

**FIGURE 22.13** Approximate regions of chemical shifts for different types of protons in organic compounds.

**TABLE 22.2** Characteristic  $^1\text{H}$  NMR chemical shifts in  $\text{CDCl}_3$

Compound	Chemical shift ( $\delta$ , ppm)
TMS	0.0
Alkanes (C-C-H)	0.8–1.9
Amines (C-N-H)	0.6–4.5
Alcohols (C-O-H)	0.5–5.0
Alkenes <sup>a</sup> (C=C-C-H)	1.5–2.6
Alkynes (C≡C-H)	1.7–3.1
Carbonyl compounds (O=C-C-H)	1.9–3.3
Halides (X-C-H)	2.1–4.5
Aromatic compounds <sup>b</sup> (Ar-C-H)	2.2–3.0
Alcohols, esters, ethers (O-C-H)	3.2–5.3
Alkenes (C=C-H)	4.5–8.5
Phenols (Ar-O-H)	4.0–8.0
Amides (O=C-N-H)	5.5–9.5
Aromatic compounds (Ar-H)	6.5–9.0
Aldehydes (O=C-H)	9.5–10.5
Carboxylic acids (O=C-O-H)	9.7–12.5

a. Allylic protons.

b. Benzylic protons.

**TABLE 22.4 Additive parameters for predicting NMR chemical shifts of aromatic protons in CDCl<sub>3</sub>**

Group	Base value		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
—CH <sub>3</sub>	-0.18	-0.11	-0.21
—CH(CH <sub>3</sub> ) <sub>2</sub>	-0.14	-0.08	-0.20
—CH <sub>2</sub> Cl	0.02	-0.01	-0.04
—CH=CH <sub>2</sub>	0.04	-0.04	-0.12
—CH=CHAr	0.14	-0.02	-0.11
—CH=CHCO <sub>2</sub> H	0.19	0.04	0.05
—CH=CH(C=O)Ar	0.28	0.06	0.05
Group	<i>ortho</i>	<i>meta</i>	<i>para</i>
—Ar	0.23	0.07	-0.02
—(C=O)H	0.53	0.18	0.28
—(C=O)R	0.60	0.10	0.20
—(C=O)Ar	0.45	0.12	0.23
—(C=O)CH=CHAr	0.67	0.14	0.21
—(C=O)OCH <sub>3</sub>	0.68	0.08	0.19
—(C=O)OCH <sub>2</sub> CH <sub>3</sub>	0.69	0.06	0.17
—(C=O)OH	0.77	0.11	0.25
—(C=O)Cl	0.76	0.16	0.33
—(C=O)NH <sub>2</sub>	0.46	0.09	0.17
—C≡N	0.29	0.12	0.25
—F	-0.32	-0.05	-0.25
—Cl	-0.02	-0.07	-0.13
—Br	0.13	-0.13	-0.08
—OH	-0.53	-0.14	-0.43
—OR	-0.45	-0.07	-0.41
—OAr	-0.36	-0.04	-0.28
—O(C=O)R	-0.27	0.02	-0.13
—O(C=O)Ar	-0.14	0.07	-0.09
—NH <sub>2</sub>	-0.71	-0.22	-0.62
—N(CH <sub>3</sub> ) <sub>2</sub>	-0.68	-0.15	-0.73
—NH(C=O)R	0.14	-0.07	-0.27
—NO <sub>2</sub>	0.87	0.20	0.35

a. Base value is the measured chemical shift of benzene in CDCl<sub>3</sub> (1% solution).

**TABLE 22.3 Additive parameters for predicting NMR chemical shifts of alkyl protons in  $\text{CDCl}_3$ <sup>a</sup>**

Group (Y)	Base values		
	Alpha ( $\alpha$ ) substituent	Beta ( $\beta$ ) substituent	Gamma ( $\gamma$ ) substituent
	Methyl	0.9 ppm	
	Methylene	1.2 ppm	
	Methine	1.5 ppm	
	$\begin{array}{c}   \\ \text{H}-\text{C}-\text{Y} \\   \end{array}$	$\begin{array}{c}   \quad   \\ \text{H}-\text{C}-\text{C}-\text{Y} \\   \quad   \end{array}$	$\begin{array}{c}   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Y} \\   \quad   \quad   \end{array}$
—R	0.0	0.0	0.0
—C=C	0.8	0.2	0.1
—C=C—Ar <sup>b</sup>	0.9	0.1	0.0
—C=C(C=O)OR	1.0	0.3	0.1
—C≡C—R	0.9	0.3	0.1
—C≡C—Ar	1.2	0.4	0.2
—Ar	1.4	0.4	0.1
—(C=O)OH	1.1	0.3	0.1
—(C=O)OR	1.1	0.3	0.1
—(C=O)H	1.1	0.4	0.1
—(C=O)R	1.2	0.3	0.0
—(C=O)Ar	1.7	0.3	0.1
—(C=O)NH <sub>2</sub>	1.0	0.3	0.1
—(C=O)Cl	1.8	0.4	0.1
—C≡N	1.1	0.4	0.2
—Br	2.1	0.7	0.2
—Cl	2.2	0.5	0.2
—OH	2.3	0.3	0.1
—OR	2.1	0.3	0.1
—OAr	2.8	0.5	0.3
—O(C=O)R	2.8	0.5	0.1
—O(C=O)Ar	3.1	0.5	0.2
—NH <sub>2</sub>	1.5	0.2	0.1
—NH(C=O)R	2.1	0.3	0.1
—NH(C=O)Ar	2.3	0.4	0.1

a. There may be differences of 0.1–0.5 ppm in the chemical shift values calculated from this table and those measured from individual spectra.

b. Ar = aromatic group.

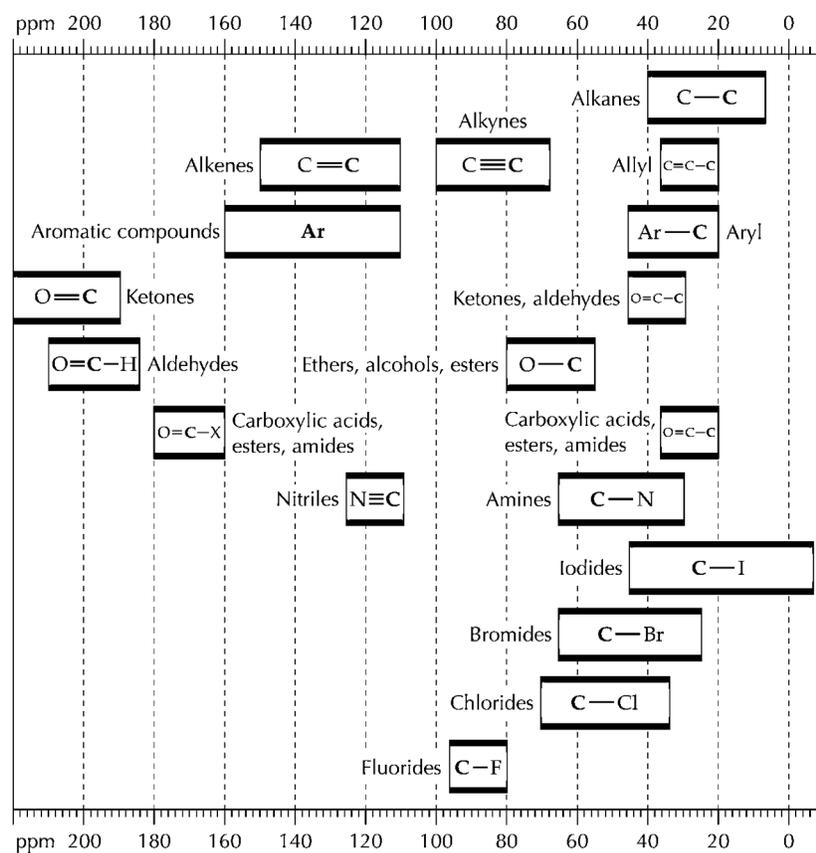


FIGURE 23.4 Approximate regions of  $^{13}\text{C}$  chemical shifts for different types of carbon atoms in organic compounds.

TABLE 23.1 Characteristic  $^{13}\text{C}$  NMR chemical shifts in  $\text{CDCl}_3$

Compound	Chemical shift (ppm)
TMS	0.0
$\text{CDCl}_3$ (t)	77
Alkane (C— $\text{CH}_3$ )	7–30
Alkane (C— $\text{CH}_2$ )	15–40
Alkane (C—CH) and (C—C)	15–40
Carboxylic acids, esters, and amides (C—C=O)	20–35
Allyl (C—C=C)	20–35
Arene (C—Ar)	20–45
Ketones, aldehydes (C—C=O)	30–45
Amines (C—N)	30–65
Iodides (C—I)	-5–45
Bromides (C—Br)	25–65
Chlorides (C—Cl)	35–70
Fluorides (C—F)	80–95
Alcohols (C—OH), ethers (C—OR), esters (C—O[C=O]R)	55–80
Alkyne (C $\equiv$ C)	70–100
Alkene (C=C)	110–150
Aromatic	110–160
Nitriles (C $\equiv$ N)	110–125
Carboxylic acids, esters, and amides (C=O)	160–180
Aldehydes (C=O)	185–210
Ketones (C=O)	190–220