11.27 The following $^1$H NMR absorptions were obtained on a spectrometer operating at 200 MHz and are given in hertz downfield from the TMS standard. Convert the absorptions to δ units
(a) 436 Hz (b) 956 Hz (c) 1504 Hz

The equation to use is: ppm = shift in Hz/ strength of the NMR in MHz
(a) 436 Hz/ 200 MHz = 2.18 ppm
(b) 956 Hz/ 200 MHz = 4.78 ppm
(c) 1504 Hz/ 200 MHz = 7.52 ppm

11.29 When measured on a spectrometer operating at 200 MHz, chloroform (CHCl3) shows a single sharp absorption at 7.3 δ.

(a) How many parts per million downfield from TMS does chloroform absorb?
7.3 ppm. δ is the symbol used to represent ppm.

(b) How many hertz down from TMS would chloroform absorb if the measurement were carried out on a spectrometer operating at 360 MHz?
Using the same equation, ppm = shift in Hz/ strength of the NMR in MHz
7.3 ppm = x Hz/ 360 MHz = 2628 Hz.

(c) What would be the position of the chloroform absorption in δ units when measured on a 360 MHz spectrometer?
7.3 δ. That doesn’t change with changes in the magnetic strength.

11.30 How many signals would you expect each of the following molecules to have in its $^1$H and $^{13}$C NMR spectra?

![Chemical structures](attachment:image.png)

11.31 How many absorptions would you expect to observe in the $^{13}$C NMR spectra of the following compounds?
(a) 1,1-dimethylcyclohexane
(b) CH3CH2OCH3
(c) tert-Butylcyclohexane
(d) 3-Methylpent-1-yne
(e) trans-1,2-Dimethylcyclohexane
(f) Cyclohexanone

The first step here is to draw the structures, and then you can count how many unique carbon atoms there are:

11.33 Is a nucleus that absorbs at 6.50 $\delta$ more shielded or less shielded than a nucleus that absorbs at 3.20 $\delta$? Does the nucleus that absorbs at 6.50 $\delta$ require a stronger applied field or a weaker applied field to come into resonance than the nucleus that absorbs at 3.20 $\delta$?

The nucleus at 6.50 $\delta$ is less shielded, and therefore requires a weaker applied field to come into resonance.

11.44 Identify the indicated sets of protons as unrelated, homotopic, enantiotopic, or diastereotopic

a. Homotopic – regardless of which one you replaced with an X, the resulting product would be identical.

b. These are enantiotopic. There is a prochiral center in the molecule – a carbon atom that is not chiral right now, but will become chiral if one of the hydrogens were replaced with an X group.

c. These protons are diastereotopic. Two different diastereomers would result if you replaced the protons.

11.35 How many types of nonequivalent protons are present in each of the following molecules?
11.37 The following compounds all show a single line in their \(^1\)H NMR spectra. List them in expected order of increasing chemical shift.

\(\text{CH}_4, \text{CH}_2\text{Cl}_2, \text{cyclohexane}, \text{CH}_3\text{COCH}_3, \text{H}_2\text{C=CH}_2, \text{benzene}\)

It never hurts to draw these molecules to make sure you understand their structures.

In general, saturated sp3-carbons shield more than unsaturated compounds, and electronegative atoms deshield. With these basic guidelines in mind, we can arrive at the following order, listed from lowest chemical shift to highest chemical shift:

\(\text{CH}_4, \text{cyclohexane}, \text{CH}_3\text{COCH}_3, \text{CH}_2\text{Cl}_2, \text{H}_2\text{C=CH}_2, \text{benzene}\)

11.40 How could you use \(^1\)H NMR to distinguish between the following pairs of compounds?

a. The first compound has a double bond, so the proton directly attached to that double bond (called a vinylic proton) will have a characteristic signal at approximately 5-6 ppm. Protons attached to a cyclopropane ring have a much lower ppm value because they are shielded by the surrounding electron-rich environment.

b. The first compound is highly symmetrical, so you will see signals for only two distinct proton environments. The second compound has four different proton environments, including a singlet from the methoxy group.
c. The ester group in the first compound will make the neighboring protons less shielded than they will be just from the ketone group in the second compound.

d. These compounds only really differ in the placement of the methyl group – whether it is on the carbon directly attached to the ketone, or the terminal carbon. The methyl group will be less shielded in the first compound compared to in the second compound due to its proximity to the ketone.

11.45 How could you use $^1$H NMR, $^{13}$C NMR, IR, and UV spectroscopy to help you distinguish between the following structures?

![Structures](image)

$^1$H NMR spectroscopy: The second compound has an isolated methyl group which will give a singlet in the $^1$H NMR spectrum. The second compound also has an isolated methyl group which will give a singlet, however it is likely to be more shielded than the singlet of the second compound (because it is further away from the electron-withdrawing carbonyl group).

$^{13}$C NMR spectroscopy: The alkene carbons which are part of an unsaturated ketone system are going to have a different chemical shift compared to alkene carbons that are not part of the unsaturated ketone system.

UV-Vis: The first compound is an unsaturated ketone, and will absorb light in the ultraviolet region. The second compound has an isolated double bond and a saturated ketone, neither of which are likely to absorb ultraviolet light.

IR spectroscopy: Unsaturated ketones have a different characteristic carbonyl stretch compared to saturated ketones.

11.46 The compound whose $^1$H NMR spectrum is shown has the molecular formula C$_3$H$_8$Br$_2$. Propose a structure.

The $^1$H NMR shows two different proton signals, with an intensity of 2.00 protons at 3.56 ppm and 1.00 proton at 2.33 ppm. This means that there are two different types of protons in the compound. Because there are 6 total protons, there must be 4 of one kind of proton and 2 of another kind of proton. Also, the signal at 3.56 ppm is split into a triplet, which means that it is next to a carbon with two protons attached, and the signal at 2.33 ppm is split into a quintet, which means that is next to a carbon (or carbons) with four other protons attached. All of this information fits the structure shown below:

![Signal Diagram](image)

11.50 Propose structures for the two compounds whose $^1$H NMR spectra are shown.

(a) C$_4$H$_9$Br
Three different signals: the signal at 3.31 ppm corresponds to 2 protons and is split into a doublet, the signal at 1.97 ppm corresponds to 1 proton and is split into 9 different signals, and the signal at 1.05 ppm corresponds to six protons and is split into a doublet.

(b) $\text{C}_4\text{H}_8\text{Cl}_2$

Four different signals: the signal at 4.25 ppm is a multiplet corresponding to 1 proton, signal at 3.72 ppm is another multiplet corresponding to two protons, signal at 2.13 ppm corresponding to 2 protons which is a quartet, and the signal at 1.56 ppm which corresponds to 3 protons and is a doublet.

11.52 Assign as many of the resonances as you can to specific carbon atoms in the $^{13}\text{C}$ NMR spectrum of ethyl benzoate.

The easiest peak to assign is the carbonyl peak around 168 ppm. There are four peaks in the aromatic region (between 120 ppm and 140 ppm), which corresponds to the four chemically distinct carbon signals in the aromatic ring of the molecule. The peak at 60 ppm corresponds to the saturated carbon closest to the ester, and the peak around 15 ppm corresponds to the terminal methyl group.

11.53 The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound A, $\text{C}_9\text{H}_9\text{Br}$, are shown. Propose a structure for A, and assign peaks in the spectra to your structure.

You definitely have an aromatic ring in this compound, with two distinct sets of signals, each of which is a doublet corresponding to 2 protons. This pattern means that the aromatic ring is para-substituted. The quartet at 2.58 ppm corresponding to two protons, and the triplet at 1.20 corresponding to 3 protons, means that you have an ethyl group in the molecule as well. The structure based on the $^1\text{H}$ NMR spectrum alone is shown below:
This structure is further confirmed by the $^{13}$C NMR spectrum, which shows four aromatic signals (two strong ones, which have protons attached to them), and two weak ones that do not have attached protons. There are also two signals in the aliphatic region of the $^{13}$C NMR spectrum corresponding to the ethyl group.

11.57 Propose a structure for compound C, which has $M^+$ = 86 in its mass spectrum, an IR absorption at 3400 cm$^{-1}$, and the following $^{13}$C NMR spectral data:

Broadband-decoupled $^{13}$C NMR: 30.2, 31.9, 61.8, 114.7, 138.4 δ

DEPT-90: 138.4 δ

DEPT-135: positive peak at 138.4 δ; negative peaks at 30.2, 31.9, 61.8, 114.7 δ

We can figure out what environments each of the $^{13}$C NMR signals are in, using the following information: In a DEPT-90 spectrum, only signals due to CH appear, and in a DEPT-135 spectrum, CH$_3$ and CH show positive signals, CH$_2$ shows negative signals, and carbons with no hydrogens do not appear. Combining all this data gives us the following information

30.2 ppm: CH$_2$; 31.9 ppm: CH$_2$; 61.8 ppm: CH$_2$; 114.7 ppm: CH$_2$; 138.4 ppm: CH

IR absorption at 3400 cm$^{-1}$ also indicates that an alcohol is likely. Because this compound has no CH$_3$ signals, I am going to assume that it has a ring structure (otherwise the straight carbon chain would have to terminate in a CH$_3$ group), and draw a cyclic hydrocarbon that meets these basic requirements:

This compound has 4 CH$_2$ groups, one CH group, an alcohol group, and a mass of 86 g/mol.

11.63 Carboxylic acids (RCO$_2$H) react with alcohols in the presence of an acid catalyst. The reaction product of propanoic acid with methanol has the following spectroscopic properties. Propose a structure.

MS: $M^+$ = 88

IR: 1735 cm$^{-1}$

$^1$H NMR: 1.11 δ (3 H, triplet, $J$ = 7 Hz); 2.32 δ (2 H, quartet, $J$ = 7 Hz); 3.65 δ (3 H, singlet)

$^{13}$C NMR: 9.3, 27.6, 51.4, 174.6 δ

The compound structure is shown below. I will go through how the spectral data confirm this.

Mass spectrometry: Molecular weight is 88.1 g/mol
IR spectroscopy: Molecule has an ester group with a strong carbonyl stretch at 1735 cm\(^{-1}\).

\(^1\)H NMR spectroscopy:

- Signal at 2.32 ppm; split into quartet by the 3 green protons
- Signal at 1.11 ppm; split into triplet by the blue protons

\(^13\)C NMR spectroscopy:

- Signal at 27.6 ppm; somewhat deshielded by proximity to carbonyl, less so than the red carbon
- Most shielded carbon signal at 9.3 ppm
- Signal at 51.4 ppm - deshielded due to ester proximity
- Signal at 174.6 ppm; characteristic range for carbonyls