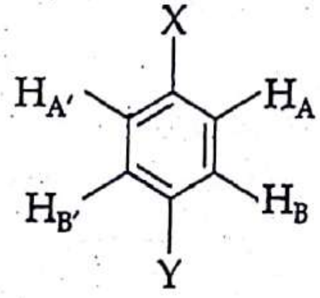
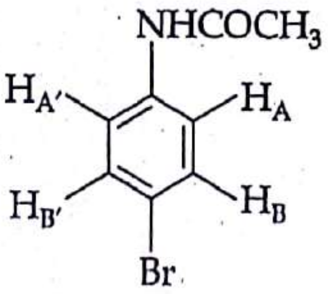
8.3 Spectroscopic Analysis

p - Disubstituted benzene with non identical substituents :



For these compounds H_A and $H_{A/}$ are chemically equivalent as both of them are ortho w.r.t X and meta w.r.t Y. Thus the δ value is the same for both H_A and $H_{A/}$. The same is true for H_B and $H_{B/}$. However /. H_A and $H_{A/}$ are magnetically non equivalent as they couple with H_B and $H_{B/}$ with unequal coupling constants. Similarly H_B and $H_{B/}$ are also magnetically non equiva lent for their coupling with H_A and $H_{A/}$ with different coupling constants. This type of system is referred to as AA/BB/ system. Usually these aromatic protons appear as doublet due to ortho coupling with a J value of 7-9 Hz (para coupling is usually not seen). δ Values of the aromatic protons depend on the nature of the substituents X and Y.

8.3.1 4-Bromoacetanilide



- **^{1}H-NMR Spectrum :**

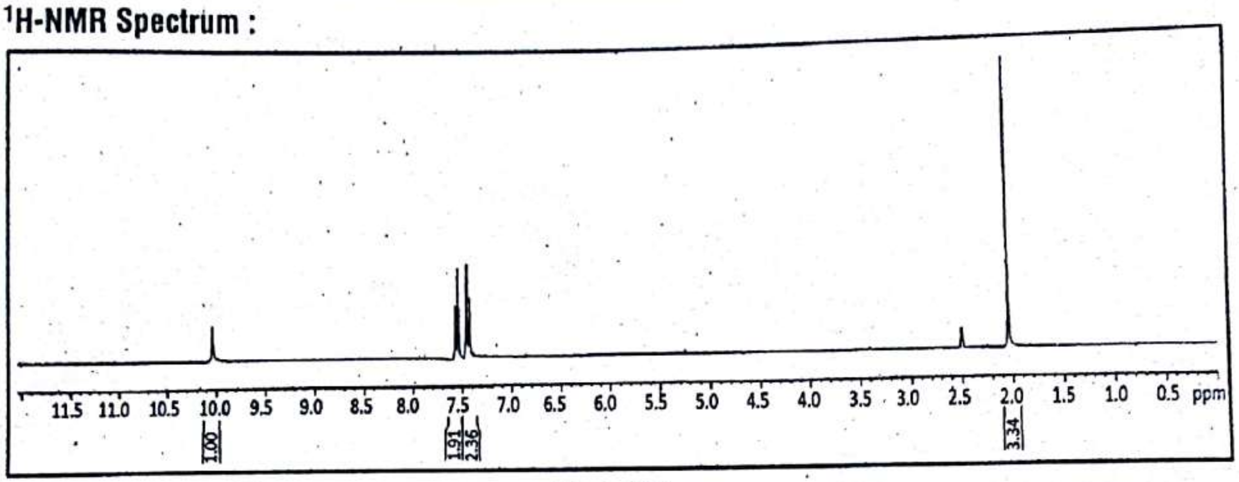


Figure-8,3

Chemical Shift (δ ppm)	Multiplicity J Hz	Assignment to proton	Explanation
2.05	Singlet (3H)	$-CH_3$	Deshielding by carbonyl causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
7.44	Doublet (2H) (7.5 Hz)	H_A and $H_{A'}$	Mesomeric electron release by $-NHCOMe$ may cause slight shielding. The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
7.56	Doublet (2H) (7.5 Hz)	H_B and $H_{B'}$.	The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
10.05	Broad singlet (1H)	$-NH$	The signal appears as a singlet due to absence of any coupling partner. Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet.

- **IR Spectrum :**

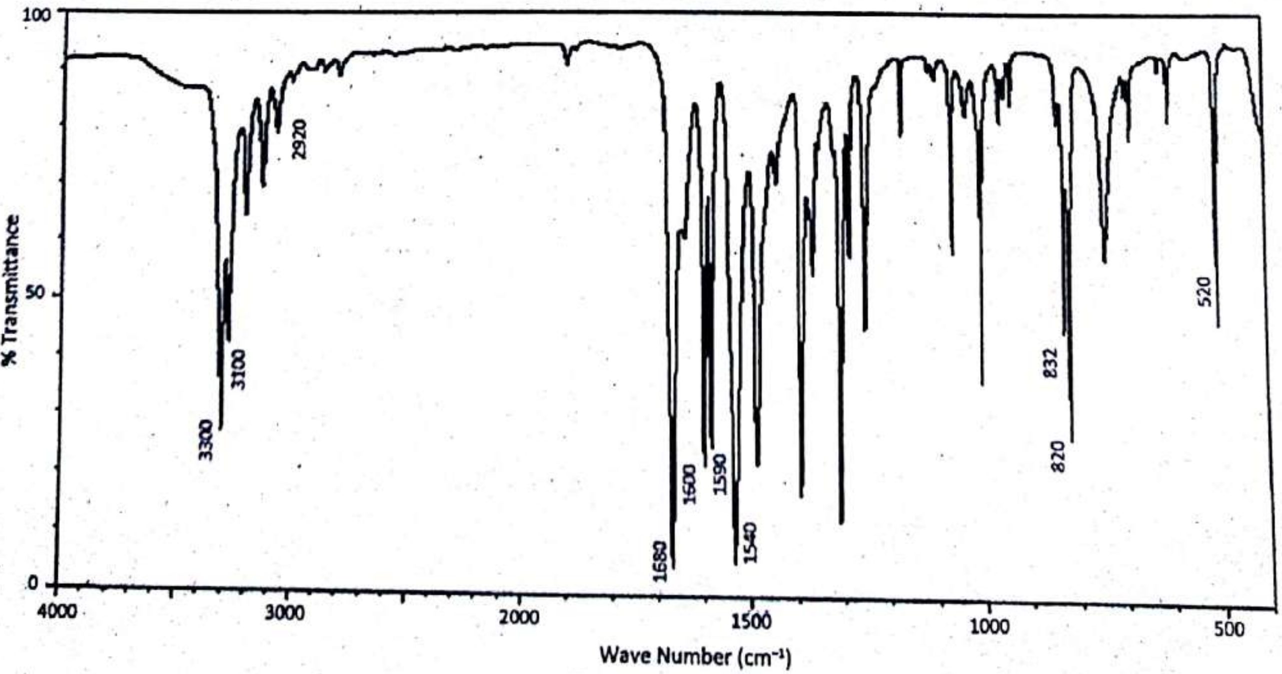
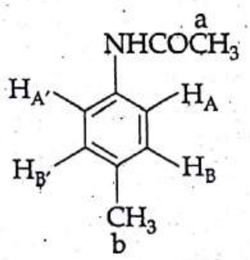


Figure-8.4

Wave no (cm^{-1})	Assignment	Explanation
520	C–Br stretching	
820, 832	C–H def. (*p*-disubstitution)	
1540	N–H bending (amide II)	
1590, 1600	Aromatic C=C stretching	
1680	C=O stretching	Nitrogen lone pair is partly involved in resonance with the phenyl ring. So its conjugation with the carbonyl group diminishes increasing the carbonyl stretching from the normal value of amide.
2920	C-H stretching of $-CH_3$	
3100	Aromatic C–H stretching	
3300	N–H stretching	

8.3.2 4-Methyl acetanilide



- **^{1}H-NMR Spectrum :**

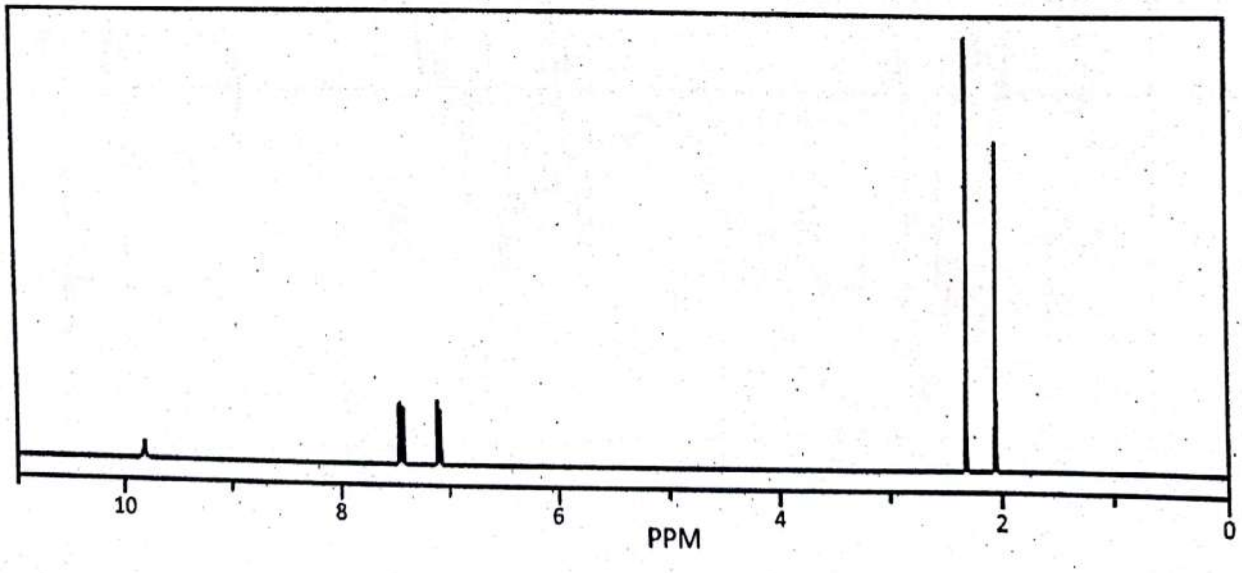


Figure-8.5

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.10	Singlet (3H)	$-CH_3$ (a)	Deshielding by carbonyl causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
2.30	Singlet (3H)	$-CH_3$ (b)	Deshielding by phenyl nucleus causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
7.08	Doublet (2H) (8.2Hz)	H_B and $H_{B'}$.	Hyperconjugative electron release by –Me may cause slight shielding. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
7.54	Doublet (2H) (8.2 Hz)	H_A and $H_{A'}$	The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
9.81	Broad singlet (1H)	$-NH$	The signal appears as a singlet due to absence of any coupling partner. Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet.

■ **IR Spectrum :**

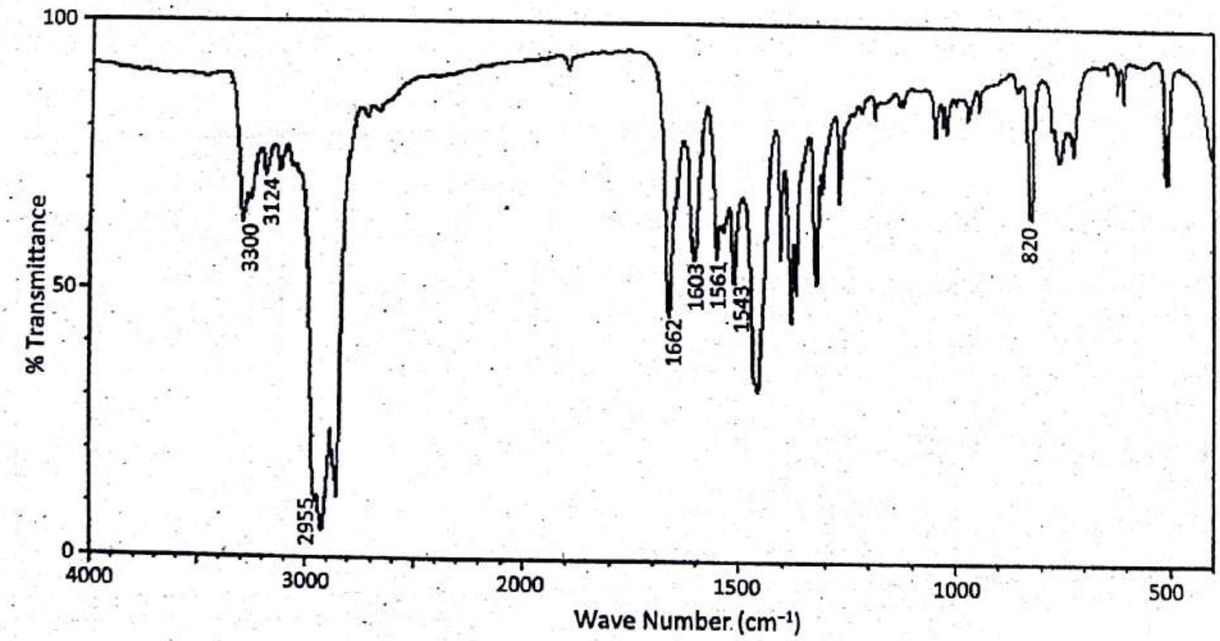


Figure-8.6

[illegible]	[illegible]	Explanation
820	C–H def. (*p*-disubstitution)	
1543	N–H bending (amide II)	
1561, 1603	Aromatic C=C stretching	

^1H-NMR Spectrum :

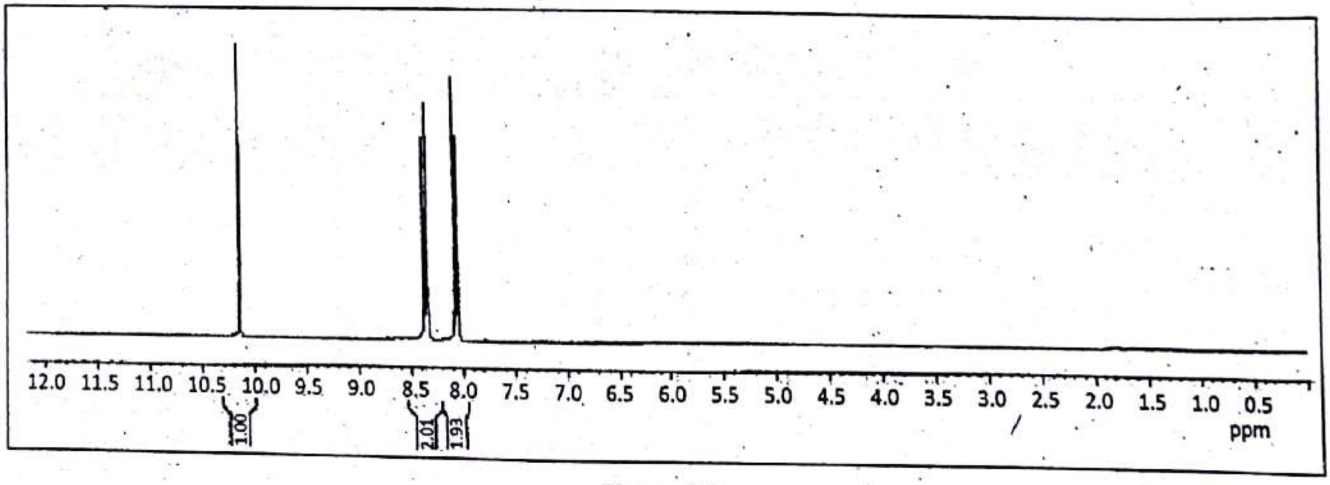


Figure-8.9

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
8.06	Doublet (2H) (9 Hz)	H_A and $H_{A'}$.	Deshielding is caused by the magnetic anisotropy of the carbonyl function. The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
8.35	Doublet (2H) (9 Hz)	H_B and $H_{B'}$	Deshielding is caused by the magnetic anisotropy of the nitro group to a greater extent than that of the carbonyl function. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
10.14	Singlet (1H)	–CHO	Magnetic anisotropy of the C=O unit causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

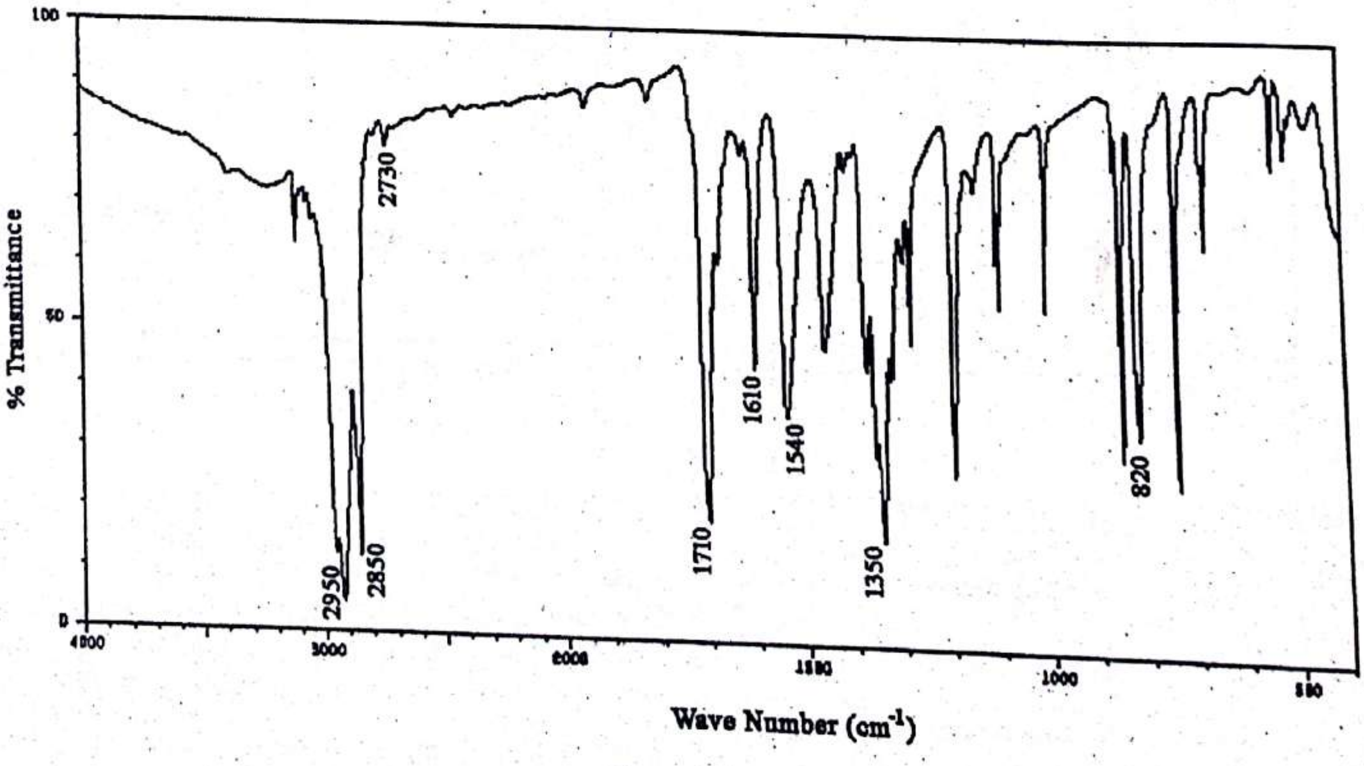
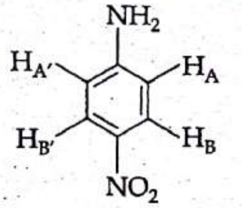


Figure-8.10

Wave no (cm^{-1})	Assignment	Explanation
820	C-H def. (*p*-disubstitution)	
1350, 1540	Symmetric and asymmetric stretching respectively of $-NO_2$.	
1610	Aromatic C=C stretching	
1710	C=O stretching	Mesomeric electron withdrawal by nitro group increases carbonyl stretching frequency.
2730, 2850	C−H stretching of −CHO	
2950	Aromatic C−H stretching	

8.3.5 4-Nitroaniline



- **¹H-NMR Spectrum :**

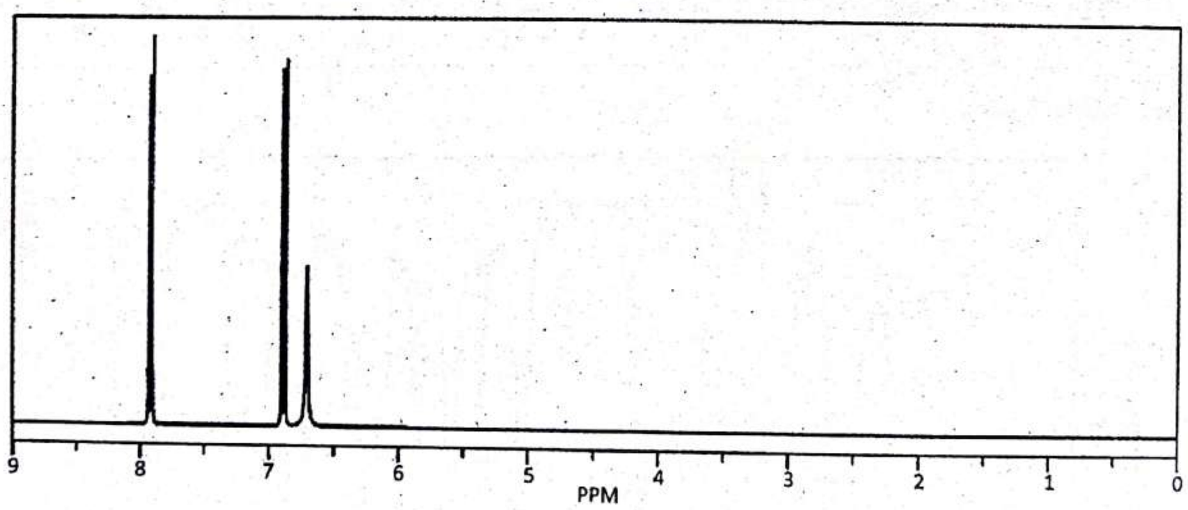


Figure-8.11

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
6.71	Singlet (2H)	$-NH_2$	Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet. The signal appears as a singlet due to absence of any coupling partner.
6.82	Doublet (2H) (9 Hz)	H_A and $H_{A'}$.	Mesomeric electron release by –amino function causes some shielding. The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
7.92	Doublet (2H) (9 Hz)	H_B and $H_{B'}$.	Deshielding is caused by the magnetic anisotropy of the nitro group. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.

IR Spectrum :

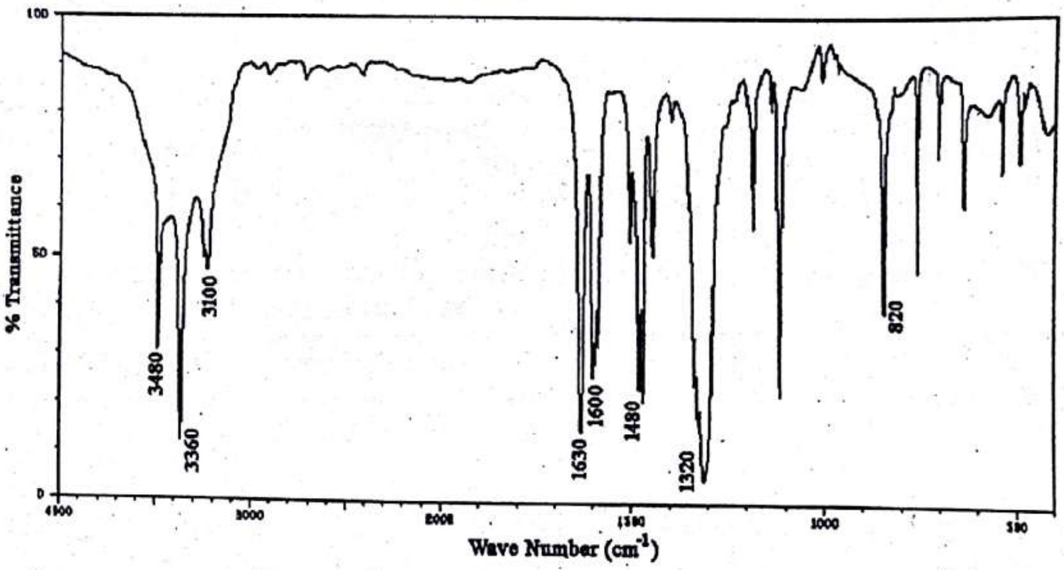
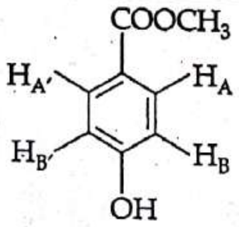


Figure-8.12

Wave no (cm^{-1})	Assignment	Explanation
820	C-H def. (*p*-disubstitution)	
1320, 1480	Symmetric and asymmetric stretching respectively of $-NO_2$.	
1600	Aromatic C=C stretching	
1630	N−H bending	
3100	Aromatic C−H stretching	
3360, 3480	Symmetric and asymmetric N−H stretching respectively of $-NH_2$	

8.3.6 Methyl-4-hydroxybenzoate



^{1}H-NMR Spectrum :

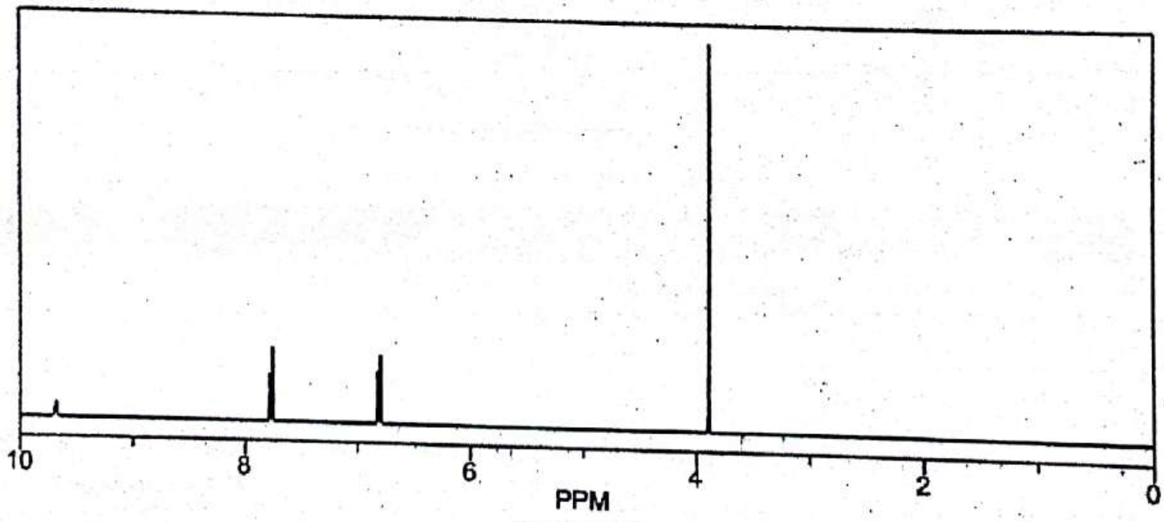


Figure-8.13

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
3.85	Singlet (3H)	$-OCH_3$	Deshielding by $-COO$ unit causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
6.81	Doublet (2H) (9 Hz)	H_B and $H_{B'}$	Mesomeric electron release by -OH function causes some shielding. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
7.77	Doublet (2H) (9 Hz)	H_A and $H_{A'}$	Deshielding is caused by the magnetic anisotropy of C=O of the methoxycarbonyl group The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
9.68	Singlet (1H)	$-OH$	The signal appears as a singlet due to absence of any coupling partner.

- **IR Spectrum :**

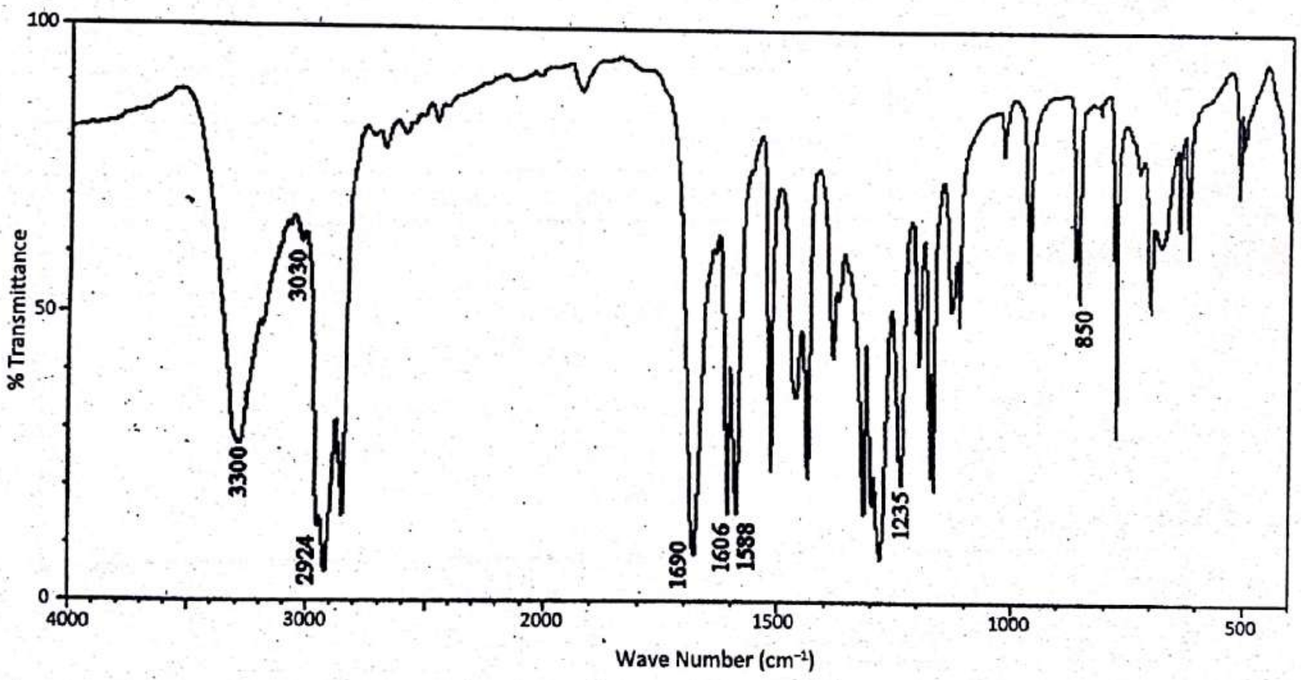
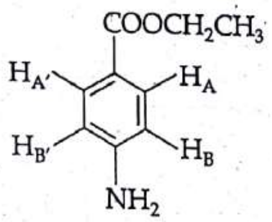


Figure-8.14

Wave no. (cm^{-1})	Assignment	Explanation
850	C–H def. (p-disubstitution)	
1235	C–O stretching	
1588, 1606	Aromatic C=C stretching	
1690	C=O stretching	Mesomeric electron release by -OH group diminishes carbonyl stretching frequency
2924	C–H stretching of $-CH_3$	
3030	Aromatic C–H stretching	
3300	O–H stretching	

8.3.7 Ethyl-4-amino benzoate



■ **^{1}H-NMR Spectrum :**

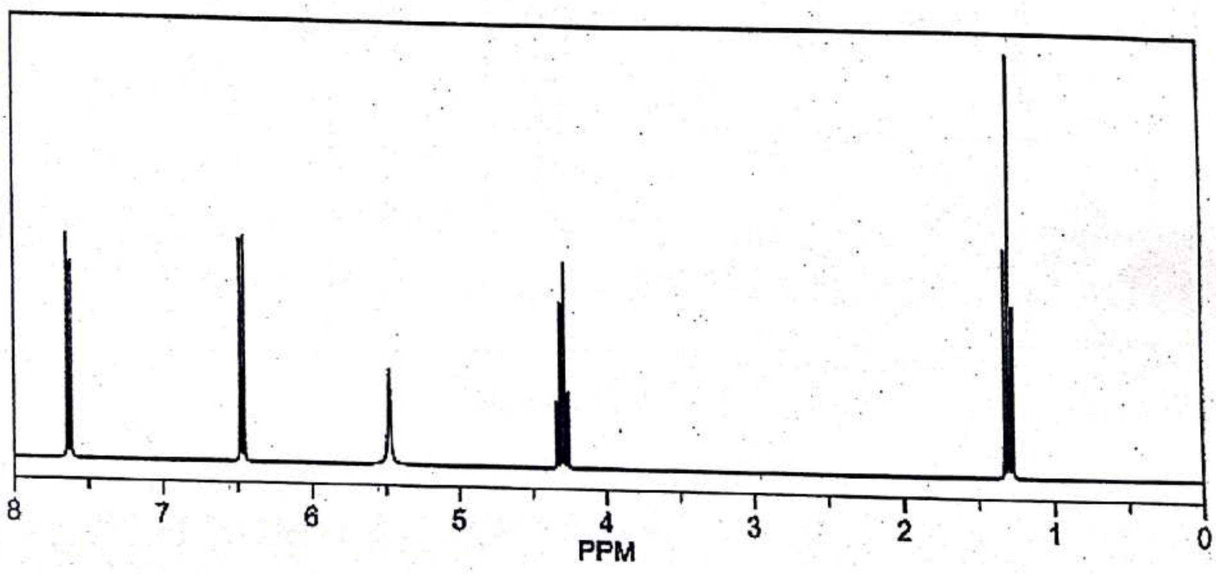


Figure-8.15

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
1.3	Triplet (3H) (7 Hz)	$-CH_3$	These protons are coupled by adjacent methylene protons.
4.3	Quartet (2H) (7 Hz)	$-CH_2$	These protons are coupled by adjacent methyl protons.
5.48	Singlet (2H)	$-NH_2$	Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet. Appearance as a singlet is attributed to the absence of any coupling partner.
6.47	Doublet (2H) (9 Hz)	H_B and $H_{B'}$.	Mesomeric electron release by –amino function causes some shielding. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
7.63	Doublet (2H) (9 Hz)	H_A and $H_{A'}$	Deshielding is caused by the magnetic anisotropy of C=O of the ethoxycarbonyl group. The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.

IR Spectrum :

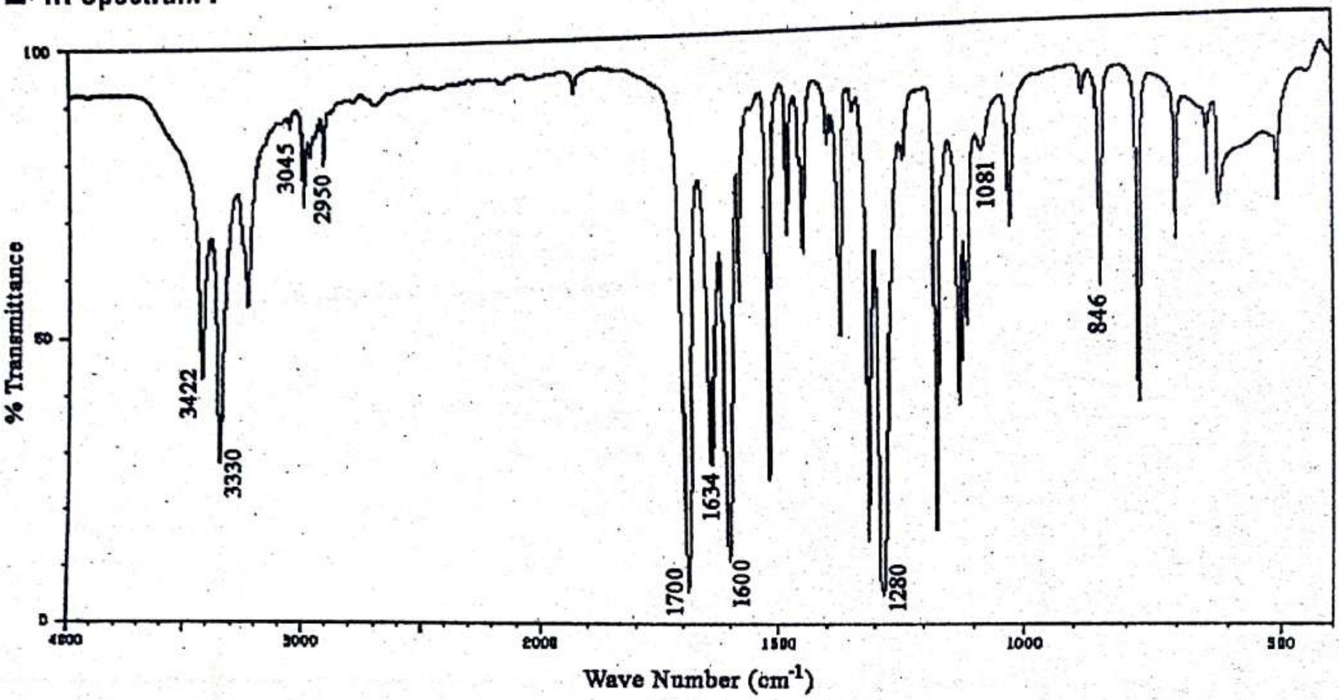
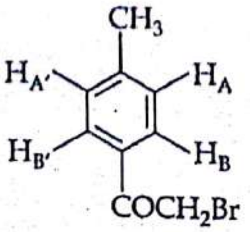


Figure-8.16

Wave no (cm^{-1})	Assignment	Explanation
846	C$-$H def. (*p*-disubstitution)	
1081	O$-$CH$_2$ stretching	
1280	C$-$O stretching of ester	
1600	Aromatic C=C stretching	
1634	N$-$H bending	
1700	C=O stretching	Mesomeric electron release by amino group decreases the stretching frequency of ester carbonyl from its normal value
2950	C$-$H stretchingof $-$CH$_2$CH$_3$	
3045	Aromatic C-H stretching	
3330, 3422	Symmetric and asymmetric N$-$H stretching respectively of $-$NH$_2$.	

8.3.8 4-Methyl phenacyl bromide



^{1}H-NMR Spectrum :

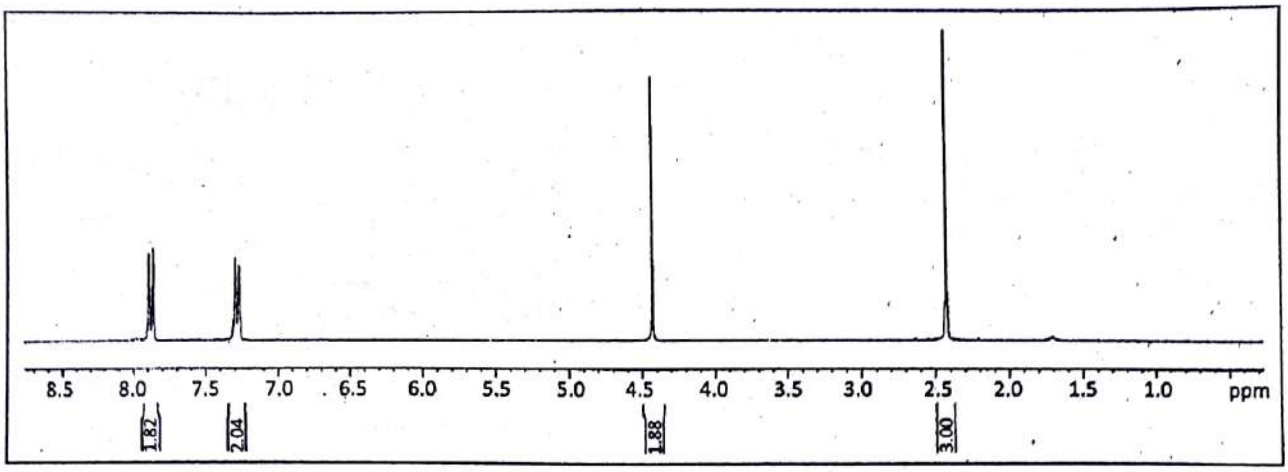


Figure-8.17

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.40	singlet	$-CH_3$	Appearance as a singlet is attributed to the absence of any coupling partner.
4.43	singlet	$-CH_2$	Deshielding is caused by carbonyl and Br. Appearance as a singlet is attributed to the absence of any coupling partner.
7.28	Doublet (8.2Hz)	H_A and $H_{A'}$	The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
7.88	Doublet (8.2 Hz)	H_B and $H_{B'}$.	Deshielding is caused by magnetic anisotropy of the carbonyl function. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.

IR Spectrum :

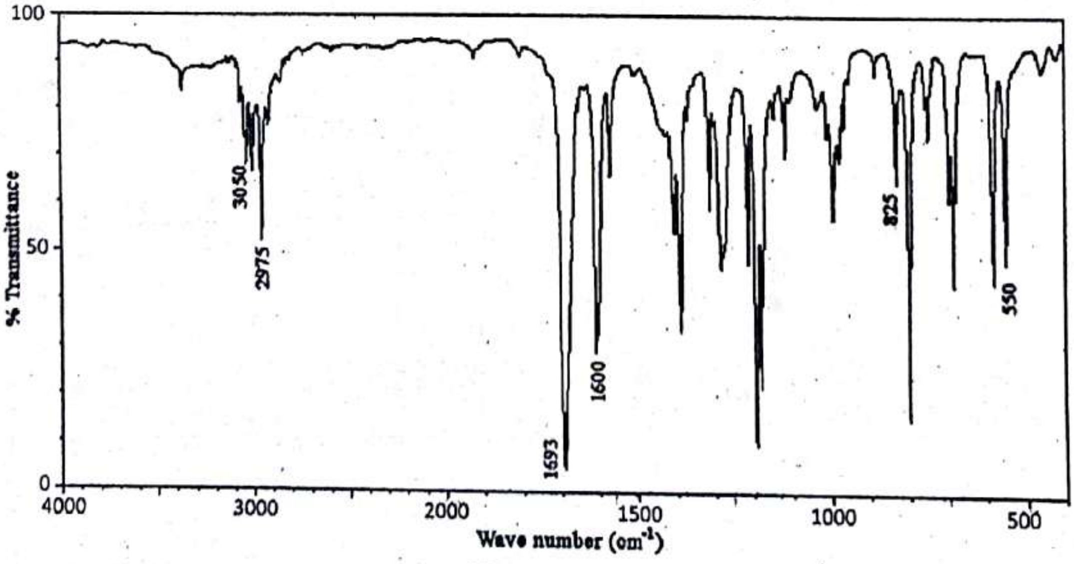
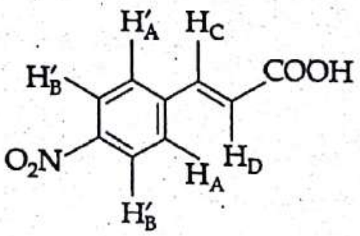


Figure-8.18

Wave no (cm^{-1})	Assignment	Explanation
550	C–Br stretching	
825	C–H def. (*p*-disubstitution)	
1600	Aromatic C═C stretching	
1693	C═O stretching	Inductive electron withdrawal by bromine increases the stretching frequency of conjugated carbonyl from its normal value
2975	(sp^3) C–H stretching.	
3050	Aromatic C–H stretching	

8.3.9 4-Nitrocinnamic acid



■ **^{1}H-NMR Spectrum :**

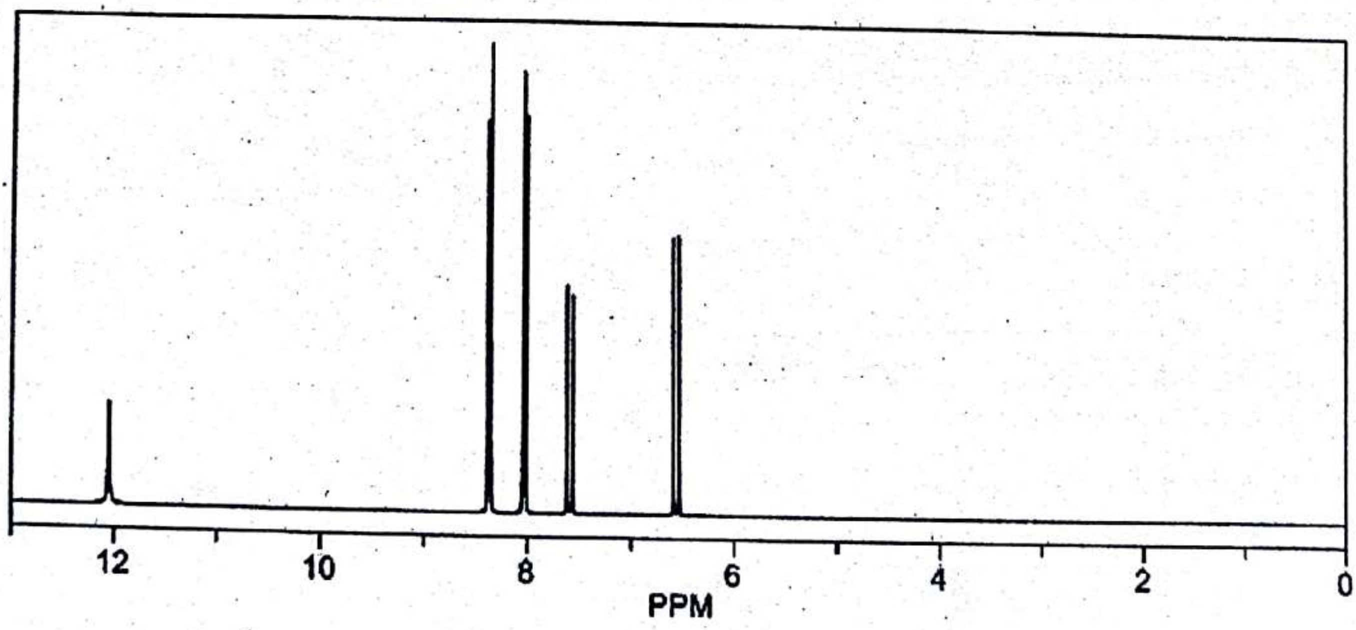


Figure-8.19

[illegible]	[illegible]	[illegible]	Explanation
6.56	Doublet (1H)	H_D	The signal appears as doublet due to coupling with HB. The trans coupling constant is very high.
7.59	Doublet (1H)	H_C	Mesomeric electron withdrawal by the -COOH group causes high downfield shift. The signal appears as doublet due to coupling with HA. The trans coupling constant is very high.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
8.03	Doublet (2H) (9 Hz)	H_A and $H_{A'}$	The signal appears as a doublet due to ortho coupling with H_B and $H_{B'}$.
8.37	Doublet (2H) (9 Hz)	H_B and $H_{B'}$	Deshielding is caused by the magnetic anisotropy of the nitro group. The signal appears as a doublet due to ortho coupling with H_A and $H_{A'}$.
12.05	Singlet (1H)	$-COOH$	Strong hydrogen bonding causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

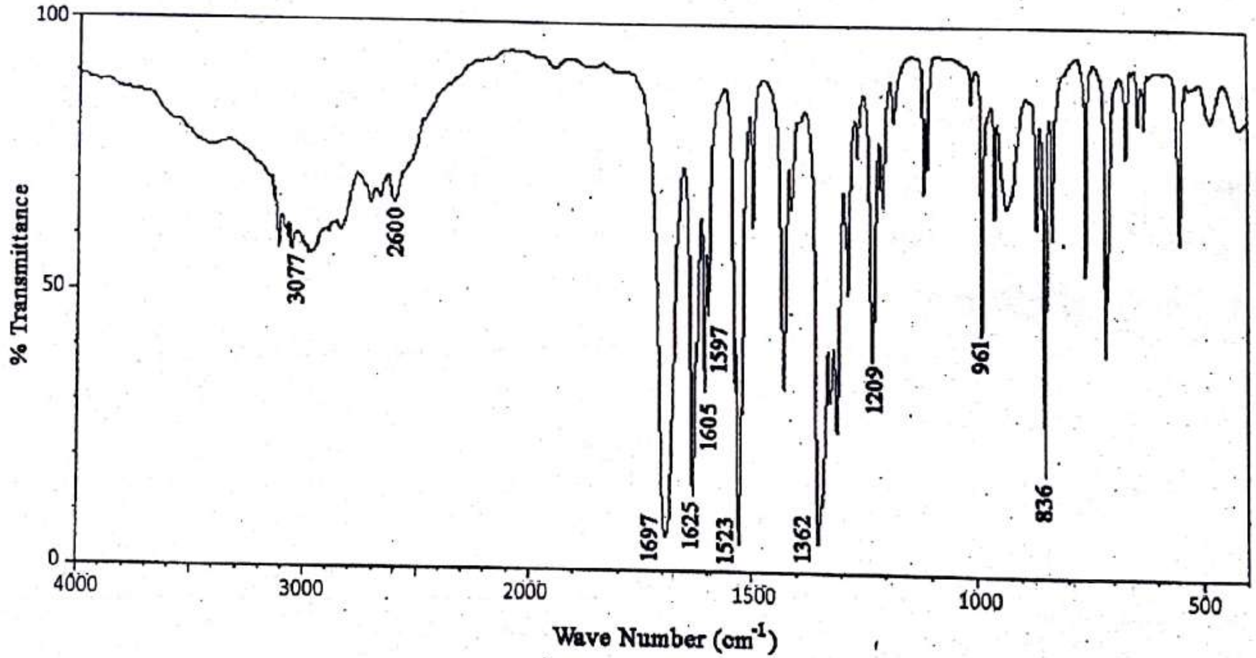
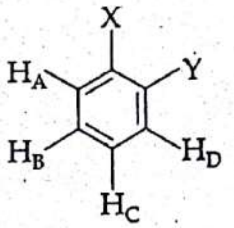


Figure-8.20

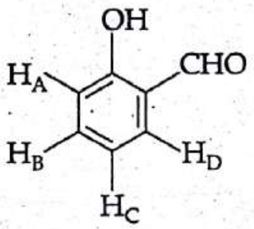
Wave number (cm^{-1})	Assignment	Explanation
836	C-H def. (*p*-disubstitution)	
961	C−H def. (trans olefin)	
1209	C−O stretching	
1362, 1523	Symmetric and asymmetric stretching of $-NO_2$	
1597, 1605	Aromatic C=C stretching	
1625	Olefinic C=C stretching	
1697	C=O stretching	Hydrogen bonding and conjugation with olefinic segment lowers the carbonyl stretching frequency.
2600	O−H stretching.	Strong hydrogen bonding is responsible for lowering of O−H stretching frequency and broadening of the band
3077	Aromatic C−H stretching	

o-Disubstituted benzene with non-identical substituents



For these compounds H_A,H_B, H_C and H_D' are chemically as well as magnetically non-equivalent. *Ortho, meta* and *para* coupling are possible for HA and HD whereas *ortho* and *meta* coupling are possible for H_B and H_C. So the splitting pattern of aromatic protons are highly complex and cannot be recognized unless subjected to hyperfine splitting. Theoretically doublet of doublet of doublet is the predicted splitting pattern for the aromatic protons. However in most of the cases they appear as complex multiplets.

8.3.10 Salicylaldehyde



- **^{1}H-NMR Spectrum :**

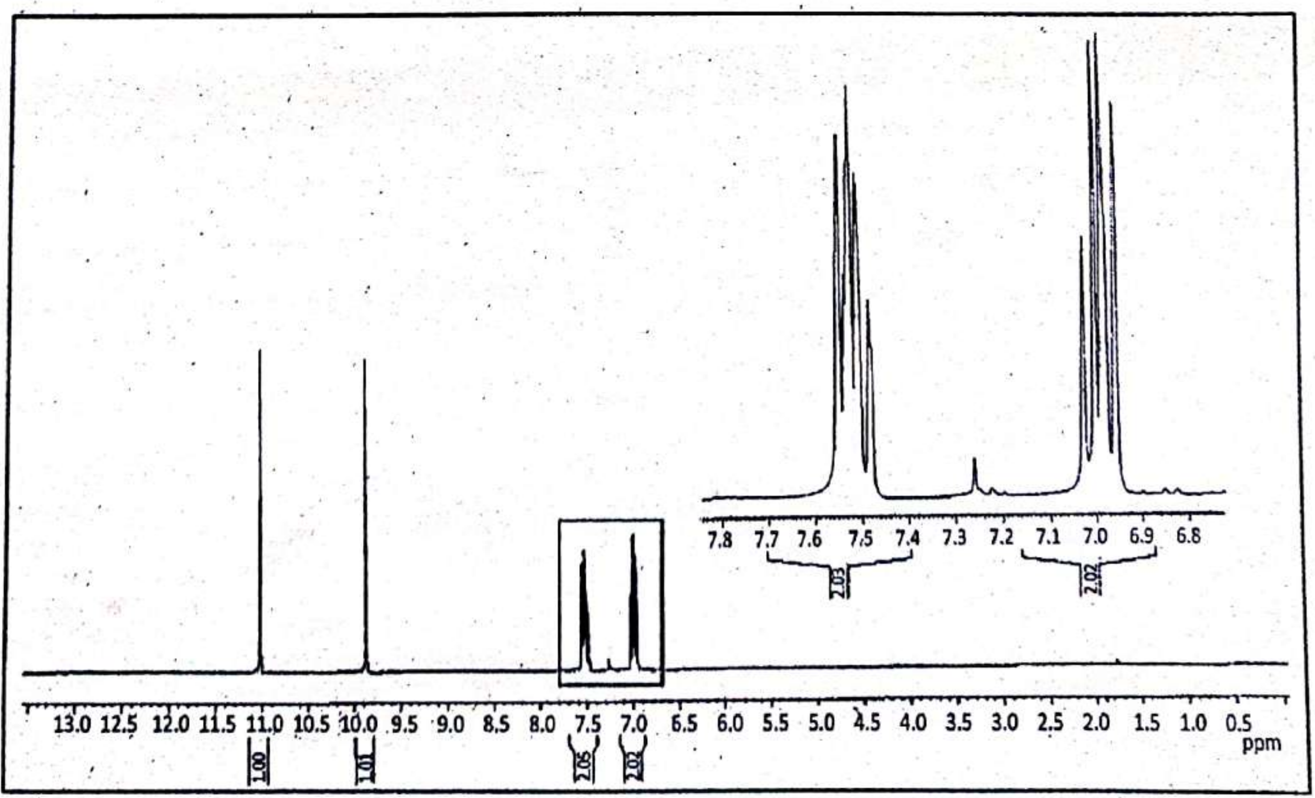


Figure-8.21

Chemical Shift (δ ppm)	Multiplicity (J, Hz)	Assignment to proton	Explanation
6.96-7.03	Complex multiplet (2H)	H_A and H_C	Mesomeric electron release by –OH function may cause some shielding. The signal for H_A appears as a doublet due to strong ortho coupling with H_B. The signal for H_C should appear as a triplet or doublet of doublet due to coupling with H_B and H_D. However the signals are close enough not to find out the discrete splitting pattern.
7.48-7.55	Complex multiplet (2H)	H_B and H_D	Mesomeric electron withdrawal by aldehydic carbonyl causes deshielding. Deshielding of H_D is also attributed to magnetic anisotropy of the carbonyl function. The signal for H_D appears as a doublet due to strong ortho coupling with H_C. The signal for H_B should appear as a triplet or doublet of doublet due to coupling with H_A and H_C. However the signals are close enough not to find out the discrete splitting pattern.
9.87	Singlet (1H)	–CHO	Magnetic anisotropy of the C═O unit causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.
11.1	Singlet (1H)	–OH	Magnetic anisotropy of the C═O unit and strong intramolecular hydrogen bonding cause very high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

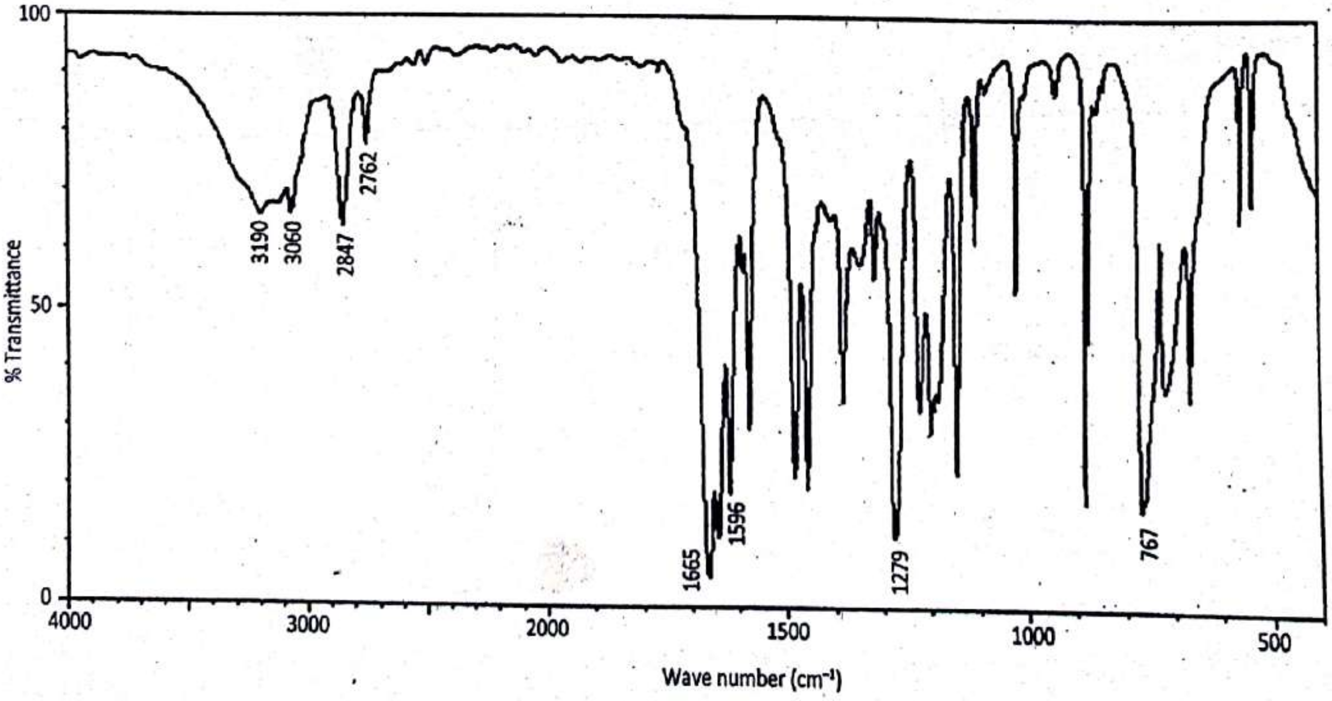
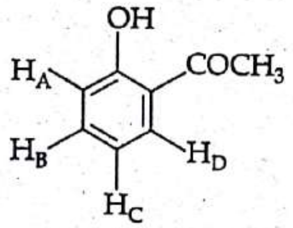


Figure-8.22

Wave number (cm^{-1})	Assignment	Explanation
767	C–H def. (*o*-disubstitution)	
1279	C–O stretching	
1596	Aromatic C=C stretching	
1665	C=O stretching	Strong intramolecular hydrogen bonding decreases the carbonyl stretching frequency
2762, 2847	C–H stretching of –CHO	
3060	Aromatic C–H stretching.	
3190	O–H stretching	Strong intramolecular hydrogen bonding decreases the –OH stretching frequency and broadens the signal

8.3.11 2-Hydroxyacetophenone



■ **^{1}H-NMR Spectrum :**

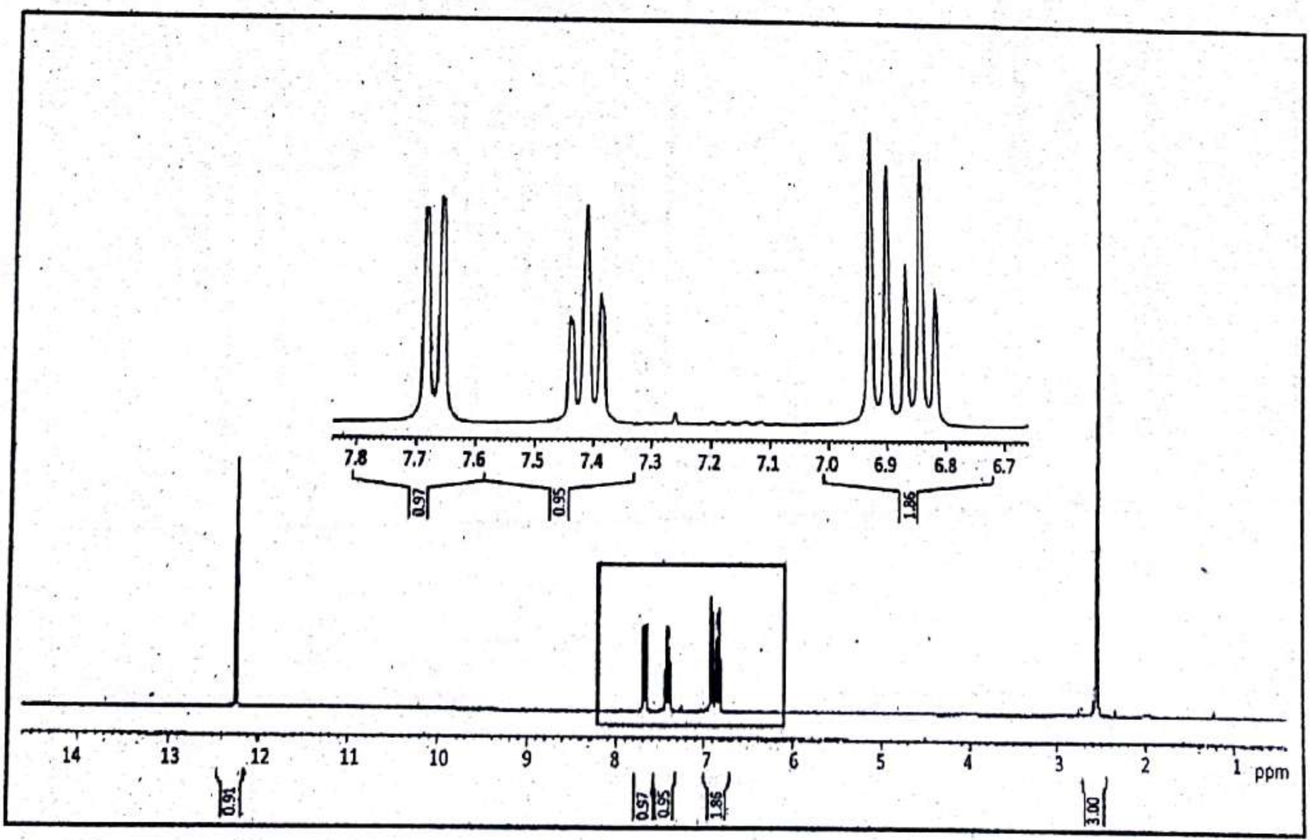


Figure-8.23

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.5	Singlet (3H)	$-COCH_3$	Deshielding by carbonyl causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
6.81-6.93	Complex multiplet (2H)	H_A and H_C	Mesomeric electron release by $-OH$ function may cause some shielding. The signal for H_A should appear as a doublet due to ortho coupling with H_B and the signal for H_C should appear as a triplet due to ortho coupling with H_B and H_D. Here meta coupling is too weak to be seen.
7.41	Triplet (1H)	H_B	Mesomeric electron withdrawal by ketonic carbonyl causes deshielding. The signal appears as a triplet due to ortho coupling with H_A and H_C. Meta coupling with H_D is too weak to be seen.
7.67	Doublet of doublet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as a doublet of doublet due to strong ortho coupling with H_C and weak meta coupling with H_B.
12.4	Singlet (1H)	$-OH$	Magnetic anisotropy of the C=O unit and strong intramolecular hydrogen bonding cause very high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

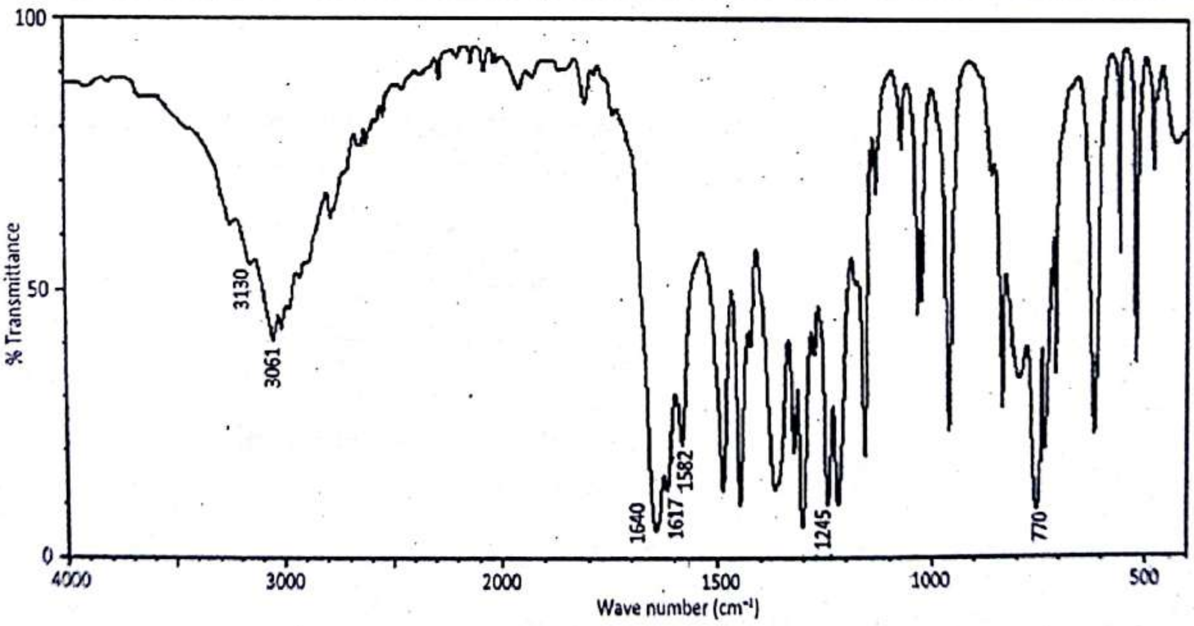
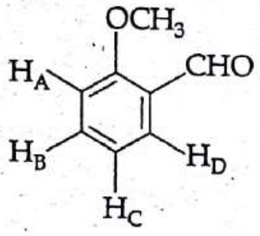


Figure-8.24

Wave number (cm⁻¹)	Assignment	Explanation
770	C–H def. (*o*-disubstitution)	
1245	C–O stretching	
1582, 1617	Aromatic C=C stretching	
1640	C=O stretching	Strong intramolecular hydrogen bonding decreases the carbonyl stretching frequency

Wave number (cm^{-1})	Assignment	Explanation
3061	Aromatic C=H stretching	
3130	O−H stretching.	Strong intramolecular hydrogen bonding decreases the −OH stretching frequency and broadens the signal

8.3.12 2-Methoxybenzaldehyde



■ ^{1}H-NMR Spectrum :

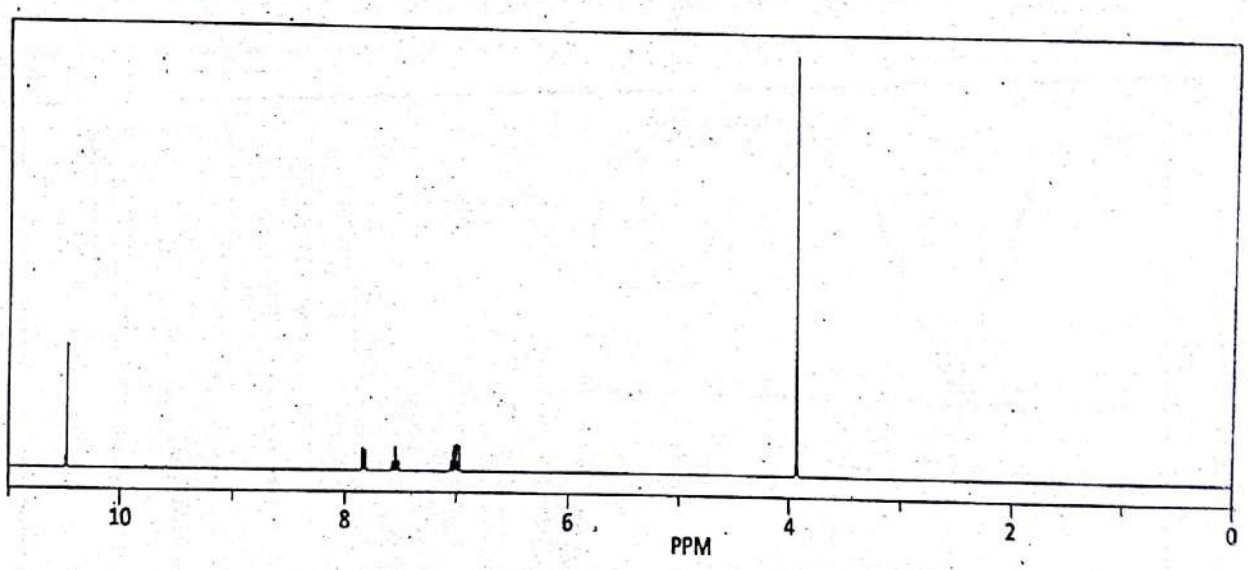


Figure-8.25

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
3.93	Singlet (3H)	$-OCH_3$	Inductive electron withdrawal by methoxyl oxygen causes deshielding to lower the δ value than the normal value of 0.9 ppm for methyl protons. The signal appears as a singlet due to absence of any coupling partner.
6.99-7.03	Complex multiplet (2H)	H_A and H_C	Mesomeric electron release by $-OCH_3$ function may cause some shielding.
7.55	Triplet (1H)	H_B	Mesomeric electron withdrawal by aldehydic carbonyl causes deshielding. The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.83	Complex multiplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as a complex multiplet due to ortho, meta and para coupling with H_C, H_B and H_A respectively.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
10.48	Singlet (1H)	$-CHO$	Magnetic anisotropy of the C=O unit causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

■ **IR Spectrum :**

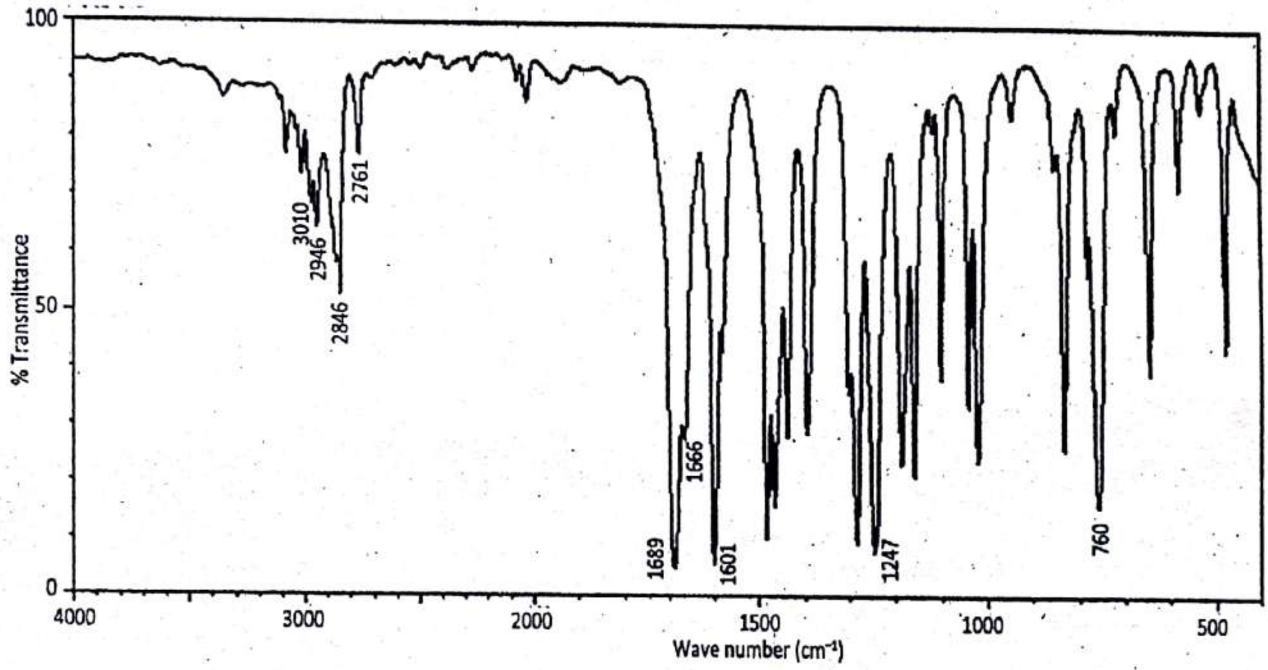
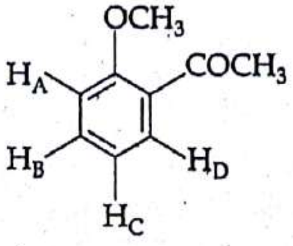


Figure-8.26

Wave number (cm⁻¹)	Assignment	Explanation
760	C–H def. (o-disubstitution)	
1247	C–O stretching	
1601	Aromatic C=C stretching	
1666, 1689	C=O stretching	When C=O and $-OCH_3$ are on opposite sides, C=O stretching frequency is lowered. When C=O and $-OCH_3$ are on the same side, C=O stretching frequency is raised as the carbon-oxygen double bond undergoes less charge separation to minimize dipole-dipole repulsion.
2761, 2846	C–H stretching of $-CHO$	
2946	C–H stretching of $-CH_3$	
3010	Aromatic C–H stretching.	

8.3.13 2-Methoxyacetophenone



- **^{1}H-NMR Spectrum :**

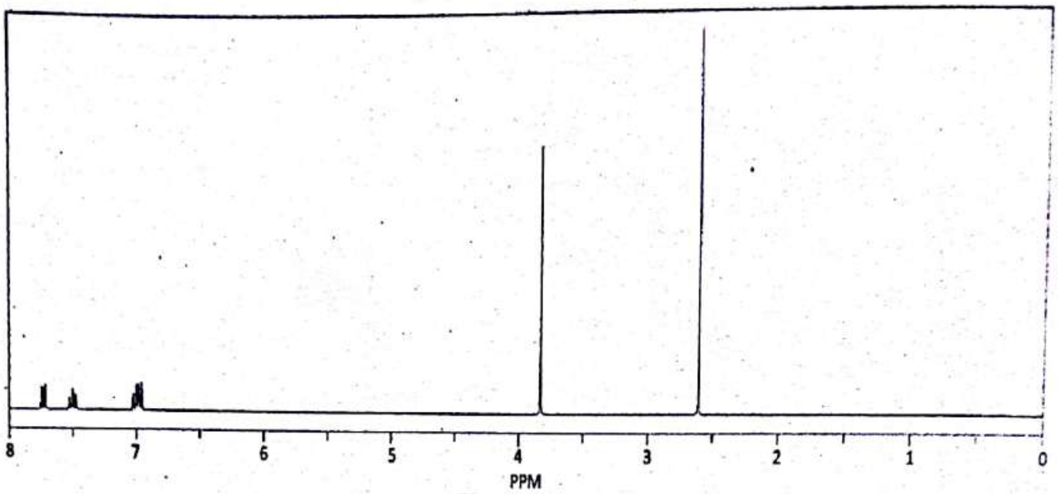


Figure-8.27

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.61	Singlet (3H)	$-COCH_3$	Deshielding by carbonyl causes downfield shift from the normal value of δ 0.9 ppm for methyl protons. Appearance as a singlet is attributed to the absence of any coupling partner.
3.83	Singlet (3H)	$-OCH_3$	Inductive electron withdrawal by methoxyl oxygen causes deshielding to lower the δ value than the normal value of 0.9 ppm for methyl protons. The signal appears as a singlet due to absence of any coupling partner.
6.97-7.00	Complex multiplet (2H)	H_A and H_C	Mesomeric electron release by $-OCH_3$ function may cause some shielding. The signal appears as a complex multiplet due to *ortho* and meta coupling.
7.50	Triplet (1H)	H_B	Mesomeric electron withdrawal by aldehydic carbonyl causes deshielding. The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.73	Complex multiplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as a complex multiplet due to ortho, meta and para coupling with H_C, H_B and H_A respectively.

- **IR Spectrum :**

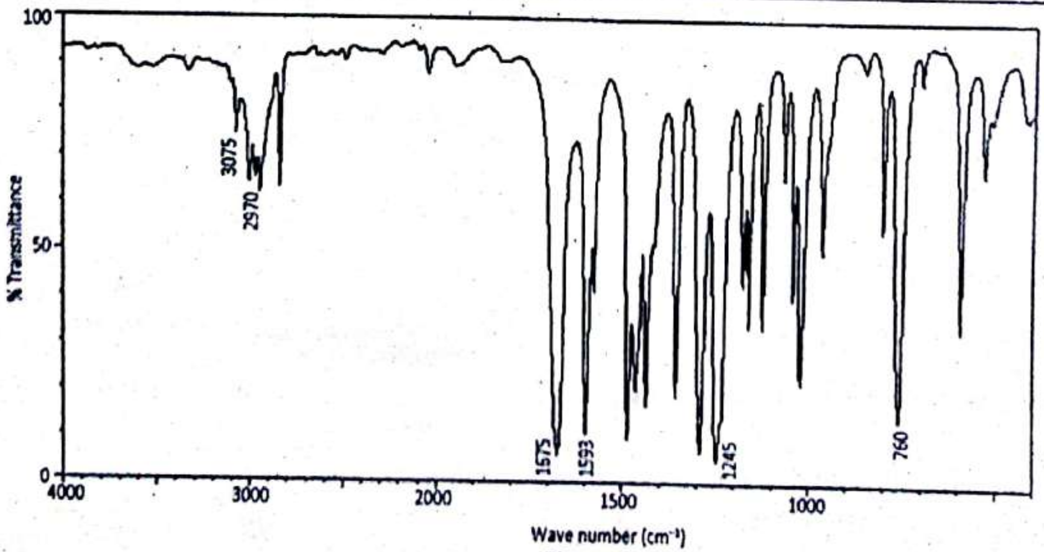
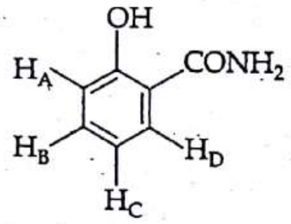


Figure-8.28

Wave number (cm^{-1})	Assignment	Explanation
760	C−H def. (*o*-disubstitution)	
1236	C−O stretching	
1593	Aromatic C=C stretching	
1675	C=O stretching	Mesomeric electro release by methoxy group. decreases the carbonyl stretching frequency.
2970	C−H stretching of $-CH_3$	
3075	Aromatic C−H stretching.	

8.3.14 Salicylamide



^{1}H-NMR Spectrum :

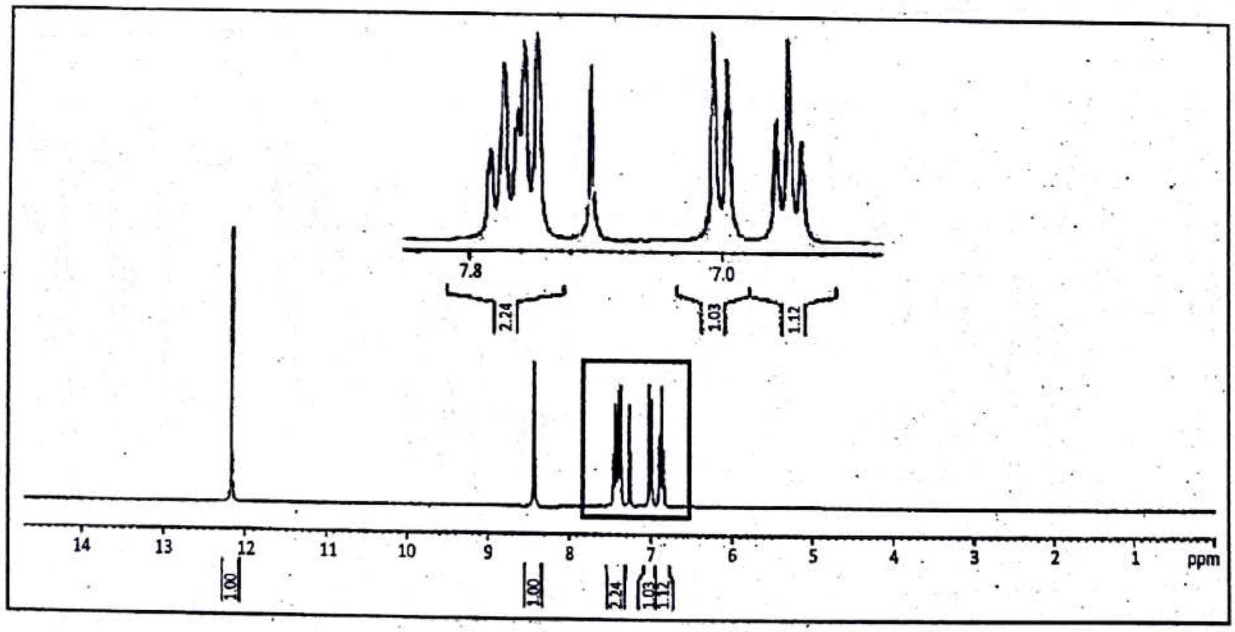


Figure-8.29

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
6.86	Triplet (1H)	H_C	Mesomeric electron release by −OH function may cause some shielding. The signal appears as triplet due to ortho coupling with H_B and H_D.
7.00	Doublet (1H)	H_A	Mesomeric electron release by −OH function may cause some shielding. The signal appears as a doublet due to ortho coupling with H_B.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
7.50-7.60	Complex multiplet (2H)	H_B and H_D	Mesomeric electron withdrawal and magnetic anisotropy of amide carbonyl cause deshielding. The signal appears as a complex multiplet due to ortho coupling of H_B with H_A and H_C and meta coupling with H_D. H_D experiences ortho coupling with H_C and meta coupling with H_B. Signals are too closely spaced to identify the splitting pattern clearly.
8.4	Broad singlet (2H)	$-CONH_2$	The signal appears as a singlet due to absence of any coupling partner.
12.2	Singlet (1H)	$-OH$	Magnetic anisotropy of the C═O unit and strong intramolecular hydrogen bonding cause very high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

■ IR Spectrum :

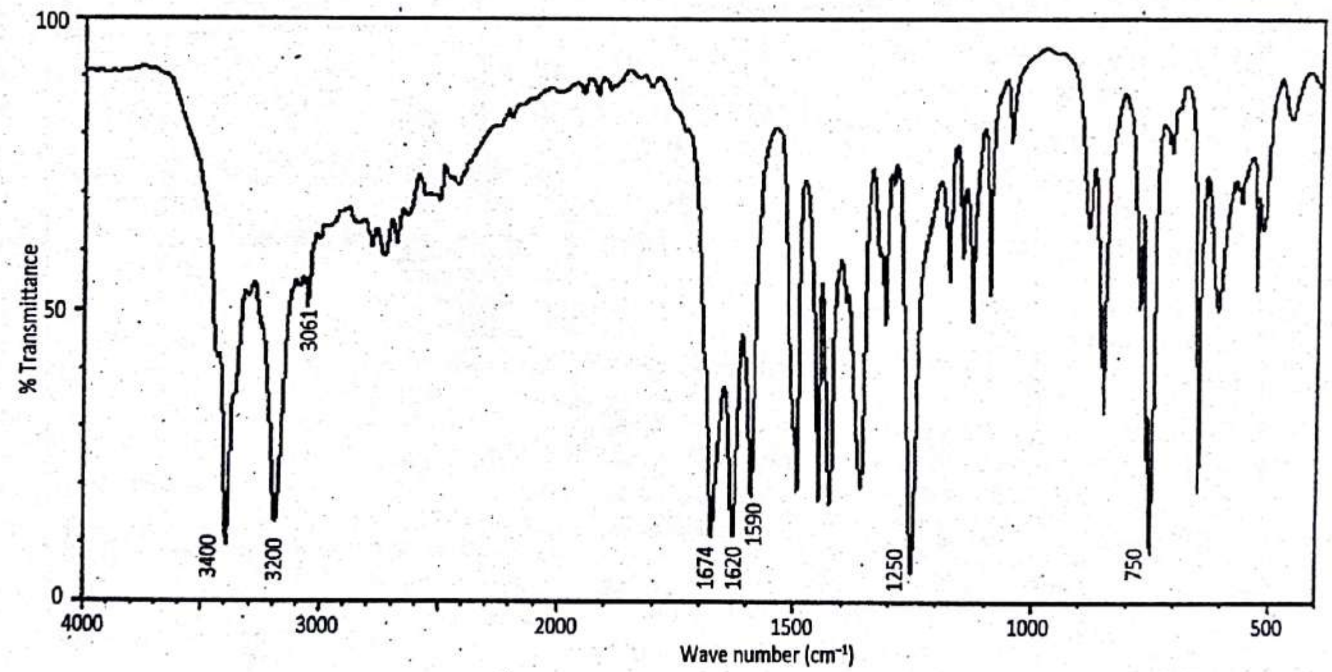
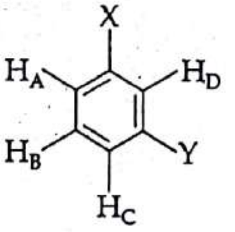


Figure-8.30

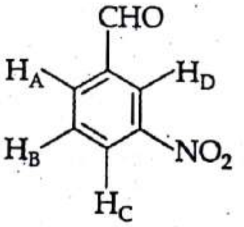
Wave number (cm⁻¹)	Assignment	Explanation
750	C–H def. (*o*-disubstitution)	
1250	C–O stretching	
1590, 1620	Aromatic C═C stretching	
1674	C═O stretching	Intramolecular hydrogen bonding decreases the carbonyl stretching frequency.
3061	Aromatic C═H stretching	
3200, 3400	Symmetric and asymmetric N–H stretching respectively	

m-Disubstituted benzene with non-identical substituents



For these compounds H_A, H_B, H_C and H_D are chemically as well as magnetically non-equivalent. Ortho and meta coupling are possible for H_A and H_C. Ortho and para coupling are possible for H_B. Meta and para coupling are possible for H_D. So the splitting pattern of aromatic protons are highly complex and cannot be recognized unless subjected to hyperfine splitting. Theoretically doublet of doublet of doublet and doublet of doublet of doublet are the predicted splitting pattern for H_A and H_C respectively. H_B and H_D are expected to appear as a doublet of doublet (neglecting the para coupling). However, in most of the cases they appear as complex multiplets.

8.3.15 3-Nitrobenzaldehyde



- **^{1}H-NMR Spectrum :**

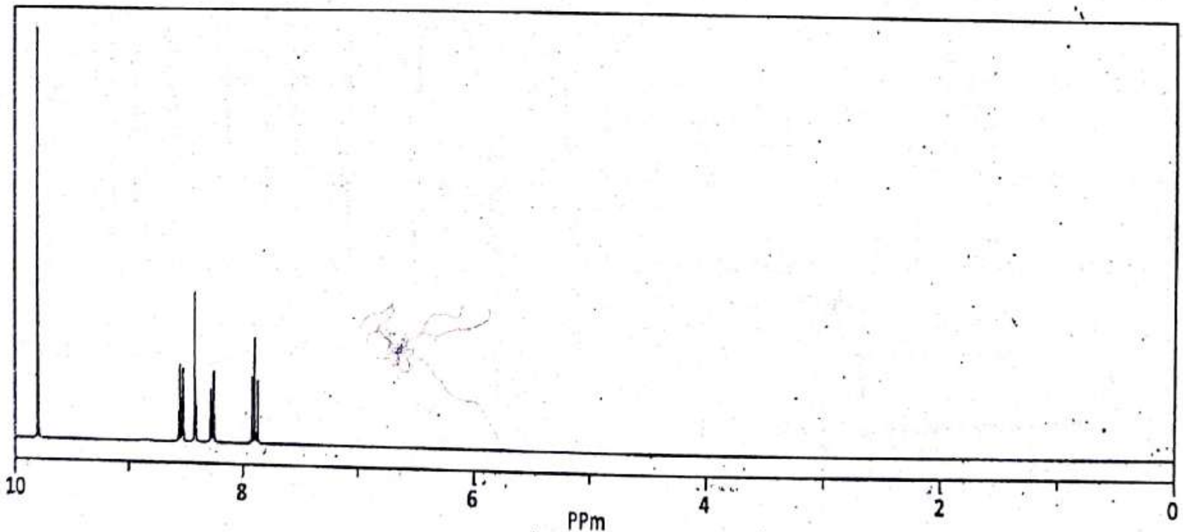


Figure-8.31

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
7.90	Triplet (1H)	H_B	Least deshielded among the aromatic protons as it is away from both the aldehyde and nitro functions. Appearance as a triplet is ascribed to strong ortho coupling with H_A and H_C.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
8.27	Doublet of doublet (1H)	H_A	Deshielding is caused by strong magnetic anisotropy of the carbonyl function.The signal appears as a doublet of doublet due to strong ortho coupling with H_B and weak meta coupling with H_C.
8.42	Complex multiplet (1H)	H_C	Deshielding is caused by strong magnetic anisotropy of the nitro function. Probably this effect is stronger than that caused by the carbonyl group.The signal appears as a complex multiplet due to ortho coupling with H_B and meta coupling with H_A and H_D respectively..
8.65	Triplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the nitro and carbonyl functions. The signal appears as a triplet due to weak meta coupling with H_A and H_C.
9.80	Singlet (1H)	CHO	Magnetic anisotropy of the C=O unit causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

■ IR Spectrum :

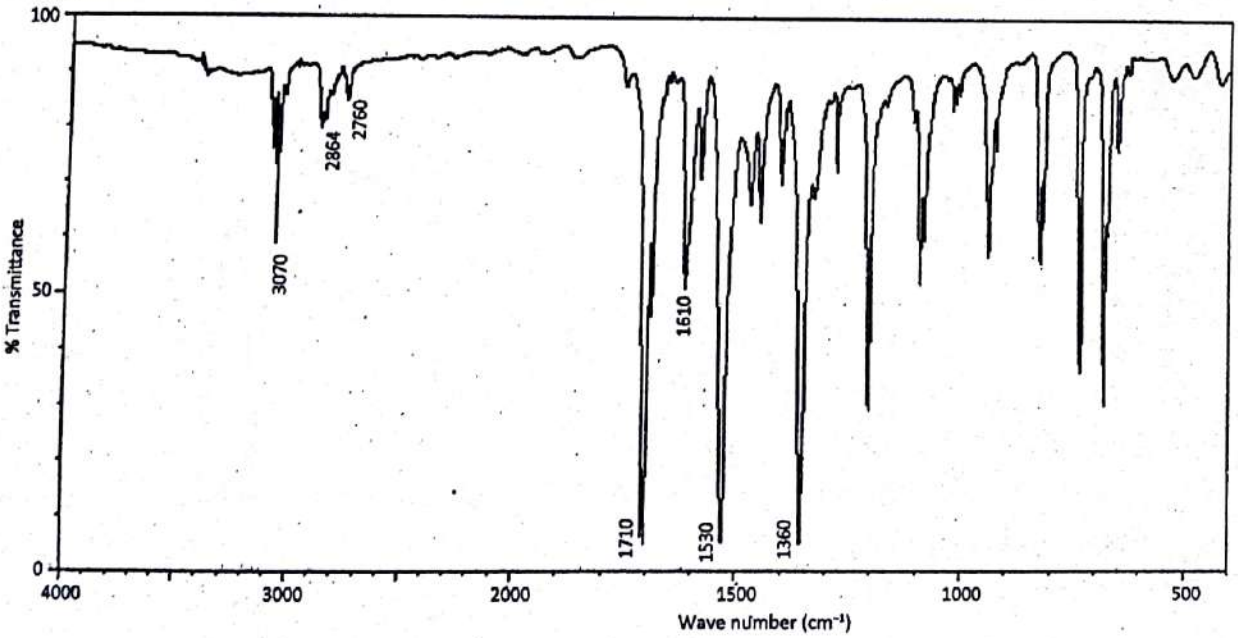
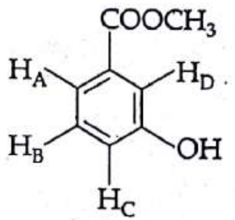


Figure-8.32

Wave number (cm⁻¹)	Assignment	Explanation
1360, 1530	Symmetric and asymmetric stretching of $-NO_2$	
1610	Aromatic C=C stretching	
1710	C=O stretching	Conjugation with the phenyl ring decreases the carbonyl stretching frequency.
2760, 2864	C–H stretching of –CHO.	
3070	Aromatic C–H stretching	

8.3.16 Methyl-3-hydroxybenzoate



^{1}H-NMR Spectrum :

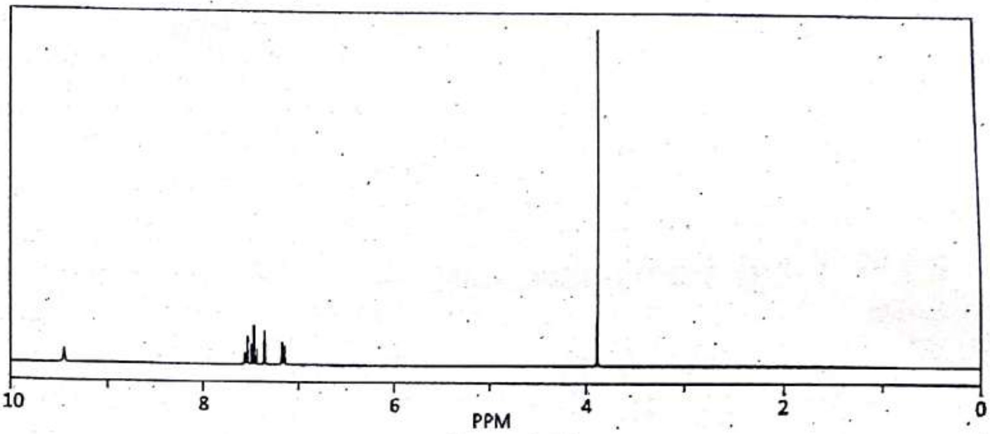


Figure-8.33

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
3.89	Singlet (3H)	COOCH$_3$	Deshielding is caused by −COO unit. Appearance as a singlet is ascribed to absence of any coupling partner.
7.16	Triplet (1H)	H$_B$	The signal appears as a triplet due to strong ortho coupling with H$_A$ and H$_C$.
7.36	Complex multiplet (1H)	H$_C$	The signal appears as a complex multiplet due to ortho coupling with HB and meta coupling with H$_A$ and H$_D$.
7.47-7.55	Complex multiplet (2H)	H$_A$ and H$_D$	Deshielding is caused by strong magnetic anisotropy of the carbonyl function.
9.45	Broad singlet (1H)	OH	The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

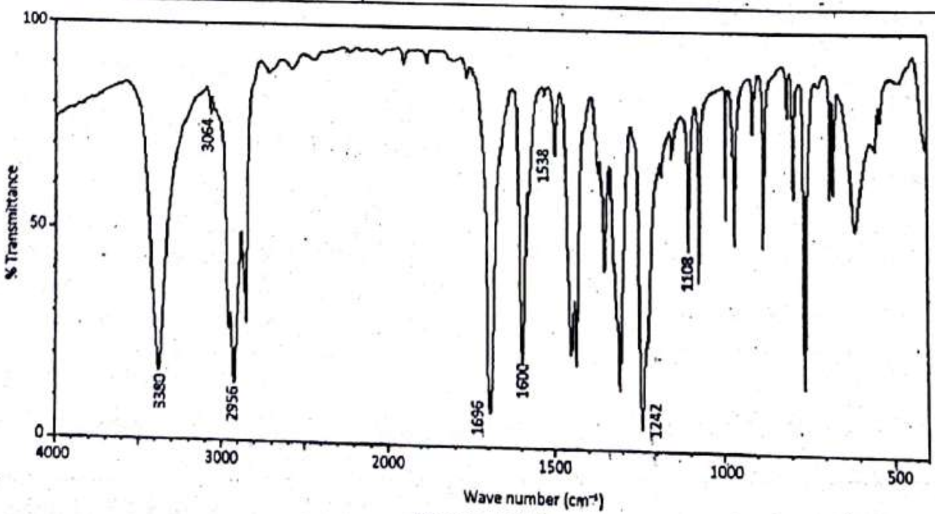
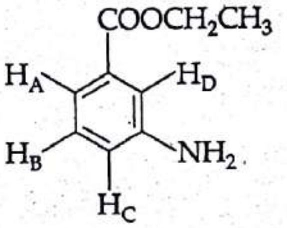


Figure-8.34

Wave number (cm⁻¹)	Assignment	Explanation
1108	$O-CH_3$ stretching	
1242	C(O)–O stretching	
1538, 1600	Aromatic C=C stretching	
1696	C=O stretching	Conjugation with the phenyl ring decreases the carbonyl stretching frequency.
2956	C–H stretching of $-CH_3$.	
3064	Aromatic C–H stretching	
3380	–OH stretching	

8.3.17 Ethyl-3-aminobenzoate



■ ^{1}H-NMR Spectrum :

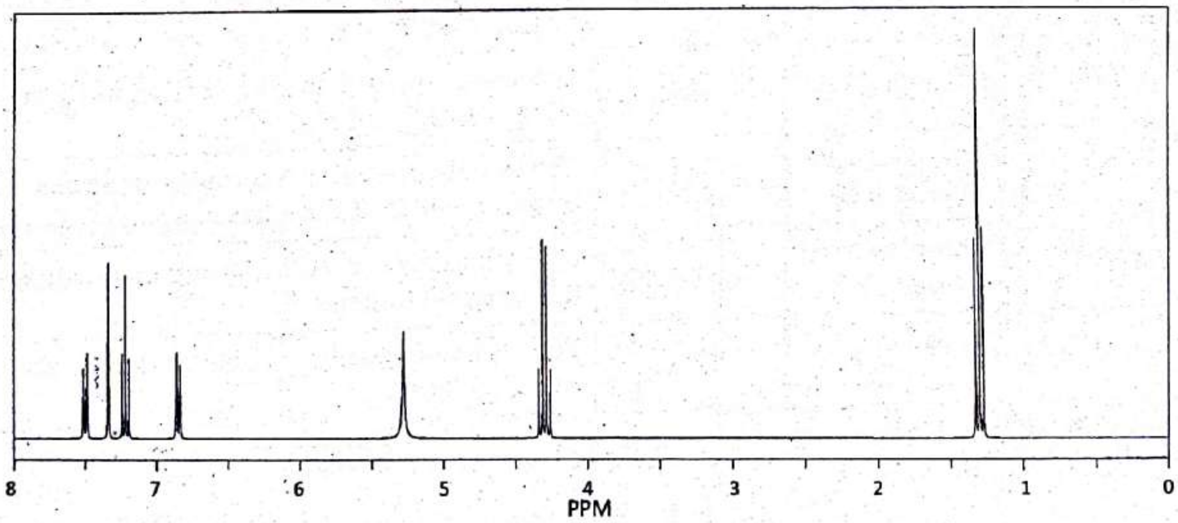


Figure-8.35

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
1.30	Triplet (3H)	$-CH_3$	Appearance as a triplet is ascribed to coupling with adjacent methylene protons
4.30	Quartet (2H)	$-CH_2$	Deshielding is caused by –COO function. The signal appears as a quartet is ascribed to coupling with adjacent methyl protons
5.28	Broad singlet (2H)	$-NH_2$	The signal appears as a singlet due to absence of any coupling partner. Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
6.85	Complex multiplet (1H)	H_C	The signal appears as a complex multiplet due to ortho coupling with H_B and meta coupling with H_A and H_D.
7.22	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.34	Triplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as a triplet due to weak meta coupling with H_A and H_C.
7.50	Complex multiplet (1H)	H_A	Deshielding is caused by strong magnetic anisotropy of the carbonyl function.The signal appears as complex multiplet due to strong ortho coupling with H_B and weak meta coupling with H_C and H_D.

IR Spectrum :

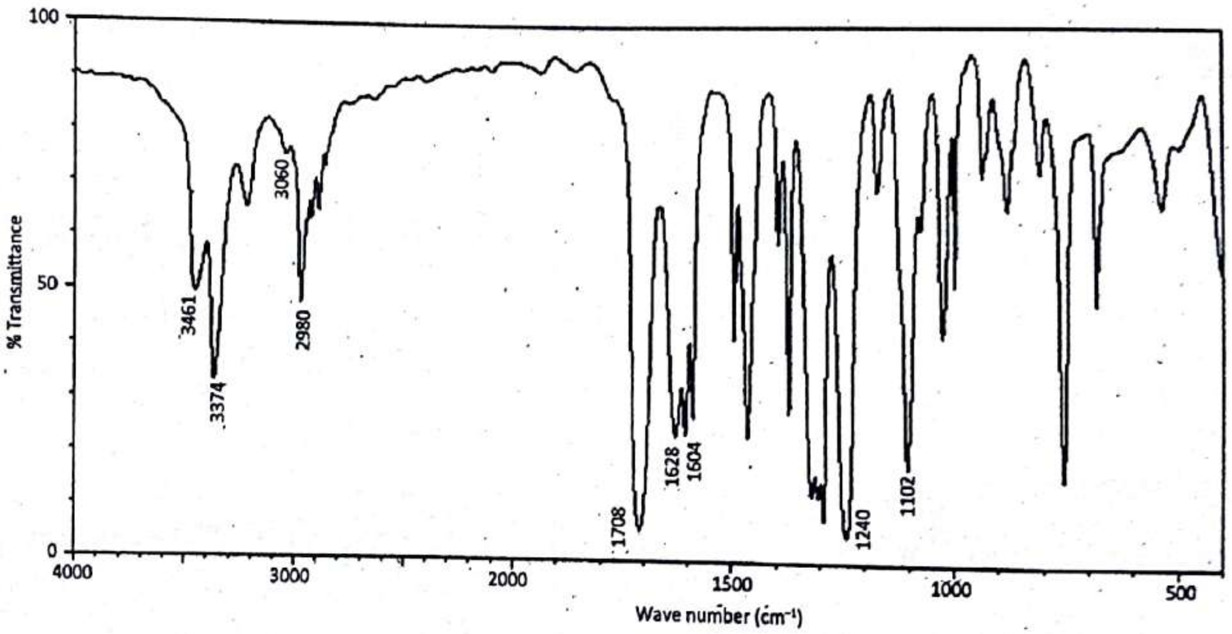
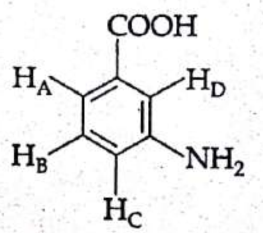


Figure-8.36

Wave number (cm⁻¹)	Assignment	Explanation
1102	$O-CH_2$ stretching	
1240	$C(O)-O$ stretching	
1588, 1604	Aromatic $C{=}C$ stretching	
1628	$N{=}H$ stretching	
1708	$C{=}O$ stretching	Conjugation with the phenyl ring decreases the carbonyl stretching frequency.
2980	$C-H$ stretching of $-CH_2CH_3$.	
3060	Aromatic $C-H$ stretching	
3374, 3461	Symmetric and asymmetric $-NH_2$ stretching.	

8.3.18 3-Aminobenzoic acid



- **^{1}H-NMR Spectrum :**

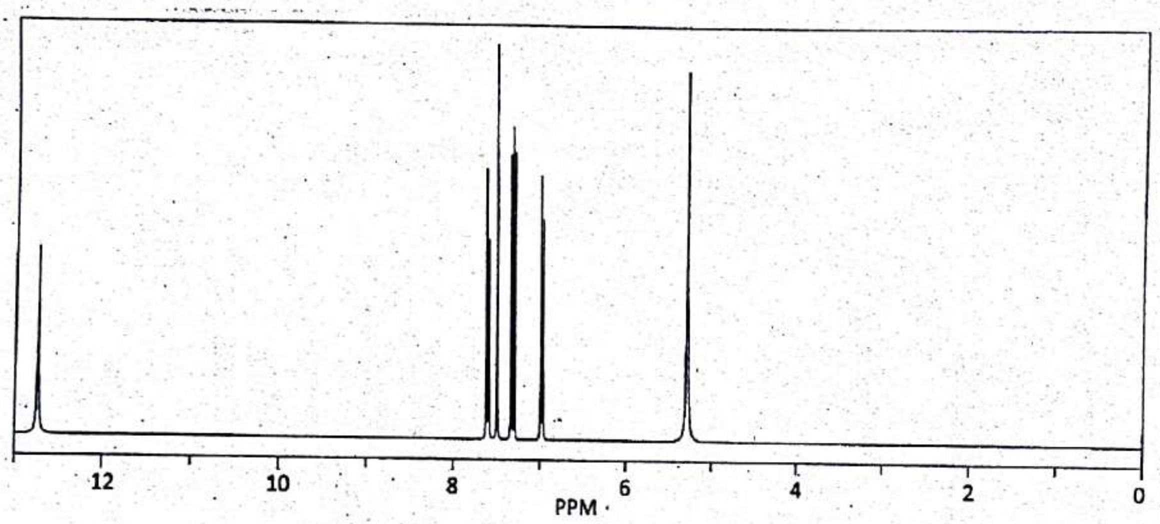


Figure-8.37

Chemical shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
5.28	Broad singlet (2H)	$-NH_2$	The signal appears as a singlet due to absence of any coupling partner. Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet.
6.98	Complex multiplet (1H)	H_C	The signal appears as a complex multiplet due to ortho coupling with H_B and meta coupling with H_A and H_D.
7.32	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.50	Triplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as a triplet due to weak meta coupling with H_A and H_C.
7.61	Complex multiplet (1H)	H_A	Deshielding is caused by strong magnetic anisotropy of the carbonyl function. The signal appears as complex multiplet due to strong ortho coupling with H_B and weak meta coupling with H_C and H_D.
12.74	Broad singlet (1H)	COOH	Strong hydrogen bonding causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner

IR Spectrum :

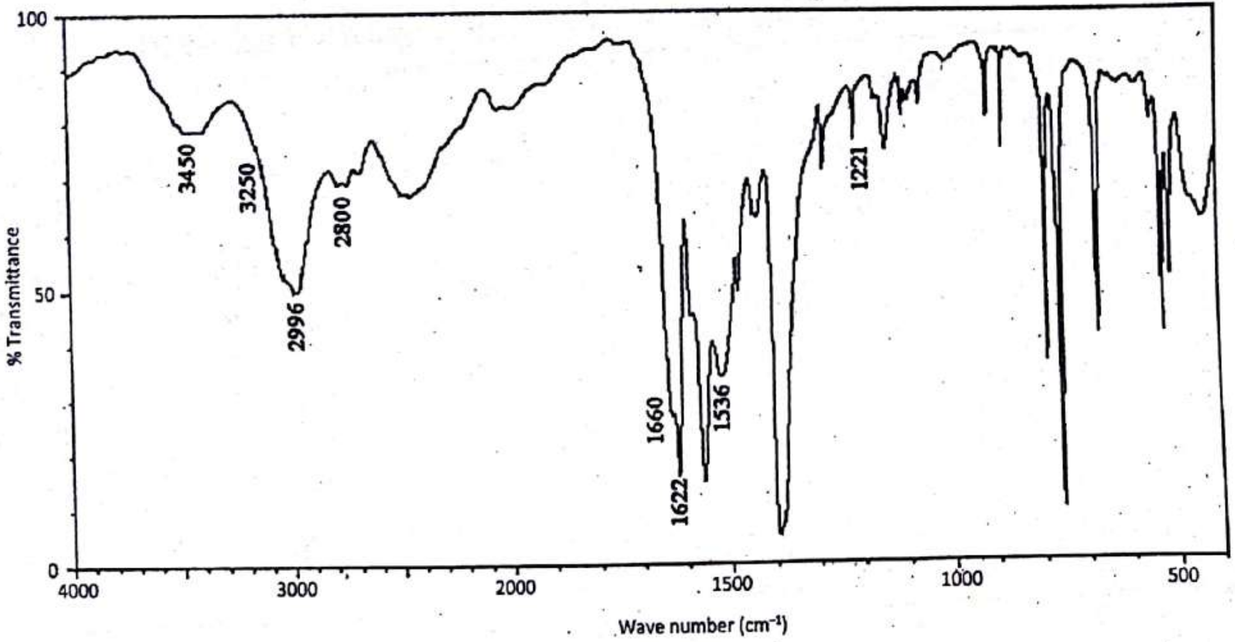
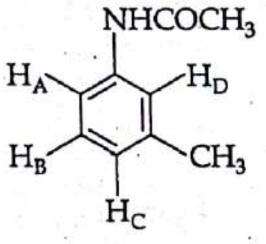


Figure-8.38

Wave number (cm^{-1})	Assignment	Explanation
1221	C(O)—O stretching	
1536, 1622	Aromatic C═C stretching	
1660	C═O stretching	Conjugation with phenyl ring and strong hydrogen bonding decreases the carbonyl stretching frequency.
2800	O—H stretching	Strong hydrogen bonding decreases the -OH stretching frequency and broadens the peak.
2996	Aromatic C—H stretching	
3250, 3450	Symmetric and asymmetric $-NH_2$ stretching.	

8.3.19 3-Methylacetanilide



■ ^{1}H-NMR Spectrum :

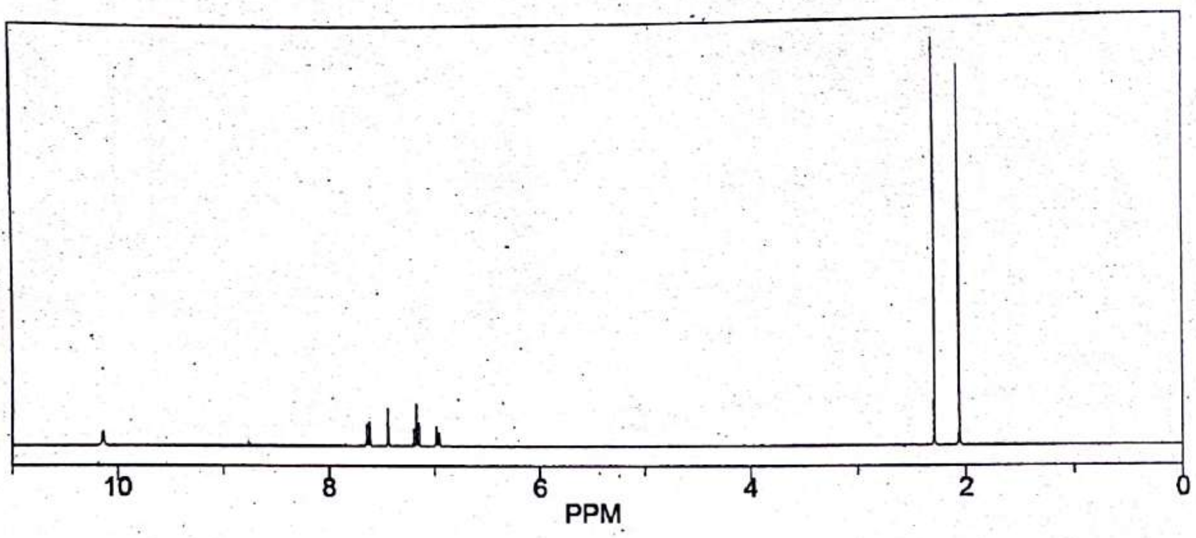


Figure-8.39

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.04	Singlet (3H)	$NHCOCH_3$	The signal appears as a singlet due to absence of any coupling partner.
2.34	Singlet (3H)	C_3-CH_3	The signal appears as a singlet due to absence of any coupling partner.
6.97	Complex multiplet (1H)	H_C	The signal appears as a complex multiplet due to ortho coupling with H_B and meta coupling with H_A and H_D.
7.31	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.42	Complex multiplet (1H)	H_A	The signal appears as complex multiplet due to strong ortho coupling with H_B and weak meta coupling with H_C and H_D.
7.54	Triplet (1H)	H_D	The signal appears as a triplet due to weak meta coupling with H_A and H_C.
10.2	Broad singlet (1H)	NH	The signal appears as a singlet due to absence of any coupling partner. Nuclear quadruple broadening by nitrogen may be responsible for the appearance of broad singlet.

IR Spectrum :

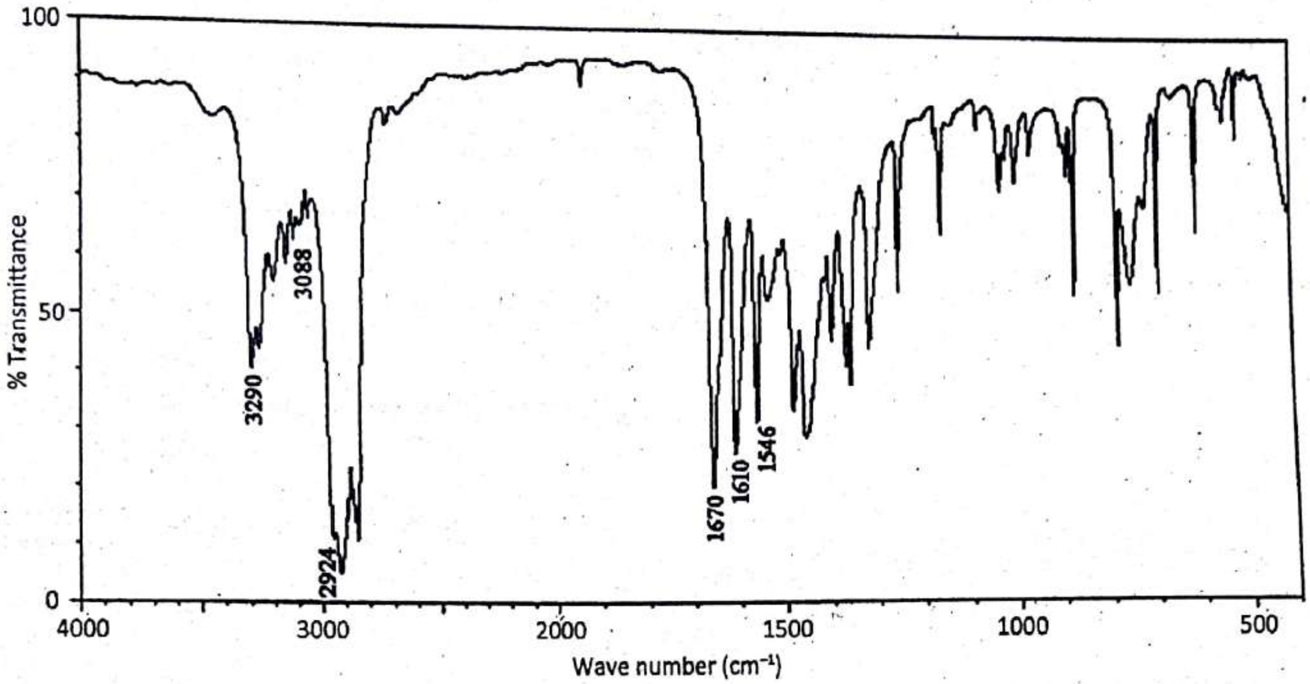
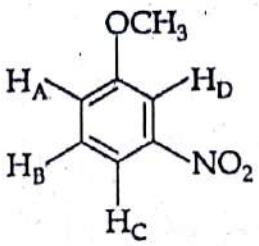


Figure-8.40

Wave number (cm⁻¹)	Assignment	Explanation
1546	N–H bending (amide II)	
1610	Aromatic C=C stretching	
1670	C=O stretching	Nitrogen lone pair is partly involved in resonance with the phenyl ring. So its conjugation with the carbonyl group diminishes increasing the carbonyl stretching from the normal value of amide.
2924	C–H stretching of $-CH_3$	
3088	Aromatic C–H stretching	
3290	N–H stretching	

8.3.20 3-Nitroanisole



¹H-NMR Spectrum :

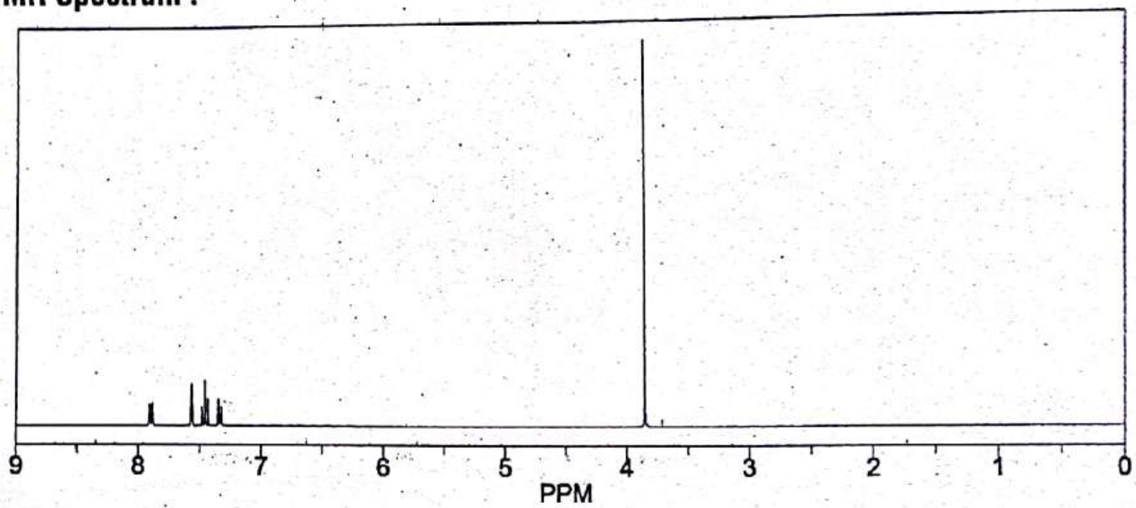


Figure-8.41

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
3.85	Singlet (3H)	OCH_3	The signal appears as a singlet due to absence of any coupling partner.
7.33	Complex multiplet (1H)	H_A	The signal appears as a complex multiplet due to ortho coupling with H_B and meta coupling with H_C and H_D.
7.45	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.56	Triplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of the nitro function. The signal appears as a triplet due to weak meta coupling with H_A and H_C.
7.89	Complex multiplet (1H)	H_C	Deshielding is caused by strong magnetic anisotropy of the nitro function. The signal appears as complex multiplet due to strong ortho coupling with H_B and weak meta coupling with H_A and H_D.

IR Spectrum :

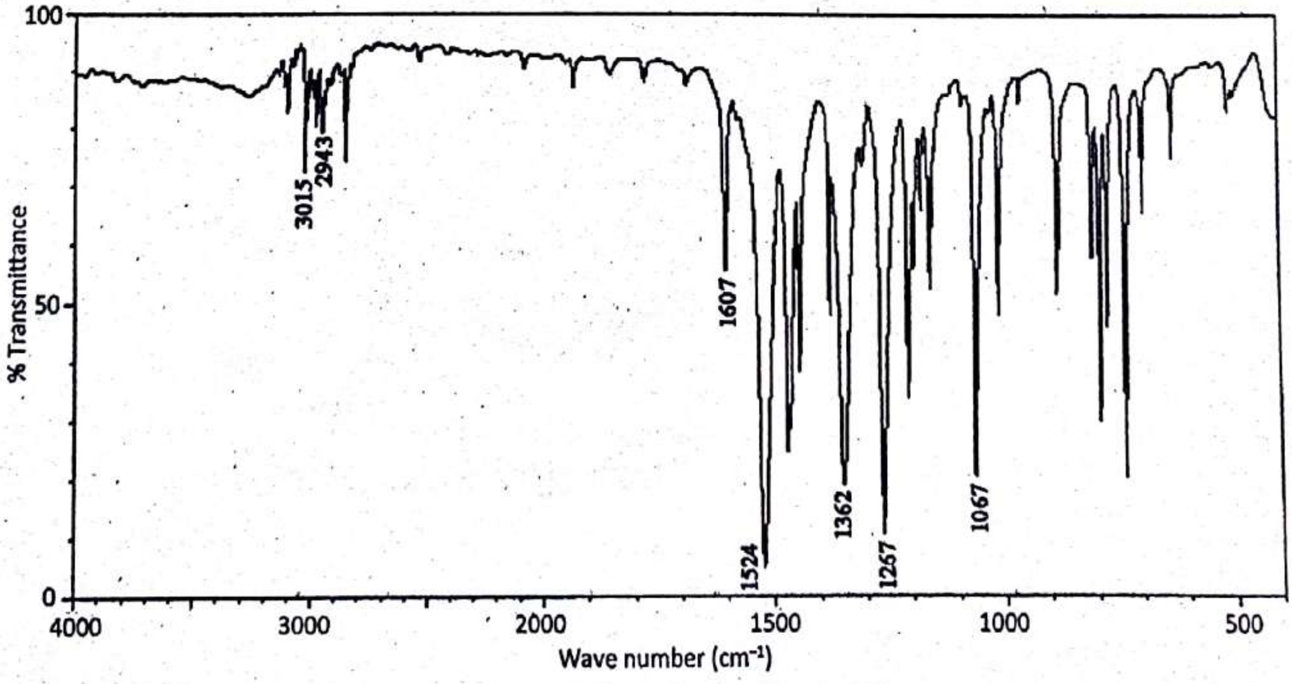
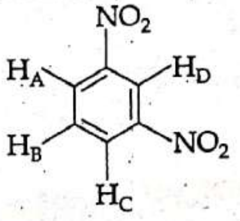


Figure-8.42

Wave number (cm^{-1})	Assignment	Explanation
1067, 1267	C–O stretching	
1362, 1524	Symmetric and asymmetric stretching of $-NO_2$	
1607	Aromatic C=C stretching	
2943	C–H stretching of $-CH_3$	
3015	Aromatic C–H stretching	

m-Disubstituted benzene with identical substituents

8.3.21 1,3-Dinitrobenzene



■ **^{1}H-NMR Spectrum :**

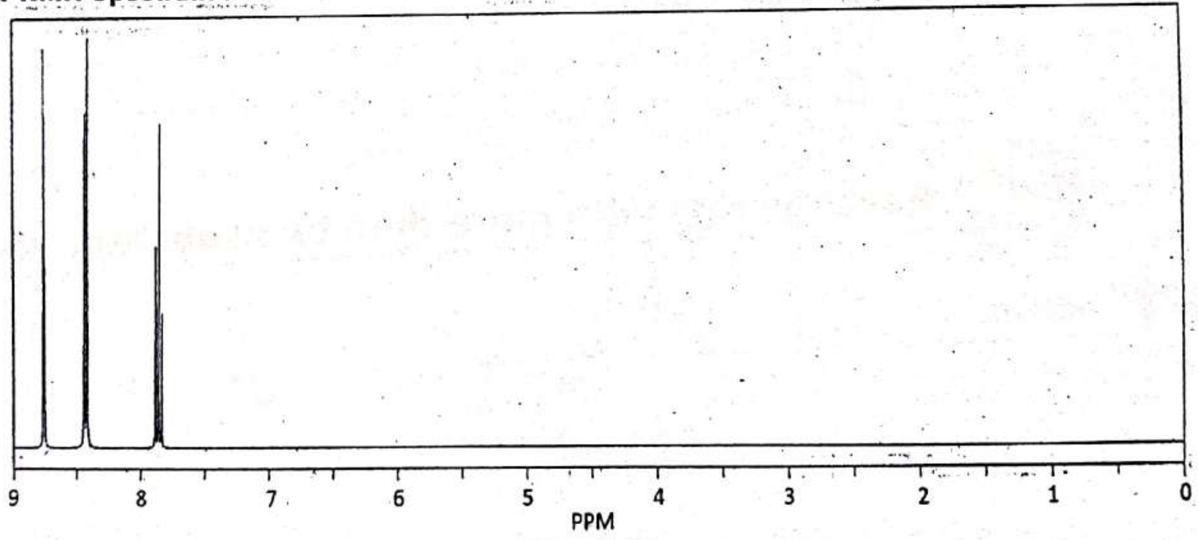


Figure-8.43

Chemical Shift (δ ppm)	Multiplicity [illegible]	Assignment [illegible]	Explanation
7.86	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with two H_A,
8.43	Doublet of doublet (2H)	H_A	Deshielding is caused by strong magnetic anisotropy of the nitro function. The signal appears as a doublet of doublet due to strong ortho coupling with H_B and weak meta coupling with H_D.
8.76	Triplet (1H)	H_D	Deshielding is caused by strong magnetic anisotropy of two nitro functions. The signal appears as triplet due to weak meta coupling with two H_A.

IR Spectrum :

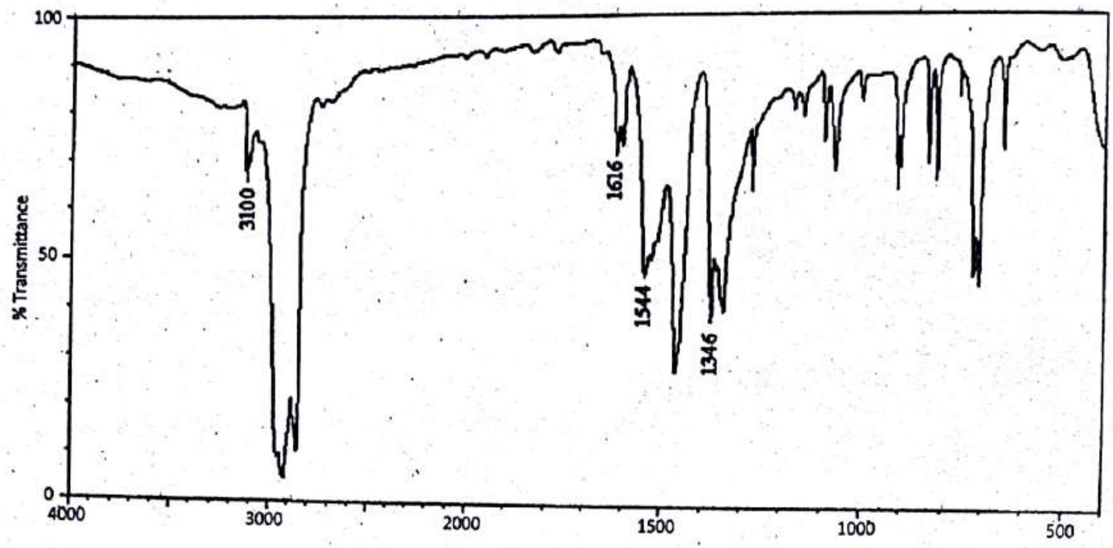
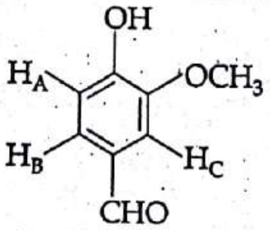


Figure-8.44

Wave number (cm⁻¹)	Assignment	Explanation
1346, 1544	Symmetric and asymmetric stretching of $-NO_2$	
1616	Aromatic C=C stretching	
3100	Aromatic C–H stretching	

Benzene ring with more than two substituents

8.3.22 Vanillin



¹H-NMR Spectrum :

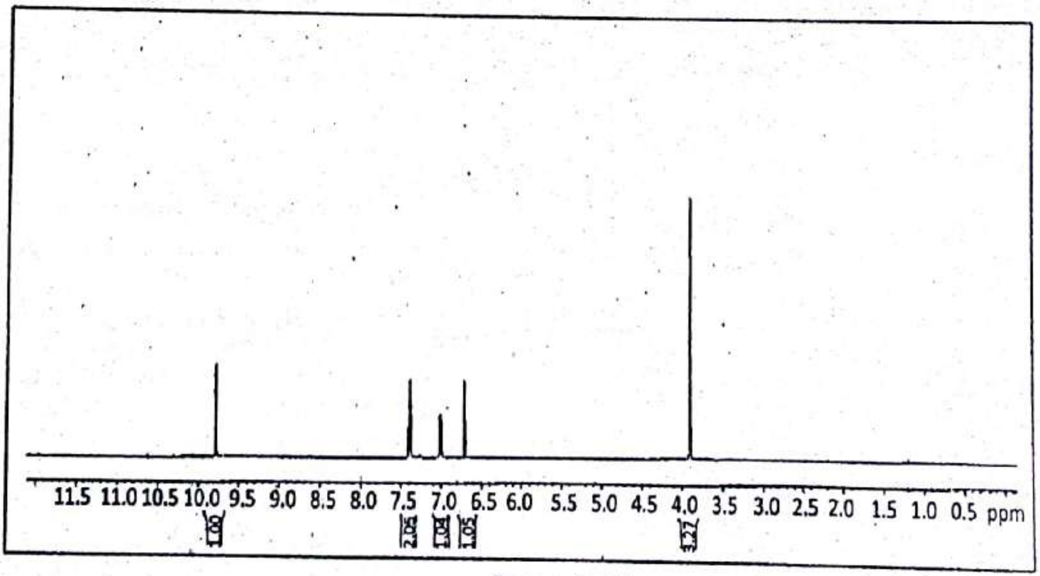


Figure-8.45

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
3.9	Singlet (3H)	OCH_3	The signal appears as a singlet due to absence of any coupling partner.
6.7	Singlet (1H)	OH	The signal appears as a singlet due to absence of any coupling partner.
7.00	Doublet (1H)	H_A	The signal appears as a doublet due to ortho coupling with H_B.
7.38-7.40	Complex multiplet (2H)	H_B and H_C	Deshielding is caused by magnetic anisotropy of the carbonyl function. H_B experiences ortho coupling with H_A and meta coupling with H_C. H_C experiences meta coupling with H_B. Proximity of the signals prevents observation of the splitting pattern clearly.
9.80	Singlet (1H)	CHO	Magnetic anisotropy of the C=O unit causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

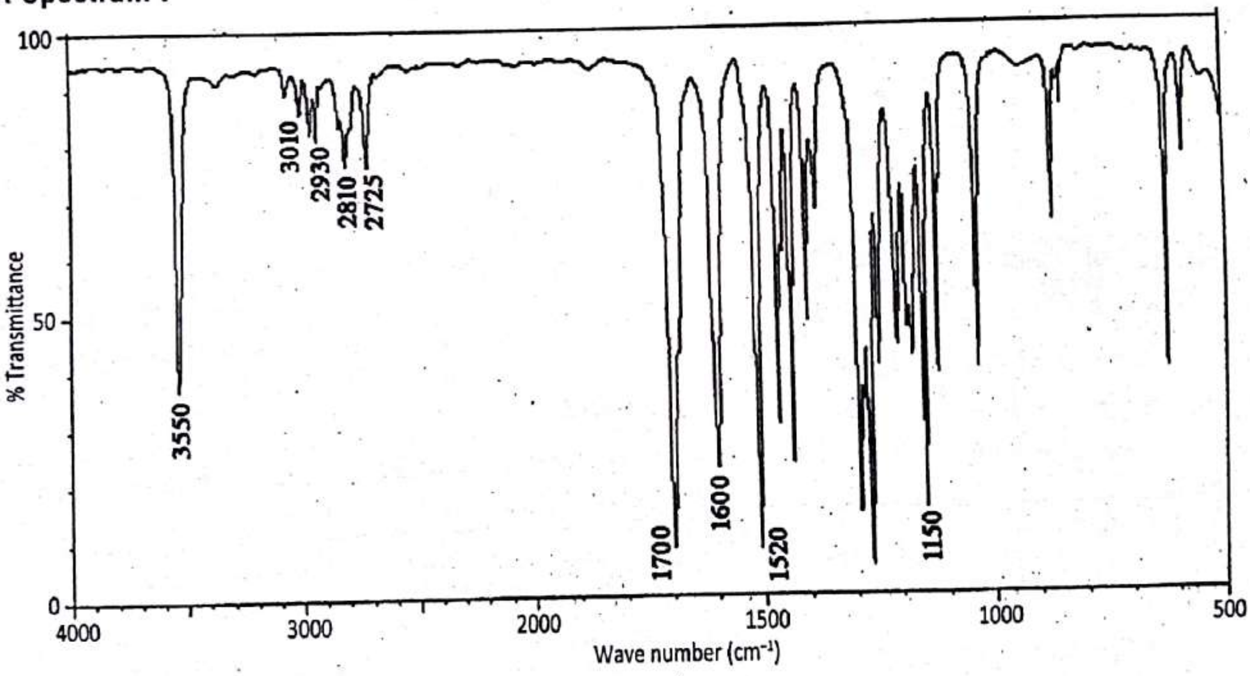
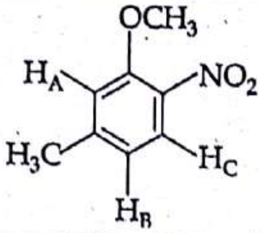


Figure-8.46

Wave number (cm⁻¹)	Assignment	Explanation
1150	C–O stretching	
1520, 1600	Aromatic C=C stretching	
1700	C=O stretching	
2725, 2810	C–H stretching of –CHO	
2930	C–H stretching of $-CH_3$	
3010	Aromatic C–H stretching	
3550	O–H stretching	

8.3.23 5-Methyl-2-nitroanisole



- **^{1}H-NMR Spectrum :**

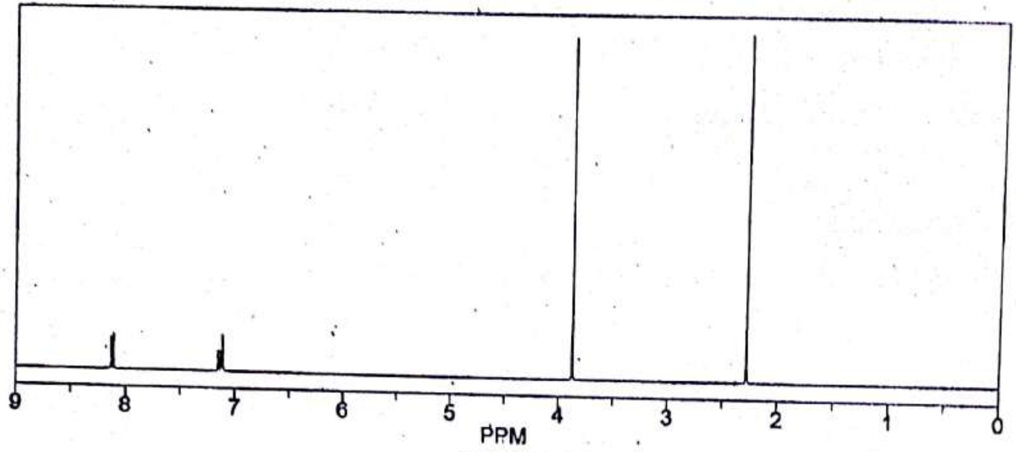


Figure-8.47

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.34	Singlet (3H)	$C-CH_3$	The signal appears as a singlet due to absence of any coupling partner.
3.84	Singlet (3H)	OCH_3	The signal appears as a singlet due to absence of any coupling partner.
7.11-7.14	Doublet of doublet (2H)	H_A and H_B	H_A undergoes meta coupling with H_B and H_B undergoes ortho coupling with H_C and meta coupling with H_A.
8.12	Doublet (1H)	H_C	Deshielding is caused by magnetic anisotropy of the nitro function. The signal appears as a doublet due to strong ortho coupling with H_B.

- **IR Spectrum :**

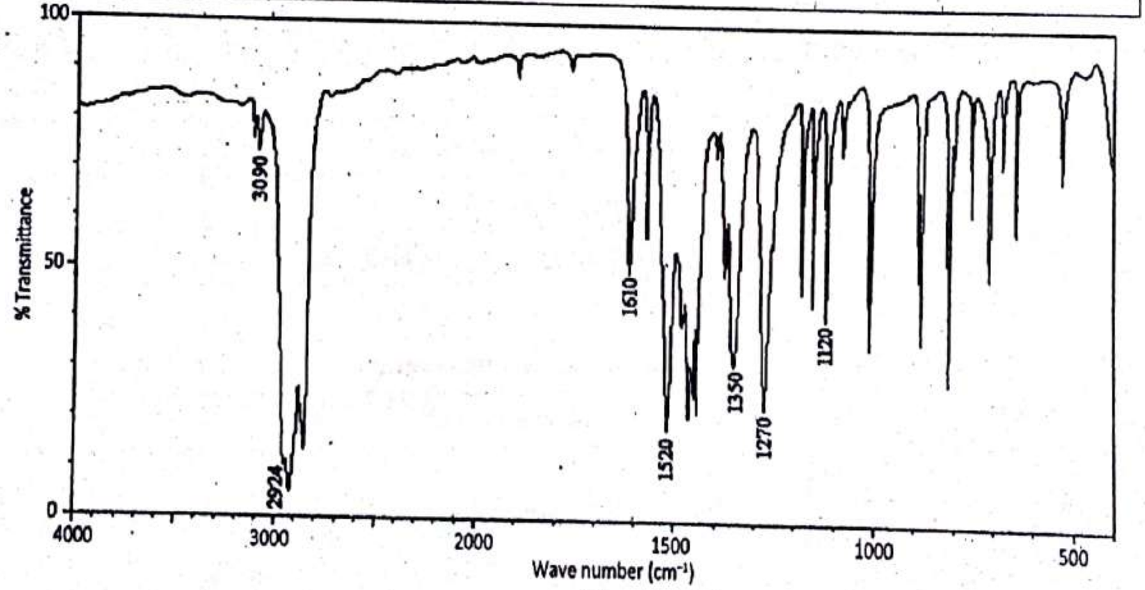
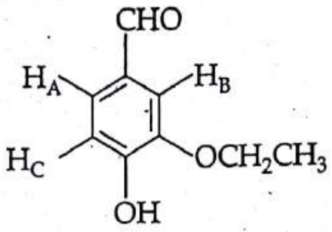


Figure-8.48

70

Wave number (cm^{-1})	Assignment	Explanation
1120	$O-CH_3$ stretching	
1270	Ar$-$O stretching	
1350, 1520	Symmetric and asymmetric stretching of $-NO_2$	
1610	Aromatic C=C stretching	
2924	C$-$H stretching of $-CH_3$	
3090	Aromatic C$-$H stretching	

8.3.24 3-Ethoxy-4-hydroxybenzaldehyde



^{1}H-NMR Spectrum :

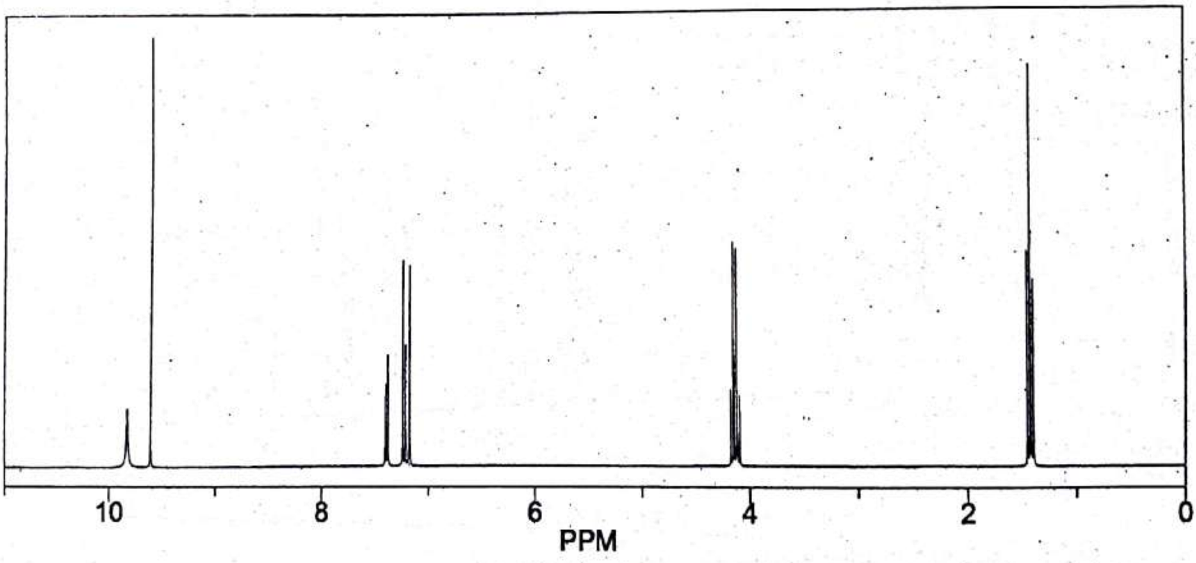


Figure-8.49

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
1.32	Triplet (3H)	$-CH_3$	The signal appears as a triplet due to coupling with adjacent methylene protons.
4.11	Quartet (2H)	$-CH_2$	The signal appears as a quartet due to coupling with adjacent methyl protons.
7.20 -7.24	Complex multiplet (2H)	H_B and H_C	H_B experiences meta coupling with H_A. H_C experiences ortho coupling with H_A. Proximity of the signals prevents clear identification of the splitting pattern.
7.38	Doublet of doublet(1H)	H_A	Deshielding is caused by magnetic anisotropy of the carbonyl function. The signal appears as a doublet of doublet due to strong ortho coupling with H_C and weak meta coupling with H_B.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
9.61	Singlet (1H)	CHO	Magnetic anisotropy of the C=O unit causes high down-field shift. The signal appears as a singlet due to absence of any coupling partner.
9.83	Broad singlet (1H)	–OH	The signal appears as a singlet due to absence of any coupling partner.

- **IR Spectrum.:**

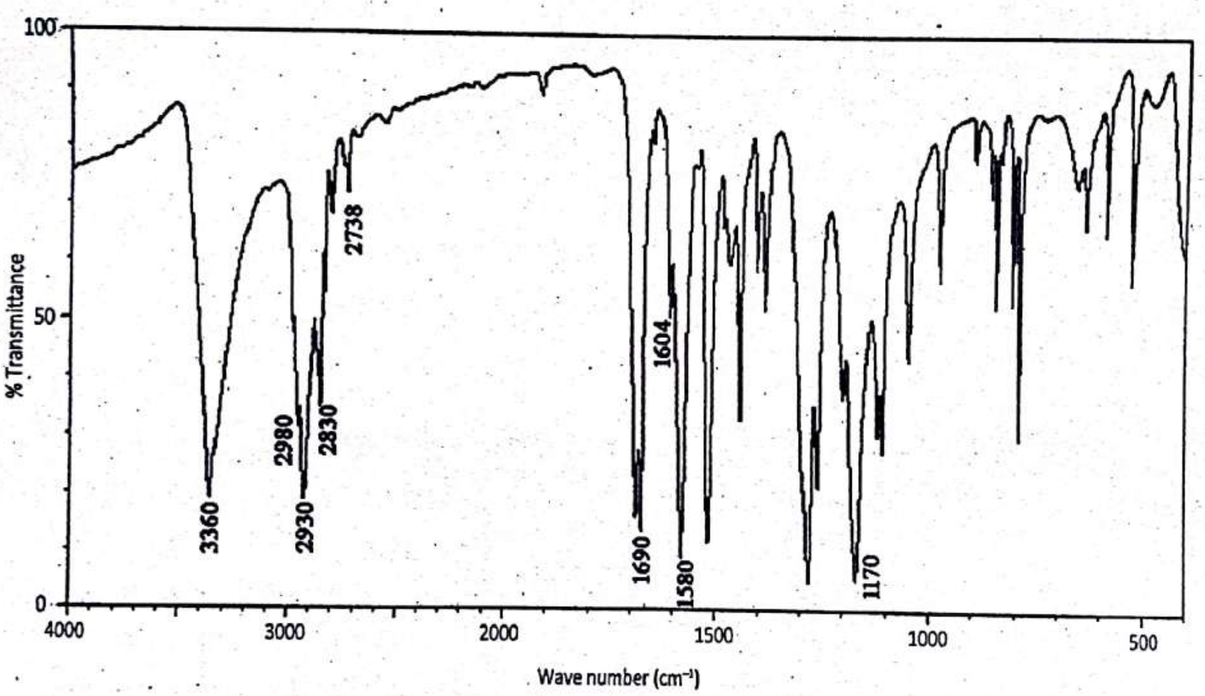
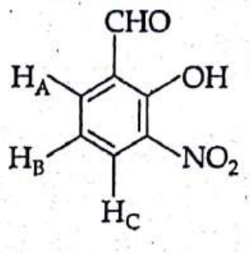


Figure-8.50

Wave number (cm^{-1})	Assignment	Explanation
1170	C–O stretching	
1580, 1604	Aromatic C=C stretching	
1690	C=O stretching	
2738, 2830	C–H stretching of –CHO	
2930	C–H stretching of –CH_2CH_3	
2980	Aromatic C–H stretching	
3360	O-H stretching	

8.3.25 2-Hydroxy-3-nitrobenzaldehyde



110

^{1}H-NMR Spectrum :

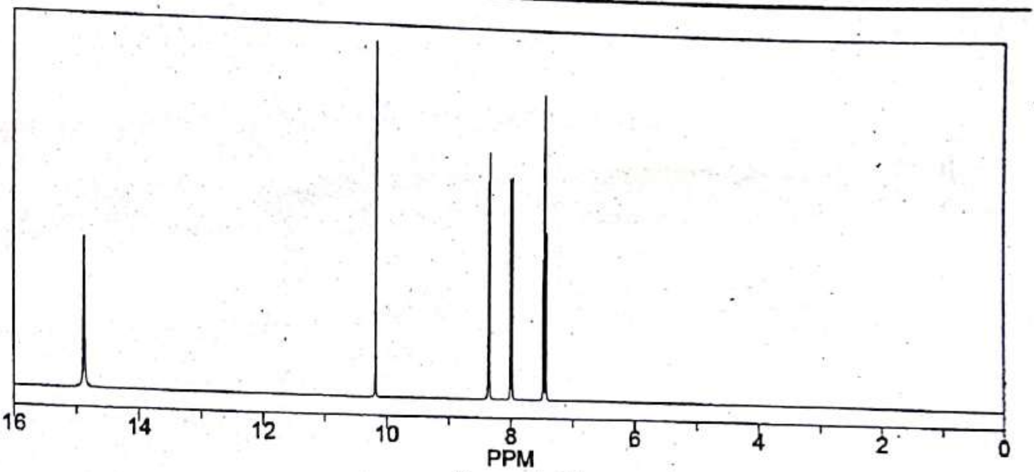


Figure-8.51

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
7.46	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
8.01	Doublet of doublet (1H)	H_A	Magnetic anisotropy of the C=O unit causes high downfield shift. The signal appears as doublet of doublet due to ortho coupling with H_B and meta coupling with H_C.
8.37	Doublet of doublet (1H)	H_C	Magnetic anisotropy of the nitro function causes high downfield shift. The effect is stronger than that of the carbonyl group. The signal appears as doublet of doublet due to ortho coupling with H_B and meta coupling with H_A.
10.26	Singlet (1H)	–CHO	Magnetic anisotropy of the C=O unitcauses high downfield shift. The signal appears as a singlet due to absence of any coupling partner.
14.89	Singlet (1H)	–OH	Magnetic anisotropy of the C=O unit and strong intramolecular hydrogen bonding cause very high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

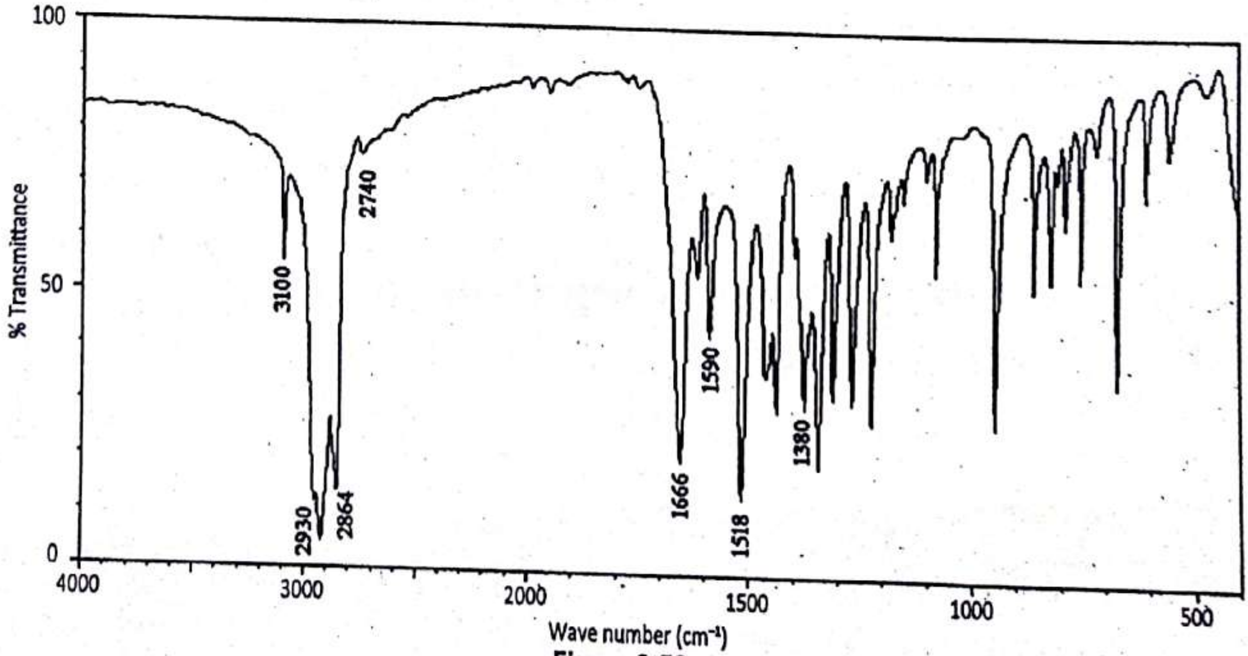
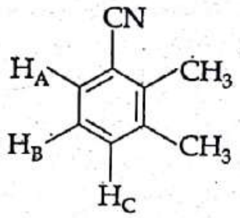


Figure-8.52

Wave number (cm^{-1})	Assignment	Explanation
1380, 1518	Symmetric and asymmetric stretching of $-NO_2$	
1590	Aromatic C=C stretching	
1666	C=O stretching	Conjugation with phenyl group and strong intramolecular hydrogen bonding with $-OH$ function decreases the carbonyl stretching frequency.
2740, 2864	C−H stretching of $-CHO$	
2930	Aromatic C−H stretching	
3100	O−H stretching	Strong intramolecular hydrogen bonding with $-CHO$ and $-NO_2$ groups drastically lowers the $-OH$ stretching frequency

8.3.26 2,3-Dimethylbenzonitrile



- **^{1}H-NMR Spectrum :**

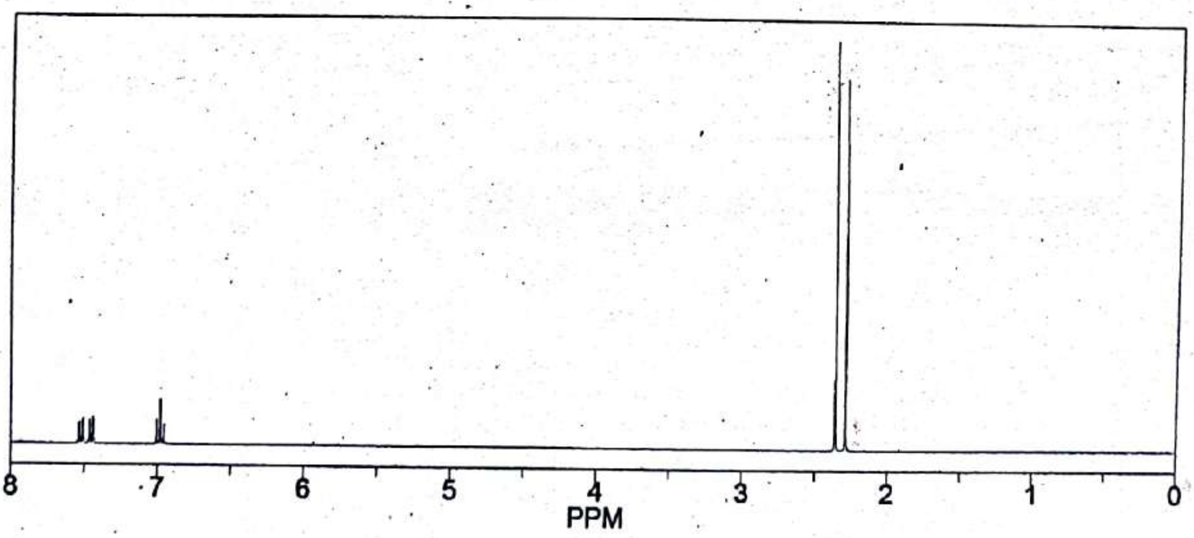


Figure-8.53

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
2.34	Singlet (3H)	C_3-CH_3	The signal appears as singlet due to absence of any coupling partner.
2.41	Singlet (3H)	C_2-CH_3	Slightly more deshielded than C_3-CH_3 as a result of electron withdrawal by $-CN$ group. The signal appears as singlet due to absence of any coupling partner.

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
6.98	Triplet (1H)	H_B	The signal appears as a triplet due to ortho coupling with H_A and H_C.
7.45	Doublet of doublet (1H)	H_A	The signal appears as a doublet of doublet due to ortho coupling with H_B and meta coupling with H_C.
7.53	Doublet of doublet (1H)	H_C	The signal appears as doublet of doublet due to ortho coupling with H_B and meta coupling with H_A.

- **IR Spectrum :**

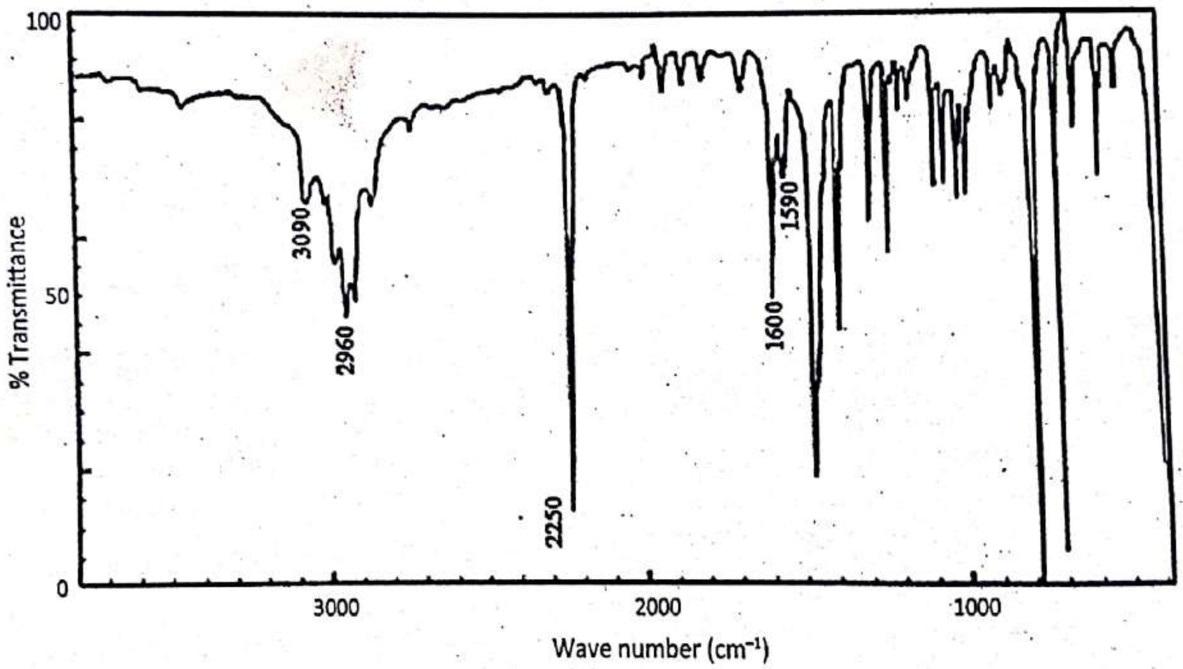
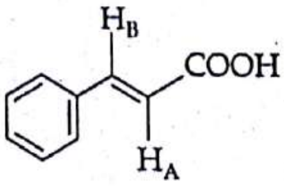


Figure-8.54

Wave number (cm⁻¹)	Assignment	Explanation
1590, 1600	Aromatic C=C stretching	
2250	CN stretching	
2900	C–H stretching of $-CH_3$	
3040	Aromatic C–H stretching	

Monosubstituted benzene derivative

8.3.27 *trans* - Cinnamic acid



■ ^{1}H-NMR Spectrum :

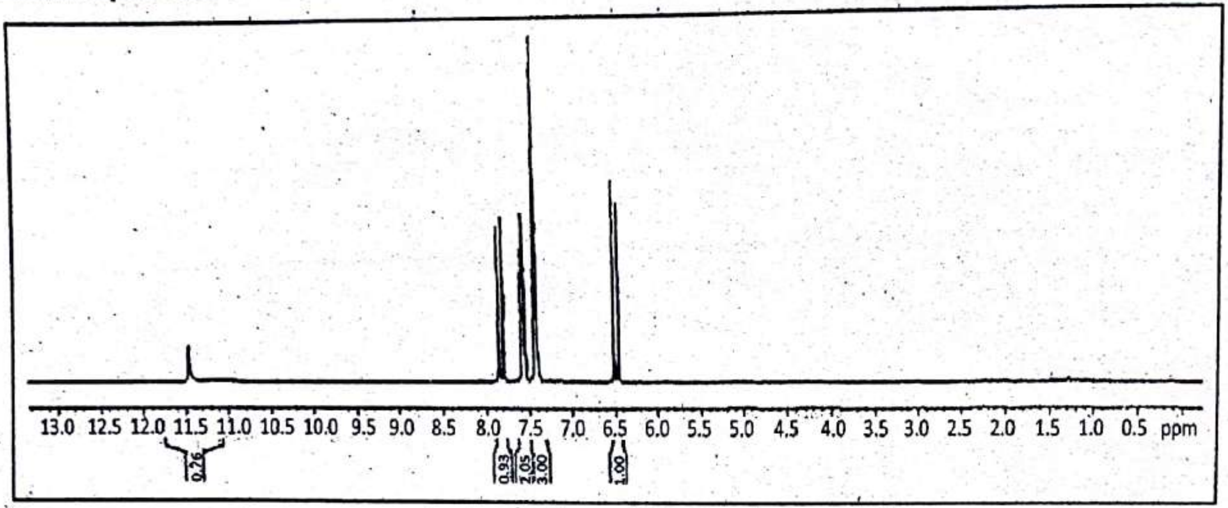


Figure-8.55

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
6.48	Doublet (1H)	H_A	The signal appears as doublet due to coupling with HB. The trans coupling constant is very high.
7.42	Multiplet (3H)	Two meta and one para ring protons	The signal appears as a multiplet due to ortho and meta coupling.
7.60	Multiplet (2H)	Two ortho ring protons	The signal appears as a multiplet due to ortho and meta coupling.
7.82	Doublet (1H)	H_B	Mesomeric electron withdrawal by the –COOH group causes high downfield shift. The signal appears as doublet due to coupling with H_A. The trans coupling constant is very high.
11.5	Broad singlet (1H)	COOH	Strong hydrogen bonding causes high downfield shift. The signal appears as a singlet due to absence of any coupling partner.

■ IR Spectrum :

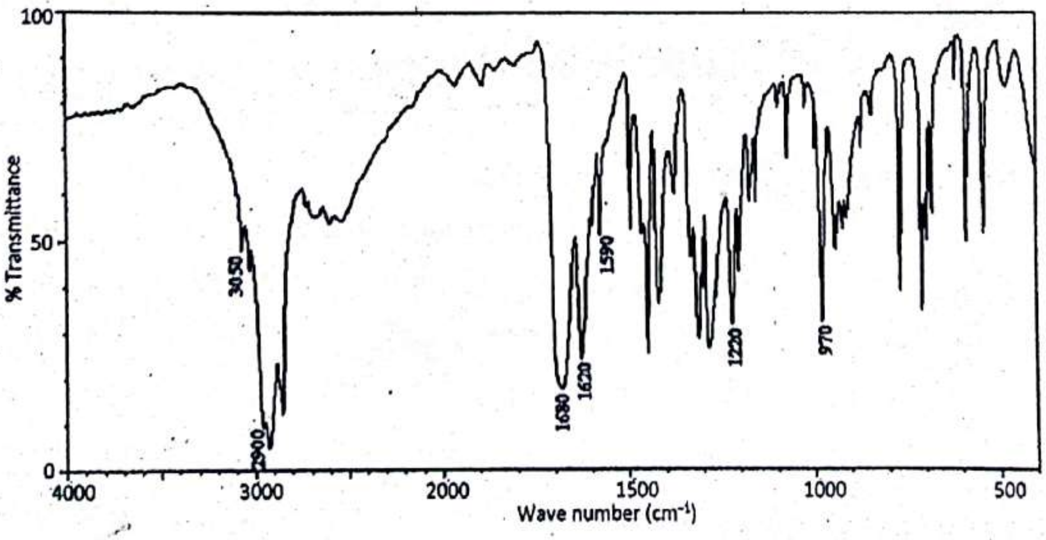
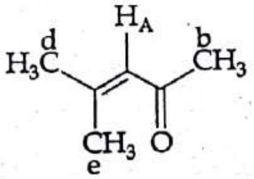


Figure-8.56

Wave number (cm^{-1})	Assignment	Explanation
970	C-H def. (trans olefin)	
1220	C−O stretching	
1590	Aromatic C=C stretching	
1620	Olefinic C=C stretching	
1680	C=O stretching	Hydrogen bonding and conjugation with olefinic segment lowers the carbonyl stretching frequency.
2900	O−H stretching.	Strong hydrogen bonding is responsible for lowering of O−H stretching frequency and broadening of the band
3050	Aromatic C−H stretching	

Some aliphatic compounds

8.3.28 Mesityl oxide



■ ^{1}H-NMR Spectrum :

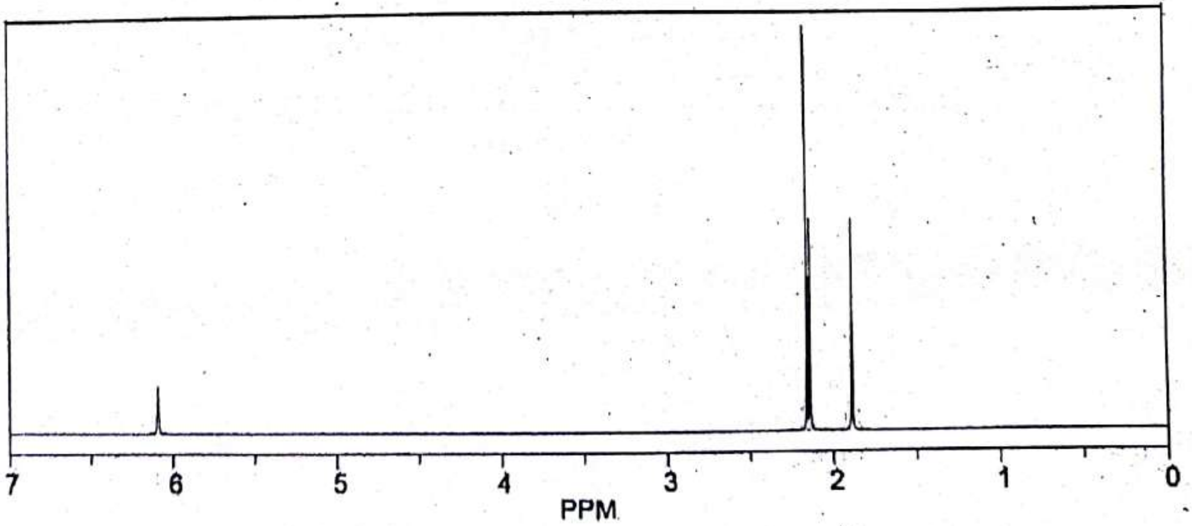


Figure-8.57

Chemical shift (δ ppm)	Multiplicity (# H)	Assignment to proton	Explanation
1.89	Doublet (3H)	CH_3(d)	The signal appears as a doublet due to allylic coupling with H_A.
2.14	Doublet (3H)	CH_3(e)	The signal appears as a doublet due to allylic coupling with H_A.
2.16	Singlet (3H)	CH_3(b)	The signal appears as singlet due to absence of any coupling partner.
6.09	Broad singlet (1H)	H_A	The signal should appear as a multiplet due to allylic coupling with CH_3(d) and CH_3(e). However, these long-range couplings are so weak that the actual splitting pattern is not seen.

- **IR Spectrum :**

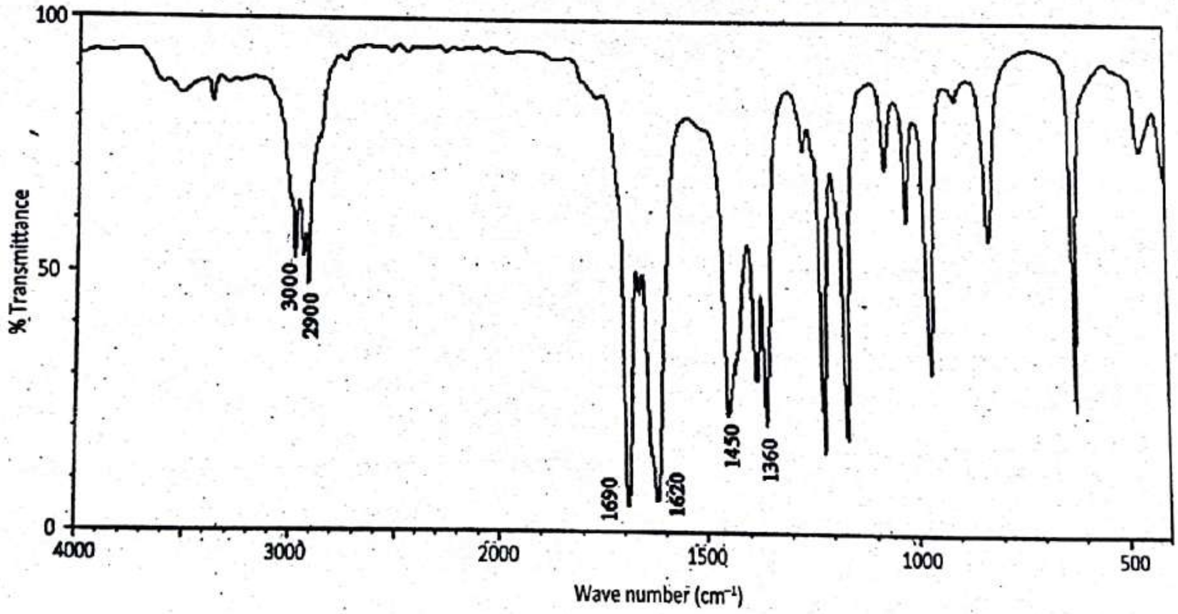
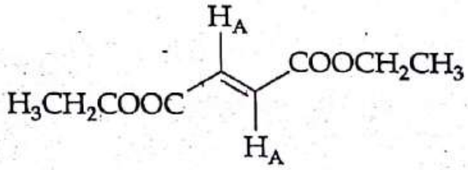


Figure-8.58

Wave number (cm⁻¹)	Assignment	Explanation
1360, 1450	Symmetric and asymmetric CMe_2 Stretching	
1620	C═C stretching	
1690	C═C stretching	Conjugation with C=C slightly lowers the carbonyl stretching frequency
2900	$C(sp^3)-H$ stretching	
3000	C═C–H stretching	

8.3.29 Diethyl fumarate



■ ^{1}H-NMR Spectrum :

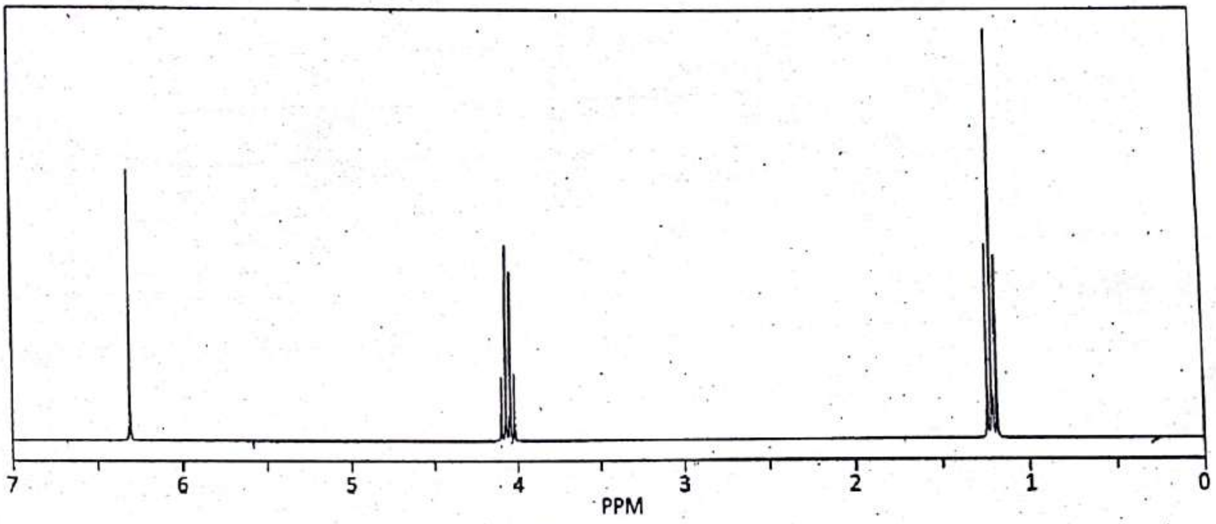


Figure-8.59

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
1.21	Triplet (6H)	$-CH_3$	The signal appears as triplet due to coupling with adjacent methylene protons.
4.06	Quartet (4H)	$-CH_2$	The signal appears as quartet due to coupling with adjacent methyl protons.
6.31	Singlet (2H)	H_A	The signal appears as a singlet as two H_A are homotopic and so chemically and magnetically equivalent.

■ IR Spectrum :

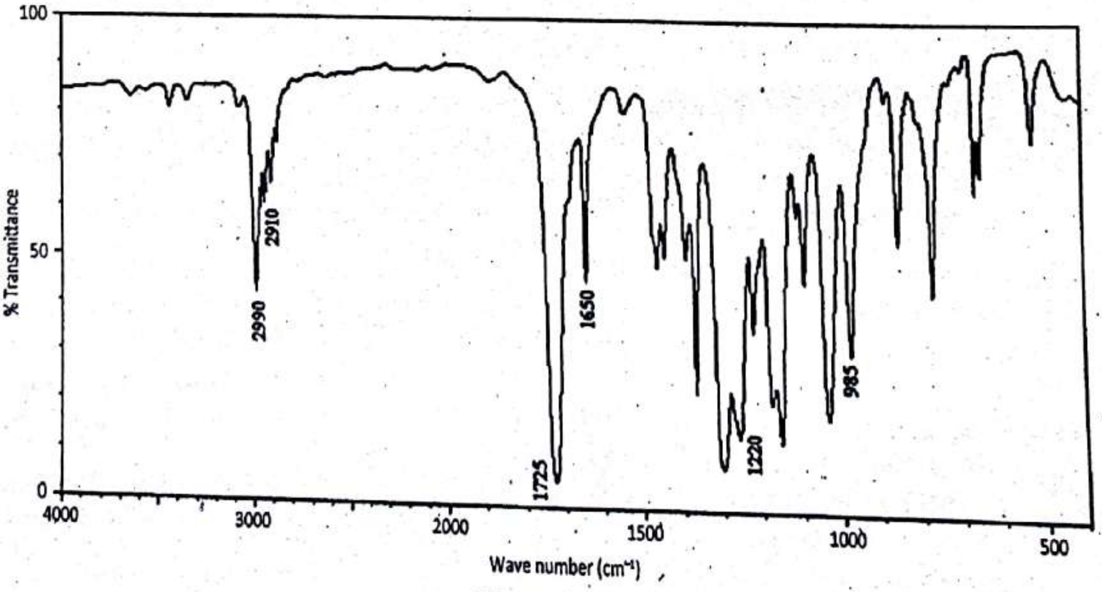
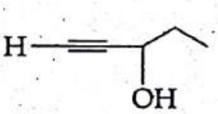


Figure-8.60

Wave number (cm⁻¹)	Assignment	Explanation
985	C–H def. (trans olefin)	
1220	C–O stretching	
1650	C=C stretching	
1725	C=O stretching	
2910	C(sp^3)–H stretching	
2990	C=C–H stretching	

8.3.30 Pent-1-yn-3-ol



- **¹H-NMR Spectrum :**

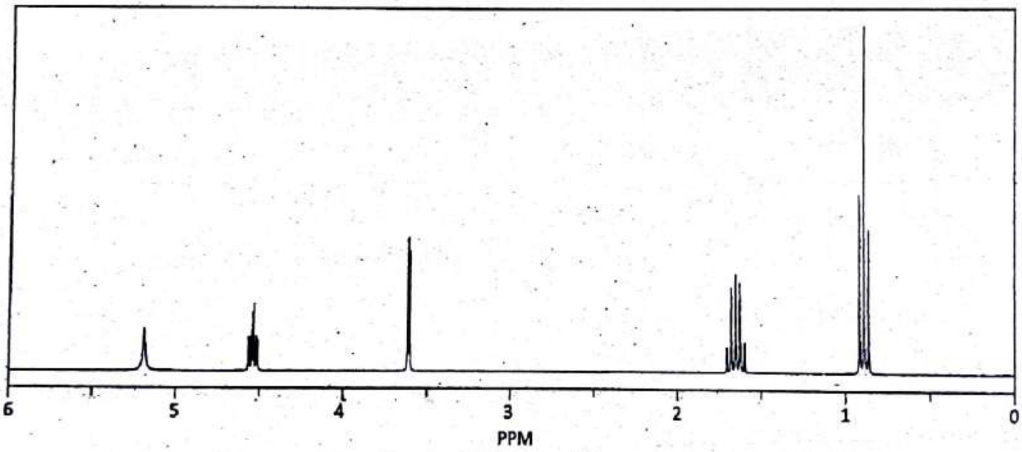


Figure-8.61

Chemical Shift (δ ppm)	Multiplicity (J Hz)	Assignment to proton	Explanation
0.89	Triplet (3H)	$-CH_3$	The signal appears as triplet due to coupling with adjacent methylene protons.
1.65	Quartet (4H)	$-CH_2$	The signal appears as quintet due to coupling with adjacent methyl and methine protons. Coupling constants with methyl and methine protons are almost the same which make the doublet of quartet coalesce into a quintet.
3.61	Doublet (1H)	Acetylenic proton	The signal appears as a doublet due to long range coupling with methine proton. The coupling constant is low.
4.54	Doublet of triplet (1H)	CHOH	The signal appears as a doublet of triplet (dt) due to coupling with adjacent methyl protons (with high coupling constant) and long-range coupling with methine proton (with low coupling constant).
5.19	Broad singlet (1H)	OH	The signal appears as a singlet due to absence of any coupling partner.

IR Spectrum :

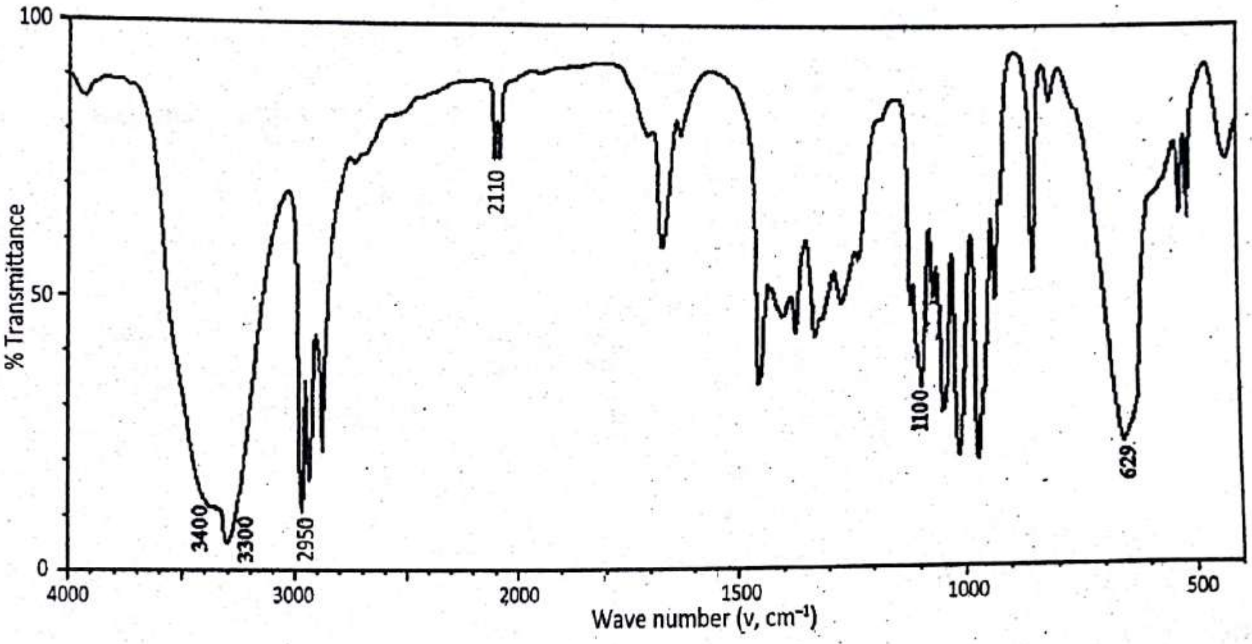


Figure-8.62

Wave number (cm⁻¹)	Assignment	Explanation
629	$C(sp)-H$ def.	
1100	$C-O$ stretching	
2110	$C(sp)-C(sp)$ stretching	
2950	$C(sp^3)$-H stretching	
3300	$C(sp)-H$ stretching	
3400	$O-H$ stretching	

Question for viva-voce

1. Why the aldehydic C−H stretching absorption appears as a doublet and at a lower wave number than an alkenyl C−H?

Hint : Interaction between n orbital on carbonyl oxygen and σ of *C−H decreases the force constant of aldehydic C−H. Appearance as a doublet is ascribed to interaction between fundamental C−H stretching and overtone of C−H bending.

2. Why hydrogen bonded O−H appears as broad band?

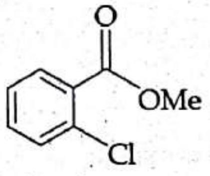
Hint : Due to thermal motion of molecules strengths of all the hydrogen bonds in a molecular assembly are not identical. So hydrogen bonding diminishes the force constants in such a way that a large number of O−H bonds with closely spaced force constants are created.

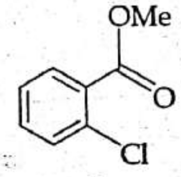
3. How can you distinguish between 4-methyl benzamide and 4-amino acetophenone by IR spectroscopy?

Hint: By the presence and absence of the characteristic amide bands. Comparison of carbonyl stretching frequency is not safe due to lowering of force constant of $C=O$ in 4-amino acetophenone through mesomeric electron release by the amino group.

4. Two $C=O$ stretching absorptions are observed in methyl-2-chloro benzoate. Explain.

Hint: In rotamer B $C=O$ bond acquires less single bond character to minimise dipole-dipole repulsion with $C-Cl$. So force constant of $C=O$ becomes greater for B than for A which is responsible for the higher carbonyl stretching displayed by B than by A.


A


B

5. 2-Hydroxy-3-nitro acetophenone displays two carbonyl stretching frequencies at 1692 and 1658 cm-1. Explain.

Hint: The hydroxyl function may separately be engaged in intramolecular hydrogen bonding with $-NO_2$ and $C=O$. Therefore signals for nonbonded $C=O$ ($1692\ cm^{-1}$) and bonded $C=O$ ($1658\ cm^{-1}$) are observed.

6. How many PMR signals do you expect for the following compounds?
(i) R-2-bromobutane (ii) Propene (iii) p-dichlorobenzene

Hint: (i) 5 (ii) 4 (iii) 1

7. What type of protons undergo D_2O exchange?

Hint: Labile protons like $-OH$, $-COOH$, $-SH$, $-CONH-$, active methylene and methine etc.

8. Which nuclei are NMR active?

Hint: Nuclei with spin quantum number greater than zero are NMR active.

9. Which compound is used as internal standard during D_2O exchange?

Hint: Sodium salt of 3-(trimethyl silyl)-propanesulfonic acid as TMS is insoluble in water or in D_2O.

10. Between enantiotopic and diastereotopic protons which can be distinguished by PMR spectroscopy?

Hint: Diastereotopic protons as PMR is an achiral probe.

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