

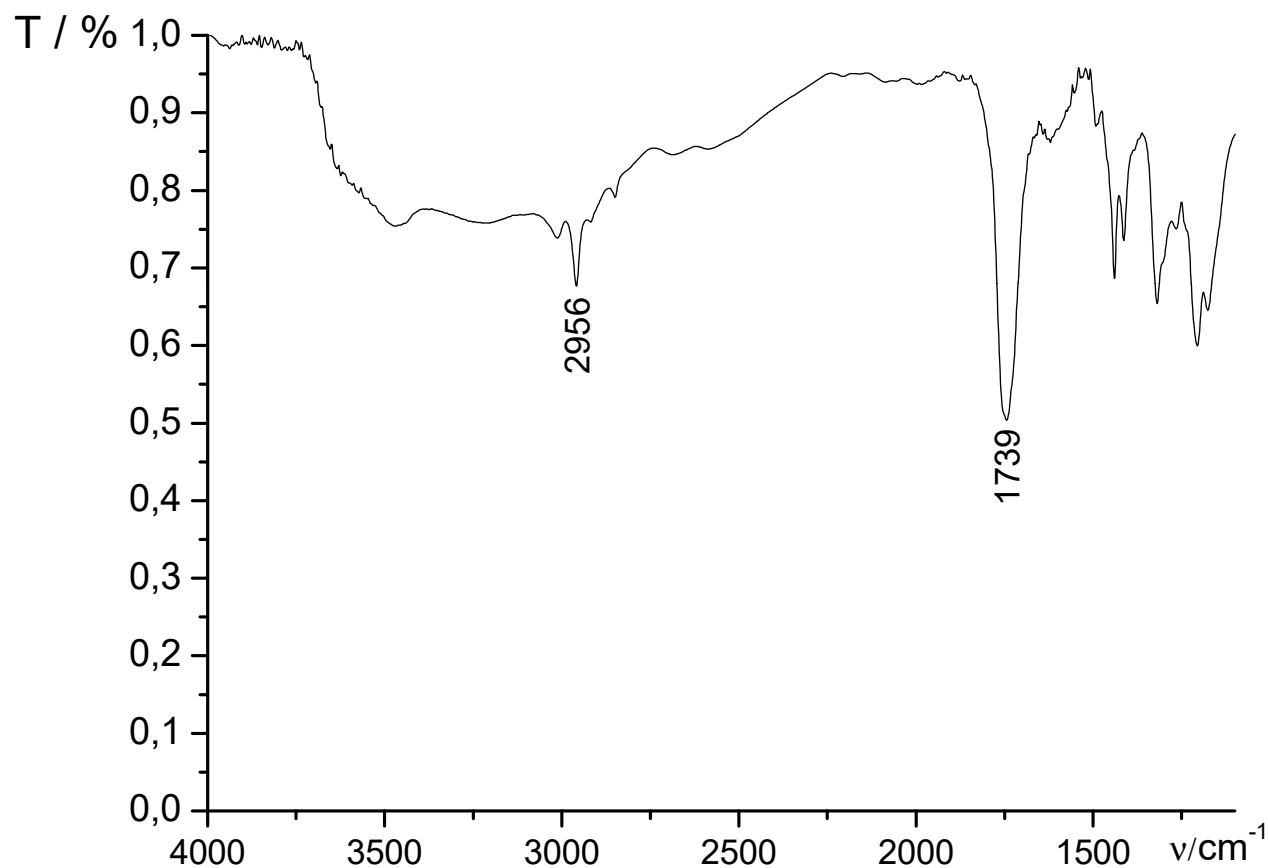
Spektroskopska strukturna analiza

prof. dr. sc. Predrag Novak
izv. prof. dr. sc. Tomislav Jednačak; ak. god. 2024./25.

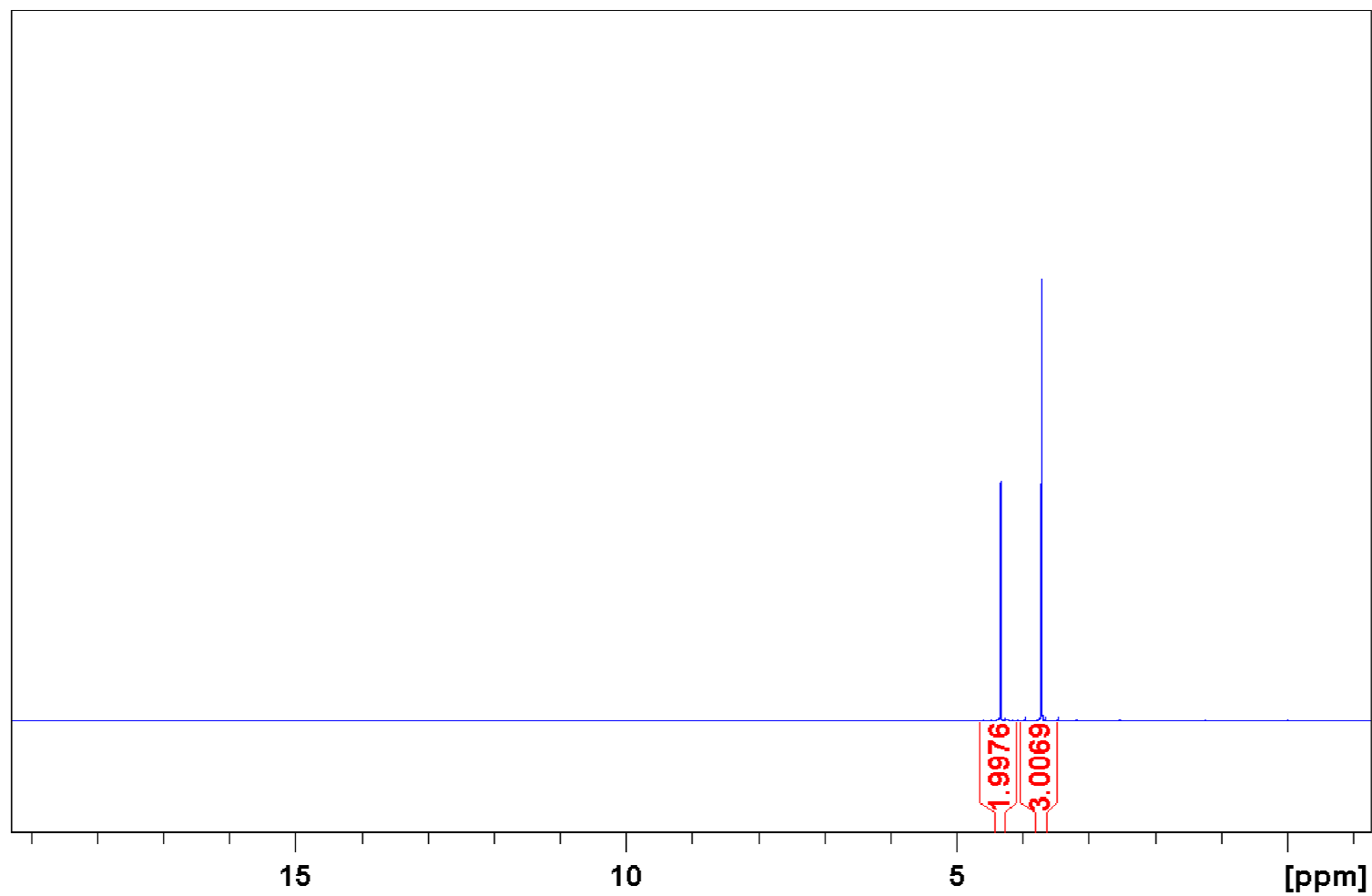
Literatura

1. P. Novak, T. Jednačak, *Strukturna analiza spojeva spektroskopskim metodama*, TIVA, Varaždin, 2013.
2. J. B. Lambert, S. Gronert, H. F. Shurvell, D. A. Lightner, *Organic Structural Spectroscopy*, Pearson, Amsterdam, 2011.
3. R. M. Silverstein, F. X. Webster, D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, 2005.
4. E. Pretsch, P. Bühlmann i C. Affolter, *Structure Determination of Organic Compounds - Tables of Spectral Data*, Springer, Berlin, 2000.
5. M. Hesse, H. Meier i B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 2005.
6. T. D. W. Claridge, *High Resolution NMR Techniques in Organic Chemistry*, Pergamon, Amsterdam, 2009.
7. H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, Wiley-VCH, Weinheim, 2005.
8. E. de Hoffman, V. Stroobant, *Mass Spectrometry - Principles and Applications*, Wiley, Chichester, 2003.

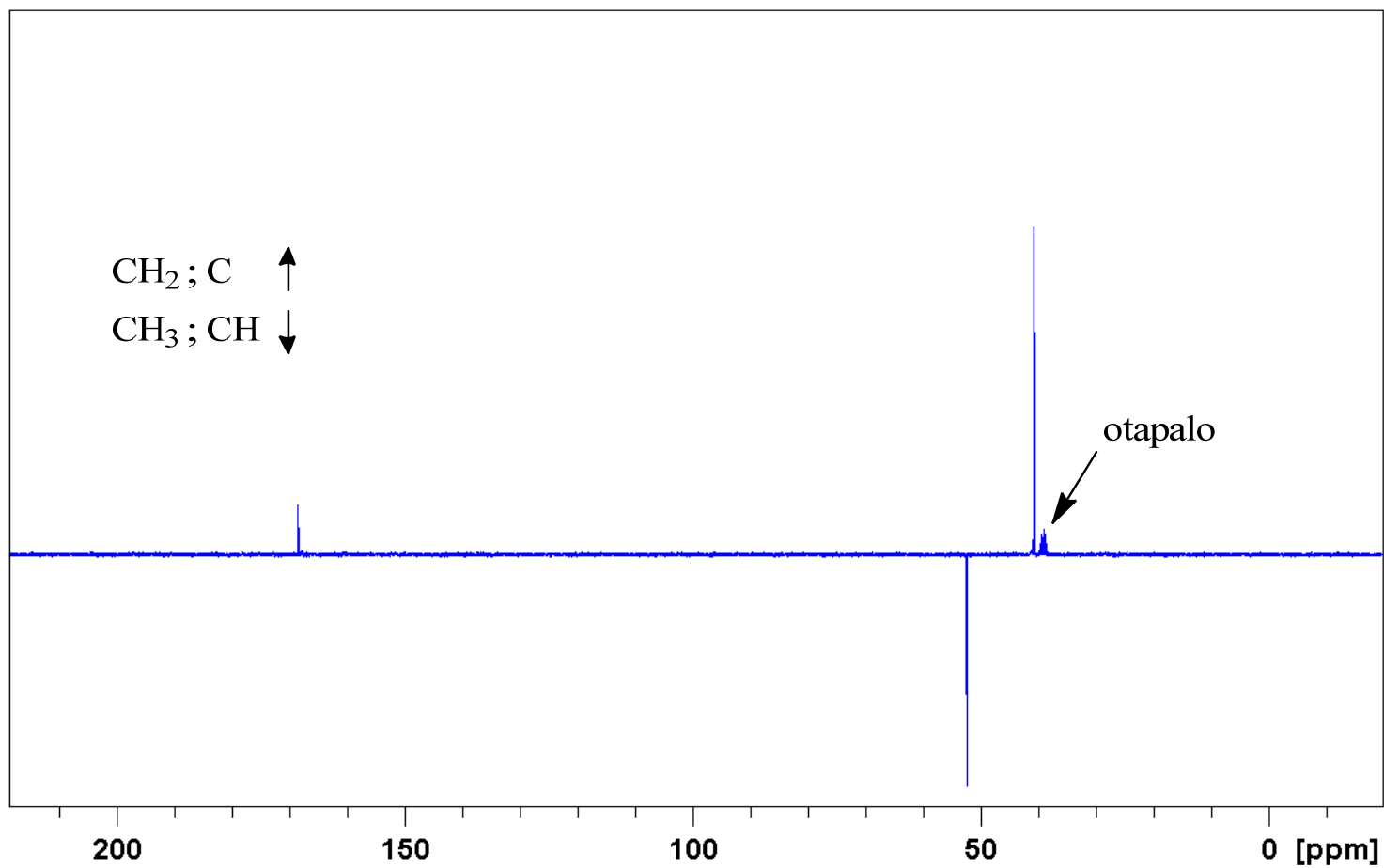
1. Odredite strukturu spoja molekulske mase 108 g/mol na temelju njegovog infracrvenog, ^1H NMR i APT spektra



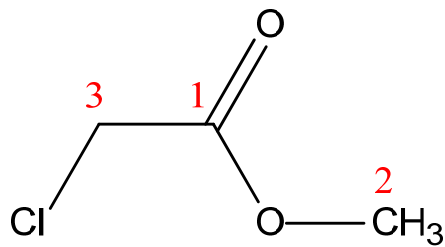
Infracrveni spektar spoja snimljen u tekućinskoj kiveri od CaF_2 .



^1H NMR spektar spoja snimljen u DMSO- d_6 .



APT spektar spoja snimljen u DMSO-d₆.



Struktura spoja i brojanje atoma.

Karakteristične vibracijske vrpce u infracrvenom spektru spoja

ν / cm^{-1}	Način vibracije
2956	$\nu (\text{C-H})_{\text{alifatsko}}$
1739	$\nu (\text{C=O})$

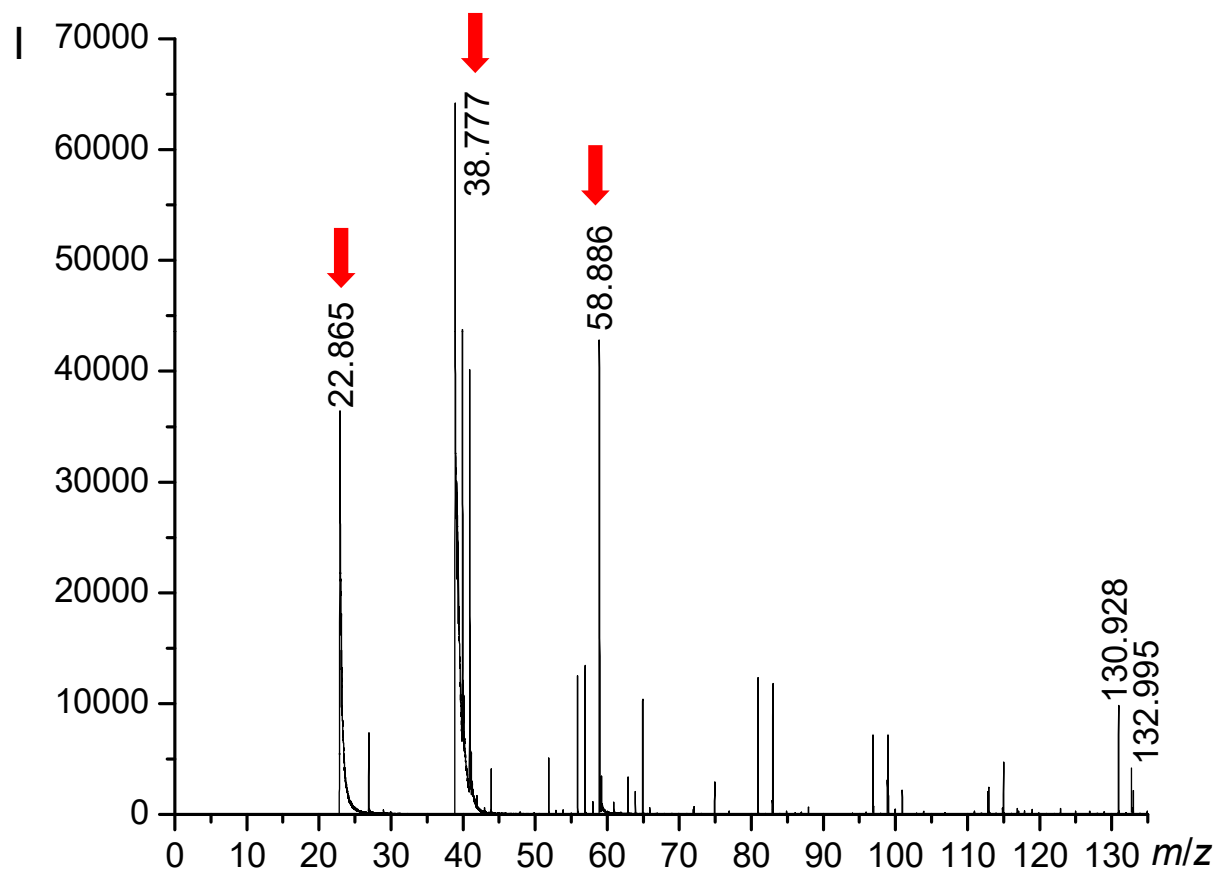
Asignacija ^1H NMR kemijskih pomaka spoja

H-atom	δ / ppm	Intenzitet	Multipletnost
1			
2	3,7	3,01	s
3	4,3	1,99	s

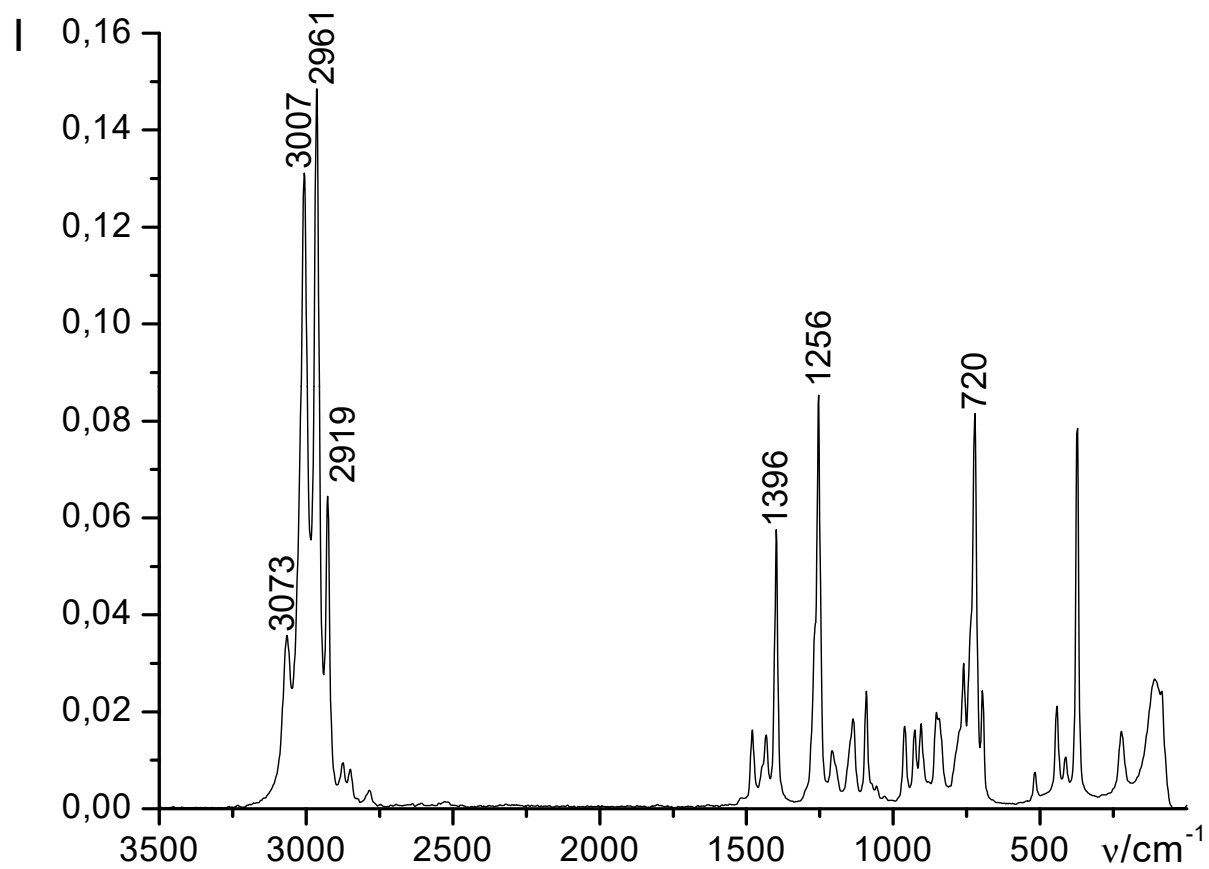
Asignacija ^{13}C NMR kemijskih pomaka spoja

C-atom	δ / ppm
1	170
2	53
3	40

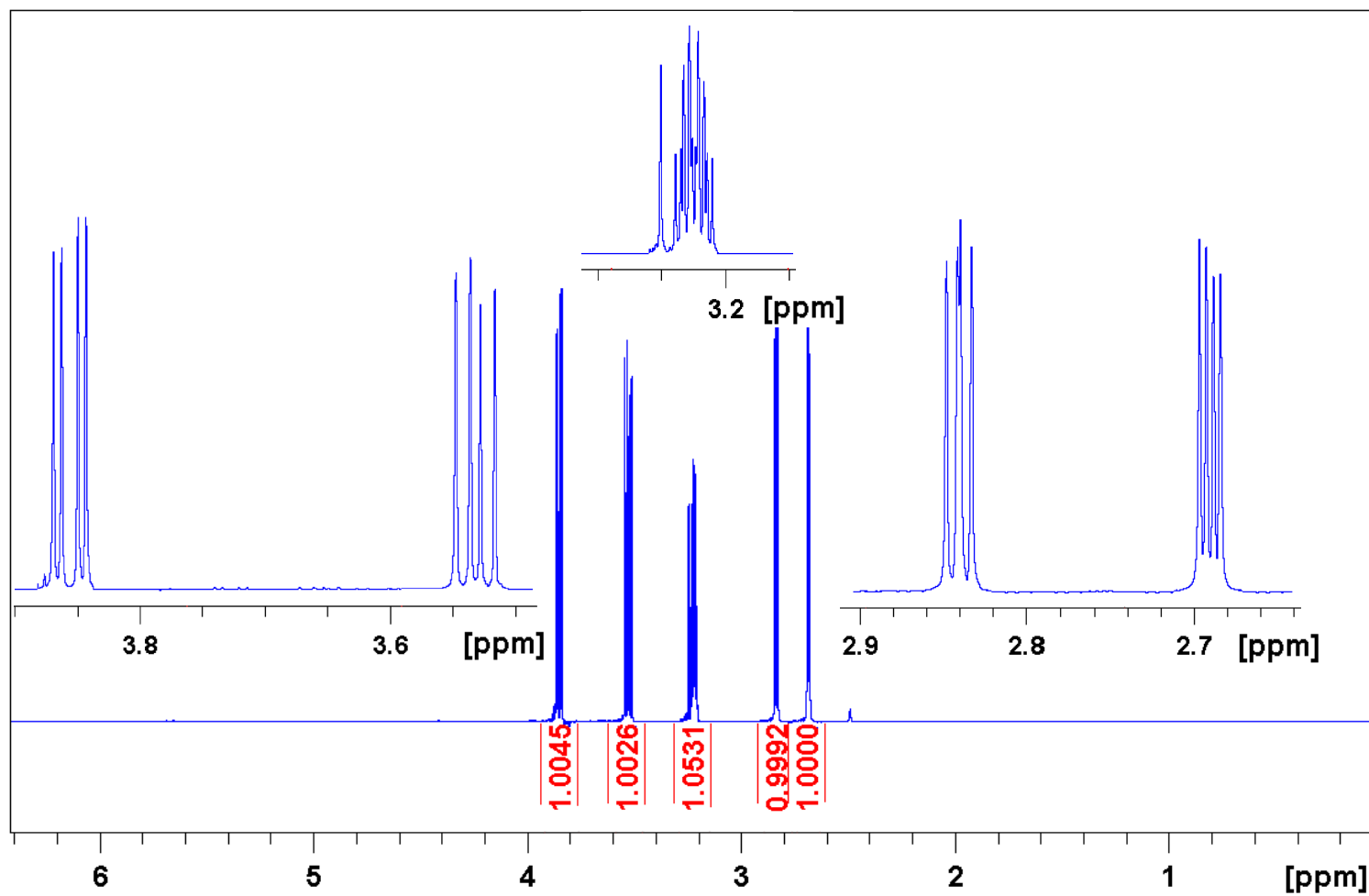
2. Odredite strukturu spoja na temelju njegovog MS, Ramanovog, ^1H NMR, APT, COSY i HSQC spektra.



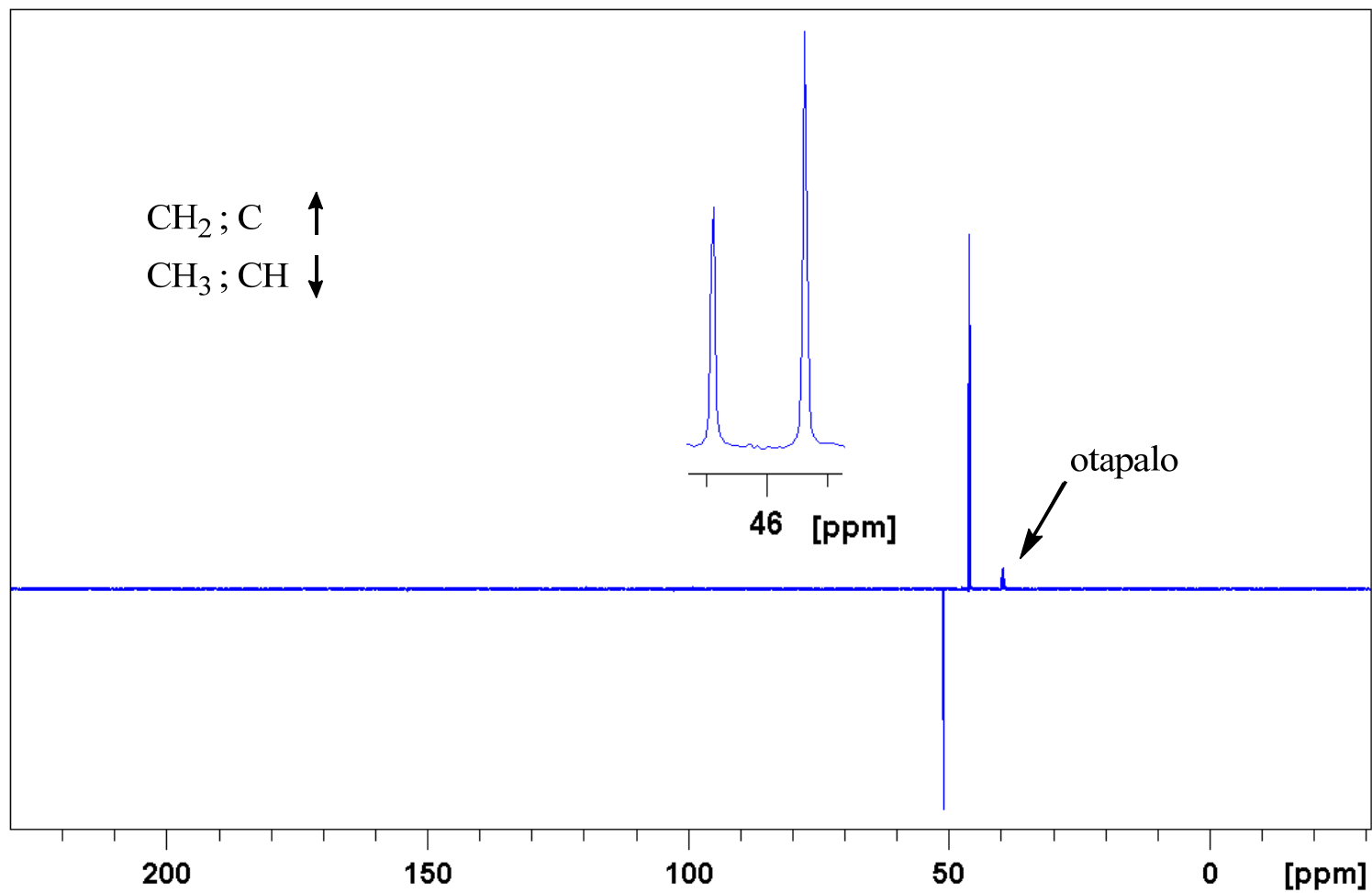
Spektar masa spoja dobiven tehnikom MALDI-TOF. Uzorak je otopljen u smjesi acetona i vode (v/v=1:1). Signali označeni crvenim strelicama odgovaraju ionima Na^+ , K^+ i Cl^- koji su prisutni u matrici uzorka te njihovim aduktima.



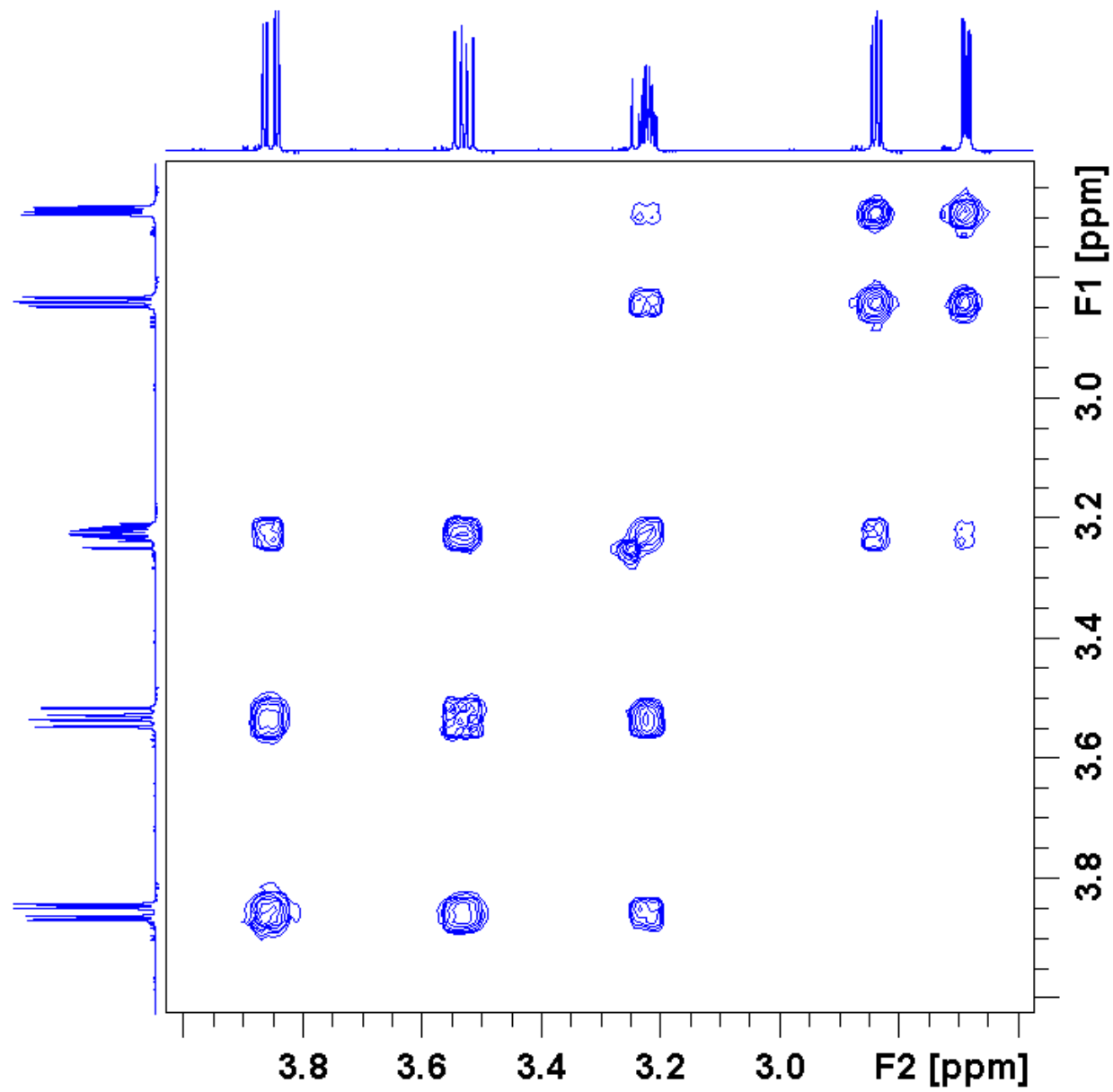
Ramanov spektar spoja.



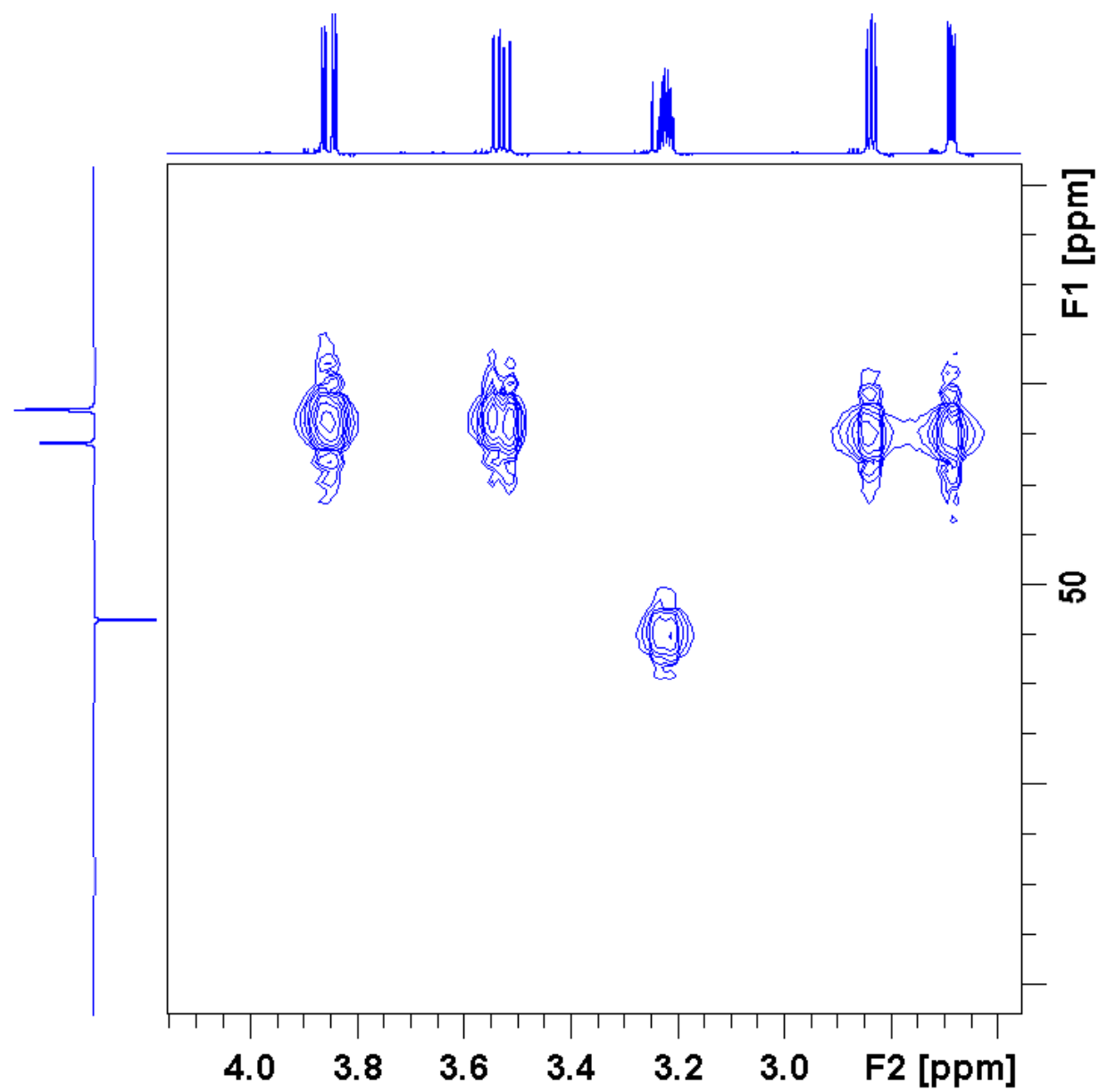
^1H NMR spektar spoja snimljen u DMSO-d_6 uz uvećani prikaz područja koja odgovaraju pojedinim signalima.



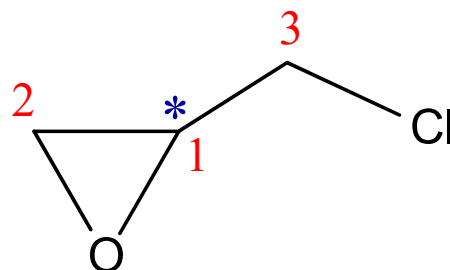
APT spektar spoja snimljen u DMSO-d₆ uz uvećani prikaz područja koja odgovaraju pojedinim signalima.



COSY spektar spoja snimljen u DMSO-d₆.



HSQC spektar spoja snimljen u DMSO- d_6 .



Struktura spoja i brojanje atoma. Simbolom * označen je kiralni centar.

Asignacija karakterističnih fragmenata u spektru masa spoja

Signal	m/z
bazni signal	38,777
Na ⁺	22,885
K ⁺	38,777
NaCl ^{•+}	58,886
(M+K) ⁺	130,928
(M+2+K) ⁺	132,995

Karakteristične vibracijske vrpce u Ramanovom spektru spoja

ν / cm^{-1}	Način vibracije
3073; 3007; 2961; 2919	$\nu (\text{C-H})$
1396	$\delta (\text{CH}_2)$
1256	$\nu_s (\text{C-O})$
720	$\nu_{as} (\text{C-O})$

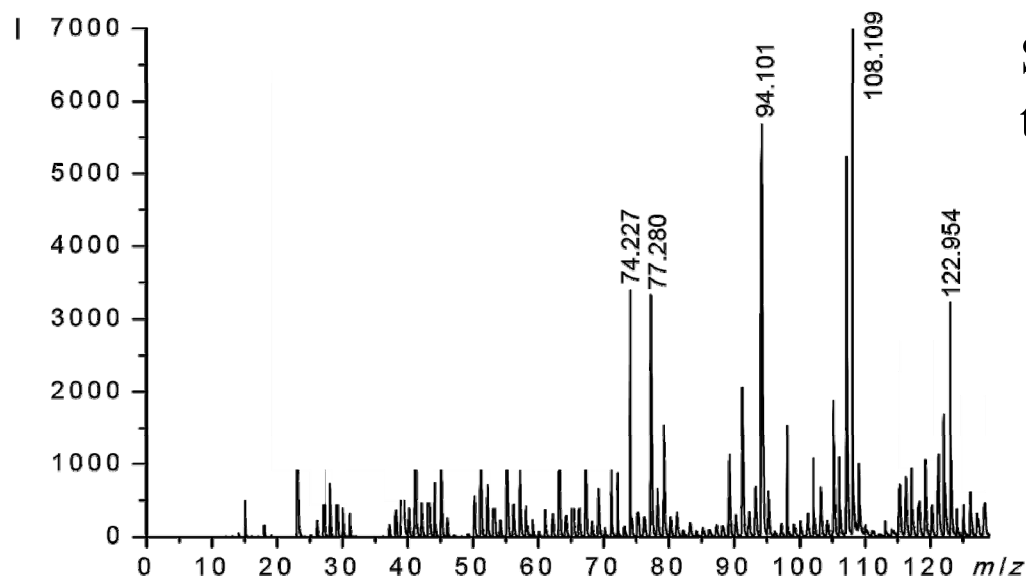
Asignacija ^1H NMR kemijskih pomaka spoja

H-atom	δ / ppm	Intenzitet	Multipletnost
1	3,12	1,0	m
2	2,69; 2,84	2,0	dd
3	3,83; 3,56	2,0	dd

Asignacija ^{13}C NMR kemijskih pomaka spoja

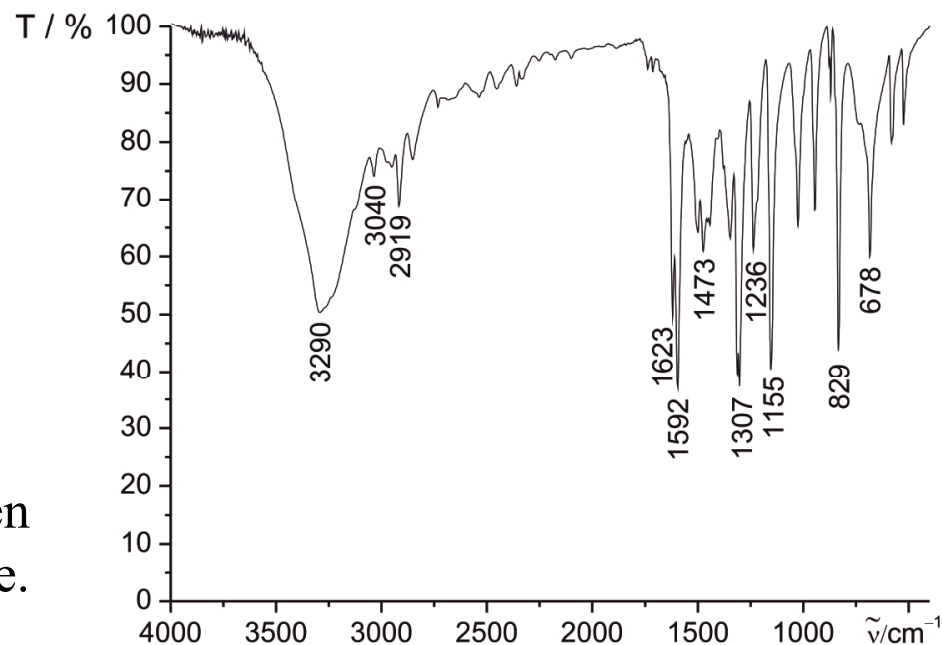
C-atom	δ / ppm
1	52
2	46,2
3	45,8

3. Odredite strukturu spoja na temelju njegovog MS, IR, ^1H NMR, APT, HSQC i HMBC spektra

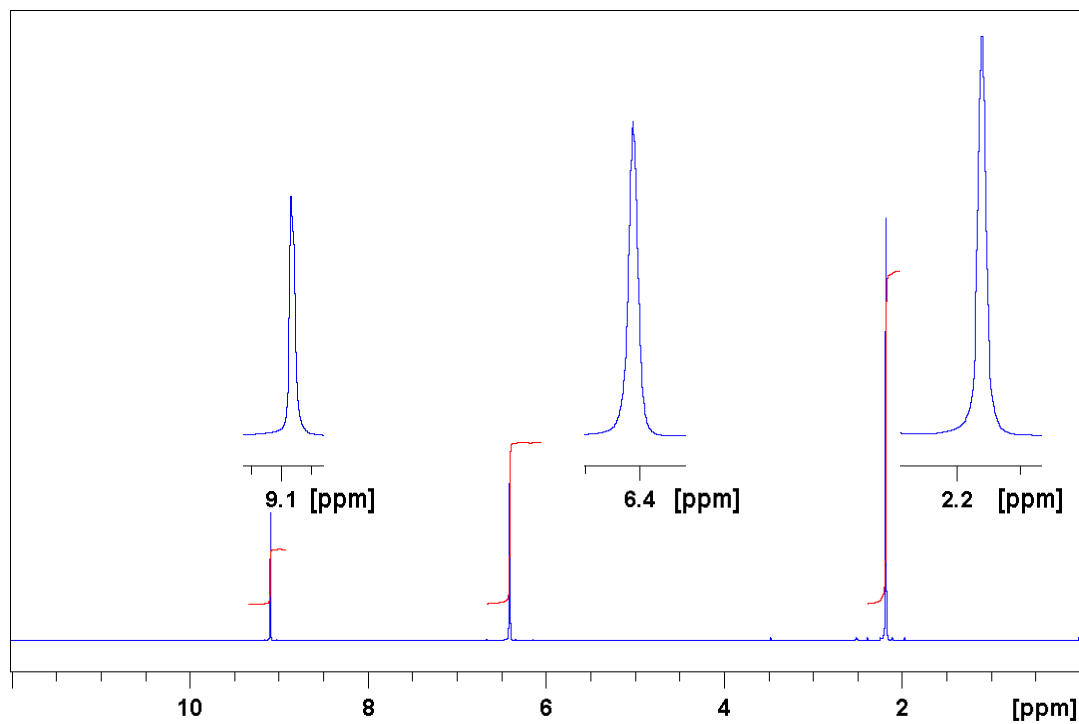


Spektar masa spoja dobiven tehnikom MALDI-TOF.

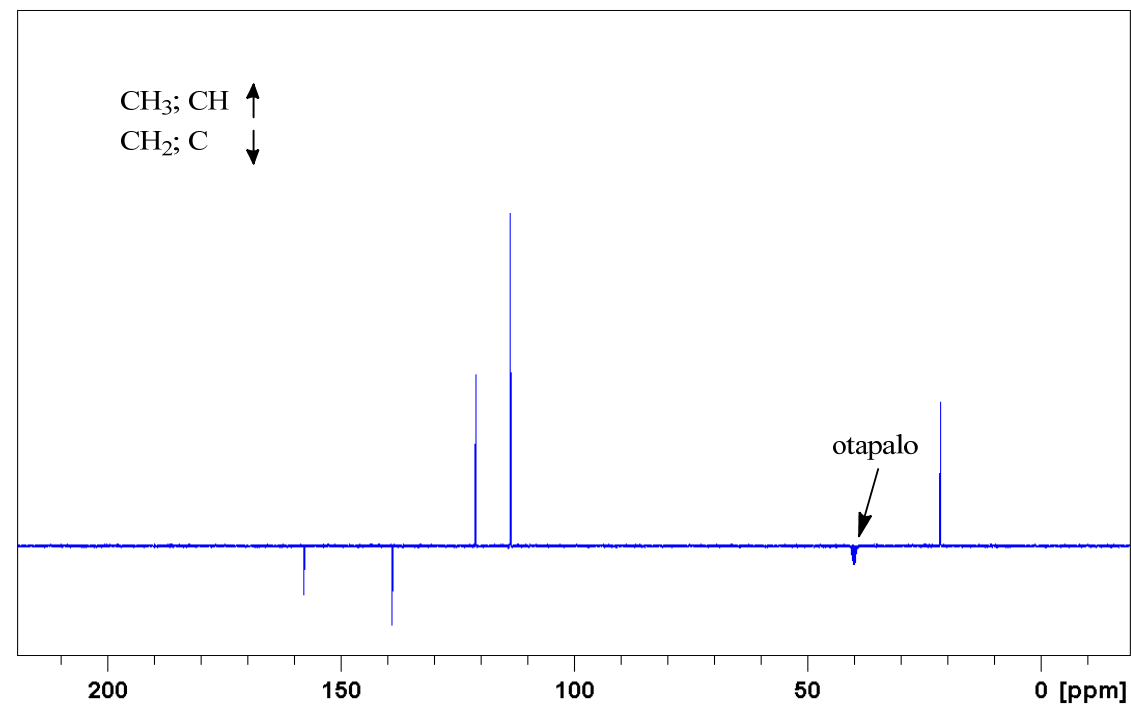
IR spektar spoja snimljen tehnikom KBr pastile.

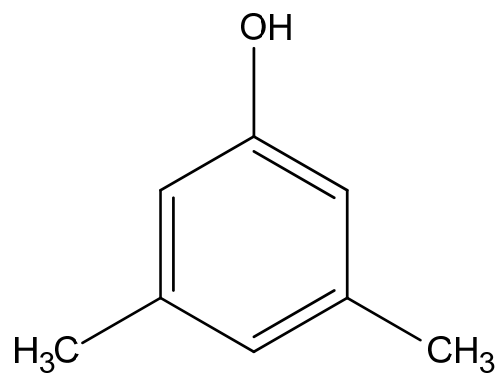
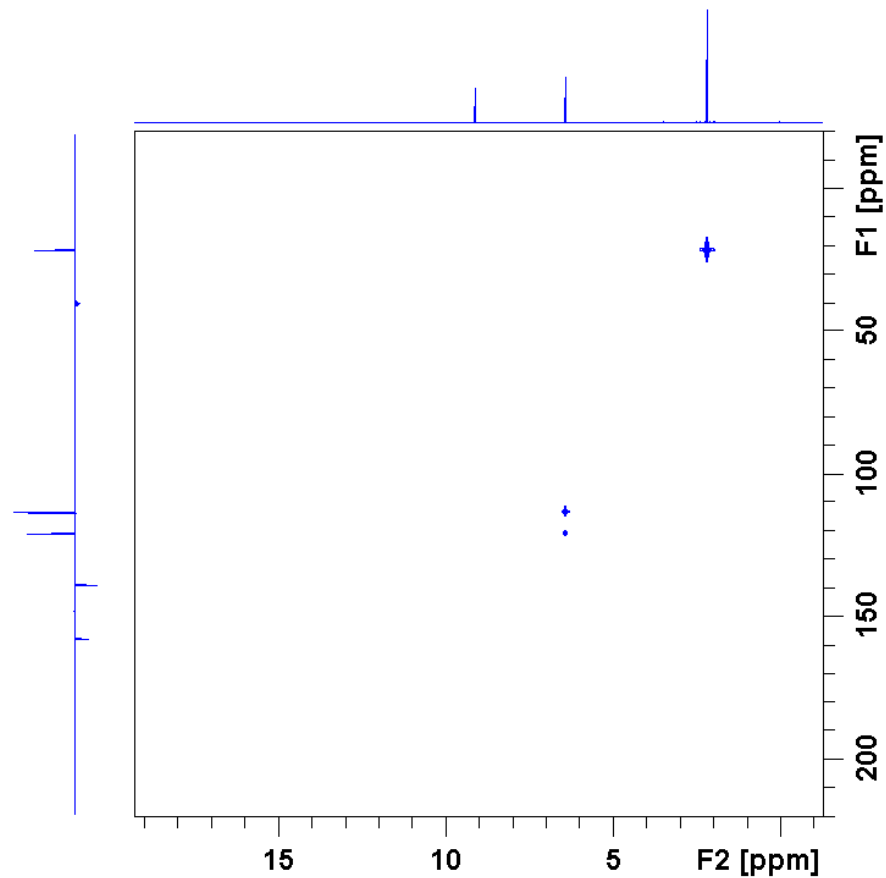


^1H NMR spektar spoja
snimljen u DMSO- d_6 .



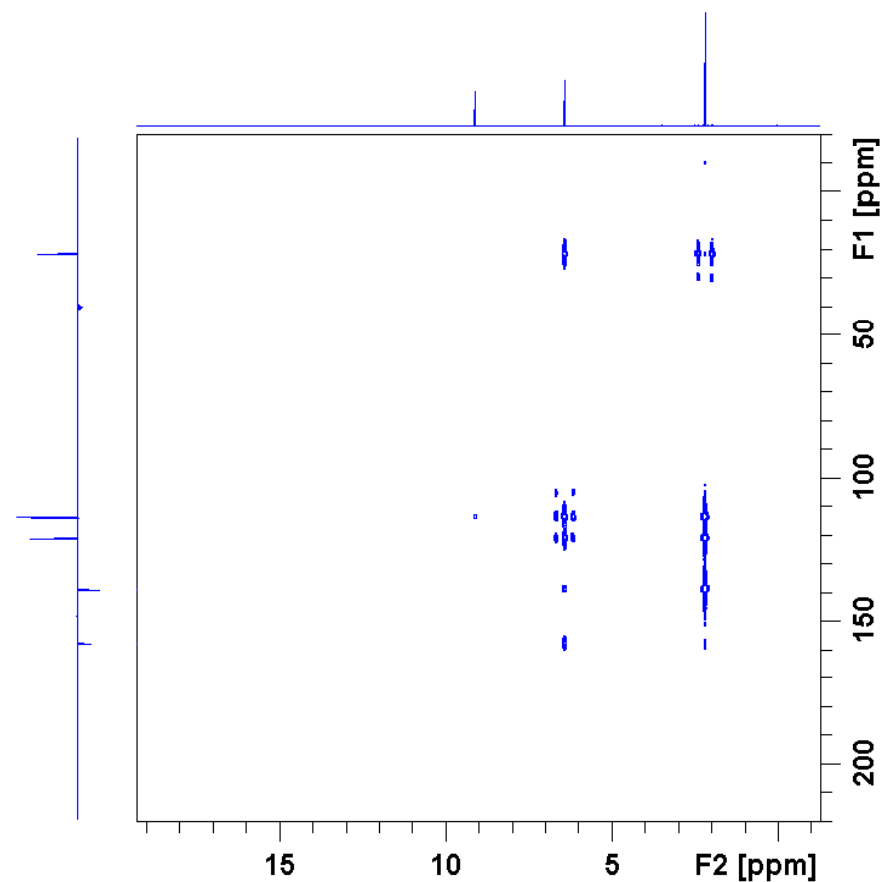
APT spektar spoja
snimljen u DMSO- d_6 .





3,5-dimetilfenol

HSQC spektar spoja
snimljen u DMSO- d_6 .



HMBC spektar spoja snimljen u DMSO- d_6 .

Asignacija karakterističnih fragmenata u spektru masa spoja

Signal	m/z
KCl^+	74,227
$(\text{C}_6\text{H}_5)^+$	77,280
$(\text{C}_6\text{H}_6\text{O})^+$	94,101
bazni signal	108,109
$(\text{M}+\text{H})^+$	122,954

Karakteristične vibracijske vrpce u IR spektru spoja

ν / cm^{-1}	Način vibracije
3290	$\nu (\text{O}-\text{H})$
3040	$\nu (\text{C}-\text{H})_{\text{aromat.}}$
2919	$\nu (\text{C}-\text{H})_{\text{alifat.}}$
1623; 1592	$\nu (\text{C}=\text{C})$
1307	$\nu (\text{C}-\text{O})$
1236; 1155	$\delta (\text{C}-\text{H})_{\text{i.p.}}$
829; 678	$\delta (\text{C}-\text{H})_{\text{o.o.p.}}$

i.p. = u ravnini (engl. *in plane*);

o.o.p. = izvan ravnine (engl. *out of plane*)

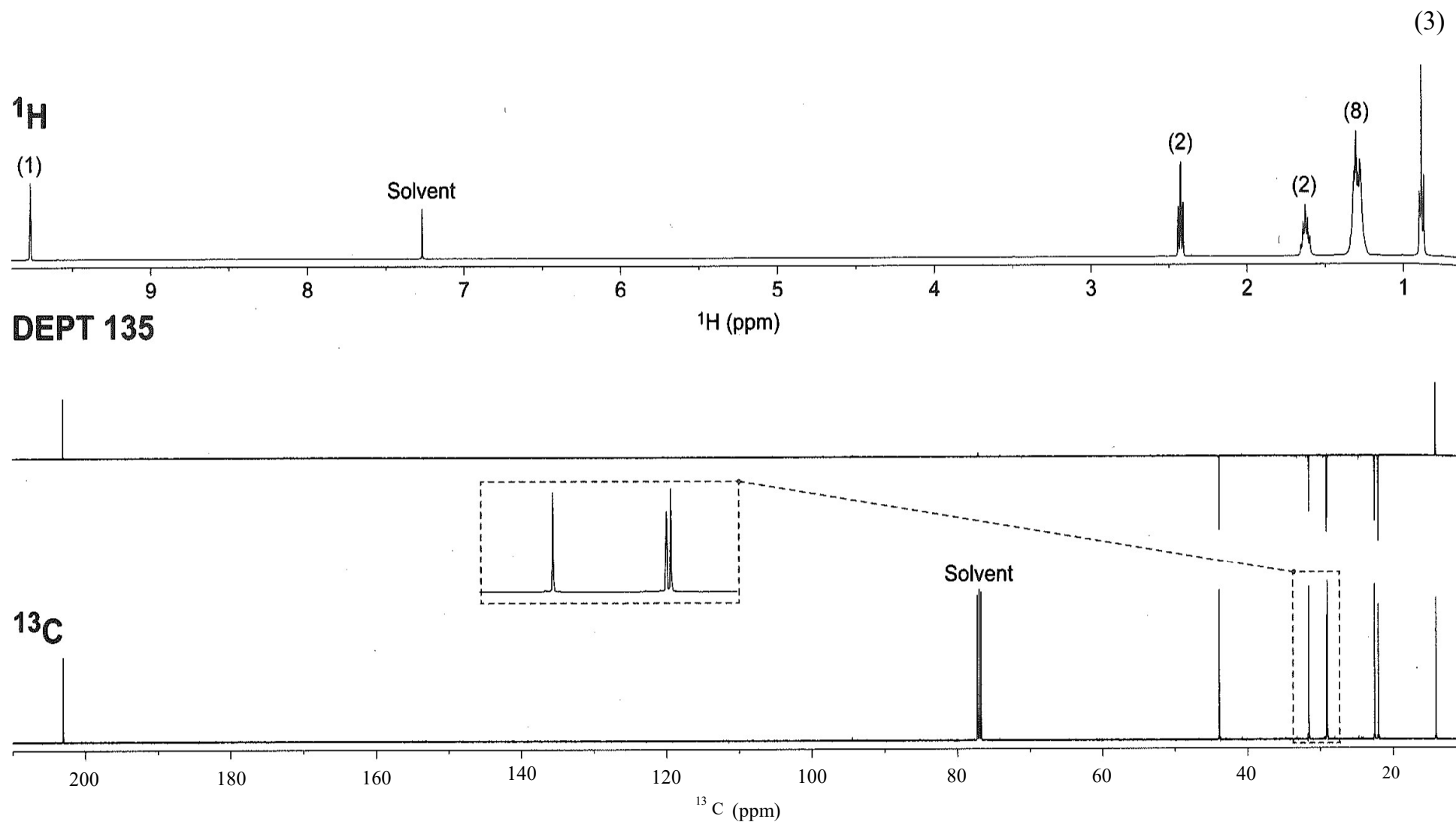
Asignacija ^1H NMR kemijskih pomaka spoja

H-atom	δ / ppm	Intenzitet	Multipletnost
CH_3	2,19	6	s
CH, CH	6,42	3	s
OH	9,09	1	s

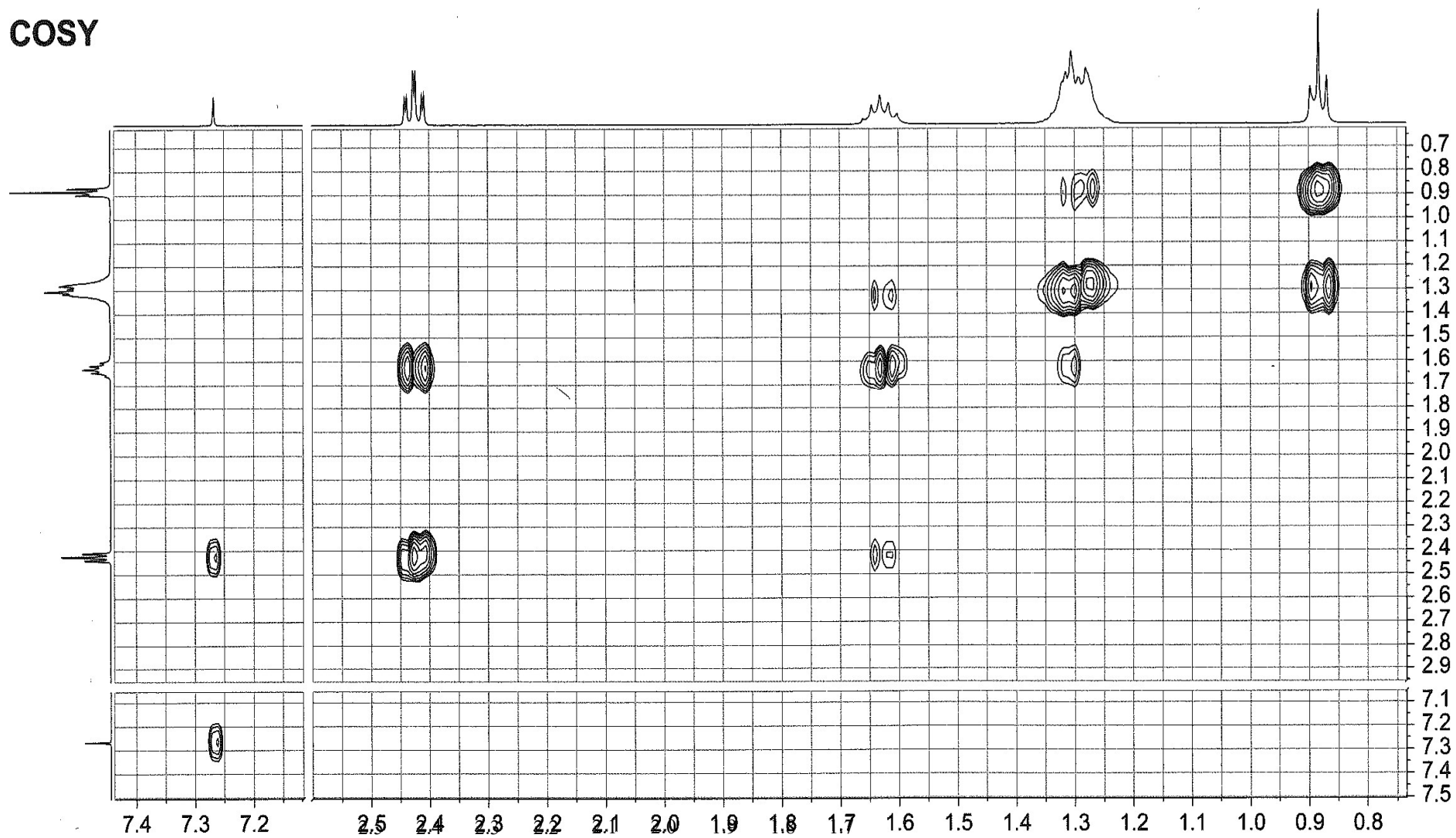
Asignacija ^{13}C NMR kemijskih pomaka spoja

C-atom	δ / ppm
CH_3	20
CH	112
CH	120
C	139
C	159

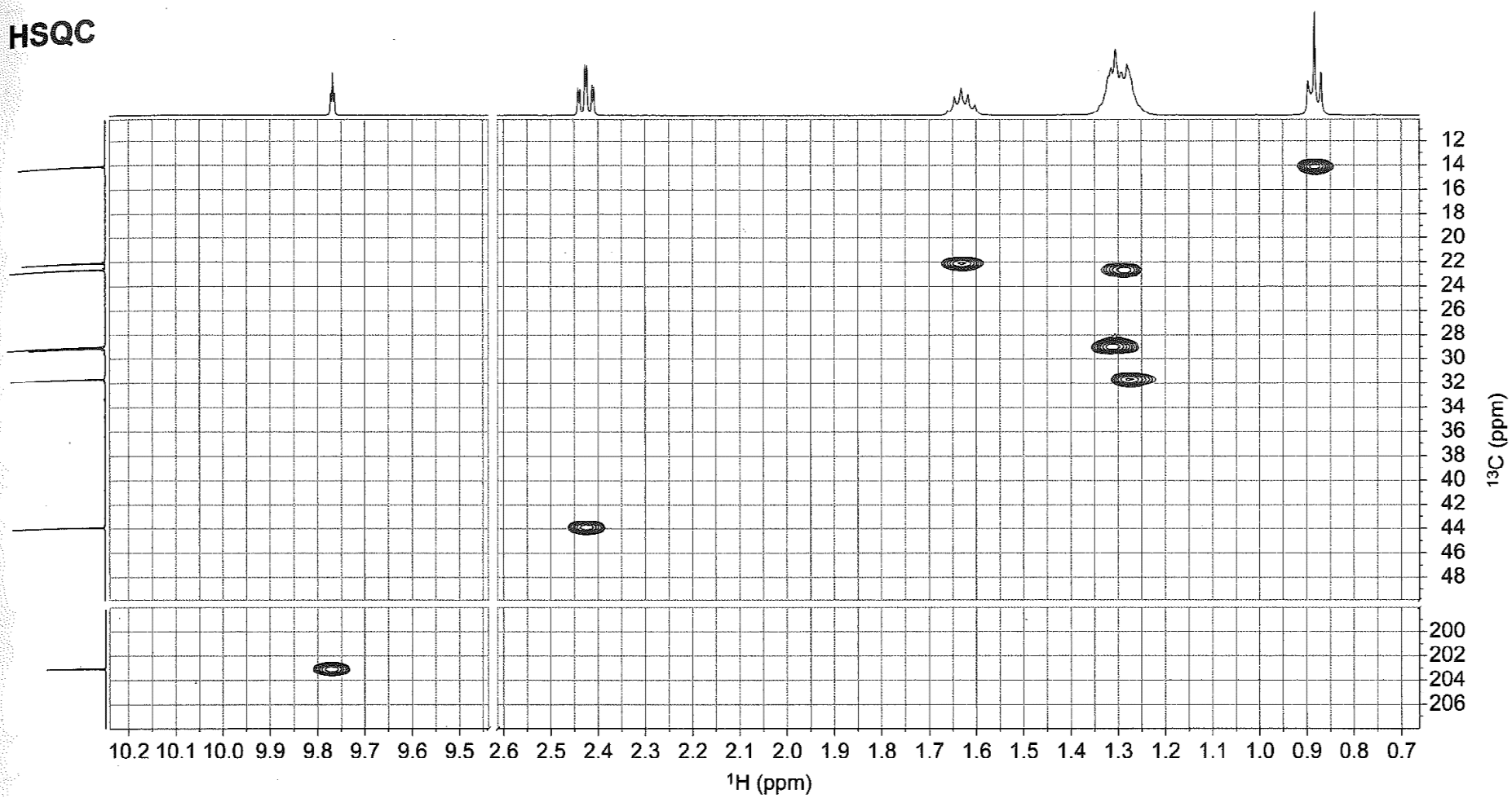
4. Odredite strukturu spoja molekulske formule $C_8H_{16}O$ na temelju njegovog 1H NMR, ^{13}C NMR, COSY, HSQC i HMBC spektra



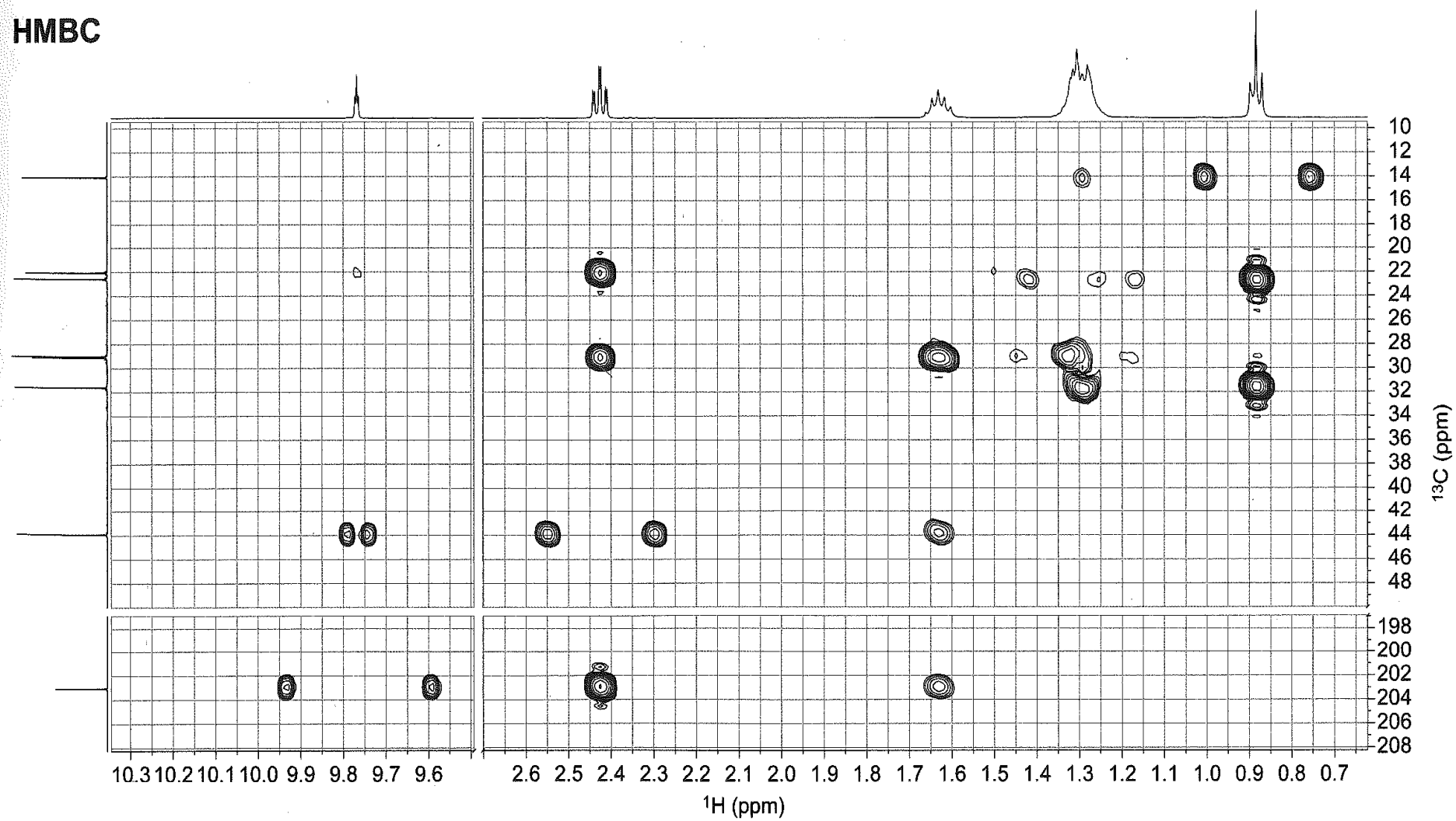
COSY



HSQC



HMBC

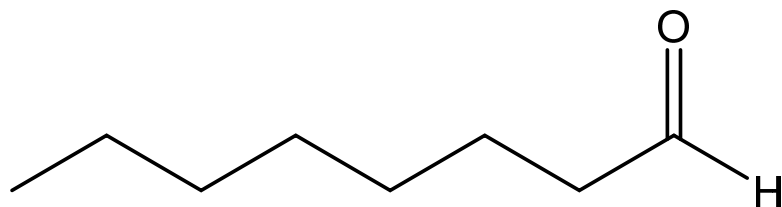


- informacije iz ^1H NMR:

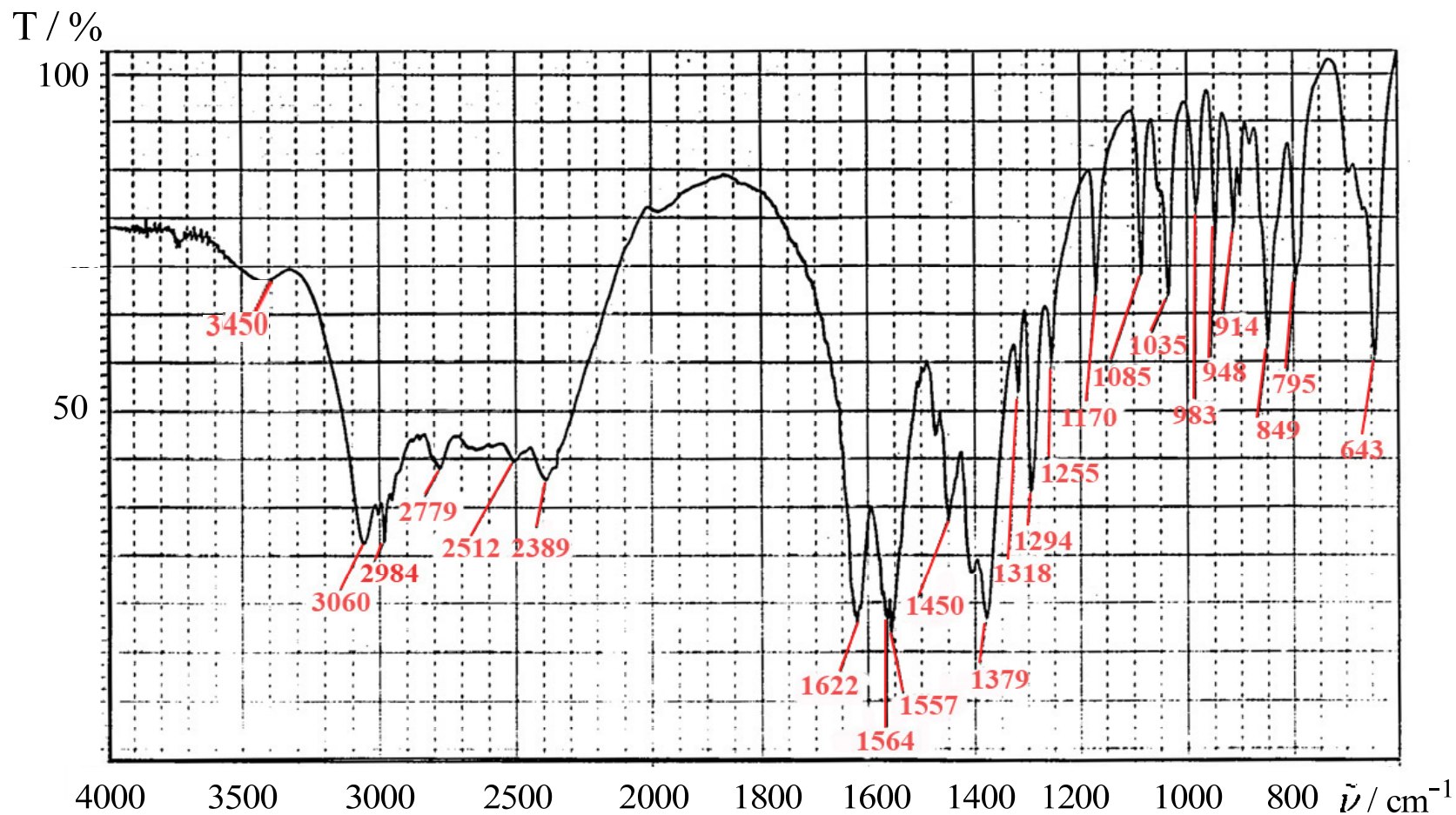
$\delta(^1\text{H}) / \text{ppm}$	multiplet	H-atom
0,88	t	$-\text{CH}_3$
1,28	m	$-\text{CH}_2-$
1,29	m	$-\text{CH}_2-$
1,31	m	$-\text{CH}_2-$
1,31	m	$-\text{CH}_2-$
1,62	m	$-\text{CH}_2-$
2,42	dt	$-\text{CH}_2-$
9,77	t	$\text{HC}=\text{O}$

- informacije iz ^{13}C NMR:

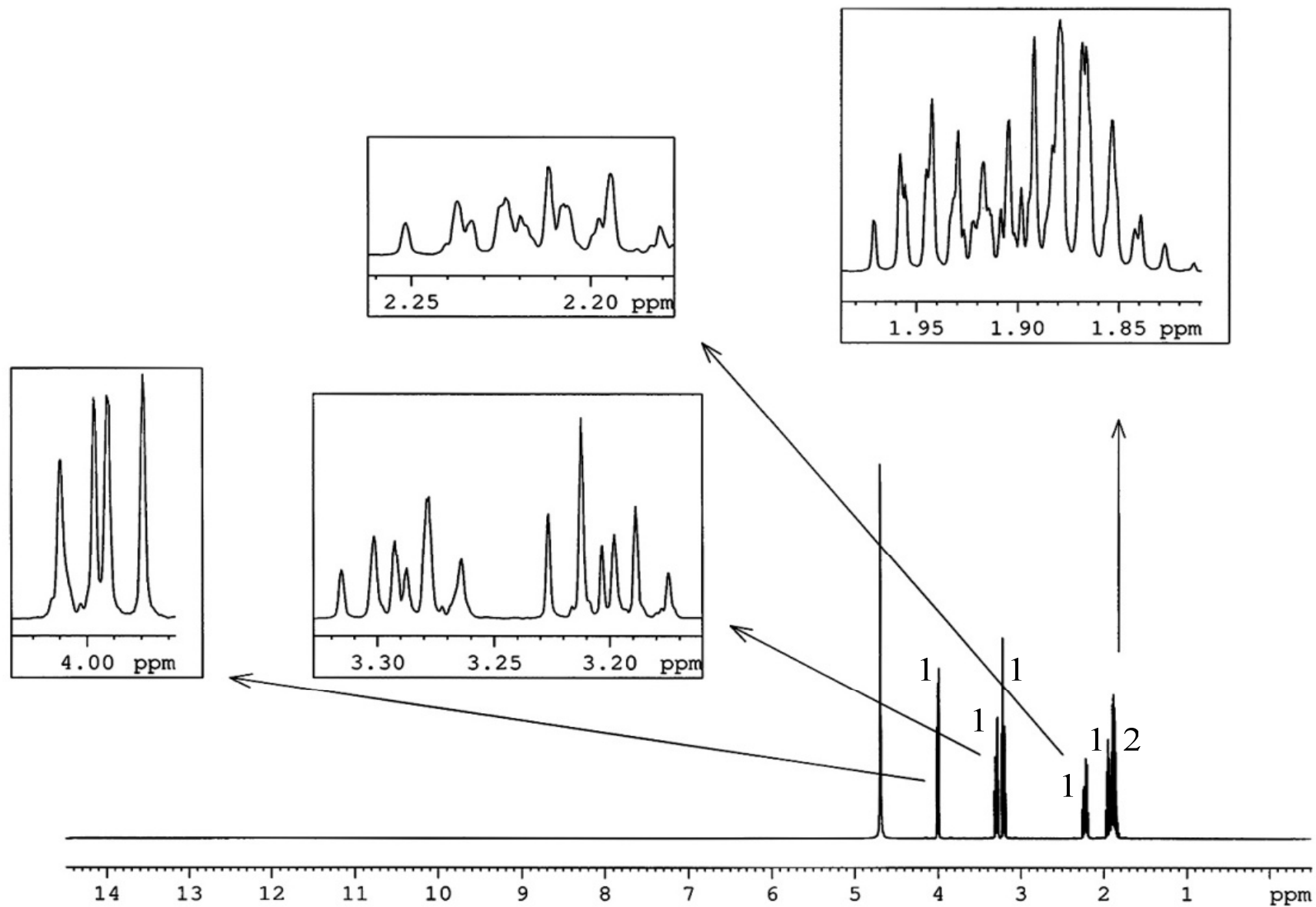
$\delta(^{13}\text{C}) / \text{ppm}$	C-atom
14,1	$-\text{CH}_3$
22,2	$-\text{CH}_2-$
22,6	$-\text{CH}_2-$
29,1	$-\text{CH}_2-$
29,1	$-\text{CH}_2-$
31,7	$-\text{CH}_2-$
44,0	$-\text{CH}_2-$
203,1	$\text{C}=\text{O}$



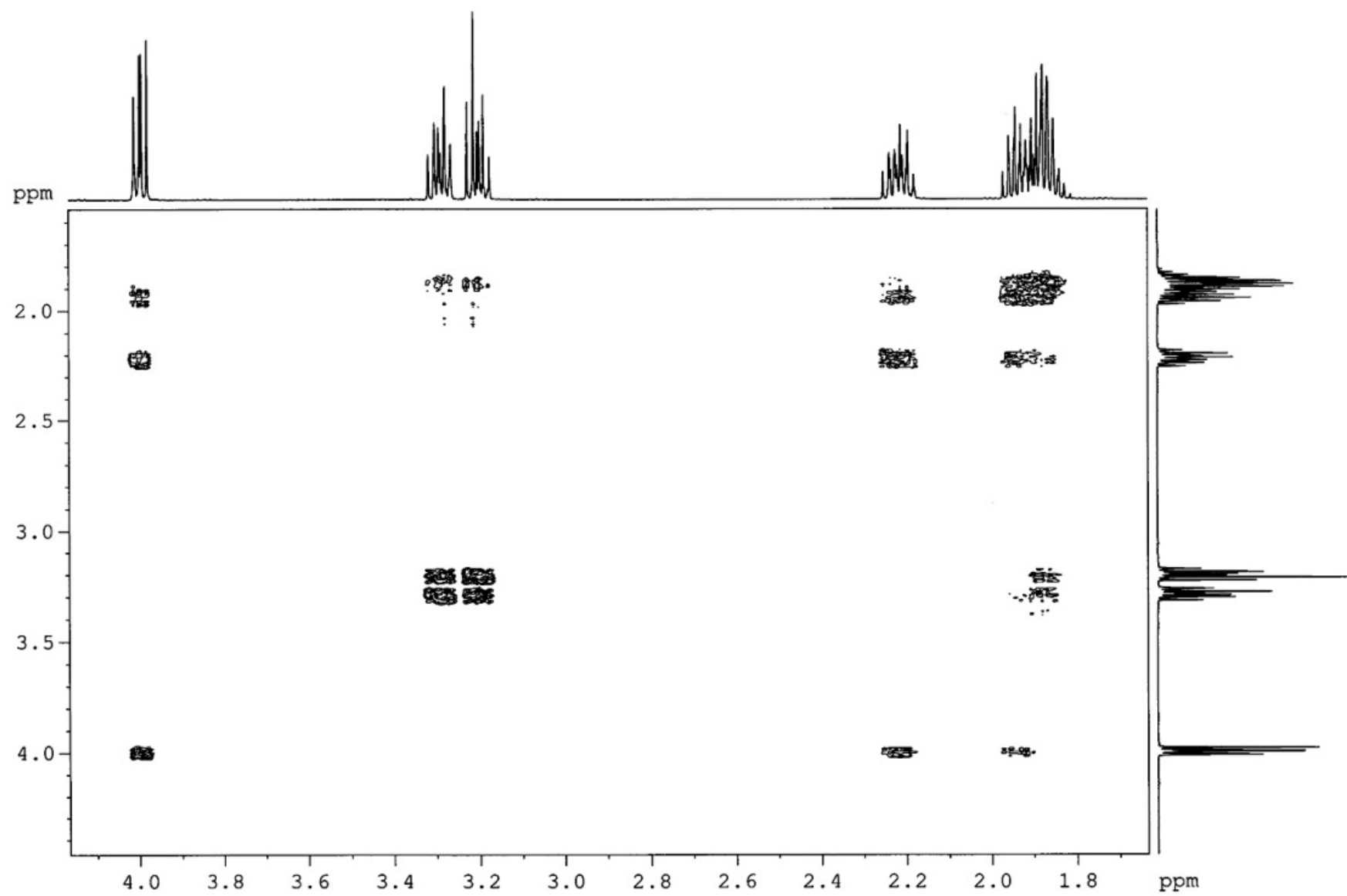
5. Odredite strukturu spoja molekulske mase 115 Da na temelju njegovog IR, ^1H NMR, COSY, HMQC i HMBC spektra



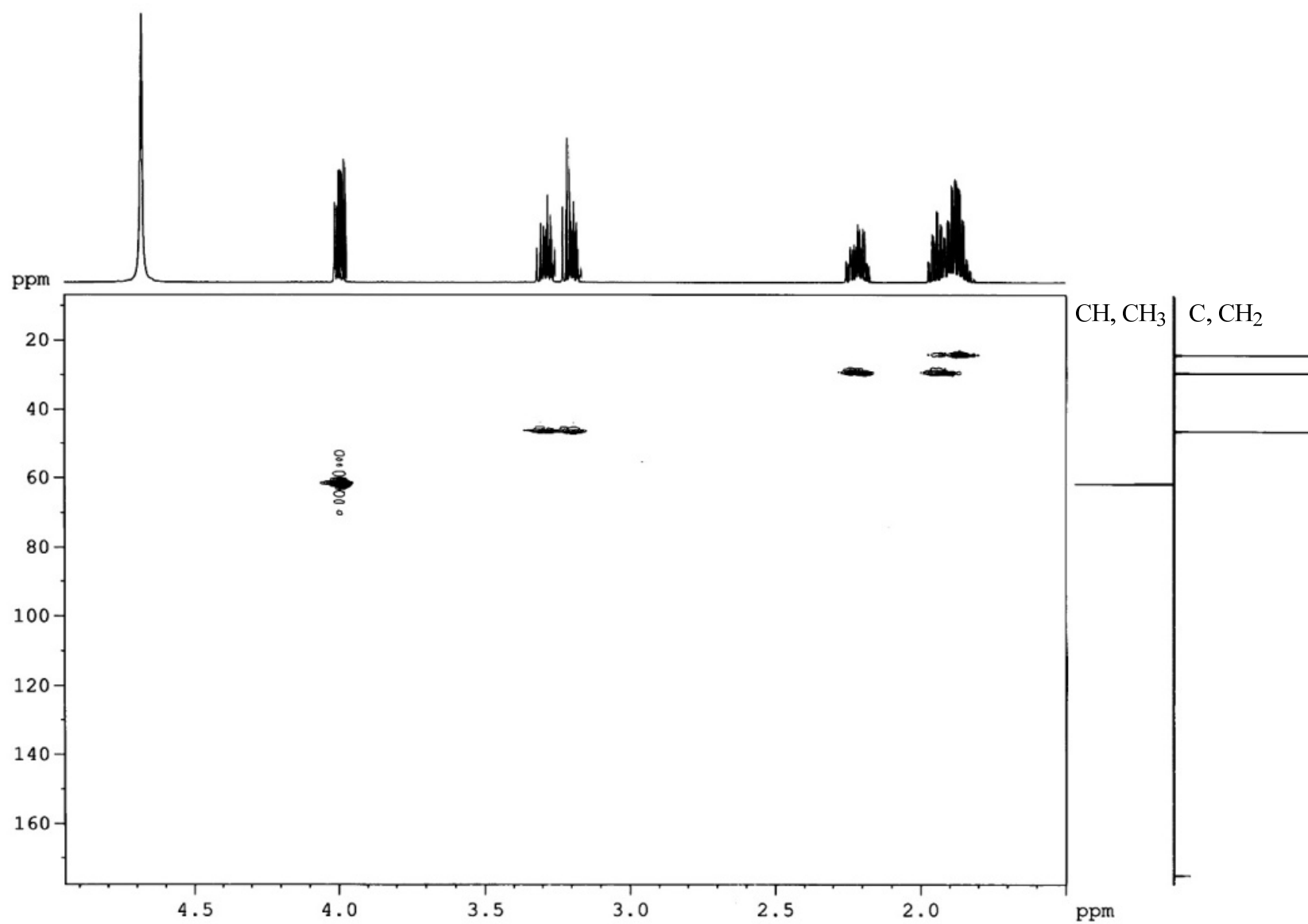
IR spektar spoja snimljen tehnikom KBr pastile.



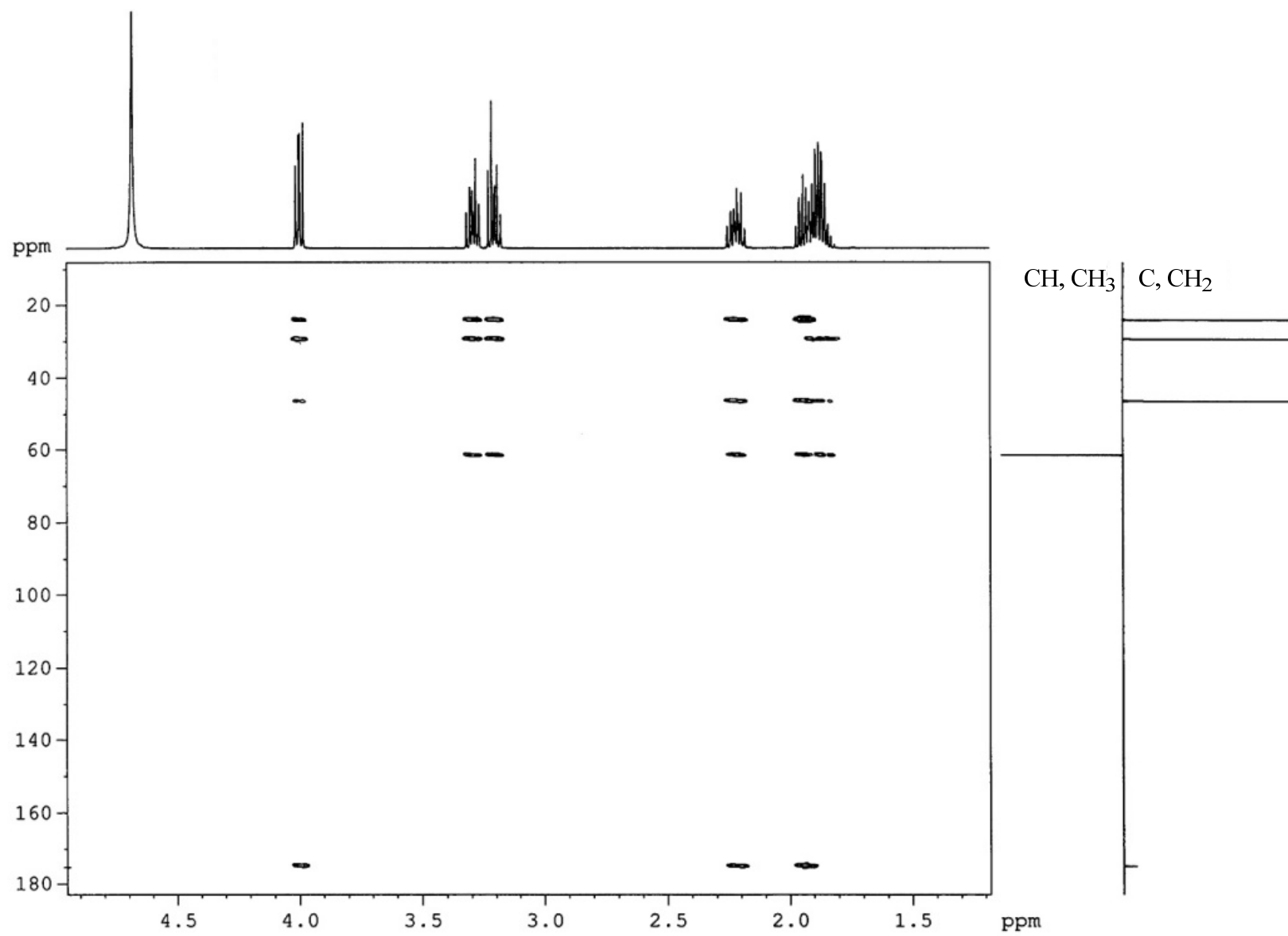
^1H NMR spektar spoja snimljen u D_2O uz uvećani prikaz područja koja odgovaraju pojedinim signalima.



COSY spektar spoja snimljen u D₂O.



HMQC spektar spoja snimljen u D_2O .



HMBC spektar spoja snimljen u D_2O .

Karakteristične vibracijske vrpce u IR spektru

ν / cm^{-1}	Način vibracije
3200–2000	$\nu(\text{NH}_2^+)$
3060, 2984	$\nu(\text{C-H})$
1622	$\delta(\text{NH}_2^+)$
1564	$\nu_{\text{as}}(\text{COO}^-)^{\text{a}}$
1450	$\nu_{\text{s}}(\text{COO}^-)^{\text{b}}$

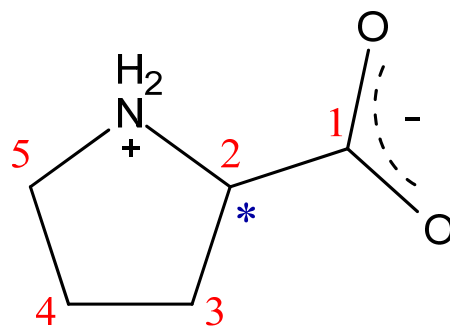
^a asimetrično istežanje; ^b simetrično istežanje

Asignacija ^1H NMR kemijskih pomaka

H-atom	δ / ppm	Intenzitet	Multipletnost
1			
2	4,00	1	dd
3	1,95	1	m
3	2,22	1	m
4	1,87	2	m
5	3,20	1	m
5	3,30	1	m

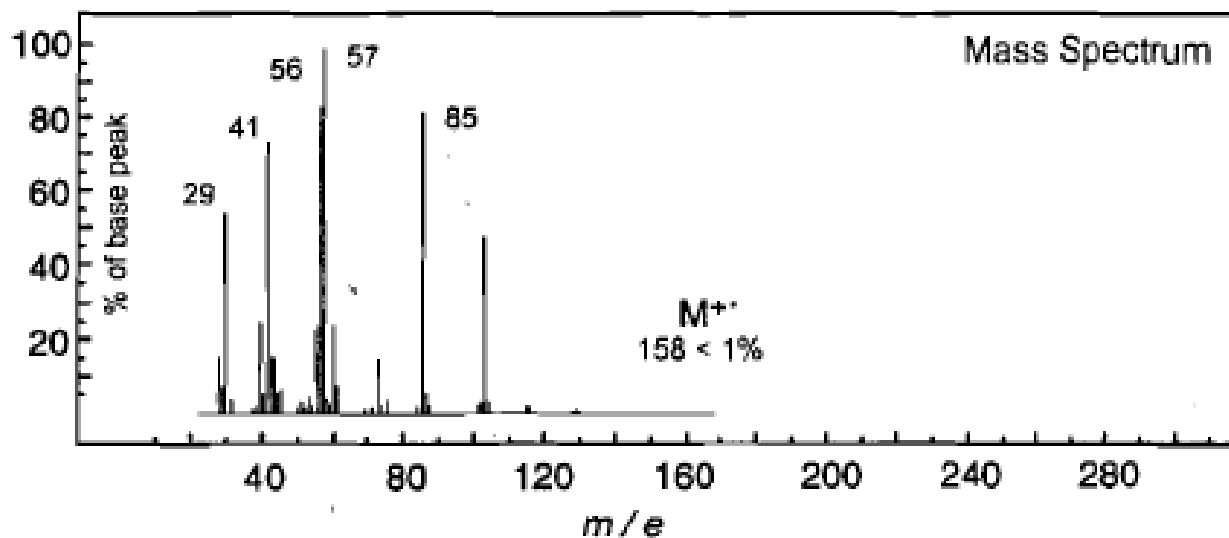
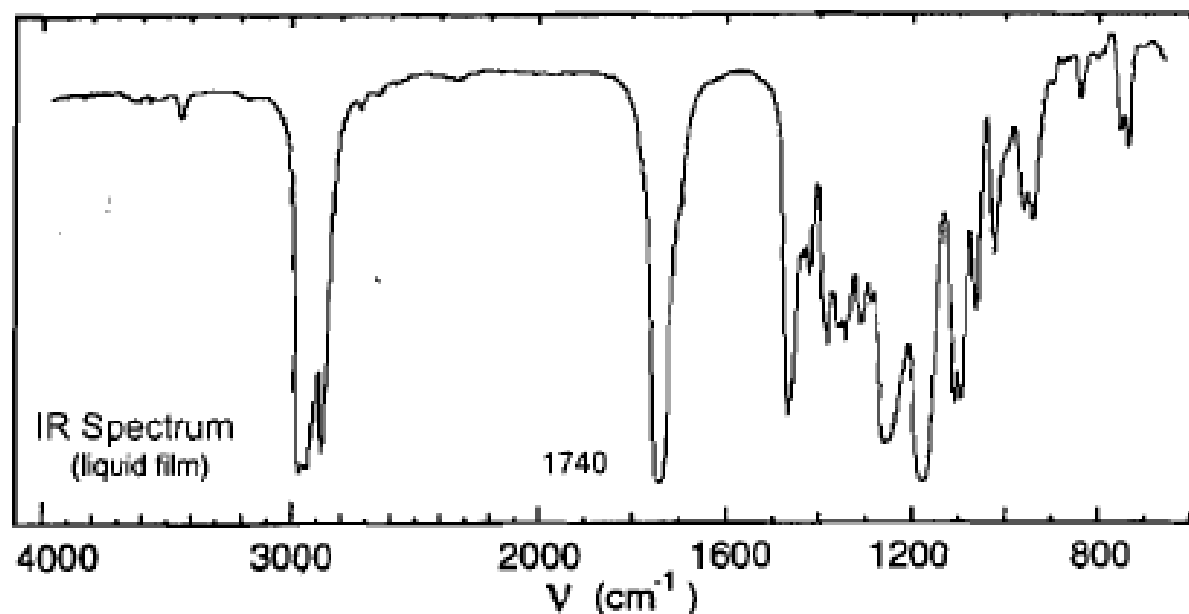
Asignacija ^{13}C NMR kemijskih pomaka

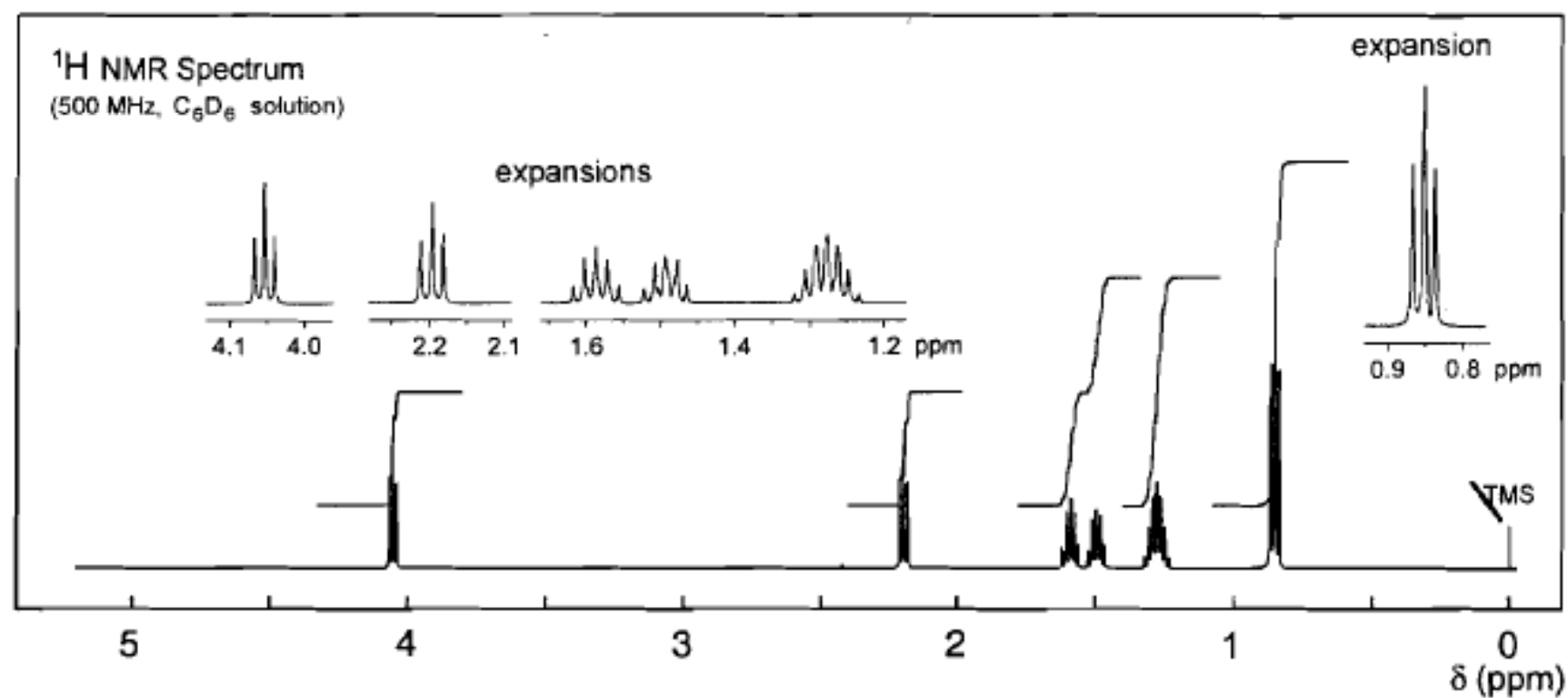
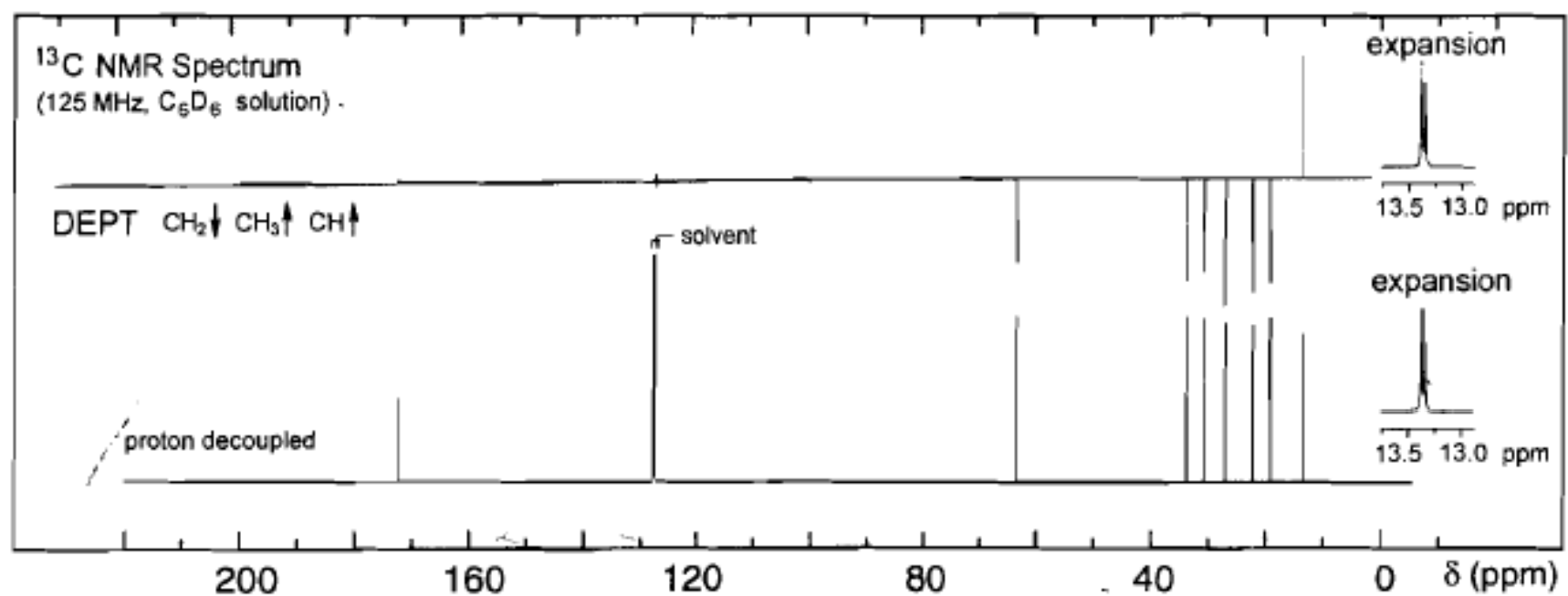
C-atom	δ / ppm
1	175
2	63
3	30
4	25
5	43

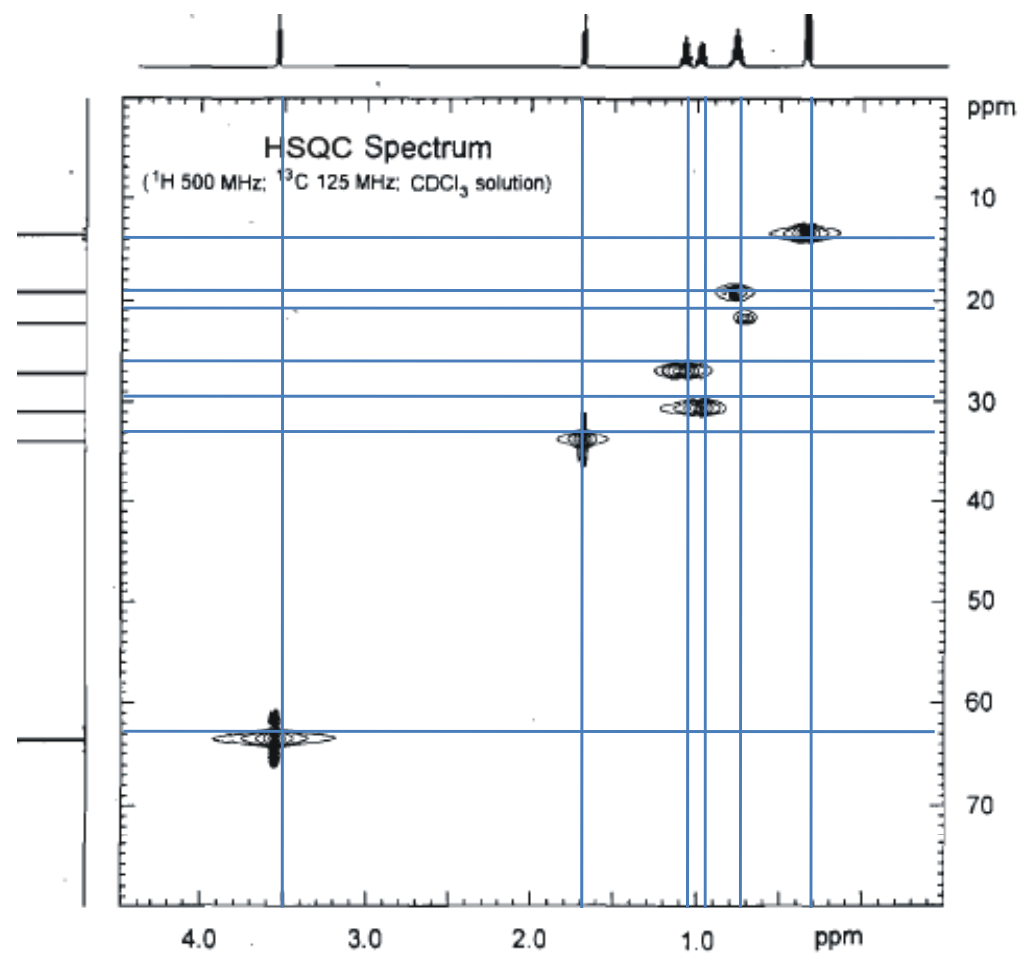
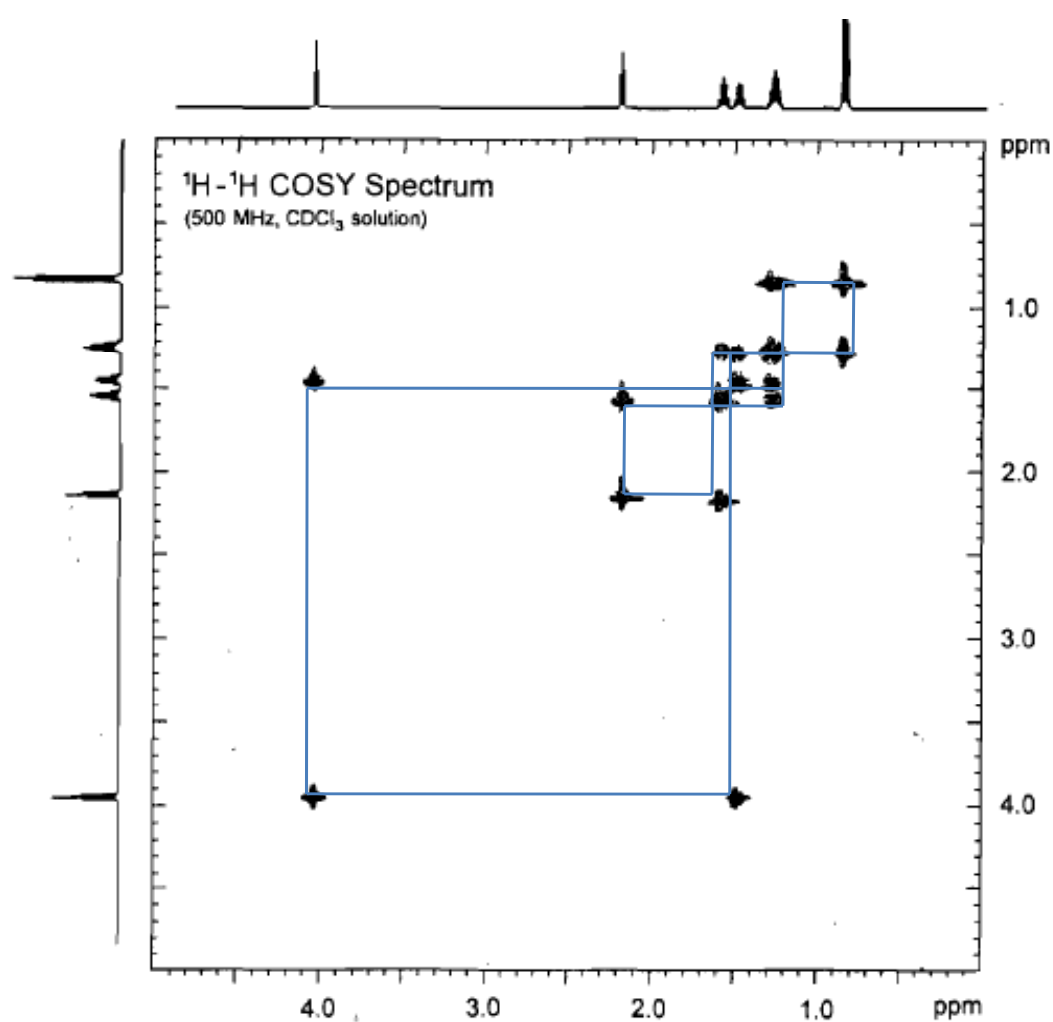


Struktura spoja i brojanje atoma. Simbolom * označen je kiralni centar.

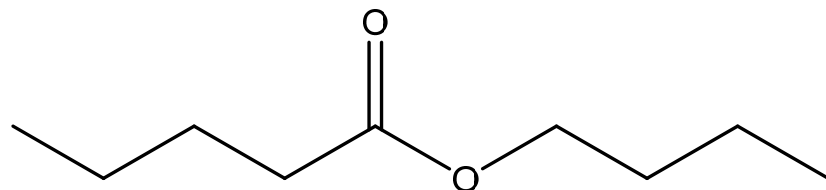
6. Odredite strukturu spoja na temelju njegovog IR, MS, ^1H NMR, ^{13}C NMR, COSY i HSQC spektra.







- informacije iz MS:
bazni pik: 57
 $M^+ = 158$



- informacije iz ^1H NMR:

$\delta(^1\text{H}) / \text{ppm}$	multiplet	H-atom
0,85	t	$-\text{CH}_3$
1,27	m (septet)	$-\text{CH}_2-$
1,49	m (kvintet)	$-\text{CH}_2-$
1,59	m (kvintet)	$-\text{CH}_2-$
2,20	t	$-\text{CH}_2-$
4,05	t	$-\text{CH}_2-$

- informacije iz IR:
 2950 cm^{-1} C–H alifatsko istežanje
 1740 cm^{-1} C=O istežanje

- informacije iz ^{13}C NMR:

$\delta(^{13}\text{C}) / \text{ppm}$	C-atom
13,3	$-\text{CH}_3$
13,4	$-\text{CH}_3$
19	$-\text{CH}_2-$
22	$-\text{CH}_2-$
27	$-\text{CH}_2-$
31	$-\text{CH}_2-$
34	$-\text{CH}_2-$
63	$-\text{CH}_2-$
173	C=O