ADVANCED
NUCLEAR MAGNETIC RESONANCE (ANMR)
UNIT 6: OTHER NUCLEI IN NMR

1. ^{1}H-OTHER NUCLEI COUPLING

   ^{1}H-^{19}F; ^{1}H-^{2}H; ^{1}H-^{31}P; ^{1}H-^{29}Si; ^{1}H-^{13}C

2. ^{13}C-OTHER NUCLEI COUPLING

   ^{13}C-^{19}F; ^{13}C-^{2}H; ^{13}C-^{31}P; ^{13}C-^{29}Si; ^{13}C-^{1}H

3. OTHER NUCLEI NUCLEAR MAGNETIC RESONANCE

   ^{15}N; ^{19}F; ^{31}P

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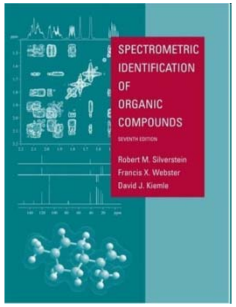
Bibliografía:

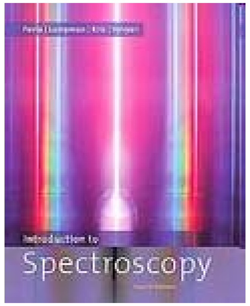
Spectrometric Identification of Organic Compounds, 7th Ed.

Robert M. Silverstein, Francis X. Webster, David J. Kiemle

Chapter 6

***NMR spectrometry of other important spin ½ nuclei* (page 216)**





Introduction to Spectroscopy, 4th Ed.

Donald L. Pavia, Gary M. Lampman, George S. Kriz, James R. Vyvyan

Chapter 4: Nuclear Magnetic Resonance Spectroscopy
***Part two: Carbon-13 spectra, including heteronuclear coupling with other nuclei* (page 177)**

Tablas para la determinación estructural por métodos espectroscópicos

Ernö Pretsch, Joseph Seibl, Wilhelm Simon, Thomas Clerc

ADVANCED NUCLEAR MAGNETIC RESONANCE (ANMR)

UNIT 6: OTHER NUCLEI IN NMR

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3. OTHER NUCLEI NUCLEAR MAGNETIC RESONANCE

   ^{15}N; ^{19}F; ^{31}P

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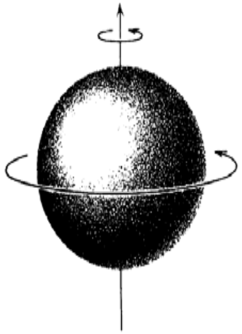
1. ^{1}H–Other Nuclei Coupling
Introduction



Nuclei with *I* ≠ 0?

I	Atomic Mass	Atomic Number	Examples (*I*)
Half-integer	Odd	Even or Odd	$^{1}_{1}H$ (1/2) $^{17}_{8}O$ (5/2) $^{15}_{7}N$ (1/2)
Integer	Even	Odd	$^{2}_{1}H$ (1) $^{10}_{5}B$ (3) $^{14}_{7}N$ (1)
Zero	Even	Even	$^{12}_{6}C$ (0) $^{16}_{8}O$ (0) $^{34}_{16}S$ (0)

$$\hbar = h/2\pi$$

$$L = I\hbar = Ih/2\pi$$

$$\mu = \gamma L$$

$$\gamma = \mu/I\hbar = 2\pi\mu/Ih$$

$$\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$$

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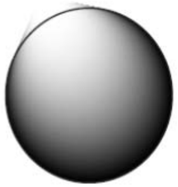
1. ^{1}H–Other Nuclei Coupling Introduction

ELECTRIC QUADRUPOLE MOMENT

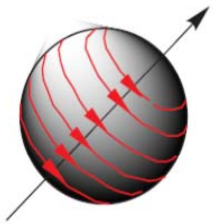
A. Non-spinning sphere



Nuclear Spin *I* = 0
Angular Moment *p* = 0
Magnetic Moment $\mu = 0$
Quadrupolar Moment *Q* = 0

I = 0 (^{12}C, ^{18}O, ^{32}S)
Atomic Mass (A) and Atomic number (Z) Even

B. Spinning sphere



Nuclear Spin *I* = 1/2
Angular Moment *p* = 1/2 (h/2π)
Magnetic Moment $\mu \neq 0$
Quadrupolar Moment *Q* = 0

I = 1/2 (^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P)
Atomic Mass (A) Odd
Atomic Number (Z) Even or Odd

Diapositiva 5

MA4 Throughout the document, some footnotes are in Spanish. I understand this is not included in the version of the powerpoint that the students will be getting.
Otherwise they should be translated into English.
María Abad; 20/10/2014

1. ^{1}H–Other Nuclei Coupling
Introduction

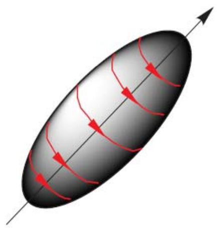
ELECTRIC QUADRUPOLE MOMENT

C. Spinning ellipse

When I ≥ 1 ⟶ Ellipsoidal charge distribution

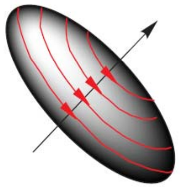
Nuclear Spin $I \geq 1$ (1, 3/2, 5/2,…)
Angular Moment p = I (h/2π)
Magnetic Moment $\mu \neq 0$
Quadrupolar Moment $Q \neq$ (positive for I = 1, negative for I > 1

Prolate Spheroid



I = 1 (^{2}H, ^{14}N)

Oblate Spheroid



I > 1 [^{17}O (I = 5/2), ^{35}Cl (I = 3/2)]

1. ^{1}H–Other Nuclei Coupling Introduction

Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
^{13}C	1.11	1/2	0.70220	75.432	$1.59x10^{-2}$	6.728
^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
^{15}**N**	0.37	1/2	-0.28304	30.398	$1.04x10^{-3}$	-2.712
^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

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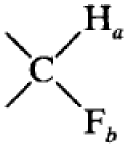
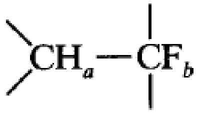
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{19}F



44–81



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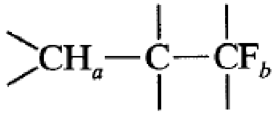

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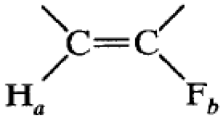

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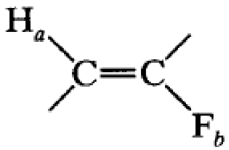

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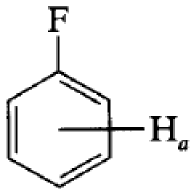
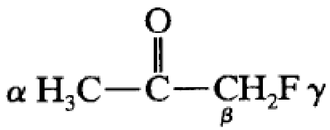


o 6–10
m 5–6
p 2



$\alpha\gamma$ 4.3
$\beta\gamma$ 48

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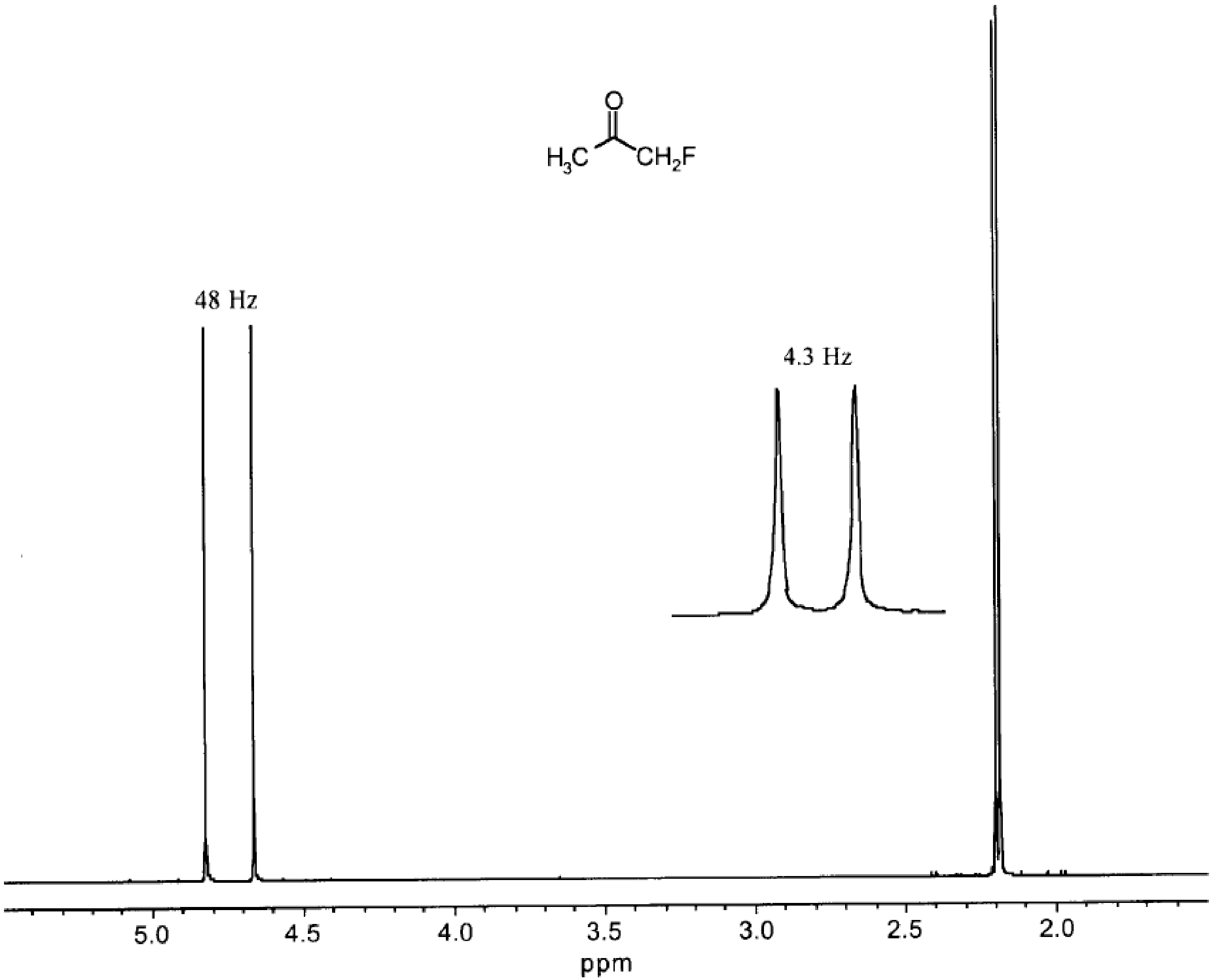
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{19}F



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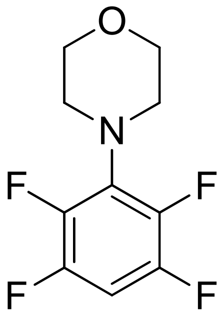
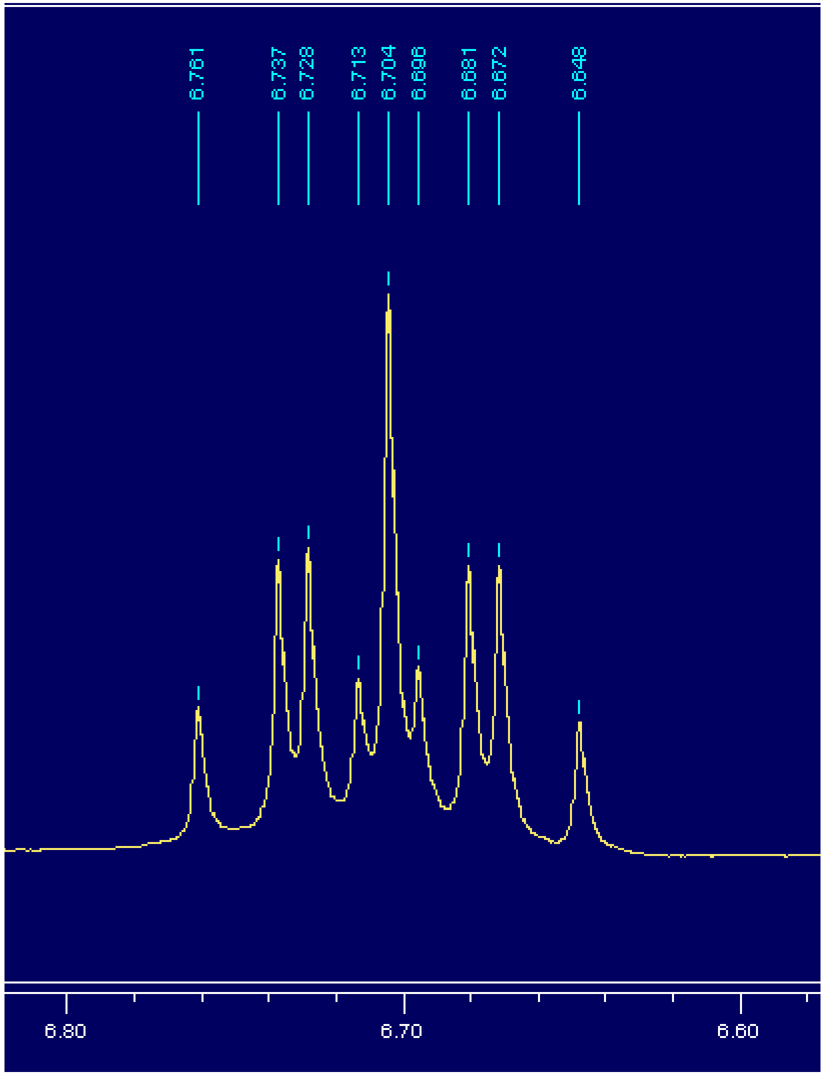
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{19}F





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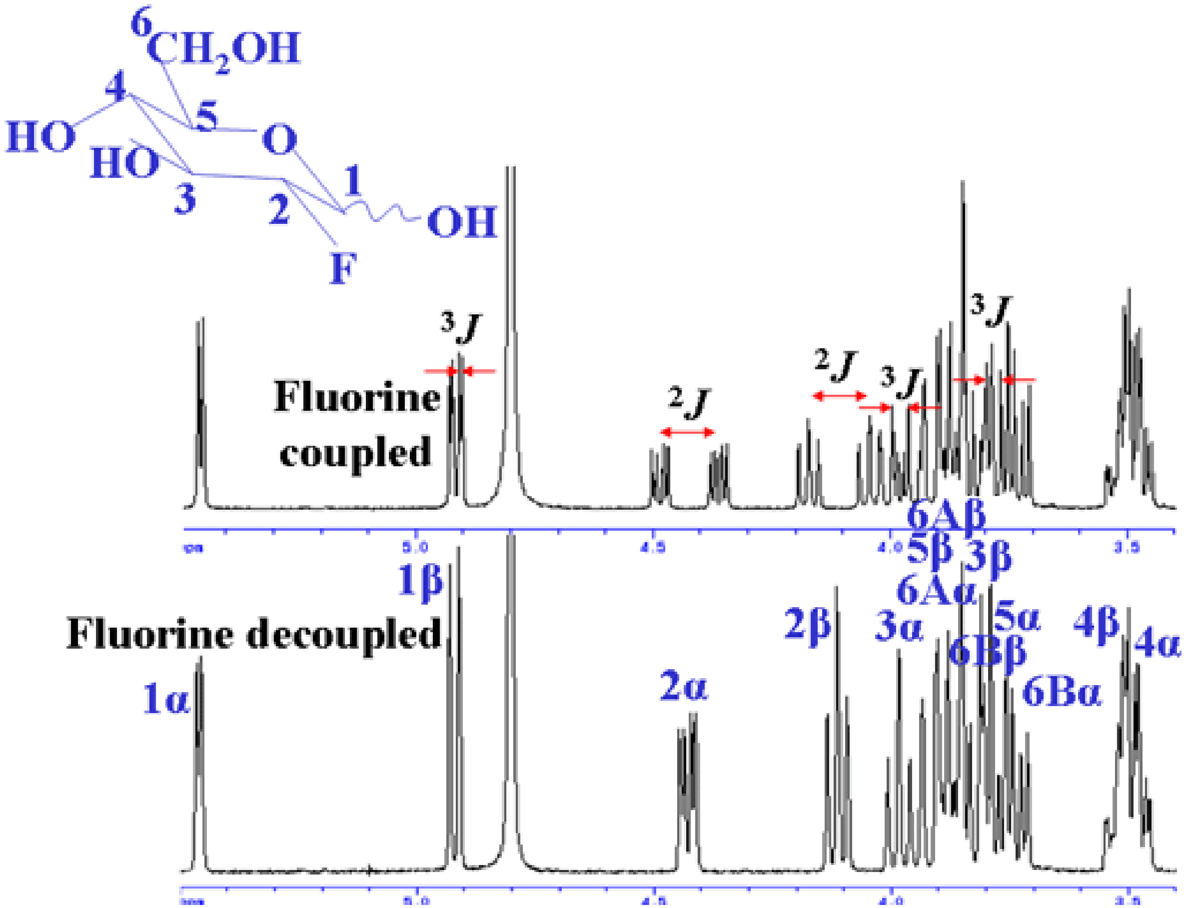
1. ^1H–Other Nuclei Coupling

^1H–^{19}F



1. ^{1}H–Other Nuclei Coupling

^{1}H–^{2}H

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1. ^{1}H–Other Nuclei Coupling

^{1}H–^{2}H

Solvent	M	δ (multiplicity)
Acetic acid-d_4	64.078	11.53 (1)
		2.03 (5)
Acetone-d_6	64.117	2.04 (5)
Acetonitrile-d_3	44.071	1.93 (5)
Benzene-d_6	84.152	7.15 (br)
Chloroform-d	120.384	7.26 (1)
Cyclohexane-d_{12}	96.236	1.38 (br)
Deuterium oxide	20.028	4.63 (ref. DSS)[c]
		4.67 (ref. TSP)[c]
1,2-Dichloroethane-d_4	102.985	3.72 (br)
Diethyl-d_{10} ether	84.185	3.34 (m)
		1.07 (m)
Diglyme-d_{14}	148.263	3.49 (br)
		3.40 (br)
		3.22 (5)
Nitromethane-d_3	64.059	4.33 (5)
Isopropyl alcohol-d_8	68.146	5.12 (1)
		3.89 (br)
		1.10 (br)
Pyridine-d_5	84.133	8.71 (br)
		7.55 (br)
		7.19 (br)
Tetrahydrofuran-d_8	80.157	3.58 (br)
		1.73 (br)
Toluene-d_8	100.191	7.09 (m)
		7.00 (br)
		6.98 (m)
		2.09 (5)
Trifluoroacetic acid-d	115.030	11.50 (1)
2,2,2-Trifluoroethyl alcohol-d_3	103.059	5.02 (1)
		3.88 (4 × 3)
N,N-Dimethylformamide-d_7	80.138	8.01 (br)
		2.91 (5)
		2.74 (5)
Dimethyl-d_6 sulphoxide	84.170	2.49 (5)
p-Dioxane-d_8	96.156	3.53 (m)
Ethyl alcohol-d_6 (anh)	52.106	5.19 (1)
		3.55 (br)
		1.11 (m)
Glyme-d_{10}	100.184	3.40 (m)
		3.22 (5)
Hexafluoroacetone deuterate	198.067	5.26 (1)
HMPT-d_{18}	197.314	2.53 (2 × 5)
Methyl alcohol-d_4	36.067	4.78 (1)
		3.30 (5)
Methylene chloride-d_2	86.945	5.32 (3)
Nitrobenzene-d_5	128.143	8.11 (br)
		7.67 (br)
		7.50 (br)

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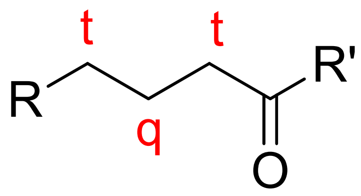
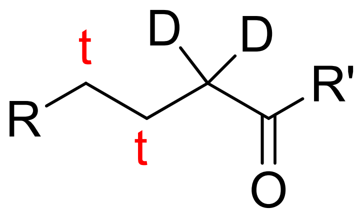
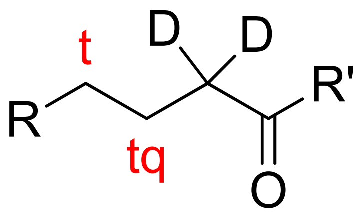
^{1}H–^{2}H



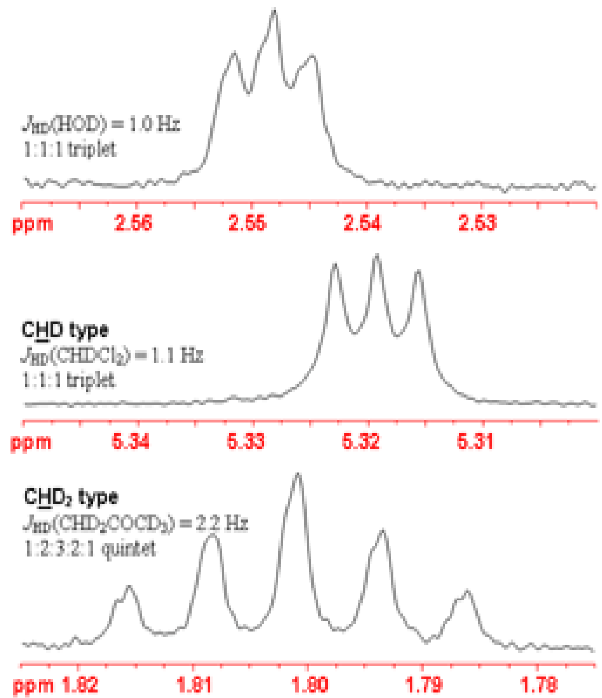


Low resolution



High Resolution

J = 7, 1 Hz



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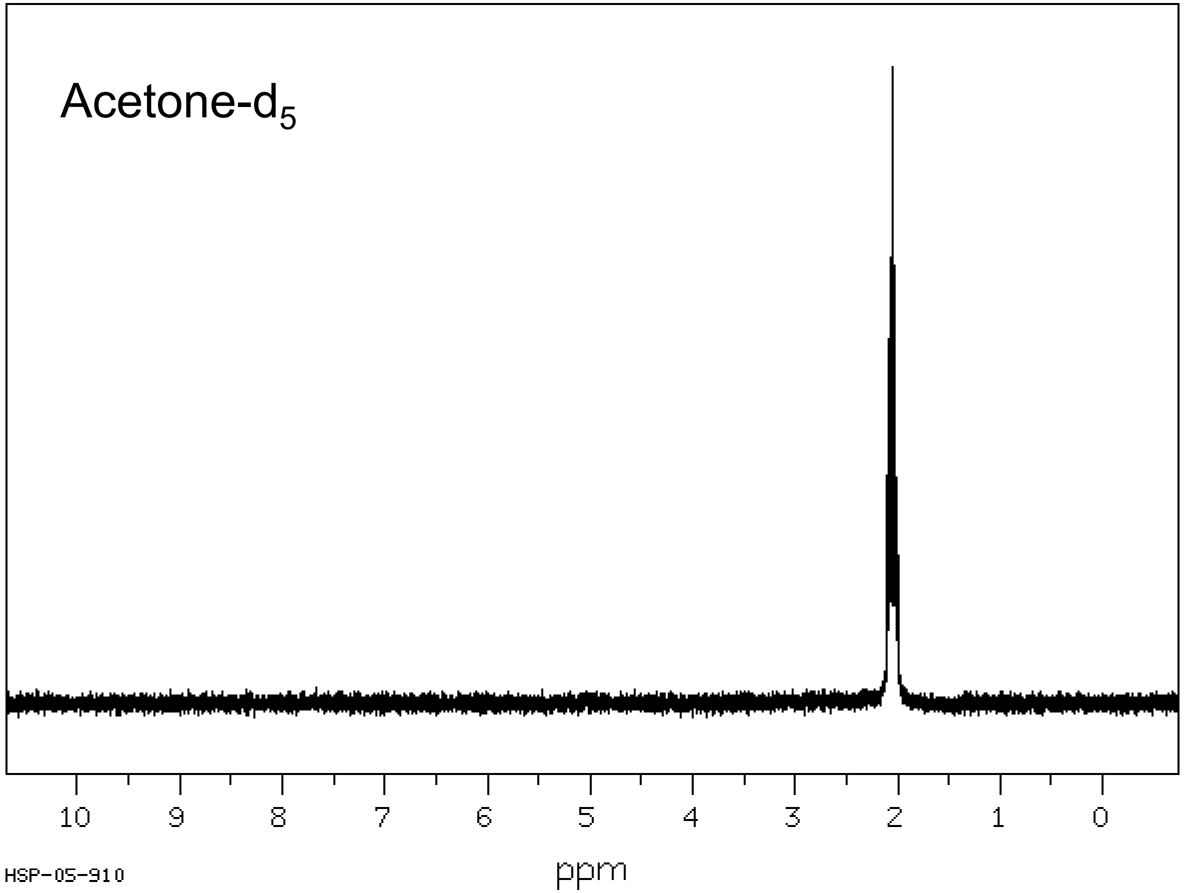
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{2}H



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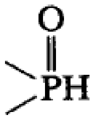
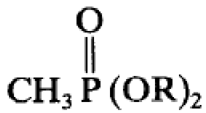
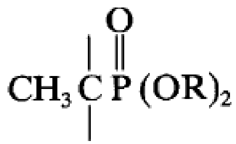
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{31}P

J (H-P) = 200-700 Hz; *J* (HC-P) = 0.5-20 Hz

	630–707	
$(CH_3)_3P$	2.7	
$(CH_3)_3P{=}O$	13.4	
$(CH_3CH_2)_3P$	0.5 (HCCP)	13.7 (HCP)
$(CH_3CH_2)_3P{=}O$	11.9 (HCCP)	16.3 (HCP)
	10–13	
	15–20	
$CH_3OP(OR)_2$	10.5–12	
$P[N(CH_3)_2]_3$	8.8	
$O{=}P[N(CH_3)_2]_3$	9.5	

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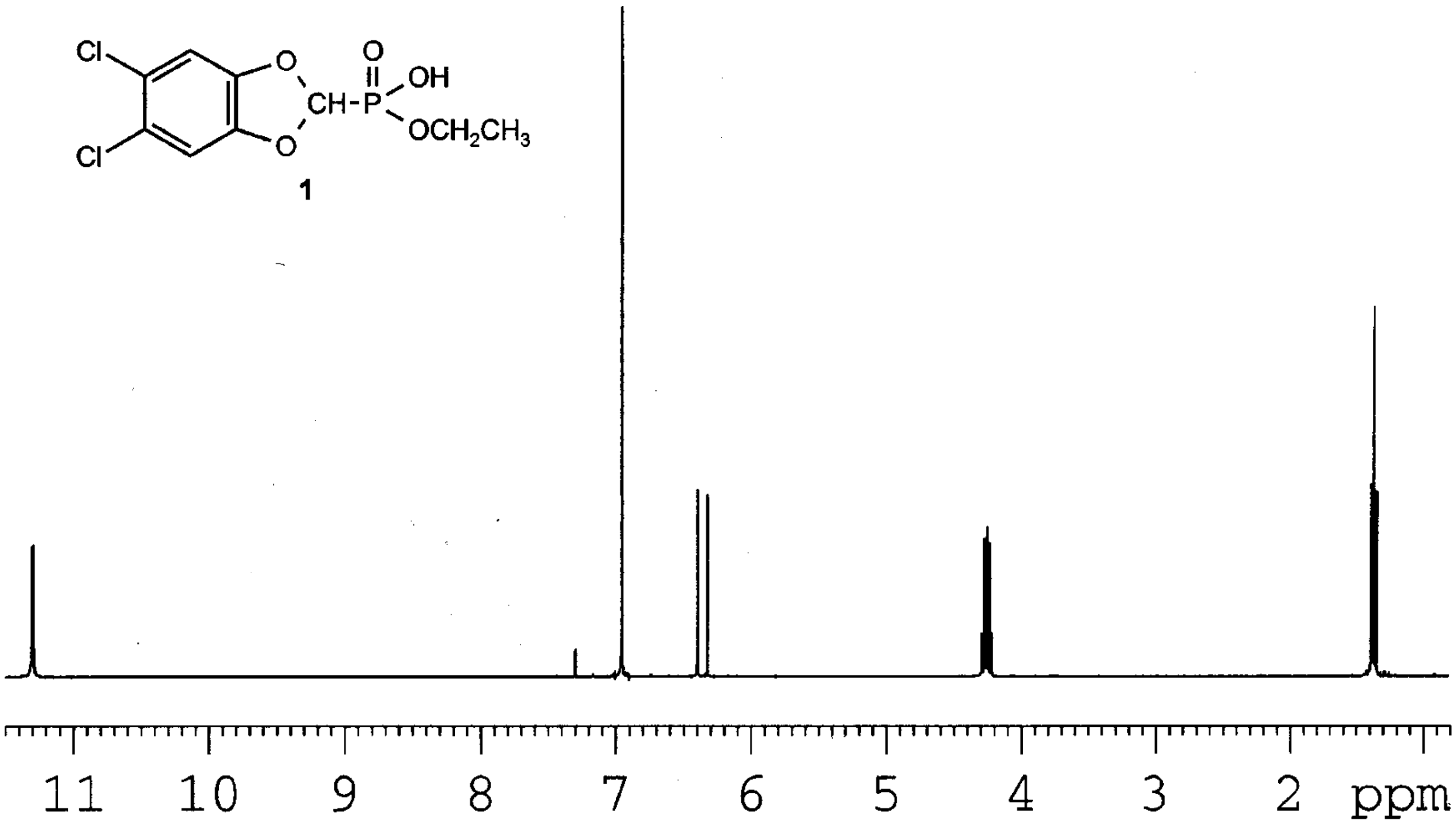
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{31}P



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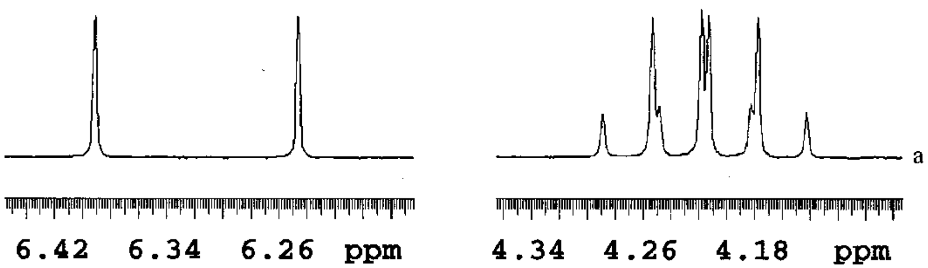
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{31}P



H	δ (ppm)	*J* (^{1}H–^{31}P) (Hz)
OH	11.58	0
ArCH	6.92	–
CHP	6.32	28.7
CH_2	4.20	8.0
CH_3	1.33	0.6

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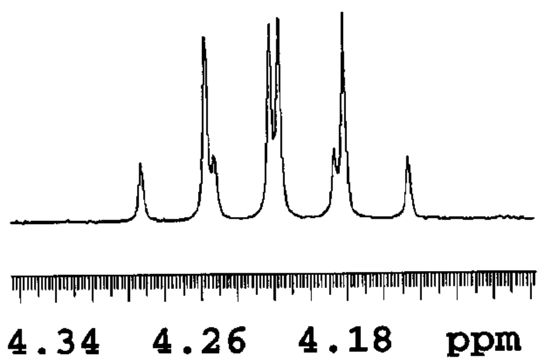
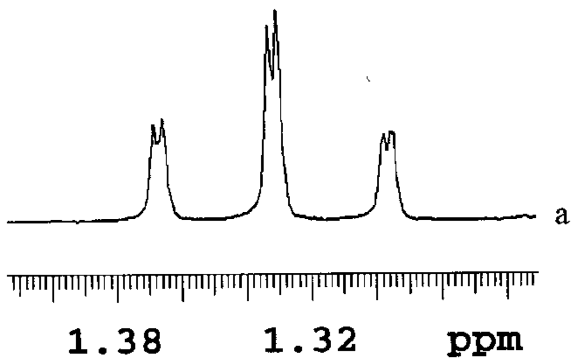
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{31}P





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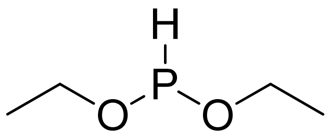
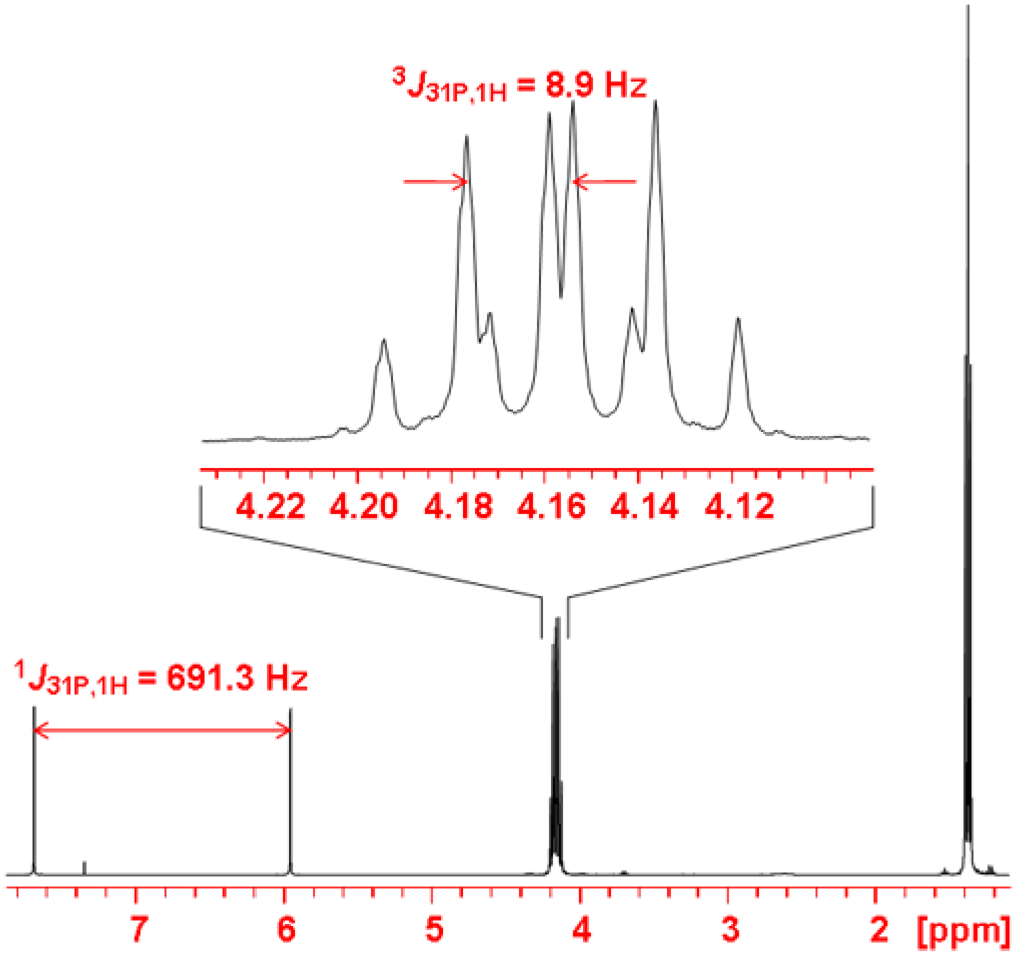
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{31}P

J (H-P) = 200-700 Hz; J (HC-P) = 0.5-20 Hz





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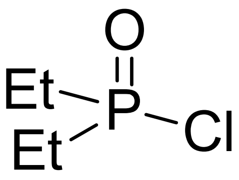
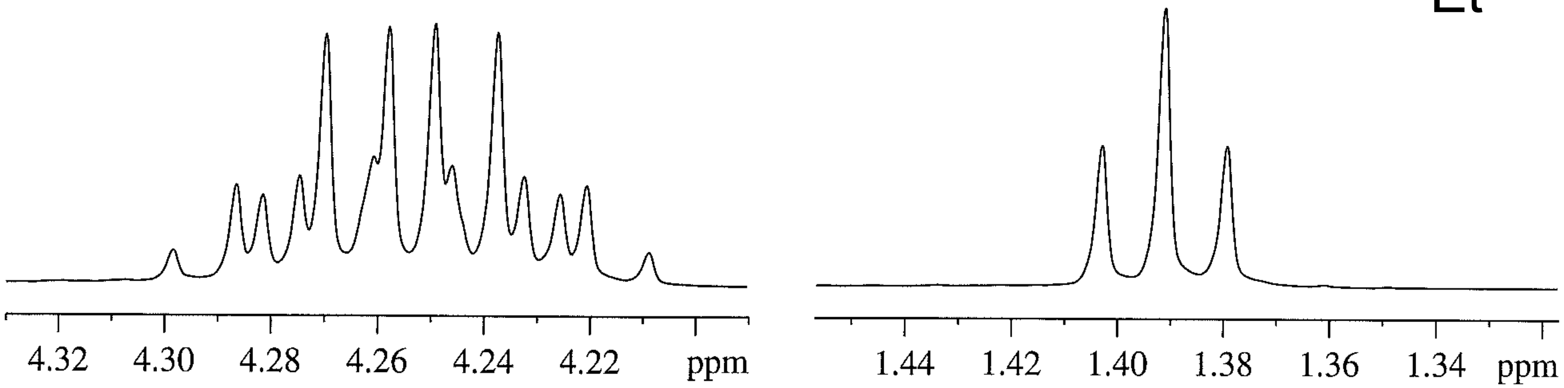
1. ^{1}H–Other Nuclei Coupling

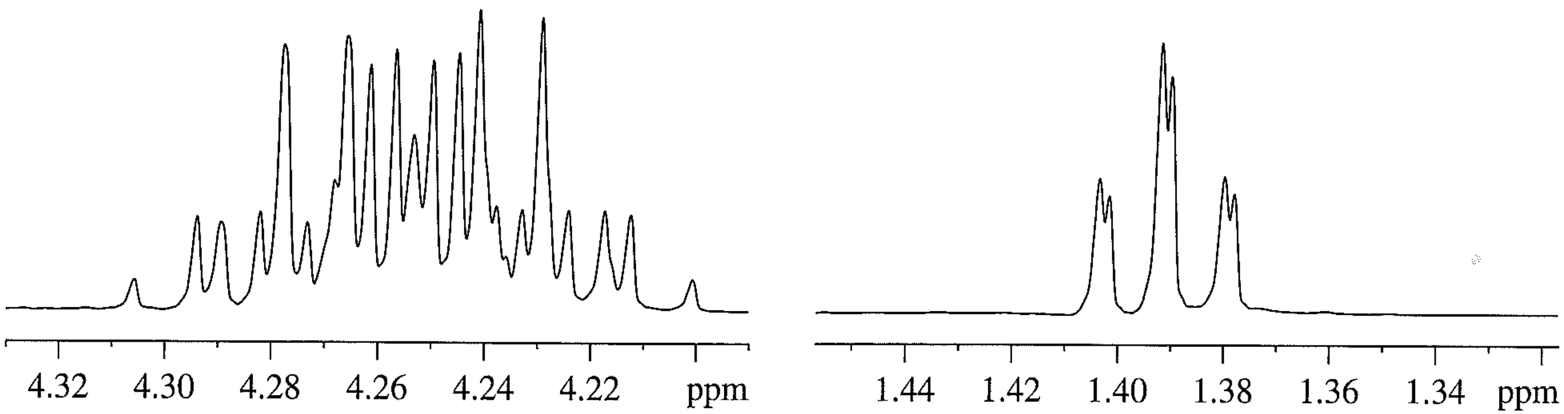
^{1}H–^{31}P



^{1}H NMR 600 MHz ^{31}P decoupled



^{1}H NMR 600 MHz coupled ^{31}P



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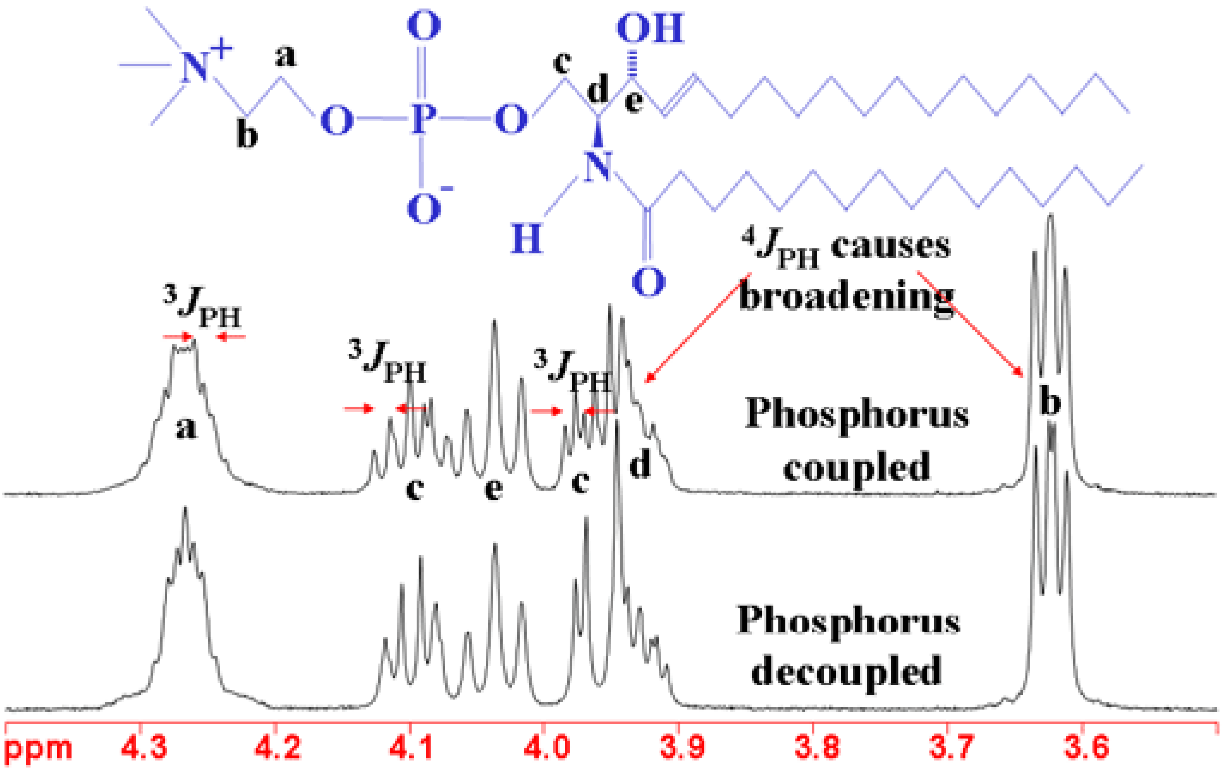
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{31}P



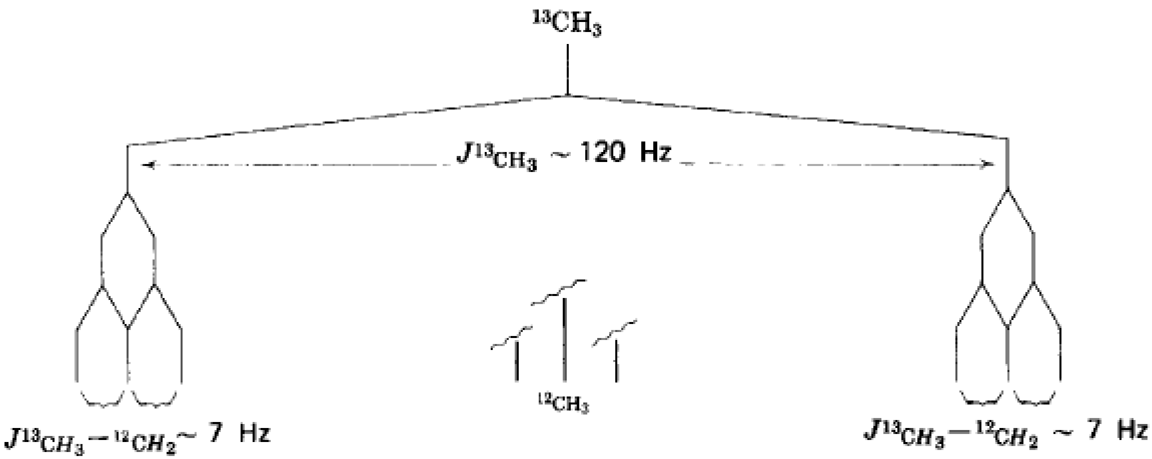
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{13}C

Isotope	Natural Abundance (%)	Nuclear Spin (*I*)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
^{13}C	1.11	1/2	0.70220	75.432	$1.59x10^{-2}$	6.728
^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
^{15}N	0.37	1/2	-0.28304	30.398	$1.04x10^{-3}$	-2.712
^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

1. ^{1}H–Other Nuclei Coupling
^{1}H–^{13}C

J (^{13}C-H) = 110-320 Hz; J (^{13}C-^{13}C-H) = – 5 to 60 Hz (typically 7)



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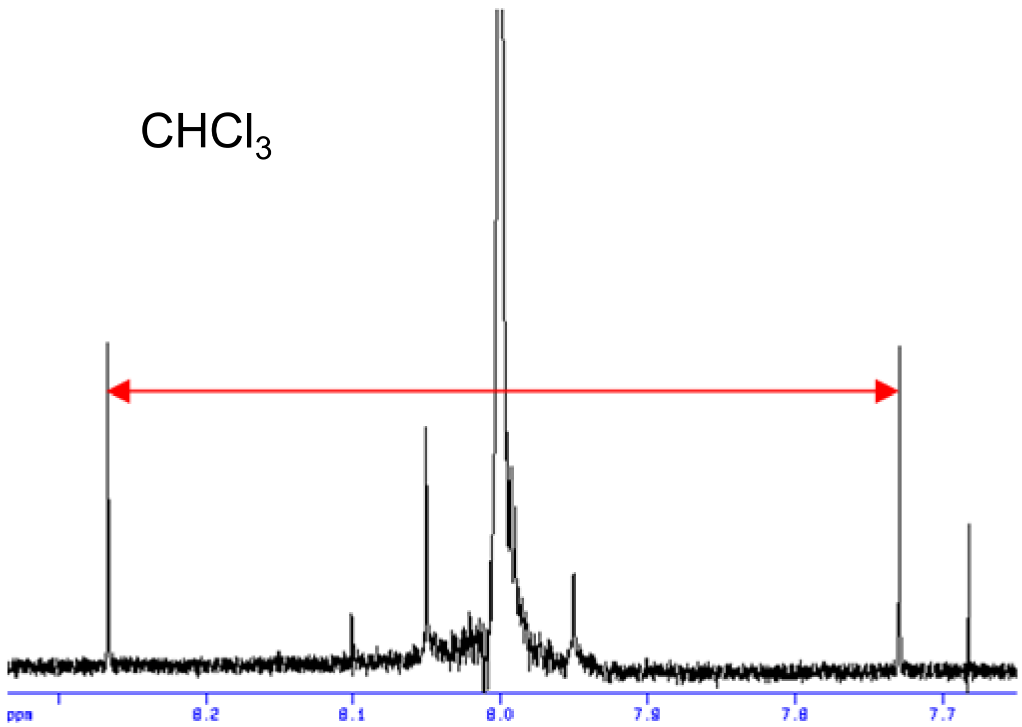
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{13}C

J (^{13}C-H) = 110-320 Hz (typically 125-160 Hz); *J* (^{13}C-^{13}C-H) = - 5 to 60 Hz (typically 7)



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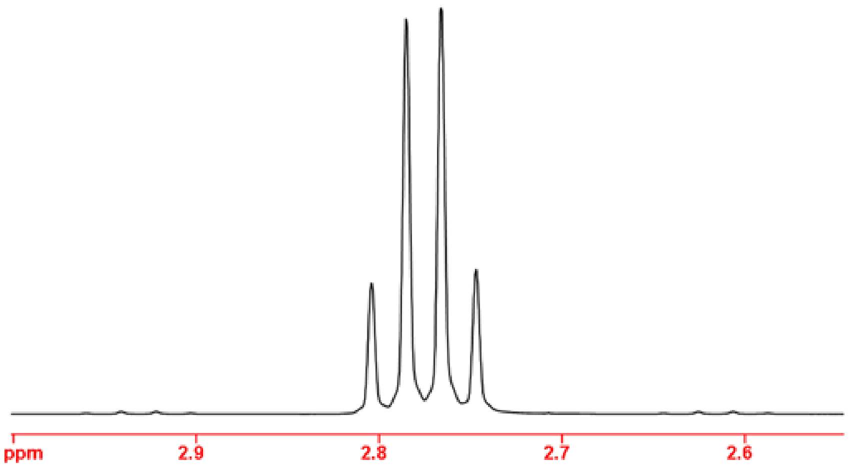
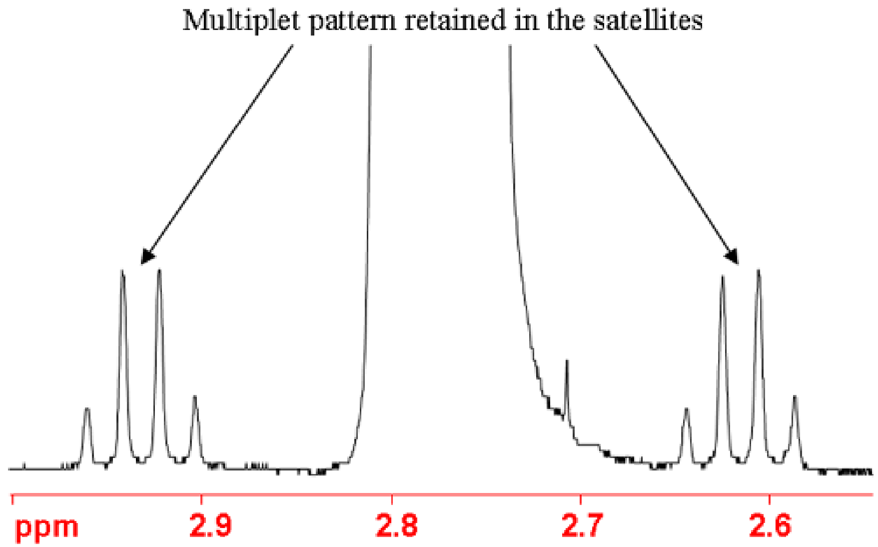
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{13}C





AX_3

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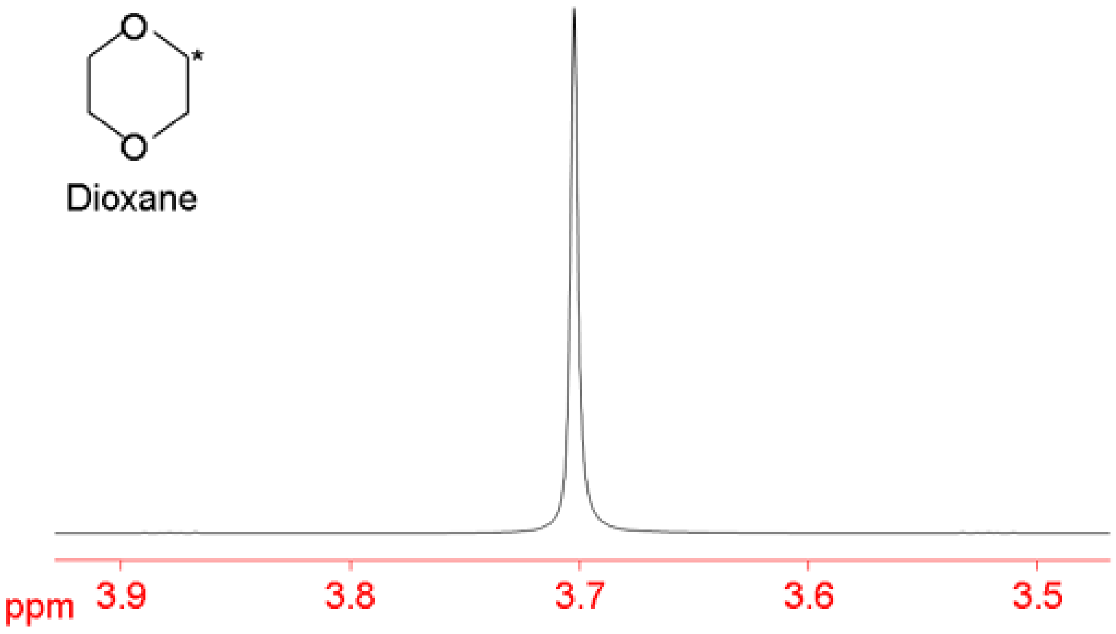
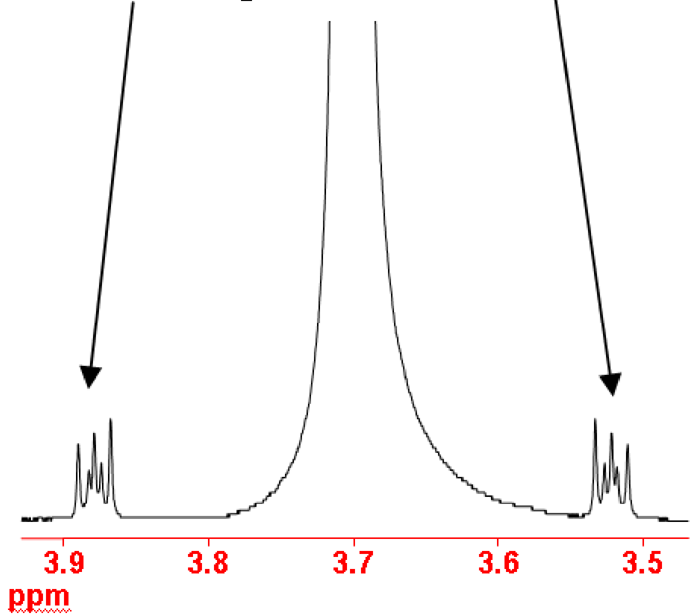
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{13}C





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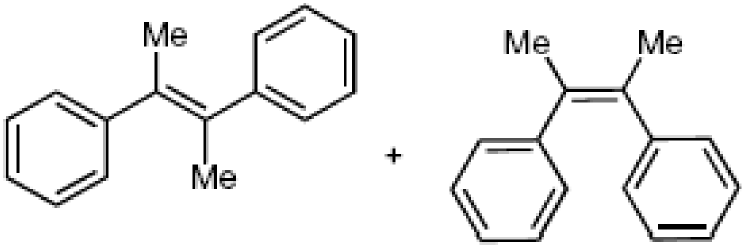
1. ^{1}H–Other Nuclei Coupling
^{1}H–^{13}C

Wrong assigment in literature



3a 3b

initially assigned **3a** as the (*Z*)-isomer (1.89 ppm and 25.1 ppm, H_{arom} at 7.2–7.4 ppm) and **3b** as the (*E*)-isomer (2.19 ppm and 21.4 ppm, H_{arom} at 6.9–7.1 ppm).[5]

Tetrahedron Lett. **2005**, *46*, 3793-3795

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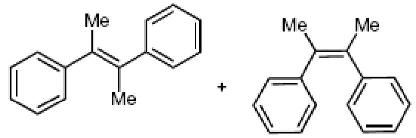
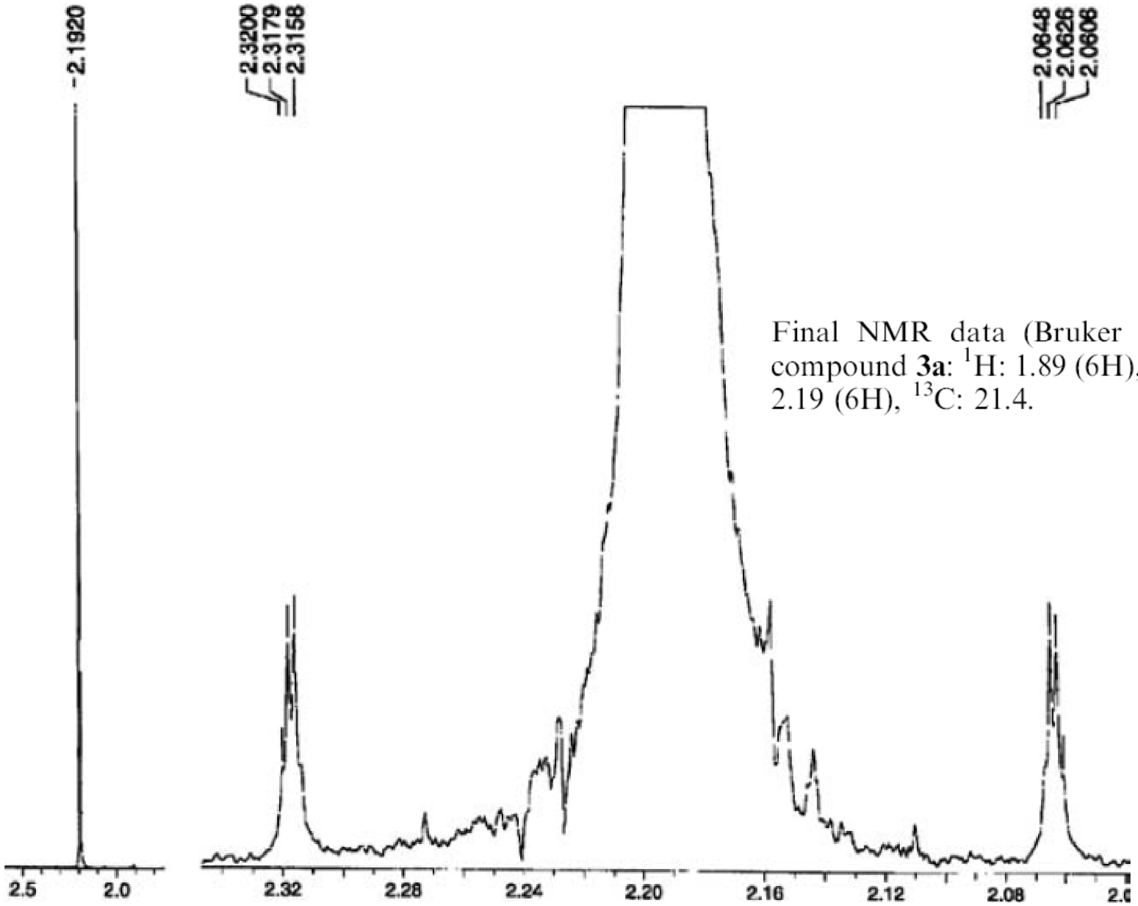
1. ^{1}H–Other Nuclei Coupling

^{1}H–^{13}C



3a 3b

trum. The isomer **3a** revealed quartet sidebands with a ^5J coupling constant of 1.5 Hz for the 2.01 ppm signal, whereas **3b** showed a coupling constant of 1.1 Hz on the multiplet satellite of the 2.32 ppm peak (Scheme 4).



Final NMR data (Bruker Avance 500, in $CDCl_3$) for compound **3a**: ^{1}H: 1.89 (6H), ^{13}C: 25.1; compound **3b**: ^{1}H: 2.19 (6H), ^{13}C: 21.4.

Scheme 4. Coupling constants of **3b** ^{13}C-satellites.

Tetrahedron Lett. **2005**, *46*, 3793-3795

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1. ^{1}H–Other Nuclei Coupling
^{1}H–^{29}Si

Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
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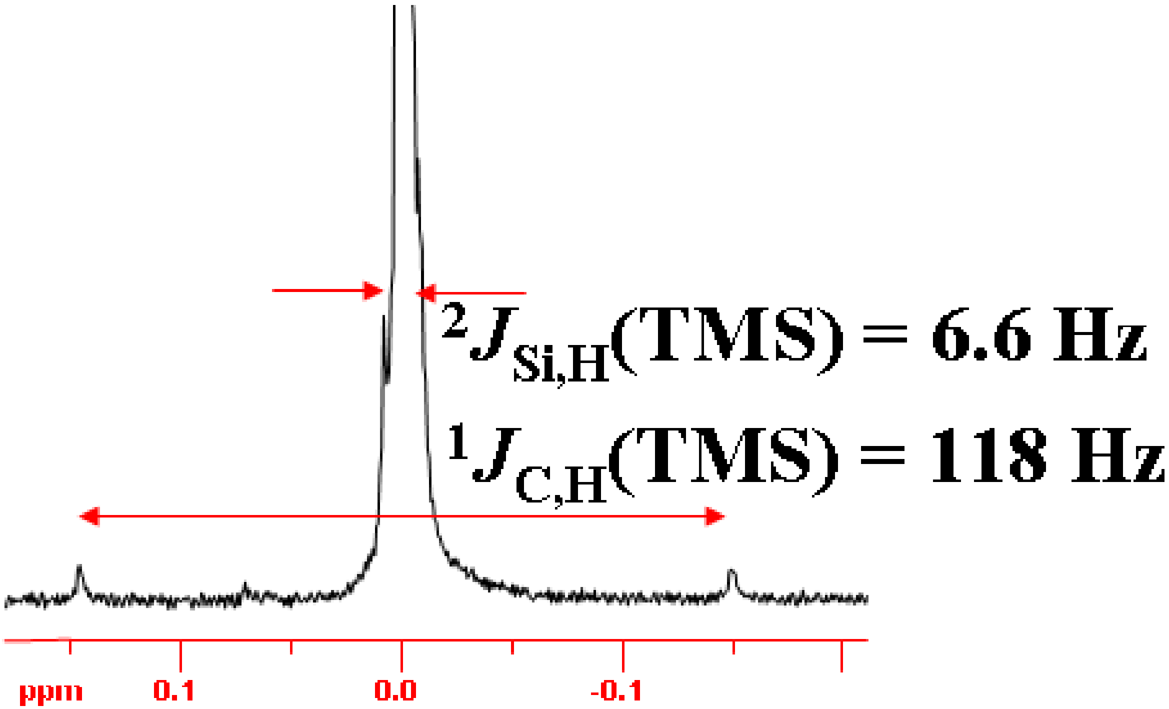
^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
^{15}N	0.37	1/2	-0.28304	30.398	$1.04x10^{-3}$	-2.712
^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

1. ^{1}H–Other Nuclei Coupling
^{1}H–^{29}Si

J (HC-Si) = 6 Hz



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1. ^1H–Other Nuclei Coupling

^1H–^{14}N

Isotope	Natural Abundance (%)	Nuclear Spin (*I*)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
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^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
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^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

1. ^{1}H–Other Nuclei Coupling
Introduction

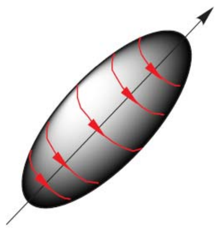
ELECTRIC QUADRUPOLE MOMENT

C. Spinning Ellipse

When I ≥ 1 ⟶ Ellipsoidal charge distribution

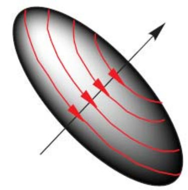
Nuclear Spin $I \geq 1$ (1, 3/2, 5/2,…)
Angular Moment p = I (h/2π)
Magnetic Moment $\mu \neq 0$
Quadrupolar Moment $Q \neq$ (positive for I = 1, negative for I > 1

Prolate Spheroid



I = 1 (^{2}H, ^{14}N)

Oblate Spheroid



I > 1 [^{17}O (I = 5/2), ^{35}Cl (I = 3/2)]

1. ^{1}H–Other Nuclei Coupling
^{1}H–^{14}N

NH : ^{14}N: I=1; 2nI+1 lines

A ^{1}H bonded to the N or in the α-C should give a triplet (3 lines) of the same intensity

However: ^{1}H interchange and the ^{14}N electric quadrupolar moment (Q) usually produce broad signals

- **Amines**:

Fast or moderate interchange
Not usual to see coupling (sharp singlet or broad singlet)
Aliphatic amines: δ ~ 3 - 0.5 ppm
Aromatic amines: δ ~ 3 - 5 ppm

- **Amide, Pyrrole, Indole, Carbamate**:

NH broad singlet
~ 5 - 8 ppm MA6
CHα couples with NH

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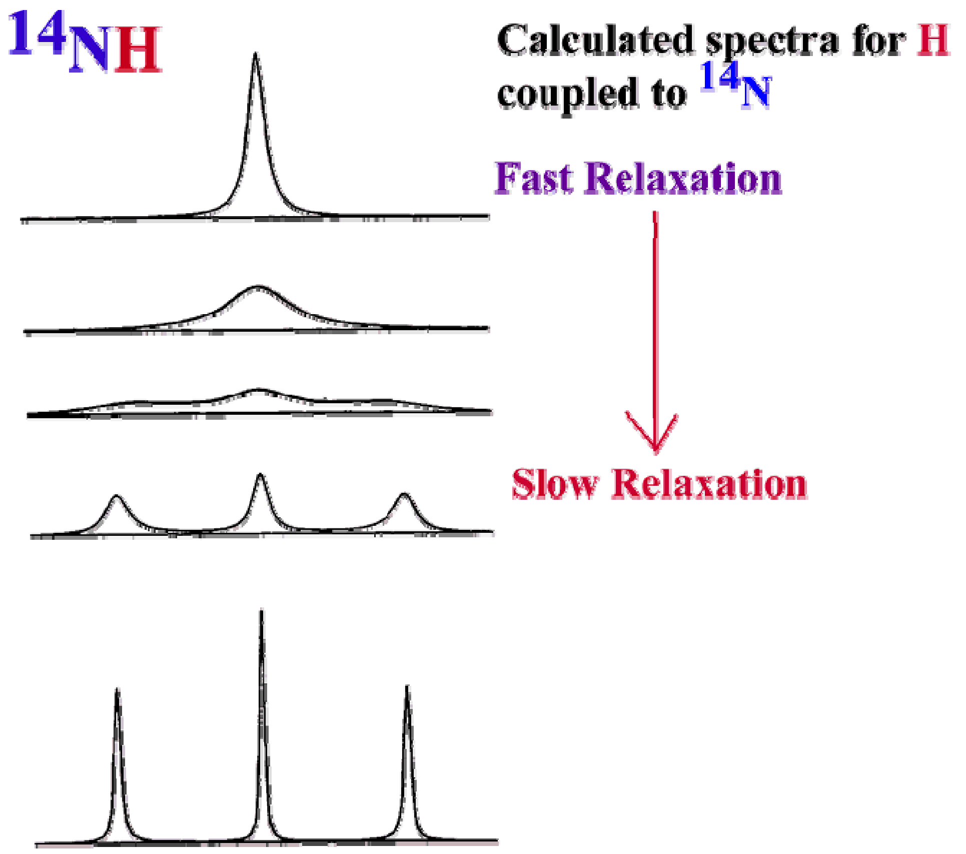
Diapositiva 35

MA6 with

María Abad; 27/10/2014

1. ^{1}H–Other Nuclei Coupling

^{1}H–^{14}N



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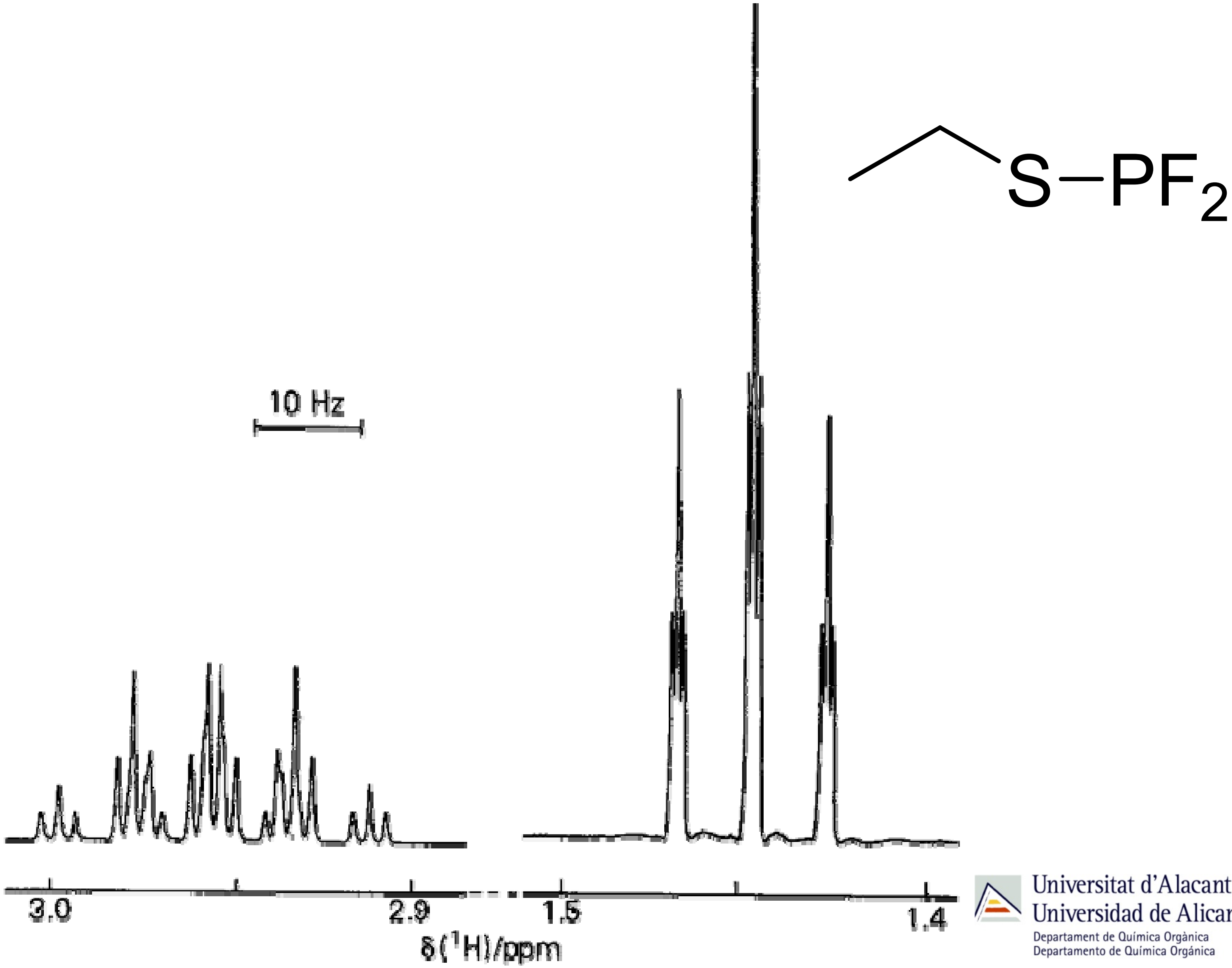
1. ¹H–Other Nuclei Coupling
Examples



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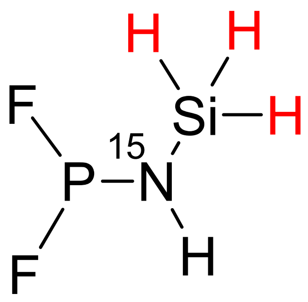
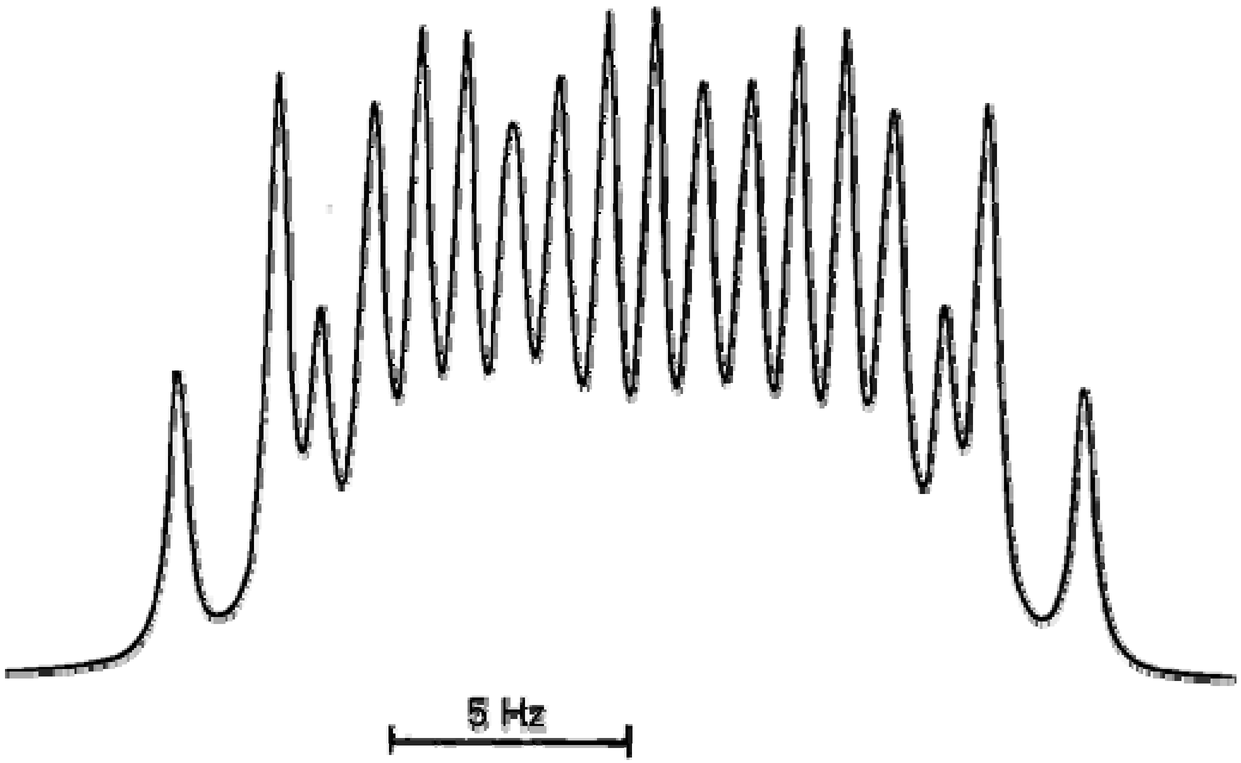
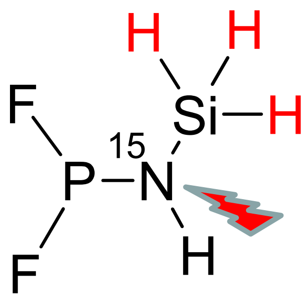
1. ^{1}H–Other Nuclei Coupling
Examples



$^{3}J_{PH}$ (8 Hz); $^{3}J_{HH}$ (4 Hz); $^{2}J_{NH}$ (3 Hz); $^{4}J_{FH}$ (2 Hz)
dddt

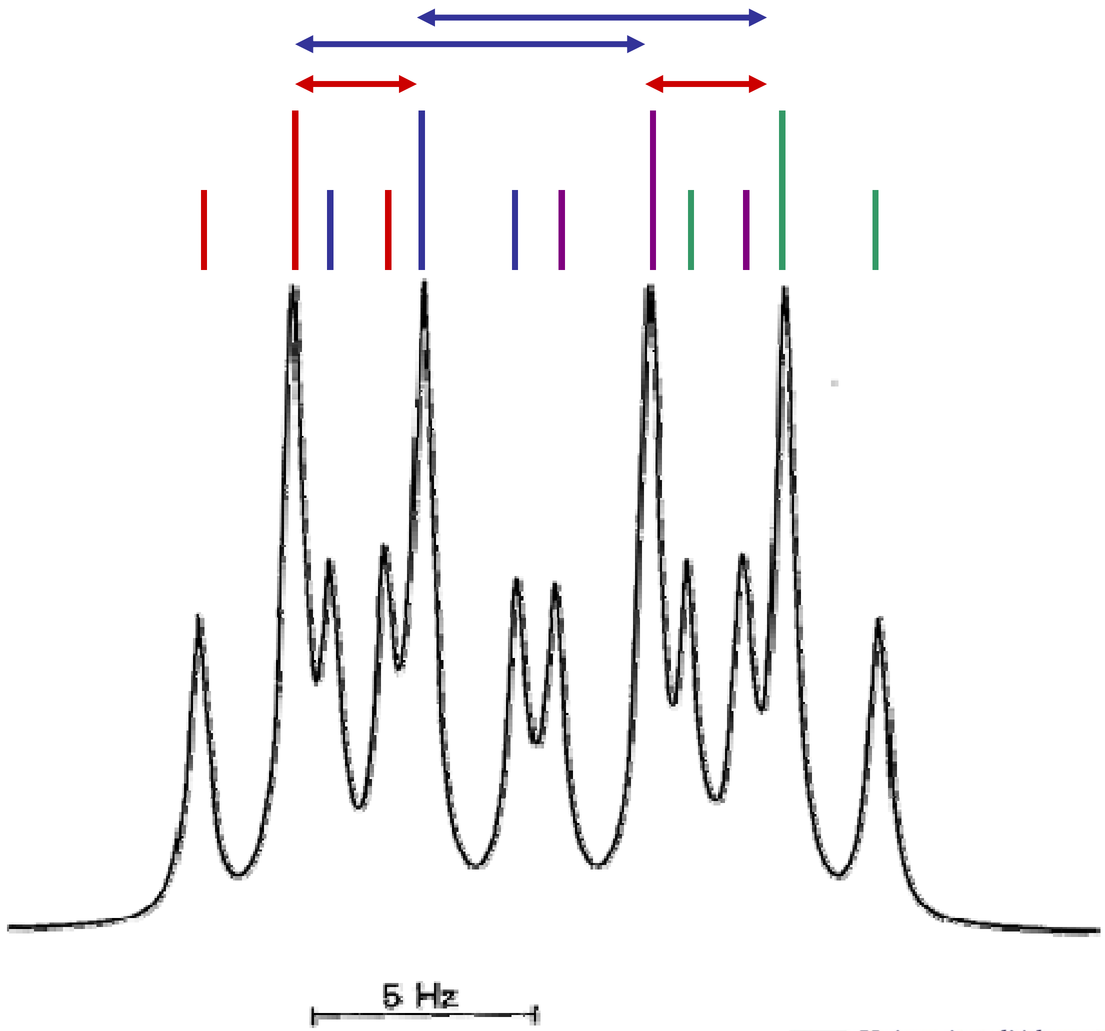


1. ^{1}H–Other Nuclei Coupling
Examples



$^{3}J_{PH}$ (8 Hz); $^{3}J_{HH}$ (4 Hz); $^{4}J_{FH}$ (2 Hz)

ddt



ADVANCED
NUCLEAR MAGNETIC RESONANCE (ANMR)
UNIT 6: OTHER NUCLEI IN NMR

1. ^{1}H-OTHER NUCLEI COUPLING

   ^{1}H-^{19}F; ^{1}H-^{2}H; ^{1}H-^{31}P; ^{1}H-^{29}Si; ^{1}H-^{13}C

1. ^{13}C-OTHER NUCLEI COUPLING

   ^{13}C-^{19}F; ^{13}C-^{2}H; ^{13}C-^{31}P; ^{13}C-^{29}Si; ^{13}C-^{1}H

3. OTHER NUCLEI NUCLEAR MAGNETIC RESONANCE

   ^{15}N; ^{19}F; ^{31}P

2. ^{13}C–Other Nuclei Coupling
^{13}C–^{1}H

Isotope	Natural Abundance (%)	Nuclear Spin (*I*)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
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^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
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^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

2. ^{13}C–Other Nuclei Coupling

^{13}C–^{1}H

J (^{13}C-H) = 110-320 Hz; J (^{13}C-^{13}C-H) = – 5 to 60 Hz (typically 7)

Table 5.17 Some $^{1}J_{CH}$ Values

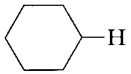
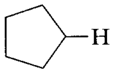
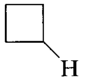
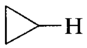
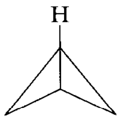
Compound	*J* (Hz)
sp^3	
CH_3CH_3	124.9
$CH_3CH_2CH_3$	119.2
$(CH_3)_3CH$	114.2
CH_3NH_2	133.0
CH_3OH	141.0
CH_3Cl	150.0
CH_2Cl_2	178.0
$CHCl_3$	209.0
	123.0
	128.0
	134.0
	161.0
	205.0
sp^2	
$CH_2{=}CH_2$	156.2
$CH_3\underline{C}H{=}C(CH_3)_2$	148.4
$CH_3\underline{C}H{=}O$	172.4
$NH_2\underline{C}H{=}O$	188.3
C_6H_6	159.0
sp	
$CH{\equiv}CH$	249.0
$C_6H_5C{\equiv}CH$	251.0
$HC{\equiv}N$	269.0

Table 5.18 Some $^{2}J_{CH}$ Values

Compound	*J* (Hz)
sp^3	
$C\underline{H}_3\underline{C}H_3$	−4.5
$C\underline{H}_3\underline{C}Cl_3$	5.9
$\underline{C}H_3C\underline{H}{=}O$	26.7
sp^2	
$C\underline{H}_2{=}\underline{C}H_2$	−2.4
$(C\underline{H}_3)_2\underline{C}{=}O$	5.5
$CH_2{=}\underline{C}HC\underline{H}{=}O$	26.9
*C_6H_6	1.0
sp	
$C\underline{H}{\equiv}\underline{C}H$	49.3
$C_6H_5O\underline{C}{\equiv}C\underline{H}$	61.0

* ^{2}J = 7.6 (>^{2}J)

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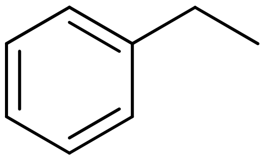
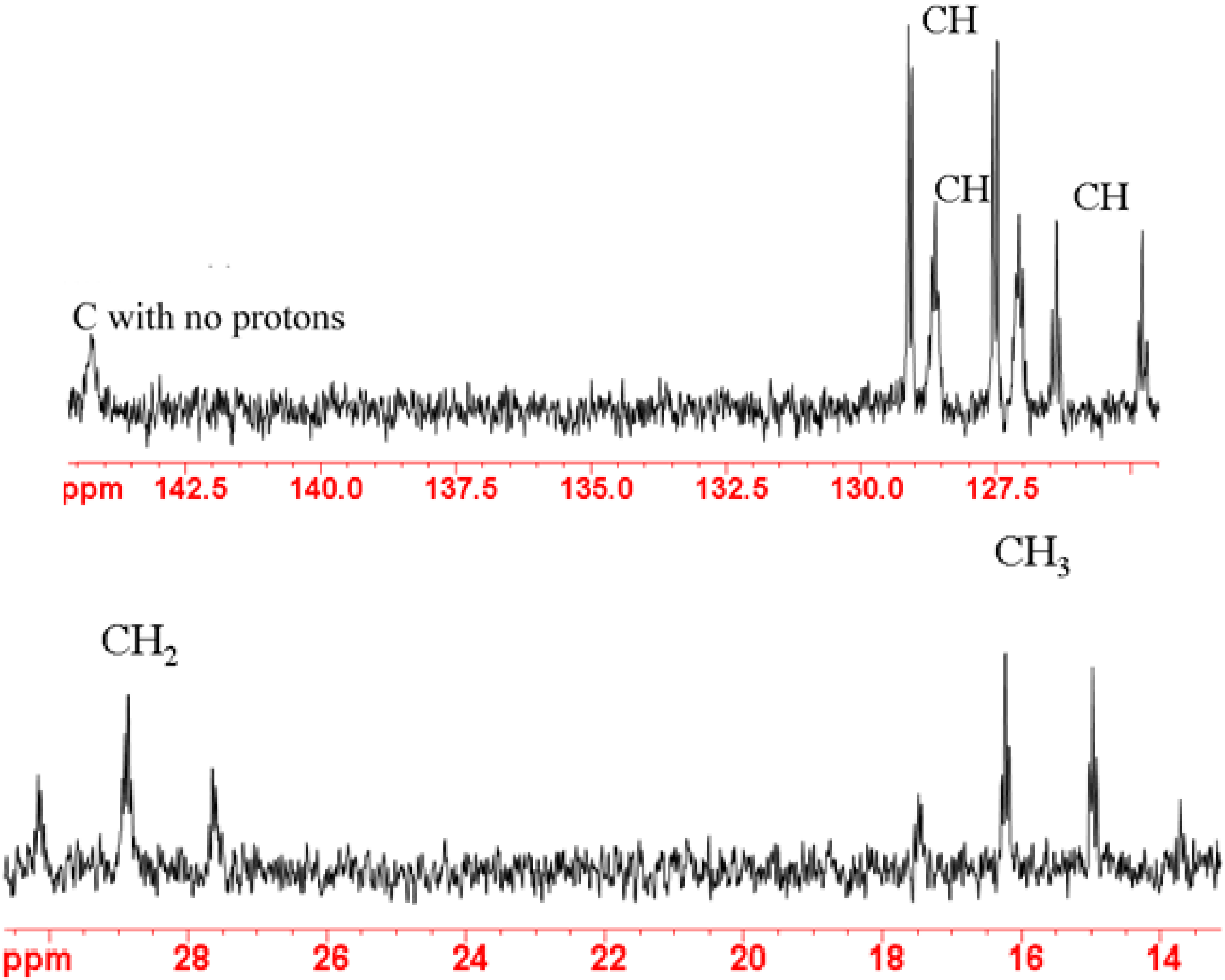
2. ^{13}C–Other Nuclei Coupling
^{13}C–^{1}H

J (^{13}C-H) = 110-320 Hz; J (^{13}C-^{13}C-H) = – 5 to 60 Hz (typically 7)





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2. ^{13}C–Other Nuclei Coupling

^{13}C–^{1}H

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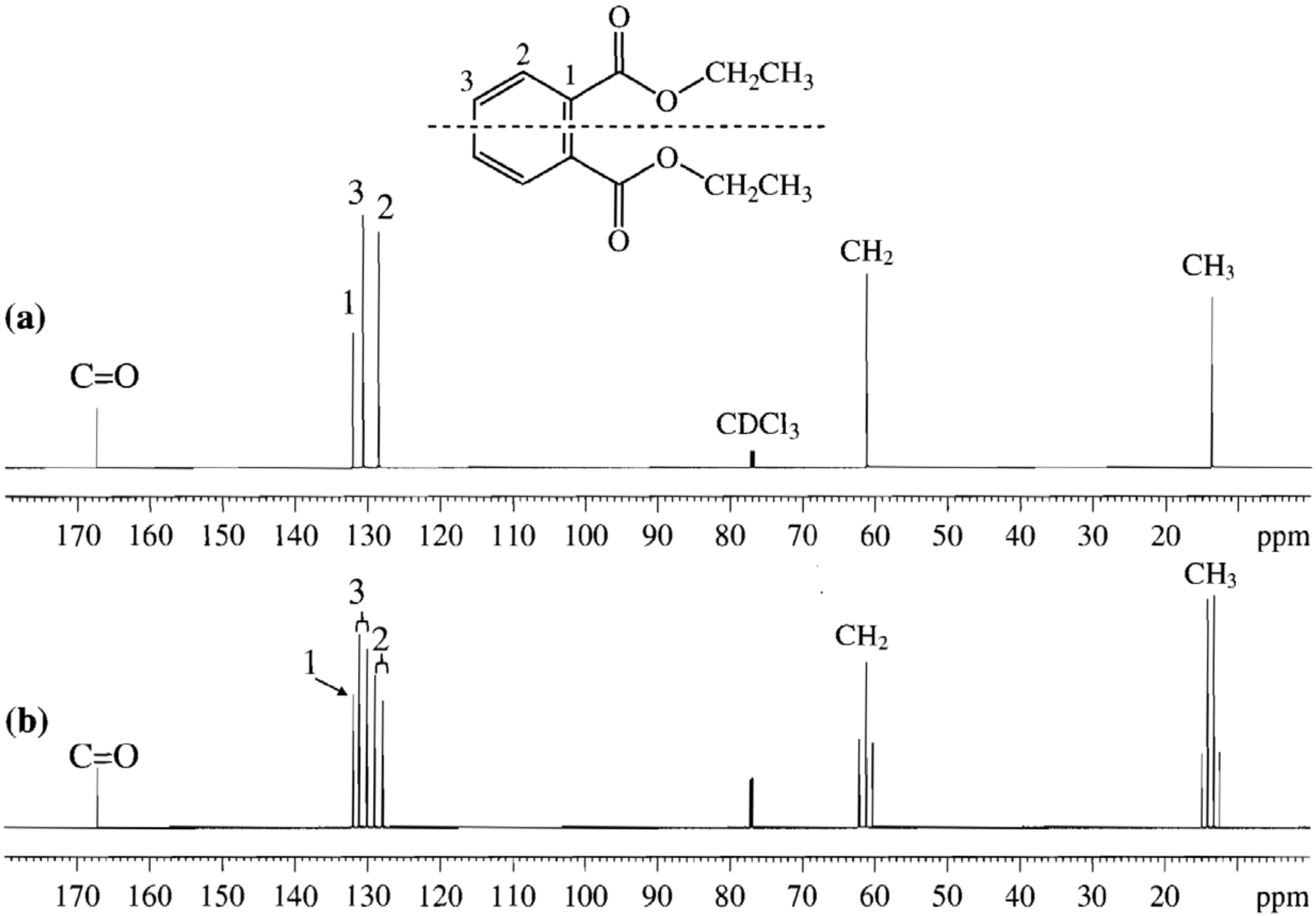
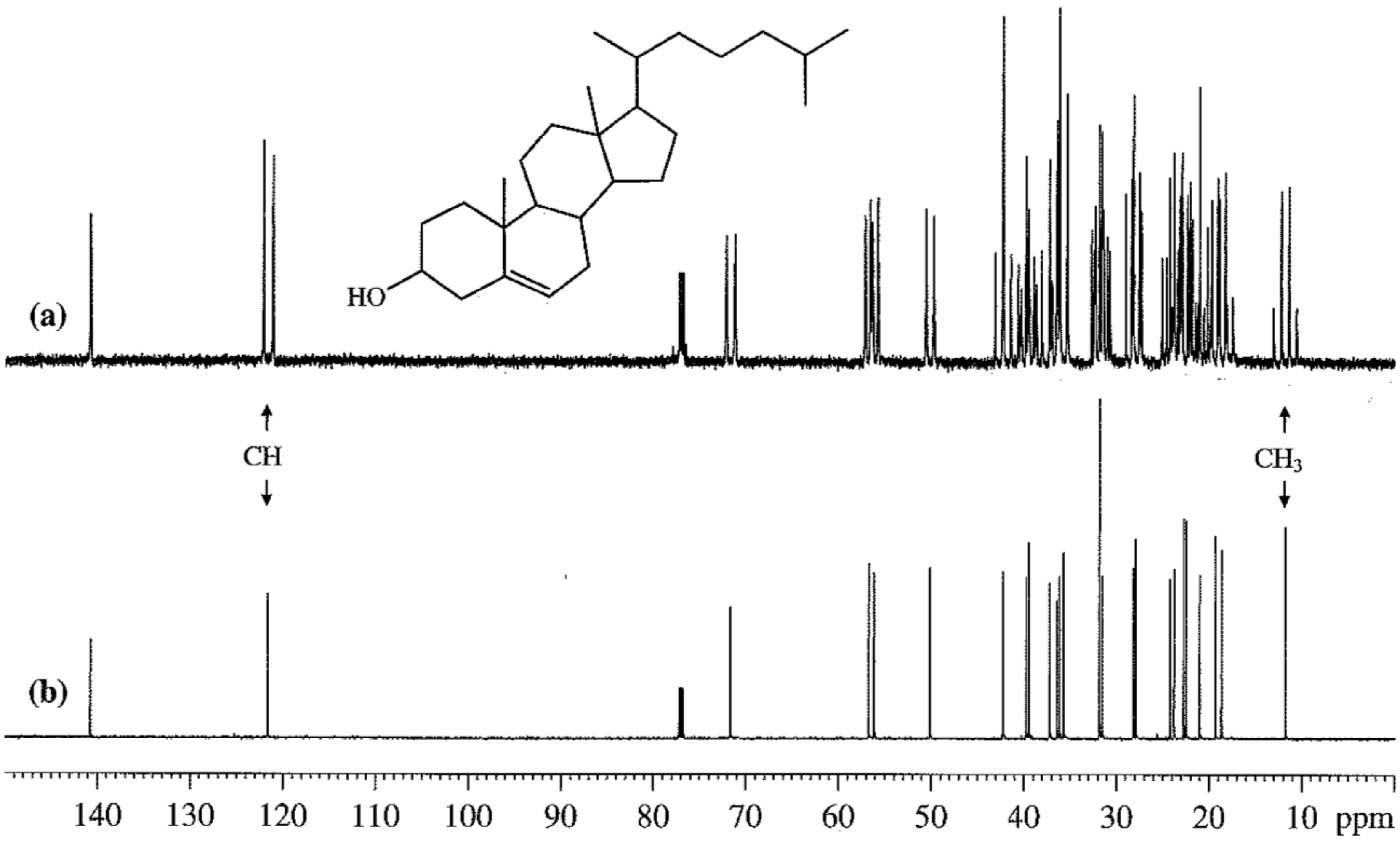


2. ^{13}C–Other Nuclei Coupling
^{13}C–^{1}H



Cholesterol ^{13}CNMR spectrum: (a) coupled, (b) broad-band decoupled

2. ^{13}C–Other Nuclei Coupling

^{13}C–^{2}H

Isotope	Natural Abundance (%)	Nuclear Spin (*I*)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
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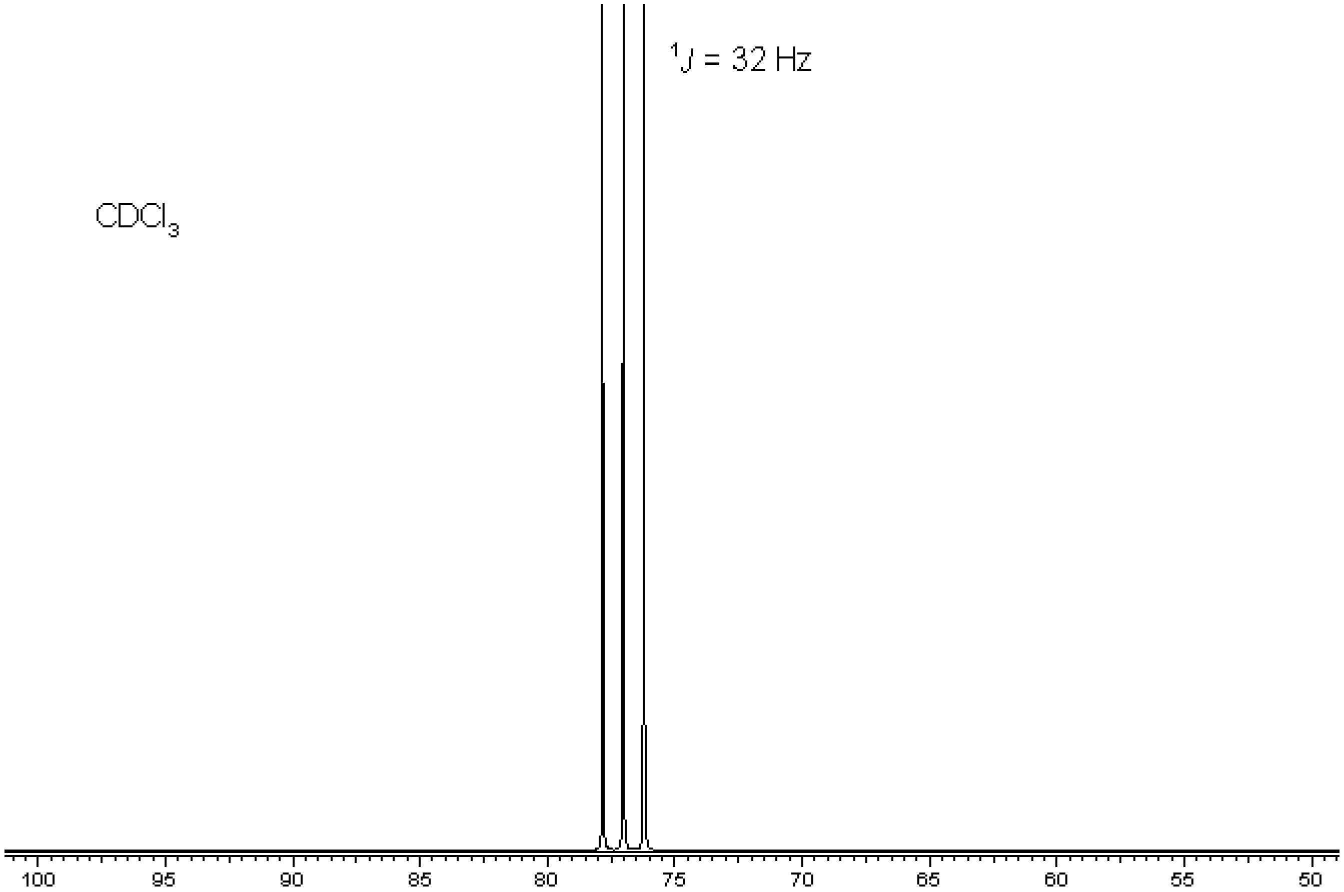
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

2. ^{13}C–Other Nuclei Coupling
^{13}C–^{2}H

TABLE 4.3 Coupling Constants for ^{19}F, ^{31}P, D Coupled to ^{13}C

Compound	^1J(Hz)	^2J(Hz)	^3J(Hz)	^4J(Hz)
CH_3CF_3	271			
CF_2H_2	235			
CF_3CO_2H	284	43.7		
C_6H_5F	245	21.0	7.7	3.3
$(C_4H_9)_3P$	10.9	11.7	12.5	
$(CH_3CH_2)_4P^+ Br^-$	49.0	4.3		
$(C_6H_5)_3P^+ CH_3I^-$	88.0	10.9		
	^1J(Hz) of CH_3 = 52			
$C_2H_5(P{=}O)(OC_2H_5)_2$	143	7.1 (J_{COP})	6.9 (J_{CCOP})	
$(C_6H_5)_3P$	12.4	19.6	6.7	
$CDCl_3$	31.5			
$CD_3(C{=}O)CD_3$	19.5			
$(CD_3)_2SO$	22.0			
C_6D_6	25.5			

2. ^{13}C–Other Nuclei Coupling
^{13}C–^{2}H

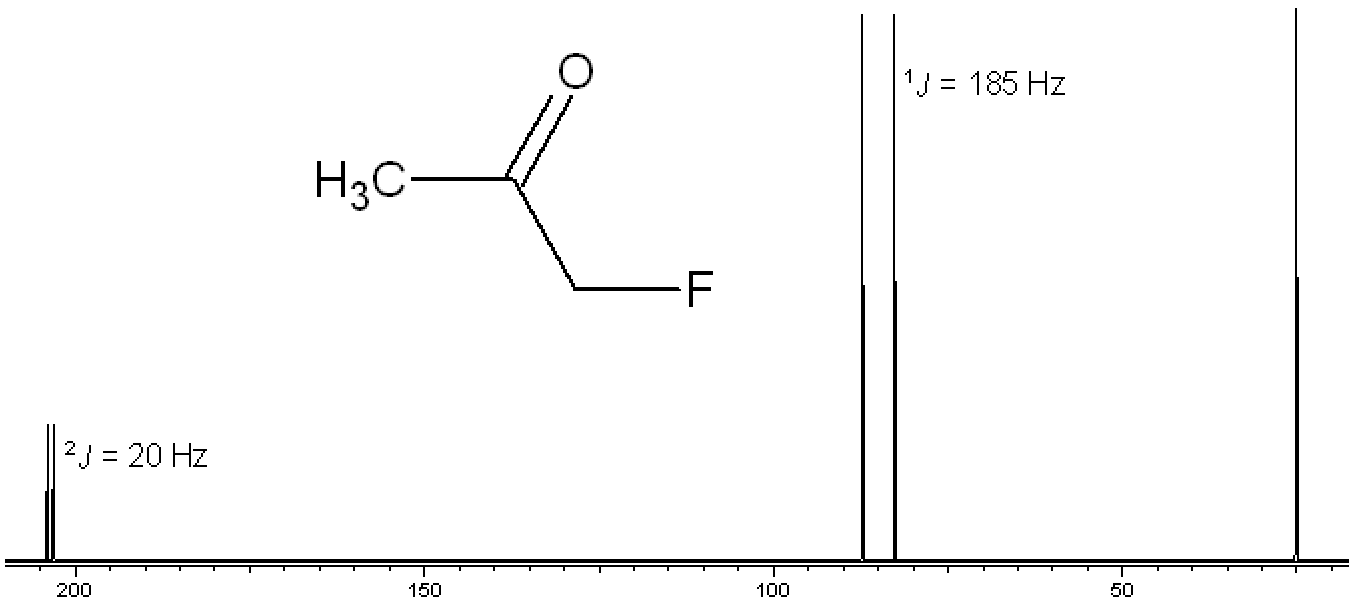


2. ^{13}C–Other Nuclei Coupling
^{13}C–^{19}F

Isotope	Natural Abundance (%)	Nuclear Spin (*I*)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
^{13}C	1.11	1/2	0.70220	75.432	$1.59x10^{-2}$	6.728
^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
^{15}N	0.37	1/2	-0.28304	30.398	$1.04x10^{-3}$	-2.712
^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

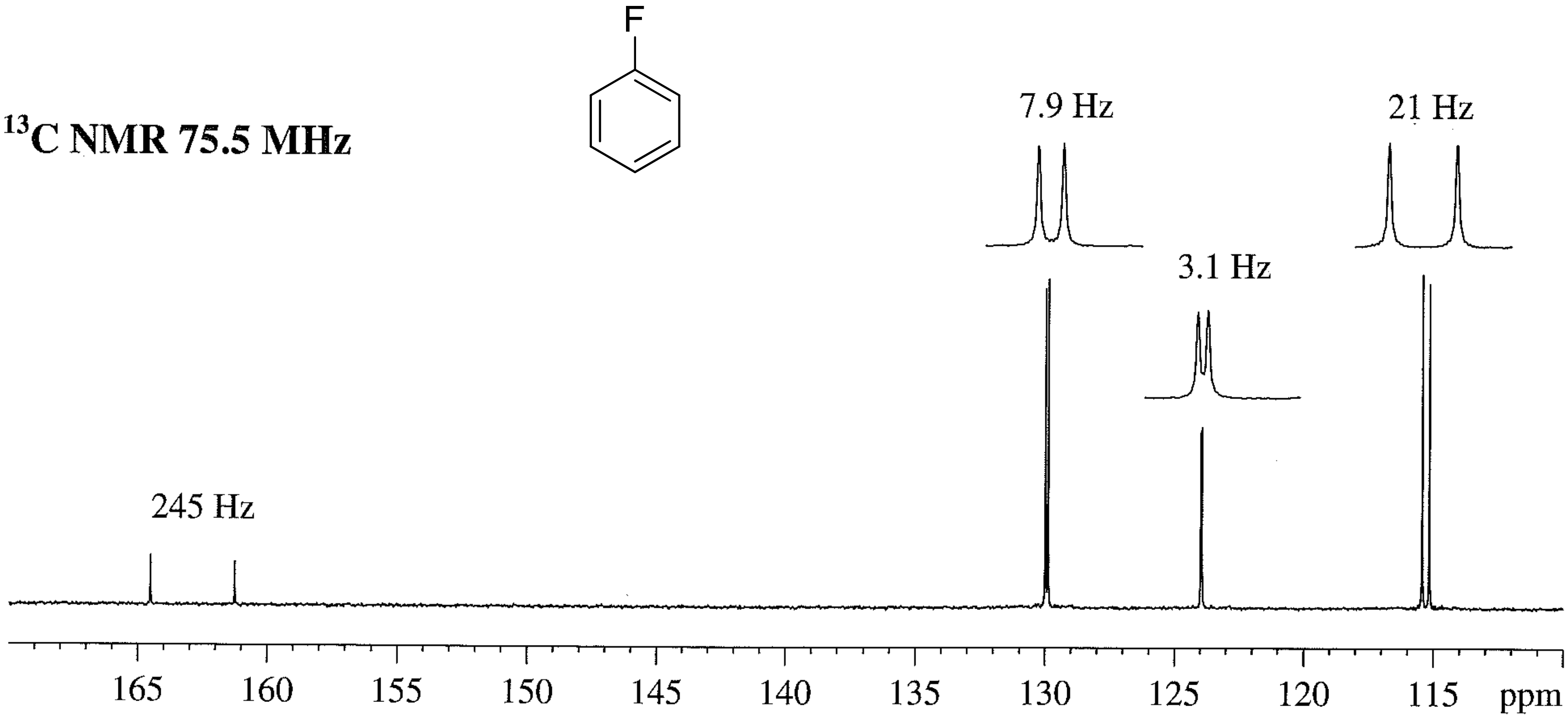
2. ^{13}C–Other Nuclei Coupling
^{13}C–^{19}F

J (^{13}C-^{19}F) = 185 Hz (típica); J (^{13}C-^{13}C-^{19}F) = typically 20 Hz



2. ^{13}C–Other Nuclei Coupling

^{13}C–^{19}F



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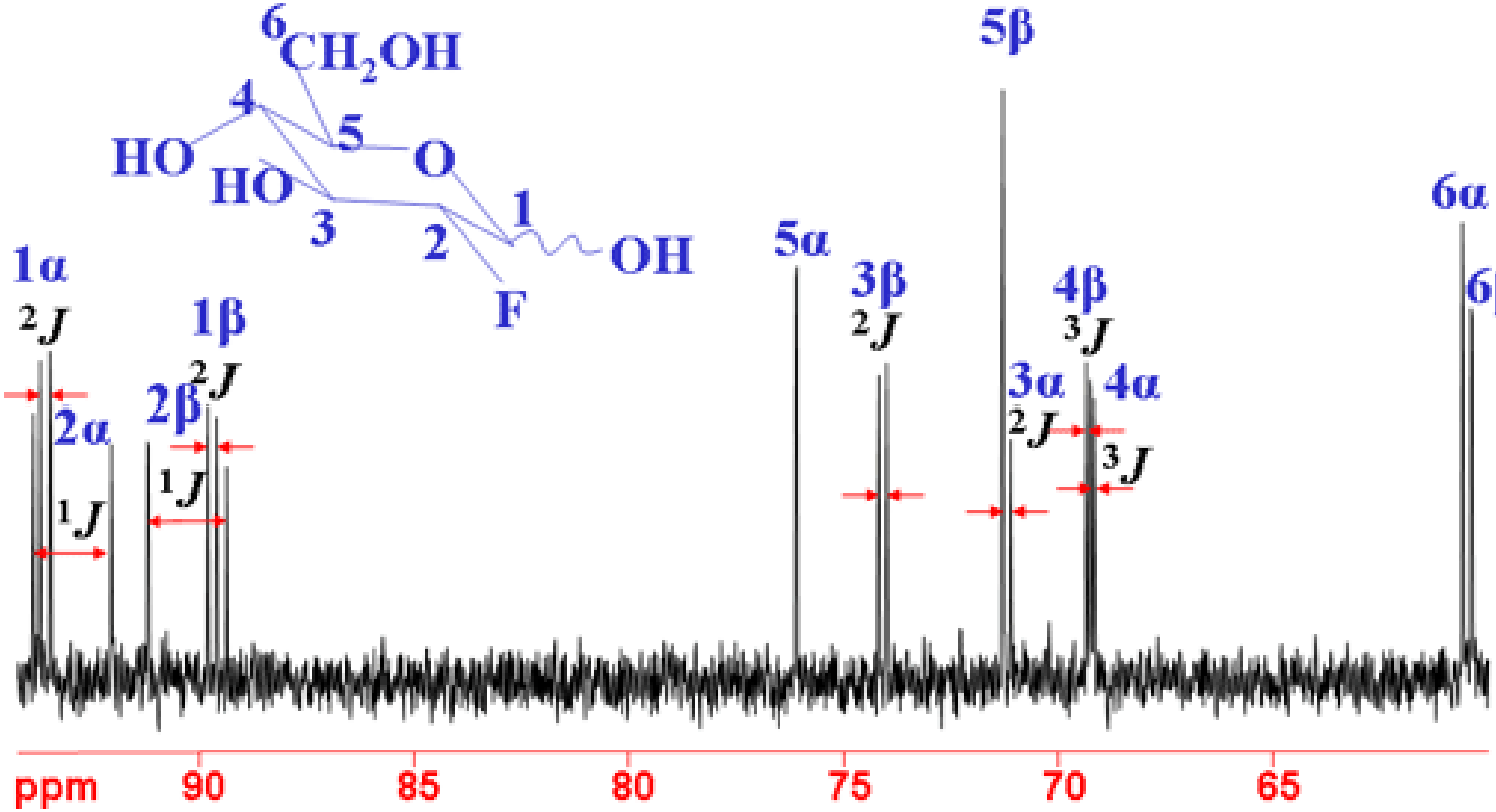
2. ^{13}C–Other Nuclei Coupling
^{13}C–^{19}F



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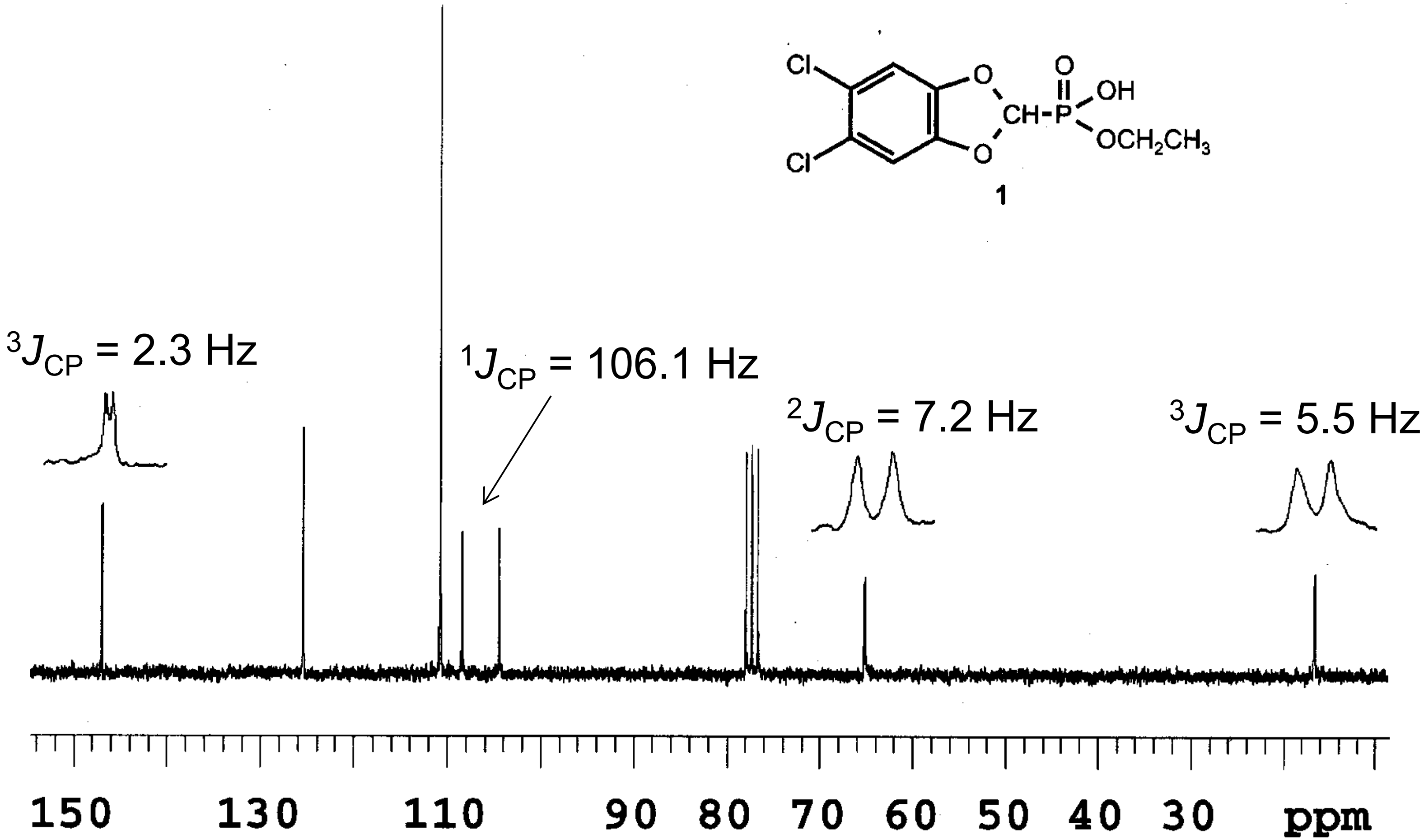
2. ^{13}C–Other Nuclei Coupling
^{13}C–^{19}F

Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetic Moment (μ)	Resonance Frequency (MHz) (7.04T)	Relative Sensitivity (Constant Field)	Magnetogyric Ratio (γ) (rad s^{-1} G^{-1})
^{1}H	99.9885	1/2	2.79268	300	1	26.753
^{2}H	0.0115	1	0.85739	46.051	$9.64x10^{-3}$	4.107
^{13}C	1.11	1/2	0.70220	75.432	$1.59x10^{-2}$	6.728
^{14}N	99.63	1	0.40358	21.671	$1.01x10^{-3}$	1.933
^{15}N	0.37	1/2	-0.28304	30.398	$1.04x10^{-3}$	-2.712
^{17}O	0.04	5/2	-1.8930	40.670	$2.91x10^{-2}$	-3.628
^{19}F	100.00	1/2	2.6273	282.231	0.834	25.179
^{31}P	100.00	1/2	1.1305	121.442	$6.64x10^{-2}$	10.840
^{29}Si	4.68	1/2	-0.96179	59.595	$6.63x10^{-2}$	-5.319

2. ^{13}C–Other Nuclei Coupling

^{13}C–^{19}F



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ADVANCED
NUCLEAR MAGNETIC RESONANCE (ANMR)
UNIT 6: OTHER NUCLEI IN NMR

1. ^{1}H-OTHER NUCLEI COUPLING

   ^{1}H-^{19}F; ^{1}H-^{2}H; ^{1}H-^{31}P; ^{1}H-^{29}Si; ^{1}H-^{13}C

1. ^{13}C-OTHER NUCLEI COUPLING

   ^{13}C-^{19}F; ^{13}C-^{2}H; ^{13}C-^{31}P; ^{13}C-^{29}Si; ^{1}H-^{13}C

3. OTHER NUCLEI NUCLEAR MAGNETIC RESONANCE

   ^{15}N; ^{19}F; ^{31}P

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3. Other Nuclei NMR

TABLE 6.1 Useful Magnetic Resonance Data for Nuclei Discussed in this Chapter

Isotope	Spin	Natural Abundundance %	Sensitivity Relative[a]	Sensitivity Absolute[b]	MHz at T of 7.0463	Reference Compound	Detection Range ppm
^{1}H	1/2	99.98	1.00	1.00	300.000	$Si(CH_3)_4$	10 to 0
^{2}H	1	1.5×10^{-2}	9.65×10^{-3}	1.45×10^{-6}	46.051	$Si(CD_3)_4$	10 to 0
^{3}H	1/2	0	1.21	0	319.990	$Si(CT_3)_4$	10 to 0
^{13}C	1/2	1.108	1.59×10^{-2}	1.76×10^{-4}	75.432	$Si(CH_3)_4$	220 to 0
^{14}N	1	99.63	1.01×10^{-3}	1.01×10^{-3}	21.671	$^{14}NH_3$ (1)[c]	900 to 0
^{15}N	1/2	0.37	1.04×10^{-3}	3.85×10^{-6}	30.398	$^{15}NH_3$ (1)[c]	900 to 0
^{17}O	5/2	3.7×10^{-2}	2.91×10^{-2}	1.08×10^{-5}	40.670	H_2O	1700 to −50
^{19}F	1/2	100	0.83	0.83	282.231	$CFCl_3$	276 to −280
^{29}Si	1/2	4.7	7.84×10^{-3}	3.69×10^{-4}	59.595	$Si(CH_3)_4$	80 to −380
^{31}P	1/2	100	6.63×10^{-2}	6.63×10^{-2}	121.442	85% H_3PO_4	270 to −480

[a] At constant field for equal number of nuclei
[b] Product of relative sensitivity and natural abundance
[c] At 25°C

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IMPORTANT ISSUES: Isotopic abundance; sensitivity*, Q (I > ½), T_1, references

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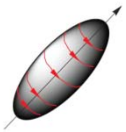
3. Other Nuclei NMR: Nitrogen

TABLE 6.1 Useful Magnetic Resonance Data for Nuclei Discussed in this Chapter

Isotope	Spin	Natural Abundundance %	Sensitivity Relative[a]	Sensitivity Absolute[b]	MHz at T of 7.0463	Reference Compound	Detection Range ppm
^{1}H	1/2	99.98	1.00	1.00	300.000	$Si(CH_3)_4$	10 to 0
^{2}H	1	1.5×10^{-2}	9.65×10^{-3}	1.45×10^{-6}	46.051	$Si(CD_3)_4$	10 to 0
^{3}H	1/2	0	1.21	0	319.990	$Si(CT_3)_4$	10 to 0
^{13}C	1/2	1.108	1.59×10^{-2}	1.76×10^{-4}	75.432	$Si(CH_3)_4$	220 to 0
^{14}N	1	99.63	1.01×10^{-3}	1.01×10^{-3}	21.671	$^{14}NH_3$ (l)[c]	900 to 0
^{15}N	1/2	0.37	1.04×10^{-3}	3.85×10^{-6}	30.398	$^{15}NH_3$ (l)[c]	900 to 0
^{17}O	5/2	3.7×10^{-2}	2.91×10^{-2}	1.08×10^{-5}	40.670	H_2O	1700 to −50
^{19}F	1/2	100	0.83	0.83	282.231	$CFCl_3$	276 to −280
^{29}Si	1/2	4.7	7.84×10^{-3}	3.69×10^{-4}	59.595	$Si(CH_3)_4$	80 to −380
^{31}P	1/2	100	6.63×10^{-2}	6.63×10^{-2}	121.442	85% H_3PO_4	270 to −480

[a] At constant field for equal number of nuclei
[b] Product of relative sensitivity and natural abundance
[c] At 25°C

In theory, none of the two Nitrogen isotopes is appropriate for NMR experiments

^{14}N  **"prolate"**

***I* = 1, Q ≠ 0, "Interchange"**

^{15}N 

***I* = 1/2, Q = 0**

Abundance, sensitivity, T_1~ 80 seg

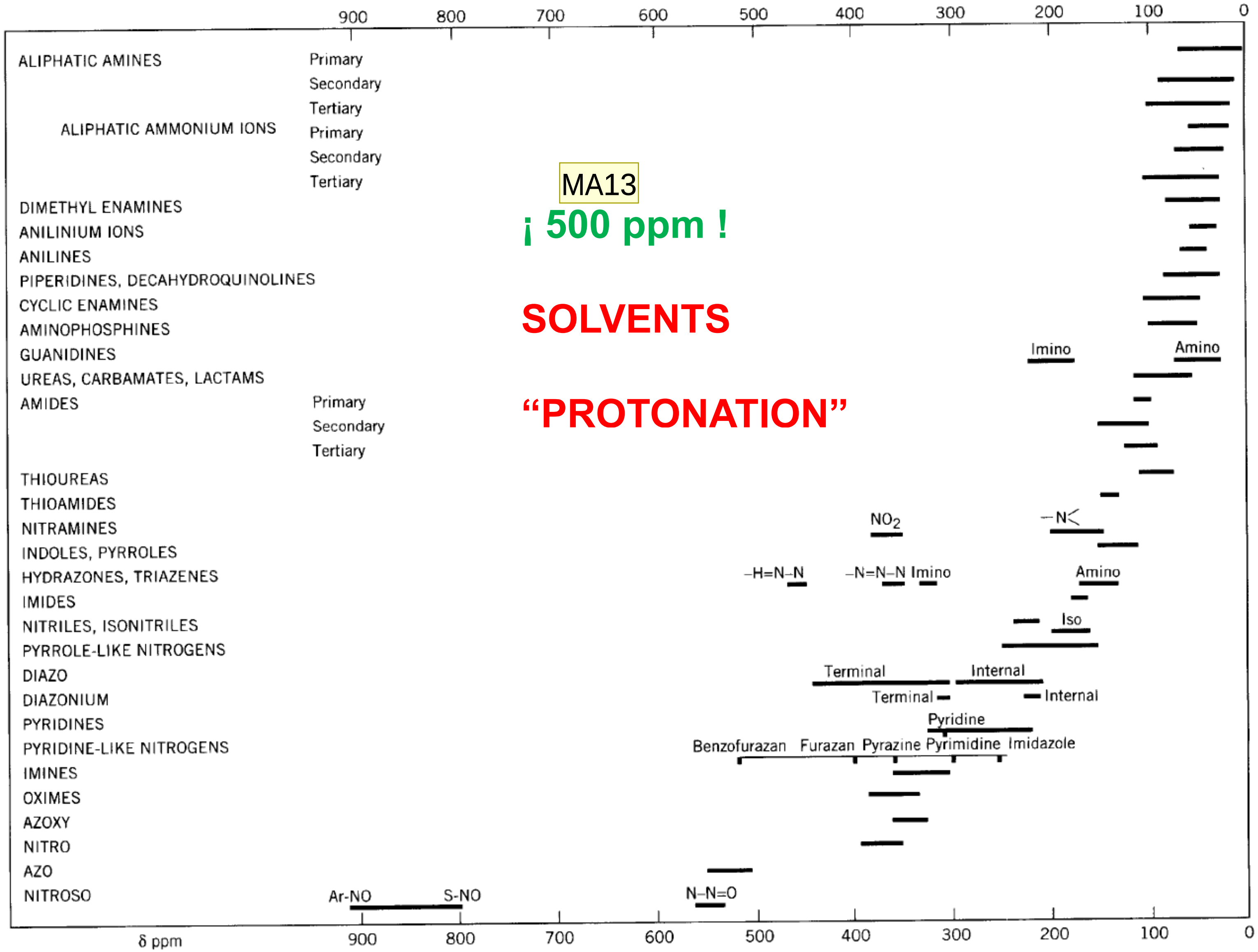
$Cr(acac)_3$ or NOE effect

Highest NOE effect (^{13}C/^{1}H): $\gamma_H/2\gamma_C$ = 26753/(2x6728) : 1.98

Highest NOE effect (^{15}N/^{1}H): $\gamma_H/2\gamma_N$ = 26753/[2x(–2712)] : –4.93

3. Other Nuclei NMR: ^{15}N

Table 7.2 Chemical Shift Ranges for Various Nitrogen-containing Compounds. Adapted from Levy and Lichter (1979).



MA13

¡ 500 ppm !

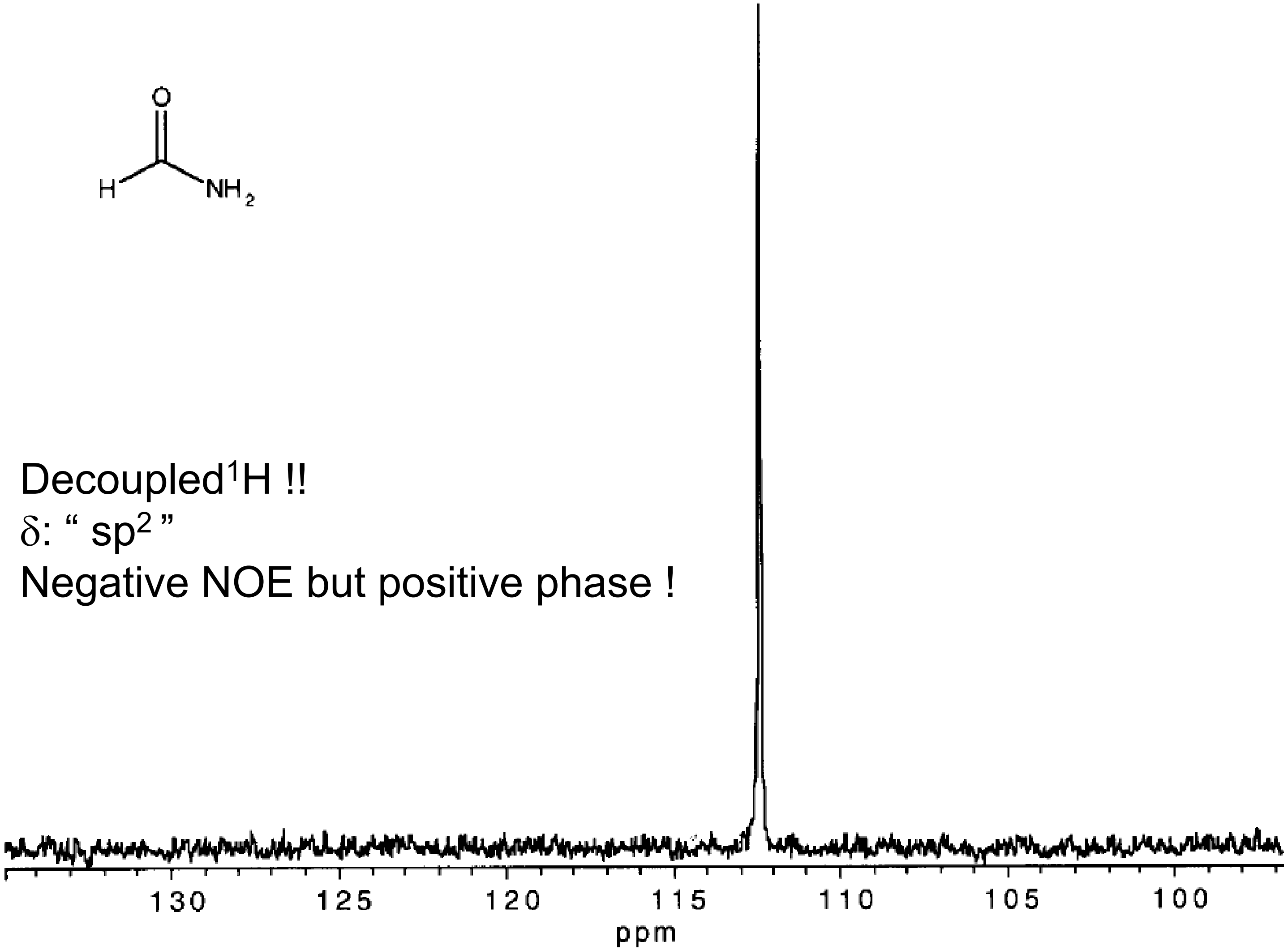
SOLVENTS

“PROTONATION”

MA13 500 ppm!

(Remember to remove the Spanish exclamation mark!)
María Abad; 27/10/2014

3. Other Nuclei NMR: ^{15}N



Decoupled ^{1}H !!
δ: " sp^{2} "
Negative NOE but positive phase !

FIGURE 7.1. The proton-decoupled ^{15}N (30.4-MHz) NMR spectrum of formamide in $CDCl_3$ referenced to external NH_3.

3. Other Nuclei NMR: ^{15}N

$^{1}J_{NH}$ = 75-135 Hz

$^{2}J_{NH}$ = 0-20 Hz

$^{3}J_{NH}$ = 0-10 Hz

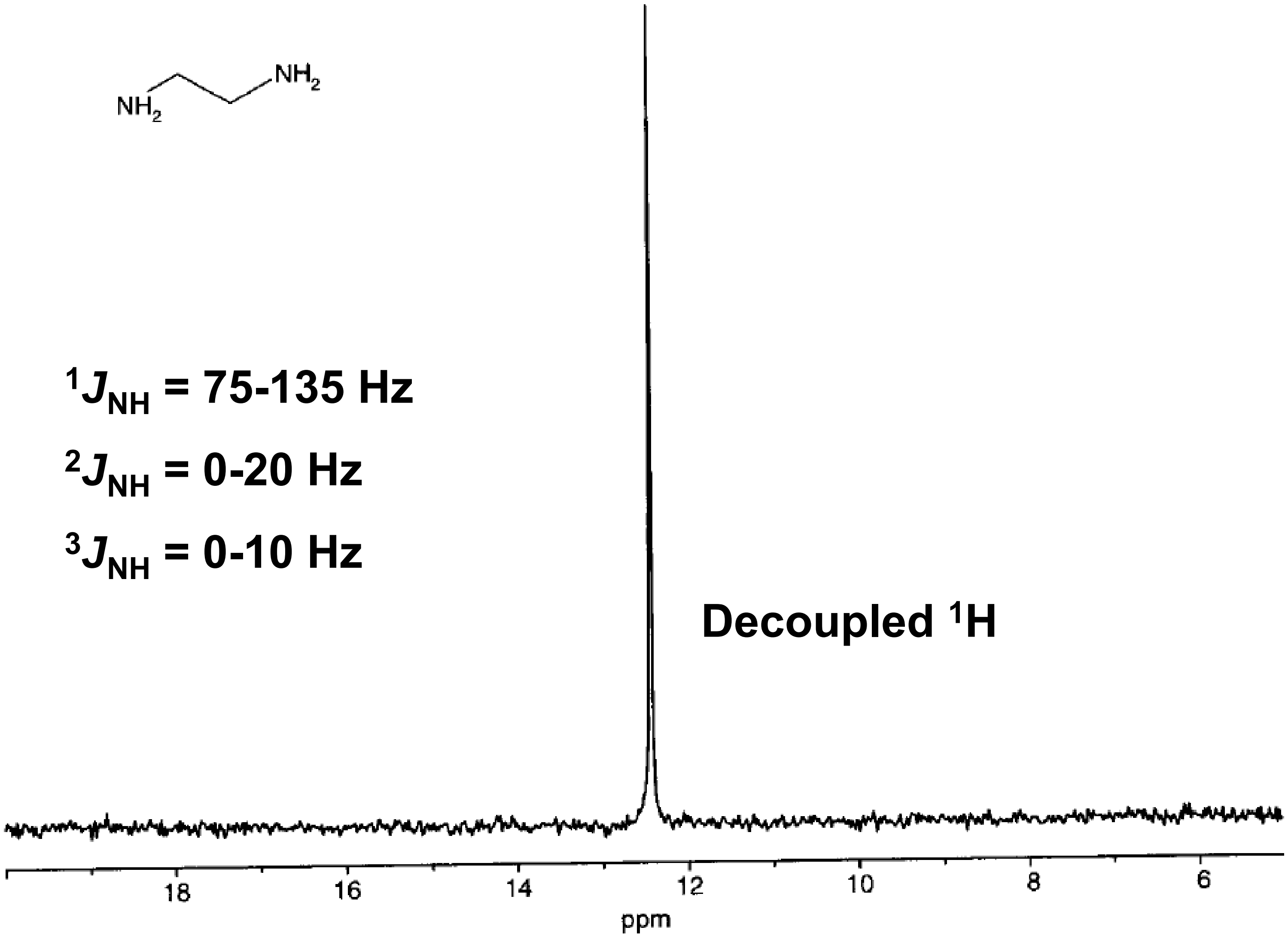


FIGURE 7.2. The proton-decoupled ^{15}N NMR spectrum (30.4 MHz) of ethylenediamine in $CDCl_3$. The proton-coupled spectrum is shown in the inset.

3. Other Nuclei NMR: ^{15}N

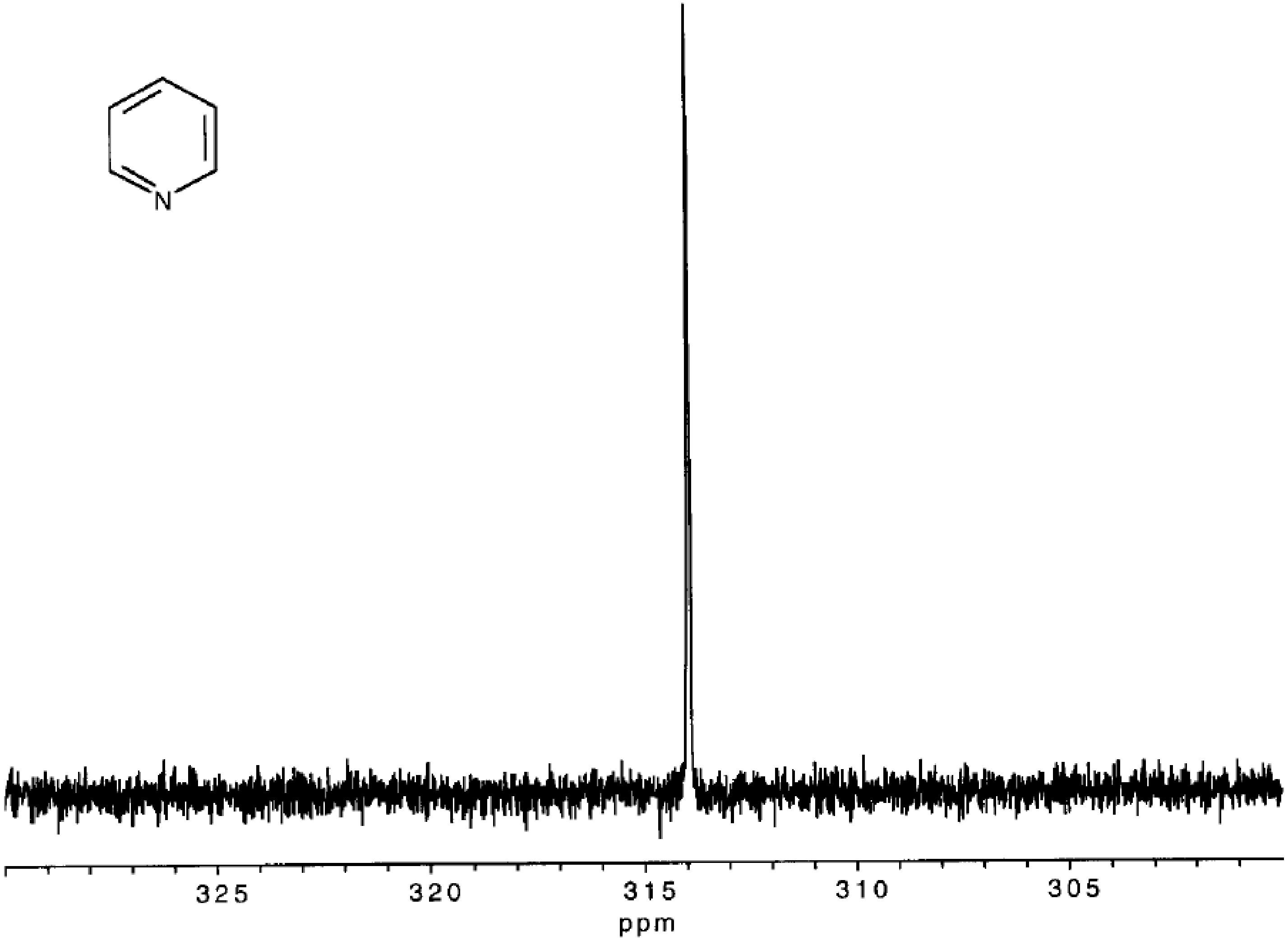


FIGURE 7.4. The proton-decoupled ^{15}N spectrum (30.4 MHz) of pyridine in $CDCl_3$.

3. Other Nuclei NMR: ^{15}N

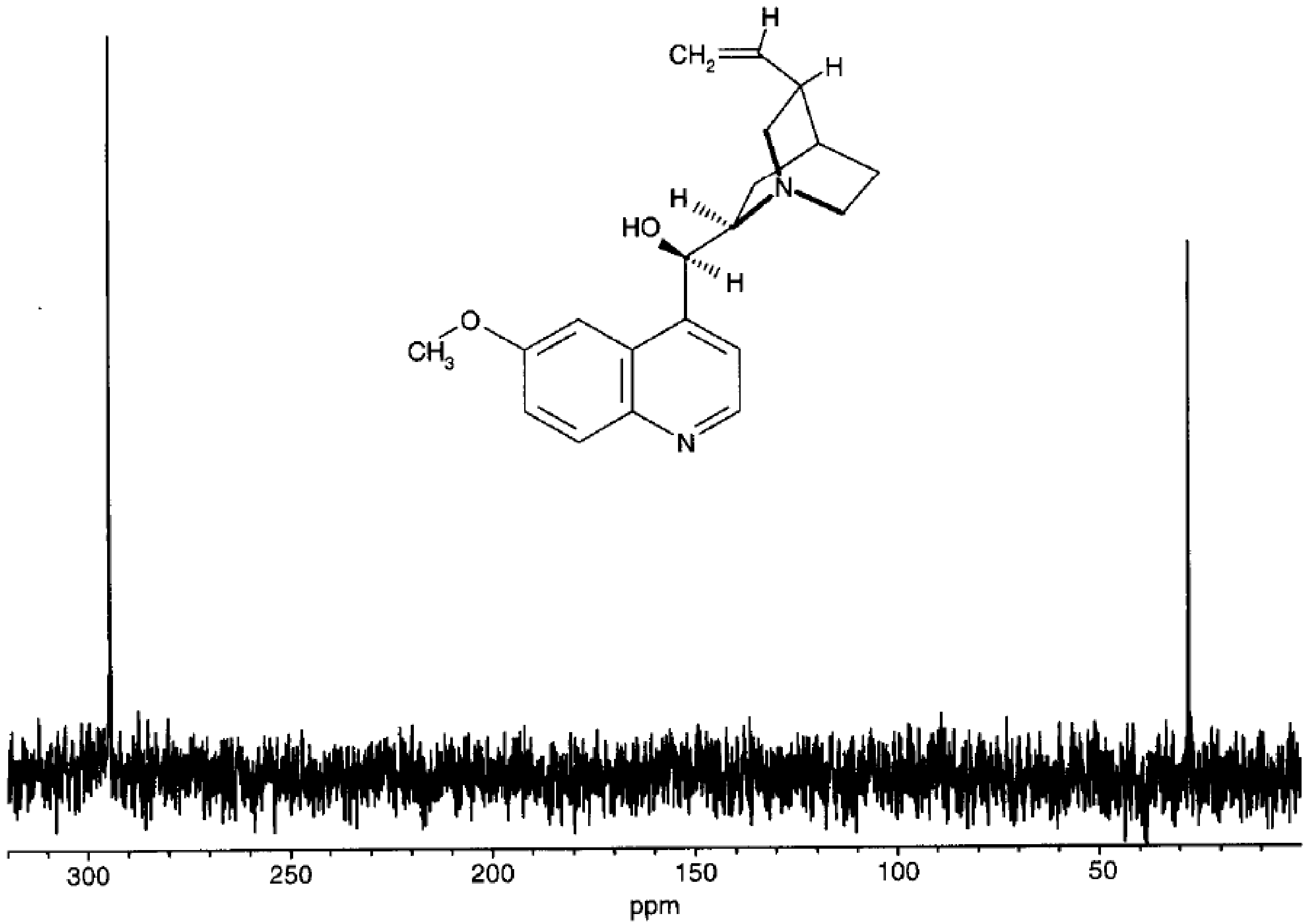


FIGURE 7.5. The proton-decoupled ^{15}N (30.4-MHz) spectrum of quinine in $CDCl_3$.

3. Other Nuclei NMR: ^{19}F

TABLE 6.1 Useful Magnetic Resonance Data for Nuclei Discussed in this Chapter

Isotope	Spin	Natural Abundundance %	Sensitivity		MHz at T of 7.0463	Reference Compound	Detection Range ppm
			Relative[a]	Absolute[b]			
^{1}H	1/2	99.98	1.00	1.00	300.000	$Si(CH_3)_4$	10 to 0
^{2}H	1	1.5×10^{-2}	9.65×10^{-3}	1.45×10^{-6}	46.051	$Si(CD_3)_4$	10 to 0
^{3}H	1/2	0	1.21	0	319.990	$Si(CT_3)_4$	10 to 0
^{13}C	1/2	1.108	1.59×10^{-2}	1.76×10^{-4}	75.432	$Si(CH_3)_4$	220 to 0
^{14}N	1	99.63	1.01×10^{-3}	1.01×10^{-3}	21.671	$^{14}NH_3$ (1)[c]	900 to 0
^{15}N	1/2	0.37	1.04×10^{-3}	3.85×10^{-6}	30.398	$^{15}NH_3$ (1)[c]	900 to 0
^{17}O	5/2	3.7×10^{-2}	2.91×10^{-2}	1.08×10^{-5}	40.670	H_2O	1700 to −50
^{19}F	1/2	100	0.83	0.83	282.231	$CFCl_3$	276 to −280
^{29}Si	1/2	4.7	7.84×10^{-3}	3.69×10^{-4}	59.595	$Si(CH_3)_4$	80 to −380
^{31}P	1/2	100	6.63×10^{-2}	6.63×10^{-2}	121.442	85% H_3PO_4	270 to −480

[a] At constant field for equal number of nuclei
[b] Product of relative sensitivity and natural abundance
[c] At 25°C

$CFCl_3$ (0 ppm) versus CF_3CO_2H (-78.5 ppm)

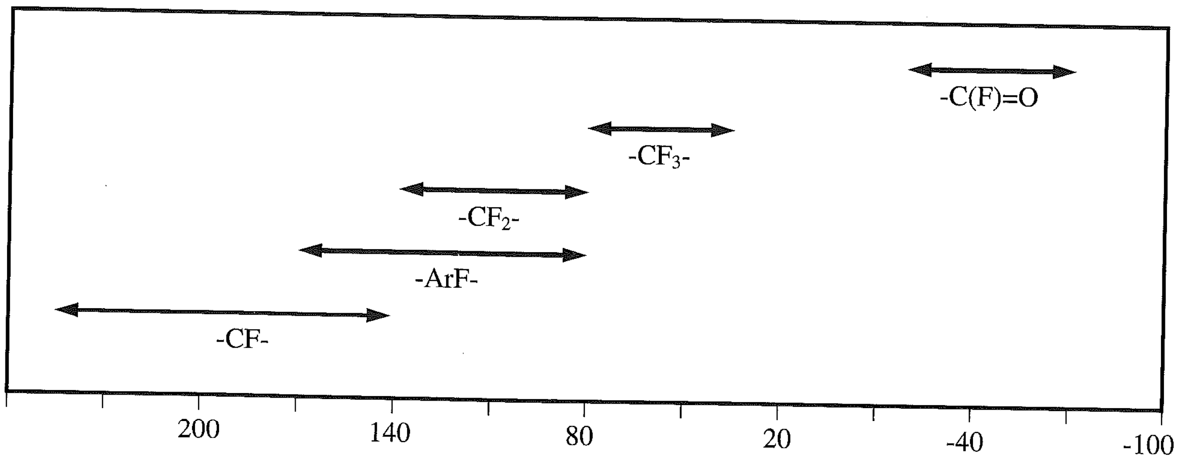


FIGURE 6.5 Chemical shift ranges for various fluorine-containing compounds.

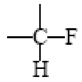
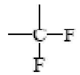
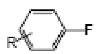
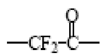
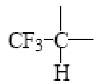
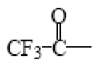
3. Other Nuclei NMR: ^{19}F

TABLE 6.2 Chemical Shifts for Various Fluorine-containing Compounds

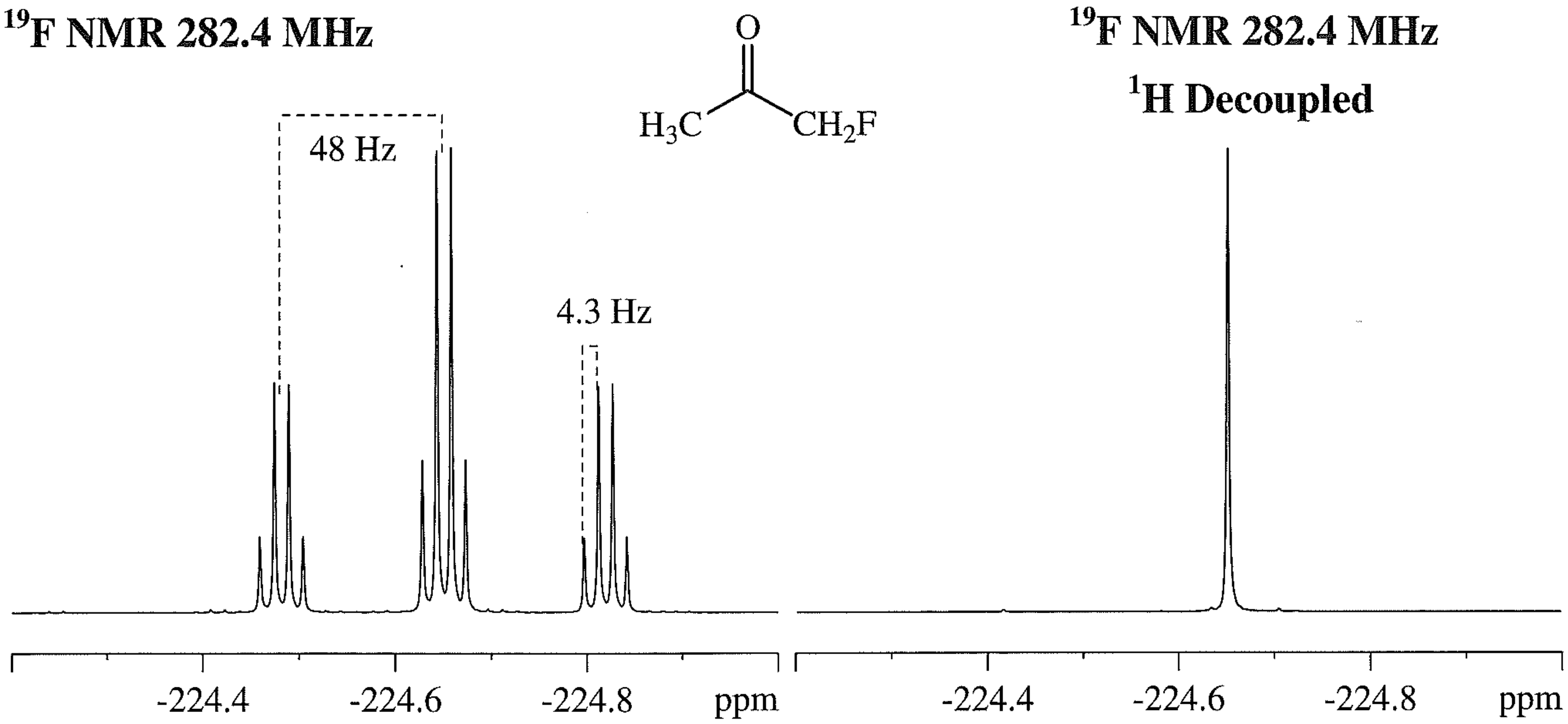
Compound	Chemical Shift (ppm)[a]
$CFCl_3$ Reference	0.0
CF_2Cl_2	−8.0
CF_3Cl	−28.6
$CFBr_3$	7.4
CF_2Br_2	7.0
$CFBr_3$	7.0
CFH_3	−271.9
CF_2H_2	−1436.0
CF_3H	−78.6
CF_4	−62.3
C_4F_8	−135.15
C_5F_{10}	−132.9
$(CF_3)_2CO$	−84.6
$CF_3C(O)OH$	−76.5
$CF_3C(O)OCH_3$	−74.2
CF_3COOEt	−78.7
$(CF_3)_3N$	−56.0
CH_2FCN	−251.0
$FCH{=}CH_2$	−114.0
$F_2C{=}CH_2$	−81.3
$F_2C{=}CF_2$	−135.0
C_6F_6	−164.9
C_6H_5F	−113.5
p−$C_6H_4F_2$	−106.0
$C_6H_5CFH_2$	−207
$C_6H_5C(O)OCF_3$	−73.9
$C_6H_5C(CF_3)_2OH$	−74.7
$C_6H_5CF_3$	−63.7
F_2 (elemental)	422.9
SF_6	57.4
SiF_4	−163.3
HF (aqueous)	−204.0
KF (aqueous F^-)	−125.3

[a] Most literature references historically reversed the sign convention (i.e., negative shifts are reported as positive).

Difficult to predict!!
Electronegativity; Oxidation state of neighbour;
Stereochemistry; Effect of more distant group

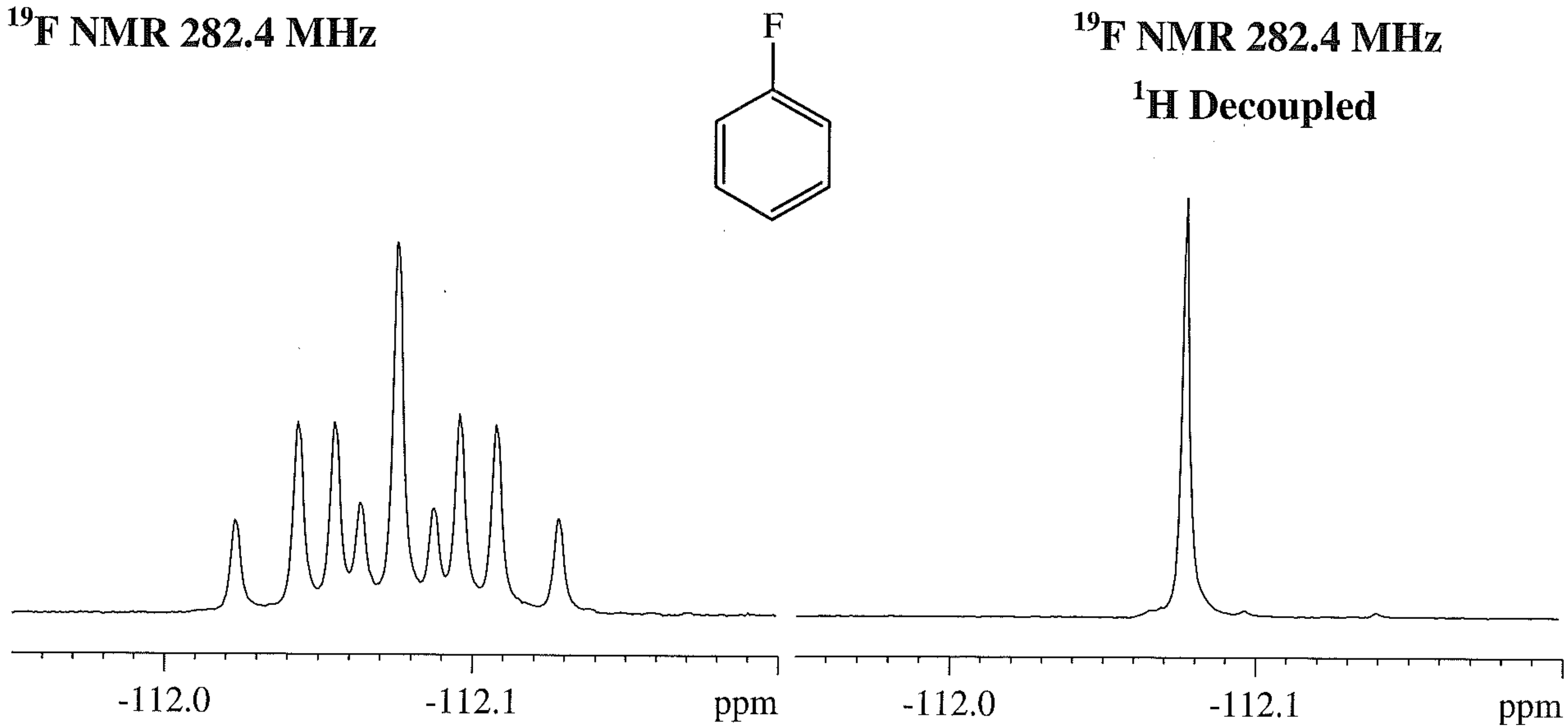
Chemical group	σ relative to $CFCl_3$, ppm	σ relative to CF_3COOH, ppm	σ relative to C_6H_5F, ppm
	-210	-131	-96
	-140	-69	-26
	-140	-60	-26
	-125	-46	-11
	-75	4	39
	-81	-2	33
$-SO_2F$	50	129	164

3. Other Nuclei NMR: ^{19}F

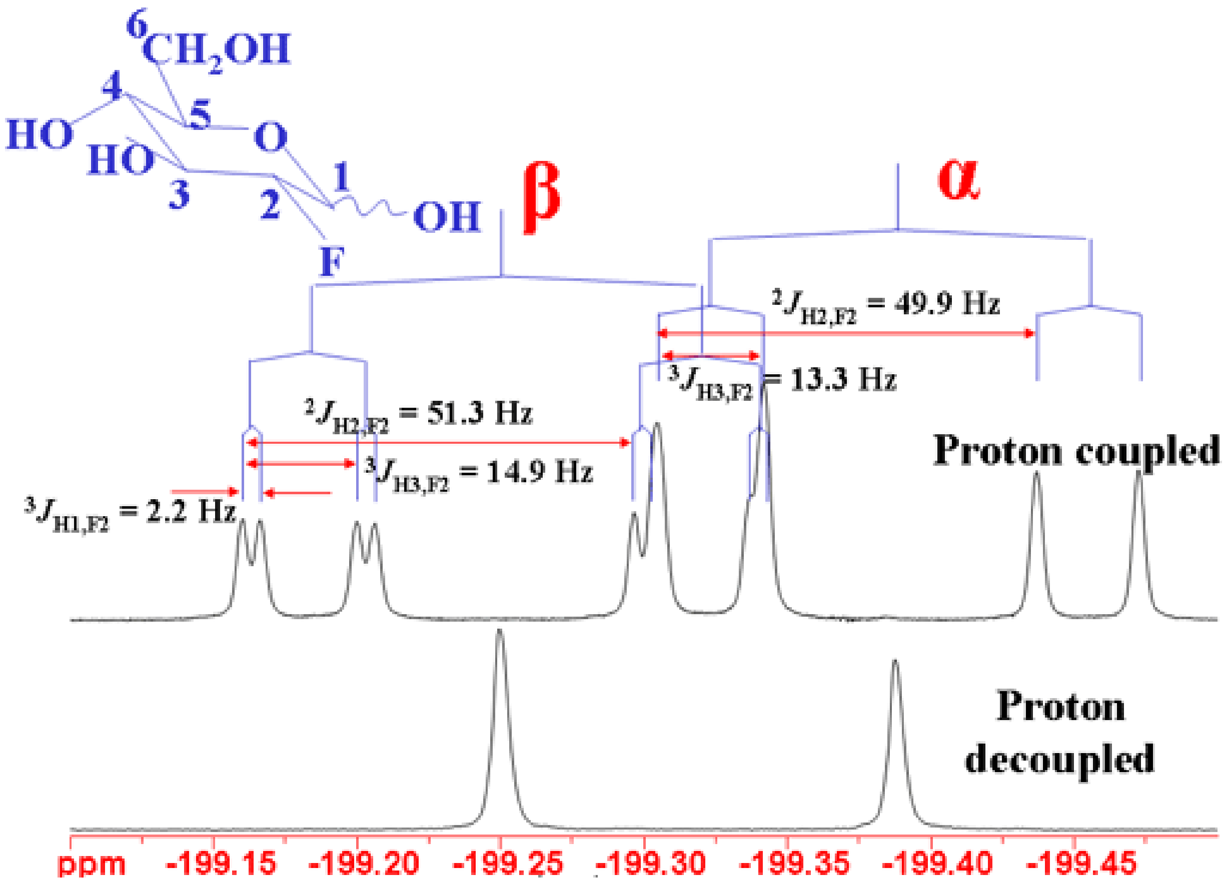


NOE EFFECT IS NOT A DECISIVE FACTOR

3. Other Nuclei NMR: ^{19}F



3. Other Nuclei NMR: ^{19}F



3. Other Nuclei NMR: ^{31}P

TABLE 6.1 Useful Magnetic Resonance Data for Nuclei Discussed in this Chapter

Isotope	Spin	Natural Abundundance %	Sensitivity Relative[a]	Sensitivity Absolute[b]	MHz at T of 7.0463	Reference Compound	Detection Range ppm
^{1}H	1/2	99.98	1.00	1.00	300.000	$Si(CH_3)_4$	10 to 0
^{2}H	1	1.5×10^{-2}	9.65×10^{-3}	1.45×10^{-6}	46.051	$Si(CD_3)_4$	10 to 0
^{3}H	1/2	0	1.21	0	319.990	$Si(CT_3)_4$	10 to 0
^{13}C	1/2	1.108	1.59×10^{-2}	1.76×10^{-4}	75.432	$Si(CH_3)_4$	220 to 0
^{14}N	1	99.63	1.01×10^{-3}	1.01×10^{-3}	21.671	$^{14}NH_3$ (1)[c]	900 to 0
^{15}N	1/2	0.37	1.04×10^{-3}	3.85×10^{-6}	30.398	$^{15}NH_3$ (l)[c]	900 to 0
^{17}O	5/2	3.7×10^{-2}	2.91×10^{-2}	1.08×10^{-5}	40.670	H_2O	1700 to −50
^{19}F	1/2	100	0.83	0.83	282.231	$CFCl_3$	276 to −280
^{29}Si	1/2	4.7	7.84×10^{-3}	3.69×10^{-4}	59.595	$Si(CH_3)_4$	80 to −380
^{31}P	1/2	100	6.63×10^{-2}	6.63×10^{-2}	121.442	85% H_3PO_4	270 to −480

[a] At constant field for equal number of nuclei
[b] Product of relative sensitivity and natural abundance
[c] At 25°C

Biological importance

Highest NOE ($^{31}P/^{1}H$): $\gamma_H/2\gamma_P$ = 26.753/(2x10.840) : 1.23

(^{1}H-^{31}P): ^{1}J (600-700 Hz); ^{2}J (20-30 Hz); ^{3}J (5-10 Hz); ^{4}J (< 1Hz)

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3. Other Nuclei NMR: ^{31}P

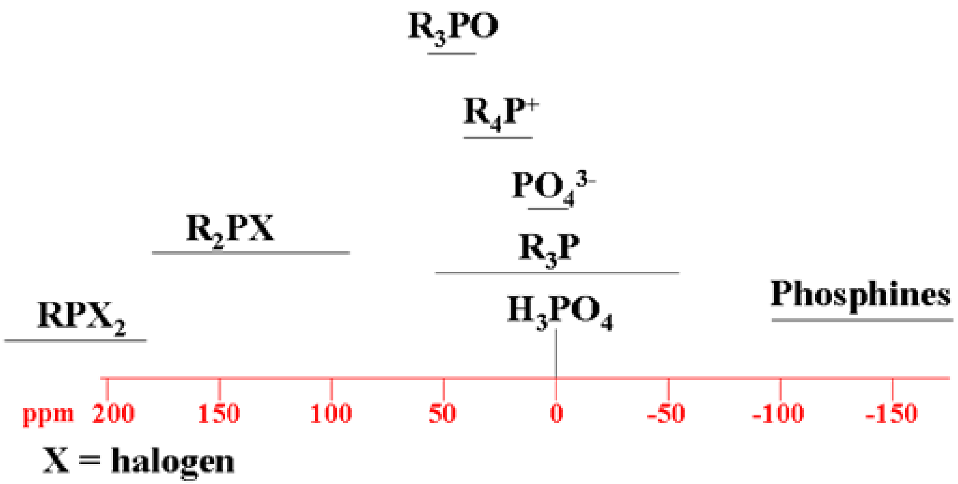

TABLE 6.3 Chemical Shifts for Various Phosphorus-containing Compounds. Adapted from Bruker Almanac 1995.

Phosphorous (III) Compounds	(ppm)[a]	Phosphorous (V) Compounds	(ppm)[a]
PMe_3	−62	Me_3PO	36.2
PEt_3	−20	Et_3PO	48.3
$PPr(n)_3$	−33	$[Me_4P]^{+1}$	24.4
$PPr(i)_3$	19.4	$[PO_4]^{-3}$	6
$PBu(n)_3$	−32.5	PF_5	−80.3
$PBu(i)_3$	−45.3	PCl_5	−80
$PBu(s)_3$	7.9	$MePF_4$	−29.9
$PBu(t)_3$	63	Me_3PF_2	−158
$PMeF_2$	245	Me_3PS	59.1
$PMeH_2$	−163.5	Et_3PS	54.5
$PMeCl_2$	192	$[Et4p]^{+1}$	40.1
$PMeBr_2$	184	$[PS_4]^{-3}$	87
PMe_2F	186	$[PF_6]^{-1}$	−145
PMe_2H	−99	$[PCl_4]^{+1}$	86
PMe_2Cl	−96.5	$[PCl_6]^{-1}$	−295
PMe_2Br	−90.5	Me_2PF_3	8

[a] Reference to 85% H_3PO_4 at 0 ppm

One-bond couplings are typically 600 to 700 Hz, two-bond 20 to 30 Hz, three-bond 5 to 10 Hz and four-bond <1 Hz.

3. Other Nuclei NMR: ^{31}P

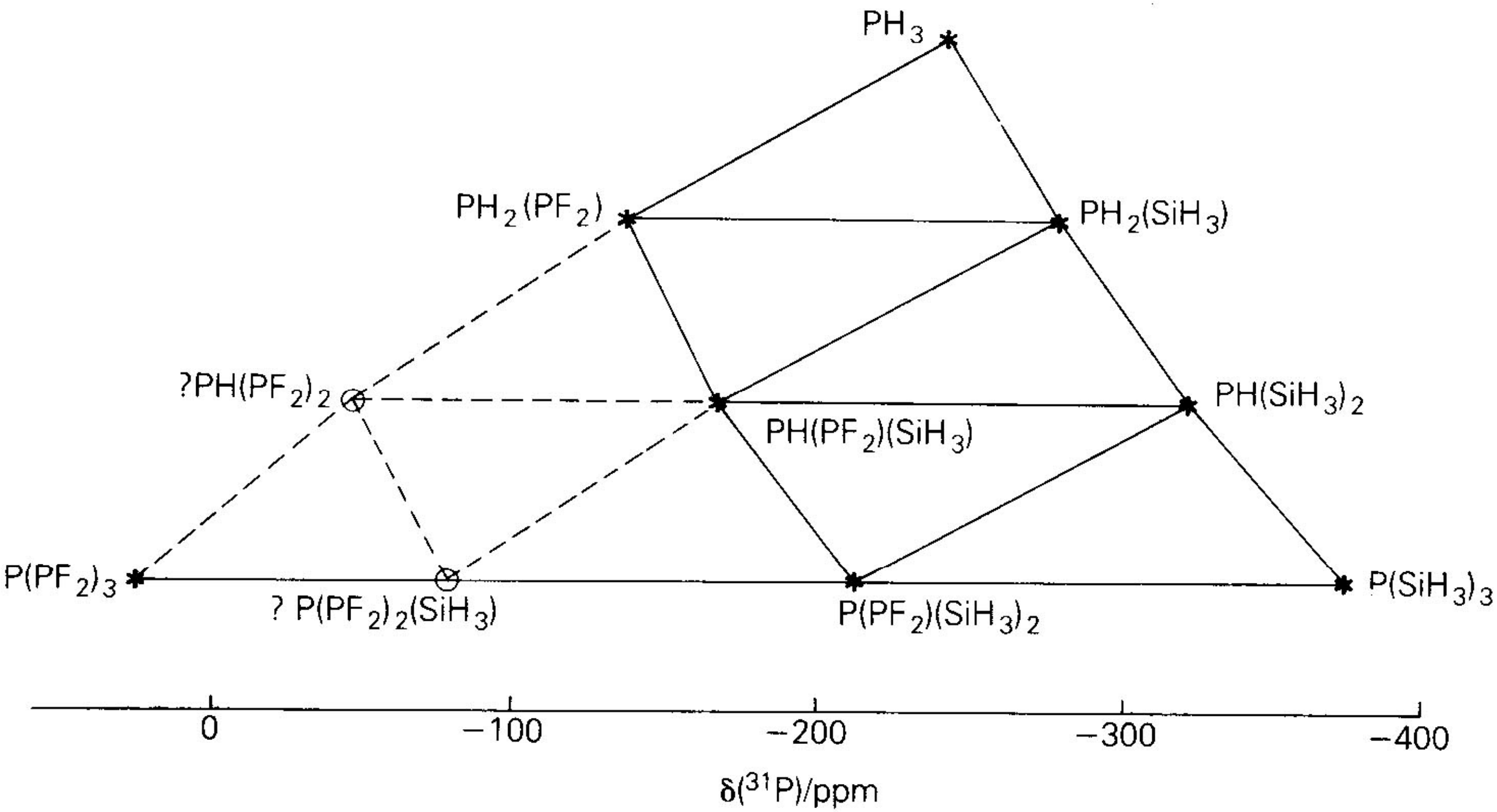

Fig 2.6 Representation of ^{31}P chemical shifts of phosphines with H, SiH_3 and PF_2 substituents. The regularity of the changes enables the chemical shifts of the unknown compounds $PH(PF_2)_2$ and $P(PF_2)_2(SiH_3)$, to be predicted.

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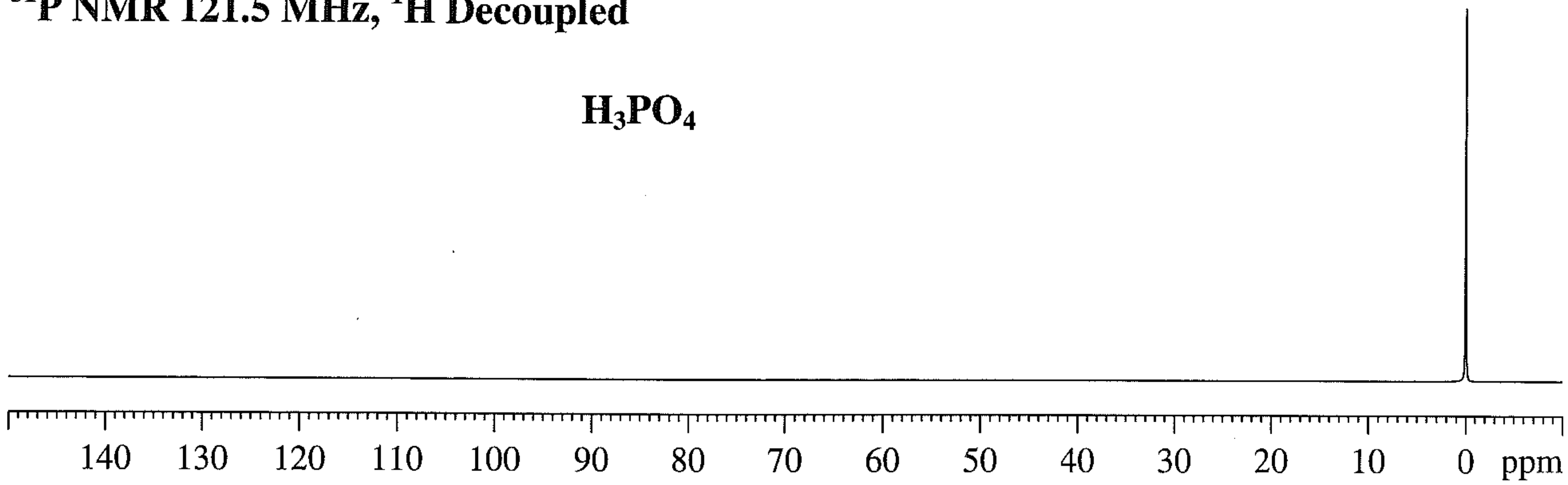
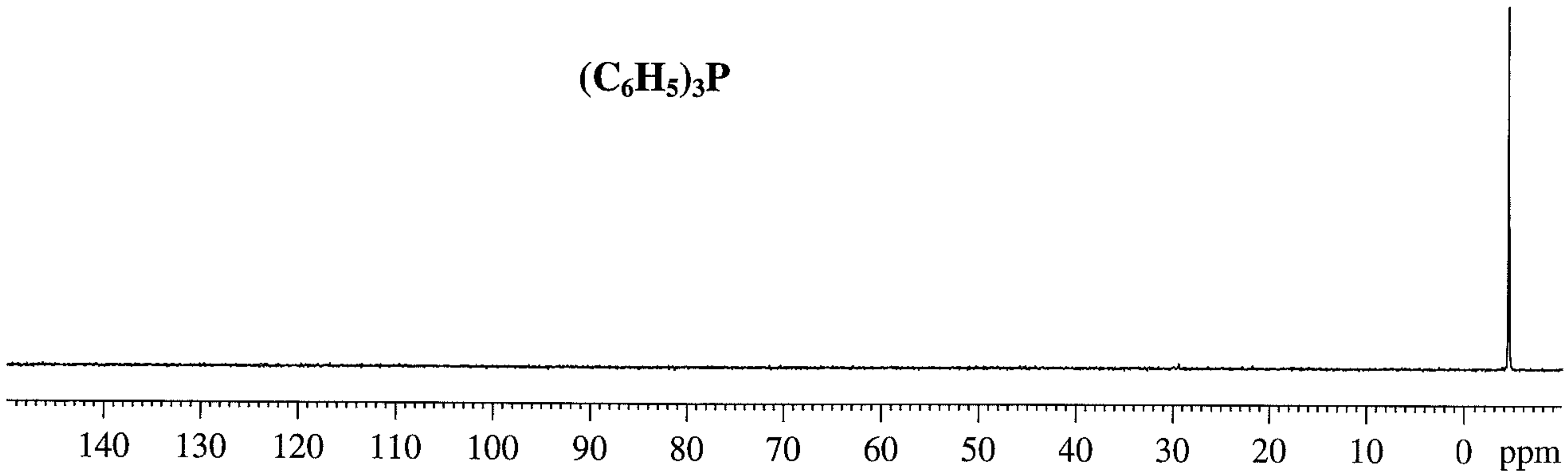
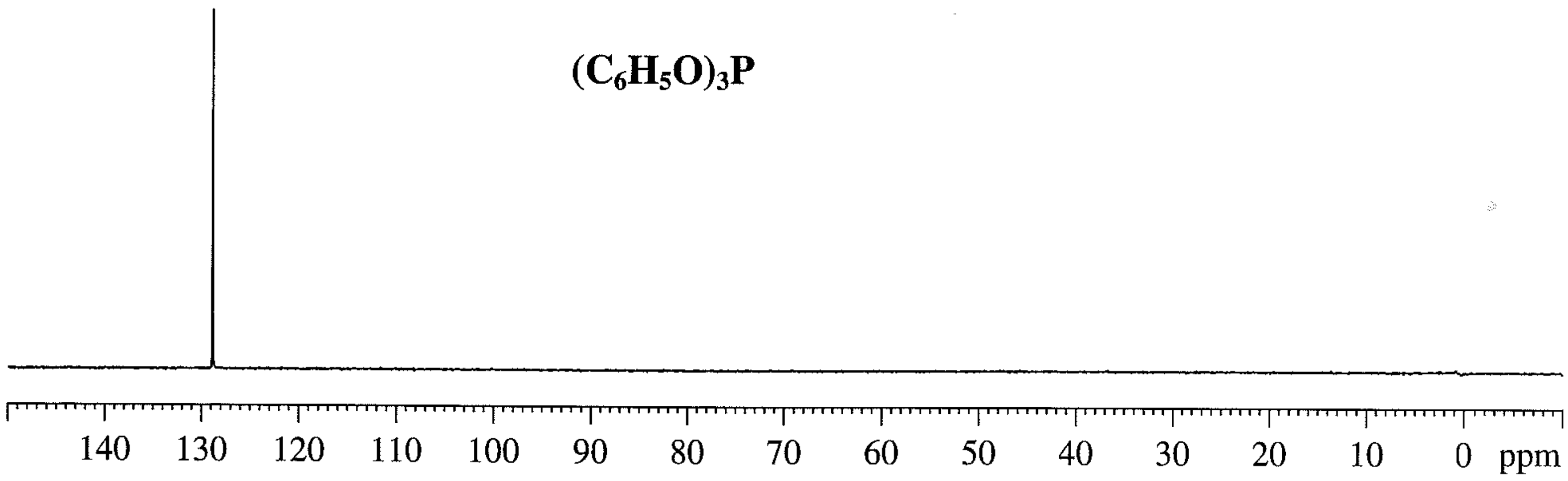
3. Other Nuclei NMR: ^{31}P

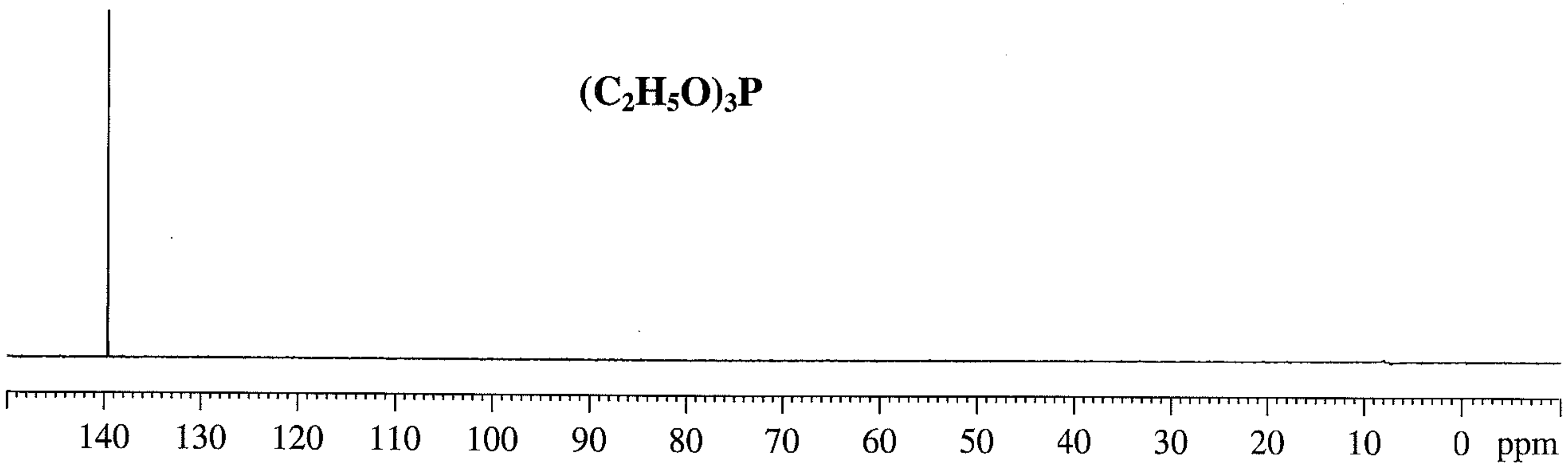
^{31}P NMR 121.5 MHz, ^{1}H Decoupled





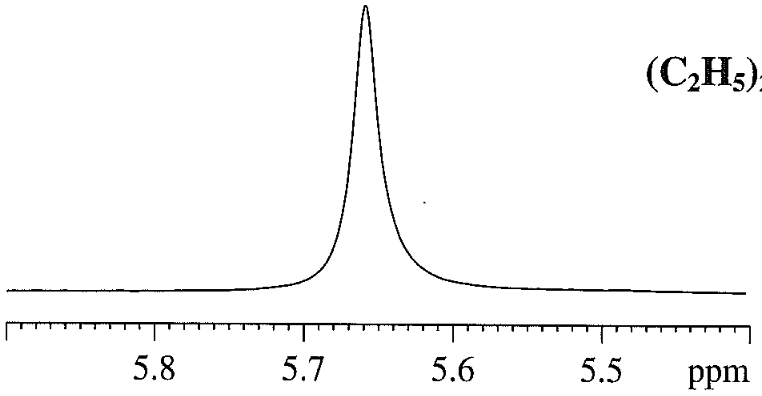
3. Other Nuclei NMR: ^{31}P





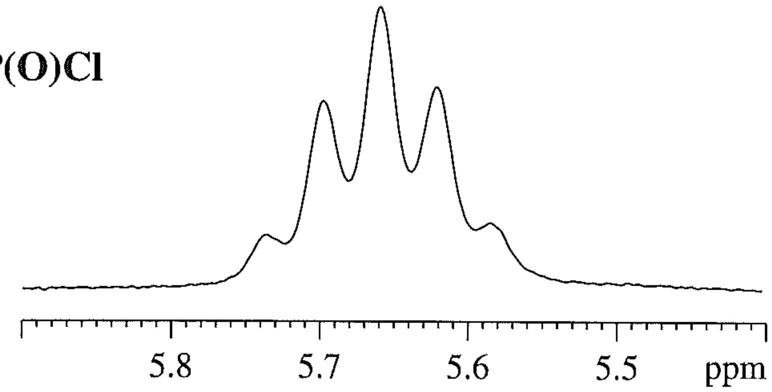
3. Other Nuclei NMR: ^{31}P

^{31}P NMR 242.9 MHz ^{1}H decoupled

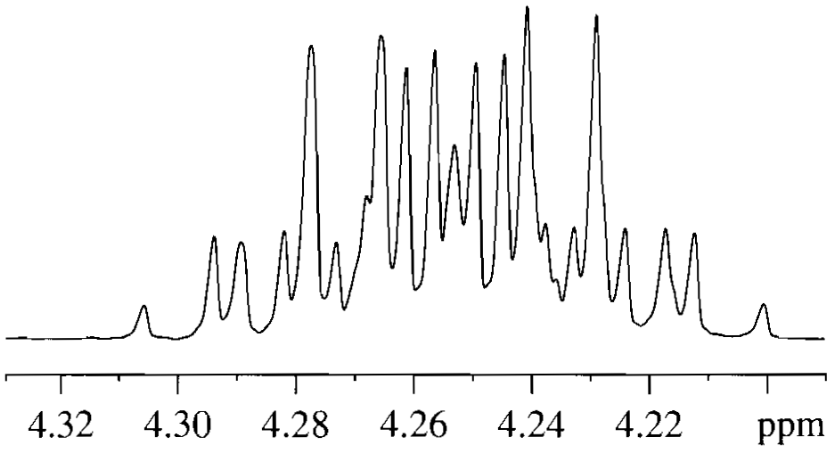


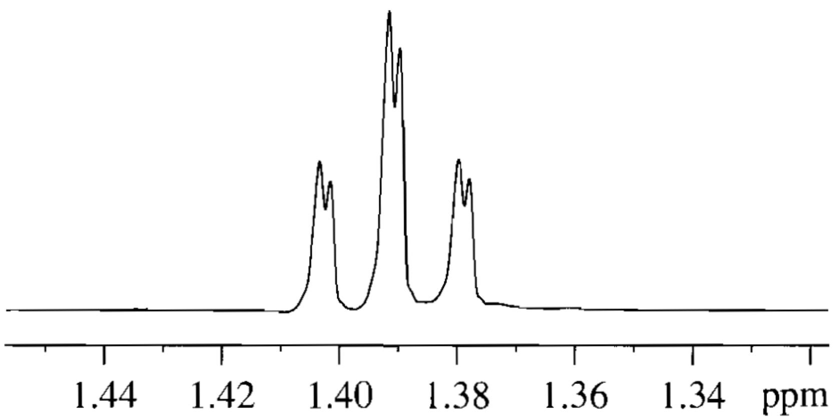
$(C_2H_5)_2P(O)Cl$

^{31}P NMR 242.9 MHz ^{1}H coupled

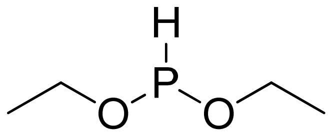


^{1}H NMR 600 MHz coupled ^{31}P

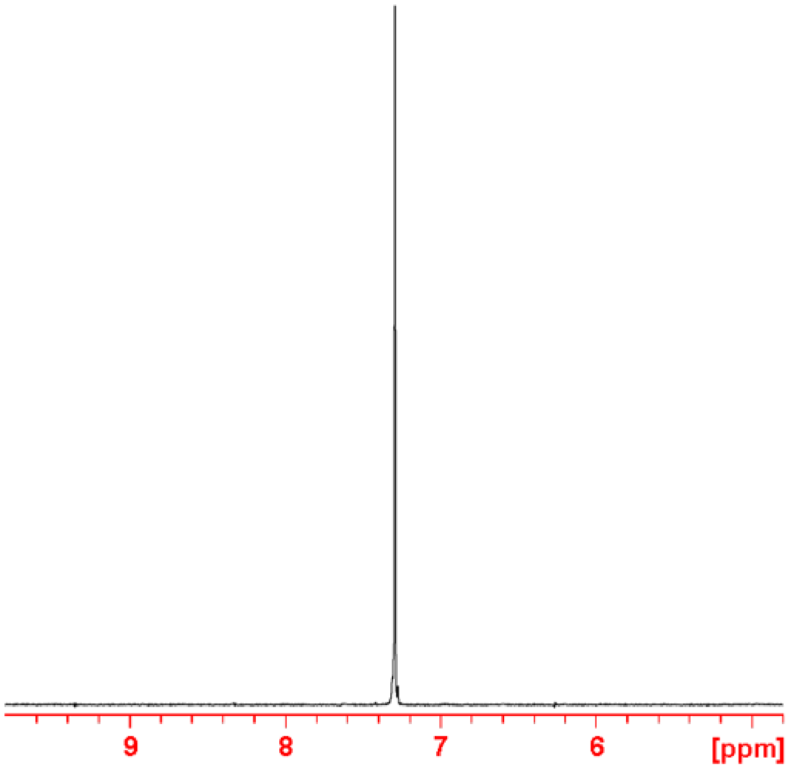


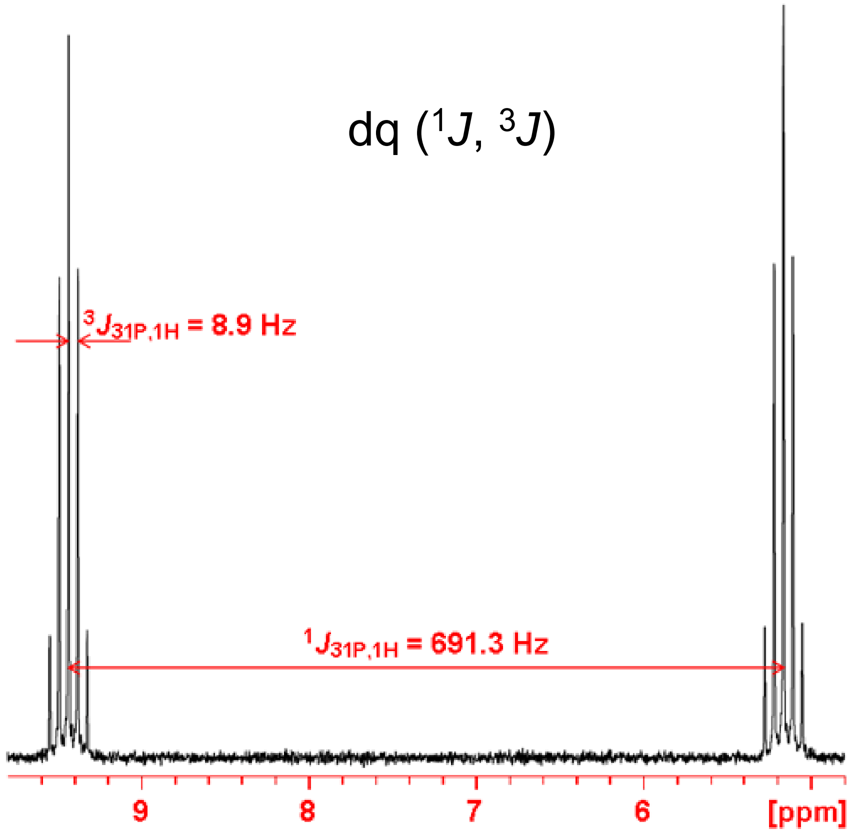


3. Other Nuclei NMR: ^{31}P

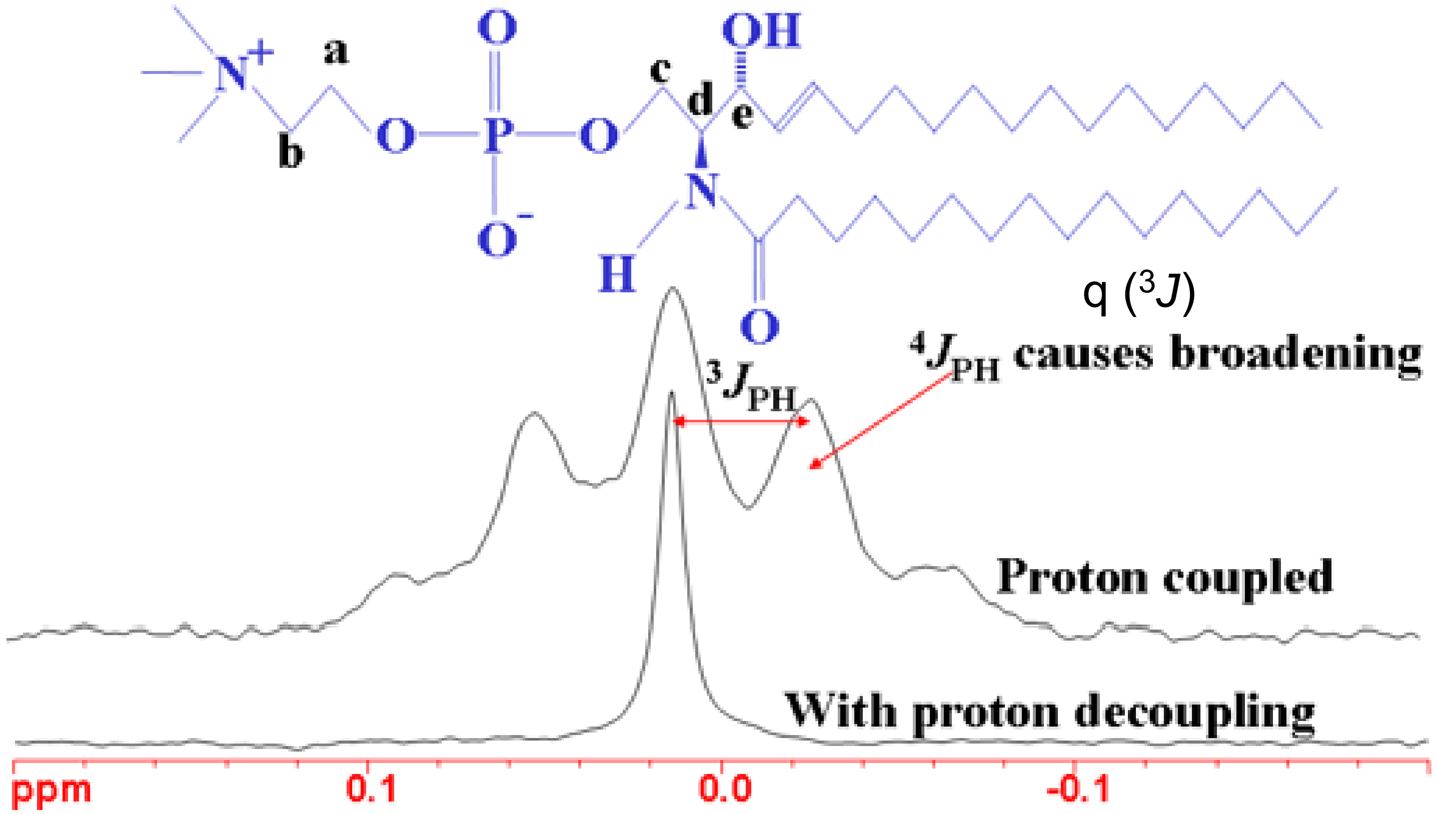


^{1}H decoupled experiment





3. Other Nuclei NMR: ^{31}P



3. Other Nuclei NMR: ^{29}Si

TABLE 6.1 Useful Magnetic Resonance Data for Nuclei Discussed in this Chapter

Isotope	Spin	Natural Abundundance %	Sensitivity Relative[a]	Sensitivity Absolute[b]	MHz at T of 7.0463	Reference Compound	Detection Range ppm
^{1}H	1/2	99.98	1.00	1.00	300.000	$Si(CH_3)_4$	10 to 0
^{2}H	1	1.5×10^{-2}	9.65×10^{-3}	1.45×10^{-6}	46.051	$Si(CD_3)_4$	10 to 0
^{3}H	1/2	0	1.21	0	319.990	$Si(CT_3)_4$	10 to 0
^{13}C	1/2	1.108	1.59×10^{-2}	1.76×10^{-4}	75.432	$Si(CH_3)_4$	220 to 0
^{14}N	1	99.63	1.01×10^{-3}	1.01×10^{-3}	21.671	$^{14}NH_3$ (1)[c]	900 to 0
^{15}N	1/2	0.37	1.04×10^{-3}	3.85×10^{-6}	30.398	$^{15}NH_3$ (l)[c]	900 to 0
^{17}O	5/2	3.7×10^{-2}	2.91×10^{-2}	1.08×10^{-5}	40.670	H_2O	1700 to −50
^{19}F	1/2	100	0.83	0.83	282.231	$CFCl_3$	276 to −280
^{29}Si	1/2	4.7	7.84×10^{-3}	3.69×10^{-4}	59.595	$Si(CH_3)_4$	80 to −380
^{31}P	1/2	100	6.63×10^{-2}	6.63×10^{-2}	121.442	85% H_3PO_4	270 to −480

[a] At constant field for equal number of nuclei
[b] Product of relative sensitivity and natural abundance
[c] At 25°C

3. Other Nuclei NMR: ^{29}Si

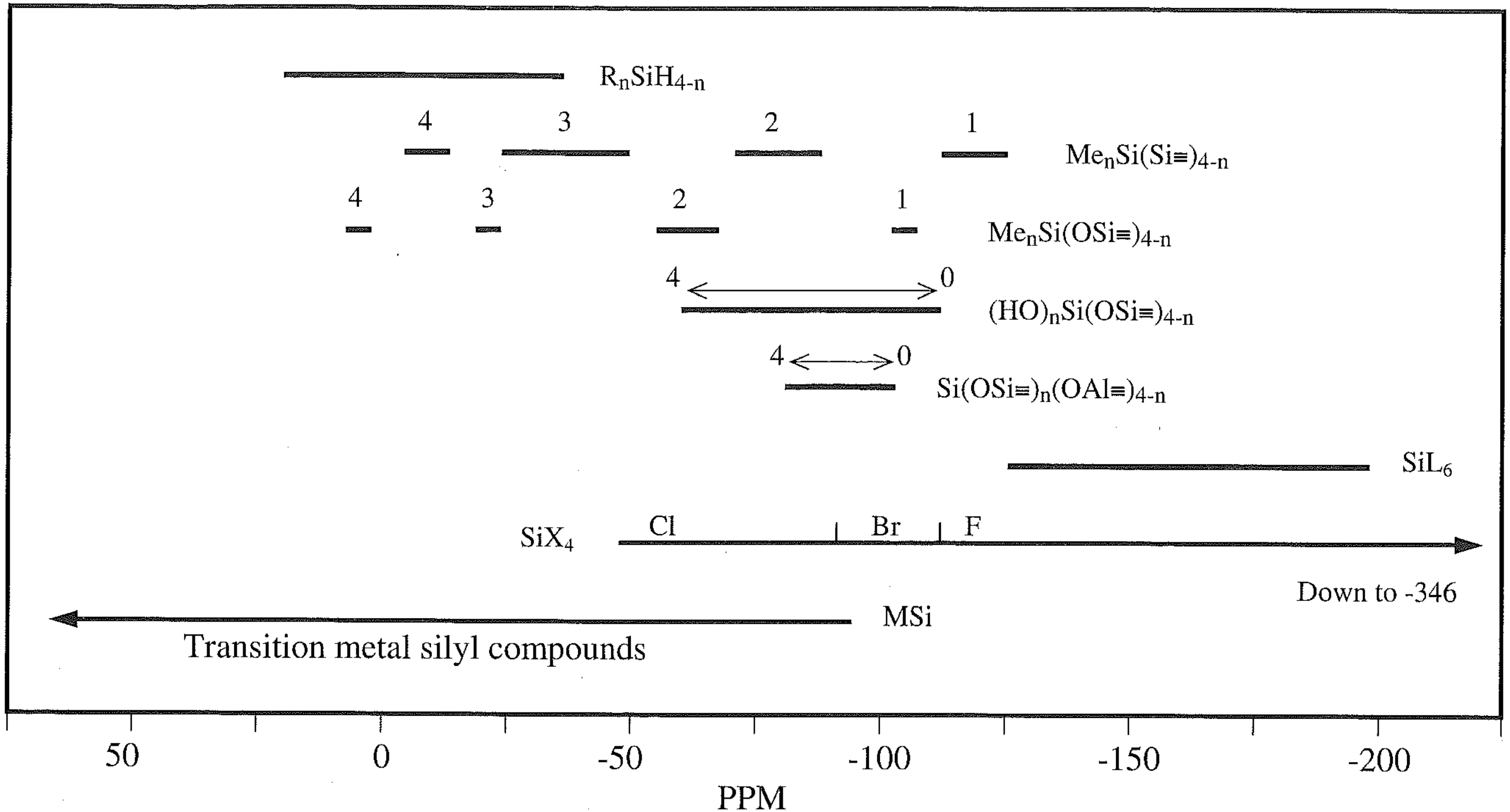


FIGURE 6.8 Chemical shift ranges for various silicon-containing compounds. Adapted from Bruker Almanac 1995.

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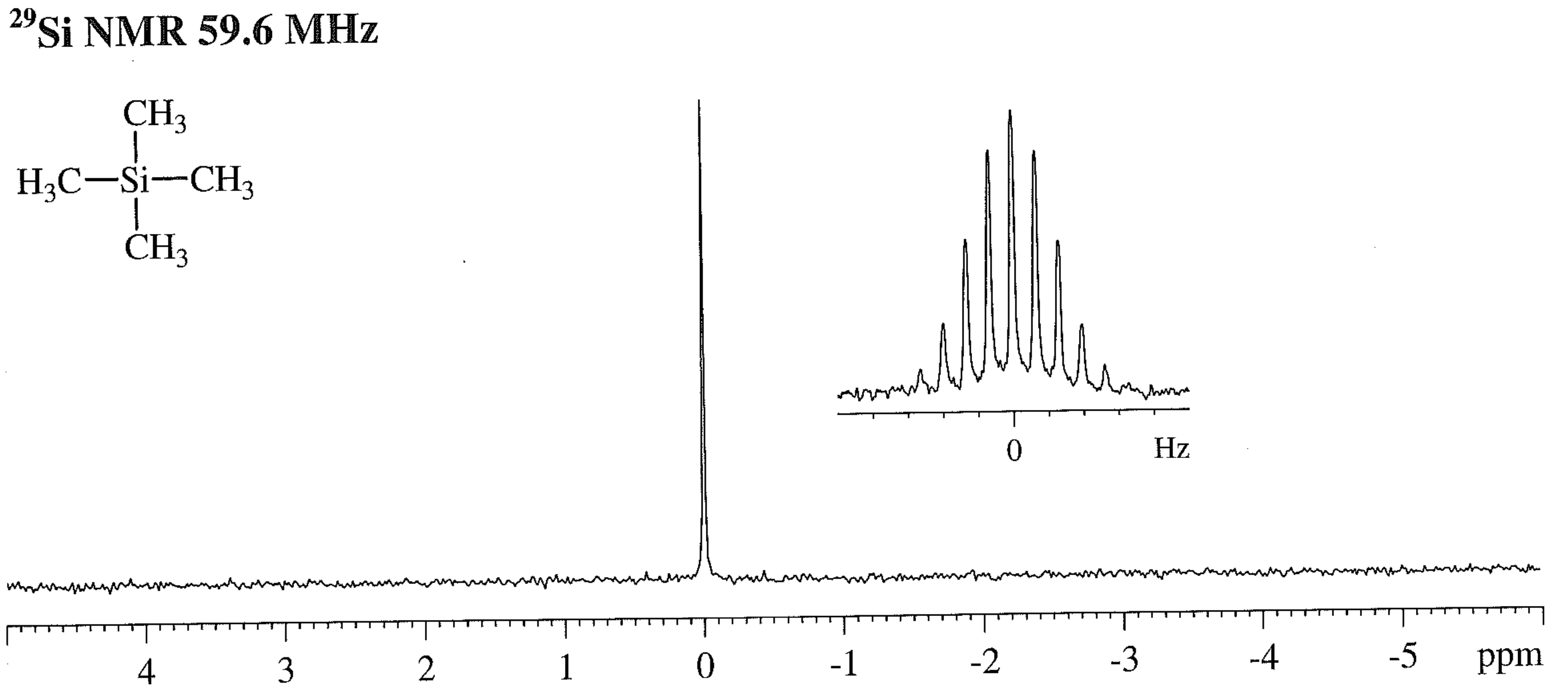
3. Other Nuclei NMR: ^{29}Si



^{2}J (Si-H) ~ 6 Hz

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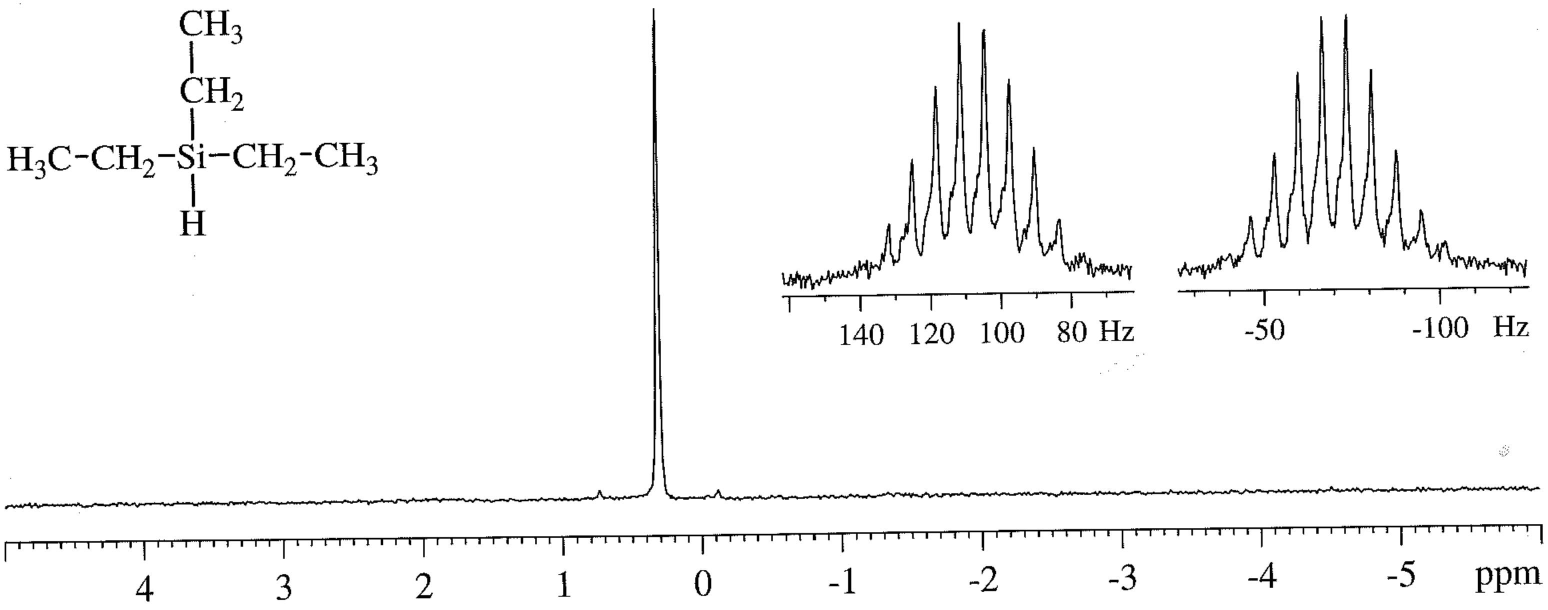
3. Other Nuclei NMR: ^{29}Si



^{1}J (Si-H) ~ 175 Hz

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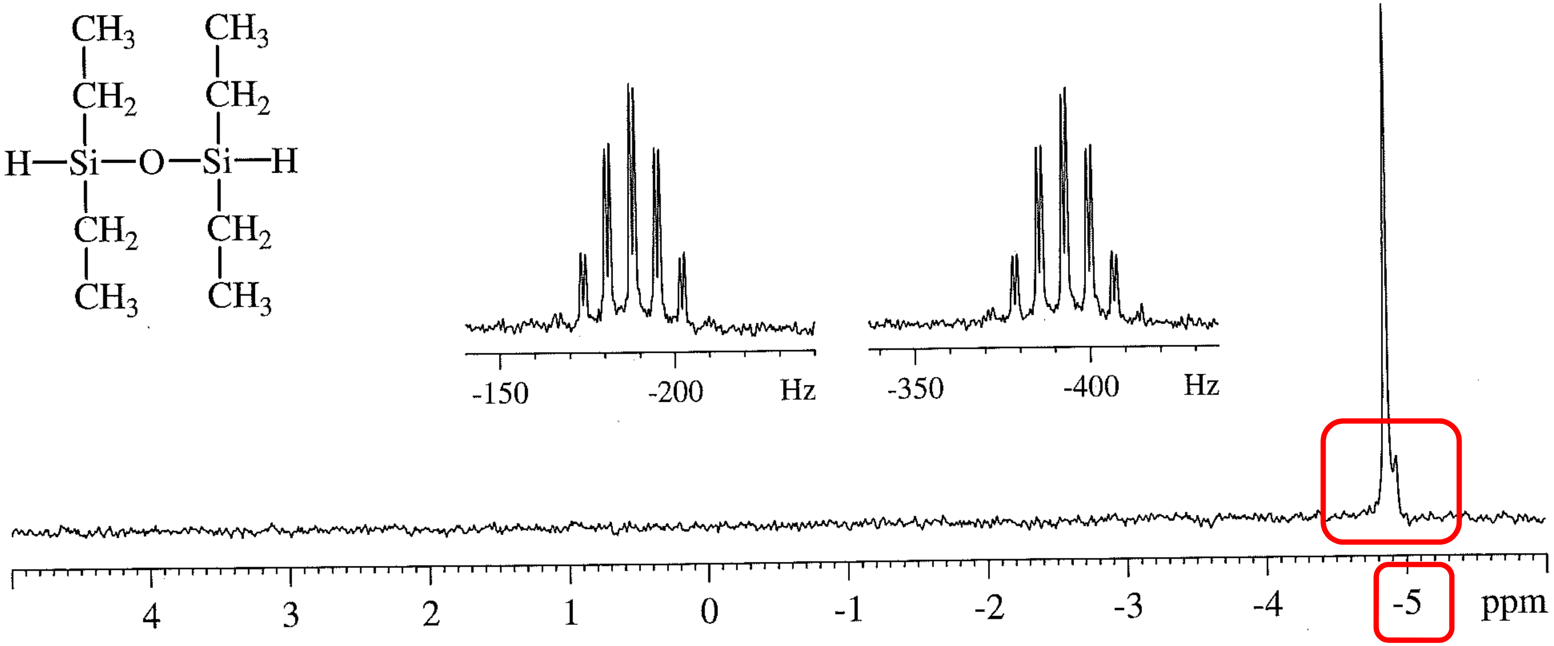
3. Other Nuclei NMR: ^{29}Si



^{1}J (Si-H) ~ 215 Hz

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