NMR SPECTROSCOPY OF OTHER IMPORTANT NUKLEI

^{13}C, ^{19}F

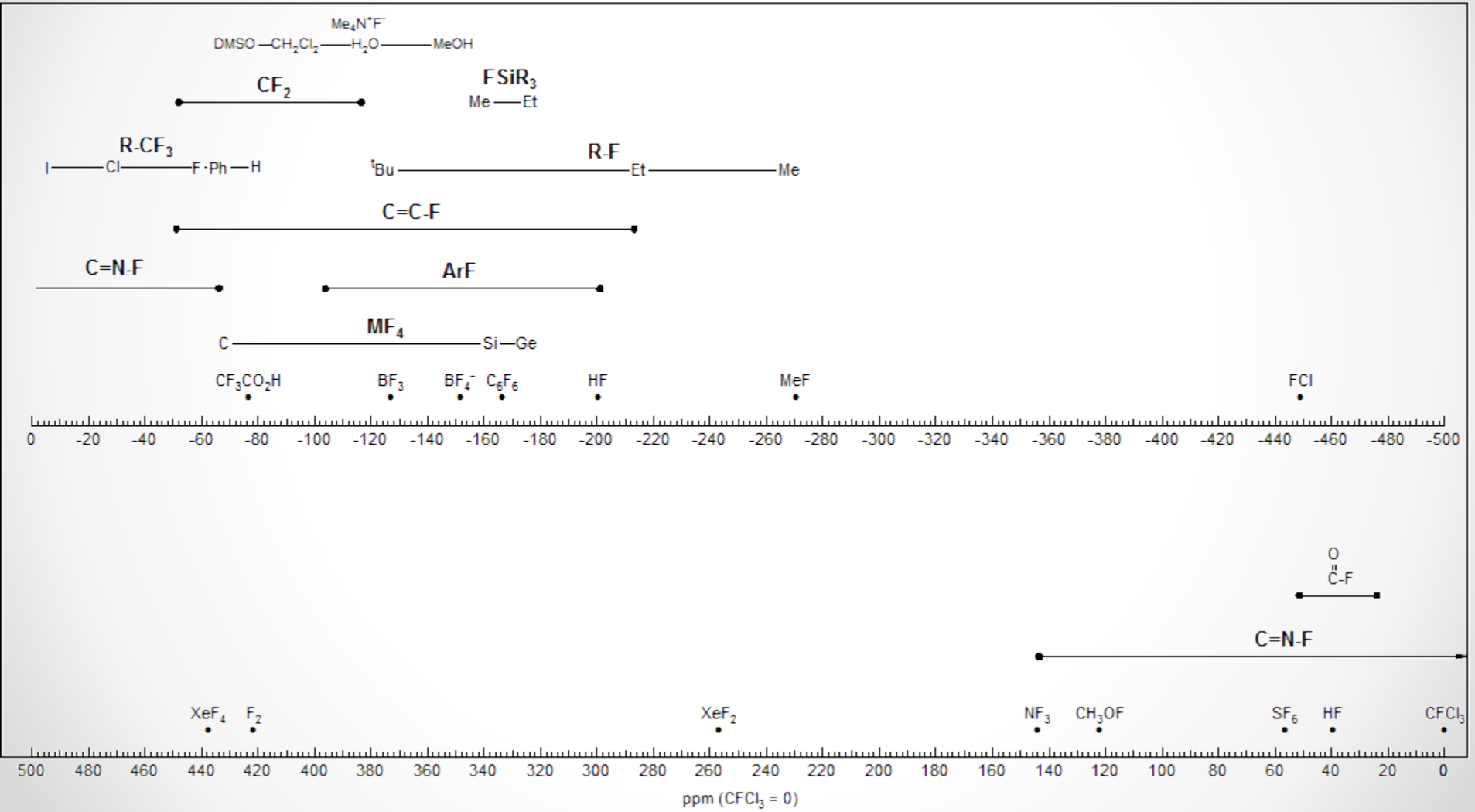
Department of Organic Chemistry
Dr hab. Sławomir Makowiec prof. PG

Magnetic Resonance Data for Nuclei

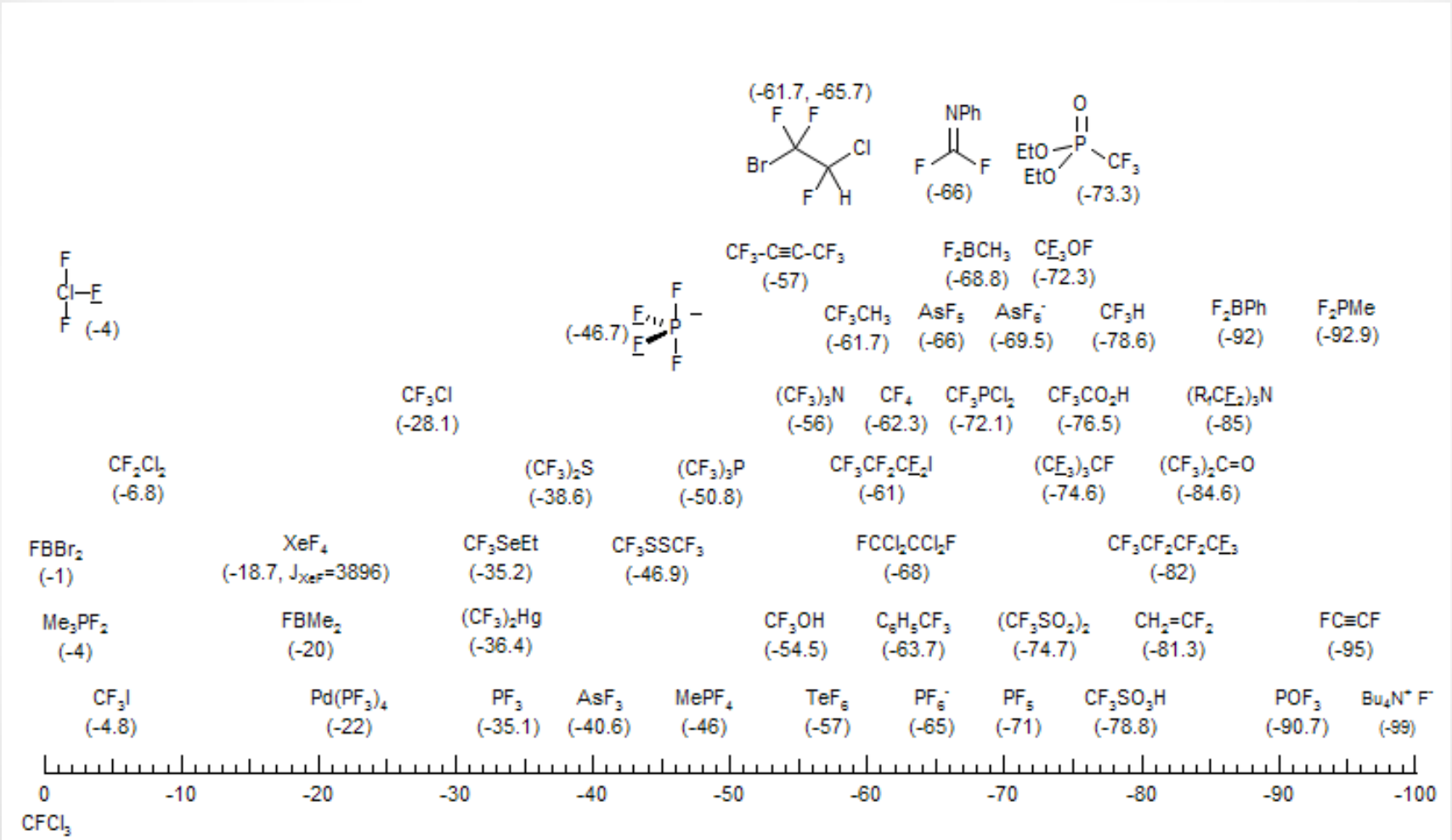
Isotope	Spin	Natural Abundance %	Sensivity		Frequency [MHz] at 7.04 T	Reference compound	Detection range ppm
			Relative	Absolute			
^{1}H	1/2	99,98	1,00	1.00	300	$Si(CH_3)_4$	0 to 10
^{3}H	1/2	0	1,21	0	319	$Si(CT_3)_4$	0 to 10
^{13}C	1/2	1.108	$1.59x10^{-2}$	$1.76x10^{-4}$	75	$Si(CH_3)_4$	0 to 220
^{15}N	1/2	0.37	$1.04x10^{-3}$	$3.85x10^{-6}$	30.3	$^{15}NH_3$	0 to 900
^{17}O	5/2	$3x10^{-2}$	$2.91x10^{-2}$	$1.08x10^{-5}$	40.6	H_2O	-50 to 1700
^{19}F	1/2	100	0.83	0.83	282	$CFCl_3$	-280 to 276
^{31}P	1/2	100	$6,63x10^{-2}$	$6,63x10^{-2}$	121	H_3PO_4	-480 to 270

Fluorine NMR

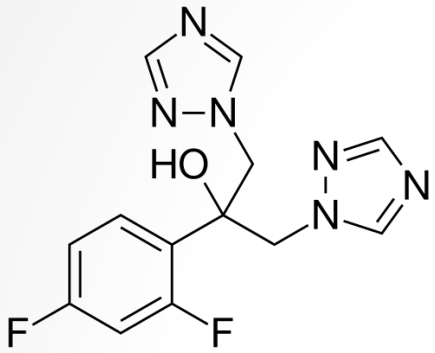
- Fluorine Shifts Overview



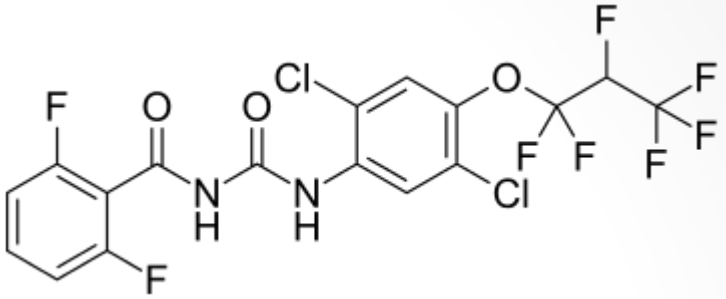
^{19}F chemical shifts



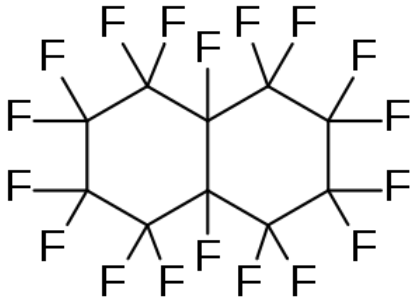
Fluorine NMR – target molecules



Fluconazole (antifungal)



Lefenuron (pesticide and antifungal)

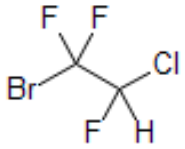
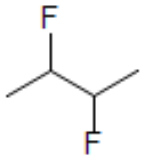
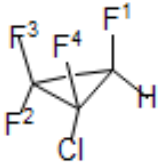
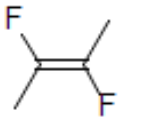
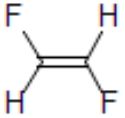
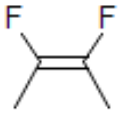
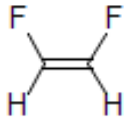
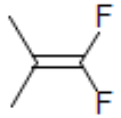
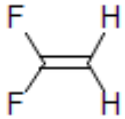
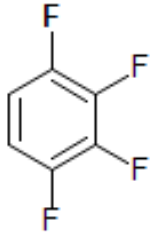


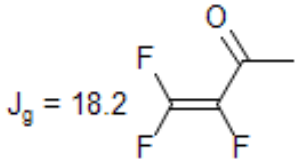
Perfluorodecaline (Fluosol - artificial blood
100 mL of perfluorodecalin can dissolve 49 mL of O_2

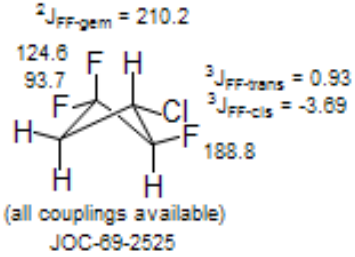
Fluorine NMR – reference compounds

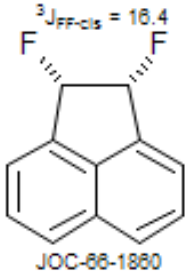
$CFCl_3$ (trichlorofluoromethane)	0.00
CF_3COOH (trifluoroacetic acid)	-76.55
C_6F_6 (hexafluorobenzene)	-164.9
C_6H_5F (fluorobenzene)	-113.15
CF_3Cl (trifluorochloromethane)	-28.6
F_2 (elemental fluorine)	+422.92
FCH_2CN (fluoroacetonitrile)	-251.
$CFCl_2CFCl_2$ (difluorotetrachloroethane)	-67.80
$C_6H_5CF_3$ (trifluorotoluene)	-63.72
SiF_4 (tetrafluorosilane)	-163.3
SF_6 (sulfur hexafluoride)	+57.42
$S_2O_5F_2$	+47.2
$(CF_3)_2CO$ (hexafluoro acetone)	-84.6
p-FC_6H_4F (para-difluorobenzene)	-106.0
BF_3	-131.
HF (aq)	-204.0
CF_4	-62.5
Aqueous F- (KF)	-125.3

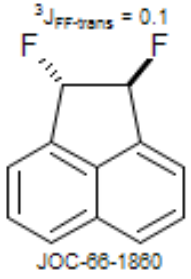
Fluorine NMR – J_{FF} coupling

Type	Range	Examples
	$^{2}J_{FF\text{-}gem}$ 40-370 Hz	 $^{2}J_{FF\text{-}g}$ = 174.1 $^{3}J_{FF}$ = 18.00, 18.04 JA-73-182
	$^{3}J_{HF\text{-}vic}$ 0-45 Hz	 JOC-70-678* $^{2}J_{23}$ = 184 $^{3}J_{13}$ = 7.5 $^{3}J_{12}$ = 4.9 $^{3}J_{34}$ = 4.8 $^{3}J_{24}$ = 2.1
	$^{3}J_{FF\text{-}trans}$ 100-150 Hz	 $^{3}J_{FF}$ = -132.0 JA-72-34
	$^{3}J_{FF\text{-}cis}$ 0-60 Hz	 $^{3}J_{FF}$ = 19.1 JA-72-34
	$^{2}J_{FF\text{-}gem}$ 0-110 Hz	 $^{2}J_{FF}$ = 31.1 JA-72-34
	$^{3}J_{FF\text{-}o}$ 18-35 Hz $^{4}J_{FF\text{-}m}$ 0-15 $^{5}J_{FF\text{-}p}$ 4-16	

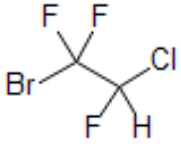
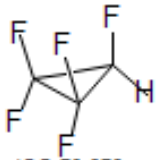
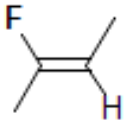
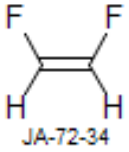
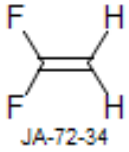
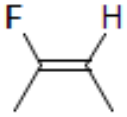
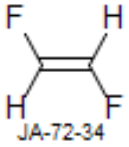
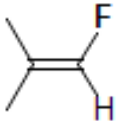
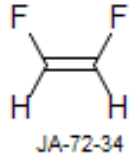
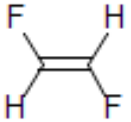




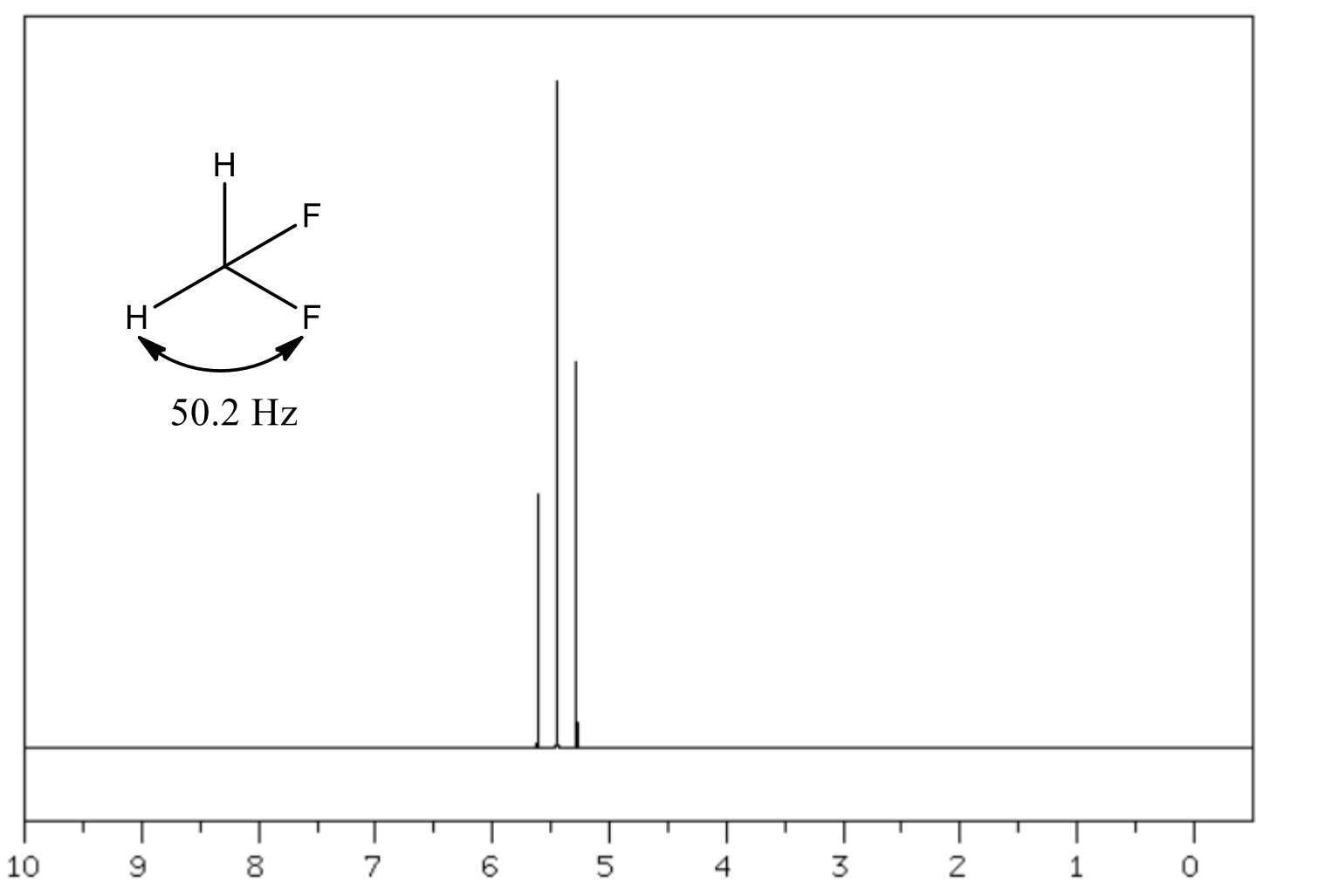




Fluorine NMR – J_{FH} coupling

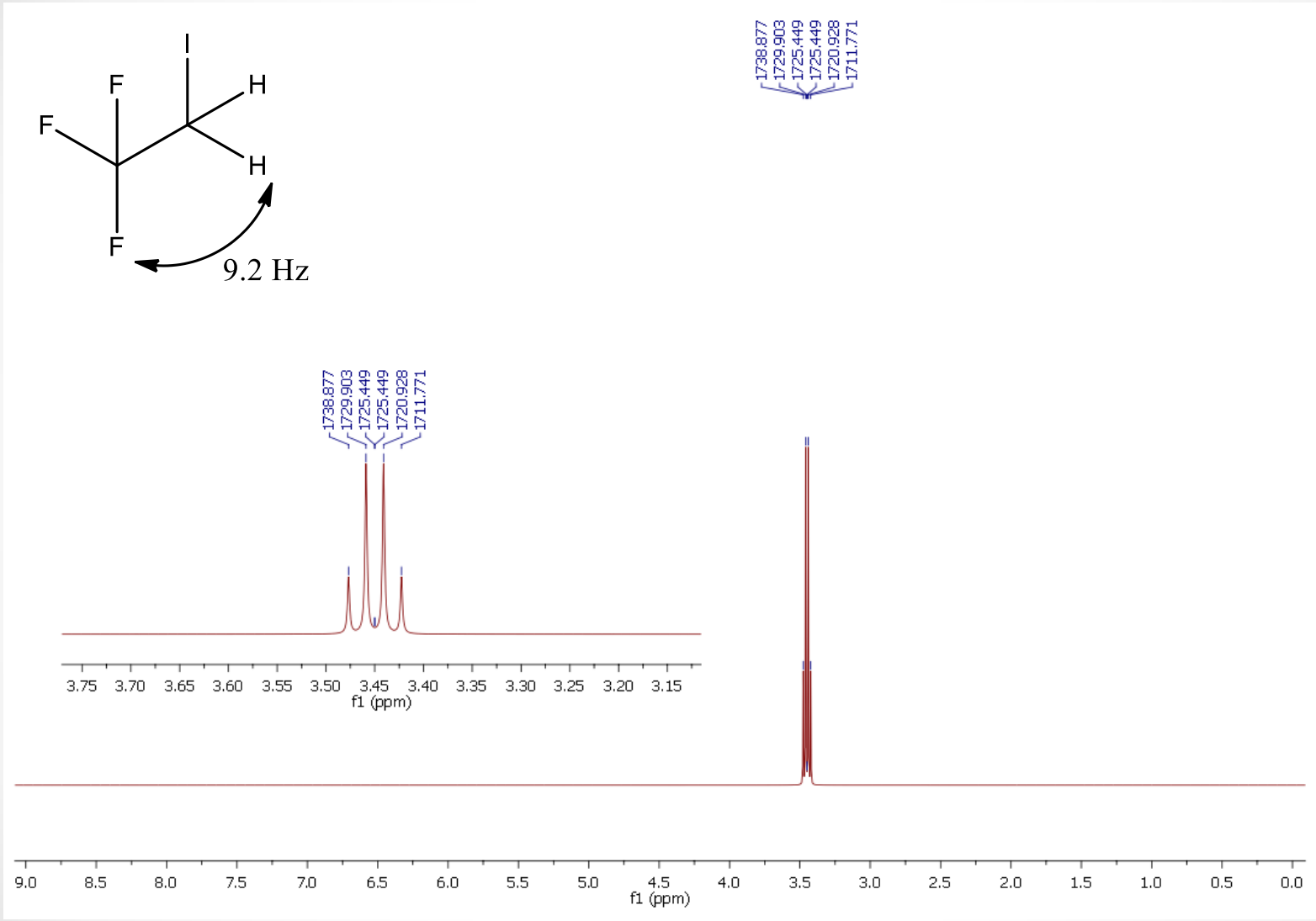
Type	Range	Examples
	$^{2}J_{HF\text{-}gem}$ 40-60 Hz	 $^{2}J_g = 48.2$ $^{3}J_v = 3.7, 6.2$ JA-73-182
	$^{3}J_{FH}$ **5–20 Hz**	 JOC-70-678 $^{2}J_g = 56$ $^{3}J_c = 13.2$ $^{3}J_t = 1.3$
	$^{3}J_{HF\text{-}trans}$ 10-50 Hz	 JA-72-34 $^{3}J_{HF} = 20.3$
		 JA-72-34 $^{3}J_{HF\text{-}c} = 0.6$ $^{3}J_{HF\text{-}t} = 34.0$
	$^{3}J_{HF\text{-}cis}$ 0-20 Hz	 JA-72-34 $^{3}J_{HF} = 3.0$
	$^{2}J_{HF\text{-}gem}$ 70-90 Hz	 JA-72-34 $^{2}J_{HF} = 72.0$
		 $^{2}J_{HF} = 75.1$

$^{2}J_{FH}$ Coupling



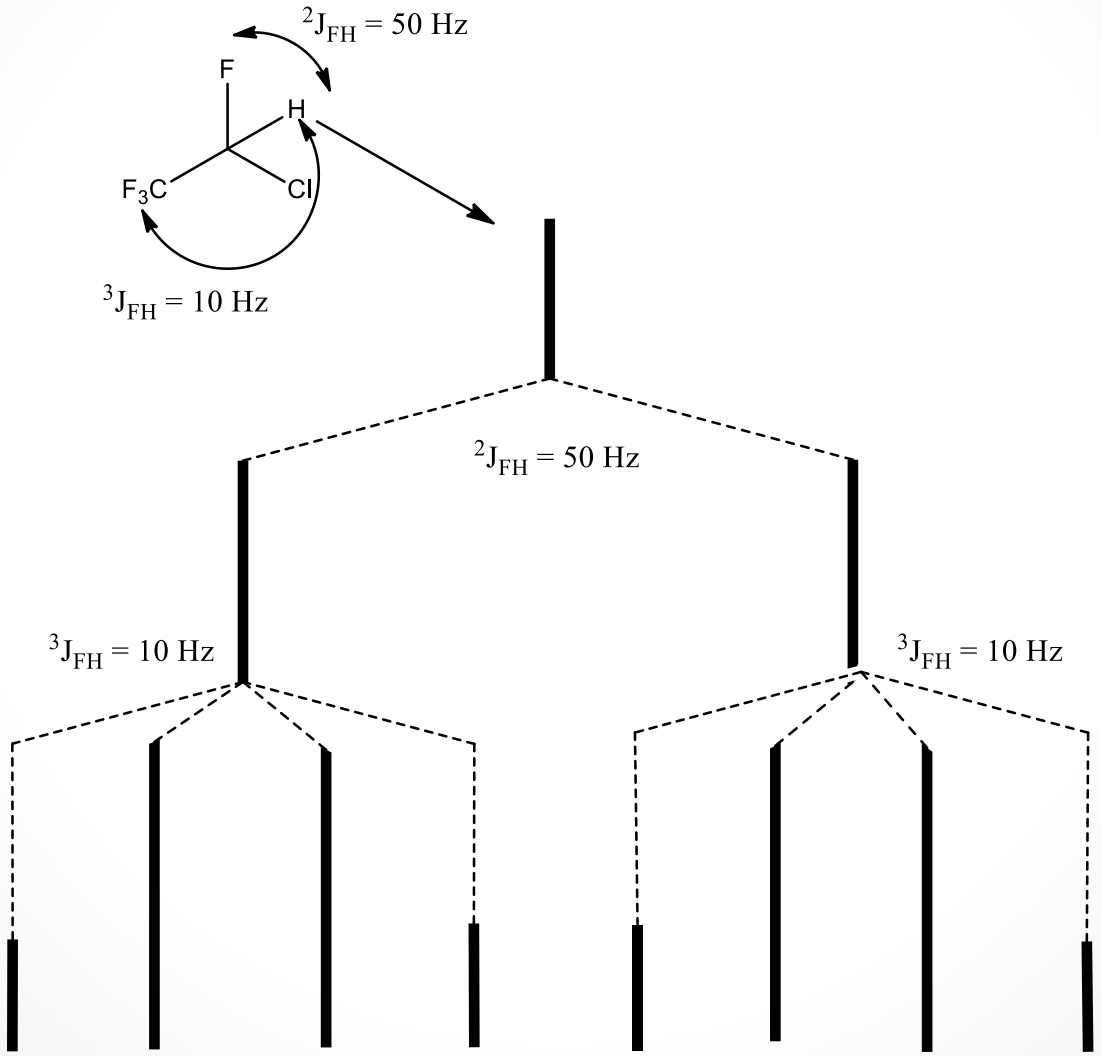
^{1}H Spectrum of difluoromethane

$^3J_{FH}$ Coupling

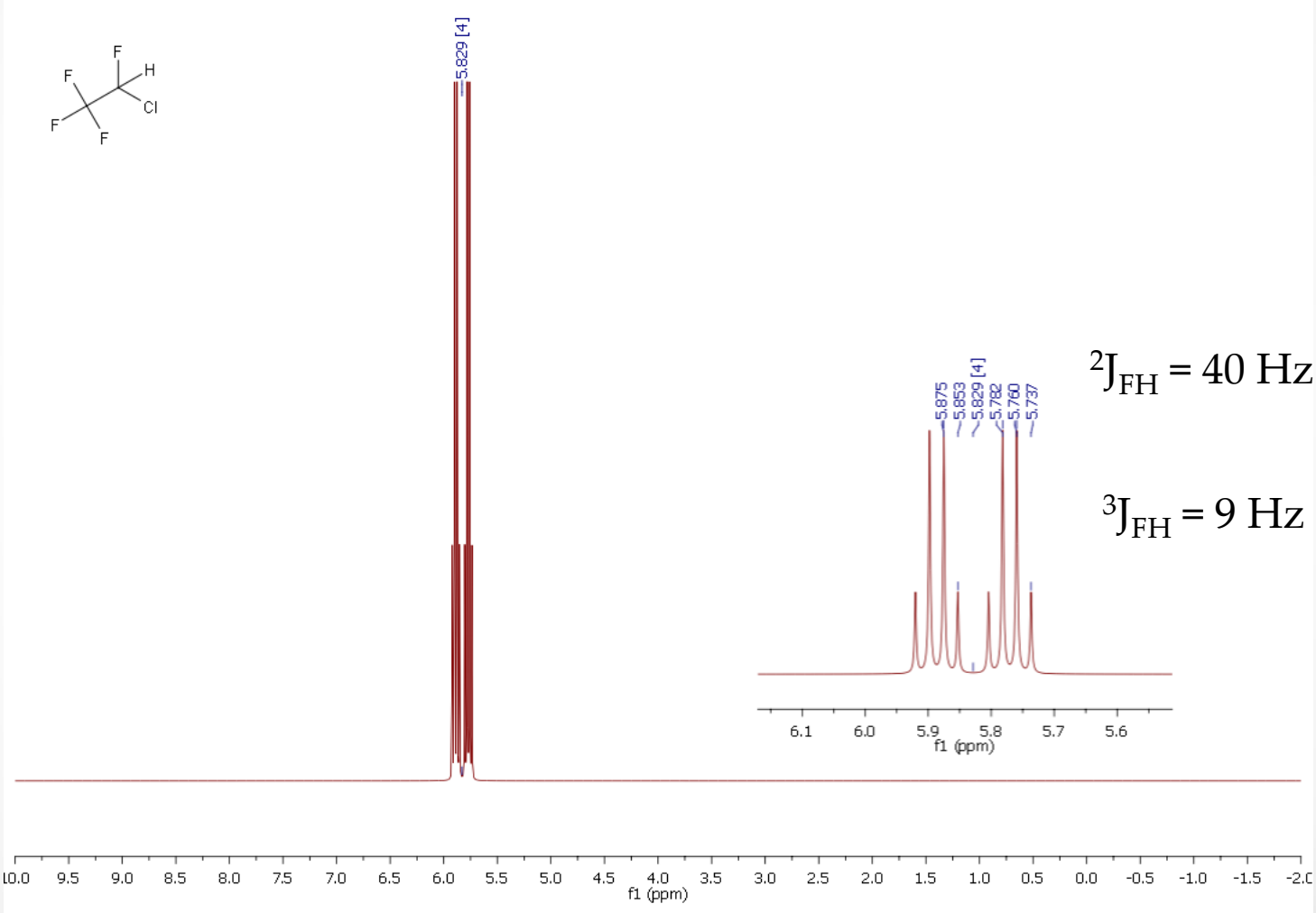


^{1}H Spectrum of 1,1,1-trifluoro-2-iodoethane

Spin system of CF_3CHFCl



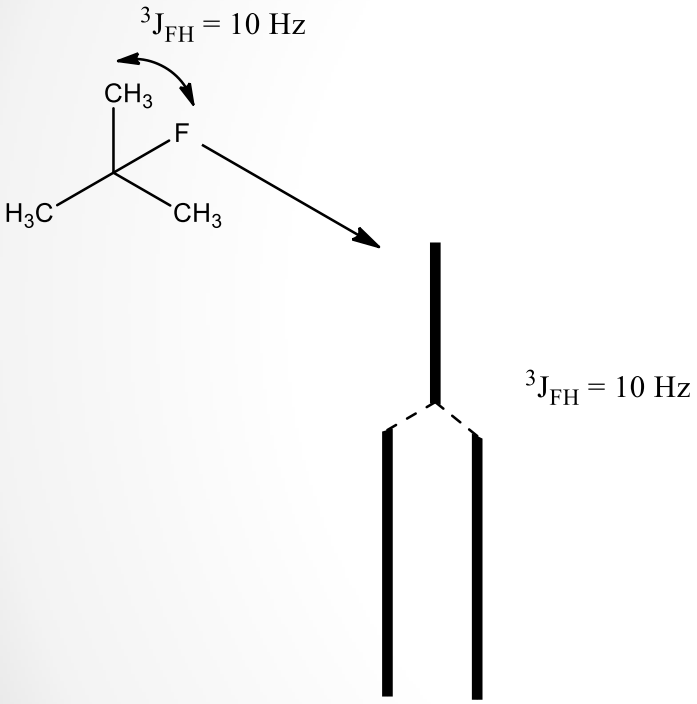
^{1}H Spectrum of CF_3CHFCl



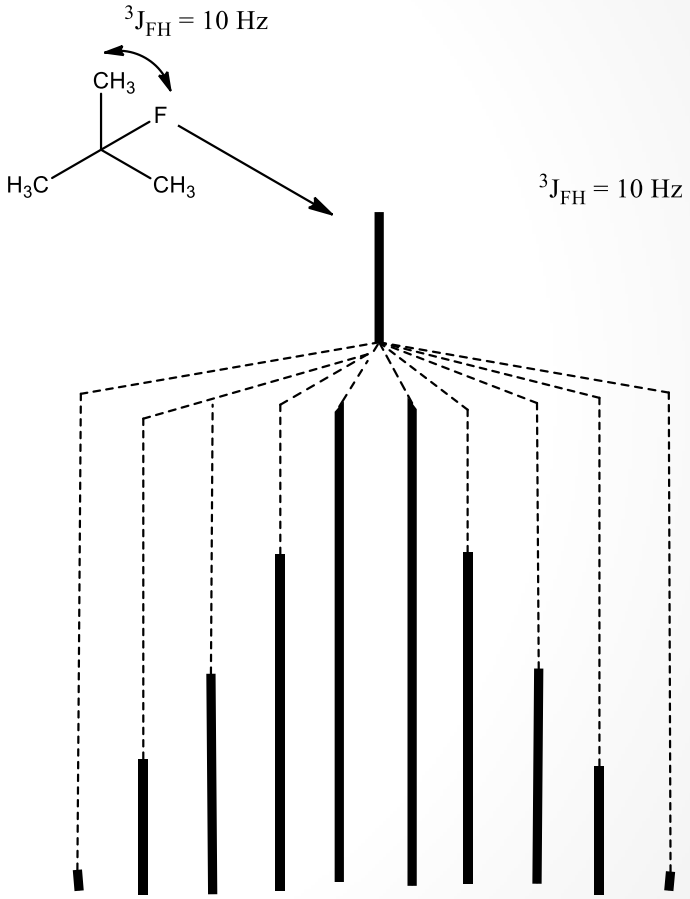
$^{2}J_{FH} = 40$ Hz

$^{3}J_{FH} = 9$ Hz

^{1}H and ^{19}F Spectra prediction for $(CH_3)_3CF$

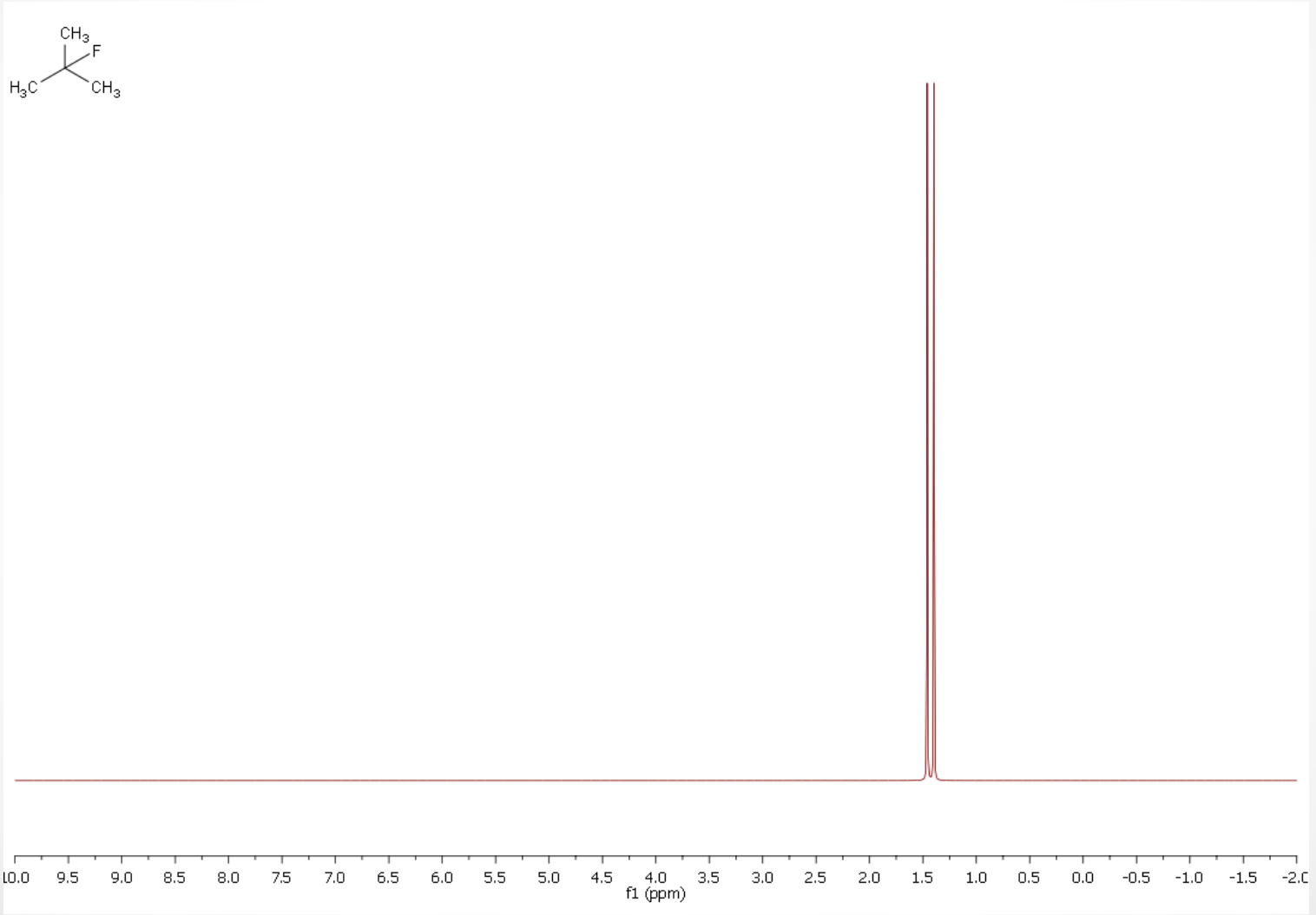


^{1}H Spectrum

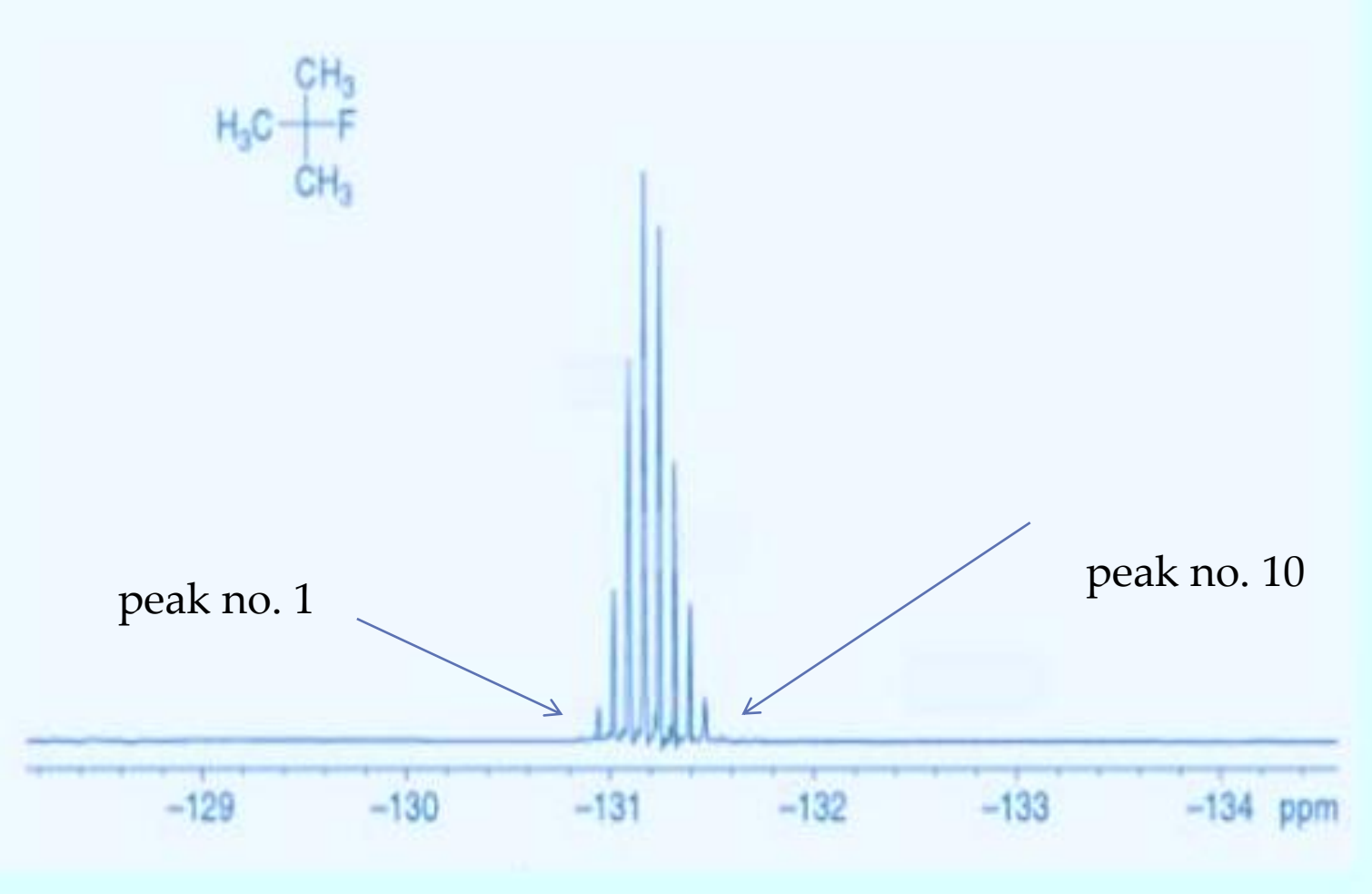


^{19}F Spectrum

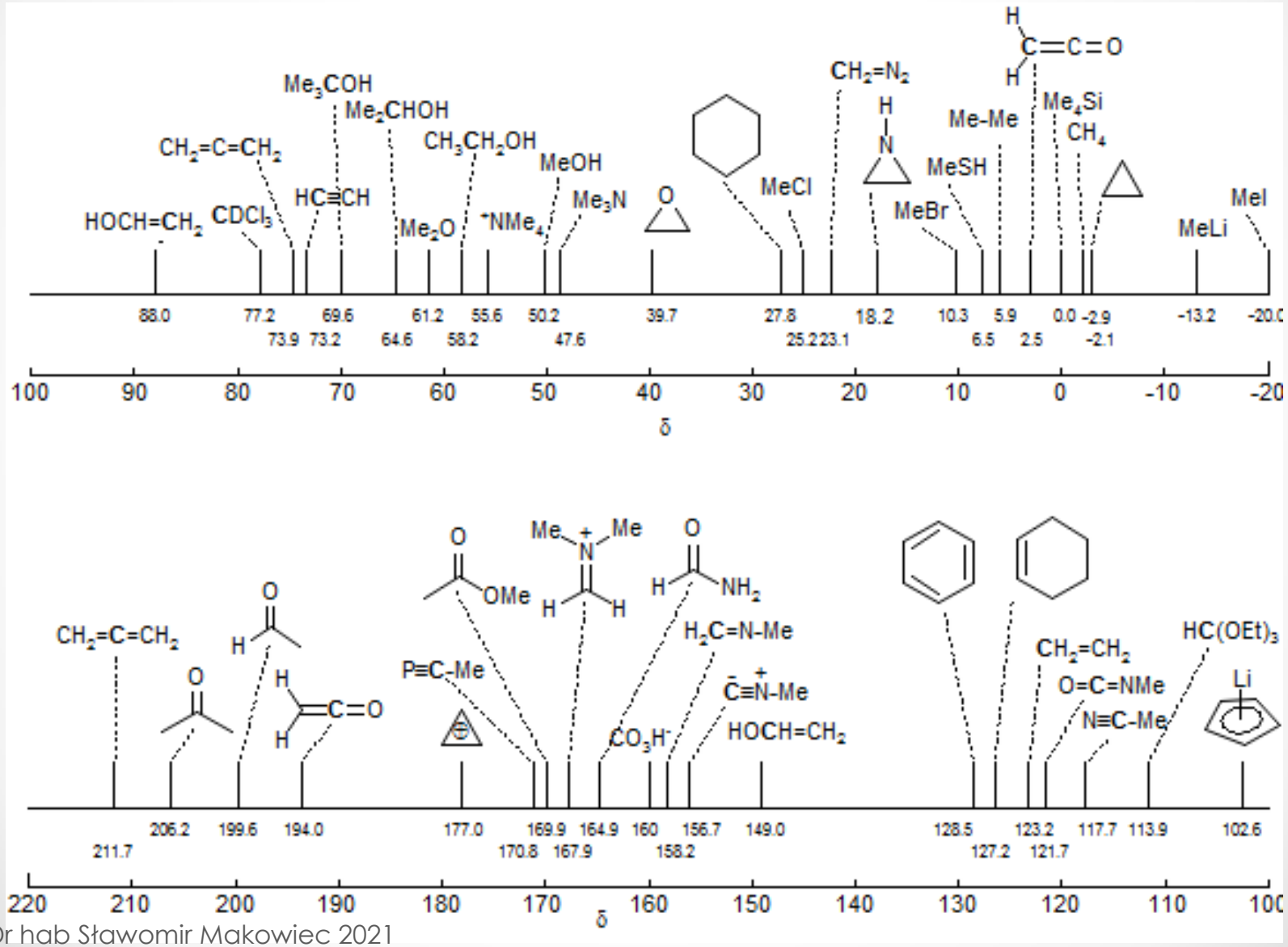
$(CH_3)_3CF$ ^1H Spectrum



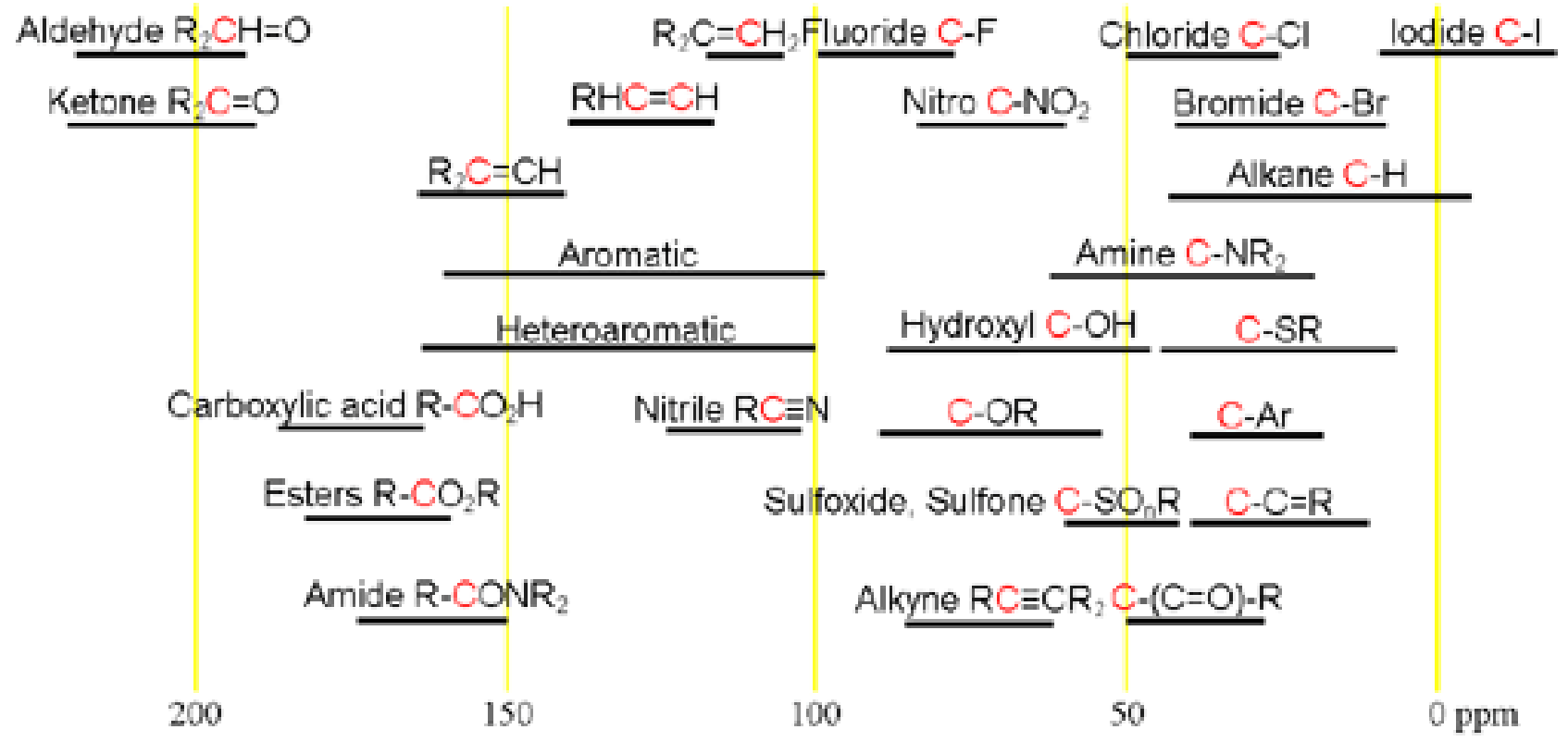
$(CH_3)_3CF$ ^{19}F Spectrum



^{13}C NMR


HOCH=CH2
CDCl3
CH2=C=CH2
HC≡CH
Me3COH
Me2CHOH
CH3CH2OH
Me2O
+NMe4
MeOH
Me3N
O
MeCl
CH2=N2
H
N
MeBr
MeSH
Me-Me
H
C=C=O
H
Me4Si
CH4
MeLi
MeI
88.0
77.2
73.9
73.2
69.6
64.6
61.2
58.2
55.6
50.2
47.6
39.7
27.8
25.2
23.1
18.2
10.3
6.5
5.9
2.5
0.0
-2.1
-2.9
-13.2
-20.0
100
90
80
70
60
50
40
30
20
10
0
-10
-20
δ
CH2=C=CH2
O
H
O
H
H
C=O
H
P≡C-Me
O
OMe
Me
+
N
Me
H
H
O
H
NH2
H2C=N-Me
C≡N-Me
CO3H-
HOCH=CH2
CH2=CH2
O=C=NMe
N≡C-Me
HC(OEt)3
Li
211.7
206.2
199.6
194.0
177.0
170.8
169.9
167.9
164.9
160
158.2
156.7
149.0
128.5
127.2
123.2
121.7
117.7
113.9
102.6
220
210
200
190
180
170
160
150
140
130
120
110
100
δ

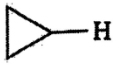
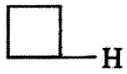
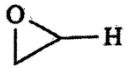
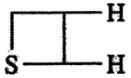
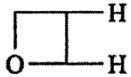
^{13}C NMR chemical shifts



^{13}C NMR – $^{1}J_{CH}$ coupling constants

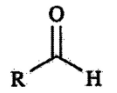
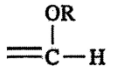
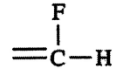
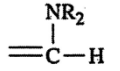
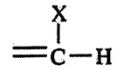
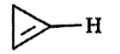
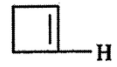
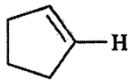
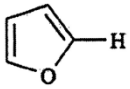
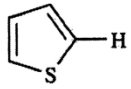
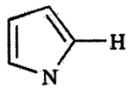
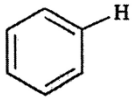
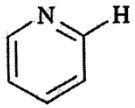
sp³ carbons

^{1}H-^{13}C

Type	*J* (Hz)	Type	*J* (Hz)
CH_3-H	125	CH_3Li	98
Ph-CH_2-H	129	Cl_2CH-H	178
RC≡C-CH_2-H	132	O_2N-CH_2-H	147
R_2NCH_2-H	133	FCH_3-H	149
$RSCH_2$-H	138	$ClCH_2$-H	150
$ROCH_2$-H	140	ICH_2-H	151
$(NC)_2CH$-H	145	$BrCH_2$-H	152
	161	$(CH_3O)_2CH$-H	162
	134		180
	137		137
	150		150

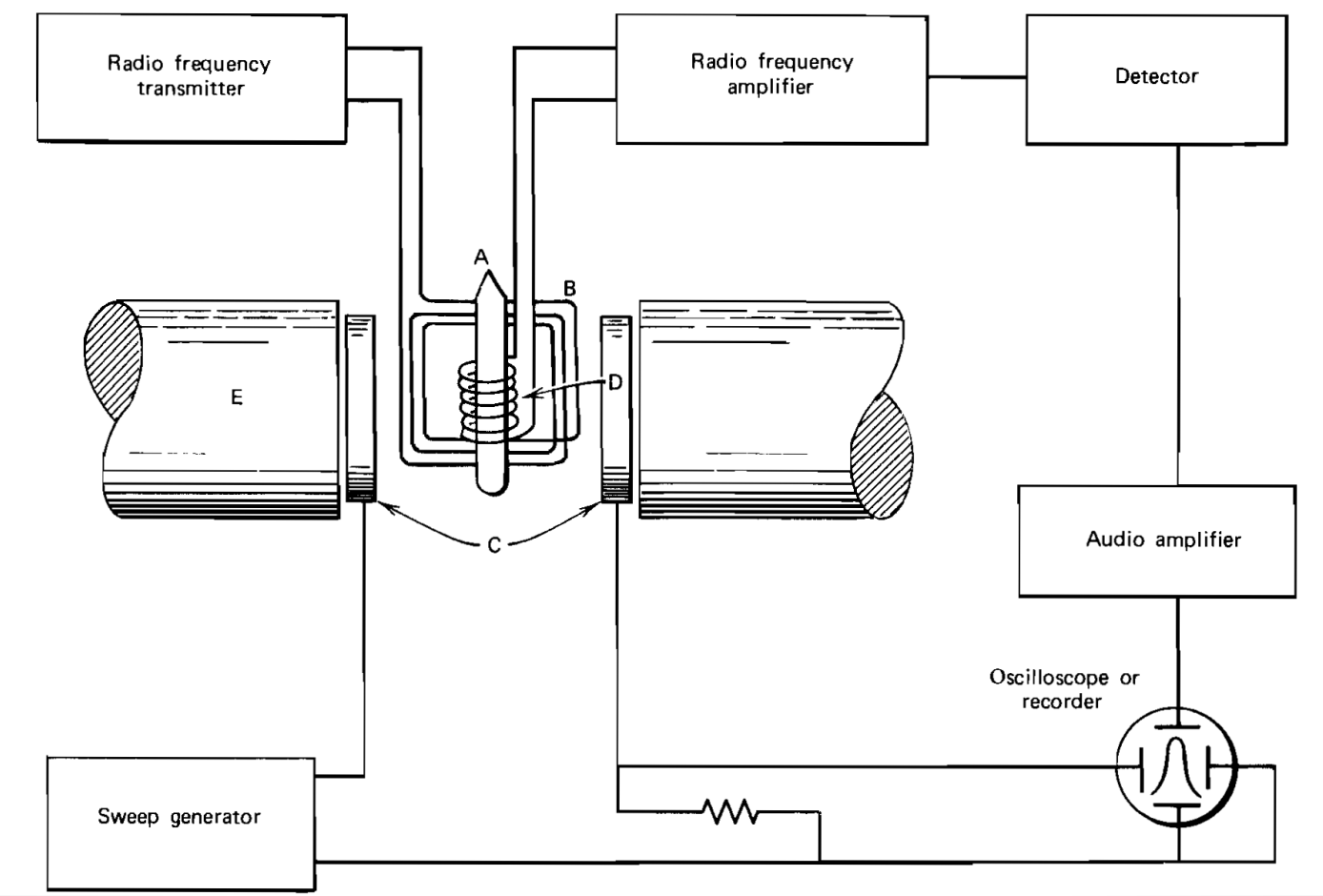
sp² carbons

^{1}H-^{13}C

Type	*J* (Hz)	Type	*J* (Hz)
=C-H	157	C=C=C-H	168
	172		195
	200		195
 X=Halogen	~198		238
	170		160
	202		189
	182		159
	178		

$^{1}J_{CH} \approx 125$ -180 Hz $^{2}J_{CH} \approx 5$ -10 Hz $^{3}J_{CH} \approx 0$ -1 Hz

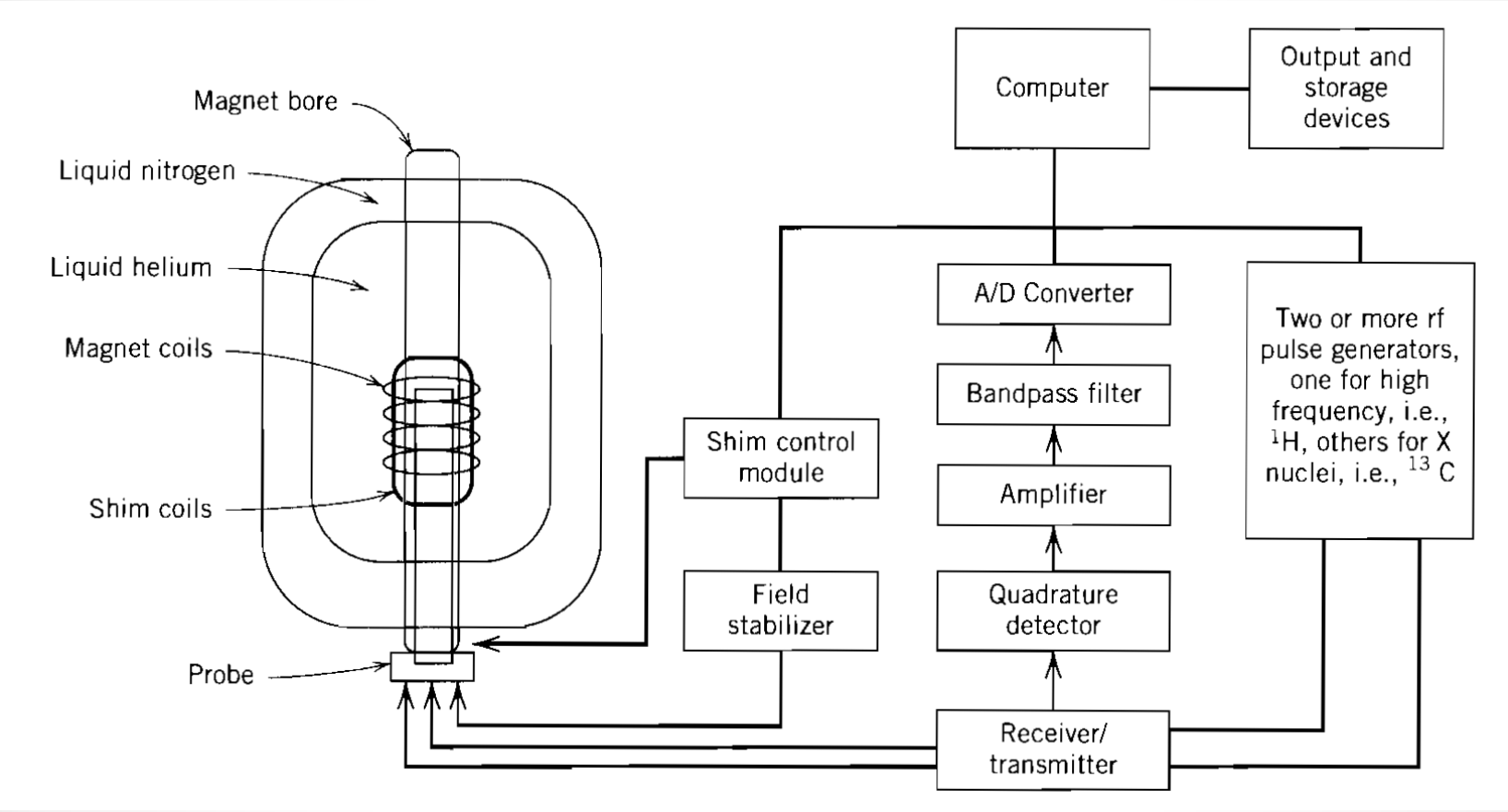
Continuous Wave ver. Fourier Transformation



Schematic diagram of CW NMR spectrometer:

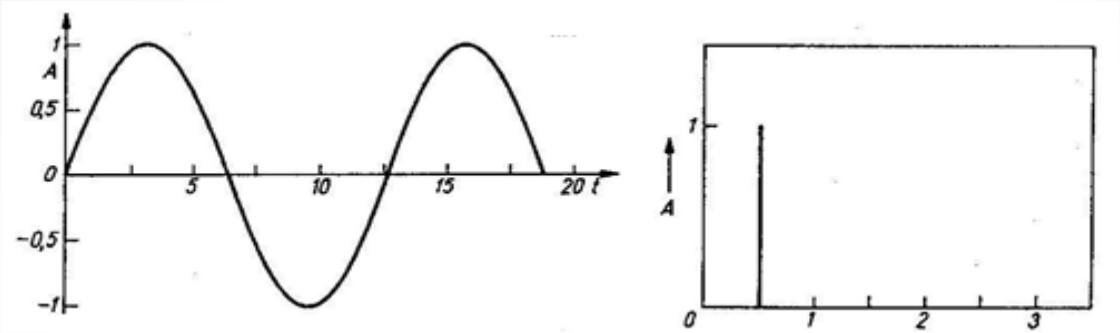
A: Sample (Tube is perpendicular to the *z* axis of the magnet), B: Transmitter coil, C: Sweep coils, D: Receiver coil, E: Magnet

Fourier Transformation Spectrometer

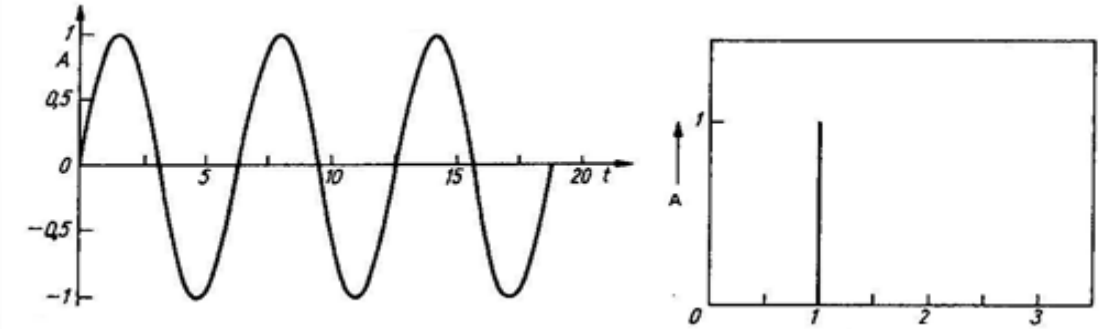


Schematic diagram of Fourier transformation spectrometer,
Tube with sample is parallel with the *z* axis of the magnet, which is cooled with liquid helium.

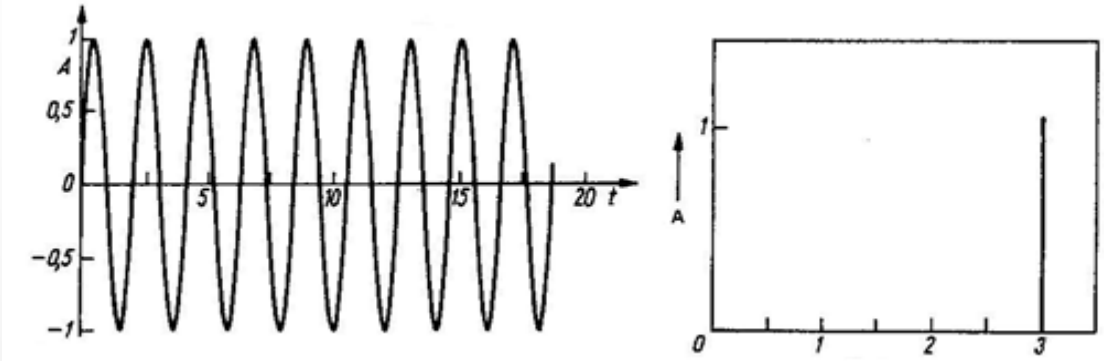
Continuous Wave – Spectra Acquisition



ν^{o}=100 MHz



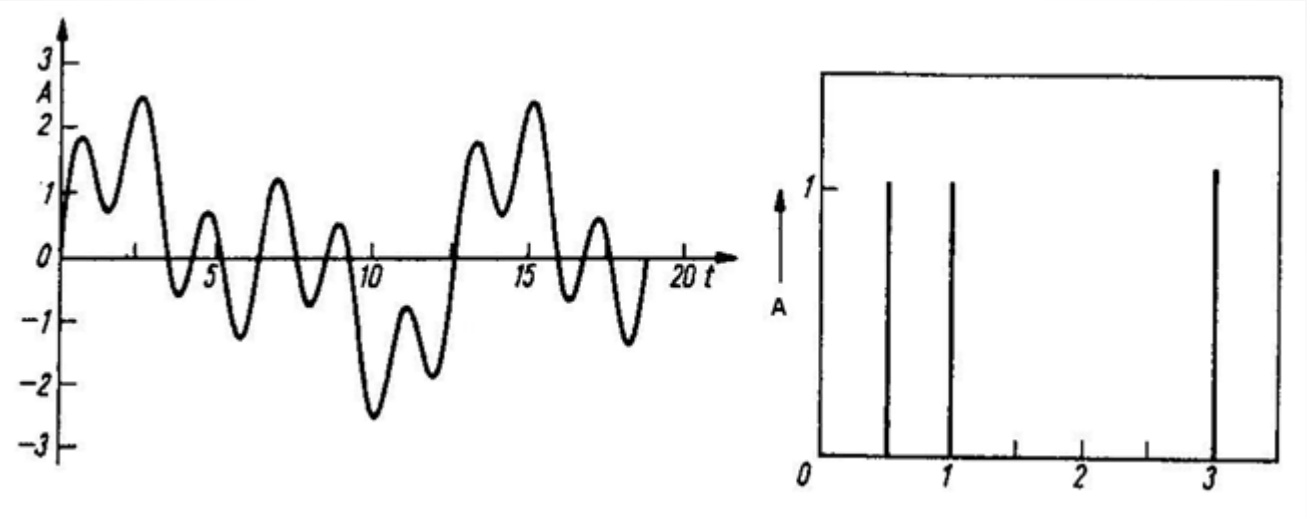
ν=100000050 Hz

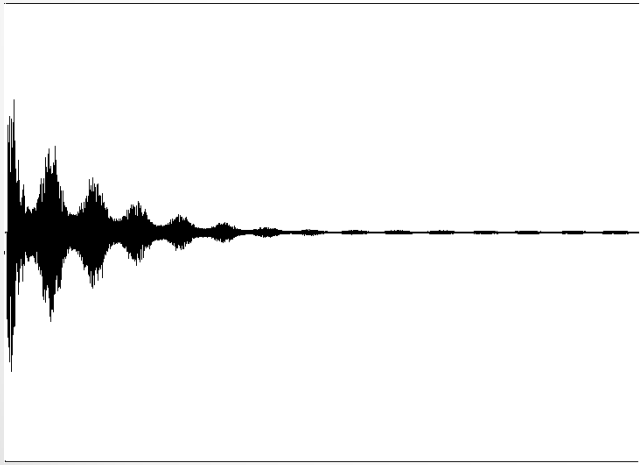


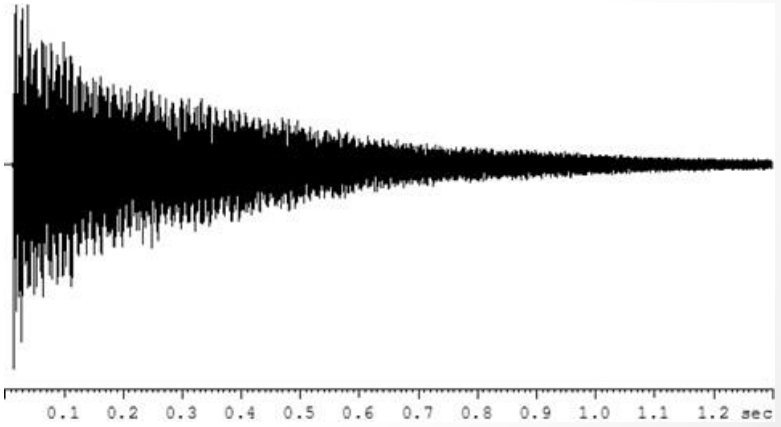
ν=100000100 Hz

ν=100000300 Hz

Fourier Transformation – Spectra Acquisition



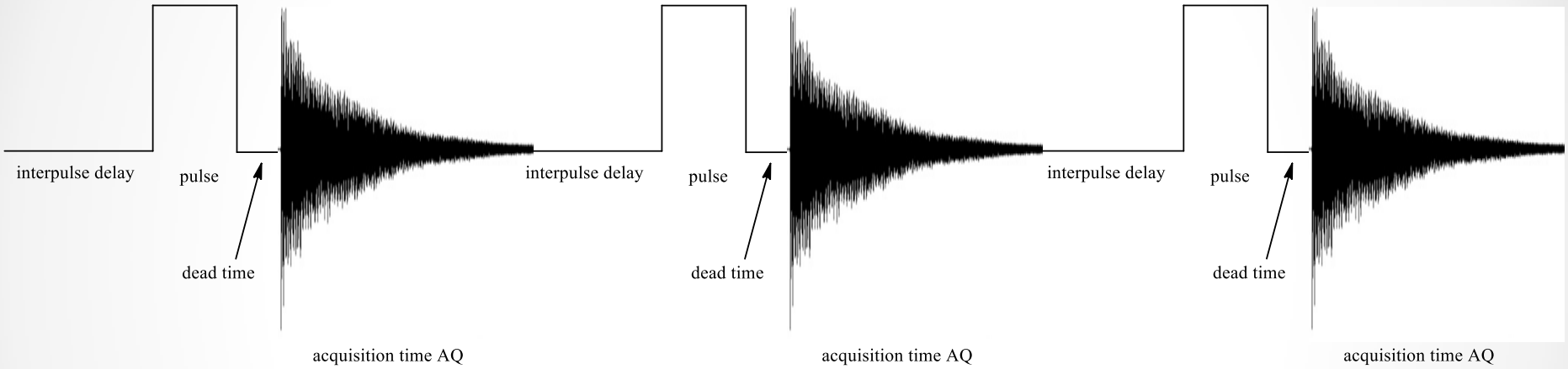




FID Free Induction Decay

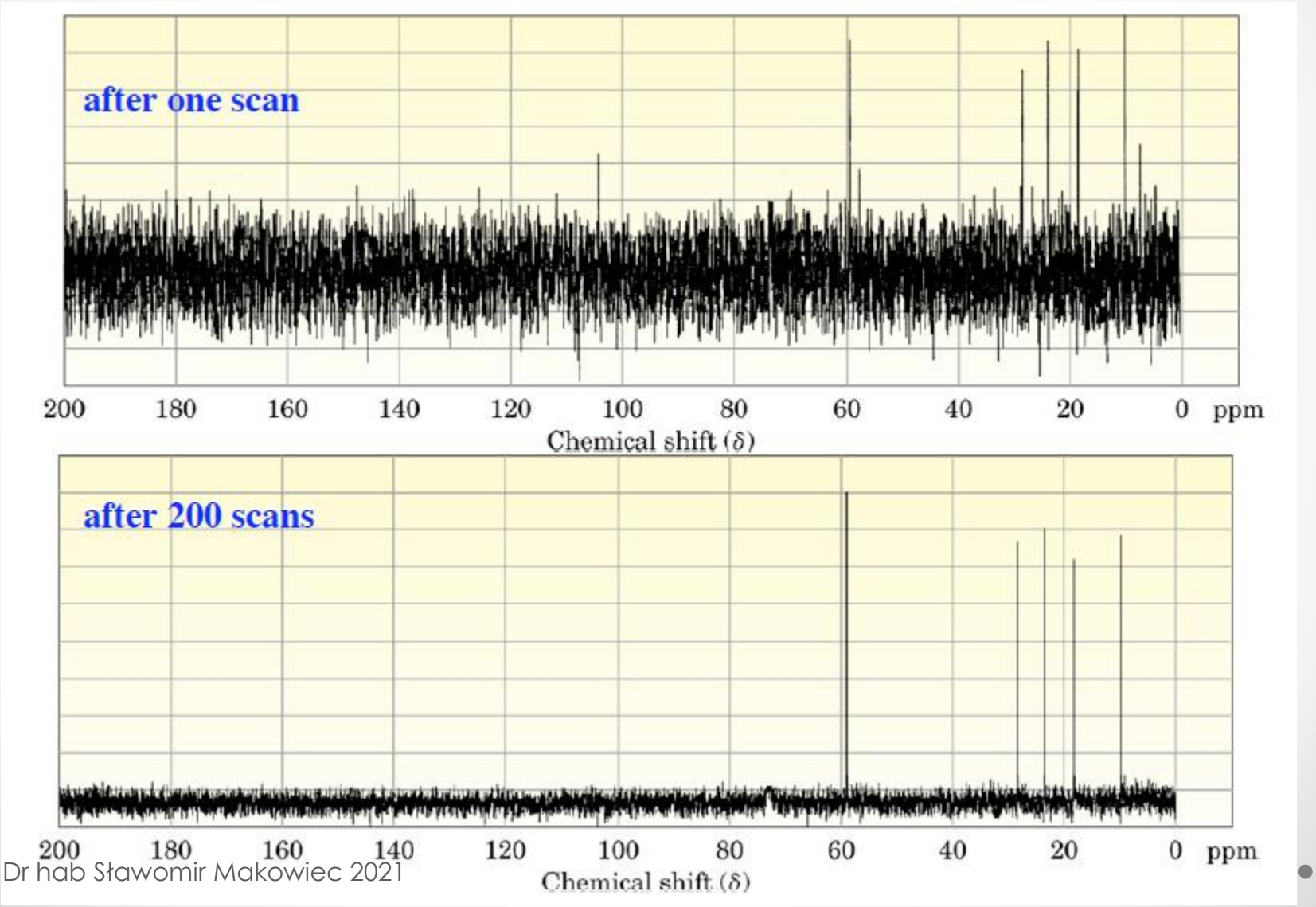
The signal can be seen to decay due to nuclear relaxation processes following the RF excitation

Fourier Transformation – Spectra Acquisition

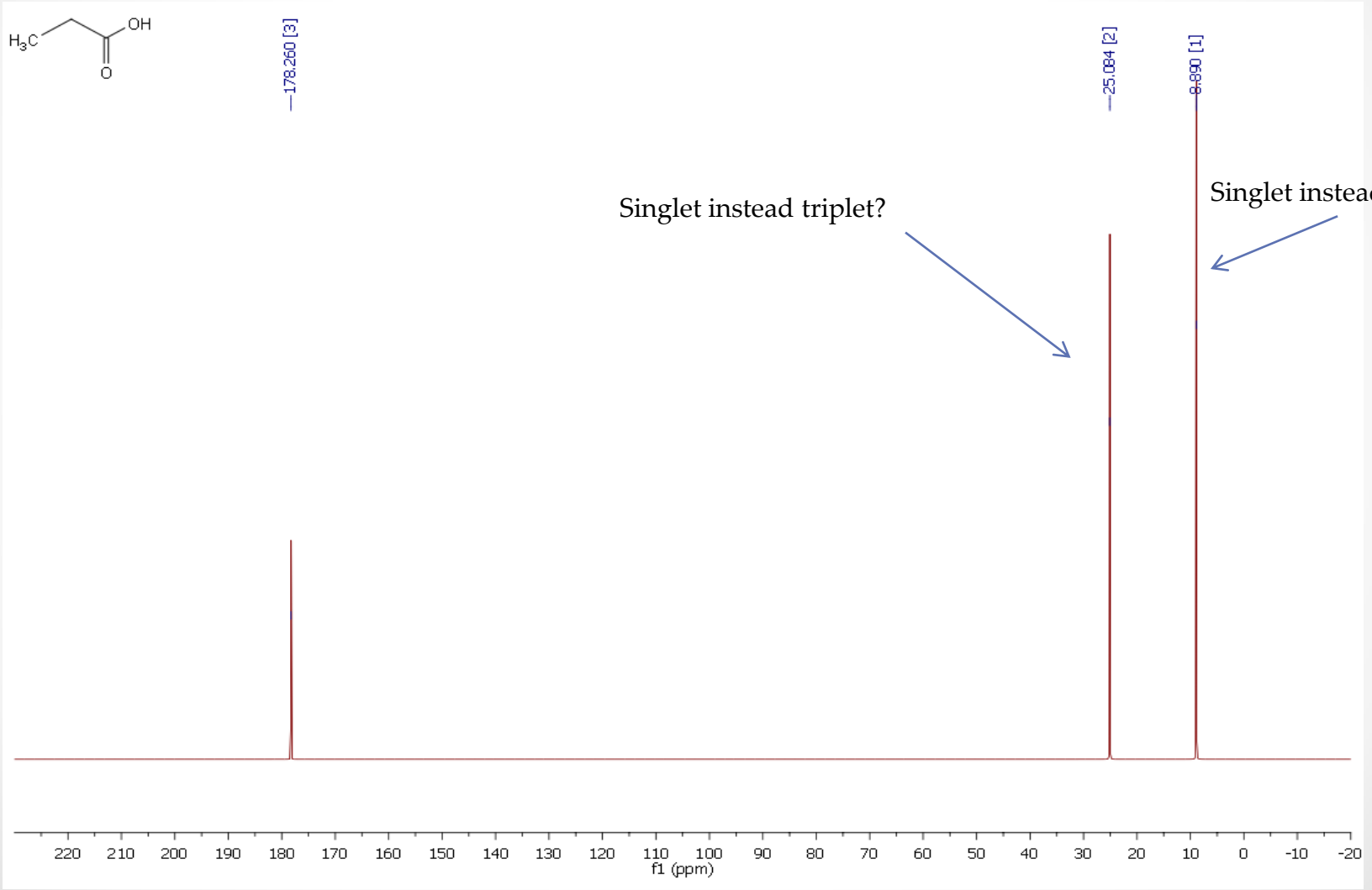


$$\frac{Signal}{Noise} = \sqrt{Number\ of\ acquisitions}$$

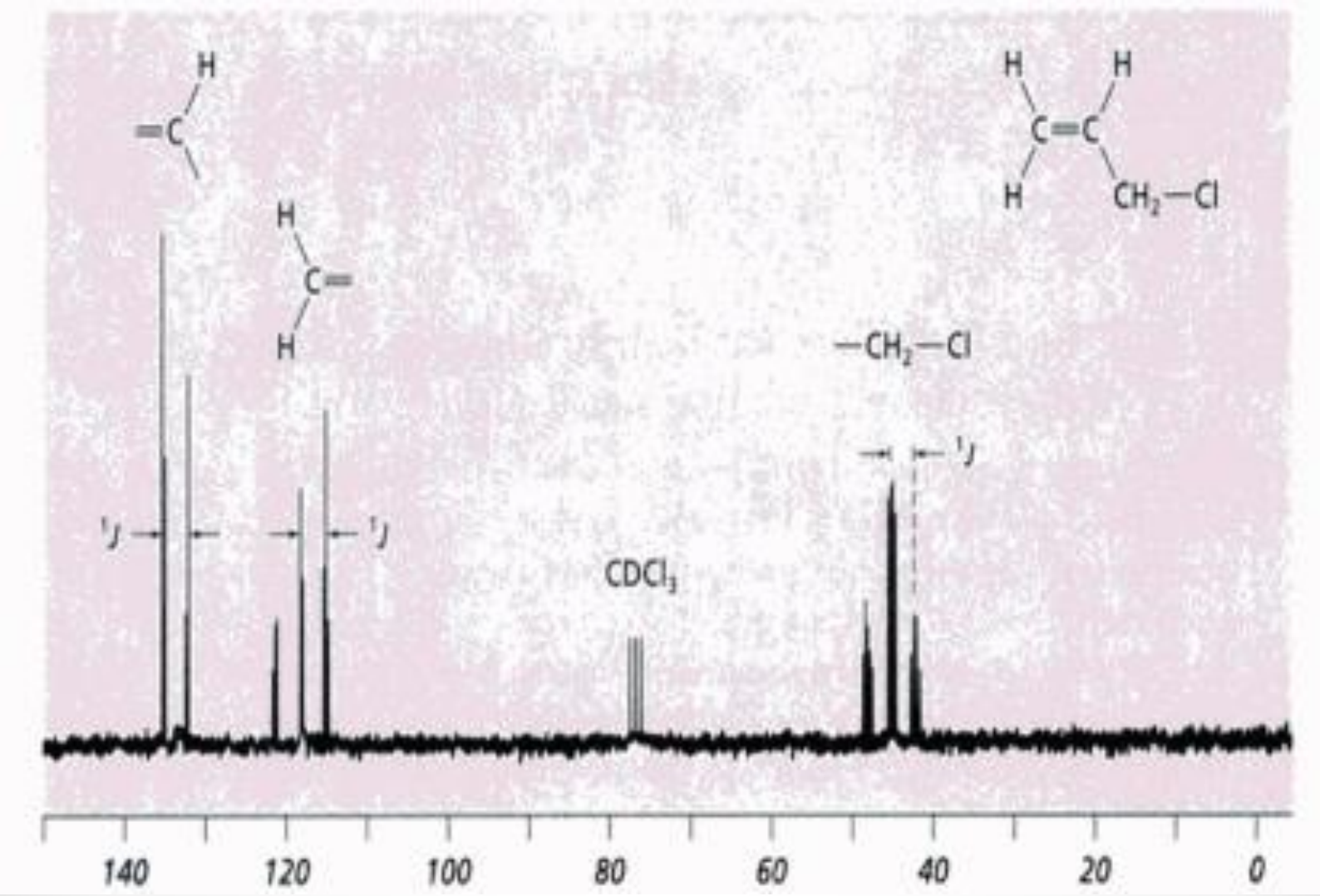
^{13}C NMR spectra of $CH_3CH_2CH_2CH_2CH_2OH$



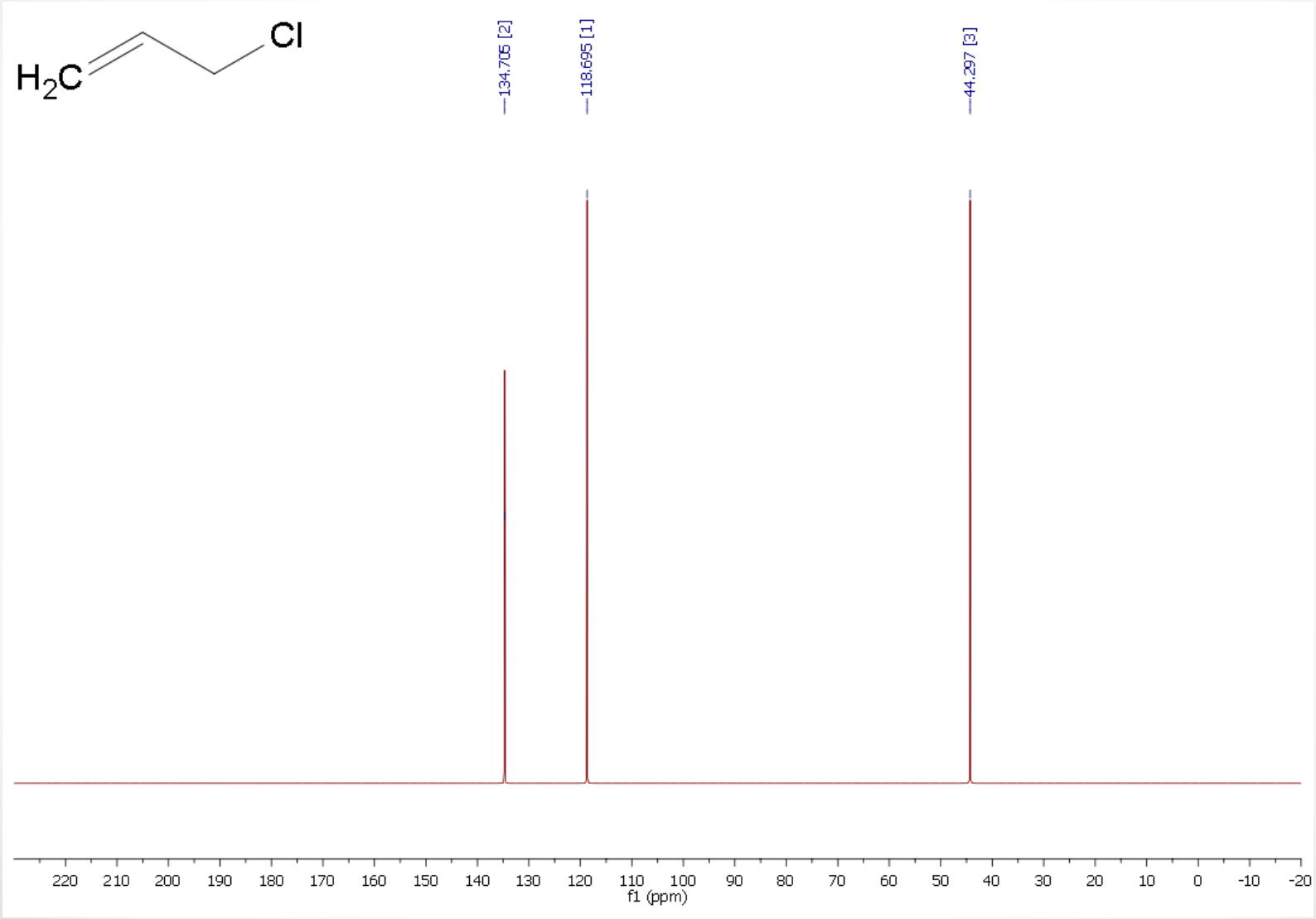
Propionic acid 13 C spectra (100MHz)



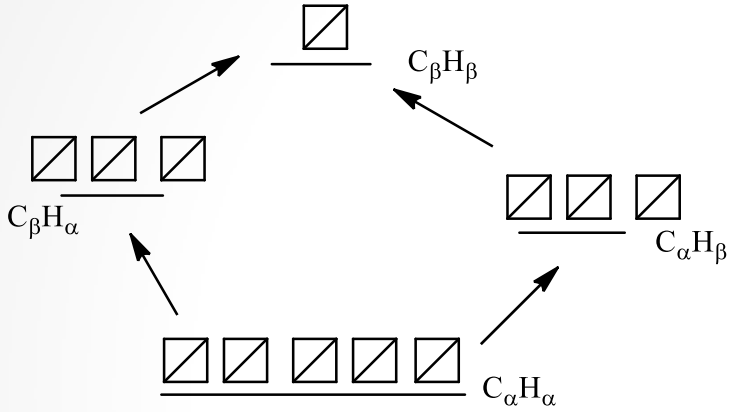
^{13}C spectrum of allyl chloride (75MHz)

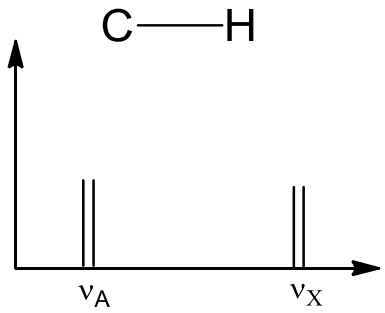


Broad band decoupling

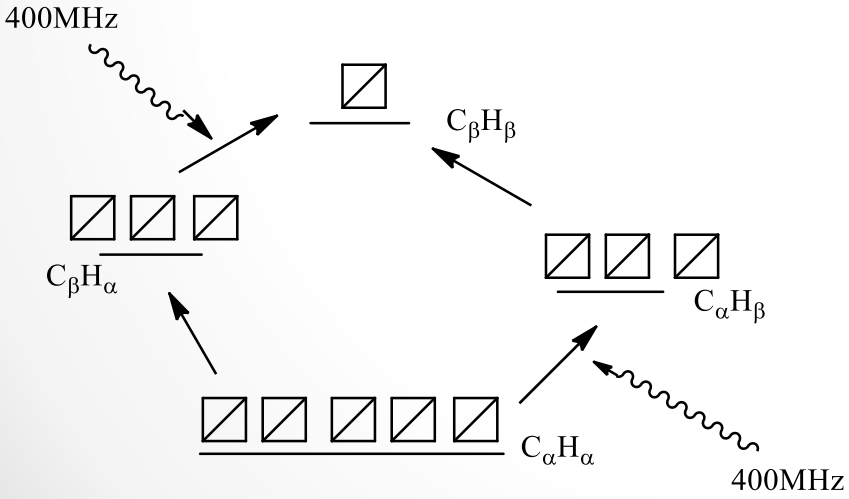


Nuclear Overhauser Effect



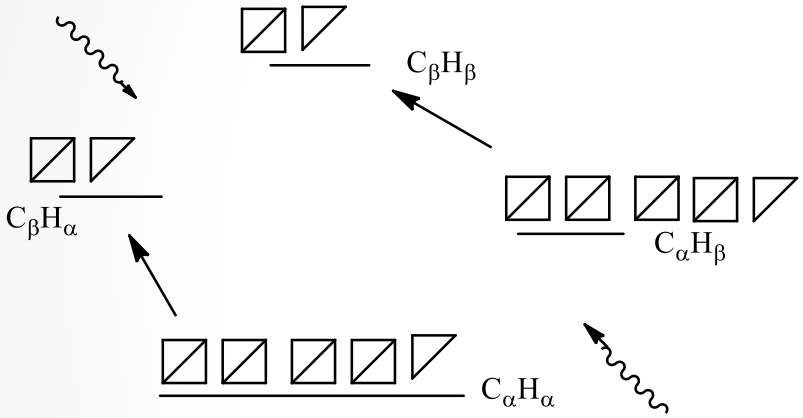


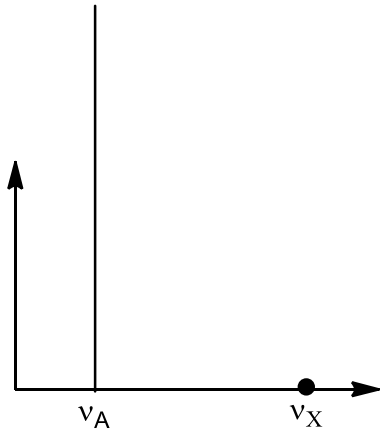
undisturbed system



Irradiation of protons

Nuclear Overhauser Effect

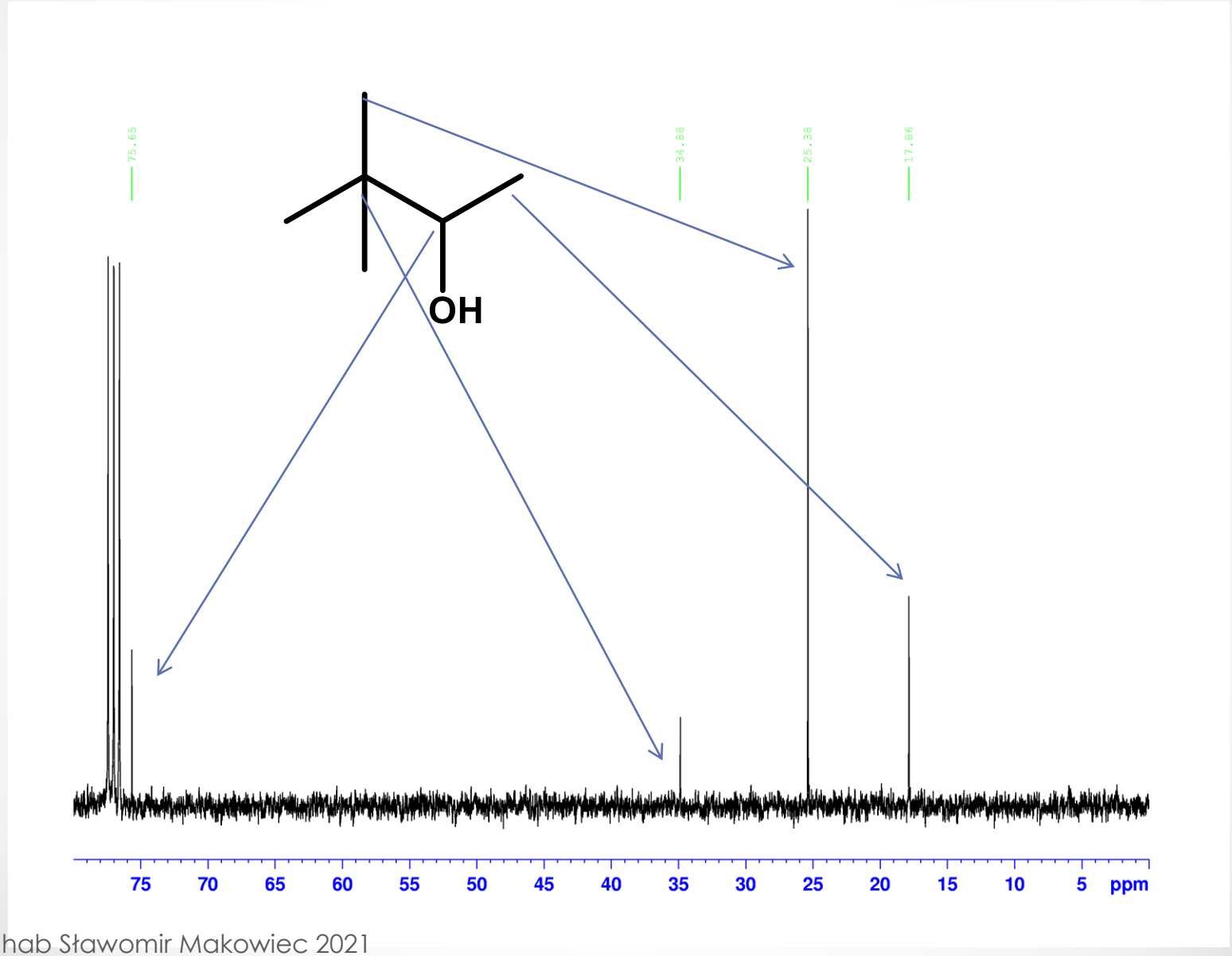




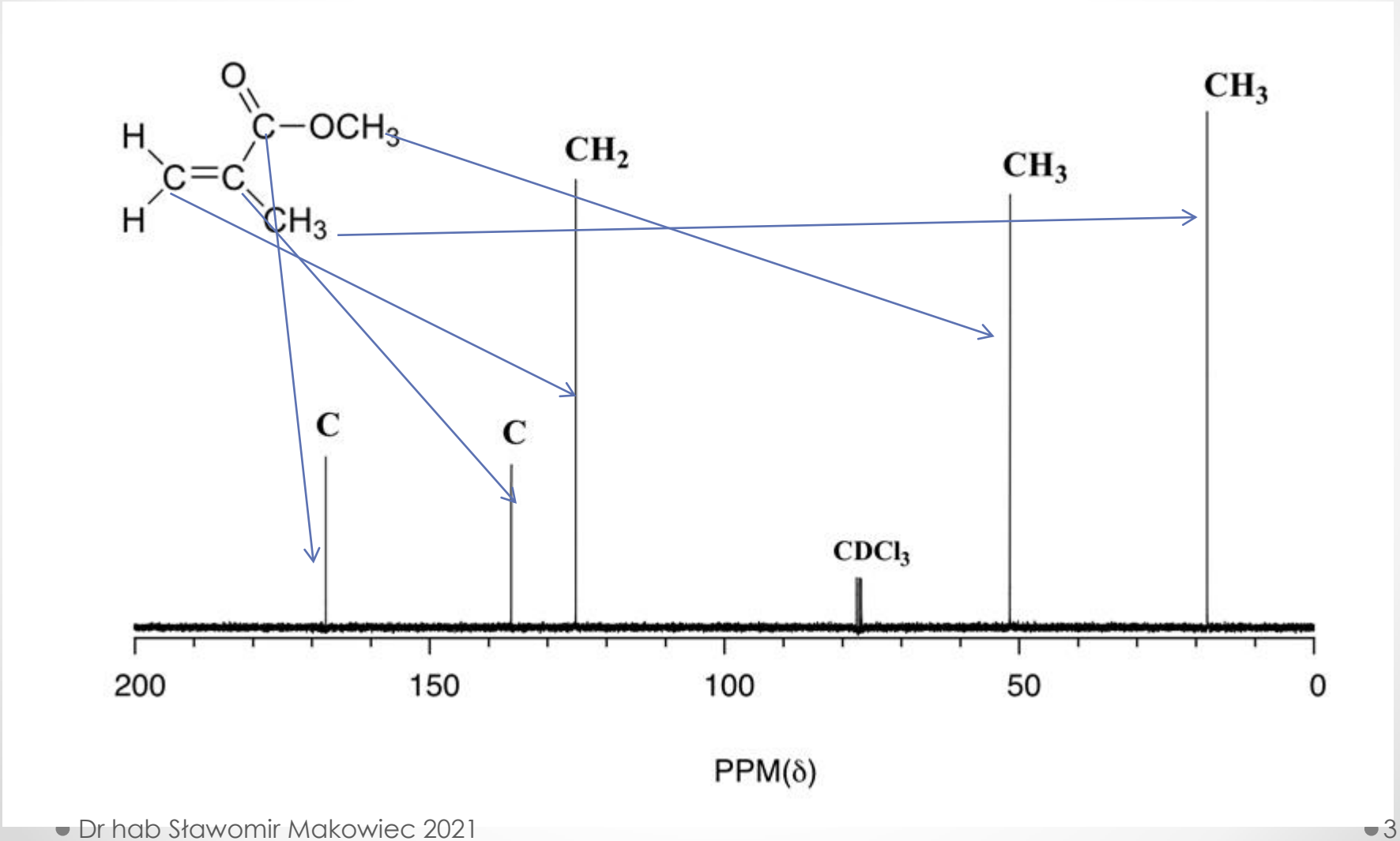
Saturated protons

NOE = 0 for quaternary carbon atoms,
-CN, -COOH, -COOR, -C(O)R, R_4C

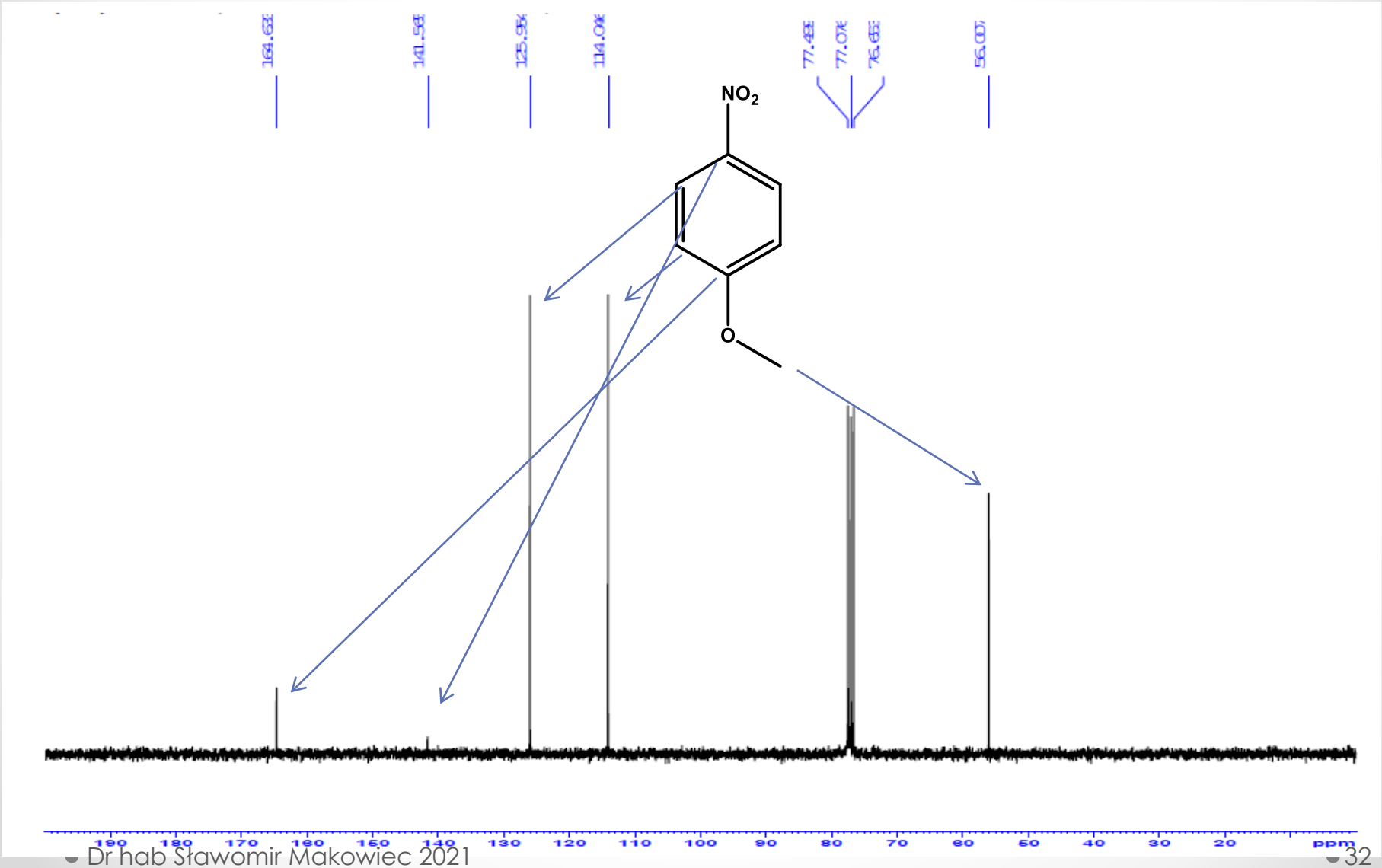
^{13}C-NMR spectrum of 3,3-dimethyl-2-butanol



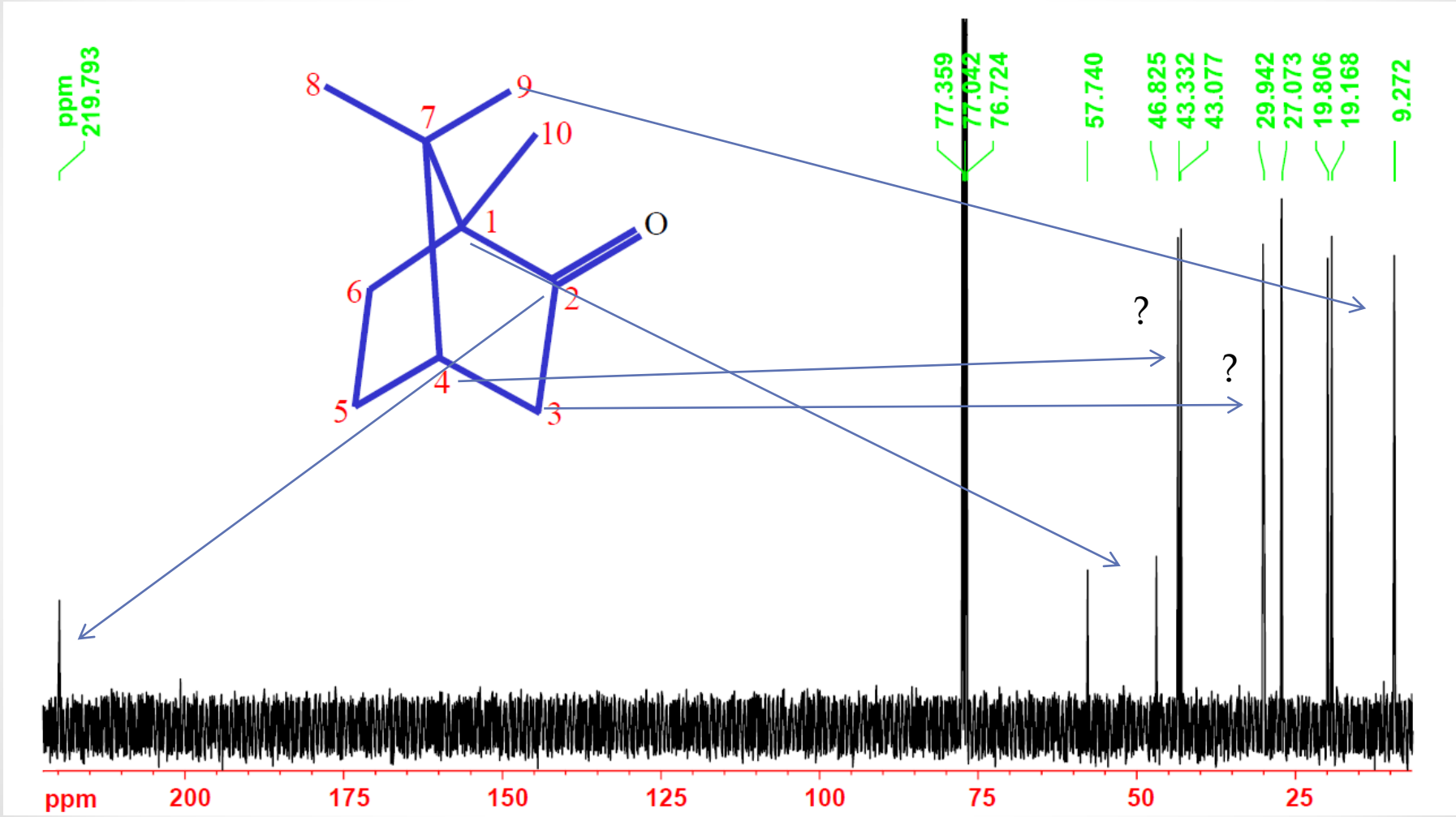
^{13}C-NMR methyl methacrylate



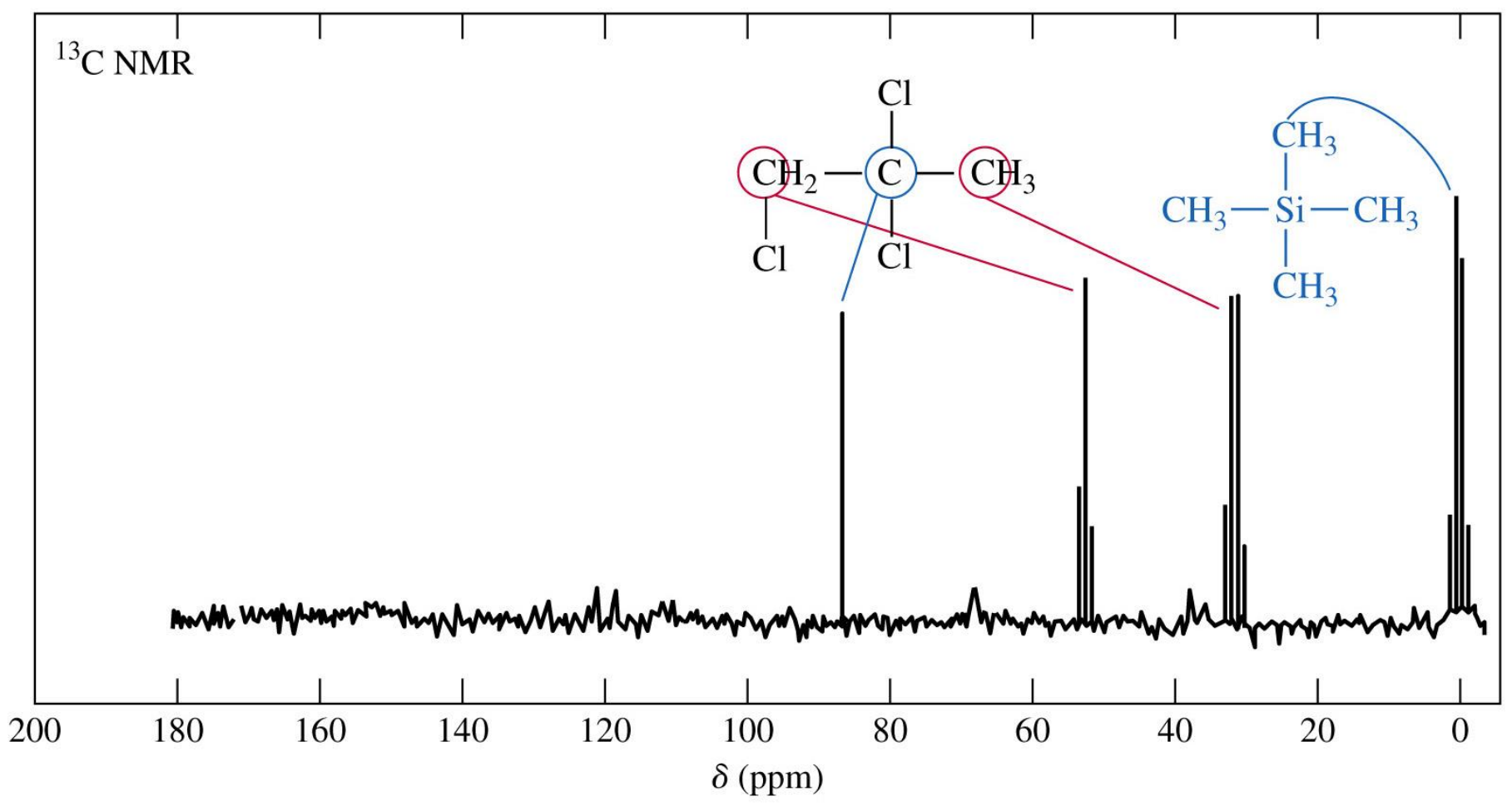
^{13}C-NMR 4-nitroanisole



^{13}C-NMR camphor

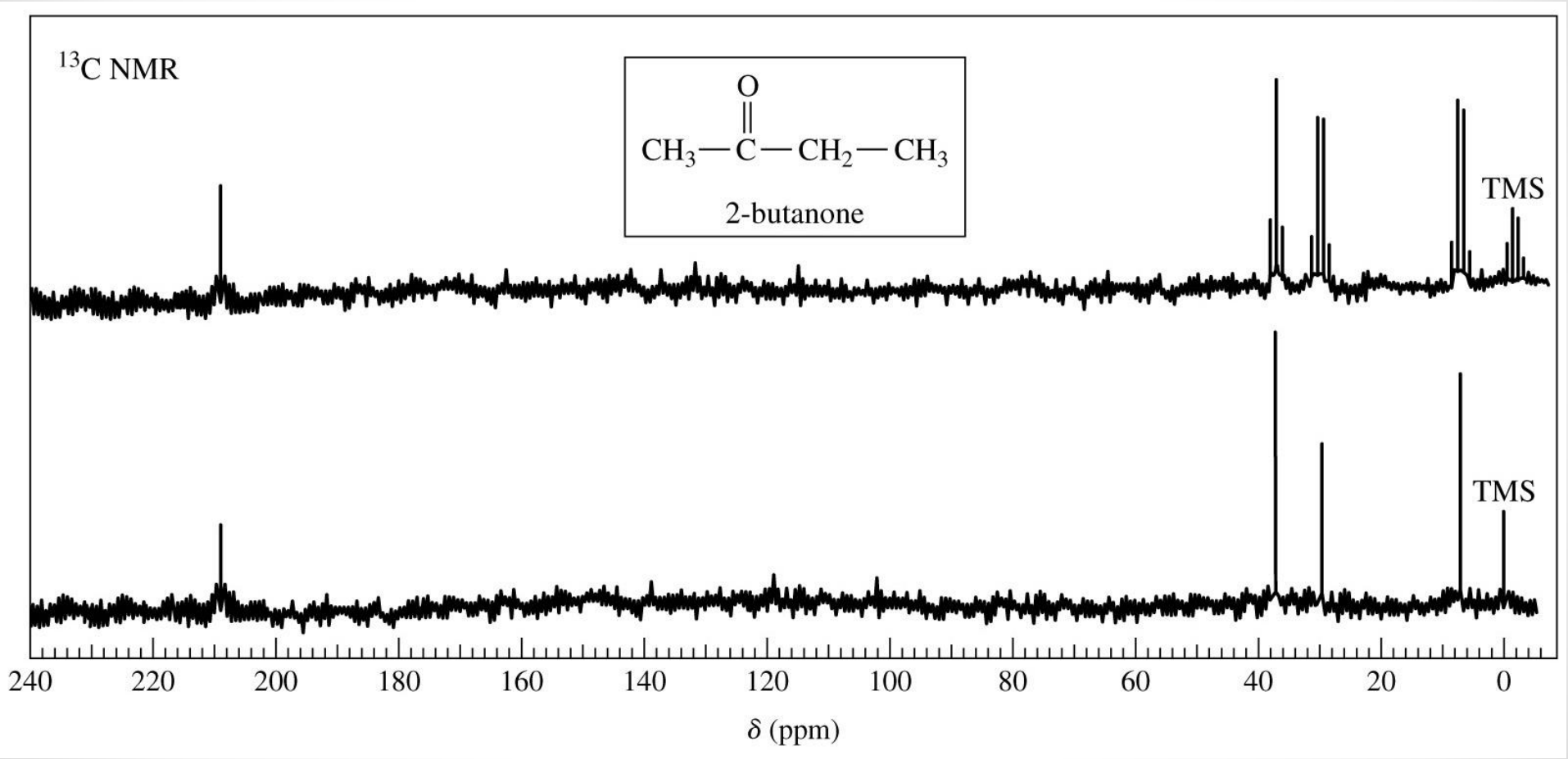


Off-resonance decoupling of ^{1}H from ^{13}C nuclei

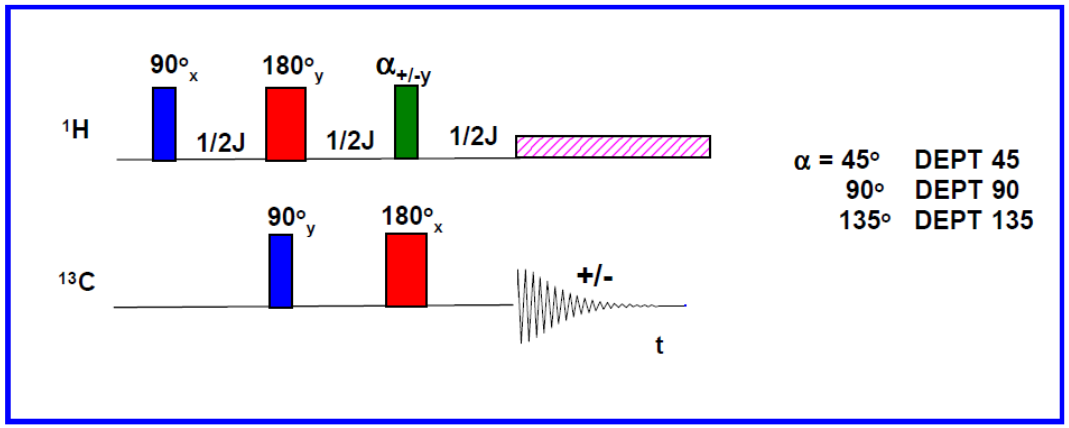


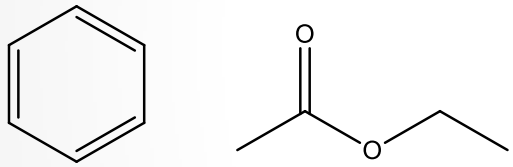
(partial decoupling, only $^{1}J_{CH}$ coupling are observed)

Off-resonance decoupling

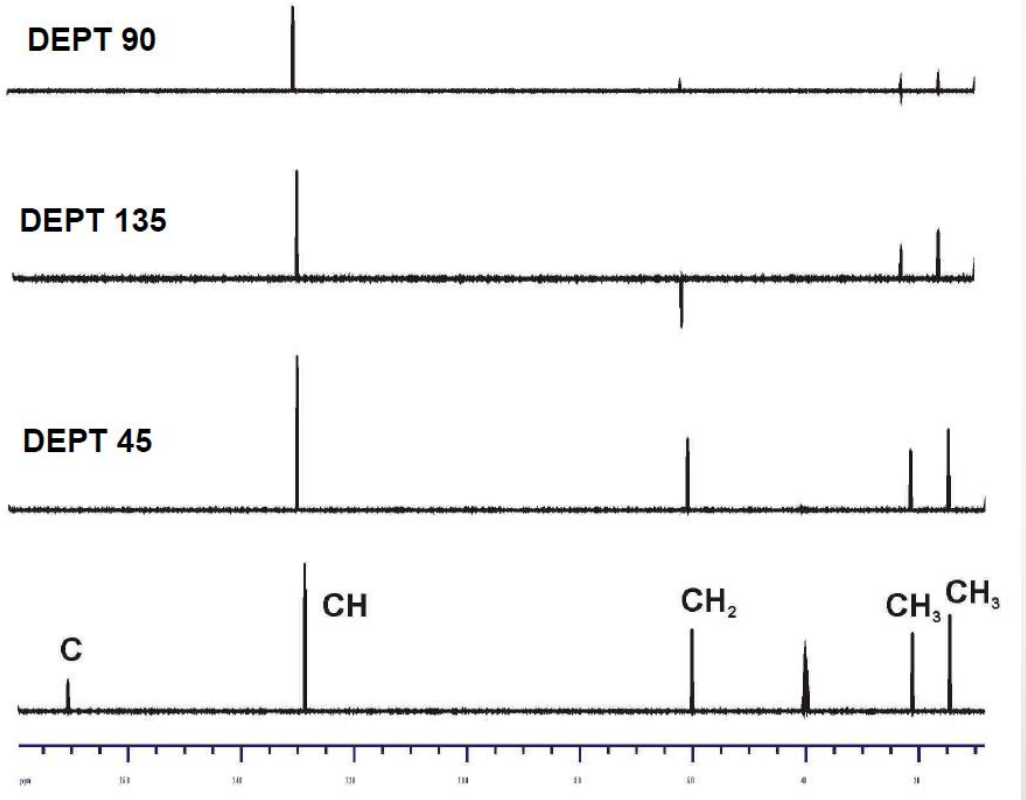


DEPT - *Distortionless Enhancement of Polarisation Transfer*





mixture of two compounds

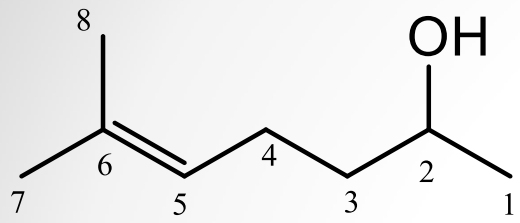


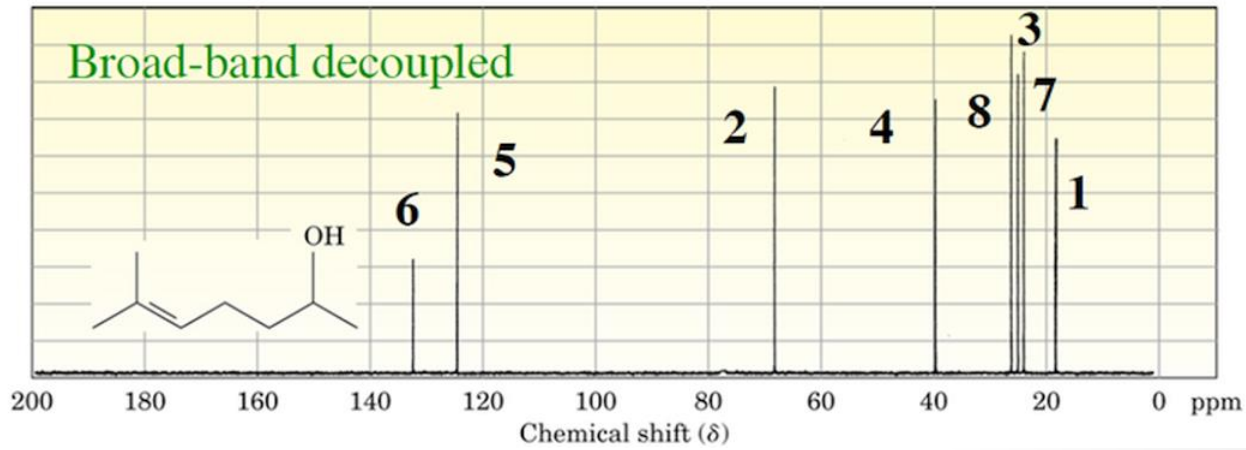
45° gives all carbons with attached protons (regardless of number) in phase

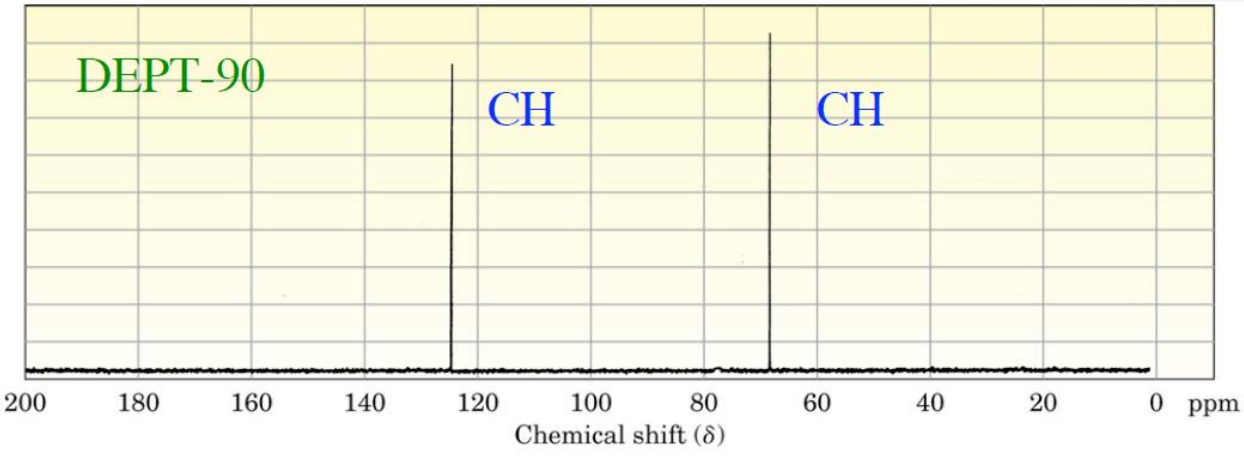
135° gives all CH and CH_3 in phase, opposite to CH_2;

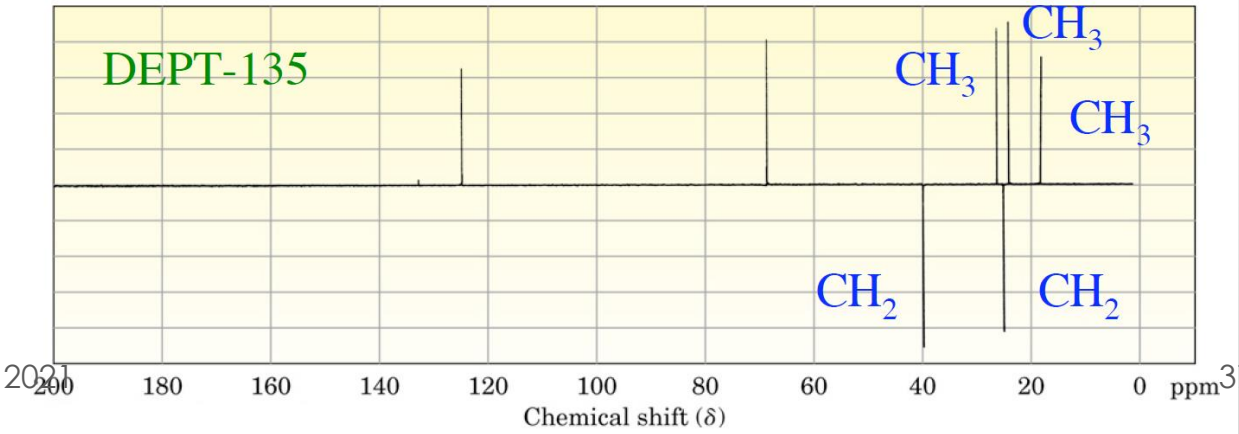
90° angle gives only CH groups, the others being suppressed;

DEPT


8
OH
6
4
2
7
5
3
1


Broad-band decoupled
OH
6
5
2
4
8
3
7
1
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)


DEPT-90
CH
CH
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)


DEPT-135
CH3
CH3
CH3
CH2
CH2
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)

^{13}C-NMR spectrum of camphor + DEPT