

Spring semester 2011, CHE 233, ^{13}C NMR spectroscopy

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^{13}C NMR Spectra

The common isotope of carbon is ^{12}C , which has a nuclear spin number of zero, so it cannot be examined by NMR techniques.

However, about 1.1% of carbon atoms in nature consist of the isotope, ^{13}C , which is magnetically active. ^{13}C has a nuclear spin quantum number of 1/2, so, like the ^1H nucleus, it can assume two spin states in the magnetic field of the NMR spectrometer. The ability to examine the carbon atoms in a molecule provides a much more sensitive probe of molecular structure than does ^1H NMR since carbon atoms occupy a central position in an organic molecule, while H atoms are in more peripheral locations.

Obtaining ^{13}C spectra is more difficult than ^1H spectra for two reasons:

- 1) Unlike hydrogen, where >99% of atoms in nature are the magnetically-active isotope ^1H , only ~1.1% of all in natural abundance are atoms of ^{13}C .
- 2) ^{13}C nuclei give weaker signals than ^1H nuclei, even if the ^{13}C concentration is enriched to 99% like ^1H .

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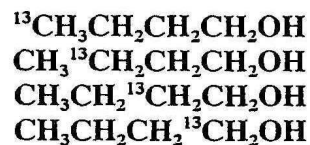
Because of these problems, scanning the ^{13}C spectrum a single time gives signals that are so weak that they cannot be distinguished for random electronic noise. To obtain a useful ^{13}C spectrum it is necessary to scan the spectrum many times (typically hundreds or thousands of times) and average the data. As more and more spectra are averaged, the actual ^{13}C signals reinforce each other, getting stronger and stronger, and random electronic noise cancels out.

In earlier days it required several minutes to acquire a single spectrum, so the time required to collect enough scans to get a useful spectrum was several hours or days, and at that time the power of a main frame computer was required to process the data. The rapid advances in computer technology have put more computer power in your pocket than the main frame of that day could provide. Obtaining a single NMR "scan" now requires only seconds using the technique of "Fourier Transform" (FT) analysis. Using FT all of the ^{13}C nuclei are excited in one blast of energy. A very complex wave is produced as the excited nuclei decay in a matter of seconds, and the computer can analyze this signal and convert the information into a conventional spectrum. One can accumulate hundreds of spectral "scans" in short order and average the data of the multiple scans to produce in a matter of minutes a spectrum that would have taken days using earlier methods.

Since the natural abundance of ^{13}C is only 1.1%, a relatively small organic molecule may contain no ^{13}C atoms or only a single ^{13}C atom, while the remaining carbons are magnetically inactive ^{12}C atoms.

However, in a sample containing billions of molecules, one will encounter a range of molecules in which every carbon atom is represented among the ^{13}C labeled population.

e.g., in an NMR sample of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ there are equal numbers of molecules of the types:



Most of the molecules contain no ^{13}C atoms at all, but the composite spectrum has signals representing all of the different types of carbons in the molecule.

Spin-Spin Coupling:

- 1) **Coupling between ^{13}C atoms:**
Since coupling is only observed between magnetically active nuclei within the same molecule, coupling between two ^{13}C atoms is not observed in the spectrum. This is because the probability of a molecule containing two ^{13}C adjacent to each other is negligible.
- 2) **Coupling between ^{13}C atoms with ^1H atoms:**
Since ^{13}C and ^1H atoms are both magnetically active, ^{13}C atoms can couple with ^1H atoms. The largest coupling is between a ^{13}C atom and hydrogen atoms that are directly attached to it. However, ^{13}C atoms also exhibit coupling with hydrogen atoms attached to neighboring carbons, and even on carbon atoms farther removed. This coupling could result in very complex multiplets that would be difficult to interpret.

In the interest of simplifying the signals, the spectrum is usually "decoupled". Decoupling involves irradiating the sample with broad-band radio frequency energy in the ^1H region at the same time the ^{13}C region is being analyzed. This has the effect of scrambling the spin states of the H atoms so they do not establish coupling interactions with ^{13}C atoms. Broad-band decoupling gives signals in the ^{13}C spectrum that are all single sharp lines (singlets).

Another type of decoupling is called "off-resonance decoupling". In off-resonance decoupling the ^1H region is irradiated with radio frequency energy sufficient to wipe out long range couplings. This produces a spectrum in which the signal for a particular ^{13}C is coupled only with the ^1H atoms that carbon. This gives multiplets, and the multiplicity of the ^{13}C signal depends upon the number of H atoms attached directly to that carbon. The multiplicity obeys the same $(n + 1)$ rule that is applied in predicting the effect of a set of "n" neighboring protons on the multiplicity of a signal in the ^1H NMR spectrum.

$-\text{CH}_3$ gives a quartet $(3 + 1) = 4$

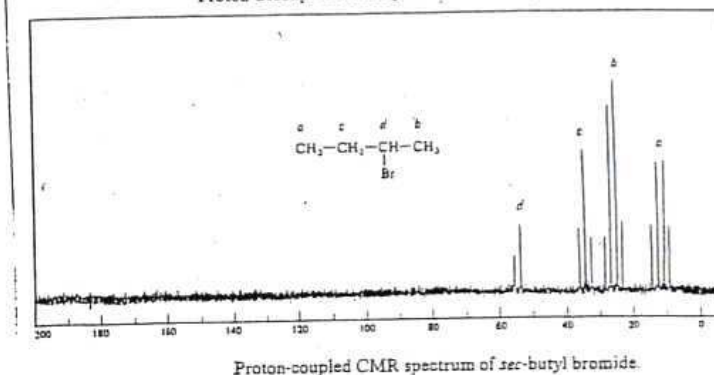
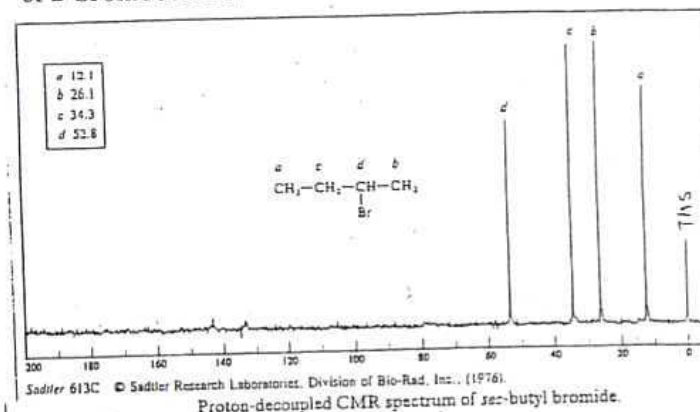
$-\text{CH}_2-$ gives a triplet $(2 + 1) = 3$

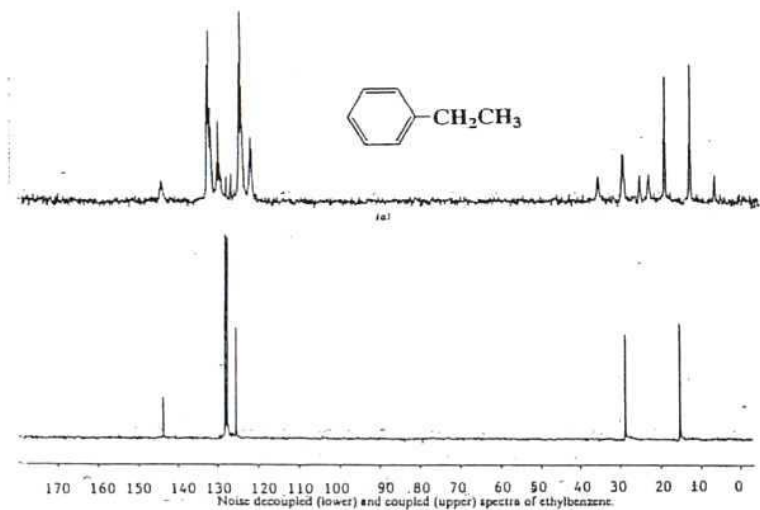
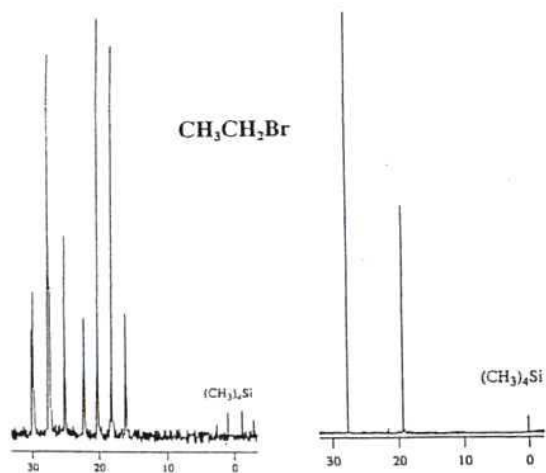
$\begin{array}{c} \text{H} \\ | \\ -\text{C}- \\ | \end{array}$ gives a doublet $(1 + 1) = 2$

$\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$ gives a singlet $(1 + 0) = 1$

The off-resonance decoupled spectrum is sometimes called the "proton-coupled" spectrum.

The spectra below are the proton-decoupled spectrum and proton-coupled (off-resonance decoupled) spectrum of 2-bromobutane.





Peak areas of signals in ¹³C NMR spectra:

In ¹H NMR spectra the peak areas are directly related to the numbers of H atoms represented by the signals. "Integration" of the ¹H spectrum could be used to determine relative numbers of H atoms represented by each signal.

In ¹³C NMR spectra other factors besides number of ¹³C affect peak areas. As a result, it is not possible to determine relative numbers of ¹³C atoms represented by the signals by measuring relative peak areas.

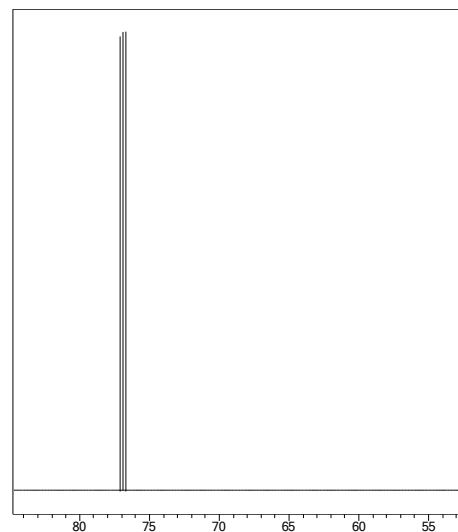
An important factor related to the signal area of a ¹³C signal is its "relaxation time", which is the time it takes for an excited ¹³C atom to decay back to the lower energy spin state. The strongest signals are exhibited by ¹³C atoms with short relaxation times, while atoms with longer relaxation times give weaker signals.

The relaxation time of a ¹³C nucleus is affected by the number of H atoms attached to that carbon. During decoupling the irradiation of H atoms causes them to interact with the ¹³C atoms to which they are connected that results in an increase in the signal size for that ¹³C atom. The phenomenon is known as the "nuclear Overhauser effect" (nOe or NOE).

¹³C atoms which have no H atoms connected to them give particularly weak signals in the ¹³C NMR spectrum, making them relatively easy to assign.

Deuterium coupling to ^{13}C :

The solvent most commonly used in CMR spectroscopy is CDCl_3 , deuteriochloroform. The carbon in deuteriochloroform contains ^{13}C in its usual natural abundance, so it produces a signal in the CMR spectrum. The signal for the ^{13}C atom in deuteriochloroform has a chemical shift of 77 ppm and is split into a multiplet by coupling with the deuterium atom. The deuterium nucleus has a spin quantum number of $3/2$ and splits the ^{13}C signal of CDCl_3 into three lines of equal size. This signal is often used as the reference signal for ^{13}C spectra when CDCl_3 is the solvent.

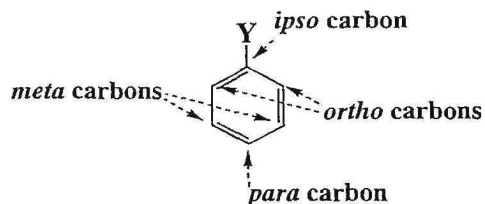


Chemical shifts in ^{13}C NMR:

One advantage of ^{13}C NMR compared with ^1H NMR is that the ^{13}C atoms are much more sensitive to differences in their molecular environments than are ^1H atoms. As a result the range of chemical shifts is much broader for CMR signals than for PMR signals. A consequence of this is that overlap of signals for ^{13}C atoms which are chemically non-equivalent is relatively uncommon, while overlapping of signals for chemically non-equivalent H atoms in the PMR spectrum is quite common.

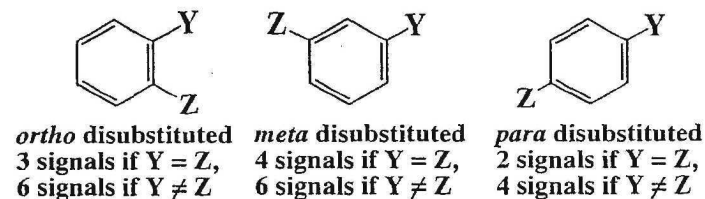
In benzene C_6H_6 , the chemical shift of ^{13}C is 128.5 ppm and is a single sharp peak, since all six of the carbon atoms are equivalent.

Attaching a single substituent to the benzene ring in place of one of the hydrogen atoms results in a situation where the six carbon atoms of the ring fall into 4 categories in terms of their chemical non-equivalency.

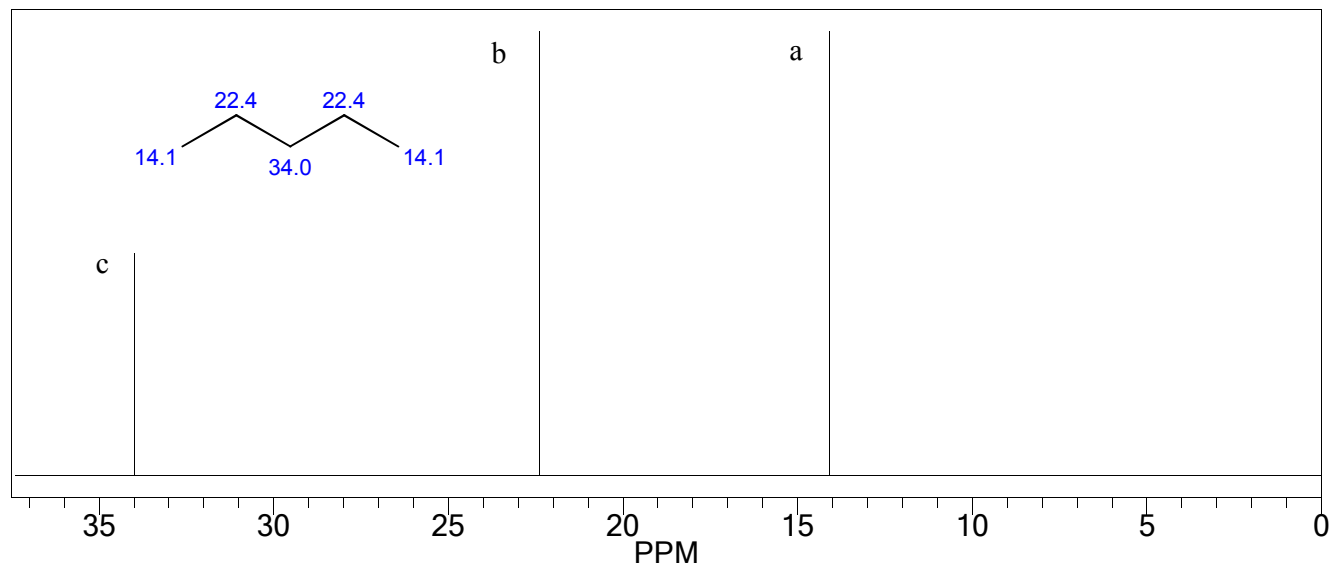


The aromatic ^{13}C region of the spectrum for a monosubstituted benzene usually contains 4 signals, one signal for the carbon atom C-1 to which the substituent is connected (sometimes called the "ipso" position), a signal for the two equivalent *ortho* carbons, a signal for the two equivalent *meta* carbons, and a signal for the *para* carbon. In a monosubstituted benzene the *ipso* carbon typically gives a very weak signal relative to the other carbons, because the *ipso* carbon has no hydrogen atom attached to it. The nOe effect of the hydrogens attached to the other carbons causes enhancement of the strength of their signals.

For disubstituted benzene derivatives, the number of signals expected depends upon whether the two substituents are the same or different and whether they are located *ortho*, *meta*, or *para* to each other.



It is possible to predict the approximate chemical shifts of the carbon atoms of a substituted benzene by applying substituent constants that have been determined experimentally. The effect of a particular substituent on the chemical shifts of the ring carbons depends upon whether the carbon is the one to which the substituent is connected (C-1 or *ipso*), or if the carbon is *ortho*, *meta*, or *para* to the point of connection.

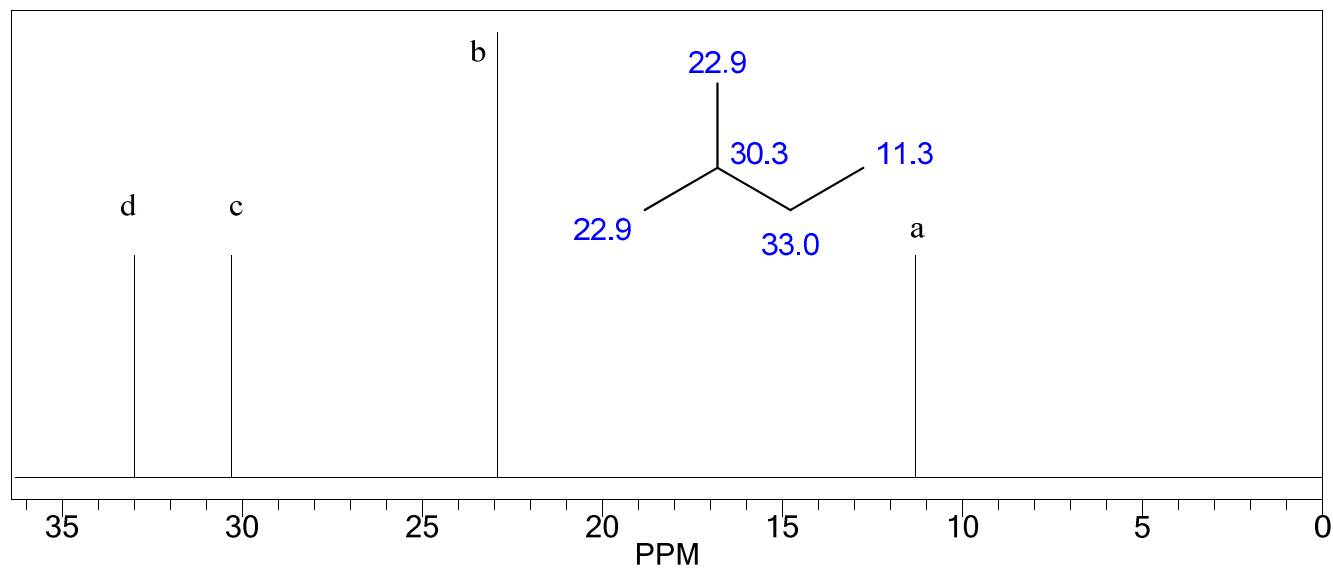


proton coupled spectrum

a = quartet

b = triplet

c = triplet



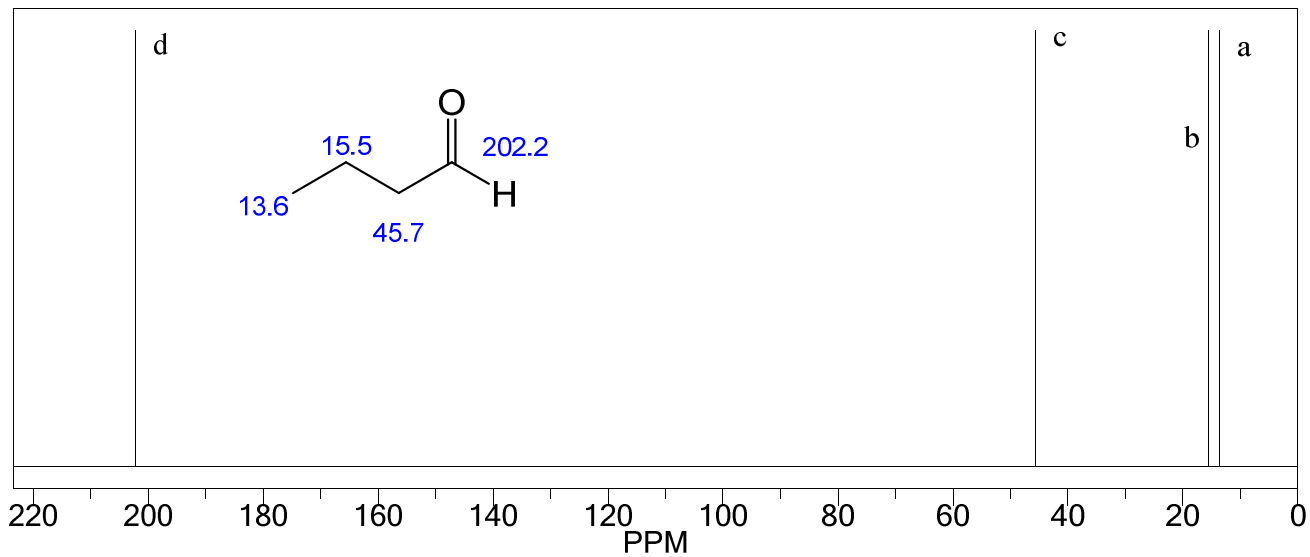
proton coupled spectrum

a = quartet

b = quartet

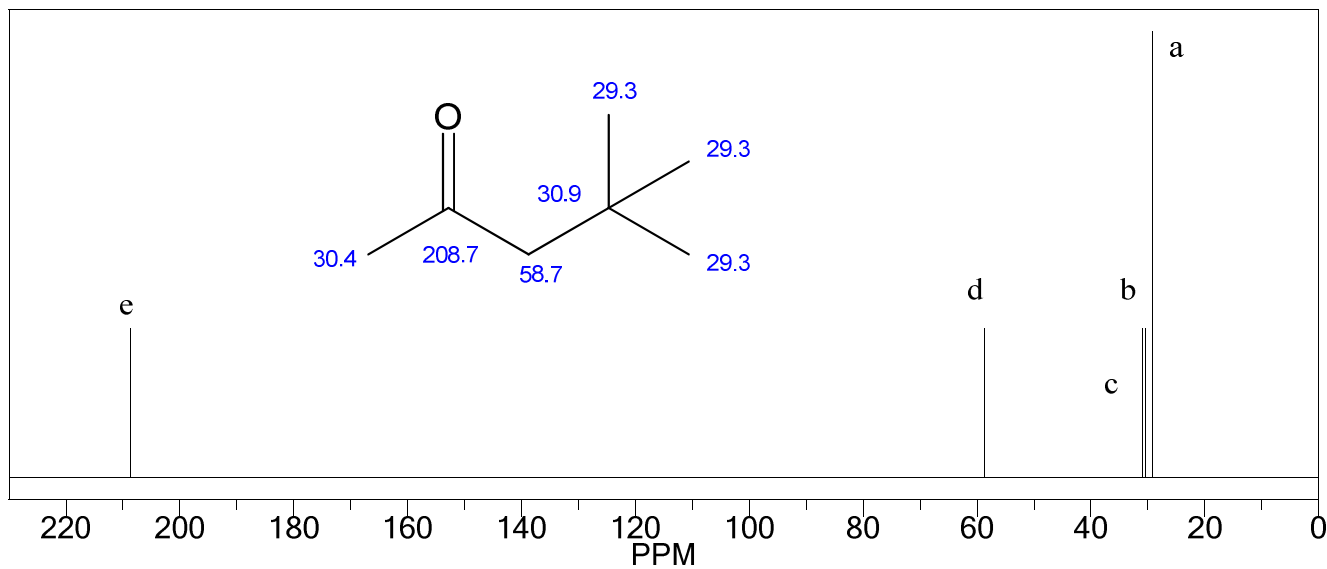
c = doublet

d = triplet



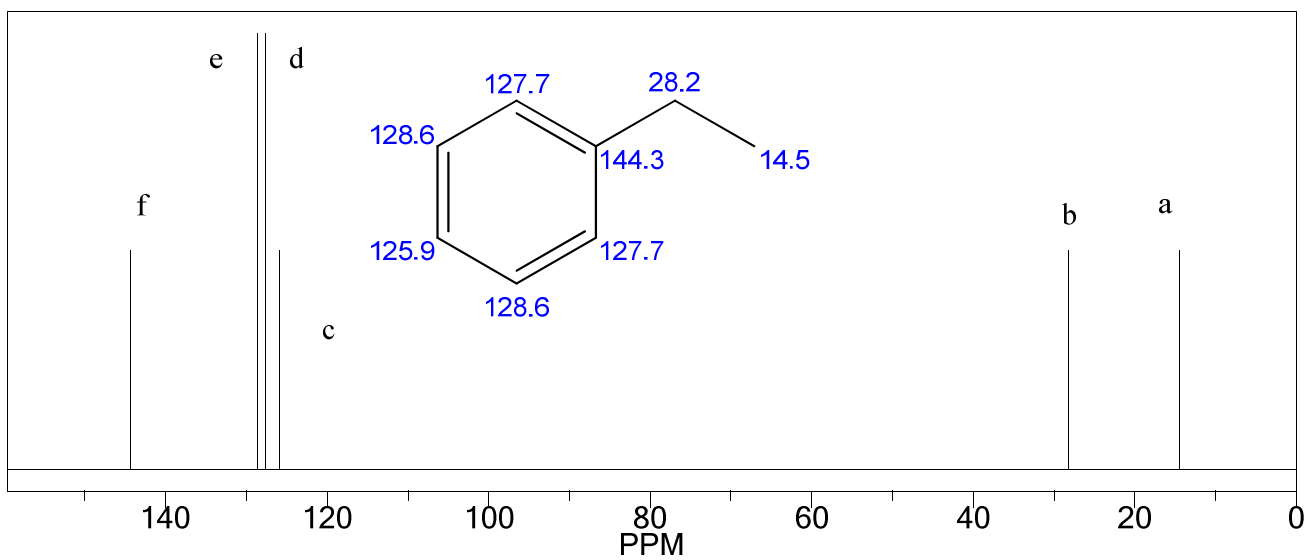
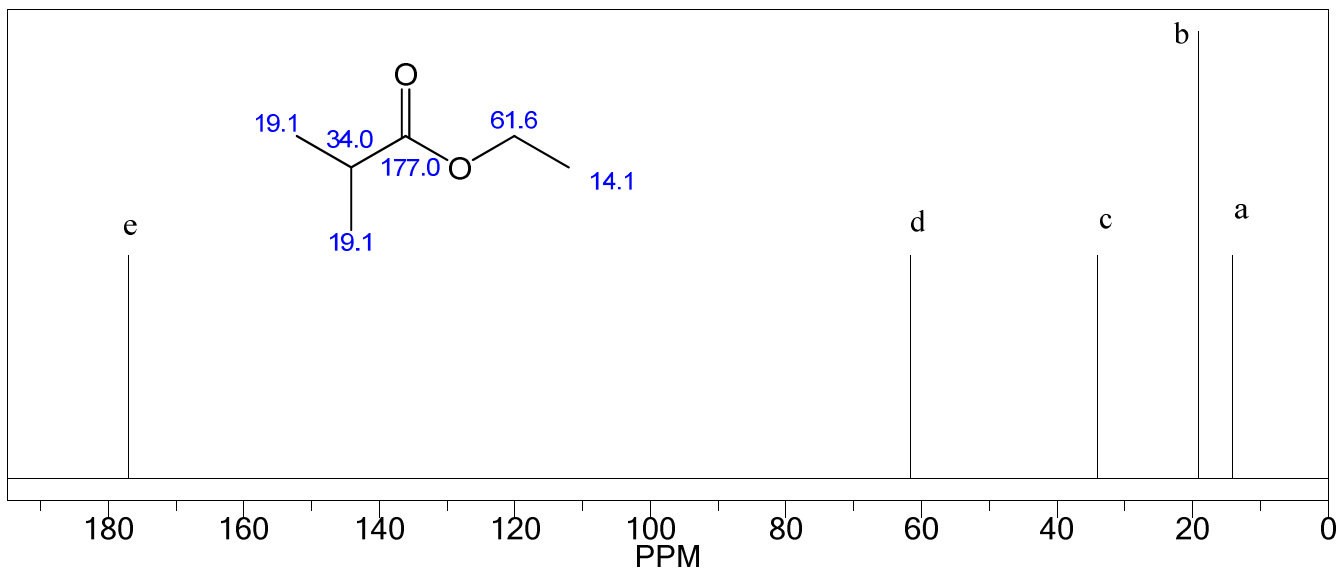
proton coupled spectrum

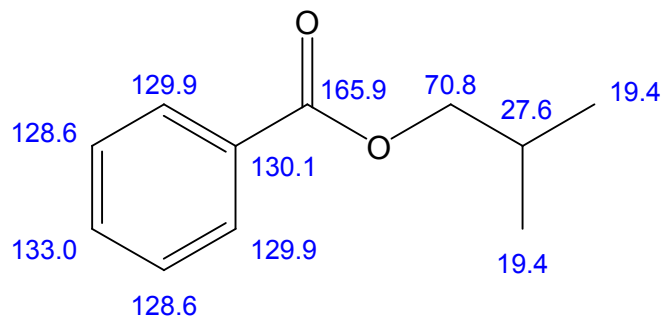
- a = quartet
- b = triplet
- c = triplet
- d = doublet



proton coupled spectrum

- a = quartet
- b = quartet
- c = singlet
- d = triplet
- e = singlet





proton coupled spectrum

- a = quartet
- b = doublet
- c = triplet
- d = doublet (128.6 ppm)
- e = doublet (129.9 ppm)
- f = singlet (130.1 ppm, the ipso carbon)
- g = doublet (133.0 ppm)
- h = singlet

