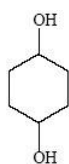
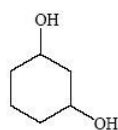
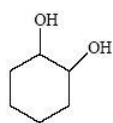


Q1. Three cyclic alcohols, cyclohexan-1,2-diol, cyclohexan-1,3-diol and cyclohexan-1,4-diol were compared using ^{13}C n.m.r. spectroscopy.

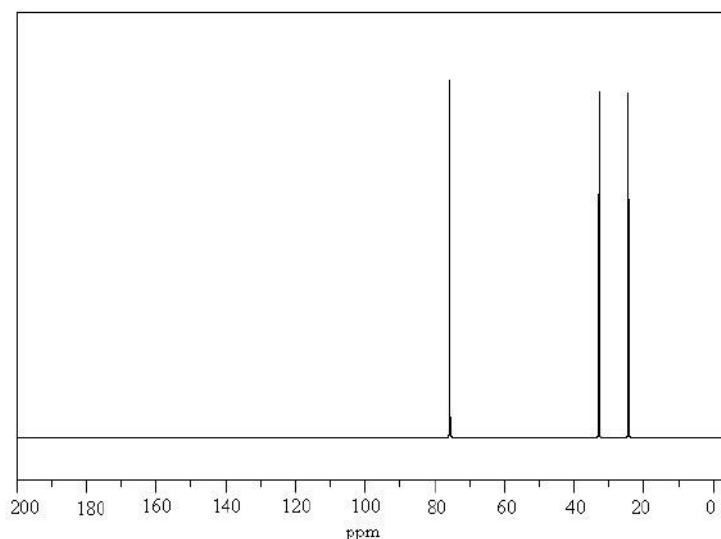


cyclohexan-1,2-diol

cyclohexan-1,3-diol

cyclohexan-1,4-diol

The ^{13}C n.m.r. spectrum of cyclohexan-1,2-diol is shown below.



- (a) (i) Explain why there are three peaks.

- (ii) Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for ^{13}C vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan-1,2-diol.

- (b) (i) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,3-diol.

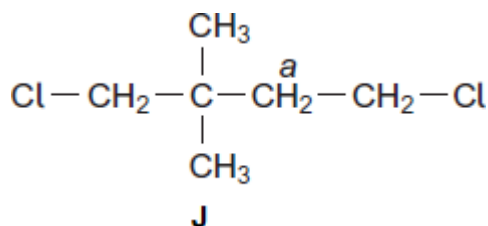
- (ii) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,4-diol.

- (c) Suggest why the structures drawn above represents several stereoisomers.

(Total 5 marks)

Q2. N.m.r. spectroscopy can be used to study the structures of organic compounds.

(a) Compound **J** was studied using ^1H n.m.r. spectroscopy.



(i) Identify a solvent in which **J** can be dissolved before obtaining its ^1H n.m.r. spectrum.

(1)

(ii) Give the number of peaks in the ^1H n.m.r. spectrum of **J**.

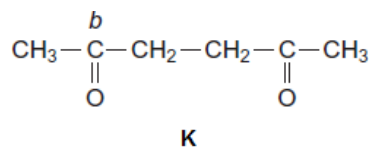
(1)

(iii) Give the splitting pattern of the protons labelled *a*.

(1)

(iv) Give the IUPAC name of **J**.

(b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.



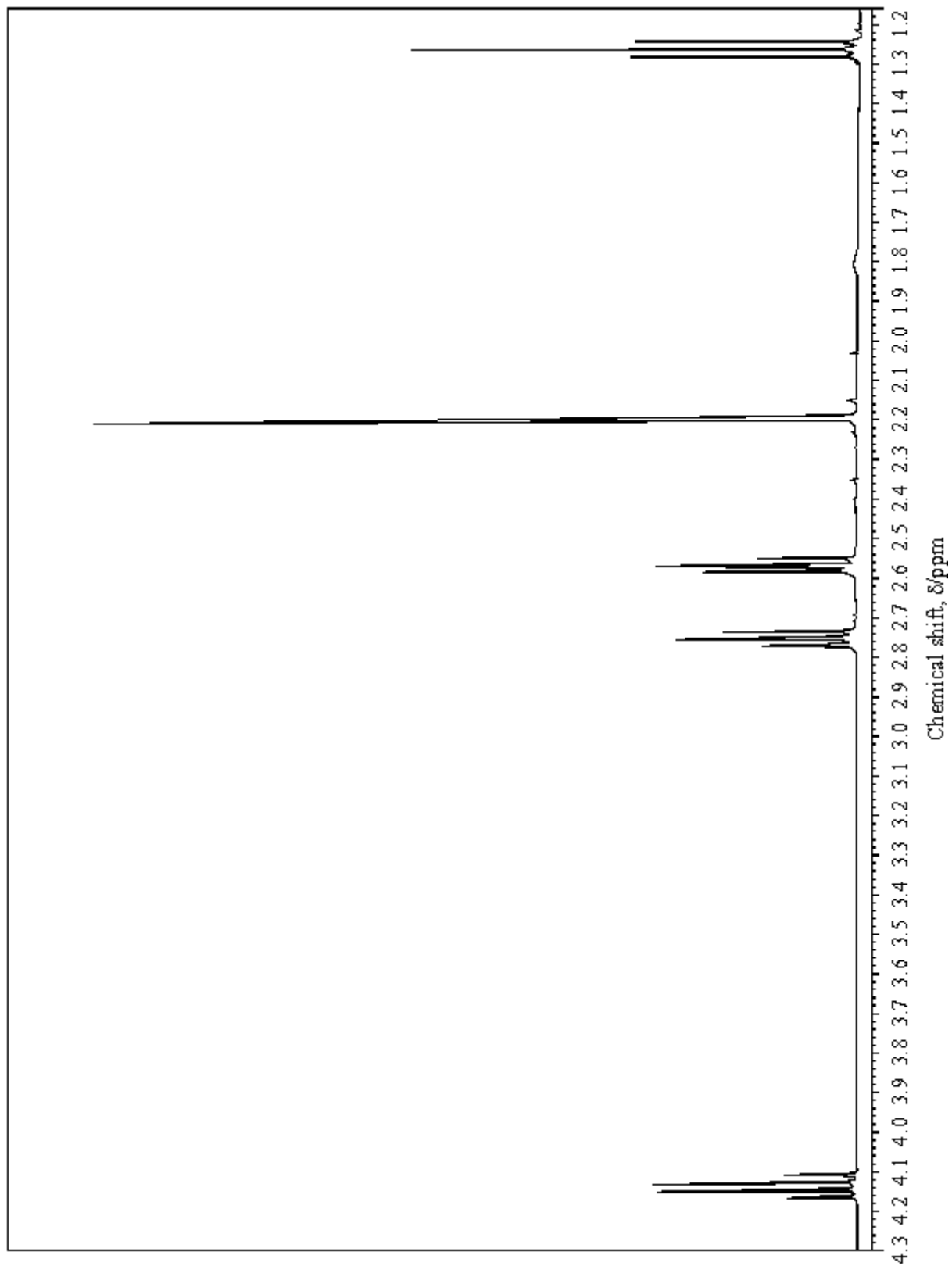
(i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

(ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

(iii) Give the IUPAC name of **K**.

(Total 7 marks)

Q3. The proton n.m.r. spectrum of compound **X** is shown below.



Compound **X**, $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

Chemical shift, δ /ppm	4.13	2.76	2.57	2.20	1.26
Integration ratio	0.8	0.8	0.8	1.2	1.2

Refer to the spectrum, the information given above and the data below the Periodic Table provided to answer the following questions.

- (a) How many different types of proton are present in compound **X**?

(1)

- (b) What is the whole-number ratio of each type of proton in compound **X**?

(1)

- (c) Draw the part of the structure of **X** which can be deduced from the presence of the peak at δ 2.20.

(1)

- (d) The peaks at δ 4.13 and δ 1.26 arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

Alkyl group _____

Explanation _____

(3)

- (e) Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at δ 2.76 and δ 2.57.

(1)

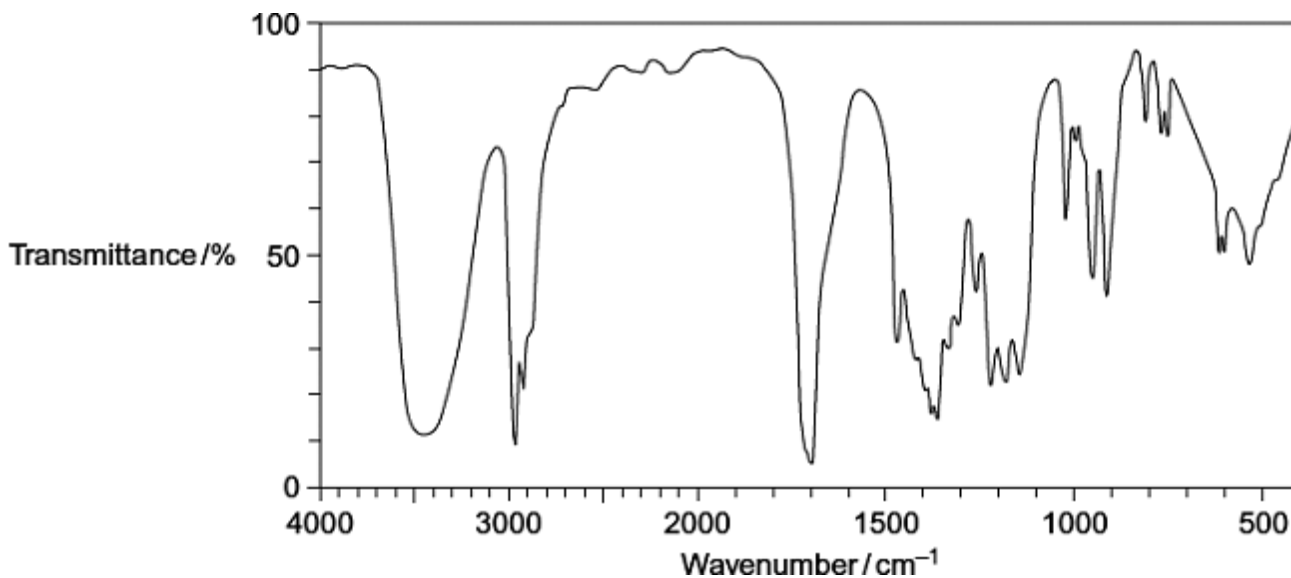
- (f) Deduce the structure of compound **X**.

(2)

(Total 9 marks)

Q4. Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

- (a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm^{-1} in the spectrum.

(1)

- (b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ /ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i) The peak at $\delta = 2.6$

(1)

(ii) The peak at $\delta = 2.2$

(1)

(iii) The peak at $\delta = 1.2$

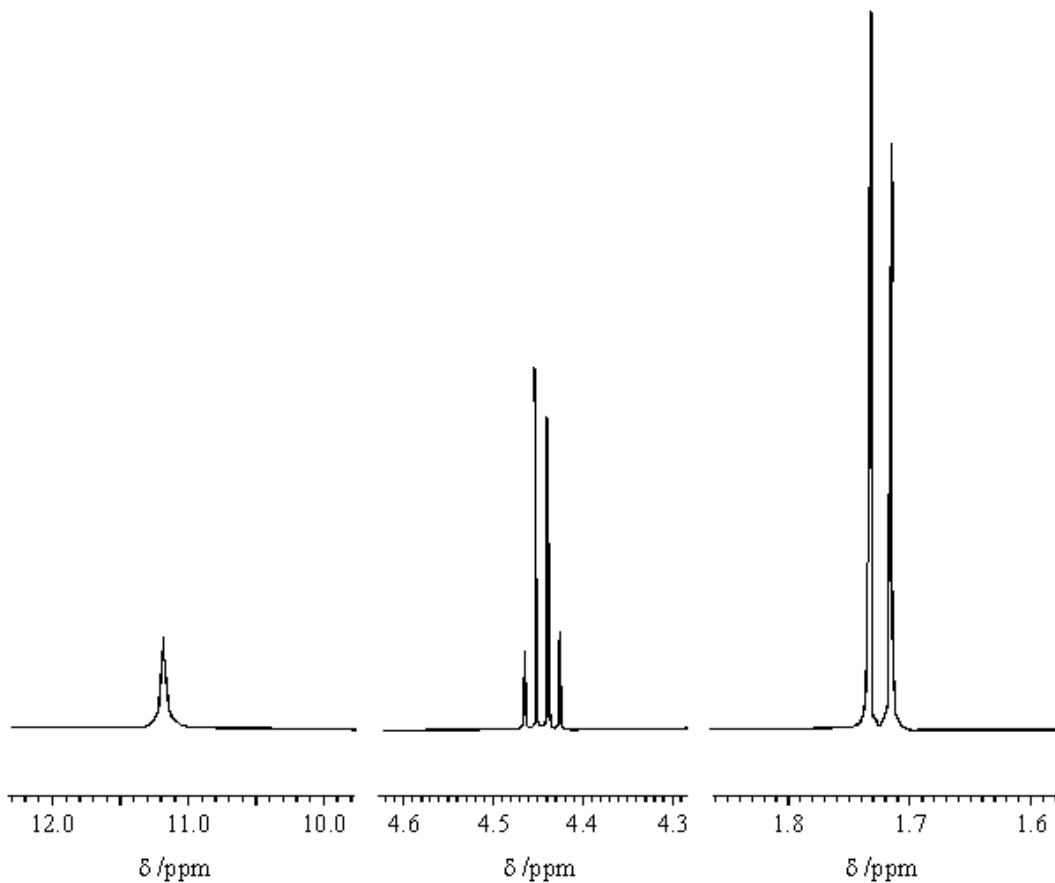
(1)

(iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

(1)

(Total 5 marks)

Q5. Three sections of the proton n.m.r. spectrum of $\text{CH}_3\text{CHClCOOH}$ are shown below.



(a) Name the compound $\text{CH}_3\text{CHClCOOH}$

(1)

(b) Explain the splitting patterns in the peaks at δ 1.72 and δ 4.44

(2)

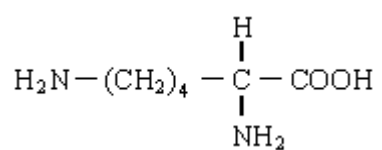
(c) Predict the splitting pattern that would be seen in the proton n.m.r. spectrum of the isomeric compound $\text{ClCH}_2\text{CH}_2\text{COOH}$

(1)

- (d) The amino acid *alanine* is formed by the reaction of $\text{CH}_3\text{CHClCOOH}$ with an excess of ammonia. The mechanism is nucleophilic substitution. Outline this mechanism, showing clearly the structure of *alanine*.

(5)

- (e) The amino acid *lysine* has the structure



Draw structures to show the product formed in each case when lysine reacts with

- (i) an excess of aqueous HCl,

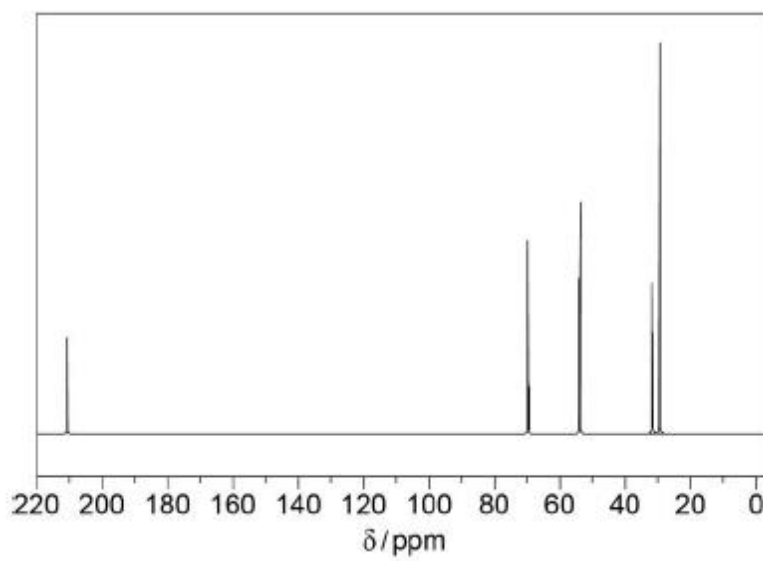
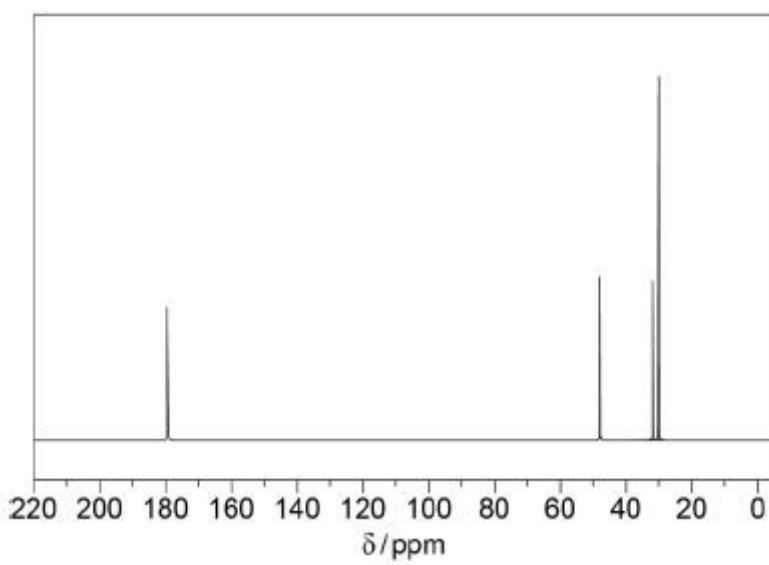
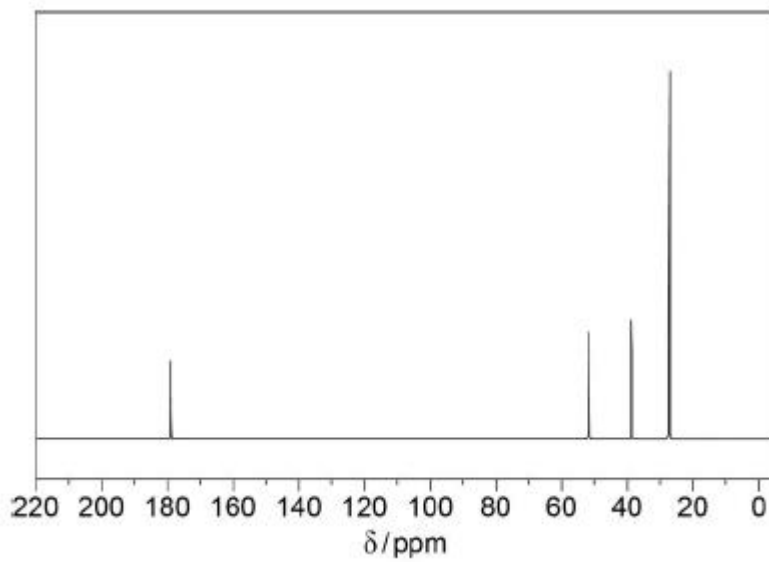
- (ii) an excess of aqueous NaOH,

- (iii) another molecule of lysine.

(3)

(Total 12 marks)

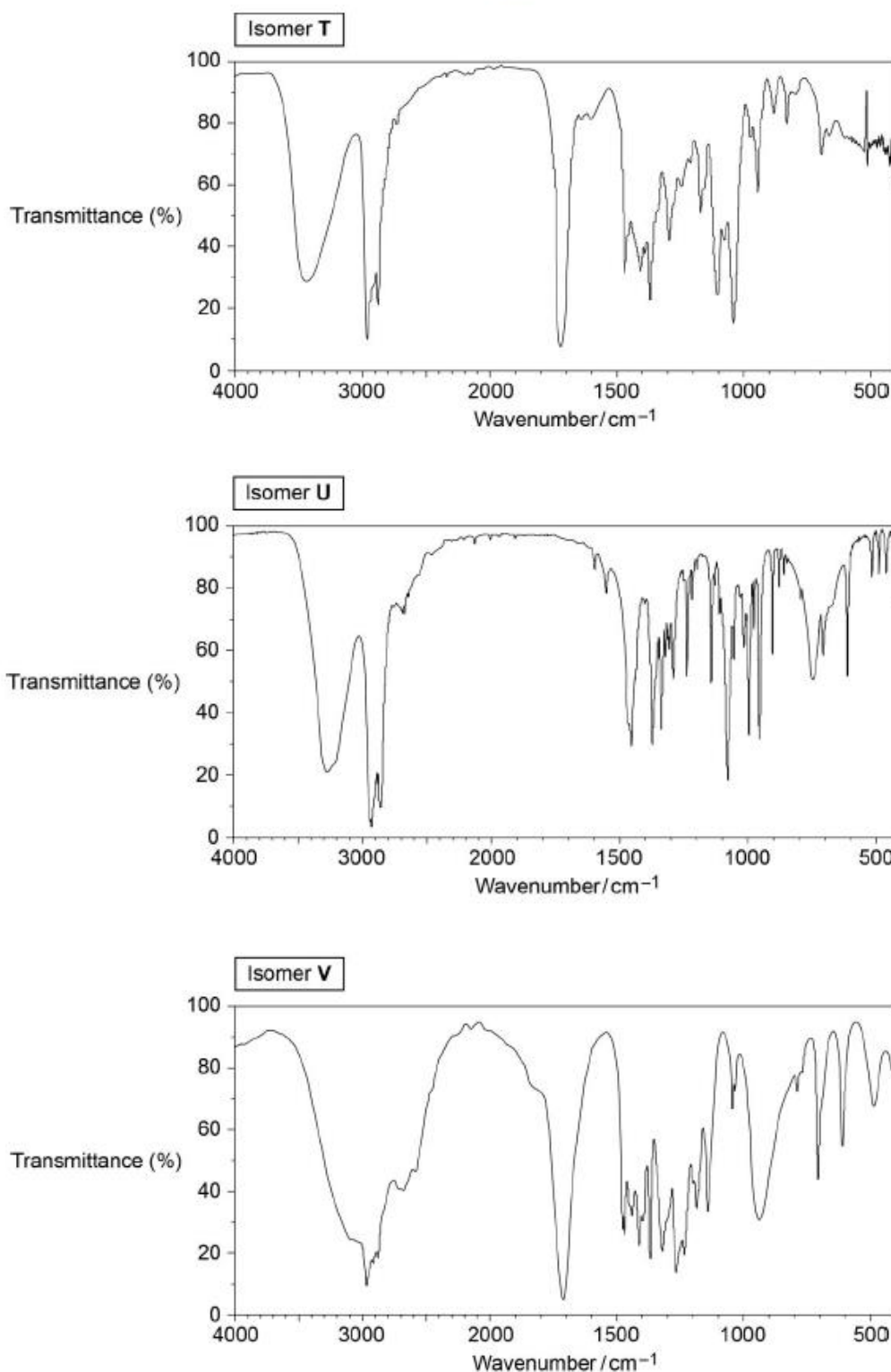
Figure 2



(3)

- (c) The infrared spectra shown in **Figure 3** are those of three different isomers of $C_6H_{12}O_2$, isomers **T**, **U** and **V**.

Figure 3



Identify the functional group(s) present in each isomer **T**, **U** and **V** of $C_6H_{12}O_2$ using **Table A** in the Data Booklet.

Explain your answer.

(6)

- (d) The integration values for the peaks in the ^1H NMR spectrum of **X**, a different isomer of $\text{C}_6\text{H}_{12}\text{O}_2$, are given in the table below.

Chemical shift, δ/ppm	3.7	3.5	2.6	2.2	1.1
Integration value	0.6	0.6	0.6	0.9	0.9
Splitting pattern	triplet	quartet	triplet	singlet	triplet

Deduce the simplest ratio of the relative numbers of protons in each environment in compound **X**.

(1)

- (e) Use the data in the table above and **Table B** in the Data Booklet to help you answer this question.

Deduce the part of the structure of **X** that causes the signal at $\delta = 3.5$ and the part of the structure at **X** that causes the signal at $\delta = 2.2$.

Explain the splitting patterns of these peaks.

Signal at $\delta = 3.5$ _____

Signal at $\delta = 2.2$ _____

(4)

- (f) Deduce the structure of compound **X**, $\text{C}_6\text{H}_{12}\text{O}_2$

Use your answer from part (e) to help you.

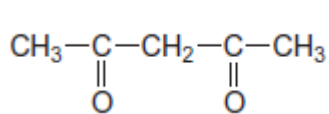
You are **not** required to explain how you deduced the structure.

(2)

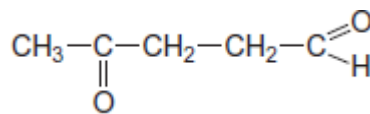
(Total 17 marks)

- (b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.



J



K

(5)

- (c) Draw the structure of each of the following isomers of $\text{C}_5\text{H}_8\text{O}_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^1H n.m.r. spectrum.

(5)

(Total 19 marks)

Mark schemes

Q1.

- (a) (i) There are three pairs of equivalent carbon atoms 1
- (ii) 75ppm 1
- (b) (i) 4 1
- (ii) 2 1
- (c) Each structure can represent a pair of cis/Z and trans/E isomers
OR
Optical isomers 1

[5]

Q2.

- (a) (i) CDCl_3 or CD_2Cl_2 or C_6D_6 or CCl_4
Not D_2O Allow CD_3Cl 1
- (ii) **4 or four** 1
- (iii) Triplet or 3 or three 1
- (iv) 1,4-dichloro-2,2-dimethylbutane
Do not penalise different or missing punctuation or extra spaces.
Spelling must be exact and order of letters and numbers as here. 1
- (b) (i) 3 or three 1
- (ii) 190-220 (cm^{-1})
Allow a single number within the range.
OR *a smaller range entirely within this range.* 1
- (iii) hexane-2,5-dione
Do not penalise different or missing punctuation or extra spaces.
Spelling must be exact and order of letters and numbers as here.
NB so must have middle e 1

Q3.

(a) 5 (1) 1

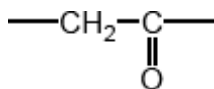
(b) 2:2:2:3:3 (1)
any order but not multiples 1(c) $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - (\text{R})$ (1) 1(d) CH_3CH_2 or C_2H_5 or ethyl (1)
 $\delta 4.13$ (quartet) : CH_2 peak split by CH_3 / next to CH_3 (1)
 $\delta 1.26$ (triplet) : CH_3 peak split by CH_2 / next to CH_2 (1) 3(e) CH_2CH_2 (1) 1(f) $\text{CH}_3 - \overset{(\text{CO})}{\parallel}{\text{C}} - \text{CH}_2\text{CH}_2 - \overset{(\text{CO})}{\parallel}{\text{C}} - \text{OCH}_2\text{CH}_3$ (2)
allow (1) for $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OCOCH}_2\text{CH}_3$
or $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$
Must be $\text{C}_7\text{H}_{12}\text{O}_3$ 2

[9]

Q4.

(a) OH alcohols 1

(b) (i) 2.6

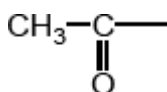


Ignore any group on RHS

Must clearly indicate relevant **two** H on a C next to $\text{C}=\text{O}$ On LHS, penalise H or CH or CH_2 or CH_3

Ignore missing trailing bonds or attached R groups 1

(ii) 2.2

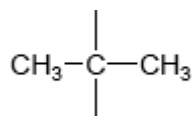


Ignore all groups on RHS

Must clearly indicate relevant **three** H on C next to C=O
 Ignore missing trailing bonds or attached R group

1

(iii) 1.2



Or in words: two equivalent CH₃ groups

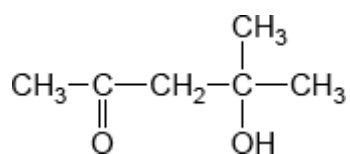
Must clearly indicate two equivalent methyl groups.

Penalise attached H

Ignore missing trailing bonds or attached R groups

1

(iv)



1

[5]

Q5.

(a) 2-chloropropanoic acid (1)

1

(b) δ 1.72 Doublet \therefore next to CH (1)

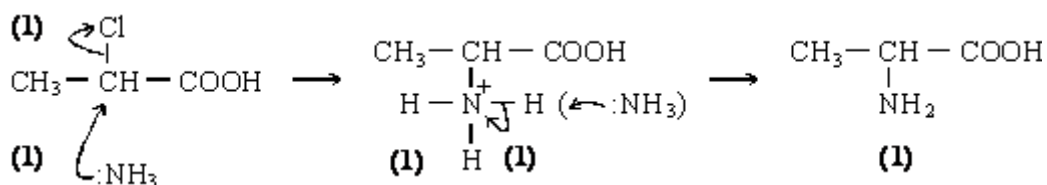
δ 4.44 Quartet \therefore next to CH₃ (1)

2

(c) Two triplets (1)

1

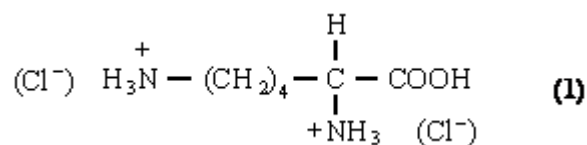
(d)



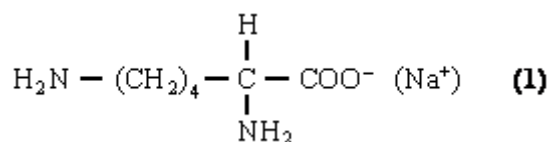
Allow S_N1

5

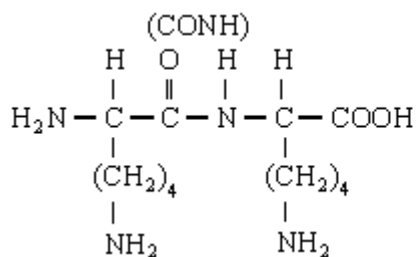
(e) (i)



(ii)

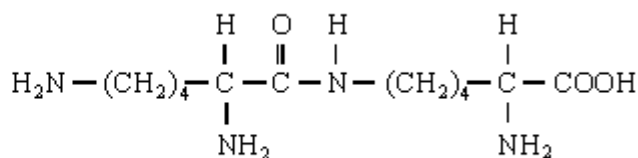


(iii)



(1)

or



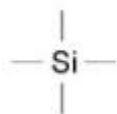
Or anhydride

3

[12]

Q6.

(a)



1xAO1

1

(b) **S**

1

R

1

Q

1

(c) (Isomer T)

signals due to OH (alcohol) at 3230–3350 and C=O at 1680–1750

1

OH and C=O (functional groups) separated in molecule.

Allow not a carboxylic acid.

1

(Isomer U)

(only) signal for OH (alcohol) at 3230–3350

1

2 × OH groups present / diol / OH & cyclo(ether) structure.

Allow OH but not C=O.

1

(Isomer V)

signals due to OH (acid) at 2500–3000 (and C=O at 1680–1750)

carboxylic acid group / –COOH present.

1

1

(d) 2:2:2:3:3

Any order.

1

(e) (The quartet at $\delta=3.5$ is for a CH_2 group) next to $-\text{O}-\text{CH}_2$ OR shifted significantly downfield by electronegative O

1

(is a quartet) because of an adjacent CH_3 group / couple with 3 adjacent protons

1

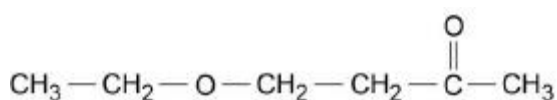
(singlet at $\delta=2.2$ is for a CH_3 group) attached to $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ OR shifted downfield by electronegative $\text{C}=\text{O}$

1

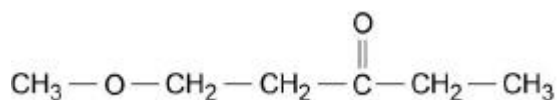
(is a singlet) because there are no adjacent protons / no coupling.

1

(f)



Allow 1 mark for:



2

[17]

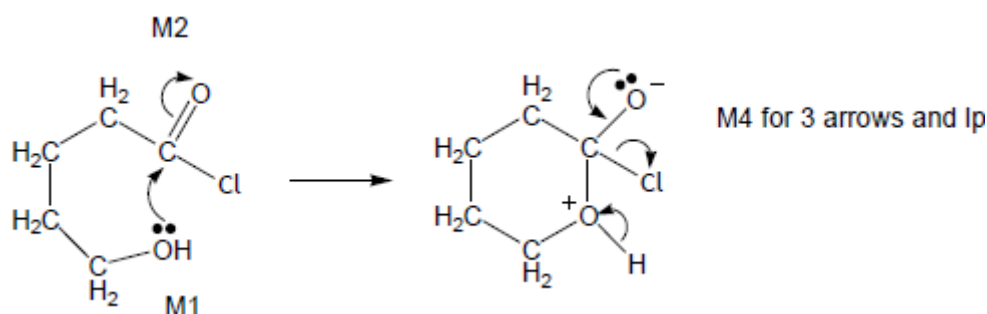
Q7.

(a) (i) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

Ignore esterification

1



M3 for structure

- If wrong nucleophile used or $\text{O}-\text{H}$ broken in first step, can only score M2.
- M2 not allowed independent of M1, but allow M1 for correct attack on C^+
- + rather than δ^+ on $\text{C}=\text{O}$ loses M2.
- If Cl lost with $\text{C}=\text{O}$ breaking lose M2.

- M3 for correct structure with charges but lone pair on O is part of M4.
- Only allow M4 after correct / very close M3.
- Ignore HCl shown as a product.

4

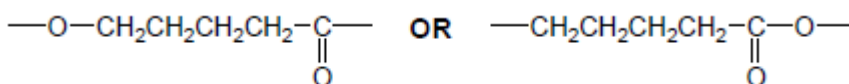
a 20-50 (ppm) or single value or range entirely within this range
If values not specified as a or b then assume first is a.

1

b 50-90 (ppm) or single value or range entirely within this range

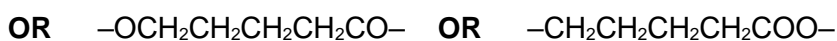
1

(ii)

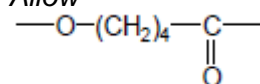


Must have trailing bonds, but ignore n.

1



Allow



but not $\text{—C}_4\text{H}_8\text{—}$

one unit only

Condensation

1

(b)

	Tollens'	Fehling's / Benedicts	Acidified potassium dichromate
--	----------	-----------------------	--------------------------------

Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on.

1

J	No reaction / no (visible) change / no silver mirror	No reaction / no (visible) change / stays blue / no red ppt	No reaction / no (visible) change / stays orange / does not turn green
----------	--	---	--

Ignore 'clear', 'nothing'.

Penalise wrong starting colour for dichromate.

1

K	Silver <u>mirror</u> / grey <u>ppt</u>	Red <u>ppt</u> (allow brick red or	(orange) turns green
----------	--	---------------------------------------	----------------------

		red-orange)	
--	--	-------------	--

1

J Two (peaks)
 Allow trough, peak, spike.

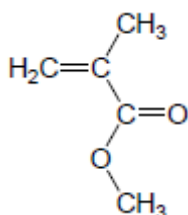
1

K Four (peaks)
 Ignore details of splitting.
 If values not specified as J or K then assume first is J.

1

(c) If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.

L
 ester



OR $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$

All $\text{C}_5\text{H}_8\text{O}_2$ L to P must have $\text{C}=\text{C}$.

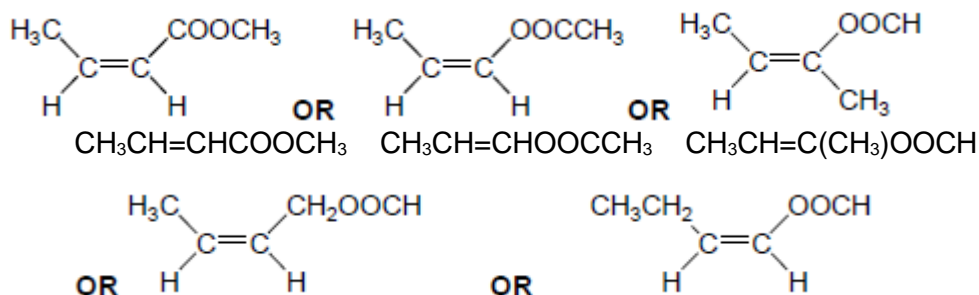
Allow CH_3^- .

Allow $-\text{CO}_2\text{CH}_3$ etc.

Allow $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$.

1

M
 ester



$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OOCH}$

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHOOCH}$

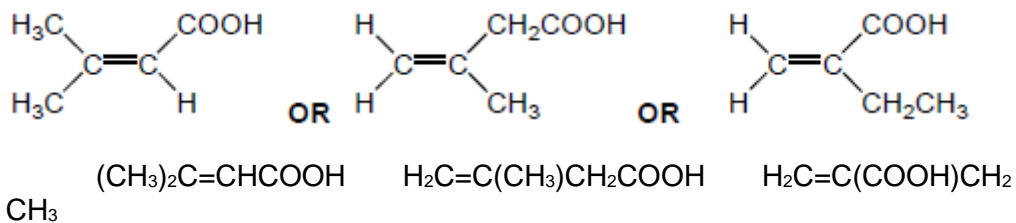
Allow either *E-Z* isomer.

Allow CH_3^- or C_2H_5^- but not CH_2CH_3^- .

Allow $\text{CH}_3\text{CHCHCOOCH}_3$ etc.

1

N
 acid

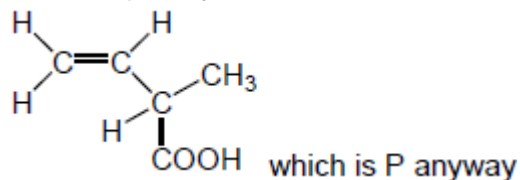


Allow CH₃- or C₂H₅- but not CH₂CH₃-.

Allow -CO₂H.

Not cyclic isomers.

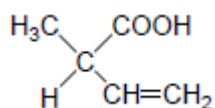
Not the optically active isomer.



Allow (CH₃)₂CCHCOOH etc.

1

P
acid



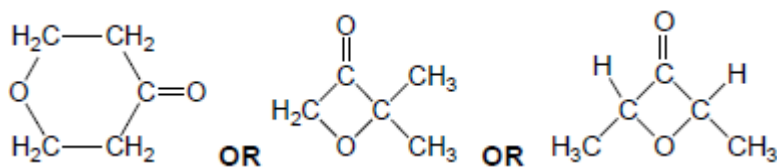
Allow -CO₂H.



Allow CH₃CH(CO₂H)CHCH₂ or
CH₃CH(CO₂H)C₂H₃.

1

Q



Not cyclic esters.

1

[19]