Wykład 2

Efekt NOE

Jądrowy efekt Overhausera

(NOE - NUCLEAR OVERHAUSER EFFECT)

zmiana natężenia sygnału NMR jądra A na skutek naświetlania oddziałującego z nim dipolowo spinu X

η, a τ_c

$\eta \sim r^{-6}$

współczynnik wzmocnienia NOE: $\eta_A = (I_A - I_A^0)/I_A^0$

I_A i I_A^0 – intensywność sygnału rezonansowego jader A, w obecności naświetlania i bez naświetlania

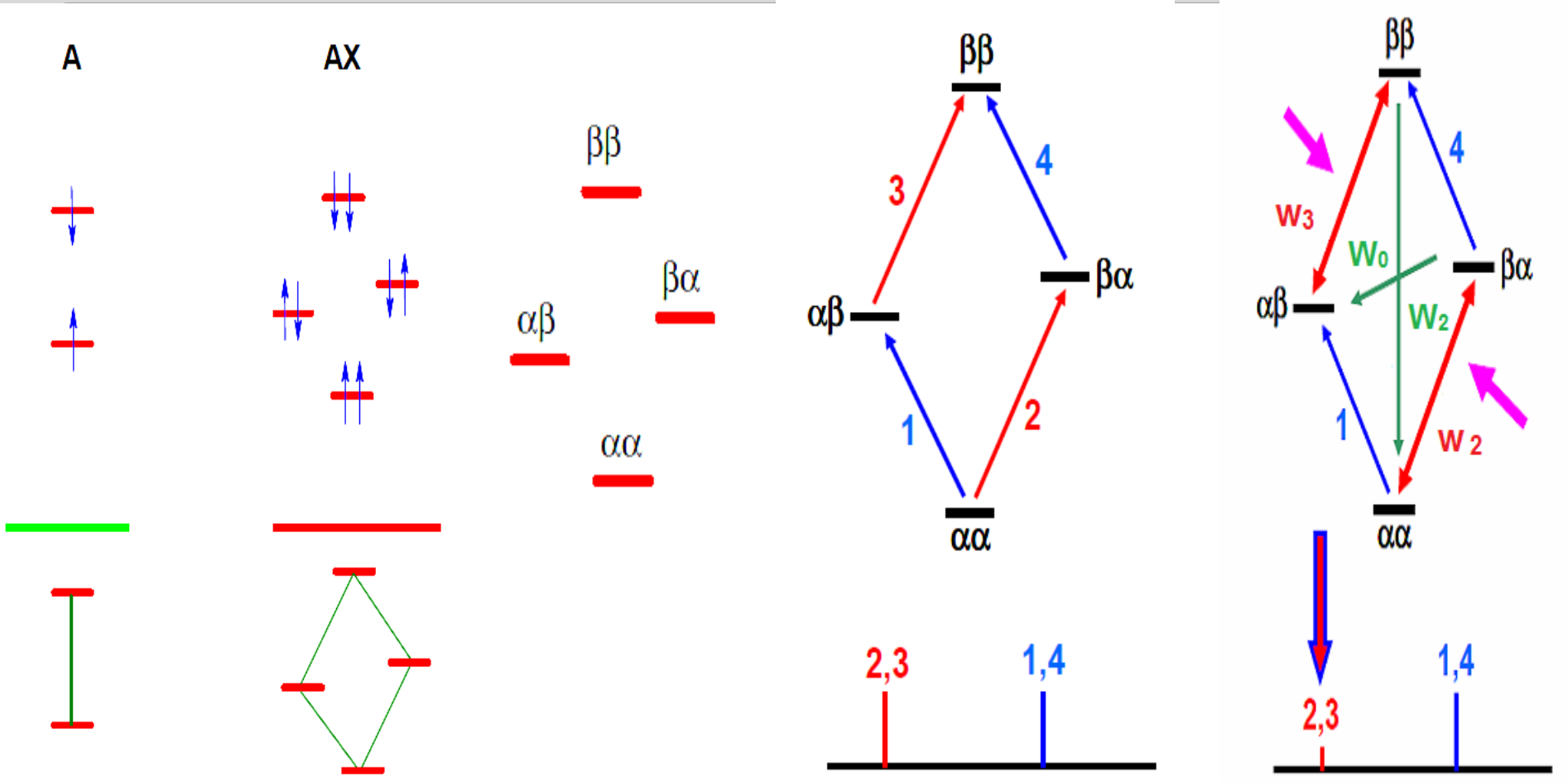
N-15 γ=-2,712

Ujemny NOE

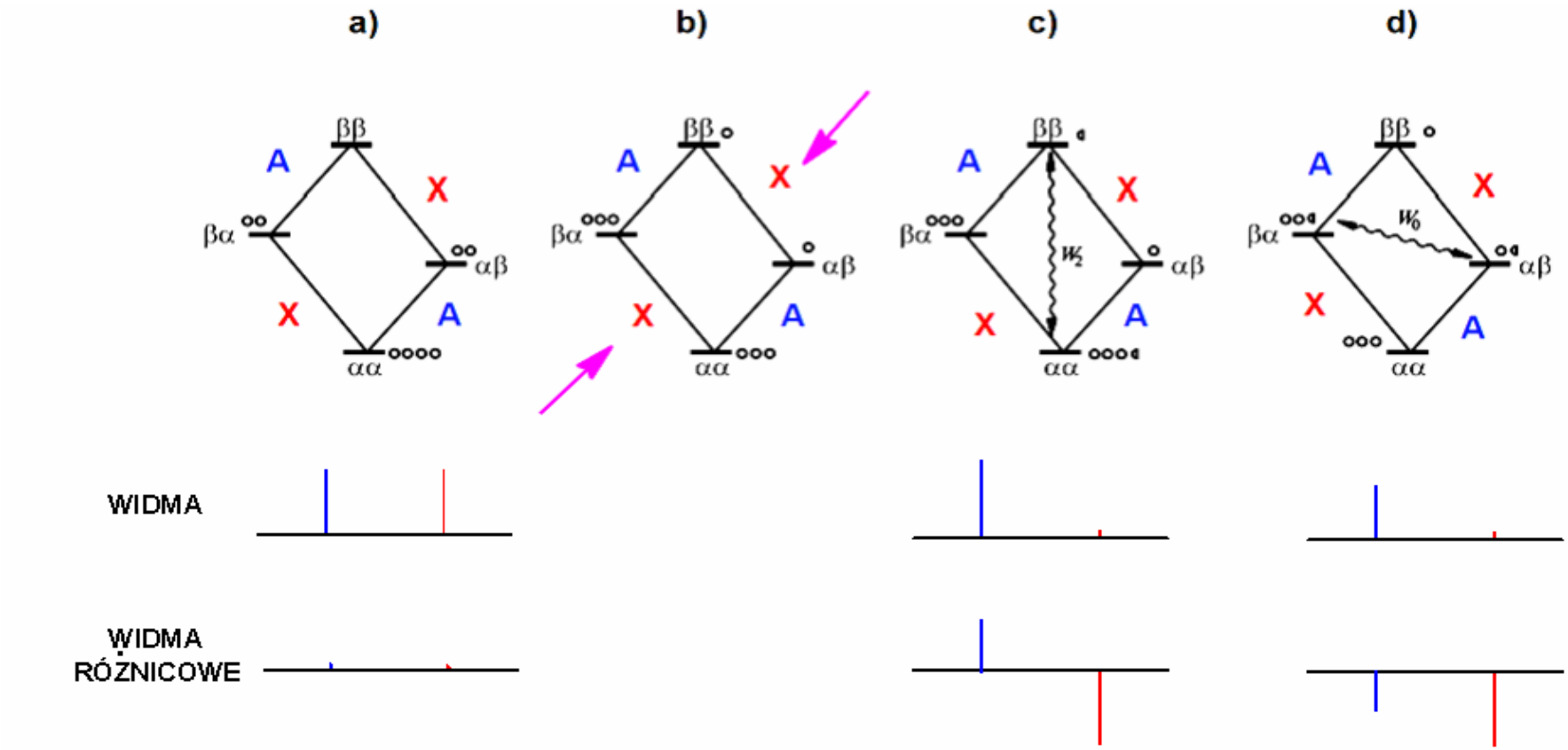
dla małych cząsteczek: $\eta_{max} = \gamma_H/2\gamma_X$

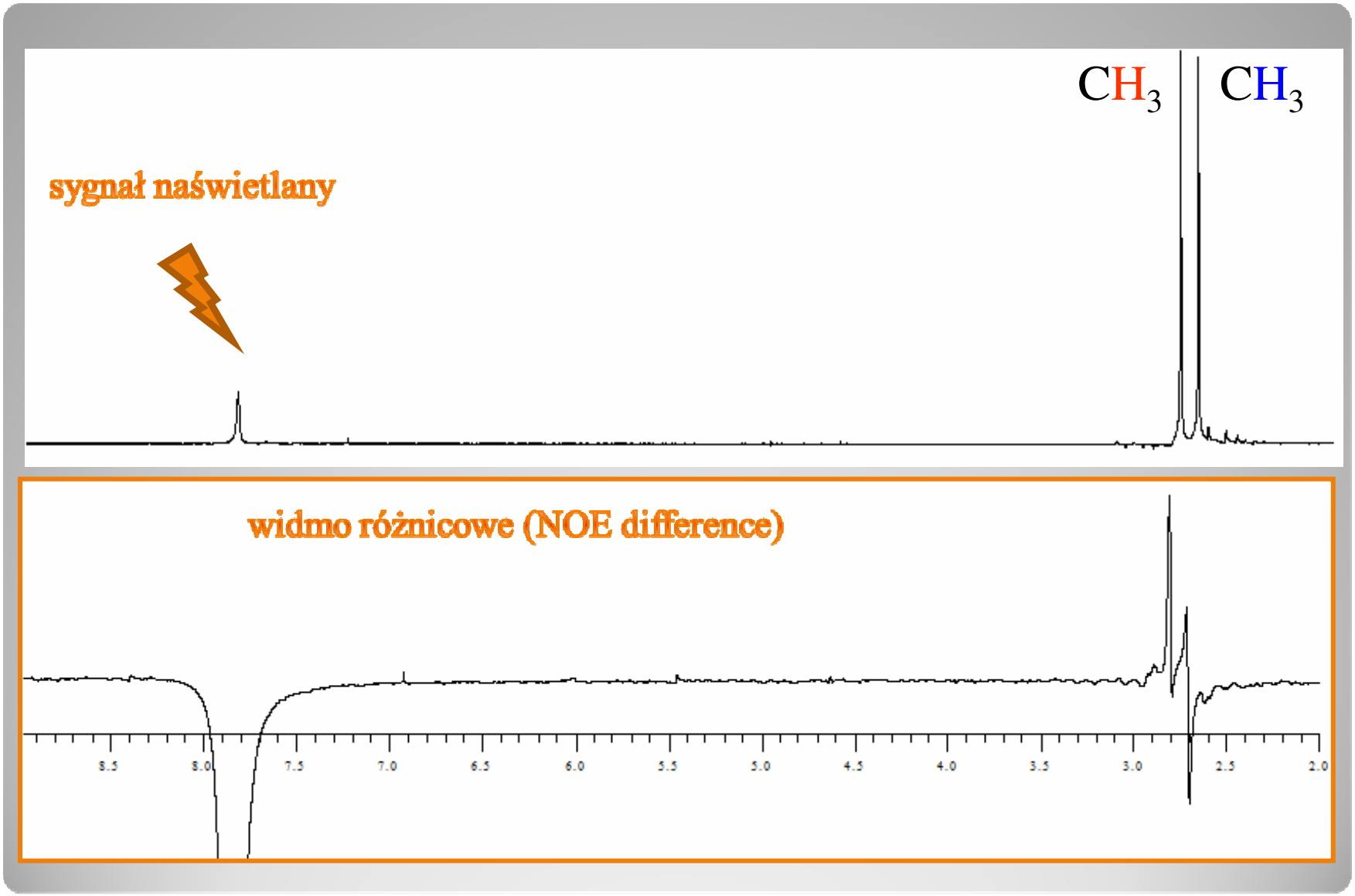
dla 1H-1H +50%

Naświetlanie → polaryzacja poziomów energetycznych jąder sprzężonych dipolowo → relaksacja wzajemna → wzmocnienie sygnału


A
AX
ββ
βα
αβ
αα
ββ
βα
αβ
αα
3
4
1
2
2,3
1,4
ββ
βα
αβ
αα
W3
W0
W2
W 2
4
1
2,3
1,4

Generowanie efektu Overhausera dwóch jąder **A** i **X**



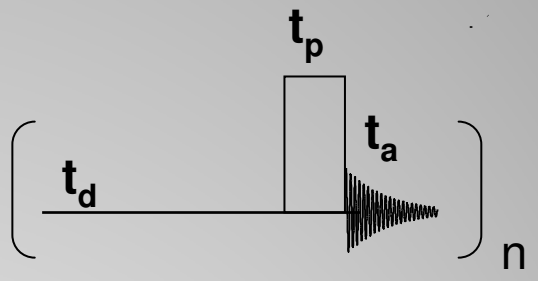

CH3
CH3
sygnał naświetlany
widmo różnicowe (NOE difference)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

Pomiar widma

Sekwencje pomiarowe - 1D NMR:

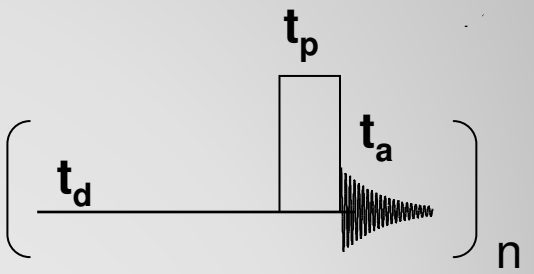
(1)^{1}H NMR:

^{1}H: $[(t_d) - (t_p) - (t_a)]_n$



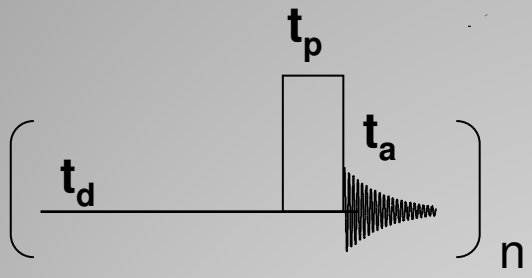
(2) ^{13}C NMR z odprzęganiem protonów:

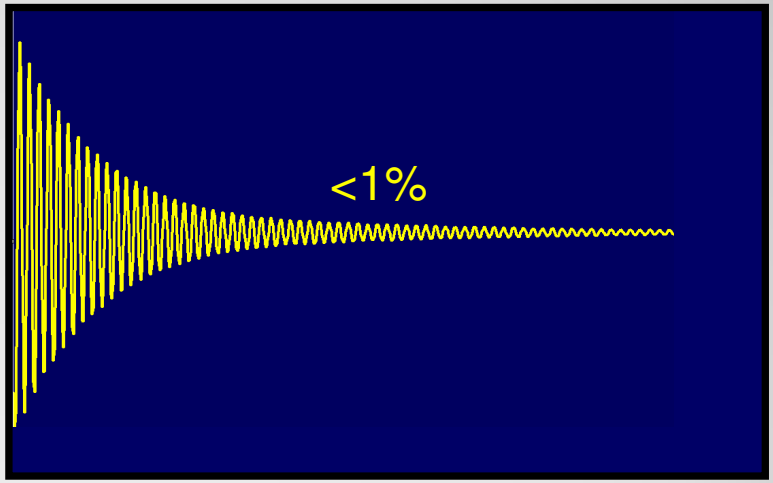
^{13}C: $[(t_d) - (t_p) - (t_a)]_n$



^{1}H: [odprzęganie włączone]

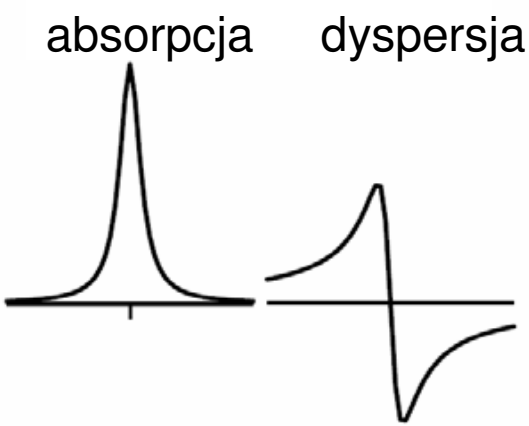
BB decoupling

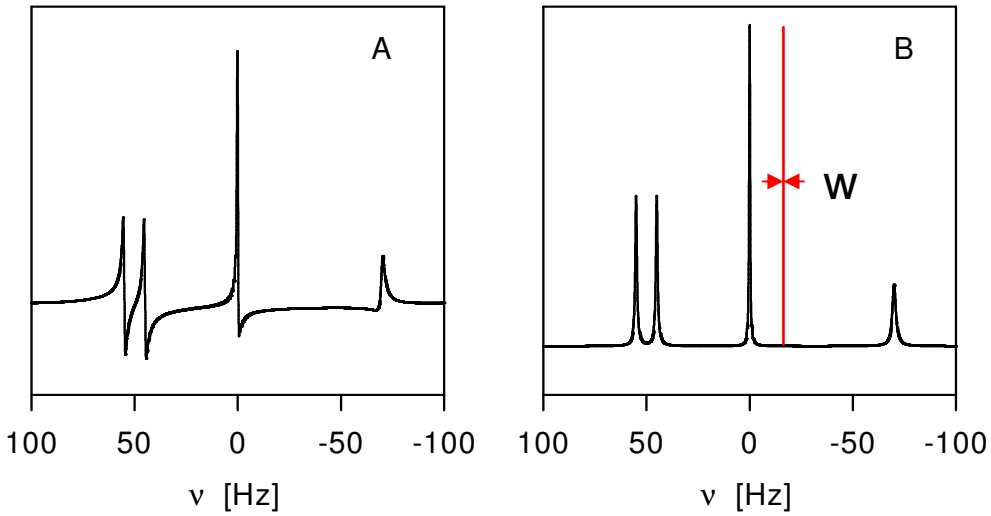

t_p
t_a
t_d
n


<1%

Transformacja Fouriera i linia Lorenca:

$$\text{Widmo}(\omega) = A \int_0^{\infty} FID(t)\cos(\omega_t)dt$$





Absorpcyjna i dyspersyjna krzywa Lorenca: A-przed korekcją fazową; B- po korekcji fazy; W - szerokość linii

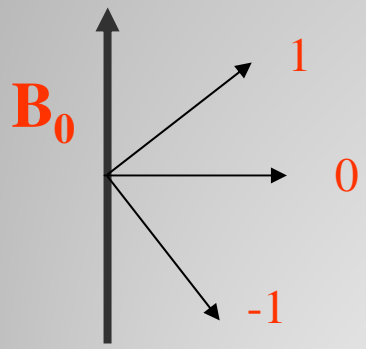
SPEKTROSKOPIA ^{13}C NMR

$I(^1H) = ½$	$I(^{12}C) = 0$	$I(^{13}C) = ½$
$\gamma(^1H) = 26,75$		$\gamma(^{13}C) = 6,73$

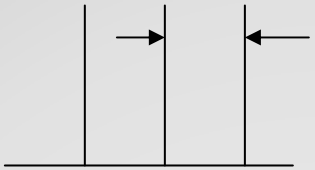
- ✓ naturalna zawartość ^{13}C w przyrodzie: 1,1%
- ✓ **CZUŁOŚĆ ^1H = 5600xCZUŁOŚĆ ^{13}C**
- ✓ **długie T_1 (zwłaszcza IV rz.)**
- ✓ **Efekt NOE**

SYGNAŁ ROZPUSZCZALNIKA

I(D) = 1

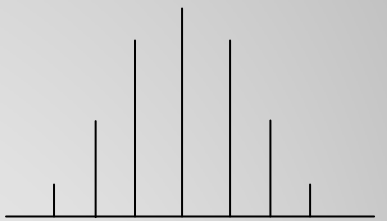


$CDCl_3$



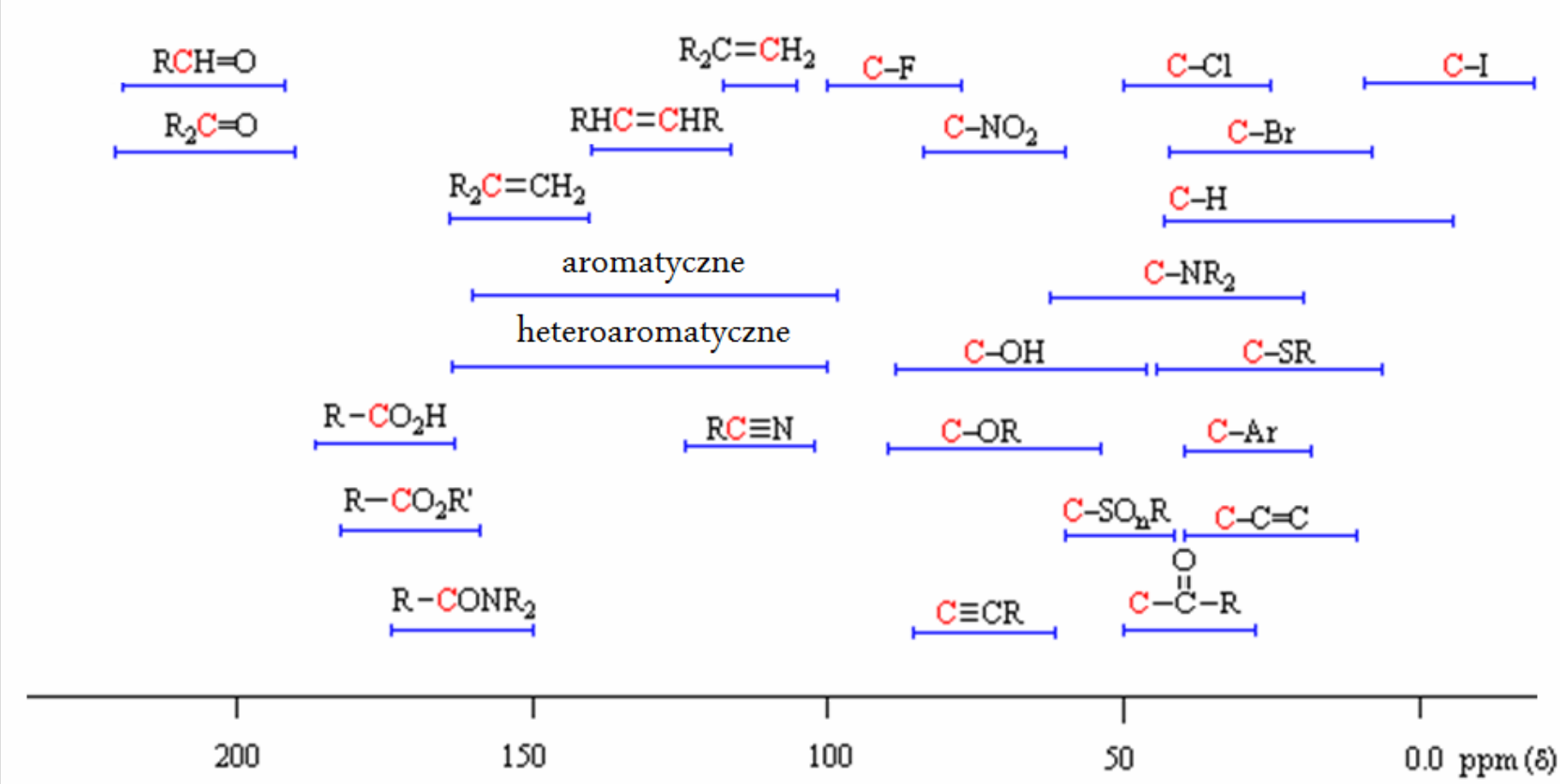
$J(D,^{13}C) = 31,5$ Hz

CD_3COCD_3

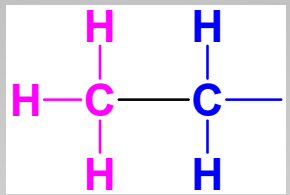


$J(D,^{13}C) = 19,5$ Hz

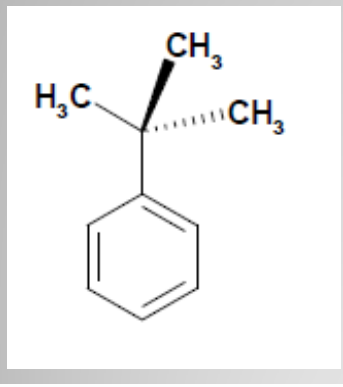
ZAKRESY WYSTĘPOWANIA SYGNAŁÓW ^{13}C MRJ

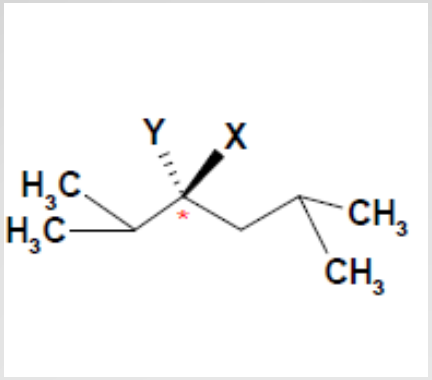


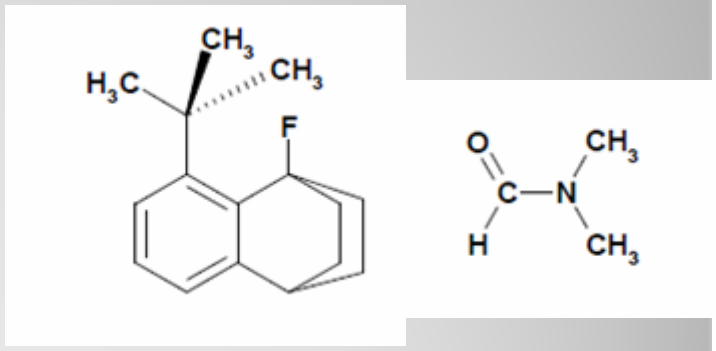
Liczba sygnałów w widmie ^{13}C NMR

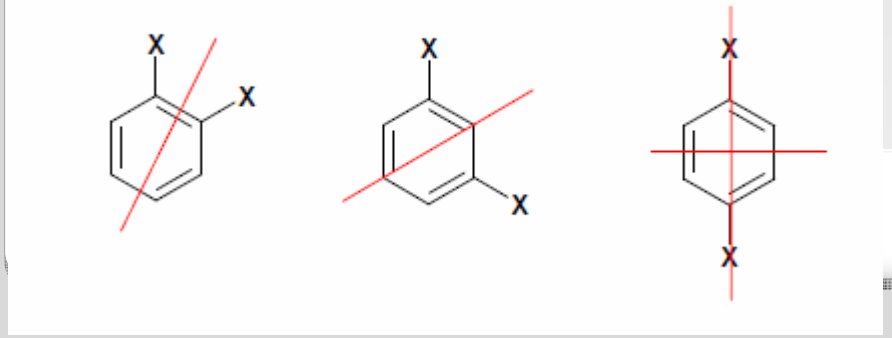


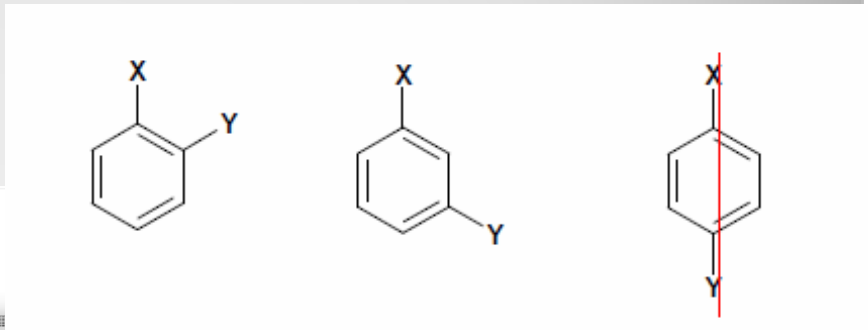
- kwartet: sprzężenia atomu węgla grupy CH_3 z protonami grupy CH_3 $^1J(^{13}C\text{-}^1H)$
- tryplet: sprzężenia atomu węgla grupy CH_2 z protonami grupy CH_2 $^1J(^{13}C\text{-}^1H)$





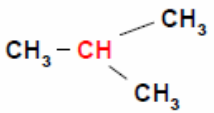
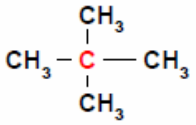




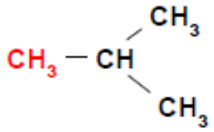
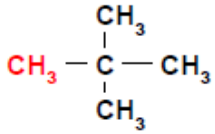


Przesunięcie chemiczne w widmie ^{13}C NMR (δ, ppm)

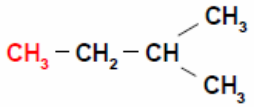
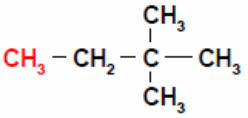
Efekt α

	ppm
CH_4	- 2.1
CH_3-CH_3	5.9
$CH_3-CH_2-CH_3$	16.1
	25.2
	27.9

Efekt β

	ppm
CH_3-CH_3	5.9
$CH_3-CH_2-CH_3$	15.6
	24.3
	31.5

Efekt γ

	ppm
$CH_3-CH_2-CH_3$	15.6
$CH_3-CH_2-CH_2-CH_3$	13.2
	11.5
	8.7

Zmiana przesunięcia chemicznego w ppm

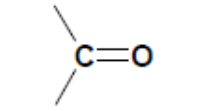
ε	δ	γ	β	α	
CH_3	CH_2	CH_2	CH_2	CH_2	X
0.0	0.2	- 6.6	8.1	70.0	F
- 0.1	- 0.6	- 5.2	10.1	30.5	Cl
0.0	- 0.6	- 4.0	10.2	19.2	Br
- 0.1	- 1.0	- 2.0	10.6	- 7.5	I
0.3	0.3	- 2.6	2.4	20.4	COOH
0.6	0.6	- 5.8	10.4	49.0	OH

Elektroujemność efekt ciężkiego atomu

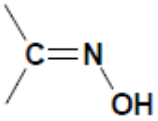
CF_4 / CHF_3 / CH_2F_2 / CH_3F	120 - 75 ppm
CCl_4 / $CHCl_3$ / CH_2Cl_2 / CH_3Cl	100 - 20 ppm
CBr_4 / CH_2Br_2 / $CHBr_3$ / CH_3Br	30 - 7 ppm
CH_3I / CH_2I_2 / CHI_3 / CI_4	(- 20) - (-295) ppm

Przesunięcie chemiczne w widmie ^{13}C NMR (δ, ppm)

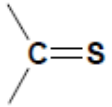
Grupy funkcyjne



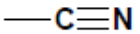
220 - 140 ppm



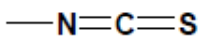
165 - 145 ppm



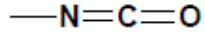
210 - 180 ppm



125 - 110 ppm

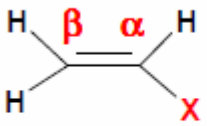


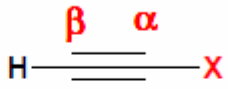
140 - 110 ppm



130 - 120 ppm

Elektroujemność podstawnika

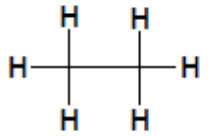




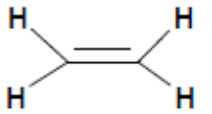
- 34.3	24.9	F
- 5.4	3.3	Cl
- 0.7	- 7.2	Br
7.7	- 37.4	I
- 37.3	30.3	OCH_3
14.9	15.8	CHO

- 59.7	14.8
- 16.9	- 13.3
- 5.9	- 31.6
11.1	- 73.3

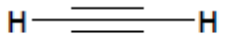
Wpływ hybrydyzacji atomu węgla



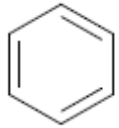
5.9

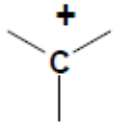


122.8



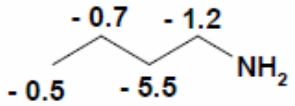
72.8


128.5

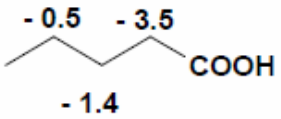


kation
330 - 100 ppm

Wpływ protonowania



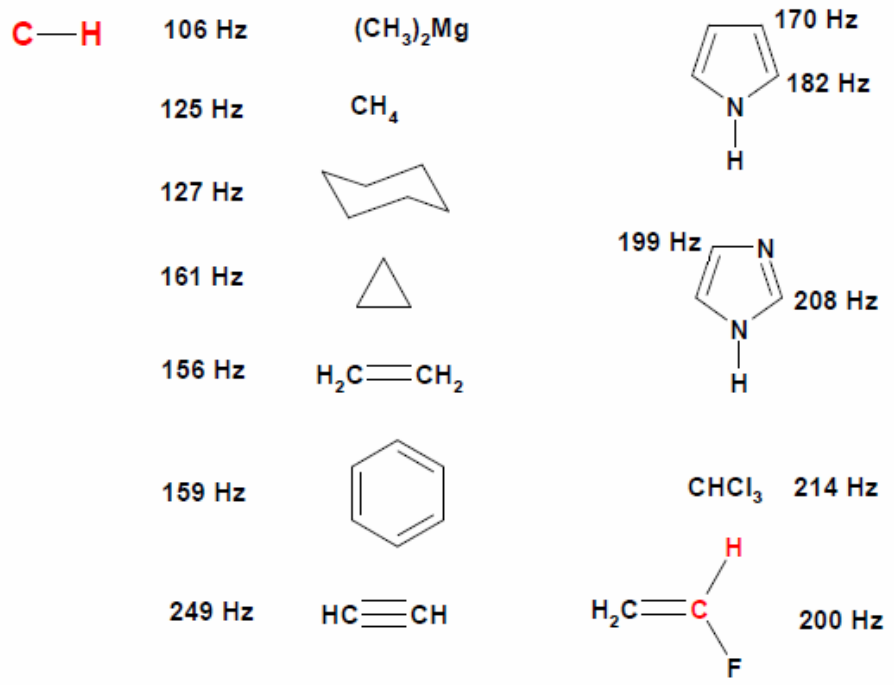
$\delta_{sól}$ vs. δ_{amina}



$\delta_{sól}$ vs. δ_{kwas}

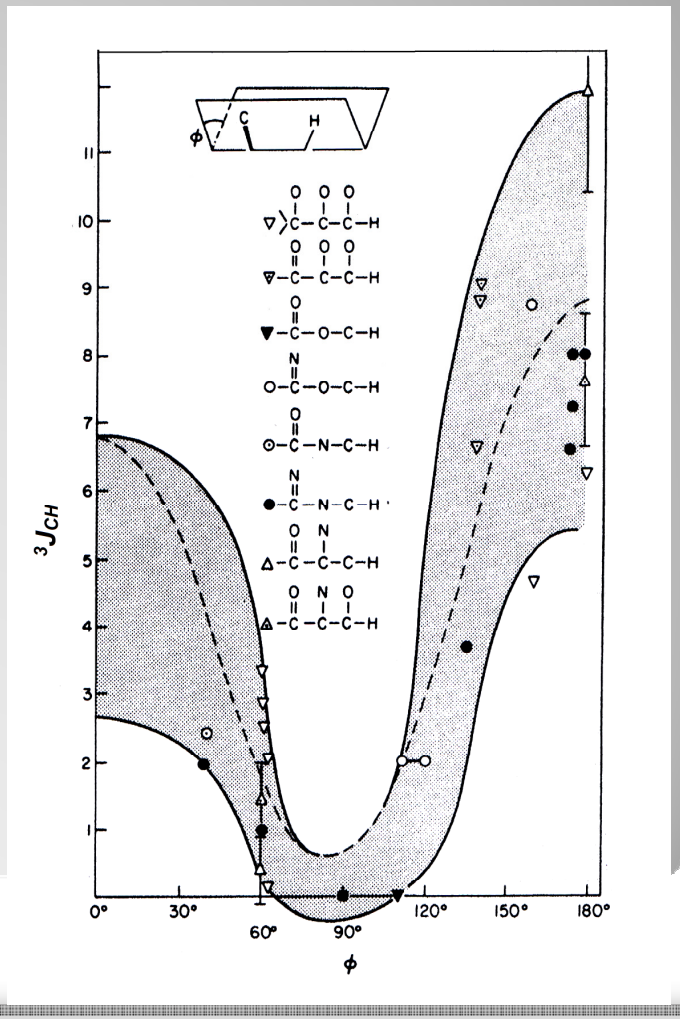
Stała sprzężenia ^{13}C- ^{1}H (Hz)

- ^{1}J -przez 1 wiązanie:



- ^{3}J –(wicynalna): do 10 Hz

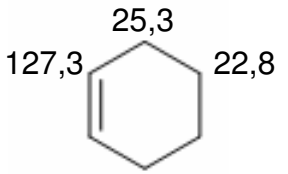
(obowiązuje zależność Karplusa)

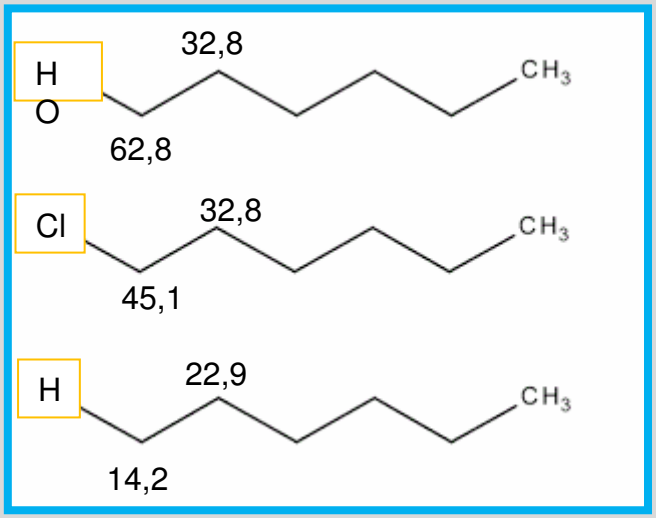


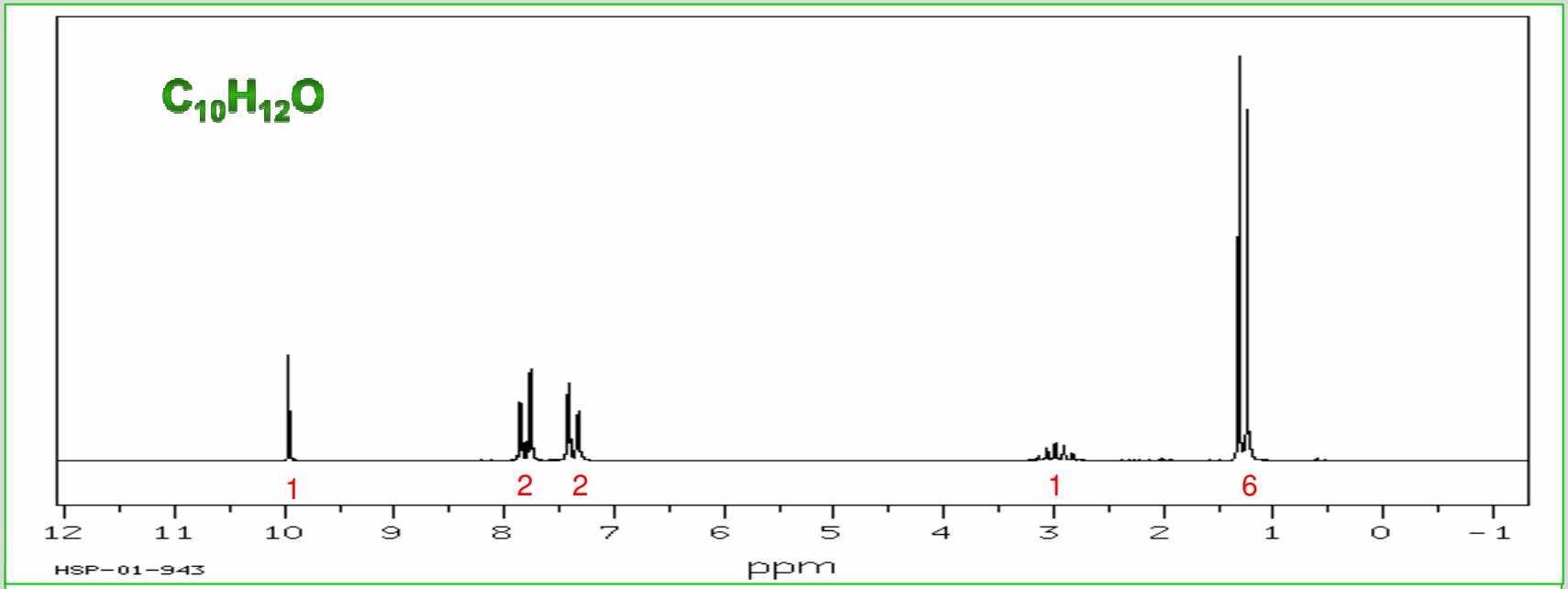
Co wpływa na przesunięcie chemiczne?

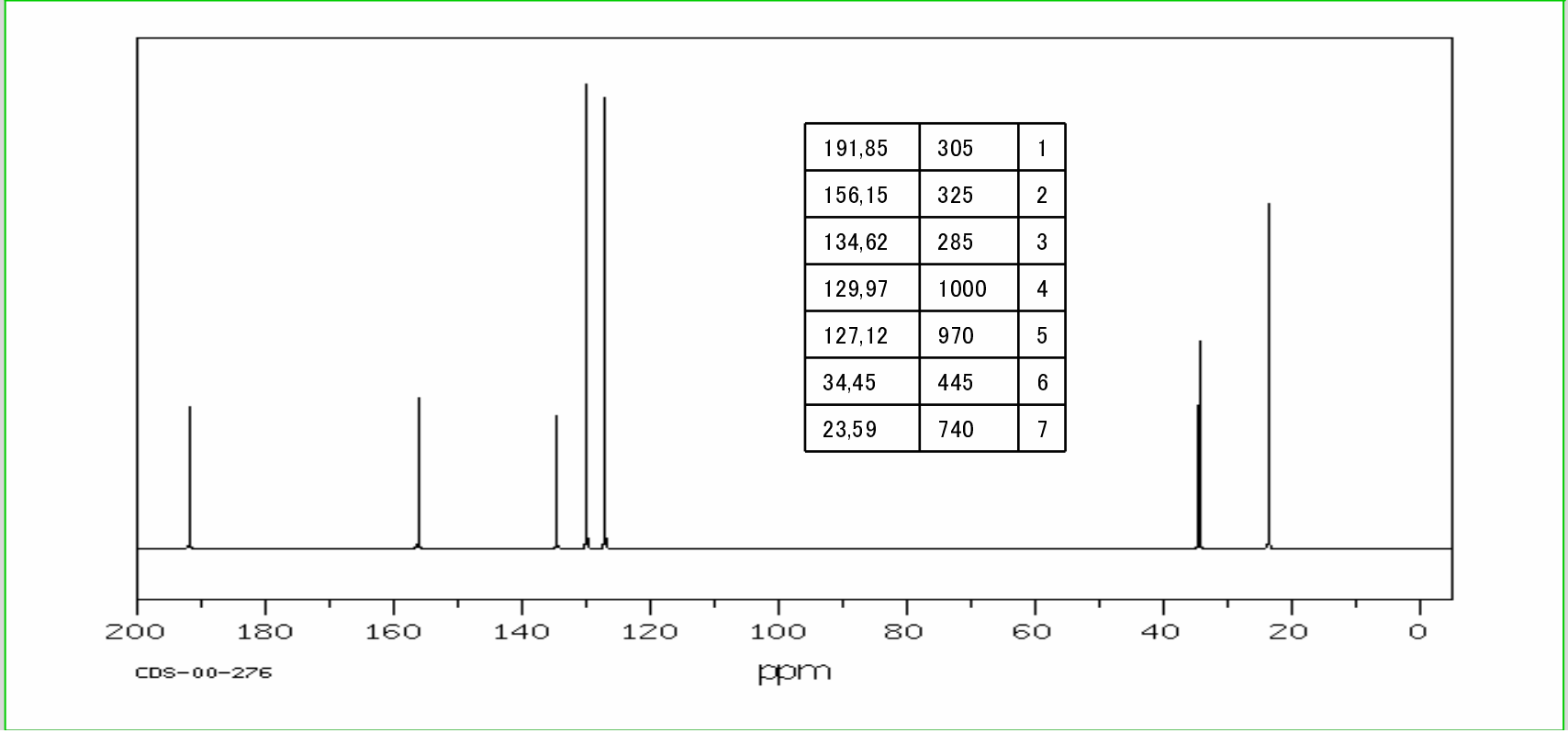
- ❑Hybrydyzacja atomu węgla
- ❑Efekty indukcyjne podstawników
- ❑Efekty steryczne
- ❑Efekty mezometyczne
- ❑Efekt ciężkiego atomu (np, J, Br)
- ❑Efekt anizotropowy

$\delta(sp^3) < \delta(sp) < \delta(sp^2)$

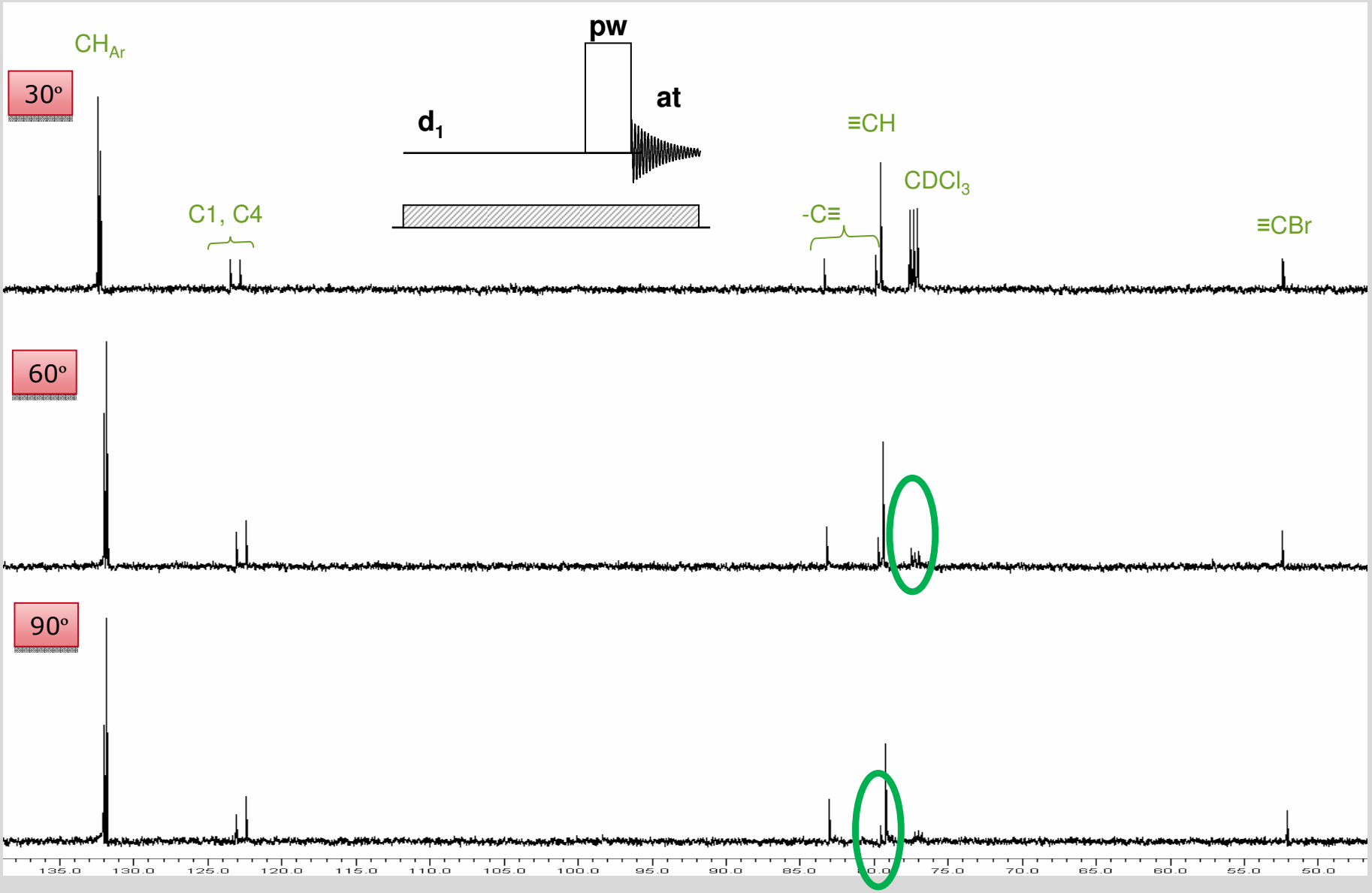


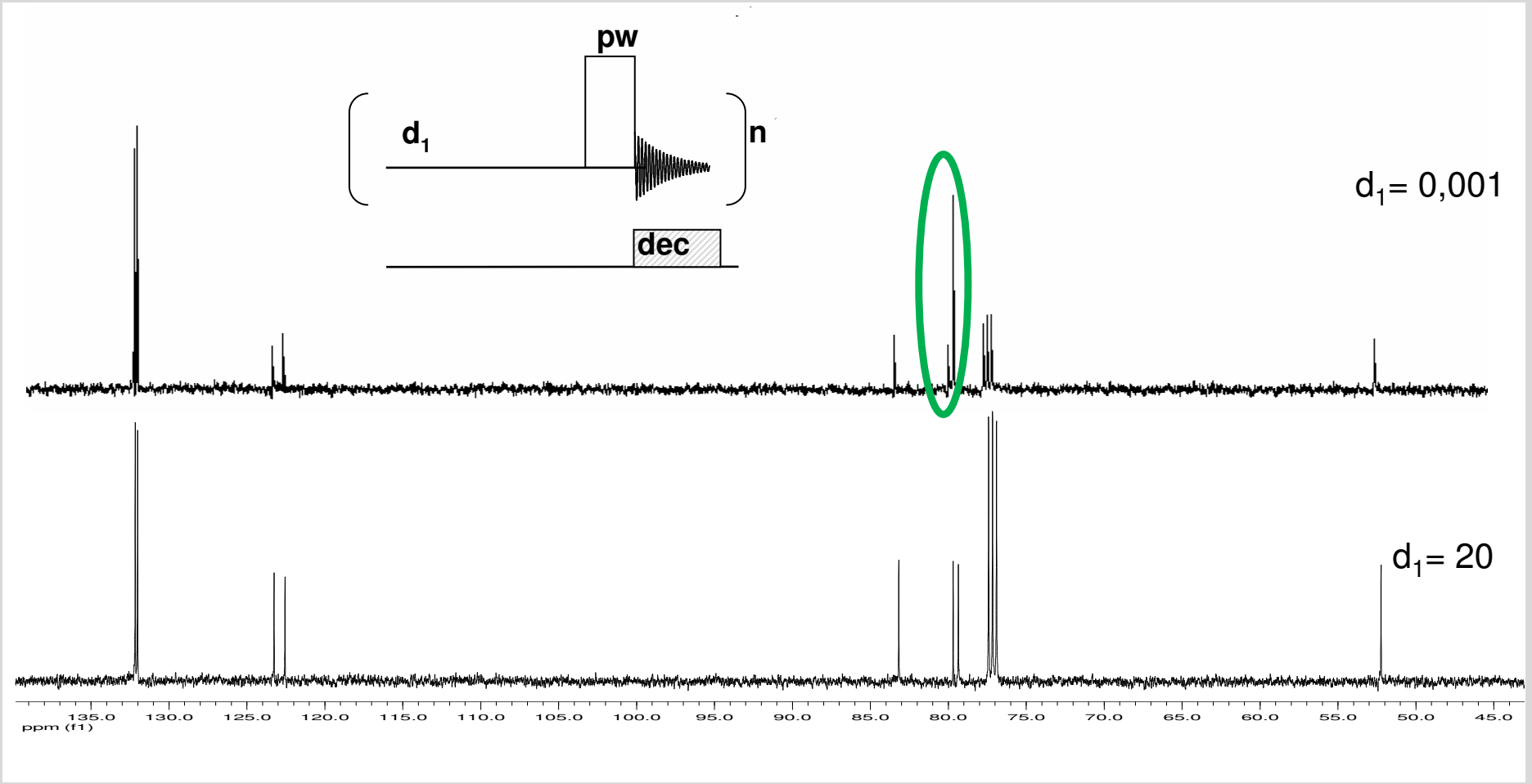


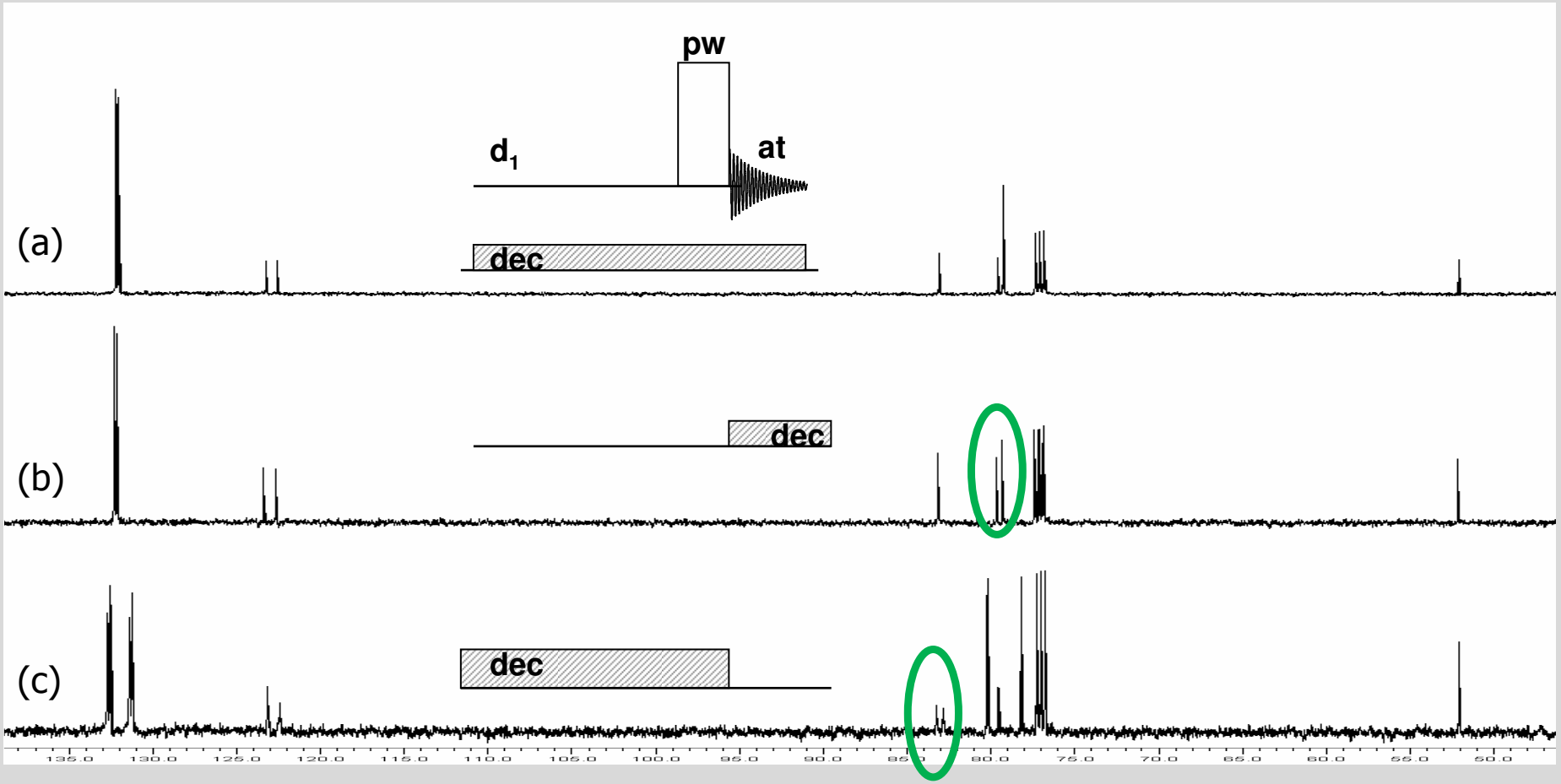


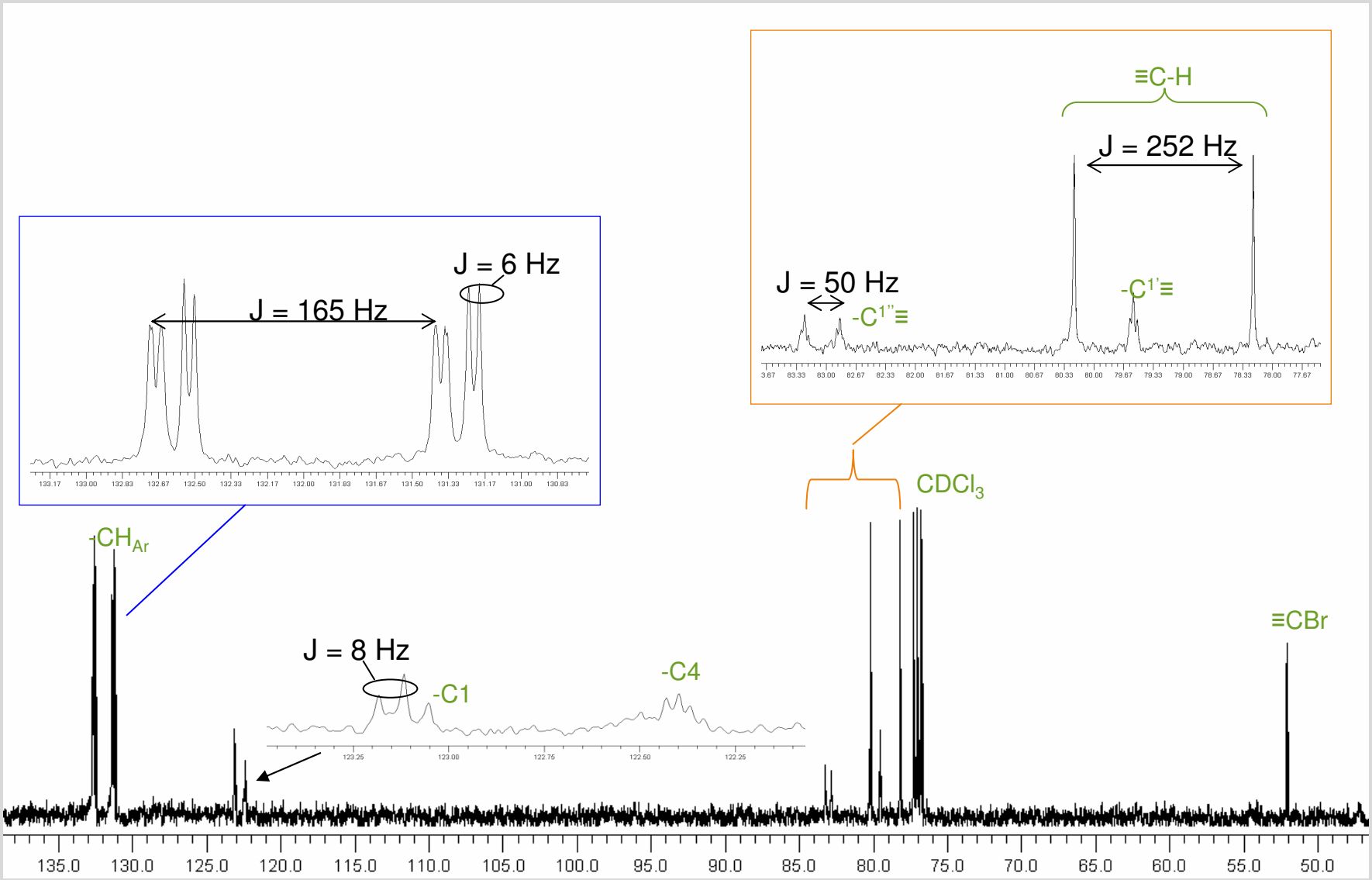


191,85	305	1
156,15	325	2
134,62	285	3
129,97	1000	4
127,12	970	5
34,45	445	6
23,59	740	7

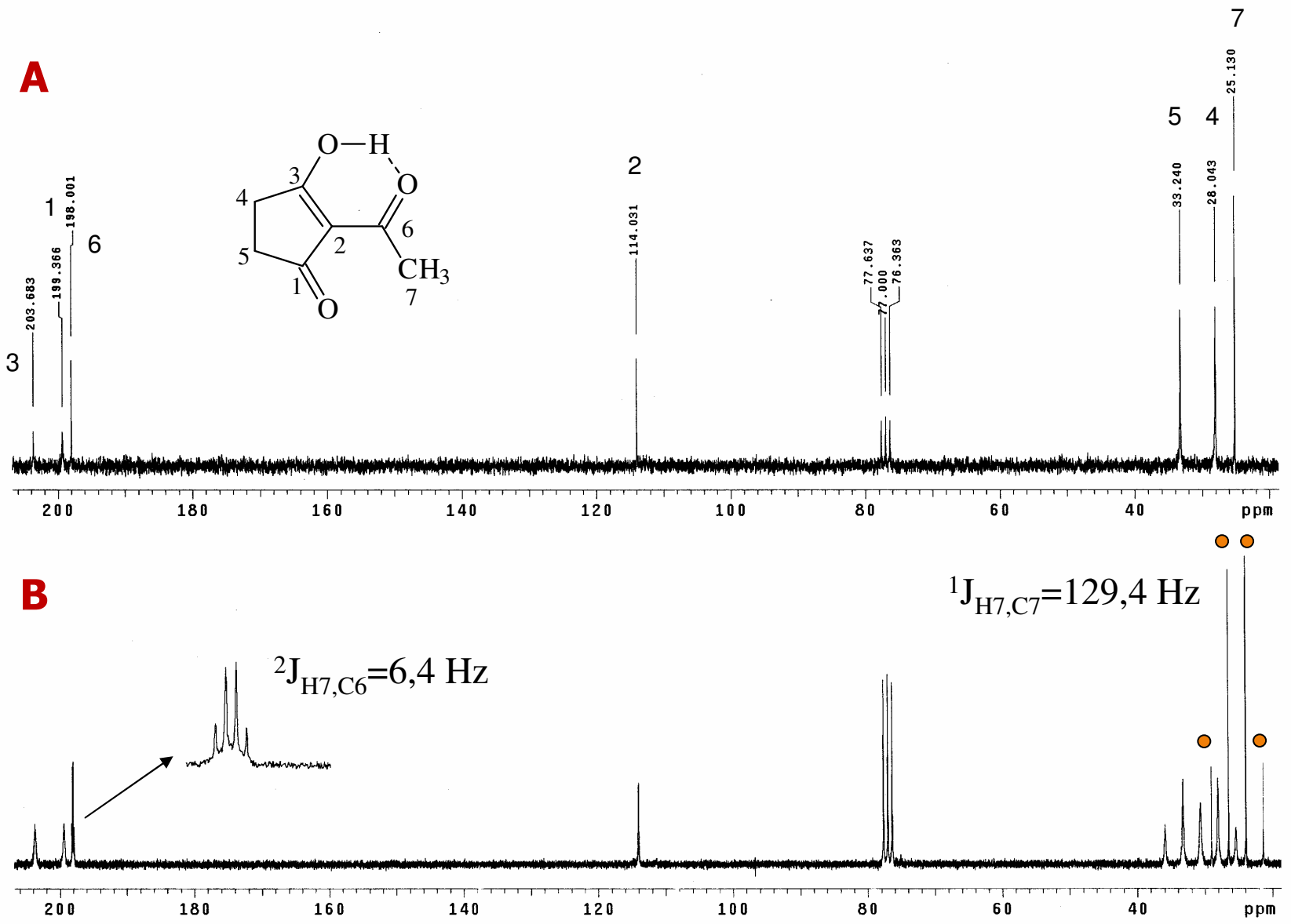

CH$_{Ar}$
30º
pw
d$_1$
at
≡CH
CDCl$_3$
C1, C4
-C≡
≡CBr
60º
90º
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0


pw
d1
n
dec
d1= 0,001
d1= 20
135.0 130.0 125.0 120.0 115.0 110.0 105.0 100.0 95.0 90.0 85.0 80.0 75.0 70.0 65.0 60.0 55.0 50.0 45.0
ppm (f1)


pw
d1
at
dec
(a)
dec
(b)
dec
(c)
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0


≡C-H
J = 252 Hz
J = 50 Hz
-C1''≡
-C1'≡
J = 6 Hz
J = 165 Hz
-CHAr
CDCl3
J = 8 Hz
-C1
-C4
≡CBr
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0

^{13}C NMR ODSPRZĘŻONE (A) i SPRZĘŻONE Z PROTONAMI (B)

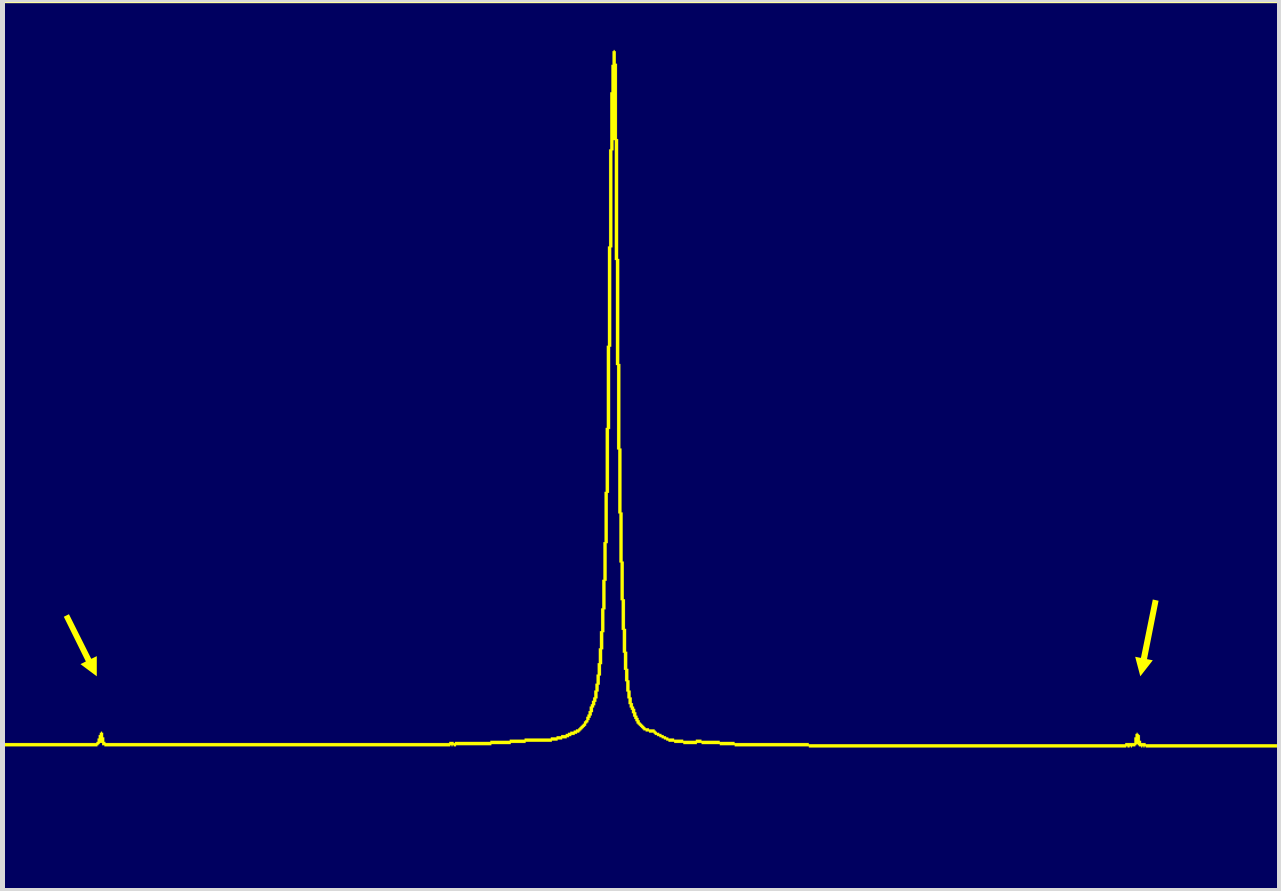


Sztuczne zwiększanie polaryzacji jądrowej

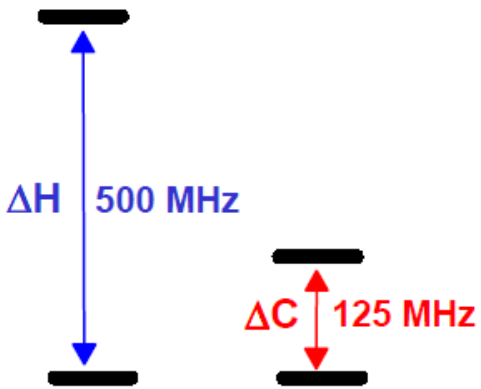
1. NOE – jądrowy efekt Overhausera

2. Przeniesienie polaryzacji *S* (sensitive) ⟶ *I* (insensitive)

3. Detekcja odwrotna: widmo *I* na podstawie rejestracji sygnału S



Przeniesienie polaryzacji (Polarisation Transfer)



$\Delta H > \Delta C$

$\Delta \sim \exp(-\Delta E / kT)$

$CHCl_3$

$^{1}H - ^{13}CCl_3$ 1%

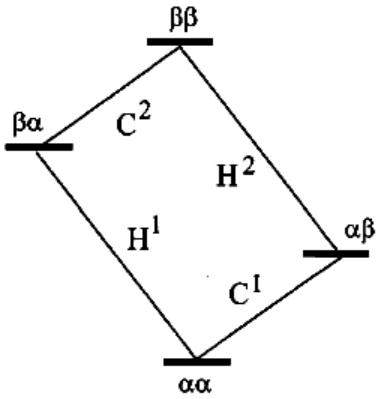
$^{1}H - ^{12}CCl_3$ 99%

czułość:

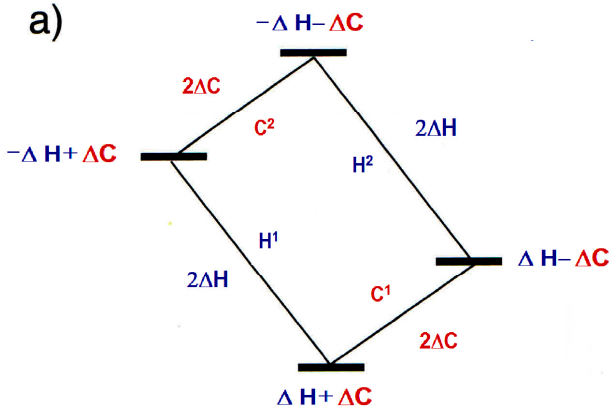
$^{1}H : ^{13}C = 1 : 0.0159$

Przeniesienie polaryzacji (Polarisation Transfer)

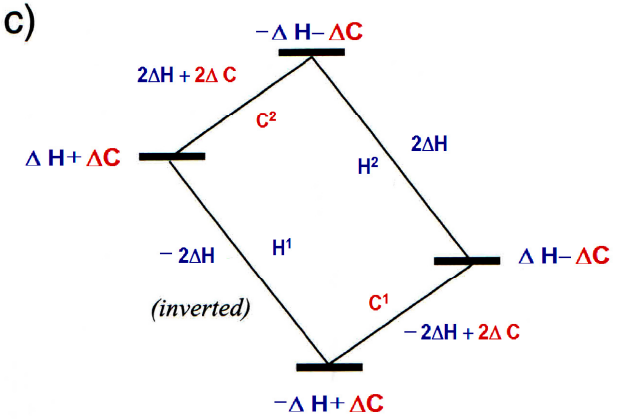
SPT – Selective Population Transfer
SPI – Selective Population Inversion



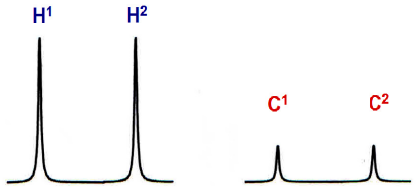
a)



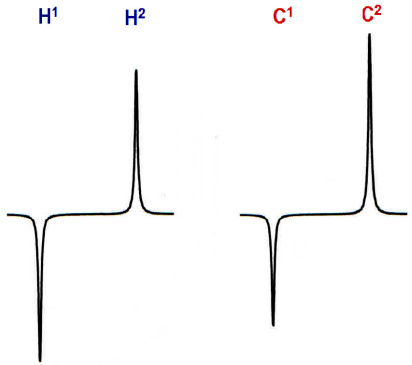
c)

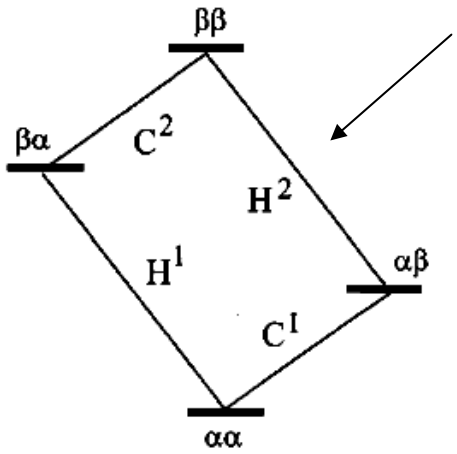


b)



d)



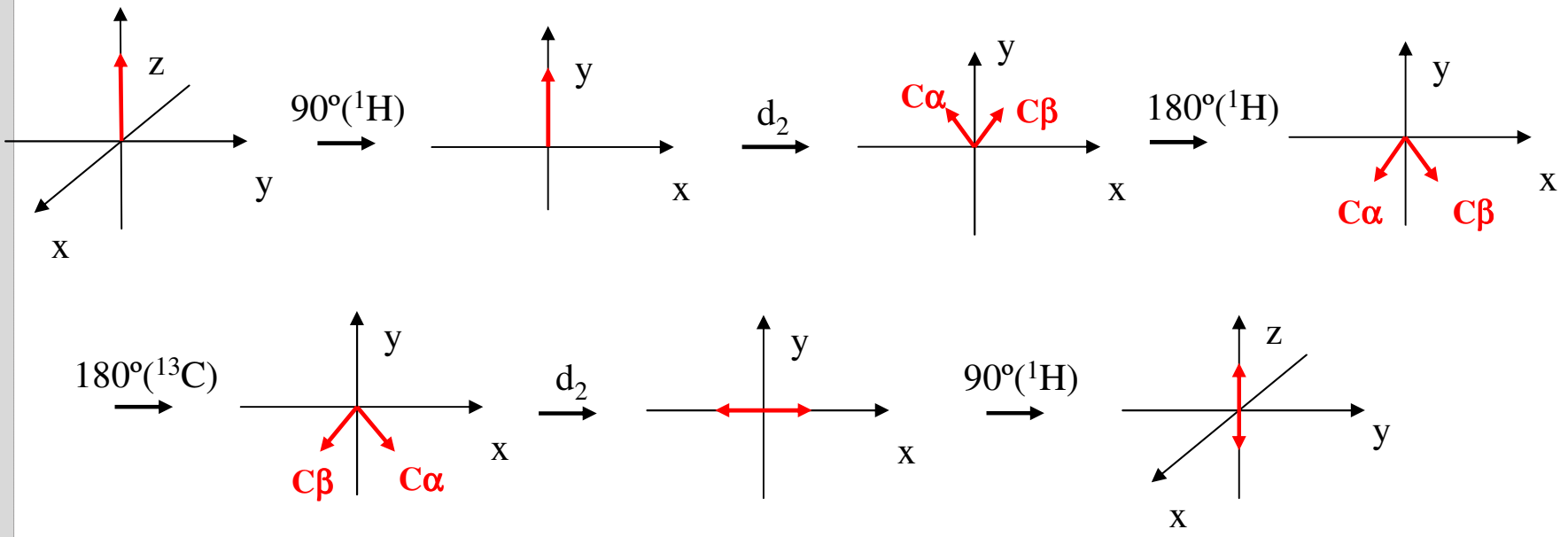


	Stan równowagi	Po impulsie selektywnym 180(H_2)
p(**ββ**)	0,25-h-c	0,25+h-c
p(**βα**)	0,25-h+c	0,25-h+c
p(**αβ**)	0,25+h-c	0,25-h-c
p(**αα**)	0,25+h+c	0,25+h+c

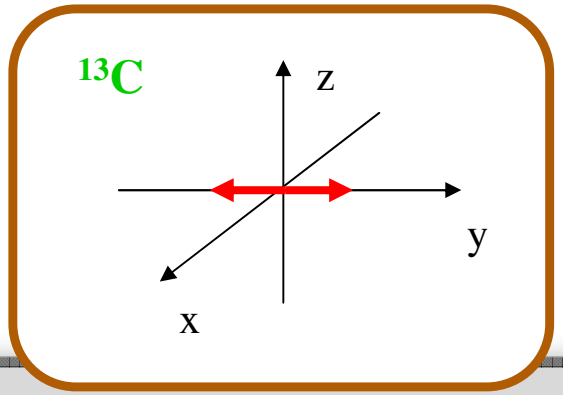
	Int(C_2)= p(**βα**) – p(**ββ**)	Int(C_1)= p(**αα**) – p(**αβ**)
Stan równowagi	2c	2c
Po selektywnym impulsie 180(H_2)	2c – 2h	2c + 2h

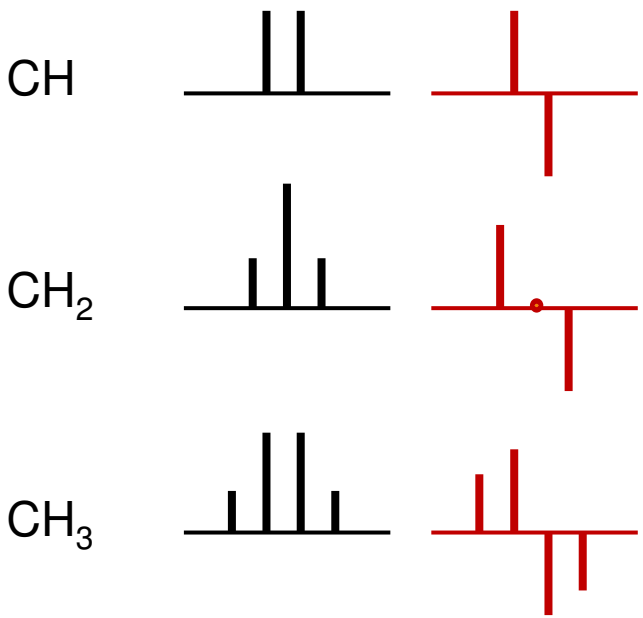
Technika INEPT

Przebieg zmian magnetyzacji dla układu $^{1}H^{13}C$



$$\Theta = 2\pi J d_2 = 2\pi J(1/4J) = \pi/2$$

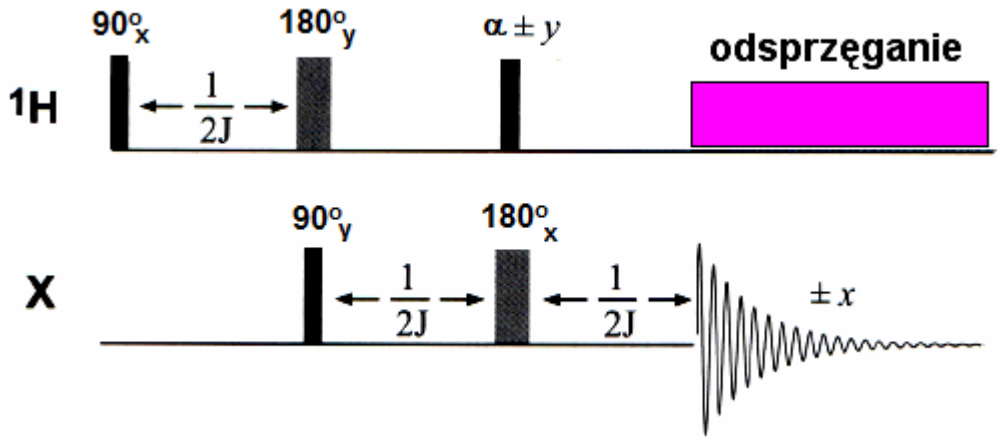



CH
CH2
CH3

Schemat sekwencji DEPT
(DEPT = distortionless enhancement by polarisation transfer)

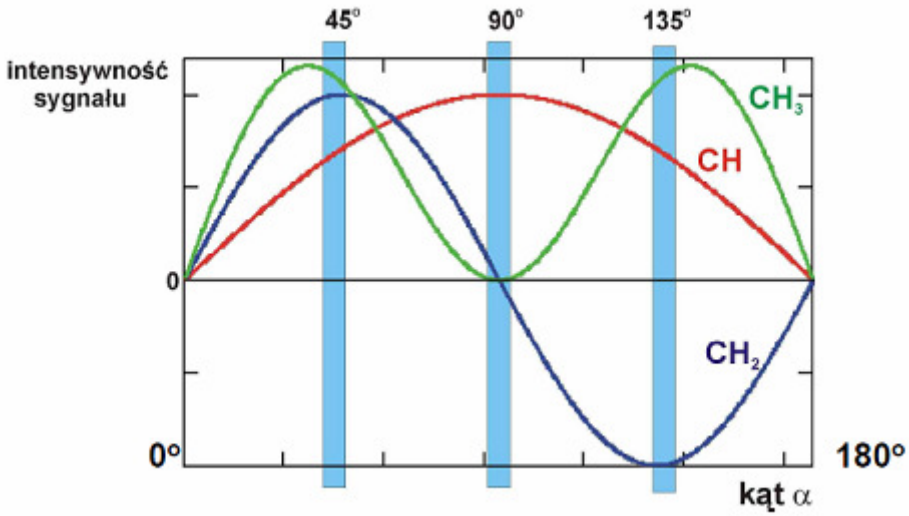
Optymalizacja

- **wartość J**
- **kąt α**
- **$E=(\gamma_H/\gamma_C)\sin\alpha$**

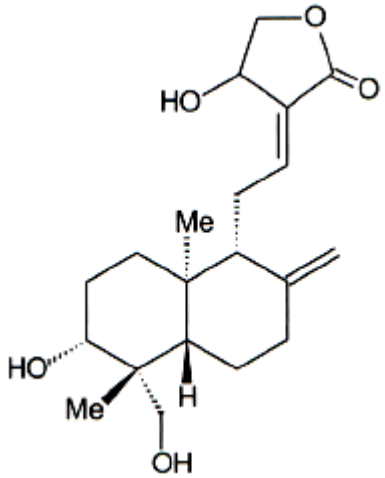


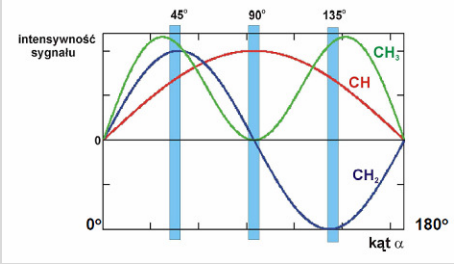
Znak sygnałów multipletów w widmach DEPT

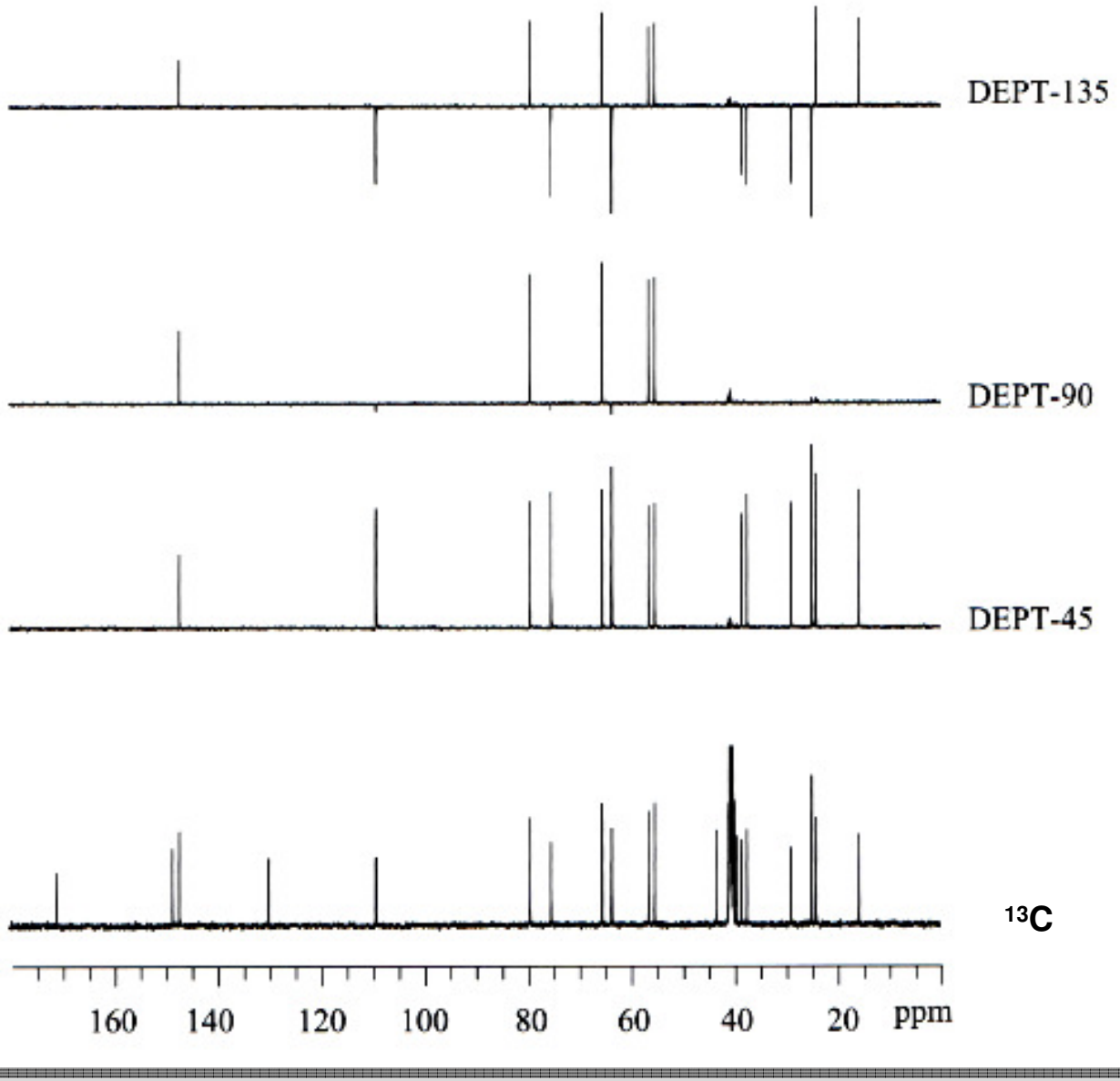
	DEPT-45	DEPT-90	DEPT-135
XH (CH)	+	+	+
XH_2 (CH_2)	+	0	−
XH_3 (CH_3)	+	0	+



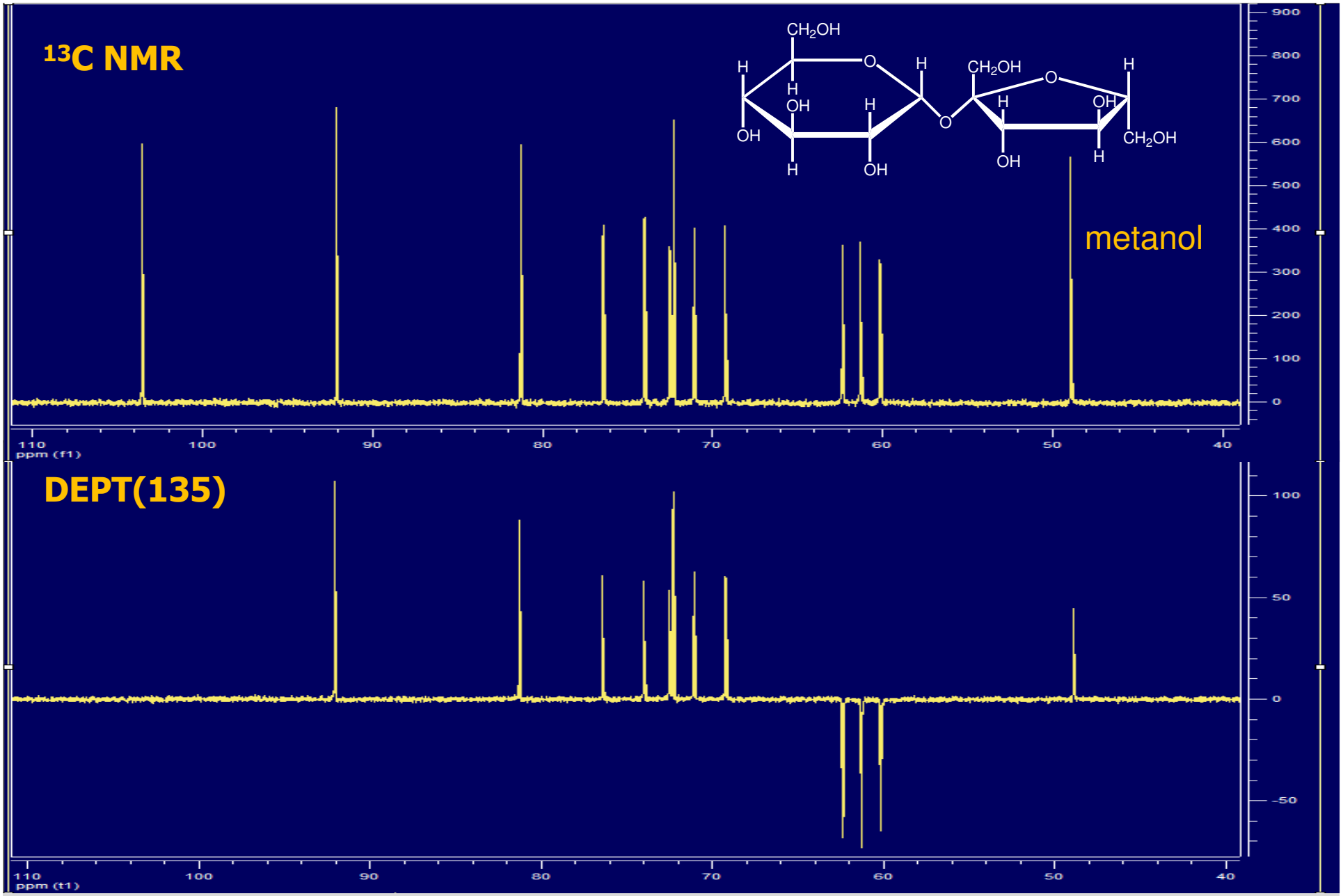
Terpen - andrografolid





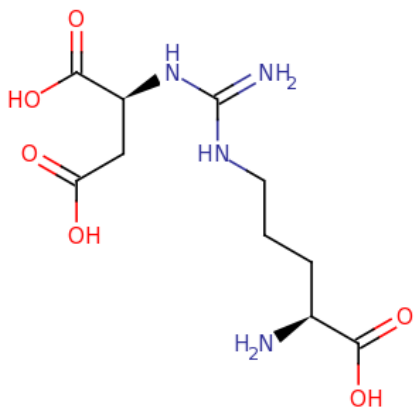


^{13}C


13C NMR
metanol
DEPT(135)
ppm (f1)
ppm (t1)

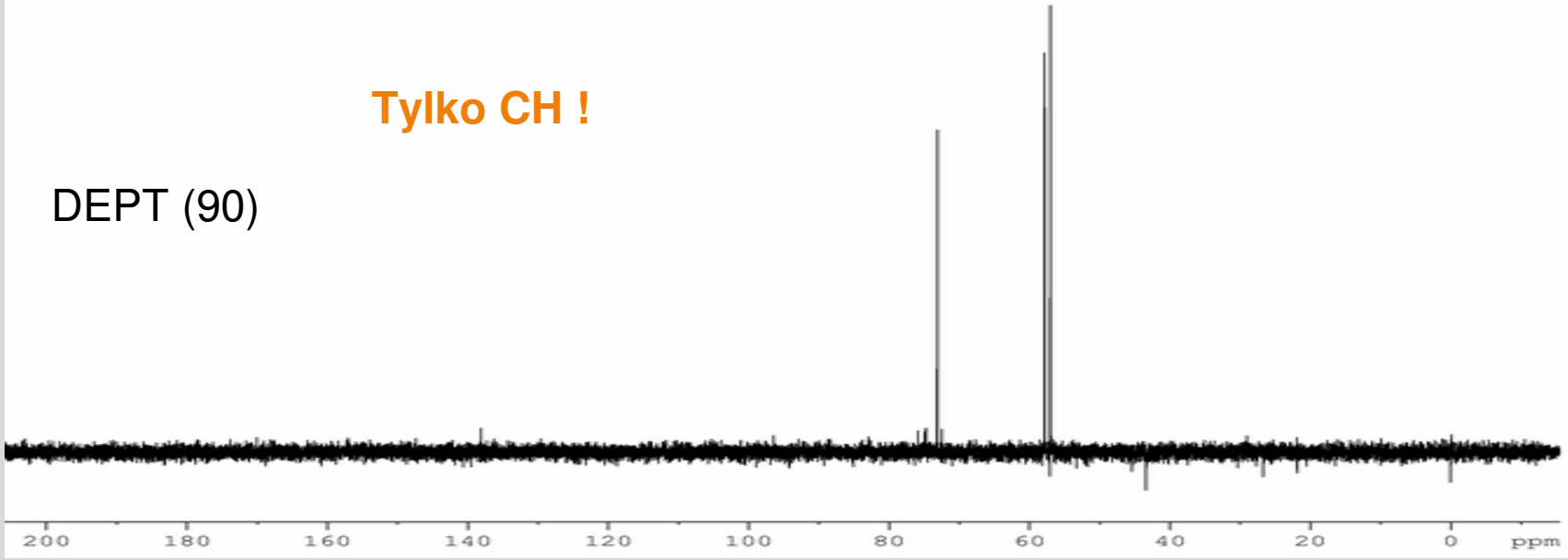
Kwas argininobursztynowy

13C NMR

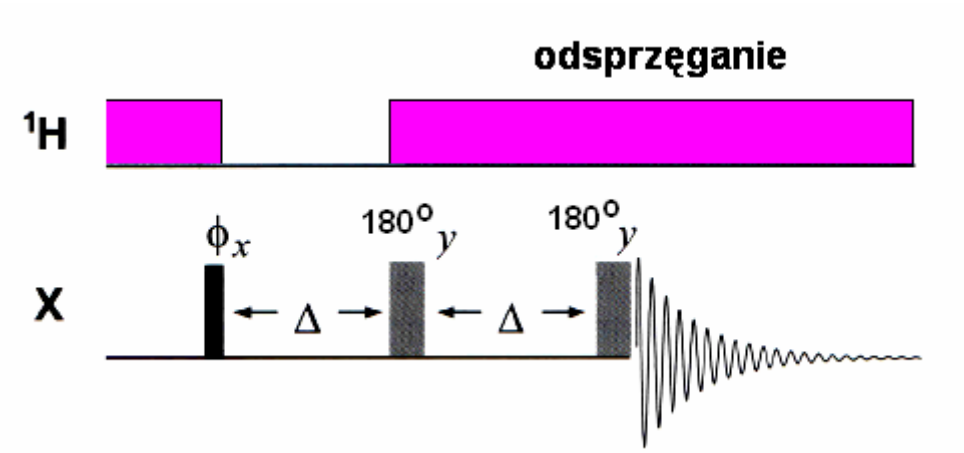


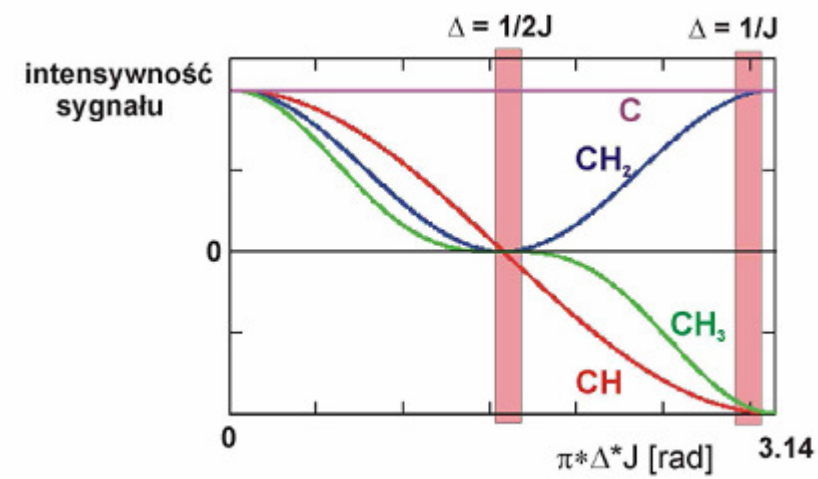
Tylko CH !

DEPT (90)

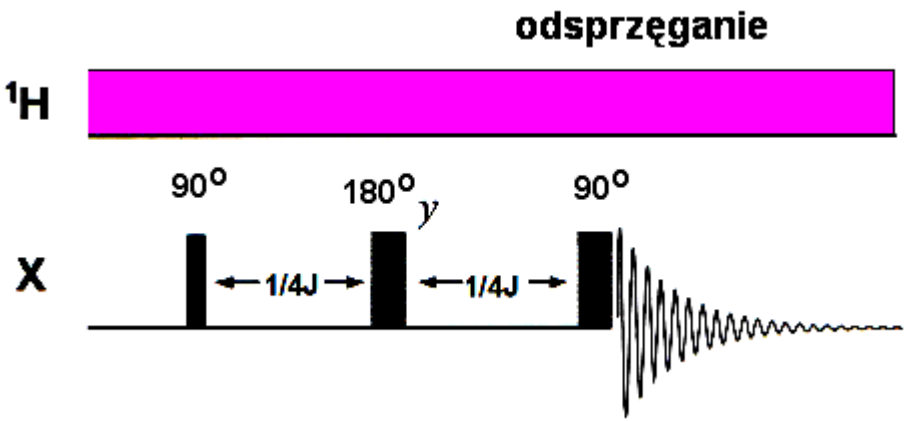


APT- Attached Proton Test





INADEQUATE -Incredible Natural Abundance DoublE QUAntum Transfer Experiment



- Sekwencja impulsów usuwa sygnały izolowanych atomów ^{13}C (singlety) pozostawia sygnały par ^{13}C-^{13}C (dublety)
- Do optymalizacji parametrów eksperymentu konieczna jest znajomość stałej sprzężenia ^{13}C-^{13}C, a więc wielkości która ma być mierzona

^{13}C—^{12}C—^{13}C

^{13}C—^{13}C—^{12}C

CH_3—CH_2—OH

98%

$^{13}CH_3$—$^{13}CH_2$—OH

0.01%

$^{13}CH_3$—CH_2—OH

1%

CH_3—$^{13}CH_2$—OH

1%

$^1J(^{13}C\text{-}^{13}C)$

36.6 etan

67.0 etylen

56.0 benzen

171.5 acetylen

12.4 cyklopropan

$^nJ(^{13}C\text{-}^{13}C)$

kilka-kilkanaście Hz