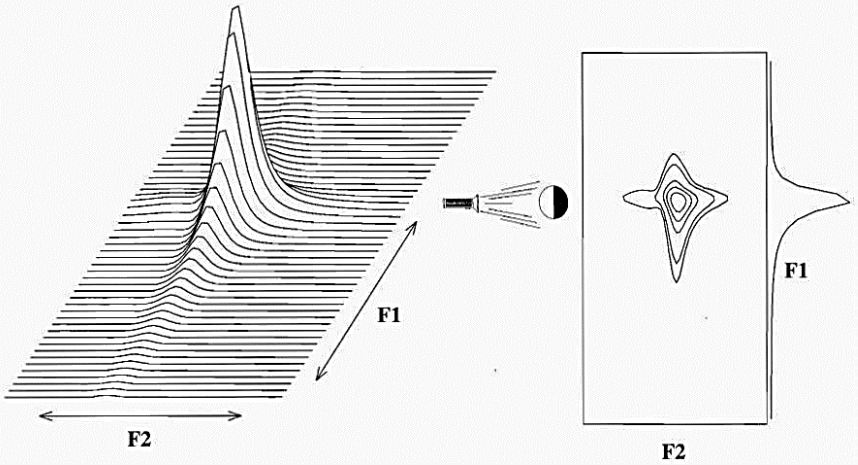
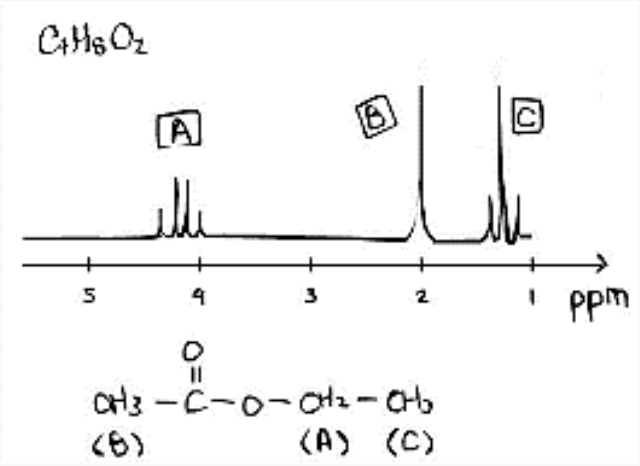
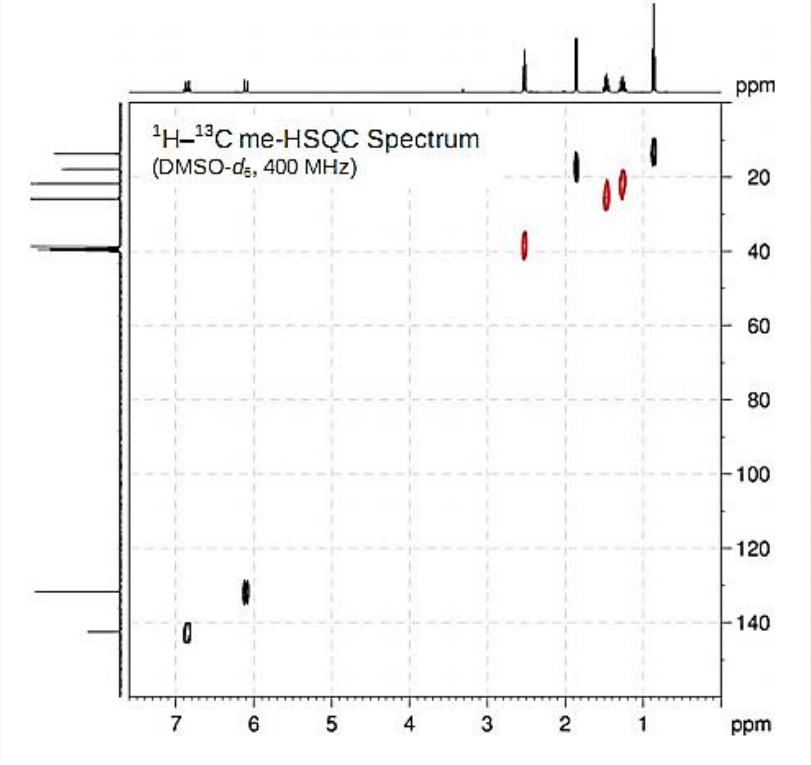
2D NMR Spectroscopy


F1
F2
F1
F2


C4H8O2
A
B
C
5
4
3
2
1
ppm
O
CH3 – C – O – CH2 – CH3
(B)
(A)
(C)


ppm
1H–13C me-HSQC Spectrum
(DMSO-d6, 400 MHz)
20
40
60
80
100
120
140
7
6
5
4
3
2
1
ppm

- 1971, the idea of 2D NMR, Jean Jeener.

- 1975, “ two-dimensional spectroscopy, application to Nuclear magnetic resonance”, Ernst Paper.

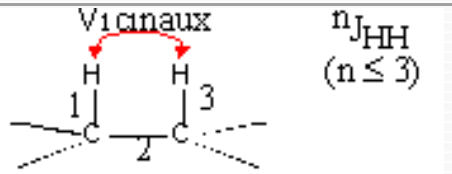
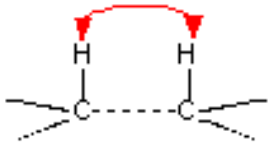
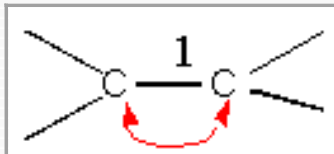
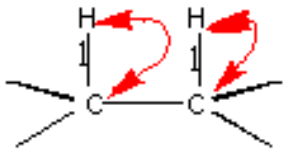
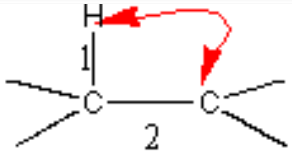
- 1980-present, application of NMR to protein structures.

- 1991, Nobel Prize in Chemistry, Fourier Transform NMR, Ernst Paper.

2D NMR طیف های

- COSY
- HETCOR
- TOCSY
- NOESY
- ROESY
- HMBC
- 2D INADEQUATE

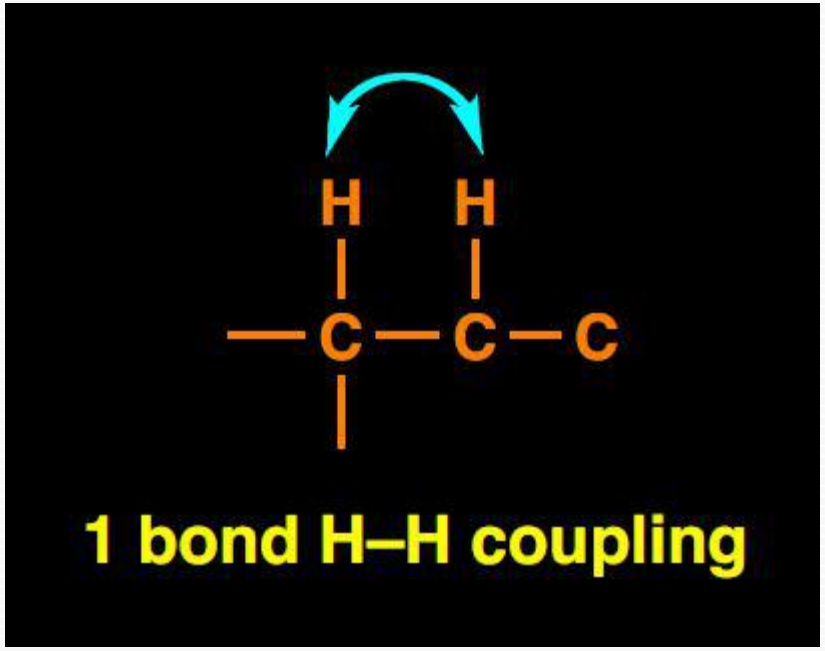
Table summarising 2D NMR spectroscopy
2D Homonuclear and Heteronuclear

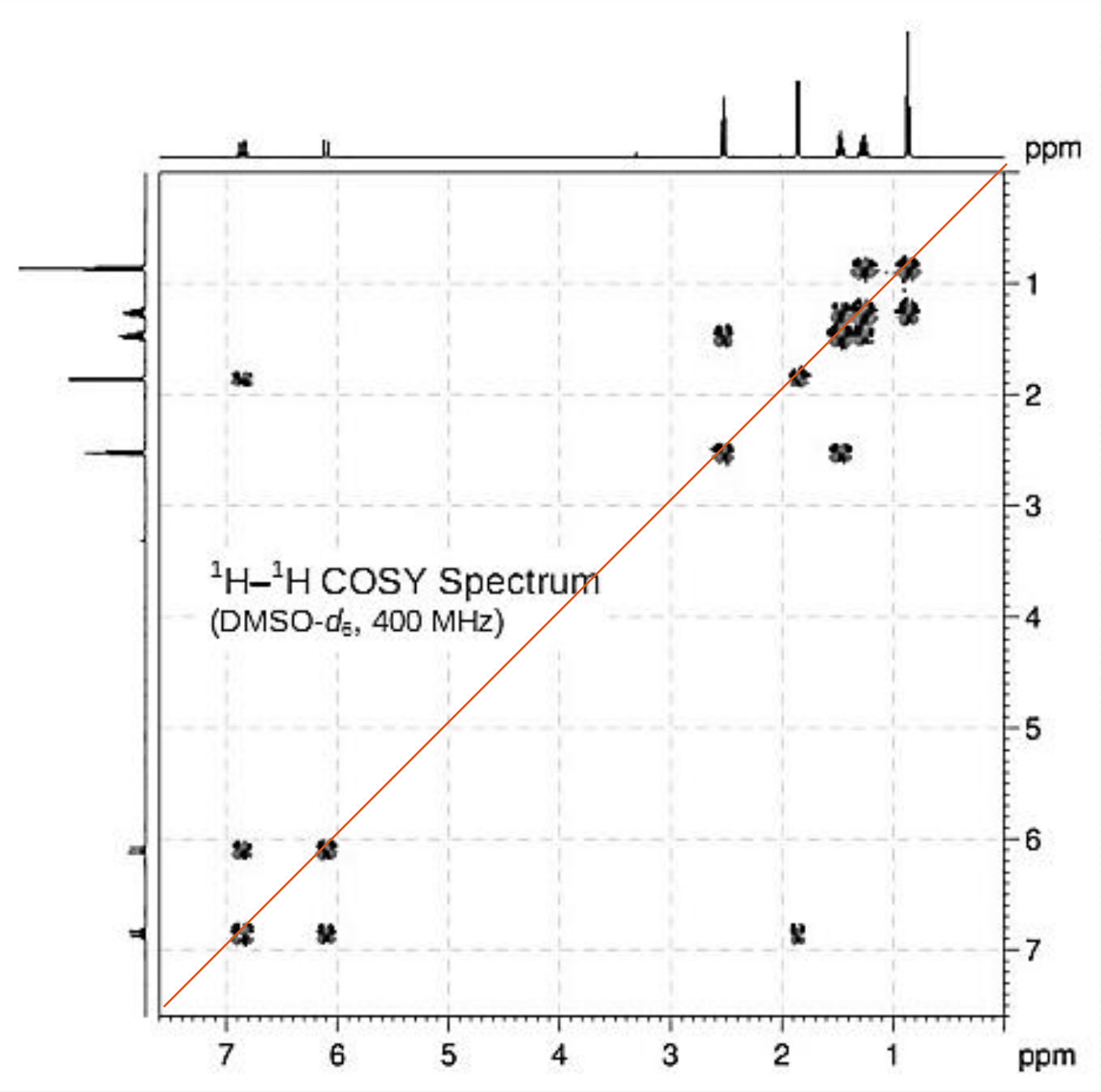
Experiments	F2 Dimension	F1 Dimension	Type of informations: (With n as the number of bonds).
Homonuclear Correlations:			
• COSY • TOCSY.	δ_H, J_{HH}	δ_H, J_{HH}	 $^nJ_{HH}$ ($n \leq 3$)
• NOESY. • ROESY.	δ_H, J_{HH}	δ_H, J_{HH}	 N.O.E
• 2D-Inadequate.	δ_C, J_{CC}	δ_C, J_{CC}	 $^1J_{CC}$
Heteronuclear Correlations:			
• HSQC • HMQC	δ_C	δ_H, J_{HH}	 $^1J_{CH}$
• Long-Range • HSBC	δ_C	δ_H, J_{HH}	 $^1J_{CH}$ ($n>1$)

COSY

Correlation Spectroscopy

H-H COSY




ppm
1
2
3
4
5
6
7
^{1}H–^{1}H COSY Spectrum
(DMSO-d_6, 400 MHz)
7
6
5
4
3
2
1
ppm

H-H COSY Spectrum

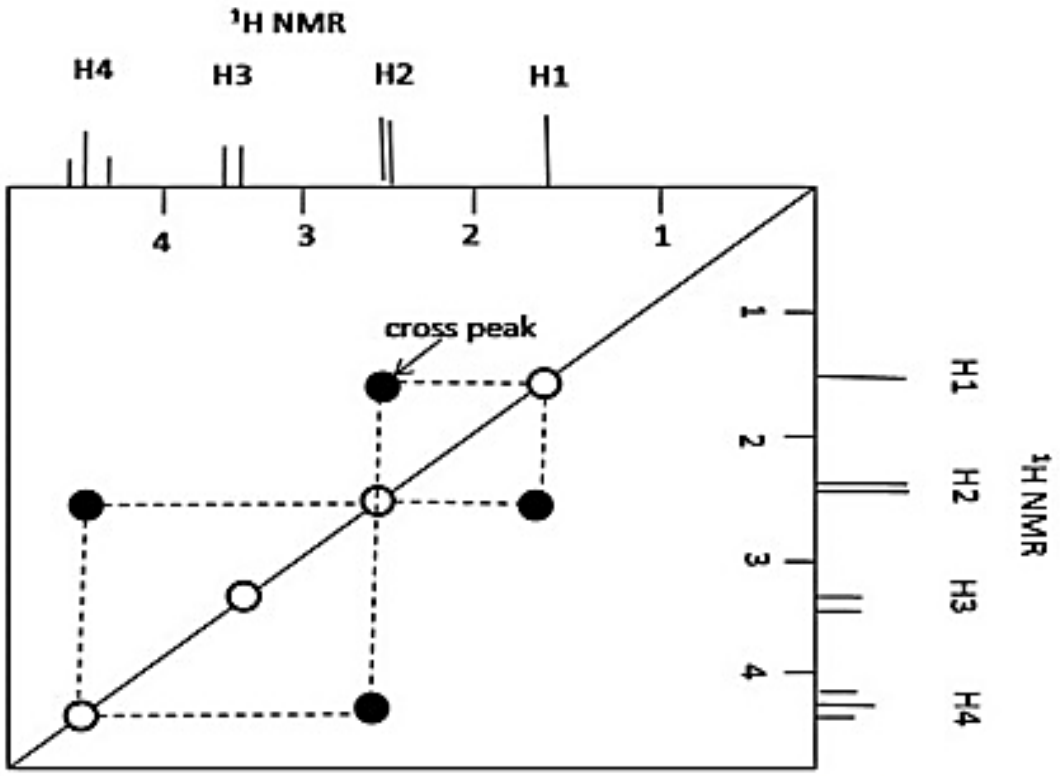
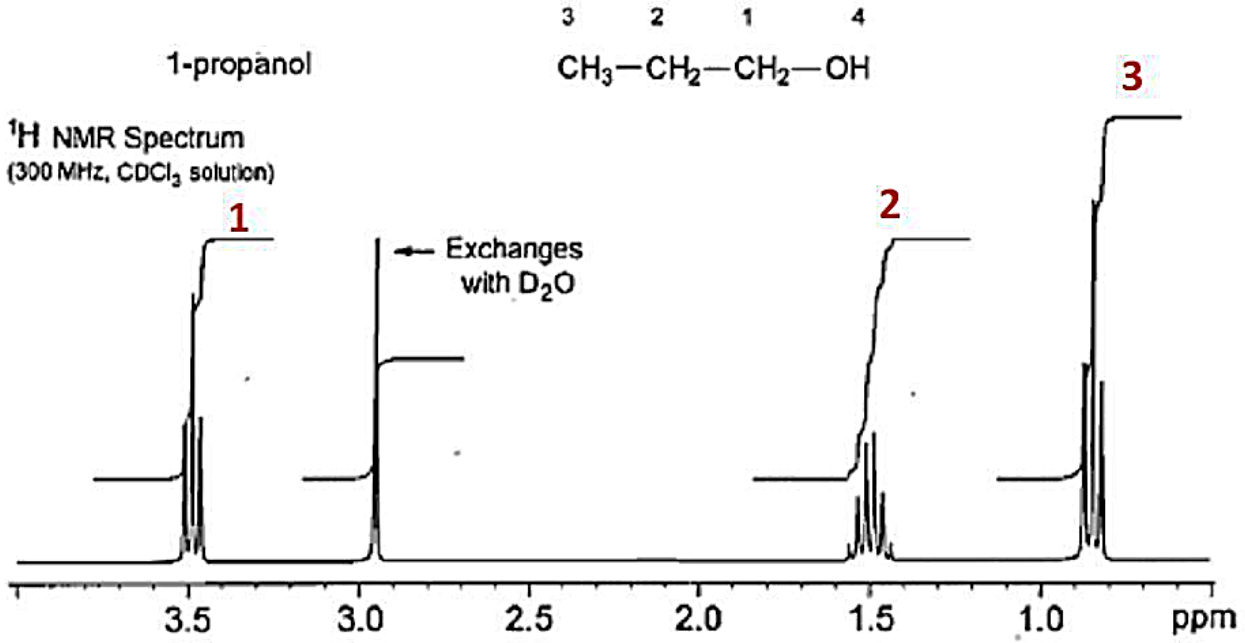


Fig 12. ^{1}H-^{1}H COSY spectrum

Problem 292

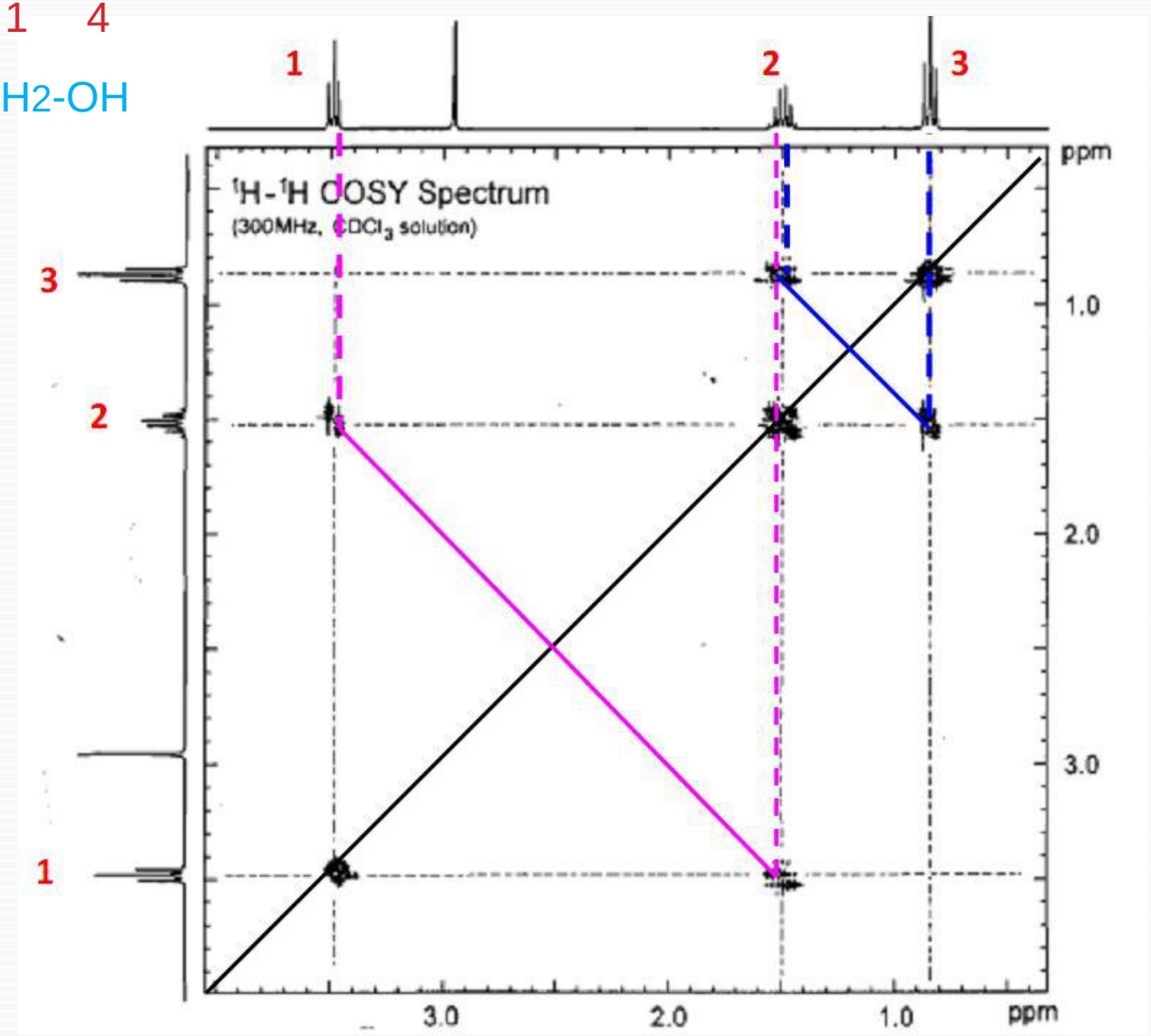
The ^{1}H and ^{13}C NMR spectra of 1-propanol (C_3H_8O) recorded in $CDCl_3$ solution at 298K are given below. The 2-dimensional ^{1}H-^{1}H COSY spectrum and the C-H correlation spectrum are given on the facing page. From the COSY spectrum, assign the proton spectrum and then use the C-H correlation spectrum to assign the ^{13}C spectrum *i.e.* determine the chemical shift corresponding to each of the protons and each of the carbons in the molecule.

1-propanol



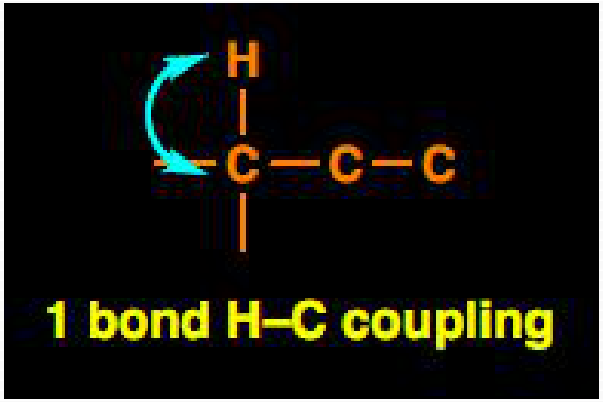
3 2 1 4

CH_3-CH_2-CH_2-OH



HMQC , HMBC, HSQC, HETCOR,...

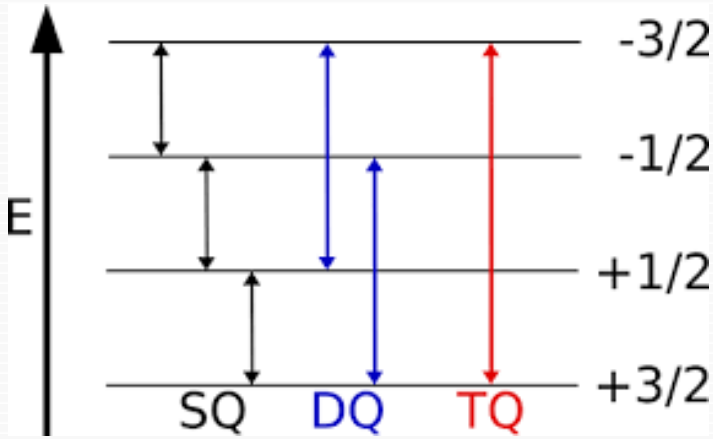
HMQC , HETCOR, HSQC

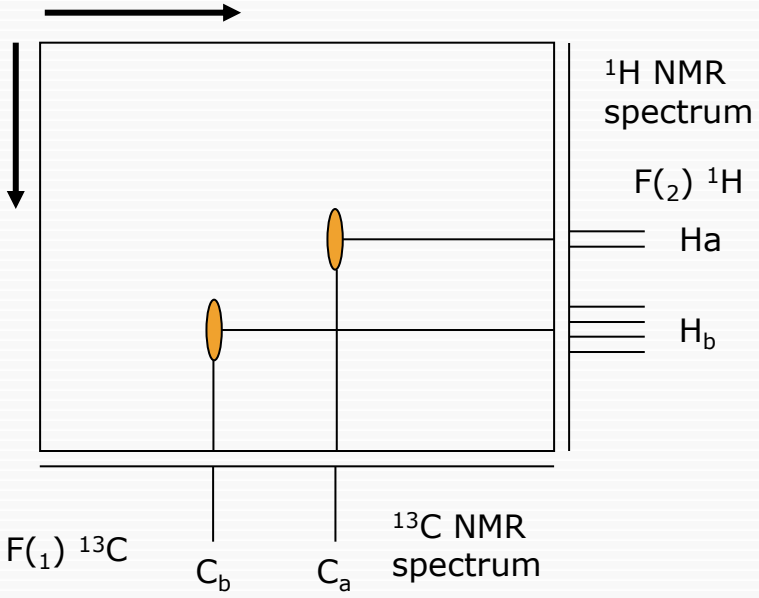


HMQC

Heteronuclear Multiple Quantum Correlation

- ✓ ^{13}C-^{1}H COSY.
- ✓ Cross peaks are usually seen only for protons directly attached to the carbon.
- ✓ Peaks occur at a position where the protons in the spectrum on the F2 axis is coupled to a carbon in the spectrum on the F1 axis.
- ✓ Ha is coupled to Ca and Hb is coupled to Cb
- ✓ Does not have diagonal peaks



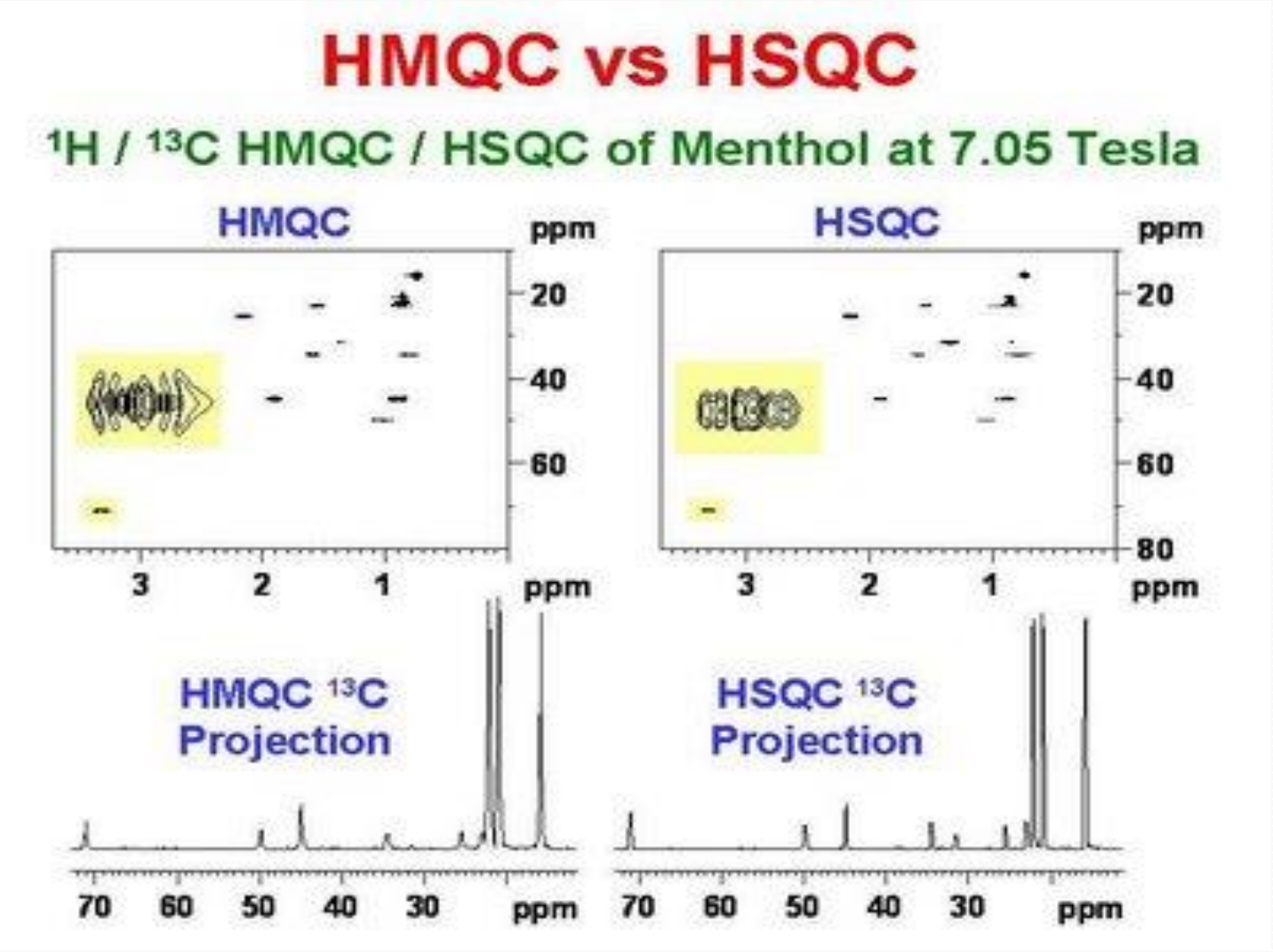


HSQC

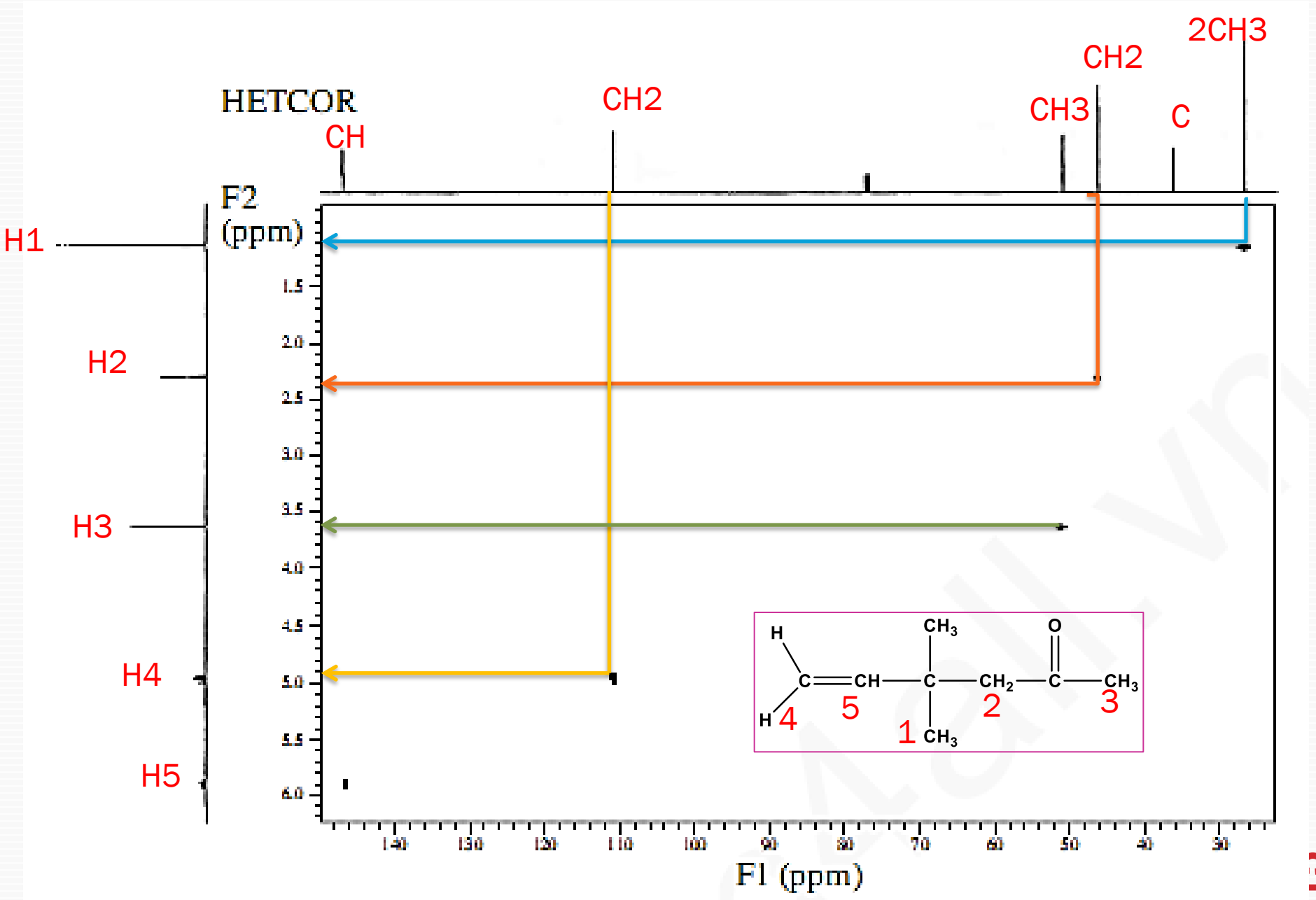
Heteronuclear Single Quantum Correlation

- ✓ A 2D proton-detected heteronuclear shift correlation experiment which provides the same information as the closely related HMQC, that is, one-bond ^{1}H-^{13}C correlations.
- ✓ Principle advantage - slightly better resolution (in homonuclear proton couplings) than in HMQC.
- ✓ For most routine applications this difference is barely noticeable, but where crowding occurs, the HSQC should provide better results.

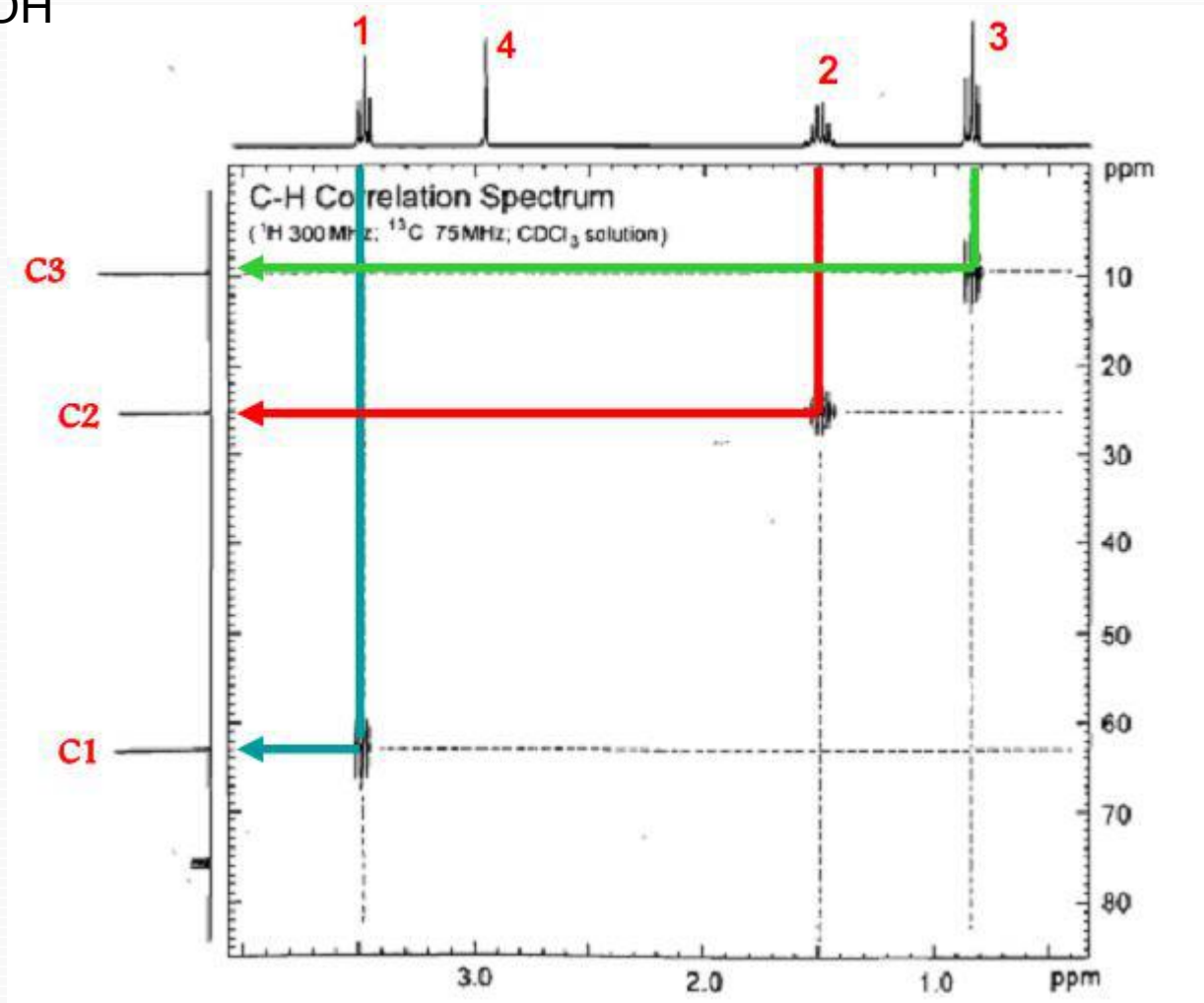
Both the HSQC and HMQC provide the exact same information. The differences are technical and involve signal-to-noise ratio.



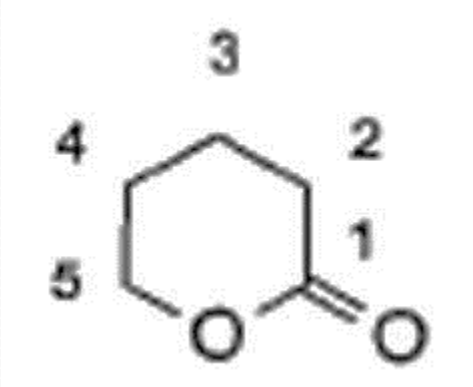
HETCOR (HETERONUCLEAR COSY)

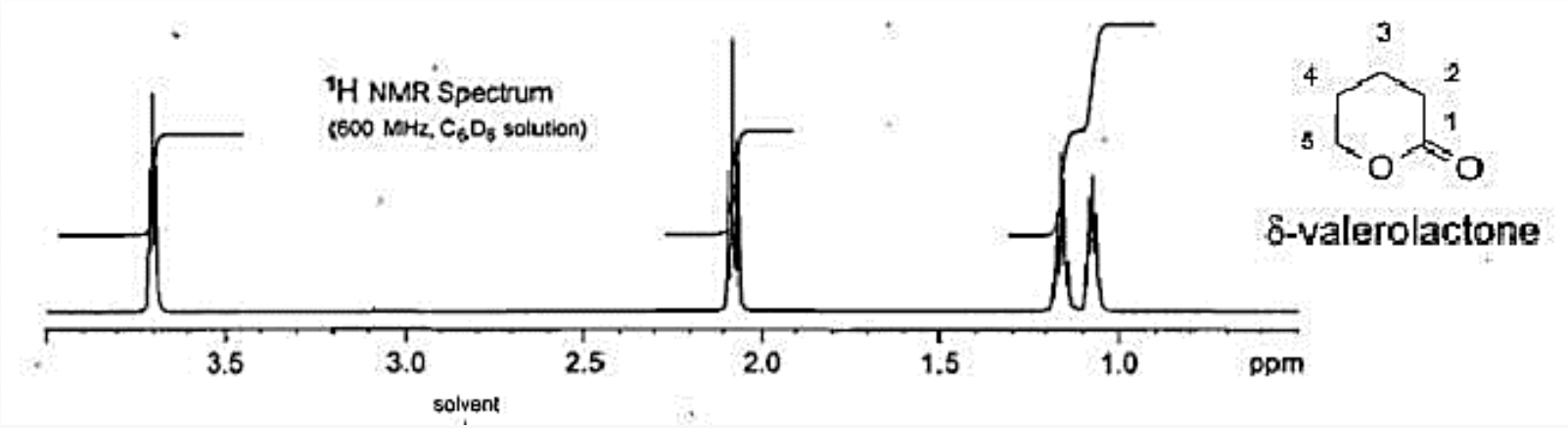


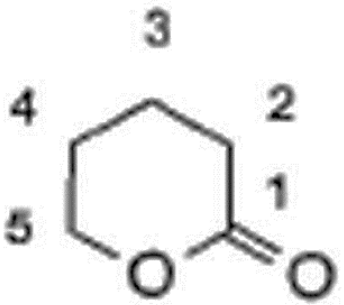
CH3--CH2--CH2--OH

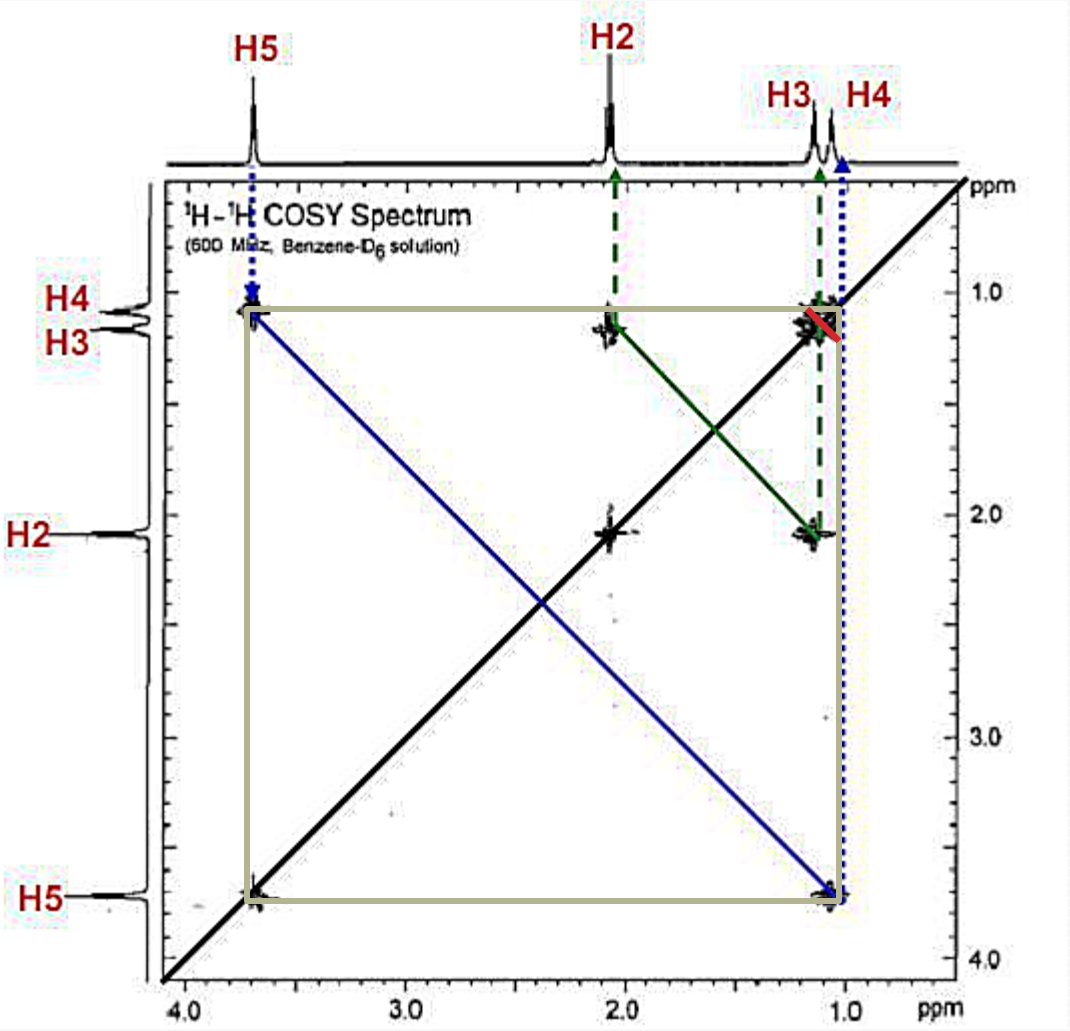


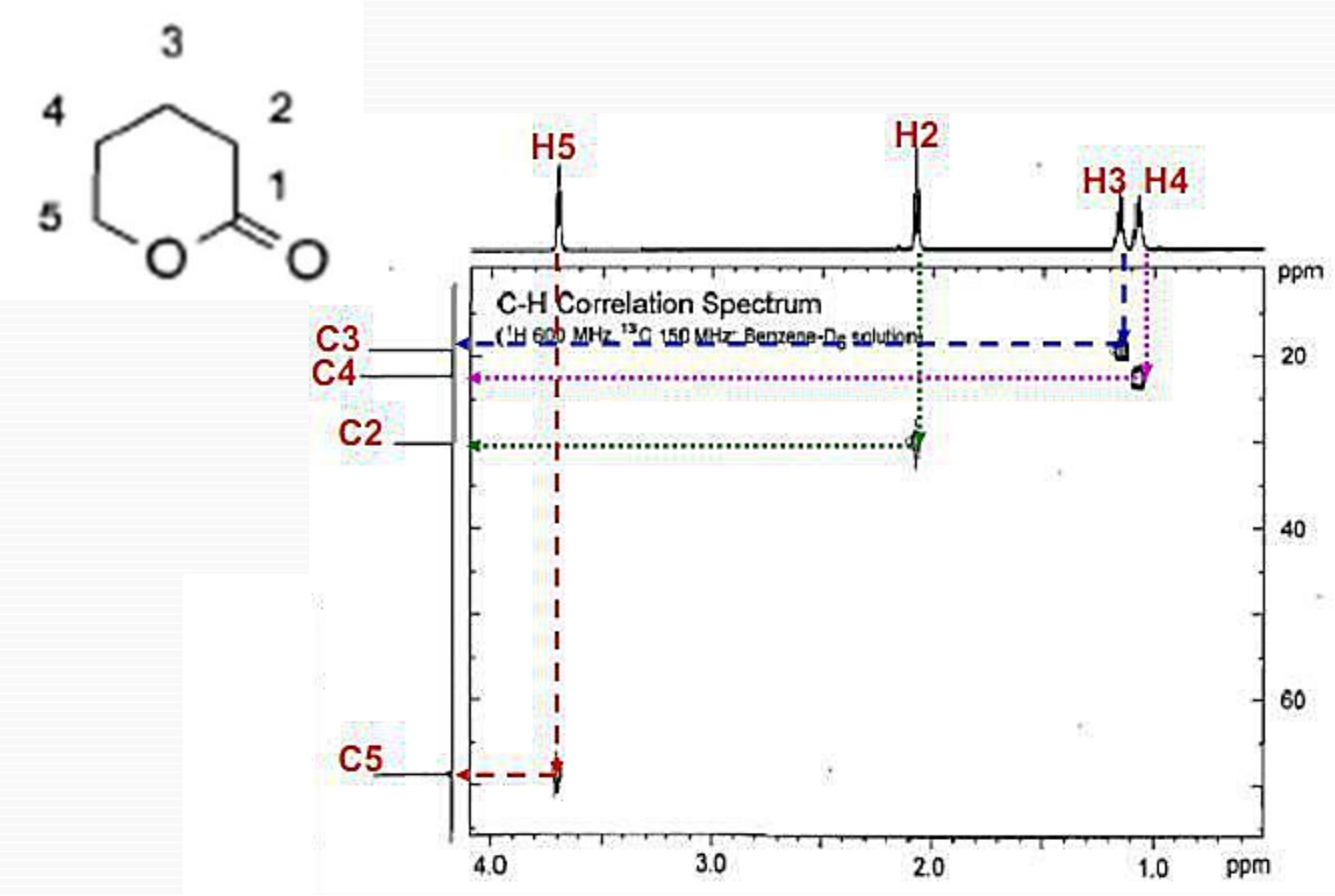
سوال ۲۹۶ کالمن

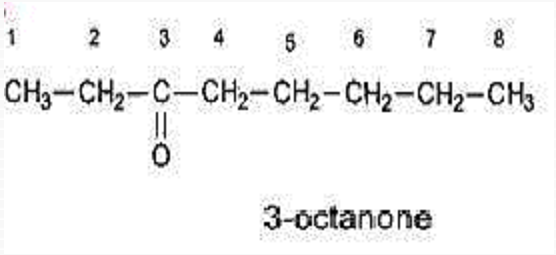


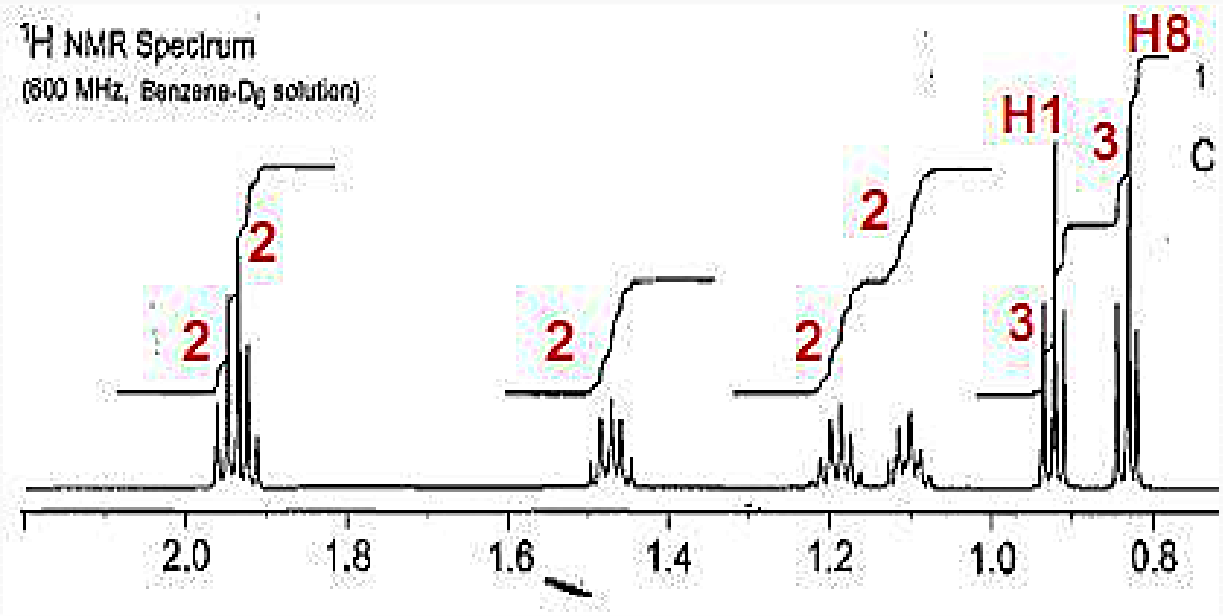


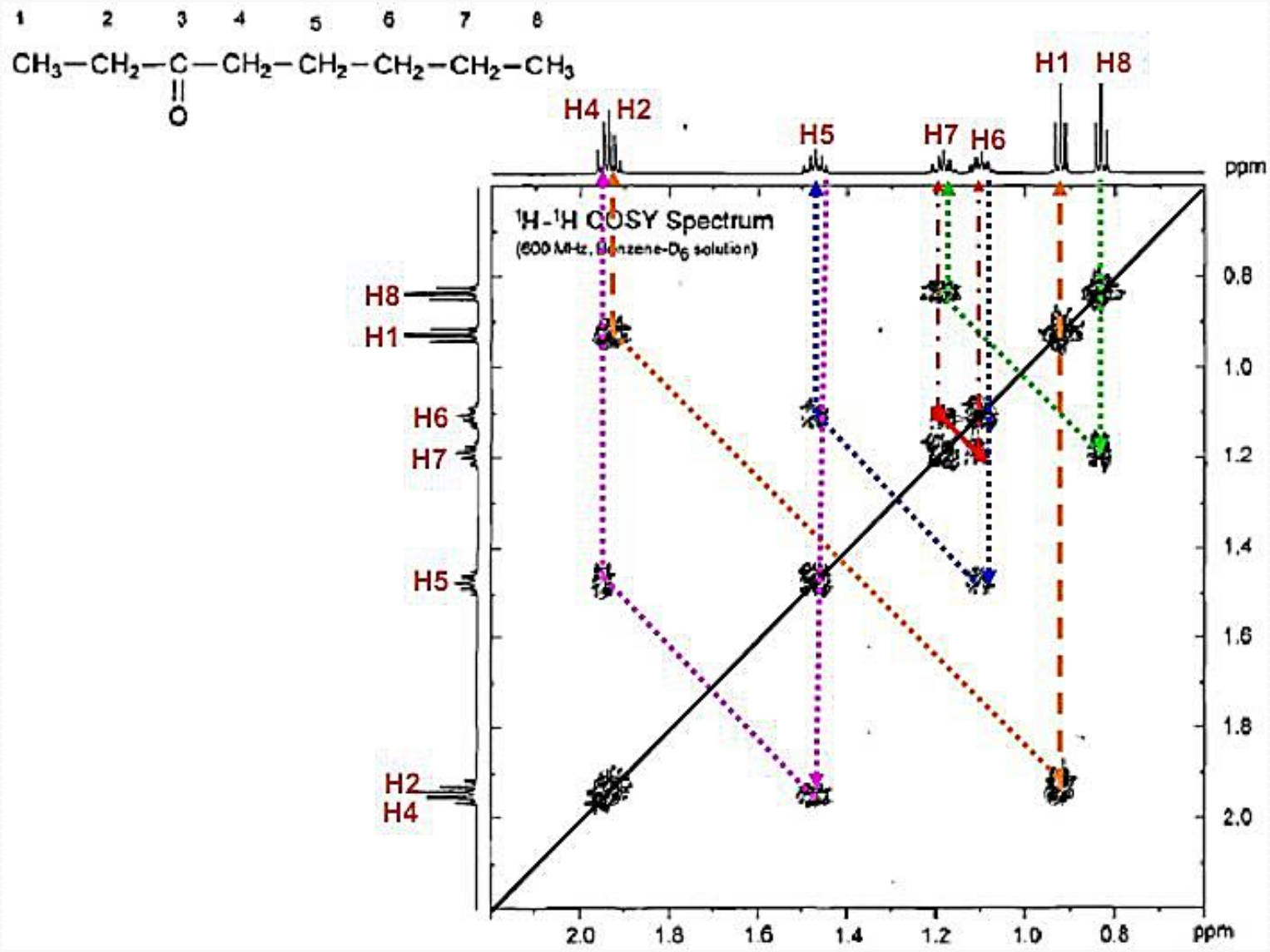

3
4
2
1
5
O
O

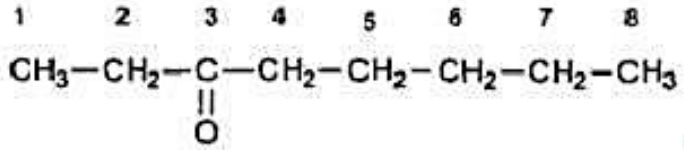

H5
H2
H3
H4
^{1}H-^{1}H COSY Spectrum
(600 MHz, Benzene-D$_6$ solution)
H4
H3
H2
H5
ppm
1.0
2.0
3.0
4.0
4.0
3.0
2.0
1.0
ppm


3
4
2
1
5
O
O
H5
H2
H3
H4
C-H Correlation Spectrum
C3
C4
C2
C5
ppm
20
40
60
4.0
3.0
2.0
1.0
ppm

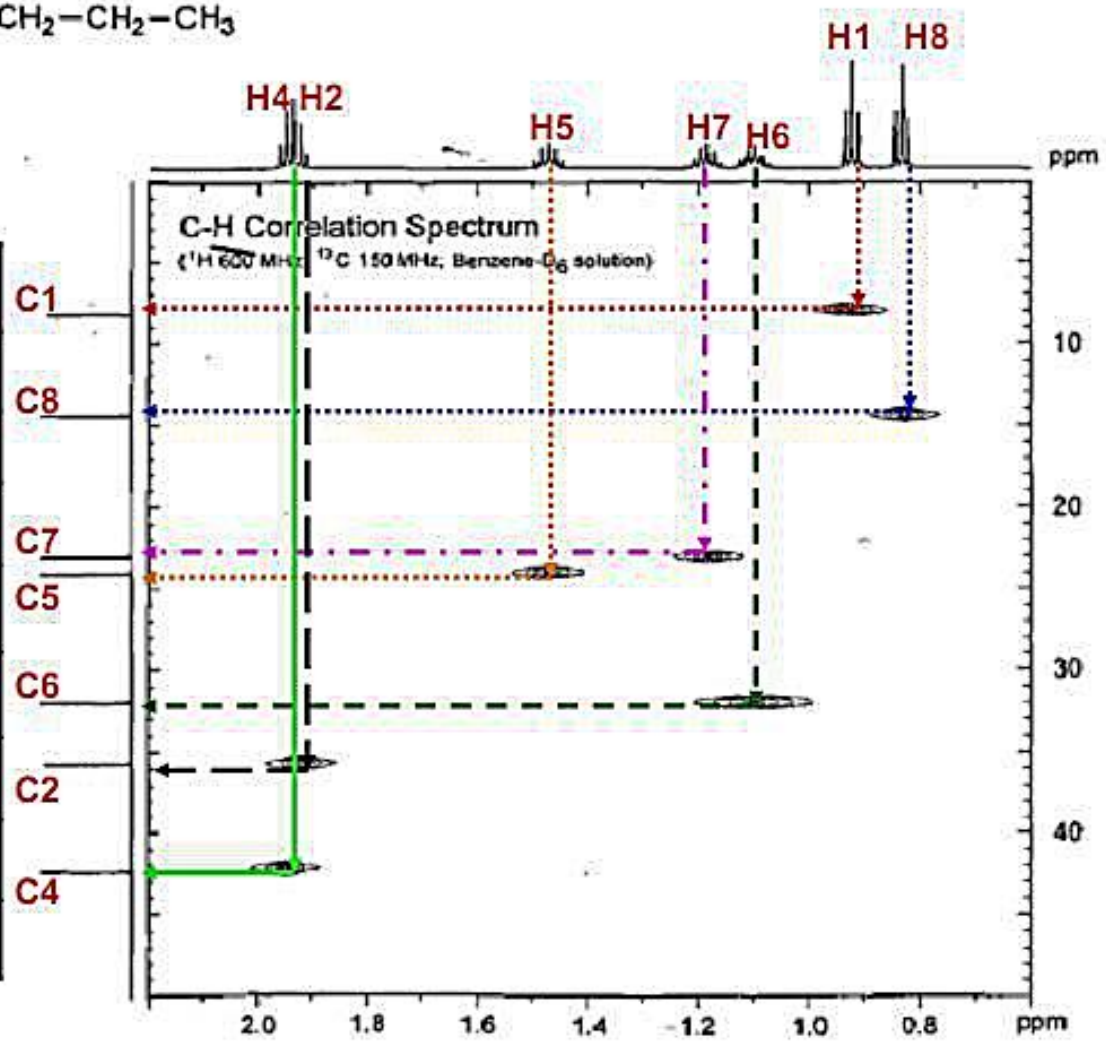

1 2 3 4 5 6 7 8
CH3–CH2–C–CH2–CH2–CH2–CH2–CH3
O
3-octanone


¹H NMR Spectrum
(600 MHz, Benzene-D6 solution)
H8
H1
2
2
2
2
3
3
2.0
1.8
1.6
1.4
1.2
1.0
0.8


1 2 3 4 5 6 7 8
CH3—CH2—C—CH2—CH2—CH2—CH2—CH3
O
H4 H2
H5
H7 H6
H1 H8
ppm
¹H-¹H COSY Spectrum
(600 MHz, Benzene-D6 solution)
H8
H1
H6
H7
H5
H2
H4
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm



پروتون	δ ppm	کربن	δ ppm
H1	0.92	C1	7.8
H2	1.92	C2	35.4
		C3	209
H4	1.94	C4	42.1
H5	1.47	C5	23.7
H6	1.11	C6	31.7
H7	1.19	C7	22.7
H8	0.82	C8	14



U=(C+1)-1/2H

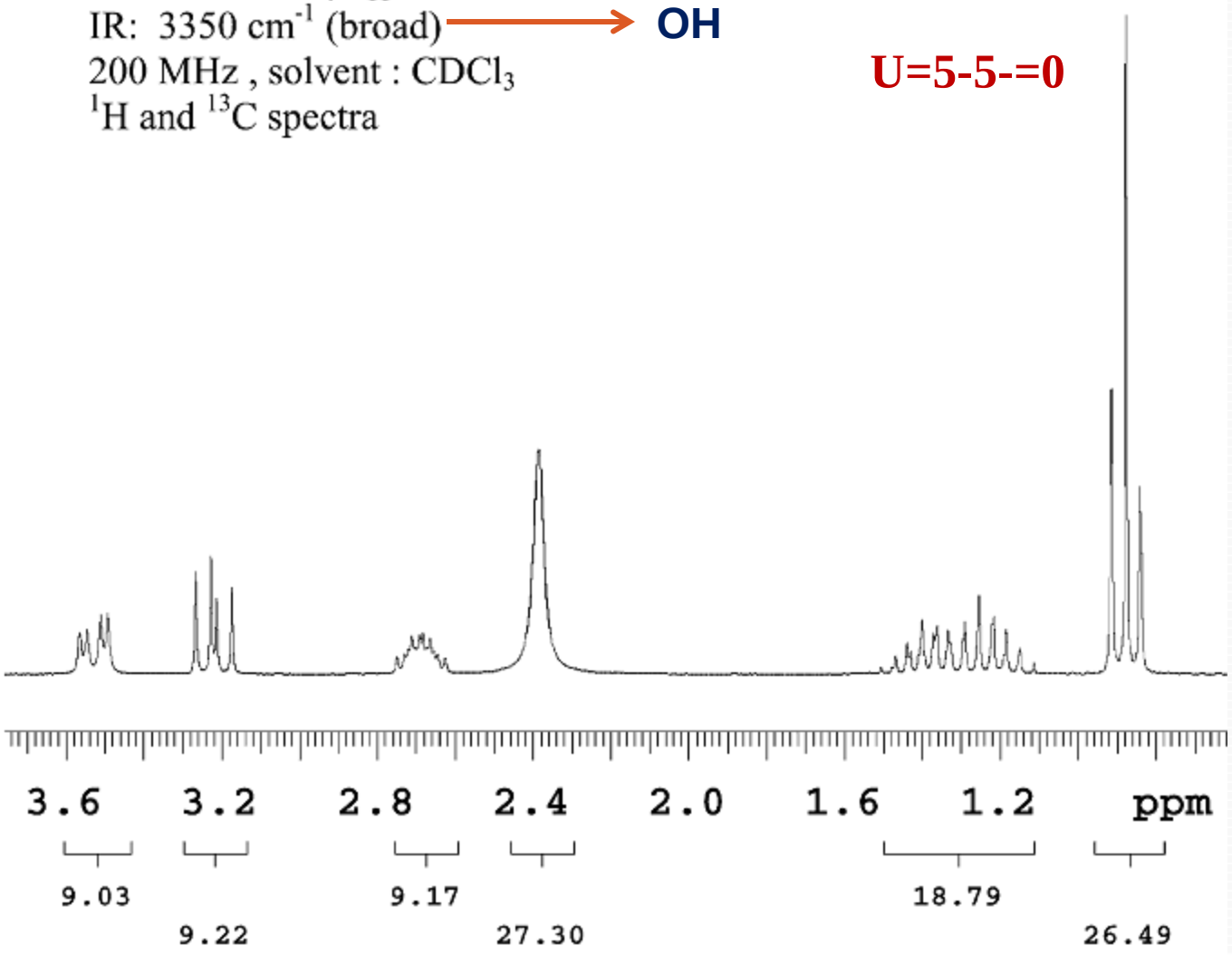
Problem 4 : $C_4H_{11}NO$

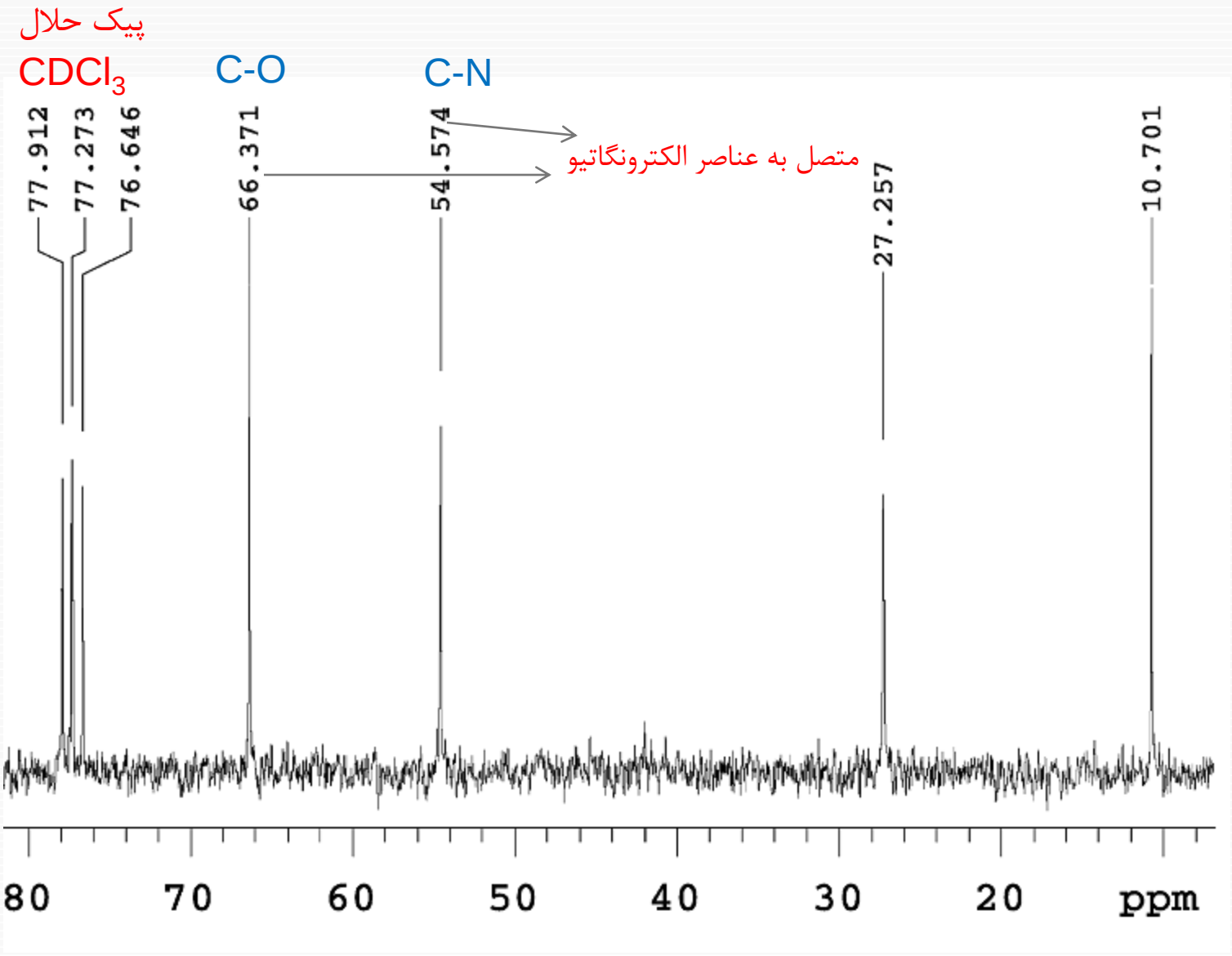
IR: 3350 cm^{-1} (broad) → OH

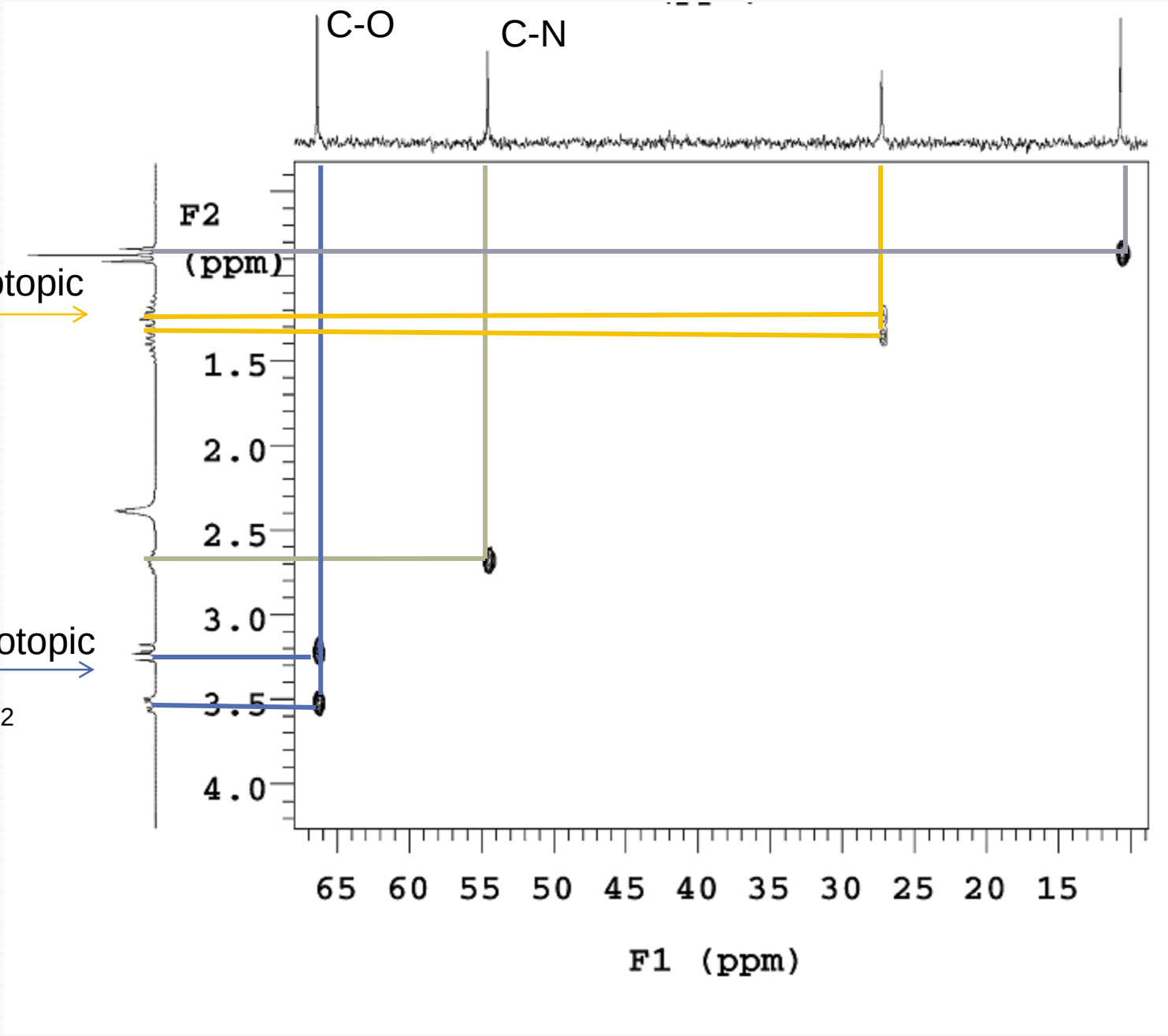
200 MHz , solvent : $CDCl_3$

^1H and ^{13}C spectra

U=5-5-=0




پیک حلال
$CDCl_3$
C-O
C-N
متصل به عناصر الکترونگاتیو
77.912
77.273
76.646
66.371
54.574
27.257
10.701
80
70
60
50
40
30
20
ppm



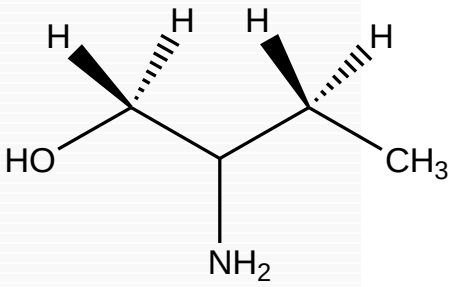
Diastereotopic CH_2

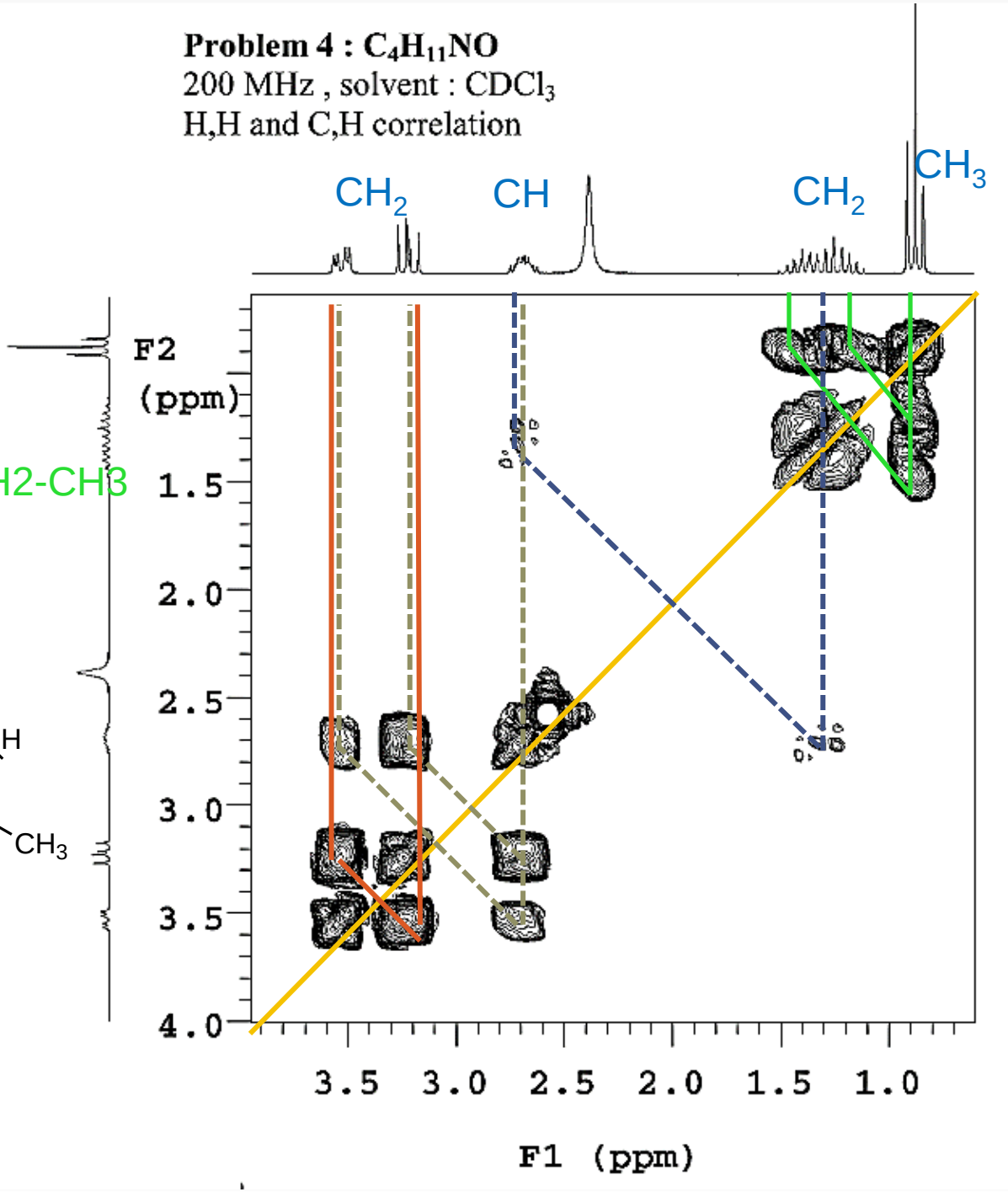
Diastereotopic CH_2

Problem 4 : $C_4H_{11}NO$
200 MHz , solvent : $CDCl_3$
H,H and C,H correlation

CH_2-CH_3

OH-CH2-CH-CH2-CH3





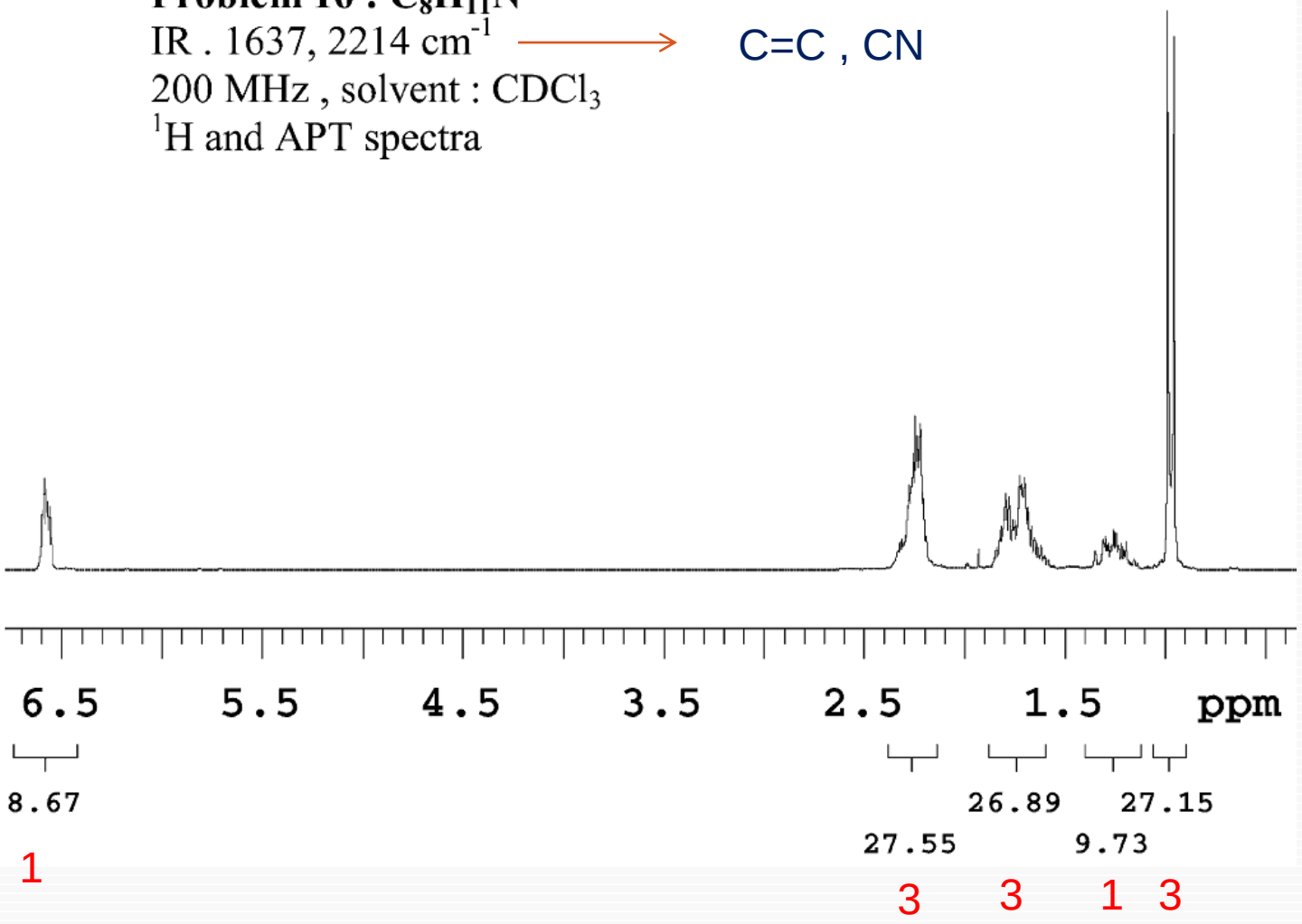
D.U: 4

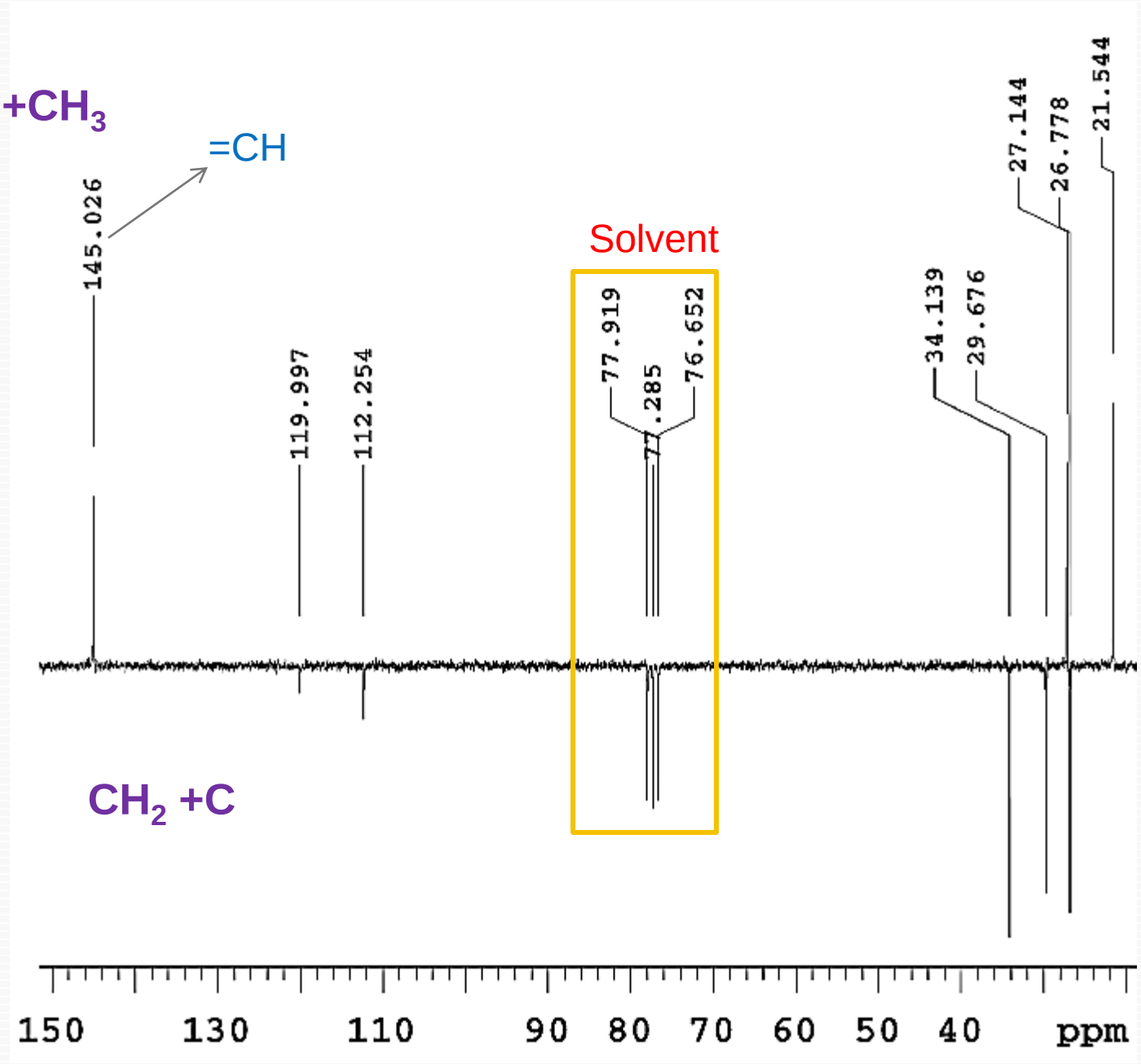
Problem 16 : $C_8H_{11}N$

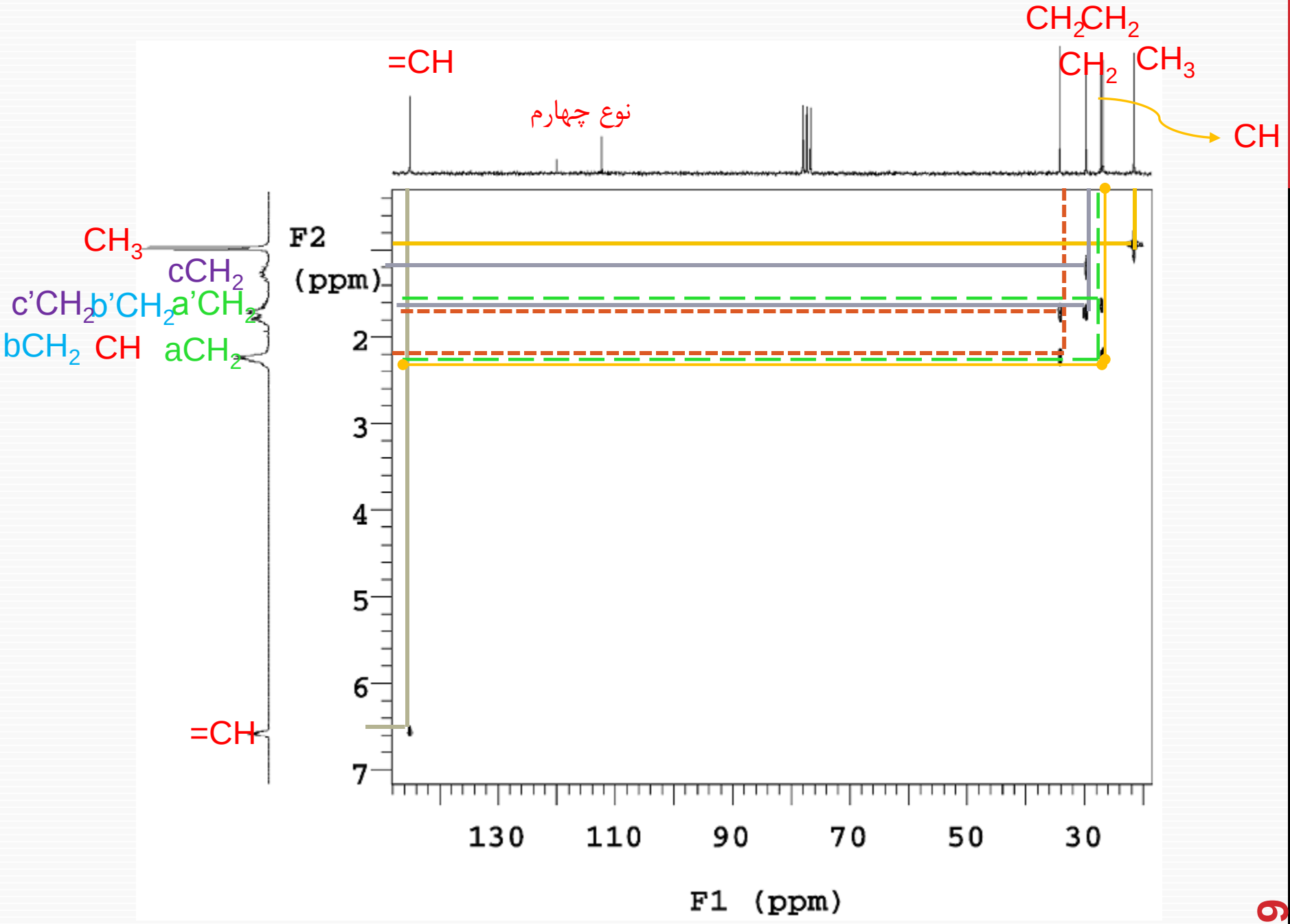
IR . 1637, 2214 cm^{-1} ⟶ C=C , CN

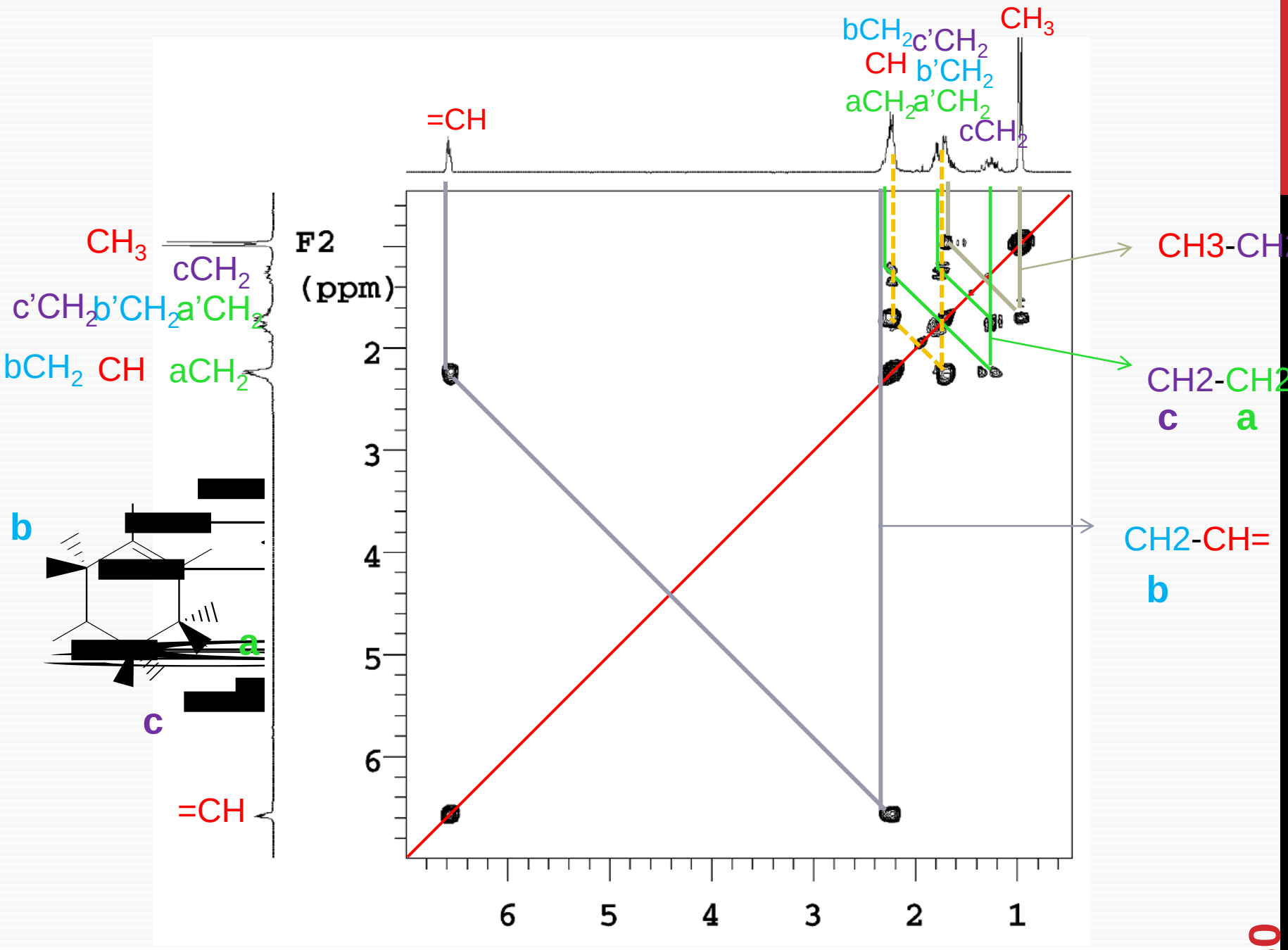
200 MHz , solvent : $CDCl_3$

^1H and APT spectra




CH +CH3
=CH
145.026
119.997
112.254
77.919
77.285
76.652
Solvent
34.139
29.676
27.144
26.778
21.544
CH2 +C
150
130
110
90
80
70
60
50
40
ppm


=CH
نوع چهارم
CH2CH2
CH2
CH3
CH
CH3
cCH2
c'CH2b'CH2a'CH2
bCH2 CH aCH2
=CH
F2
(ppm)
2
3
4
5
6
7
130
110
90
70
50
30
F1 (ppm)


CH3
cCH2
c'CH2b'CH2a'CH2
bCH2 CH aCH2
b
a
c
=CH
F2
(ppm)
bCH2c'CH2
CH b'CH2
aCH2a'CH2
cCH2
CH3
=CH
2
3
4
5
6
6
5
4
3
2
1
CH3-CH2
CH2-CH2
c a
CH2-CH=
b

NOESY

Nuclear Overhauser Effect Spectroscopy

- همانطور که از نام این نوع طیف بر می آید از اثر تقویت هسته ای اورهاوزر یا NOE در آن استفاده شده است.

- وقتی یک طیف ^{13}C واجفت شده از پروتون به دست می آید شدت بسیاری از رزونانسهای کربن نسبت به طیف جفت شده با پروتون به طور قابل توجهی افزایش می یابد . اتم های کربنی که اتم های هیدروژن به آن متصل است بیشترین افزایش شدت را تجربه کرده و هر قدر تعداد هیدروژن های متصل افزایش یابد میزان شدت بیشتر می شود . این اثر به نام اثر هسته ای اورهاوزر شناخته می شود و این میزان افزایش در سیگنال را تقویت هسته ای اورهاوزر گویند.

- در واقع یک طیف NOE اطلاعات کمی و کیفی از فاصله بین هسته ها به ما میدهد یعنی پروتون هایی که از طریف فضا کوپل می شود اطلاعاتش را به ما می دهد.

- در یک طیف ^{13}C واجفت شده از پروتو ن، هر قدر تعداد هیدروژن های همسایه افزایش یابد; NOE کل برای یک کربن به خصوص افزایش می یابد. پس شدت سیگنال ها در یک طیف ^{13}C به ترتیب زیر است.

$$CH_3 > CH_2 > CH \gg C$$

این اثر همچنین با فاصله ارتباط دارد و با افزایش فاصله این اثر کم میشود.

$$C \xrightarrow{r} H \qquad NOE = f\left(\frac{1}{r^3}\right)$$

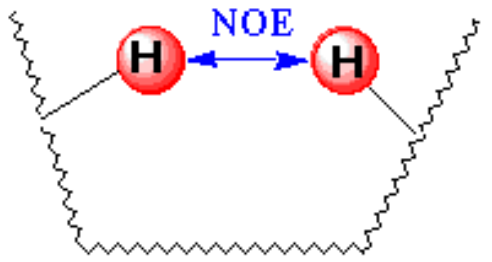
- NOESY: در این نوع طیف از این اثر استفاده می شود و در آن دوهسته ای که فاصله ی کمتر از ۵ آنگستروم دارند با یکدیگر کوپل میگردد . و در واقع ارتباط از طریق فضا صورت می گیرد.

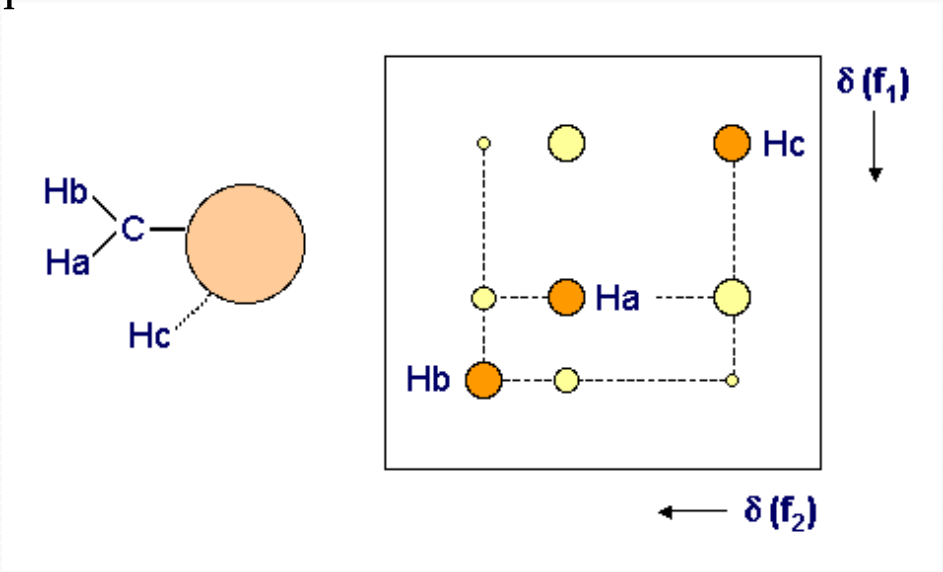
NOESY – Relies on the Nuclear overhauser effect (NOE) and shows that pairs of nuclei are close together in space.

Similar in appearance to COSY, consisting of a symmetrical spectrum that has the ^{1}HNMR spectrum of the substance as both of the chemical shift axis (F_1 and F_2).

NOESY: gives information on through-space coupling (stereochemistry and configuration).

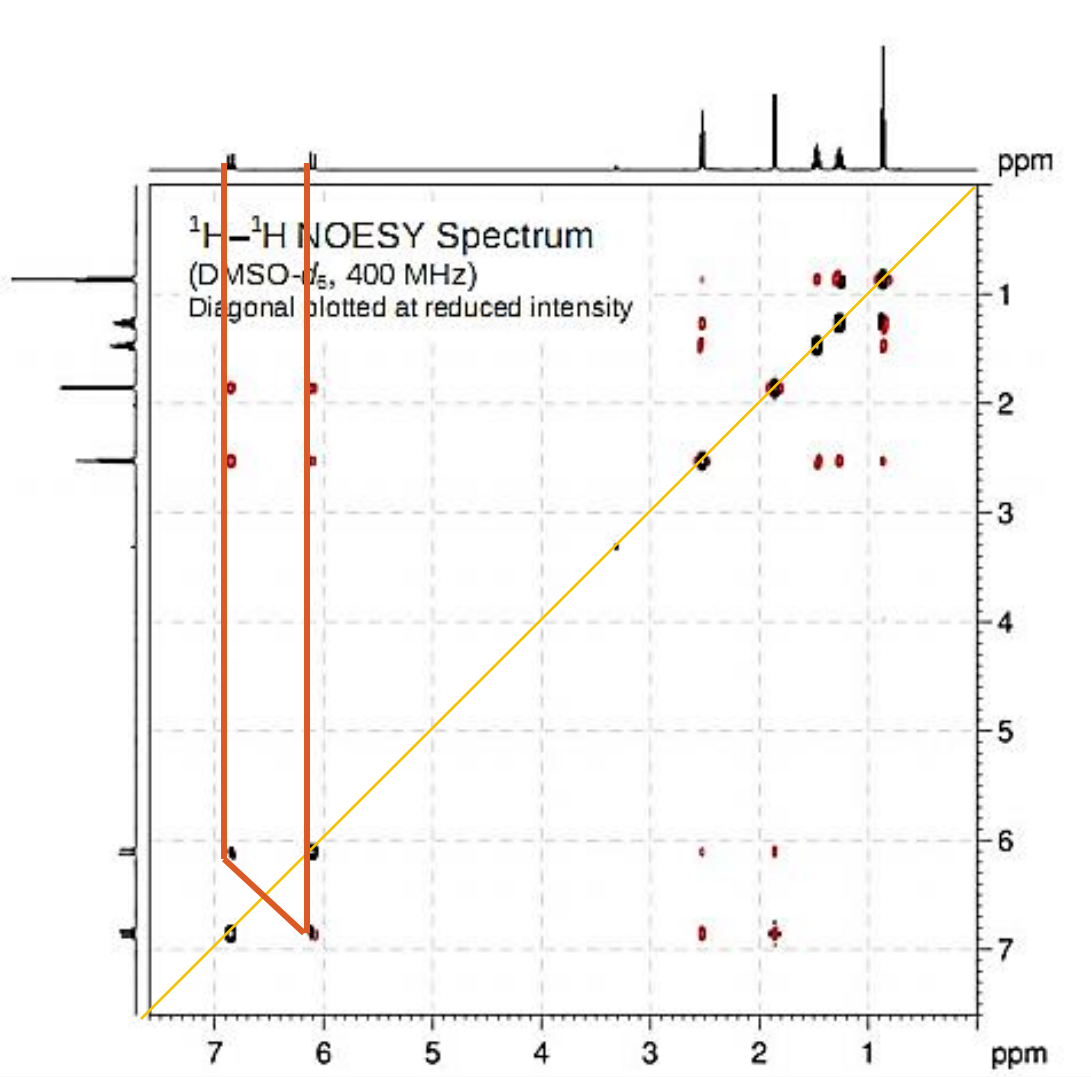
The intensity of the crosspeak often quantifies the interaction.





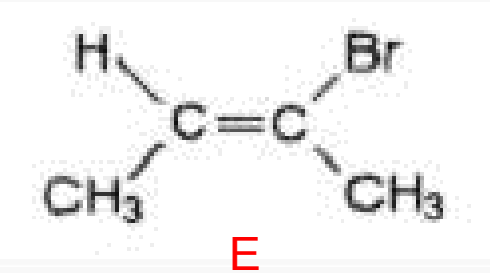
این نوع طیف نیز کاملا شبیه H-H COSY می باشد.

تنها یکی از تفاوت هایی که طیف COSY با NOESY دارد این است که پیک های عرضی یا Diagonal یعنی آنها که روی قطر هستند بسیار قویتر دیده می شوند.

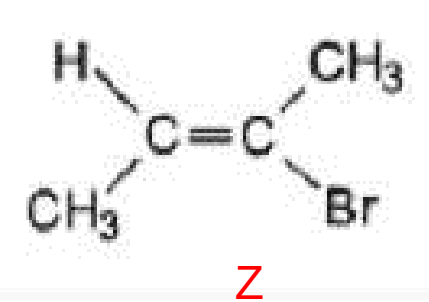


تمرین کالمن ۳.۳

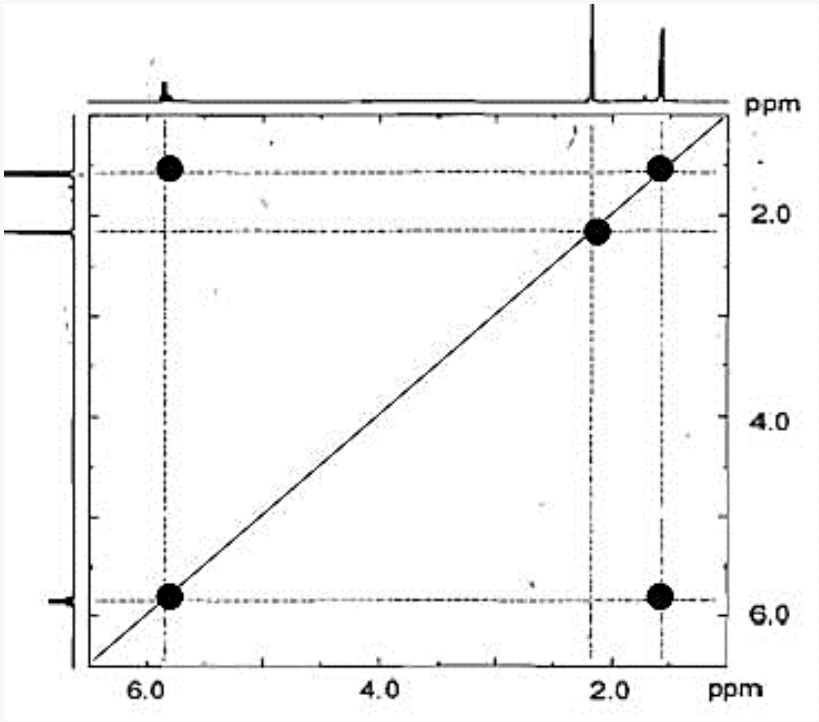
سوال در واقع تشخیص دو ایزومر Z , E ترکیب ۲-برومو ۲- بوتن می باشد. که راه تشخیص آن از NOESY است.



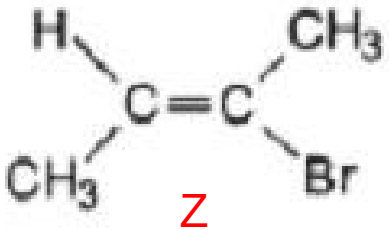
E



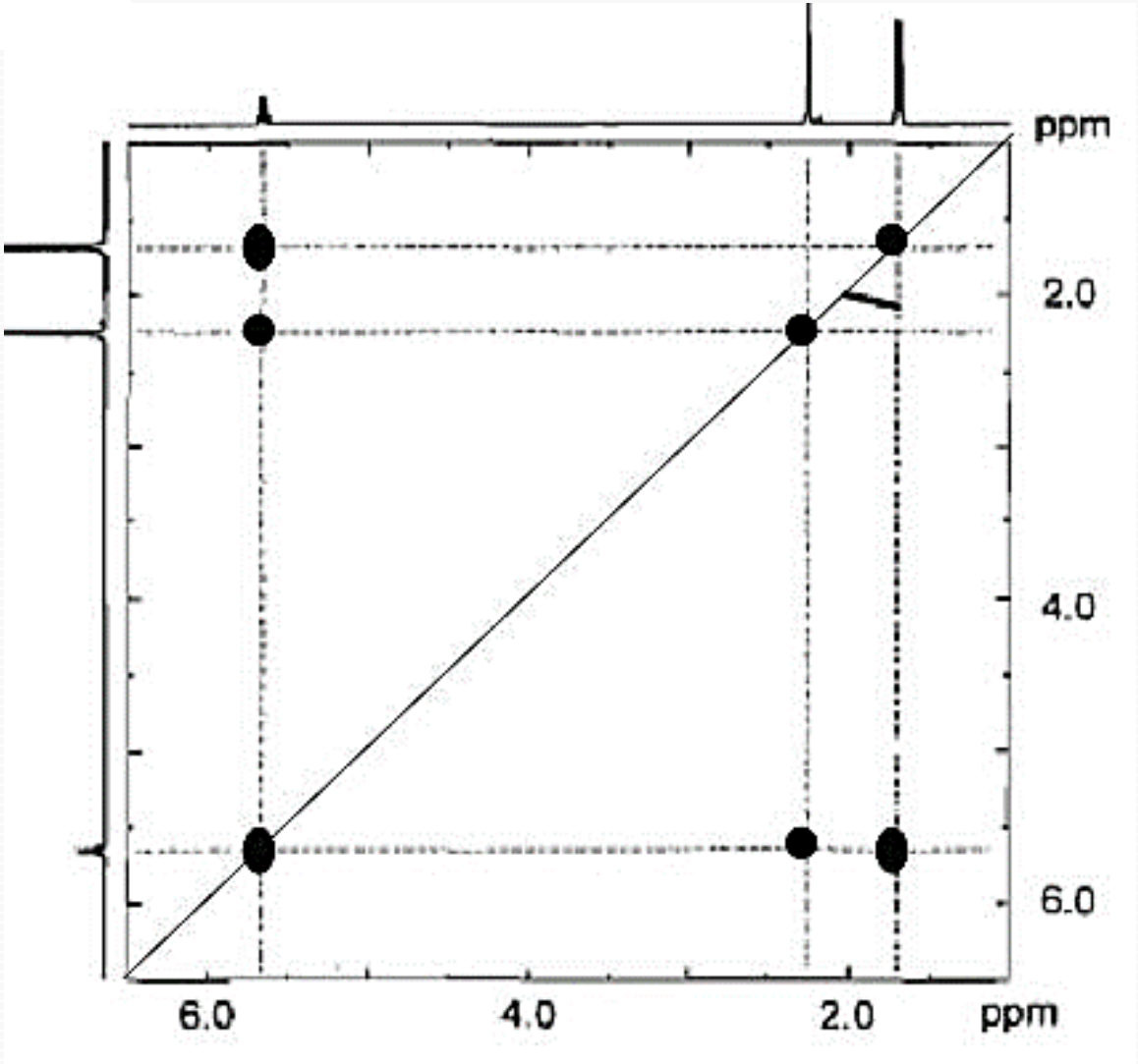
Z



طیف مربوط به ایزومر Z

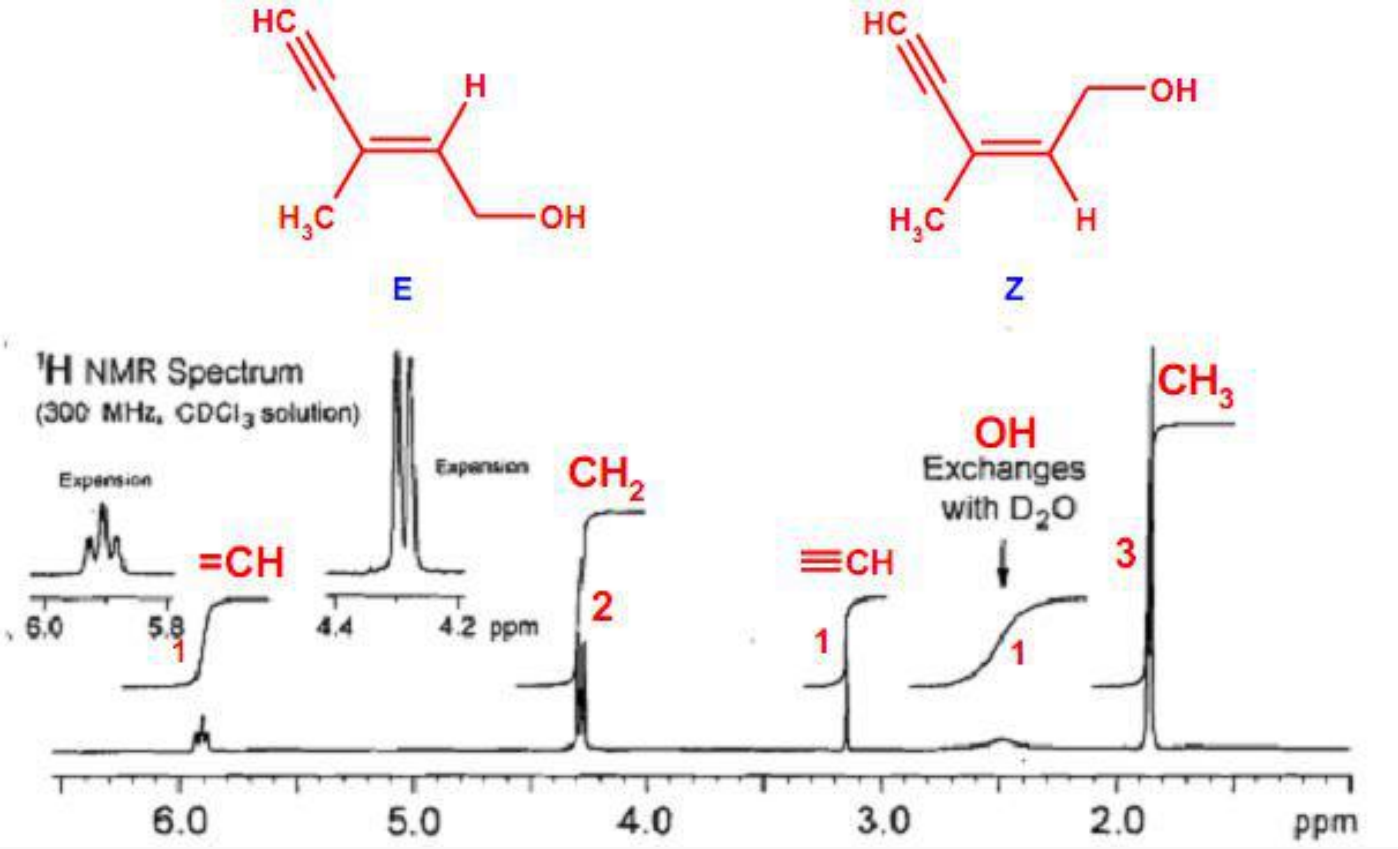


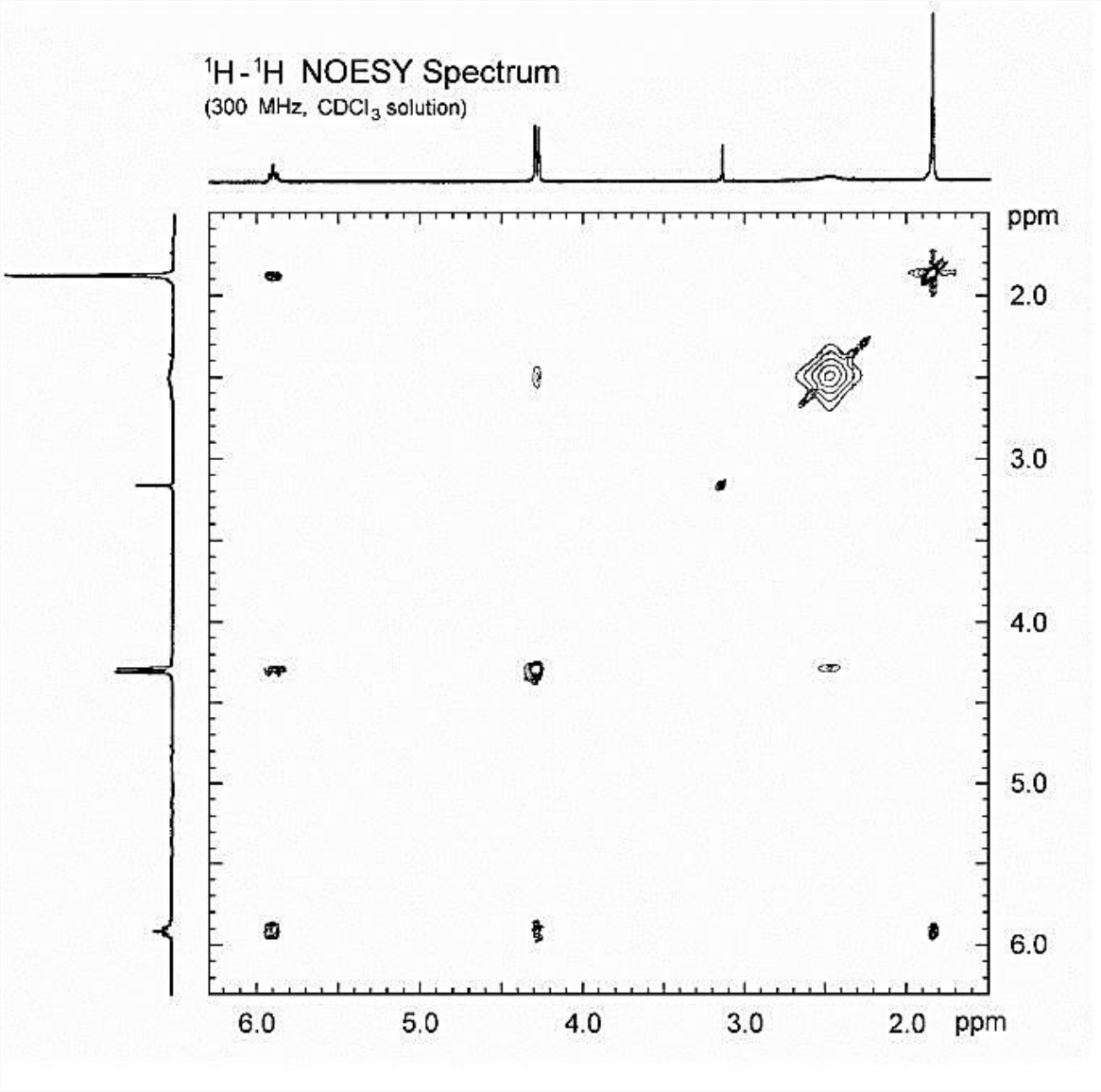
Z



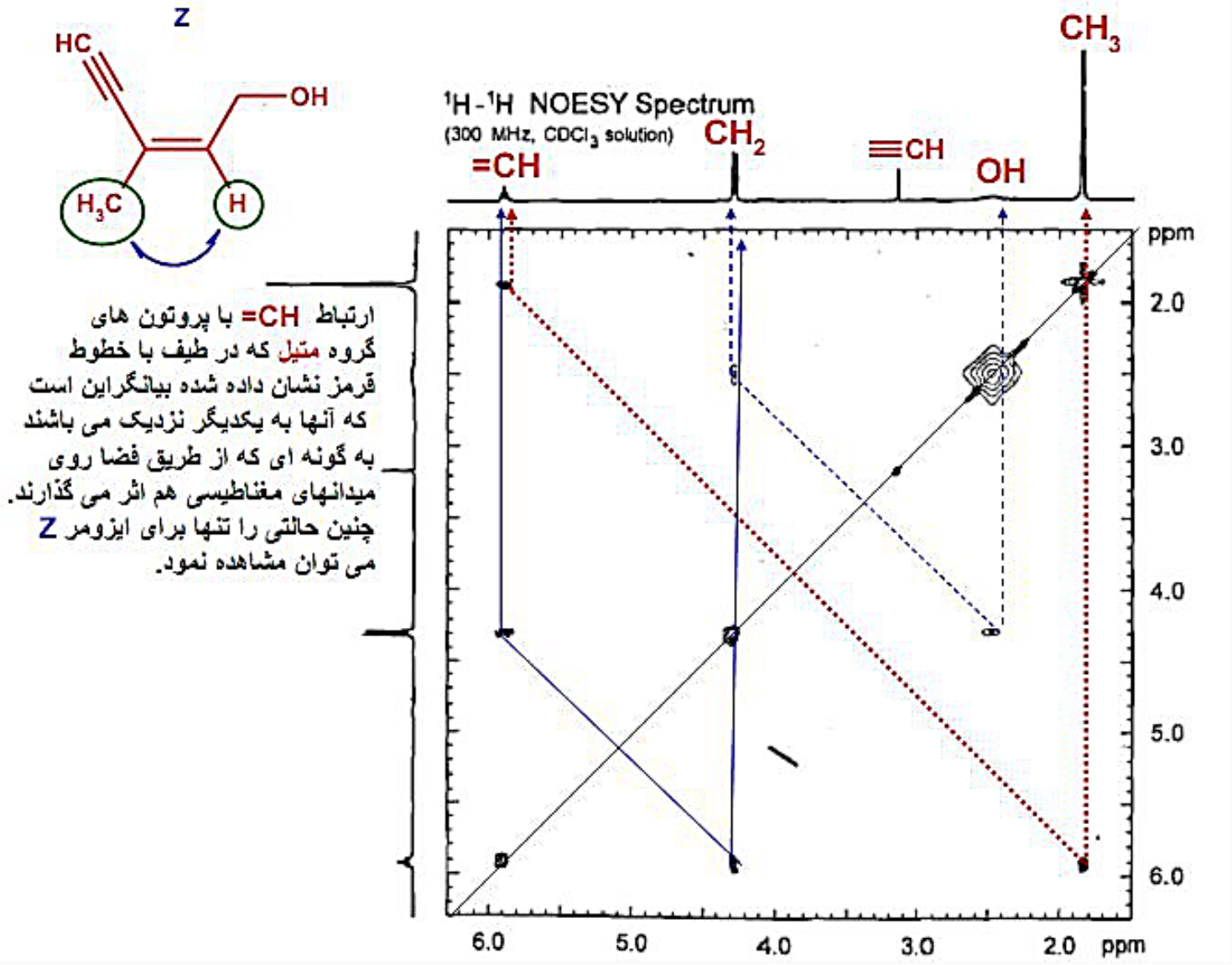
The ^{1}H NMR spectrum of one stereoisomer of 3-methylpent-2-en-4-yn-1-ol [HC≡ C(CH_3)C=CHCH_2OH] is given below. The 2-dimensional ^{1}H NOESY spectrum is also given. Determine the stereochemistry of the compound and draw a structural formula for the compound indicating the stereochemistry.

این تمرین نیز مجدد مربوط می شود به تشخیص دو نوع ایزومر E , Z



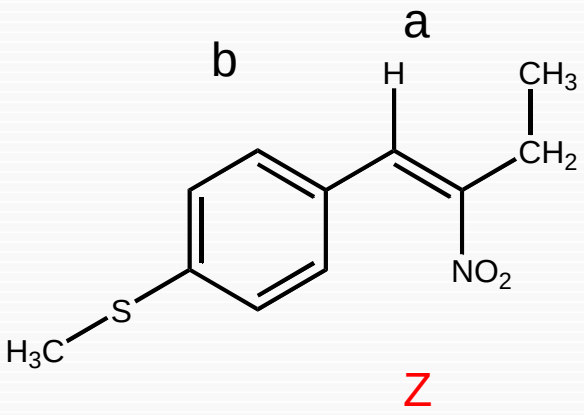


به نظر شما با توجه به طیف H-H NOESY کدام ایزومر می باشد؟

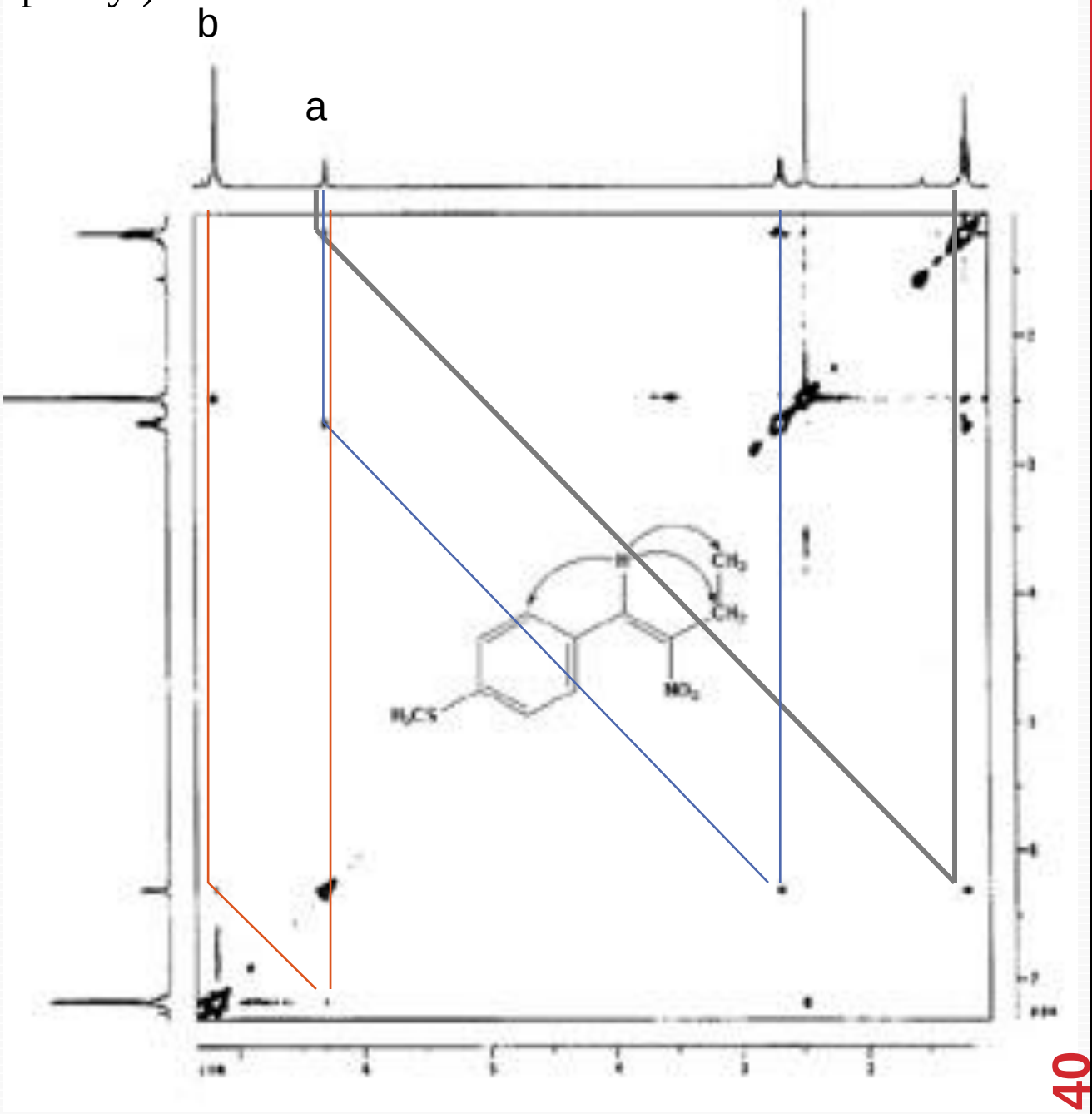


ارتباط =CH با پروتون های گروه متیل که در طیف با خطوط قرمز نشان داده شده بیانگراین است که آنها به یکدیگر نزدیک می باشند به گونه ای که از طریق فضا روی میدانهای مغناطیسی هم اثر می گذارند. چنین حالتی را تنها برای ایزومر Z می توان مشاهده نمود.

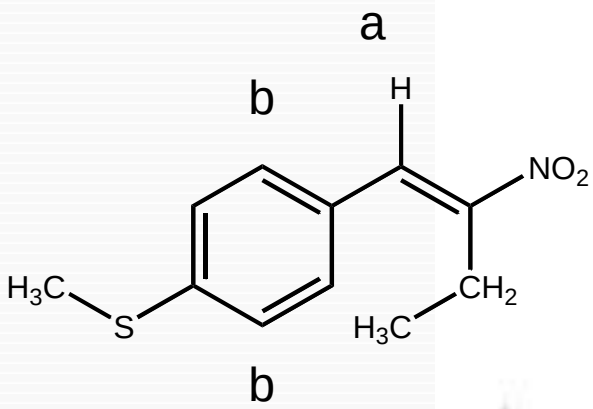
NOESY of 1-(4-methylthiophenyl)-2-nitroalkenes



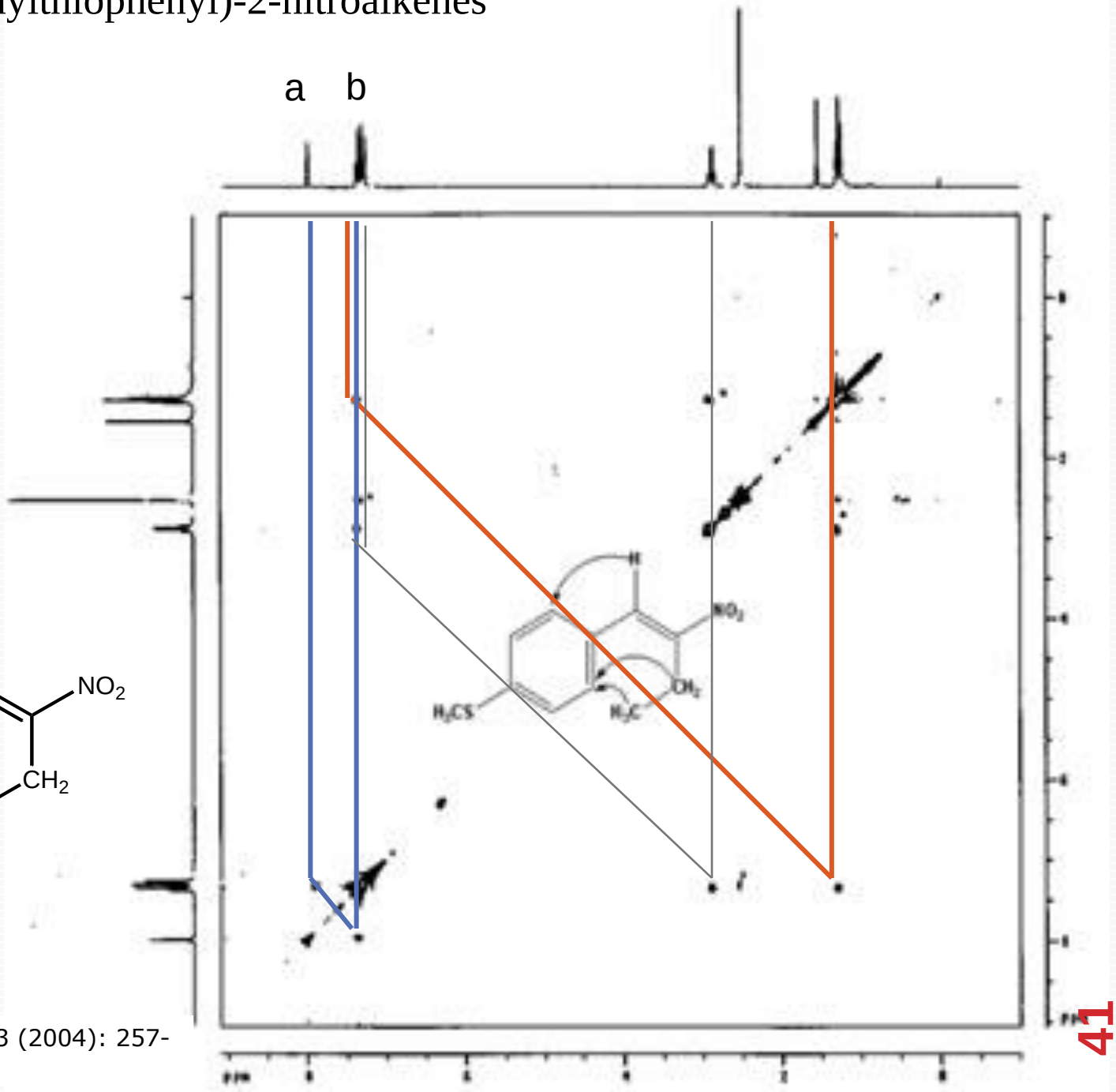
Z



NOESY of 1-(4-methylthiophenyl)-2-nitroalkenes



E

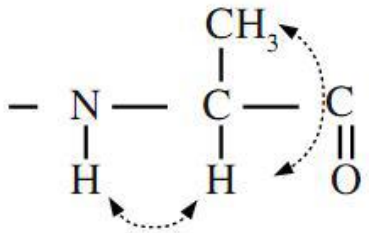


J. Chil. Chem. Soc., 49, N 3 (2004): 257-260

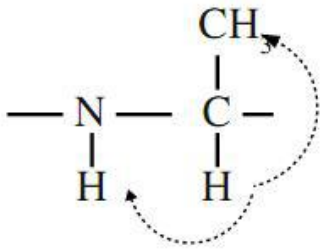
1H–1H TOCSY

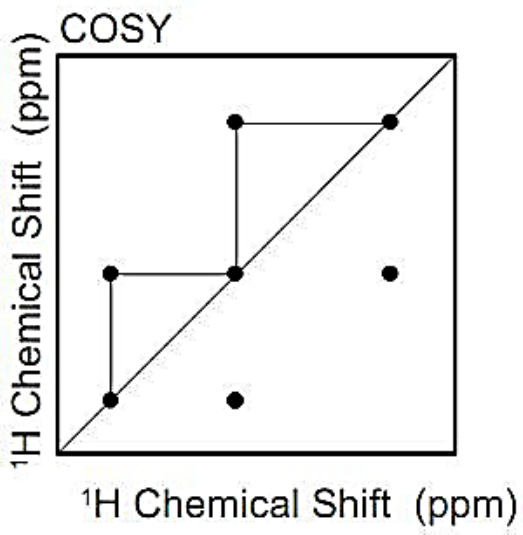
(Total Correlation Spectroscopy)

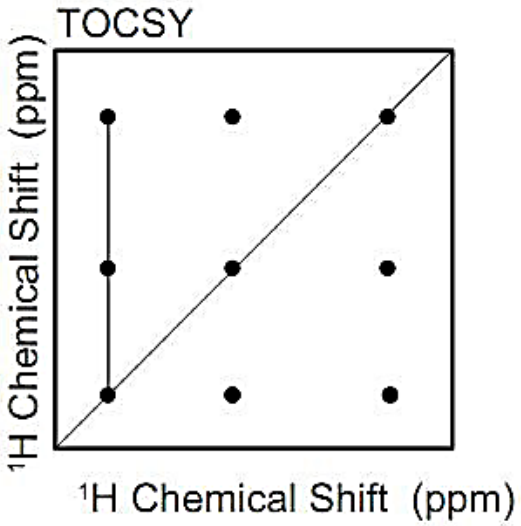
COSY



TOCSY



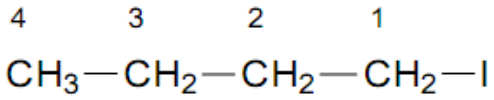




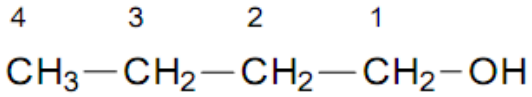
Problem 302

The ^{1}H NMR spectrum of a mixture of 1-iodobutane and 1-butanol recorded at 298K in $CDCl_3$ solution is given below. There is some overlap between the spectra of the components of the mixture. The TOCSY spectrum and the COSY spectrum are given on the facing page. Use the TOCSY and COSY spectra to determine the chemical shifts of all of the protons in 1-butanol and 1-iodobutane.

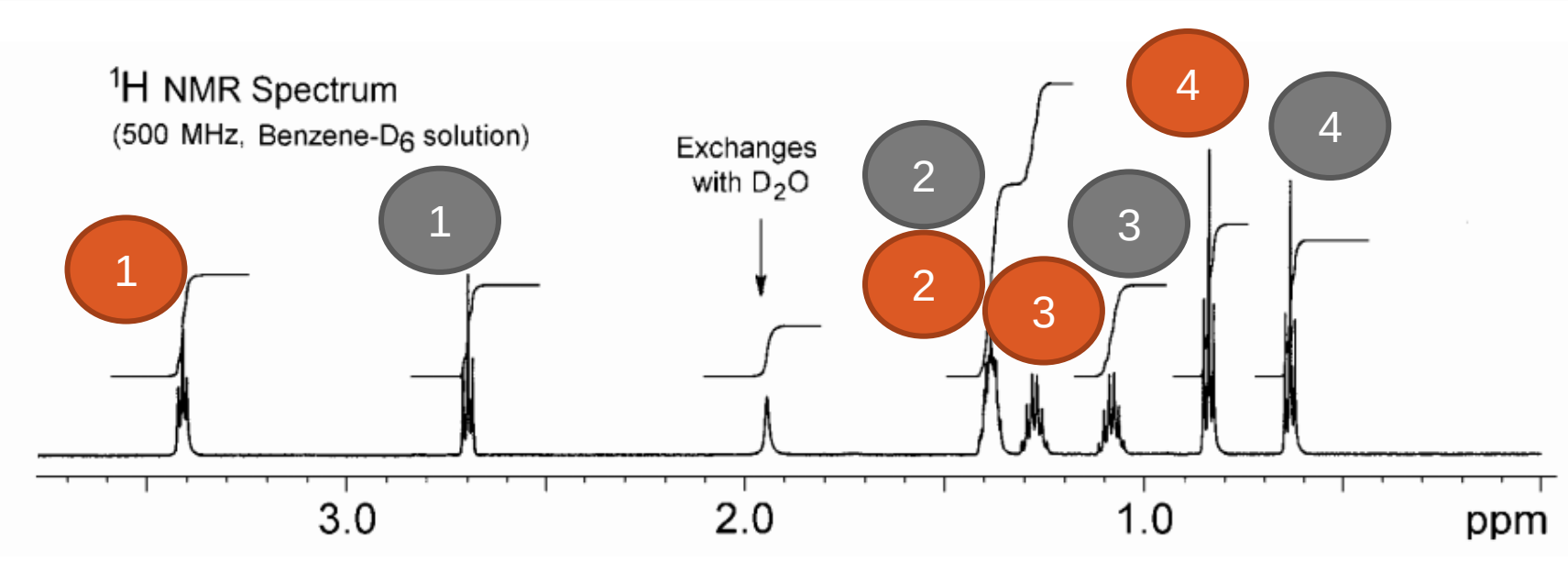
1-iodobutane



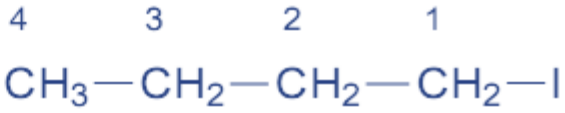
1-butanol



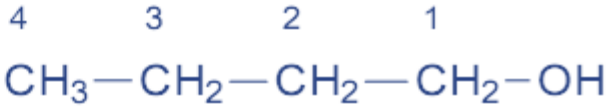
در اینجا از آنجایی که ید الکترونگاتیوته کمتری از اکسیژن دارد پس اولین triplet مربوط به ترکیب ۱-یدوبوتان است. حال ادامه کار را با طیف TOCSY دنبال می کنیم



1-iodobutane



1-butanol

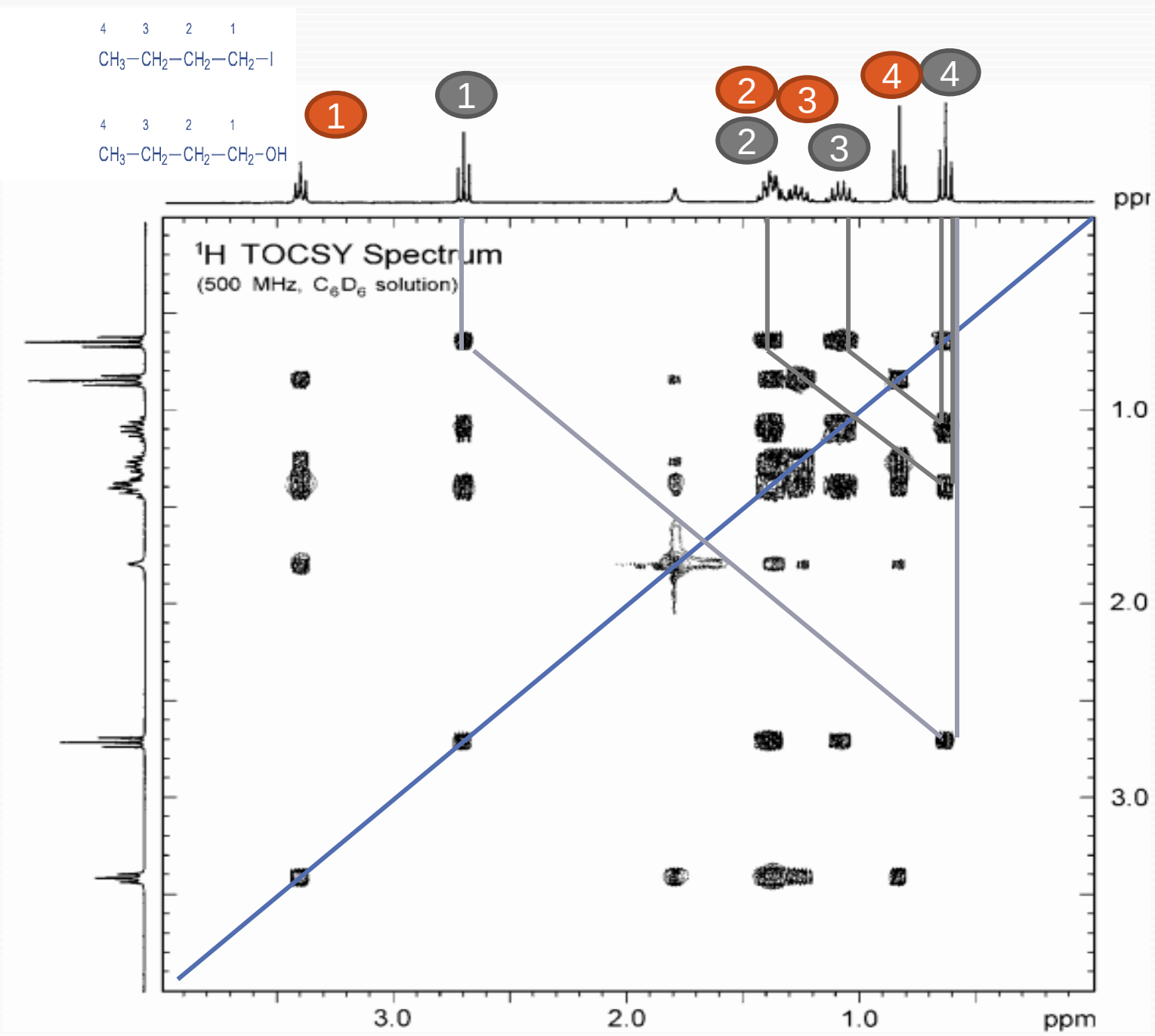


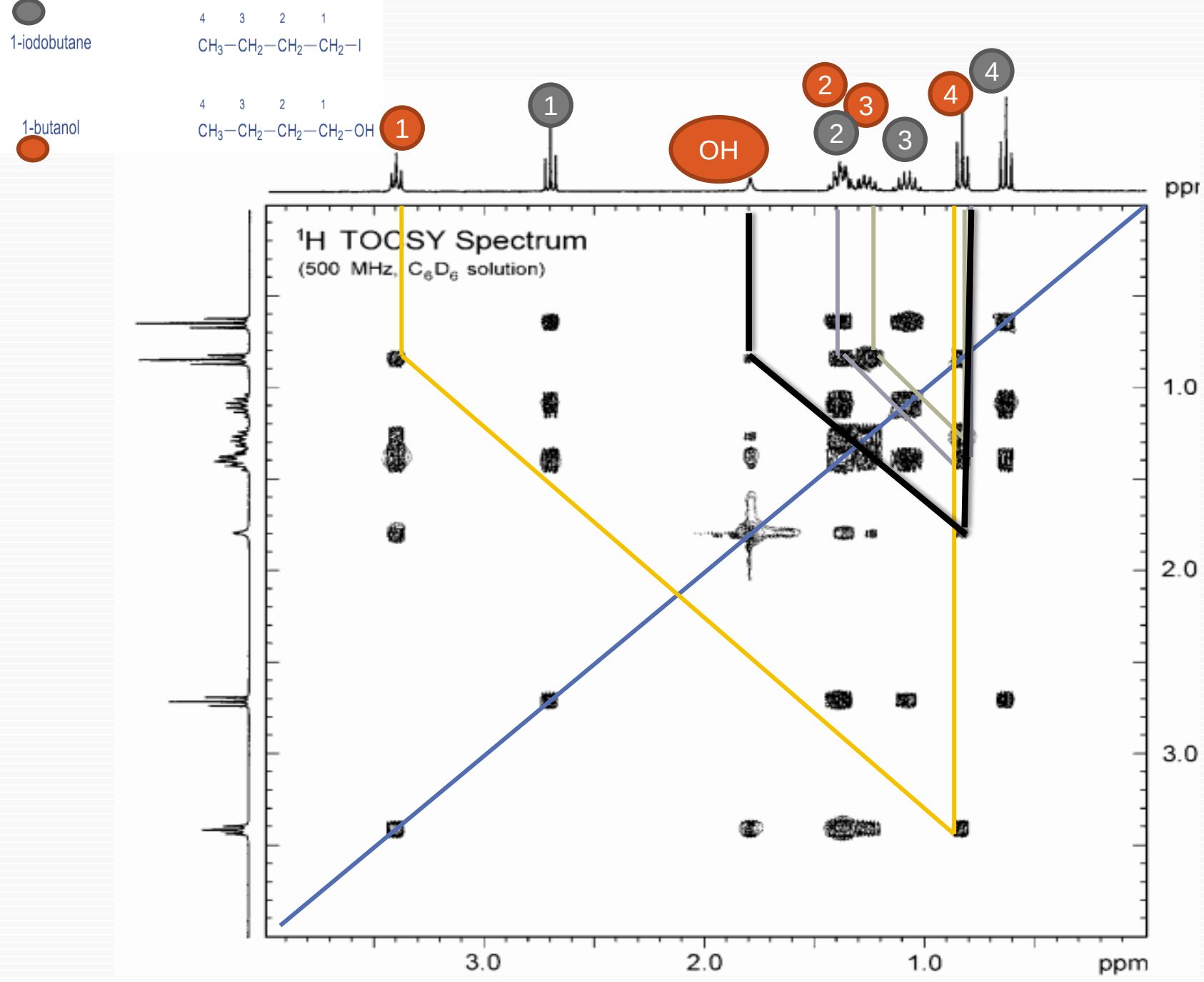
1-iodobutane

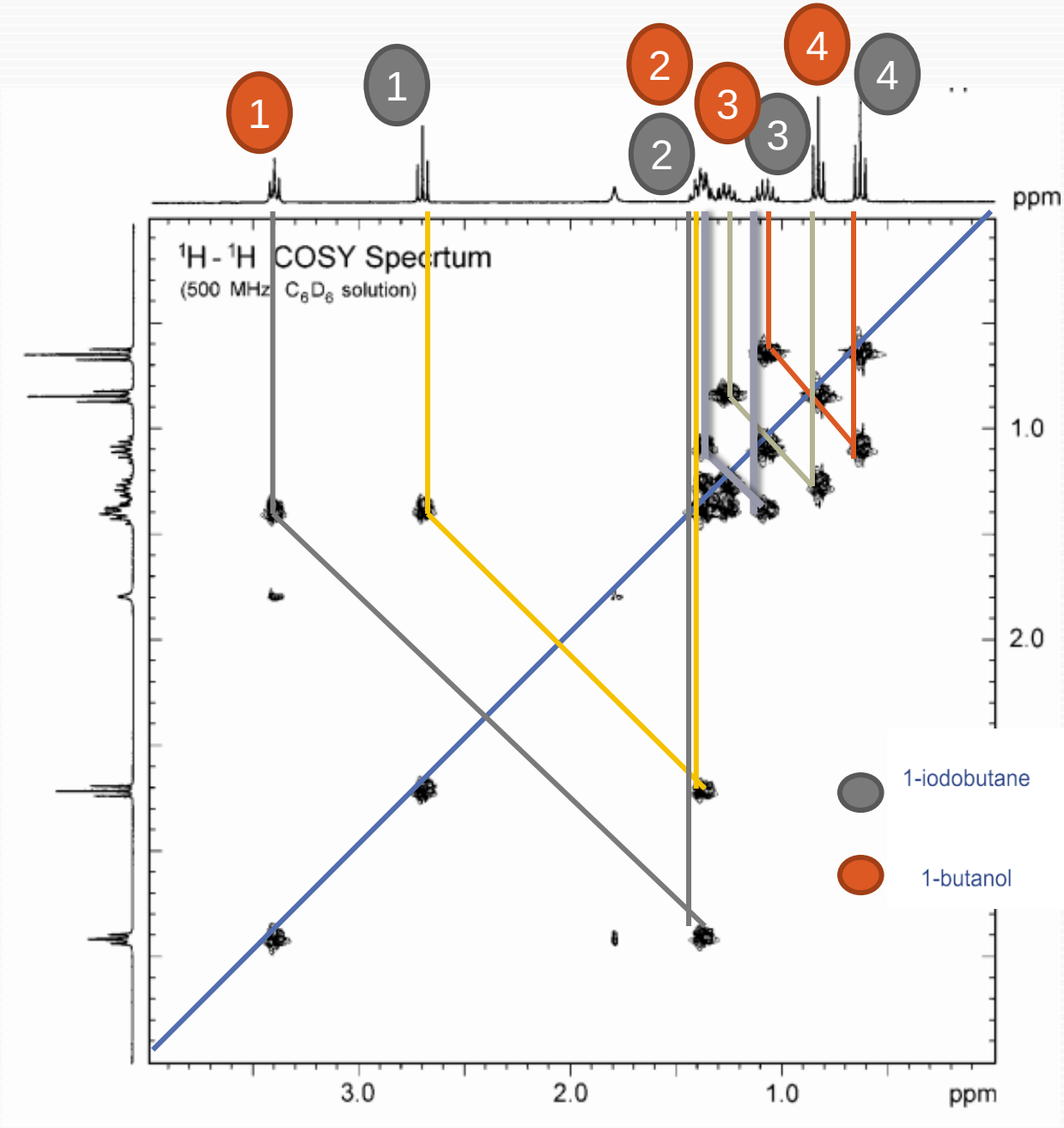
4 3 2 1
$CH_3-CH_2-CH_2-CH_2-I$

1-butanol

4 3 2 1
$CH_3-CH_2-CH_2-CH_2-OH$



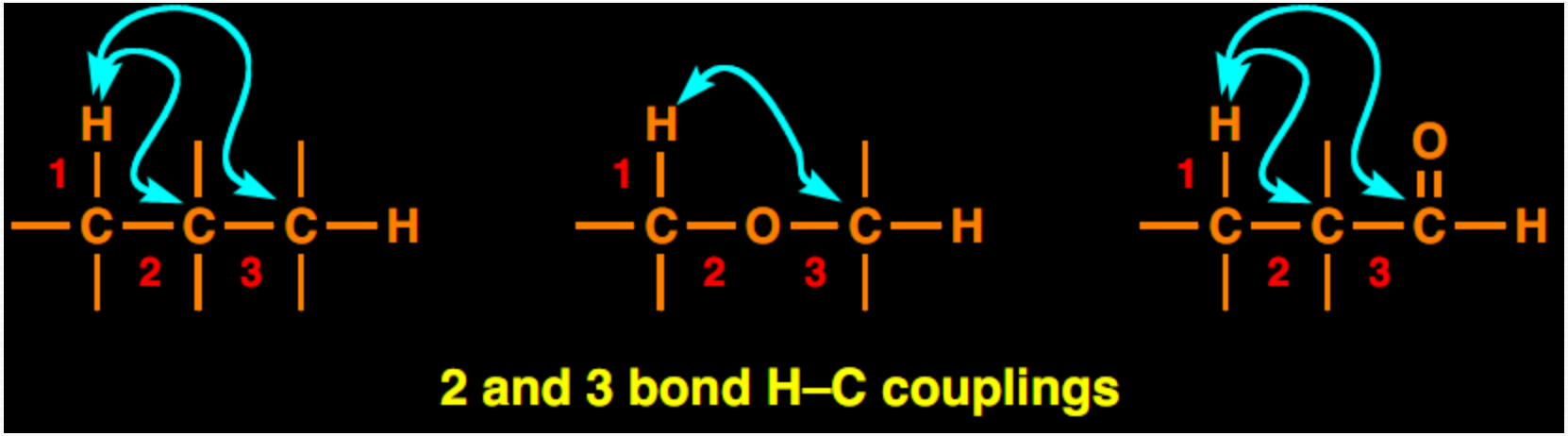

1-iodobutane
4 3 2 1
CH3—CH2—CH2—CH2—I
1-butanol
4 3 2 1
CH3—CH2—CH2—CH2—OH
1
1
OH
2
3
2
3
4
4
ppr
1H TOCSY Spectrum
(500 MHz, C6D6 solution)
1.0
2.0
3.0
3.0
2.0
1.0
ppm


1
1
2
2
3
3
4
4
ppm
^{1}H - ^{1}H COSY Spectrum
(500 MHz C_6D_6 solution)
1.0
2.0
3.0
2.0
1.0
ppm
1-iodobutane
1-butanol
4 3 2 1
$CH_3—CH_2—CH_2—CH_2—I$
4 3 2 1
$CH_3—CH_2—CH_2—CH_2—OH$

HMBC

Heteronuclear Multiple Bond Coherence

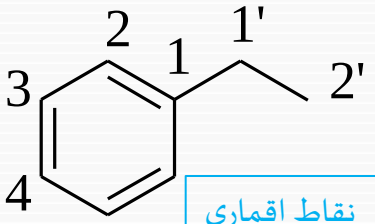
- A 2D experiment (closely related to HMQC, its 1-bond analogue), used to identify long-range couplings between protons and carbons (^{1}H-^{13}C COSY with long range heteronuclear correlation)
- HMBC experiment differs from the HMQC and HSQC in that multiple-bond couplings – over two or three bonds (J = 2-15Hz) are utilized. Cross peaks are between protons and carbons that are two or three bonds away. Direct one-bond cross-peaks are suppressed.
- Some 2- and 3-bond correlations may be absent due to the variations in the magnitude of the coupling constant.



2 and 3 bond H–C couplings

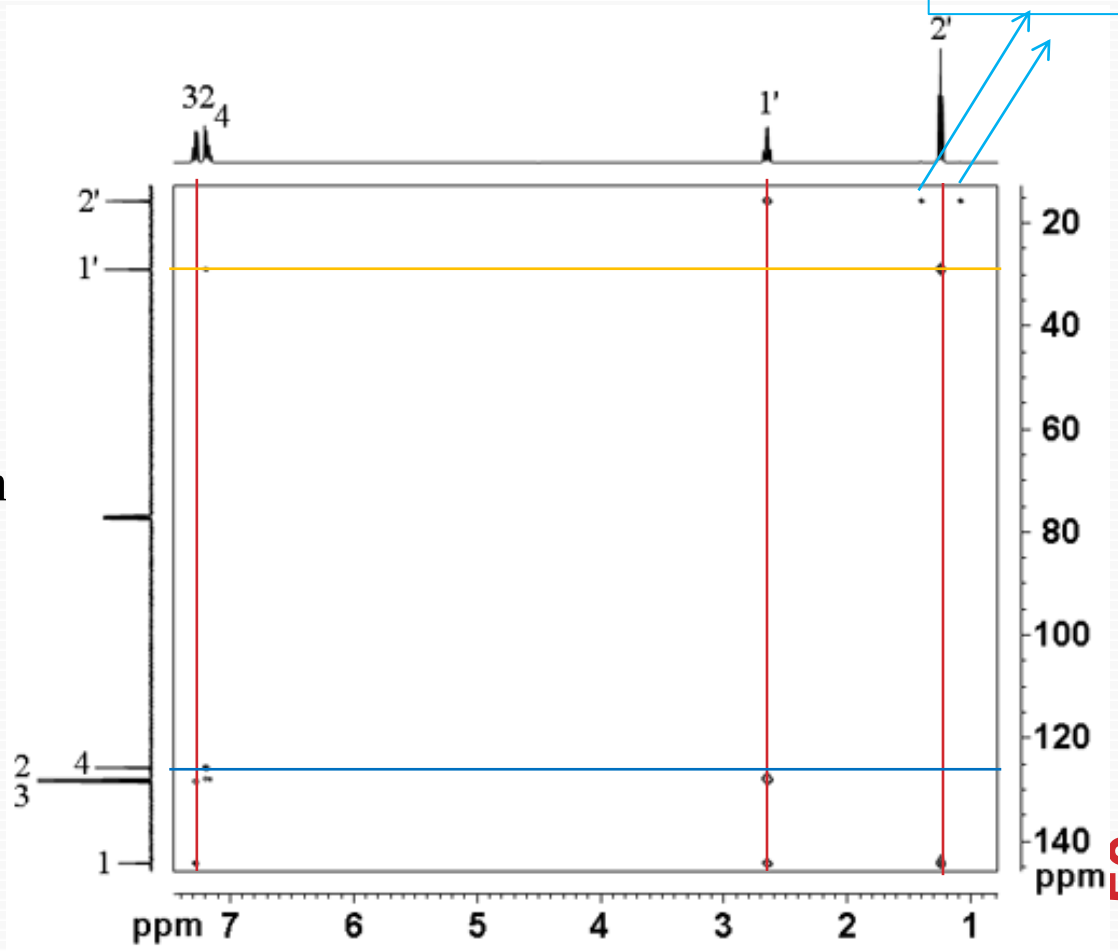
2D HMBC spectrum of ethylbenzene

In the case of ethylbenzene, all the three-bond correlations and some two-bond correlations appear strongly.



For example H2' correlates with C1' via a 2 bond correlation and with C1 via a 3 bond correlation

Those signals in the 1D spectrum that do not correlate do not appear in the 2D spectrum.



INADEQUATE

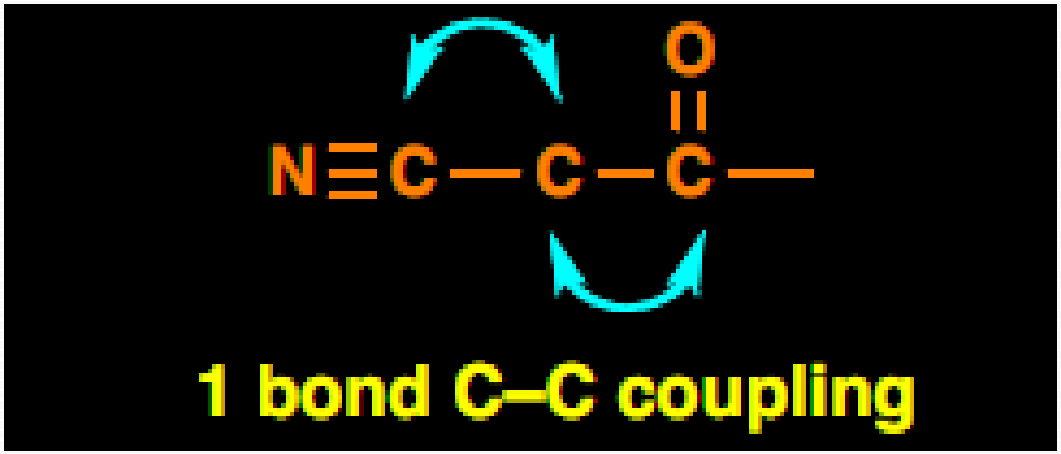
Incredible Natural Abundance Double Quantum Transfer Experiment

- ✓ A 2D INADEQUATE spectrum that yields one bond correlations *via* spin–spin coupling. The spectrum does not appear in the same form as a COSY spectrum

- ✓ It a ^{13}C-^{13}C COSY which gives cross peaks for 1-bond couplings but the low sensitivity is a deterrent.

- ✓ Useful for determining which signals arise from neighbouring carbons.

- ✓ It is very insensitive as 0.01% of the carbons are excited at natural abundance. Use this experiment as a last resort when all else fails.

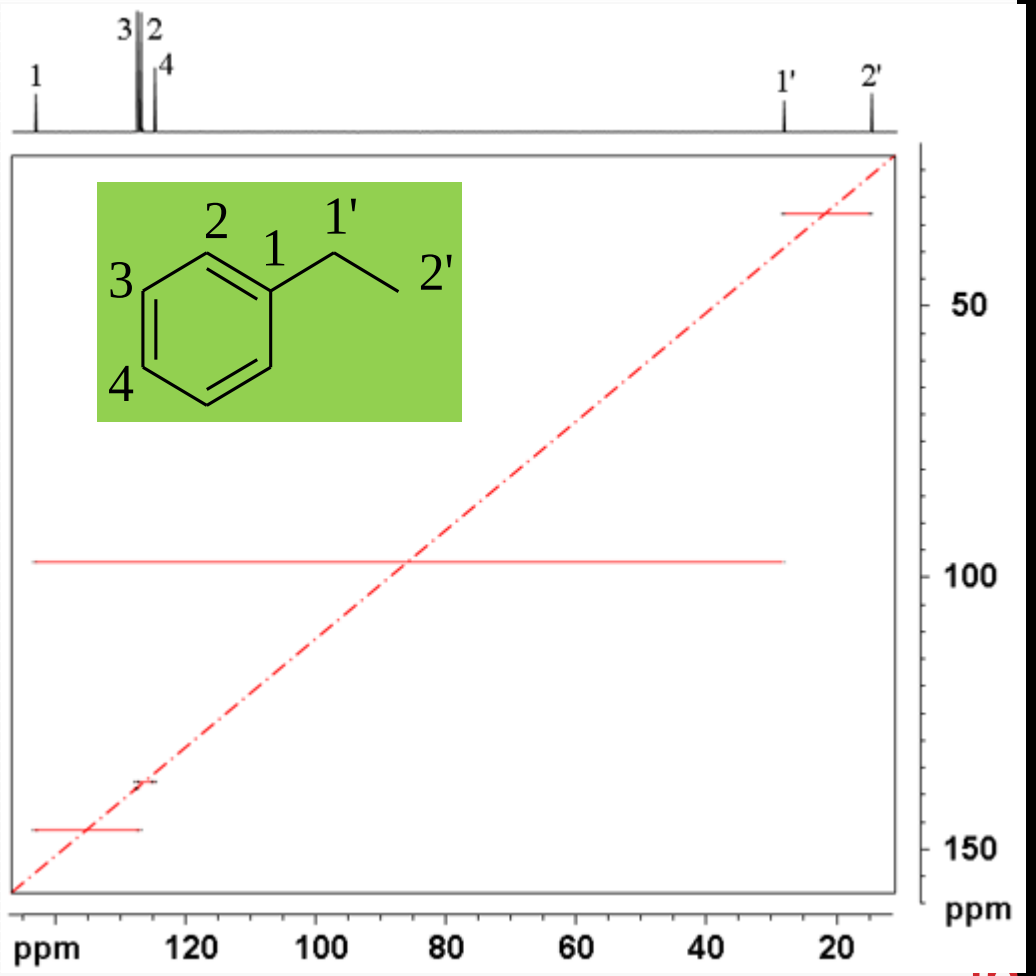

O
N≡C—C—C—
1 bond C–C coupling

2D INADEQUATE

Spectrum of ethylbenzene

When two neighboring carbons have similar chemical shifts, the cross-peak is weaker

- The cross-peaks are distributed symmetrically and horizontally either side of the diagonal (red dashed).
- The connection between each pair of carbons is shown as a solid red line in the diagram below. Each cross-peak is a doublet split by carbon-carbon coupling.
- The carbon connectivity can be followed through the molecule from 2' to1' to 1 to 2 to 3 to 4.



Summary of 2D NMR experiments

Homonuclear correlation

Through bond: COSY, TOCSY, 2D-INADEQUATE
Through space: NOESY, ROESY

Heteronuclear correlation

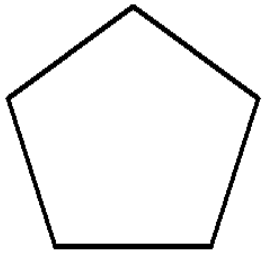
One-bond correlation: HSQC, HMQC, HETCOR
Long-range correlation: HMBC

درجه ی غیر اشباع شدگی(ضریب کمبود هیدوژن)

ضریب کمبود هیدروژن (U) نشان دهنده ی تعداد پیوندهای پای یا حلقه های موجود در واکنش است

U از فرمول مولکولی یک ماده ی مجهول واز مقایسه ی ان با فرمول ترکیب اشباع غیر حلقوی مشابه بدست می اید

اگر اختلاف تعداد Hدو فرمول را نصف کنیم ضریب کمبود هیدروژن بدست می اید



C5H12 ← فرمول آلکان

C5H10 ← فرمول ترکیب براساس قواعد فرمول اشباع

2/2=1

C_5H_{10}

بدست اوردن فرمول اشباع:

۱–به ازای هر کدام از عناصر N.As.Sb.Bi.P یک هیدروژن اضافی به فرمول اضافه شود

C2H6. C2H7N . C2H8N2

۲– به ازای عناصر گروه ۶ تغییری در تعداد هیدروژ ن ها داده نمی شود O.S Se

C2H6. C2H6O. C2H6O2

۳– به ازای هر یک از هالوژن ها یک هیدروژن از فرمول کاسته می شود

C2H6- C2H5F- C2H4F2

U=1

وجود حلقه یا پیوند دوگانه

U=2

وجود یک پیوند سه گانه یا دو پیوند دوگانه یا دو حلقه

U=>4

یک حلقه ارو ماتیک

بدست اوردن فرمول اشباع:

۱-به ازای هر کدام از عناصرN.As.Sb.Bj.P

یک هیدروژن اضافی به فرمول اضافه شود

C2H6. C2H7N . C2H8N2

۲- به ازای عناصر گروه ۶ تغییری در تعداد هیدروژ ن ها داده نمی شود

O.S Se.Te

C2H6. C2H6O. C2H6O2

ضریب کمبود هیدروژن (u) نشان دهنده ی تعداد پیوندهای پای یا حلقه های موجود در واکنش است

Problem 11

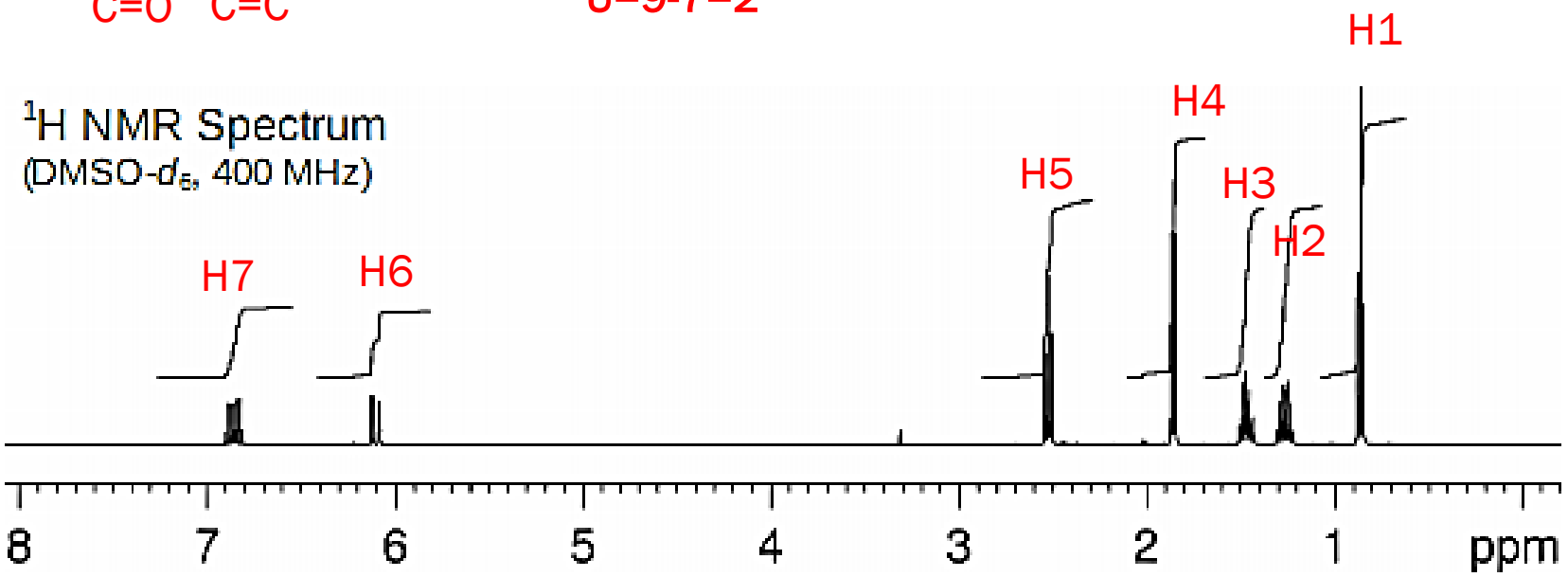
Identify the following compound.
Molecular Formula: $C_8H_{14}O$
IR: 1698, 1638 cm^{-1}

C=O C=C

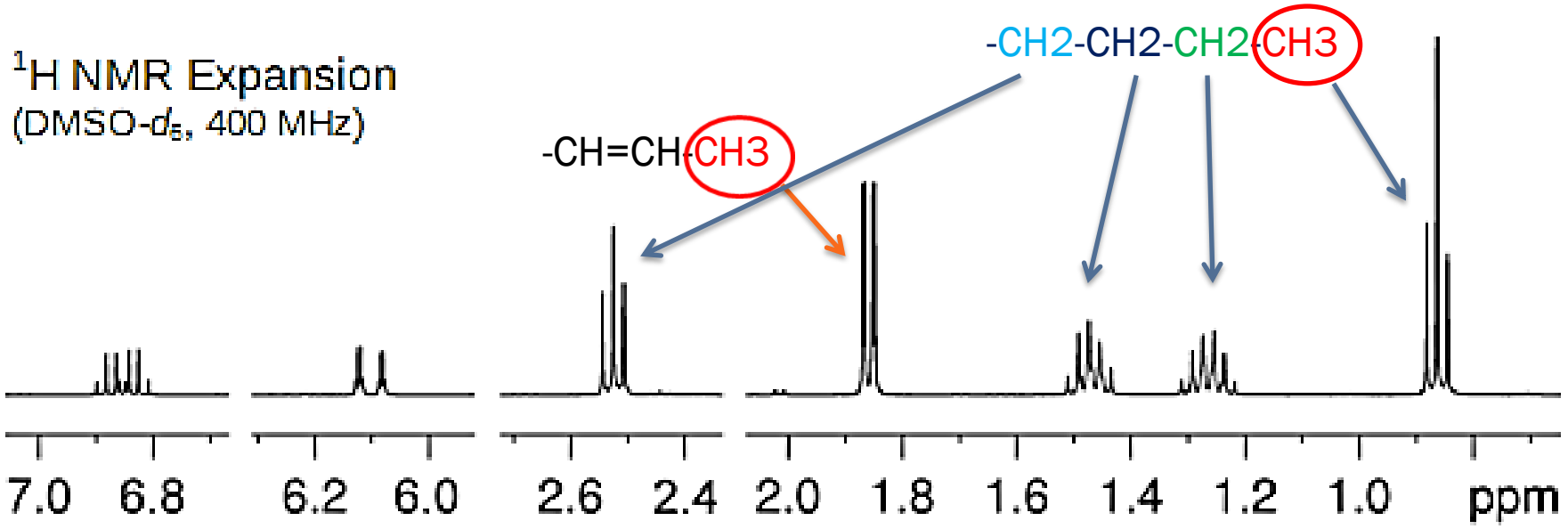
U=9-7=2

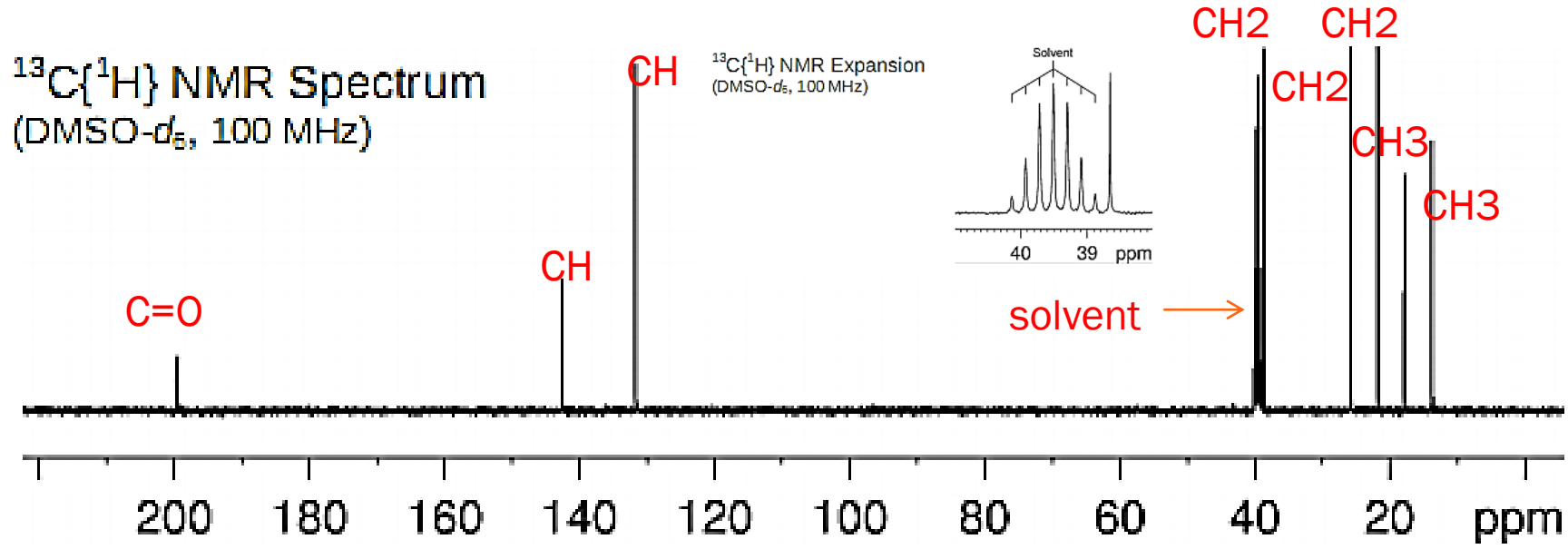
نکته در IR: مزدوج شدن C=O با C=C (β,α- کتون غیر اشباع):

در ناحیه ۱۶۷۵-۱۷۰۰ C=O و در ۱۶۱۷-۱۶۴۴C=C

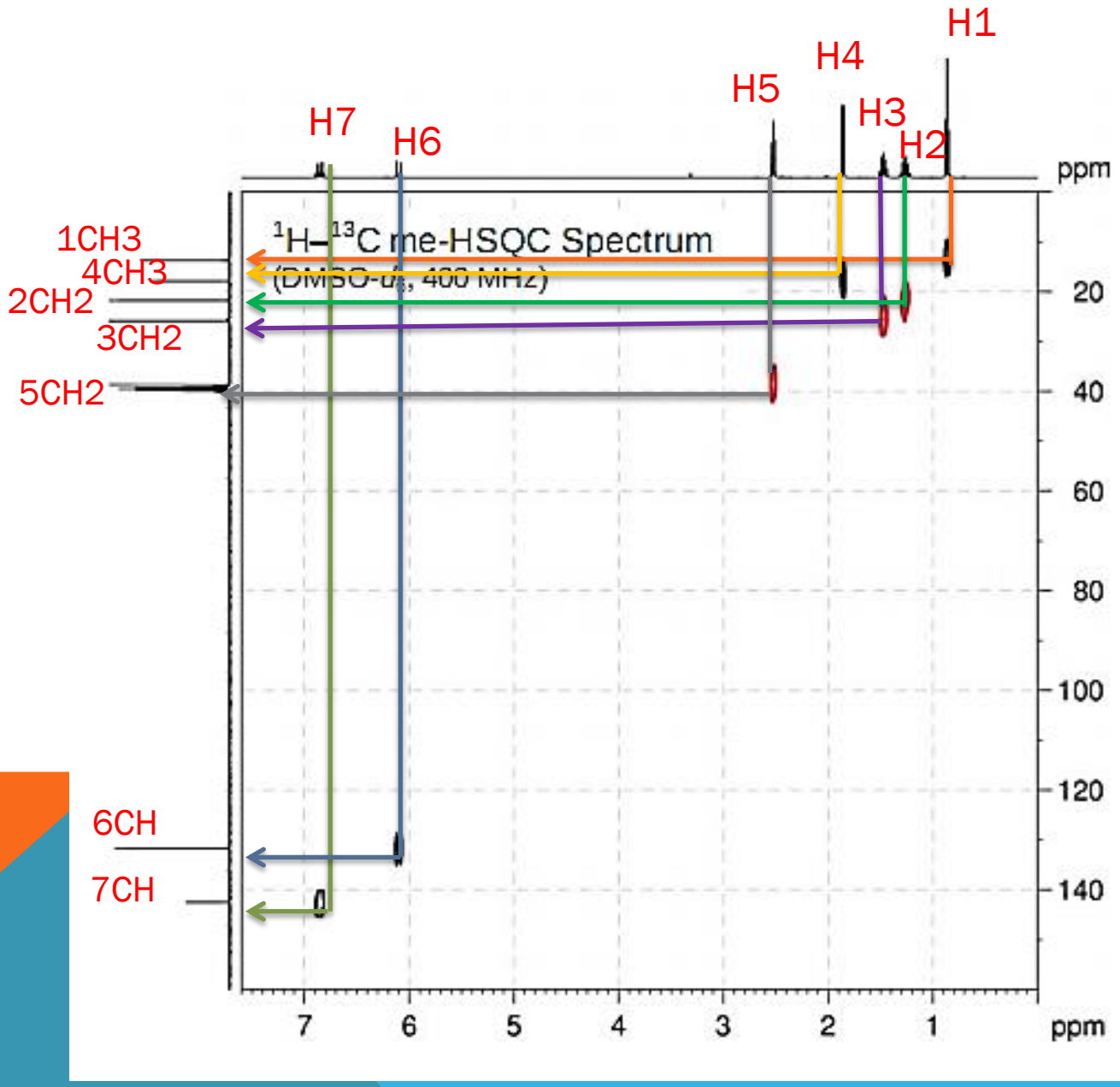


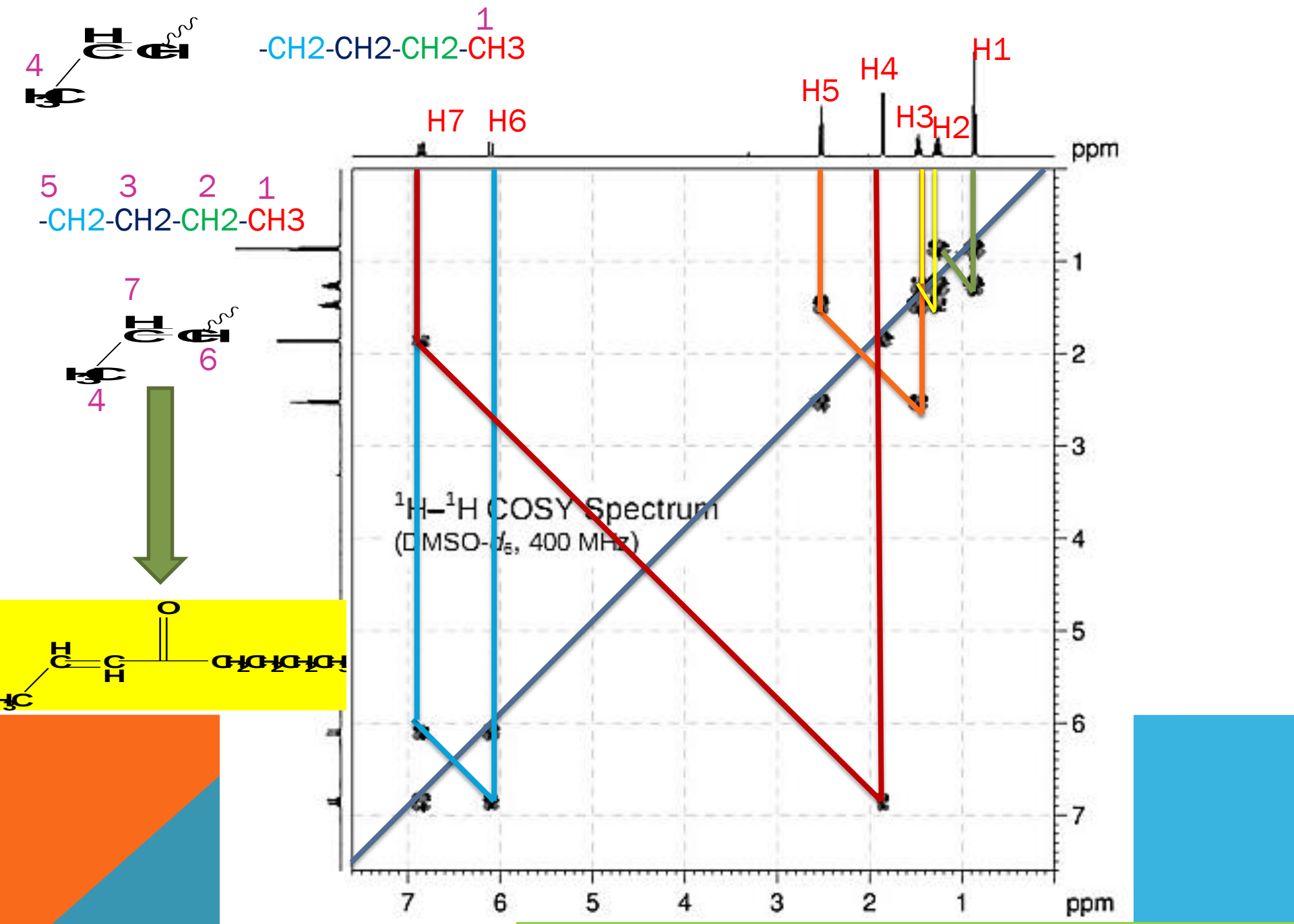
C8H14O U=2 → C=O C=C



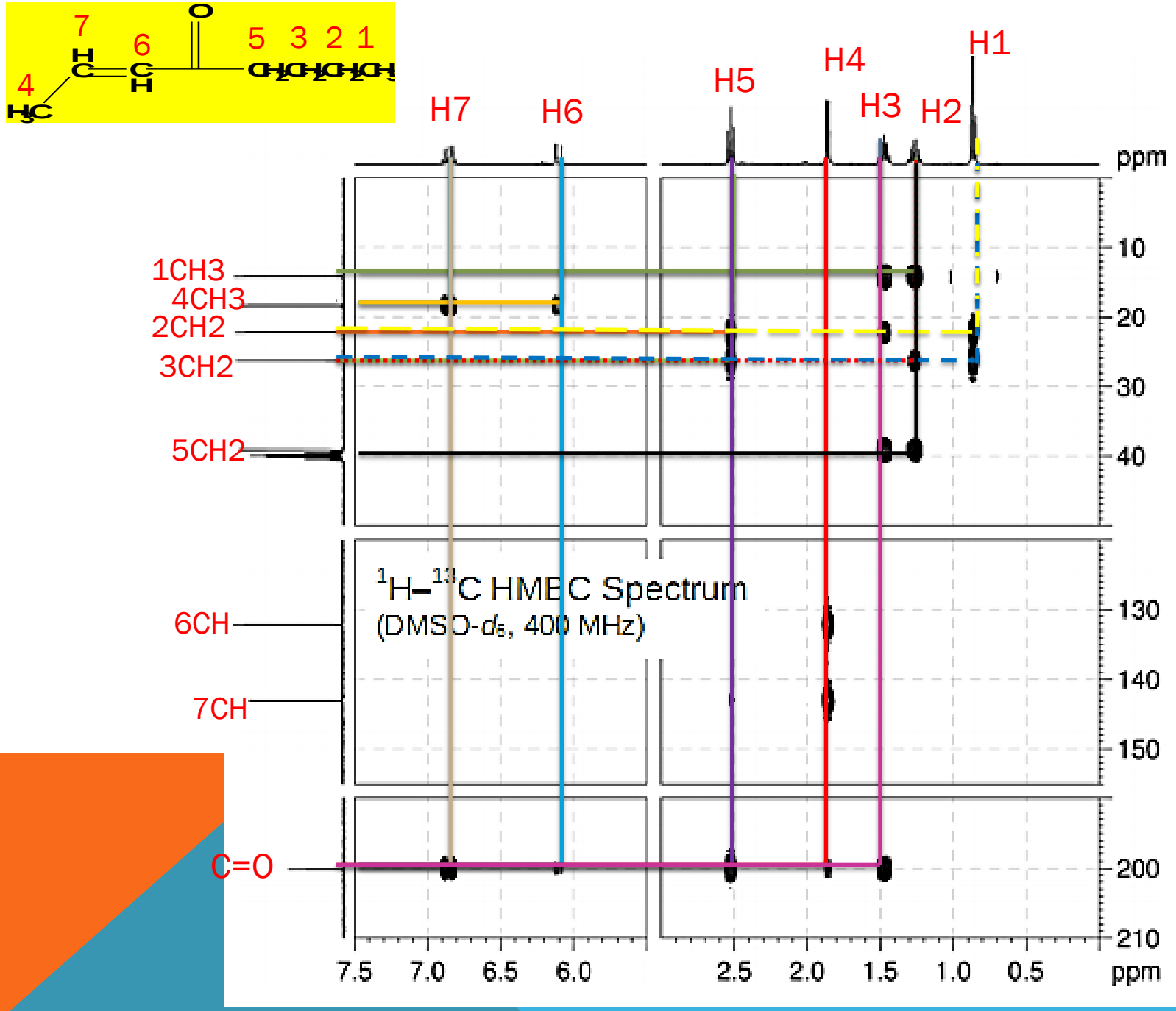


Trans-2-Octen-4-One

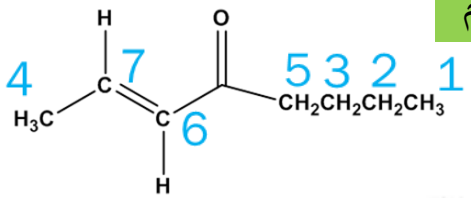




نکته: در ترکیبات الفا-بتا کربونیل غیر اشباع، کربن و هیدروژن بتا خیلی دشیلدتر از الفا است


7
6
5 3 2 1
4
H7
H6
H5
H4
H3
H2
H1
ppm
1CH3
4CH3
2CH2
3CH2
5CH2
6CH
7CH
C=O
^{1}H–^{13}C HMBC Spectrum
(DMSO-d_6, 400 MHz)
10
20
30
40
130
140
150
200
210
7.5
7.0
6.5
6.0
2.5
2.0
1.5
1.0
0.5
ppm

با توجه به ارتباط ۶ با ۴ آلکن ترانس داریم



Problem 20

Identify the following compound.

Molecular Formula: $C_{14}H_{12}O_2$

IR: 1751 cm^{-1}

U=15-6=9

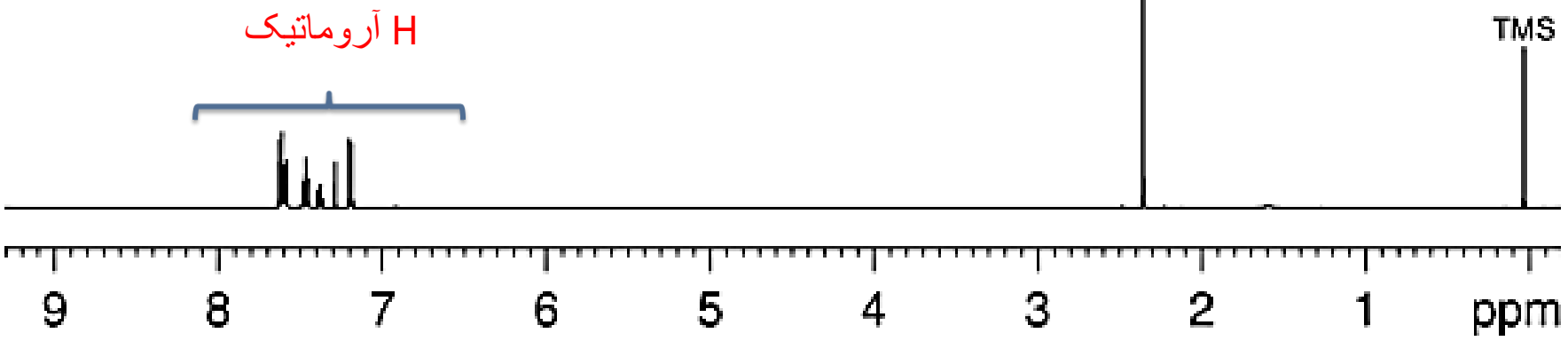
C=O

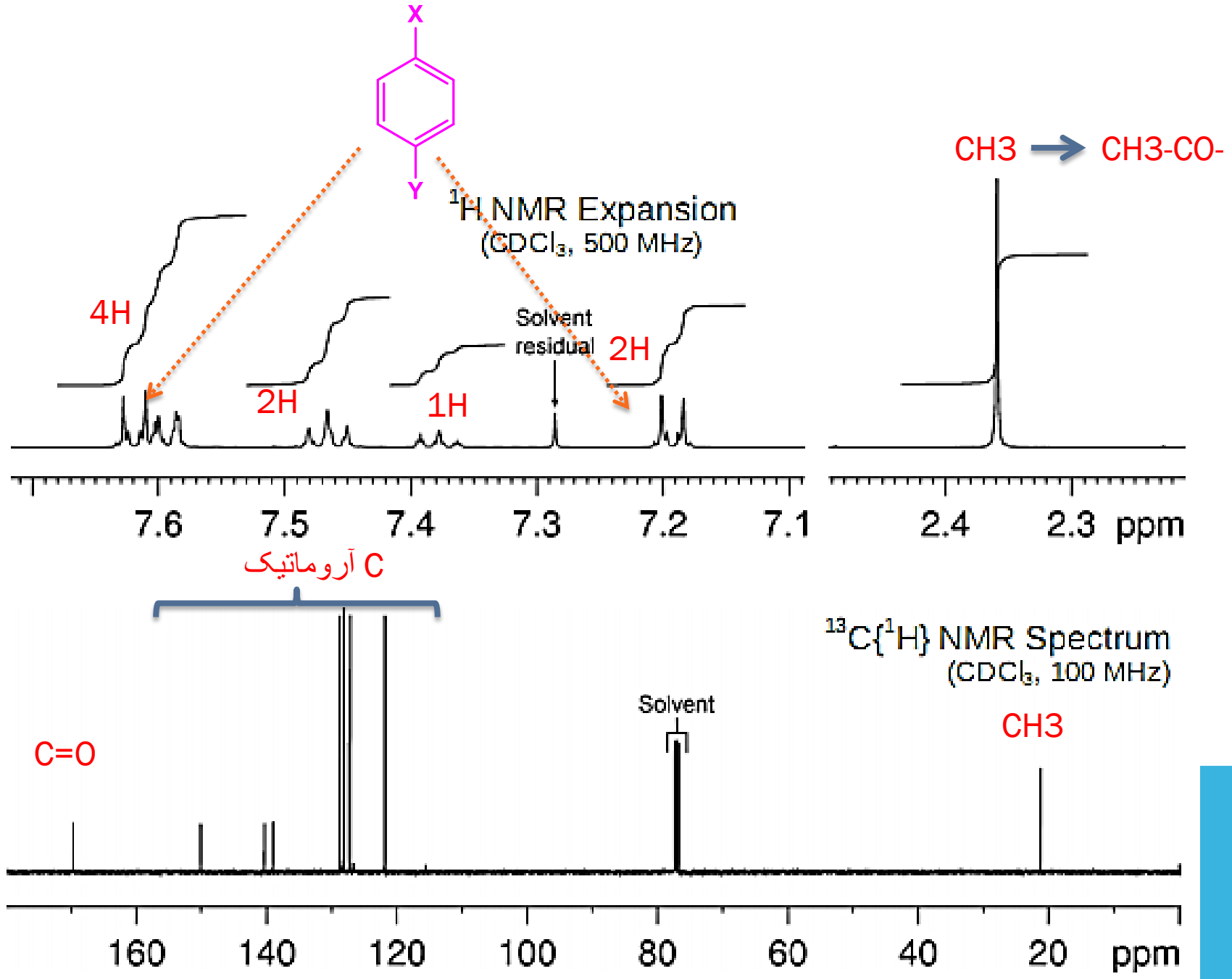
2حلقه اروماتیک

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

3H

آروماتیک H

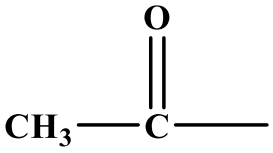



X
Y
^{1}H NMR Expansion
($CDCl_3$, 500 MHz)
4H
2H
1H
Solvent residual
2H
7.6
7.5
7.4
7.3
7.2
7.1
CH3 → CH3-CO-
2.4
2.3 ppm
C آروماتیک
$^{13}C\{^1H\}$ NMR Spectrum
($CDCl_3$, 100 MHz)
Solvent
C=O
CH3
160
140
120
100
80
60
40
20
ppm

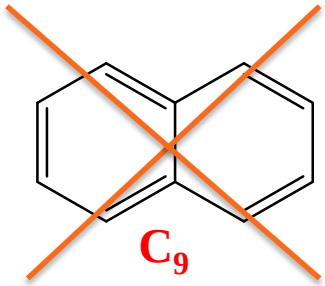
U=15-6=9

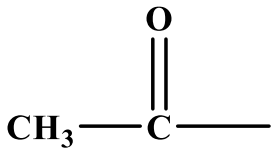
C=O

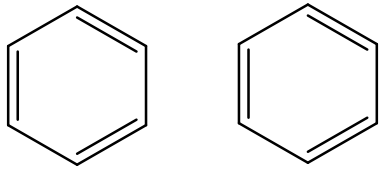
2حلقه اروماتیک



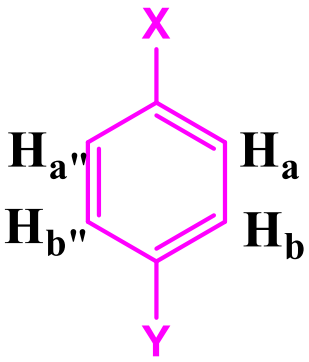
$C_{14}H_{12}O_2$







O



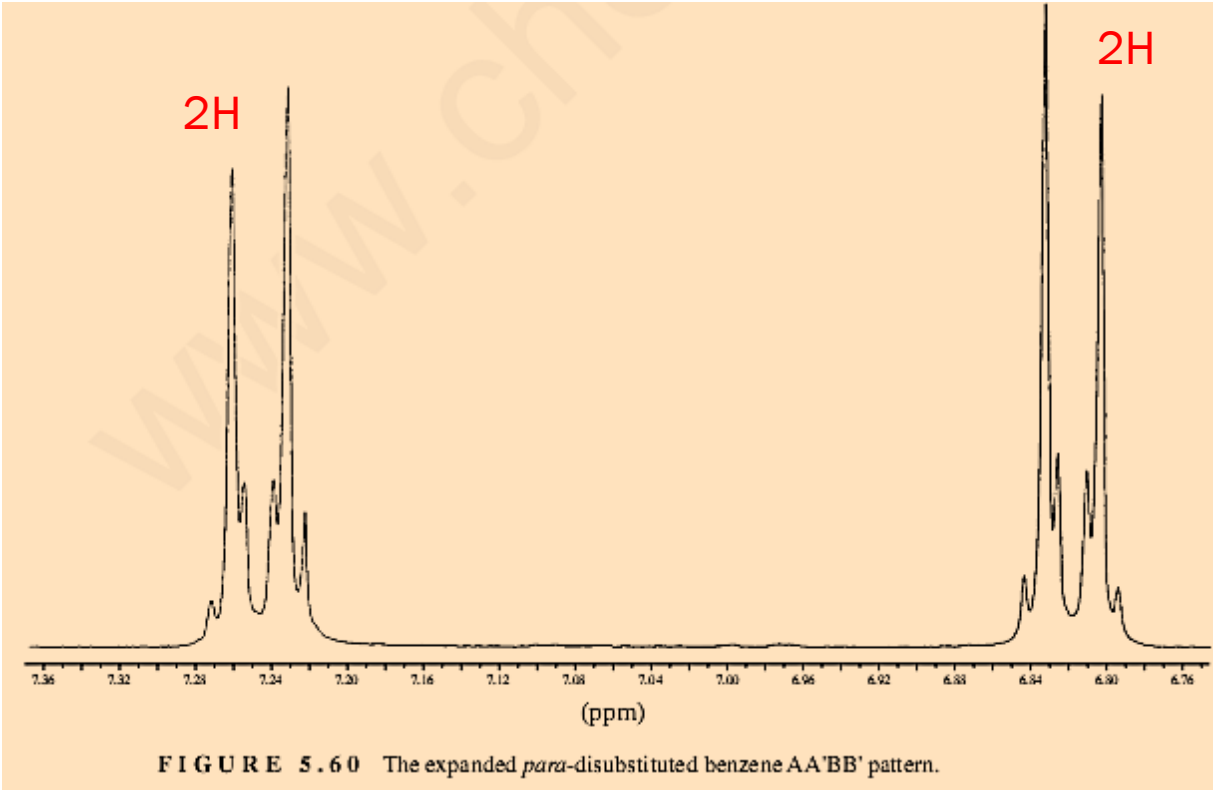
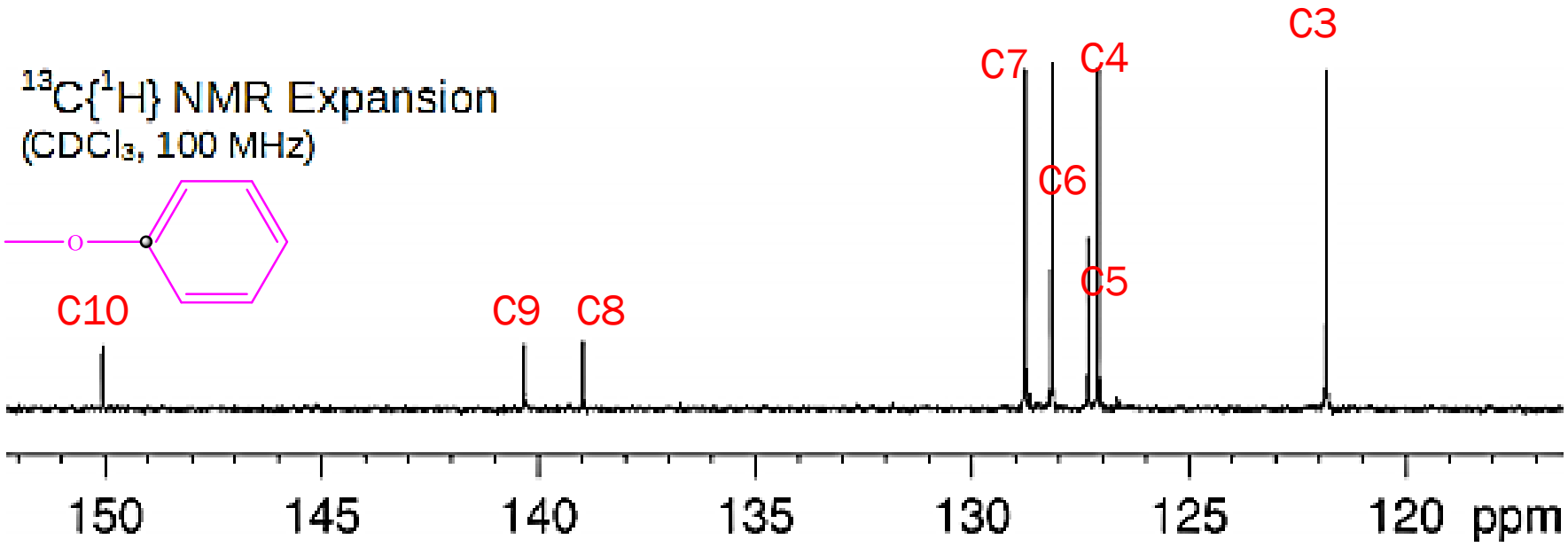
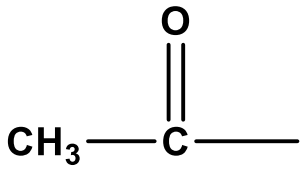
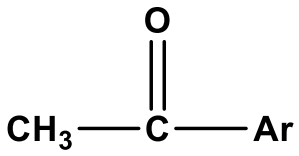


FIGURE 5.60 The expanded *para*-disubstituted benzene AA'BB' pattern.

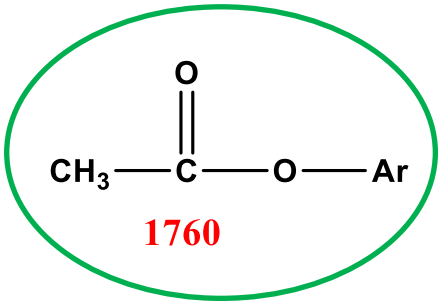

$^{13}C\{^{1}H\}$ NMR Expansion
(CDCl3, 100 MHz)
O
C10
C9
C8
C7
C4
C3
C6
C5
150
145
140
135
130
125
120
ppm



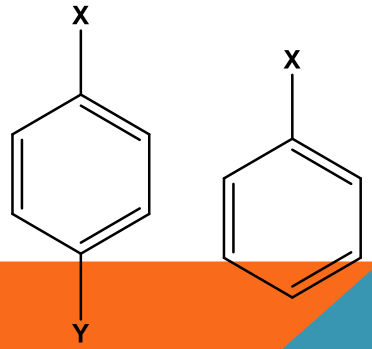
با توجه به طیف های IR, HNMR, CNMR :



1680-1700



IR

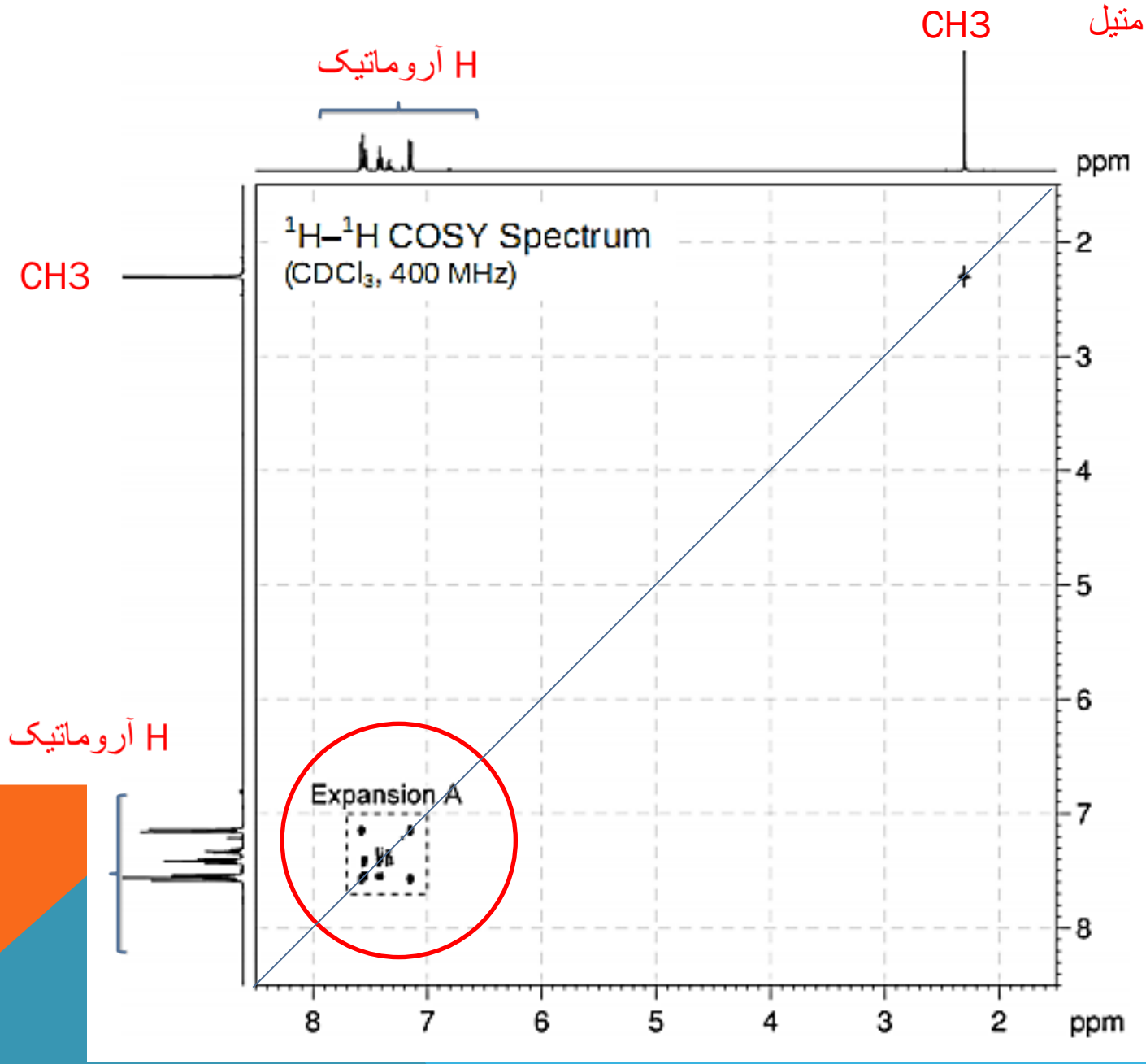


از ۱۴ کربن، ۱۲ کربن در ناحیه آروماتیک :

بنابراین دو حلقه آروماتیک جدا از هم داریم

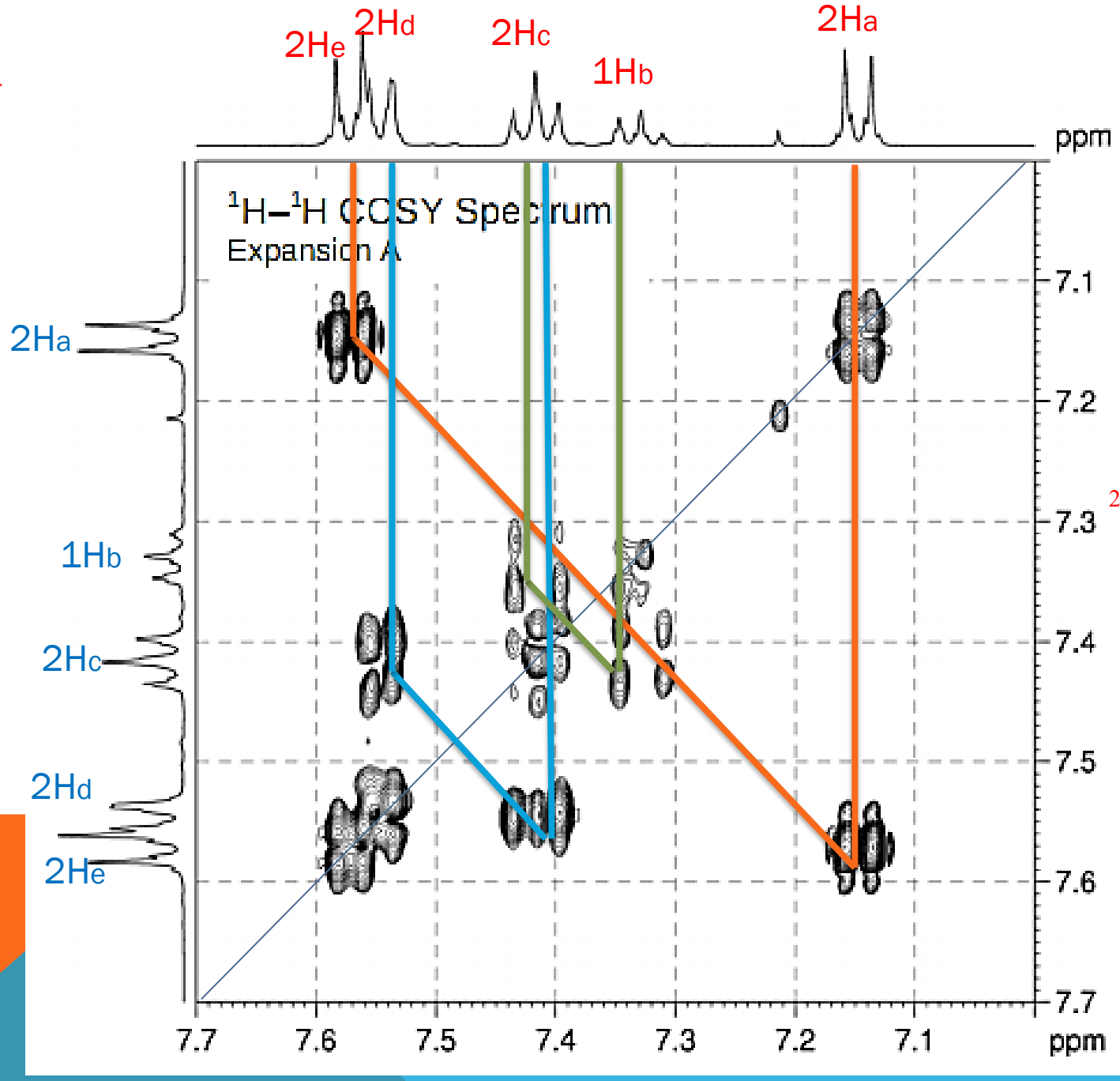
هیچ ارتباطی برای متیل وجود ندارد

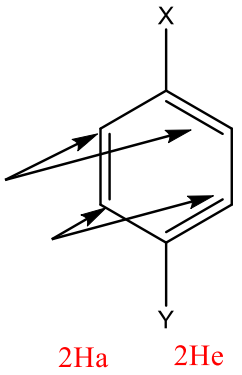
CH3-CO-

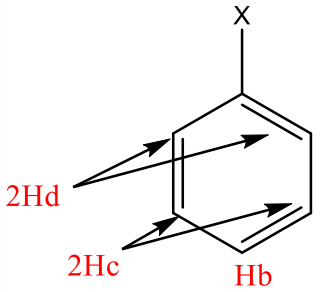


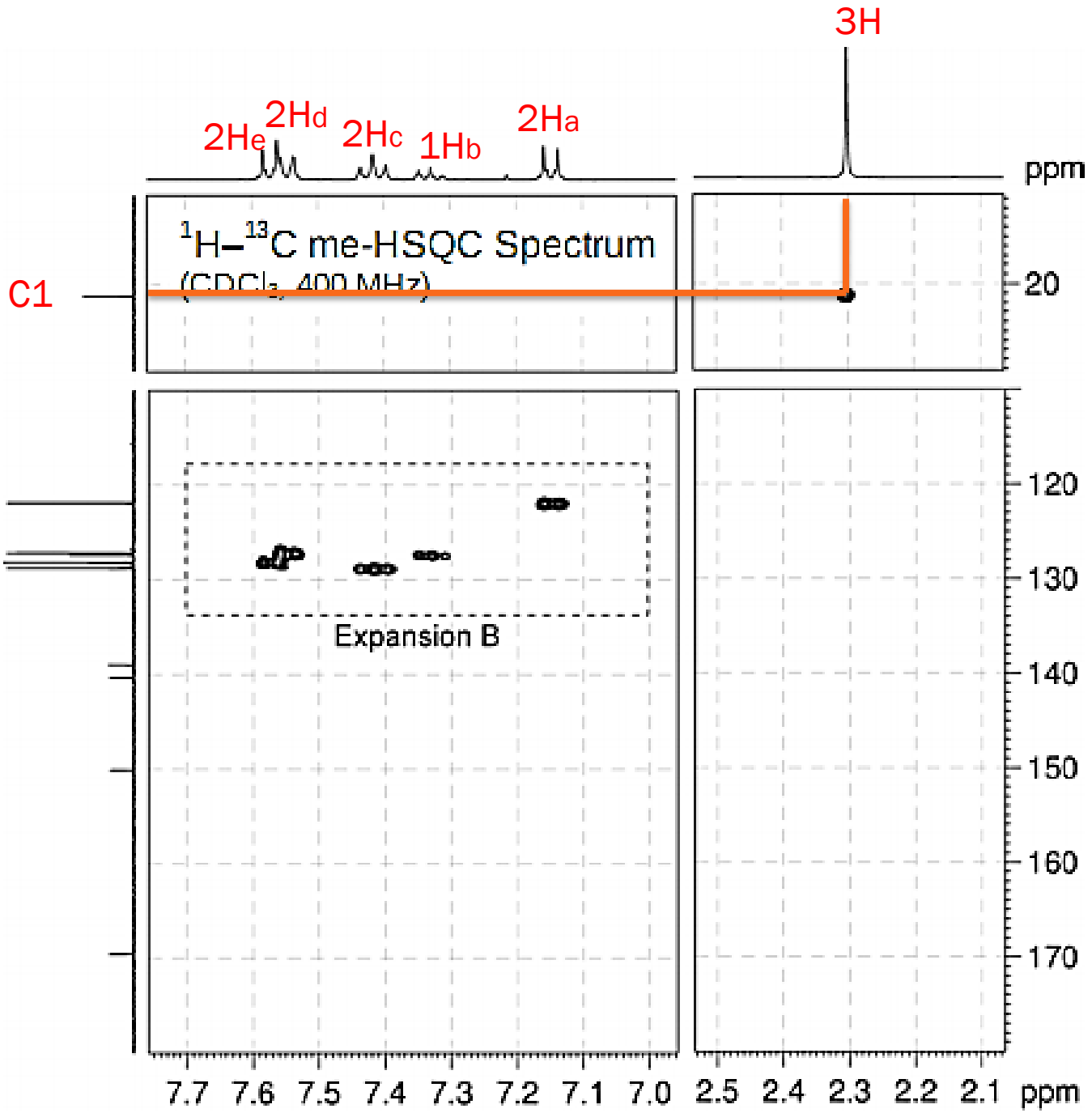
-Hb-Hc-Hd-

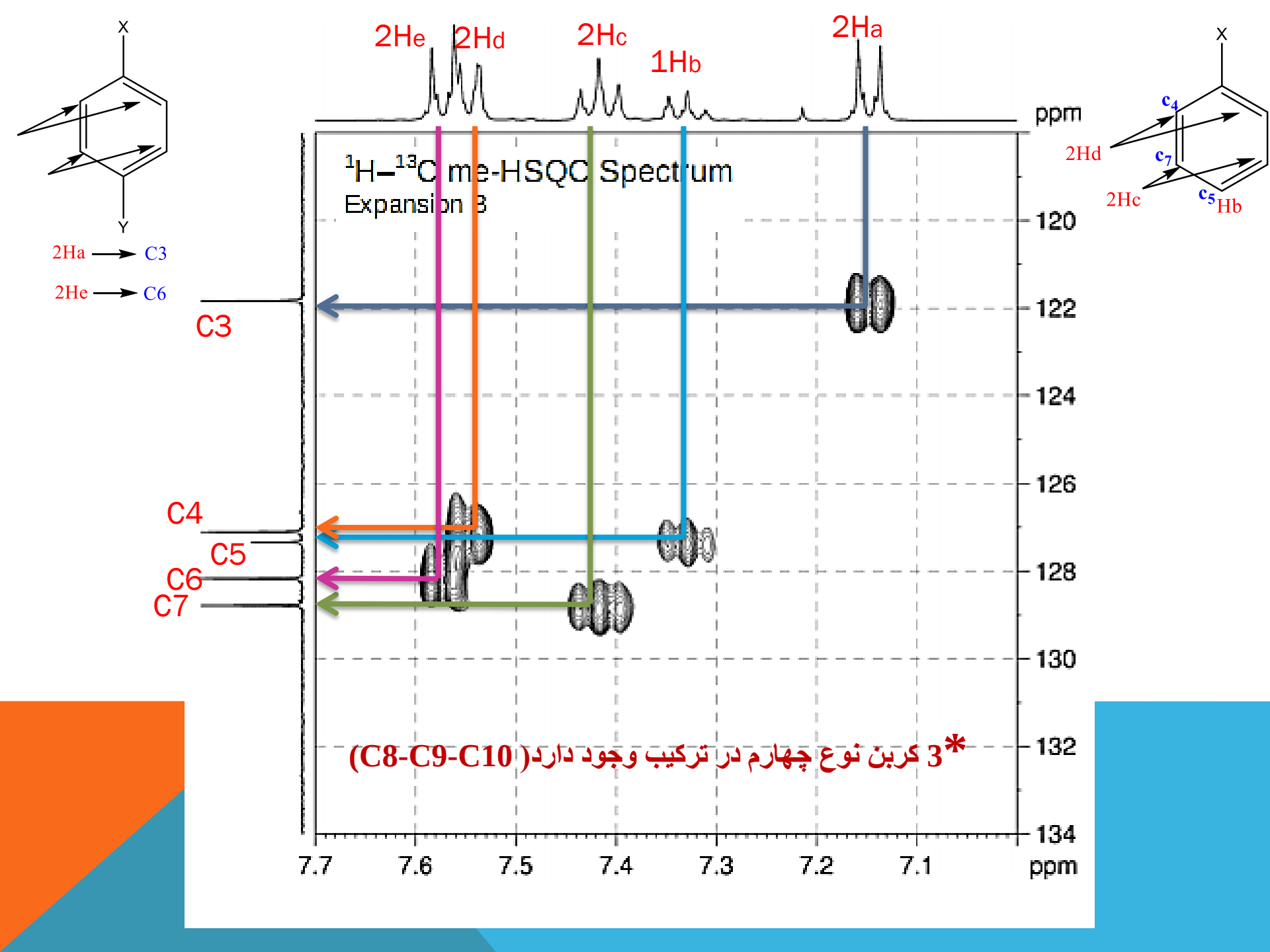
-He-Ha-


2He
2Hd
2Hc
1Hb
2Ha
ppm
^{1}H–^{1}H COSY Spectrum
Expansion A
2Ha
1Hb
2Hc
2Hd
2He
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm

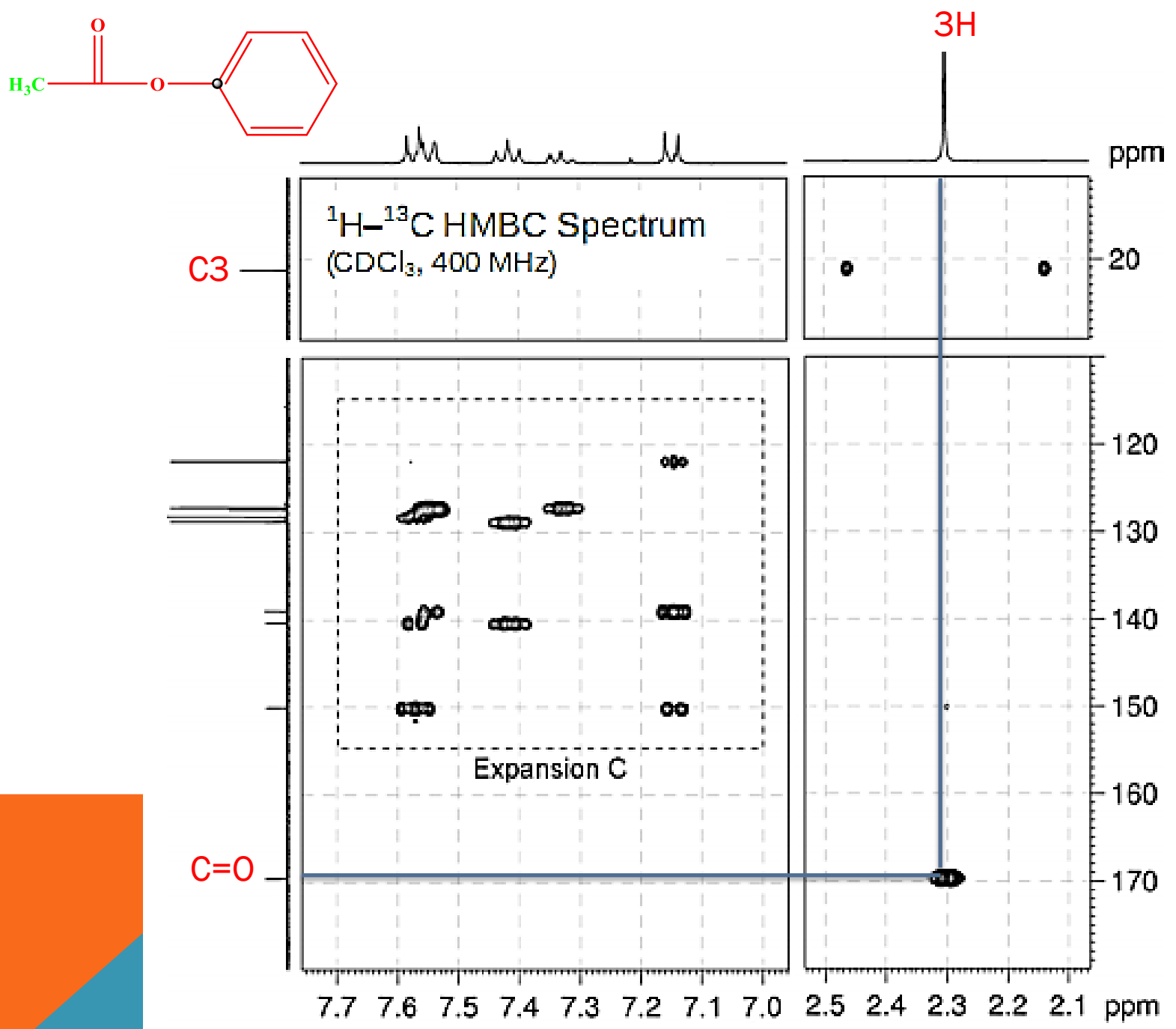

X
Y
2Ha
2He

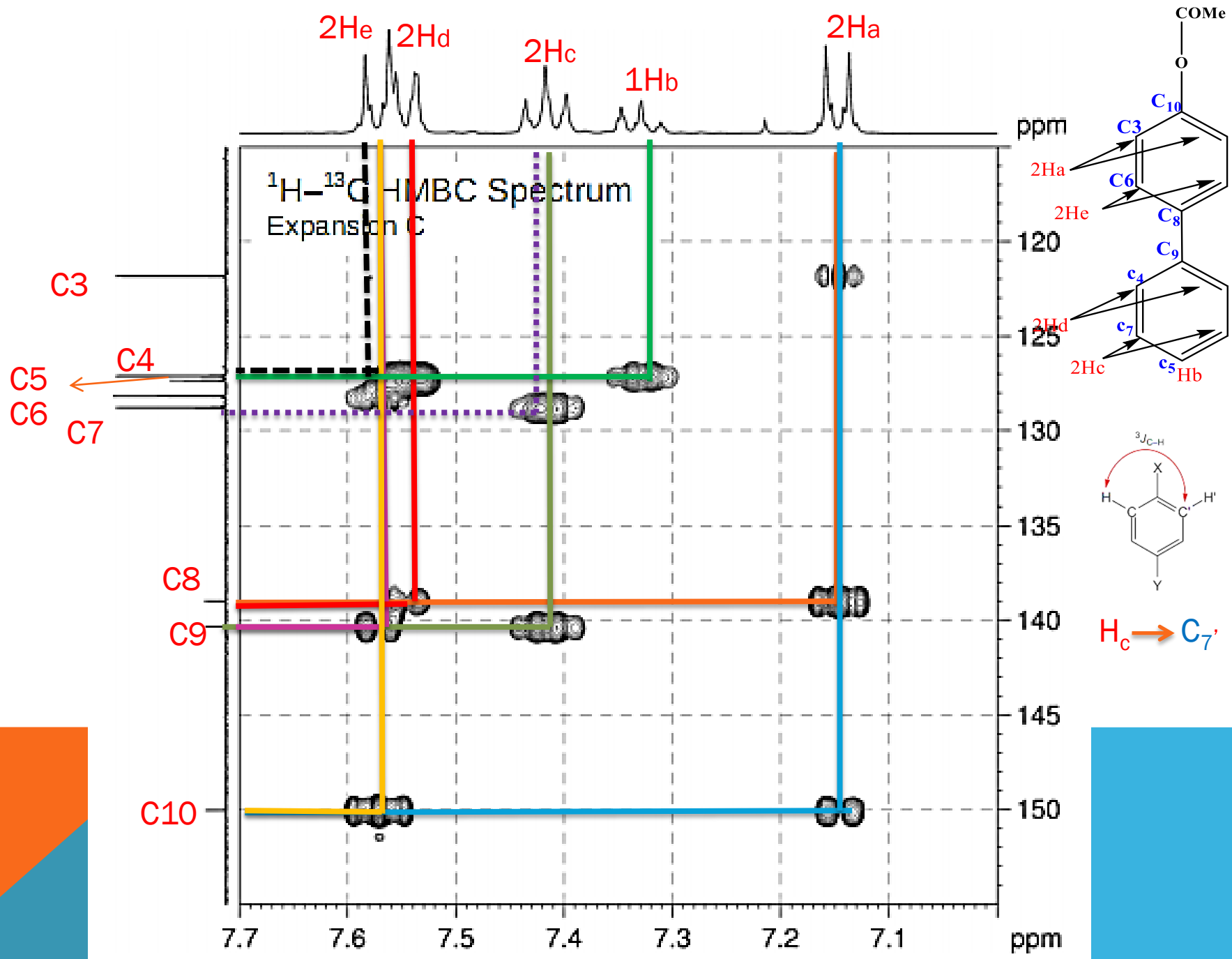

X
2Hd
2Hc
Hb


3H
2He
2Hd
2Hc
1Hb
2Ha
ppm
^{1}H–^{13}C me-HSQC Spectrum
(CDCl3, 400 MHz)
C1
20
120
130
140
150
160
170
Expansion B
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
2.5 2.4 2.3 2.2 2.1 ppm



3* کربن نوع چهارم در ترکیب وجود دارد (C8-C9-C10)

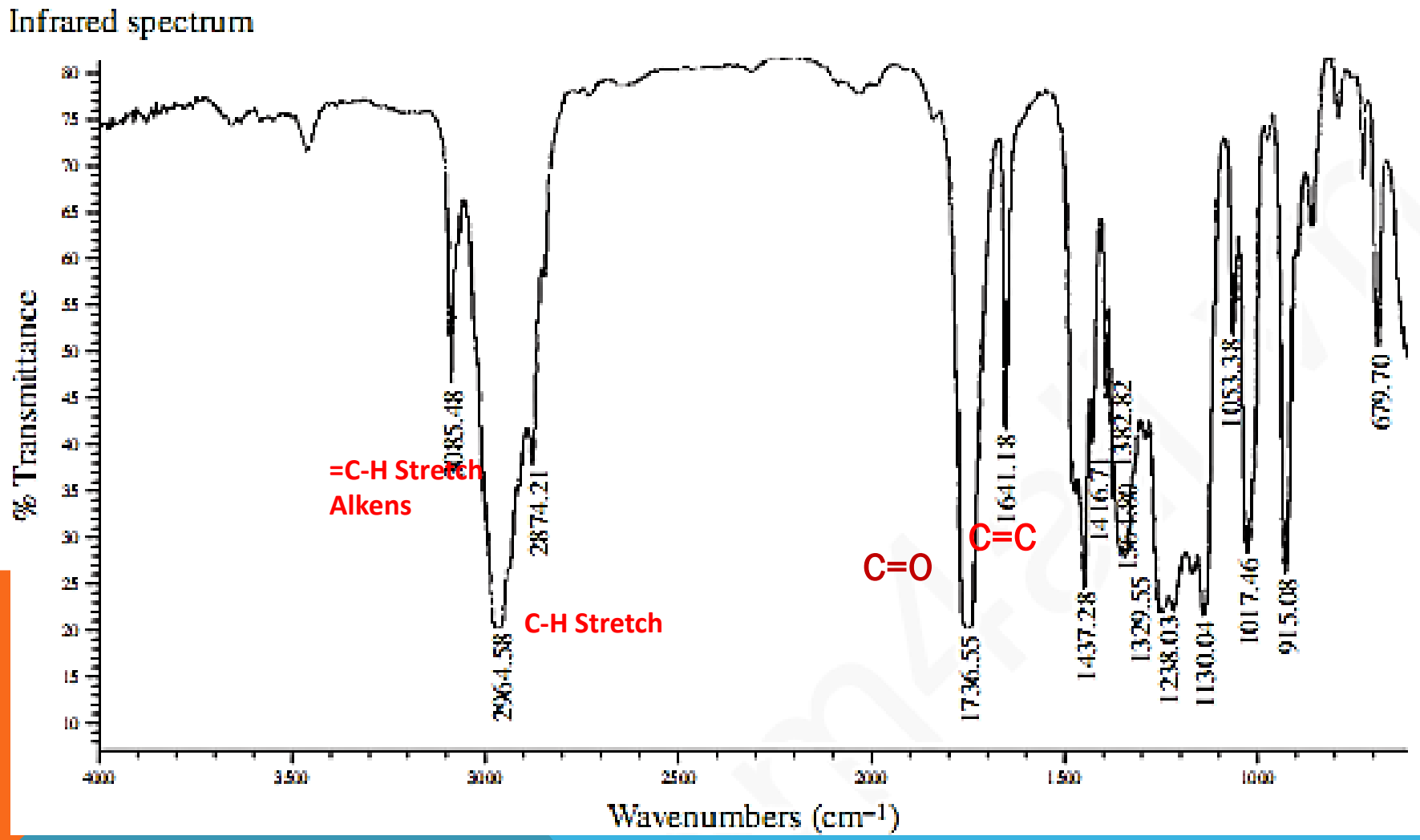

O
H3C
O
3H
ppm
1H–13C HMBC Spectrum
(CDCl3, 400 MHz)
C3
C=O
20
120
130
140
150
160
170
Expansion C
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
2.5 2.4 2.3 2.2 2.1 ppm


2He
2Hd
2Hc
1Hb
2Ha
ppm
^{1}H–^{13}C HMBC Spectrum
Expansion C
C3
C4
C5
C6
C7
C8
C9
C10
120
125
130
135
140
145
150
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
COMe
O
C10
C3
2Ha
C6
2He
C8
C9
c4
2Hd
c7
2Hc
c5
Hb
$^3J_{C-H}$
X
H
C
C'
H'
Y
H_c → $C_{7'}$

نگرشی بر طیف سنجی (پاویا): فصل ۱۰، تمرین ۱۰، صفحه ۷۰۲

10. Determine the structure for a compound with formula $C_8H_{14}O$. The IR spectrum, ^1H NMR spectrum and expansions, ^{13}C NMR spectrum, DEPT spectrum, COSY spectrum, and HETCOR (HSQC) spectrum are included in this problem.

U=(C+1)-1/2H **U=9-7=2** **$C_8H_{14}O$**


Infrared spectrum
% Transmittance
Wavenumbers (cm⁻¹)
4000
3500
3000
2500
2000
1500
1000
3085.48
2964.58
2874.21
1736.55
1641.18
1437.28
1416.71
1382.82
1329.55
1238.03
1130.04
1053.38
1017.46
915.08
679.70
=C-H Stretch
Alkens
C-H Stretch
C=O
C=C

$C_8H_{14}O$

C=O

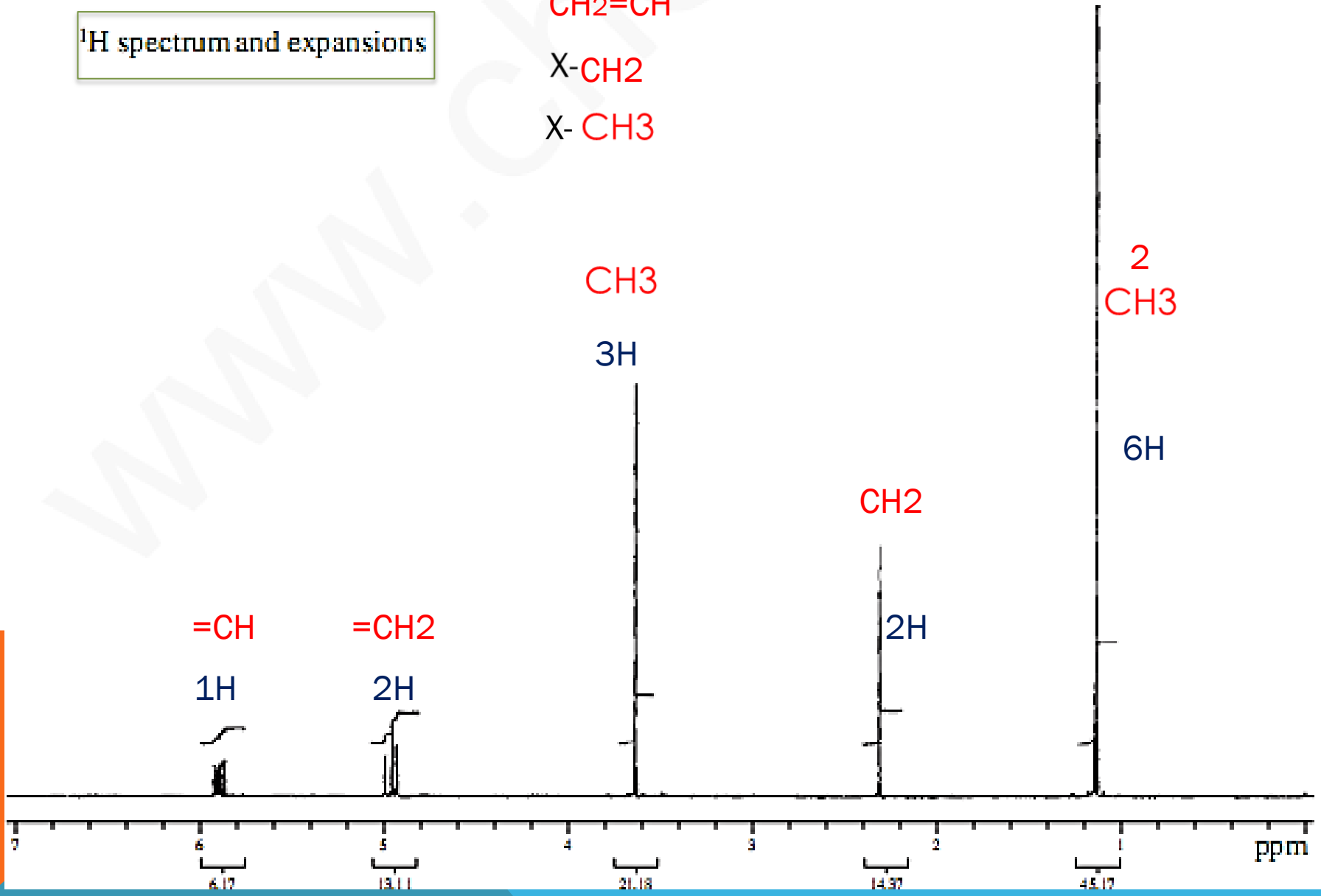
2 CH3

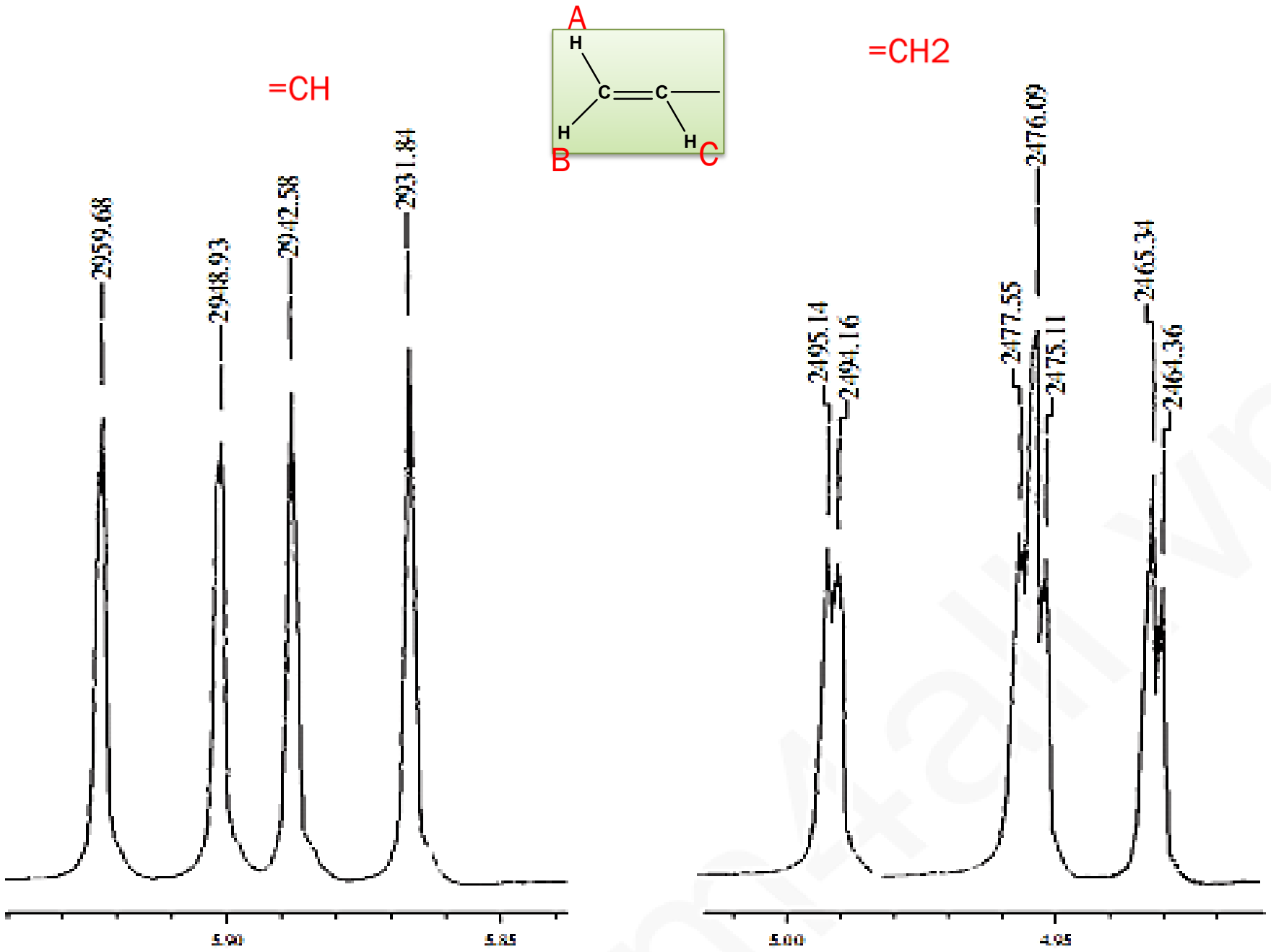
CH_2=CH

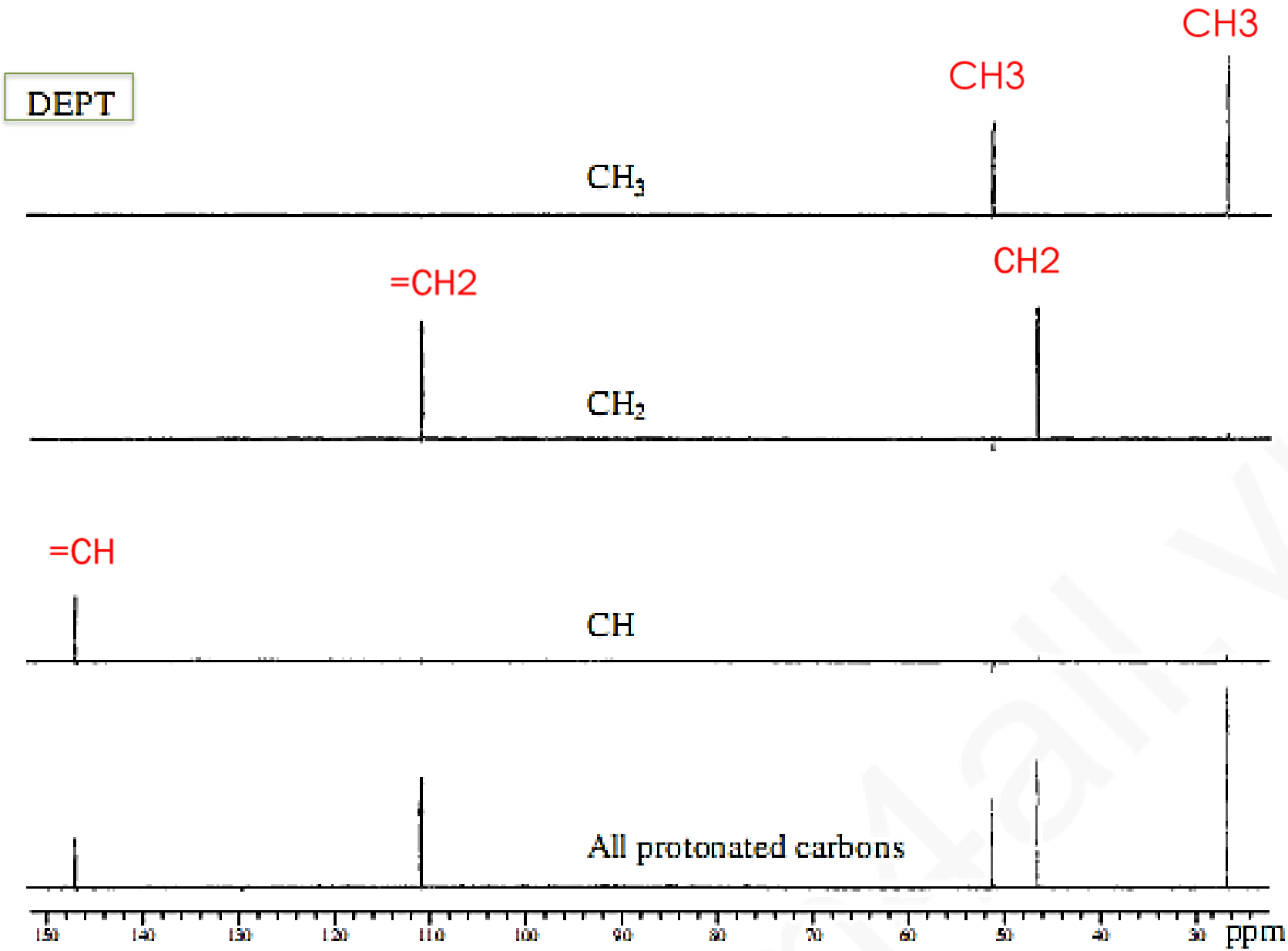
X-CH_2

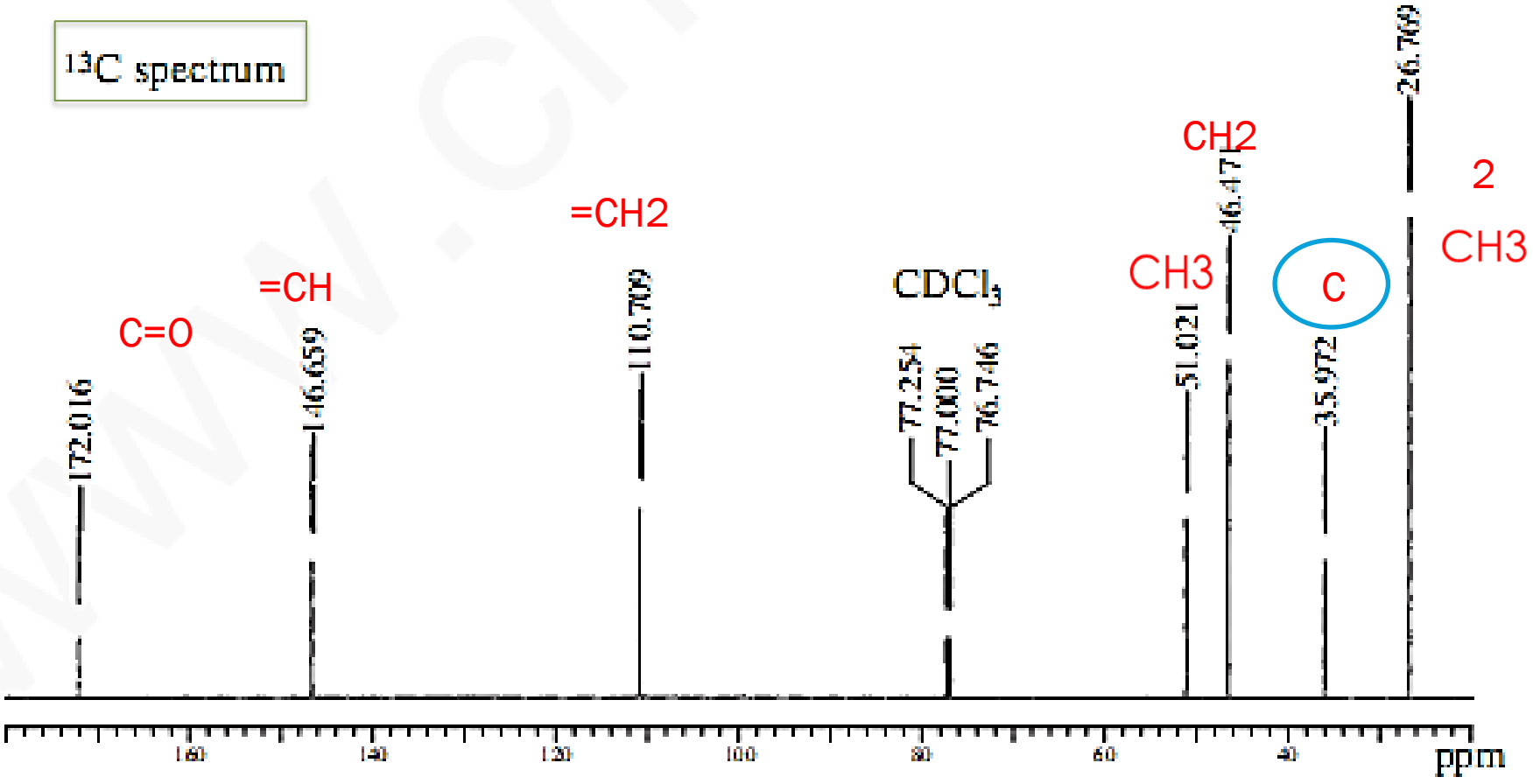
X- CH3

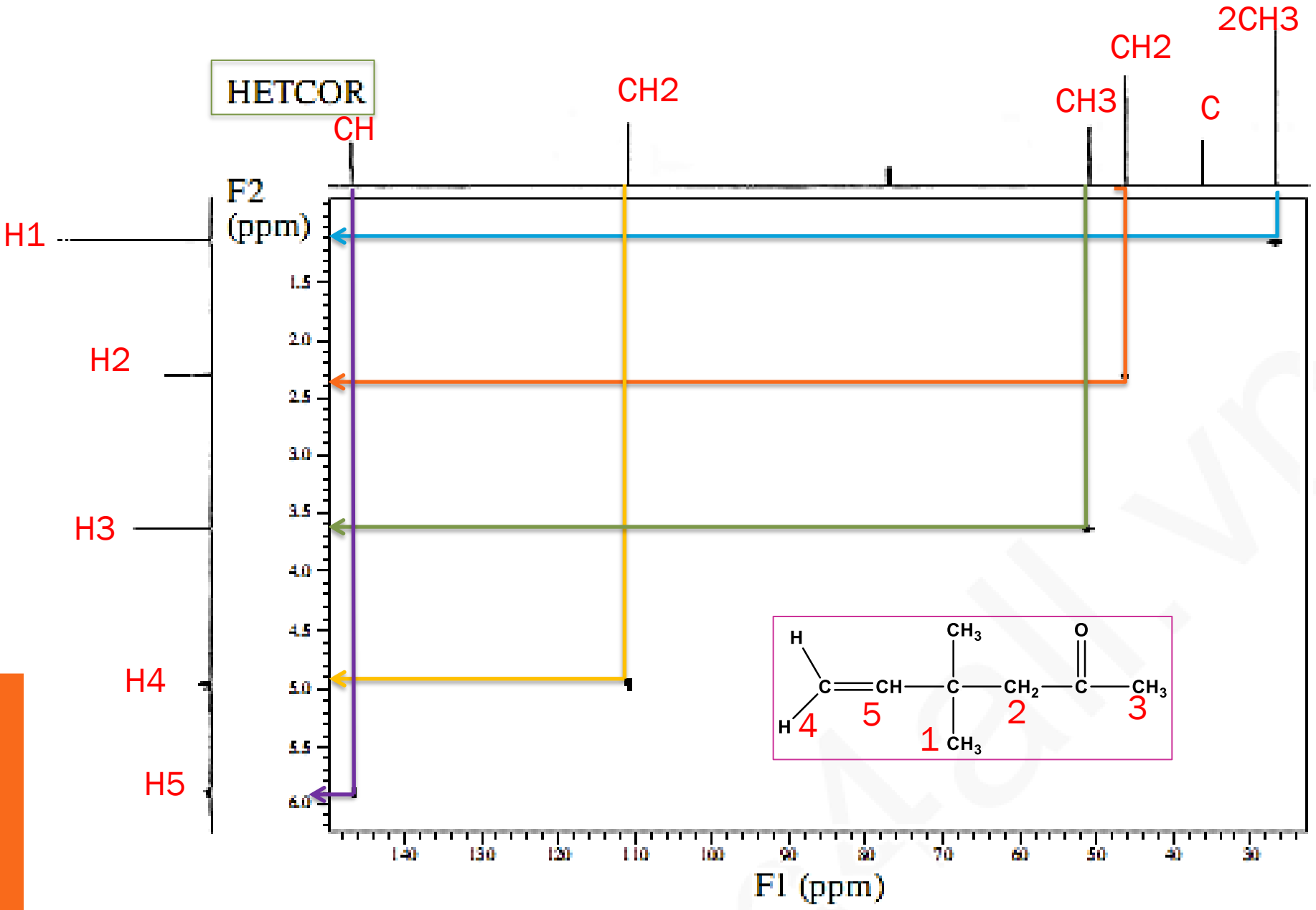
^{1}H spectrum and expansions

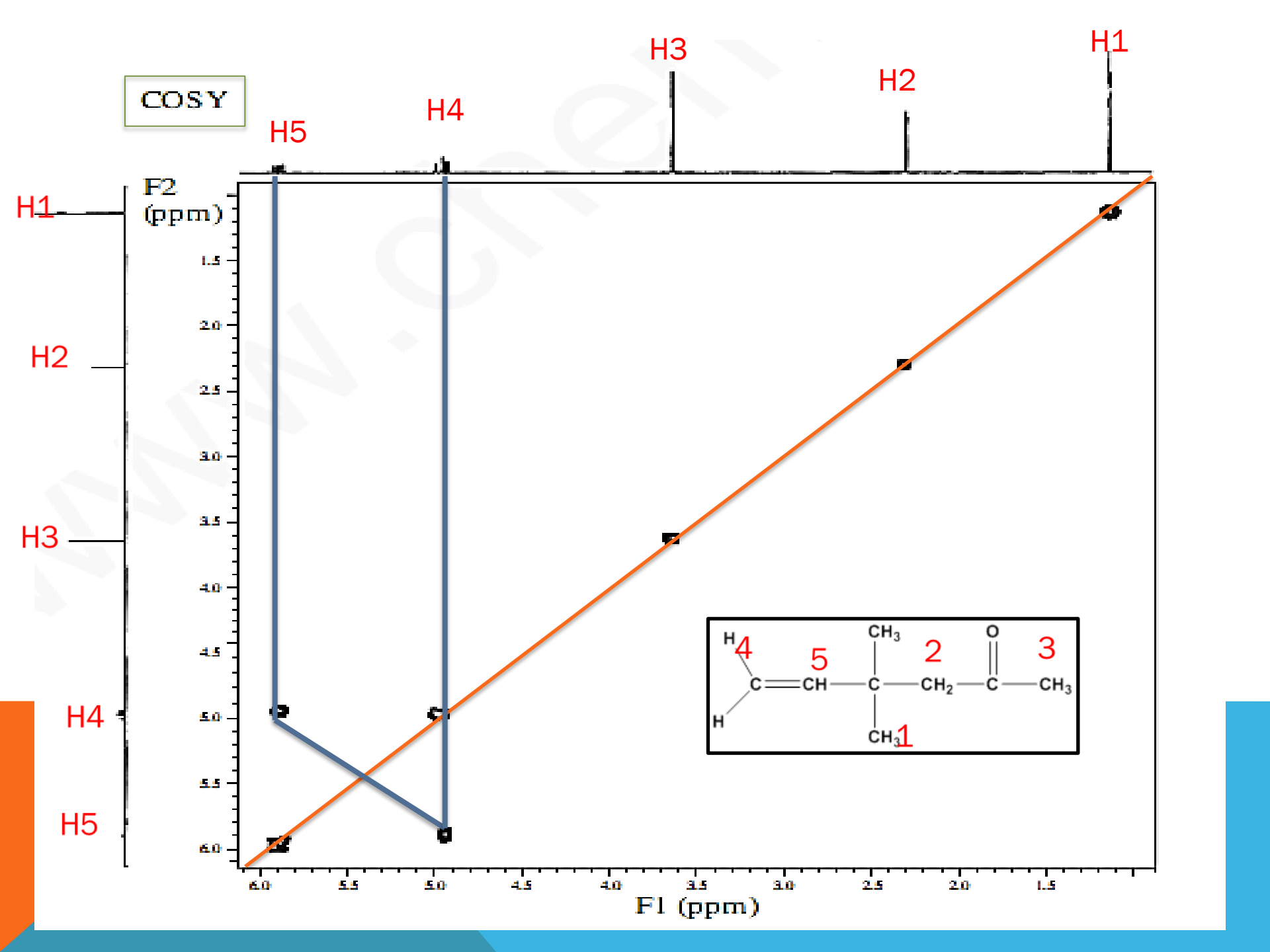



A
B
C
=CH
=CH2
2959.68
2918.93
2912.58
2931.84
2495.14
2494.16
2477.55
2476.09
2475.11
2465.34
2464.36
5.90
5.85
5.00
4.95


DEPT
CH3
CH3
CH3
=CH2
CH2
=CH
All protonated carbons
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


^{13}C spectrum
C=O
=CH
=CH2
CDCl3
CH3
CH2
C
2
CH3
172.016
146.659
110.709
77.254
77.000
76.746
51.021
46.471
35.972
26.769
160
140
120
100
80
60
40
ppm

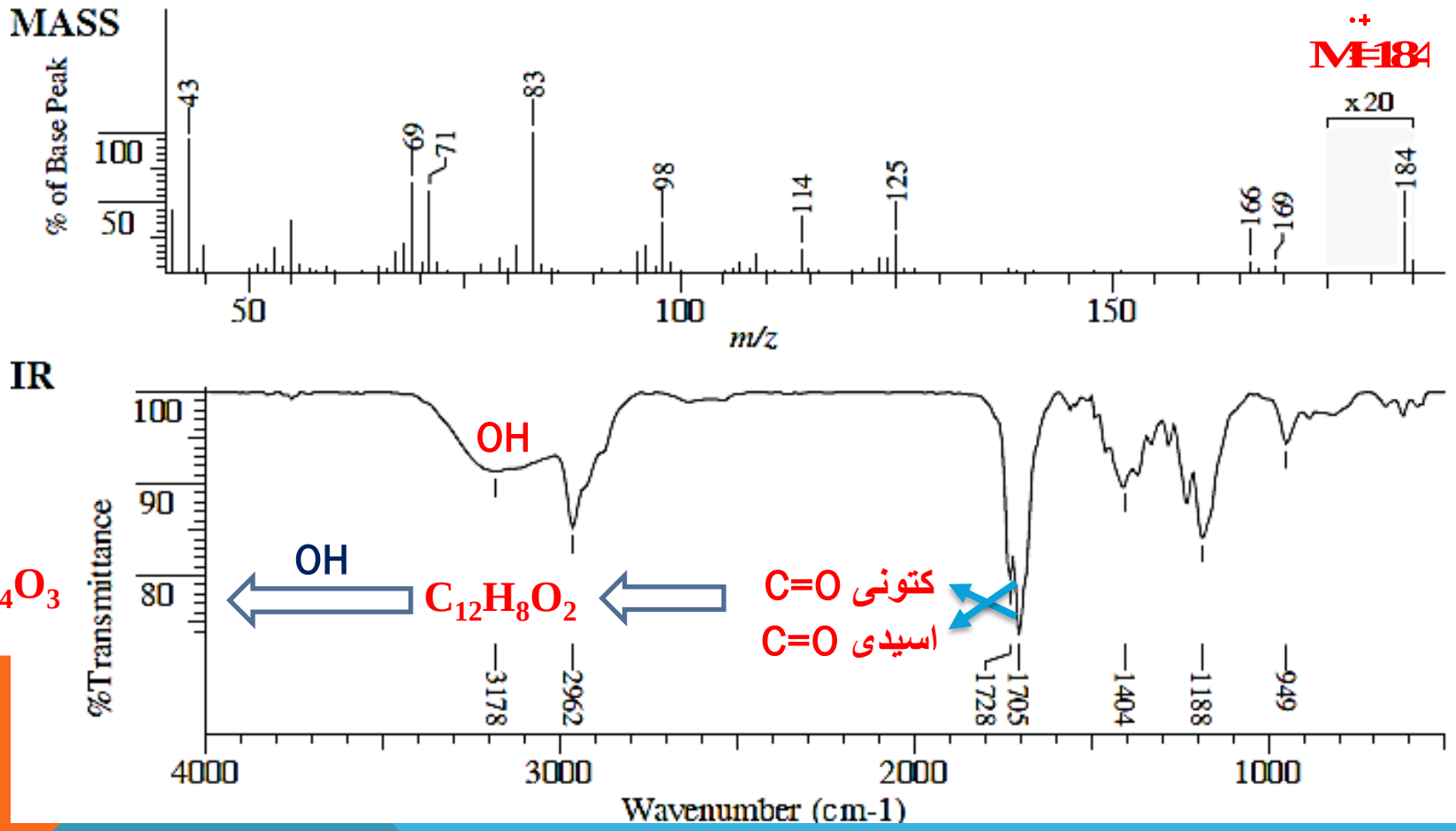

HETCOR
CH
CH2
CH3
C
2CH3
F2 (ppm)
H1
H2
H3
H4
H5
F1 (ppm)
H
CH3
O
C
CH
CH2
C
CH3
H
4
5
1
2
3
CH3


COSY
H5
H4
H3
H2
H1
F2 (ppm)
F1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
H
4
5
CH3
2
O
3
C
CH
C
CH2
C
CH3
H
CH3
1

Chapter 8 Additional Problems 11

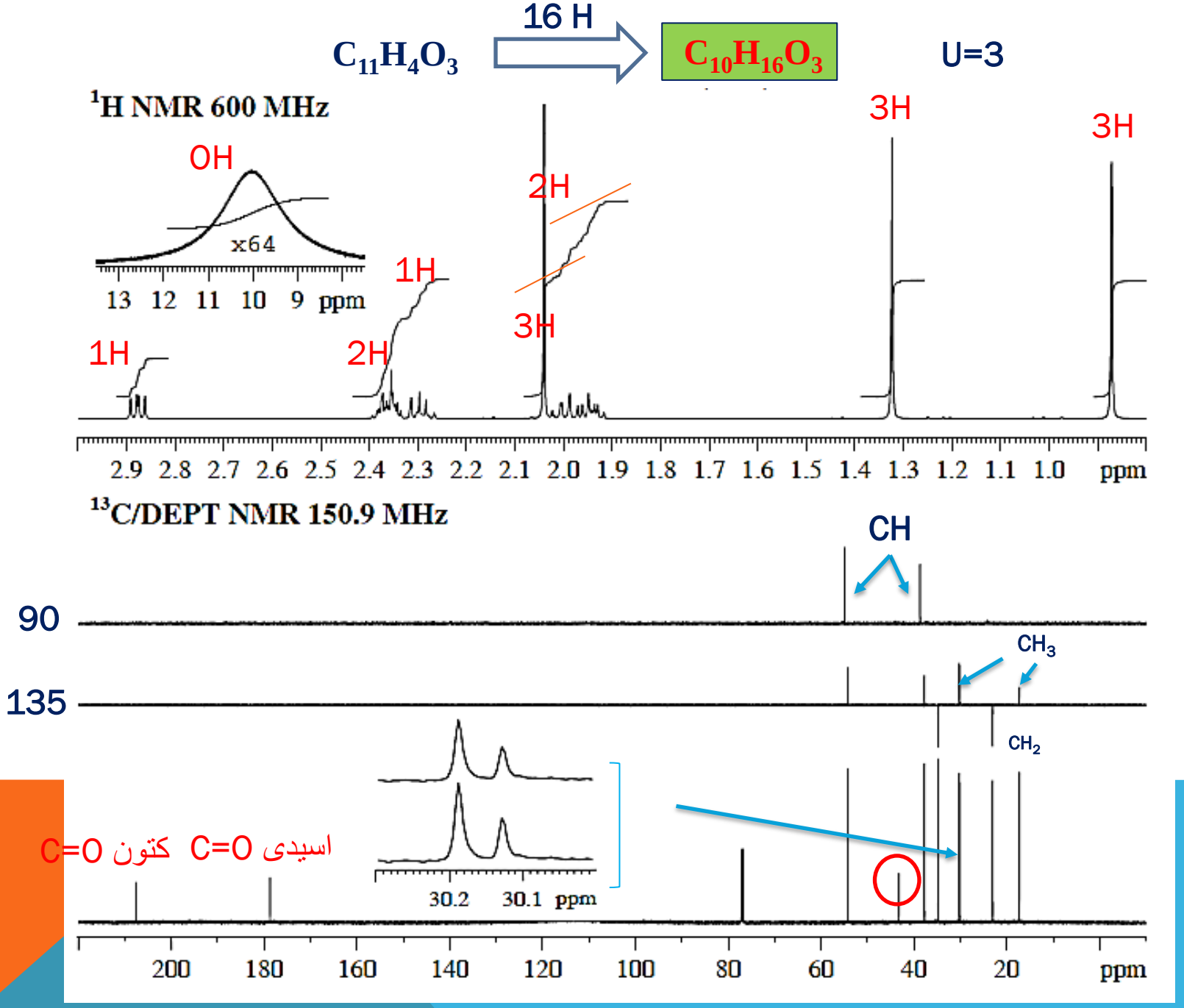
$M^{\cdot+}=184/13=14\frac{2}{13}$

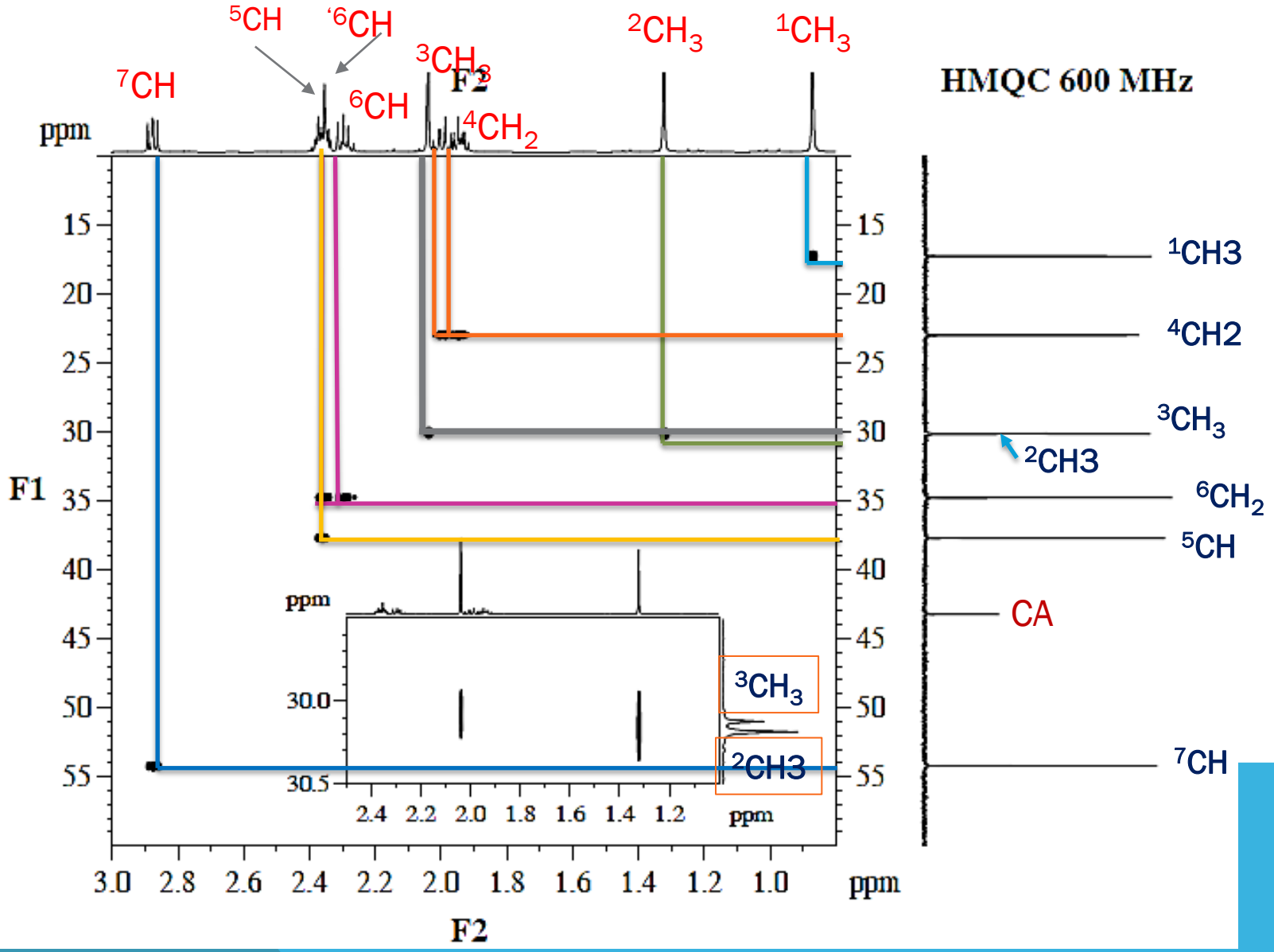
با استفاده از قاعده ی ۱۳ = $C_{14}H_{16}$



$C_{11}H_4O_3$

$C_{12}H_8O_2$


16 H
$C_{11}H_4O_3$
$C_{10}H_{16}O_3$
U=3
^{1}H NMR 600 MHz
OH
x64
13 12 11 10 9 ppm
1H
2H
1H
3H
3H
3H
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 ppm
^{13}C/DEPT NMR 150.9 MHz
CH
90
135
CH_3
CH_2
30.2 30.1 ppm
C=O کتون
C=O اسیدی
200 180 160 140 120 100 80 60 40 20 ppm


HMQC 600 MHz
5CH
'6CH
7CH
6CH
3CH2
4CH2
2CH3
1CH3
F2
ppm
F1
15
20
25
30
35
40
45
50
55
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm
F2
30.0
30.5
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm
3CH3
2CH3
1CH3
4CH2
3CH3
2CH3
6CH2
5CH
CA
7CH

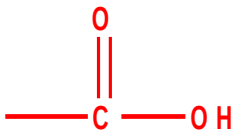
$C_{10}H_{16}O_3$

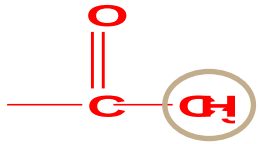
U=3

CH_3 CH_2 CH C OH

CH_3 CH_2 CH C=O

CH_3 C=O



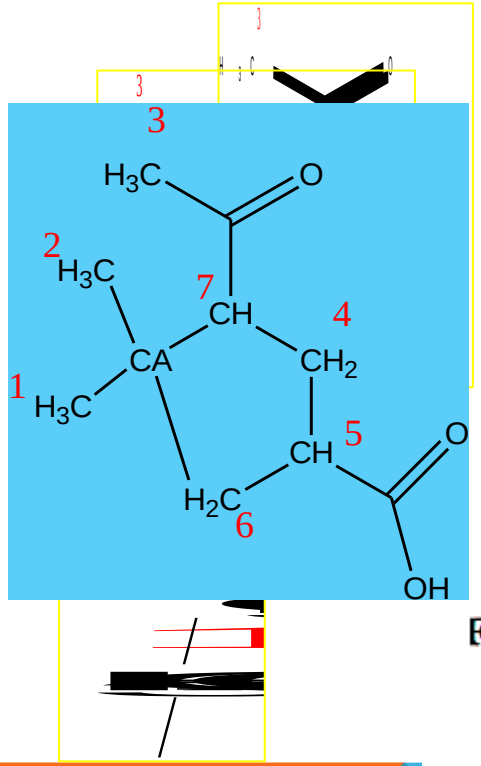


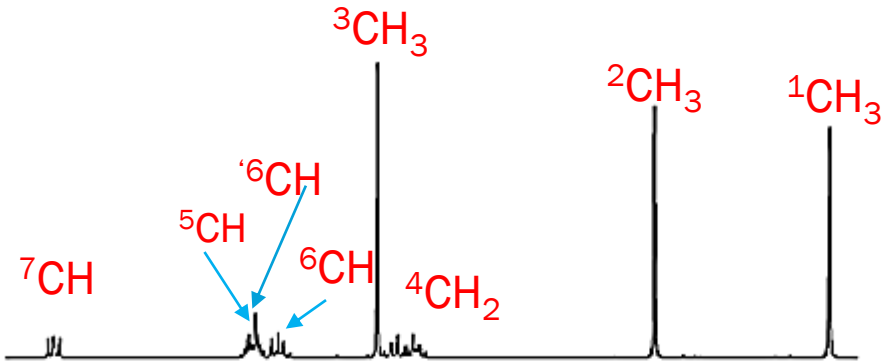
یک حلقه

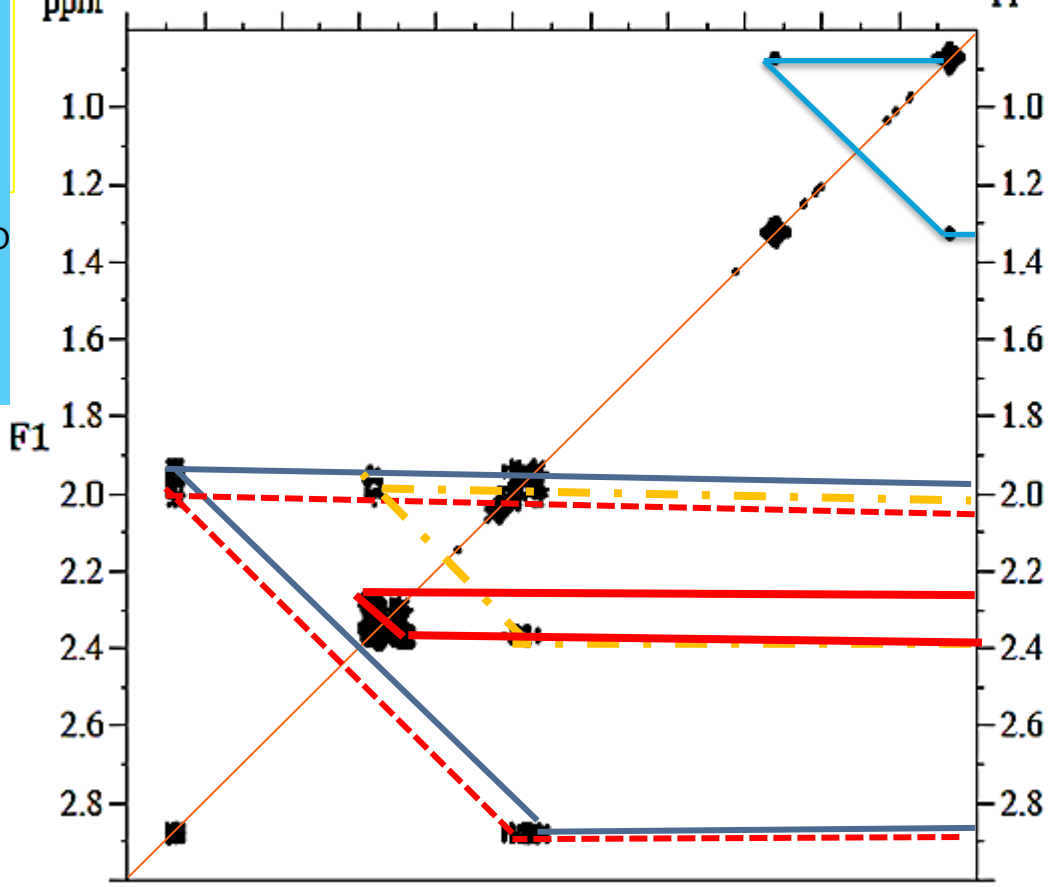
$^{1}CH_3$ — $^{2}CH_3$

$^{6}CH_2$ — ^{5}CH — $^{4}CH_2$ — ^{7}CH

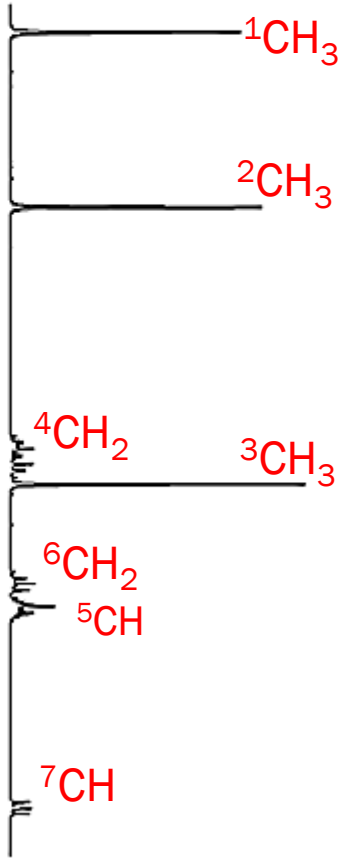
$^{3}CH_3$ — ^{7}CH

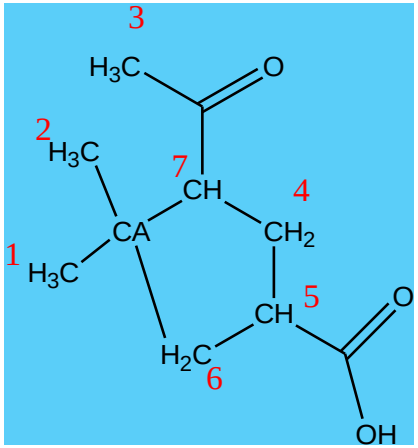


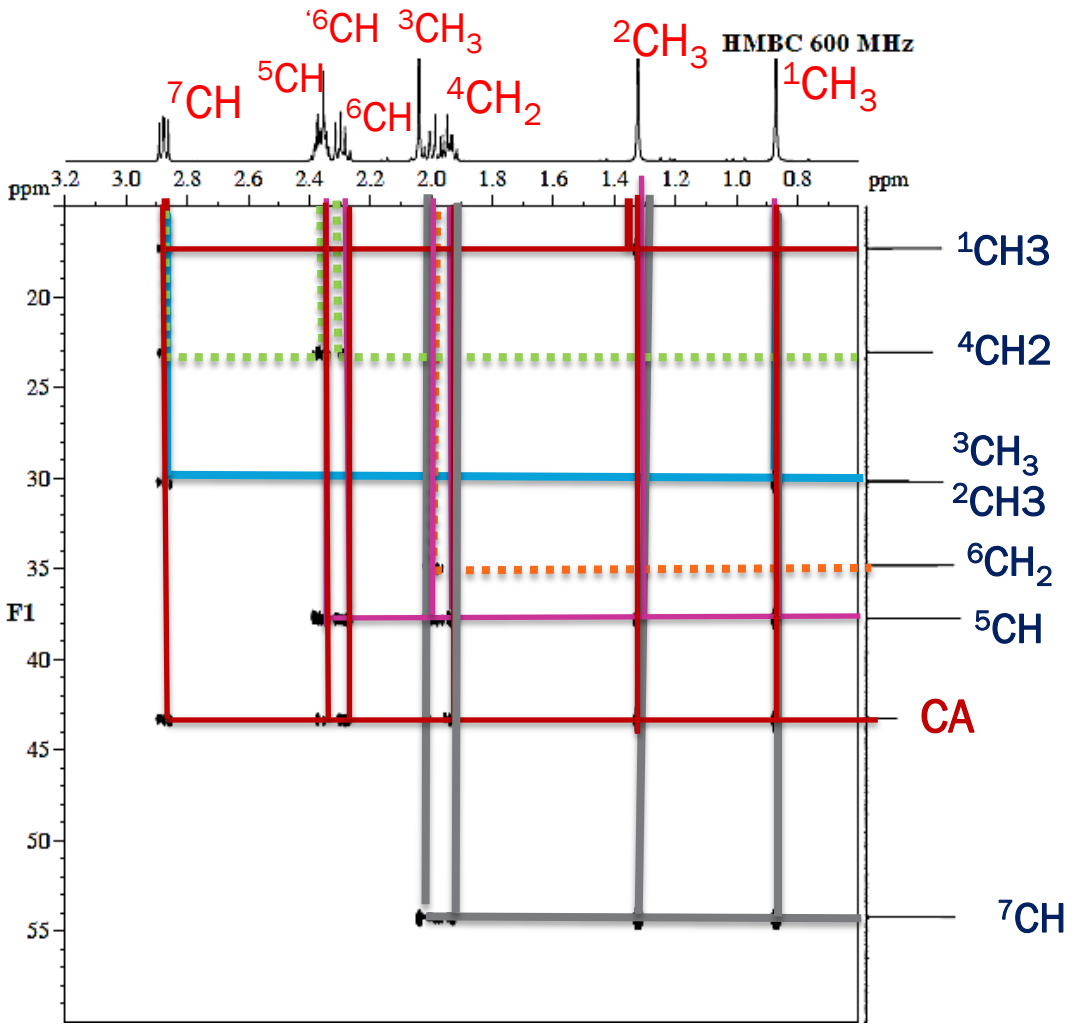


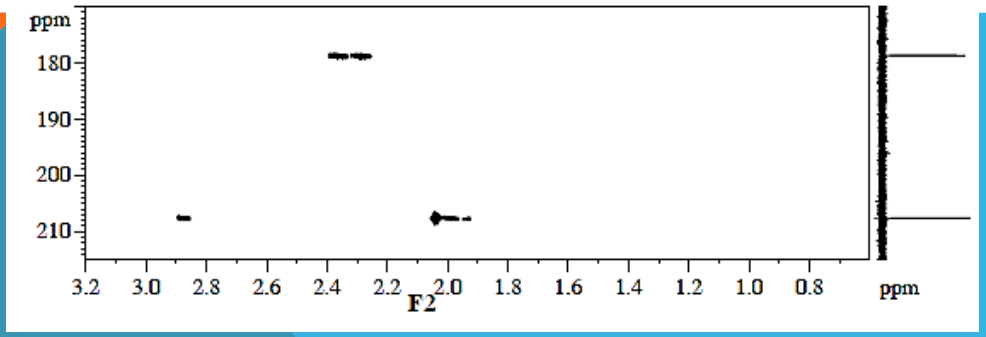


COSY 600 MHz









اسیدی C=O

کتونC=O