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Chapter 13

Nuclear Magnetic Resonance Spectroscopy

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Nuclear Magnetic Resonance

- ◆ **Two Nobel Prizes have been awarded for the development of NMR**
 - **Isidor Isaac Rabi (1938 Nobel Prize in Physics)**
 - **Felix Bloch and Edward Purcell (1952 Nobel Prize in Physics)**

**WHY ARE WE LEARNING ABOUT
PHYSICS IN ORGANIC
CHEMISTRY?!?**

Molecular Spectroscopy

- ◆ **Nuclear magnetic resonance (NMR) spectroscopy:** A spectroscopic technique that gives us information about the number and types of atoms in a molecule, for example, about the number and types of
 - hydrogen atoms using ^1H -NMR spectroscopy.
 - carbon atoms using ^{13}C -NMR spectroscopy.
 - phosphorus atoms using ^{31}P -NMR spectroscopy.

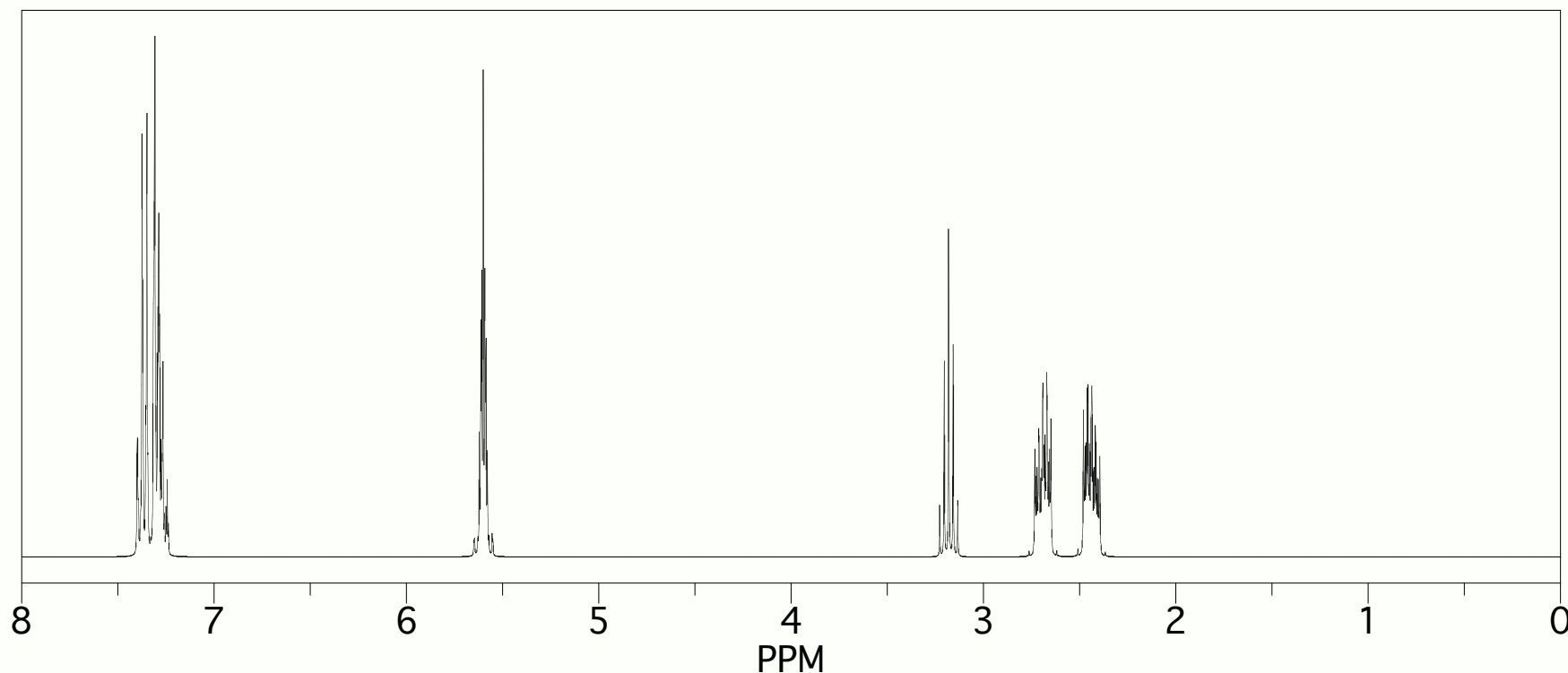
^1H NMR is the most common spectroscopic technique used by organic chemists to determine structure, and is usually the primary mode of structure determination

General Concept of NMR

- ◆ The Theory behind NMR is beyond the scope of what you are expected to know. However, a general understanding of the underlying principles can help make sense of some of the phenomena.
- ◆ **Your primary objective should be to be able to interpret ^1H NMR**

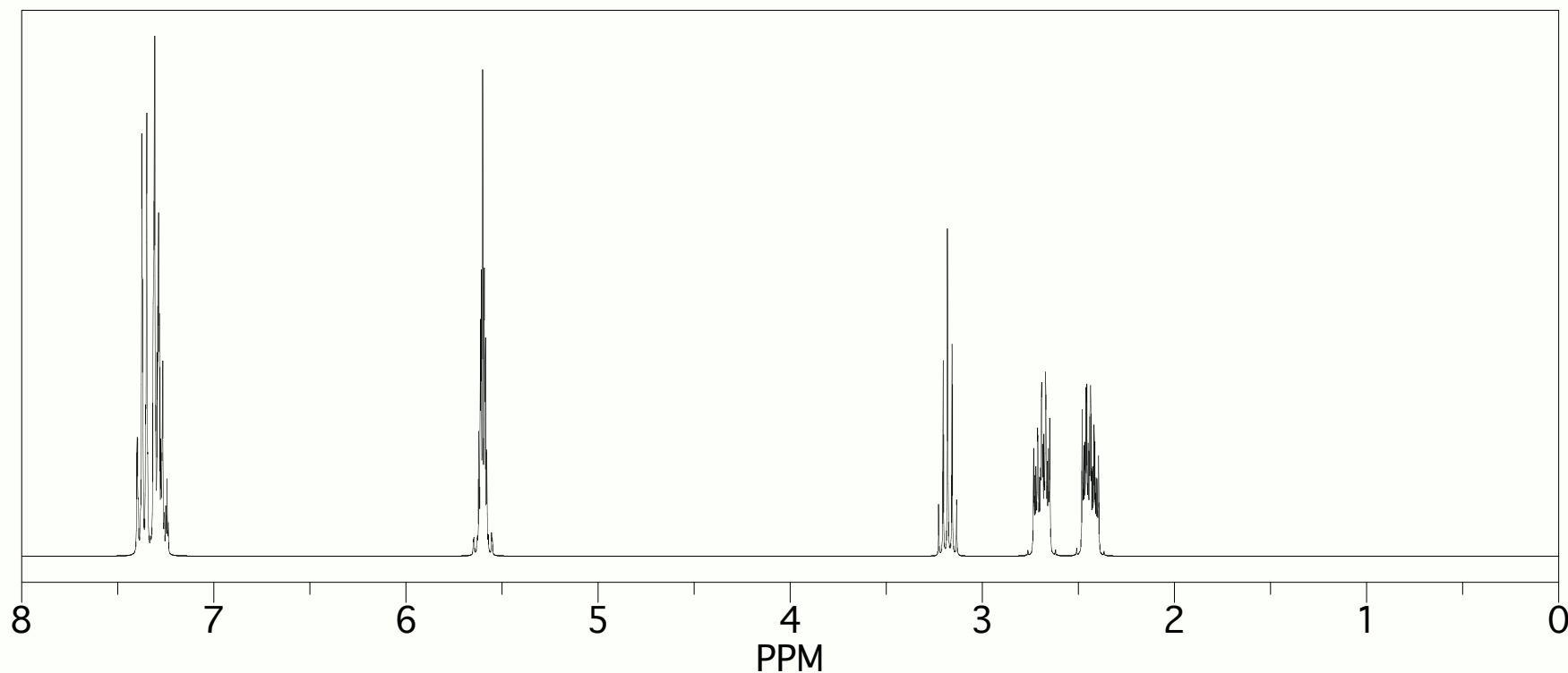
Sample NMR QUESTION

- ◆ The following is a ^1H NMR Spectrum of a molecule with the molecular formula $\text{C}_{11}\text{H}_{12}$. Show a structure that is consistent with the information given



Information of NMR

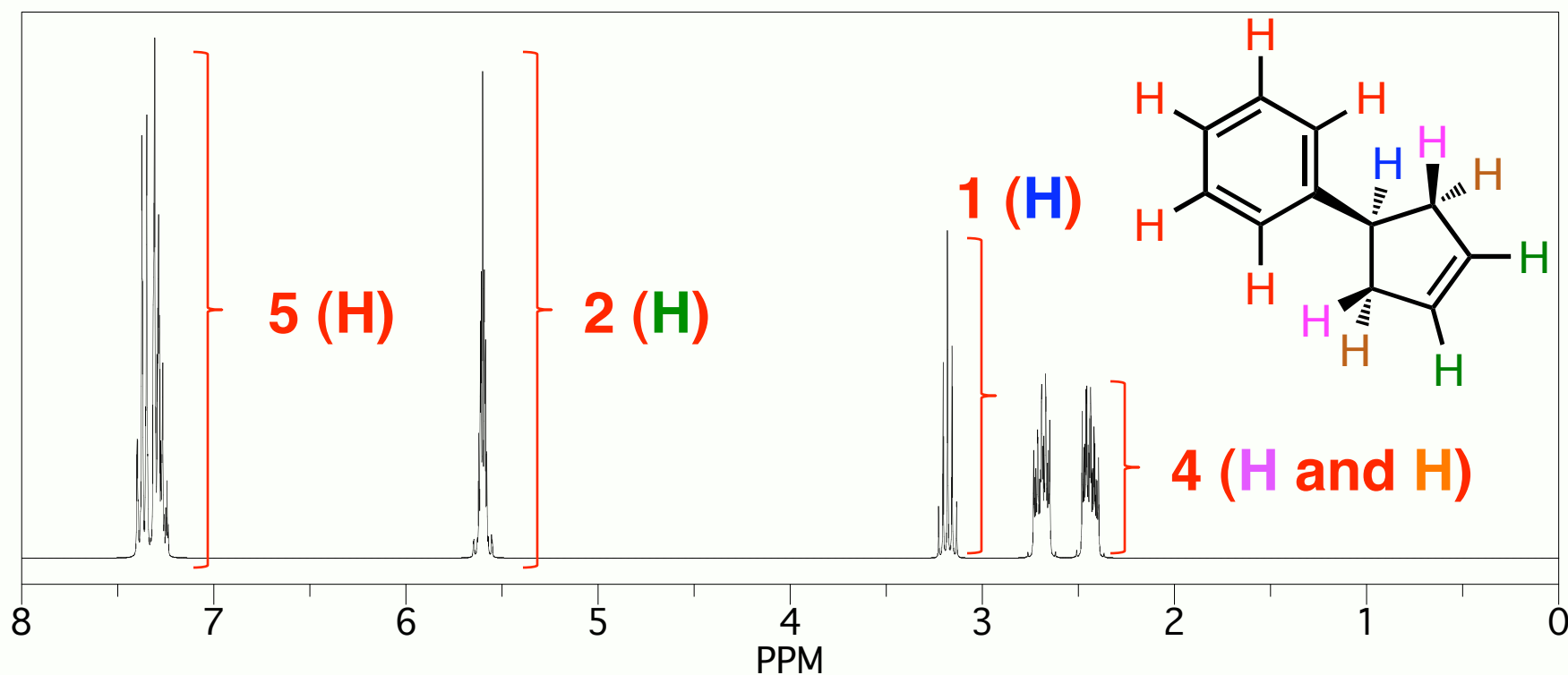
- ◆ **3 Pieces of Information can be gained from the NMR**
 - **Integration**: Number of Protons Corresponding to a given peak
 - **Chemical Shift**: Electronic Environment of Proton
 - **Coupling**: What protons are nearby (on adjacent carbon)



Information of NMR

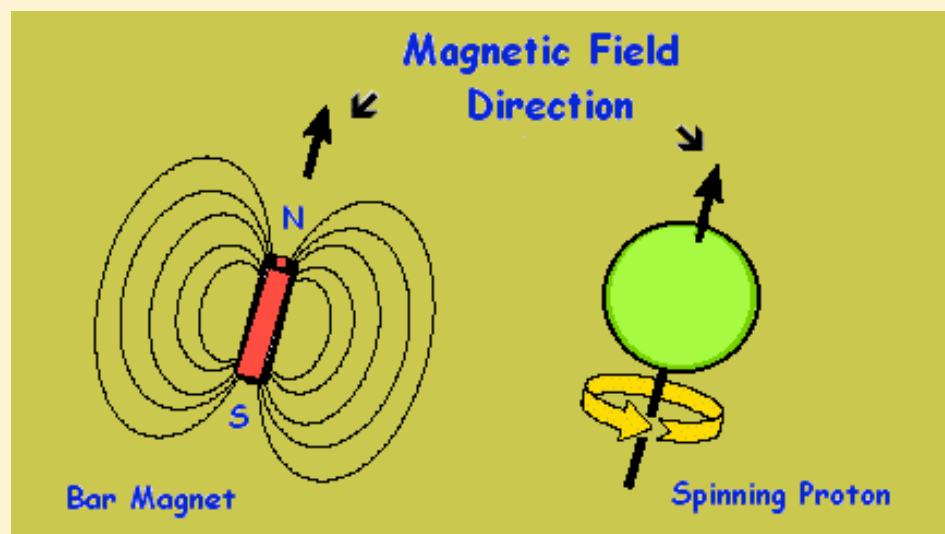
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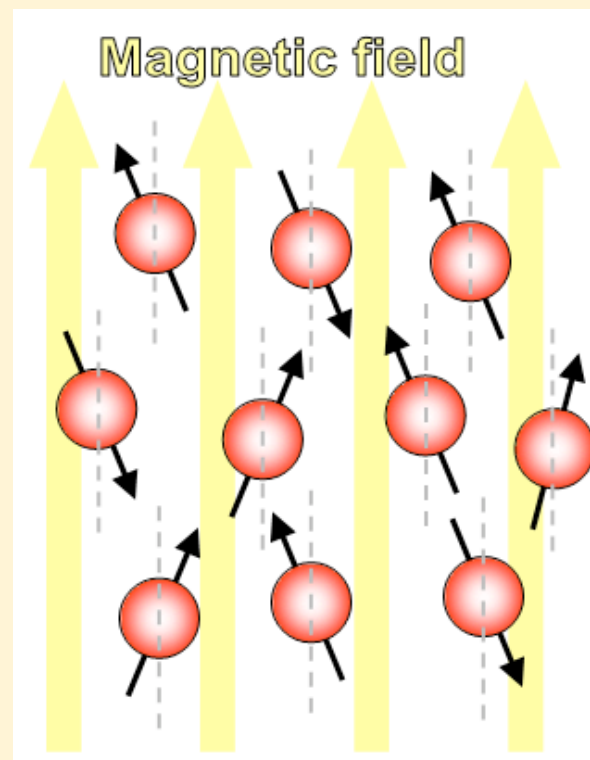
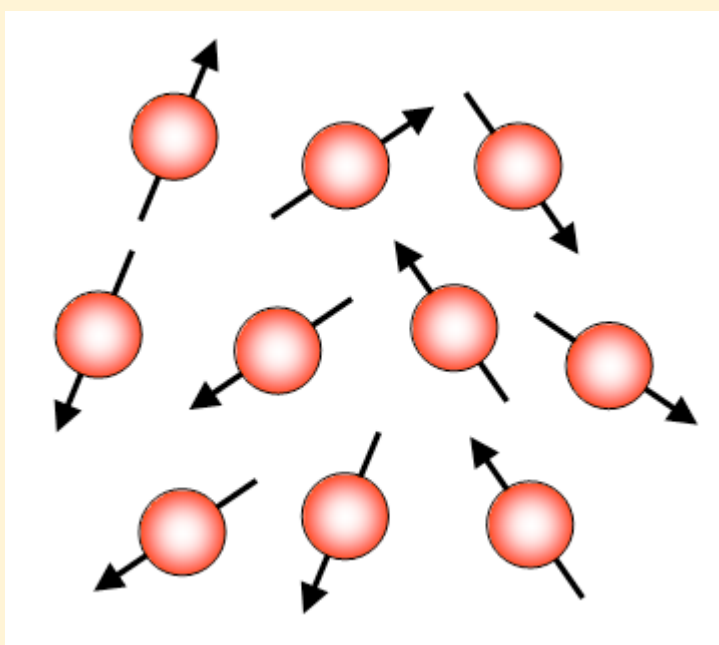
General Concept of NMR

- ◆ Some nuclei (usually those with odd # masses such as ^1H and ^{13}C) create a magnetic field as they spin.
- ◆ Like the earth, the magnetic field is related to the direction of the spin.



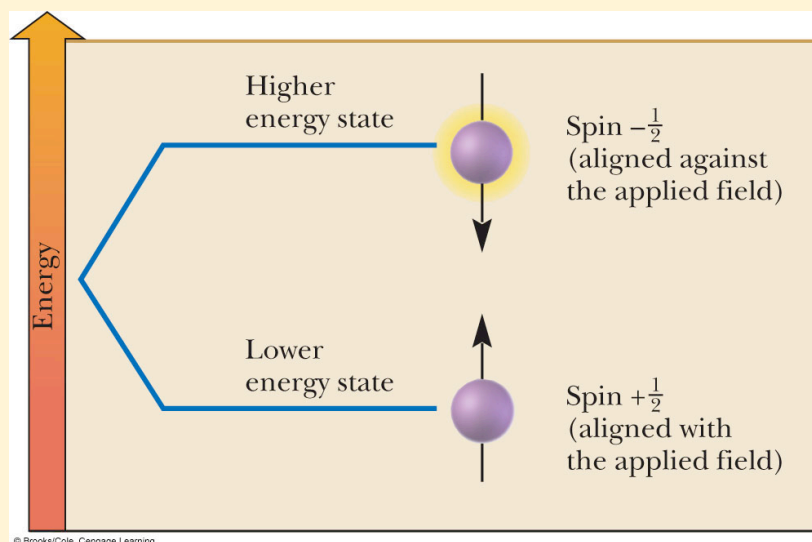
General Concept of NMR

- ◆ Nuclei in general have no inherent preference to spin one way or another.
- ◆ However, when a magnetic field is applied, nuclei will align themselves either with or against the field



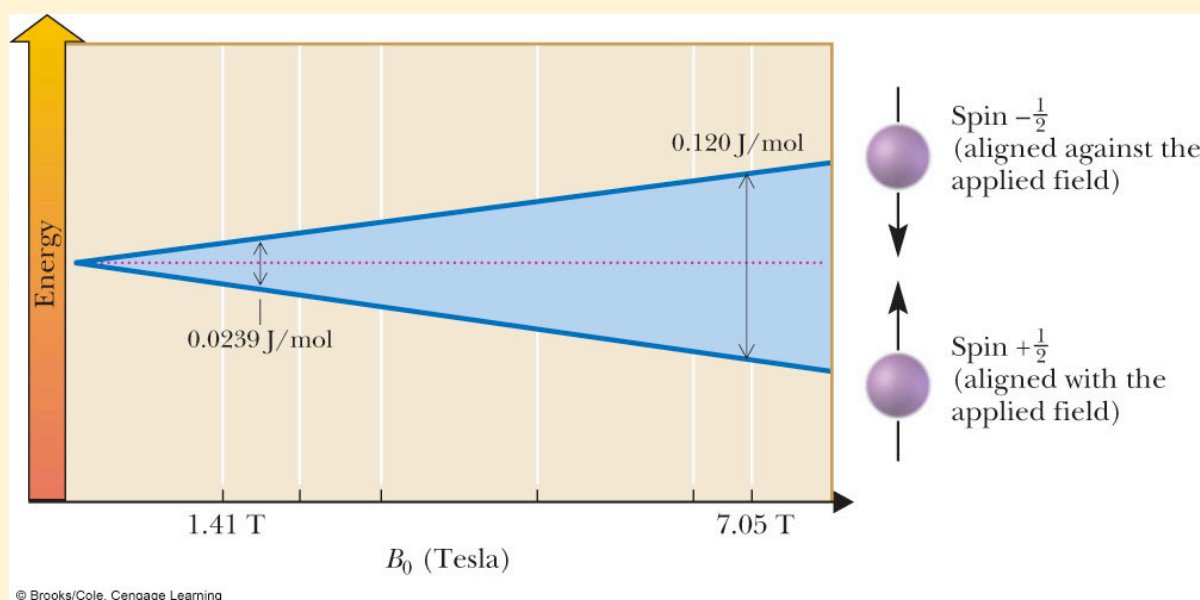
General Concept of NMR

- ◆ Nuclei aligned with magnetic field (α -state) are lower in energy than nuclei aligned against magnetic field (β -state), and thus there are more in α -state.
- ◆ When subjected to electromagnetic radiation, α -state can be excited to the β -state, and this change can be observed.
- ◆ **IN ORDER FOR A “FLIP” TO TAKE PLACE, ENERGY OF PHOTON MUST BE EQUAL TO THE ENERGY DIFFERENCE OF THE SPIN STATES**



Nuclear Spin in B_0

- The energy difference between allowed spin states increases linearly with applied field strength.
- Values shown here are for ^1H nuclei.



Thus, the energy needed to induce a “flip” will be different depending on field strength

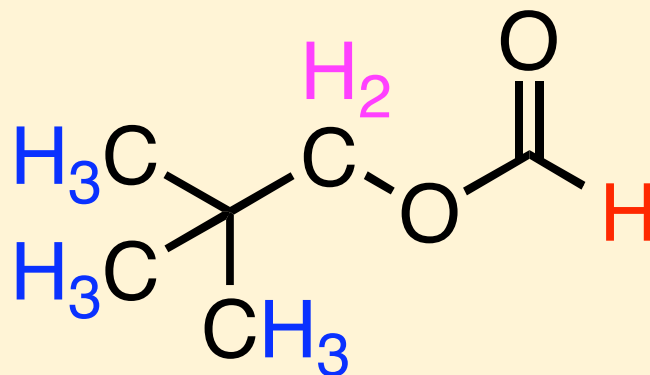
General Concept of NMR

- ◆ **The difference in the energy between the two states changes based on the local magnetic field strength at that nucleus.**
- ◆ **Two different internal factors can change the magnetic field**
 - **Electron density**
 - Electrons circulating around the nuclei can serve as a buffer for the applied external magnetic field, thereby changing the . The higher the electron density, the more “shielded” the nuclei is. The lower amount of electron density, the more “deshielded the nuclei is.
 - **Magnetic Moments Caused by Nearby Nuclei**
 - The magnetic field caused by the rotation of nearby nuclei can slightly alter the magnetic field around a nuclei

INTERPRETATION OF NMR RELIES ENTIRELY ON THE CHANGES THAT THESE PHENOMENON HAVE ON A NUCLEI

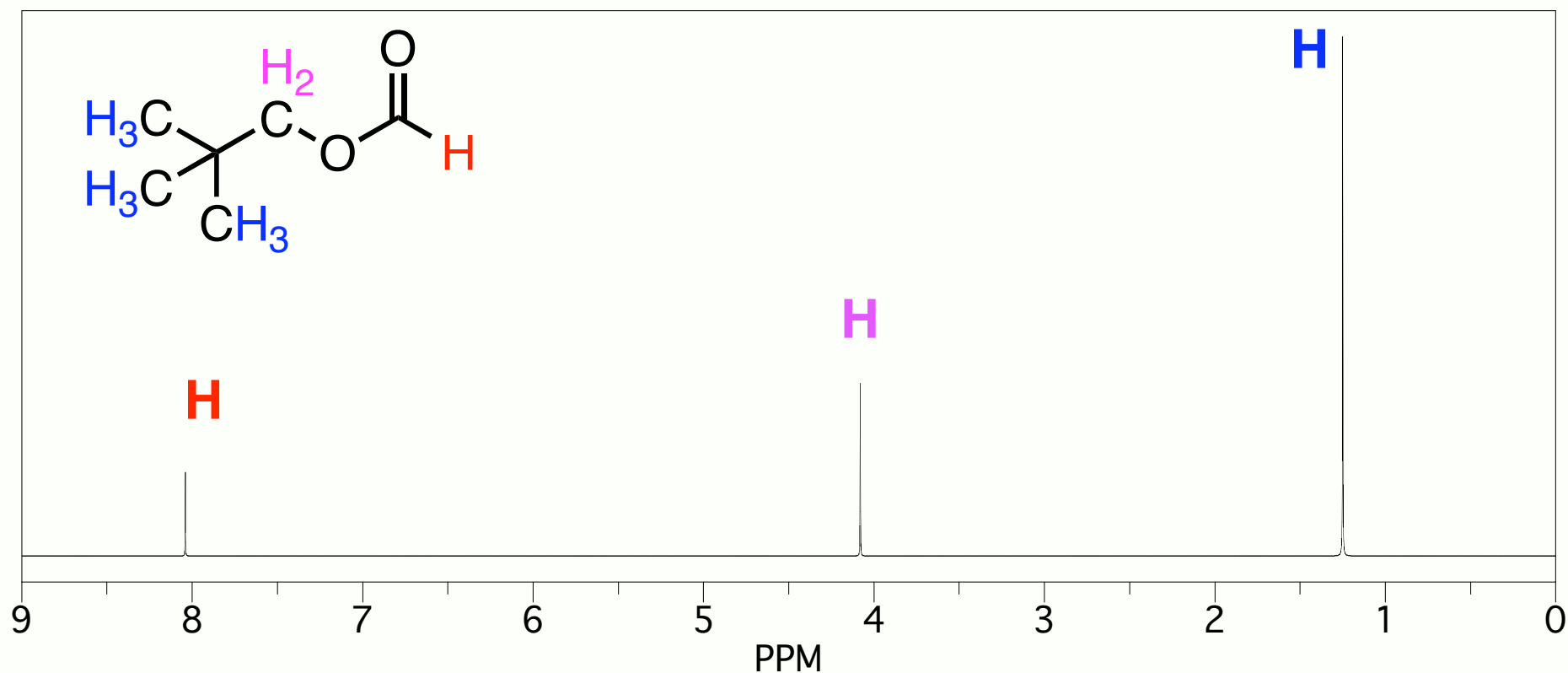
Effects of Shielding on NMR

- ◆ Nuclei that are “deshielded” generally have electron-withdrawing groups nearby
- ◆ They show up at higher numbers on an NMR spectrum



Order the protons based on estimated electron density

Effects of Shielding on NMR

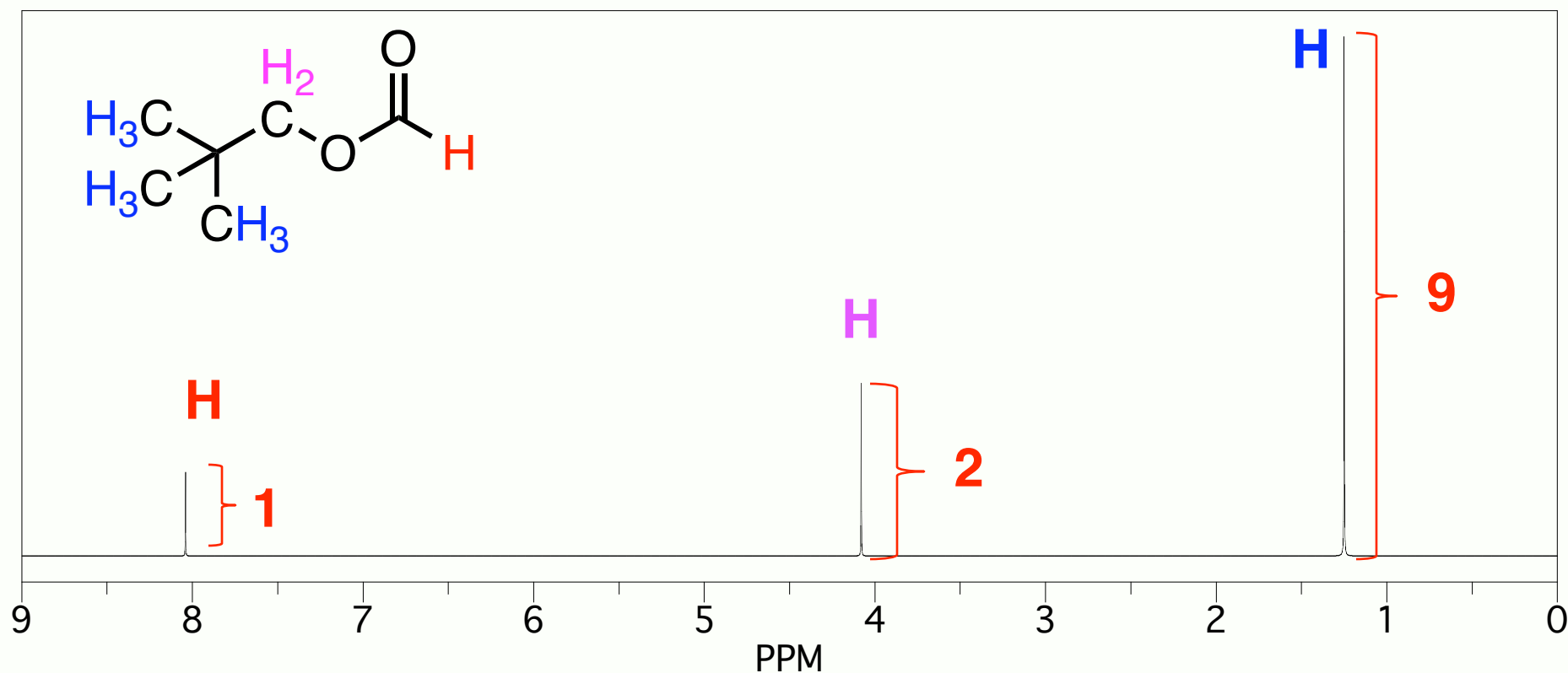


H is an aldehyde proton. Extremely deshielded.

H are on carbon connected to an oxygen, which is electron withdrawing and deshields slightly.

H are on carbon connected to carbon connected to another carbon. Nothing particularly electron withdrawing in proximity to have a noticeable effect.

Effects of Shielding on NMR



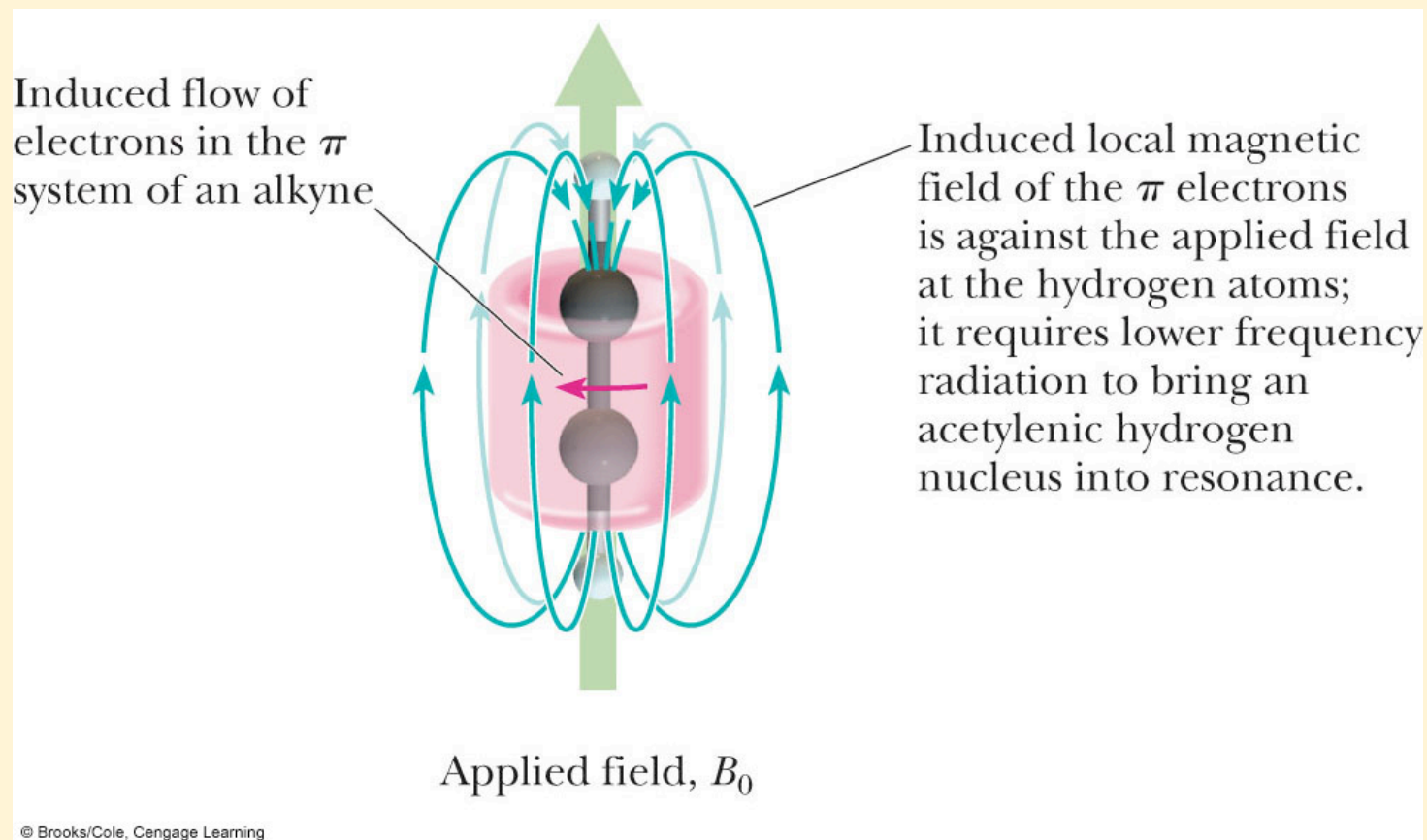
In addition, in ¹H NMR, areas underneath peak are directly related to # of protons represented by that peak

Affects of π bonds on ^1H NMR

- ◆ **Molecules with π bonds have distinct chemical shifts**
 - H on sp^2 hybridized carbons show up around 4.5-5.5 ppm
 - H on sp hybridized carbons show up around 2-3
 - H on aromatic protons show up around 7-8.
- ◆ **This is due to 2 effects**
 - More s character of carbon attached to H makes carbon more electronegative
 - **Diamagnetic effects from π bonds**
 - Flow of electrons π bonds create a magnetic current that impacts the chemical shift

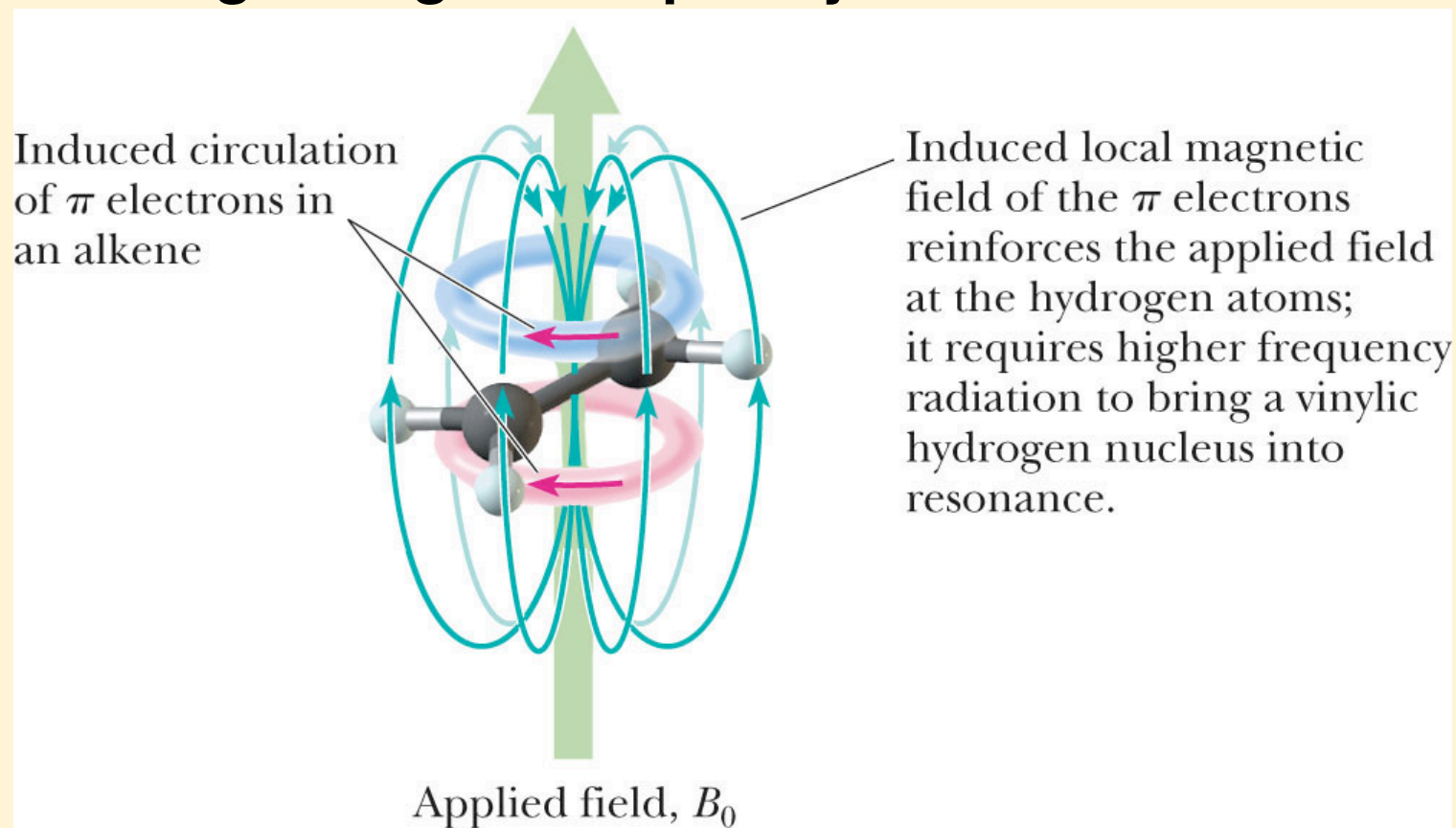
Affects of π bonds on ^1H NMR

- Magnetic induction in the π bonds of a carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal lower frequency.



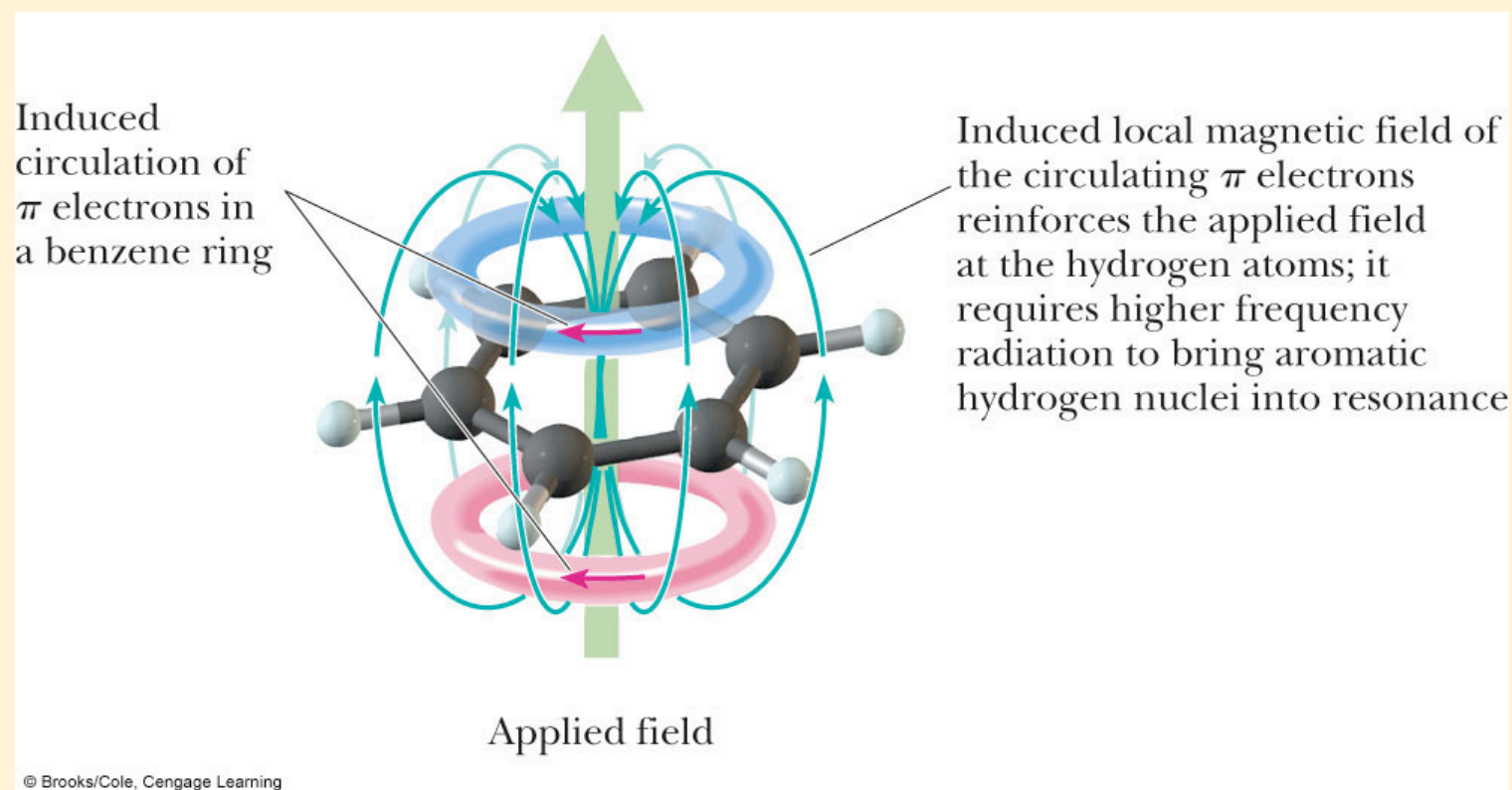
Affects of π bonds on ^1H NMR

- Magnetic induction in the π bond of a carbon-carbon double bond deshields vinylic hydrogens and shifts their signal higher frequency.



Affects of π bonds on ^1H NMR

- The magnetic field induced by circulation of π electrons in an aromatic ring deshields the hydrogens of the aromatic ring and shifts their signal to higher frequency.



Summary of Chemical Shifts

- ◆ The location of the peaks on an NMR are related to the electronic environment surrounding that proton, and will shift to higher numbers or lower numbers based on deshielding or shielding affects, respectively.

HOMEWORK: MEMORIZE THE APPROXIMATE LOCATION OF ANY PROTON ON AN ORGANIC MOLECULE

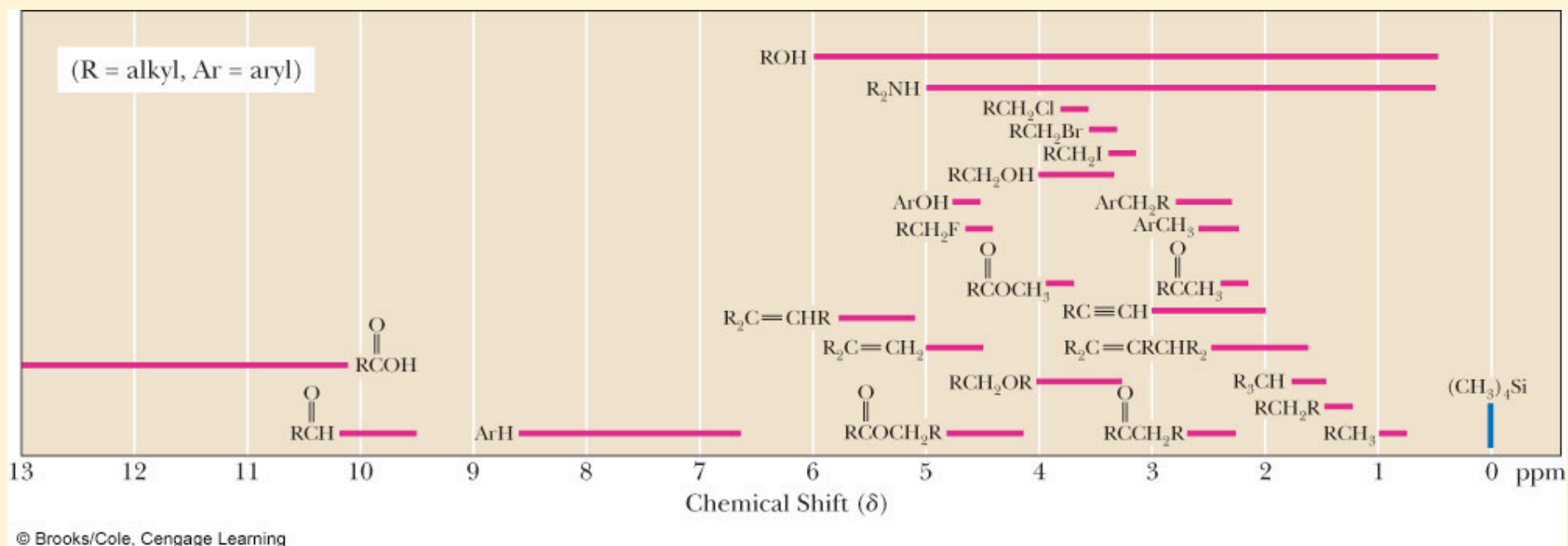
LIST OF CHEMICAL SHIFTS TO KNOW

Chemical Shifts ¹H-NMR

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
(CH ₃) ₄ Si	0 (by definition)		
RCH ₃	0.8-1.0	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_3 \end{array}$	3.7-3.9
RCH ₂ R	1.2-1.4	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_2\text{R} \end{array}$	4.1-4.7
R ₃ CH	1.4-1.7	RCH ₂ I	3.1-3.3
R ₂ C=CRCH ₂ R	1.6-2.6	RCH ₂ Br	3.4-3.6
RC≡CH	2.0-3.0	RCH ₂ Cl	3.6-3.8
ArCH ₃	2.2-2.5	RCH ₂ F	4.4-4.5
ArCH ₂ R	2.3-2.8	ArOH	4.5-4.7
ROH	0.5-6.0	R ₂ C=CH ₂	4.6-5.0
RCH ₂ OH	3.4-4.0	R ₂ C=CHR	5.0-5.7
RCH ₂ OR	3.3-4.0	ArH	6.5-8.5
R ₂ NH	0.5-5.0	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCH} \end{array}$	9.5-10.1
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCCCH}_3 \end{array}$	2.1-2.3	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$	10-13
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCCCH}_2\text{R} \end{array}$	2.2-2.6		

Chemical Shift - $^1\text{H-NMR}$

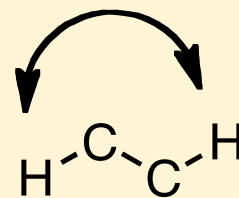
- ◆ Average values of chemical shifts of representative types of hydrogens.



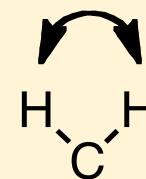
Magnetic Field of Adjacent Nuclei

- ◆ Nearby nuclei with magnetic moment can have a subtle effect on the shift of the peaks.
- ◆ Protons with identical chemical shifts split one another, but the spectra almost* never show it.
- ◆ Focus on **Blue H's**.
 - They will all have identical chemical shifts, and have one H Adjacent to them (**H**)
- ◆ This **H** will be spinning either against or with the magnetic field, and thus can shift the peak either left or right on the spectrum

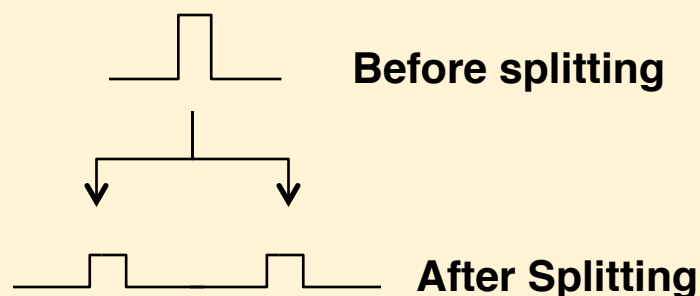
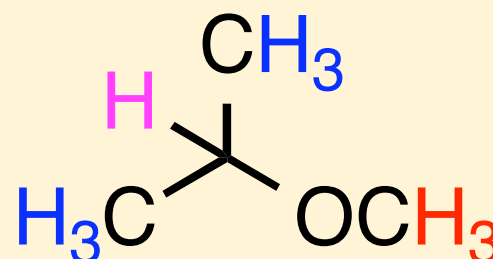
* In the context of this course, they will never split one another



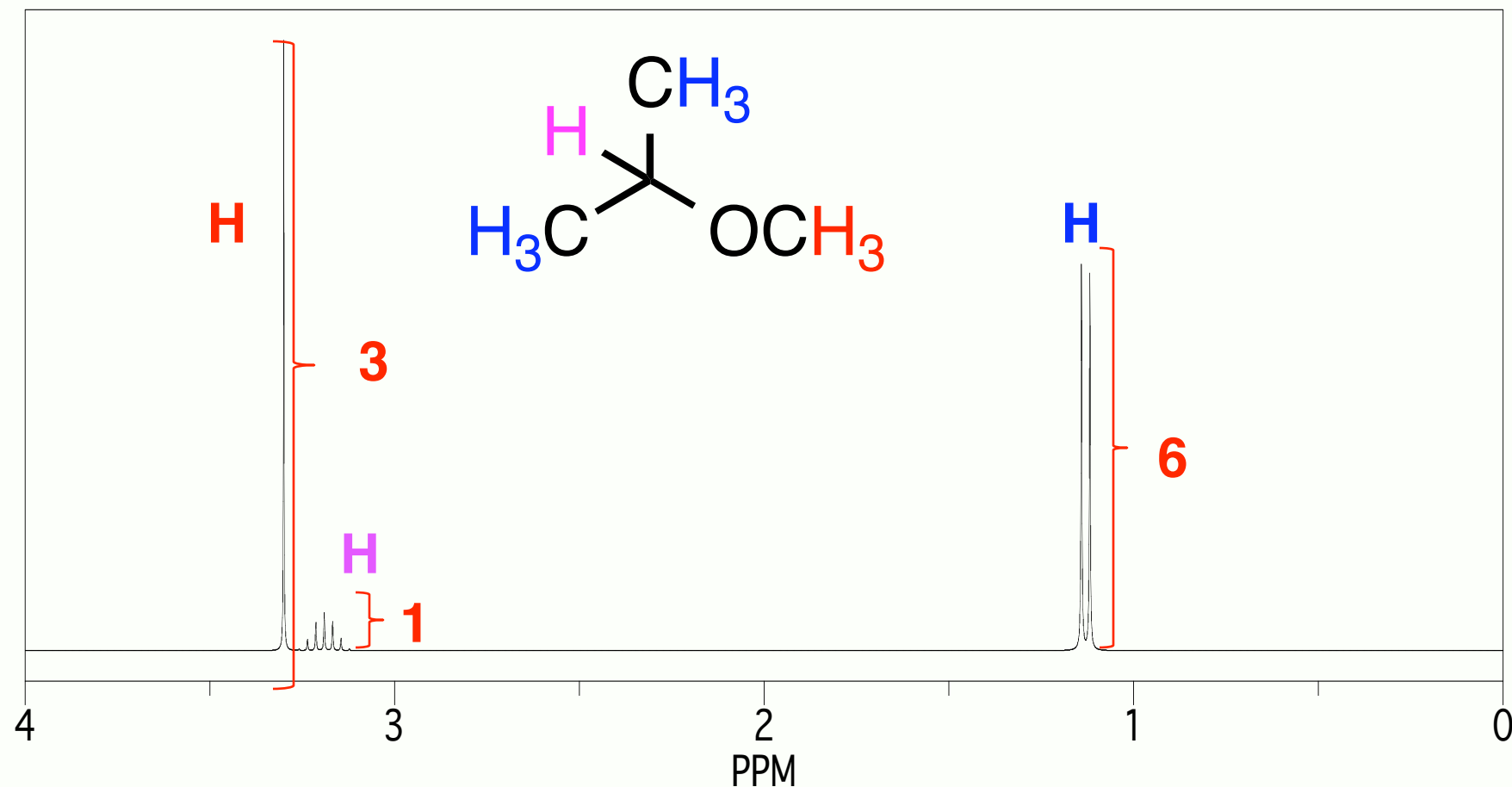
vicinal



geminal

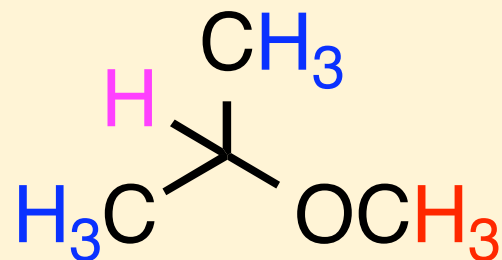


Magnetic Field of Adjacent Nuclei



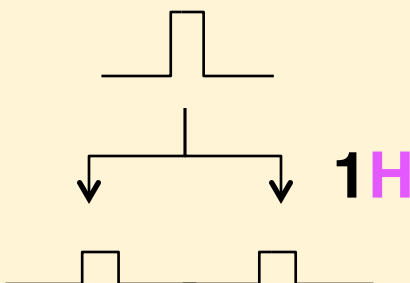
Note that **H** is split into a doublet, and **H** is a singlet.
What is going on with **H**?

Splitting in NMR



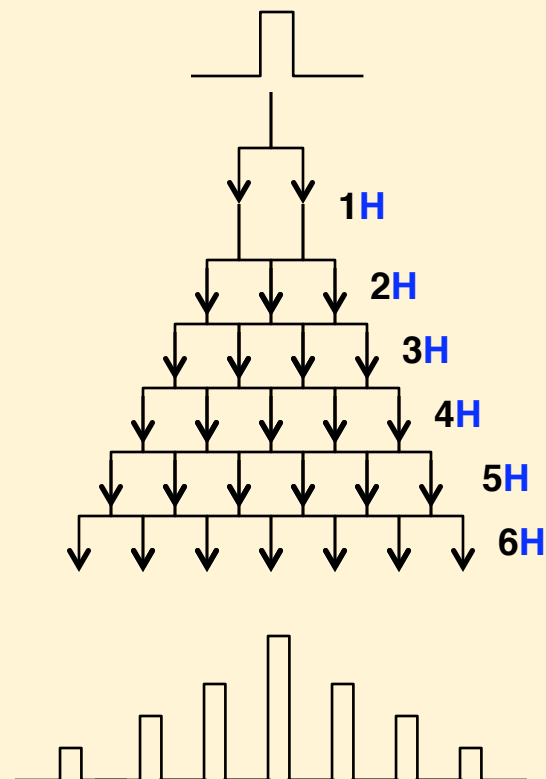
When split equivalently by multiple protons, an NMR will split to a pattern of $n+1$, where n is the number of protons doing the splitting

H split by 1 H



doublet
($1+1 = 2$)

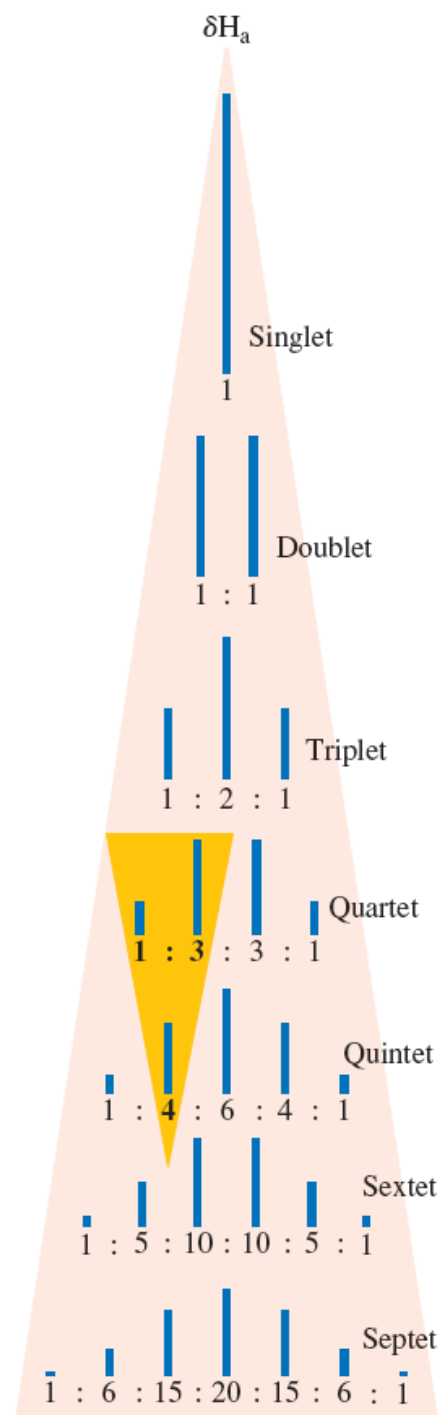
H split by 6 H



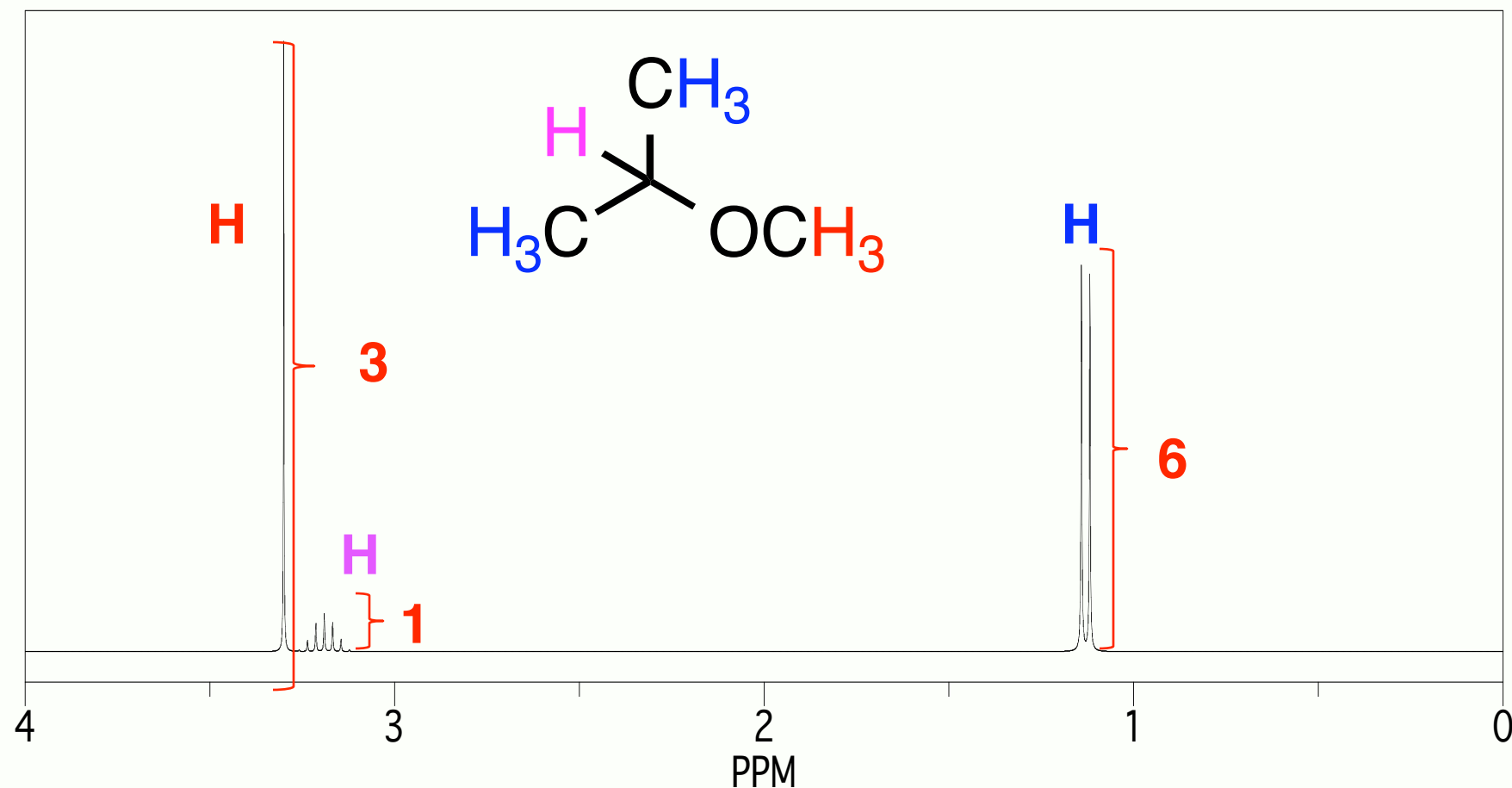
septet
($6+1 = 7$)

Signal Splitting

- ◆ **Pascal's triangle.**
 - As illustrated by the highlighted entries, each entry is the sum of the values immediately above it to the left and the right.



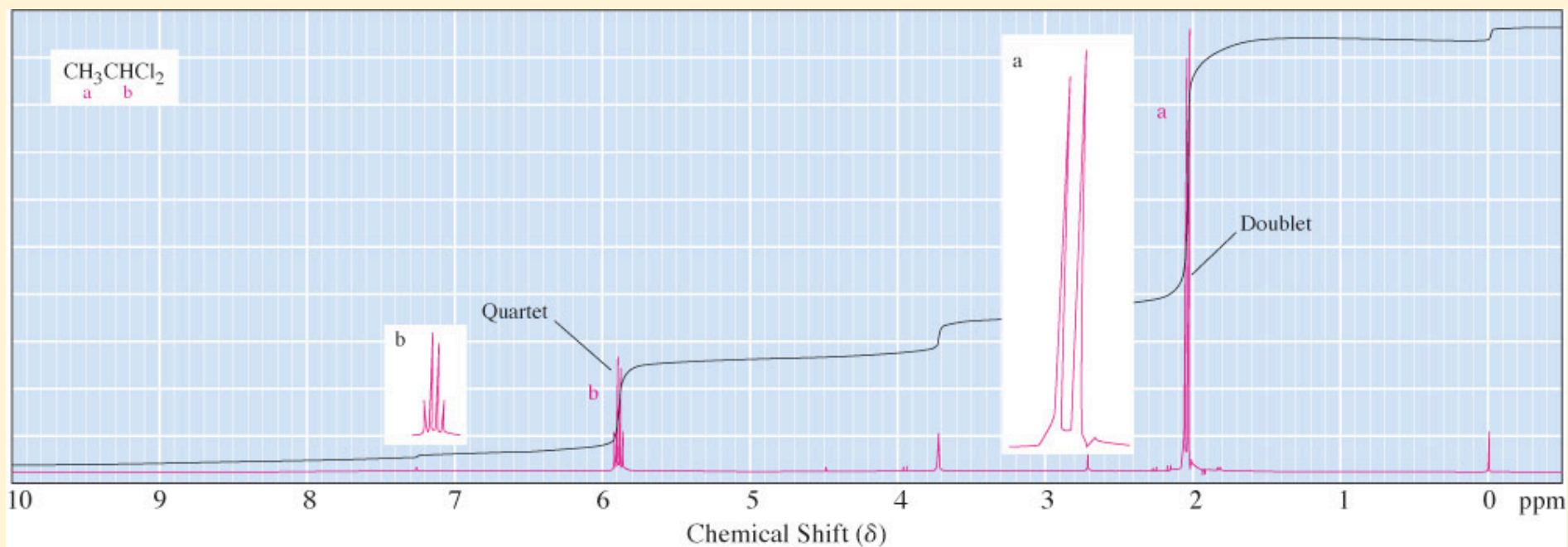
Magnetic Field of Adjacent Nuclei



Note the septet splitting pattern of H. Once it gets to the corners it becomes difficult to see because the outermost peaks are so small

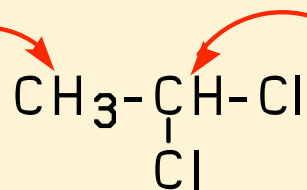
Signal Splitting ($n + 1$)

- $^1\text{H-NMR}$ spectrum of 1,1-dichloroethane.



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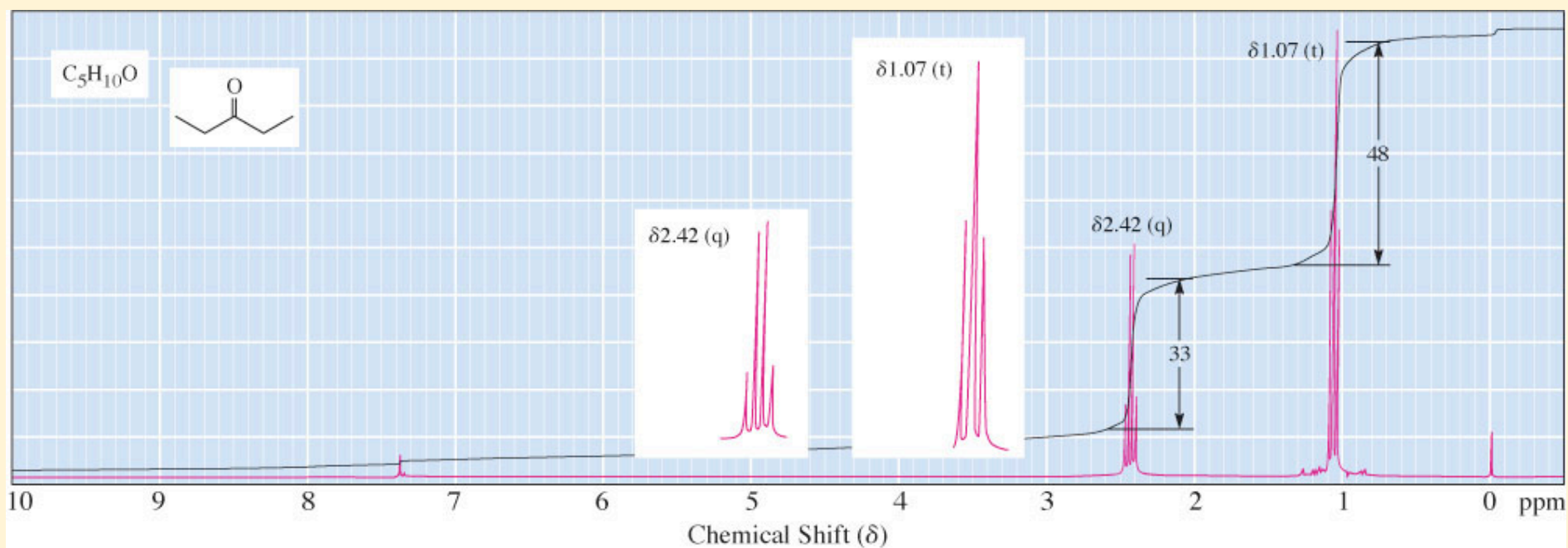
For these hydrogens, $n = 1$;
their signal is split into
 $(1 + 1) = 2$ peaks; a doublet



For this hydrogen, $n = 3$;
its signal is split into
 $(3 + 1) = 4$ peaks; a quartet

Origins of Signal Splitting

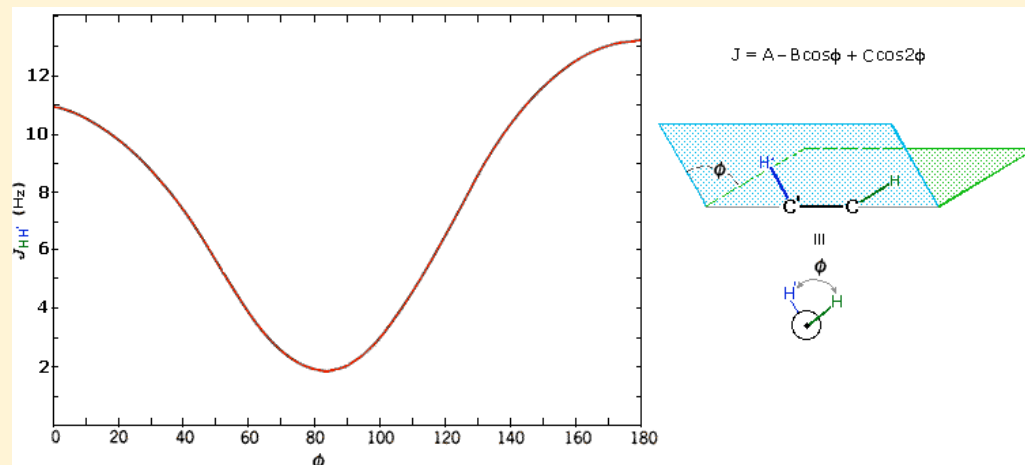
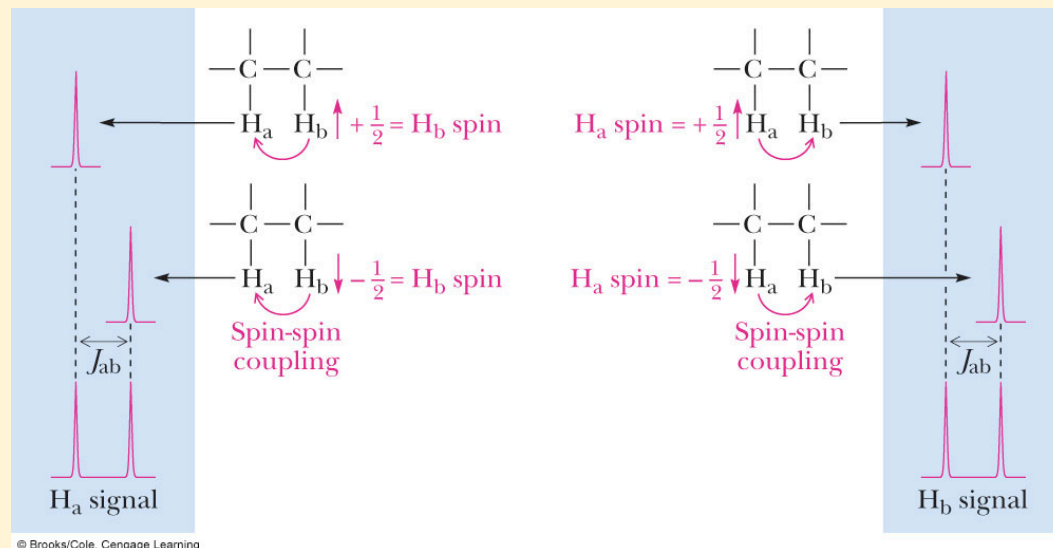
- The quartet-triplet $^1\text{H-NMR}$ signals of 3-pentanone showing the original trace and a scale expansion to show the signal splitting more clearly.



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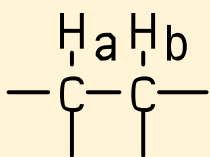
Coupling Constants

- ◆ **Coupling constant (J):**
The separation on an NMR spectrum (in hertz) between adjacent peaks in a multiplet.
- ◆ Degree of splitting is related to angle of between nuclei.
- ◆ The Karplus Curve (right) can help anticipate and explain approximate J values relative to dihedral angle on vicinal protons

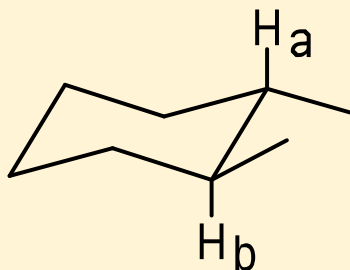


Coupling Constants

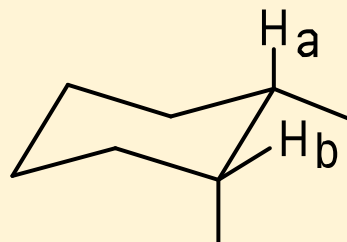
- ◆ **Coupling constant (J):** The distance between peaks in a split signal, expressed in hertz.
 - The value is a quantitative measure of the magnetic interaction of nuclei whose spins are coupled.



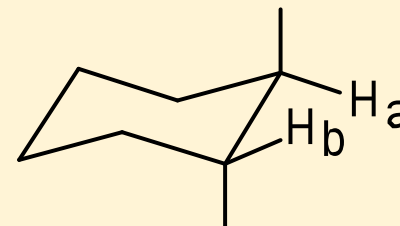
6-8 Hz



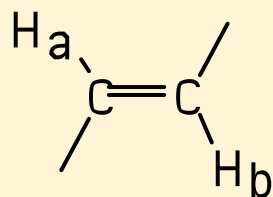
8-14 Hz



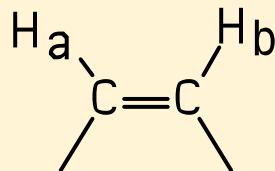
0-5 Hz



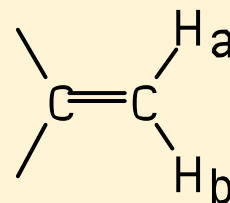
0-5 Hz



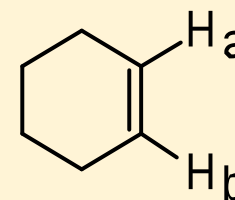
11-18 Hz



5-10 Hz



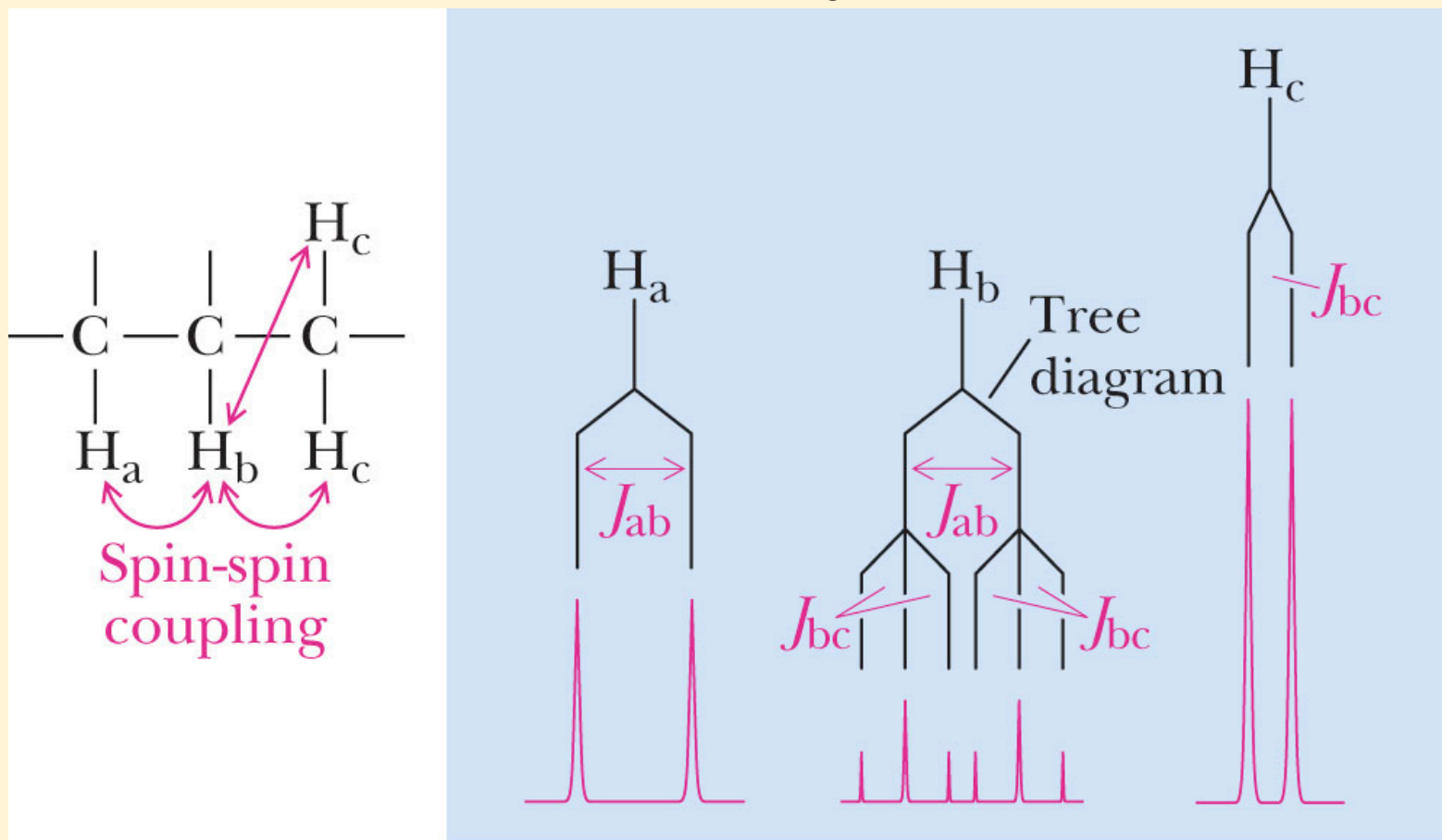
0-5 Hz



8-11 Hz

More Complex Splitting Patterns

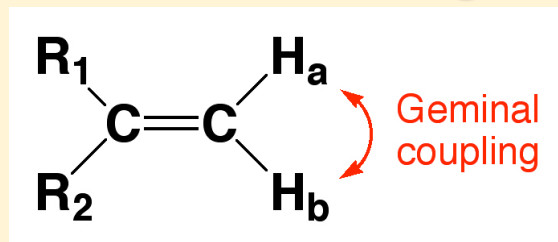
- Complex coupling that arises when H_b is split by H_a and two equivalent atoms H_c .



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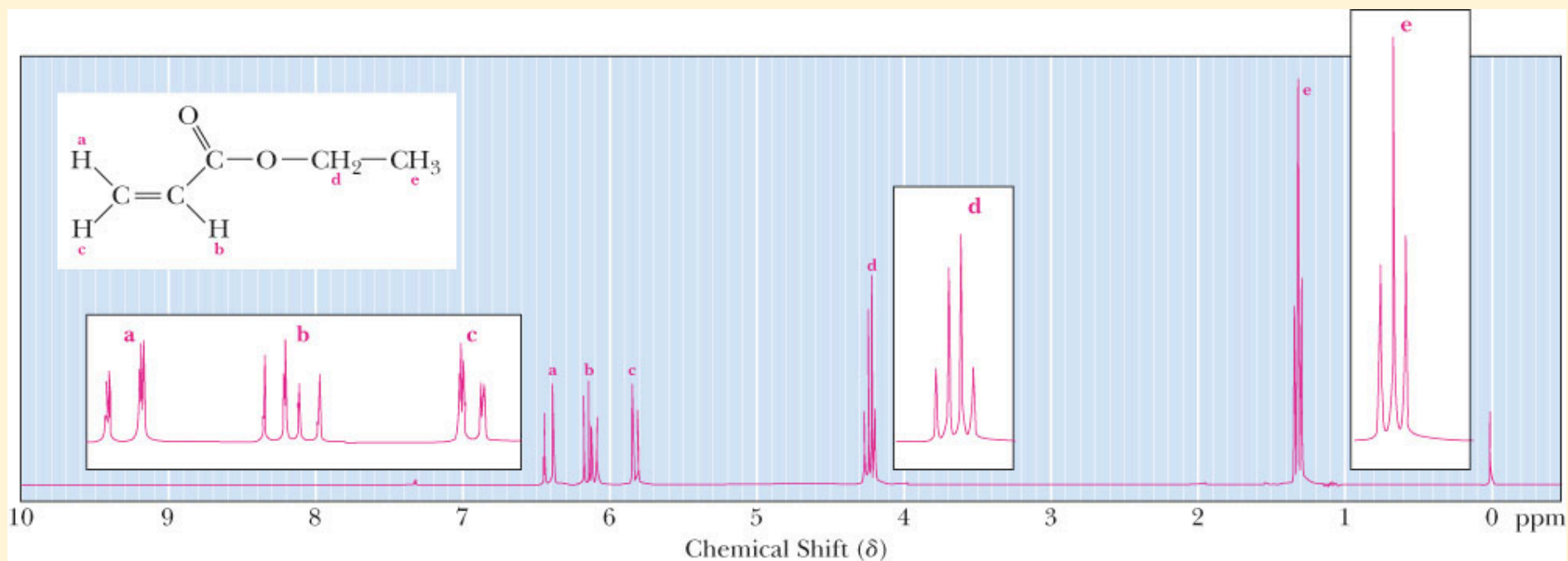
More Complex Splitting Patterns

- Because the angle between C-H bond determines the extent of coupling, bond rotation is a key parameter.
- In molecules with relatively free rotation about C-C sigma bonds, H atoms bonded to the same carbon in CH₃ and CH₂ groups generally are equivalent.
- If there is restricted rotation, as in alkenes and cyclic structures, H atoms bonded to the same carbon may not be equivalent.
- Nonequivalent H on the same carbon will couple and cause signal splitting.
- This type of coupling is called **geminal coupling**.



More Complex Splitting Patterns

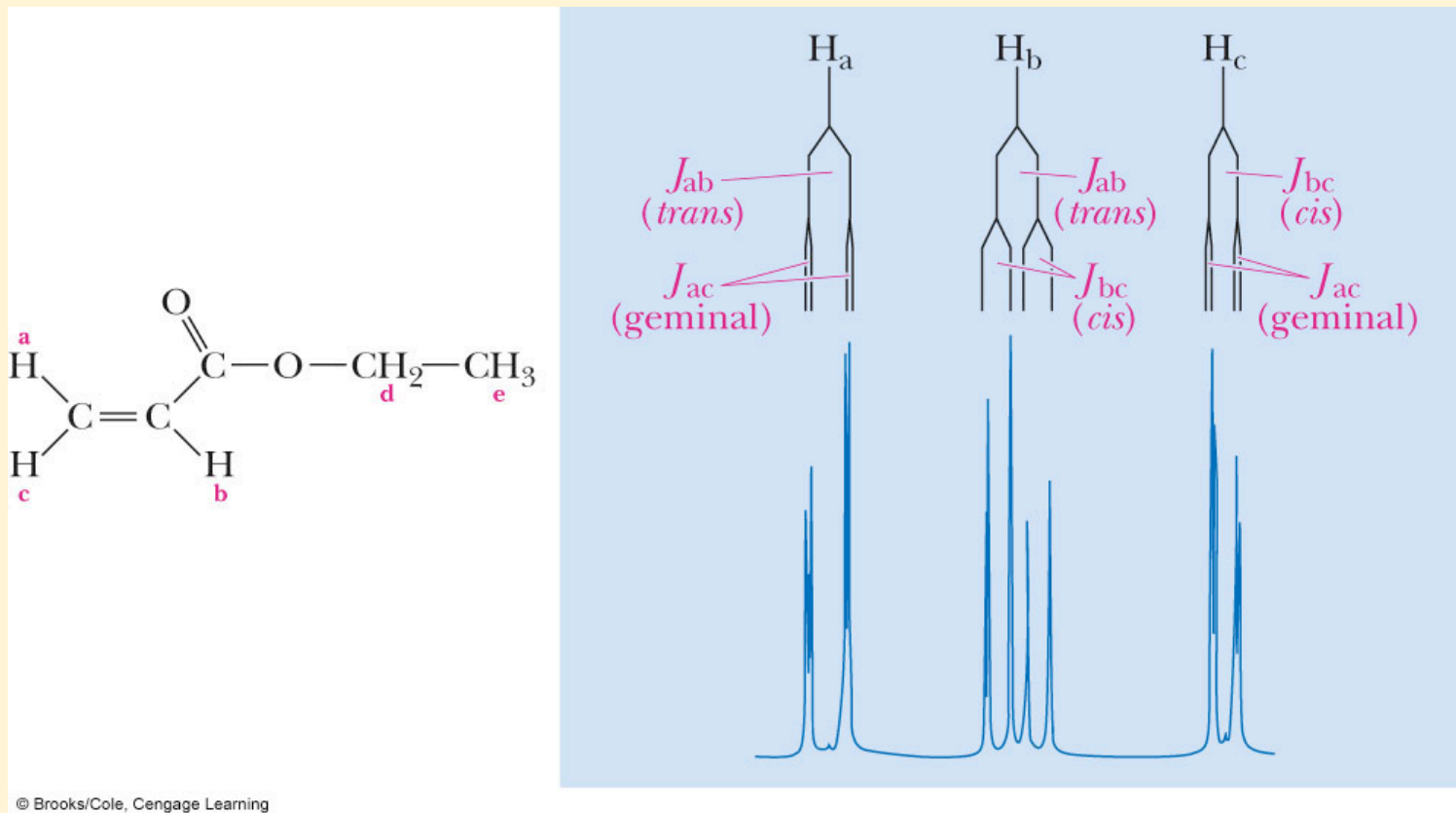
- In ethyl propenoate, an unsymmetrical terminal alkene, the three vinylic hydrogens are nonequivalent.



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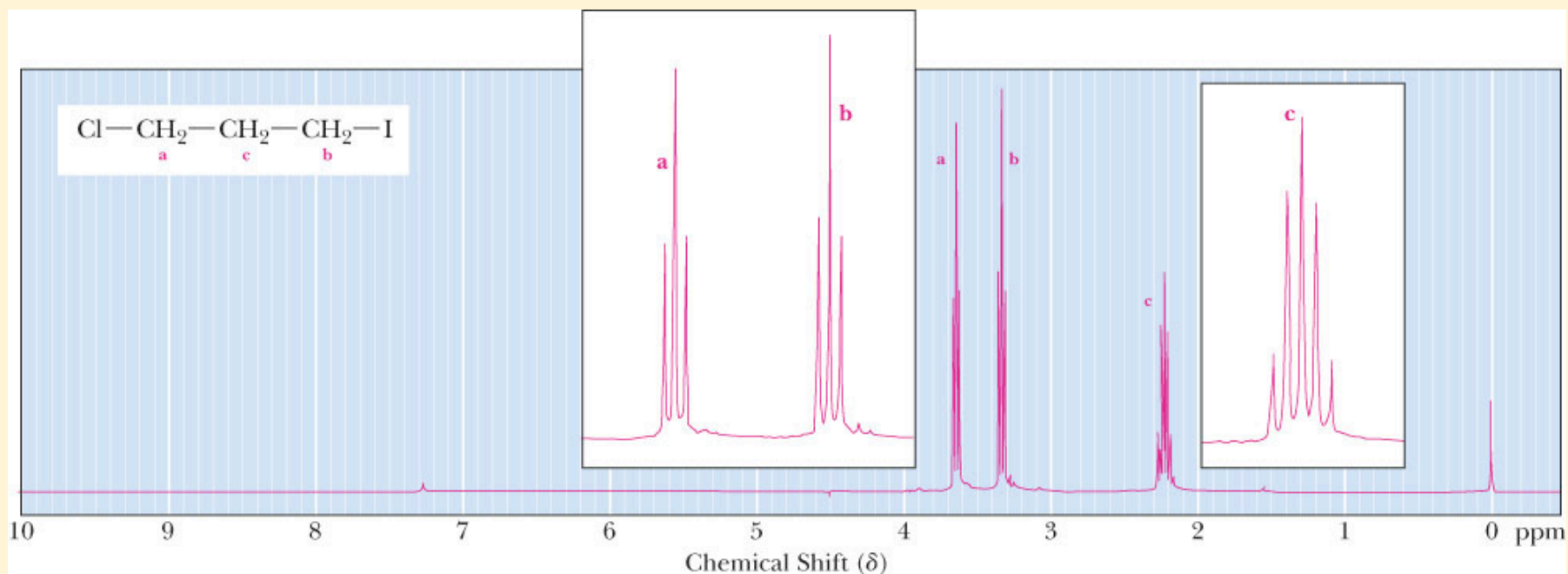
More Complex Splitting Patterns

- Tree diagram for the complex coupling seen for the three alkenyl H atoms in ethyl propenoate.



More Complex Splitting Patterns

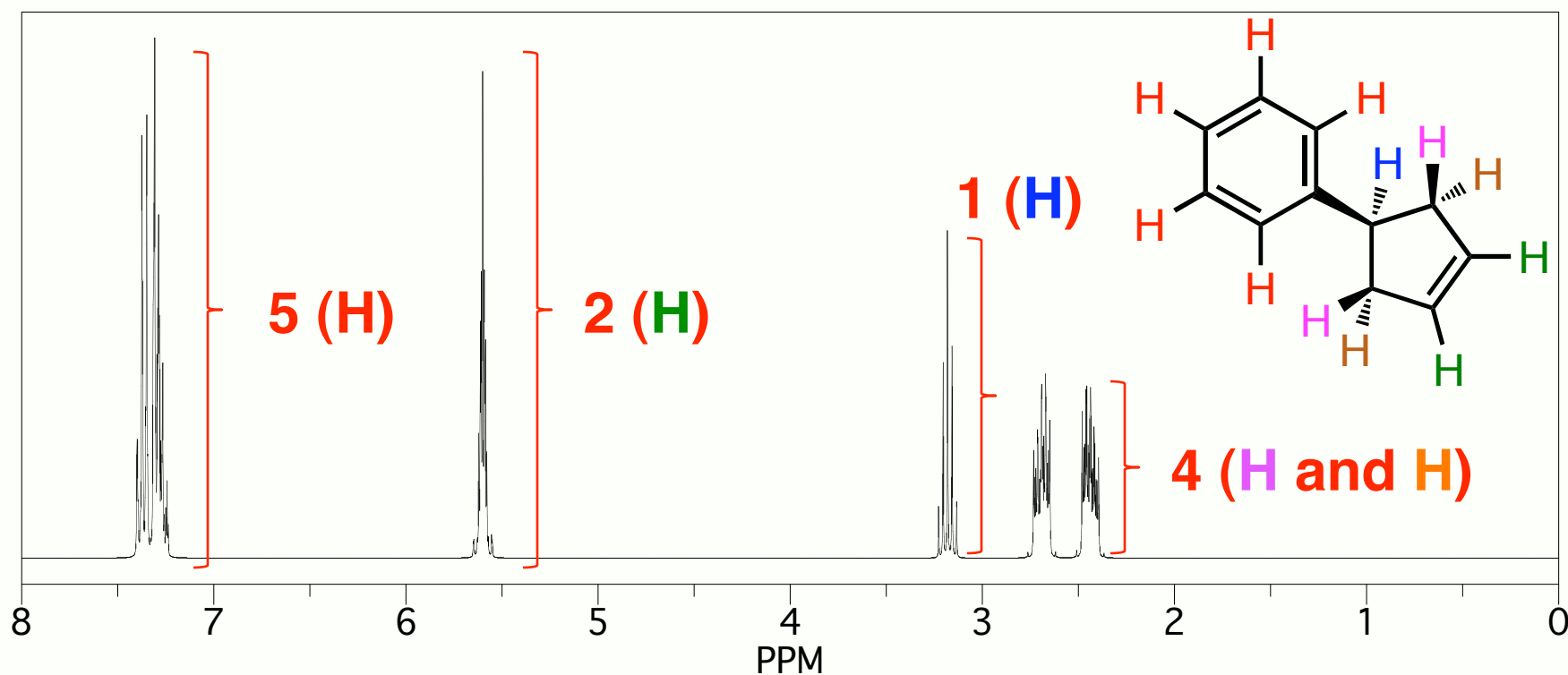
- An example of peak overlap occurs in the spectrum of 1-chloro-3-iodopropane.
- The central CH₂ (H_c) has the possibility for $3 \times 3 = 9$ peaks (a triplet of triplets) but because J_{ab} and J_{bc} are so similar, only $4 + 1 = 5$ peaks are distinguishable.



Information of NMR

◆ 3 Pieces of Information can be gained from the NMR

- **Integration:** Number of Protons Corresponding to a given peak
- **Chemical Shift:** Electronic Environment of Proton
- **Coupling:** What protons are nearby (on adjacent carbon)

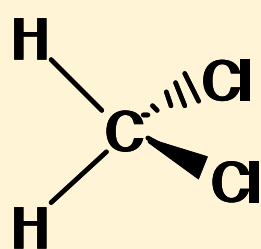


Stereochemistry & Topicity

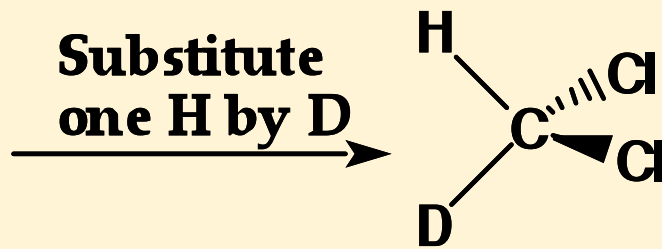
- ◆ Depending on the symmetry of a molecule, otherwise equivalent hydrogens may be
 - homotopic.
 - enantiotopic.
 - diastereotopic.
- ◆ The simplest way to visualize topicity is to substitute an atom or group by an isotope; is the resulting compound
 - the same as its mirror image?
 - different from its mirror image?
 - are diastereomers possible?

Stereochemistry & Topicity

◆ Homotopic atoms or groups



Dichloro-
methane
(achiral)



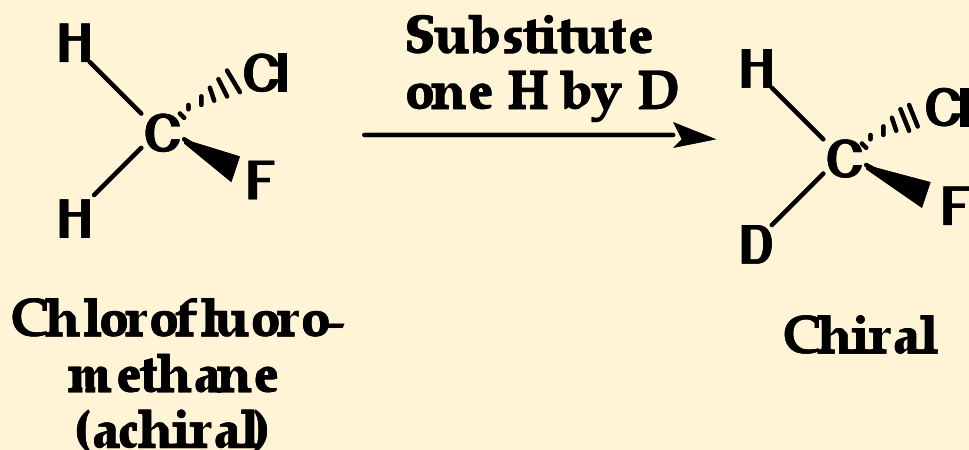
Achiral

Substitution does not
produce a stereocenter;
therefore hydrogens
are homotopic.

- Homotopic atoms or groups have identical chemical shifts under all conditions.

Stereochemistry & Topicity

◆ Enantiotopic groups



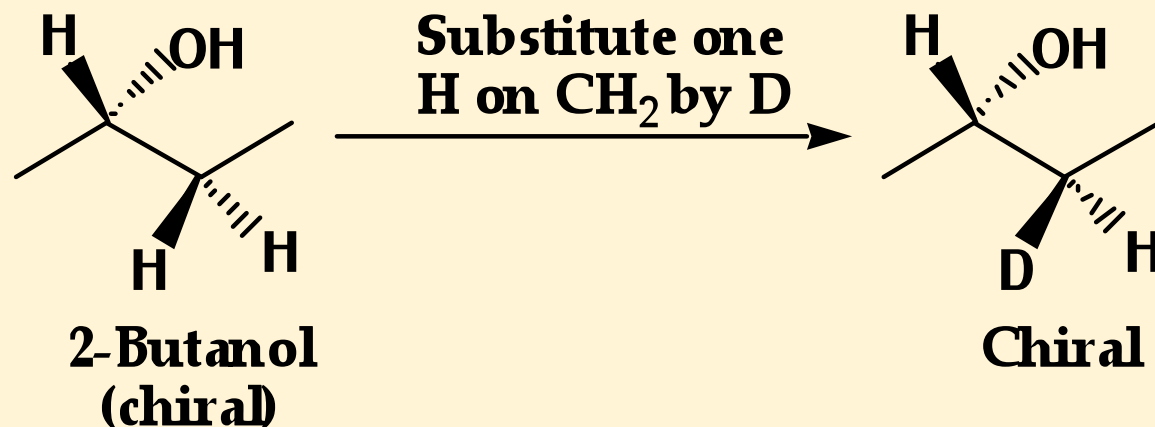
Substitution produces a stereocenter; therefore, hydrogens are enantiotopic. Both hydrogens are prochiral; one is pro-R-chiral, the other is pro-S-chiral.

- Enantiotopic atoms or groups have identical chemical shifts in achiral environments.
- They have different chemical shifts in chiral environments.

Stereochemistry & Topicity

◆ Diastereotopic groups

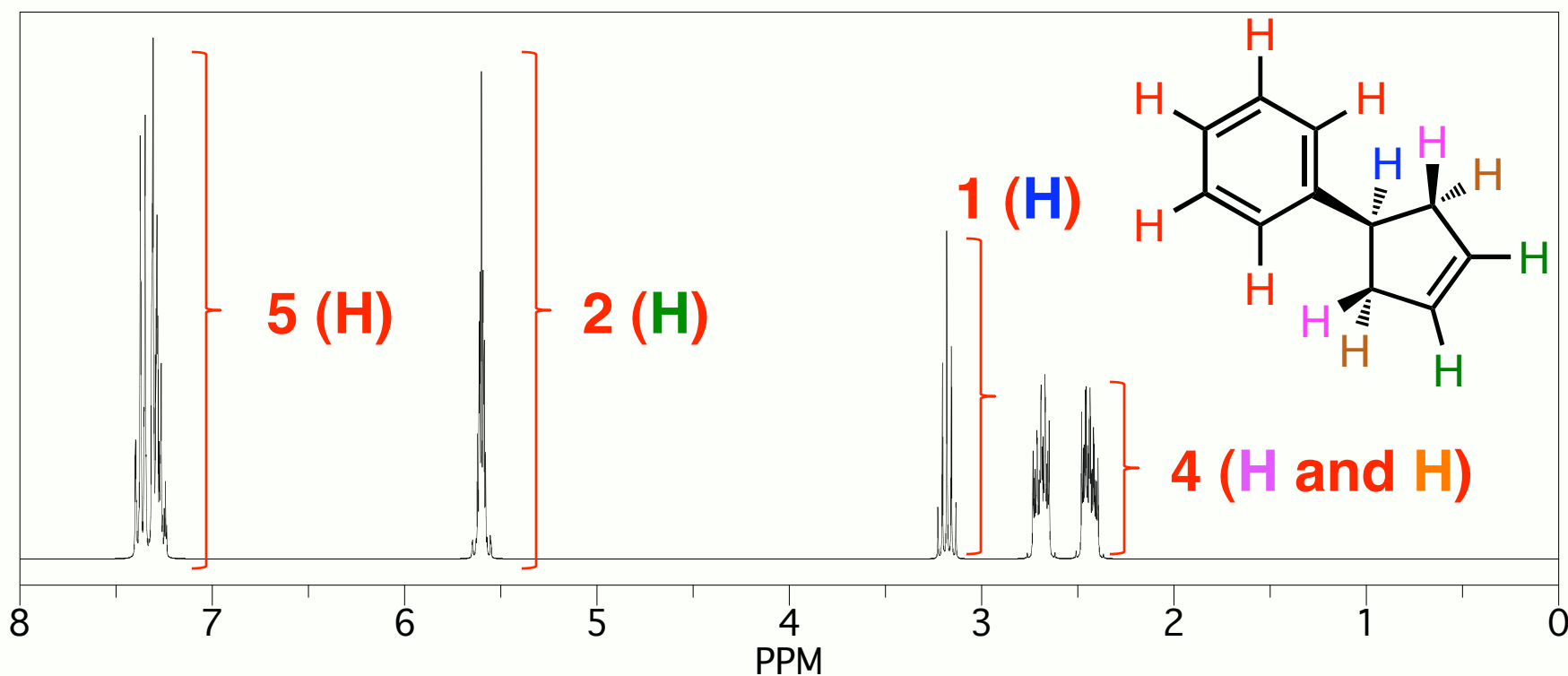
- H atoms on C-3 of 2-butanol are diastereotopic.
- Substitution by deuterium creates a chiral center.
- Because there is already a chiral center in the molecule, diastereomers are now possible.



- Diastereotopic hydrogens have different chemical shifts under all conditions.

Information of NMR

- ◆ **3 Pieces of Information can be gained from the NMR**
 - **Integration:** Number of Protons Corresponding to a given peak
 - **Chemical Shift:** Electronic Environment of Proton
 - **Coupling:** What protons are nearby (on adjacent carbon)



Interpreting NMR Spectra

◆ Alkanes

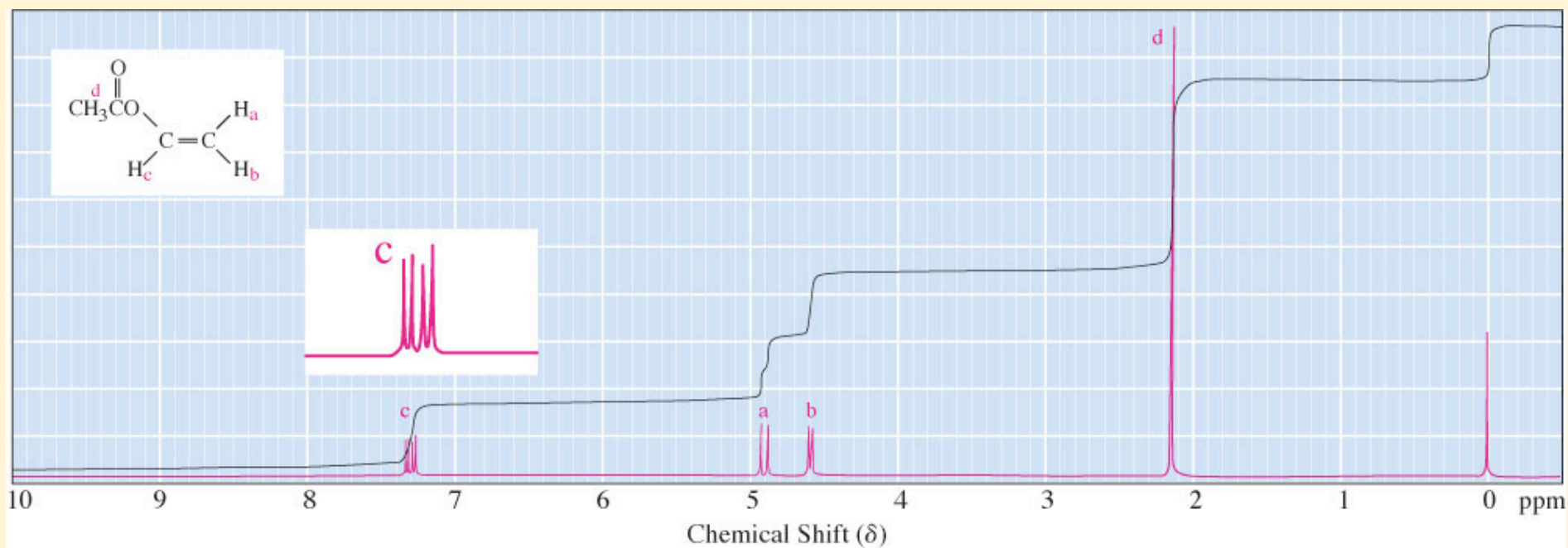
- ^1H -NMR signals appear in the range of δ 0.8-1.7.

◆ Alkenes

- ^1H -NMR signals appear in the range δ 4.6-5.7.
- ^1H -NMR coupling constants are generally larger for *trans*-vinylic hydrogens ($J= 11-18$ Hz) compared with *cis*-vinylic hydrogens ($J= 5-10$ Hz).

Interpreting NMR Spectra

- ^1H -NMR spectrum of vinyl acetate.



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Interpreting NMR Spectra

◆ Alcohols

- ◆ $^1\text{H-NMR}$ O-H chemical shift often appears in the range δ 3.0-4.0, but may be as low as δ 0.5.
 - $^1\text{H-NMR}$ chemical shifts of hydrogens on the carbon bearing the -OH group are deshielded by the electron-withdrawing inductive effect of the oxygen and appear in the range δ 3.0-4.0.

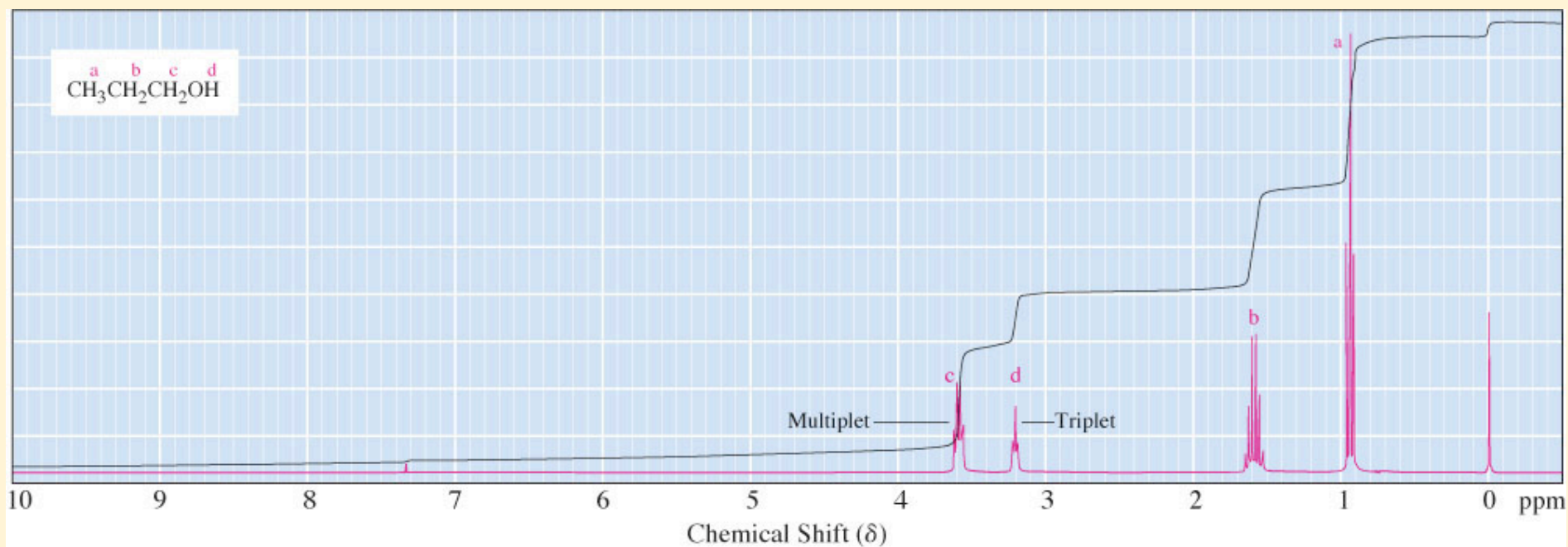
It is not uncommon to not see alcohol O-H peak at all

◆ Ethers

- A distinctive feature in the $^1\text{H-NMR}$ spectra of ethers is the chemical shift, δ 3.3-4.0, of hydrogens on the carbons bonded to the ether oxygen.

Interpreting NMR Spectra

- ^1H -NMR spectrum of 1-propanol.



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Interpreting NMR Spectra

◆ Aldehydes and ketones

- $^1\text{H-NMR}$: aldehyde hydrogens appear at δ 9.5-10.1.
- $^1\text{H-NMR}$: α -hydrogens of aldehydes and ketones appear at δ 2.2-2.6.

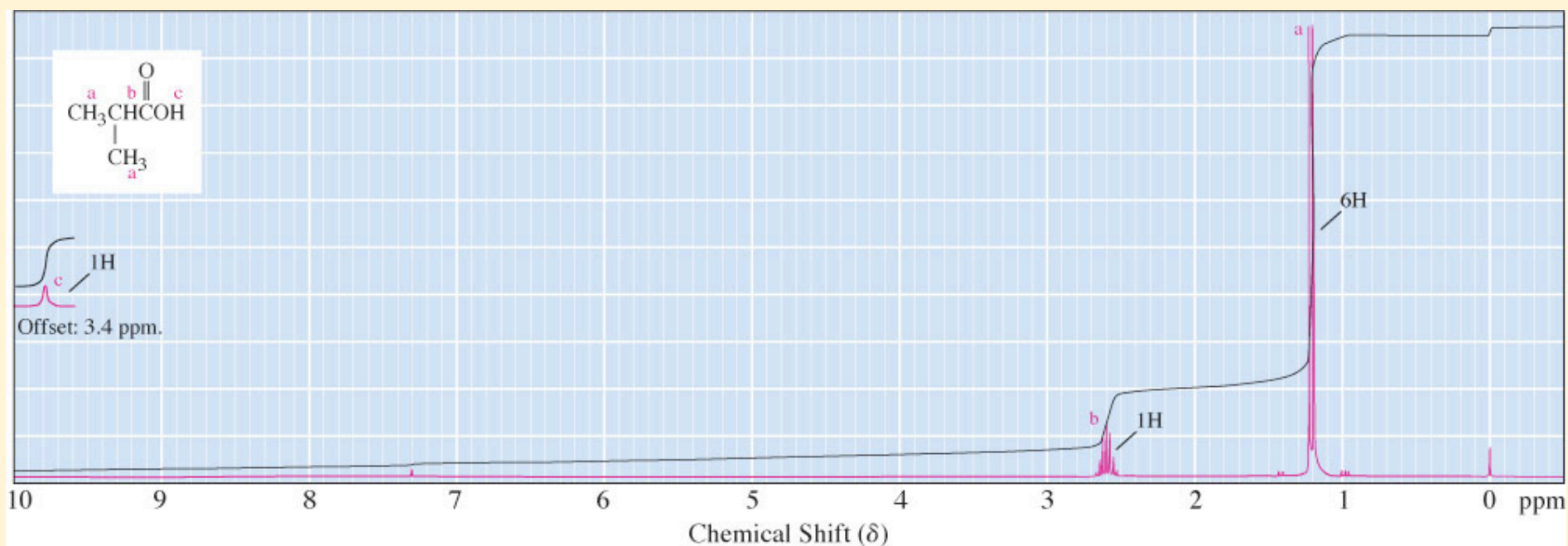
◆ Amines

- $^1\text{H-NMR}$: amine hydrogens appear at δ 0.5-5.0 depending on conditions.

Interpreting NMR Spectra

◆ Carboxylic acids

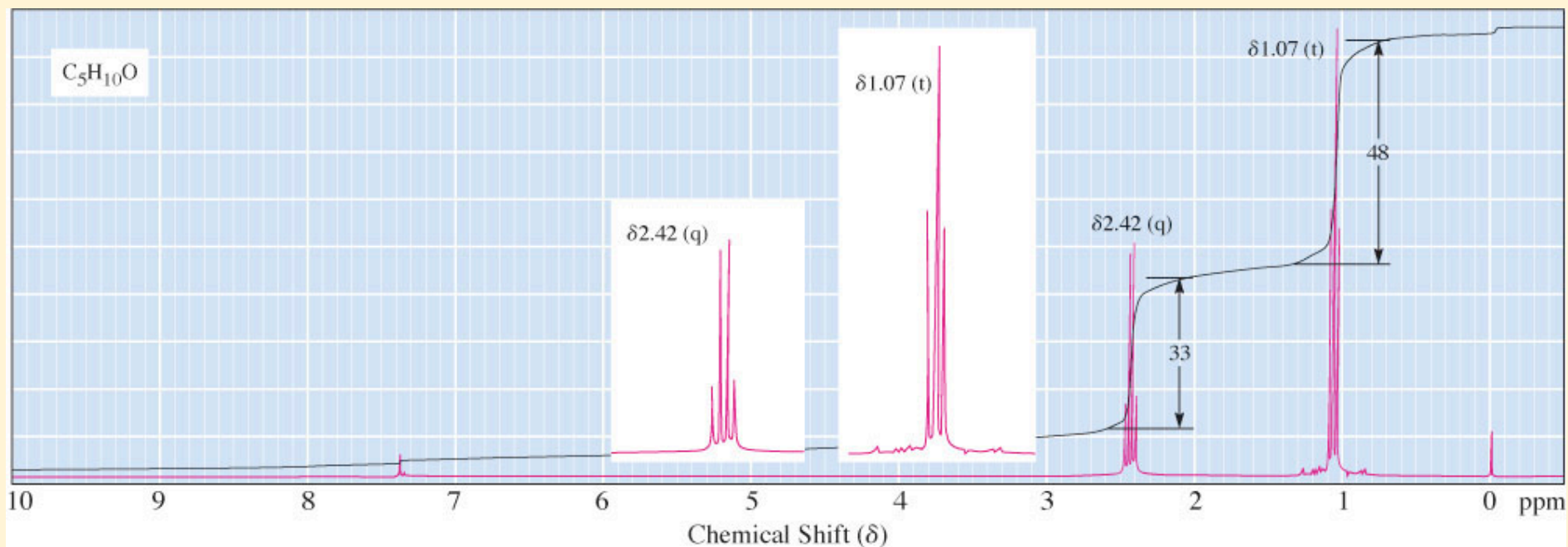
- $^1\text{H-NMR}$: carboxyl hydrogens appear at δ 10-13, to higher frequency of most other types of hydrogens.



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Interpreting NMR Spectra

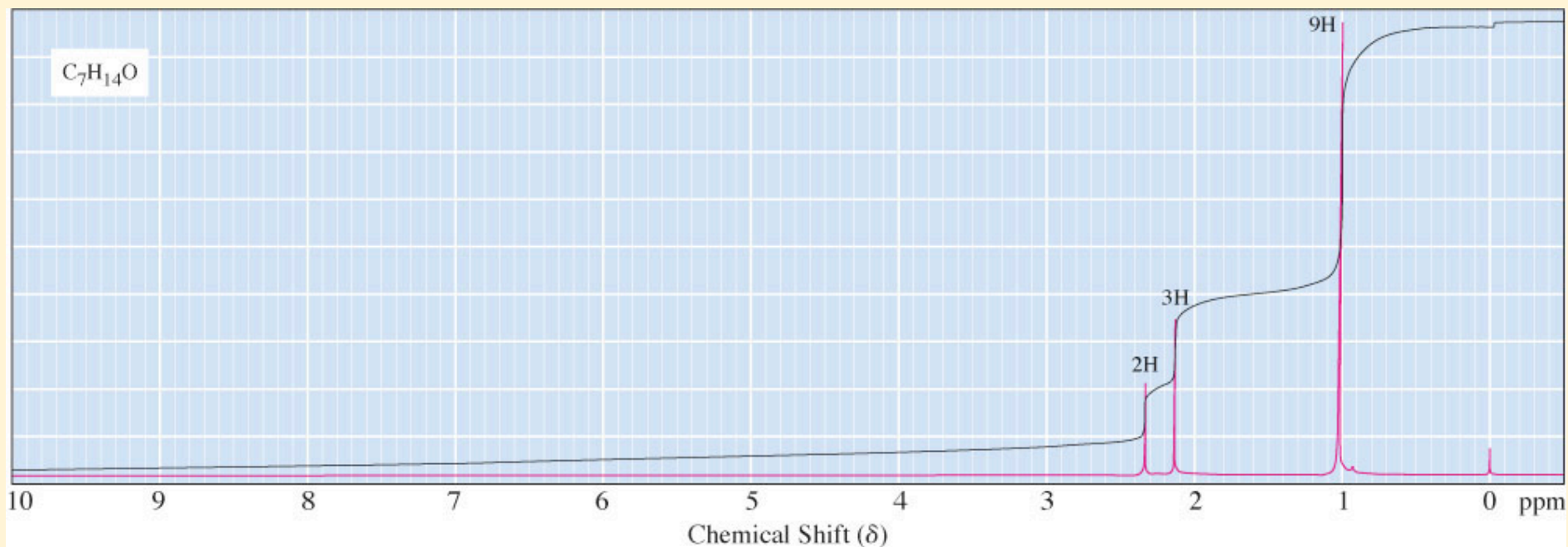
◆ Spectral Problem 1; molecular formula $C_5H_{10}O$.



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Interpreting NMR Spectra

◆ Spectral Problem 2; molecular formula $C_7H_{14}O$.



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