

Spectroscopy in Organic Chemistry



Spectroscopy

Spectrum - dealing with light, or more specifically, radiation

Scope - to see

Organic Spectroscopy therefore deals with examining how organic molecules interact with radiation (visible, ultra-violet, infrared, radio waves, etc.)

Organic chemists use spectroscopy to determine **structural information** about molecules. This helps to identify functional groups that are present, which also includes determining if chemical reactions occurred.

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Types of Spectroscopy in Organic



Spectroscopy typical to Organic Chemistry

- **Proton Nuclear Magnetic Resonance** (_____)
-deals with hydrogens and their environment
- **Carbon Nuclear Magnetic Resonance** (_____)
-deals with carbons and their environment
- **Infrared Absorption** (_____)
-identifies functional groups
- **Ultra-violet - Visible Absorption** (_____)
-deals with conjugation (alternating single and double-bonds)
- **Mass Spectrometry** (_____)
-deals with the mass of a molecule and the mass of fragments
[since it's not dealing with radiation, *technically* MS is not spectroscopy]

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^1H NMR - 3 Major Clues...



Because virtually all organic molecules have protons, the H^1 NMR is probably the most powerful tool for spectroscopy

There are 3 items in a ^1H NMR that can help to give clues about the structure of an organic molecule. Each item tells you something different and provides clues...

- _____ (ppm, δ)
 - where in the spectrum is the signal found
 - chemical environment of the proton
- _____
 - how big is the signal
 - number of protons causing the signal
- _____
 - how many peaks in the signal
 - how many proton neighbors there are

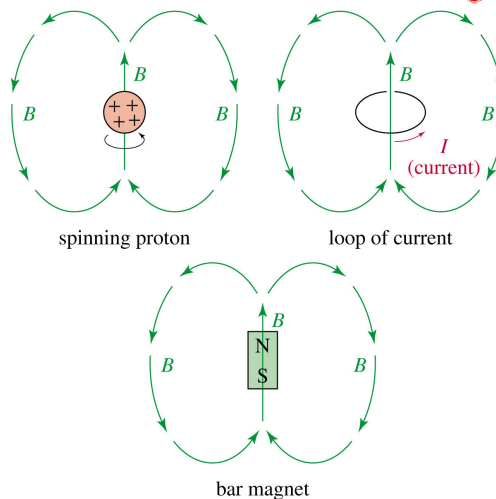
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The nucleus of the hydrogen atom



- The spinning nucleus of the hydrogen atom is just a proton and it acts like it is a magnet.
- Therefore, when another magnetic field is applied to this system, they can affect each other.
- This gives rise to nuclear resonance spectroscopy (NMR).
- This means that they also act differently around each other.



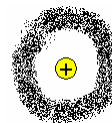
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Effect of electron density on NMR chemical shifts



When a nucleus is buried under a lot of electrons, the applied external magnetic field (from the instrument) doesn't have that much effect on the nucleus. It is said to be _____.



When a nucleus has fewer electrons around it, the effect of the applied magnetic field is greater and it is said to be _____.



_____ (electron rich) nuclei give signals closer towards 0 ppm (also known as being shifted _____).

Shielded →

0 ppm

_____ (electron poor) nuclei give signals that are shifted further away from 0 ppm (or _____).

← Deshielded

0 ppm

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Shielded and Upfield Positioning



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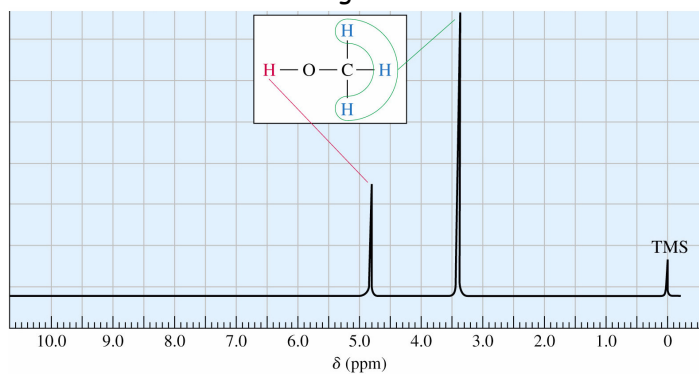
Chemical shift example - Methanol



Methanol, CH_3OH , has 2 different kinds of protons.

One is attached to an oxygen and three are on a carbon.

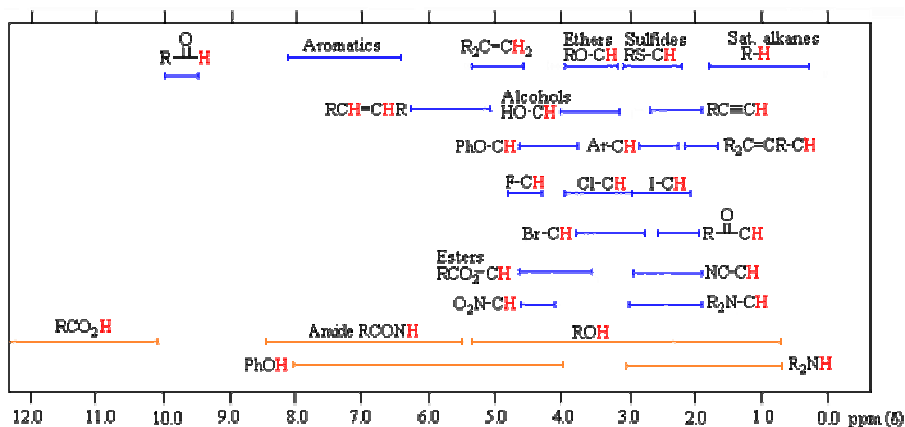
Which atom is more electronegative? What does that mean?



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General Chemical Shift Regions



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Table O' NMR Data



TABLE 13-3 Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-\text{CH}_3$)	0.9	$\text{>C}=\text{C}< \begin{matrix} \diagup \\ \text{CH}_3 \end{matrix}$	1.7
alkane ($-\text{CH}_2-$)	1.3	Ph- H	7.2
alkane ($-\text{CH}-$)	1.4	Ph- CH_3	2.3
$\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{CH}_3 \end{matrix}$	2.1	R- CHO	9-10
$-\text{C}\equiv\text{C}-\text{H}$	2.5	R- COOH	10-12
R- CH_2 -X (X = halogen, O)	3-4	R- OH	variable, about 2-5
$\text{>C}=\text{C}< \begin{matrix} \diagdown \\ \text{H} \end{matrix}$	5-6	Ar- OH	variable, about 4-7
		R- NH_2	variable, about 1.5-4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

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Integration



One of the most useful aspects of NMR is the fact that it can be _____.

What this means is that the _____ corresponds to the _____ that is causing that signal.

Three equivalent protons will create a signal that is three times larger than just a single proton.

Think of it like this, what is louder, a single voice screaming at me, or three voices screaming at me all at the same time. (How much louder would it be?) Louder means more signal.

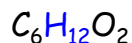
By comparing the _____ to the area under _____, you can assign the number of hydrogens for each set of peaks. (Given the total # of H's)

Let's look at the example on the next page...

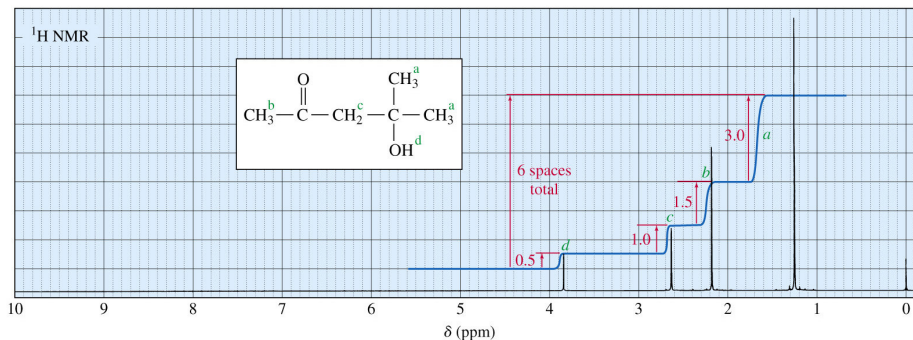
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NMR spectrum of 4-methyl-4-hydroxy-2-pentanone



(12 Hydrogens, 6 total blocks high, 0.5 block per hydrogen)



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Splitting in H^1 NMR - MulticPLICITY



If one proton on an atom "sees" another proton on an adjacent atom, the signal will be split...one peak is split into two.

The peak is split one additional time for every "other" hydrogen that is seen (in general, adjacent atoms only).

In general, protons are only split by "neighbors" (adjacent atoms), not by "roommates" (same atom), unless the "roommate" is VERY different. (i.e. examine $\text{CH}_3\text{-CH}=\underline{\text{CH}}_2$)

This gives a lot of information about the structure.

Therefore if you get a doublet (split into 2 peaks), that means that one set of hydrogens "sees" one other hydrogen.

If you get a quartet (split into 4 peaks), that means that one set of hydrogens "sees" three other hydrogens.

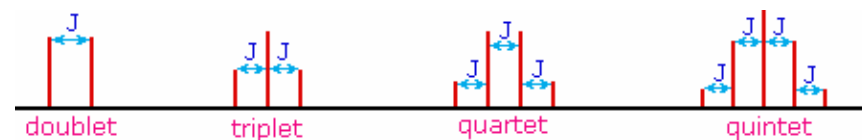
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Ratios of Multiplicity



Number of Peaks Symbol Name Ratios



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Coupling Constants - Distance between the splittings

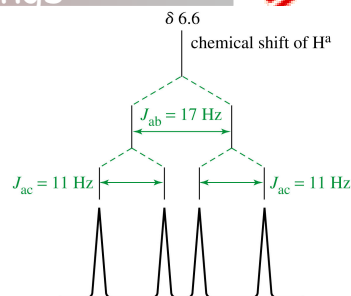


To make sure that a quartet is really a quartet, you need to be sure that there really is a 1:3:3:1 ratio.

You must make sure that all four of the peaks are equally spaced apart.

If they are NOT, then **you don't have a true quartet** and it may really be a doublet that has been split into another doublet (a.k.a doublet of doublets), or just two doublets close to each other.

The bottom line is that within a splitting, the distance between the peaks must be the same. This distance is known as a coupling constant, represented by J .

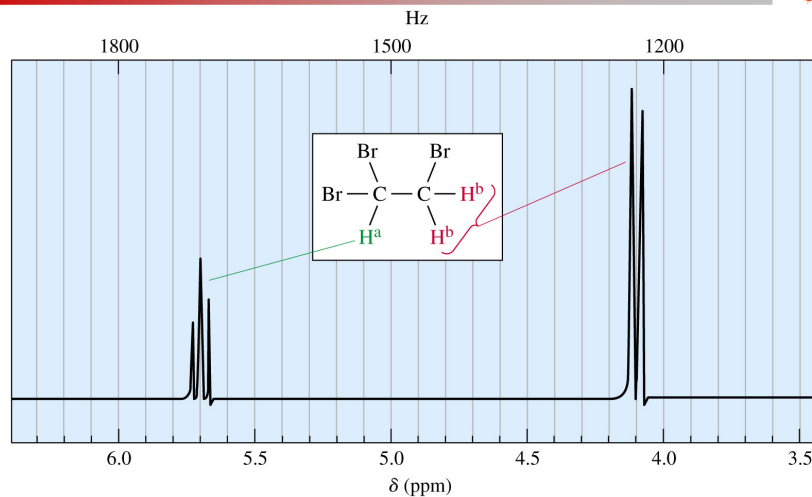


The coupling constant is in units of hertz (Hz) and is a function of the dihedral angle between the hydrogens causing the coupling.

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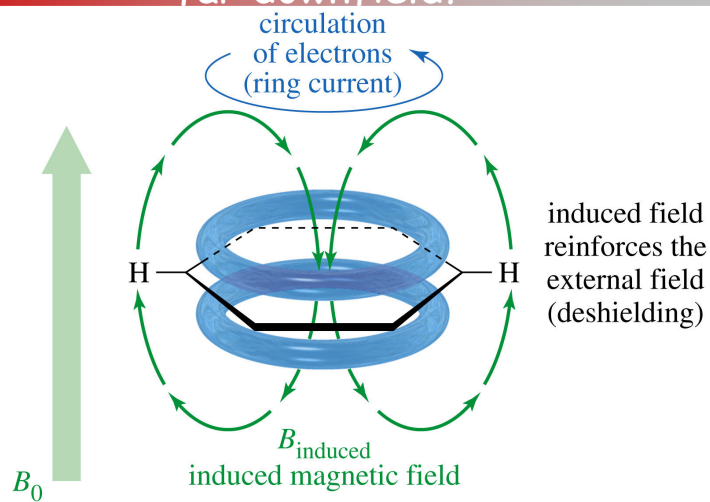
Example of simple NMR splitting



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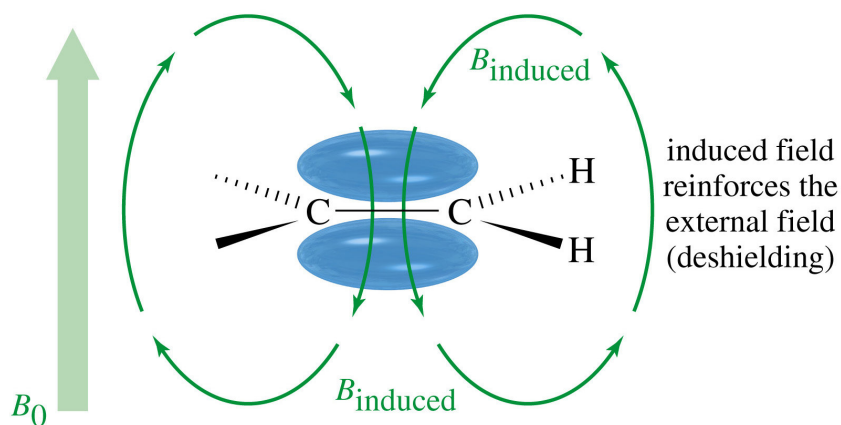
Why are aromatic protons shifted so far downfield?



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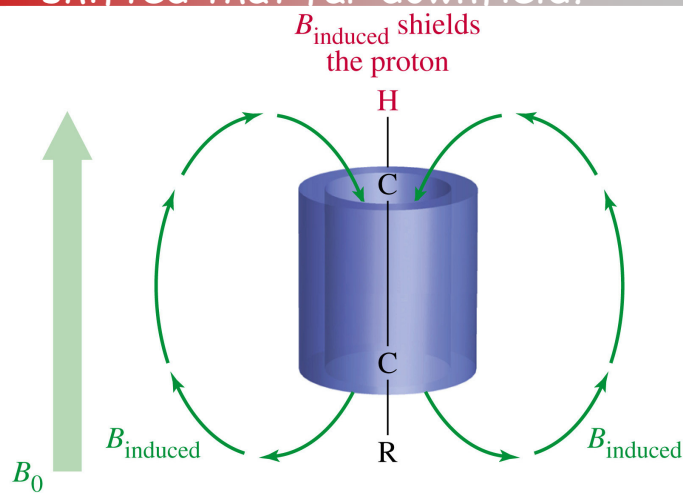
Why are vinylic protons shifted so far downfield?



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Why are acetylinic protons not shifted that far downfield?



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How to analyze proton NMR spectra



1. Look at the molecular formula (if available), and look at the total integration of the spectrum.
2. Determine how many hydrogens are causing each signal.
3. Look at the splitting pattern so you get an idea of what hydrogens are around that group.
4. Try to assemble the molecule with the clues you have gathered. (Think of it as a puzzle...)
5. If you have other spectroscopic information (like IR), make sure your analysis is consistent with all available data.

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Tricky Aspects of ^1H NMR



- Remember that the NMR active nuclei is the ^1H (spin=1/2).
- Therefore, a deuteron ($^2\text{H} = \text{D}$) is not NMR active.
- Solvents like CDCl_3 , D_2O , or C_6D_6 are themselves _____ on the ^1H NMR since they do not contain simple ^1H hydrogens.
- Any group that can _____ with water will effectively have the ^1H replaced with a D and become NMR invisible on those positions (OH, NH, CO₂H) when the solvent is _____.
- Sometimes you can determine if a signal is due to one of these hydrogen-bonding groups by the addition of D_2O . If these protons exchange with solvent (by hydrogen bonding) then they will _____.

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Tricky Aspects of ^1H NMR

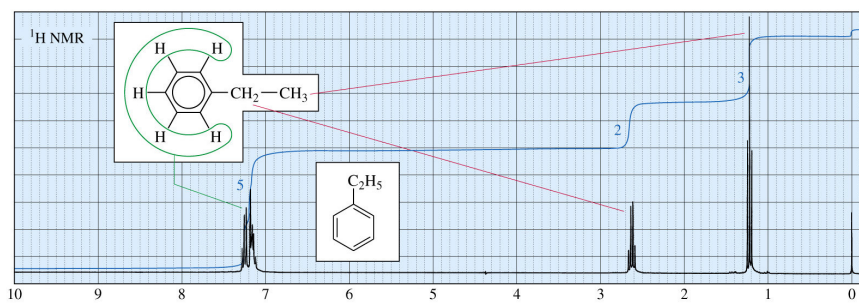


- Fluorine atoms have the same spin as a proton, therefore they will _____, although they _____ themselves.
- Sometimes protons on alcohols and amines can be seen and will split with neighbors, sometimes they won't... be prepared for this behavior.
- If a proton is coupled by two *different* sets of other protons, then each one will couple the initial proton independently. Therefore if one proton sees 2 hydrogens on one side for a triplet and one on the other side for a doublet, the result may look like a triplet with each peak being split into doublets and not necessarily a quartet. (more pronounced in rigid or ring systems)

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NMR of ethylbenzene



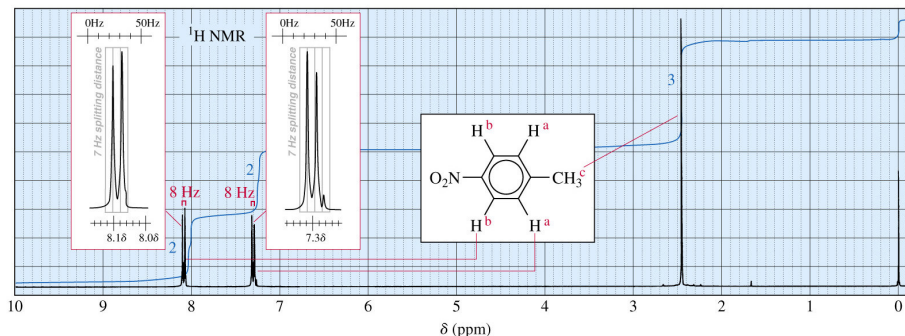
Note the messy multiplet around δ 7.2 that corresponds to 5 H. This is characteristic of a mono-substituted aromatic ring.

A _____ simply means it's too complicated to analyze. This is usually caused by either very complicated splitting or many different signals all overlapping each other.

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NMR of *p*-nitrotoluene

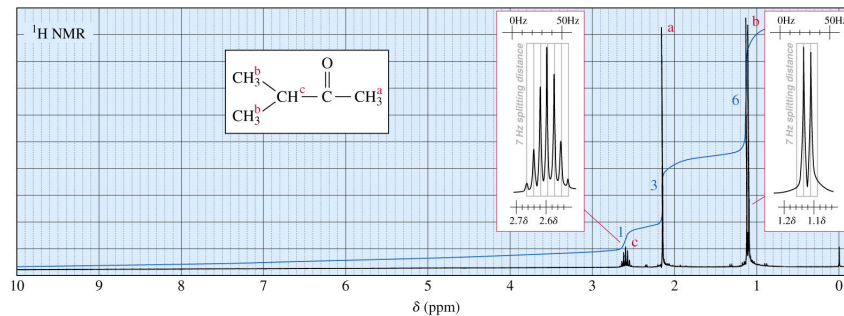


Note the two characteristic doublets in the aromatic region (2 H each); this is characteristic of a para (1,4 relationship) di-substituted aromatic ring.

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NMR of 3-methyl-2-butanone



This is how the data is often represented. Notice that the chemical shifts, integrations, and splittings are all included. (Sometimes the coupling constants are also included.)

δ 1.20 (d, 6 H)

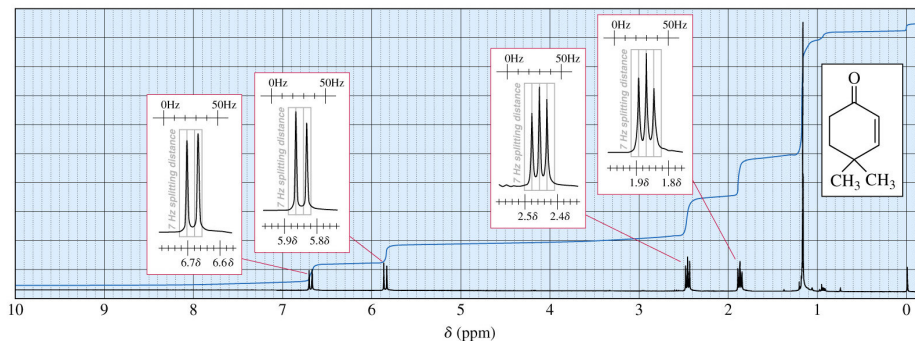
δ 2.15 (s, 3 H)

δ 2.68 (sept., 1 H)

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4,4-dimethylcyclohexa-2-ene-1-one

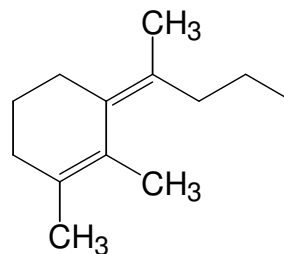
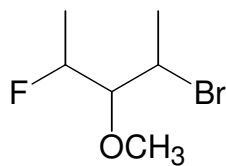
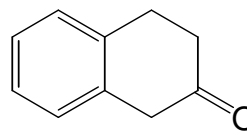
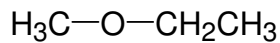
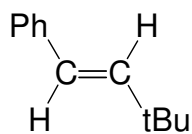


Analyze the ^1H NMR spectrum of the molecule above and write out the NMR data in the accepted method described earlier.

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Try to predict the proton NMR spectra of these compounds



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Try to draw the structure of the compounds given the following NMRs



1. C_3H_8O ; δ 1.22 (d, 6 H), 2.5 (s, 1 H), 4.05 (sept., 1 H)
2. $C_{10}H_{12}O_2$; δ 2.0 (s, 3 H) 2.9 (t, 2 H), 4.3 (t, 2 H), 7.3 (m, 5 H)
3. C_3H_6ClBr ; δ 2.3 (p, 2 H), 3.6 (t, 2 H), 3.8 (t, 2 H)
4. $C_{11}H_{16}$; δ 0.9 (s, 9 H), 2.5 (s, 2 H), 7.2 (m, 5 H)

Some people prefer to sketch out the spectrum from the data and others prefer to list the data from a given spectrum. Be able to do both for exams.