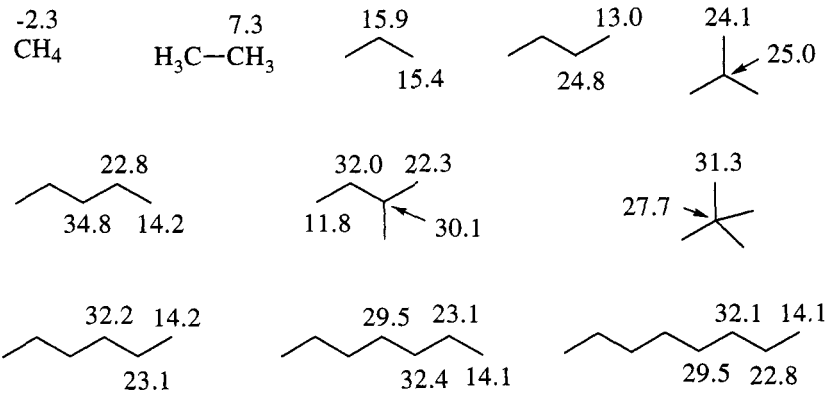
4 ^{13}C NMR Spectroscopy

4.1 Alkanes

4.1.1 Chemical Shifts

^{13}C Chemical Shifts of Alkanes (δ in ppm relative to TMS)



^{13}C *Chemical Shifts of Methyl Groups* (δ *in ppm relative to TMS*)

	Substituent X	δ_{CH_3-X}		Substituent X	δ_{CH_3-X}
	–H	-2.3		–3-indolyl	9.8
C	$-CH_3$	7.3		–4-indolyl	21.6
	$-CH_2CH_3$	15.4		–5-indolyl	21.5
	$-CH(CH_3)_2$	24.1		–6-indolyl	21.7
	$-C(CH_3)_3$	31.3		–7-indolyl	16.6
	$-(CH_2)_6CH_3$	14.1	H	–F	71.6
	$-CH_2$–phenyl	15.7	a	–Cl	25.6
	$-CH_2F$	15.8	l	–Br	9.6
	$-CH_2Cl$	18.7		–I	-24.0
	$-CH_2Br$	19.1	O	–OH	50.2
	$-CH_2I$	20.4		$-OCH_3$	60.9
	$-CHCl_2$	31.6		$-OCH_2CH_3$	57.6
	$-CHBr_2$	31.8		$-OCH(CH_3)_2$	54.9
	$-CCl_3$	46.3		$-OC(CH_3)_3$	49.4
	$-CBr_3$	49.4		$-OCH_2CH{=}CH_2$	57.4
	$-CH_2OH$	18.2		–O–cyclohexyl	55.1
	$-CH_2OCH_3$	14.7		$-OCH{=}CH_2$	52.5
	$-CH_2OCH_2CH_3$	15.4		–O–phenyl	54.8
	$-CH_2OCH{=}CH_2$	14.6		$-OCOCH_3$	51.5
	$-CH_2O$–phenyl	14.9		–OCO–cyclohexyl	51.2
	$-CH_2OCOCH_3$	14.4		$-OCOCH{=}CH_2$	51.5
	$-CH_2NH_2$	19.0		–OCO–phenyl	51.8
	$-CH_2NHCH_3$	14.3		$-OCOOCH_3$	54.9
	$-CH_2N(CH_3)_2$	12.8		$-OSO_2$–4-tolyl	56.3
	$-CH_2NO_2$	12.3		$-OSO_2OCH_3$	59.1
	$-CH_2SH$	19.7	N	$-NH_2$	28.3
	$-CH_2SO_2CH_3$	6.7		$-NH_3^+$	26.5
	$-CH_2SO_3H$	8.0		$-NHCH_3$	38.2
	$-CH_2CHO$	5.2		–NH–cyclohexyl	33.5
	$-CH_2COCH_3$	7.0		–NH–phenyl	30.2
	$-CH_2COOH$	9.6		$-N(CH_3)_2$	47.5
	–cyclopentyl	20.5		–*N*–pyrrolidinyl	42.7
	–cyclohexyl	23.1		–*N*–pyperidinyl	47.7
	$-CH{=}CH_2$	18.7		$-N(CH_3)$phenyl	39.9
	$-C{\equiv}CH$	3.7		–*N*-pyrrolyl	35.9
	–phenyl	21.4		–*N*-imidazolyl	32.2
	–1-naphthyl	19.1		–*N*-pyrazolyl	38.4
	–2-naphthyl	21.5		–*N*-indolyl	32.1
	–2-pyridyl	24.2		$-NHCOCH_3$	26.1
	–3-pyridyl	18.0		$-N(CH_3)CHO$	31.5; 36.5
	–4-pyridyl	20.6		$-N(CH_3)COCH_3$	35.0; 38.0
	–2-furyl	13.7		$-NO_2$	61.2
	–2-thienyl	14.7		–CN	1.7
	–2-pyrrolyl	11.8		–NC	26.8
	–2-indolyl	13.4		–NCS	29.1

Substituent X		δ_{CH_3-X}	Substituent X	δ_{CH_3-X}
S	–SH	6.5	$-COO^-$	24.4
	$-SCH_3$	19.3	$-COOCH_3$	20.6
	–S–*n*-C_8H_{17}	15.5	$-COOCOCH_3$	21.8
	–S–phenyl	15.6	$-CONH_2$	22.3
	$-SSCH_3$	22.0	$-CON(CH_3)_2$	21.5
	$-SOCH_3$	40.1	–COSH	32.6
	$-SO_2CH_3$	42.6	$-COSCH_3$	30.2
	$-SO_2CH_2CH_3$	39.3	$-COCOCH_3$	23.2
	$-SO_2Cl$	52.6	–COCl	33.6
	$-SO_3H$	39.6	–COBr	39.1
	$-SO_3Na$	41.1	$-COSi(CH_3)_3$	35.7
O	–CHO	31.2		
||	$-COCH_3$	30.7		
C	$-COCH_2CH_3$	27.5		
/\	$-COCCl_3$	21.1		
	$-COCH{=}CH_2$	25.7		
	–CO–cyclohexyl	27.6		
	–CO–phenyl	25.7		
	–COOH	21.7		

^{13}C Chemical Shifts of Monosubstituted Alkanes

(δ in ppm relative to TMS)

Substituent		Methyl	Ethyl		1-Propyl		
		$-CH_3$	$-CH_2$	$-CH_3$	$-CH_2$	$-CH_2$	$-CH_3$
	–H	-2.3	7.3	7.3	15.4	15.9	15.4
C	$-CH{=}CH_2$	18.7	27.4	13.4	36.2	22.4	13.6
	$-C{\equiv}CH$	3.7	12.3	13.8	20.6	22.2	13.4
	–phenyl	21.4	29.1	15.8	38.3	24.8	13.8
H	–F	71.6	80.1	15.8	85.2	23.6	9.2
a	–Cl	25.6	39.9	18.9	46.8	26.3	11.6
l	–Br	9.6	27.6	19.4	35.6	26.4	13.0
	–I	-24.0	-1.6	20.6	9.1	27.0	15.3
O	–OH	50.2	57.8	18.2	64.2	25.9	10.3
	$-OCH_3$	60.9	67.7	14.7	74.5	23.2	10.5
	$-OCH_2CH_3$	57.6	66.0	15.4	72.5	23.2	10.7
	$-OCH(CH_3)_2$	54.9					
	$-OC(CH_3)_3$	49.4	56.8	16.4			
	–O–phenyl	54.8	63.2	14.9	69.4	22.8	10.6
	$-OCOCH_3$	51.5	60.4	14.4	66.2	22.4	10.5
	–OCO–phenyl	51.8	60.8	14.4	66.4	22.2	10.5
	$-OSO_2$–4-tolyl	56.3	66.9	14.7	72.2	22.3	10.0
N	$-NH_2$	28.3	36.9	19.0	44.6	27.4	11.5
	$-NHCH_3$	38.2	45.9	14.3	54.0	23.2	12.5
	$-N(CH_3)_2$	47.6	53.6	12.8	61.8	20.6	11.9
	$-NHCOCH_3$	26.1	34.4	14.6	40.7	22.5	11.1
	$-NO_2$	61.2	70.8	12.3	77.4	21.2	10.8
	–CN	1.7	10.8	10.6	19.3	19.0	13.3
	–NC	26.8	36.4	15.3	43.4	22.9	11.0
S	–SH	6.5	19.1	19.7	26.4	27.6	12.6
	$-SCH_3$	19.3					
	$-SSCH_3$	22.0	31.8	14.7			
	$-SOCH_3$	40.1					
	$-SO_2CH_3$	42.6	48.2	6.7	56.3	16.3	13.0
	$-SO_2Cl$	52.6	60.2	9.1	67.1	18.4	12.1
	$-SO_2OH$	39.6	46.7	8.0	53.7	18.8	13.7
O	–CHO	31.3	36.7	5.2	45.7	15.7	13.3
||	$-COCH_3$	30.7	35.2	7.0	45.2	17.5	13.5
C	–CO–phenyl	25.7	31.7	8.3	40.4	17.7	13.8
/ \	–COOH	21.7	28.5	9.6	36.2	18.7	13.7
	$-COOCH_3$	20.6	27.2	9.2	35.6	18.9	13.8
	$-CONH_2$	22.3	29.0	9.7			
	–COCl	33.6	41.0	9.3	48.9	18.8	13.0

^{13}C Chemical Shifts of Monosubstituted Alkanes (contd.)

(δ in ppm relative to TMS)

Substituent		Isopropyl		*tert*-Butyl	
		–CH	$-CH_3$	–C	$-CH_3$
	–H	15.9	15.4	25.0	24.1
C	$-CH=CH_2$	32.3	22.1	33.8	29.4
	$-C\equiv CH$	20.3	22.8	27.4	31.1
	–phenyl	34.3	24.0	34.6	31.4
H	–F	87.3	22.6	93.5	28.3
a	–Cl	53.7	27.3	66.7	34.6
l	–Br	44.8	28.5	62.1	36.4
	–I	20.9	31.2	43.0	40.4
	–OH	64.0	25.3	68.9	31.2
	$-OCH_3$	72.6	21.4	72.7	27.0
	$-OCH_2CH_3$			72.6	27.7
	$-OCH(CH_3)_2$	68.5	23.0	73.0	28.5
	$-OC(CH_3)_3$	63.5	25.2	76.3	33.8
	–O–phenyl	69.3	22.0		
	$-OCOCH_3$	67.5	21.9	79.9	28.1
	–OCO–phenyl	68.2	21.9	80.7	28.2
N	$-NH_2$	43.0	26.5	47.2	32.9
	$-NHCH_3$	50.5	22.5	50.4	28.2
	$-N(CH_3)_2$	55.5	18.7	53.6	25.4
	$-NHCOCH_3$	40.5	22.3	49.9	28.6
	$-NO_2$	78.8	20.8	85.2	26.9
	–CN	19.8	19.9	28.1	28.5
	–NC	45.5	23.4	54.0	30.7
S	–SH	29.9	27.4	41.1	35.0
	$-SCH_2CH_3$	34.4	23.4		
	$-SO_2CH_3$	53.5	15.2	57.6	22.7
	$-SO_2Cl$	67.6	17.1	74.2	24.5
	$-SO_2OH$	52.9	16.8	55.9	25.0
O	–CHO	41.1	15.5	42.4	23.4
||	$-COCH_3$	41.6	18.2	44.3	26.5
C	–CO–phenyl	35.2	19.1	43.5	27.9
/ \	–COOH	34.1	18.8	38.7	27.1
	$-COOCH_3$	34.1	19.1	38.7	27.3
	$-CONH_2$	34.9	19.5	38.6	27.6
	–COCl	46.5	19.0	49.4	27.1

^{13}C Chemical Shifts of 1-Substituted n-*Octanes*

(δ in ppm relative to TMS)

Substituent	1 $-CH_2$	2 $-CH_2$	3 $-CH_2$	4 $-CH_2$	5 $-CH_2$	6 $-CH_2$	7 $-CH_2$	8 $-CH_3$
–H	14.1	22.8	32.1	29.5	29.5	32.1	22.8	14.1
C –$CH{=}CH_2$	34.5	~29.6	~29.6	~29.6	~29.6	32.2	23.0	13.9
–phenyl	36.2	31.7	~29.6	~29.6	~29.6	32.1	22.8	14.1
Hal –F	84.2	30.6	25.3	29.3	29.3	31.9	22.7	14.1
Hal –Cl	45.1	32.8	27.0	29.0	29.2	31.9	22.8	14.1
Hal –Br	33.8	33.0	28.3	28.8	29.2	31.8	22.7	14.1
–I	6.9	33.7	30.6	28.6	29.1	31.8	22.6	14.1
O –OH	63.1	32.9	25.9	29.5	29.4	31.9	22.8	14.1
–O–*n*-C_8H_{17}	71.1	30.0	26.3	29.6	29.4	32.0	22.8	14.1
–ONO	68.3	29.2	26.0	29.3	29.3	31.9	22.7	14.0
N –NH_2	42.4	34.1	27.0	29.6	29.4	31.9	22.7	14.1
–$N(CH_3)_2$	60.1	29.5*	≈27.9*	≈27.7*	29.7*	32.0	22.8	14.4
–NO_2	75.8	26.2	27.9	≈29.6	≈29.6	31.4	22.6	14.0
–CN	17.2	25.5	≈29.9	≈29.9	≈29.9	31.8	22.7	14.0
S –SH	24.7	34.2	28.5	29.2	29.1	31.9	22.7	14.1
–SCH_3	34.5	29.0	29.4	29.4	29.4	31.9	22.8	14.1
–SO–*n*-C_8H_{17}	52.6	≈29.1	≈29.1	≈29.1	≈29.1	31.8	22.7	14.1
O –CHO	44.0	22.2	≈29.3	≈29.3	≈29.3	31.9	22.7	14.1
|| –$COCH_3$	43.7	24.1	≈29.5	≈29.5	≈29.5	32.0	22.8	14.1
C –CO–phenyl	38.6	24.4	29.5	29.5	29.5	31.9	22.7	14.0
/ \ –COOH	34.2	24.8	≈29.3	≈29.3	≈29.3	31.9	22.7	14.1
–$COOCH_3$	34.2	25.1	29.3	29.3	29.3	31.9	22.8	14.1
–$CONH_2$	35.5	25.4	29.1	29.1	29.1	31.6	22.3	14.0
–COCl	47.2	25.1	28.5	29.1	29.1	31.8	22.7	14.1

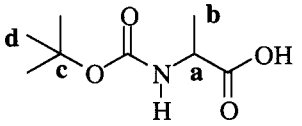
* assignment uncertain

Estimation of ^{13}C Chemical Shifts of Aliphatic Compounds (in ppm relative to TMS)

The chemical shifts of sp^3-hybridized carbon atoms can be estimated with the help of an additivity rule using the shift value of methane (-2.3 ppm) and increments for substituents in α-, β-, γ-, and δ-position (see next pages). Some substituents occupy two positions. Thus, the quaternary carbon atom **c** in the example given below is in δ-position relative to the carbon atom **a** since the sp^3-hybridized oxygen of the β-COO group occupies the γ-position. This simple linear model needs corrections in case of strong branching of the observed C atom and/or its neighbors (steric corrections, S). Substituents for which such corrections are necessary are those with varying branching, i.e., a varying number of directly bonded H atoms. They are marked with an asterisk (*) in the Table of Increments. Further correction terms are needed if γ-substituents are in a sterically fixed position (conformational corrections, K).

The chemical shifts estimated with this additivity rule differ in general by less than about 4 ppm from the experimental values. Larger discrepancies may be expected for highly branched systems (particularly for quaternary carbon atoms). For carbon atoms bearing several halogen, oxygen, and/or other strongly deshielding substituents, additional correction terms are needed [1]. Without such corrections, deviations can be so large as to render the rule useless.

Example: Estimation of chemical shifts for *N-tert*-butoxycarbonylalanine



a	base value	-2.3
	1 α-C	9.1
	1 α-COOH	20.1
	1 α-NH	28.3
	1 β-COO	2.0
	1 δ-C	0.3
	1 S(tert,2)	-3.7
	estimated	53.8
	exp	49.0

b	base value	-2.3
	1 α-C	9.1
	1 β-COOH	2.0
	1 β-NH	11.3
	1 γ-COO	-2.8
	1 S(prim,3)	-1.1
	estimated	16.2
	exp	17.3

c	base value	-2.3
	3 α-C	27.3
	1 α-OCO	56.5
	1 γ-NH	-5.1
	1 δ-C	0.3
	3 S(quat,1)	-4.5
	estimated	72.2
	exp	78.1

d	base value	-2.3
	1 α-C	9.1
	2 β-C	18.8
	1 β-OCO	6.5
	1 δ-NH	0.0
	1 S(prim,4)	-3.4
	estimated	28.7
	exp	28.1

Estimation of ^{13}C Chemical Shifts of Aliphatic Compounds

(δ in ppm relative to TMS)

$$\delta = -2.3 + \sum_i Z_i + \sum_j S_j + \sum_k K_k$$

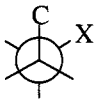
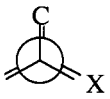
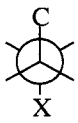
Substituent		Increment Z_i for substituents in position			
		α	β	γ	δ
	–H	0.0	0.0	0.0	0.0
	—C⋞	9.1	9.4	-2.5	0.3
	–C*=C	19.5	6.9	-2.1	0.4
	–C≡C–	4.4	5.6	-3.4	-0.6
	–phenyl	22.1	9.3	-2.6	0.3
Hal	–F	70.1	7.8	-6.8	0.0
Hal	–Cl	31.0	10.0	-5.1	-0.5
Hal	–Br	18.9	11.0	-3.8	-0.7
	–I	–7.2	10.9	-1.5	-0.9
O	–O–*	49.0	10.1	-6.2	0.3
	–OCO–	56.5	6.5	-6.0	0.0
	–ONO	54.3	6.1	-6.5	-0.5
N	—N⋞	28.3	11.3	-5.1	0.0
	—N^+⋞	30.7	5.4	-7.2	-1.4
	–NH_3^+	26.0	7.5	-4.6	0.0
	–NO_2	61.6	3.1	-4.6	-1.0
	–CN	3.1	2.4	-3.3	-0.5
	–NC	31.5	7.6	-3.0	0.0
S	–S*–	10.6	11.4	-3.6	-0.4
	–SCO–	17.0	6.5	-3.1	0.0
	–S*O–	31.1	7.0	-3.5	0.5
	–S*O_2–	30.3	7.0	-3.7	0.3
	–SO_2Cl	54.5	3.4	-3.0	0.0
	–SCN	23.0	9.7	-3.0	0.0
O ‖ C / \	–CHO	29.9	-0.6	-2.7	0.0
	–CO–	22.5	3.0	-3.0	0.0
	–COOH	20.1	2.0	-2.8	0.0
	–COO^-	24.5	3.5	-2.5	0.0
	–COO–	22.6	2.0	-2.8	0.0
	–CO–N<	22.0	2.6	-3.2	-0.4
	–COCl	33.1	2.3	-3.6	0.0
	–C=NOH syn	11.7	0.6	-1.8	0.0
	–C=NOH anti	16.1	4.3	-1.5	0.0
	–CS–N<	33.1	7.7	-2.5	0.6
	–Sn	-5.2	4.0	-0.3	0.0

Steric Corrections, S

Observed ^{13}C-center	S, for number of substituents at the α-atom[a]			
	1	2	3	4
primary (CH_3)	0.0	0.0	-1.1	-3.4
secondary (CH_2)	0.0	0.0	-2.5	-6.0
tertiary (CH)	0.0	-3.7	-8.5	-10.0
quaternary (C)	-1.5	-8.0	-10.0	-12.5

[a] To be applied to each of the neighboring atoms, which may have a variable number of non-hydrogen substituents (marked with an asterisk (*) in the Table of Increments).

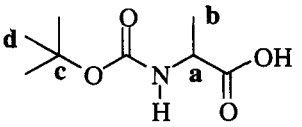
Conformational Corrections, K, for γ-Substituents

Conformation		K
synperiplanar		-4.0
synclinal		-1.0
anticlinal		0.0
antiperiplanar		2.0
not fixed		0.0

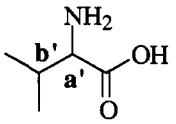
One can also use the chemical shifts of a reference compound as the base value if its structure is closely related to that assumed for the unknown. The increments corresponding to the structural elements missing in the reference compound are then added to the base value, while those of structural elements present in the reference but absent in the unknown are subtracted.

Example: Estimation of the chemical shifts for the carbon atoms **a** and **b** in *N-tert*-butoxycarbonylalanine using the chemical shifts of valine as base values (**a'**, **b'**):

Target:



Reference:



a	base value	61.6
	1 β-COO	2.0
	1 δ-C	0.3
	1 S(tert,2)	-3.7
	- 2 β-C	-18.8
	- 1 S(tert,3)	8.5
	estimated	49.9
	exp	49.0

b	base value	30.2
	1 γ-COO	-2.8
	1 S(prim,3)	-1.1
	- 2 α-C	-18.2
	- 1 S(tert,3)	8.5
	estimated	16.6
	exp	17.3

4.1.2 Coupling Constants

^{13}C-^{1}H Coupling Constants

Coupling through one bond ($^{1}J_{CH}$ in Hz)

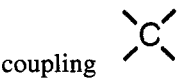
The ^{13}C-^{1}H coupling constant of 125 Hz in methane increases in the presence of electronegative substituents and can be estimated by using the following additivity rule:

$$^{1}J_{CH}\ Z_1Z_2Z_3 = 125.0 + \sum_i Z_i$$

Substituent	Increments Z_i	Substituent	Increments Z_i
–H	0.0	–Br	27.0
$-CH_3$	1.0	–I	26.0
$-C(CH_3)_3$	-3.0	–OH	18.0
$-CH_2Cl$	3.0	–O-phenyl	18.0
$-CH_2Br$	3.0	$-NH_2$	8.0
$-CH_2I$	7.0	$-NHCH_3$	7.0
$-CHCl_2$	6.0	$-N(CH_3)_2$	6.0
$-CCl_3$	9.0	–CN	11.0
–C≡C	7.0	$-SOCH_3$	13.0
–phenyl	1.0	–CHO	2.0
–F	24.0	$-COCH_3$	-1.0
–Cl	27.0	–COOH	5.5

Example: Estimation of ^{13}C-^{1}H coupling constant of $CHCl_3$:
J = 125.0 + 3 × 27.0 = 206.0 Hz (exp: 209.0 Hz).

Coupling through more than one bond ($|J_{CH}|$ *in Hz*)

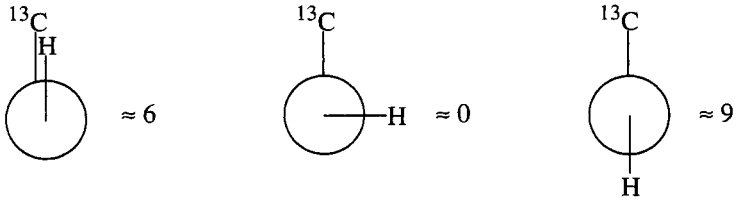


The coupling constants can be estimated from the corresponding ^1H-^1H coupling constants [2]:

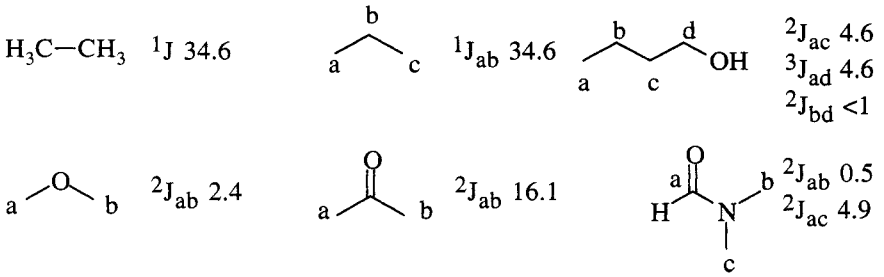
$$J_{CH} \approx 0.62\ J_{HH}$$

$^2J_{CH}$	1– 6	$^1H–CH_2–^{13}CH_3$	4.5
$^3J_{CH}$	0–10	$^1H–CH_2–CH_2–^{13}CH_3$	5.8

The ^{13}C-^1H coupling constants for coupling across three bonds depend on the dihedral angle in the same way as the vicinal ^1H-^1H coupling constants (see Chapter 5.1):



^{13}C-^{13}C *Coupling Constants* ($|J_{CC}|$ *in Hz*)



The ^{13}C-^{13}C coupling constants for coupling over three bonds depend on the dihedral angle in the same way as the vicinal ^1H-^1H (see Chapter 5.1) and ^{13}C-^1H coupling constants. Maximum values of ca. 4–6 Hz are observed for dihedral angles of 0° and 180° and minimal values around 0 Hz at 90°.

4.1.3 References

[1] A. Fürst, E. Pretsch, W. Robien, A comprehensive parameter set for the prediction of the ^{13}C NMR chemical shifts of sp^3-hybridized carbon atoms in organic compounds, Anal. Chim. Acta **1990**, *233*, 213.

[2] J.L. Marshall, Carbon-carbon and carbon-proton NMR couplings, Verlag Chemie International, Deerfield Beach, FL, 1983.

4.2 Alkenes

C=C

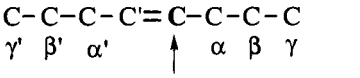
4.2.1 Chemical Shifts

^{13}C Chemical Shifts of Alkenes (δ in ppm relative to TMS)

The ^{13}C chemical shifts of the carbons of C=C double bonds typically range from ca. 80–160 ppm; a wider range of 40–210 ppm is observed with O- and N-substituents. In unsaturated *acyclic hydrocarbons*, they can be predicted with high accuracy (see below). To estimate the ^{13}C chemical shifts in all other *substituted alkenes*, one can use the substituent effects listed for chemical shifts in vinyl groups. However, since no configuration-dependent parameters are available, the values thus estimated are less accurate than those for unsaturated acyclic hydrocarbons.

The ^{13}C chemical shifts of sp^3-hybridized carbon atoms in the vicinity of double bonds can be estimated using the additivity rule given on page 78. The conformational correction factors, K, for γ-substituents of *cis*- vs. *trans*-disubstituted alkenes differ by 6 ppm because the relative position of these substituents is fixed by the double bond.

Estimation of the ^{13}C Chemical Shifts of sp^2-Hybridized Carbon Atoms in Unsaturated Acyclic Hydrocarbons
(δ in ppm relative to TMS)



Base value: 123.3

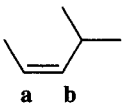
Increments for C-substituents:

at C-atom under consideration (C)		at neighboring C-atom (C')	
α	10.6	α'	-7.9
β	4.9	β'	-1.8
γ	-1.5	γ'	1.5

Steric corrections:

• for each pair of *cis*-α,α'-substituents	-1.1
• for a pair of geminal α,α-substituents	-4.8
• for a pair of geminal α',α'-substituents	2.5
• if one or more β-substituents are present	2.3

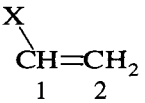
Example: Estimation of chemical shifts of *cis*-4-methyl-2-pentene



C=C

a	base value	123.3	**b**	base value	123.3
	1 α-C	10.6		1 α-C	10.6
	1 α'-C	-7.9		2 β-C	9.8
	2 β'-C	-3.6		1 α'-C	-7.9
	cis-α,α'	-1.1		*cis*-α,α'	-1.1
	estimated	121.3		1 β-substituent	2.3
	exp	121.8		estimated	137.0
				exp	138.8

Effect of Substituents on the ^{13}C Chemical Shifts of Vinyl Compounds *(in ppm relative to TMS)*



$\delta_{C_i} = 123.3 + Z_i$

	Substituent X	Z_1	Z_2		Substituent X	Z_1	Z_2
	–H	0.0	0.0	**O**	–OH	25.7	-35.3
C	$-CH_3$	12.9	-7.4		$-OCH_3$	29.4	-38.9
	$-CH_2CH_3$	17.2	-9.8		$-OCH_2CH_3$	28.8	-37.1
	$-CH_2CH_2CH_3$	15.7	-8.8		$-O(CH_2)_3CH_3$	28.1	-40.4
	$-CH(CH_3)_2$	22.7	-12.0		$-OCOCH_3$	18.4	-26.7
	$-(CH_2)_3$	14.6	-8.9	**N**	$-N(CH_3)_2$	28.0*	-32.0*
	$-C(CH_3)_3$	26.0	-14.8		$-N^+(CH_3)_3$	19.8	-10.6
	$-CH_2Cl$	10.2	-6.0		–*N*–pyrrolidonyl	6.5	-29.2
	$-CH_2Br$	10.9	-4.5		$-NO_2$	22.3	-0.9
	$-CH_2I$	14.2	-4.0		–CN	-15.1	14.2
	$-CH_2OH$	14.2	-8.4		–NC	-3.9	-2.7
	$-CH_2OCH_2CH_3$	12.3	-8.8	**S**	$-SCH_2CH_3$	9.0	-12.8
	$-CH=CH_2$	13.6	-7.0		$-SO_2CH=CH_2$	14.3	7.9
	$-C\equiv CH$	-6.0	5.9	**O**	–CHO	15.3	14.5
	–phenyl	12.5	-11.0	‖	$-COCH_3$	13.8	4.7
H	–F	24.9	-34.3	**C**	–COOH	5.0	9.8
a	–Cl	2.8	-6.1	/\	$-COOCH_2CH_3$	6.3	7.0
l	–Br	-8.6	-0.9		–COCl	8.1	14.0
	–I	-38.1	7.0		$-Si(CH_3)_3$	16.9	6.7
					$-SiCl_3$	8.7	16.1

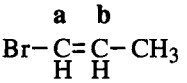
* estimated values

The values listed on the preceding page can also be used to estimate the ^{13}C chemical shifts of sp^2-hybridized carbon atoms in alkenes with more than one substituent (note that the *cis/trans* configuration is not taken into account):

$$\delta_{C_i} = 123.3 + \sum_i Z_i$$

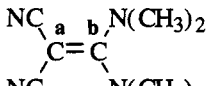
C = C

Example: Estimation of chemical shifts of 1-bromo-1-propene

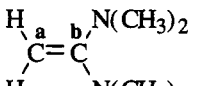


a	base value	123.3		**b**	base value	123.3	
	Z_1(Br)	-8.6			Z_2(Br)	-0.9	
	Z_2(CH_3)	-7.4			Z_1(CH_3)	12.9	
	estimated	107.3			estimated	135.3	
	exp	108.9	(*cis*)		exp	129.4	(*cis*)
		104.7	(*trans*)			132.7	(*trans*)

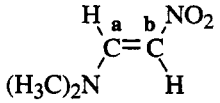
The following examples show some larger deviations between measured and estimated (in parentheses) chemical shifts. This is usually to be expected when several substituents are present that strongly interact with the π-electrons of the double bond:



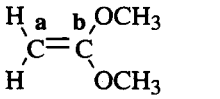
a	39.1 (29.1)
b	171.0 (207.7)



a	69.2 (59.3)
b	163.0 (179.3)

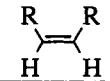
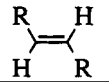


a	151.0 (150.4)
b	111.4 (113.6)



a	54.7 (45.5)
b	167.9 (182.1)

^{13}C Chemical Shifts of cis- and trans-1,2-Disubstituted Alkenes *(δ in ppm relative to TMS)*

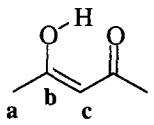
Substituent R		
–CH_3	123.3	124.5
–CH_2CH_3	131.2	131.3
–Cl	118.1	119.9
–Br	116.4	109.4
–I	96.5	79.4
–CN	120.8	120.2
–OCH_3	130.3	135.2
–COOH	130.4	134.2
–$COOCH_3$	130.1	133.5

^{13}C *Chemical Shifts of Enols* (δ *in ppm relative to TMS)*

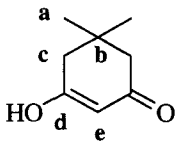
The carbon atom bonded to the enolic OH group is strongly deshielded so that its shift is close to that of a carbonyl carbon. The other carbon atom is strongly shielded.

C=C

Enol:

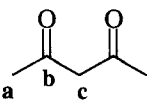


a	22.5
b	190.5
c	99.0

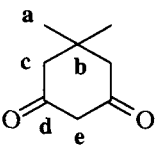


a	28.3
b	32.8
c	46.2
d	191.1
e	103.3

Ketone:



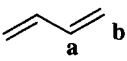
a	28.5
b	201.1
c	56.6



a	28.3
b	31.0
c	54.2
d	203.6
e	57.3

^{13}C *Chemical Shifts of Aliphatic Dienes* (δ *in ppm relative to TMS)*

Conjugated Dienes



a	136.9
b	116.3

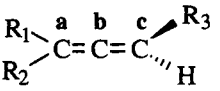
Allenes

$$\overset{213.5}{CH_2}=\overset{74.8}{C}=CH_2$$

Estimation of the chemical shifts of sp^2-hybridized carbon atoms in substituted allenes: see [1].

^{13}C Chemical Shifts of Substituted Allenes
(δ in ppm relative to TMS)

C = C



R_1	R_2	R_3	a	b	c
–H	–H	–H	74.8	213.5	74.8
$-CH_3$	–H	–H	84.4	210.4	74.1
$-CH_3$	$-CH_3$	–H	93.4	207.3	72.1
$-CH_3$	–H	$-CH_3$	85.4	207.1	85.4
$-CH_2CH_3$	–H	–H	91.7	208.9	75.3
$-C(CH_3)_3$	$-C(CH_3)_3$	–H	119.6	207.0	75.8
$-CH=CH_2$	–H	–H	93.9	211.4	75.1
$-C\equiv CH$	–H	–H	74.8	217.7	77.3
–phenyl	–H	–H	94.4	210.0	78.8
–F	–H	–H	129.8	200.2	93.9
–Cl	–H	–H	88.8	207.9	84.5
–Br	–H	–H	72.7	207.6	83.8
–I	–H	–H	35.3	208.0	78.3
$-OCH_3$	–H	–H	123.1	202.0	90.3
$-N(CH_3)_2$	–H	–H	113.1	204.2	85.5
–CN	–H	–H	67.4	218.7	80.7
$-SCH_3$	–H	–H	90.0	206.1	81.3
–COOH	–H	–H	88.1	217.7	80.0

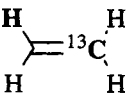
4.2.2 Coupling Constants

^{13}C-^{1}H Coupling Constants ($|J_{CH}|$ in Hz)

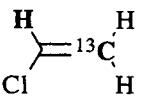
Coupling through one bond

$CH_2=CH_2$ $^1J_{CH}$ 156.4 $CH_2=C=CH_2$ $^1J_{CH}$ 167.8

Coupling through two bonds *(typical range: 0–16)*



$^2J_{CH}$ -2.4



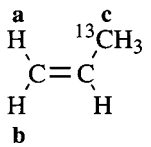
$^2J_{CH}$ 6.9

Additivity rule for the estimation of $^2J_{CH}$ of alkenes: see [2].

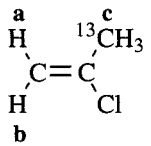
Coupling through three bonds:

The *trans*-^{1}H–C=C–^{13}C coupling constant of alkenes is always larger than the corresponding *cis* coupling constant so that an assignment is possible if both isomers are available: see [3].

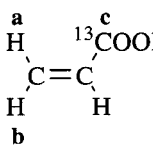
C=C



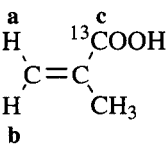
$^{3}J_{ac}$ 7.6
$^{3}J_{bc}$ 12.6



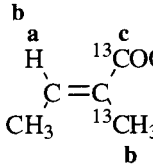
$^{3}J_{ac}$ 4.1
$^{3}J_{bc}$ 8.1



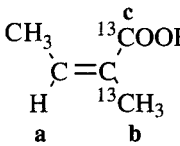
$^{3}J_{ac}$ 7.6
$^{3}J_{bc}$ 14.1



$^{3}J_{ac}$ 7.6
$^{3}J_{bc}$ 14.1

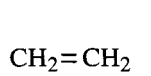


$^{3}J_{ab}$ 7.7
$^{3}J_{ac}$ 7.4

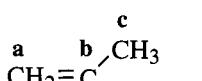


$^{3}J_{ab}$ 6.9
$^{3}J_{ac}$ 13.2

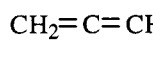
^{13}C-^{13}C Coupling Constants ($|^{1}J_{CC}|$ *in Hz*)



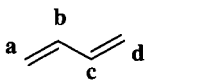
$^{1}J_{CC}$ 67.6



$^{1}J_{ab}$ 70.0
$^{1}J_{bc}$ 41.9



$^{1}J_{CC}$ 98.7



$^{1}J_{ab}$ 68.8
$^{1}J_{bc}$ 53.7
$^{2}J_{ac}$ < 1
$^{3}J_{ad}$ 9.0

4.2.3 References

[1] R.H.A.M. Janssen, R.J.J.Ch. Lousberg, M.J.A. de Bie, An additivity relation for carbon-13 chemical shifts in substituted allenes, J. R. Neth. Chem. Soc. **1981**, *100*, 85.

[2] U. Vögeli, D. Herz, W. von Philipsborn, Geminal C,H spin coupling in substituted alkenes, Org. Magn. Reson. **1980**, *13*, 200.

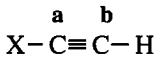
[3] U. Vögeli, W. von Philipsborn, Vicinal C,H spin coupling in substituted alkenes. Stereochemical significance and structural effects, Org. Magn. Reson. **1975**, *7*, 617.

4.3 Alkynes

4.3.1 Chemical Shifts

C≡C

^{13}C Chemical Shifts of Alkynes (δ in ppm relative to TMS)



	Substituent X	a	b
	–H	71.9	71.9
C	$-CH_3$	80.4	68.3
	$-CH_2CH_3$	85.5	67.1
	$-CH_2CH_2CH_3$	84.0	68.7
	$-CH_2CH_2CH_2CH_3$	83.0	66.0
	$-CH(CH_3)_2$	89.2	67.6
	$-C(CH_3)_3$	92.6	66.8
	–cyclohexyl	88.7	68.3
	$-CH_2OH$	83.0	73.8
	$-CH{=}CH_2$	82.8	80.0
	$-C{\equiv}C-CH_3$	68.8	64.7
	–phenyl	84.6	78.3
O	$-OCH_2CH_3$	90.9	26.5
S	$-SCH_2CH_3$	72.6	81.4
O	–CHO	81.8	83.1
‖	$-COCH_3$	81.9	78.1
C	–COOH	74.0	78.6
/\	$-COOCH_3$	74.8	75.6

Additivity rule for estimating the chemical shifts of *sp*-hybridized carbon atoms in alkynes: see [1].

4.3.2 Coupling Constants

^{13}C-^{1}H Coupling Constants ($|J_{CH}|$ in Hz) [2]

a b c H−^{13}C≡C−H	$^{1}J_{ab}$	249		
	$^{2}J_{bc}$	49.3 (in substituted acetylenes: 40–60)		
a b c d e H−C≡C−CH$_3$	$^{2}J_{ac}$	50.1	$^{3}J_{ad}$	3.4
	$^{2}J_{ce}$	-10.4	$^{3}J_{be}$	4.7
a b c CH$_3$−C≡C−CH$_3$	$^{2}J_{ab}$	-10.3	$^{3}J_{ac}$	4.3

C≡C

With acetylenes, the results of multipulse experiments (such as DEPT, INEPT, SEFT, or APT) to determine the number of protons attached to the carbon atoms must be interpreted with care. As a consequence of the unusually large ^{13}C-^{1}H coupling constants through one and two bonds, the sign of the signals may be opposite to the expected one.

^{13}C-^{13}C Coupling Constants ($|^{1}J_{CC}|$ in Hz)

H−C≡C−H	$^{1}J_{CC}$	171.5	a b c H−C≡C−C≡C−H	$^{1}J_{ab}$	190.3
				$^{1}J_{bc}$	153.4

4.3.3 References

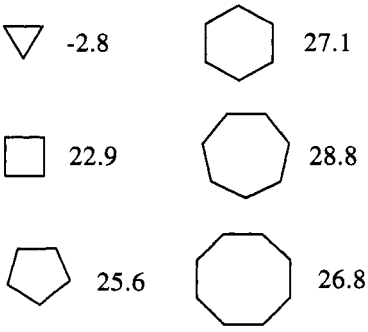
[1] W. Höbold, R. Radeglia, D. Klose, Inkrementen-Berechnung von ^{13}C-chemischen Verschiebungen in *n*-Alkinen, J. Prakt. Chem. **1976**, *318*, 519.

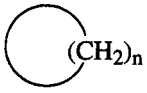
[2] K. Hayamizu, O. Yamamoto, ^{13}C,^{1}H Spin coupling constants of dimethylacetylene, Org. Magn. Reson. **1980**, *13*, 460.

4.4 Alicyclics

4.4.1 Chemical Shifts

Saturated Monocyclic Alicyclics (δ in ppm relative to TMS)





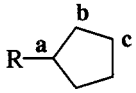
n	δ
9	26.0
10	25.1
11	26.3
12	23.8
13	26.2
14	25.2
15	27.0
20	28.0
30	29.3
40	29.4
72	29.7

^{13}C Chemical Shifts of Monosubstituted Cyclopropanes (δ in ppm relative to TMS) [1]

Substituent X		a	b	other
	–H	-2.8	-2.8	
C	$-CH_3$	4.9	5.6	CH_3 19.4
	$-CH_2CH_3$	12.8	4.1	CH_2 27.8, CH_3 13.6
	$-CH_2CH_2CH_2CH_3$	10.9	4.4	1-CH_2 34.7, 2-CH_2 32.0
	$-C(CH_3)_3$	22.7	0.3	C 29.3, CH_3 28.2
	$-CH_2Cl$	13.6	5.5	CH_2 50.3
	$-CH_2OH$	12.7	2.2	CH_2 66.5
	$-CH{=}CH_2$	14.7	6.6	CH 142.4, CH_2 111.5
	–phenyl	15.3	9.2	C 143.9, CH 125.3–128.2
H	–Cl	27.3	8.9	
a	–Br	14.2	9.1	
l	–I	-20.1	10.4	
O	–OH	45.7	6.8	
N	$-NH_2$	24.0	7.4	
	$-NO_2$	54.3	11.7	
	–CN	-4.5	6.2	CN 121.5
O	–CHO	22.7	7.4	CO 202.1
||	$-COCH_3$	20.1	9.6	CO 207.3, CH_3 29.1
C	–COOH	12.7	8.9	CO 181.6
/\	$-COOCH_3$	12.2	7.7	CO 174.7, CH_3 51.1

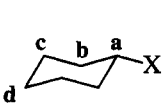
^{13}C Chemical Shifts of Monosubstituted Cyclopentanes

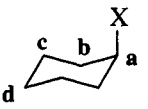
(δ in ppm relative to TMS) [2]



	Substituent X	a	b	c	other
	–H	25.5	25.5	25.5	
C	$-CH_3$	34.8	34.8	25.4	CH_3 21.4
	$-CH_2CH_3$	42.3	32.6	25.4	CH_2 29.2, CH_3 13.2
	$-CH(CH_3)_2$	47.4	30.0	24.7	CH 33.9, CH_3 21.7
	$-C(CH_3)_3$	50.3	26.5	25.1	C 32.5, CH_3 27.6
	$-CH_2OH$	41.2	28.3	24.5	CH_2 67.0
H	–F	95.5	32.8	22.5	$^1J_{CF}$ 173.5, $^2J_{CF}$ 22.1, $^3J_{CF}$ <1.5
a	–Cl	61.8	37.5	23.3	
l	–Br	53.1	38.4	23.7	
	–I	28.7	40.7	24.9	
O	–OH	72.5	34.5	22.7	
	$-OCH_3$	82.2	31.4	23.1	CH_3 56.0
	$-OCOCH_3$	77.7	33.8	24.9	CO 170.8, CH_3 21.7
N	$-NH_2$	52.5	35.5	23.0	
	$-NO_2$	87.0	32.6	24.8	
	–CN	27.0	30.5	24.2	CN 123.4
S	–SH	38.3	37.7	24.6	
	–COOH	43.0	29.2	25.1	CO 183.8

^{13}C Chemical Shifts of Equatorially and Axially Monosubstituted Cyclohexanes (*δ in ppm relative to TMS*)



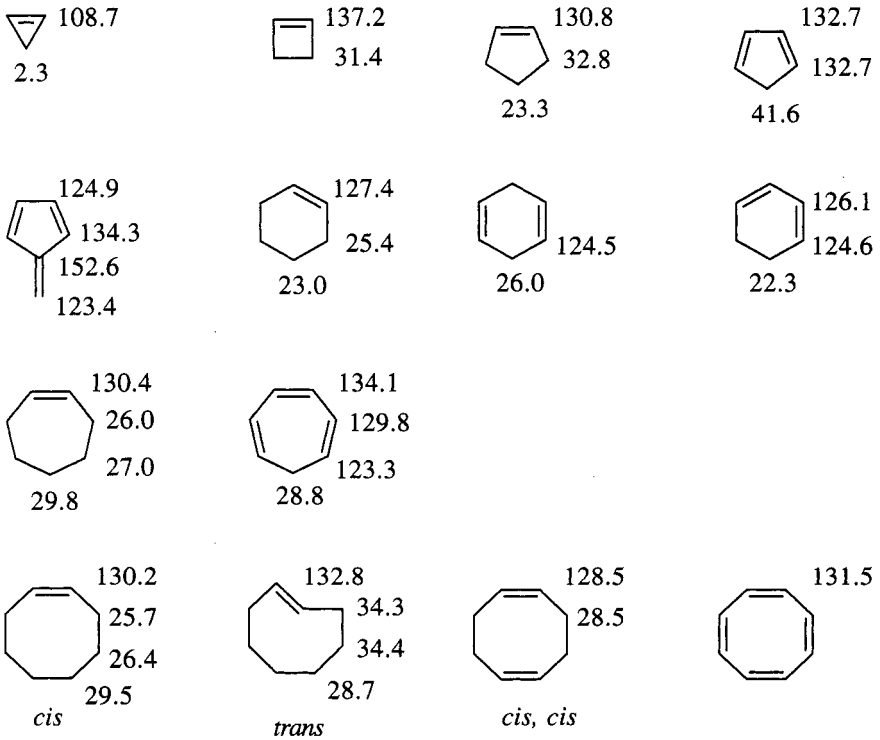


	Substituent X	a	b	c	d	a	b	c	d
	–H	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1
C	$-CH_3$	33.2	36.0	27.1	27.0	28.4	32.4	20.6	26.9
	$-CH_2CH_3$	40.1	33.4	26.9	27.2	35.5	30.0	21.4	27.1
	$-CH_2CH_2CH_3$	40.0	33.6	26.6	26.9				
	$-CH(CH_3)_2$	44.6	30.0	26.8	27.3	41.1	30.2	21.6	27.1
	$-CH_2CH_2CH_2CH_3$	38.4	34.1	27.1	27.3				
	$-C(CH_3)_3$	48.8	28.1	27.7	27.1				
	–cyclohexyl	44.3	30.8	27.4	27.4				
	$-CH=CH_2$	42.1	32.3	26.0	27.1	37.0	30.0	21.2	27.1
	$-C\equiv CH$	28.7	32.1	25.2	24.4	28.0	30.0	21.2	25.7
	–phenyl	45.1	34.9	27.4	26.7				
H	–F	91.0	32.8	23.6	25.3	88.1	30.1	19.8	25.0
a	–Cl	59.8	37.4	26.1	25.4	60.1	33.9	20.4	26.0
l	–Br	52.4	38.3	27.3	25.6	55.4	34.9	21.5	26.4
	–I	31.2	40.1	28.3	25.4	38.3	36.0	22.8	26.1
O	–OH	70.4	35.8	25.1	26.3	65.5	33.2	20.5	27.1
	$-OCH_3$	79.2	32.2	24.5	26.4	74.9	30.0	21.1	26.6
	$-OCOCH_3$	72.3	32.2	24.4	26.1				
	–OCO–phenyl	72.8	31.5	24.1	24.7	69.0	29.3	20.3	24.7
	$-OSi(CH_3)_3$	70.5	36.0	24.7	25.0	66.1	33.1	19.8	25.0
N	$-NH_2$	51.1	37.6	25.8	26.3	47.4	33.8	20.0	27.1
	$-NHCH_3$	58.7	32.7	25.7	26.8				
	$-N(CH_3)_2$	64.3	29.2	26.5	26.9				
	$-NH_3^+Cl^-$	51.8	32.2	24.8	25.2				
	–N=C=N–cyclohexyl	55.7	35.0	24.8	25.5				
	$-NO_2$	84.6	31.4	24.7	25.5				
	$-N_3$	59.5	31.5	24.5	24.5	56.8	29.0	20.1	25.2
	–CN	28.0	29.6	24.6	25.1	26.4	27.4	21.9	25.0
	–NC	51.9	33.7	24.4	25.2	50.3	30.5	20.1	25.2
	–NCS	55.3	33.9	24.5	24.8	50.3	30.5	20.1	25.2
S	–SH	38.3	38.1	26.6	25.3	35.9	33.1	19.4	25.7
O	–CHO	50.1	26.0	25.2	26.1	46.4	24.7	22.7	27.1
||	$-COCH_3$	51.5	29.0	26.6	26.3				
C	–COOH	43.7	29.6	26.2	26.6				
/\	$-COO^-$	47.2	30.9	26.9	26.9				
	$-COOCH_3$	43.4	29.6	26.0	26.4	39.1	27.7	24.1	26.7
	–COCl	55.4	29.7	25.5	25.9				

Estimation of ^{13}C Chemical Shifts of Alicyclic Compounds
(in ppm relative to TMS)

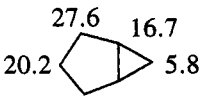
The chemical shift of the parent compound (e.g., 22.9 for cyclobutane, 25.6 for cyclopentane, and 27.1 ppm for cyclohexane) and the same increments as for alkanes (see Chapter 4.1) can be used to estimate the chemical shifts of sp^3-hybridized carbon atoms of alicyclic compounds. Appropriate use of the conformational correction terms, K (page 79), is especially important with axial and equatorial substituents in cyclohexanes. The additivity rule is, however, not suitable for estimating chemical shifts of substituted cyclopropanes.

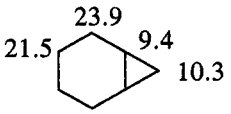
^{13}C Chemical Shifts of Unsaturated Alicyclics
(δ in ppm relative to TMS)

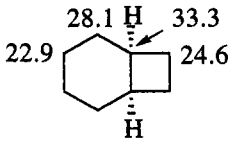


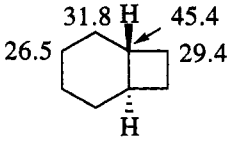
^{13}C Chemical Shifts of Condensed Alicyclics

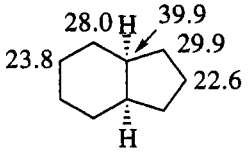
(δ in ppm relative to TMS)

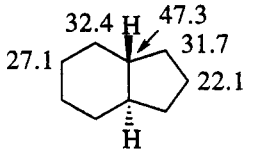


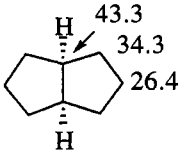


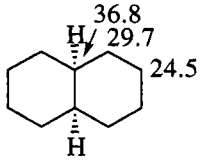


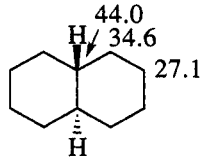


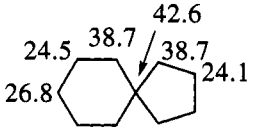


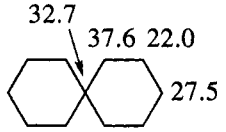


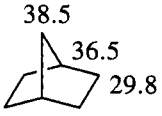


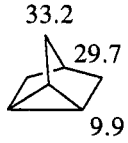


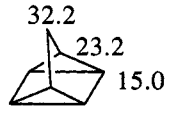


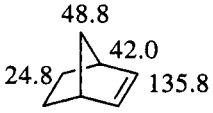


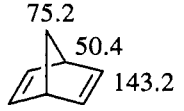


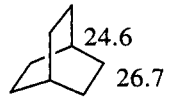


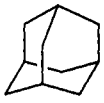


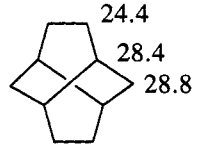


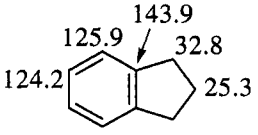


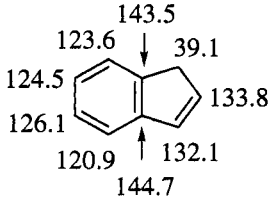


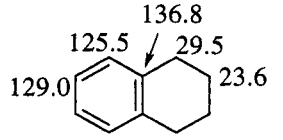












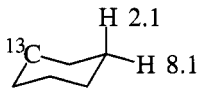
4.4.2 Coupling Constants

^{13}C-^{1}H Coupling Constants

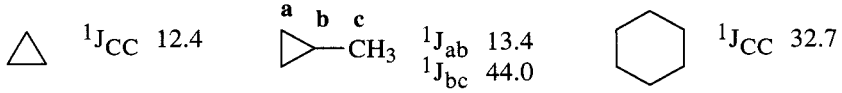
Coupling through one bond *($|^1J_{CH}|$ in Hz)*

Coupling through two bonds *($|^2J_{CH}|$ in Hz)*

Coupling through three bonds *($|^3J_{CH}|$ in Hz)*



^{13}C-^{13}C Coupling Constants *($|^1J_{CC}|$ in Hz)*



4.4.3 References

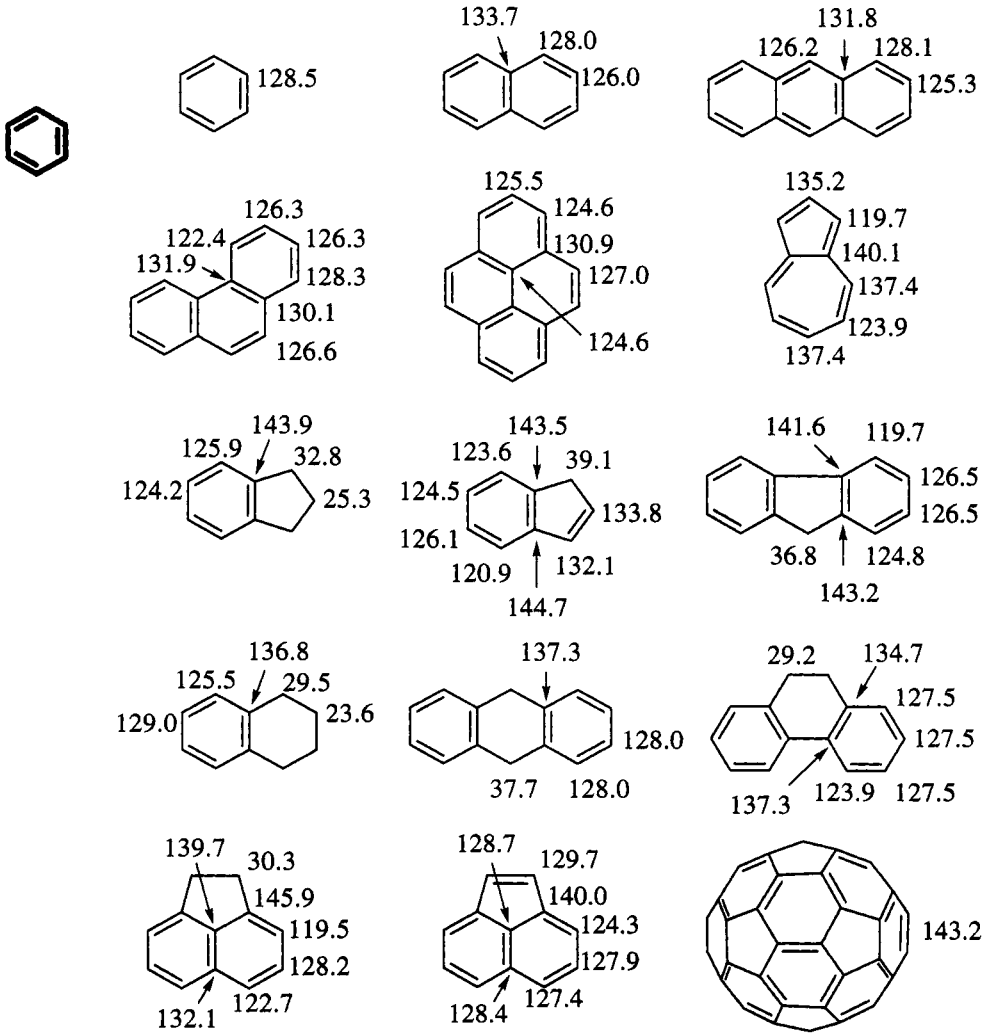
[1] N.C. Rol, A.D.H. Clague, ^{13}C NMR Spectroscopy of cyclopropane derivatives, Org. Magn. Reson. **1981**, *16*, 187.

[2] H.-J. Schneider, N. Nguyen-Ba, F. Thomas, Force field and ^{13}C NMR investigations of substituted cyclopentanes. A concept for the adaption of ^{13}C NMR shifts to varying torsional arrangements in flexible conformers, Tetrahedron **1982**, *38*, 2327.

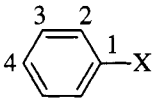
4.5 Aromatic Hydrocarbons

4.5.1 Chemical Shifts

^{13}C Chemical Shifts in Aromatic Hydrocarbons
(δ in ppm relative to TMS) [1]



Effect of Substituents on ^{13}C Chemical Shifts of Monosubstituted Benzenes *(in ppm relative to TMS)*



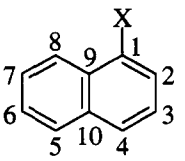
$\delta_{C_i} = 128.5 + Z_i$

	Substituent X	Z_1	Z_2	Z_3	Z_4
	–H	0.0	0.0	0.0	0.0
C	$-CH_3$	9.2	0.7	-0.1	-3.0
	$-CH_2CH_3$	11.7	-0.6	-0.1	-2.8
	$-CH_2CH_2CH_3$	10.3	-0.2	0.1	-2.7
	$-CH(CH_3)_2$	20.2	-2.2	-0.3	-2.8
	$-CH_2CH_2CH_2CH_3$	10.9	-0.2	-0.2	-2.8
	$-C(CH_3)_3$	18.6	-3.3	-0.4	-3.1
	–cyclopropyl	15.1	-3.3	-0.6	-3.6
	–cyclopentyl	17.8	-1.5	-0.4	-2.9
	–cyclohexyl	16.3	-1.8	-0.3	-2.8
	–1–adamantyl	22.2	-2.9	-0.5	-3.1
	$-CH_2F$	8.5	-0.7	0.4	0.5
	$-CF_3$	2.5	-3.2	0.3	3.3
	$-CH_2Cl$	9.3	0.3	0.2	0.0
	$-CHCl_2$	11.9	-2.4	0.1	1.2
	$-CCl_3$	16.3	-1.7	-0.1	1.8
	$-CH_2Br$	9.5	0.7	0.3	0.2
	$-CH_2I$	10.5	0.0	0.0	-0.9
	$-CH_2OH$	12.4	-1.2	0.2	-1.1
	$-CH_2OCH_3$	8.7	-0.9	-0.1	-0.9
	$-CH_2NH_2$	14.9	-1.4	-0.2	-2.0
	$-CH_2NHCH_3$	12.6	-0.3	-0.3	-1.8
	$-CH_2N(CH_3)_2$	7.8	0.5	-0.3	-1.5
	$-CH_2NO_2$	2.2	2.2	2.2	1.2
	$-CH_2CN$	1.6	0.5	-0.8	-0.7
	$-CH_2SH$	12.5	-0.6	0.0	-1.6
	$-CH_2SCH_3$	9.8	0.4	-0.1	-1.6
	$-CH_2S(O)CH_3$	0.8	1.5	0.4	-0.2
	$-CH_2SO_2CH_3$	-0.1	2.1	0.6	0.6
	$-CH_2CHO$	7.4	1.3	0.5	-1.1
	$-CH_2COCH_3$	5.8	0.8	0.1	-1.6
	$-CH_2COOH$	6.5	1.4	0.4	-1.2
	$-CH_2Li$	32.2	-22.0	-0.4	-24.3
	$-CH=CH_2$	8.9	-2.3	-0.1	-0.8
	$-C(CH_3)=CH_2$	12.6	-3.1	-0.4	-1.2
	$-C\equiv CH$	-6.2	3.6	-0.4	-0.3
	–phenyl	8.1	-1.1	0.5	-1.1
	–2-pyridyl	11.2	-1.4	0.5	-1.4
	–4-pyridyl	9.6	-1.6	0.5	0.5

	Substituent X	Z_1	Z_2	Z_3	Z_4
Hal	–F	33.6	-13.0	1.6	-4.4
	–Cl	5.3	0.4	1.4	-1.9
	–Br	-5.4	3.3	2.2	-1.0
	–I	-31.2	8.9	1.6	-1.1
O	–OH	28.8	-12.8	1.4	-7.4
	–ONa	39.6	-8.2	1.9	-13.6
	–OCH_3	33.5	-14.4	1.0	-7.7
	–$OCH{=}CH_2$	28.2	-11.5	0.7	-5.8
	–O–phenyl	27.6	-11.2	-0.3	-6.9
	–$OCOCH_3$	22.4	-7.1	0.4	-3.2
	–$OSi(CH_3)_3$	26.8	-8.4	0.9	-7.1
	–$OPO(O\text{–phenyl})_2$	21.9	-8.4	1.2	-3.0
	–OCN	25.0	-12.7	2.6	-1.0
N	–NH_2	18.2	-13.4	0.8	-10.0
	–$NHCH_3$	15.0	-16.2	0.8	-11.6
	–$N(CH_3)_2$	16.0	-15.4	0.9	-10.5
	–NH–phenyl	14.7	-10.6	0.9	-10.5
	–$N(phenyl)_2$	13.1	-7.0	0.9	-5.6
	–NH_3^+	0.1	-5.8	2.2	2.2
	–$NH_2{}^+CH(CH_3)_2$	5.5	-4.1	1.1	0.7
	–$N^+(CH_3)_3$	19.5	-7.3	2.5	2.4
	–$N(O)(CH_3)_2$	26.2	-8.4	0.8	0.6
	–$NHCOCH_3$	9.7	-8.1	0.2	-4.4
	–NHOH	21.5	-13.1	-2.2	-5.3
	–$NHNH_2$	22.8	-16.5	0.5	-9.6
	–$N(NO)CH_3$	13.7	-9.4	0.9	-1.3
	–N=CH–phenyl	24.7	-6.5	1.3	-1.5
	–$N{=}NCH_3$	22.2	-6.2	0.5	-3.0
	–NO	37.4	-7.6	0.8	7.1
	–NO_2	19.9	-4.9	0.9	6.1
	–CN	-16.0	3.5	0.7	4.3
	–NC	-1.8	-2.2	1.4	0.9
	–NCO	5.1	-3.7	1.1	-2.8
	–NCS	3.0	-2.7	1.3	-1.0
	$-N^+{\equiv}N$	-12.7	6.0	5.7	16.0
S	–SH	4.0	0.7	0.3	-3.2
	–SCH_3	10.0	-1.9	0.2	-3.6
	–$SC(CH_3)_3$	4.5	9.0	-0.3	0.0
	–$S(CH_3)_2{}^+$	-1.0	3.1	2.2	6.3
	–$SCH{=}CH_2$	5.8	2.0	0.2	-1.8
	–S–phenyl	7.3	2.5	0.6	-1.5
	–S–S–phenyl	7.5	-1.3	0.8	-1.1
	–$S(O)CH_3$	17.6	-5.0	1.1	2.4
	–SO_2CH_3	12.3	-1.4	0.8	5.1
	–SO_2OH	15.0	-2.2	1.3	3.8
	–SO_2OCH_3	6.4	-0.6	1.5	5.9
	–SO_2F	4.6	0.0	1.5	7.5

	Substituent X	Z_1	Z_2	Z_3	Z_4
	$-SO_2Cl$	15.6	-1.7	1.2	6.8
	$-SO_2NH_2$	10.8	-3.0	0.3	3.2
	-SCN	-3.7	2.5	2.2	2.2
O	-CHO	8.2	1.2	0.5	5.8
||	$-COCH_3$	8.9	0.1	-0.1	4.4
C	$-COCF_3$	-5.6	1.8	0.7	6.7
/\	$-COC{\equiv}CH$	7.4	1.0	0.0	5.9
	-CO-phenyl	9.3	1.6	-0.3	3.7
	-COOH	2.1	1.6	-0.1	5.2
	-COONa	9.7	4.6	2.2	4.6
	$-COOCH_3$	2.0	1.2	-0.1	4.3
	$-CONH_2$	5.0	-1.2	0.1	3.4
	$-CON(CH_3)_2$	6.0	-1.5	-0.2	1.0
	-COF	4.2	1.6	-0.7	5.3
	-COCl	4.7	2.7	0.3	6.6
	-COSH	6.2	-0.6	0.2	5.4
	$-CH{=}NCH_3$	8.8	0.5	0.1	2.3
	-CS-phenyl	18.7	1.0	-0.6	2.4
	-CS-(1-piperidyl)	15.0	-3.1	-0.2	-0.2
	-Li	-43.2	-12.7	2.4	3.1
	-MgBr	-35.8	-11.4	2.7	4.0
Si	$-SiH_3$	-0.5	7.3	-0.4	1.3
	$-SiH_2CH_3$	4.8	6.3	-0.5	1.0
	$-Si(CH_3)_3$	11.6	4.9	-0.7	0.4
	$-Si(phenyl)_3$	5.8	7.9	-0.6	1.1
	$-SiCl_3$	3.0	4.6	0.1	4.2
	$-Ge(CH_3)_3$	13.7	4.5	-0.5	-0.2
	$-Sn(CH_3)_3$	13.2	7.2	-0.4	-0.4
	$-Pb(CH_3)_3$	20.1	8.0	-0.1	-1.0
P	$-P(CH_3)_2$	13.6	1.6	-0.6	-1.0
	$-P(phenyl)_2$	8.9	5.2	0.0	0.1
	$-P^+(phenyl)_2CH_3$	-9.7	5.2	2.0	6.7
	$-PO(CH_3)_2$	2.5	1.1	0.1	3.0
	$-PO(-phenyl)_2$	5.8	3.9	-0.1	3.0
	$-PO(OH)_2$	-1.9	3.6	1.5	5.6
	$-PO(OCH_2CH_3)_2$	1.6	3.6	-0.2	3.4
	$-PS(CH_3)_2$	6.7	2.0	0.2	2.9
	$-PS(OCH_2CH_3)_2$	6.1	2.8	-0.4	3.4
	$-AsH_2$	1.7	7.9	0.8	0.0
	$-As(phenyl)_2$	11.1	5.0	0.1	-0.1
	$-AsO(OH)_2$	3.8	1.6	0.8	4.5
	$-SeCH{=}CH_2$	0.7	4.7	0.4	-1.4
	-SeCN	-5.3	5.1	2.9	2.1
	$-Sb(phenyl)_2$	9.8	7.7	0.3	0.0
	-Hg-phenyl	41.6	9.3	-0.9	-1.6
	-HgCl	22.5	8.0	-0.6	-0.9

Effect of Substituents in Position 1 on the ^{13}C Chemical Shifts of Monosubstituted Naphthalenes *(in ppm relative to TMS)*



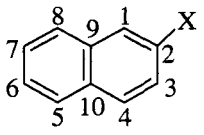
for X: H $\delta_{C_1} = 128.0$

$\delta_{C_2} = 125.9$

$\delta_{C_9} = 133.6$

	Substituent X	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
C	$-CH_3$	6.0	0.5	0.6	-1.8	0.3	-0.7	-0.5	-4.1	-1.1	-0.2
	$-C(CH_3)_3$	17.9	-2.8	-0.9	-0.6	1.6	-1.4	-1.4	-1.2	-1.6	2.2
	$-CH_2Br$	4.0	1.1	-0.9	1.3	0.5	-0.1	0.3	-4.6	-2.8	0.1
	$-CH_2OH$	8.2	-0.9	-0.6	0.1	0.5	-0.3	0.1	-4.5	-2.6	0.0
	$-CF_3$		-1.3	-1.8	5.0	1.0	0.8	2.0	-3.4	1.0	-3.9
H	-F	31.5	-16.1	0.1	-3.8	0.1	1.4	0.7	-7.1	-9.3	2.1
a	-Cl	3.9	0.2	-0.2	-0.9	0.2	3.1	0.8	-3.6	-2.8	1.0
l	-Br	-5.4	3.6	-0.2	-0.5	-0.1	0.4	1.0	-1.3	-2.0	0.6
	-I	-28.4	12.3	1.7	1.7	1.4	1.6	2.6	4.4	1.3	1.3
O	-OH	23.5	-17.2	-0.1	-7.3	-0.4	0.5	0.3	-6.6	-9.3	1.0
	$-OCH_3$	27.3	-22.3	-0.2	-7.9	-0.7	0.3	-0.9	-6.1	-8.1	0.8
	$-OCOCH_3$	18.6	-7.9	-0.6	-2.1	0.0	0.4	0.4	-6.9	-6.9	0.9
N	$-NH_2$	14.0	-16.5	0.3	-9.3	0.3	-0.3	-1.3	-7.3	-10.2	0.6
	$-N(CH_3)_2$	23.7	-11.2	0.6	-4.6	1.0	0.4	-0.3	-3.2	-3.9	2.1
	$-NH_3^+$	-3.8	-4.6	-0.9	3.4	1.4	2.1	2.8	-9.0	-7.4	1.2
	$-NO_2$	18.5	-2.1	-2.0	6.5	0.5	1.3	3.4	-5.1	-8.7	0.6
	-CN	-19.2	5.1	-2.4	3.8	-0.7	0.2	1.2	-4.5	-2.8	-2.2
O	-CHO	2.9	10.8	-1.4	6.7	0.2	0.6	2.7	-3.5	-3.6	-0.3
||	$-COCH_3$	6.9	2.9	-1.7	4.9	0.3	0.4	2.0	-2.0	-3.5	0.2
C	-COOH	-1.5	3.6	-2.4	4.3	-0.6	-0.9	0.6	-3.2	-3.2	-0.8
/\	$-COOCH_3$	-0.9	4.5	-1.2	5.4	0.7	0.5	1.9	-1.8	-1.9	0.5
	$-CON(CH_3)_2$	6.8	-2.1	-0.8	0.9	0.4	0.4	1.0	0.1	-4.1	-0.2
	-COCl	1.2	10.6	-0.5	9.3	1.9	2.1	4.5	-2.1	-2.1	1.0
	$-Si(CH_3)_3$	9.8	5.1	-0.4	1.7	1.2	-0.8	-0.7	0.1	3.8	0.2

Effect of Substituents in Position 2 on the ^{13}C Chemical Shifts of Monosubstituted Naphthalenes *(in ppm relative to TMS)*



for X: H $\delta_{C_1} = 128.0$

$\delta_{C_2} = 125.9$

$\delta_{C_9} = 133.6$

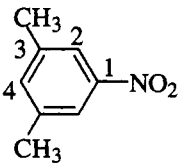
Substituent X		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
C	$-CH_3$	-1.3	9.3	2.0	-0.8	-0.5	-1.1	-0.2	-0.6	-0.1	-2.0
	$-C(CH_3)_3$	-3.3	22.5	-3.0	-0.4	0.0	-0.7	-0.2	-0.6	0.4	-1.3
	$-CH_2Br$	-1.7	9.0	1.9	-0.4	-0.5	0.7	0.3	0.6	-0.6	-0.7
	$-CH_2OH$	-2.7	12.3	-4.4	-0.1	-0.4*	-0.2*	0.1*	-0.2*	-0.3	-0.8
	$-CF_3$	-2.0		-4.2	1.1*	0.1*	2.4*	1.5	1.1	-1.1	1.3
H	-F	-17.0	34.9	-9.6	2.4	0.0	-0.7	1.1	-0.6	0.7	-3.0
a	-Cl	-1.4	5.7	0.8	1.5	-0.2	0.2	1.1	-1.1	0.7	-1.9
l	-Br	1.8	-6.2	3.1	1.5	-0.3	0.2	0.8	-1.1	-2.0	0.7
	-I	9.2	-34.1	9.0	2.3	0.5	1.3	1.5	-0.6	2.1	-0.8
O	-OH	-18.6	27.3	-8.3	1.8	-0.3	-2.4	0.5	-1.7	0.9	-4.7
	$-OCH_3$	-22.2	31.8	-7.1	1.5	-0.3	-2.2	0.5	-1.2	1.0	-4.3
	$-OCOCH_3$	-9.5	22.5	-4.8	1.3	-0.4	-0.3	0.6	-0.4	0.1	-2.2
N	$-NH_2$	-20.6	16.7	-8.9	-0.2	-1.6	-4.8	-0.9	-3.5	-0.1	-7.0
	$-N(CH_3)_2$	-21.1	23.6	-8.8	1.2	0.0	-3.4	0.7	-1.1	2.4	-5.9
	$-NH_3^+$	-5.9	-0.3	-6.5	3.2	0.2	2.3	2.0	0.2	0.1	-0.3
	$-NO_2$	-3.4	20.0	-6.7	1.7	0.1	4.0	2.2	2.1	-1.1	2.4
	-CN	5.8	-16.7	0.1	1.0	-0.2	3.0	1.6	0.2	-1.6	0.7
O	-CHO	6.2	7.9	-3.6	0.8	-0.3	2.9	0.9	1.8	2.4	-1.4
||	$-COCH_3$	1.9	8.3	-2.2	0.2	-0.4	2.3	0.7	1.4	1.8	-1.3
C	-COOH	2.7	2.4	-0.6	0.2	-0.3	2.4	0.9	1.3	-1.3	1.5
/\	$-COOCH_3$	3.0	1.8	-0.5	0.2	-0.1	2.4	0.9	1.4	-1.0	1.9
	-COCl	2.5	9.1	-0.7	0.2*	-0.4	2.2*	0.8	1.2		-1.4
	$-Si(CH_3)_3$	5.8	11.9	3.9	-1.0	0.1	0.3	-0.2	0.1	-0.5	0.2

* assignment uncertain

Estimation of ^{13}C Chemical Shifts of Multiply Substituted Benzenes and Naphthalenes

The ^{13}C chemical shifts of multiply substituted benzenes and naphthalenes can be estimated using the substituent effects in the corresponding monosubstituted hydrocarbons.

Example: Estimation of the chemical shifts for 3,5-dimethylnitrobenzene



C-1 base value	128.5
$Z_1(NO_2)$	19.9
$2\,Z_3(CH_3)$	-0.2
estimated	148.2
exp	148.5

C-2 base value	128.5
$Z_2(NO_2)$	-4.9
$Z_2(CH_3)$	0.7
$Z_4(CH_3)$	-3.0
estimated	121.3
exp	121.7

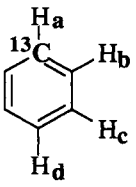
C-3 base value	128.5
$Z_1(CH_3)$	9.2
$Z_3(CH_3)$	-0.1
$Z_3(NO_2)$	0.9
estimated	138.5
exp	139.6

C-4 base value	128.5
$2\ Z_2(CH_3)$	1.4
$Z_4(NO_2)$	6.1
estimated	136.0
exp	136.2

Larger discrepancies between estimated and experimental values are to be expected if the substituents are *ortho* to each other or if strongly electron-donating and electron-accepting groups occur simultaneously.

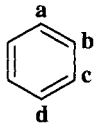
4.5.2 Coupling Constants

^{13}C-^{1}H Coupling Constants ($|J|$ in Hz)

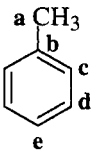


	In benzene:	In derivatives:
$^1J_{C_aH_a}$	159.0	
$^2J_{C_aH_b}$	1.0	1–4
$^3J_{C_aH_c}$	7.6	7–10
$^4J_{C_aH_d}$	-1.3	

^{13}C-^{13}C Coupling Constants ($|^1J_{CC}|$ in Hz)



$^1J_{ab}$	57.0
$^2J_{ac}$	2.5
$^3J_{ad}$	10.0



$^1J_{ab}$	44.2
$^2J_{ac}$	3.1
$^3J_{ad}$	3.8
$^4J_{ae}$	0.9

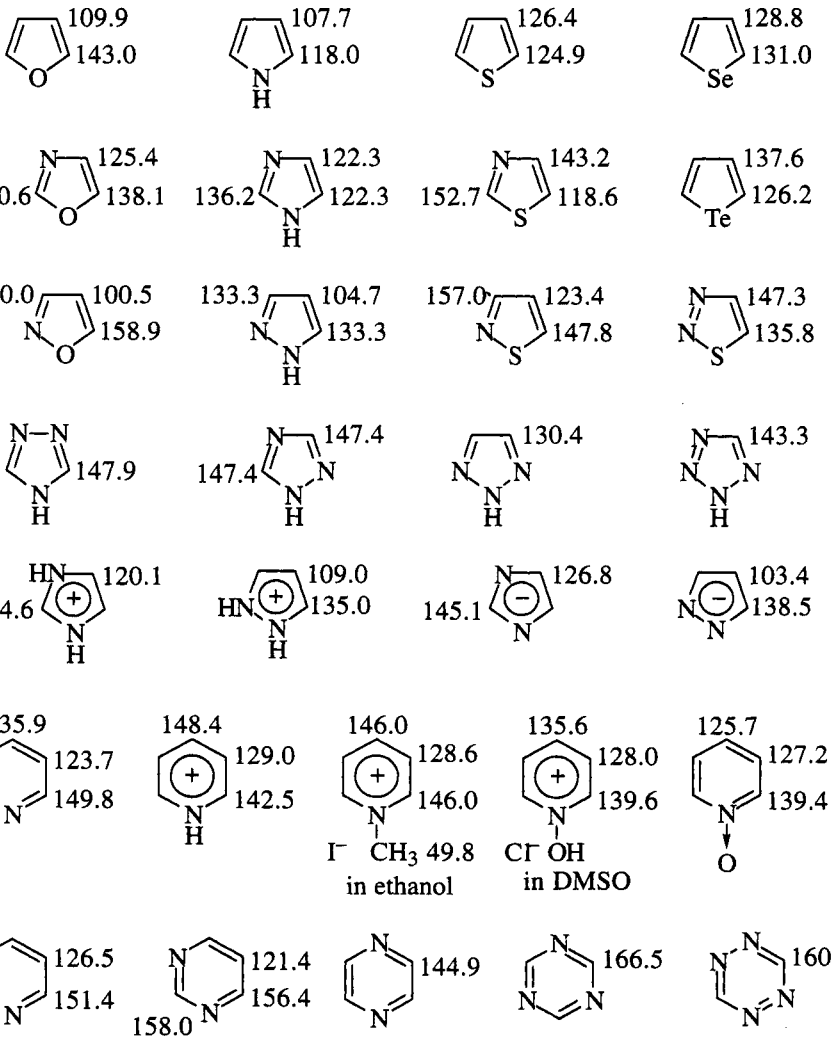
4.5.3 References

[1] P.E. Hansen, ^{13}C NMR of polycyclic aromatic hydrocarbons. A review, Org. Magn. Reson. **1979**, *12*, 109.

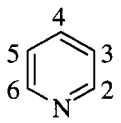
4.6 Heteroaromatic Compounds

4.6.1 Chemical Shifts

^{13}C Chemical Shifts of Heteroaromatic Compounds
(δ in ppm relative to TMS)



Effect of Substituents on the ^{13}C Chemical Shifts of Monosubstituted Pyridines *(in ppm relative to TMS)*



$\delta_{C\text{-}2} = 149.8 + Z_{i,2}$
$\delta_{C\text{-}3} = 123.7 + Z_{i,3}$
$\delta_{C\text{-}4} = 135.9 + Z_{i,4}$
$\delta_{C\text{-}5} = 123.7 + Z_{i,5}$
$\delta_{C\text{-}6} = 149.8 + Z_{i,6}$

	Substituent in position 2 or 6	$Z_{22} = Z_{66}$	$Z_{23} = Z_{65}$	$Z_{24} = Z_{64}$	$Z_{25} = Z_{63}$	$Z_{26} = Z_{62}$
	–H	0.0	0.0	0.0	0.0	0.0
C	$-CH_3$	8.6	-0.5	0.3	-3.0	-0.7
	$-CH_2CH_3$	13.7	-1.7	0.4	-2.8	-0.6
	$-CH{=}CH_2$	5.9	-1.3	1.1	-2.5	-0.3
	–phenyl	7.7	-1.6	0.8	-3.2	0.2
H	–F	13.9	-14.0	5.4	-2.5	-2.0
a	–Cl	1.8	0.8	2.8	-1.4	0.0
l	–Br	-7.5	4.6	2.6	-1.1	0.5
	–I	-31.6	11.3	1.7	-0.8	1.0
O	–OH	15.5	-3.6	-1.1	-17.0	-8.2
	$-OCH_3$	14.3	-12.7	2.6	-7.1	-2.9
	–O–phenyl	13.9	-12.2	3.5	-5.3	-2.0
	$-OCOCH_3$	7.6	-7.3	3.4	-1.8	-1.6
N	$-NH_2$	8.4	-15.1	1.8	-9.7	-1.6
	$-NHCH_3$	10.9	-16.2	1.5	-11.3	-1.3
	$-N(CH_3)_2$	9.6	-17.9	1.2	-12.3	-1.9
	$-NHCOCH_3$	1.4	-9.8	2.6	-3.9	-2.1
	$-NO_2$	6.9	-5.7	3.9	5.4	-0.8
	–CN	-15.8	4.8	1.1	3.2	1.4
S	–SH	30.4	10.7	2.1	-10.6	-12.1
	$-SCH_3$	10.2	-4.6	0.0	-2.2	-0.5
	$-S(=O)CH_3$	16.2	-4.4	2.2	0.9	-0.2
	$-S(=O)_2CH_3$	8.5	-2.6	2.4	3.7	0.3
O	–CHO	3.0	-2.0	1.2	4.2	0.4
||	$-COCH_3$	3.8	-2.1	0.9	3.4	-0.8
C	–COOH	-3.7	0.0	2.5	4.2	-1.7
/\	$-COOCH_3$	-1.7	1.5	1.1	3.3	0.0
	$-CONH_2$	-0.3	-1.2	1.4	2.8	-1.5
	$-Si(CH_3)_3$	18.6	5.0	-2.0	-1.1	0.3
	$-Sn(CH_3)_3$	23.3	7.6	-2.7	-1.7	0.6
	$-Pb(CH_3)_3$	33.4	9.2	-2.6	-2.3	1.1

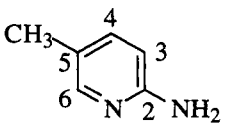
	Substituent in position 3 or 5	$Z_{32} = Z_{56}$	$Z_{33} = Z_{55}$	$Z_{34} = Z_{54}$	$Z_{35} = Z_{53}$	$Z_{36} = Z_{52}$
	–H	0.0	0.0	0.0	0.0	0.0
C	$-CH_3$	1.3	8.9	0.0	-0.9	-2.3
	$-CH_2CH_3$	-0.4	15.4	-0.8	-0.5	-2.7
	–phenyl	-1.4	12.8	-1.8	-0.3	-1.3
Hal	–F	-11.5	36.1	-13.2	0.8	-3.9
	–Cl	-0.3	8.1	-0.4	0.6	-1.4
	–Br	2.1	-2.7	2.7	1.1	-0.9
	–I	7.1	-28.5	8.9	2.3	0.3
O	–OH	-10.7	31.3	-12.4	1.2	-8.6
	$-OCH_3$	-12.5	31.5	-15.9	0.1	-8.4
	$-OCOCH_3$	-6.5	23.4	-7.0	-0.1	-3.2
N	$-NH_2$	-11.9	21.4	-14.4	0.8	-10.8
	$-NHCH_3$	-13.6	23.1	-18.2	0.6	-11.9
	$-N(CH_3)_2$	-14.0	23.3	-17.1	0.1	-11.6
	–CN	3.6	-13.8	4.2	0.5	4.2
S	–SH	-12.8	26.1	-11.3	7.3	-2.8
	$-SCH_3$	-13.6	24.6	-11.7	10.6	-3.0
O	–CHO	2.4	7.8	-0.2	0.5	5.4
||	$-COCH_3$	3.5	8.5	-0.7	-0.2	0.0
C	–COOH	-6.4	13.0	11.1	4.3	-6.0
/\	$-COOCH_3$	-0.6	1.0	-0.5	-1.8	1.8
	$-CONH_2$	2.7	5.9	1.1	1.2	-1.5
	$-Si(CH_3)_3$	2.7	9.1	3.0	-2.3	-1.2
	$-Ge(CH_3)_3$	3.9	12.8	4.2	-0.4	-0.1
	$-Sn(CH_3)_3$	5.9	13.0	7.1	0.1	-0.3
	$-Sn(n\text{-}C_4H_9)_3$	6.6	12.6	7.7	0.0	-0.4
	$-Pb(n\text{-}C_4H_9)_3$	7.1	21.7	8.5	0.9	-1.8

	Substituent in position 4	$Z_{42} = Z_{46}$	$Z_{43} = Z_{45}$	Z_{44}
	–H	0.0	0.0	0.0
C	$-CH_3$	0.5	0.7	10.6
	$-CH_2CH_3$	-0.1	-0.5	16.8
	$-CH(CH_3)_2$	0.4	-1.9	21.2
	$-C(CH_3)_3$	0.9	-2.6	23.9
	$-CH=CH_2$	0.3	-3.0	8.4
	–phenyl	0.4	-2.2	12.2
H	–F	2.7	-11.9	32.8
a	–Br	3.0	3.3	-3.2
l	–I	0.2	9.1	-30.8
O	$-OCH_3$	0.9	-13.9	29.0
	$-OCOCH_3$	1.7	-6.7	23.9
N	$-NH_2$	0.7	-13.8	19.3
	$-NHCH_3$	0.5	-15.9	19.8
	$-N(CH_3)_2$	0.6	-16.3	19.2
	–CN	2.1	2.1	-15.9
S	–SH	-16.9	5.9	54.3
	$-SCH_3$	0.1	-3.3	14.6
O	–CHO	1.7	-0.7	5.3
||	$-COCH_3$	1.6	-2.7	6.6
C	$-COOCH_3$	1.0	-0.8	1.4
/\	$-CONH_2$	0.4	-0.9	6.2
	$-Si(CH_3)_3$	-2.8	2.4	11.9
	$-Ge(CH_3)_3$	-1.1	4.4	16.8
	$-Sn(CH_3)_3$	-1.1	7.3	16.2
	$-Pb(CH_3)_3$	-0.5	9.1	24.6

Estimation of ^{13}C Chemical Shifts of Multiply Substituted Pyridines

The ^{13}C chemical shifts in multiply substituted pyridines can be estimated using the substituent effects in the monosubstituted parent compound.

Example: Estimation of the chemical shifts for 2-amino-5-methylpyridine



C-2 base value		149.8
	$Z_{22}(NH_2)$	8.4
	$Z_{52}(CH_3)$	-2.3
	estimated	155.9
	exp	156.9

C-3 base value		123.7
	$Z_{23}(NH_2)$	-15.1
	$Z_{53}(CH_3)$	-0.9
	estimated	107.7
	exp	108.4

C-4 base value		135.9
	$Z_{24}(NH_2)$	1.8
	$Z_{54}(CH_3)$	0.0
	estimated	137.7
	exp	138.6

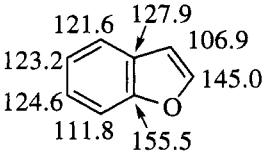
C-5 base value		123.7
	$Z_{25}(NH_2)$	-9.7
	$Z_{55}(CH_3)$	8.9
	estimated	122.9
	exp	122.5

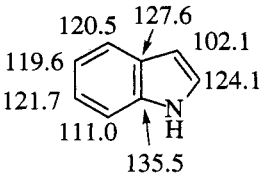
C-6 base value		149.8
	$Z_{26}(NH_2)$	-1.6
	$Z_{56}(CH_3)$	1.3
	estimated	149.5
	exp	147.6

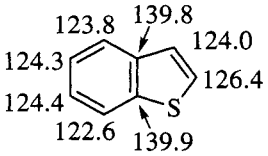
Larger discrepancies between estimated and experimental values are to be expected if the substituents are *ortho* to each other and if strongly electron-donating and -accepting groups occur simultaneously. Also, tautomerization and zwitterion formation have large effects on ^{13}C chemical shifts.

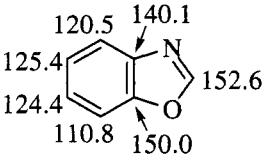
^{13}C *Chemical Shifts of Condensed Heteroaromatic Rings*

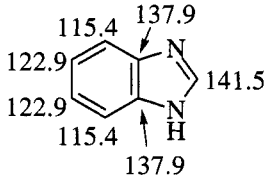
(δ in ppm relative to TMS)

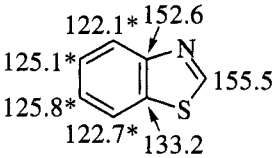


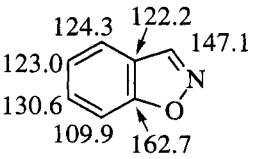


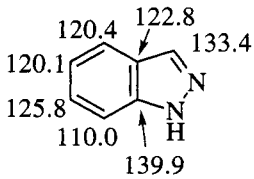


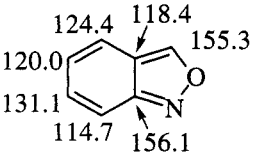


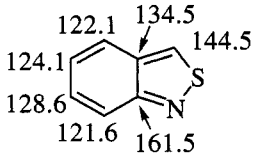


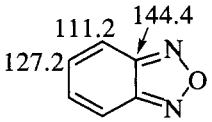


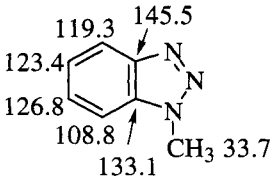


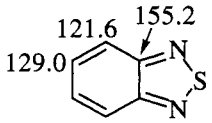


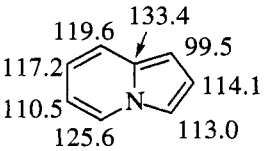


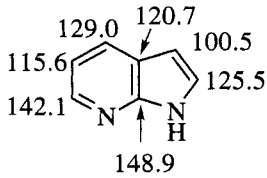


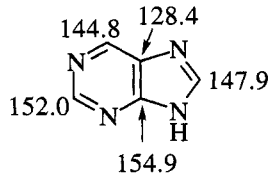




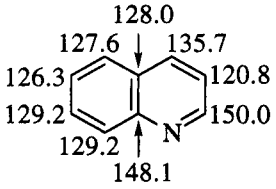


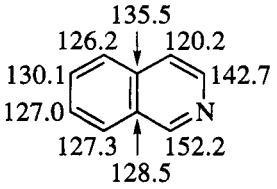


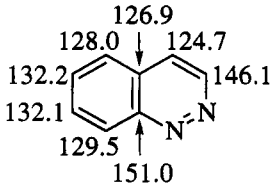


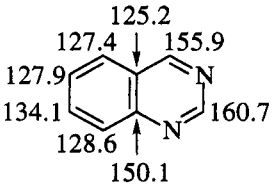


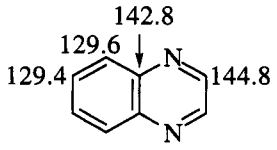
* assignment uncertain

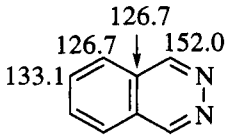


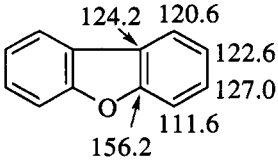


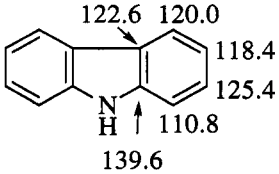


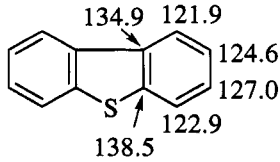


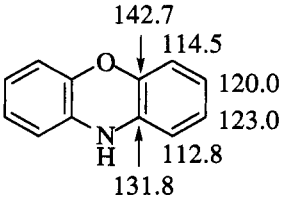


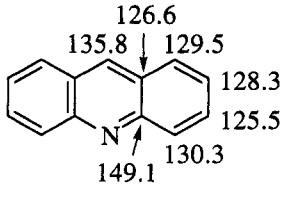


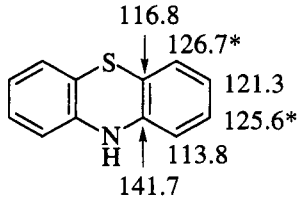


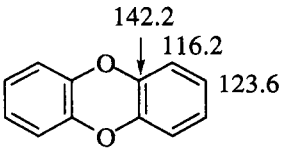


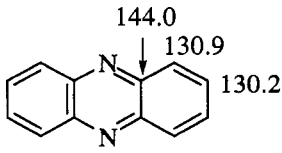


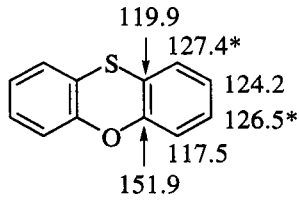










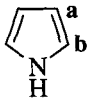


* assignment uncertain

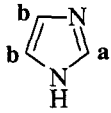
4.6.2 Coupling Constants

^{13}C-^{1}H Coupling Constants ($|J|$ in Hz)

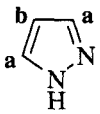
$^{1}J_{CaHa}$ 175
$^{1}J_{CbHb}$ 202



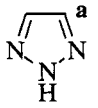
$^{1}J_{CaHa}$ 169
$^{1}J_{CbHb}$ 183



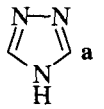
$^{1}J_{CaHa}$ 206
$^{1}J_{CbHb}$ 189



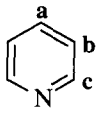
$^{1}J_{CaHa}$ 186
$^{1}J_{CbHb}$ 177



$^{1}J_{CaHa}$ 194



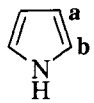
$^{1}J_{CaHa}$ 209



$^{1}J_{CaHa}$ 161
$^{1}J_{CbHb}$ 163
$^{1}J_{CcHc}$ 178

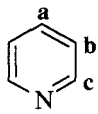
^{13}C-^{13}C Coupling Constants ($|J_{CC}|$ in Hz)

$^{1}J_{CaCb}$ 69,1



$^{1}J_{CaCb}$ 65.6

$^{1}J_{CaCb}$ 64.2



$^{1}J_{CaCb}$ 53.7
$^{1}J_{CbCc}$ 54.3

4.7 Halogen Compounds

The additivity rules for estimating the ^{13}C chemical shifts of various skeletons can be applied to those haloalkanes that do not have more than one halogen atom at a given carbon atom. In all other cases, the simple linear models fail but correction terms for non-additivity are available for halomethanes and derivatives (see [1, 2]).

4.7.1 Fluoro Compounds

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

^{13}C Chemical Shifts and ^{19}F-^{13}C Coupling Constants of Fluoro Compounds *(δ in ppm relative to TMS, $|J|$ in Hz)*

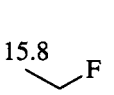
71.6 CH_3F J_{CF} 161.9

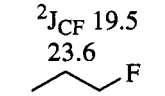
109.0 CH_2F_2 J_{CF} 234.8

116.4 CHF_3 J_{CF} 274.3

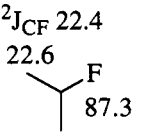
118.5 CF_4 J_{CF} 259.2

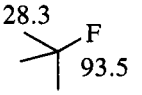
Hal

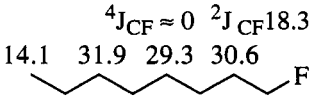




$^3J_{CF}$ 6.7 $^1J_{CF}$ 163.3



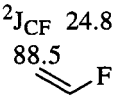




$^3J_{CF}$ 6.2 $^1J_{CF}$ 164.8

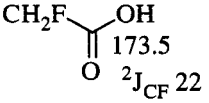
116.2
CF_3–CF_3

$^1J_{CF}$ 271
$^2J_{CF}$ 48.1

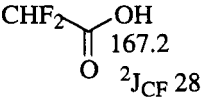


$^1J_{CF}$ 267.2

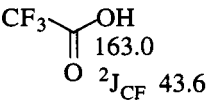
$^1J_{CF}$ 177
78.9

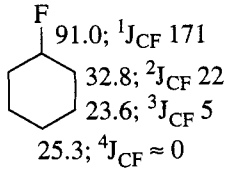


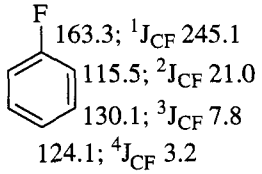
$^1J_{CF}$ 239
108.1

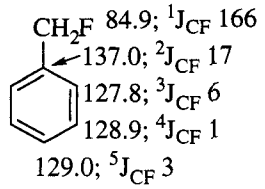


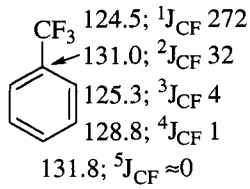
$^1J_{CF}$ 283.2
115.0

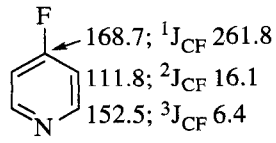


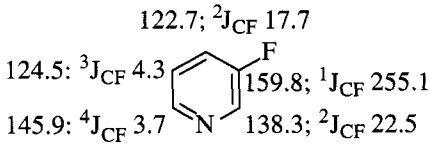


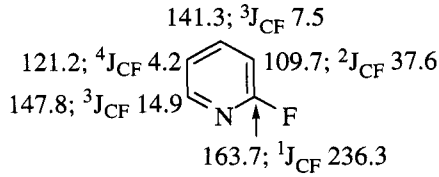












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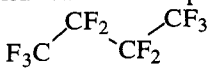
Estimation of ^{13}C Chemical Shifts of Linear Perfluoroalkanes *(δ in ppm relative to TMS)* [3]

$$\delta = 124.8 + \sum_i Z_i$$

Increments Z_i for the CF_2- or CF_3-substituent in position:		
α	β	γ
-8.6	1.8	0.5

Example: Estimation of the chemical shifts in perfluorobutane



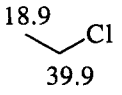
CF_3	base value	124.8
	1 α CF_2	-8.6
	1 β CF_2	1.8
	1 γ CF_3	0.5
	estimated	118.5
	exp	118.5

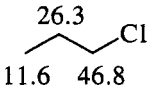
CF_2	base value	124.8
	1 α CF_3	-8.6
	1 α CF_2	-8.6
	1 β CF_3	1.8
	estimated	109.4
	exp	109.3

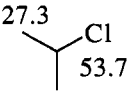
4.7.2 Chloro Compounds

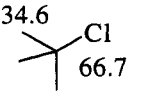
^{13}C Chemical Shifts of Chloro Compounds (δ in ppm relative to TMS)

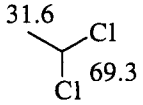
25.6 CH_3Cl | 54.0 CH_2Cl_2 | 77.2 $CHCl_3$ | 96.1 CCl_4

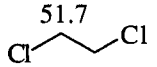


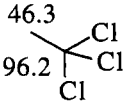




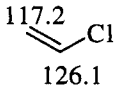


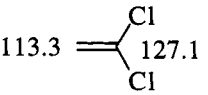


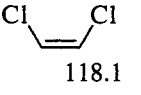


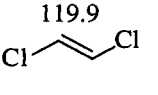


105.3 CCl_3–CCl_3









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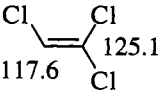
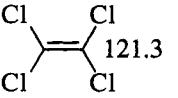
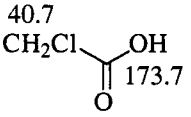
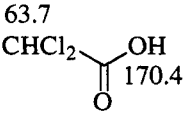
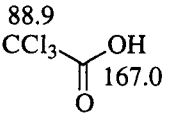
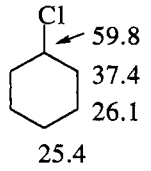


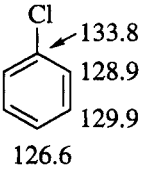


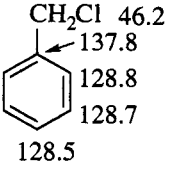


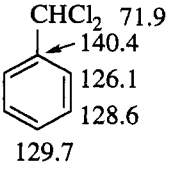


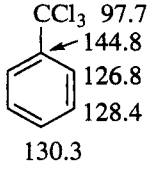


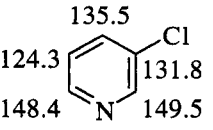


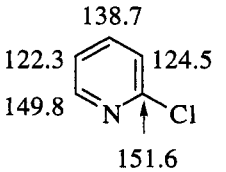






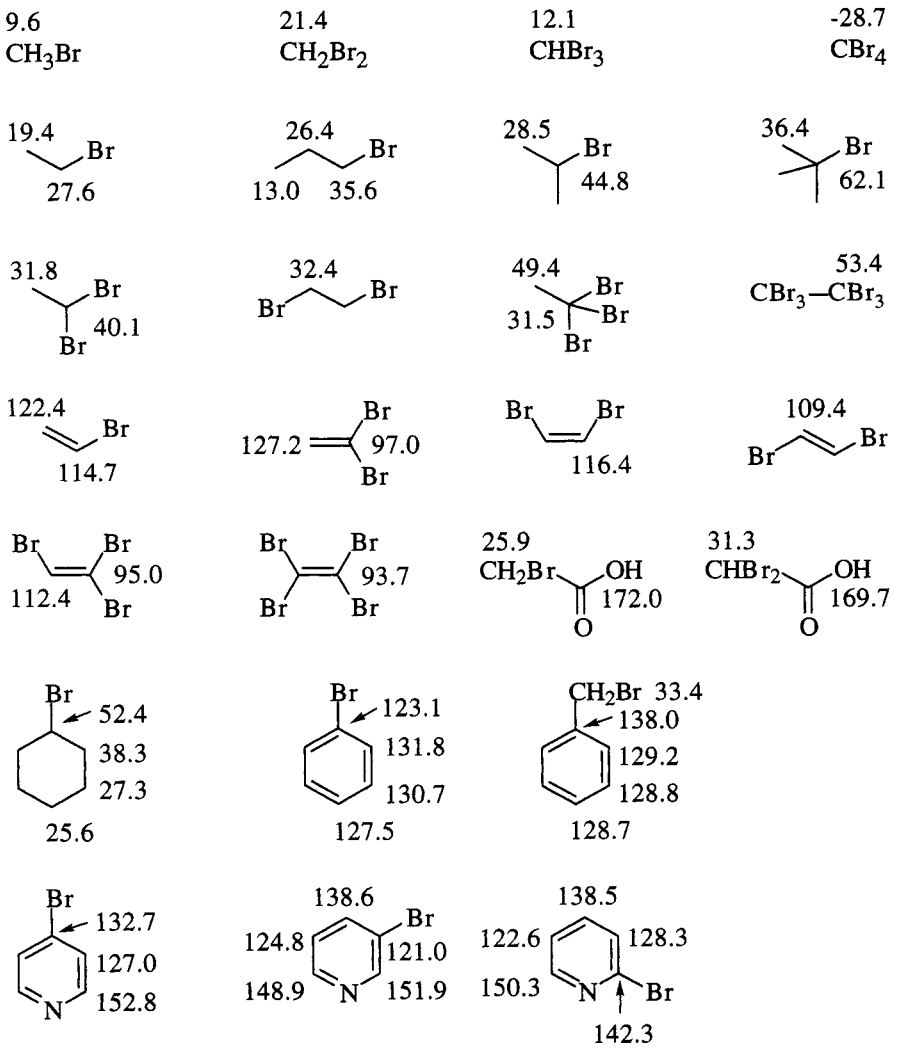






4.7.3 Bromo Compounds

^{13}C Chemical Shifts of Bromo Compounds (δ in ppm relative to TMS)



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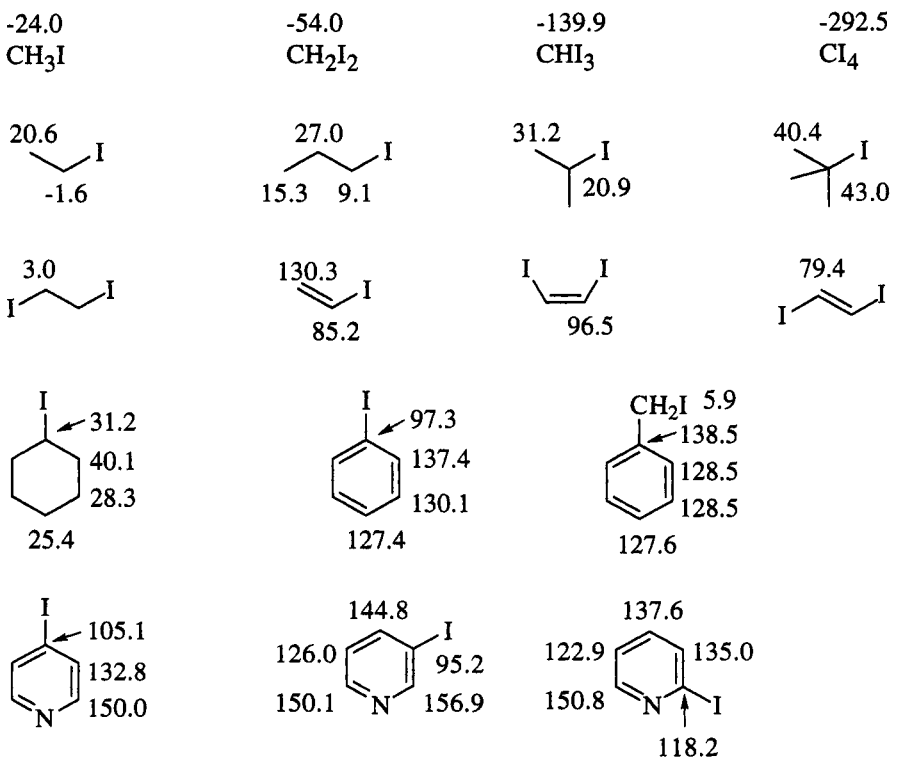
4.7.4 Iodo Compounds

^{13}C Chemical Shifts of Iodo Compounds (δ in ppm relative to TMS)



4.7.5 References

[1] G.R. Somayajulu, J.R. Kennedy, T.M. Vickrey, B.J. Zwolinski, Carbon-13 chemical shifts for 70 halomethanes, J. Magn. Reson. **1979**, *33*, 559.

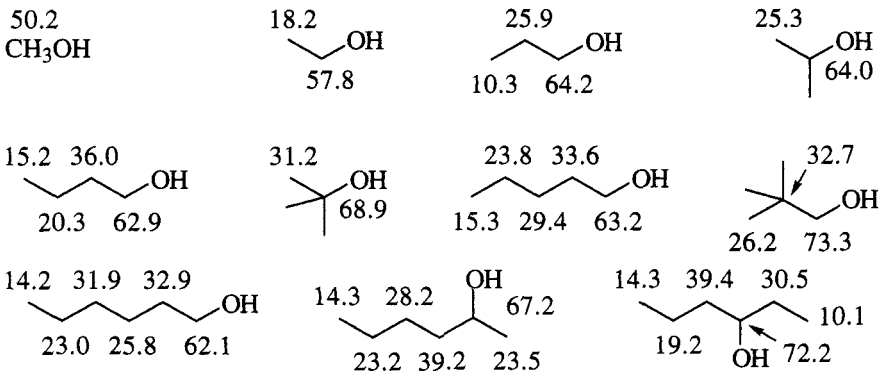
[2] A. Fürst, W. Robien, E. Pretsch, A comprehensive parameter set for the prediction of the ^{13}C NMR chemical shifts of sp^3-hybridized carbon atoms in organic compounds, Anal. Chim. Acta **1990**, *233*, 213.

[3] D.W. Ovenall, J.J. Chang, Carbon-13 NMR of fluorinated compounds using wide-band fluorine decoupling, J. Magn. Reson. **1977**, *25*, 361.

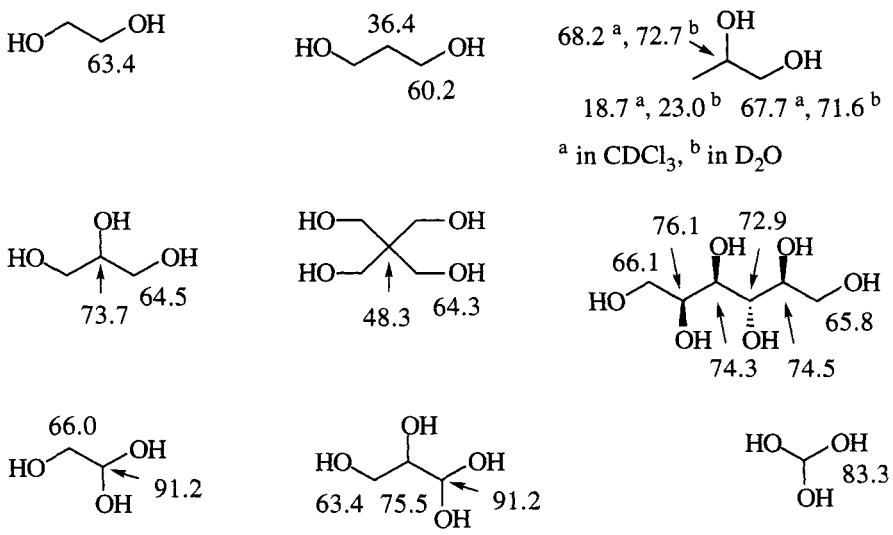
4.8
Alcohols, Ethers, and Related Compounds

4.8.1
Alcohols

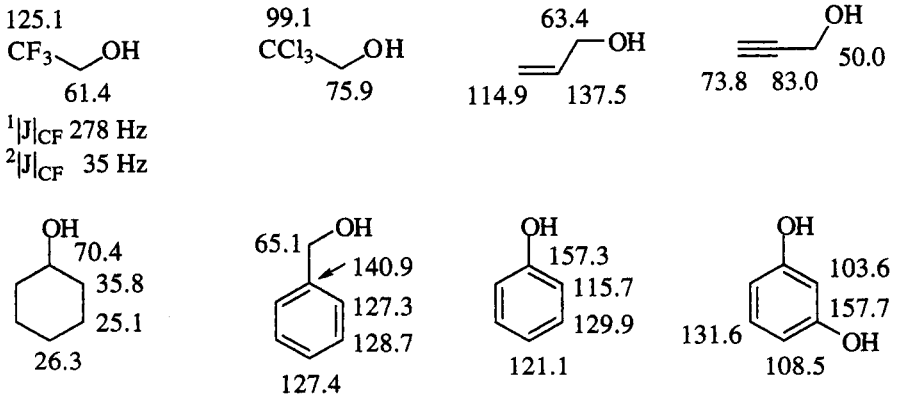
^{13}C Chemical Shifts of Aliphatic Alcohols (δ in ppm relative to TMS)



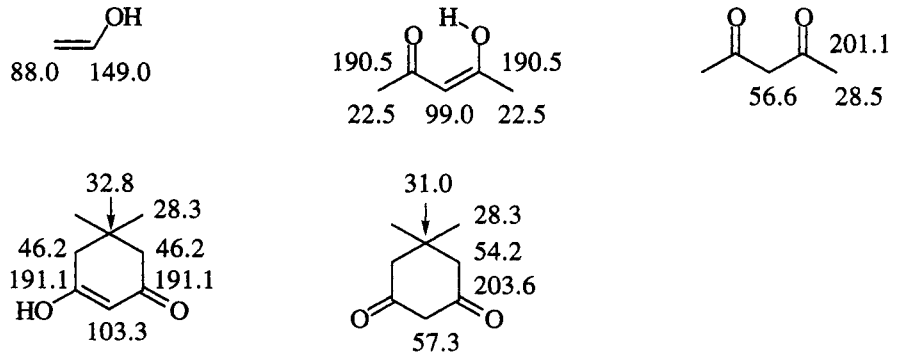
^{13}C Chemical Shifts of Aliphatic Glycols and Polyols (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Alcohols (δ in ppm relative to TMS)

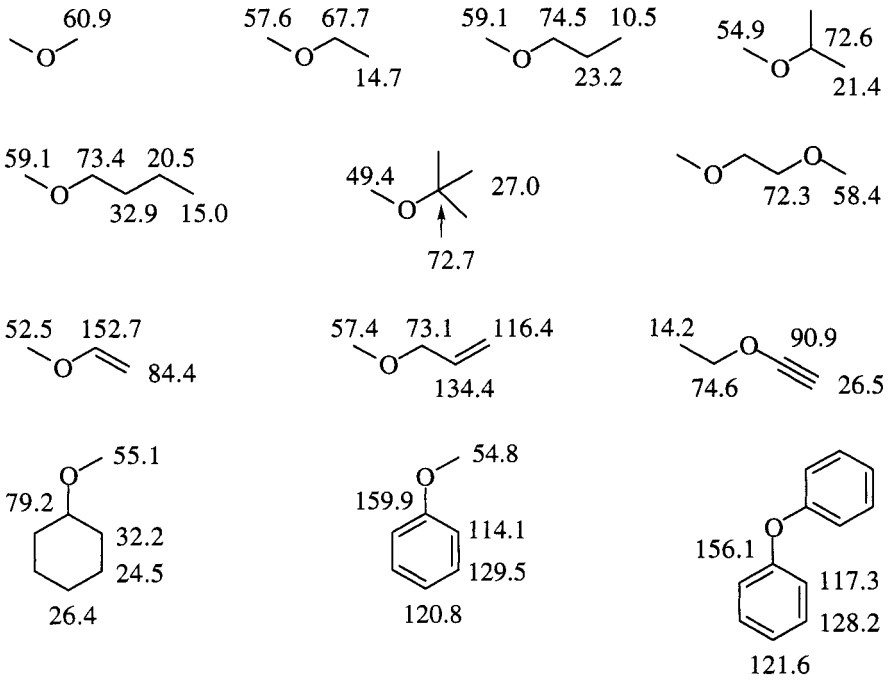


^{13}C Chemical Shifts of Enols (δ in ppm relative to TMS)

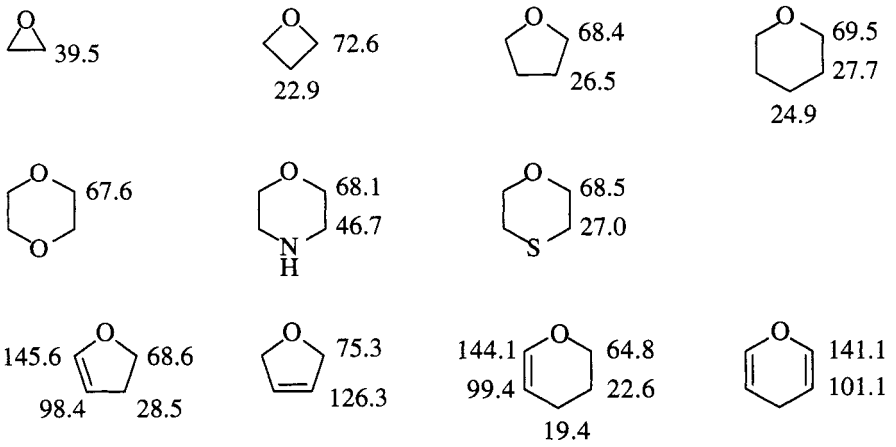


4.8.2 Ethers

^{13}C Chemical Shifts of Ethers (δ in ppm relative to TMS)

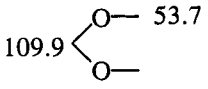


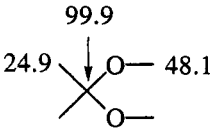
^{13}C Chemical Shifts of Cyclic Ethers (δ in ppm relative to TMS)

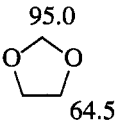


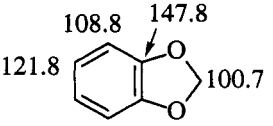
^{13}C Chemical Shifts of Acetals, Ketals and Ortho Esters

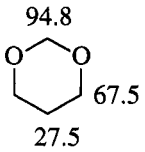
(δ in ppm relative to TMS)

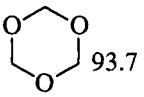


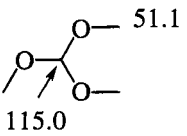


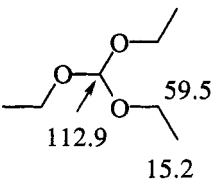


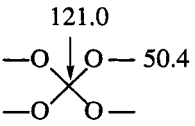












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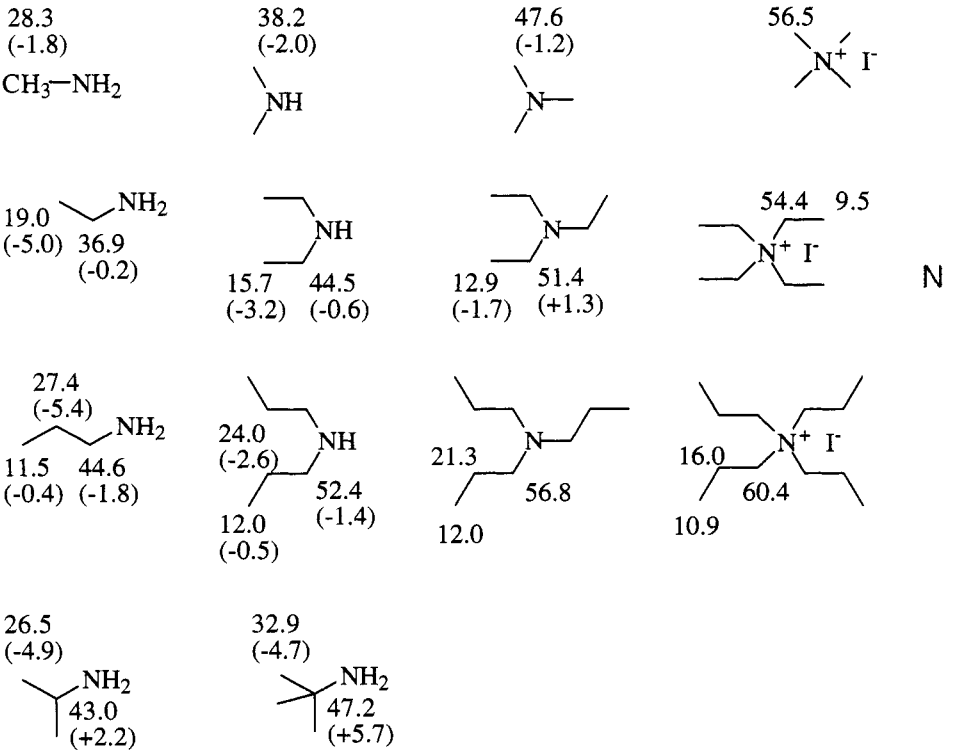
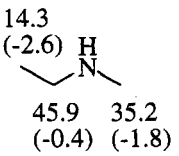
4.9
Nitrogen Compounds

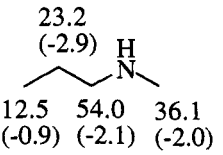
4.9.1
Amines

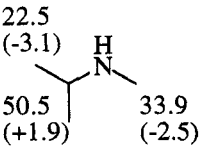
^{13}C Chemical Shifts of Amines *(δ in ppm relative to TMS)* ***as well as Shifts Induced by Protonation*** *(in parentheses: $\delta_{amine\ hydrochloride} - \delta_{amine}$, measured in D_2O)*

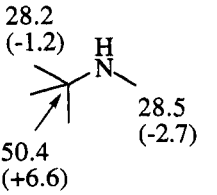
The protonation of amines causes a shielding of the carbon atoms in the vicinity of the nitrogen. This shielding amounts to -2 ppm for an α-carbon atom, -3 to -4 for a β-carbon, and -0.5 to -1.0 ppm for a γ-carbon. The most frequent exceptions occur in branched systems: Tertiary and quaternary carbon atoms in the α-position are generally deshielded by protonation of the nitrogen ($\Delta\delta$ = +0.5 to + 9 ppm) [1].

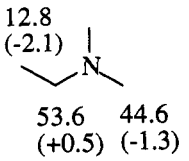


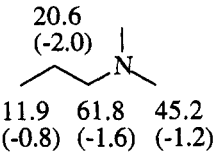


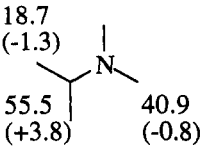


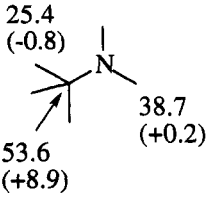


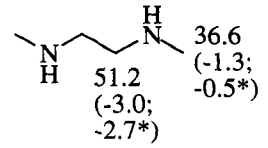




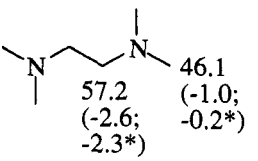




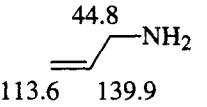


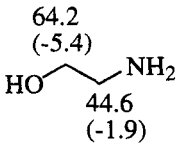


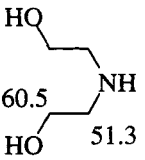
*doubly protonated form

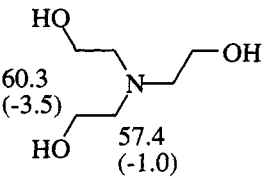


*doubly protonated form









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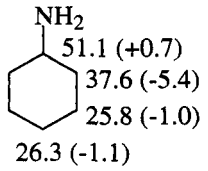
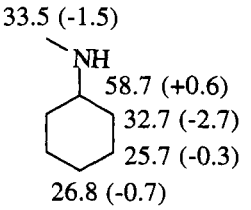
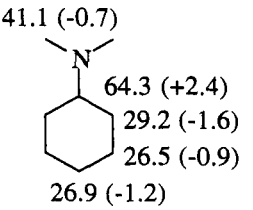
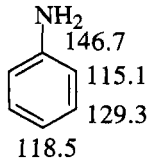
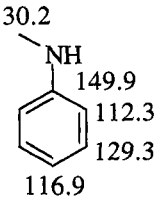
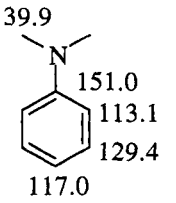


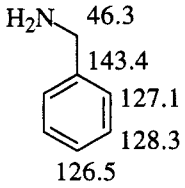


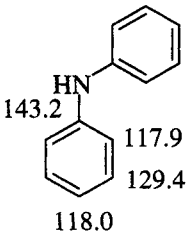


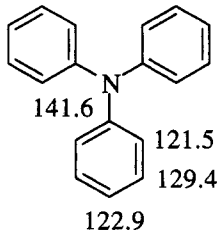




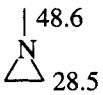


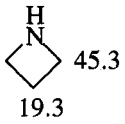


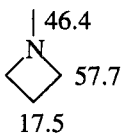


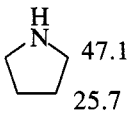


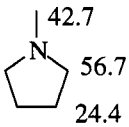
^{13}C Chemical Shifts of Cyclic Amines *(δ in ppm relative to TMS)*

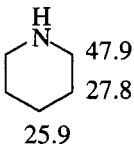


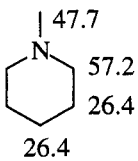


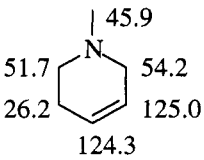


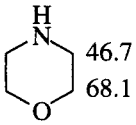


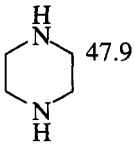


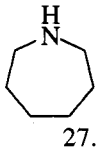








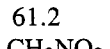


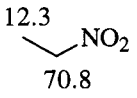


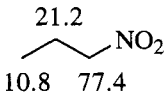
N

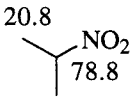
4.9.2 Nitro and Nitroso Compounds

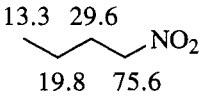
^{13}C Chemical Shifts of Nitro and Nitroso Compounds
(δ in ppm relative to TMS)

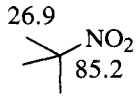


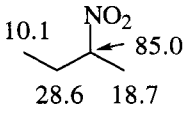


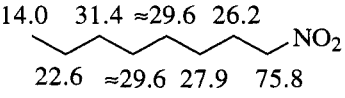


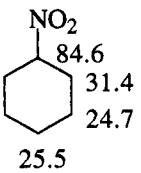


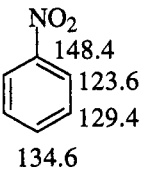


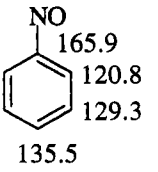






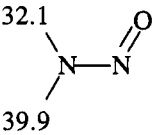


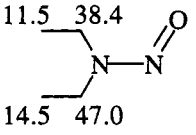


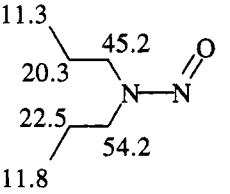


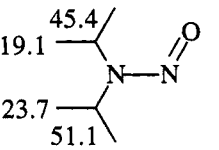
4.9.3 Nitrosamines and Nitramines

^{13}C Chemical Shifts of Nitrosamines (δ in ppm relative to TMS)

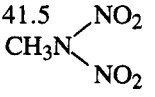


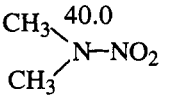






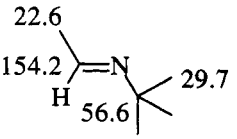
^{13}C Chemical Shifts of Nitramines (δ in ppm relative to TMS)

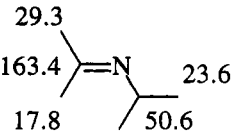


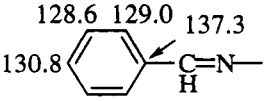


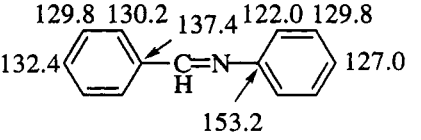
4.9.4 Imines and Oximes

^{13}C Chemical Shifts of Imines (δ in ppm relative to TMS)

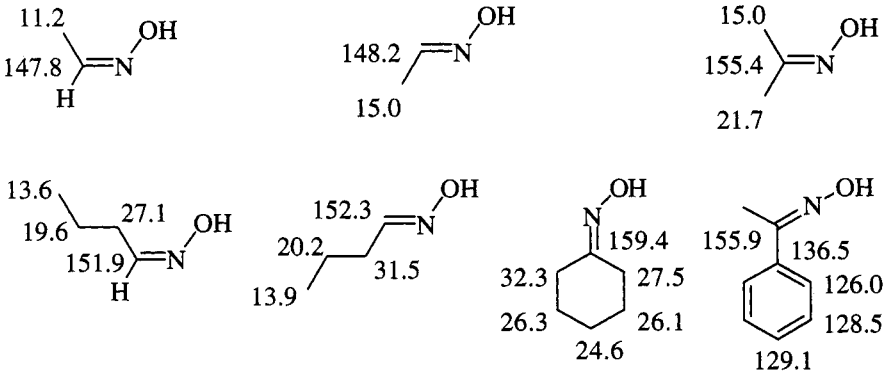






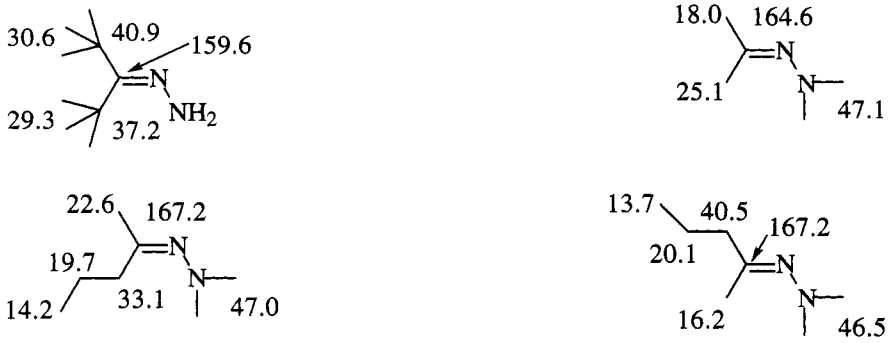


^{13}C Chemical Shifts of Oximes (δ in ppm relative to TMS)



4.9.5 Hydrazones and Carbodiimides

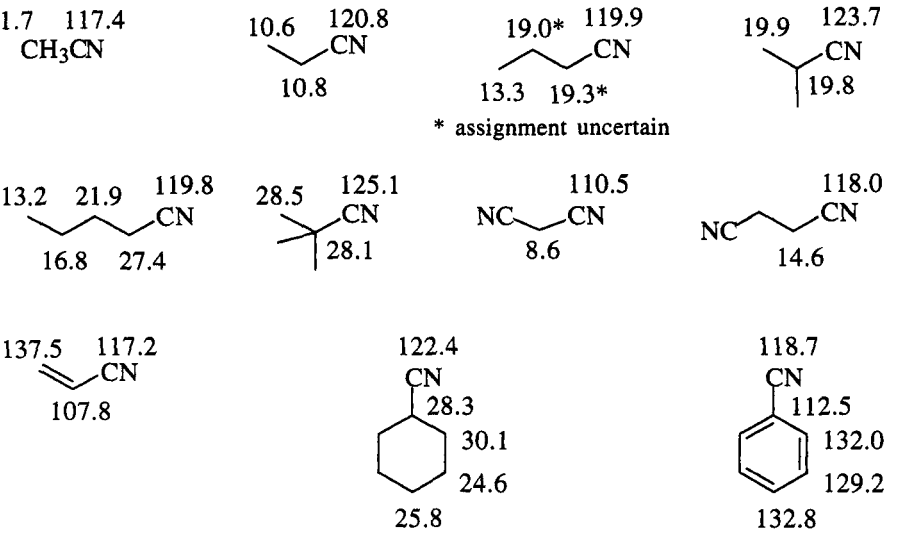
^{13}C Chemical Shifts of Hydrazones (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Carbodiimides (δ in ppm relative to TMS)

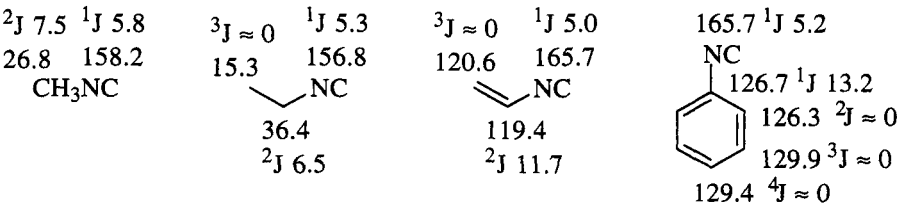
4.9.6 Nitriles and Isonitriles

^{13}C Chemical Shifts of Nitriles (δ in ppm relative to TMS)



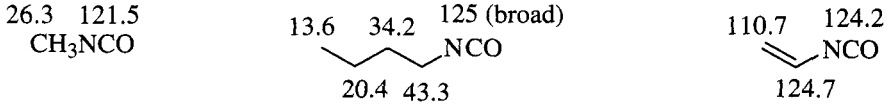
^{13}C Chemical Shifts of Isonitriles
(δ in ppm relative to TMS, $|J|_{CN}$ in Hz)

N Because of the symmetrical electron distribution around the nitrogen atom, the ^{13}C–^{14}N-coupling can be observed in the ^{13}C NMR spectra of isonitriles: triplets with relative intensities of 1:1:1 (spin quantum number of ^{14}N: I = 1, natural abundance 99.6%).

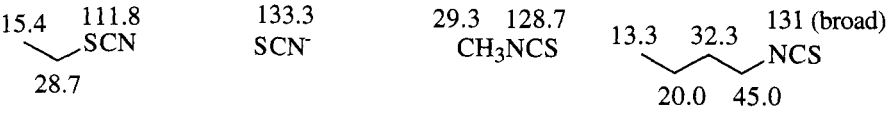


4.9.7 Isocyanates, Thiocyanates and Isothiocyanates

^{13}C Chemical Shifts of Isocyanates (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Thiocyanates and Isothiocyanates (δ in ppm relative to TMS)



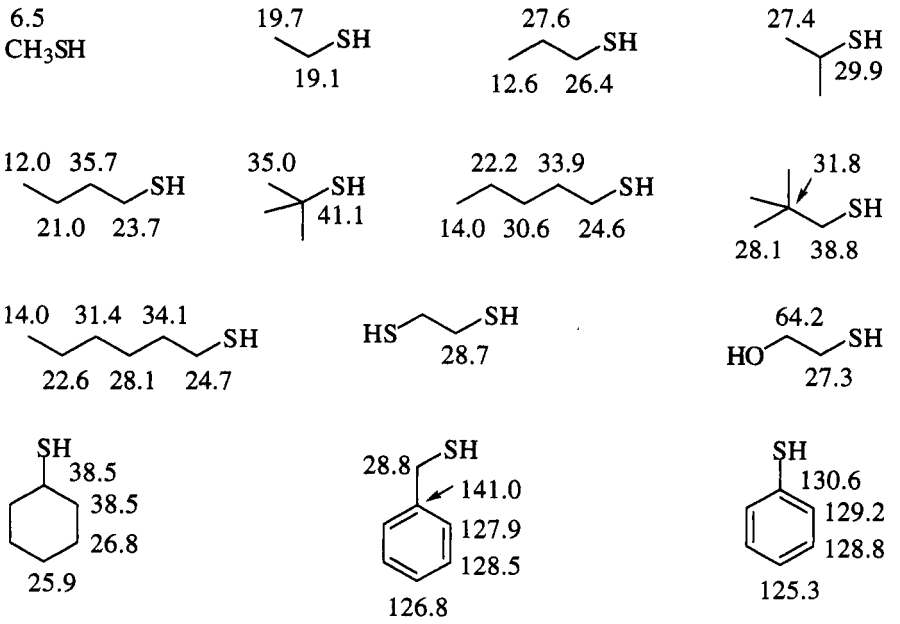
4.9.8 References

[1] J.E. Sarneski, H.L. Surprenant, F.K. Molen, Ch.N. Reilley, Chemical shifts and protonation shifts in carbon-13 nuclear magnetic resonance studies of aqueous amines, Anal. Chem. **1975**, *47*, 2116.

4.10 Sulfur-Containing Functional Groups

4.10.1 Thiols

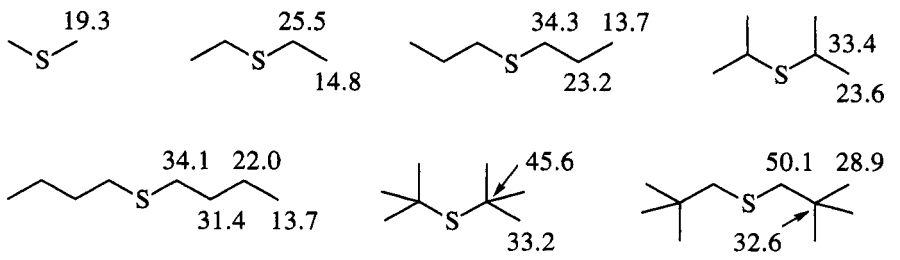
^{13}C Chemical Shifts of Thiols (δ in ppm relative to TMS)

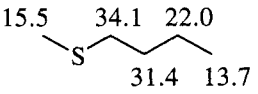


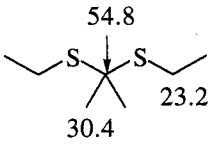
S

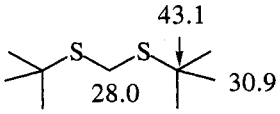
4.10.2 Sulfides

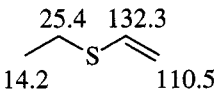
^{13}C Chemical Shifts of Sulfides (δ in ppm relative to TMS)

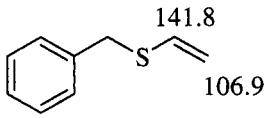


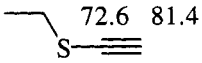


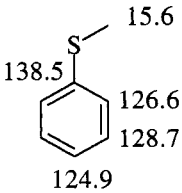


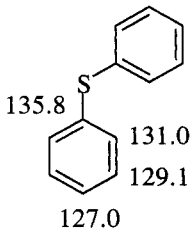




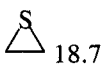


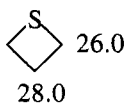


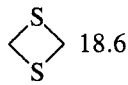


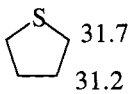


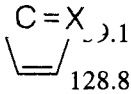
^{13}C Chemical Shifts of Cyclic Sulfides *(δ in ppm relative to TMS)*

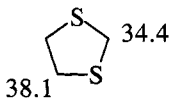


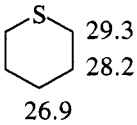


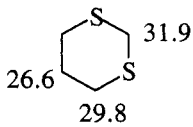


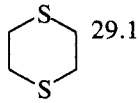


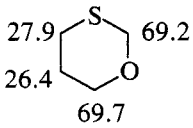


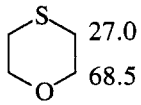






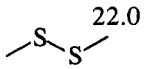


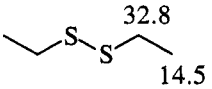


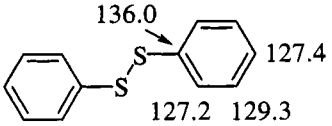


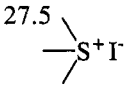
4.10.3 Disulfides and Sulfonium Salts

^{13}C Chemical Shifts of Disulfides and Sulfonium Salts
(δ in ppm relative to TMS)



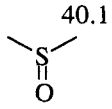


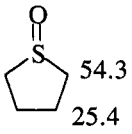


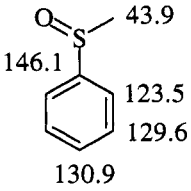


4.10.4 Sulfoxides and Sulfones

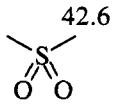
^{13}C Chemical Shifts of Sulfoxides and Sulfones
(δ in ppm relative to TMS)

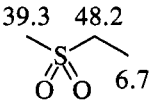


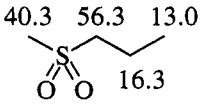


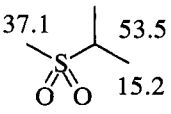


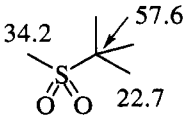
S

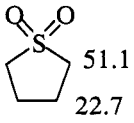


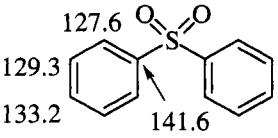






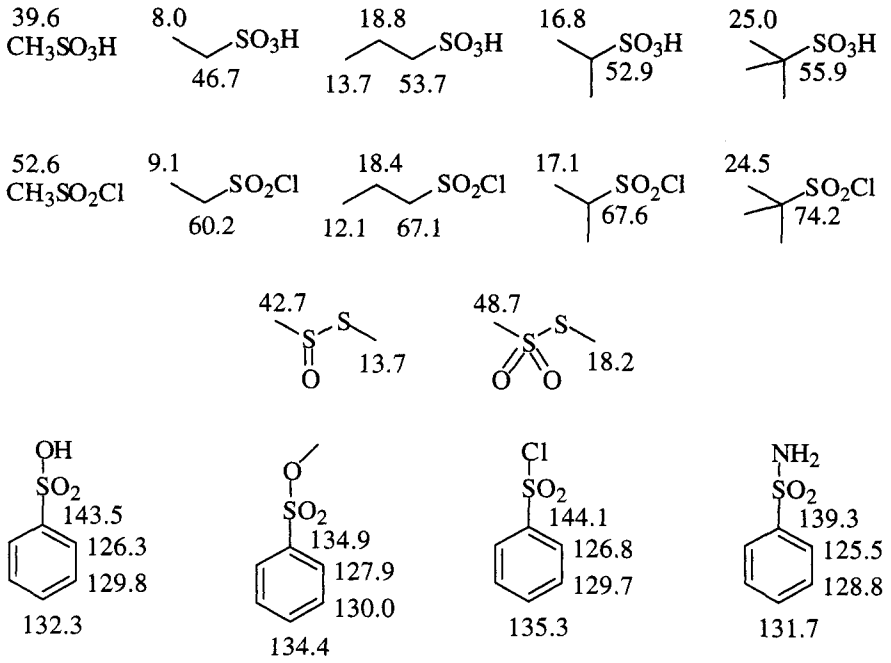






4.10.5
Sulfonic and Sulfinic Acids and Derivatives

^{13}C Chemical Shifts of Sulfonic and Sulfinic Acids and Derivatives *(δ in ppm relative to TMS)*



4.10.6
Sulfurous and Sulfuric Acid Derivatives

S

^{13}C Chemical Shifts of Sulfurous and Sulfuric Acid Derivatives *(δ in ppm relative to TMS)*

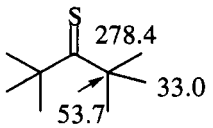
4.10.7 Sulfur-Containing Carbonyl Derivatives

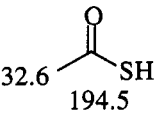
^{13}C Chemical Shifts of Sulfur-Containing Carbonyl Derivatives (δ in ppm relative to TMS)

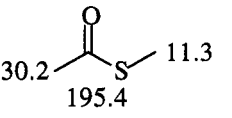
The chemical shifts of thiocarbonyl groups are higher by about 30 ppm than those of the corresponding carbonyl groups:

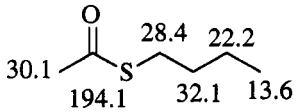
$$\delta_{C=S} \approx 1.5\ \delta_{C=O} - 57.5$$

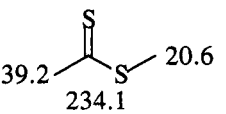
Carbonyl groups of thiocarboxylic acids and their esters are deshielded by about 20 ppm with respect to the corresponding oxygen compounds.

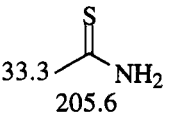


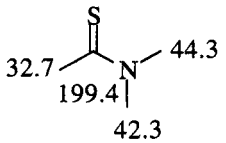


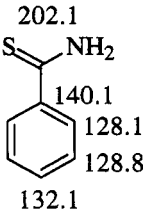












4.11 Carbonyl Compounds

4.11.1 Aldehydes

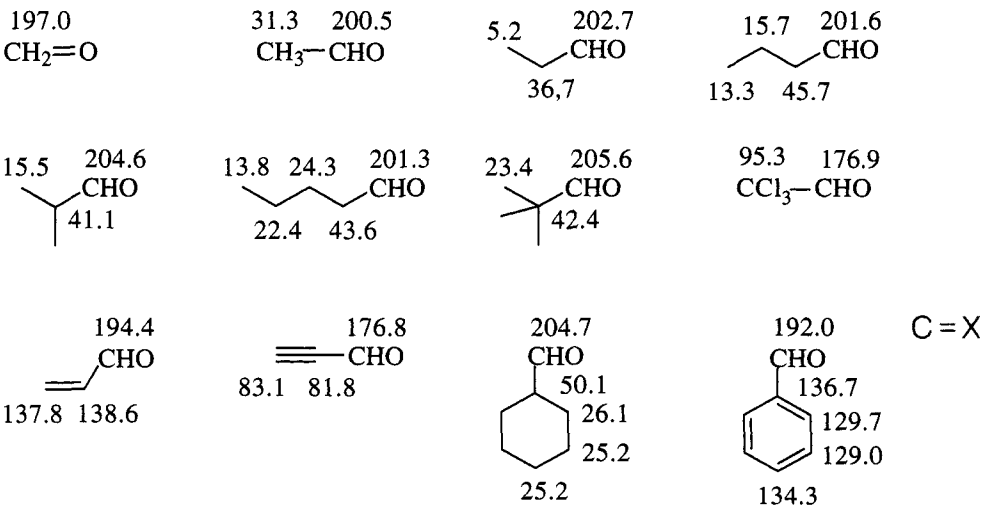
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Aldehyde Carbonyl Carbon Atoms *(δ in ppm relative to TMS)*

$$\delta_{C=O} = 193.0 + \sum_i Z_i$$

$$-C_\beta-C_\alpha-CHO$$

Substituent i	Z_α	Z_β
$-C\equiv$	6.5	2.6
$-CH=CH_2$	-0.8	0.0
$-CH=CH-CH_3$	0.2	0.0
-phenyl	-1.2	0.0

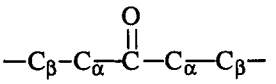
^{13}C Chemical Shifts of Aldehydes *(δ in ppm relative to TMS)*



4.11.2 Ketones

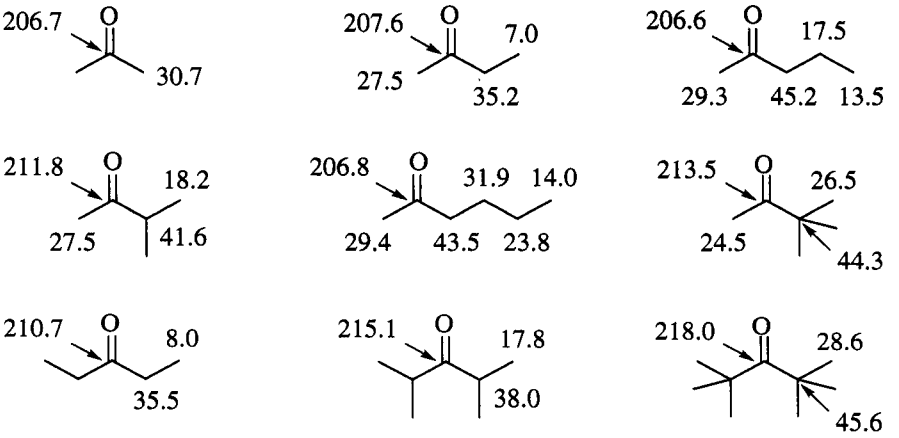
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Ketone Carbonyl Carbon Atoms *(δ in ppm relative to TMS)*

$$\delta_{C=O} = 193.0 + \sum_i Z_i$$



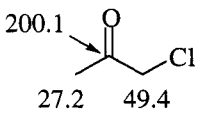
Substituent i	Z_α	Z_β
$-C\leqslant$	6.5	2.6
$-CH=CH_2$	-0.8	0.0
$-CH=CH-CH_3$	0.2	0.0
-phenyl	-1.2	0.0

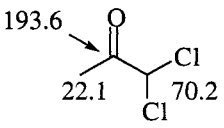
^{13}C Chemical Shifts of Aliphatic Ketones *(δ in ppm relative to TMS)*

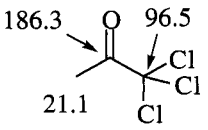


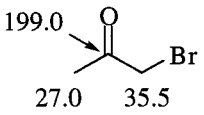
C=X

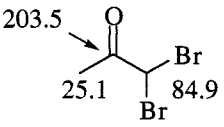
^{13}C Chemical Shifts of Halogenated Ketones
(δ in ppm relative to TMS)

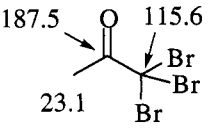


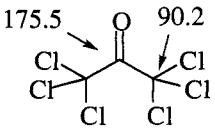




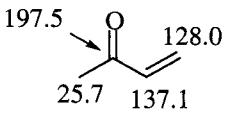


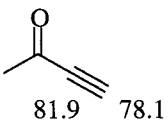


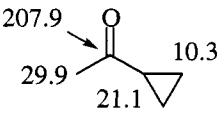


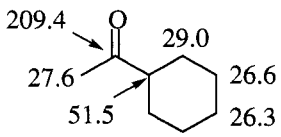


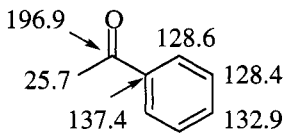
^{13}C Chemical Shifts of Unsaturated and Alicyclic Ketones
(δ in ppm relative to TMS)

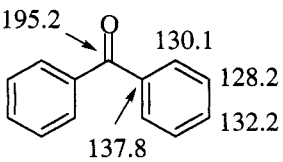




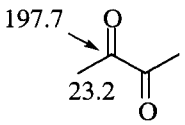


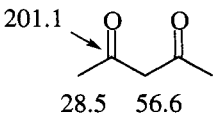


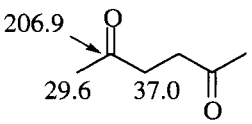




^{13}C Chemical Shifts of Diketones *(δ in ppm relative to TMS)*



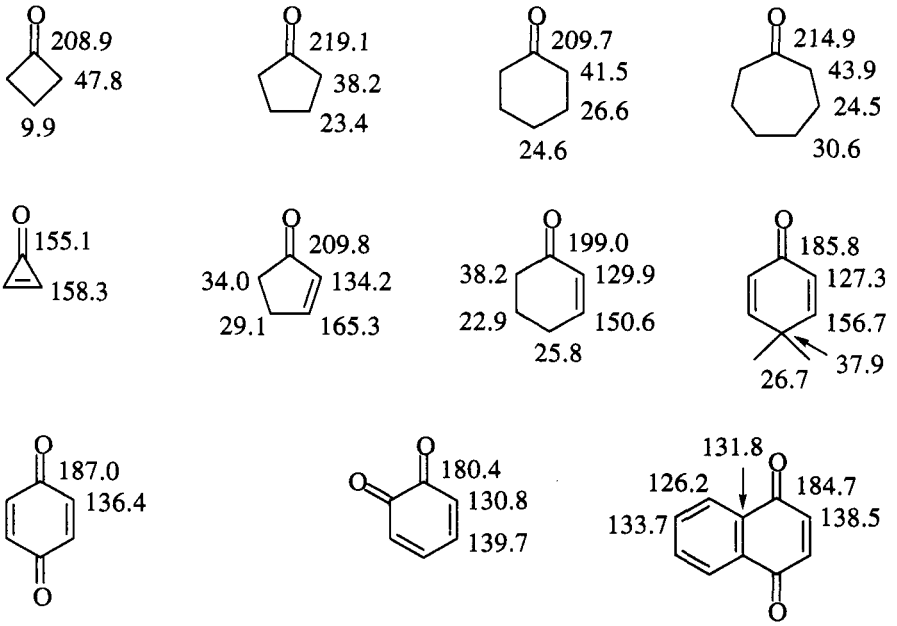




C=X

Enol form: see Chapter 4.8

^{13}C Chemical Shifts of Cyclic Ketones and Quinones *(δ in ppm relative to TMS)*



4.11.3 Carboxylic Acids and Carboxylates

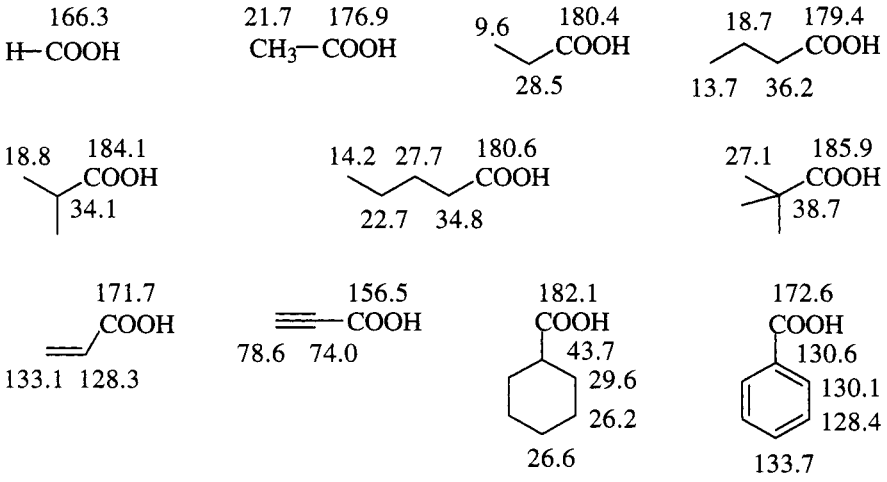
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Carboxyl Carbon Atoms *(δ in ppm relative to TMS)*

$$\delta_{C=O} = 166.0 + \sum_i Z_i$$

$$—C_\gamma—C_\beta—C_\alpha—COOH$$

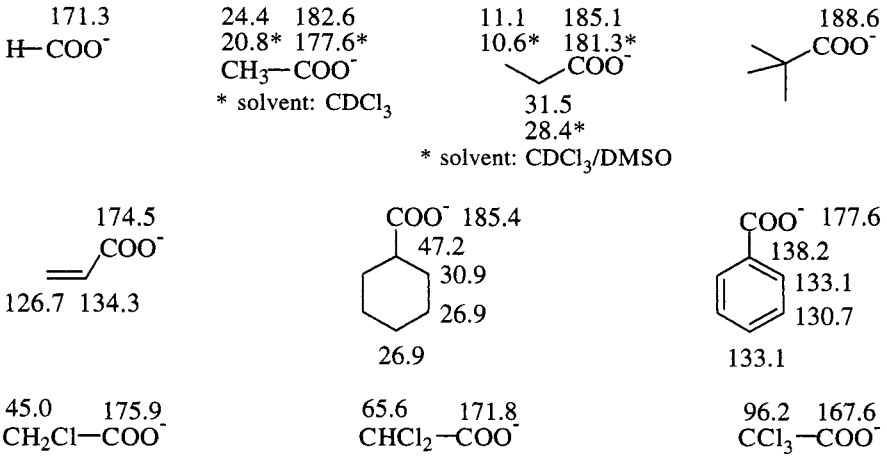
Substituent i	Z_α	Z_β	Z_γ
–C≡	11.0	3.0	-1.0
–CH=CH$_2$	5.0		
–phenyl	6.0	1.0	

^{13}C Chemical Shifts of Carboxylic Acids (*δ in ppm relative to TMS*)



^{13}C Chemical Shifts of Carboxylate Anions

(δ in ppm relative to TMS; measured in water unless indicated otherwise)



C = X

4.11.4 Esters and Lactones

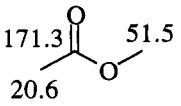
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Ester Carbonyl Carbon Atoms *(δ in ppm relative to TMS)*

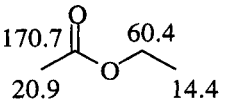
$$\delta_{C=O} = 166.0 + \sum_i Z_i$$

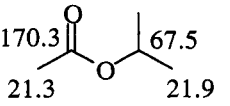
$$-C_\gamma-C_\beta-C_\alpha-COO-C_{\alpha'}-$$

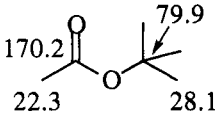
Substituent i	Z_α	Z_β	Z_γ	$Z_{\alpha'}$
$-C\equiv$	11.0	3.0	-1.0	-5.0
$-CH=CH_2$	5.0			-9.0
-phenyl	6.0	1.0		-8.0

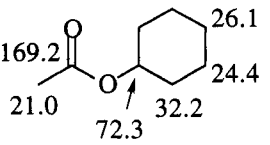
^{13}C Chemical Shifts of Acetic Acid Esters *(δ in ppm relative to TMS)*

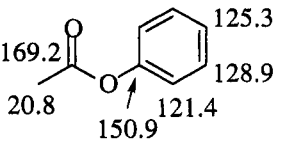






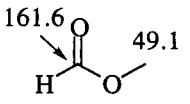


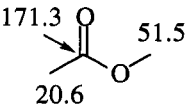


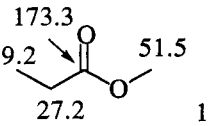


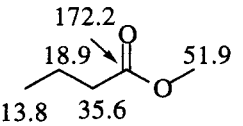
^{13}C Chemical Shifts of Methyl Esters *(δ in ppm relative to TMS)*

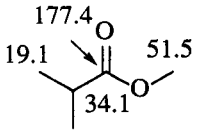
C=X

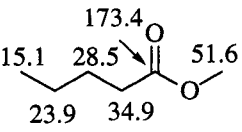


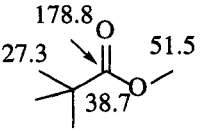


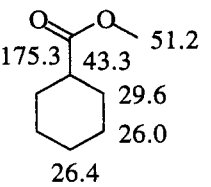


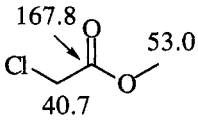


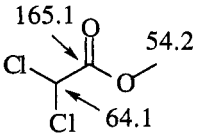


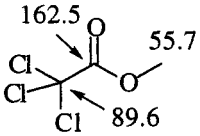


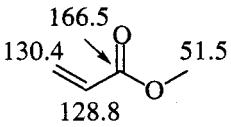


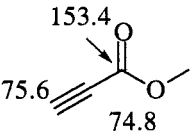


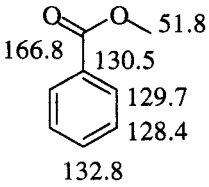


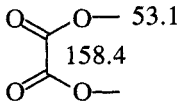


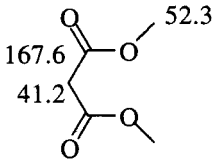


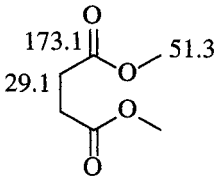


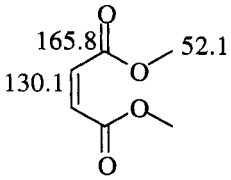


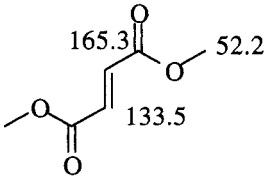


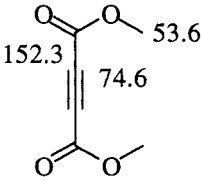




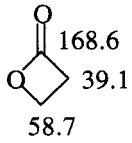


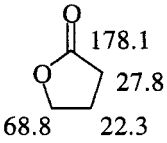


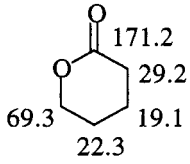




^{13}C Chemical Shifts of Lactones *(δ in ppm relative to TMS)*







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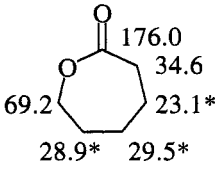
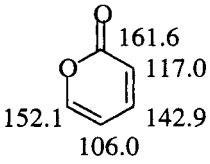


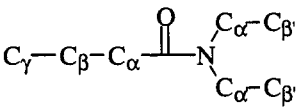


* assignment uncertain

4.11.5 Amides and Lactams

Additivity Rule for Estimating the ^{13}C Chemical Shifts of Amide Carbonyl Carbon Atoms *(δ in ppm relative to TMS)*

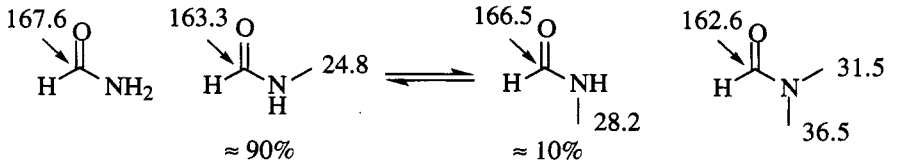
$$\delta_{C=O} = 165.0 + \sum_i Z_i$$

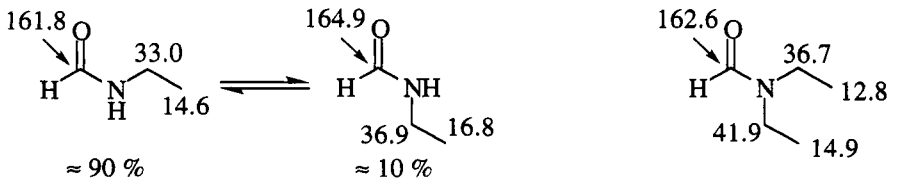


Substituent i	Z_α	Z_β	Z_γ	$Z_{\alpha'}$	$Z_{\beta'}$
–C≤	7.7	4.5	-0.7	-1.5	-0.3
–CH=CH$_2$	3.3				
–phenyl	4.7			-4.5	

^{13}C Chemical Shifts of Amides *(δ in ppm relative to TMS)*

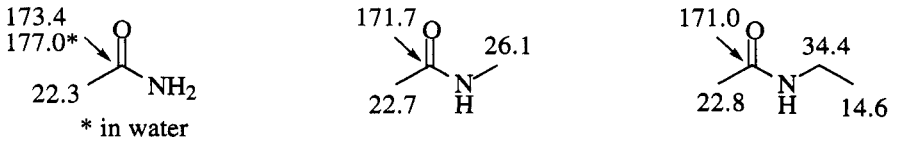
Formamides:

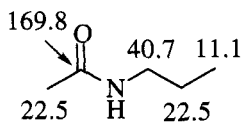


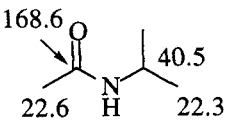


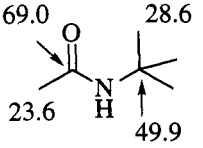
C=X

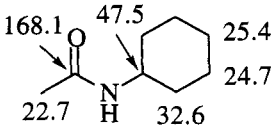
Primary and Secondary Acetamides:

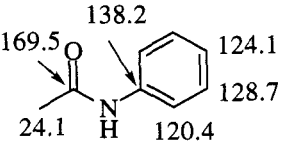




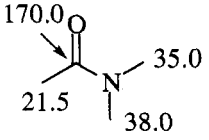


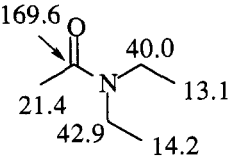


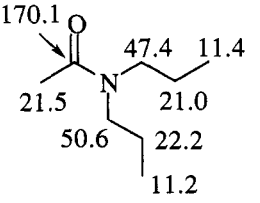


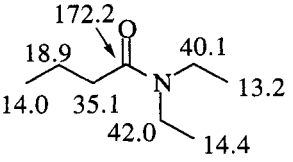


Tertiary Aliphatic Amides:

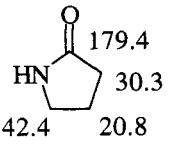


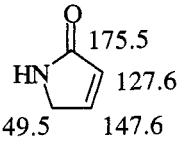


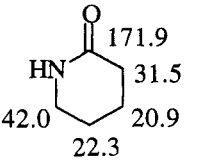




^{13}C Chemical Shifts of Lactams *(δ in ppm relative to TMS)*







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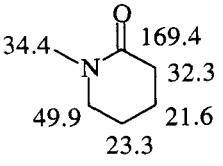
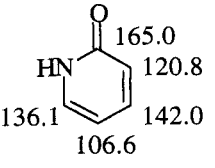
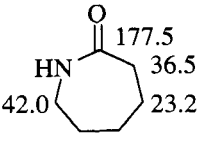


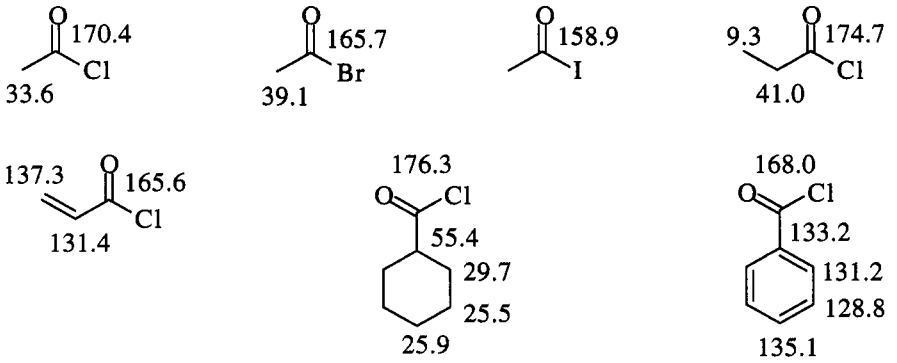




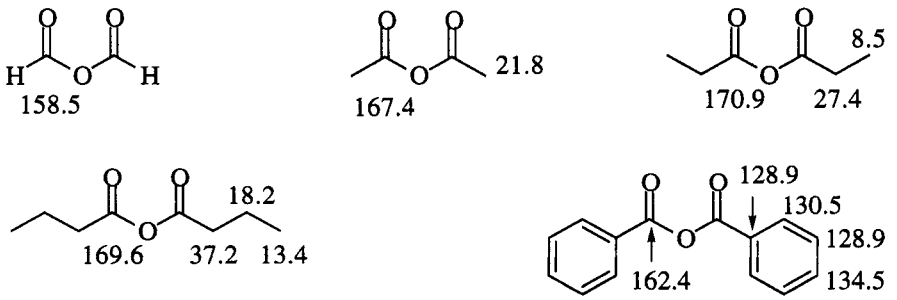
* assignment uncertain

4.11.6
Miscellaneous Carbonyl Derivatives

^{13}C Chemical Shifts of Carboxylic Acid Halides
(δ in ppm relative to TMS)



^{13}C Chemical Shifts of Carboxylic Acid Anhydrides
(δ in ppm relative to TMS)



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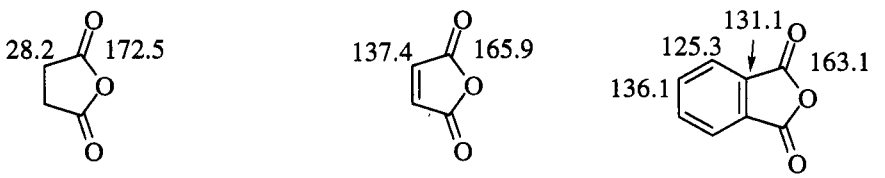
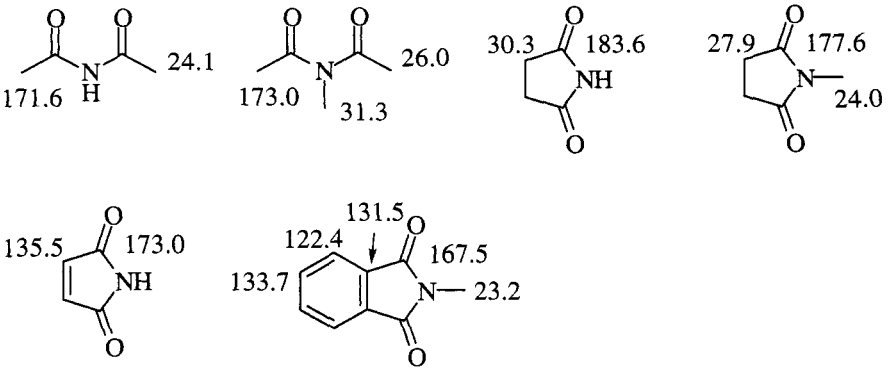
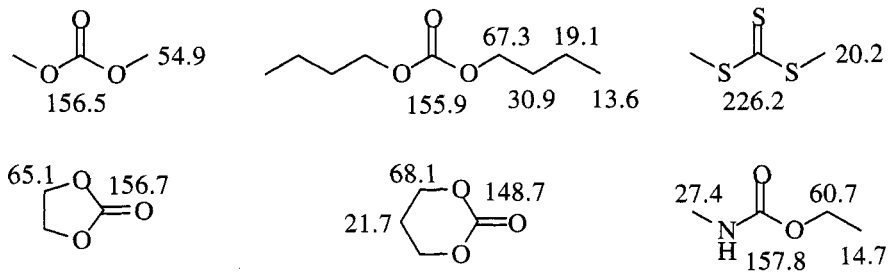


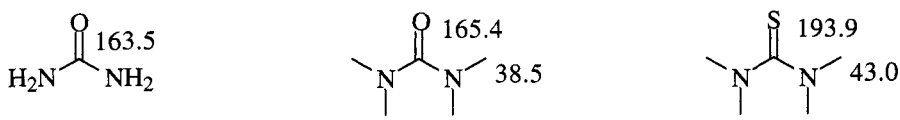
^{13}C Chemical Shifts of Carboxylic Acid Imides
(δ in ppm relative to TMS)



^{13}C Chemical Shifts of Carbonic Acid Derivatives
(δ in ppm relative to TMS)

CO 181.3 CO_2 124.2 CO_3^{2-} 168.2 CS_2 192.8

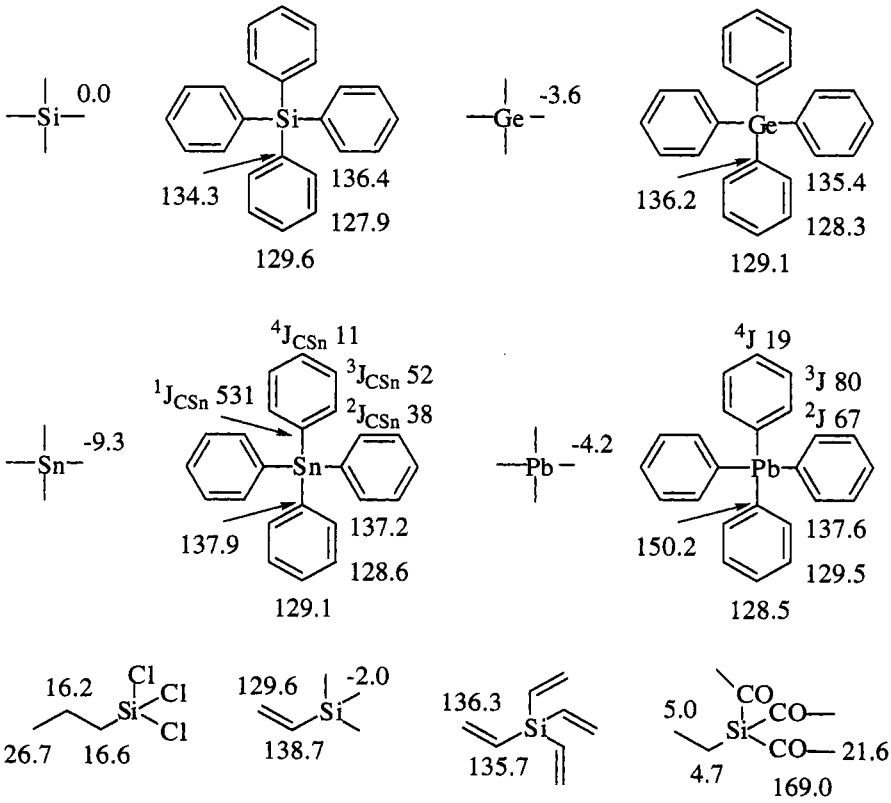




4.12 Miscellaneous Compounds

4.12.1 Derivatives of Group IV Elements

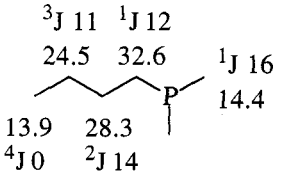
^{13}C Chemical Shifts and Coupling Constants of Derivatives of Group IV Elements *(δ in ppm relative to TMS, $|J|$ in Hz)*

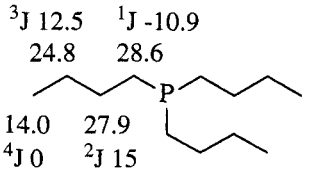


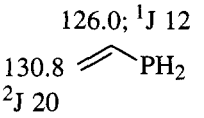
Misc.

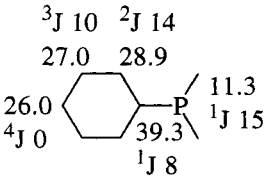
4.12.2 Phosphorus Compounds

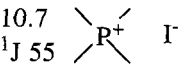
^{13}C Chemical Shifts and ^{31}P-^{13}C Coupling Constants of Aliphatic Phosphorus Compounds *(δ in ppm relative to TMS, $|J|$ in Hz)*

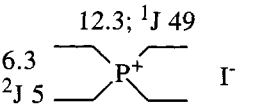


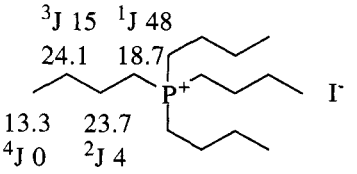


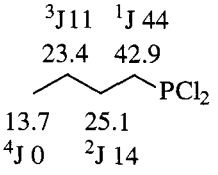


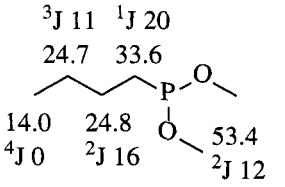


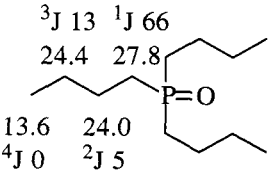


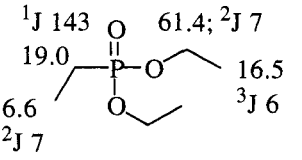


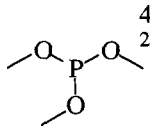


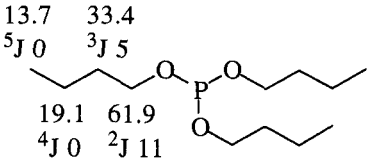


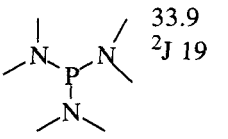




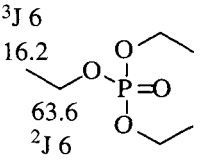


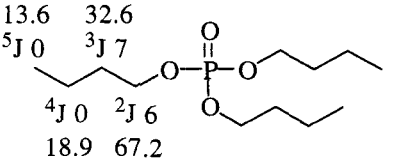


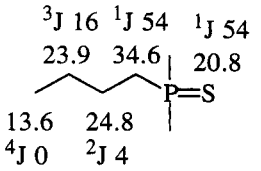


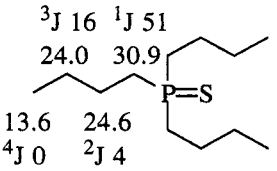


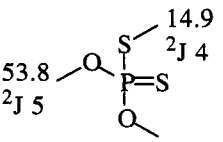
Misc.



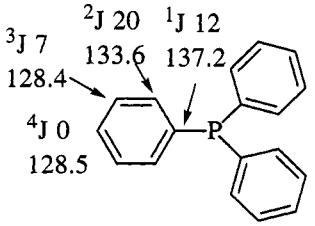


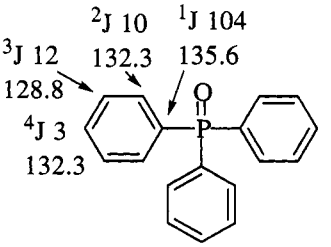


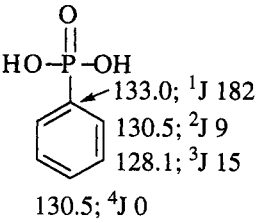


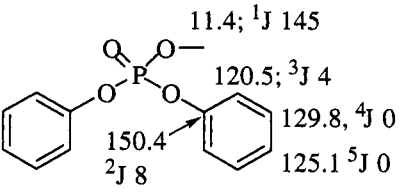


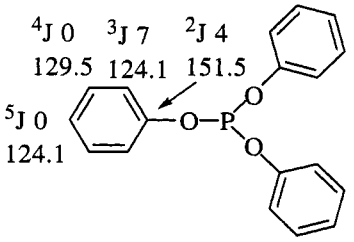
^{13}C Chemical Shifts and ^{31}P-^{13}C Coupling Constants of Aromatic Phosphorus Compounds *(δ in ppm relative to TMS, $|J|$ in Hz)*

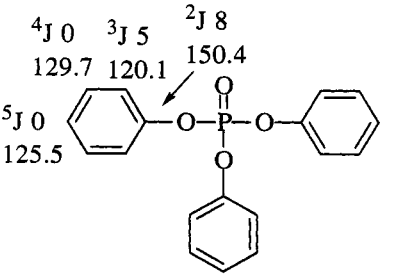






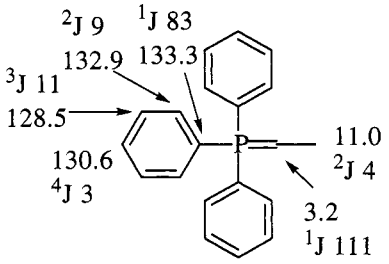


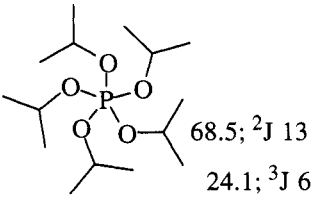




Misc.

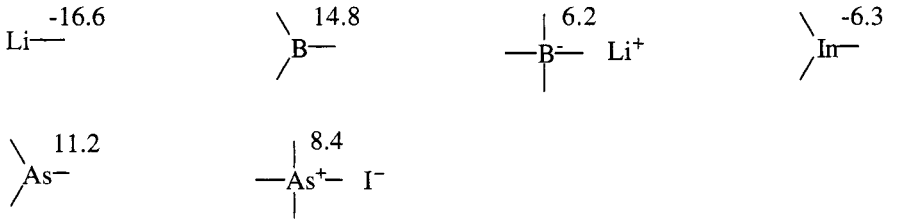
^{13}C Chemical Shifts and ^{31}P-^{13}C Coupling Constants of Phosphoranes *(δ in ppm relative to TMS, $|J|$ in Hz)*

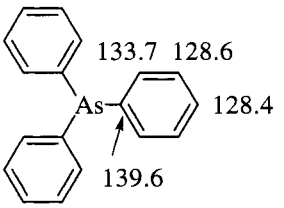


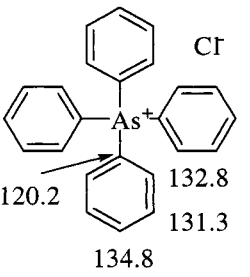


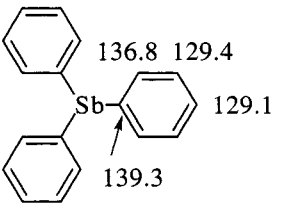
4.12.3 Miscellaneous Organometallic Compounds

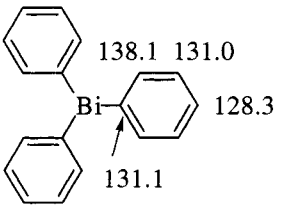
^{13}C Chemical Shifts and Coupling Constants of Miscellaneous Organometallics *(δ in ppm relative to TMS, $|J|$ in Hz)*

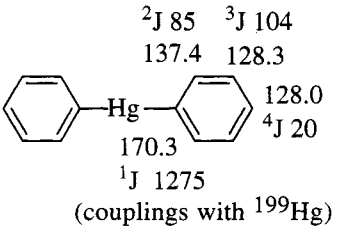








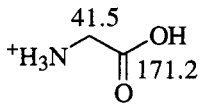




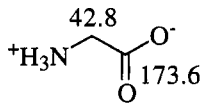
4.13 Natural Products

4.13.1 Amino Acids

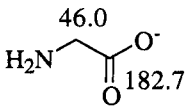
^{13}C Chemical Shifts of Amino Acids
(δ in ppm relative to TMS; solvent: water)



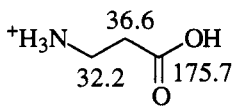
(pH 0.45)



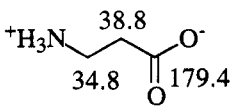
(pH 4.53)



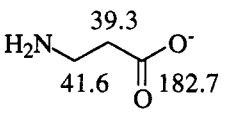
(pH 12.01)



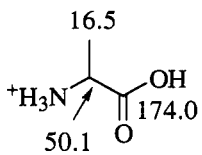
(pH 0.49)



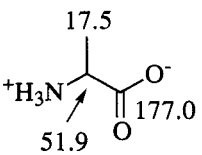
(pH 5.03)



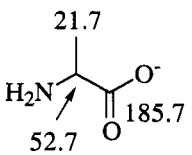
(pH 12.56)



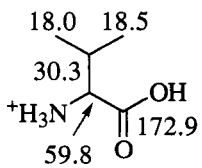
(pH 0.43)



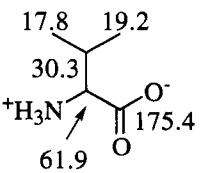
(pH 4.96)



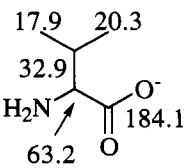
(pH 12.52)



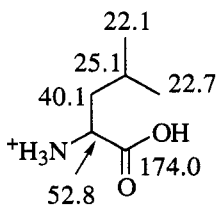
(pH 3.0)



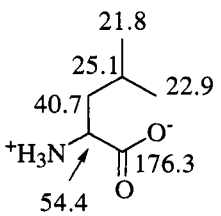
(pH 5.64)



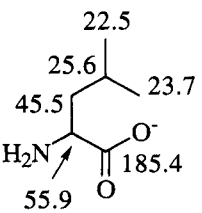
(pH 12.60)



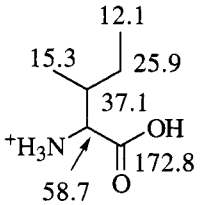
(pH 0.37)



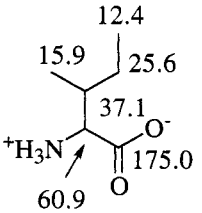
(pH 7.00)



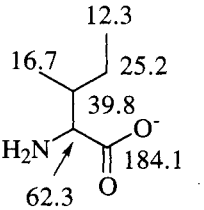
(pH 13.00)



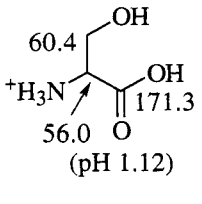
(pH 0.28)



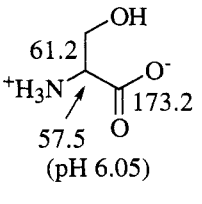
(pH 6.04)



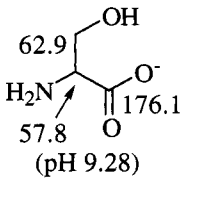
(pH 12.84)



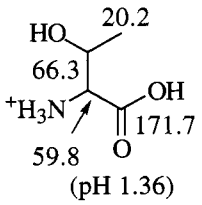
(pH 1.12)



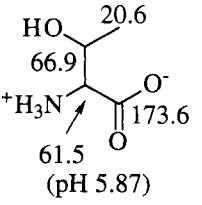
(pH 6.05)



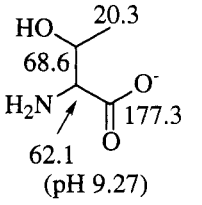
(pH 9.28)



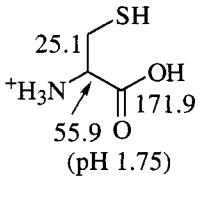
(pH 1.36)



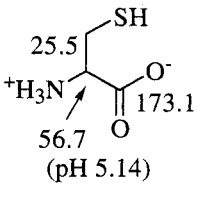
(pH 5.87)



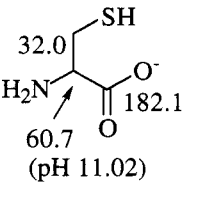
(pH 9.27)



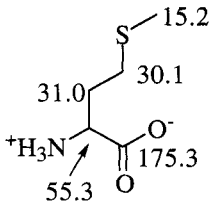
(pH 1.75)

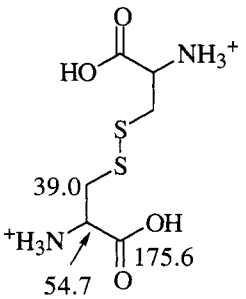


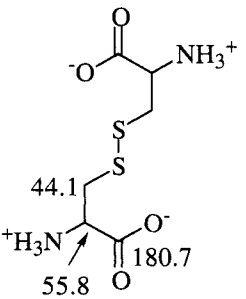
(pH 5.14)



(pH 11.02)

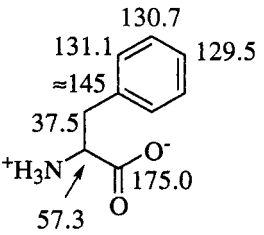


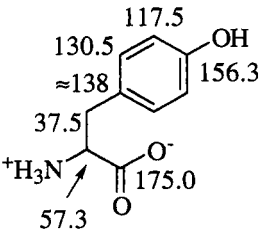


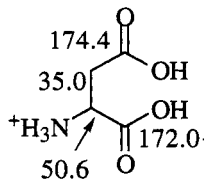


(in D_2O)

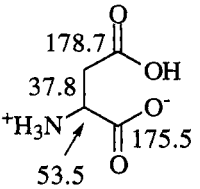
Natural Products



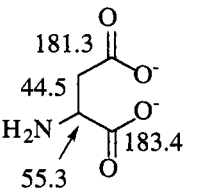




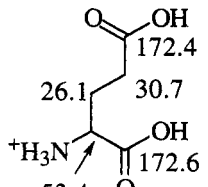
(pH 0.41)



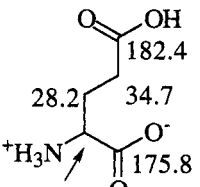
(pH 6.73)



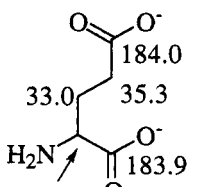
(pH 12.73)



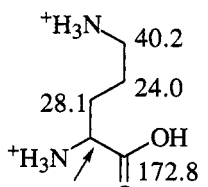
(pH 0.32)



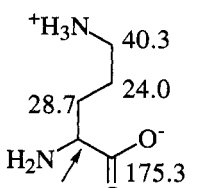
(pH 6.95)



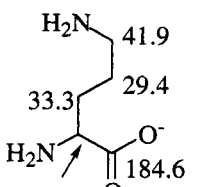
(pH 12.51)



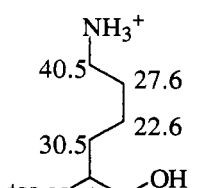
(pH 0.46)



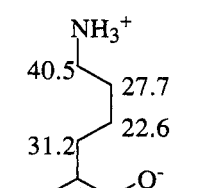
(pH 5.02)



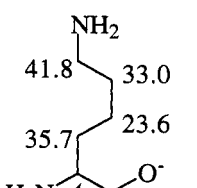
(pH 13.53)



(pH 0.50)

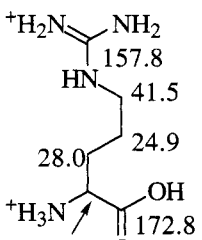


(pH 6.03)

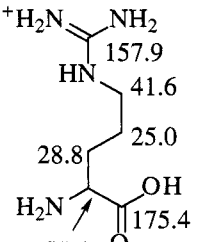


(pH 13.85)

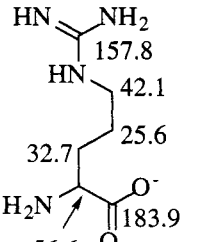
Natural Products



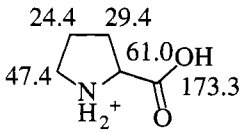
(pH 1.33)



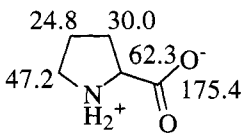
(pH 7.87)



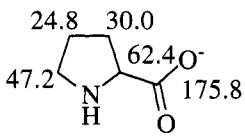
(pH 11.52)



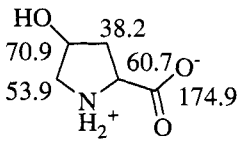
(pH 1.27)

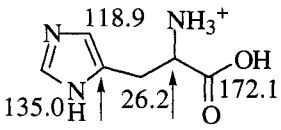


(pH 7.26)

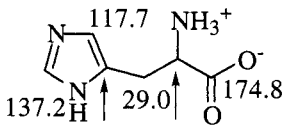


(pH 9.8)

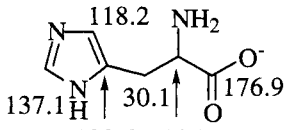




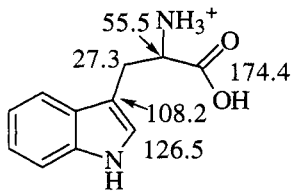
(pH 1.74)

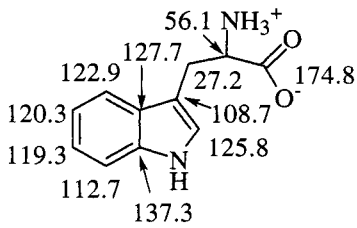


(pH 7.82)



(pH 9.21)





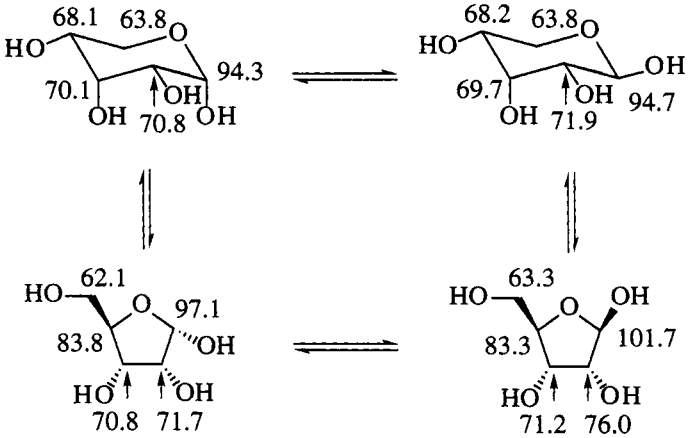
(in D2O, sat., 80 °C)

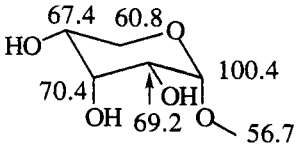
Natural Products

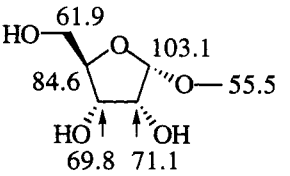
4.13.2 Carbohydrates

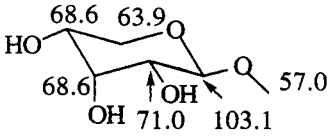
^{13}C Chemical Shifts of Monosaccharides
(δ in ppm relative to TMS)

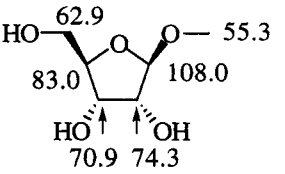
Ribose



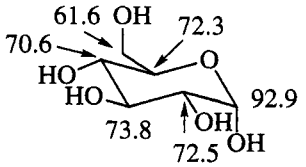


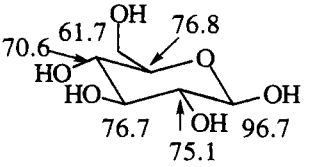


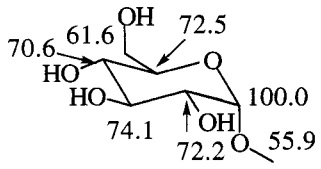


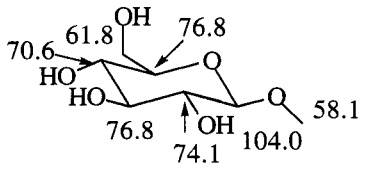


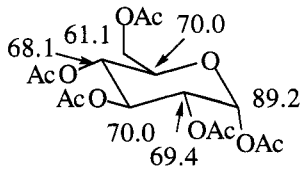
Glucose

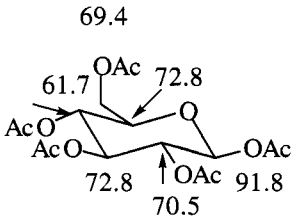




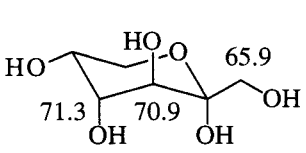




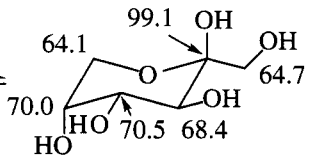




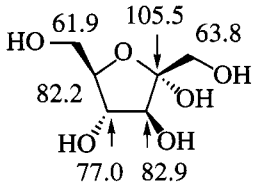
Fructose



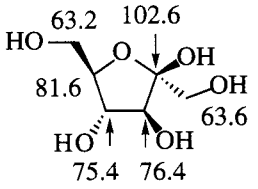
in water and in DMSO: traces



in water: 75%; in DMSO: 25%

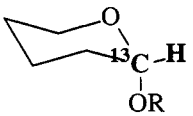


in water: 4%; in DMSO: 20%

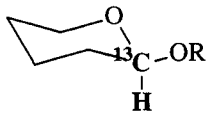


in water: 21%; in DMSO: 55%

^{13}C-^{1}H Coupling Constants through one Bond ($^{1}J_{CH}$ *in Hz*)



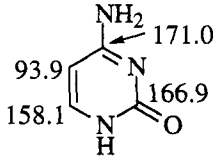
$^{1}J_{CH}$ 169–171



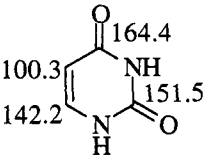
$^{1}J_{CH}$ 158–162

4.13.3 Nucleotides and Nucleosides

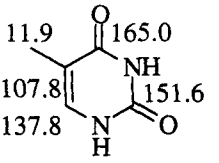
^{13}C Chemical Shifts of Nucleotides and Nucleosides
(δ in ppm relative to TMS)



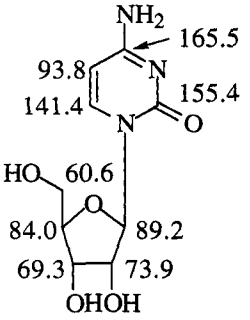
(in DMSO/water, 1:2)



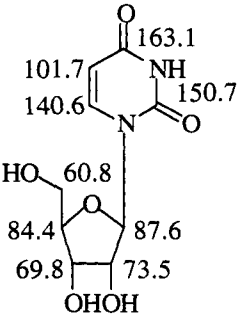
(in DMSO)



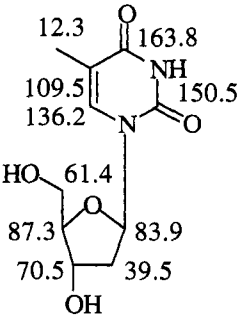
(in D_2O)



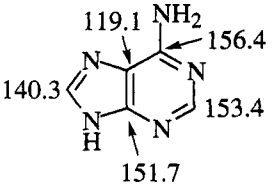
(in D_2O)



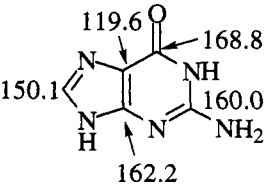
(in D_2O)



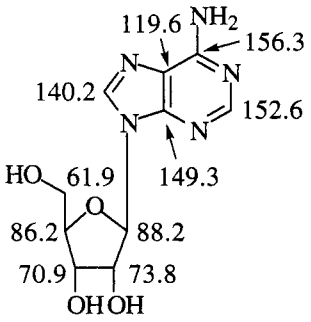
(in D_2O)



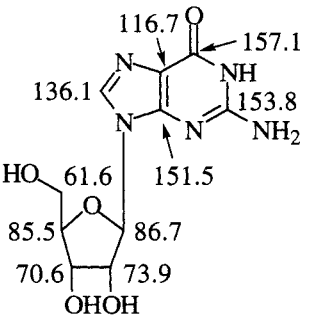
(in DMSO)



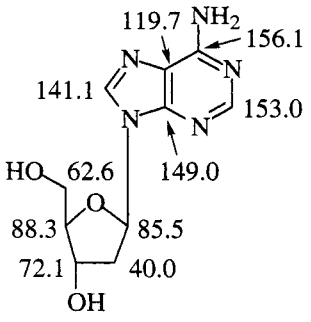
(in D_2O)



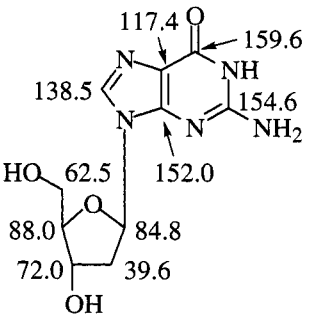
(in DMSO)



(in DMSO)



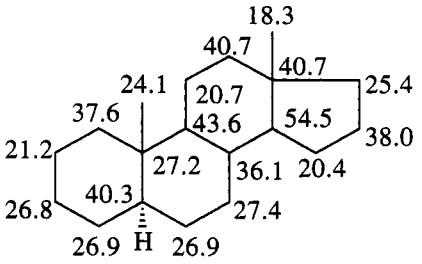
(in D_2O)

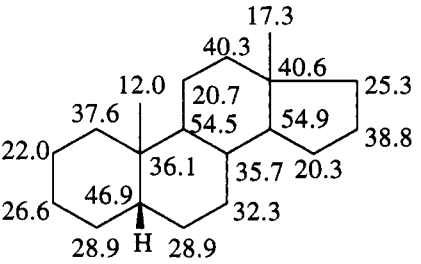


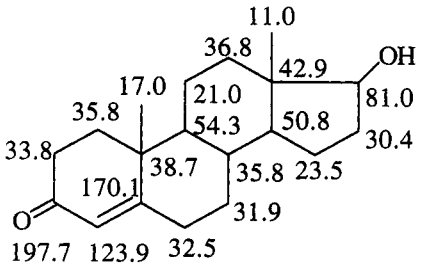
(in D_2O)

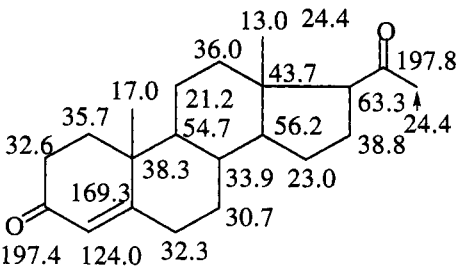
4.13.4 Steroids

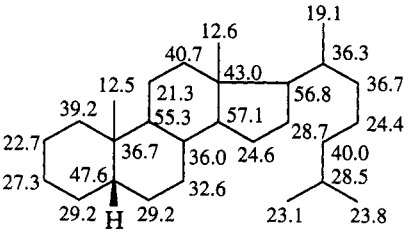
^{13}C Chemical Shifts of Steroids (δ *in ppm relative to TMS*)

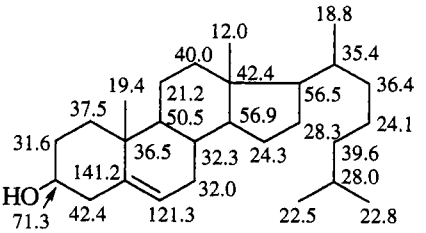










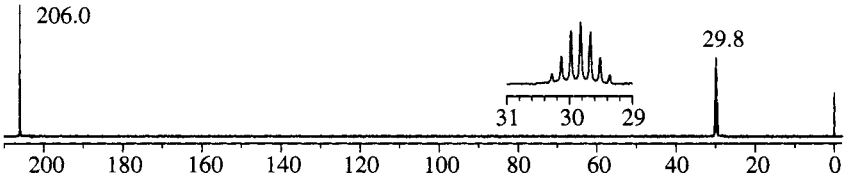


4.14
Spectra of Solvents and Reference Compounds

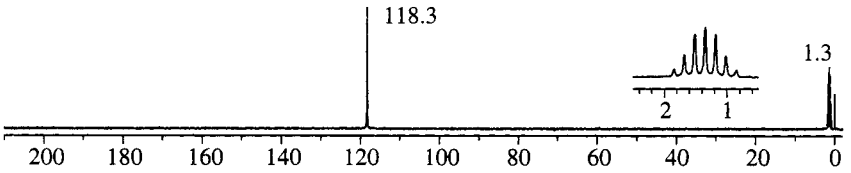
4.14.1
^{13}C NMR Spectra of Common Deuterated Solvents

(125 MHz, δ in ppm relative to TMS)

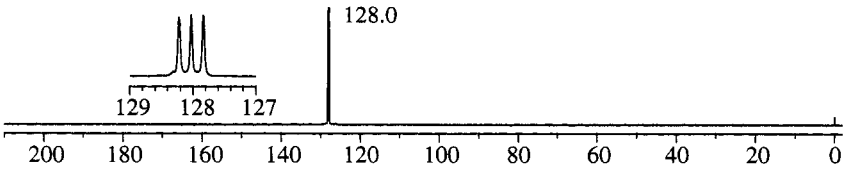
Acetone-d_6



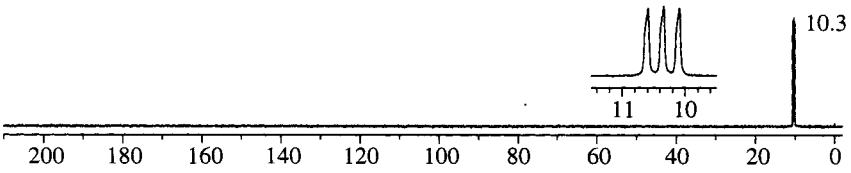
Acetonitrile-d_3



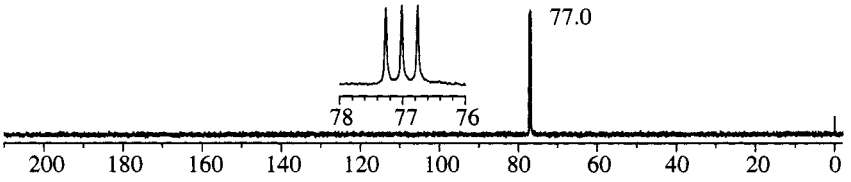
Benzene-d_6



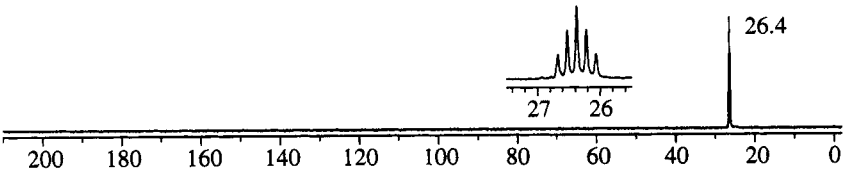
Bromoform-*d*



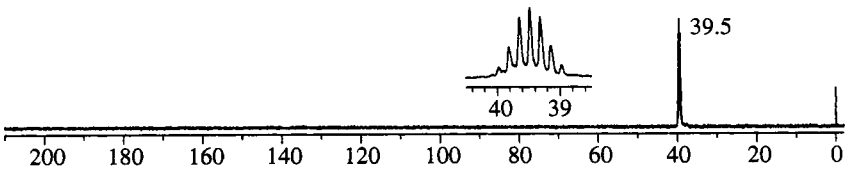
Chloroform-*d*



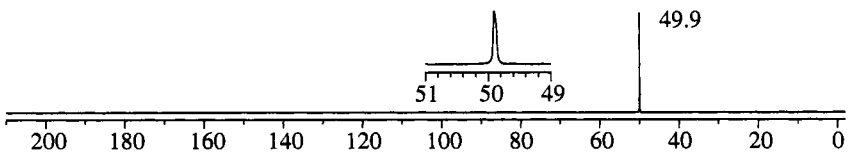
Cyclohexane-d_{12}



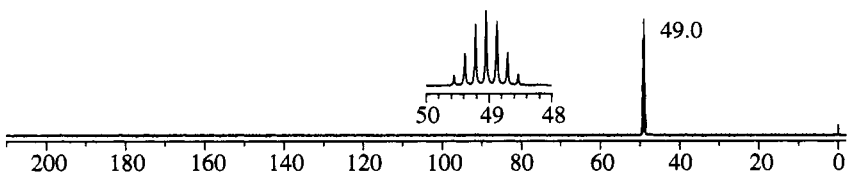
Dimethyl sulfoxide-d_6



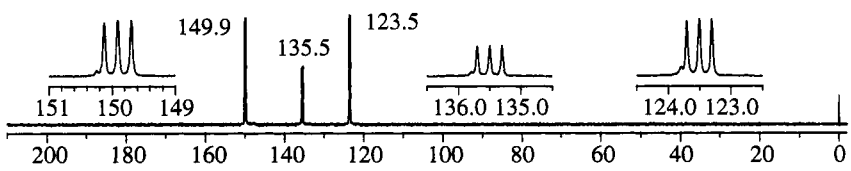
Methanol-d_1



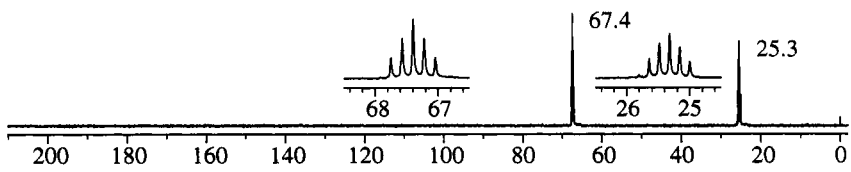
Methanol-d_4



Pyridine-d_5



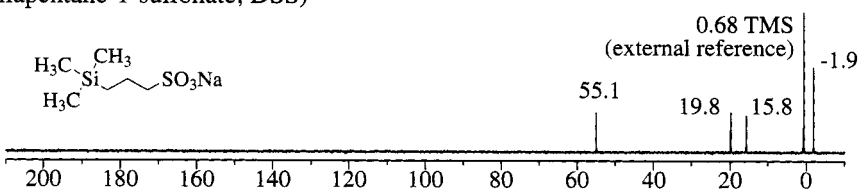
Tetrahydrofuran-d_8



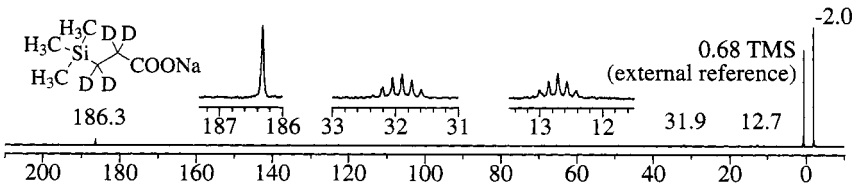
4.14.2
^{13}C NMR Spectra of Secondary Reference Compounds

Chemical shifts in ^{13}C NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS), which is added as an internal reference. When TMS is not sufficiently soluble in the sample, use of a capillary containing TMS as external reference is recommended. Owing to the different volume susceptibilities, the local magnetic fields differ in the solvent and reference. Therefore, the position of the reference must be corrected. For a D_2O solution in a cylindrical sample and 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 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 secondary reference compounds in D_2O were measured at 125 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. 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



4.14.3
^{13}C NMR Spectrum of a Mixture of Common Nondeuterated Solvents

This broad band-decoupled ^{13}C NMR spectrum of a $CDCl_3$ sample with 20 common solvents (0.05-0.4 vol%) is shown as a guide for the identification of solvent impurities (125 MHz, δ in ppm relative to TMS). Chemical shifts of signals marked with an asterisk (*) may change up to a few ppm if the sample contains solutes with functional groups that can form hydrogen bonds. DMF: dimethyl formamide; THF: tetrahydrofuran; EGDME: ethylene glycol dimethyl ether.