

Tables de déplacements chimiques et couplages RMN

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ref : D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill

Table 3.17 ^1H Chemical shifts in methyl, methylene, and methine groups

	<i>Methyl protons</i>	δ_{H}	<i>Methylene protons</i>	δ_{H}	<i>Methine protons</i>	δ_{H}
C	$\text{CH}_3\text{-R}$	0.9	$\text{R-CH}_2\text{-R}$	1.4	>CH-R	1.5
	$\text{CH}_3\text{-C-C=C}$	1.1	$\text{R-CH}_2\text{-C-C=C}$	1.7		
	$\text{CH}_3\text{-C-O}$	1.3	$\text{R-CH}_2\text{-C-O}$	1.9	>CH-C-O	2.0
	$\text{CH}_3\text{-C-N}$	1.1	$\text{R-CH}_2\text{-C-N}$	1.4		
	$\text{CH}_3\text{-C-NO}_2$	1.6	$\text{R-CH}_2\text{-C-NO}_2$	2.1		
	$\text{CH}_3\text{-C=C}$	1.6	$\text{R-CH}_2\text{-C=C}$	2.3		
	$\text{CH}_3\text{-Ar}$	2.3	$\text{R-CH}_2\text{-Ar}$	2.7	>CH-Ar	3.0
	$\text{CH}_3\text{-C=CC=O}$	2.0	$\text{R-CH}_2\text{-C=CC=O}$	2.4		
	$\text{C=C(CH}_3\text{)-C=O}$	1.8	$\text{C=C(CH}_2\text{-R)-C=O}$	2.4		
	$\text{CH}_3\text{-C}\equiv\text{C}$	1.8	$\text{R-CH}_2\text{-C}\equiv\text{C}$	2.2	$\text{>CH-C}\equiv\text{C}$	2.6
	$\text{CH}_3\text{-CO-R}$	2.2	$\text{R-CH}_2\text{-CO-R}$	2.4	>CH-CO-R	2.7
	$\text{CH}_3\text{-CO-Ar}$	2.6	$\text{R-CH}_2\text{-CO-Ar}$	2.9	>CH-CO-Ar	3.3
	$\text{CH}_3\text{-CO-OR}$	2.0	$\text{R-CH}_2\text{-CO-OR}$	2.2	>CH-CO-OR	2.5
	$\text{CH}_3\text{-CO-OAr}$	2.4				
	$\text{CH}_3\text{-CO-N}$	2.0	$\text{R-CH}_2\text{-CO-N}$	2.2	>CH-CO-N	2.4
			$\text{R-CH}_2\text{-C}\equiv\text{N}$	2.3	$\text{>CH-C}\equiv\text{N}$	2.7
	N	$\text{CH}_3\text{-N}$	2.3	$\text{R-CH}_2\text{-N}$	2.5	>CH-N
$\text{CH}_3\text{-N-Ar}$		3.0				
$\text{CH}_3\text{-N-CO-R}$		2.9	$\text{R-CH}_2\text{-N-CO-R}$	3.2	>CH-N-CO-R	4.0
$\text{CH}_3\text{-N}^+$		3.3	$\text{R-CH}_2\text{-N}^+$	3.3		
			$\text{R-CH}_2\text{-NO}_2$	4.4	>CH-NO_2	4.7
O			$\text{R-CH}_2\text{-OH}$	3.6	>CH-OH	3.9
	$\text{CH}_3\text{-OR}$	3.3	$\text{R-CH}_2\text{-OR}$	3.4	>CH-OR	3.7
	$\text{CH}_3\text{-O-C=C}$	3.8	$\text{R-CH}_2\text{-O-C=C}$	3.7		
	$\text{CH}_3\text{-OAr}$	3.8	$\text{R-CH}_2\text{-OAr}$	4.3	>CH-OAr	4.5
	$\text{CH}_3\text{-O-CO-R}$	3.7	$\text{R-CH}_2\text{-O-CO-R}$	4.1	>CH-O-CO-R	4.8
			$\text{RO-CH}_2\text{-OR}$	4.8		
Hal			$\text{R-CH}_2\text{-F}$	4.4		
			$\text{R-CH}_2\text{-Cl}$	3.6	>CH-Cl	4.2
			$\text{R-CH}_2\text{-Br}$	3.5	>CH-Br	4.3
			$\text{R-CH}_2\text{-I}$	3.2	>CH-I	4.3
Other	$\text{CH}_3\text{-Si}$	0.0	$\text{R-CH}_2\text{-Si}$	0.5	>CH-Si	1.2
	$\text{CH}_3\text{-S}$	2.1	$\text{R-CH}_2\text{-S}$	2.4	>CH-S	3.2
	$\text{CH}_3\text{-S(O)R}$	2.5				
	$\text{CH}_3\text{-S(O}_2\text{)R}$	2.8	$\text{R-CH}_2\text{-S(O}_2\text{)R}$	2.9		
		$\text{RS-CH}_2\text{-SR}$	4.2			

R = alkyl group. These values will usually be within ± 0.2 p.p.m. unless electronic or anisotropic effects from other groups are strong. An obsolete scale used τ values; these are related to δ values by the simple equation $\tau = 10 - \delta$.

Estimation of ^1H chemical shifts in substituted alkanes

$$\text{R}^1\text{R}^2\text{R}^3\text{CH} \quad \delta_{\text{H}} = 1.50 + \sum z_i \quad (3.19)$$

Table 3.18 Substituent constants z for Eq. 3.19

R^i	z	R^i	z	R^i	z
H—	-0.3	$\text{HC}\equiv\text{C}$ —	0.9	MeO—	1.5
alkyl—	0.0	OHC—	1.2	PhO—	2.3
$\text{CH}_2=\text{CHCH}_2$ —	0.2	MeCO—	1.2	AcO	2.7
MeCOCH ₂ —	0.2	RO ₂ C—	0.8	Cl—	2.0
HOCH ₂ —	0.3	NC—	1.2	Br—	1.9
ClCH ₂ —	0.5	H ₂ N—	1.0	I—	1.4
$\text{CH}_2=\text{CH}$ —	0.8	O ₂ N—	3.0	MeS—	1.0
Ph—	1.3	HO—	1.7	Me ₃ Si—	-0.7

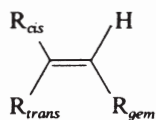
Table 3.19 ^1H Chemical shifts of methylene groups in some cyclic compounds

Structure	δ_{H}	Structure	δ_{H}	Structure	δ_{H}	Structure	δ_{H}
	0.3		1.96		1.51		1.44
at -100° H_{ax} 1.1 H_{eq} 1.6 Axial protons generally come into resonance at higher field than their equatorial counterparts.							
	0.92		2.57		1.90		1.65
	7.01		5.95		2.28		1.96
	7.01		5.95		5.60		5.59
	1.6		2.6		2.3		
	0.0						
	1.6		2.1		1.8		2.1
	2.7		2.2		2.3		2.3
	2.0		3.4		3.7		2.8
	1.5		1.6		1.6		1.6-1.8
	1.5		2.3		3.6		2.6
	2.7		3.2		4.09		3.31
	1.8		~8		1.6		1.6
	3.9-4.1		4.7-4.9		5.9		3.6
	4.7-4.9						2.9
							1.9

Table 3.20 ^1H Chemical shifts of protons attached to multiple bonds

Structure	δ_{H}	Structure	δ_{H}
RCHO	9.4-10.0	$\text{>C}=\text{CH}$ —	4.5-6.0
ArCHO	9.7-10.5	$\text{>C}=\text{CHCO}$ —	5.8-6.7
—OCHO	8.0-8.2	— $\text{HC}=\text{CCO}$ —	6.5-8.0
>NCHO	8.0-8.2	— $\text{HC}=\text{C}-\text{O}$ —	4.0-5.0
— $\text{C}\equiv\text{CH}$	1.8-3.1	$\text{>C}=\text{CH}-\text{O}$ —	6.0-8.1
$\text{>C}=\text{C}=\text{CH}$ —	4.0-5.0	— $\text{HC}=\text{C}-\text{N}$ —	3.7-5.0
ArH	6.0-9.0	$\text{>C}=\text{CH}-\text{N}$ —	5.7-8.0

Estimation of ^1H chemical shift in alkenes



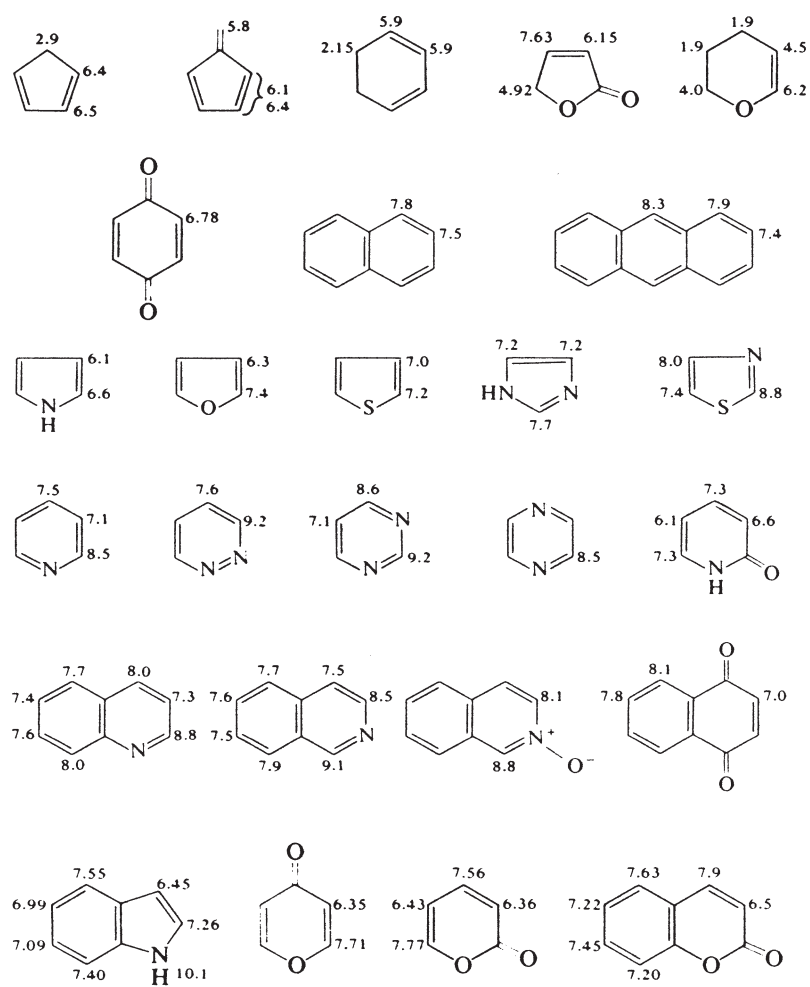
$$\delta_{\text{H}} = 5.25 + z_{\text{gem}} + z_{\text{cis}} + z_{\text{trans}} \quad (3.20)$$

Table 3.21 Substituent constants z for Eq. 3.20

	R	z_{gem}	z_{cis}	z_{trans}
C	H—	0	0	0
	alkyl—	0.45	-0.22	-0.28
	ring-alkyl—	0.69	-0.25	-0.28
	CO—CH ₂ — or NC—CH ₂ —	0.69	-0.08	-0.06
	Ar—CH ₂ —	1.05	-0.29	-0.32
	N—CH ₂ —	0.58	-0.10	-0.08
	O—CH ₂ —	0.64	-0.10	-0.02
	Hal—CH ₂ —	0.70	0.11	-0.04
	S—CH ₂ —	0.71	-0.13	-0.22
	isolated C=C—	1.00	-0.09	-0.23
	conjugated C=C—	1.24	0.02	-0.05
	Ar—	1.38	0.36	-0.07
	OHC—	1.02	0.95	1.17
	isolated RCO—	1.10	1.12	0.87
	conjugated RCO—	1.06	0.91	0.74
	isolated HO ₂ C—	0.97	1.41	0.71
	conjugated HO ₂ C—	0.80	0.98	0.32
	isolated RO ₂ C—	0.80	1.18	0.55
	conjugated RO ₂ C—	0.78	1.01	0.46
	N—CO—	1.37	0.98	0.46
	Cl—CO—	1.11	1.46	1.01
—C≡C—	0.47	0.38	0.12	
N≡C—	0.27	0.75	0.55	
N	alkyl-N—	0.80	-1.26	-1.21
	conjugated alkyl or aryl-N—	1.17	-0.53	-0.99
	—CO—N—	2.08	-0.57	-0.72
	O ₂ N—	1.87	1.30	0.62
O	alkyl-O—	1.22	-1.07	-1.21
	conjugated alkyl or aryl-O—	1.21	-0.60	-1.00
	—CO—O—	2.11	-0.35	-0.64
Hal	F—	1.54	-0.40	-1.02
	Cl—	1.08	0.18	0.13
	Br—	1.07	0.45	0.55
	I—	1.14	0.81	0.88
Other	R ₃ Si—	0.90	0.90	0.60
	RS—	1.11	-0.29	-0.13
	RSO—	1.27	0.67	0.41
	RSO ₂ —	1.55	1.16	0.93

Use the 'conjugated' values when either the substituent or the double bond is further conjugated. Use the 'ring-alkyl' values when the double bond and the alkyl group are part of a five- or six-membered ring.

Table 3.22 ^1H Chemical shifts of protons attached to double bonds in some unsaturated cyclic systems†



† For simple cycloalkenes, see Table 3.19.

Table 3.23 Substituent constants for Eq. 3.21

	R	Z_{ortho}	Z_{meta}	Z_{para}
C	H—	0	0	0
	Me—	-0.20	-0.12	-0.22
	Et—	-0.14	-0.06	-0.17
	Pr ⁱ —	-0.13	-0.08	-0.18
	Bu ^t —	0.02	-0.08	-0.21
	H ₂ NCH ₂ — or HOCH ₂ —	-0.07	-0.07	-0.07
	ClCH ₂ —	0.00	0.00	0.00
	F ₃ C—	0.32	0.14	0.20
	Cl ₃ C—	0.64	0.13	0.10
	CH ₂ =CH—	0.06	-0.03	-0.10
	Ph—	0.37	0.20	0.10
	OHC—	0.56	0.22	0.29
	MeCO—	0.62	0.14	0.21
	H ₂ NCO—	0.61	0.10	0.17
	HO ₂ C—	0.85	0.18	0.27
	MeO ₂ C—	0.71	0.1	0.21
	ClCO—	0.84	0.22	0.36
	HC≡C—	0.15	-0.02	-0.01
	N≡C—	0.36	0.18	0.28
N	H ₂ N—	-0.75	-0.25	-0.65
	Me ₂ N—	-0.66	-0.18	-0.67
	AcNH—	0.12	-0.07	-0.28
	O ₂ N—	0.95	0.26	0.38
O	HO—	-0.56	-0.12	-0.45
	MeO—	-0.48	-0.09	-0.44
	AcO—	-0.25	0.03	-0.13
Hal	F—	-0.26	0.00	-0.04
	Cl—	0.03	-0.02	-0.09
	Br—	0.18	-0.08	-0.04
	I—	0.39	-0.21	0.00
Other	Me ₃ Si—	0.22	-0.02	-0.02
	(MeO) ₂ P(=O)—	0.48	0.16	0.24
	MeS—	0.37	0.20	0.10

These parameters are simply the shifts measured on the corresponding monosubstituted benzene ring; they are not accurately taken over to polysubstituted benzenes, but the estimation of chemical shift is usually fairly good. Errors are particularly likely to occur when substituents *ortho* to one another interfere with conjugation to the ring.

Table 3.25 ^{13}C and residual ^1H chemical shifts in the common deuterated solvents

Solvent	Deuterated solvent				Undeuterated solvent
	$\delta_{\text{H}}^\dagger$	Multi- plicity \ddagger	δ_{C}	Multi- plicity \ddagger	δ_{C}
Acetic acid	2.05 11.5§				21.1 178.1
Acetone	2.05	quintet	29.8 205.7	septet	30.5 205.4
Acetonitrile	1.95	quintet	1.2 117.8	septet	1.6 117.8
Benzene	7.3		128.0	triplet	128.5
t-Butanol	1.28¶				
Carbon disulphide					192.8
Carbon tetrachloride					96.1
Chloroform	7.25		77.0	triplet	77.2
Cyclohexane	1.40	triplet	26.3	quintet	27.6
Water	4.7§				
Dimethylformamide (DMF)	2.75 2.95 8.05	quintet quintet triplet			
Dimethylsulphoxide (DMSO)	2.5	quintet	39.7	septet	40.6
water in DMSO	3.3§				
Dioxan	3.55	triplet			67.3
Hexamethylphosphoramide (HMPA)	2.60	double $\ddagger\ddagger$ quintet			
Methanol	3.35 4.8§	quintet	49.0	septet	49.9
Dichloromethane (methylene dichloride)	5.35	triplet			54.0
Pyridine	7.0 7.35 8.5		123.4 135.3 149.8	triplet triplet triplet	123.9 135.9 150.3
Toluene	2.3 7.2	quintet			
Trifluoroacetic acid (TFA)	11.3§				115.7 $\ddagger\ddagger$ 163.8§§

\dagger Residual protons in the deuterated solvent.

\ddagger A singlet unless otherwise stated.

§ Variable, depends upon the solvent and its concentration.

¶ $(\text{CH}_3)_3\text{COD}$ is usually used, not the fully deuterated solvent.

$\ddagger\ddagger$ Coupling to P, $J = 9$ Hz.

$\ddagger\ddagger\ddagger$ Quartet from coupling to F, $J = 294$ Hz.

§§ Quartet from coupling to F, $J = 46$ Hz.

Table 3.26 Geminal ($^2J_{\text{HH}}$) coupling constants (Hz)

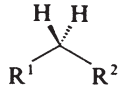
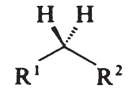
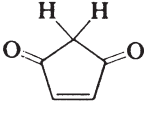
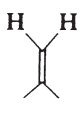
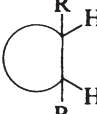
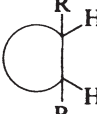




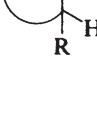
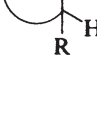
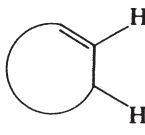
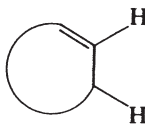
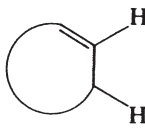
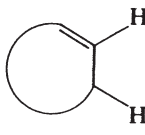
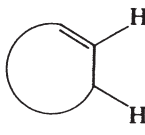
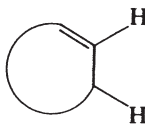
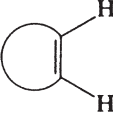
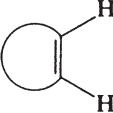
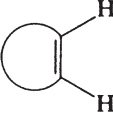
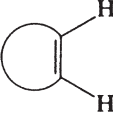
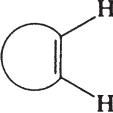
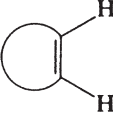
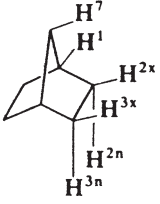
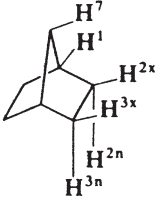
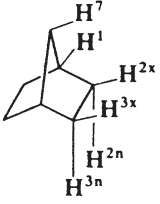
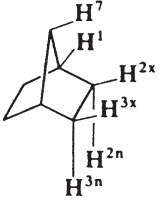
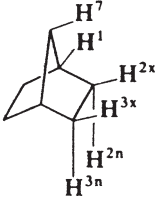
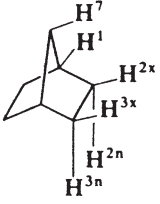
	$^2J_{\text{HH}}$		$^2J_{\text{HH}}$
H H	-12.4	H H	-16.2
R R	-8...-18	H CN	-14.9
-(CH ₂) ₂ -	-3...-9	H COMe	-21.5
-(CH ₂) ₃ -	-11...-17		-3...+3
-(CH ₂) ₄ -	-8...-18		-8...-10
-(CH ₂) ₅ -	-11...-14		
H Ph	-14.3		
H OH	-10.8		
H Cl	-10.8		
-O(CH ₂) ₂ O-	~0		
-O(CH ₂) ₃ O-	-5...-6		

Table 3.27 Vicinal ($^3J_{\text{HH}}$) coupling constants in some aliphatic compounds (Hz)

Open chain compounds			Cyclic compounds		
Structure	$^3J_{\text{HH}}$ range	Typical value	Structure	Ring size	$^3J_{\text{HH}}$ range
CH ₃ -CH ₂ -	6-8	7		cis 3	7-13
CH ₃ -CH<	5-7	6		trans 3	4-9.5
-CH ₂ -CH ₂ -	5-8	7		cis 4	4-12
>CH-CH<	0-8	7		trans 4	2-10
>C=CH-CH<	4-11	6		cis 5	5-10
>C=CH-CH=C<	6-13	11§		trans 5	5-10
>CH-CHO	0-3	2		cis 6	8-13
>C=CH-CHO	5-8	7		trans 6	2-6†
cis-CH=CH-	0-12	8		3	1.8‡
trans-CH=CH-	12-18	15		4	-0.8‡
				5	0.5‡
				6	1.5‡
				7	3.7‡
				8	5.3‡
				3	0.5-2
				4	2.5-4
				5	5-7
				6	8.5-10.5
				7	9-12.5
				8	10-13
				1-2x	3-4
				1-2n	0-2
				2x-3x	9-10
				2n-3n	6-7
				2x-3n	2-5
				1-7	0-3

† $J_{\text{aa}} = 8-13$, $J_{\text{ee}} = 2-5$; note that J_{ee} is usually 1 Hz smaller than J_{ae} .

‡ Value for the unsubstituted cycloalkene.

§ Found in dienes adopting the *s-trans* conformation.

Table 3.28 Vicinal ($^3J_{\text{HH}}$) coupling constants (Hz) in some heterocyclic and aromatic compounds

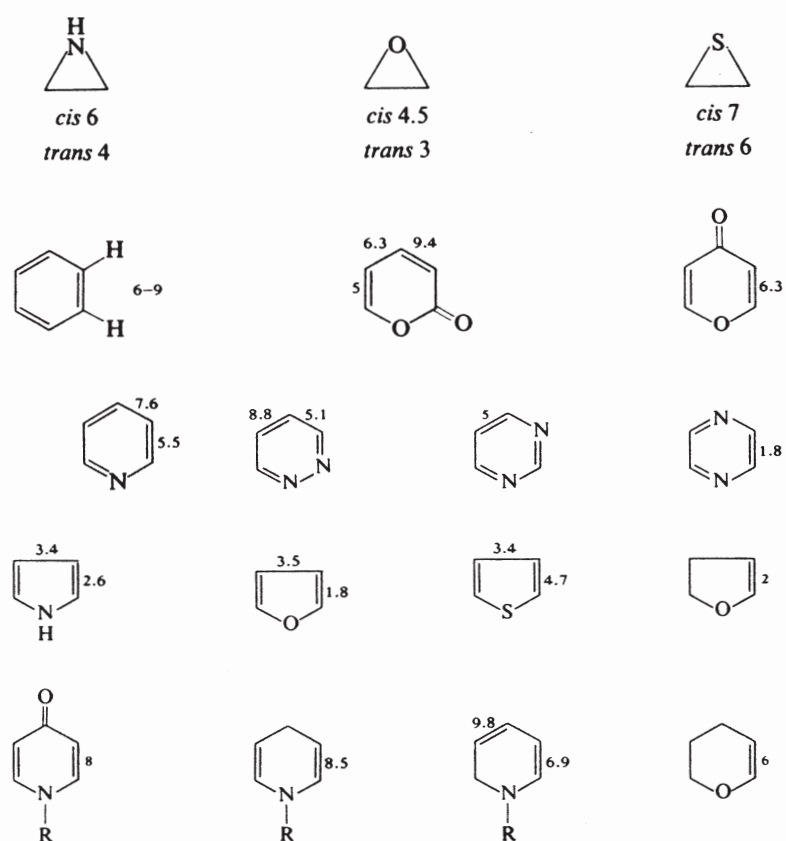


Table 3.29 Long-range ($^4J_{\text{HH}}$ and $^5J_{\text{HH}}$) coupling constants (Hz)

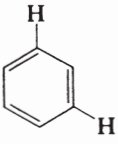
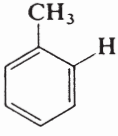
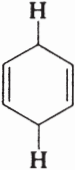
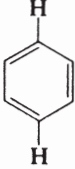



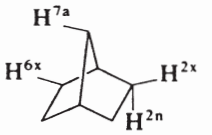
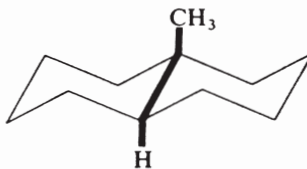
Structure	$^4J_{\text{HH}}$	Structure	$^5J_{\text{HH}}$
$-\text{CH}=\text{C}-\text{CH}\langle$	0-3	$\rangle\text{CH}-\text{C}=\text{C}-\text{CH}\langle$	0-2
	1-3	$-\text{HC}=\text{C}=\text{C}-\text{CH}\langle$	2-3
	0.6-0.9	$\rangle\text{CH}-\text{C}\equiv\text{C}-\text{CH}\langle$	1-3
$-\text{HC}=\text{C}=\text{CH}-$	4-6		8-10
$\text{HC}\equiv\text{C}-\text{CH}\langle$	1-3		0-1
	1-2		1-1.5
	7-8		
	7a-2n 3-4 2x-6x 1-2		
		signal perceptibly broadened by 4J coupling	

Table 3.30 ^1H - ^{19}F coupling constants (Hz)

Structure	J	Structure	J	
$^2J_{\text{HF}}$	45-52		<i>ortho</i> 6-11	
	60-65		<i>meta</i> 3-9	
	72-90		<i>para</i> 0-4	
$^3J_{\text{HF}}$ $\text{CH}_3\text{-CF}$ <	20-24		<i>ortho</i> 2.5	
> CH-CF <	0-45†			<i>meta</i> 1.5
<i>cis</i> - HC=CF-	3-20			<i>para</i> 0
<i>trans</i> - HC=CF-	12-53			
$^4J_{\text{HF}}$ > HC-C-CF <	0-9‡			
<i>cis</i> - FC=C-CH <	2-4			
<i>trans</i> - FC=C-CH <	0-6			

† 0-12 when gauche and 10-45 when anti-periplanar.

 ‡ The higher end of the range (≥ 3.5) when the atoms are held in a W conformation.

Table 3.31 ^{31}P - ^1H coupling constants (Hz)†

Type of coupling	Class of compound		
	Phosphines	Phosphonium salts	Phosphine oxides
$^1J_{\text{PH}}$	(150) 185-220 (250)	400-900	200-750
$^2J_{\text{PH}}$	(-5) 0-15 (27) 46‡	(0) 10-18 30‡	5-25 40‡
$^3J_{\text{PCCH}}$	(10) 13-17 (20)	(0) 10-20 (57)	14-30
$^3J_{\text{PC=CH}}$	<i>trans</i> (5) 12-41 <i>cis</i> § 6-20	<i>trans</i> 28-50 (80) <i>cis</i> § 10-20 (35)	
		Phosphites	Phosphates
$^3J_{\text{POCH}}$		(0) 5-14 (20)	(0) 5-20 (30)
	All compounds		
$^4J_{\text{PH}}$	0-3 (5)¶		

† The coupling constants are often strongly dependent upon the groups attached to phosphorus, and therefore values outside the quoted ranges may occasionally be observed; values in parentheses are 'extreme' values so far reported.

 ‡ Values observed in $\text{P}-\overset{\text{C}}{\parallel}-\text{H}$ systems.

 § *Trans* coupling is usually about twice that of *cis* coupling.

 ¶ In the system $\text{P}-\text{C}=\text{C}=\text{H}$.

Table 3.32 $\text{Eu}(\text{dpm})_3$ -induced shifts of protons in some common environments†

Functional group	Shift [<i>p.p.m.</i> /mol of $\text{Eu}(\text{dpm})_3$ per mol of substrate]
<i>RCH</i> ₂ <i>NH</i> ₂	~150
<i>RCH</i> ₂ <i>OH</i>	~100
<i>RCH</i> ₂ <i>NH</i> ₂	30-40
<i>RCH</i> ₂ <i>OH</i>	20-25
<i>RCH</i> ₂ <i>COR'</i>	10-17
<i>RCH</i> ₂ <i>CHO</i>	19
<i>RCH</i> ₂ <i>CHO</i>	11
<i>RCH</i> ₂ <i>OCH</i> ₂ <i>R</i>	10
<i>RCH</i> ₂ <i>CO</i> ₂ <i>CH</i> ₃	7
<i>RCH</i> ₂ <i>CO</i> ₂ <i>CH</i> ₃	6.5
<i>RCH</i> ₂ <i>CN</i>	3-7

† The shifts refer to the protons indicated in italics.