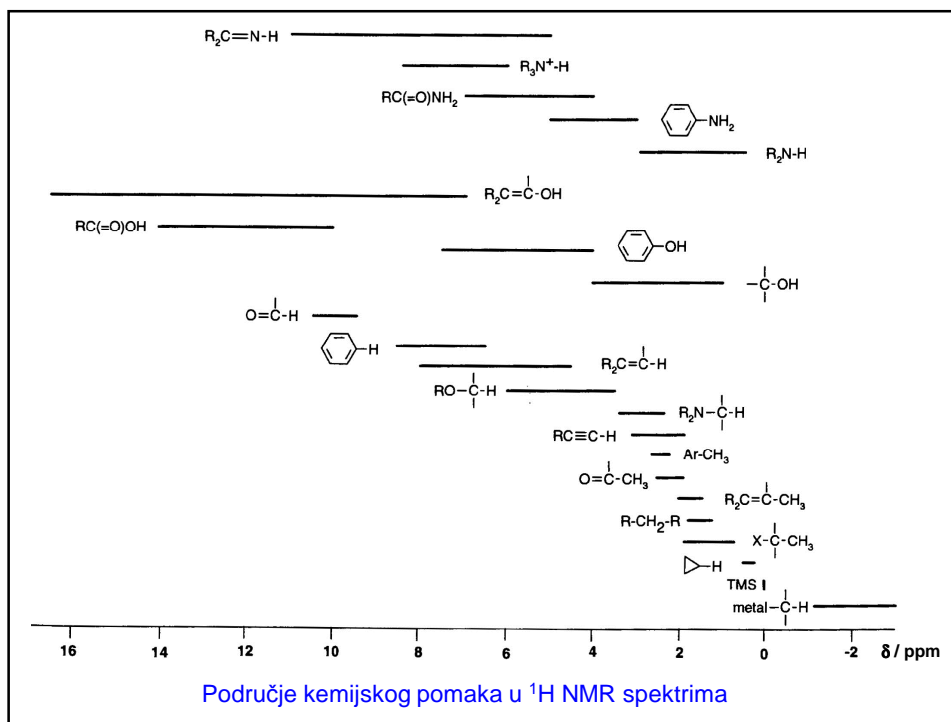






ANALITIČKA KEMIJA II

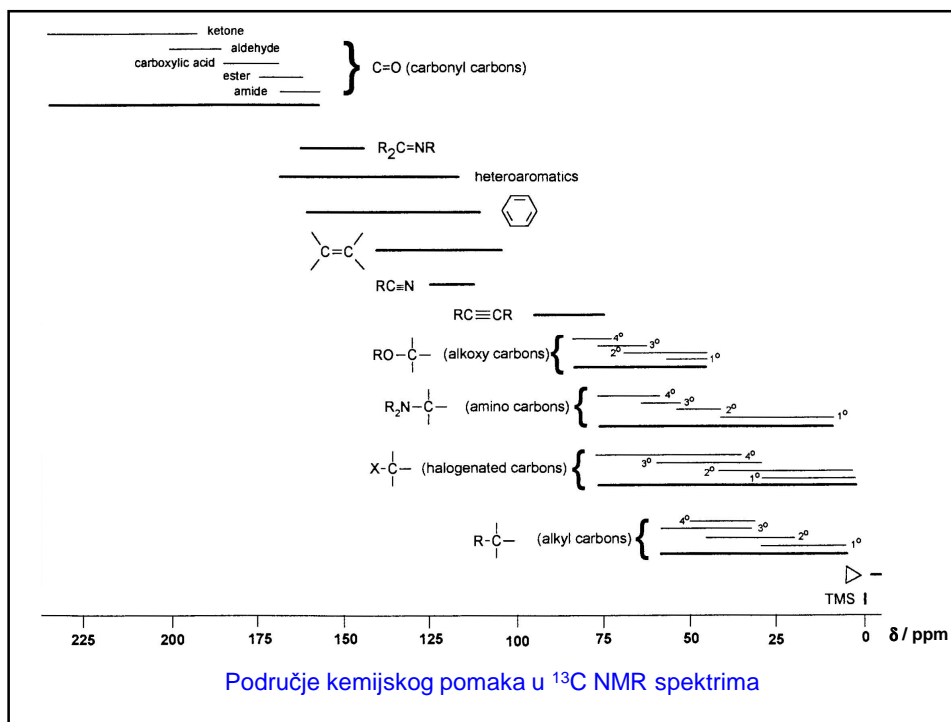
- ➔ uvodno predavanje
- ➔ općenito - uzorkovanje; norme i standardi; intelektualno vlasništvo
- ➔ STATISTIKA - osnove
- ➔ EKSTRAKCIJA, KROMATOGRAFIJA - osnove
- ➔ ELEKTROANALITIČKE METODE
- ➔ BOLTZMANNOVA RAZDIOBA
- ➔ SPEKTROSKOPIJA - osnove; zadaci
- ➔ INSTRUMENTACIJA - osnove; zadaci
- ➔ ATOMSKA SPEKTROSKOPIJA; zadaci
- ➔ MOLEKULSKA SPEKTROSKOPIJA - UV/VIS, fluorescencija
- ➔ IR i Ramanova spektroskopija
- ➔ NMR - uvod
- ➔ NMR - tehnike
- ➔ NMR - seminar
- ➔ **NMR - seminar2**

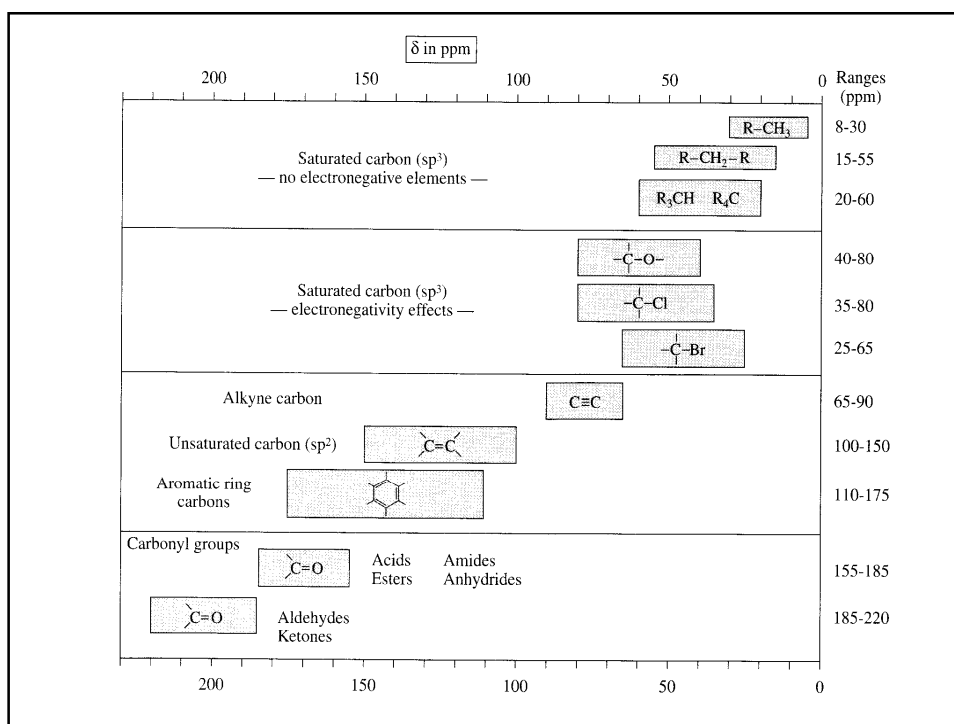
nositelj: prof.dr.sc. P. Novak; šk.g. 2012/13.
održala: Katarina Čuljak, dipl. ing.



APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS*

$R-CH_3$	0.7 - 1.3	$R-NH-CH_2$	2.2 - 2.9
$R-CH_2-R$	1.2 - 1.4	$R-S-CH_2$	2.0 - 3.0
$R-CH$	1.4 - 1.7	$I-CH_2$	2.0 - 4.0
$R-C=C-H$	1.6 - 2.6	$Br-CH_2$	2.7 - 4.1
$R-C(=O)-CH_2-H, H-C(=O)-CH_2-H$	2.1 - 2.4	$Cl-CH_2$	3.1 - 4.1
$RO-C(=O)-CH_2-H, HO-C(=O)-CH_2-H$	2.1 - 2.5	$R-S(=O)_2-CH_2-H$	ca. 3.0
$NH-C(=O)-H$	2.1 - 3.0	$RO-CH_2-H, HO-CH_2-H$	3.2 - 3.8
	2.3 - 2.7	$R-C(=O)-O-CH_2-H$	3.5 - 4.8
$R-C\equiv C-H$	1.7 - 2.7	O_2N-CH_2-H	4.1 - 4.3
$R-S-H$	var	$F-CH_2$	4.2 - 4.8
$R-N-H$	var	$R-C(=C)-H$	4.5 - 6.5
$R-O-H$	var		6.5 - 8.0
	var	$R-C(=O)-H$	9.0 - 10.0
	var	$R-C(=O)-OH$	11.0 - 12.0
$R-C(=O)-N-H$	var		



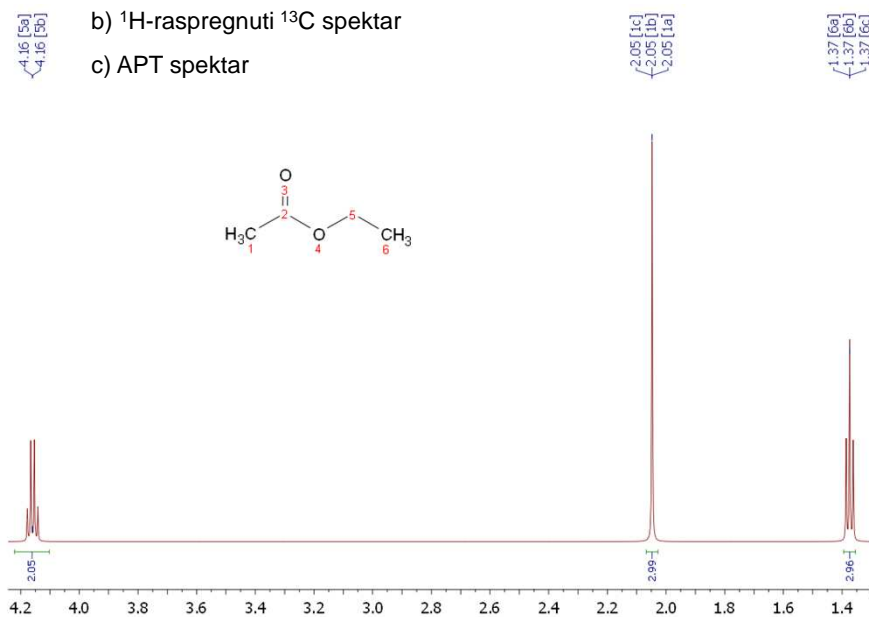


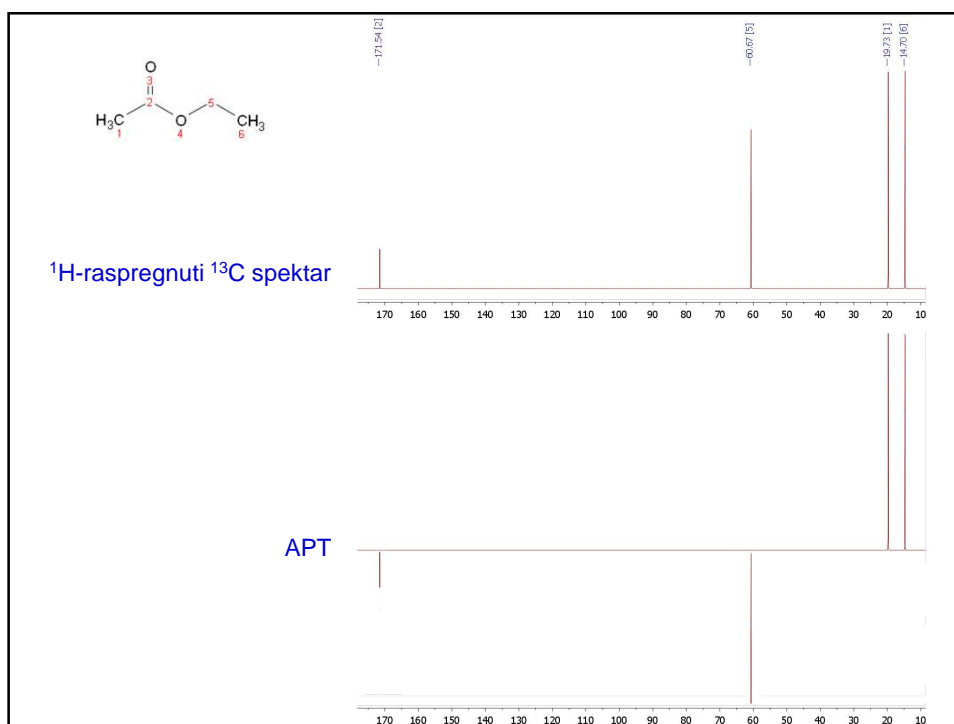
1) Za molekulu etil-acetata skicirajte sljedeće NMR spektre:

a) ¹H spektar

b) ¹H-raspregnuti ¹³C spektar

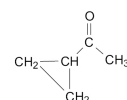
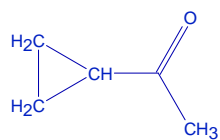
c) APT spektar



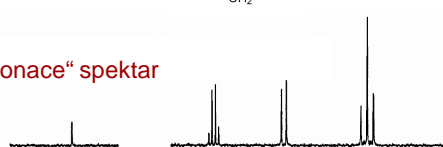


2) Za molekulu ciklopropil-metil-ketona nacrtajte sljedeće ¹³C spektre:

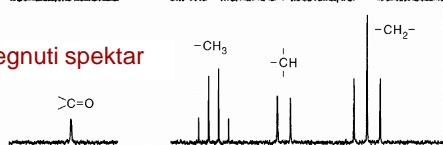
- a) ¹H-raspregnuti spektar
 b) APT spektar
 c) ¹H-spregnuti spektar
 d) "off resonance" spektar



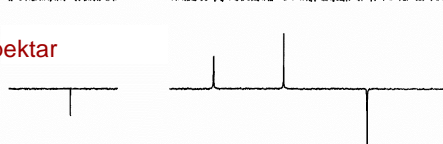
c) "off resonance" spektar



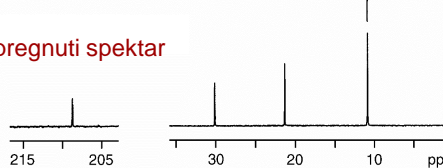
c) ¹H-spregnuti spektar



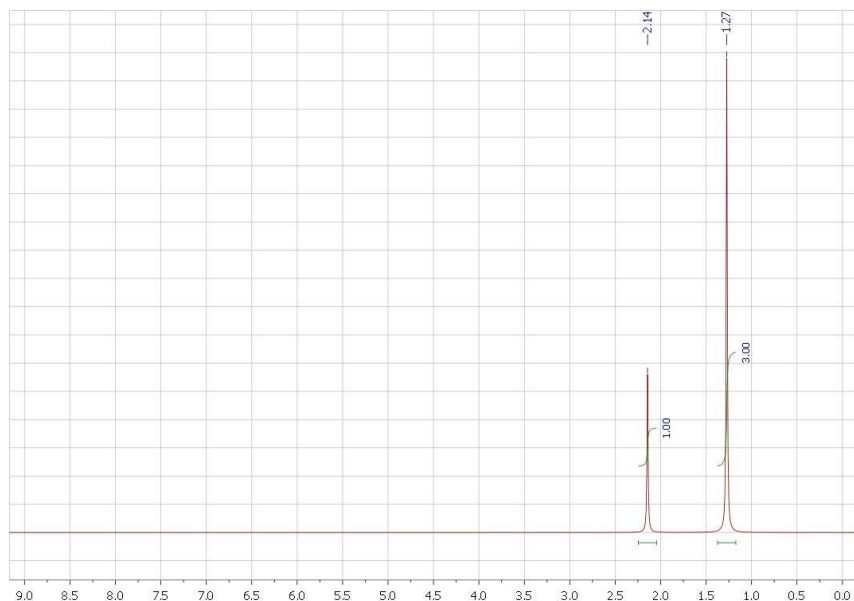
b) APT spektar



a) ¹H-raspregnuti spektar



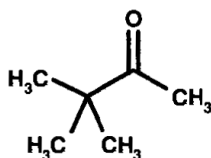
3) Odredite strukturu spoja čiji je ^1H NMR spektar prikazan na slici. Molekulska formula navedenog spoja je $\text{C}_6\text{H}_{12}\text{O}$.



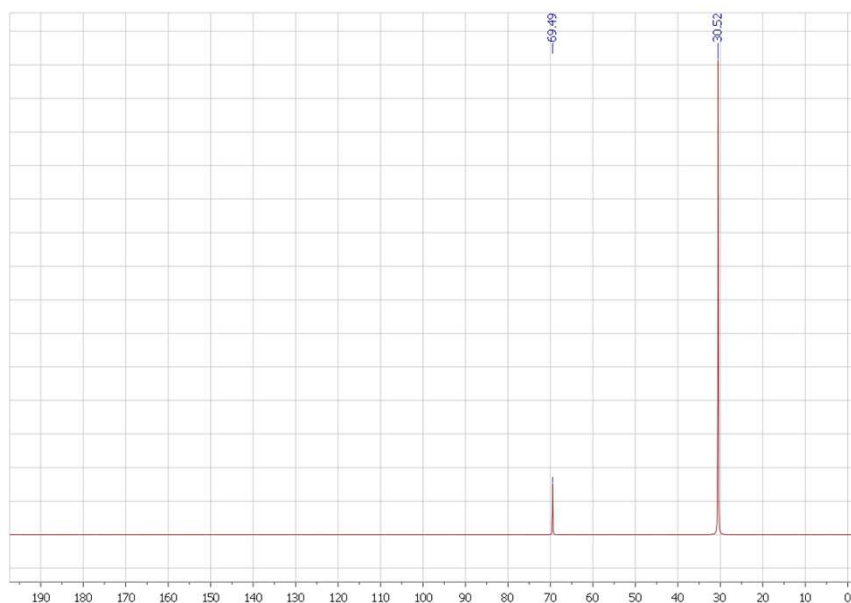
-indeks manjka vodika, *index of hydrogen deficiency* (IHD)

$$\text{IHD} = \frac{1}{2}[2C + 2 + N - (H + X)]$$

- za ovaj spoj: $\text{IHD} = [2 \cdot 6 + 2 - 12] / 2 = 1$
- jedan prsten ili dvostruka veza
- 12 H atoma
- 9 ekvivalentnih H atoma pri 1,15 ppm i 3 ekvivalentna H atoma pri 2,14 ppm
- *tert*-butilna skupina, $(\text{CH}_3)_3\text{C}-$, pri 1,15 ppm
- metilna skupina, CH_3- , vezana za karbonilnu, $\text{C}=\text{O}$, pri 2,14 ppm
- rješenje:



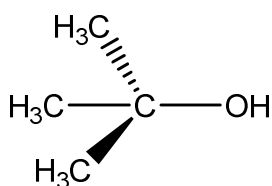
4) Odredite strukturu spoja čiji je ^{13}C NMR spektar prikazan na slici. Molekulska formula navedenog spoja je $\text{C}_4\text{H}_{10}\text{O}$.



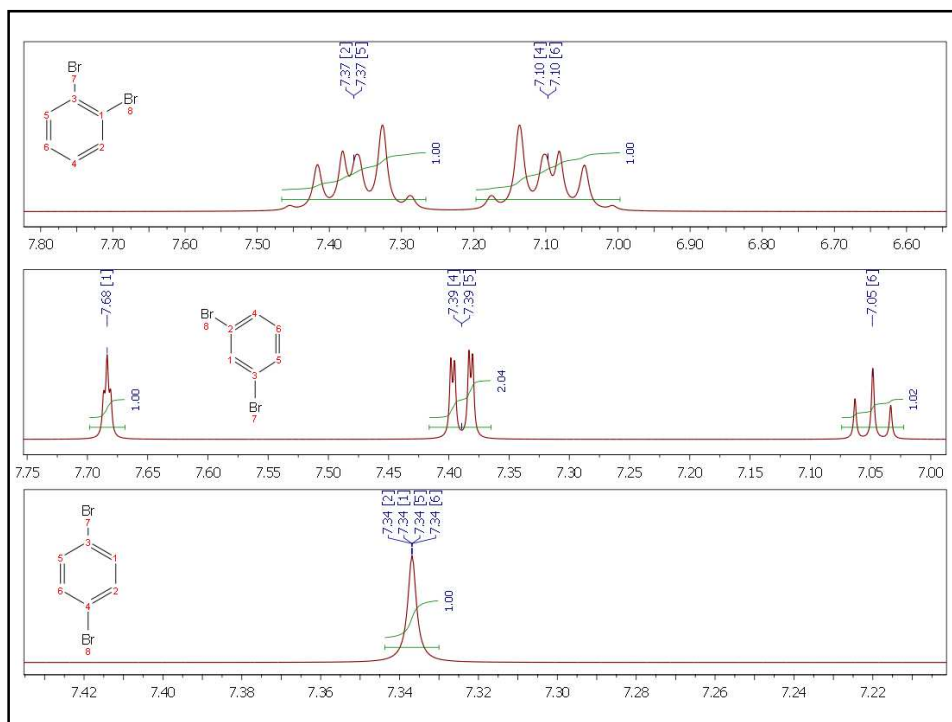
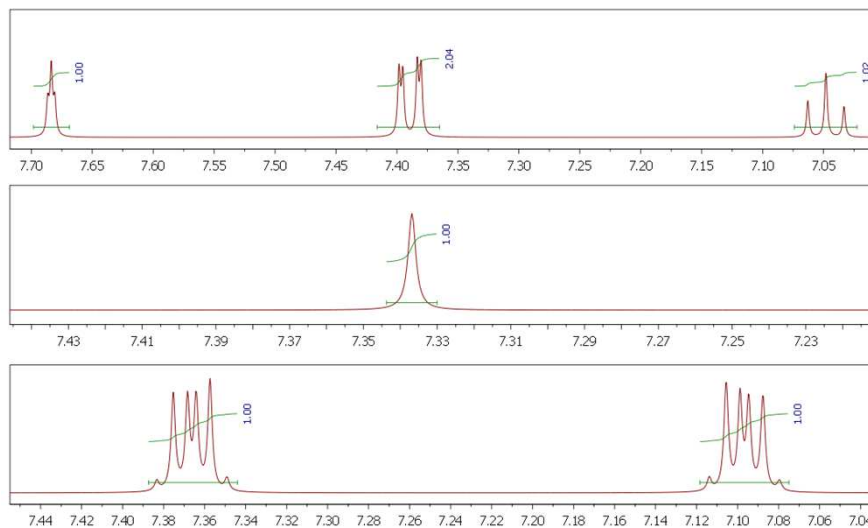
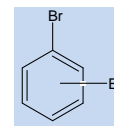
$$\text{IHD} = [2 \cdot 4 + 2 - 10] / 2 = 0$$

$\delta(^{13}\text{C})/\text{ppm}$	C-atom
30,1	-CH ₃
60,9	

-rješenje:

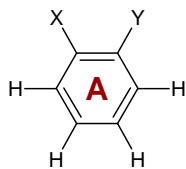


5) Na temelju prikazanih ^1H NMR spektara odredite položaj supstitucije u izomerima dibrombenzena.

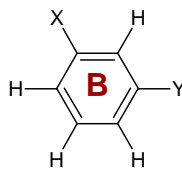


6) Koliko signala u ^1H i ^{13}C NMR spektrima očekujete za svaku navedenu strukturu:

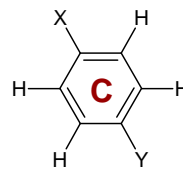
- a) ako je $X = Y \neq \text{H}$
 b) ako je $X \neq Y \neq \text{H}$?



orto



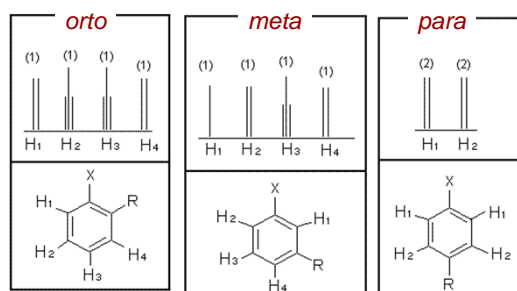
meta



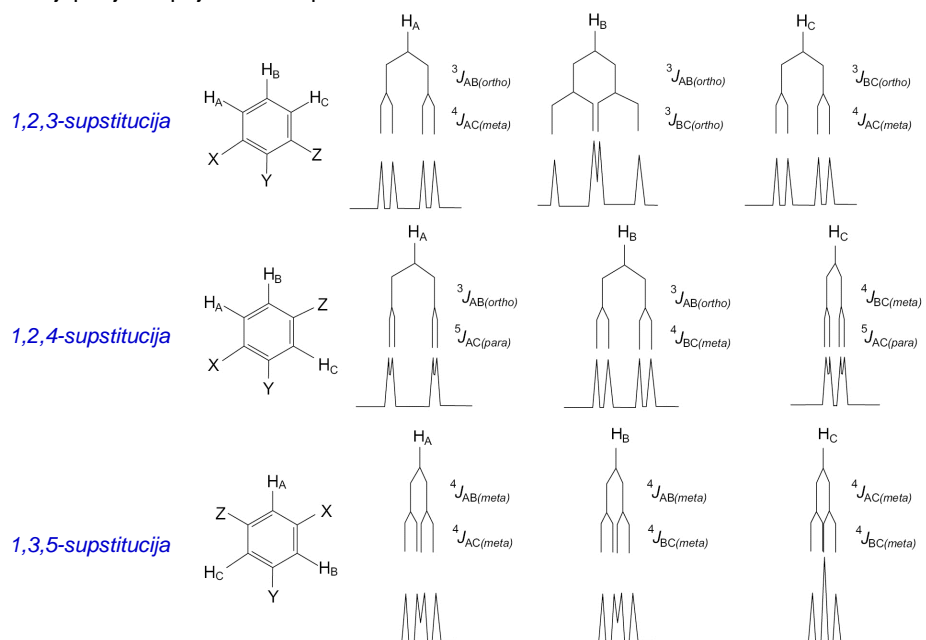
para

a) ^1H	2	3	1
^{13}C	3	4	2
b) ^1H	4	4	2
^{13}C	6	6	4

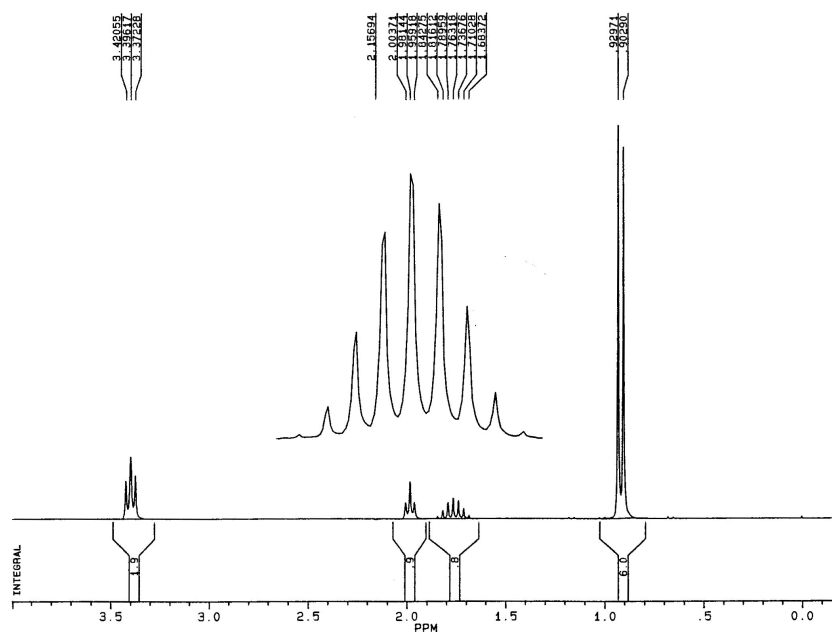
Shematski prikaz multipljeta protona za disupstituirani benzen; $X \neq R \neq \text{H}$



7) Nacrtajte multiplete protona u trisupstutuiranom benzenu te skicirajte dijagram cijepanja za pojedini multiplet.

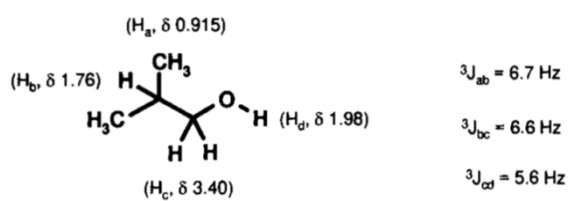


8) Prikazani spektar pripada organskom spoju molarne mase 74 g/mol, koji sadrži ugljik, vodik i kisik. Identificirajte spoj.

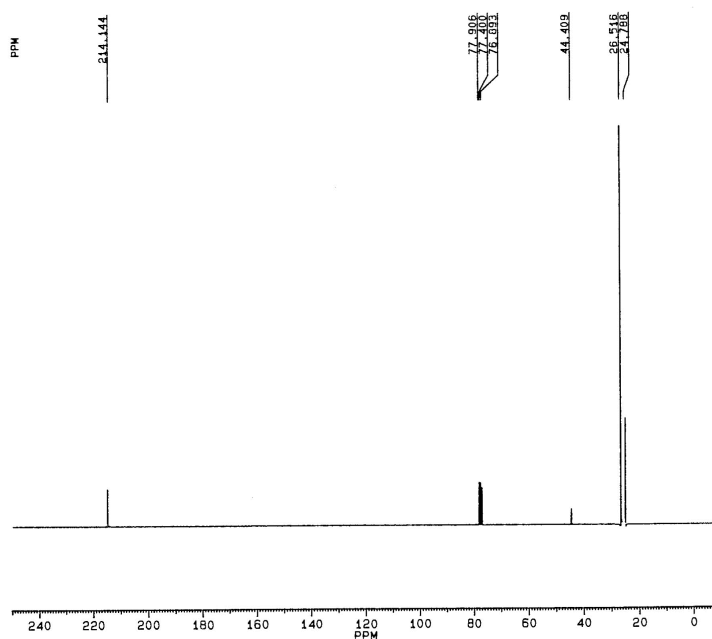


$\delta(^1\text{H})/\text{ppm}$	integral	multipletnost	H-atom
0,91	6,0	d	-CH ₃
1,75	0,8	m (nonet)	>CH
1,98	0,9	t	-OH
3,40	1,9	t	-CH ₂ -

- rješenje:



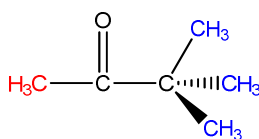
- 9) Identificirajte spoj molekulske formule C₆H₁₂O čiji je ¹³C NMR spektar prikazan na slici. Otkuda potječu signali pri 76,9 ppm, 77,4 ppm i 77,9 ppm?



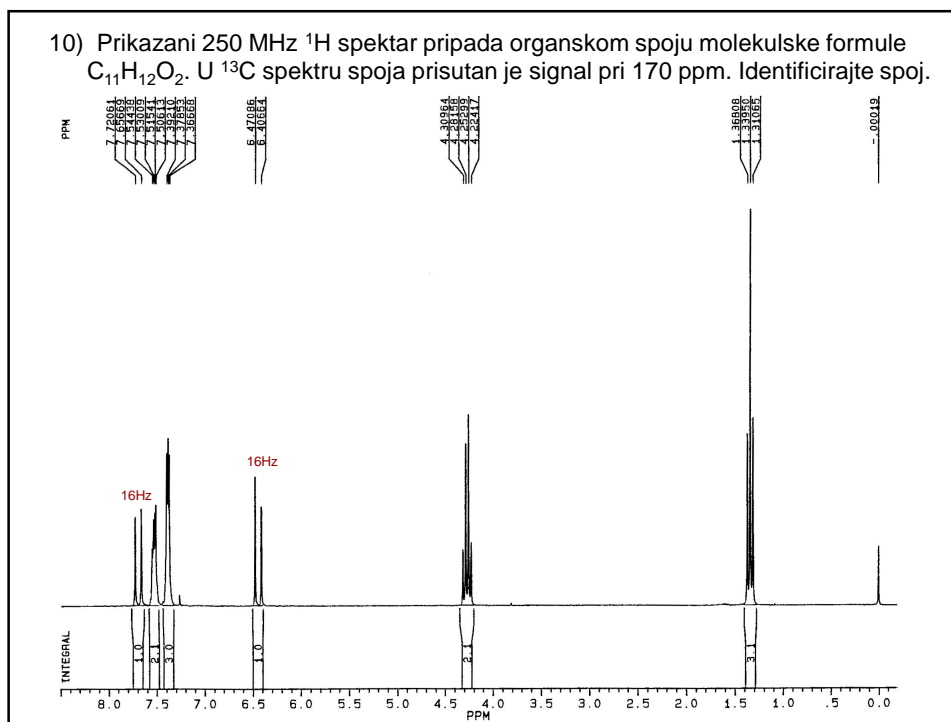
$$\text{IHD} = [2 \cdot 6 + 2 - 12] / 2 = 1$$

$\delta(^{13}\text{C})/\text{ppm}$	C-atom
24,7	-CH ₃
26,5	-CH ₃
44,4	
214,1	



-rješenje:



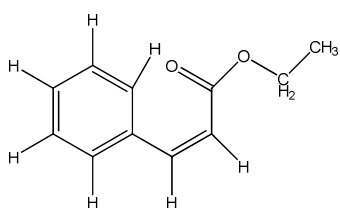
-Signali pri 76,9 ppm, 77,4 ppm i 77,9 ppm potječu od rezonancije deuteriranog kloroforma



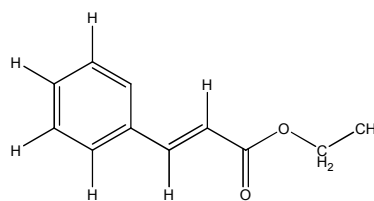
$$\text{IHD} = [2 \cdot 11 + 2 - 12] / 2 = 6$$

$\delta(^1\text{H})/\text{ppm}$	integral	multiplet	H-atom
1,34	3,1	t	-CH ₃
4,27	2,1	q	-CH ₂ -
6,44	1,0	d	=CH-
7,37	3,0	m	aromatski 
7,51	2,0	m	aromatski 
7,68	1,0	d	=CH-

- moguće strukture:



A



B

$J=16$ Hz

cis-sprega: 10-12 Hz

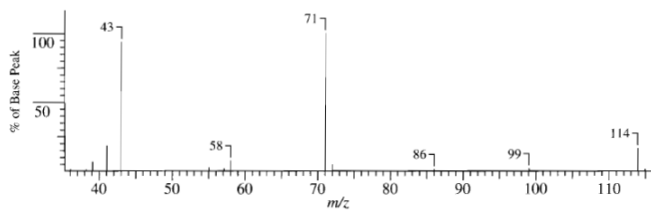
trans-sprega: 16-18 Hz

rješenje:

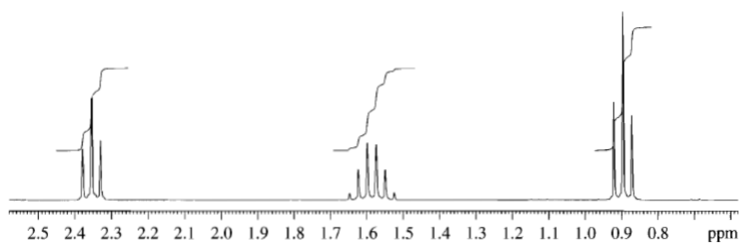
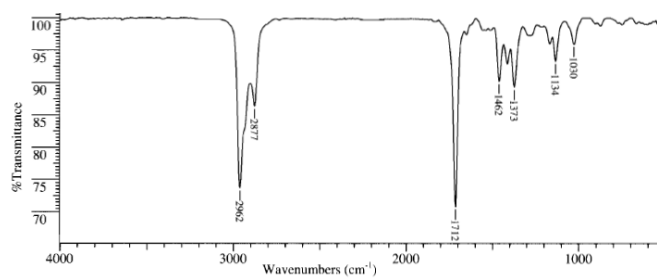
izomer B (*trans*-izomer)

11) Identificirajte spoj na temelju njegovih MS, IR i ^1H NMR spektara.

MS spektar



IR spektar



^1H NMR spektar

-informacije iz MS:

M^+ = 114

bazni pik: $m/z=71$

-informacije iz IR:

1712 cm^{-1} C=O

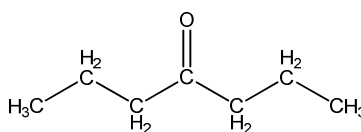
2877 cm^{-1} C-H istezanje

2962 cm^{-1} C-H istezanje

- informacije iz ^1H NMR:

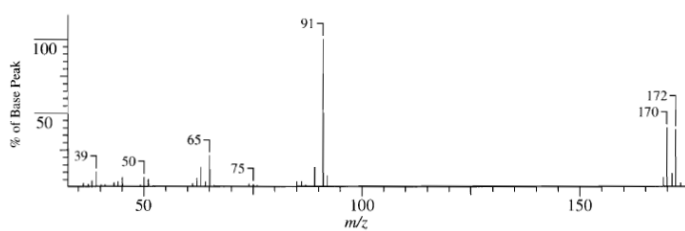
$\delta(^1\text{H})/\text{ppm}$	integral	multiplet	H-atom
0,90	3	t	$-\text{CH}_3$
1,57	2	m	$-\text{CH}_2-$
2,35	2	t	$-\text{CH}_2-$

- rješenje:

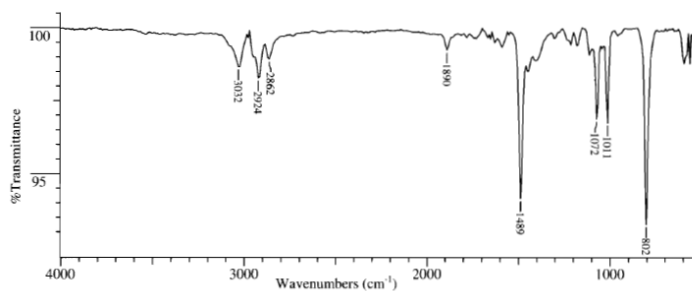


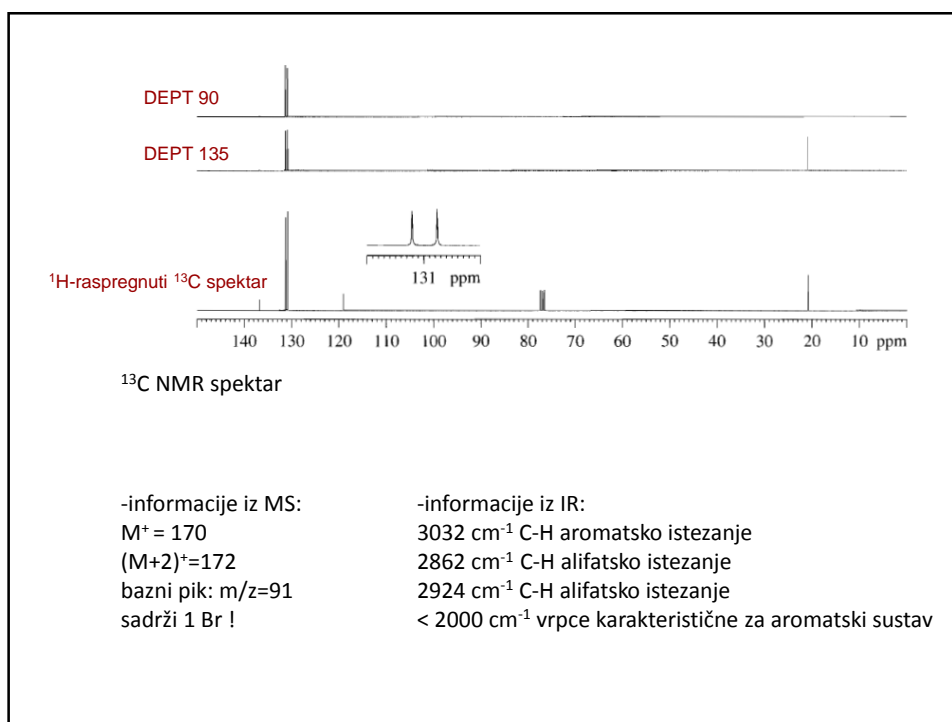
12) Identificirajte spoj na temelju njegovih MS, IR i ^{13}C NMR spektara.

MS spektar







IR spektar

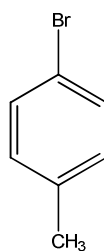




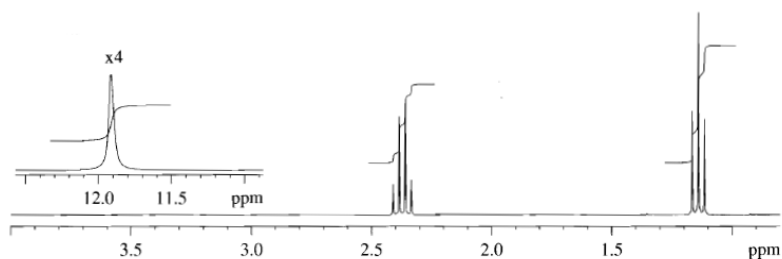
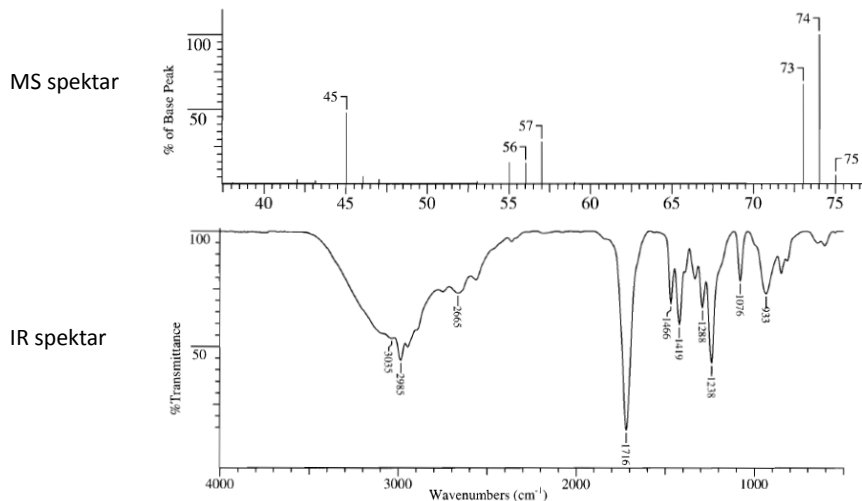
- informacije iz ¹³C NMR:

$\delta(^{13}\text{C})/\text{ppm}$	C-atom
21,0	-CH ₃
118,0	aromatski 
130,8	aromatski 
131,2	aromatski 
137,0	aromatski 

- rješenje:



13) Identificirajte spoj na temelju njegovih MS, IR i ^1H NMR spektara.



^1H NMR spektar

-informacije iz MS:

$M^+ = 74$

$(M+1)^+ = 75$

bazni pik: $m/z = 74$

-informacije iz IR:

$3500 - 2500\text{ cm}^{-1}$ O-H istezanje

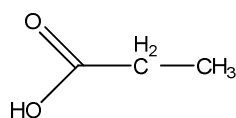
1716 cm^{-1} C=O istezanje

2985 cm^{-1} C-H alifatsko istezanje

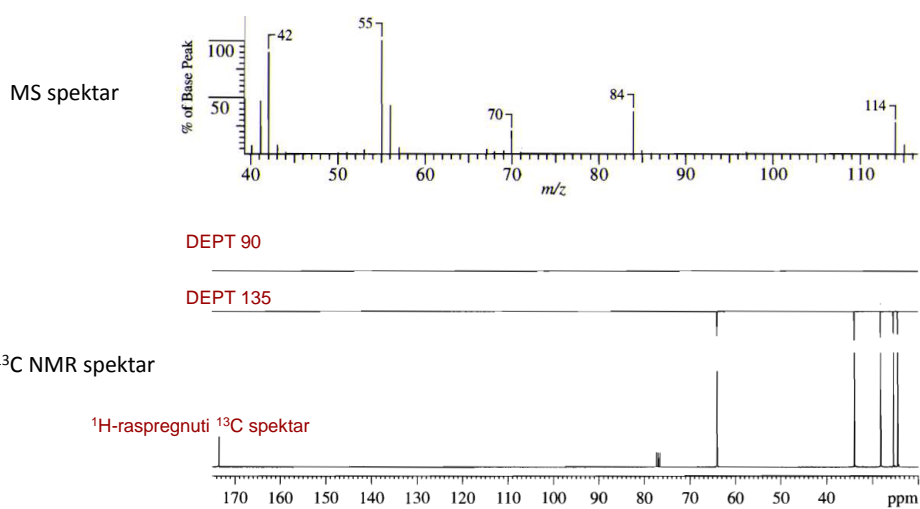
- informacije iz ^1H NMR:

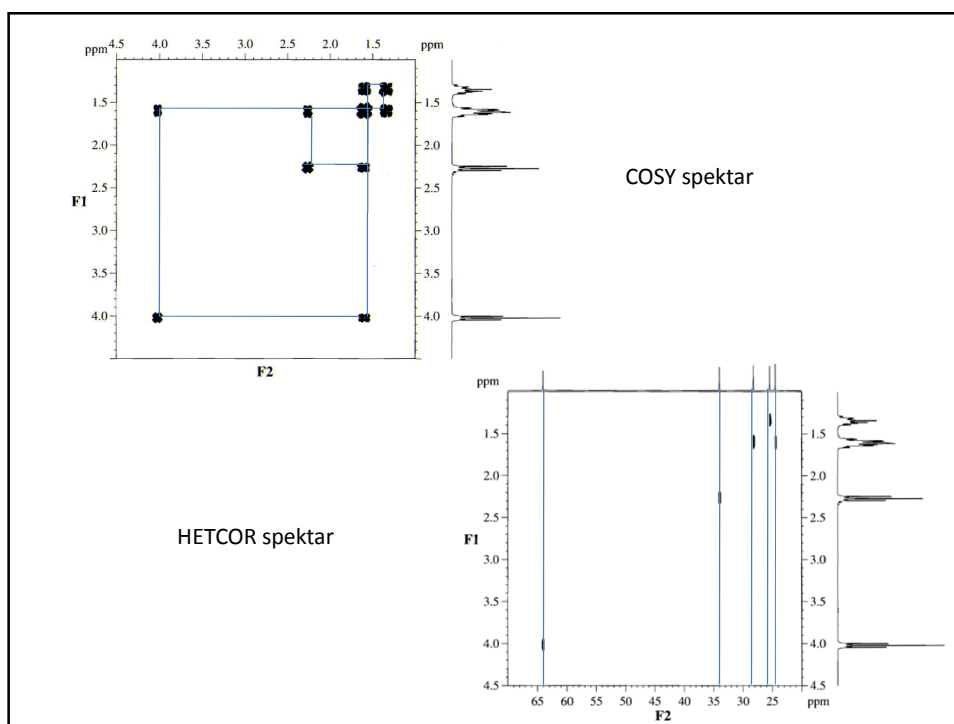
$\delta(^1\text{H})/\text{ppm}$	integral	multiplet	H-atom
1,15	3	t	$-\text{CH}_3$
2,35	2	q	$-\text{CH}_2-$
11,90	1	s	$-\text{OH}$

- rješenje:



14) Riješite strukturu spoja na temelju njegovih IR, ^{13}C , COSY i HETCOR spektara.





-informacije iz MS:

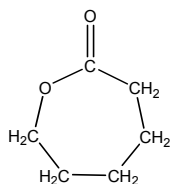
$M^+ = 114$

bazni pik: $m/z=55$

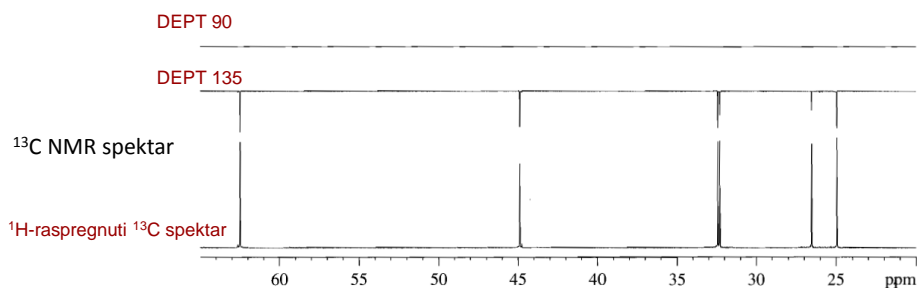
- informacije iz ^{13}C NMR:

$\delta(^{13}\text{C})/\text{ppm}$	C-atom
24	$-\text{CH}_2-$
26	$-\text{CH}_2-$
28	$-\text{CH}_2-$
34	$-\text{CH}_2-$
63	$-\text{CH}_2-$
173	$\text{C}=\text{O}$

- rješenje:



15) Riješite strukturu spoja molarne mase 136, a koji sadrži 1 atom klora na temelju njegovih ^{13}C NMR, COSY i HMQC spektara.



- informacije iz ^{13}C NMR:

$\delta(^{13}\text{C})/\text{ppm}$	C-atom
25,0	$-\text{CH}_2-$
26,5	$-\text{CH}_2-$
32,2	$-\text{CH}_2-$
32,5	$-\text{CH}_2-$
45,0	$-\text{CH}_2-$
62,5	$-\text{CH}_2-$

