1. Sketch the $^1H$ NMR spectrum of the vinyl protons appearing around.

![Chemical structure with NMR spectrum]

$J_{ab} = 3\text{ Hz}$

$J_{bc} = 10\text{ Hz}$

$J_{ac} = 16\text{ Hz}$

2. Which of the structures has the $^{13}C$ NMR spectrum shown? Assign the carbons.

![Chemical structures with NMR spectrum]

3. The $^1H$ NMR signals for the aromatic hydrogens of methyl $p$-hydroxybenzoate appear as doublets at approximately 7.05 and 8.04 $\delta$. Assign these two doublets to the respective hydrogens that produce each signal. Justify your assignments using arguments of relative electron density based on contributing resonance structures.

![Chemical structures with NMR spectrum and additional structures]
4. The three isomers of dimethylbenzene are commonly named ortho-xylene, meta-xylene and para-xylene.

(a) Describe how carbon NMR distinguishes these isomers.

- **O-xylene** has 4 distinct resonances in $^{13}$C NMR
- **m-xylene** has 5 distinct resonances in $^{13}$C NMR
- **p-xylene** has 3 distinct resonances in $^{13}$C NMR

(b) Explain why they are difficult to distinguish by proton NMR.

- The 'H NMR of the three isomers are too similar to distinguish them by 'H NMR alone.
- The J of the aromatic and methyl protons are too similar (aromatic resonances may also overlap)

5. Analyze, assign and explain the spectra of the methoxynitrobenzenes using their chemical shifts and splittings. The spectra are on the next page.
6. An unknown compound has the following molecular formula, C₉H₇Br. It's ^1H NMR shows the following absorptions.

\[
\text{Integrals: } S^{7.1} = \frac{44}{44 + 130 + 67} = \approx 0.18 \times 10 = 1.8 \approx 2
\]

singlet, δ7.1, integral 44 mm

\[
S^{2.2} = \frac{130}{44 + 130 + 67} = \approx 0.54 \times 10 = 5.4 \approx 6
\]

singlet, δ2.2, integral 130 mm

\[
S^{2.3} = \frac{67}{44 + 130 + 67} = \approx 0.28 \times 10 = 2.8 \approx 3
\]

Propose a structure for this compound.

- The molecule is likely symmetrical
- 1HD = 4 \rightarrow most likely a benzene ring
- Singlets suggest isolated protons with no short-range coupling

![Chemical structure](attachment:Chemical%20Structure.png)

\[
S^{7.1} = H_a, 2H \\
S^{2.2} = H_b, 6H \\
S^{2.3} = H_c, 3H
\]
Isomeric Methoxynitrobenzenes

Problem R-19B (C₇H₇NO₂)
300 MHz ¹H NMR spectrum in CDCl₃
Source: Aldrich Spectra Viewer/Reich

1. Hα
   2. Hβ, Hδ
   3. Hα

2. Hα
   1. Hβ, Hδ
   3. Hα

3. Hα
   2. Hβ