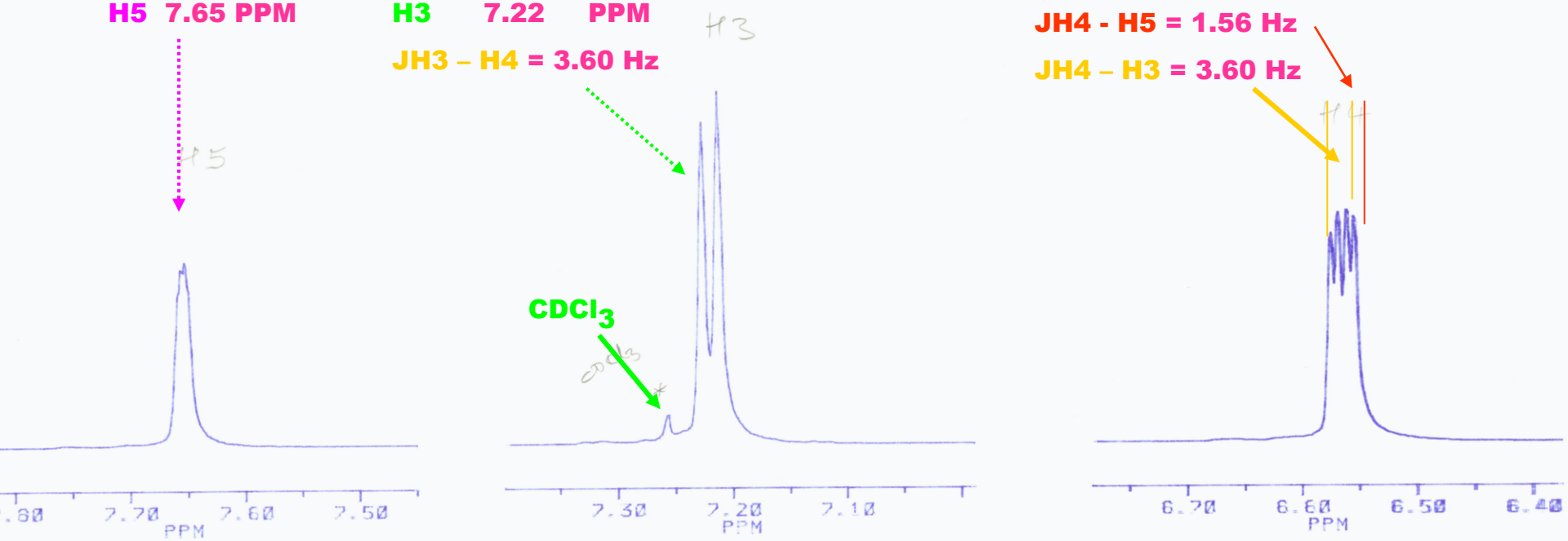
H3 7.22 PPM

JH3 – H4 = 3.60 Hz

H4 6.56 PPM

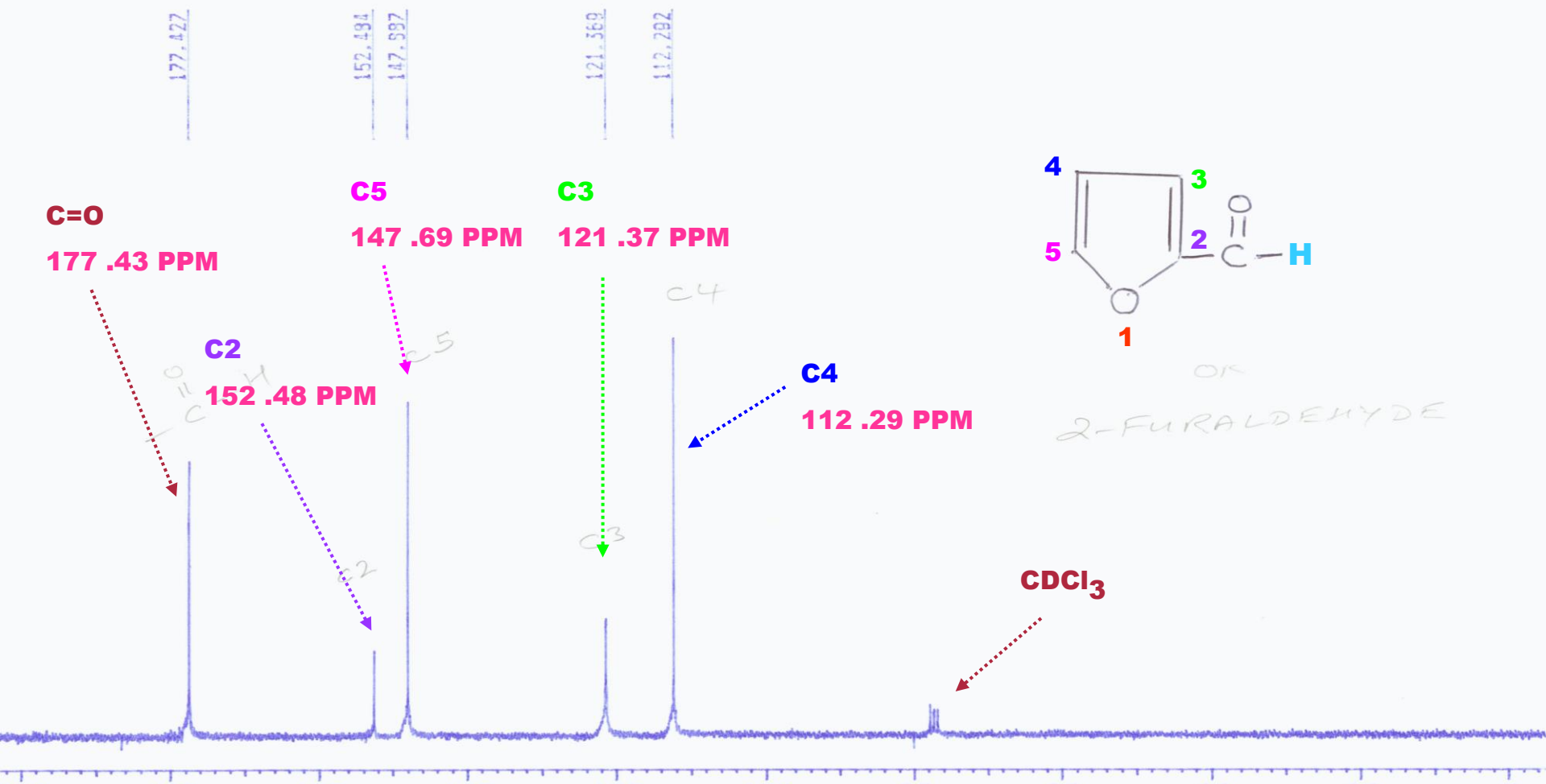
JH4 - H5 = 1.56 Hz

JH4 – H3 = 3.60 Hz



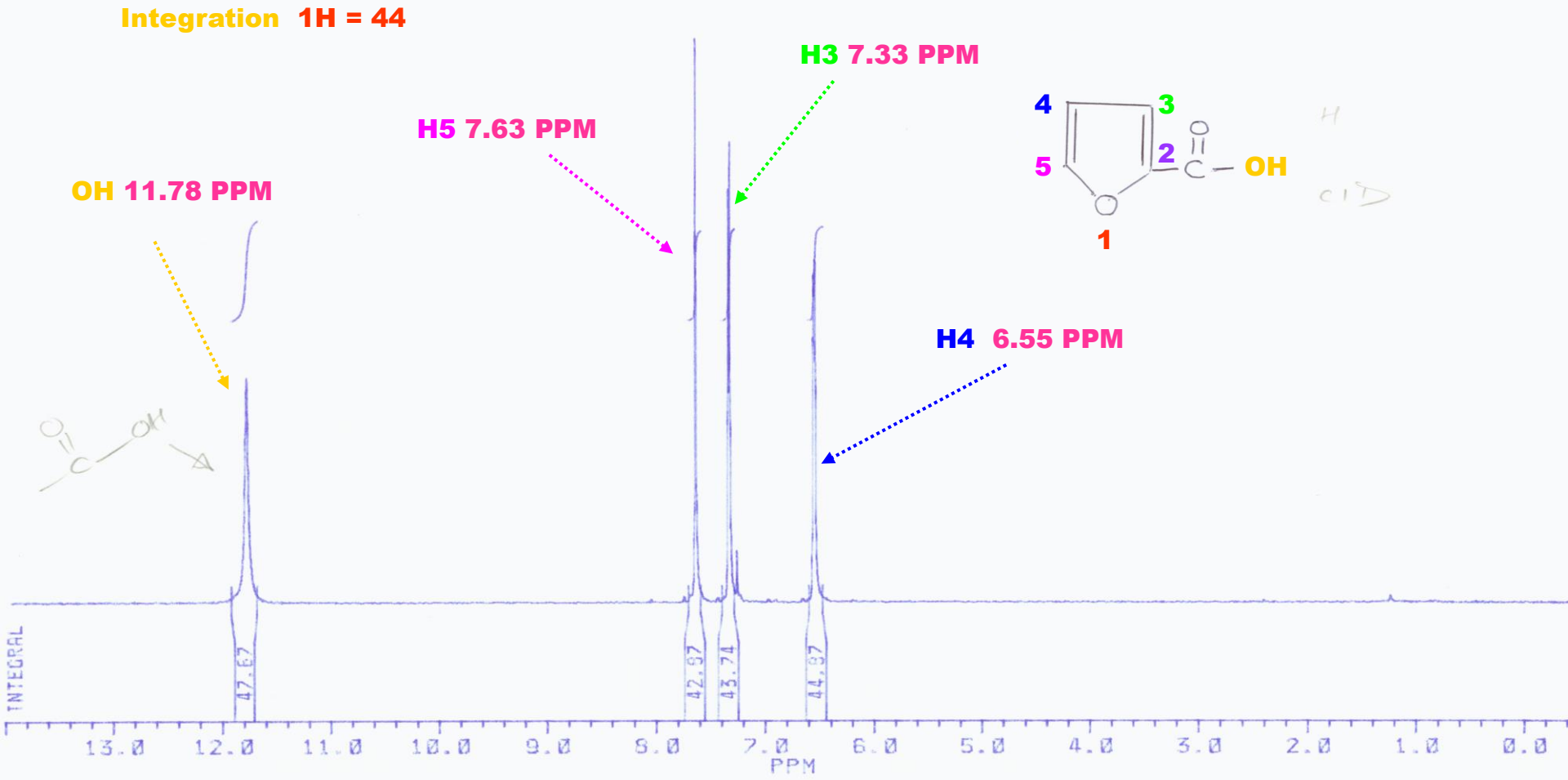
Analysis and interpretation of ^{13}C NMR Spectrum of Furfural (2-Furaldehyde)

C_4H_3O-CHO



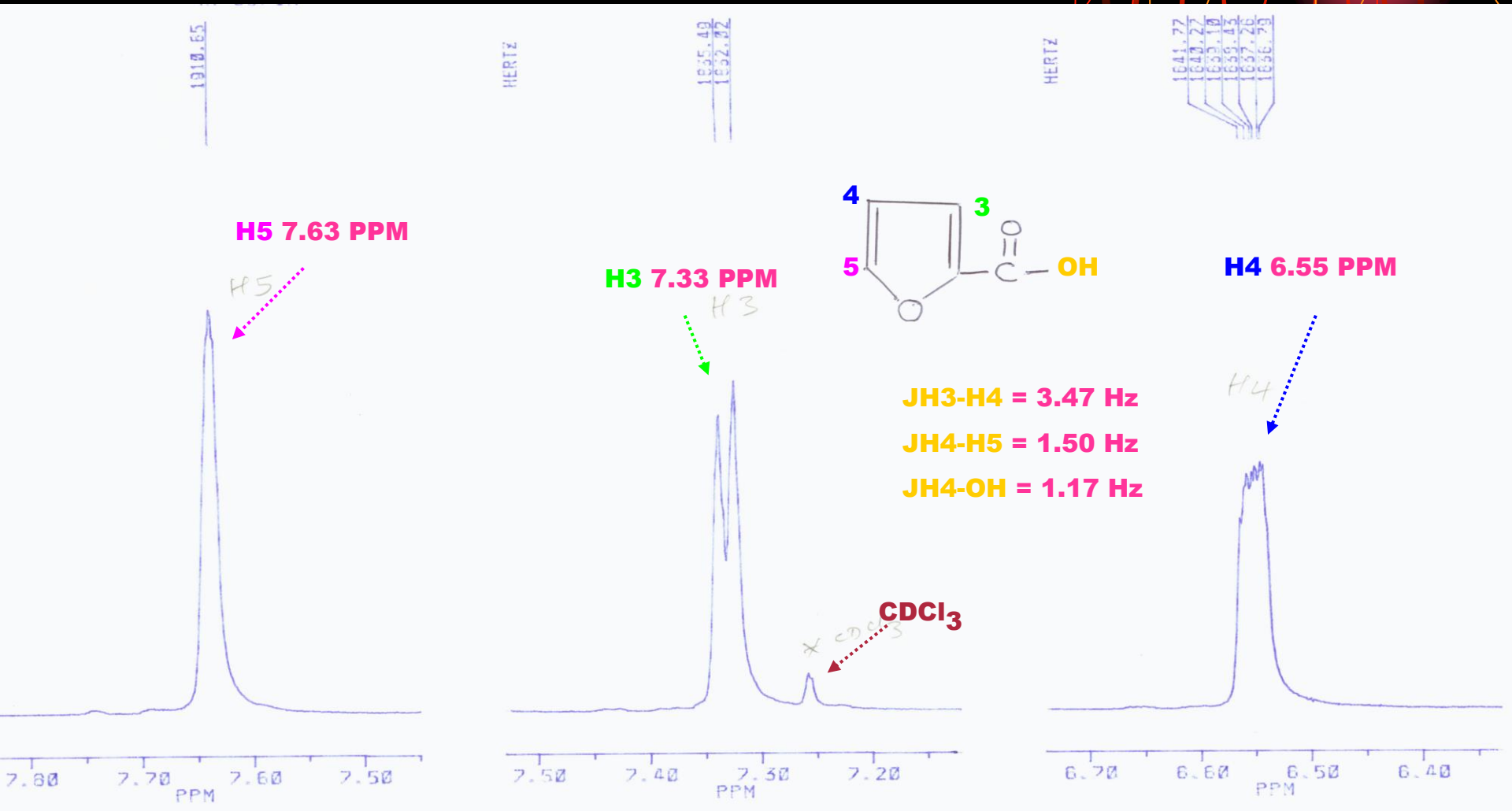
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 2-Furoic Acid

C_4H_3O-(CO-OH) ^{1}H NMR Spectrum



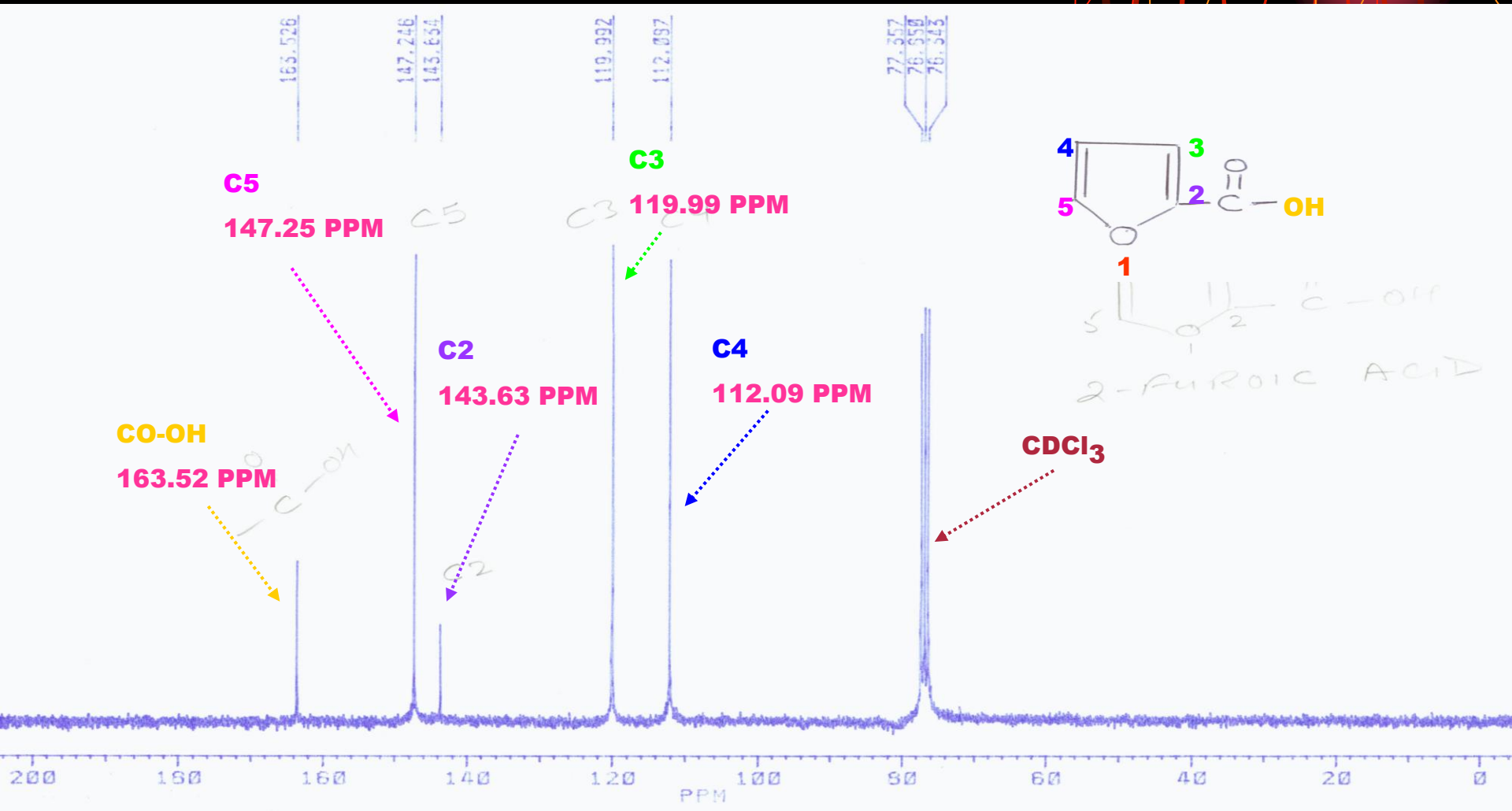
Analysis and interpretation of ^{1}H & ^{13}C NMR Spectra of 2-Furoic Acid

C_4H_3O-(CO-OH) Expansion of ^{1}H NMR Spectrum



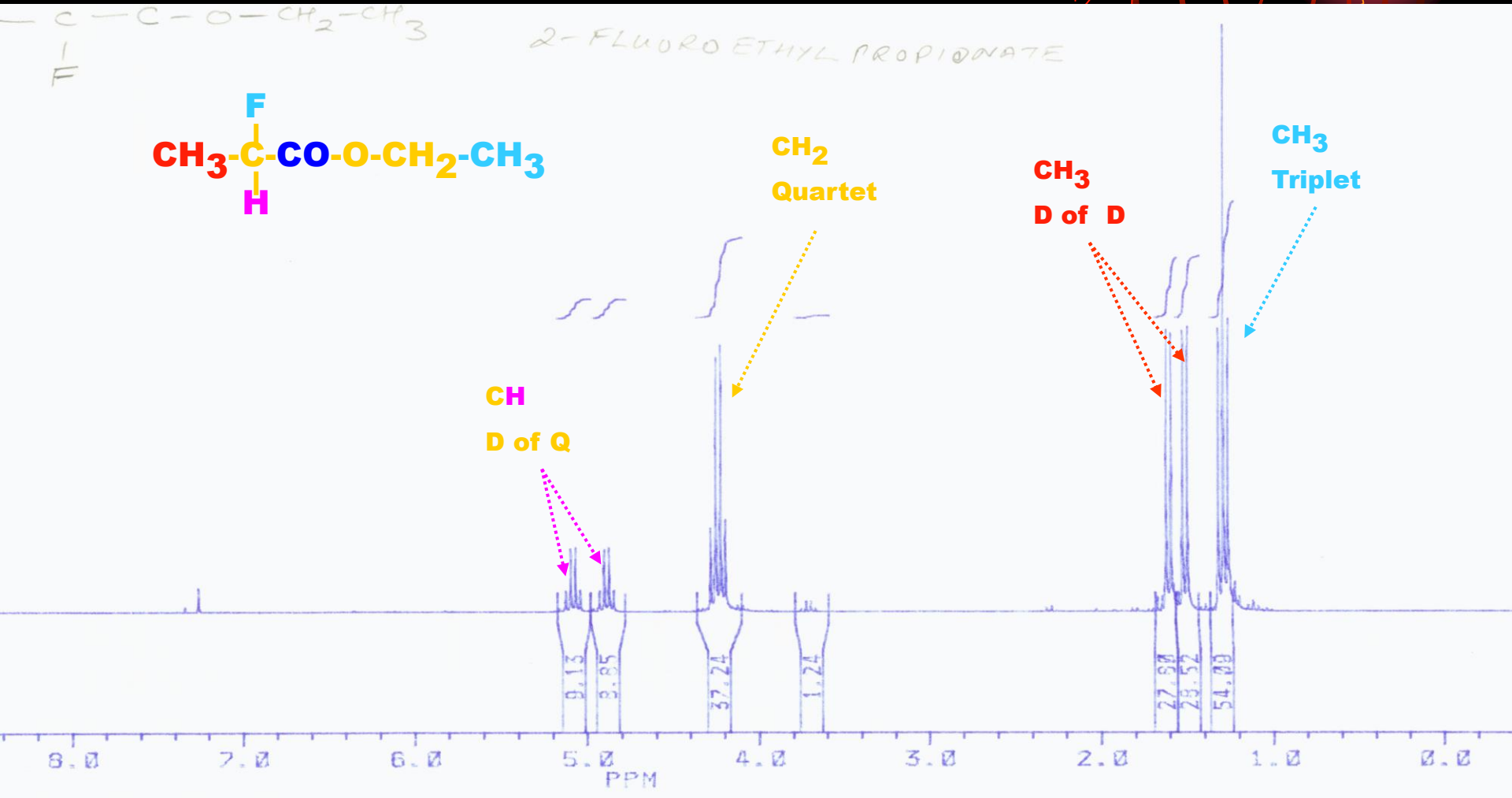
Analysis and interpretation of ^{13}C NMR Spectra of 2-Furoic Acid

C_4H_3O-(CO-OH) ^{13}C NMR Spectrum

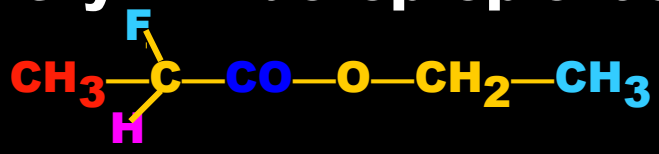


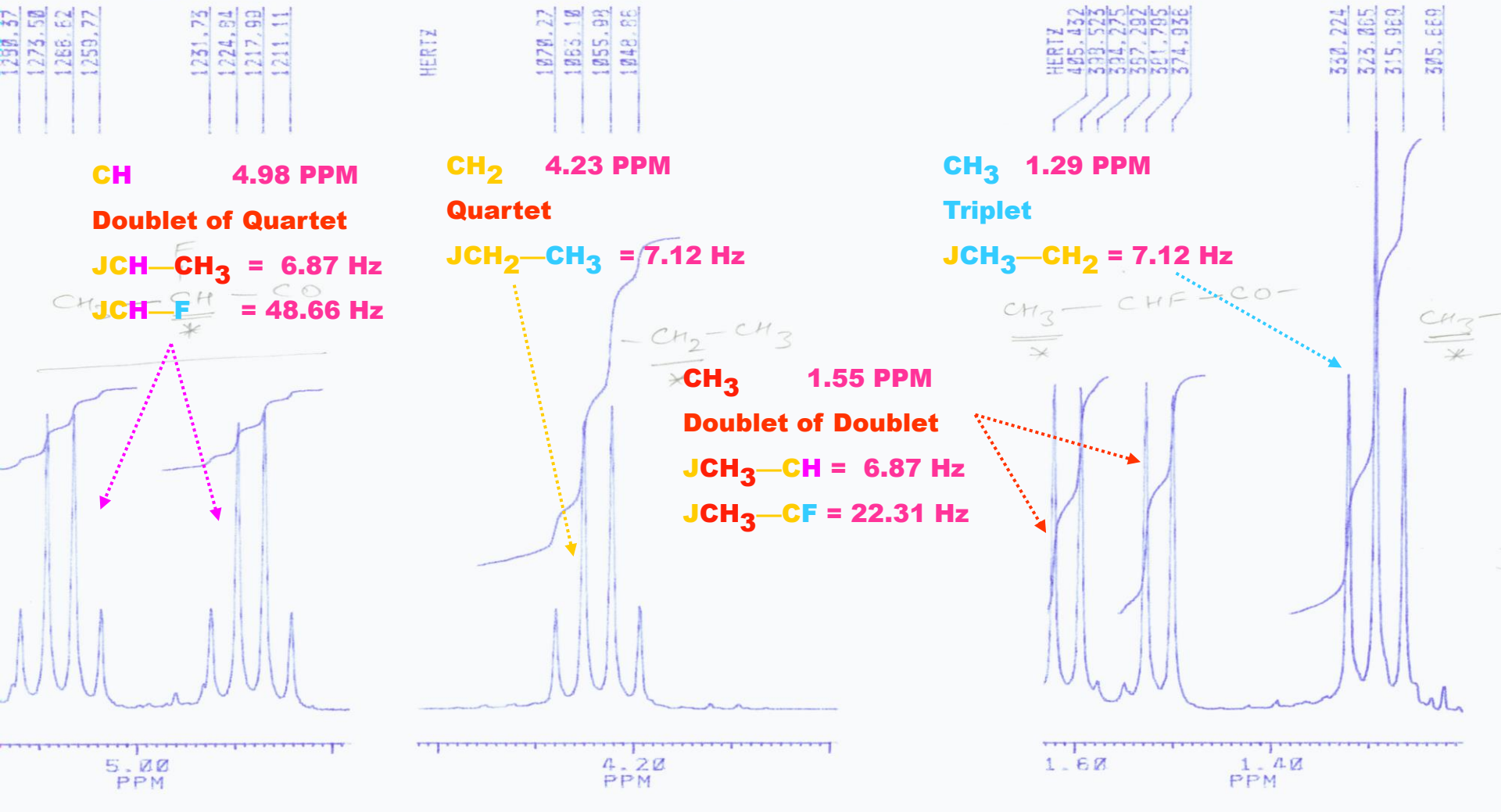
Analysis and Interpretation of ^{1}H NMR Spectrum of Ethyl-2-Fluoropropionate

CH_3-CHF-CO-O-CH_2CH_3



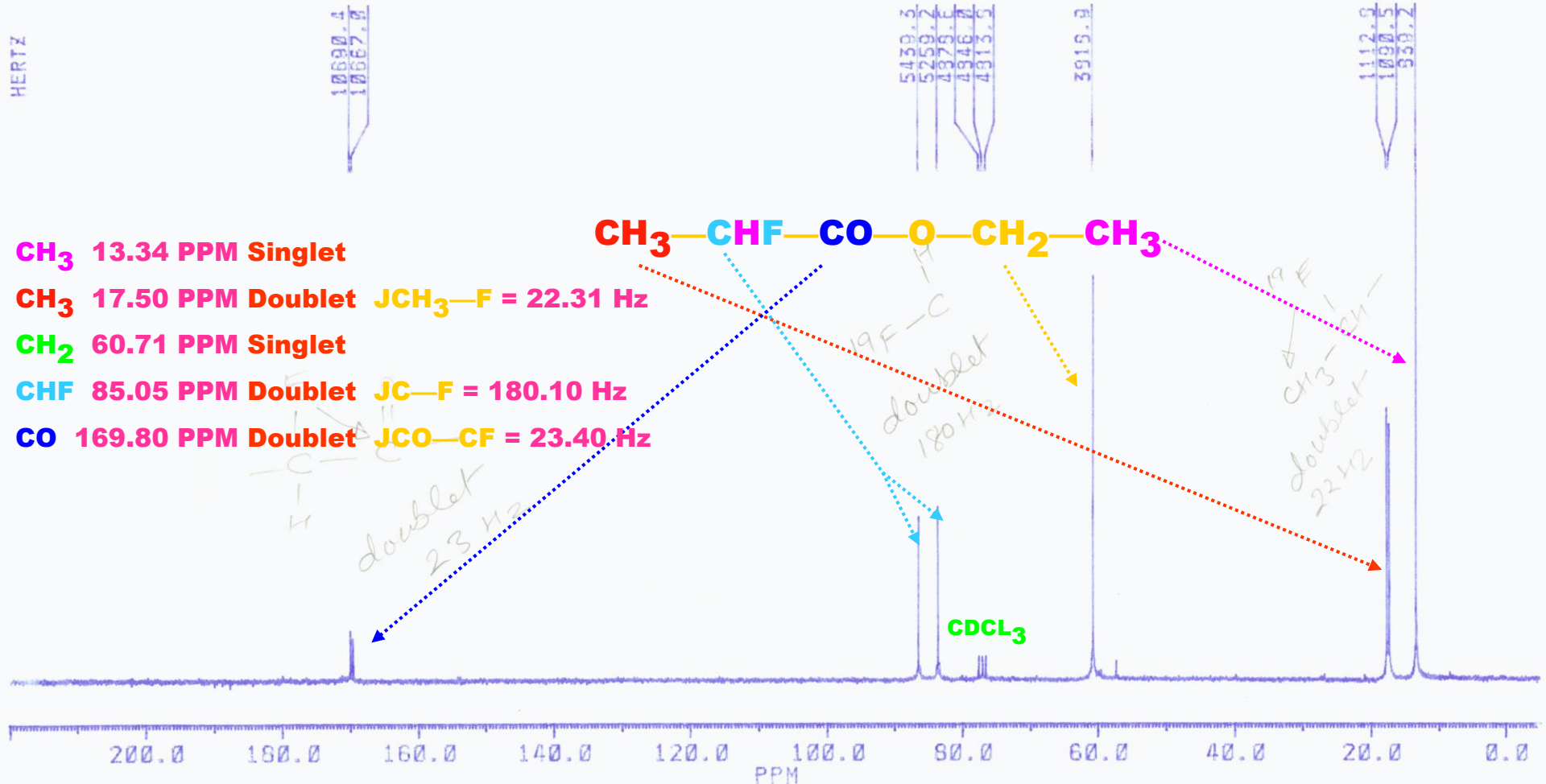
Analysis and Interpretation of ^{1}H NMR Spectrum of Ethyl-2-Fluoropropionate CH_3-CHF-CO-O-CH_2CH_3





Analysis and Interpretation of ^{13}C NMR Spectrum of Ethyl-2-Fluoropropionate

CH_3-CHF-CO-O-CH_2CH_3



Analysis and Interpretation of ^{13}C NMR Spectrum of Ethyl-2-Fluoropropionate (Expansion)

CH_3-CHF-CO-O-CH_2CH_3

^{19}F spin I = ½

No. Peak = 2nI + 1

= n + 1

= 1 + 1

= 2 (Doublet)

Here n=1 F nucleus

Hence all are doublets

^{13}C is coupling to ^{19}F

CH_3—CHF—CO—O—CH_2—CH_3

CH_3—CF doublet

17.50 PPM

^2J = 22.31 HZ

C—F Doublet

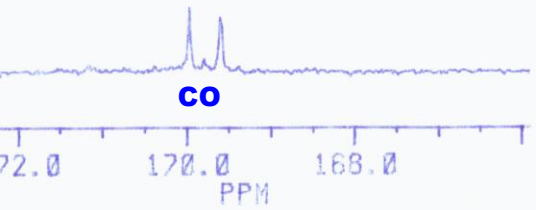
85.05 PPM

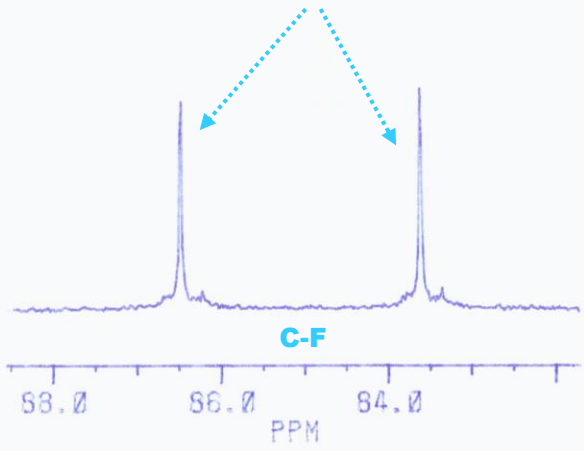
^1J = 180.10 Hz

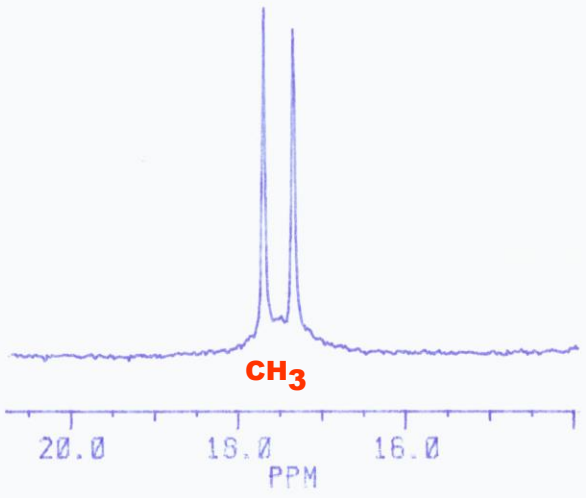
CO—CF Doublet

169.80 PPM

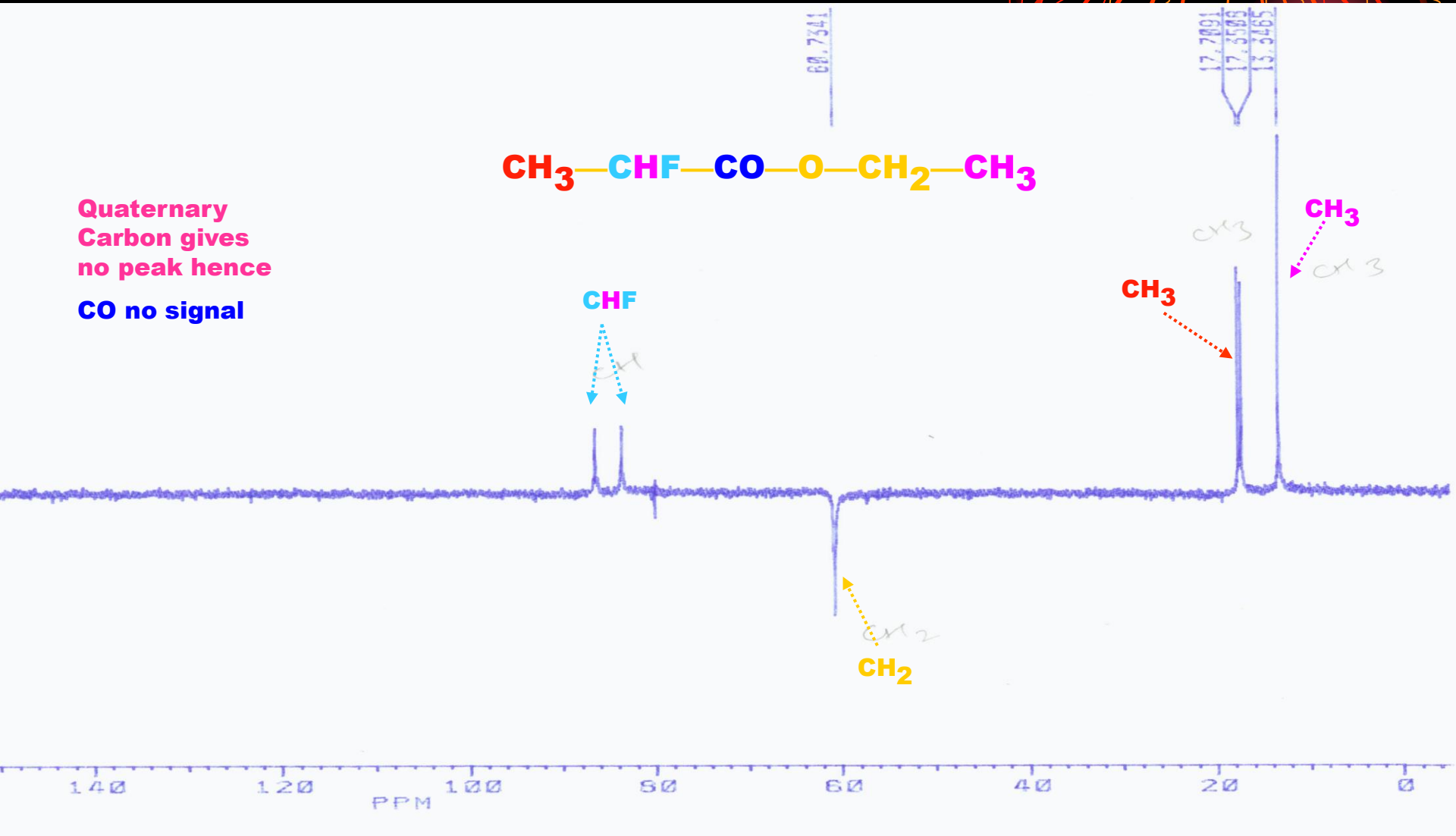
^2J = 23.40 Hz





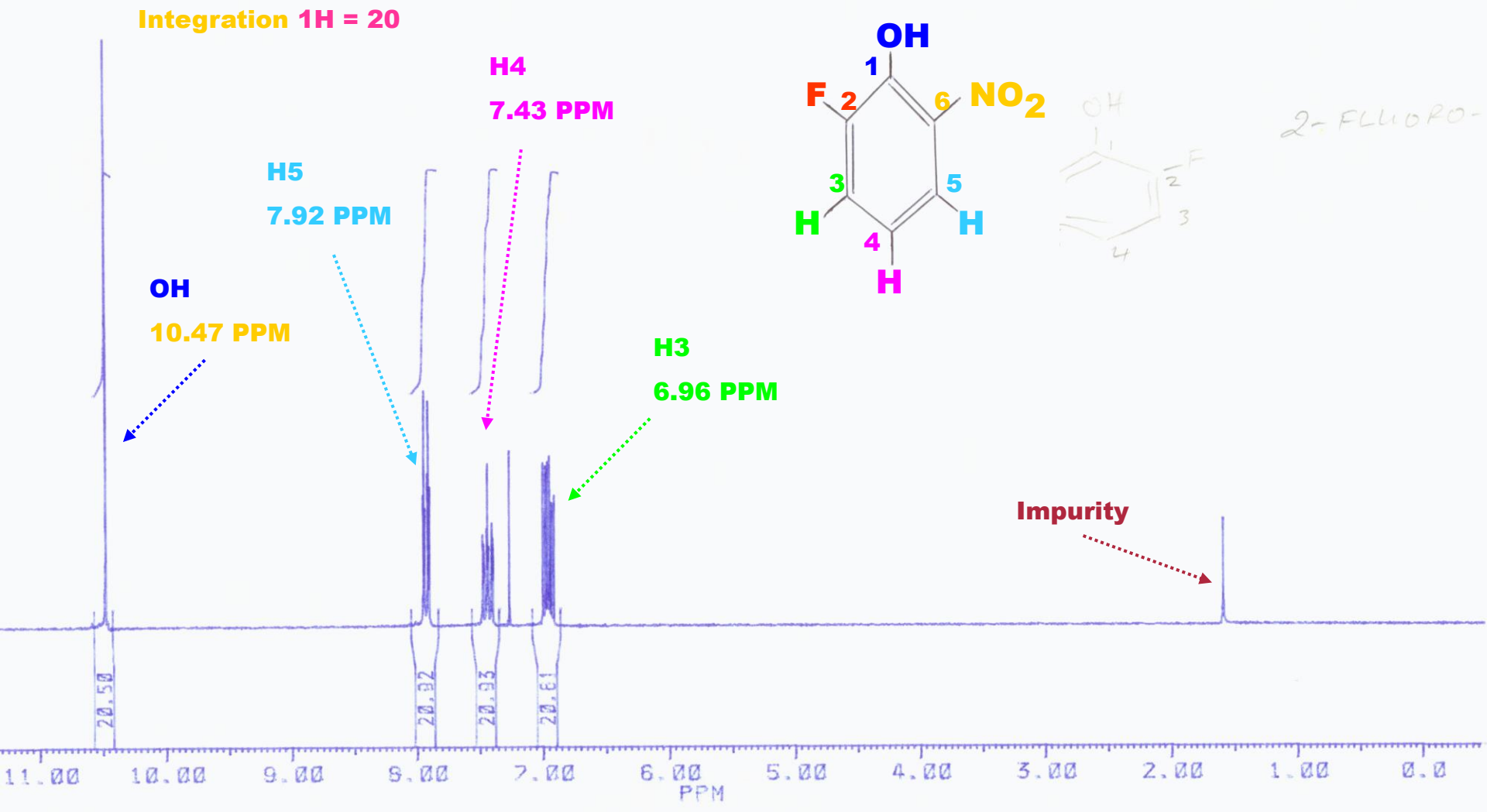


Analysis and Interpretation of ^{13}C NMR Spectrum of Ethyl-2-Fluoropropionate (Dept 135) CH_3-CHF-CO-O-CH_2CH_3



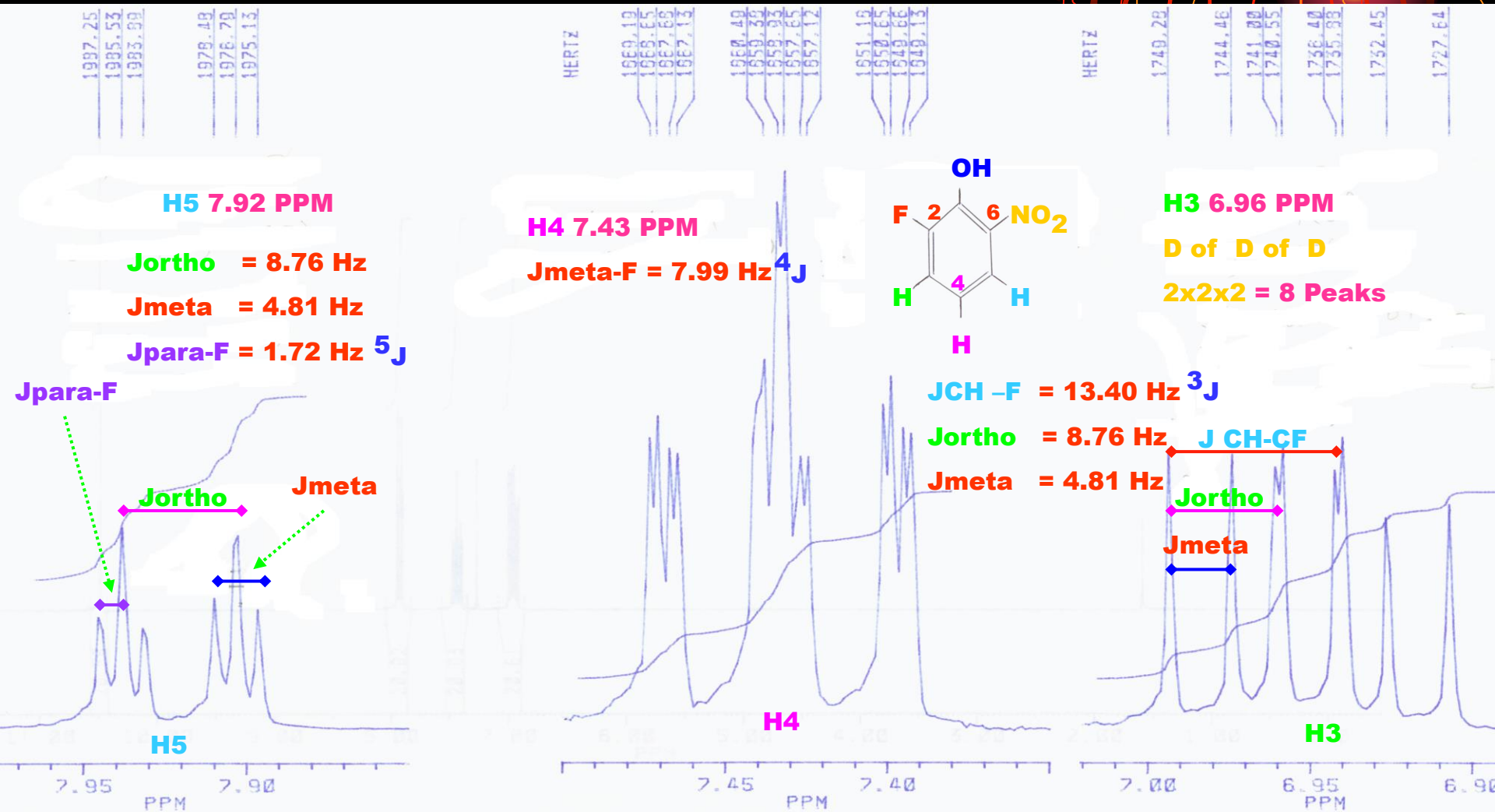
^{1}H NMR spectrum of 2-Fluoro-6-Nitrophenol

$C_6H_3(F)(NO_2)(OH)$



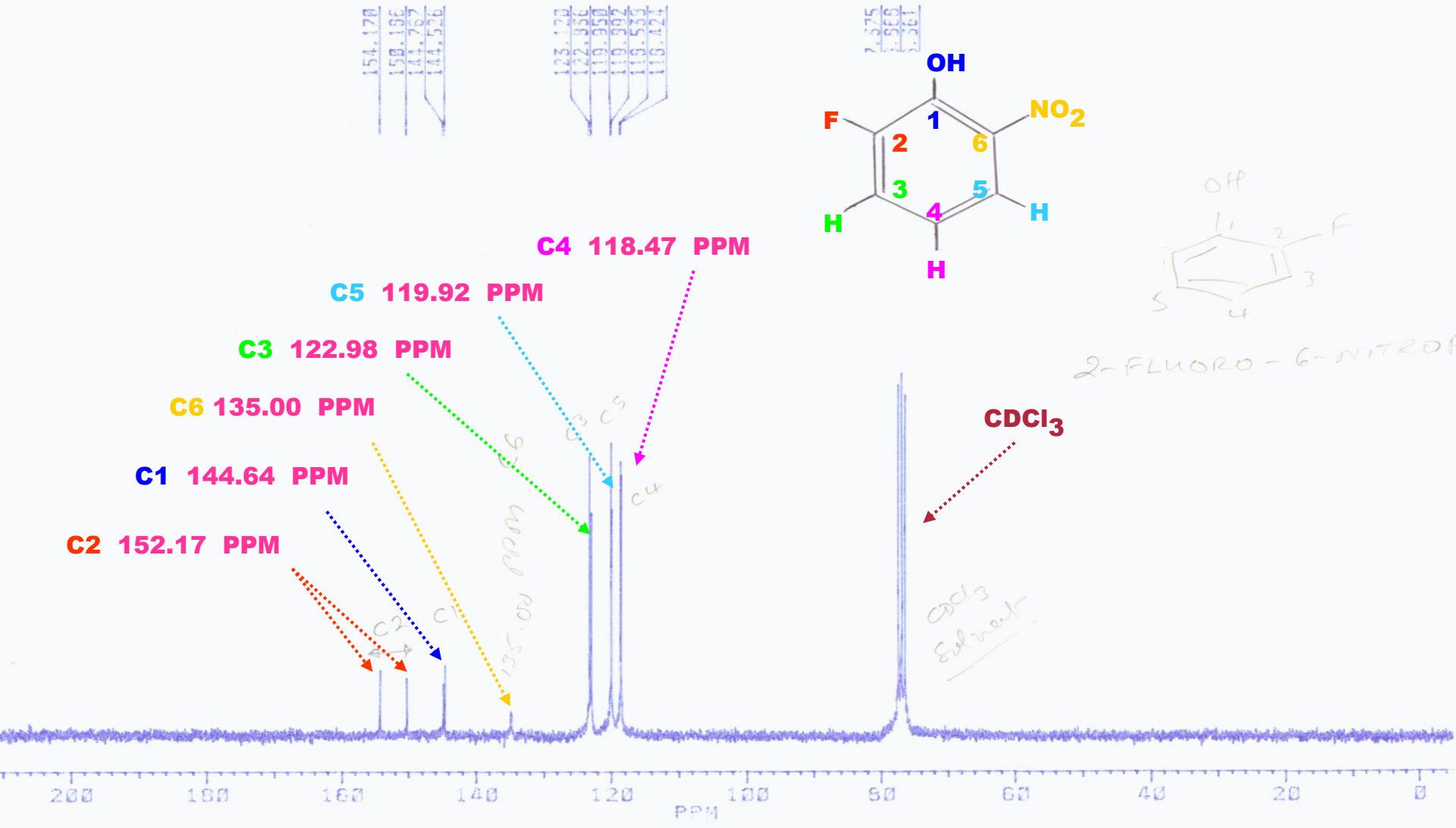
^{1}H NMR spectrum of 2-Fluoro-6-Nitrophenol

$C_6H_3(F)(NO_2)(OH)$



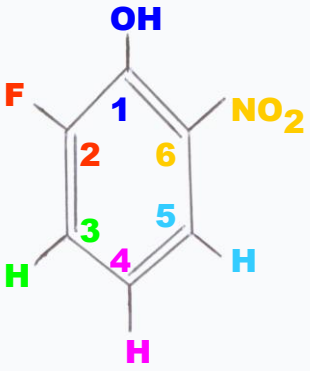
^{13}C NMR spectrum of 2-Fluoro-6-Nitrophenol

$C_6H_3(F)(NO_2)(OH)$



Expansion of ^{13}C NMR spectrum of 2-Fluoro-6-Nitrophenol

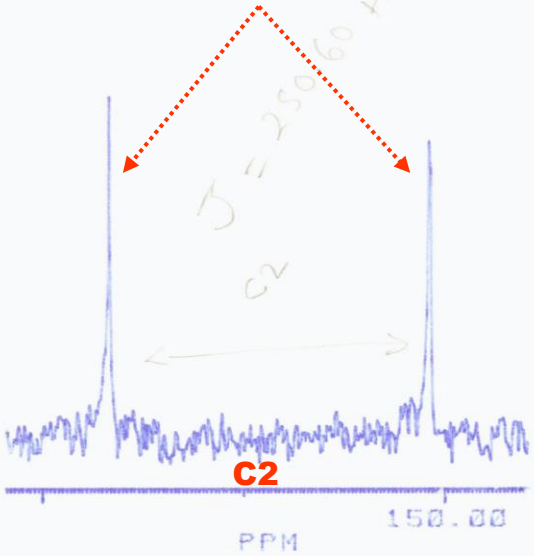
$C_6H_3(F)(NO_2)(OH)$



^{19}F has long range coupling which can be seen in the following example

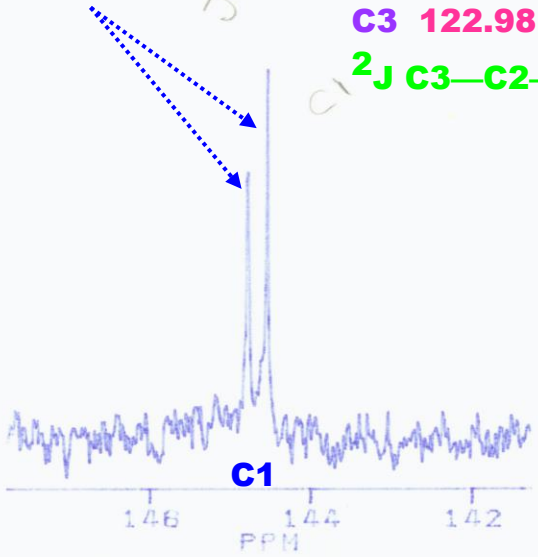
C2 153.17 PPM

^{1}J C2—F = 250.60 Hz



C1 144.64 PPM

^{2}J C1—C2—F = 15.15 Hz



C3 122.98 PPM

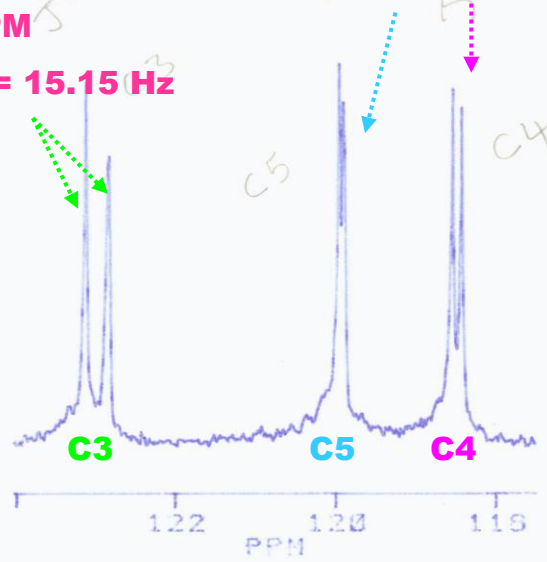
^{2}J C3—C2—F = 15.15 Hz

C4 118.47 PPM

^{3}J C4—C3—C2—F = 7.22Hz

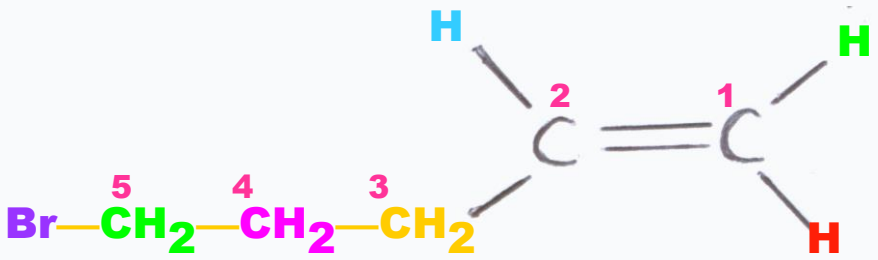
C5 119.92 PPM

^{4}J C5—C4—C3—C2—F = 3.65 Hz



^{1}H NMR Spectrum of 5-Bromopent-1-ene
Br-CH_2-CH_2-CH_2-CH=CH_2

Integration 1H = 7.5



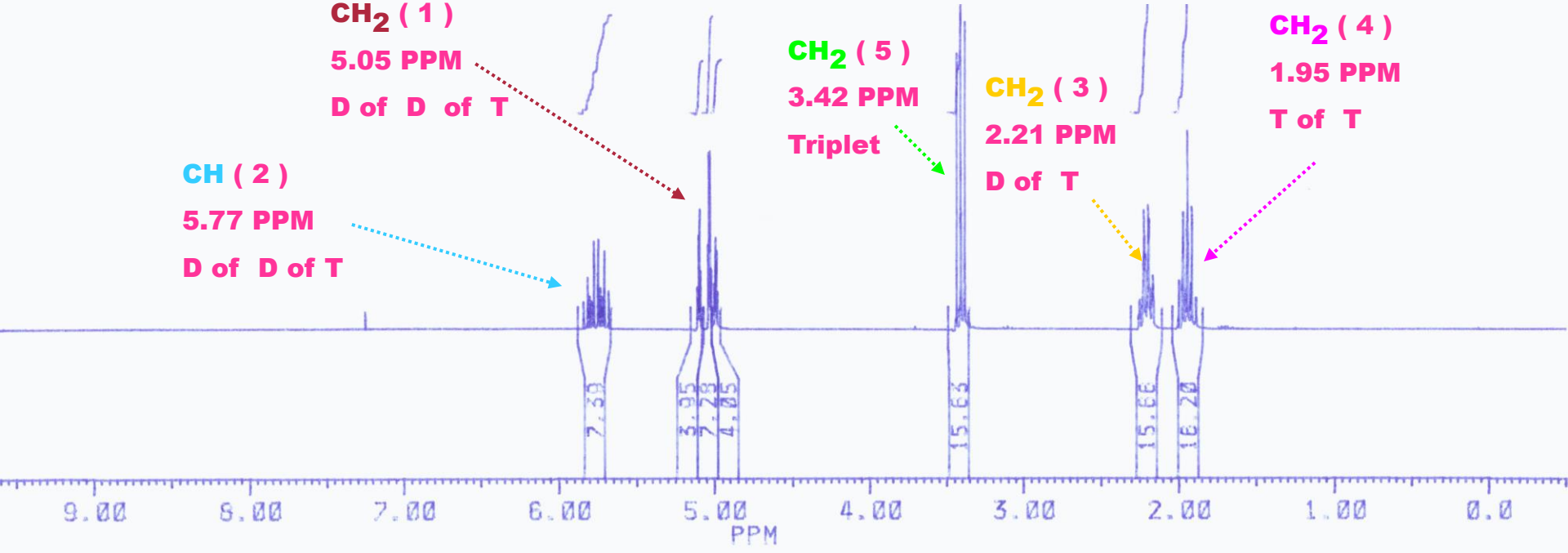
CH_2 (1)
5.05 PPM
D of D of T

CH (2)
5.77 PPM
D of D of T

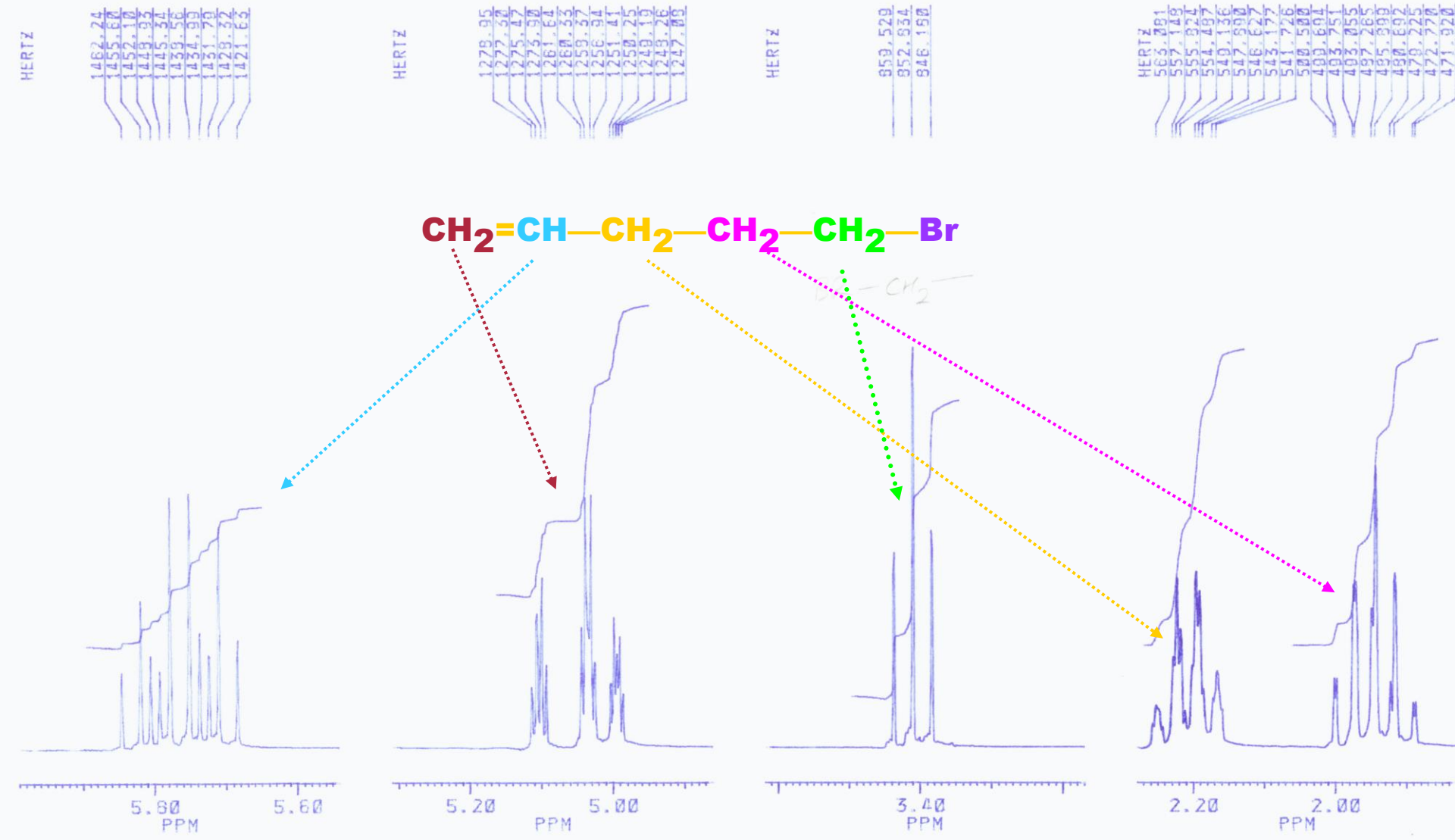
CH_2 (5)
3.42 PPM
Triplet

CH_2 (3)
2.21 PPM
D of T

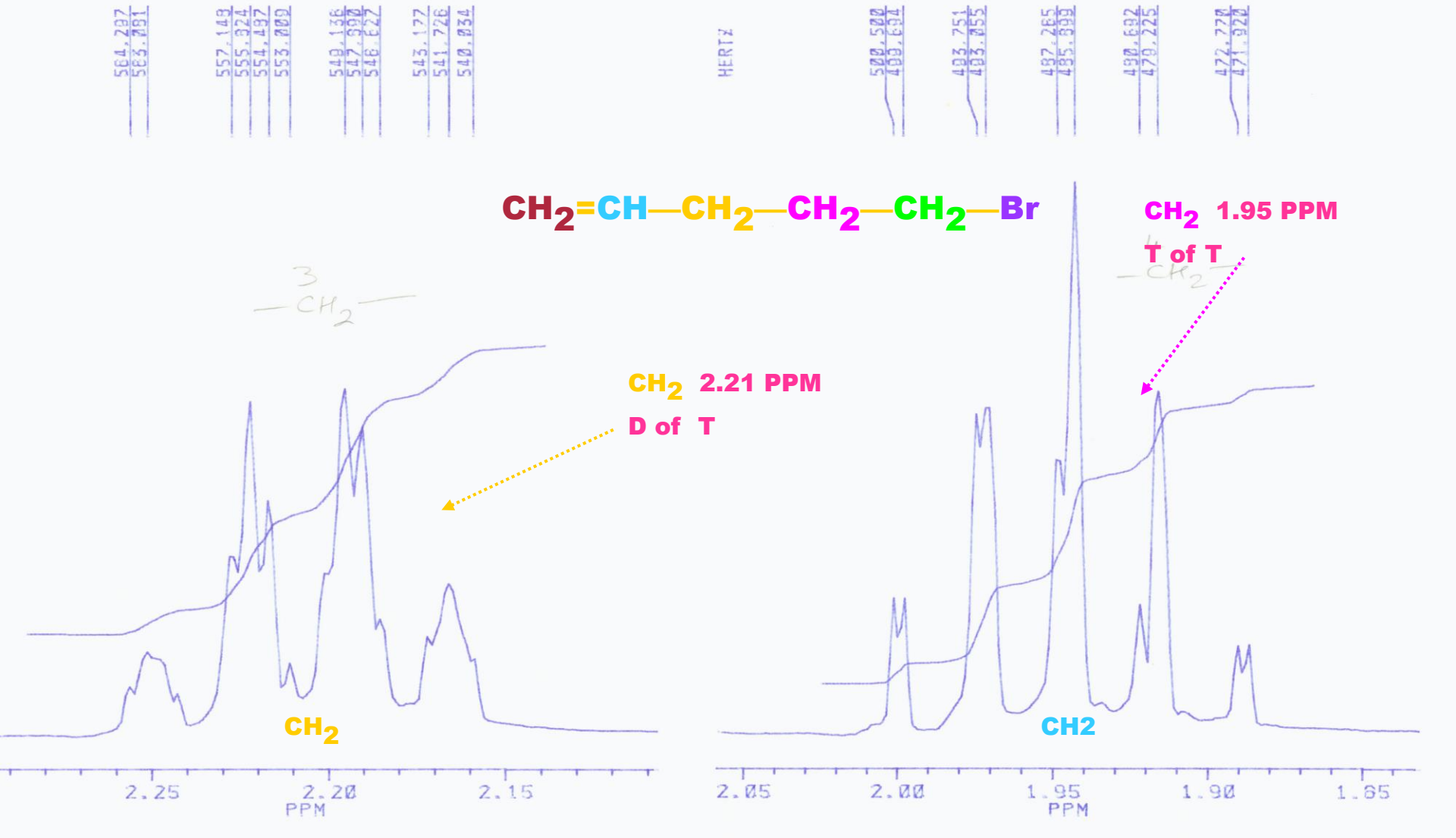
CH_2 (4)
1.95 PPM
T of T



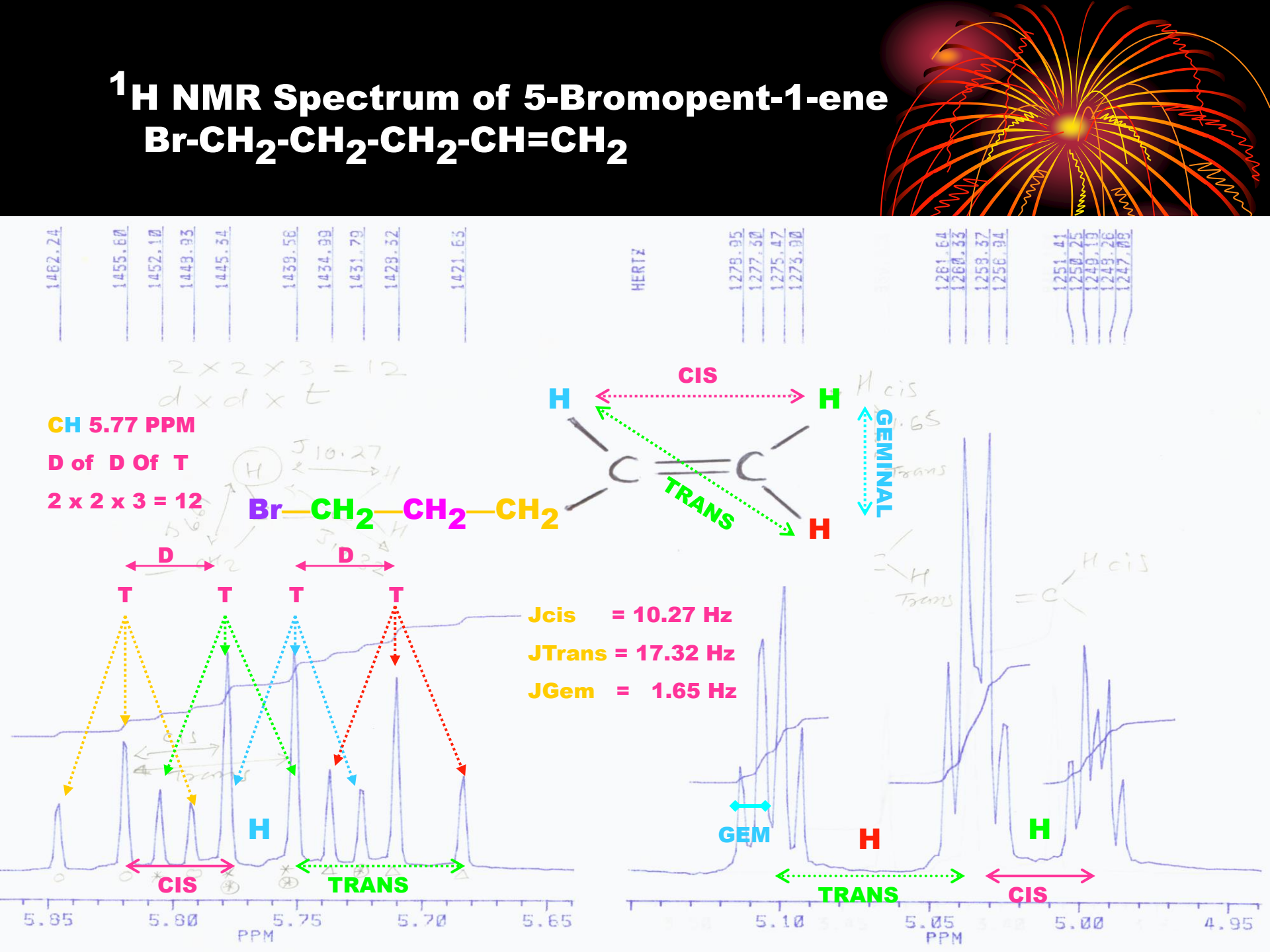
^{1}H NMR Spectrum of 5-Bromopent-1-ene
$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$



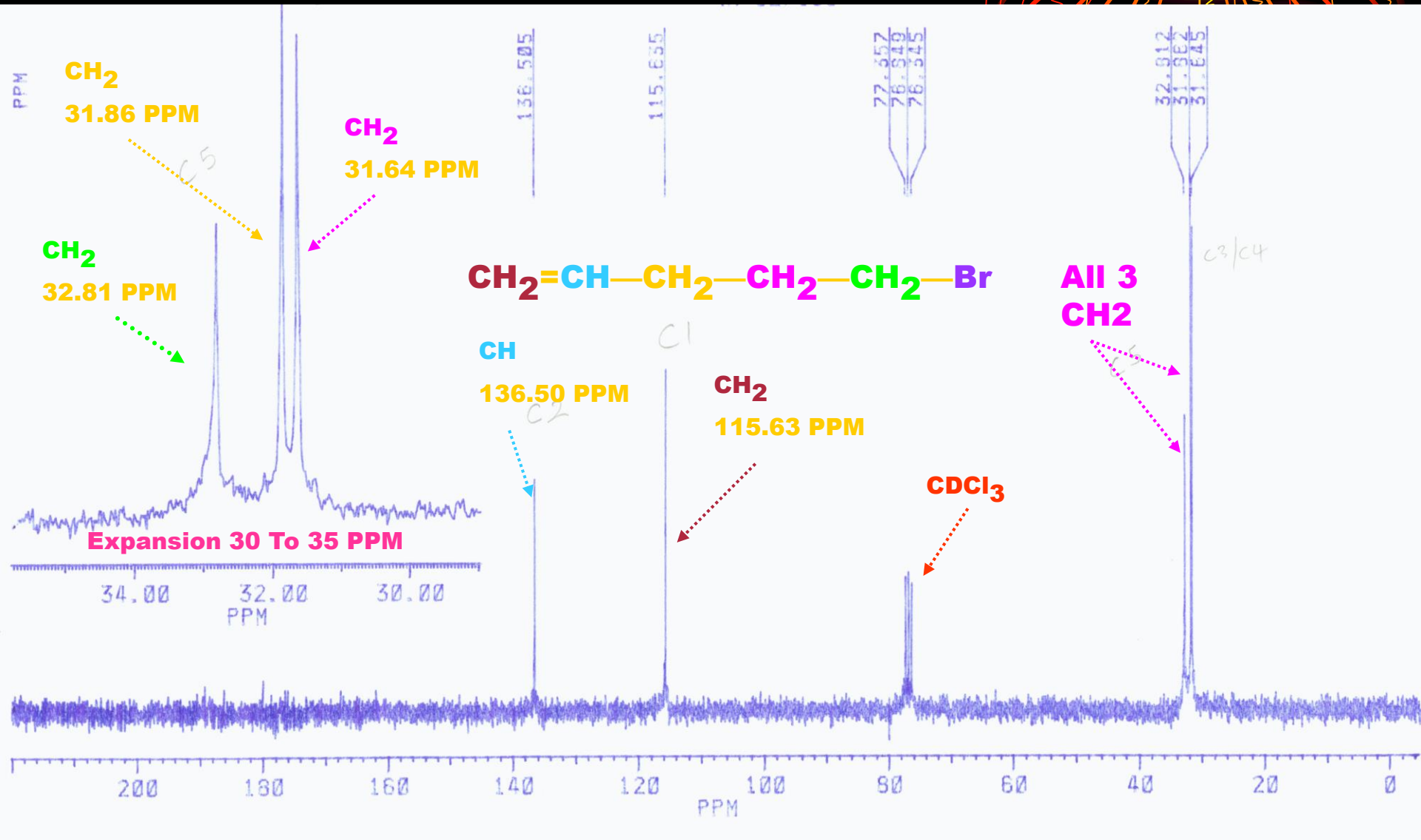
^{1}H NMR Spectrum of 5-Bromopent-1-ene
Br-CH_2-CH_2-CH_2-CH=CH_2



^{1}H NMR Spectrum of 5-Bromopent-1-ene
$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$



^{13}C NMR Spectrum of 5-Bromopent-1-ene
$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$

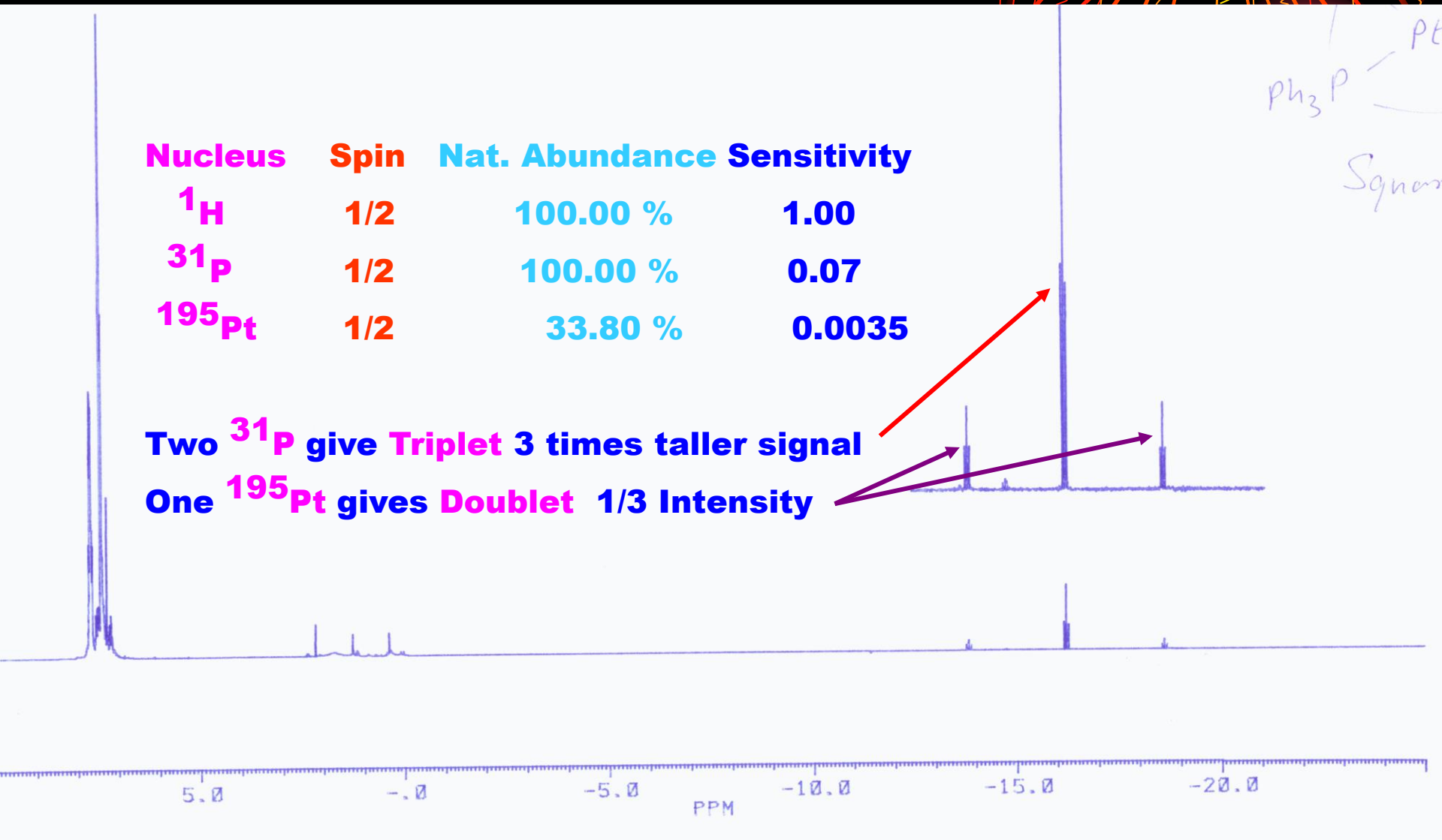


^{1}H NMR Spectrum of $[(C_6H_5)_3P]_2PtHCl$ in $CDCl_3$
DiPhosphine Platinum Hydrochloride Complex
+ 10.00 to – 25.00 PPM Range

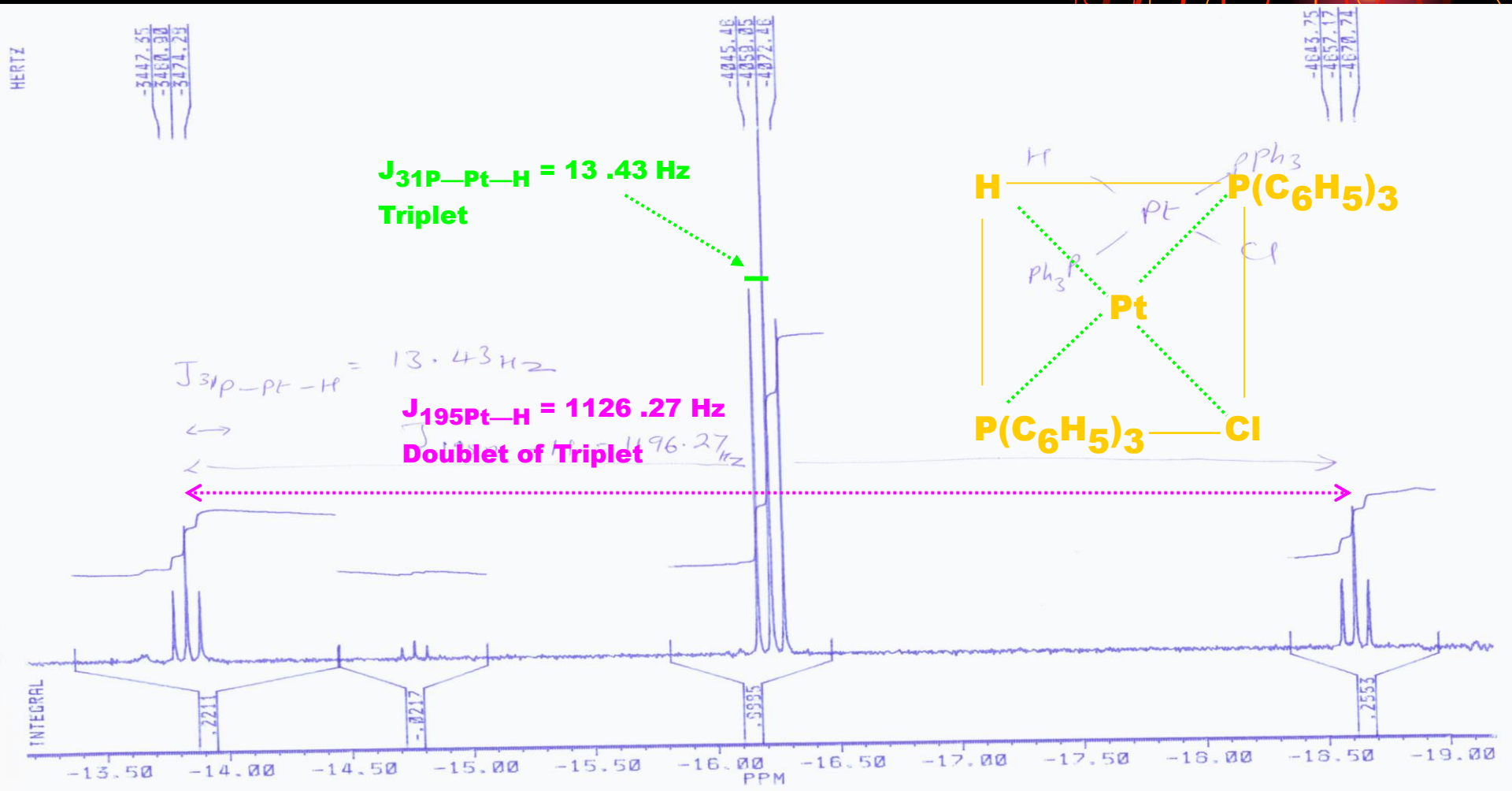
Nucleus	Spin	Nat. Abundance	Sensitivity
^{1}H	1/2	100.00 %	1.00
^{31}P	1/2	100.00 %	0.07
^{195}Pt	1/2	33.80 %	0.0035

Two ^{31}P give Triplet 3 times taller signal

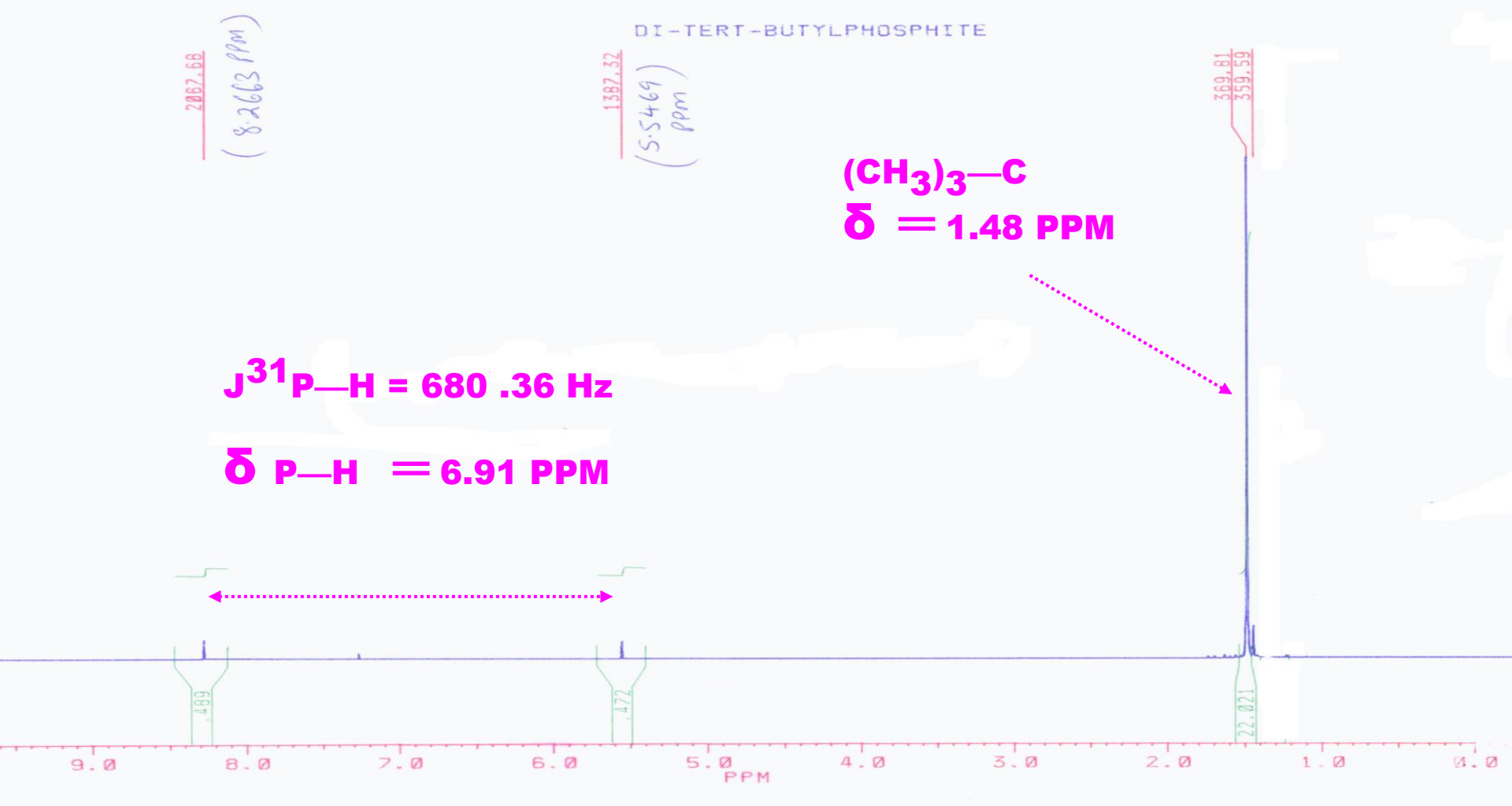
One ^{195}Pt gives Doublet 1/3 Intensity



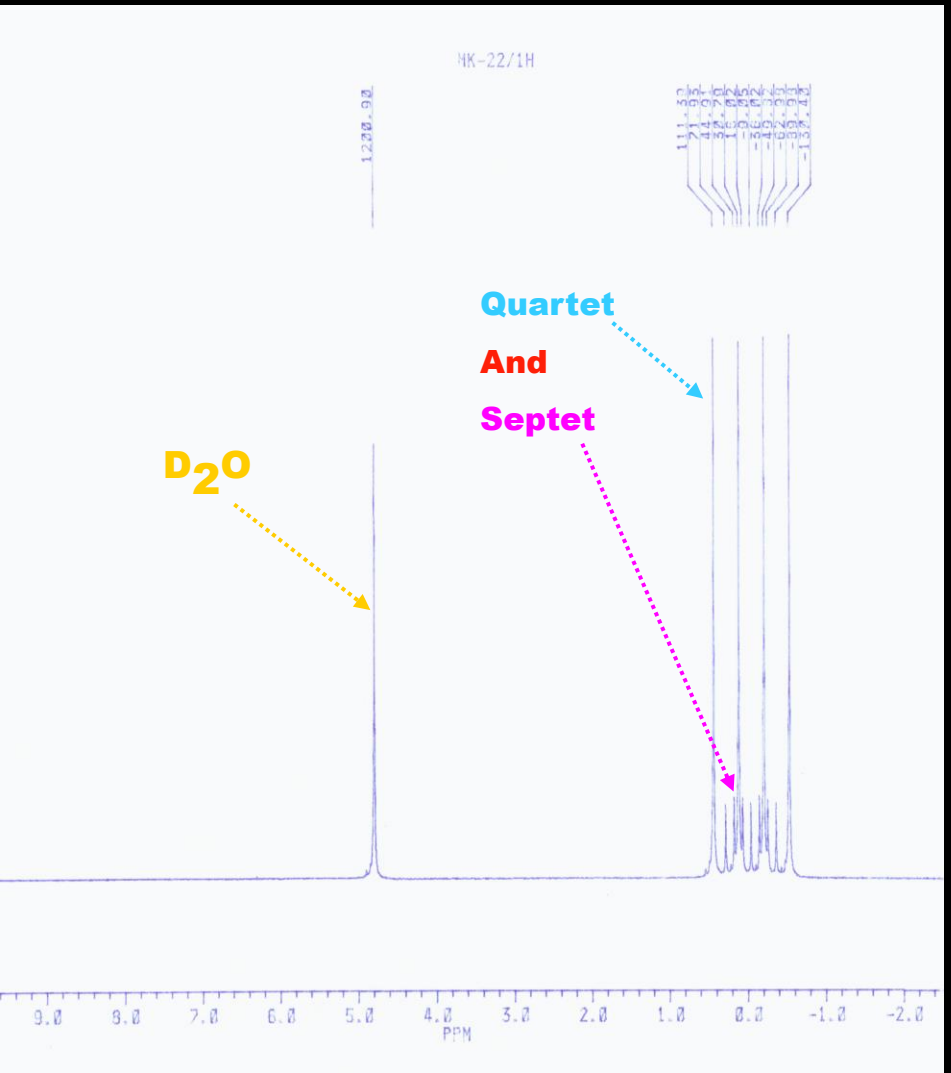
^{1}H NMR Spectrum of $[(C_6H_5)_3P]_2PtHCl$ in $CDCl_3$
DiPhosphine Platinum Hydrochloride Complex
expansion of 13.00 PPM to 19.00PPM



^{1}H NMR Spectrum of Ditertiary Butylphosphite $[(CH_3)_3C\text{-}O\text{-}]_2P(O)H$

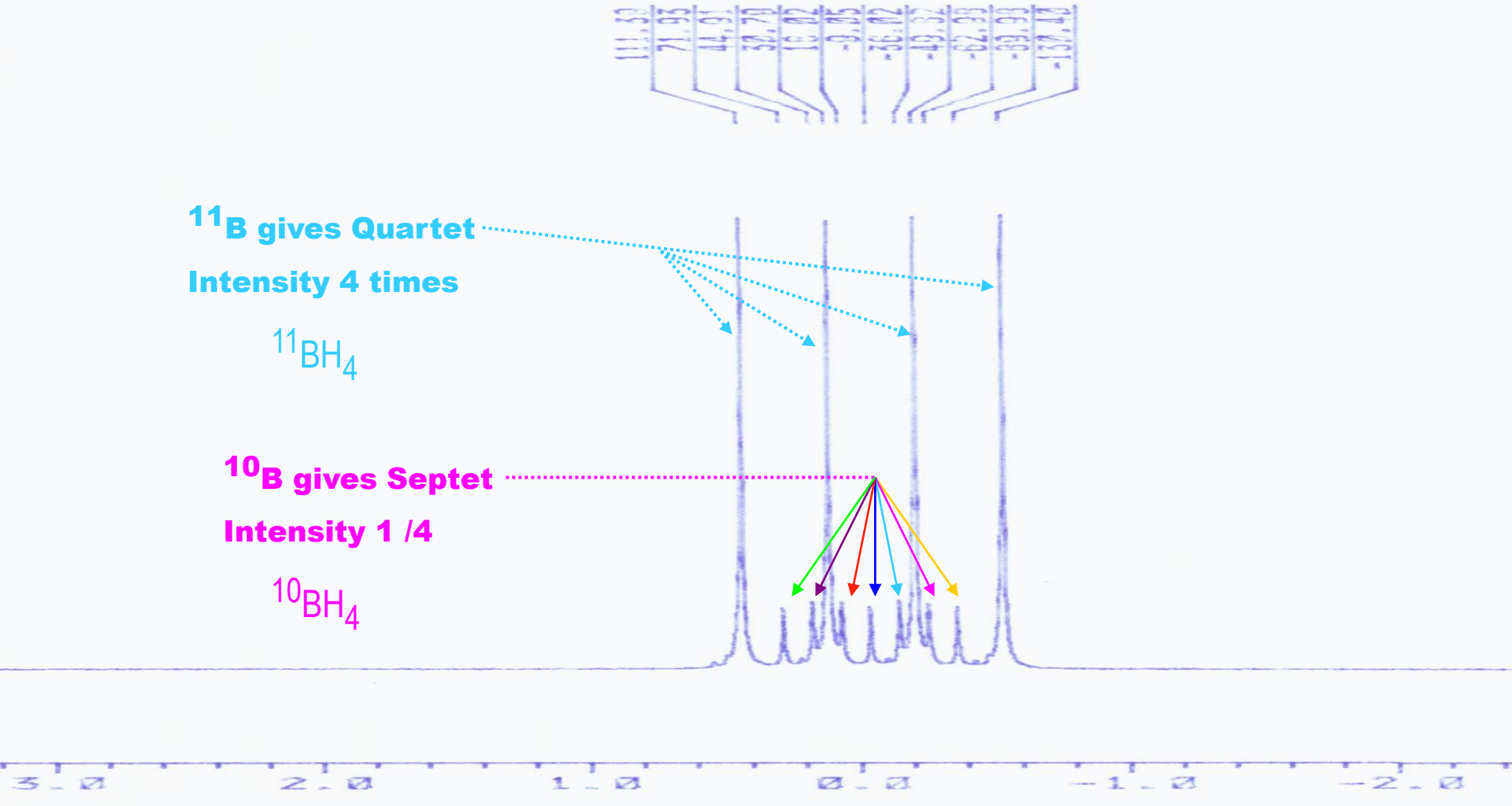


^{1}H NMR Spectrum Of Sodium Borohydride in D_2O
$NaBH_4$ 10.00 to – 2.00 PPM Range

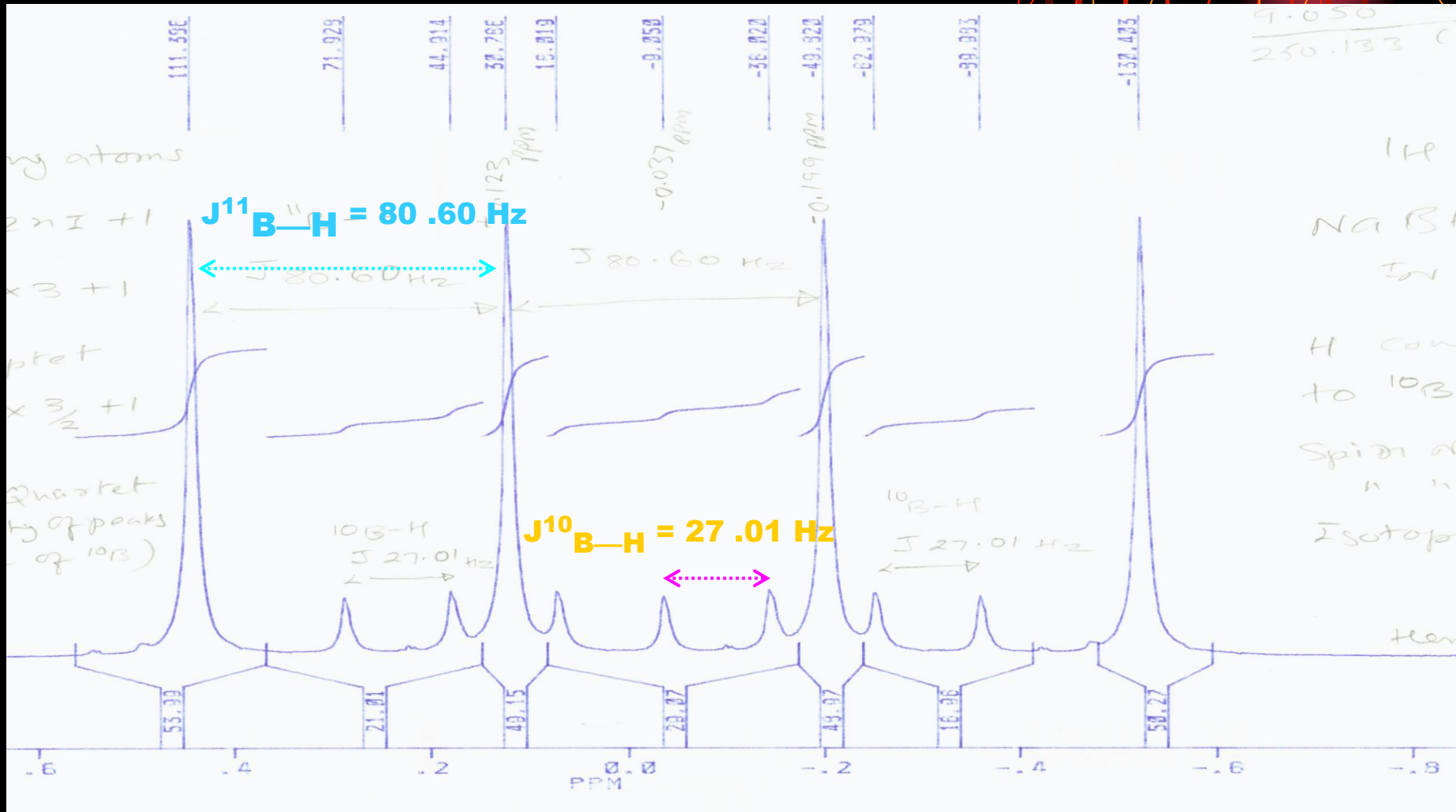


- Coupling from the same atom of different spin
- Isotope % Spin No. SF MHz
- I
- ^{10}B 19 .90 3 26 .875
- ^{11}B 80 .10 3 /2 80 .243
- For ^{1}H No. of peaks = 2 x n x I + 1
- (n = 1) Spin active nucleus neighbour (Boron)
- ^{10}B interaction to ^{1}H
- No. of Peaks = 2 x 1 x 3 +1 = 7 septet
- ^{11}B interaction to ^{1}H
- No. of Peaks = 2 x 1 x3 /2 +1
- = 3 + 1 = 4 Quartet
- Intensity Ratio of NMR Signal from
- ^{10}B & ^{11}B will be 1 : 4 reflecting its
- Isotopic concentration in the atom.
- Hence Quartet is four times taller than
- Septet.

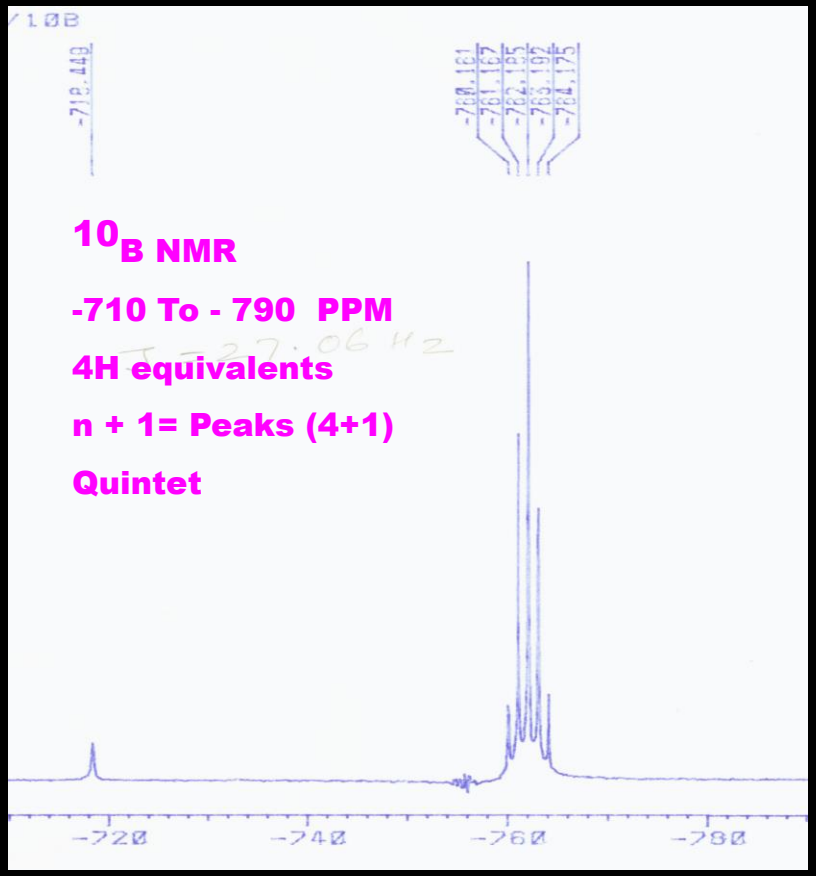
Expansion of ^{1}H NMR Spectrum Of Sodium Borohydride in D_2O
$NaBH_4$



Expansion of ^{1}H NMR Spectrum Of Sodium Borohydride in D_2O
$NaBH_4$



^{10}B & ^{11}B NMR Spectra Of Sodium Borohydride in D_2O
$NaBH_4$



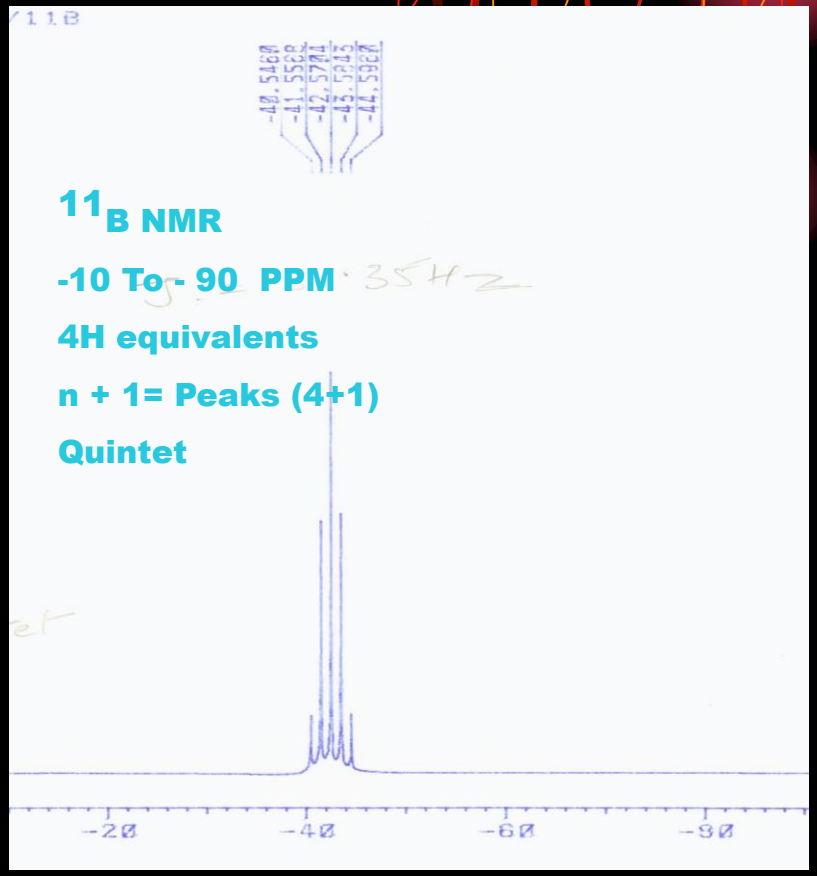
^{10}B NMR

-710 To - 790 PPM

4H equivalents

n + 1= Peaks (4+1)

Quintet



^{11}B NMR

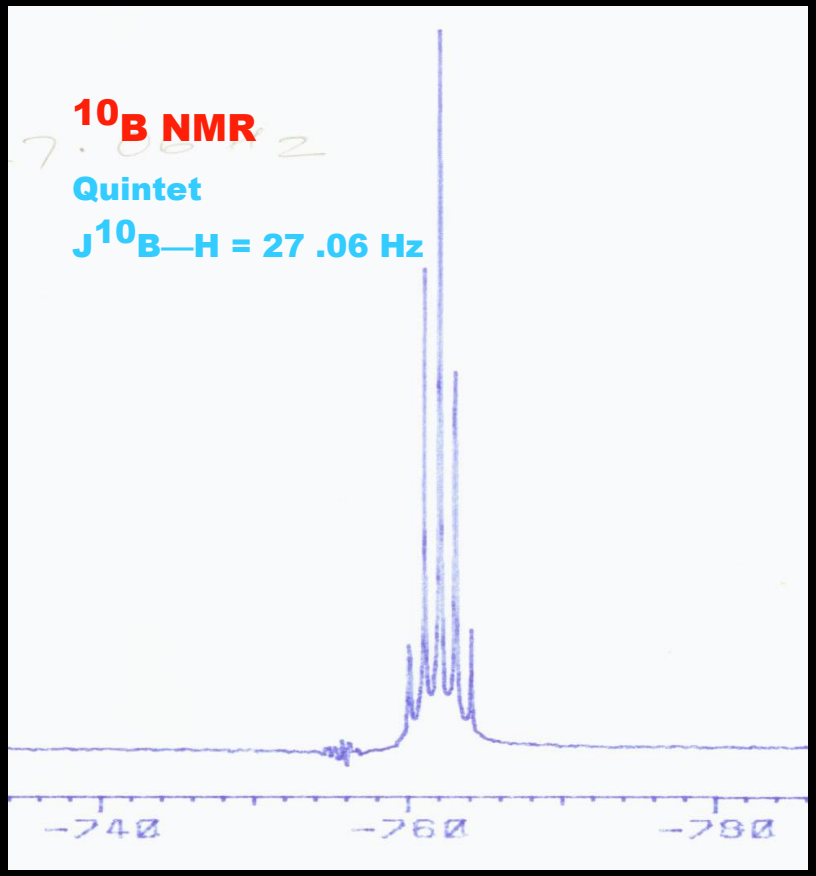
-10 To - 90 PPM

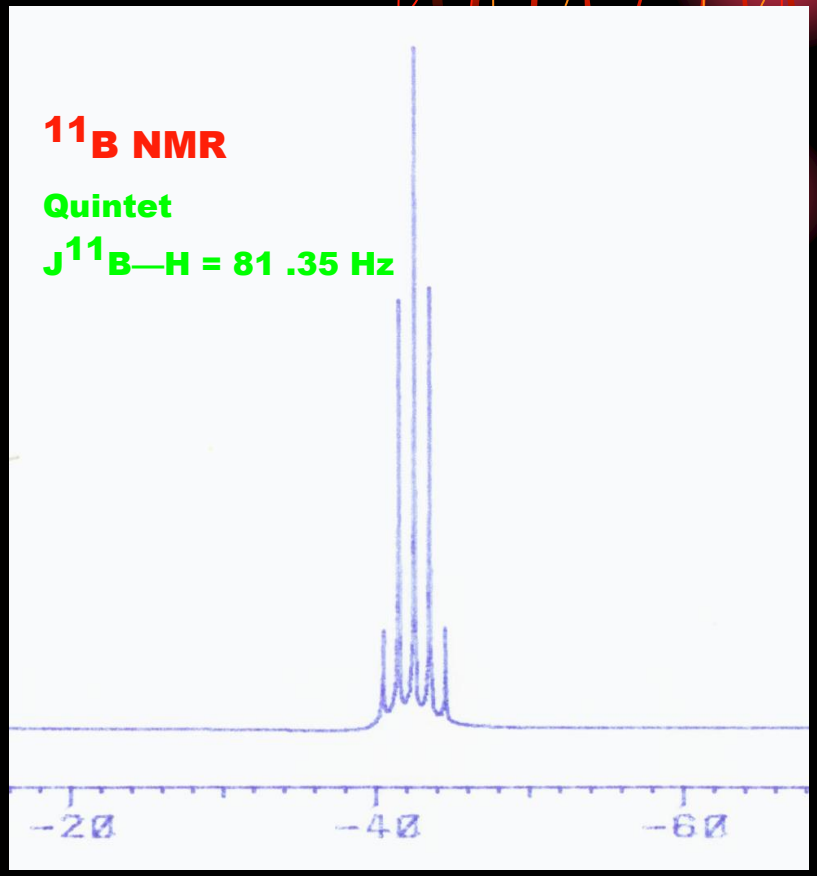
4H equivalents

n + 1= Peaks (4+1)

Quintet

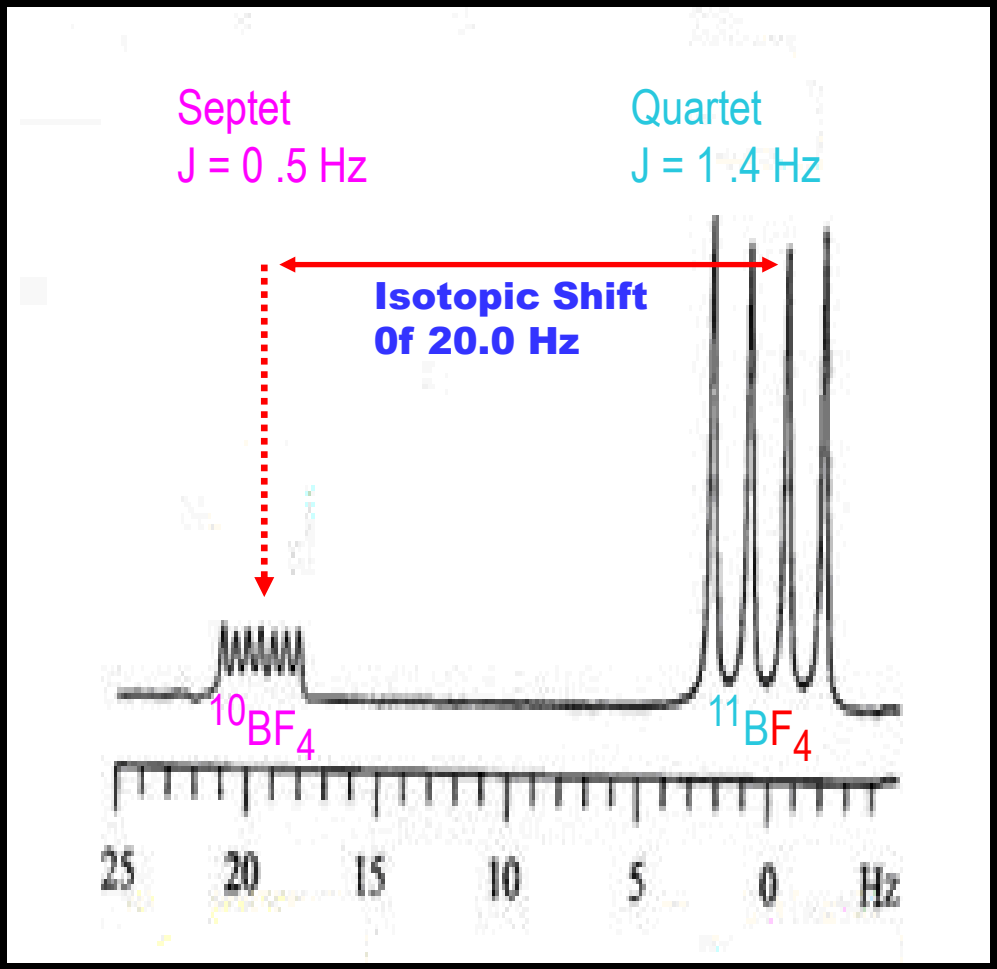
^{10}B & ^{11}B NMR Spectra Of Sodium Borohydride in D_2O
$NaBH_4$





^{19}F NMR of Sodium tetrafluoroborate In D_2O

$NaBF_4$



Coupling from the same atom of different spin

Isotope	%	Spin No. I	SF MHz
^{10}B	19 .90	3	26 .875
^{11}B	80 .10	3 /2	80 .243

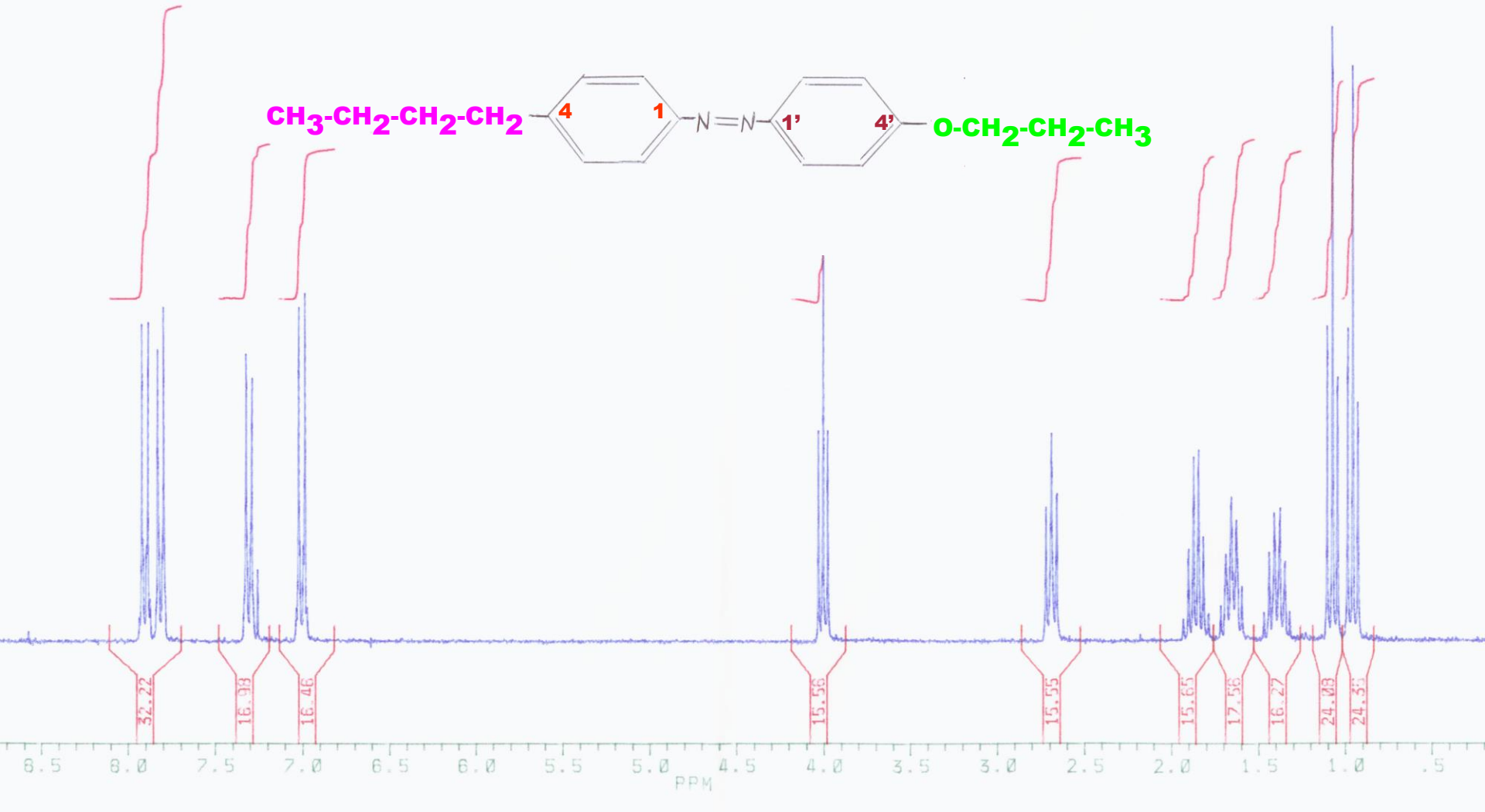
For 19F No. of peaks = 2 x n x I + 1
(n = 1) Spin active nucleus neighbour (Boron)

^{10}B interaction to ^{19}F
No. of Peaks = 2 x 1 x 3 +1 = 7 septet

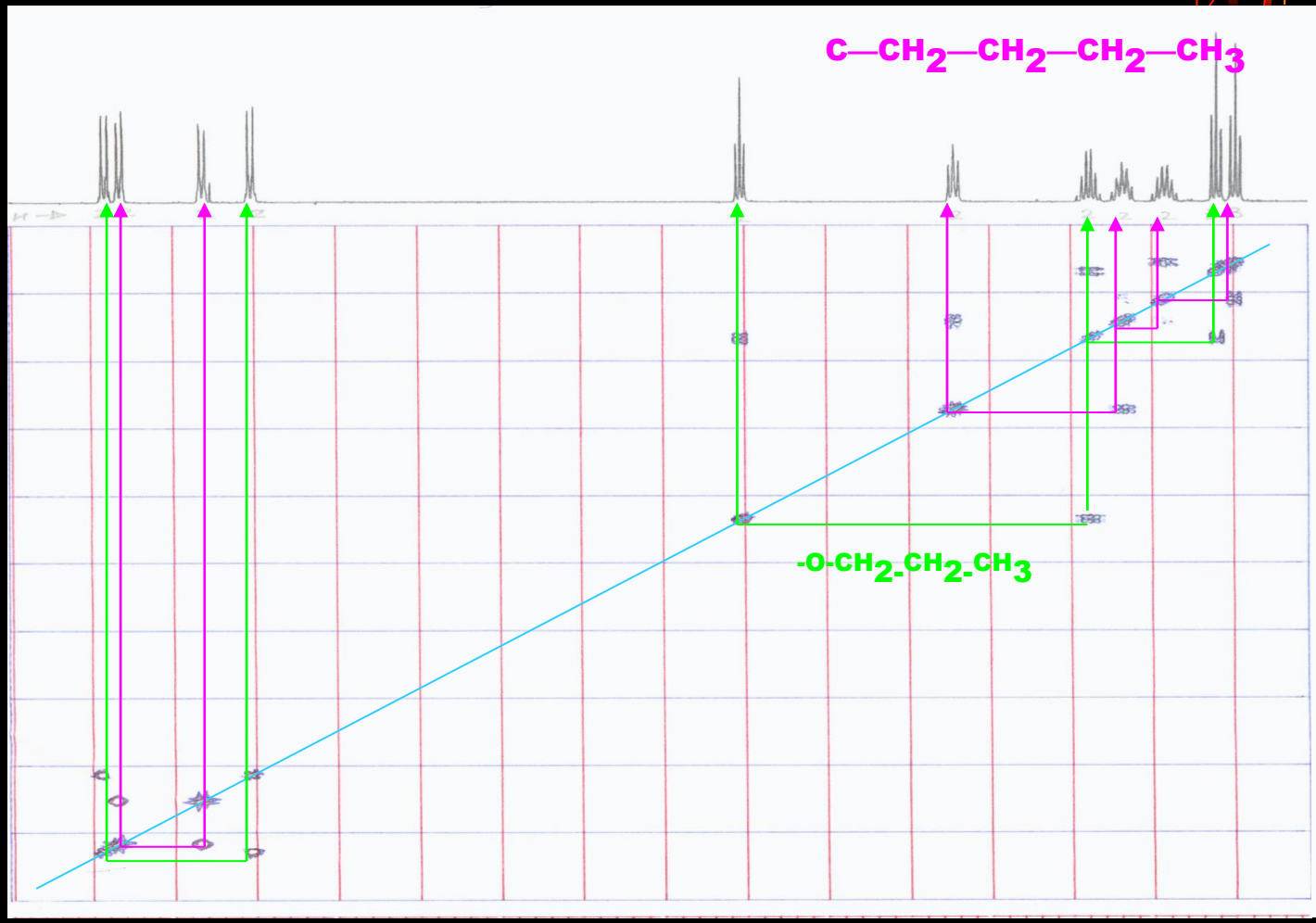
^{11}B interaction to ^{19}F
No. of Peaks = 2 x 1 x3 /2 +1
= 3 + 1 = 4 Quartet

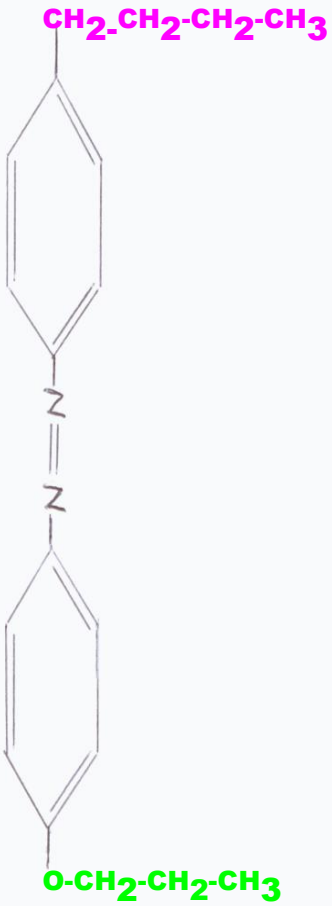
Intensity Ratio of NMR Signal from ^{10}B & ^{11}B will be 1 : 4 reflecting its Isotopic concentration in the atom.
Hence Quartet is four times taller than Septet.

^{1}H NMR Spectrum of $CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$
4-n-Butyl, 4'-Propoxy Diazobenzene

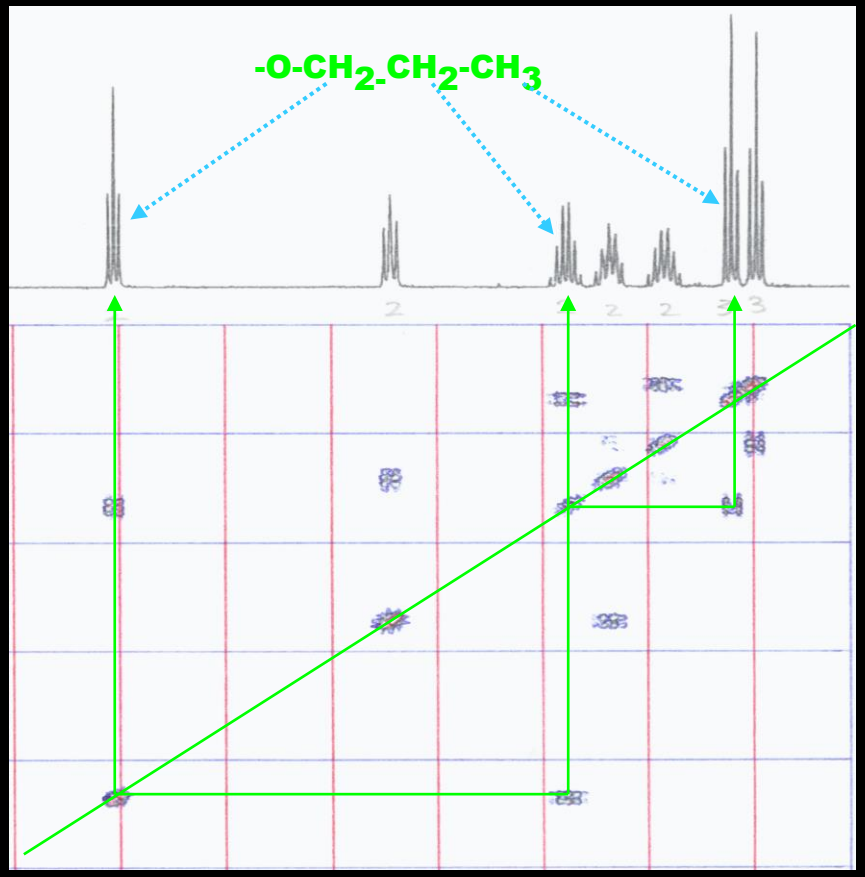


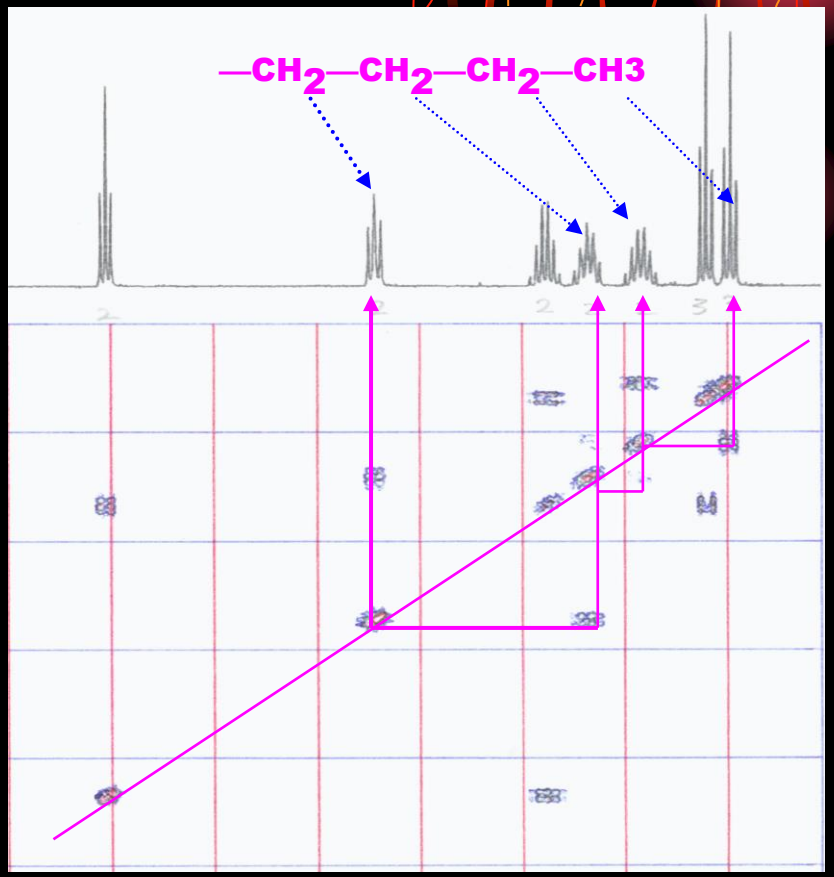
^{1}H COSY 2D NMR Spectrum of $CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$ 4-n-Butyl, 4'-n-Propoxy Diazobenzene



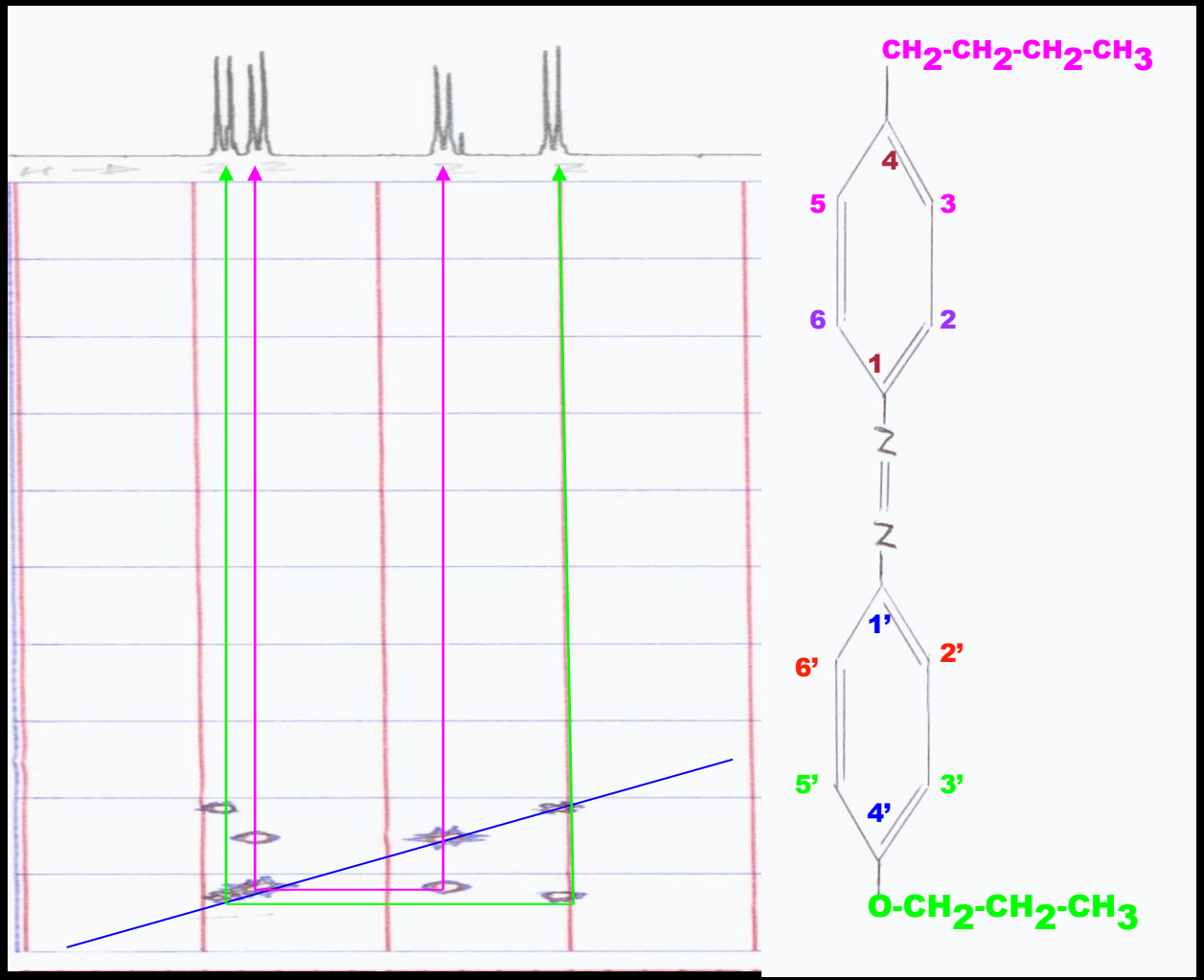


^{1}H COSY 2D NMR Spectrum of $CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$
4-n-Butyl, 4'-n-Propoxy Diazobenzene





^{1}H COSY 2D NMR Spectrum of $CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$ 4-n-Butyl, 4'-n-Propoxy Diazobenzene



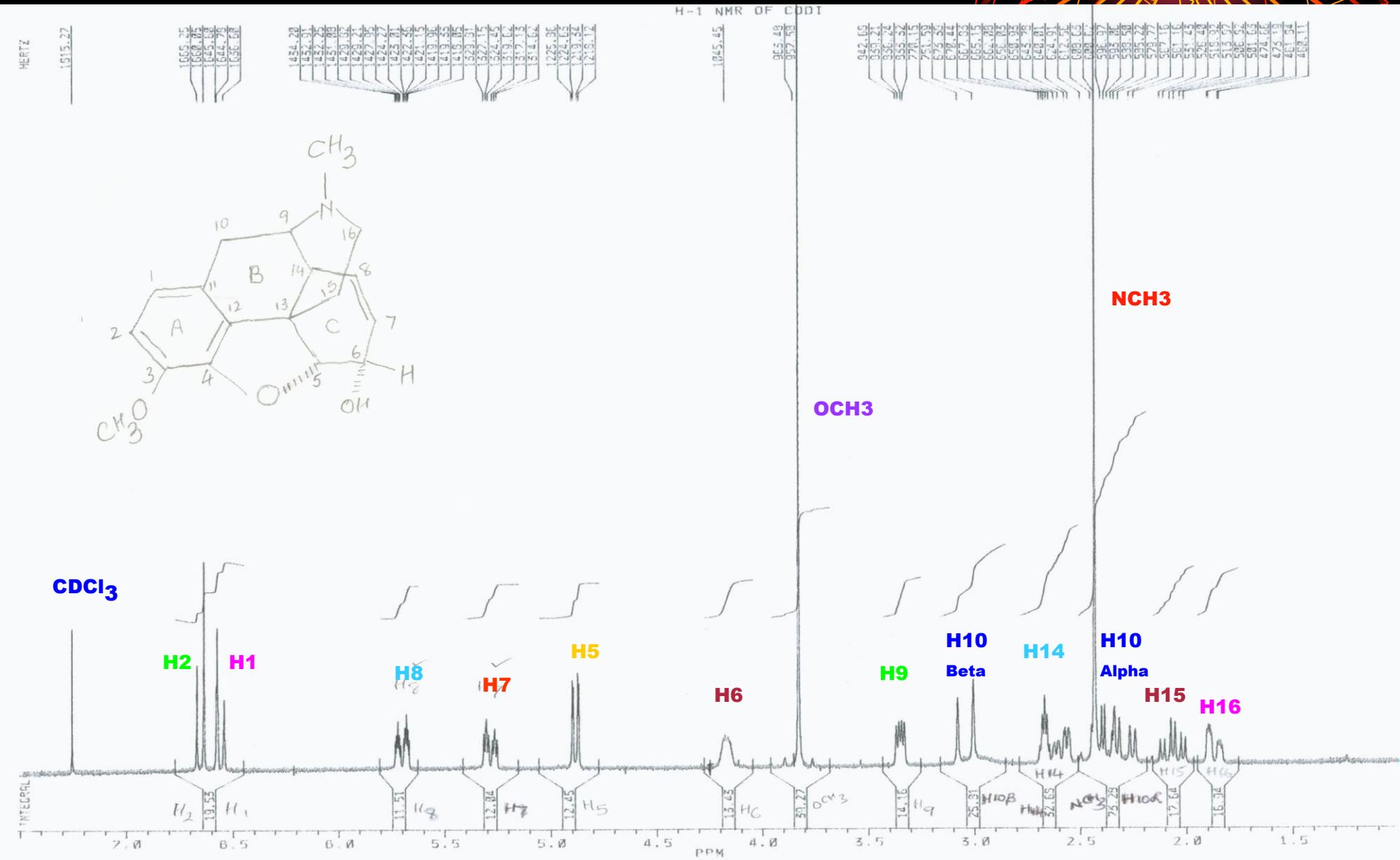
3 , 5 1H 7 .35 PPM &
2 , 6 1H 7 .85 PPM
Inner Doublets

Due to Shielding effects of n-Propoxy group

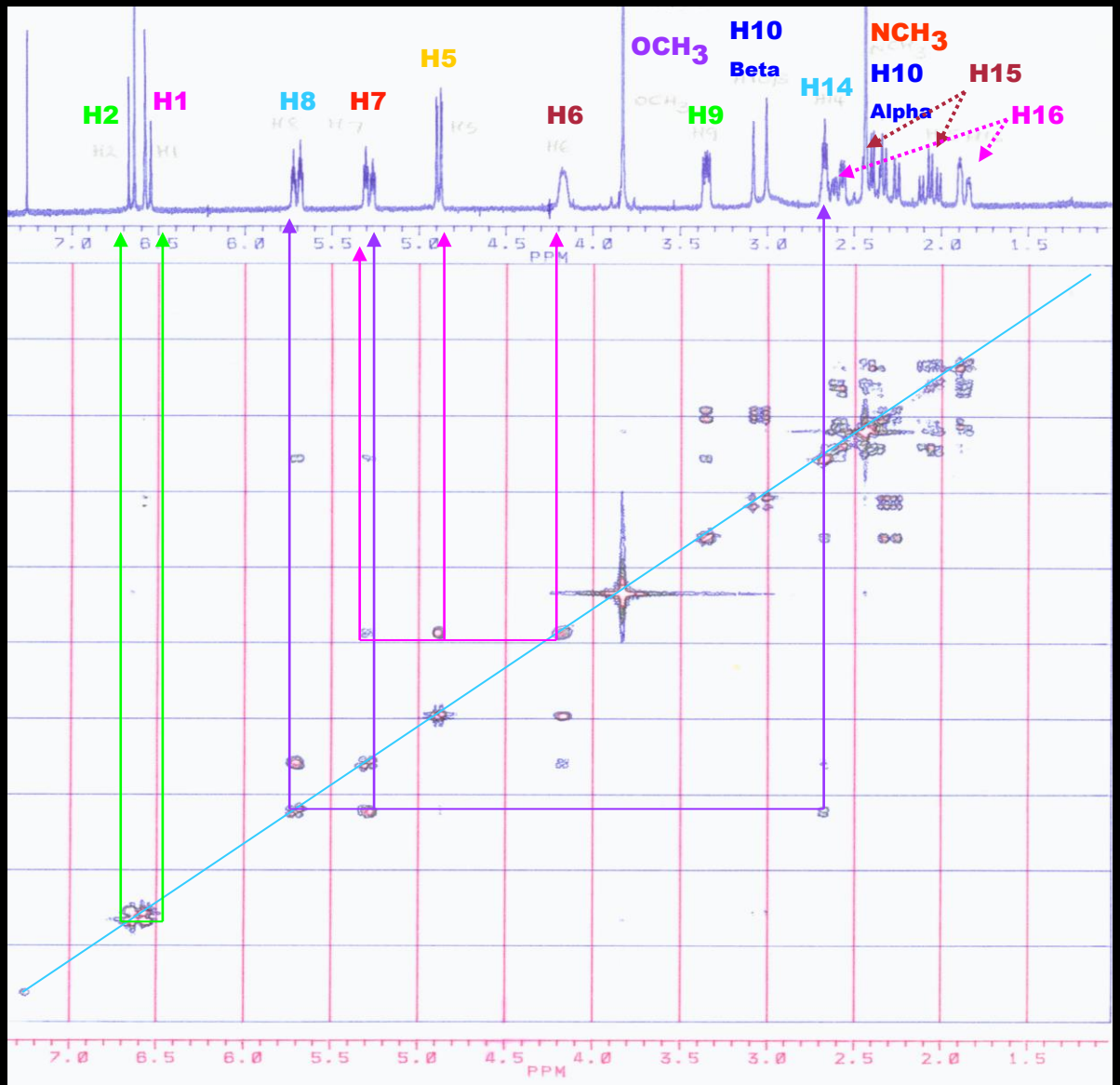
3', 5' ortho 1H 7 .00 PPM &
2', 6' meta 1H 7 .90 PPM
Outer Doublets Green Trac

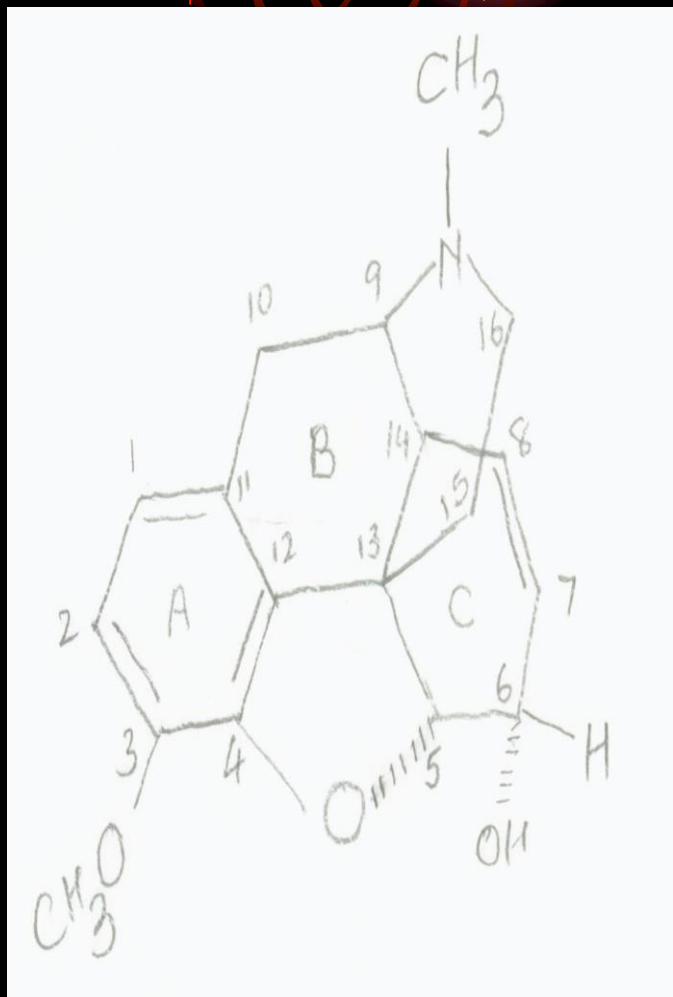
In the above example 2D COSY NMR spectrum is very useful to sort out th Complexity of peaks.

^{1}H NMR of Codeine In $CDCl_3$

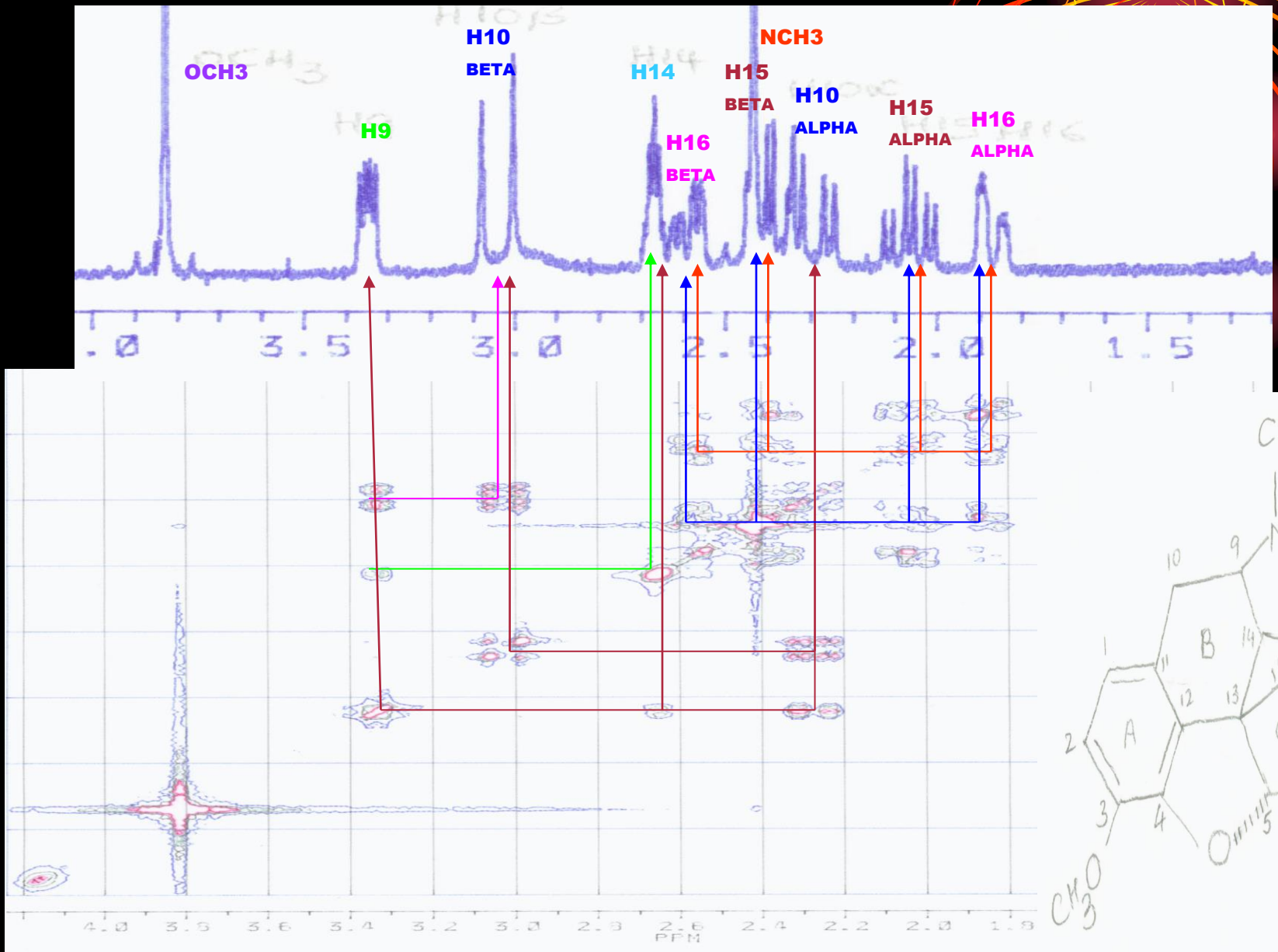


2D COSY NMR Spectrum of Codeine In $CDCl_3$

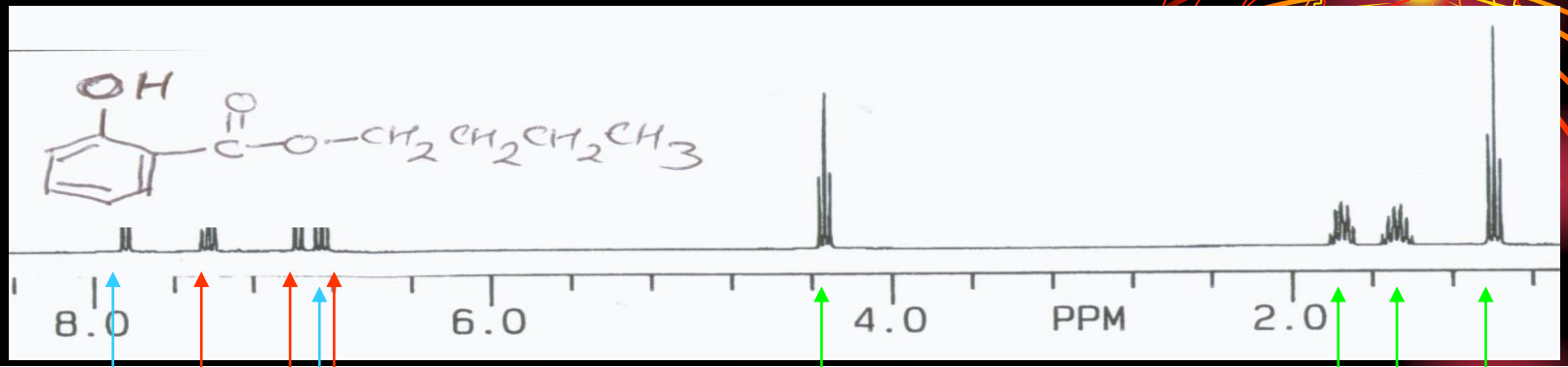


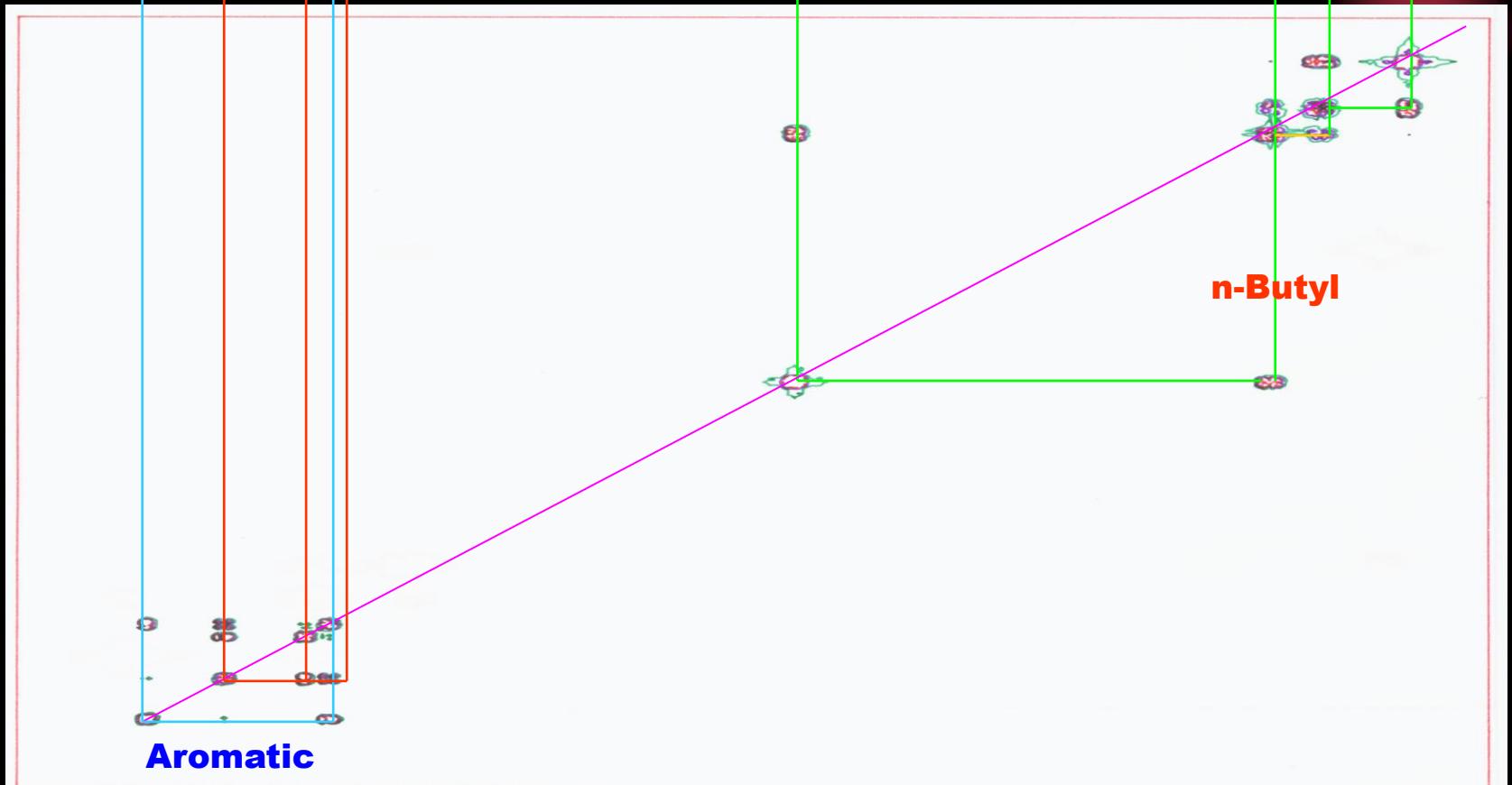


2D COSY NMR Spectrum of Codeine In $CDCl_3$
Expansion from 4.00 To 1.40 PPM Range

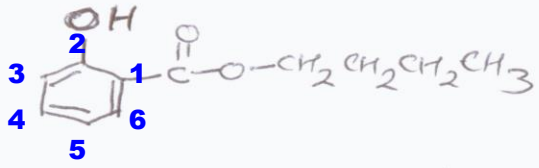


2D COSY ^{1}H NMR Spectrum of n-Butyl salicylate



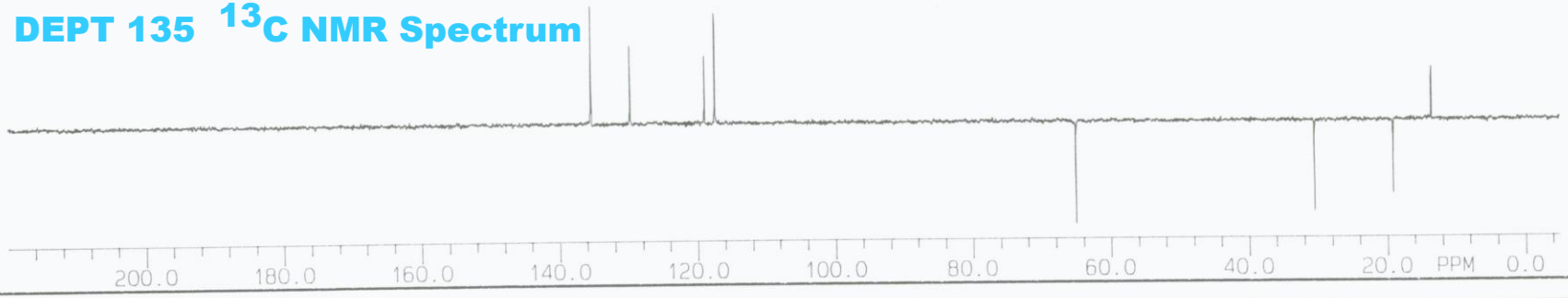


^{13}C NMR Spectrum of n-Butyl Salicylate

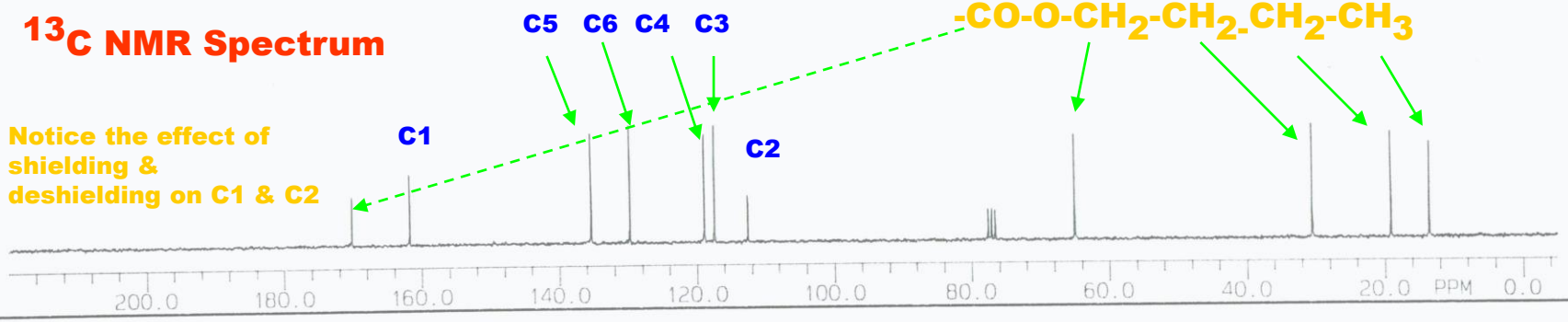


INEPT ^{13}C NMR Spectrum

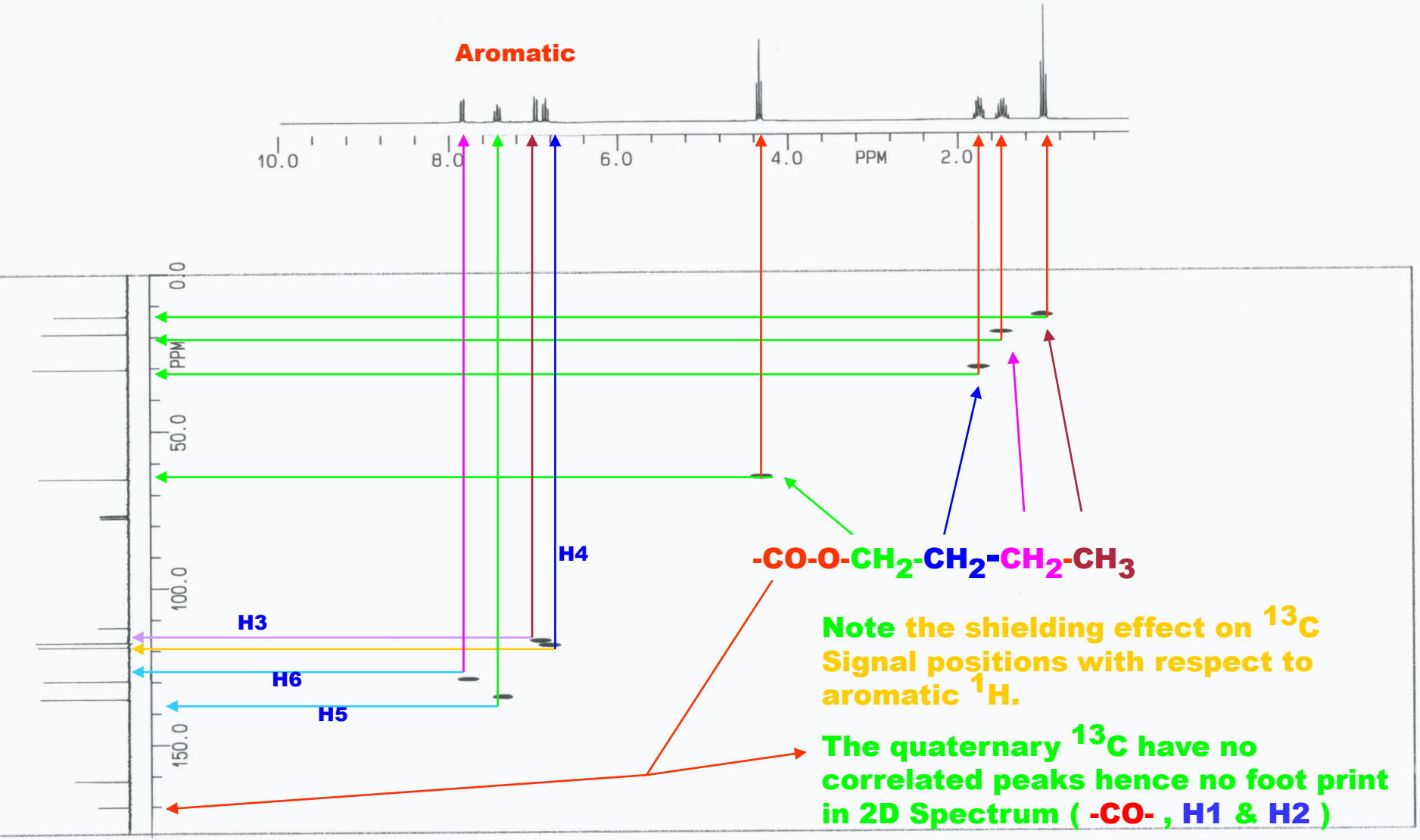
DEPT 135 ^{13}C NMR Spectrum



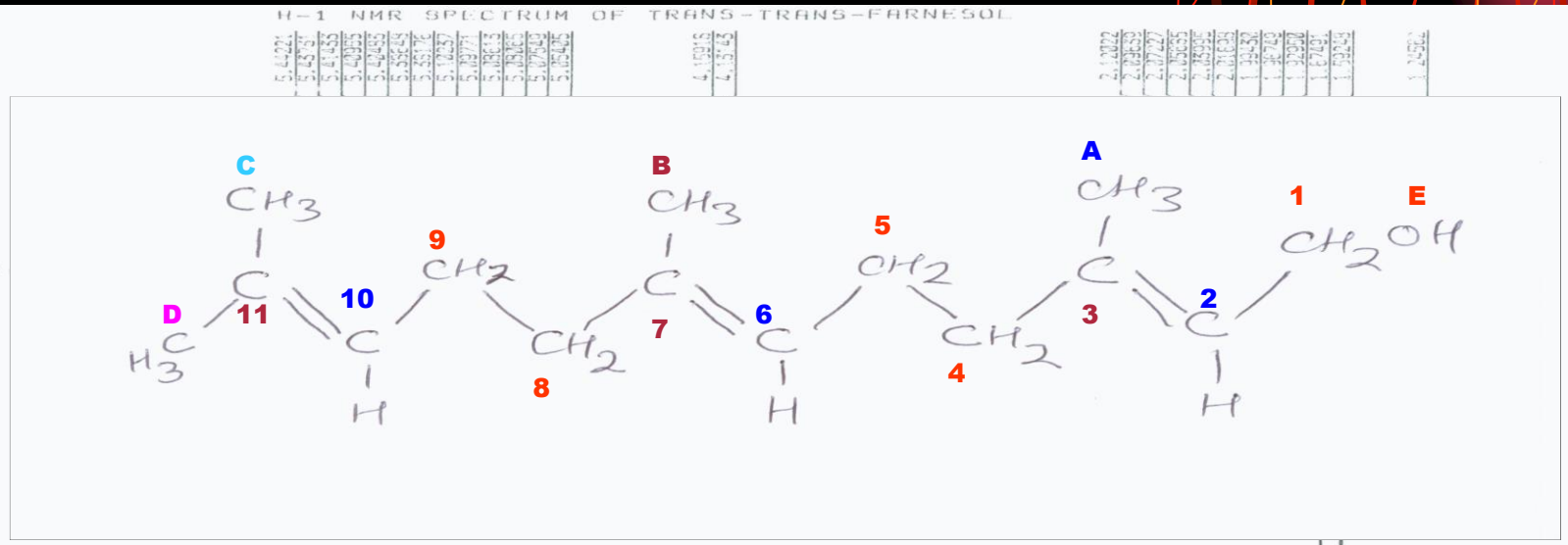
^{13}C NMR Spectrum



$^{1}H—^{13}C$ CORR Spectrum n-Butyl Salicylate

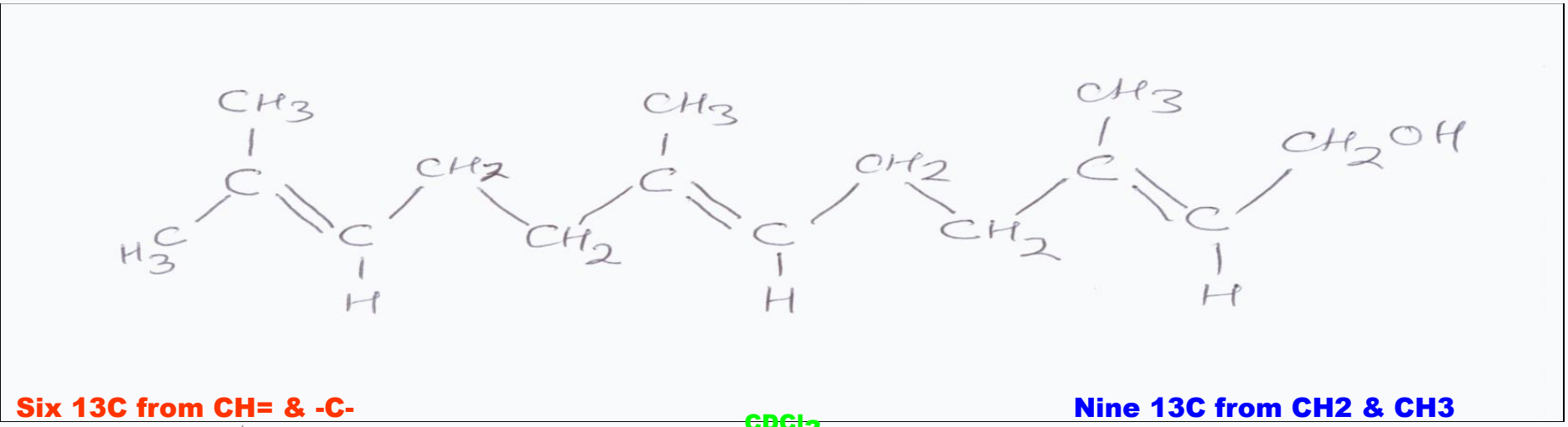


^{1}H NMR 0f Trans FARNESOL $C_{15}H_{26}O$



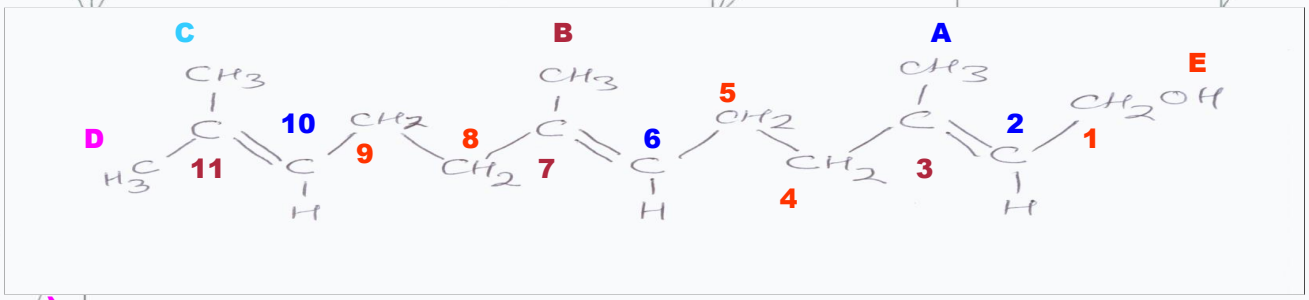
^{13}C NMR Spectrum of Trans FARNESOL In $CDCl_3$

$C_{15}H_{26}O$



^{13}C & DEPT 135 NMR Spectra of Trans Farnesol In $CDCl_3$

$C_{15}H_{26}O$



CH (Three)

DEPT - 135

10 6 2

DEPT 135 NMR

CH_3 (Four)

A C B D

CH_2(Five)

1 4 5 8 9

Quaternary ^{13}C

3 7 11

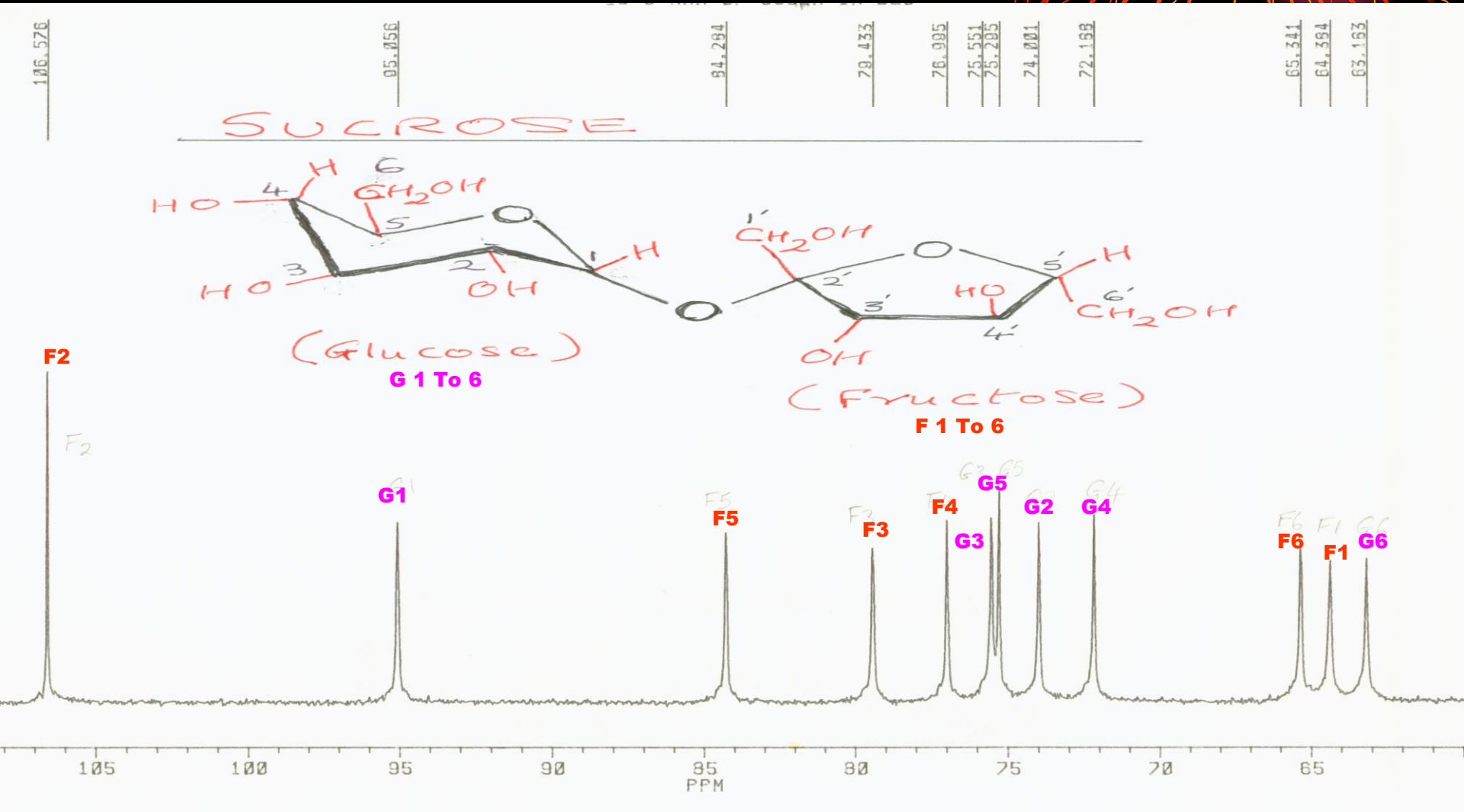
$CDCl_3$

140 130 120 110 100 90 80 70 60 50 40 30 20 10

PPM

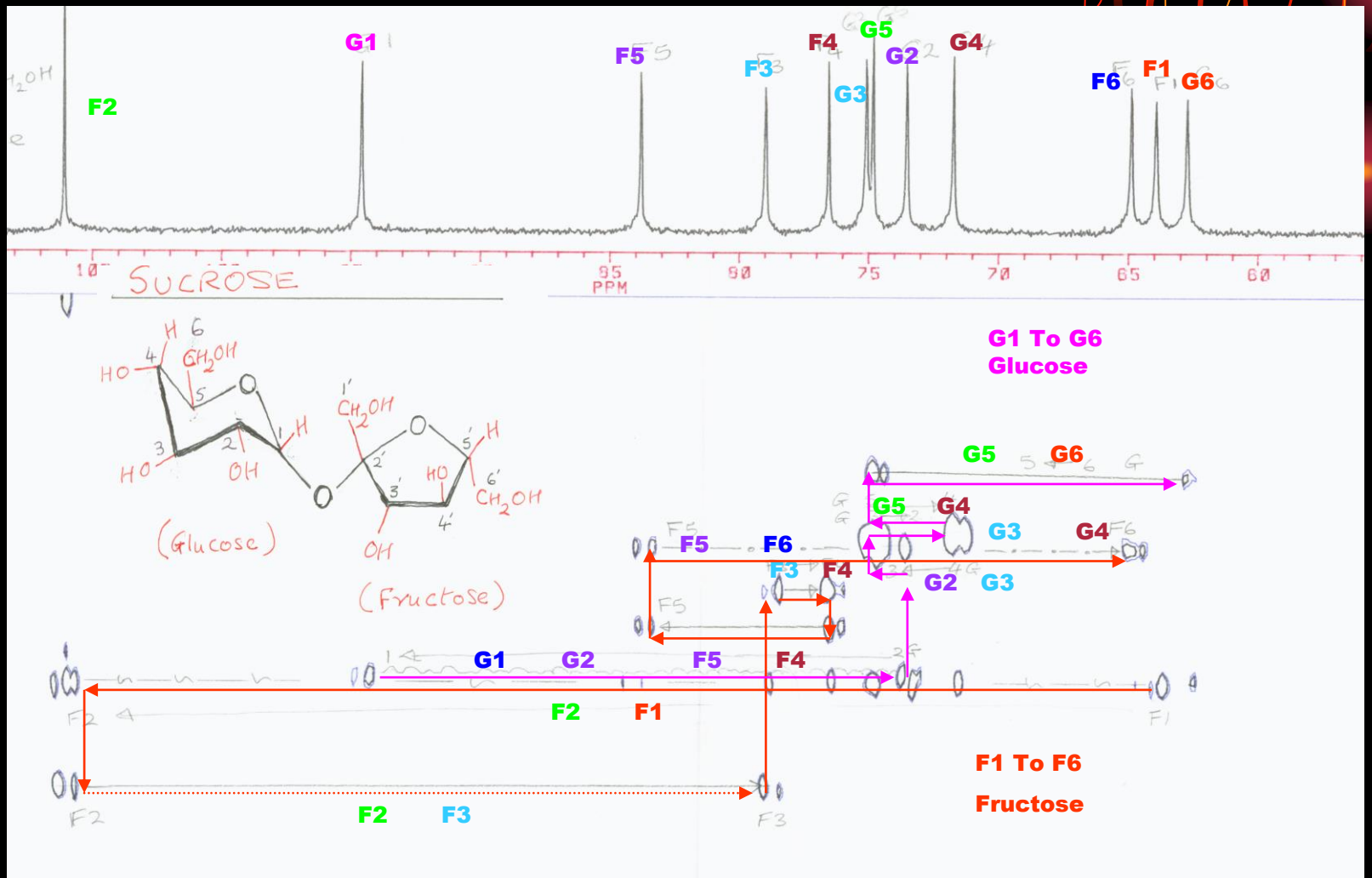
^{13}C NMR Spectrum of sucrose In D_2O

$C_{12}H_{22}O_{11}$



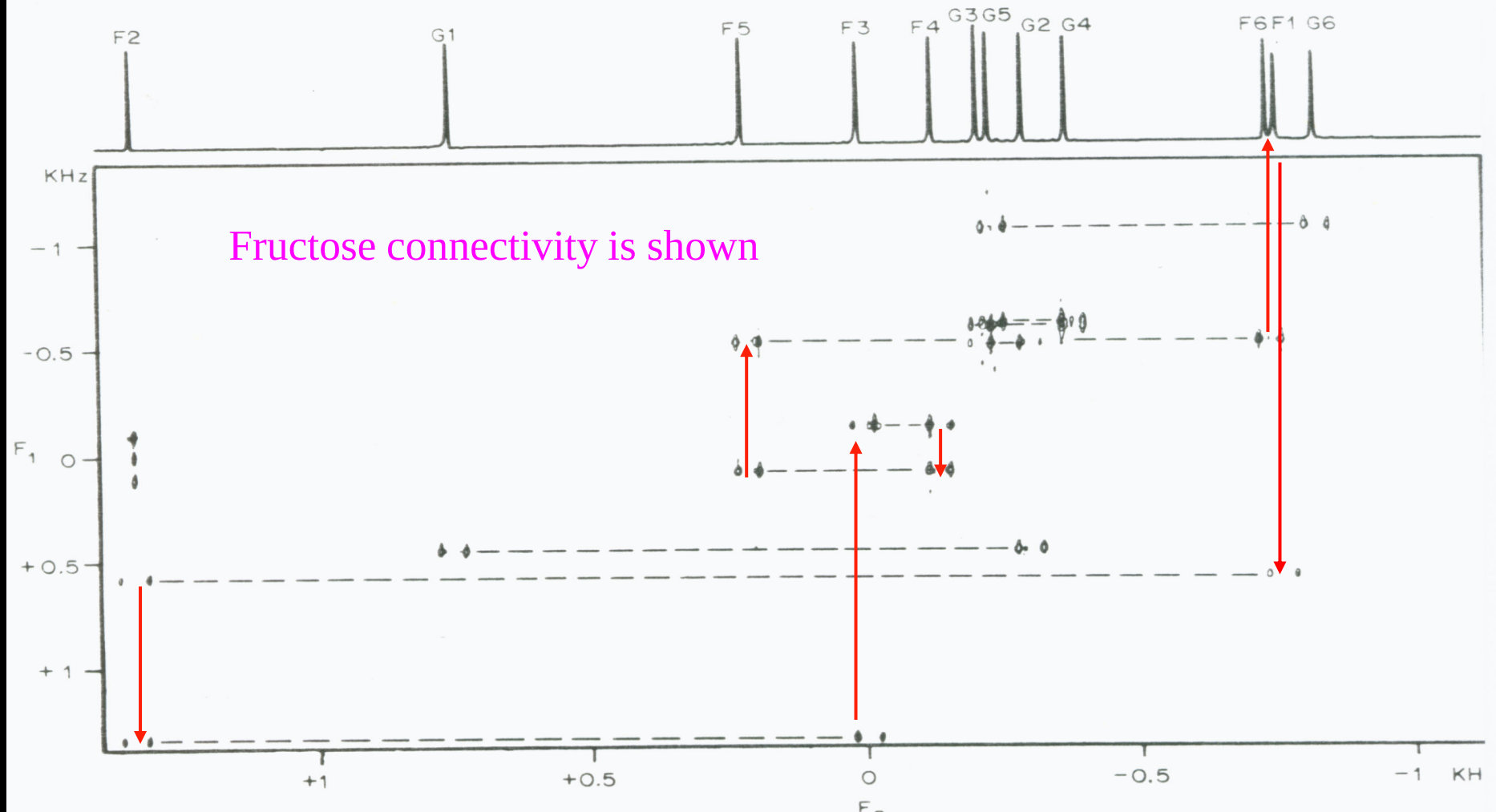
2D ^{13}C Connectivity NMR Spectrum of sucrose In D_2O

$C_{12}H_{22}O_{11}$

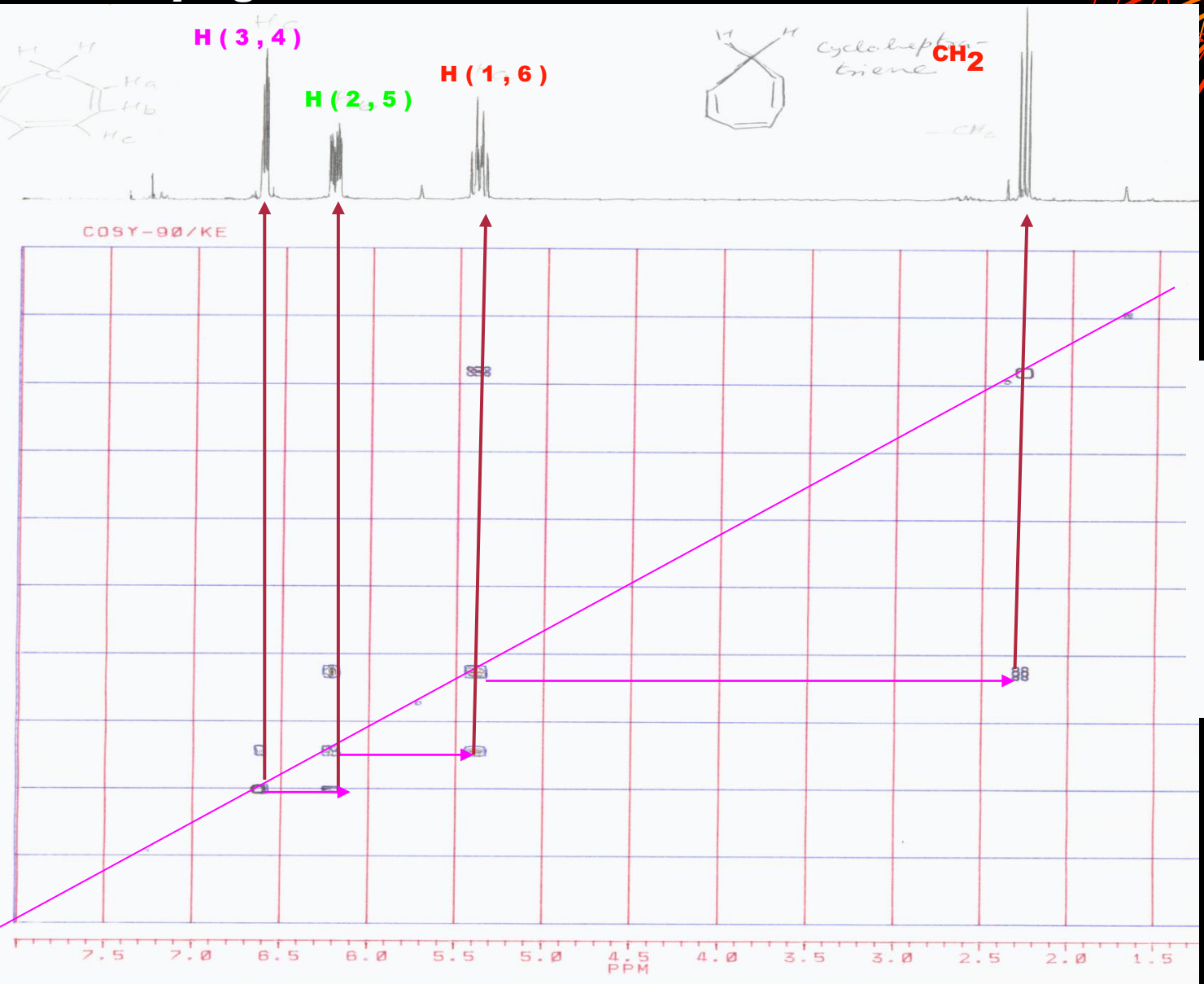


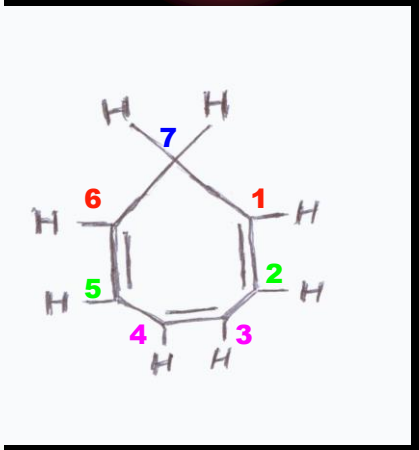
2D ^{13}C Connectivity NMR Spectrum of sucrose In D_2O

$C_{12}H_{22}O_{11}$

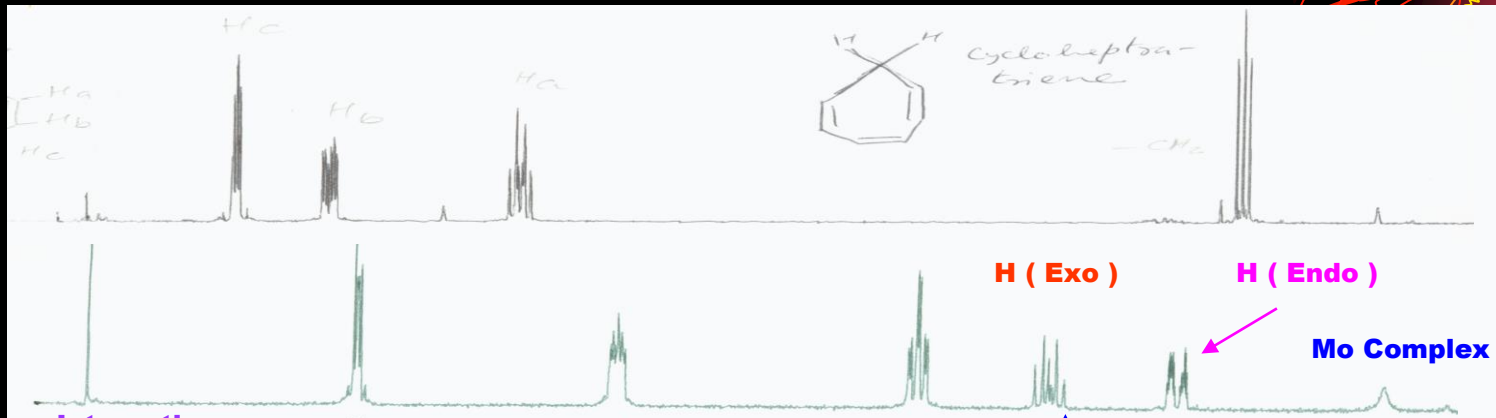


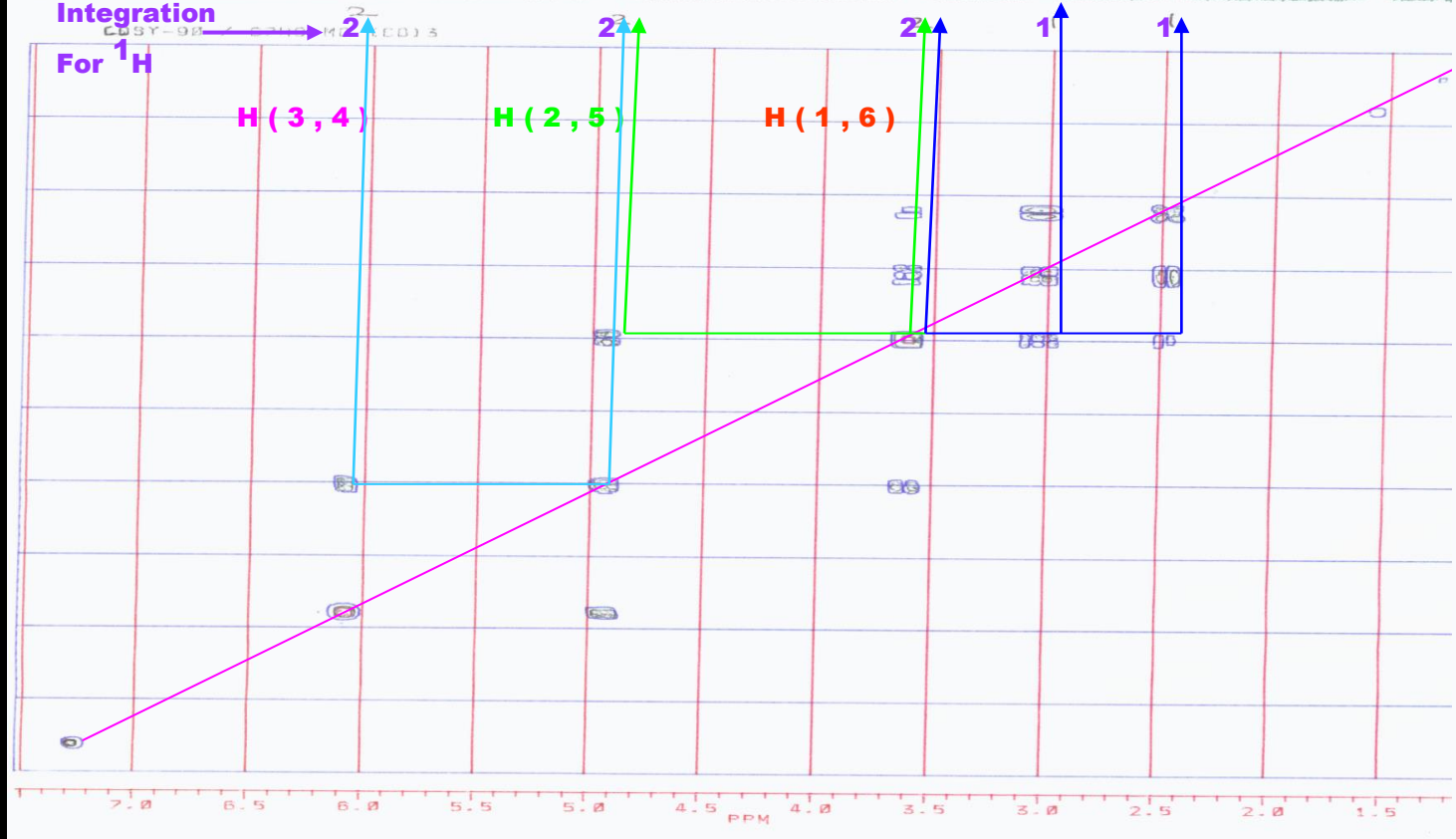
^{1}H 2D COSY 90 NMR Spectrum of Cycloheptatriene C_7H_8

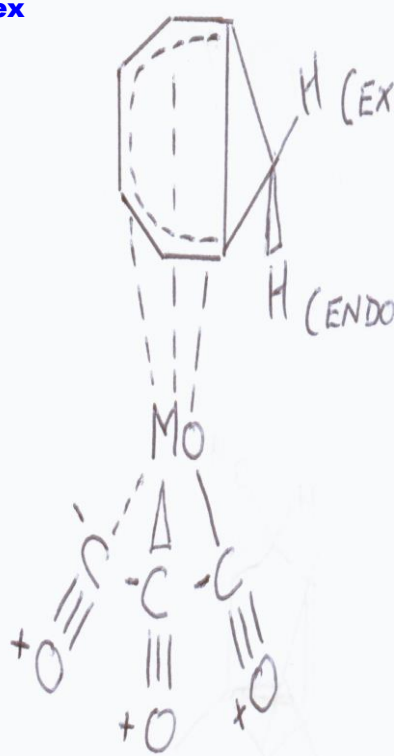




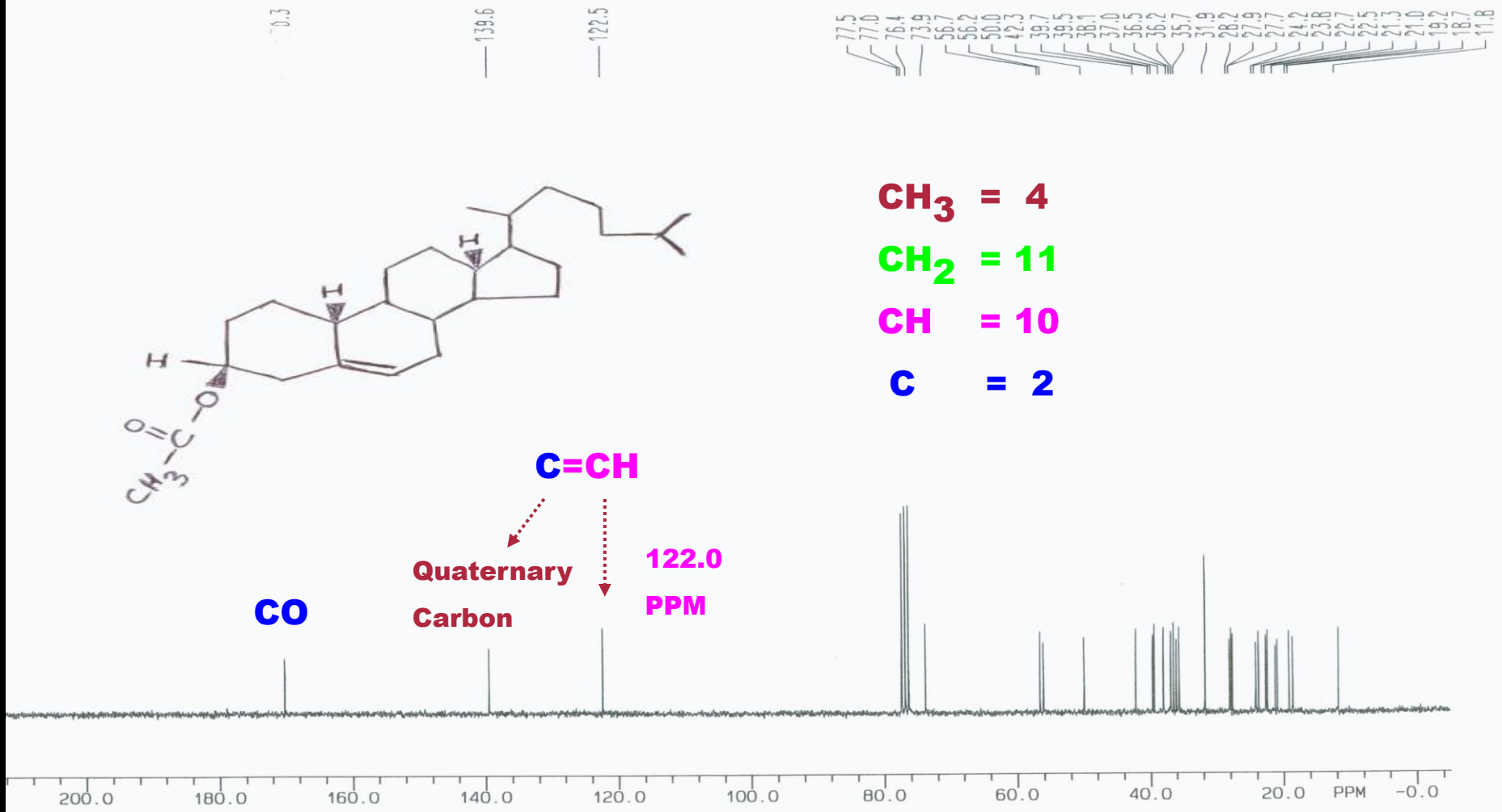
^{1}H 2D COSY 90 NMR Spectrum of Cycloheptatriene Molybdenum Tricarbonyl Complex C_7H_8 Mo $(CO)_3$



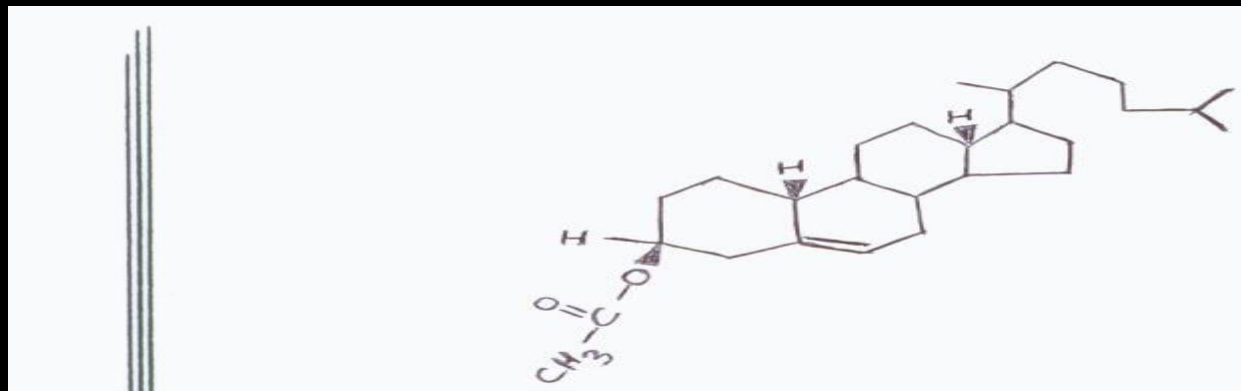




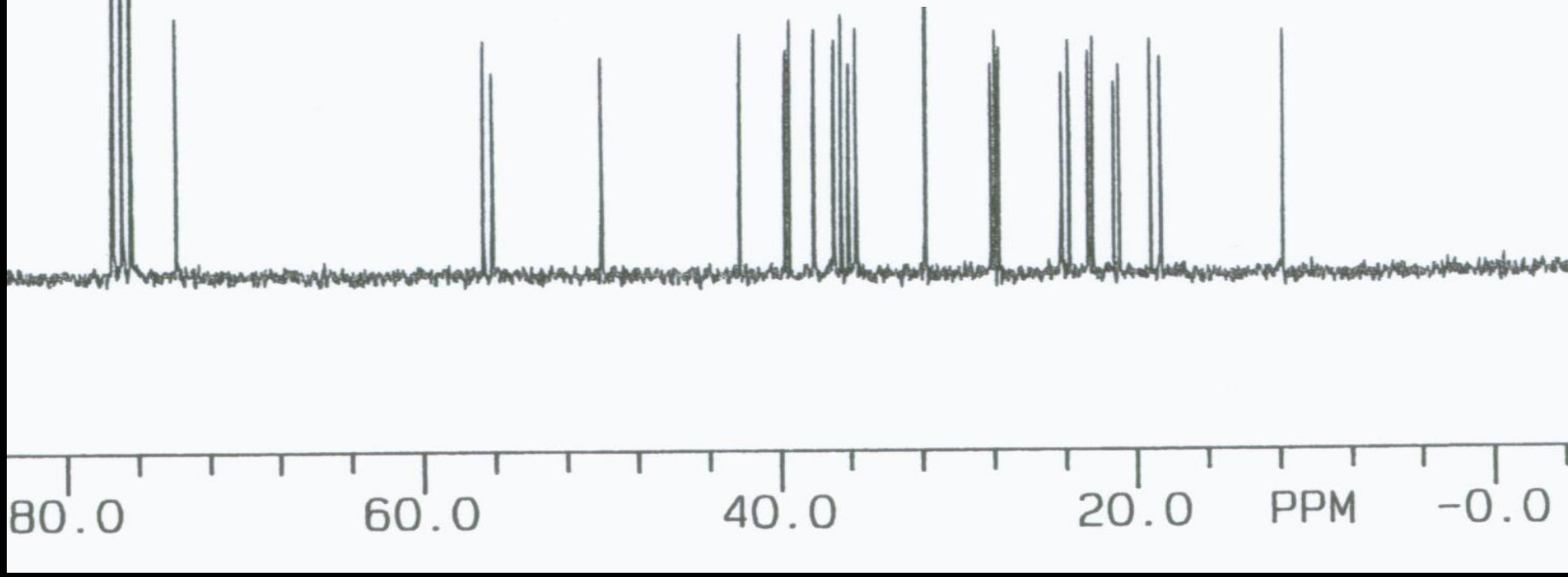
^{13}C NMR Spectrum of Cholesteryl Acetate
$C_{25}H_{45}$-OCOCH$_3$



Expansion of ^{13}C NMR Spectrum of Cholesteryl Acetate
0.0 To 80.0 PPM $C_{25}H_{45}$-$OCOCH_3$

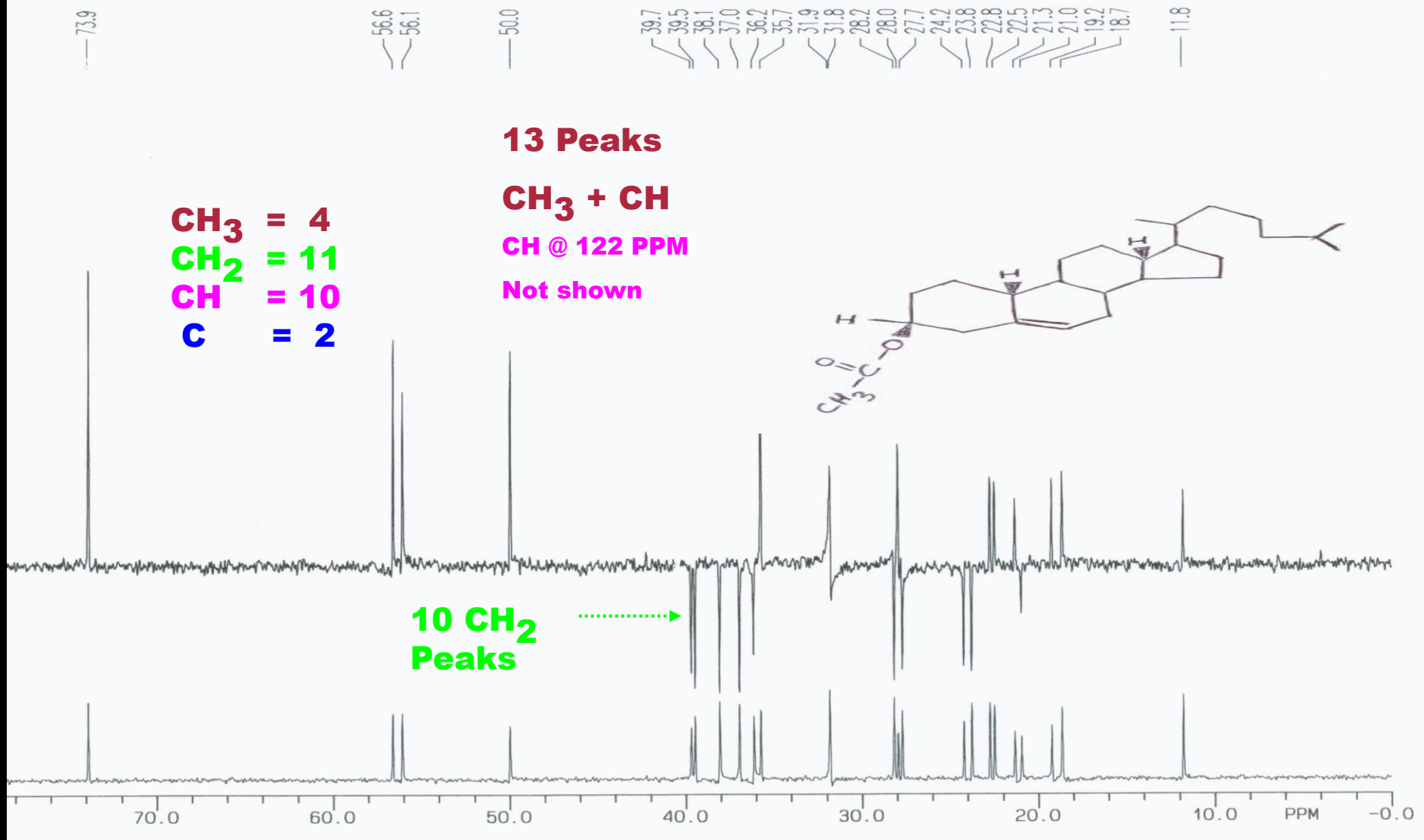


CH_3 = 4
CH_2 = 11
CH = 10
C = 2



^{13}C DEPT 135 NMR Spectrum of Cholesteryl Acetate

$C_{25}H_{45}$-$OCOCH_3$ 80.0 to 0.0 PPM



^{31}P NMR Spectrum of $PF_2H(NH_2)_2$ With Labelled ^{15}N

P-H Doublets **P-F2** Triplets **P-N** Triplets **P-H** Quintets

2 x 3 x 3 x 5 = 90 Lines NMR Spectrum