$^1H/^{13}C$ NMR SPECTROSCOPY

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^{1}H NMR SPECTROSCOPY

Nuclear Magnetic Resonance Spectroscopy

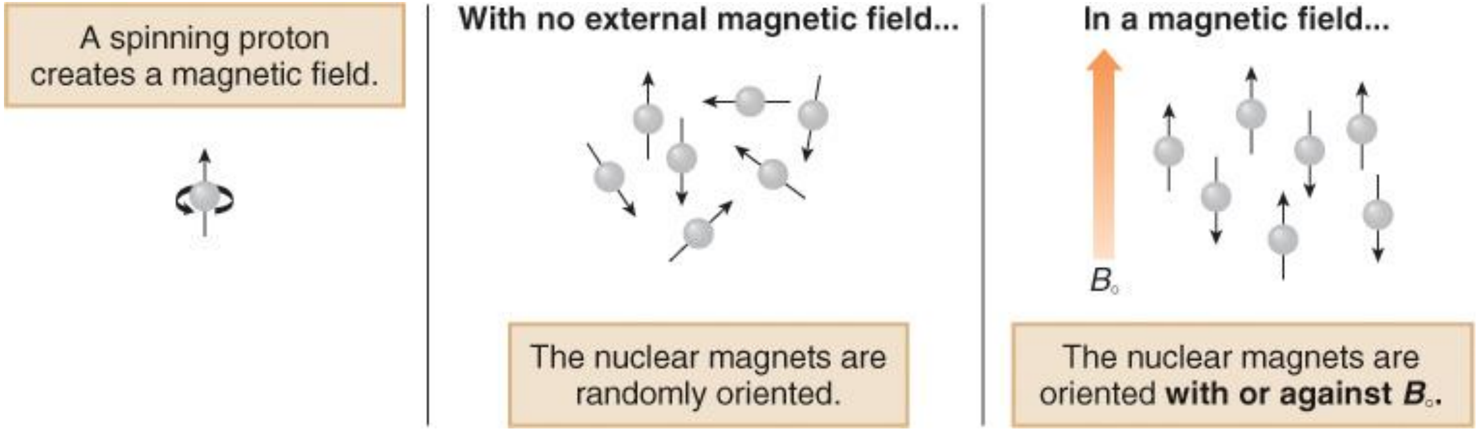
Introduction to NMR Spectroscopy

- **Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.**
- **Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of H atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.**
- **The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.**
- **When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ^{1}H and ^{13}C.**

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- **When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.**
- **Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0, they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.**
- **The energy difference between these two states is very small (<0.1 cal).**



Nuclear Magnetic Resonance

Nuclear spin

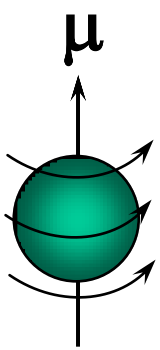
$$\mu = \gamma \, I \, h$$

μ - magnetic moment

γ - gyromagnetic ratio

I - spin quantum number

h - Planck’s constant



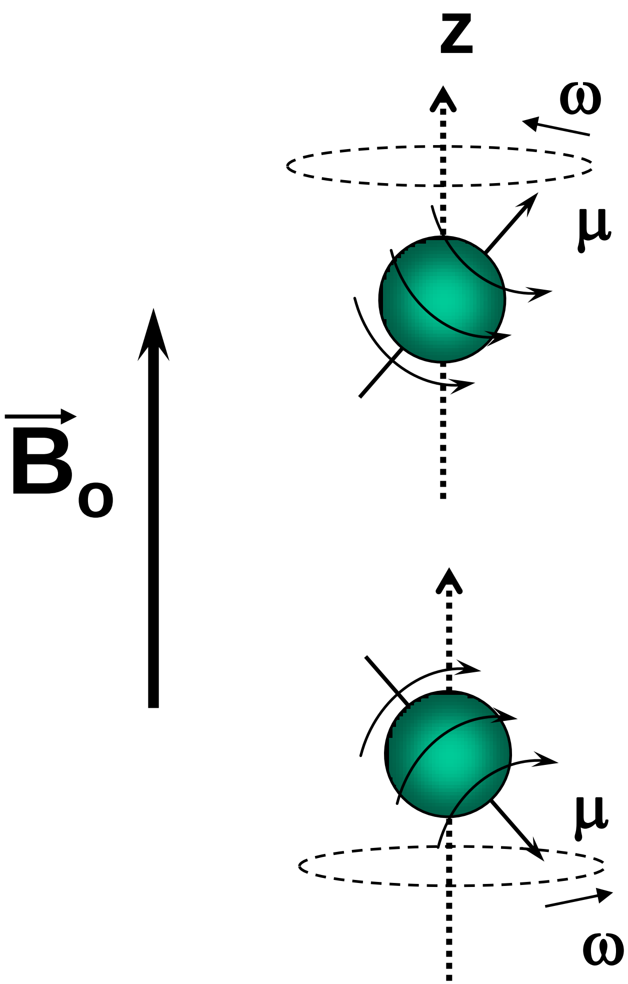
I is a property of the nucleus

Mass #	Atomic #	I
Odd	Even or odd	1/2, 3/2, 5/2,…
Even	Even	0
Even	Odd	1, 2, 3

As an exercise determine I for each of the following ^{12}C, ^{13}C, ^{1}H, ^{2}H, ^{15}N .

Apply an external magnetic field

(i.e., put your sample in the magnet)



$\omega = \gamma B_o = \nu / 2\pi$

ω - resonance frequency
in radians per second,
also called Larmor frequency

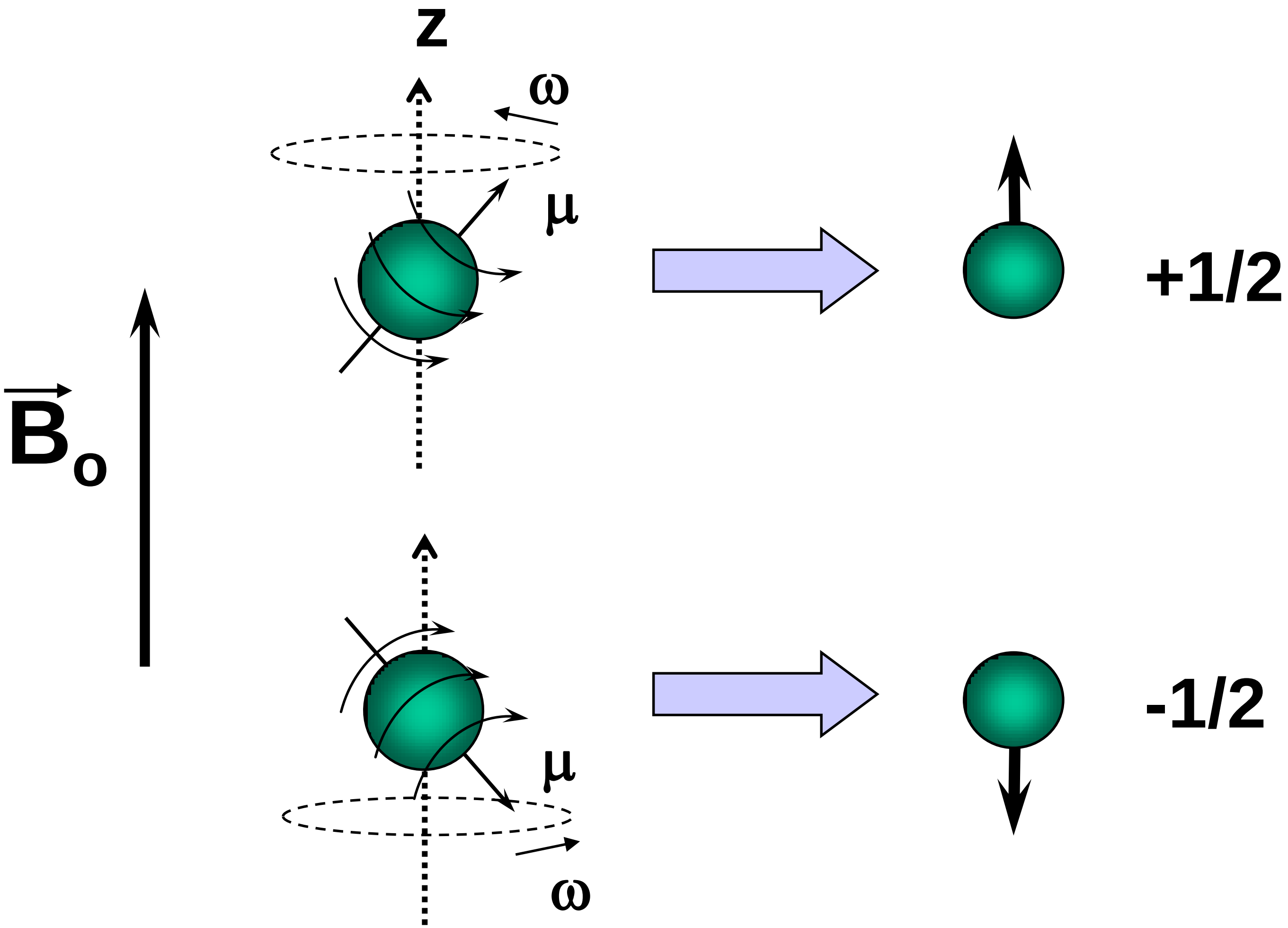
ν - resonance frequency
in cycles per second, Hz

γ - gyromagnetic ratio

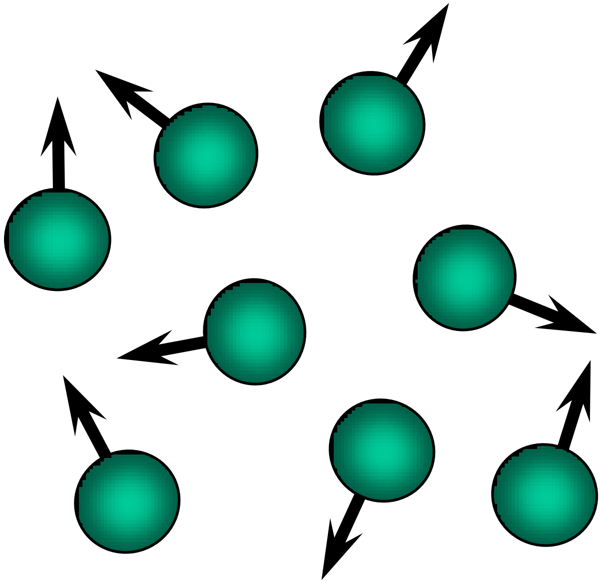
B_o - external magnetic
field (the magnet)

Spin 1/2 nuclei will have two orientations in a magnetic field +1/2 and -1/2.

Net magnetic moment

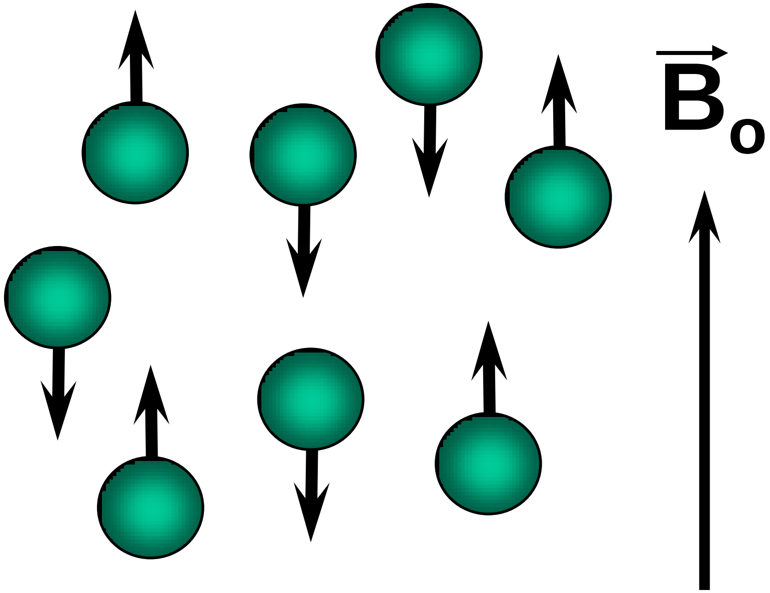


Ensemble of Nuclear Spins



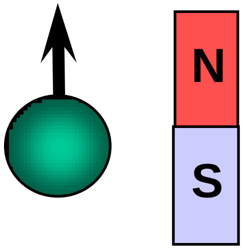
$\vec{B}_o = 0$

Randomly oriented



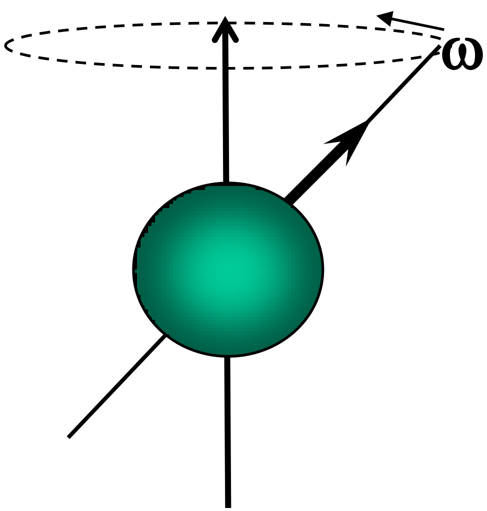
$\vec{B}_o > 0$

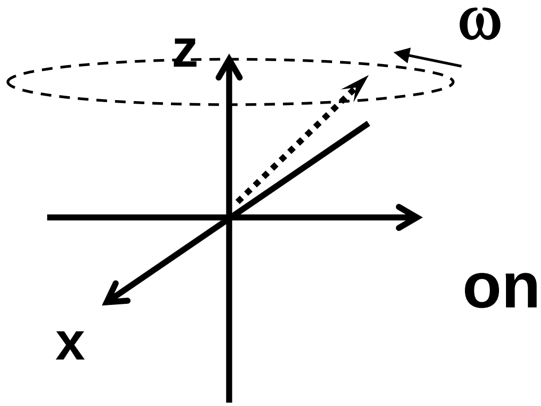
Highly oriented



Each nucleus behaves like a bar magnet.

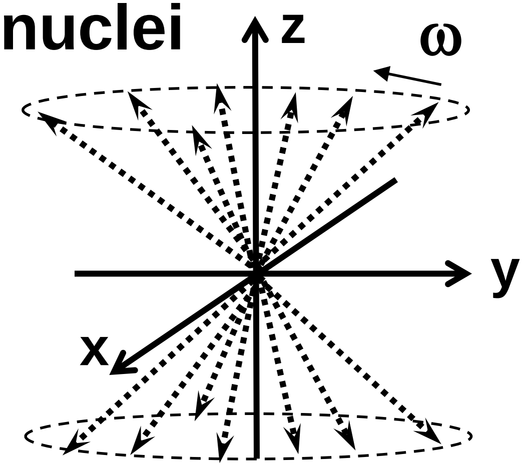
The net magnetization vector



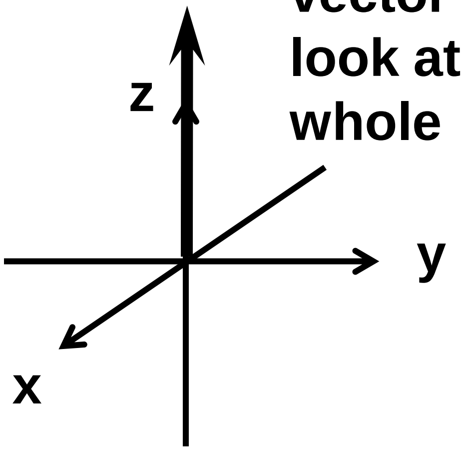


one nucleus

many nuclei

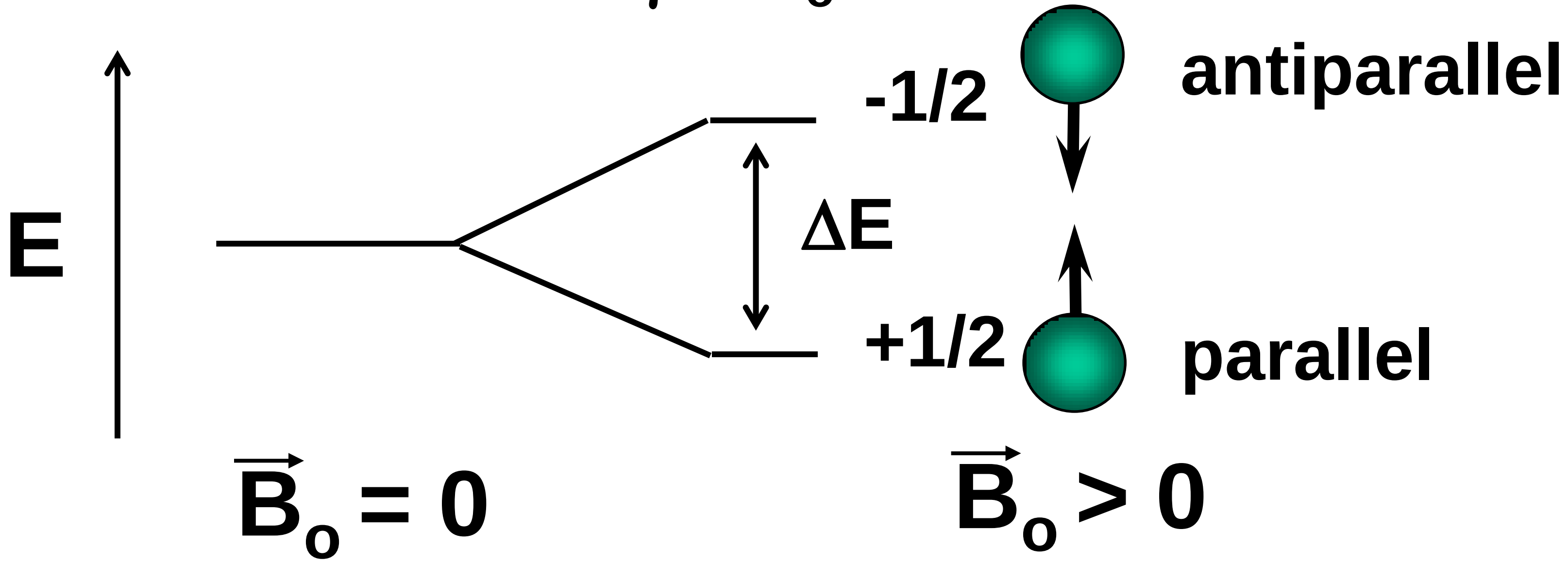


M_o - net magnetization vector allows us to look at system as a whole



Allowed Energy States for a Spin 1/2 System

$$\Delta E = \gamma\, h\, \vec{B}_o = h\, \nu$$



E

-1/2

antiparallel

ΔE

+1/2

parallel

$\vec{B}_o = 0$

$\vec{B}_o > 0$

Therefore, the nuclei will absorb light with energy ΔE resulting in a change of the spin states.

Nuclear Magnetic Resonance Spectroscopy

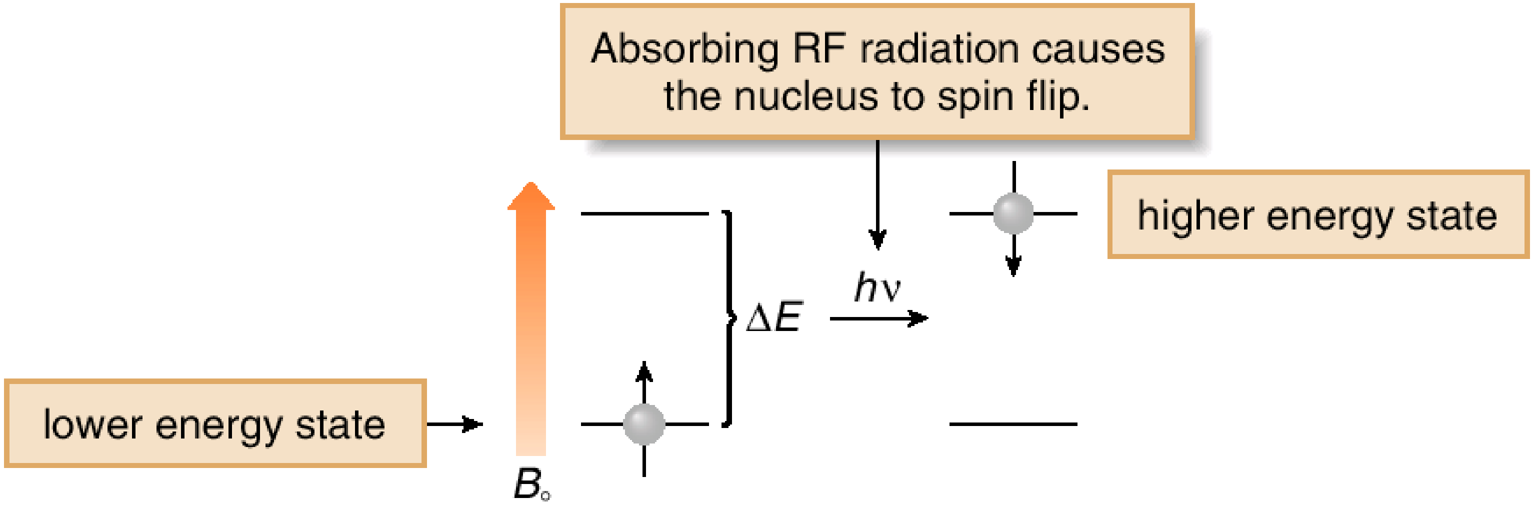
Introduction to NMR Spectroscopy

- **In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B_0, and a higher energy state in which the nucleus aligned against B_0.**
- **When an external energy source ($h\nu$) that matches the energy difference (ΔE) between these two states is applied, energy is absorbed, causing the nucleus to "spin flip" from one orientation to another.**
- **The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.**

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- Thus, two variables characterize NMR: an applied magnetic field B_0, the strength of which is measured in tesla (T), and the frequency ν of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).


Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

lower energy state

- A nucleus is in *resonance* when it absorbs RF radiation and "spin flips" to a higher energy state.

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

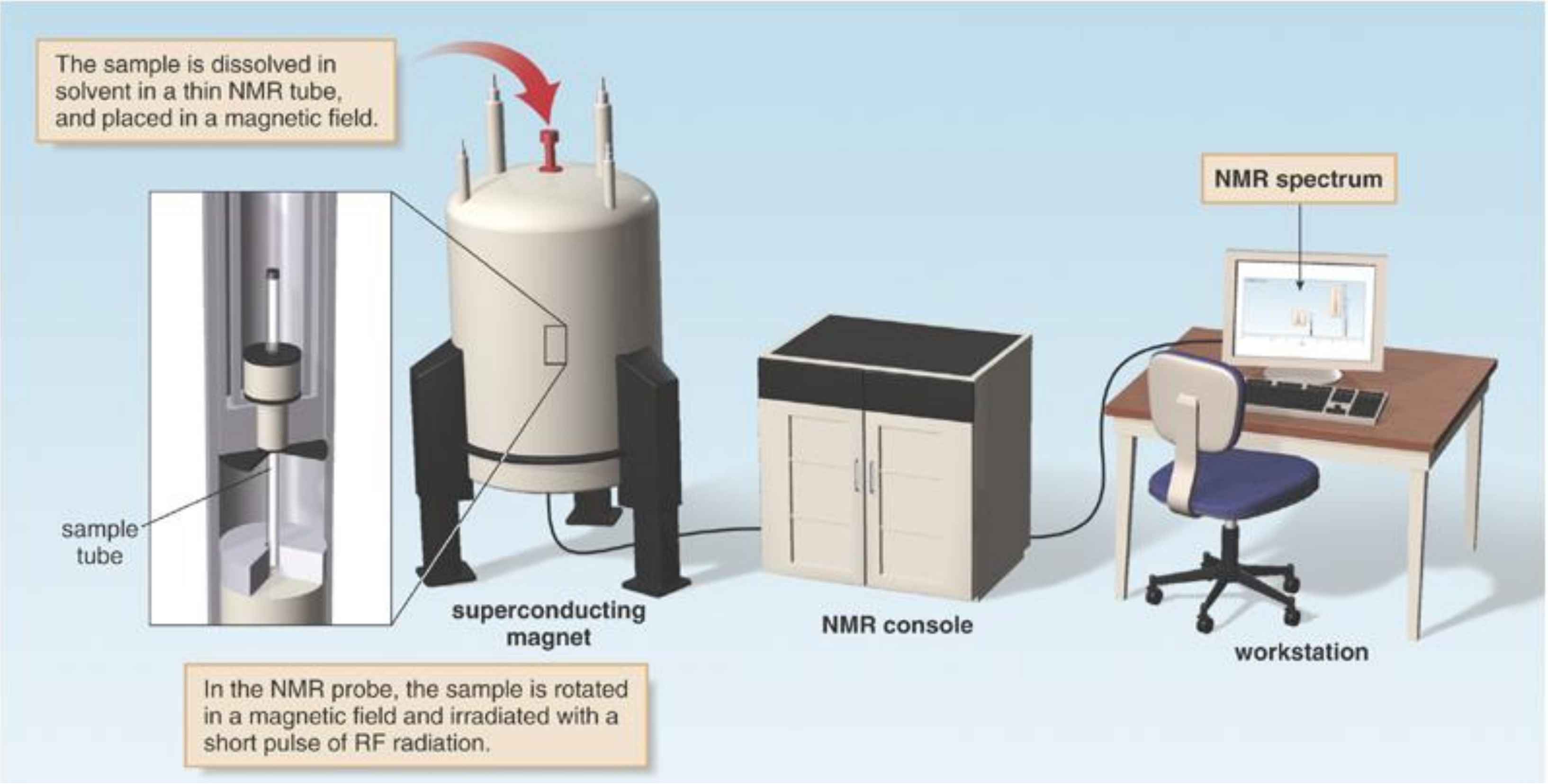
- The frequency needed for resonance and the applied magnetic field strength are proportionally related.

- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.
- These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

Schematic of an NMR spectrometer



The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.

In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.

An NMR spectrometer. The sample is dissolved in a solvent, usually $CDCl_3$ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

Nuclear Magnetic Resonance Spectroscopy

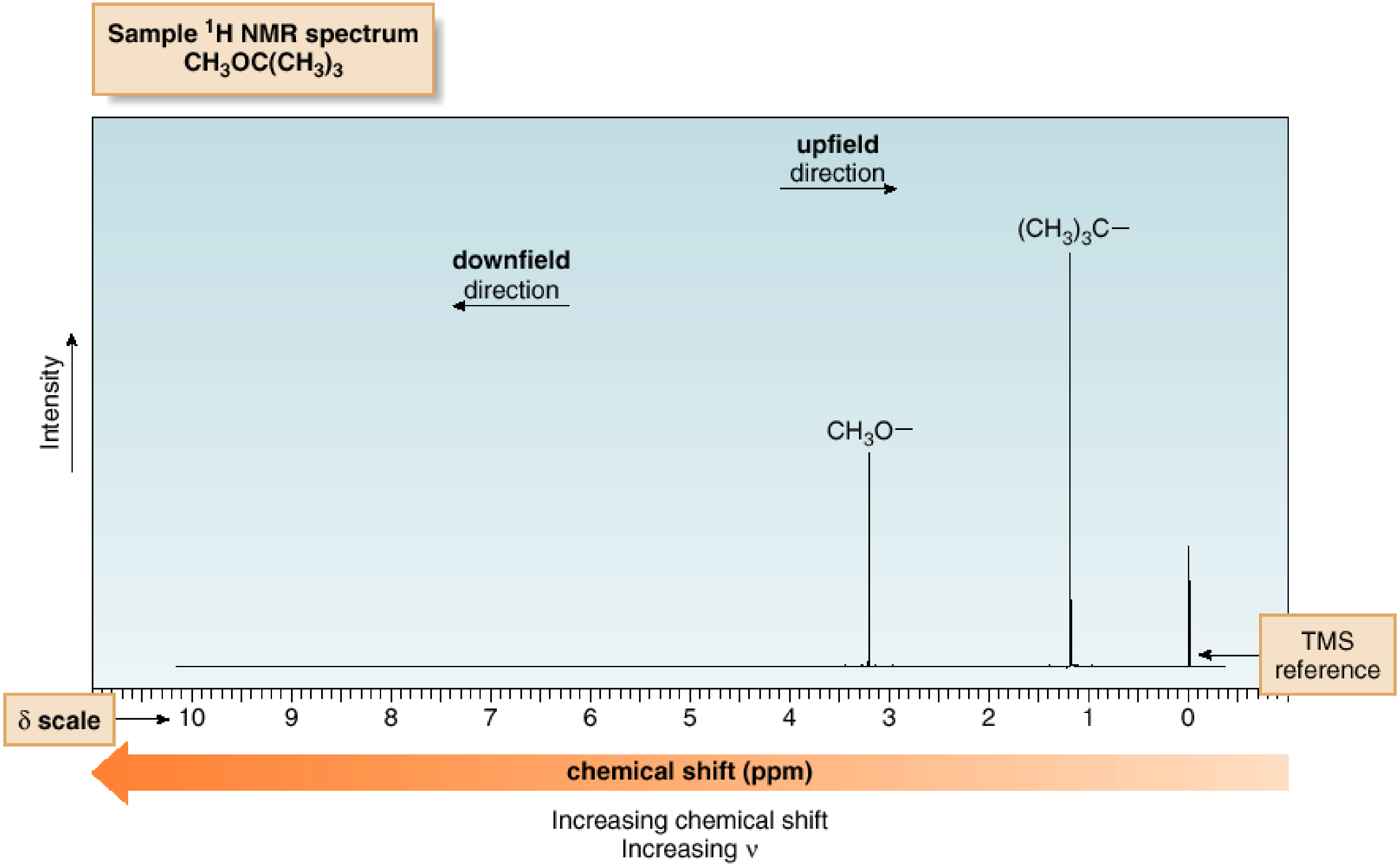
Introduction to NMR Spectroscopy

- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength B_0, and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as ^{1}H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^{2}H and ^{14}N) give rise to NMR signals.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—The Spectrum

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).



Nuclear Magnetic Resonance Spectroscopy

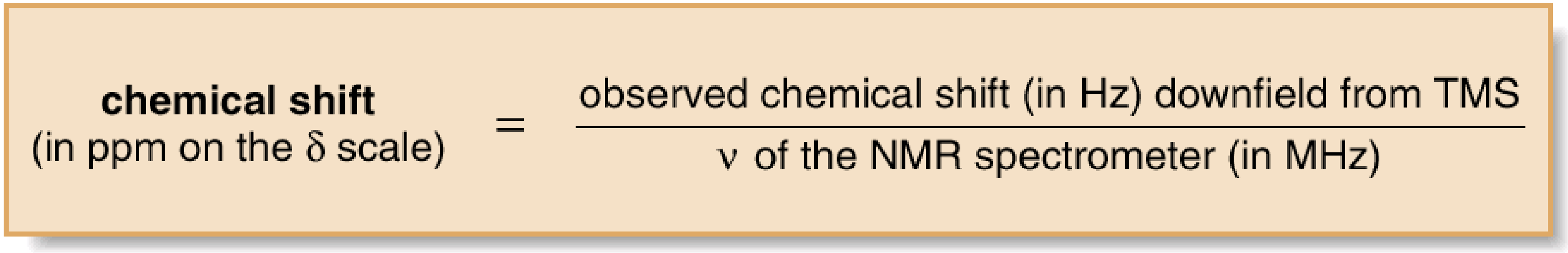
^{1}H NMR—The Spectrum

- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from right to left.
- Most protons absorb between 0-10 ppm.
- The terms “upfield” and “downfield” describe the relative location of peaks. Upfield means to the right. Downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—The Spectrum

- The chemical shift of the *x* axis gives the position of an NMR signal, measured in ppm, according to the following equation:



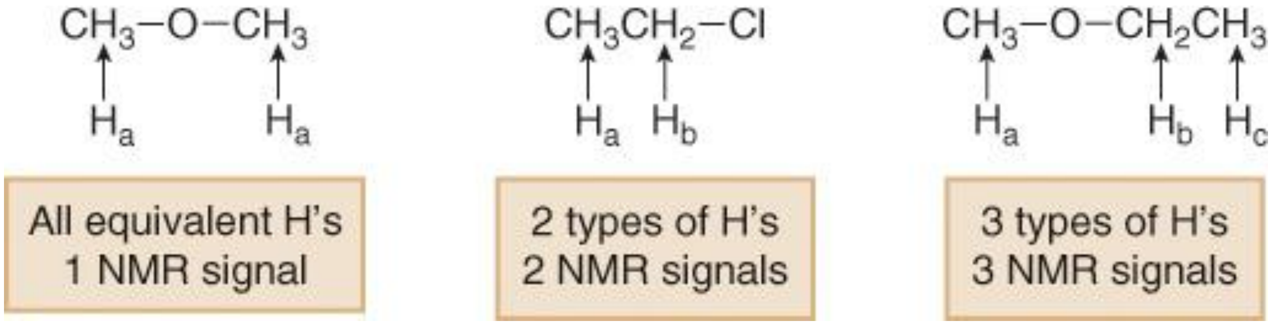
$$\text{chemical shift (in ppm on the } \delta \text{ scale)} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}$$

- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.
- Four different features of a ^{1}H NMR spectrum provide information about a compound’s structure:
  - a. Number of signals
  - b. Position of signals
  - c. Intensity of signals.
  - d. Spin-spin splitting of signals.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.

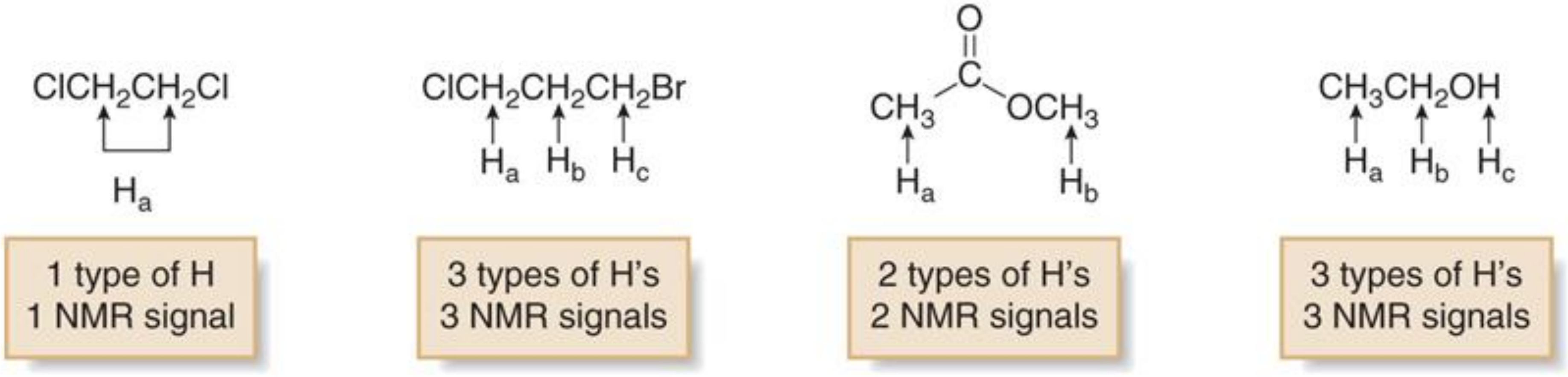


- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.

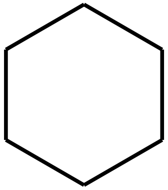
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

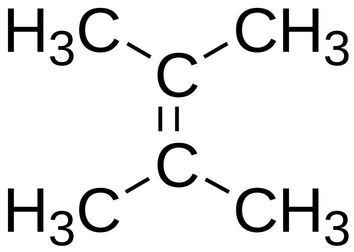
The number of ^{1}H NMR signals of some representative organic compounds



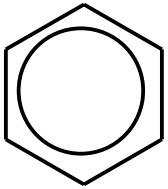
number of signals?



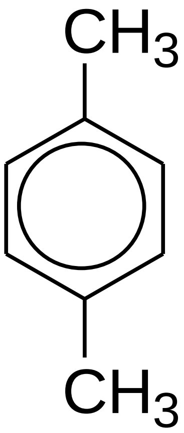
one



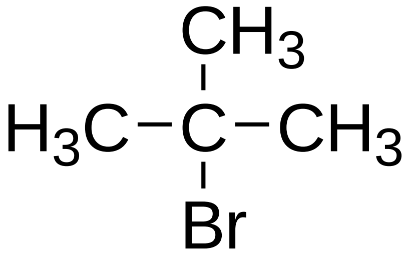
one



one



two



$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ Br \end{array}$$

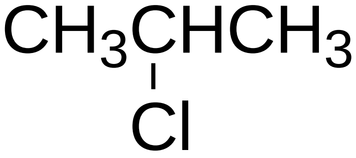
one

$CH_3CH_2\text{-}Br$

two

$CH_3CH_2CH_2\text{-}Br$

three



$$\begin{array}{c} CH_3CHCH_3 \\ | \\ Cl \end{array}$$

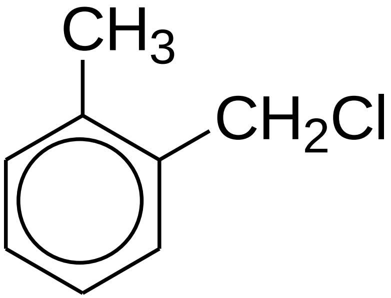
two

$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_2CH_3}$$

four

$Cl\text{-}CH_2CH_2CH_2\text{-}Cl$

two

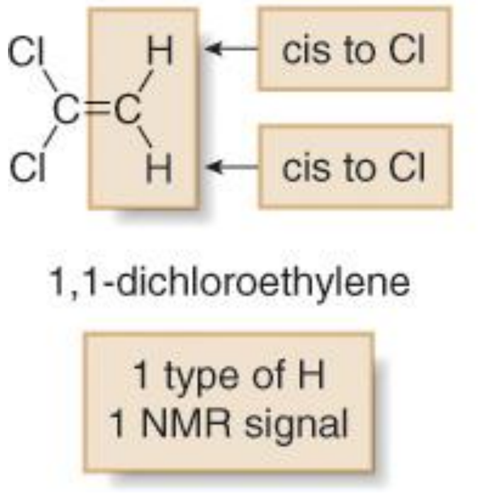


three

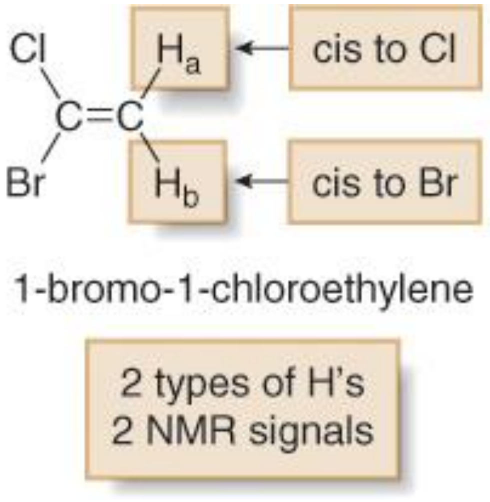
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

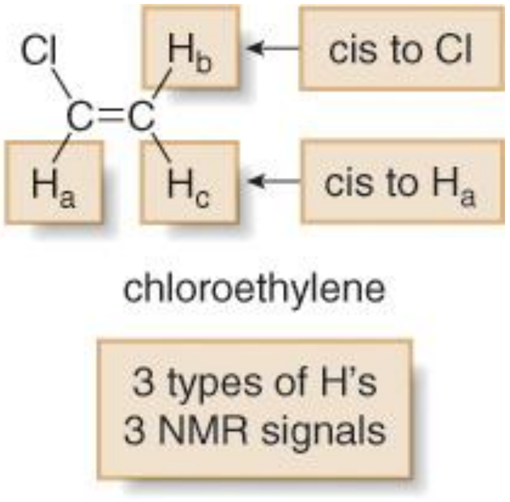
- In comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups.



1,1-dichloroethylene



1-bromo-1-chloroethylene

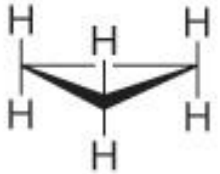


chloroethylene

Nuclear Magnetic Resonance Spectroscopy

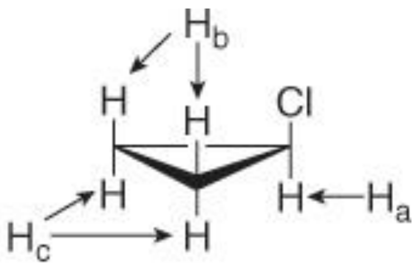
^{1}H NMR—Number of Signals

- Proton equivalency in cycloalkanes can be determined similarly.



cyclopropane

All H's are equivalent.
1 NMR signal

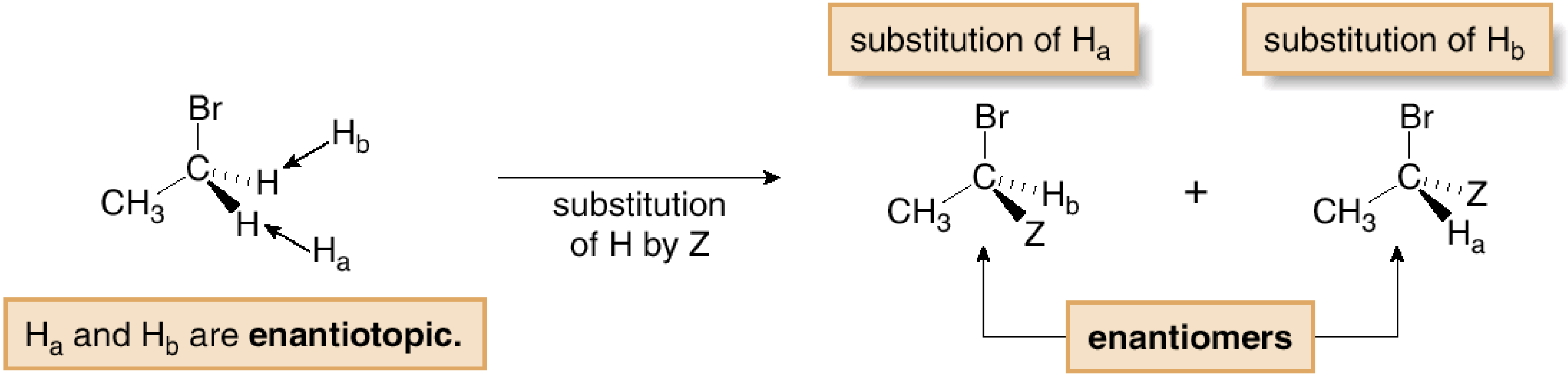


chlorocyclopropane

3 types of H's
3 NMR signals

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Enantiotopic Protons.



substitution of H by Z

substitution of H$_a$

substitution of H$_b$

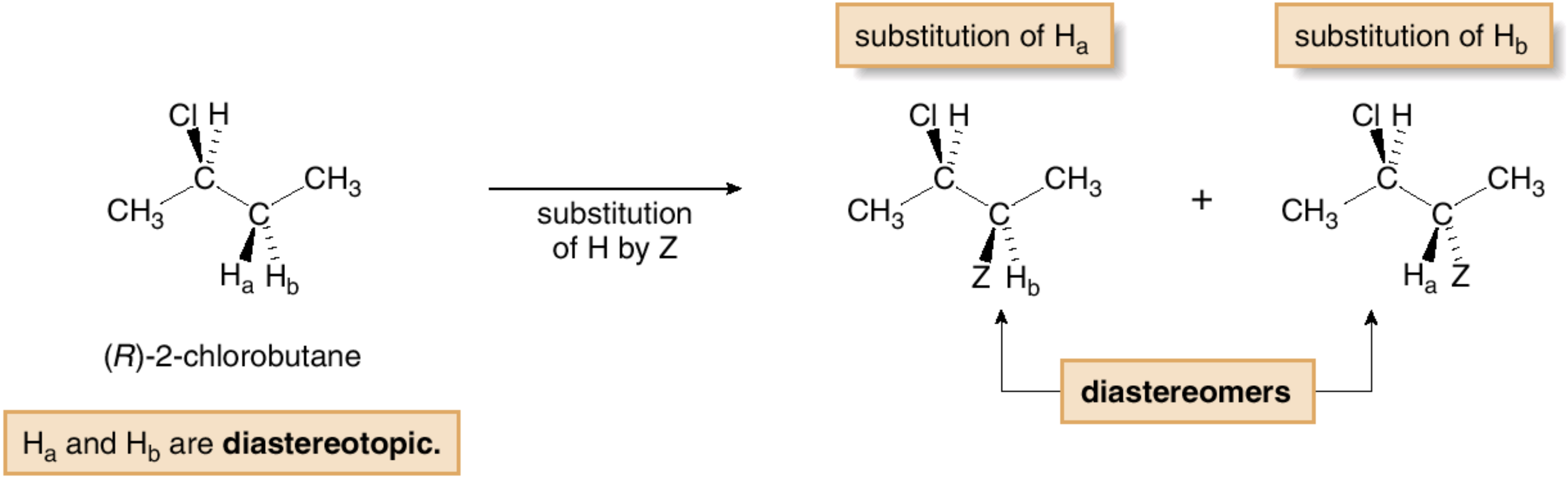
H$_a$ and H$_b$ are **enantiotopic.**

enantiomers

- When substitution of two H atoms by Z forms enantiomers, the two H atoms are equivalent and give a single NMR signal. These two H atoms are called *enantiotopic* protons.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR— Diastereotopic Protons.



(*R*)-2-chlorobutane

substitution of H_a

substitution of H_b

diastereomers

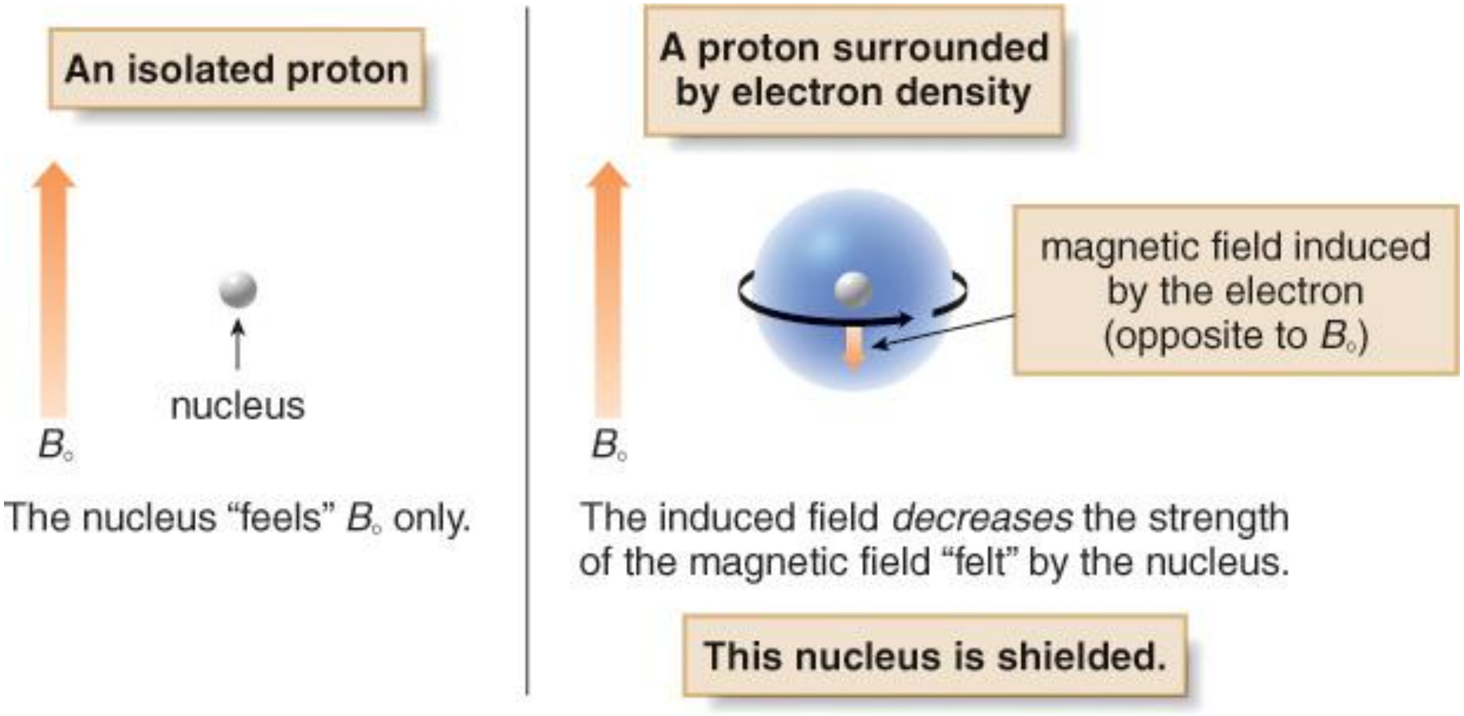
H_a and H_b are **diastereotopic.**

- When substitution of two H atoms by Z forms diastereomers, the two H atoms are not equivalent, and give two NMR signals. These two H atoms are called *diastereotopic* protons.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

- **In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton "feels".**
- **Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward a lower chemical shift, so shielding shifts the absorption upfield.**



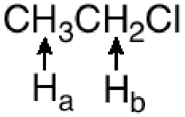
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

- The less shielded the nucleus becomes, the more of the applied magnetic field (B_0) it feels.
- This deshielded nucleus experiences a higher magnetic field strength, to it needs a higher frequency to achieve resonance.
- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so deshielding shifts an absorption downfield.
- Protons near electronegative atoms are deshielded, so they absorb downfield.

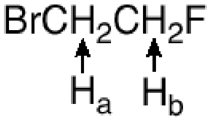
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals



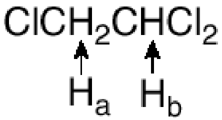
$\mathrm{CH_3CH_2Cl}$

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.



$\mathrm{BrCH_2CH_2F}$

- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**



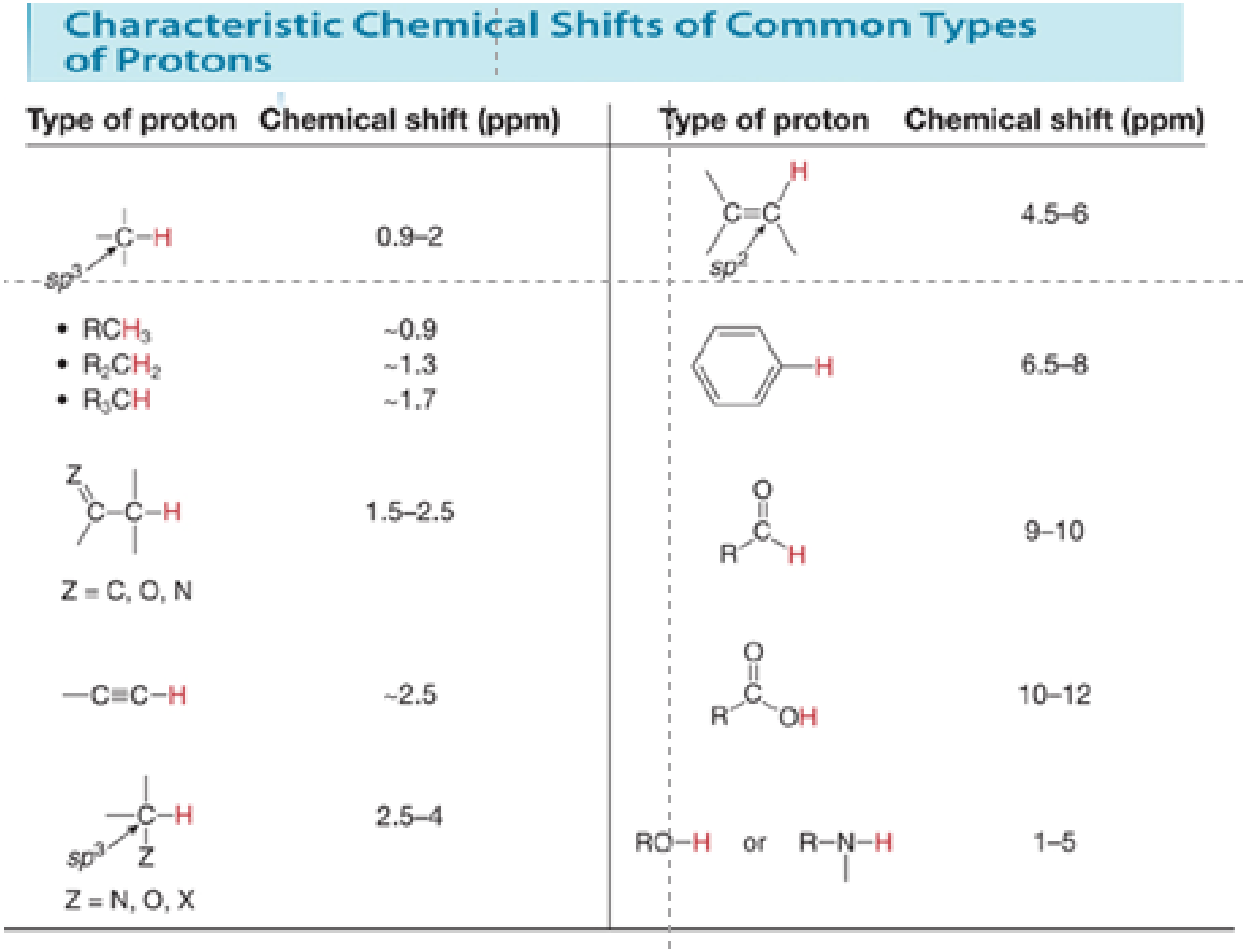
$\mathrm{ClCH_2CHCl_2}$

- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- **Protons in a given environment absorb in a predictable region in an NMR spectrum.**



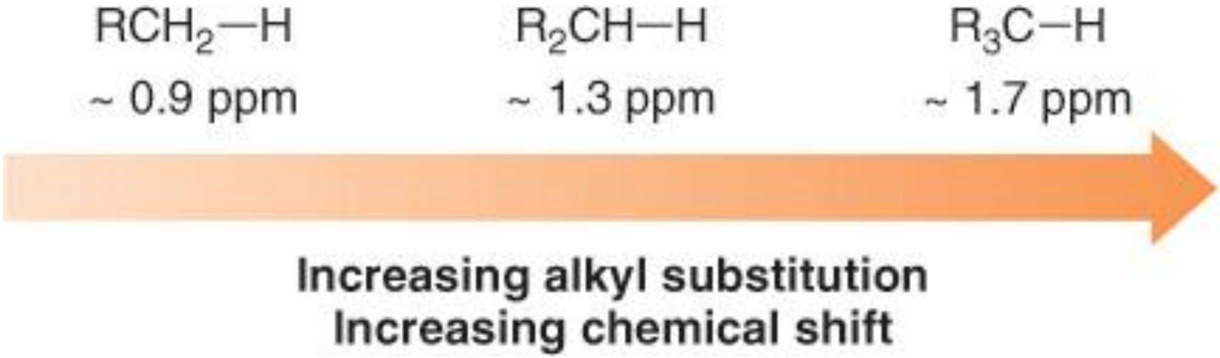
Characteristic Chemical Shifts of Common Types of Protons

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
$-C-H$ (sp^3)	0.9–2	$C=C$–H (sp^2)	4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7	C_6H_5–H	6.5–8
$Z=C-C-H$ Z = C, O, N	1.5–2.5	$RCHO$	9–10
$-C\equiv C-H$	~2.5	$RCOOH$	10–12
sp^3 $Z-C-H$ Z = N, O, X	2.5–4	RO–H or R–N–H	1–5

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

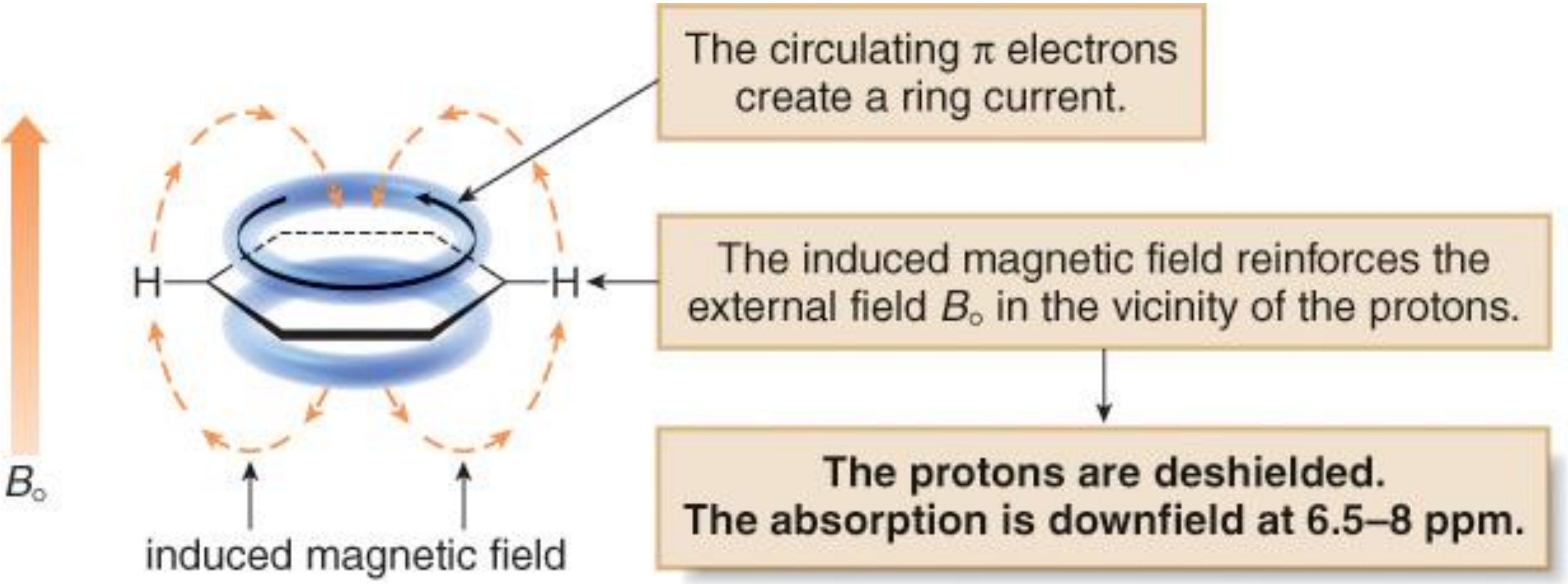
- The chemical shift of a C—H bond increases with increasing alkyl substitution.



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- In a magnetic field, the six π electrons in benzene circulate around the ring creating a ring current.
- The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons.
- The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.



The circulating π electrons create a ring current.

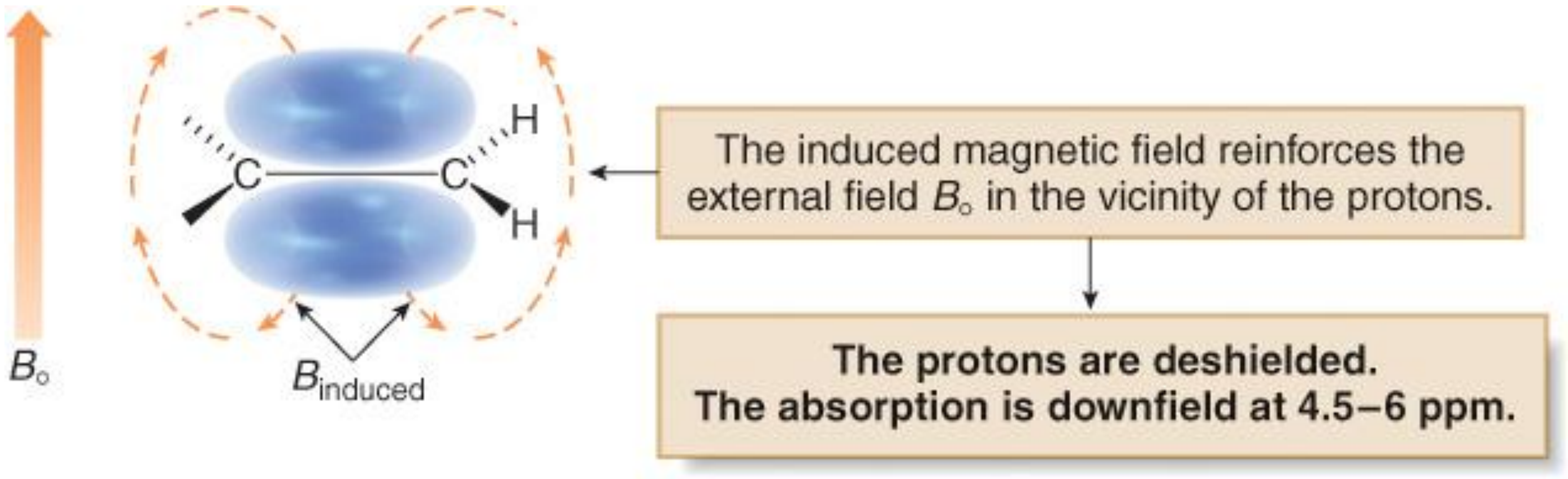
The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

**The protons are deshielded.
The absorption is downfield at 6.5–8 ppm.**

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- In a magnetic field, the loosely held π electrons of the double bond create a magnetic field that reinforces the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.



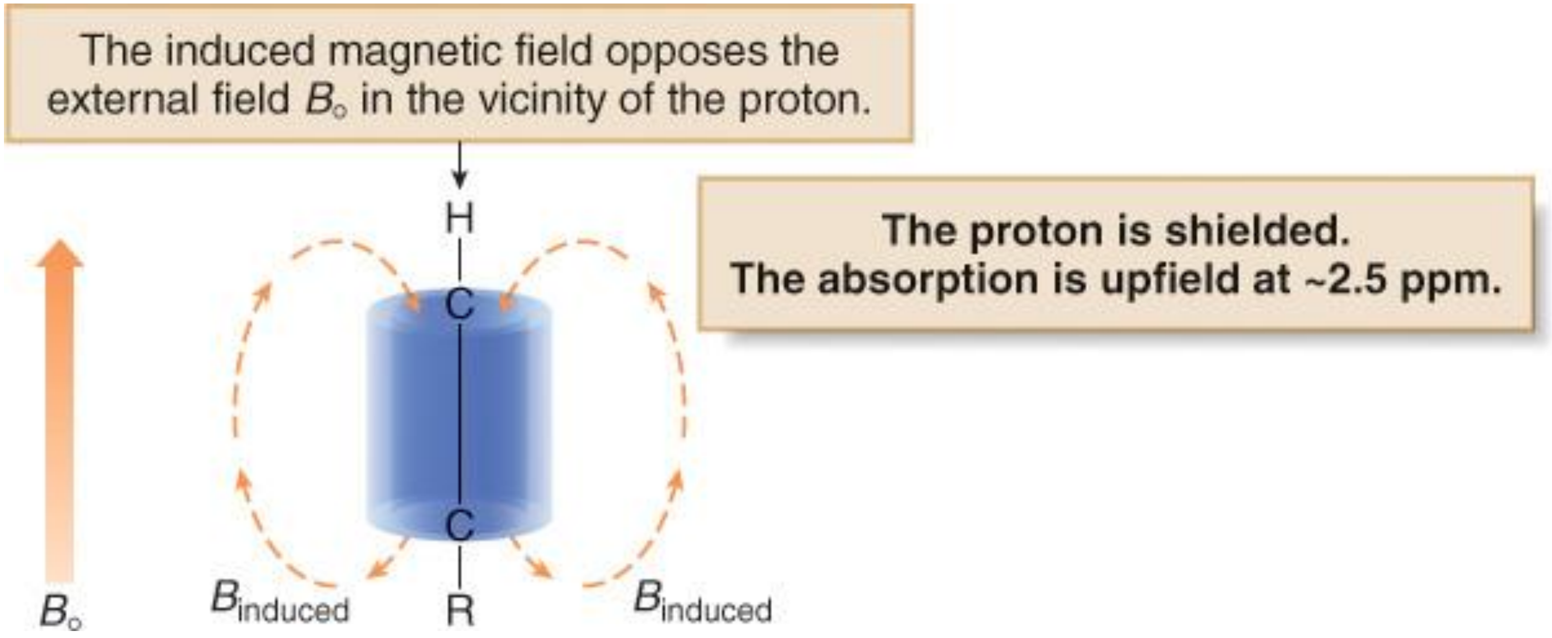
The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded.
The absorption is downfield at 4.5–6 ppm.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- In a magnetic field, the π electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field (B_0).
- Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.



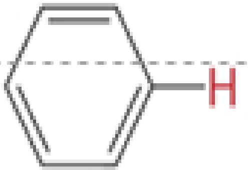
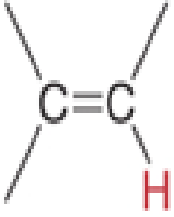
The induced magnetic field opposes the external field B_o in the vicinity of the proton.

The proton is shielded.
The absorption is upfield at ~2.5 ppm.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

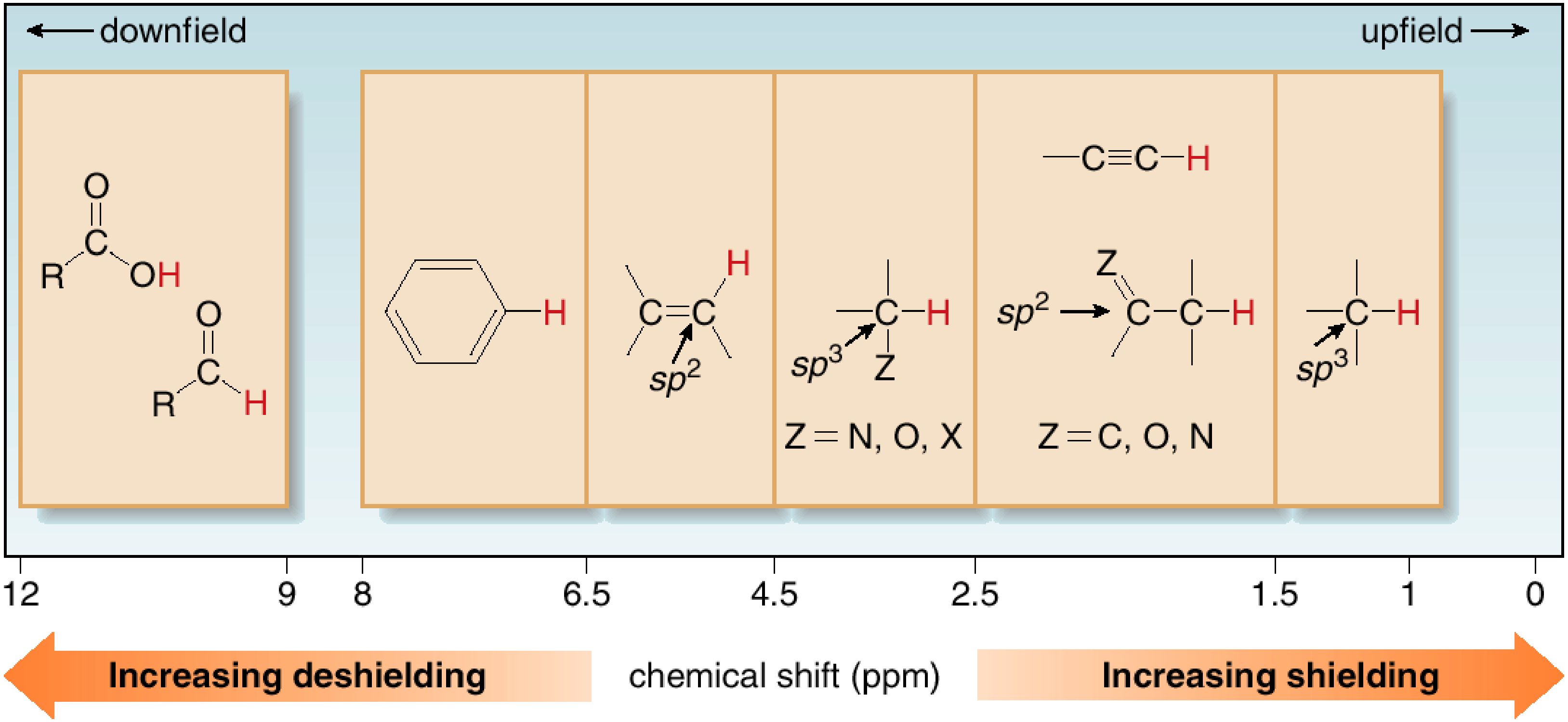
Effect of π Electrons on Chemical Shift Values

Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
$-C\equiv C-H$	shielded	~2.5

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values)

Regions in the ^{1}H NMR spectrum



- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

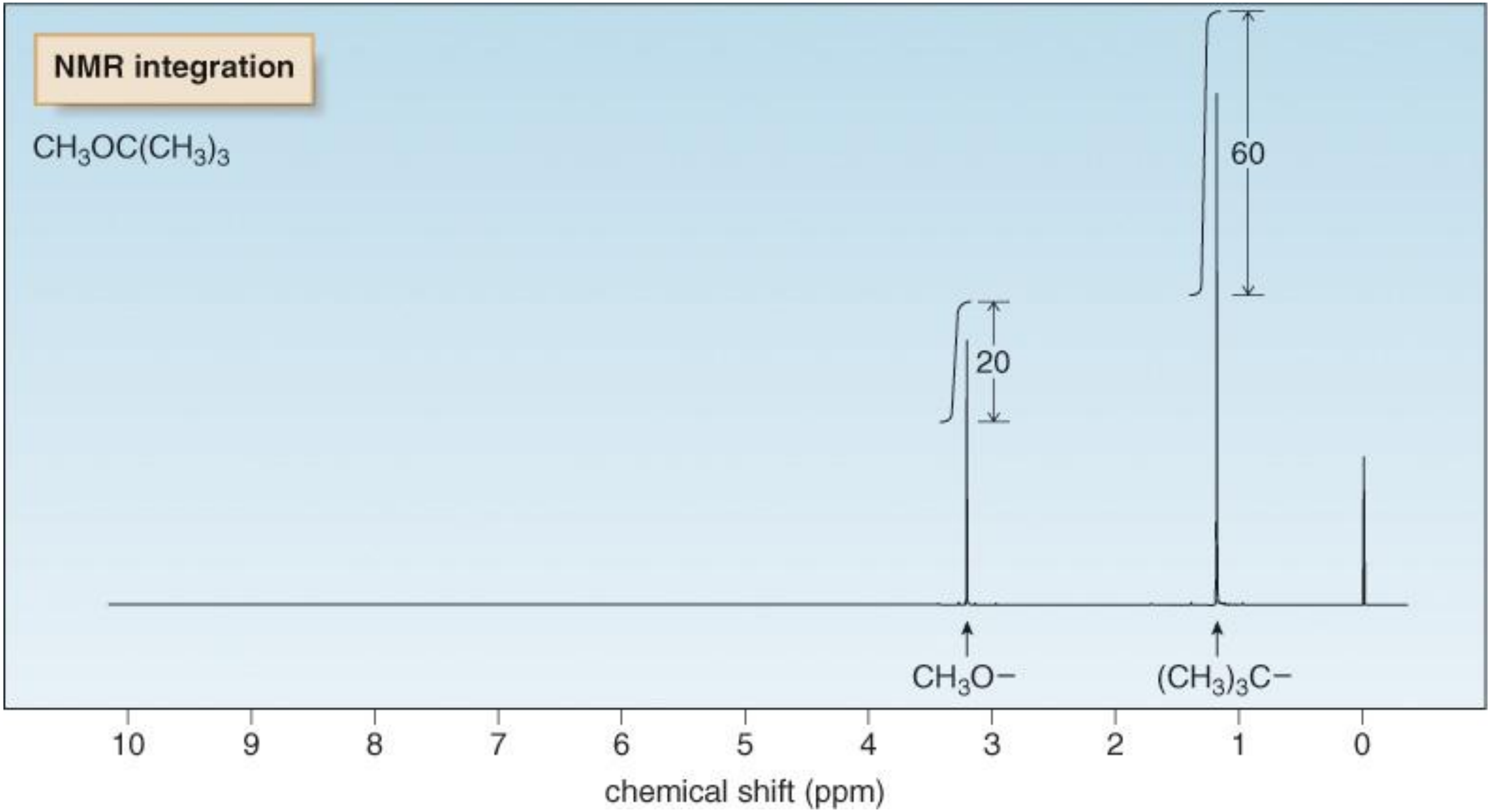
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Intensity of Signals

- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.
- The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.
- Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.
- The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.

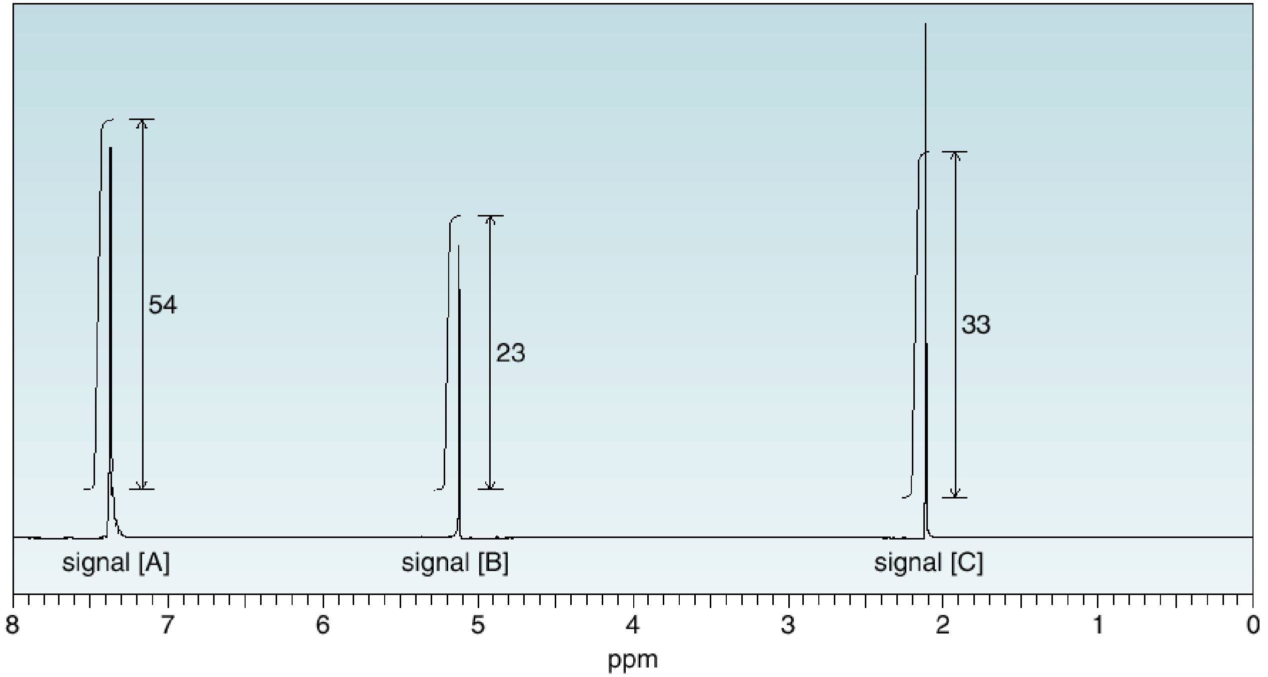
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Intensity of Signals



How To Determine the Number of Protons Giving Rise to an NMR Signal

Example A compound of molecular formula $C_9H_{10}O_2$ gives the following integrated ^1H NMR spectrum. How many protons give rise to each signal?



Step [1] **Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.**

- Total number of integration units: 54 + 23 + 33 = 110 units
- Total number of protons = 10
- Divide: 110 units/10 protons = **11 units per proton**

Step [2] **Determine the number of protons giving rise to each signal.**

- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

Signal [A]: $\frac{54}{11} = 4.9 \approx \boxed{5\ H}$

Signal [B]: $\frac{23}{11} = 2.1 \approx \boxed{2\ H}$

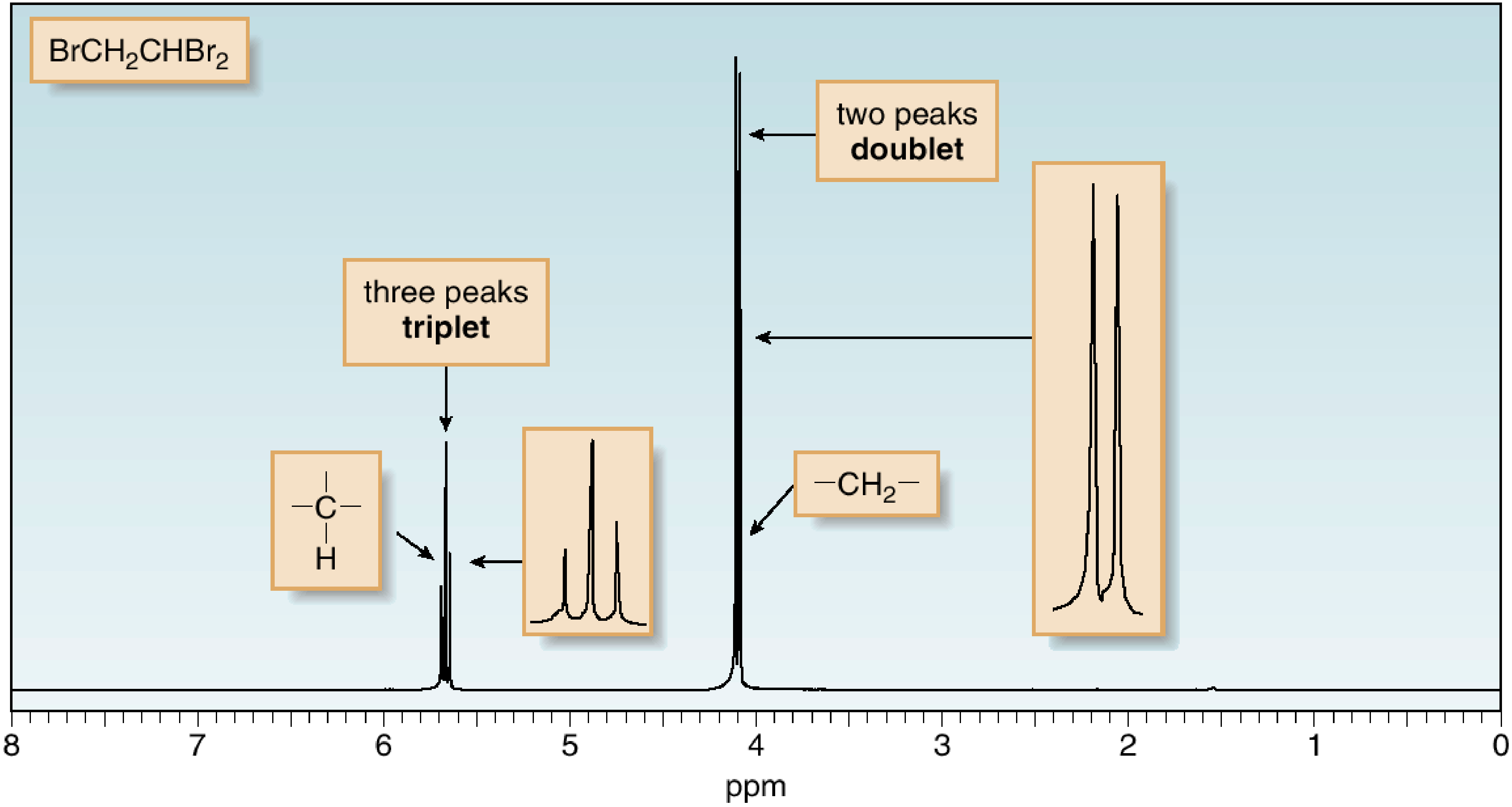
Signal [C]: $\frac{33}{11} = \boxed{3\ H}$

Answer: 5 H, 2 H, 3 H

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

- **Consider the spectrum below:**



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

- **Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.**

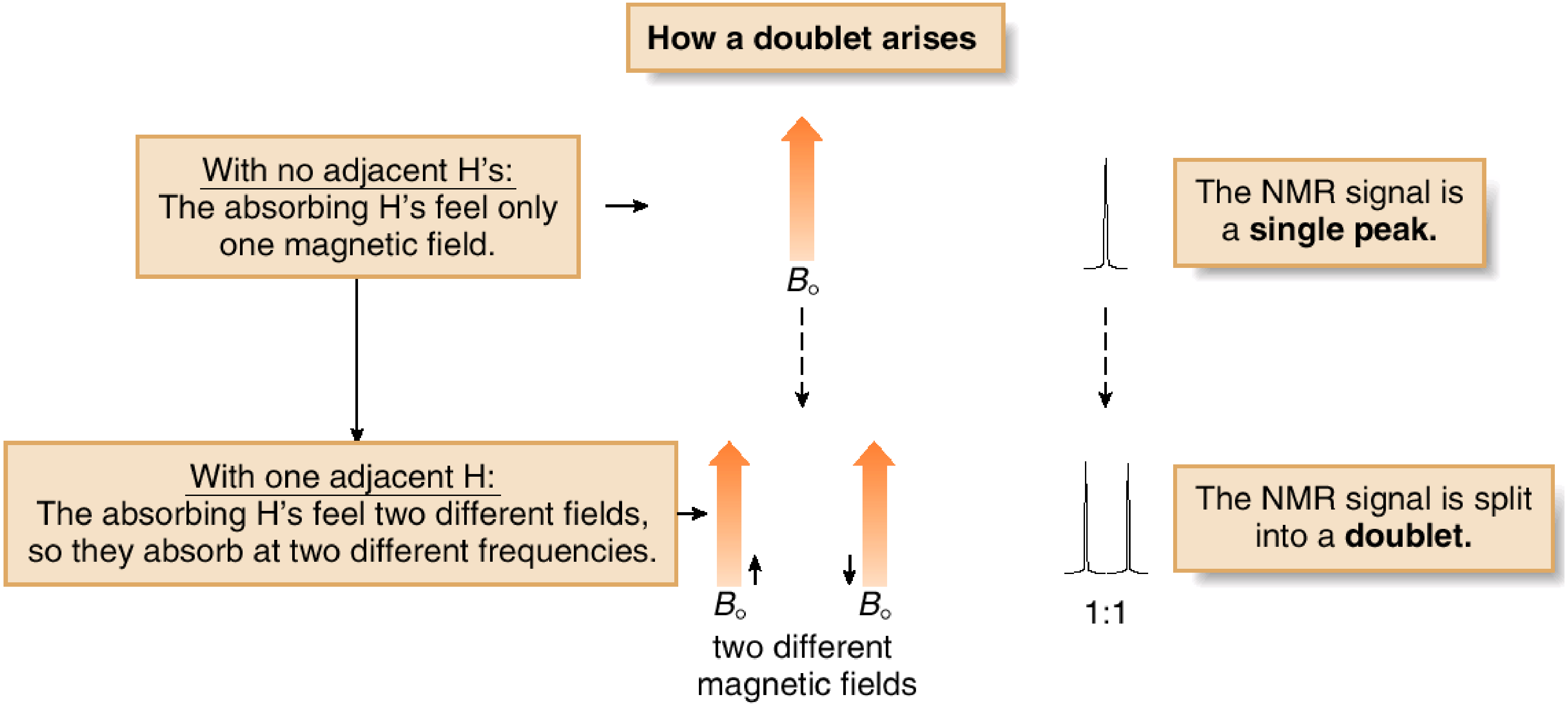
Let us consider how the doublet due to the CH_2 group on $BrCH_2CHBr_2$ occurs:

- **When placed in an applied electric field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0.**
- **Thus, the absorbing CH_2 protons feel two slightly different magnetic fields—one slightly larger than B_0, and one slightly smaller than B_0.**
- **Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.**

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

The frequency difference, measured in Hz between two peaks of the doublet is called the coupling constant, *J*.



How a doublet arises

With no adjacent H's:
The absorbing H's feel only one magnetic field.

The NMR signal is a **single peak.**

With one adjacent H:
The absorbing H's feel two different fields, so they absorb at two different frequencies.

The NMR signal is split into a **doublet.**

- One adjacent proton splits an NMR signal into a doublet.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

Let us now consider how a triplet arises:

- **When placed in an applied magnetic field (B_0), the adjacent protons H_a and H_b can each be aligned with (↑) or against (↓) B_0.**
- **Thus, the absorbing proton feels three slightly different magnetic fields—one slightly larger than B_0, one slightly smaller than B_0, and one the same strength as B_0.**

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

- **Because the absorbing proton feels three different magnetic fields, it absorbs at three different frequencies in the NMR spectrum, thus splitting a single absorption into a triplet.**

- **Because there are two different ways to align one proton with B_0, and one proton against B_0—that is, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$—the middle peak of the triplet is twice as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:2:1.**

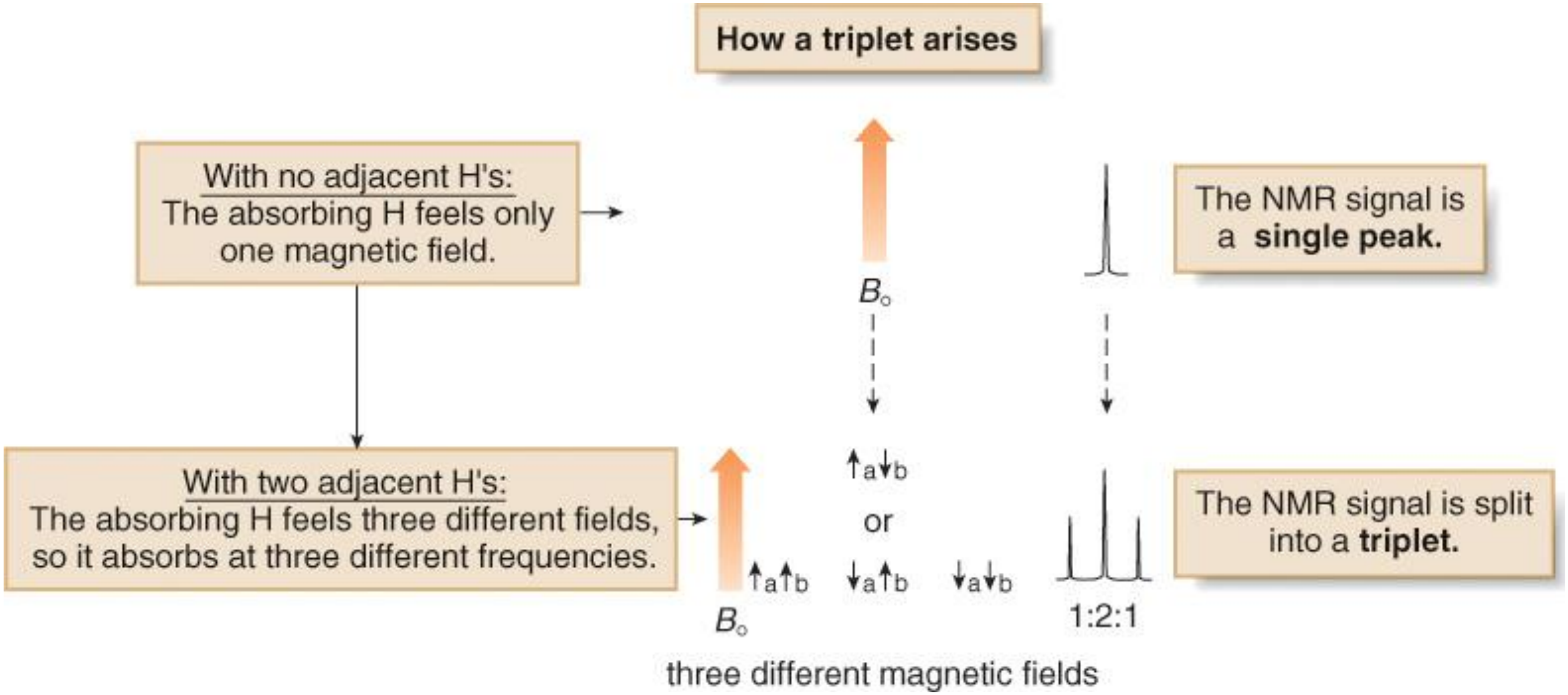
- **Two adjacent protons split an NMR signal into a triplet.**

- **When two protons split each other, they are *said to be coupled*.**

- **The spacing between peaks in a split NMR signal, measured by the *J* value, is equal for coupled protons.**

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting



How a triplet arises

With no adjacent H's:
The absorbing H feels only one magnetic field.

The NMR signal is a **single peak.**

With two adjacent H's:
The absorbing H feels three different fields, so it absorbs at three different frequencies.

The NMR signal is split into a **triplet.**

Nuclear Magnetic Resonance Spectroscopy

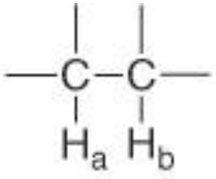
^{1}H NMR—Spin-Spin Splitting

Three general rules describe the splitting patterns commonly seen in the ^{1}H NMR spectra of organic compounds.

1. **Equivalent protons do not split each other's signals.**
2. **A set of n nonequivalent protons splits the signal of a nearby proton into n + 1 peaks.**
3. **Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.**

If H_a and H_b are not equivalent, splitting is observed when:

H_a and H_b are on the **same** carbon.

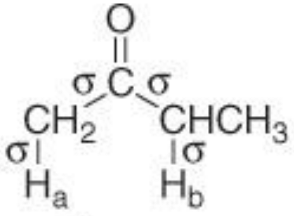


H_a and H_b are on **adjacent** carbons.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

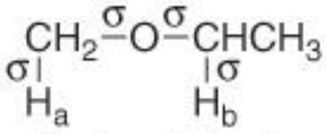
Splitting is not generally observed between protons separated by more than three σ bonds.



2-butanone

H_a and H_b are separated by four σ bonds.

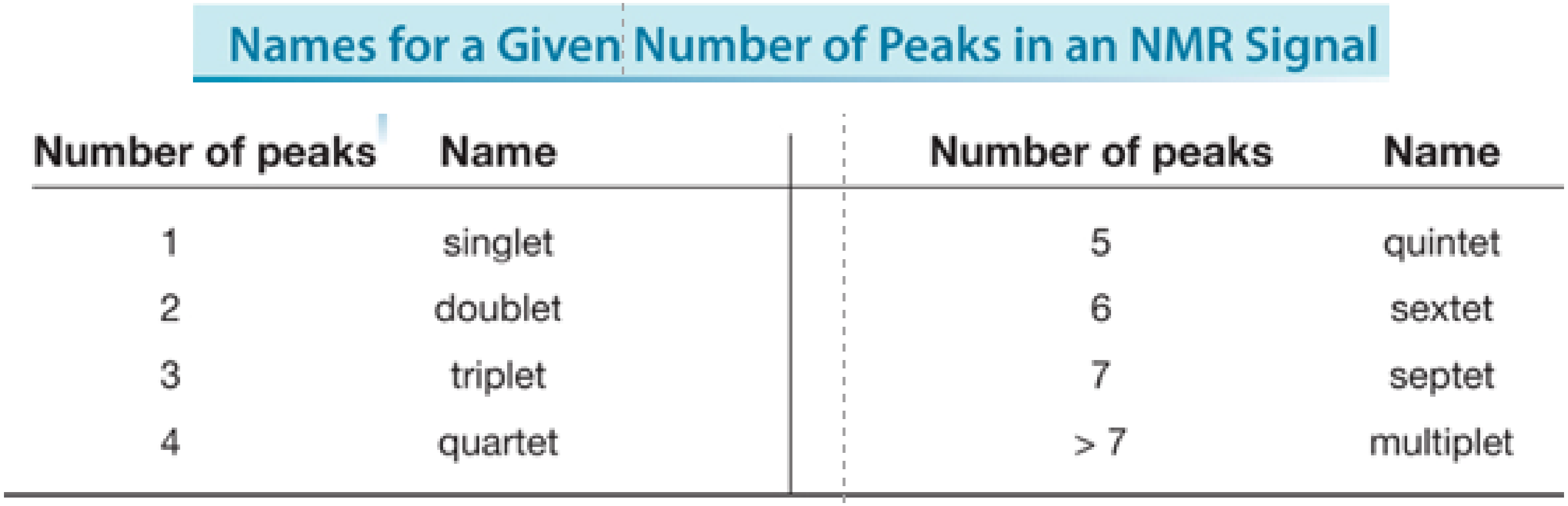
no splitting between H_a and H_b



ethyl methyl ether

H_a and H_b are separated by four σ bonds.

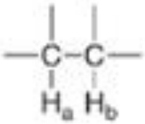
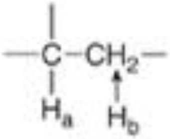
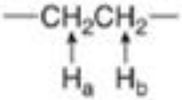
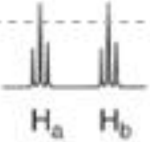
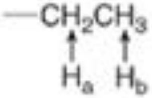
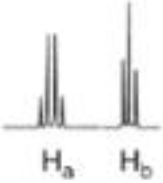
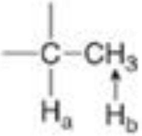
no splitting between H_a and H_b



Names for a Given Number of Peaks in an NMR Signal

Number of peaks	Name	Number of peaks	Name
1	singlet	5	quintet
2	doublet	6	sextet
3	triplet	7	septet
4	quartet	> 7	multiplet

Common Splitting Patterns Observed in ^{1}H NMR

	Example	Pattern	Analysis (H_a and H_b are not equivalent.)
[1]			• H_a: one adjacent H_b proton → two peaks → a **doublet** • H_b: one adjacent H_a proton → two peaks → a **doublet**
[2]			• H_a: two adjacent H_b protons → three peaks → a **triplet** • H_b: one adjacent H_a proton → two peaks → a **doublet**
[3]			• H_a: two adjacent H_b protons → three peaks → a **triplet** • H_b: two adjacent H_a protons → three peaks → a **triplet**
[4]			• H_a: three adjacent H_b protons → four peaks → a **quartet*** • H_b: two adjacent H_a protons → three peaks → a **triplet**
[5]			• H_a: three adjacent H_b protons → four peaks → a **quartet*** • H_b: one adjacent H_a proton → two peaks → a **doublet**

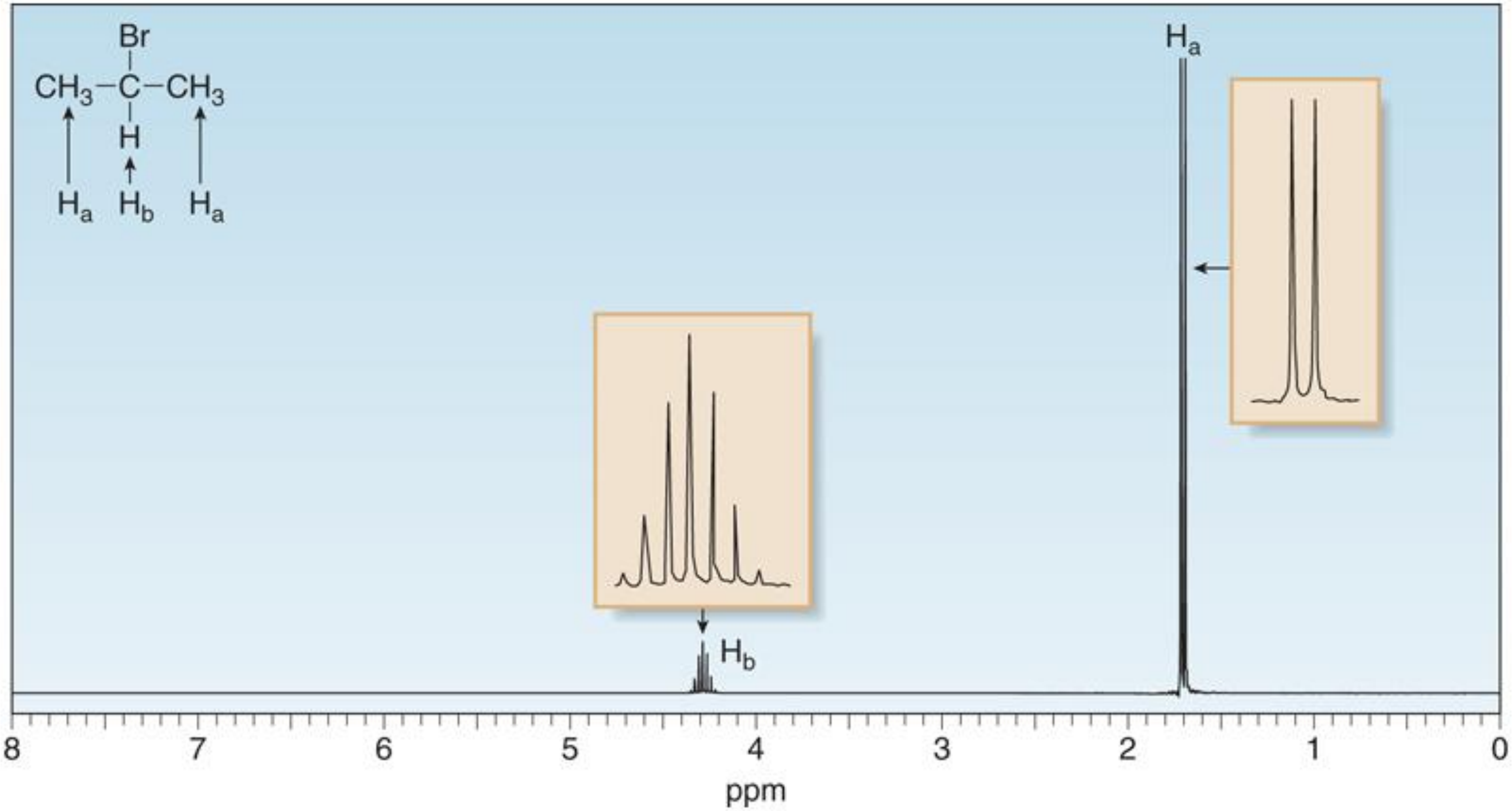
*The relative area under the peaks of a quartet is 1:3:3:1.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.

The 1H NMR spectrum of 2-bromopropane, [$(CH_3)_2CHBr$]

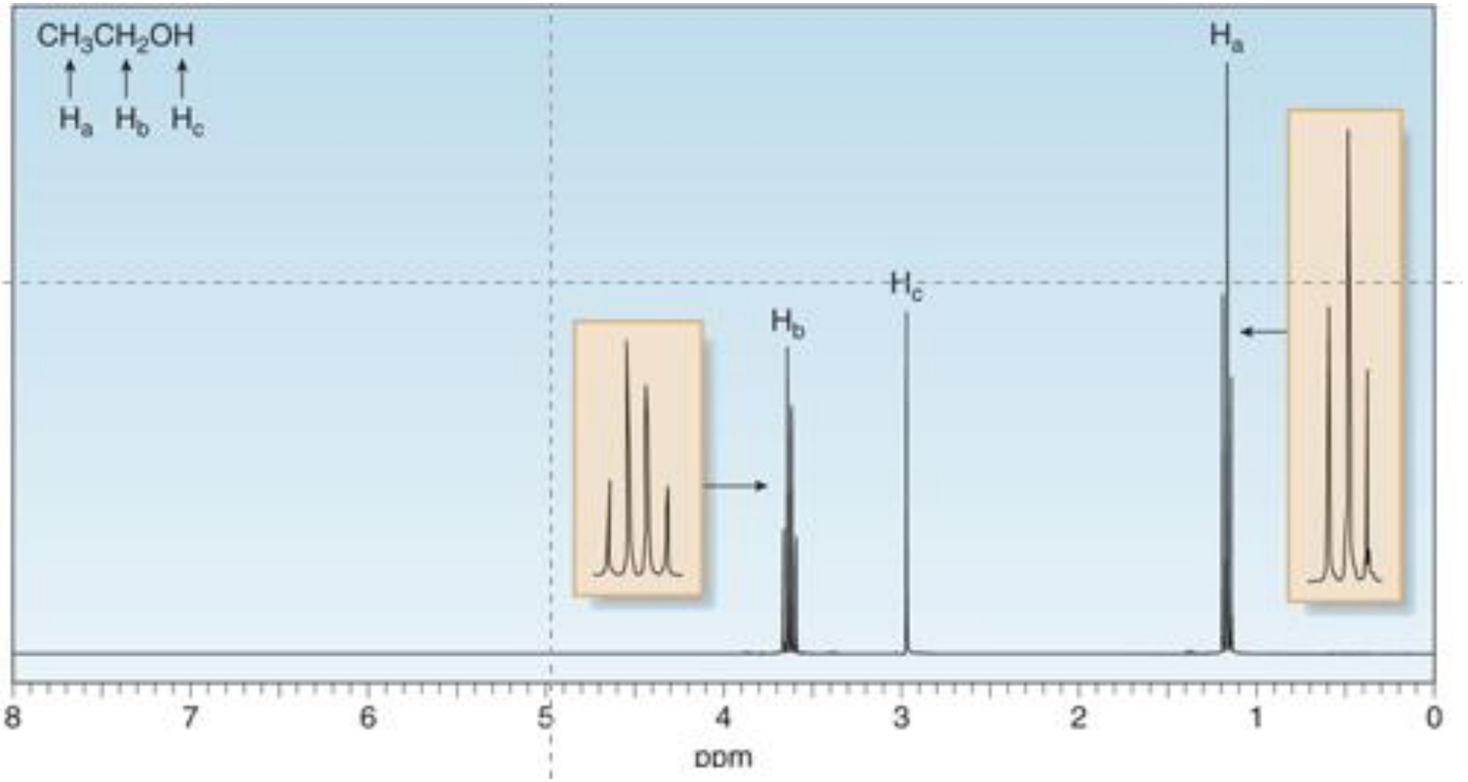


Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

Now consider the spectrum of 1-bromopropane. Since H_a and H_c are not equivalent to each other, we cannot merely add them together and use the n + 1 rule.

The 1H NMR spectrum of 1-bromopropane, $CH_3CH_2CH_2Br$

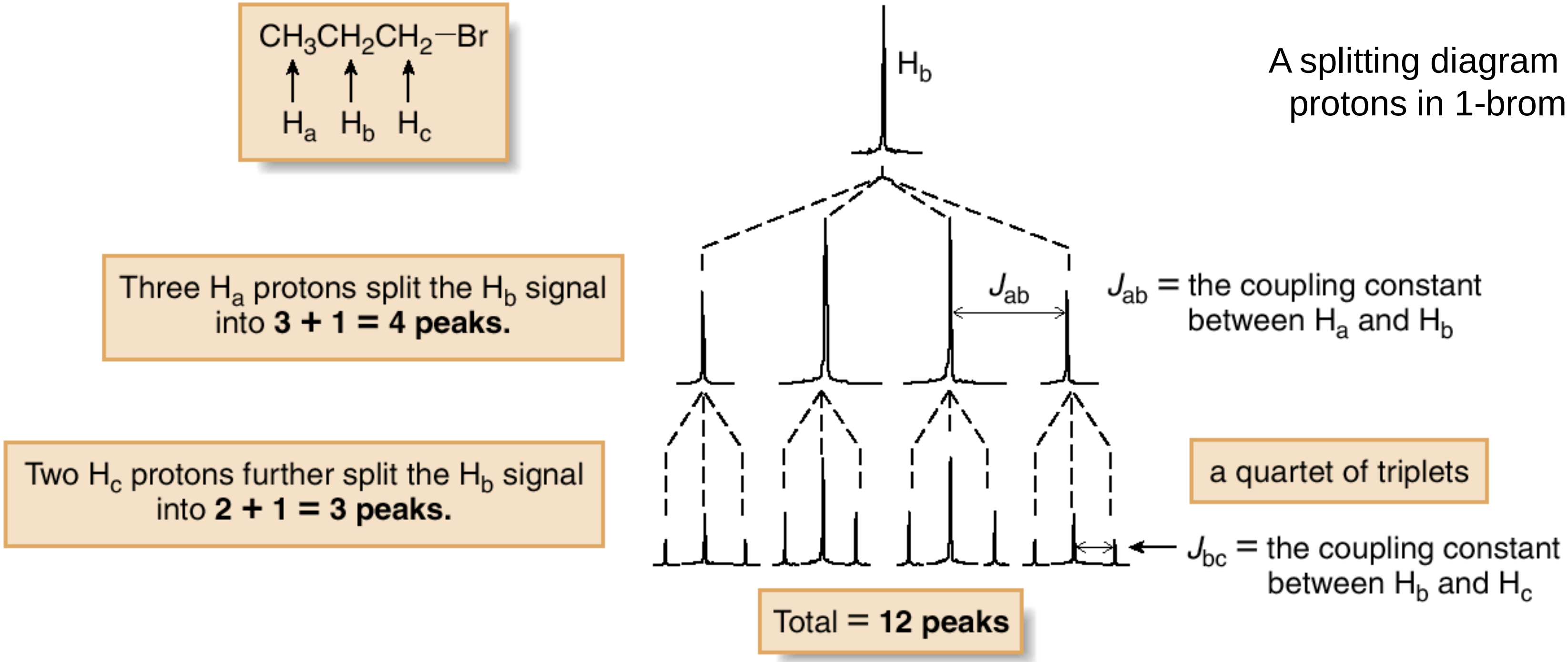


- H_a and H_c are both triplets.
- H_b is split into 12 peaks, labeled as a multiplet. Fewer peaks are seen because some peaks overlap.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

When two sets of adjacent protons are different from each other (n protons on one adjacent carbon and m protons on the other), the number of peaks in an NMR signal = (n + 1)(m + 1).



$CH_3CH_2CH_2{-}Br$

H_a H_b H_c

A splitting diagram for the H_b protons in 1-bromopropane

H_b

Three H_a protons split the H_b signal into **3 + 1 = 4 peaks.**

J_{ab}

J_{ab} = the coupling constant between H_a and H_b

Two H_c protons further split the H_b signal into **2 + 1 = 3 peaks.**

a quartet of triplets

J_{bc} = the coupling constant between H_b and H_c

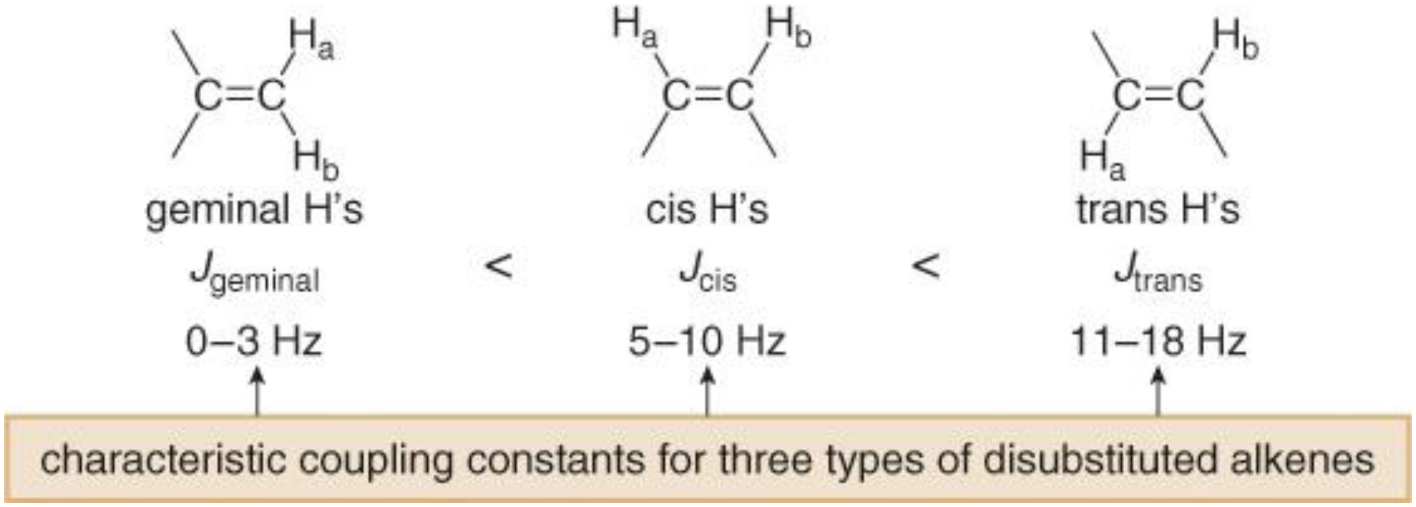
Total = **12 peaks**

- The H_b signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants, J_{ab} and J_{bc}. When $J_{ab} >> J_{bc}$, as drawn in this diagram, all 12 lines of the pattern are visible. When J_{ab} and J_{bc} are similar in magnitude, peaks overlap and fewer lines are observed.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

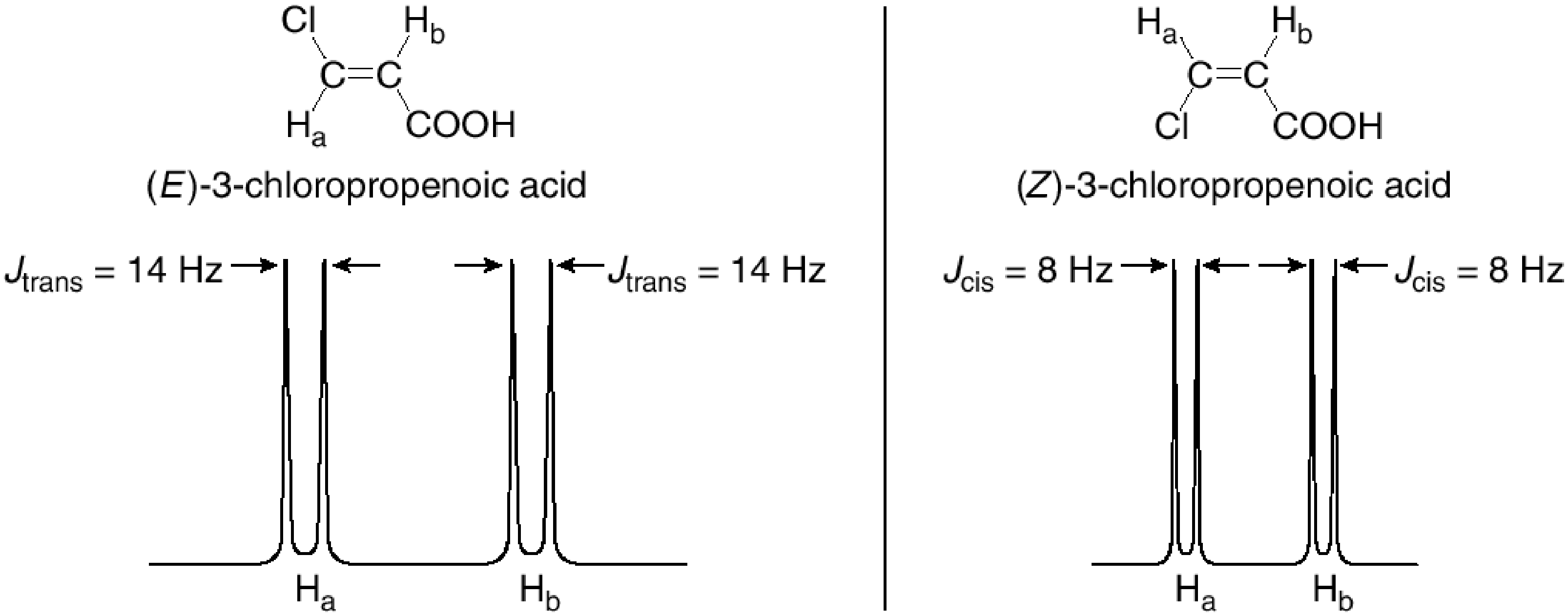
- Protons on carbon-carbon double bonds often give characteristic splitting patterns.
- A disubstituted double bond can have two geminal protons, two cis protons, or two trans protons.
- When these protons are different, each proton splits the NMR signal of the other so that each proton appears as a doublet.
- The magnitude of the coupling constant *J* for these doublets depends on the arrangement of hydrogen atoms.



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

^{1}H NMR spectra for the alkenyl protons of (*E*)- and (*Z*)-3-chloropropenoic acid

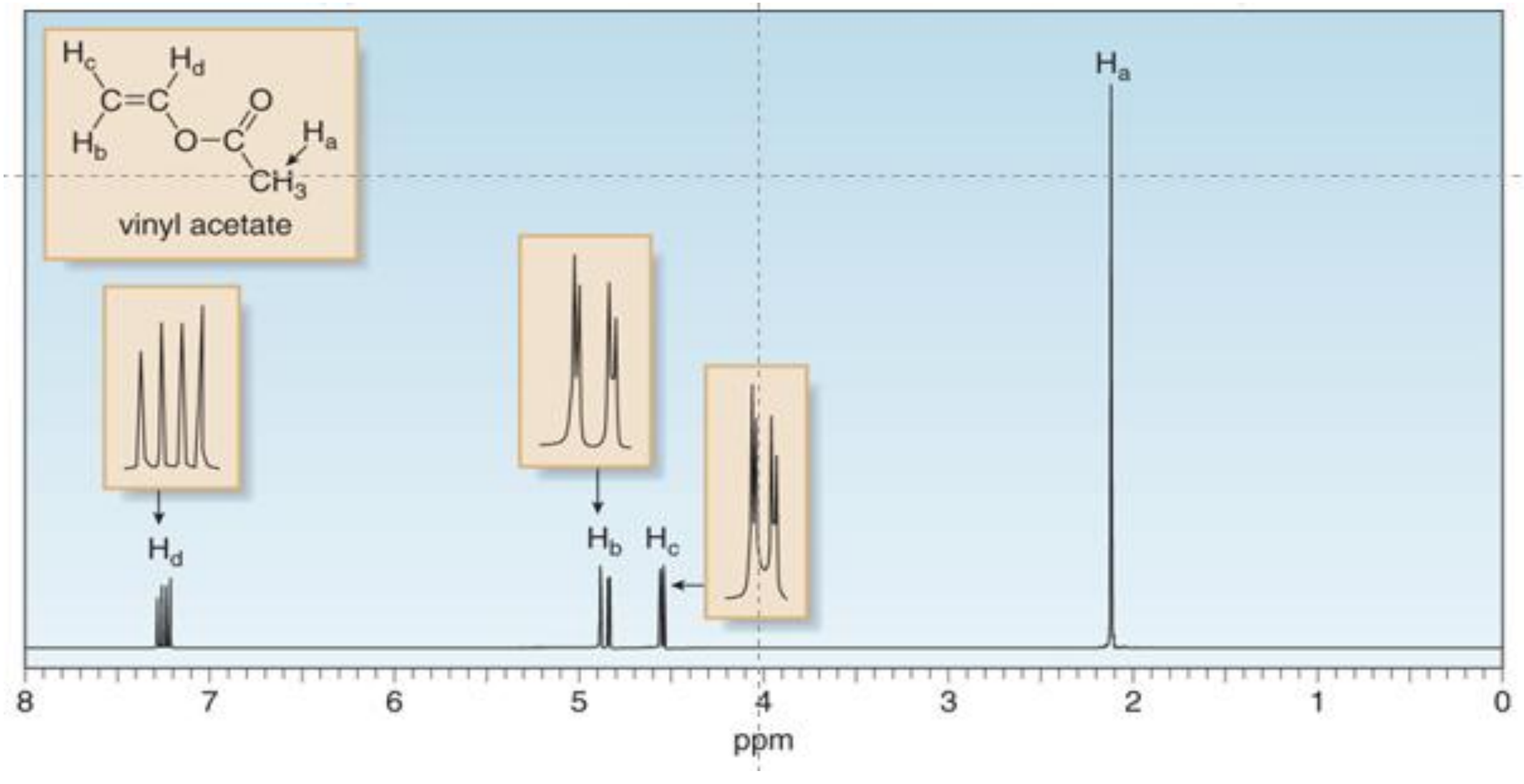


- Although both (*E*)- and (*Z*)-3-chloropropenoic acid show two doublets in their ^{1}H NMR spectra for their alkenyl protons, $J_{trans} > J_{cis}$.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

The ^{1}H NMR spectrum of vinyl acetate (CH_2=$CHOCOCH_3$)

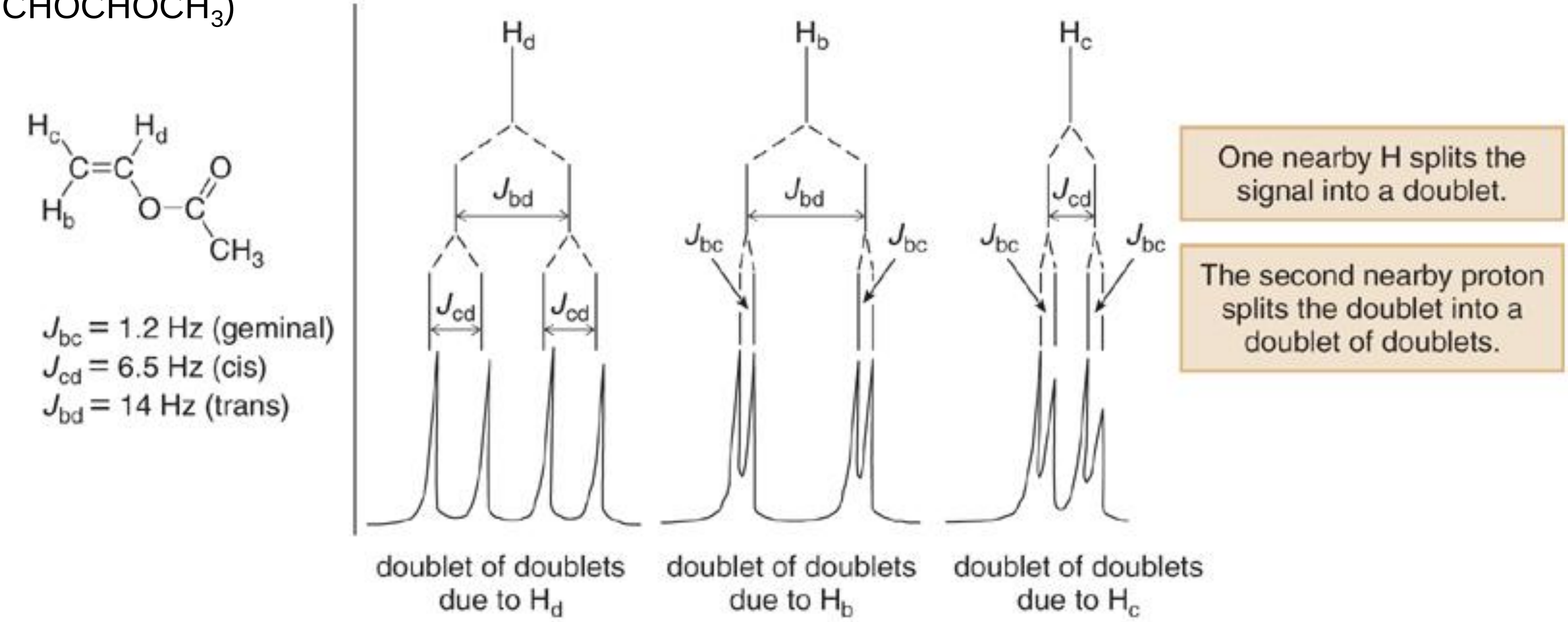


Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

Splitting diagrams for the alkenyl protons in vinyl acetate are shown below. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.

Splitting diagram for the alkenyl protons in vinyl acetate (CH_2=CHOCHOCH_3)



One nearby H splits the signal into a doublet.

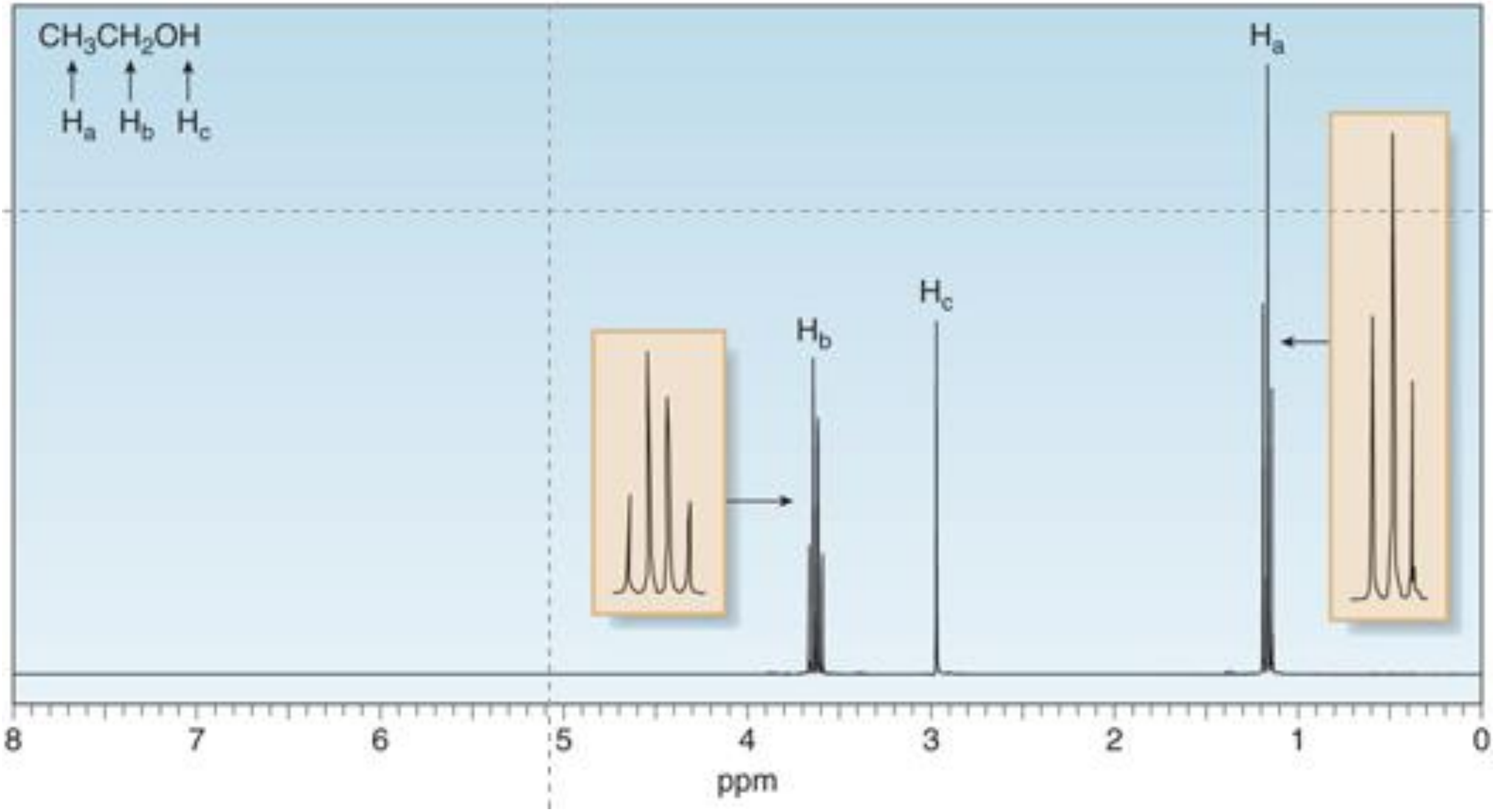
The second nearby proton splits the doublet into a doublet of doublets.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—OH Protons

- Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.
- The signal due to an OH proton is not split by adjacent protons.

The ^{1}H spectrum of ethanol (CH_3CH_2OH)



Nuclear Magnetic Resonance Spectroscopy

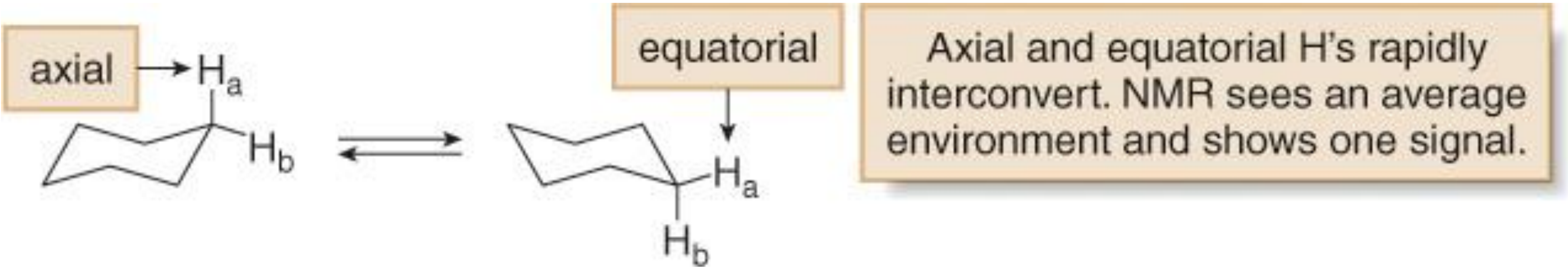
^{1}H NMR—OH Protons

- Ethanol (CH_3CH_2OH) has three different types of protons, so there are three signals in its NMR spectrum.
- The H_a signal is split by the two H_b protons into three peaks (a triplet).
- The H_b signal is split only by the three H_a protons into four peaks, a quartet. The adjacent OH proton does not split the signal due to H_b.
- H_c is a singlet because OH protons are not split by adjacent protons.
- Protons on electronegative atoms rapidly exchange between molecules in the presence of trace amounts of acid or base. Thus, the CH_2 group of ethanol never “feels” the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another.
- This phenomenon usually occurs with NH and OH protons.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Cyclohexane Conformers

- Recall that cyclohexane conformers interconvert by ring flipping.
- Because the ring flipping is very rapid at room temperature, an NMR spectrum records an average of all conformers that interconvert.
- Thus, even though each cyclohexane carbon has two different types of hydrogens—one axial and one equatorial—the two chair forms of cyclohexane rapidly interconvert them, and an NMR spectrum shows a single signal for the average environment that it "sees".



Axial and equatorial H's rapidly interconvert. NMR sees an average environment and shows one signal.

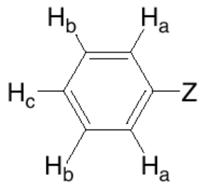
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Protons on Benzene Rings

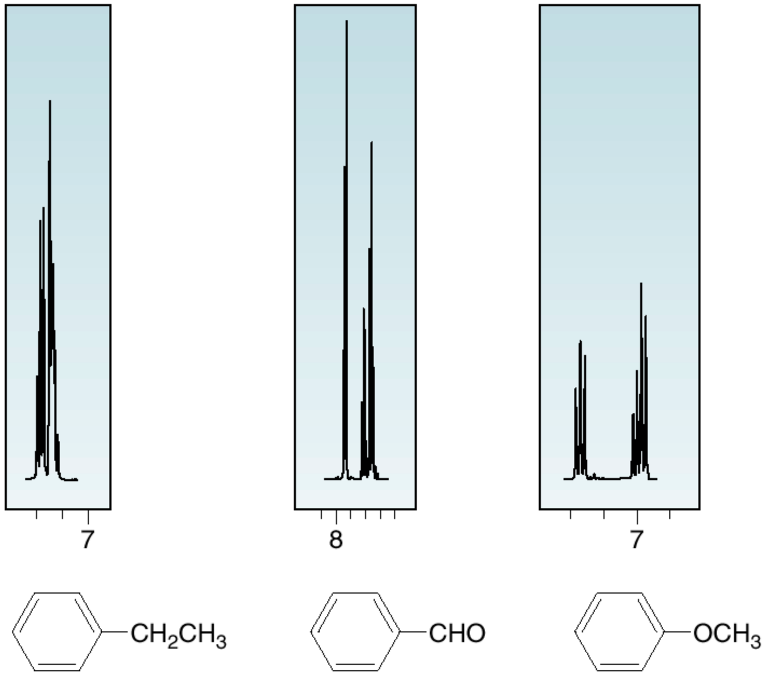
- Benzene has six equivalent deshielded protons and exhibits a single peak in its ^{1}H NMR spectrum at 7.27 ppm.
- Monosubstituted benzenes contain five deshielded protons that are no longer equivalent, and the appearance of these signals is highly variable, depending on the identity of Z.

The 6.5–8 ppm
region of the 1H NMR spectrum of
three benzene derivatives

A benzene ring with one substituent Z

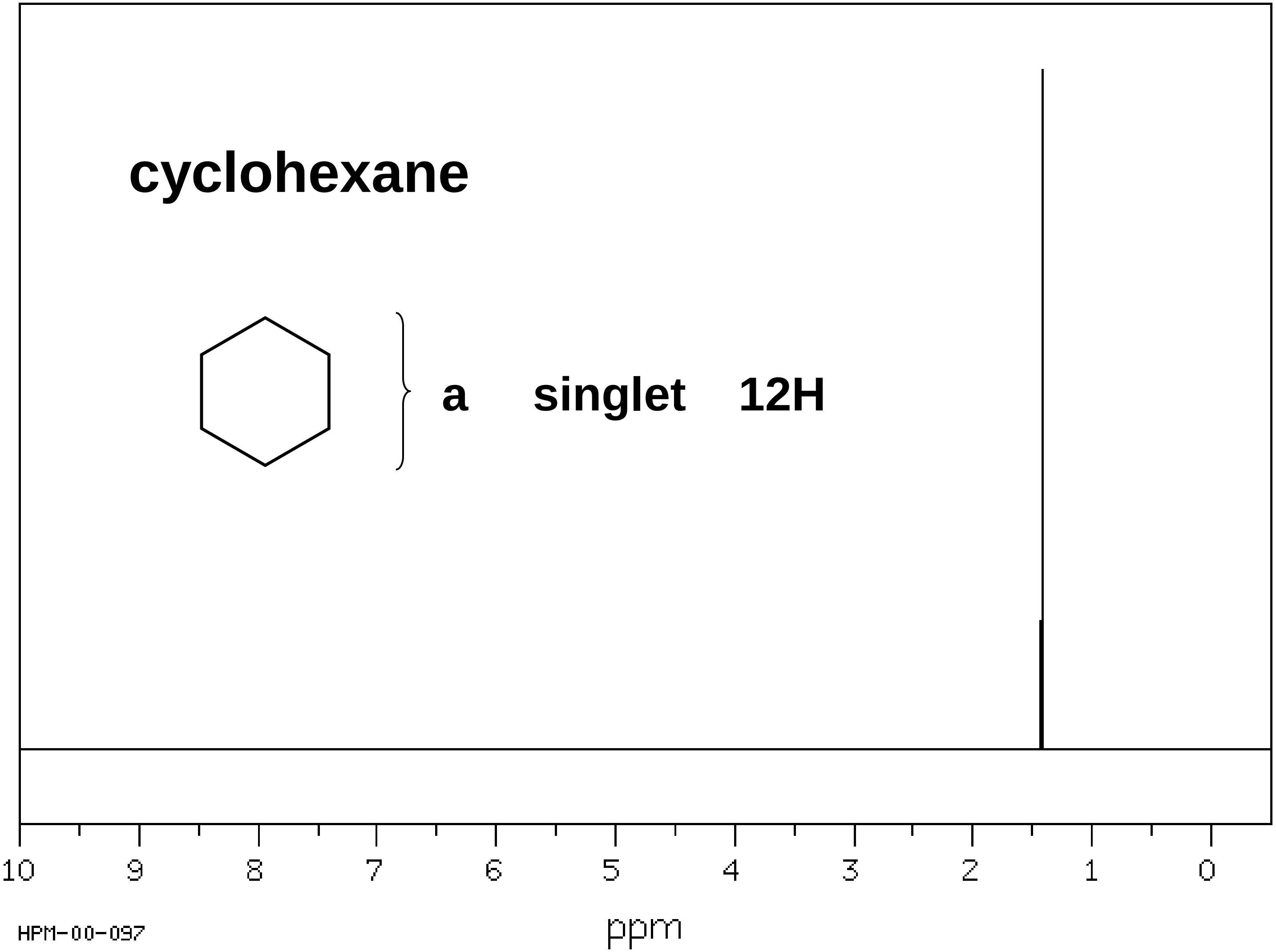


A monosubstituted benzene ring has three different types of H atoms: H_a, H_b, and H_c.



- The appearance of the signals in the 6.5–8 ppm region of the ^{1}H NMR spectrum depends on the identity of Z in C_6H_5Z.

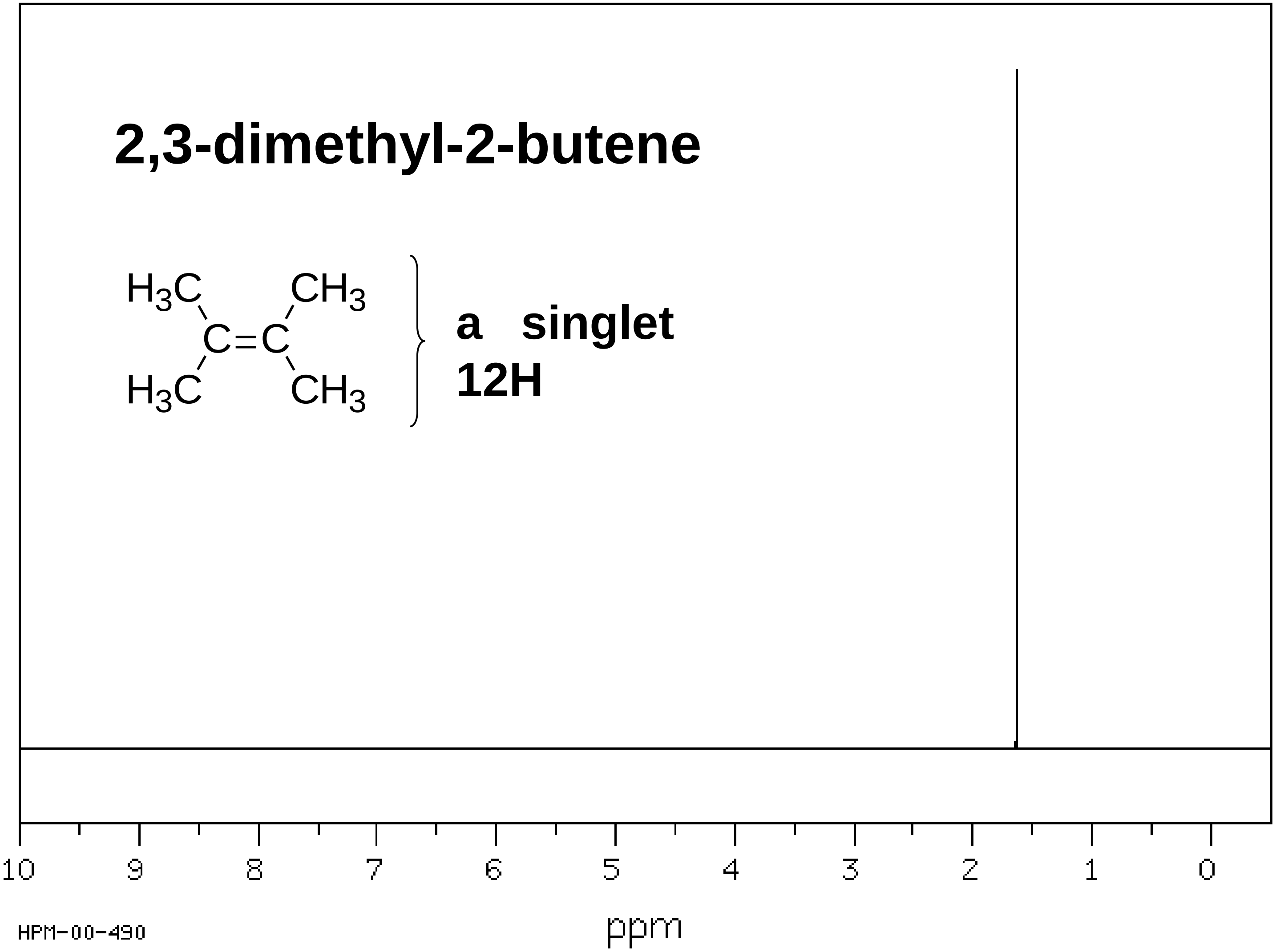
Examples



cyclohexane

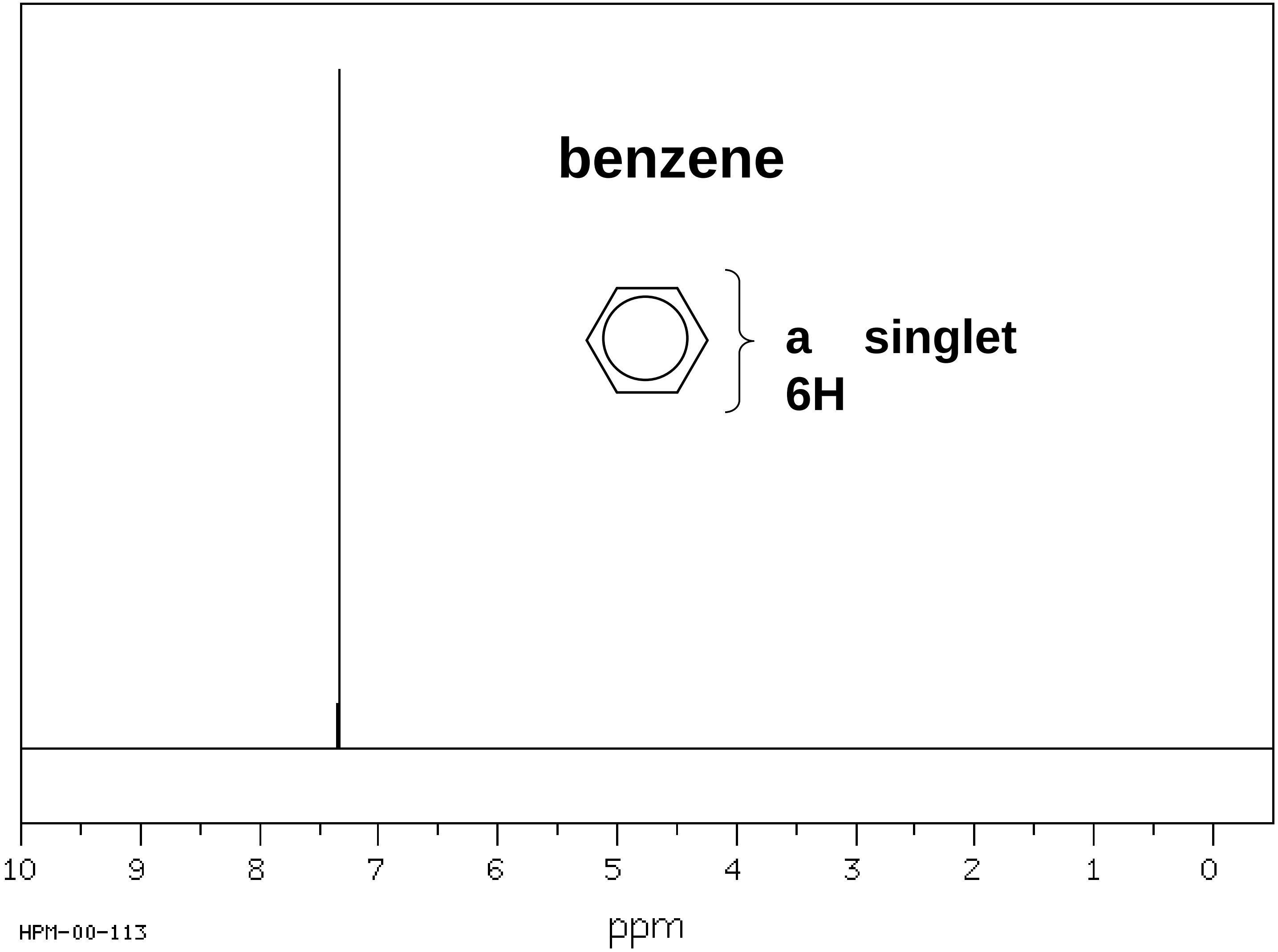
a singlet 12H

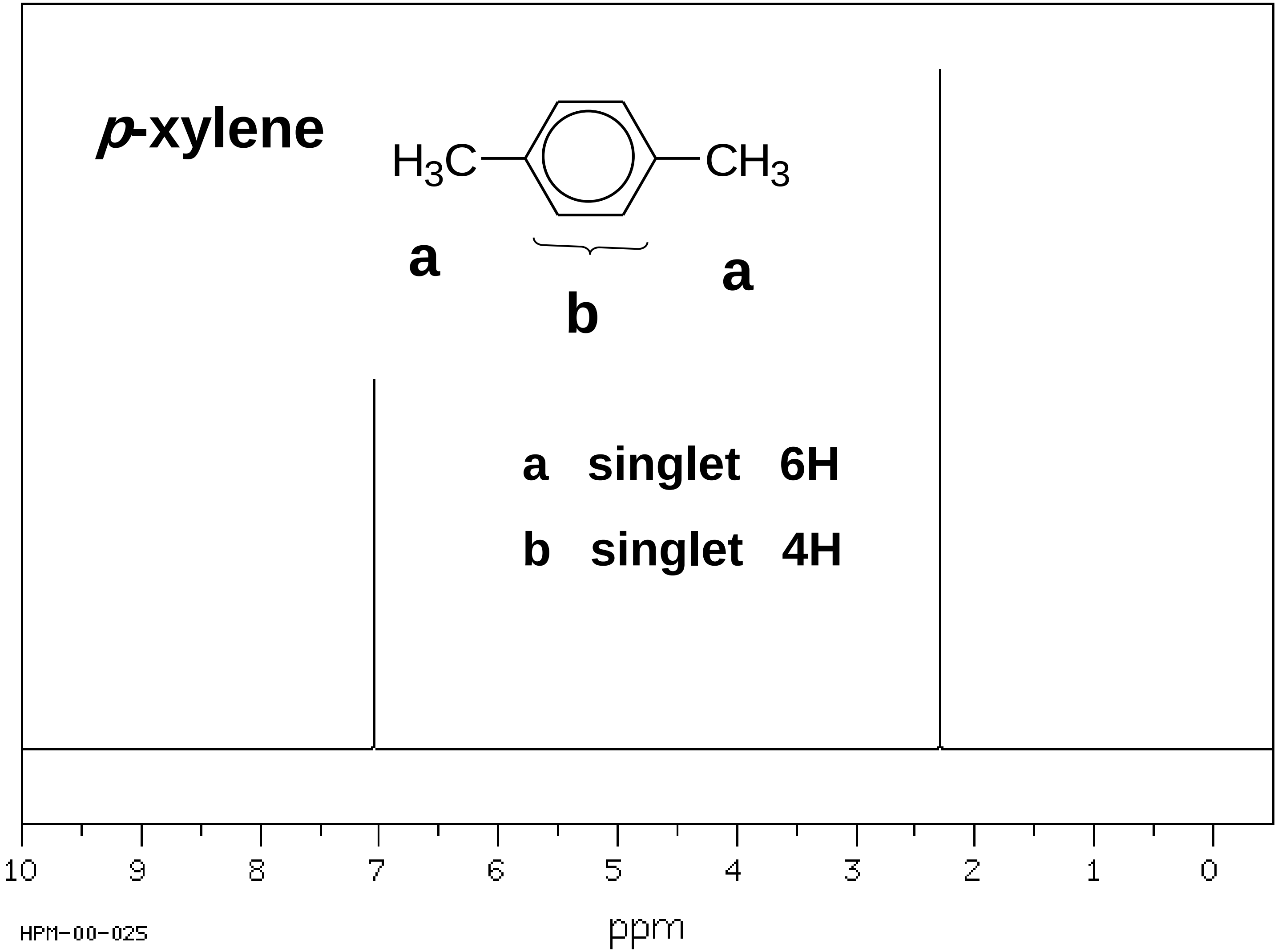
2,3-dimethyl-2-butene



a singlet

12H


benzene
a singlet
6H
10
9
8
7
6
5
4
3
2
1
0
ppm
HPM-00-113

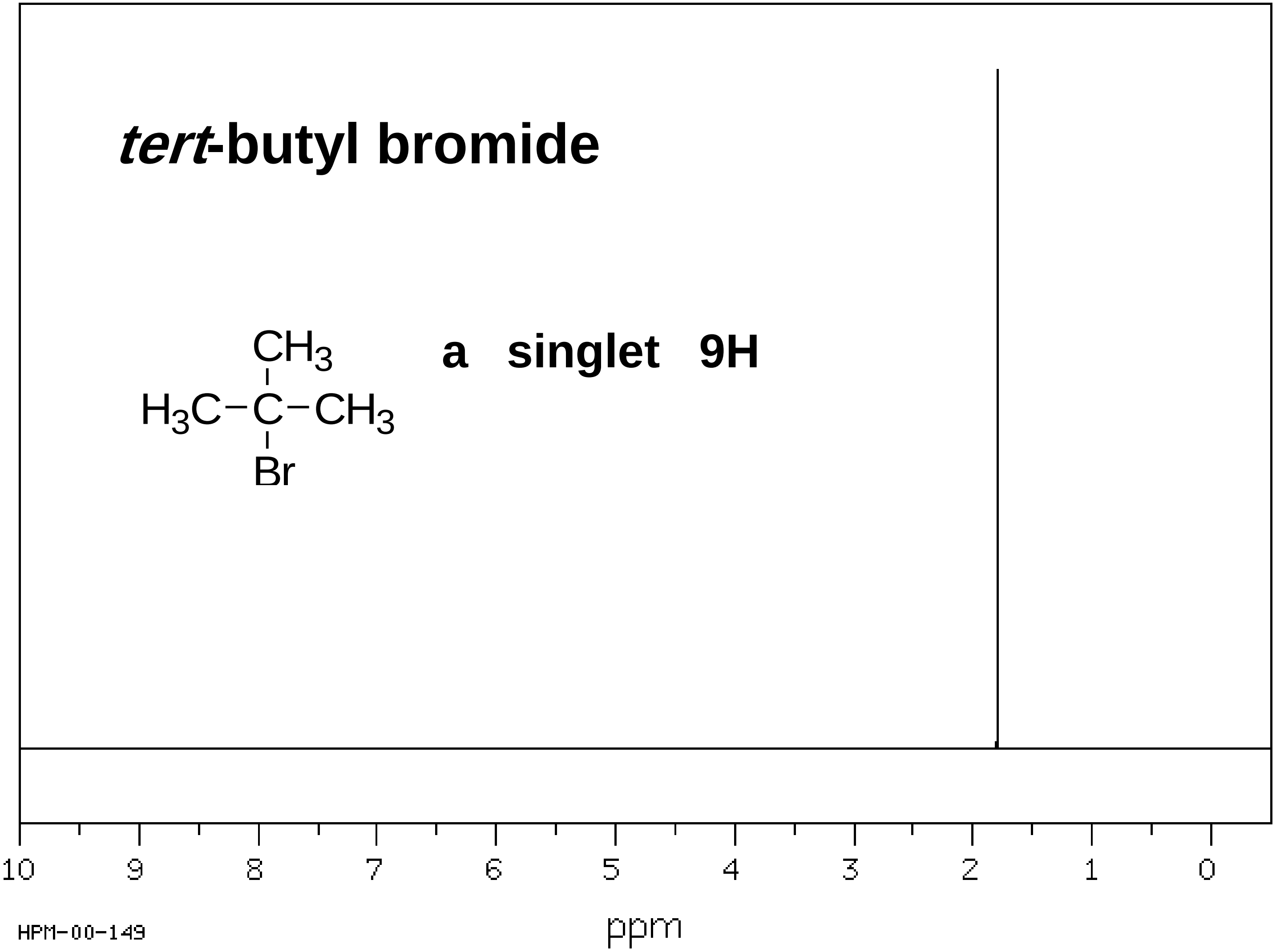


***p*-xylene**

a singlet 6H

b singlet 4H

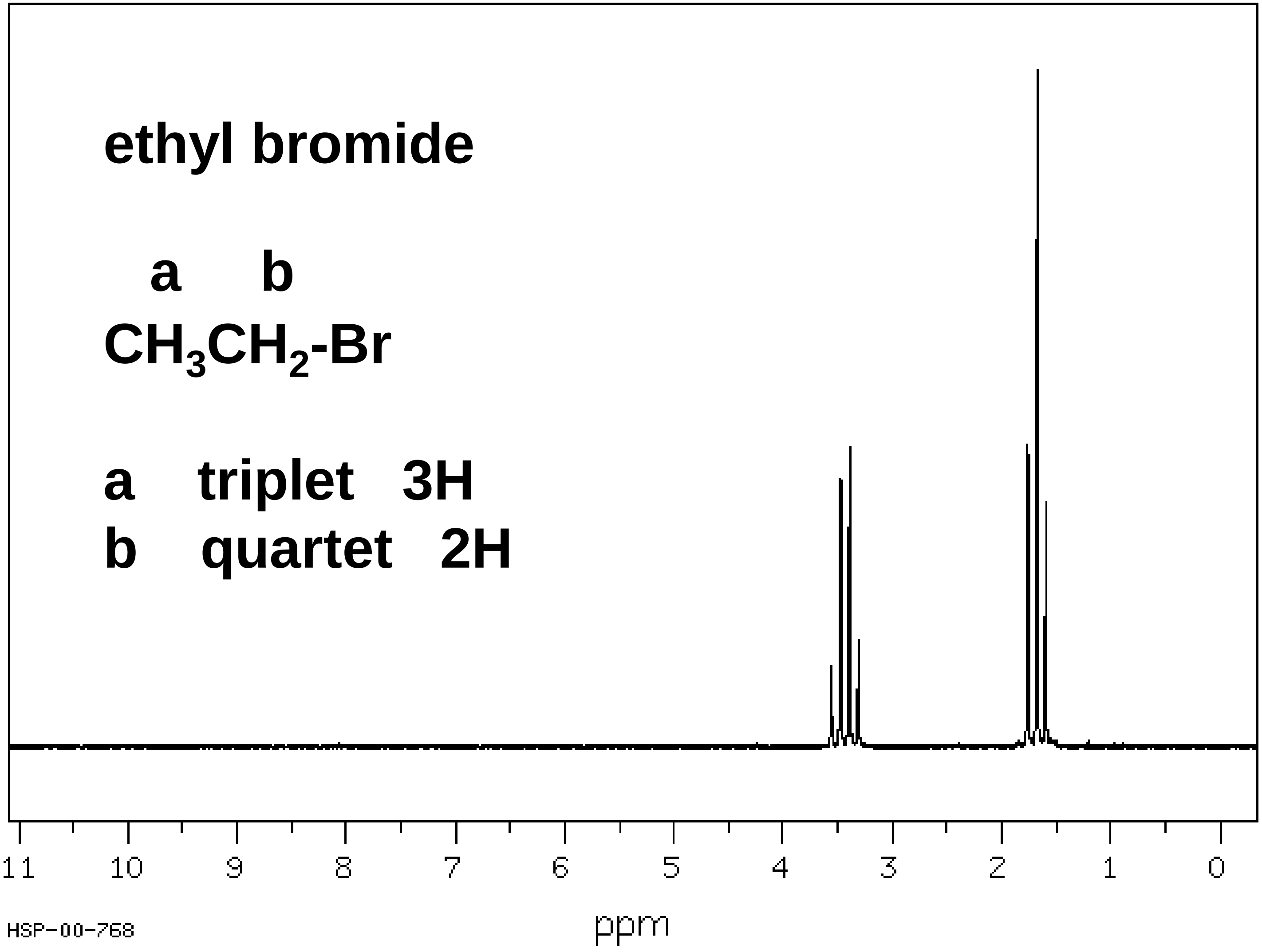
tert-butyl bromide



$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ Br \end{array}$$

a singlet 9H

HPM-00-149



ethyl bromide

$\overset{a}{CH_3}\overset{b}{CH_2}\text{-Br}$

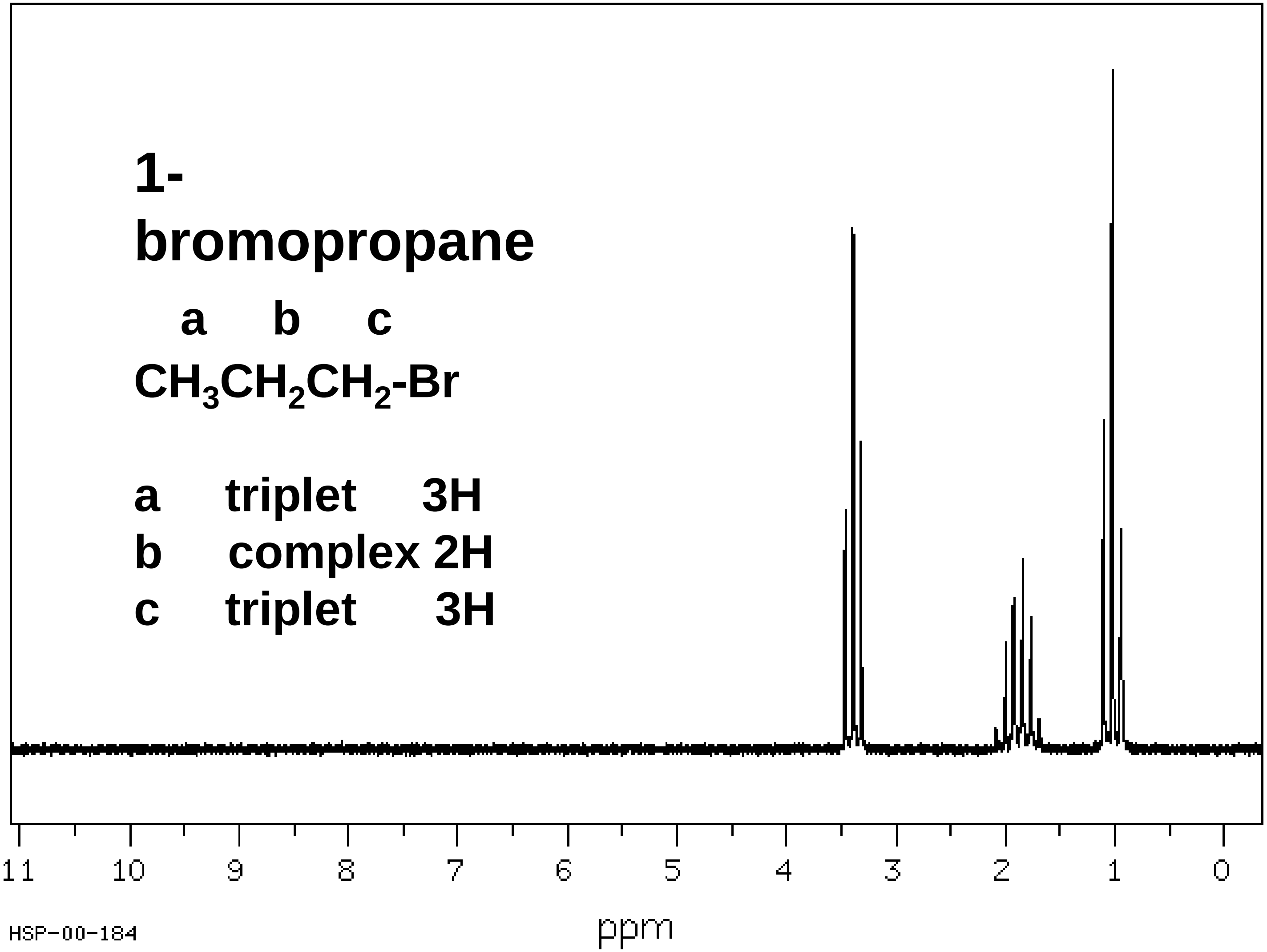
a triplet 3H
b quartet 2H

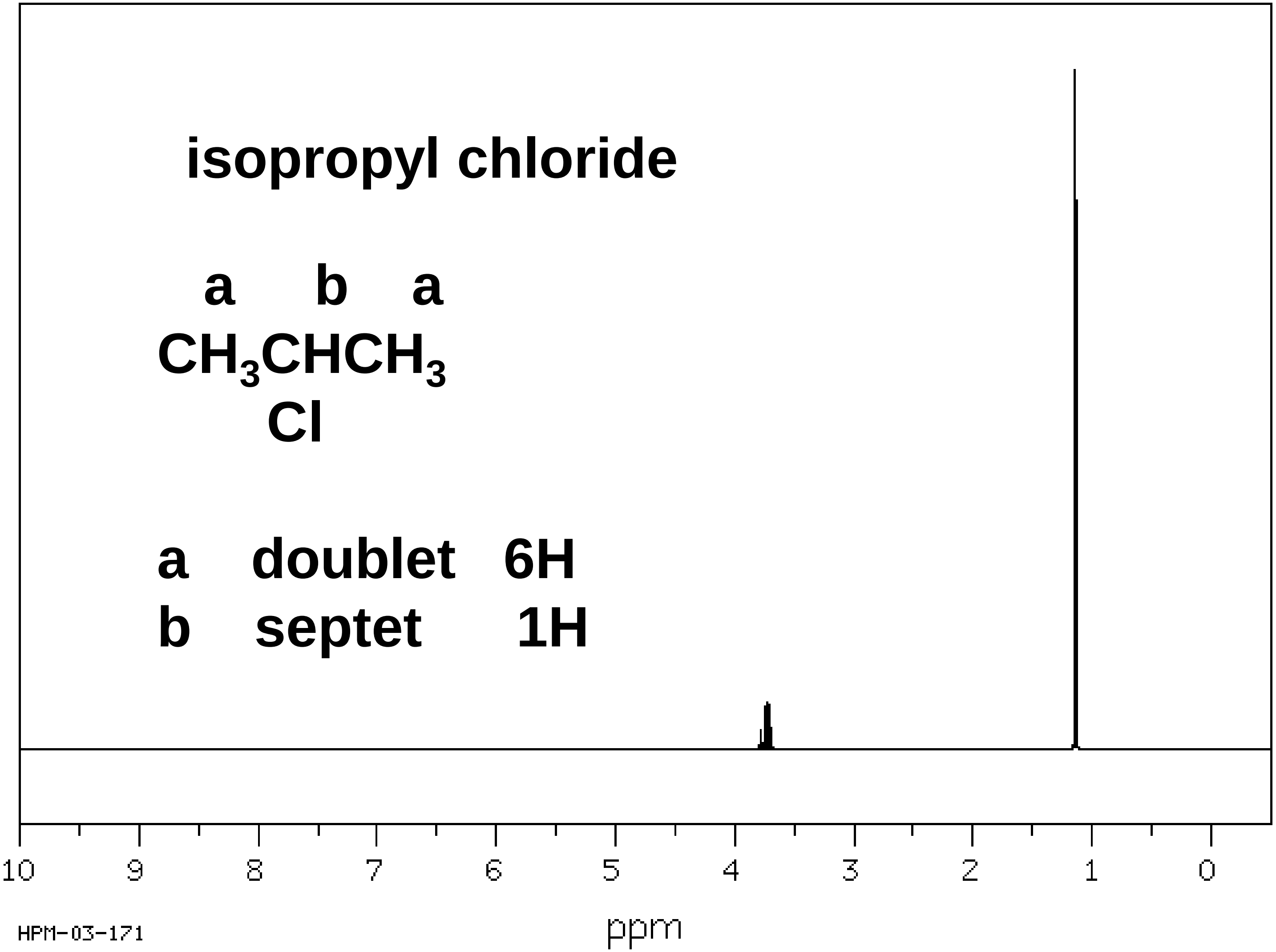
1-bromopropane

a b c

$CH_3CH_2CH_2$-Br

a triplet 3H
b complex 2H
c triplet 3H

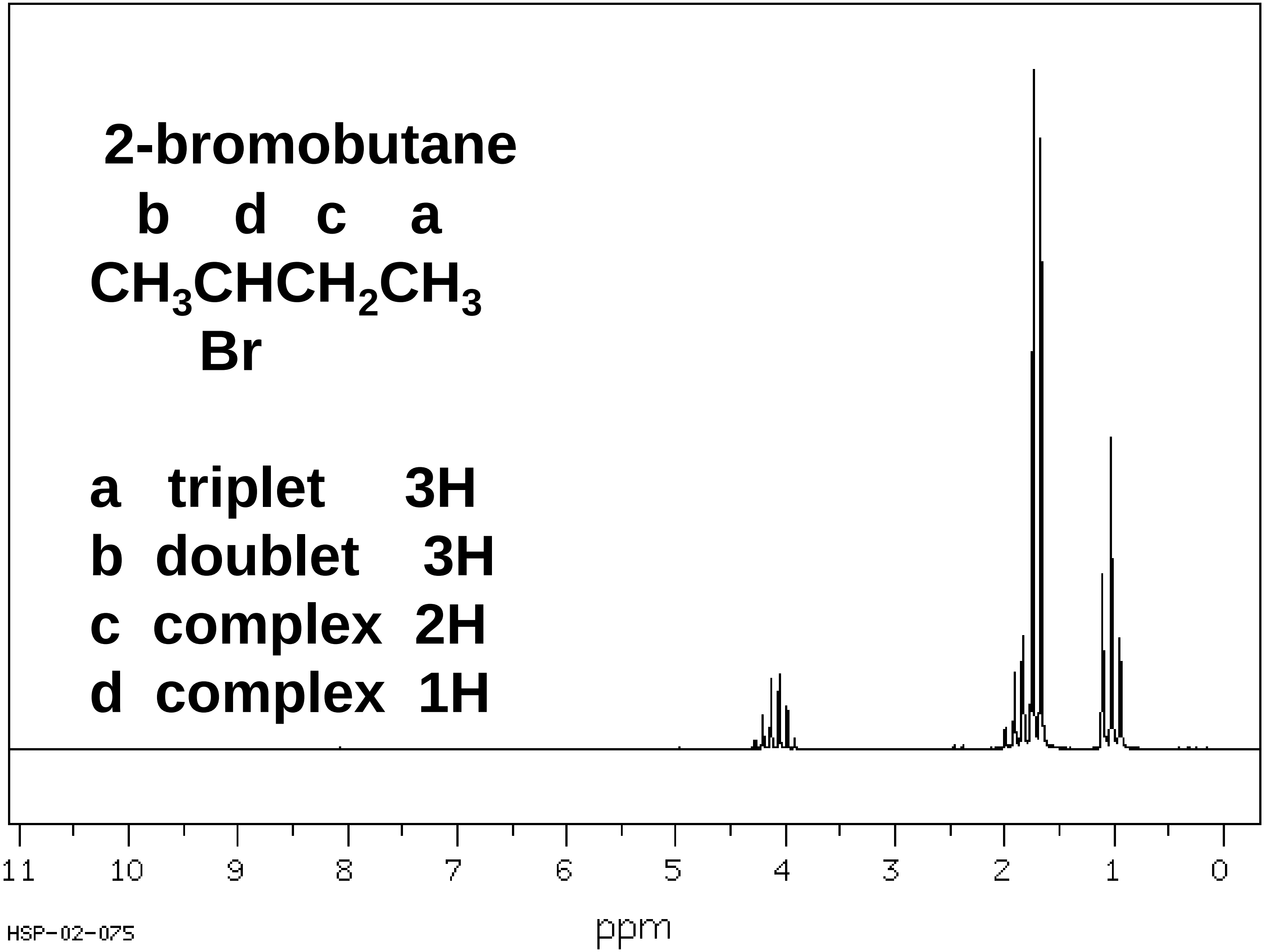




isopropyl chloride

$$\overset{a}{CH_3}\underset{Cl}{\overset{b}{CH}}\overset{a}{CH_3}$$

a	doublet	6H
b	septet	1H

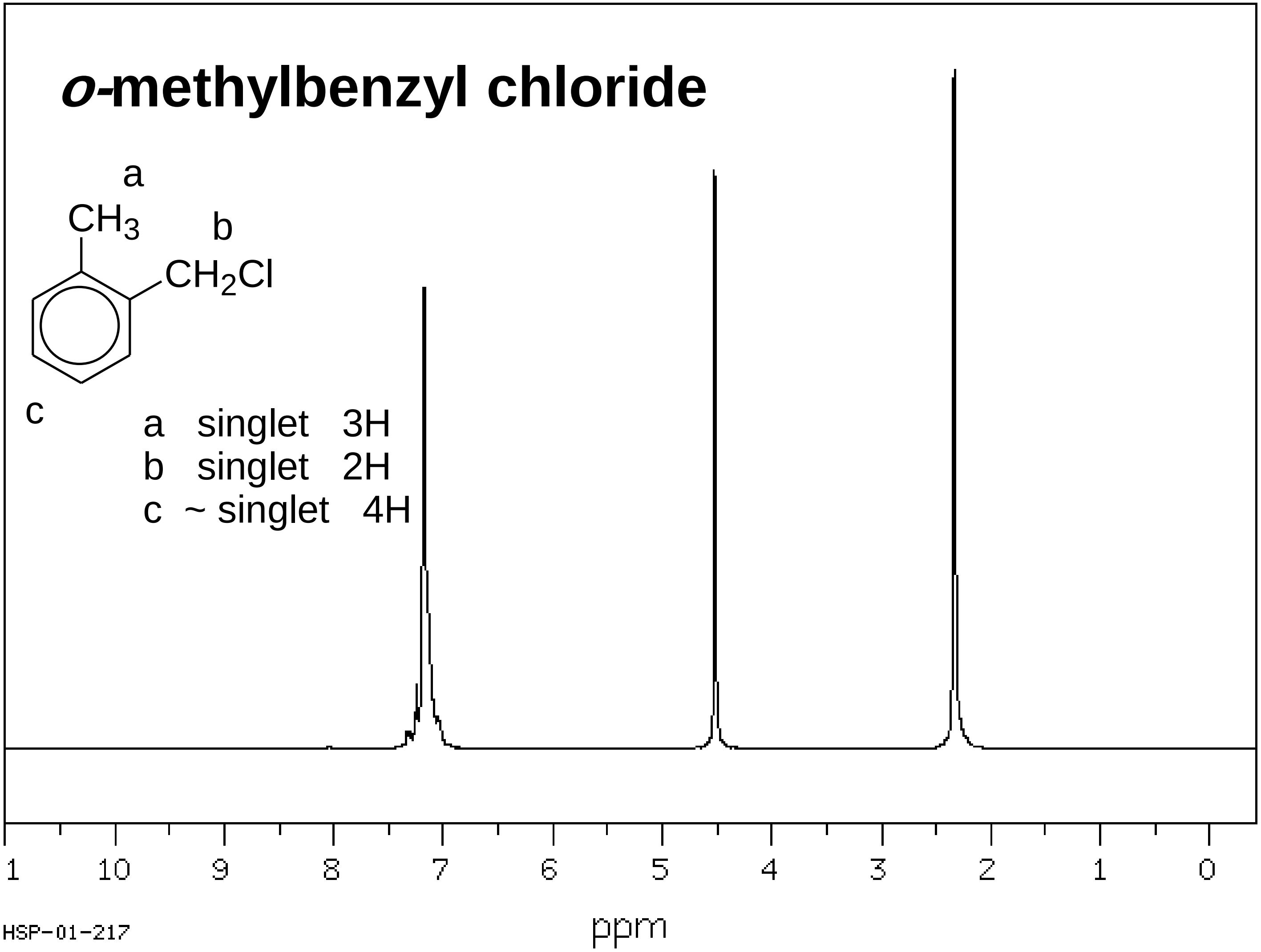


2-bromobutane

$$\overset{b}{CH_3}\underset{Br}{\overset{d}{CH}}\overset{c}{CH_2}\overset{a}{CH_3}$$

a	triplet	3H
b	doublet	3H
c	complex	2H
d	complex	1H

o-methylbenzyl chloride



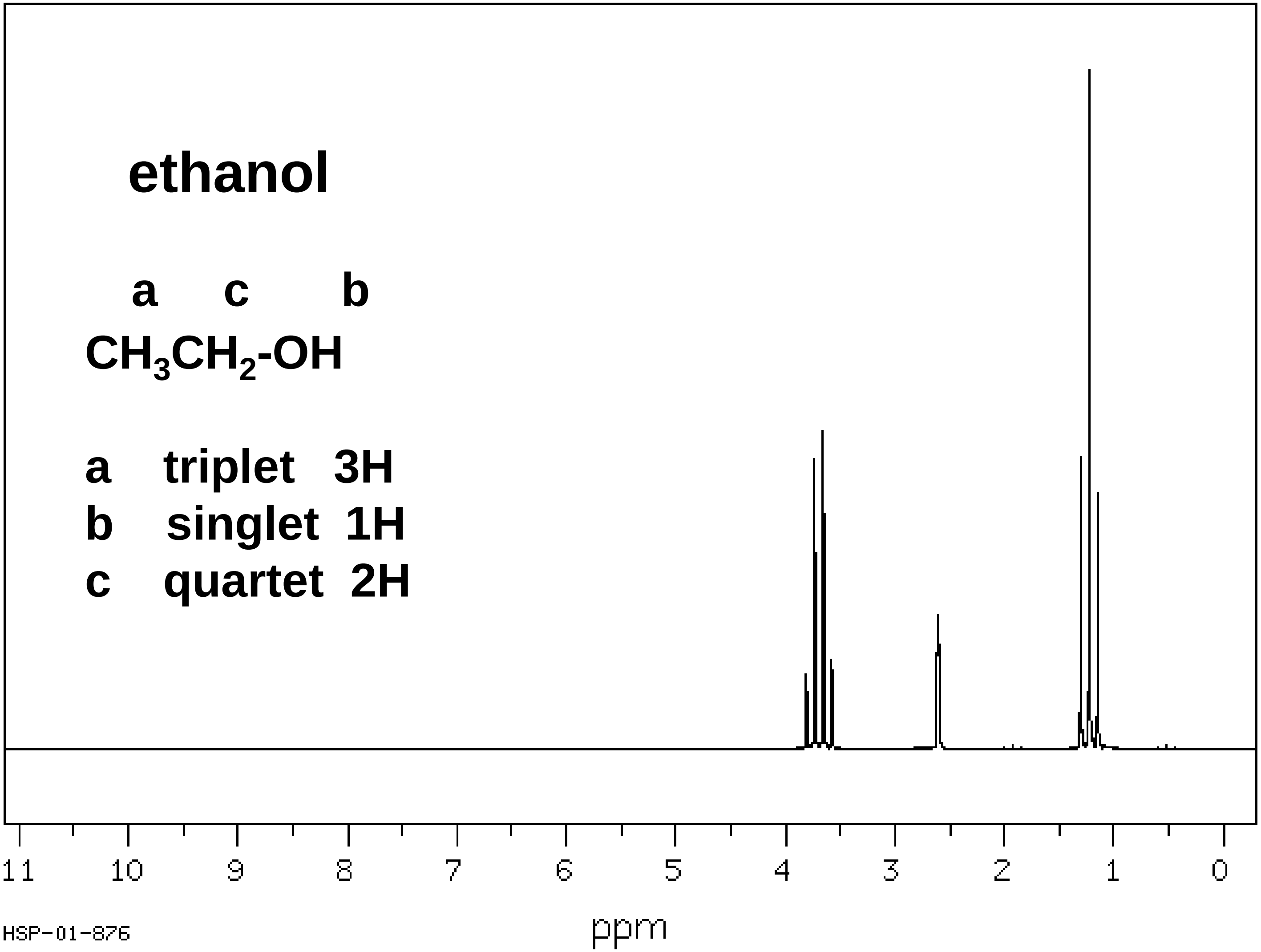
a singlet 3H
b singlet 2H
c ~ singlet 4H

HSP-01-217

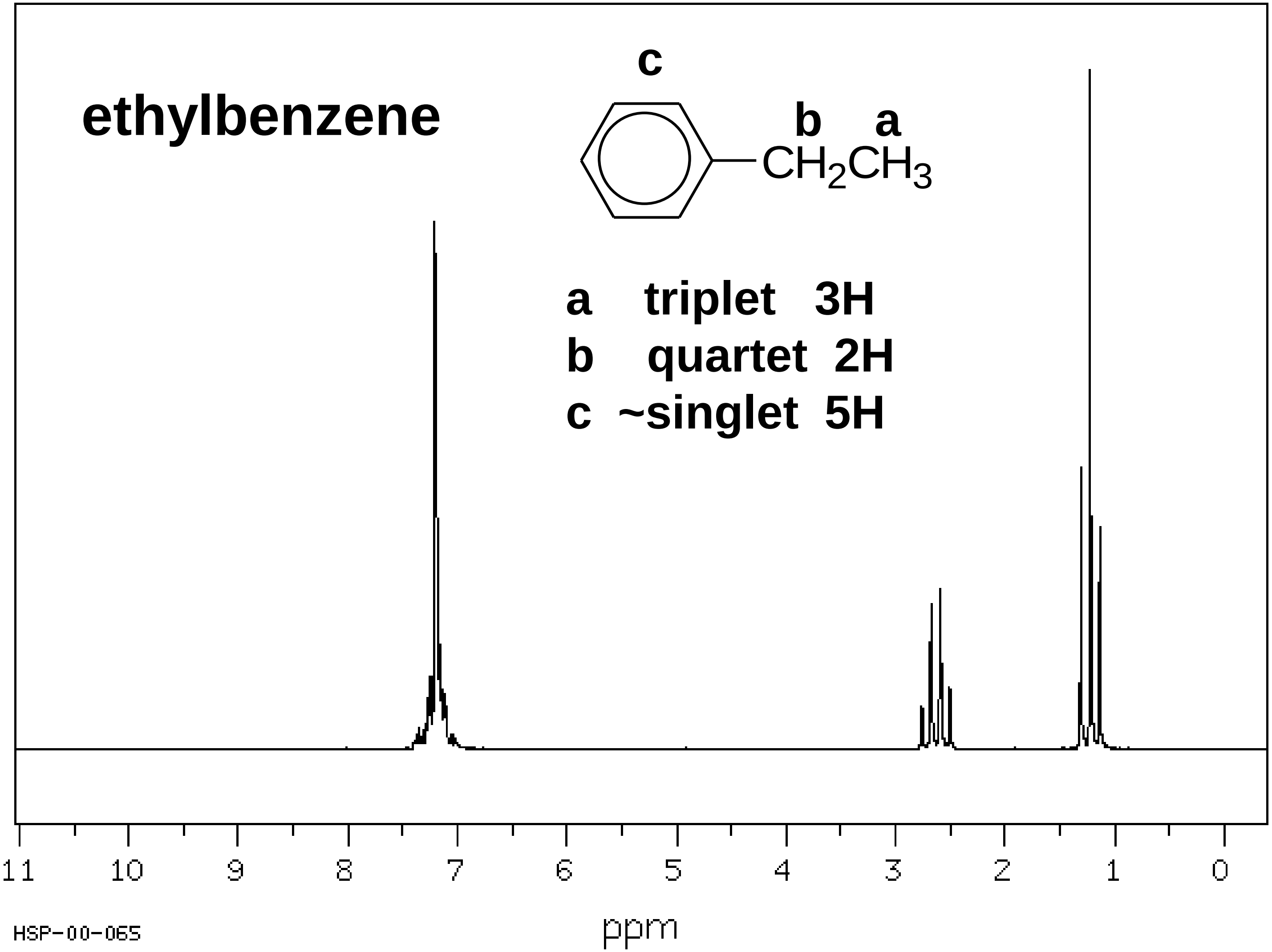
ethanol

a c b
CH_3CH_2-OH

a triplet 3H
b singlet 1H
c quartet 2H



ethylbenzene

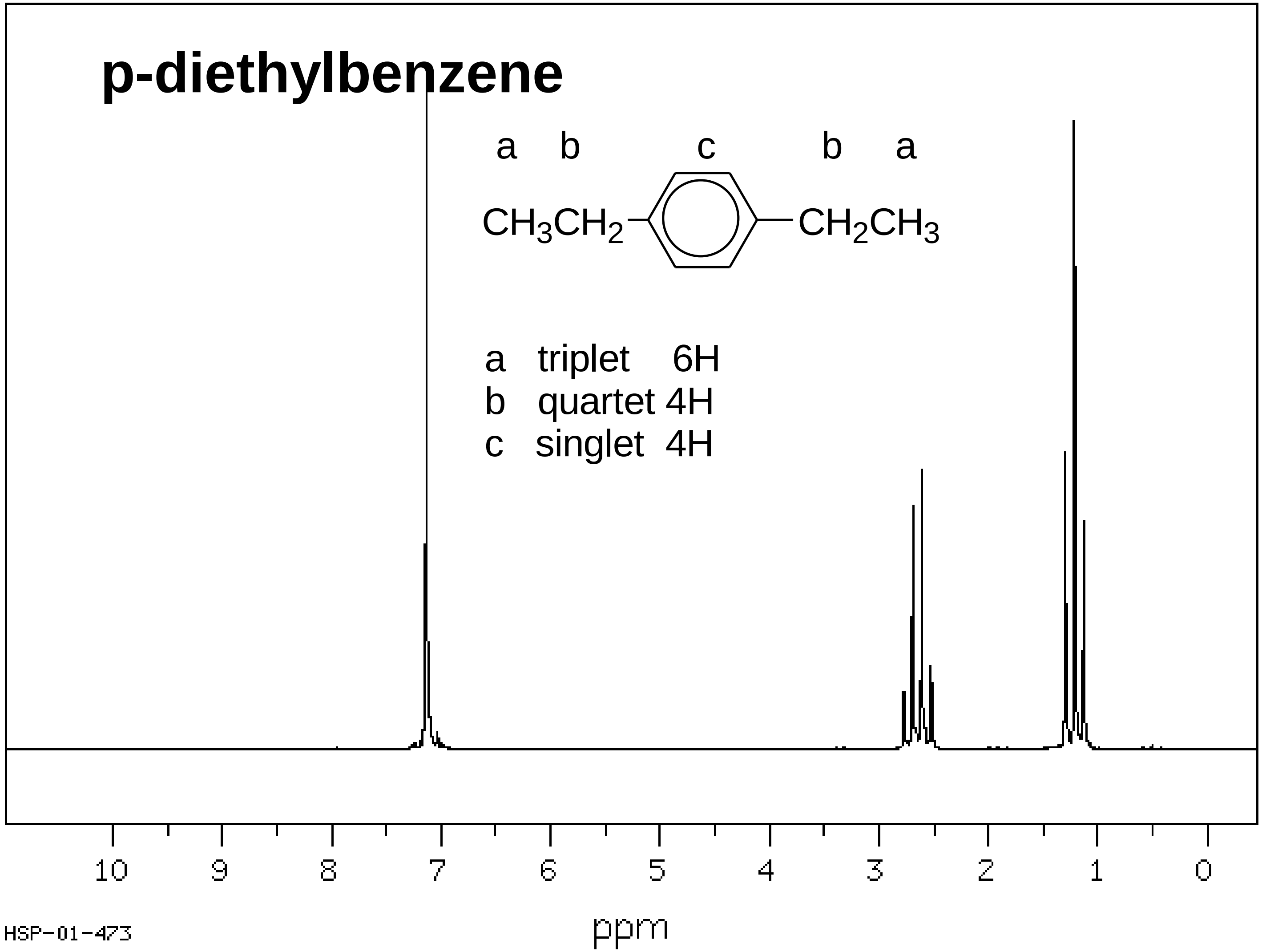


a triplet 3H

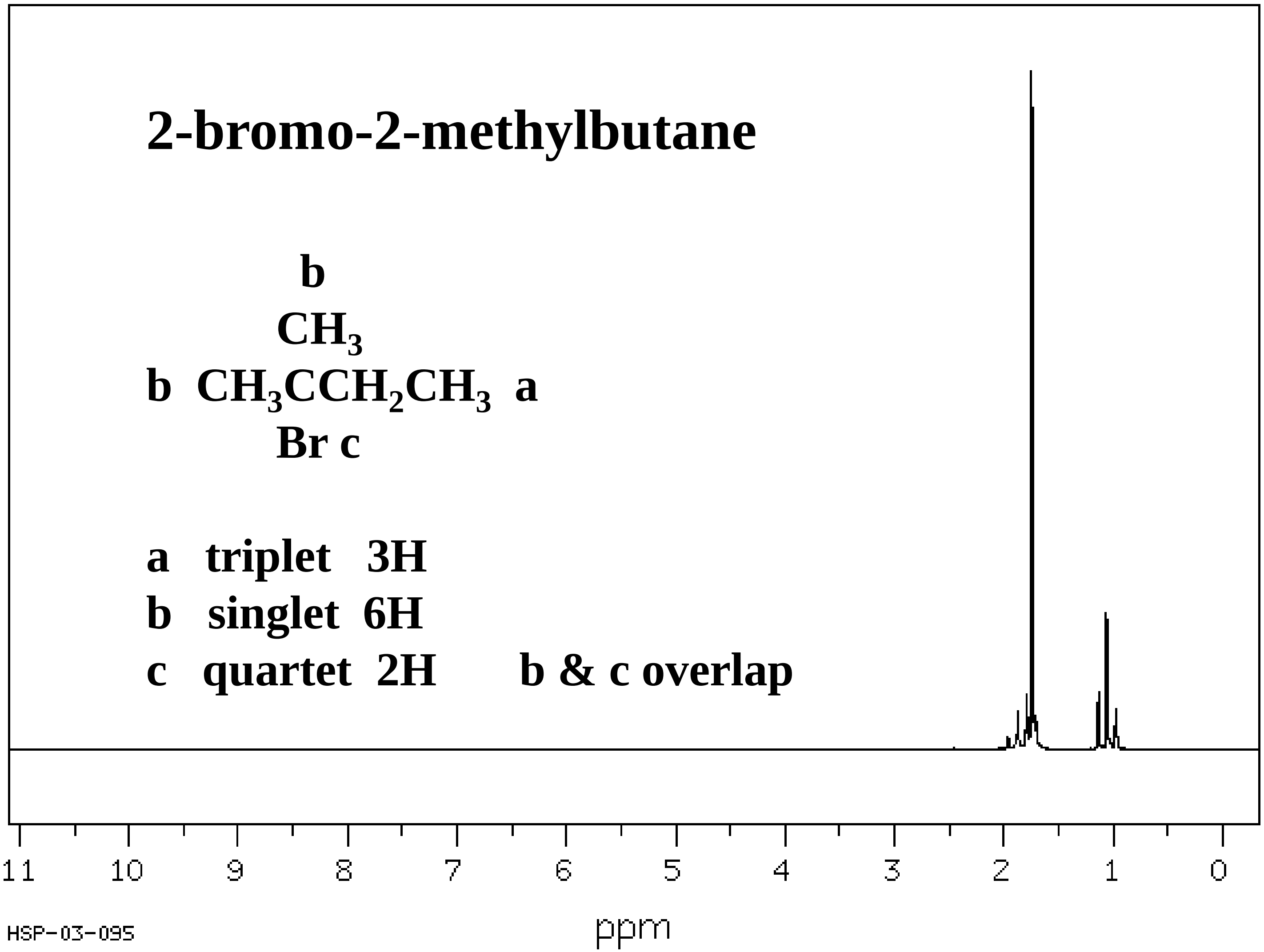
b quartet 2H

c ~singlet 5H

p-diethylbenzene



a triplet 6H
b quartet 4H
c singlet 4H



2-bromo-2-methylbutane

$$\begin{array}{l} \qquad\quad b \\ \qquad CH_3 \\ b\ \ CH_3CCH_2CH_3\ \ a \\ \qquad Br\ c \end{array}$$

a triplet 3H

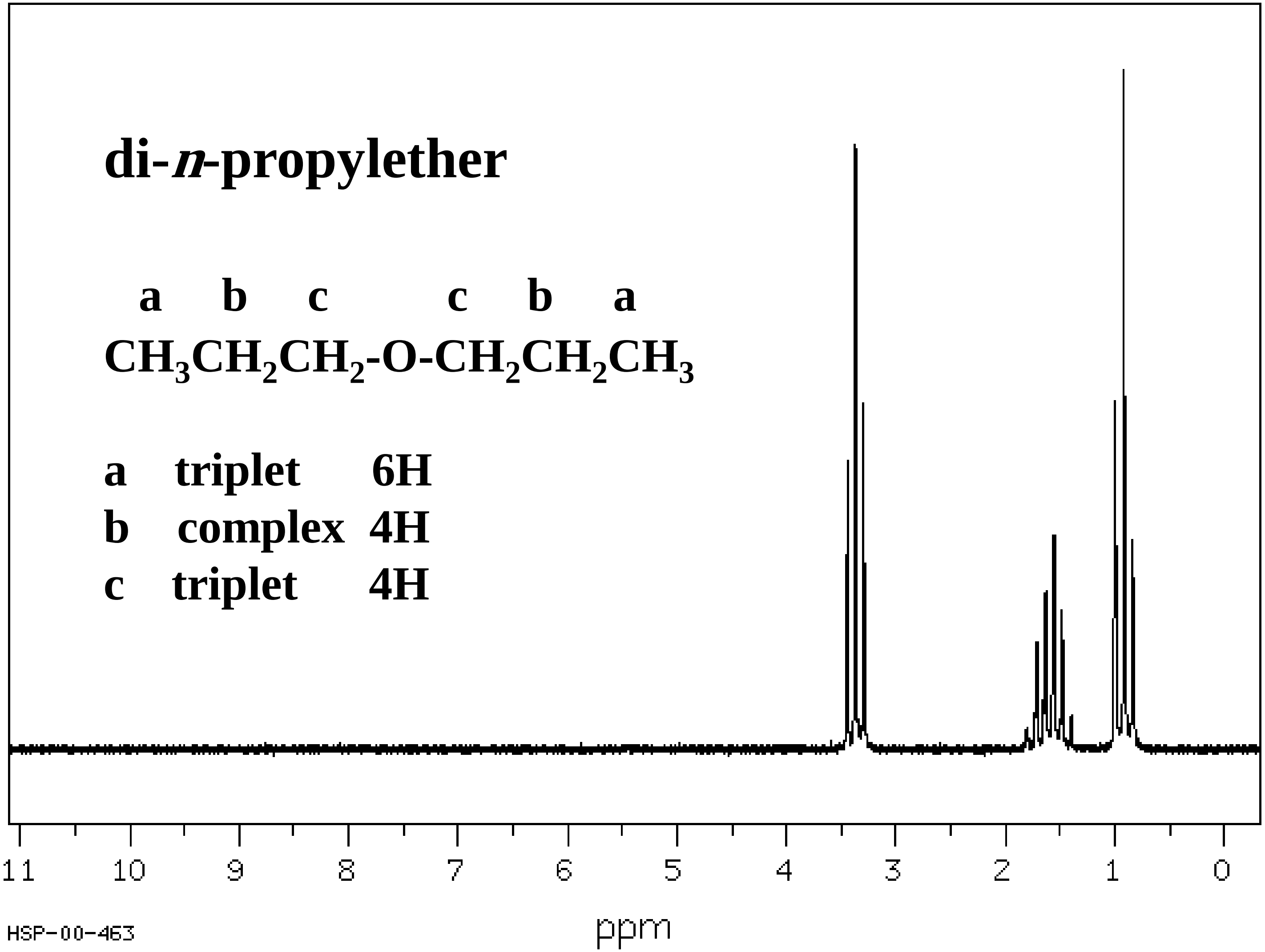
b singlet 6H

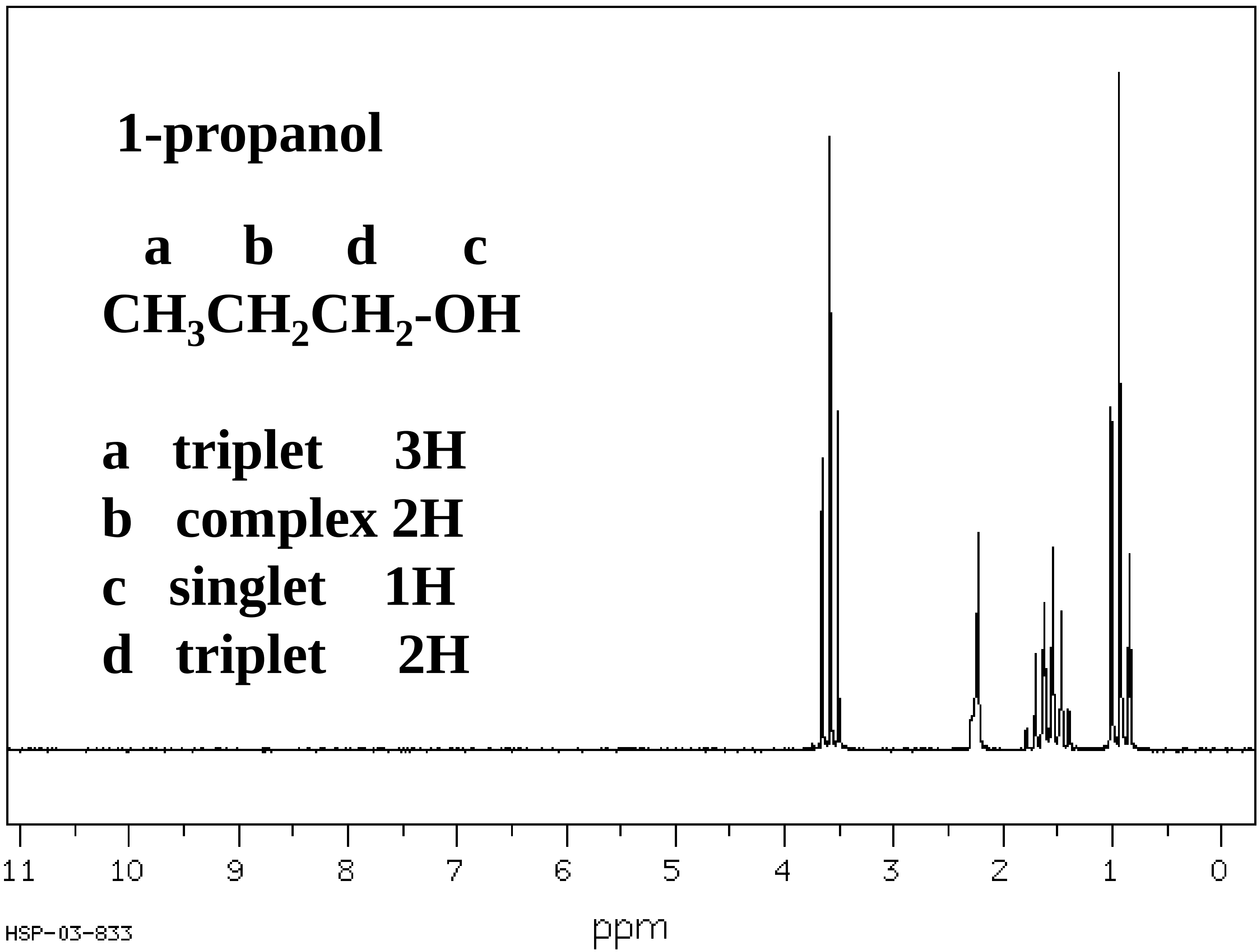
c quartet 2H b & c overlap

di-*n*-propylether

$\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}\text{-O-}\overset{c}{CH_2}\overset{b}{CH_2}\overset{a}{CH_3}$

a	**triplet**	**6H**
b	**complex**	**4H**
c	**triplet**	**4H**





1-propanol

a b d c

$CH_3CH_2CH_2\text{-}OH$

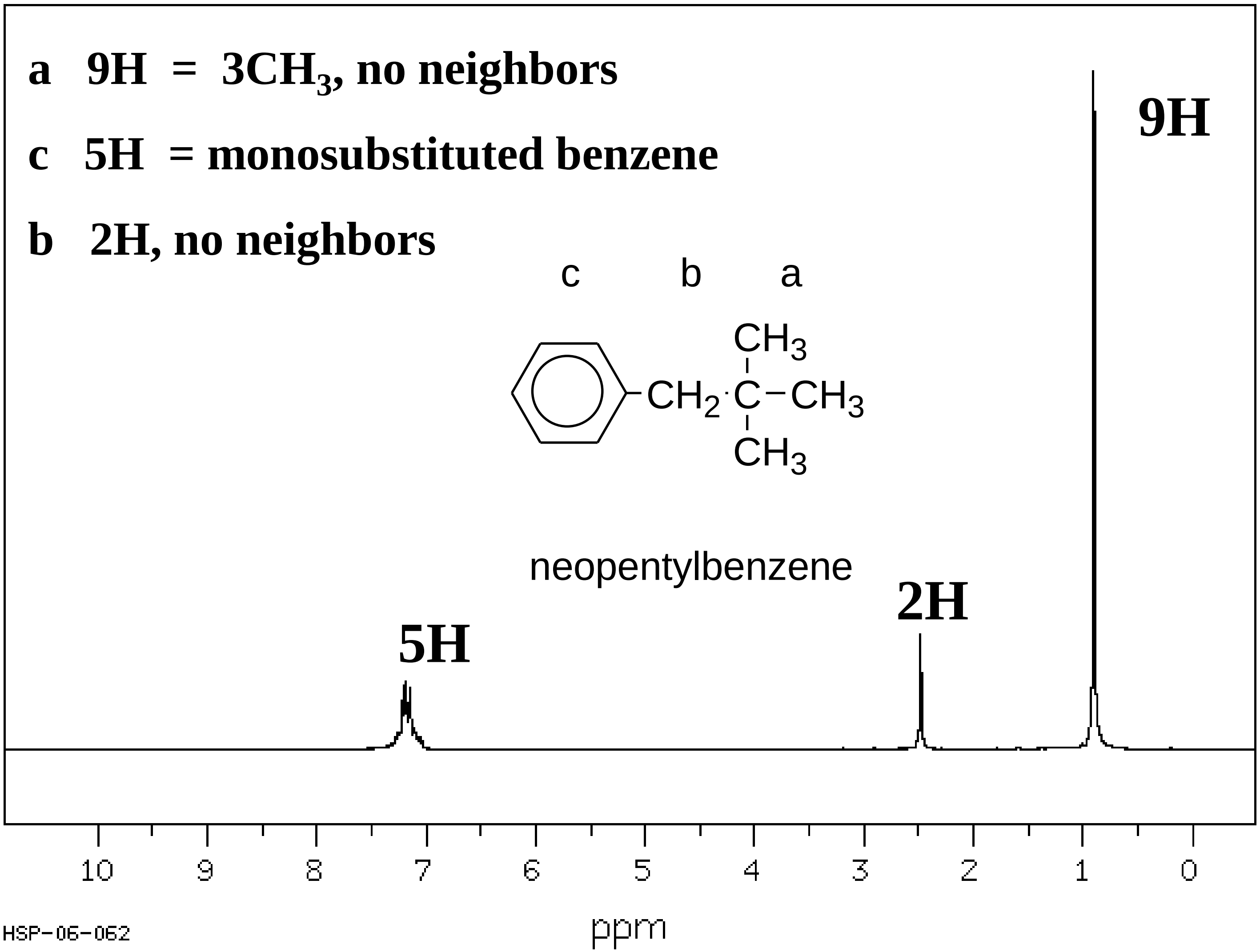
a	triplet	3H
b	complex	2H
c	singlet	1H
d	triplet	2H

$C_{11}H_{16}$

a 9H = $3CH_3$, no neighbors

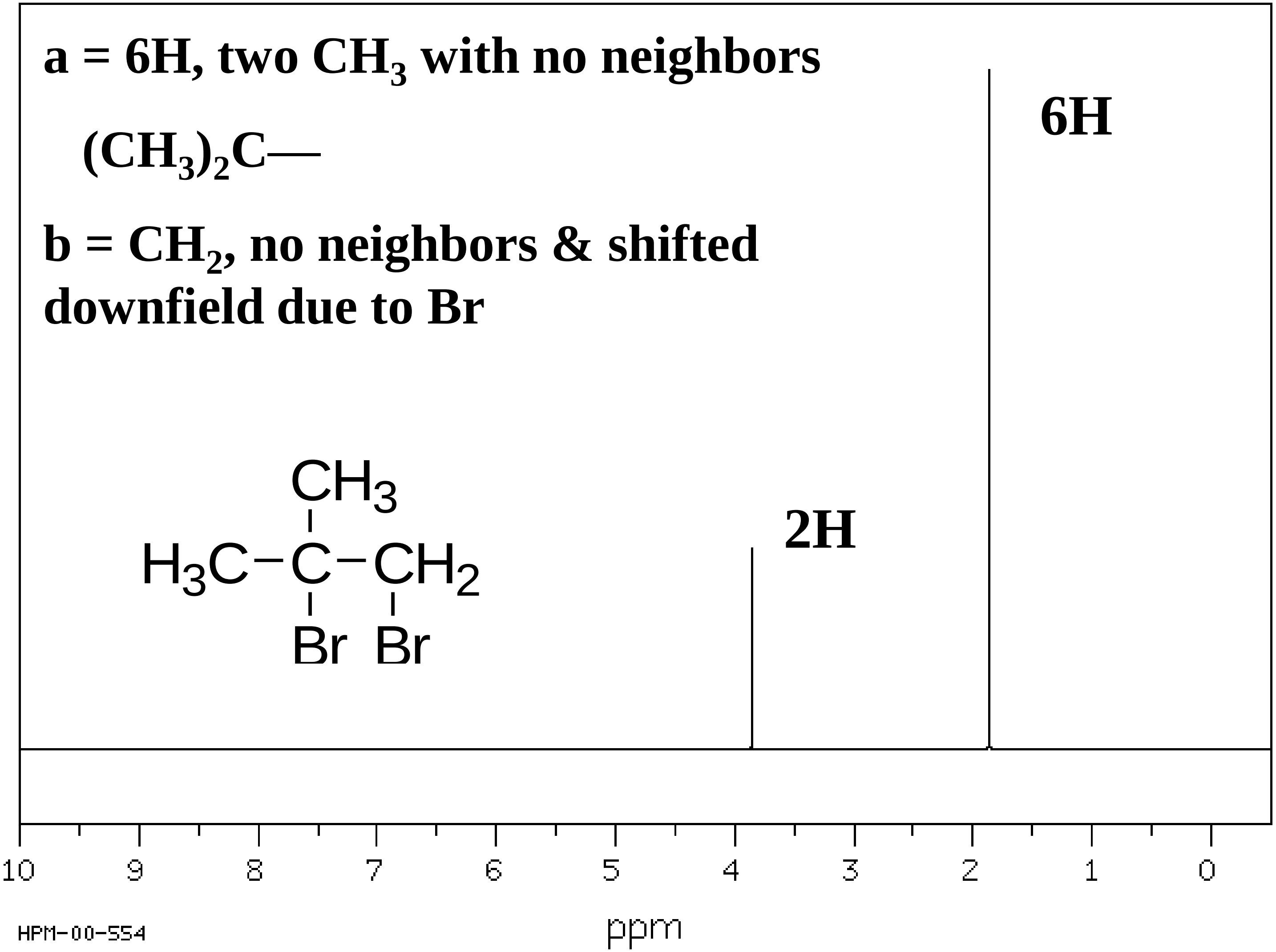
c 5H = monosubstituted benzene

b 2H, no neighbors



HSP-06-062

$C_4H_8Br_2$



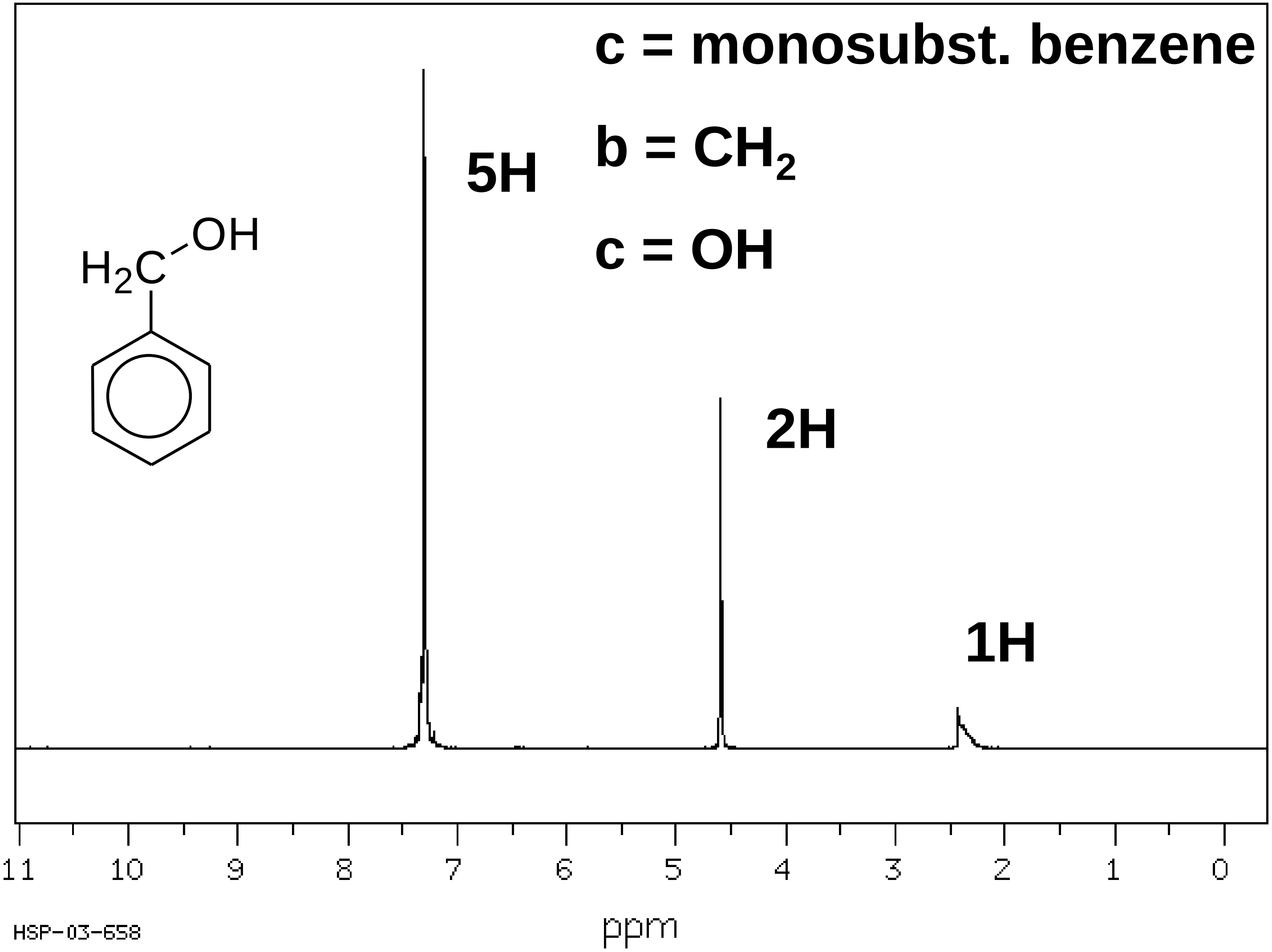
a = 6H, two CH_3 with no neighbors

$(CH_3)_2C$—

b = CH_2, no neighbors & shifted downfield due to Br

$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-\underset{\displaystyle Br}{CH_2}$$

C_7H_8O



c = monosubst. benzene

b = CH_2

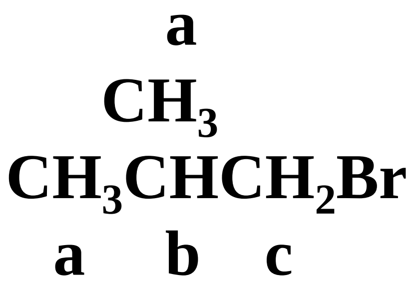
c = OH

C_4H_9Br

a	doublet	1.04 ppm	6H
b	complex	1.95 ppm	1H
c	doublet	3.33 ppm	2H

a = two equivalent CH_3’s with one neighboring H (b?)

c = CH_2 with one neighbor H (also b)



$$\underset{a}{CH_3}\underset{b}{\overset{\overset{a}{CH_3}}{CH}}\underset{c}{CH_2}Br$$

a	6H	doublet
b	1H	complex
c	2H	doublet

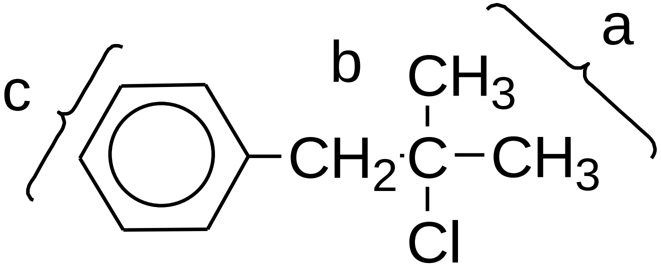
$C_{10}H_{13}Cl$

a singlet 1.57 ppm 6H
b singlet 3.07 ppm 2H
c singlet 7.27 ppm 5H

a = two-equilalent CH_3’s with no neighbors

c = monosubstituted benzene ring

b = CH_2



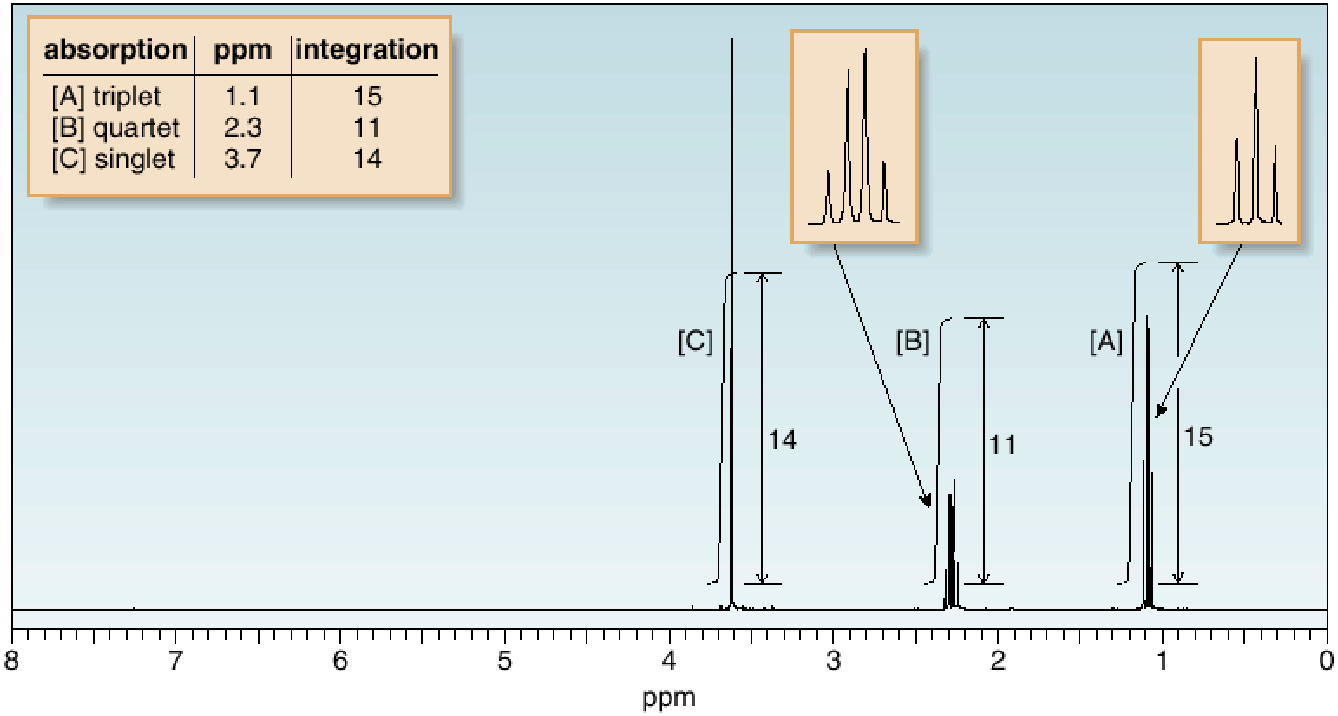
a singlet 6H
b singlet 2H
c singlet 5H

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

How To Use ^{1}H NMR Data to Determine a Structure

Example Using its ^{1}H NMR spectrum, determine the structure of an unknown compound **X** that has molecular formula $C_4H_8O_2$ and contains a C=O absorption in its IR spectrum.



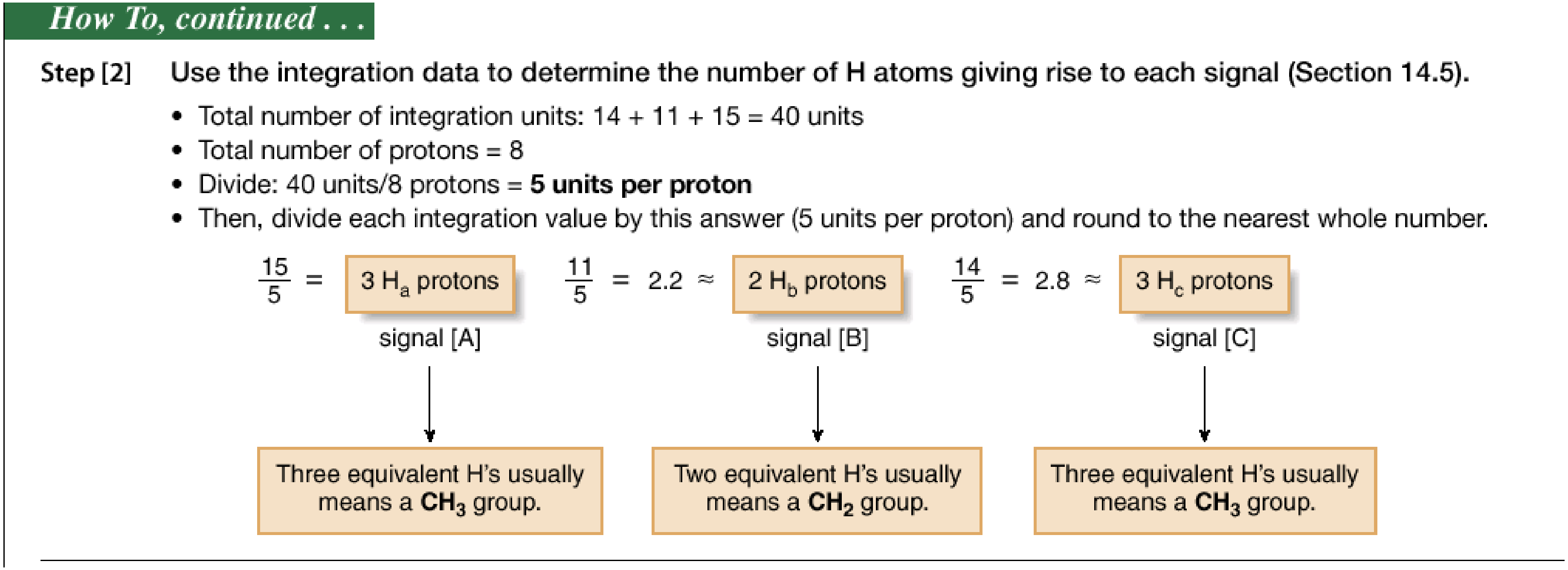
absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14

Step [1] **Determine the number of different kinds of protons.**

- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a, H_b, and H_c).

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination



How To, continued . . .

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).

- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

$\frac{15}{5}$ = 3 H_a protons

signal [A]

Three equivalent H's usually means a $\mathbf{CH_3}$ group.

$\frac{11}{5} = 2.2 \approx$ 2 H_b protons

signal [B]

Two equivalent H's usually means a $\mathbf{CH_2}$ group.

$\frac{14}{5} = 2.8 \approx$ 3 H_c protons

signal [C]

Three equivalent H's usually means a $\mathbf{CH_3}$ group.

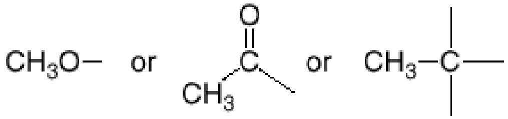
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

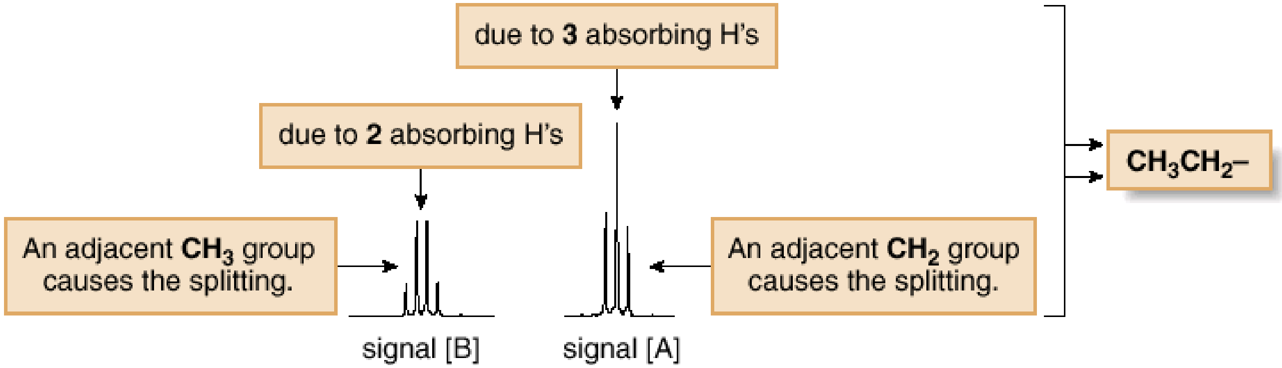
How To, continued . . .

Step [3] **Use individual splitting patterns to determine what carbon atoms are bonded to each other.**

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group $\dashrightarrow$ CH_3CH_2-.



due to **3** absorbing H's

due to **2** absorbing H's

An adjacent **CH_3** group causes the splitting.

An adjacent **CH_2** group causes the splitting.

CH_3CH_2-

To summarize, **X** contains CH_3-, CH_3CH_2-, and $C{=}O$ (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a ^{1}H NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

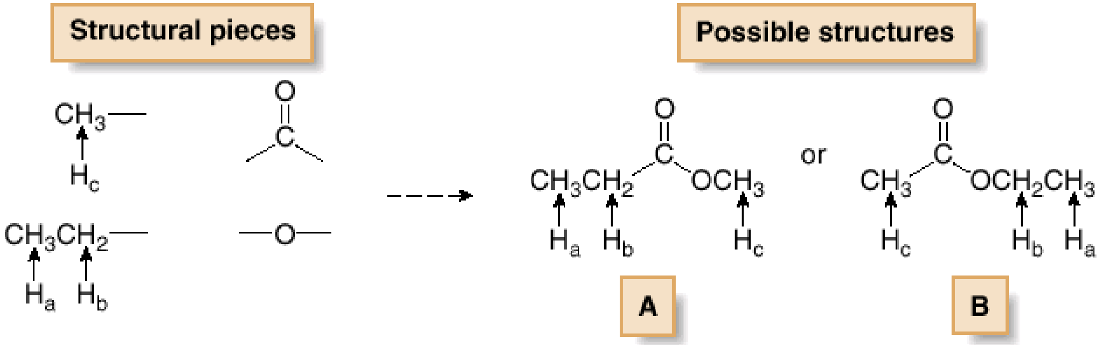
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

How To, continued . . .

Step [4] Use chemical shift data to complete the structure.

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:



- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**

^{13}C NUCLEAR
MAGNETIC RESONANCE

✓ ^{13}C occurs naturally as 1.11% of total C and the NMR signal is weaker than ^{1}H.

Therefore, acquisition of a spectrum usually takes much longer than in ^{1}H NMR. Fourier Transform NMR is used to collect a spectrum.

✓ The magnetogyric ratio of the ^{13}C nucleus is about 1/4 that of the ^{1}H nucleus. Therefore, the resonance frequency in ^{13}C NMR:

is much lower than in ^{1}H NMR.

(75 MHz for ^{13}C as opposed to 300 MHz for ^{1}H in a 7.04 Tesla field).

✓ At these lower frequencies, the excess population of nuclei in the lower spin state is reduced, which, in turn, reduces the sensitivity of NMR detection.

✓ ^{13}C resonances occur:

from 0 to 200 ppm (δ) so there is little interference with ^{1}H δ values.

✓ Unlike ^{1}H NMR, the area of a peak is not proportional to the number of carbons giving rise to the signal. Therefore, integrations are usually not done.

✓ Each unique carbon in a molecule gives rise to a ^{13}C NMR signal. Therefore, if there are fewer signals in the spectrum than carbon atoms in the compound, the molecule must possess symmetry.

✓ ^{13}C peaks are :

split by the attached hydrogens.

- ✓ **When running a spectrum:**

The *protons are usually decoupled from their respective carbons* to give a singlet for each carbon atom.

This is called a *proton-decoupled spectrum*.

- ✓ **Broadband decoupling:**

eliminates splitting of C by Hs attached to that C.

- ✓ **Off-resonance decoupling:**

eliminates interactions of hydrogens on adjacent carbons.

- ✓ ***Peaks in a ^{13}C NMR spectrum are: typically singlets***

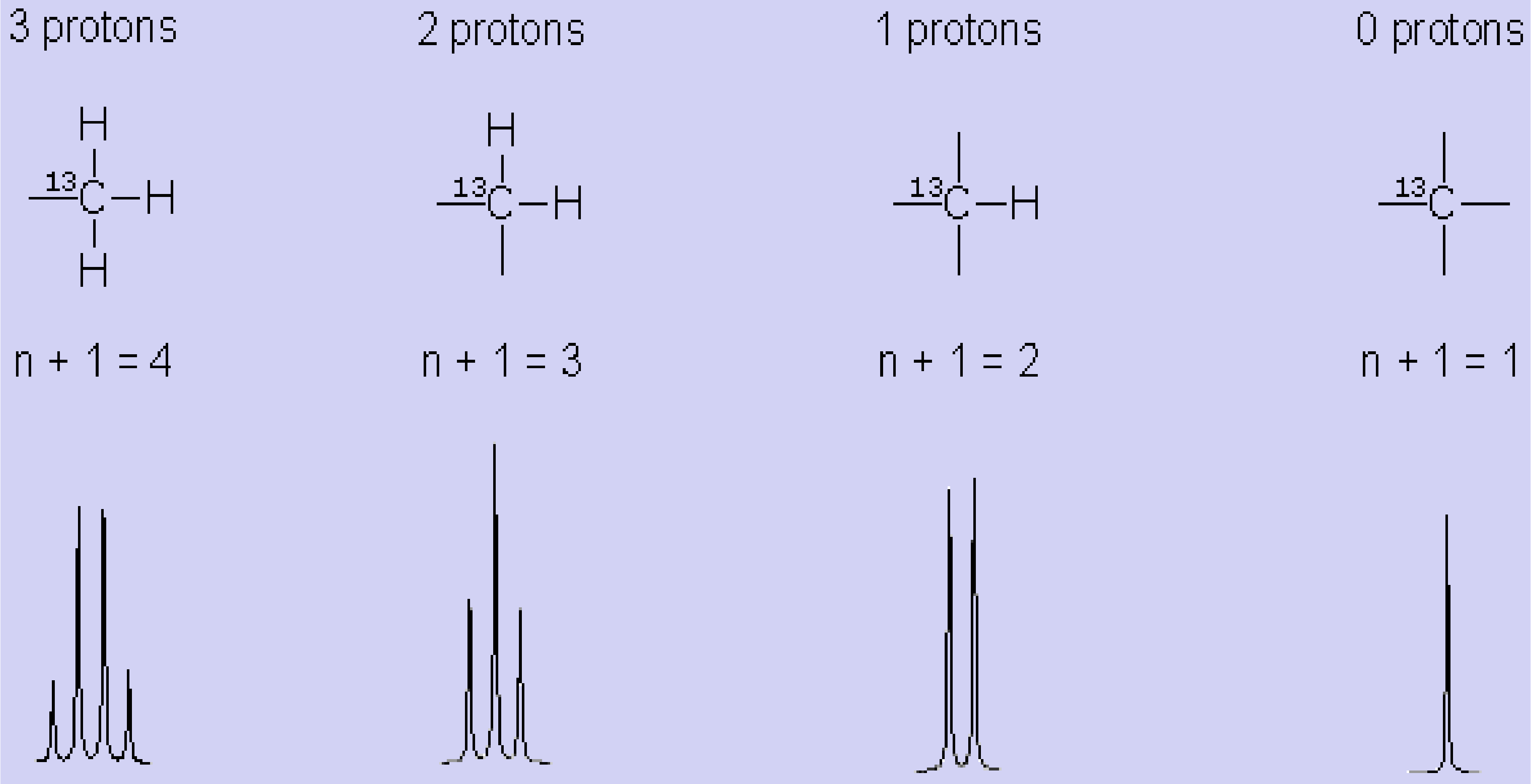
- ✓ ***$^{13}C—^{13}C$ splitting is not seen:***

  because the probability of two ^{13}C nuclei being in the same molecule is very small.

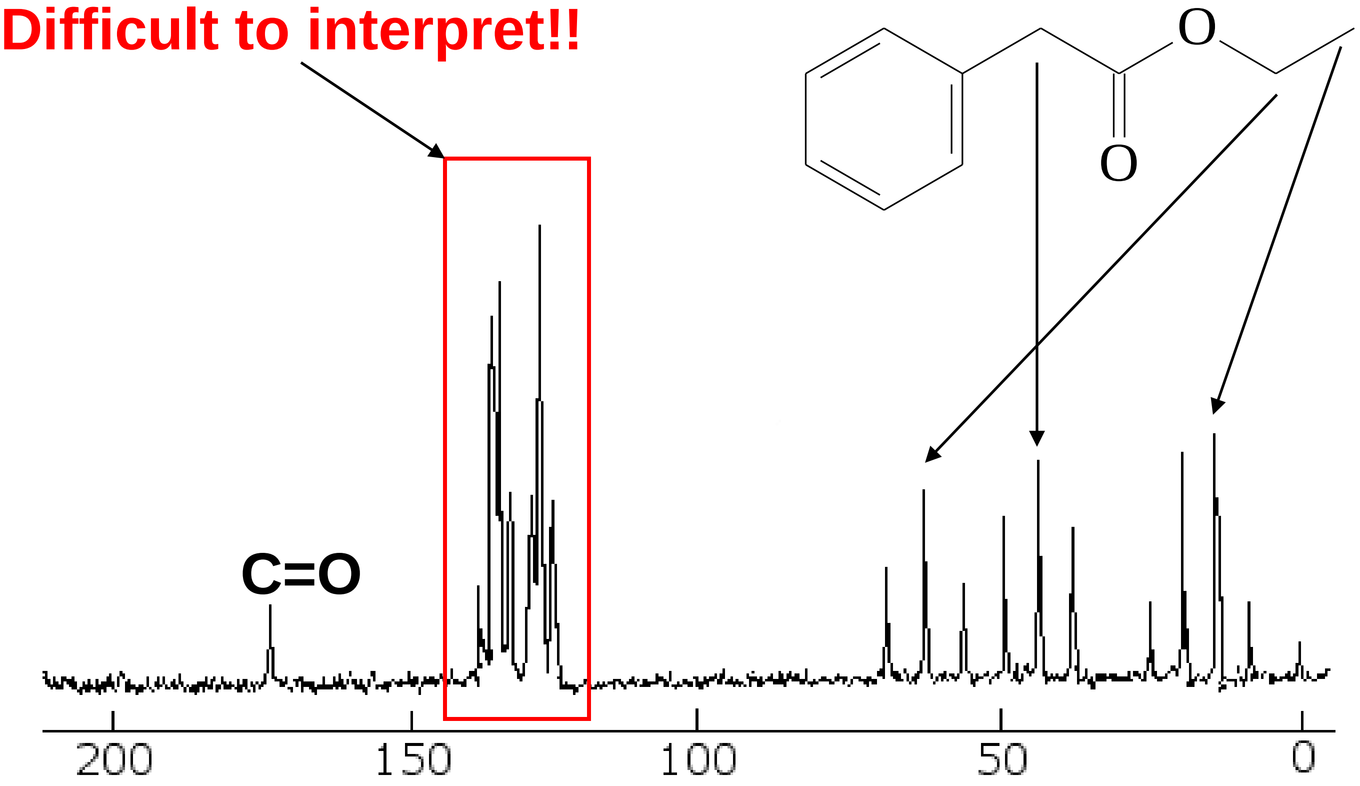
- ✓ ***$^{13}C—^{1}H$ splitting is not seen:***

  because spectrum is measured under conditions that suppress this splitting (*broadband decoupling*).

Carbon-13 Proton-Coupled Patterns

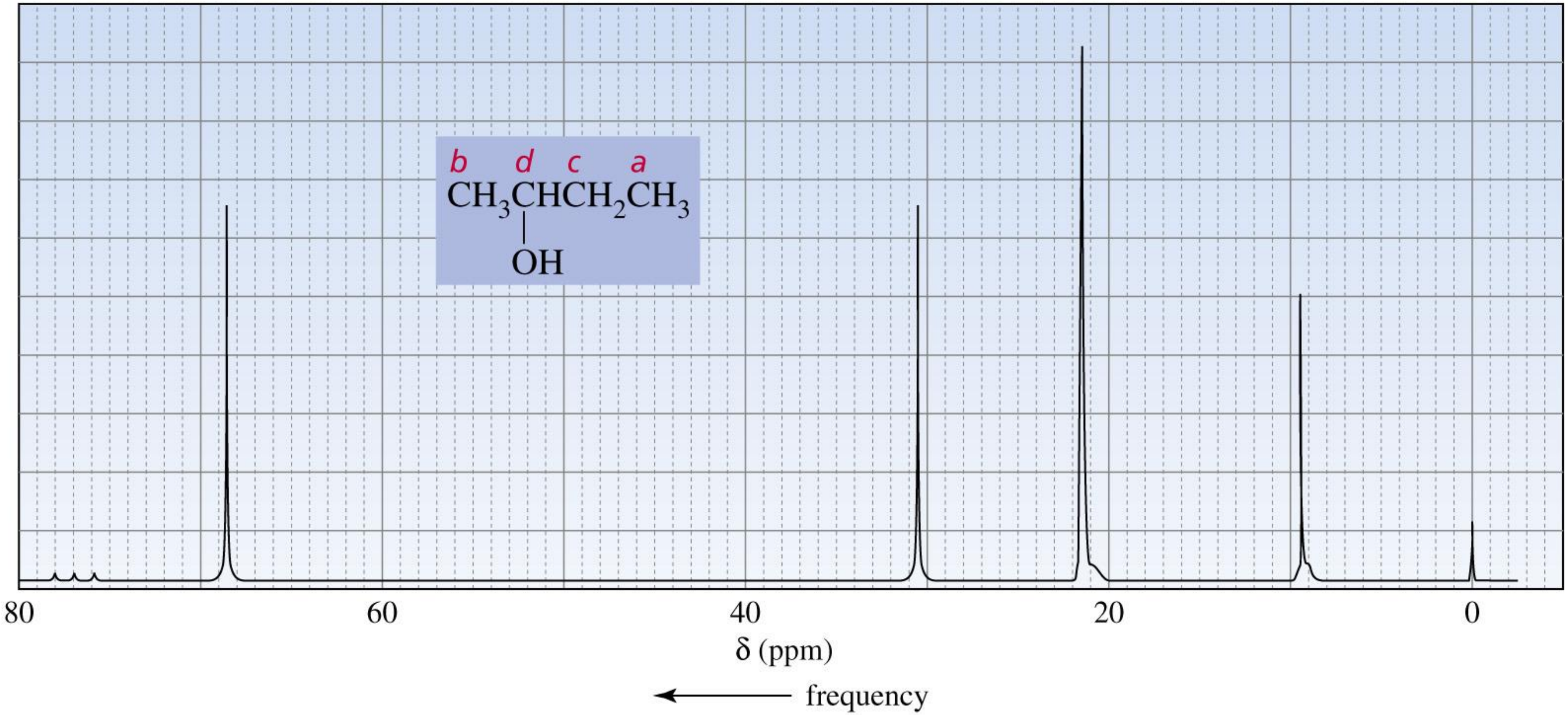


Carbon-13 Proton-Coupled Spectrum of Ethyl Phenylacetate

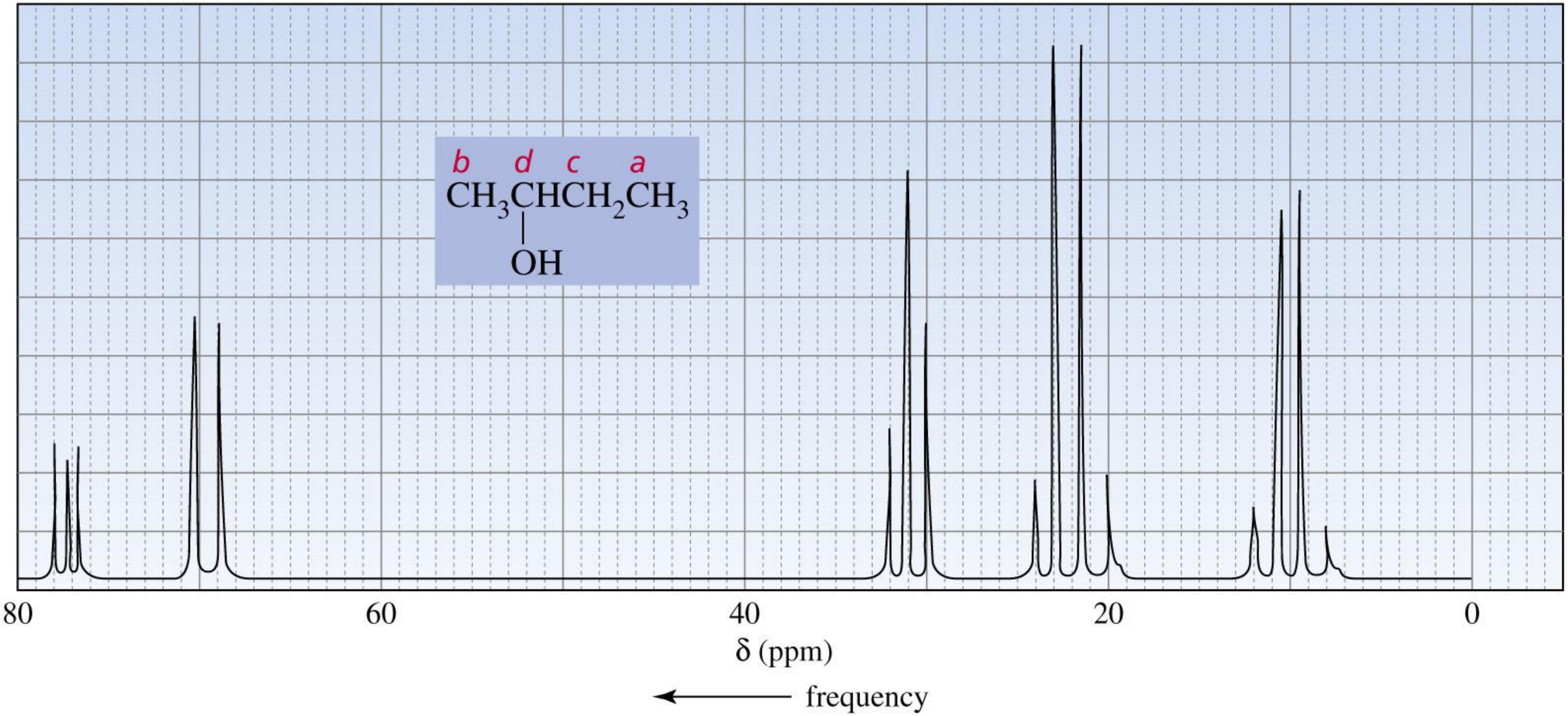

Difficult to interpret!!

Typical coupling constants for ^{13}C-^{1}H one-bond couplings are between *100 to 250 Hz*.

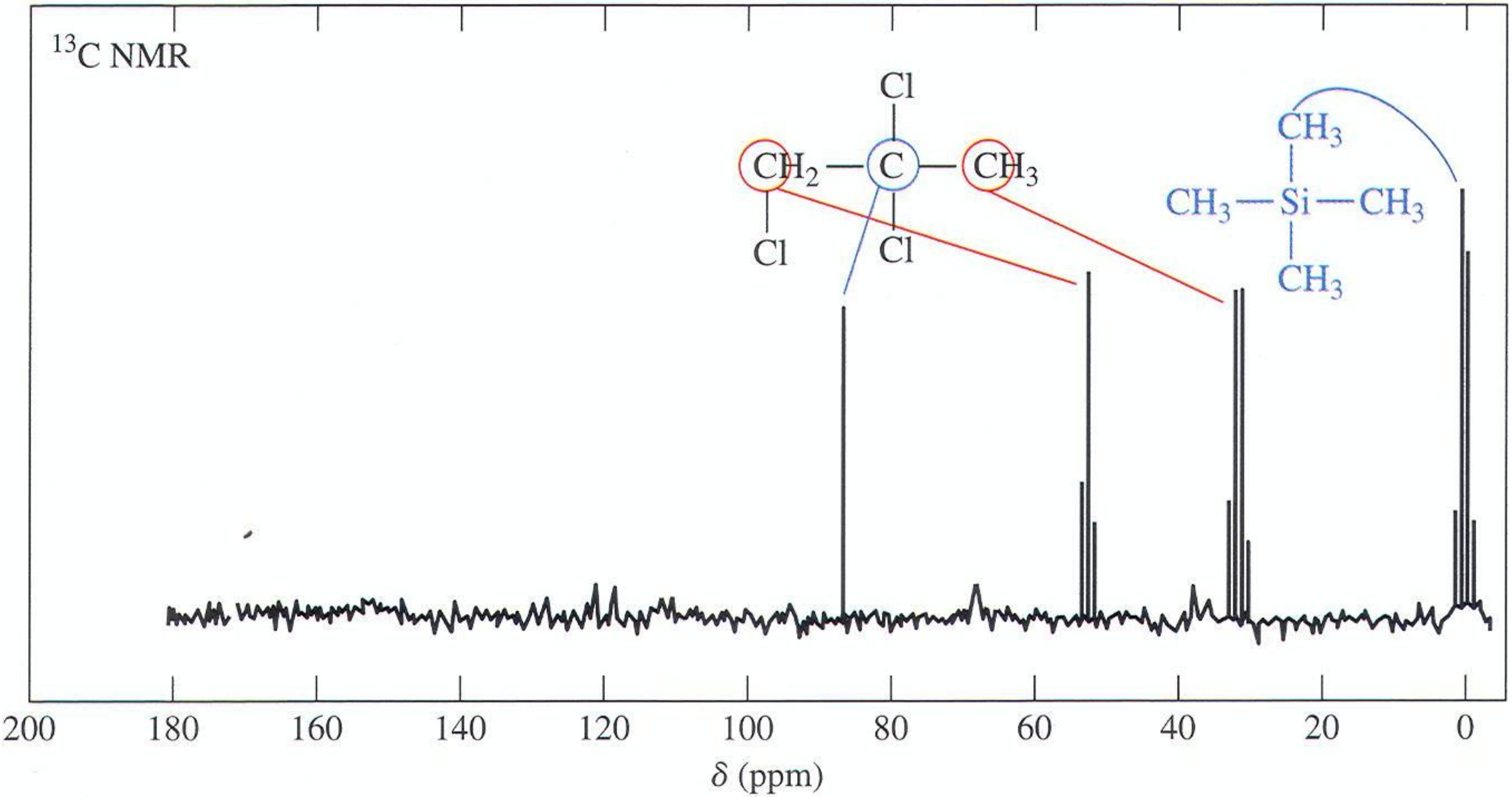
Proton-Decoupled ^{13}C NMR of 2-Butanol



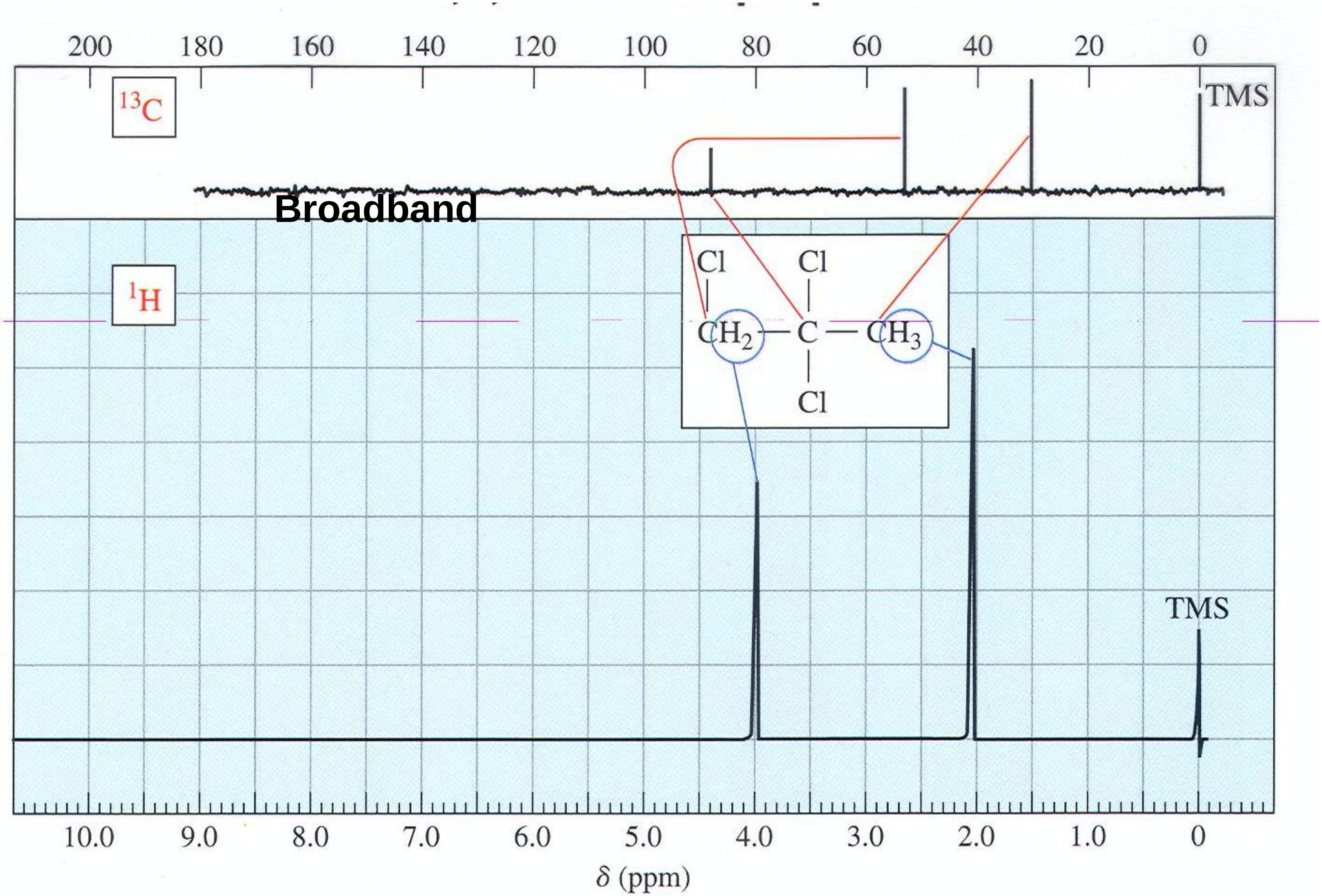
Proton-Coupled ^{13}C NMR of 2-Butanol



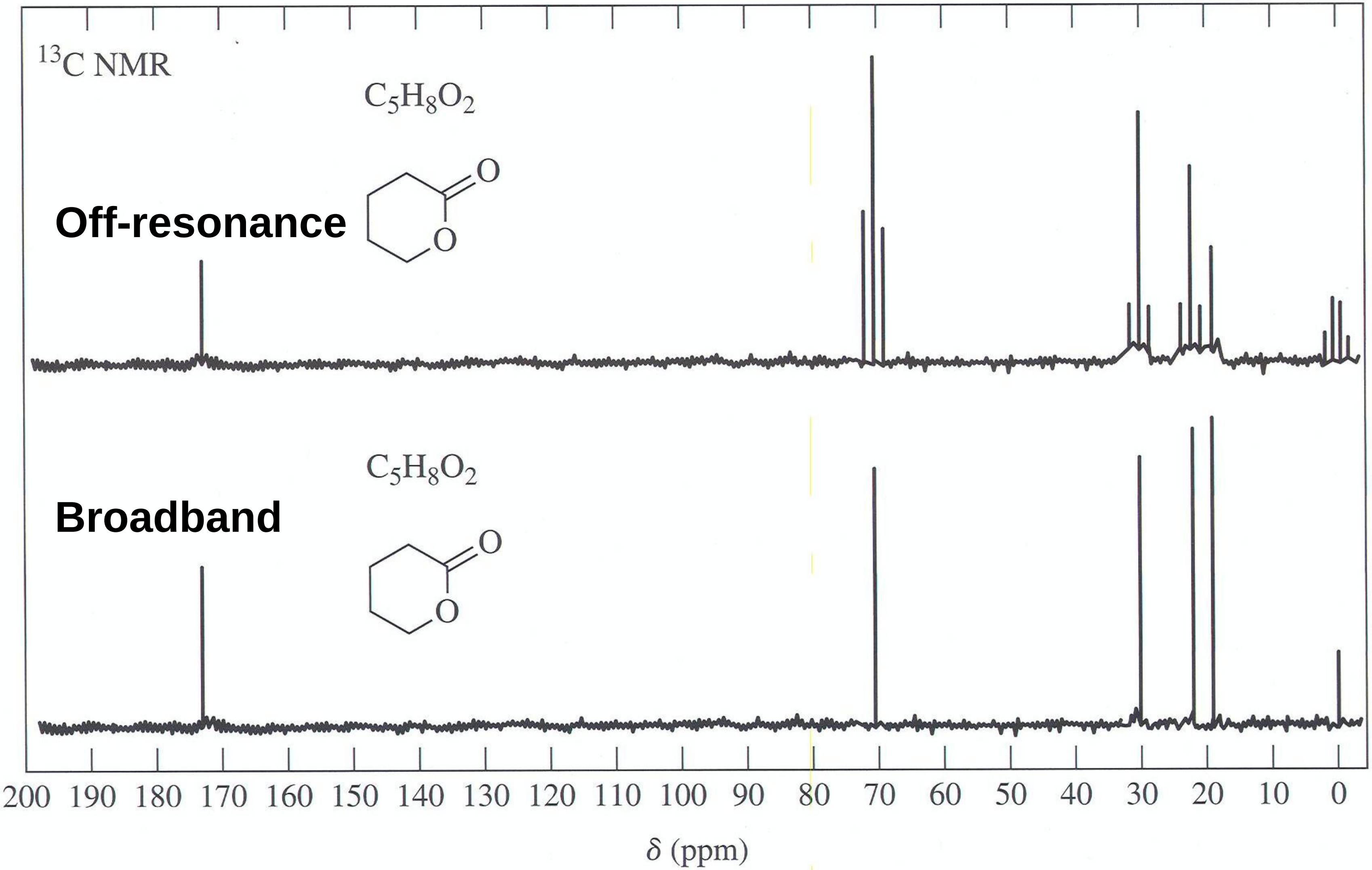
^{13}C Off-resonance decoupled spectrum



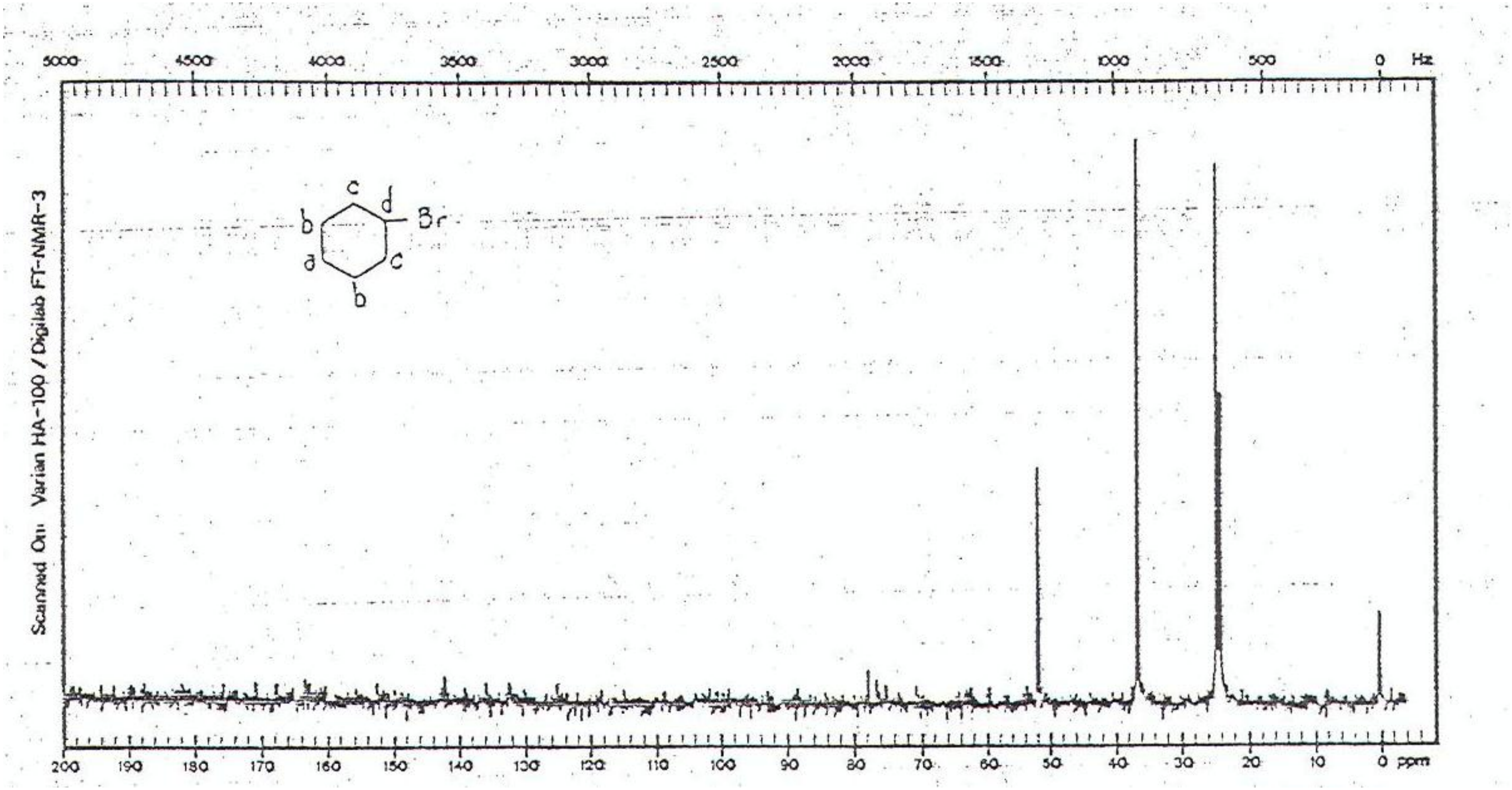
^1H & ^{13}C NMR: 1,1,2-trichloropropane



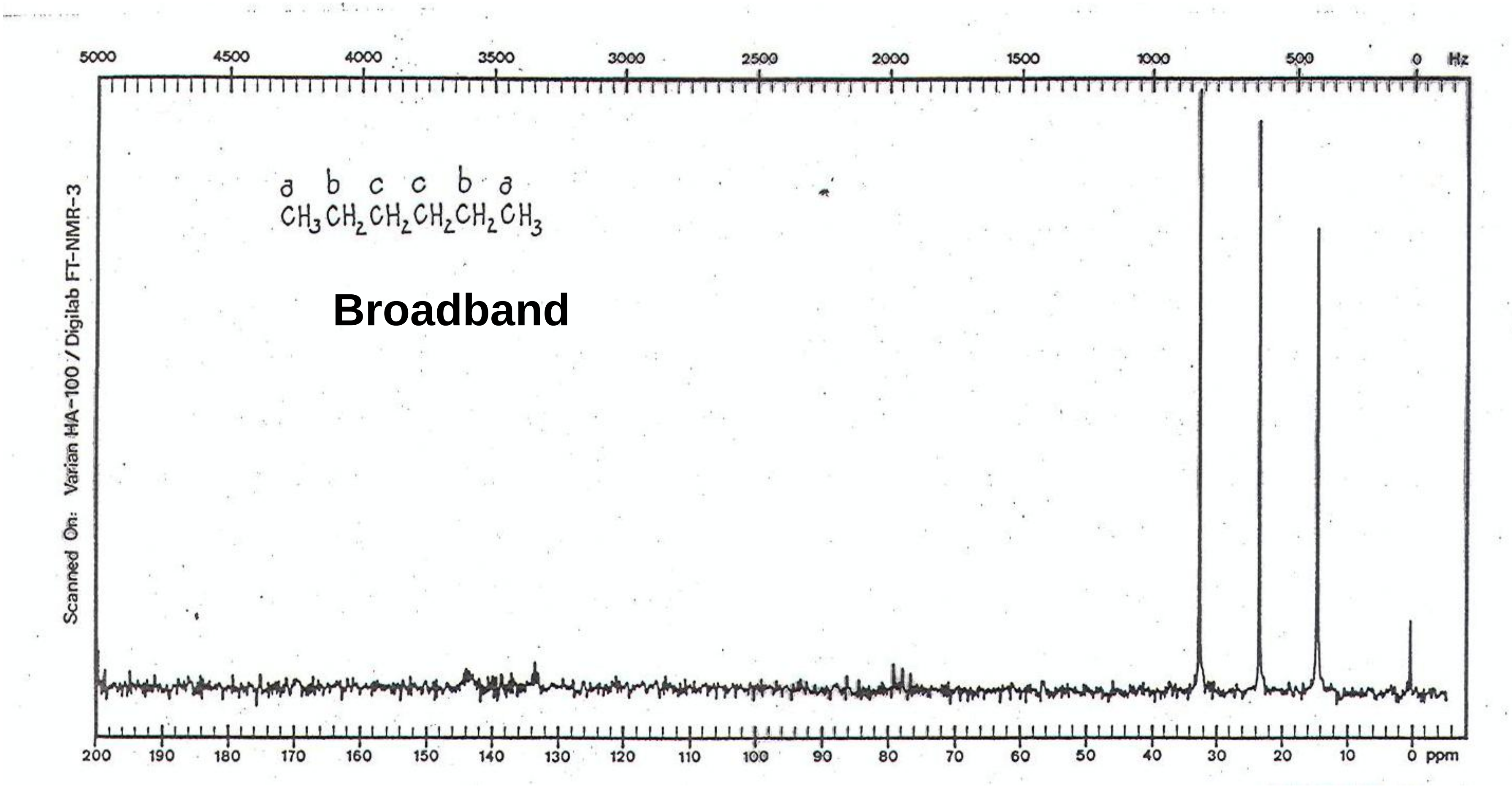
^{13}C Off-resonance & Broadband decoupled spectra



^{13}C Broadband decoupled spectrum

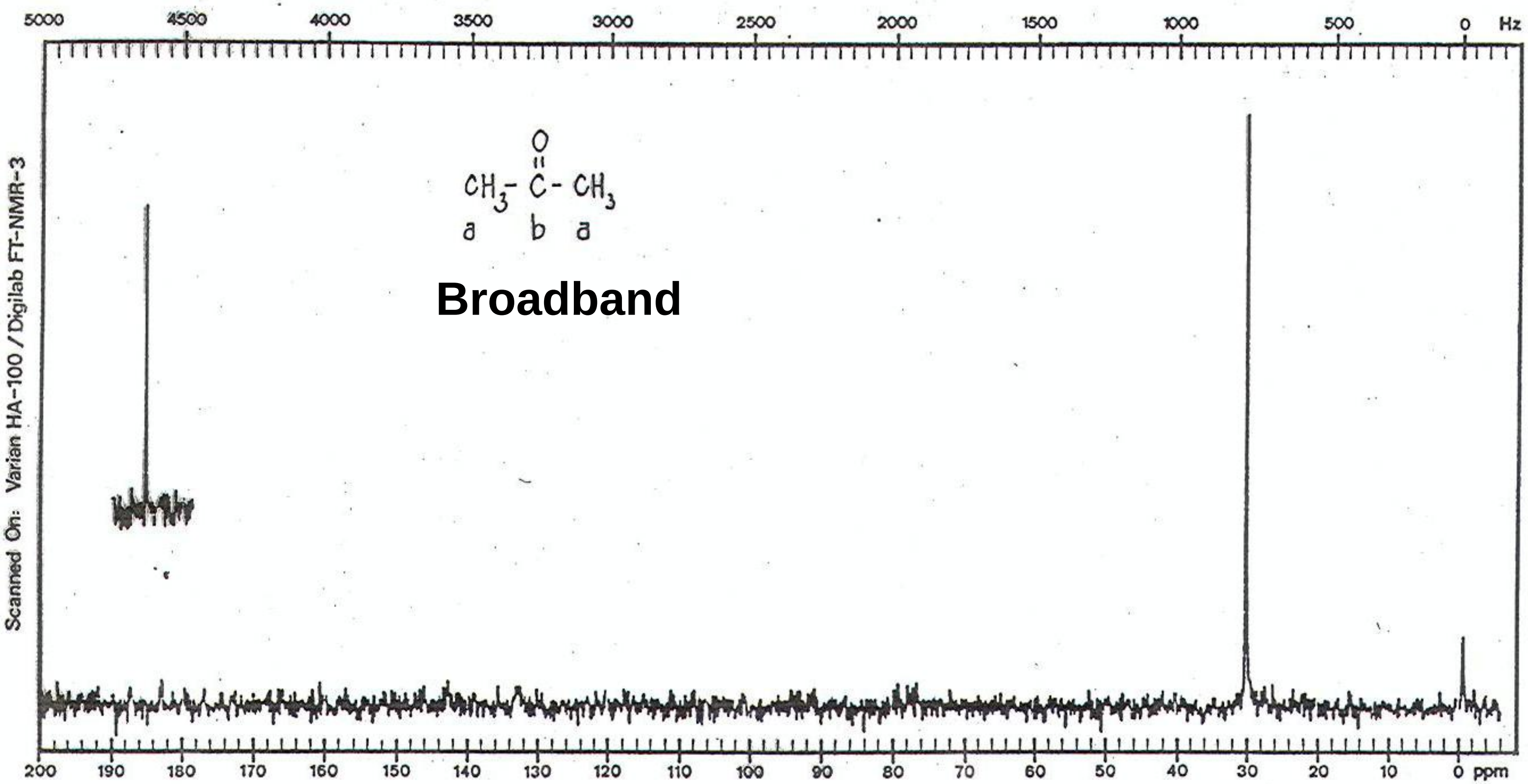


^{13}C NMR – n-Hexane



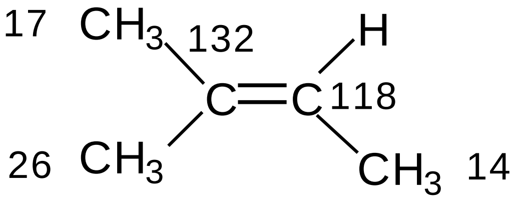
Broadband

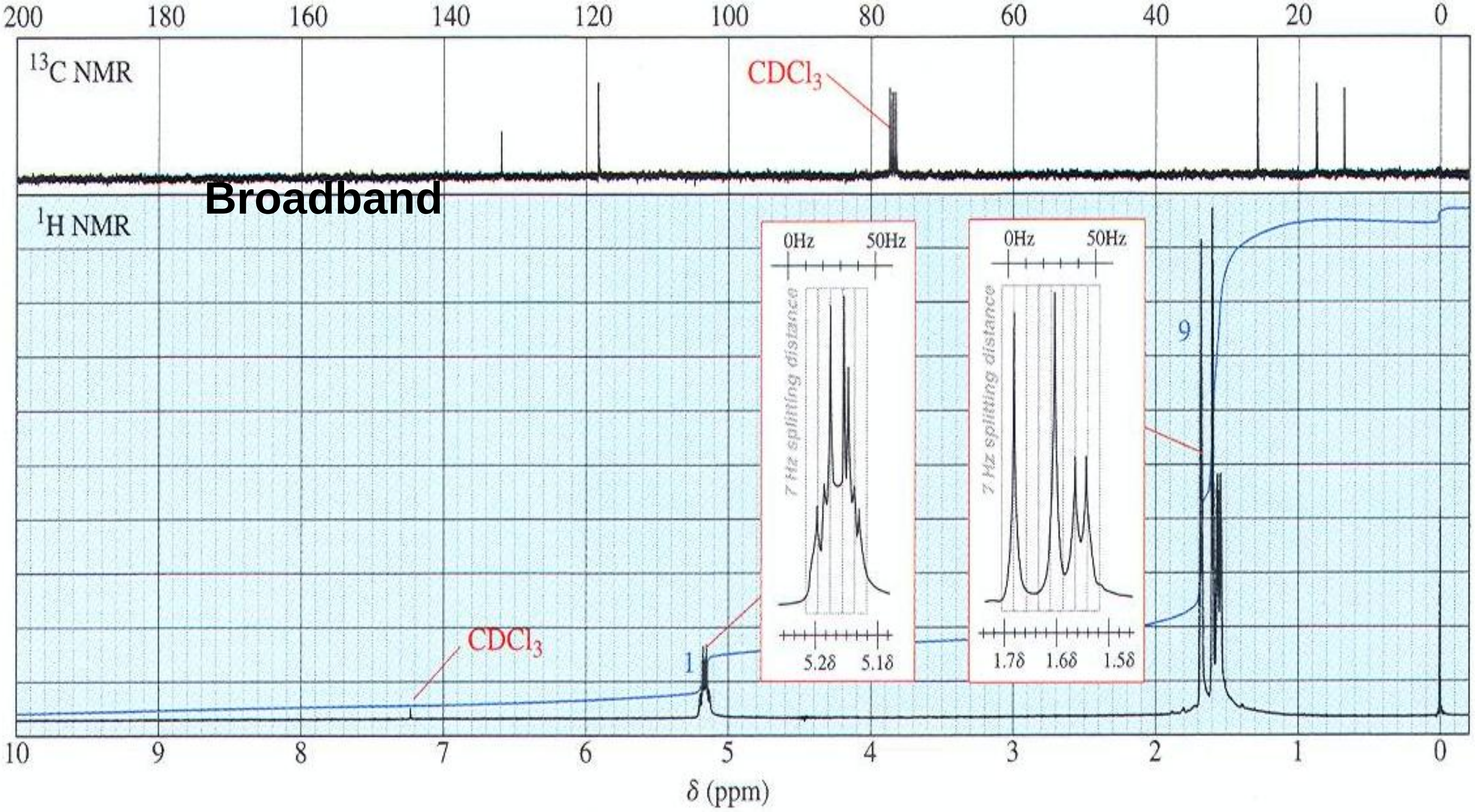
^{13}C NMR – Acetone



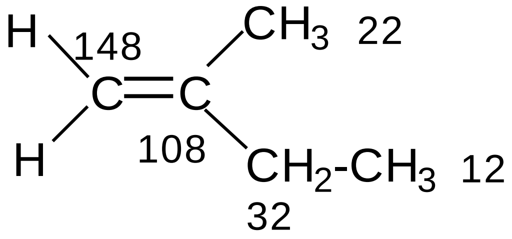
Broadband

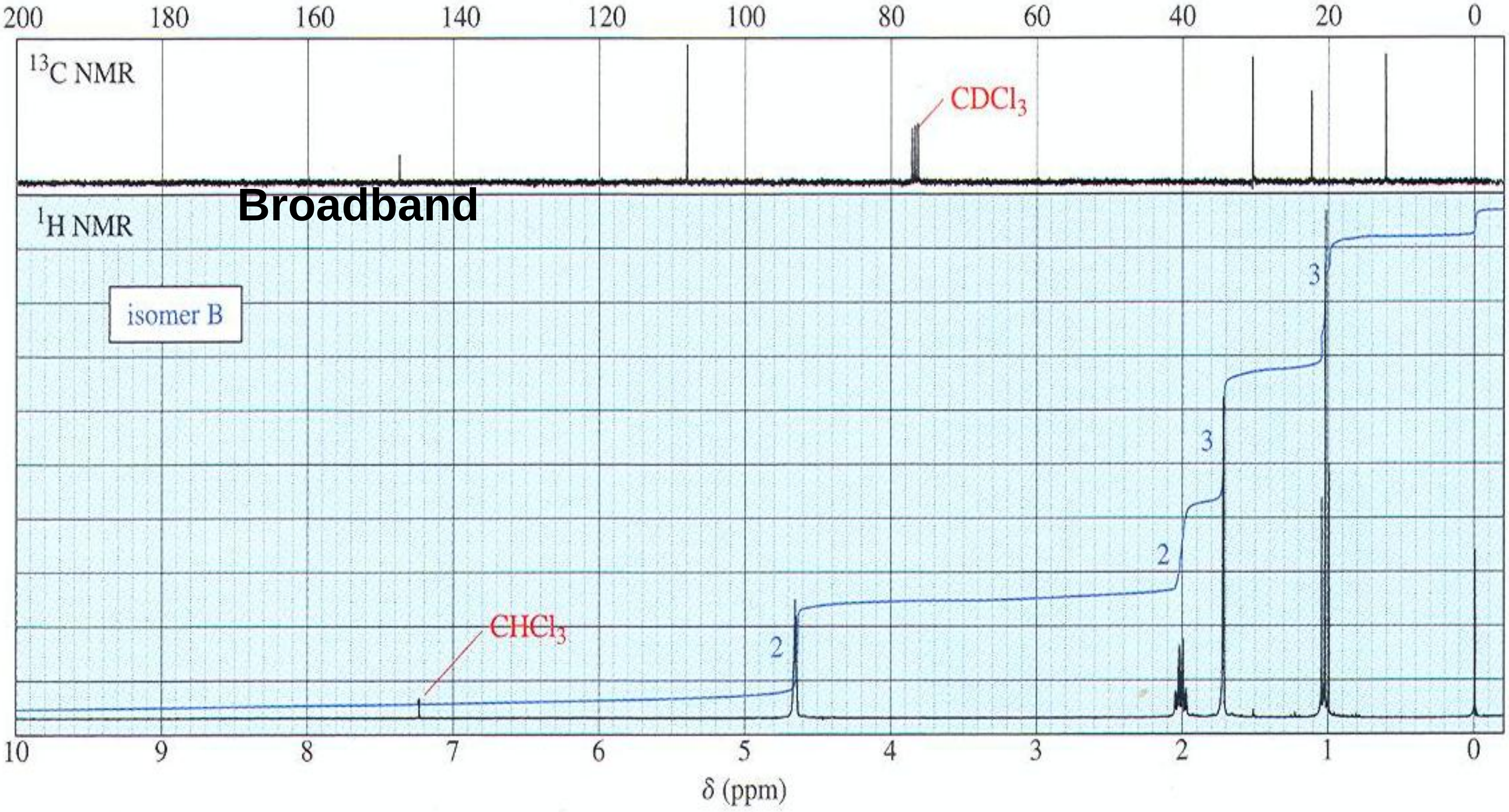
^{1}H & ^{13}C NMR: 2-methyl-2-butene




Broadband

^{1}H & ^{13}C NMR: 2-methyl-1-butene

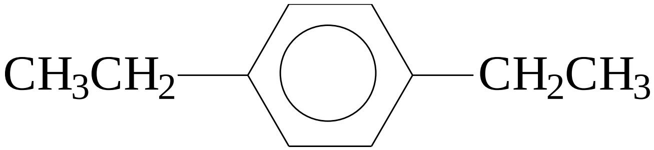


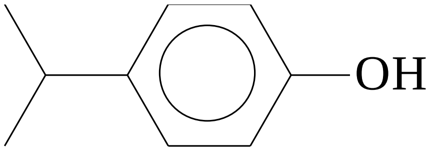

Broadband

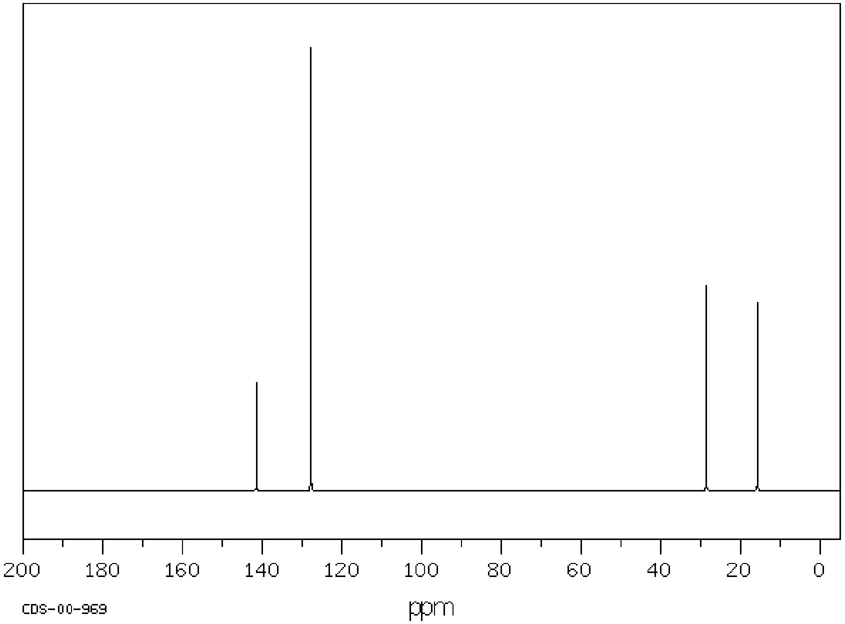
Symmetry in ^{13}C NMR

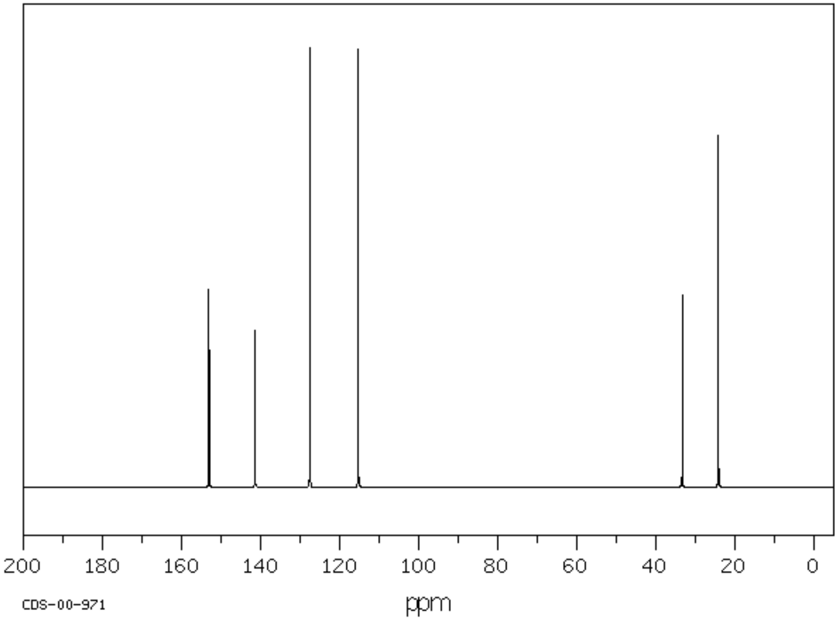
✓ **If there are fewer signals in the spectrum than carbon atoms in the compound, the molecule must possess symmetry.**

Examples:

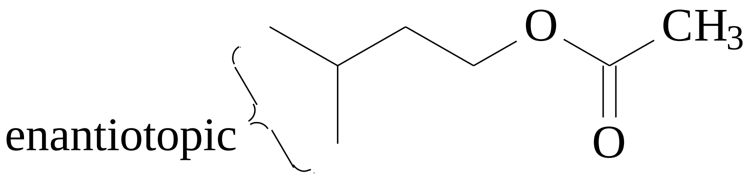


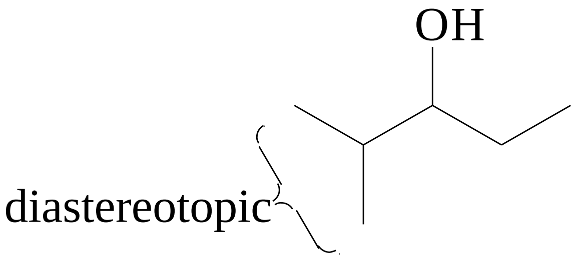


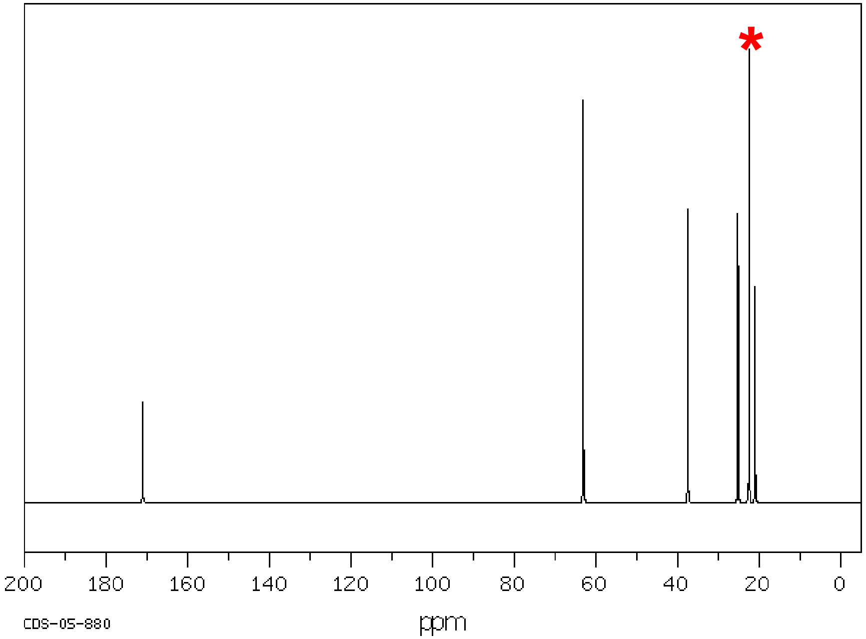


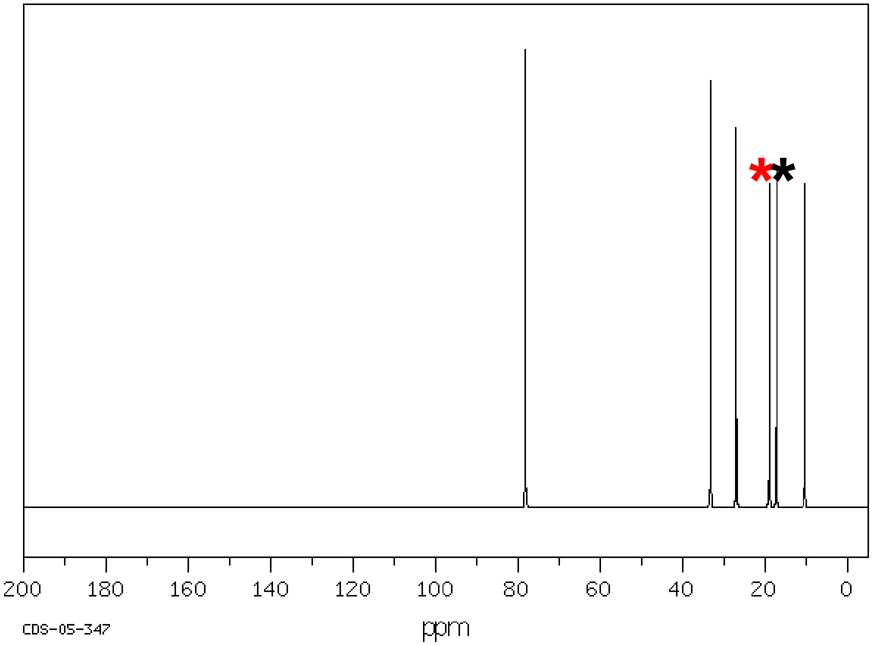


Enantiotopic vs Diastereotopic CH$_3$'s

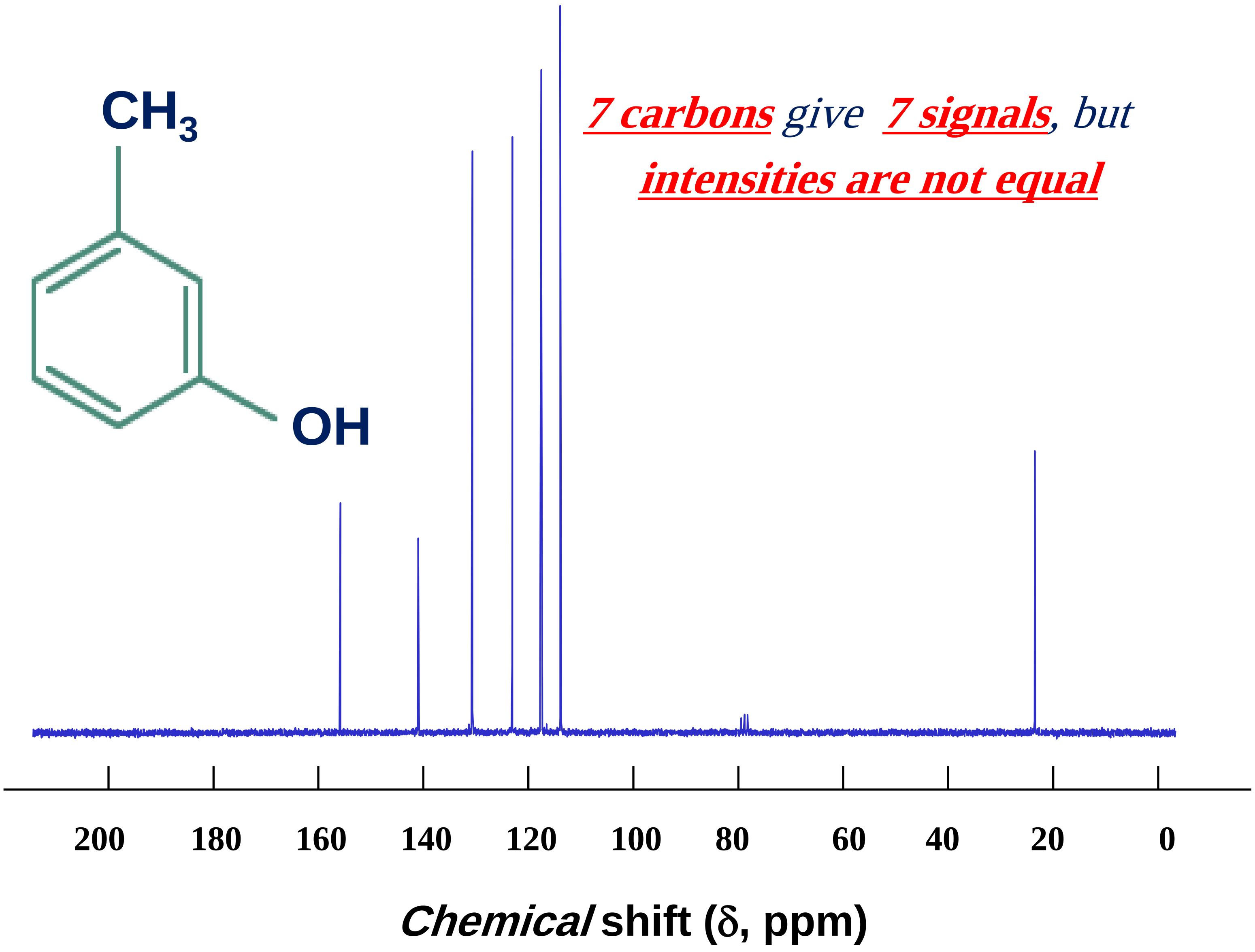








^{13}C NMR and Peak Intensities



7 carbons *give* ***7 signals***, *but*
intensities are not equal

^{1}H and ^{13}C NMR compared

- ✓ Both give us information about the **number of chemically nonequivalent nuclei** (***nonequivalent hydrogens or nonequivalent carbons***)
- ✓ Both give us information about the **environment of the nuclei:**

*Ex:(**hybridization state**, **attached atoms**, etc.)*

- ✓ ^{13}C **signals** are spread over a **much wider range than ^{1}H signals** making it easier to identify and count individual nuclei

^{13}C Chemical Shifts

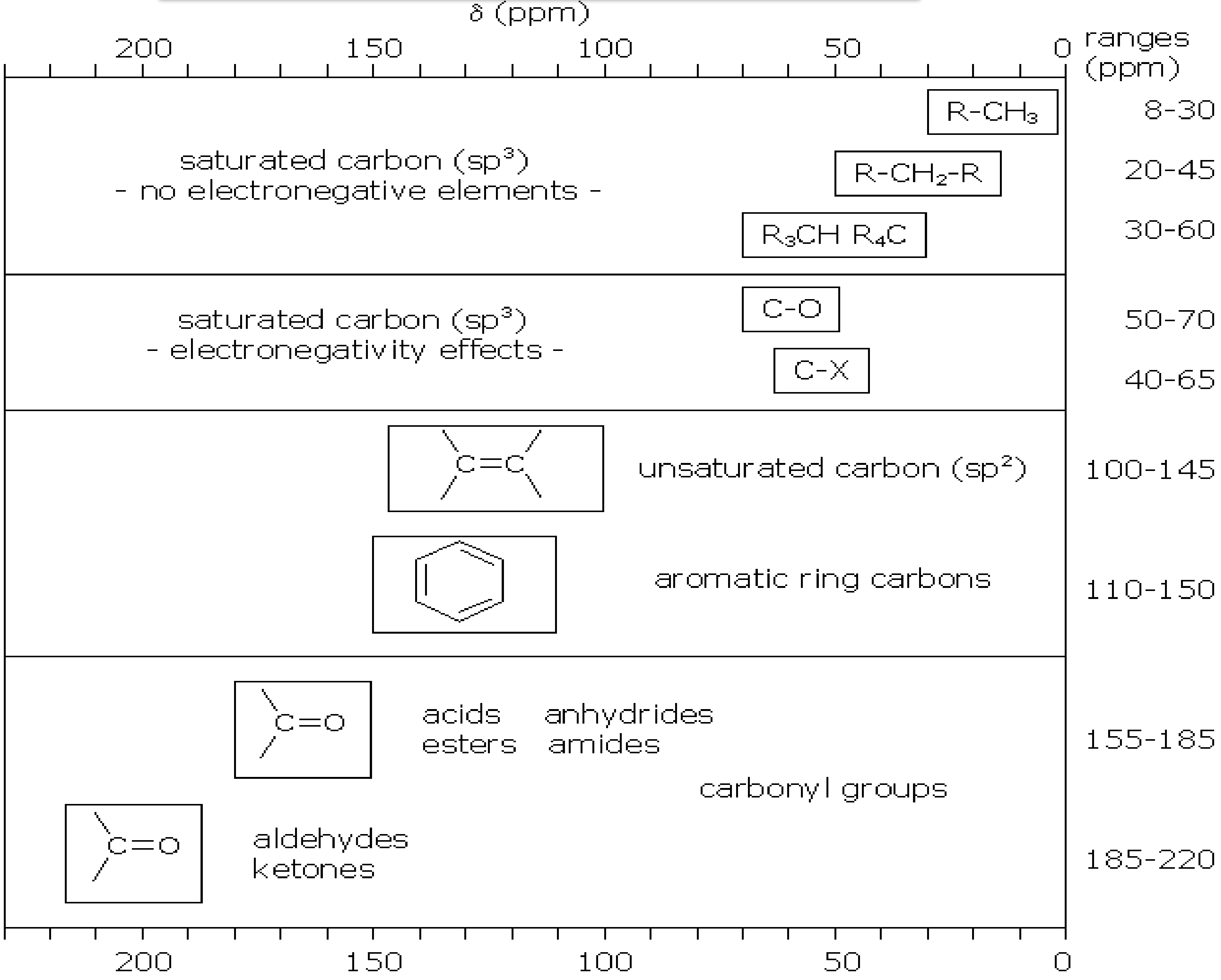
are measured in **ppm (δ)** ***from the carbons of TMS***

^{13}C NMR

C environment			**δ ppm**
Saturated carbons			0-55
	primary	$R\text{-}\mathbf{C}H_3$	4-30
	secondary	$R_2\text{-}\mathbf{C}H_2$	12-50
	tertiary	$R_3\text{-}\mathbf{C}H$	22-54
	quaternary	$R_4\text{-}\mathbf{C}$	29-47
Olefinic carbons			100-165
		$R_2C{=}\mathbf{C}H_2$	100-110
		$R\text{-}CH{=}\mathbf{C}H_2$	110-120
		$R\text{-}CH{=}\mathbf{C}H\text{-}R$	125-150
		$CH_2{=}\mathbf{C}H\text{-}R$	130-154
		$CH_2{=}\mathbf{C}R_2$	140-165
Allenes			
		$\mathbf{C}{=}C{=}\mathbf{C}$	70-95
		$C{=}\mathbf{C}{=}C$	200-215

C environment		δ ppm
Acetylenic	$\text{-}\mathbf{C}{\equiv}\mathbf{C}\text{-}$	60-90
Benzenoid		120-140
Carbonyl	$\mathbf{C}{=}O$	150-220
	amides & imides	150-180
	esters & anhydrides	155-185
	acids	170-190
	ketones	185-220
	aldehydes	190-210
Nitriles	$R\text{-}\mathbf{C}{\equiv}N$	115-125
Azomethine	$R_2\mathbf{C}{=}N\text{-}R$	145-165

Carbon-13 Chemical Shift Table



saturated carbon (sp^3)
- no electronegative elements -

$R-CH_3$ 8-30

$R-CH_2-R$ 20-45

R_3CH R_4C 30-60

saturated carbon (sp^3)
- electronegativity effects -

C-O 50-70

C-X 40-65

unsaturated carbon (sp^2) 100-145

aromatic ring carbons 110-150

carbonyl groups

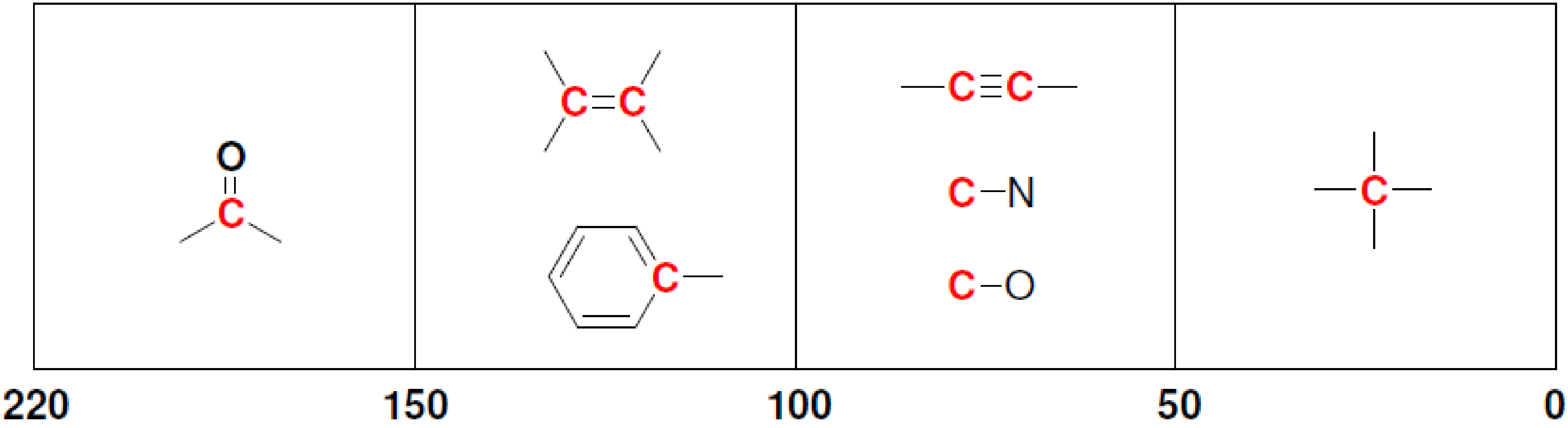
acids anhydrides
esters amides
155-185

aldehydes
ketones
185-220

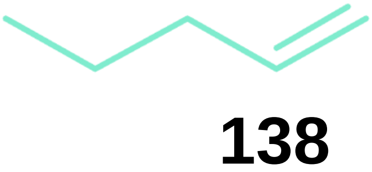
^{13}C Chemical Shifts are most affected by:

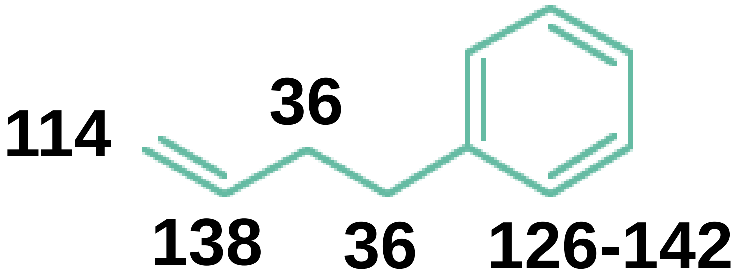
- ✓ ***hybridization state*** of carbon
- ✓ ***electronegativity of groups*** attached to the carbon:

electronegativity has an even: ***greater effect on ^{13}C*** chemical shifts **than it does on ^{1}H** chemical shifts.



Hybridization Effects





- ✓ sp^3 hybridized carbon is more shielded than sp^2.

$$\begin{array}{cccccc} H- & C\equiv & C- & CH_2- & CH_2- & CH_3 \\ & 68 & 84 & 22 & 20 & 13 \end{array}$$

- ✓ sp hybridized carbon is more shielded than sp^2, but less shielded than sp^3.

Electronegativity Effect

23

61

138

202

✓ ***an electronegative atom* deshields the carbon to which it is attached.**

Types of Carbons

	Classification	Chemical shift, δ	
		^{1}H	^{13}C
CH_4		0.2	2
CH_3CH_3	primary	0.9	8
$CH_3CH_2CH_3$	secondary	1.3	16
$(CH_3)_3CH$	tertiary	1.7	25
$(CH_3)_4C$	quaternary		28

Replacing H with C (more electronegative) *deshields C to which it is attached*.

Electronegativity Effects on CH_3

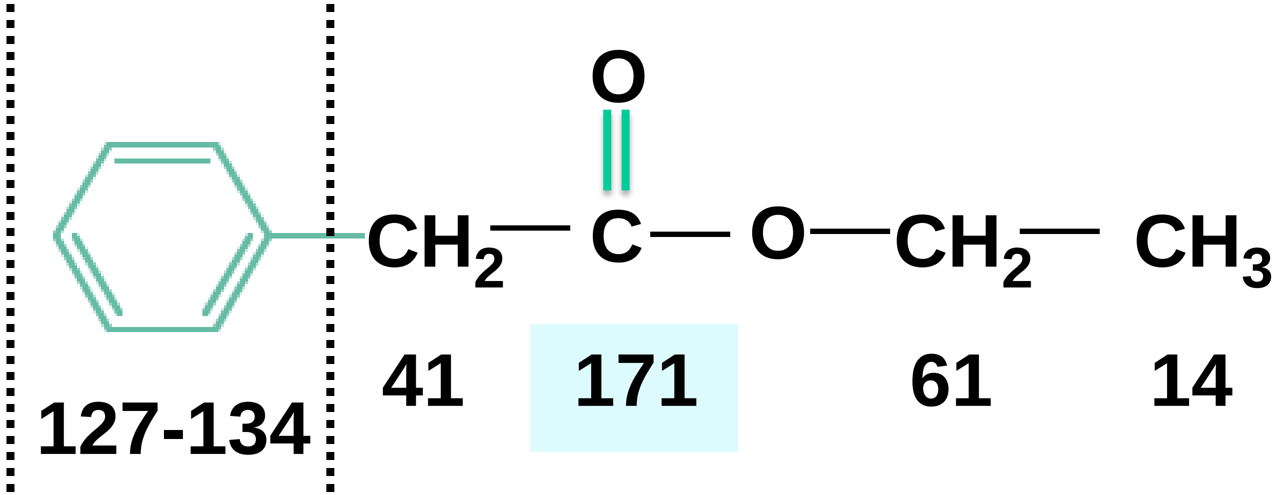
	Chemical shift, δ (ppm)	
	^{1}H	^{13}C
CH_4	0.2	2
$CH_3\underline{N}H_2$	2.5	27
$CH_3\underline{O}H$	3.4	50
$CH_3\underline{F}$	4.3	75

Electronegativity Effects and Chain Length

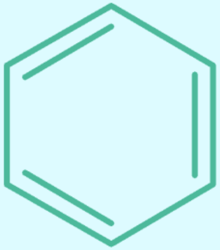
$Cl-$	CH_2-	CH_2-	CH_2-	CH_2-	CH_3
δ (ppm)	**45**	**33**	**29**	**22**	**14**

- ✓ **Deshielding effect of Cl decreases as number of bonds between Cl and C increases.**

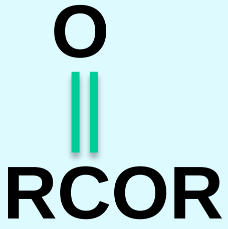
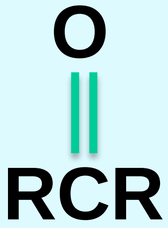
Carbonyl Carbons ***are Especially*** ***Deshielded***



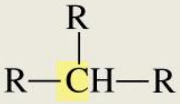
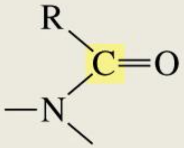
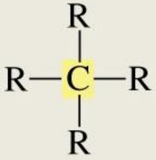
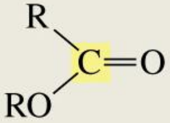
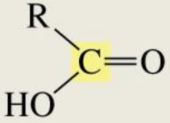
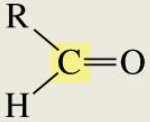
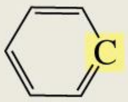
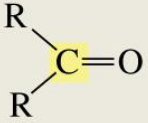
Type of carbon	***Chemical shift (δ), ppm***
$R\underline{C}H_3$	**0-35**
$R_2\underline{C}H_2$	**15-40**
$R_3\underline{C}H$	**25-50**
$R_4\underline{C}$	**30-40**

Type of carbon	***Chemical shift (δ), ppm***
$RC\equiv CR$	**65-90**
$R_2C{=}CR_2$	**100-150**
	**110-175**

Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40
RCH_2Cl	25-50
RCH_2NH_2	35-50
RCH_2OH	50-65
RCH_2OR	50-65

Type of carbon	Chemical shift (δ), ppm
$RC\equiv N$	110-125
 $\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR}$	160-185
 $\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$	190-220

Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C—I$	0–40
$R—CH_3$	8–35	$C—Br$	25–65
$R—CH_2—R$	15–50	$C—Cl$ $C—N$ $C—O$	35–80 40–60 50–80
 $R—CH(R)—R$	20–60		165–175
 $R—C(R)(R)—R$	30–40		165–175
$\equiv C$	65–85		175–185
$=C$	100–150		190–200
	110–170		205–220

Measuring a ^{13}C NMR spectrum involves

1- Equilibration of the nuclei between the lower and higher spin states under the influence of a magnetic field.

2- Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state.

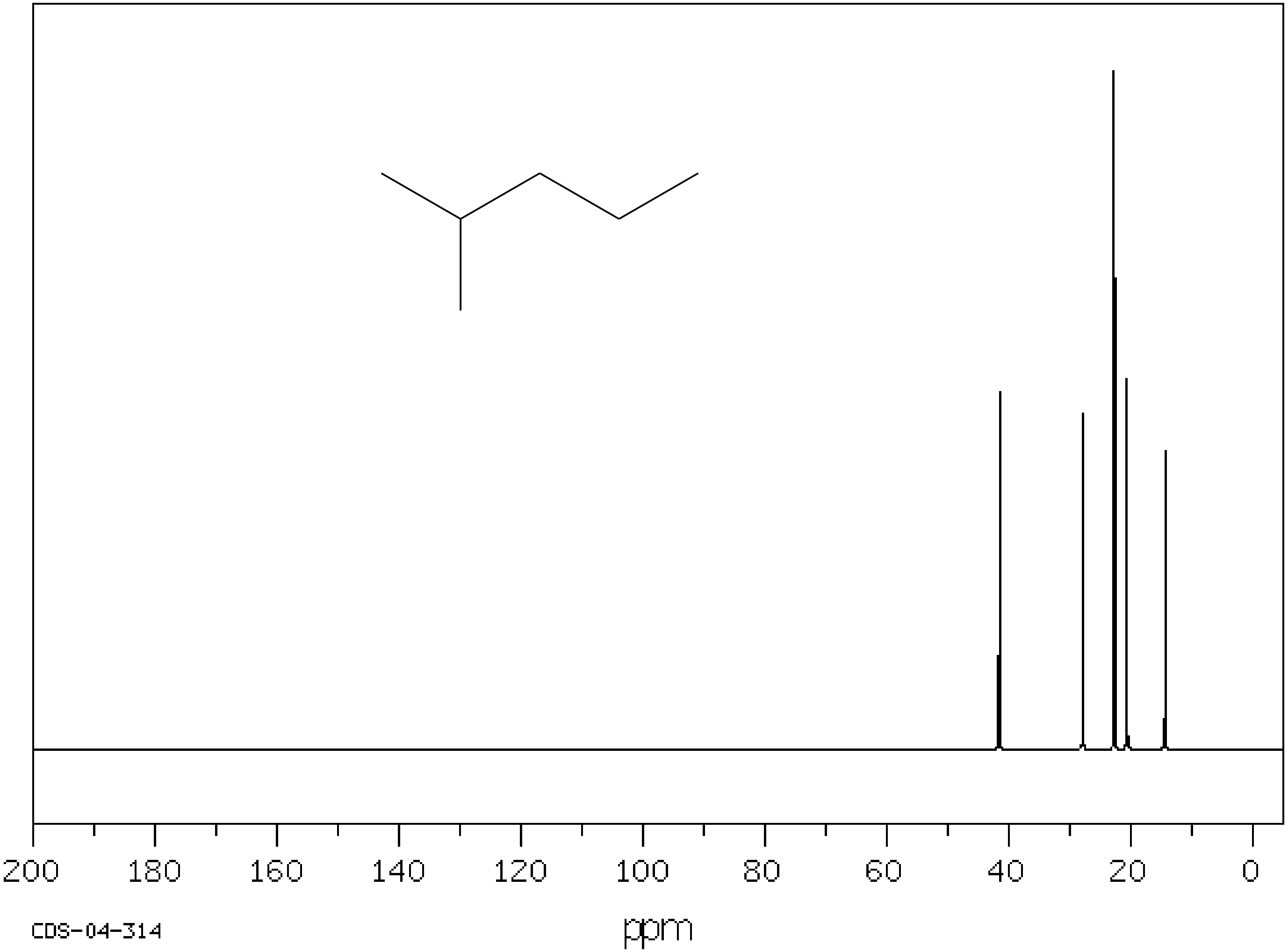
3- Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restore

4- Mathematical manipulation (Fourier transform) of the data to plot a spectrum

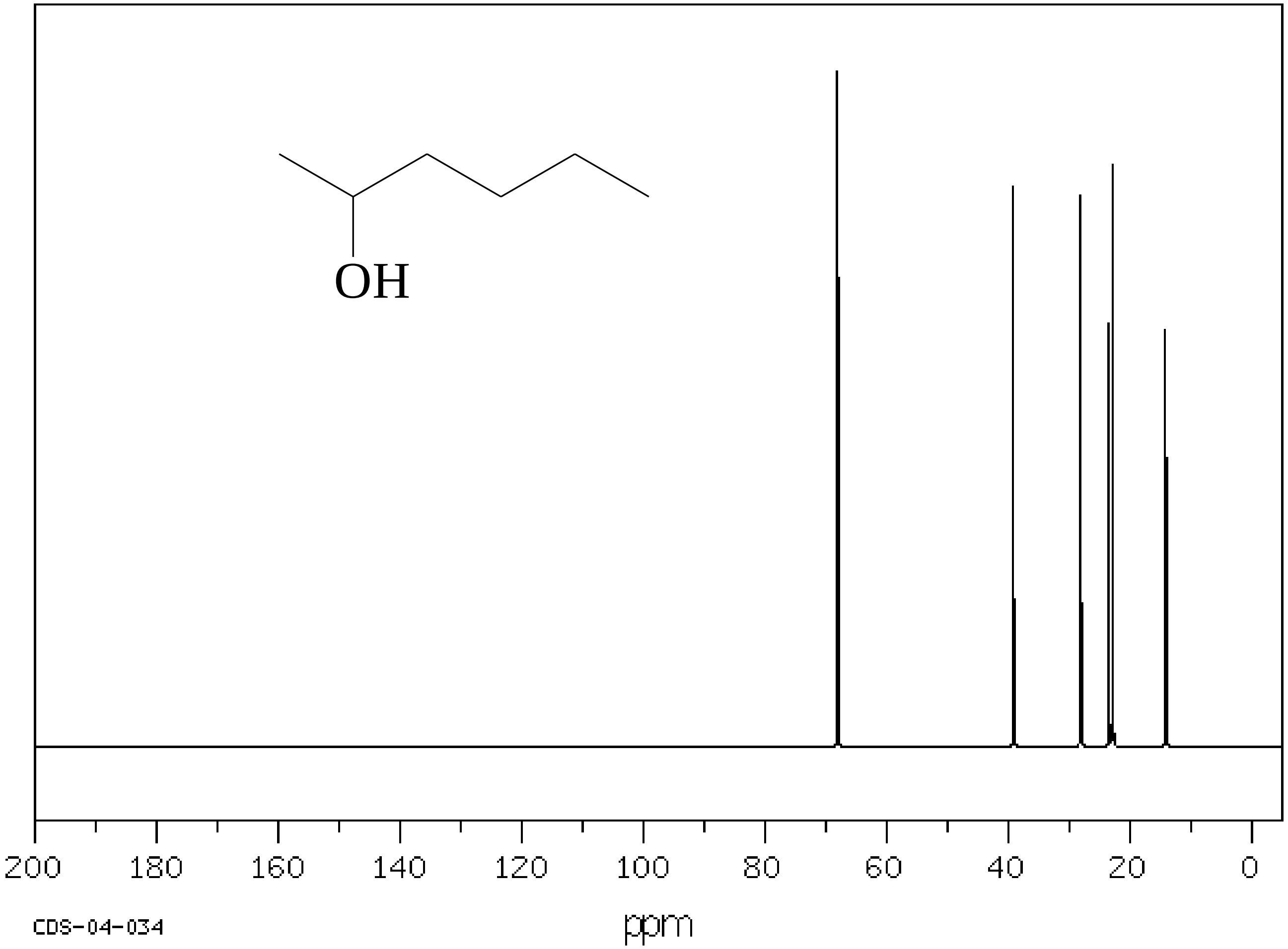
5- Steps 2 and 3 can be repeated hundreds of times to enhance the signal-noise ratio

Alkane: 2-methylpentane

Example 1:

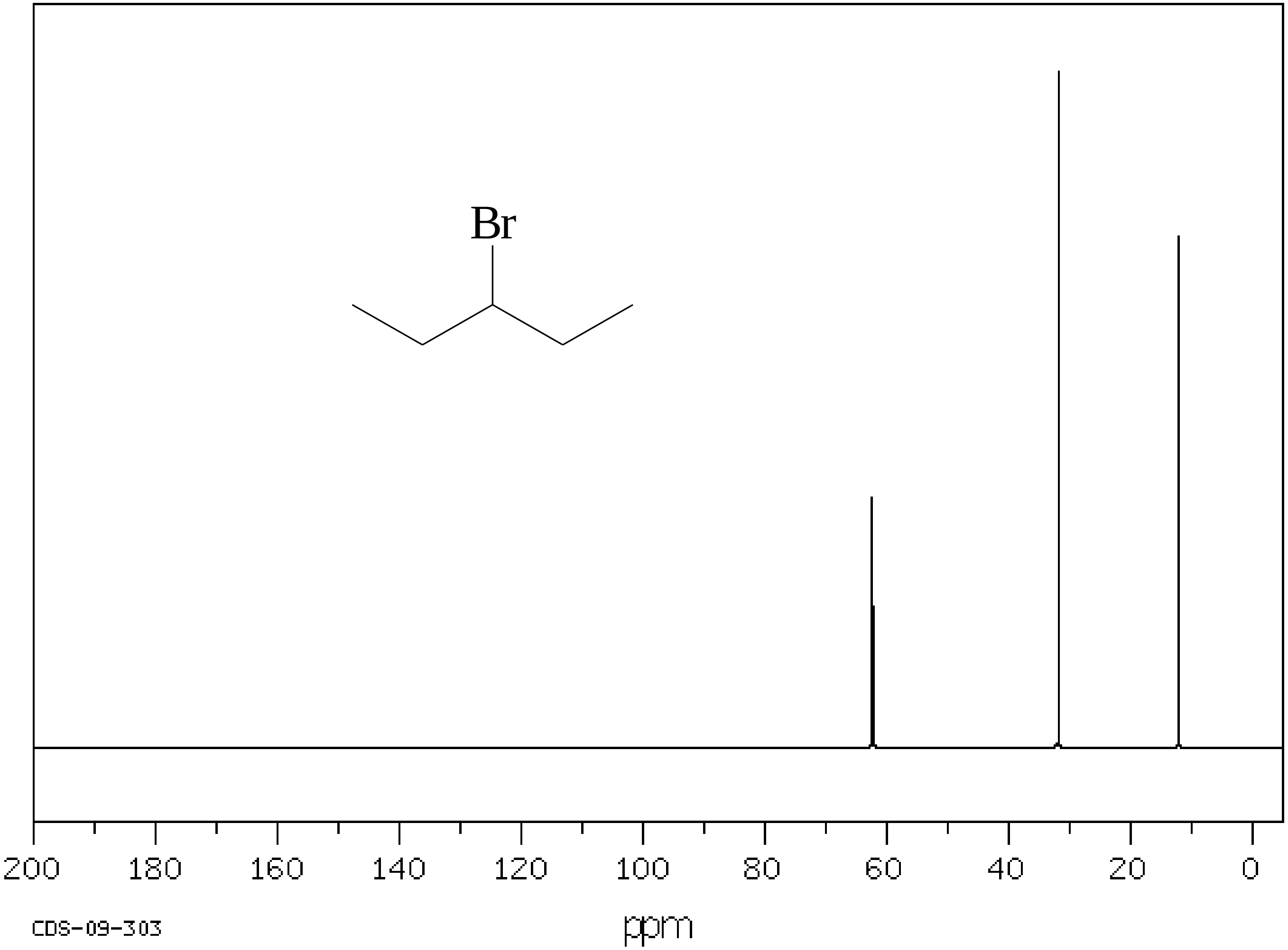


Example 2: Alcohol: 2-hexanol



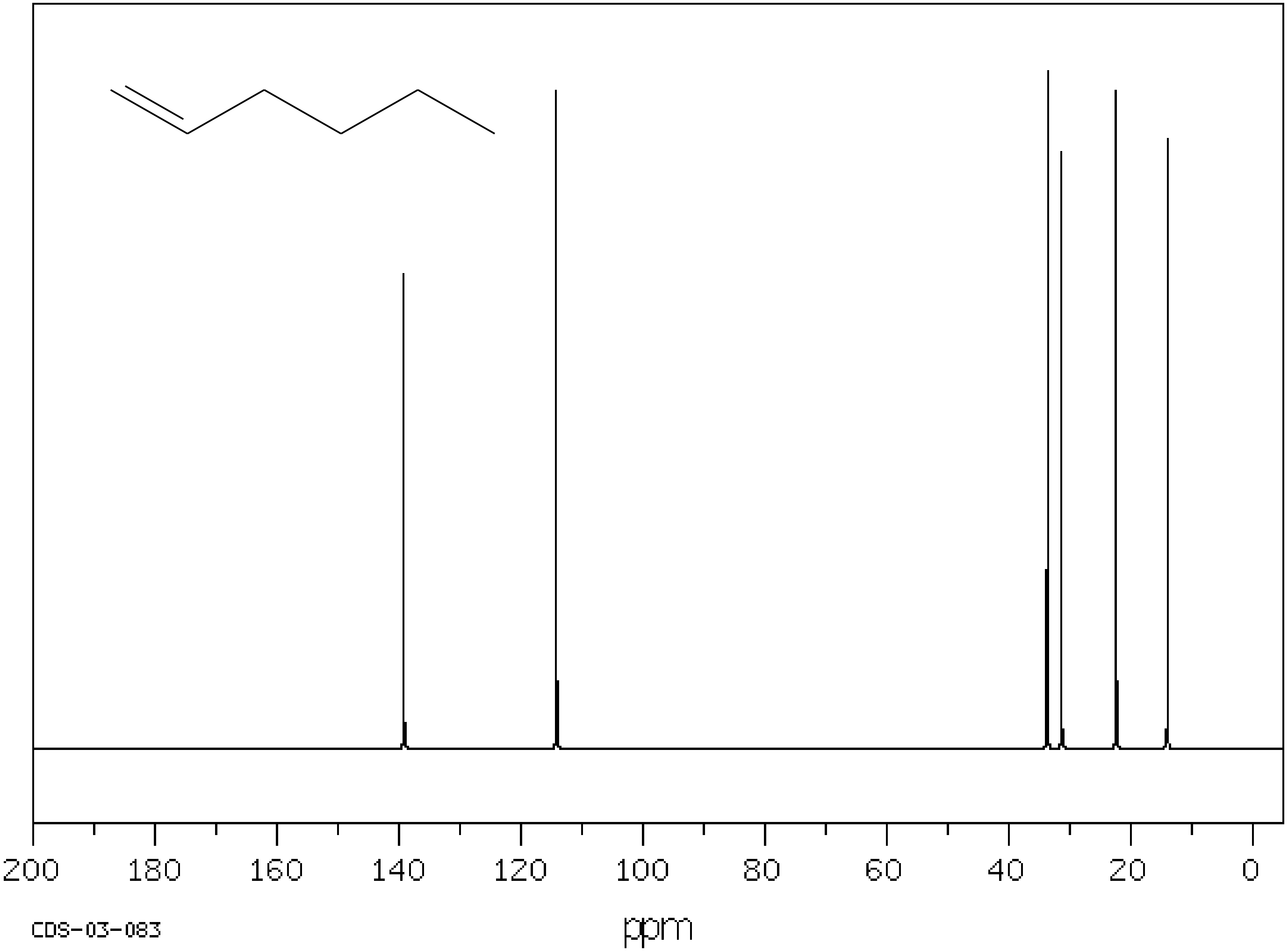
Example 3:

Alkyl Halide: 3-bromopentane



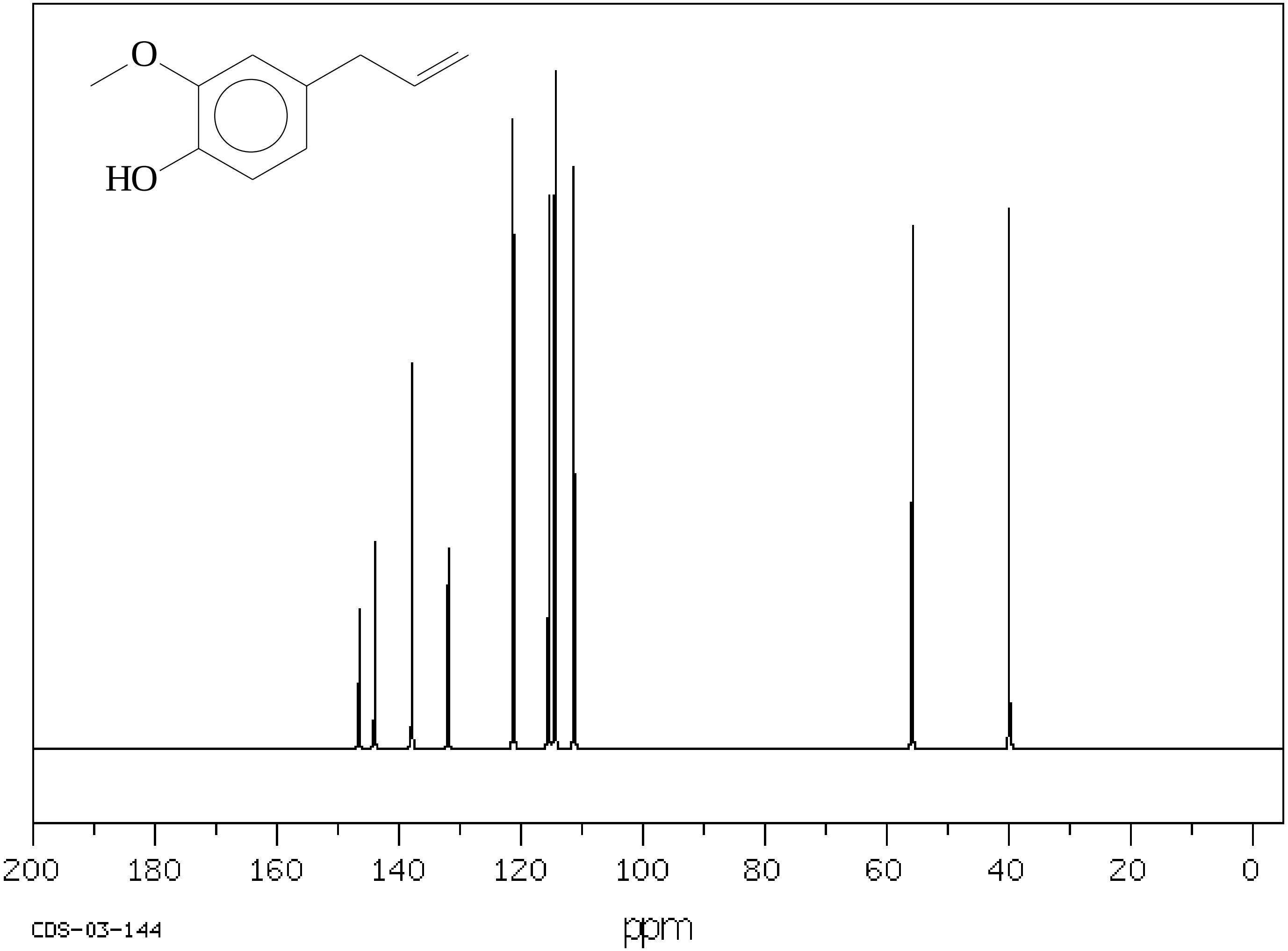
Example 4: **Alkene:** 1-hexene

-

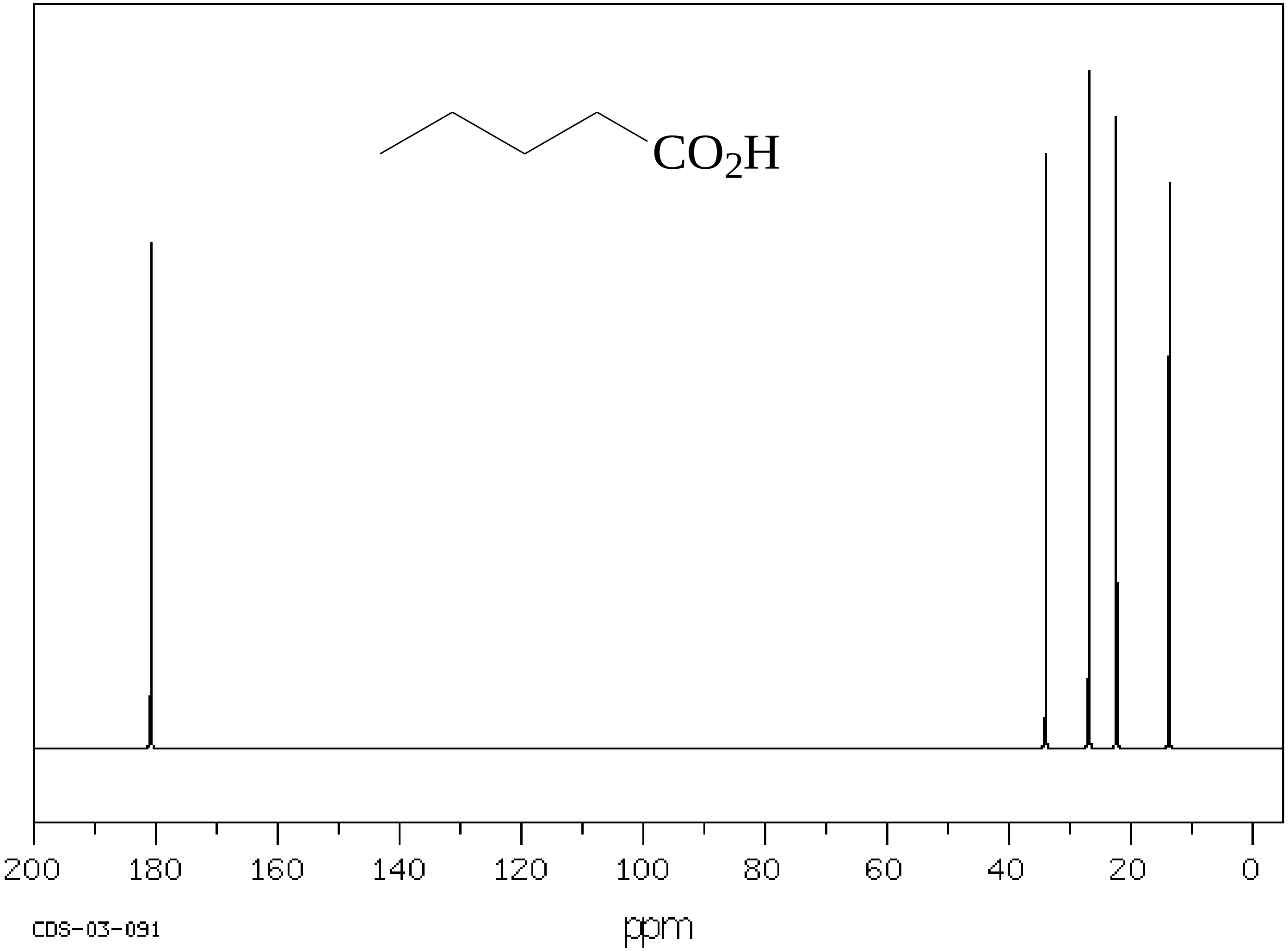


Example 5:

Aromatic Ring: eugenol

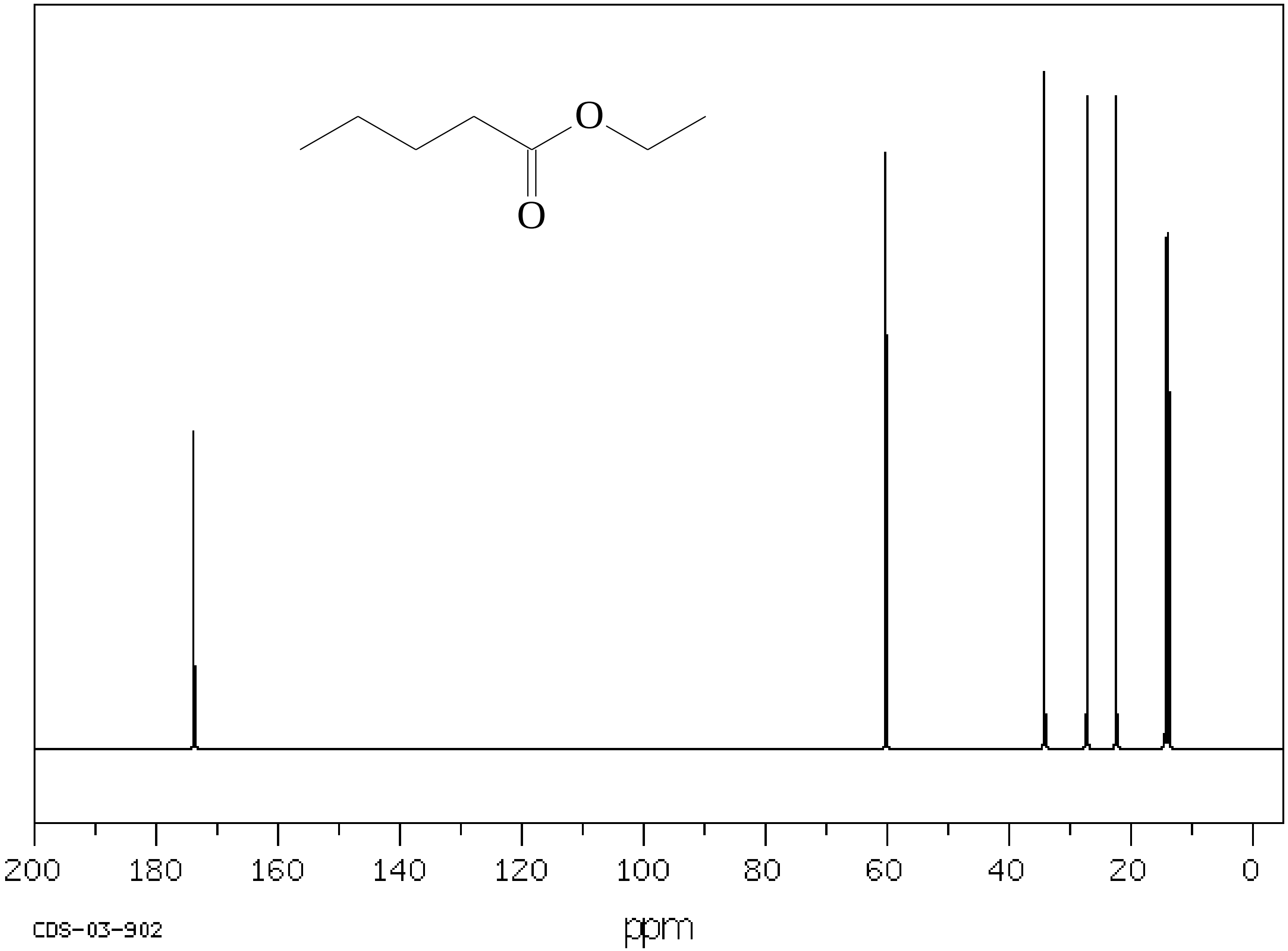


Example 6: Carboxylic Acid: pentanoic acid



Example 7:

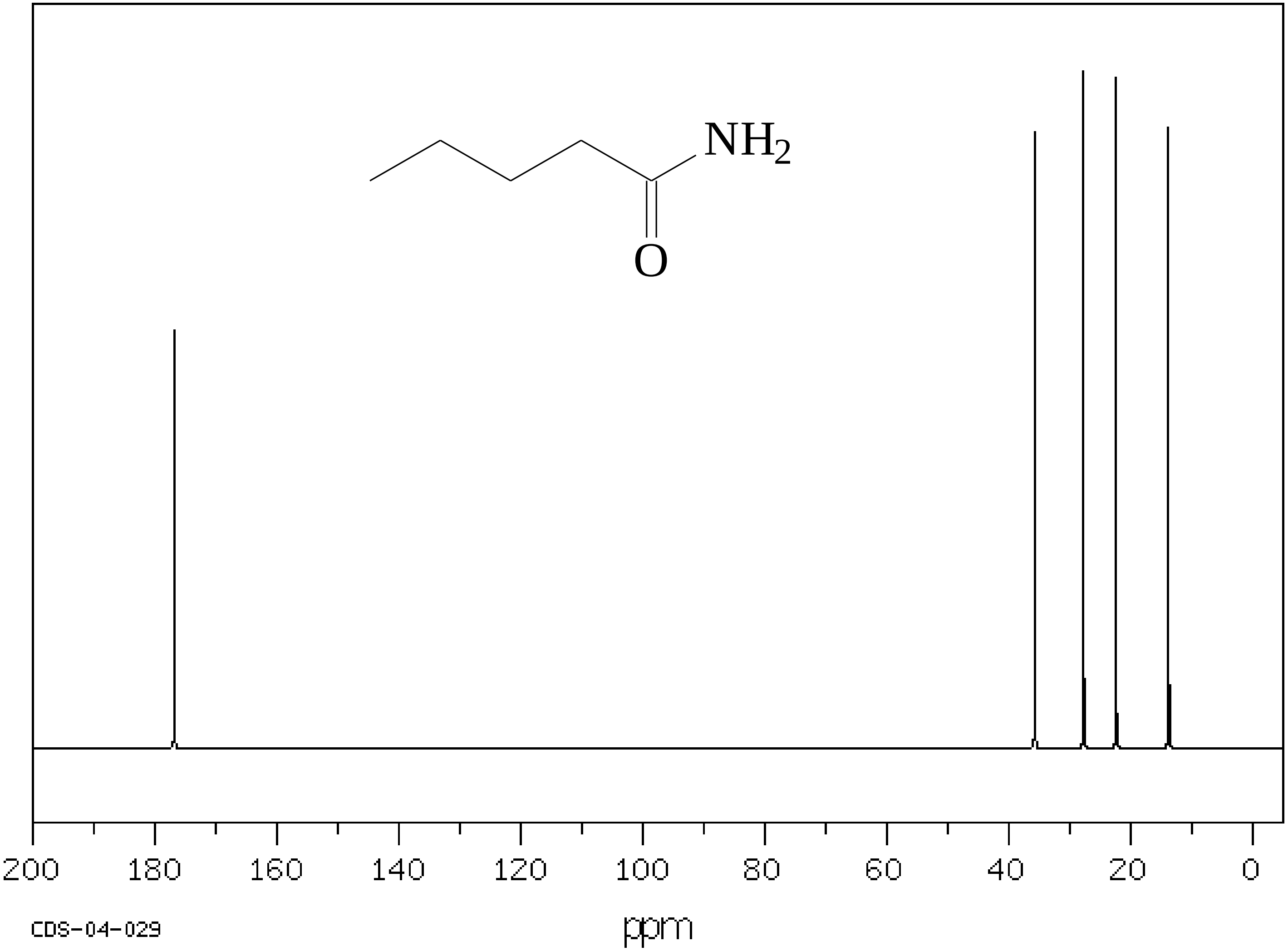
Ester: ethyl valerate



Example 8:

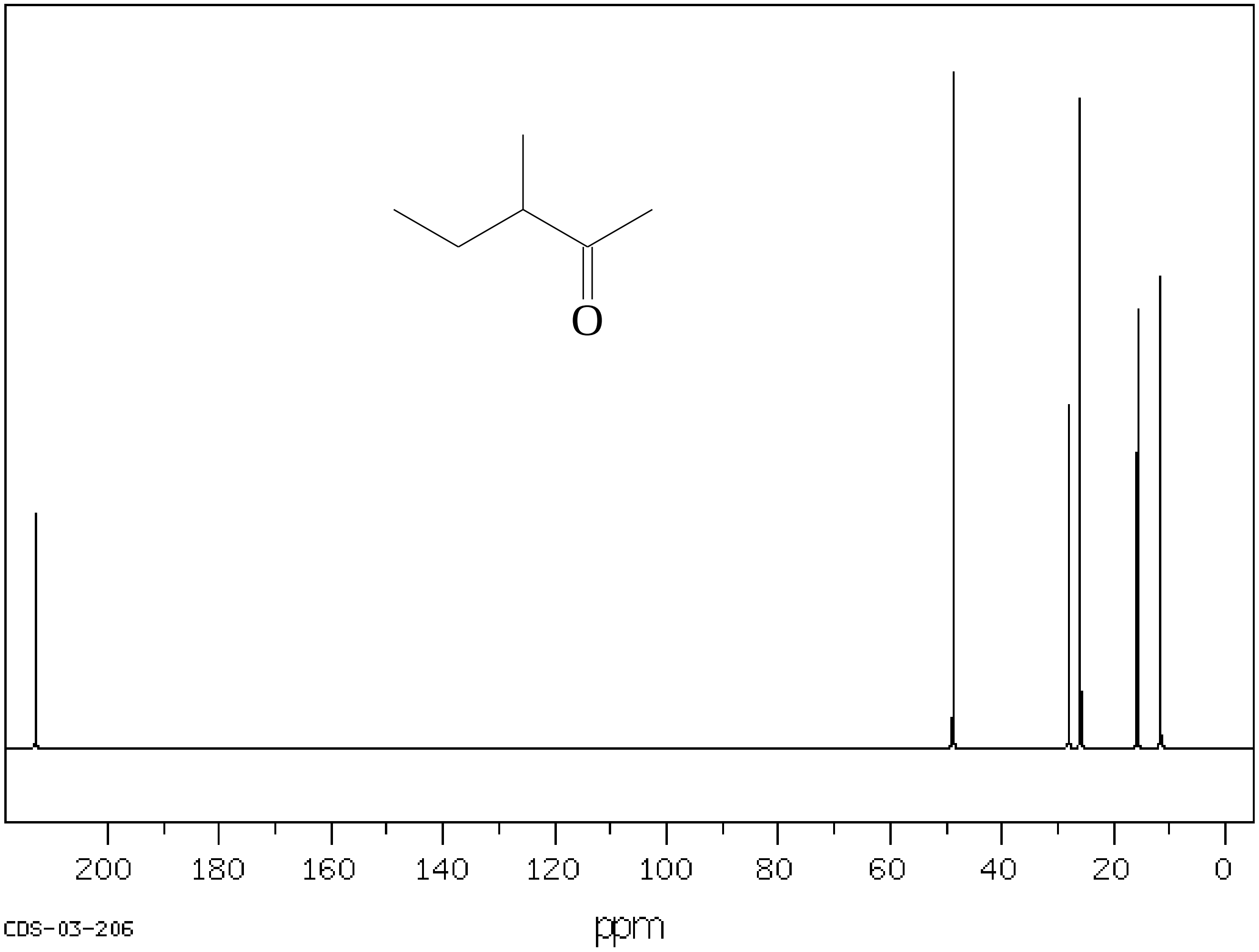
Amide: pentanamide

-



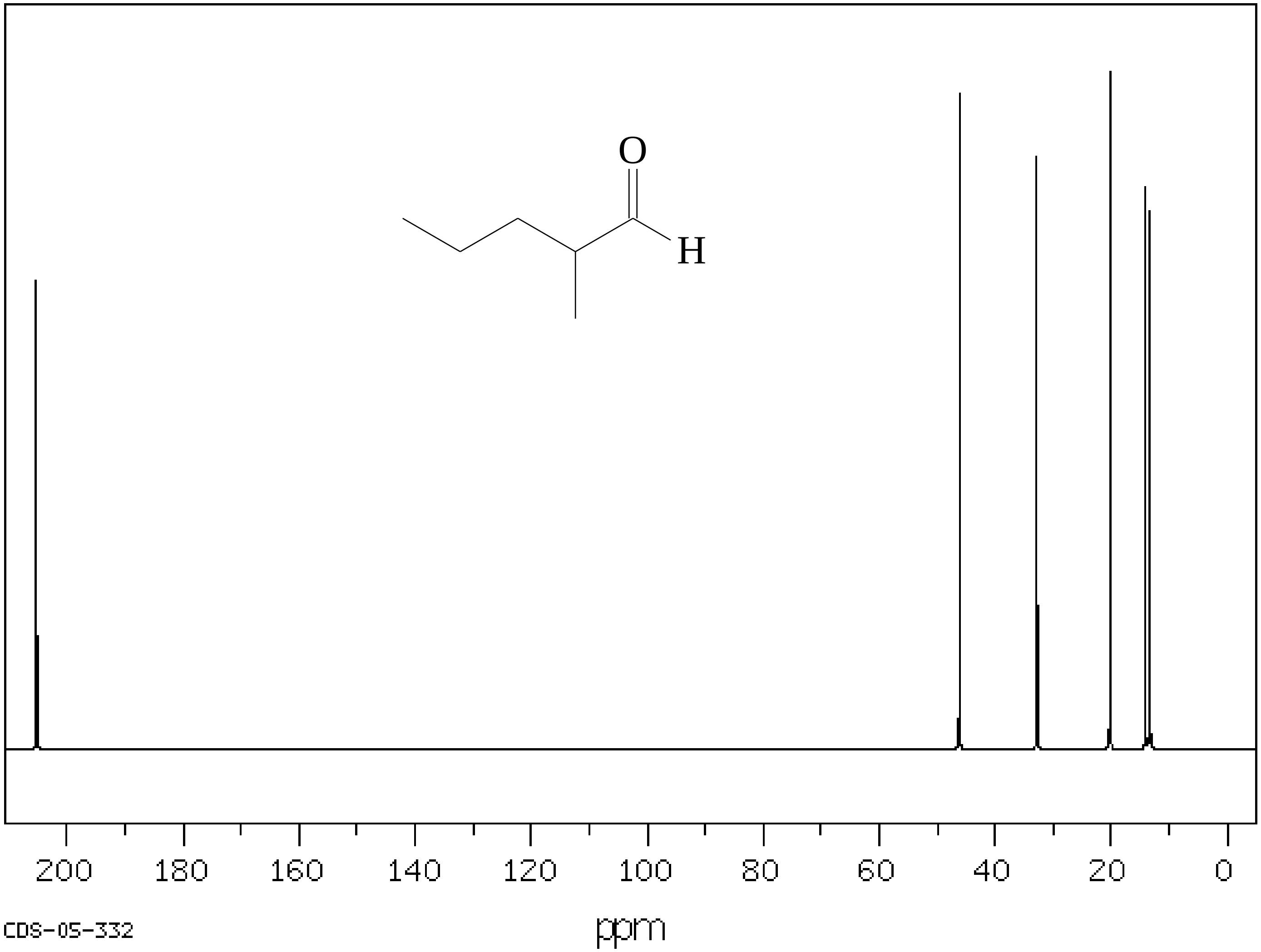
Example 9:

Ketone: 3-methyl-2-pentanone



Example 10:

Aldehyde: 2-methylpentanal



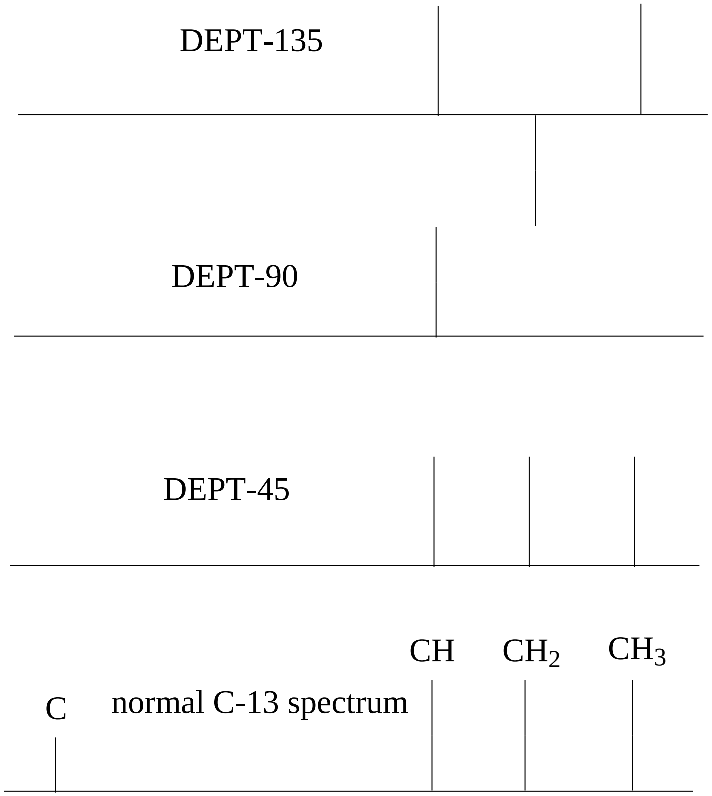
DEPT ^{13}C NMR Spectra

- **DISTORTIONLESS ENHANCEMENT BY POLARIZATION TRANSFER (DEPT) ^{13}C NMR** provides information the ***number of hydrogen atoms attached to each carbon***.
  - ✓ Some ^{13}C signals ***stay the same***
  - ✓ Some ^{13}C signals ***disappear***
  - ✓ Some ^{13}C signals ***are inverted***

- **Full decoupled ^{13}C** spectrum shows **all carbon peaks.**
- In a **DEPT-90**, only **CH** signals appear.
- In a **DEPT-135**, **CH_3** and **CH** give (+) signals, and **CH_2** give (–) signals.

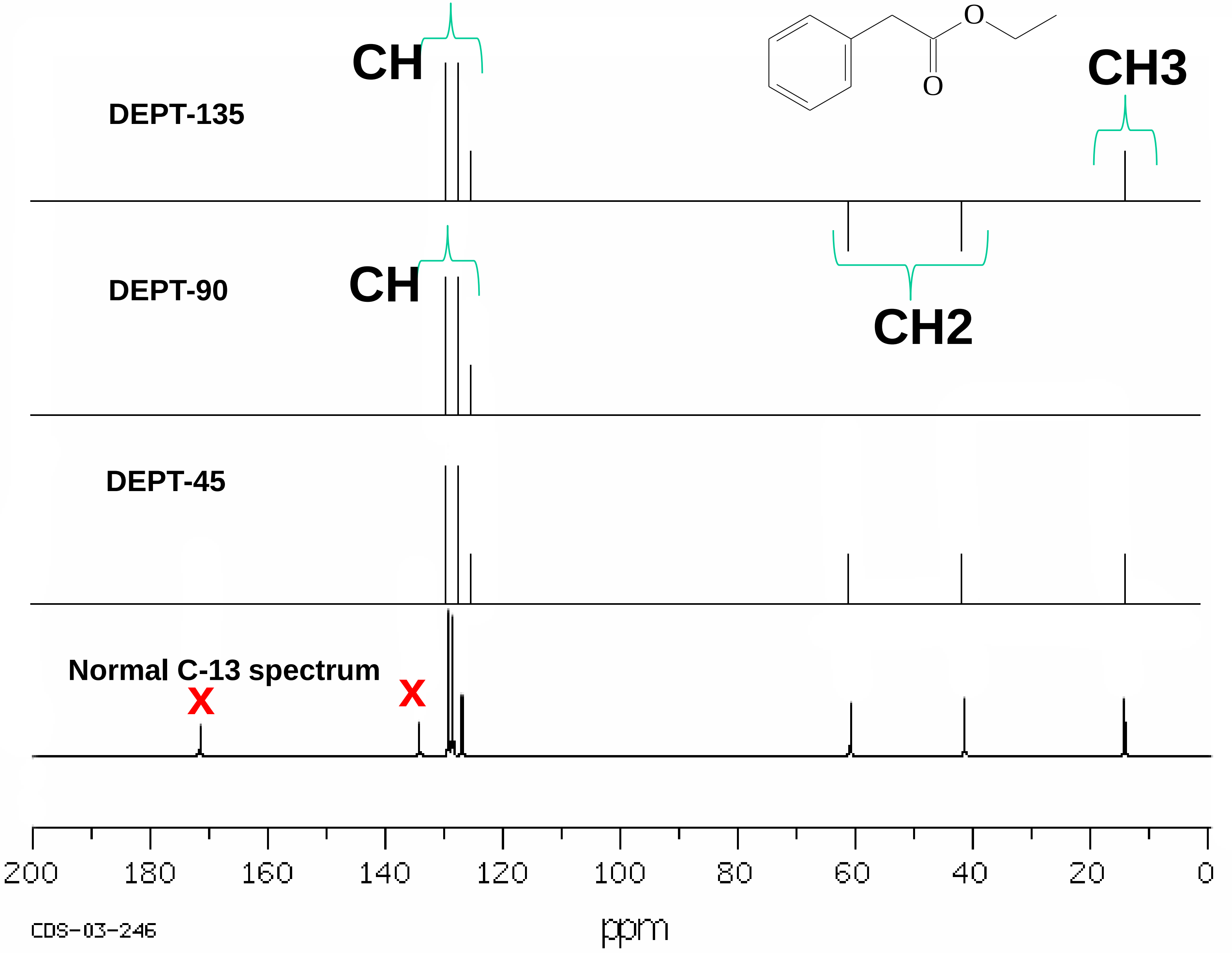
DEPT Spectra

	CH_3	CH_2	CH	C
Broadband-decoupled				
DEPT-90	—	—		—
DEPT-135				—

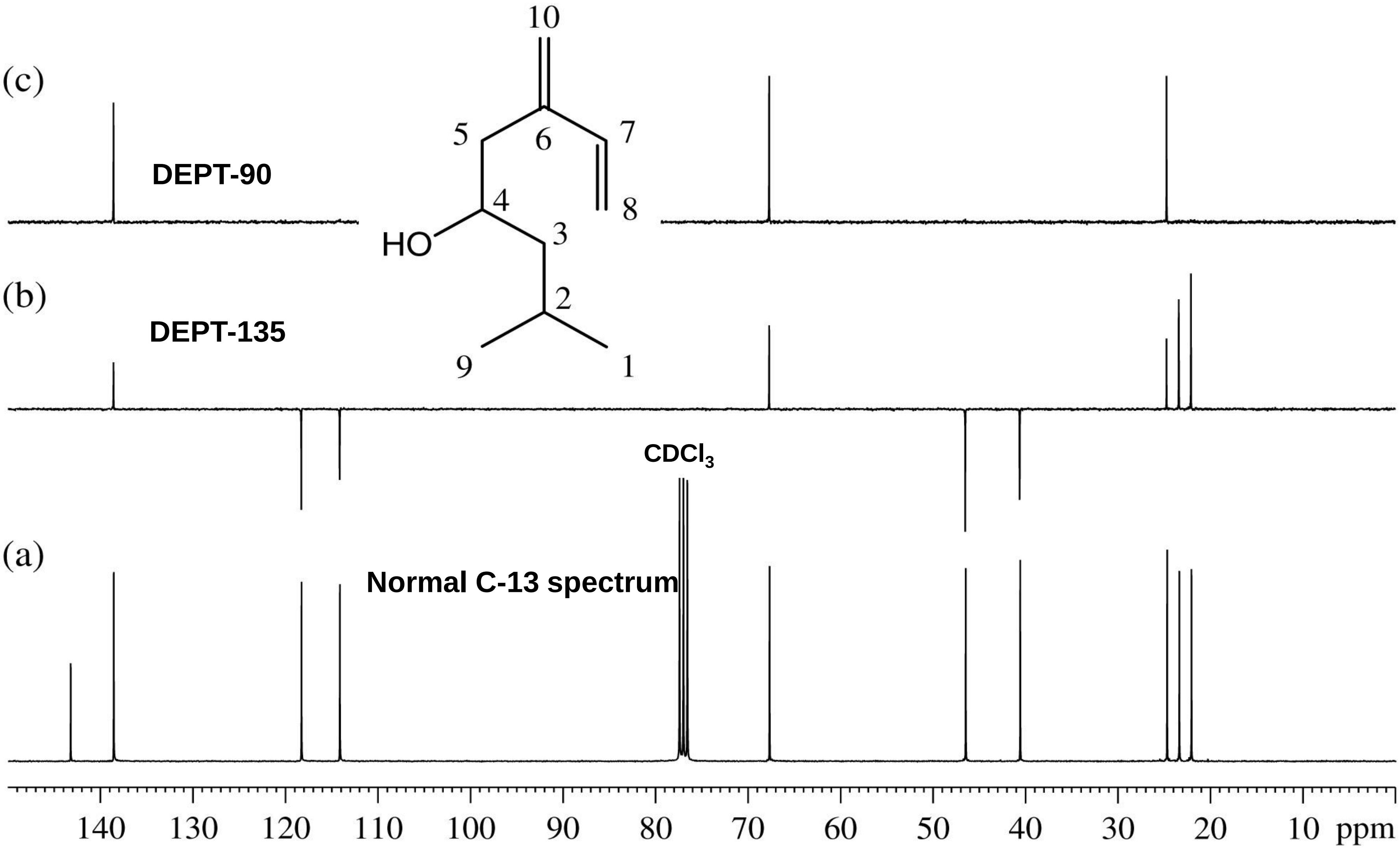


Quaternary carbons (C) do <u>not</u> show up in DEPT.

Simulated DEPT Spectra of Ethyl Phenylacetate



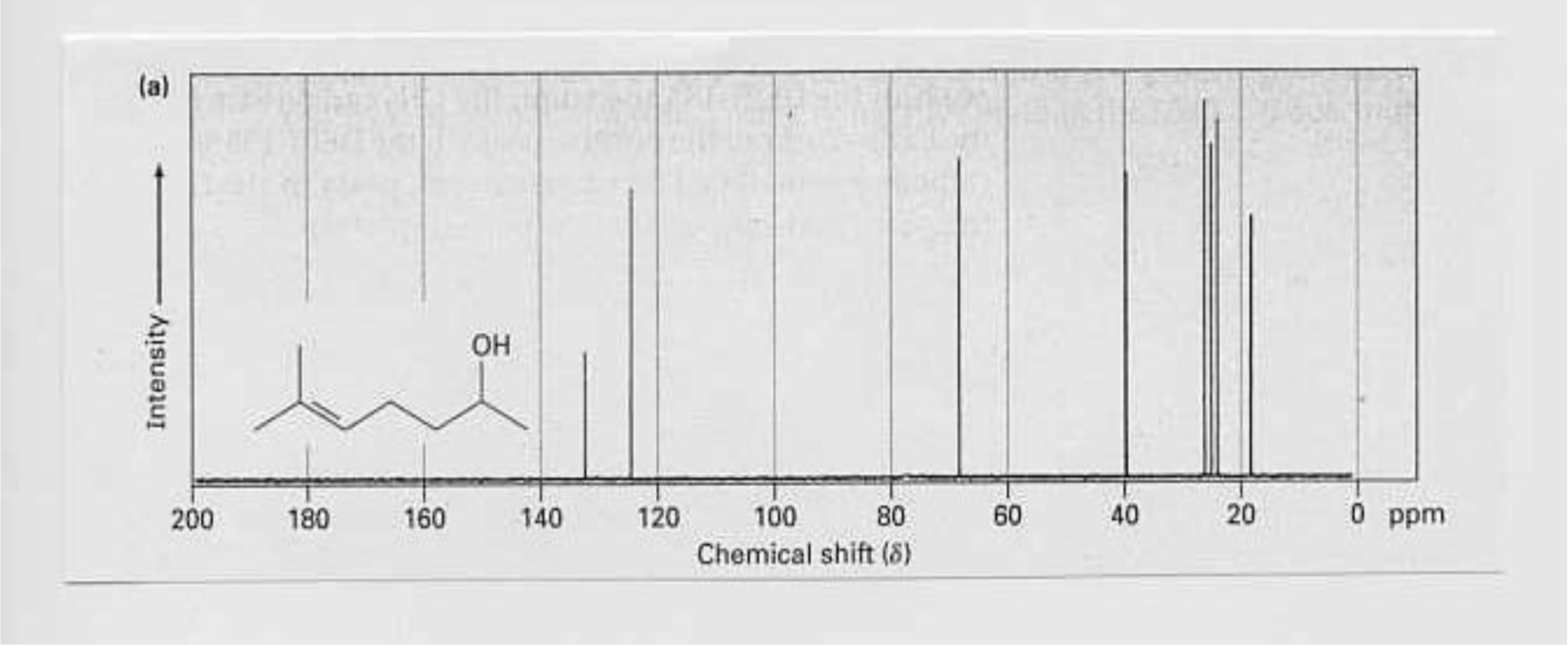
DEPT Spectra of Ipsenol



^{13}C NMR – 6-methyl-5-hepten-2-ol

Broadband

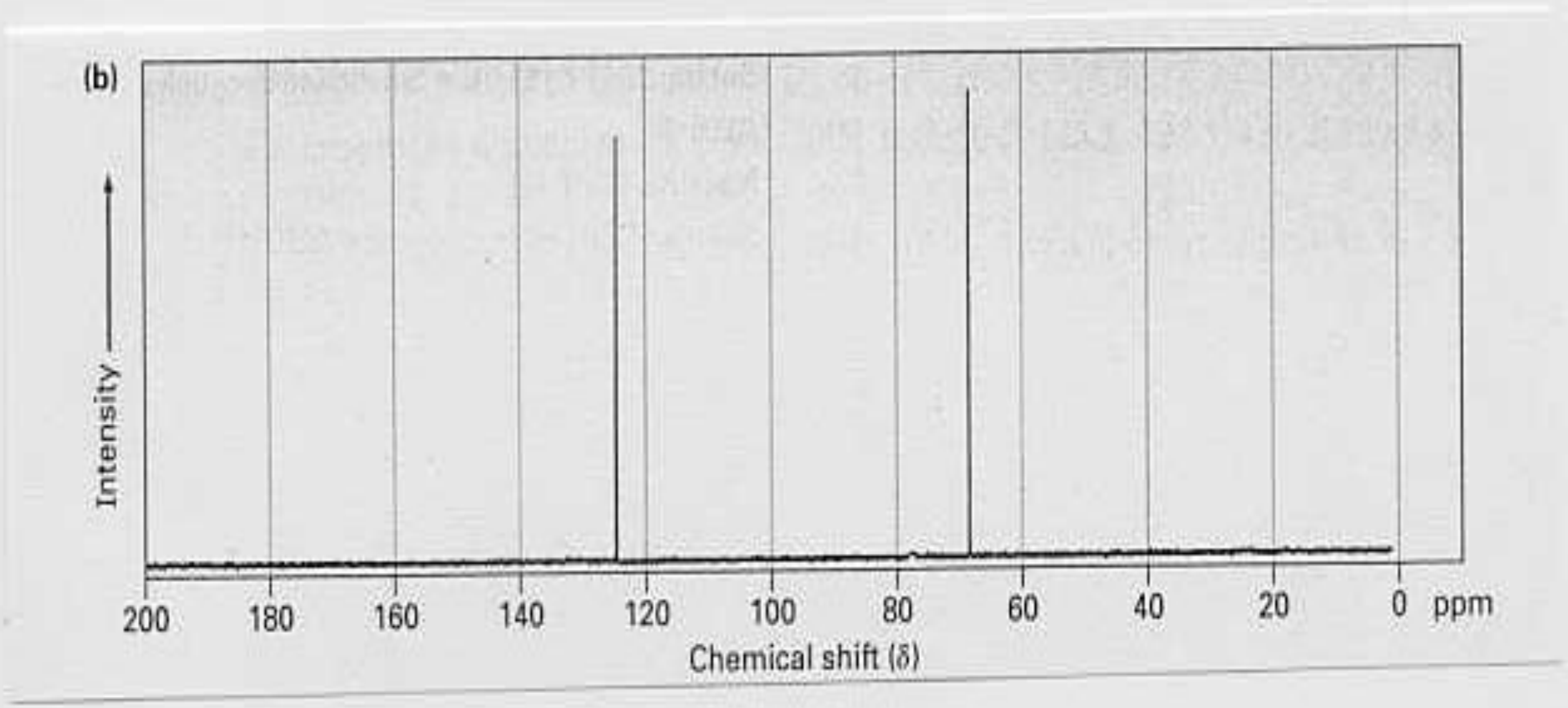
All carbons as singlets



^{13}C NMR – 6-methyl-5-hepten-2-ol

DEPT 90

Only CH carbons



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