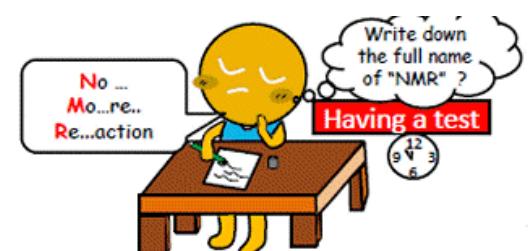




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# *Protonska nuklearna magnetska rezonancija ( $^1\text{H}$ NMR)*



# ✓ Pascalov trokut



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## n Multiplicitet

**0 Singlet (s)**

**1 Doublet (d)**

**2 Triplet (t)**

**3 Quartet (q)**

**4 Quintet**

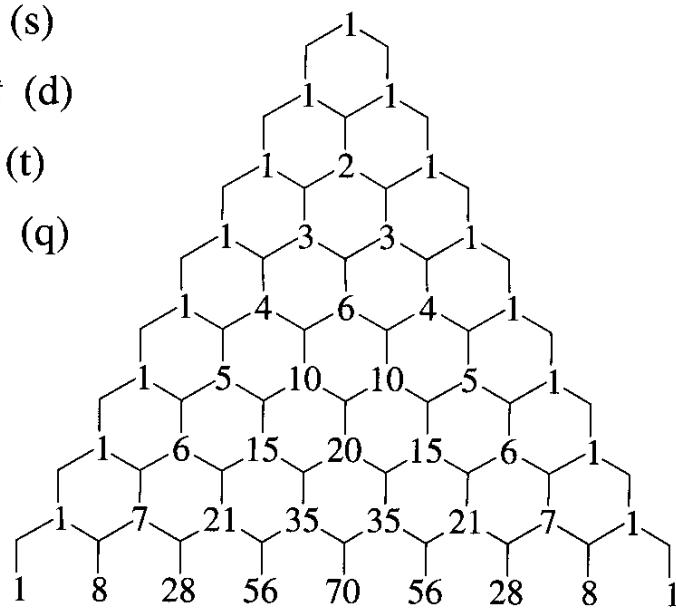
**5 Sextet**

**6 Septet**

**7 Octet**

**8 Nonet**

## Relativni intenzitet



## Spinovi

$n = 1$

$n = 2$

$n = 3$

$n = 4$

$n = 5$

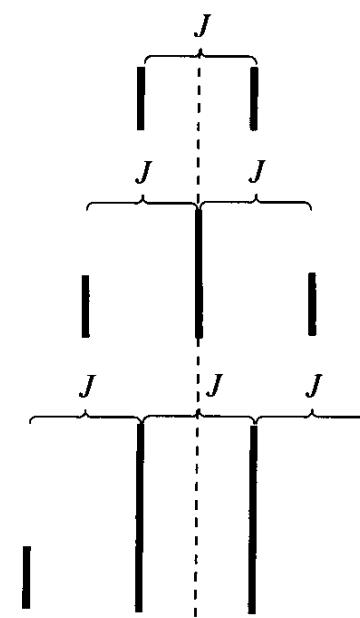
$n = 6$

$n = 7$

$n = 8$

$n = 9$

## Signali sprezanja



Relativni intenzitet multipleta ( $n$  = broj ekvivalentnih jezgara (sa spinom  $1/2$ ) koje se sprežu)

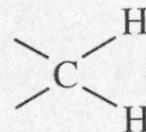
# ✓ *Geminalna sprega*



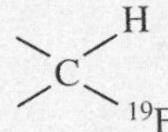
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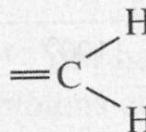
## Primjeri nekih konstanti sprega ( $^2J$ )



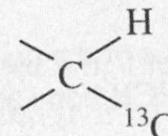
-9 to -15 Hz



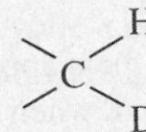
~50 Hz<sup>a</sup>



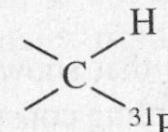
0 to 2 Hz



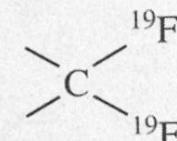
~5 Hz<sup>a</sup>



~2 Hz<sup>a</sup>



7 - 14 Hz



~160 Hz<sup>a</sup>

<sup>a</sup>Absolute values.

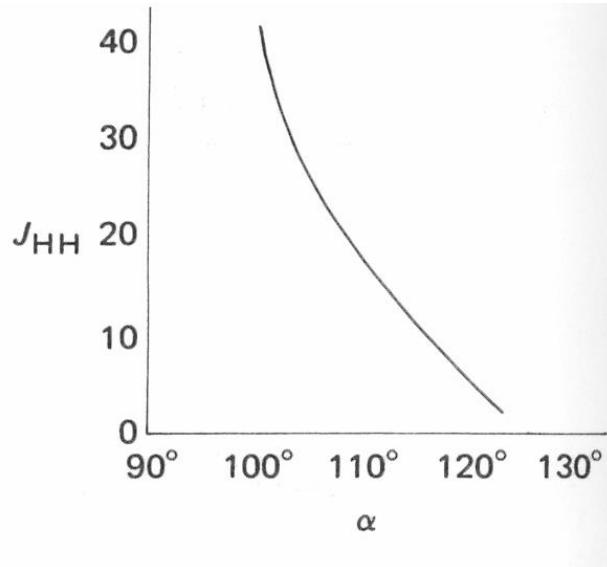
## ✓ Geminale sprege ( $^2J$ )



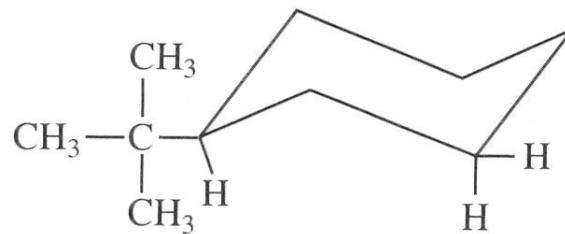
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- Geminale sprege se pojavljuju u spektru samo onda kada ta dva protona na istom ugljiku dođu u rezonanciju kod različitih frekvencija.
- Geminale  $\text{CH}_2$  sprege kroz dvije veze ovise o H-C-H kutu;
  - metilenske skupine: u fuzioniranom cikloheksanu ( $^2J \sim 12 - 18$  Hz),  
u ciklopropanu ( $^2J \sim 5$  Hz),  
terminalne  $=\text{CH}_2$  ( $^2J \sim 0 - 3$  Hz).
  - elektronegativni supstituenti smanjuju geminalne konstante sprege;
  - $sp^2$  ili  $sp$  hibridizirani C-atomi ih povećavaju;
  - geminalne konstante su obično negativne brojke ali se predznak ignorira.

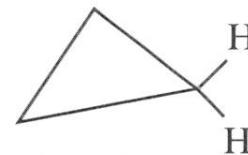


✓ Ovisnost veličine geminalne konstante sprega  $^2J_{\text{HCH}}$  o HCH veznom kutu  $\alpha$ .



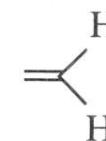
$$\alpha \approx 109^\circ$$

$$^2J_{\text{HH}} \approx 12-18 \text{ Hz}$$



$$\alpha \approx 118^\circ$$

$$^2J_{\text{HH}} \approx 5 \text{ Hz}$$

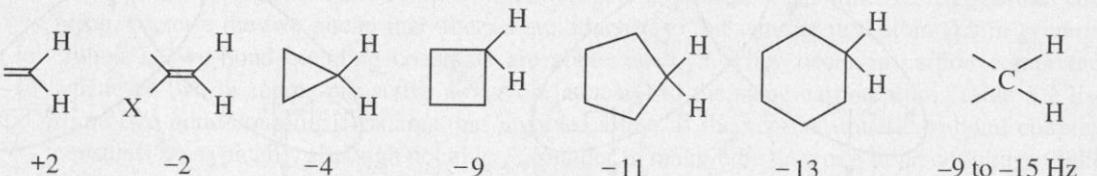


$$\alpha \approx 120^\circ$$

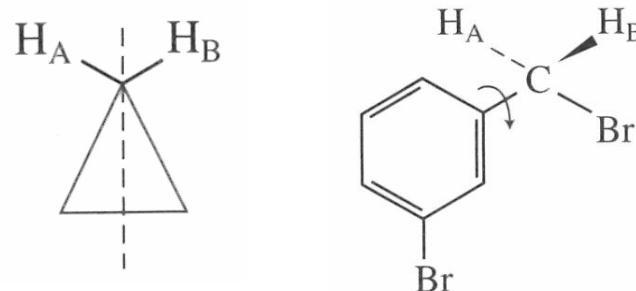
$$^2J_{\text{HH}} \approx 0-3 \text{ Hz}$$

✓ Primjeri nekih geminalnih konstanti sprega  $^2J_{\text{HCH}}$ . Vidi se da se povećanjem kuta smanjuje veličina  $^2J_{\text{HCH}}$ .

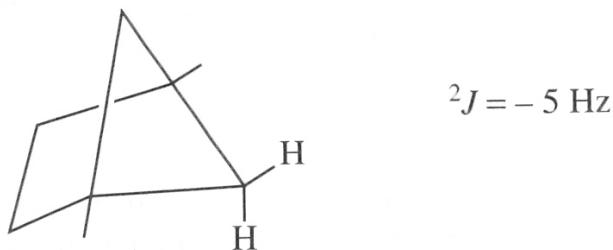
## Promjene veličine ${}^2J_{\text{HCH}}$ ovisno o hibridizaciji i veličini prstena



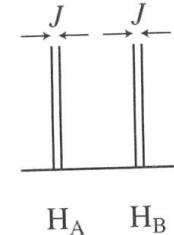
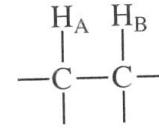
- U nekim slučajevima nema sprezanja spinova (niti geminalne konstante sprege) ili uslijed postojanja ravnine simetrije ili uslijed mogućnosti slobodne rotacije koja geminalne protone čini ekvivalentnim.



- Kako se i iz gornje tablice vidi, geminalne konstante sprege ipak postoje u pojedinim slučajevima, (npr. kod cikličkih spojeva) iako smo ranije naveli da protone na istom ugljiku možemo smatrati 1 skupinom u kojoj nema spin-spin sprege između njih. Ipak, kada je riječ o konformacijski-rigidnim cikličkim sustavima kao što su biciklički spojevi (biciklo[2.1.1]heksan), geminalna konstanta sprege postoji.



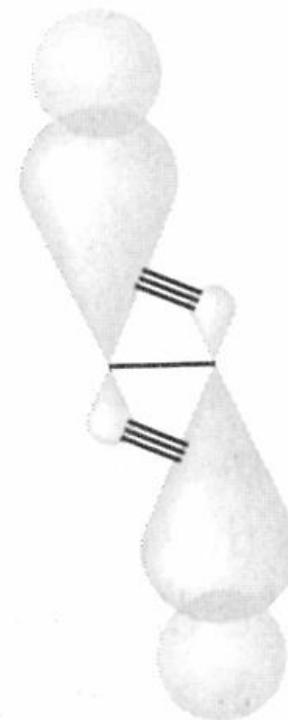
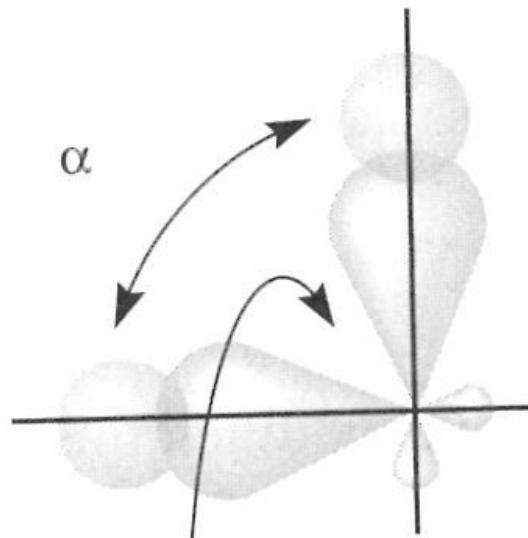
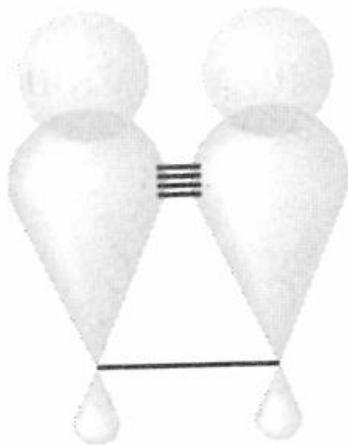
# ✓ Vicinalna sprega ( $\beta J$ )



$\alpha = 0^\circ$

$\alpha = 90^\circ$

$\alpha = 180^\circ$



- Nema preklapanja (ili minimalno) ukoliko su orbitale okomite jedna u odnosu na drugu

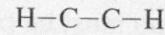
# ✓ *Vicinalna sprega ( $^3J$ )*



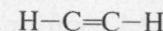
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## Dodatni primjeri nekih konstanti sprega ( $^3J$ )



6–8 Hz

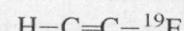


*cis* 6–15 Hz

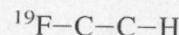
*trans* 11–18 Hz



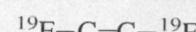
5 Hz



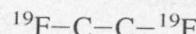
*cis* 18 Hz



5–20 Hz

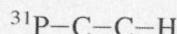


*cis* 30–40 Hz

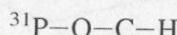


–3 to –20

*trans* 40 Hz



13 Hz

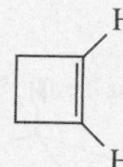


5–15 Hz

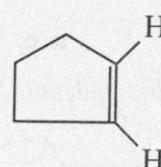
Razlike u konstantama sprega ( $^3J[\text{Hz}]$ ) ovisno o valentnom  
kutu u cikličkim alkenima



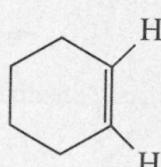
0–2



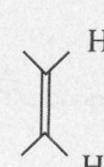
2–4



5–7



8–11

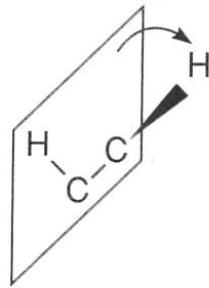


6–15

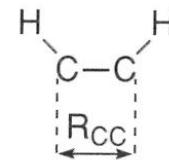
# ✓ Karplusova krivulja

aproksimativnog odnosa  
konstante sprege  $^3J$   
o diedarskom kutu

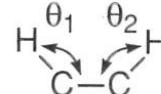
Osim diedarskog kuta ima i drugih faktora koji utječu na veličinu vicinalne konstante sprege a to su duljina veze, valentni kutevi te elektronegativnost bilo kojeg supstituenta vezanog na ugljikove atome.



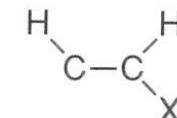
dihedral angle  
diedarski kut



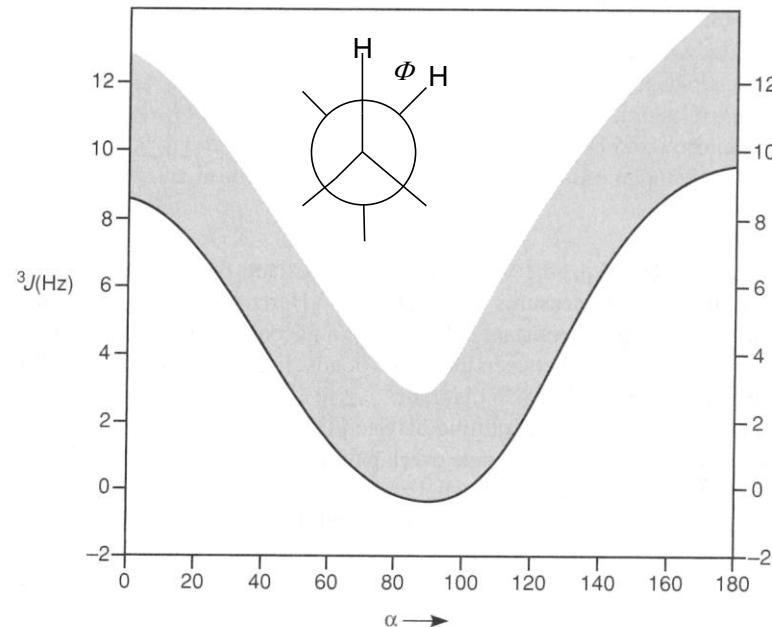
bond length  
duljina veze



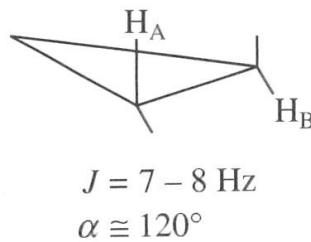
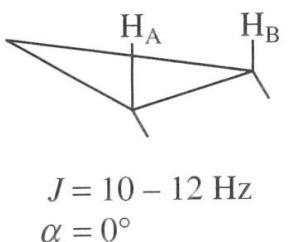
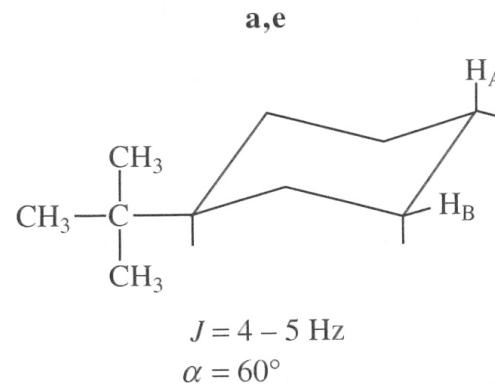
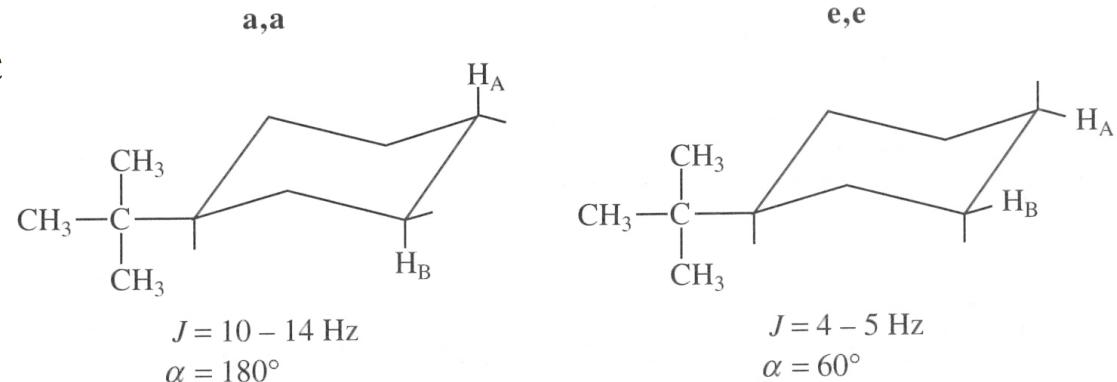
valence angles  
valentni kut



electronegative substituents  
elektronegativni supstituenti



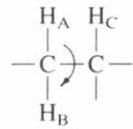
✓ Primjer Karplusove ovisnosti na rigidnoj strukturi cikloheksana



✓ Ciklopropan kao konformacijski rigidna struktura

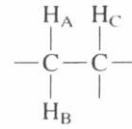
# ✓ Neekvivalentnost u okviru skupine-slučaj kada $n+1$ pravilo ne vrijedi!

(a) FREE ROTATION  
THE  $n + 1$  RULE APPLIES

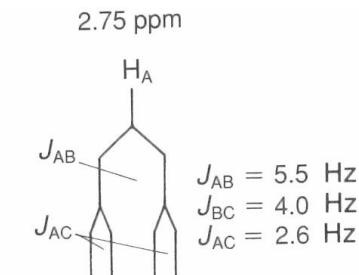
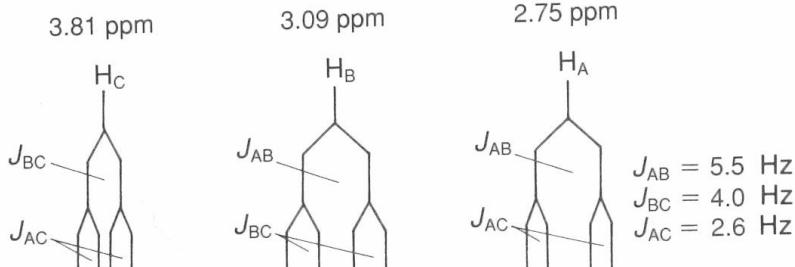
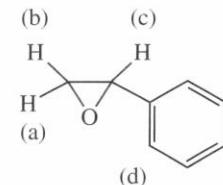
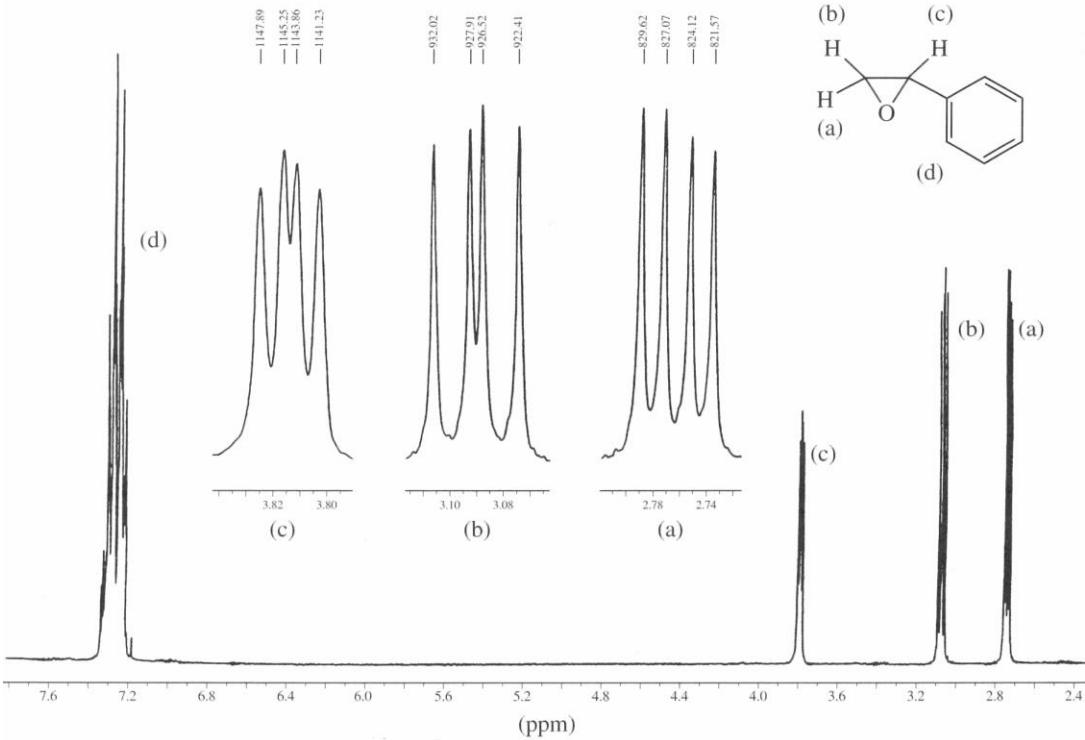


$$\begin{aligned}\delta_A &= \delta_B \\ J_{AC} &= J_{BC} \\ J_{AB} &= 0\end{aligned}$$

(b) LOCKED CONFORMATION  
A TREE DIAGRAM IS REQUIRED



$$\begin{aligned}\delta_A &\neq \delta_B \\ J_{AC} &\neq J_{BC} \\ J_{AB} &\neq 0\end{aligned}$$



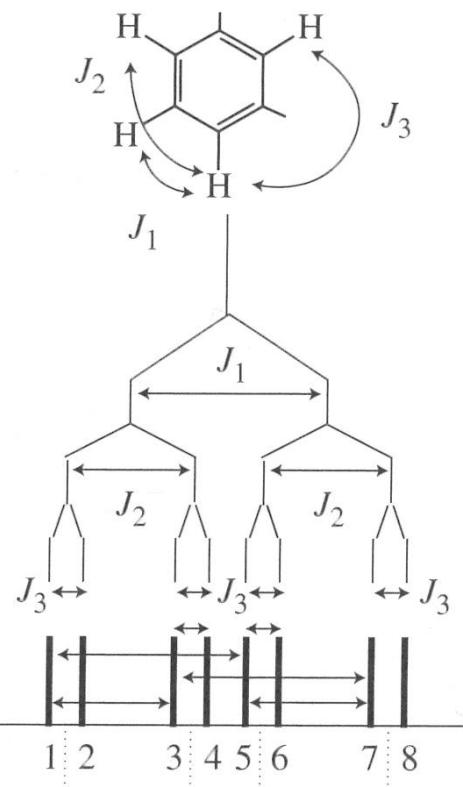
✓  $^1\text{H}$  NMR spektar **stiren-oksida** i sprezanje tri neekvivalentna protona



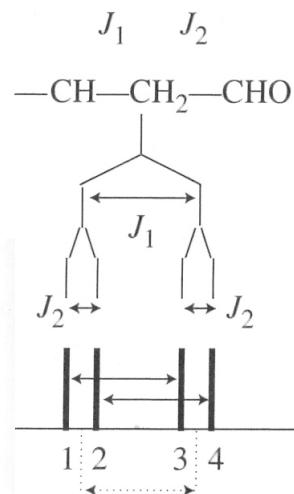
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# ✓ Kompleksniji multipleti



A number of approaches are possible. Generally you should choose an appropriately spaced pair of peaks based on their intensities and sharpness.

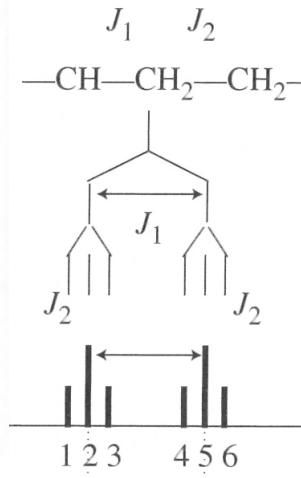


## Doublet of Doublets (dd)

To obtain  $J_1$  measure the difference between lines 1 and 3, or 2 and 4, in Hz.\*

\*Do not try to find the centers of the doublets!

$J_2$  is the spacing between lines 1 and 2, or 3 and 4

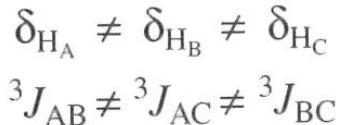
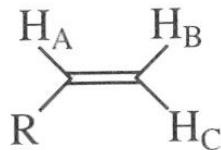


## Doublet of Triplets (dt)

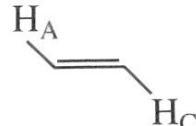
To obtain  $J_1$  measure the difference between the most intense lines (2 and 5) in Hz

$J_2$  is the spacing between lines 1 and 2, or 2 and 3, or those in the other triplet.

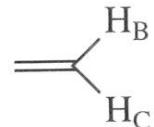
# ✓ *Cis-trans izomerija*



*cis*-izomer



*trans*-izomer



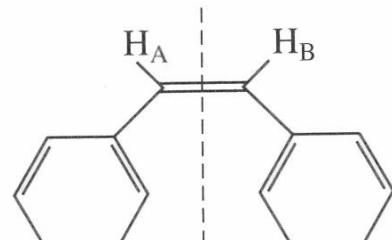
terminalni metilenski (geminalni) vodici

$$^3J \cong 6 - 15 \text{ Hz}$$

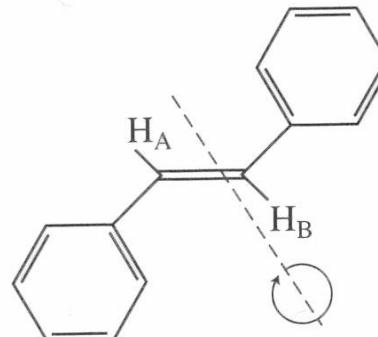
$$^3J \cong 11 - 18 \text{ Hz}$$

$$^2J \cong 0 - 5 \text{ Hz}$$

- ❑ U oba geometrijska izomera stilbena, vinilni protoni u NMR spektru daju samo singletni rezonancijski pik bez sprezanja.

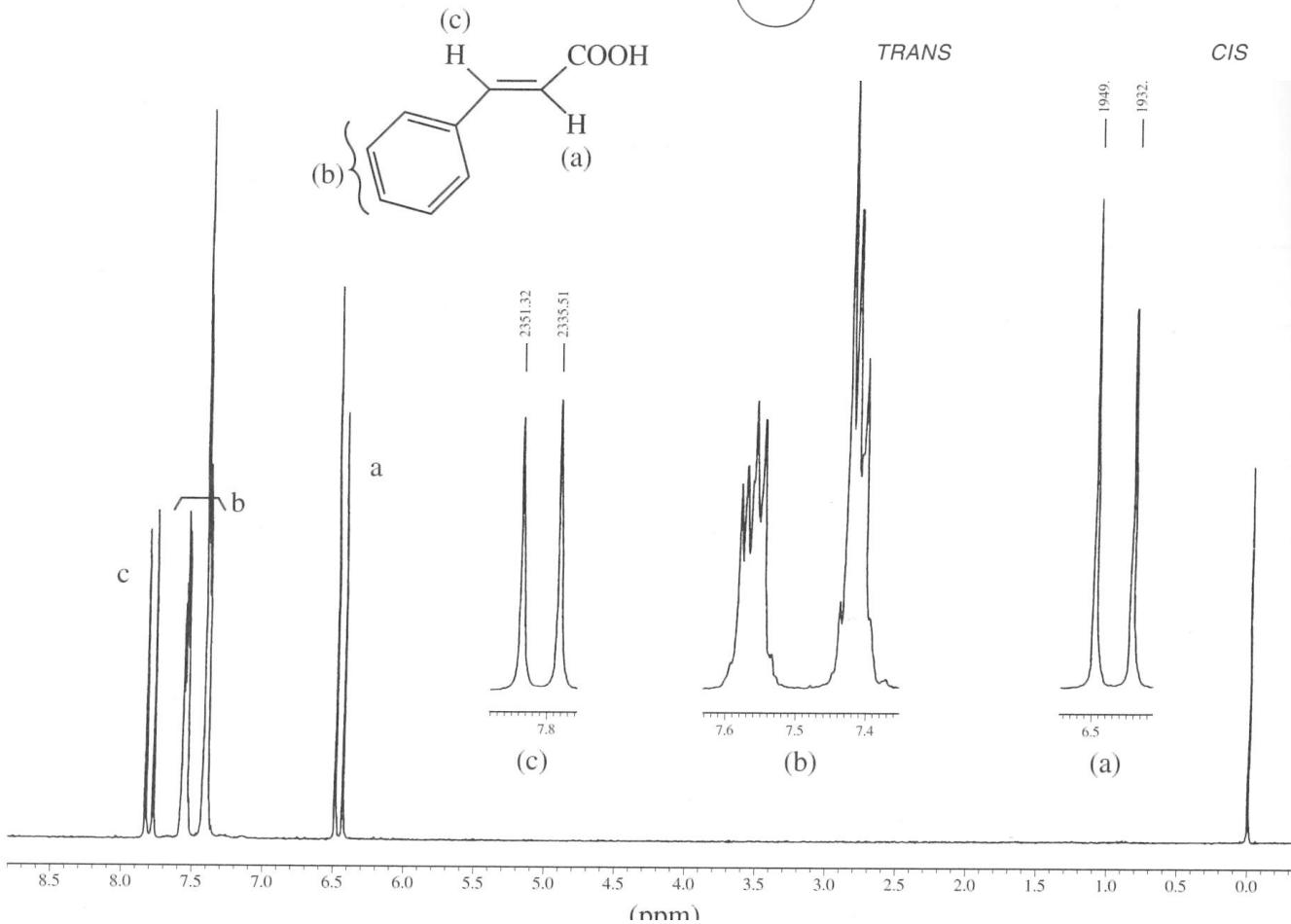
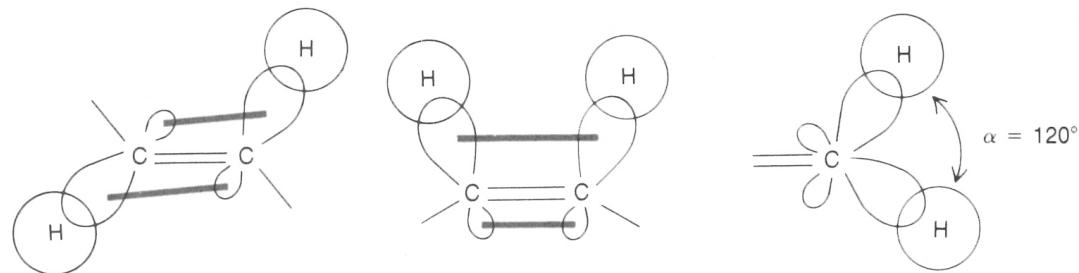


ravnina simetrije  
*cis*-stilben



os simetrije  
*trans*-stilben

✓ Razlika u konstantama  
sprezanja u *cis*- i *trans*-  
izomerima



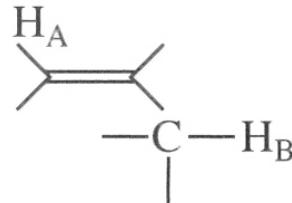
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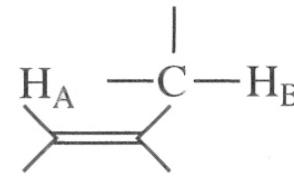
# ✓ Sprege dalekog dosega ( $^4J - ^nJ$ )



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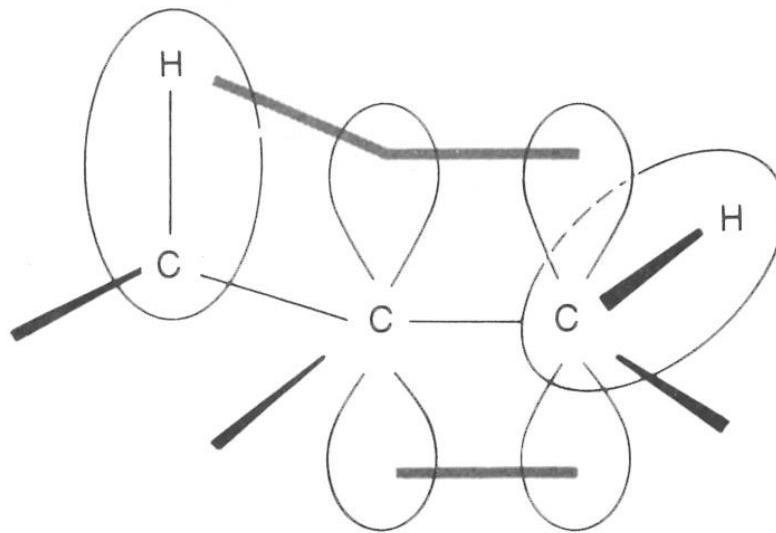


$$^4J \sim 0 - 3 \text{ Hz}$$

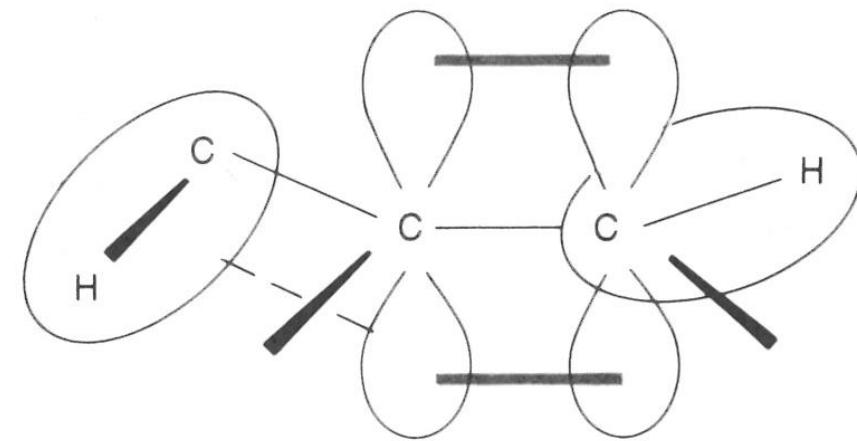


$$^4J \sim 0 - 3 \text{ Hz}$$

✓ Raspored u prostoru s maksimalnim i minimalnim *alilnim sprezanjem*



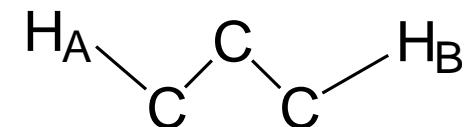
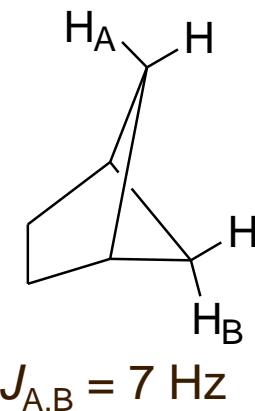
maksimalna interakcija



minimalna interakcija

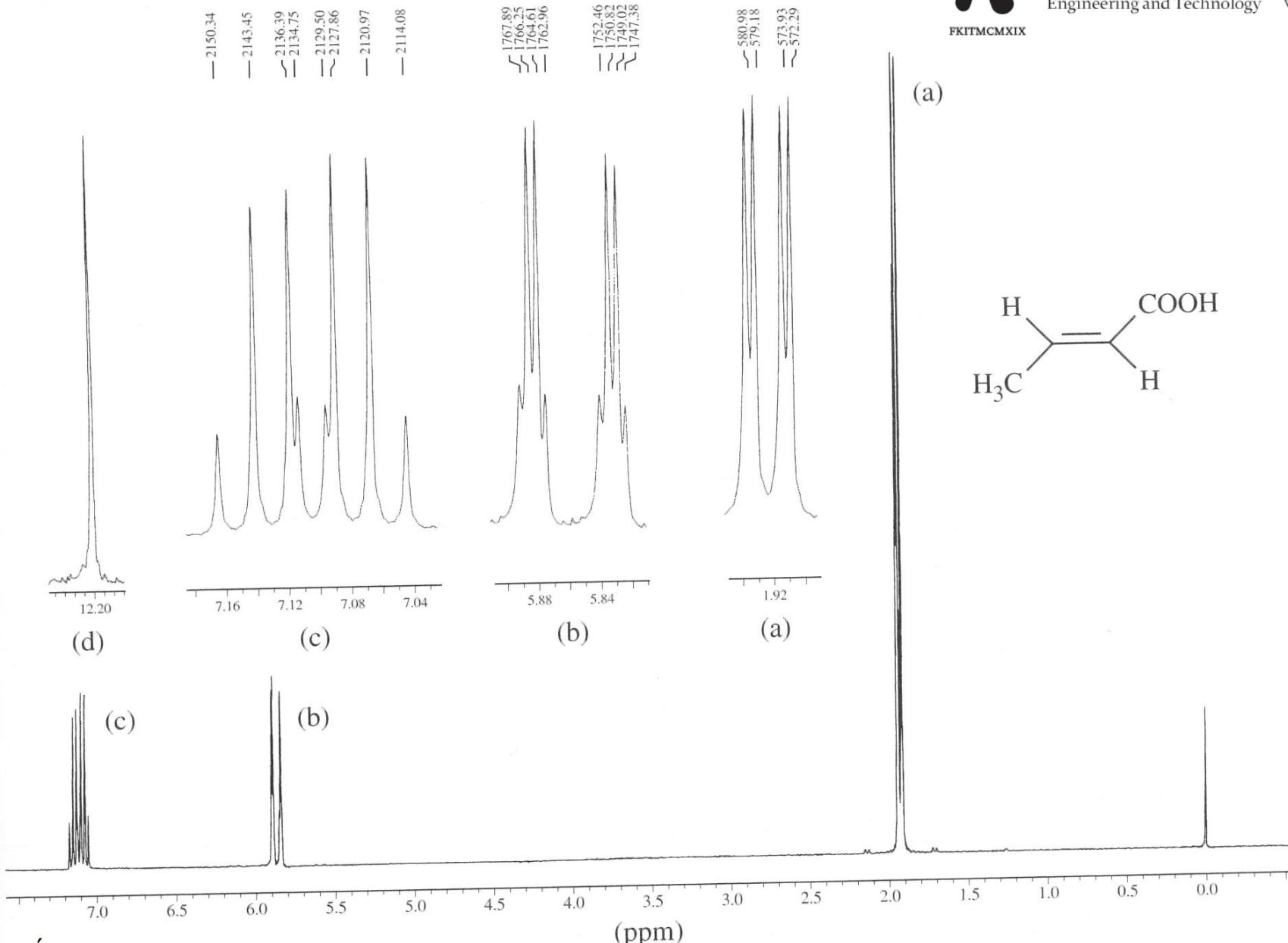
## ✓ Sprege dalekog dosega (*long range coupling*)

- alilne sprege (**H-C-C=C-H**):  $^4J$  oko 1,6 Hz
- u butadienu:  $^5J$  oko 1,3 Hz
- **meta**-sprega u benzenu: 1-3 Hz
- **para**-sprega u benzenu: 0-1 Hz
- 5-člani heteroaromatski spoj:  $^4J$  je 0-2 Hz



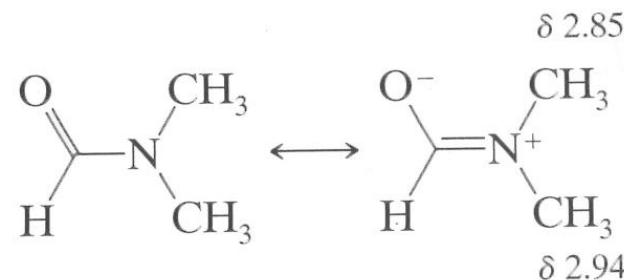
"W konformacija"  
4 σ veza između  $H_A$  i  $H_B$

# ✓ Primjer ( $^1\text{H}$ NMR spektar *krotonske* kiseline)

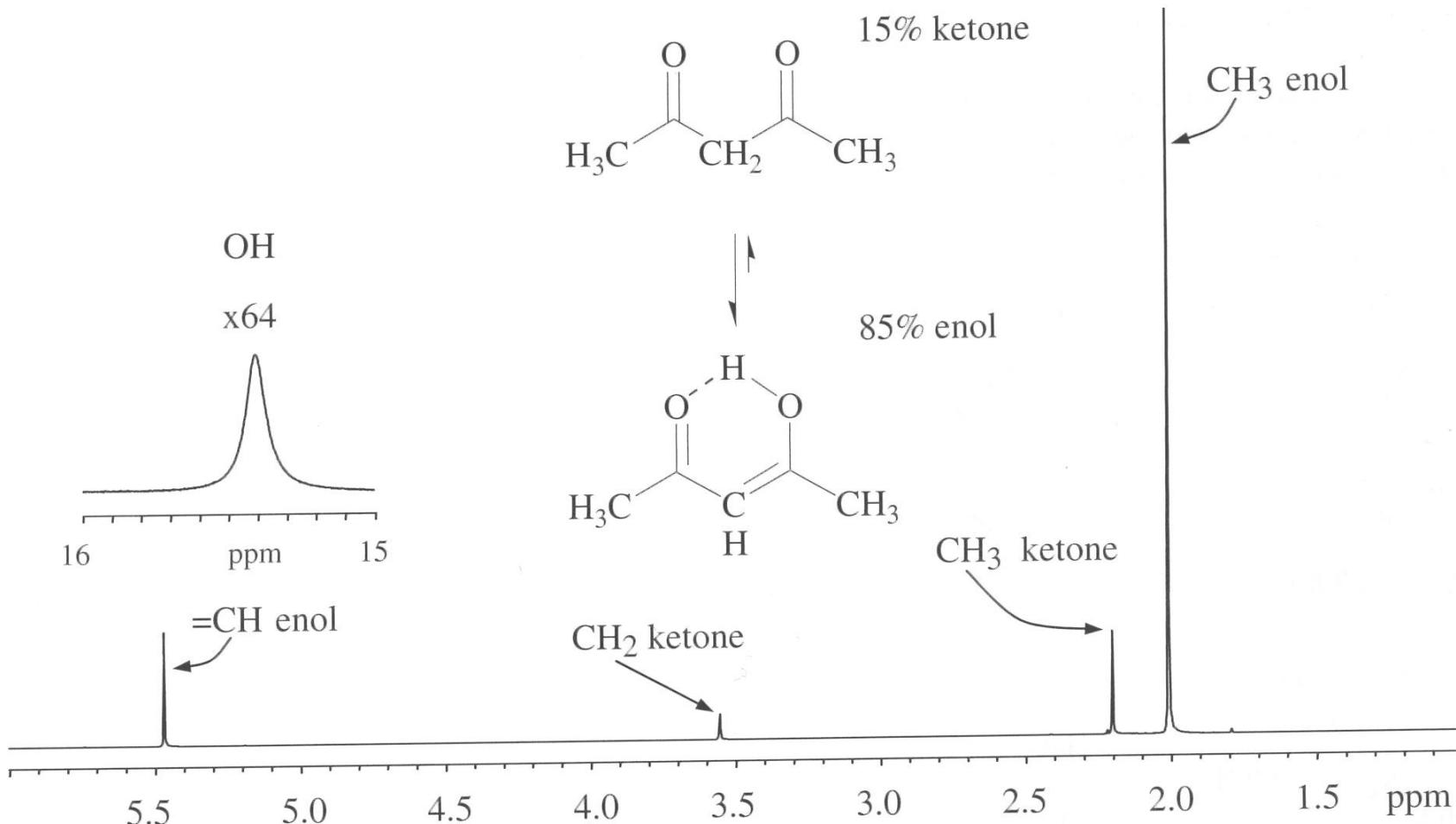


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## ■ Keto-enolna tautomerija

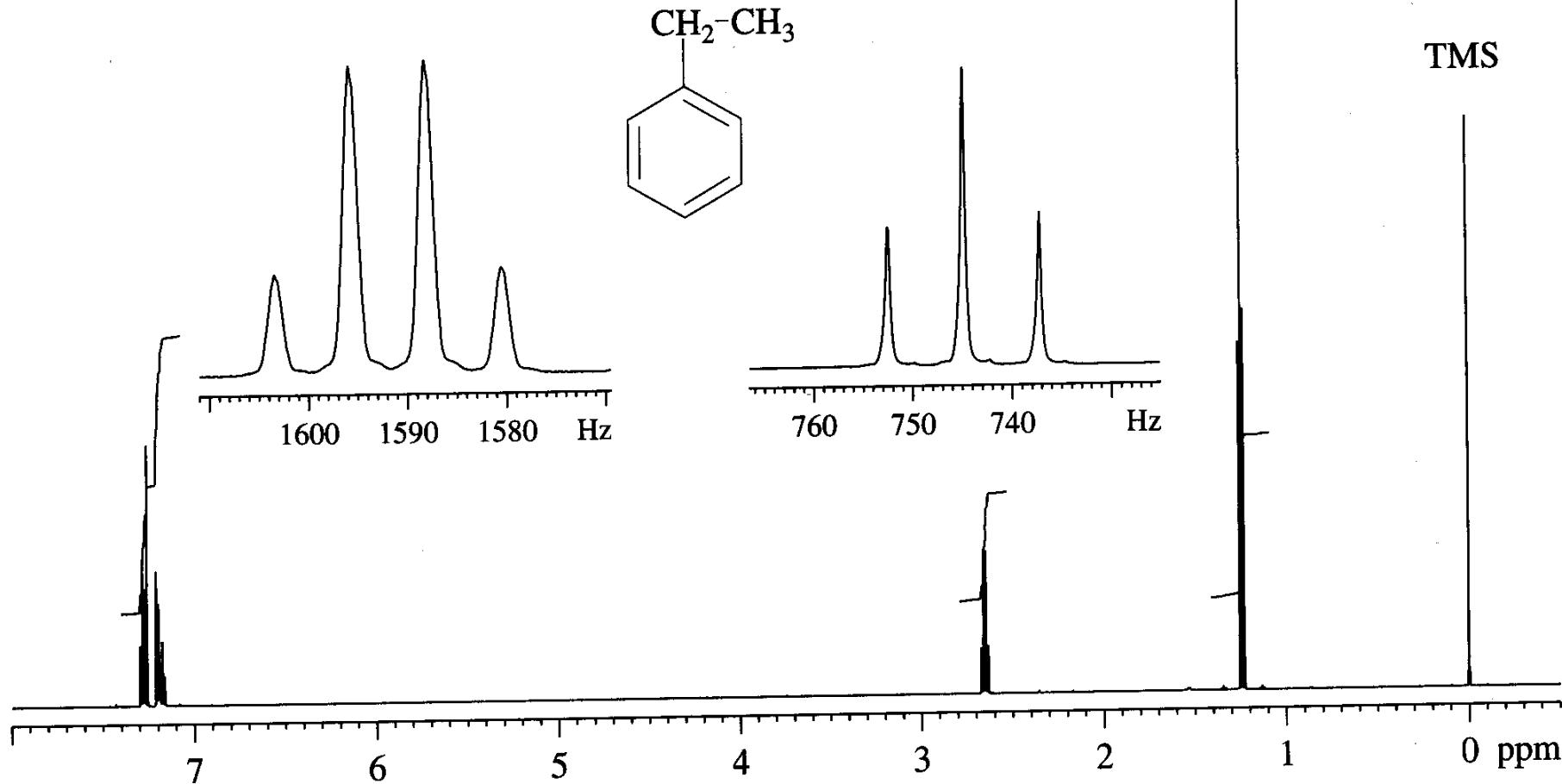


**FIGURE 3.45** Acetylacetone in  $\text{CDCl}_3$  at 300 MHz and 32°C. The enol-keto ratio was measured by integration of the  $\text{CH}_3$  peaks.

# ✓ Primjer

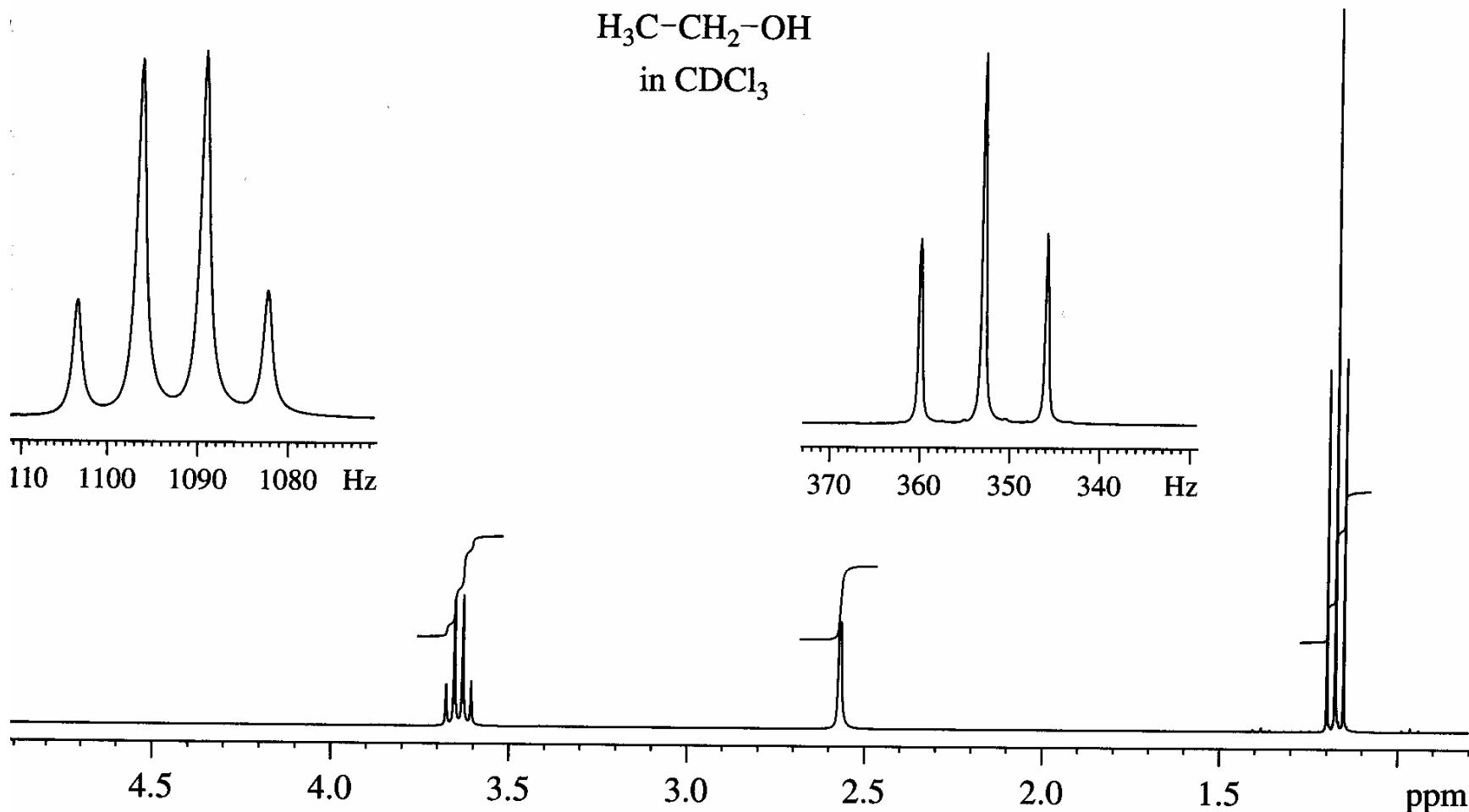


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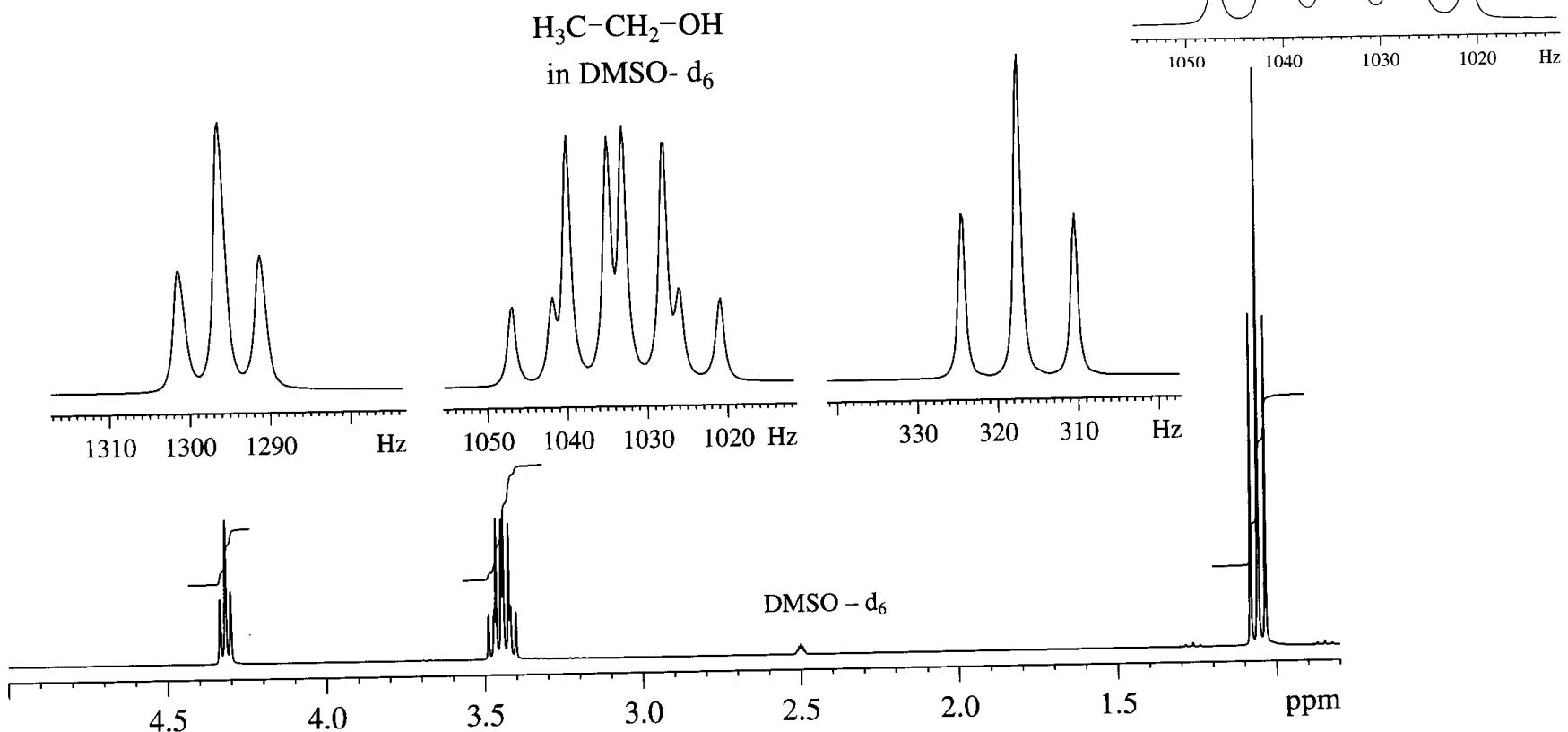


**FIGURE 3.34** Ethylbenzene in  $\text{CDCl}_3$  at 600 MHz. The ethyl moiety is recognized by the  $\text{CH}_3$  triplet and the  $\text{CH}_2$  quartet.

- Spektar etanola snimljen na 300 MHz, nakon što je uzorak u otapalu ostavljen na sobnoj temperaturi na zraku preko noći



- Spektar etanola snimljen na 300 MHz u suhom deuteriranom DMSO (dimetilsulfoksidu)



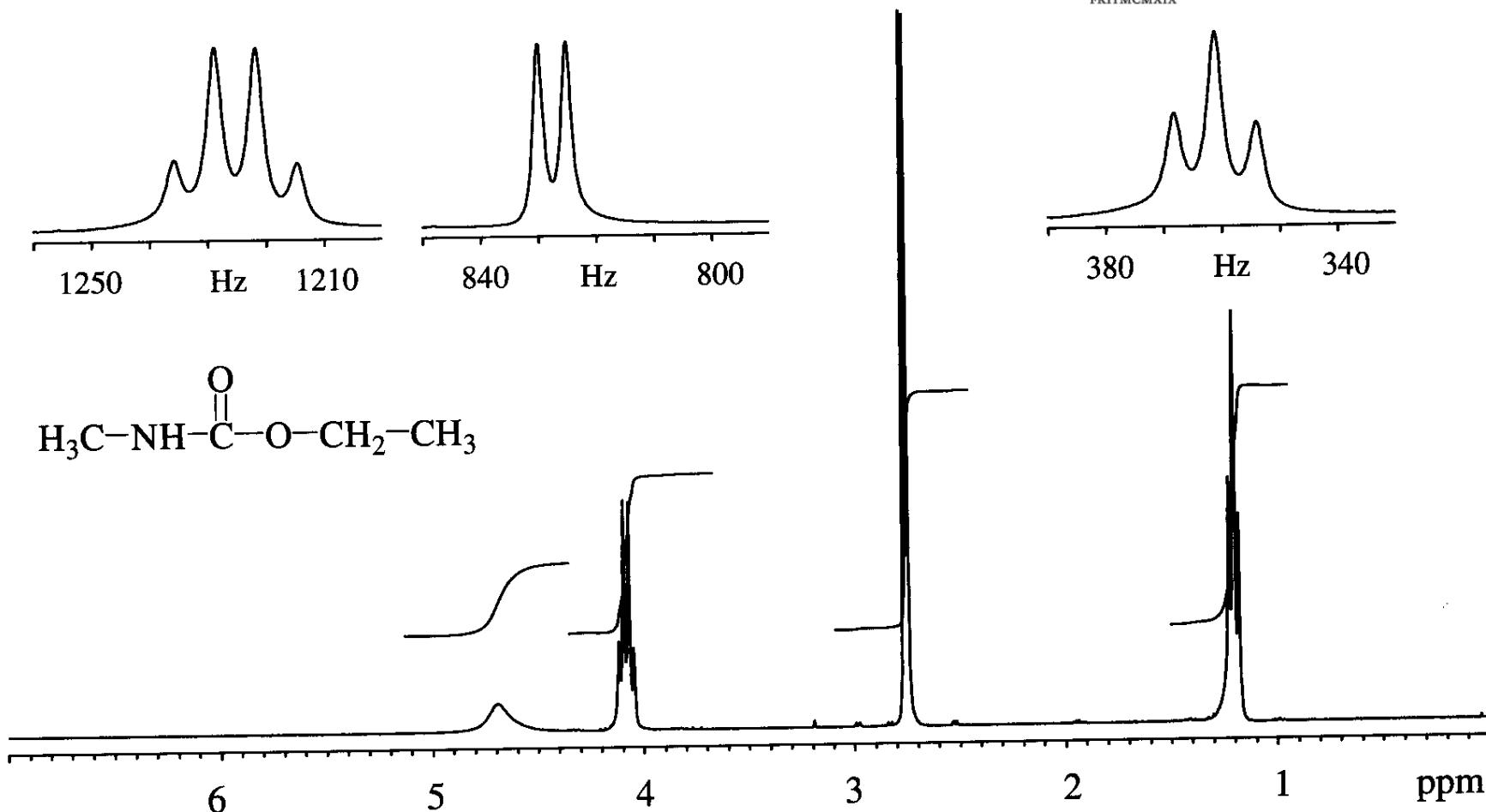
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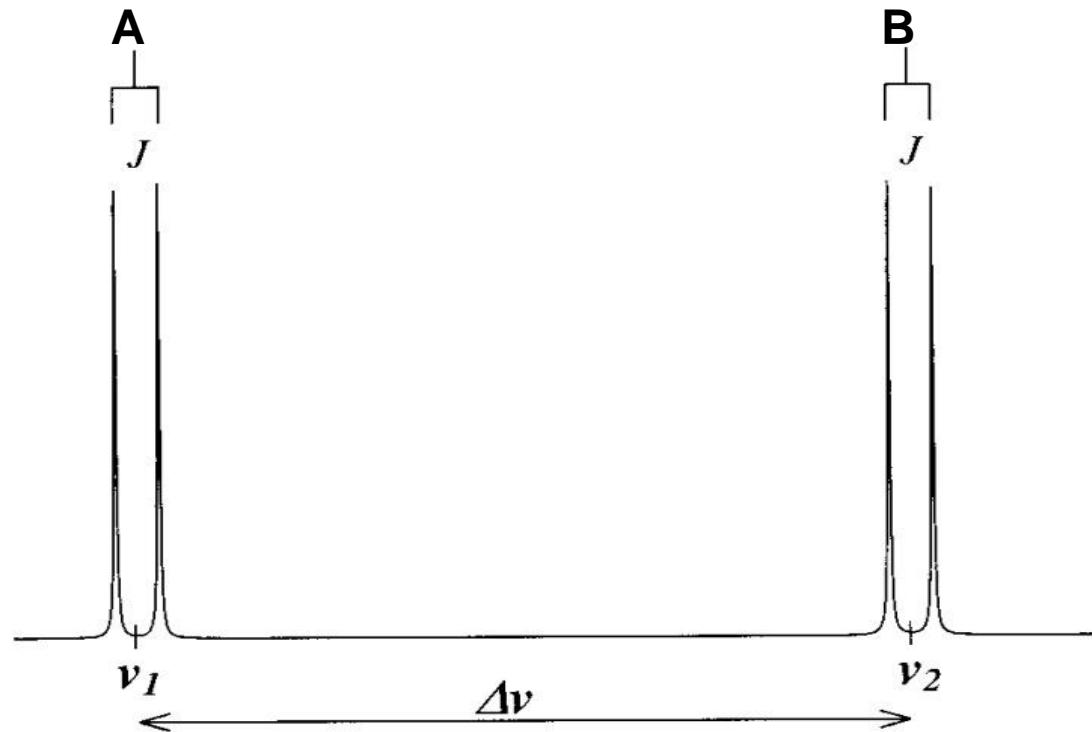


**FIGURE 3.40** Ethyl *N*-methylcarbamate, at 300 MHz in  $\text{CDCl}_3$ .

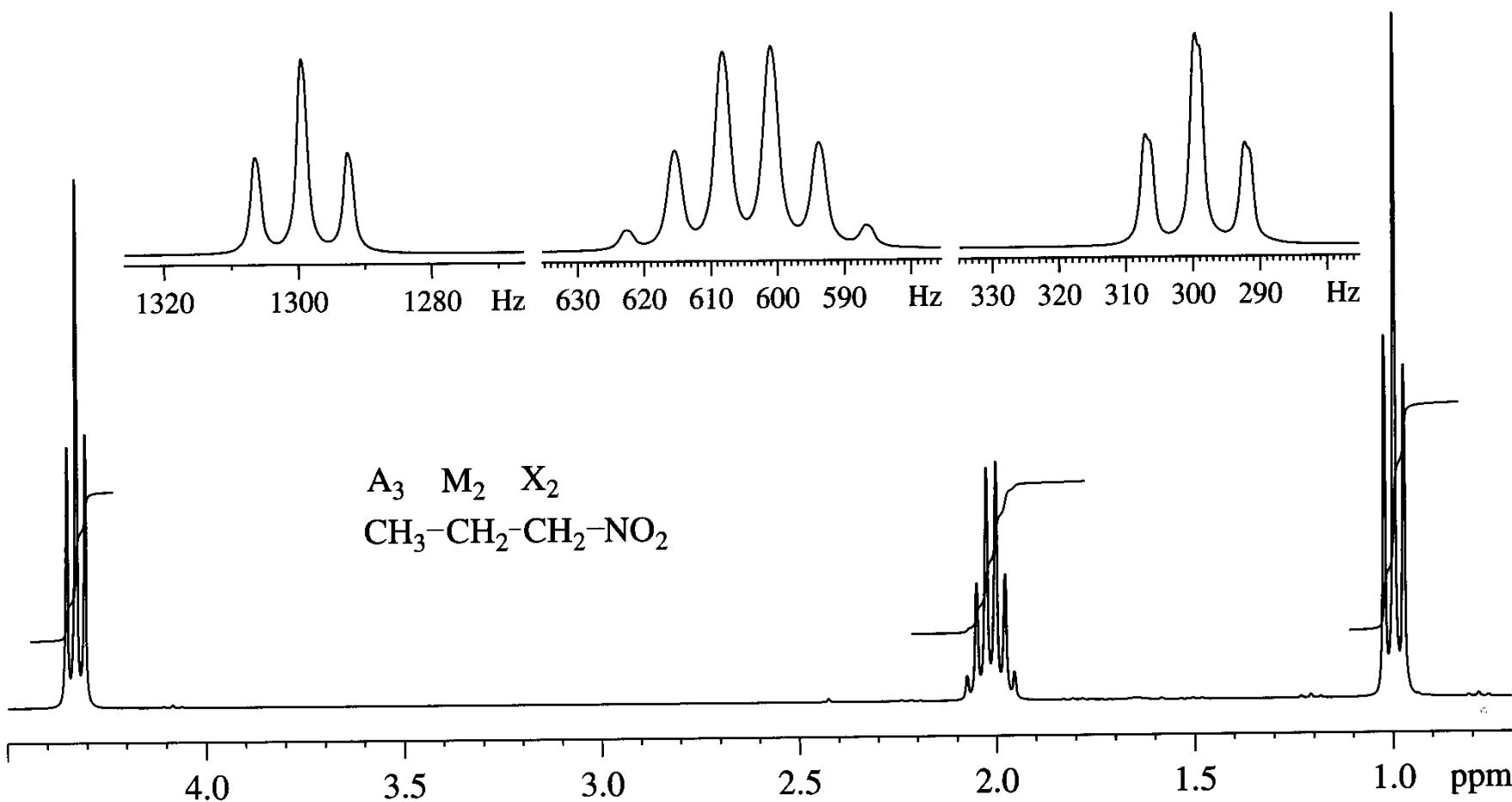
✓ Neki jednostavni sustavi  $^1\text{H} - ^1\text{H}$  sprezanja



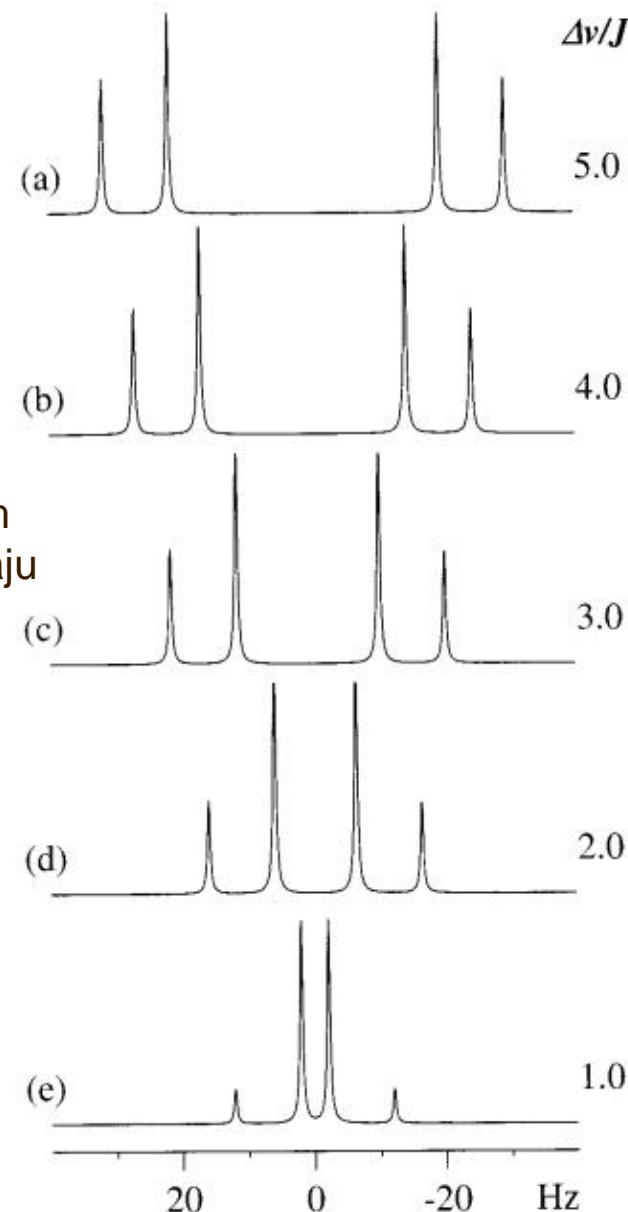
- ✓ **prema konvenciji** – **A, B, C** protoni: bliski po kemijskim pomacima;  
**X, Y, Z** protoni: oni koji su daleko od ovih prethodnih;  
**M, N, O** protoni: negdje u sredini.



Spinska sprega između dva protona s vrlo različitim kemijskim pomacima  
( $\Delta\nu / J$  je iznad ~8).



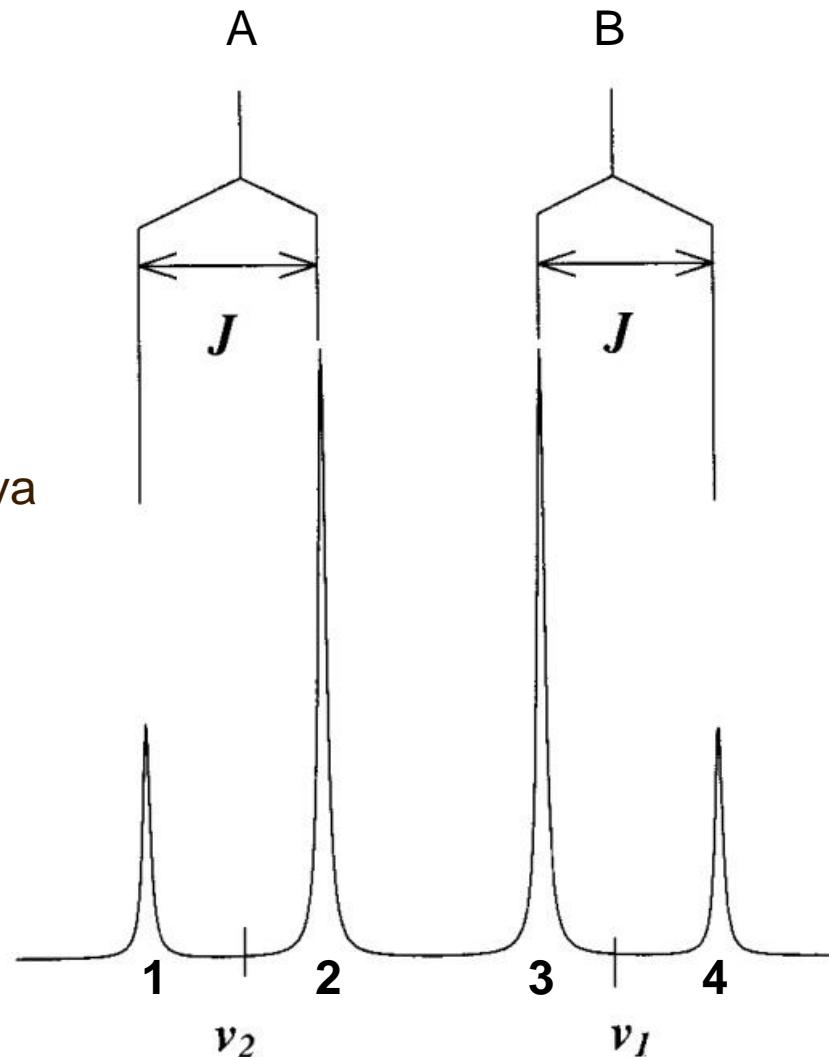
**FIGURE 3.51** 1-Nitropropane in  $\text{CDCl}_3$  at 300 MHz.



✓ Dvoprotonski sustav, spinsko sprezanje sa smanjenom razlikom ( $\Delta\nu / J$ ) u kemijskom pomaku dvaju protona i velikom konstantom sprege (10 Hz).

$$\Delta\nu = \sqrt{(1-4)(2-3)}$$

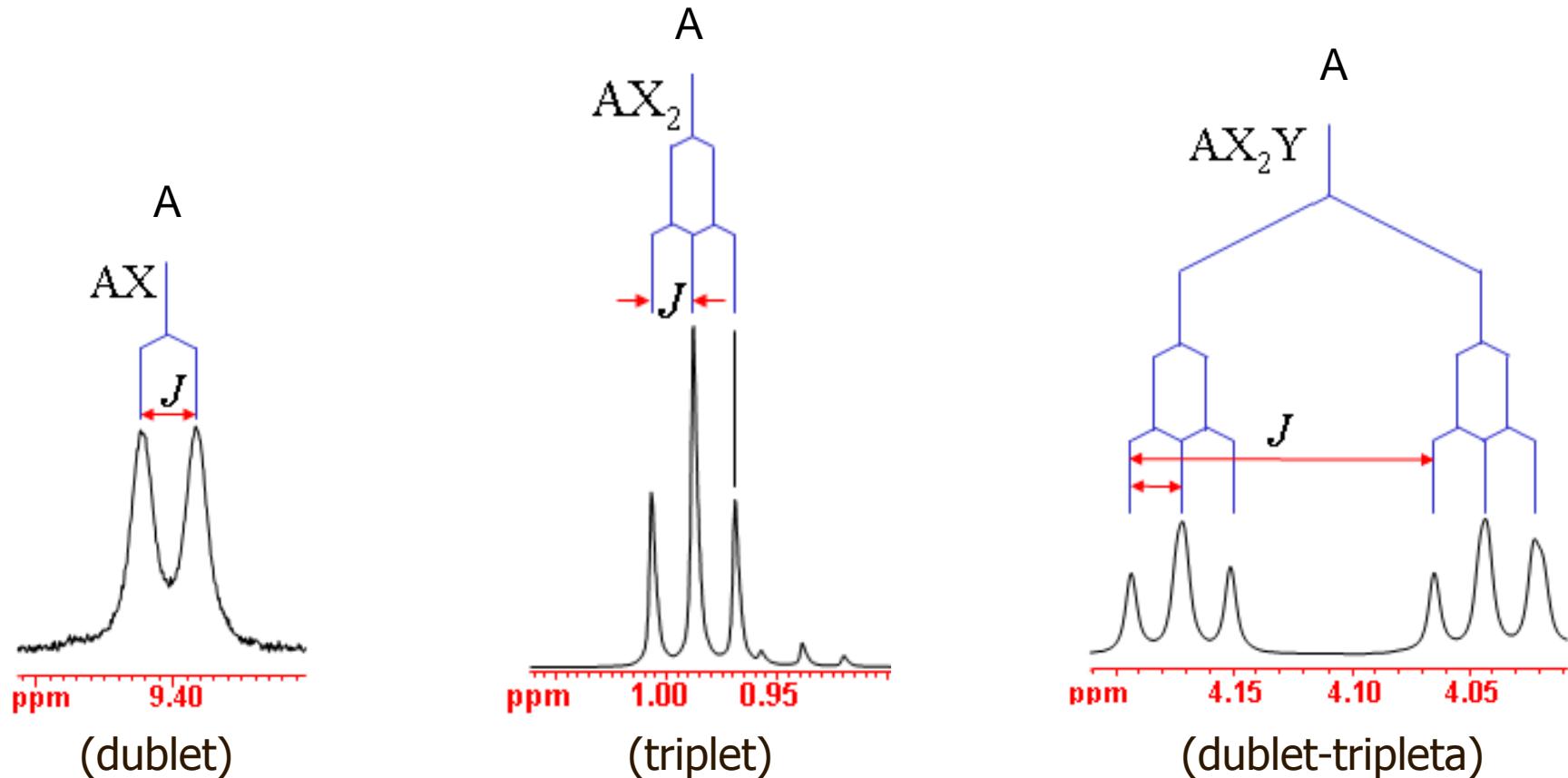
(pozicije signala (1, 2, 3, 4) s lijeva u desno u Hz; kemijski pomak svakog protona je  $\Delta\nu/2$  od sredine skupine signala)

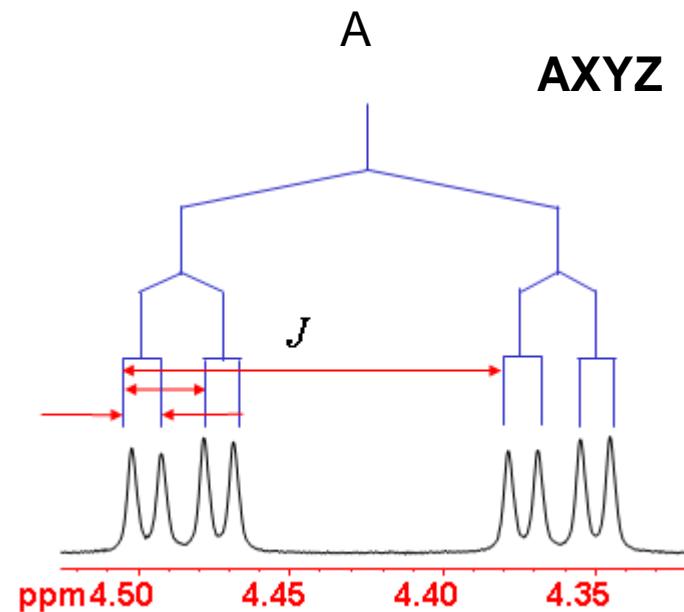
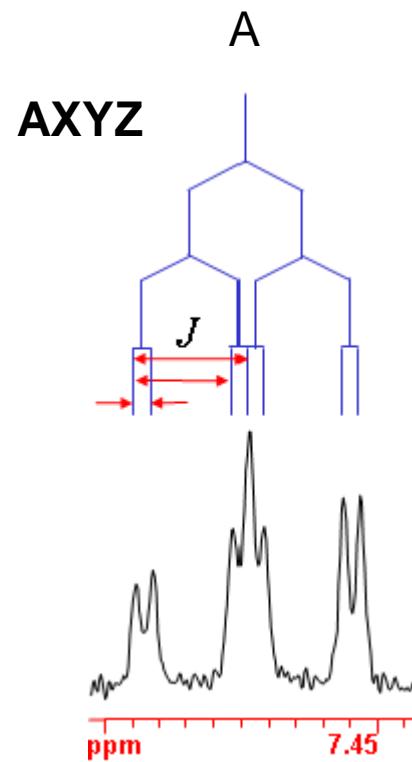
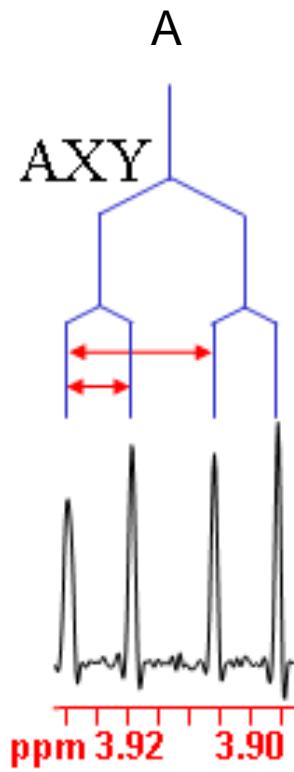


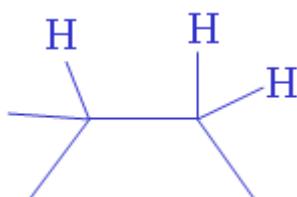
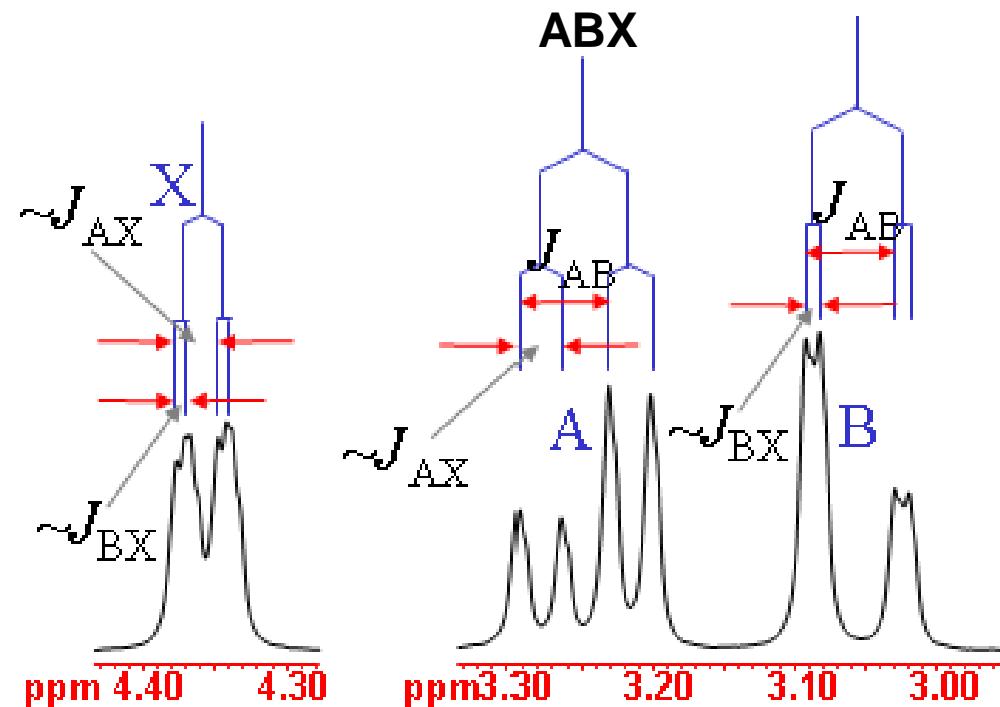
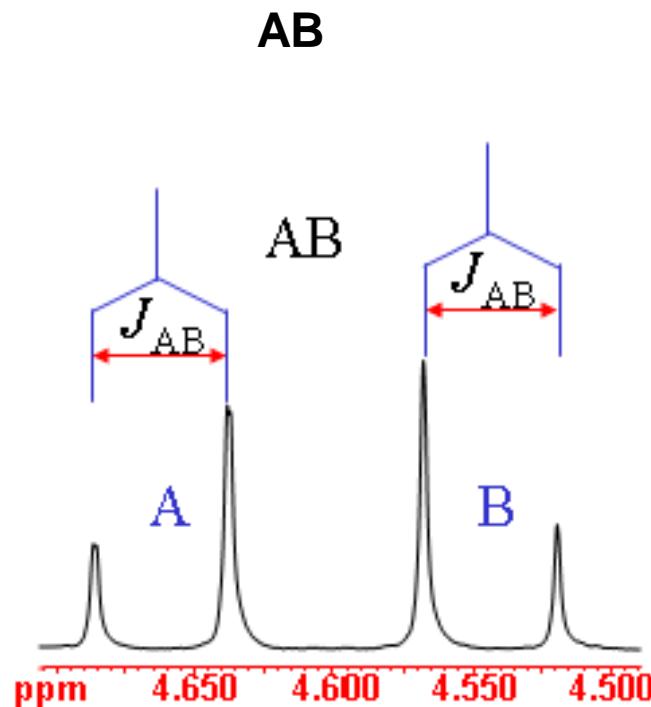
## ✓ Sprezanja protona A i X...Y... :

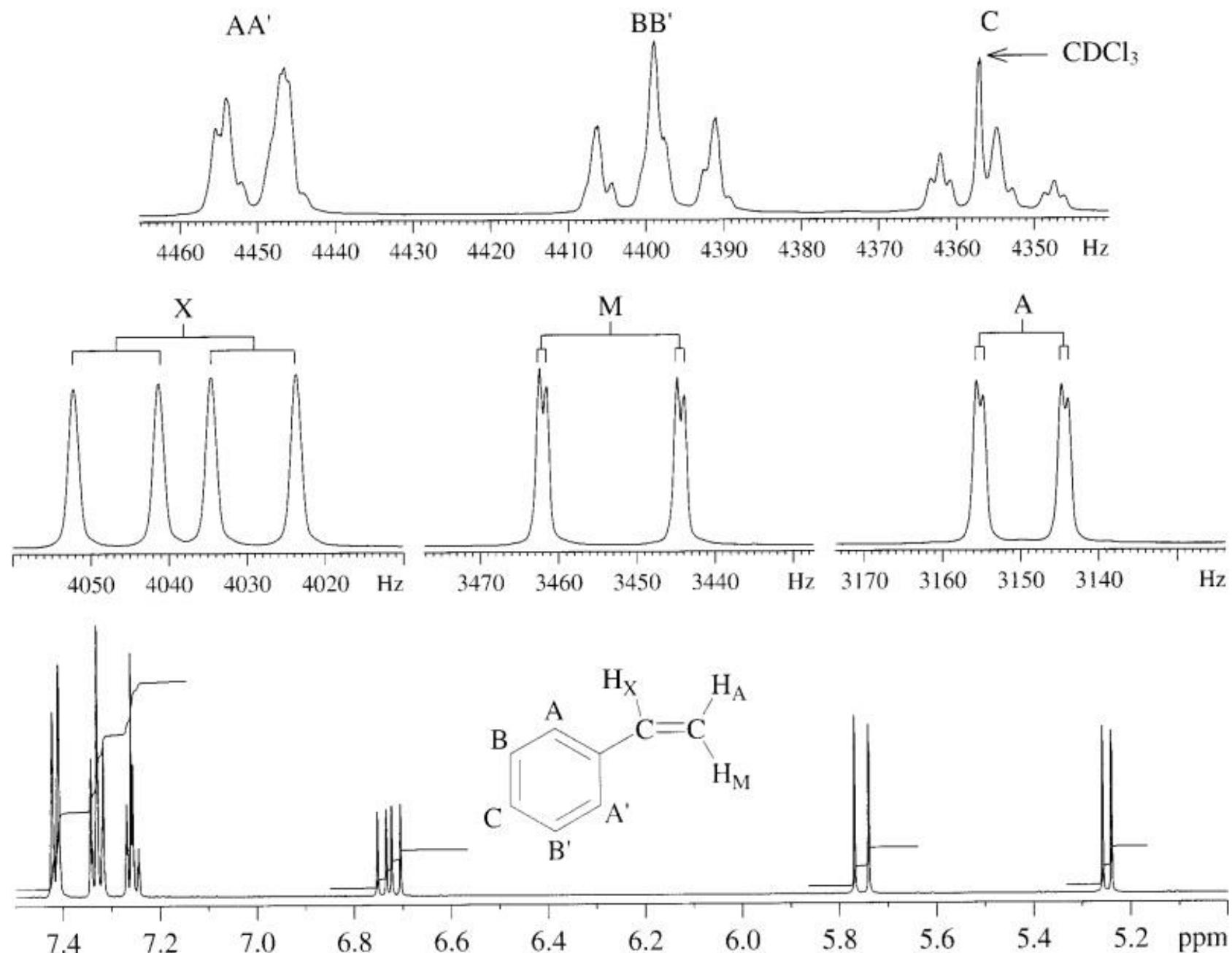


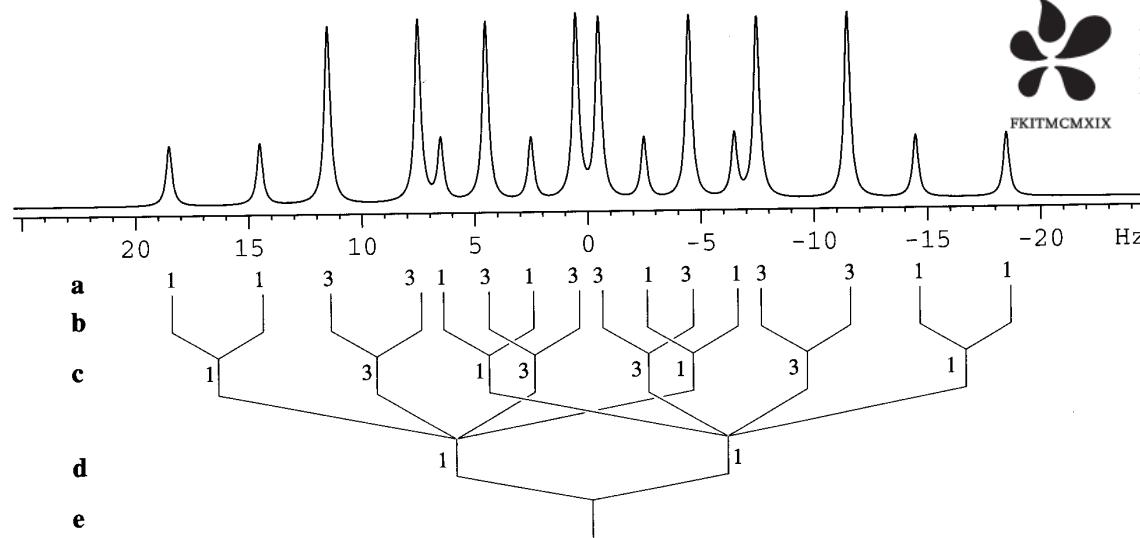
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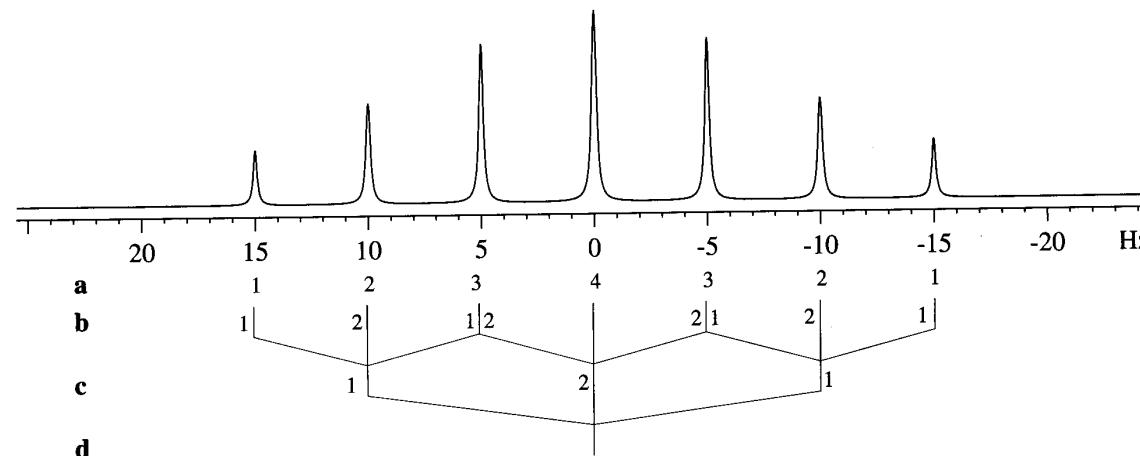






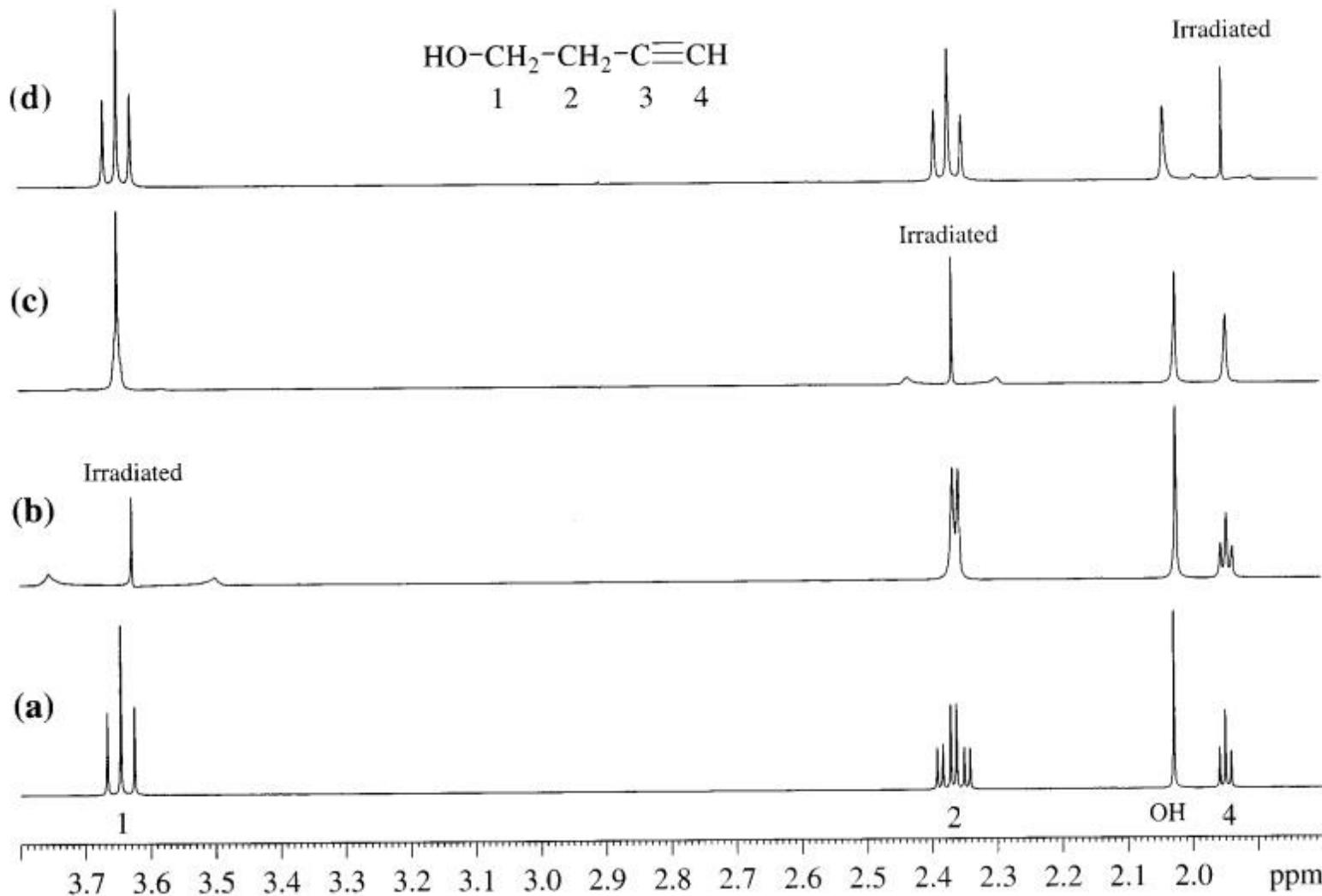


- Konstante sprega prikazanog multipleta sastoje se od 2 dubleta s 4 i 12 Hz i 2 kvarteta od 7 Hz. Na horizontalnoj skali je 10 mm = 5 Hz.



- Podudaranje pikova koji potječu od tripleta-tripleta s konstantama sprega od 5 i 10 Hz dovodi do pojednostavljenja ukupnog signala.

## ✓ Selektivno spinsko rasprezanje (*double resonance*)



$^1\text{H} - ^1\text{H}$  rasprezanja kroz veze

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✓ **Kemijski pomaci metilne skupine u  $\text{CH}_3\text{-X}$**



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<b>Spoj, <math>\text{CH}_3\text{X}</math></b>	$\text{CH}_3\text{F}$	$\text{CH}_3\text{O}$ H	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$	$\text{CH}_4$	$(\text{CH}_3)_4$ Si
<b>X</b>	F	O	Cl	Br	I	H	Si
<b>elektronegativnost X</b>	4.0	3.5	3.1	2.8	2.5	2.1	1.8
<b>kemijski pomak, <math>\delta</math> / ppm</b>	4.26	3.4	3.05	2.68	2.16	0.23	0

- kemijski pomak ( $\delta$  / ppm) se mijenja ovisno o elektronskoj gustoći oko protona;
- elektronegativne skupine uz C-H sustav smanjuju elektronsku gustoću oko protona, kažemo da je proton manje zaklonjen (ili nezaklonjen) i kemijski pomak se povećava;



Spoj	CH <sub>4</sub>	CH <sub>3</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
δ / ppm	0.23	3.05	5.30	7.27

- utjecaj susjednih skupina je kumulativan – prisutnost više elektronegativnih skupina jače otklanja, veći kemijski pomaci

<b>H signal</b>	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> Br
δ / ppm	1.25 1.69 3.30

- ove induktivne efekte osjećaju i drugi protoni u lancu ali utjecaj znatno opada s udaljenosti od elektronegativne skupine



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# $^{13}\text{C}$ nuklearna magnetska rezonancija ( $^{13}\text{C}$ NMR)

## ■ $^{13}\text{C}$ NMR spektroskopija

- Izotop  $^{13}\text{C}$  obuhvaća 1,1% ugljika iz prirodnih izvora
  - $^{12}\text{C}$  nema magnetski spin i ne daje NMR signal
- Jedan pik za svaki ugljikov atom
  - Ugljik-ugljik sprege su vrlo rijetke
  - $^1\text{H}$  i  $^{13}\text{C}$  jezgre se međusobno također sprežu
    - Proces uklanjanja sprege jezgre  $^1\text{H}$  s ugljikovom jezgrom na koju je vezan, naziva se “broadband (BB) proton decoupling”
  - Većina  $^{13}\text{C}$  NMR spektara, uslijed toga, pokazuje samo jedan pik za svaki pojedini ugljik

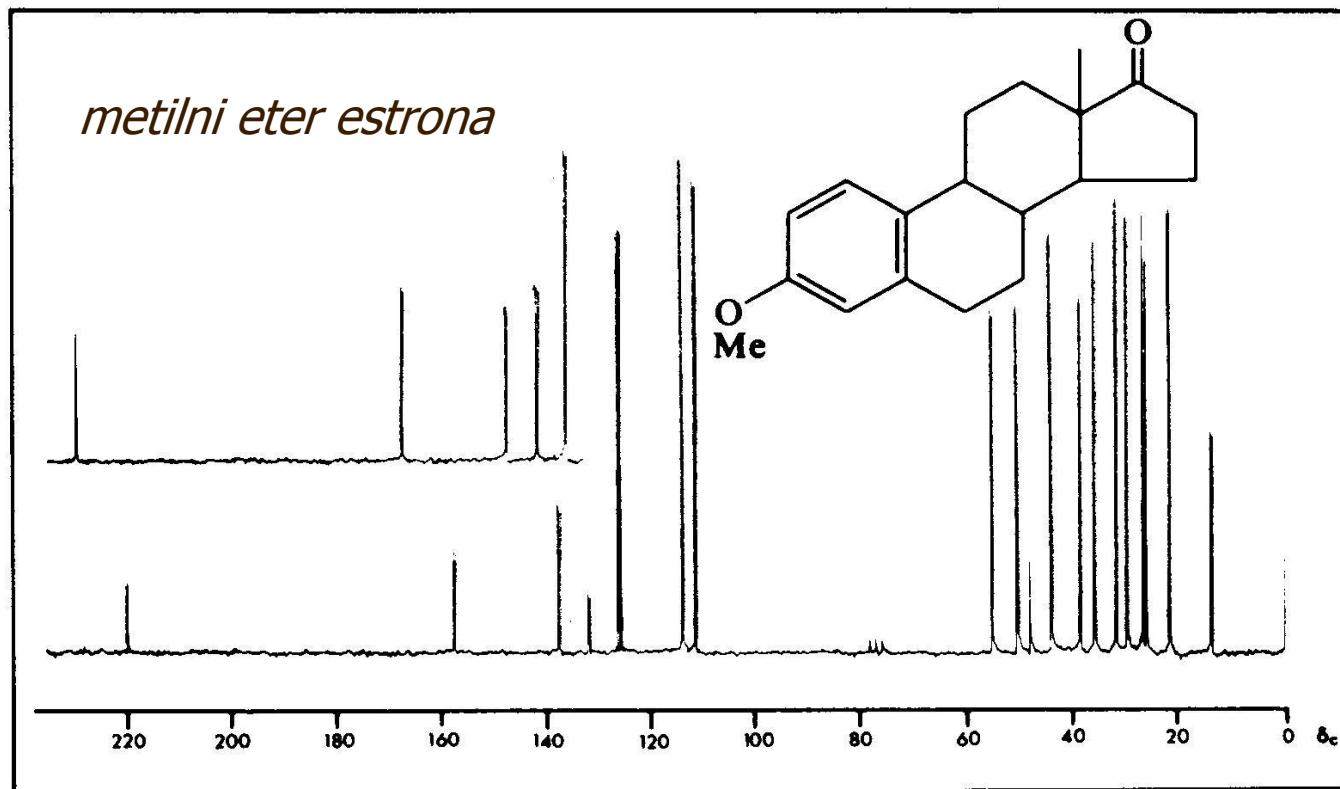
## $^{13}\text{C}$ kemijski pomaci

- Kao i u  $^1\text{H}$  NMR spektroskopiji, kemijski pomaci u  $^{13}\text{C}$  NMR spektrima ovise o elektronskoj gustoći oko jezgre ugljika
  - Opadanje elektronske gustoće uzrokuje pomak signala u niže magnetsko polje (*deshielding*)
  - Povećanje elektronske gustoće uzrokuje pomak u više magnetsko polje (*shielding*)
- Uslijed širokog područja kemijskih pomaka, vrlo je rijetko slučajno podudaranje  $^{13}\text{C}$  signala
- Grupa od 3 linije pikova na  $\delta$  77 ppm potječe od uobičajenog NMR signala deuterokloroform-a kao otapala i ne treba se uzimati u obzir

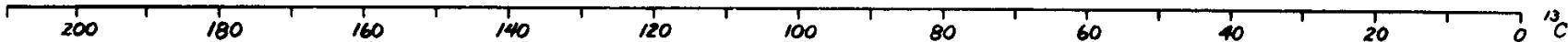


## ✓ $^{13}\text{C}$ NMR

**NE vrijedi** isto pravilo - veličina signala za C-atom nije proporcionalna s brojem C-atoma - brzina relaksacije ugljikovih atoma direktno vezanih na vodikove atome je puno veća nego ugljikovih atoma koji nisu tako vezani. (moguće je povećati intenzitet slabih signala dodatkom paramagnetskih soli, koje ubrzavaju relaksaciju).



- ✓ (nejednako veliki signali, 19 C-atoma, 5 signala niskog intenziteta odgovara 5 kvaternim C-atomima)



Aldehydes

Aromatic

Conjugated Alkene Terminal Methylene

Alkene

>CH-O

-CH<sub>2</sub>-O

-O-CH<sub>3</sub>

>CH-N<-CH<sub>2</sub>-N<,CH<sub>3</sub>-N<

-C≡C-H

>CH-C(=O)-, -CH<sub>2</sub>-C(=O)-, CH<sub>3</sub>-C(=O)-

\*CH<sub>3</sub>-C=C<

>C-\*CH<sub>2</sub>-C< H H

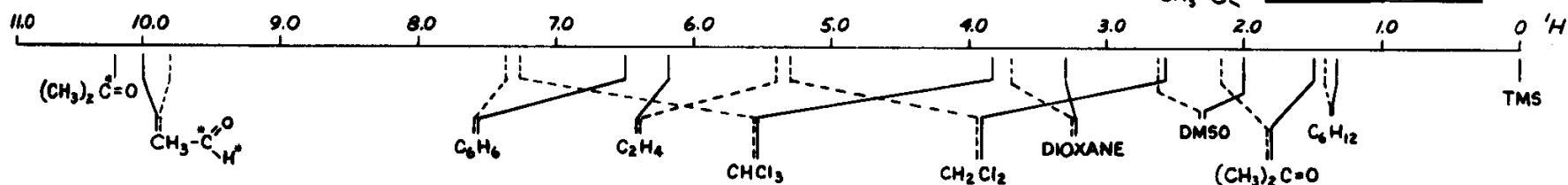
CH<sub>3</sub>-C<

$$\delta_C = 20 \cdot \delta_H$$



$$\delta_H = 5,28 \text{ ppm}$$

$$\delta_C = 123,3 \text{ ppm}$$



Legend:  $^1\text{H}$  ---  $^{13}\text{C}$  —

✓ Usporedba  $^1\text{H}$  i  $^{13}\text{C}$  kemijskih pomaka

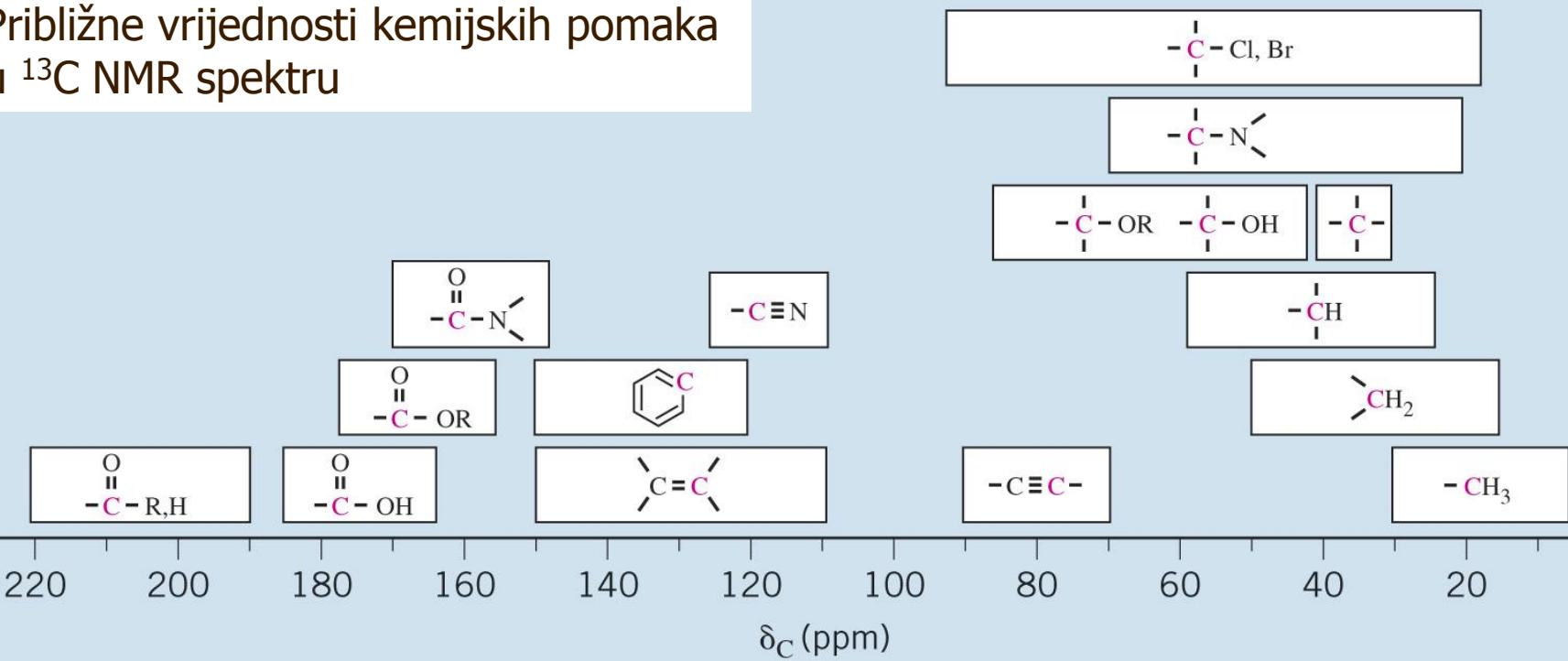


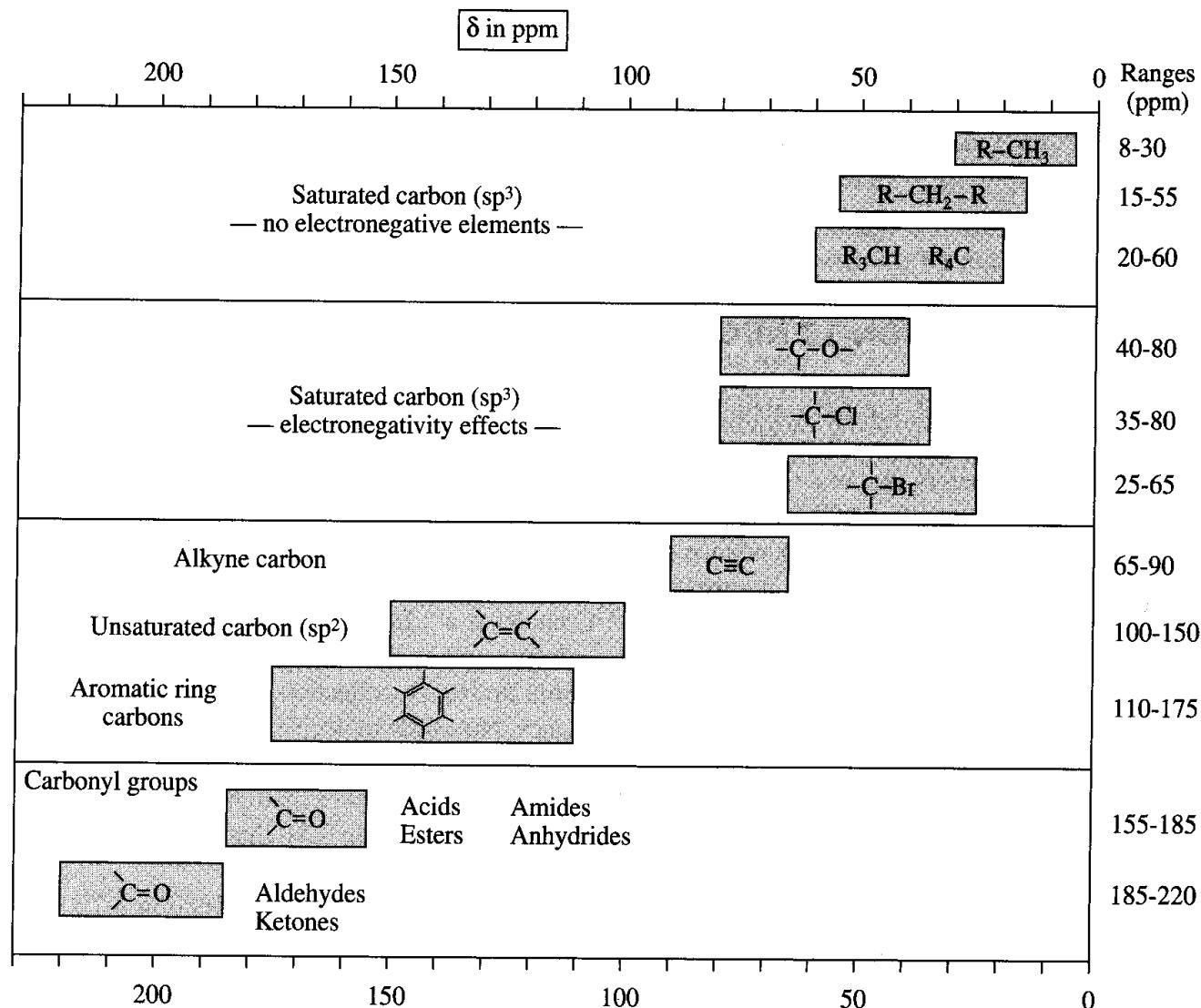
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## Približne vrijednosti kemijskih pomaka u $^{13}\text{C}$ NMR spektru

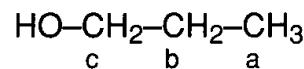




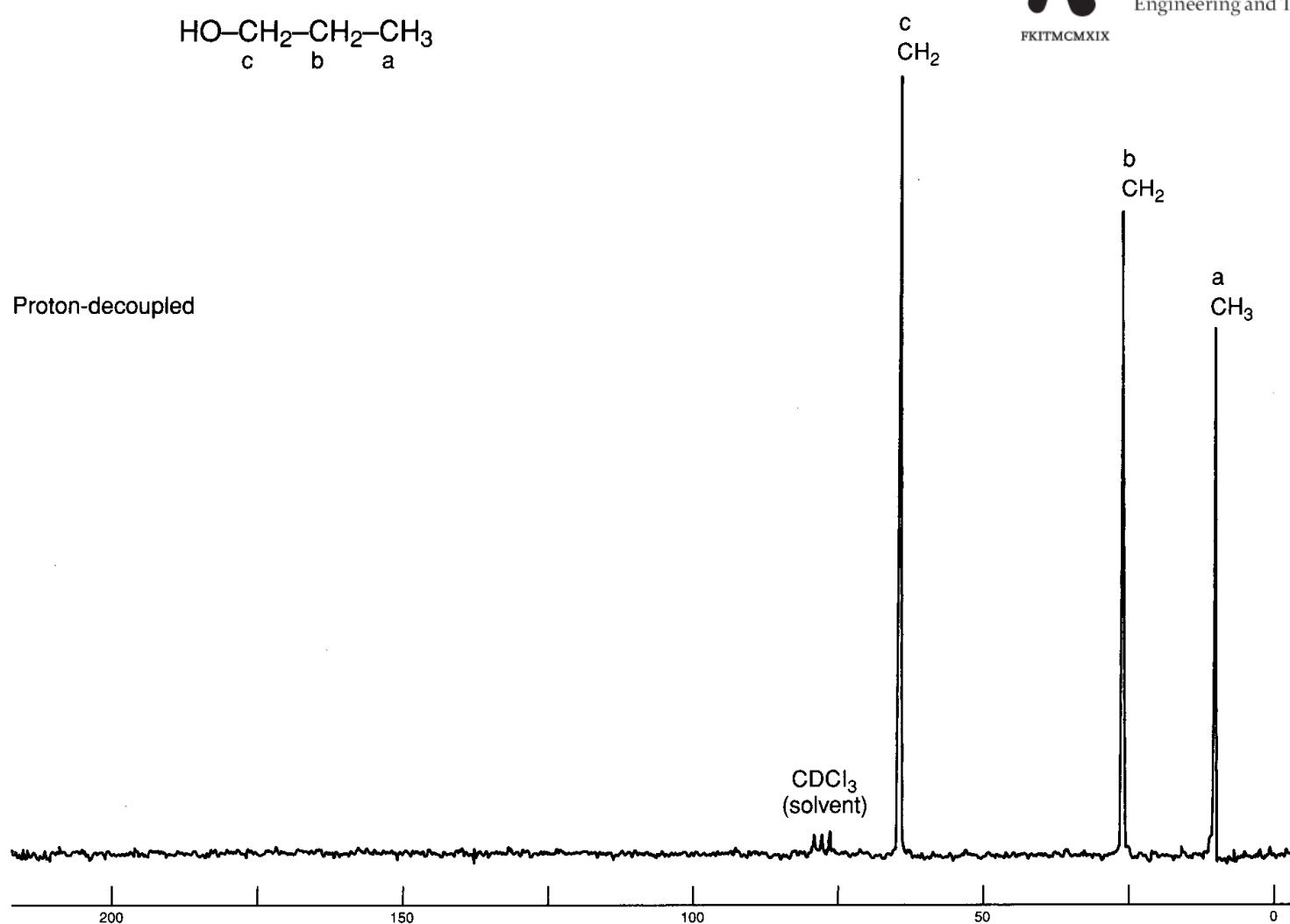
**FIGURE 4.1** A correlation chart for  $^{13}\text{C}$  chemical shifts (chemical shifts are listed in parts per million from TMS).



# ✓ Primjer



Proton-decoupled



**FIGURE 4.5** The proton-decoupled  $^{13}\text{C}$  spectrum of 1-propanol (22.5 MHz).



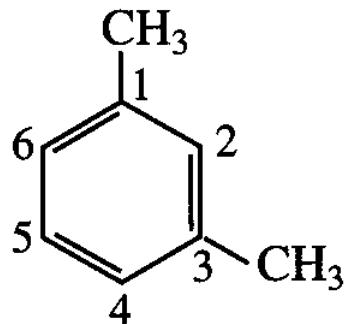
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# ✓ Računanje $^{13}\text{C}$ kemijskih pomaka



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$$\text{C1} = \text{base} + \text{ipso} + \text{meta} = 128.5 + 9.3 + (-0.1) = 137.3 \text{ ppm}$$

$$\text{C2} = \text{base} + \text{ortho} + \text{ortho} = 128.5 + 0.7 + 0.7 = 129.9 \text{ ppm}$$

$$\text{C3} = \text{C1}$$

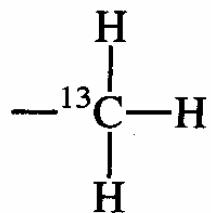
$$\text{C4} = \text{base} + \text{ortho} + \text{para} = 128.5 + 0.7 + (-2.9) = 126.3 \text{ ppm}$$

$$\text{C5} = \text{base} + \text{meta} + \text{meta} = 128.5 + 2(-0.1) = 128.3 \text{ ppm}$$

$$\text{C6} = \text{C4}$$

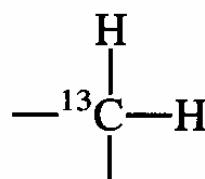
# ✓ Utjecaj vezanih protona na rezonanciju $^{13}\text{C}$ jezgre

3 protons



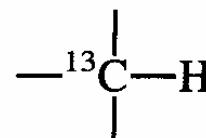
$$n + 1 = 3 + 1 \\ = 4$$

2 protons



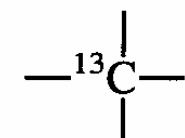
$$n + 1 = 3$$

1 proton

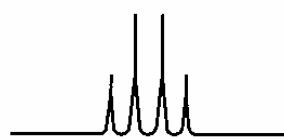


$$n + 1 = 2$$

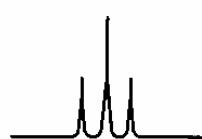
0 protons



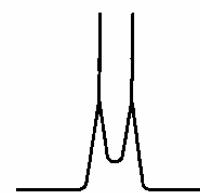
$$n + 1 = 1$$



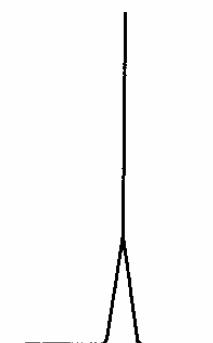
Methyl  
carbon



Methylene  
carbon



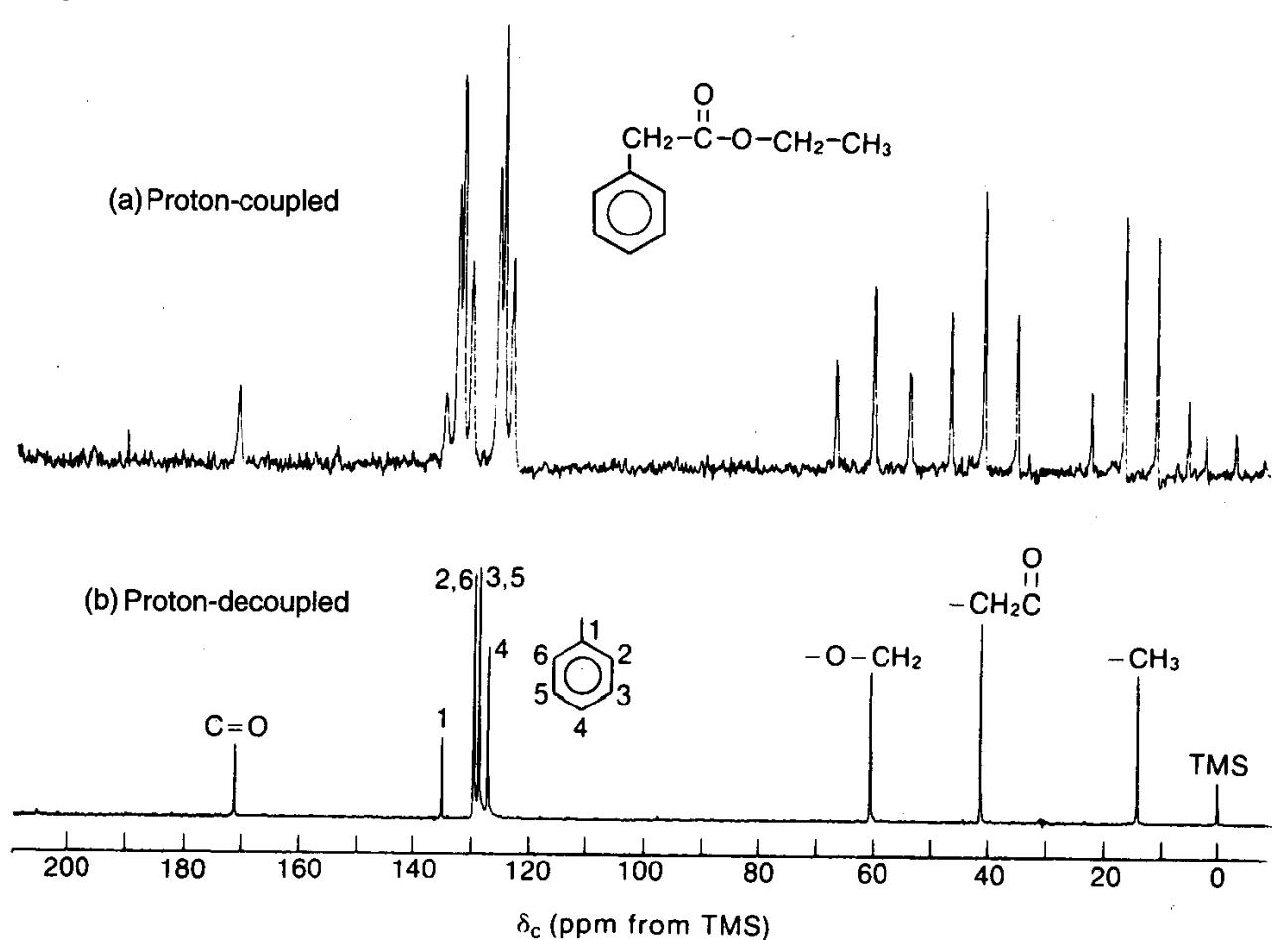
Methine  
carbon



Quaternary  
carbon



✓ "Proton-coupled" (gore) i "proton-decoupled" (dolje)  
 $^{13}\text{C}$  NMR spektar etilfenilacetata



**FIGURE 4.4** Ethyl phenylacetate. (a) The proton-coupled  $^{13}\text{C}$  spectrum (20 MHz). (b) The proton-decoupled  $^{13}\text{C}$  spectrum (20 MHz). (From Moore, J. A., and D. L. Dalrymple, *Experimental Methods in Organic Chemistry*, W. B. Saunders, Philadelphia, 1976.)

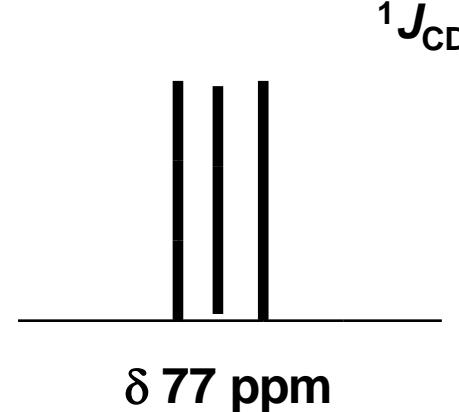
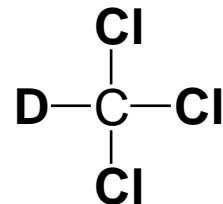
# ✓ Spin – spin sprezanja



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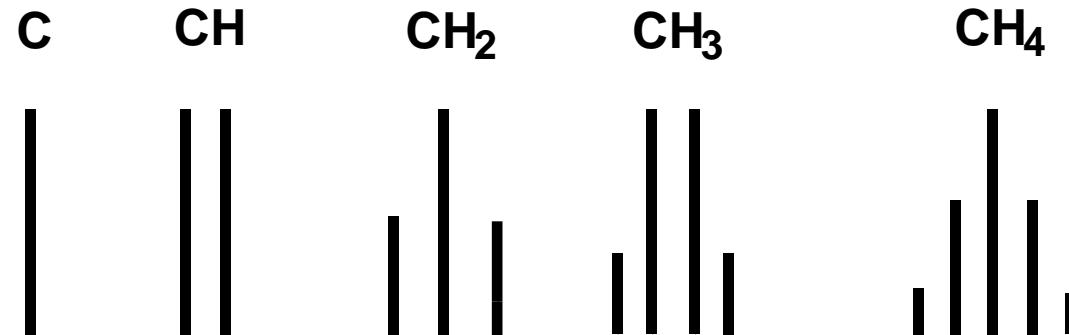


$^{13}\text{C} - ^2\text{H}$  sprege



deuterij :  $I = 1$ ;  $2I + 1 = 3$

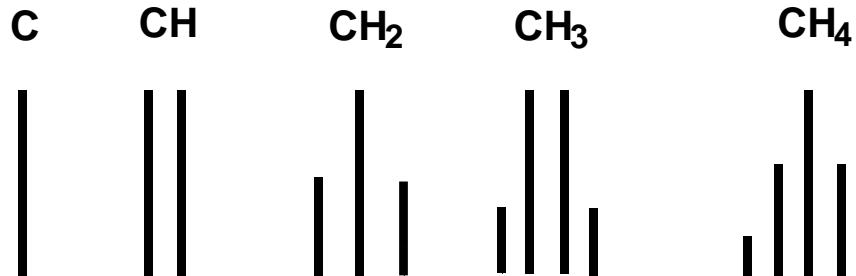
$^{13}\text{C} - ^1\text{H}$  sprege



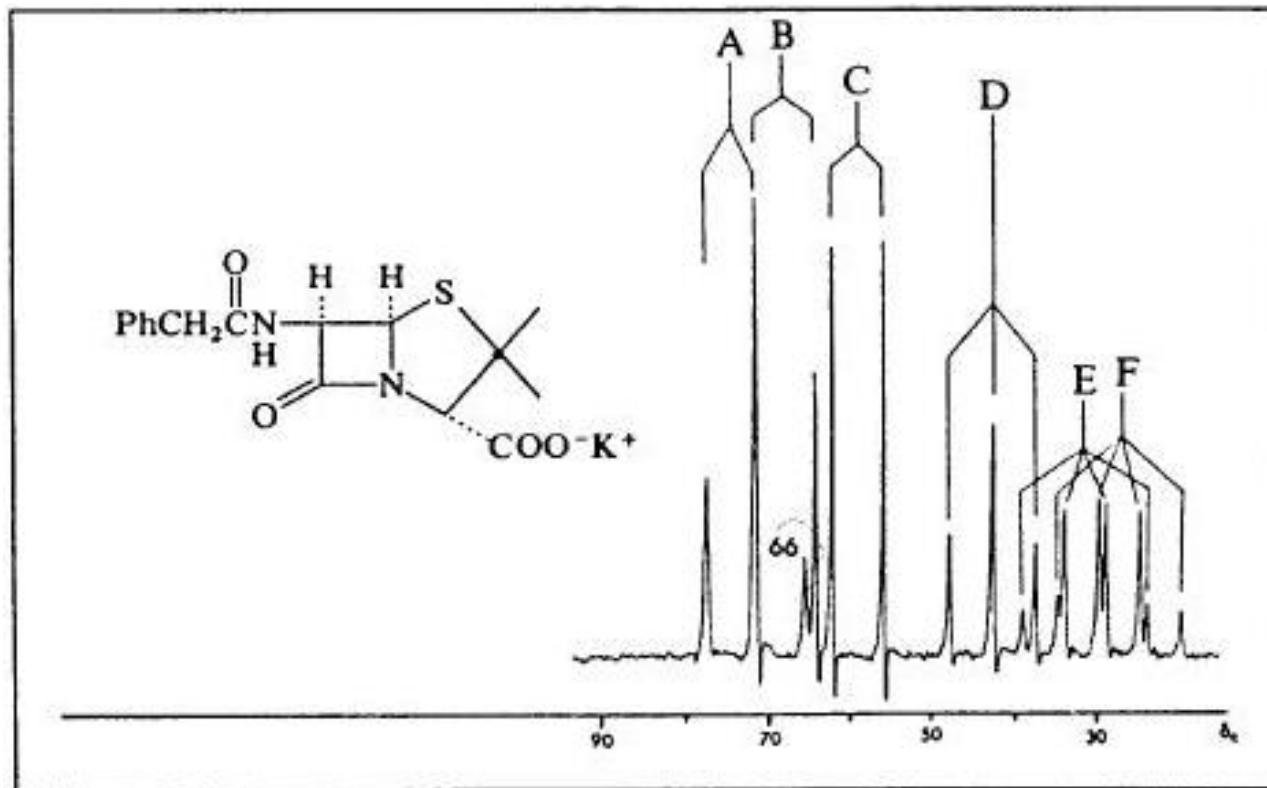
## ✓ *Neraspregnuti spektar*



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(n+1) linija  
intenziteti: prema koeficijentima  
 $(x+1)^n$





✓ Veličina konstanti sprega

$J_{\text{CH}}$ :

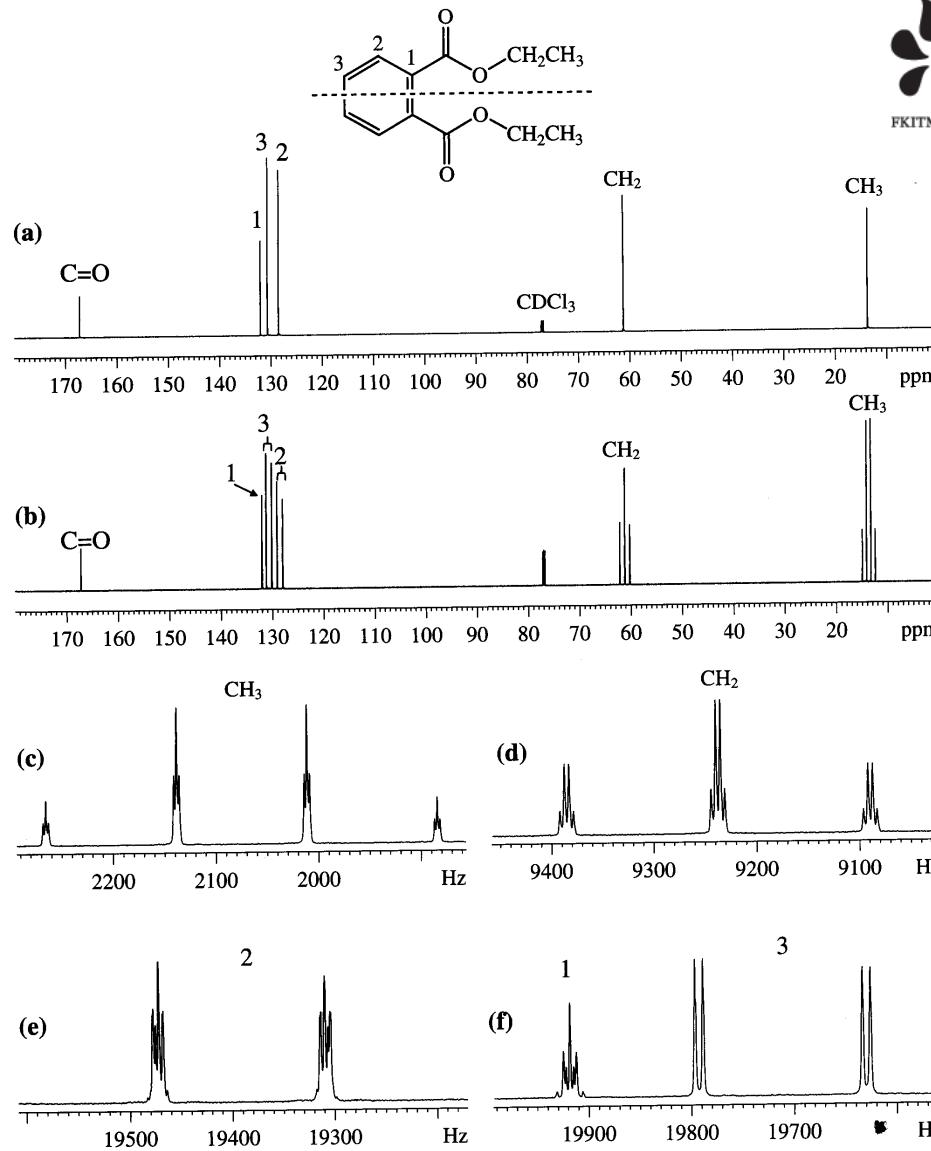
$J_{\text{CH}} \text{ } (sp^3) = 120 - 150 \text{ Hz}$

$(sp^2) = 155 - 205 \text{ Hz}$

$(sp) = \sim 250 \text{ Hz}$

**$^{13}\text{C} - ^{13}\text{C}$  sprege**

✓ Zbog niskog udjela izotopa  $^{13}\text{C}$  – ne vidi se signal ili je jako slabi (rijetkost je da jedna  $^{13}\text{C}$  jezgra bude vezana za drugu  $^{13}\text{C}$  jezgru).

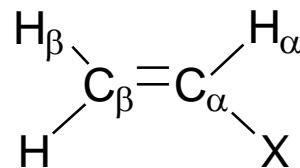


**FIGURE 4.6** (a) Diethyl phthalate, decoupled  $^{13}\text{C}$  spectrum at 150.9 MHz in  $\text{CDCl}_3$ , (b) coupled  $^{13}\text{C}$  spectrum (c–f) expansions of coupled  $^{13}\text{C}$  spectrum.

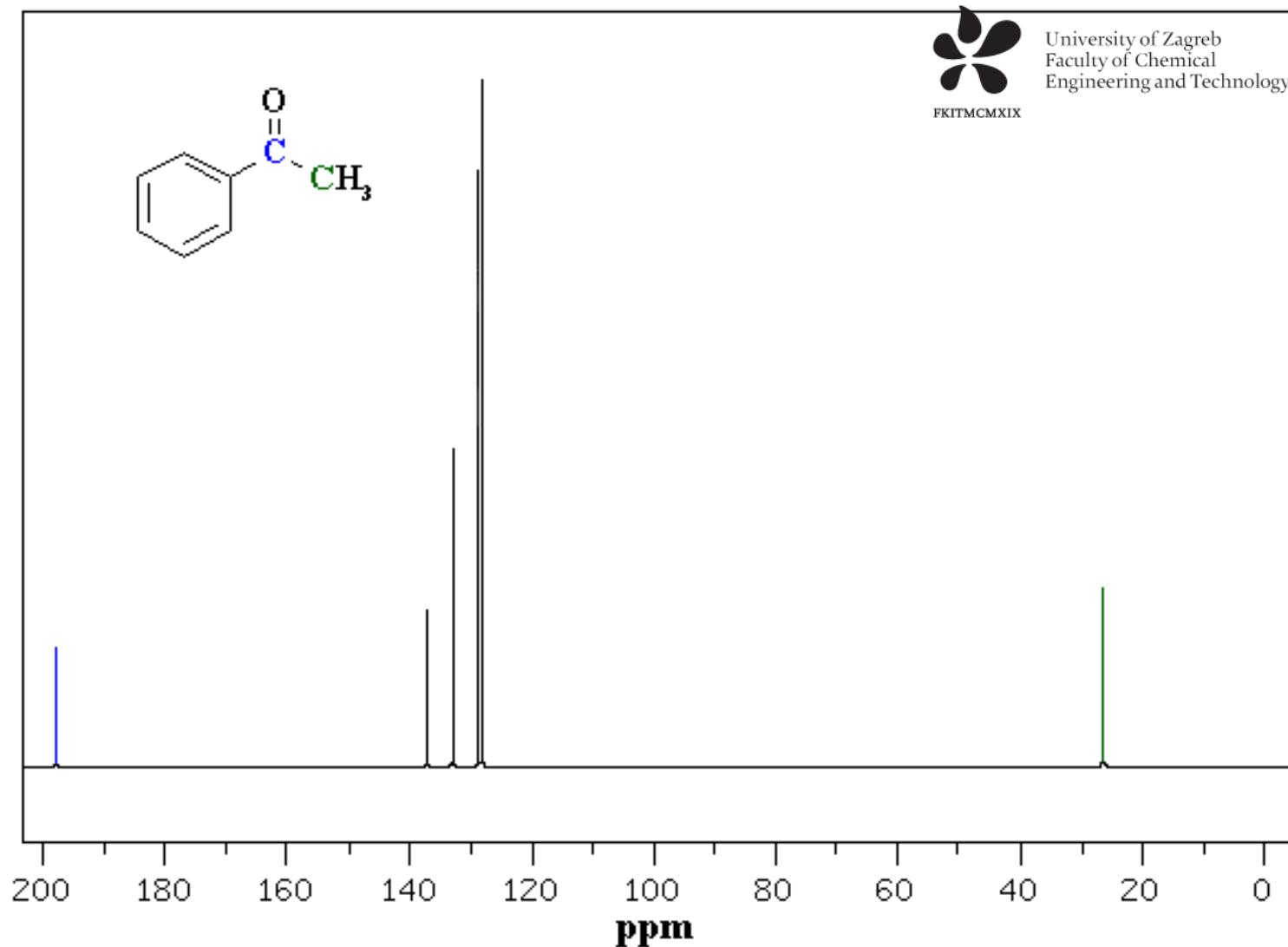
□ Kemijski pomaci ugljika i vodika u, na i pokraj višestrukih veza:

<i>Compound</i>	$\delta_{\text{C}}$	$\delta_{\text{H}}$	<i>Compound</i>	$\delta_{\text{C}}$	$\delta_{\text{H}}$
$\text{CH}_3\text{H}$	-2.3	0.23	$\text{CH}_3\text{CHO}$	31.2	2.20
$\text{CH}_3\text{CH}=\text{CH}_2$	22.4	1.71	$\text{CH}_3\text{COCH}_3$	28.1	2.09
$\text{CH}_3\text{C}\equiv\text{CH}$		1.80	$\text{CH}_3\text{CN}$	1.30	1.98
$\text{CH}_2=\text{CH}_2$	123.3	5.25	$\text{CH}_3\text{CHO}$	199.7	9.80
$\text{CH}_3\text{C}\equiv\text{CH}$	66.9	1.80	$\text{CH}_3\text{COCH}_3$	206.0	
$\text{CH}_3\text{C}\equiv\text{CCH}_3$	79.2		$\text{CH}_3\text{CN}$	117.7	

□ Konjugativni efekti na kemijske pomake supstituiranih alkena:



X	<i>Electronic nature</i>	$\delta_{\text{C}\beta}$	$\delta_{\text{C}\alpha}$	$\delta_{\text{H}\beta}$	$\delta_{\text{H}\alpha}$
H	Reference compound	123.3	123.3	5.28	5.28
Me	Weak $\pi$ - and $\sigma$ -donor	115.4	133.9	4.88	5.73
OMe	$\pi$ -donor, $\sigma$ -acceptor	84.4	152.7	3.85	6.38
Cl	$\sigma$ -acceptor, weak $\pi$ -donor	117.2	125.9	5.02	5.94
$\text{CH}=\text{CH}_2$	Simple conjugation	130.3	136.9	5.06	6.27
SiMe <sub>3</sub>	$\pi$ -acceptor, $\sigma$ -donor	129.6	138.7	5.87	6.12
COMe	$\pi$ -acceptor, $\sigma$ -acceptor	129.1	138.3	6.40	5.85

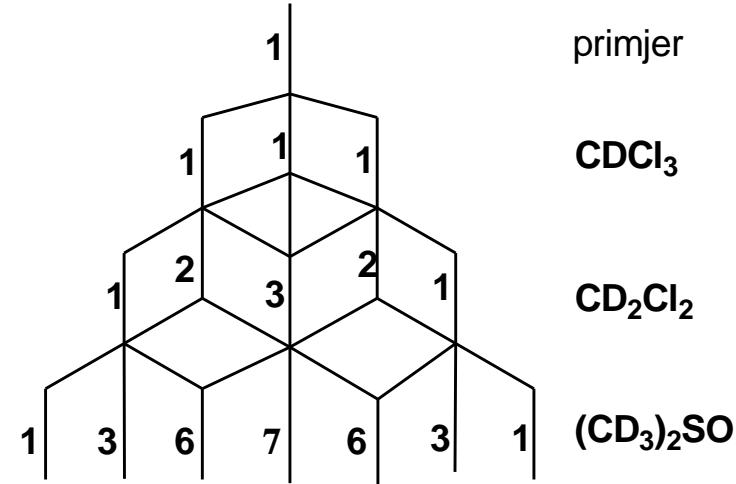


✓ **acetofenon**: 6 različitih C, 6 signala

## ✓ Deuterirana otapala

- otapalo **CDCl<sub>3</sub>** - u protonskom spektru singlet na  $\delta$  7,26 ppm je posljedica malih količina CHCl<sub>3</sub> u CDCl<sub>3</sub>;
  - u <sup>13</sup>C spektru triplet (1:1:1) na  $\delta$  77 ppm posljedica je cijepanja <sup>13</sup>C pika s deuterijem [multiplicitet =  $2nl+1 = 2 \times 1 \times 1 + 1 = 3$ ];
- otapalo **(CD<sub>3</sub>)<sub>2</sub>S=O** – dimetil-d<sub>6</sub>-sulfoksid (DMSO):
  - u protonskom spektru kvintet na  $\delta$  2,49 ppm je posljedica malih količina HCD<sub>2</sub>-S(=O)-CD<sub>3</sub> [**H** cijepan s 2 deuterija; multiplicitet =  $2nl+1 = 2 \times 2 \times 1 + 1 = 5$ ];
  - u <sup>13</sup>C spektru septet na  $\delta$  39,7 (1:3:6:7:6:3:1) [multiplicitet:  $2nl+1 = 2 \times 3 \times 1 + 1 = 7$ ].

✓ dijagram Pascalovog trokuta za deuterirana otapala



**THE  $^{13}\text{C}$  CHEMICAL SHIFTS, COUPLINGS, AND MULTIPLICITIES**  
**APPENDIX A OF COMMON NMR SOLVENTS**

Structure	Name	$\delta$ (ppm)	$J_{\text{C}-\text{D}}$ (Hz)	Multiplicity <sup>a</sup>
<chem>CDCl3</chem>	Chloroform- $d_1$	77.0	32	Triplet
<chem>CD3OD</chem>	Methanol- $d_4$	49.0	21.5	Septet
<chem>CD3SOCD3</chem>	DMSO- $d_6$	39.7	21	Septet
<chem>O=C([CD3])C([CD3])2</chem>	DMF- $d_7$	30.1 35.2 167.7	21 21 30	Septet Septet Triplet
<chem>C6D6</chem>	Benzene- $d_6$	128.0	24	Triplet
<chem>CC1(C)CO[C@H]1C</chem>	THF- $d_8$	25.2 67.4	20.5 22	Quintet Quintet
<chem>CC1(OCC2[C@H]1OC[C@H]2C)OC[C@H]1OC[C@H]2OC[C@H]1O</chem>	Dioxane- $d_8$	66.5	22	Quintet
<chem>C1=CC2=C(C=C1)N(C)C(=D)C2</chem>	Pyridine- $d_5$	123.5 (C-3,5) 135.5 (C-4) 149.2 (C-2,6)	25 24.5 27.5	Triplet Triplet Triplet
<chem>CD3CCD3</chem>	Acetone- $d_6$	29.8 (methyl) 206.5 (carbonyl)	20 <1	Septet Septet <sup>b</sup>
<chem>CD3CN</chem>	Acetonitrile- $d_3$	1.3 (methyl) 118.2 (CN)	32 <1	Septet Septet <sup>b</sup>
<chem>CD3NO2</chem>	Nitromethane- $d_3$	60.5	23.5	Septet
<chem>CD3CD2OD</chem>	Ethanol- $d_6$	15.8 (C-2) 55.4 (C-1)	19.5 22	Septet Quintet
<chem>CD3CD2O</chem>	Ether- $d_{10}$	13.4 (C-2) 64.3 (C-1)	19 21	Septet Quintet
<chem>[(CD3)2N]3P=O</chem>	HMPA- $d_{18}$	35.8	21	Septet
<chem>CD3CO2D</chem>	Acetic acid- $d_4$	20.2 (C-2) 178.4 (C-1)	20 <1	Septet Septet <sup>b</sup>
<chem>CD2Cl2</chem>	Dichloromethane- $d_2$ (Methylene chloride- $d_2$ )	53.1	29	Quintet

<sup>a</sup>Triplet intensities = 1:1:1, quintet = 1:2:3:2:1, septet = 1:3:6:7:6:3:1.

<sup>b</sup>Unresolved, long-range coupling.

Source: Breitmaier, E., and Voelter, W. (1987). *Carbon-13 NMR Spectroscopy*, 3rd ed. New York: VCH, p. 109; with permission. Also Merck & Co., Inc.