

A Guide to Solving NMR Problems

NMR spectroscopy is a great tool for determining structures of organic compounds. As you know ^1H spectra have three features, chemical shift, signal intensity, and multiplicity, each providing helpful information. In this document we show how you use these features together to assign structures from ^1H and ^{13}C spectra. Use this approach.

I Begin with a general examination of the spectrum:

- a) determine how many signals (clusters) there are in the ^1H spectrum and note their chemical shifts, and count the signals in the ^{13}C spectrum;
- b) determine how many ^1H nuclei are present in each cluster (look at the integration);
- c) determine the multiplicity of each signal cluster (count the peaks or read the label attached to the peak);
- d) determine what additional information is available (often the molecular formula is given; that gives you a chance to subtract groups you've identified and to check what is left to identify);
- e) compare the number of ^1H signals with those in the ^{13}C spectrum; this may tell you whether all carbon atoms bear ^1H nuclei or whether there are carbons without ^1H nuclei attached.

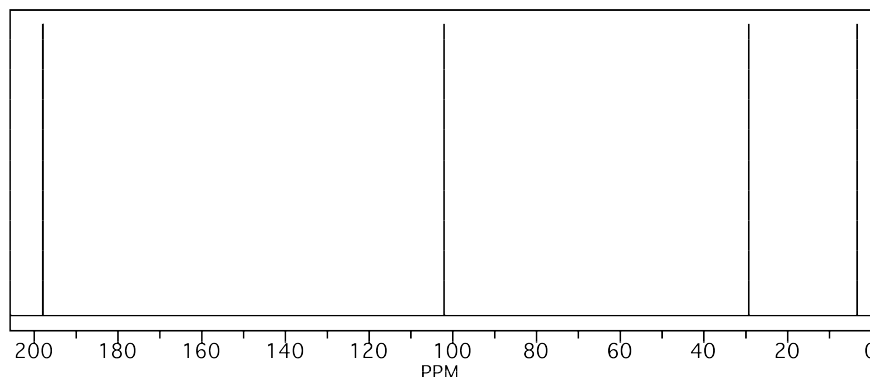
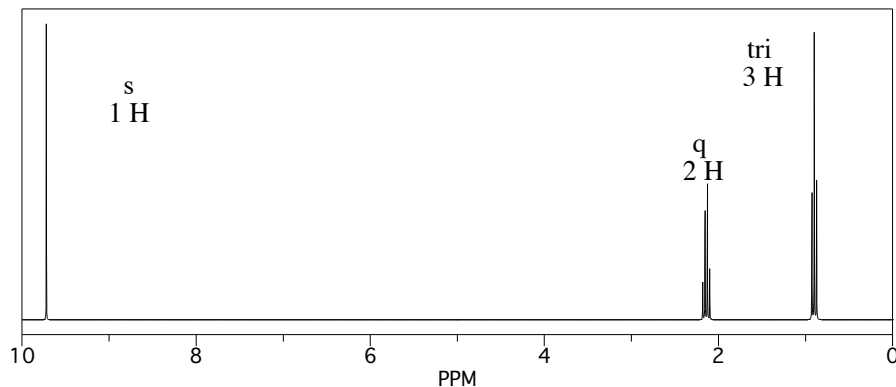
II Now proceed to the interpretation of the spectrum:

- f) for each peak match the number of ^1H nuclei and its multiplicity with a corresponding peak and combine them to groups (coupling is mutual);
- g) record each group you recognize (that'll give you partial credit ☺);
- h) when you have assigned all ^1H groups that you recognize, add their formulas up and compare with the molecular formula; the difference will be a group or groups that you haven't identified as yet or cannot see in the ^1H spectrum; step e) above will give you similar information.
- i) enter the "difference" and combine all fragments.

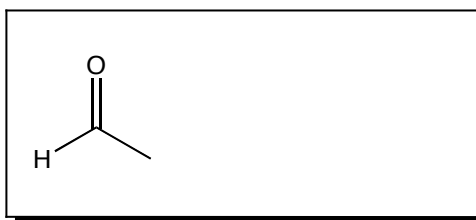
III Check your work: make sure that you have accounted for all signals and for every atom of the molecular structure and that your combined structure satisfies all chemical shifts. That's all, folks.

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Lets begin by looking at a really quite simple compound; it has a molecular formula of $C_4H_6Cl_2$. The 1H spectrum has 3 signals and the ^{13}C spectrum shows 4 signals; make a note that there must be a C without any H attached.

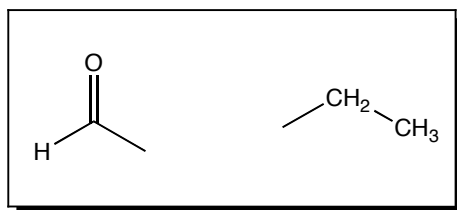


For your interpretation of the individual peaks, it's best to start at one of the edges, low field or high, left or right. At low field (left) our spectrum has a singlet (1 H) at 9.7 ppm; that chemical shift is unmistakable: it can only indicate an aldehyde. Because this signal is a singlet ($n + 1 = 1$; $n = 0$), there cannot be any 1H nuclei on the adjacent carbon. You can enter the aldehyde fragment without neighbor in the "box provided" for your first piece of partial credit. (I place groups with low-field signals on the left, but that is not crucial).



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Now we go to high field (right): there is a triplet (3 H) at 0.9 ppm; 3 H at high field is almost always a methyl group. The signal is a triplet ($n + 1 = 3$); therefore, the methyl group must have ($n =$) 2 ^1H neighbors; that must be a CH_2 group. The CH_2 signal is a quartet ($n + 1 = 4$), so it must have ($n =$) 3 ^1H neighbors; that can only be the CH_3 group. You also know that there cannot be any ^1H neighbor on the other side. Note that the combination of a “triplet, 3 H” with a “quartet, 2 H” is ALWAYS a C_2H_5 group. You can enter an ethyl group into the “box provided”, joining the aldehyde group (and increasing your partial credit).



IMPORTANT: it does NOT matter in what order we probe the spectrum. If we had started with the high field region (C_2H_5 before CHO), the conclusion would be the same.

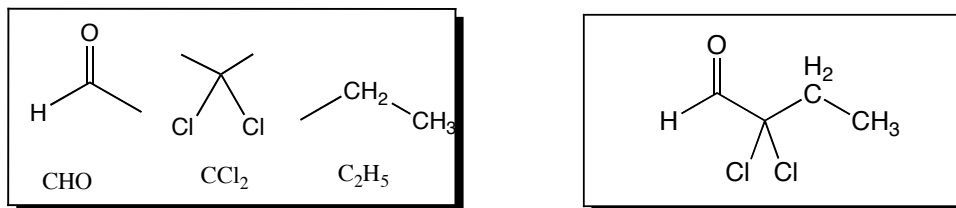
So far we have no information how the two groups are connected. The answer could come from the composition or from a ^{13}C spectrum. Working with the empirical formula, $\text{C}_4\text{H}_6\text{Cl}_2$, you subtract the two fragments, CHO and C_2H_5 ($\text{C}_4\text{H}_6\text{Cl}_2 - \text{CHO} - \text{C}_2\text{H}_5 = \text{CCl}_2$) and are left with a dichloromethylene unit (more partial credit).

We find support for our structure fragments in the ^{13}C spectrum. The four signals, 198 ppm for the aldehyde carbon, 102 ppm for the CCl_2 carbon next to the $\text{C}=\text{O}$ group, and 30 and 5 ppm, respectively, for the (slightly deshielded) CH_2 and the (shielded) CH_3 of the ethyl group, are in accord with the fragments we identified. Note, that we base the CCl_2

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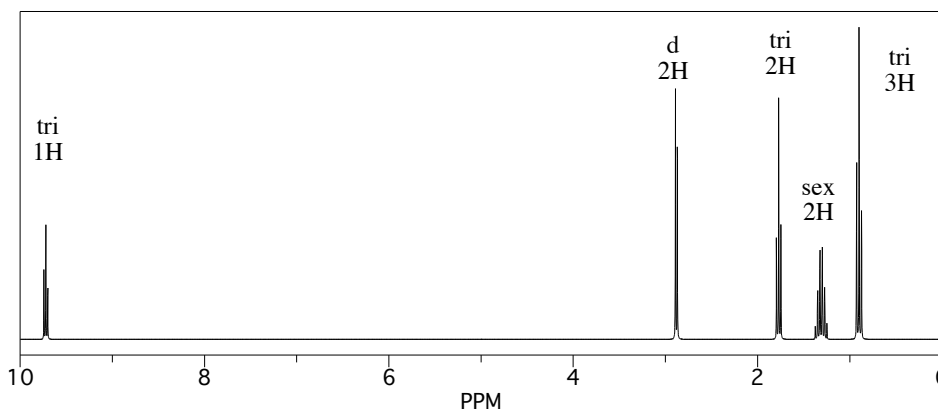
group on the ^{13}C spectrum and use non-spectroscopic information (the composition) in order to derive this part of the target structure.

There is only one way how the three units can be connected into a molecule.



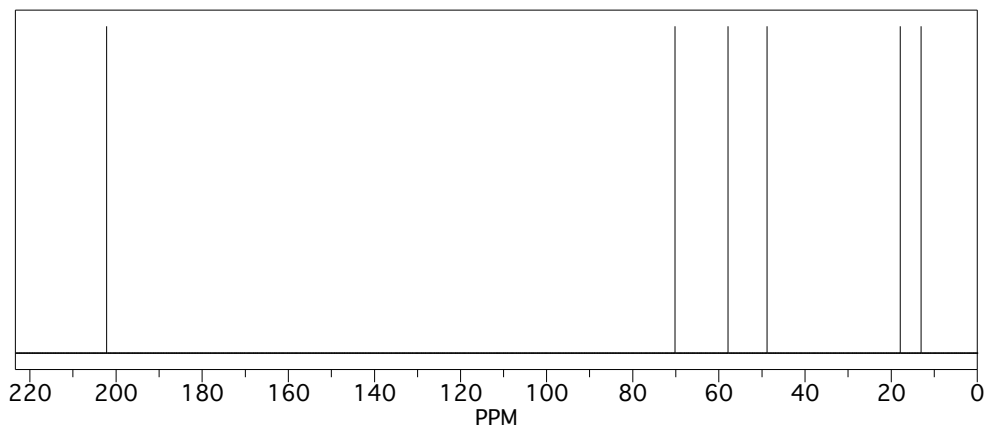
At this point (or earlier, if you wish) you can use the composition to check the degrees of unsaturation ($H_{\text{sat}} = 2 \times 4 + 2 = 10$; $- 2$ for $\text{Cl}_2 = 8$; $H_{\text{act}} = 6$; $H_{\text{sat}} - H_{\text{act}} = 2$; $D(U) = 1$). The $D(U)$ count is in accord with the presence of the $\text{C}=\text{O}$ group. This gives you additional confidence that your assignment is correct. So much for a simple spectrum.

Are you ready for a slightly more difficult spectrum with two more carbon atoms and two additional signals each in ^1H and ^{13}C spectra? Its composition is $\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}$.

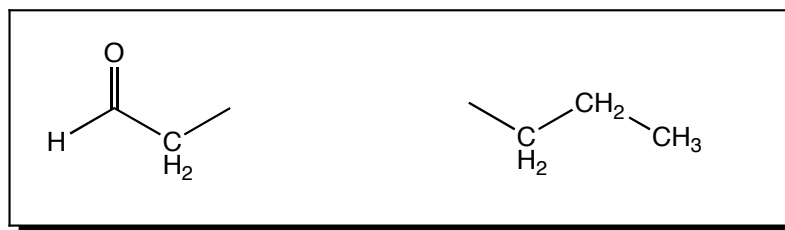


This spectrum has a triplet (1 H) at 9.8 ppm, clearly indicating the presence of an aldehyde group; because the signal is a triplet ($n + 1 = 3$), there must be two ^1H nuclei on the adjacent carbon ($n = 2$). We find a 2 H signal, a doublet, at 2.9 ppm, indicating that it has 1 ^1H neighbor (the coupling between groups is always mutual). The group is slightly deshielded, indicating that it resides near a group, like $\text{C}=\text{C}$ or $\text{C}=\text{O}$. This suggests that we combine the aldehyde function with the CH_2 group and enter them into the “box provided”.

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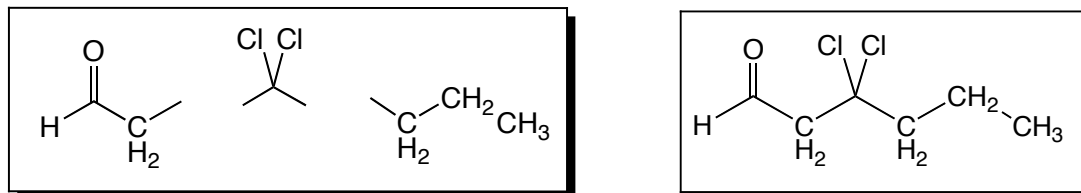


Turning to the high-field side of the spectrum, there is a triplet (3 H) at 0.9 ppm; any 3 H at high field must be a methyl group; the triplet ($n + 1 = 3$) indicates that the methyl group must have ($n =$) 2 ¹H neighbors, i.e., a CH₂ group. There are two CH₂ groups in the spectrum, at 1.4 and 1.8 ppm; which one should we choose? The signal at 1.8 ppm is a triplet ($n + 1 = 3$); attachment to the CH₃ group ($n = 3$) would require at least a quartet. The CH₂ signal is a sextet ($n + 1 = 6$), requiring 5 ¹H neighbors; since we have 3 neighbors at high field (the CH₃ group), we need 2 more at lower field, the triplet at 1.8 ppm. We combine these three groups to a slightly deshielded propyl group, which we enter into the “box provided”. Note: the combination of triplet (3H) – sextet (2H) – triplet (2H) is always a propyl group. Once again the result is independent of the sequence: examining the high field signals before the low field ones yields the same result as the sequence used above.



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In order to determine how these groups are connected, we consult the composition ($C_6H_{10}Cl_2O$). If we subtract from the empirical formula, $C_6H_{10}Cl_2O$, the fragments, $CHOCH_2$ and C_3H_8 , we are left with CCl_2 , a dichloromethylene unit. Again, there is only one way how the resulting three units can be connected into a molecule.

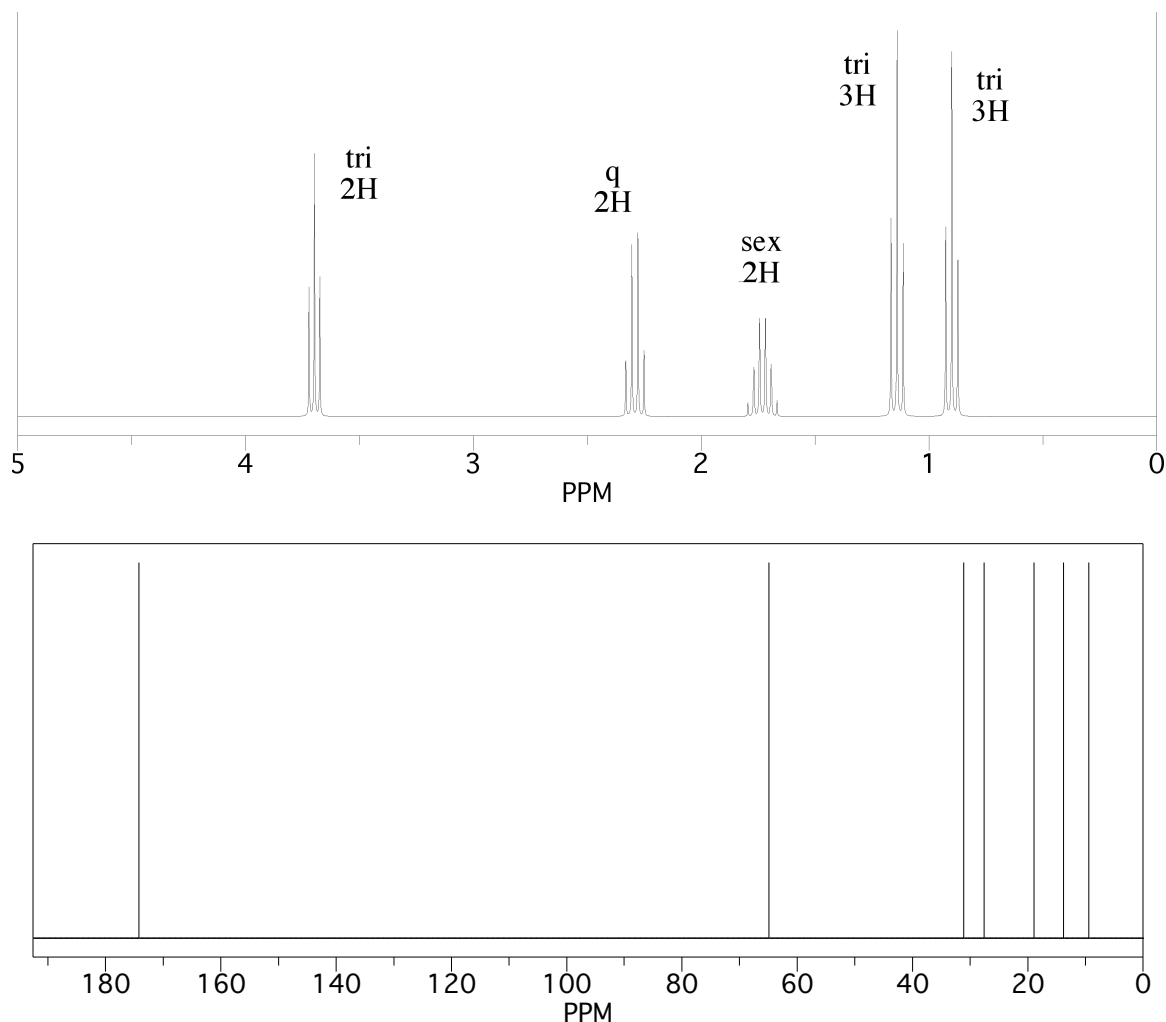


We check the ^{13}C spectrum whether it fits the assigned structure. It has five signals: a shift of 202 ppm is characteristic for a $C=O$ group; 70 ppm for the CCl_2 carbon (not directly next to the $C=O$ group as in our first spectrum); 58 and 48 ppm for the deshielded CH_2 groups next to $C=O$ and CCl_2 ; and 18 and 13 ppm for the shielded CH_2 and CH_3 belonging to the propyl group. This ^{13}C spectrum fully supports the structure we derived.

Checking the degrees of unsaturation (you could have done this earlier, if you wanted): $H_{sat} = 2 \times 6 + 2 = 14$; -2 for $Cl_2 = 12$; $H_{act} = 10$; $H_{sat} - H_{act} = 2$; $D(U) = 1$). The presence of the $C=O$ group is in accord with one element of unsaturation (the $C=O$) group. This agreement gives you additional confidence that your assignment is correct.

So far we have dealt with spectra in which the signals of the structure fragments were well separated. Maybe we should try to solve a problem where the signals of the structure fragments fall into the same region. Let us consider the spectrum of a compound, whose chemical formula is $C_6H_{12}O_2$; the spectra, shown below, have five 1H and six ^{13}C signals.

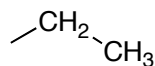
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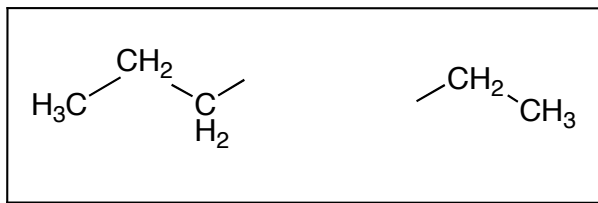
This time let's start with the degrees of unsaturation (there is nothing magical about the sequence): $H_{\text{sat}} = 2 \times 6 + 2 = 14$; $H_{\text{act}} = 12$; $H_{\text{sat}} - H_{\text{act}} = 2$; $D(U) = 1$: that means we have to expect one double bond or one ring.

Our ^1H spectrum has two methyl groups, at 0.9 and 1.2 ppm; both are triplets ($n + 1 = 3$), so both must be adjacent to a CH_2 group. We have three CH_2 groups to choose from, at 1.7, 2.3, and 3.7 ppm; they are slightly to significantly deshielded. The group at 2.3 ppm is a quartet ($n + 1 = 4$); obviously, it is located next to a methyl group. Combining the two gives you an ethyl group – “bank” it.

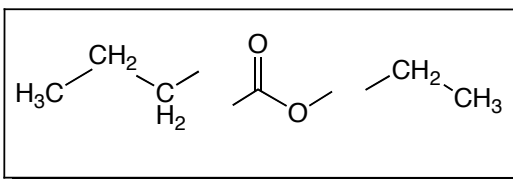
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Of the remaining three groups, the sextet ($n + 1 = 6$) at 1.7 ppm requires $n = 5$ ^1H neighbors; it just so happens that we have one CH_3 and one CH_2 group (3.7 ppm) left. This could amount to a propyl group, whose open-ended CH_2 is significantly deshielded. As you place it in the “box provided”, you may remember that the combination, triplet (3H) – sextet (2H) – triplet (2H), is always a propyl group.



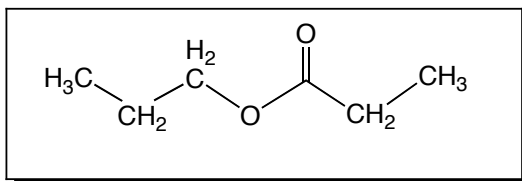
How could these groups be connected? In order to answer that question we remember the composition, $\text{C}_6\text{H}_{12}\text{O}_2$, and subtract from it the two fragments C_2H_5 and C_3H_7 , giving us CO_2 ; this represents an “ester” linkage, $-\text{O}-\text{C}(=\text{O})-$. The $\text{C}=\text{O}$ function takes care of the degree of unsaturation we expected. [You will learn much more about esters in Chem 308.]



In this case there are two ways to connect the three fragments: either the propyl or the ethyl group could be attached to the O and the remaining group to the $\text{C}=\text{O}$. The answer lies in the chemical shifts of the triplet at 3.7 ppm (part of the propyl group) and of the quartet at 2.3 ppm (part of the ethyl group). The shift of 3.7 ppm is exactly what we expect from a

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group attached to the electronegative O; therefore we attach the propyl group to the O. 2.3 ppm is what we expect for a CH₂ near a (C=O) double bond; accordingly, we attach the ethyl group to the C=O group.



Checking the ¹³C spectrum: an ester carbon has a very characteristic ¹³C chemical shift (~175 ppm), clearly seen in the spectrum below. The other notable peak is the signal at 65 ppm, representing the CH₂ carbon (of the propyl group), which is attached to the O. The remaining five signals are unexceptional CH₂ and CH₃ resonances

One question remains (which does not affect the structure, but is still of interest): which of the methyl signals belongs to the propyl and which belongs to the ethyl group. We base this decision on chemical shift evidence: the CH₃ group of the ethyl group is closer to a deshielding unit (C=O); therefore we assign the signal at 1.2 ppm to that group and the triplet at 0.9 ppm to the CH₃ group of the propyl group. There, we have assigned a structure and identified every signal unambiguously.

We hope that working through these three sets of spectra with additional supporting information gives you some familiarity with the methodology and confidence to approach the spectra you will encounter in your future exams. Good luck.

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Typical ^1H and ^{13}C Chemical Shift in Organic Molecules	
Chemical Shift	Type of Hydrogen
0.8 – 1.0	Primary alkyl, RCH_3
1.2 – 1.4	Secondary alkyl, $\text{RCH}_2\text{R}'$
1.4 – 1.7	Tertiary alkyl, R_3CH
1.6 – 1.9	Allylic, $\text{R}_2\text{C}=\text{CR}'\text{CH}_3$
2.2 – 2.5	Benzylic, ArCH_2R
2.1 – 2.6	Next to carbonyl, $\text{R}(\text{C}=\text{O})\text{CH}_2\text{R}'$
1.7 – 3.1	Alkyne, $\text{RC}\equiv\text{CH}$
3.4 – 3.6	RCH_2Br
3.6 – 3.8	RCH_2Cl
3.3 – 4.0	RCH_2OH , $\text{RCH}_2\text{OR}'$
0.5 – 5.0	OH , SH , NH_2
4.6 – 5.0	Terminal alkene, $\text{RHC}=\text{CH}_2$
– 5.6	Terminal alkene near electronegative atoms
5.2 – 5.7	Internal alkene $\text{RHC}=\text{CH}_2$
– 6.5	Internal alkene near electronegative atoms
6.0 – 9.5	Benzene and aromatics, ArH
9.5 – 9.9	Aldehyde, $\text{R}(\text{C}=\text{O})\text{H}$
Chemical Shift	Type of Carbon
5 – 20	Primary alkyl, RCH_3
20 – 30	Secondary alkyl, $\text{RCH}_2\text{R}'$
30 – 50	Tertiary alkyl, R_3CH
30 – 45	Quaternary alkyl, R_4C
20 – 40	Allylic, $\text{R}'_2\text{C}=\text{CRCH}_3$
20 – 40	RCH_2Br
25 – 50	RCH_2Cl
50 – 90	RCH_2OH , $\text{RCH}_2\text{OR}'$
65 – 95	Alkyne, $\text{RC}\equiv\text{CH}$
100 – 160	Alkene, Aromatic
170 – 175	Ester, $\text{R}(\text{C}=\text{O})\text{OR}'$
190 – 210	Aldehyde or Ketone, $\text{R}(\text{C}=\text{O})\text{H}$, $\text{R}(\text{C}=\text{O})\text{R}'$

