NMR SPECTROSCOPY

SEM-4, CC-8
PART-7, PPT-19

Contents (Part-7)

Interpretation of NMR Spectra of Common Organic Compounds

1. *^{1}H NMR Absorptions of Benzene*
2. *^{1}H NMR Absorptions of Toluene*
3. *^{1}H NMR Absorptions of Benzaldehyde*
4. *^{1}H NMR Absorptions of Nitrobenzene*
    - *Spectral Analysis of Common Organic Compounds*
    - *^{1}H NMR Spectroscopic Problems*

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Nuclear Magnet Resonance (NMR) Spectroscopy (PART-7, PPT-19)

^{1}H NMR Spectral Analysis of Benzene

All the six protons in benzene are equivalent as the protons are in a similar chemical environment. Therefore, absorption frequency of all the protons in benzene is identical. Since all the protons are equivalent, question of spin-spin coupling does not arise. Aromatic protons are highly deshielded due to diamagnetic anisotropic deshielding effect of the benzene ring (ring current effect). Benzene shows a sharp singlet (6H) at δ 7.27 in its ^{1}H NMR spectrum.

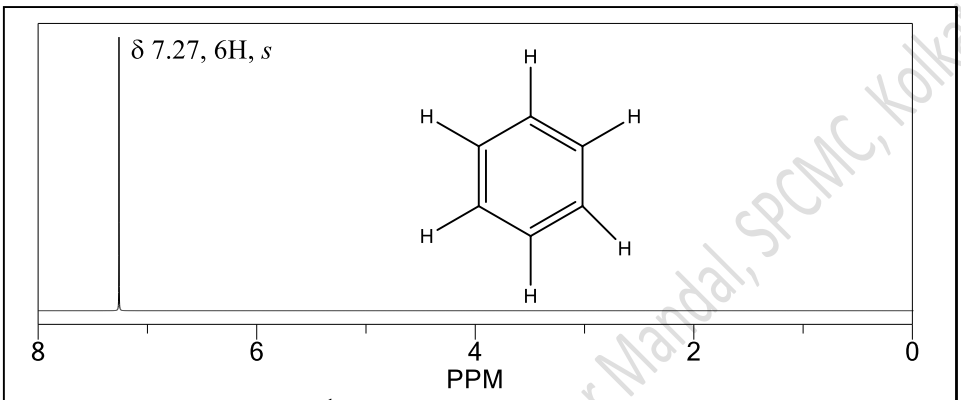


Figure 1: ^{1}H NMR spectrum of benzene

^{1}H NMR Spectral Analysis of Toluene

Some substituents like methyl, ethyl, etc., do not perturb the chemical shifts of the benzenoid hydrogens to a significant extent, so that all absorb at about the similar frequency to display a broad *singlet* (*s*). This is usually the case when the substituent is an alkyl group or group that about the same electronegativity as carbon and cannot create much difference in electron density on the *ortho*, *meta*, and *para* positions.

Such an absorption (a *singlet* for benzenoid hydrogens) is displayed by toluene, but methyl group resides in a different environment compared to the benzenoid protons, hence appears at δ 2.34 (3H, *s*). The comparatively higher δ value of methyl protons in toluene is due to the influence of the aromatic ring (ring current effect).

Toluene shows two signals in its ^{1}H NMR spectrum as shown in Figure 2. As expected, methyl protons appear as a *singlet* because of the absence of neighbouring interacting proton. Aromatic protons, on the other hand, appear as a broad *singlet*. Though aromatic protons appear almost at the similar position in the spectrum, all of them are not chemically equivalent. All the aromatic protons in toluene are magnetically nonequivalent. As a result of additional coupling among protons with small coupling constant, they appear as a *broad* signal.

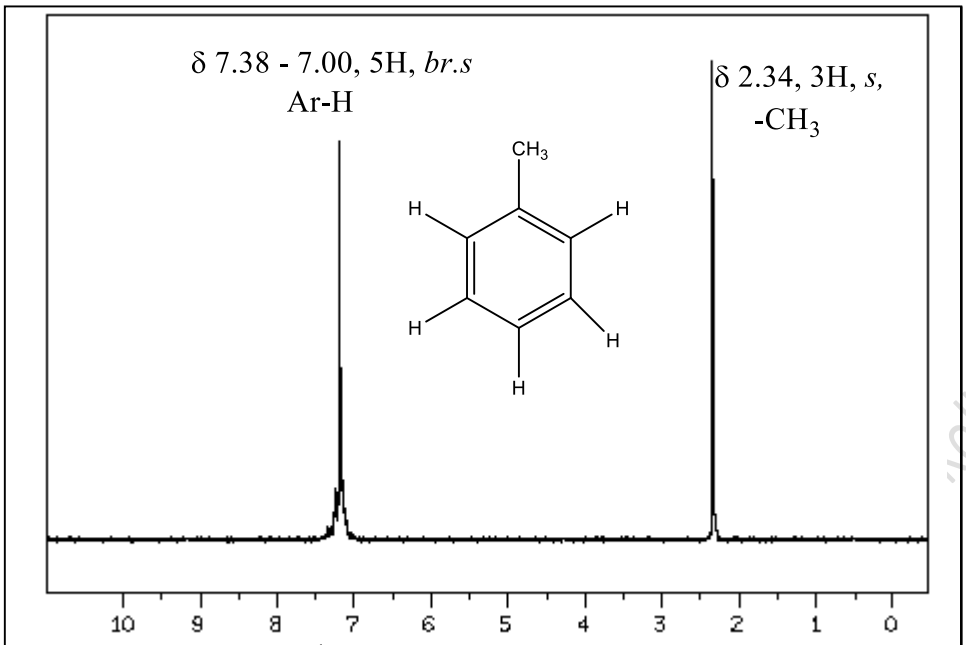
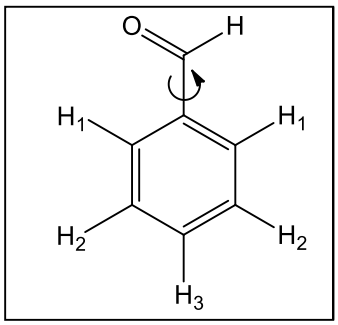


Figure 2: ^{1}H NMR spectrum of toluene

^{1}H NMR Spectral Analysis of Benzaldehyde

Formyl (-CHO) group is a strongly electron withdrawing group, so in benzaldehyde electron density at *ortho*, *meta*, and *para* positions with respect to –CHO group will be different. Thus aldehydic proton and benzenoid protons H_1 (2H), H_2 (2H) and H_3 (1H) all are chemically nonequivalent, i.e., has different chemical shift values. Consequently, four signals appear in the ^{1}H NMR spectrum of the compound.

Aldehydic proton is mostly deshielded by the diamagnetic anisotropic deshielding effect of the carbonyl group, and appears at δ 9.88 (1H, *s*). Presence of electron withdrawing carbonyl group and benzene ring (ring current effect) also play a role. Since –CHO is a powerful electron withdrawing group, so all the benzenoid protons will be deshielded compared to benzene itself.



Consequently, all the benzenoid protons (H_1, H_2, and H_3) resonated at higher frequency and appeared at higher δ values compared to that of benzene (δ_H for benzene is 7.27), but the extent of deshielding will be different depending upon the influence of –CHO group at the ring carbons: $\delta_{H1} > \delta_{H3} > \delta_{H2}$.

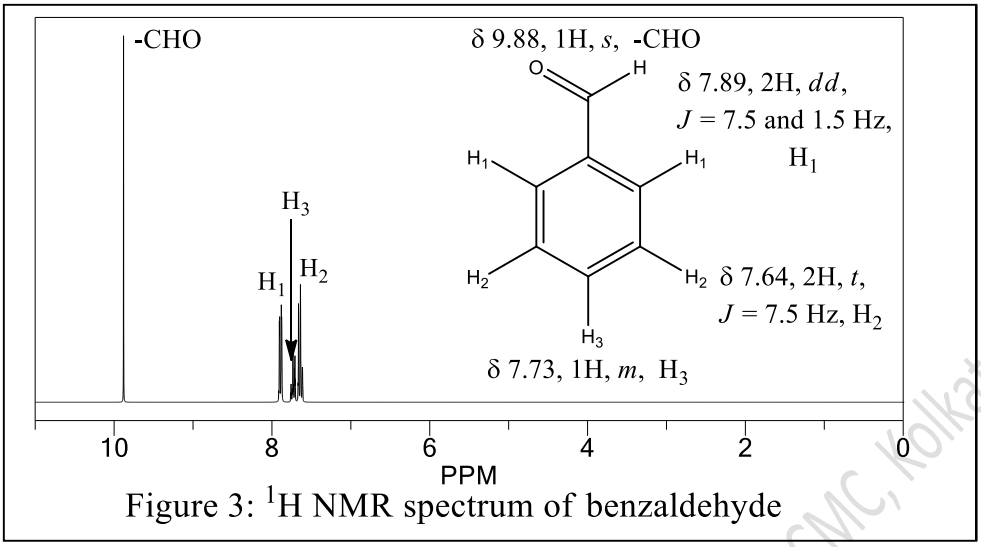


Figure 3: ^{1}H NMR spectrum of benzaldehyde

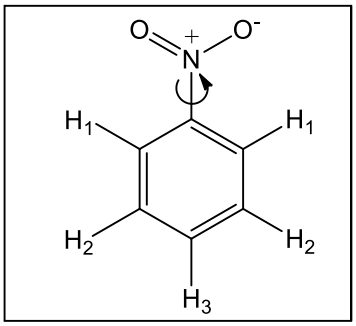
The aldehydic (-CHO) proton appears as a *singlet* (*s*) because it has no coupling partner. The proton, H_1, couples with the proton, H_2, (*ortho* coupling) and proton, H_3, (*meta* coupling). Therefore, it appears as a *doublet of doublets* (*dd*) with *J* values 7.5 Hz and 1.5 Hz. If weak *meta* coupling were ignored, H_1 proton would appear as a *doublet* (*d*).

The proton, H_2, interacts with proton, H_1, (*ortho* coupling) and proton, H_3, (*ortho* coupling). Therefore, it appears as a *triplet* (*t*) with J = 7.5 Hz. The proton, H_3, couples with two H_2 protons (*ortho* coupling) and two H_1 protons (*meta* coupling). Therefore, it appears as a *multiplet* (*m*). If weak *meta* coupling were ignored, H_3 proton would appear as a *triplet* with J = 7.5 Hz.

^{1}H NMR Spectral Analysis of Nitrobenzene

Nitro group (-NO_2) is a strongly electron withdrawing group, so in nitrobenzene electron density at *ortho*, *meta*, and *para* positions with respect to –NO_2 group will be different. Thus, benzenoid protons H_1 (2H), H_2 (2H) and H_3(1H) all are chemically nonequivalent, i.e., has different chemical shift values. Consequently, three signals appear in the ^{1}H NMR spectrum of the compound.

Since –NO_2 group is a strong electron withdrawing group, so all the benzenoid protons will be deshielded compared to benzene itself. The *ortho* (H_1) protons are mostly deshielded by the diamagnetic anisotropic deshielding effect of the benzene ring as well as that of –N=O bond. –I effect of –NO_2 group is also responsible for the deshielding.



Consequently, all the benzenoid protons (H_1, H_2, and H_3) appear at higher δ values than 7.27 (δ_H for benzene), but the extent of deshielding will be different: $\delta_{H1} > \delta_{H3} > \delta_{H2}$.

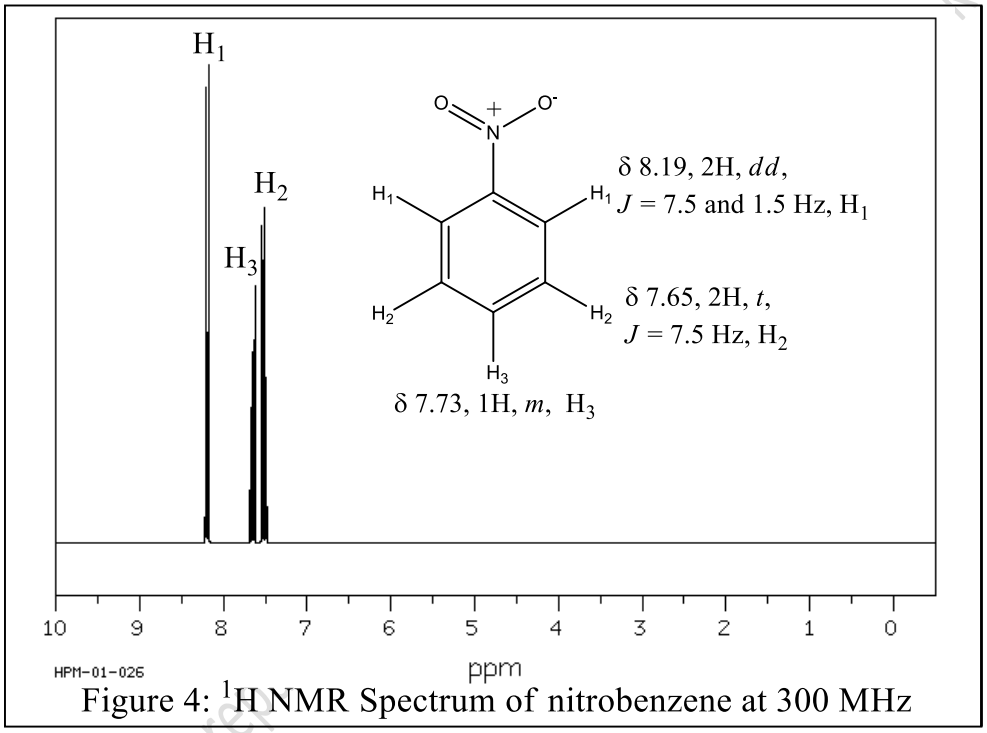


Figure 4: ^{1}H NMR Spectrum of nitrobenzene at 300 MHz

^{1}H NMR Spectral Analysis of nitrobenzene

In nitrobenzene, the proton, H_1, couples with the proton, H_2, (*ortho* coupling) and proton, H_3, (*meta* coupling). Therefore, it appears as a *doublet of doublets* (*dd*) with *J* values 7.5 Hz and 1.5 Hz. If weak *meta* coupling were ignored, H_1 proton would appear as a *doublet* (*d*). The proton, H_2, interacts with proton, H_1, (*ortho* coupling) and proton, H_3, (*ortho* coupling). Therefore, it appears as a *triplet* (*t*) with J = 7.5 Hz.

The proton, H_3, couples with two H_2 protons (*ortho* coupling) and two H_1 protons (*meta* coupling). Therefore, it appears as a *multiplet* (*m*). If weak *meta* coupling were ignored, H_3 proton would appear as a *triplet* with J = 7.5 Hz.

^{1}H NMR Spectral Assignment of 4-Nitroaniline

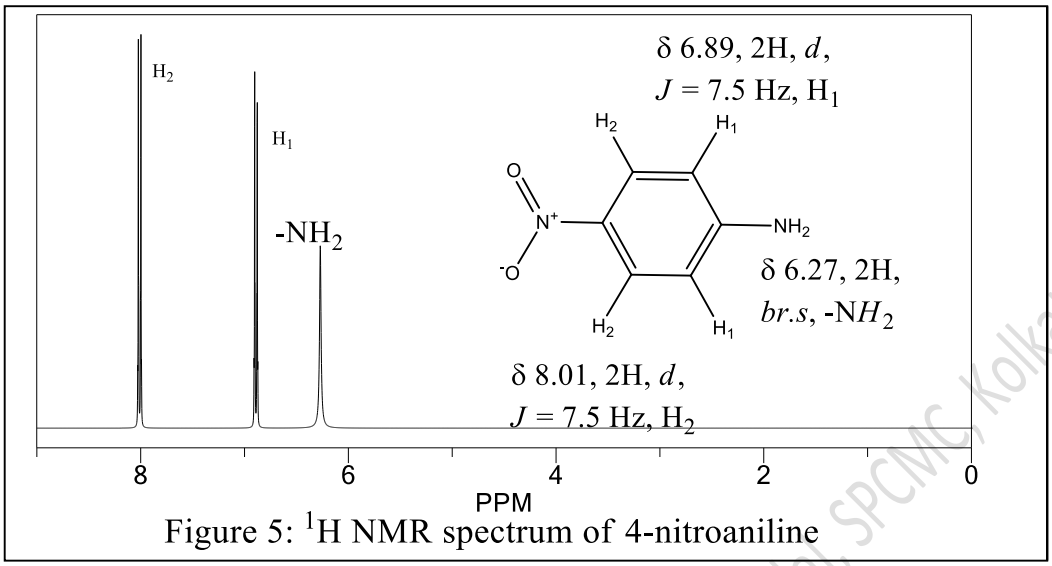


Figure 5: ^{1}H NMR spectrum of 4-nitroaniline

^{1}H NMR Spectral Assignment of 3-Nitrobenzaldehyde

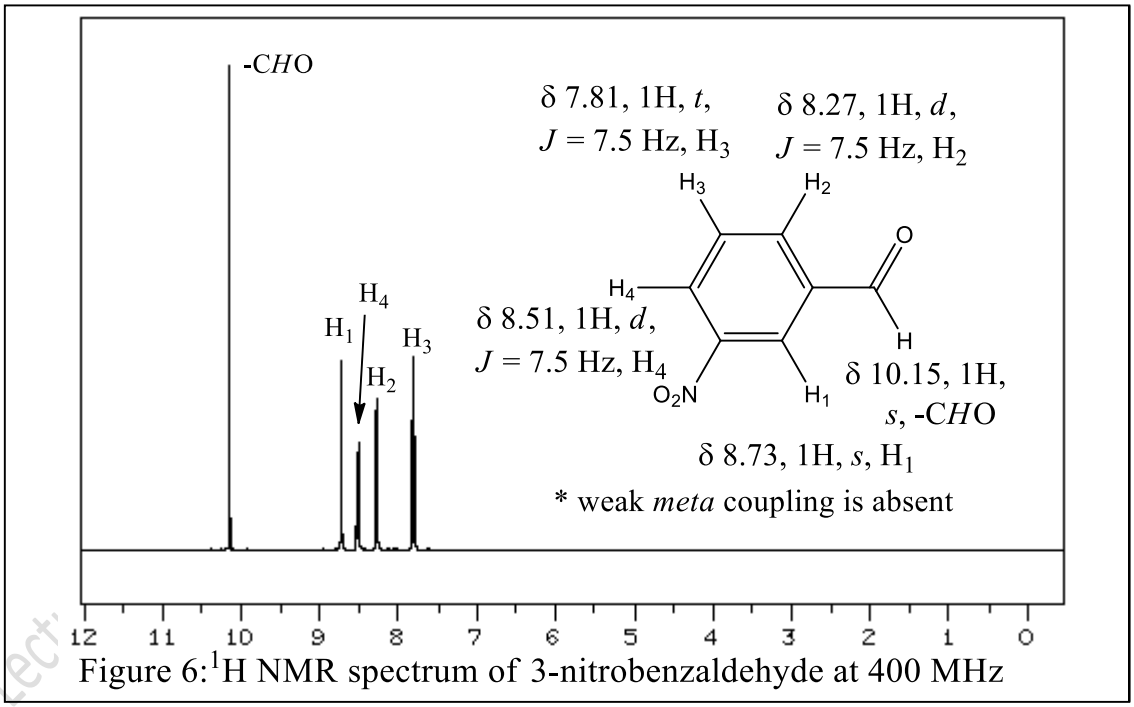


Figure 6:^{1}H NMR spectrum of 3-nitrobenzaldehyde at 400 MHz

^{1}H NMR Spectral Assignment of 4-Methoxyacetophenone

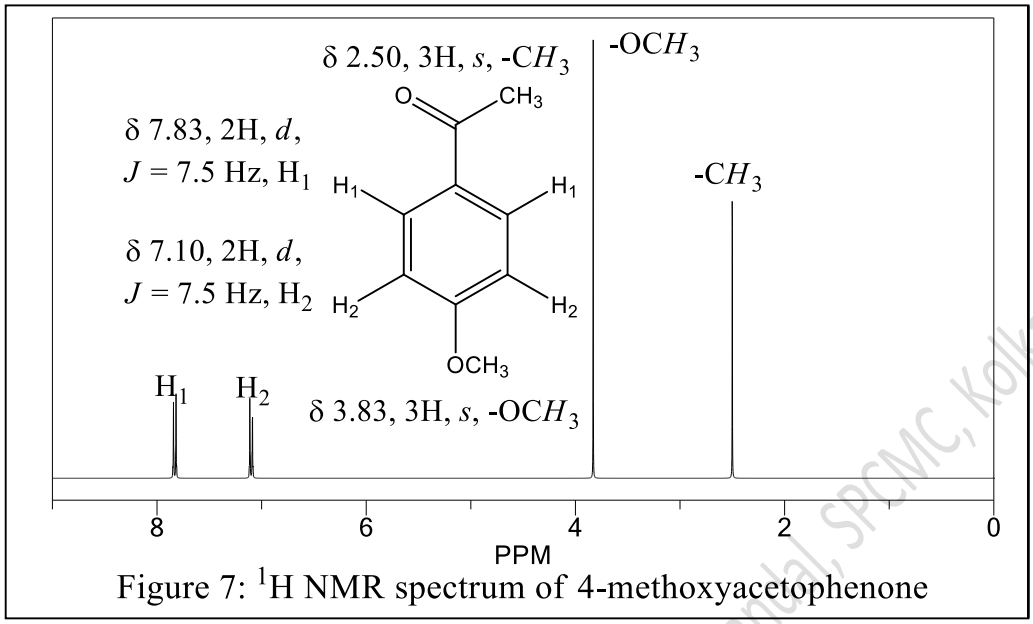
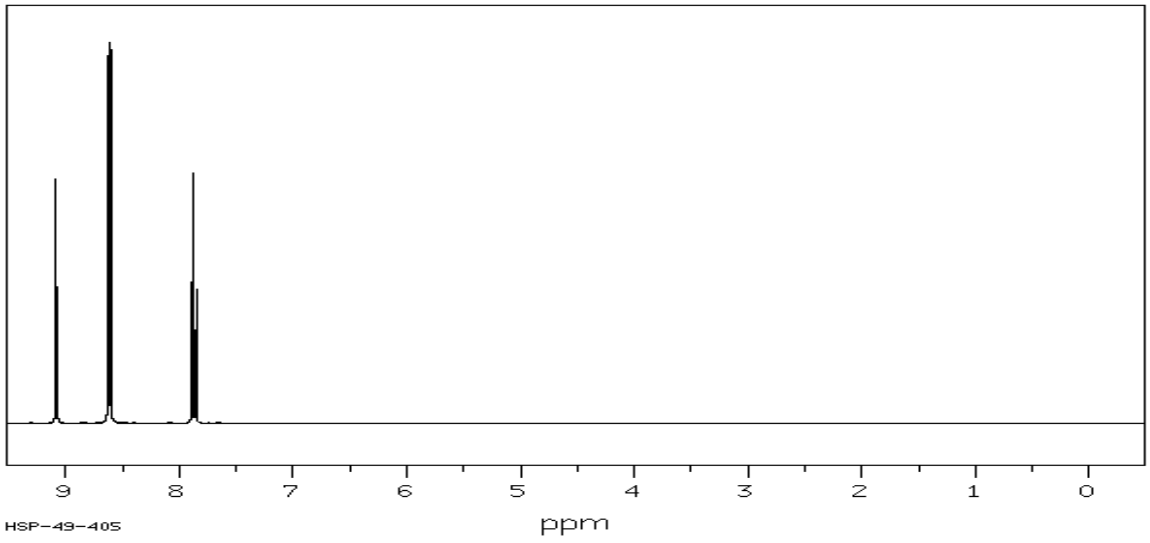


Figure 7: ^{1}H NMR spectrum of 4-methoxyacetophenone

Unknown Compound 1

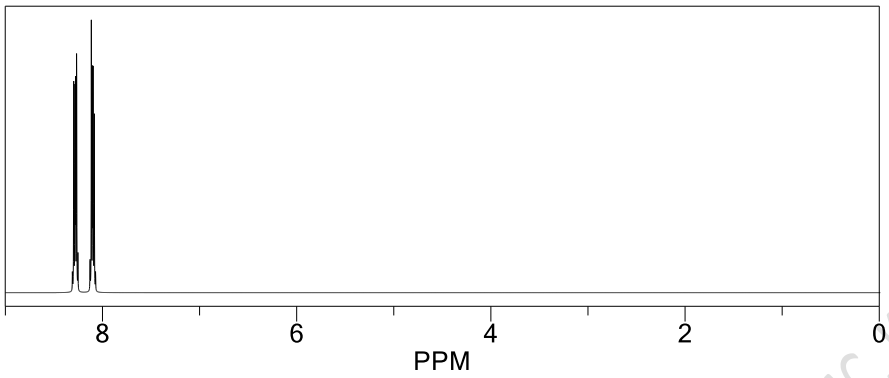
- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An aromatic disubstituted compound
- M. F.: $C_6H_4O_4N_2$
- ^{1}H NMR signals: δ 9.08, 8.62, and 7.87



Unknown Compound 2

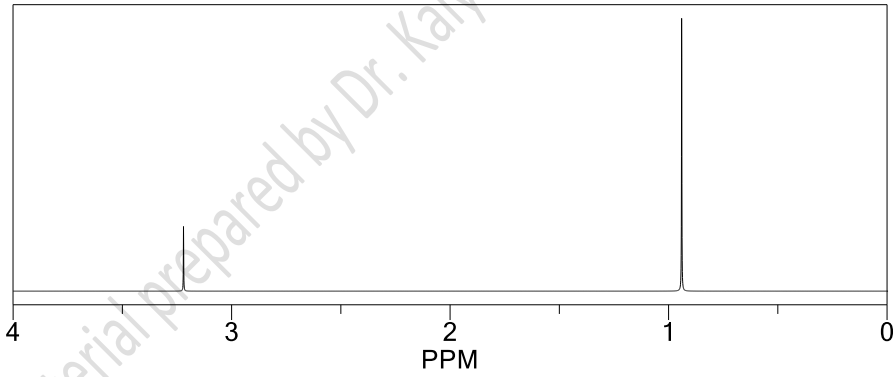
- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals: An aromatic disubstituted compound

- M. F.: $C_6H_4O_4N_2$
- ^{1}H NMR signals: δ 8.28, and 8.10



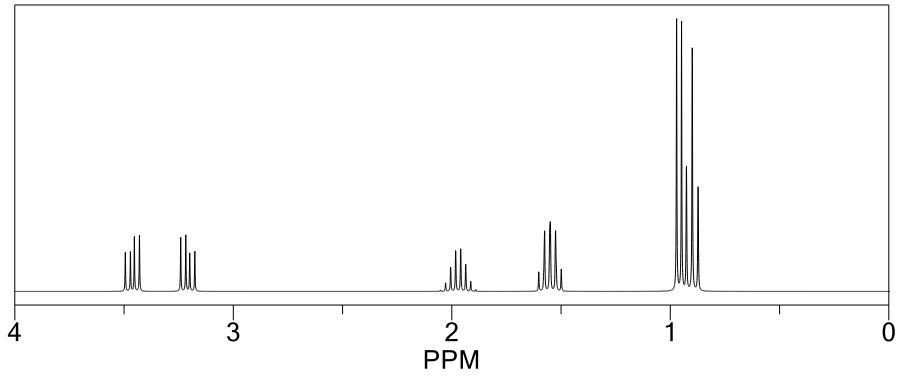
Unknown Compound 3

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_5H_{11}Cl$
- ^{1}H NMR signals: δ 3.30, and 0.94



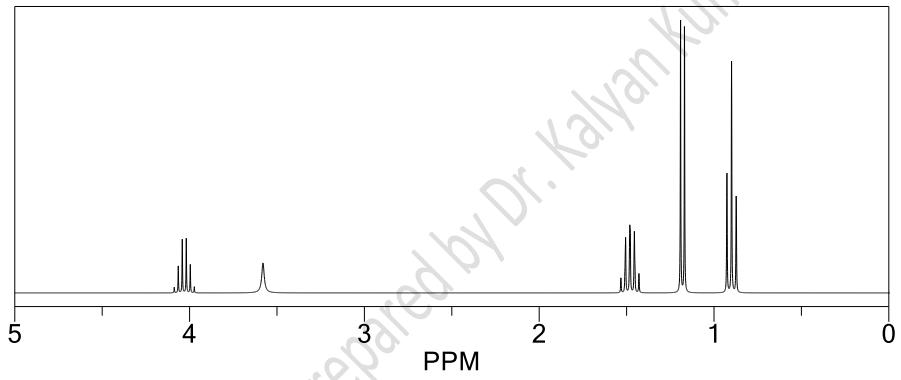
Unknown Compound 4

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_5H_{11}Cl$
- ^{1}H NMR signals: δ 3.46, 3.21, 1.97, 1.55, 0.96, and 0.90



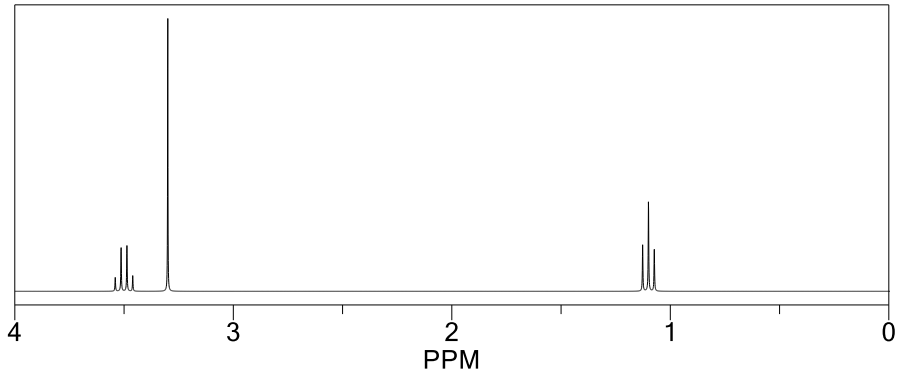
Unknown Compound 5

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_4H_{10}O$
- ^{1}H NMR signals: δ 4.03, 3.58, 1.48, 1.18, and 0.90



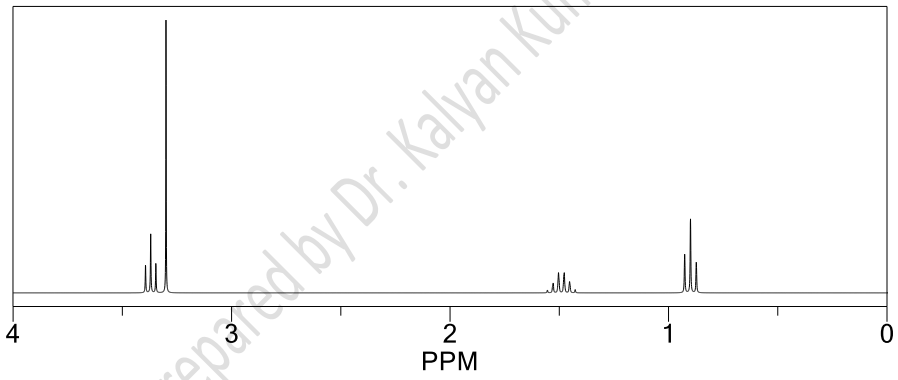
Unknown Compound 6

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: C_3H_8O
- ^{1}H NMR signals: δ 3.50, 3.30, and 1.10



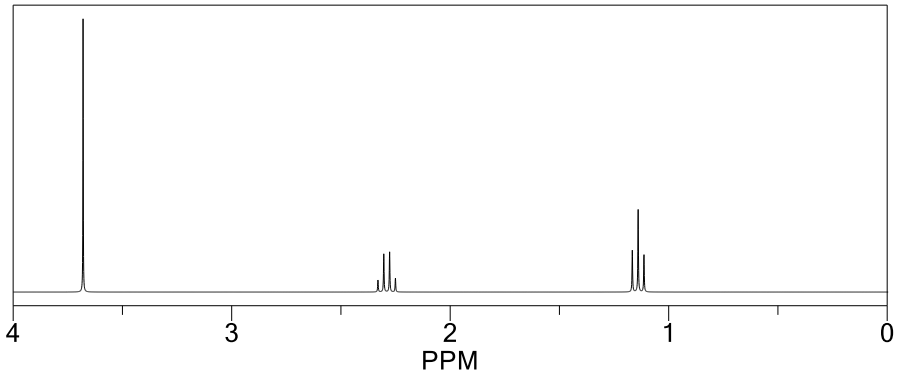
Unknown Compound 7

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acrylic compound
- M. F.: $C_4H_{10}O$
- ^{1}H NMR signals: δ 3.37, 3.30, 1.49, and 0.90



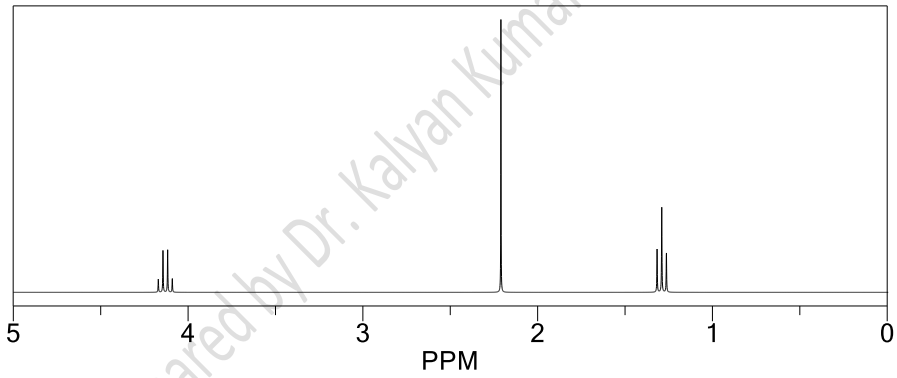
Unknown Compound 8

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_4H_8O_2$
- ^{1}H NMR signals: δ 3.68, 2.29, and 1.14



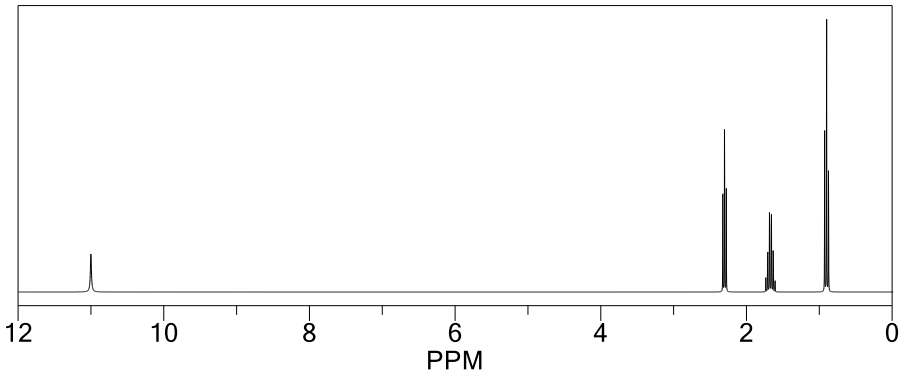
Unknown Compound 9

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_4H_8O_2$
- ^{1}H NMR signals: δ 4.13, 2.21, and 1.29



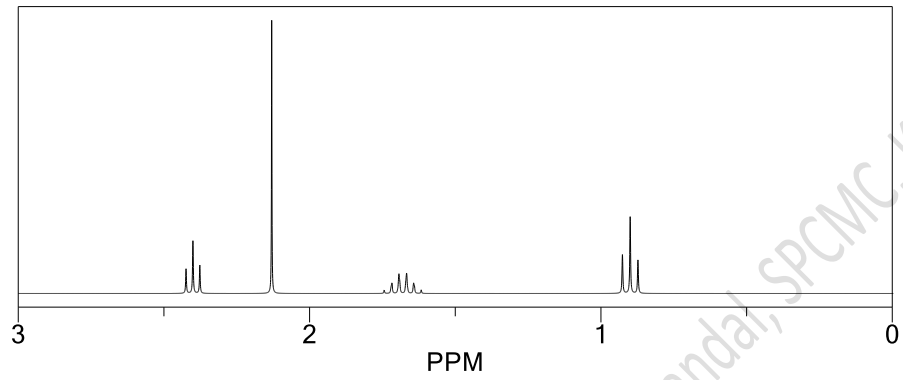
Unknown Compound 10

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_4H_8O_2$
- ^{1}H NMR signals: δ 11.0, 2.30, 1.67, and 0.90



Unknown Compound 11

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_5H_{10}O$
- ^{1}H NMR signals: δ 2.40, 2.13, 1.68, and 0.90



Unknown Compound 12

- Identify the following compound from the given spectral data/information and assign the ^{1}H NMR signals:
- An acyclic compound
- M. F.: $C_5H_{10}O$
- ^{1}H NMR signals: δ 9.72, 2.40, 1.58, 1.31, and 0.90