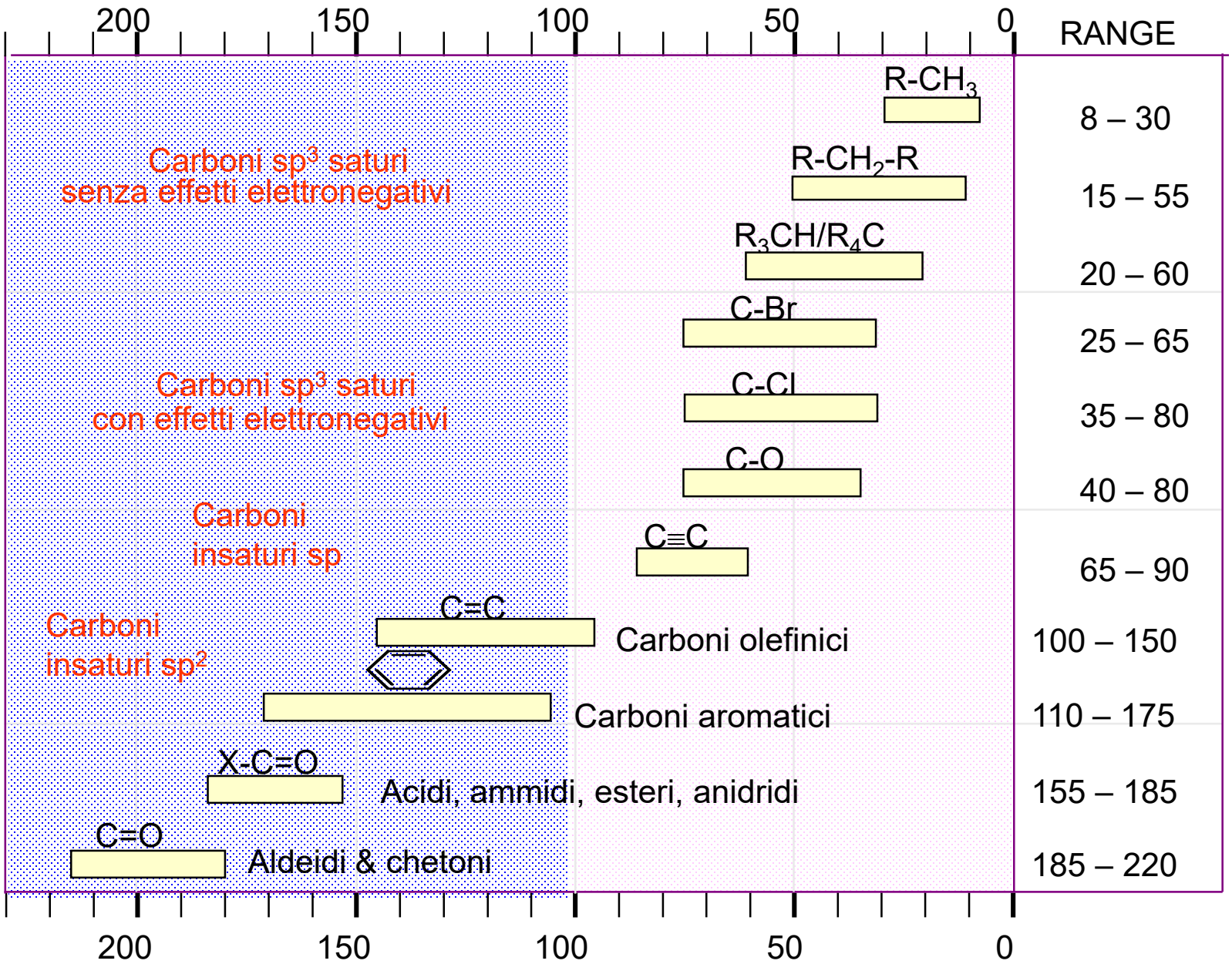
CHEMICAL SHIFT DEL ^{13}C

Il range del chemical shift è maggiore di quello dei protoni

0 - 200 ppm

Tabella di correlazione per il Chemical Shift del ^{13}C (ppm)



^{13}C NMR Chemical Shift Correlations	
Type of carbon	**Chemical Shift (δ) ppm**
1° alkyl, RCH_3	0-40
2° alkyl, RCH_2R	10-50
3° alkyl, $RCHR_2$	15-50
4° alkyl, R_4C	15-50
R_3CBr, R_3CCl, R_3C-N-R_2	10-65
R_3-C-O-H, R_3-C-O-R	50-90
RC≡CR	60-90
RC=CR	100-170
Aromatic	100-170
R-C≡N	120-130
Amide carbonyl (C=O)	150-180
Carboxylic acid carbonyl	160-185
Aldehyde or ketone carbonyl	182-215
Ester carbonyl	160-185

CHEMICAL SHIFT DEL ^{13}C

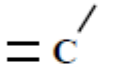
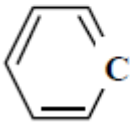
- IBRIDAZIONE
- EFFETTI DEL SOSTITUENTE:
  a. Elettronegatività
  b. Effetto dell'atomo pesante
  c. Effetti di risonanza
  d. Effetti sterici
  e. Effetti di campo elettrico
  f. Effetti di anisotropia magnetica
  g. Effetti isotopici

1. IBRIDAZIONE

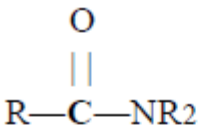
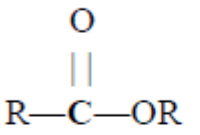
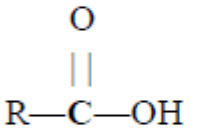
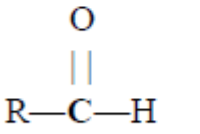
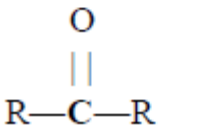
Chemical shift Csp^3 < Csp< Csp^2

Stesso trend dell ^1H

$R—CH_3$	8-35
R_2CH_2	15-50
R_3CH	20-60
R_4C	30-40

	65-85
	100-150
	110-170

C-O	50-80
C-N	40-60
C-Cl	35-80
C-Br	25-65

	165-175
	165-175
	175-185
	190-200
	205-220

Effetti del sostituente X

Il chemical shift del ^{13}C è estremamente sensibile all'effetto induttivo di sostituenti in α (deschermo) , ma questi effetti si trasmettono anche sui Cβ (deschermo) e sui Cγ (schermo). Quest'ultimo è un effetto sterico (gauche).
Inoltre dobbiamo considerare l'effetto dell'atomo pesante.

Elettronegatività	X—CH_2—	α	β	γ
2.1	H	0	0	0
2.5	Me	+9	+9	-2
2.5	SH	+11	+12	-6
3.0	NH_2	+29	+11	-5
3.0	Cl	+31	+11	-4
4.0	F	+68	+9	-4

Contributi additivi

Contributo negativo: schermo
Contributo positivo deschermo

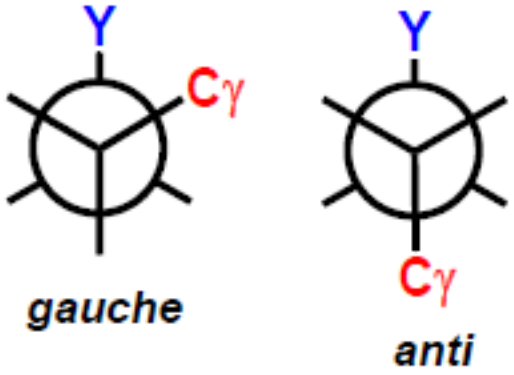
Effetto dell'atomo pesante

	F	Cl	Br	I
CH_3X	75	24.9	9.8	-20.8
CHX_3	116	77	12.1	-139.9

Sostituzione Br e I provoca un effetto di schermatura

Effetto γ (gauche)

E’ un effetto sterico

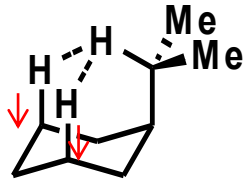


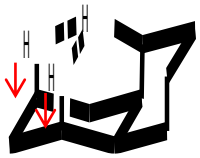
I chemical shift del Cγ sono a campi più alti a causa della compressione sterica nota come effetto Gauche

E’un effetto piccolo nel caso delle molecole lineari

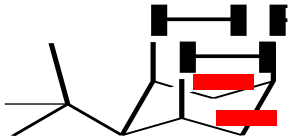
Effetto γ (gauche)

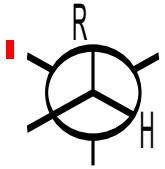
IMPORTANTE IN SISTEMA ALICICLICI

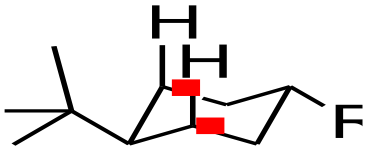




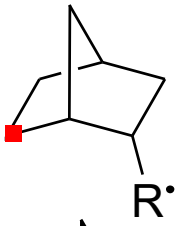
COMPRESSIONE STERICA

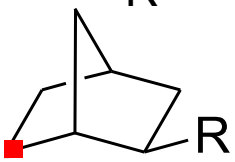


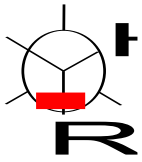


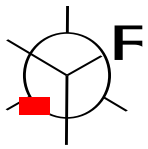


	CIS	TRANS
H	28.0	
OH	21.0	25.7
F	21.5	25.3
Cl	21.2	27.8
SCH3	21.9	27.6



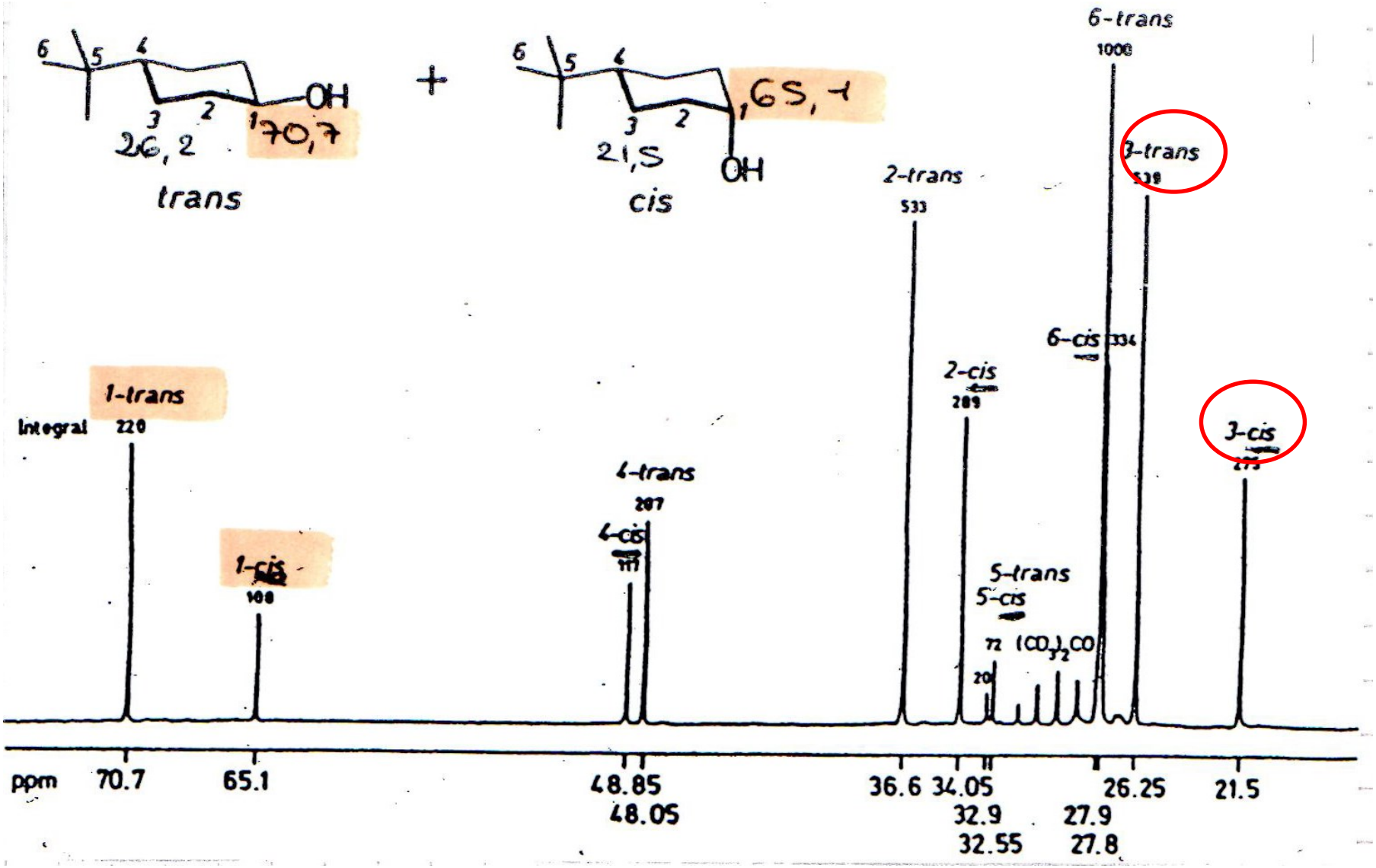






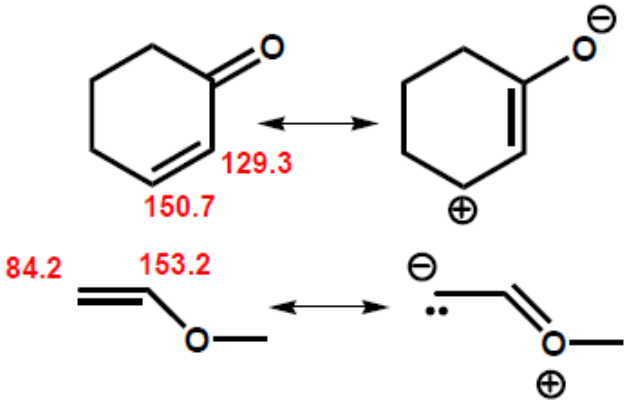
	endo	eso
H	30.1	
CH3	22.4	29.0
OH	20.4	24.9
OCH3	20.5	27.6
NH2	20.6	27.0

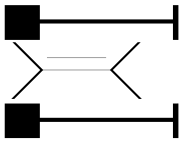
4-terbutilcicloesanolo



Effetti di risonanza

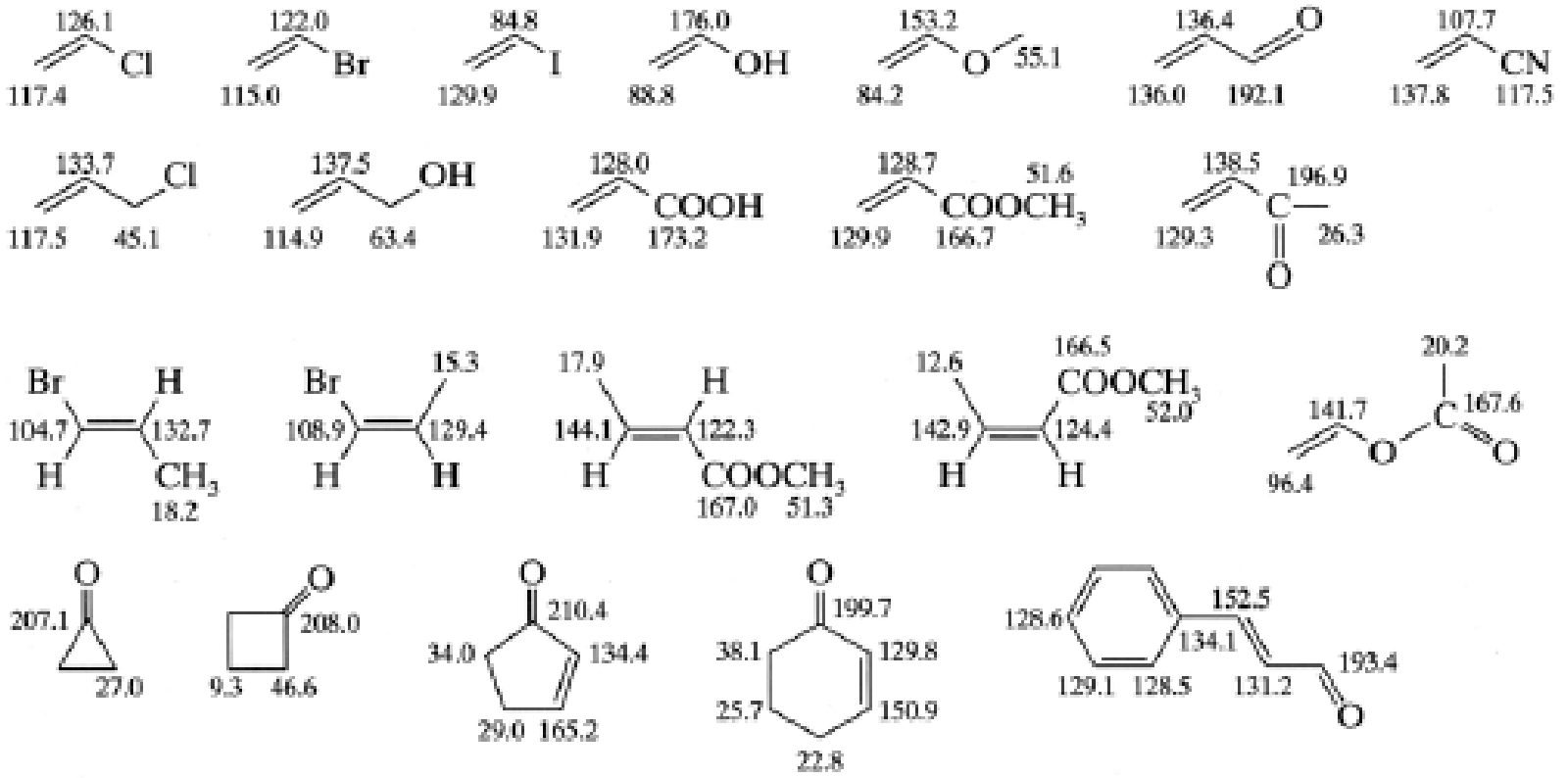
Mentre gli effetti induttivi si trasmettono in massima parte sul Cα, quelli di risonanza agiscono maggiormente sul Cβ





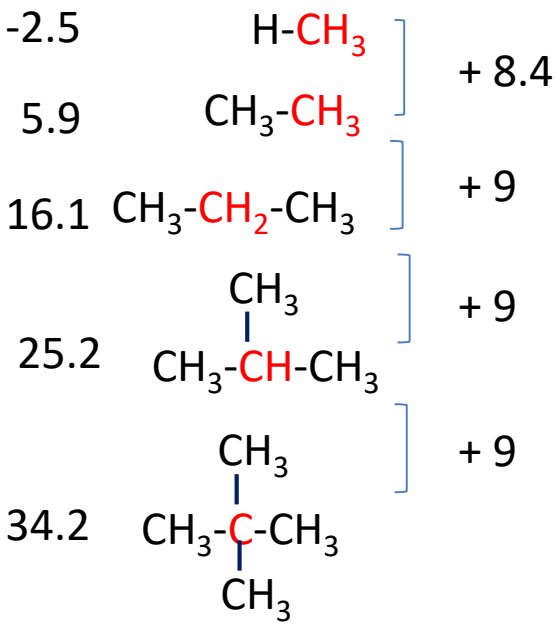
123.3 ppm

Esempi

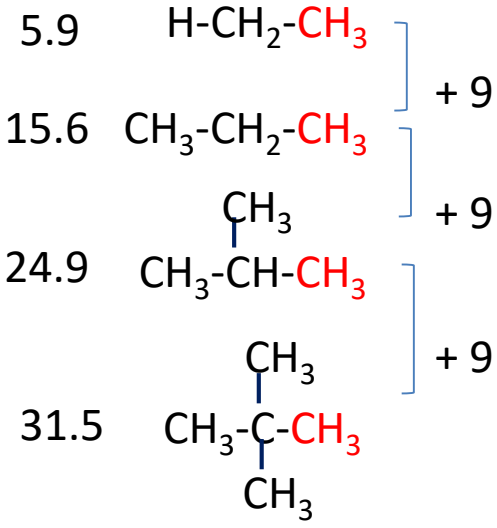

126.1
Cl
117.4
122.0
Br
115.0
84.8
I
129.9
176.0
OH
88.8
153.2
O
55.1
84.2
136.4
O
136.0
192.1
107.7
CN
137.8
117.5
133.7
Cl
117.5
45.1
137.5
OH
114.9
63.4
128.0
COOH
131.9
173.2
128.7
51.6
COOCH3
129.9
166.7
138.5
196.9
C
129.3
26.3
O
Br
H
104.7
132.7
H
CH3
18.2
Br
15.3
108.9
129.4
H
H
17.9
H
144.1
122.3
H
COOCH3
167.0
51.3
12.6
166.5
COOCH3
52.0
142.9
124.4
H
H
20.2
141.7
C
167.6
O
O
96.4
O
207.1
27.0
O
208.0
9.3
46.6
O
210.4
34.0
134.4
29.0
165.2
O
199.7
38.1
129.8
25.7
150.9
22.8
128.6
152.5
134.1
193.4
129.1
128.5
131.2
O

C sp^3 0 – 60 ppm

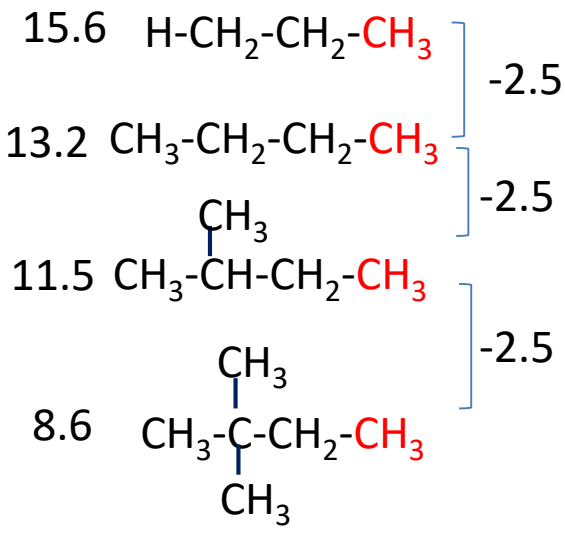
Effetto α
del Metile : + 9 ppm

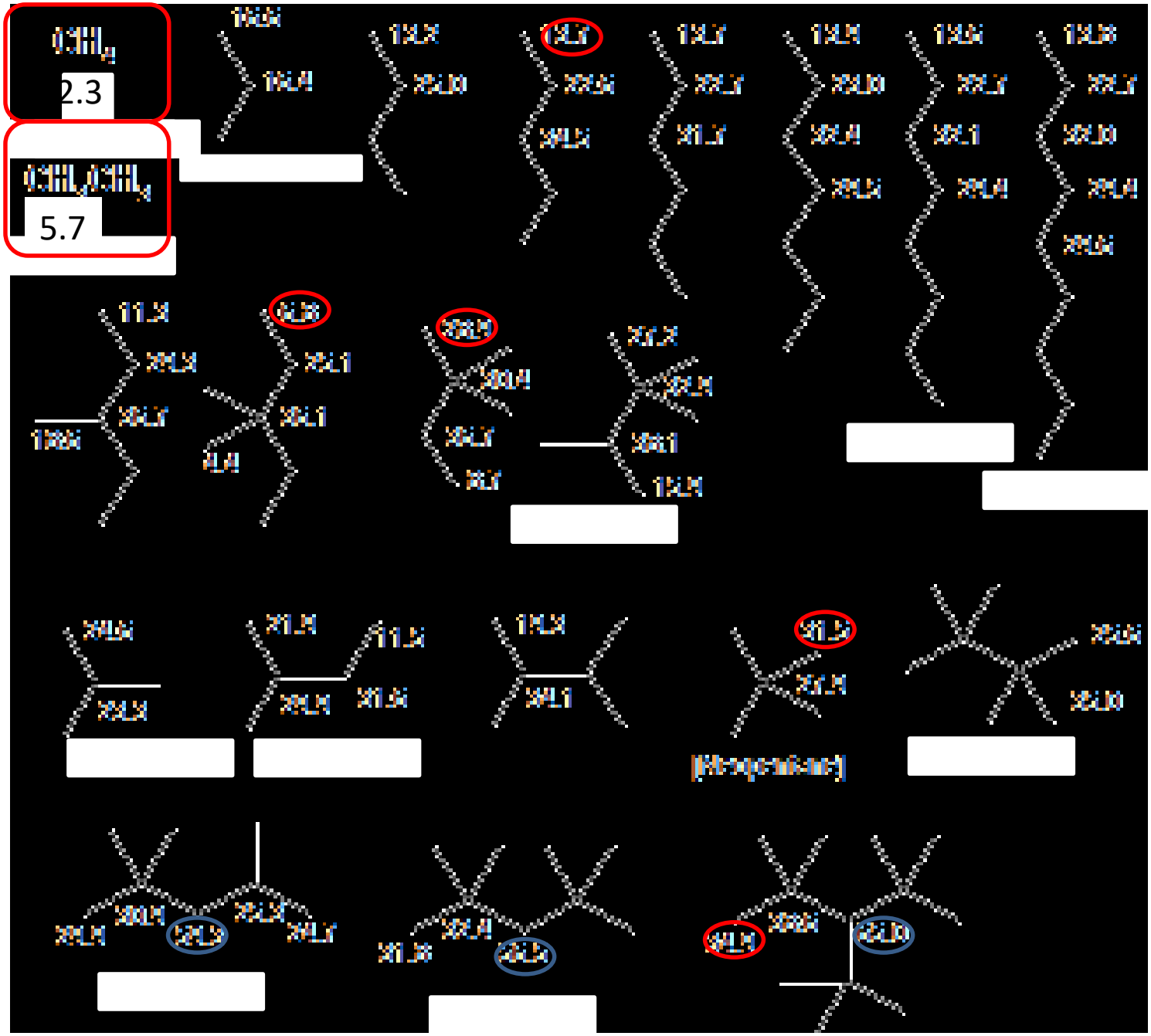


Effetto β
del Metile: + 9 ppm



Effetto γ
del Metile: -2.5 ppm

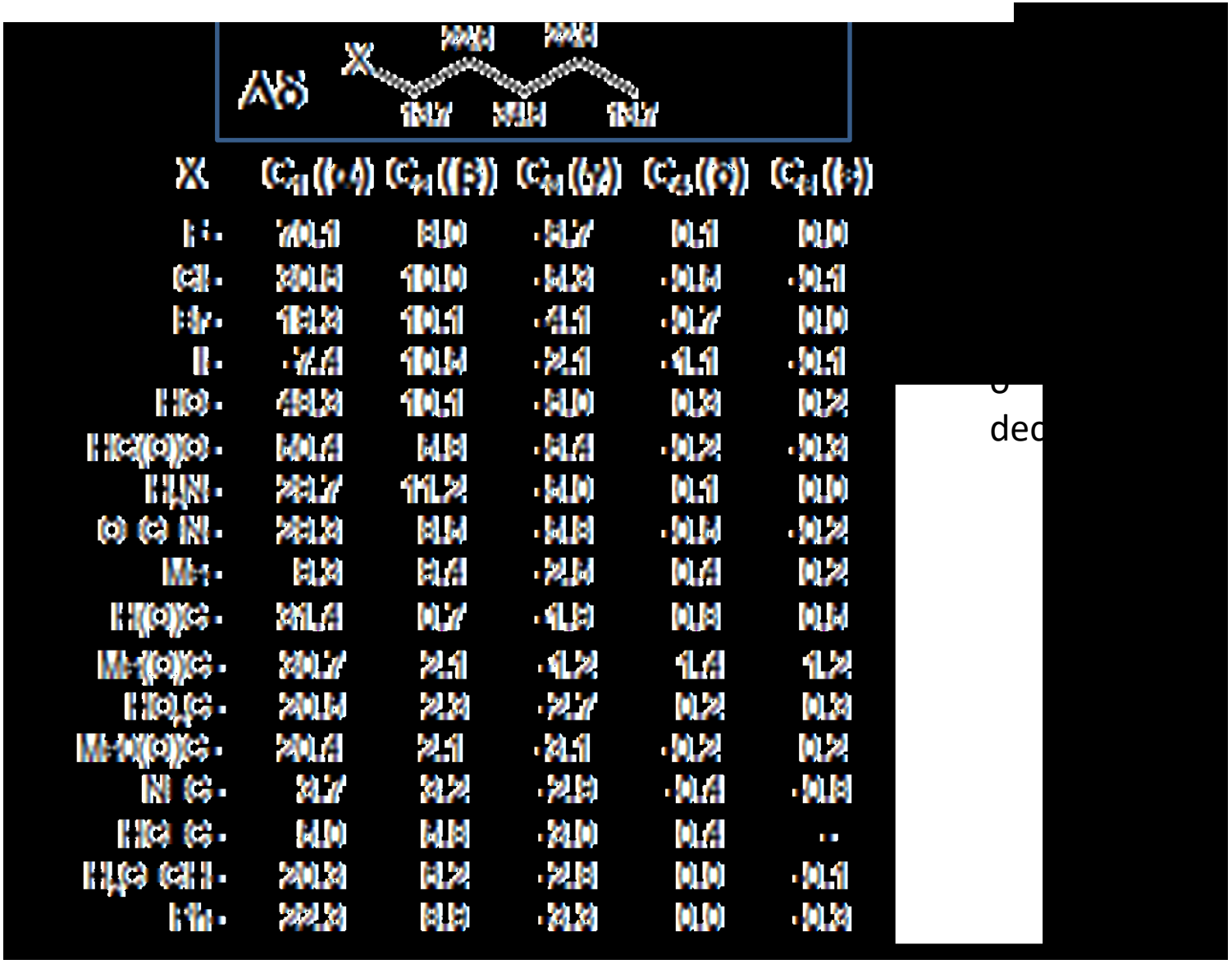



2.3
5.7

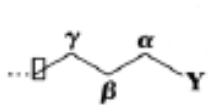
Chemical shift ^{13}C per alcani lineari e ramificati

Compound	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3			
Butane	13.4	25.2			
Pentane	13.9	22.8	34.7		
Hexane	14.1	23.1	32.2		
Heptane	14.1	23.2	32.6	29.7	
Octane	14.2	23.2	32.6	29.9	
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

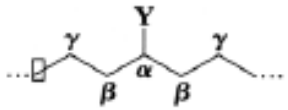
ALCANI SOSTITUITI



Incrementi per alcani sostituiti



Terminal

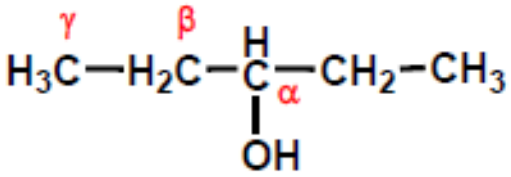


Internal

	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	9	6	10	8	−2
$CH{=}CH_2$	20		6		−0.5
$C{\equiv}CH$	4.5		5.5		−3.5
COOH	21	16	3	2	−2
COO^-	25	20	5	3	−2
COOR	20	17	3	2	−2
COCl	33	28		2	
$CONH_2$	22		2.5		−0.5
COR	30	24	1	1	−2
CHO	31				−2
Phenyl	23	17	9	7	−2
OH	48	41	10	8	−5
OR	58	51	8	5	−4
OCOR	51	45	6	5	−3
NH_2	29	24	11	10	
NH_3^+	26	24	8	6	−5
NHR	37	31	8	6	−4
NR_2	42		6		−3
NR_3^+	31		5		−7
NO_2	63	57	4	4	
CN	4	1	3	3	−3
SH	11	11	12	11	−4
SR	20		7		−3
F	68	63	9	6	−4
Cl	31	32	11	10	−4
Br	20	25	11	10	−3
I	−6	4	11	12	−1

Aggiungere gli incrementi al valore dell'appropriato carbonio del corrispondente alcano saturo mostrato nella tabella affianco.

ESEMPIO 3-PENTANOLO



Cα = 34.7 + 41 = 75.7 (73.8)
Cβ = 22.8 + 8 = 30.8 (29.7)
Cγ = 13.9 – 5 = 8.9 (9.8)

C sp 60 - 95 ppm 

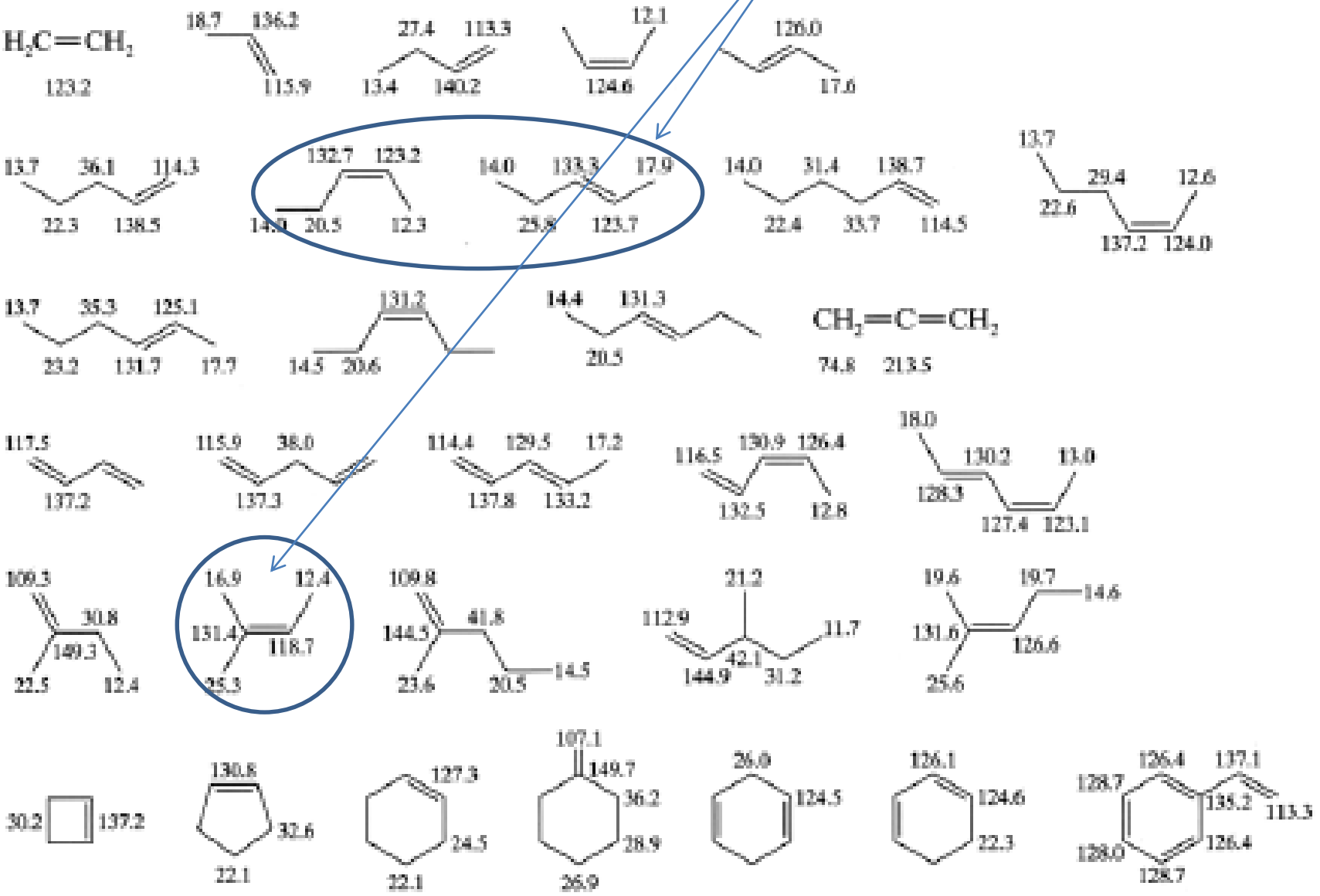
112 – 126 ppm 

C sp^2 110 - 150 ppm

$CH_2=CH_2$ 123.3 ppm

ALCHENI

Compressione sterica



ALCHENI

X-$\overset{1}{C}H=\overset{2}{C}H_2$ $\quad \delta 1 = 123.3 + I_1$

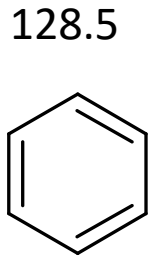
$\delta 2 = 123.3 + I_2$

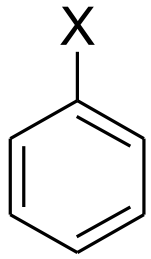
X-$\overset{1}{C}H=\overset{2}{C}H$-Y $\quad \delta 1 = 123.3 + I_{X1} + I_{Y2}$

$\delta 2 = 123.3 + I_{Y1} + I_{X2}$

Sostituente	Incrementi	
	I_1	I_2
—H	0	0
—CH_3	10,6	− 8,0
—C_2H_5	15,5	− 9,7
—CH_2—CH_2—CH_3	14,0	− 8,2
—$CH(CH_3)_2$	20,3	−11,5
—$(CH_2)_2$—CH_3	14,7	− 9,0
—$C(CH_3)_3$	25,3	−13,3
—CH=CH_2	13,6	− 7,0
—C≡C—R	− 7,5	8,9
—C_6H_5	12,5	−11,0
—CH_2Cl	10,2	− 6,0
—CH_2Br	10,9	− 4,5
—CH_2OR	13,0	− 8,6
—CH=O	13,1	12,7
—CO—CH_3	15,0	5,9
—COOH	4,2	8,9
—COOR	6,0	7,0
—CN	−15,1	14,2
—OR	28,8	−39,5
—O—CO—R	18,0	−27,0
—NR_2	16,0	−29,0
—$\overset{+}{N}(CH_3)_3$	19,8	−10,6
—NO_2	22,3	− 0,9
—SR	19,0	−16,0
—F	24,9	−34,3
—Cl	2,6	− 6,1
—Br	− 7,9	− 1,4
—I	−38,1	7,0

AROMATICI



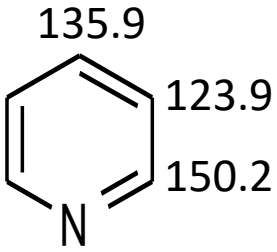


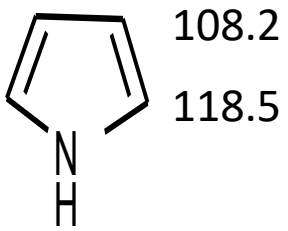
C-1 96.7 – 168.3 (Risente dell'elettronegatività di X)

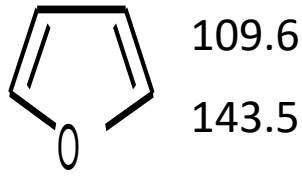
C-orto range 15 ppm
C-meta 127.2 – 131.6
C para range 15 ppm

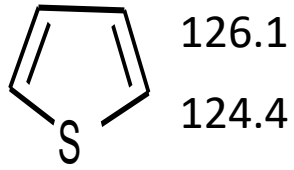
} C orto > C para

ETEROAROMATICI

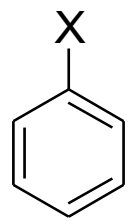








Benzene monosostituito

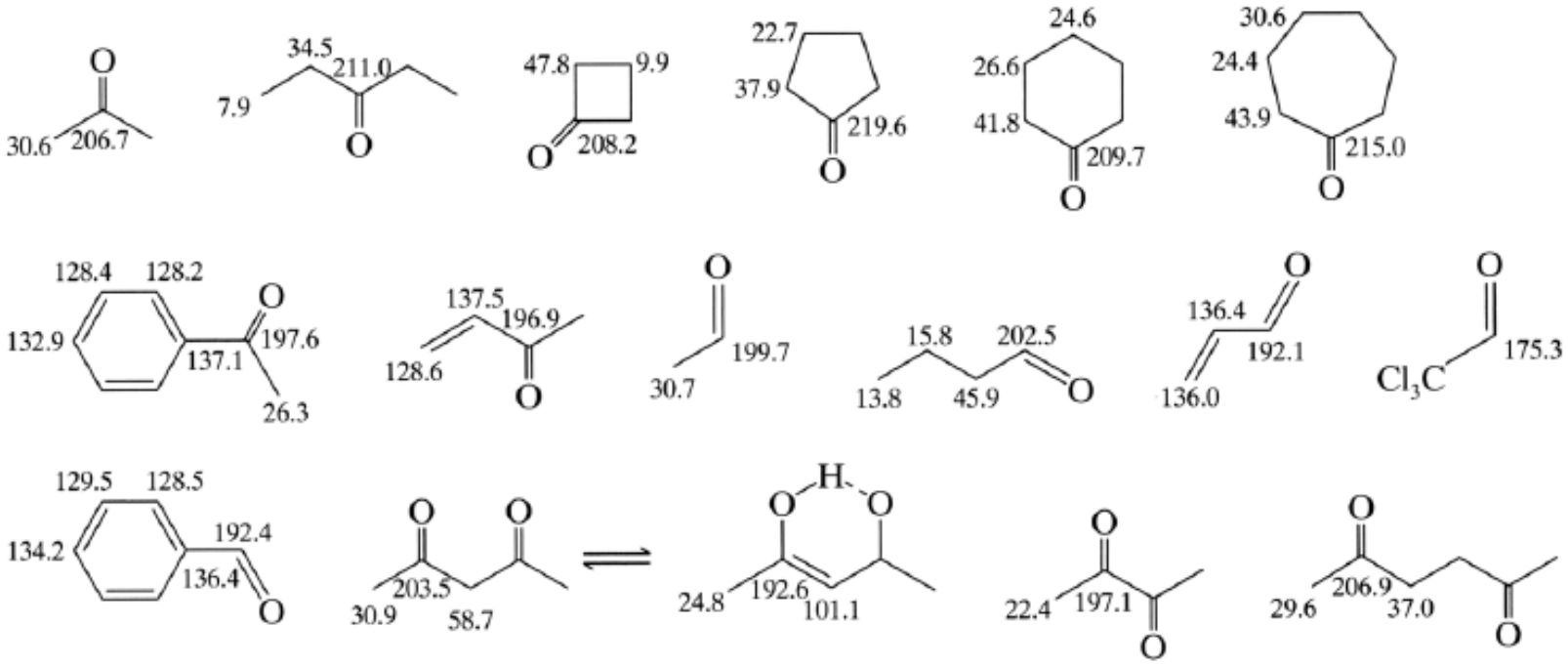


$128 + I_1 + I_2 + I_3 + I_4$

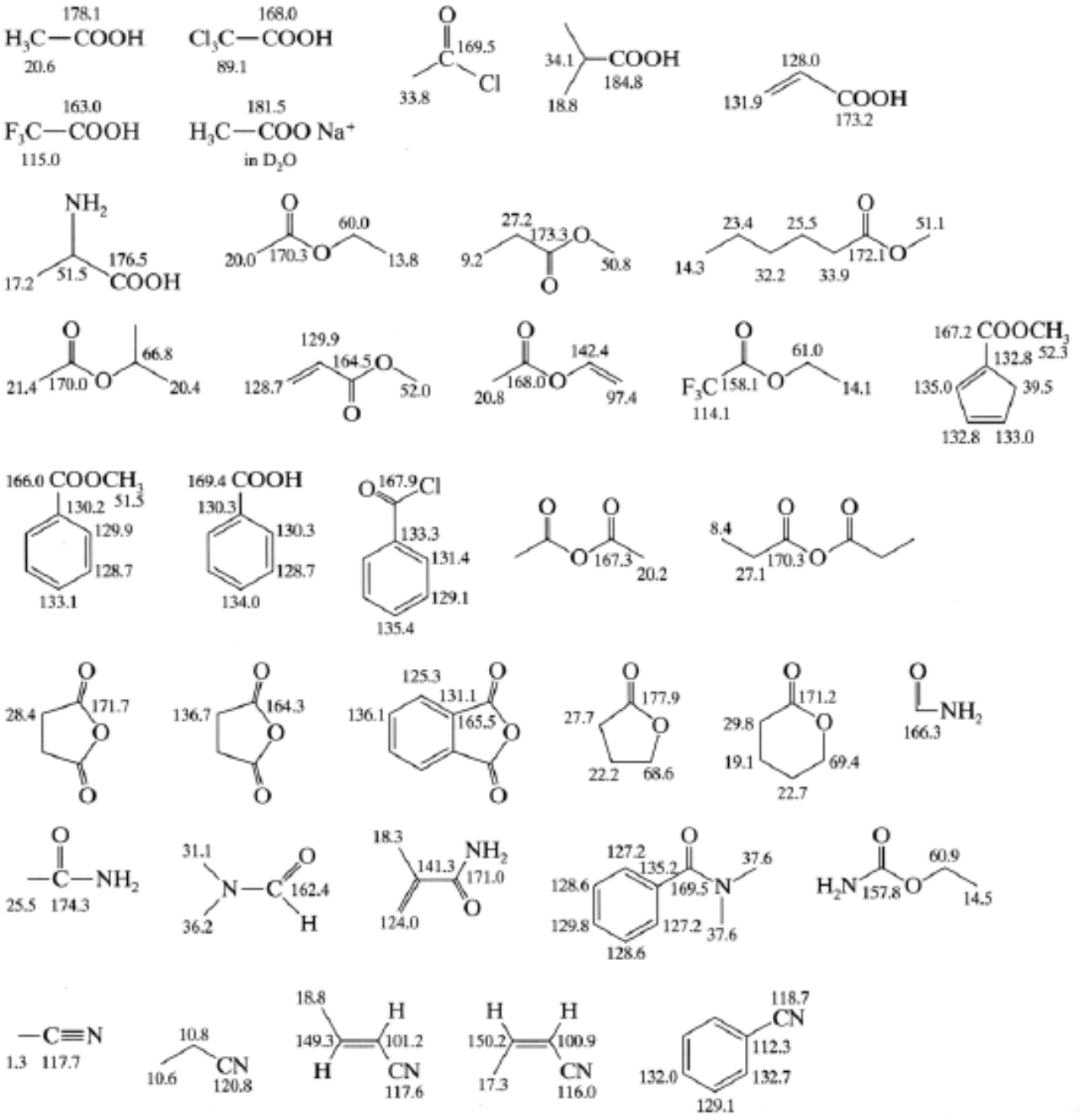
Substituent	C-1 (Attachment)	C-2	C-3	C-4
H	0.0	0.0	0.0	0.0
CH_3	9.3	0.7	−0.1	−2.9
CH_2CH_3	15.6	−0.5	0.0	−2.6
$CH(CH_3)_2$	20.1	−2.0	0.0	−2.5
$C(CH_3)_3$	22.2	−3.4	−0.4	−3.1
$CH{=}CH_2$	9.1	−2.4	0.2	−0.5
$C{\equiv}CH$	−5.8	6.9	0.1	0.4
C_6H_5	12.1	−1.8	−0.1	−1.6
CH_2OH	13.3	−0.8	−0.6	−0.4
$CH_2O(C{=}O)CH_3$	7.7	~0.0	~0.0	~0.0
OH	26.6	−12.7	1.6	−7.3
OCH_3	31.4	−14.4	1.0	−7.7
OC_6H_5	29.0	−9.4	1.6	−5.3
$O(C{=}O)CH_3$	22.4	−7.1	−0.4	−3.2
$(C{=}O)H$	8.2	1.2	0.6	5.8
$(C{=}O)CH_3$	7.8	−0.4	−0.4	2.8
$(C{=}O)C_6H_5$	9.1	1.5	−0.2	3.8
$(C{=}O)F_3$	−5.6	1.8	0.7	6.7
$(C{=}O)OH$	2.9	1.3	0.4	4.3
$(C{=}O)OCH_3$	2.0	1.2	−0.1	4.8
$(C{=}O)Cl$	4.6	2.9	0.6	7.0
$(C{=}O)NH_2$	5.0	−1.2	0.0	3.4
$C{\equiv}N$	−16	3.6	0.6	4.3
NH_2	19.2	−12.4	1.3	−9.5
$N(CH_3)_2$	22.4	−15.7	0.8	−11.8
$NH(C{=}O)CH_3$	11.1	−9.9	0.2	−5.6
NO_2	19.6	−5.3	0.9	6.0
$N{=}C{=}O$	5.7	−3.6	1.2	−2.8
F	35.1	−14.3	0.9	−4.5
Cl	6.4	0.2	1.0	−2.0
Br	−5.4	3.4	2.2	−1.0
I	−32.2	9.9	2.6	−7.3
CF_3	2.6	−3.1	0.4	3.4
SH	2.3	0.6	0.2	−3.3
SCH_3	10.2	−1.8	0.4	−3.6
SO_2NH_2	15.3	−2.9	0.4	3.3
$Si(CH_3)_3$	13.4	4.4	−1.1	−1.1

Carbonile

Aldeidi e chetoni 190 – 210 ppm



Acidi carbossilici e derivati
150 – 180 ppm



ACCOPPIAMENTO C-F

CF3COOH CF3COOH

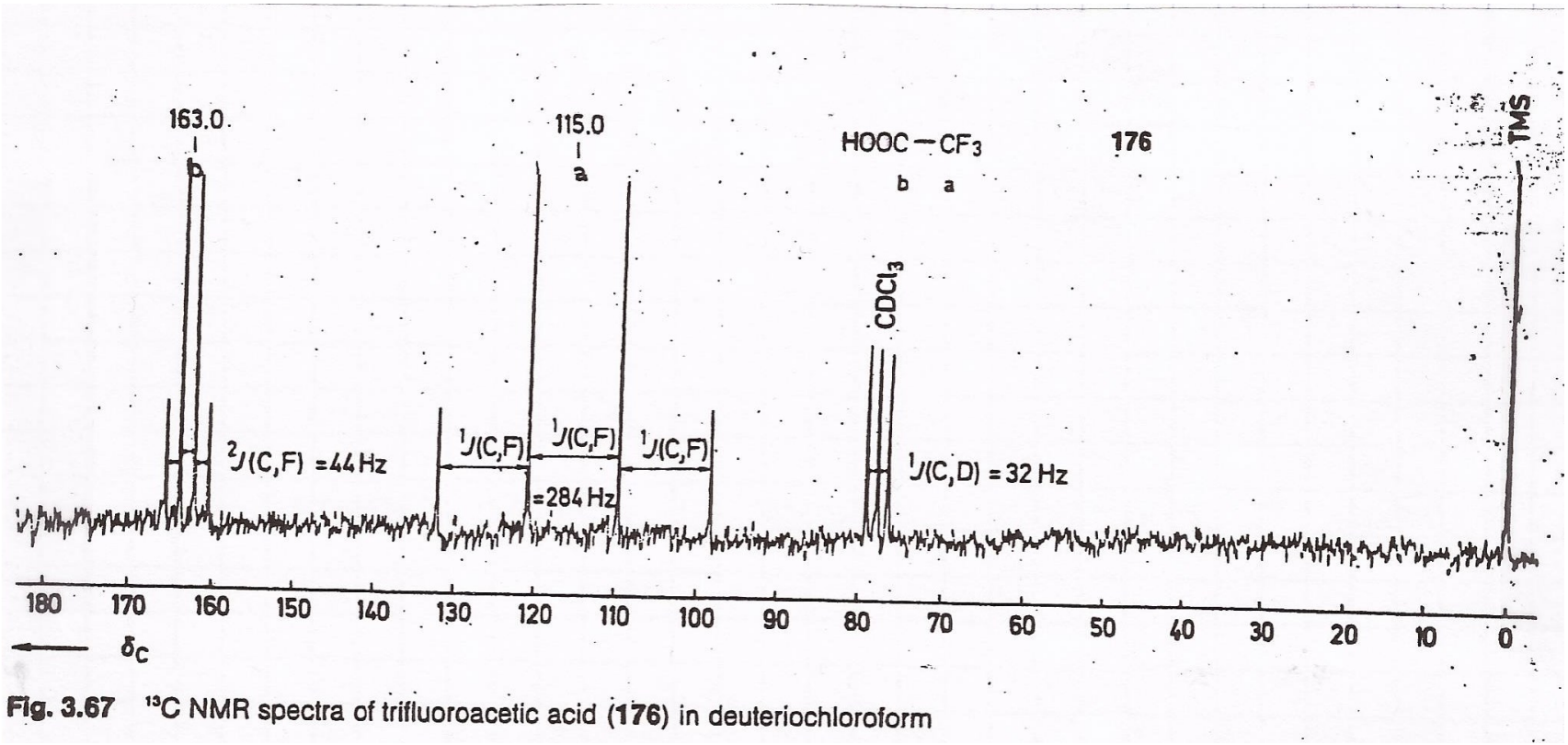


Fig. 3.67 ^{13}C NMR spectra of trifluoroacetic acid (**176**) in deuteriochloroform

ALOGENO DERIVATI

Compound	C-1	C-2	C-3
CH_4	−2.3		
CH_3F	75.4		
CH_3Cl	24.9		
CH_2Cl_2	54.0		
$CHCl_3$	77.5		
CCl_4	96.5		
CH_3Br	10.0		
CH_2Br_2	21.4		
$CHBr_3$	12.1		
CBr_4	−28.5		
CH_3I	−20.7		
CH_2I_2	−54.0		
CHI_3	−139.9		
CI_4	−292.5		
CH_3CH_2F	79.3	14.6	
CH_3CH_2Cl	39.9	18.7	
CH_3CH_2Br	28.3	20.3	
CH_3CH_2I	−0.2	21.6	
$CH_3CH_2CH_2Cl$	46.7	26.5	11.5
$CH_3CH_2CH_2Br$	35.7	26.8	13.2
$CH_3CH_2CH_2I$	10.0	27.6	16.2

È osservato l'effetto dell'atomo pesante per la sostituzione geminale con Br e I. Cl e Br mostrano l'effetto di schermo γ-gauche