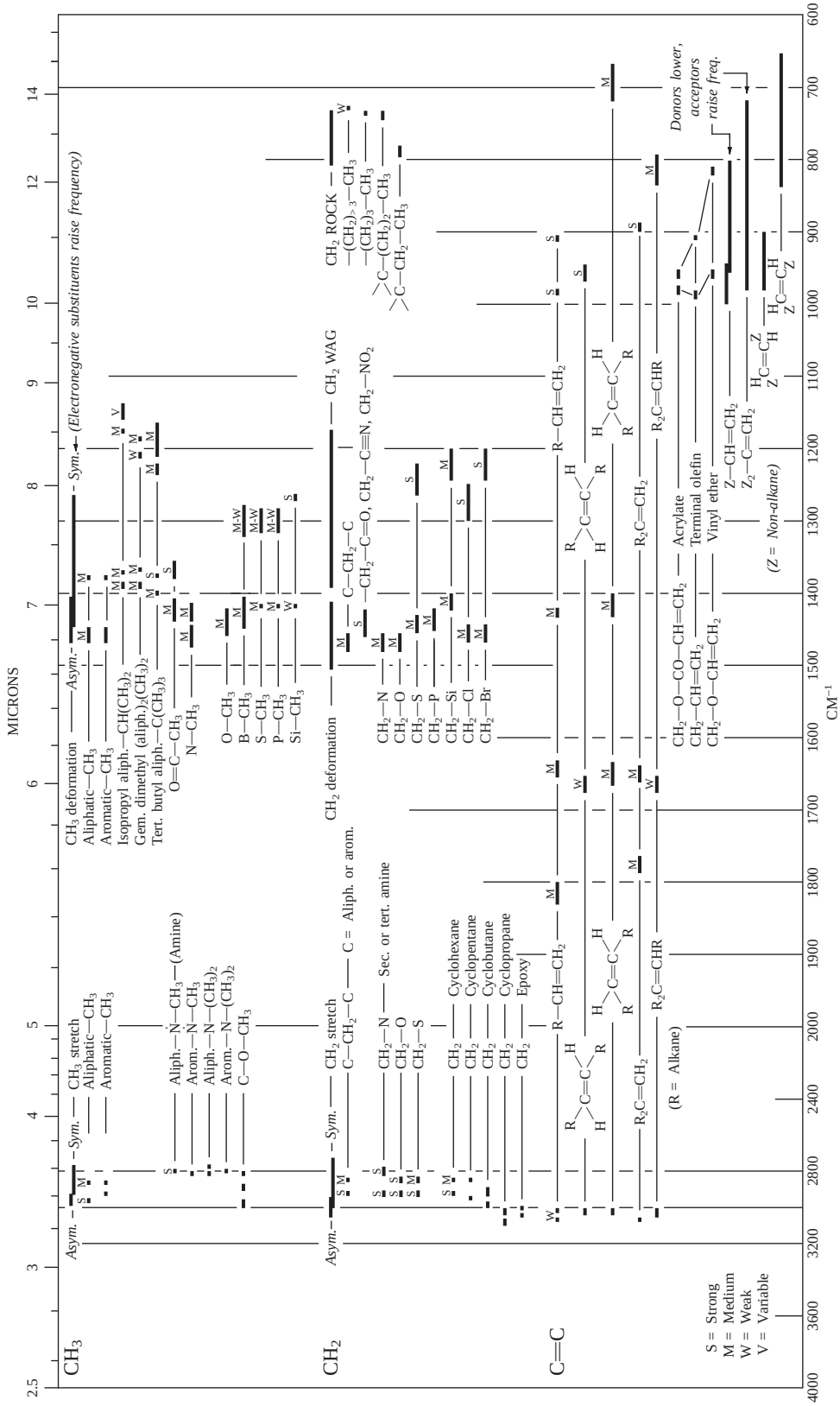
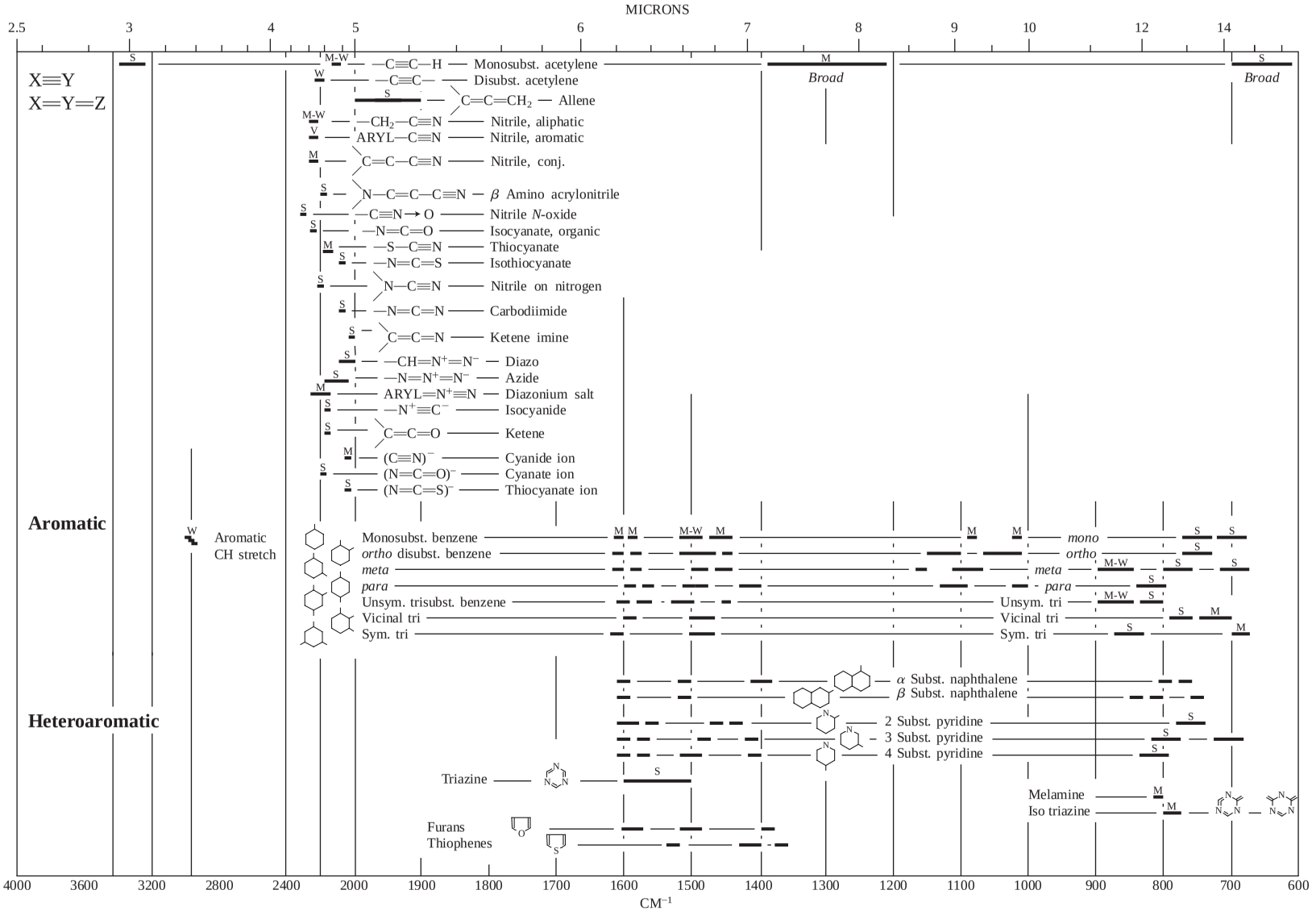
APPENDICES

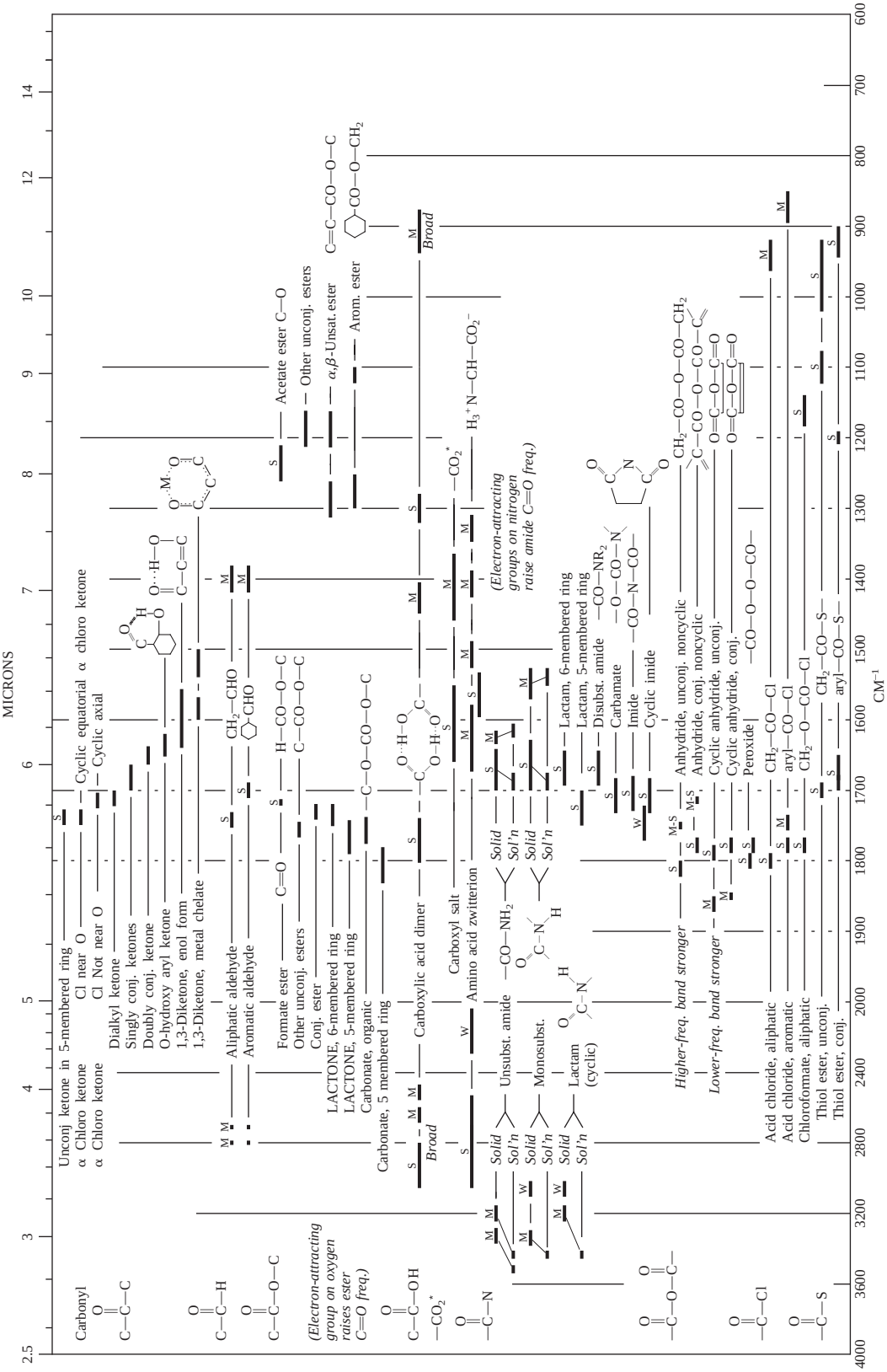
APPENDIX 1

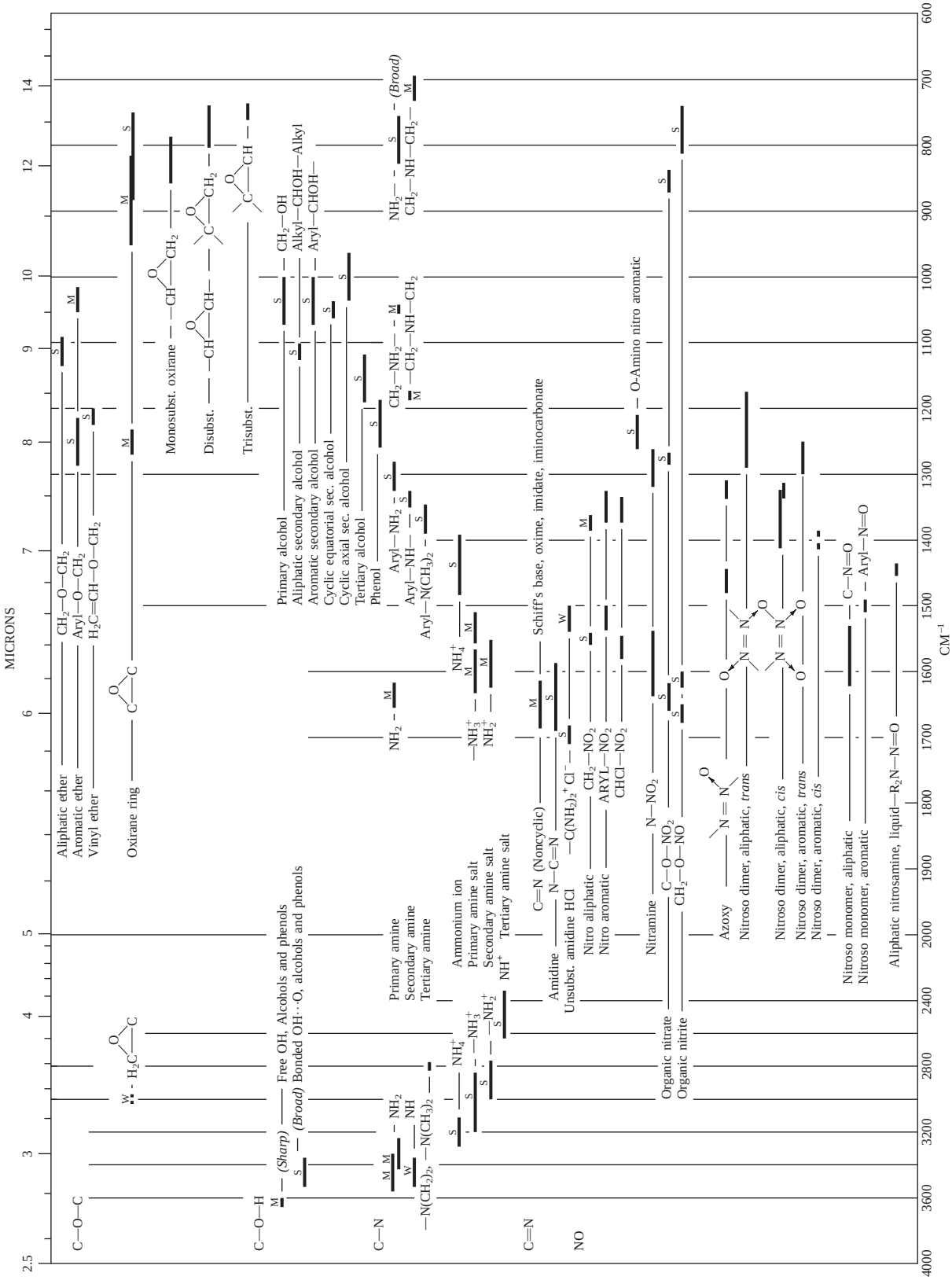
Infrared Absorption Frequencies of Functional Groups

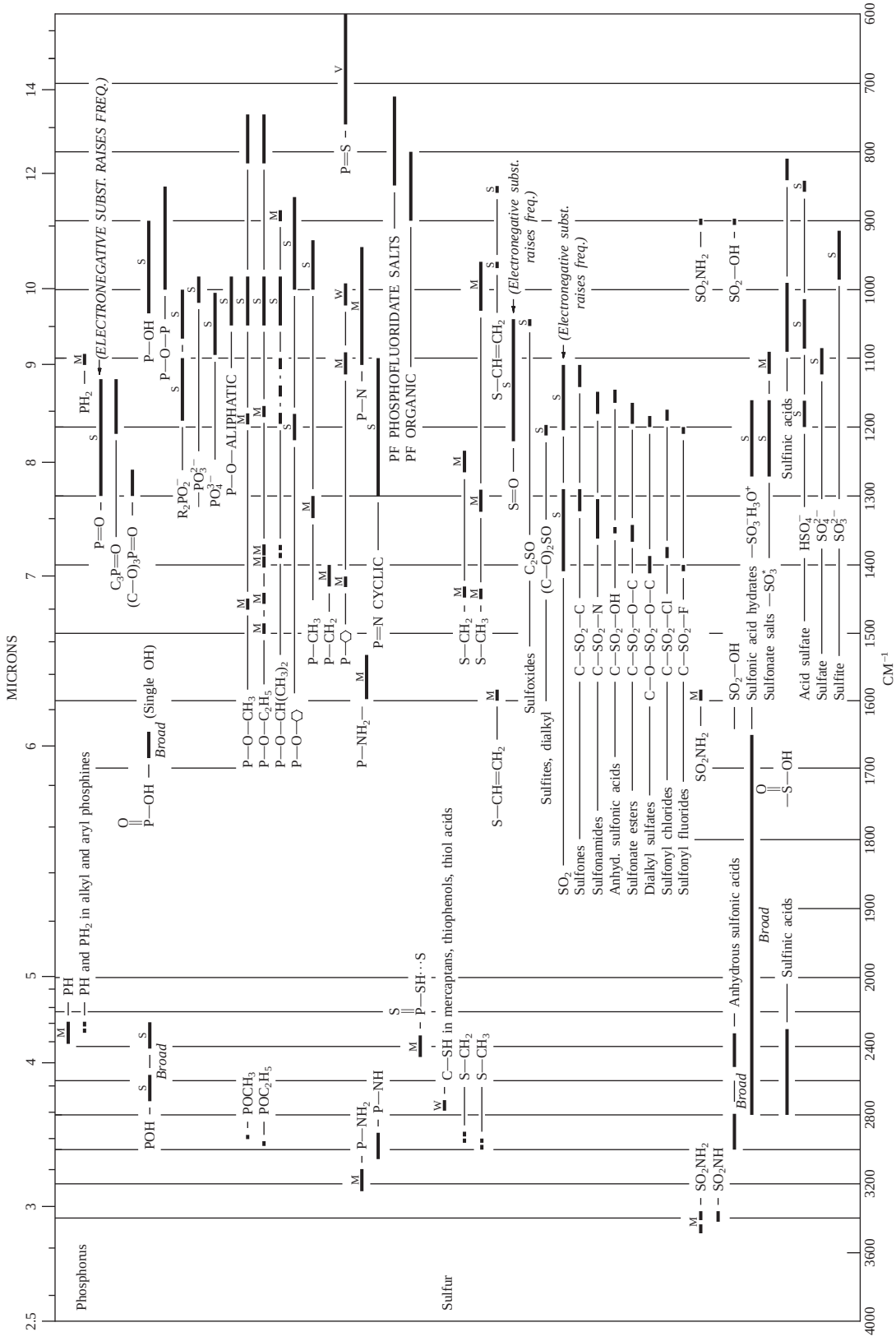


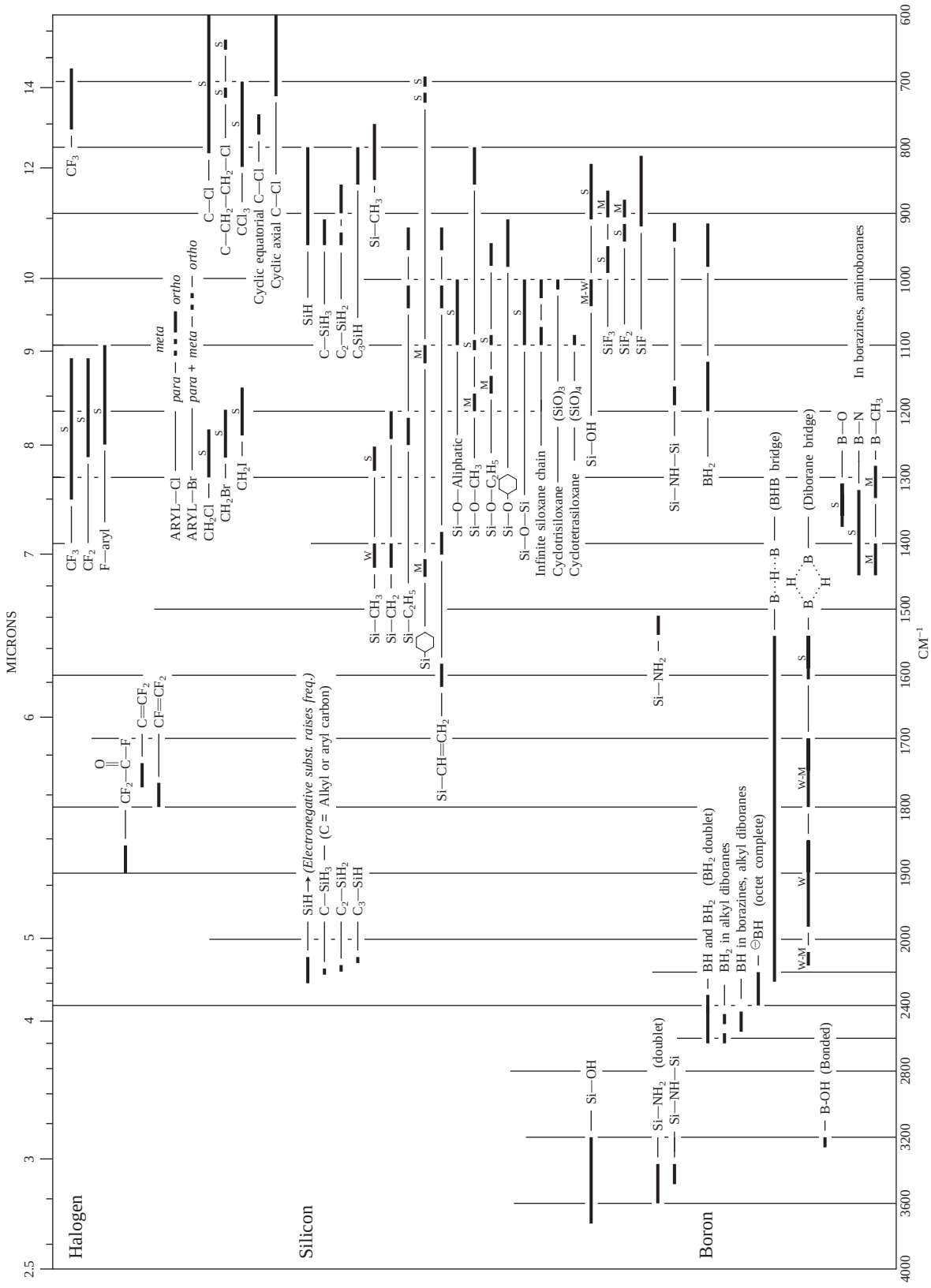
Colthup spectra–structure correlation charts for infrared frequencies in the 4000–600 cm^{-1} region from Lin-Vien, D., N. B. Colthup, W. G. Fateley, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, New York, 1991.


MICRONS
2.5
3
4
5
6
7
8
9
10
12
14
X≡Y
X=Y=Z
—C≡C—H — Monosubst. acetylene
—C≡C— — Disubst. acetylene
C=C=CH2 — Allene
—CH2—C≡N — Nitrile, aliphatic
ARYL—C≡N — Nitrile, aromatic
C=C—C≡N — Nitrile, conj.
N—C=C—C≡N — β Amino acrylonitrile
—C≡N→O — Nitrile N-oxide
—N=C=O — Isocyanate, organic
—S—C≡N — Thiocyanate
—N=C=S — Isothiocyanate
N—C≡N — Nitrile on nitrogen
—N=C=N — Carbodiimide
C=C=N — Ketene imine
—CH=N+=N− — Diazo
—N=N+=N− — Azide
ARYL=N+≡N — Diazonium salt
—N+≡C− — Isocyanide
C=C=O — Ketene
(C≡N)− — Cyanide ion
(N=C=O)− — Cyanate ion
(N=C=S)− — Thiocyanate ion
Broad
Broad
Aromatic
Aromatic CH stretch
Monosubst. benzene
ortho disubst. benzene
meta
para
Unsym. trisubst. benzene
Vicinal tri
Sym. tri
mono
ortho
meta
para
Unsym. tri
Vicinal tri
Sym. tri
Heteroaromatic
α Subst. naphthalene
β Subst. naphthalene
2 Subst. pyridine
3 Subst. pyridine
4 Subst. pyridine
Triazine
Melamine
Iso triazine
Furans
Thiophenes
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM−1


MICRONS
CM⁻¹
Carbonyl
Unconj ketone in 5-membered ring
α Chloro ketone
α Chloro ketone
Cl near O
Cl Not near O
Cyclic equatorial α chloro ketone
Cyclic axial
Dialkyl ketone
Singly conj. ketones
Doubly conj. ketone
O-hydroxy aryl ketone
1,3-Diketone, enol form
1,3-Diketone, metal chelate
Aliphatic aldehyde
Aromatic aldehyde
Formate ester
Other unconj. esters
Conj. ester
LACTONE, 6-membered ring
LACTONE, 5-membered ring
Carbonate, organic
Carbonate, 5 membered ring
(Electron-attracting group on oxygen raises ester C=O freq.)
Broad
Carboxylic acid dimer
Carboxyl salt
Amino acid zwitterion
Unsubst. amide
Monosubst. amide
Lactam (cyclic)
Solid
Sol'n
Higher-freq. band stronger
Lower-freq. band stronger
Acid chloride, aliphatic
Acid chloride, aromatic
Chloroformate, aliphatic
Thiol ester, unconj.
Thiol ester, conj.
Acetate ester C—O
Other unconj. esters
α,β-Unsat. ester
Arom. ester
(Electron-attracting groups on nitrogen raise amide C=O freq.)
Lactam, 6-membered ring
Lactam, 5-membered ring
Disubst. amide
Carbamate
Imide
Cyclic imide
Anhydride, unconj. noncyclic
Anhydride, conj. noncyclic
Cyclic anhydride, unconj.
Cyclic anhydride, conj.
Peroxide
Broad

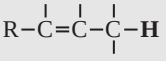
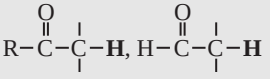
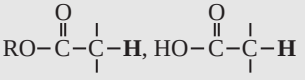
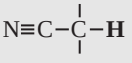
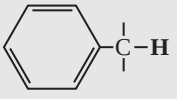
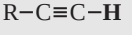
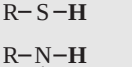
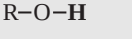
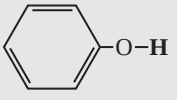
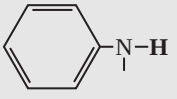
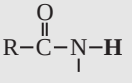
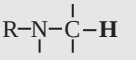
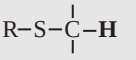
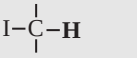
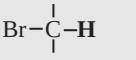
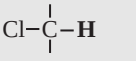
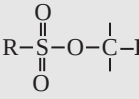
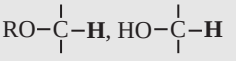
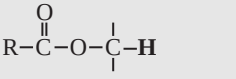
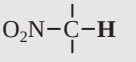
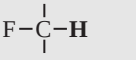
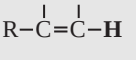
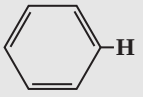
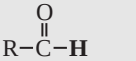
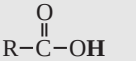

MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM⁻¹
C—O—C
Aliphatic ether
Aromatic ether
Vinyl ether
Oxirane ring
Monosubst. oxirane
Disubst.
Trisubst.
C—O—H
(Sharp)
(Broad) Bonded OH···O, alcohols and phenols
Free OH, Alcohols and phenols
Primary alcohol
Aliphatic secondary alcohol
Aromatic secondary alcohol
Cyclic equatorial sec. alcohol
Cyclic axial sec. alcohol
Tertiary alcohol
Phenol
Alkyl—CHOH—Alkyl
Aryl—CHOH—
C—N
Primary amine
Secondary amine
Tertiary amine
Ammonium ion
Primary amine salt
Secondary amine salt
Tertiary amine salt
Aryl—NH—
Aryl—N(CH3)2
Aryl—NH2
(Broad)
C=N
C=N (Noncyclic)
Schiff's base, oxime, imidate, iminocarbonate
Amidine
Unsubst. amidine HCl
NO
Nitro aliphatic
Nitro aromatic
Nitramine
Organic nitrate
Organic nitrite
O-Amino nitro aromatic
Azoxy
Nitroso dimer, aliphatic, trans
Nitroso dimer, aliphatic, cis
Nitroso dimer, aromatic, trans
Nitroso dimer, aromatic, cis
Nitroso monomer, aliphatic
Nitroso monomer, aromatic
Aliphatic nitrosamine, liquid
Aryl—N=O
S
M
W


MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM⁻¹
Phosphorus
Sulfur
PH and PH2 in alkyl and aryl phosphines
PH
PH2
(ELECTRONEGATIVE SUBST. RAISES FREQ.)
P=O
C3P=O
(C—O)3P=O
P—OH
Broad
(Single OH)
P—O—P
P—OH
R2PO2−
PO3−
PO43−
P—O—ALIPHATIC
P—O—CH3
P—O—C2H5
P—O—CH(CH3)2
P—O—⬠
P—CH3
P—CH2
P—⬠
P—NH2
P=N CYCLIC
P—N
P=S
PF PHOSPHOFLUORIDATE SALTS
PF ORGANIC
POH
POCH3
POC2H5
P—NH2
P—NH
P—SH··S
C—SH in mercaptans, thiophenols, thiol acids
S—CH2
S—CH3
S—CH=CH2
Sulfoxides
C2SO
Sulfites, dialkyl
(C—O)2SO
(Electronegative subst. raises freq.)
SO2
Sulfones
C—SO2—C
Sulfonamides
C—SO2—N
Anhyd. sulfonic acids
C—SO2—OH
Sulfonate esters
C—SO2—O—C
Dialkyl sulfates
C—O—SO2—O—C
Sulfonyl chlorides
C—SO2—Cl
Sulfonyl fluorides
C—SO2—F
SO2NH2
SO2NH
Anhydrous sulfonic acids
SO2—OH
Sulfonic acid hydrates
—SO3−H3O+
Sulfonate salts
—SO3−
Broad
Sulfinic acids
—S—OH
Acid sulfate
HSO4−
Sulfate
SO42−
Sulfite
SO32−
Sulfinic acids
SO2NH2
SO2—OH


MICRONS
CM⁻¹
Halogen
Silicon
Boron
CF3
CF2
F—aryl
ARYL—Cl
ARYL—Br
CH2Cl
CH2Br
CH2I
meta
para
para + meta
ortho
ortho
C—Cl
C—CH2—CH2—Cl
CCl3
Cyclic equatorial C—Cl
Cyclic axial C—Cl
SiH
C—SiH3
C2—SiH2
C3SiH
Si—CH3
Si—CH2
Si—C2H5
Si—CH=CH2
Si—O—Aliphatic
Si—O—CH3
Si—O—C2H5
Si—O—
Si—O—Si
Infinite siloxane chain
Cyclotrisiloxane
Cycloterasiloxane
(SiO)3
(SiO)4
Si—OH
SiF3
SiF2
SiF
Si—NH—Si
BH2
B···H···B
(BHB bridge)
(Diborane bridge)
B—O
B—N
B—CH3
In borazines, aminoboranes
Si—NH2
BH and BH2 (BH2 doublet)
BH2 in alkyl diboranes
BH in borazines, alkyl diboranes
⊖BH (octet complete)
B-OH (Bonded)
SiH → (Electronegative subst. raises freq.)
C—SiH3 — (C = Alkyl or aryl carbon)
C2—SiH2
C3—SiH
Si—NH2 (doublet)
Si—NH—Si
Si—OH
CF2—C—F
O
C=CF2
CF=CF2

APPENDIX 2

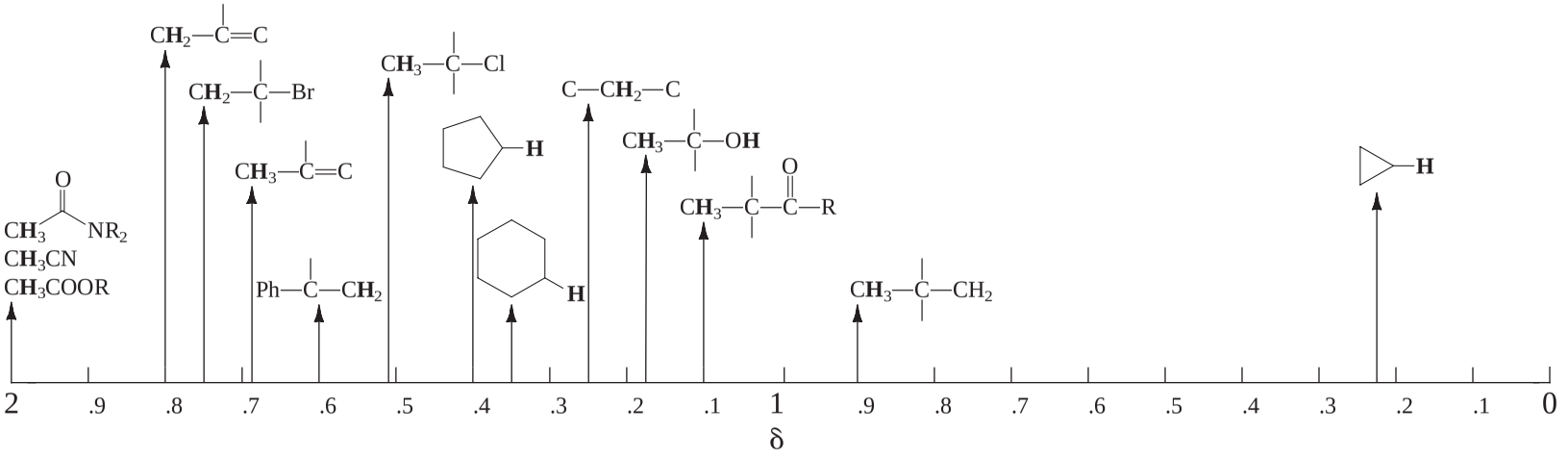
Approximate ^{1}H Chemical Shift Ranges (ppm) for Selected Types of Protons[a]

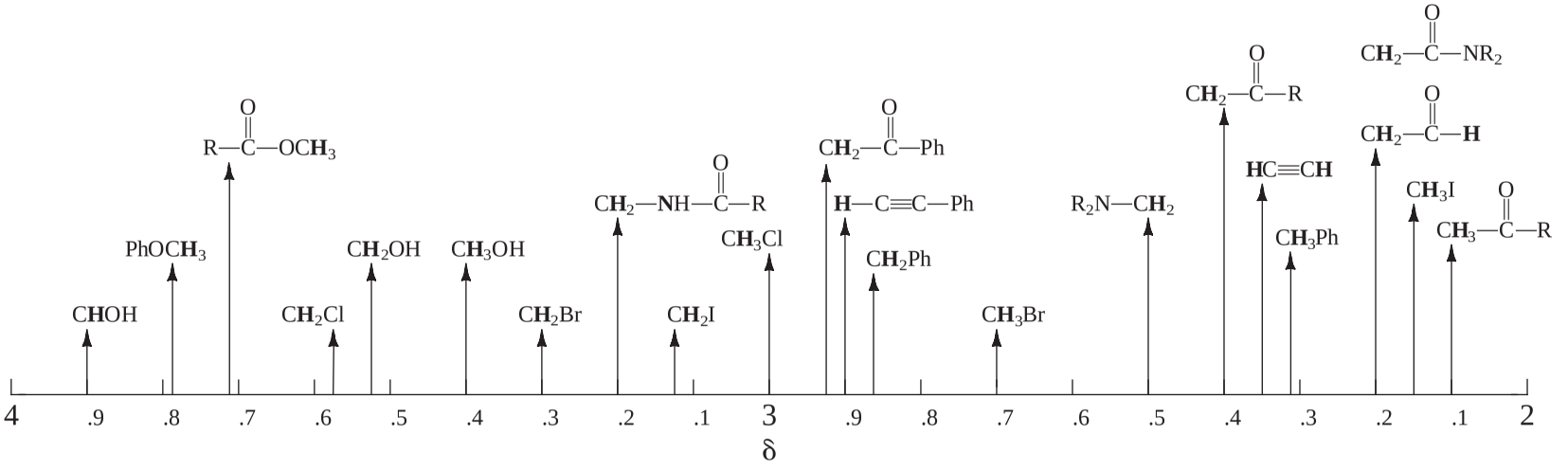
$R-CH_3$		0.7 – 1.3
$R-CH_2-R$		1.2 – 1.4
R_3CH		1.4 – 1.7
		1.6 – 2.6
		2.1 – 2.4
		2.1 – 2.5
		2.1 – 3.0
		2.3 – 2.7
		1.7 – 2.7
	var	1.0 – 4.0[b]
	var	0.5 – 4.0[b]
	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
	var	5.0 – 9.0[b]
		2.2 – 2.9
		2.0 – 3.0
		2.0 – 4.0
		2.7 – 4.1
		3.1 – 4.1
		ca. 3.0
		3.2 – 3.8
		3.5 – 4.8
		4.1 – 4.3
		4.2 – 4.8
		4.5 – 6.5
		6.5 – 8.0
		9.0 – 10.0
		11.0 – 12.0

[a] *For those hydrogens shown as*  *, if that hydrogen is part of a methyl group (CH_3) the shift is generally at the low end of the range given, if the hydrogen is in a methylene group ($-CH_2-$) the shift is intermediate, and if the hydrogen is in a methine group (*  *) the shift is typically at the high end of the range given.*

[b] *The chemical shift of these groups is variable, depending not only on the chemical environment in the molecule, but also on concentration, temperature, and solvent.*

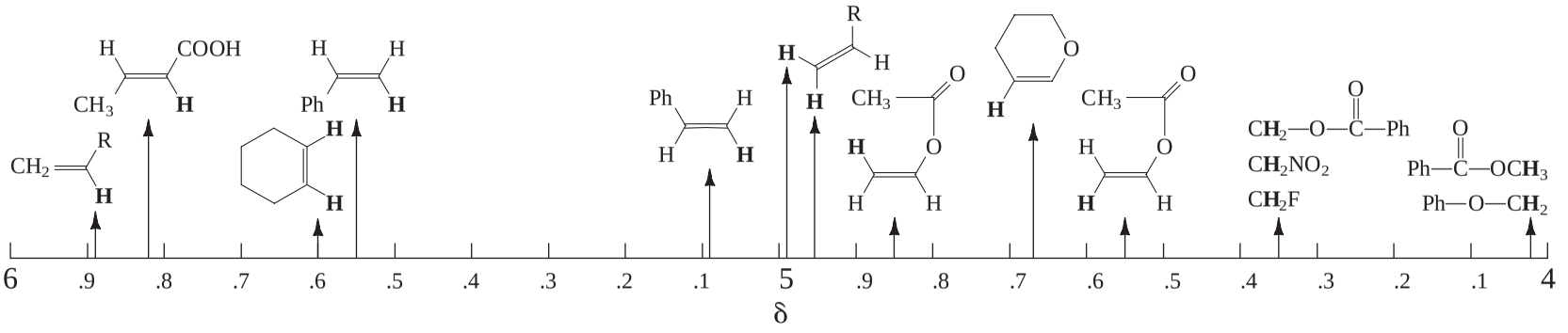
Some Representative ^{1}H Chemical Shift Values[a] for Various Types of Protons[b]

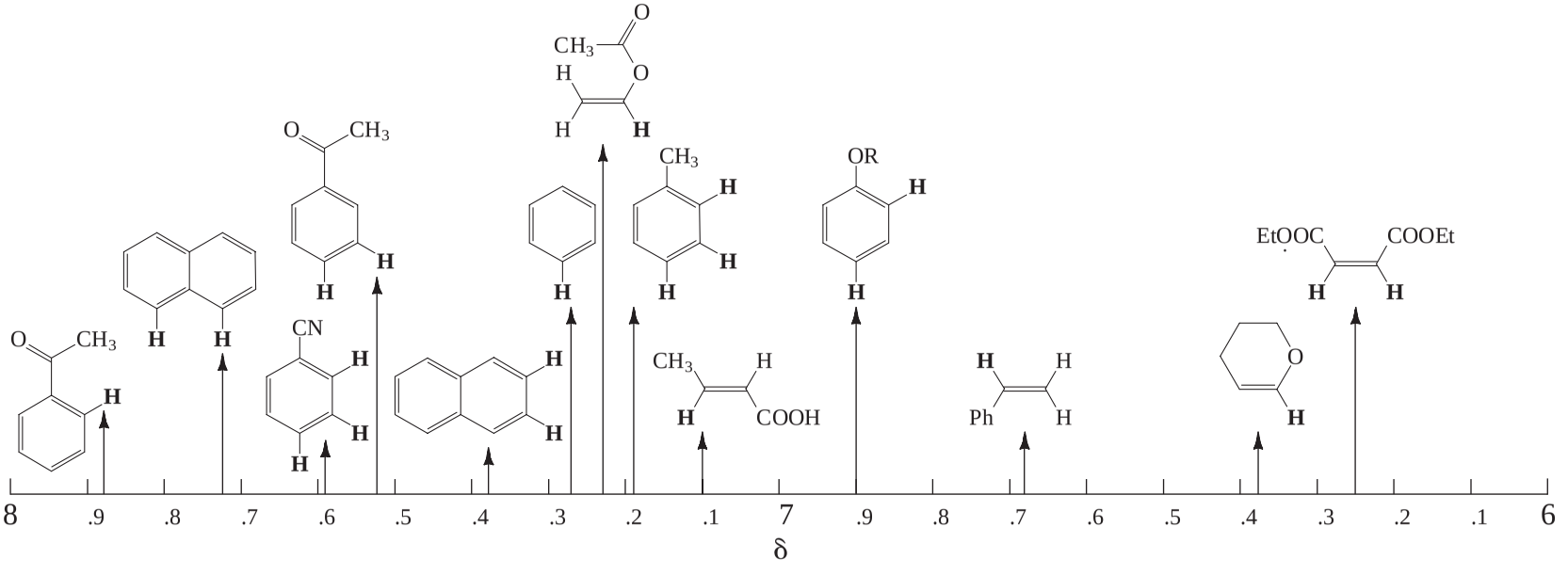


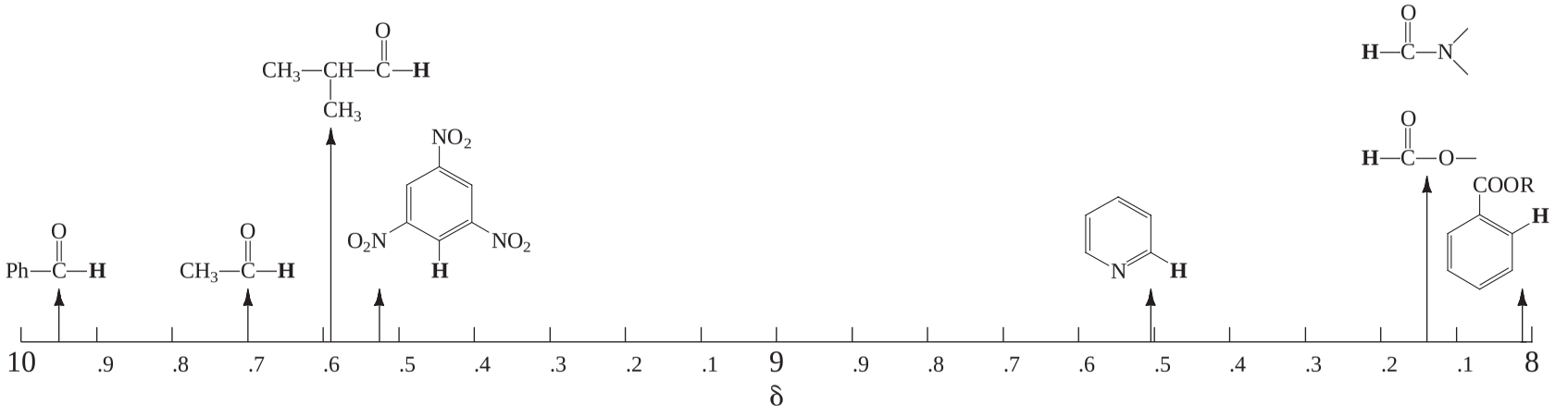


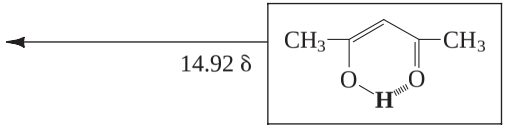
[a]Chemical shift values refer to the boldface protons **H,** not to regular H.

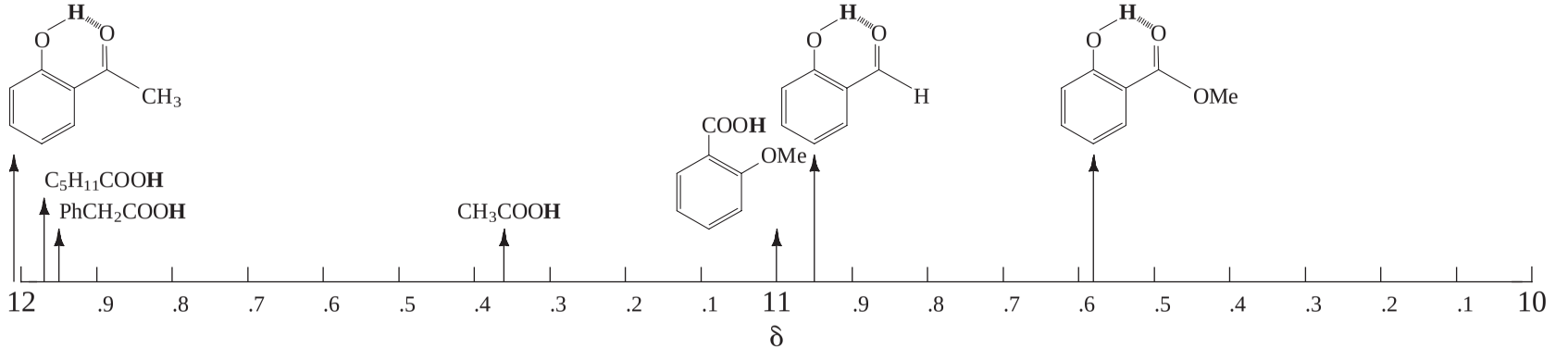
[b]Adapted with permission from Landgrebe, J. A., *Theory and Practice in the Organic Laboratory*, 4th ed., Brooks/Cole Publishing, Pacific Grove, CA, 1993.


6 .9 .8 .7 .6 .5 .4 .3 .2 .1 5 .9 .8 .7 .6 .5 .4 .3 .2 .1 4
δ


8 .9 .8 .7 .6 .5 .4 .3 .2 .1 7 .9 .8 .7 .6 .5 .4 .3 .2 .1 6
δ

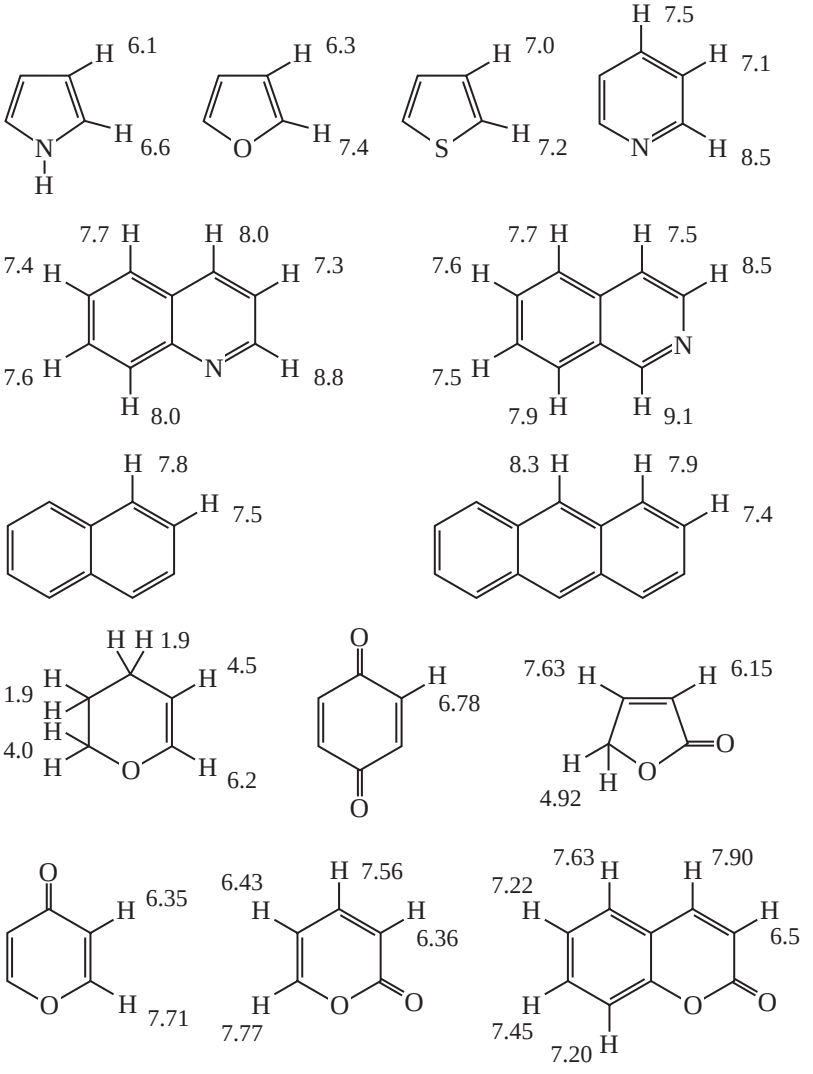

Ph—C—H
CH3—C—H
CH3—CH—C—H
CH3
NO2
O2N
NO2
H
N
H
H—C—N
H—C—O—
COOR
H
10 .9 .8 .7 .6 .5 .4 .3 .2 .1 9 .9 .8 .7 .6 .5 .4 .3 .2 .1 8
δ


14.92 δ
CH3
CH3
O
H
O


CH3
C5H11COOH
PhCH2COOH
CH3COOH
COOH
OMe
H
OMe
12 .9 .8 .7 .6 .5 .4 .3 .2 .1 11 .9 .8 .7 .6 .5 .4 .3 .2 .1 10
δ

A P P E N D I X 4

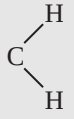
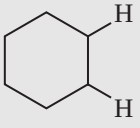
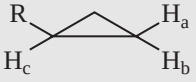
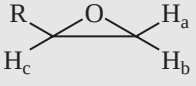
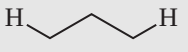
^{1}H Chemical Shifts of Selected Heterocyclic and Polycyclic Aromatic Compounds



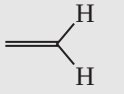
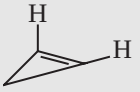
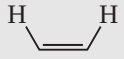
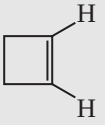
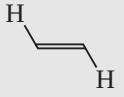
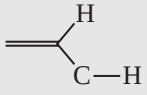
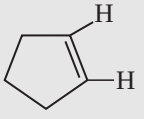
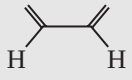
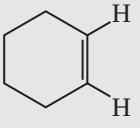
APPENDIX 5

Typical Proton Coupling Constants

ALKANES AND SUBSTITUTED ALKANES

Type			Typical Value (Hz)	Range (Hz)	
	^2J	geminal	12	12–15	(For a 109° H—C—H angle)
	^3J	vicinal	7	6–8	(Depends on HCCH dihedral angle)
	^3J ^3J ^3J	a,a a,e e,e	10 5 3	8–14 0–7 0–5	In conformationally rigid systems (in systems undergoing inversion, all $J \approx 7$–8 Hz)
	^3J ^3J ^2J	*cis* (H_bH_c) *trans* (H_aH_c) *gem* (H_aH_b)	9 6 6	6–12 4–8 3–9	
	^3J ^3J ^2J	*cis* (H_bH_c) *trans* (H_aH_c) *gem* (H_aH_b)	4 2.5 6	2–5 1–3 4–6	
	^4J		0	0–7	(*W*-configuration obligatory—strained systems have the larger values)

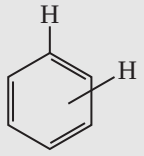
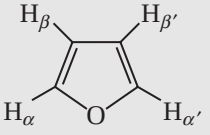
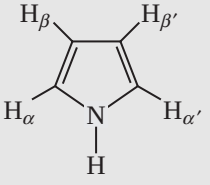
ALKENES AND CYCLOALKENES (^2J AND ^3J)

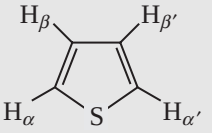
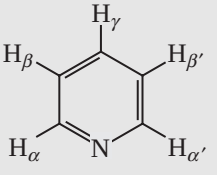
Type		Typical Value (Hz)	Range (Hz)	Type		Typical Value (Hz)	Range (Hz)
	^2J *gem*	<1	0–5		^3J	2	0–2
	^3J *cis*	10	6–15		^3J	4	2–4
	^3J *trans*	16	11–18				
	^3J	5	4–10		^3J	6	5–7
	^3J	10	9–13		^3J	10	8–11

ALKENES AND ALKYNES (^4J AND ^5J)

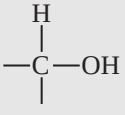
Type		Typical Value (Hz)	Range (Hz)	Type		Typical Value (Hz)	Range (Hz)
H−C=C−C−H Allylic	^4J (*cis* or *trans*)	1	0–3	H−C≡C−C−H Allylic	^4J	2	2–3
H−C−C=C−C−H Homoallylic	^5J	0	0–1.5	H−C−C≡C−C−H Homoallylic	^5J	2	2–3

AROMATICS AND HETEROCYCLES

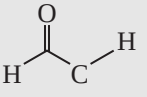
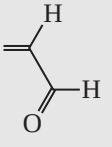
Type		Typical Value (Hz)	Range (Hz)
	^3J *ortho*	8	6–10
	^4J *meta*	3	1–4
	^5J *para*	<1	0–2
	^3J $\alpha\beta$		1.6–2.0
	^4J $\alpha\beta'$		0.3–0.8
	^4J $\alpha\alpha'$		1.3–1.8
	^3J $\beta\beta'$		3.2–3.8
	^3J $\alpha\beta$		2.0–2.6
	^4J $\alpha\beta'$		1.0–1.5
	^4J $\alpha\alpha'$		1.8–2.3
	^3J $\beta\beta'$		2.8–4.0

Type		Range (Hz)
	^3J $\alpha\beta$	4.6–5.8
	^4J $\alpha\beta'$	1.0–1.5
	^4J $\alpha\alpha'$	2.1–3.3
	^3J $\beta\beta'$	3.0–4.2
	^3J $\alpha\beta$	4.9–5.7
	^4J $\alpha\gamma$	1.6–2.0
	^5J $\alpha\beta'$	0.7–1.1
	^4J $\alpha\alpha'$	0.2–0.5
	^3J $\beta\gamma$	7.2–8.5
	^4J $\beta\beta'$	1.4–1.9

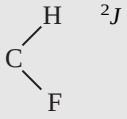
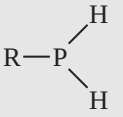
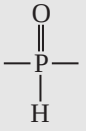
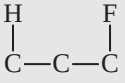
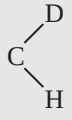
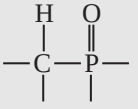
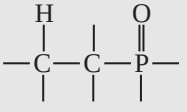
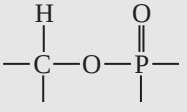
ALCOHOLS

Type		Typical Value (Hz)	Range (Hz)
	^3J	5	4–10
(No exchange occurring)			

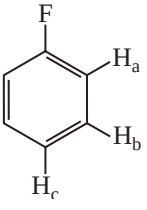
ALDEHYDES

Type		Typical Value (Hz)	Range (Hz)
	^3J	2	1–3
	^3J	6	5–8

PROTON–OTHER NUCLEUS COUPLING CONSTANTS

Type		Typical Value (Hz)	Type		Typical Value (Hz)	Type	Typical Value (Hz)
	^2J	44–81		^1J	~190	N—H	~52
							0
	^3J	3–25		^1J	~650		
	^4J	~0					
	^2J	~2		^2J	~13		
	^3J	<1 (Leads only to peak broadening)		^3J	~17		
				^3J	~8		

Example:



7.03 ppm, doublet of douiblets 2H (H_aH_b = 8.8 Hz, ^3J H_aF = 8.9 Hz). Looks like a triplet with fine structure

7.30 ppm, triplet of doublets, 2H (H_bH_a and H_bH_c = 7.8, ^4J H_bF = 5.8. Looks like a quartet, with fine structure

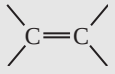
7.10 ppm, triplet of doublets 1H (H_cH_b = 7.4, ^5JH_cF = 0.8. Looks like a triplet

APPENDIX 6

Calculation of Proton (^{1}H) Chemical Shifts

TABLE A6.1
^{1}H CHEMICAL-SHIFT CALCULATIONS FOR DISUBSTITUTED METHYLENE COMPOUNDS

$X-CH_2-X$ or $X-CH_2-Y$ $\quad \delta_H$ ppm = 0.23 + Σ constants

Substituents	Constants	Substituents	Constants
Alkanes, alkenes, alkynes, aromatics		Bonded to oxygen	
−R	0.47	−OH	2.56
	1.32	−OR	2.36
−C≡C−	1.44	−OCOR	3.13
$-C_6H_5$	1.85	$-OC_6H_5$	3.23
Bonded to nitrogen and sulfur		Bonded to halogen	
$-NR_2$	1.57	−F	4.00
−NHCOR	2.27	−Cl	2.53
$-NO_2$	3.80	−Br	2.33
−SR	1.64	−I	1.82
Ketones		Derivatives of carboxylic acids	
−COR	1.70	−COOR	1.55
$-COC_6H_5$	1.84	$-CONR_2$	1.59
		−C≡N	1.70

Example Calculations

The formula allows you to calculate the *approximate* chemical-shift values for protons (^{1}H) based on methane (0.23 ppm). Although it is possible to calculate chemical shifts for any proton (methyl, methylene, or methine), agreement with actual experimental values is best with *disubstituted* compounds of the type $X-CH_2-Y$ or $X-CH_2-X$.

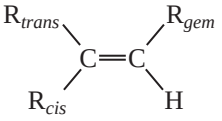
$Cl-\mathbf{CH_2}-Cl$ $\quad \delta_H = 0.23 + 2.53 + 2.53 = 5.29$ ppm; actual = 5.30 ppm

$C_6H_5-\mathbf{CH_2}-O-\overset{\overset{O}{\|}}{C}-CH_3$ $\quad \delta_H = 0.23 + 1.85 + 3.13 = 5.21$ ppm; actual = 5.10 ppm

$C_6H_5-\mathbf{CH_2}-\overset{\overset{O}{\|}}{C}-O-CH_3$ $\quad \delta_H = 0.23 + 1.85 + 1.55 = 3.63$ ppm; actual = 3.60 ppm

$CH_3-CH_2-\mathbf{CH_2}-NO_2$ $\quad \delta_H = 0.23 + 3.80 + 0.47 = 4.50$ ppm; actual = 4.38 ppm

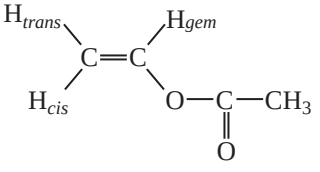
TABLE A6.2
^{1}H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED ALKENES



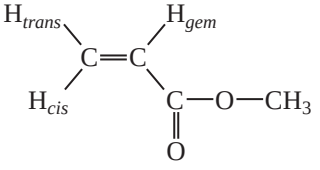
$$\delta_H \text{ ppm} = 5.25 + \delta_{gem} + \delta_{cis} + \delta_{trans}$$

Substituents (−R)	δ_{gem}	δ_{cis}	δ_{trans}
Saturated carbon groups			
Alkyl	0.44	–0.26	–0.29
$-CH_2-O-$	0.67	–0.02	–0.07
Aromatic groups			
$-C_6H_5$	1.35	0.37	–0.10
Carbonyl, acid derivatives, and nitrile			
COR	1.10	1.13	0.81
−COOH	1.00	1.35	0.74
−COOR	0.84	1.15	0.56
$-C\equiv N$	0.23	0.78	0.58
Oxygen groups			
−OR	1.18	–1.06	–1.28
−OCOR	2.09	–0.40	–0.67
Nitrogen groups			
$-NR_2$	0.80	–1.26	–1.21
$-NO_2$	1.87	1.30	0.62
Halogen groups			
−F	1.54	–0.40	–1.02
−Cl	1.08	0.19	0.13
−Br	1.04	0.40	0.55
−I	1.14	0.81	0.88

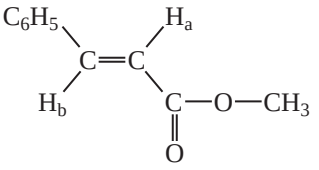
Example Calculations



H_{gem} = 5.25 + 2.09 = 7.34 ppm; actual = 7.25 ppm
H_{cis} = 5.25 – 0.40 = 4.85 ppm; actual = 4.85 ppm
H_{trans} = 5.25 – 0.67 = 4.58 ppm; actual = 4.55 ppm



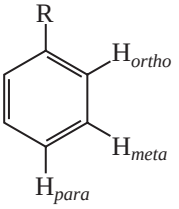
H_{gem} = 5.25 + 0.84 = 6.09 ppm; actual = 6.14 ppm
H_{cis} = 5.25 + 1.15 = 6.40 ppm; actual = 6.42 ppm
H_{trans} = 5.25 + 0.56 = 5.81 ppm; actual = 5.82 ppm



H_a { δ_{gem} for $-COOR = 0.84$; δ_{cis} for $-C_6H_5 = 0.37$; $H_a = 5.25 + 0.84 + 0.37 = 6.46$ ppm; actual = 6.43 ppm

H_b { δ_{gem} for $-C_6H_5 = 1.35$; δ_{cis} for $-COOR = 1.15$; $H_b = 5.25 + 1.35 + 1.15 = 7.75$ ppm; actual = 7.69 ppm

TABLE A6.3
^{1}H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED BENZENE RINGS

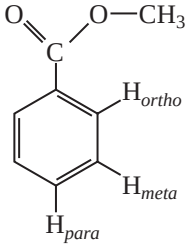


$$\delta_H \text{ ppm} = 7.27 + \Sigma\delta$$

Substituents (−R)	δ_{ortho}	δ_{meta}	δ_{para}
Saturated carbon groups			
Alkyl	–0.14	–0.06	–0.17
$-CH_2OH$	–0.07	–0.07	–0.07
Aldehydes and ketones			
−CHO	0.61	0.25	0.35
−COR	0.62	0.14	0.21
Carboxylic acids and derivatives			
−COOH	0.85	0.18	0.34
−COOR	0.71	0.10	0.21
−C≡N	0.25	0.18	0.30
Oxygen groups			
−OH	–0.53	–0.17	–0.45
$-OCH_3$	–0.48	–0.09	–0.44
$-OCOCH_3$	–0.19	–0.03	–0.19
Nitrogen groups			
$-NH_2$	–0.80	–0.25	–0.65
$-NO_2$	0.95	0.26	0.38
Halogen groups			
−F	–0.29	–0.02	–0.23
−C1	0.03	–0.02	–0.09
−Br	0.18	–0.08	–0.04
−I	0.38	–0.23	–0.01

Example Calculations

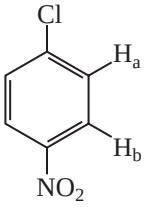
The formula allows you to calculate the *approximate* chemical-shift values for protons (^{1}H) on a benzene ring. Although the values given in the table are for *monosubstituted benzenes*, it is possible to estimate chemical shifts for disubstituted and trisubstituted compounds by adding values from the table. The calculations for *meta*- and *para*-disubstituted benzenes often agree closely with actual values. More significant deviations from the experimental values are expected with *ortho*-disubstituted and trisubstituted benzenes. With these types of compounds, steric interactions cause groups such as carbonyl and nitro to turn out of the plane of the ring and thereby lose conjugation. Calculated values are often lower than the actual chemical shifts for *ortho*-disubstituted and trisubstituted benzenes.



$H_{ortho} = 7.27 + 0.71 = 7.98$ ppm; actual = 8.03 ppm

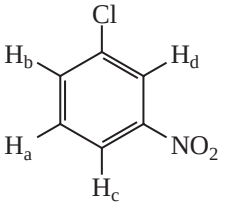
$H_{meta} = 7.27 + 0.10 = 7.37$ ppm; actual = 7.42 ppm

$H_{para} = 7.27 + 0.21 = 7.48$ ppm; actual = 7.53 ppm



H_a { δ_{ortho} for $-Cl = 0.03$; δ_{meta} for $-NO_2 = 0.26$; $H_a = 7.27 + 0.03 + 0.26 = 7.56$ ppm; actual = 7.50 ppm

H_b { δ_{meta} for $-Cl = -0.02$; δ_{ortho} for $-NO_2 = 0.95$; $H_b = 7.27 - 0.02 + 0.95 = 8.20$ ppm; actual = 8.20 ppm



H_a { δ_{meta} for $-Cl = -0.02$; δ_{meta} for $-NO_2 = 0.26$; $H_a = 7.27 - 0.02 + 0.26 = 7.51$ ppm; actual = 7.51 ppm

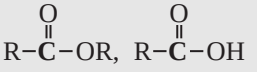
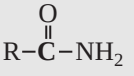
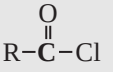
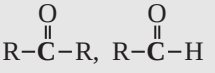
H_b { δ_{ortho} for $-Cl = 0.03$; δ_{para} for $-NO_2 = 0.38$; $H_b = 7.27 + 0.03 + 0.38 = 7.68$ ppm; actual = 7.69 ppm

H_c { δ_{para} for $-Cl = -0.09$; δ_{ortho} for $-NO_2 = 0.95$; $H_c = 7.27 - 0.09 + 0.95 = 8.13$ ppm; actual = 8.12 ppm

H_d { δ_{ortho} for $-Cl = 0.03$; δ_{ortho} for $-NO_2 = 0.95$; $H_d = 7.27 + 0.03 + 0.95 = 8.25$ ppm; actual = 8.21 ppm

APPENDIX 7

Approximate ^{13}C Chemical-Shift Values (ppm) for Selected Types of Carbon

Types of Carbon	Range (ppm)	Types of Carbon	Range (ppm)
R−**C**H$_3$	8–30	**C**≡**C**	65–90
R$_2$**C**H$_2$	15–55	**C**=**C**	100–150
R$_3$**C**H	20–60	**C**≡N	110–140
C−I	0–40		110–175
C−Br	25–65		155–185
C−N	30–65		155–185
C−Cl	35–80		160–170
C−O	40–80		185–220

APPENDIX 8

Calculation of ^{13}C Chemical Shifts

TABLE A8.1
^{13}C CHEMICAL SHIFTS OF SELECTED HYDROCARBONS (PPM)

Compound	Formula	C1	C2	C3	C4	C5
Methane	CH_4	–2.3				
Ethane	CH_3CH_3	5.7				
Propane	$CH_3CH_2CH_3$	15.8	16.3			
Butane	$CH_3CH_2CH_2CH_3$	13.4	25.2			
Pentane	$CH_3CH_2CH_2CH_2CH_3$	13.9	22.8	34.7		
Hexane	$CH_3(CH_2)_4CH_3$	14.1	23.1	32.2		
Heptane	$CH_3(CH_2)_5CH_3$	14.1	23.2	32.6	29.7	
Octane	$CH_3(CH_2)_6CH_3$	14.2	23.2	32.6	29.9	
Nonane	$CH_3(CH_2)_7CH_3$	14.2	23.3	32.6	30.0	30.3
Decane	$CH_3(CH_2)_8CH_3$	14.2	23.2	32.6	31.1	30.5
2-Methylpropane		24.5	25.4			
2-Methylbutane		22.2	31.1	32.0	11.7	
2-Methylpentane		22.7	28.0	42.0	20.9	14.3
2,2-Dimethylpropane		31.7	28.1			
2,2-Dimethylbutane		29.1	30.6	36.9	8.9	
2,3-Dimethylbutane		19.5	34.4			
Ethylene	$CH_2{=}CH_2$	123.3				
Cyclopropane		–3.0				
Cyclobutane		22.4				
Cyclopentane		25.6				
Cyclohexane		26.9				
Cycloheptane		28.4				
Cyclooctane		26.9				
Cyclononane		26.1				
Cyclodecane		25.3				
Benzene		128.5				

TABLE A8.2
^{13}C CHEMICAL-SHIFT CALCULATIONS FOR LINEAR AND BRANCHED ALKANES

$$\delta_C = -2.3 + 9.1\alpha + 9.4\beta - 2.5\gamma + 0.3\delta + 0.1\varepsilon + \Sigma \text{ (steric corrections) ppm}$$

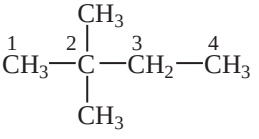
α, β, γ, δ, and ε are the numbers of carbon atoms in the α, β, γ, δ, and ε positions relative to the carbon atom being observed.

$$\cdots\cdots C_\varepsilon - C_\delta - C_\gamma - C_\beta - C_\alpha - \mathbf{C} - C_\alpha - C_\beta - C_\gamma - C_\delta - C_\varepsilon \cdots\cdots$$

Steric corrections are derived from the following table (use all that apply, even if they apply more than once).

Steric Corrections (ppm)				
	Type of Carbons Attached			
Carbon Atom Observed	**Primary**	**Secondary**	**Tertiary**	**Quaternary**
Primary	0	0	–1.1	–3.4
Secondary	0	0	–2.5	–7.5
Tertiary	0	–3.7	–8.5	–10.0
Quaternary	–1.5	–8.4	–10.0	–12.5

Example



2,2-Dimethylbutane

Actual values: C1 29.1 ppm
C2 30.6 ppm
C3 36.9 ppm
C4 8.9 ppm

C1 = –2.3 + 9.1(1) + 9.4(3) – 2.5(1) + 0.3(0) + 0.1(0) **+ [1(–3.4)]** = 29.1 ppm
Steric correction (boldface) = primary with 1 adjacent quaternary

C2 = –2.3 + 9.1(4) + 9.4(1) – 2.5(0) + 0.3(0) + 0.1(0) **+ [3(–1.5)] + [1(–8.4)]** = 30.6 ppm
Steric corrections = quaternary/3 adj. primary, and quaternary/1 adj. secondary

C3 = –2.3 + 9.1(2) + 9.4(3) – 2.5(0) + 0.3(0) + 0.1(0) **+ [1(0)] + [1(–7.5)]** = 36.6 ppm
Steric corrections = secondary/1 adj. primary, and secondary/1 adj. quaternary

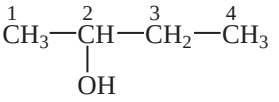
C4 = –2.3 + 9.1(1) + 9.4(1) – 2.5(3) + 0.3(0) + 0.1(0) **+ [1(0)]** = 8.7 ppm
Steric correction = primary/1 adj. secondary

TABLE A8.3
^{13}C SUBSTITUENT INCREMENTS FOR ALKANES AND CYCLOALKANES (PPM)[a]

	Terminal: Y−C_α−C_β−C_γ			*Internal*: C_γ−C_β−C_α(Y)−C_β−C_γ		
Substituent Y	α	β	γ	α	β	γ
−D	–0.4	–0.1	0			
−CH_3	9	10	–2	6	8	–2
−CH=CH_2	19.5	6.9	–2.1			–0.5
−C≡CH	4.5	5.4	–3.5			–3.5
−C_6H_5	22.1	9.3	–2.6	17	7	–2
−CHO	29.9	–0.6	–2.7			
−$COCH_3$	30	1	–2	24	1	–2
−COOH	20.1	2	–2.8	16	2	–2
−COOR	22.6	2	–2.8	17	2	–2
−$CONH_2$	22	2.5	–3.2			–0.5
−CN	3.1	2.4	–3.3	1	3	–3
−NH_2	29	11	–5	24	10	–5
−NHR	37	8	–4	31	6	–4
−NR_2	42	6	–3			–3
−NO_2	61.6	3.1	–4.6	57	4	
−OH	48	10	–6.2	41	8	–5
−OR	58	8	–4	51	5	–4
−$OCOCH_3$	56.5	6.5	–6.0	45	5	–3
−F	70.1	7.8	–6.8	63	6	–4
−Cl	31	10	–5.1	32	10	–4
−Br	20	11	–3	25	10	–3
−I	–7.2	10.9	–1.5	4	12	–1

[a]*Add these increments to the values given in Table A8.1.*

Example 1

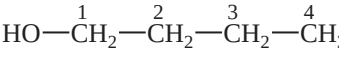


2-Butanol

Using the values for butane listed in Table A8.1 and the internal substituent corrections from Table A8.3, we calculate:

	Actual value
C1 = 13.4 + 8 = 21.4 ppm	22.6 ppm
C2 = 25.2 + 41 = 66.2 ppm	68.7 ppm
C3 = 25.2 + 8 = 33.2 ppm	32.0 ppm
C4 = 13.4 + (–5) = 8.4 ppm	9.9 ppm

Example 2

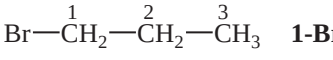


1-Butanol

Using the values for butane listed in Table A8.1 and the terminal substituent corrections from Table A8.3, we calculate:

	Actual value
C1 = 13.4 + 48 = 61.4 ppm	61.4 ppm
C2 = 25.2 + 10 = 35.2 ppm	35.0 ppm
C3 = 25.2 + (–6.2) = 19.0 ppm	19.1 ppm
C4 = 13.4 = 13.4 ppm	13.6 ppm

Example 3

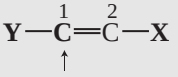


1-Bromopropane

Using the values for propane listed in Table A8.1 and the terminal substituent corrections from Table A8.3, we calculate:

	Actual value
C1 = 15.8 + 20 = 35.8 ppm	35.7 ppm
C2 = 16.3 + 11 = 27.3 ppm	26.8 ppm
C3 = 15.8 + (–3) = 12.8 ppm	13.2 ppm

TABLE A8.4
^{13}C SUBSTITUENT INCREMENTS FOR ALKENES (PPM)[a,b]



Substituent	Y	X
−H	0	0
$-CH_3$	12.9	–7.4
$-CH_2CH_3$	19.2	–9.7
$-CH_2CH_2CH_3$	15.7	–8.8
$-CH(CH_3)_2$	22.7	–12.0
$-C(CH_3)_3$	26.0	–14.8
$-CH=CH_2$	13.6	–7
$-C_6H_5$	12.5	–11
$-CH_2Cl$	10.2	–6.0
$-CH_2Br$	10.9	–4.5
$-CH_2I$	14.2	–4.0
$-CH_2OH$	14.2	–8.4
−COOH	5.0	9.8
$-NO_2$	22.3	–0.9
$-OCH_3$	29.4	–38.9
$-OCOCH_3$	18.4	–26.7
−CN	–15.1	14.2
−CHO	15.3	14.5
$-COCH_3$	13.8	4.7
−COCl	8.1	14.0
$-Si(CH_2)_3$	16.9	6.7
−F	24.9	–34.3
−Cl	2.6	–6.1
−Br	–8.6	–0.9
−I	–38.1	7.0

[a]*Corrections for C1; add these increments to the base value of ethylene (123.3 ppm).*

[b]*Calculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.*

Example 1

$$\mathrm{Br{-}\overset{1}{C}H{=}\overset{2}{C}H{-}\overset{3}{C}H_3}$$ **1-Bromopropene**

	Actual values	
	cis	*trans*
C1 = 123.3 + (–8.6) + (–7.4) = 107.3 ppm	108.9	104.7 ppm
C2 = 123.3 + 12.9 + (–0.9) = 135.3 ppm	129.4	132.7 ppm

Example 2

$$\mathrm{HOO\overset{1}{C}{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_3}$$ **Crotonic acid**

	Actual value (*trans*)
C2 = 123.3 + 5 + (–7.4) = 120.9 ppm	122.0 ppm
C3 = 123.3 + 12.9 + 9.8 = 146.0 ppm	147.0 ppm

TABLE A8.5
^{13}C CHEMICAL-SHIFT CALCULATIONS FOR LINEAR AND BRANCHED ALKENES[a]

$$\delta_{C1} = 123.3 + [10.6\alpha + 7.2\beta - 1.5\gamma] - [7.9\alpha' + 1.8\beta' - 1.5\gamma'] + \Sigma \text{ (steric corrections)}$$

α, β, γ and α', β', γ' are the numbers of carbon atoms in those same positions relative to C1:

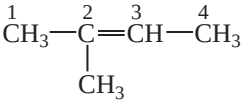
$$\mathrm{C\gamma{-}C\beta{-}C\alpha{-}\overset{1}{\underset{\uparrow}{C}}{=}\overset{2}{C}{-}C\alpha'{-}C\beta'{-}C\gamma'}$$

Steric corrections are applied as follows (use all that apply):

Cα and Cα' are *trans* (*E*-configuration)	0
Cα and Cα' are *cis* (*Z*-configuration)	–1.1
Two alkyl substituents at C1 (two Cα)	–4.8
Two alkyl substituents at C2 (two Cα')	+2.5
Two or three alkyl substituents at Cβ	+2.3

[a]*Calculate C1 as shown in the diagram. Redefine C2 as C1 when calculating values for C2.*

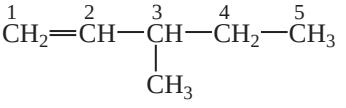
Example 1



2-Methyl-2-butene

	Actual value
C2 = 123.3 + [10.6(2)] – [7.9(1)] + [(–4.8) + (–1.1)] = 130.7 ppm	131.4 ppm
C3 = 123.3 + [10.6(1)] – [7.9(2)] + [(+2.5) + (–1.1)] = 119.5 ppm	118.7 ppm

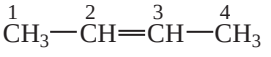
Example 2



3-Methyl-1-pentene

		Actual value
C1 = 123.3 + [0] – [7.9(1) + 1.8(2) – 1.5(1)]	= 113.3 ppm	112.9 ppm
C2 = 123.3 + [10.6(1) + 7.2(2) – 1.5(1)] – [0] + [(+2.3)]	= 149.1 ppm	144.9 ppm

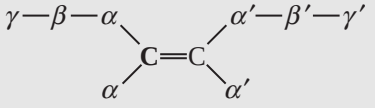
Example 3



2-Butene

		Actual value
C2 (*cis* isomer) = C3 = 123.3 + [10.6(1)] – [7.9(1)] + [(–1.1)]	= 124.9 ppm	124.6 ppm
C2 (*trans* isomer) = C3 = 123.3 + [10.6(1)] – [7.9(1)] + [0]	= 126.0 ppm	126.0 ppm

TABLE A8.6
^{13}C SUBSTITUENT INCREMENTS FOR ALKENE (VINYL) CARBONS[a,b]

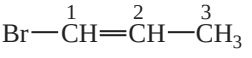


Substituent	α	β	γ	α′	β′	γ′
Carbon	10.6	7.2	–1.5	–7.9	–1.8	–1.5
$-C_6H_5$	12			–11		
−OR	29	2		–39	–1	
−OCOR	18			–27		
−COR	15			6		
−COOH	4			9		
−CN	–16			15		
−Cl	3	–1		–6	2	
−Br	–8	0		–1	2	
−I	–38			7		

[a] *In the upper chains, if a group is in the β or γ position, the preceding atoms (α and/or β) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3 ppm).*

[b] *Calculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.*

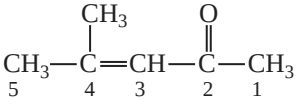
Example 1



1-Bromopropene

	Actual values	
	cis	*trans*
C1 = 123.3 – 8 – 7.9 = 107.4 ppm	108.9	104.7 ppm
C2 = 123.3 + 10.6 – 1 = 132.9 ppm	129.4	132.7 ppm

Example 2



Mesityl oxide

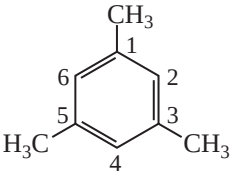
	Actual value
C3 = 123.3 + 15 – 7.9 – 7.9 = 122.5 ppm	124.3 ppm
C4 = 123.3 + 10.6 + 10.6 + 6 = 150.5 ppm	154.6 ppm

TABLE A8.7
^{13}C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)[a]

Substituent Y	α (*ipso*)	o (*ortho*)	m (*meta*)	p (*para*)
$-CH_3$	9.3	0.7	–0.1	–2.9
$-CH_2CH_3$	11.7	–0.5	0	–2.6
$-CH(CH_2)_2$	20.1	–2.0	–0.3	–2.5
$-C(CH_3)_3$	18.6	–3.4	–0.4	–3.1
$-CH{=}CH_2$	9.1	–2.4	0.2	–0.5
$-C{\equiv}CH$	–6.2	3.6	–0.4	–0.3
$-C_6H_5$	8.1	–1.1	–0.5	–1.1
$-CHO$	8.2	1.2	0.6	5.8
$-COCH_3$	8.9	–0.1	–0.1	4.4
$-COC_6H_5$	9.1	1.5	–0.2	3.8
$-COOH$	2.1	1.6	–0.1	5.2
$-COOCH_3$	2.0	1.2	–0.1	4.3
$-CN$	–16.0	3.6	0.6	4.3
$-NH_2$	18.2	–13.4	0.8	–10.0
$-N(CH_3)_2$	16.0	–15.7	0.8	–10.5
$-NHCOCH_3$	9.7	–8.1	0.2	–4.4
$-NO_2$	19.6	–4.9	0.9	6.0
$-OH$	28.8	–12.7	1.6	–7.3
$-OCH_3$	33.5	–14.4	1.0	–7.7
$-OCOCH_3$	22.4	–7.1	–0.4	–3.2
$-F$	33.6	–13.0	1.6	–4.5
$-Cl$	5.3	0.4	1.4	–1.9
$-Br$	–5.4	3.4	2.2	–1.0
$-I$	–31.2	8.9	1.6	–1.1

[a]*Add these increments to the base value for benzene-ring carbons (128.5 ppm).*

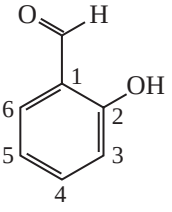
Example 1



Mesitylene

	Observed
C1,C3,C5 = 128.5 + 9.3 – 0.1 – 0.1 = 137.6 ppm	137.4 ppm
C2,C4,C6 = 128.5 + 0.7 + 0.7 – 2.9 = 127.0 ppm	127.1 ppm

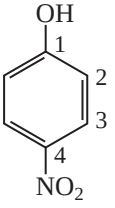
Example 2



Salicylaldehyde

	Observed
C1 = 128.5 + 8.2 – 12.7 = 124.0 ppm	121.0 ppm
C2 = 128.5 + 28.8 + 1.2 = 158.5 ppm	161.4 ppm
C3 = 128.5 – 12.7 + 0.6 = 116.4 ppm	117.4 ppm
C4 = 128.5 + 1.6 + 5.8 = 135.9 ppm	136.6 ppm
C5 = 128.5 – 7.3 + 0.6 = 121.8 ppm	119.6 ppm
C6 = 128.5 + 1.2 + 1.6 = 131.3 ppm	133.6 ppm

Example 3



4-Nitrophenol

	Observed
C1 = 128.5 + 28.8 + 6.0 = 163.3 ppm	161.5 ppm
C2 = 128.5 – 12.7 + 0.9 = 116.7 ppm	115.9 ppm
C3 = 128.5 + 1.6 – 4.9 = 125.2 ppm	126.4 ppm
C4 = 128.5 + 19.6 + 7.3 = 140.8 ppm	141.7 ppm

APPENDIX 9

^{13}C Coupling Constants

^{13}C–proton coupling constants (^1J)

sp^3	^{13}C−H	115–125 Hz
sp^2	^{13}C−H	150–170 Hz
sp	^{13}C−H	250–270 Hz

^{13}C–proton coupling constants (^2J)

^{13}C−C−H		0–60 Hz

^{13}C–deuterium coupling constants (^1J)

^{13}C−D		20–30 Hz

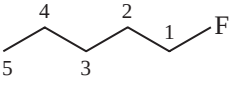
^{13}C–fluorine coupling constants (^1J)

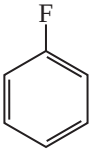
^{13}C−F		165–370 Hz

^{13}C–fluorine coupling constants (^2J)

^{13}C−C−F		18–45 Hz

Example





C1 162.9 ppm, doublet, ^{1}J = 245 Hz
C2 115.3 ppm, doublet, ^{2}J = 20.7 Hz
C3 129.9 ppm, doublet, ^{3}J = 8.5 Hz
C4 124.0 ppm, doublet, ^{4}J = 2.5 Hz

C1 = 84.2 ppm, doublet, ^{1}J = 165 Hz
C2 = 30.2 ppm, doublet, ^{2}J = 19.5 Hz
C3 = 27.4 ppm, doublet, ^{3}J = 6.1 Hz
C4 = 22.4 ppm, singlet, ^{4}J = 0 Hz
C5 = 13.9 ppm, singlet, ^{5}J = 0 Hz

^{13}C–phosphorus coupling constants (^1J)

^{13}C−P		48–56 Hz

^{13}C–phosphorus coupling constants (^2J)

^{13}C−C−P		4–6 Hz

Example

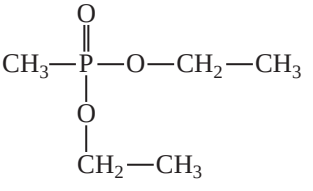
$(CH_3-CH_2)_4P^+X^-$

^{13}C–phosphorus coupling constants (^1J)

^{13}C−P		143 Hz

^{13}C–phosphorus coupling constants (^2J and ^3J)

^{13}C−O−P		6–7 Hz
^{13}C−C−O−P		6–7 Hz



APPENDIX 10

^{1}H and ^{13}C Chemical Shifts for Common NMR Solvents

TABLE A10.1
^{1}H CHEMICAL-SHIFT VALUES (PPM) FOR SOME COMMON NMR SOLVENTS

Solvent	Deuterated Form	Chemical Shift (Multiplicity)[a]
Acetone	Acetone-d_6	2.05 (5)
Acetonitrile	Acetonitrile-d_3	1.93 (5)
Benzene	Benzene-d_6	7.15 (broad)
Carbon tetrachloride	—	—
Chloroform	Chloroform-d	7.25 (1)
Dimethylsulfoxide	Dimethylsulfoxide-d_6	2.49 (5)
Water	Deuterium oxide	4.82 (1)
Methanol	Methanol-d_4	4.84 (1) hydroxyl
		3.30 (5) methyl
Methylene chloride	Methylene chloride-d_2	5.32 (3)

[a]*Where multiplets apply, the center peak is given and the number of lines is indicated in parentheses. No proton peak should be observed in the completely deuterated solvents listed. However, multiplets will arise from coupling of a proton with deuterium because the solvents are not 100% isotopically pure. For example, acetone-d_6 has a trace of acetone-d_5 in it, while $CDCl_3$ has some $CHCl_3$ present.*

TABLE A10.2
^{13}C CHEMICAL-SHIFT VALUES FOR SOME COMMON NMR SOLVENTS (PPM)

Solvent	Deuterated Form	Chemical Shift (Multiplicity)[a]
Acetone	Acetone-d_6	206.0 (1) carbonyl
		29.8 (7) methyl
Acetonitrile	Acetonitrile-d_3	118.3(1) CN
		1.3(7) methyl
Benzene	Benzene-d_6	128.0 (3)
Chloroform	Chloroform-d	77.0 (3)
Dimethylsulfoxide	Dimethylsulfoxide-d_6	39.5 (7)
Dioxane	Dioxane-d_8	66.5 (5)
Methanol	Methanol-d_4	49.0 (7)
Methylene chloride	Methylene chloride-d_2	54.0 (5)

[a]*Where multiplets apply, the center peak is given and the number of lines is indicated in parentheses. These multiplets arise from the coupling of carbon with the deuterium.*

APPENDIX 11

Tables of Precise Masses and Isotopic Abundance Ratios for Molecular Ions under Mass 100 Containing Carbon, Hydrogen, Nitrogen, and Oxygen[a]

	Precise Mass	*M* + 1	*M* + 2
16			
CH_4	16.0313	1.15	
17			
NH_3	17.0266	0.43	
18			
H_2O	18.0106	0.07	0.20
26			
C_2H_2	26.0157	2.19	0.01
27			
CHN	27.0109	1.48	
28			
N_2	28.0062	0.76	
CO	27.9949	1.12	
C_2H_4	28.0313	2.23	0.01
29			
CH_3N	29.0266	1.51	
30			
CH_2O	30.0106	1.15	0.20
C_2H_6	30.0470	2.26	0.01
31			
CH_5N	31.0422	1.54	
32			
O_2	31.9898	0.08	0.40
N_2H_4	32.0375	0.83	
CH_4O	32.0262	1.18	0.20
40			
C_3H_4	40.0313	3.31	0.04
41			
C_2H_3N	41.0266	2.59	0.02
42			
CH_2N_2	42.0218	1.88	0.01
C_2H_2O	42.0106	2.23	0.21
C_3H_6	42.0470	3.34	0.04

[a]*Adapted with permission from Beynon, J. H.,* Mass Spectrometry and Its Application to Organic Chemistry, *Elsevier, Amsterdam, 1960. The precise masses are calculated on the basis of the most abundant isotope of carbon having a mass of 12.0000.*

	Precise Mass	*M* + 1	*M* + 2
43			
CH_3N_2	43.0297	1.89	0.01
C_2H_5N	43.0422	2.62	0.02
44			
N_2O	44.0011	0.80	0.20
CO_2	43.9898	1.16	0.40
CH_4N_2	44.0375	1.91	0.01
C_2H_4O	44.0262	2.26	0.21
C_3H_8	44.0626	3.37	0.04
45			
CH_3NO	45.0215	1.55	0.21
C_2H_7N	45.0579	2.66	0.02
46			
NO_2	45.9929	0.46	0.40
CH_2O_2	46.0054	1.19	0.40
CH_4NO	46.0293	1.57	0.21
CH_6N_2	46.0532	1.94	0.01
C_2H_6O	46.0419	2.30	0.22
47			
CH_5NO	47.0371	1.58	0.21
48			
O_3	47.9847	0.12	0.60
CH_4O_2	48.0211	1.22	0.40
52			
C_4H_4	52.0313	4.39	0.07
53			
C_3H_3N	53.0266	3.67	0.05
54			
$C_2H_2N_2$	54.0218	2.96	0.03
C_3H_2O	54.0106	3.31	0.24
C_4H_6	54.0470	4.42	0.07
55			
C_2HNO	55.0058	2.60	0.22
C_3H_5N	55.0422	3.70	0.05
56			
$C_2H_4N_2$	56.0375	2.99	0.03
C_3H_4O	56.0262	3.35	0.24
C_4H_8	56.0626	4.45	0.08
57			
CH_3N_3	57.0328	2.27	0.02
C_2H_3NO	57.0215	2.63	0.22
C_3H_7N	57.0579	3.74	0.05

	Precise Mass	*M* + 1	*M* + 2
58			
CH_2N_2O	58.0167	1.92	0.21
$C_2H_2O_2$	58.0054	2.27	0.42
$C_2H_6N_2$	58.0532	3.02	0.03
C_3H_6O	58.0419	3.38	0.24
C_4H_{10}	58.0783	4.48	0.08
59			
$CHNO_2$	59.0007	1.56	0.41
CH_5N_3	59.0484	2.31	0.02
C_2H_5NO	59.0371	2.66	0.22
C_3H_9N	59.0736	3.77	0.05
60			
CH_4N_2O	60.0324	1.95	0.21
$C_2H_4O_2$	60.0211	2.30	0.04
$C_2H_8N_2$	60.0688	3.05	0.03
C_3H_8O	60.0575	3.41	0.24
61			
CH_3NO_2	61.0164	1.59	0.41
CH_7N_3	61.0641		
C_2H_7NO	61.0528	2.69	0.22
62			
CH_2O_3	62.0003	1.23	0.60
CH_6N_2O	62.0480	1.98	0.21
$C_2H_6O_2$	62.0368	2.34	0.42
63			
CH_5NO_2	63.0320	1.62	0.41
64			
CH_4O_3	64.0160	1.26	0.60
66			
C_5H_6	66.0470	5.50	0.12
67			
C_4H_5N	67.0422	4.78	0.09
68			
$C_3H_4N_2$	68.0375	4.07	0.06
C_4H_4O	68.0262	4.43	0.28
C_5H_8	68.0626	5.53	0.12
69			
$C_2H_3N_3$	69.0328	3.35	0.04
C_3H_3NO	69.0215	3.71	0.25
C_4H_7N	69.0579	4.82	0.09
70			
$C_2H_2N_2O$	70.0167	3.00	0.23
$C_3H_2O_2$	70.0054	3.35	0.44
$C_3H_6N_2$	70.0532	4.10	0.07
C_4H_6O	70.0419	4.46	0.28
C_5H_{10}	70.0783	5.56	0.13

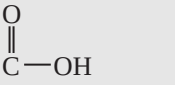
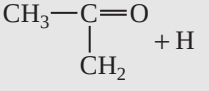
	Precise Mass	*M* + 1	*M* + 2
71			
C_2HNO_2	71.0007	2.64	0.42
$C_2H_5N_3$	71.0484	3.39	0.04
C_3H_5NO	71.0371	3.74	0.25
C_4H_9N	71.0736	4.85	0.09
72			
$C_2H_4N_2O$	72.0324	3.03	0.23
$C_3H_4O_2$	72.0211	3.38	0.44
$C_3H_8N_2$	72.0688	4.13	0.07
C_4H_8O	72.0575	4.49	0.28
C_5H_{12}	72.0939	5.60	0.13
73			
$C_2H_3NO_2$	73.0164	2.67	0.42
$C_2H_7N_3$	73.0641	3.42	0.04
C_3H_7NO	73.0528	3.77	0.25
$C_4H_{11}N$	73.0892	4.88	0.10
74			
$C_2H_2O_3$	74.0003	2.31	0.62
$C_2H_6N_2O$	74.0480	3.06	0.23
$C_3H_6O_2$	74.0368	3.42	0.44
$C_3H_{10}N_2$	74.0845	4.17	0.07
$C_4H_{10}O$	74.0732	4.52	0.28
75			
$CHNO_3$	74.9956	1.60	0.61
$C_2H_5NO_2$	75.0320	2.70	0.43
$C_2H_9N_3$	75.0798	3.45	0.05
C_3H_9NO	75.0684	3.81	0.25
76			
$C_2H_4O_3$	76.0160	2.34	0.62
$C_2H_8N_2O$	76.0637	3.09	0.24
$C_3H_8O_2$	76.0524	3.45	0.44
77			
CH_3NO_3	77.0113	1.63	0.61
$C_2H_7NO_2$	77.0477	2.73	0.43
78			
$C_2H_6O_3$	78.0317	2.38	0.62
C_6H_6	78.0470	6.58	0.18
79			
CH_5NO_3	79.0269	1.66	0.61
C_5H_5N	79.0422	5.87	0.14
80			
C_6H_8	80.0626	6.61	0.18
81			
C_5H_7N	81.0579	5.90	0.14

	Precise Mass	*M* + 1	*M* + 2
82			
$C_4H_6N_2$	82.0532	4.18	0.11
C_5H_6O	82.0419	5.54	0.32
C_6H_{10}	82.0783	6.64	0.19
83			
$C_3H_5N_3$	83.0484	4.47	0.08
C_4H_5NO	83.0371	4.82	0.29
C_5H_9N	83.0736	5.93	0.15
84			
$C_3H_4N_2O$	84.0324	4.11	0.27
$C_4H_4O_2$	84.0211	4.47	0.48
$C_4H_8N_2$	84.0688	5.21	0.11
C_5H_8O	84.0575	5.57	0.33
C_6H_{12}	84.0939	6.68	0.19
85			
$C_3H_3NO_2$	85.0164	3.75	0.45
$C_3H_7N_3$	85.0641	4.50	0.08
C_4H_7NO	85.0528	4.86	0.29
$C_5H_{11}N$	85.0892	5.96	0.15
86			
$C_3H_2O_3$	86.0003	3.39	0.64
$C_3H_6N_2O$	86.0480	4.14	0.27
$C_4H_6O_2$	86.0368	4.50	0.48
$C_4H_{10}N_2$	86.0845	5.25	0.11
$C_5H_{10}O$	86.0732	5.60	0.33
C_6H_{14}	86.1096	6.71	0.19
87			
C_2HNO_3	86.9956	2.68	0.62
$C_3H_5NO_2$	87.0320	3.78	0.45
$C_3H_9N_3$	87.0798	4.53	0.08
C_4H_9NO	87.0684	4.89	0.30
$C_5H_{13}N$	87.1049	5.99	0.15
88			
$C_3H_4O_3$	88.0160	3.42	0.64
$C_3H_8N_2O$	88.0637	4.17	0.27
$C_4H_8O_2$	88.0524	4.53	0.48
$C_4H_{12}N_2$	88.1001	5.28	0.11
$C_5H_{12}O$	88.0888	5.63	0.33
89			
$C_2H_3NO_3$	89.0113	2.71	0.63
$C_3H_7NO_2$	89.0477	3.81	0.46
$C_3H_{11}N_3$	89.0954	4.56	0.84
$C_4H_{11}NO$	89.0841	4.92	0.30
90			
$C_3H_6O_3$	90.0317	3.46	0.64
$C_3H_{10}N_2O$	90.0794	4.20	0.27
$C_4H_{10}O_2$	90.0681	4.56	0.48

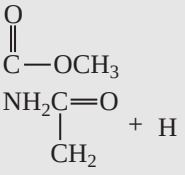
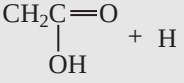
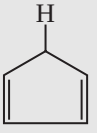
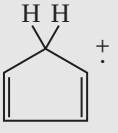
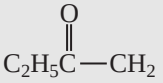
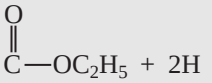
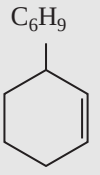
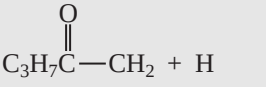
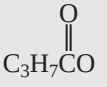
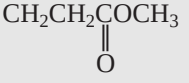
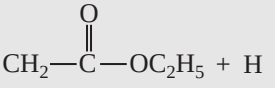
	Precise Mass	*M* + 1	*M* + 2
91			
$C_2H_5NO_3$	91.0269	2.74	0.63
$C_2H_9N_3O$	91.0746	3.49	0.25
$C_3H_9NO_2$	91.0634	3.85	0.46
92			
$C_3H_8O_3$	92.0473	3.49	0.64
C_7H_8	92.0626	7.69	0.26
93			
$C_2H_7NO_3$	93.0426	2.77	0.63
C_6H_7N	93.0579	6.98	0.21
94			
$C_5H_6N_2$	94.0532	6.26	0.17
C_6H_6O	94.0419	6.62	0.38
C_7H_{10}	94.0783	7.72	0.26
95			
$C_4H_5N_3$	95.0484	5.55	0.13
C_5H_5NO	95.0371	5.90	0.34
C_6H_9N	95.0736	7.01	0.21
96			
$C_4H_4N_2O$	96.0324	5.19	0.31
$C_5H_4O_2$	96.0211	5.55	0.53
$C_5H_8N_2$	96.0688	6.29	0.17
C_6H_8O	96.0575	6.65	0.39
C_7H_{12}	96.0939	7.76	0.26
97			
$C_4H_3NO_2$	97.0164	4.83	0.49
$C_4H_7N_3$	97.0641	5.58	0.13
C_5H_7NO	97.0528	5.94	0.35
$C_6H_{11}N$	97.0892	7.04	0.21
98			
$C_4H_6N_2O$	98.0480	5.22	0.31
$C_5H_6O_2$	98.0368	5.58	0.53
$C_5H_{10}N_2$	98.0845	6.33	0.17
$C_6H_{10}O$	98.0732	6.68	0.39
C_7H_{14}	98.1096	7.79	0.26
99			
$C_4H_5NO_2$	99.0320	4.86	0.50
$C_4H_9N_3$	99.0798	5.61	0.13
C_5H_9NO	99.0684	5.97	0.35
$C_6H_{13}N$	99.1049	7.07	0.21
100			
$C_4H_8N_2O$	100.0637	5.25	0.31
$C_5H_8O_2$	100.0524	5.61	0.53
$C_5H_{12}N_2$	100.1001	6.36	0.17
$C_6H_{12}O$	100.0888	6.72	0.39
C_7H_{16}	100.1253	7.82	0.26

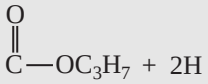
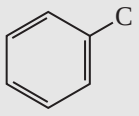
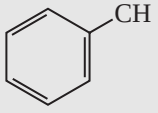
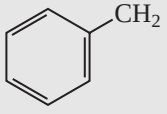
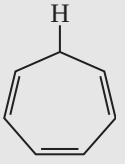
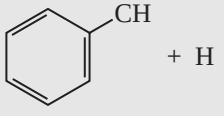
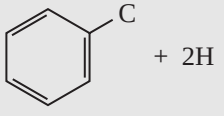
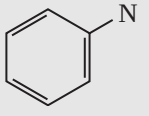
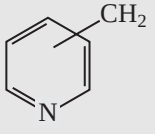
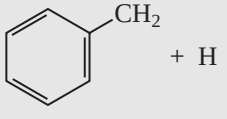
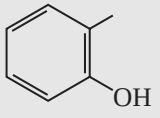
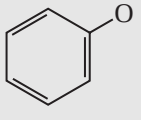
APPENDIX 12

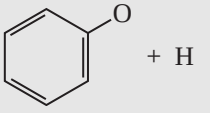
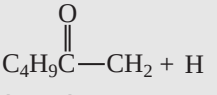
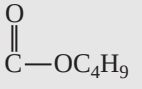
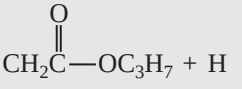
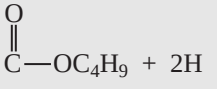
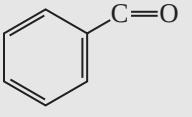
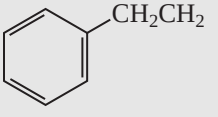
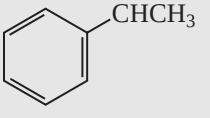
Common Fragment Ions under Mass 105[a]

m/z	Ions	*m/z*	Ions
14	CH_2	44	$CH_2CH{=}O + H$
15	CH_3		CH_3CHNH_2
16	O		CO_2
17	OH		$NH_2C{=}O$
18	H_2O		$(CH_3)_2N$
	NH_4	45	CH_3CHOH
19	F		CH_2CH_2OH
	H_3O		CH_2OCH_3
26	$C{\equiv}N$		
27	C_2H_3		
28	C_2H_4		$CH_3CH{-}O + H$
	CO	46	NO_2
	N_2 (air)	47	CH_2SH
	$CH{=}NH$		CH_3S
29	C_2H_5	48	$CH_3S + H$
	CHO	49	CH_2Cl
30	CH_2NH_2	51	CHF_2
	NO		C_4H_3
31	CH_2OH	53	C_4H_5
	OCH_3	54	$CH_2CH_2C{\equiv}N$
32	O_2 (air)	55	C_4H_7
33	SH		$CH_2{=}CHC{=}O$
	CH_2F	56	C_4H_8
34	H_2S	57	C_4H_9
35	Cl		$C_2H_5C{=}O$
36	HCl	58	
39	C_3H_3		
40	$C{\equiv}N$		$C_2H_5CHNH_2$
41	C_3H_5		$(CH_3)_2NHCH_2$
	$CH_2C{=}H + H$		$C_2H_5NHCH_2$
	C_2H_2NH		C_2H_2S
42	C_3H_6		
43	C_3H_7		
	$CH_3C{=}O$		
	C_2H_5N		

[a]*Adapted with permission from Silverstein, R. M. and F. X. Webster,* Spectrometric Identification of Organic Compounds, *6th ed., John Wiley & Sons, New York, 1998.*

m/z	Ions
59	$(CH_3)_2COH$
	$CH_2OC_2H_5$
	
	CH_3OCHCH_3
	CH_3CHCH_2OH
60	
	CH_2ONO
61	
	CH_2CH_2SH
	CH_2SCH_3
65	 (or C_5H_5)
66	 (or C_5H_6)
67	C_5H_7
68	$CH_2CH_2CH_2C{\equiv}N$
69	C_5H_9
	CF_3
	$CH_3CH{=}CHC{=}O$
	$CH_2{=}C(CH_3)C{=}O$
70	C_5H_{10}
71	C_5H_{11}
	$C_3H_7C{=}O$
72	
	$C_3H_7CHNH_2$
	$(CH_3)N{=}C{=}O$
	$C_2H_5NHCHCH_3$ and isomers
73	Homologs of 59
74	
75	
	$CH_2SC_2H_5$
	$(CH_3)_2CSH$
	$(CH_3O)_2CH$
77	C_6H_5
78	$C_6H_5 + H$
79	$C_6H_5 + 2H$
	Br
80	$CH_3SS + H$
81	
82	$CH_2CH_2CH_2CH_2C{\equiv}N$
	CCl_2
	C_6H_{10}
83	C_6H_{11}
	$CHCl_2$
85	C_6H_{13}
	$C_4H_9C{=}O$
	$CClF_2$
86	
	$C_4H_9CHNH_2$ and isomers
87	
	Homologs of 73
	
88	

m/z	Ions
89	
	
90	CH_3CHONO_2
	
91	 or 
	
	
	$(CH_2)_4Cl$
	
92	
	
93	CH_2Br
	
	C_7H_9
	

m/z	Ions
94	
96	$CH_2CH_2CH_2CH_2CH_2C{\equiv}N$
97	C_7H_{13}
99	C_7H_{15}
	$C_6H_{11}O$
100	
	$C_5H_{11}CHNH_2$
101	
102	
103	
	$C_5H_{11}S$
	$CH(OCH_2CH_3)_2$
104	$C_2H_5CHONO_2$
105	
	
	

APPENDIX 13

A Handy-Dandy Guide to Mass Spectral Fragmentation Patterns

Alkanes

Good M^+
14-amu fragments

Alkenes

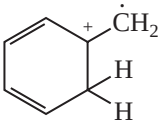
Distinct M^+
Loss of 15, 29, 43, and so on

Cycloalkanes

Strong M^+
Loss of $CH_2{=}CH_2$ $M - 28$
Loss of alkyl

Aromatics

Strong M^+
$C_7H_7^+$ $m/z = 91$, weak $m/z = 65$ ($C_5H_5^+$)



$m/z = 92$ Transfer of *gamma* hydrogens

Halides

Cl and Br doublets (M^+ and $M + 2$)
$m/z = 49$ or 51 $CH_2{=}Cl^+$
$m/z = 93$ or 95 $CH_2{=}Br^+$
$M - 36$ Loss of HCl

$m/z = 91$ or 93 

$m/z = 135$ or 137 

$M - 79$ ($M - 81$) Loss of Br·
$M - 127$ Loss of I·

Alcohols

M^+ weak or absent
Loss of alkyl
$CH_2{=}OH^+$ $m/z = 31$
$RCH{=}OH^+$ $m/z = 45, 59, 73, \ldots$
$R_2C{=}OH^+$ $m/z = 59, 73, 87, \ldots$
$M - 18$ Loss of H_2O
$M - 46$ Loss of $H_2O + CH_2{=}CH_2$

Phenols

Strong M^+
Strong $M - 1$ Loss of H·
$M - 28$ Loss of CO

Ethers

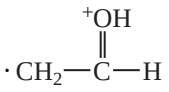
M^+ stronger than alcohols
Loss of alkyl
Loss of OR′ $M - 31$, $M - 45$, $M - 59$, and so on
$CH_2{=}OR'^+$ $m/z = 45, 59, 73, \ldots$

Amines

M^+ weak or absent
Nitrogen Rule
$m/z = 30$ $CH_2{=}NH_2^+$ (base peak)
Loss of alkyl

Aldehydes

Weak M^+
$M - 29$ Loss of HCO
$M - 43$ Loss of $CH_2{=}CHO$
$m/z = 44$



Transfer of *gamma* hydrogens

or 58, 72, 86, . . .

Aromatic Aldehydes

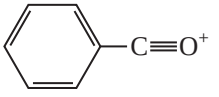
Strong M^+
$M - 1$ Loss of H·
$M - 29$ Loss of H· and CO

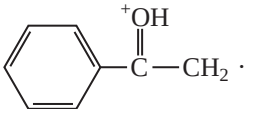
Ketones

M^+ intense
$M - 15$, $M - 29$, $M - 43$, . . . Loss of alkyl group
$m/z = 43$ CH_3CO^+
$m/z = 58, 72, 86, \ldots$ Transfer of *gamma* hydrogens
$m/z = 55$ $^+CH_2{-}CH{=}C{=}O$ Base peak for cyclic ketones

$m/z = 83$  in cyclohexanone

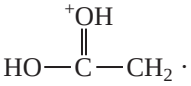
$m/z = 42$  in cyclohexanone

$m/z = 105$  in aryl ketones

$m/z = 120$  Transfer of *gamma* hydrogens

Carboxylic Acids

M^+ weak but observable
$M - 17$ Loss of OH
$M - 45$ Loss of COOH
$m/z = 45$ ^+COOH

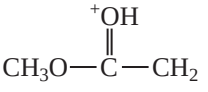
$m/z = 60$  Transfer of *gamma* hydrogens

Aromatic Acids

M^+ large
$M - 17$ Loss of OH
$M - 45$ Loss of COOH
$M - 18$ *Ortho* effect

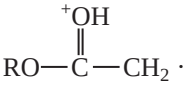
Methyl Esters

M^+ weak but observable
$M - 31$ Loss of OCH_3
$m/z = 59$ $^+COOCH_3$

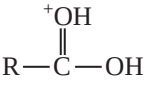
$m/z = 74$  Transfer of *gamma* hydrogens

Higher Esters

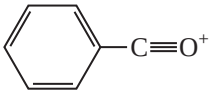
M^+ weaker than for $RCOOCH_3$
Same pattern as in methyl esters
$M - 45$, $M - 59$, $M - 73$ Loss of OR
$m/z = 73, 87, 101$ ^+COOR

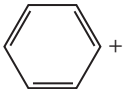
$m/z = 88, 102, 116$  Transfer of *gamma* hydrogens

$m/z = 28, 42, 56, 70$ *Beta* hydrogens on alkyl group

$m/z = 61, 75, 89$  Long alkyl chain

$m/z = 108$ Loss of $CH_2{=}C{=}O$ Benzyl or acetate ester

$m/z = 105$ 

$m/z = 77$  weak

$M - 32$, $M - 46$, $M - 60$ *ortho* effect—loss of ROH

APPENDIX 14

Index of Spectra

Infrared Spectra

Mass Spectra

^{1}H NMR Spectra

^{13}C NMR Spectra

COSY Spectra

DEPT Spectra

HETCOR Spectra

NOE Difference Spectra

Ultraviolet-Visible Spectra