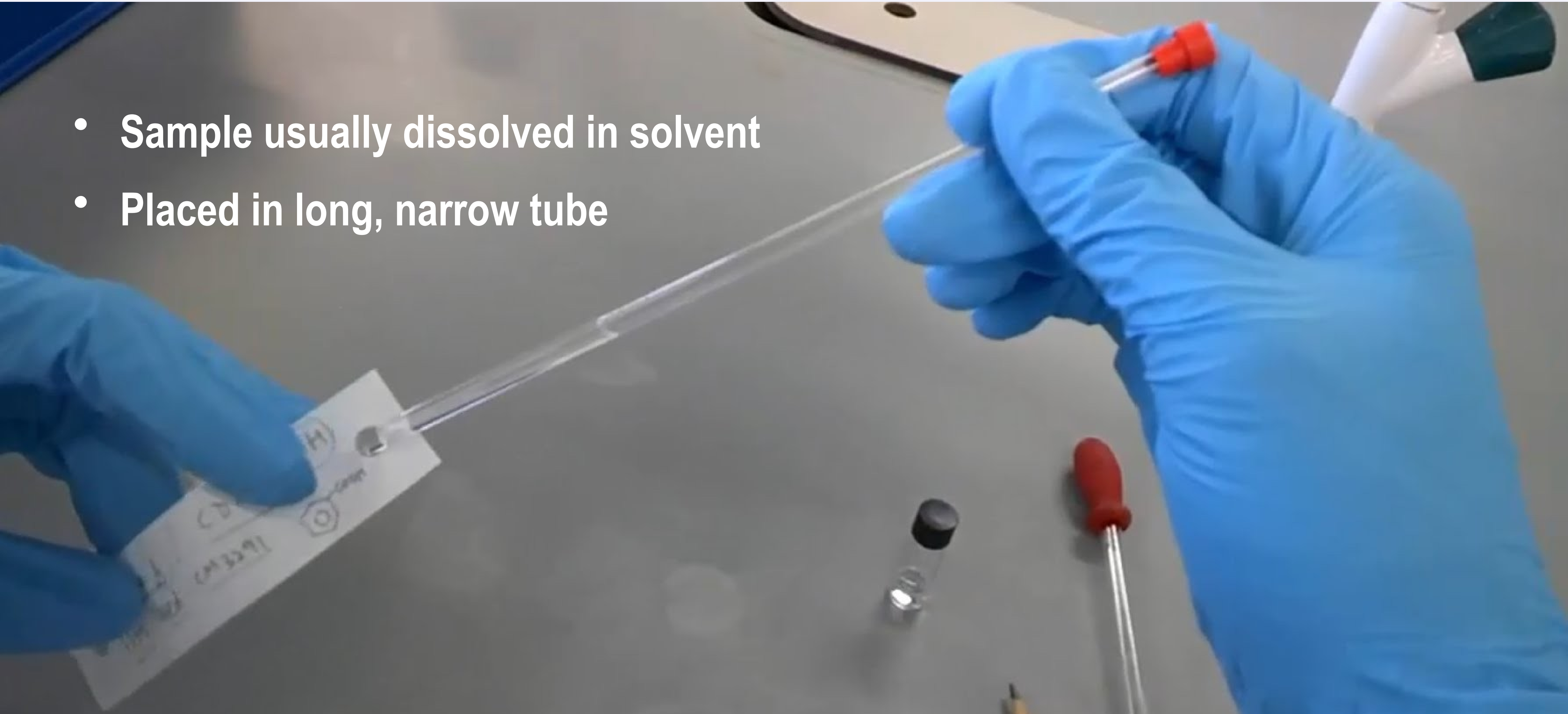
WWW.CHEMSHEETS.CO.UK

NMR

SPECTROSCOPY

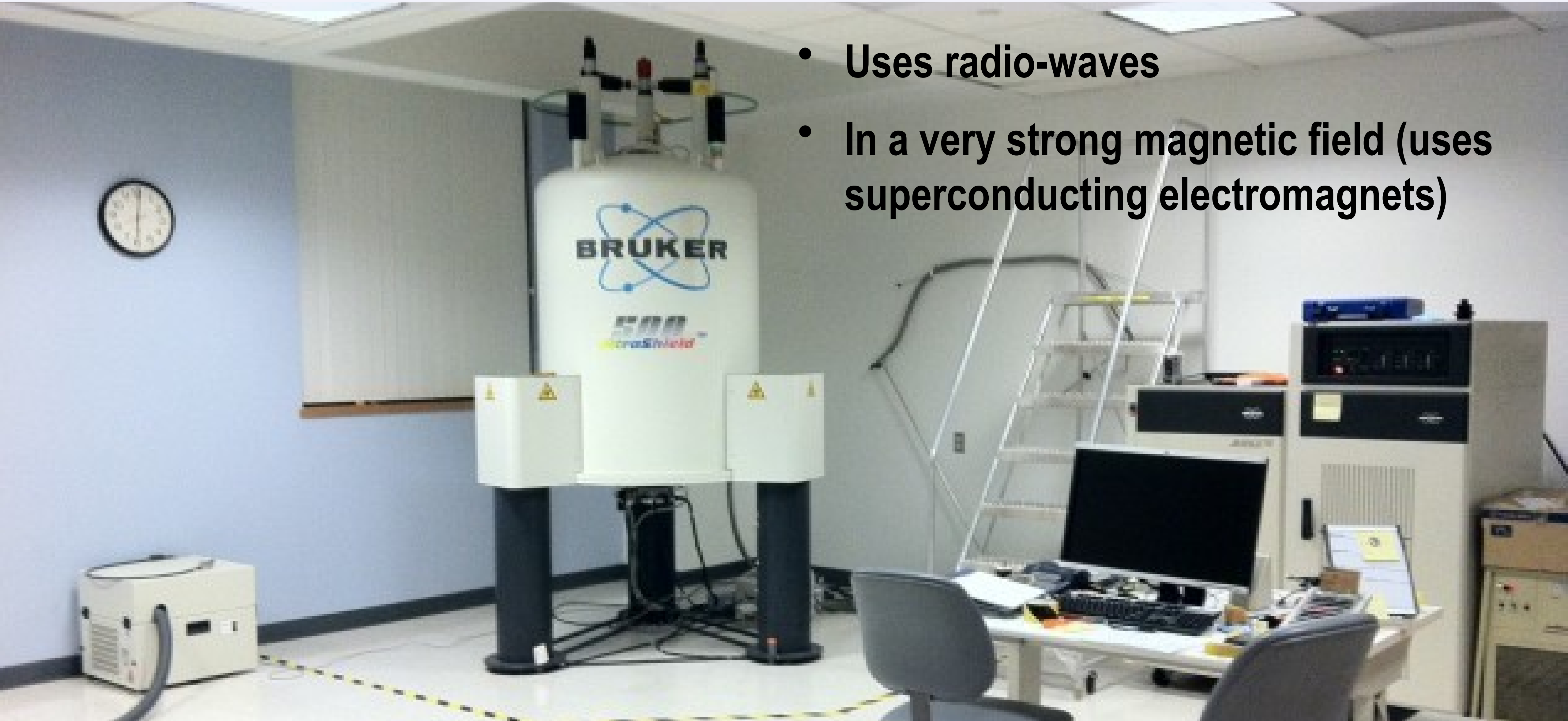
RUNNING A SPECTRUM



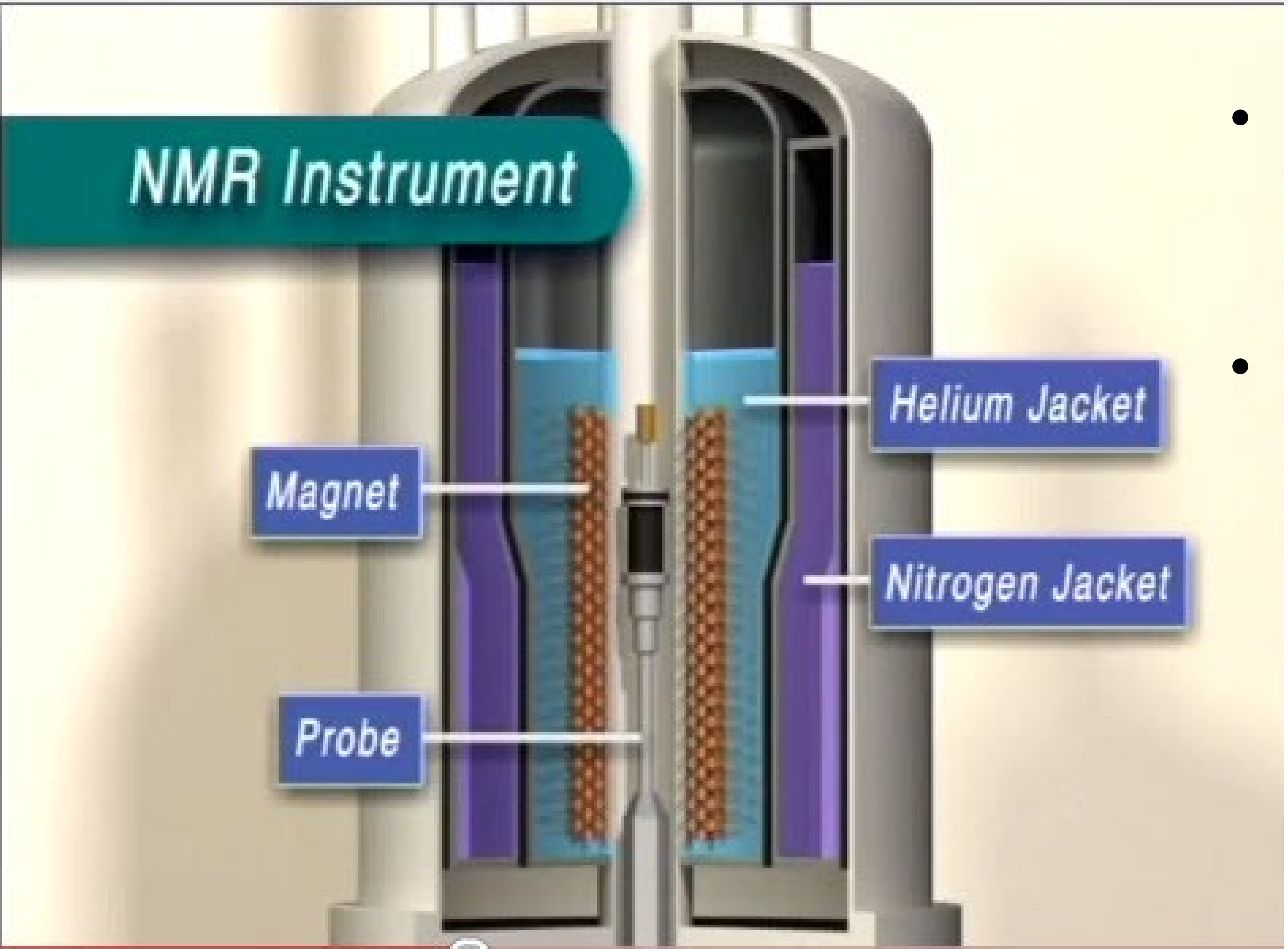
- Sample usually dissolved in solvent
- Placed in long, narrow tube

RUNNING A SPECTRUM

- Uses radio-waves
- In a very strong magnetic field (uses superconducting electromagnets)

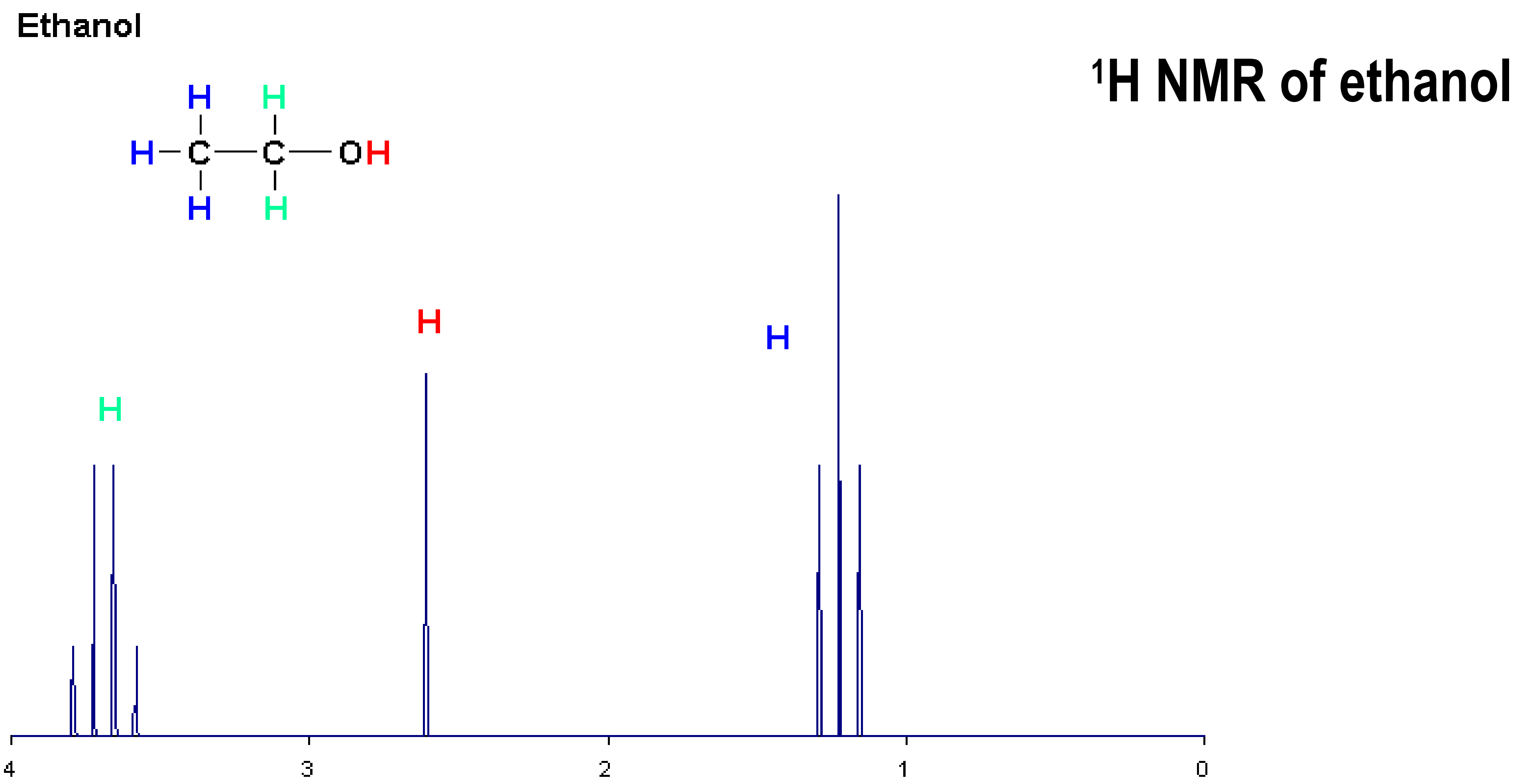


RUNNING A SPECTRUM



- Compound absorbs radio-waves to change the direction of 'spin' of the nucleus
- Used by organic chemists to look at ^{1}H and ^{13}C atoms

RUNNING A SPECTRUM

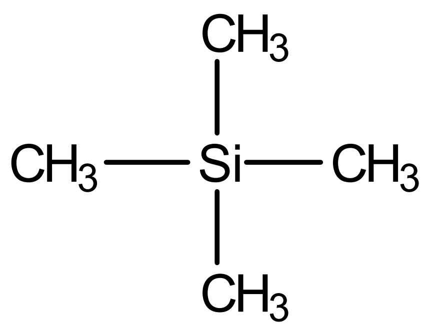


SOLVENTS

- Samples are dissolved in solvents free of ^1H atoms
- e.g. CCl_4, $CDCl_3$

CALIBRATION

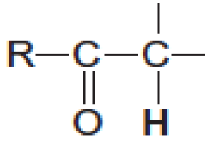
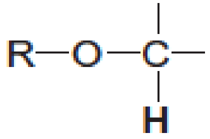
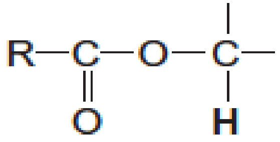
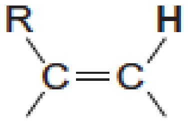
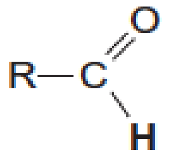
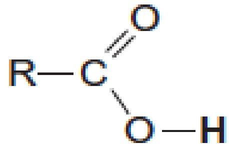
- Radio-wave absorptions are measured relative to those for TMS (tetramethylsilane) in ppm – this is called the chemical shift (δ)

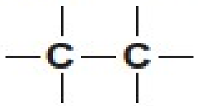
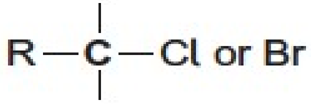
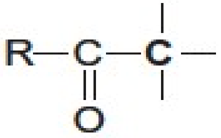
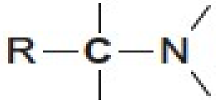
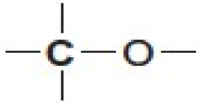
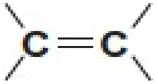
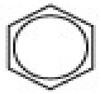
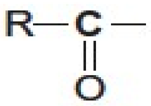
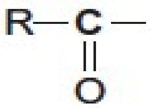


- TMS is used because:
  - its signal is away from all the others
  - it only gives one signal
  - it is non-toxic
  - it is inert

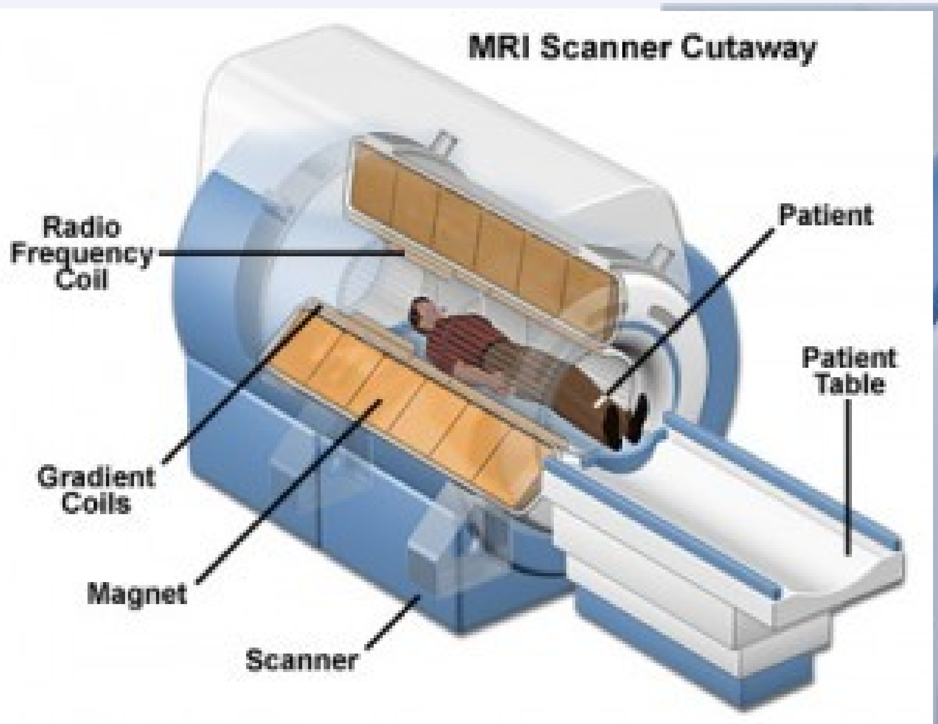
CHEMCIAL SHIFT

Chemical shift (δ) – the closer the H/C is to electronegative atoms and/or double bonds – the bigger the chemical shift

Type of proton	δ/ppm
ROH	0.5 – 5.0
RCH_3	0.7 – 1.2
RNH_2	1.0 – 4.5
R_2CH_2	1.2 – 1.4
R_3CH	1.4 – 1.6
	2.1 – 2.6
	3.1 – 3.9
RCH_2Cl or Br	3.1 – 4.2
	3.7 – 4.1
	4.5 – 6.0
	9.0 – 10.0
	10.0 – 12.0

Type of carbon		δ/ppm
		5 – 40
		10 – 70
		20 – 50
		25 – 60
	alcohols, ethers or esters	50 – 90
		90 – 150
$R-C\equiv N$		110 – 125
		110 – 160
	esters or acids	160 – 185
	aldehydes or ketones	190 – 220

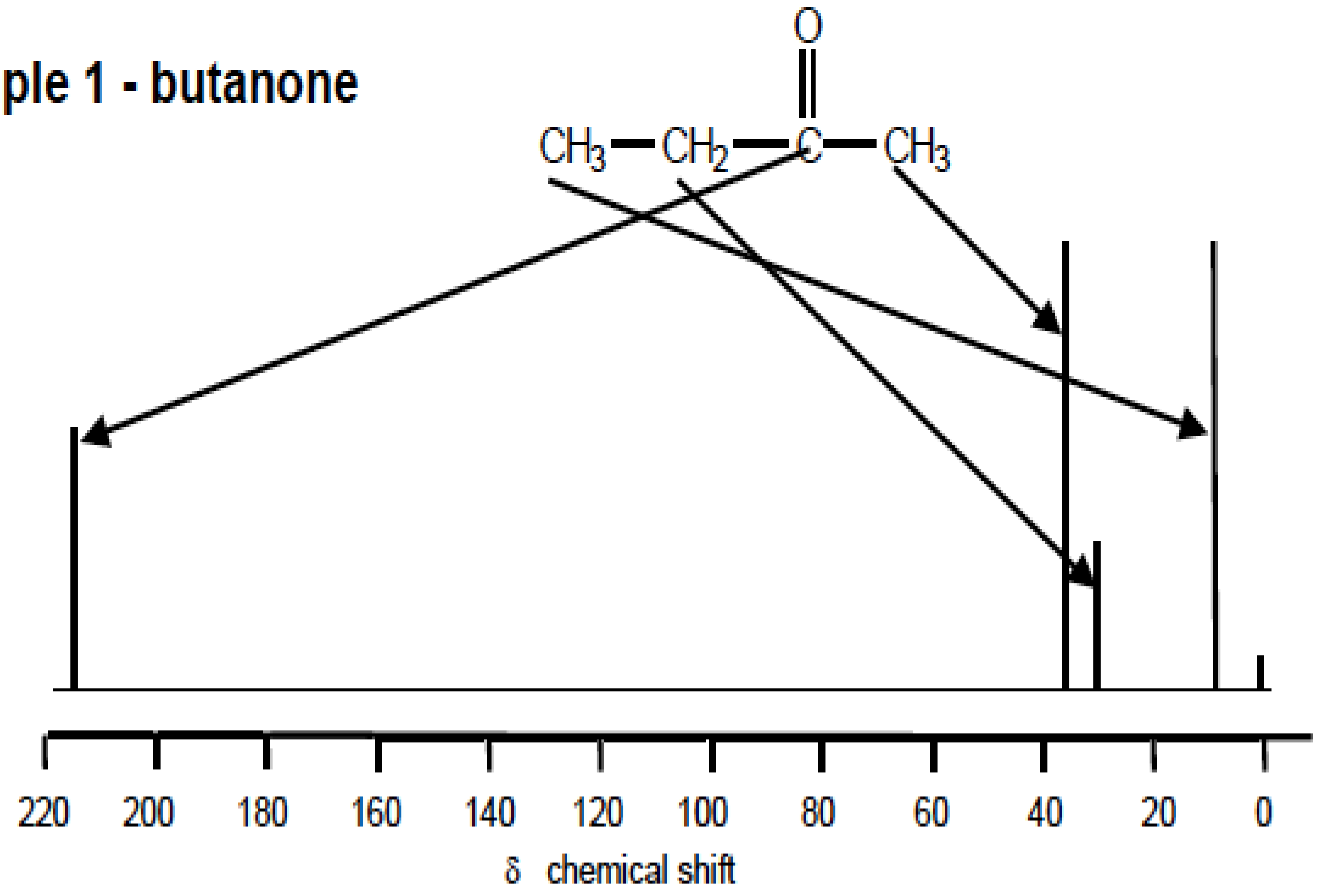
MRI SCANNERS



	Similar or different	^{1}H NMR	^{13}C NMR
Number of signals	similar	One signal for each set of equivalent ^{1}H or ^{13}C atoms	
Position of signal	similar	The closer the atom to a very electronegative atom and/or double bond, the greater the chemical shift	
Relative size of signals	different	Relative area of signals related to relative number of ^{1}H atoms	No link between area of signal to number of ^{13}C atoms
Splitting of signals	different	Signal split by ^{1}H atoms on adjacent atom (into doublets, triplets, etc)	No splitting

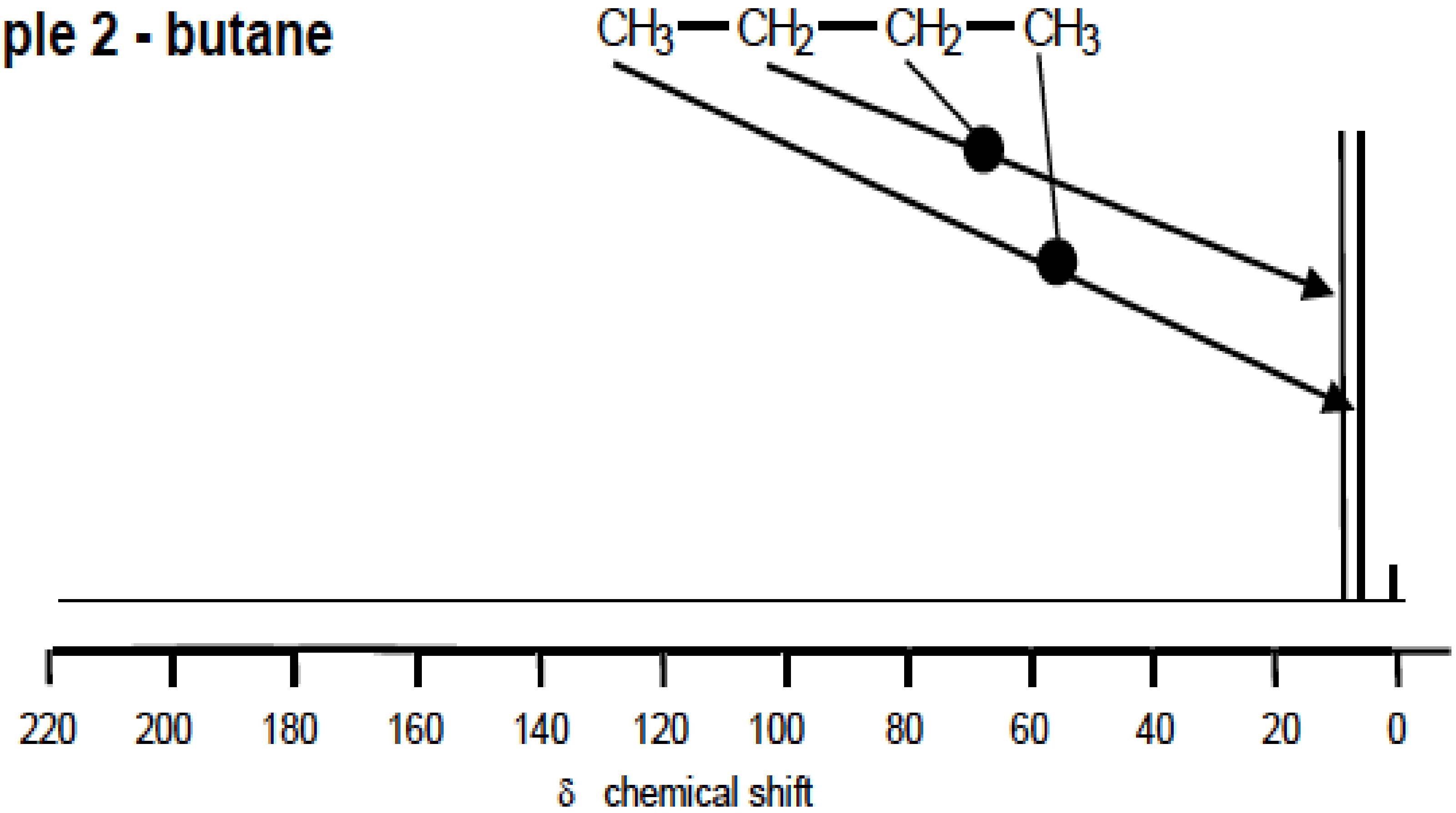
13C NMR SPECTROSCOPY

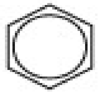
Example 1 - butanone



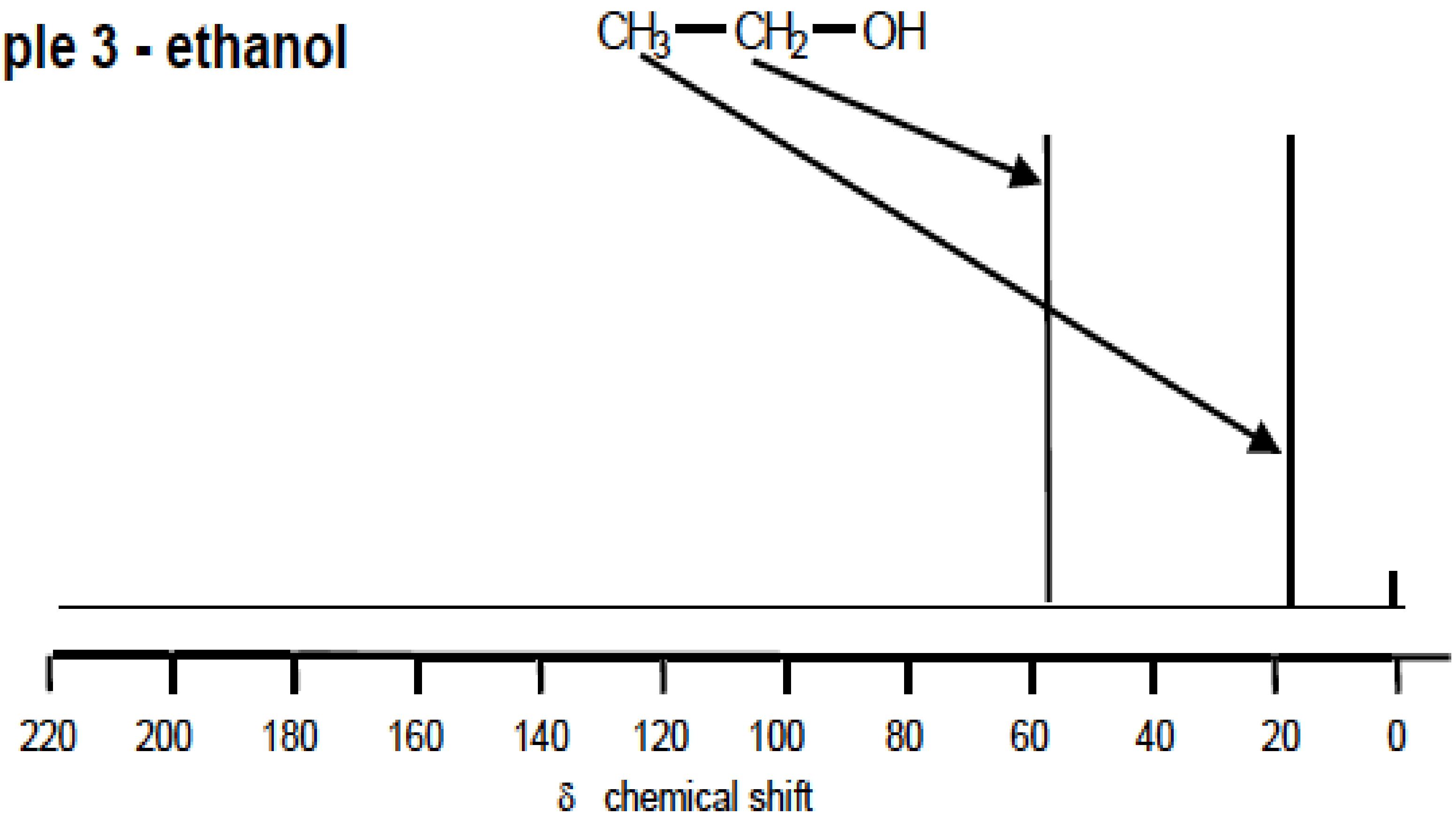
Type of carbon		δ/ppm
—C—C—		5 – 40
R—C—Cl or Br		10 – 70
R—C(=O)—C—		20 – 50
R—C—N		25 – 60
—C—O—	alcohols, ethers or esters	50 – 90
C=C		90 – 150
R—C≡N		110 – 125
benzene ring		110 – 160
R—C(=O)—	esters or acids	160 – 185
R—C(=O)—	aldehydes or ketones	190 – 220

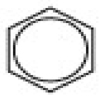
Example 2 - butane



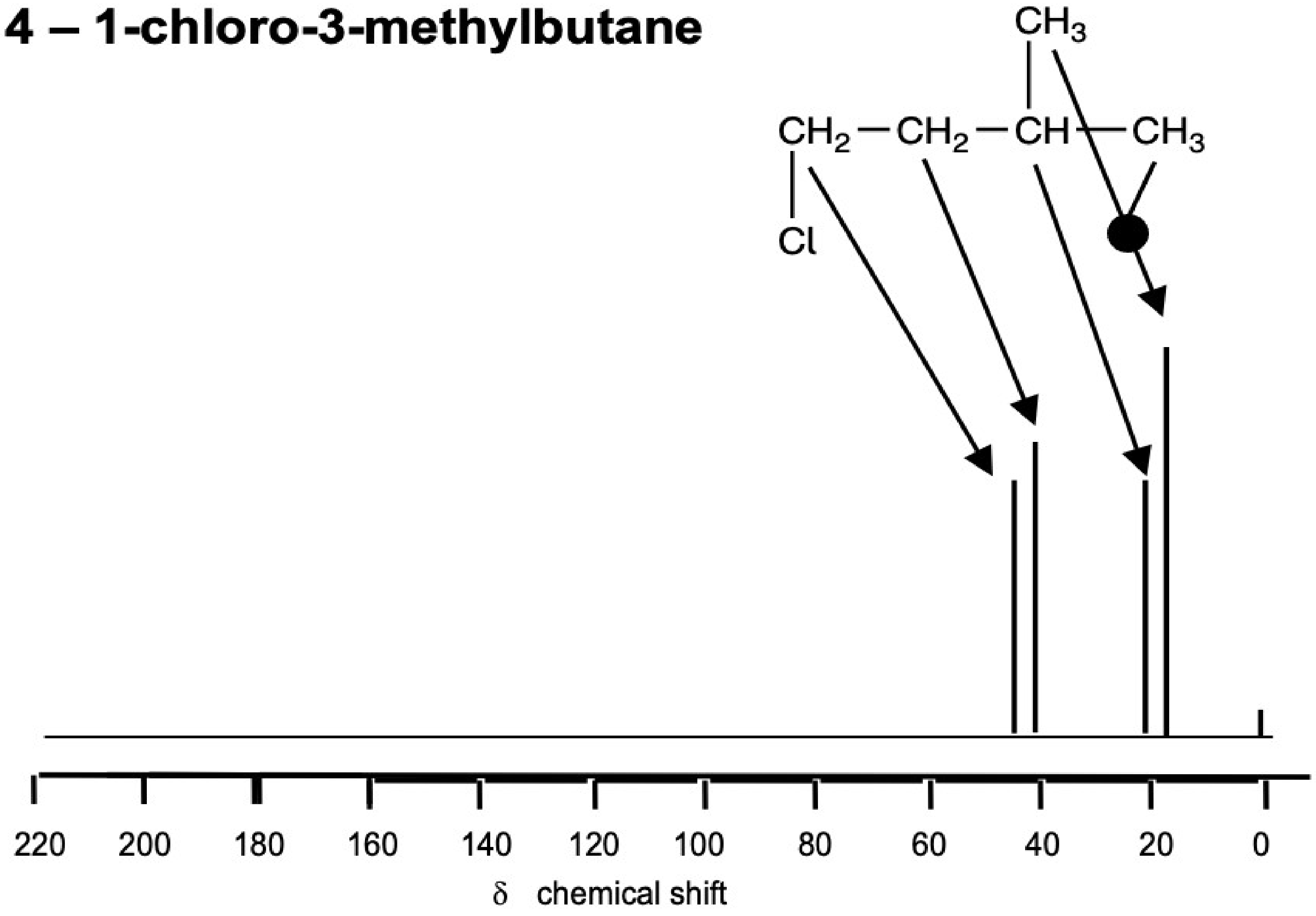
Type of carbon	δ/ppm
—C—C—	5 – 40
R—C—Cl or Br	10 – 70
R—C(=O)—C—	20 – 50
R—C—N	25 – 60
—C—O— alcohols, ethers or esters	50 – 90
C=C	90 – 150
R—C≡N	110 – 125
	110 – 160
R—C(=O)— esters or acids	160 – 185
R—C(=O)— aldehydes or ketones	190 – 220

Example 3 - ethanol



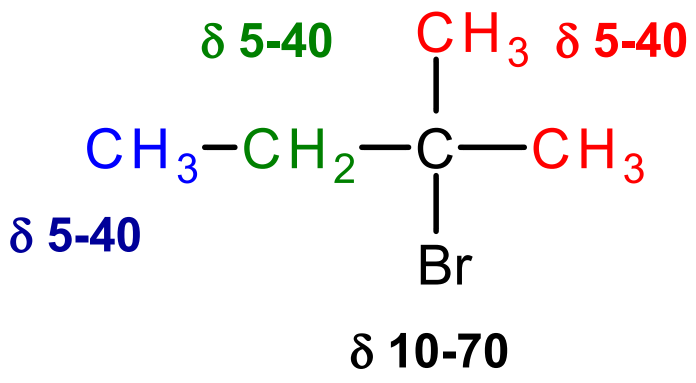
Type of carbon		δ/ppm
—C—C—		5–40
R—C—Cl or Br		10–70
R—C(=O)—C—		20–50
R—C—N		25–60
—C—O—	alcohols, ethers or esters	50–90
C=C		90–150
R—C≡N		110–125
		110–160
R—C(=O)—	esters or acids	160–185
R—C(=O)—	aldehydes or ketones	190–220

Example 4 – 1-chloro-3-methylbutane

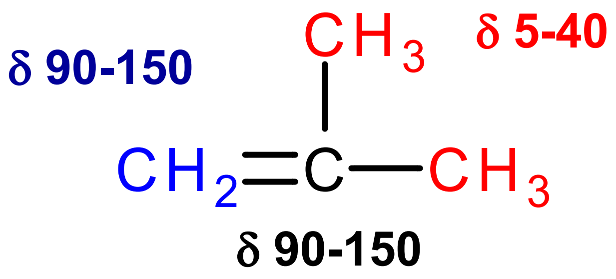


Type of carbon	δ/ppm
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	5 – 40
R – C – Cl or Br	10 – 70
R – C(=O) – C –	20 – 50
R – C – N	25 – 60
– C – O – alcohols, ethers or esters	50 – 90
C = C	90 – 150
R – C ≡ N	110 – 125
Benzene ring	110 – 160
R – C(=O) – esters or acids	160 – 185
R – C(=O) – aldehydes or ketones	190 – 220

TASK 1



4 signals



3 signals

Type of carbon	δ/ppm
—C—C—	5–40
R—C—Cl or Br	10–70
R—C(=O)—C—	20–50
R—C—N	25–60
—C—O— alcohols, ethers or esters	50–90
C=C	90–150
R—C≡N	110–125
benzene ring	110–160
R—C(=O)— esters or acids	160–185
R—C(=O)— aldehydes or ketones	190–220

TASK 1

δ 90-150 — 3 signals

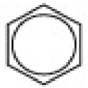
$CH_2{=}CH{-}CH_3$

δ 90-150 — δ 5-40

δ 5-40

$CH_3{-}CH(Cl){-}CH_3$

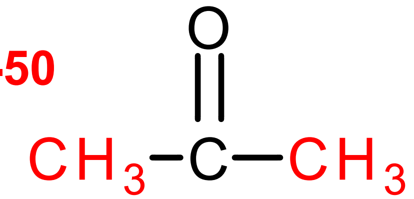
δ 10-70 — 2 signals

Type of carbon		δ/ppm
–C–C–		5–40
R–C–Cl or Br		10–70
R–C(=O)–C–		20–50
R–C–N		25–60
–C–O–	alcohols, ethers or esters	50–90
C=C		90–150
R–C≡N		110–125
		110–160
R–C(=O)–	esters or acids	160–185
R–C(=O)–	aldehydes or ketones	190–220

TASK 1

2 signals

δ 20-50



δ 190-220

δ 25-60

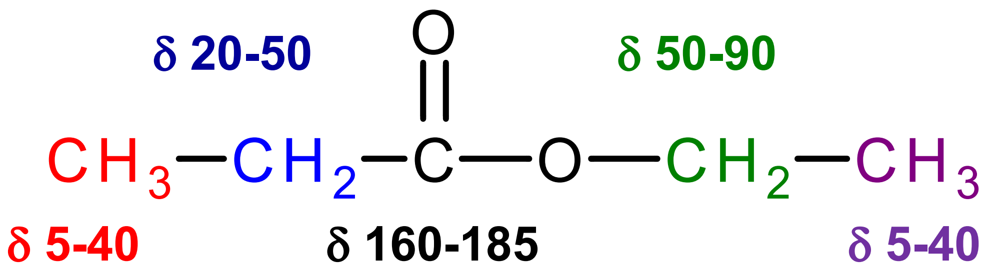
CH_3-NH_2

1 signal

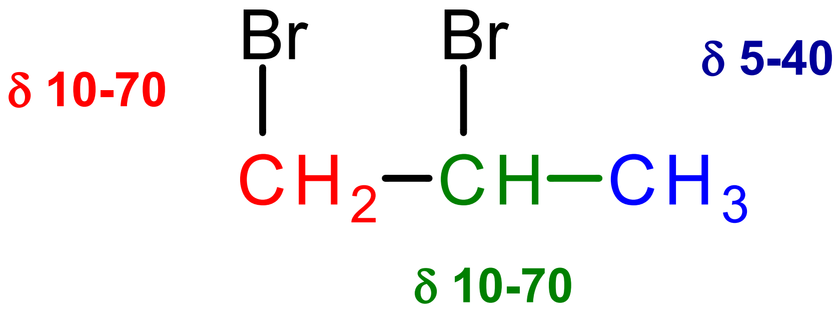
Type of carbon		δ/ppm
–C–C–		5–40
R–C–Cl or Br		10–70
R–C(=O)–C–		20–50
R–C–N		25–60
–C–O–	alcohols, ethers or esters	50–90
C=C		90–150
R–C≡N		110–125
benzene ring		110–160
R–C(=O)–	esters or acids	160–185
R–C(=O)–	aldehydes or ketones	190–220

TASK 1

5 signals



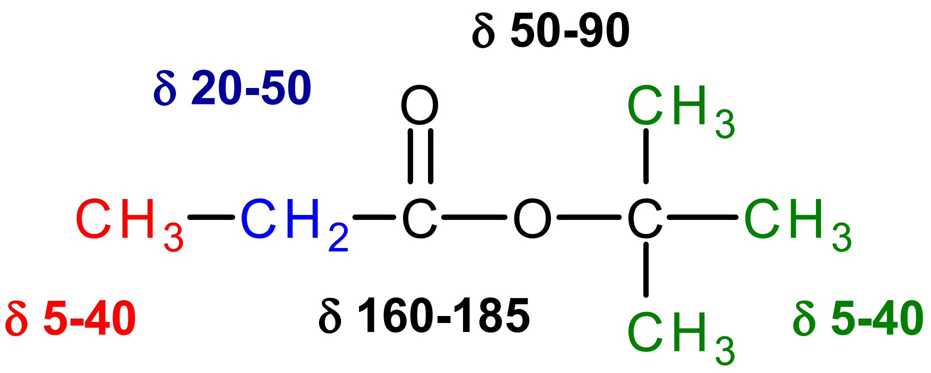
3 signals

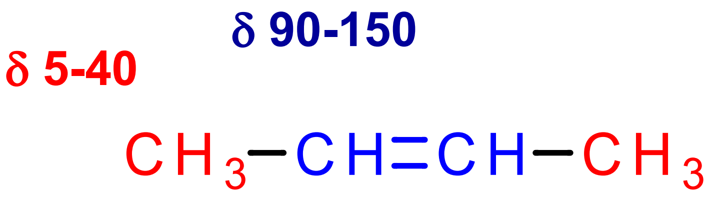


Type of carbon		δ/ppm
–C–C–		5 – 40
R–C–Cl or Br		10 – 70
R–C(=O)–C–		20 – 50
R–C–N		25 – 60
–C–O–	alcohols, ethers or esters	50 – 90
C=C		90 – 150
R–C≡N		110 – 125
benzene ring		110 – 160
R–C(=O)–	esters or acids	160 – 185
R–C(=O)–	aldehydes or ketones	190 – 220

TASK 1

5 signals



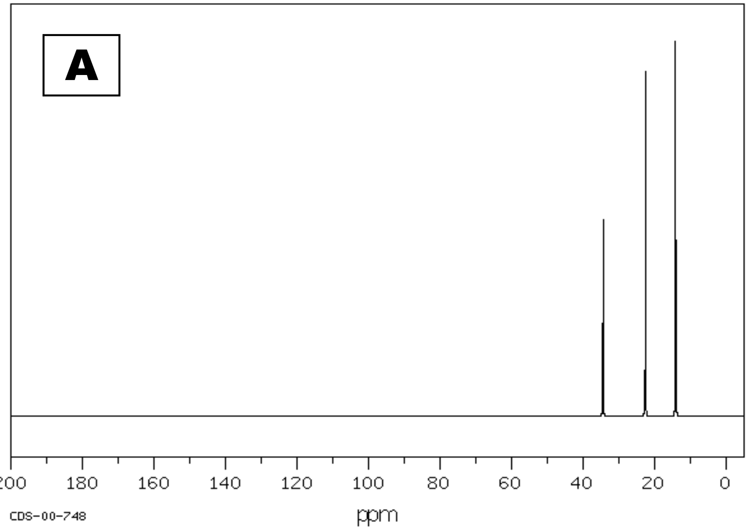


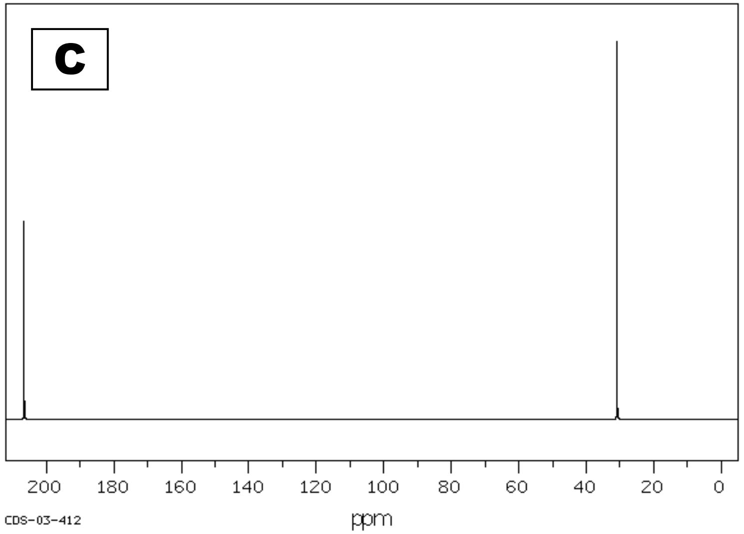
2 signals

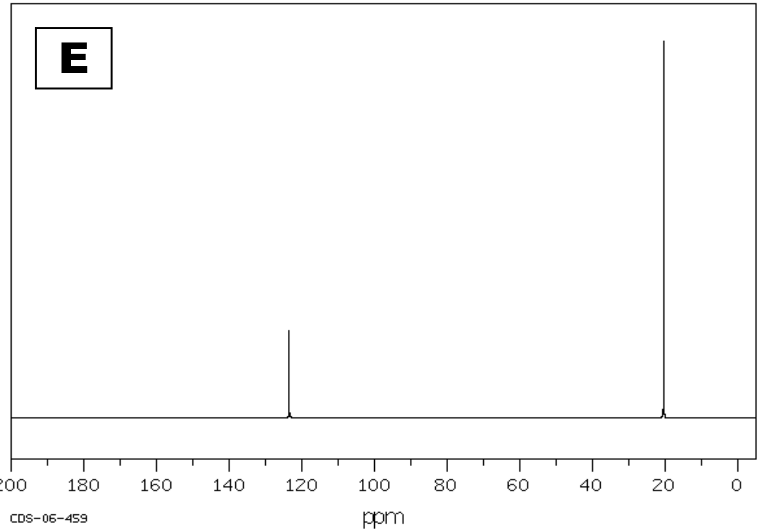
Type of carbon		δ/ppm
—C—C—		5–40
R—C—Cl or Br		10–70
R—C(=O)—C—		20–50
R—C—N		25–60
—C—O—	alcohols, ethers or esters	50–90
C=C		90–150
R—C≡N		110–125
benzene ring		110–160
R—C(=O)—	esters or acids	160–185
R—C(=O)—	aldehydes or ketones	190–220

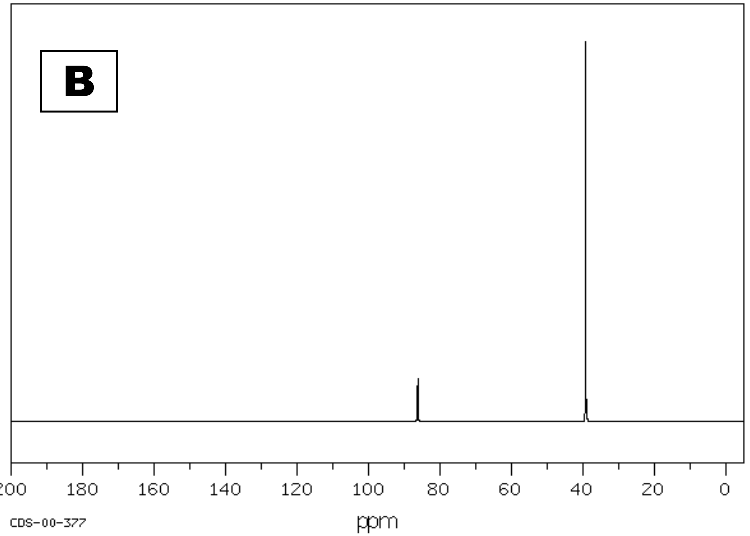
TASK 2

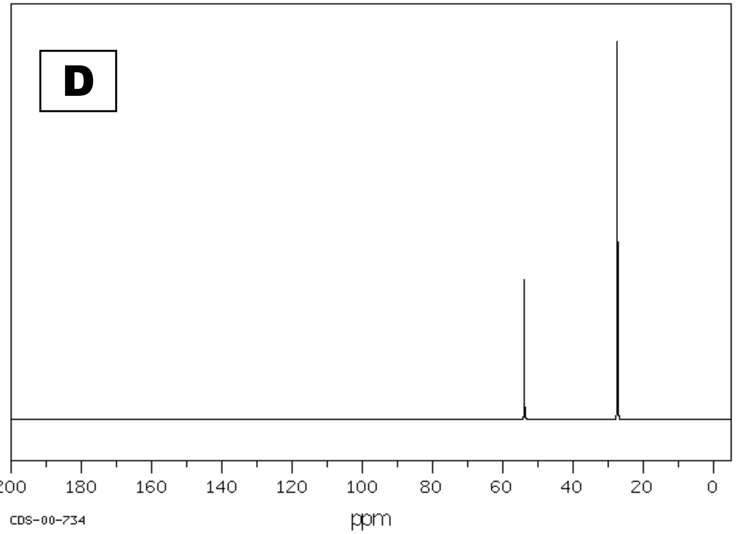
propanoic acid	pentane	2-chlorpropane
propanone	2,2-dichloropropane	2,3-dimethylbut-2-ene

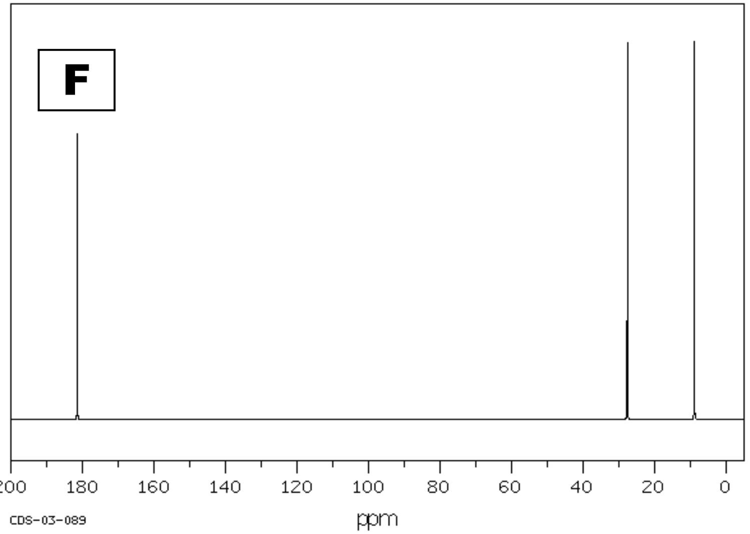




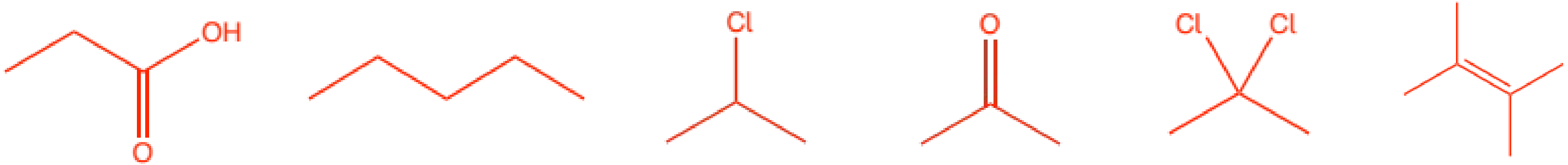


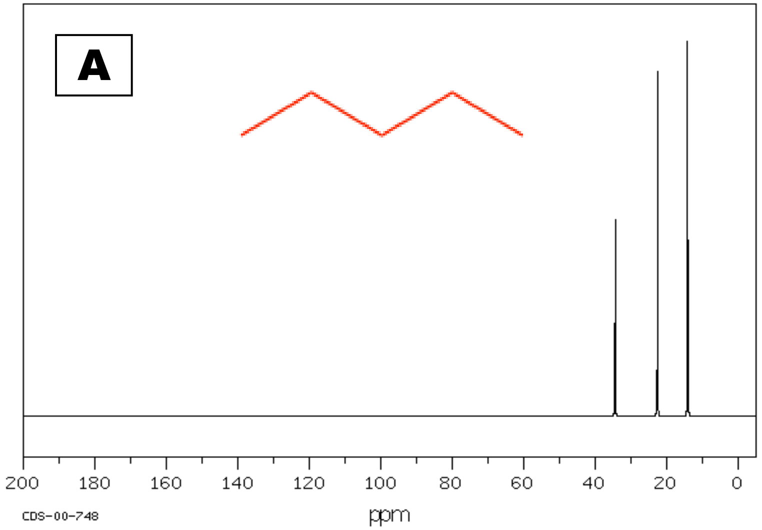


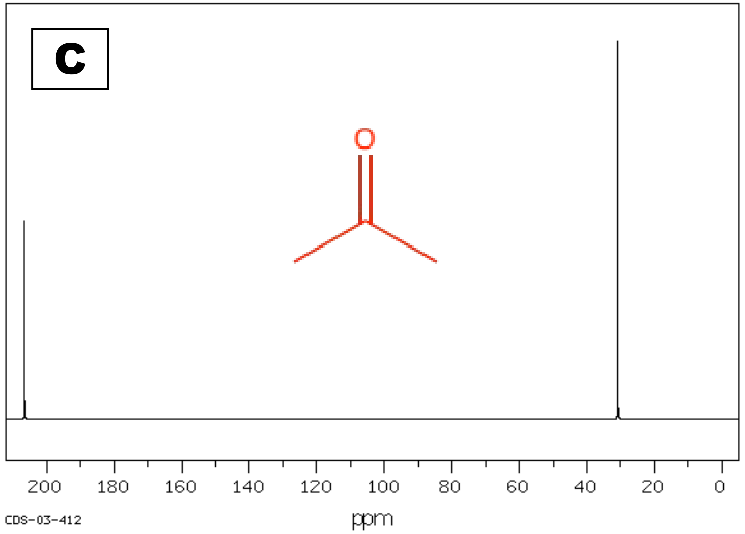


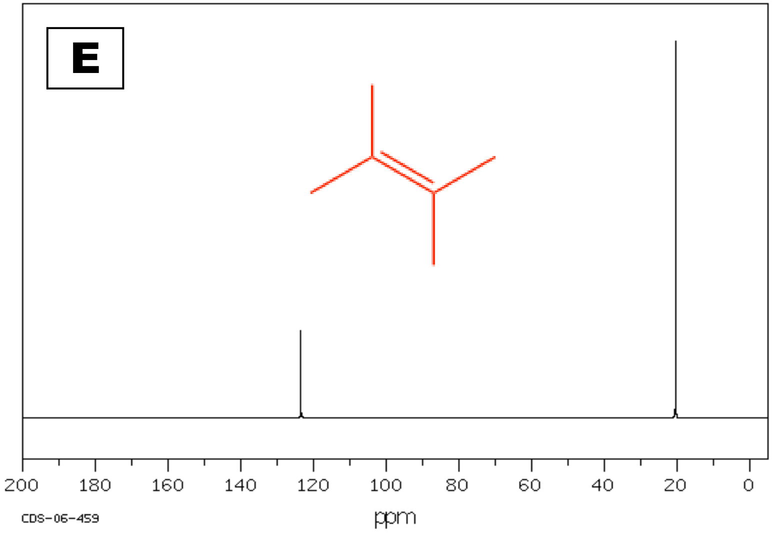


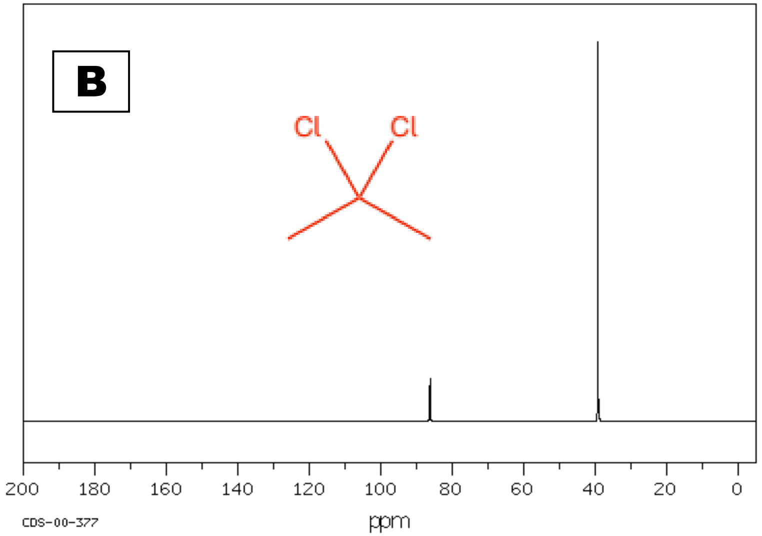
TASK 2

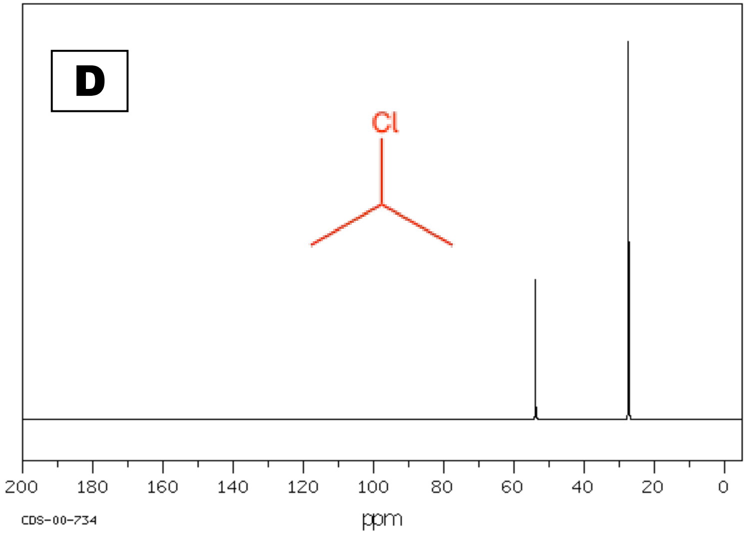

OH
O
Cl
O
Cl Cl


A
200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-00-748


C
O
200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-03-412


E
200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-06-459


B
Cl Cl
200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-00-377


D
Cl
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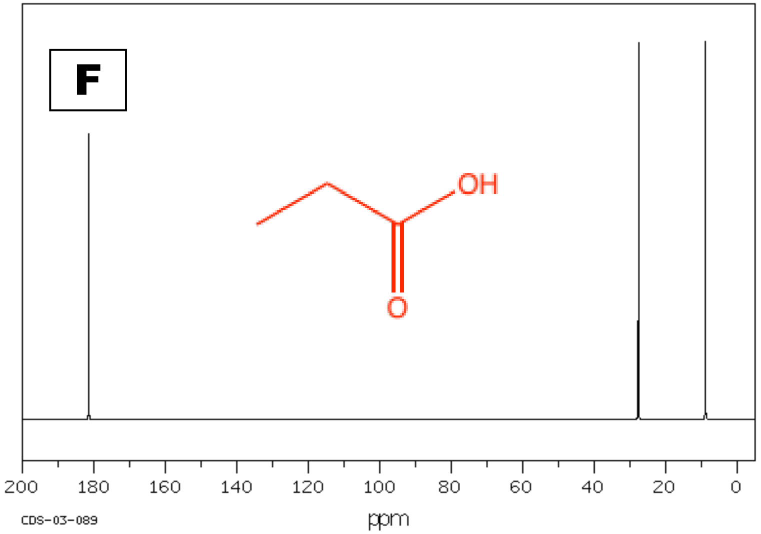
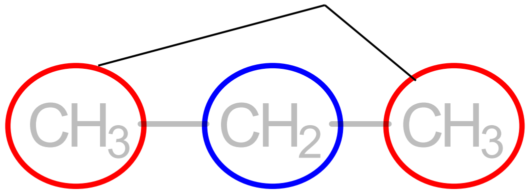
ppm
CDS-00-734

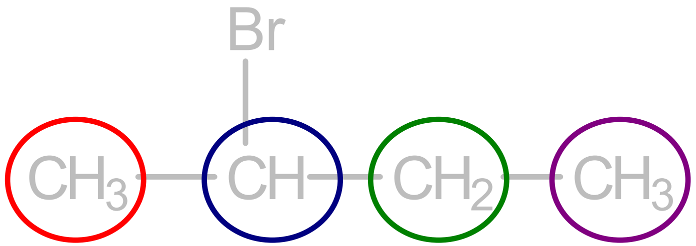

F
OH
O
200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-03-089

1H NMR SPECTROSCOPY

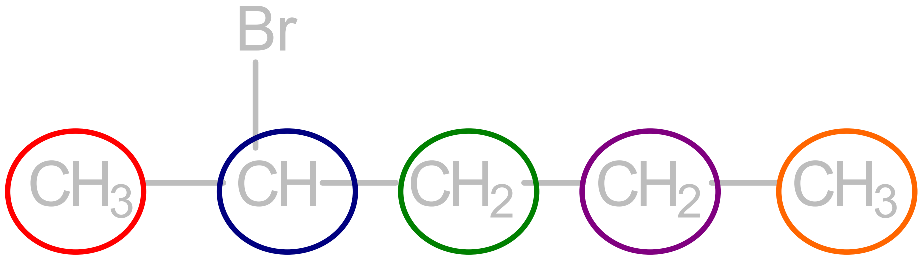
	Similar or different	^{1}H NMR	^{13}C NMR
Number of signals	similar	One signal for each set of equivalent ^{1}H or ^{13}C atoms	
Position of signal	similar	The closer the atom to a very electronegative atom and/or double bond, the greater the chemical shift	
Relative size of signals	different	Relative area of signals related to relative number of ^{1}H atoms	<u>No link</u> between area of signal to number of ^{13}C atoms
Splitting of signals	different	Signal split by ^{1}H atoms on adjacent atom (into doublets, triplets, etc)	<u>No splitting</u>



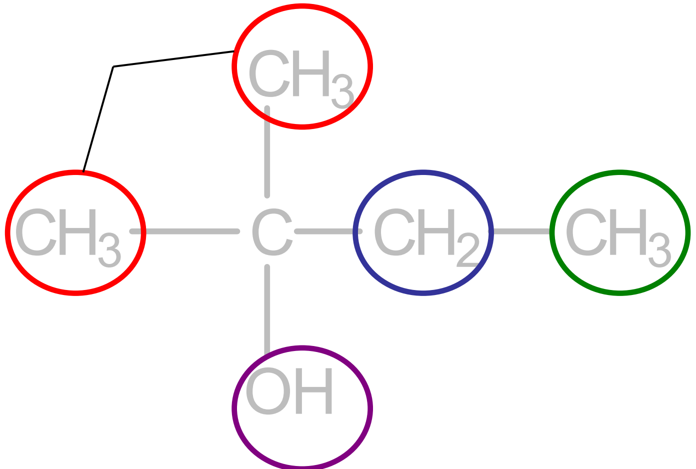
2 sets of equivalent H's: ratio 6:2 (3:1)



4 sets of equivalent H's: ratio 3:1:2:3

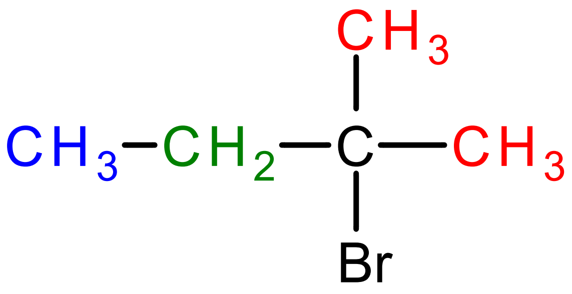


5 sets of equivalent H's: ratio 3:1:2:2:3



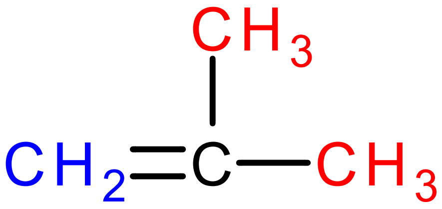
4 sets of equivalent H's: ratio 6:1:2:3

TASK 3a

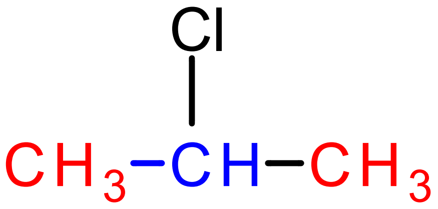


3 signals: ratio 3:2:6

3 signals: ratio 2:1:3

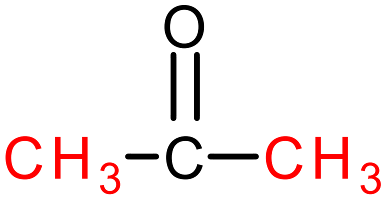


2 signals: ratio 6:2 (3:1)

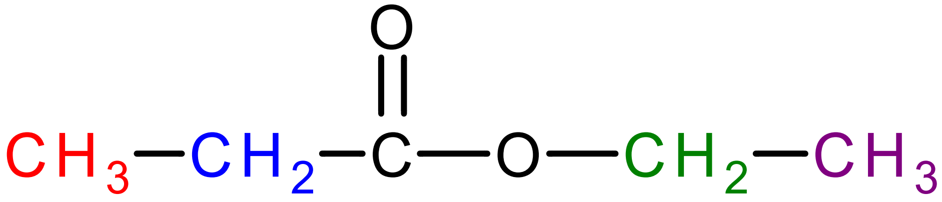


2 signals: ratio 6:1

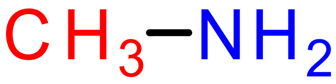
TASK 3a



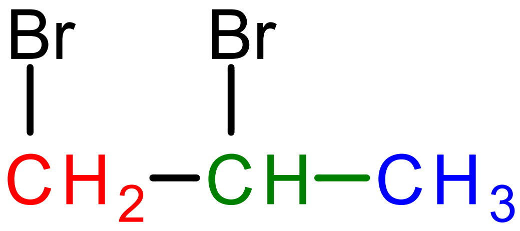
1 signal



4 signals: ratio 3:2:2:3

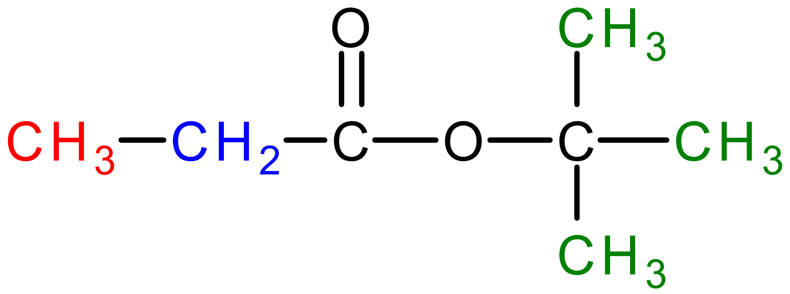


2 signals: ratio 3:2

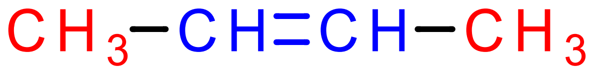


3 signals: ratio 2:1:3

TASK 3a

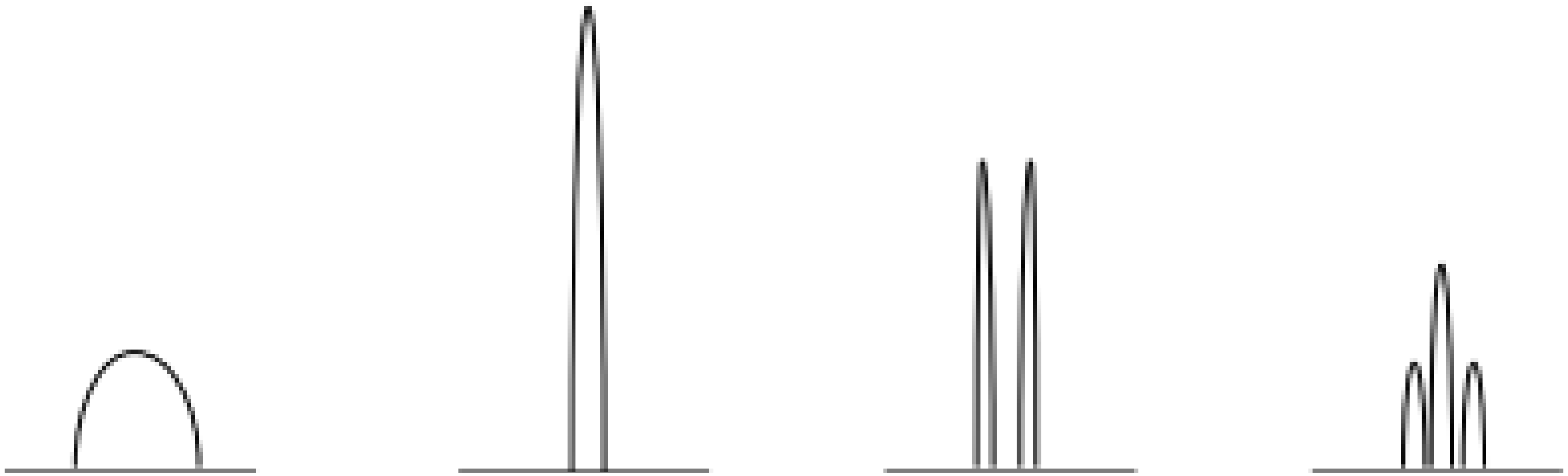


3 signals: ratio 3:2:9



2 signals: ratio 6:2 (3:1)

RELATIVE INTENSITY



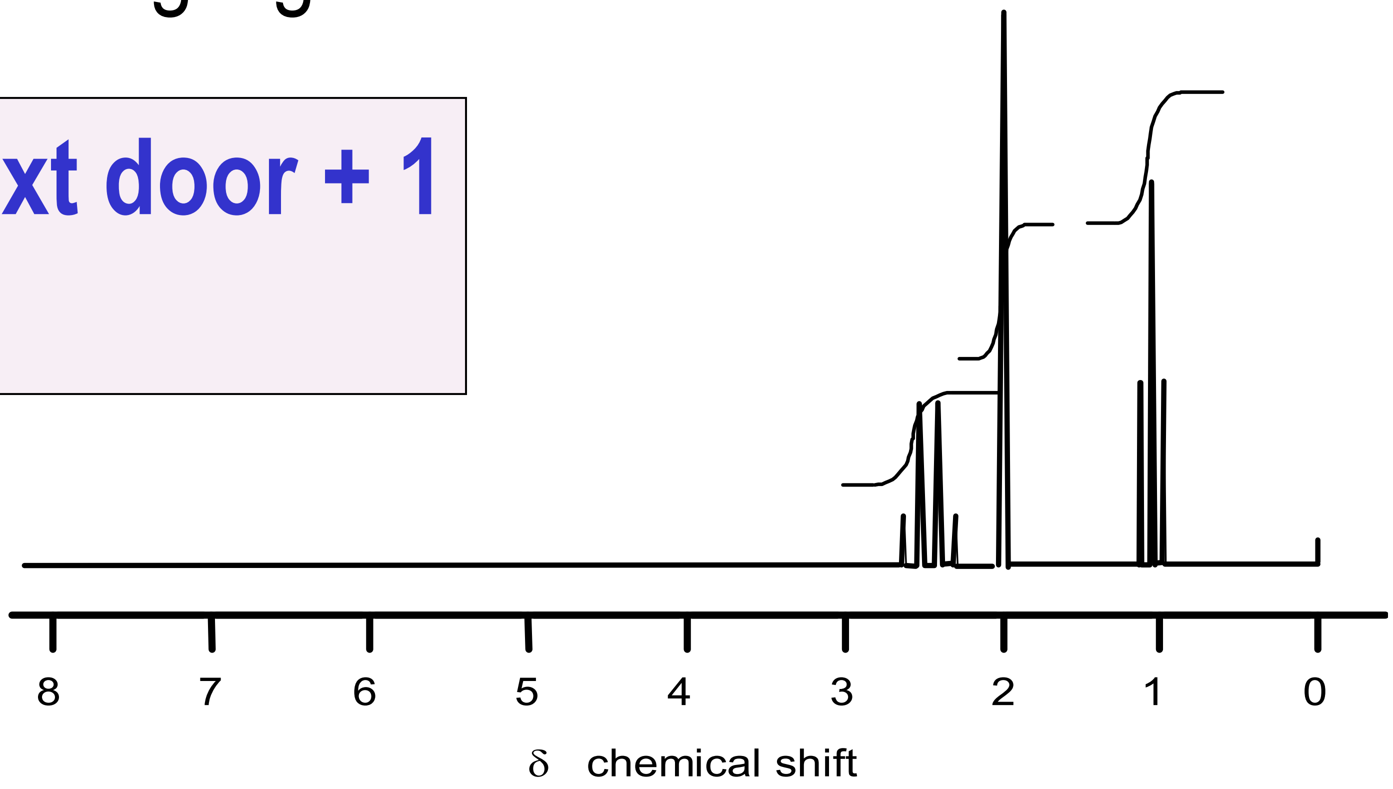
These four signals have the same overall area and represent the same number of H atoms

SPIN-SPIN COUPLING

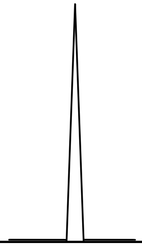
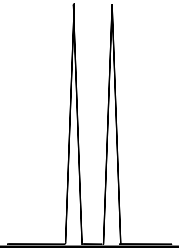
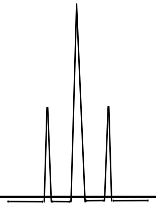
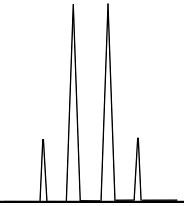
H atoms **couple** together splitting signals

Lines = number of H next door + 1

n+1 rule



SPIN-SPIN COUPLING

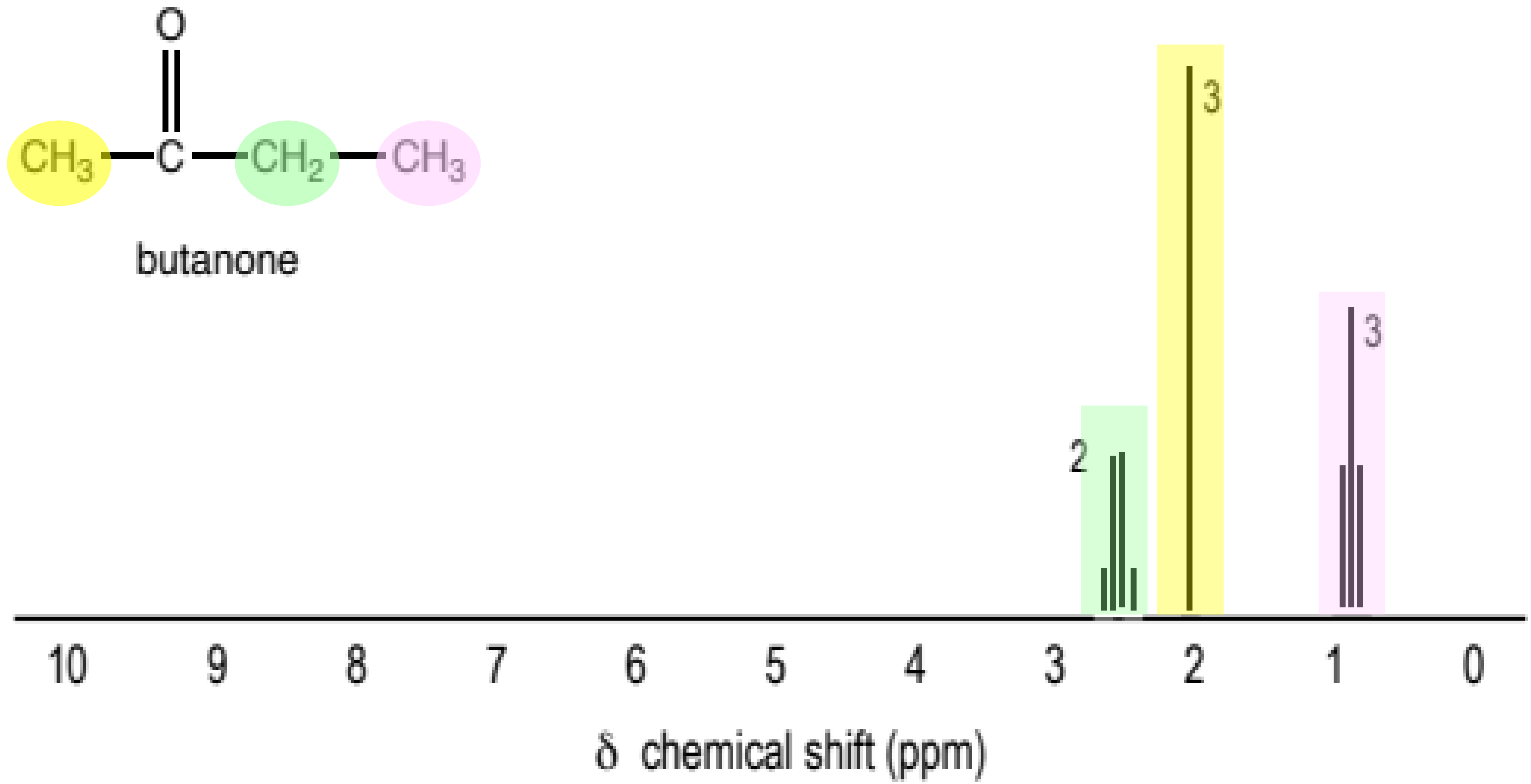
signal	singlet	doublet	triplet	quartet
appearance				
number of lines	1	2	3	4
number of H's next door	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

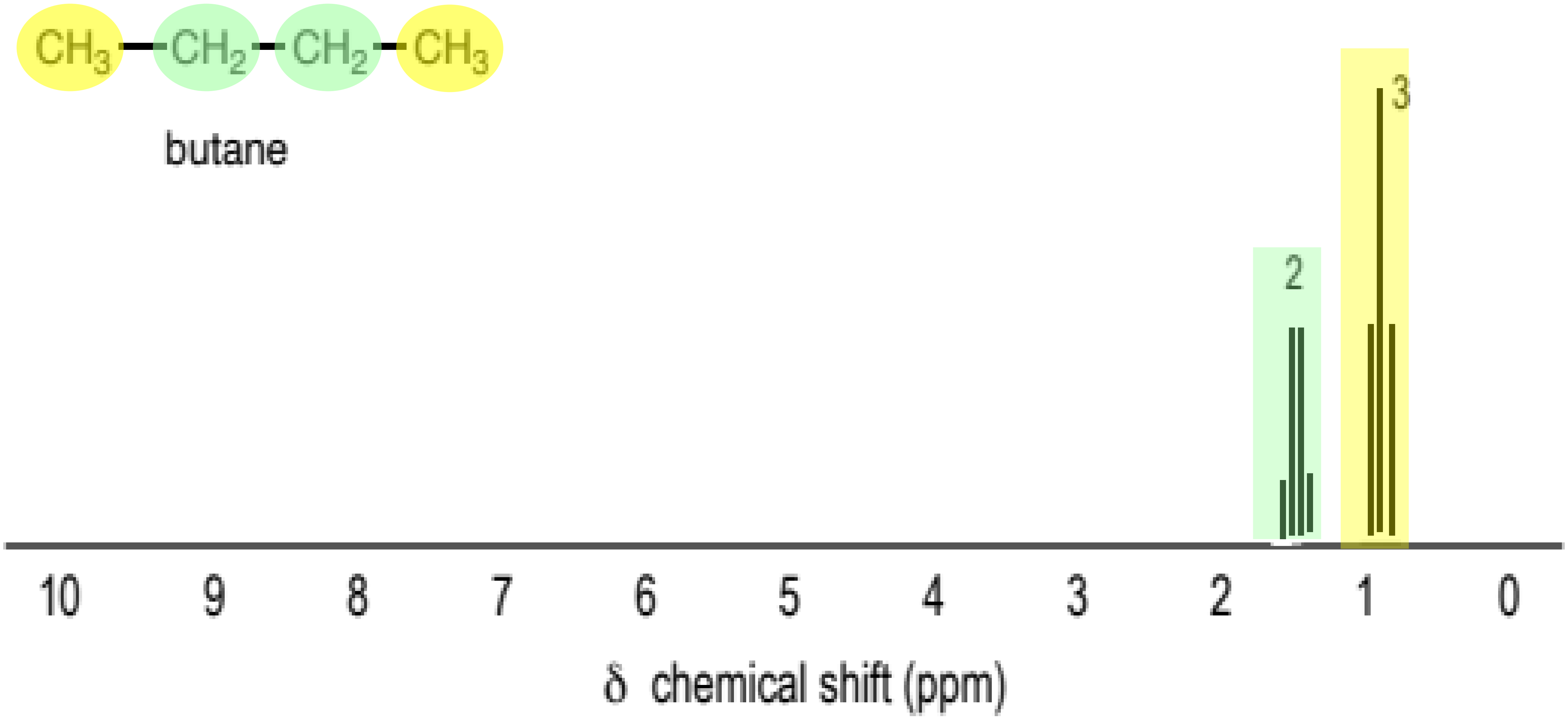
Lines = number of H next door + 1

n+1 rule

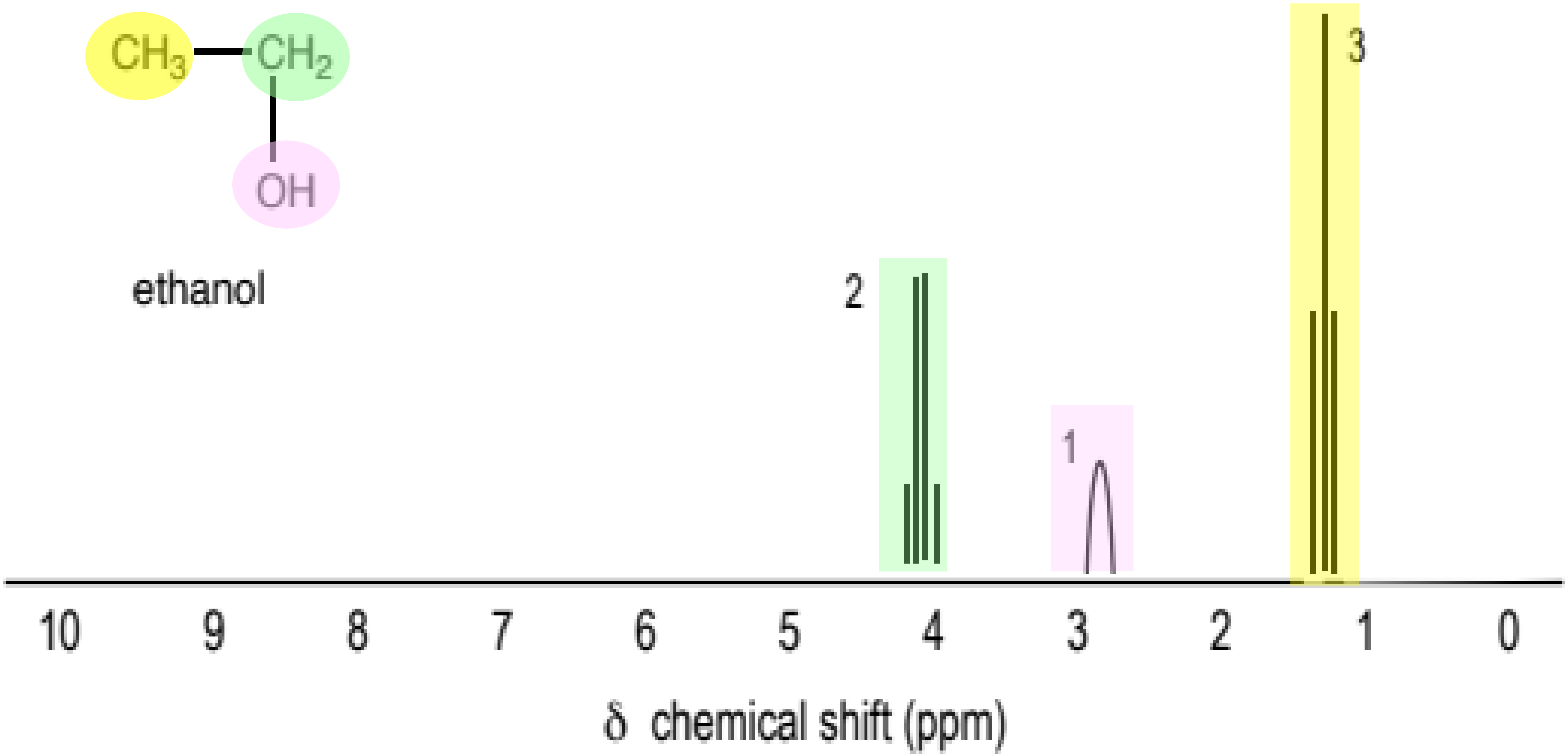
But H atoms do not couple to

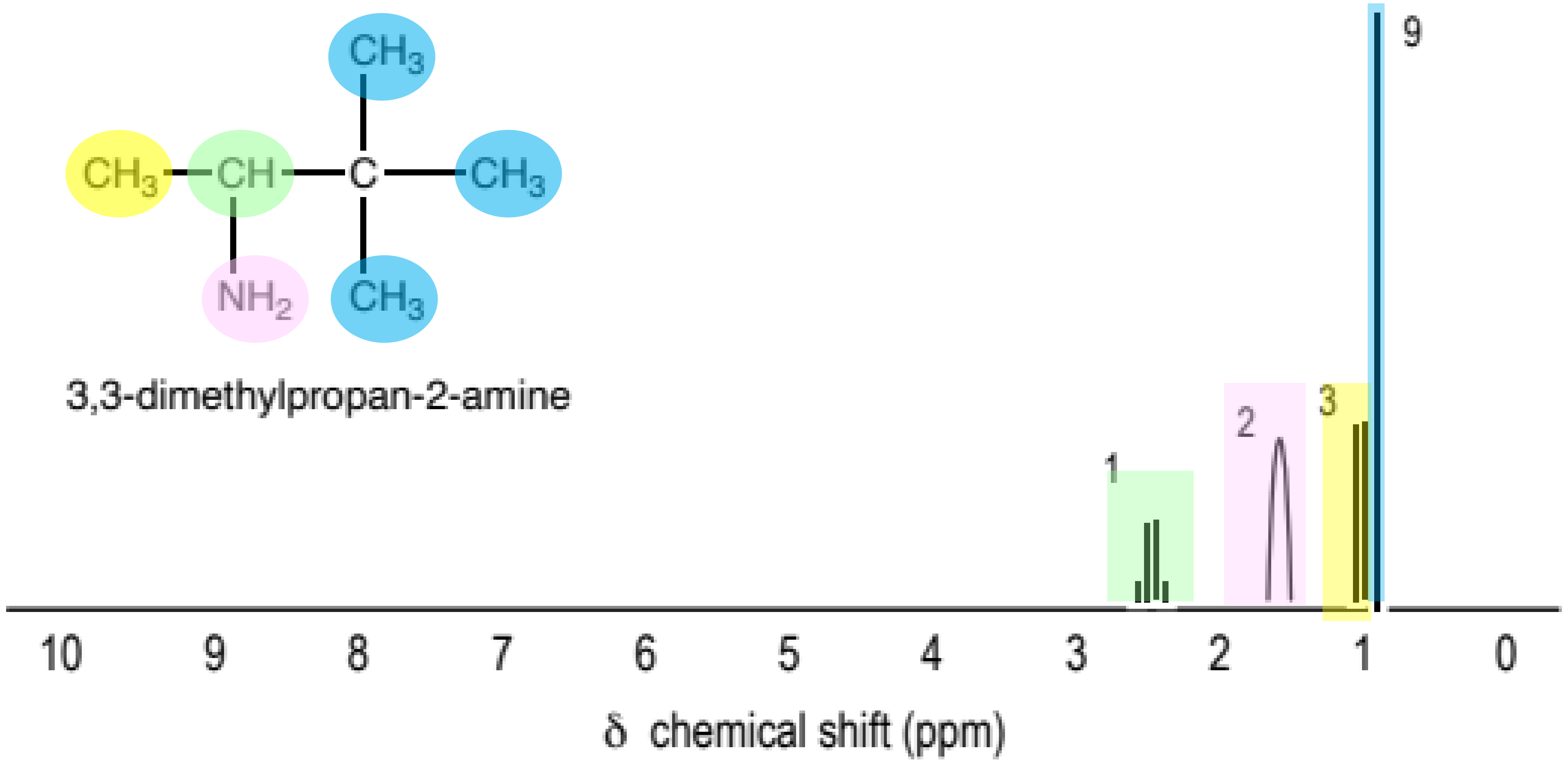
- H's that are equivalent
- H's on O/N

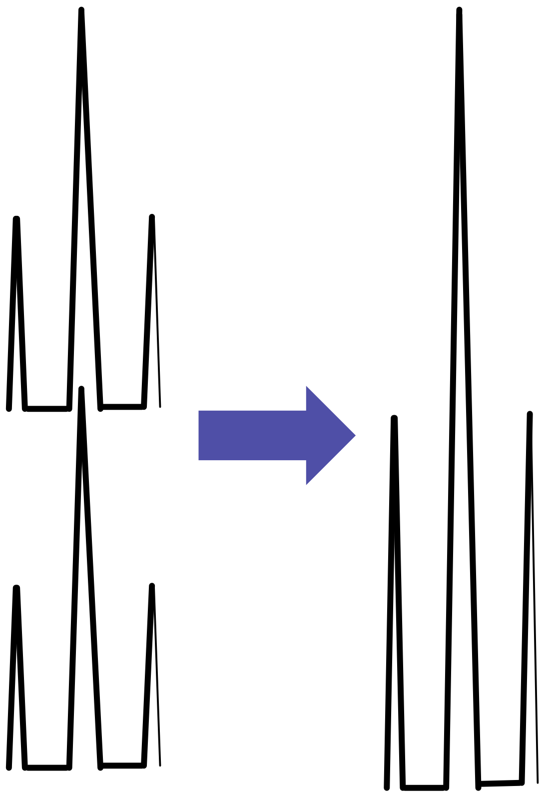

O
CH3
C
CH2
CH3
butanone
3
2
3
10
9
8
7
6
5
4
3
2
1
0
δ chemical shift (ppm)

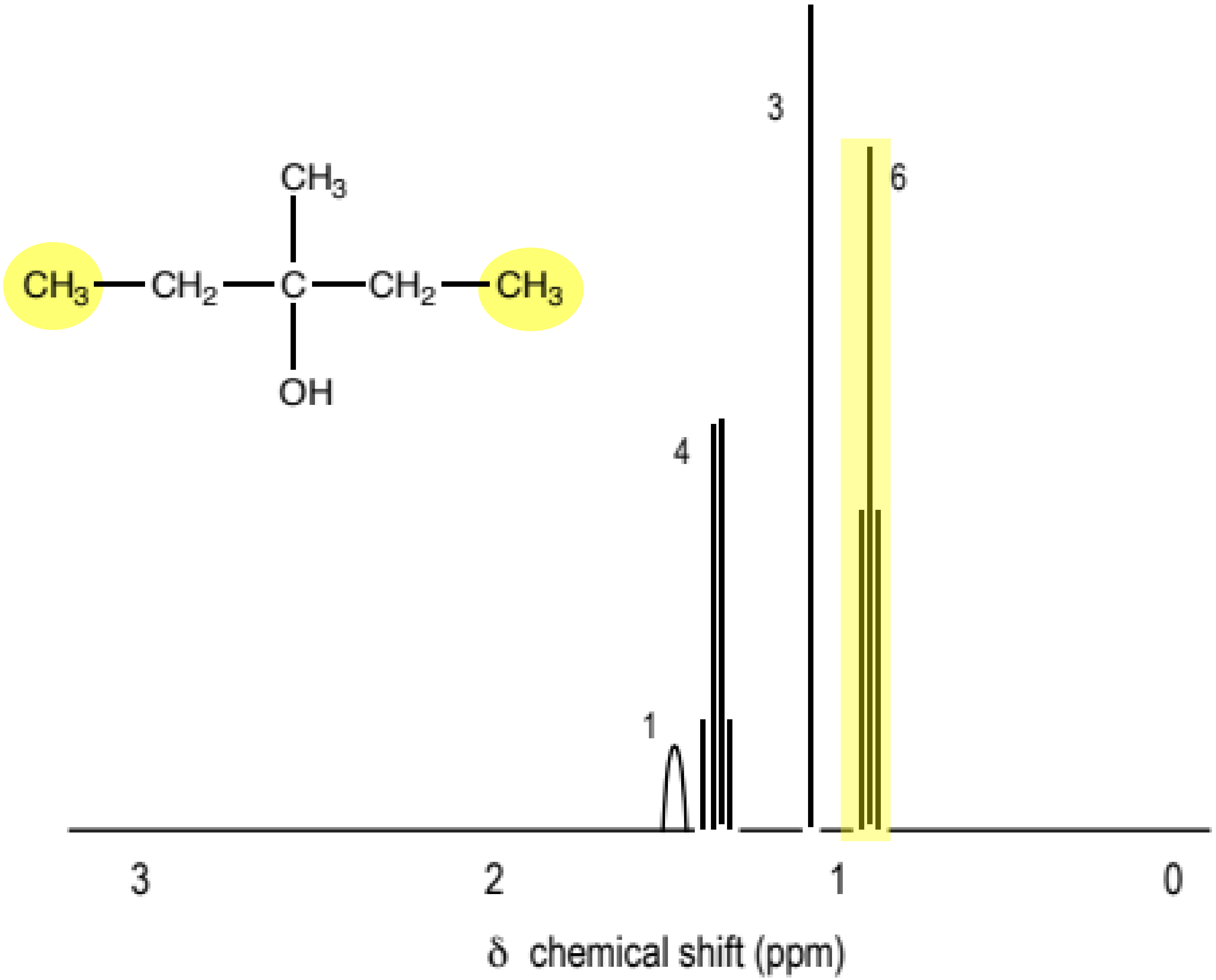


CH3
CH2
CH2
CH3
butane
2
3
10
9
8
7
6
5
4
3
2
1
0
δ chemical shift (ppm)


CH3
CH2
OH
ethanol
2
1
3
10
9
8
7
6
5
4
3
2
1
0
δ chemical shift (ppm)

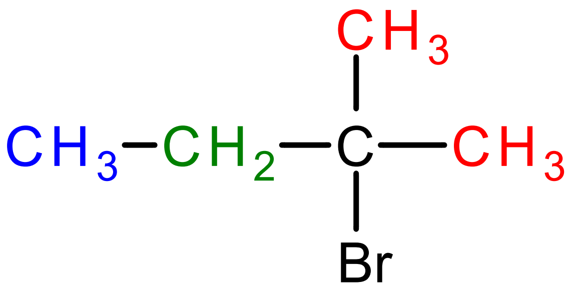

CH_3
CH_3
CH
C
CH_3
NH_2
CH_3
3,3-dimethylpropan-2-amine
9
1
2
3
10
9
8
7
6
5
4
3
2
1
0
δ chemical shift (ppm)





Two identical sets of ^{1}H atoms produce one signal that is twice the size that one set would produce (not two signals!)

TASK 3b

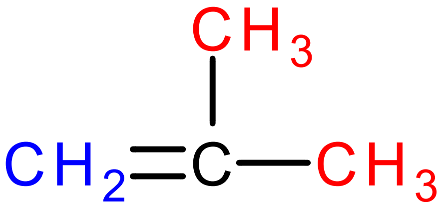


3 signals: ratio 3:2:6

t q s

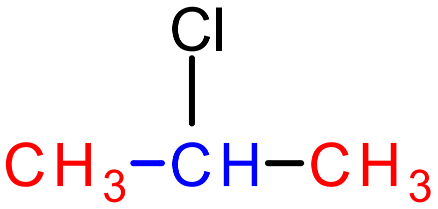
3 signals: ratio 2:1:3

d m d



2 signals: ratio 6:2 (3:1)

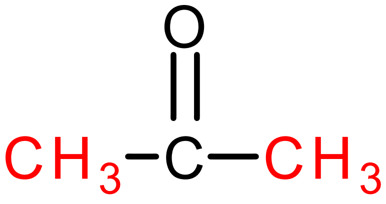
s s



2 signals: ratio 6:1

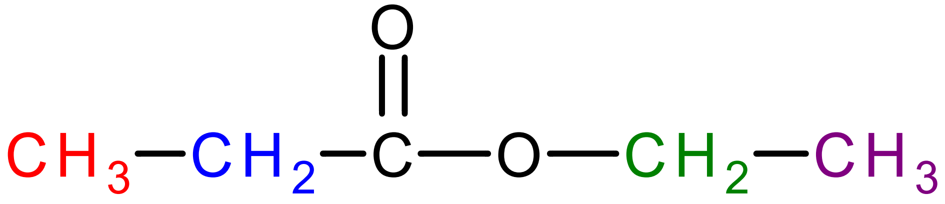
d m

TASK 3b



1 signal

s



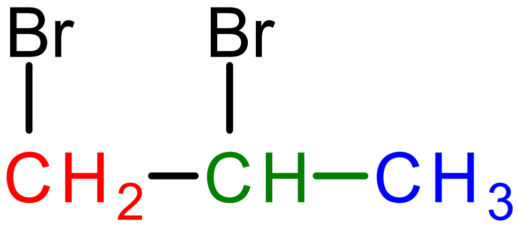
4 signals: ratio 3:2:2:3

t q q t

CH_3-NH_2

2 signals: ratio 3:2

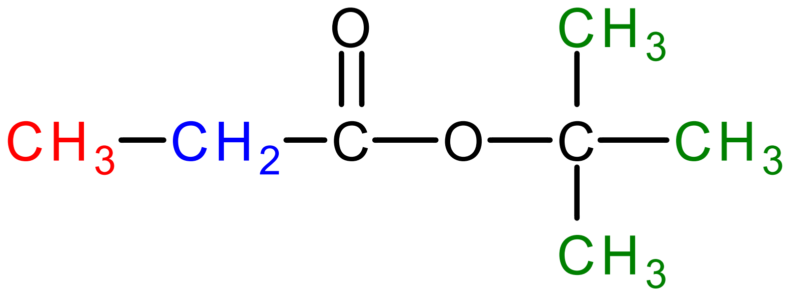
t q



3 signals: ratio 2:1:3

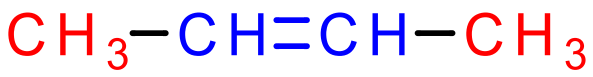
d m d

TASK 3b



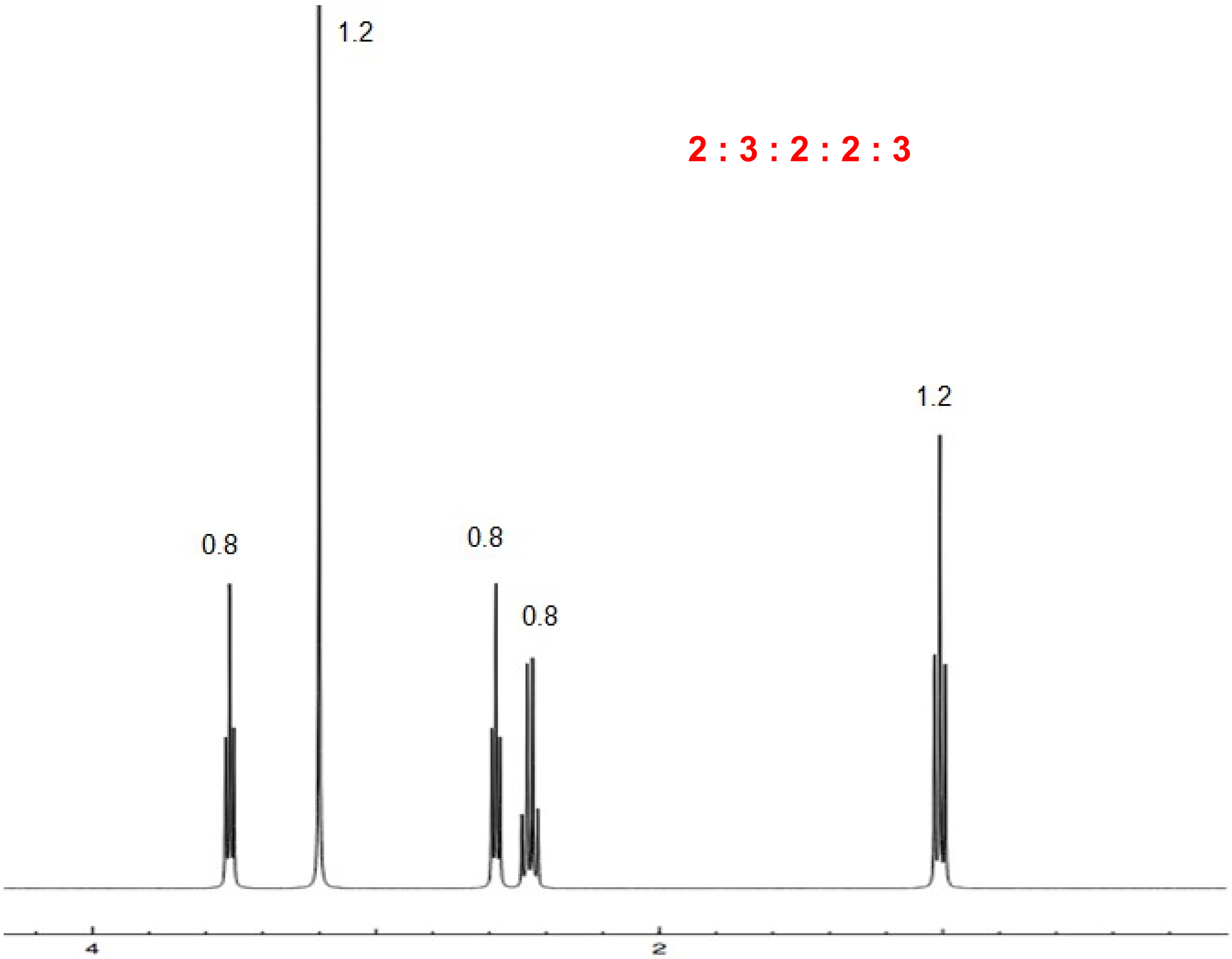
3 signals: ratio 3:2:9

t q s

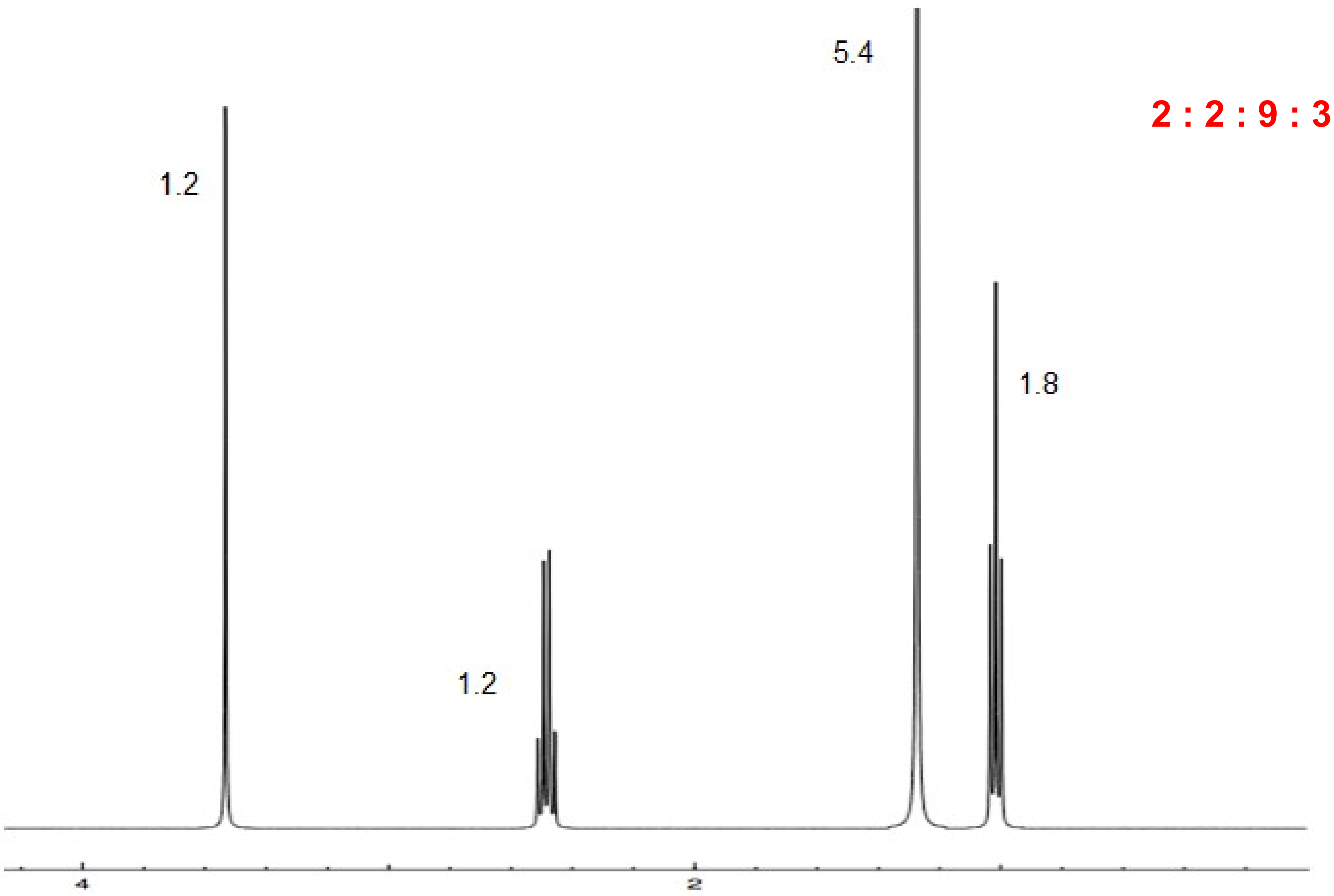


2 signals: ratio 6:2 (3:1)

d q

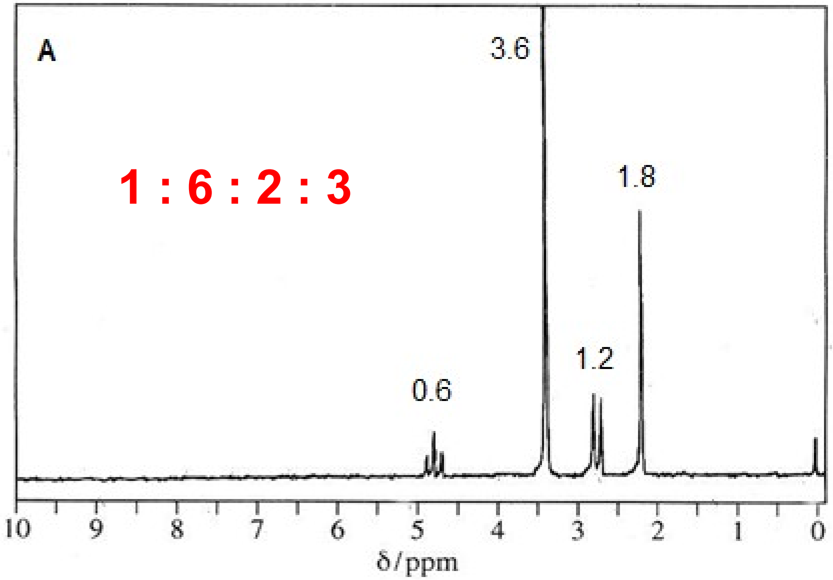


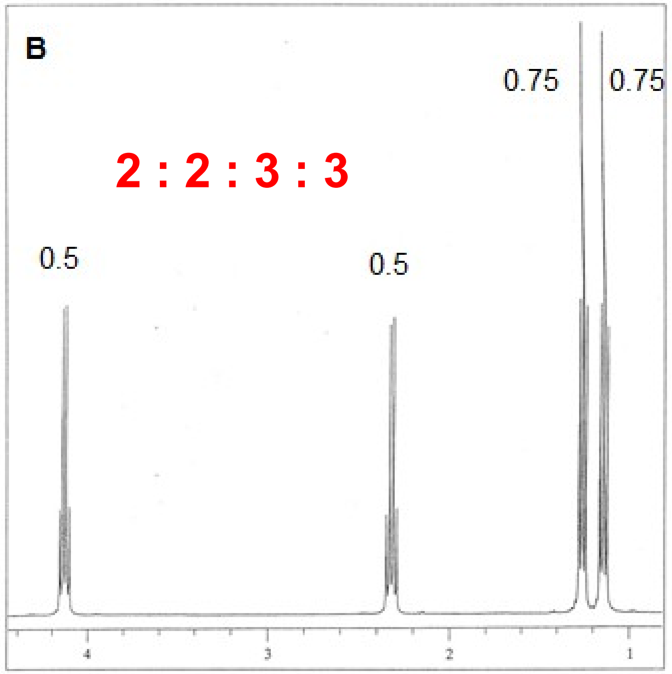
2 : 3 : 2 : 2 : 3

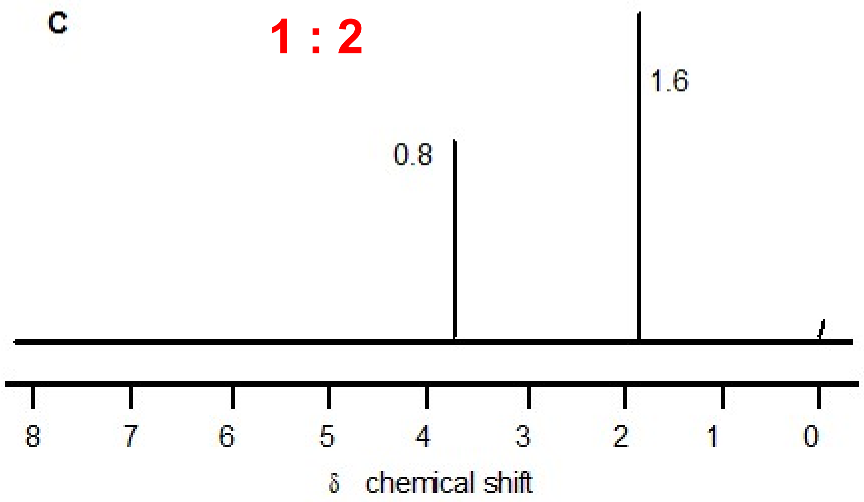


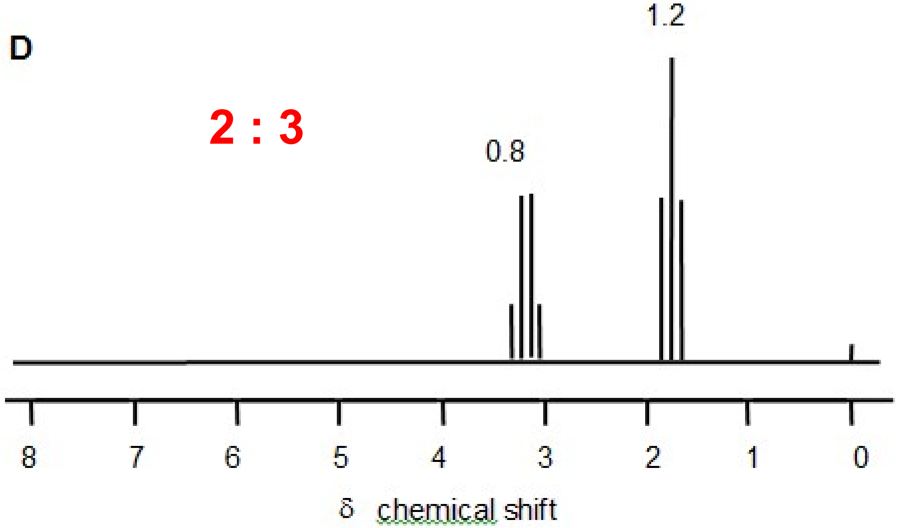
2 : 2 : 9 : 3

TASK 4

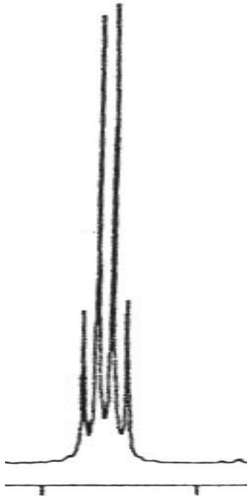

A
1 : 6 : 2 : 3
3.6
1.8
1.2
0.6
10 9 8 7 6 5 4 3 2 1 0
δ/ppm


B
2 : 2 : 3 : 3
0.75
0.75
0.5
0.5
4 3 2 1

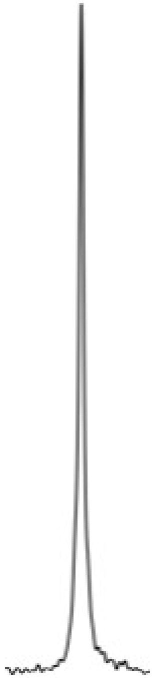

C
1 : 2
1.6
0.8
8 7 6 5 4 3 2 1 0
δ chemical shift


D
1.2
2 : 3
0.8
8 7 6 5 4 3 2 1 0
δ chemical shift

TASK 5

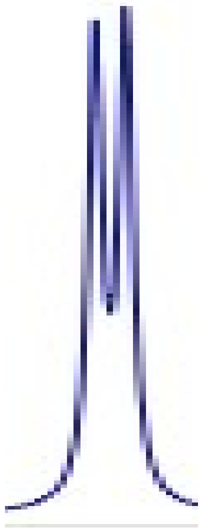


q

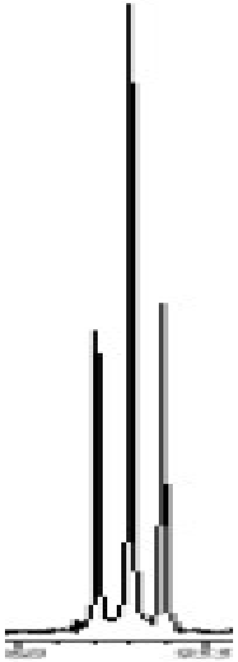


s

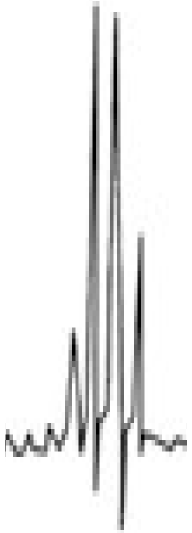
q



d

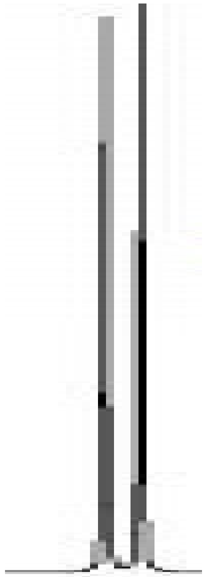


t

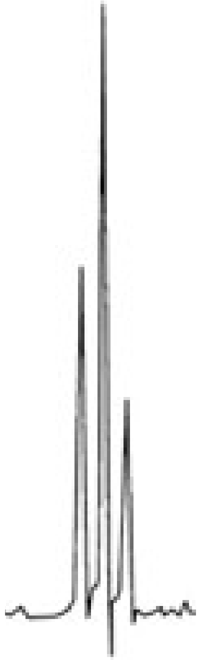


q

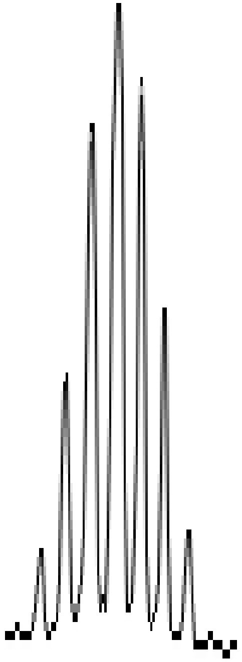
TASK 5



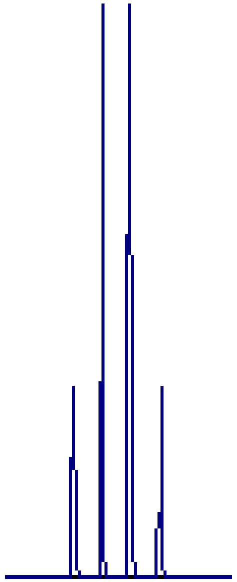
d



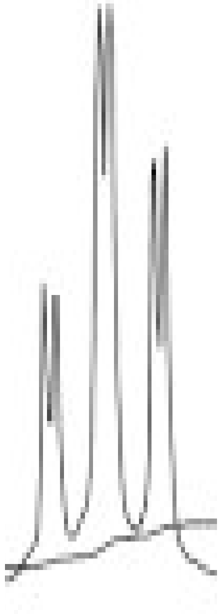
t



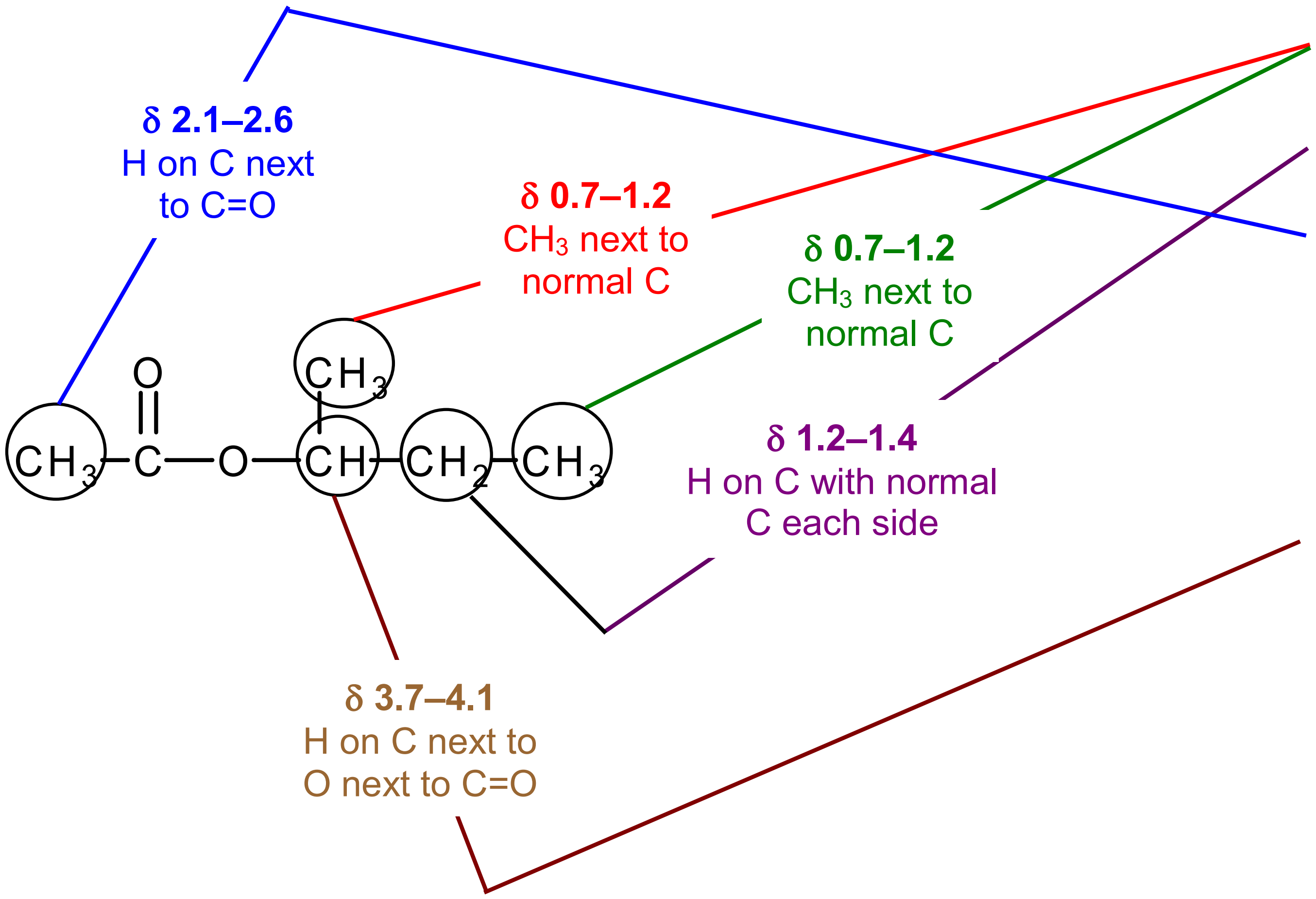
m



q

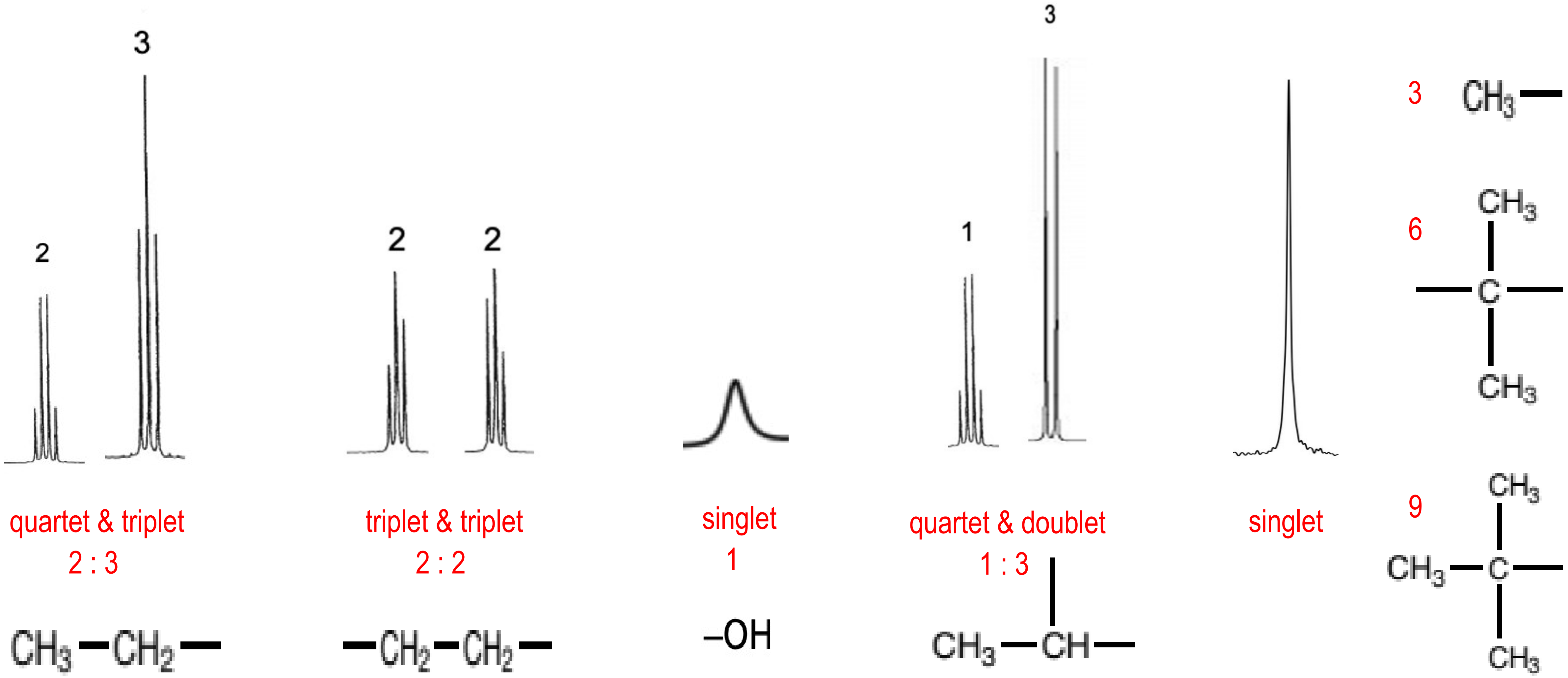


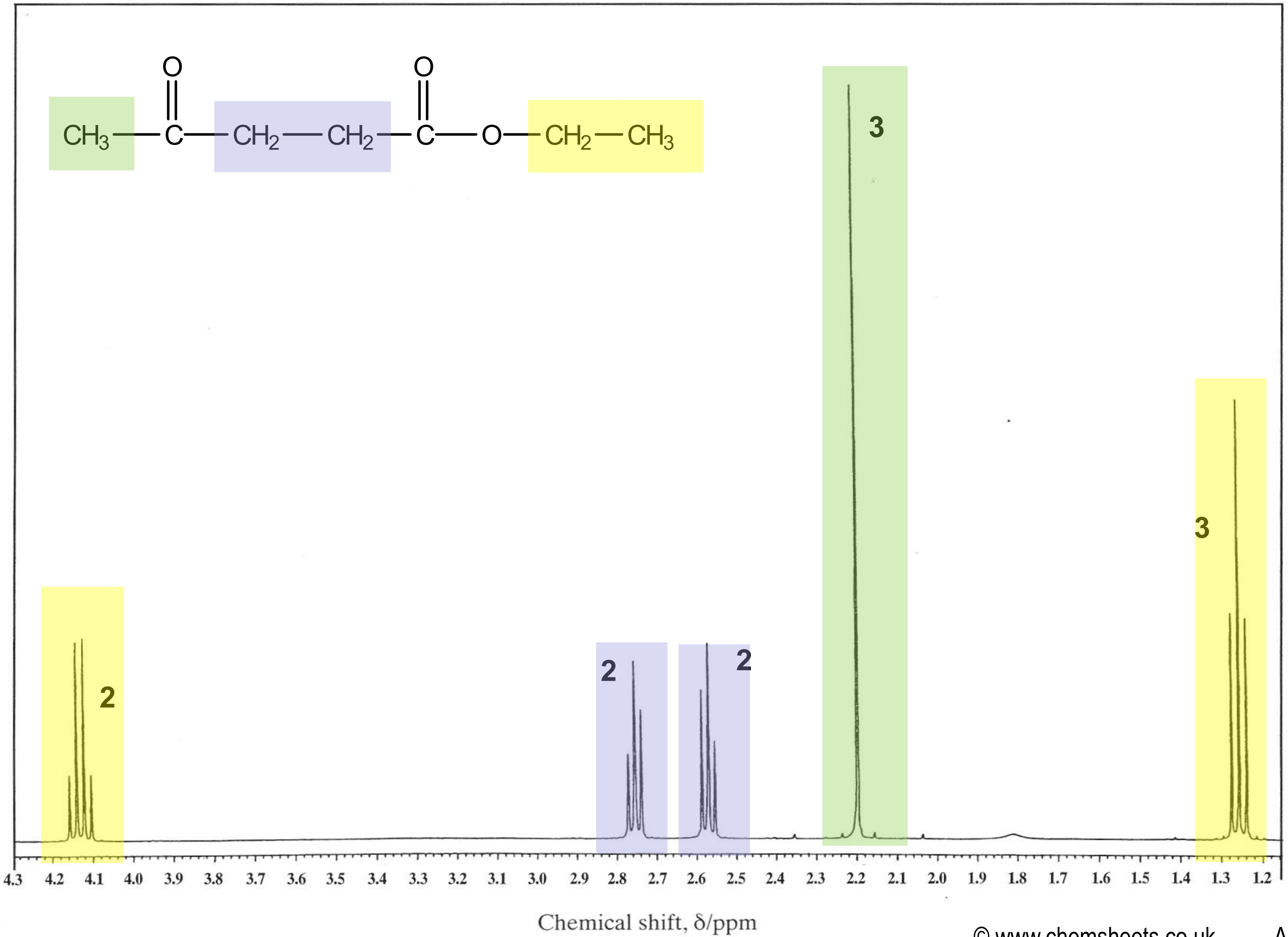
m



Type of proton	δ/ppm
ROH	0.5 – 5.0
RCH_3	0.7 – 1.2
RNH_2	1.0 – 4.5
R_2CH_2	1.2 – 1.4
R_3CH	1.4 – 1.6
R–C(=O)–C(–H)–	2.1 – 2.6
R–O–C(–H)–	3.1 – 3.9
RCH_2Cl or Br	3.1 – 4.2
R–C(=O)–O–C(–H)–	3.7 – 4.1
R(–)C=C(–)H	4.5 – 6.0
R–C(=O)–H	9.0 – 10.0
R–C(=O)–O–H	10.0 – 12.0

KEY SIGNALS


2
3
quartet & triplet
2 : 3
CH3–CH2–
2
2
triplet & triplet
2 : 2
–CH2–CH2–
singlet
1
–OH
1
3
quartet & doublet
1 : 3
CH3–CH–
singlet
3
CH3–
6
CH3
C
CH3
9
CH3
CH3–C–
CH3


CH3
C
O
CH2
CH2
C
O
O
CH2
CH3
3
3
2
2
2
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 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
Chemical shift, δ/ppm