

# <sup>13</sup>C NMR Spectroscopy

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from chapter \_\_\_\_\_ in the recommended text

## A. Introduction

## B. Fundamental Physics Of NMR (Nuclear Magnetic Resonance)

*Nuclear* spin is the property that defines NMR active nuclei.

NMR is caused by *flipping* these spins between aligned and counter-aligned states by applying a *radiofrequency*

*low* energy range of the electromagnetic spectrum, *ie low* frequency and *high* wavelength.

For <sup>13</sup>C and <sup>1</sup>H the nuclear spin is  $\frac{1}{2}$ , and for <sup>12</sup>C the nuclear spin is *0*.

The natural abundance of <sup>1</sup>H is *high*, but that of <sup>13</sup>C is *low* (*1.1* %),

FT-NMR spectra are *averaged over multiple scans* to increase *both these parameters*.

NMR transitions are much *less* than those between vibrational states in IR, and *less* than the quanta

NMR active nuclei *are* sensitive to large external magnetic fields

energy difference between nuclear spins is *zero*.

The larger the applied magnetic field, the *larger* the energy gap between nuclear spin states.

are aligned and opposed to an external field is governed by *both these parameters* (*the energy gap between the nuclear spin states / Boltzman distributions*).

NMR active nuclei *are* sensitive to the electron density  
these nuclei in different parts of the molecule flip when *different* field strength(s) are/is applied

Spectroscopists may say that electron environment "*shield*" each other

an applied magnetic field is *deshielded* relative to one that is insulated

### C. Chemical Shifts In General

for  $^1\text{H}$  the reference is  $\text{SiMe}_4$ .

Chemical shift on this scale reflects how much less the frequency is for an NMR active nuclei to flip, or *resonate*, relative to that standard

Most chemical shift values are *positive*.

Nuclei with positive chemical shifts are *deshielded*

0 in  $^1\text{H}$  NMR corresponds to *the operating frequency of the machine* so a 200 MHz NMR spectrometer sets 0 at *200,000,000* Hz.

One millionth of this is *200* so on part per million (ppm) corresponds to *200*, ie *200* Hz.

on a 250 MHz machine, 1 ppm corresponds to 250 Hz in proton NMR spectra  
on a 400 MHz machine, 1 ppm corresponds to 400 Hz in proton NMR spectra  
on an 800 MHz machine, *10 ppm* corresponds to 8000 Hz in proton NMR spectra

0.05 ppm are separated by a frequency of 25 Hz.

to a chemical shift difference of 0.1 ppm.

to a chemical shift difference of 0.1 ppm.

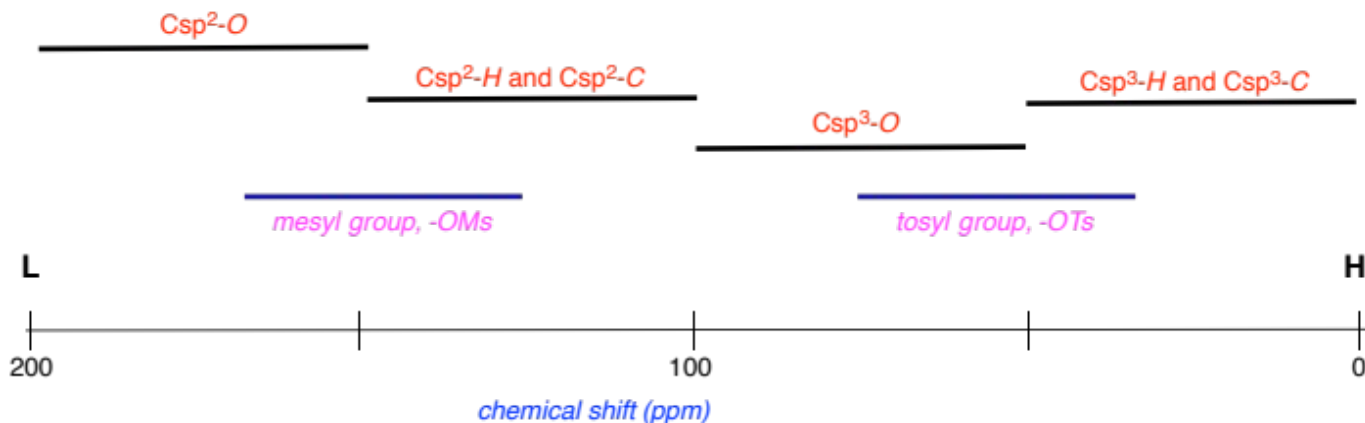
are 60 Hz apart will be *greater* on a 60 MHz

100 Hz apart will be *greater* on a 100 MHz

resonances at *fixed frequencies* appear to be *less* as the operating frequency

## D. Chemical Shifts In $^{13}\text{C}$ Spectra

this is called the *upfield* region and corresponds to *shielded*



this is called the *downfield* region and corresponds to *deshielded*

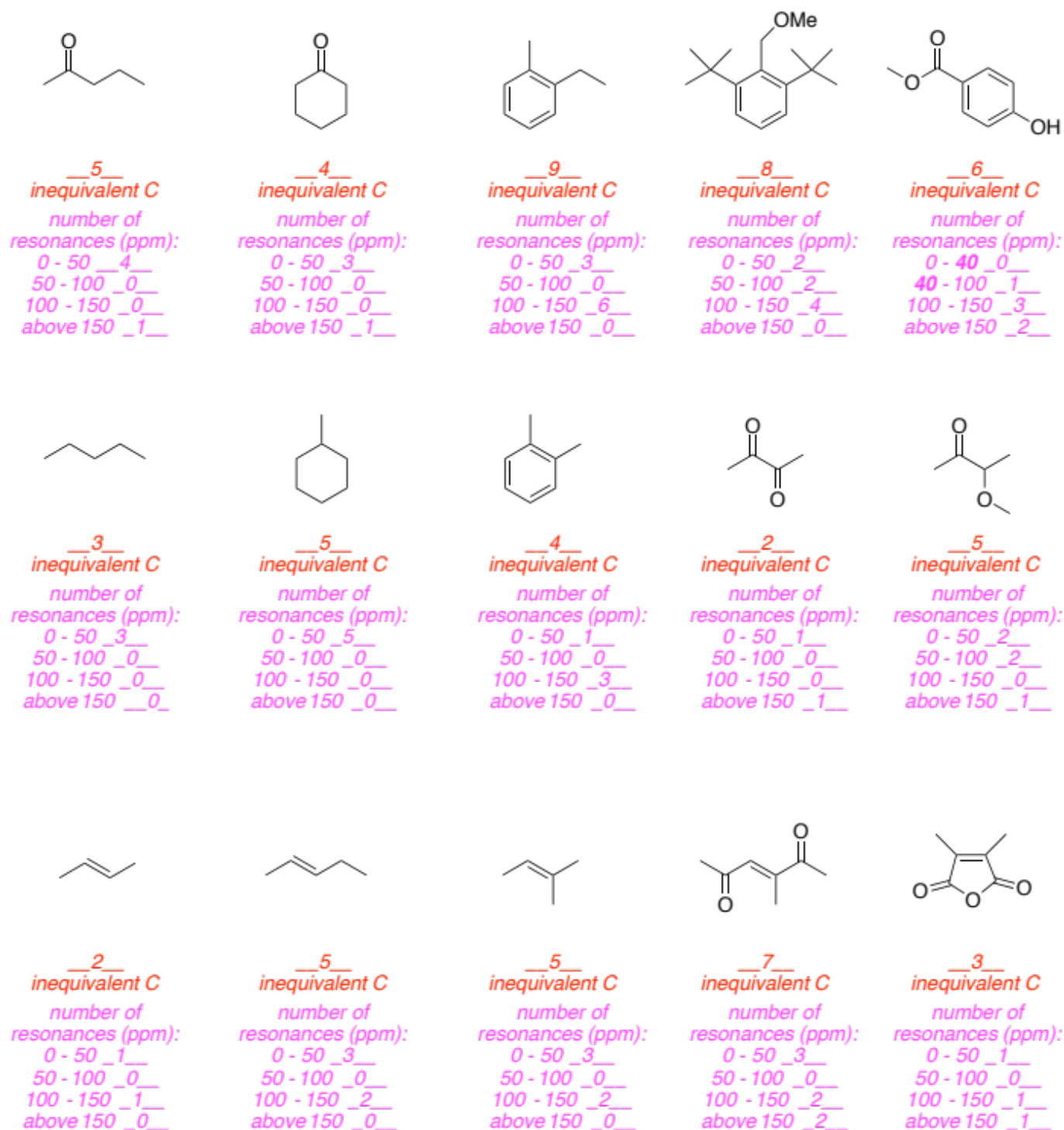
deduce electronegative atoms that *attract* electron density tend to *deshield* adjacent  $^{13}\text{C}$  nuclei, electron withdrawing groups will also tend to *deshield* adjacent  $^{13}\text{C}$  nuclei.

$\text{sp}^2$ -hybridized carbons tend to be *less* shielded

then those carbons are *inequivalent* except

$^{13}\text{C}$  NMR spectra resonate at *the same* chemical shifts, and inequivalent ones usually resonate at *different*  $^{13}\text{C}$  NMR spectra resonate at

this is *the same as* the number of resonances that are expected



Note: For some carbons, it is quite difficult to know in which range it will resonate in, so these are educated approximations.



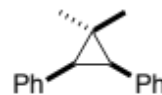
1  
inequivalent C  
number of resonances (ppm):  
0 - 50 1  
50 - 100 0  
100 - 150 0  
above 150 0



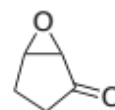
3  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 0  
100 - 150 0  
above 150 0



6  
inequivalent C  
number of resonances (ppm):  
0 - 50 2  
50 - 100 0  
100 - 150 4  
above 150 0



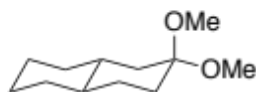
8  
inequivalent C  
number of resonances (ppm):  
0 - 50 4  
50 - 100 0  
100 - 150 4  
above 150 0



5  
inequivalent C  
number of resonances (ppm):  
0 - 40 2  
40 - 100 2  
100 - 150 0  
above 150 1



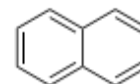
6  
inequivalent C  
number of resonances (ppm):  
0 - 50 4  
50 - 100 2  
100 - 150 0  
above 150 0



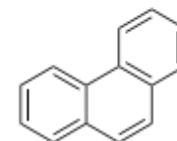
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inequivalent C  
number of resonances (ppm):  
0 - 50 9  
50 - 100 3  
100 - 150 0  
above 150 0



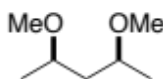
8  
inequivalent C  
number of resonances (ppm):  
0 - 50 8  
50 - 100 0  
100 - 150 0  
above 150 0



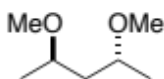
3  
inequivalent C  
number of resonances (ppm):  
0 - 50 0  
50 - 100 0  
100 - 150 3  
above 150 0



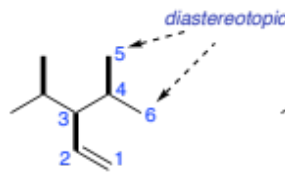
7  
inequivalent C  
number of resonances (ppm):  
0 - 50 0  
50 - 100 0  
100 - 150 7  
above 150 0



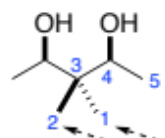
4  
inequivalent C  
number of resonances (ppm):  
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50 - 100 2  
100 - 150 0  
above 150 0



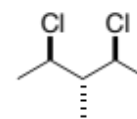
4  
inequivalent C  
number of resonances (ppm):  
0 - 50 2  
50 - 100 2  
100 - 150 0  
above 150 0



6  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 0  
100 - 150 2  
above 150 0



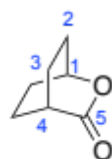
5  
inequivalent C  
number of resonances (ppm):  
0 - 50 4  
50 - 100 1  
100 - 150 0  
above 150 0



4  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 1  
100 - 150 0  
above 150 0



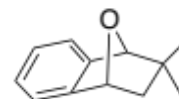
2  
inequivalent C  
number of resonances (ppm):  
0 - 50 2  
50 - 100 0  
100 - 150 0  
above 150 0



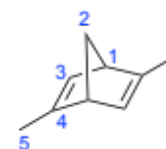
5  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 1  
100 - 150 0  
above 150 1



3  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 0  
100 - 150 0  
above 150 0



12  
inequivalent C  
number of resonances (ppm):  
0 - 50 4  
50 - 100 2  
100 - 150 6  
above 150 0

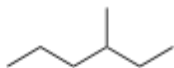


5  
inequivalent C  
number of resonances (ppm):  
0 - 50 3  
50 - 100 0  
100 - 150 2  
above 150 0

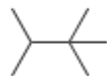
Note: For some carbons, it is quite difficult to know in which range it will resonate in, so these are educated approximations.

soccer-ball-like molecule  $C_{60}$ , has 6  $^{13}C$  resonances.

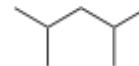
so they usually *cannot* be reliably used to ascertain the number



7 inequivalent C



4 inequivalent C



3 inequivalent C

## E. Coupling In $^{13}C$ NMR

### $^{13}CH$ Spin Systems

The  $^1H$  nucleus *is* NMR active

magnetic effect on her compass would be *different* to another molecule

into *two* peaks of almost equal intensity; this is called a *doublet*.

The chemical shift of that carbon is *exactly at the center of* these resonances.

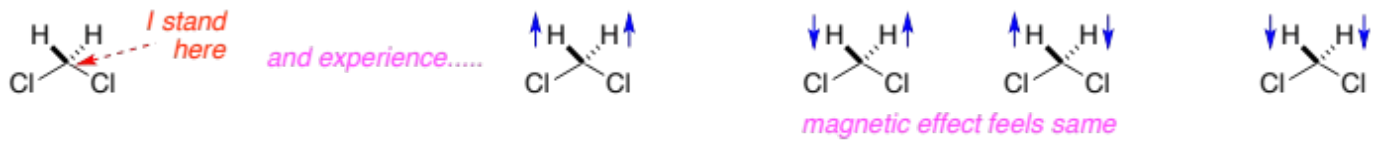
$^{13}C$  NMR spectra the effects of *coupling* with protons with protons in the molecule are completely

$^{13}C$  spectra of  $^{13}CHCl_3$  and  $^{13}CCl_4$  then we would see a *doublet and a singlet*, respectively.

In that experiment it *would* be possible to distinguish between  $^{13}CHCl_3$  and  $^{13}CCl_4$

### $^{13}\text{C}_2\text{H}_2$ Spin Systems

Energetically, the effect is *the same* for the *ao* and *oa* cases.



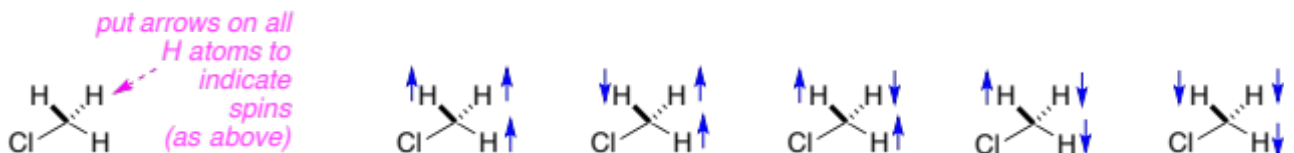
3 different magnetic field strengths influence that  $^{13}\text{C}$ , ratio 1:2:1

experiencing *three* different magnetic fields and the relative probability is 1:2:1.

$^{13}\text{CH}_2\text{Cl}_2$  would show a *triplet* for the carbon and it *could* be differentiated from  $^{13}\text{CHCl}_3$  and  $^{13}\text{CCl}_4$

### $^{13}\text{CH}_3$ Spin Systems

$^{13}\text{CH}_3\text{Cl}$  would show a *quartet* for the carbon and it *could* thus be differentiated from



4 different magnetic field strengths influence that  $^{13}\text{C}$ , ratio 1:3:3:1

The relative probabilities for finding the spins in a or o states is 1:3:3:1.

it will be split into  $n + 1$  peaks.

the number  $n$  refers to the number of nuclei *doing the splitting* and not those *being observed*.

The relative intensities of these peaks *follows Pascal's triangle*.

$^{13}\text{C}$  atoms adjacent to each other in a chain are *rare* and *can* be ignored.

## Differentiating CH, CH<sub>2</sub>, And CH<sub>3</sub> In <sup>13</sup>C Spectra



splitting pattern is called the *coupling* constant and it is expressed in *Hz*.

as chemical shift differences would be the *different* on machines operating at different field strengths they are *never* quoted in this way.

DEPT Spectra To Differentiate Quaternary, Methine-, Methylene-, and Methyl-Carbons  
Carbons with no hydrogen atoms on them, *quaternary*, *do not* show up in DEPT spectra.

DEPT 135 spectra are usually presented with CH & CH<sub>3</sub> *positive* peaks,  
and resonances for CH<sub>2</sub> carbons *negative*.

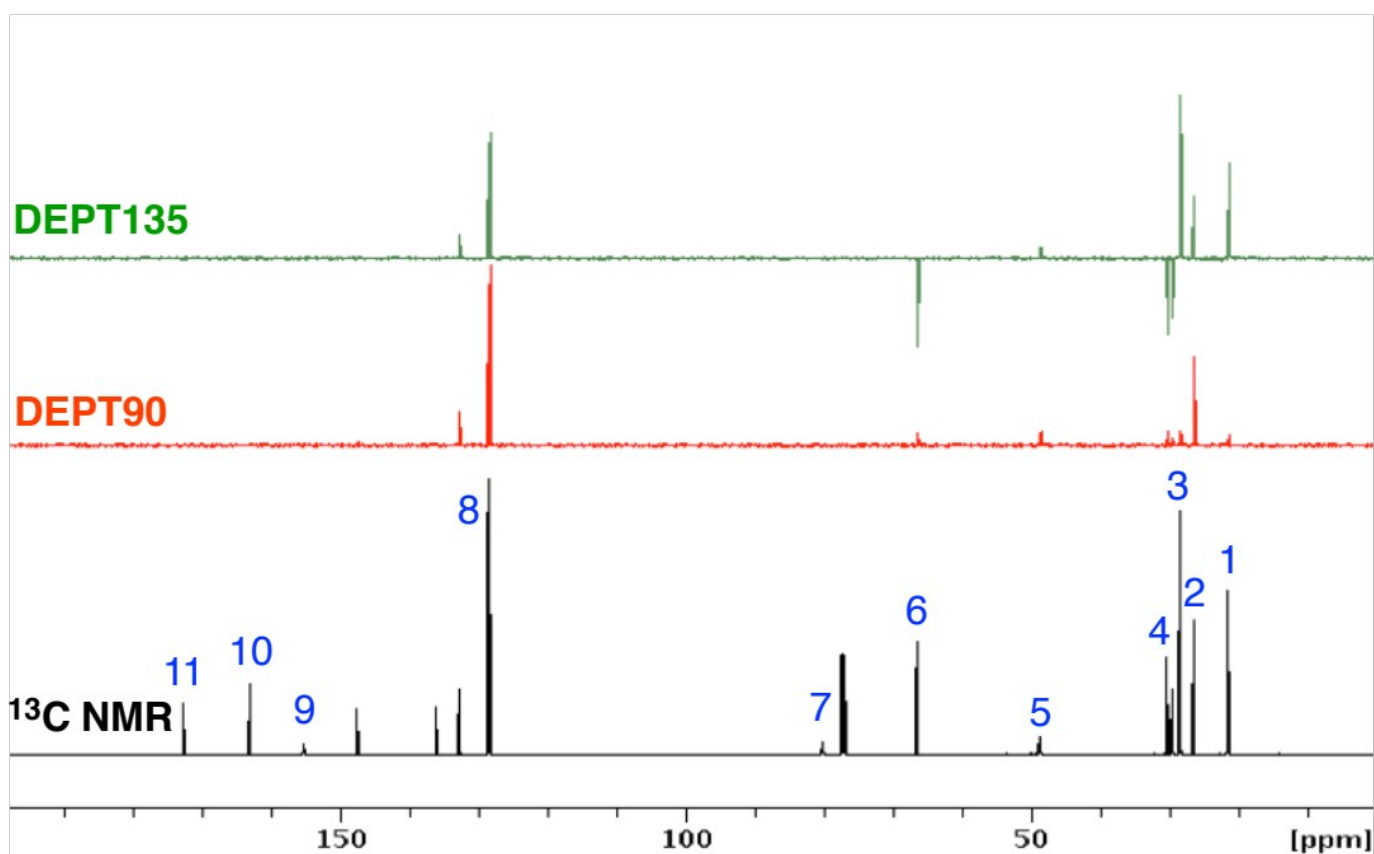
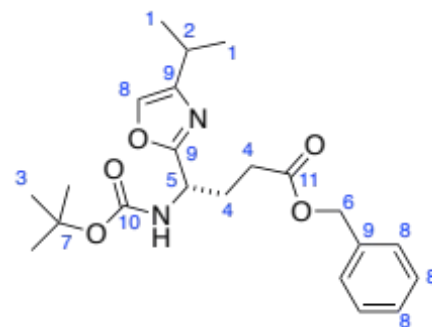
DEPT 90 spectra only show *CH* peaks.

Variations of DEPT *can* allow CH & CH<sub>3</sub> groups to be differentiated

DEPT is a *more* effective way of differentiating methyl, methylene, methane, and quaternary



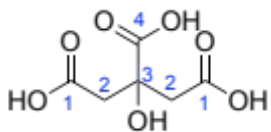
(Some inequivalent carbon atoms are given the same number if they are indistinguishable in the spectra, eg C<sup>4</sup>, C<sup>8</sup> and C<sup>9</sup>).



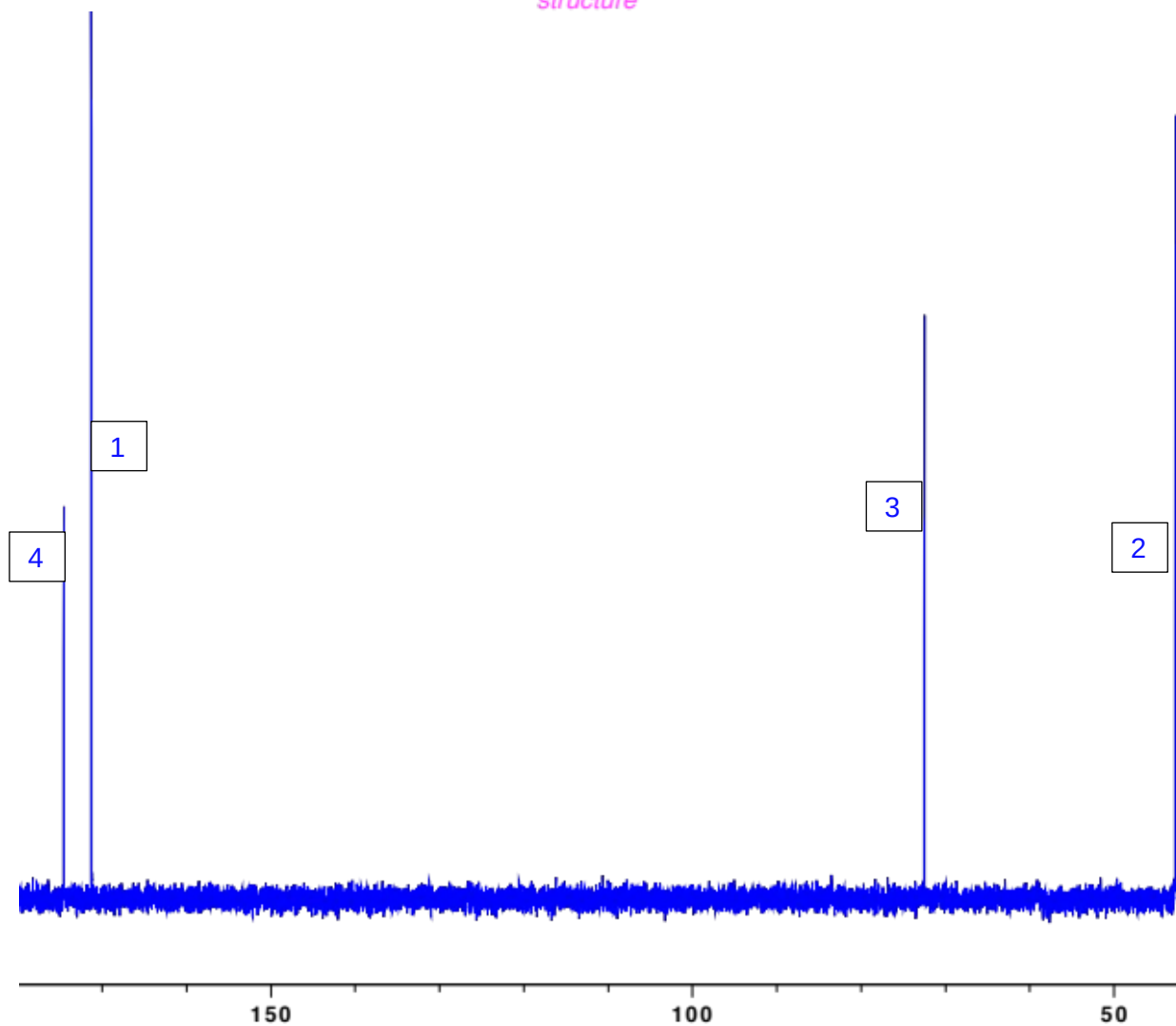
proton-proton couplings in <sup>1</sup>H NMR spectra are *nearly always shown*.

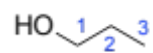
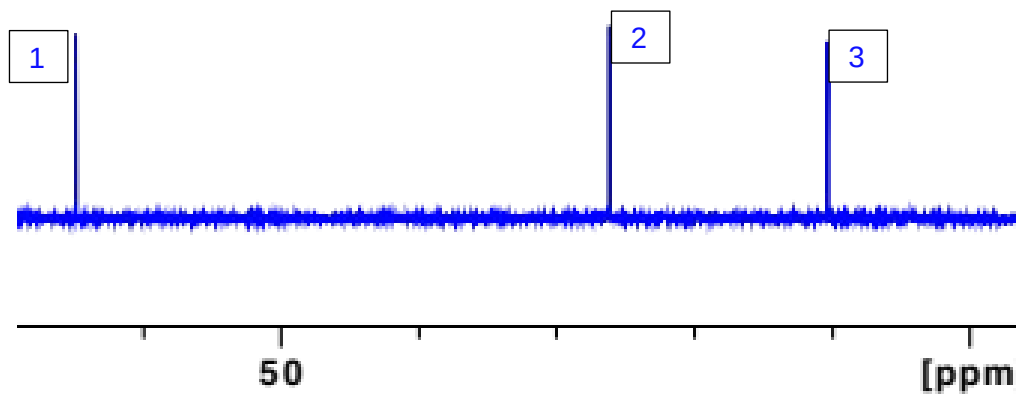
spectroscopy can correlate <sup>13</sup>C- with *<sup>1</sup>H-NMR signals of the protons attached to them*.

## F. Some Problems Involving Interpretation Of $^{13}\text{C}$ Spectra

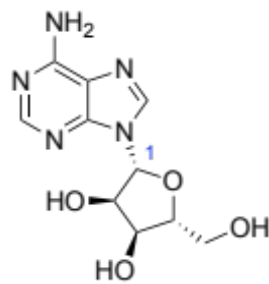


*structure*

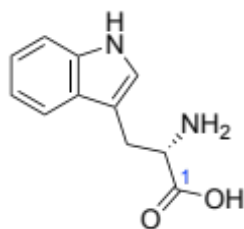
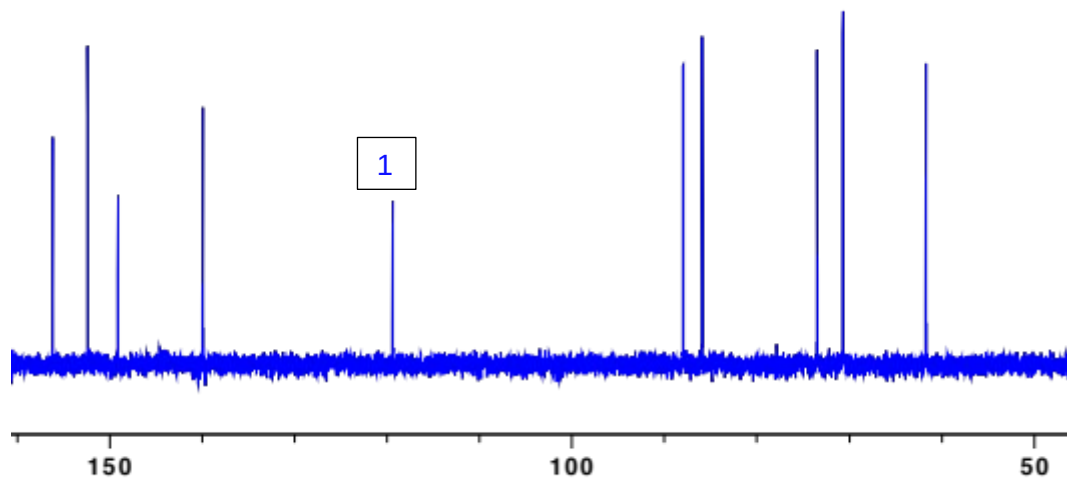




structure



structure



structure

