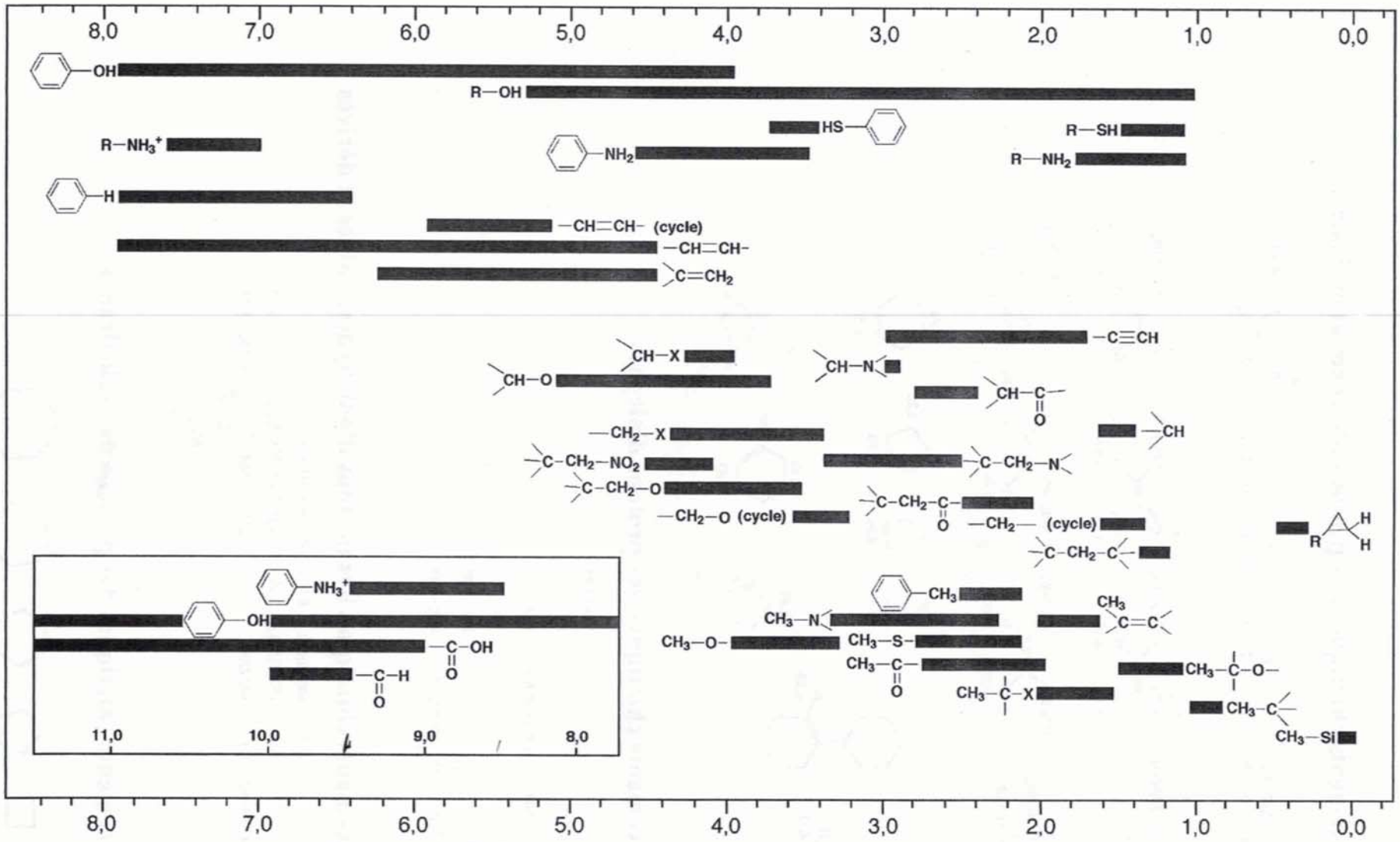
^{1}H NMR

Table de déplacements chimiques du proton



Remarque importante : Cette table n'est pas exhaustive. Par ailleurs, les limites indiquées ns sont pas absolues.

appendix b. effect on chemical shifts of two or three functional groups (Y-CH_2-Z, and Y-CH(W)-Z)

Shoolery's rules (B. P. Dailey and J. W. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955) permit calculation of a shift position of a methylene group attached to two functional groups by the additive effect of the shielding constants in Table 1, below. The sum of the constants is added to δ 0.23, the position for CH_4.

Thus, to calculate the shift for the $-CH_2-$ protons of $C_6H_5CH_2Br$:

C_6H_5 =	1.85	0.23
Br =	2.33	4.18
	4.18	4.41 = δ value for the $-CH_2-$ group.

Table I. Shielding Constants

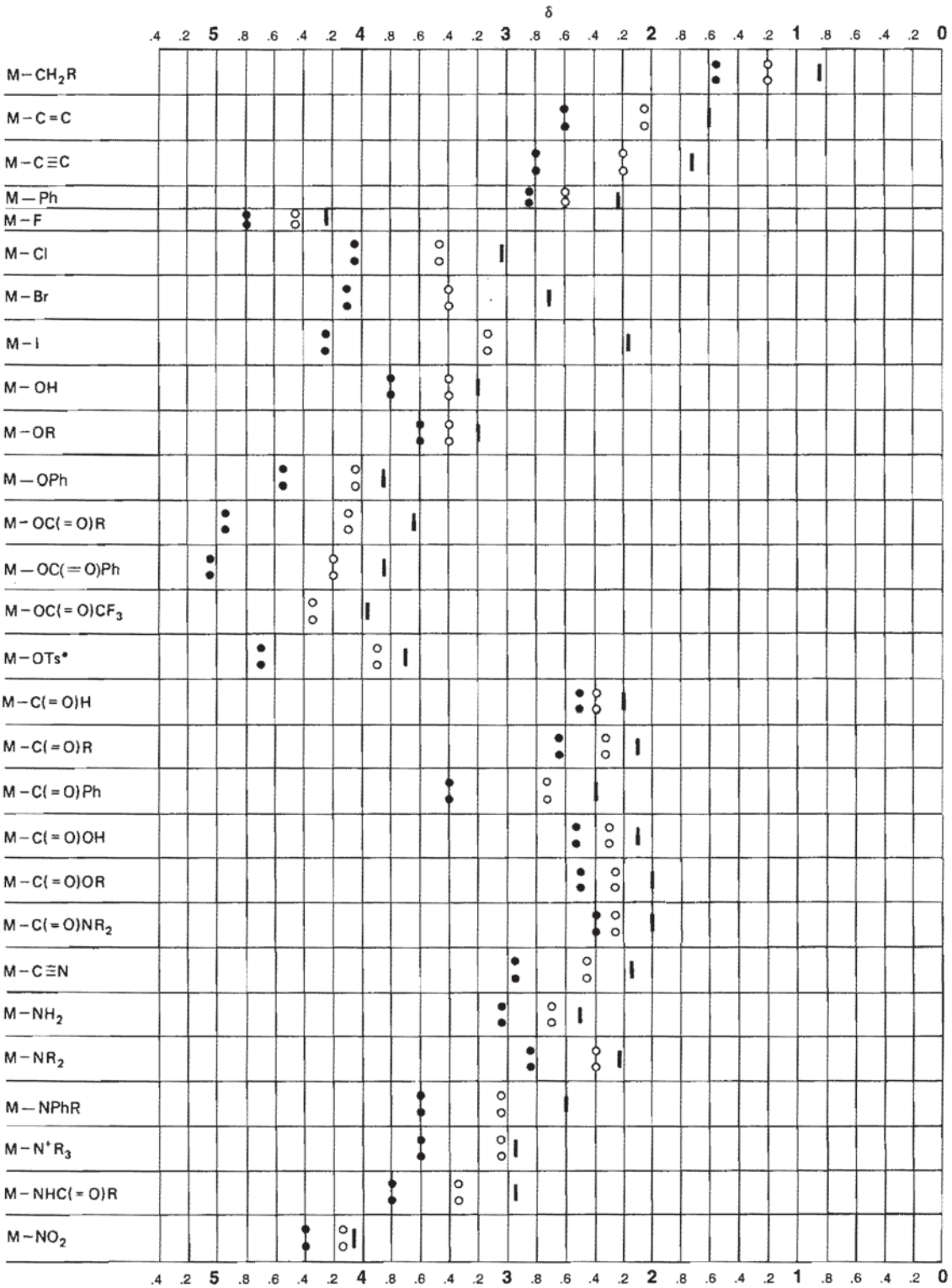
Y or *Z*	Shielding Constants	*Y* or *Z*	Shielding Constants
$-CH_3$	0.47	$-C(=O)NR_2$	1.59
$-C=C$	1.32	$-C\equiv N$	1.70
$-C\equiv C$	1.44	$-NR_2$	1.57
$-\phi$	1.85	$-NHC(=O)R$	2.27
$-CF_2$	1.21	$-N_3$	1.97
$-CF_3$	1.14	$-SR$	1.64
$-Cl$	2.53	$-OSO_2R$	3.13
$-Br$	2.33		
$-I$	1.82		
$-OH$	2.56		
$-OR$	2.36		
$-O\phi$	3.23		
$-OC(=O)R$	3.13		
$-C(=O)R$	1.70		
$-C(=O)\phi$	1.84		
$-C(=O)OR$	1.55		

The shielding constants have been used to prepare the chart on page 224. Several values have been added to the original set of constants.

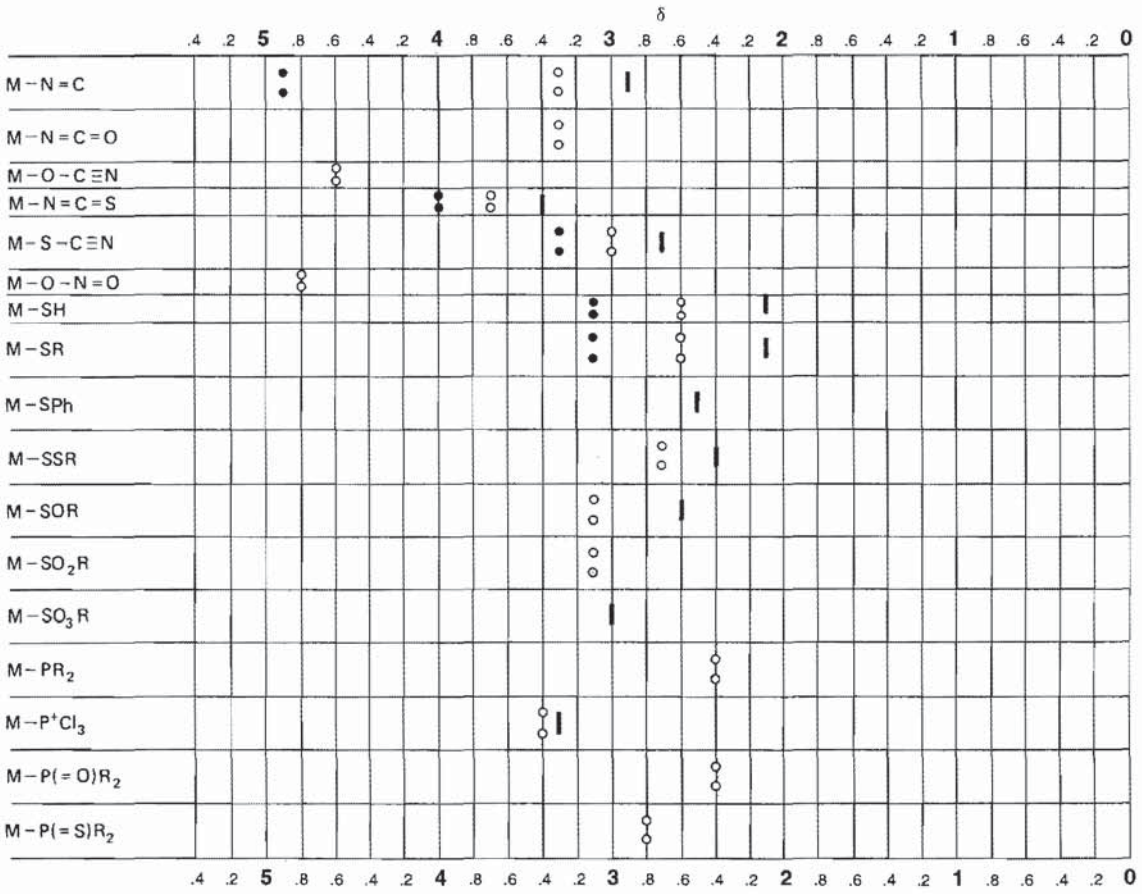
Alternatively, Chart 1 can be used to find the shift position of a methylene group attached to two functional groups from the δ values in the box at the intersection of the horizontal and diagonal groups ("mileage chart"). The upper number in each box is an experimental value; the lower number is calculated from Shoolery's constants.

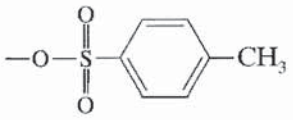
APPENDIX A CHART A.1 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—Y)

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



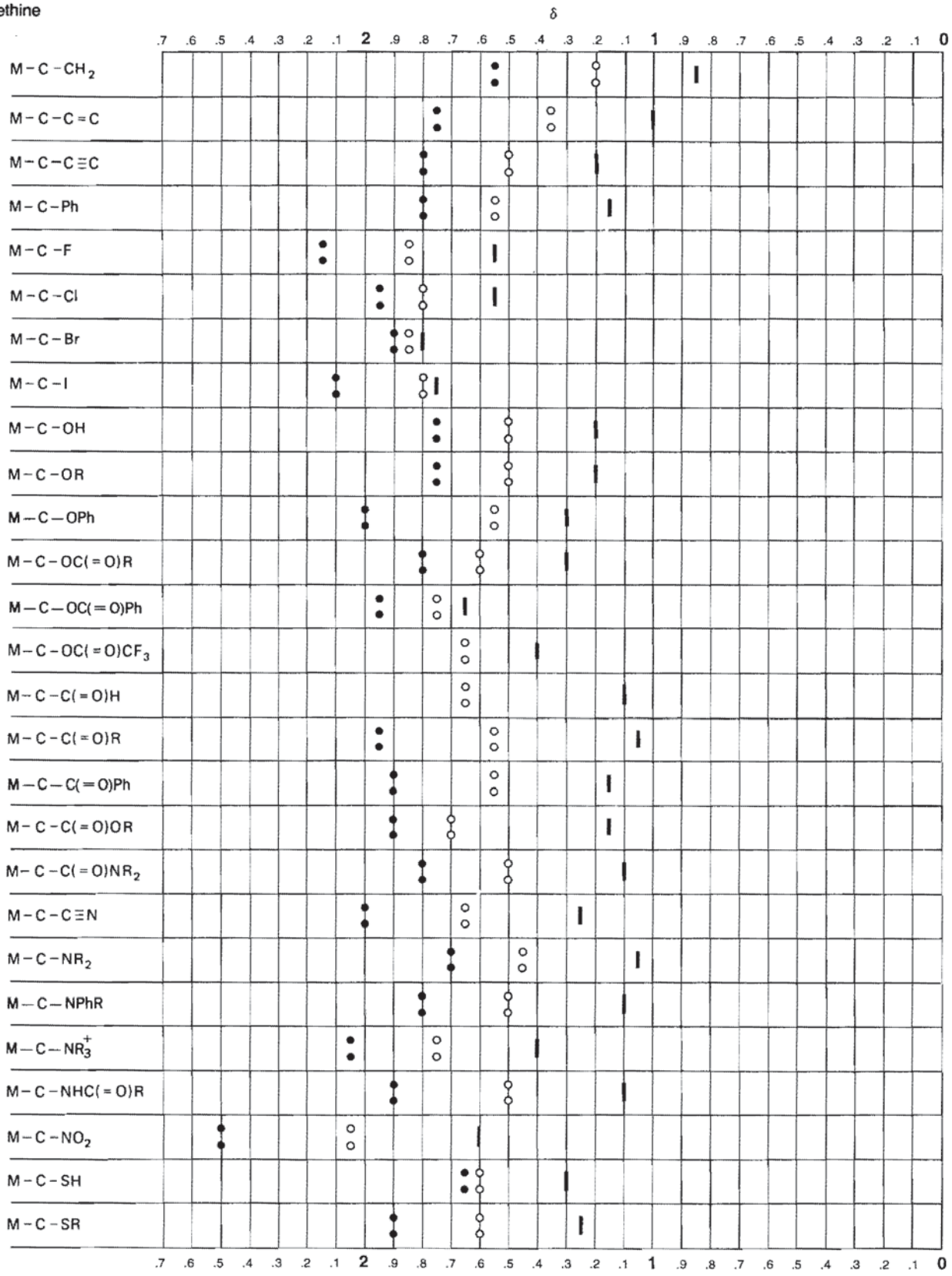
APPENDIX A *(Continued)*



*OTS is 

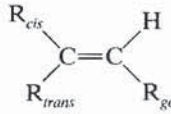
APPENDIX A CHART A.2 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ONCE REMOVED (β POSITION) FROM A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—C—Y)

▮ M = methyl
▯ M = methylene
⋮ M = methine



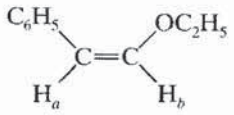
APPENDIX D CHEMICAL SHIFTS IN UNSATURATED AND AROMATIC SYSTEMS

(See Table D.1)



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

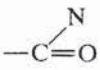
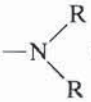
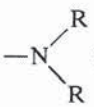
For example, the chemical shifts of the alkene protons in



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.

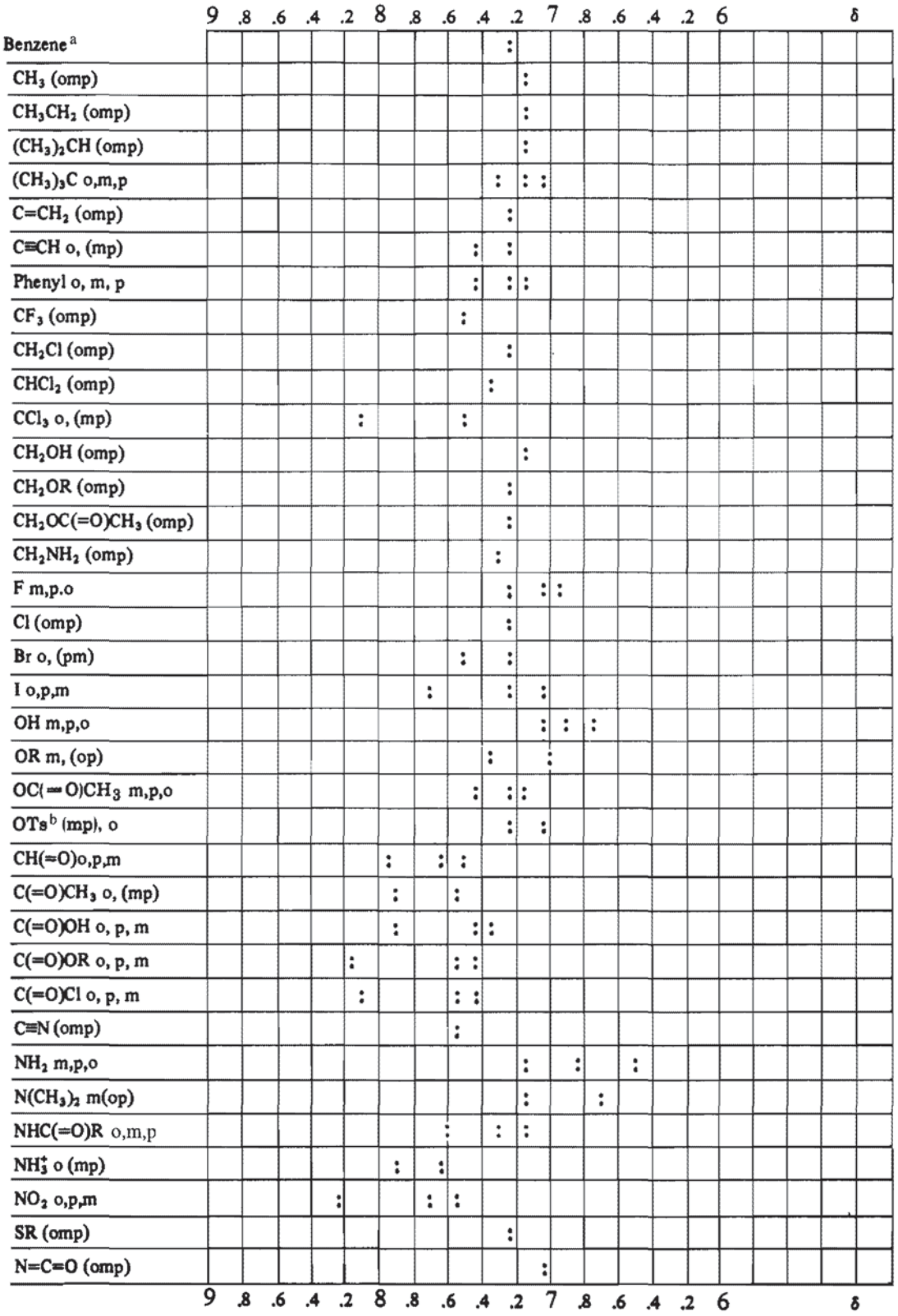
	Z				Z		
Substituent R	*gem*	*cis*	*trans*	**Substituent R**	*gem*	*cis*	*trans*
—H	0	0	0				
—Alkyl	0.44	−0.26	−0.29		1.03	0.97	1.21
—Alkyl-ring[a]	0.71	−0.33	−0.30				
—CH_2O, —CH_2I	0.67	−0.02	−0.07		1.37	0.93	0.35
—CH_2S	0.53	−0.15	−0.15				
—CH_2Cl, —CH_2Br	0.72	0.12	0.07		1.10	1.41	0.99
—CH_2N	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.

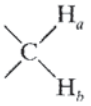
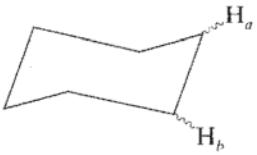
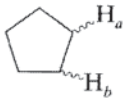
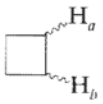
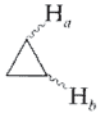
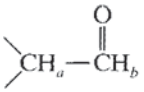
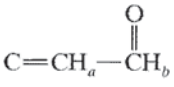
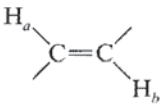
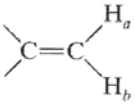
Source: Pascual C., Meier, J., and Simon, W. (1966) *Helv. Chim. Acta*, **49**, 164.

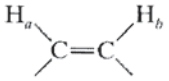
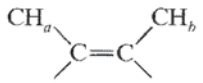
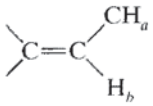
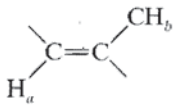
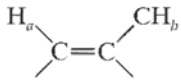
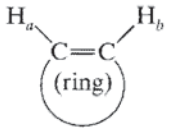
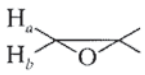
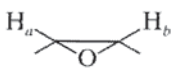
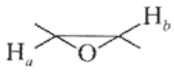
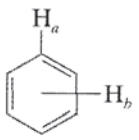
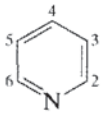
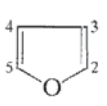
CHART D.1 CHEMICAL SHIFTS OF PROTONS ON MONOSUBSTITUTED BENZENE RINGS



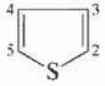
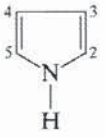
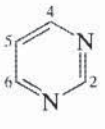
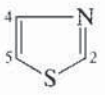
[a] The benzene ring proton is at δ 7.27, from which the shift increments are calculated as shown at the end of Section 3.4.
[b] OTS = *p*-toluenesulfonyloxy group.

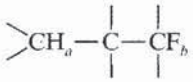
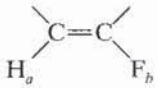
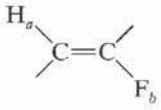
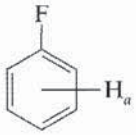
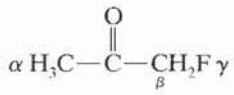
APPENDIX F PROTON SPIN-COUPLING CONSTANTS

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

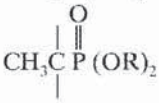
Type	J_{ab} (Hz)	J_{ab} Typical
	6–12	10
	0–3	1–2
	4–10	7
	0–3	1.5
	0–3	2
$C=CH_a—CH_b=C$	9–13	10
	3 member 4 member 5 member 6 member 7 member 8 member	0.5–2.0 2.5–4.0 5.1–7.0 8.8–11.0 9–13 10–13
$CH_a—C\equiv CH_b$	2–3	
$—CH_a—C\equiv C—CH_b—$	2–3	
		6
		4
		2.5
	*J (ortho)* *J (meta)* *J (para)*	6–10 1–3 0–1	9 3 ~0
	*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	5 8 1.5 1.5 1 ~0
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (2–5)	1.3–2.0 3.1–3.8 0–1 1–2	1.8 3.6 ~0 1.5

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 C CHEMICAL SHIFTS IN ALICYCLIC AND HETEROCYCLIC RINGS

TABLE C.1 Chemicals Shifts in Alicyclic Rings.

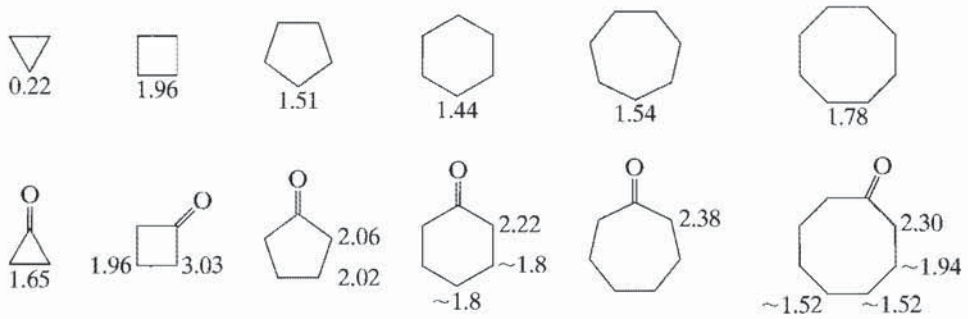


TABLE C.2 Chemical Shifts in Heterocyclic Rings.

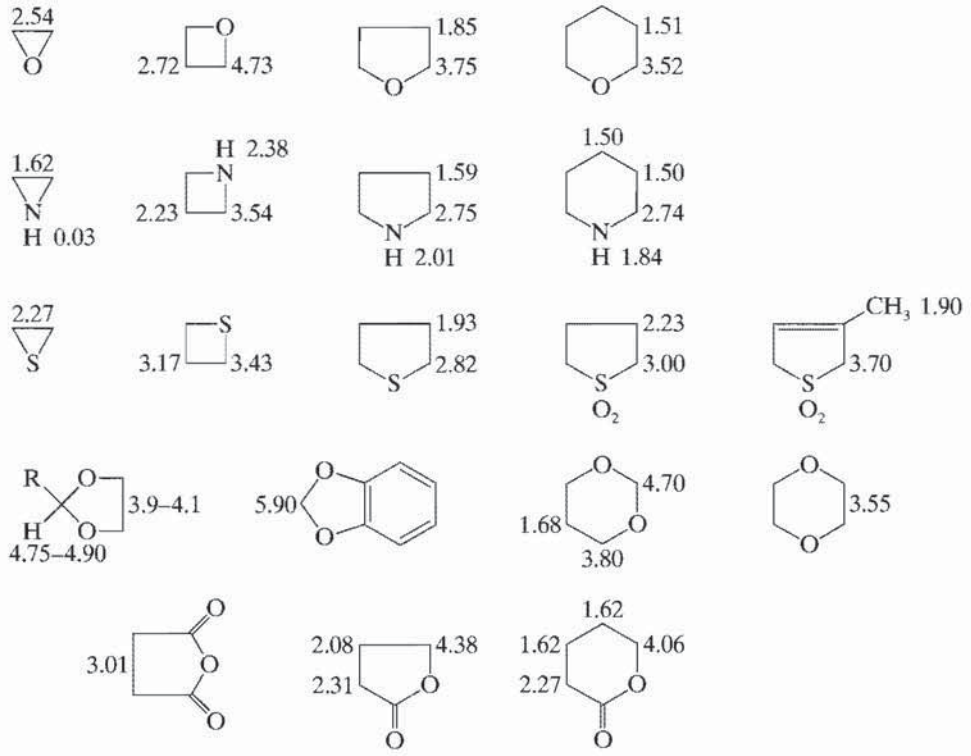


TABLE D.2 Chemical Shifts of Miscellaneous Alkenes

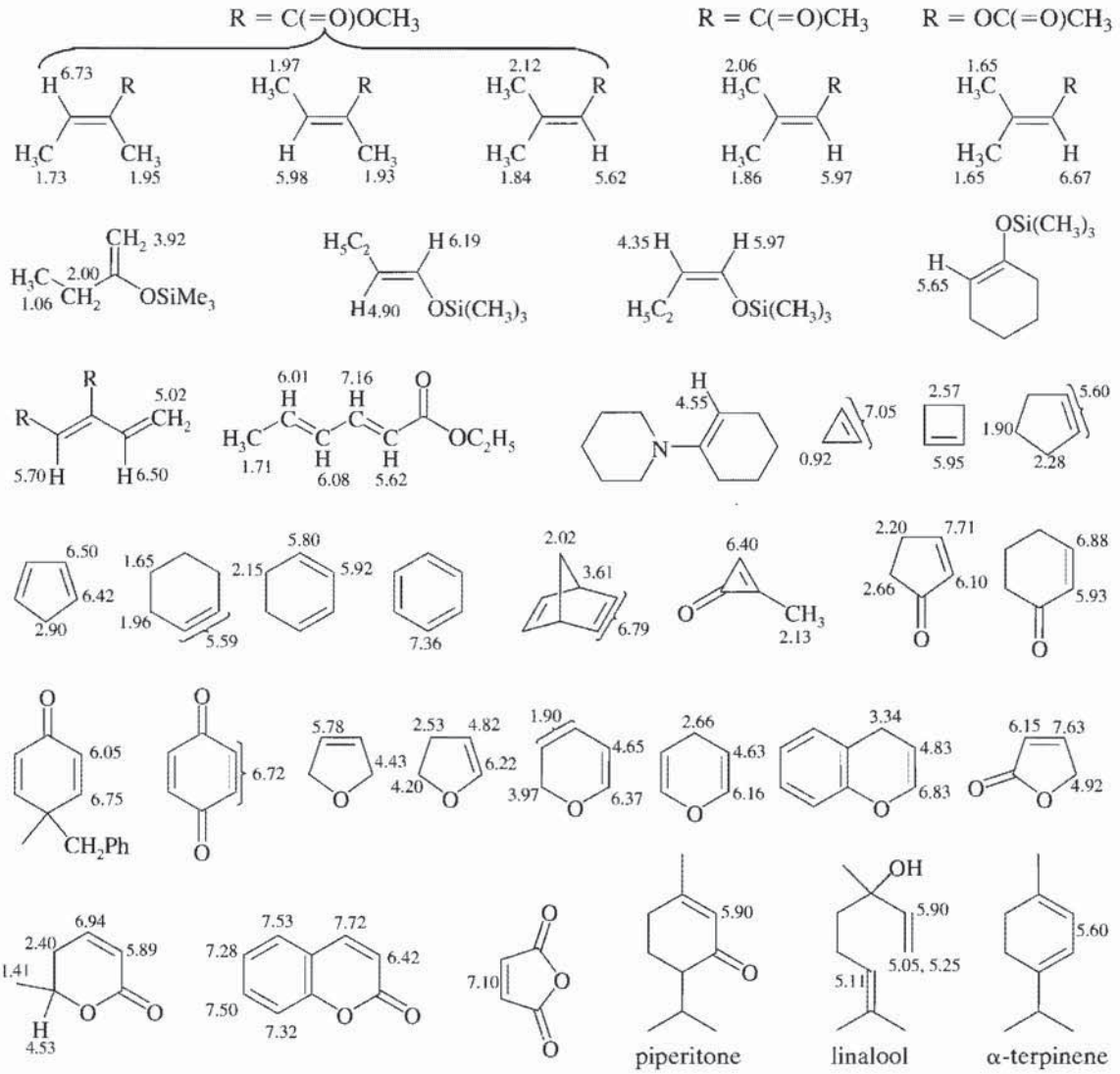


TABLE D.3 Chemical Shifts of Alkyne Protons

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