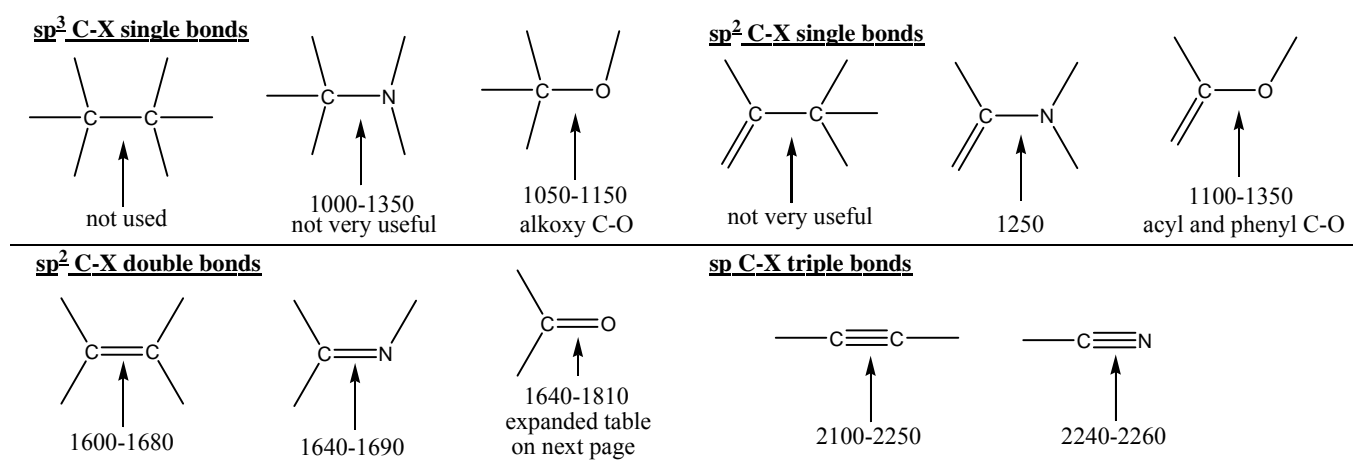
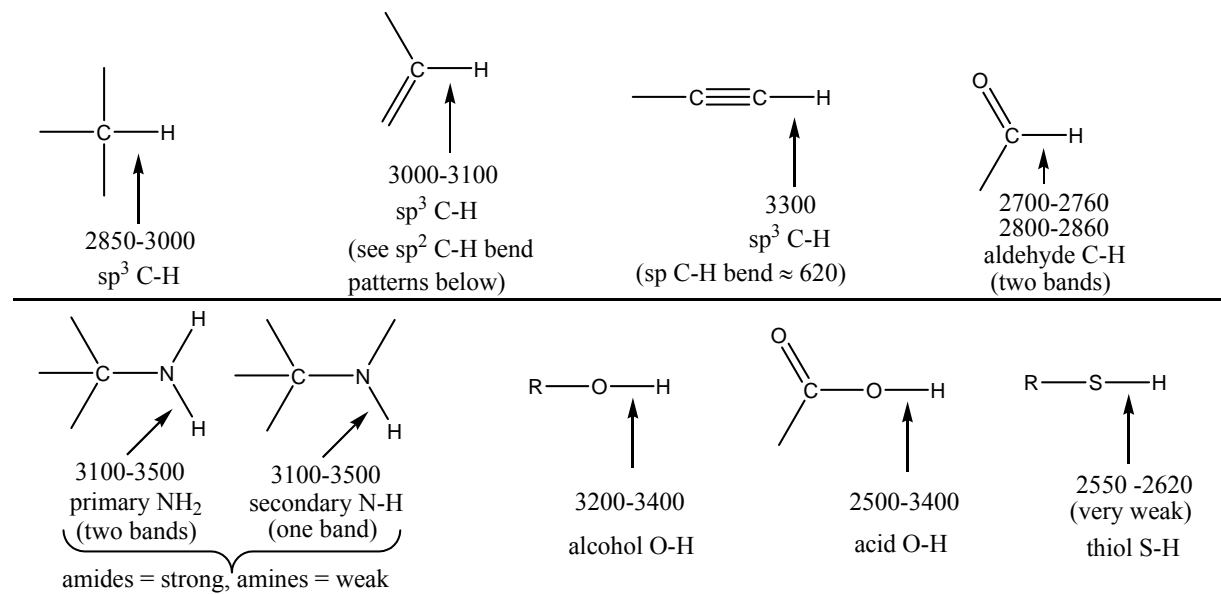


Infrared Tables (short summary of common absorption frequencies)

The values given in the tables that follow are typical values. Specific bands may fall over a range of wavenumbers, cm^{-1} . Specific substituents may cause variations in absorption frequencies. Absorption intensities may be stronger or weaker than expected, often depending on dipole moments. Additional bands may confuse the interpretation. In very symmetrical compounds there may be fewer than the expected number of absorption bands (it is even possible that all bands of a functional group may disappear, i.e. a symmetrically substituted alkyne!). Infrared spectra are generally informative about what functional groups are present, but not always. The ^1H and ^{13}C NMR's are often just as informative about functional groups, and sometimes even more so in this regard. Information obtained from one spectroscopic technique should be verified or expanded by consulting the other spectroscopic techniques.

IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1} **Bonds to Carbon (stretching wave numbers)**

Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands (sometimes none).

Bonds to Hydrogen (stretching wave numbers)

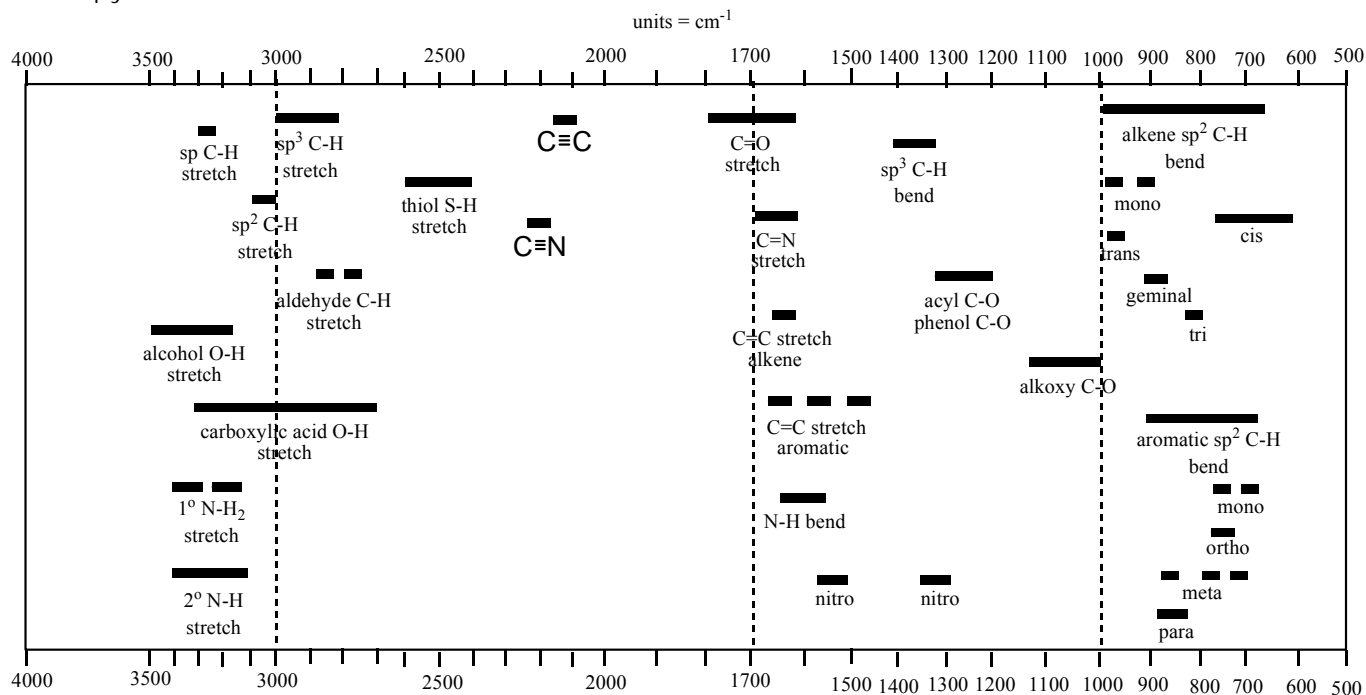
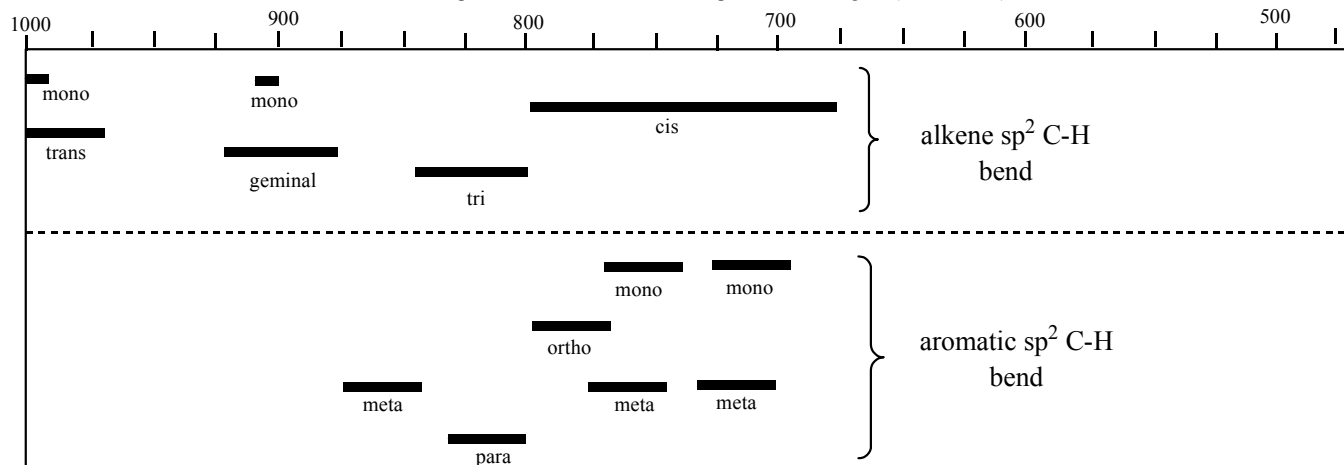
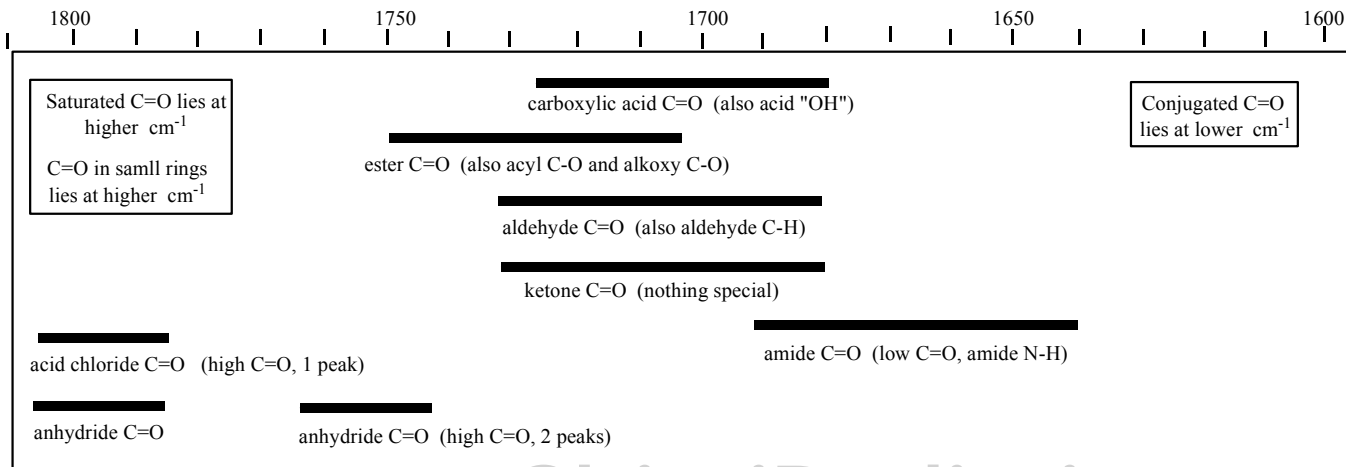
Carbonyl Highlights (stretching wave numbers)

Aldehydes	Ketones	Esters	Acids
saturated = 1725 conjugated = 1690 aromatic = 1700	saturated = 1715 conjugated = 1680 aromatic = 1690 6 atom ring = 1715 5 atom ring = 1745 4 atom ring = 1780 3 atom ring = 1850	saturated = 1735 conjugated = 1720 aromatic = 1720 6 atom ring = 1735 5 atom ring = 1775 4 atom ring = 1840	saturated = 1715 conjugated = 1690 aromatic = 1690
Amides	Anhydrides	Acid Chlorides	nitro
saturated = 1650 conjugated = 1660 aromatic = 1660 6 atom ring = 1670 5 atom ring = 1700 4 atom ring = 1745 3 atom ring = 1850	saturated = 1760, 1820 conjugated = 1725, 1785 aromatic = 1725, 1785 6 atom ring = 1750, 1800 5 atom ring = 1785, 1865	saturated = 1800 conjugated = 1770 aromatic = 1770	asymmetric = 1500-1600 symmetric = 1300-1390
	Very often there is a very weak C=O overtone at approximately $2 \times \bar{\nu}$ ($\approx 3400 \text{ cm}^{-1}$). Sometimes this is mistaken for an OH or NH peak.		

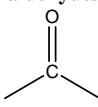
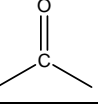
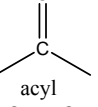
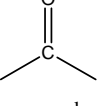
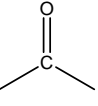
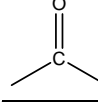
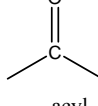
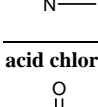
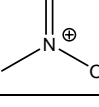
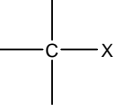
sp² C-H bend patterns for alkenes**sp² C-H bend patterns for aromatics**

alkene substitution pattern	descriptive alkene term	absorption frequencies (cm ⁻¹) due to sp ² CH bend	aromatic substitution pattern	descriptive aromatic term	absorption frequencies (cm ⁻¹) due to sp ² CH bend
	monosubstituted alkene	985-1000 900-920		monosubstituted aromatic	690-710 730-770
	cis disubstituted alkene	675-730 (broad)		ortho disubstituted aromatic	735-770
	trans disubstituted alkene	960-990		meta disubstituted aromatic	680-725 750-810 880-900 (sometimes)
	geminal disubstituted alkene	880-900		para disubstituted aromatic	790-840
	trisubstituted alkene	790-840			
	tetrasubstituted alkene	none			

Aromatic compounds have characteristic weak overtone bands that show up between 1650-2000 cm⁻¹. Some books provide pictures for comparison (not here). A strong C=O peak will cover up most of this region.

expansion of alkene & aromatic sp^2 C-H bend region (units = cm^{-1})expansion of carbonyl (C=O) stretch region (units = cm^{-1})

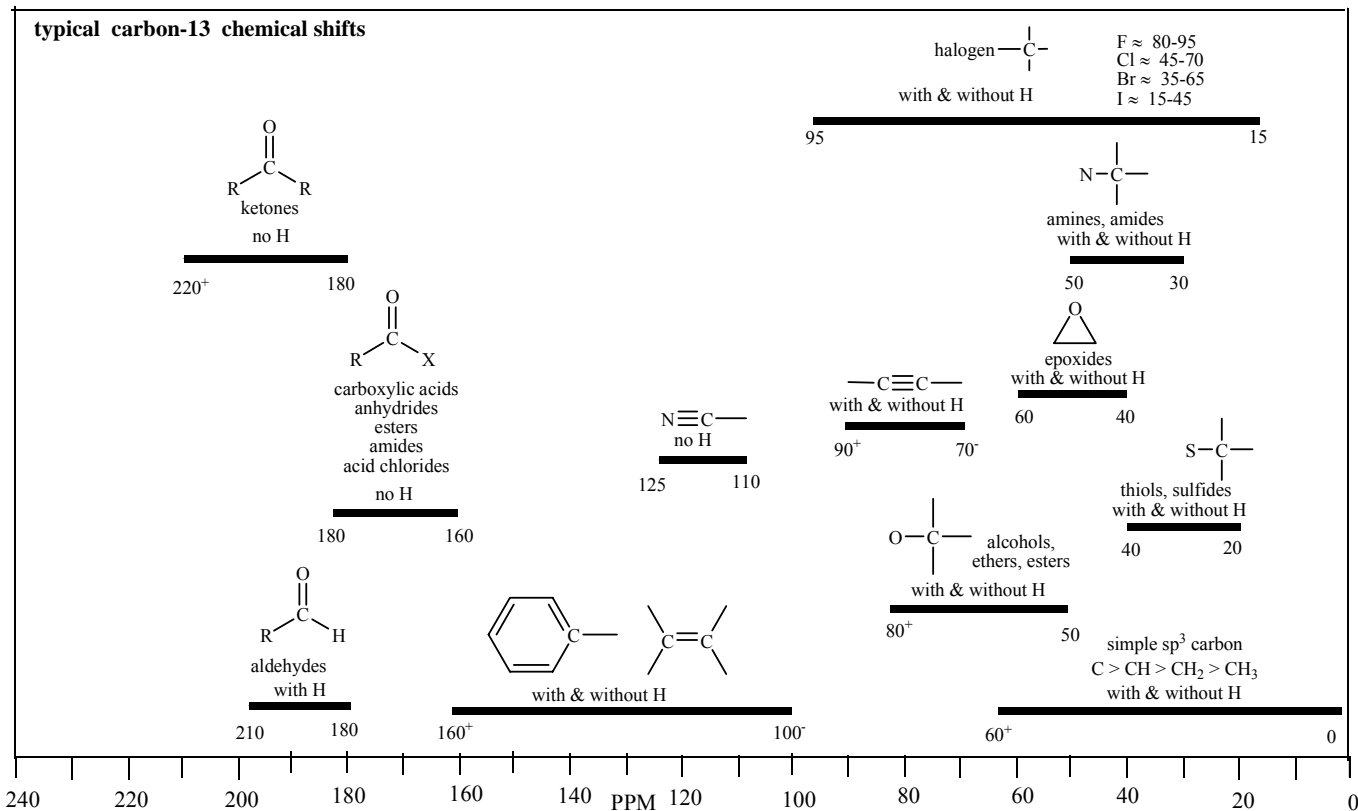
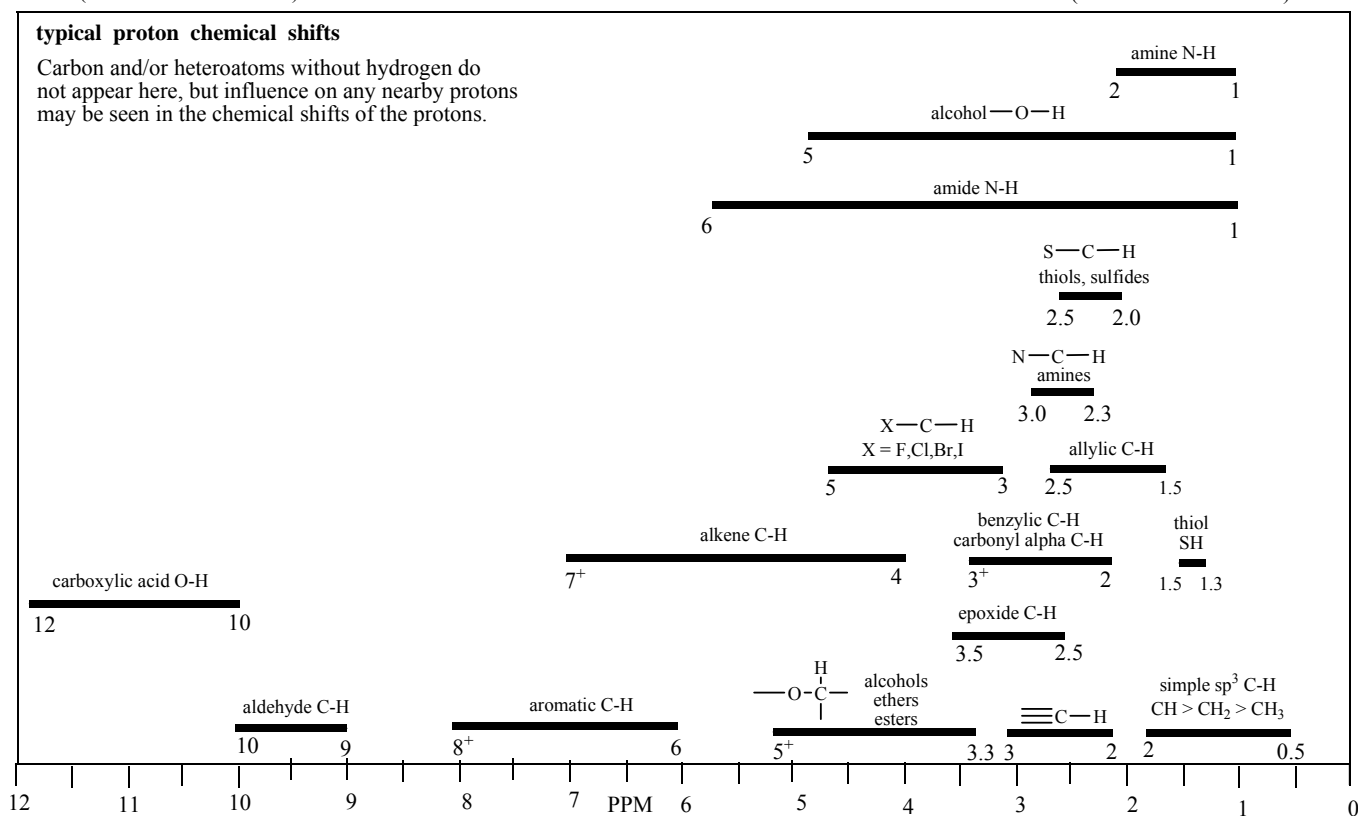
IR Flowchart to determine functional groups in a compound (all values in cm^{-1}).**IR Spectrum**

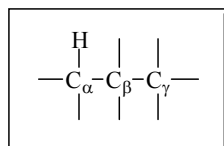
IR Spectrum		has C=O band (1650-1800 cm^{-1}) very strong	does not have C=O band						
<p>aldehydes</p>  <p>1725-1740 (saturated) 1660-1700 (unsaturated)</p> <p>2860-2800 ← sometimes lost 2760-2700 in sp^3 CH peaks (both weak)</p> <p>aldehyde C-H</p>		<p>alkanes</p> <table border="1"> <tr><td>sp^3 C-H stretch</td><td>2850-3000</td></tr> <tr><td>sp^3 C-H bend</td><td>1460 & 1380</td></tr> <tr><td>C—C</td><td>not useful</td></tr> </table>		sp^3 C-H stretch	2850-3000	sp^3 C-H bend	1460 & 1380	C—C	not useful
sp^3 C-H stretch	2850-3000								
sp^3 C-H bend	1460 & 1380								
C—C	not useful								
<p>ketones</p>  <p>1710-1720 (saturated) 1680-1700 (unsaturated) 1715-1810 (rings: higher in small rings)</p>		<p>nitriles</p> <p>$\text{C}\equiv\text{N}$</p> <p>≈ 2250 sharp, stronger than alkynes, a little lower when conjugated</p>							
<p>esters - rule of 3</p>  <p>1735-1750 (saturated) 1715-1740 (unsaturated) 1735-1820 (higher in small rings)</p> <p>acyl C—O 1150-1350 (acyl, strong)</p> <p>alkoxy C—O (1000-1150, alkoxy, medium)</p>		<p>alkynes</p> <p>$\text{C}\equiv\text{C}$ 2150 (variable intensity)</p> <p>not present or weak when symmetrically substituted, a little lower when conjugated</p> <table border="1"> <tr><td>sp C-H stretch</td><td>3300 sharp, strong</td></tr> <tr><td>sp C-H bend</td><td>620</td></tr> </table>		sp C-H stretch	3300 sharp, strong	sp C-H bend	620		
sp C-H stretch	3300 sharp, strong								
sp C-H bend	620								
<p>acids</p>  <p>1700-1730 (saturated) 1715-1740 (unsaturated) 1680-1700 (higher in small rings)</p> <p>acyl C—O 1210-1320 (acyl, strong)</p> <p>acid O—H 2400-3400, very broad (overlaps C-H stretch)</p>		<p>All IR values are approximate and have a range of possibilities depending on the molecular environment in which the functional group resides. Resonance often modifies a peak's position because of electron delocalization (C=O lower, acyl C-O higher, etc.). IR peaks are not 100% reliable. Peaks tend to be stronger (more intense) when there is a large dipole associated with a vibration in the functional group and weaker in less polar bonds (to the point of disappearing in some completely symmetrical bonds).</p>							
<p>amides</p>  <p>1630-1680 (saturated) 1745 (in 4 atom ring)</p> <p>1° 3350 & 3180, two bands for 1° amides, one band for 2° amides, stronger than in amines, extra overtone sometimes at 3100</p> <p>2°</p> <p>N—H N-H bend, 1550-1640, stronger in amides than amines</p>		<p>Alkene sp^2 C-H bending patterns</p> <p>monosubstituted (985-1000, 900-920) geminal disubstituted (960-990) cis disubstituted (675-730) trans disubstituted (880-900) trisubstituted (790-840) tetrasubstituted (none, no sp^2 C-H)</p>							
<p>acid chlorides</p>  <p>1800 (saturated) 1770 (unsaturated)</p> <p>Inductive pull of Cl increases the electron density between C and O.</p>		<p>Aromatic sp^2 C-H bending patterns</p> <p>monosubstituted (730-770, 690-710) ortho disubstituted (735-770) meta disubstituted (880-900, sometimes, 750-810, 680-725) para disubstituted (790-840)</p>							
<p>anhydrides</p>  <p>1760 & 1820 (saturated) 1725-1785 (unsaturated) two strong bands</p> <p>acyl C—O 1150-1350 (acyl, strong)</p>		<p>There are also weak overtone bands between 1660 and 2000, but are not shown here. You can consult pictures of typical patterns in other reference books. If there is a strong C=O band, they may be partially covered up.</p>							
<p>ethers</p>  <p>alkoxy C—O 1120 (aliphatic) 1040 & 1250 (aromatic)</p>		<p>nitro compounds</p>  <p>1500-1600, asymmetric (strong) 1300-1390, symmetric (medium)</p>							
<p>carbon-halogen bonds</p>  <p>usually not very useful</p> <p>X = F, Cl, Br, I</p>									

deshielding side = less electron rich
(inductive & resonance)

Typical ^1H and ^{13}C NMR chemical shift values.

shielding side = more electron rich
(inductive & resonance)



Calculation of chemical shifts for protons at sp^3 carbons

Estimation of sp^3 C-H chemical shifts with multiple substituent parameters for protons within 3 C's of consideration.

α = directly attached substituent, use these values when the hydrogen and substituent are attached to the same carbon

β = once removed substituent, use these values when the hydrogen and substituent are on adjacent (vicinal) carbons

γ = twice removed substituent, use these values when the hydrogen and substituent have a 1,3 substitution pattern

X = substituent	α	β	γ
R- (alkyl)	0.0	0.0	0.0
R ₂ C=CR- (alkenyl)	0.8	0.2	0.1
RCC- (alkynyl)	0.9	0.3	0.1
Ar- (aromatic)	1.4	0.4	0.1
F- (fluoro)	3.2	0.5	0.2
Cl- (chloro)	2.2	0.5	0.2
Br- (bromo)	2.1	0.7	0.2
I- (iodo)	2.0	0.9	0.1
HO- (alcohol)	2.3	0.3	0.1
RO- (ether)	2.1	0.3	0.1
epoxide	1.5	0.4	0.1
R ₂ C=CRO- (alkenyl ether)	2.5	0.4	0.2
ArO- (aromatic ether)	2.8	0.5	0.3
RCO ₂ - (ester, oxygen side)	2.8	0.5	0.1
ArCO ₂ - (aromatic ester, oxygen side)	3.1	0.5	0.2
ArSO ₃ - (aromatic sulfonate, oxygen)	2.8	0.4	0.0
H ₂ N- (amine nitrogen)	1.5	0.2	0.1
RCONH- (amide nitrogen)	2.1	0.3	0.1
O ₂ N- (nitro)	3.2	0.8	0.1
HS- (thiol, sulfur)	1.3	0.4	0.1
RS- (sulfide, sulfur)	1.3	0.4	0.1
OHC- (aldehyde)	1.1	0.4	0.1
RCO- (ketone)	1.2	0.3	0.0
ArCO- (aromatic ketone)	1.7	0.3	0.1
HO ₂ C- (carboxylic acid)	1.1	0.3	0.1
RO ₂ C- (ester, carbon side)	1.1	0.3	0.1
H ₂ NOC- (amide, carbon side)	1.0	0.3	0.1
ClOC- (acid chloride)	1.8	0.4	0.1
NC- (nitrile)	1.1	0.4	0.2
RSO- (sulfoxide)	1.6	0.5	0.3
RSO ₂ - (sulfone)	1.8	0.5	0.3

Starting value and equations for CH₃'s

$$\delta \text{CH}_3 = 0.9 + \alpha \quad \text{H}_3\text{C}-\alpha$$

$$\delta \text{CH}_3 = 0.9 + \sum(\beta + \gamma) \quad \text{H}_3\text{C}-\text{C}_\beta-\text{C}_\gamma-$$

Σ is the summation symbol for all substituents considered

Starting value and equation for CH₂'s

In a similar manner we can calculate chemical shifts for methylenes (CH₂) using the following formula

$$\delta \text{CH}_2 = 1.2 + \sum(\alpha + \beta + \gamma) \quad \text{H}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma-$$

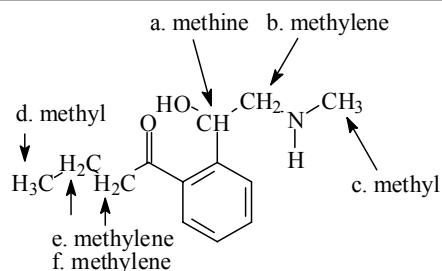
Σ is the summation symbol for all substituents considered

Starting value and equation for CH's

In a similar manner we can calculate chemical shifts for methines (CH) using the following formula

$$\delta \text{CH} = 1.5 + \sum(\alpha + \beta + \gamma) \quad \text{H}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma-$$

Σ is the summation symbol for all substituents considered



$$\begin{aligned} \text{a. methine} &= 1.5 + (1.4)_\alpha + (2.3)_\alpha + (0.2)_\beta = 5.4 \text{ ppm} \\ \text{actual} &= 5.2 \end{aligned}$$

$$\begin{aligned} \text{b. methylene} &= 1.2 + (1.5)_\alpha + (0.4)_\beta + (0.3)_\beta = 3.4 \text{ ppm} \\ \text{actual} &= 3.0 \text{ and } 3.2 \end{aligned}$$

$$\begin{aligned} \text{c. methyl} &= 0.9 + (1.5)_\alpha = 2.4 \text{ ppm} \\ \text{actual} &= 2.6 \end{aligned}$$

$$\begin{aligned} \text{d. methyl} &= 0.9 + (0.1)_\alpha = 1.0 \text{ ppm} \\ \text{actual} &= 1.0 \end{aligned}$$

$$\begin{aligned} \text{e. methylene} &= 1.2 + (0.3)_\alpha = 1.5 \text{ ppm} \\ \text{actual} &= 1.7 \end{aligned}$$

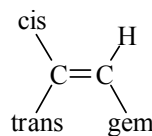
$$\begin{aligned} \text{f. methylene} &= 1.2 + (1.7)_\alpha = 2.9 \text{ ppm} \\ \text{actual} &= 2.9 \end{aligned}$$

Calculations are generally close to actual chemical shifts for a single substituent, but are less reliable as the number of substituent factors goes up. Multiple substituent factors tend to overestimate an actual chemical shift.

Estimated chemical shifts for protons at alkene sp^2 carbons

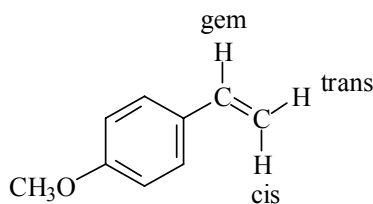
Substituent	α_{geminal}	α_{cis}	α_{trans}
H- Hydrogen	0.0	0.0	0.0
R- Alkyl	0.5	-0.2	-0.3
$C_6H_5CH_2$ - Benzyl	0.7	-0.2	-0.2
X- CH_2 - Halomethyl	0.7	0.1	0.0
(H)/ $ROCH_2$ - alkoxymethyl	0.6	0.0	0.0
(H) $_2$ / R_2NCH_2 - aminomethyl	0.6	-0.1	-0.1
$RCOCH_2$ - α -keto	0.7	-0.1	-0.1
$NCCH_2$ - α -cyano	0.7	-0.1	-0.1
$R_2C=CR$ - Alkenyl	1.2	0.0	0.0
C_6H_5 - Phenyl	1.4	0.4	-0.1
F- Fluoro	1.5	-0.4	-1.0
Cl- Chloro	1.1	0.2	0.1
Br- Bromo	1.1	0.4	0.6
I- Iodo	1.1	0.8	0.9
RO - alkoxy (ether)	1.2	-1.1	-1.2
RCO_2 - O-ester	2.1	-0.4	-0.6
(H) $_2$ / R_2N - N-amino	0.8	-1.3	-1.2
$RCONH$ - N-amide	2.1	-0.6	-0.7
O_2N - Nitro	1.9	1.3	0.6
RS - Thiol	1.1	-0.3	-0.1
OHC - Aldehyde	1.0	1.0	1.2
ROC - Ketone	1.1	0.9	0.7
HO_2C - C-acid	0.8	1.0	0.3
RO_2C - C-ester	0.8	1.0	0.5
H_2NOC - C-amide	0.4	1.0	0.5
NC - Nitrile	0.3	0.8	0.6

Substitution relative to calculated "H"



$$\delta(\text{ppm}) = 5.2 + \alpha_{\text{gem}} + \alpha_{\text{cis}} + \alpha_{\text{trans}}$$

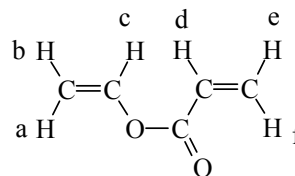
Example Calculation



$$\begin{aligned} \delta_{\text{gem}} &= 5.2 + 1.4 = 6.6 \\ \text{actual} &= 6.6 \end{aligned}$$

$$\begin{aligned} \delta_{\text{trans}} &= 5.2 - 0.1 = 5.1 \\ \text{actual} &= 5.1 \end{aligned}$$

$$\begin{aligned} \delta_{\text{cis}} &= 5.2 + 0.4 = 5.7 \\ \text{actual} &= 5.6 \end{aligned}$$



$$\begin{aligned} \delta_a &= 5.2 + (-0.4) = 4.8 \\ \text{actual} &= 4.9 \text{ (} J = 14, 1.6 \text{ Hz)} \end{aligned}$$

$$\begin{aligned} \delta_b &= 5.2 + (-0.6) = 4.6 \\ \text{actual} &= 4.6 \text{ (} J = 6, 1.6 \text{ Hz)} \end{aligned}$$

$$\begin{aligned} \delta_c &= 5.2 + 2.1 = 7.3 \\ \text{actual} &= 7.4 \text{ (} J = 14, 6 \text{ Hz)} \end{aligned}$$

$$\begin{aligned} \delta_d &= 5.2 + 0.8 = 6.0 \\ \text{actual} &= 6.2 \text{ (} J = 18, 11 \text{ Hz)} \end{aligned}$$

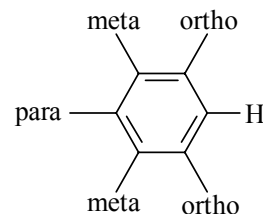
$$\begin{aligned} \delta_e &= 5.2 + 0.5 = 5.7 \\ \text{actual} &= 5.8 \text{ (} J = 11, 1.4 \text{ Hz)} \end{aligned}$$

$$\begin{aligned} \delta_f &= 5.2 + 1.0 = 6.2 \\ \text{actual} &= 6.4 \text{ (} J = 18, 1.4 \text{ Hz)} \end{aligned}$$

Estimated chemical shifts for protons at aromatic sp^2 carbons

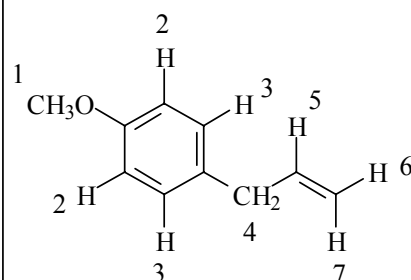
Substituent	α ortho	α meta	α para
H- Hydrogen	0.0	0.0	0.0
CH ₃ - Methyl	-0.2	-0.1	-0.2
ClCH ₂ - Chloromethyl	0.0	0.0	0.0
Cl ₃ C- Halomethyl	0.6	0.1	0.1
HOCH ₂ - Hydroxymethyl	-0.1	-0.1	-0.1
R ₂ C=CR- Alkenyl	0.1	0.0	-0.1
C ₆ H ₅ - Phenyl	1.4	0.4	-0.1
F- Fluoro	-0.3	0.0	-0.2
Cl- Chloro	0.0	0.0	-0.1
Br- Bromo	0.2	-0.1	0.0
I- Iodo	0.4	-0.2	0.9
HO- Hydroxy	-0.6	-0.1	-0.5
RO- Alkoxy	-0.5	-0.1	-0.4
RCO ₂ - O-ester	-0.3	0.0	-0.1
(H) ₂ /R ₂ N- N-amino	-0.8	-0.2	-0.7
RCONH- N-amide	0.1	-0.1	-0.3
O ₂ N- Nitro	1.0	0.3	0.4
RS- thiol/sulfide	-0.1	-0.1	-0.2
OHC- Aldehyde	0.6	0.2	0.3
ROC- Ketone	0.6	0.1	0.2
HO ₂ C- C-acid	0.9	0.2	0.3
RO ₂ C- C-ester	0.7	0.1	0.2
H ₂ NOC- C-amide	0.6	0.1	0.2
NC- Nitrile	0.4	0.2	0.3

Substitution relative to calculated "H"



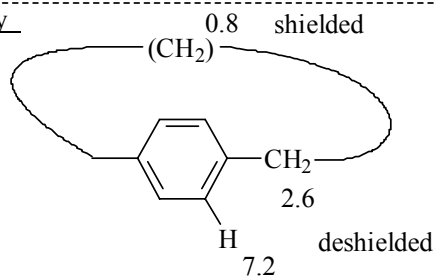
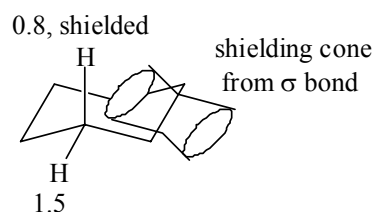
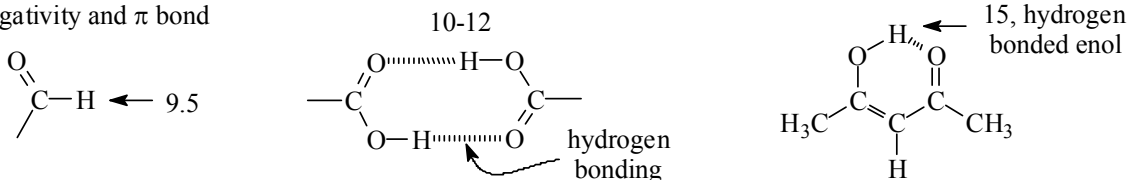
$$\delta(\text{ppm}) = 7.3 + \alpha_{\text{ortho}} + \alpha_{\text{meta}} + \alpha_{\text{para}}$$

Example Calculation

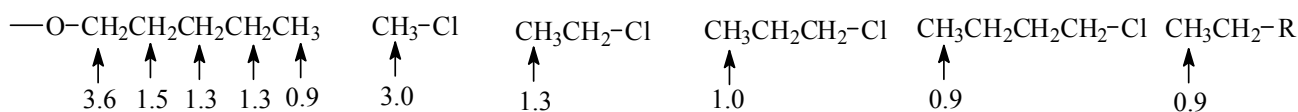


- $\delta(\text{CH}_3) = 0.9 + 2.8 = 3.7$
actual = 3.8
- $\delta(2) = 7.3 + (-0.5)_{\text{ortho}} + (-0.1)_{\text{para}} = 6.7$
actual = 6.8
- $\delta(3) = 7.3 + (-0.2)_{\text{ortho}} + (-0.4)_{\text{para}} = 6.7$
actual = 7.1
- $\delta(\text{CH}_2) = 1.2 + (0.8)\alpha + (1.4)\alpha = 3.4$
actual = 3.3
- $\delta(5) = 5.2 + (0.7)_{\text{gem}} = 5.9$
actual = 5.9
- $\delta(6) = 5.2 + (-0.2)_{\text{trans}} = 5.0$
actual = 5.1
- $\delta(7) = 5.2 + (-0.2)_{\text{cis}} = 5.0$
actual = 5.1

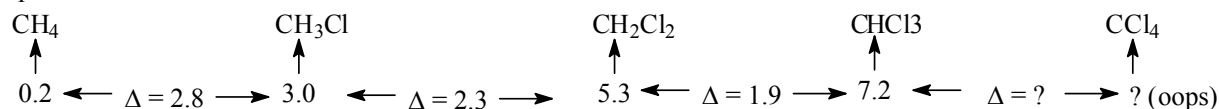
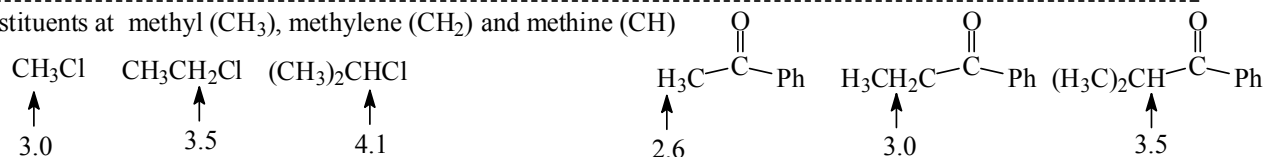
Real Examples of Combination Effects on Chemical Shifts

 π bond anisotropy σ bond example tooelectronegativity and π bond

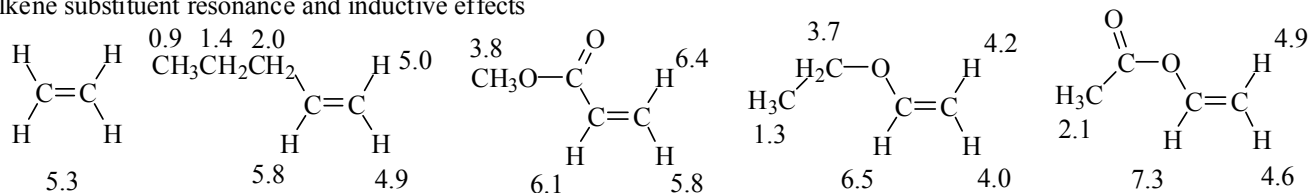
electronegative substituent and distance from protons



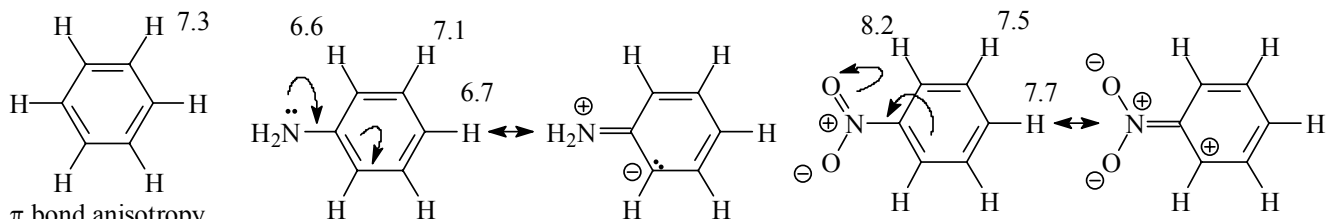
multiple substituents

substituents at methyl (CH₃), methylene (CH₂) and methine (CH)

alkene substituent resonance and inductive effects



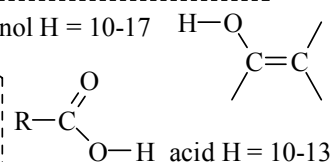
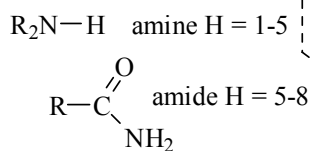
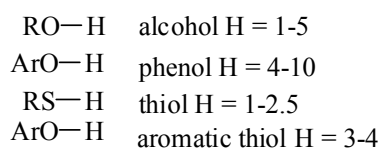
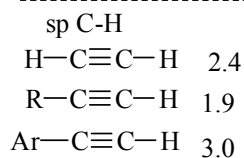
aromatic resonance and inductive effects



π bond anisotropy produces deshielding effect on aromatic protons.

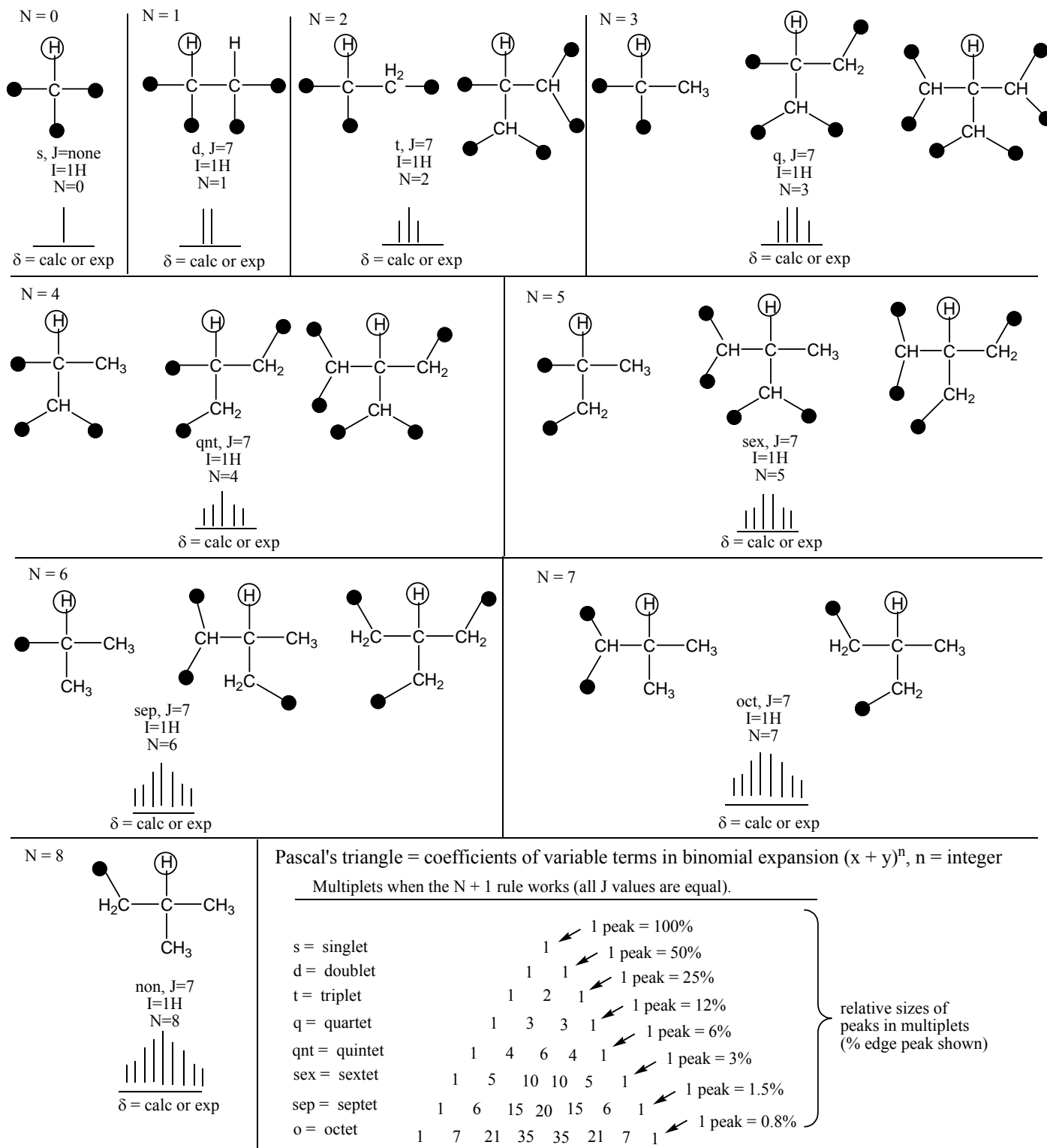
Extra electron density via resonance produces shielding effect on aromatic protons, especially at ortho/para positions.

Withdrawal of electron density via resonance produces deshielding effect on aromatic protons, especially at ortho/para positions.




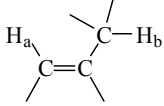
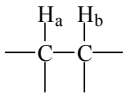
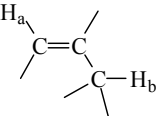
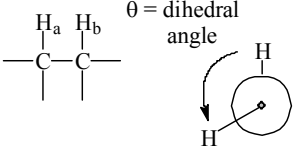
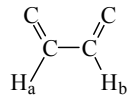
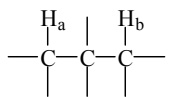
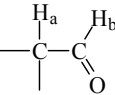
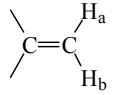
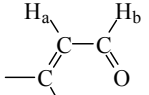
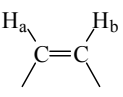
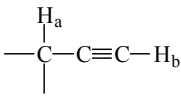
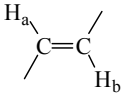
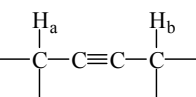
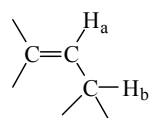
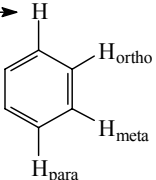
Splitting patterns when the N+1 rule works (common, but not always true)

● = group without any coupled proton(s)



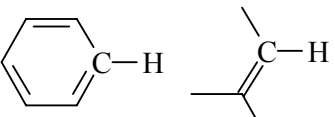
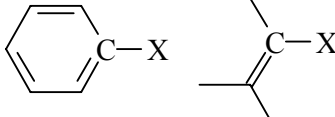
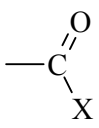
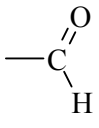
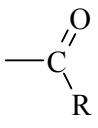
Combinations of these are possible.

dd = doublet of doublets; ddd = doublet of doublet of doublets; dddd = doublet of doublet of doublet of doublets; dt = doublet of triplets; td = triplet of doublets; etc.

	<u>Range</u>	<u>Typical</u>		<u>Range</u>	<u>Typical</u>
 geminal protons - can have different chemical shifts and split one another if they are diastereotopic	0-30 Hz	14 Hz	 cis / allylic coupling, notice through 4 bonds	0-3 Hz	1 Hz
 vicinal protons are on adjacent atoms, when freely rotating coupling averages out to about 7 Hz	6-8 Hz	7 Hz	 trans / allylic coupling, notice through 4 bonds	0-3 Hz	1 Hz
 θ = dihedral angle depends on dihedral angle, see plot of Karplus equation	0-12 Hz	7 Hz	 sp^2 vicinal coupling (different π bonds)	9-13 Hz	10 Hz
 protons rarely couple through 4 chemical bonds unless in a special, rigid shapes (i.e. W coupling)	0-1 Hz	0 Hz	 sp^3 vicinal aldehyde coupling	1-3 Hz	2 Hz
 sp^2 geminal coupling	0-3 Hz	2 Hz	 sp^2 vicinal aldehyde coupling	5-8 Hz	6 Hz
 sp^2 cis (acyclic) coupling (always smaller than the trans isomer)	5-11 Hz	10 Hz	 sp / propargylic coupling notice through 4 bonds	2-3 Hz	2 Hz
 sp^2 trans coupling (always larger than the cis isomer)	11-19 Hz	17 Hz	 bis-propargylic coupling notice through 5 bonds	2-3 Hz	3 Hz
 sp^2 / sp^3 vicinal coupling	4-10 Hz	7 Hz	ortho, meta and para coupling to this proton 	ortho 6-10 Hz meta 2-3 Hz para 0-1 Hz	9 Hz 2 Hz 0 Hz

When J values are less than 1 Hz, it is often difficult to resolve them and a peak may merely appear wider and shorter.

Similar chemical shift information presented in a different format. Remember, proton decoupled carbons appear as singlets. When carbons are coupled to their hydrogens, carbons follow the N+1 rule. Methyls = q, methylenes = t, methines = d, and carbons without hydrogen appear as singlets = s. DEPT provides the same information. Carbon chemical shifts are spread out over a larger range than proton chemical shifts (they are more dispersed), so it is less likely that two different carbon shifts will fall on top of one another. The relative positions of various types of proton and carbon shifts have many parallel trends (shielded protons tend to be on shielded carbons, etc.)

Simple alkane carbons	CH_3- $d \approx 0 - 30 \text{ ppm}$ (q)	CH_2- $d \approx 20 - 40 \text{ ppm}$ (t)	$-\text{CH}-$ $d \approx 30 - 50 \text{ ppm}$ (d)	$-\text{C}-$ $d \approx 30 - 60 \text{ ppm}$ (s)	
sp^3 carbon next to oxygen	CH_3-O $d \approx 50 - 60 \text{ ppm}$ (q)	CH_2-O $d \approx 55 - 80 \text{ ppm}$ (t)	$-\text{CH}-\text{O}$ $d \approx 60 - 80 \text{ ppm}$ (d)	$-\text{C}-\text{O}$ $d \approx 70 - 90 \text{ ppm}$ (s)	
sp^3 carbon next to nitrogen	CH_3-N $d \approx 10 - 50 \text{ ppm}$ (q)	CH_2-N $d \approx 35 - 55 \text{ ppm}$ (t)	$-\text{CH}-\text{N}$ $d \approx 50 - 70 \text{ ppm}$ (d)	$-\text{C}-\text{N}$ $d \approx 50 - 70 \text{ ppm}$ (s)	
sp^3 carbon next to bromine or chlorine (X = Cl, Br)		CH_2-X $d \approx 25 - 50 \text{ ppm}$ (t)	$-\text{CH}-\text{X}$ $d \approx 60 - 80 \text{ ppm}$ (d)	$-\text{C}-\text{X}$ $d \approx 60 - 80 \text{ ppm}$ (s)	
sp carbon (alkynes)	$-\text{C}\equiv\text{C}-$ $\delta \approx 70 - 90 \text{ ppm}$		sp carbon (nitriles)	$-\text{C}\equiv\text{N}$ $\delta \approx 110 - 125 \text{ ppm}$	
sp^2 carbon (alkenes and aromatics)	 $\delta \approx 100 - 140 \text{ ppm}$ simple sp^2 carbon resonance donation moves δ lower, resonance withdrawal moves δ higher		 $\delta \approx 140 - 160^+ \text{ ppm}$ sp^2 carbon attached to an electronegative atom (X = oxygen, nitrogen, halogen) or C_β carbon conjugated with a carbonyl group		
	 $\delta \approx 160 - 180 \text{ ppm}$ carboxyl carbons (acids, esters, amides) (s)			 $\delta \approx 180 - 210 \text{ ppm}$ aldehyde carbons, lower values when conjugated (d)	 $\delta \approx 180 - 220 \text{ ppm}$ ketone carbons, lower values when conjugated (s)

Calculations of alkane ^{13}C chemical shifts not listed above. sp^3 Carbon Chemical Shift Calculations

Calculations for sp^3 carbon ^{13}C chemical shifts of functionalized carbon skeletons can be performed starting from the actual shifts found in the corresponding alkane skeleton, and introducing correction factors based on the functionality present in the molecule. This assumes that the alkane ^{13}C shifts are available, which is why several examples are provided below.

Examples of C_n alkanes as possible starting points for calculation ^{13}C shifts in ppm.

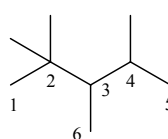
Steric Corrections for sp^3 carbon chemical shift calculations

The attached C_α carbons are:

The calculated carbon atom is:	primary	secondary	tertiary	quaternary
primary	0	0	-1.1	-3.4
secondary	0	0	-2.5	-7.5
tertiary	0	-3.7	-9.5	-15.0
quaternary	-1.5	-8.4	-15.0	-25.0

Approximate ^{13}C shift calculation from scratch.

$$\delta_{\text{C}} = -(2) + 9x(\#\alpha + \#\beta) - 2x(\#\gamma) + \text{steric corrections}$$



$$\text{C1} = -2 + 9(1+3) - 2(2) + (-3) = 29 \quad (\text{actual} = 28.3)$$

$$\text{C2} = -2 + 9(4+2) - 2(2) + [3x(-1.5) + (-15.0)] = 28 \quad (\text{actual} = 34.0)$$

$$\text{C3} = -2 + 9(3+5) - 0(2) + [(-9.5) + (-15.0)] = 45 \quad (\text{actual} = 47.9)$$

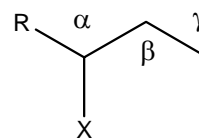
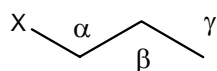
$$\text{C4} = -2 + 9(3+2) - 3(2) + (-9.5) = 27 \quad (\text{actual} = 27.2)$$

$$\text{C5} = -2 + 9(1+2) - 2(2) + (-1) = 20 \quad (\text{actual} = 19.5)$$

$$\text{C6} = -2 + 9(1+2) - 5(2) + (-1) = 14 \quad (\text{actual} = 8.5)$$

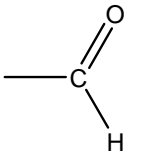
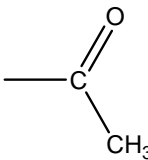
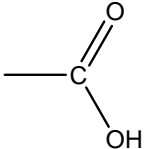
 ^{13}C shifts for various carbon alkane skeletons - useful starting points for calculating sp^3 carbon chemical shifts

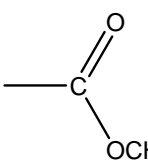
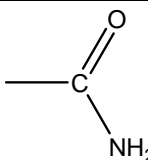
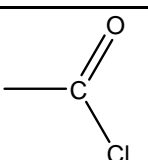
CH_4 -2.3 C ₂ 5.9	C_3 16.3 15.8	C_4 25.0 13.8	C_5 25.4 25.0 22.6 14.1 34.4	C_6 22.3 30.2 11.8 31.9 32.0 29.7 32.0
C_6 22.9 14.1 32.9	C_7 22.7 27.9 20.6 41.5 14.4	C_8 11.5 36.3 29.3 18.8	C_9 29.0 30.4 8.9 36.5	C_{10} 19.5 33.9
C_7 22.9 14.1 32.1 29.3	C_8 22.7 28.1 39.0 23.1 29.9 14.1	C_9 11.4 29.7 34.4 39.2 14.5 19.2 20.3	C_{10} 29.8 33.4 17.5 48.3 15.0 31.8 40.6 26.9 12.0	C_{11} 22.9 25.6 48.9 25.6 27.0 9.1 35.3 36.4 11.0 25.2 42.3 27.0 37.2 38.0 17.9
C_8 22.9 14.1 32.1 29.5	C_9 22.7 28.1 39.2 32.3 14.1 27.2 22.8	C_{10} 29.6 11.5 34.6 29.7 14.1 36.5 19.3	C_{11} 14.5 20.3 39.6 32.4 19.7 32.4	C_{12} 10.9 25.6 40.3 35.4 20.1 14.6
C_9 22.8 14.1 32.1 29.6 29.8	C_{10} 22.9 14.2 32.2 29.6 29.9			

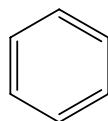


Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
---CH_3	9	9	-2	6	8	-2
$\text{---CH}_2\text{CH}_3$	18	7	-2	9	6	-2
$\text{---CH}(\text{CH}_3)_2$	26	4	-2	14	3	-2
$\text{---C}(\text{CH}_3)_3$	32	2	-2	20	1	-2
$\text{---}\underset{\text{H}}{\text{C}}=\text{CH}_2$	20	6	-1	15	5	-1
$\text{---C}\equiv\text{CH}$	5	5	-4	2	6	-4
	23	9	-2	17	7	-2

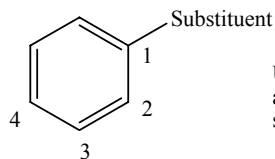
Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
---OH	48	10	-6	44	7	-4
---OR	60	7	-6	57	5	-6
	51	6	-6	49	5	-6
---NH_2	28	10	-5	24	8	-5
$\text{---NH}(\text{CH}_3)$	38	8	-5	32	5	-4
$\text{---N}(\text{CH}_3)_2$	45	5	-5	37	3	-4
	26	7	-5	21	5	-5
---NO_2	62	5	-5	58	2	-5

Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C _α correction	C _β correction	C _γ correction	C _α correction	C _β correction	C _γ correction
—F	70	8	-7	67	5	-7
—Cl	31	10	-5	36	8	-5
—Br	20	10	-4	28	10	-4
—I	-7	11	-2	7	11	-2
	30	0	-3	24	-1	-3
	31	1	-3	26	0	-3
	22	2	-3	18	1	-3

Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C _α correction	C _β correction	C _γ correction	C _α correction	C _β correction	C _γ correction
	20	2	-3	16	2	-3
	25	3	-3	19	2	-3
—C≡N	3	3	-3	3	3	-3
	33	2	-3	30	2	-3
—SH	11	10	-3	12	8	-3
—SR	22	8	-3	20	6	-3

Additional starting point for calculating ^{13}C chemical shifts (ppm) of substituted benzene rings (just a few possibilities)

128 ppm starting point for benzene carbon

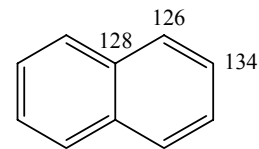


Use correction term for carbon atom in relative position to the substituent. Start with 128 ppm.

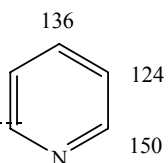
Substituent	Z ₁	Z ₂	Z ₃	Z ₄
-H	0	0	0	0
-CH ₃	9	1	0	-3
-CH ₂ CH ₃	12	-1	0	-3
-CH ₂ CH ₂ CH ₃	10	0	0	-3
-CH ₂ CH ₂ CH ₂ CH ₃	11	0	0	-3
-CH(CH ₃) ₂	20	-2	0	-3
-C(CH ₃) ₃	19	-3	0	-3
-CH ₂ F	8	-1	0	0
-CH ₂ Cl	9	0	0	0
-CH ₂ Br	9	1	0	0
-CH ₂ I	11	-1	0	-1
-CH ₂ OH	12	-1	0	-1
-CH ₂ NH ₂	15	-1	0	-2
-CH ₂ NO ₂	2	2	1	1
-CH ₂ CN	2	0	-1	-1
-CH ₂ SH	12	-1	0	-2
-CH ₂ CHO	7	1	0	-1
-CH ₂ COCH ₃	6	1	0	-2
-CH ₂ CO ₂ H	6	1	0	-1
-CH ₂ =CH ₂	13	-3	0	-1
-CCH	-6	4	0	0
-C ₆ H ₅	8	-1	0	-1
-F	34	-13	2	-4
-Cl	5	0	1	2
-Br	-5	3	2	-1
-I	-31	9	2	-1

Substituent	Z ₁	Z ₂	Z ₃	Z ₄
-OH	29	-13	1	-7
-OCH ₃	34	-14	1	-8
-OC ₆ H ₅	28	-11	0	-7
-NH ₂	18	-13	1	-10
-NHCOCH ₃	10	-8	0	-4
-NHOH	22	-13	-2	-5
-NHNH ₂	23	-16	1	-10
-N=N-R	22	-6	0	-3
-NO	37	-8	1	7
-NO ₂	20	-5	1	6
-SH	4	1	0	-3
-SCH ₃	10	-2	0	-4
-S(O)CH ₃	18	-5	1	2
-SO ₂ CH ₃	12	-1	1	5
-SO ₂ Cl	16	-2	1	7
-CN	-16	3	1	4
-CHO	8	1	0	6
-COCH ₃	9	0	0	4
-CO ₂ H	2	2	0	5
-CO ₂ CH ₃	2	1	0	4
-CONH ₂	5	-1	0	3
-COCl	11	0	0	-3
-Li	-43	-13	2	3
-MgBr	-36	-11	3	4

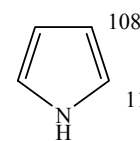
Starting points for other common ring systems. (ppm). No correction terms included for substituents.



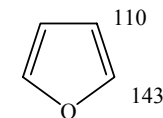
naphthalene



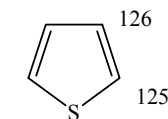
pyridine



pyrrole



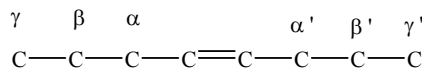
furan



thiophene

Additional starting point for calculating ^{13}C chemical shifts (ppm) of substituted alkenes (just a few possibilities)

123 ppm starting point for alkene carbon



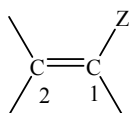
123 + correction factors

increments for directly attached carbon atoms

$$\begin{array}{l} \alpha = 11 \quad \alpha' = -8 \\ \beta = 5 \quad \beta' = -2 \\ \gamma = -2 \quad \gamma' = 2 \end{array}$$

steric corrections

for each pair of cis- α, α' substituents	-1
for each pair of geminal- α, α' substituents	-5
for each pair of geminal- α, α' substituents	3
if one or more β substituents are present	2



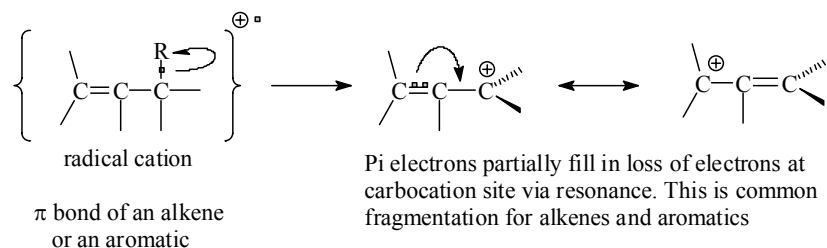
$$\delta_{\text{C}} = 123 \text{ ppm} + Z_i$$

Effect of substituents on alkene ^{13}C shifts (ppm)

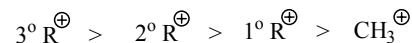
Substituent	Z ₁	Z ₂	Substituent	Z ₁	Z ₂
-H	0	0	-F	24	-34
-CH ₃	13	-7	-Cl	3	-6
-CH ₂ CH ₃	17	-10	-Br	-9	-1
-CH ₂ CH ₂ CH ₃	16	-9	-I	-38	7
-CH(CH ₃) ₂	23	-12	-OCH ₃	29	-39
-C(CH ₃) ₃	26	-15	-O ₂ CCH ₃	18	-27
-CH ₂ Cl	10	-6	-N(CH ₃) ₂	28	-32
-CH ₂ Br	11	-5	-NO ₂	22	-1
-CH ₂ I	14	-4	-CN	-15	14
-CH ₂ OH	14	-8	-SCH ₂ CH ₃	9	-13
-CH=CH ₂	14	-7	-CHO	15	14
-CCH	-6	6	-COCH ₃	14	5
-C ₆ H ₅	12	-11	-CO ₂ H	5	10
			-COCl	8	14

Common fragmentation patterns in mass spectroscopy

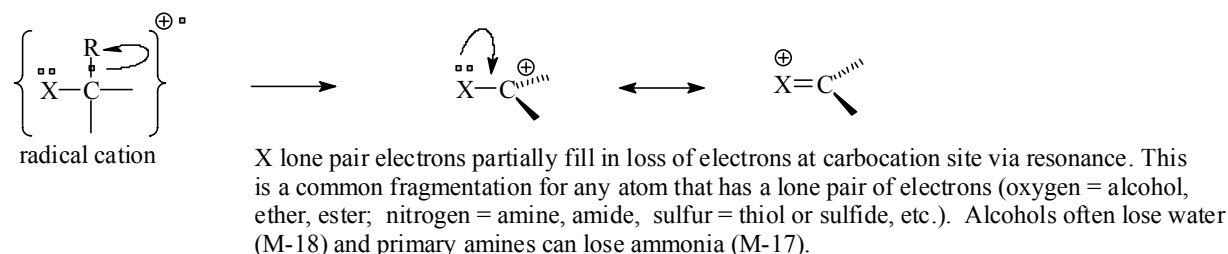
1. Branch next to a π bond



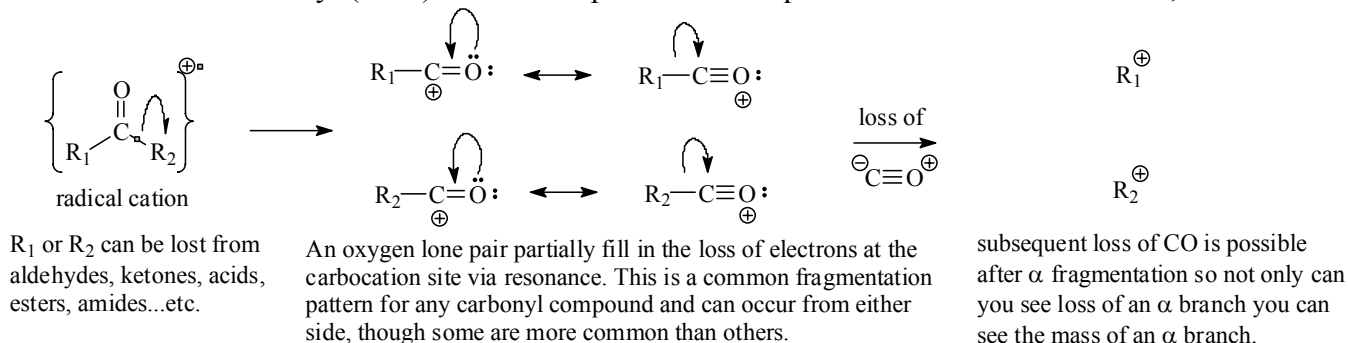
Characteristic carbocation stability also applies.



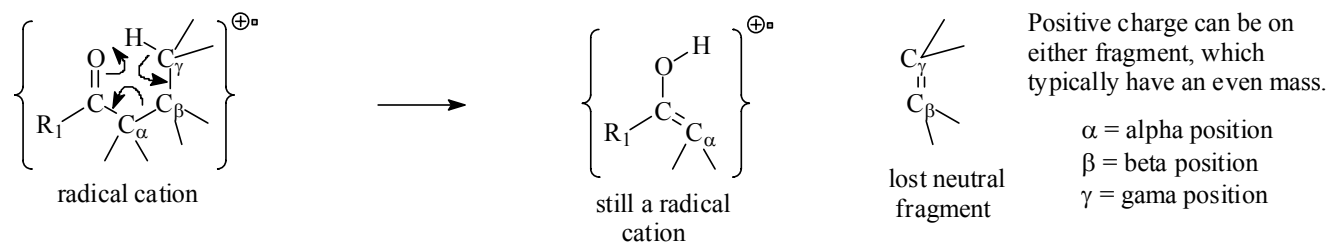
2. Branch next to an atom with a lone pair of electrons



3. Branch next to a carbonyl (C=O) bond...and possible subsequent loss of carbon monoxide, CO

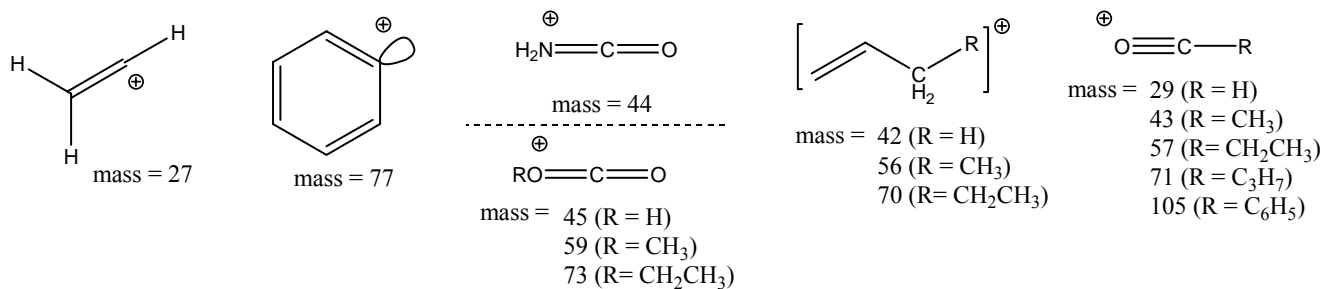
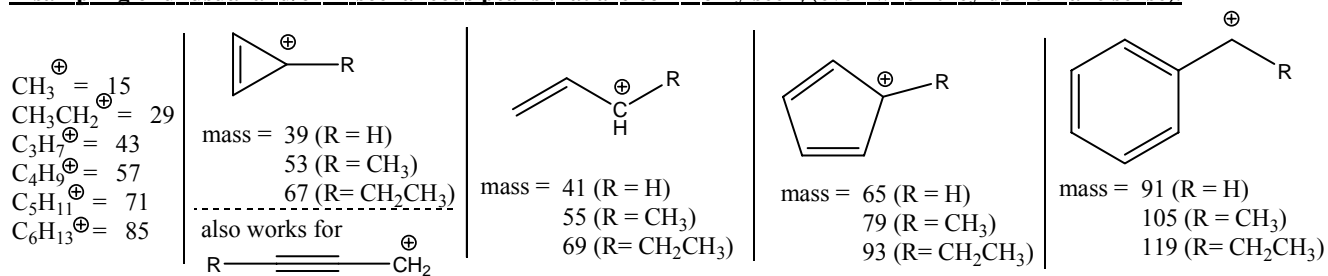


4. McLafferty Rearrangement



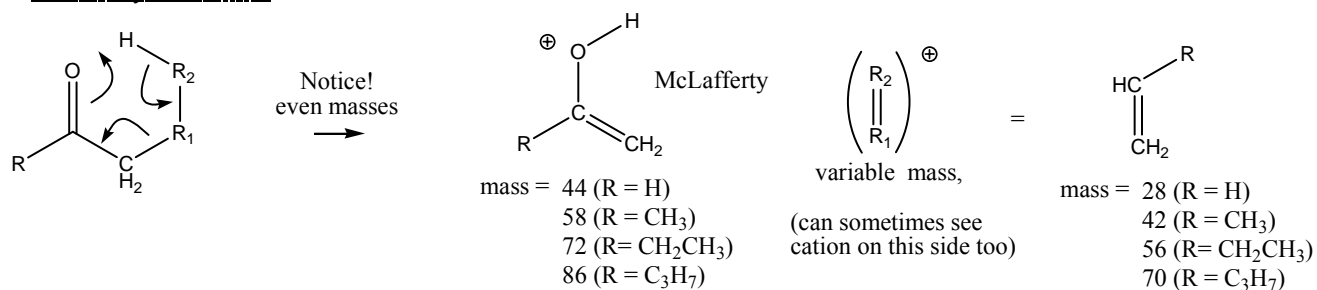
This is another common fragmentation pattern for carbonyl compounds (and other pi systems as well: alkenes, aromatics, alkynes, nitriles, etc.). If the pi bond has at least 3 additional nonhydrogen atoms attached and a hydrogen on the "gamma" atom, the branch can curve around to a comfortable 6 atom arrangement and the pi bond can pick up a hydrogen atom and cut off a fragment between the C_α and C_β positions. The positive charge can be seen on either fragment and usually the fragments have an even mass (unless there is an odd number of nitrogen atoms).

Knowing these few fragmentation patterns will allow you to make many useful predictions and interpretations. Loss of small molecules, via elimination is common: $\text{H}_2\text{O} = 18$, $\text{H}_2\text{S} = 34$, $\text{CH}_3\text{OH} = 32$, $\text{C}_2\text{H}_5\text{OH} = 46$, $\text{NH}_3 = 17$, $\text{CH}_3\text{CO}_2\text{H} = 62$, $\text{HF} = 20$, $\text{HCl} = 36/38$, $\text{HBr} = 80/82$, etc.

A sampling of unusual and/or miscellaneous peaks that are commonly seen, (even when they don't make sense).

Loss of small molecules via elimination reactions.

H ₂ O	H ₂ S	CH ₃ OH	C ₂ H ₅ OH	NH ₃	CH ₃ CO ₂ H	HF	HCl	HBr
mass = 18	34	32	46	17	62	20	36 38	80 82

McLafferty PossibilitiesSimilar Patterns