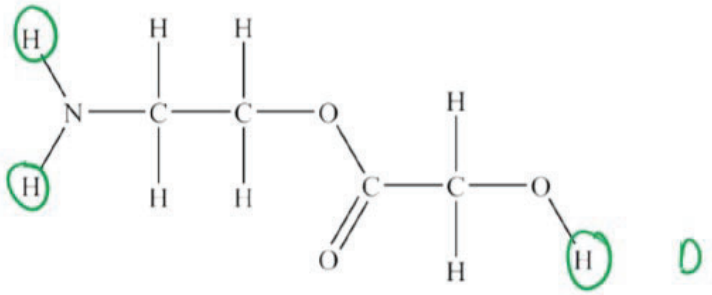
1. The structure of molecule **Z** is shown below.



Which of the following statements is/are true?

✓ **1:** The carbon-13 NMR spectrum of **Z** shows four peaks → 4 C environments

✓ **2:** The proton NMR spectrum of **Z** shows five peaks → 5 H environments

✓ **3:** The proton NMR spectrum of **Z** run in D_2O shows three peaks

5 − 2 = 3

↓

D replaces H bonded to O or N so peaks no longer show in the spectrum.

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer **A**

[1]

2. 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

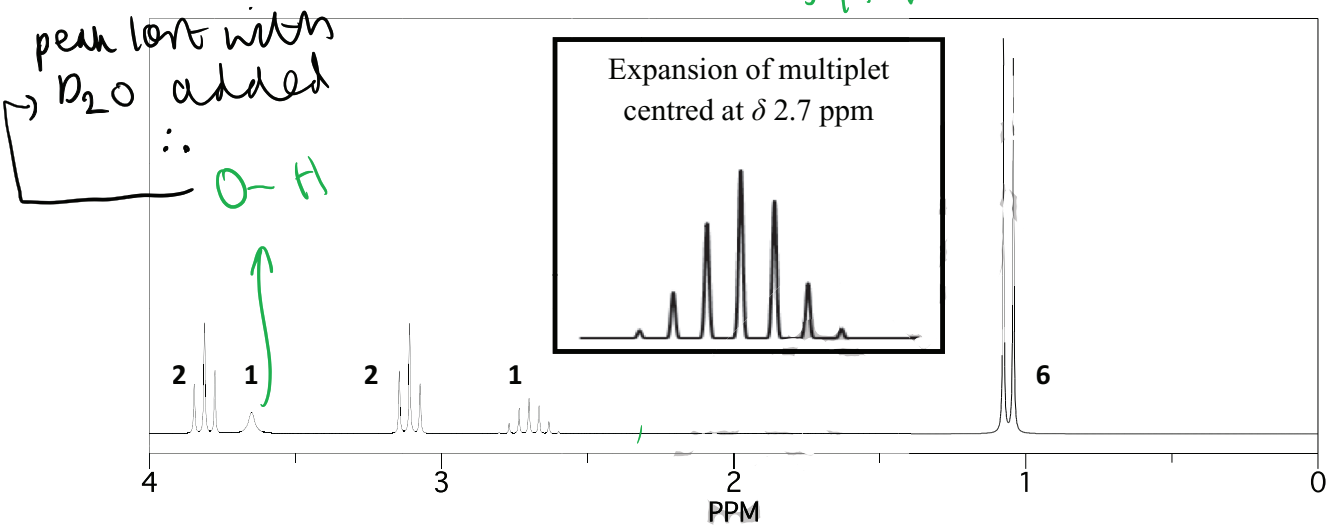
Molecular ion peak at m/z = 116.0.

^{1}H NMR spectra

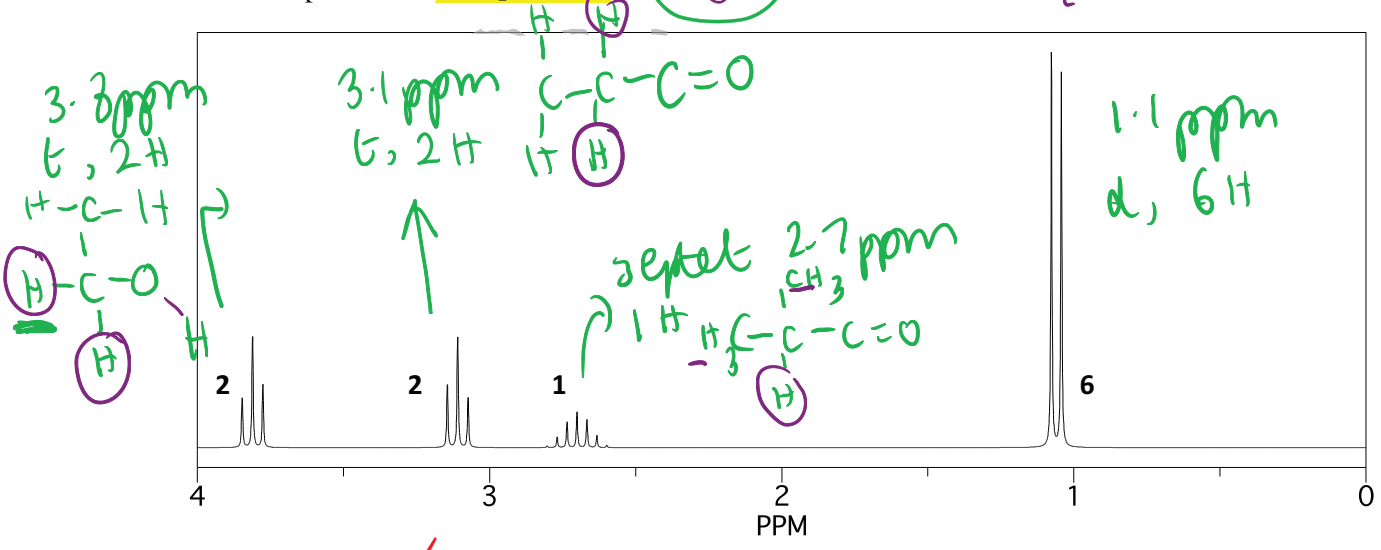
The numbers next to each signal represent the number of ^{1}H responsible for that signal.

Two ^{1}H NMR spectra were obtained: one without D_2O and one with D_2O added.

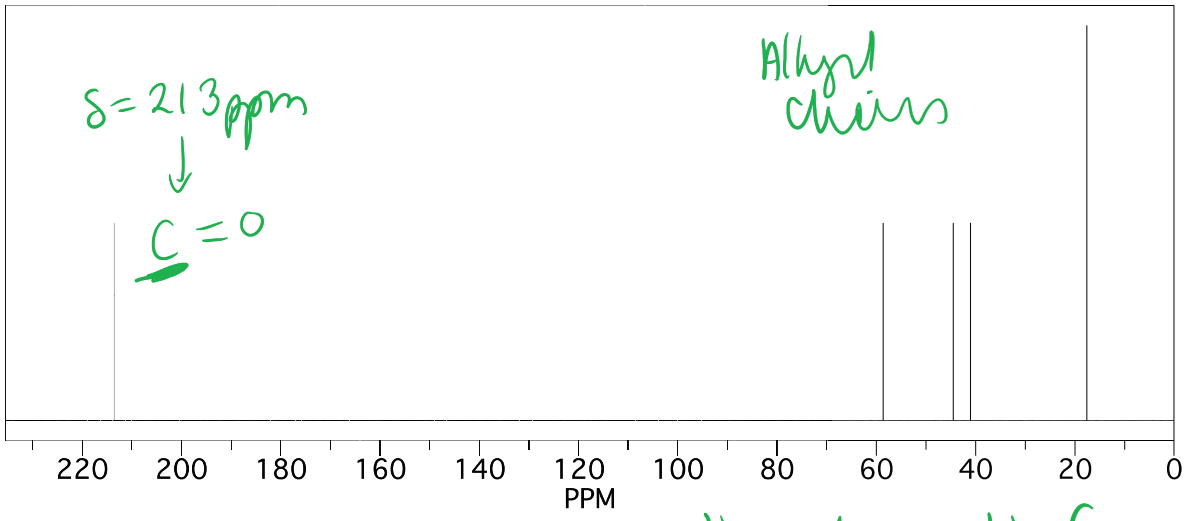
^{1}H NMR spectrum with no D_2O:



^{1}H NMR spectrum with D_2O added:



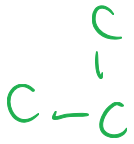
^{13}C NMR spectrum:



peaks = # C environments

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

Give your reasoning.



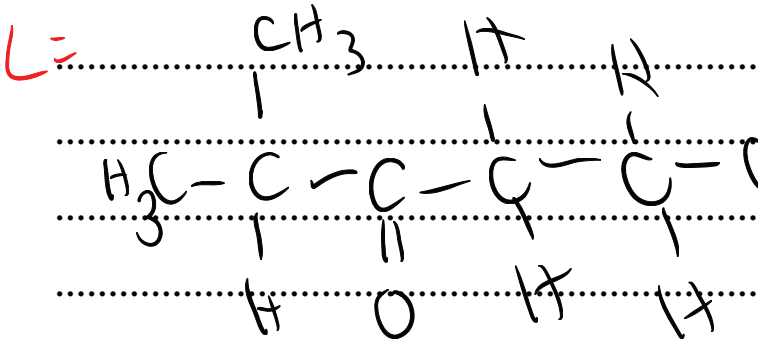
5 peaks

Molecular formula = $C_6H_{12}O_2$ ✓

5 C environments; C=O bond peak @ 213 ppm (13C NMR).

Ketone, no δ = 9–10 ppm on ^1H NMR. (aldehyde).

L =



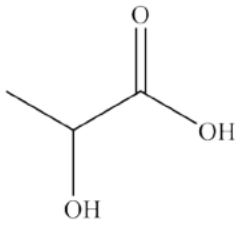
(H) → peak lost (^1H NMR) added D_2O.

- peak environment, splitting, integration needed (shown on previous page) for full marks.

[6]

3. This question is about organic acids.

(a) Lactic acid, shown below, has two functional groups.



Lactic acid reacts with bases and with many metals.

- An aqueous solution containing 1.125 g of lactic acid is reacted with an excess of magnesium producing hydrogen gas.
- The excess magnesium is removed.
  The water is evaporated, leaving a white solid, **A**.

(i) Name the type of reaction of lactic acid with bases and with metals.

reaction with bases: neutralisation

reaction with metals: redox

[1]

(ii) Calculate the volume of $H_2(g)$ produced, measured at room temperature and pressure.

mass / mol x RFM

$\frac{1.125}{(12\times3)+(16\times3)+6} = 0.0125$ mol

$\frac{0.0125}{2} \times 24000 = 150\,cm^3$

$\frac{\text{Volume}}{24000} = \text{mol}$

x2 mol of lactic acid than H_2

volume of H_2 = 150 cm^3 **[2]**

(iii) What is the empirical formula of the white solid **A**?

$[C_3H_6O_3]^-$ ion of lactic acid

Mg^{2+} so x2 ions of lactic acid needed

$C_6H_{12}O_6Mg$ **[1]**

(iv) Predict **two** reactions of lactic acid, each involving a different functional group.

Do **not** include reactions with bases or metals.

For each reaction,

- state the type of reaction, the reagents and conditions
- draw the structures of any organic products formed.

COOH: esterification

CH_3OH, H_2SO_4

any alcohol

ester link $R_2-\overset{\overset{O}{\|}}{C}-O-R_1$

$CH_3(CHOH)COOCH_3$

2° OH: oxidation

$K_2Cr_2O_7$, H_2SO_4 + heat

$CH_3(CO)COOH$

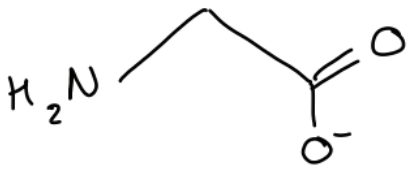
2° alcohol → ketone

[4]

(b) In basic conditions, α-amino acids form anions with the general formula, $RCH(NH_2)COO^-$. These anions can act as bidentate ligands.

Copper(II) ions can form a square planar complex with anions of the amino acid glycine (R = H). There are two stereoisomers of this complex, **B** and **C**.

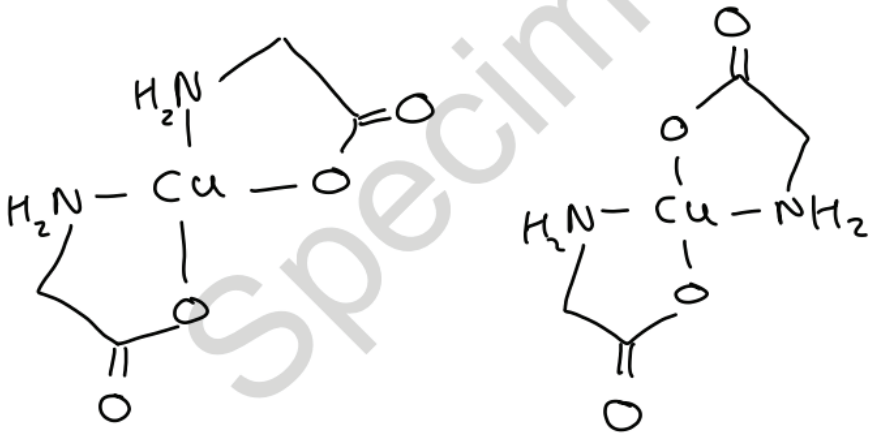
(i) Draw the **skeletal** formula of the anion of glycine.



[1]

(ii) Draw diagrams of stereoisomers **B** and **C**.

In your structures, show the ligands as skeletal formulae.



[2]

(iii) Anion ligands of the amino acid alanine (R = CH_3) would be expected to form more than two square planar stereoisomers with copper(II) ions.

Explain this statement.

alanine has a chiral centre

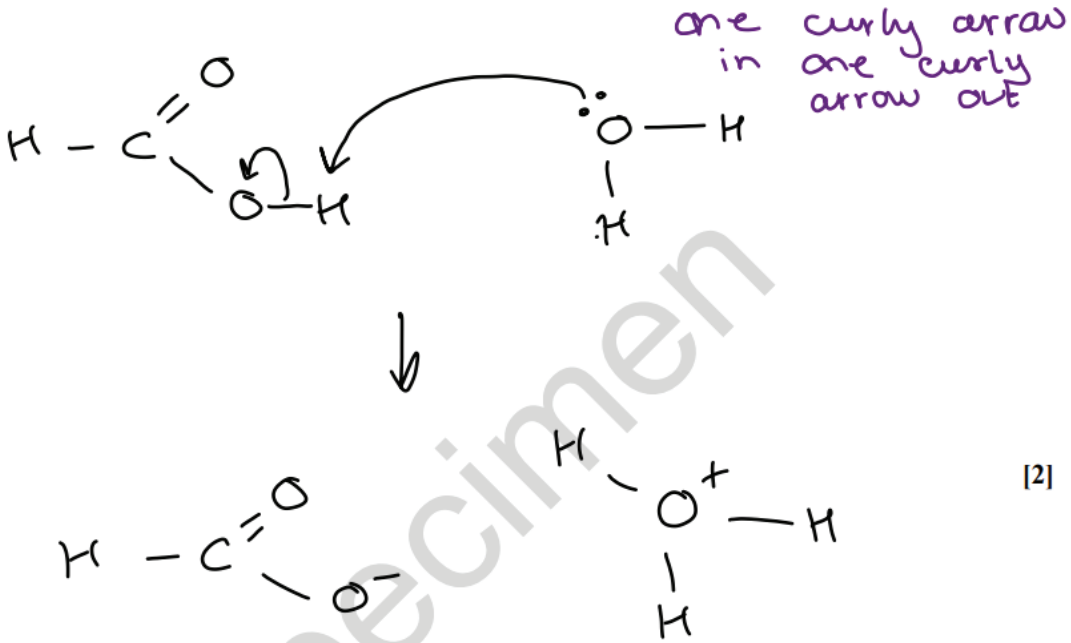
.....

[1]

(c) Methanoic acid is added to water. An acid–base equilibrium is set up containing two acid–base pairs.

Suggest a mechanism for the forward reaction in this equilibrium.

Your mechanism should use displayed formulae and curly arrows, and show all species present at equilibrium.



[2]

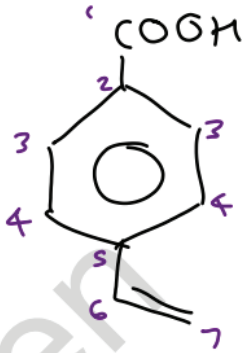
(d) Information about a monobasic organic acid **D** is shown below.

- **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.

7 ^{13}C NMR peaks



electrophilic substitution = benzene ring

electrophilic addition = alkene (C=C)

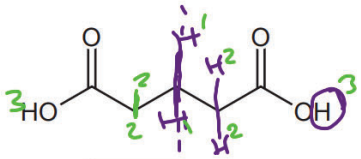
molecular formula: [O], C=C, COOH

$C_9H_8O_2$

acid

[5]

4. The compound below is analysed by ^{1}H NMR spectroscopy.



How many peaks are observed in the ^{1}H NMR spectrum?

3 unique environments

A 5

B 4

C 3

D 2

Your answer C

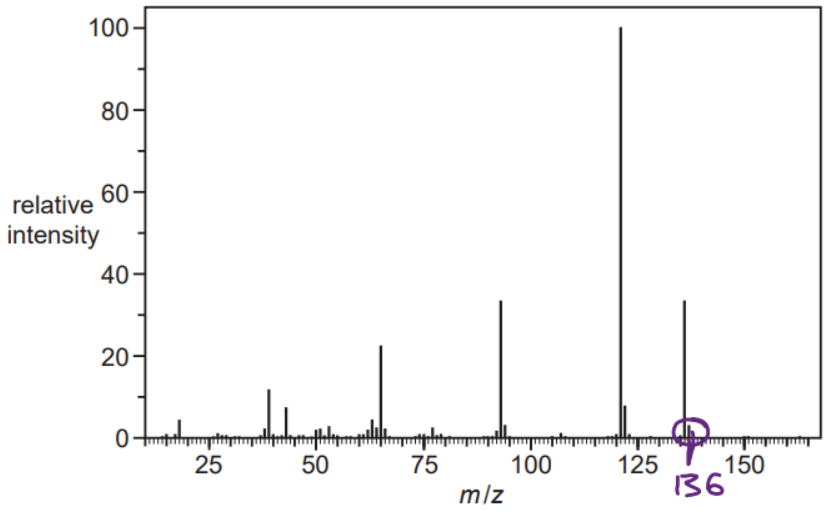
[1]

5. A chemist analyses a naturally occurring aromatic compound.

(a) 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.

C_4H_4O has an RFM of: $(12\times4)+4+16 = 68$ so multiply by 2

C: $\frac{70.58}{12} = 5.88$

H: $\frac{5.92}{1} = 5.92$

O: $\frac{23.50}{16} = 1.46875$

$\frac{5.92}{1.46875} = 4$

$\frac{5.88}{1.46875} = 4$

$\frac{1.46875}{1.46875} = 1$

molecular formula = $C_8H_8O_2$ **[3]**

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

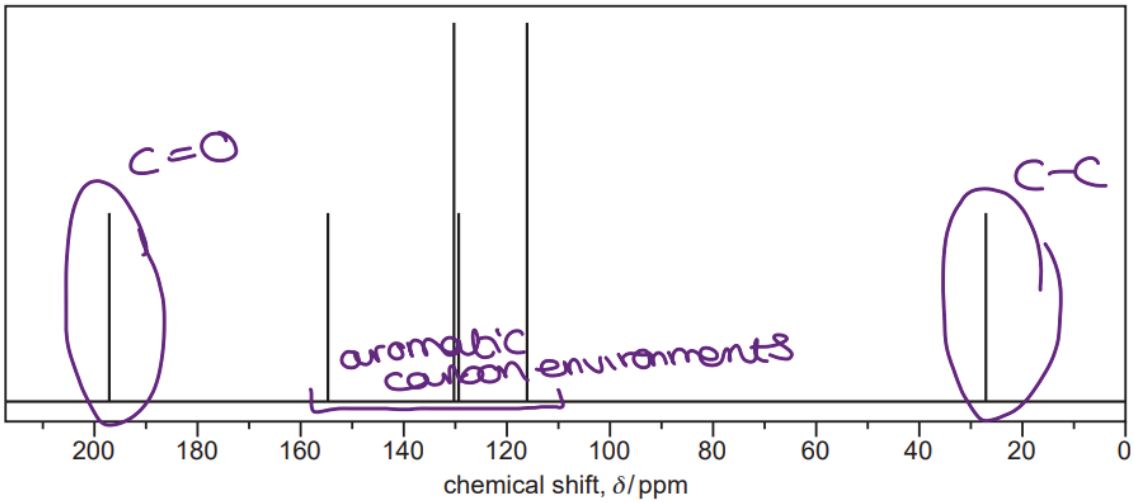
Test	Acidity	Na_2CO_3(aq)	2,4-DNP	Tollens' reagent
		test for COOH	test for C=O	test for $-C\overset{O}{\underset{H}{}}$
Observation	pH = 5 weak acid	No observable change if present effervesces	Orange precipitate	No observable change if present silver mirror

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

Functional groups ketone, phenol

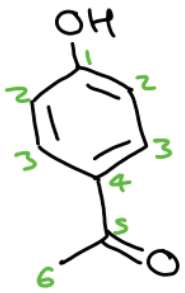
Explanation phenols are weak acids not carboxylic acid as no reaction with Na_2CO_3, but C=O group present as orange ppt in 2,4 DNP but no silver mirror in Tollens reagent so not an aldehyde. **[3]**

(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.

peaks between 110 - 160 ppm are the 4 aromatic carbon environments. Peaks between 190 - 200 ppm is a C=O peak between 20 - 30 ppm is C-C.



Structure of compound

[3]

6. Which compound is used as a standard for NMR chemical shift measurements?

A $Si(CH_3)_4$

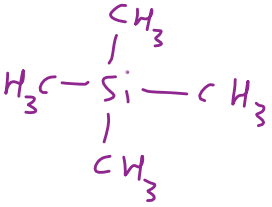
B $CDCl_3$ – no peak in ^1H NMR.

C D_2O – no peak in ^{13}C NMR

D CCl_4 – no peak in ^1H NMR

$D = {}^2H$

} solvents



Your answer A

[1]

n° peaks = n° environments

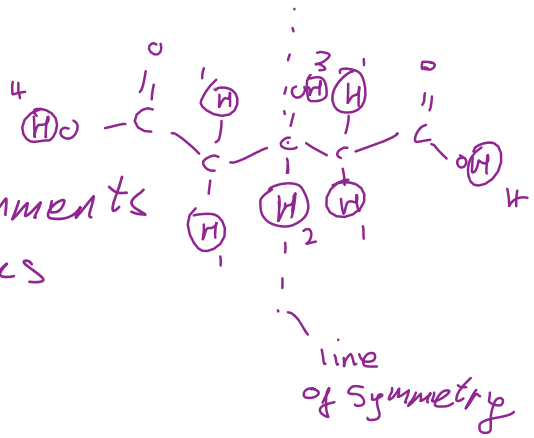
7. What is the number of peaks in the ^{1}H NMR spectrum of $HOOCCH_2CHOHCH_2COOH$?

A 3

B 4

C 5

D 6

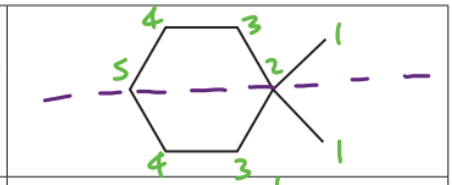
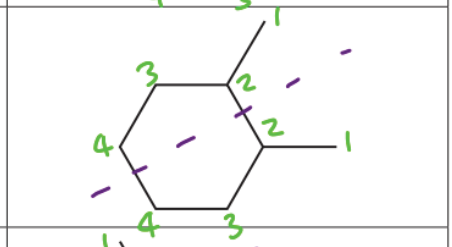
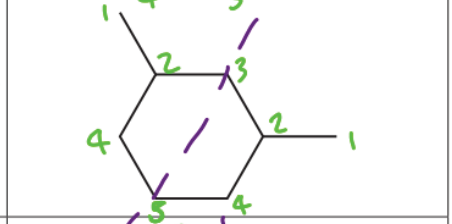
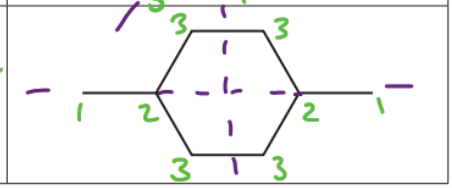


4 environments
∴ 4 peaks

Your answer B

[1]

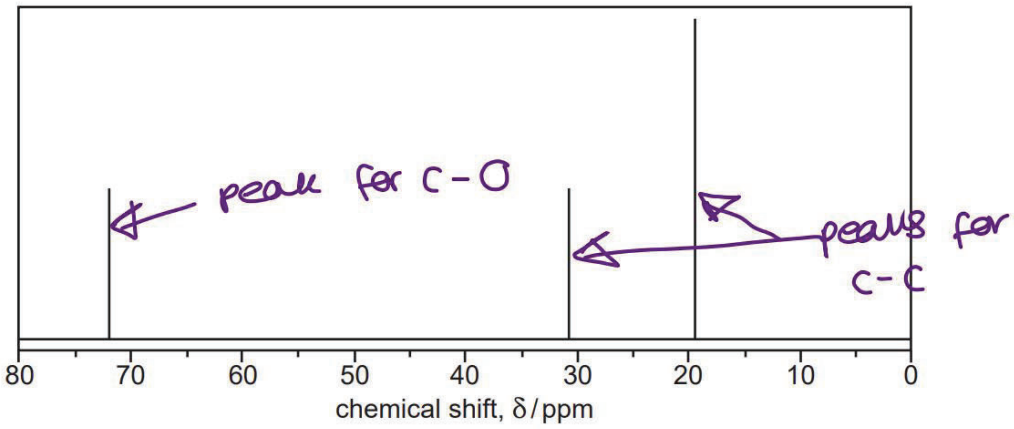
8. Which compound shows 4 peaks in its carbon-13 NMR spectrum?

A	 5 peaks
B	 4 peaks
C	 5 peaks
D	 3 peaks

Your answer B

[1]

9. A compound produces the ^{13}C NMR spectrum below.



3 peaks

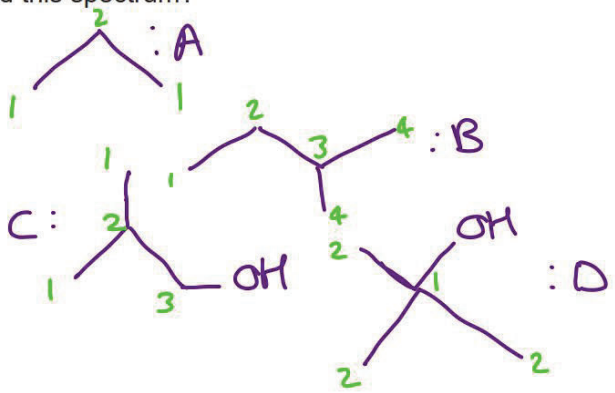
Which compound could have produced this spectrum?

~~A~~ Propane

~~B~~ 2-Methylbutane

C 2-Methylpropan-1-ol

~~D~~ 2-Methylpropan-2-ol

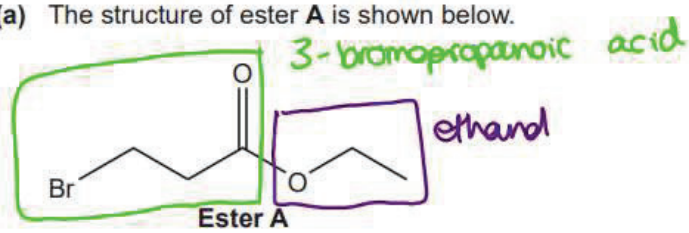


Your answer C

[1]

10. This question is about esters.

(a) The structure of ester **A** is shown below.



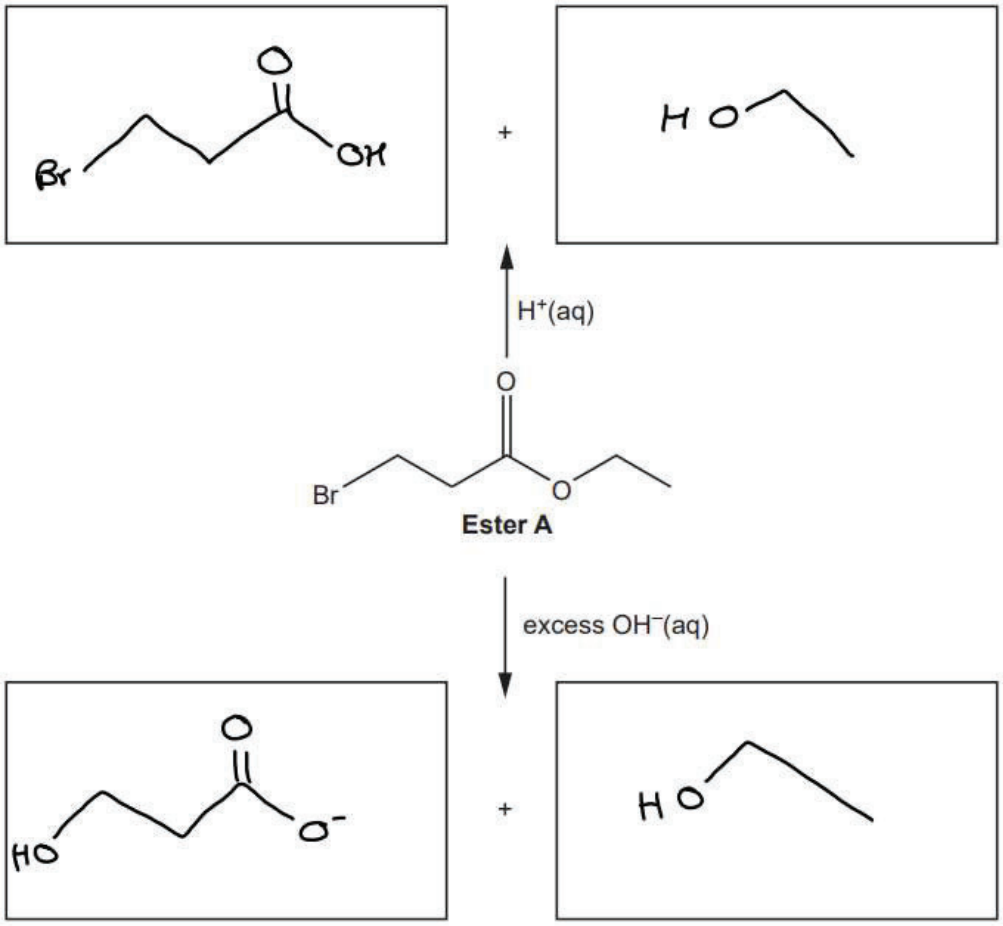
Ester A

(i) What is the systematic name of ester **A**?

ethyl 3-bromopropanoate ..... **[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.

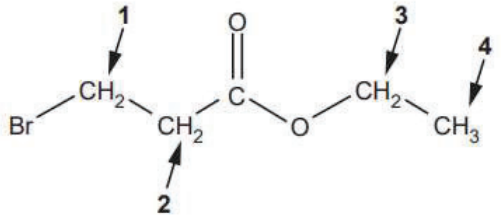


[5]

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

hydrolysis ..... **[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	3.0-4.3	triplet
2	2.0-3.0	triplet
3	3.0-4.3	quartet
4	0.5-1.9	triplet

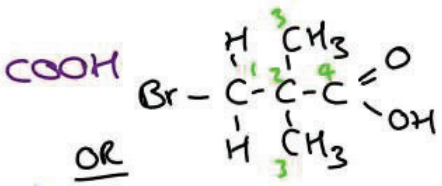
[4]

$C_5H_9O_2Br$

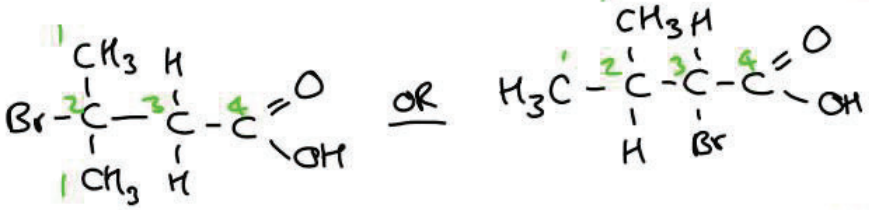
(c) Compound **B** is a structural isomer of ester **A**.

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

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

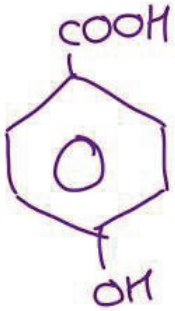


OR



[1]

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



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

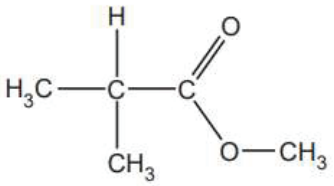
$(12 \times 7) + 6 + ((16 \times 3) = 138 \text{ g mol}^{-1}$

$138 \times 200 = 27600 \text{ g mol}^{-1}$

$27600 - ((99 \times 18) = 24018$

M_r = ... 24018 ..... 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]**

$\frac{12.75}{(12\times5)+10+(16\times2)} = 0.125$ mol of ester C

$0.125 \times \frac{100}{40} = 0.3125$ mol of 2methyl-propanal

$((12\times4)+8+16) \times 0.3125 = 22.50$g of 2-methyl propanal

1: $(CH_3)_2CHCHO + [O] \rightarrow (CH_3)_2CHCOOH$

$[O]$: $Cr_2O_7^{2-}/H^+$ and reflux

2: $(CH_3)_2CHCOOH + CH_3OH \xrightarrow[\text{reflux}]{H^+} (CH_3)_2CHCOOCH_3 + H_2O$

Additional answer space if required

.....

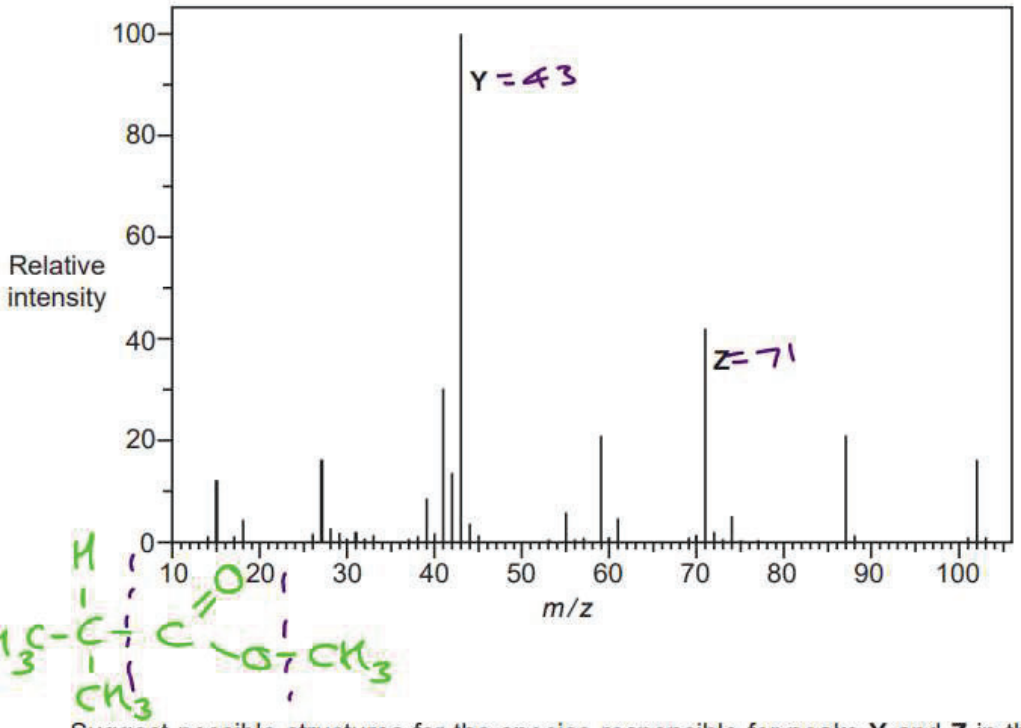
.....

.....

.....

.....

(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.

$(CH_3)_2CH^+$	$(CH_3)_2CHCO^+$
Y	**Z**

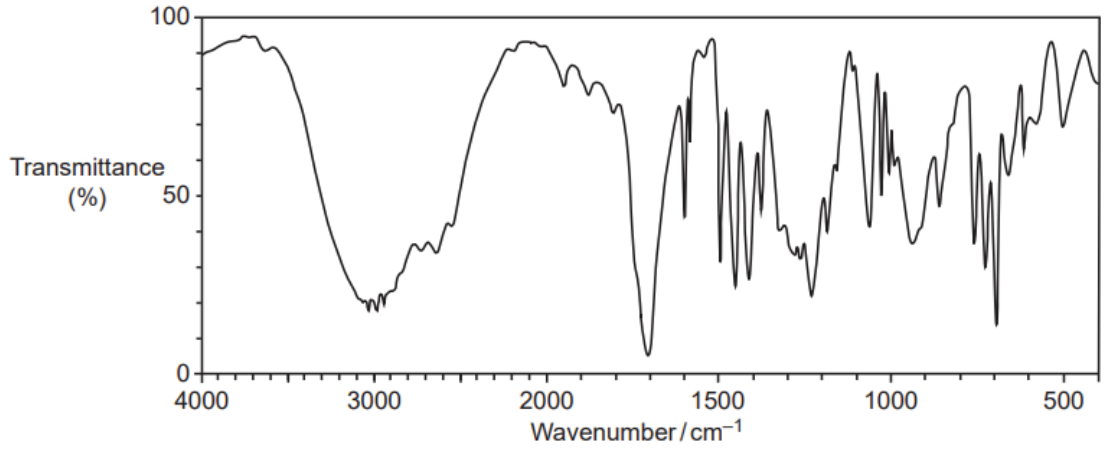
[2]

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

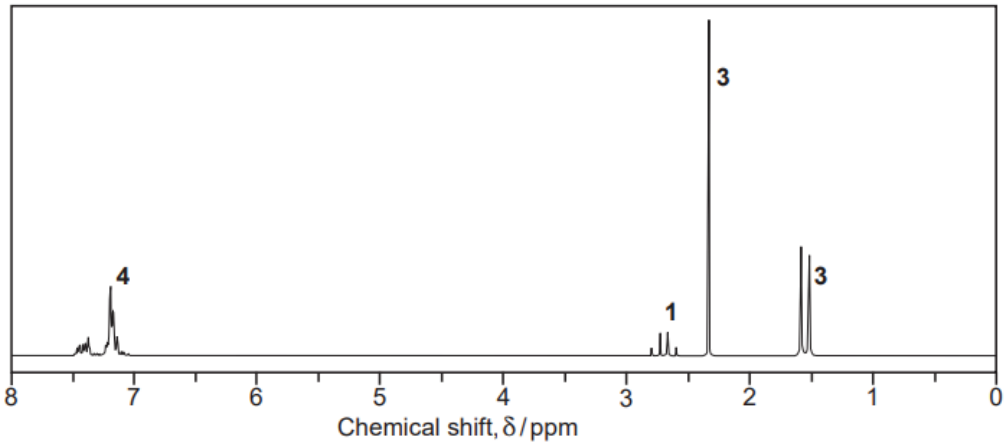
Elemental analysis by mass
C: 73.17%; H: 7.32%; O: 19.51% empirical formula

Mass spectrum
Molecular ion peak at m/z = 164.0 molecular formula

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]**

empirical formula: C_5H_6O

C: $\frac{73.17}{12} = 6.0975$ H: $\frac{7.32}{1} = 7.32$ O: $\frac{(9.51)}{16} = 1.22$

$\frac{6.0975}{1.22} = 5$ $\frac{7.32}{1.22} = 6$ $\frac{1.22}{1.22} = 1$

$(5 \times 12) + 6 + 16 = 82$ ← $\times 2 = 164$

molecular formula: $C_{10}H_{12}O_2$

IR:

- peak at 2300-3700 cm^{-1} (OH)
- peak at ~ 1720 cm^{-1} (C=O)

so COOH present

^1H NMR:

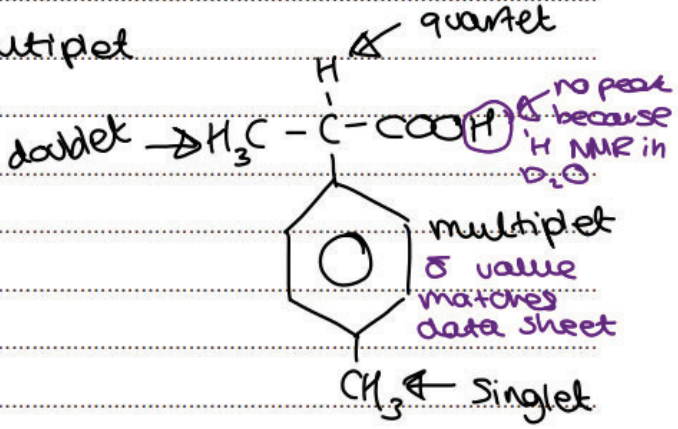
δ = 1.6 ppm, doublet

δ = 2.3 ppm, singlet

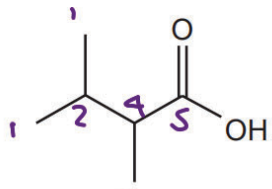
Additional answer space if required

δ = 2.7 ppm, quartet

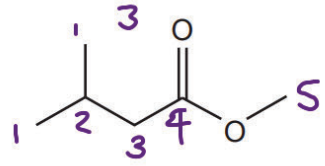
δ = 7.1 - 7.5 ppm, multiplet



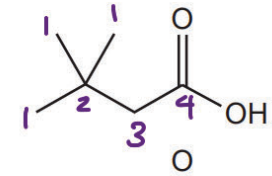
12. Which isomer of $C_6H_{12}O_2$ produces the smallest number of peaks in its ^{13}C NMR spectrum?

A 

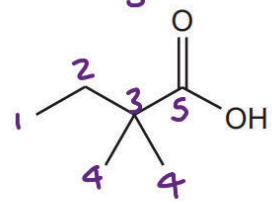
5 peaks

B 

5 peaks

C 

4 peaks

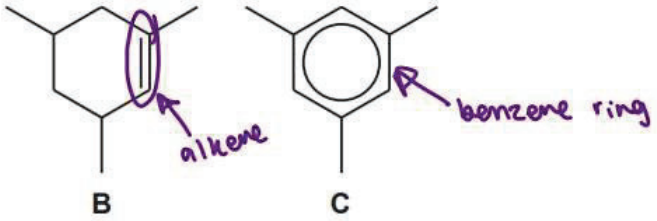
D 

5 peaks

Your answer C

[1]

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

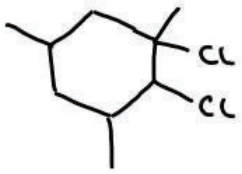
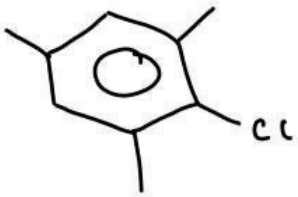


B **C**

(a) Compound **B** reacts with chlorine at room temperature, but compound **C** requires the presence of a halogen carrier.

In both reactions, the organic compound reacts with chlorine in a 1:1 molar ratio.

(i) Draw the structures of the organic product of each reaction.

electrophilic addition 	electrophilic substitution 
Organic product with **B**	Organic product with **C**

[2]

(ii) Explain the relative resistance to chlorination of compound **C** compared with compound **B**.

In B the electrons / π bond is localised
In C the electrons / π ring system is delocalised
In B the electron density is higher so is more susceptible to electrophilic attack / B attracts / accepts the electrophile (CCl_2) more / B polarises the electrophile (CCl_2) more.

[3]

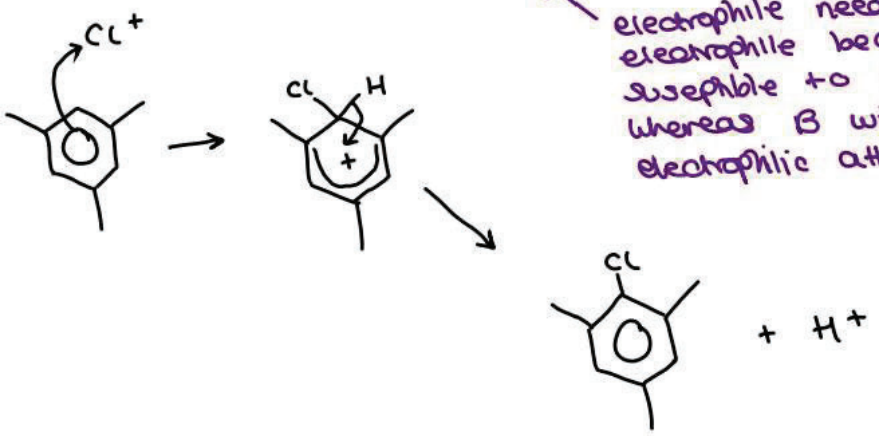
(iii) Outline the mechanism for the reaction of compound **C** with chlorine.

Show the role of the halogen carrier.

forming electrophile

$AlCl_3 + Cl_2 \longrightarrow Cl^+ + AlCl_4^-$

electrophile needs a stronger electrophile because C is less susceptible to electrophilic attack whereas B will undergo electrophilic attack with $Cl^{\delta+}$



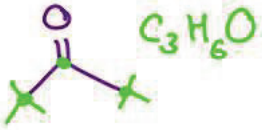
$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

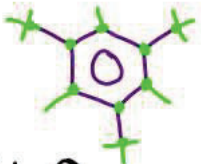
regenerating halogen carrier

[5]

(b) Compound **C** can be prepared by 'trimerisation' of propanone using concentrated sulfuric acid as a catalyst.

Suggest an equation for this reaction, using **molecular** formulae.





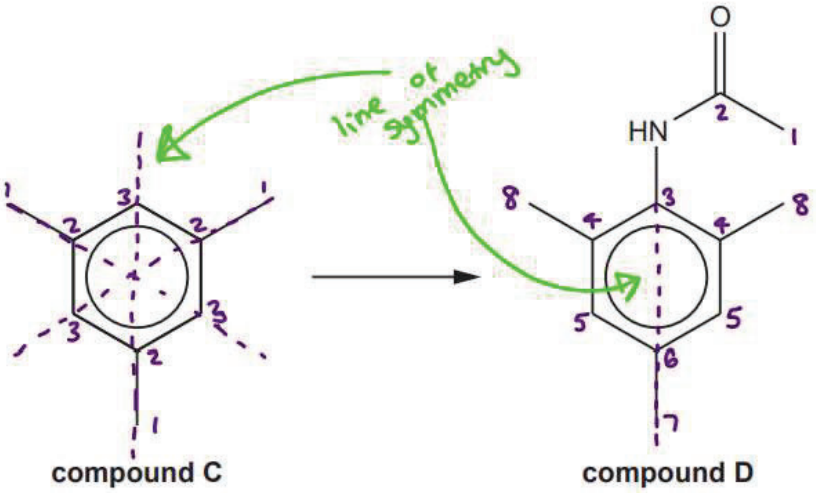
C_9H_{12}

Question confirms 9 carbons in compound C

$3C_3H_6O \longrightarrow C_9H_{12} + 3H_2O$ **[3]**

(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**

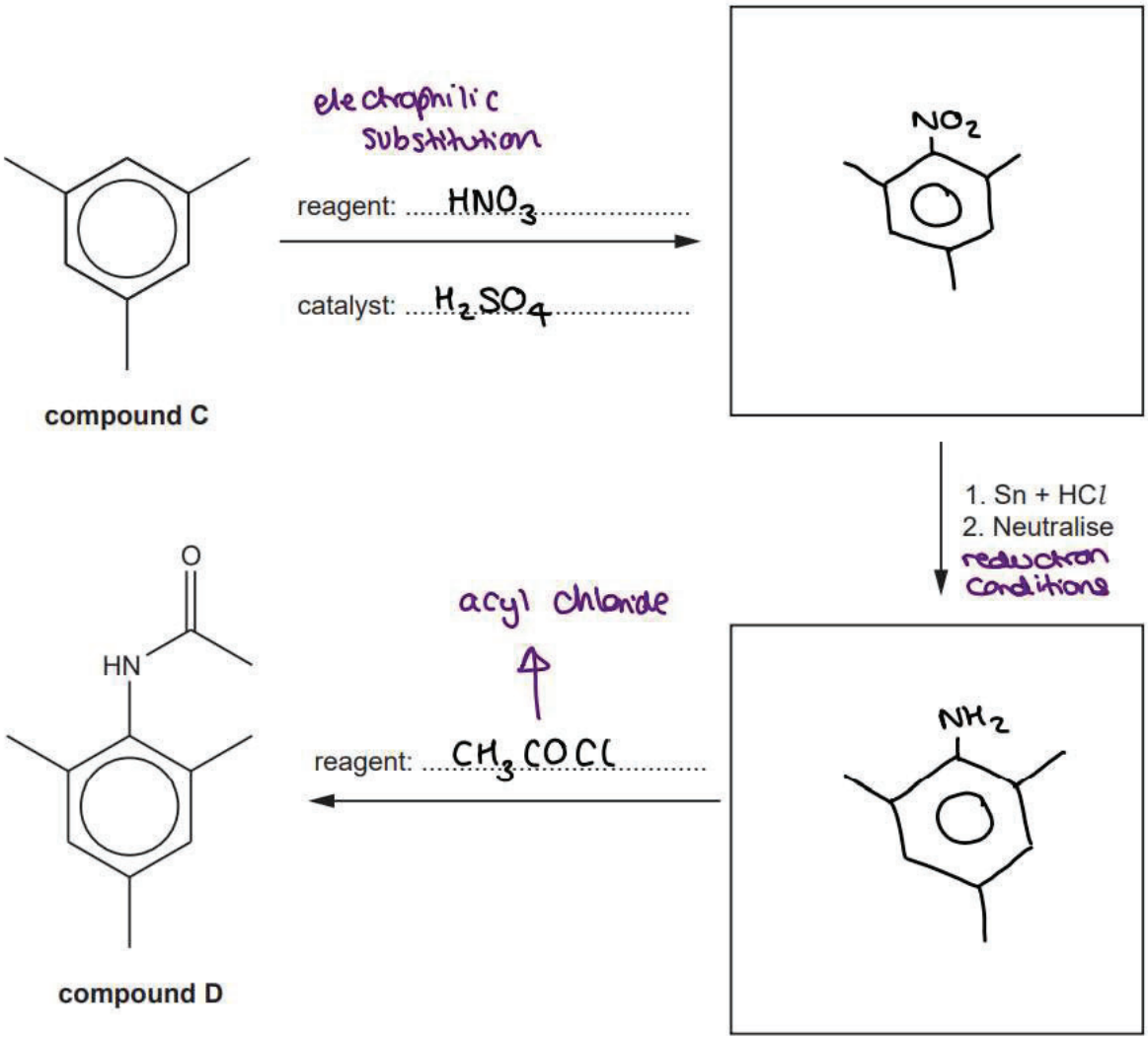
(i) Predict the number of peaks in the ^{13}C NMR spectra of compounds **C** and **D**.

	Compound **C**	Compound **D**
Number of peaks	3	8

[2]

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

Complete the flowchart.
Show structures for organic compounds.

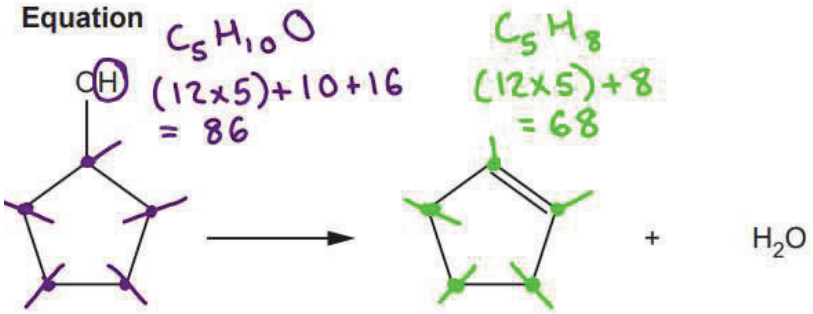


[5]

14. Cyclopentanol can be reacted to form cyclopentene.
Cyclopentene is a liquid with a boiling point of 44 °C and a density of 0.74 g cm^{-3}.
→ temp. to redistill at

A student plans to prepare 4.00 g of cyclopentene by reacting cyclopentanol (boiling point 140 °C) with an acid catalyst.

Equation

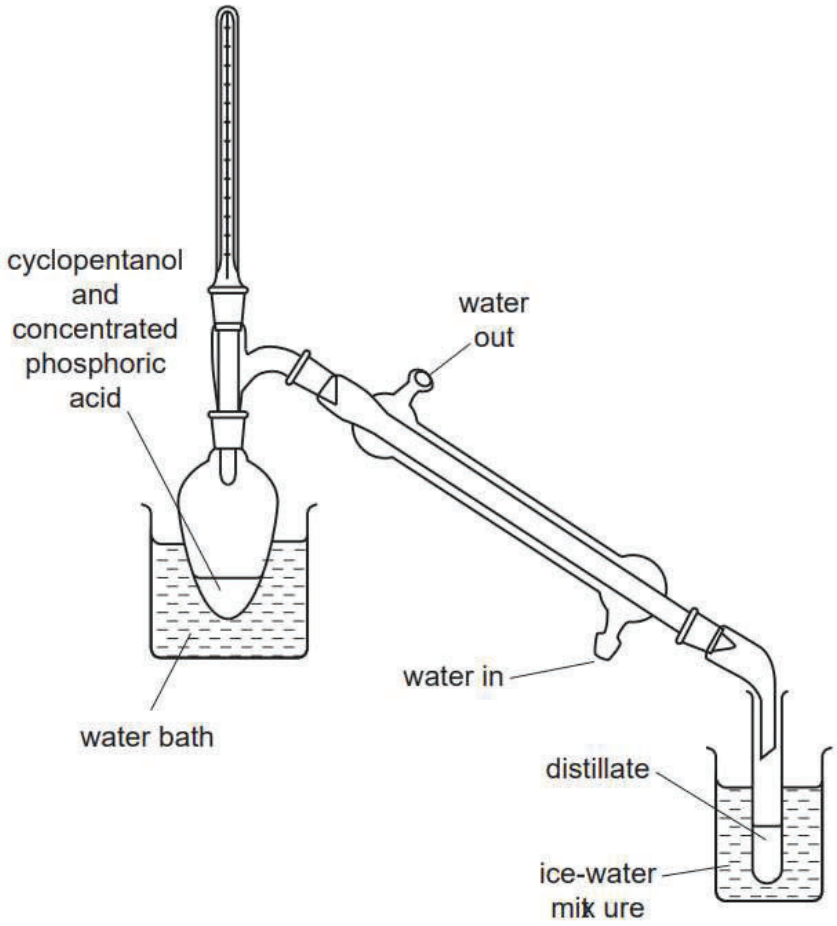


The expected percentage yield of cyclopentene is 64.0%.

Method

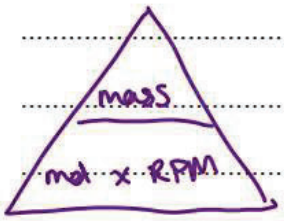
The student carries out the preparation using apparatus set up for distillation, as shown below.

1 The reaction mixture is heated gently, and a distillate containing impure cyclopentene is collected.



2 The distillate has an aqueous layer and an organic layer.
The student purifies the cyclopentene from the distillate.

(a)* Calculate the mass of cyclopentanol that the student should use and explain how pure cyclopentene could be obtained from the distillate. **[6]**



$\frac{4.00}{68} = 0.0588$ mol of cyclopentene

$0.0588 \times \frac{100}{64} = 0.0919$ mol of cyclopentanol

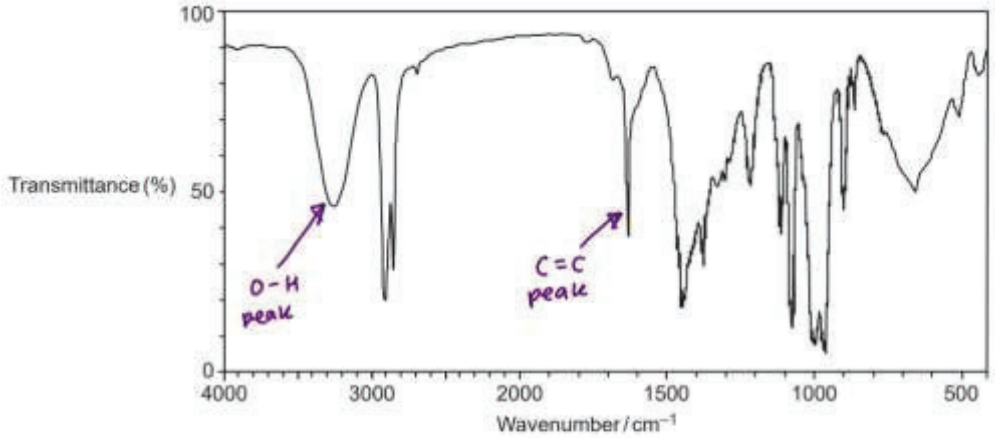
$0.0919 \times 86 = 7.90\text{g}$ (2dp.)

purification:

- Add a neutralising agent such as Na_2CO_3
- In a separating funnel the organic layer is on top (cyclopentene is less dense so on top)
- Drying with anhydrous salt such as, $MgSO_4$ / Na_2SO_4 / $CaCl_2$ (removes traces of water)
- Redistill at approx. 44 °C

Additional answer space if required

(b) The organic layer in the distillate was analysed by IR spectroscopy.
The IR spectrum is shown below.



Explain how the IR spectrum of the organic layer suggests that cyclopentene has been formed and that the reaction is incomplete.

Same cyclopentanol and cyclopentene present in IR

O-H / alcohol peak in region 3200 - 3600 cm⁻¹

C=C / alkene peak in region 1620 - 1680 cm⁻¹

[2]

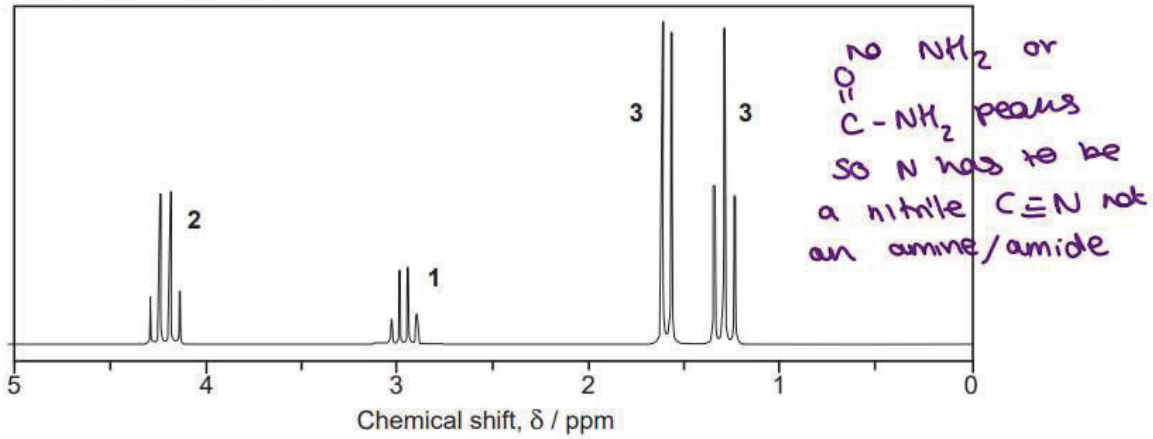
15. An organic compound **I** is analysed, using a combination of techniques. The analytical data is shown below.

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



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

chloroform-d
$CDCl_3$ used as a solvent

D_2O used to identify OH or NH peaks

when D_2O used the OH or NH peaks disappear but when D_2O not used OH or NH peaks are present [2]

(b)* Determine the structure of compound I, showing **all** your reasoning. **[6]**

$\frac{56.69}{12}$ $\frac{7.09}{1}$ $\frac{11.02}{14}$ $\frac{25.2}{16}$

$\frac{=4.72}{0.787}$ $\frac{=7.09}{0.787}$ $\frac{=0.787}{0.787}$ $\frac{=1.575}{0.787}$

$= 6$ $= 9$ $= 1$ $= 2$

$C_6H_9NO_2$ empirical formula and molecular formula

$(6\times12) + 9 + 14 + (16\times2) = 127.0$

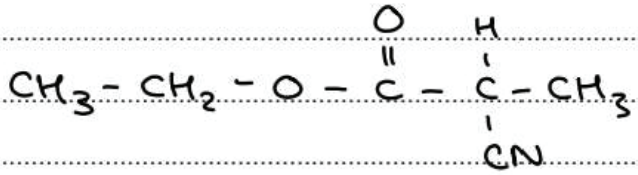
$\delta = 4.2$ ppm quartet, 2H $CH_3-\underline{CH_2}-O$

$\delta = 2.9$ ppm quartet, 1H $\underset{\underset{O}{\|}}{C}-\underline{CH}-CH_3$

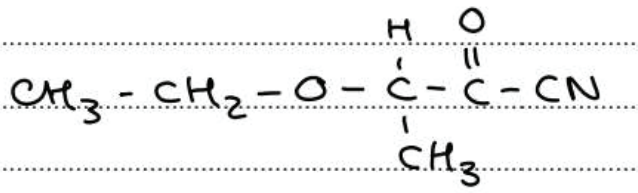
$\delta = 1.7$ ppm doublet, 3H $CH-\underline{CH_3}$

$\delta = 1.3$ ppm triplet $\underline{CH_3}-CH_2$

Additional answer space if required



ester nitrile



ketone nitrile ether