คณะวิทยาศาสตร์ มหาวิทยาลัยแม่โจ้

Spectroscopy in Organic Chemistry (คม 351)

Ultraviolet and Visible Spectroscopy (UV-VIS)
Infrared Spectroscopy (IR)
Nuclear Magnetic Resonance Spectroscopy (NMR)
- **^{1}H-NMR**
- **^{13}C-NMR (4.5 h = 9 + 3%)**

Mass Spectrometry (MS) (12 h = 20 + 3%)
Combined Structure Problems (7.5 h = 12 + 3%)

Referents

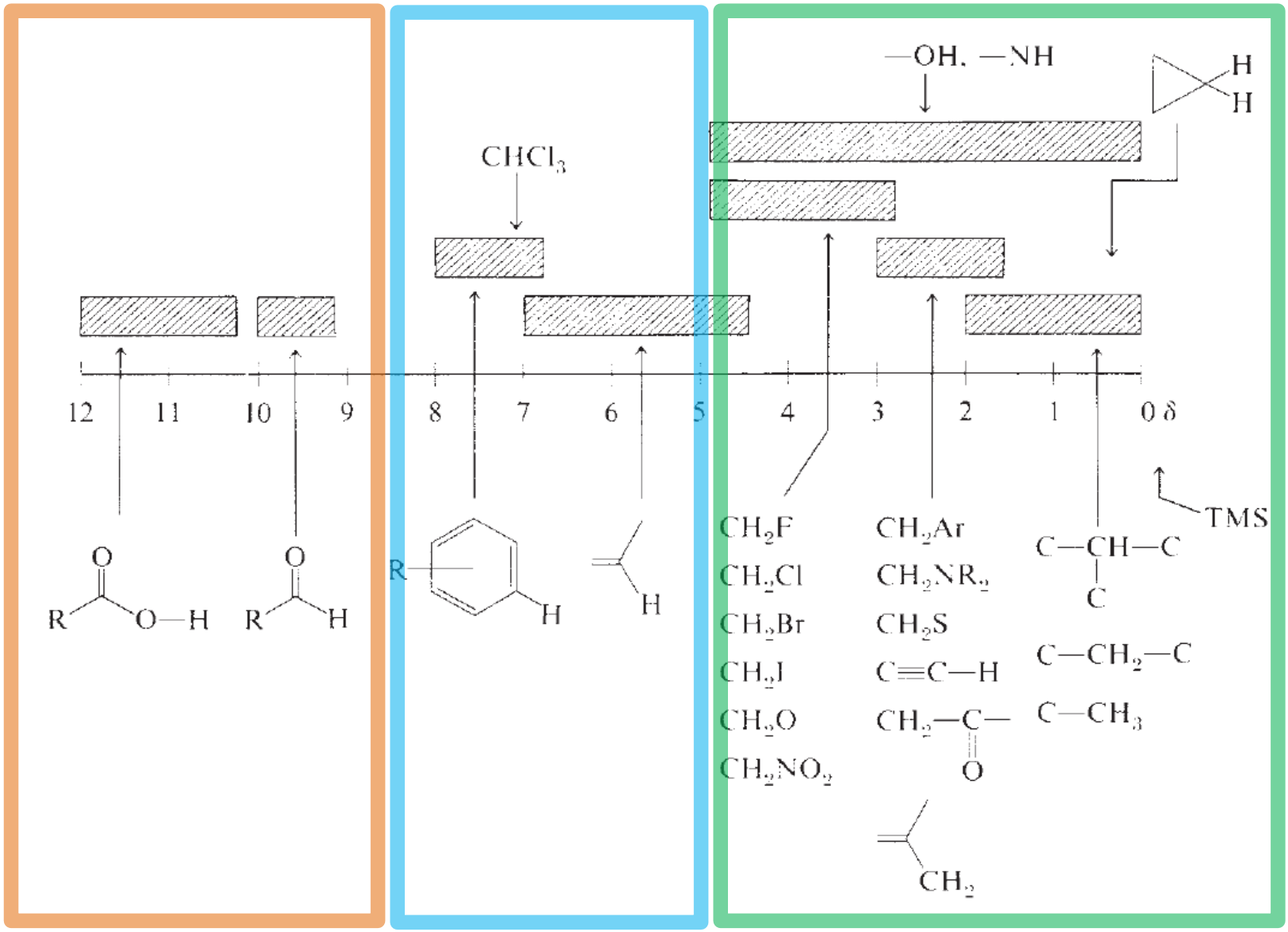
Introduction to Spectroscopy, 4th 2009 and International 2010 Edition
Donald L. Pavia.; Gary M. Lampman.; George S. Kriz.; James a. Vyvyan.

Spectrometric Identification of Organic Compounds, 6th 1996 and 7th 2005Edition
Robert M. Silverstein.; Francis X. Webster.

Organic Structures from Spectra, 4th Edition
Leslie D. Field.; Sev Stermhell.; John R. Kalman.
http://files.rushim.ru/books/spectroscopia/organic-structures-from-spectra-2008.pdf

สเปกโทรสโกปีสำหรับเคมีอินทรีย์, เย็นหทัย แน่นหนา

อาจารย์ ดร.วชิระ ชุ่มมงคล


—OH, —NH
H
H
CHCl3
12
11
10
9
8
7
6
5
4
3
2
1
0 δ
TMS
R
O
O—H
R
O
R
H
R
H
H
CH2F
CH2Cl
CH2Br
CH2I
CH2O
CH2NO2
CH2Ar
CH2NR2
CH2S
C≡C—H
CH2—C—
O
CH2
C—CH—C
C
C—CH2—C
C—CH3

ทบทวน 4 กระบวนท่า (IIPC)

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

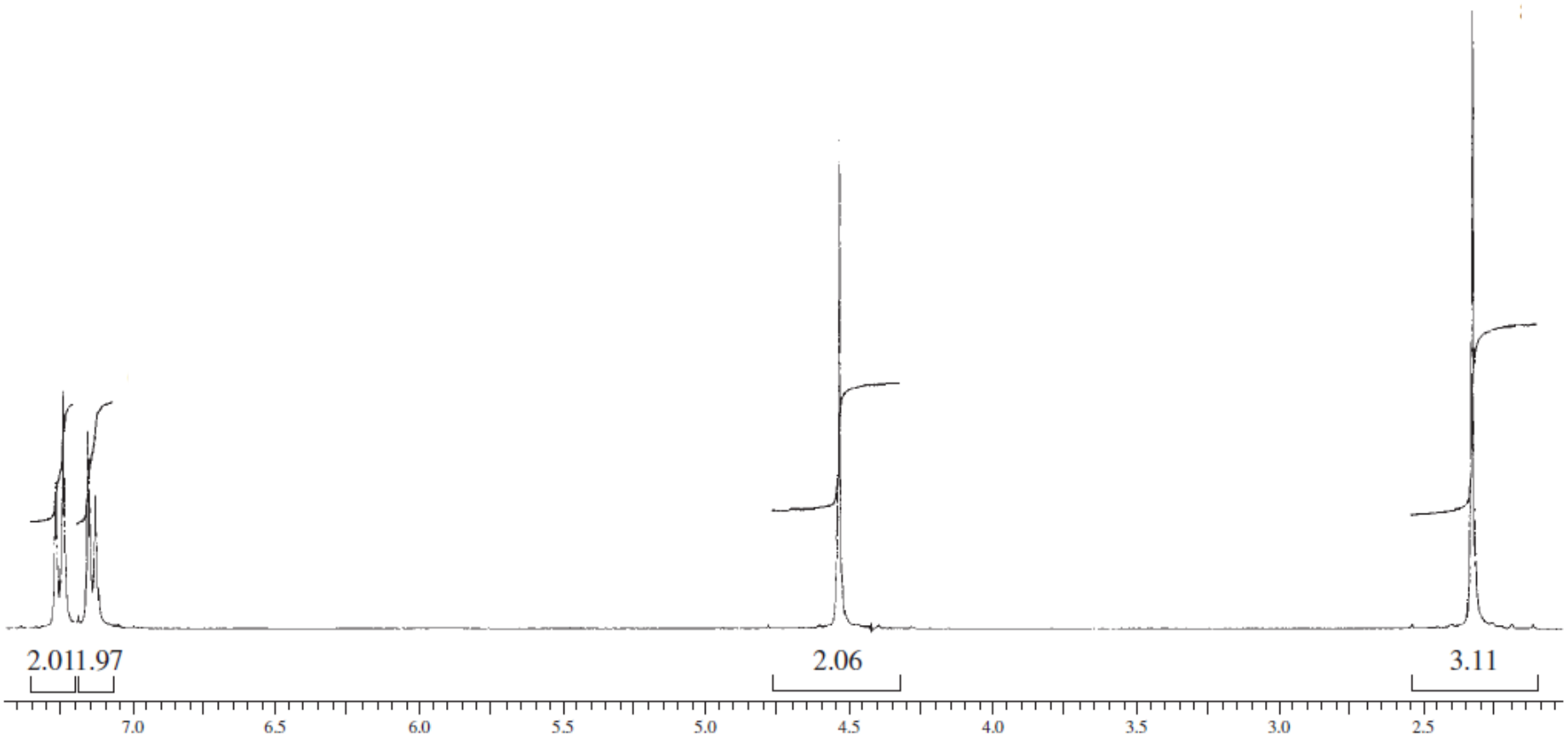
2) Integration บอกจำนวน H ของแต่ละพีค

3) Spin-Spin Splitting (n+1) (ลักษณะพีค) and *J*-coupling constant บอกจำนวน H ข้างเคียง

4) Chemical Shift (ตำแหน่งที่ขึ้น)
   - Inductive effect
   - Anisotropy effect
   - Hybridization effect
   - Hydrogen bonding effect

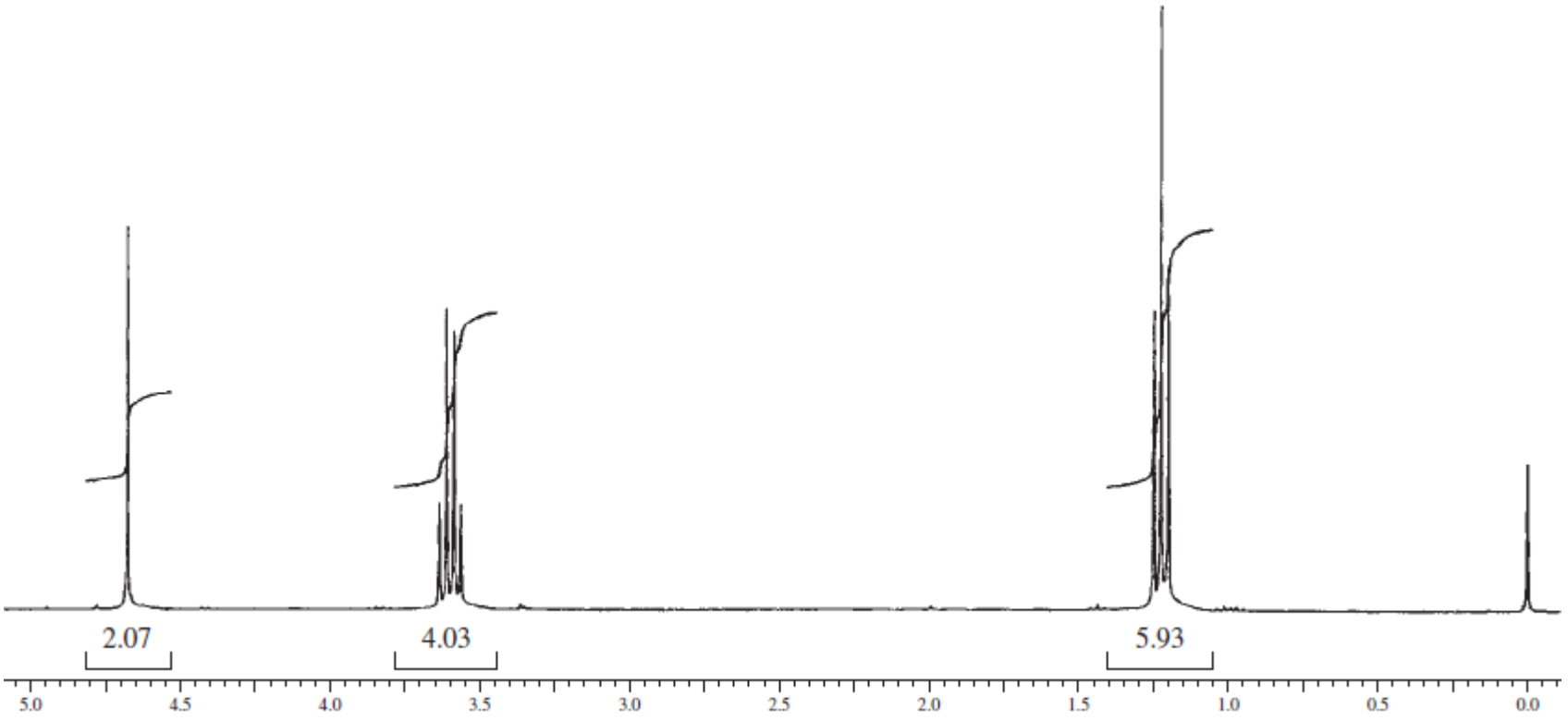
ทบทวน

C_8H_9Cl



ทบทวน

$C_5H_{12}O_2$



ทบทวน

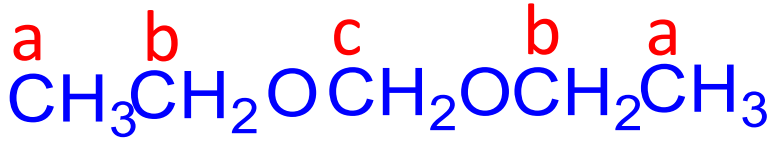
2) Integration บอกจำนวน H ของแต่ละพีค

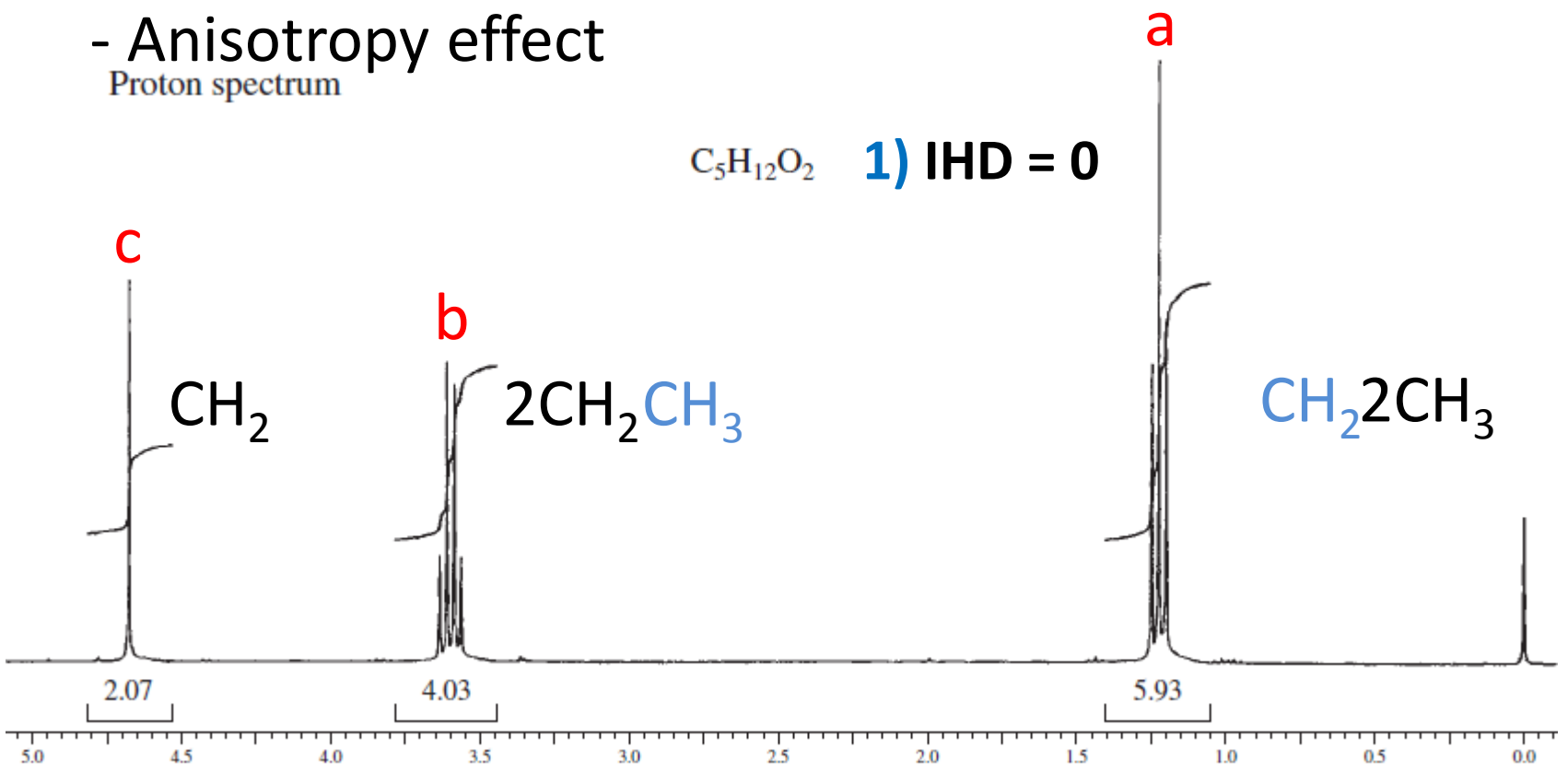
3) Peak Types or *J*-coupling constant

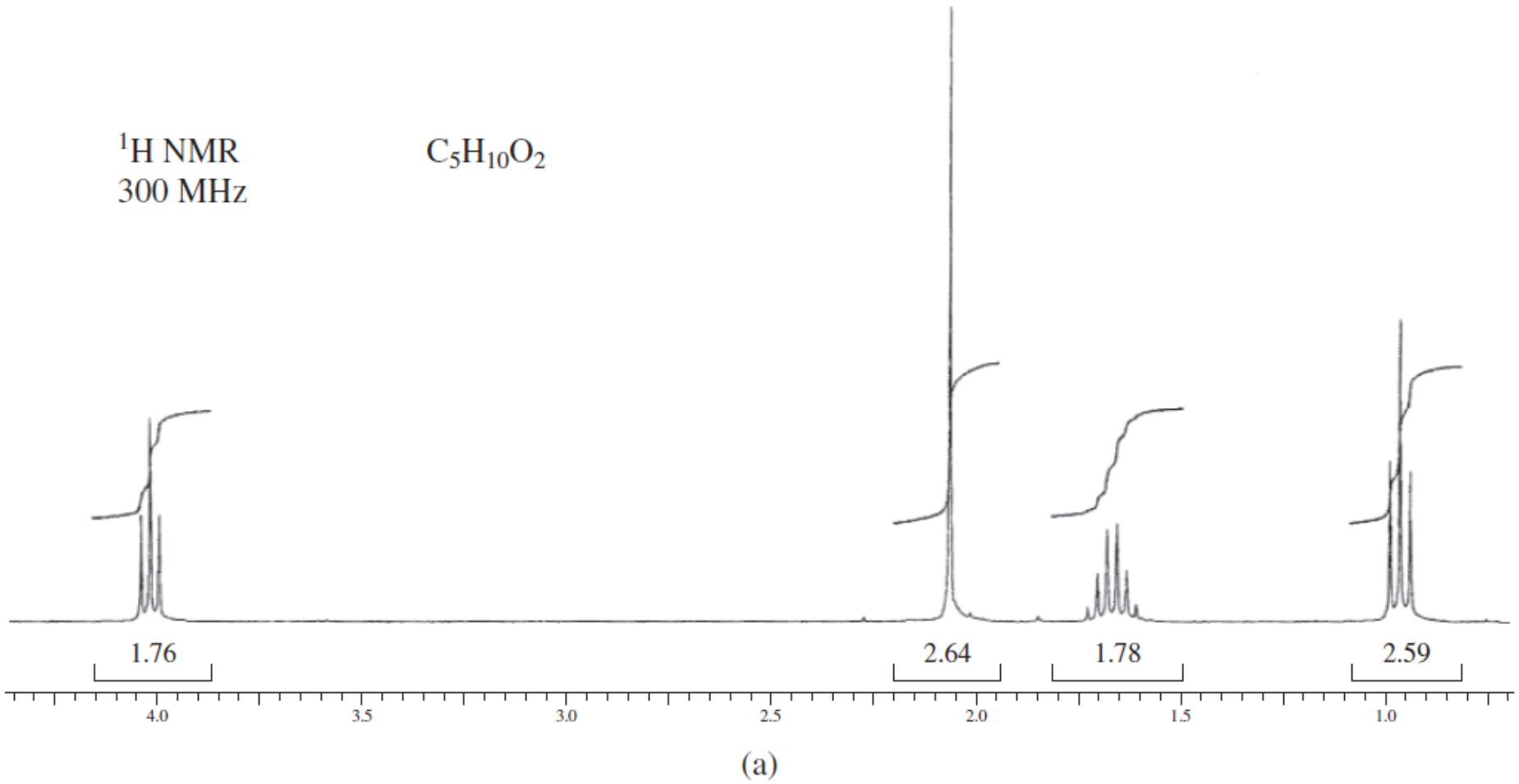
บอกจำนวน H ข้างเคียง

4) Chemical Shift

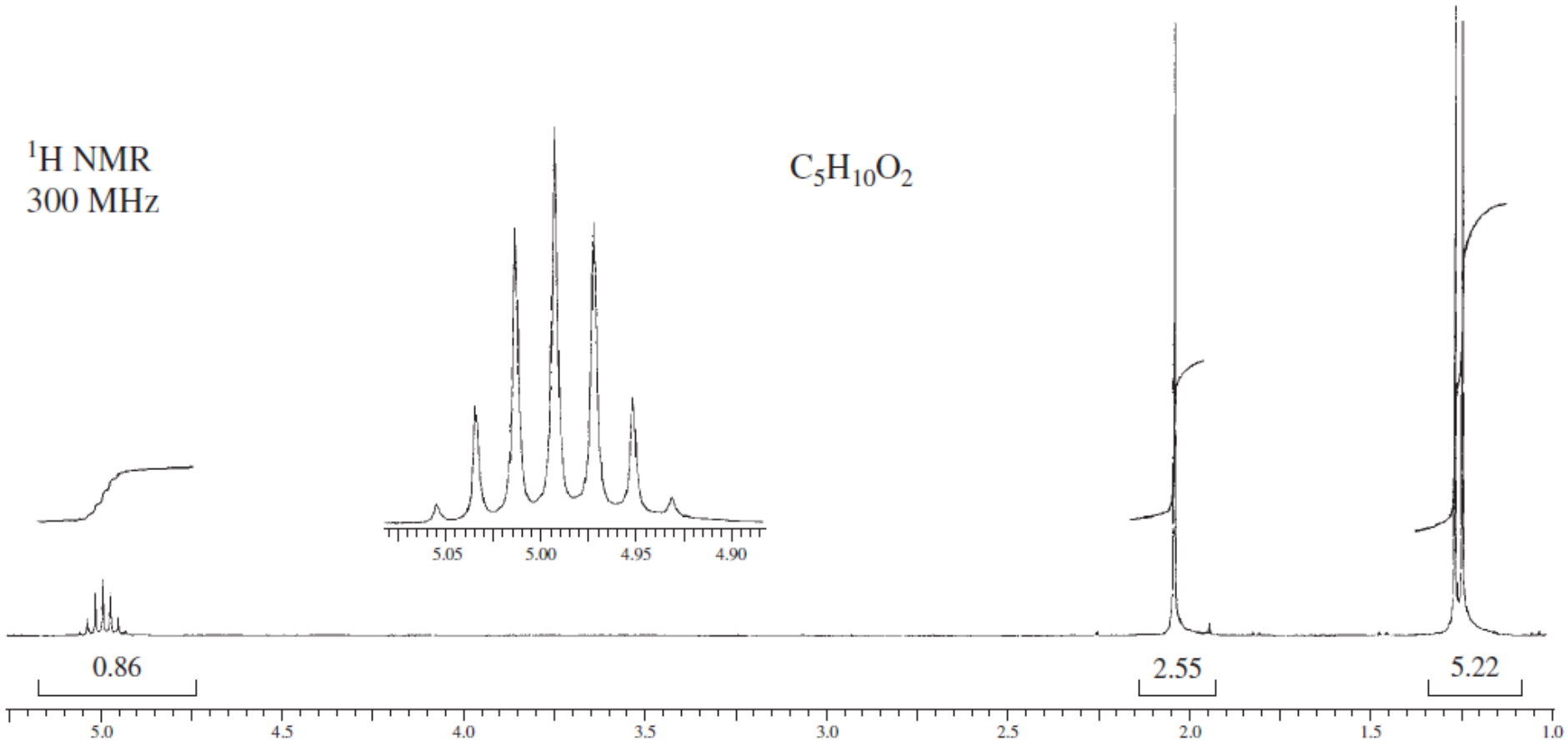
- Inductive effect
- Anisotropy effect





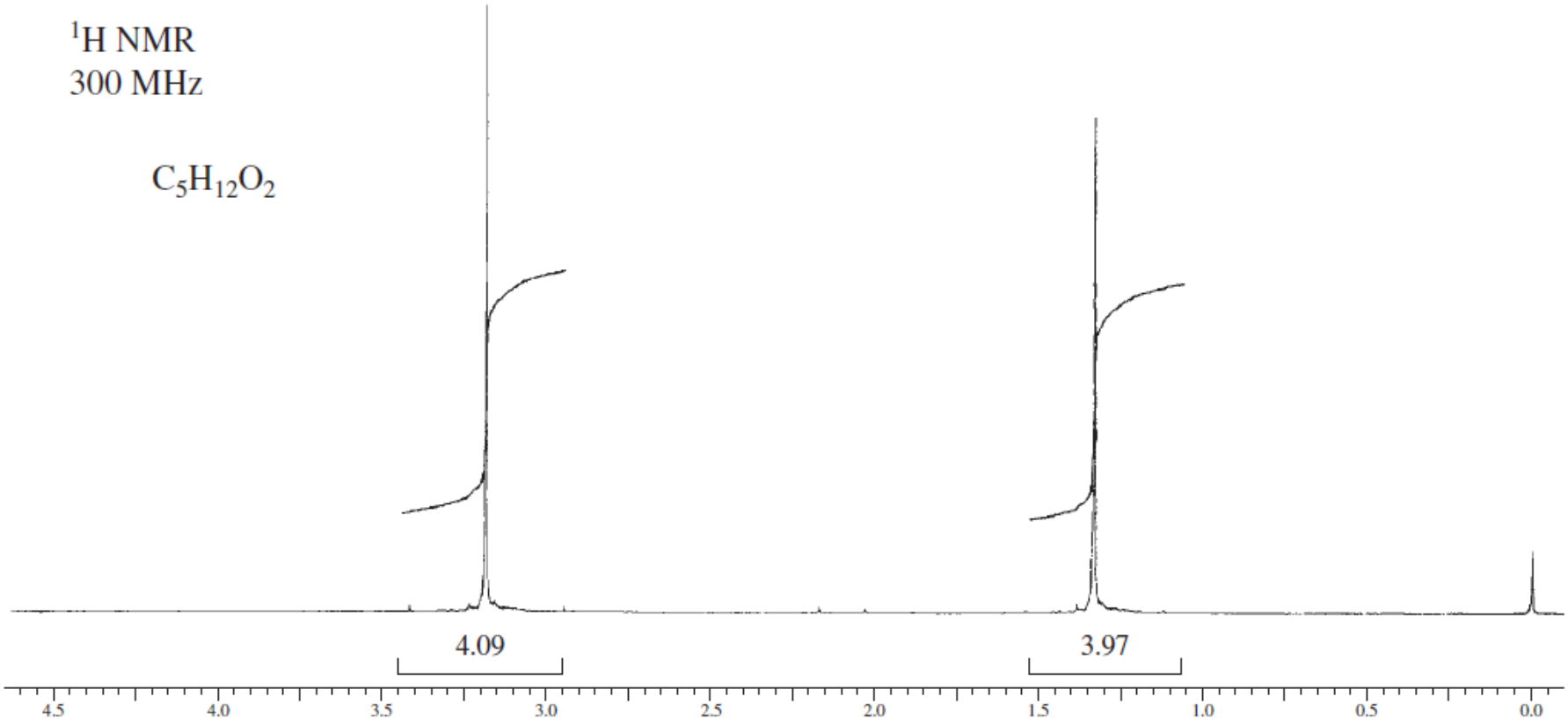


(a)


^{1}H NMR
300 MHz
$C_5H_{10}O_2$
5.05
5.00
4.95
4.90
0.86
2.55
5.22
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

(b)

*19. Draw the structure of an ether with formula $C_5H_{12}O_2$ that fits the following NMR spectrum:



Carbon-13 NMR

- เข้าใจความหมายของ ^{13}C-NMR

  Peaks Integration

  Chemical Shift

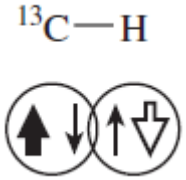
  Peaks type/Carbon type/DEPT

- สามารถเขียนและแปรโครงสร้างของสารประกอบจากสเปคตรัมได้

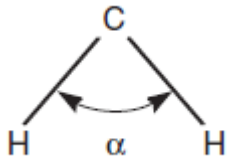
1. Proton-Coupled ^{13}C of C-13 Signals

Coupling constants

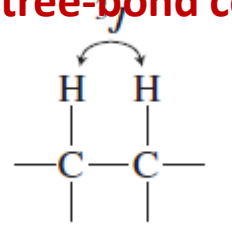
^1J (one-bond couplings)

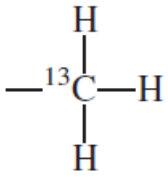
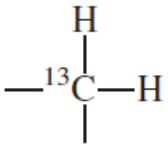
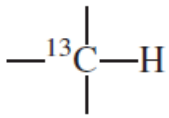
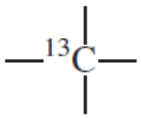
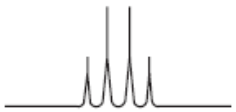
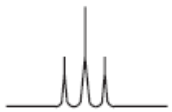
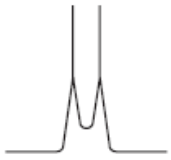


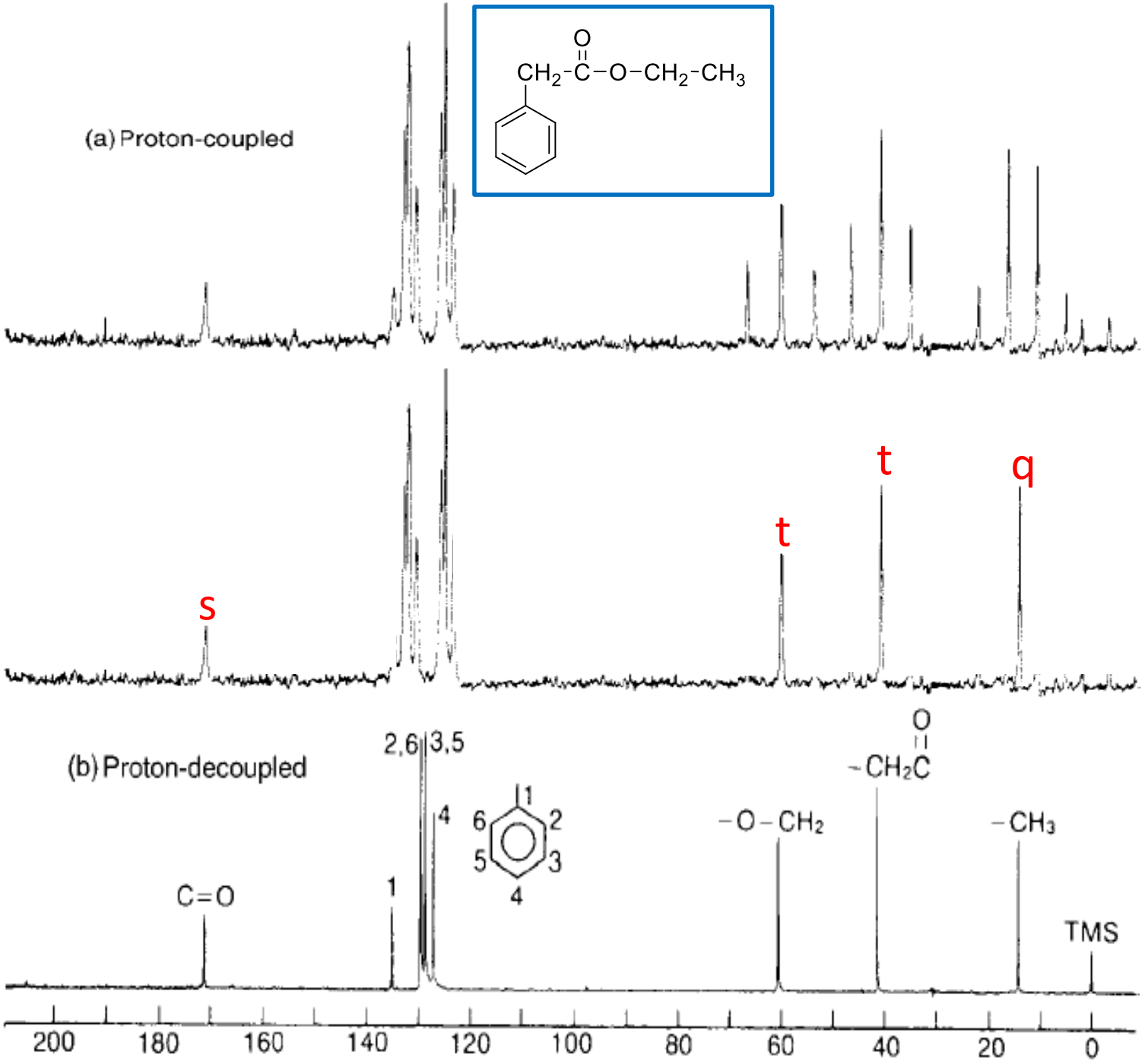
^2J (two-bond couplings)



^3J (tree-bond couplings)

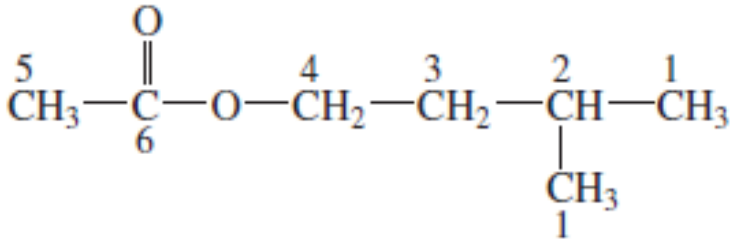


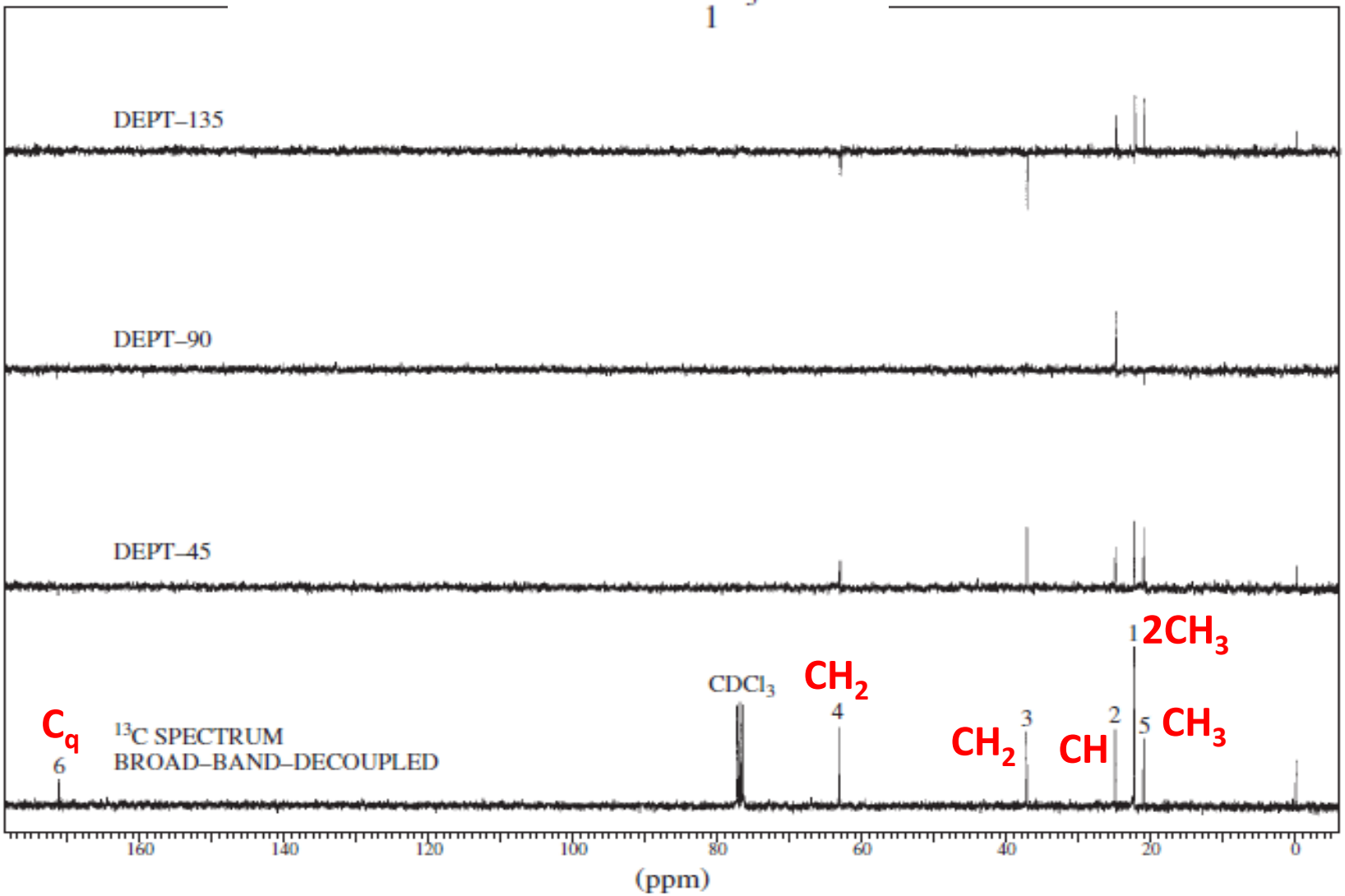
3 protons	2 protons	1 proton	0 protons
			
$n + 1 = 3 + 1 = 4$	$n + 1 = 3$	$n + 1 = 2$	$n + 1 = 1$
			
Methyl carbon	Methylene carbon	Methine carbon	Quaternary carbon


(a) Proton-coupled
O
CH2-C-O-CH2-CH3
s
t
t
q
(b) Proton-decoupled
2,6
3,5
4
1
C=O
1
2
3
4
5
6
-O-CH2
O
-CH2C
-CH3
TMS
200
180
160
140
120
100
80
60
40
20
0

Distortionless enhancement with polarization transfer (DEPT)

เป็นเทคนิคที่ทำให้สเปคตรัมที่ได้มีเฉพาะกับคาร์บอนชนิดใดชนิดหนึ่งเท่านั้น



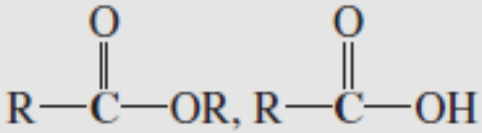
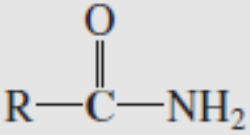
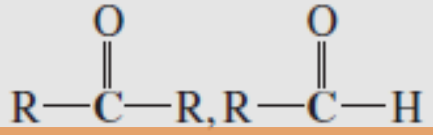


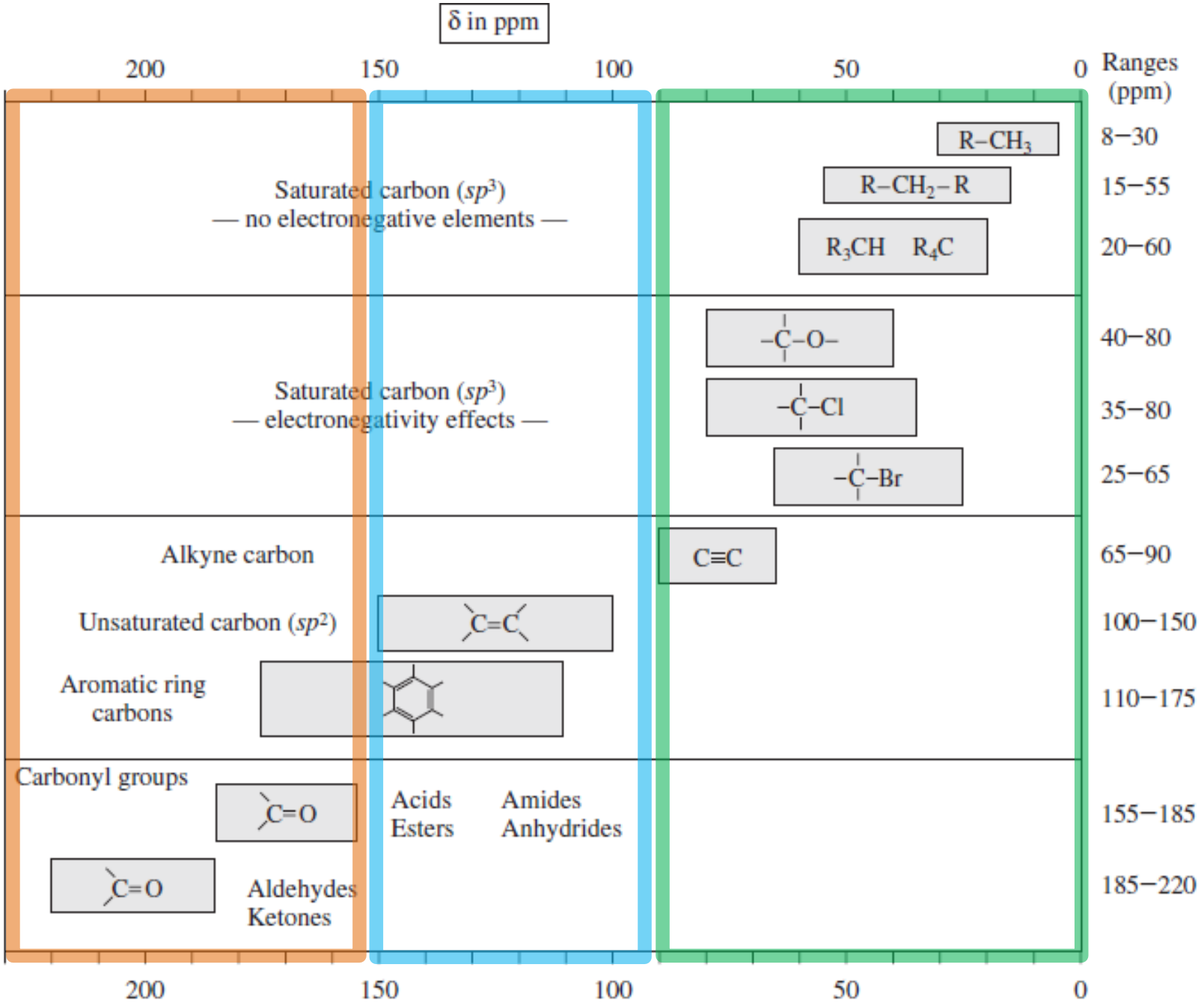
4.2 CARBON-13 CHEMICAL SHIFTS

A. Correlation Charts

APPROXIMATE ^{13}C CHEMICAL SHIFT RANGES (ppm) FOR SELECTED TYPES OF CARBON

$R-CH_3$	8–30
R_2CH_2	15–55
R_3CH	20–60
C–I	0–40
C–Br	25–65
C–N	30–65
C–Cl	35–80
C–O	40–80

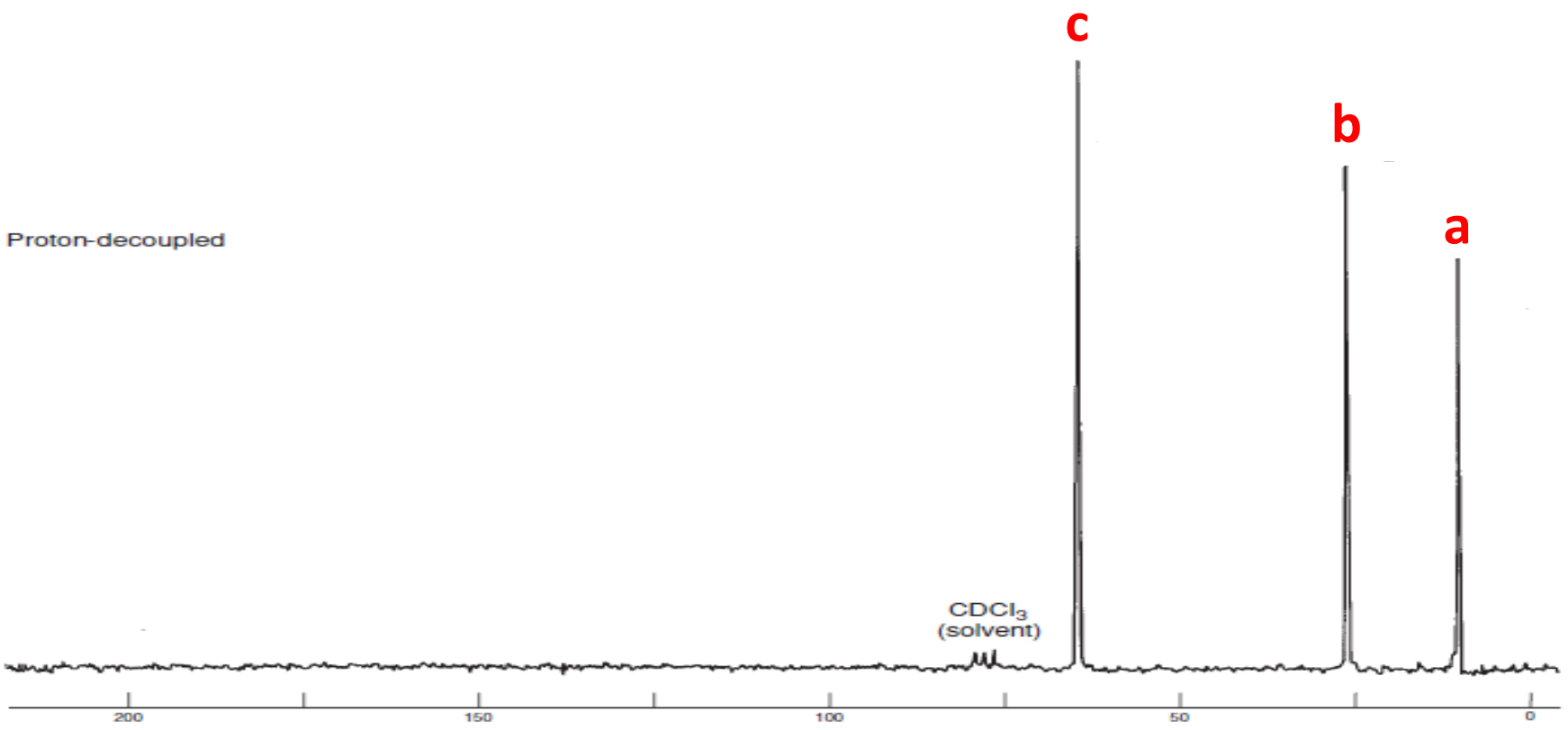
C≡C	65–90
C=C	100–150
C≡N	110–140
	110–175
	155–185
	155–185
	185–220


δ in ppm
200
150
100
50
0
Ranges (ppm)
Saturated carbon (sp^3) — no electronegative elements —
R–CH3
R–CH2–R
R3CH R4C
8–30
15–55
20–60
Saturated carbon (sp^3) — electronegativity effects —
–C–O–
–C–Cl
–C–Br
40–80
35–80
25–65
Alkyne carbon
C≡C
65–90
Unsaturated carbon (sp^2)
C=C
100–150
Aromatic ring carbons
110–175
Carbonyl groups
C=O
Acids
Esters
Amides
Anhydrides
155–185
C=O
Aldehydes
Ketones
185–220
200
150
100
50
0

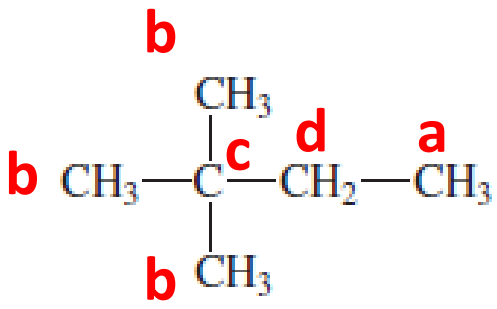
Example 1

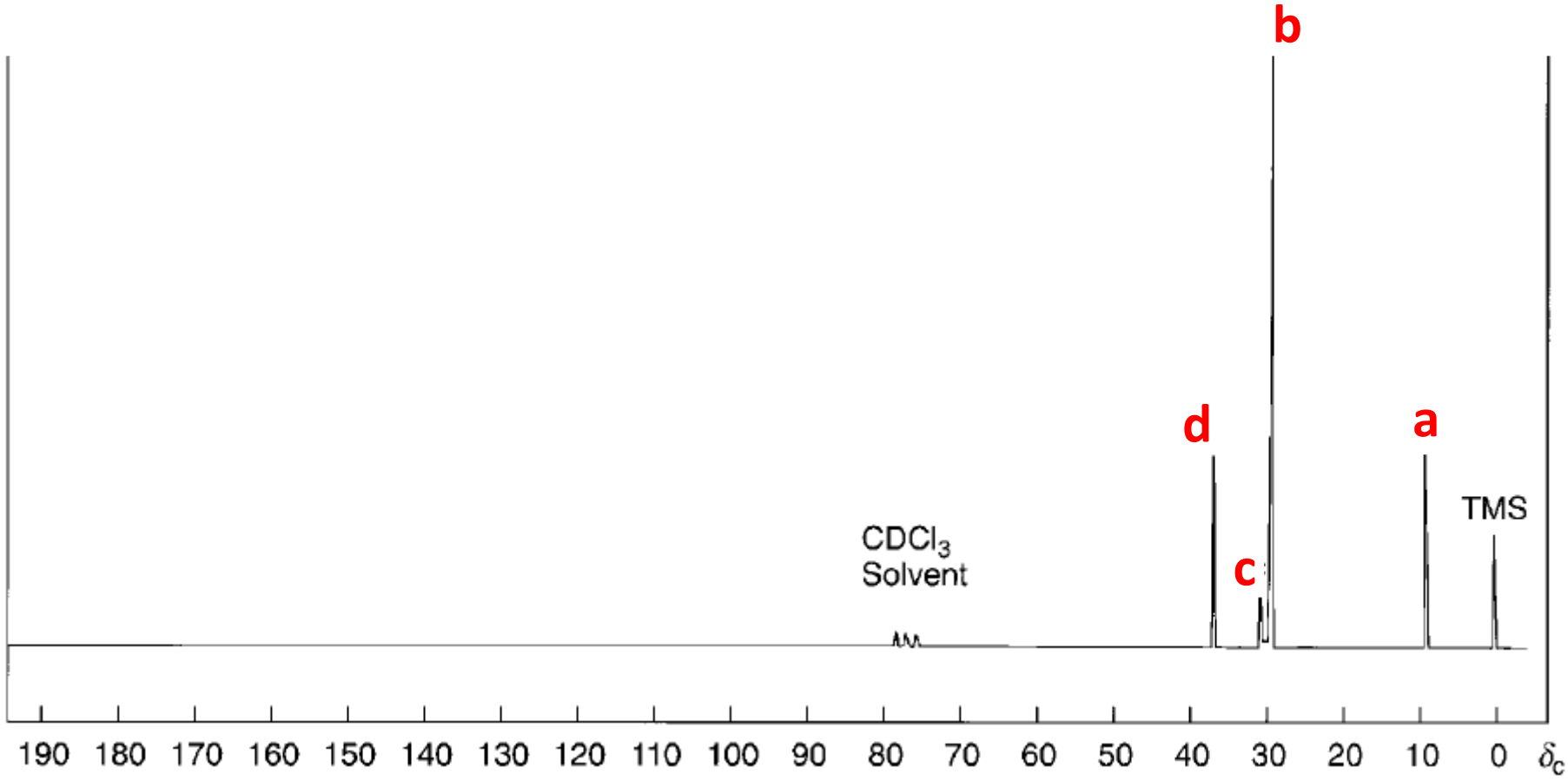
$CH_3-CH_2-CH_2-OH$

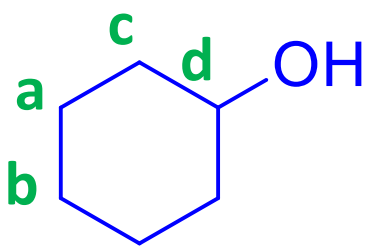
a b c inductive effect

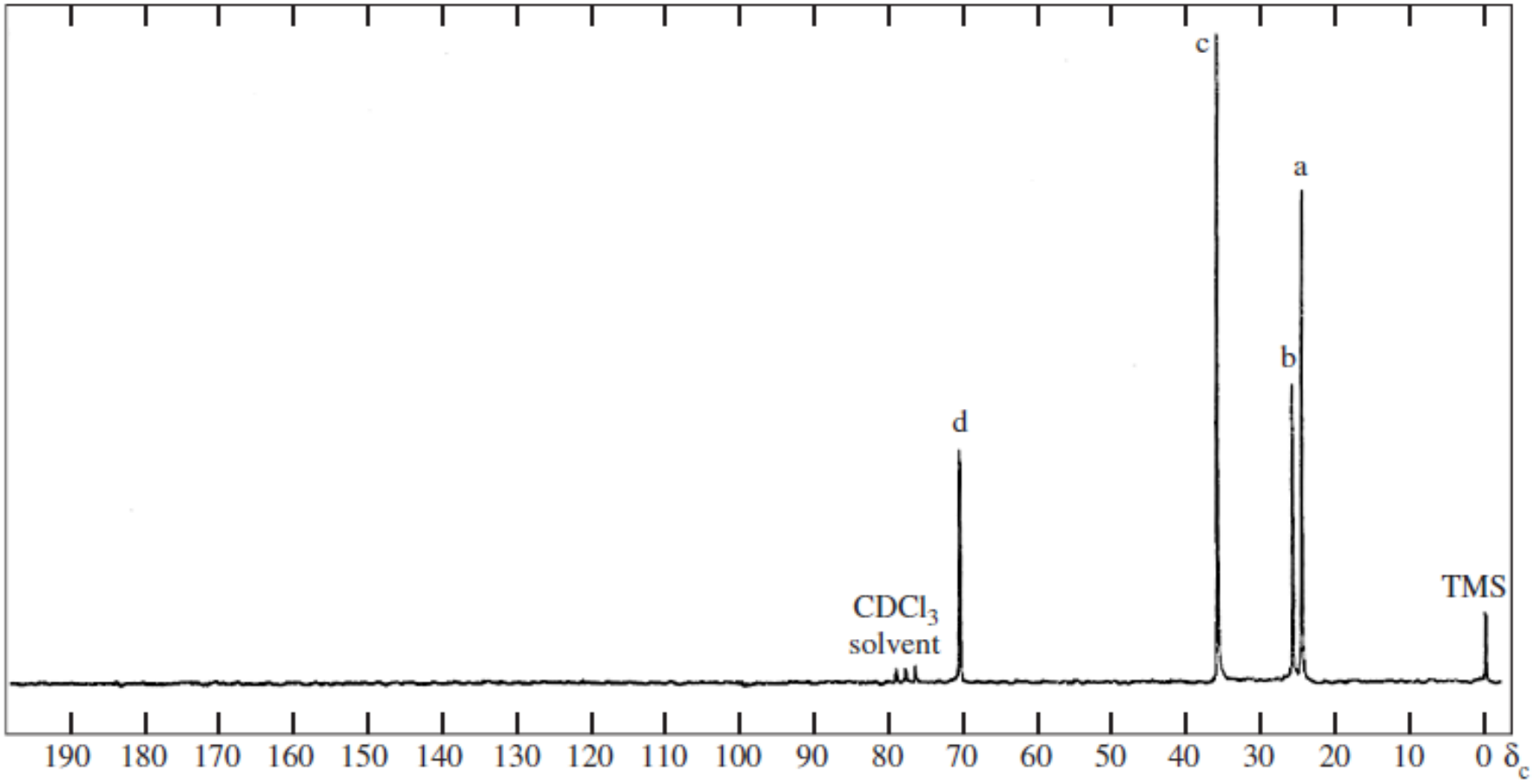


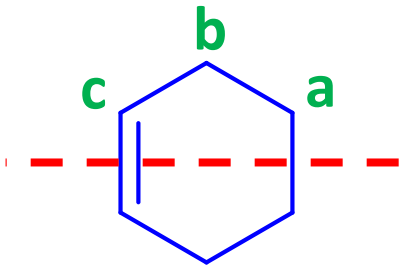
Example 2: Equivalent Carbons

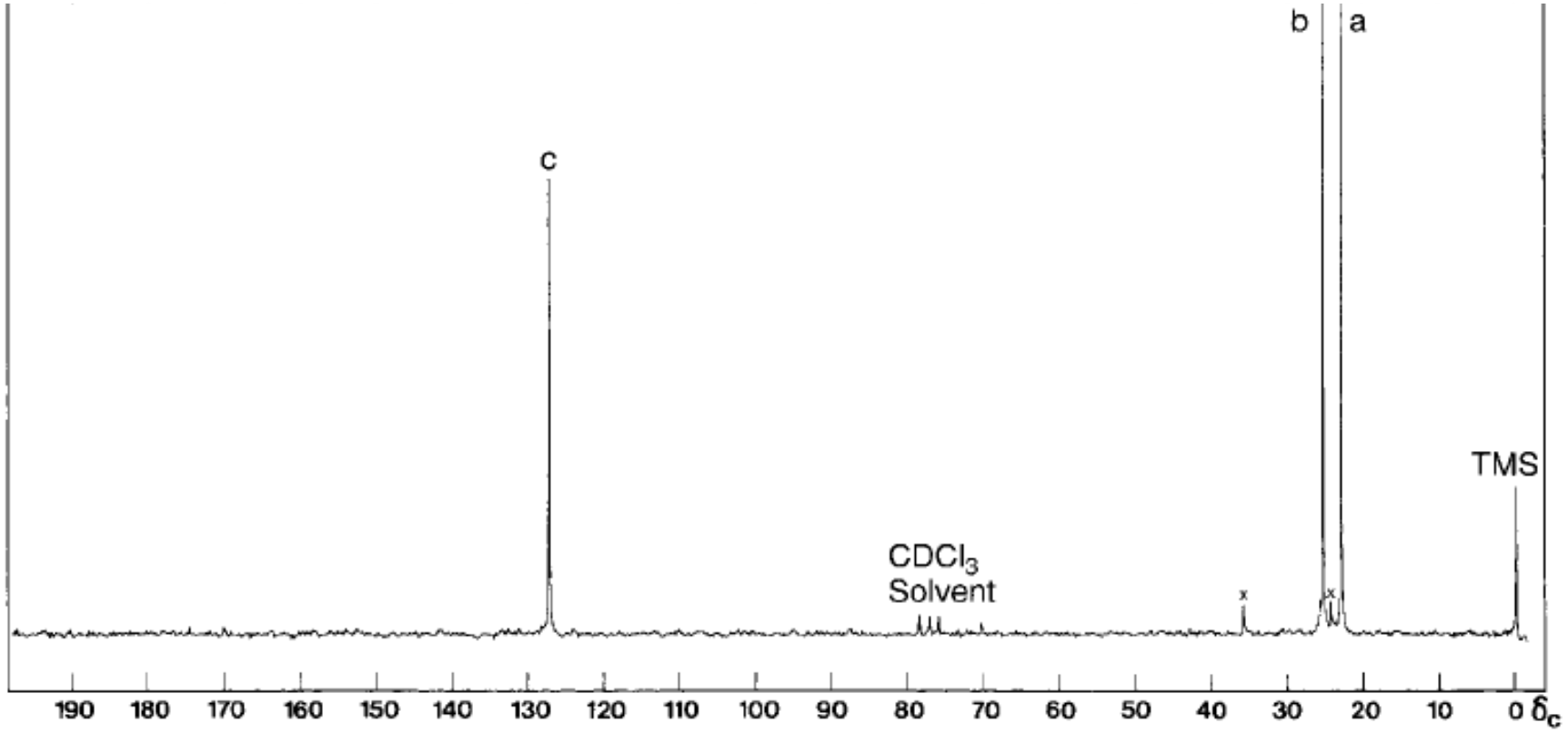


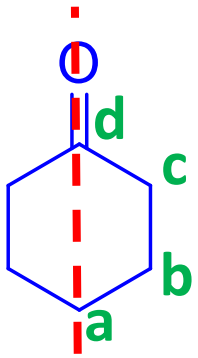


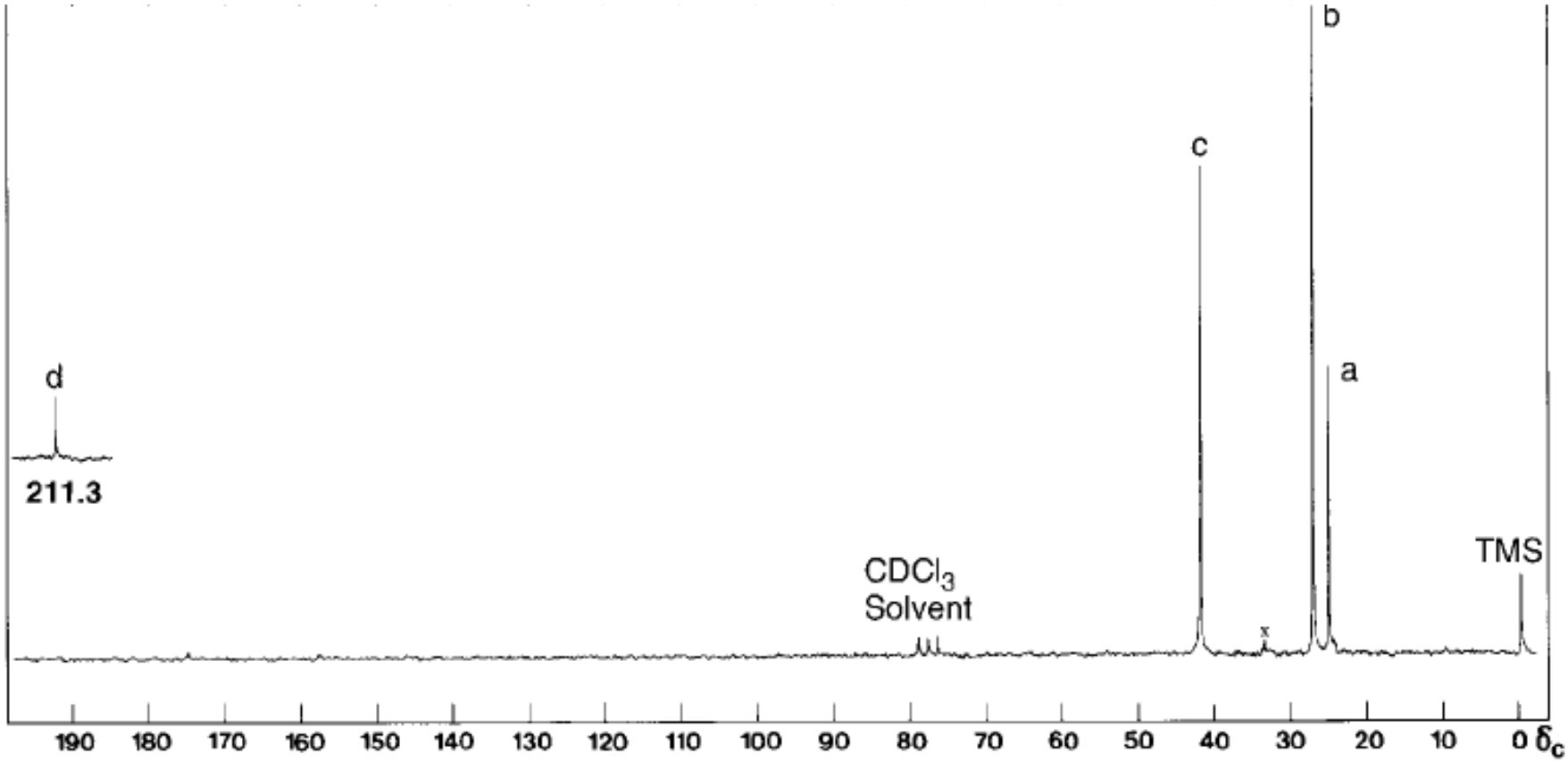

c
d
OH
a
b


c
a
b
d
CDCl3
solvent
TMS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 δc

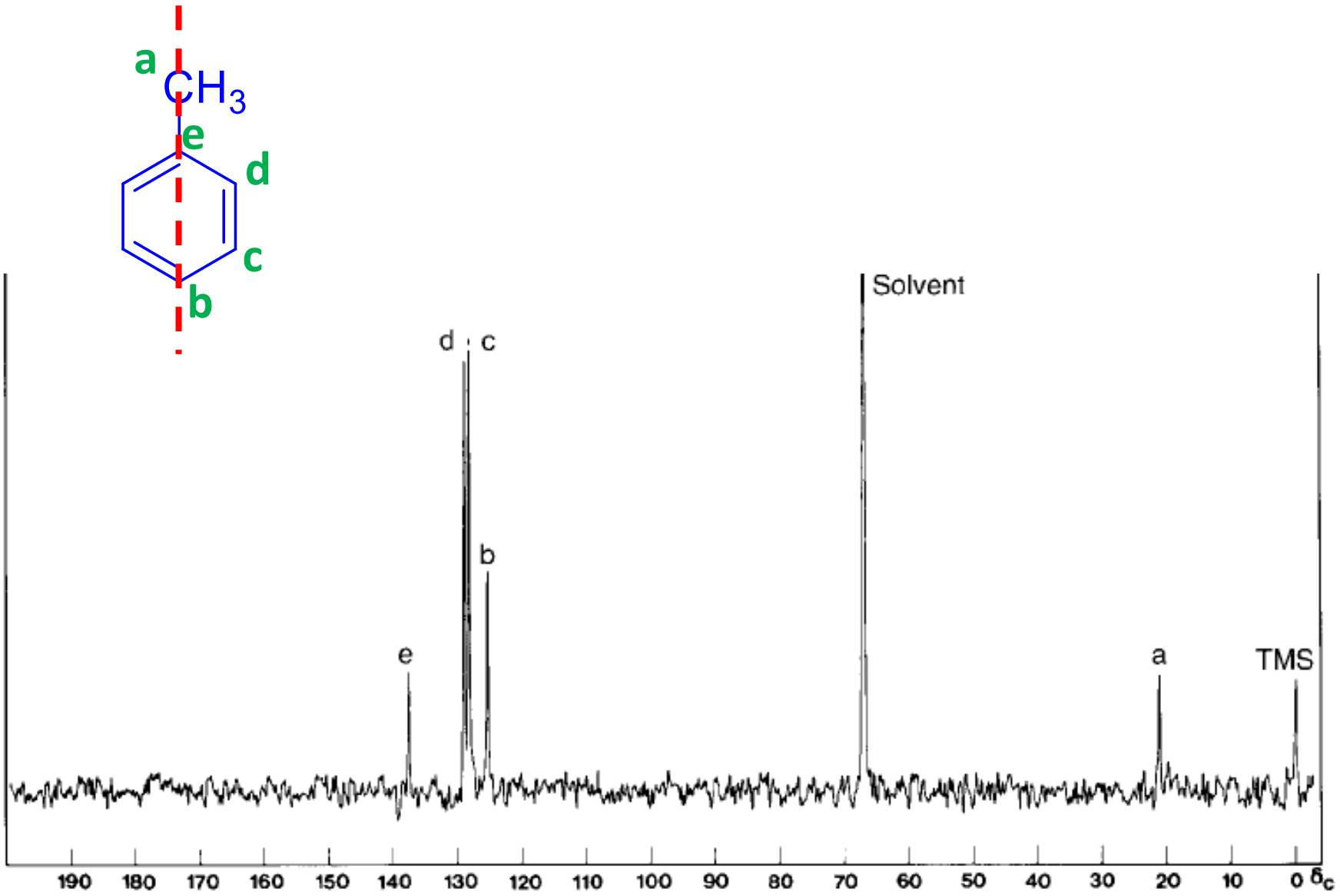

b
c
a

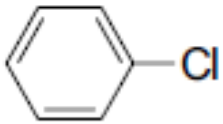
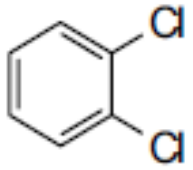
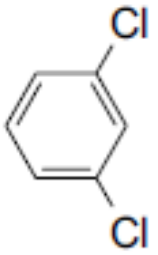

b
a
c
TMS
CDCl3
Solvent
x
x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δc

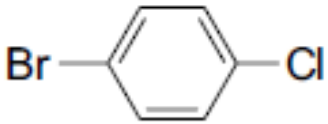
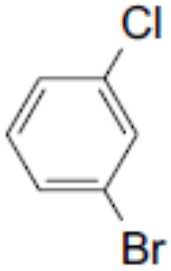
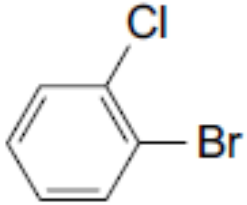

O
d
c
b
a


d
211.3
CDCl3
Solvent
c
b
a
TMS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 δc

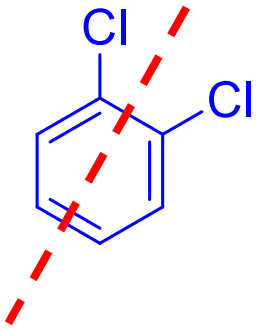
Mono-substitution Aromatic rings

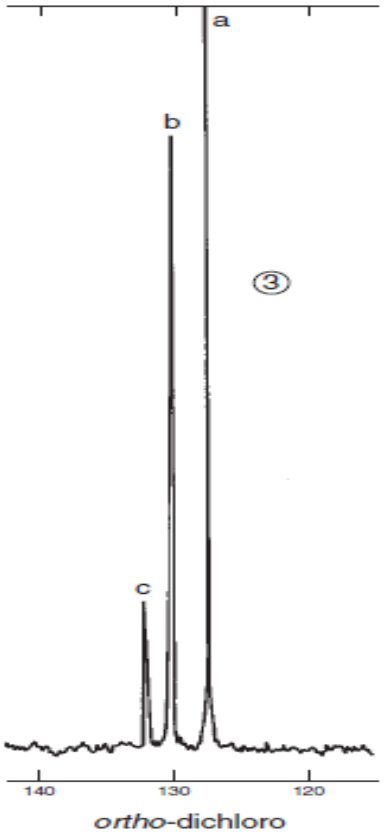


Molecule	Number of aromatic ^{13}C resonances
	1
	4
	3
	4

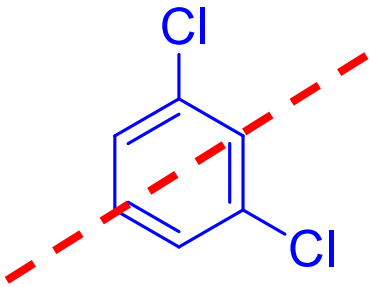
Molecule	Number of aromatic ^{13}C resonances
	2
	4
	6
	6

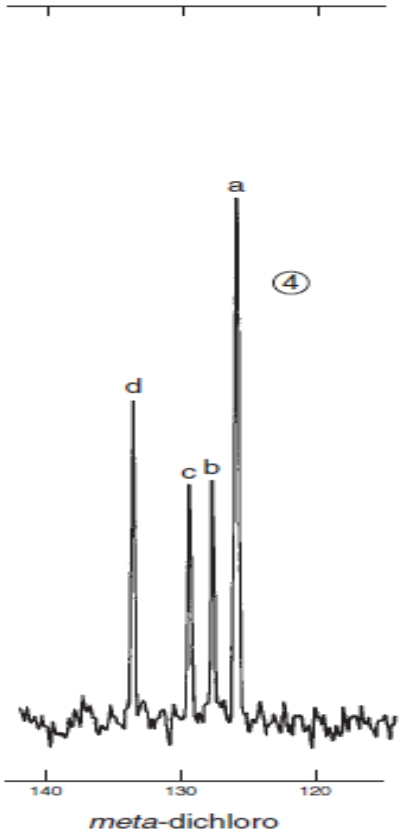
Di-substitution Aromatic rings



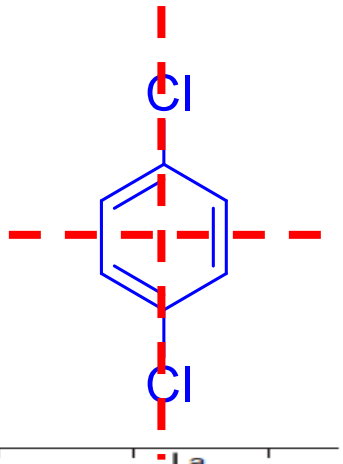


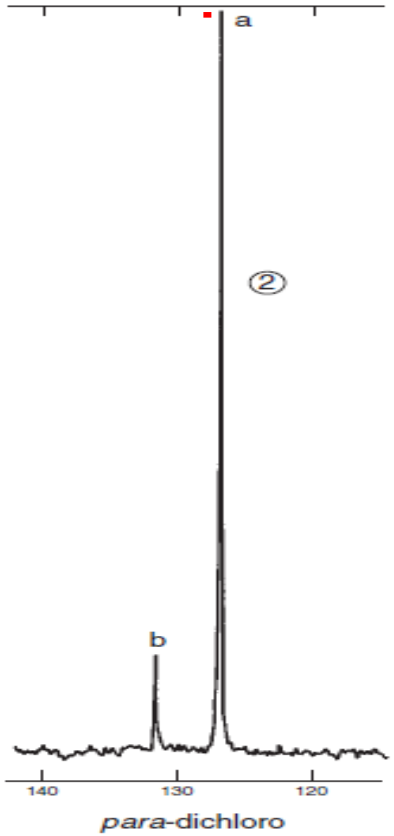
ortho-dichloro





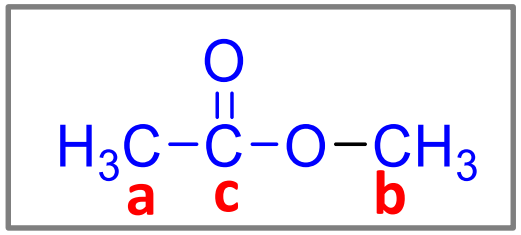
meta-dichloro



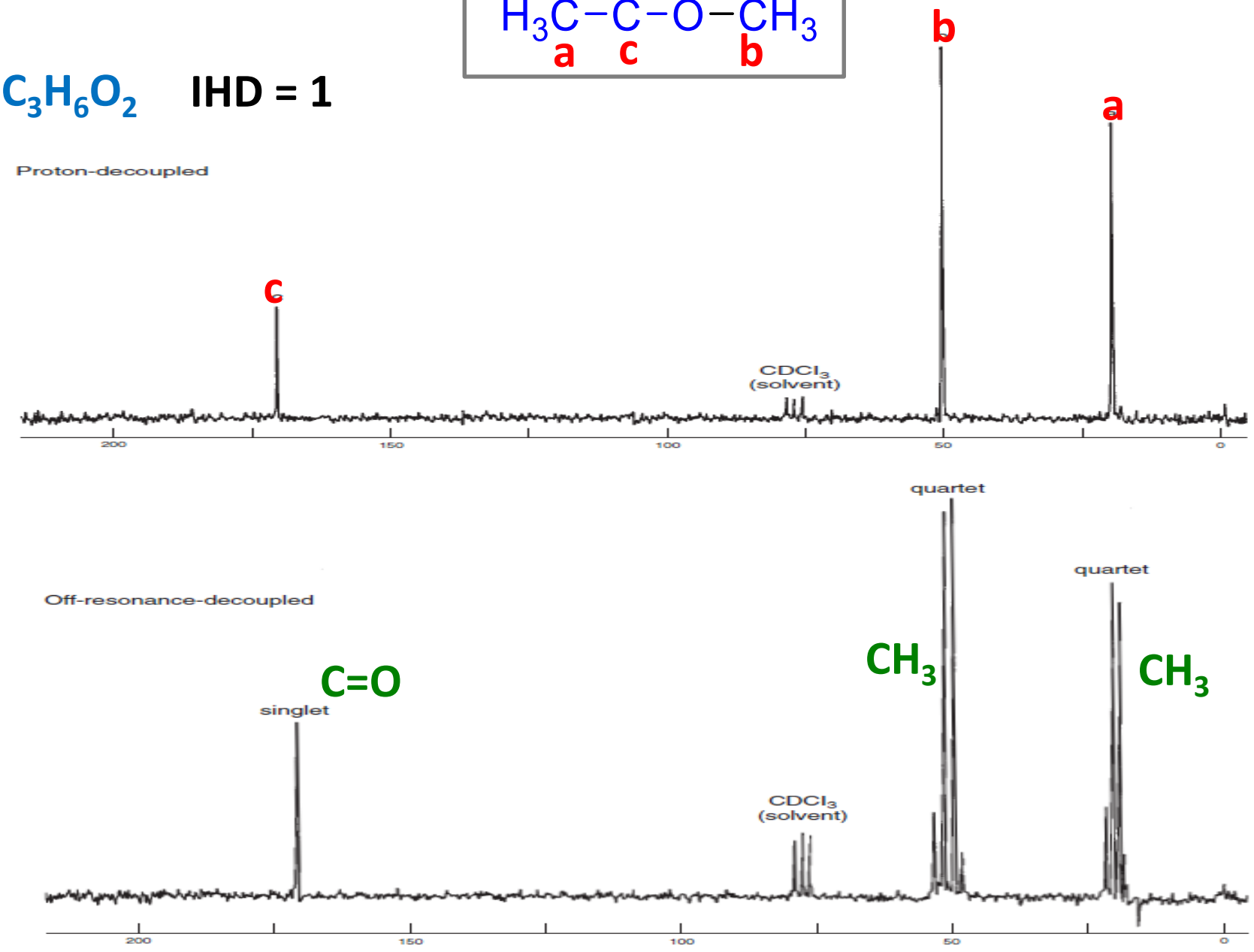


para-dichloro

Example 1



$C_3H_6O_2$ IHD = 1

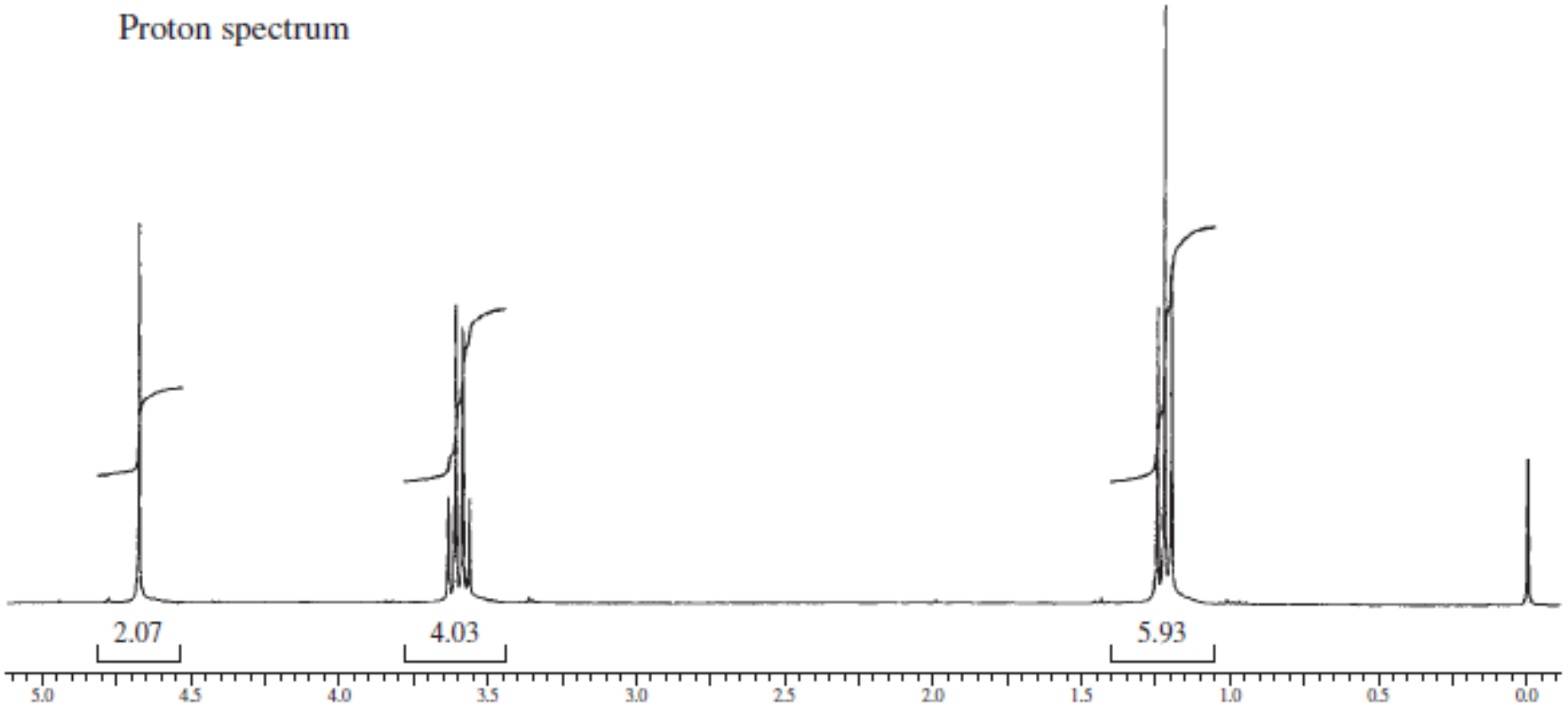


Example 2

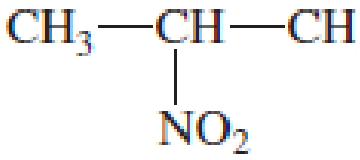
Normal Carbon	DEPT-135	DEPT-90
15 ppm	Positive	No peak
63	Negative	No peak
95	Negative	No peak

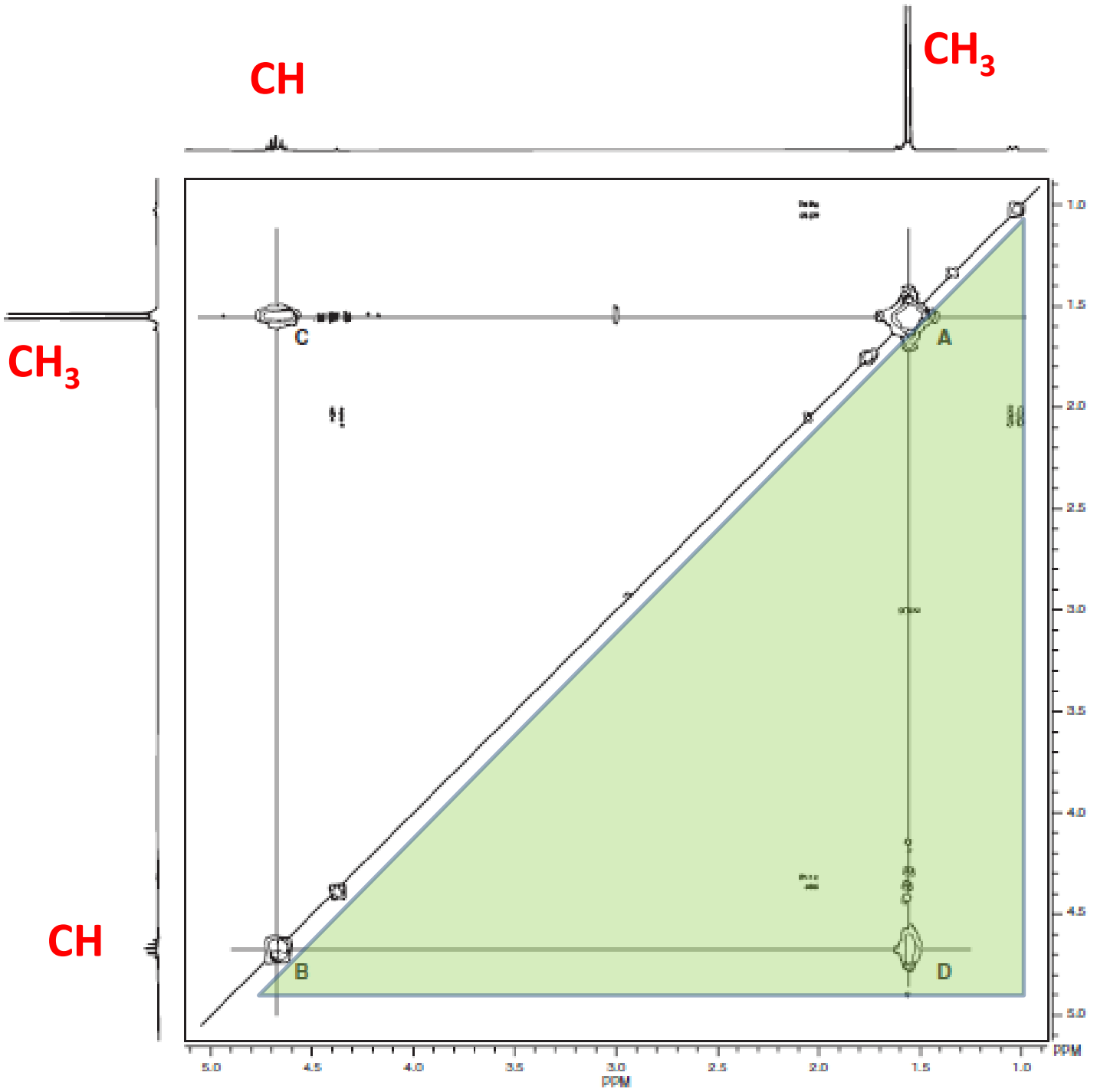
$C_5H_{12}O_2$

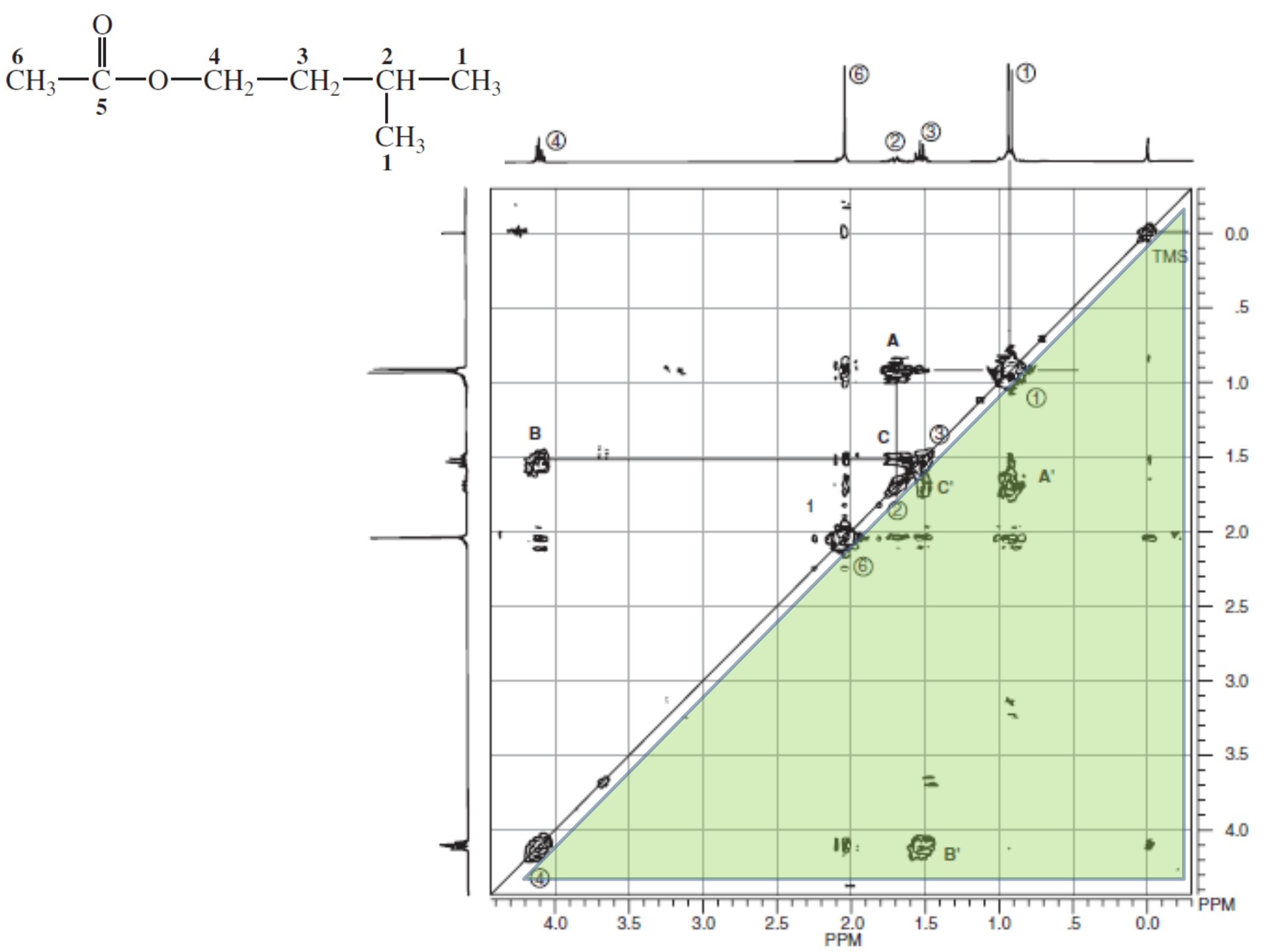
Proton spectrum



COSY





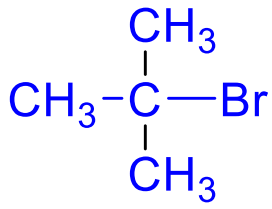

6
CH3
O
C
5
O
4
CH2
3
CH2
2
CH
CH3
1
CH3
1
⑥
①
④
②
③
A
B
C
C'
A'
B'
1
TMS
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
PPM
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

***5.** Following are the ^{1}H and ^{13}C spectra for each of four isomeric bromoalkanes with formula C_4H_9Br. Assign a structure to each pair of spectra.

Carbon spectrum
A

C_4H_9Br

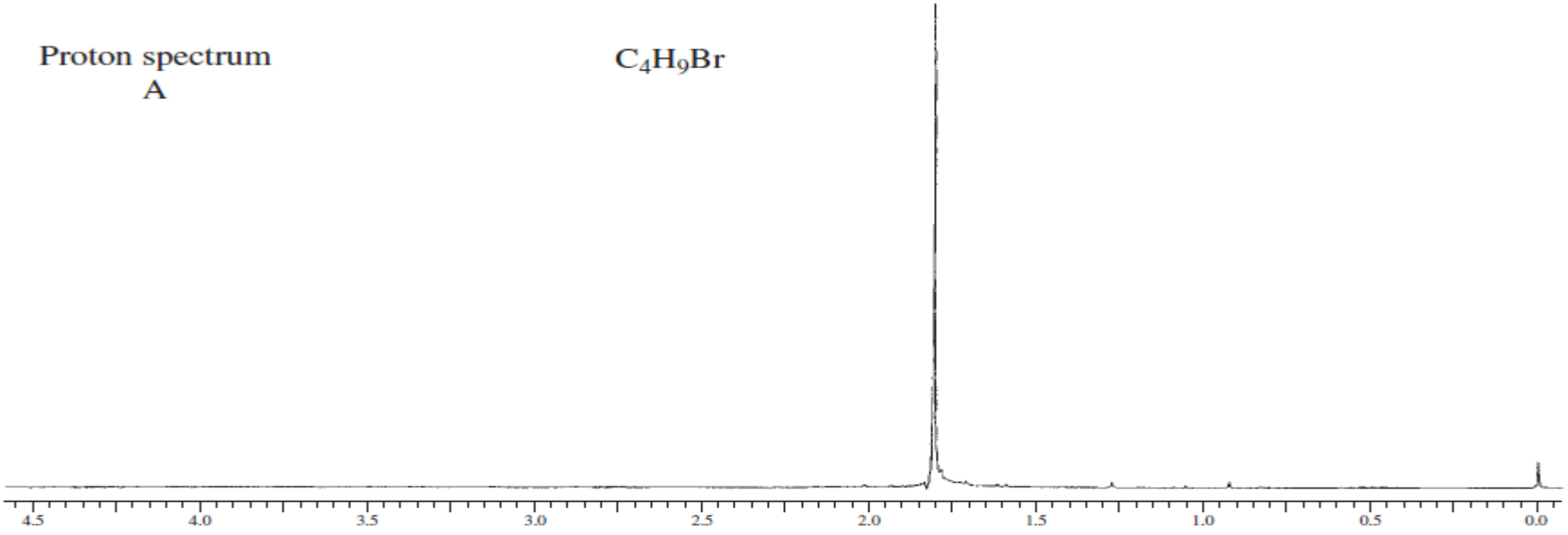
IHD = 0



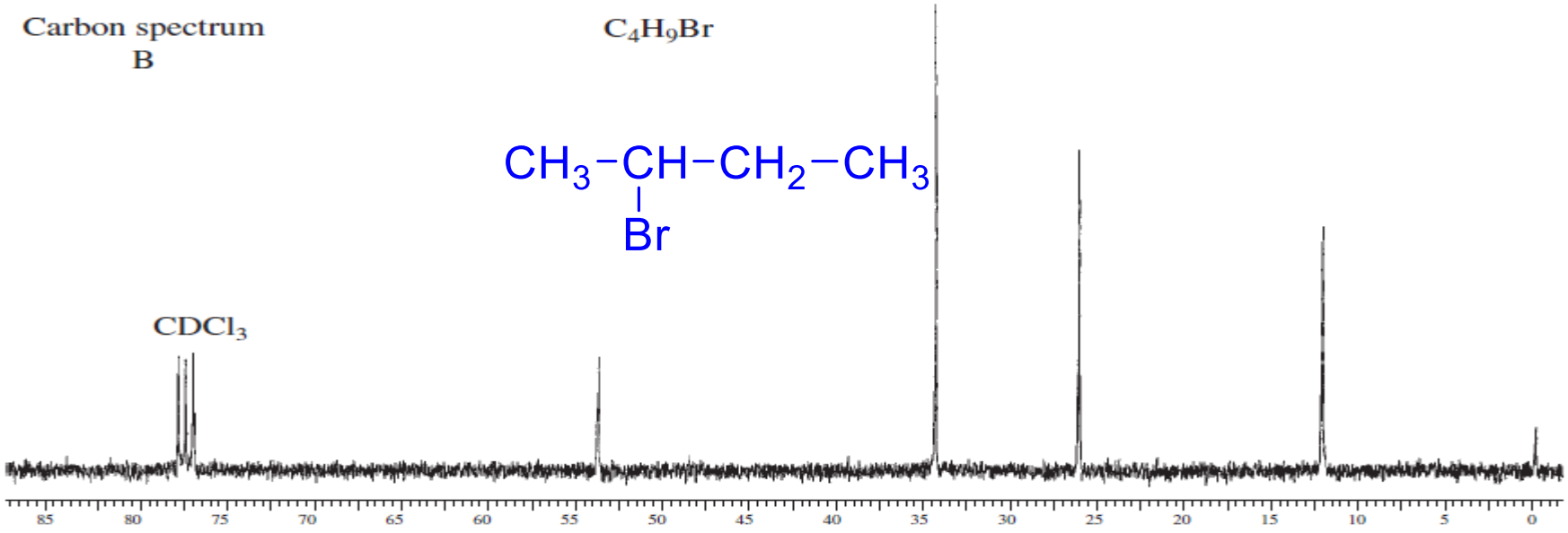
$CDCl_3$
(solvent)

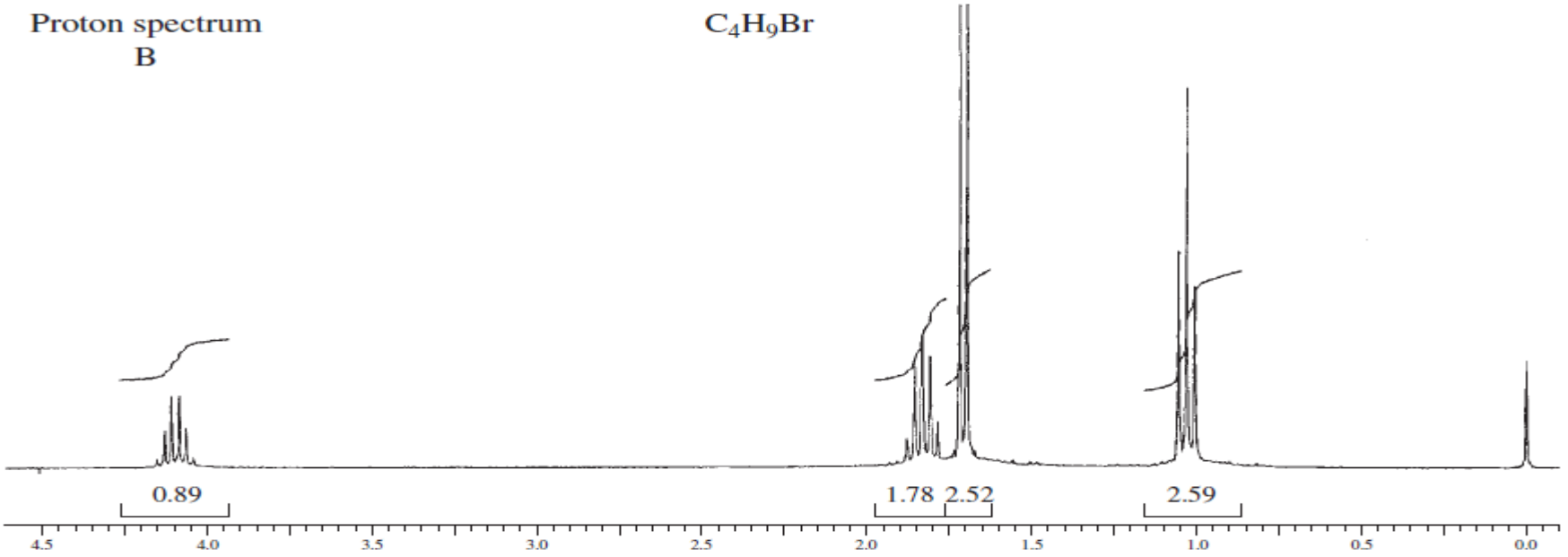
Proton spectrum
A

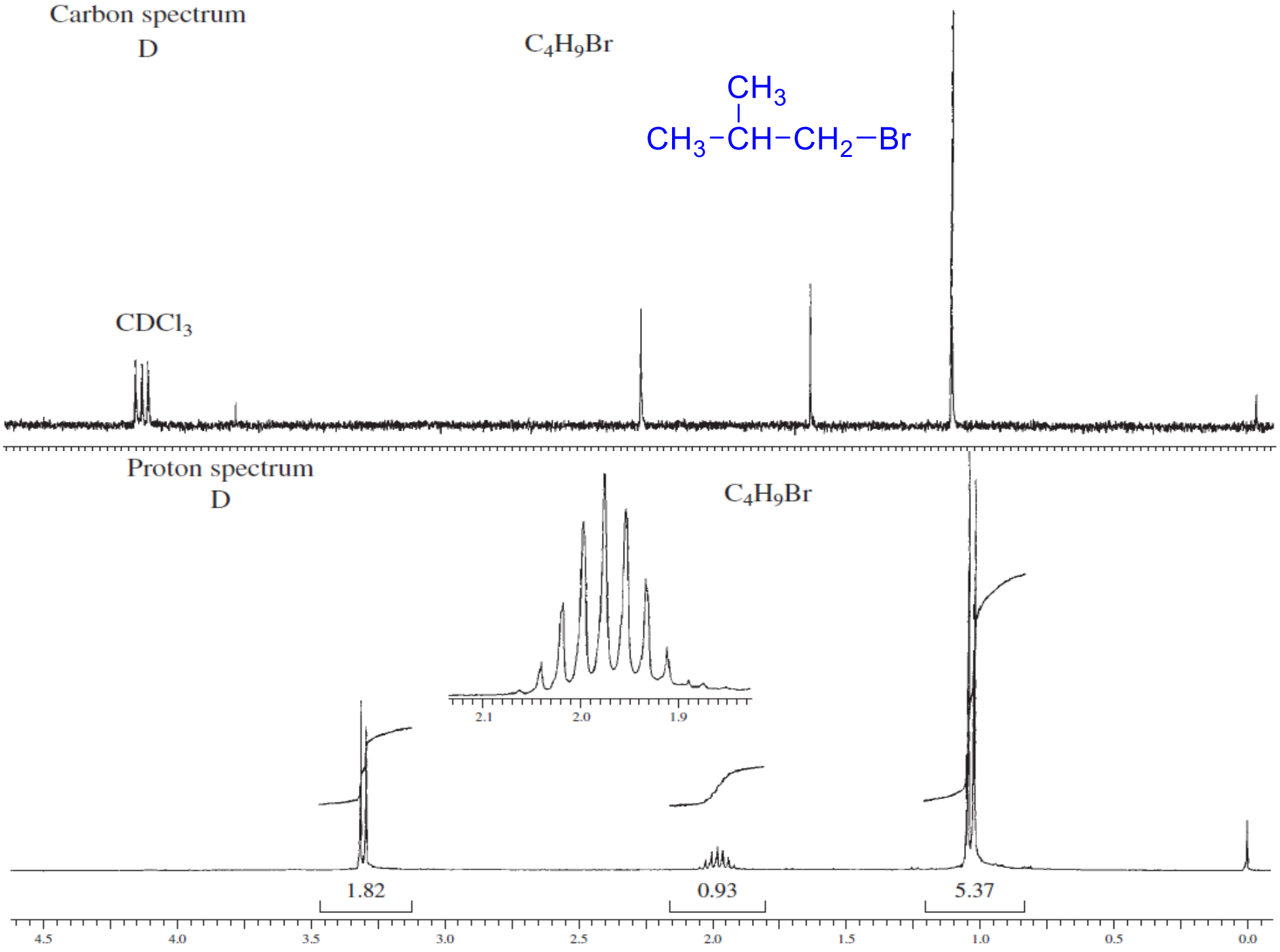
C_4H_9Br



***5.** Following are the ^{1}H and ^{13}C spectra for each of four isomeric bromoalkanes with formula C_4H_9Br. Assign a structure to each pair of spectra.

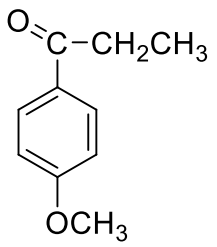




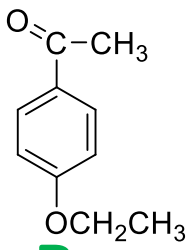

Carbon spectrum
D
C_4H_9Br
CH_3
$CH_3-CH-CH_2-Br$
$CDCl_3$
Proton spectrum
D
C_4H_9Br
2.1
2.0
1.9
1.82
0.93
5.37
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

12. The proton NMR spectrum for a compound with formula $C_{10}H_{12}O_2$ is shown below. The infrared spectrum has a strong band at 1711 cm^{-1}. The normal carbon-13 NMR spectral results are tabulated along with the DEPT-135 and DEPT-90 information. Draw the structure of this compound.

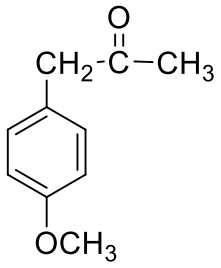
Normal Carbon	DEPT-135	DEPT-90	
29 ppm	Positive	No peak	CH_3
50	Negative	No peak	CH_2 Alkyl
55	Positive	No peak	CH_3
114	Positive	Positive	2CH
126	No peak	No peak	C_q Benzene
130	Positive	Positive	2CH
159	No peak	No peak	C_q
207	No peak	No peak	C_q Carbonyl



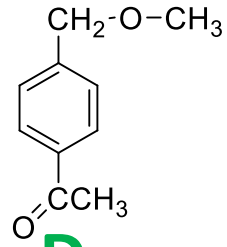
A



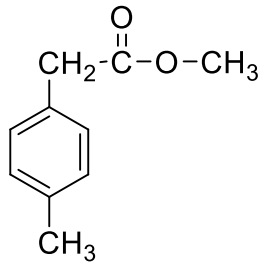
B



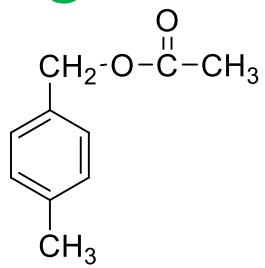
C



D



E



F

Proton

$C_{10}H_{12}O_2$

IHD = 5