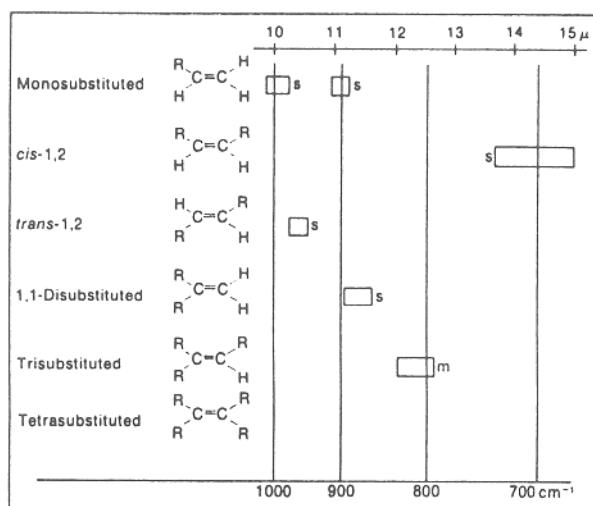


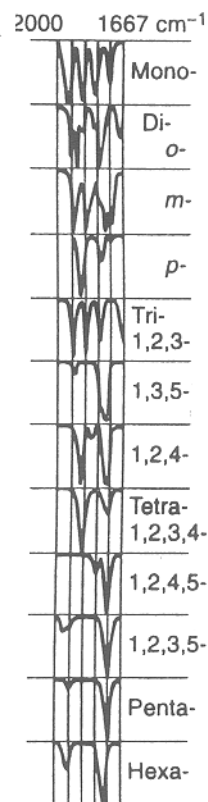
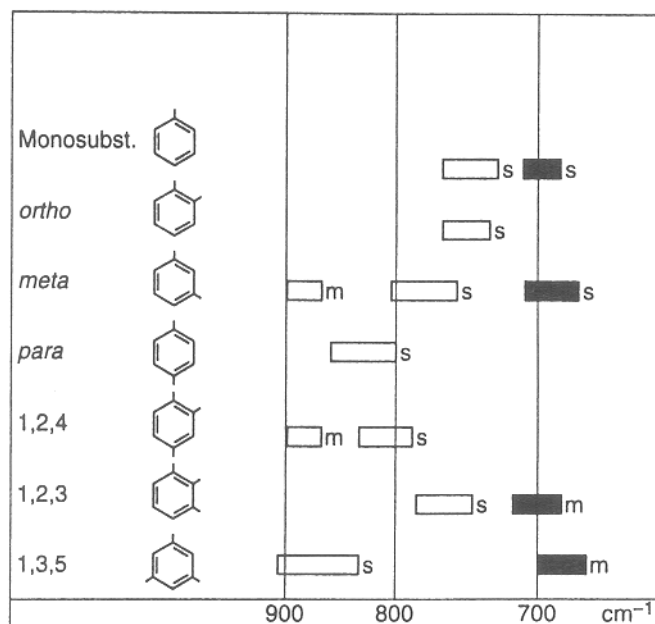
## A Simplified Correlation Chart

	Type of Vibration	Frequency (cm <sup>-1</sup> )	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH <sub>3</sub> (bend)	1450 and 1375	m	
	—CH <sub>2</sub> — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne (stretch)	ca. 3300	s	
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s
O—H	Alcohols, phenols			
	Free	3650–3600	m	
	H-bonded	3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides (stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO <sub>2</sub> )	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S=O	Sulfoxides	1050	s	
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s	
C—X	Fluoride	1400–1000	s	
	Chloride	785–540	s	
	Bromide, iodide	< 667	s	



► **FIGURE 2.22** The C—H out-of-plane bending vibrations for substituted alkenes.

Figure 2.22 shows the C—H out-of-plane bending vibrations for substituted alkenes, together with the frequency ranges.



► **FIGURE 2.28** (a) The C—H out-of-plane bending vibrations for substituted benzenoid compounds. (b) The 2000-to-1667-cm<sup>-1</sup> region for substituted benzenoid compounds (from Dyer, John R., *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, Englewood Cliffs, N.J., 1965).

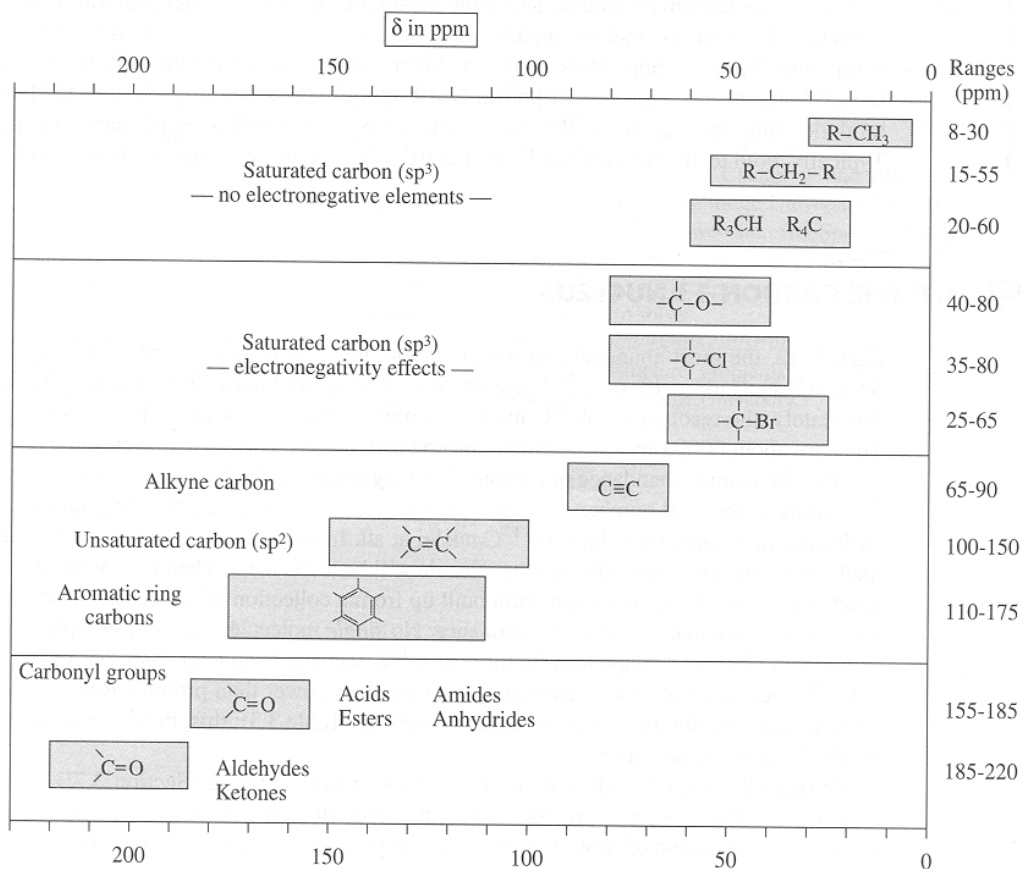


FIGURE 4.1 A correlation chart for  $^{13}\text{C}$  chemical shifts (chemical shifts are listed in parts per million from TMS).

$^{13}\text{C}$  Substituent Increments for Benzene Rings (ppm)<sup>a</sup>

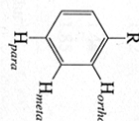
Substituent Y	$\alpha$ ( <i>ipso</i> )	<i>o</i> ( <i>ortho</i> )	<i>m</i> ( <i>meta</i> )	<i>p</i> ( <i>para</i> )
-CH <sub>3</sub>	9.3	0.7	-0.1	-2.9
-CH <sub>2</sub> CH <sub>3</sub>	15.6	-0.5	0	-2.6
-CH(CH <sub>2</sub> ) <sub>2</sub>	20.1	-2.0	0	-2.5
-C(CH <sub>3</sub> ) <sub>3</sub>	22.2	-3.4	-0.4	-3.1
-CH=CH <sub>2</sub>	9.1	-2.4	0.2	-0.5
-C≡CH	-5.8	6.9	0.1	0.4
-C <sub>6</sub> H <sub>5</sub>	12.1	-1.8	-0.1	-1.6
-CHO	8.2	1.2	0.6	5.8
-COCH <sub>3</sub>	7.8	-0.4	-0.4	2.8
-COC <sub>6</sub> H <sub>5</sub>	9.1	1.5	-0.2	3.8
-COOH	2.9	1.3	0.4	4.3
-COOCH <sub>3</sub>	2.0	1.2	-0.1	4.8
-CN	-16.0	3.6	0.6	4.3
-NH <sub>2</sub>	19.2	-12.4	1.3	-9.5
-N(CH <sub>3</sub> ) <sub>2</sub>	22.4	-15.7	0.8	-11.8
-NHCOCH <sub>3</sub>	11.1	-9.9	0.2	-5.6
-NO <sub>2</sub>	19.6	-5.3	0.9	6.0
-OH	26.6	-12.7	1.6	-7.3
-OCH <sub>3</sub>	31.4	-14.4	1.0	-7.7
-OCOCH <sub>3</sub>	22.4	-7.1	-0.4	-3.2
-F	35.1	-14.3	0.9	-4.5
-Cl	6.4	0.2	1.0	-2.0
-Br	-5.4	3.4	2.2	-1.0
-I	-32.2	9.9	2.6	-7.3

<sup>a</sup>Add these increments to the base value for benzene-ring carbons (128.5 ppm).

TABLE 3.4  
APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS<sup>a</sup>

R-CH <sub>3</sub>	0.7-1.3	R-N <sub>3</sub> -C-H	2.2-2.9
R-CH <sub>2</sub> -R	1.2-1.4	R-S-C-H	2.0-3.0
R <sub>3</sub> CH	1.4-1.7	I-C-H	2.0-4.0
R-C=C-C-H	1.6-2.6	Br-C-H	2.7-4.1
R-C-C-C-H	2.1-2.4	Cl-C-H	3.1-4.1
RO-C-C-C-H	2.1-2.5	R-S-O-C-H	ca. 3.0
N≡C-C-H	2.1-3.0	RO-C-H, HO-C-H	3.2-3.8
Ph-C-H	2.3-2.7	R-C-O-C-H	3.5-4.8
R-C≡C-H	1.7-2.7	O <sub>2</sub> N-C-H	4.1-4.3
R-S-H	1.0-4.0 <sup>b</sup>	F-C-H	4.2-4.8
R-N-H	0.5-4.0 <sup>b</sup>	R-C=C-H	4.5-6.5
R-O-H	0.5-5.0 <sup>b</sup>	Ph-H	6.5-8.0
Ph-N-H	3.0-5.0 <sup>b</sup>	R-C-H	9.0-10.0
R-C(=O)-N-H	5.0-9.0 <sup>b</sup>	R-C-OH	11.0-12.0

<sup>1</sup>H Chemical-Shift Calculations for Substituted Benzene Rings



$$\delta_H \text{ ppm} = 7.27 + \Sigma\delta$$

Substituents (-R)	$\delta_{ortho}$	$\delta_{meta}$	$\delta_{para}$
Saturated carbon groups			
Alkyl	-0.14	-0.06	-0.17
-CH <sub>2</sub> OH	-0.07	-0.07	-0.07
Aldehydes and ketones			
-CHO	0.56	0.22	0.29
-COR	0.62	0.14	0.21
Carboxylic acids and derivatives			
-COOH	0.85	0.18	0.27
-COOR	0.71	0.10	0.21
-C≡N	0.36	0.18	0.28
Oxygen groups			
-OH	-0.56	-0.12	-0.45
-OCH <sub>3</sub>	-0.48	-0.09	-0.44
-OCOCH <sub>3</sub>	-0.25	0.03	-0.13
Nitrogen groups			
-NH <sub>2</sub>	-0.75	-0.25	-0.65
-NO <sub>2</sub>	0.95	0.26	0.38
Halogen groups			
-Cl	0.03	-0.02	-0.09
-Br	0.18	-0.08	-0.04

$\delta$  in ppm