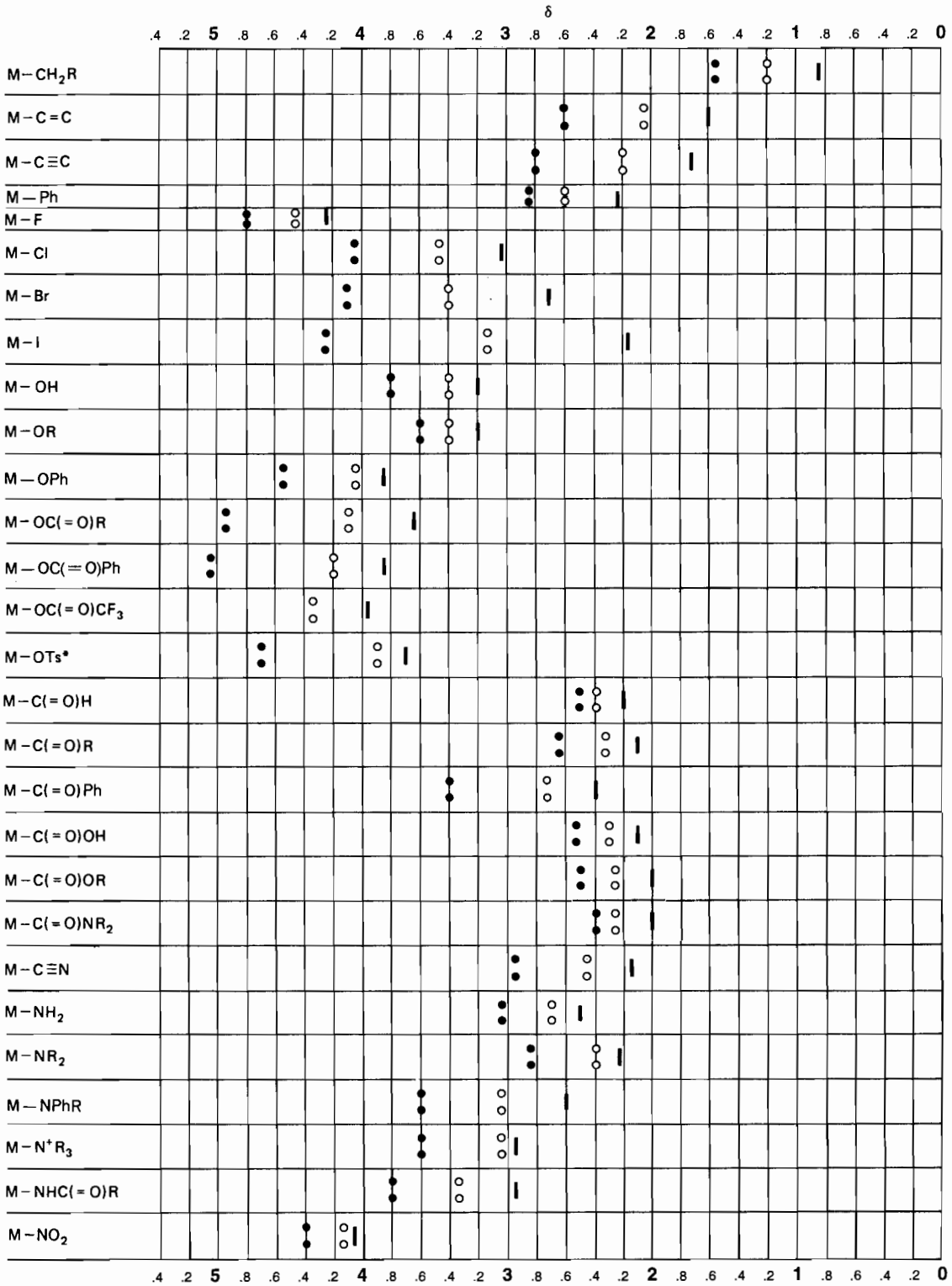
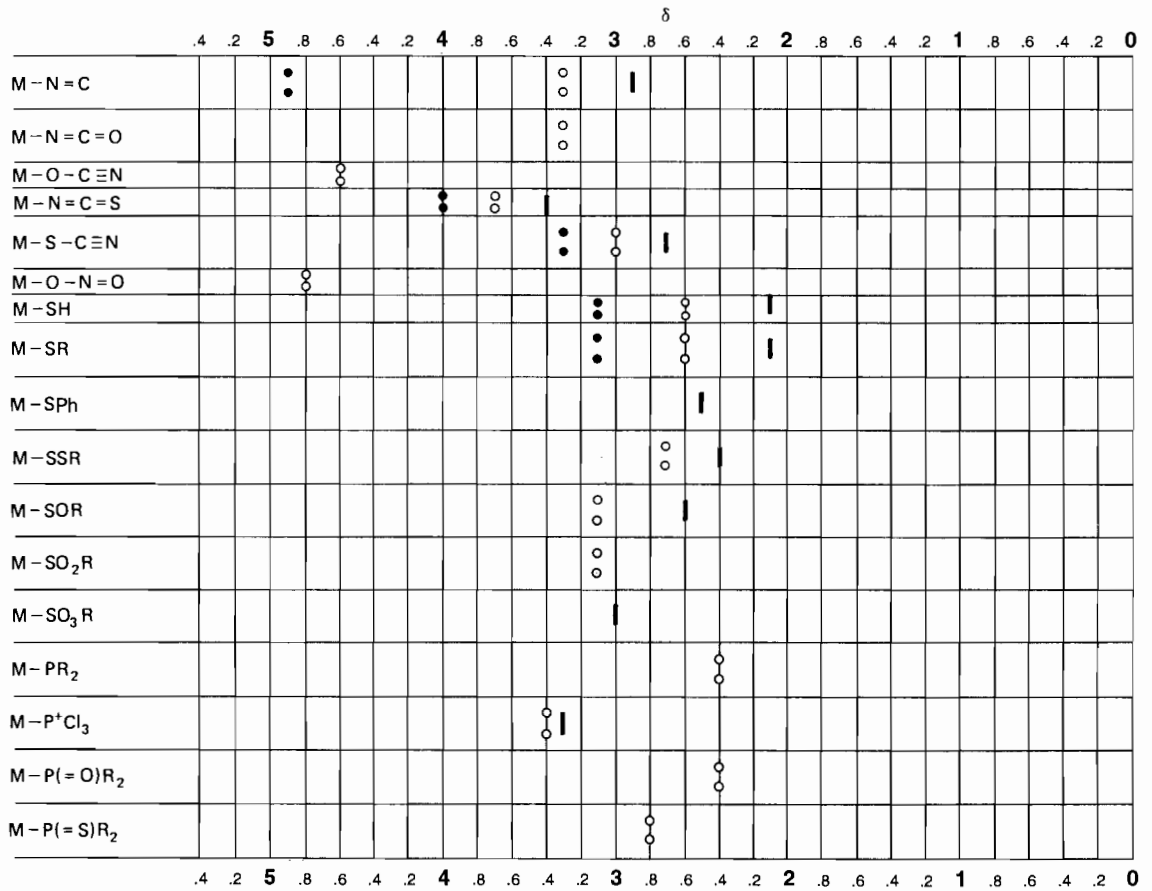
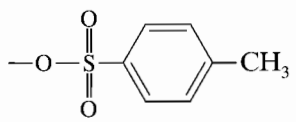
APPENDIX A CHART A.1 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—Y)

| M = methyl
| M = methylene
⋮ M = methine



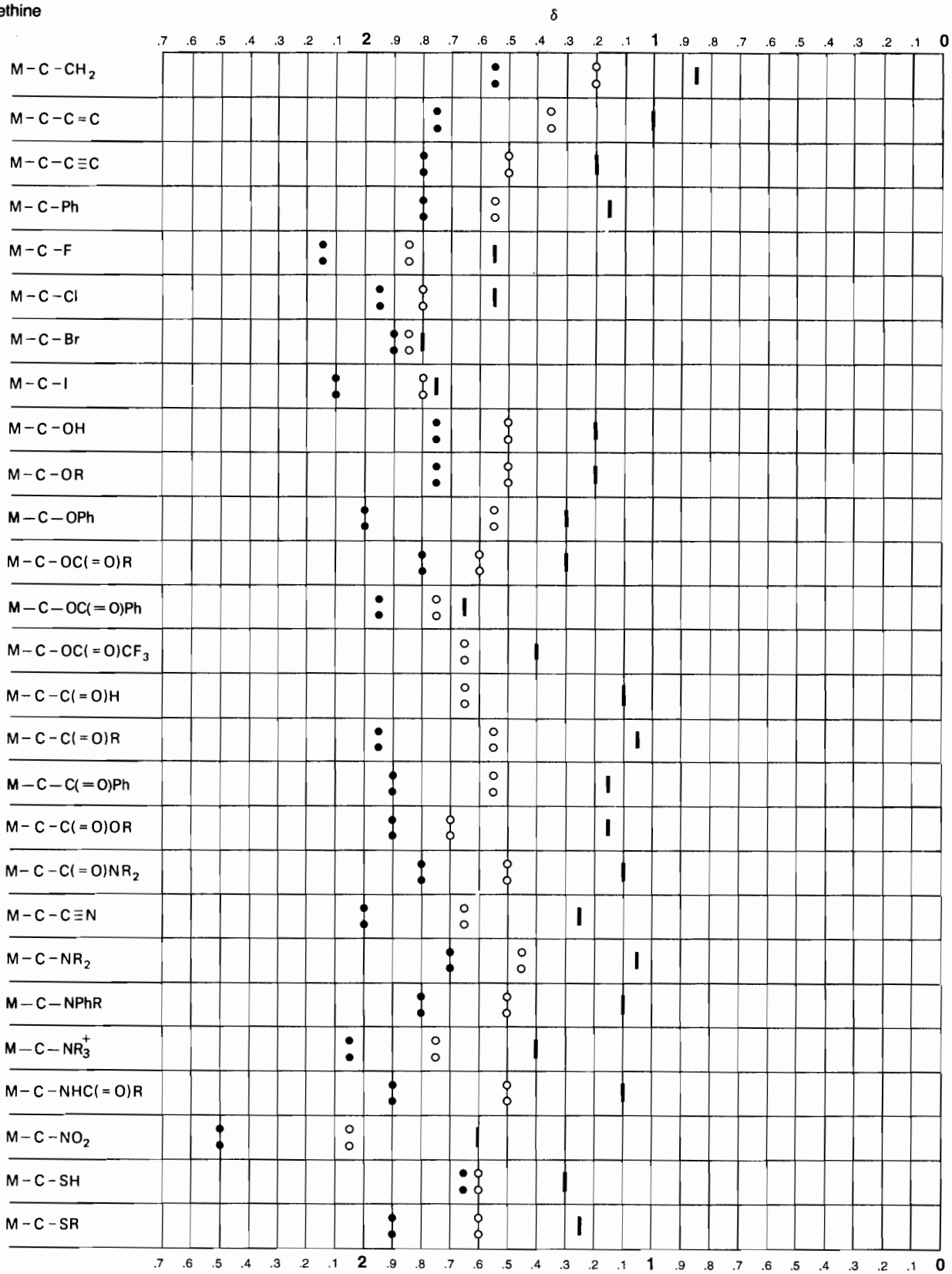
APPENDIX A *(Continued)*



*OTS is 

APPENDIX A CHART A.2 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ONCE REMOVED (β POSITION) FROM A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—C—Y)

▮ M = methyl
8 M = methylene
⁝ M = methine



APPENDIX B EFFECT ON CHEMICAL SHIFTS BY TWO OR THREE DIRECTLY ATTACHED FUNCTIONAL GROUPS

$$Y{-}CH_2{-}Z \text{ and } Y{-}\underset{\displaystyle W}{\overset{\displaystyle |}{CH}}{-}Z$$

The chemical shift of a methylene group attached to two functional groups can be calculated by means of the substituent constants (σ values) in Table B.1. Shoolery's rule* states that the sum of the constants for the attached functional groups is added to δ 0.23, the chemical shift for CH_4:

$$\delta\,(Y{-}CH_2{-}Z) = 0.23 + \sigma_Y + \sigma_Z$$

The chemical shift for the methylene protons, of $C_6H_5CH_2Br$, for example, is calculated from the σ values in Table B.1.

$$\begin{aligned} &0.23\\ \sigma_{Ph} &= 1.85\\ \sigma_{Br} &= 2.33\\ \hline \delta &= 4.41 \quad \text{Found, } \delta\ 4.43 \end{aligned}$$

Shoolery's original constants have been revised and extended in Table B.1. The observed and calculated chemical shifts for 62% of the samples tested were within ±0.2 ppm, 92% within ±0.3 ppm. 96% within 0.4 ppm, and 99% within ±0.5 ppm.† Table B.1 contains substituent constants (Friedrich and Runkle, 1984) for the more common functional groups. Note that chemical shifts of methyl protons can be calculated by using the constant for H (0.34). For example $H{-}CH_2{-}Br$ is equivalent to CH_3Br.

* Shoolery, J.N. (1959). *Varian Technical Information Bulletin*, Vol 2, No. 3. Palo Alto, CA: Varian Associates.

† Data from Friedrich, E.C., and Runkle, K.G. (1984). *J. Chem. Educ.* **61,** 830; (1986)**63,** 127.

TABLE B.1 Substituent Constants for Alkyl Methylene (and Methyl) Protons.

Y or Z	Substituent Constants (σ)	Y or Z	Substituent Constants (σ)
—H	0.34	—OC(=O)R	3.01
—CH_3	0.68	—OC(=O)Ph	3.27
—C—C	1.32	—C(=O)R	1.50
—C≡C	1.44	—C(=O)Ph	1.90
—Ph	1.83	—C(=O)OR	1.46
—CF_2	1.12	—C(=O)$NR_2(H_2)$	1.47
—CF_3	1.14	—C≡N	1.59
—F	3.30	—$NR_2(H_2)$	1.57
—Cl	2.53	—NHPh	2.04
—Br	2.33	—NHC(=O)R	2.27
—I	2.19	—N_3	1.97
—OH	2.56	—NO_2	3.36
—OR	2.36	—SR(H)	1.64
—OPh	2.94	—OSO_2R	3.13

Tables B.2a, B.2b, and B.2c: Chemical Shift Correlations for Methine Protons

Table B.2a gives the substituent constants* to be used with the formulation

$$\delta\,CHXYZ = 2.50 + \sigma_X + \sigma_Y + \sigma_Z$$

which is satisfactory if at least two of the substituents are electron-withdrawing groups. In other words, only a single substituent may be an alkyl group (R). Within these limits, the standard error of estimate is 0.20 ppm. For example, the chemical shift of the methine proton in

$$CH_3{-}\underset{\displaystyle OEt}{\overset{\displaystyle |}{CH}}{-}OEt$$

is calculated from Table B.2a as follows:

$$\delta = 2.50 + 1.14 + 1.14 + 0.00 = 4.78$$

The found value is 4.72.

Tables B.2b and B.2c are used jointly for methine protons that are substituted by at least two alkyl groups

* Bell, H.M., Bowles, D.B. and Senese, F. (1981). *Org. Magn. Reson.*, **16,** 285. With permission.

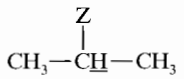
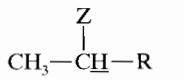
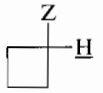
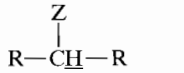
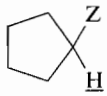
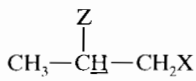
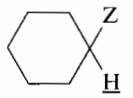
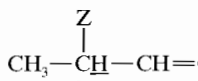
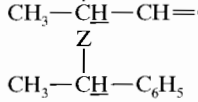
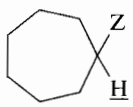
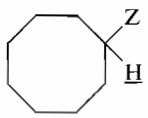
TABLE B.2a Substituent Constants for Methine Protons.

Group	(σ)
—F	1.59
—Cl	1.56
—Br	1.53
—NO_2	1.84
—NH_2	0.64
—NH_3^+	1.34
—NHCOR	1.80
—OH, —OR	1.14
—OAr	1.79
—OCOR	2.07
—Ar	0.99
—C=C	0.46
—C≡C	0.79
—C≡N	0.66
—COR, —COOR, —COOH	0.47
—$CONH_2$	0.60
—COAr	1.22
—SH, —SR	0.61
—SO_2R	0.94
—R	0

TABLE B.2b Observed Methine Proton Chemical Shifts of Isopropyl Derivatives.

$(CH_3)_2CHZ$		$(CH_3)_2CHZ$	
Z	δ (ppm) obs	Z	δ (ppm) obs
H	1.33	HO	3.94
H_3C	1.56	RO	3.55
R	1.50	C_6H_5O	4.51
XCH_2	1.85	R(H)C(=O)O	4.94
R(H)C(=O)	2.54	$C_6H_5C(=O)O$	5.22
$C_6H_5C(=O)$	3.58	$F_3CC(=O)O$	5.20
R(H)OC(=O)	2.52	$ArSO_2O$	4.70
$R_2(H_2)NC(=O)$	2.44		
C_6H_5	2.89	R(H)S	3.16
$R_2(H_2)C=CR(H)$	2.62	RSS	2.63
R(H)C≡C	2.59		
N≡C	2.67	F	4.50
		Cl	4.14
$R_2(H_2)N$	3.07	Br	4.21
R(H)C(=O)NH	4.01	I	4.24
O_2N	4.67		

TABLE B.2c Correction Factors for Methine Substituents of Low Polarity.

Open-Chain Methine Proton Systems	Δxy	Cyclic Methine Proton Systems	Δxy
	0.00		−1.0
	−0.20		+0.40
	−0.40		+0.20
	+0.20		monosub. −0.20
			axial H −0.45
	+0.40		equat. H +0.25
	+1.15		0.00
	+0.90		0.00

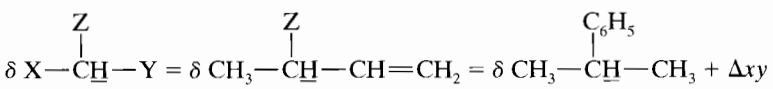
(or other groups of low polarity). Friedrich and Runkle proposed the relationship

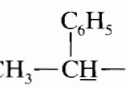
$$\delta_{CHXYZ} = \delta_{(CH_3)_2CHZ} = \Delta xy$$

in which the X and Y substituents are alkyl groups or other groups of low polarity. The Z susbstituent covers a range of polarities. Δxy is a correction factor. The relationship states that the chemical shift of a methine proton with at least two low-polarity groups is equivalent to the chemical shift of an isopropyl methine proton plus correction factor.

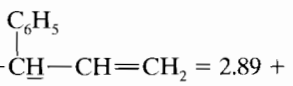
The substituent constants for a Z substituent on an isopropyl methine proton are given in Table B.2b. The Δxy correction factors are given in Table B.2c.

The following example illustrates the joint use of Tables B.2b and B.2c, with CH_3, $CH{=}CH_2$, and C_6H_5 as substituents. The most polar substituent is always designated Z.



From Table B.2b, $\delta = 2.89$ for  .

From Table B.2c, $\Delta xy = 0.00$ for CH_3. $\Delta xy = 0.40$ for $CH{=}CH_2$.

Therefore, δ  $= 2.89 + 0.00 + 0.40 = 3.29$ (Found: $\delta = 3.44$).

APPENDIX C CHEMICAL SHIFTS IN ALICYCLIC AND HETEROCYCLIC RINGS

TABLE C.1 Chemicals Shifts in Alicyclic Rings.

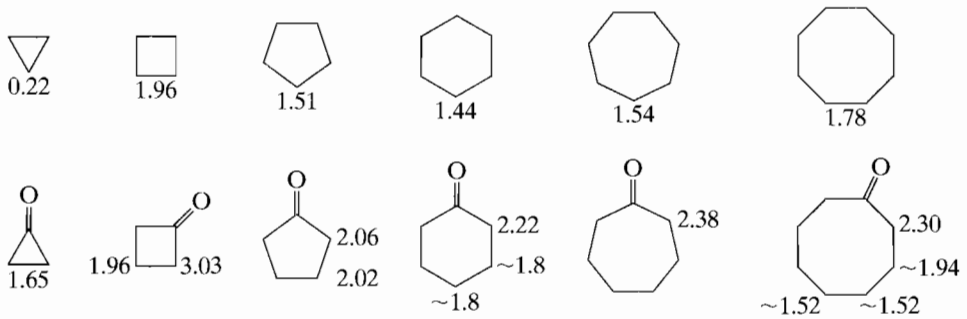
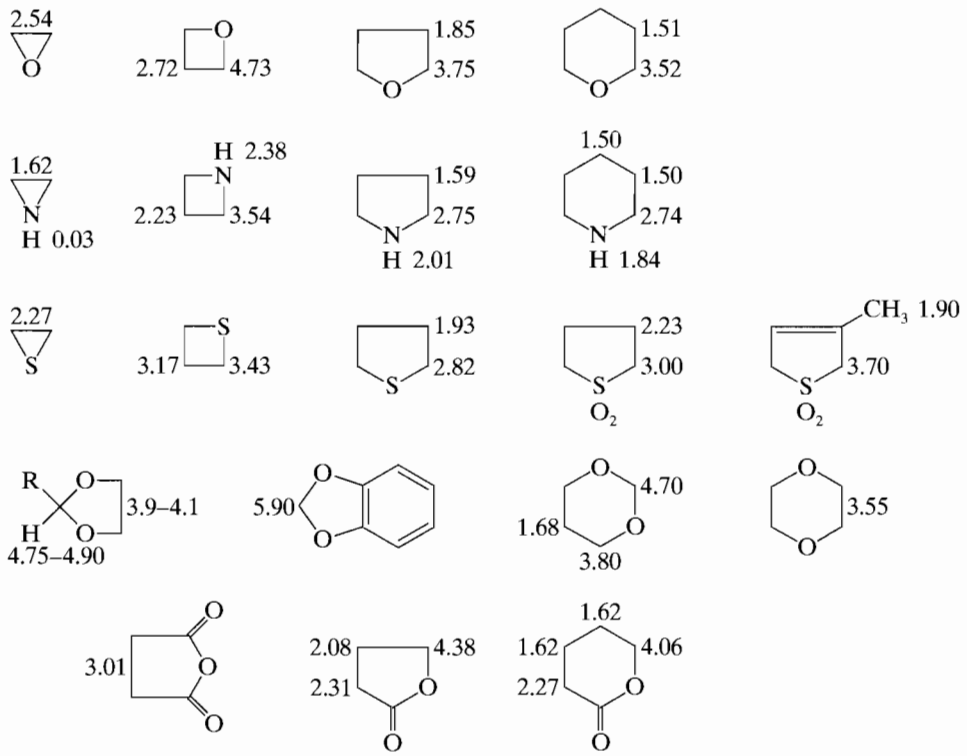
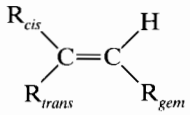


TABLE C.2 Chemical Shifts in Heterocyclic Rings.



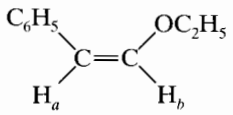
APPENDIX D CHEMICAL SHIFTS IN UNSATURATED AND AROMATIC SYSTEMS

(See Table D.1)



$$\delta_H = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

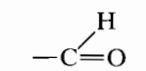
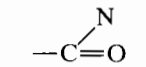
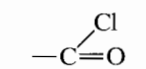
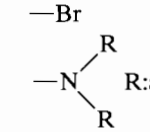
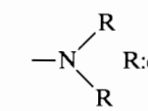
For example, the chemical shifts of the alkene protons in



are calculated:

H_a	C_6H_5 *gem*	1.35	5.25
	OR_{trans}	−1.28	0.07
		0.07	δ 5.32
H_b	OR_{gem}	1.18	5.25
	C_6H_5 *trans*	−0.10	1.08
		1.08	δ 6.33

TABLE D.1 Substituent Constants (Z) for Chemical Shifts of Substituted Ethylenes.

	Z				Z		
Substituent R	*gem*	*cis*	*trans*	**Substituent R**	*gem*	*cis*	*trans*
—H	0	0	0				
—Alkyl	0.44	−0.26	−0.29		1.03	0.97	1.21
—Alkyl-ring[a]	0.71	−0.33	−0.30				
—CH_2O, —CH_2I	0.67	−0.02	−0.07		1.37	0.93	0.35
—CH_2S	0.53	−0.15	−0.15				
—CH_2Cl, —CH_2Br	0.72	0.12	0.07		1.10	1.41	0.99
—CH_2N	0.66	−0.05	−0.23				
—C≡C	0.50	0.35	0.10	—OR, R: aliph	1.18	−1.06	−1.28
—C≡N	0.23	0.78	0.58	—OR, R: conj[b]	1.14	−0.65	−1.05
—C=C	0.98	−0.04	−0.21	—OCOR	2.09	−0.40	−0.67
—C=C conj[b]	1.26	0.08	−0.01	—Aromatic	1.35	0.37	−0.10
—C=O	1.10	1.13	0.81	—Cl	1.00	0.19	0.03
—C=O conj[b]	1.06	1.01	0.95	—Br	1.04	0.40	0.55
—COOH	1.00	1.35	0.74				
—COOH conj[b]	0.69	0.97	0.39	 R:aliph	0.69	−1.19	−1.31
—COOR	0.84	1.15	0.56	 R:conj[b]	2.30	−0.73	−0.81
—COOR conj[b]	0.68	1.02	0.33	—SR	1.00	−0.24	−0.04
				—SO_2	1.58	1.15	0.95

[a] Alkyl ring indicates that the double bond is part of the ring  .

[b] The Z factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

Source: Pascual C., Meier, J., and Simon, W. (1966) *Helv. Chim. Acta,* **49,** 164.

TABLE D.2 Chemical Shifts of Miscellaneous Alkenes

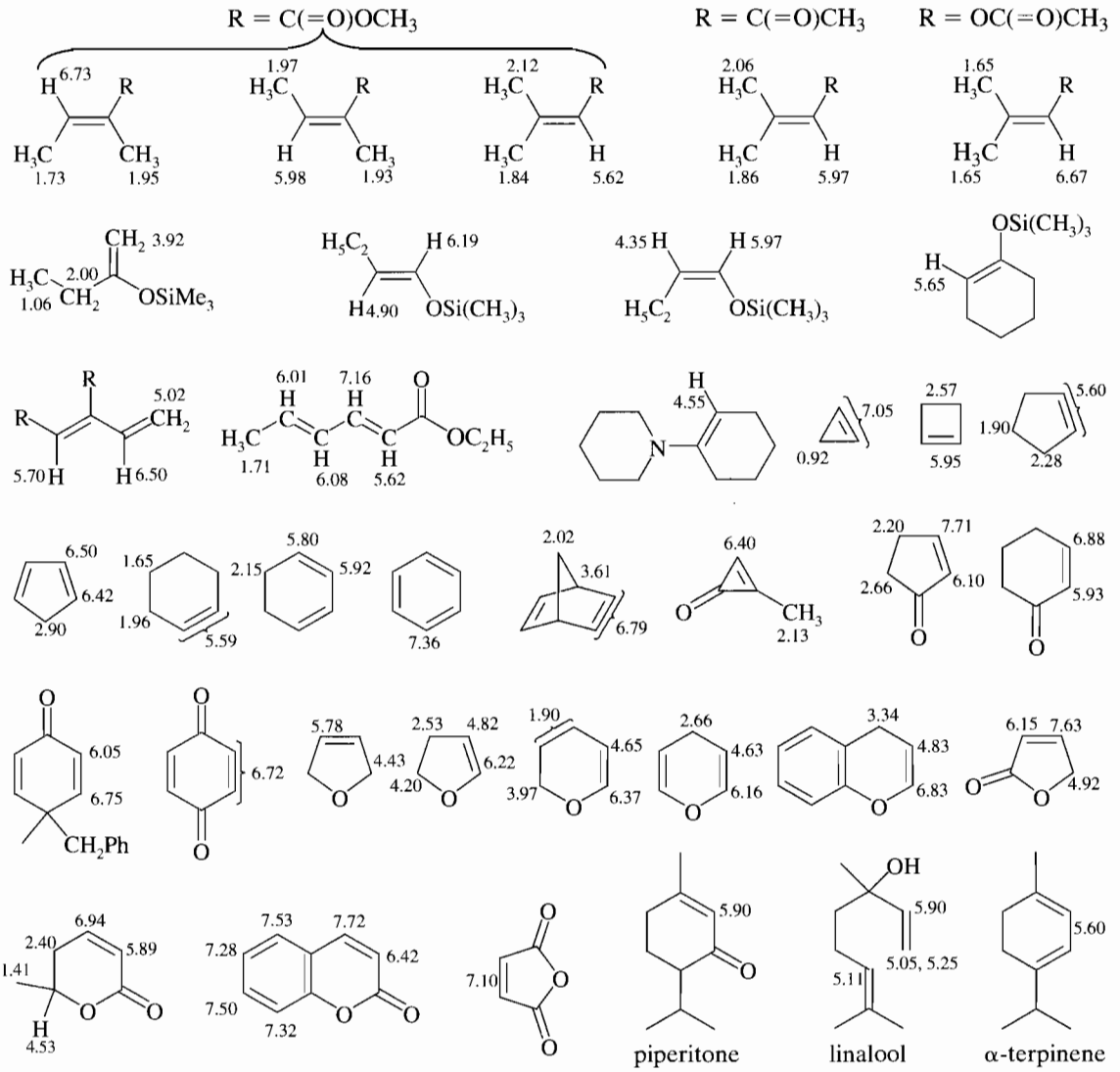


TABLE D.3 Chemical Shifts of Alkyne Protons

HC≡CR	1.73–1.88	HC≡C—COH	2.23
HC≡C—C≡CR	1.95	HC≡CH	1.80
HC≡C—Ph	2.71–3.37	HC≡C—CH=CR_2	2.60–3.10

TABLE D.4 Chemical Shifts of Protons on Fused Aromatic Rings

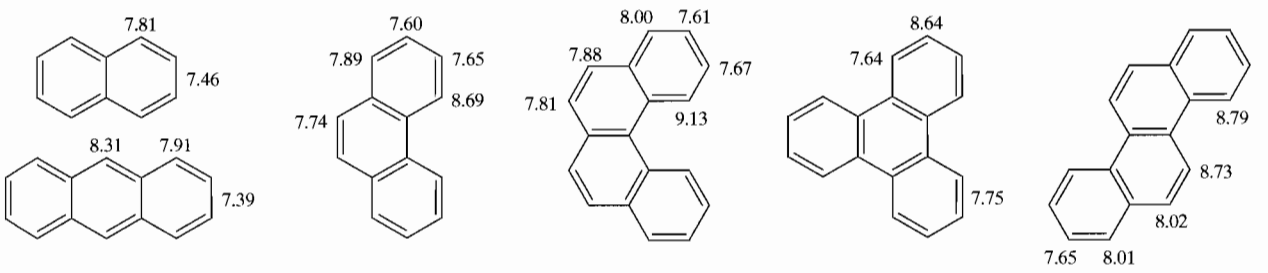
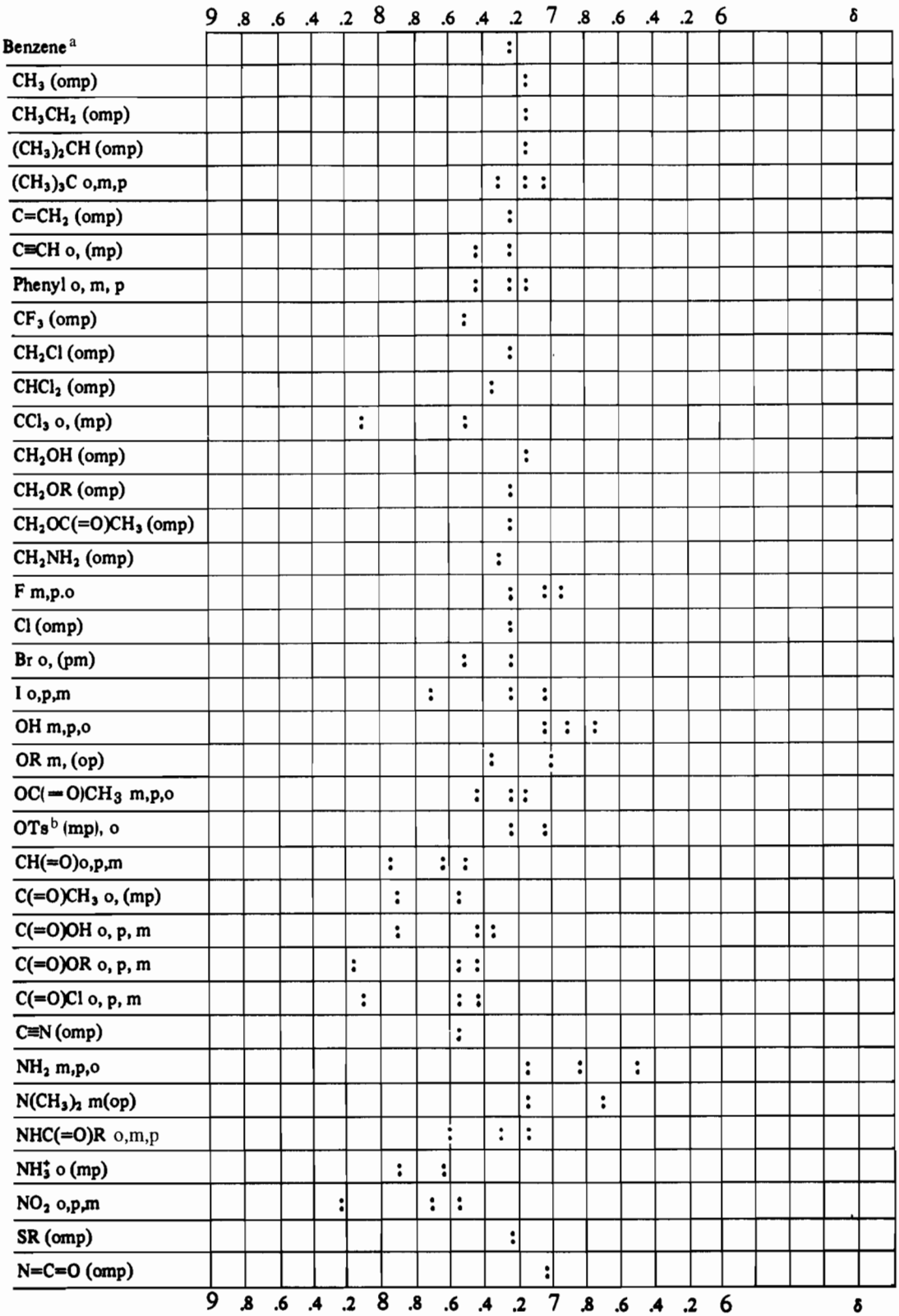


CHART D.1 CHEMICAL SHIFTS OF PROTONS ON MONOSUBSTITUTED BENZENE RINGS



[a] The benzene ring proton is at δ 7.27, from which the shift increments are calculated as shown at the end of Section 3.4.

[b] OTS = *p*-toluenesulfonyloxy group.

TABLE D.5 Chemical Shifts of Protons on Heteroaromatic Rings

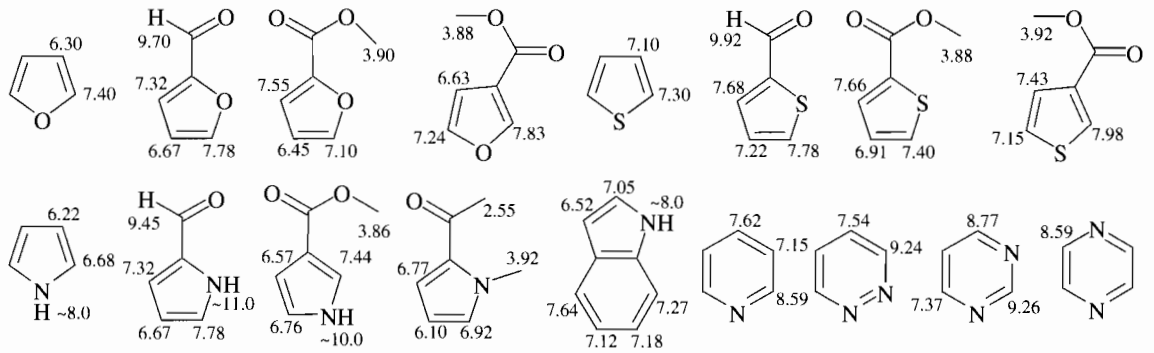
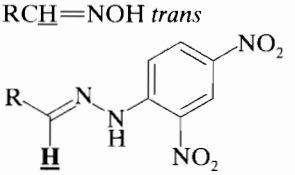
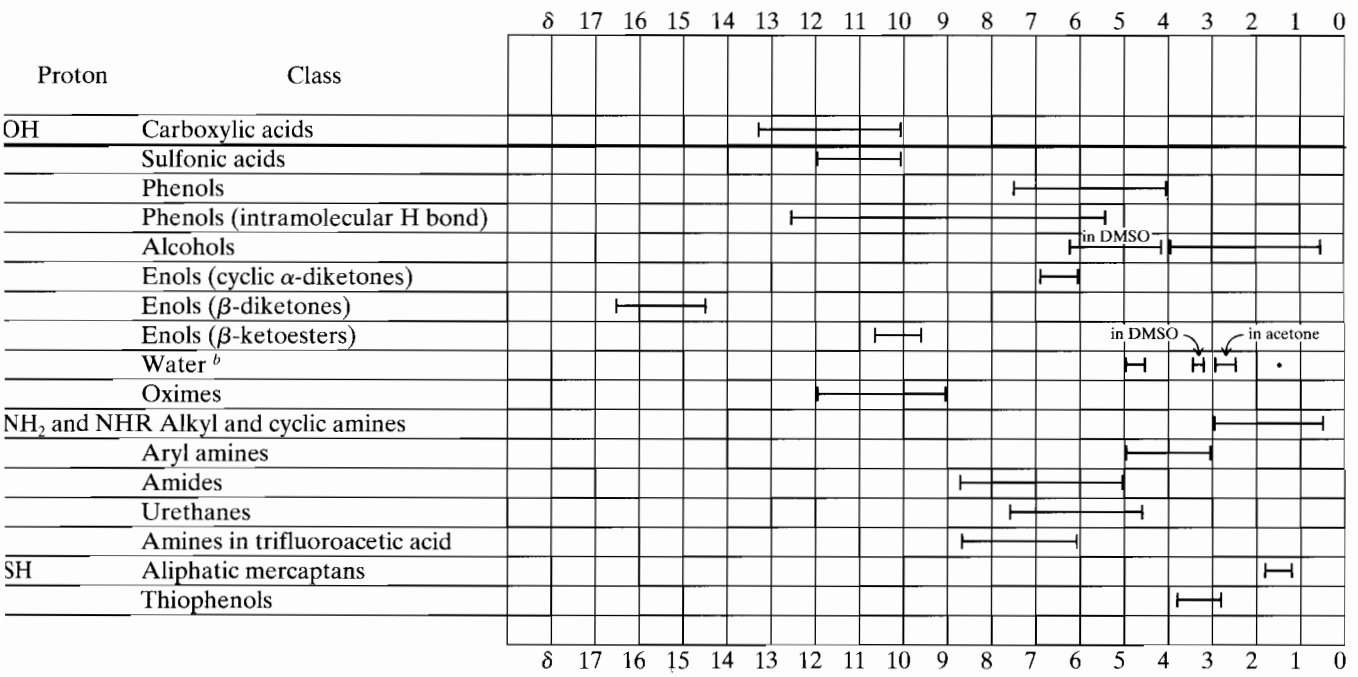


TABLE D.6 Chemical Shifts of HC=O, HC=N, and $HC(O)_3$ Protons

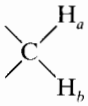
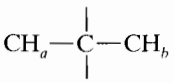
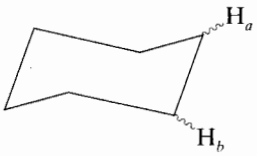
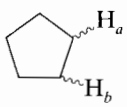
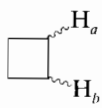
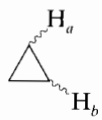
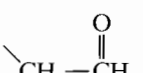
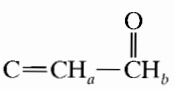
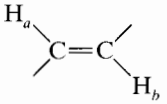
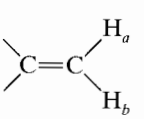
RCH=O	9.70	HC(=O)OR	8.05	RCH=NOH *cis*	7.25
PhCH=O	9.98	$HC(=O)NR_2$	8.05	RCH=NOH *trans*	6.65
RCH=CHCH=O	9.78	$HC(OR)_3$	5.00		6.05

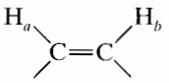
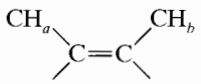
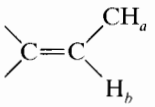
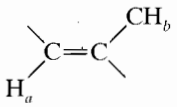
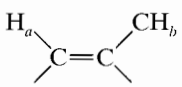
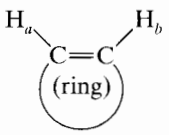
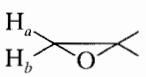
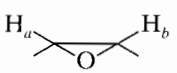
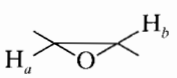
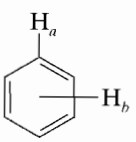
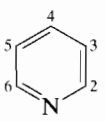
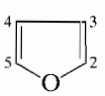
APPENDIX E PROTONS SUBJECT TO HYDROGEN-BONDING EFFECTS (PROTONS ON HETEROATOMS)[a]



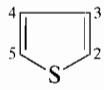
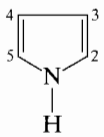
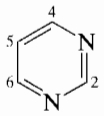
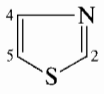
[a] Solvent $CDCl_3$. Chemical shifts within a range are a function of concentration.
[b] See Section 3.6.1.2.

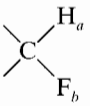
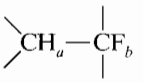
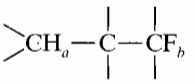
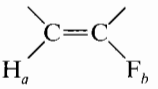
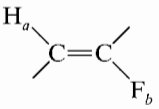
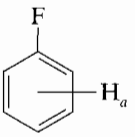
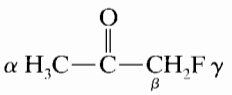
APPENDIX F PROTON SPIN-COUPLING CONSTANTS

Type	J_{ab} (Hz)	J_{ab} Typical
	0–30	12–15
$CH_a—CH_b$ (free rotation)	6–8	7
	0–1	0
		
ax–ax	6–14	8–10
ax–eq	0–5	2–3
eq–eq	0–5	2–3
 (*cis* or *trans*)	*cis* 5–10 *trans* 5–10	
 (*cis* or *trans*)	*cis* 4–12 *trans* 2–10	
 (*cis* or *trans*)	*cis* 7–13 *trans* 4–9	
$CH_a—OH_b$ (no exchange)	4–10	5
	1–3	2–3
	5–8	6
	12–18	17
	0–3	0–2

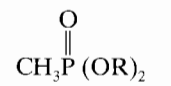
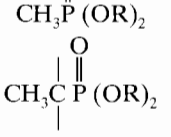
Type	J_{ab} (Hz)	J_{ab} Typical
	6–12	10
	0–3	1–2
	4–10	7
	0–3	1.5
	0–3	2
$C=CH_a—CH_b=C$	9–13	10
	3 member 4 member 5 member 6 member 7 member 8 member	0.5–2.0 2.5–4.0 5.1–7.0 8.8–11.0 9–13 10–13
$CH_a—C\equiv CH_b$	2–3	
$—CH_a—C\equiv C—CH_b—$	2–3	
		6
		4
		2.5
	*J (ortho)* *J (meta)* *J (para)*	6–10 1–3 0–1
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (3–5) *J* (2–5) *J* (2–6)	5–6 7–9 1–2 1–2 0–1 0–1
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (2–5)	1.3–2.0 3.1–3.8 0–1 1–2

APPENDIX F *(Continued)*

Type		J_{ab} (Hz)	J_{ab} Typical
	*J* (2–3)	4.9–6.2	5.4
	J (3–4)	3.4–5.0	4.0
	J (2–4)	1.2–1.7	1.5
	J (2–5)	3.2–3.7	3.4
	*J* (1–3)	2–3	
	J (2–3)	2–3	
	J (3–4)	3–4	
	J (2–4)	1–2	
	J (2–5)	1.5–2.5	
	J (4–5)	4–6	
	J (2–5)	1–2	
	J (2–4)	0–1	
	J (4–6)	2–3	
	J (4–5)	3–4	
	J (2–4)	~0	
	J (2–5)	1–2	

Type	J_{ab} (Hz)	J_{ab} Typical
Proton–Carbon-13 (See Tables 5.17, 5.18)		
Proton–Fluorine		
	44–81	
	3–25	
	0–4	
	1–8	
	12–40	
	*o* 6–10 *m* 5–6 *p* 2	
	αγ 4.3 βγ 48	

Proton–Phosphorus

	630–707
$(CH_3)_3P$	2.7
$(CH_3)_3P{=}O$	13.4
$(CH_3CH_2)_3P$	0.5 (HCCP) 13.7 (HCP)
$(CH_3CH_2)_3P{=}O$	11.9 (HCCP) 16.3 (HCP)
	10–13
	15–20
$CH_3OP(OR)_2$	10.5–12
$P[N(CH_3)_2]_3$	8.8
$O{=}P[N(CH_3)_2]_3$	9.5

Source: Complied by Varian Associates. Absolute values. Reproduced with permission.

APPENDIX G CHEMICAL SHIFTS AND MULTIPLICITIES OF RESIDUAL PROTONS IN COMMERCIALLY AVAILABLE DEUTERATED SOLVENTS (MERCK & CO., INC.)

Compound[a] Molecular Weight	δ_H (multiplet)	Compound[a] Molecular Weight	δ_H (multiplet)
Acetic acid-d_4	11.53 (1)	Nitromethane-d_3	4.33 (5)
64.078	2.03 (5)	64.059	
Acetone-d_6	2.04 (5)	Isopropyl alcohol-d_8	5.12 (1)
64.117		68.146	3.89 (br)
Acetonitrile-d_3	1.93 (5)		1.10 (br)
44.071			8.71 (br)
Benzene-d_6	7.15 (br)	Pyridine-d_5	7.55 (br)
84.152		84.133	7.19 (br)
Chloroform-d	7.26 (1)	Tetrahydrofuran-d_8	3.58 (br)
120.384		80.157	1.73 (br)
Cyclohexane-d_{12}	1.38 (br)	Toluene-d_8	7.09 (m)
96.236		100.191	7.00 (br)
Deuterium oxide	4.63 (ref. DSS)[c]		6.98 (m)
20.028	4.67 (ref. TSP)[c]		2.09 (5)
1,2-Dichloroethane-d_4	3.72 (br)	Trifluoroacetic acid-d	11.50 (1)
102.985		115.030	
Diethyl-d_{10} ether	3.34 (m)	2,2,2-Trifluoroethyl alcohol-d_3	5.02 (1)
84.185	1.07 (m)	103.059	3.88 (4 × 3)
Diglyme-d_{14}	3.49 (br)		
148.263	3.40 (br)		
	3.22 (5)		
N, N-Dimethylformamide-d_7	8.01 (br)		
80.138	2.91 (5)		
	2.74 (5)		
Dimethyl-d_6 sulphoxide	2.49 (5)		
84.170			
p-Dioxane-d_8	3.53 (m)		
96.156			
Ethyl alcohol-d_6 (anh)	5.19 (1)		
52.106	3.55 (br)		
	1.11 (m)		
Glyme-d_{10}	3.40 (m)		
100.184	3.22 (5)		
Hexafluroacetone deuterate	5.26 (1)		
198.067			
HMPT-d_{18}	2.53 (2 × 5)		
197.314			
Methyl alcohol-d_4	4.78 (1)		
36.067	3.30 (5)		
Methylene chloride-d_2	5.32 (3)		
86.945			
Nitrobenzene-d_5	8.11 (br)		
128.143	7.67 (br)		
	7.50 (br)		

[a] Purity (Atom % D) up to 99.96 % ("100 %") for several solvents.

[b] The residual proton consists of one proton of each kind in an otherwise completely deuterated molecule. For example, deuterated acetic acid has two different kinds of residual protons: CD_2H—COOD and CD_3—COOH. The CD_2H proton, coupled to two D nuclei is at δ 2.03 with a multiplicity of 5 (i.e., $2nI + 1 = 2 \times 2 \times 1 + 1 = 5$). The carboxylic proton is a singlet at δ 11.53.

[c] DSS is 3-trimethylsilyl)-1-propane sulfonic acid, sodium salt. TSP is sodium-3-trimethylpropionate-2,2,3,3-d_4. Both are reference standards used in aqueous solutions.

APPENDIX H CHEMICAL SHIFTS OF COMMON LABORATORY SOLVENTS as TRACE IMPURITIES

	proton	mult	$CDCl_3$	$(CD_3)_2CO$	$(CD_3)_2SO$	C_6D_6	CD_3CN	CD_3OD	D_2O
solvent residual peak			7.26	2.05	2.50	7.16	1.94	3.31	4.79
H_2O		s	1.56	2.84[a]	3.33[a]	0.40	2.13	4.87	
acetic acid	CH_3	s	2.10	1.96	1.91	1.55	1.96	1.99	2.08
acetone	CH_3	s	2.17	2.09	2.09	1.55	2.08	2.15	2.22
acetonitrile	CH_3	s	2.10	2.05	2.07	1.55	1.96	2.03	2.06
benzene	CH	s	7.36	7.36	7.37	7.15	7.37	7.33	
tert-butyl alcohol	CH_3	s	1.28	1.18	1.11	1.05	1.16	1.40	1.24
	OH[c]	s			4.19	1.55	2.18		
tert-butyl methyl ether	CCH_3	s	1.19	1.13	1.11	1.07	1.14	1.15	1.21
	OCH_3	s	3.22	3.13	3.08	3.04	3.13	3.20	3.22
BHT[b]	ArH	s	6.98	6.96	6.87	7.05	6.97	6.92	
	OH[c]	s	5.01		6.65	4.79	5.20		
	$ArCH_3$	s	2.27	2.22	2.18	2.24	2.22	2.21	
	$ArC(CH_3)_3$	s	1.43	1.41	1.36	1.38	1.39	1.40	
chloroform	CH	s	7.26	8.02	8.32	6.15	7.58	7.90	
cyclohexane	CH_2	s	1.43	1.43	1.40	1.40	1.44	1.45	
1,2-dichloroethane	CH_2	s	3.73	3.87	3.90	2.90	3.81	3.78	
dichloromethane	CH_2	s	5.30	5.63	5.76	4.27	5.44	5.49	
diethyl ether	CH_3	t, 7	1.21	1.11	1.09	1.11	1.12	1.18	1.17
	CH_2	q, 7	3.48	3.41	3.38	3.26	3.42	3.49	3.56
diglyme	CH_2	m	3.65	3.56	3.51	3.46	3.53	3.61	3.67
	CH_2	m	3.57	3.47	3.38	3.34	3.45	3.58	3.61
	OCH_3	s	3.39	3.28	3.24	3.11	3.29	3.35	3.37
1,2-dimethoxyethane	CH_3	s	3.40	3.28	3.24	3.12	3.28	3.35	3.37
	CH_2	s	3.55	3.46	3.43	3.33	3.45	3.52	3.60
dimethylacetamide	CH_3CO	s	2.09	1.97	1.96	1.60	1.97	2.07	2.08
	NCH_3	s	3.02	3.00	2.94	2.57	2.96	3.31	3.06
	NCH_3	s	2.94	2.83	2.78	2.05	2.83	2.92	2.90
dimethylformamide	CH	s	8.02	7.96	7.95	7.63	7.92	7.97	7.92
	CH_3	s	2.96	2.94	2.89	2.36	2.89	2.99	3.01
	CH_3	s	2.88	2.78	2.73	1.86	2.77	2.86	2.85
dimethyl sulfoxide	CH_3	s	2.62	2.52	2.54	1.68	2.50	2.65	2.71
dioxane	CH_2	s	3.71	3.59	3.57	3.35	3.60	3.66	3.75
ethanol	CH_3	t, 7	1.25	1.12	1.06	0.96	1.12	1.19	1.17
	CH_2	q, 7[d]	3.72	3.57	3.44	3.34	3.54	3.60	3.65
	OH	s[cd]	1.32	3.39	4.63		2.47		
ethyl acetate	CH_3CO	s	2.05	1.97	1.99	1.65	1.97	2.01	2.07
	CH_2CH_3	q, 7	4.12	4.05	4.03	3.89	4.06	4.09	4.14
	CH_2CH_3	t, 7	1.26	1.20	1.17	0.92	1.20	1.24	1.24
ethyl methyl ketone	CH_3CO	s	2.14	2.07	2.07	1.58	2.06	2.12	2.19
	CH_2CH_3	q, 7	2.46	2.45	2.43	1.81	2.43	2.50	3.18
	CH_2CH_3	t, 7	1.06	0.96	0.91	0.85	0.96	1.01	1.26
ethylene glycol	CH	s[e]	3.76	3.28	3.34	3.41	3.51	3.59	3.65
"grease"[f]	CH_3	m	0.86	0.87		0.92	0.86	0.88	
	CH_2	br s	1.26	1.29		1.36	1.27	1.29	
n-hexane	CH_3	t	0.88	0.88	0.86	0.89	0.89	0.90	
	CH_2	m	1.26	1.28	1.25	1.24	1.28	1.29	
HMPA[g]	CH_3	d, 9.5	2.85	2.59	2.53	2.40	2.57	2.64	2.61
methanol	CH_3	s[h]	3.49	3.31	3.16	3.07	3.28	3.34	3.34
	OH	s[gh]	1.09	3.12	4.01		2.16		
nitromethane	CH_3	s	4.33	4.43	4.42	2.94	4.31	4.34	4.40
n-pentane	CH_3	t, 7	0.88	0.88	0.86	0.87	0.89	0.90	
	CH_2	m	1.27	1.27	1.27	1.23	1.29	1.29	
2-propanol	CH_3	d, 6	1.22	1.10	1.04	0.95	1.09	1.50	1.17
	CH	sep, 6	4.04	3.90	3.78	3.67	3.87	3.92	4.02

APPENDIX H *(Continued)*

	proton	mult	$CDCl_3$	$(CD_3)_2CO$	$(CD_3)_2SO$	C_6D_6	CD_3CN	CD_3OD	D_2O
pyridine	CH(2)	m	8.62	8.58	8.58	8.53	8.57	8.53	8.52
	CH(3)	m	7.29	7.35	7.39	6.66	7.33	7.44	7.45
	CH(4)	m	7.68	7.76	7.79	6.98	7.73	7.85	7.87
silicone grease[i]	CH_3	s	0.07	0.13		0.29	0.08	0.10	
tetrahydrofuran	CH_2	m	1.85	1.79	1.76	1.40	1.80	1.87	1.88
	CH_2O	m	3.76	3.63	3.60	3.57	3.64	3.71	3.74
toluene	CH_3	s	2.36	2.32	2.30	2.11	2.33	2.32	
	CH(*o*/*p*)	m	7.17	7.1–7.2	7.18	7.02	7.1–7.3	7.16	
	CH(*m*)	m	7.25	7.1–7.2	7.25	7.13	7.1–7.3	7.16	
triethylamine	CH_3	t, 7	1.03	0.96	0.93	0.96	0.96	1.05	0.99
	CH_2	q, 7	2.53	2.45	2.43	2.40	2.45	2.58	2.57

[a] In these solvents the intermolecular rate of exchange is slow enough that a peak due to HDO is usually also observed; it appears at 2.81 and 3.30 ppm in acetone and DMSO, respectively. In the former solvent, it is often seen as a 1:1:1 triplet, with $^2J_{H,D} = 1$ Hz.

[b] 2,6-Dimethyl-4-*tert*-butylphenol.

[c] The signals from exchangeable protons were not always identified.

[d] In some cases (see note *a*), the coupling interaction between the CH_2 and the OH protons may be observed ($J = 5$ Hz).

[e] In CD_3CN, the OH proton was seen as a multiplet at δ 2.69, and extra coupling was also apparent on the methylene peak.

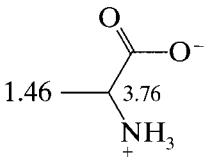
[f] Long-chain, linear aliphatic hydrocarbons. Their solubility in DMSO was too low to give visible peaks.

[g] Hexamethylphosphoramide.

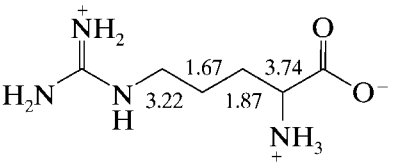
[h] In some cases (see notes *a*, *d*), the coupling interaction between the CH_3 and the OH protons may be observed ($J = 5.5$ Hz).

[i] Poly(dimethylsiloxane). Its solubility in DMSO was too low to give visible peaks.

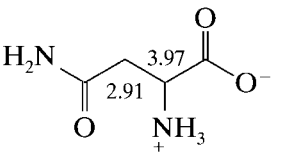
APPENDIX I PROTON NMR CHEMICAL SHIFTS OF AMINO ACIDS IN D_2O



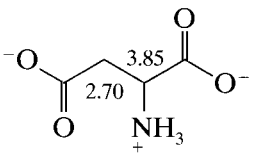
Alanine (Ala) (A)



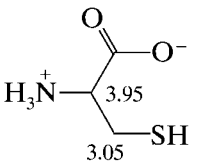
Arginine (Arg) (R)



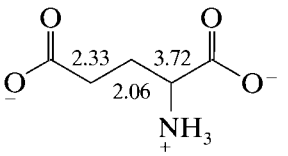
Asparagine (Asn) (N)



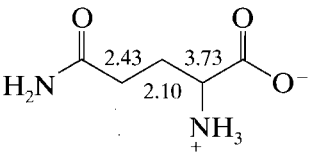
Aspartic Acid (Asp) (D)



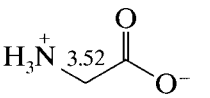
Cysteine (Cys) (C)



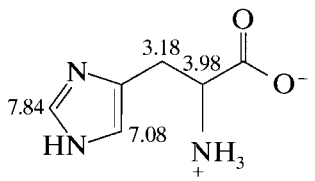
Glutamic Acid (Glu) (E)



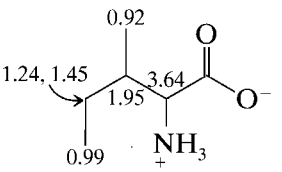
Glutamine (Gln) (Q)



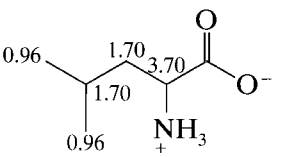
Glycine (Gly) (G)



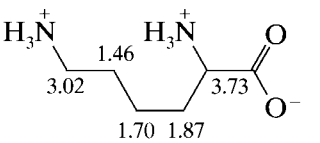
Histidine (His) (H)



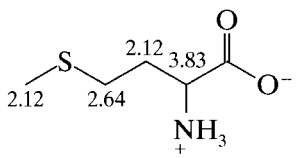
Isoleucine (Ilue) (I)



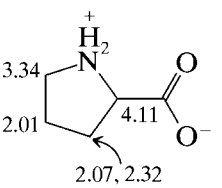
Leucine (Leu) (L)



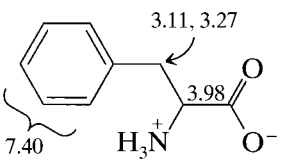
Lysine (Lys) (K)



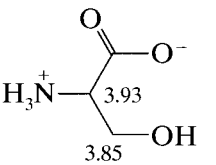
Methionine (Met) (M)



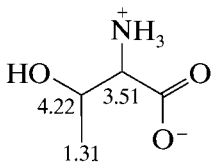
Proline (Pro) (P)



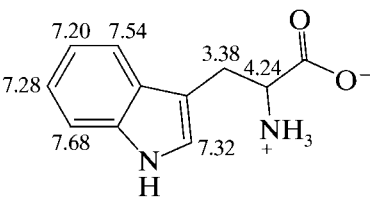
Phenylalanine (Phe) (F)



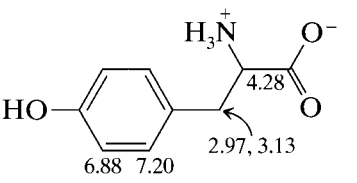
Serine (Ser) (S)



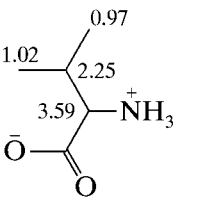
Threonine (Thr) (T)



Tryptophan (Trp) (W)



Tyrosine (Tyr) (Y)



Valine (Val) (V)