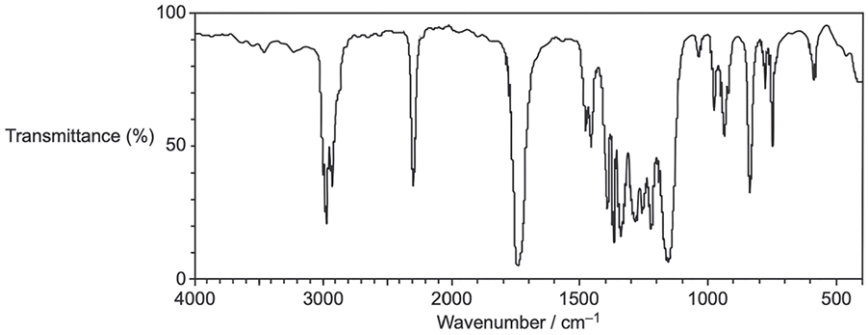
Spectroscopy

1(a). An organic compound **I** is analysed, using a combination of techniques. The analytical data is shown below.

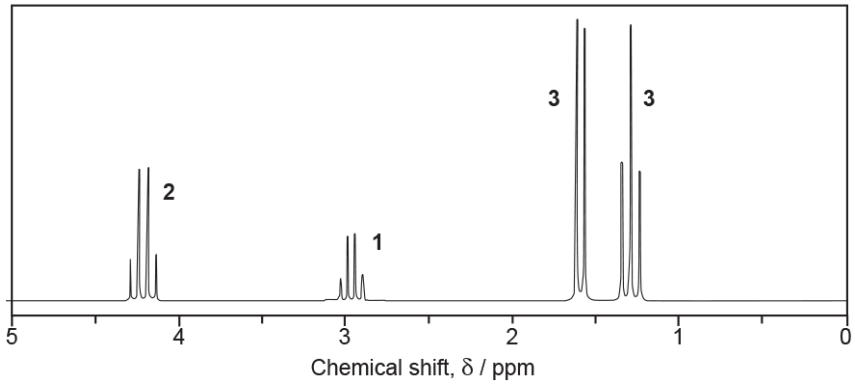
Elemental analysis by mass
C, 56.69%; H, 7.09%; N, 11.02%; O, 25.20%

Mass spectrum
Molecular ion peak at *m/z* = 127.0

IR spectrum



Proton NMR spectrum



* Determine the structure of compound **I**, showing **all** your reasoning.

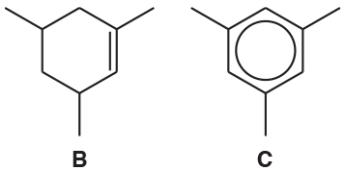
---

[6]

(b). Explain the use of two deuterated compounds in NMR spectroscopy.

[2]

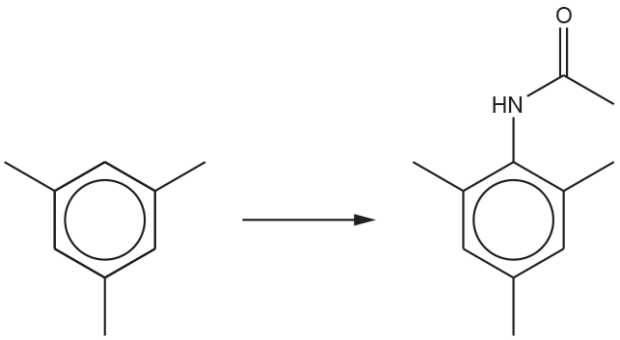
2. Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.



B **C**

An organic chemist is investigating compound **D** for possible use as a medicine.

The chemist proposes a synthesis of compound D from compound C.



compound C **compound D**

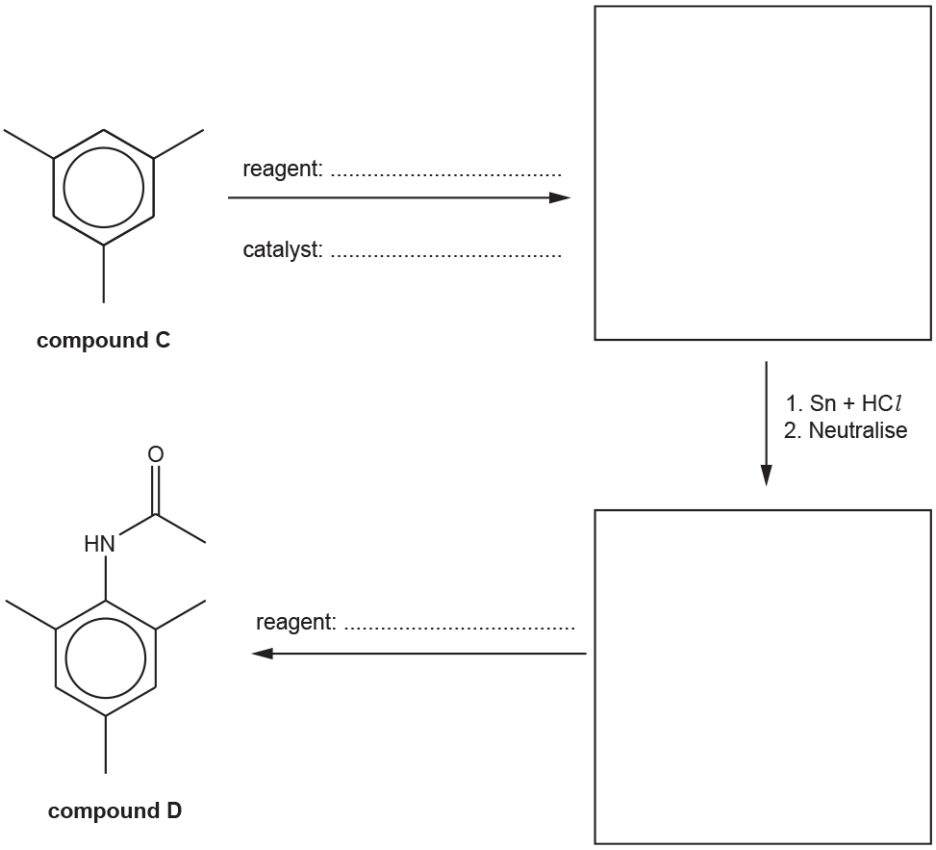
i. Predict the number of peaks in the ^{13}C NMR spectra of compounds **C** and **D**.

	Compound **C**	Compound **D**
Number of peaks	.....	.....

[2]

ii. The chemist develops a three-stage synthesis of compound **D** from compound **C**.

Complete the flowchart.
Show structures for organic compounds.

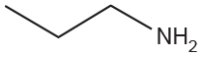
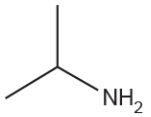
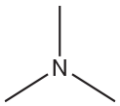


[5]

3. This question is about organic chemistry.

This part is about amines.

i. The table shows the structures and boiling points of three amines, which are structural isomers of C_3H_9N.

Amine	$CH_3CH_2CH_2NH_2$	$(CH_3)_2CHNH_2$	$(CH_3)_3N$
Skeletal formula			
Boiling point / °C	48–49 °C	33–34 °C	3–4 °C

Explain the difference in the boiling points of the three amines.

---

[4]

ii. Amine **A** is a liquid at room temperature and pressure.

When vaporised, 0.202 g of the amine produces 72.0 cm^3 of gas at 1.00×10^5 Pa and 100 °C. The ^{13}C NMR spectrum of amine **A** has 3 peaks.

Determine the molecular formula of **A** and suggest a possible structure for amine **A**.

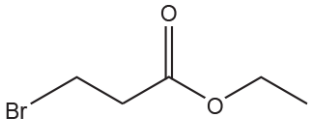
Molecular formula of **A** .....

Structure of A

[6]

4(a). This question is about esters.

The structure of ester **A** is shown below.



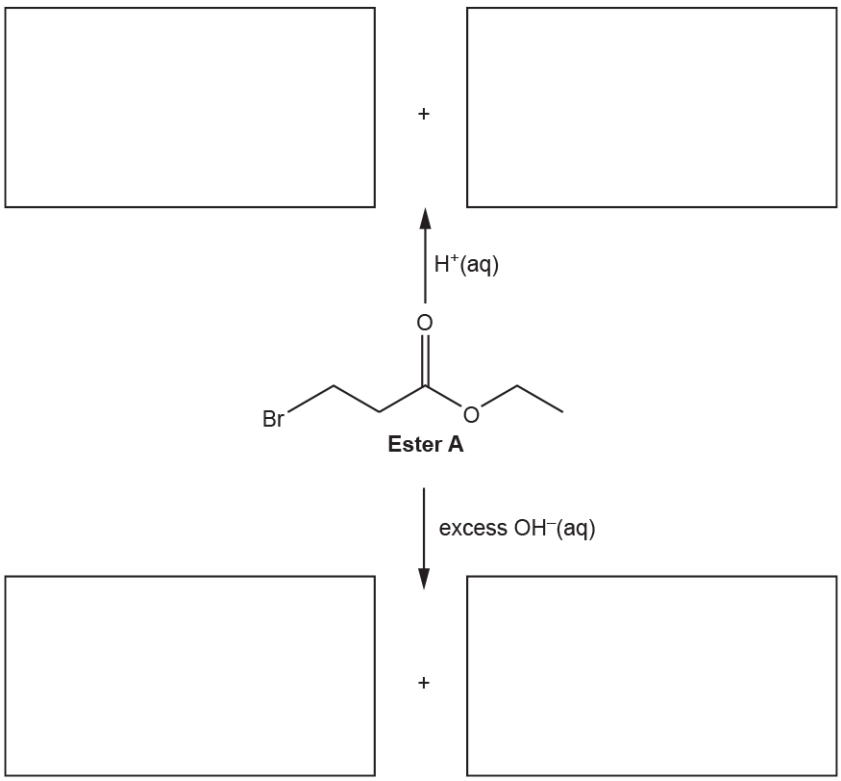
Ester A

i. What is the systematic name of ester **A**?

---

[1]

ii. In the boxes, draw the organic products for the reactions of the functional groups in ester **A** shown below.
Each reaction forms two organic products.



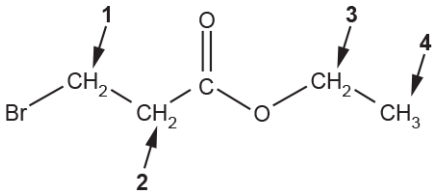
[5]

iii. Name the type of reactions of ester **A** shown in **(ii).**

---

[1]

(b). The protons in ester A are in four different environments, labelled **1– 4** on the structure below.



Complete the table to predict the **proton** NMR spectrum of ester **A.**

Proton environment	Chemical shift	Splitting pattern
1		
2		
3		
4		

[4]

(c). Compound **B** is a structural isomer of ester **A.**

- Compound **B** reacts with aqueous sodium carbonate.
- The ^{13}C NMR spectrum of **B** has 4 peaks.

Draw a possible structure for compound **B.**

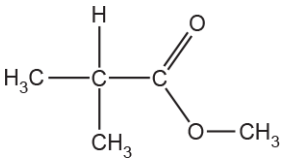
[1]

(d). A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.

What is the relative molecular mass, M_r, of the polyester?

M_r = ... g mol^{-1} **[2]**

(e). * A student intends to synthesise ester **C**.



Ester C

i. Plan a two-stage synthesis to prepare 12.75 g of ester **C** starting from 2-methylpropanal, $(CH_3)_2CHCHO$. Assume the overall percentage yield of ester **C** from 2-methylpropanal is 40%.

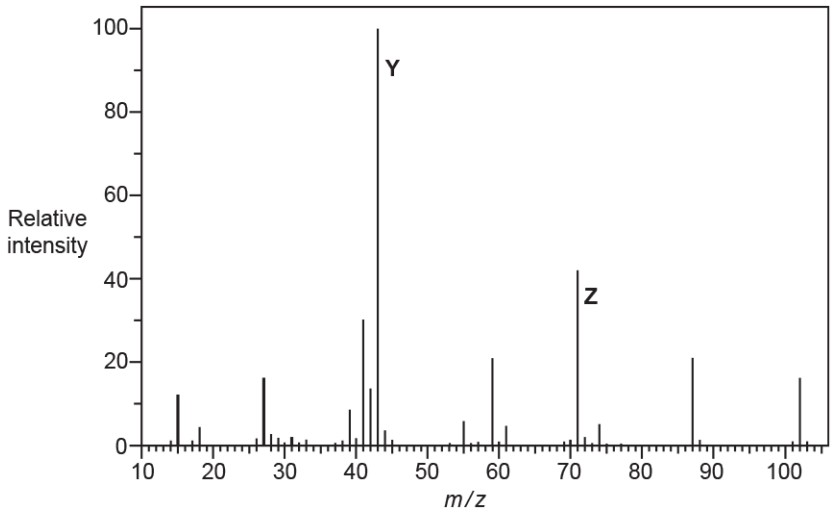
In your answer include the mass of 2-methylpropanal required, reagents, conditions and equations where appropriate.

Purification details are **not** required.

---

[6]

ii. The mass spectrum of ester **C** is shown below.



Suggest possible structures for the species responsible for peaks **Y** and **Z** in the mass spectrum.

Y	**Z**

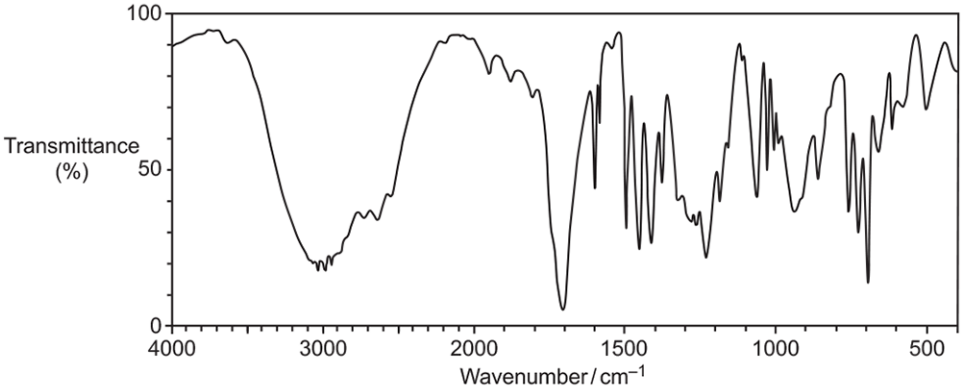
[2]

5. * Analysis of an unknown organic compound produced the following results.

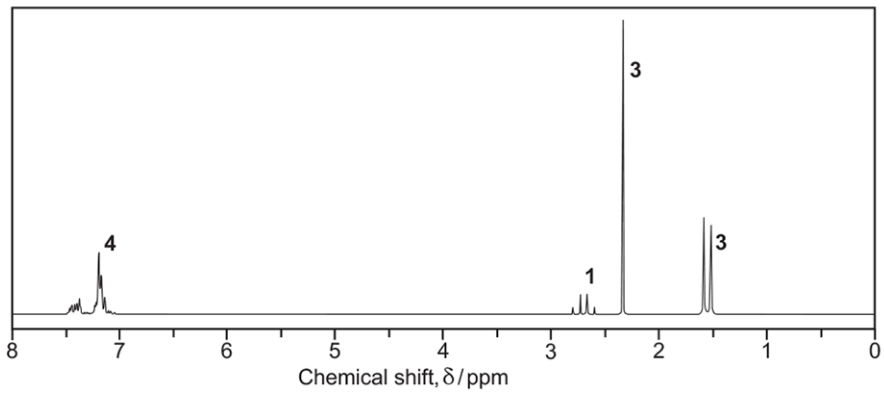
Elemental analysis by mass
C: 73.17%; H: 7.32%; O: 19.51%

Mass spectrum
Molecular ion peak at m / z = 164.0

Infrared spectrum



^{1}H NMR spectrum in D_2O



The numbers by the peaks are the relative peak areas.

Use the results to suggest **one** possible structure for the unknown compound.

Show **all** your reasoning.

---

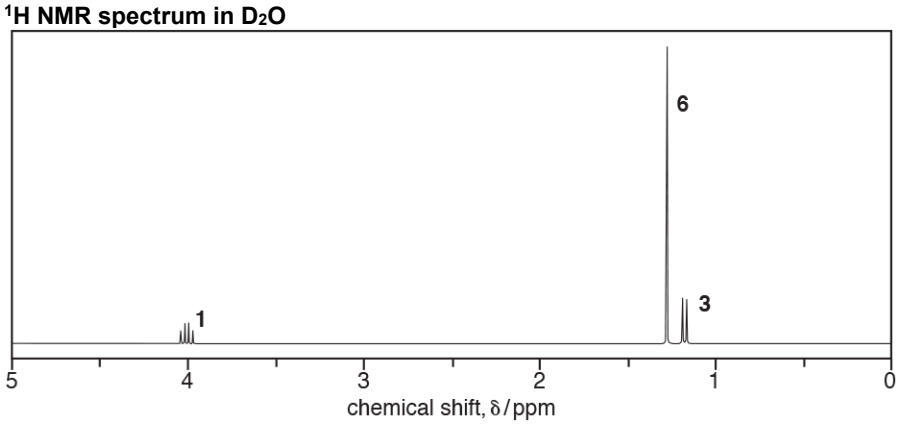
[6]

6. A scientist is researching compounds that might be suitable as fuel additives.
One of the compounds gives the analytical results below.

Elemental analysis by mass:
C: 54.54%; H: 9.10%; O: 36.36%

Mass spectrum:
Molecular ion peak at *m/z* = 132.0

^{1}H NMR spectrum in D_2O



The numbers by the peaks are the relative peak areas.

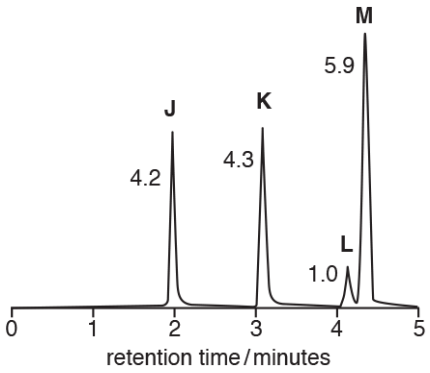
When the spectrum is run without D_2O, there are **two** additional peaks with the same relative peak areas at 11.0 ppm and 3.6 ppm.

Use the information provided to suggest a structure for the compound.

Show all your reasoning. **[6]**

7. A cosmetic product containing four esters, **J**, **K**, **L** and **M**, is analysed by gas chromatography and mass spectrometry. The results are shown below.

Gas chromatogram



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

Mass spectrometry

ester	*m/z* of molecular ion peak
J	152
K	166
L	180
M	180

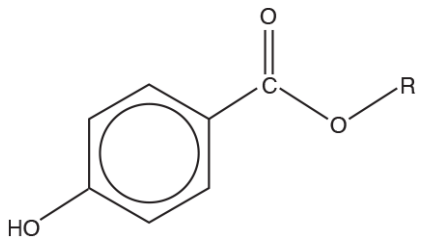
i. The concentration of ester **K** in the cosmetic product is 9.13×10^{-2} g dm^{-3}.

Using the results, calculate the concentration, in mol dm^{-3}, of ester **M** in the cosmetic product.

Give your answer to **two** significant figures.

concentration of ester **M** = _____ mol dm^{-3} **[2]**

ii. A general structure for esters **J**, **L** and **M** is shown below.



Where 'R' is an alkyl group.

Use the mass spectrometry results to deduce possible structures for esters **J**, **L** and **M**.

J	L	M

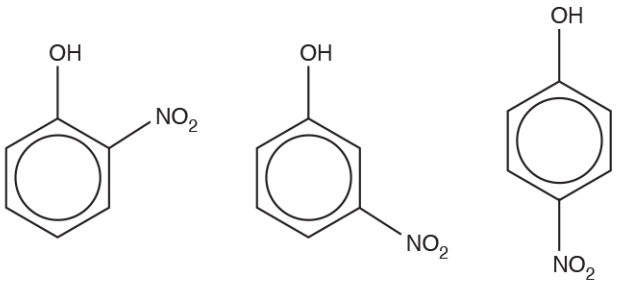
[3]

8. This question is about aromatic compounds.

Phenol undergoes nitration more readily than benzene.

i. A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.

A small amount of 3-nitrophenol is also produced.



2-nitrophenol **3-nitrophenol** **4-nitrophenol**

The student thought that ^{13}C NMR spectroscopy could be used to distinguish between these three nitrophenols.

Explain whether the student is correct.

_____

_____

_____

_____

_____

_____

_____

_____ **[3]**

ii. Explain why phenol is nitrated more readily than benzene.

_____

_____

_____

_____

_____

_____

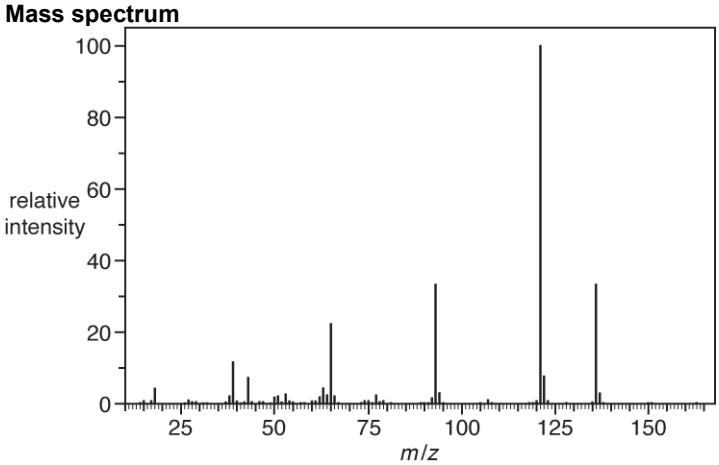
_____

_____

_____ **[3]**

9(a). A chemist analyses a naturally occurring aromatic compound.

The percentage composition and mass spectrum of the compound are shown below.
Percentage composition by mass: C, 70.58%; H, 5.92%; O, 23.50%.
Mass spectrum



Determine the molecular formula of the compound.
Show your working.

molecular formula = ... **[3]**

(b). Qualitative tests are carried out on the aromatic compound. The results are shown below.

Test	**Acidity**	**Na_2CO_3(aq)**	**2,4-DNP**	**Tollens' reagent**
Observation	pH = 5	No observable change	Orange precipitate	No observable change

Determine the functional groups in the compound. Explain your reasoning.

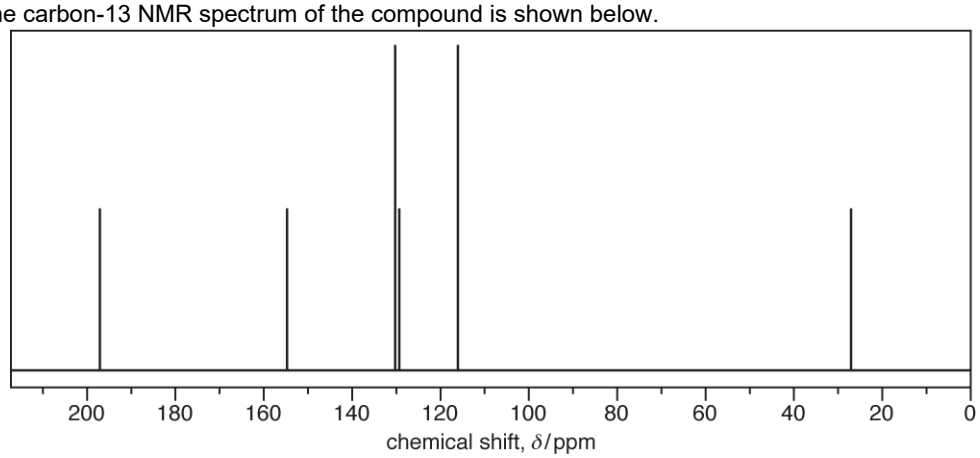
Functional groups ----------

Explanation ----------

---

[3]

(c). The carbon-13 NMR spectrum of the compound is shown below.



Using the spectrum and the results from **(a)** and **(b)**, determine the structure of the compound. Explain your reasoning.

Structure of compound

[3]

10. Fruit juice contains a mixture of organic acids.

*Acid **C** is an aliphatic organic acid present in fruit juice.

Information about acid **C** is shown below:

- 1.21×10^{-2} mol **C** has a mass of 2.323 g.
- The molecular formula of **C** is $C_xH_yO_7$.
- 1 mol of acid **C** requires 3 mol NaOH for neutralisation.
- Acid **C** contains a hydroxyl group but produces no colour change with hot acidified dichromate(VI).
- The ^{13}C NMR spectrum of **C** has four peaks.

Analyse this information to determine the structure of acid **C**.

Show **all** your reasoning.

---

[6]

11(a). A student was provided with five compounds: an aldehyde, a ketone, a carboxylic acid and two esters. The student decides to identify the type of compound by carrying out some chemical tests.

Suggest chemical tests to identify the carboxylic acid and aldehyde.

For each test, include essential reagent(s), observation(s) and a balanced equation.

In your equations, use 'R' for the alkyl group.

i. Test for carboxylic acid.

Reagent(s)
.....

Observation(s)
.....

Equation

[2]

ii. Test for aldehyde.

Reagent(s)
.....

Observation(s)
.....

Equation

[2]

(b). Suggest a chemical test to distinguish the ketone from the two esters.

Reagent(s)
.....

Observation(s)
.....

---

[1]

(c). The student wants to confirm that the other two compounds are esters. Unfortunately there is no direct test for an ester group.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

The student plans the following:

- hydrolyse the two esters using aqueous sodium hydroxide.
- separate the hydrolysis products.
- carry out tests on the hydrolysis products.

i. Write an equation for the hydrolysis of one of the two esters with aqueous sodium hydroxide.

Show the structures for the organic compounds.

[2]

ii. Suggest a chemical test on the hydrolysis products that would allow the two esters to be identified.

Write an equation for one reaction that takes place.

Show the structures for the organic compounds.

Reagent(s)
.....

Observation(s)
.....

Equation

[2]

iii. The student thought that NMR spectroscopy could be used to identify the two esters without the need to carry out chemical tests.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

Explain whether the student is correct for ^{13}C and ^{1}H NMR spectroscopy. Your answer should also clearly state any differences between the spectra of the two esters.

---

[3]

(d). The ketone and aldehyde provided to the student both contain five carbon atoms.

The ^{1}H NMR spectrum of the aldehyde contains two singlet peaks only:
a large peak at δ = 1.2 ppm and smaller peak at δ = 9.6 ppm.

Suggest **all** possible structures for the ketone and identify the aldehyde.

Show **all** your reasoning.

---

[5]

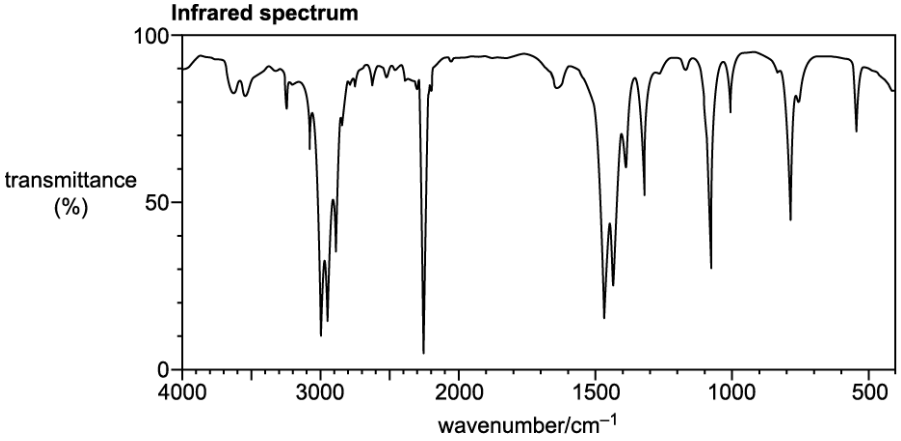
12. *Compound **J** is an organic compound containing carbon, hydrogen and nitrogen only.

A chemist analyses compound **J** and the results are shown below:

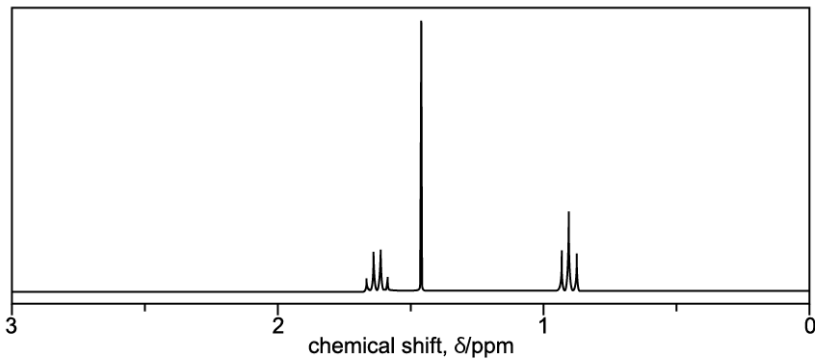
Elemental analysis by mass:
C: 74.17%; H: 11.41%; N, 14.42%

Mass spectrum
Molecular ion peak at *m/z* = 97.0

Infrared spectrum



^{1}H NMR spectrum



Use the information provided to suggest a structure for compound **J**.

Show **all** of your reasoning.

_____

_____

_____

_____

_____

_____

_____

_____ **[6]**

13(a). A chemistry teacher carries out an experiment to synthesise 2-aminopropan-1-ol, $CH_3CH(NH_2)CH_2OH$.

The teacher asks a university chemistry department to test the 2-aminopropan-1-ol using proton NMR spectroscopy and mass spectrometry.

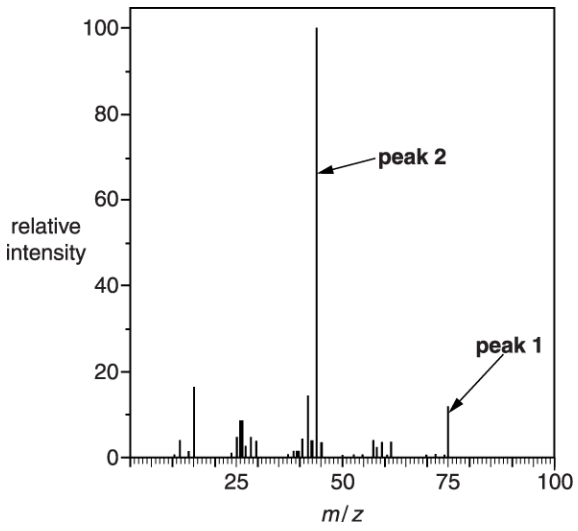
i. For the ^1H NMR analysis, the sample was dissolved in D_2O.

Complete the table to predict the ^1H NMR spectrum of $CH_3CH(NH_2)CH_2OH$ after dissolving in D_2O.

^1H NMR spectrum for $CH_3CH(NH_2)CH_2OH$, dissolved in D_2O		
Chemical shift, δ/ ppm	**Relative peak area**	**Splitting pattern**

[3]

ii. The mass spectrum for $CH_3CH(NH_2)CH_2OH$ is shown below.



Give the formulae for the species responsible for **peak 1** and **peak 2** in the mass spectrum.

peak 1

peak 2

[2]

(b). The teacher synthesises 2-aminopropan-1-ol, $CH_3CH(NH_2)CH_2OH$, from 2-chloropropan-1-ol, $CH_3CHC/\ CH_2OH$.

i. State the reagents and conditions required for this synthesis.

---

[1]

ii. The sample prepared by the teacher from 2-chloropropan-1-ol is not pure. It also contains compound **D**.

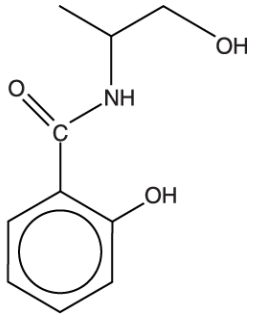
Compound **D** has a molecular formula of $C_6H_{15}NO_2$.

Suggest the structure of compound **D**.

Compound **D**

[1]

(c). In a separate experiment, the chemistry teacher prepares compound **E** from 2-aminopropan-1-ol.



compound E

i. One of the functional groups in compound **E** is a phenol.

Name the other functional groups in compound **E**.

---

[1]

ii. Draw the structures of the **two** organic products formed when compound **E** is heated under reflux with dilute hydrochloric acid.

[2]

14(a). There are several isomeric alcohols with the formula $C_5H_{11}OH$.

Pentan-1-ol, $CH_3(CH_2)_3CH_2OH$, can be prepared in the laboratory by the reduction of an aldehyde.

State a suitable reducing agent for this reaction and write an equation to show the preparation of pentan-1-ol.
Use [H] to represent the reducing agent in the equation.

Reducing agent
.....

Equation
.....

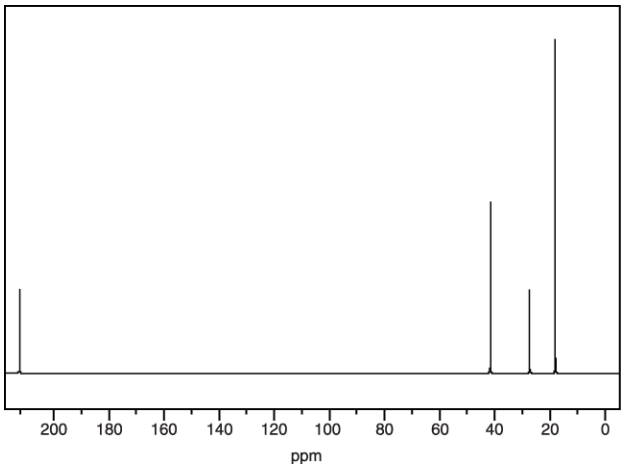
[2]

(b). Compound **F** is a structural isomer of $C_5H_{11}OH$.

Compound **F** is converted to compound **G** when heated under reflux with acidified potassium dichromate(VI) solution.

Compound **G** reacts with 2,4-dinitrophenylhydrazine to form an orange solid but compound **G** does not react with Tollens' reagent.

The ^{13}C NMR spectrum of compound **G** is shown below.



Compound **H** is a carboxylic acid. In a titration, 0.211 g of carboxylic acid **H** requires 22.8 cm^3 of 0.125 mol dm^{-3} NaOH for neutralisation.

Compound **F** reacts with compound **H** in the presence of concentrated sulfuric acid to form organic compound **I**.

Identify compounds **F**, **G**, **H** and **I** and draw their structures in the boxes below.

Show your working **only** for the identification of compound **H**.

F

G

H

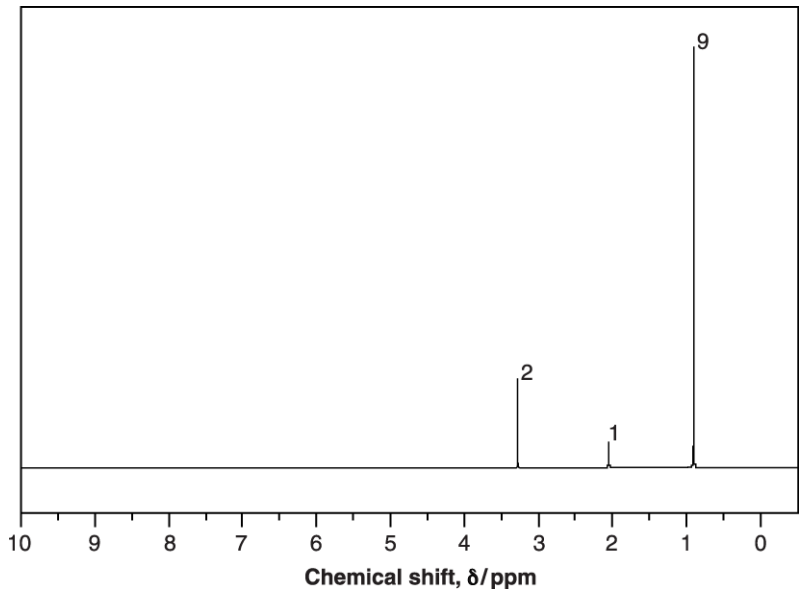
I

[7]

(c). Compound **J** is another structural isomer of $C_5H_{11}OH$.

The ^1H NMR spectrum of **J** is shown below.

The numbers next to each peak are the relative peak areas.



Identify compound **J** and draw its structure in the box below.

J

[1]

15(a). i. State the region of the electromagnetic spectrum used in ^{1}H NMR spectroscopy.

---

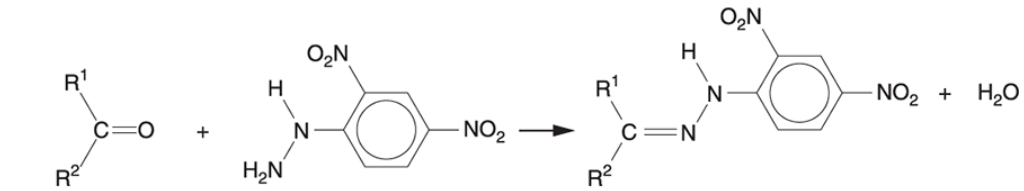
[1]

ii. Explain why $CDC\beta$ is used as a solvent in ^{1}H NMR spectroscopy.

---

[1]

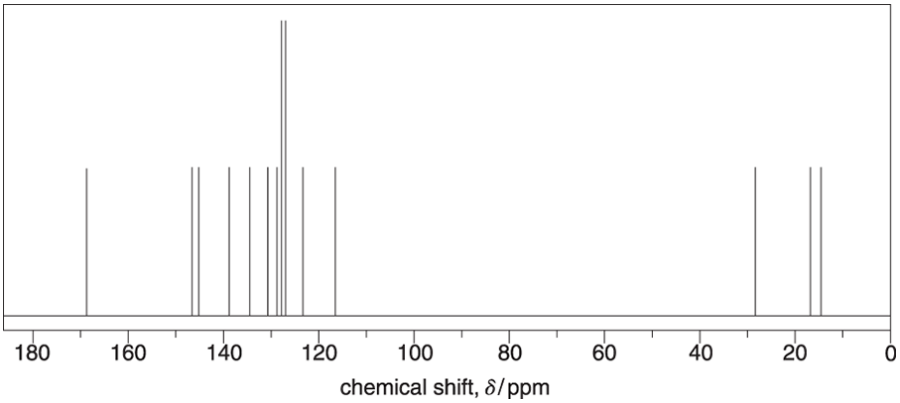
(b). A student reacts compound **K** with 2,4-dinitrophenylhydrazine. An orange precipitate, **L**, was formed.



compound K **2,4-dinitrophenylhydrazine** **orange precipitate L**

The student purifies the orange precipitate, **L**, and sends the sample for analysis using ^{1}H NMR and ^{13}C NMR spectroscopy.

The ^{13}C NMR spectrum of **L** is shown below.

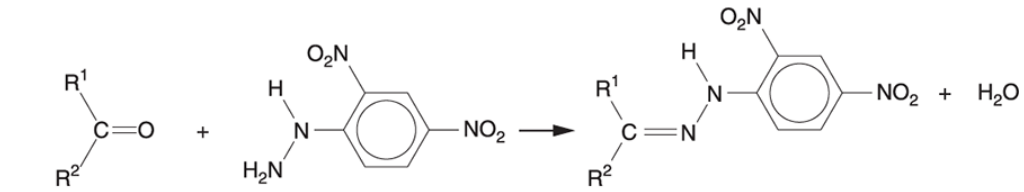


How many different carbon environments (types of carbon) are present in a molecule of compound **L**?

---

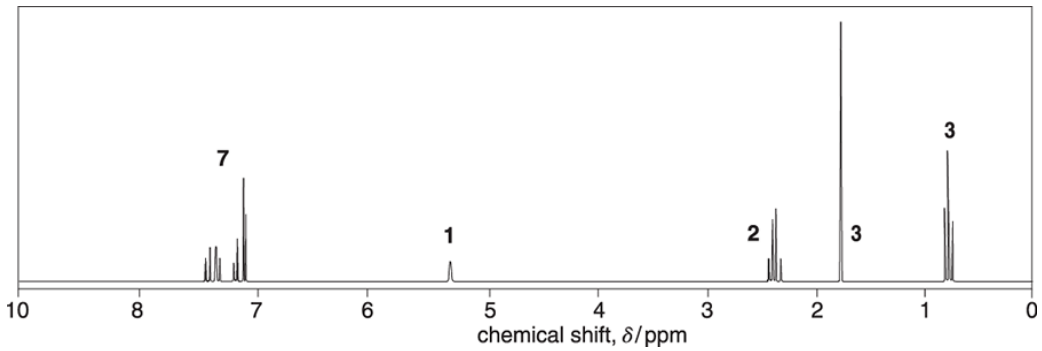
[1]

(c). The reaction of **K** to form **L** is repeated below.



compound K **2,4-dinitrophenylhydrazine** **orange precipitate L**

The ^{1}H NMR spectrum of **L** is shown below.



Use your answer to **(c)** and the data given to identify R^1, R^2 and the structure of compound **L**.

Explain how you used the chemical shifts and splitting patterns in the ^{1}H NMR spectrum and any evidence from the ^{13}C NMR spectrum.

In the ^{1}H NMR spectrum, HC–C=N– would have a peak in the range δ = 1.6–2.2 ppm.

In your answer, you should use appropriate technical terms, spelled correctly.

---

structure of compound **L**

[7]

(d). Draw the structure of compound **K**.

structure of compound **K**

[1]

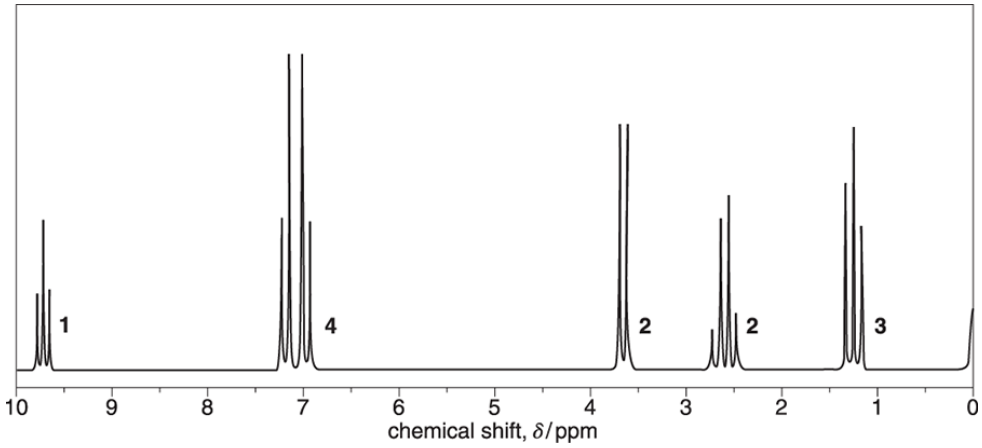
16(a). A chemist isolates compound **H** from a mixture and sends it for analysis.

Initial analysis shows that the molecular formula of compound **H** is $C_{10}H_{12}O$.

The ^{13}C NMR spectrum of compound **H** contained eight separate peaks.

The ^{1}H NMR spectrum of compound **H** is shown below.

^{1}H NMR spectrum
The numbers by each peak are the relative peak areas.



The ^{1}H NMR spectrum contains a peak at δ = 0 ppm resulting from a chemical added to the sample.

State the chemical responsible for the peak at δ = 0 ppm, and state why this chemical was added to the sample.

---**[1]**

(b). In the ^{1}H NMR spectrum, the peak at δ = 3.7 ppm would normally be expected at a chemical shift value about 1 ppm to the right, ie at 2.7 ppm.

Use the information in this question to determine the structure of compound **H**.

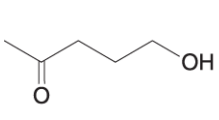
Show all your reasoning.

In your answer, you should use the appropriate technical terms, spelled correctly.

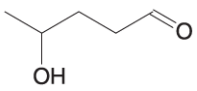
---

[9]

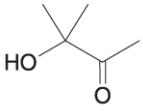
17. The following three carbonyl compounds are structural isomers of $C_5H_{10}O_2$.



compound C



compound D



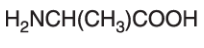
compound E

Predict the number of peaks in the ^{13}C NMR spectra of compounds **C**, **D** and **E**.

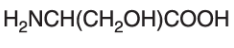
Compound	**C**	**D**	**E**
Number of peaks			

[1]

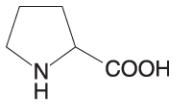
18(a). Alanine, serine and proline are α-amino acids.



alanine



serine



proline

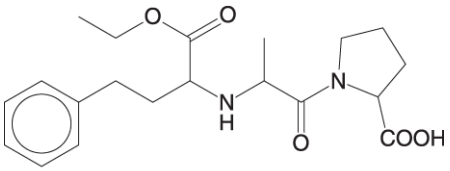
A solution of serine was shaken with a few drops of D_2O. The solution was then analysed using ^1H NMR spectroscopy.

Complete the table to predict the ^1H NMR spectrum of serine after the addition of D_2O.

^1H NMR spectrum for serine		
Chemical shift, δ / ppm	**Relative peak area**	**Splitting pattern**

[2]

(b). Enalapril is a drug used in the treatment of high blood pressure.



enalapril

i. **On the structure above**, mark each chiral centre with an asterisk (*).

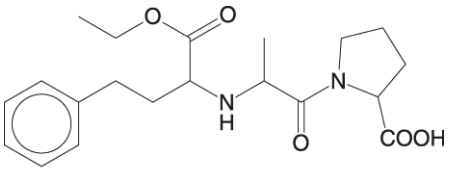
[1]

ii. Suggest **two** benefits of using single stereoisomers in the synthesis of drugs such as enalapril.

---

[2]

iii. Enalapril is broken down in the body by acid hydrolysis.



enalapril

Draw the structures of the **three** organic products of the **acid hydrolysis** of enalapril.

[4]

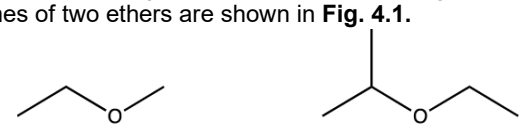
iv. A scientist hydrolysed enalapril in the laboratory. The scientist then analysed the mixture of products using GC–

Explain how GC– enables the products to be identified.

---

[1]

19(a). Ethers are a homologous series of organic compounds containing the R−O−R functional group. The structures and names of two ethers are shown in **Fig. 4.1.**



methoxyethane **2-ethoxypropane**

Fig. 4.1

Draw the **skeletal** formula of the ether, 2-ethoxy-3-methylbutane.

[1]

(b). Ethers can be prepared by nucleophilic substitution of haloalkanes with alkoxide ions, RO^-.

i. Alkoxide ions can be prepared by reacting sodium with an alcohol. A gas is also formed.

Write an equation for the formation of methoxide ions from sodium and an alcohol.

---

[1]

ii. Methoxyethane, shown in **Fig. 4.1**, can be prepared by reacting bromoethane, CH_3CH_2Br, with methoxide ions, CH_3O^-.

Suggest the mechanism for the nucleophilic substitution of CH_3CH_2Br with CH_3O^-.

Show curly arrows, charges, relevant dipoles, and products.

[3]

iii. In this mechanism, explain how CH_3O^- ions have acted as a nucleophile.

State the type of bond fission that takes place.

---

[1]

(c). 2-Ethoxypropane, shown in **Fig. 4.1**, is analysed by ^{1}H NMR spectroscopy.

Complete the table to predict the ^{1}H NMR spectrum of 2-ethoxypropane.
You may **not** need to use all the rows.

Chemical shift, δ/ppm	Relative peak area	Splitting pattern

[4]

(d). In organic reactions, alkoxide ions can also act as a base.

The diagram below shows an incomplete mechanism for the reaction of a diester with methoxide ions, CH_3O^- (**Step 1**), followed by reaction of the intermediate with bromoethane (**Step 2**).

i. For **Step 1**, add curly arrows to show how CH_3O^- reacts with the diester to form the intermediate.
In the box, draw the structure of the organic product formed in **Step 2**.

[3]

ii. Explain how CH_3O^- ions have acted as a base in this mechanism.

---

[1]

20. Information about a monobasic organic acid **D** is shown below.

- **D** reacts by both electrophilic substitution and electrophilic addition.
- The molecular formula of **D** is $C_xH_yO_2$.
- The mass spectrum of **D** has a molecular ion peak at *m/z* = 148.
- The ^{13}C NMR spectrum of **D** contains seven peaks.

Determine and draw a possible structure for **D**.

Explain your reasoning from the evidence provided.

---

[5]

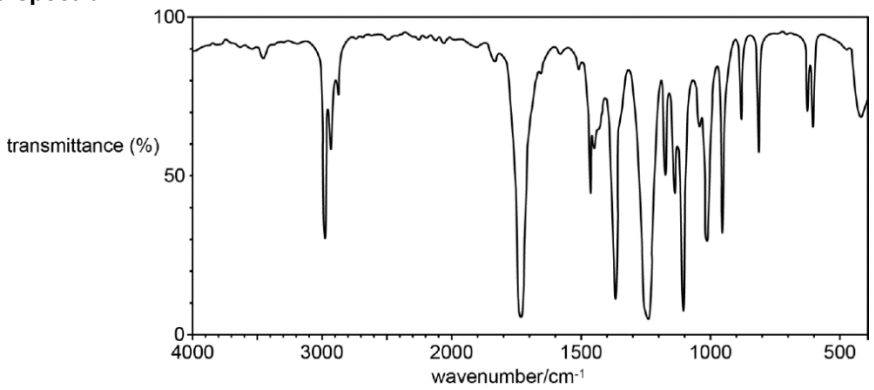
21. A scientist analyses a compound that is present in a sample of ink.

The results are shown below:

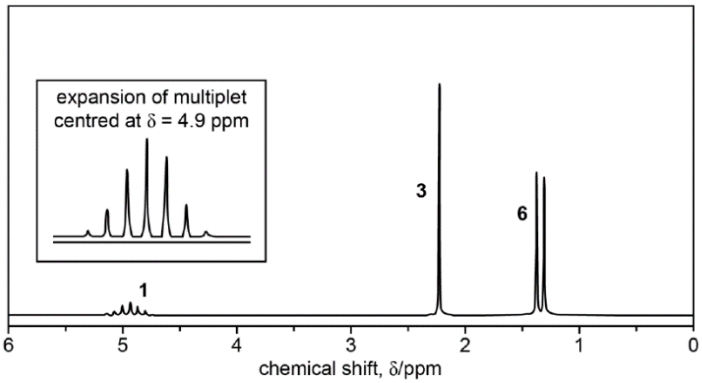
Elemental analysis by mass:
C: 58.80%; H: 9.87%; O: 31.33%

Mass spectrum
Molecular ion peak at *m*/*z* = 102.0

Infrared spectrum



^{1}H NMR spectrum



The numbers by the peaks are the relative peak areas.

From the *Data Sheet*, the peak centred at δ = 4.9 ppm would be expected at a chemical shift value about 1 ppm to the right, i.e. 3.9 ppm.

Use the results to identify the unknown compound. Show **all** your reasoning.

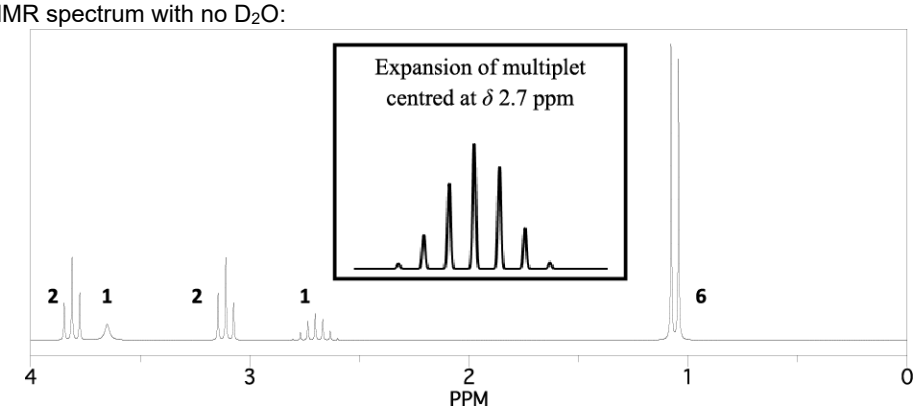
[8]

22. * A chemist isolates compound **L**, with empirical formula C_3H_6O, and sends a sample for analysis. The analytical laboratory sends back the following spectra.

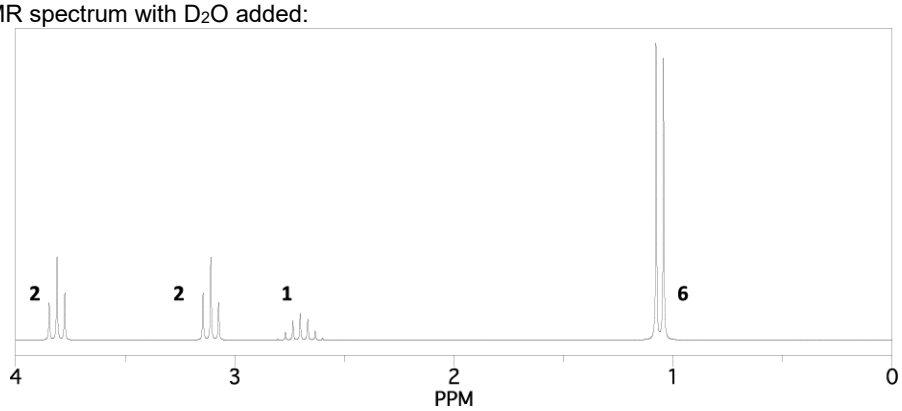
Mass spectrum
Molecular ion peak at m/z = 116.0.

^{1}H NMR spectra
The numbers next to each signal represent the number of ^{1}H responsible for that signal.
Two ^{1}H NMR spectra were obtained: one without D_2O and one with D_2O added.

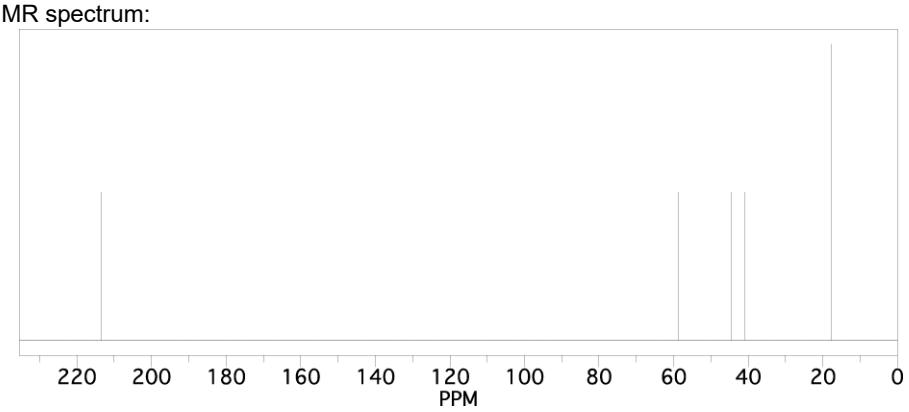
^{1}H NMR spectrum with no D_2O:



^{1}H NMR spectrum with D_2O added:



^{13}C NMR spectrum:



Use the information provided to suggest a structure for compound **L**.

Give your reasoning.

---

[6]

END OF QUESTION PAPER