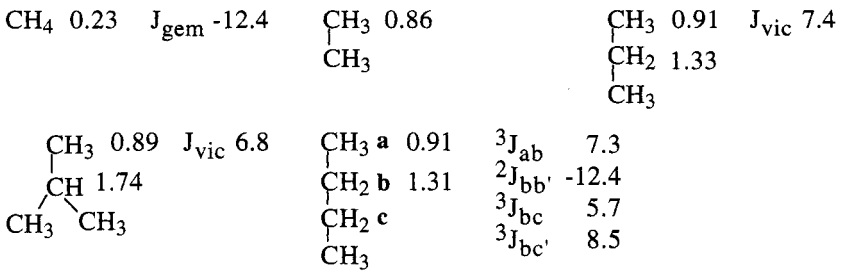
5 ^{1}H NMR Spectroscopy

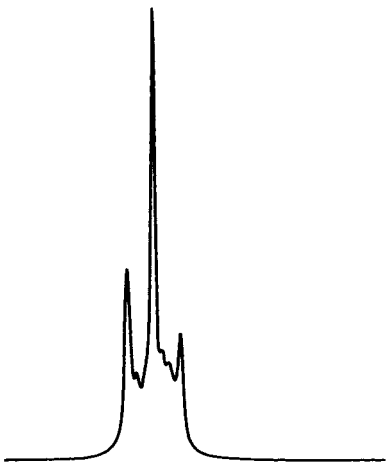
5.1 Alkanes

5.1.1 Chemical Shifts

^{1}H Chemical Shifts of Alkanes (δ in ppm relative to TMS, J in Hz)



In long-chain alkanes, the methyl groups at ca. 0.8 ppm typically show distorted triplets because of second order effects:



^1H *Chemical Shifts of Monosubstituted Alkanes*

(δ in ppm relative to TMS)

Substituent		Methyl	Ethyl		Propyl		
		$-CH_3$	$-CH_2$	$-CH_3$	$-CH_2$	$-CH_2$	$-CH_3$
	–H	0.23	0.86	0.86	0.91	1.33	0.91
C	$-CH=CH_2$	1.71	2.00	1.00	2.02	1.43	0.91
	$-C\equiv CH$	1.80	2.16	1.15	2.10	1.50	0.97
	–phenyl	2.35	2.63	1.21	2.59	1.65	0.95
H	–F	4.27	4.36	1.24	4.30	1.68	0.97
a	–Cl	3.06	3.47	1.33	3.47	1.81	1.06
l	–Br	2.69	3.37	1.66	3.35	1.89	1.06
	–I	2.16	3.16	1.88	3.16	1.88	1.03
O	–OH	3.39	3.59	1.18	3.49	1.53	0.93
	–O–alkyl	3.24	3.37	1.15	3.27	1.55	0.93
	$-OCH=CH_2$	3.16	3.66	1.21			
	–O–phenyl	3.73	3.98	1.38	3.86	1.70	1.05
	$-OCOCH_3$	3.67	4.12	1.26	4.02	1.65	0.95
	–OCO–phenyl	3.88	4.37	1.38	4.25	1.76	1.07
	$-OSO_2$–4-tolyl	3.70	4.07	1.30	3.94	1.60	0.95
N	$-NH_2$	2.47	2.74	1.10	2.61	1.43	0.93
	$-NHCH_3$	2.3					
	$-N(CH_3)_2$	2.31	2.32	1.06			
	$-NHCOCH_3$	2.79	3.26	1.14	3.18	1.55	0.96
	$-NO_2$	4.29	4.37	1.58	4.28	2.01	1.03
	–CN	1.98	2.35	1.31	2.29	1.71	1.11
	–NC	2.85	3.39	1.28			
S	–SH	2.00	2.44	1.31	2.50	1.63	0.99
	–S–alkyl	2.09	2.49	1.25	2.43	1.59	0.98
	–SS–alkyl	2.30	2.67	1.35	2.63	1.71	1.03
	$-SOCH_3$	2.50					
	$-SO_2CH_3$	2.84	2.94	2.80			
O	–CHO	2.20	2.46	1.13	2.42	1.67	0.97
||	$-COCH_3$	2.09	2.47	1.05	2.32	1.56	0.93
C	–CO–phenyl	2.55	2.92	1.18	2.86	1.72	1.02
/ \	–COOH	2.10	2.36	1.16	2.31	1.68	1.00
	$-COOCH_3$	2.01	2.32	1.15	2.22	1.65	0.98
	$-CONH_2$	2.02	2.23	1.13	2.19	1.68	0.99
	–COCl	2.66	2.93	1.24	2.87	1.74	1.00

^1H Chemical Shifts of Monosubstituted Alkanes (contd.)
(δ in ppm relative to TMS)

Substituent		Isopropyl		Butyl				*tert*-Butyl
		–CH	$-CH_3$	$-CH_2$	$-CH_2$	$-CH_2$	$-CH_3$	$-CH_3$
	–H	1.33	0.91	0.91	1.31	1.31	0.91	0.89
C	$-CH=CH_2$			2.06	≈1.5	≈1.2.	0.90	1.02
	–C≡CH	2.59	1.15	2.18	1.52	1.41	0.92	1.22
	–phenyl	2.89	1.25	2.61	1.60	1.34	0.93	1.32
H	–F			4.34	1.65		0.95	1.34
a	–Cl	4.14	1.55	3.42	1.68	1.41	0.92	1.60
l	–Br	4.21	1.73					1.76
	–I	4.24	1.89	3.20	1.80	1.42	0.93	1.95
	–OH	3.94	1.16	3.63	1.53	1.39	0.94	1.22
	–O–alkyl	3.55	1.08	3.40	1.54	1.38	0.92	1.24
	$-OCH=CH_2$	4.06	1.23	3.68	1.61	1.39	0.94	
	–O–phenyl	4.51	1.31	3.94	1.76	1.47	0.97	
	$-OCOCH_3$	4.99	1.23	4.06	1.60	1.39	0.94	1.45
	–OCO–phenyl	5.22	1.37					1.58
	$-OSO_2$–4-tolyl	4.70	1.25	4.03	1.62	1.36	0.88	
N	$-NH_2$	3.07	1.03	2.68	1.43	1.33	0.92	1.15
	$-NHCOCH_3$	4.01	1.13	3.21	1.49	1.35	0.92	1.28
	$-NO_2$	4.44	1.53	4.47	2.07	1.50	1.07	1.59
	–CN	2.67	1.35	2.34	1.63	1.50	0.96	1.37
	–NC	3.87	1.45					1.44
S	–SH	3.16	1.34	2.52	1.59	1.43	0.92	1.43
	–S–alkyl	2.93	1.25	2.49	1.56	1.42	0.92	1.39
	–SS–alkyl			2.69	1.64	1.42	0.93	1.32
	$-SO_2CH_3$	3.13	1.41					1.44
O	–CHO	2.39	1.13	2.42	1.59	1.35	0.93	1.07
||	$-COCH_3$	2.54	1.08					1.12
C	–CO–phenyl	3.58	1.22	2.95	1.72	1.41	0.96	
/ \	–COOH	2.56	1.21	2.35	1.62	1.39	0.93	1.23
	$-COOCH_3$	2.56	1.17	2.31	1.61	1.33	0.92	1.20
	$-CONH_2$	2.44	1.18	2.22	1.60	1.37	0.93	1.22
	–COCl	2.97	1.31	2.88	1.67	1.40	0.93	

Estimation of ^{1}H Chemical Shifts of Aliphatic Compounds (*δ in ppm relative to TMS*) [1]

CH$_3$ $\delta_{CH_3X} = 0.86 + Z_\alpha$

$\delta_{CH_3CXYZ} = 0.86 + \sum_i Z_{\beta_i}$

CH$_2$ $\delta_{CH_2} = 1.37 + \sum_i Z_{\alpha_i} + \sum_j Z_{\beta_j}$

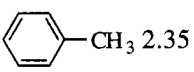
CH $\delta_{CH} = 1.50 + \sum_i Z_{\alpha_i} + \sum_j Z_{\beta_j}$

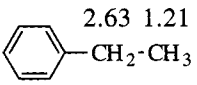
Substituent (X, Y, Z)		**CH$_3$**		**CH$_2$**		**CH**	
		Z_α	Z_β	Z_α	Z_β	Z_α	Z_β
	–C	0.00	0.05	0.00	-0.04	0.17	-0.01
	–C=C	0.85	0.20	0.63	0.00	0.68	0.03
	–C⊟C–	0.94	0.32	0.70	0.13	1.04	
	–phenyl	1.49	0.38	1.22	0.29	1.28	0.38
Hal	–F	3.41	0.41	2.76	0.16	1.83	0.27
	–Cl	2.20	0.63	2.05	0.24	1.98	0.31
	–Br	1.83	0.83	1.97	0.46	1.94	0.41
	–I	1.30	1.02	1.80	0.53	2.02	0.15
O	–OH	2.53	0.25	2.20	0.15	1.73	0.08
	–O–C	2.38	0.25	2.04	0.13	1.35	0.32
	–OC=C	2.64	0.36	2.63	0.33		
	–O–phenyl	2.87	0.47	2.61	0.38	2.20	0.50
	–O(C=O)–	2.81	0.44	2.83	0.24	2.47	0.59
N	–N	1.61	0.14	1.32	0.22	1.13	0.23
	–N$^+$	2.44	0.39	1.91	0.40	1.78	0.56
	–N(C=O)–	1.88	0.34	1.63	0.22	2.10	0.62
	–NO_2	3.43	0.65	3.08	0.58	2.31	
	–CN	1.12	0.45	1.08	0.33	1.00	
	–NCS	2.51	0.54	2.27		2.14	
S	–S–	1.14	0.45	1.23	0.26	1.06	0.31
	–SCO–	1.41	0.37	1.54	0.63	1.31	0.19
	–S(=O)–	1.64	0.36			1.25	
	–$S(=O)_2$–	1.98	0.42	2.08	0.52	1.50	
	–SCN	1.75	0.66	1.62		1.64	
O	–CHO	1.34	0.21	1.07	0.29	0.86	0.22
‖	–CO–	1.23	0.20	1.12	0.24		
C	–COOH	1.22	0.23	0.90	0.23	0.87	0.32
**/ **	–COO–	1.15	0.28	0.92	0.35	0.83	0.63
	–CO–N	1.16	0.28			0.94	
	–COCl	1.94		1.51			

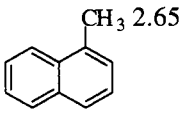
For other approaches: see [2]

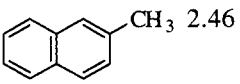
^1H Chemical Shifts of Aromatically Substituted Alkanes

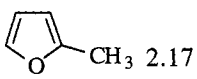
(δ in ppm relative to TMS)

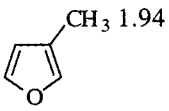


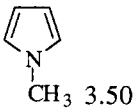


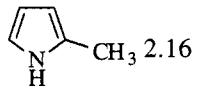


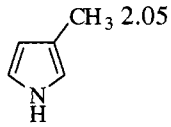


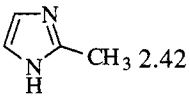


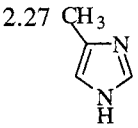


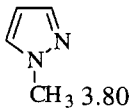


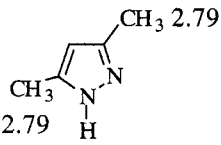


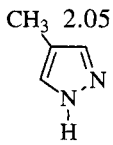


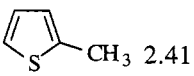


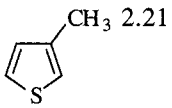


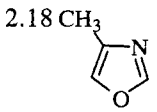


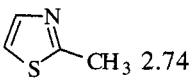


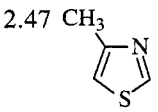


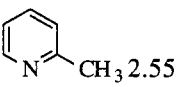


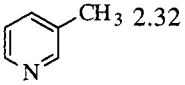


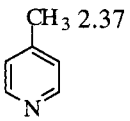


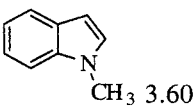


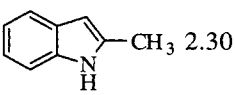


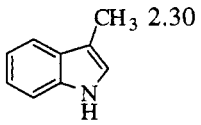










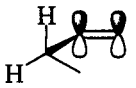


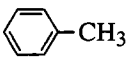
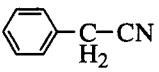
5.1.2 Coupling Constants

Geminal Coupling Constants ($^2J_{HH}$ in Hz)

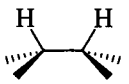
$^2J_{HCH}$ -8 to -18 Hz

Electronegative substituents cause a decrease in $|J|_{gem}$, while a double or triple bond next to the CH_2 group causes an increase. The latter effect is strongest if one of the C–H bonds is parallel to the π orbitals:



Compound	J_{gem}	Compound	J_{gem}
CH_4	-12.4	CH_3COCH_3	-14.9
CH_3Cl	-10.8	CH_3COOH	-14.5
CH_2Cl_2	-7.5	CH_3CN	-16.9
CH_3OH	-10.8	$CH_2(CN)_2$	-20.3
	-14.3		-18.5

Vicinal Coupling Constants ($^3J_{HH}$ in Hz)



conformation not fixed: $^3J_{HH} \approx 7$

fixed: $^3J_{HH} \approx 0 - 18$

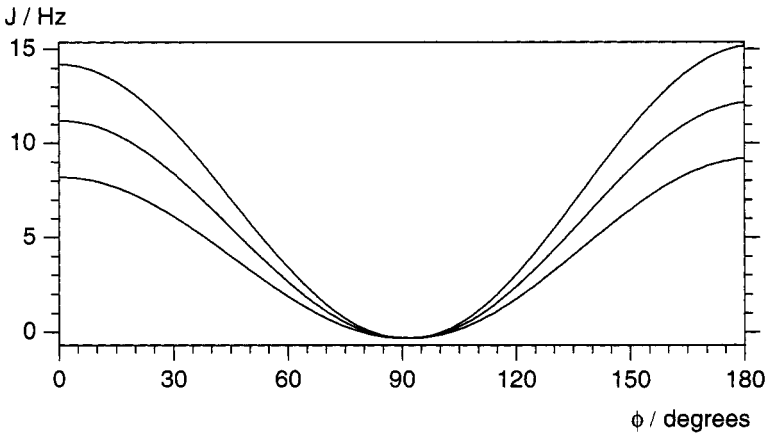
Influence of Substituents on the Vicinal Coupling Constant

Compound	J_{vic}	Compound	J_{vic}	Compound	J_{vic}
$CH_3CH–F_2$	4.5	$CH_3CH_2–OH$	6.9	$CH_3CH_2–CN$	7.6
$CH_3CH–Cl_2$	6.1	$(CH_3CH_2)_3O^+BF_4^-$	7.2	$(CH_3CH_2)_2S$	7.4
$CH_3CH_2–F$	6.9	$(CH_3CH_2)_3N$	7.1	$CH_3CH_2–Li$	8.4
$CH_3CH_2–Cl$	7.2				

Vicinal coupling constants strongly depend on the dihedral angle, ϕ (Karplus equation):

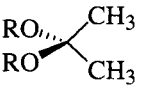
$$J = J^0 \cos^2 \phi - 0.3 \qquad 0^\circ \leq \phi \leq 90^\circ$$
$$J = J^{180} \cos^2 \phi - 0.3 \qquad 90^\circ \leq \phi \leq 180^\circ$$

The same relationship between torsional angle and vicinal coupling constant holds for substituted alkanes if appropriate values are used for J^0 and J^{180}. These limiting values depend on the electronegativity and orientation of substituents, the hybridization of carbon atoms, bond lengths, and bond angles.



Long-Range Coupling Constants ($|J|_{HH}$ *in Hz*)

Coupling constants through more than three bonds (long-range coupling) in alkanes are generally much smaller than 1 Hz and thus not visible in routine 1D NMR spectra. They are, however, much larger than 1 Hz for fixed conformations (e.g. in condensed alicyclic systems, see Chapter 5.4) and in unsaturated compounds (see Chapter 5.2). They are also significant when electronegative substituents are present between the coupling partners, as e.g.:



$^4J_{HH}$ 0.7

5.1.3 References

[1] R. Bürgin Schaller, C. Arnold, E. Pretsch, New parameters for predicting ^{1}H NMR chemical shifts of protons attached to carbon atoms, Anal. Chim. Acta **1995**, *312*, 95.

[2] E. Friedrich, K.G. Runkle, Empirical NMR chemical shift correlations for methyl and methylene protons, J. Chem. Educ. **1984**, *61*, 830.

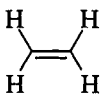
5.2 Alkenes

C=C

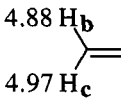
5.2.1 Substituted Ethylenes

^{1}H NMR Chemical Shifts and Coupling Constants of Alkenes

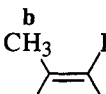
(δ in ppm relative to TMS, J in Hz)



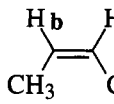
$^2J_{gem}$ 2.5
$^3J_{cis}$ 11.6
$^3J_{trans}$ 19.1



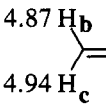
$^3J_{ab}$ 10.0
$^3J_{ac}$ 16.8
$^3J_{ad}$ 6.4
$^2J_{bc}$ 2.1
$^4J_{bd}$ -1.3
$^4J_{cd}$ -1.8



$^4J_{ab}$ -1.7
$^3J_{ac}$ 15.1
$^3J_{ad}$ 6.5
$^5J_{bd}$ 1.6



$^3J_{ab}$ 10.9
$^4J_{ac}$ -1.8
$^3J_{ad}$ 6.8
$^5J_{cd}$ 1.2



$^3J_{ab}$ 10.3
$^3J_{ac}$ 17.2
$^3J_{ad}$ 6.2
$^2J_{bc}$ 2.0
$^4J_{bd}$ -1.3
$^4J_{cd}$ -1.7

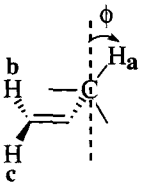
Geminal and Vicinal Coupling of Alkenes (J in Hz)

The coupling constants strongly depend on the electronegativity of the substituents (see Table on pp 170, 171). They decrease with increasing electronegativity and number of electronegative substituents. The same trend holds for the signed values of *geminal* coupling constants but not for the absolute values because J_{gem} can be positive or negative. Although the total ranges of *cis* and *trans* vicinal coupling constants overlap, $J_{trans} > J_{cis}$ always holds for given substituents.

Typical ranges: J_{gem} -4 to 4
J_{cis} 4 to 12
J_{trans} 14 to 19

Coupling Over More than Three Bonds in Alkenes (Long-Range Coupling) *(J in Hz)*

Allylic Coupling



cisoid: J_{ab} -3.0 to +2.0

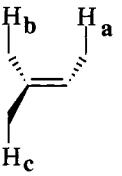
transoid: J_{ac} -3.5 to +2.5

C≡C

In acyclic systems, $|J|_{cisoid} > |J|_{transoid}$ usually holds. The magnitudes of the coupling constants depend on the conformation. Largest absolute values are observed if the C–H bond of the substituents overlaps with the π-electrons (ϕ = 0):

ϕ	J_{ab}	J_{ac}
0°	-3.0	-3.5
90°	+1.8	+2.2
180°	-3.0	-3.5
270°	0.0	0.8

Homoallylic Coupling

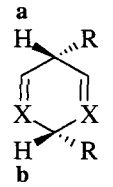


cisoid: $|J|_{ab}$ 0–3

transoid: $|J|_{ac}$ 0–3

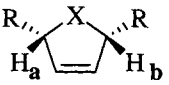
Allylic and homoallylic couplings with methyl groups are often comparable: $^4J_{H-C=C-CH_3} \approx {}^5J_{CH_3-C=C-CH_3}$

In acyclic systems, $|J|_{cisoid} < |J|_{transoid}$ usually holds. Large homoallylic coupling constants are generally observed in cyclic systems:



J_{ab} 5–11

X: CH, N
R: any substituent

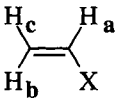


J_{ab} 0–7

X: O, NH
R: any substituent

^{1}H Chemical Shifts and Coupling Constants of Monosubstituted Ethylenes (δ in ppm relative to TMS, J in Hz)

C=C



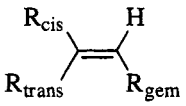
	Substituent X	H_a	H_b	H_c	J_{ab}	J_{ac}	J_{bc}	Other
	–H	5.28	5.28	5.28	19.1	11.6	2.5	
C	$-CH_3$	5.73	4.97	4.88	16.8	10.0	2.1	CH_3 1.72
	$-CH_2CH=CH_2$	5.71	4.95	4.92	16.9	10.3	2.2	CH_2 2.72
	$-CH_2$–phenyl	5.89	5.01	5.00	17.0	10.0	1.9	CH_2 3.19
	–cyclopropyl	5.32	5.04	4.84	17.1	10.4	1.8	
	–cyclohexyl	5.79	4.95	4.88	17.6	10.5	1.9	
	$-CH_2F$	5.89	5.24	5.12	17.2	10.6	1.5	CH_2 4.69
	$-CF_3$	5.90	5.85	5.56	17.5	11.1	0.2	
	$-CH_2Cl$	5.93	5.30	5.17	16.9	10.1	1.3	CH_2 3.91
	$-CH_2Br$	5.99	5.29	5.11	16.8	10.0	1.2	CH_2 3.87
	$-CH_2I$	6.04	5.23	5.95	16.5	9.7	1.3	CH_2 3.82
	$-CH_2OH$	5.98	5.26	5.12	17.4	10.5	1.7	CH_2 4.12
	$-CH_2NH_2$	5.97	5.15	5.04	17.3	10.4	1.7	CH_2 3.29
	$-CH_2NO_2$	6.11	5.46	5.49	16.7	10.7	0.8	CH_2 4.93
	$-CH=C=CH_2$	6.31	5.19	4.99	17.2	10.1	1.6	
	$-C\equiv C-CH_3$	5.62	5.39	5.24	17.0	11.1	2.3	
	–phenyl	6.72	5.72	5.20	17.9	11.1	1.0	
	–2-naphthyl	6.87	5.86	5.32				
	–2-*m*-xylyl	6.65	5.22	5.48	17.9	11.4	2.1	CH_3 2.27
	–2-nitrophenyl	7.19	5.68	5.45	17.4	10.7	1.1	
	–3-nitrophenyl	6.74	5.86	5.42	17.5	10.9	0.4	
	–4-nitrophenyl	6.77	5.90	5.48	17.4	10.9	0.8	
	–2-pyridyl	6.84	6.22	5.45	18.5	11.3	1.4	
	–4-pyridyl	6.61	5.91	5.42	17.6	10.8	0.7	
H	–F	6.17	4.37	4.03	12.8	4.7	-3.2	
a	–Cl	6.26	5.48	5.39	14.5	7.5	-1.4	
l	–Br	6.44	5.84	5.97	14.9	7.1	-1.9	
	–I	6.53	6.57	6.23	15.9	7.8	-1.5	
O	–OH	6.45	4.18	3.82				
	$-OCH_3$	6.44	4.03	3.88	14.1	7.0	-2.0	CH_3 3.16
	$-OCH_2CH_3$	6.46	4.17	3.96	14.4	6.9	-1.9	
	$-OCH=CH_2$	6.49	4.52	4.21	14.0	6.4	-1.8	
	–O–phenyl	6.64	4.74	4.40	13.7	6.1	-1.6	
	–OCHO	7.33	4.96	4.66	13.9	6.4	-1.7	CHO 8.07
	$-OCOCH_3$	7.28	4.88	4.56	14.1	6.3	-1.6	CH_3 2.13
	$-OCOCH=CH_2$	7.39	4.96	4.62	14.2	6.4	-1.6	
	–OCO–phenyl	7.52	5.04	4.67	13.8	6.3	-1.7	
	$-OPO(OCH_2CH_3)_2$	6.58	4.91	4.59	13.8	6.0	-2.1	

Substituent X		H_a	H_b	H_c	J_{ab}	J_{ac}	J_{bc}	Other
N	$-NH_2$	≈6.05	≈4.04	≈3.99				
	$-N^+(CH_3)_3Br^-$	6.50	5.76	5.54	15.1	8.2	-4.3	
	$-NHCOCH_3$	≈7.33	≈4.53	≈4.68				
	$-NO_2$	7.12	6.55	5.87	14.6	7.0	1.4	
	-CN	5.73	6.20	6.07	17.9	11.8	0.9	
	-NC	5.90	5.58	5.35	15.6	8.6	-0.5	
	-NCO	6.12	5.01	4.77	15.2	7.6	-0.1	
S	$-SCH_3$	6.35	4.84	5.08	16.4	10.3	-0.3	CH_3 2.12
	-S-phenyl	6.53	5.32	5.32	16.7	9.6	-0.2	
	$-S(O)CH_3$	6.77	6.08	5.92	16.7	9.8	-0.6	CH_3 2.61
	$-SO_2CH_3$	6.76	6.43	6.14	16.5	10.0	-0.5	CH_3 2.96
	$-SO_2CH{=}CH_2$	6.67	6.41	6.17	16.4	10.0	-0.6	
	$-SO_2OH$	6.73	6.41	6.13	16.8	10.2	-1.2	
	$-SO_2OCH_3$	6.57	6.43	6.22	16.9	10.1	-0.6	CH_3 3.85
	$-SO_2NH_2$	6.93	6.17	5.98	16.3	10.0	0.0	NH_2 6.7
	$-SO_2NH$-phenyl	6.56	6.18	5.86	16.7	10.1	-0.3	NH 9.07
	$-SF_5$	6.63	5.96	5.64	16.6	9.8	0.4	
	-SCN	6.19	5.66	5.70				
O	-CHO	6.26	6.11	6.26	17.4	10.0	1.0	CHO 9.51
‖	$-COCH_3$	6.30	6.27	5.90	18.7	10.7	1.3	CH_3 2.25
C	$-COCH{=}CH_2$	6.67	6.28	5.82	17.9	11.0	1.4	
/	-CO-phenyl	7.20	6.52	5.81	17.7	9.9	2.3	
	-COOH	6.15	6.53	5.95	17.2	10.5	1.8	COOH 12.08
	$-COOCH_3$	6.14	6.40	5.83	17.4	10.6	1.5	CH_3 3.76
	$-CONH_2$	6.48	6.17	5.71	17.3	7.9	5.0	NH_2 7.55
	$-CON(CH_3)_2$	6.64	6.12	5.55	17.0	9.8	3.4	
	-COF	6.14	6.60	6.25	17.3	10.7	0.8	
	-COCl	6.35	6.63	6.16	17.4	10.6	0.2	
P	$-P(CH_3)_2$	6.23	5.39	5.51	18.3	11.8	2.0	CH_3 0.95
	$-P(CH{=}CH_2)_2$	6.16	5.59	5.64	18.4	11.8	2.0	
	$-PCl_2$	7.48	6.64	6.68	18.6	11.7	0.4	
	$-PO(phenyl)_2$	6.72	6.25	6.21	18.9	12.9	1.8	
	$-PSCl_2$	6.42	6.13	5.90	17.5	11.0	0.3	
	$-PS(CH_3)_2$	6.60	6.26	6.14	17.9	11.8	1.8	
	$-PS(phenyl)_2$	6.82	6.34	6.17	17.9	11.7	1.6	
	-Li				23.9	19.3	7.1	
	-MgCl	6.68	5.57	6.20	23.0	17.6	7.5	
	-MgBr	6.67	5.51	6.15	23.3	17.7	7.6	
	$-Si(CH_3)_3$	6.11	5.63	5.88	20.2	14.6	3.8	CH_3 0.06
	$-Sn(CH{=}CH_2)_3$	6.39	5.75	6.21	20.7	13.4	3.1	
	$-Pb(CH{=}CH_2)_3$	6.70	5.46	6.19	19.8	12.2	2.1	
	-HgBr	6.45	5.52	5.92	18.7	11.9	3.1	

Estimation of ^{1}H Chemical Shifts of Substituted Ethylenes

(δ in ppm relative to TMS)

C = C



$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

Substituent R		Z_{gem}	Z_{cis}	Z_{trans}
	–H	0.00	0.00	0.00
C	–alkyl	0.45	-0.22	-0.28
	–alkyl ring[1]	0.69	-0.25	-0.28
	–CH_2–aromatic	1.05	-0.29	-0.32
	–CH_2X, X: F, Cl, Br	0.70	0.11	-0.04
	–CHF_2	0.66	0.32	0.21
	–CF_3	0.66	0.61	0.32
	–CH_2O	0.64	-0.01	-0.02
	–CH_2N	0.58	-0.10	-0.08
	–CH_2CN	0.69	-0.08	-0.06
	–CH_2S	0.71	-0.13	-0.22
	–CH_2CO	0.69	-0.08	-0.06
	–C=C	1.00	-0.09	-0.23
	–C=C conjugated[2]	1.24	0.02	-0.05
	–C≡C	0.47	0.38	0.12
	–aromatic	1.38	0.36	-0.07
	–aromatic, fixed[3]	1.60		-0.05
	–aromatic, *o*-substituted	1.65	0.19	0.09
H	–F	1.54	-0.40	-1.02
a	–Cl	1.08	0.18	0.13
l	–Br	1.07	0.45	0.55
	–I	1.14	0.81	0.88
O	–OC (sp^3)	1.22	-1.07	-1.21
	–OC (sp^2)	1.21	-0.60	-1.00
	–OCO–	2.11	-0.35	-0.64
	–$OPO(OCH_2CH_3)_2$	1.33	-0.34	-0.66
N	–NR_2; R: H, C (sp^3)	0.80	-1.26	-1.21
	–NR–; R: C (sp^2)	1.17	-0.53	-0.99
	–NCO–R	2.08	-0.57	-0.72
	–N=N–phenyl	2.39	1.11	0.67
	–NO_2	1.87	1.30	0.62
	–CN	0.27	0.75	0.55

Substituent R		Z_{gem}	Z_{cis}	Z_{trans}
S	–S–	1.11	-0.29	-0.13
	–SO–	1.27	0.67	0.41
	$–SO_2–$	1.55	1.16	0.93
	–SCO–	1.41	0.06	0.02
	–SCN	0.94	0.45	0.41
	$–SF_5$	1.68	0.61	0.49
O	–CHO	1.02	0.95	1.17
||	–CO–	1.10	1.12	0.87
C	–CO– conjugated[2]	1.06	0.91	0.74
/\	–COOH	0.97	1.41	0.71
	–COOH conjugated[2]	0.80	0.98	0.32
	–COOR	0.80	1.18	0.55
	–COOR conjugated[2]	0.78	1.01	0.46
	–CON	1.37	0.98	0.46
	–COCl	1.11	1.46	1.01
	$–PO(OCH_2CH_3)_2$	0.66	0.88	0.67

C≡C

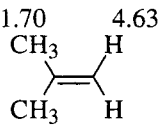
1) The increment for "alkyl ring" is to be used if the substituent and the double bond are part of a cyclic structure.

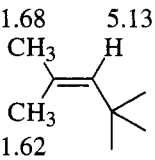
2) The increment "conjugated" is to be used if either the double bond or the substituent is conjugated to other substituents.

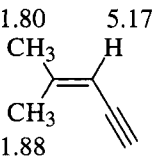
3) The increment "aromatic, fixed" is to be used if the double bond conjugated to an aromatic ring is part of a fused ring (such as in 1,2-dihydronaphthalene).

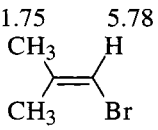
^1H Chemical Shifts of Substituted Isobutenes

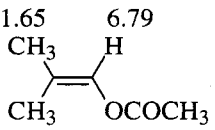
(δ in ppm relative to TMS)

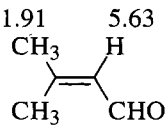


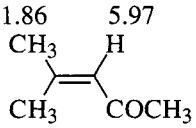


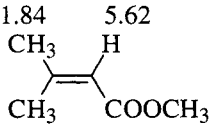


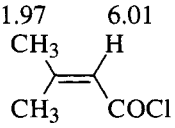






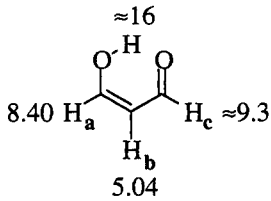




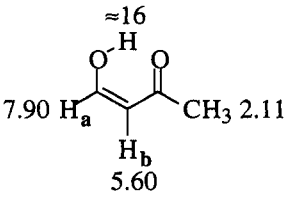


^{1}H Chemical Shifts of Enols (*δ in ppm relative to TMS, J in Hz*)

C=C



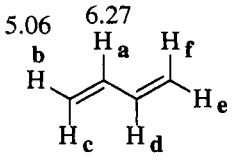
J_{ab} 9.7
J_{bc} ≈8



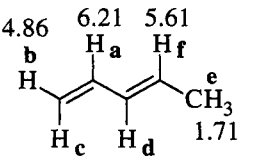
J_{ab} 5.1

5.2.2 Dienes

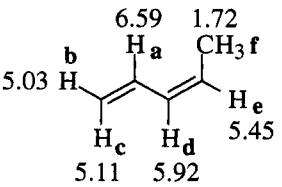
^{1}H Chemical Shifts and Coupling Constants of Conjugated Dienes (*δ in ppm relative to TMS, J in Hz*)



$^3J_{ab}$ 10.2
$^3J_{ac}$ 17.1
$^3J_{ad}$ 10.4
$^4J_{ae}$ -0.9
$^4J_{af}$ -0.8
$^2J_{bc}$ 1.8
$^5J_{be}$ 1.3
$^5J_{bf}$ 0.6
$^5J_{cf}$ 0.7

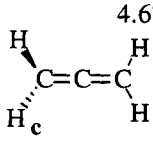


$^3J_{ab}$ 10.2
$^3J_{ac}$ 16.9
$^3J_{ad}$ 10.3
$^5J_{ae}$ 0.4
$^4J_{af}$ -0.8
$^2J_{bc}$ 1.9
$^4J_{bd}$ -0.8
$^6J_{be}$ -0.7
$^5J_{bf}$ 0.7
$^4J_{cd}$ -0.8
$^6J_{ce}$ -0.7
$^5J_{cf}$ 0.7
$^4J_{de}$ -1.6
$^3J_{df}$ 15.1
$^3J_{ef}$ 6.6

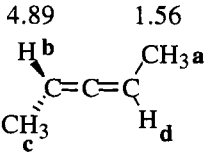


$^3J_{ab}$ 10.2
$^3J_{ac}$ 16.9
$^3J_{ad}$ 10.9
$^4J_{ae}$ -1.1
$^5J_{af}$ 0.2
$^2J_{bc}$ 2.1
$^4J_{bd}$ -0.8
$^5J_{be}$ -0.7
$^6J_{bf}$ 0.7
$^4J_{cd}$ -0.8
$^5J_{ce}$ 0.7
$^6J_{cf}$ -0.6
$^3J_{de}$ 10.8
$^4J_{df}$ -1.8
$^3J_{ef}$ 7.0

^{1}H Chemical Shifts and Coupling Constants of Allenes (*δ in ppm relative to TMS, J in Hz*)



$^2J_{ab}$ -9
$^4J_{ac}$ -6

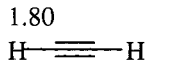


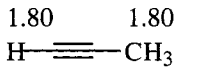
$^5J_{ab}$ 3.2
$^6J_{ac}$ 0
$^3J_{ad}$ 6.8
$^4J_{bd}$ -6.4

5.3 Alkynes

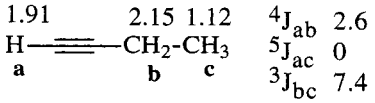
5.3.1 Chemical Shifts and Coupling Constants

^1H Chemical Shifts and Coupling Constants of Alkynes C≡C
(δ in ppm relative to TMS, J in Hz)

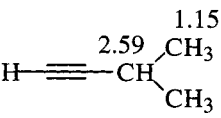


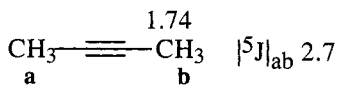


$^4J_{H,CH_3}$ 2.9

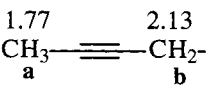


$^4J_{ab}$ 2.6
$^5J_{ac}$ 0
$^3J_{bc}$ 7.4

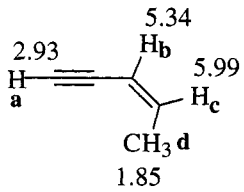




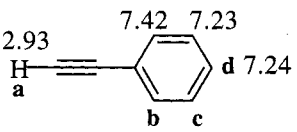
$|^5J|_{ab}$ 2.7



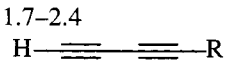
$|^5J|_{ab}$ 2.5

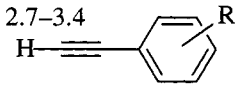


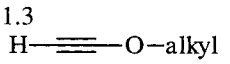
$^4J_{ab}$ 2.0
$^5J_{ac}$ 1.0
$^6J_{ad}$ 0.6
$^3J_{bc}$ 10.5
$^4J_{bd}$ 1.6
$^3J_{cd}$ 6.5

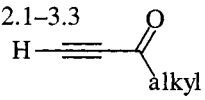


$^5J_{ab}$ 0.28
$^6J_{ac}$ -0.11
$^7J_{ad}$ 0.22









5.4 Alicyclics

^1H Chemical Shifts and Coupling Constants of Saturated Alicyclic Hydrocarbons *(δ in ppm relative to TMS, J in Hz)*


0.20

$^2J_{gem}$	-4.3
$^3J_{cis}$	9.0
$^3J_{trans}$	5.6

In derivatives:

$^2J_{gem}$	-3 to -9
$^3J_{cis}$	6 to 12
$^3J_{trans}$	2 to 9

Throughout: $J_{cis} > J_{trans}$


1.94

In derivatives:

$^2J_{gem}$	-10 to -17
$^3J_{cis}$	4 to 12
$^3J_{trans}$	2 to 10
$^4J_{cis}$	≈0
$^4J_{trans}$	≈-1


1.51

In derivatives:

$^2J_{gem}$	-8 to -18
$^3J_{cis}$	5 to 10
$^3J_{trans}$	5 to 10

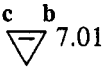

1.44

At -100 °C:
H_{ax} 1.1
H_{eq} 1.6

In derivatives:

$^2J_{gem}$	-11 to -14
$^3J_{ax,ax}$	8 to 13
$^3J_{eq,ax}$	2 to 6
$^3J_{eq,eq}$	2 to 5

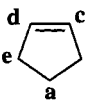
Generally: $J_{eq,ax} \approx J_{eq,eq} + 1$



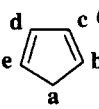
In derivatives:

$^3J_{ab}$	1.5 to 2.0
$^3J_{bc}$	0.5 to 1.5

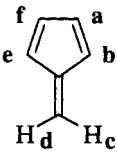
$^2J_{gem}$	-13.7
$^3J_{ab}$	1.0
$^4J_{ac}$	-0.3
$^3J_{ad,cis}$	1.8
$^3J_{ad,trans}$	4.6
$^3J_{bc}$	2.8



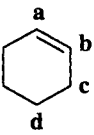
$^2J_{gem,a}$	-12.8	$^4J_{bd}$	-2.3
$^3J_{ab,cis}$	9.3	$^5J_{be,cis}$	2.1
$^3J_{ab,trans}$	5.7	$^5J_{be,trans}$	3.0
$^2J_{gem,b}$	-16.1	$^3J_{cd}$	5.8
$^3J_{bc}$	2.3		



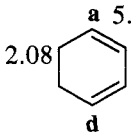
$^3J_{ab}$	1.3
$^4J_{ac}$	-1.5
$^3J_{bc}$	5.0
$^4J_{bd}$	1.1
$^5J_{be}$	2.0
$^3J_{cd}$	1.9



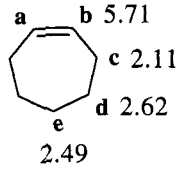
$^3J_{ab}$	5.1	$^4J_{bc}$	-0.2
$^5J_{ac}$	0.5	$^4J_{bd}$	-0.4
$^5J_{ad}$	1.4	$^4J_{be}$	2.0
$^4J_{ae}$	1.3	$^2J_{cd}$	0.1
$^3J_{af}$	2.0		



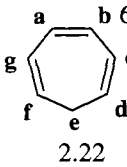
$^3J_{ab}$	≈10	$^3J_{bc}$	1.5



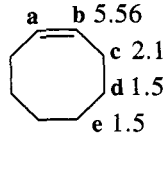
$^3J_{ab}$ 9.7
$^4J_{ac}$ 1.0
$^5J_{ad}$ 1.1
$^3J_{bc}$ 5.1



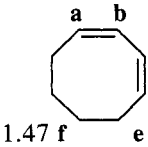
$^3J_{ab}$ ≈10
$^3J_{bc}$ 3.7



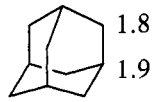
$^3J_{ab}$	11.2	$^5J_{cg}$	-0.6
$^4J_{ac}$	0.8	$^3J_{de}$	6.7
$^3J_{bc}$	5.5	$^4J_{df}$	0
$^3J_{cd}$	8.9	$^5J_{dg}$	0
$^5J_{cf}$	0	$^2J_{gem,e}$	-13.0

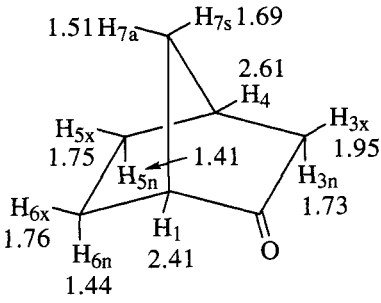


$^3J_{ab}$ ≈10
$^3J_{bc}$ 5.3



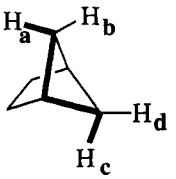
$^3J_{ab}$ 11.3
$^4J_{ac}$ -0.6
$^5J_{ad}$ 0.5
$^3J_{bc}$ 4.1



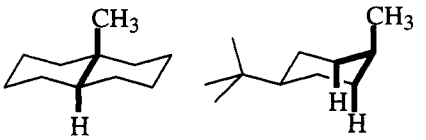


$^4J_{1,4}$	1.2	$^4J_{4,6n}$	-0.5
$^4J_{1,5n}$	-0.3	$^4J_{4,6x}$	0.7
$^4J_{1,5x}$	0.2	$^3J_{4,7a}$	2.1
$^3J_{1,6n}$	0.1	$^3J_{4,7s}$	1.6
$^3J_{1,6x}$	4.7	$^2J_{5n,5x}$	-12.8
$^3J_{1,7a}$	1.2	$^3J_{5n,6n}$	9.1
$^3J_{1,7s}$	1.6	$^3J_{5n,6x}$	4.7
$^2J_{3n,3x}$	-17.6	$^4J_{5n,7a}$	-0.1
$^3J_{3n,4}$	0	$^4J_{5n,7s}$	2.1
$^4J_{3n,7a}$	4.2	$^3J_{5x,6n}$	4.6
$^4J_{3n,7a}$	4.2	$^3J_{5x,6x}$	12.1
$^3J_{3x,4}$	4.8	$^2J_{6n,6x}$	-12.3
$^4J_{3x,5x}$	2.3	$^4J_{6n,7a}$	-0.1
$^3J_{4,5n}$	0.1	$^4J_{6n,7s}$	2.3
$^3J_{4,5x}$	4.3	$^2J_{7a,7s}$	-10.2

In condensed alicyclics, couplings over four or more bonds are often observed. Such long-range couplings are particularly large if the arrangement of the bonds between the two protons is w-shaped:

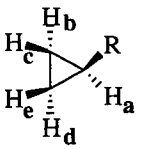


$^4J_{ac} \approx 7$
$^4J_{ad}, {}^4J_{bd} \approx 0$



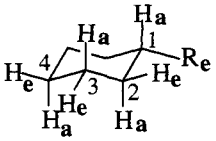
CH_3 signal broadened due to long-range coupling

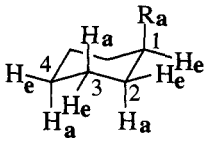
^{1}H Chemical Shifts and Coupling Constants of Monosubstituted Cyclopropanes (*δ in ppm relative to TMS, J in Hz*)



	Substituent X	H_a	$H_{b,d}$	$H_{c,e}$	$^3J_{ab}$	$^3J_{ac}$	$^2J_{bc}$	$^3J_{bd}$	$^3J_{be}$	$^3J_{ce}$
	–H	0.20	0.20	0.20	9.0	5.6	-4.3	9.0	5.6	9.0
C	–CH=CH_2	2.36	0.64	0.34	8.2	4.9	-4.5	9.3	6.2	9.0
	–phenyl	1.71	2.65	2.83	9.5	6.3	-4.5	9.5	5.2	8.9
H	–F	4.32	0.69	0.27	5.9	2.4	-6.7	10.8	7.7	12.0
a	–Cl	2.55	0.87	0.74	7.0	3.6	-6.0	10.3	7.1	10.6
l	–Br	2.83	0.96	0.81	7.1	3.8	-6.1	10.2	7.0	10.5
	–I	2.31	1.04	0.76	7.5	4.4	-5.9	9.9	6.6	10.0
O	–OH	3.35	0.59	0.34	6.2	2.9	-5.4	10.3	6.8	10.9
N	–NH_2	2.23	0.32	0.20	6.6	3.6	-4.3	9.7	6.2	9.9
	–CN	1.36	0.94	0.93	8.4	5.1	-4.7	9.2	7.1	9.5
O	–CO–cyclopropyl	1.70	0.56	1.02	7.9	4.6	-3.5	9.1	7.0	9.5
||	–COOH	1.59	0.91	1.05	8.0	4.6	-4.0	9.3	7.1	9.7
C	–$COOCH_3$	1.95	0.81	0.85	8.0	4.6	-3.4	8.8	6.9	9.6
/ \	–COF	1.66	1.20	1.11	8.0	4.6	-4.5	10.1	7.5	9.3
	–COCl	2.11	1.18	1.28	7.9	4.4	-4.5	9.2	7.6	10.0
	–Li	-2.53	0.43	-0.12	10.3	9.1	-1.6	7.7	3.2	6.5
	–B(cyclopropyl)$_2$	-0.25	0.66	0.61	8.9	5.8	-3.3	8.2	5.9	8.4
	–Hg–cyclopropyl	0.00	0.75	0.47	9.6	6.9	-3.7	8.5	4.8	7.9

^1H Chemical Shifts of Axially and Equatorially Monosubstituted Cyclohexanes (δ in ppm relative to TMS)





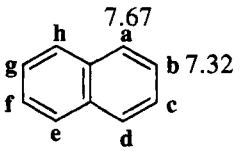
	Substituent R	1a	2a	2e	3a	3e	1e	2a	2e	3a	3e
	–D	1.12	1.12	1.60	1.12	1.60	1.60	1.12	1.60	1.12	1.60
C	$-CH_3$	1.27	0.81	1.57	1.15	1.60	1.93	1.37	1.40	1.39	1.34
	–phenyl	2.47					2.98				
H	–Cl	3.63					4.34			1.7	
a	–Br	3.81					4.62				
l	–I	3.98					4.72				
O	–OH	3.38	1.09	1.78	1.19	1.61	3.89	1.35	1.58	1.58	1.33
	$-OCOCH_3$	4.46					4.98	1.47	2.3		
N	$-NH_2$	2.52					3.15				
	$-NHCH_3$	2.08					2.70				
	$-NO_2$	4.23	2.2	1.9			4.43	1.6	2.6		
S	–SH	2.57	0.7	1.3			3.43		1.5	1.9	

5.5 Aromatic Hydrocarbons

^{1}H Chemical Shifts and Coupling Constants of Aromatic Hydrocarbons (δ in ppm relative to TMS, J in Hz)

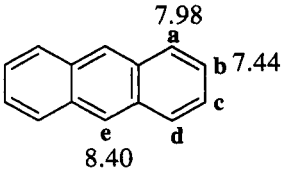
In derivatives:

$^3J_{ortho}$	6.5–8.5
$^4J_{meta}$	1.0–3.0
$^5J_{para}$	0.0–1.0



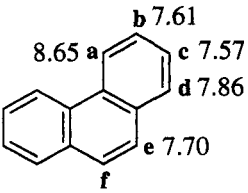
In derivatives:

$^3J_{ab}$	8–9	$^5J_{ae}$	≈0.9
$^4J_{ac}$	1–2	$^6J_{af}$	≈-0.1
$^5J_{ad}$	≈1	$^5J_{ag}$	≈0.2
$^3J_{bc}$	5–7	$^4J_{ah}$	≈-0.5
		$^7J_{bf}$	≈0.3
		$^6J_{bg}$	≈0.1



In derivatives:

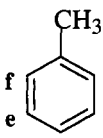
$^3J_{ab}$	8.5–9.5
$^4J_{ac}$	0.8–1.5
$^5J_{ad}$	0.6–0.9
$^5J_{ae}$	≈0.8
$^3J_{bc}$	6.5–8.0
$^4J_{de}$	≈0.4



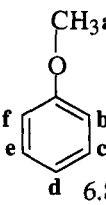
$^3J_{ab}$	8.4
$^4J_{ac}$	1.2
$^5J_{ad}$	0.7
$^3J_{bc}$	7.2
$^4J_{bd}$	1.3
$^3J_{cd}$	8.1

In derivatives:

$^3J_{ef}$	≈9

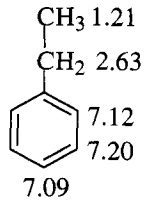


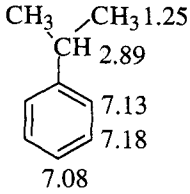
$^4J_{ab}$	-0.7	$^5J_{be}$	0.6		
$^5J_{ac}$	0.3	$^4J_{bf}$	2.0		
$^6J_{ad}$	-0.6	$^3J_{cd}$	7.5		
$^3J_{bc}$	7.7	$^4J_{ce}$	1.5		
$^4J_{bd}$	1.3				

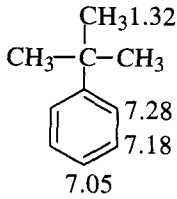


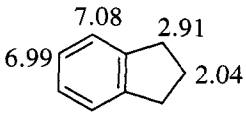
$^5J_{ab}$	≈ 0.8	$^4J_{bf}$	2.7		
$^3J_{bc}$	8.3	$^3J_{cd}$	7.4		
$^4J_{bd}$	1.0	$^4J_{ce}$	1.8		
$^5J_{be}$	0.4				

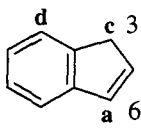
In routine spectra, the small long-range couplings between aromatic protons and aliphatic substituents are not resolved. Nevertheless, they are diagnostically highly relevant because the line broadenings caused by them are easily detected (if there is a reference line in the spectrum, e.g. from another methyl group, or in an AA'XX' spin system of the aromatic protons). As a confirmation, a decoupling experiment may be useful (line sharpening on weak irradiation of the frequency of the coupling partner) or a COSY experiment is recommended.



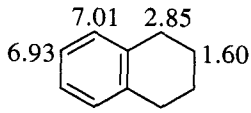


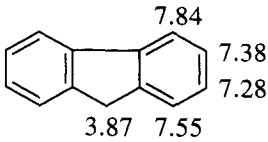


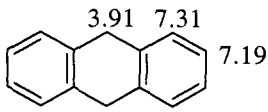


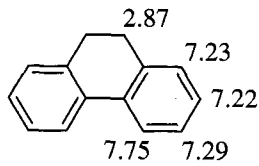


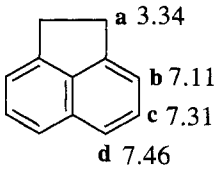
$^3J_{ab}$ 5.8
$^4J_{ac}$ 2.0
$^5J_{ad}$ 0.7
$^3J_{bc}$ 2.0



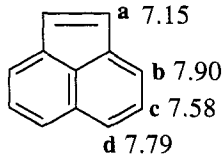






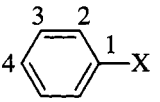


$^4J_{ab}$ 1.5
$^5J_{ac}$ 0
$^6J_{ad}$ 0.5
$^3J_{bc}$ 6.7
$^4J_{bd}$ 1.2
$^3J_{cd}$ 8.1



$^4J_{ab}$ 0
$^5J_{ac}$ 0
$^6J_{ad}$ 0
$^3J_{bc}$ 7
$^4J_{bd}$ 0.6
$^3J_{cd}$ 8

Effect of Substituents on ^1H Chemical Shifts of Monosubstituted Benzenes *(in ppm relative to TMS)*

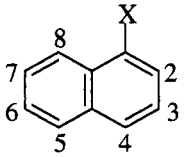


$$\delta_{H_i} = 7.26 + Z_i$$

	Substituent X	Z_2	Z_3	Z_4
	–H	0.00	0.00	0.00
C	$-CH_3$	-0.20	-0.12	-0.21
	$-CH_2CH_3$	-0.14	-0.05	-0.18
	$-CH(CH_3)_2$	-0.13	-0.08	-0.18
	$-C(CH_3)_3$	0.03	-0.08	-0.20
	$-CF_3$	0.19	-0.07	0.00
	$-CCl_3$	0.55	-0.07	-0.09
	$-CH_2OH$	-0.07	-0.07	-0.07
	$-CH=CH_2$	0.04	-0.05	-0.12
	–CH=CH–phenyl (*trans*)	0.16	0.00	-0.15
	$-C\equiv CH$	0.16	-0.03	-0.02
	–C≡C–phenyl	0.20	-0.04	-0.07
	–phenyl	0.22	0.06	-0.04
	–2-pyridyl	0.73	0.09	0.02
H	–F	-0.29	-0.02	-0.23
a	–Cl	0.01	-0.06	-0.12
l	–Br	0.17	-0.11	-0.06
	–I	0.38	-0.23	-0.01
O	–OH	-0.53	-0.17	-0.44
	$-OCH_3$	-0.49	-0.11	-0.44
	$-OCH_2CH=CH_2$	-0.45	-0.13	-0.43
	–O–phenyl	-0.34	-0.04	-0.28
	$-OCOCH_3$	-0.19	-0.03	-0.19
	–OCO–phenyl	-0.11	0.07	-0.10
	$-OSO_2CH_3$	-0.05	0.07	-0.01
N	$-NH_2$	-0.80	-0.25	-0.64
	$-NHCH_3$	-0.83	-0.22	-0.68
	$-N(CH_3)_2$	-0.67	-0.18	-0.66
	$-N^+(CH_3)_3I^-$	0.72	0.40	0.34
	$-NHCOCH_3$	0.38	-0.02	-0.26
	$-NHNH_2$	-0.60	-0.08	-0.55
	–N=N–phenyl	0.67	0.20	0.20
	–NO	0.55	0.29	0.35
	$-NO_2$	0.93	0.26	0.39
	–CN	0.25	0.18	0.30
	–NCS	-0.11	0.04	-0.02

Substituent X		Z_2	Z_3	Z_4
S	–SH	-0.08	-0.16	-0.22
	$-SCH_3$	-0.08	-0.10	-0.24
	–S–phenyl	-0.06	-0.20	-0.26
	–S–S–phenyl	0.24	0.02	-0.06
	$-SO_2CH_3$	0.68	0.35	0.39
	$-SO_2OCH_3$	0.68	0.34	0.36
	$-SO_2Cl$	0.68	0.23	0.34
	$-SO_2NH_2$	0.59	0.32	0.32
O	–CHO	0.61	0.25	0.35
||	$-COCH_3$	0.60	0.11	0.19
C	$-COCH_2CH_3$	0.63	0.08	0.18
/\	–CO–phenyl	0.44	0.10	0.19
	–CO-(2-pyridyl)	0.86	0.11	0.20
	–COOH	0.87	0.21	0.34
	$-COOCH(CH_3)_2$	0.73	0.11	0.20
	–COO–phenyl	0.88	0.15	0.25
	$-CONH_2$	0.69	0.18	0.25
	–COF	0.71	0.21	0.38
	–COCl	0.81	0.21	0.37
	–COBr	0.77	0.21	0.38
	–CH=N–phenyl	0.64	0.24	0.24
	–Li	0.77	0.26	-0.29
	–MgBr	0.40	-0.19	-0.26
	–Mg–phenyl	-0.49	0.18	0.25
	$-Si(CH_3)_3$	0.19	0.00	0.00
	$-Si(phenyl)_2Cl$	0.32	0.07	0.12
	$-SiCl_3$	0.52	≈0.2	≈0.2
P	$-Pb(phenyl)_2Cl$	0.68	0.28	0.11
	$-P(phenyl)_2$	-0.02	-0.33	-0.33
	$-PO(OCH_3)_2$	0.46	0.14	0.22
	–Zn–phenyl	-0.36	0.02	0.05
	–Hg–phenyl	0.00	0.00	-0.20

Effect of Substituents in Position 1 on the ^{1}H Chemical Shifts of Monosubstituted Naphthalenes *(in ppm relative to TMS)*



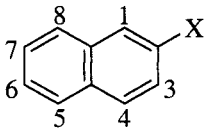
for X : H $\delta_{H_1}, \delta_{H_4}, \delta_{H_5}, \delta_{H_8}$: 7.67

$\delta_{H_2}, \delta_{H_3}, \delta_{H_6}, \delta_{H_7}$: 7.32

	Substituent X	H-2	H-3	H-4	H-5	H-6	H-7	H-8
C	$-CH_3$	-0.22	-0.13	-0.16	-0.03	-0.03	-0.01	0.10
	$-CH_2CH_3$	0.01	0.08	0.03	0.17	0.14	0.17	0.38
	$-CH_2C{\equiv}CH$	0.25	-0.07	-0.06	0.00	0.03	0.13	0.69
	$-CH_2Cl$	0.13	0.01	0.09	0.13	0.14	0.20	0.42
	$-CF_3$	0.67	0.15	0.18	0.23	0.23	0.29	0.52
H	–F	-0.22	0.01	-0.11	0.13	0.15*	0.17*	0.42
a	–Cl	0.17	-0.04	-0.02	0.07	0.11	0.16	0.54
l	–Br	0.38	-0.09	0.03	0.05	0.11	0.19	0.51
	–I	0.10	-0.48	0.18	-0.20	-0.07	-0.02	0.27
O	–OH	-0.68	-0.15	-0.36	0.01	0.03	0.06	0.41
	$-OCH_3$	-0.68	-0.09	-0.38	-0.01	0.04	0.03	0.50
	$-OCOCH_3$	-0.15	0.11	-0.10	0.03	-0.07	0.07	0.16
N	$-NH_2$	-0.77	-0.17	-0.51	-0.06	-0.02	-0.01	-0.01
	$-N(CH_3)_2$	-0.30	0.03	-0.19	0.11	0.13	0.10	0.55
	$-NHCOCH_3$	0.40	0.17	0.05	0.26	0.20	0.24	0.44
	$-NO_2$	0.80	0.14	0.19	0.33	0.21	0.32	0.72
	–NCO	-0.29	-0.15	-0.19	-0.03	0.05	0.03	0.24
	–CN	0.48	0.12	0.30	0.16	0.22	0.29	0.51
O	–CHO	0.44	0.10	0.21	0.06	0.14	0.23	1.52
‖	$-COCH_3$	0.38	-0.07	0.10	0.01	0.04	0.13	1.08
C	–COOH	1.11	0.23	0.42	0.24	0.25	0.34	1.43
/	$-COOCH_3$	0.80	0.05	0.22	0.08	0.10	0.20	1.30
	–COCl	1.17	0.17	0.37	0.17	0.21	0.30	1.04

* Assignment uncertain

Effect of Substituents in Position 2 on the ^1H Chemical Shifts of Monosubstituted Naphthalenes *(in ppm relative to TMS)*



for X: H $\delta_{H_1}, \delta_{H_4}, \delta_{H_5}, \delta_{H_8}$: 7.67

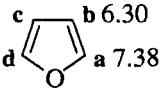
$\delta_{H_2}, \delta_{H_3}, \delta_{H_6}, \delta_{H_7}$: 7.32

	Substituent X	H-1	H-3	H-4	H-5	H-6	H-7	H-8
C	$-CH_3$	-0.21	-0.14	-0.06	0.01	-0.04	-0.01	-0.03
	$-CH_2CH_3$	-0.05	0.02	0.09	0.12	0.08	0.12	0.10
	$-CH(CH_3)_2$	-0.07	0.01	0.05	0.07	0.04	0.06	0.07
	$-CH=CH_2$	0.06	0.30	0.11	0.11	0.10	0.12	0.11
	$-CF_3$	0.45	0.30	0.23		0.25	0.22	
	-Cl	0.13	0.08	0.07	0.12	0.13	0.15	0.05
	-Br	0.23	0.14	-0.09	-0.08	0.05	0.07	0.01
O	-OH	-0.69	-0.35	-0.05	-0.04	-0.11	-0.02	-0.14
	$-OCH_3$	-0.70	-0.28	-0.07	-0.03	-0.11	0.00	-0.07
	$-OCOCH_3$	-0.19	-0.14	0.01	0.06	-0.04	0.11	0.08
N	$-NH_2$	-0.88	-0.56	-0.16	-0.12	-0.23	-0.09	-0.23
	$-N(CH_3)_2$	-0.90	-0.33	-0.13	-0.12	-0.23	-0.08	-0.16
	$-NHCOCH_3$	0.50	0.14	0.07	0.06	0.07	0.10	0.08
	$-NO_2$	0.98	0.82	0.18	0.18	0.28	0.24	0.26
	-CN	0.51	0.25	0.20	0.19	0.31	0.26	0.19
O	-CHO	0.62	0.61	0.23	0.21	0.30	0.24	0.29
||	$-COCH_3$	0.76	0.69	0.19	0.17	0.25	0.21	0.26
C	-COOH	1.00	0.73	0.37	0.36	0.36	0.32	0.48
/\	$-COOCH_3$	0.83	0.66	0.09	0.09	0.15	0.11	0.17
	-COCl	1.02	0.74	0.39	0.49	0.32	0.37	0.37

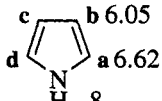
5.6 Heteroaromatic Compounds

5.6.1 Non-Condensed Heteroaromatic Rings

^1H Chemical Shifts and Coupling Constants of Non-Condensed Heteroaromatic Compounds *(δ in ppm relative to TMS, $|J|$ in Hz)*

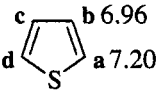


$^3J_{ab}$ 1.8
$^4J_{ac}$ 0.9
$^4J_{ad}$ 1.5
$^3J_{bc}$ 3.4

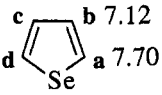


(broad)

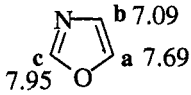
$^3J_{ab}$ 2.6
$^4J_{ac}$ 1.3
$^4J_{ad}$ 2.1
$^3J_{ae}$ 2.6
$^3J_{bc}$ 3.5
$^4J_{be}$ 2.3



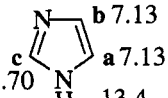
$^3J_{ab}$ 4.8
$^4J_{ac}$ 1.0
$^4J_{ad}$ 2.8
$^3J_{bc}$ 3.5



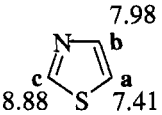
$^3J_{ab}$ 5.4
$^4J_{ac}$ 1.1
$^4J_{ad}$ 2.5
$^3J_{bc}$ 3.6



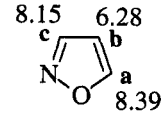
$^3J_{ab}$ 0.8
$^4J_{ac}$ 0.5
$^4J_{bc}$ 0.0



$^3J_{ab}$ 1–2
$^4J_{ac}$ 1–2
$^3J_{bc}$ ≈1
(J values in derivatives)

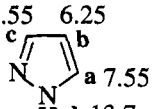


$^3J_{ab}$ 3.2
$^4J_{ac}$ 1.9
$^3J_{bc}$ 0.0

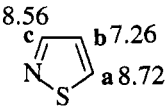


(in CS_2)

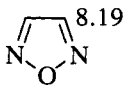
$^3J_{ab}$ 1.7
$^4J_{ac}$ 0.3
$^4J_{bc}$ 1.8

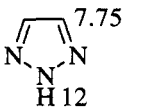


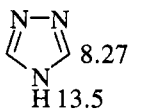
$^3J_{ab}$ 2.1
$^4J_{ac}$ 0.0
$^3J_{bc}$ 2.1

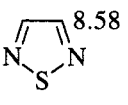


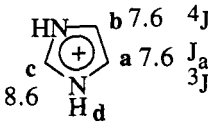
$^3J_{ab}$ 4.7
$^4J_{ac}$ <0.4
$^3J_{bc}$ 1.7





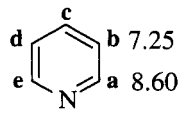






$^4J_{ac}$ 1.4
$J_{ad}+J_{bd}$ 4.4
$^3J_{cd}$ 2.4
≈12

(in H_2SO_4)

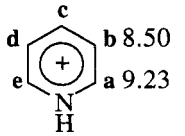


(in $CDCl_3$)

In DMSO:

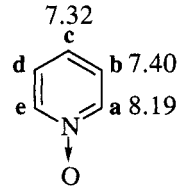
a 8.59
b 7.38
c 7.75

	In derivatives:
$^3J_{ab}$ 6.0	4–6
$^4J_{ac}$ 1.9	0–2.5
$^5J_{ad}$ 0.9	0–2.5
$^4J_{ae}$ 0.4	0–0.6
$^3J_{bc}$ 7.6	7–9
$^4J_{bd}$ 1.6	0.5–2

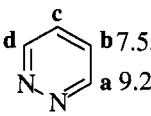


(in CD_3CN)

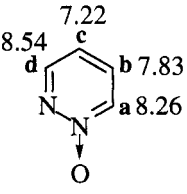
$^3J_{ab}$ 6.0
$^4J_{ac}$ 1.6
$^5J_{ad}$ 0.8
$^4J_{ae}$ 1.0
$^3J_{bc}$ 7.9
$^4J_{bd}$ 1.4



$^3J_{ab}$ 6.5
$^4J_{ac}$ 1.1
$^5J_{ad}$ 0.6
$^4J_{ae}$ 1.9
$^3J_{bc}$ 7.7
$^4J_{bd}$ 2.1

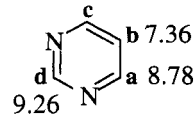


$^3J_{ab}$ 4.9
$^4J_{ac}$ 2.0
$^5J_{ad}$ 3.5
$^3J_{bc}$ 8.4

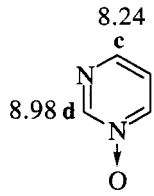


$^3J_{ab}$ 5.3
$^4J_{ac}$ 1.0
$^5J_{ad}$ 1.0
$^3J_{bc}$ 8.0
$^4J_{bd}$ 2.5
$^3J_{cd}$ 6.5

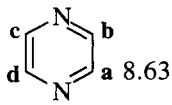
(in acetone)

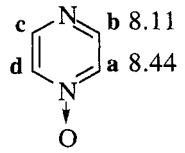


$^3J_{ab}$ 5.0
$^4J_{ac}$ 2.5
$^4J_{ad}$ 0
$^5J_{bd}$ 1.5

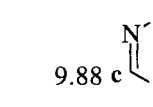


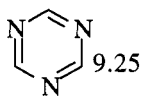
$^3J_{ab}$ 6.8
$^4J_{ac}$ 1.6
$^4J_{ad}$ 2.0
$^3J_{bc}$ 4.9
$^5J_{bd}$ 1.0
$^4J_{cd}$ 0



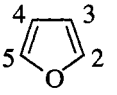


$^3J_{ab}$ 4.1
$^5J_{ac}$ 0.8
$^4J_{ad}$ 0.6
$^4J_{bc}$ 0.4





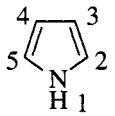
Effect of Substituents on the ^1H Chemical Shifts of Monosubstituted Furans *(in ppm relative to TMS)*



$\delta_{H\text{-}2} = 7.38 + Z_{i,2}$
$\delta_{H\text{-}3} = 6.30 + Z_{i,3}$
$\delta_{H\text{-}4} = 6.30 + Z_{i,4}$
$\delta_{H\text{-}5} = 7.38 + Z_{i,5}$

Substituent		in position 2 or 5:			in position 3 or 4:		
		Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
	–H	0.00	0.00	0.00	0.00	0.00	0.00
C	$-CH_3$	-0.42	-0.12	-0.17	-0.27	-0.17	-0.15
	$-CH_2OH$	-0.11	-0.05	-0.08			
	$-CH_2NH_2$	-0.24	-0.06	-0.10			
	–CH=CHCHO	0.70	0.35	0.42			
	–Br	-0.02	0.03	-0.01			
	–I	0.12	-0.13	-0.01	-0.13	0.04	-0.22
O	$-OCH_3$	-1.34	-0.23	-0.68	-0.46	-0.28	-0.37
N	$-NO_2$	1.21	0.55	0.51			
	–CN	0.85	0.32	0.28	0.45	0.22	-0.02
S	$-SCH_3$	-0.12	-0.06	-0.09	-0.18	-0.05	-0.15
	–SCN	0.40	0.06	0.10	0.19	0.19	0.03
O	–CHO	0.93	0.31	0.34	0.48	0.37	-0.07
||	$-COCH_3$	0.81	0.23	0.19	0.46	0.36	-0.12
C	$-COCF_3$	1.34	0.50	0.64			
/\	–COOH	0.94	0.33	0.41	0.89	0.54	0.36
	$-COOCH_3$	0.85	0.22	0.25	0.45	0.33	-0.14
	–COCl	1.20	0.39	0.48			

Effect of Substituents on the ^1H Chemical Shifts of Monosubstituted Pyrroles *(in ppm relative to TMS)*

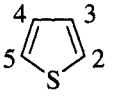


$\delta_{H\text{-}1} \approx 8$ broad, solvent-dependent
$\delta_{H\text{-}2} = 6.62 + Z_{i,2}$
$\delta_{H\text{-}3} = 6.05 + Z_{i,3}$
$\delta_{H\text{-}4} = 6.05 + Z_{i,4}$
$\delta_{H\text{-}5} = 6.62 + Z_{i,5}$

Substituent in position 1	Z_{12} Z_{15}	Z_{13} Z_{14}
–H	0.00	0.00
$-CH_3$	-0.25	-0.13
$-CH_2CH_3$	-0.16	-0.12
$-CH_2$–phenyl	-0.12	-0.04
–phenyl	0.33	0.14
$-COCH_3$	0.56	0.12
–CO–phenyl	0.57	0.18

Substituent		in position 2 or 5:			in position 3 or 4:		
		Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
	–H	0.00	0.00	0.00	0.00	0.00	0.00
C	$-CH_3$	-0.33	-0.16	-0.26	-0.34	-0.20	-0.20
N	$-NO_2$	1.06	0.24	0.43	1.04	0.70	0.13
	–CN	0.83	0.23	0.51			
S	$-SCH_3$	0.18	0.05	0.10			
	–SCN	0.48	0.10	0.28			
O	–CHO	0.93	0.27	0.61			
||	$-COCH_3$	0.78	0.10	0.44	0.79	0.63	0.15
C	$-COOCH_3$	0.79	0.13	0.29	0.90	0.73	0.16

Effect of Substituents on the ^{1}H Chemical Shifts of Monosubstituted Thiophenes *(in ppm relative to TMS)*

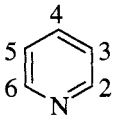


$\delta_{H\text{-}2} = 7.20 + Z_{i,2}$
$\delta_{H\text{-}3} = 6.96 + Z_{i,3}$
$\delta_{H\text{-}4} = 6.96 + Z_{i,4}$
$\delta_{H\text{-}5} = 7.20 + Z_{i,5}$

Substituent		in position 2 or 5:			in position 3 or 4:		
		Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
	–H	0.00	0.00	0.00	0.00	0.00	0.00
C	$-CH_3$	-0.36	-0.24	-0.29	-0.45	-0.22	-0.14
	$-C\equiv CH$	0.15	-0.16	-0.12			
H	–Cl	-0.25	-0.22	-0.22	-0.22	-0.11	-0.03
a	–Br	-0.05	-0.27	-0.11	-0.12	-0.08	-0.10
l	–I	0.13	-0.33	0.01	0.06	0.00	-0.19
O	–OH*	-0.72	0.59	-3.10			
	$-OCH_3$	-0.94	-0.43	-0.82	-1.10	-0.38	-0.20
N	$-NH_2$	-0.95	-0.45	-0.85	-1.25	-0.53	-0.25
	$-NO_2$	0.82	-0.03	0.30	0.95	0.60	0.03
	–CN	0.47	0.00	0.28	0.63	0.20	0.15
S	–SH	0.00	-0.20	-0.07	-0.22	-0.20	-0.10
	$-SCH_3$	-0.03	-0.18	-0.05	-0.33	-0.10	-0.03
	$-SO_2CH_3$	1.03	0.20	0.79	0.96	0.48	0.46
	$-SO_2Cl$	0.73	0.06	0.45			
	–SCN	0.30	-0.05	0.28	0.25	0.05	0.05
O	–CHO	0.65	0.10	0.45	0.79	0.45	0.03
||	$-COCH_3$	0.57	0.00	0.28	0.68	0.47	-0.02
C	–COOH	0.80	0.08	0.40	0.99	0.48	0.24
/\	$-COOCH_3$	0.70	-0.05	0.20	0.78	0.47	-0.05
	–COCl	0.88	0.06	0.44	1.05	0.50	0.03

* Present in the keto form

Effect of Substituents on the ^1H Chemical Shifts of Monosubstituted Pyridines *(in ppm relative to TMS; solvent: DMSO)*



$\delta_{H\text{-}2} = 8.59 + Z_{i,2}$
$\delta_{H\text{-}3} = 7.38 + Z_{i,3}$
$\delta_{H\text{-}4} = 7.75 + Z_{i,4}$
$\delta_{H\text{-}5} = 7.38 + Z_{i,5}$
$\delta_{H\text{-}6} = 8.59 + Z_{i,6}$

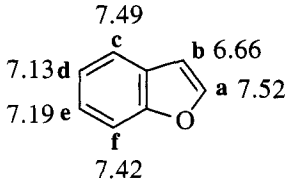
	Substituent in position 2 or 6	Z_{23} Z_{65}	Z_{24} Z_{64}	Z_{25} Z_{63}	Z_{26} Z_{62}
	–H	0.00	0.00	0.00	0.00
C	$-CH_3$	-0.11	-0.01	-0.16	0.08
	$-CH_2CH_3$	-0.09	-0.08	-0.15	0.03
	$-CH_2$–phenyl	0.12	-0.08	-0.20	0.02
	$-CH_2OH$	0.37	0.30	0.02	0.06
	$-CH_2NH_2$	0.20	0.07	-0.09	0.05
	$-CH_2S$–*n*-C_3H_7	0.04	-0.08	-0.26	-0.06
	$-CH_2SO_2$–phenyl	≈0	≈-0.3	≈0	-0.2
	$-CH{=}CH_2$	0.11	-0.14	-0.11	0.04
	–phenyl	0.16	-0.28	-0.40	-0.03
	–2-pyridyl	1.12	-0.09	-0.26	0.00
H	–F	-0.10	0.40	0.12	-0.13
a	–Cl	0.32	0.29	0.29	0.20
l	–Br	0.41	0.17	0.19	0.02
O	–OH	-0.7	0.0	-1.0	-0.9
	–O–*n*-C_4H_9	-0.53	-0.03	-0.49	-0.32
N	$-NH_2$	-0.68	-0.31	-0.78	-0.48
	$-NHCOCH_3$	0.94	0.16	-0.20	-0.10
	$-NHCOOCH_2CH_3$	0.59	0.07	-0.24	-0.21
	$-NHNO_2$	0.34	0.31	-0.03	-0.41
	$-NO_2$	1.09	0.67	0.74	0.26
	–CN	0.88	0.38	0.55	0.39
S	$-SCH_3$	-0.09	-0.11	-0.29	-0.11
O	–CHO	0.93	0.42	0.50	0.44
||	$-COCH_3$	0.82	0.37	0.39	0.28
C	–CO–phenyl	0.62	0.55	0.32	0.28
/\	–COOH	0.97	0.43	0.48	0.42
	–COO–*n*-C_4H_9	0.86	0.39	0.35	0.35
	$-CONH_2$	1.05	0.47	0.43	0.30
	$-CSNH_2$	1.41	0.37	0.33	0.25
	–CH=NOH	0.40	0.28	0.01	0.16

Substituent		in position 3 or 5:				in position 4:	
		Z_{32} Z_{56}	Z_{34} Z_{54}	Z_{35} Z_{53}	Z_{36} Z_{52}	Z_{42} Z_{46}	Z_{43} Z_{45}
	–H	0.00	0.00	0.00	0.00	0.00	0.00
C	$-CH_3$	-0.02	-0.06	-0.09	-0.02	0.01	-0.10
	$-CH_2$–phenyl					0.00	-0.15
	$-CH_2OH$	0.11	0.15	0.04	-0.04	0.07	0.14
	$-CH_2NH_2$	0.16	0.13	0.04	0.00	0.01	0.03
	$-CH_2S$-*n*-C_3H_7					-0.06	-0.13
	$-CH_2SO_2$–phenyl	-0.24	-0.15	-0.22	0.01	-0.09	-0.18
	$-CH=CH_2$					0.12	0.13
	–CH=CH–COOH	0.45	0.52	0.34	0.17		
H	–F	-0.01	0.00	0.14	-0.10	-0.07	-0.03
a	–Cl	0.20	0.24	0.19	0.09	0.00	0.05
l	–Br	0.20	0.43	0.34	0.18	0.09	0.35
O	–OH	-0.03	-0.37	0.15	-0.24		
	$-OCH_3$					0.02	-0.29
N	$-NH_2$	-0.06	-0.49	0.02	-0.36	-0.15	-0.74
	$-NHCOCH_3$	0.37	0.50	0.06	-0.16	-0.05	0.31
	–CN	0.63	0.72	0.43	0.50	0.46	0.62
S	$-SCH_2$–phenyl					-0.02	0.04
	–S–phenyl					0.05	-0.16
	$-SO_3H$	0.70	1.14	0.81	0.70		
O	–CHO	0.45	0.42	0.12	0.20	0.47	0.58
||	$-COCH_3$	0.72	0.68	0.30	0.37	0.40	0.58
C	–CO–phenyl	0.47	0.54	0.37	0.34	0.36	0.40
/\	$-COOCH_3$	0.62	0.60	0.23	0.34		
	$-COO$-*n*-C_4H_9					0.34	0.54
	$-CSNH_2$	0.68	0.67	0.24	0.26	0.35	0.68
	–CH=NOH	0.39	0.43	0.19	0.15	0.24	0.37

5.6.2
Condensed Heteroaromatic Rings

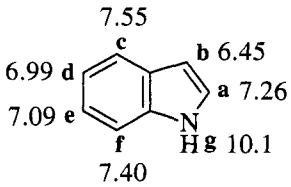
^1H Chemical Shifts of Condensed Heteroaromatic Rings

(δ in ppm relative to TMS, $|J|$ in Hz)



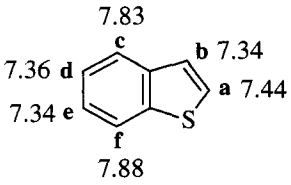
$^3J_{ab}$ 2.5
$^5J_{ac}$, $^6J_{ad}$, $^6J_{ae}$, $^5J_{af}$: 0
$^4J_{bc}$, $^5J_{bd}$, $^6J_{be}$: 0
$^5J_{bf}$ 0.9
$^3J_{cd}$ 7.9

$^4J_{ce}$ 1.2
$^5J_{cf}$ 0.8
$^3J_{de}$ 7.3
$^4J_{df}$ 0.9
$^3J_{ef}$ 8.4



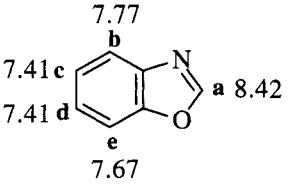
$^3J_{ab}$ 3.1
$^5J_{ac}$, $^6J_{ad}$, $^6J_{ae}$, $^5J_{af}$: 0
$^3J_{ag}$ 2.5
$^4J_{bc}$, $^5J_{bd}$, $^6J_{be}$: 0
$^5J_{bf}$ 0.7
$^4J_{bg}$ 2.0
$^3J_{cd}$ 7.8

$^4J_{ce}$ 1.2
$^5J_{cf}$ 0.9
$^5J_{cg}$ 0.8
$^3J_{de}$ 7.1
$^4J_{df}$ 1.3
$^3J_{ef}$ 8.1
$^6J_{dg}$, $^5J_{eg}$, $^4J_{fg}$: 0



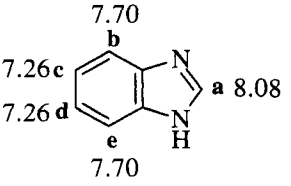
$^3J_{ab}$ 5.5
$^5J_{ac}$, $^6J_{ad}$, $^6J_{ae}$, $^5J_{af}$: 0
$^4J_{bc}$, $^5J_{bd}$, $^6J_{be}$: 0
$^5J_{bf}$ 0.8
$^3J_{cd}$ 8.0

$^4J_{ce}$ 1.1
$^5J_{cf}$ 0.9
$^3J_{de}$ 7.2
$^4J_{df}$ 1.0
$^3J_{ef}$ 8.0

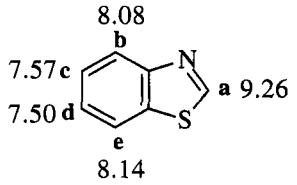


$^5J_{ab}$ 0.2
$^6J_{ac}$ -0.1
$^6J_{ad}$ 0.4
$^5J_{ae}$ 0.0
$^3J_{bc}$ 8.2

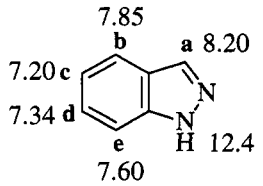
$^4J_{bd}$ 1.0
$^5J_{be}$ 0.7
$^3J_{cd}$ 7.4
$^4J_{ce}$ 1.2
$^3J_{de}$ 8.3



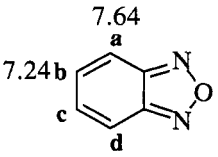
$^5J_{ab}$, $^6J_{ac}$, $^6J_{ad}$, $^5J_{ae}$: 0
$^3J_{bc}$, $^3J_{de}$ 8.2
$^4J_{bd}$, $^4J_{ce}$ 1.4
$^5J_{be}$ 0.7
$^3J_{cd}$ 7.1



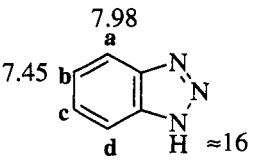
$^5J_{ab}$ 0.1
$^6J_{ac}$ -0.2
$^6J_{ad}$ 0.4
$^5J_{ae}$ 0.1
$^3J_{bc}$ 8.2
$^4J_{bd}$ 1.1
$^5J_{be}$ 0.6
$^3J_{cd}$ 7.2
$^4J_{ce}$ 1.1
$^3J_{de}$ 8.2



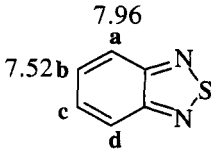
$^4J_{ab}$, $^5J_{ac}$, $^6J_{ad}$: 0
$^5J_{ae}$ 0.8
$^3J_{bc}$ 7.8
$^4J_{bd}$ 1.2
$^5J_{be}$ 1.0
$^3J_{cd}$ 7.0
$^4J_{ce}$ 1.2
$^3J_{de}$ 7.9



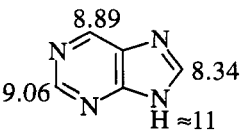
$^3J_{ab}$ 9.3
$^4J_{ac}$ 1.2
$^5J_{ad}$ 0.9
$^3J_{bc}$ 6.4

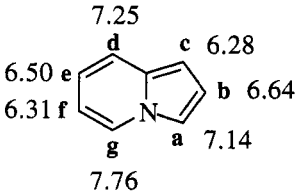


$^3J_{ab}$ 8.3
$^4J_{ac}$ 1.0
$^5J_{ad}$ 0.9

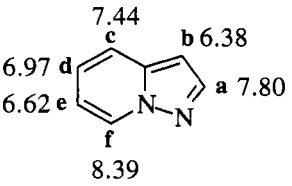


$^3J_{ab}$ 9.2
$^4J_{ac}$ 1.0
$^5J_{ad}$ 0.8
$^3J_{bc}$ ≈6

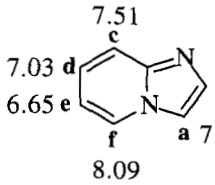




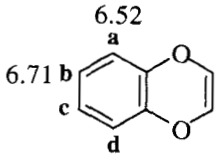
$^3J_{ab}$ 2.7
$^4J_{ac}$ 1.2
$^5J_{ad}$ 0.5
$^6J_{ae}$, $^5J_{af}$, $^4J_{ag}$: 0
$^3J_{bc}$ 3.9
$^5J_{bd}$, $^6J_{be}$, $^5J_{bg}$: 0
$^6J_{bf}$ 0.5
$^4J_{cd}$, $^5J_{ce}$, $^6J_{cf}$: 0
$^5J_{cg}$ 1.0
$^3J_{de}$ 9.0
$^4J_{df}$ 1.0
$^5J_{dg}$ 1.2
$^3J_{ef}$ 6.4
$^4J_{eg}$ 1.0
$^3J_{fg}$ 6.8



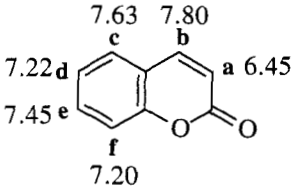
$^3J_{ab}$ 2.2
$^5J_{ac}$ 0
$^6J_{ad}$ 0.5
$^6J_{ae}$, $^5J_{af}$ 0
$^4J_{bc}$, $^5J_{bd}$, $^6J_{be}$: 0
$^5J_{bf}$ 0.9
$^3J_{cd}$ 8.9
$^4J_{ce}$ 1.2
$^5J_{cf}$ 1.0
$^3J_{de}$ 7.0
$^4J_{df}$ 1.0
$^3J_{ef}$ 6.9



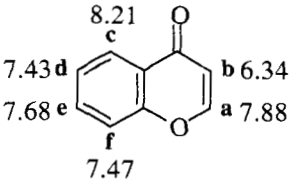
$^3J_{ab}$ 1.0
$^5J_{ac}$, $^6J_{ad}$, $^5J_{ae}$: 0
$^4J_{af}$ 0.7
$^5J_{bc}$, $^6J_{bd}$, $^6J_{be}$, $^5J_{bf}$: 0
$^3J_{cd}$ 9.3
$^4J_{ce}$ 1.0
$^5J_{cf}$ 1.0
$^3J_{de}$ 6.8
$^4J_{df}$ 1.2
$^3J_{ef}$ 6.9



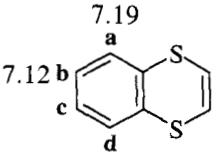
$^3J_{ab}$ 7.9
$^4J_{ac}$ 1.5
$^5J_{ad}$ 0.4
$^3J_{bc}$ 7.9



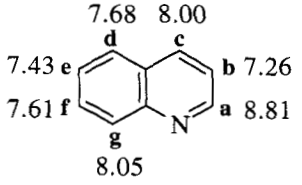
$^3J_{ab}$ 9.8
$^3J_{cd}$ 8.5
$^4J_{ce}$ 2.0
$^5J_{cf}$ 0.0
$^3J_{de}$ 8.6
$^4J_{df}$ 1.8
$^3J_{ef}$ 8.5



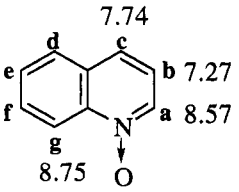
$^3J_{ab}$ 6.1
$^3J_{cd}$ 8.0
$^4J_{ce}$ 1.8
$^5J_{cf}$ 0.5
$^3J_{de}$ 7.0
$^4J_{df}$ 1.1
$^3J_{ef}$ 8.4



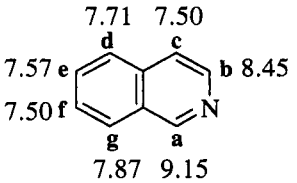
$^3J_{ab}$ 7.8
$^4J_{ac}$ 1.3
$^5J_{ad}$ 1.1
$^3J_{bc}$ 7.1



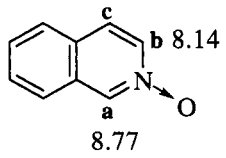
$^3J_{ab}$ 4.3 $^4J_{df}$ 1.6
$^4J_{ac}$ 1.8 $^5J_{dg}$ 0.5
$^3J_{bc}$ 8.3 $^3J_{ef}$ 6.8
$^5J_{cg}$ 0.8 $^4J_{eg}$ 1.1
$^3J_{de}$ 8.2 $^3J_{fg}$ 8.2



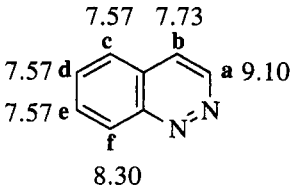
$^3J_{ab}$ 6.0
$^4J_{ac}$ 1.1
$^3J_{bc}$ 8.5



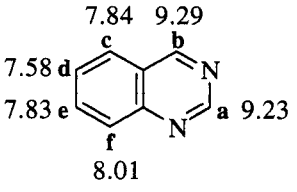
$^4J_{ab}$ 0.8 $^3J_{de}$ 8.7
$^5J_{ac}$ 0 $^4J_{df}$ 1.1
$^5J_{ad}$ <0.5 $^5J_{dg}$ 0.9
$^3J_{bc}$ 6.0 $^3J_{ef}$ 7.0
$^5J_{cg}$ 0.8 $^4J_{eg}$ 1.3
$^3J_{fg}$ 8.2



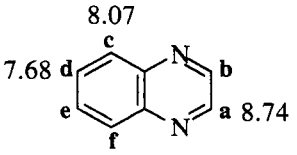
$^4J_{ab}$ 1.7
$^3J_{bc}$ 7.0



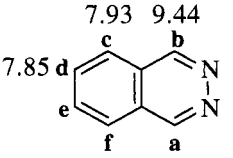
$^3J_{ab}$ 5.7 $^3J_{de}$ 6.9
$^5J_{bf}$ 0.8 $^4J_{df}$ 1.3
$^3J_{cd}$ 7.8 $^3J_{ef}$ 8.6
$^4J_{ce}$ 1.5
$^5J_{cf}$ 0.8



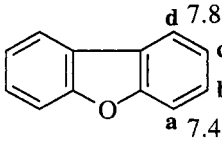
$^4J_{ab}$ 0 $^3J_{de}$ 6.9
$^5J_{bf}$ 0.5 $^4J_{df}$ 1.2
$^3J_{cd}$ 7.9 $^3J_{ef}$ 8.5
$^4J_{ce}$ 1.2
$^5J_{cf}$ 0.8



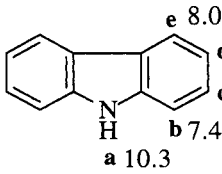
$^3J_{ab}$ 1.8
$^3J_{cd}$ 8.4
$^4J_{ce}$ 1.6
$^5J_{cf}$ 0.6
$^3J_{de}$ 6.9



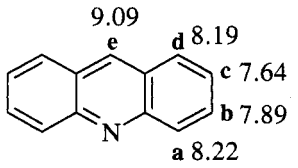
$^5J_{ac}$ 0.4
$^3J_{cd}$ 8.2
$^4J_{ce}$ 1.2
$^5J_{cf}$ 0.6
$^3J_{de}$ 6.8



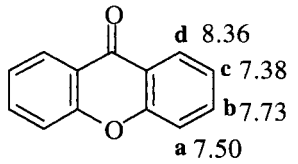
$^3J_{ab}$ 8.5 $^3J_{bc}$ 7.3
$^4J_{ac}$ 0.9 $^4J_{bd}$ 1.3
$^5J_{ad}$ 0.6 $^3J_{cd}$ 7.6



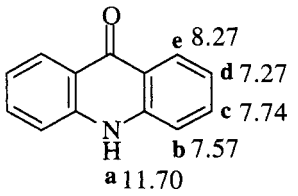
$^5J_{ae}$ 0.7 $^3J_{cd}$ 7.2
$^3J_{bc}$ 8.2 $^4J_{ce}$ 1.2
$^4J_{bd}$ 0.9 $^3J_{de}$ 7.8
$^5J_{be}$ 0.7



$^3J_{ab}$ 9.0 $^3J_{bc}$ 6.6
$^4J_{ac}$ 1.2 $^4J_{bd}$ 1.4
$^5J_{ad}$ 0.6 $^3J_{cd}$ 8.2
$^5J_{ae}$ 0.9 $^4J_{de}$ 0.4



$^3J_{ab}$ 8.4 $^3J_{bc}$ 7.1
$^4J_{ac}$ 1.1 $^4J_{bd}$ 1.8
$^5J_{ad}$ 0.5 $^3J_{cd}$ 8.0



$^5J_{ae}$ 0.4 $^3J_{cd}$ 7.0
$^3J_{bc}$ 8.6 $^4J_{ce}$ 1.4
$^4J_{bd}$ 1.0 $^3J_{de}$ 8.2
$^5J_{be}$ 0.4

5.7 Halogen Compounds

5.7.1 Fluoro Compounds

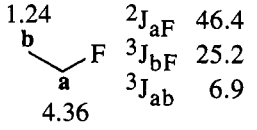
Fluorine in nature occurs 100% as ^{19}F, which exhibits a spin quantum number I = 1/2. The signals of ^{1}H atoms are split by coupling to ^{19}F up to a distance of about four bonds.

^{1}H Chemical Shifts and Coupling Constants of Fluoro Compounds *(δ in ppm relative to TMS, J in Hz)*

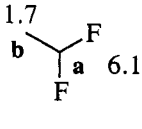
4.10
CH_3F $^2J_{HF}$ 46.4

5.45
CH_2F_2 $^2J_{HF}$ 50.2

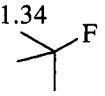
6.25
CHF_3 $^2J_{HF}$ 79.2



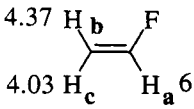
$^2J_{aF}$ 46.4
$^3J_{bF}$ 25.2
$^3J_{ab}$ 6.9



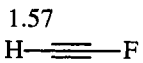
$^2J_{aF}$ 57.3
$^3J_{bF}$ 20.9
$^3J_{ab}$ 4.5



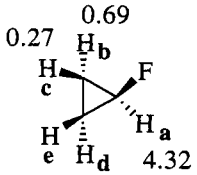
Hal



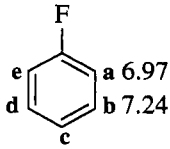
$^2J_{aF}$ 84.7 $^3J_{ab}$ 12.8
$^3J_{bF}$ 20.1 $^3J_{ac}$ 4.7
$^3J_{cF}$ 52.4 $^2J_{bc}$ -3.2



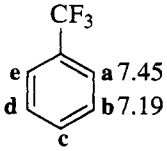
$^3J_{HF}$ 15.0



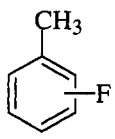
$^2J_{aF}$ 64.5 $^3J_{ab}$ 5.9
$^3J_{bF}$ 9.9 $^3J_{ac}$ 2.4
$^3J_{cF}$ 21.0 $^2J_{bc}$ -6.7
$^3J_{bd}$ 10.8
$^3J_{be}$ 7.7
$^3J_{ce}$ 12.0



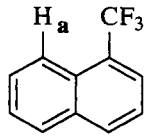
$^3J_{aF}$ 8.9 $^3J_{ab}$ 8.4
$^4J_{bF}$ 5.7 $^4J_{ac}$ 1.1
$^5J_{cF}$ 0.2 $^5J_{ad}$ 0.4
$^4J_{ac}$ 2.7
$^3J_{bc}$ 7.5
$^4J_{bd}$ 1.8



$^4J_{aF}$ -0.8 $^3J_{ab}$ 7.9
$^5J_{bF}$ 0.8 $^4J_{ac}$ 1.2
$^5J_{cF}$ -0.7 $^5J_{ad}$ 0.6
$^4J_{ac}$ 2.0
$^3J_{bc}$ 7.6
$^4J_{bd}$ 1.3



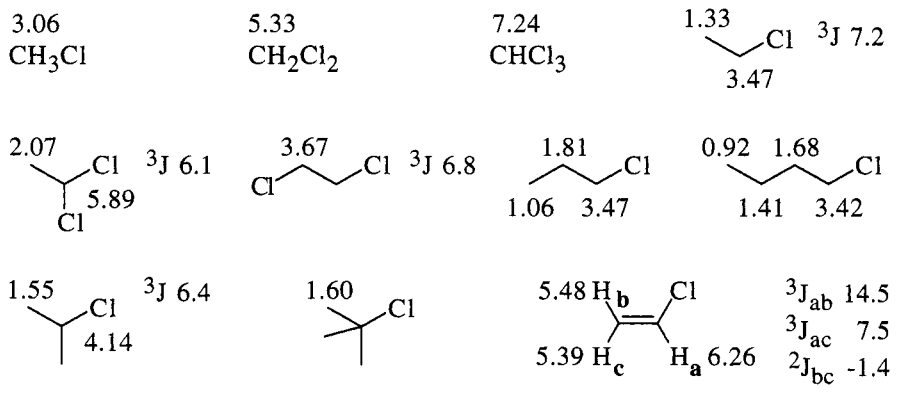
Couplings with CH_3:
^4J_o 2.5
^5J_m 0.0
^6J_p 1.5



$^5J_{aF}$ 2.2

5.7.2 Chloro Compounds

^1H Chemical Shifts and Coupling Constants of Chloro Compounds (δ in ppm relative to TMS, J in Hz)



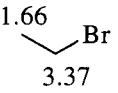
5.7.3 Bromo Compounds

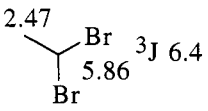
^{1}H Chemical Shifts and Coupling Constants of Bromo Compounds *(δ in ppm relative to TMS, J in Hz)*

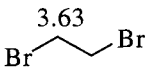
2.69
CH_3Br

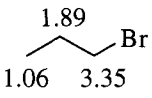
4.94
CH_2Br_2

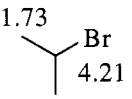
6.82
$CHBr_3$

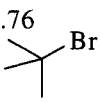


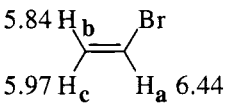




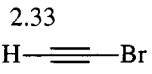








$^3J_{ab}$ 14.9
$^3J_{ac}$ 7.1
$^2J_{bc}$ -1.9



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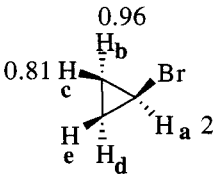
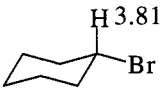
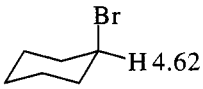
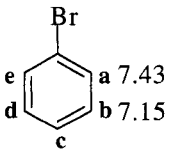


$^3J_{ab}$ 7.1
$^3J_{ac}$ 3.8
$^2J_{bc}$ -6.1
$^3J_{bd}$ 10.2
$^3J_{be}$ 7.0
$^3J_{ce}$ 10.5







$^3J_{ab}$ 8.0
$^4J_{ac}$ 1.1
$^5J_{ad}$ 0.5
$^4J_{ac}$ 2.2
$^3J_{bc}$ 7.4
$^4J_{bd}$ 1.8

5.7.4 Iodo Compounds

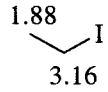
^1H Chemical Shifts and Coupling Constants of Iodo Compounds

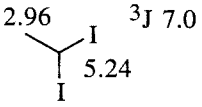
(δ in ppm relative to TMS, J in Hz)

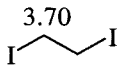
2.16
CH_3I

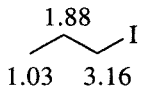
3.90
CH_2I_2

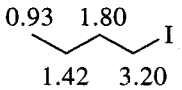
4.91
CHI_3

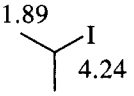


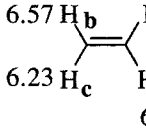




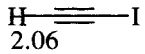








$^3J_{ab}$ 15.9
$^3J_{ac}$ 7.8
$^2J_{bc}$ -1.5



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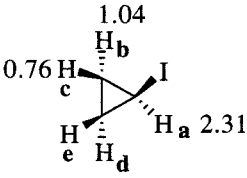
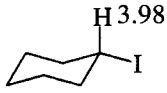
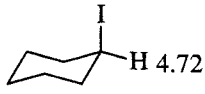
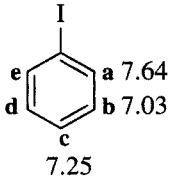


$^3J_{ab}$ 7.5
$^3J_{ac}$ 4.4
$^2J_{bc}$ -5.9
$^3J_{bd}$ 9.9
$^3J_{be}$ 6.6
$^3J_{ce}$ 10.0







$^3J_{ab}$ 7.9
$^4J_{ac}$ 1.1
$^5J_{ad}$ 0.5
$^4J_{ac}$ 1.9
$^3J_{bc}$ 7.5
$^4J_{bd}$ 1.8

5.8 Alcohols, Ethers, and Related Compounds

5.8.1 Alcohols

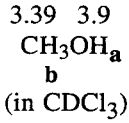
^{1}H Chemical Shifts and Coupling Constants of Alcohols

(δ in ppm relative to TMS, J in Hz)

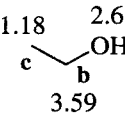
Aliphatic and alicyclic alcohols:	0.5–3.0 (in DMSO: 4–6)
Phenols:	4.0–8.0 (in DMSO: 8–12)

Hydrogen bonds strongly deshield hydroxyl protons. The position of the signal may depend heavily on the experimental conditions. If a compound contains several kinds of hydroxyl protons (–OH, –COOH, H_2O), in general only one signal at an average position is observed because of rapid exchange. In dimethyl sulfoxide (DMSO) as solvent, this exchange in most cases is so slow that isolated signals are observed. In this case, the chemical shifts of hydroxyl protons are characteristic. However, if the sample contains strong acids or amine bases, the exchange rate increases, and also in DMSO, a signal at an average position is observed. Frequently, intermediate exchange rates lead to very broad signals extending over several ppm and, therefore, sometimes not discernible in routine spectra.

As a consequence of fast intermolecular exchange of the hydroxyl protons, their coupling with the protons on the adjacent carbon atoms is usually not observed. However, in very pure (acid-free) solutions or in DMSO, the exchange is sufficiently slow so that the H-O-C-H couplings become visible. Their dependence on the conformation is analogous to that shown by the H-C-C-H couplings (Chapter 5.1). In case of fast rotation: $^3J_{HOCH} \approx 5$ Hz. In cyclohexanols, the vicinal coupling constants for axial hydroxyl protons (3.0–4.2 Hz) are lower than those of equatorial ones (4.2–5.7 Hz).



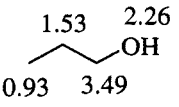
(in $CDCl_3$) in DMSO: $^3J_{ab}$ 5.2



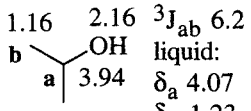
(in $CDCl_3$)

liquid: δ_a 5.27 δ_b 3.66 δ_c 1.19 $^3J_{ab}$ 4.8 $^3J_{bc}$ 6.9

in DMSO: δ_a 4.5

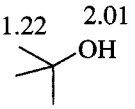


(in $CDCl_3$)

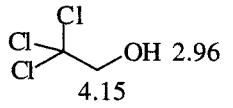


(in $CDCl_3$)

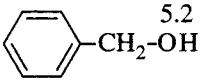
$^3J_{ab}$ 6.2
liquid:
δ_a 4.07
δ_b 1.23



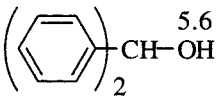
(in $CDCl_3$)



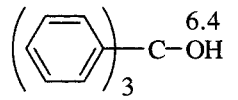
(in $CDCl_3$)
δ_{OH} in DMSO: 6.8



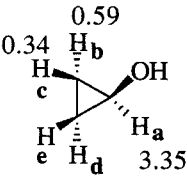
(in DMSO)



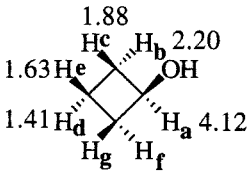
(in DMSO)



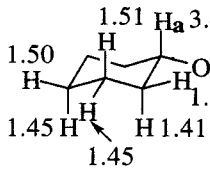
(in DMSO)



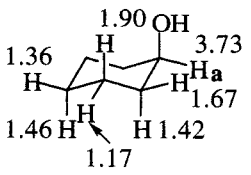
$^3J_{ab}$ 6.2
$^3J_{ac}$ 2.9
$^2J_{bc}$ -5.4
$^3J_{bd}$ 10.3
$^3J_{be}$ 6.8
$^3J_{ce}$ 10.9



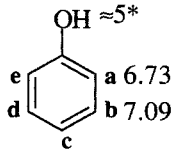
$^3J_{ab}$ 7.0
$^3J_{ac}$ 8.1
$^4J_{ad}$ 0
$^4J_{ae}$ -1.1
$^2J_{bc}$ -11.0
$^3J_{bd}$ 7.9
$^3J_{be}$ 2.3
$^4J_{bf}$ 5.2
$^3J_{cd}$ 10.4
$^3J_{ce}$ 9.7
$^4J_{cf}$ -0.9
$^4J_{cg}$ 0
$^2J_{de}$ -11.0



For derivatives in DMSO:
δ_{OH} 4.0–4.5
$^3J_{a,OH}$ 4.2–5.7

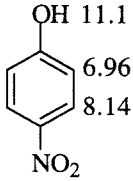


For derivatives in DMSO:
δ_{OH} 3.8–4.2
$^3J_{a,OH}$ 3.0–4.2

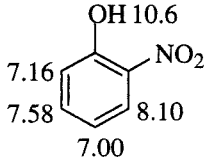


(in CCl_4)
* in DMSO: δ_{OH} 9.3

$^3J_{ab}$ 8.2
$^4J_{ac}$ 1.1
$^5J_{ad}$ 0.5
$^4J_{ae}$ 2.7
$^3J_{bc}$ 7.4
$^4J_{bd}$ 1.7

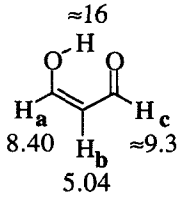


(in DMSO)

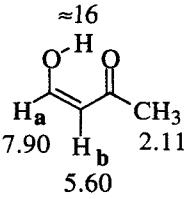


(in $CDCl_3$)

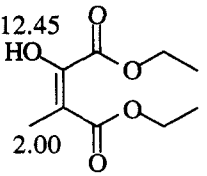
^1H Chemical Shifts of Enols (δ in ppm relative to TMS, J in Hz)



$^3J_{ab}$ 9.7
$^3J_{bc}$ ≈8



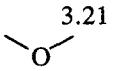
$^3J_{ab}$ 5.1



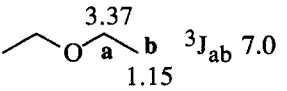
(in $CDCl_3$, partly enolized)

5.8.2 Ethers

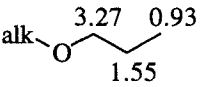
^1H Chemical Shifts and Coupling Constants of Ethers
(δ in ppm relative to TMS, J in Hz)

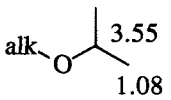


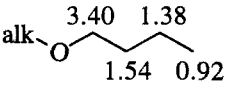
$^2J_{gem}$ -10.6

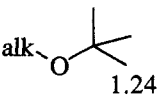


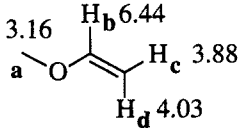
$^3J_{ab}$ 7.0





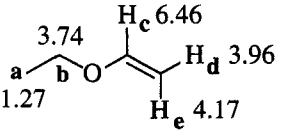






(in TMS)

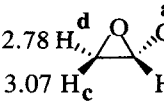
$^4J_{ab}$ 0.3
$^3J_{bc}$ 7.0
$^3J_{bd}$ 14.1
$^2J_{cd}$ -2.0



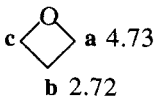
$^3J_{ab}$ 7.0
$^4J_{bc}$ 0.4
$^3J_{cd}$ 6.9
$^3J_{ce}$ 14.4
$^2J_{de}$ -1.9

^1H Chemical Shifts and Coupling Constants of Cyclic Ethers
(δ in ppm relative to TMS, J in Hz)

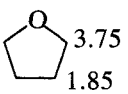
In derivatives:
$^2J_{gem}$ 5–6
$^3J_{cis}$ 4.5
$^3J_{trans}$ 3.1
Throughout:
$J_{cis} > J_{trans}$

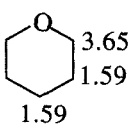


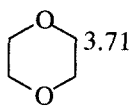
$^3J_{ab}$ 5.2
$^3J_{bc}$ 4.2
$^3J_{bd}$ 3.3
$^2J_{cd}$ 4.2

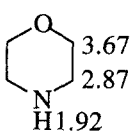


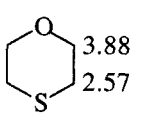
$^2J_{a,gem}$	-5.8
$^2J_{b,gem}$	-11.0
$^3J_{cis}$	8.7
$^3J_{trans}$	6.6
$^3\|J\|_{ac}$	<0.3

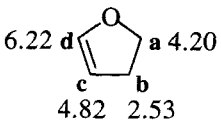




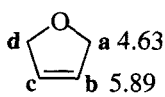




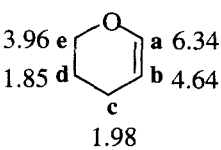




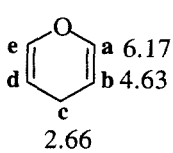
$^3J_{ab,cis}$	8.3
$^3J_{ab,trans}$	10.7
$^3J_{bc}$	2.5
$^4J_{bd}$	2.6
$^3J_{cd}$	2.6



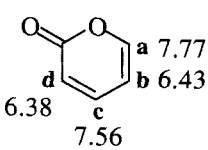
$^3J_{ab}$	1.6
$^4J_{ac}$	-2.5
$^4J_{ad,cis}$	7.1
$^4J_{ad,trans}$	4.6
$^3J_{bc}$	6.3



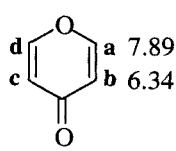
$^3J_{ab}$	6.2
$^4J_{ac}$	2.0
$^3J_{bc}$	3.8
$^4J_{bd}$	0.6



$^3J_{ab}$	7.0
$^4J_{ac}$	1.7
$^4J_{ae}$	1.5
$^3J_{bc}$	3.4

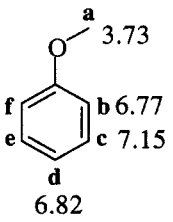


$^3J_{ab}$	5.0
$^4J_{ac}$	2.4
$^5J_{ad}$	1.2
$^3J_{bc}$	6.3
$^4J_{bd}$	1.5
$^3J_{cd}$	9.4

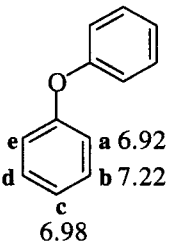


$^3J_{ab}$	6.0
$^5J_{ac}$	0.3
$^4J_{ad}$	2.7
$^4J_{bc}$	1.1

^{1}H Chemical Shifts and Coupling Constants of Aromatic Ethers (*δ in ppm relative to TMS, J in Hz*)

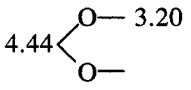


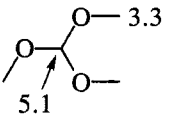
$^5J_{ab}$ ≈0.8
$^3J_{bc}$ 8.3
$^4J_{bd}$ 1.0
$^5J_{be}$ 0.4
$^4J_{bf}$ 2.7
$^3J_{cd}$ 7.4
$^3J_{ce}$ 1.8

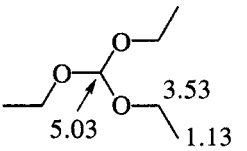


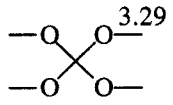
$^3J_{ab}$ 8.3
$^4J_{ac}$ 1.1
$^5J_{ad}$ 0.5
$^4J_{ae}$ 2.6
$^3J_{bc}$ 7.4
$^3J_{bd}$ 1.7

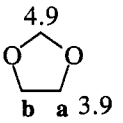
^{1}H Chemical Shifts and Coupling Constants of Acetals, Ketals, and Ortho Esters (*δ in ppm relative to TMS, J in Hz*)



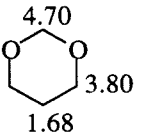


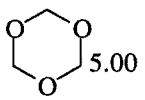


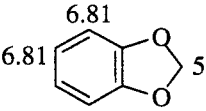




$^2J_{a,gem}$ -7.5
$^3J_{ab,cis}$ 7.3
$^3J_{ab,trans}$ 6.0







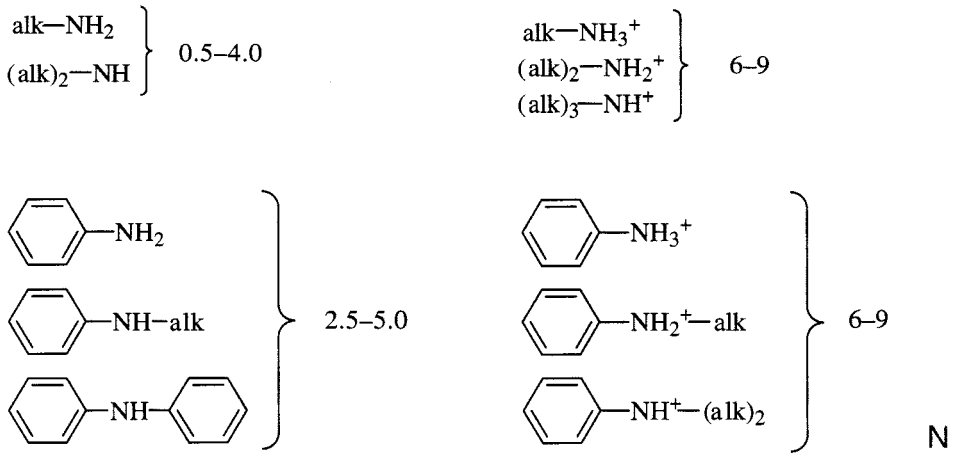
$^2J_{gem}$ 1.5

5.9 Nitrogen Compounds

5.9.1 Amines

Amine and Ammonium Protons *(δ in ppm relative to TMS, $|J|$ in Hz)*

Chemical shifts of amine protons lie around 0.5–5 ppm depending on solvent, concentration, and hydrogen bonding. Those of ammonium protons are found between ca. 6 and 9 ppm:



Coupling of amine protons with vicinal H atoms is usually not seen in aliphatic amines because of their rapid intermolecular exchange. However, for =C–NH–CH moieties (enamines, aromatic amines, amides, etc.), the exchange rate is slower and splitting is often observed. The H–C–N–H coupling depends on the conformation in a similar way as the H–C–C–H coupling (see Chapter 5.1). For N–CH_3 and N–CH_2 groups: $^3J_{HCNH} \approx 5$–6.

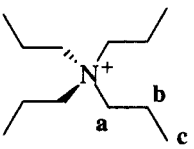
In acidic media (e.g., in trifluoroacetic acid as solvent), the exchange of the *ammonium* protons is slowed down to such an extent that the vicinal coupling H–N^+–C–H generally becomes observable. In other media, signals are usually broad owing to intermediate exchange rates.

The signals of amine and especially of ammonium protons are often broadened additionally because the ^{14}N–^1H coupling is only partly eliminated by the quadrupole relaxation of ^{14}N (spin quantum number, I = 1; natural abundance, 99.6 %; $^1J_{NH} \approx 60$). This line broadening has no effect on the vicinal H–C–N–H coupling so that sharp multiplets can be observed for neighboring H atoms. In

N

ammonium compounds of high symmetry, the quadrupole relaxation is slow and the coupling with ^{14}N leads to triplets of equal intensity for all three lines.

NH_4^+ $^1J_{NH}$ 52.8

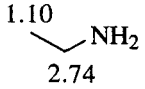


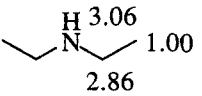
$^2J_{aN}$ 0.5
$^3J_{bN}$ 1.6
$^4J_{cN}$ 0.0

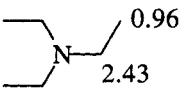
^{1}H Chemical Shifts and Coupling Constants of Amines

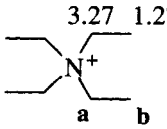
(δ in ppm relative to TMS, J in Hz)

2.47 CH_3NH_2 ≈ 2.3 $(CH_3)_2NH$ 2.31 $(CH_3)_3N$ $^2J_{gem}$ -11.7 3.3 $(CH_3)_4N^+$



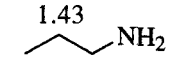


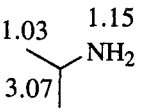




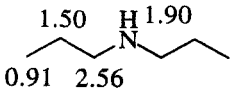
I⁻ $^2J_{aN}$ ≈0.5 $^3J_{bN}$ 1.9

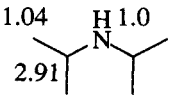
(in D_2O)

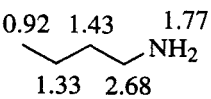


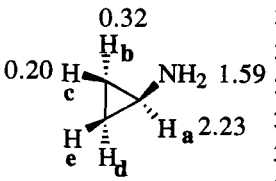


N

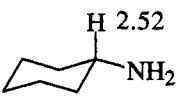


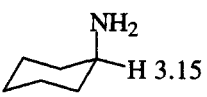


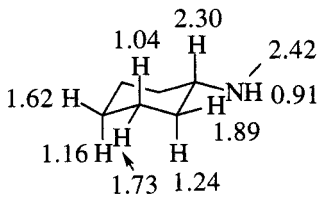


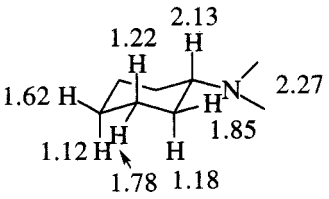


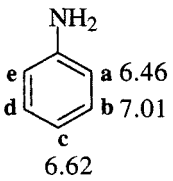
$^3J_{ab}$ 6.6
$^3J_{ac}$ 3.6
$^2J_{bc}$ -4.3
$^3J_{bd}$ 9.7
$^3J_{be}$ 6.2
$^3J_{cd}$ 9.9



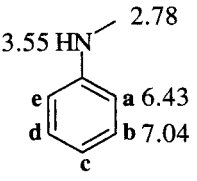




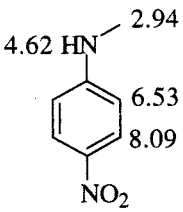




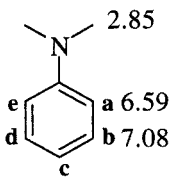
$^3J_{ab}$	8.0
$^4J_{ac}$	1.1
$^5J_{ad}$	0.5
$^4J_{ae}$	2.5
$^3J_{bc}$	7.4
$^4J_{bd}$	1.6



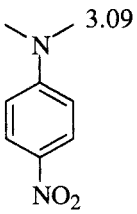
$^3J_{ab}$	8.2
$^4J_{ac}$	1.1
$^5J_{ad}$	0.4
$^4J_{ae}$	2.5
$^3J_{bc}$	7.3
$^4J_{bd}$	1.7

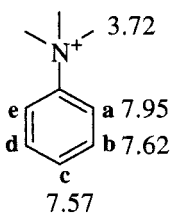


δ_{NH} in DMSO: 7.32



$^3J_{ab}$	8.4
$^4J_{ac}$	1.0
$^5J_{ad}$	0.4
$^4J_{ae}$	2.8
$^3J_{bc}$	7.3
$^4J_{bd}$	1.8

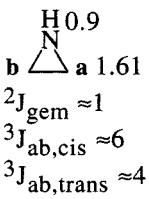




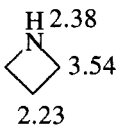
^1H Chemical Shifts and Coupling Constants of Cyclic Amines

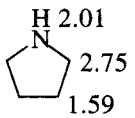
(δ in ppm relative to TMS, J in Hz)

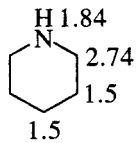
N

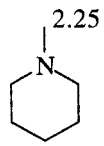


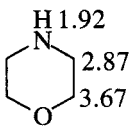
$^2J_{gem} \approx 1$
$^3J_{ab,cis} \approx 6$
$^3J_{ab,trans} \approx 4$

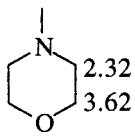


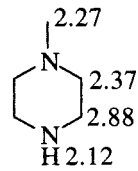






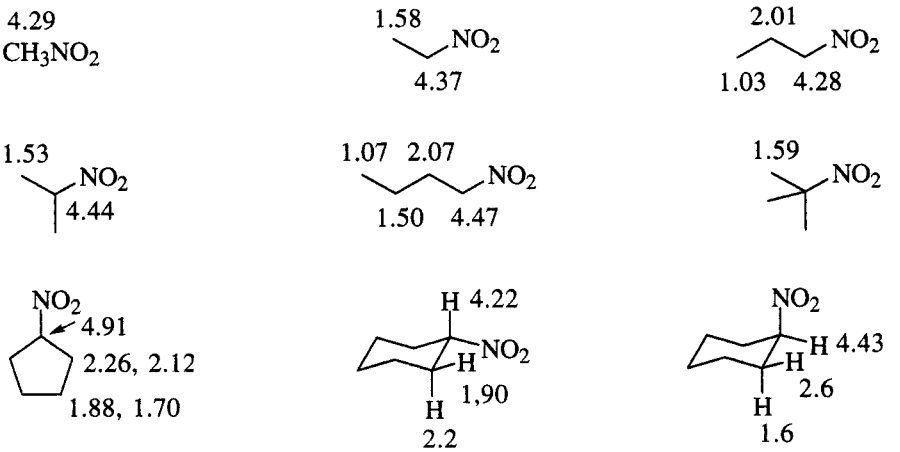






5.9.2 Nitro and Nitroso Compounds

^{1}H Chemical Shifts and Coupling Constants of Nitro and Nitroso Compounds *(δ in ppm relative to TMS, J in Hz)*



N

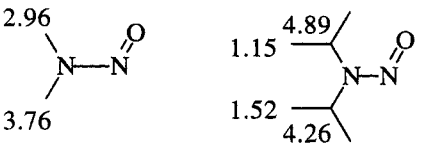
5.9.3 Nitrosamines, Azo and Azoxy Compounds

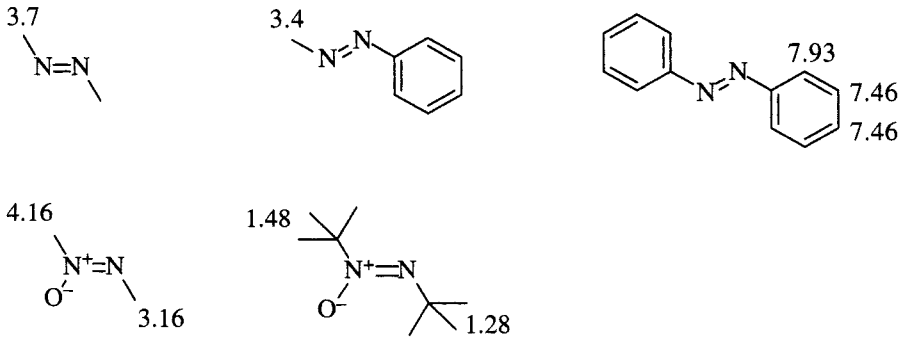
^{1}H Chemical Shifts of Nitrosamines, Azo and Azoxy Compounds *(δ in ppm relative to TMS)*

Generally:

$\delta_{cis} < \delta_{trans}$ for α-CH_3, α–CH_2, and β-CH_3 protons

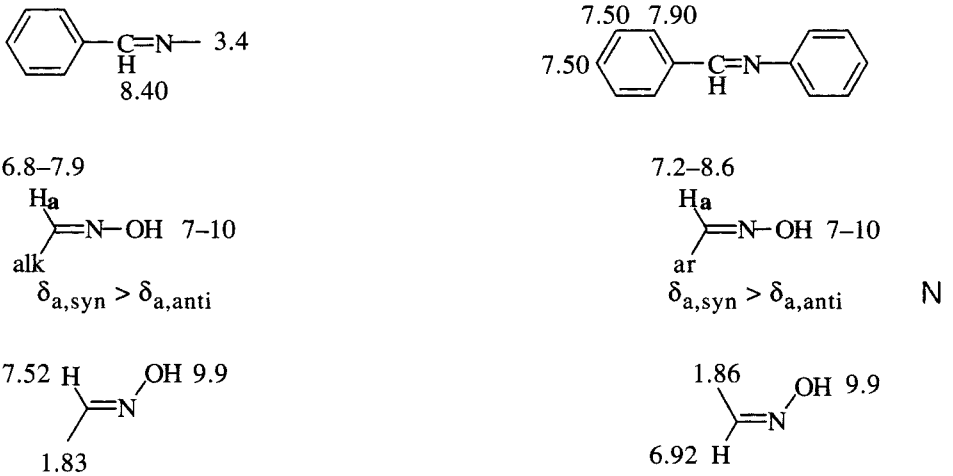
$\delta_{cis} > \delta_{trans}$ for α-CH protons



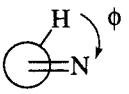


5.9.4 Imines, Oximes, Hydrazones, and Azines

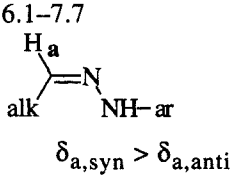
^1H Chemical Shifts and Coupling Constants of Imines, Oximes, Hydrazones, and Azines *(δ in ppm relative to TMS)*



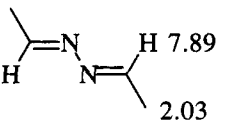
In aldoximes and ketoximes, the chemical shift difference between *syn* and *anti* protons at the α-CH groups, $\Delta\delta = \delta_{syn} - \delta_{anti}$, depends on the dihedral angle, $\phi_{H-C-C=N}$:

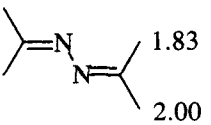


ϕ	Δδ
0°	1
60°	0
115°	-0.3



$\delta_{a,syn} > \delta_{a,anti}$



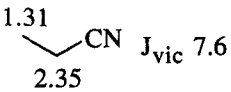


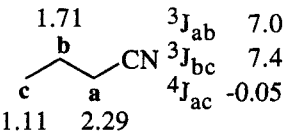
5.9.5 Nitriles and Isonitriles

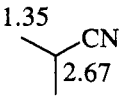
^{1}H Chemical Shifts and Coupling Constants of Nitriles

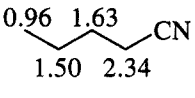
(δ in ppm relative to TMS, J in Hz)

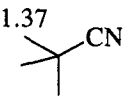
1.98
CH_3CN

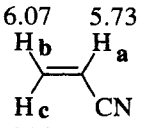


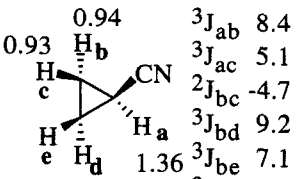


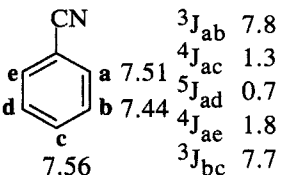








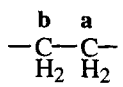




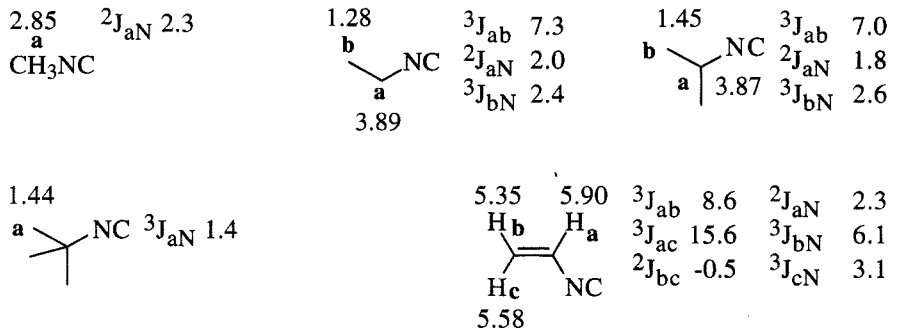
^{1}H Chemical Shifts and Coupling Constants of Isonitriles

(δ in ppm relative to TMS, J in Hz)

Because of the symmetrical electron distribution around the N atom, the quadrupole relaxation of the nitrogen nucleus is so slow that the ^{14}N-^{1}H coupling becomes observable and leads to triplets with relative intensities of 1:1:1 (spin quantum number of ^{14}N: I = 1; natural abundance, 99.6 %):

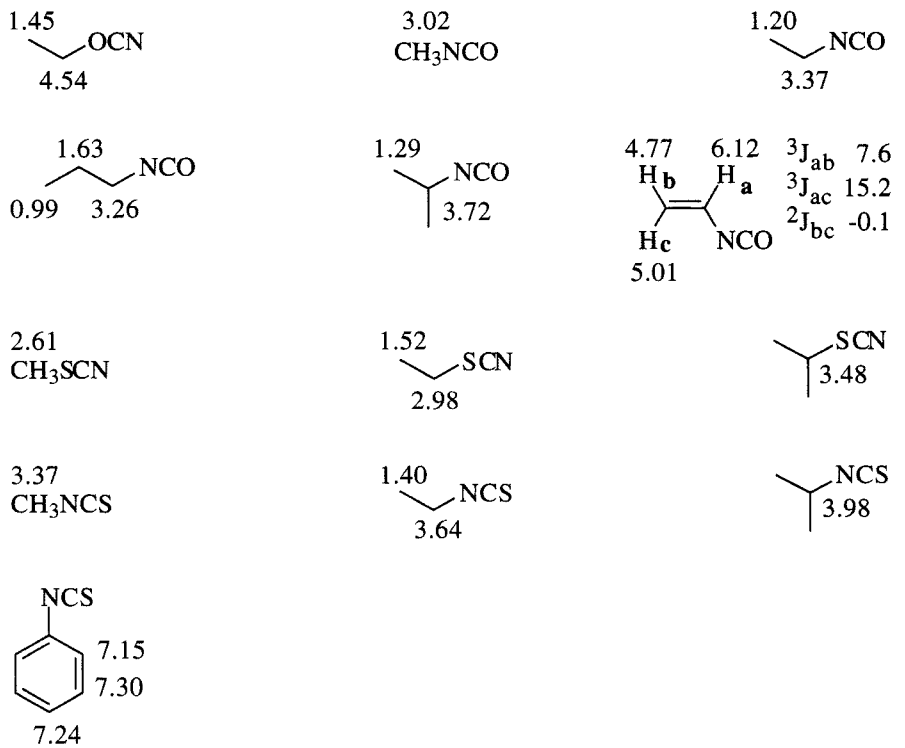


$|J|_{aN}$ 1.8–2.8
$|J|_{bN}$ 1.5–3.5



5.9.6 Cyanates, Isocyanates, Thiocyanates, and Isothiocyanates

^1H Chemical Shifts and Coupling Constants of Cyanates, Isocyanates, Thiocyanates, and Isothiocyanates
(δ in ppm relative to TMS, J in Hz)



5.10 Sulfur-Containing Functional Groups

5.10.1 Thiols

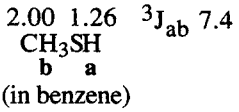
^{1}H Chemical Shifts and Coupling Constants of Thiols

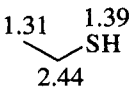
(δ in ppm relative to TMS, J in Hz)

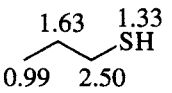
Typical ranges of SH chemical shifts:

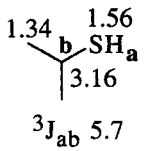
alk—SH 1–2  —SH 2–4

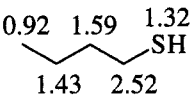
The exchange with other SH, OH, NH, or COOH protons is generally so slow that the chemical shift is characteristic and the vicinal coupling with SH protons becomes visible (5–9 Hz in aliphatic systems with fast rotation).

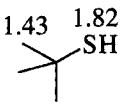


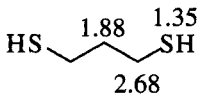




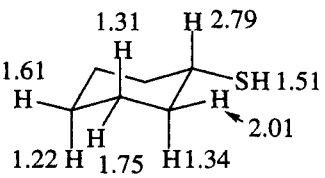


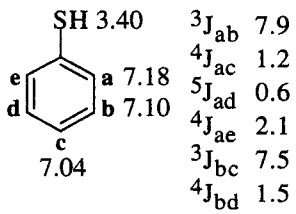






S

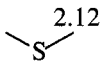


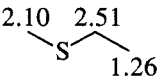


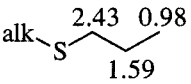
5.10.2 Sulfides

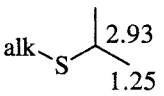
^1H Chemical Shifts and Coupling Constants of Sulfides

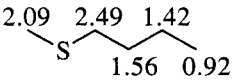
(δ in ppm relative to TMS, J in Hz)

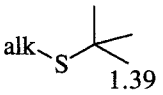


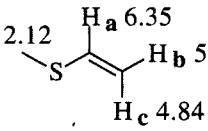






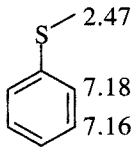


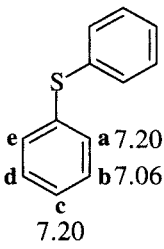




(in TMS)

$^3J_{ab}$	10.3
$^3J_{ac}$	16.4
$^2J_{bc}$	-0.3



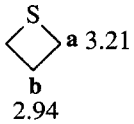


$^3J_{ab}$	7.8
$^4J_{ac}$	1.2
$^5J_{ad}$	0.6
$^4J_{ae}$	2.0
$^3J_{bc}$	7.4
$^4J_{bd}$	1.5

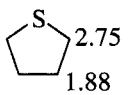
^1H Chemical Shifts and Coupling Constants of Cyclic Sulfides

(δ in ppm relative to TMS, J in Hz)

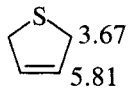
$^2J_{gem}$	0
$^3J_{cis}$	7.2
$^3J_{trans}$	5.7

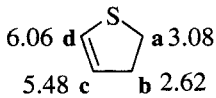


$^2J_{a,gem}$	-8.7
$^2J_{b,gem}$	-11.7
$^3J_{ab,cis}$	8.9
$^3J_{ab,trans}$	6.3
$^4J_{ac,cis}$	1.2
$^4J_{ac,trans}$	-0.2

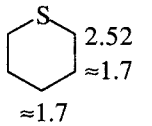


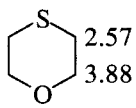
S

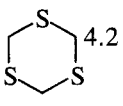


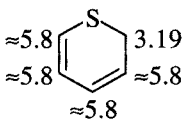


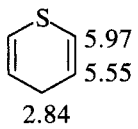
$^3J_{ab}$	9.2
$^3J_{bc}$	2.5
$^4J_{bd}$	2.2
$^3J_{cd}$	6.1





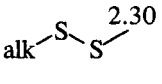


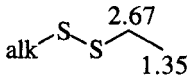


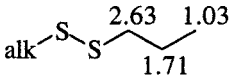


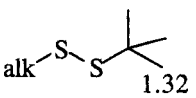
5.10.3 Disulfides and Sulfonium Salts

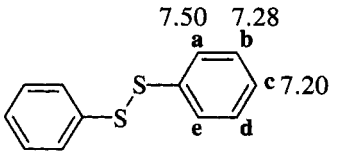
^{1}H Chemical Shifts and Coupling Constants of Disulfides and Sulfonium Salts *(δ in ppm relative to TMS, J in Hz)*



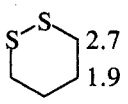


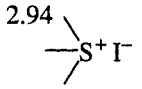






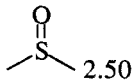
$^3J_{ab}$	7.5
$^4J_{ac}$	1.4
$^5J_{ad}$	0.5
$^4J_{ae}$	2.0
$^3J_{bc}$	7.2
$^4J_{bd}$	1.6

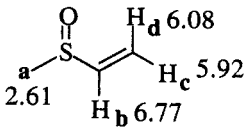




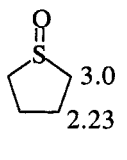
5.10.4 Sulfoxides and Sulfones

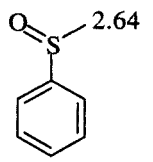
^{1}H Chemical Shifts and Coupling Constants of Sulfoxides and Sulfones *(δ in ppm relative to TMS, J in Hz)*



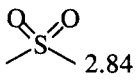


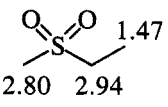
$^5J_{ac}$	0.3
$^5J_{ad}$	0
$^3J_{bc}$	9.8
$^3J_{bd}$	16.7
$^2J_{cd}$	-0.6

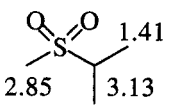


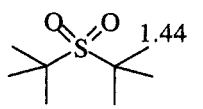


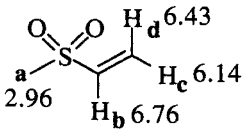
S



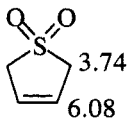


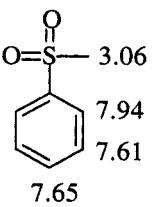






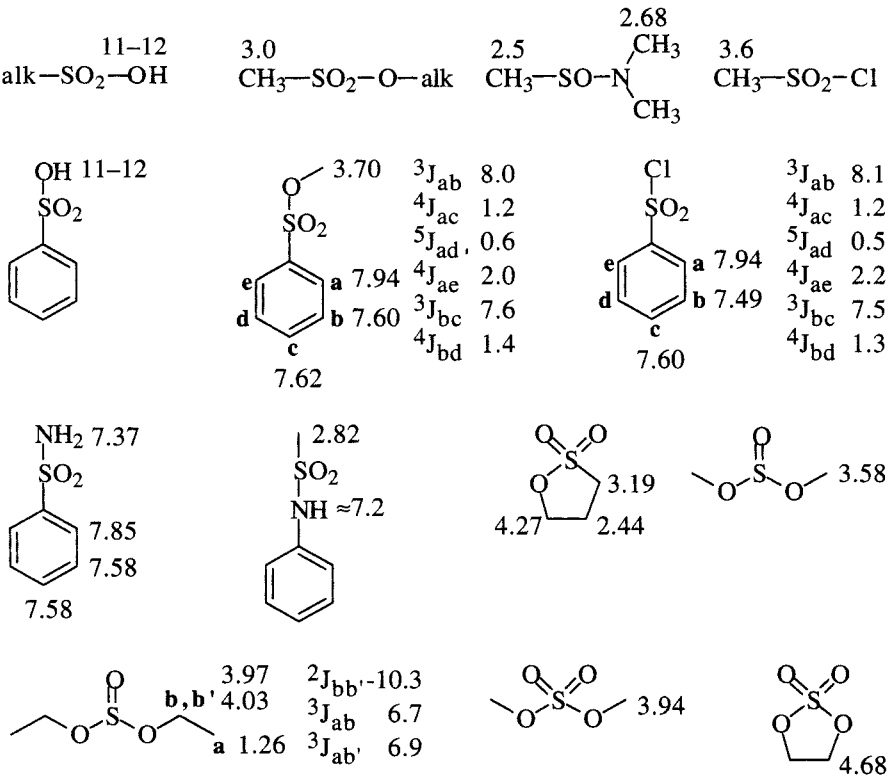
$^3J_{bc}$	10.0
$^3J_{bd}$	16.5
$^2J_{cd}$	-0.5





5.10.5 Sulfonic, Sulfinic, Sulfurous, and Sulfuric Acids and Derivatives

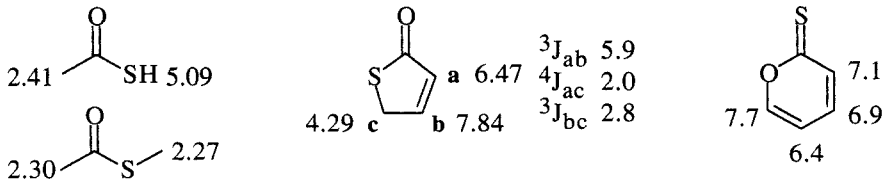
^1H Chemical Shifts and Coupling Constants of Sulfonic, Sulfinic, Sulfurous, and Sulfuric Acids and Derivatives
(δ in ppm relative to TMS, J in Hz)



S

5.10.6 Thiocarboxylate Derivatives

^1H Chemical Shifts of Thiocarboxylic Acids and Derivatives
(δ in ppm relative to TMS, $|J|$ in Hz)



5.11 Carbonyl Compounds

5.11.1 Aldehydes

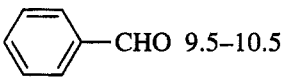
^{1}H Chemical Shifts and Coupling Constants of Aldehydes

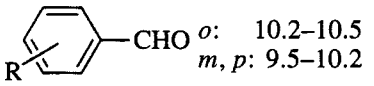
(δ in ppm relative to TMS, J in Hz)

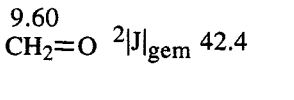
Typical ranges for chemical shifts and coupling constants of aldehyde protons:

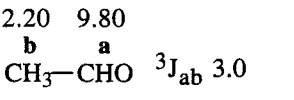
alk—CHO 9.0–10.1 $^3J_{vic}$ 0–3

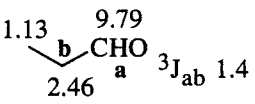
alken—CHO 9.0–10.1 $^3J_{vic}$ ≈8

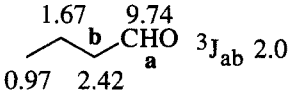


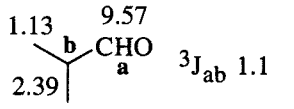


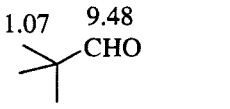




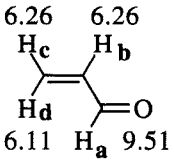




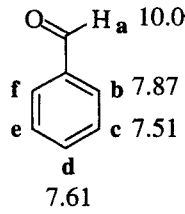




C=X



$^3J_{ab}$ ≈8.0
$^4J_{ac}$ ≈0.3
$^4J_{ad}$ ≈0.1



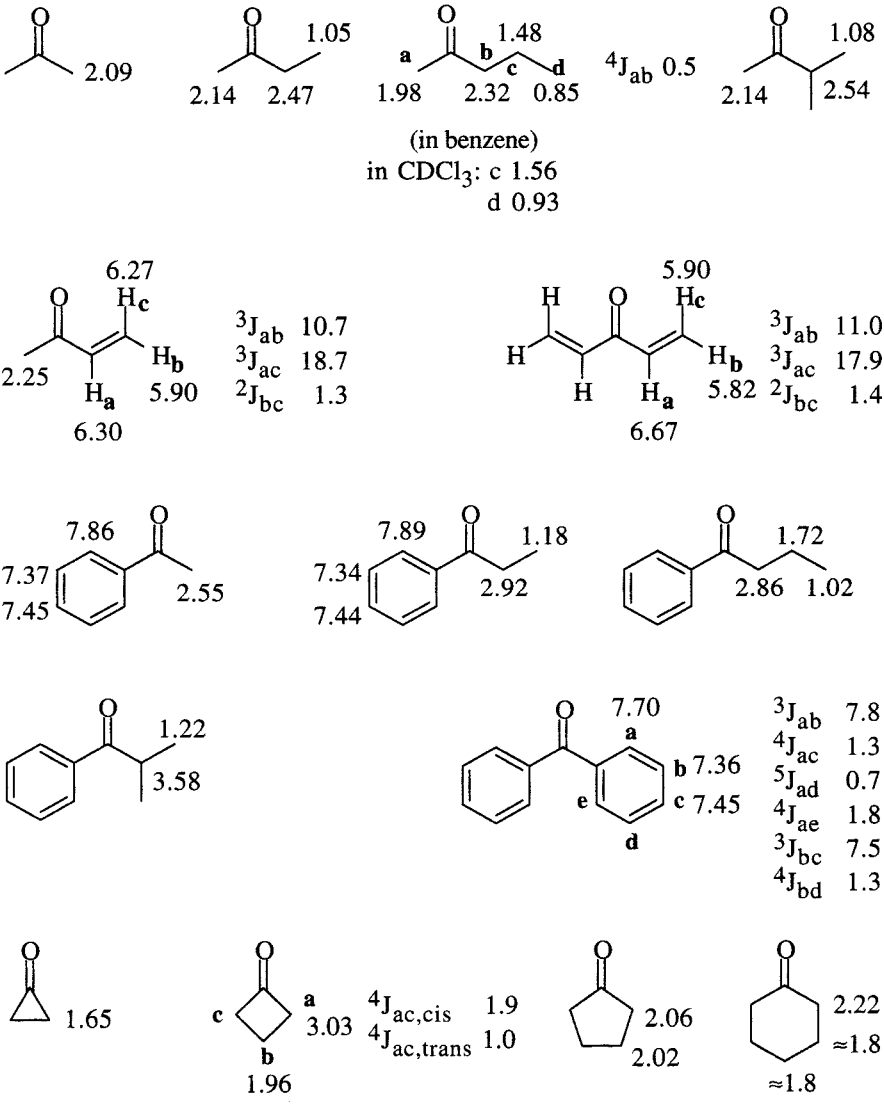
$^4J_{ab}$ ≈0.2
$^5J_{ac}$ 0
$^6J_{ad}$ 0.1
$^5J_{ae}$ 0.4–1.0

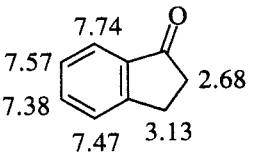
$^3J_{bc}$ 7.7
$^4J_{bd}$ 1.3
$^5J_{be}$ 0.6
$^4J_{bf}$ 1.8
$^3J_{cd}$ 7.5
$^4J_{ce}$ 1.3

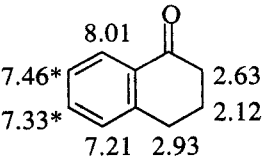
5.11.2 Ketones

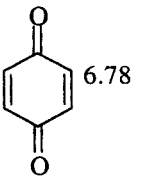
^1H Chemical Shifts and Coupling Constants of Ketones

(δ in ppm relative to TMS, J in Hz)



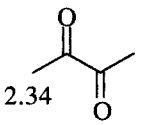


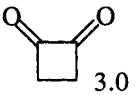


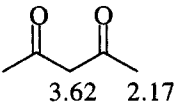


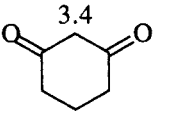
* assignment uncertain

^1H *Chemical Shifts of Diketones* (δ *in ppm relative to TMS)*





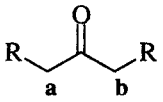




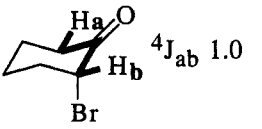
For the enol form,
see Chapter 5.8.1

Long-Range Coupling in Ketones ($|J|$ *in Hz)*

Coupling over the C=O group is often detectable for fixed conformations in W-arrangement of the coupling path:



$^4J_{ab}$ 0–0.5



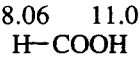
$^4J_{ab}$ 1.0

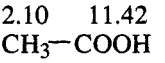
5.11.3 Carboxylic Acids and Carboxylates

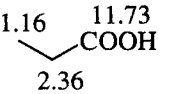
C=X

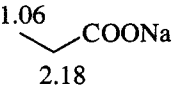
^1H *Chemical Shifts of Carboxyl Protons* (δ *in ppm relative to TMS, J in Hz)*

The position of the COOH signal depends on the solvent, the concentration, and the presence of other exchangeable protons. Intermediate rates of exchange with other protons may induce very broad lines, which are sometimes not even detected.

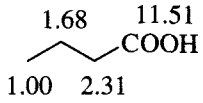


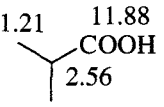


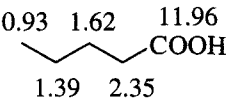


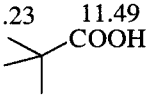


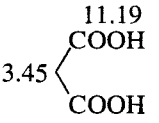
(in D_2O)

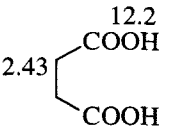




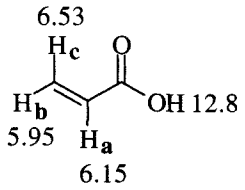




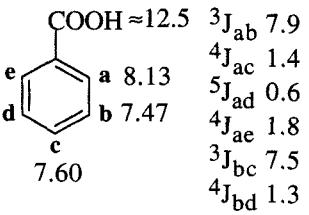




(in DMSO)



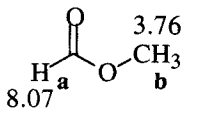
$^3J_{ab}$ 10.5
$^3J_{ac}$ 17.2
$^2J_{bc}$ 1.8



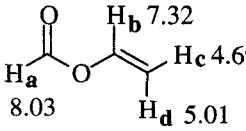
$^3J_{ab}$ 7.9
$^4J_{ac}$ 1.4
$^5J_{ad}$ 0.6
$^4J_{ae}$ 1.8
$^3J_{bc}$ 7.5
$^4J_{bd}$ 1.3

5.11.4 Esters and Lactones

^1H Chemical Shifts and Coupling Constants of Aliphatic Carboxylic Acid Esters *(δ in ppm relative to TMS, J in Hz)*

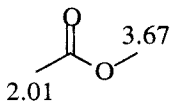


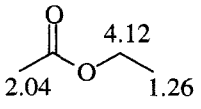
$^4|J|_{ab}$ 0.8

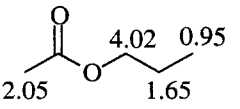


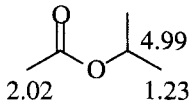
$^4J_{ab}$ -0.7 $^3J_{bc}$ 6.4
$^5J_{ac}$ 1.6 $^3J_{bd}$ 13.9
$^5J_{ad}$ 0.8 $^2J_{cd}$ -1.7

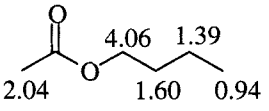
C = X

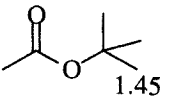


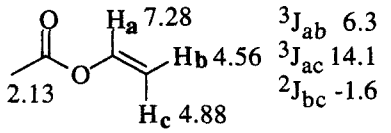


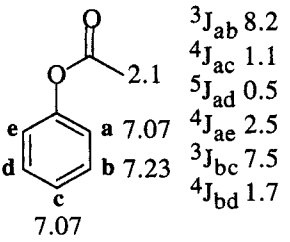


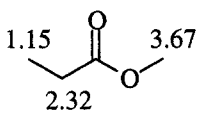


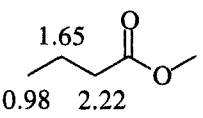


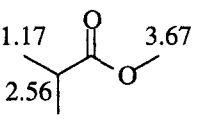


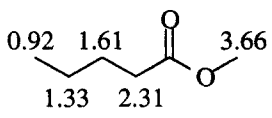


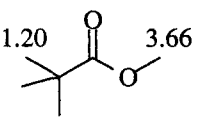






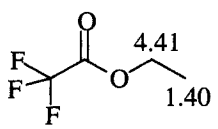


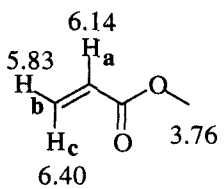


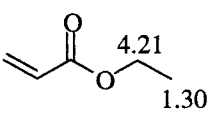


For esters of boronic, nitric, and sulfuric acid, see Chapter 5.12.

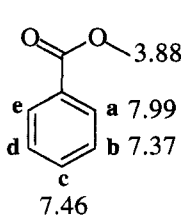
^{1}H Chemical Shifts and Coupling Constants of Alkyl Esters
(δ in ppm relative to TMS)

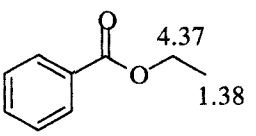


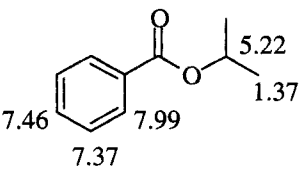




C=X

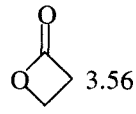


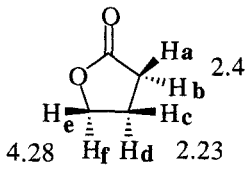




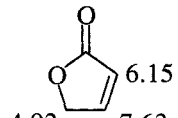
^1H Chemical Shifts and Coupling Constants of Lactones

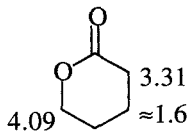
(δ in ppm relative to TMS, J in Hz)

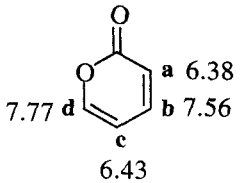




$^2J_{ab}$ -17.5 $^2J_{cd}$ -12.7
$^3J_{ac}$ 9.5 $^3J_{ce}$ 7.9
$^3J_{ad}$ 6.9 $^3J_{cf}$ 6.3
$^4J_{ae}$ 0.3 $^2J_{ef}$ -8.8
$^4J_{af}$ -0.5



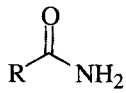




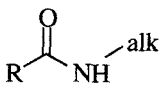
$^3J_{ab}$ 9.4
$^4J_{ac}$ 1.5
$^5J_{ad}$ 1.3
$^3J_{bc}$ 6.3
$^4J_{bd}$ 2.4
$^3J_{cd}$ 5.0

5.1.1.5 Amides and Lactams

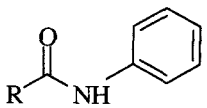
Amide Protons *(δ in ppm relative to TMS, J in Hz)*



R: alk, ar



R: alk, ar



R: alk, ar

Line Widths

The signals of the NH protons are often broad because the ^{14}N-^1H coupling is only partly eliminated by the quadrupole relaxation of ^{14}N (spin quantum number, $I = 1$; $^1J_{NH} \approx 60$). In primary amides, the hindered rotation around the CO–N bond is another reason for line broadening. At slow rotation, the chemical shifts of the two primary amide protons differ by about 0.5–1 ppm.

C=X

Vicinal Coupling H–C–N–H

Due to the slow intermolecular exchange of amide protons, their coupling to neighboring hydrogen atoms is usually detectable. The splitting of the C–H signal is clearly observed even in those cases where the signal of the NH proton is broad and featureless. The H–C–N–H coupling depends on the conformation in a similar way as the H–C–C–H coupling (see Chapter 5.1). For N–CH_3 and N–CH_2 groups: $^3J_{HCNH} \approx 7$.

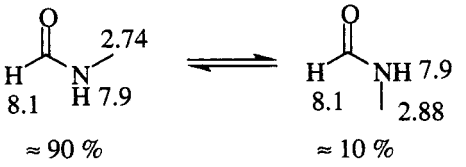
Tertiary Alkylamides

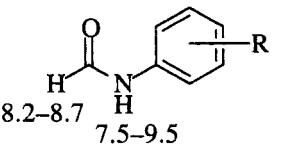
The rotation around the CO–N bond is usually so slow that, with different N-substituents, two separate signals are observed for the two conformers. In general, the following relationships hold:

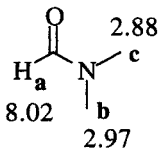
for NCH_3, NCH_2CH_3, and $NCH(CH_3)_2$	$\delta_{cis\ to\ O} \leq \delta_{trans\ to\ O}$
for $NCH(CH_3)_2$ and $NC(CH_3)_3$	$\delta_{trans\ to\ O} \leq \delta_{cis\ to\ O}$
for NCH_2	$\delta_{cis\ to\ O} \approx \delta_{trans\ to\ O}$

Formamides (δ *in ppm relative to TMS,* $|J|$ *in Hz)*

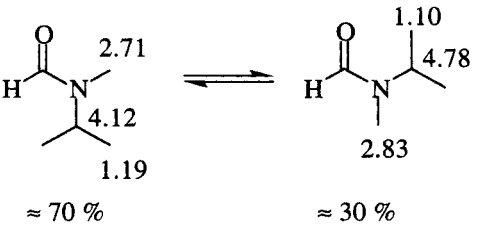
In the more stable conformer of *monosubstituted* formamides, the substituent occupies the *cis* position relative to the carbonyl oxygen. In the more stable conformer of asymmetrically *disubstituted* formamides, the larger substituent occupies the *trans* position relative to the carbonyl oxygen.







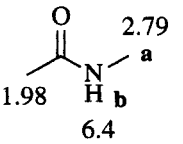
$^4J_{ab}$ ≈0.3
$^4J_{ac}$ ≈0.7



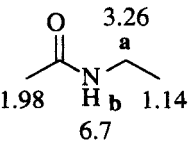
Acetamides (δ *in ppm relative to TMS, J in Hz)*

C=X

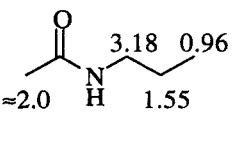
In *monosubstituted* acetamides, the substituent of the only observable conformer is *cis* to the carbonyl oxygen. In *disubstituted* acetamides, the more stable conformer has the larger substituent *cis* to the carbonyl oxygen.

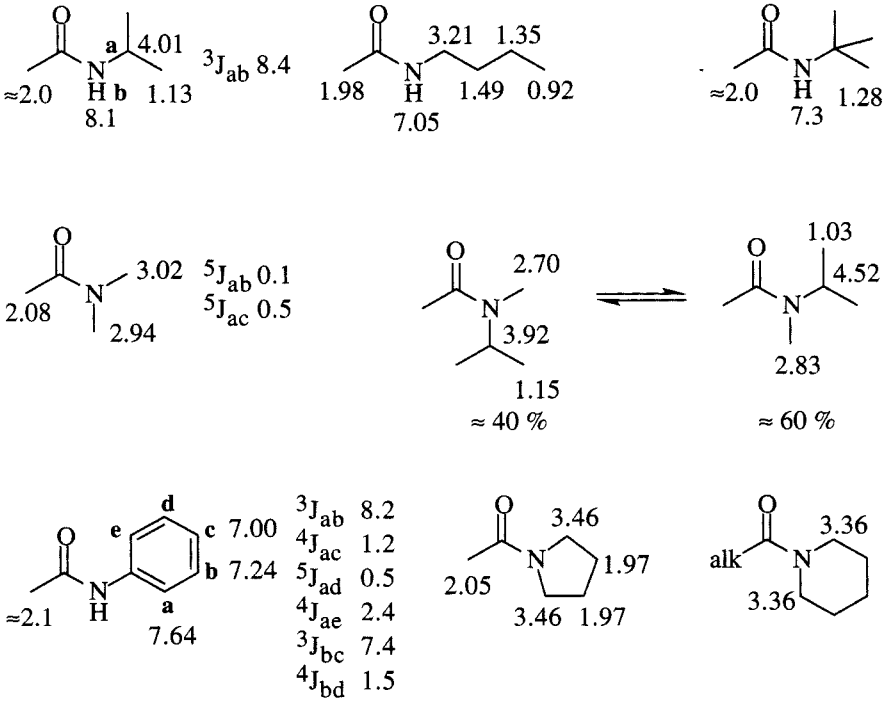


$^3J_{ab}$ 4.8

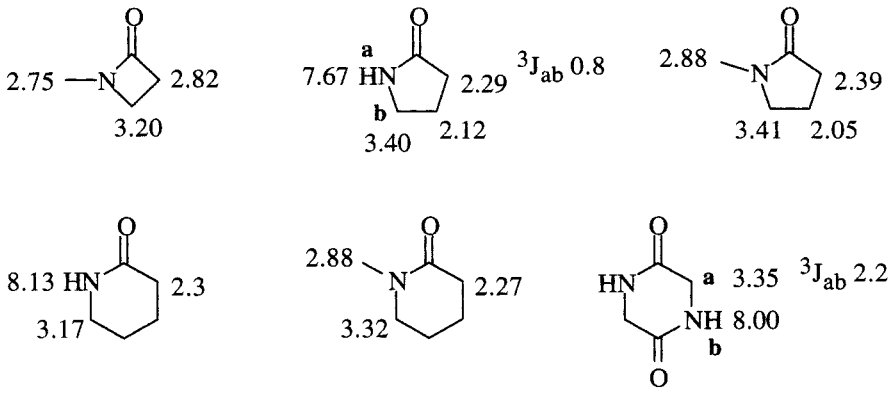


$^3J_{ab}$ 5.9





^1H *Chemical Shifts of Lactams* (δ *in ppm relative to TMS*)

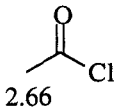


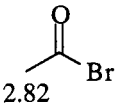
C = X

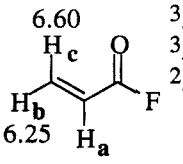
5.11.6 Miscellaneous Carbonyl Derivatives

^{1}H Chemical Shifts of Carboxylic Acid Halides

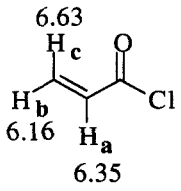
(δ in ppm relative to TMS, J in Hz)



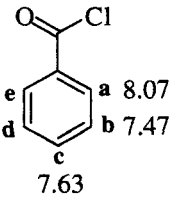




$^3J_{ab}$ 10.7
$^3J_{ac}$ 17.3
$^2J_{bc}$ 0.8



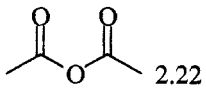
$^3J_{ab}$ 10.6
$^3J_{ac}$ 17.4
$^2J_{bc}$ 0.2

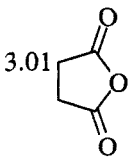


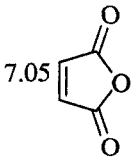
$^3J_{ab}$ 8.0
$^4J_{ac}$ 1.2
$^5J_{ad}$ 0.6
$^4J_{ae}$ 2.0
$^3J_{bc}$ 7.5
$^4J_{bd}$ 1.4

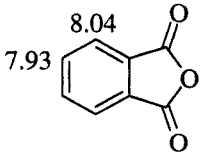
^{1}H Chemical Shifts of Carboxylic Acid Anhydrides

(δ in ppm relative to TMS)



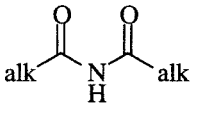


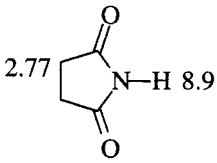


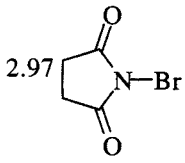


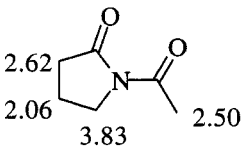
C=X

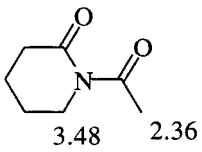
^1H Chemical Shifts of Carboxylic Acid Imides
(δ in ppm relative to TMS)



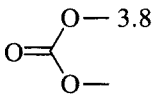


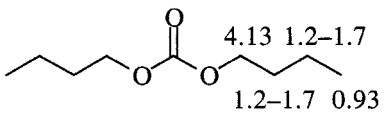


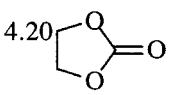


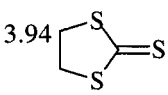


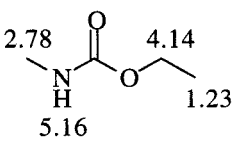
^1H Chemical Shifts of Carbonic Acid Derivatives
(δ in ppm relative to TMS)

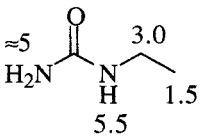


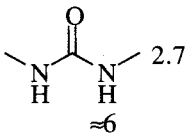


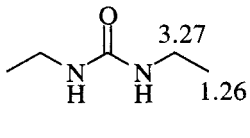










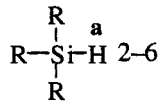


C=X

5.12 Miscellaneous Compounds

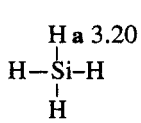
5.12.1 Silicon Compounds

^{1}H Chemical Shifts and Coupling Constants of Silanes and Silanols *(δ in ppm relative to TMS, J in Hz)*

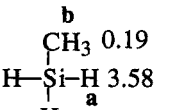


For R: H, SiX_3: 2–4
other: 3–6

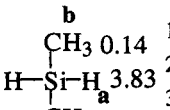
$^1J_{aSi}$ -150 to -380
(4.7% natural abundance of ^{29}Si, "Si satellites")



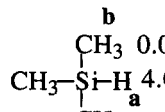
$^1J_{aSi}$ -202.5



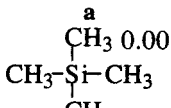
$^1J_{aSi}$ -202.5
$^3J_{ab}$ 4.7



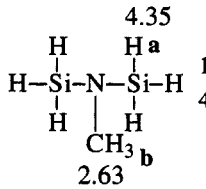
$^1J_{aSi}$ -202.5
$^2J_{bSi}$ 7.7
$^3J_{ab}$ 4.3



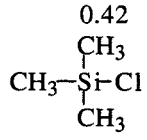
$^1J_{aSi}$ -190
$^2J_{bSi}$ 7.5
$^3J_{ab}$ 3.8

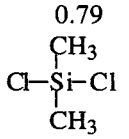


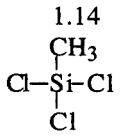
$^2J_{aSi}$ 5.5



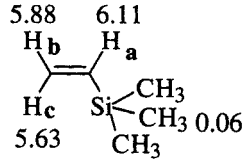
$^1J_{aSi}$ -209.4
$^4J_{ab}$ 0.3



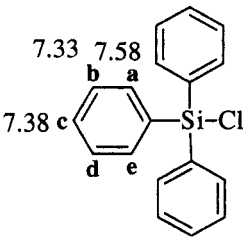




Misc.

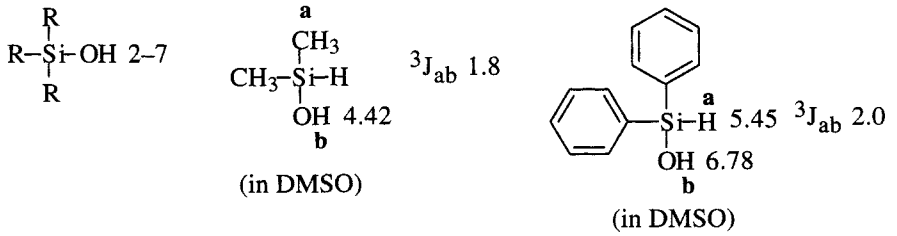


$^3J_{ab}$ 14.6
$^3J_{ac}$ 20.2
$^2J_{bc}$ 3.8



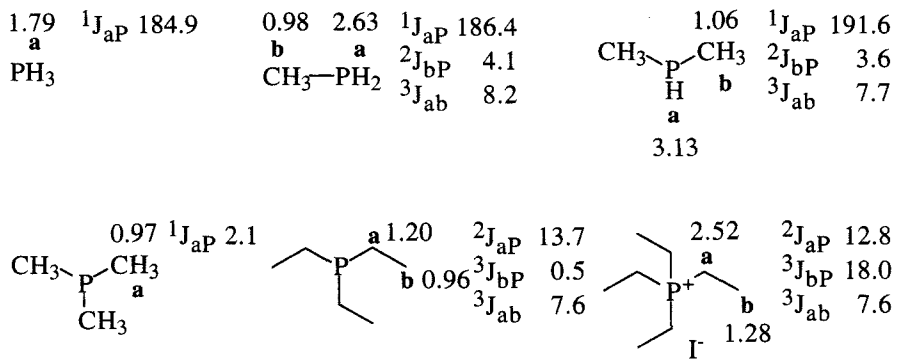
$^3J_{ab}$ 7.5
$^4J_{ac}$ 1.4
$^5J_{ad}$ 0.7
$^3J_{ae}$ 1.4
$^3J_{bc}$ 7.5
$^4J_{bd}$ 1.2

The silanol hydrogen is exchangeable with D_2O. Slow intermolecular exchange is observed in dimethyl sulfoxide as solvent so that the vicinal coupling in H–Si–OH is detectable.

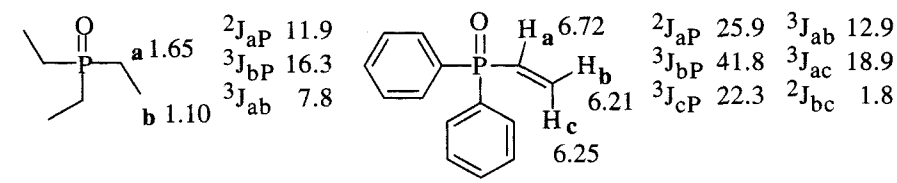


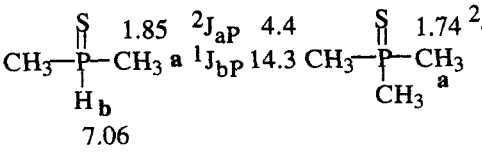
5.12.2 Phosphorus Compounds

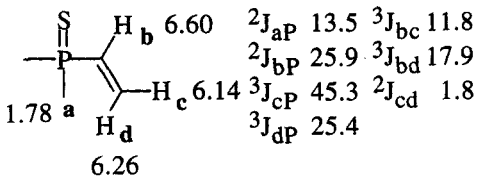
^1H Chemical Shifts and Coupling Constants of Phosphines and Phosphonium Compounds *(δ in ppm relative to TMS, $|J|$ in Hz)*



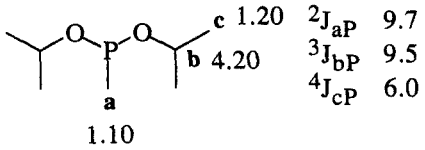
^1H Chemical Shifts and Coupling Constants of Phosphine Oxides and Sulfides *(δ in ppm relative to TMS, $|J|$ in Hz)*

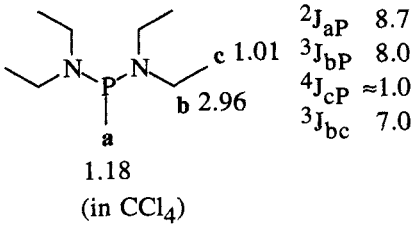


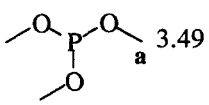




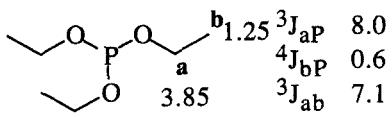
^1H Chemical Shifts and Coupling Constants of Phosphonous Acid Derivatives *(δ in ppm relative to TMS, $|J|$ in Hz)*

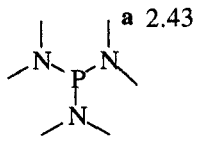






$^3J_{aP}$ 10.8

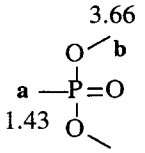




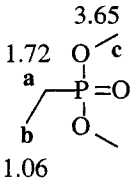
$^3J_{aP}$ 8.9

Misc.

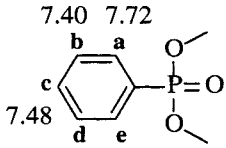
^1H Chemical Shifts and Coupling Constants of Phosphonic and Phosphoric Acid Derivatives (δ in ppm relative to TMS, J in Hz)



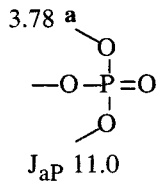
$^2J_{aP}$ 17.3
$^3J_{bP}$ 11.0

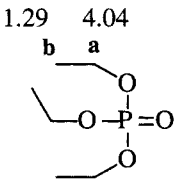


$^2J_{aP}$ -18.0
$^3J_{bP}$ 19.5
$^3J_{cP}$ 10.0
$^3J_{ab}$ 7.5

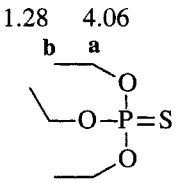


$^3J_{aP}$ 13.3
$^4J_{bP}$ 4.1
$^5J_{cP}$ 1.2
$^3J_{ab}$ 7.7
$^4J_{ac}$ 1.4
$^5J_{ad}$ 0.6
$^4J_{ae}$ 1.6
$^3J_{bc}$ 7.6
$^4J_{bd}$ 1.4



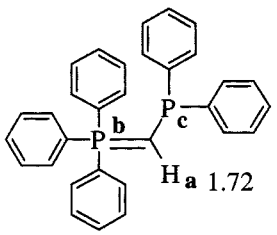


$^3J_{aP}$ 8.5
$^4J_{bP}$ 0.7
$^3J_{ab}$ ≈7

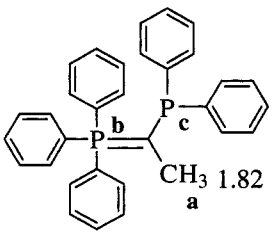


$^3J_{aP}$ 10.0
$^4J_{bP}$ 0.7
$^3J_{ab}$ ≈7

^1H Chemical Shifts and Coupling Constants of Phosphorus Ylids (δ in ppm relative to TMS, J in Hz)



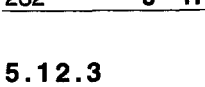
$^2J_{ab}$ 12.7
$^2J_{ac}$ -1.2

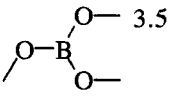


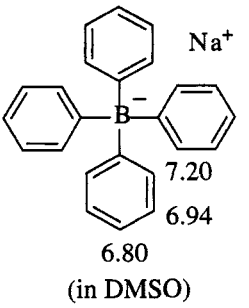
$^3J_{ab}$ 15.9
$^3J_{ac}$ 3.6

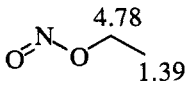
5.12.3 Miscellaneous Compounds

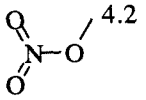
^{1}H Chemical Shifts and Coupling Constants of Miscellaneous Compounds *(δ in ppm relative to TMS)*

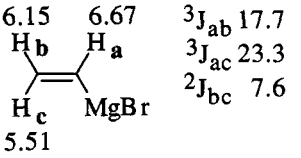


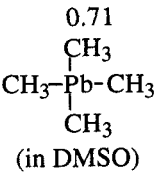


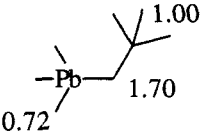


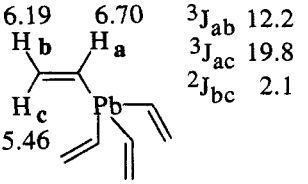


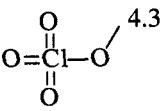


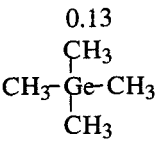


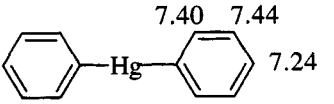








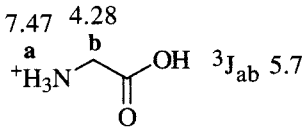




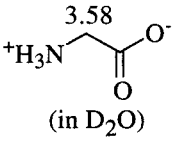
5.13 Natural Products

5.13.1 Amino Acids

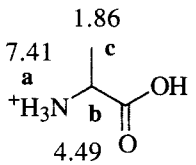
^1H Chemical Shifts and Coupling Constants of Amino Acids *(δ in ppm relative to TMS; J in Hz, solvent: trifluoroacetic acid (TFA) or D_2O)* [1]



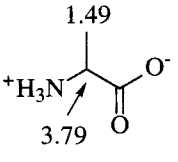
(in TFA)



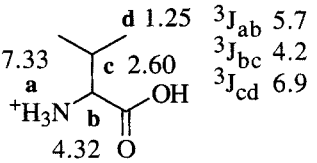
(in D_2O)



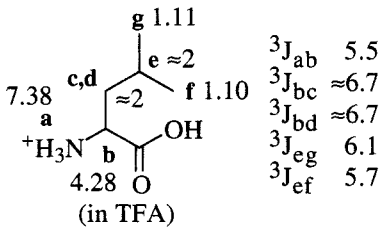
(in TFA)



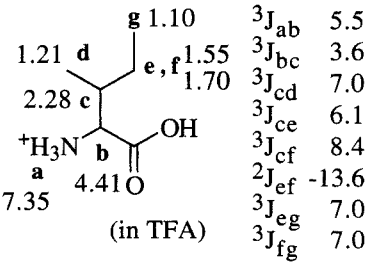
(in D_2O)



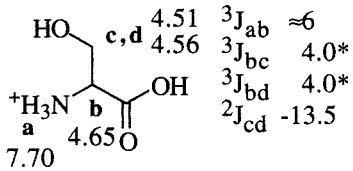
(in TFA)



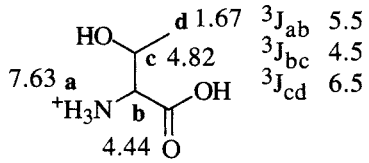
(in TFA)



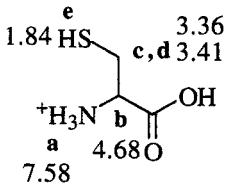
(in TFA)



(in TFA)
* average value

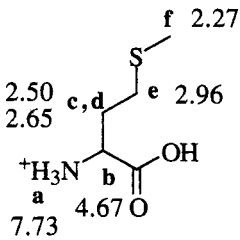


(in TFA)



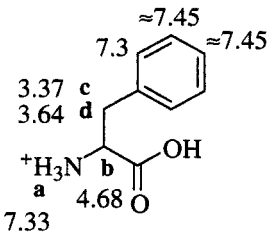
(in TFA)
* average value

$^3J_{ab}$	5.3
$^3J_{bc}$	5.0*
$^3J_{bd}$	5.0*
$^2J_{cd}$	-15.5
$^3J_{ce}$	9.1*
$^3J_{de}$	9.1*



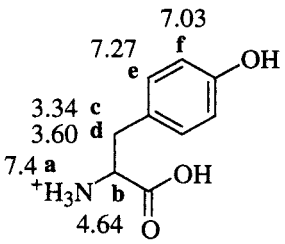
(in TFA)
* average value

$^3J_{ab}$	5.5
$^3J_{bc}$	7.7
$^3J_{bd}$	4.4
$^2J_{cd}$	-15.7
$^3J_{ce}$	6.5*
$^3J_{de}$	6.5*



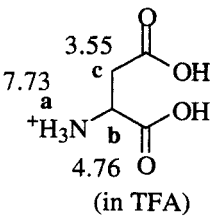
(in TFA)

$^3J_{bc}$	8.5
$^3J_{bd}$	4.5
$^2J_{cd}$	-14.5



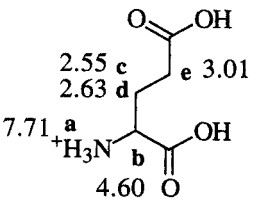
(in TFA)

$^3J_{bc}$	8.5
$^3J_{bd}$	4.5
$^2J_{cd}$	-15.0
$^3J_{ef}$	8.5



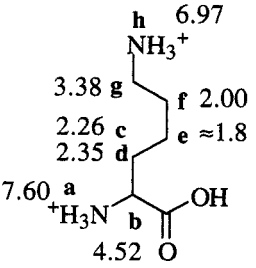
(in TFA)

$^3J_{ab}$	5.1
$^3J_{bc}$	4.7



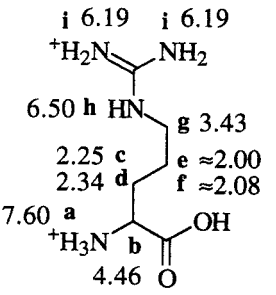
(in TFA)
* average value

$^3J_{ab}$	5.5
$^3J_{bc}$	5.6*
$^3J_{bd}$	5.6*
$^2J_{cd}$	-15.5
$^3J_{ce}$	6.2*
$^3J_{de}$	6.2*



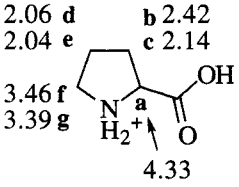
(in TFA)
* average value

$^3J_{ab}$	5.8
$^3J_{bc}$	5.6*
$^3J_{bd}$	5.6*
$^2J_{cd}$	≈-15.0
$^3J_{ce}$	6.0*
$^3J_{de}$	6.0*
$^3J_{fg}$	≈6.0
$^3J_{gh}$	≈6.0



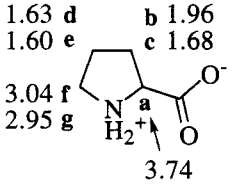
(in TFA)
* average value

$^3J_{ab}$	5.5
$^3J_{bc}$	5.3*
$^3J_{bd}$	5.3*
$^2J_{cd}$	≈-15.0
$^3J_{ce}$	≈6*
$^3J_{cf}$	≈6*
$^3J_{de}$	≈6*
$^3J_{df}$	≈6*
$^3J_{eg}$	6.5*
$^3J_{fg}$	6.5*
$^3J_{gh}$	5.3



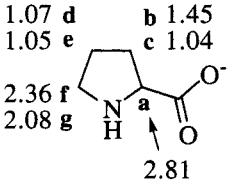
(in D_2O, pH 2.0)

$^3J_{ab}$	8.5
$^3J_{ac}$	6.5
$^2J_{bc}$	-13.5
$^3J_{bd}$	7.5
$^3J_{be}$	5.5
$^4J_{bf}$	-0.4
$^4J_{bg}$	0.0
$^3J_{cd}$	5.5
$^3J_{ce}$	7.5
$^2J_{de}$	-13.0
$^3J_{df}$	5.5
$^3J_{dg}$	7.5
$^3J_{ef}$	7.5
$^3J_{eg}$	5.5
$^2J_{fg}$	-11.0



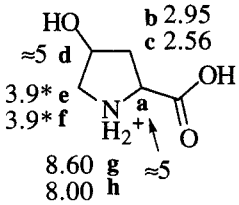
(in D_2O, pH 7.0)

$^3J_{ab}$	8.4
$^3J_{ac}$	6.2
$^2J_{bc}$	-13.5
$^3J_{bd}$	7.6
$^3J_{be}$	5.4
$^4J_{bf}$	-0.4
$^4J_{bg}$	0.0
$^3J_{cd}$	5.6
$^3J_{ce}$	7.8
$^2J_{de}$	-13.0
$^3J_{df}$	5.7
$^3J_{dg}$	7.9
$^3J_{ef}$	7.9
$^3J_{eg}$	5.7
$^2J_{fg}$	-11.0



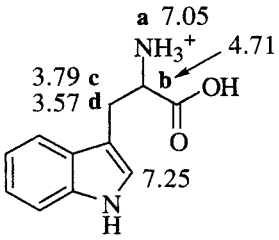
(in D_2O, pH 13.0)

$^3J_{ab}$	8.6
$^3J_{ac}$	6.6
$^2J_{bc}$	-12.0
$^3J_{bd}$	8.1
$^3J_{be}$	5.9
$^4J_{bf}$	-0.6
$^4J_{bg}$	0.0
$^3J_{cd}$	6.7
$^3J_{ce}$	8.5
$^2J_{de}$	-11.0
$^3J_{df}$	5.5
$^3J_{dg}$	8.1
$^3J_{ef}$	7.7
$^3J_{eg}$	5.7
$^2J_{fg}$	-10.5



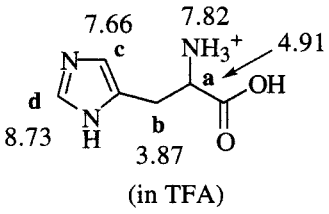
(in TFA)
* average value

$^3J_{ab}$	8.2
$^3J_{ac}$	10.4
$^2J_{bc}$	-15.0
$^3J_{bd}$	<2
$^3J_{cd}$	4.2



(in TFA)

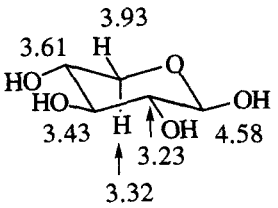
$^2J_{bc}$	4.0
$^3J_{bd}$	8.0
$^2J_{cd}$	-15.5



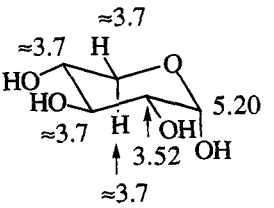
(in TFA)

$^3J_{ab}$	6.4
$^4J_{cd}$	1.4

5.13.2 Carbohydrates [2–4]

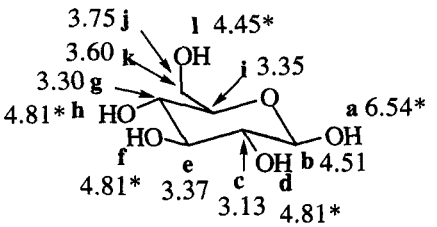


(in D_2O)



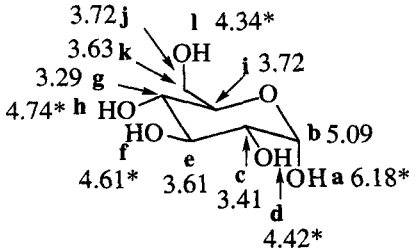
(in D_2O)

Glucose



(in D_2O, relative to internal acetone at $\delta = 2.12$)
* in DMSO

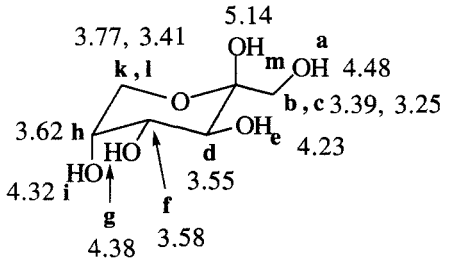
In D_2O		In DMSO	
$^3J_{bc}$	7.8	$^3J_{ab}$	6.5
$^3J_{ce}$	9.5	$^3J_{cd}$	4.5–6
$^3J_{eg}$	9.5	$^3J_{ef}$	4.5–6
$^3J_{gi}$	9.5	$^3J_{gh}$	4.5–6
$^3J_{ij}$	2.8	$^3J_{jl}$	5.5
$^3J_{ik}$	5.7	$^3J_{kl}$	6.0
$^2J_{jk}$	-12.8		



(in D_2O, relative to internal acetone at $\delta = 2.12$)
* in DMSO

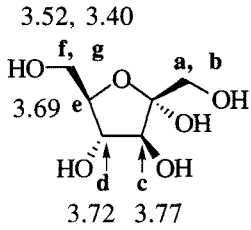
In D_2O		In DMSO	
$^3J_{bc}$	3.6	$^3J_{ab}$	4.5
$^3J_{ce}$	9.5	$^3J_{cd}$	6.8
$^3J_{eg}$	9.5	$^3J_{ef}$	4.8
$^3J_{gi}$	9.5	$^3J_{gh}$	5.5
$^3J_{ij}$	2.8	$^3J_{jl}$	5.7
$^3J_{ik}$	5.7	$^3J_{kl}$	6.2
$^2J_{jk}$	-12.8		

Fructose



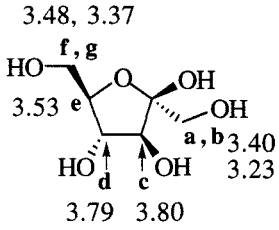
(in DMSO, 25% β-D)

In DMSO (at 70 °C)		In DMSO (at 25 °C)		δ in D_2O (75% β-D)	
$^2J_{bc}$	-11.3	$^3J_{ab}$	7.4	**b**	3.68
$^3J_{df}$	10.1	$^3J_{ac}$	5.4	**c**	3.53
$^3J_{fh}$	4.0	$^3J_{de}$	6.8	**d**	3.76
$^3J_{hk}$	1.9	$^3J_{fg}$	5.8	**f**	3.86
$^3J_{hl}$	1.6	$^3J_{hi}$	3.8	**h**	3.96
$^2J_{kl}$	-12.1			**k**	4.00
				l	3.68



$^3J_{de}$ 5
$^3J_{ef}$ 3
$^2J_{fg}$ -11.6

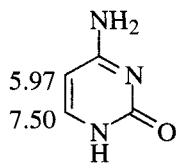
(in DMSO, 20% α-D)
Coupling constants: at 70 °C, tentative values



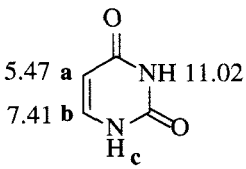
$^2J_{ab}$ -11.0
$^3J_{cd}$ 7.1
$^3J_{de}$ 5.9
$^3J_{ef}$ 2.3
$^3J_{eg}$ 3.6
$^2J_{fg}$ -11.3

(in DMSO, 55% β-D)
Coupling constants: at 70 °C

5.13.3 Nucleotides and Nucleosides

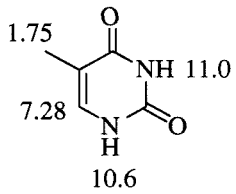


(in D_2O)

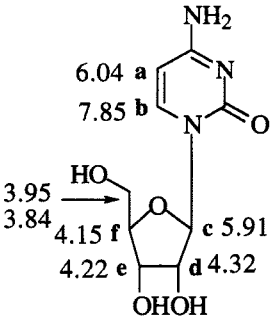


(in DMSO)

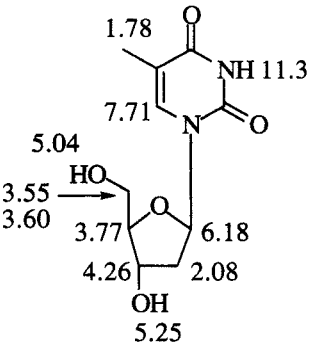
$^3J_{ab}$ 7.5
$^3J_{bc}$ 5.7



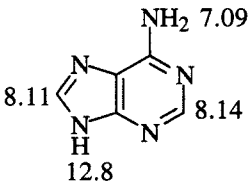
(in DMSO)



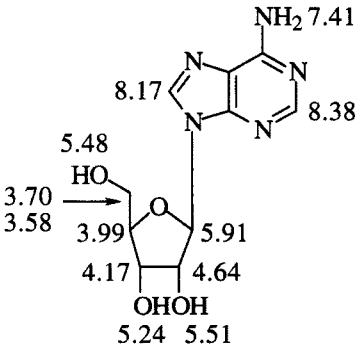
(in D_2O)



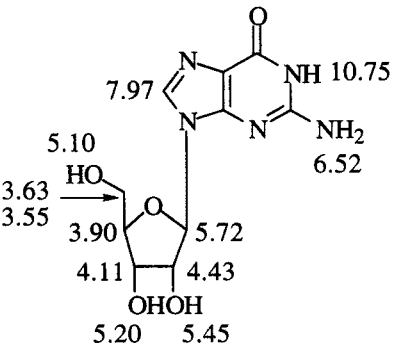
(in DMSO)



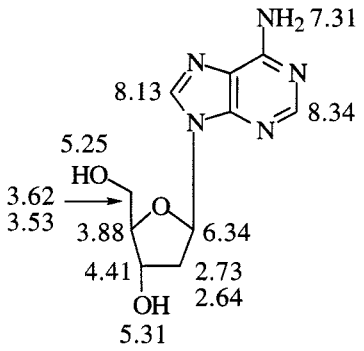
(in $CDCl_3$)



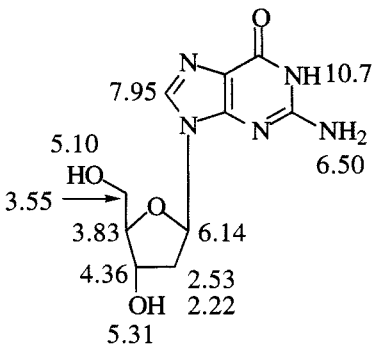
(in DMSO)



(in DMSO)



(in DMSO)



(in DMSO)

5.13.4 References

[1] B. Bak, C. Dambmann, F. Nicolaisen, E.J. Pedersen, N.S. Bhacca, Proton magnetic resonance at 220 MHz of amino acids, J. Mol. Spectrosc. **1968**, *26*, 78.

[2] B. Gillet, D. Nicole, J.-J. Delpuech, B. Gross, High field nuclear magnetic resonance spectra of hydroxyl protons of aldoses and ketoses, Org. Magn. Reson. **1981**, *17*, 28.

[3] M. Jaseja, A.S. Perlin, P. Dais, Two-dimensional NMR spectral study of the tautomeric equilibria of D-fructose and related compounds, Magn. Reson. Chem. **1990**, *28*, 283.

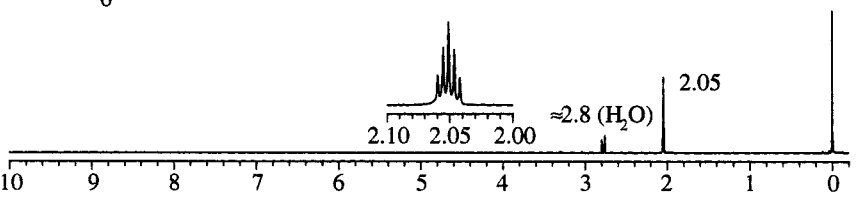
[4] C. Altona, C.A.G. Haasnoot, Prediction of *anti* and *gauche* vicinal proton-proton coupling constants in carbohydrates: a simple additivity rule for pyranose rings, Org. Magn. Reson. **1980**, *13*, 417.

5.14
Spectra of Solvents and Reference Compounds

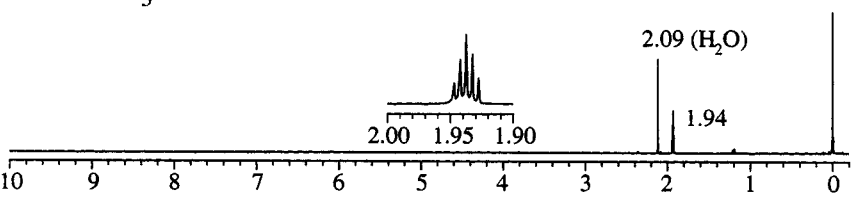
5.14.1
^{1}H NMR Spectra of Common Deuterated Solvents

(500 MHz; ≈1'000 data points per 1 ppm; δ in ppm relative to TMS)

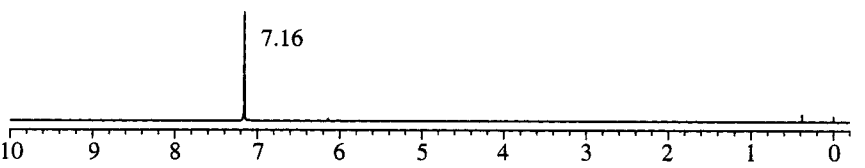
Acetone-d_6



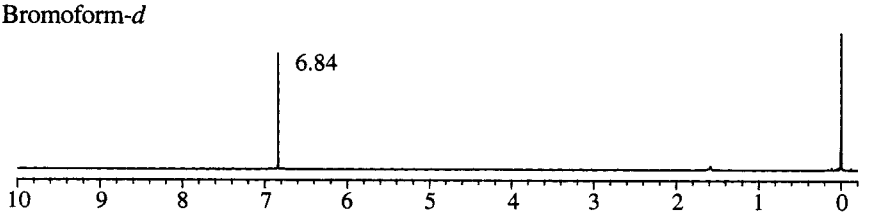
Acetonitrile-d_3



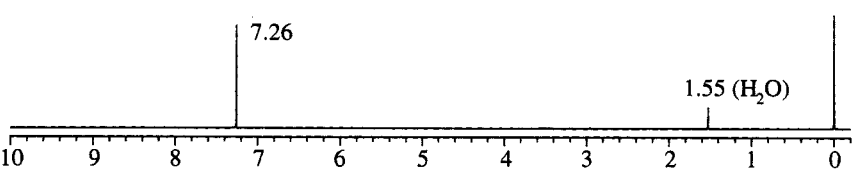
Benzene-d_6



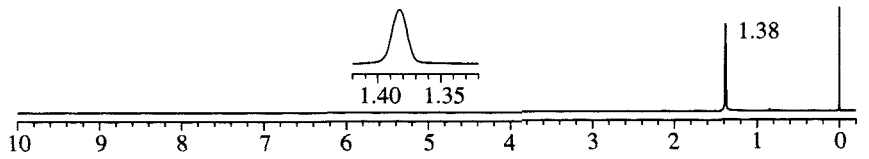
Bromoform-*d*



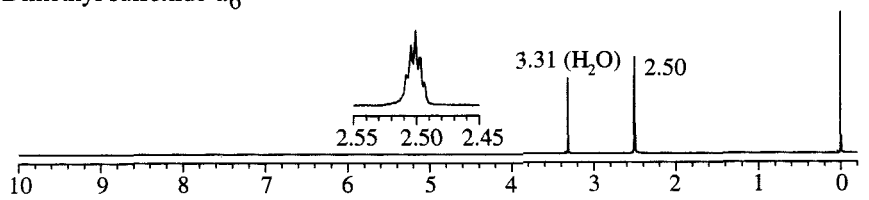
Chloroform-*d*



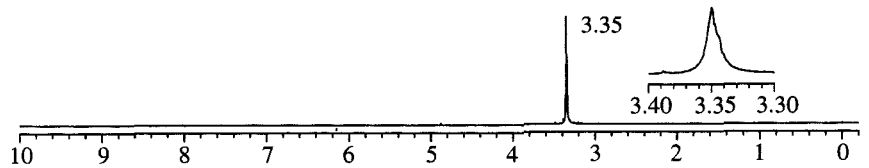
Cyclohexane-d_{12}



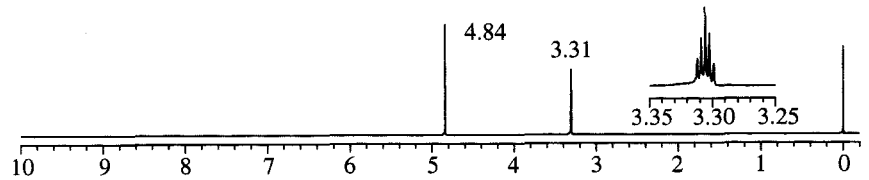
Dimethyl sulfoxide-d_6



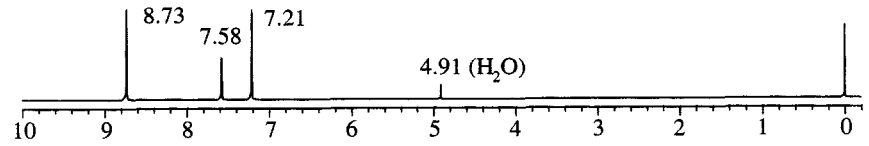
Methanol-d_1



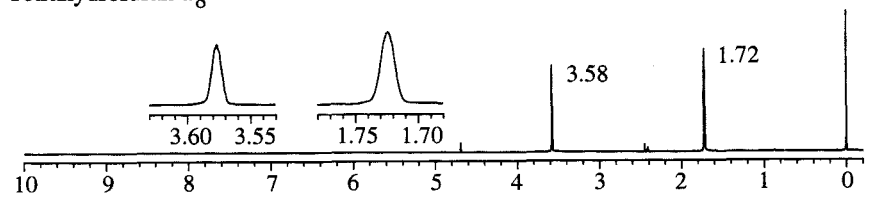
Methanol-d_4



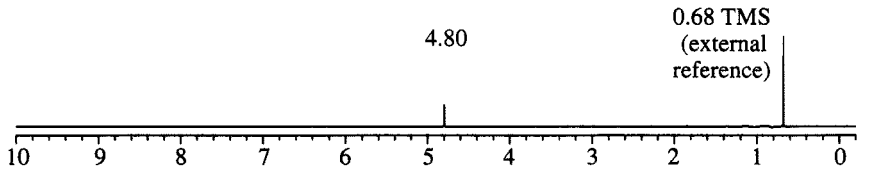
Pyridine-d_5



Tetrahydrofuran-d_8



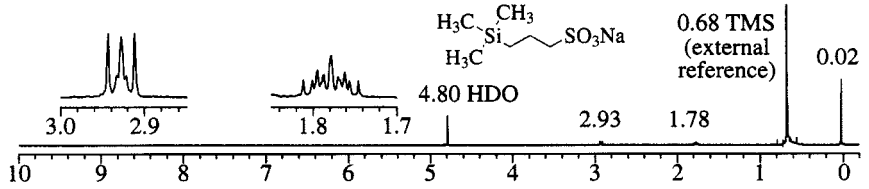
Water-d_2



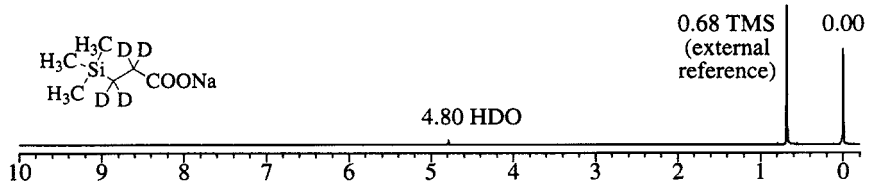
5.14.2 ^{1}H NMR Spectra of Secondary Reference Compounds

Chemical shifts in ^{1}H NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS) added to the sample as an internal reference. If TMS is not sufficiently soluble, a capillary with TMS may be used as external reference. In this case, owing to the different volume susceptibilities, the local magnetic fields in solvent and reference differ, and the peak position of the reference must be corrected. For a D_2O solution in a cylindrical sample and neat TMS in a capillary, the correction amounts to +0.68 and -0.34 ppm for superconducting and electromagnets, respectively. These values must be subtracted from the chemical shifts relative to external TMS if its position is set to 0.00 ppm. Alternatively, secondary references with $(CH_3)_3SiCH_2$ groups may be used. The following spectra of two such secondary reference compounds in D_2O were measured at 500 MHz with TMS as external reference. Chemical shifts are reported in ppm relative to TMS upon correction for the difference in the volume susceptibilities of D_2O and TMS. As a result, the peak for the external TMS appears at 0.68 ppm.

3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (sodium 4,4-dimethyl-4-silapentane-1-sulfonate; DSS)



2,2,3,3-D_4-3-(Trimethylsilyl)propionic acid sodium salt



5.14.3 ^{1}H NMR Spectrum of a Mixture of Common Nondeuterated Solvents

The following ^{1}H NMR spectrum (500 MHz, δ in ppm relative to TMS) of $CDCl_3$ containing 18 common solvents (0.05–0.4 vol%) is shown as a guide for the identification of possible impurities. Where the signals of several solvents overlap, insets show signals for the individual compounds from separate spectra. Peaks in these insets are labeled with the corresponding chemical shifts from the main spectrum but their values may differ by up to 0.03 ppm. Signals that are particularly prone to vary in their position are marked with *. THF: tetrahydrofuran; EGDME: ethylene glycol dimethyl ether.