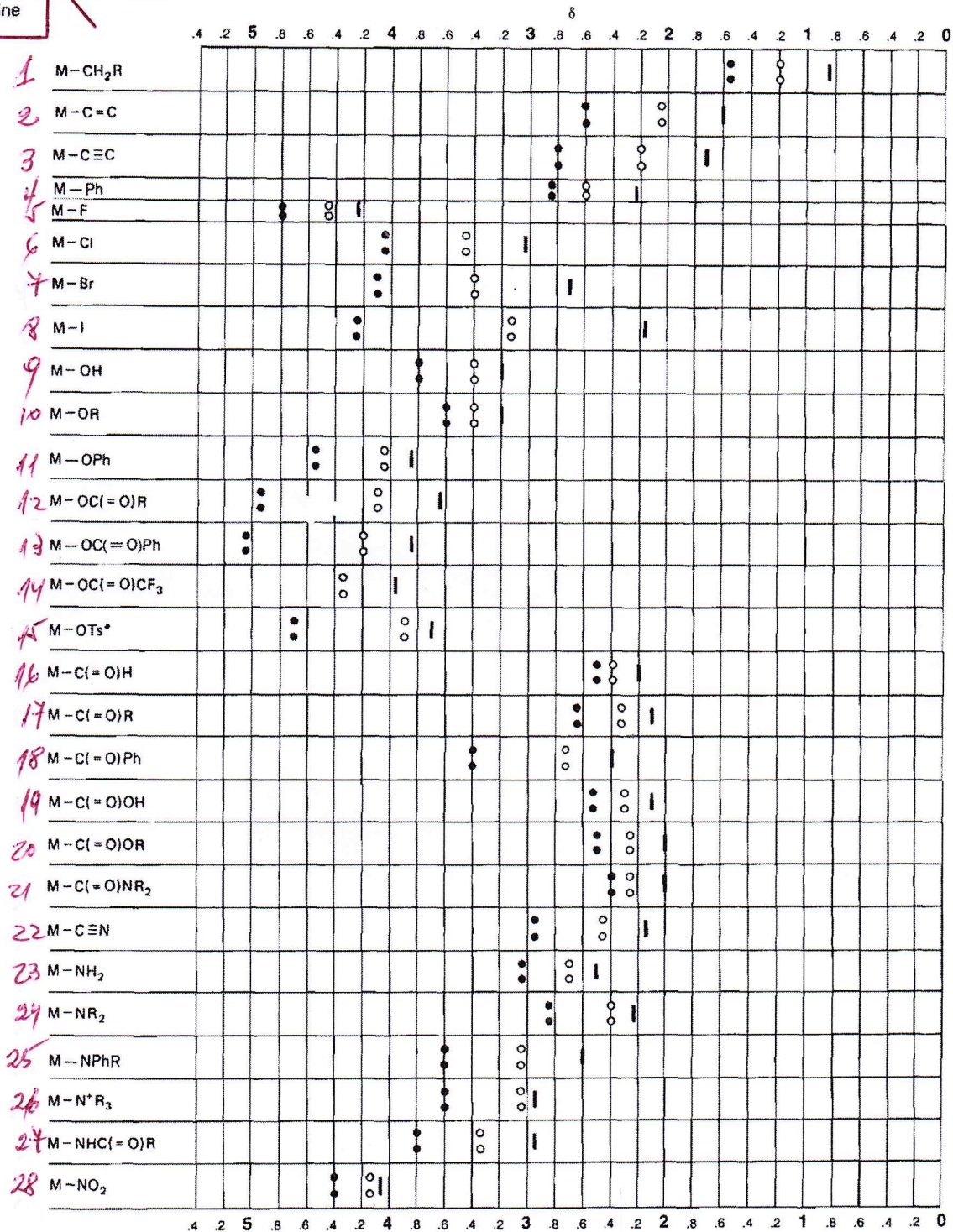
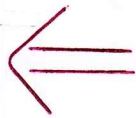


I

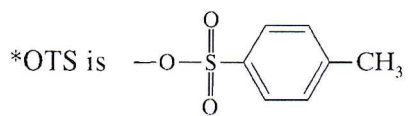
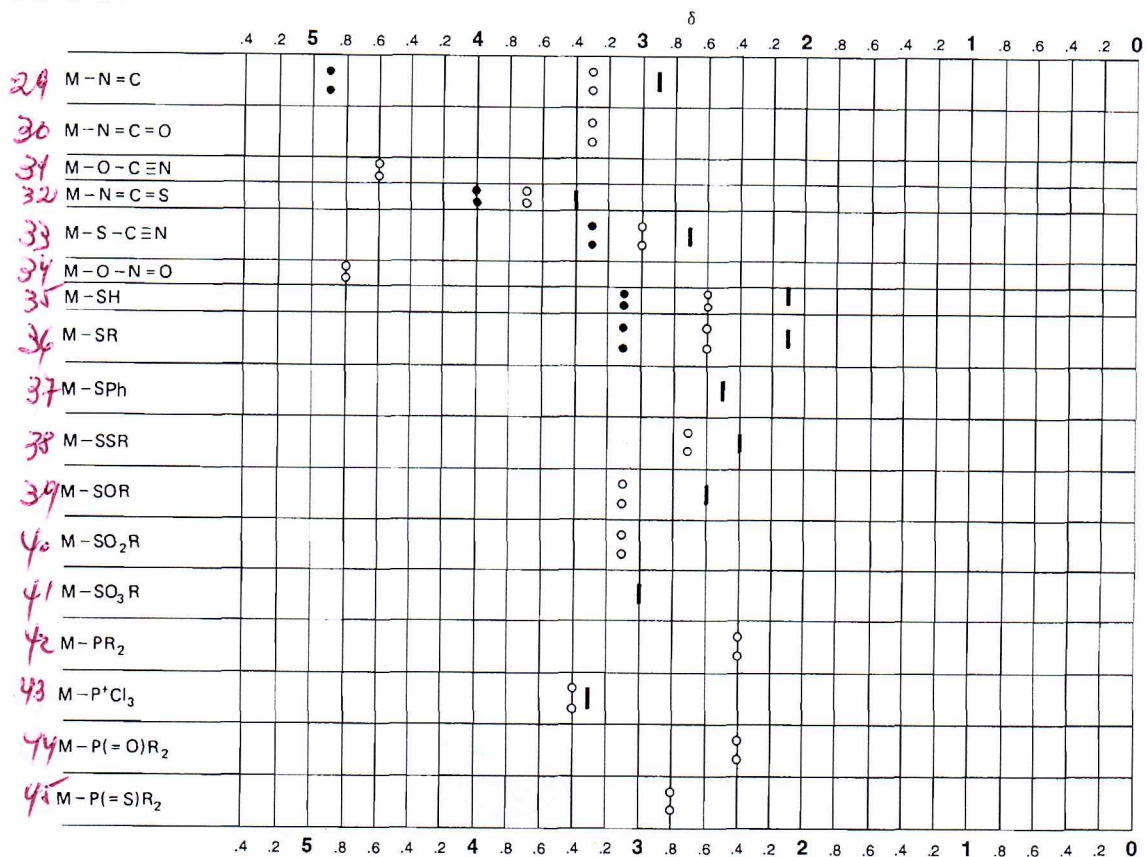
CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—Y)

| | |
|---|---------------|
| | M = methyl |
| o | M = methylene |
| : | M = methine |



I

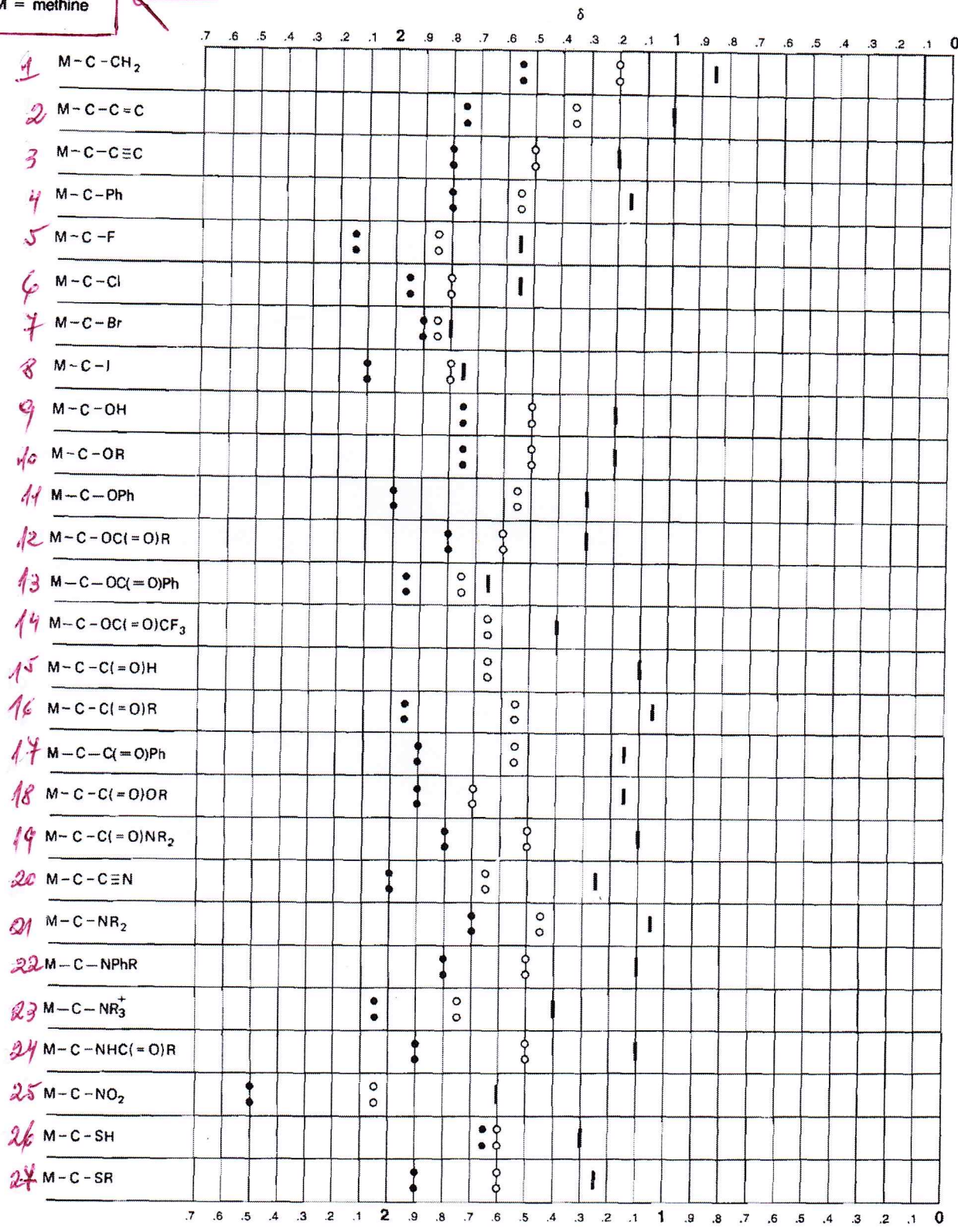
(Continued)



II

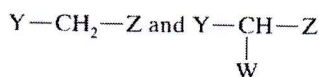
CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ONCE REMOVED (β POSITION) FROM A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—C—Y)

■ M = methyl
 ○ M = methylene
 ◐ M = methine





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



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. Shooley's rule* states that the sum of the constants for the attached functional groups is added to $\delta 0.23$, 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.

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

Shooley'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

* Shooley, 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 ₂ R | 3.13 |

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 .

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



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.

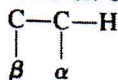
Tables B.2b and B.2c are used jointly for methine protons that are substituted by at least two alkyl groups

* 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 ₂ R | 0.94 |
| -R | 0 |

Substituent Effects on Chemical Shift^a



| Substituent | Type of Hydrogen ^b | Alpha Shift | Beta Shift |
|--|-------------------------------|--------------------|------------|
| —C=C— | 1 CH ₃ | 0.78 | |
| | 2 CH ₂ | 0.75 | 0.10 |
| —C=C—C—R X (X = C or O) | 3 CH | | |
| | 4 CH ₃ | 1.08 | |
| Aryl | 5 CH ₃ | 1.40 | 0.35 |
| | 6 CH ₂ | 1.45 | 0.53 |
| | 7 CH | 1.33 | |
| —Cl | 8 CH ₃ | 2.43 | 0.63 |
| | 9 CH ₂ | 2.30 | 0.53 |
| | 10 CH | 2.55 | 0.03 |
| —Br | 11 CH ₃ | 1.80 | 0.83 |
| | 12 CH ₂ | 2.18 | 0.60 |
| | 13 CH | 2.68 | 0.25 |
| —I | 14 CH ₃ | 1.28 | 1.23 |
| | 15 CH ₂ | 1.95 | 0.58 |
| | 16 CH | 2.75 | 0.00 |
| —OH | 17 CH ₃ | 2.50 | 0.33 |
| | 18 CH ₂ | 2.30 | 0.13 |
| | 19 CH | 2.20 | |
| —OR (R is saturated) | 20 CH ₃ | 2.43 | 0.33 |
| | 21 CH ₂ | 2.35 | 0.15 |
| | 22 CH | 2.00 | |
| —OC(=O)—R, —OC(=O)—OR, —OAr | 23 CH ₃ | 2.88 | 0.38 |
| | 24 CH ₂ | 2.98 | 0.43 |
| | 25 CH | 3.43 (esters only) | |
| —CR(=O), where R is alkyl, aryl, OH, OR', H, CO, or N | 26 CH ₃ | 1.23 | 0.18 |
| | 27 CH ₂ | 1.05 | 0.31 |
| | 28 CH | 1.05 | |
| —NRR' | 29 CH ₃ | 1.30 | 0.13 |
| | 30 CH ₂ | 1.33 | 0.13 |
| | 31 CH | 1.33 | |

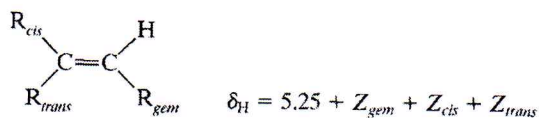
^aFrom the Ph.D. dissertation of T. J. Curphey, Harvard University, by permission.

^bStandard positions are CH₃, δ 0.87; CH₂, δ 1.20; CH, δ 1.55.

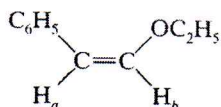
See also chemical shift correlations for methine proton, *Source*: E. C. Friedrich and K. G. Runkle, *J. Chem. Educ.*, **63**, 127 (1986).

CHEMICAL SHIFTS IN UNSATURATED AND AROMATIC SYSTEMS

(See Table D.1)



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.

| Substituent R | Z | | | Substituent R | Z | | |
|--|------|-------|-------|--|------|-------|-------|
| | gem | cis | trans | | gem | cis | trans |
| -H | 0 | 0 | 0 | $\begin{array}{c} H \\ \\ -C=O \end{array}$ | 1.03 | 0.97 | 1.21 |
| -Alkyl | 0.44 | -0.26 | -0.29 | $\begin{array}{c} N \\ \\ -C=O \end{array}$ | 1.37 | 0.93 | 0.35 |
| -Alkyl-ring ^a | 0.71 | -0.33 | -0.30 | $\begin{array}{c} Cl \\ \\ -C=O \end{array}$ | 1.10 | 1.41 | 0.99 |
| -CH ₂ O, -CH ₂ I | 0.67 | -0.02 | -0.07 | -OR, R: aliph | 1.18 | -1.06 | -1.28 |
| -CH ₂ S | 0.53 | -0.15 | -0.15 | -OR, R: conj ^b | 1.14 | -0.65 | -1.05 |
| -CH ₂ Cl, -CH ₂ Br | 0.72 | 0.12 | 0.07 | -OCOR | 2.09 | -0.40 | -0.67 |
| -CH ₂ N | 0.66 | -0.05 | -0.23 | -Aromatic | 1.35 | 0.37 | -0.10 |
| -C≡C | 0.50 | 0.35 | 0.10 | -Cl | 1.00 | 0.19 | 0.03 |
| -C≡N | 0.23 | 0.78 | 0.58 | -Br | 1.04 | 0.40 | 0.55 |
| -C=C | 0.98 | -0.04 | -0.21 | $\begin{array}{c} R \\ / \\ -N \\ \backslash \\ R \end{array}$ R:aliph | 0.69 | -1.19 | -1.31 |
| -C=C conj ^b | 1.26 | 0.08 | -0.01 | $\begin{array}{c} R \\ / \\ -N \\ \backslash \\ R \end{array}$ R:conj ^b | 2.30 | -0.73 | -0.81 |
| -C=O | 1.10 | 1.13 | 0.81 | -SR | 1.00 | -0.24 | -0.04 |
| -C=O conj ^b | 1.06 | 1.01 | 0.95 | -SO ₂ | 1.58 | 1.15 | 0.95 |
| -COOH | 1.00 | 1.35 | 0.74 | | | | |
| -COOH conj ^b | 0.69 | 0.97 | 0.39 | | | | |
| -COOR | 0.84 | 1.15 | 0.56 | | | | |
| -COOR conj ^b | 0.68 | 1.02 | 0.33 | | | | |

^a Alkyl ring indicates that the double bond is part of the ring $\begin{array}{c} C \\ | \\ R \\ || \\ C \end{array}$.

^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.

(Continued)

PROTON SPIN-COUPLED CONSTANTS

| Type | J_{ab} (Hz) | J_{ab} Typical | Type | J_{ab} (Hz) | J_{ab} Typical | Type | J_{ab} (Hz) | J_{ab} Typical |
|---|--------------------------------------|------------------|---|---------------|------------------|------|---------------|------------------|
| | 0-30 | 12-15 | | 6-12 | 10 | | 4.9-6.2 | 5.4 |
| CH_2-CH_2 (free rotation) | 6-8 | 7 | | 0-3 | 1-2 | | 3.4-5.0 | 4.0 |
| | 0-1 | 0 | | 4-10 | 7 | | 1.2-1.7 | 1.5 |
| | | | | 0-3 | 1.5 | | 3.2-3.7 | 3.4 |
| ax-ax | 6-14 | 8-10 | | 0-3 | 2 | | 2-3 | 2-3 |
| ax-eq | 0-5 | 2-3 | $\text{C}=\text{CH}_2-\text{CH}_2=\text{C}$ | 9-13 | 10 | | 2-3 | 2-3 |
| eq-eq | 0-5 | 2-3 | | 3 member | 0.5-2.0 | | 4-6 | 4-6 |
| | <i>cis</i> 5-10 <i>trans</i> 5-10 | | | 4 member | 2.5-4.0 | | 1-2 | 1-2 |
| (<i>cis</i> or <i>trans</i>) | | | | 5 member | 5.1-7.0 | | 0-1 | 0-1 |
| | <i>cis</i> 4-12 <i>trans</i> 2-10 | | | 6 member | 8.8-11.0 | | 2-3 | 2-3 |
| (<i>cis</i> or <i>trans</i>) | | | | 7 member | 9-13 | | 3-4 | 3-4 |
| | | | | 8 member | 10-13 | | 3-4 | 3-4 |
| (<i>cis</i> or <i>trans</i>) | | | $\text{CH}_2-\text{C}\equiv\text{CH}_2$ $-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-$ | 2-3 | 2-3 | | 0-1 | 0-1 |
| CH_2-OH_2 (no exchange) | 4-10 | 5 | | 2-3 | | | 1-2 | 1-2 |
| | 1-3 | 2-3 | | 2-3 | | | 1-2 | 1-2 |
| $\text{C}=\text{CH}_2-\text{CH}_3$ | 5-8 | 6 | | 2-3 | | | 1-2 | 1-2 |
| | 12-18 | 17 | | 2-3 | | | 1-2 | 1-2 |
| | 0-3 | 0-2 | | 2-3 | | | 1-2 | 1-2 |
| | 0-3 | 0-2 | | 2-3 | | | 1-2 | 1-2 |

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

VI

Proton-Carbon-13
(See Tables 5.17, 5.18)

Proton-Fluorine

α H_a H_b

β H_a H_b

γ H_a H_b

δ H_a H_b

ϵ H_a H_b

ζ H_a H_b

η H_a H_b

θ H_a H_b

ι H_a H_b

κ H_a H_b

λ H_a H_b

μ H_a H_b

ν H_a H_b

ξ H_a H_b

\omicron H_a H_b

π H_a H_b

ρ H_a H_b

σ H_a H_b

τ H_a H_b

υ H_a H_b

ϕ H_a H_b

χ H_a H_b

ψ H_a H_b

ω H_a H_b

η H_a H_b

θ H_a H_b

ι H_a H_b

κ H_a H_b

λ H_a H_b

μ H_a H_b

ν H_a H_b

ξ H_a H_b

\omicron H_a H_b

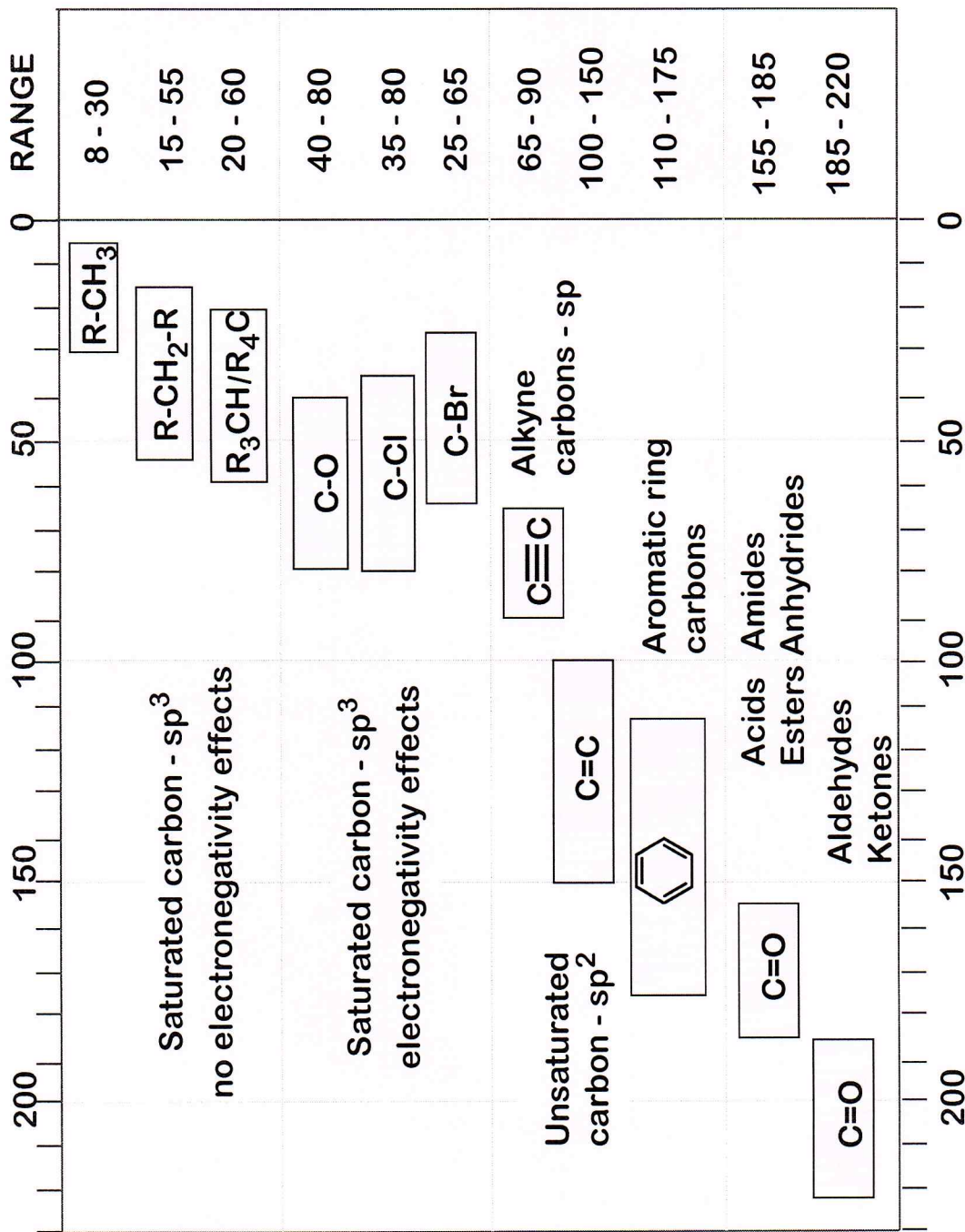
π H_a H_b

ρ H_a H_b

σ H_a H_b

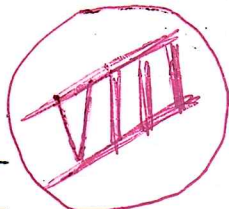
τ H_a H_b

υ H_a H_b



Correlation chart for ^{13}C Chemical Shifts (ppm)

VII



Substituent Chemical Shifts ($\Delta\delta$) in Benzenes*

| Substituent | $\Delta\delta_H$ | | | $\Delta\delta_C$ | | | |
|---|------------------|-------|-------|------------------|-------|------|-------|
| | ortho | meta | para | C ₁ | ortho | meta | para |
| NO ₂ | 0.95 | 0.26 | 0.38 | 20.0 | -4.8 | 0.9 | 5.8 |
| CO.OCH ₃ | 0.71 | 0.11 | 0.21 | 1.8 | 1.0 | -0.2 | 5.3 |
| CO.CH ₃ | 0.62 | 0.14 | 0.21 | 9.1 | 0.1 | 0.0 | 4.2 |
| CHO | 0.56 | 0.22 | 0.29 | 8.6 | 1.3 | 0.6 | 5.5 |
| CN | 0.36 | 0.18 | 0.28 | -15.4 | 3.6 | 0.6 | 3.9 |
| F | -0.29 | -0.02 | -0.23 | 34.8 | -12.9 | 1.4 | -4.5 |
| Cl | 0.03 | -0.02 | -0.09 | 6.2 | 0.4 | 1.3 | -1.9 |
| Br | 0.18 | -0.08 | -0.04 | -5.5 | 3.4 | 1.7 | -1.6 |
| I | 0.39 | -0.21 | 0.00 | -34.1 | 8.7 | 1.4 | -1.4 |
| OH | -0.56 | -0.12 | -0.45 | 26.9 | -12.7 | 1.4 | -7.3 |
| OCH ₃ | -0.48 | -0.09 | -0.44 | 31.4 | -14.4 | 1.0 | -7.7 |
| O.CO.CH ₃ | -0.25 | 0.03 | -0.13 | 19.3 | -9.8 | -2.2 | -6.9 |
| CH ₃ | -0.20 | -0.12 | -0.22 | 8.9 | 0.7 | -0.1 | -2.9 |
| NH ₂ | -0.75 | -0.25 | -0.65 | 18.0 | -13.3 | 0.9 | -9.8 |
| NMe ₂ | -0.66 | -0.18 | -0.67 | 22.6 | -15.6 | 1.0 | -11.5 |
| CH ₂ OH | — | — | — | 12.2 | -1.7 | -0.3 | -1.3 |
| CH ₂ F | — | — | — | 8.6 | -0.9 | 0.2 | 0.2 |
| CH ₂ CH ₂ CO ₂ CH ₂ CH ₃ | — | — | — | 12.2 | 0.1 | -0.1 | -2.2 |
| CO.Ph | 0.53 | 0.20 | 0.31 | 9.1 | 1.5 | -0.2 | 3.9 |
| SO ₂ .Ph | 0.69 | 0.26 | 0.27 | 13.1 | -0.9 | 0.7 | 4.6 |

*In ppm from benzene (δ_H , 7.262; δ_C , 128.5).

Substituent Effects on ¹³C Chemical Shifts ($\Delta\delta_c$) in 1-Substituted Pentanes*

| Substituent | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ |
|--------------------|----------------|----------------|----------------|----------------|----------------|
| F | 70.1 | 8.0 | -6.7 | 0.1 | 0.0 |
| Cl | 30.6 | 10.0 | -5.3 | -0.5 | -0.1 |
| Br | 19.3 | 10.1 | -4.1 | -0.7 | 0.0 |
| I | -7.4 | 10.5 | -2.1 | -1.1 | -0.1 |
| CH ₃ | 9.3 | 9.4 | -2.5 | 0.4 | 0.2 |
| NH ₂ | 29.7 | 11.2 | -5.0 | 0.1 | 0.0 |
| OH | 48.3 | 10.1 | -6.0 | 0.3 | 0.2 |
| CHO | 31.4 | 0.7 | -1.9 | 0.8 | 0.5 |
| CO.CH ₃ | 30.7 | 2.1 | -1.2 | 1.4 | 1.2 |
| COOH | 20.5 | 2.3 | -2.7 | 0.2 | 0.3 |
| C≡N | 3.7 | 3.2 | -2.9 | -0.4 | -0.8 |
| C≡CH | 5.0 | 5.8 | -3.0 | 0.4 | — |
| CH=CH ₂ | 20.3 | 6.2 | -2.8 | 0.0 | -0.1 |

*In ppm from pentane (C₁, 13.7; C₂, 22.6; C₃, 34.5).

Substituent Effects on ¹³C Chemical Shifts ($\Delta\delta_c$) in 1-Substituted Ethylenes*

| Substituent | C ₁ | C ₂ |
|------------------|----------------|----------------|
| F | 24.9 | -34.3 |
| Cl | 3.3 | -5.4 |
| Br | -7.2 | -0.7 |
| I | -37.4 | 7.7 |
| CH ₃ | 10.3 | -7.8 |
| OCH ₃ | 30.3 | -37.3 |
| CHO | 13.6 | 13.2 |
| COOH | 5.2 | 9.1 |
| CN | -15.1 | 15.0 |

*In ppm from ethylene (δ_C , 123.3).

Table I. ¹³C Shift Parameters in Some Linear and Branched Hydrocarbons

| ¹³ C Atoms | Shift (ppm) (A) |
|-----------------------|-----------------|
| α | +9.1 |
| β | +9.4 |
| γ | -2.5 |
| δ | +0.3 |
| c | +0.1 |
| 1° (3°) ^a | -1.1 |
| 1° (4°) ^a | -3.4 |
| 2° (3°) ^a | -2.5 |
| 2° (4°) | -7.2 |
| 3° (2°) | -3.7 |
| 3° (3°) | -9.5 |
| 4° (1°) | -1.5 |
| 4° (2°) | -8.4 |

^aThe notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₂CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₂CH group—and so forth.

BASE: -2.5 ppm

Regra dos 13

The rule of 13 for the base formula \longrightarrow $\frac{M}{13} = n + \frac{r}{13}$ \longrightarrow C_nH_{n+r} **Fórmula base**

The rule of 13 and U are connected by \longrightarrow $U = \frac{(n - r + 2)}{2}$

**TABLE 1.3
CARBON/HYDROGEN EQUIVALENTS FOR SOME COMMON ELEMENTS**

| Add Element | Subtract Equivalent | Add ΔU | Add Element | Subtract Equivalent | Add ΔU |
|-----------------|--------------------------------|----------------|------------------|--------------------------------|----------------|
| C | H ₁₂ | 7 | ³⁵ Cl | C ₂ H ₁₁ | 3 |
| H ₁₂ | C | -7 | ⁷⁹ Br | C ₆ H ₇ | -3 |
| O | CH ₄ | 1 | ⁷⁹ Br | C ₃ H ₁₉ | 4 |
| O ₂ | C ₂ H ₈ | 2 | F | CH ₇ | 2 |
| O ₃ | C ₃ H ₁₂ | 3 | Si | C ₂ H ₄ | 1 |
| N | CH ₂ | 1 | P | C ₂ H ₇ | 2 |
| N ₂ | C ₂ H ₄ | 1 | I | C ₉ H ₁₉ | 0 |
| S | C ₂ H ₆ | 2 | I | C ₁₀ H ₇ | 7 |

