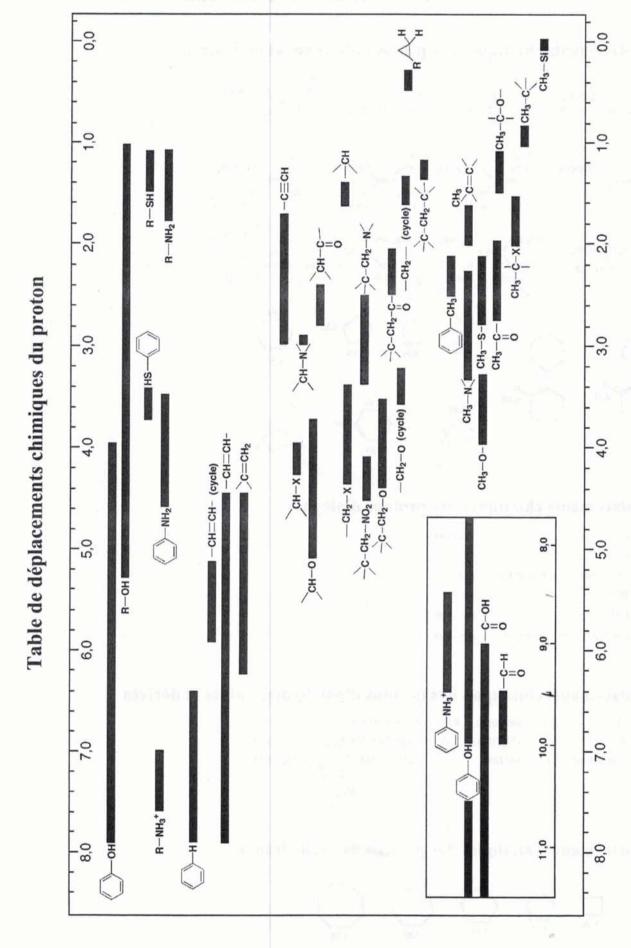
¹H NMR



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

SHOOLERY's rules

appendix b. effect on chemical shifts of two or three functional groups (Y-CH₂-Z, and Y-CH-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 CH₄.

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 4.41 = δ value for the -CH₂- 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≡N	1.70
-C≡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
-C1	2.53	-OSO ₂ R	3.13
-Br	2.33	1.77	
-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.

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

M = methyl

8 M = methylene

M = methine

	.4 .	2 5		B .(6 .	4 .	2 4	3.	В .	6 .	4 .	2 3	3. 8	3 .6	6 .4	4 .:	2 2	2 .	8 .		.4	T	1	.8	.6	.4 T	.2
M-CH ₂ R																				•		<u> </u>		ı			
M-C=C																	0										
M-C≡C																	}		ı								
M — Ph					0								•	- 8	3								1	İ		1	T
M – F M – Cl	+			Ĭ	8	-	•		-	0											+	+	-	+	+	+	+
	+			_	_		•			٥	-								-	_	_	-	\vdash	+	+	\perp	+
M – Br				L		L	•		_		}			1					L		L	L	L		1	\perp	\perp
M - i						:						0					l					L					
M-OH								3		0	}																
M-OR											5																
M — OPh					•		0	ı																T			
M - OC(= O)R			•				0		ı																		
M - OC(= 0)Ph		•					ò	١																			
M - OC(= O)CF ₃						0		ı																T			
M-OTs*				:				0	ı																		
M-C(= O)H															:	5											
M -C(=0)R														•		0 0	1										T
M - C(= 0) Ph														0 0												T	
M-C(=0)OH															•	0 0	i										
M-C(=0)OR															:	00											T
M-C(=0)NR ₂																0									T		
M-C≘N													•		0		١										
M-NH ₂												:		0 0	ı											T	T
M-NR ₂													•			3 1											T
M - NPhR												0															T
M-N+R ₃												0	ı														
M-NHC(=0)R											0 0		ı														Ī
M-NO ₂						İ	°I											Г						Ī	T	Γ	T

			Т-	1	T	- 1	_ 1					T	2	T		T	Т	 T	T		T	
M - N = C	:						0		1													
M - N = C = O							0															
M-O-CEN		8										T			\neg				T			
M - N = C = S				:	00																	
M-S-C≣N							:		}	ı												
M-O-N=0	1	3													\neg							
M-SH								:		6	3		П									
M-SR								•		0			ı			i-ci.						
M-SPh											1				1							
M-SSR										0 0												
M-SOR								0 0														
M-SO ₂ R								0 0														
M-SO ₃ R																					1	
M-PR ₂											ò											
M-P+CI ₃						ò	1															
M-P(=0)R ₂											9											
M - P(= S)R ₂			T	T						1		1		T	1				T	T		

*OTS is
$$-0 \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$
 $-CH_3$

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

M = methyl
M = methylene

* M = met

M-C-CH ₂		TT	T						•		4 .:		}	Γ	ı	8 .			.3 .	Ė
	_	-	 -						•			-	-	_	'					Ļ
M - C - C = C							•				0 0									L
M-C-C≡C										>										
M – C – Ph									0 0				1							
И−С −F			:			0 0			ı											
M-C-CI					•		}		ı											
M - C - Br						0														
M-C-I			:				31													
и-с-он							•		3	>		1								
M-C-OR							•		3	>										
#-C-OPh				3					0											
1-C-OC(=0)R								3	2											
M - C - OC(= 0)Ph					:		0	ı												
M-C-OC(=0)CF ₃								0 0												
Λ C - C(= O)H								0												
M-C-C(=O)R					:				00					ı						
A - C - C(= O)Ph									0 0				1							
1-C-C(=0)OR					3		3	5					ı							
1- C-C(=0)NR ₂						3			3	>			١							Γ
M-C-C∃N				;				0 0				ı								Γ
M-C-NR ₂							3			0 0				ı						
1-C-NPhR									3											
I-C-NR3				•			0													
1-C-NHC(=0)R					:				3	>			ı							
1-C-NO ₂				0																
1 – C – SH								• 6												
1-C-SR					•			3	}			ı						- "		

CHEMICAL SHIFTS IN UNSATURATED APPENDIX D AND AROMATIC SYSTEMS

(See Table D.1)

$$R_{cis}$$
 R_{gem} R_{gem} $R_{gem} + Z_{cis} + Z_{trans}$

For example, the chemical shifts of the alkene protons in

are calculated:

$$\begin{array}{ccccc} H_{a} & C_{6}H_{5\;gem} & 1.35 & 5.25 \\ OR_{trans} & -\frac{1.28}{0.07} & \frac{0.07}{5.32} \\ H_{b} & OR_{gem} & 1.18 & 5.25 \\ C_{6}H_{5\;trans} & -\frac{0.10}{1.08} & \frac{1.08}{6.33} \\ \end{array}$$

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

	550	Z				Z	
Substituent R	gem	cis	trans	Substituent R	gem	cis	trans
—н	0	0	0	Н			
—Alkyl	0.44	-0.26	-0.29	2	1.03	0.97	1.21
—Alkyl-ring ^a	0.71	-0.33	-0.30	-c=0			
-CH2O, -CH2I	0.67	-0.02	-0.07	N			
-CH ₂ S	0.53	-0.15	-0.15	-c-0	1.37	0.93	0.35
-CH ₂ Cl, -CH ₂ Br	0.72	0.12	0.07	C-0			
−CH ₂ N	0.66	-0.05	-0.23	,Cl	1.10	1.41	0.99
$-C \equiv C$	0.50	0.35	0.10	-c=0			
$-C \equiv N$	0.23	0.78	0.58	-OR, R: aliph	1.18	-1.06	-1.28
-c=c	0.98	-0.04	-0.21	-OR, R: conjb	1.14	-0.65	-1.05
−C=C conj ^b	1.26	0.08	-0.01	-OCOR	2.09	-0.40	-0.67
-c=0	1.10	1.13	0.81	-Aromatic	1.35	0.37	-0.10
−C=O conj ^b	1.06	1.01	0.95	—Cl	1.00	0.19	0.03
—СООН	1.00	1.35	0.74	—Br	1.04	0.40	0.55
—СООН $conj^b$	0.69	0.97	0.39	-N R:aliph	0.69	-1.19	-1.31
—COOR	0.84	1.15	0.56	$-N \stackrel{R}{\underset{R}{\bigcap}} R:conj^b$	2.30	-0.73	-0.81
—COOR conj ^b	0.68	1.02	0.33	—SR —SO ₂	1.00 1.58	-0.24 1.15	-0.04 0.95

 $^{^4}$ Alkyl ring indicates that the double bond is part of the ring $\overset{\text{C}}{\underset{\text{C}}{\mathbb{R}}}$.

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

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

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

	9	,8	.6	.4	.2	88	.8 .	.6	4 .	2	7 .	.8	.6	.4	.2	6		ł	5
Benzene ^a		Τ							:					T	T				
CH ₃ (omp)										:									
CH ₃ CH ₂ (omp)		T	Τ							:									
(CH ₃) ₂ CH (omp)	T	T	Т					Г		:									
(CH ₃) ₃ C o,m,p		T							:	: :									
C=CH ₂ (omp)			1						:										
C≡CH o, (mp)								:	:										
Phenyl o, m, p		\top	T					:	:	:			-						Г
CF ₃ (omp)			1		1			:							1	1			
CH ₂ Cl (omp)									:		-								
CHCl ₂ (omp)		\top	1	\dagger		T	†		:		\vdash				T				T
CCl ₃ o, (mp)	T	+-	+		:		<u> </u>	:		_				\vdash	T	T			
CH ₂ OH (omp)	T									:				1		1			
CH ₂ OR (omp)	T		\dagger			\top			:					<u> </u>	T	\top	<u> </u>		
CH ₂ OC(=O)CH ₃ (omp)	\dagger					1			:	\vdash				T					
CH ₂ NH ₂ (omp)	\vdash	\top	\top			<u> </u>	1		:					\vdash	T		1		
F m,p.o		\uparrow							:		:			1			T		
Cl (omp)							_		:					\vdash	 	1			
Br o, (pm)	†	T	T		 	†		:	:		†		ļ	 	1	—			
I o,p,m		†	+			\top	:		:					\vdash	T	†			
OH m,p,o	T		+	 						:	:	:		\vdash	T		T		
OR m, (op)					1				:	Г	:			T					
OC(=O)CH ₃ m,p,o								:	:	:	T					<u> </u>			
OTs ^b (mp), o		1	\top		1				:	:					T	Ţ			
CH(=0)o,p,m	T	1	1	 		:	:	:						\vdash	T	1			
C(=O)CH ₃ o, (mp)	T	T	\top			:		:							T				
C(=O)OH o, p, m	T	\top	\top		 	:	T	:	:					T	T	\top			
C(=O)OR o, p, m		T		T	:			::						\vdash					
C(=O)Cl o, p, m		T	1	1	:			::	-	Г	\vdash			\top					Г
C≡N (omp)	T	T						:		Г						\top			Π
NH ₂ m,p,o		T	1	1			1			:	:		:	Г	T				
N(CH ₃) ₂ m(op)	T		T	T		T				:		:		T	T				
NHC(=O)R o,m,p					Γ				:	:				\top	1				
NH ₃ o (mp)						:	:									T			
NO ₂ o,p,m	T		T				:	:						T	T				Г
SR (omp)	T		\top		\vdash				:					T	T	†			\vdash
N=C=O (omp)	Τ		\top			1	T							\top	T				Г

^a The benzene ring proton is at δ7.27, 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

Туре	J _{ab} (Hz)	J _{ab} Typical	Туре		J _{ab} (Hz)	J _{ab} Typical
H_a	0-30	12–15	H_a $C=C$ H_b		6-12	10
CH_a — CH_b (free rotation)	6-8	7	CH_a		0-3	1-2
$CH_a - CH_b$	0-1	0	$C = C$ H_{a}		4-10	7
H_b			$C = C$ CH_b		0-3	1.5
ax-ax	6-14	8-10	H_a $C = C$		0-3	2
ax-eq	0-5	2-3	/c-c			
eq-eq	0-5	2-3	$C = CH_a - CH_b = C$		9-13	10
H_a (cis or trans)	cis 5-10 trans 5-10		$C = C$ $(ring)$ H_b		3 member 4 member 5 member 6 member 7 member	0.5-2.0 2.5-4.0 5.1-7.0 8.8-11.0 9-13
H_a	cis 4–12 trans 2–10		$CH_a - C \equiv CH_b$ $-CH_a - C \equiv C - CH$	H_b —	8 member 2-3 2-3	10-13
(cis or trans) H_a M_b (cis or trans)	cis 7–13 trans 4–9		H_a H_b O H_b H_a O H_b			6
CH _a —OH _b (no exchange)	4-10	5				2.5
CH _a -CH _b	1-3	2–3	<u></u>	J (ortho) J (meta) J (para)	6-10 1-3 0-1	9 3 ~0
$C = CH_a - CH_b$	5-8	6		J (2-3) J (3-4)	5-6 7-9	5 8
$CH_{a}-CH_{b}$ $C=CH_{a}-CH_{b}$ H_{a} $C=C$ H_{b} $C=C$	12-18	17	$ \begin{array}{c c} 5 & 3 \\ 6 & 2 \end{array} $	J (2-4) J (3-5) J (2-5) J (2-6)	1-2 1-2 0-1 0-1	1.5 1.5 1 ~0
$C = C H_a$	0-3	0-2	4 5	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)

Туре		J _{ab} (Hz)	J _{ab} Typical	Туре	J _{ab} (Hz)	J _{ab} Typical
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	J (2-3) J (3-4) J (2-4) J (2-5) J (1-3) J (2-3) J (3-4) J (2-4)	4.9-6.2 3.4-5.0 1.2-1.7 3.2-3.7 2-3 2-3 3-4 1-2	5.4 4.0 1.5 3.4	Proton – Carbon-13 (See Tables 5.17, 5.18) Proton – Fluorine H _a F _b	44-81	
H 5 4 N 2	J (2-5) J (4-5) J (2-5) J (2-4) J (4-6)	1.5-2.5 4-6 1-2 0-1 2-3		$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \\ \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \end{array} \\$	3-25 0-4	
$\frac{4}{5}$ N_2	J (4-5) J (2-4) J (2-5)	3-4 ~0 1-2		$C = C$ H_a H_a	1-8	
				$C=C'_{F_b}$	12-40	
				H_a	o 6-10 m 5-6 p 2	
				$\alpha H_3C - \overset{\parallel}{C} - \overset{\leftarrow}{C}H_2F\gamma$	αγ 4.3 βγ 48	
			Proton-	Phosphorus		
		>PH		630-707		
			P=0 $H_2)_3P$ $H_2)_3P=0$	2.7 13.4 0.5 (HCCP) 13.7 (HCP) 11.9 (HCCP) 16.3 (HCP)		
			(OR) ₂	10-13		
		measure	O P (OR) ₂	15-20		
		P[N(CI	P (OR) ₂ H ₃) ₂] ₃ N(CH ₃) ₂] ₃	10.5-12 8.8 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.

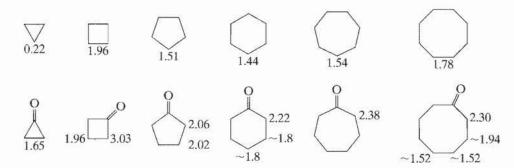


TABLE C.2 Chemical Shifts in Heterocyclic Rings.

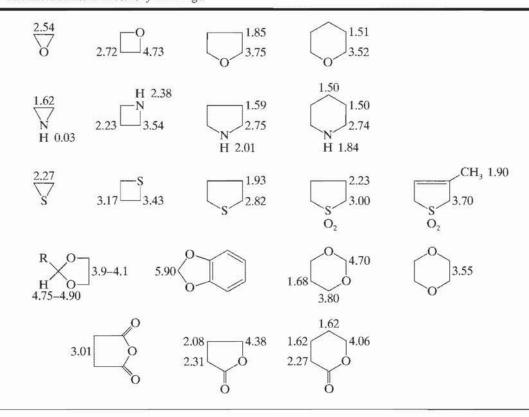


TABLE D.3 Chemical Shifts of Alkyne Protons

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	$HC \equiv C - CH = CR_2$	2.60-3.10	

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