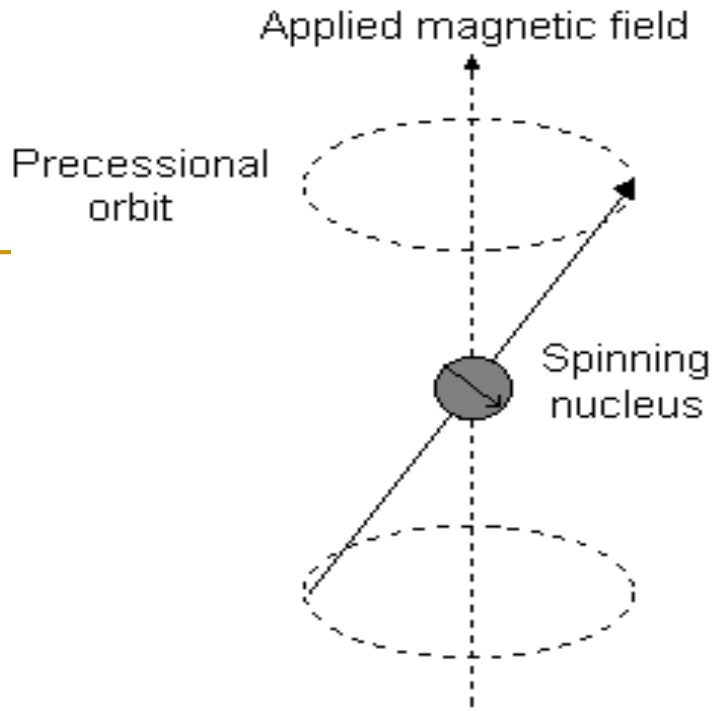
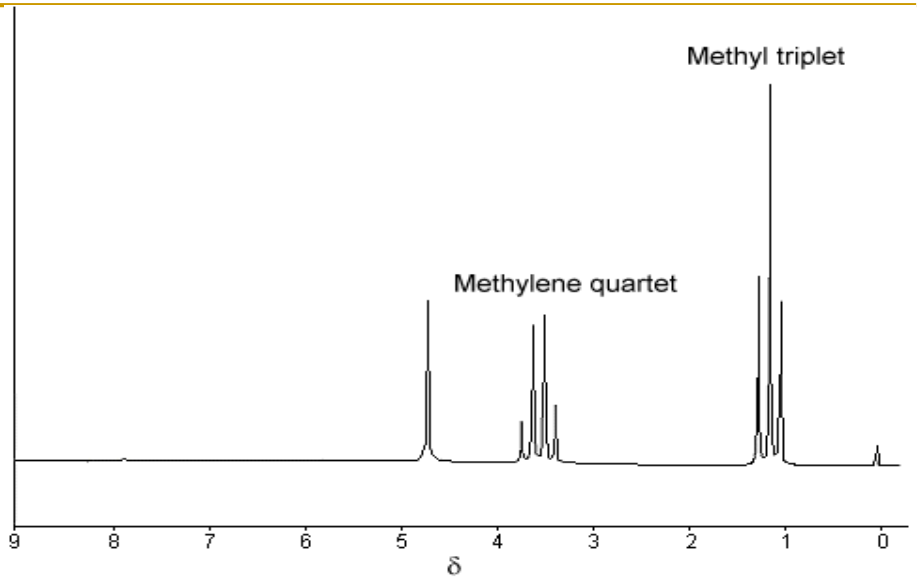
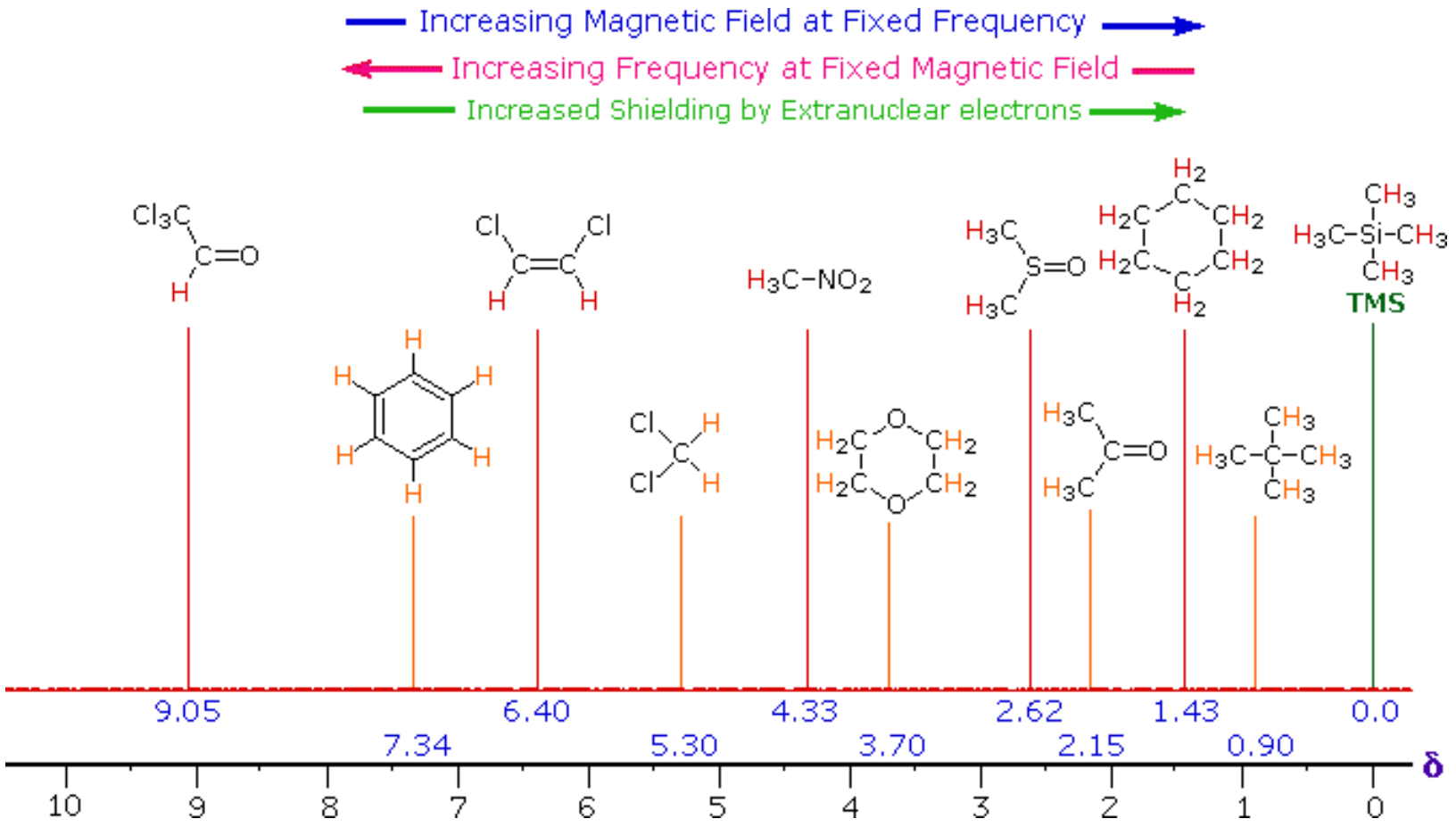
NMR Spectroscopy



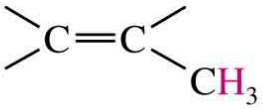
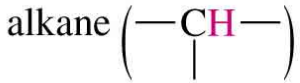
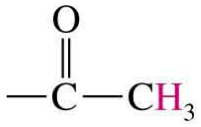
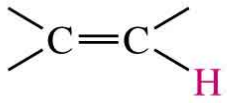
NMR Signals



- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms.


Increasing Magnetic Field at Fixed Frequency
Increasing Frequency at Fixed Magnetic Field
Increased Shielding by Extranuclear electrons
TMS
9.05
7.34
6.40
5.30
4.33
3.70
2.62
2.15
1.43
0.90
0.0
δ
10
9
8
7
6
5
4
3
2
1
0

Typical Values

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9		1.7
alkane ($-CH_2-$)	1.3	Ph—H	7.2
alkane 	1.4	Ph—CH_3	2.3
	2.1	R—CHO	9–10
—C≡C—H	2.5	R—COOH	10–12
R—CH_2—X (X = halogen, O)	3–4	R—OH	variable, about 2–5
		Ar—OH	variable, about 4–7
	5–6	R—NH_2	variable, about 1.5–4

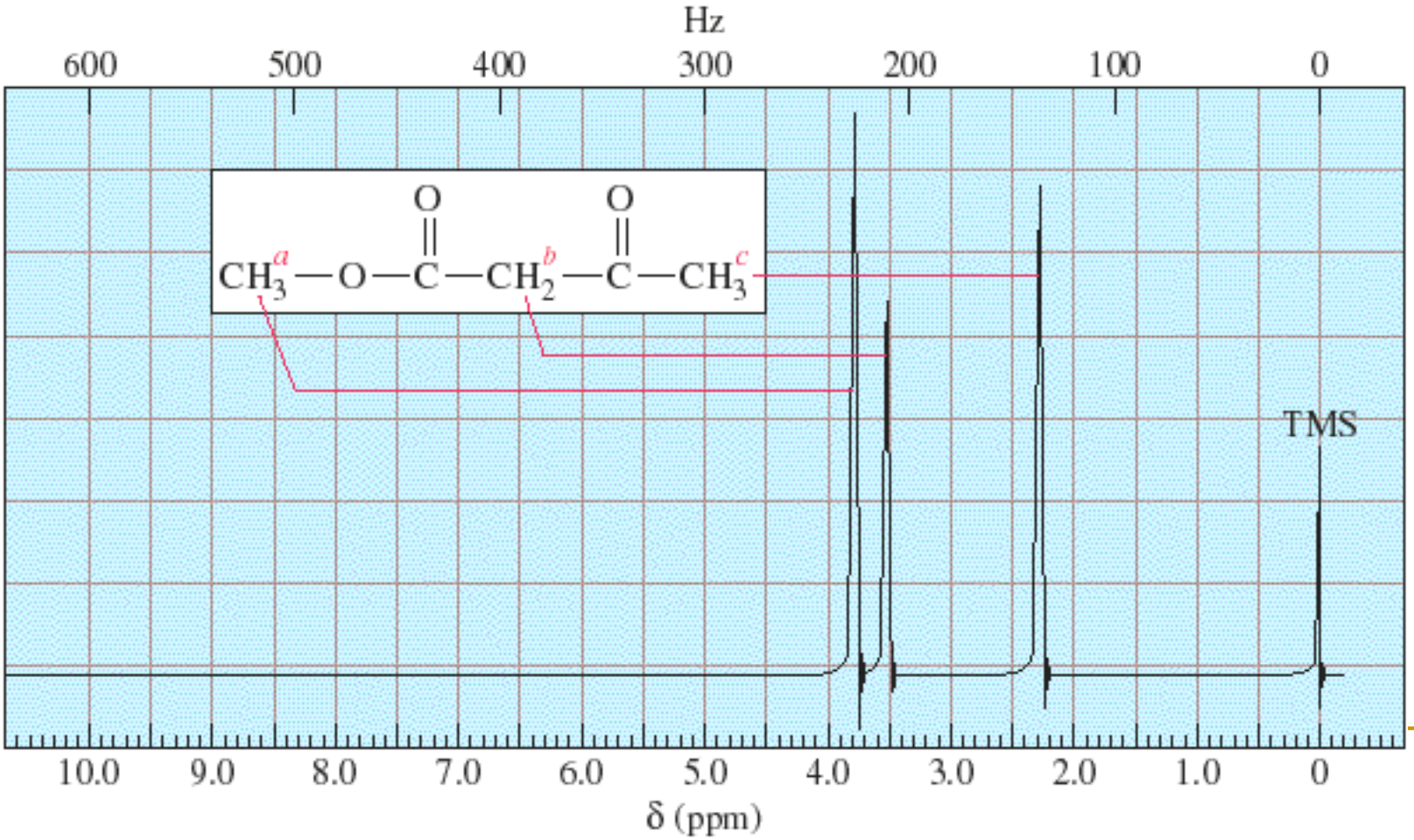
Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

=>

Number of Signals

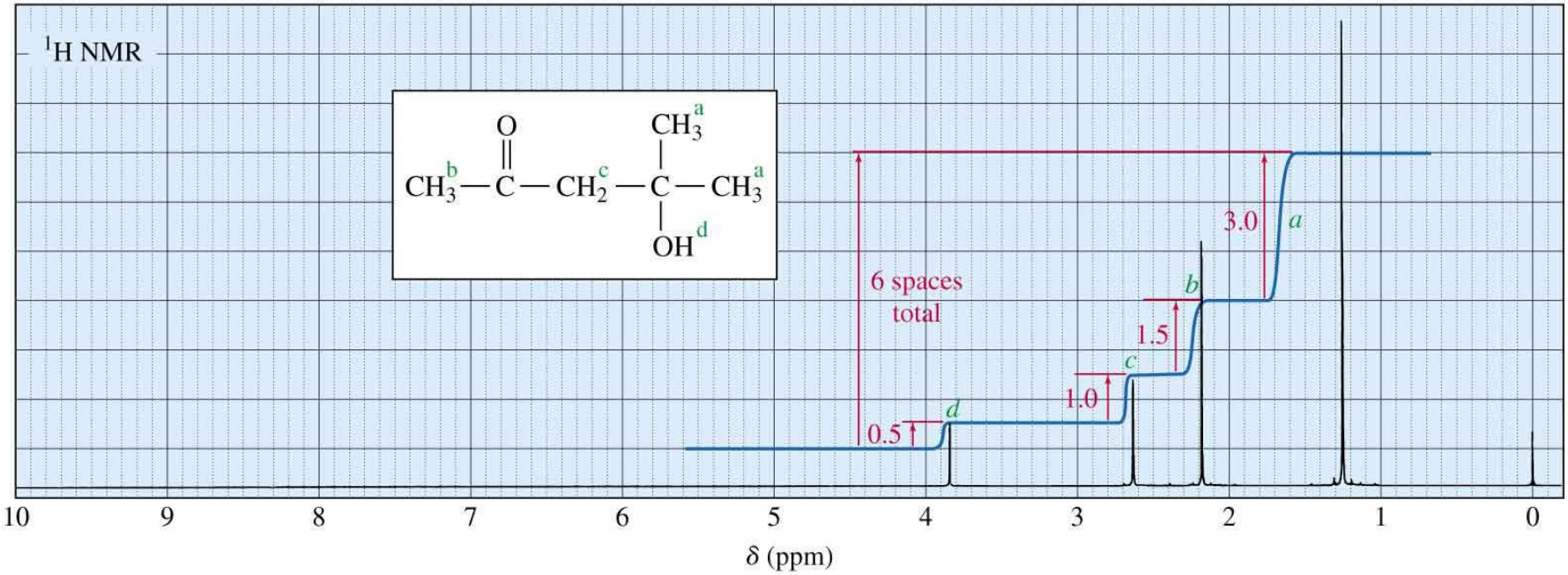
Equivalent hydrogens have the same chemical shift.

The ***number*** of signals shows how many different kinds of protons are present



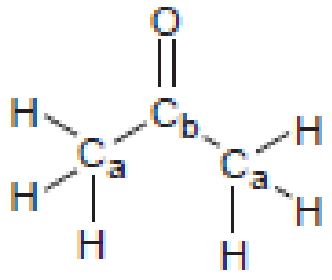
=>

How Many Hydrogens?

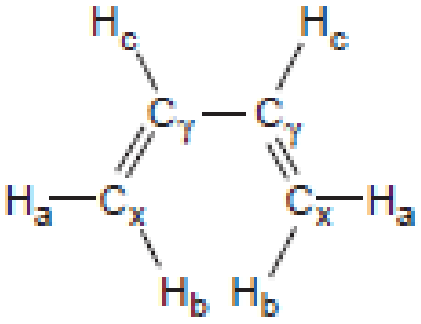


=>

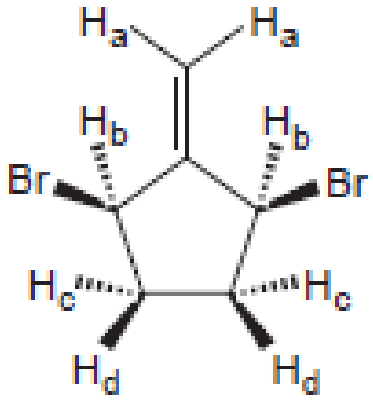
A

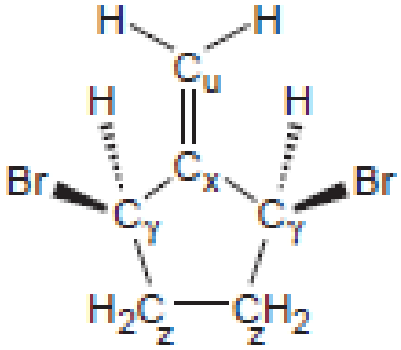


All Hs are equivalent
There are 2 types of C



3 types of H
2 types of C

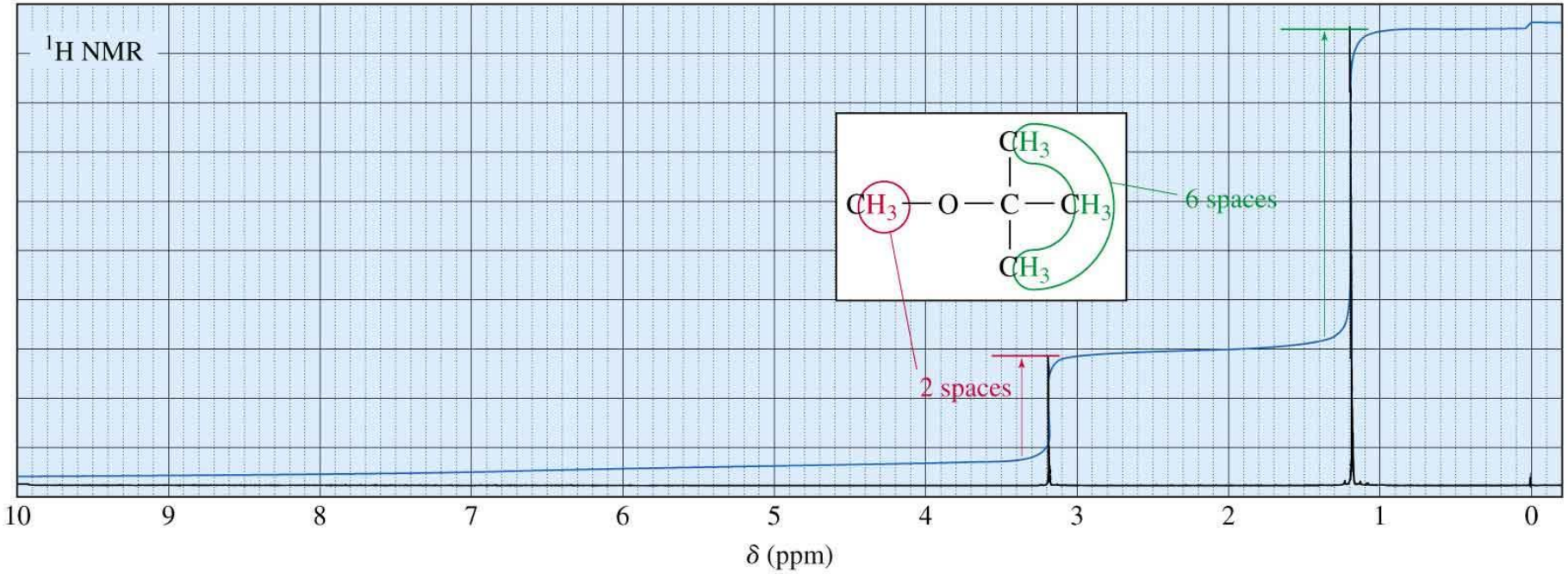




4 types of H and 4 types of C

Intensity of Signals

- The area under each peak is proportional to the number of protons. (Shown by integral trace).
- proportional to the molar concentration of the sample
- The NMR spectrum of equal molar amounts of benzene and cyclohexane.????



Multiplicity and spin–spin coupling

- Each proton signal is split into two or more lines by the presence of neighbouring proton(s) following the n+1 rule, where n is the number of neighbouring protons.
- This is known as the multiplicity or splitting or coupling pattern of each signal.

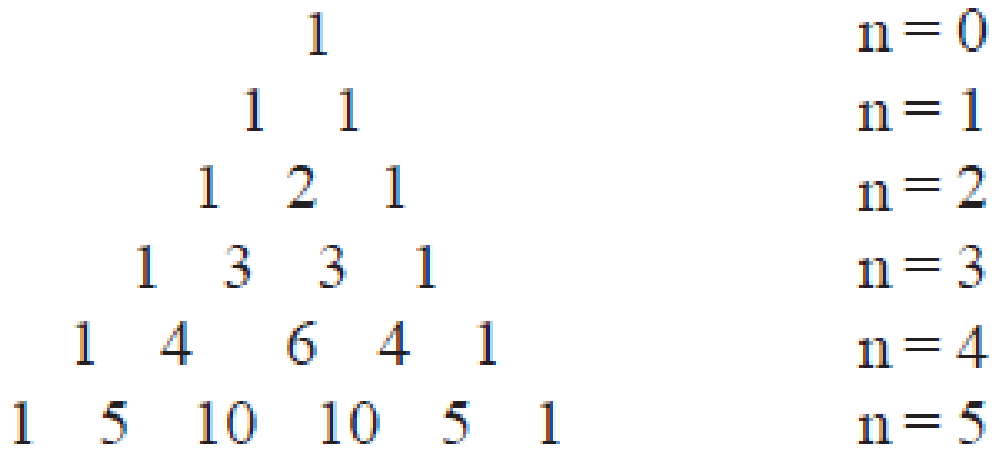
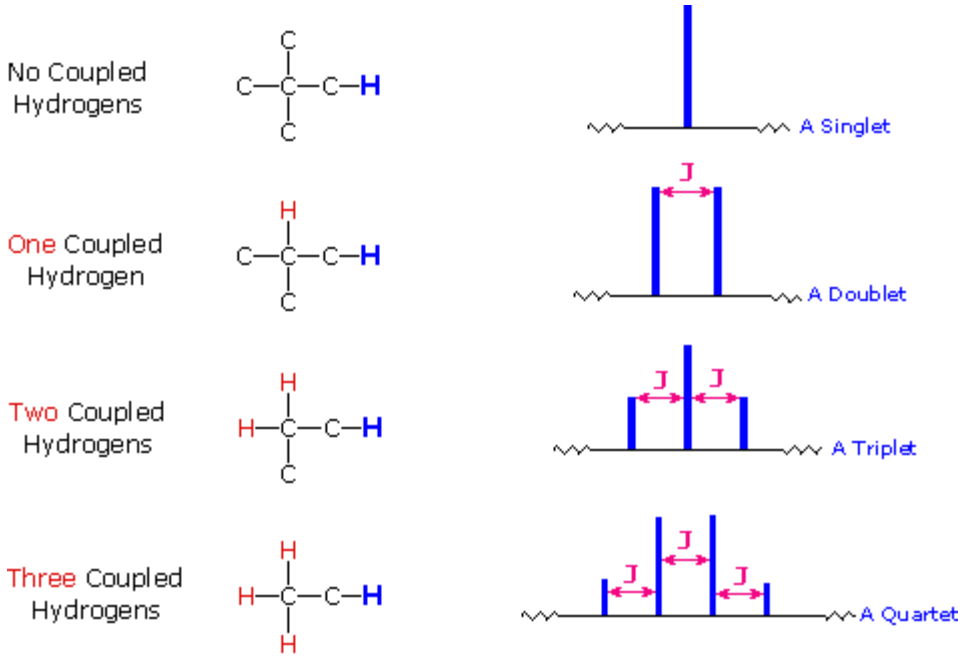
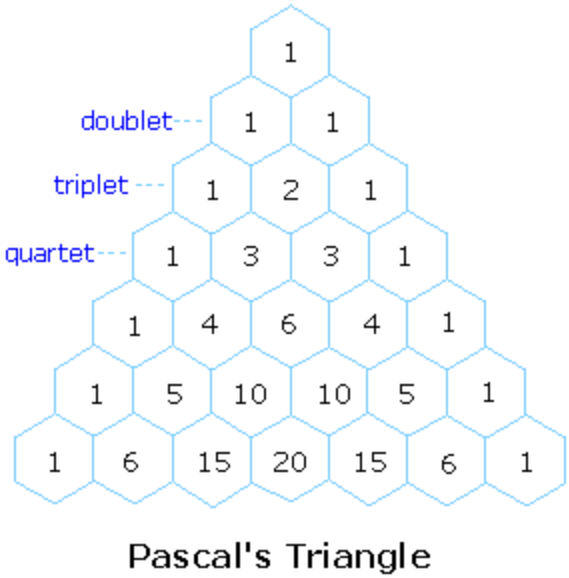


Fig. 8.11
Pascal's triangle indicating the pattern of lines produced by a particular number of adjacent protons having the same coupling constants to a particular signal.

Spin-Spin Splitting and Coupling

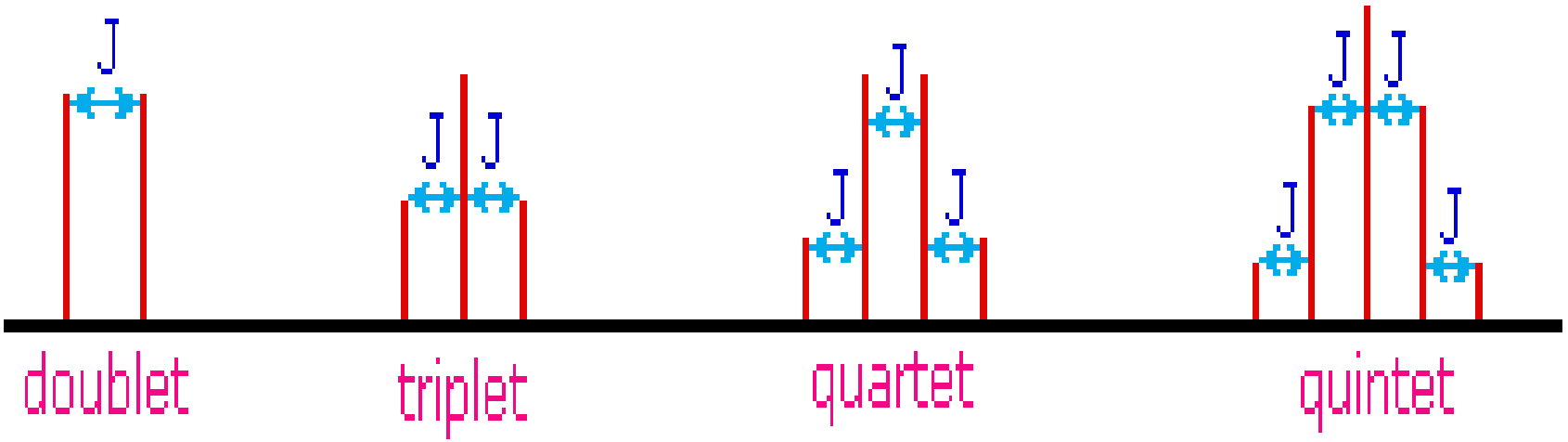


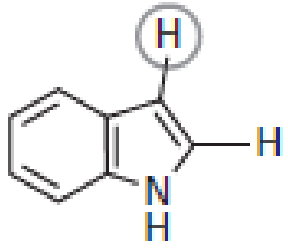


Pascal's Triangle

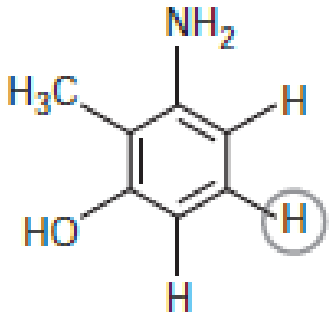
Scalar coupling: Coupling through bond

n + 1 lines

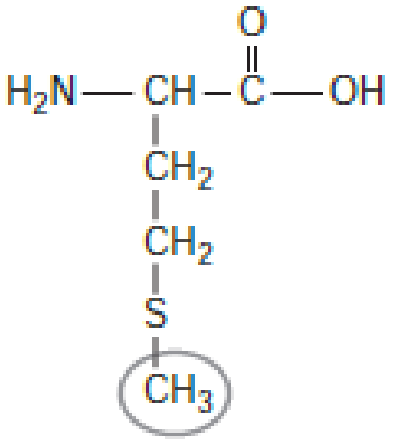

J
J J
J J J
J J J J
doublet
triplet
quartet
quintet


H
H
N
H

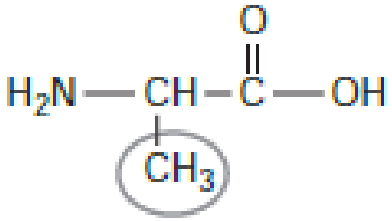
1


NH2
H3C
H
HO
H
H

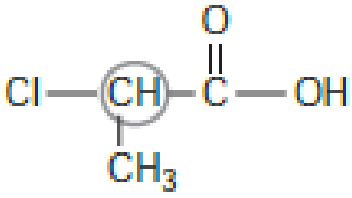
2


O
H2N
CH
C
OH
CH2
CH2
S
CH3

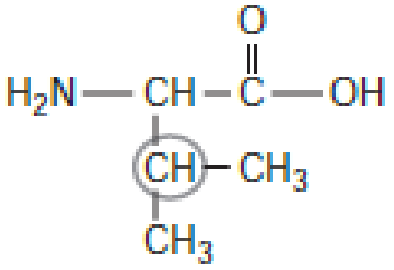
3


O
H2N
CH
C
OH
CH3

4


O
Cl
CH
C
OH
CH3

5

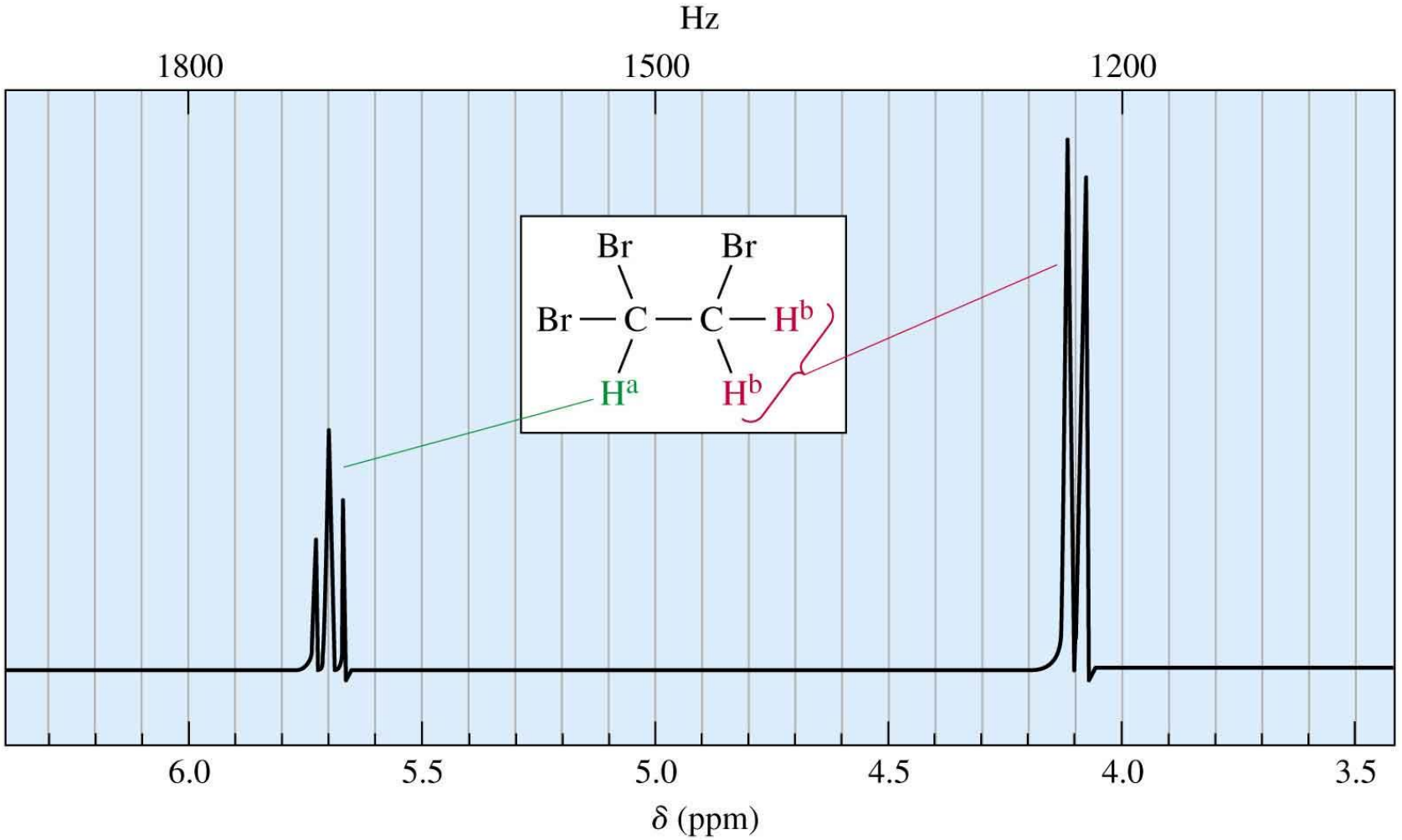

O
H2N
CH
C
OH
CH
CH3
CH3

6

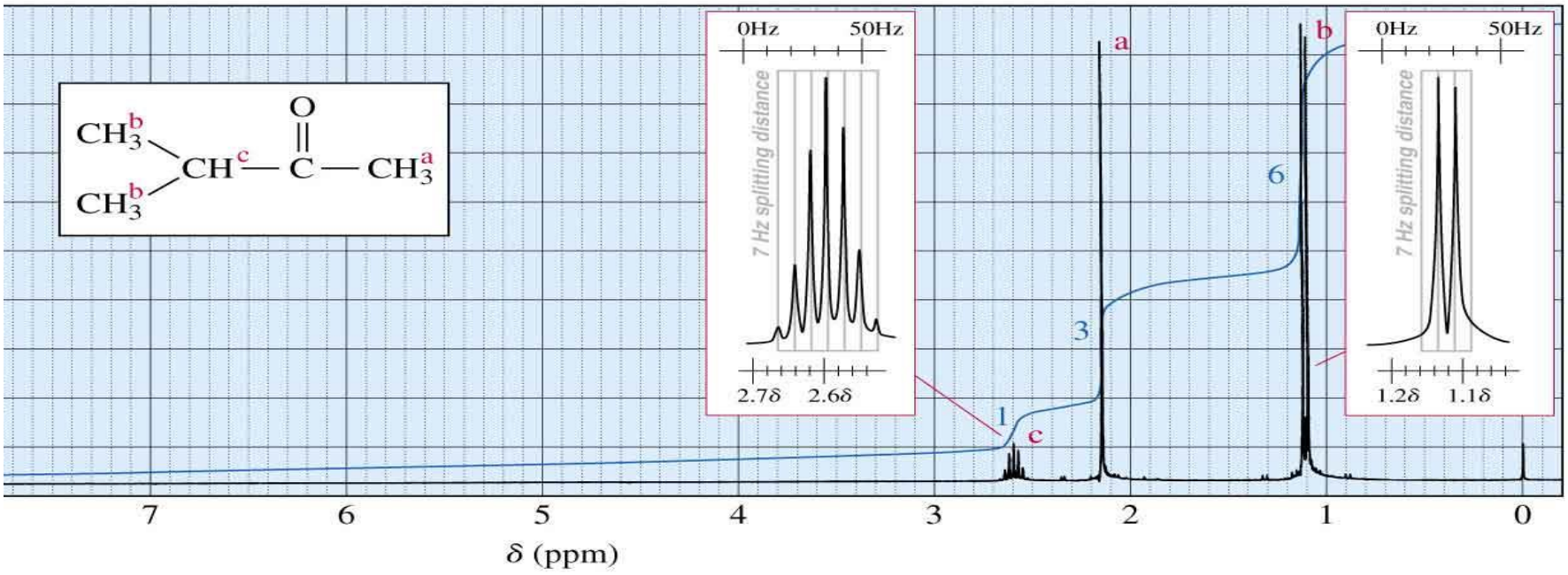
Interpretation of NMR Spectrum

- Different kinds of protons present in molecule
- The chemical shifts of the signals/peaks shown in the spectrum
- The intensity of a signal relative to others in the spectrum (integration).
- The splitting of peaks (multiplicity).

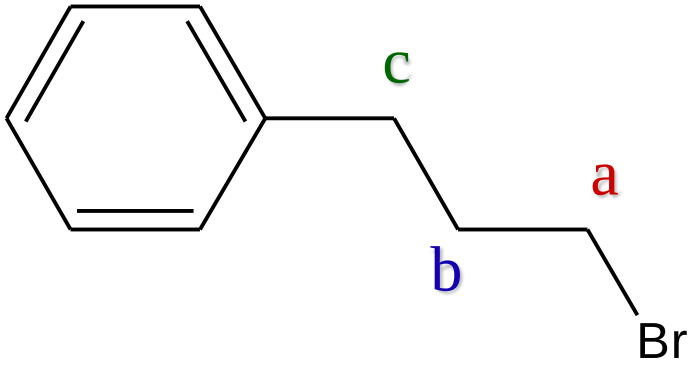
$C_2H_3Br_3$

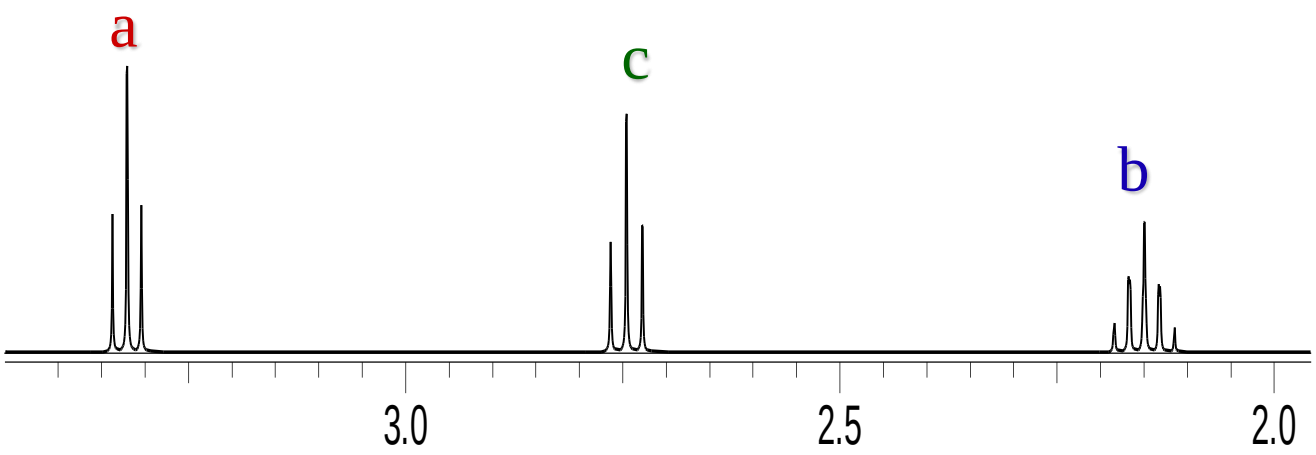


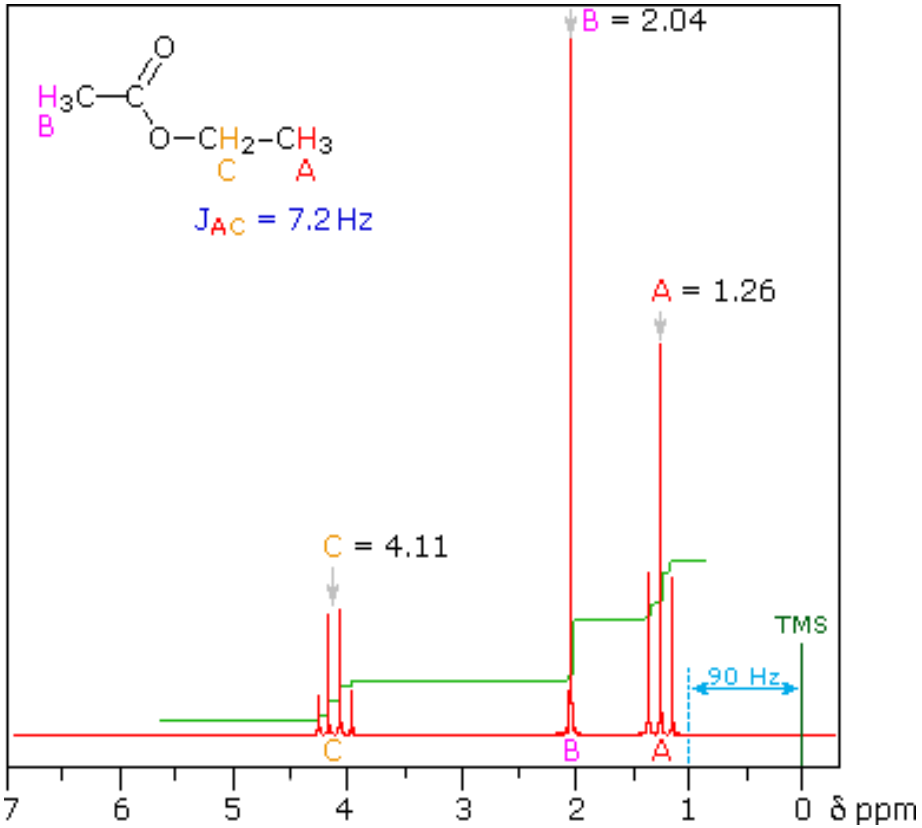
$C_5H_{10}O$

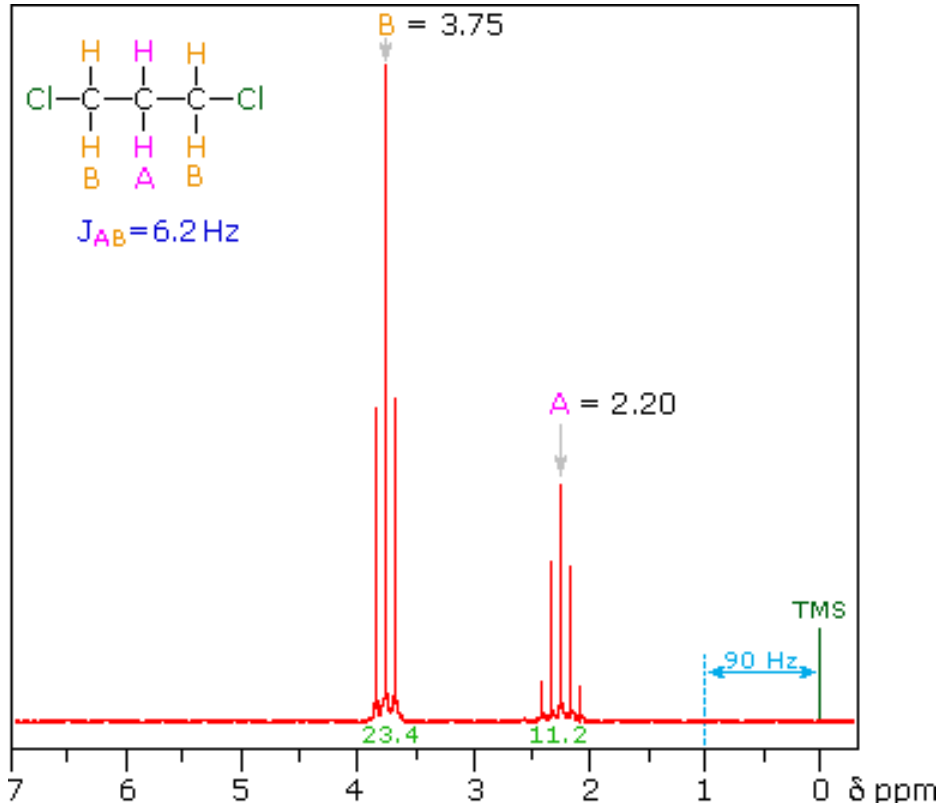

CH3b
CH3b
CHc
O
C
CH3a
0Hz
50Hz
7 Hz splitting distance
2.7δ
2.6δ
0Hz
50Hz
7 Hz splitting distance
1.2δ
1.1δ
a
b
c
1
3
6
7
6
5
4
3
2
1
0
δ (ppm)

2 x triplet
1 quintet



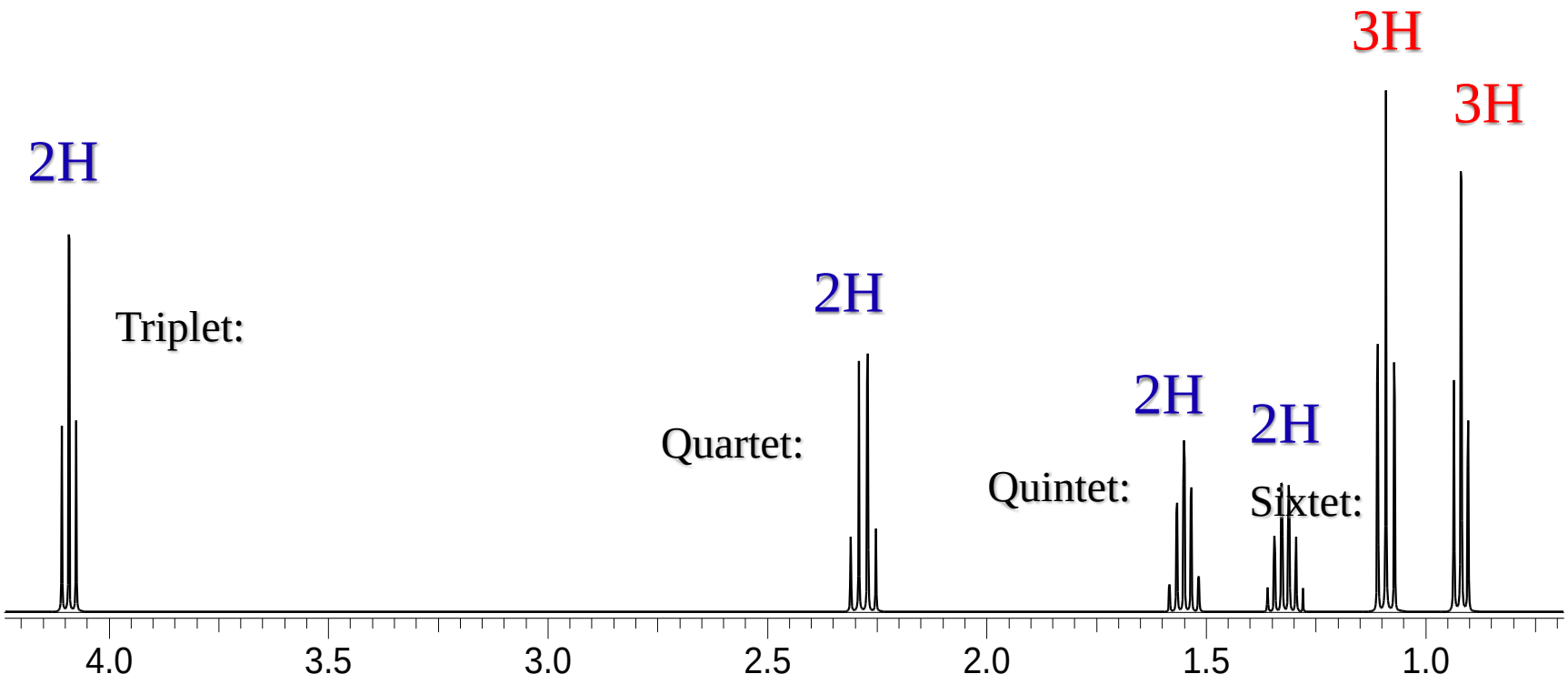


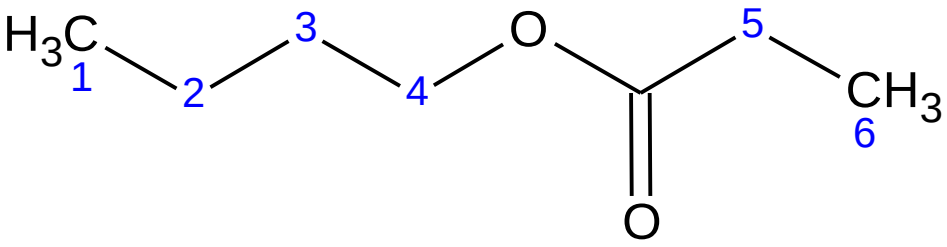

B = 2.04
A = 1.26
C = 4.11
TMS
90 Hz
C
B
A
7
6
5
4
3
2
1
0 δ ppm
JAC = 7.2 Hz

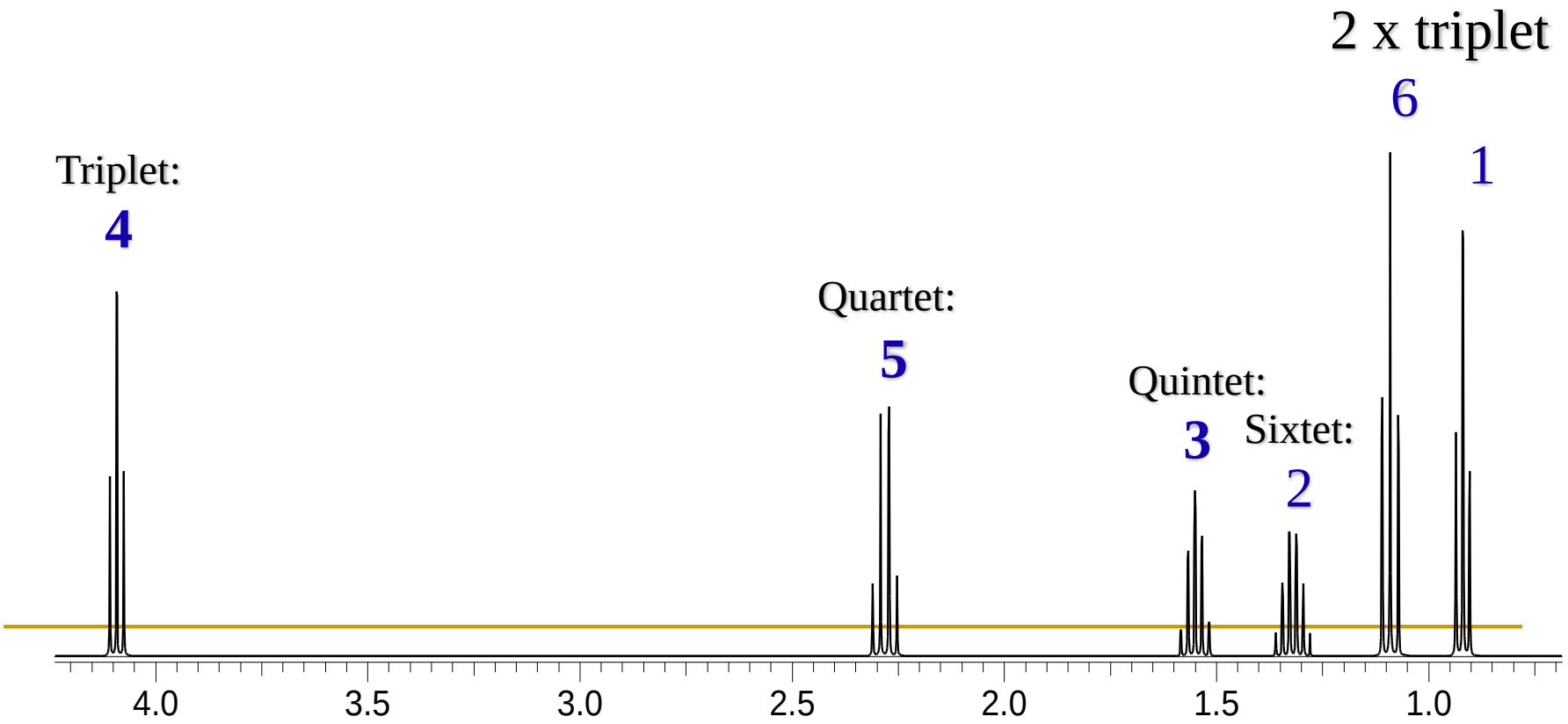

B = 3.75
A = 2.20
TMS
90 Hz
23.4
11.2
7
6
5
4
3
2
1
0 δ ppm
JAB = 6.2 Hz

C7 H14 O2
DU = 1

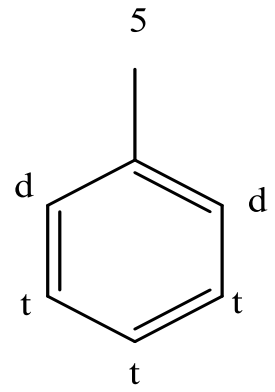
2 x triplet



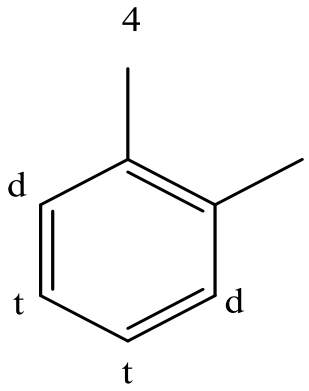

H3C
1
2
3
4
O
5
CH3
6
O

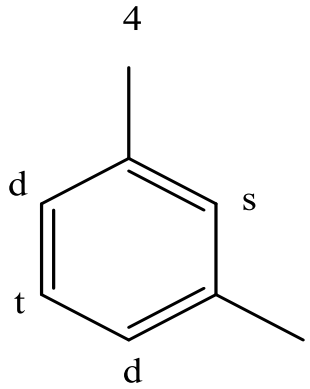

2 x triplet
6
1
Triplet:
4
Quartet:
5
Quintet:
3
Sixtet:
2
4.0
3.5
3.0
2.5
2.0
1.5
1.0

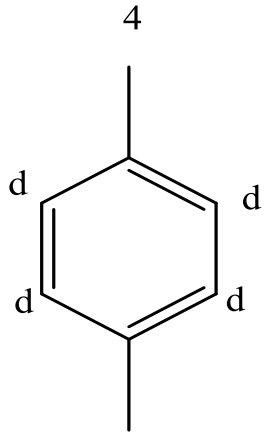
Aromatic Protons



Monosubistituted

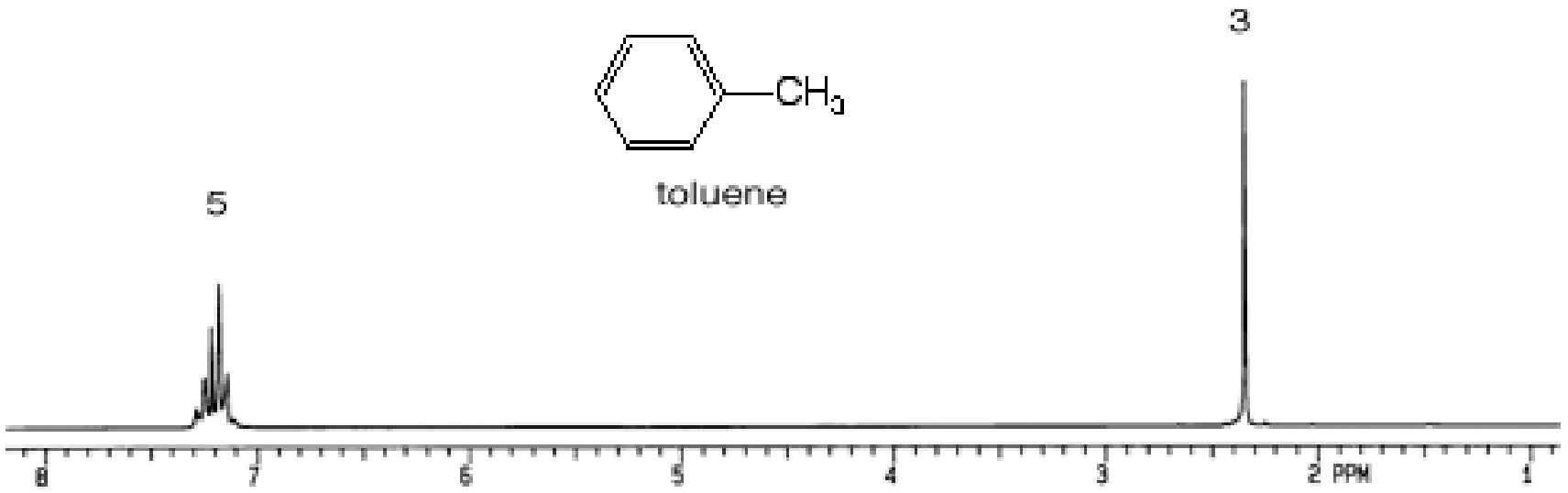


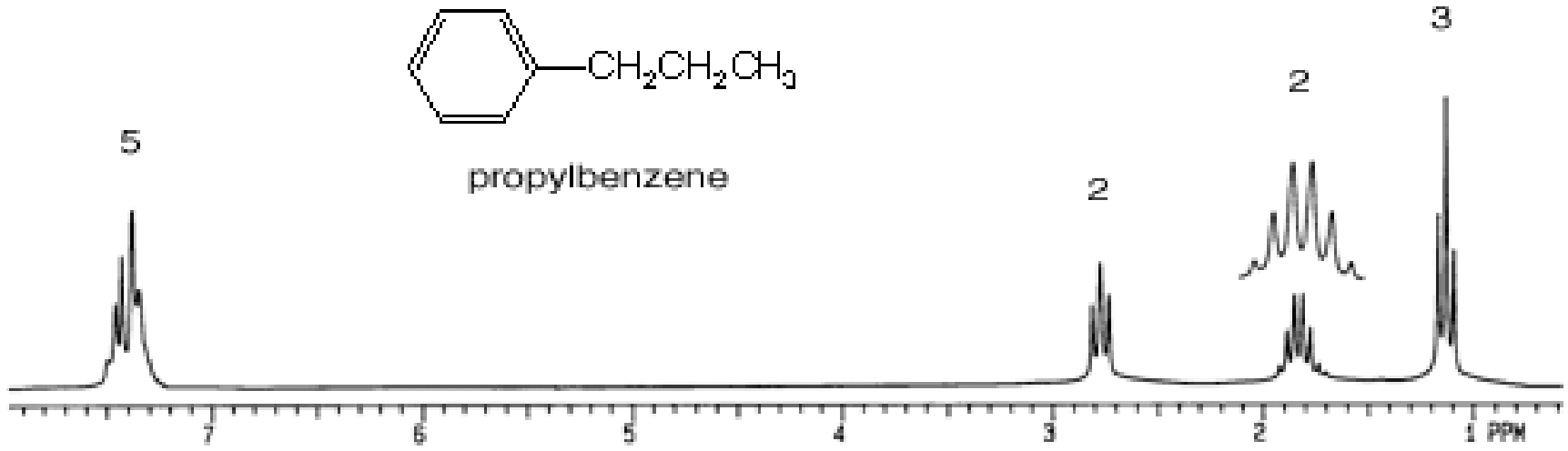


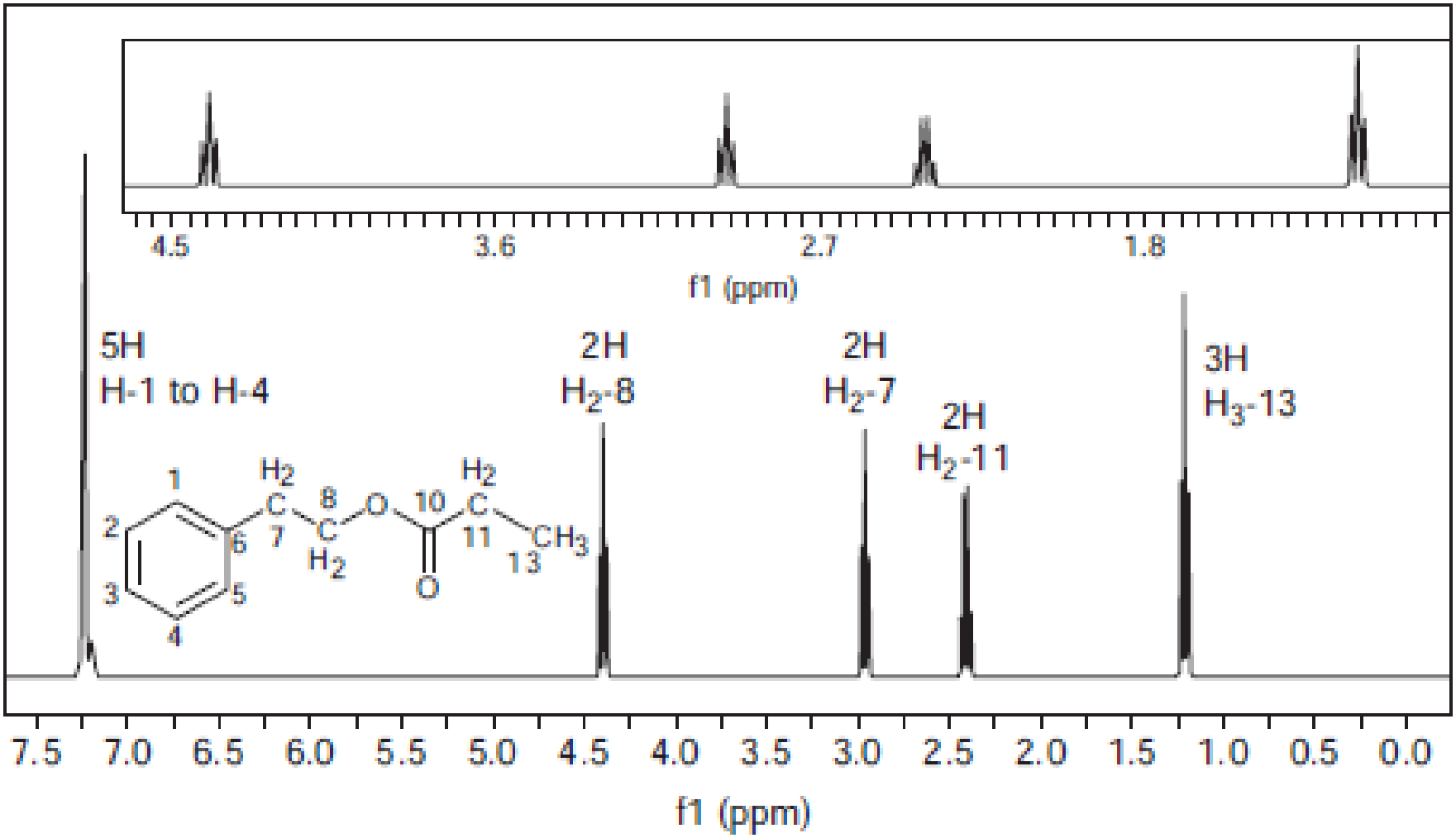


Disubistituted

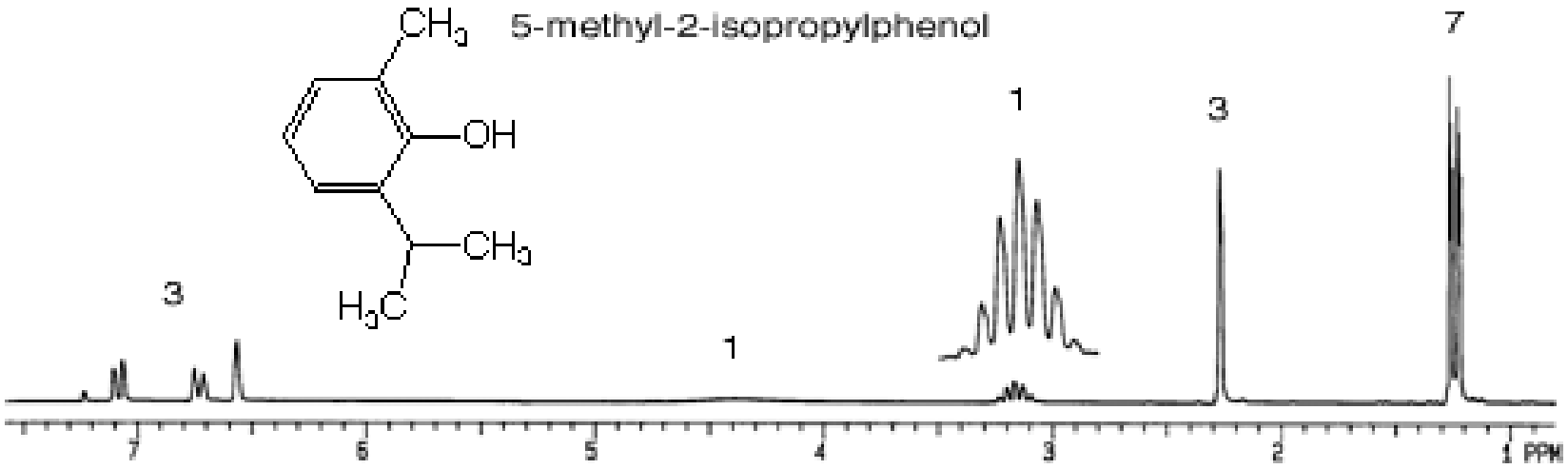
Aromatic Protons

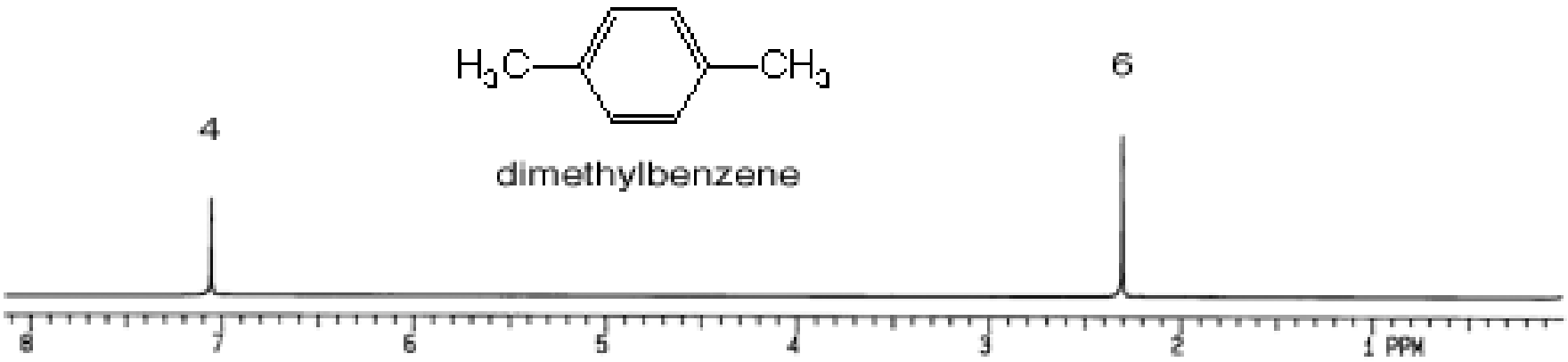


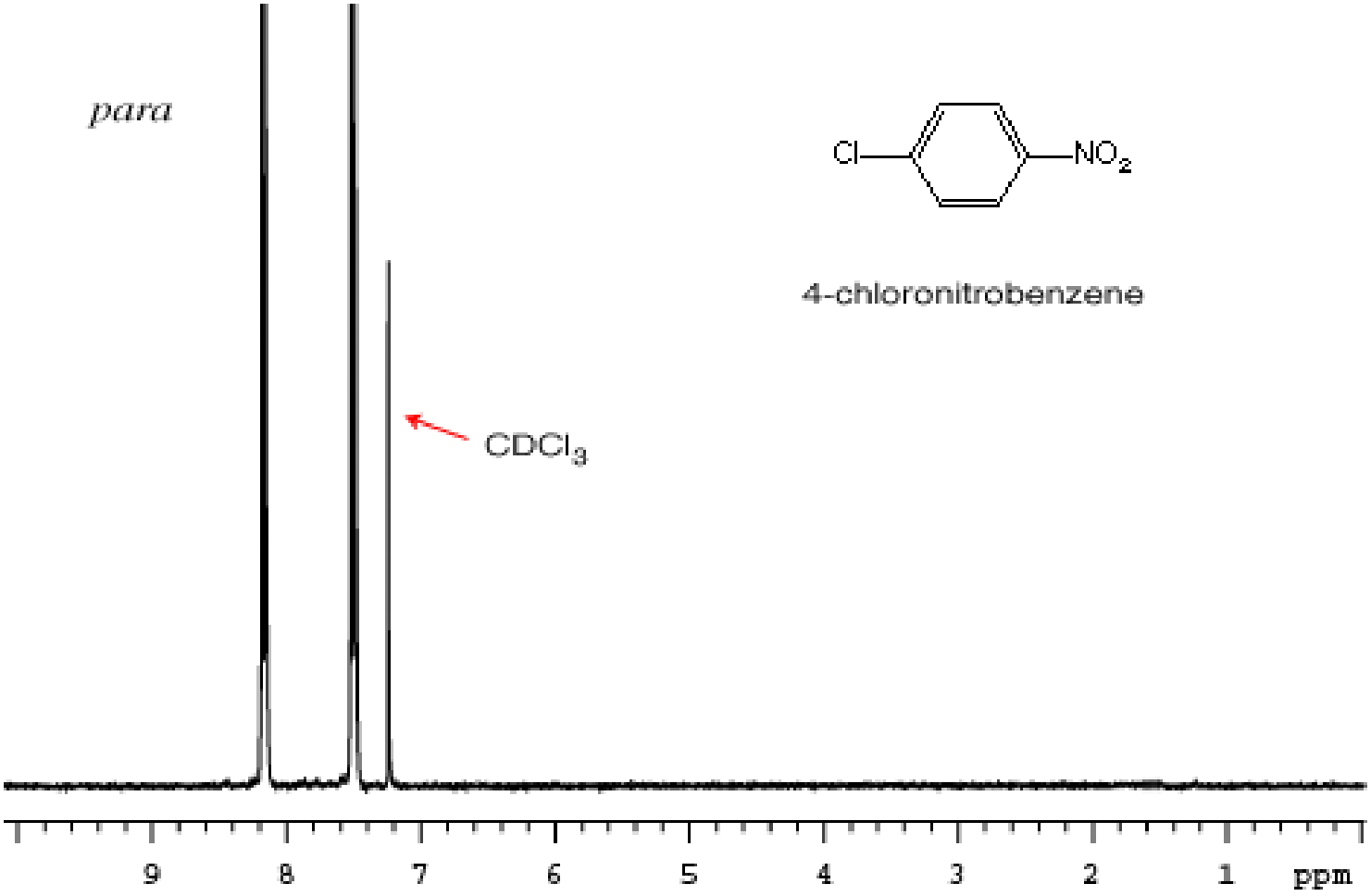



4.5
3.6
2.7
1.8
f1 (ppm)
5H
H-1 to H-4
2H
H2-8
2H
H2-7
2H
H2-11
3H
H3-13
1
2
3
4
5
6
H2
C
7
8
C
H2
O
10
O
H2
C
11
CH3
13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

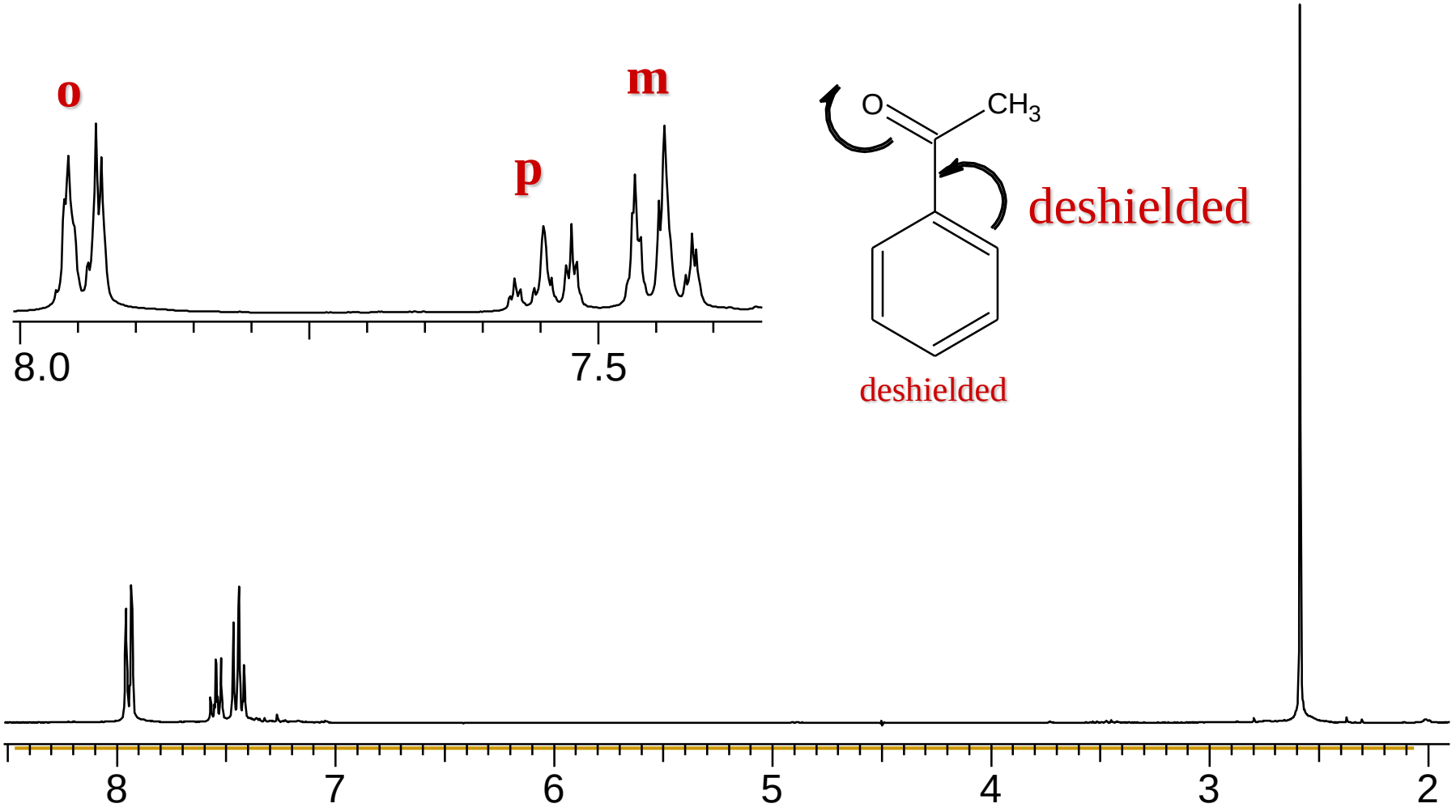
Aromatic Protons

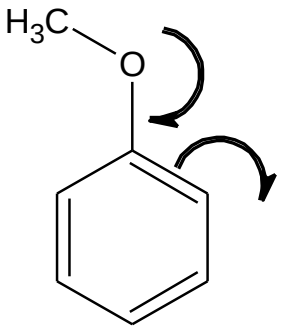





para
Cl
NO2
4-chloronitrobenzene
CDCl3
9
8
7
6
5
4
3
2
1
ppm

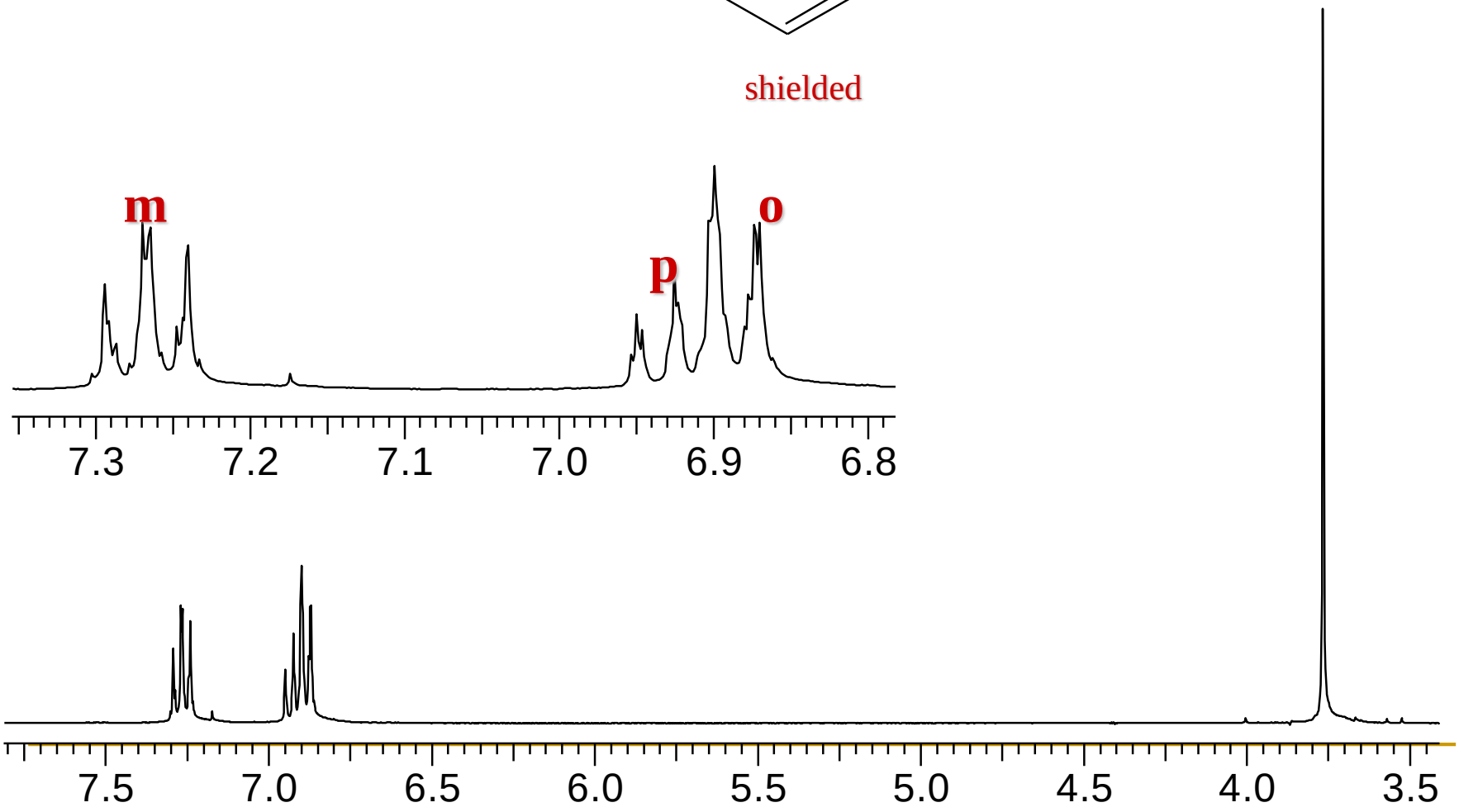
Electronic effects: conjugation with carbonyl



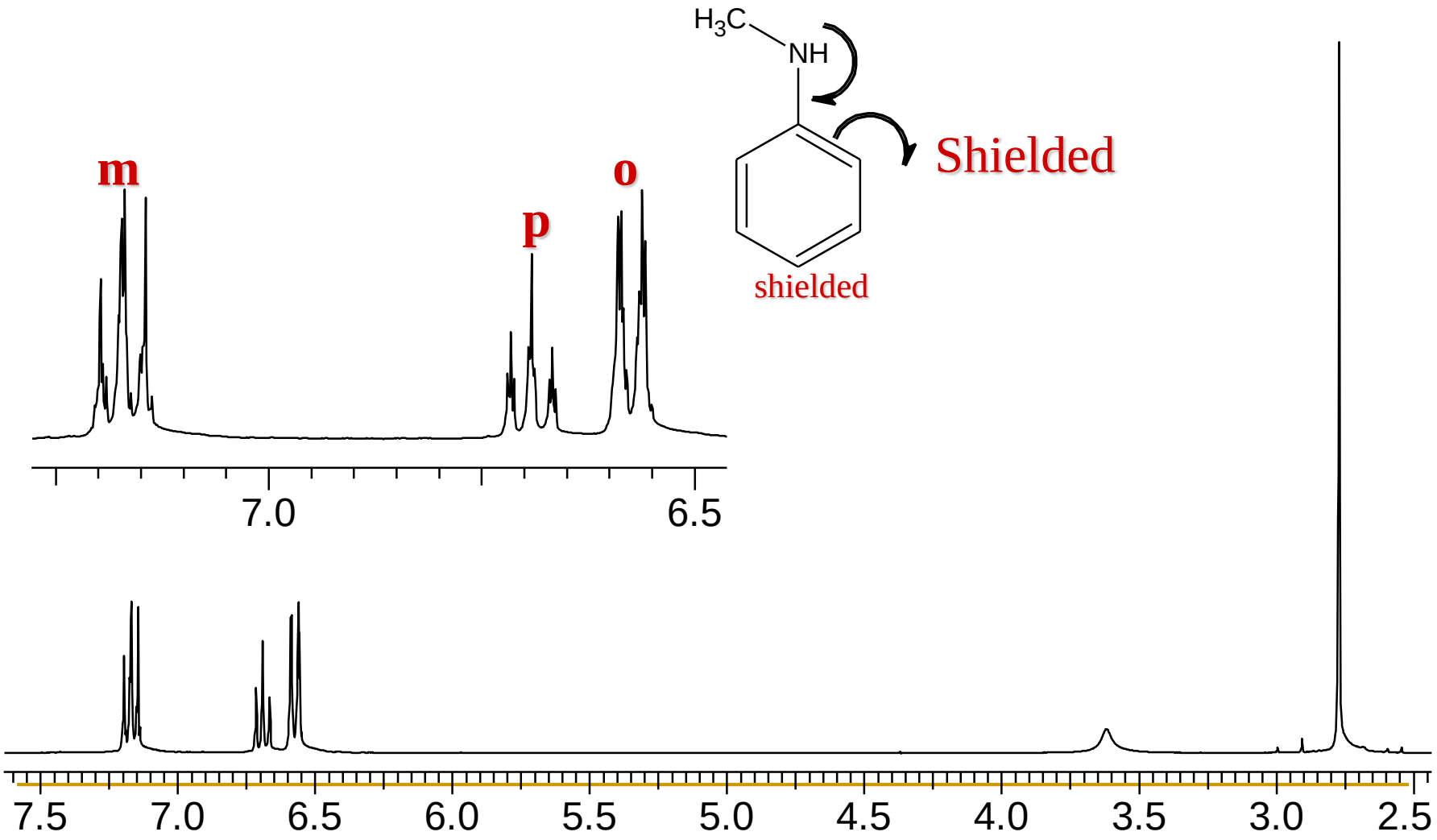


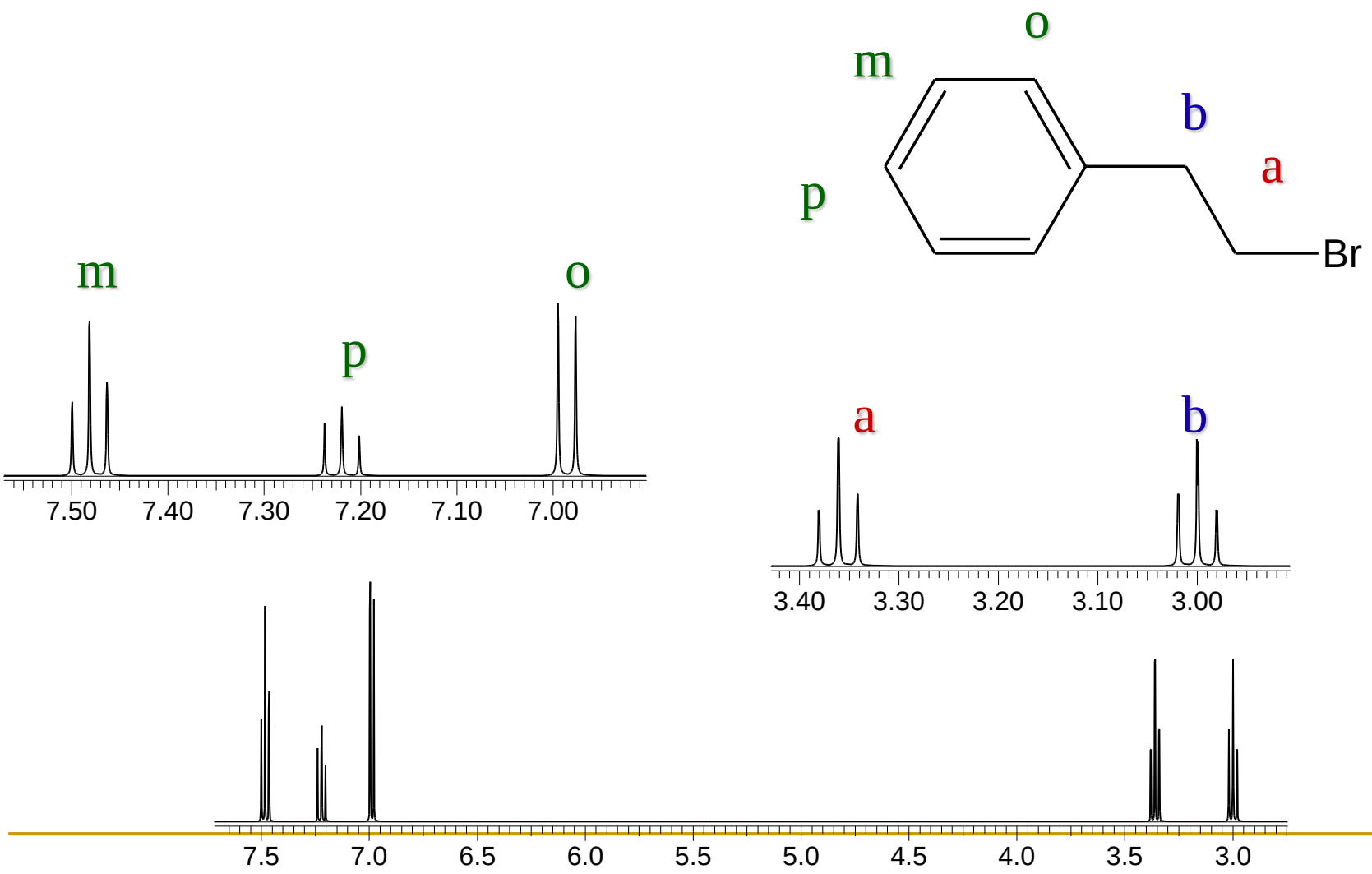
Shielded

shielded

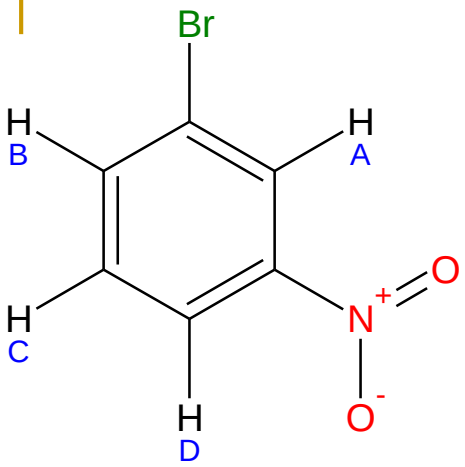


Electronic effects: conjugation with heteroatom



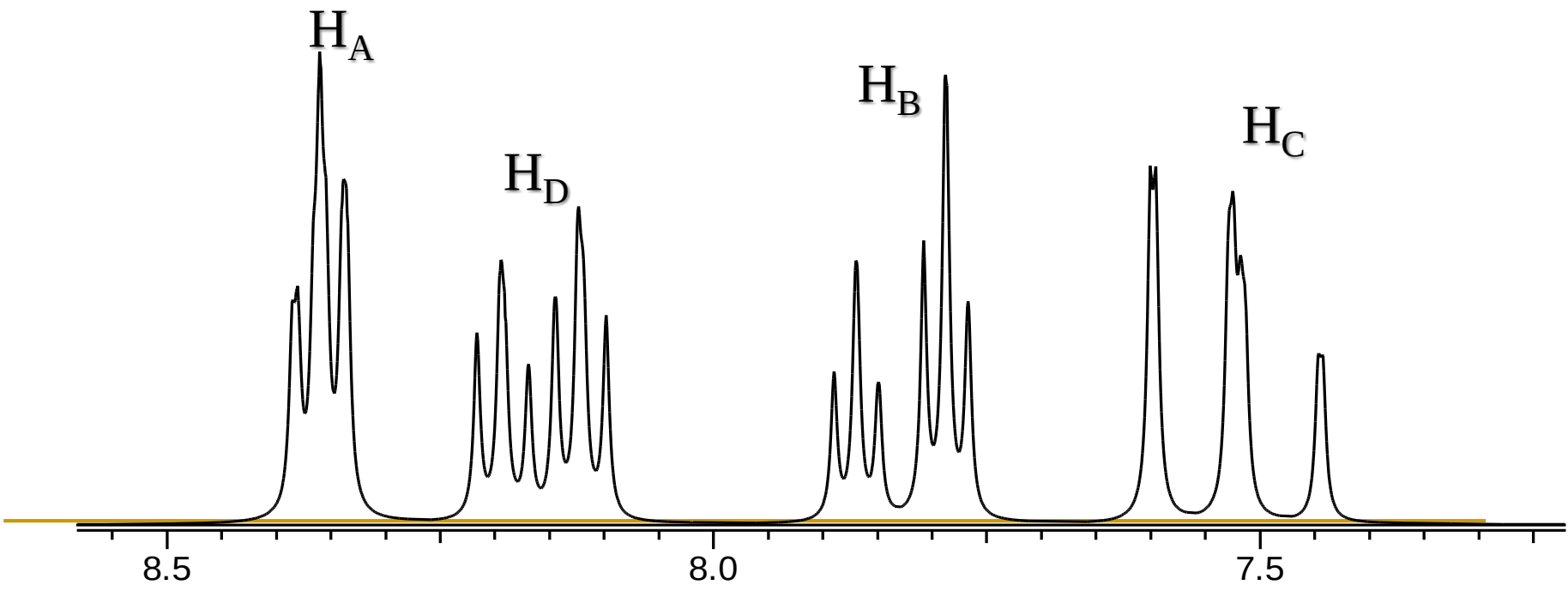

o
m
b
a
p
Br
m
o
p
7.50
7.40
7.30
7.20
7.10
7.00
a
b
3.40
3.30
3.20
3.10
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

meta bromo nitro benzene

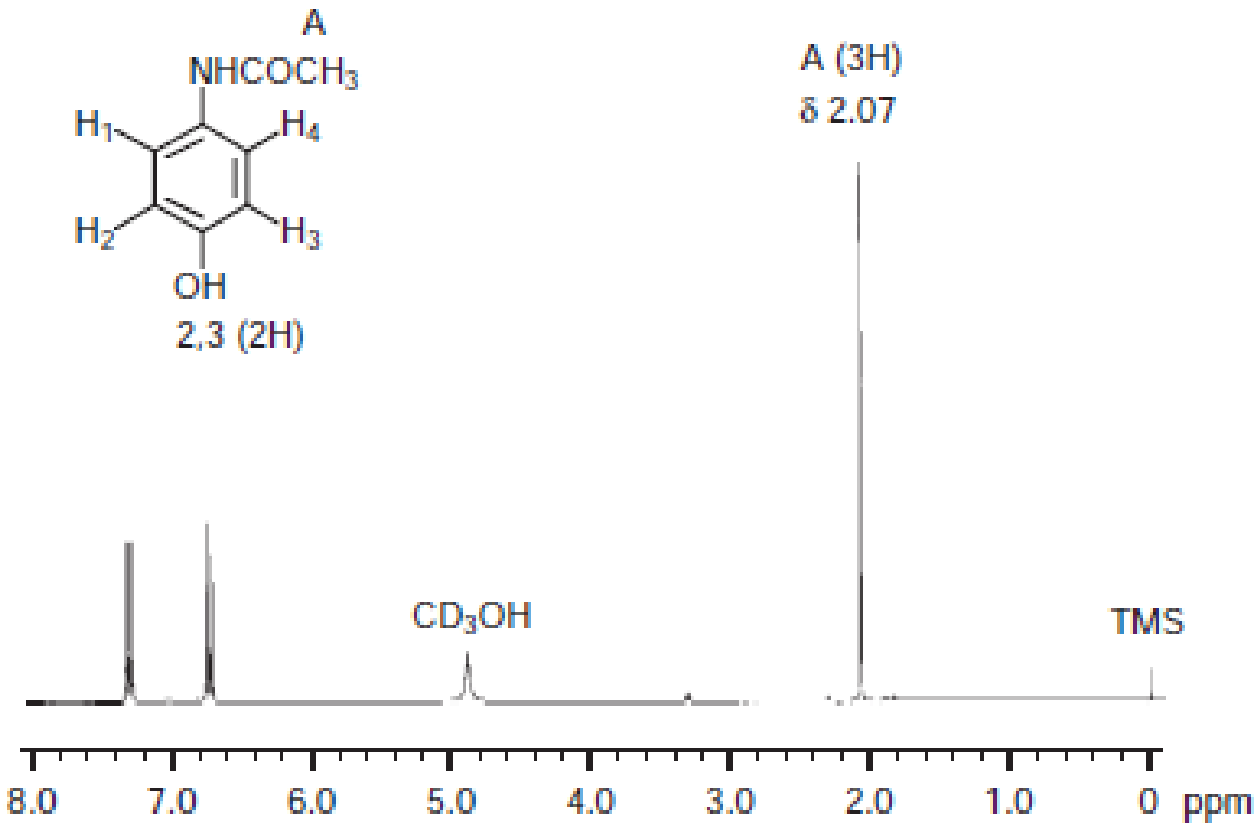


Calculated shifts

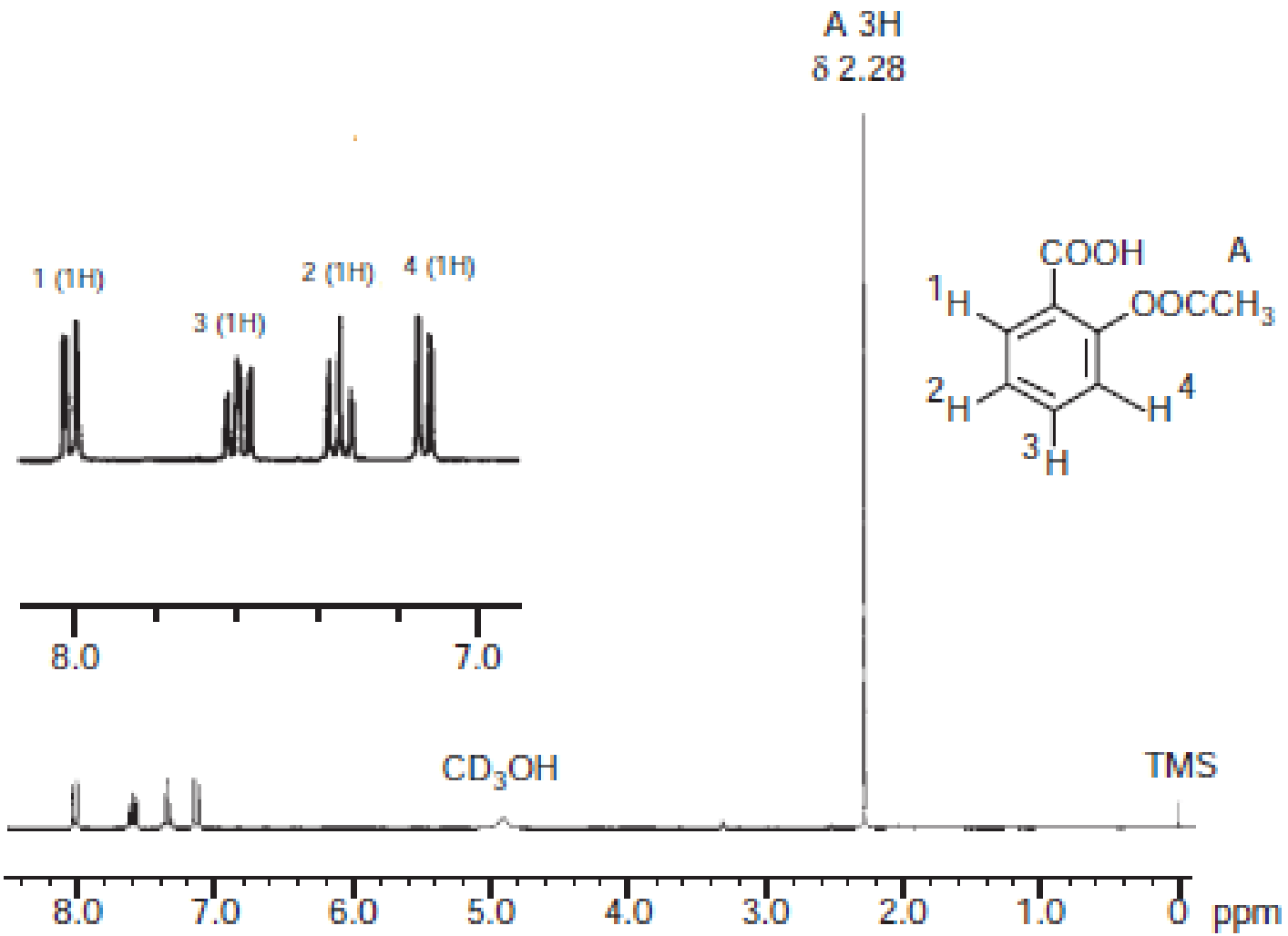
δH_A=8.44 δH_B=7.82 δH_C=7.31 δH_D=8.19

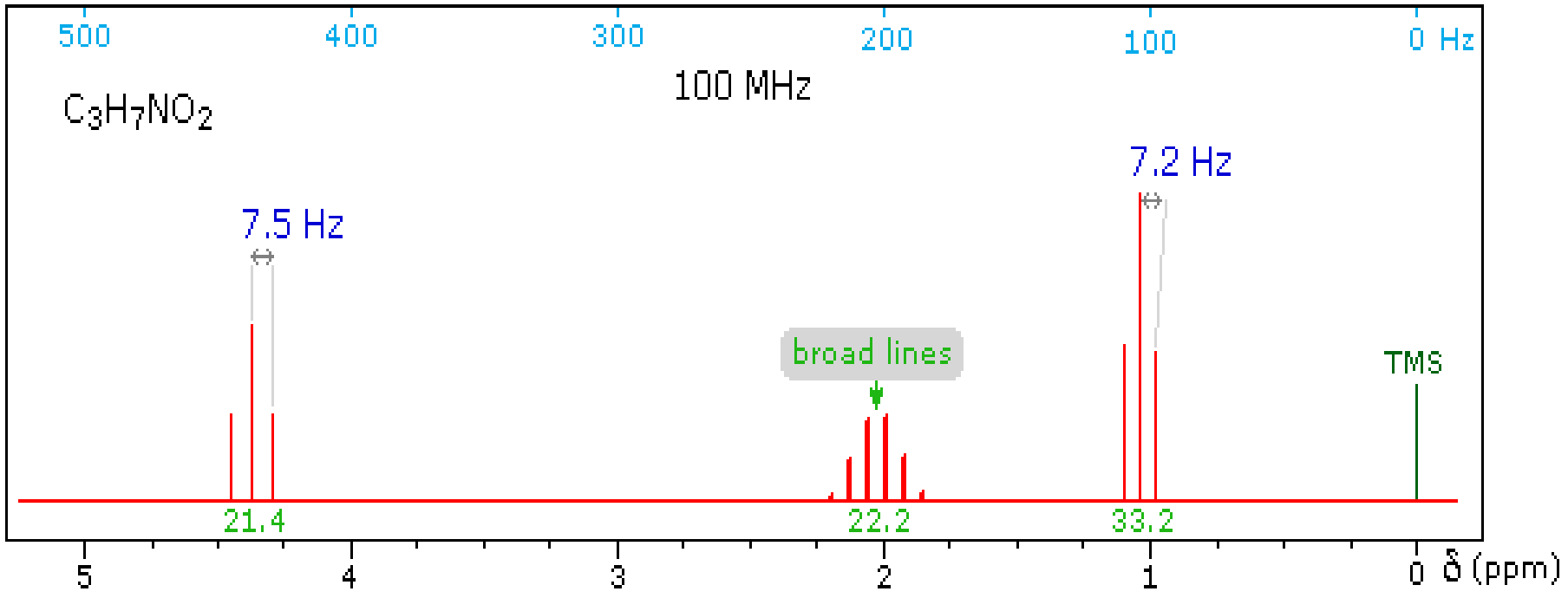


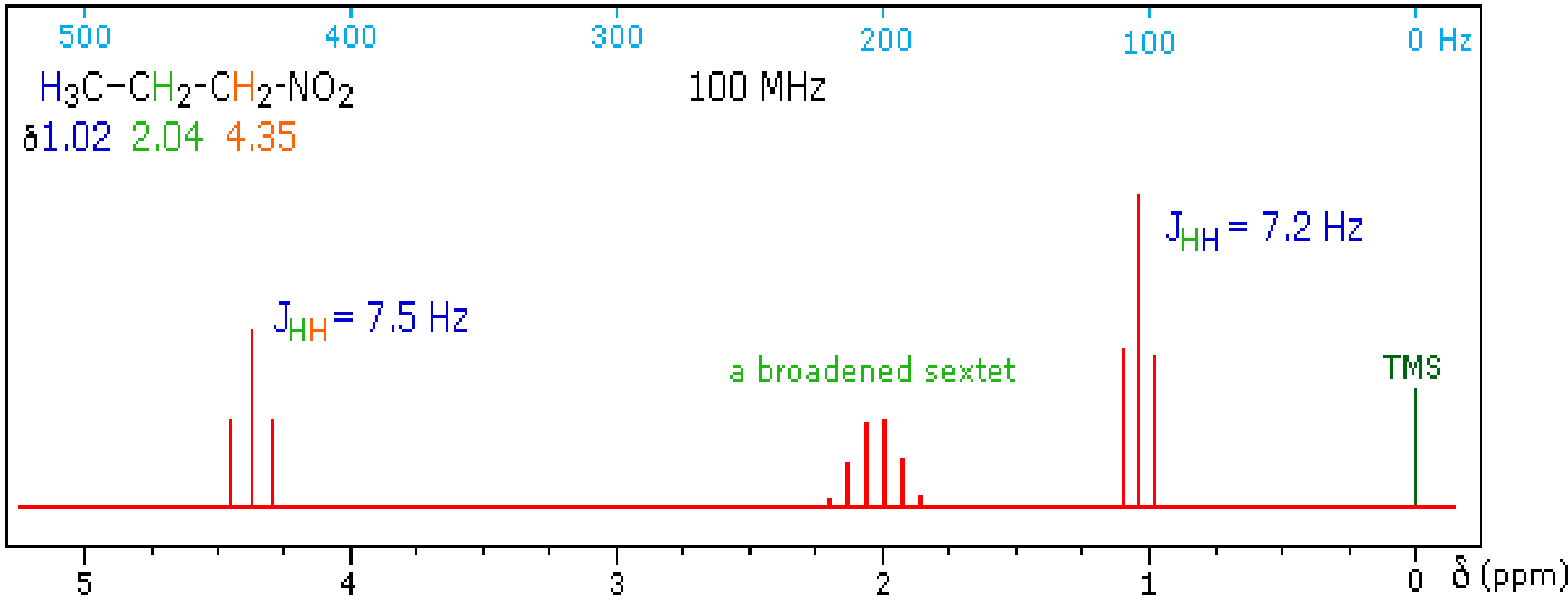
Paracetamol



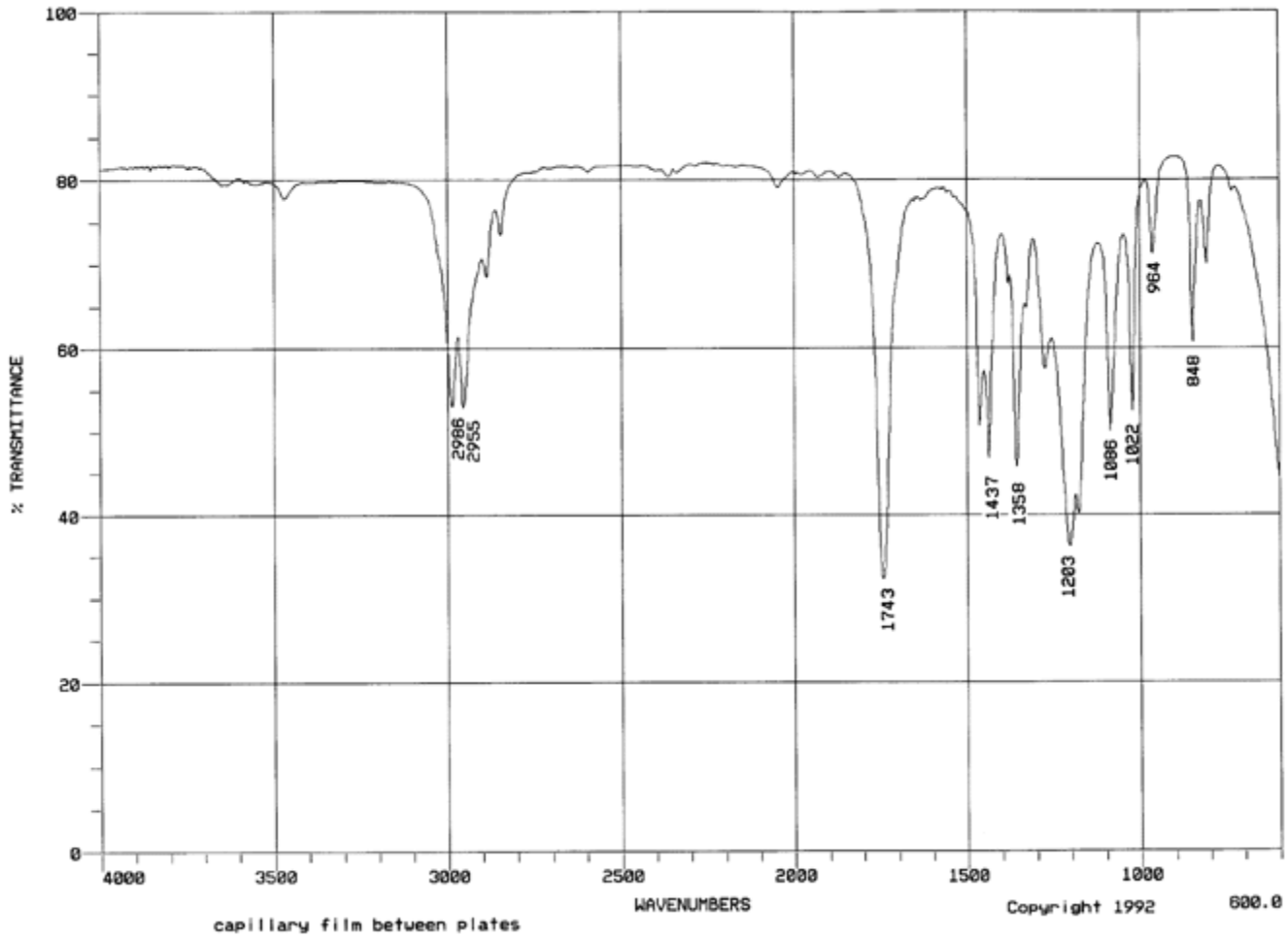
Aspirin

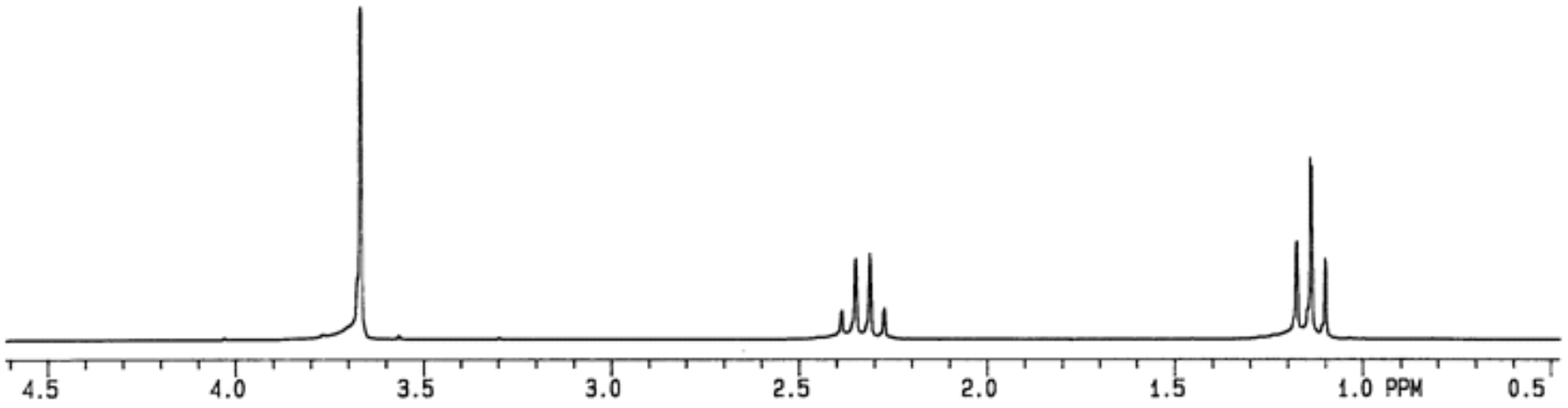

A 3H
δ 2.28
1 (1H)
3 (1H)
2 (1H)
4 (1H)
8.0
7.0
COOH
A
^{1}H
OOCCH$_3$
^{2}H
H^4
^{3}H
CD$_3$OH
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

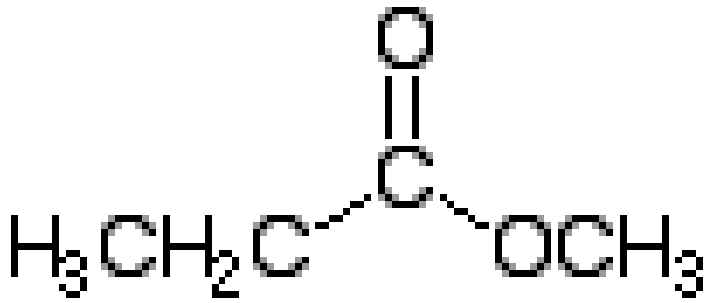

500
400
300
200
100
0 Hz
100 MHz
C3H7NO2
7.5 Hz
7.2 Hz
broad lines
TMS
21.4
22.2
33.2
5
4
3
2
1
0 δ (ppm)


500
400
300
200
100
0 Hz
H3C–CH2–CH2–NO2
100 MHz
δ1.02 2.04 4.35
JHH = 7.2 Hz
JHH = 7.5 Hz
a broadened sextet
TMS
5
4
3
2
1
0
δ (ppm)

$C_4H_8O_2$


100
80
60
40
20
0
% TRANSMITTANCE
2986
2955
1743
1437
1358
1203
1086
1022
964
848
4000
3500
3000
2500
2000
1500
1000
600.0
WAVENUMBERS
Copyright 1992
capillary film between plates


4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


O
C
H3CH2C
OCH3