

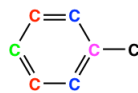
6.8: ^{13}C NMR Spectroscopy

For carbon element, the most abundant isotope ^{12}C (with ~99% natural abundance) does not have a nuclear magnetic moment, and thus is NMR-inactive. The C NMR is therefore based on the ^{13}C isotope, that accounts for about 1% of carbon atoms in nature and has a magnetic dipole moment just like a proton. The theories we have learned about ^1H NMR spectroscopy also applies to ^{13}C NMR, however with several important differences about the spectrum.

The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton, meaning that ^{13}C NMR signals are inherently much weaker than proton signals. This, combined with the low natural abundance of ^{13}C , means that it is much more difficult to observe carbon signals. Usually, sample with high concentration and large number of scans (thousands or more) are required in order to bring the signal-to-noise ratio down to acceptable levels for ^{13}C NMR spectra.

Chemical Equivalent

For carbons that are chemical equivalent, they only show one signal in ^{13}C NMR as like protons for ^1H NMR. So it is very important to be able to identify equivalent carbons in the structure, in order to interpret ^{13}C NMR spectrum correctly. Taking toluene as an example, there are five sets of different carbon atoms (shown in different colors), so there are five signals in the ^{13}C NMR spectrum of toluene.



toluene molecule has 5 different sets of carbon atoms
(hydrogen atoms are omitted)

Chemical Shift

^{13}C nuclei has different value of g (the magnetogyric ratio) comparing to ^1H nuclei, so the resonance frequencies of ^{13}C nuclei is different to those of protons in the same applied field (referring to **formula. 6.4**, in section 6.5). In an instrument with a 7.05 Tesla magnet, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^1H NMR, tetramethylsilane (TMS) is also used as the standard compound in ^{13}C NMR experiments to define the 0 ppm, however it is the signal from the four equivalent **carbon** atoms in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range of about 220 ppm (see **Table 6.3**).

Type of Carbon	Chemical Shift (ppm)	Type of Carbon	Chemical Shift (ppm)
$\text{R}-\text{CH}_3$	0 – 35	$\text{R}-\text{C}=\text{C}-\text{R}$	80 – 150
$\text{R}-\text{CH}_2$	15 – 55	C_6H_5	110 – 170
$\text{R}-\text{CH}$	25 – 55	$\text{R}-\text{C}(=\text{O})\text{OR}$	165 – 175
$\text{R}-\text{C}-\text{R}$	30 – 40	$\text{R}-\text{C}(=\text{O})\text{OH}$	175 – 185
$\text{C}-\text{X}$ (X: Cl, Br or N)	10 – 65	$\text{R}-\text{C}(=\text{O})\text{H}$	190 – 200
$\text{C}-\text{O}-\text{C}$	50 – 90	$\text{R}-\text{C}(=\text{O})\text{R}$	200 – 220
$\text{R}-\text{C}\equiv\text{C}$	70 – 90		

Table 6.3 Approximate ^{13}C NMR chemical shifts of some common groups

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The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence the chemical shift a proton: the deshielding effect of electronegative atoms and anisotropy effects tend to shift signals downfield (higher resonance frequency, with

higher chemical shifts). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen.

Integration and Coupling in ^{13}C NMR

Unlike ^1H NMR, the area under a ^{13}C NMR signal **cannot** easily be used to determine the number of carbons to which it corresponds. The signals for some types of carbons are inherently weaker than for other types, for example peaks corresponding to carbonyl carbons are much smaller than those for methyl or methylene (CH_2) peaks. For this reason, signal integration is generally not useful in ^{13}C NMR spectroscopy.

Because of the low natural abundance of ^{13}C nuclei, the spin-spin coupling between two nonequivalent ^{13}C atoms is negligible. ^{13}C nuclei are coupled to nearby protons, however, which results in complicated spectra. For clarity, chemists generally use a technique called **broadband decoupling**, which essentially ‘turns off’ C-H coupling, resulting in a spectrum in which **all carbon signals are singlets**. Below is the proton-decoupled ^{13}C NMR spectrum of ethyl acetate in CDCl_3 (**Fig. 6.8a**), showing the expected four signals, one for each of the carbons.

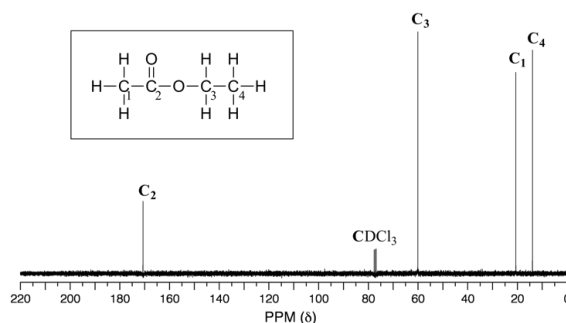
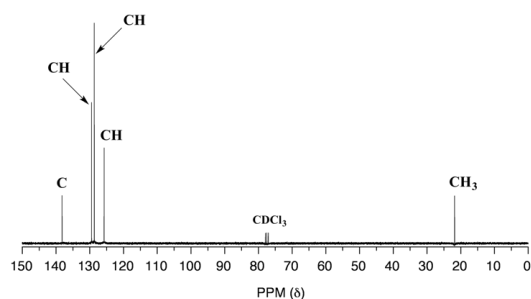
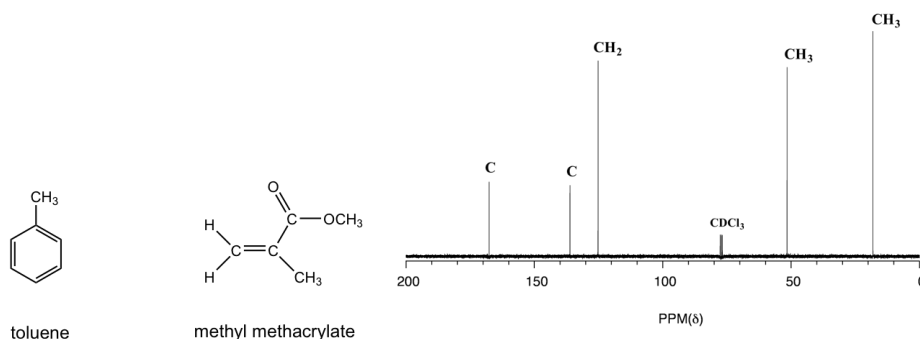


Figure 6.8a The ^{13}C NMR spectrum of ethyl acetate

For our class purpose, ^{13}C NMR spectra are usually used as supporting information to confirm the structure of a compound.

Exercises 6.2

Below are ^{13}C NMR spectra for methylbenzene (common name toluene) and methyl methacrylate. Refer to **Table 6.3** to match the spectra to the correct structure.



Answers to Practice Questions Chapter 6

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