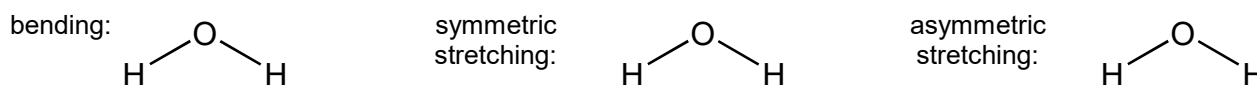
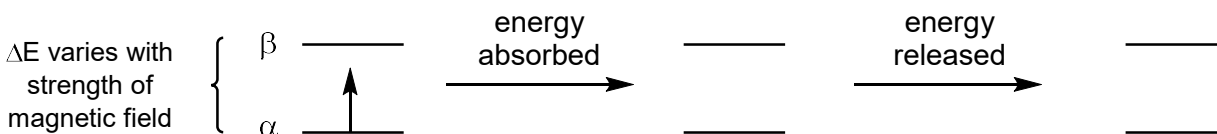
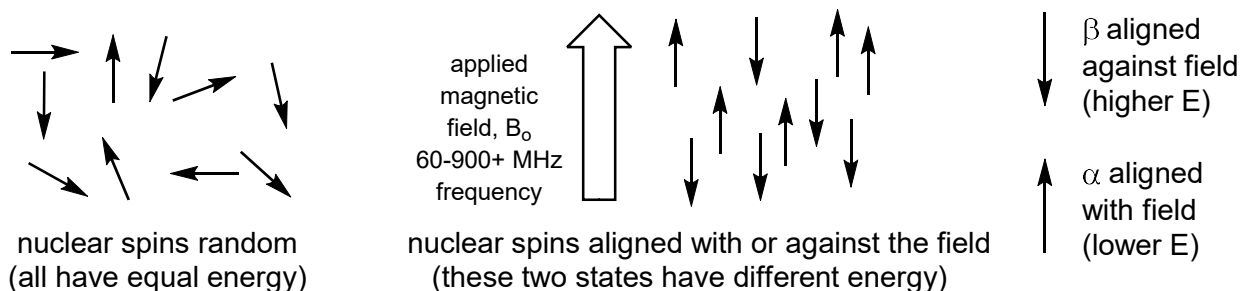


**Infrared (IR) spectroscopy** reveals which **functional groups** are present in a molecule. When certain wavelengths of IR light are absorbed, specific bonds are vibrationally excited: they stretch or bend. For example,  $\sim 1700\text{ cm}^{-1}$  light will cause a carbonyl (C=O) bond to stretch, so an absorption in that region indicates the presence of a ketone or aldehyde functional group.

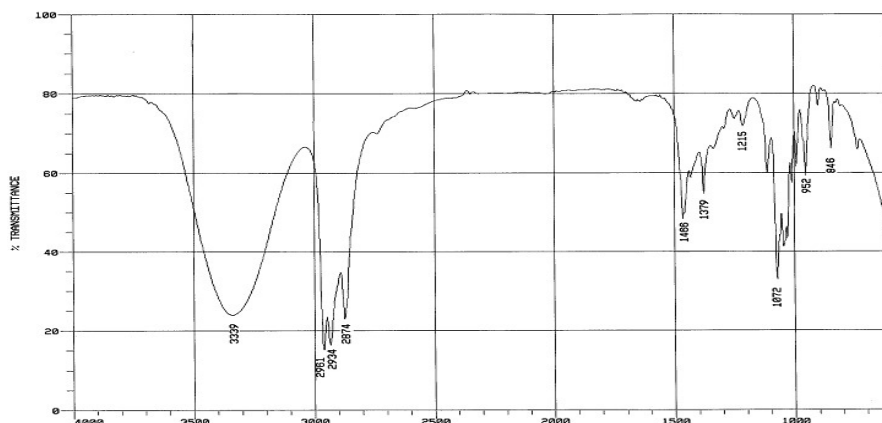


**Acquiring an NMR spectrum (15.1, 15.2)** Like all spectroscopic methods, NMR involves the use of electromagnetic energy to excite a molecule. By observing this interaction, we can learn something about the structure of the sample. In NMR spectroscopy, radio frequency waves are used (60,000,000 Hz or 60 MHz, also 200, 360, 500, etc.) and the result is a change in the spin of a nucleus. The nuclei which can be observed include  $^1\text{H}$  "proton NMR,"  $^{13}\text{C}$  "C-13 NMR,"  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ . These all have magnetic moments (like tiny magnets) and will interact with an applied magnetic field. Each of these nuclei has a spin quantum number  $I=1/2$  and has two spin states of equal energy. When a magnetic field is applied, these spin states will align **with** ( $\alpha$ ) or **against** ( $\beta$ ) the field. Those aligned with the field are lower in energy than those aligned against the field; the difference in energy between  $\alpha$  and  $\beta$  is proportional to the strength of the magnet used. Application of radio waves at just the right frequency will cause certain nuclei to absorb energy and "flip" from the  $\alpha$  to the  $\beta$  spin state. As the excited nucleus relaxes back to the ground state, a signal is recorded and an NMR spectrum can be obtained. The frequency of this energy transition depends on the electronic environment of the nucleus.

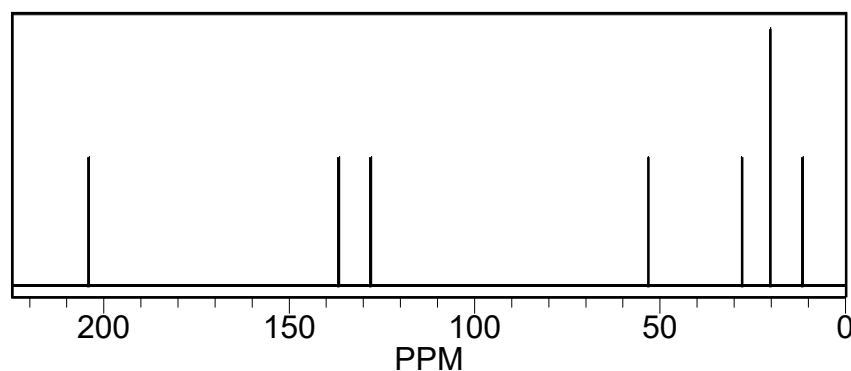


**IR spectrum** shows functional groups (see Klein Chapter 14 & CHM 3140L lab)

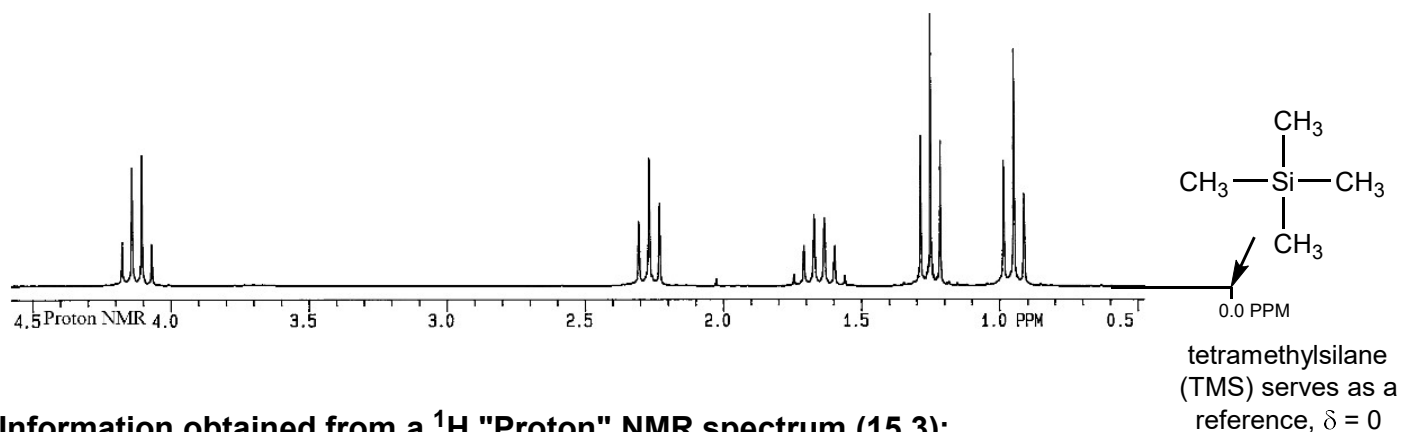
15-2



**<sup>13</sup>C NMR spectrum** shows how many different types of carbons are in a molecule, and whether each carbon is in an electron-rich or electron-deficient environment.



**<sup>1</sup>H NMR (Proton NMR) spectrum**



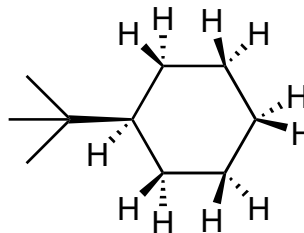
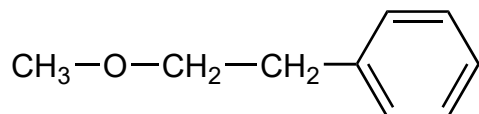
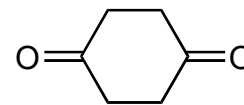
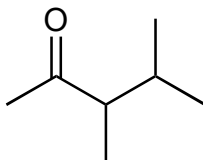
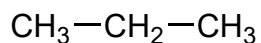
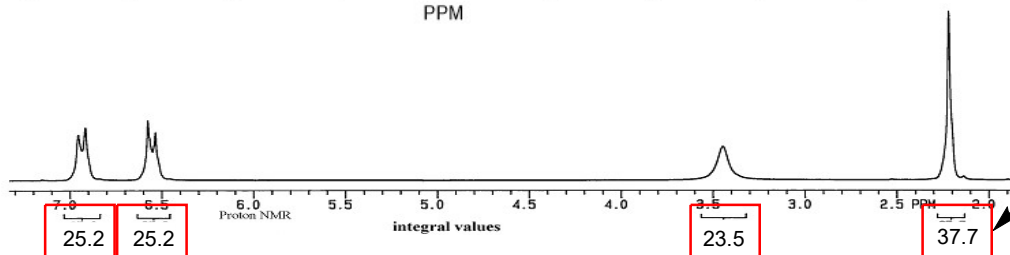
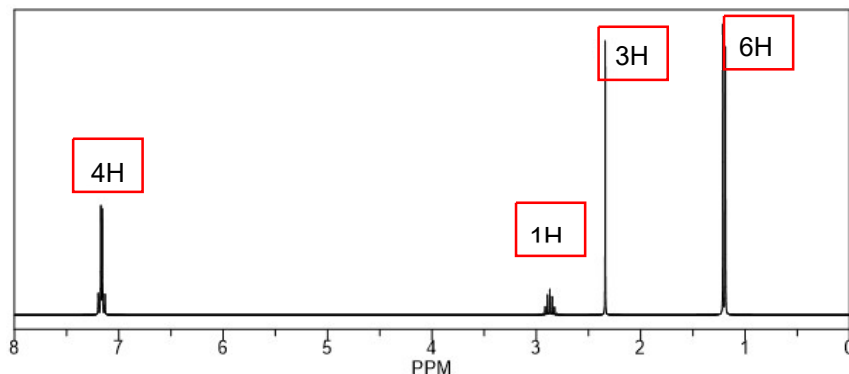
**Information obtained from a <sup>1</sup>H "Proton" NMR spectrum (15.3):**

- 1) **# of signals** indicates the number of different types of hydrogens (chemical equivalence).
- 2) **Integration** or peak area indicates how many hydrogens are in each signal. It is given as a ratio.
- 3) **Chemical shifts** are given as  $\delta$  (delta) values, in ppm (~0-10). The chemical shift indicates the electronic environment of the hydrogens (electron-rich/shielded or electron-poor/deshielded).
- 4) **Splitting patterns** indicate the # of *neighboring* hydrogens. The magnitude of the coupling constants (given as  $J$  values) depend on the spatial relationship (dihedral angle) of the two protons.

**1) Number of NMR Signals: chemical equivalence of protons (or carbons) (15.4)**

How many unique H's (label a, b, c...) and C's (label 1, 2, 3...) are on each compound?

8 H atoms, so 8 signals?

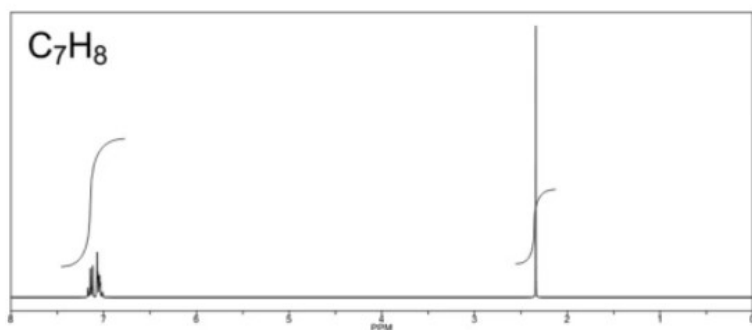
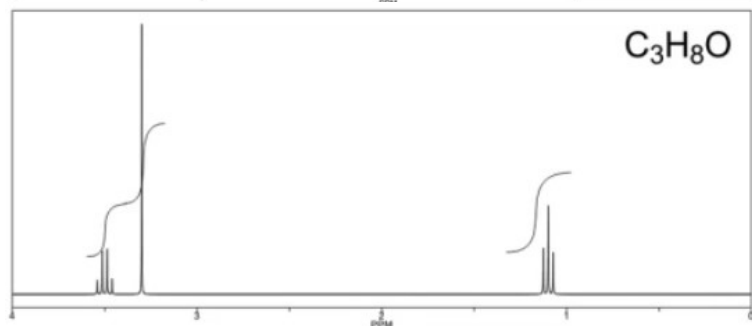
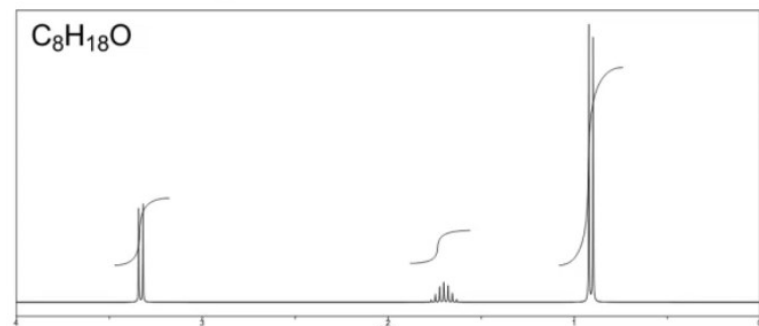
**homotopic** H's: equivalent in NMR (same chemical shift/ $\delta$  value)**enantiotopic** H's: equivalent in NMR (same chemical shift/ $\delta$  value)**diastereotopic** H's: not equivalent in NMR (different  $\delta$  values,  $J$  values, split each other, etc.)**2) Peak Integration: number of protons giving rise to signal (15.6)**numerical value of  
integral trail height  
(see next page)

see SkillBuilders 15.1, 15.2, 15.4

## Using Integral Trails

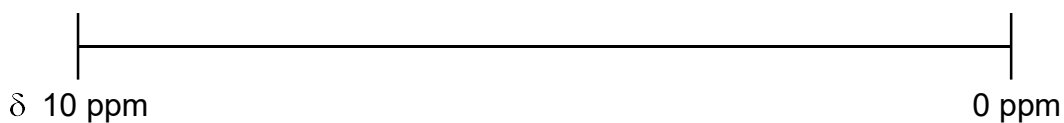
15-4

- Consider height for each peak
- Assume smallest integral = 1H
- Determine # H's for each signal
- Adjust as needed (whole numbers; account for all H's in formula)



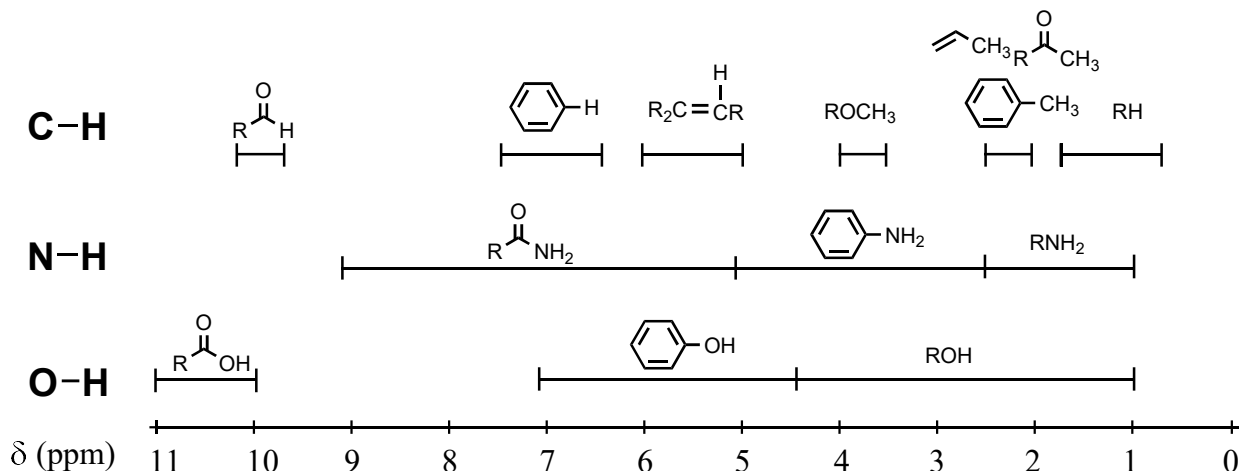
### 3) Chemical Shift ( $\delta$ value): where signal occurs on spectrum (15.5)

- $\delta$  (delta) value given in ppm
- tetramethylsilane (TMS) reference  $\delta = 0$  ppm
- low ppm = "upfield" (shielded protons)
- high ppm = "downfield" (deshielded protons)



Delta values are given in parts per million (ppm) relative to the reference compound tetramethylsilane (TMS) which resonates at  $\delta = 0.0$  ppm.

15-5



### Protons on Carbon

Type of C-H	$\delta$ (ppm)	Description of Proton
R-CH <sub>3</sub>	0.9	alkyl (methyl)
R-CH <sub>2</sub> -R	1.3	alkyl (methylene)
R <sub>3</sub> C-H	1.5-2	alkyl (methine)
	1.8	allylic (C is next to a pi bond)
	2-2.3	$\alpha$ to carbonyl (C is next to C=O)
Ar-CH <sub>3</sub>	2.3	benzylic (C is next to Ph)
RC $\equiv$ C-H	2.5	alkynyl
R <sub>2</sub> N-CH <sub>3</sub>	2-3	$\alpha$ to nitrogen (C is attached to N)
R-CH <sub>2</sub> -X	3-3.5	$\alpha$ to halogen (C attached to Cl/Br/I)
RO-CH <sub>3</sub>	3.8	$\alpha$ to oxygen (C is attached to O)
R-CH <sub>2</sub> -F	4.5	$\alpha$ to fluorine (C is attached to F)
	5-5.3	vinyl (H is attached to alkene C)
Ar-H	7.3	aromatic (H is on phenyl ring)
	9.7	aldehyde (H is on C=O)

Note: aldehyde proton (-CHO) has small coupling with neighboring H's, so it usually appears as a singlet

### Protons on Oxygen/Nitrogen\*

Type of H	$\delta$ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
	10-13	carb. acid
RNH <sub>2</sub>	0.5-5	amine
ArNH <sub>2</sub>	3-5	aniline
	5-9	amide

\*Protons on N or O typically have wide ranges of expected chemical shifts; the actual  $\delta$  value depends on the solvent used, the concentration, temp., etc. Because these protons are acidic and, therefore, *exchangeable*, they may be broad peaks and usually do not couple with neighboring protons (typically they are *broad singlets*). If a protic deuterated solvent is used (e.g., D<sub>2</sub>O or CD<sub>3</sub>OD), then the NH and OH protons will exchange with the deuterium and the peaks will shrink or disappear entirely, since D (<sup>2</sup>H) does not show up in the <sup>1</sup>H NMR spectrum.

R = alkyl group

Ar = aromatic ring, such as phenyl (Ph)

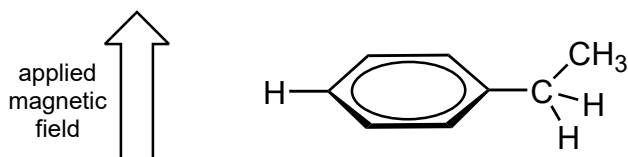
## Effects of pi electrons on chemical shift (anisotropy)

15-6

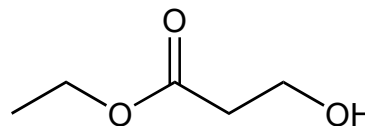
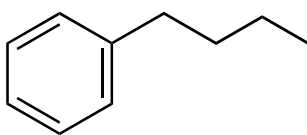
Type of C-H	$\delta$ (ppm)	Description of Proton
	1.8	allylic (C is next to a pi bond)
Ar-CH <sub>3</sub>	2.3	benzylic (C is next to Ph)
	5-5.3	vinyllic (H is attached to alkene C)
Ar-H	7.3	aromatic (H is on phenyl ring)

Why are protons that are on pi bonds or adjacent to pi bonds shifted downfield?

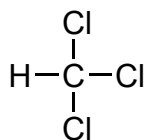
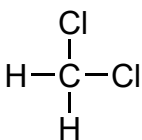
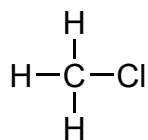
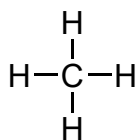
The external magnetic field causes the circulation of pi electrons which generates a ring current. These **anisotropic effects** cause **deshielding**, so protons attached to the benzene ring  $\sim 7$  ppm.



Estimate the **integration** and **chemical shift** for each unique proton:



**Electron-withdrawing effects are additive**



(Why no CCl<sub>4</sub> listed?)

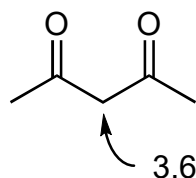
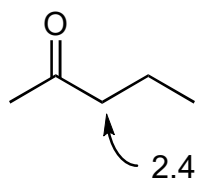
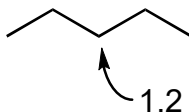
$\delta$  (ppm) 0.9

3.1

5.5

7.3

$\delta$   
(ppm)

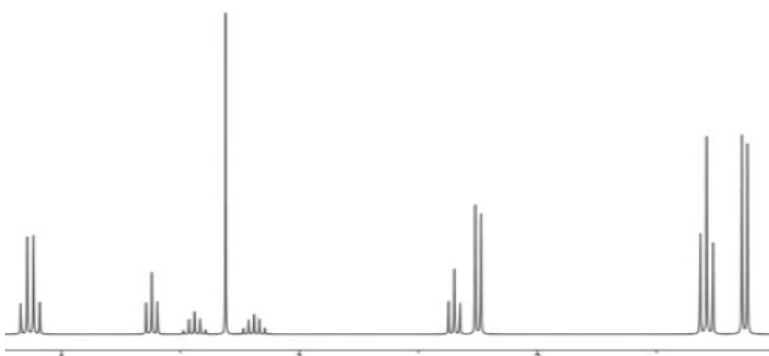


NOTE: You can skip Calculating Chemical Shift & Effects of Resonance

see SkillBuilder 15.3

#### 4) Shape of the Signal: splitting patterns and the n+1 rule (15.7)

15-7

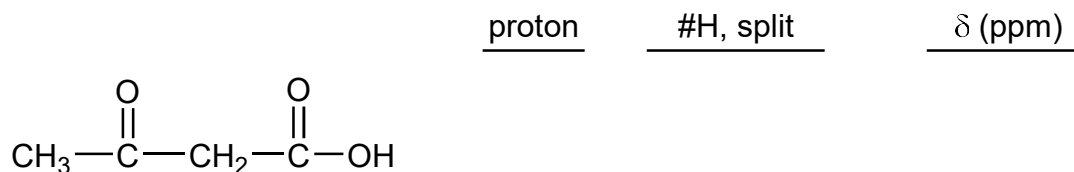
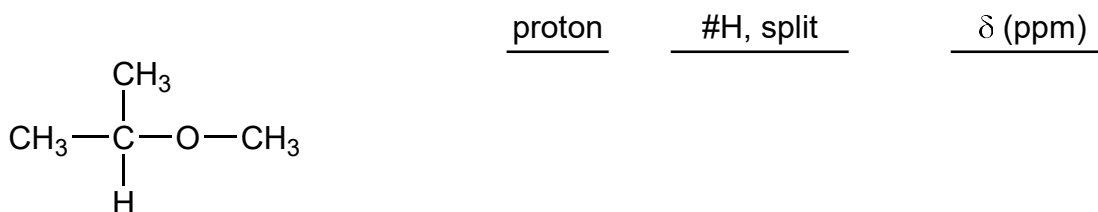


Each proton acts like a tiny magnet, causing a splitting of its neighbors' signals. Neighboring protons are said to be "coupled" and the size of the splitting is described by the coupling constant,  $J$ .  
**Exceptions:**  $\text{OH}$ ,  $\text{NH}$  and aldehyde ( $-\text{CHO}$ ) protons typically do not couple with neighboring protons and typically appear as a singlet (no splitting).

# peaks ( $n+1$ )	# of nonequivalent neighboring H's ( $n$ )	ratio of peaks
1		
2		
3		
4		
5		

see SkillBuilder 15.5

#### Putting it all together: predicting a $^1\text{H}$ NMR spectrum (15.8, 15.9)

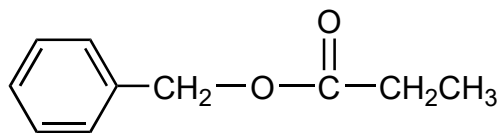


see SkillBuilders 15.6, 15.7

Predicting a  $^1\text{H}$  NMR spectrum (continued)

15-8

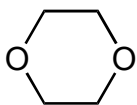
*\*skip calculation of benzylic  $\text{CH}_2$ . We can estimate  $\delta > 3.8 \text{ ppm}$*



proton

#H, split

$\delta$  (ppm)\*

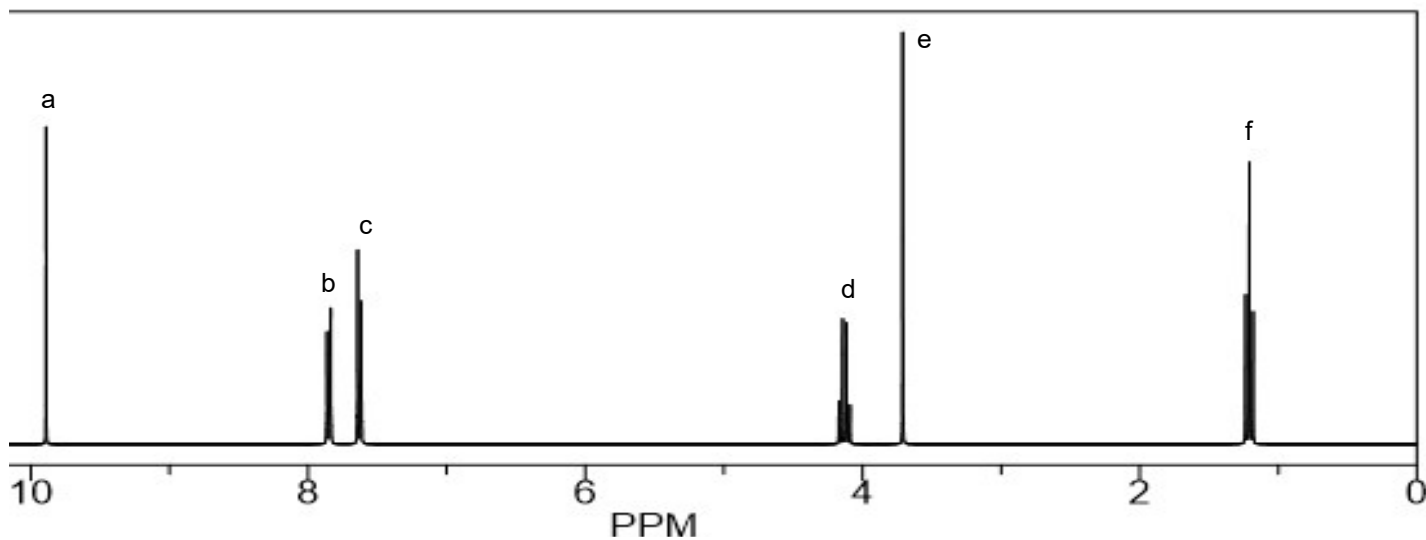
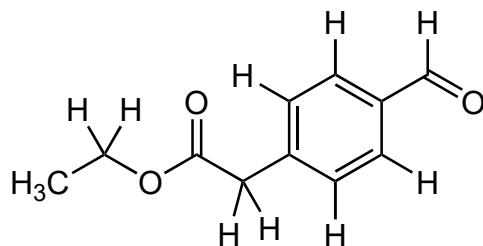


proton

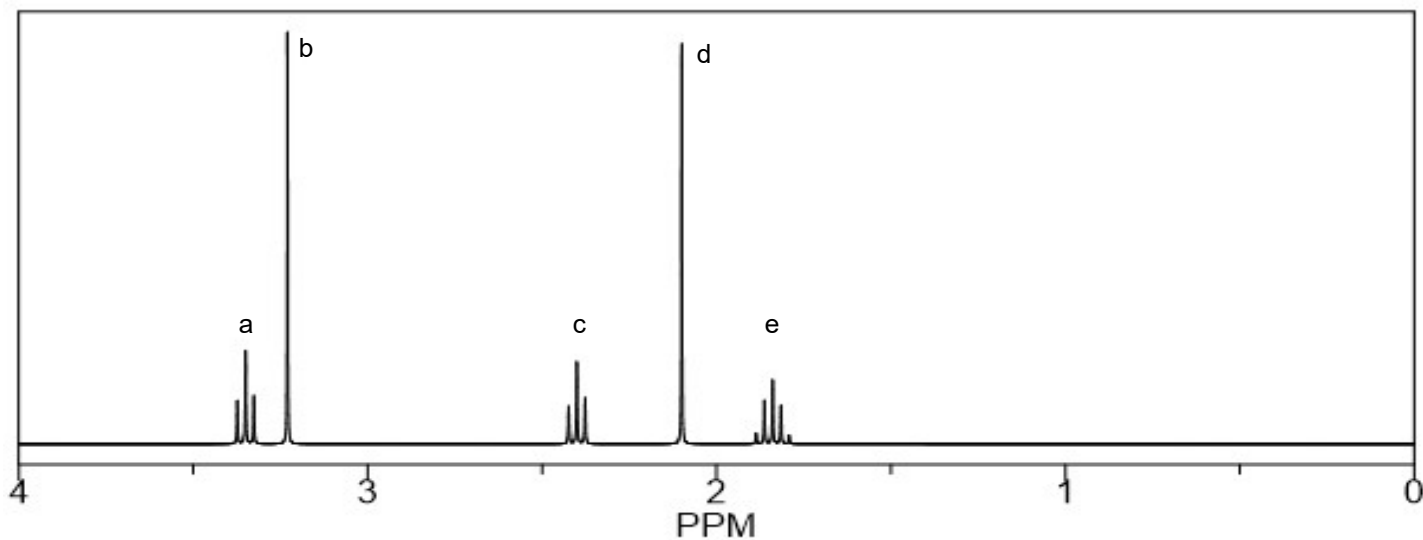
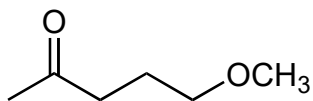
#H, split

$\delta$  (ppm)

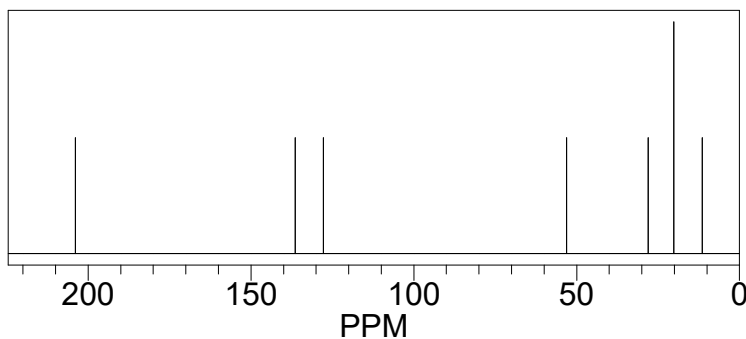
Match the labeled peaks in the NMR with the protons on the given structure.







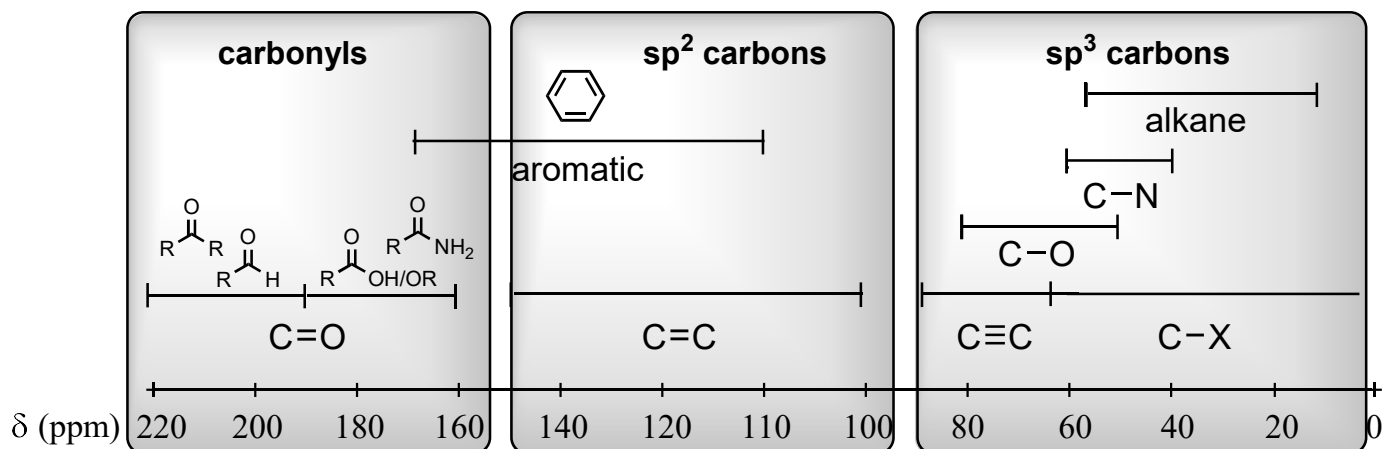
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**Interpreting  $^{13}\text{C}$  NMR Spectra (15.12) Educator lecture: NMR, Part II (1:44:49 - 1:50:16)**

- one signal for each unique carbon type
- chemical shifts ~ 0 to 220 ppm
- signals are typically all singlets ("proton-decoupled" or "broadband decoupled")
- # of hydrogens attached to each carbon can be determined by DEPT experiment (15.13)
- $^{13}\text{C}$  isotope ~1% of carbon atoms, so  $^{13}\text{C}$  NMR requires more sample and/or more scans

While it is possible to acquire a "proton coupled" spectrum that shows the splitting of each carbon by its attached hydrogens (e.g., a  $\text{CH}_3$  would appear as a quartet), such spectra are rarely used and "broadband-decoupled"  $^{13}\text{C}$  spectra are far more common. Proton-decoupled  $^{13}\text{C}$  spectra give a singlet peak for each unique carbon. In order to determine the number of hydrogens on each carbon, a series of experiments with varying pulse sequences, known as DEPT experiments, are employed (see Klein 15.13 and SkillBuilder 15.10, but we will not be covering DEPT in CHM 3140).

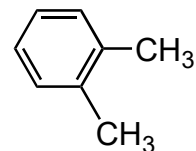
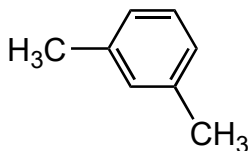
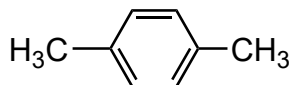
### $^{13}\text{C}$ NMR Chemical Shifts



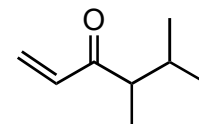
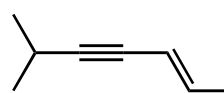
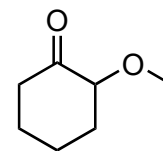
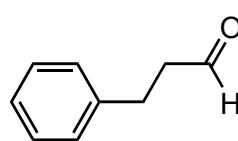
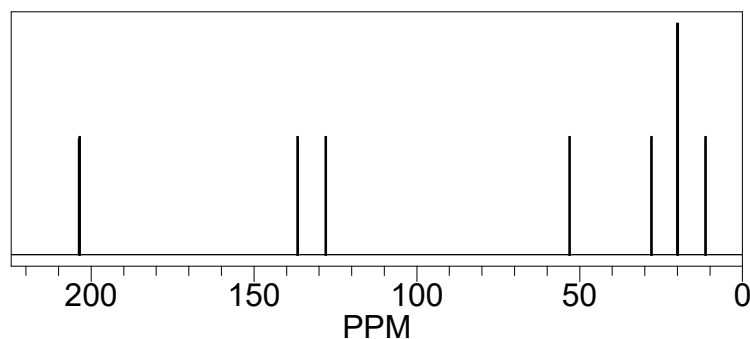
Type of carbon	$\delta$ (ppm)	Description of carbon
$\text{R}-\text{CH}_3$	10-30	primary alkyl (methyl)
$\text{R}-\text{CH}_2-\text{R}$	15-55	secondary alkyl (methylene)
$\text{R}_3\text{C}-\text{H}$ $\begin{matrix} \text{R} \\   \\ \text{R}-\text{C}-\text{R} \\   \\ \text{R} \end{matrix}$	20-60	tertiary or quaternary alkyl
$\text{C}-\text{I}$	0-40	attached to iodine
$\text{C}-\text{Br}$	25-65	attached to bromine
$\text{C}-\text{N}$	40-60	attached to nitrogen
$\text{C}-\text{Cl}$	35-80	attached to chlorine
$\text{C}-\text{O}$	40-80	attached to oxygen
$\text{RC}\equiv\text{CR}$	65-90	alkynyl
$\text{R}_2\text{C}=\text{CR}_2$	100-150	alkenyl
	110-170	aromatic (phenyl ring C)
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$ $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	165-185	$\text{C}=\text{O}$ , carboxylic acid, ester, amide
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	185-220	$\text{C}=\text{O}$ , ketone or aldehyde

How could you use  $^{13}\text{C}$  NMR to distinguish between the three isomers of dimethylbenzene?

15-11

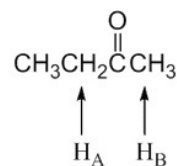
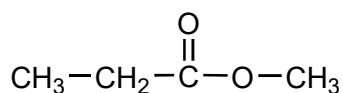
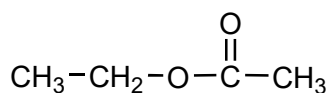


Each of the compounds shown has seven signals in its  $^{13}\text{C}$  NMR spectrum. Which structure matches the spectrum provided? Explain



see SkillBuilder 15.9

Which would be better to distinguish the following compounds,  $^1\text{H}$  or  $^{13}\text{C}$  NMR (or are they equally suitable)? Explain, and describe the peak(s) to look for.



Which of the following gives the multiplicities of the signals for the protons designated  $\text{H}_A$  and  $\text{H}_B$  in the  $^1\text{H}$  NMR spectrum of the compound shown?

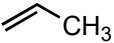
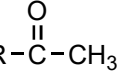
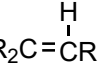

- |    | $\text{H}_A$ | $\text{H}_B$ |
|----|--------------|--------------|
| A) | Singlet      | Singlet      |
| B) | Triplet      | Doublet      |
| C) | Septet       | Singlet      |
| D) | Quartet      | Triplet      |
| E) | Quartet      | Singlet      |

Chapter 15 textbook problems for Exam II:  
SkillBuilders 15.1-15.7 ( $^1\text{H}$  NMR) and 15.9 ( $^{13}\text{C}$ )

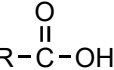
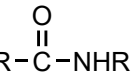
Do the following problems: 1-22, 26, 35-39, 41, 42, 45, 47, 48, 50, 63-71.

Exam III (interpreting  $^1\text{H}$  NMR spectra): SkillBuilder 15.8 and problems: 23-25, 57-59, 64.

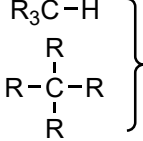

**<sup>1</sup>H NMR: Protons on Carbon**

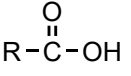
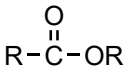
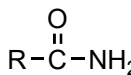
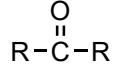
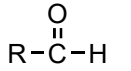
Type of C-H	δ (ppm)	Description
R-CH <sub>3</sub>	0.9	alkyl (methyl)
R-CH <sub>2</sub> -R	1.3	alkyl (methylene)
R <sub>3</sub> C-H	1.5-2	alkyl (methine)
	1.8	allylic
	2-2.3	α to carbonyl
Ar-CH <sub>3</sub>	2.3	benzylic
RC≡C-H	2.5	alkynyl
R <sub>2</sub> N-CH <sub>3</sub>	2-3	α to nitrogen
R-CH <sub>2</sub> -X	3-3.5	α to halogen
RO-CH <sub>3</sub>	3.8	α to oxygen
R-CH <sub>2</sub> -F	4.5	α to fluorine
	5-5.3	vinylic
Ar-H	7.3	aromatic
	9.7	aldehyde

**<sup>1</sup>H NMR: Protons on Oxygen/Nitrogen**

Type of H	δ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
	10-13	carb. acid
RNH <sub>2</sub>	0.5-5	amine
ArNH <sub>2</sub>	3-5	aniline
	5-9	amide

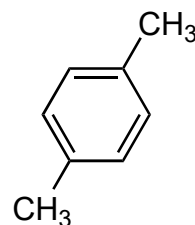
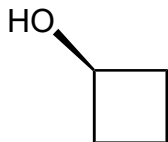
**<sup>13</sup>C NMR: Carbons**

Type of carbon	δ (ppm)	Description
R-CH <sub>3</sub>	10-30	methyl
R-CH <sub>2</sub> -R	15-55	methylene
	20-60	methine or quaternary
C-I	0-40	
C-Br	25-65	
C-N	40-60	
C-Cl	35-80	
C-O	40-80	
RC≡CR	65-90	alkynyl
R <sub>2</sub> C=CR <sub>2</sub>	100-150	alkenyl
	110-170	aromatic

	165-185	C=O, carboxylic acid, ester, amide
		
		
	185-220	C=O, ketone or aldehyde
		

R = alkyl group  
 Ar = aromatic ring, such as phenyl (Ph)

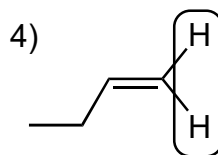
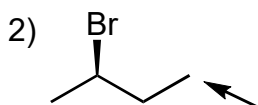
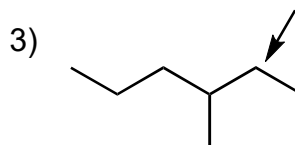
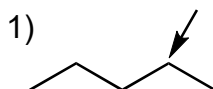
How many signals are expected for each compound? Label each unique proton type (a/b/c).



Draw the dichloropentane isomer that has exactly two <sup>1</sup>H NMR signals.

Describe the relationship of the indicated protons:

- a) enantiotopic (one signal in NMR)
- b) enantiotopic (separate signals in NMR)
- c) diastereotopic (one signal in NMR)
- d) diastereotopic (separate signals in NMR)
- e) homotopic (one signal in NMR)

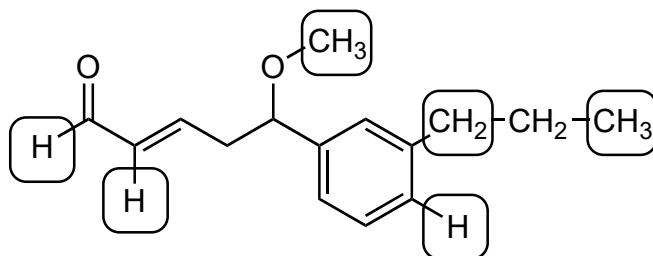


Match each highlighted proton with its approximate chemical shift:

1, 2, 4, 5, 7, 10 ppm

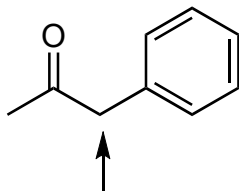
Also, predict the splitting pattern for each highlighted proton.

*Note: aldehyde protons typically do not couple with neighboring protons.*



What is the expected splitting pattern for the indicated protons?

Do you predict the chemical shift to be closer to  $\delta = 2.5$  ppm or  $\delta = 3.5$  ppm? Explain



There are two isomeric carboxylic acids with the formula C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>Cl. Provide a structure that matches each set of <sup>1</sup>H NMR data.

**Isomer A**

1.7 ppm 3H d  
4.4 ppm 1H q  
12.4 ppm 1H s

**Isomer B**

2.9 ppm 2H t  
3.8 ppm 2H t  
11.7 ppm 1H s

Predict the number of <sup>13</sup>C NMR signals (label a/b/c) and the approximate chemical shifts for each.

