

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Tuesday 11 June 2019 – Afternoon

A Level Chemistry A

H432/02 Synthesis and analytical techniques

**Time allowed: 2 hours 15 minutes
plus your additional time allowance**

YOU MUST HAVE:
the Data Sheet for Chemistry A

YOU MAY USE:
a scientific or graphical calculator

Please write clearly in black ink.

Centre number

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Candidate number

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First name(s) _____

Last name _____

READ INSTRUCTIONS OVERLEAF



INSTRUCTIONS

Use black ink. You may use an HB pencil for graphs and diagrams.

Answer ALL the questions.

Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.

Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.

INFORMATION

The total mark for this paper is 100.

The marks for each question are shown in brackets [].

Quality of extended responses will be assessed in questions marked with an asterisk (*).

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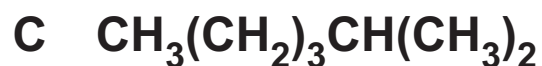
SECTION A

You should spend a maximum of 20 minutes plus your additional time allowance on this section.

Write your answer to each question in the box provided.

Answer ALL the questions.

1 Which alkane has the highest boiling point? [1]



Your answer

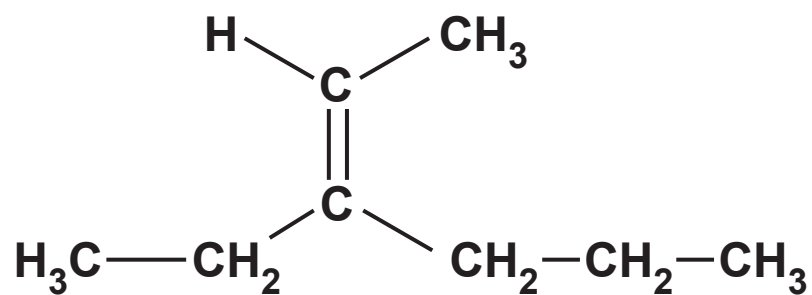
- 2 Butane reacts with chlorine in the presence of ultraviolet radiation to form a mixture of organic products.

Which equation shows a propagation step in the mechanism for this reaction? [1]



Your answer

3 What is the name of the compound below? [1]



A 3-Propylpent-2-ene

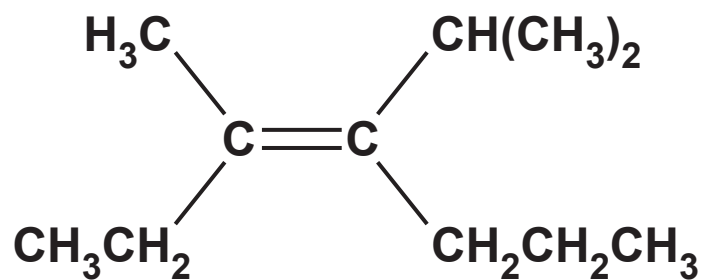
B 3-Propylpent-3-ene

C 3-Ethylhex-2-ene

D 4-Ethylhex-4-ene

Your answer

4 The structure of a stereoisomer is shown below.



Which term correctly describes this stereoisomer? [1]

A *cis*-

B *trans*-

C *E*-

D *Z*-

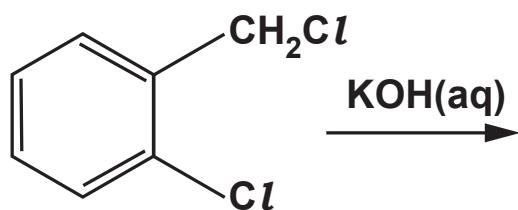
Your answer

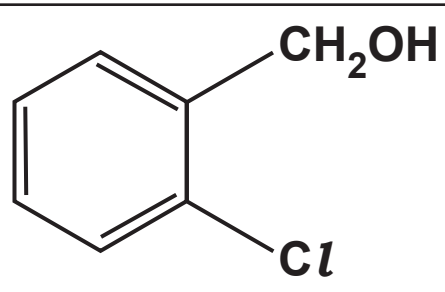
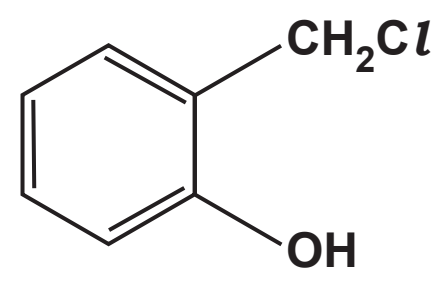
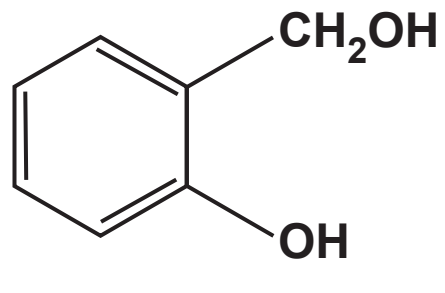
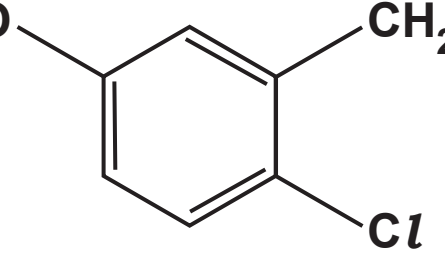
5 Which types of bonds are broken and formed in the reaction of ethene and bromine? [1]

	Types of bond broken	Types of bond formed
A	σ	π
B	π	σ
C	σ and π	π
D	σ and π	σ

Your answer

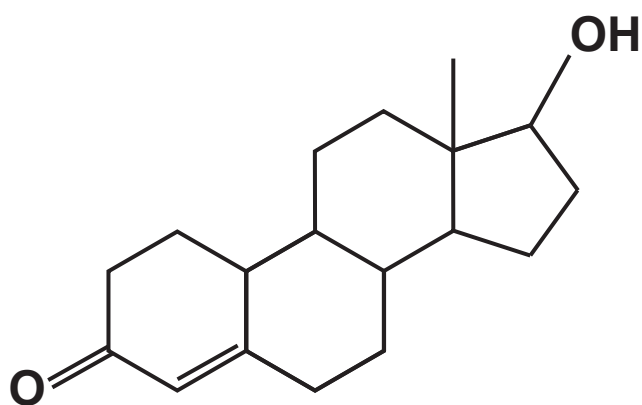
6 What is the organic product of the reaction below? [1]



A	 <chem>OC1=CC=CC=C1Cl</chem>
B	 <chem>ClCC1=CC=CC=C1O</chem>
C	 <chem>OC1=CC=CC=C1O</chem>
D	 <chem>ClCC1=CC=C(O)C=C1Cl</chem>

Your answer

7 What is the number of chiral carbon atoms in the steroid molecule below? [1]



A 5

B 6

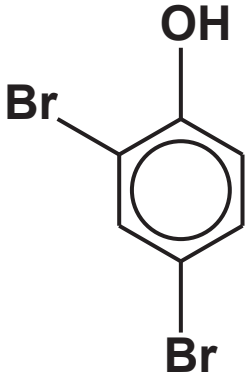
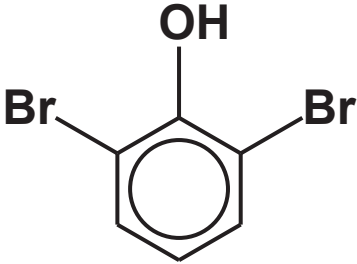
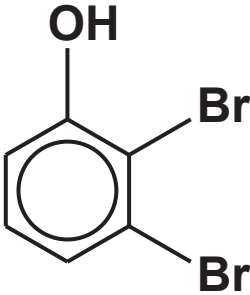
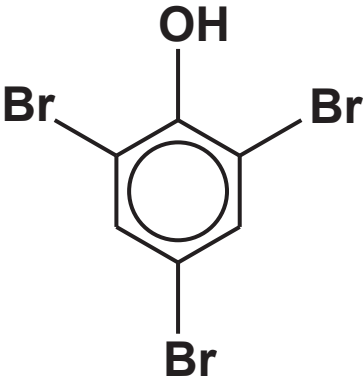
C 7

D 8

Your answer

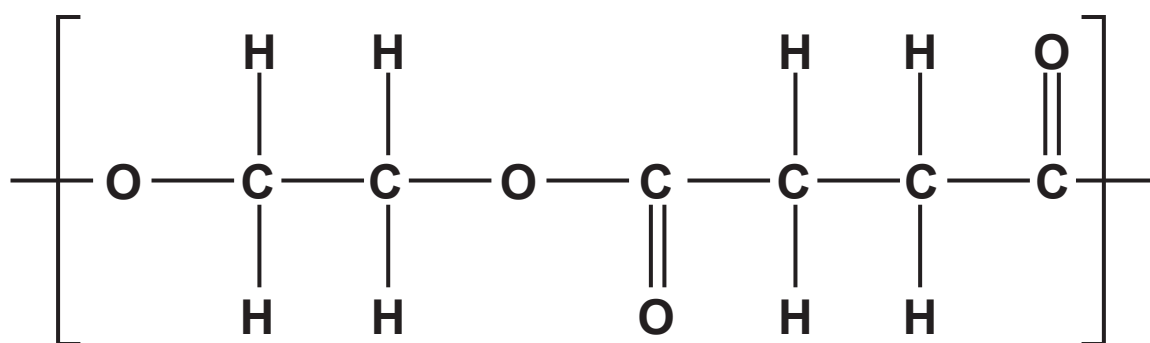
8 Phenol reacts with bromine.

Which is the LEAST likely organic product? [1]

A	
B	
C	
D	

Your answer

9 The repeat unit of a polymer is shown below.

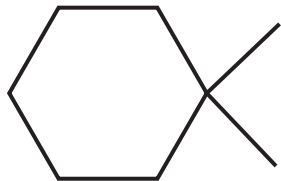
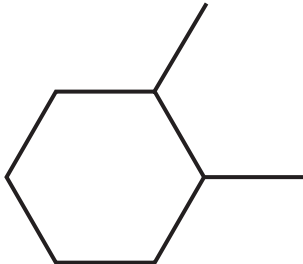
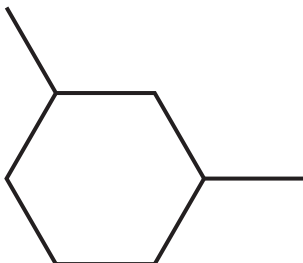
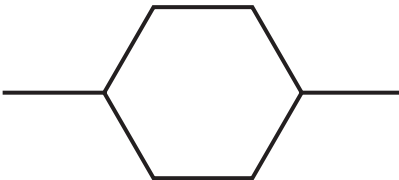


Which monomers could form this polymer? [1]

A		
B		
C		
D		

Your answer

10 Which compound shows 4 peaks in its carbon-13 NMR spectrum? [1]

A	
B	
C	
D	

Your answer

- 11 A student reacts 4.50 g of $\text{C}_6\text{H}_5\text{NH}_2$ with excess CH_3COCl in the reaction below.



$$M_r = 93.0$$

$$M_r = 135.0$$

The reaction produces 3.25 g of $\text{C}_6\text{H}_5\text{NHCOCH}_3$.

What is the percentage yield of $\text{C}_6\text{H}_5\text{NHCOCH}_3$? [1]

A 49.8

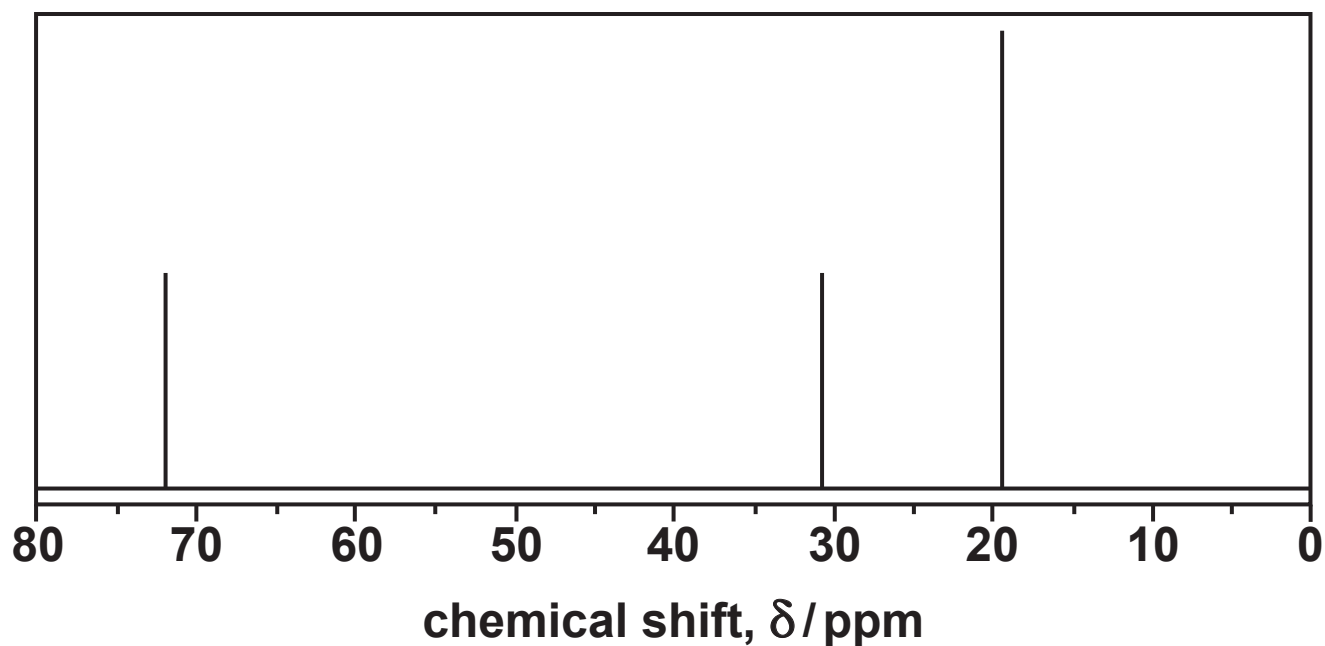
B 68.9

C 72.2

D 95.4

Your answer

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



Which compound could have produced this spectrum? [1]

- A Propane
- B 2-Methylbutane
- C 2-Methylpropan-1-ol
- D 2-Methylpropan-2-ol

Your answer

13 A carbonyl compound is reacted with NaBH_4 .

Which compound(s) could be formed? [1]

1 2-Methylpentan-2-ol

2 2-Methylpentan-1-ol

3 3-Methylpentan-2-ol

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

14 Which chemical(s) can react with phenol? [1]

1 Potassium hydroxide

2 Ethanoyl chloride

3 Nitric acid

A 1, 2 and 3

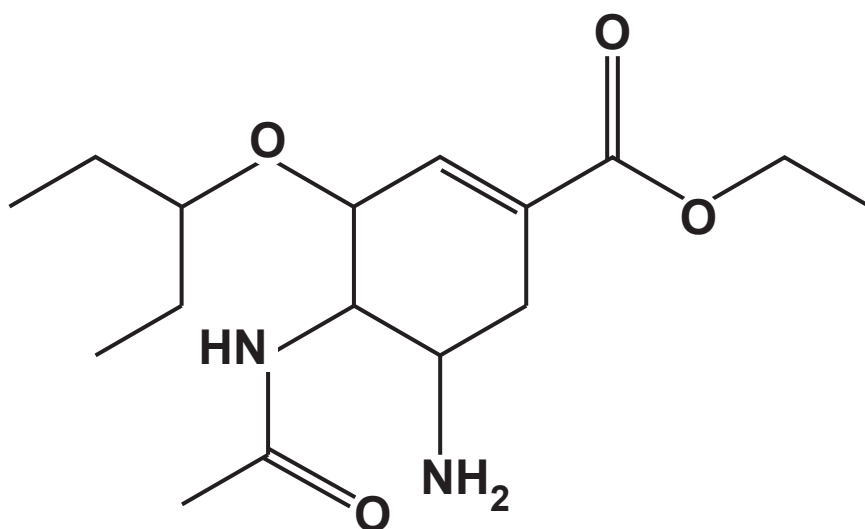
B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

15 The structure of a compound used to treat influenza is shown below.



Which functional group(s) is/are in a molecule of the compound? [1]

- 1 Ester
- 2 Secondary amide
- 3 Ketone

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

☐

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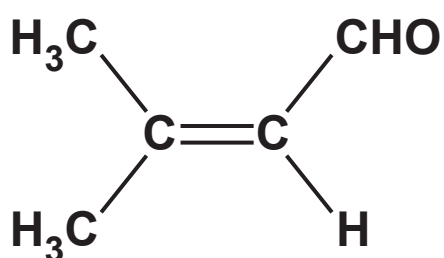
SECTION B

Answer ALL the questions.

16 This question is about unsaturated aldehydes and alcohols.

(a) 3-Methylbut-2-enal, shown below, is used as a food flavouring.

3-Methylbut-2-enal



3-Methylbut-2-enal is reacted with hydrogen bromide, forming a mixture of two organic products.

One of the organic products forms in a much greater quantity than the other organic product.

- (i) Outline the reaction mechanism for the formation of ONE of the organic products.**

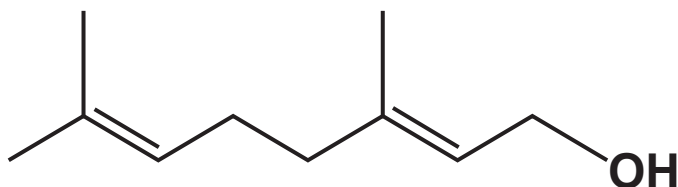
Include curly arrows and relevant dipoles. Use the space below. [4]

- (ii) Explain why one of the organic products forms in a much greater quantity than the other organic product.**

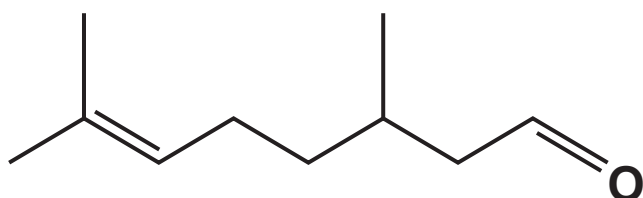
[2]

- (b) Geraniol and citronellal, shown below, are isomers present in 'citronella oil', used as an insect repellent.

Geraniol



Citronellal



Geraniol and citronellal are structural isomers of each other.

They also show stereoisomerism.

- (i) Describe how the observations from a chemical test would distinguish between geraniol and citronellal.

[2]

(ii) What is the molecular formula of geraniol?

_____ **[1]**

(iii) Explain why geraniol and citronellal are structural isomers of each other.

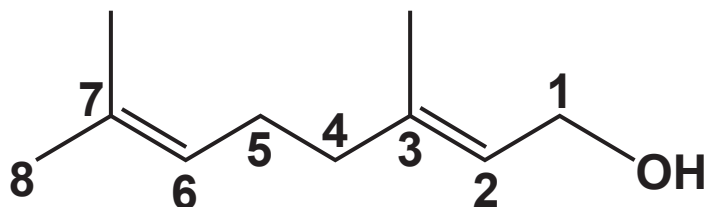
_____ **[1]**

(iv) Explain the term STEREOISOMERISM.

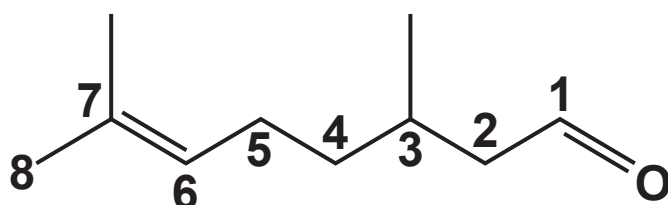
_____ **[1]**

- (v) The structures of geraniol and citronellal are repeated below with the carbon atoms numbered.

Geraniol



Citronellal



Explain the types of stereoisomerism shown by geraniol and citronellal.

**In your answer,
refer to the numbered carbon atoms in the
structures above**

**draw diagrams clearly showing any
stereoisomers. [4]**

GERANIOL STEREOISOMERS

CITRONELLAL STEREOISOMERS

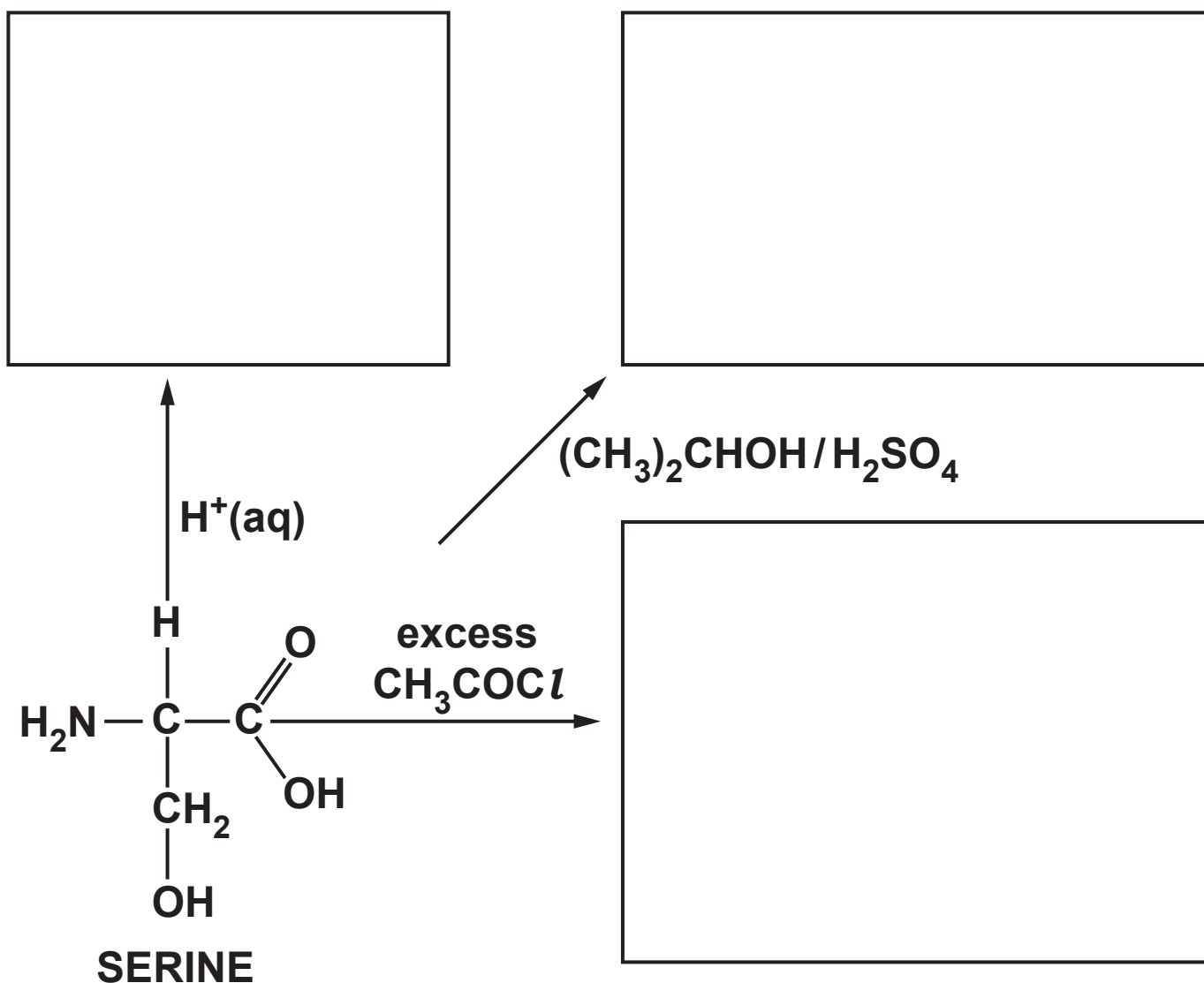
17 This question is about α -amino acids, $\text{RCH}(\text{NH}_2)\text{COOH}$.

(a) TABLE 17.1 shows the R groups in four amino acids.

TABLE 17.1

Amino acid	R group
alanine (ala)	CH_3-
serine (ser)	HOCH_2-
leucine (leu)	$(\text{CH}_3)_2\text{CHCH}_2-$
glycine (gly)	$\text{H}-$

(i) In the boxes, draw the organic products for the reactions of serine shown below. [4]



- (ii) A student is provided with one of the four amino acids in TABLE 17.1.

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 cm^3 in a volumetric flask.

The student titrates this solution with 25.0 cm^3 of 0.150 mol dm^{-3} hydrochloric acid.

21.30 cm^3 of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

**Determine which amino acid the student used.
Use the space below. [4]**

(b) The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in TABLE 17.1 opposite, using two different solvents, W and X.

(i) What is the R_f value of serine (ser) in solvent W?

$R_f =$ _____ **[1]**

(ii) Analyse the chromatograms to identify the unknown amino acid.

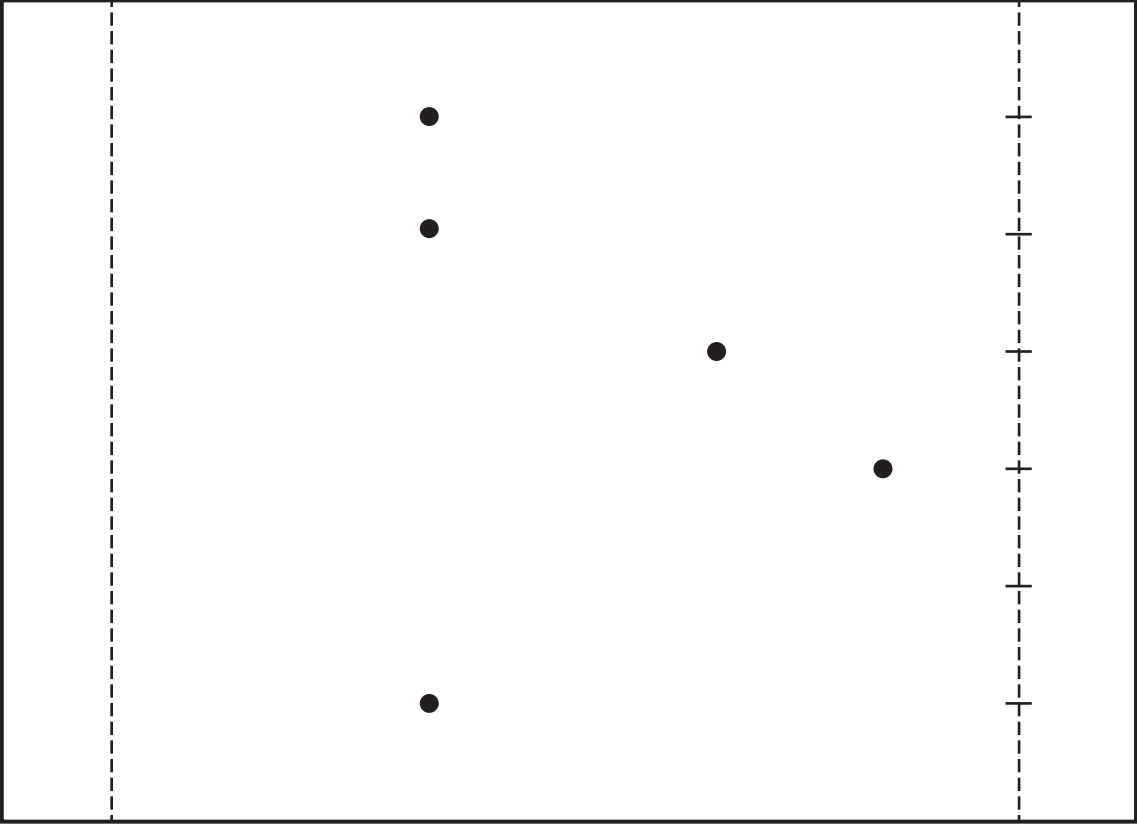
Explain your reasoning.

Name of unknown amino acid _____

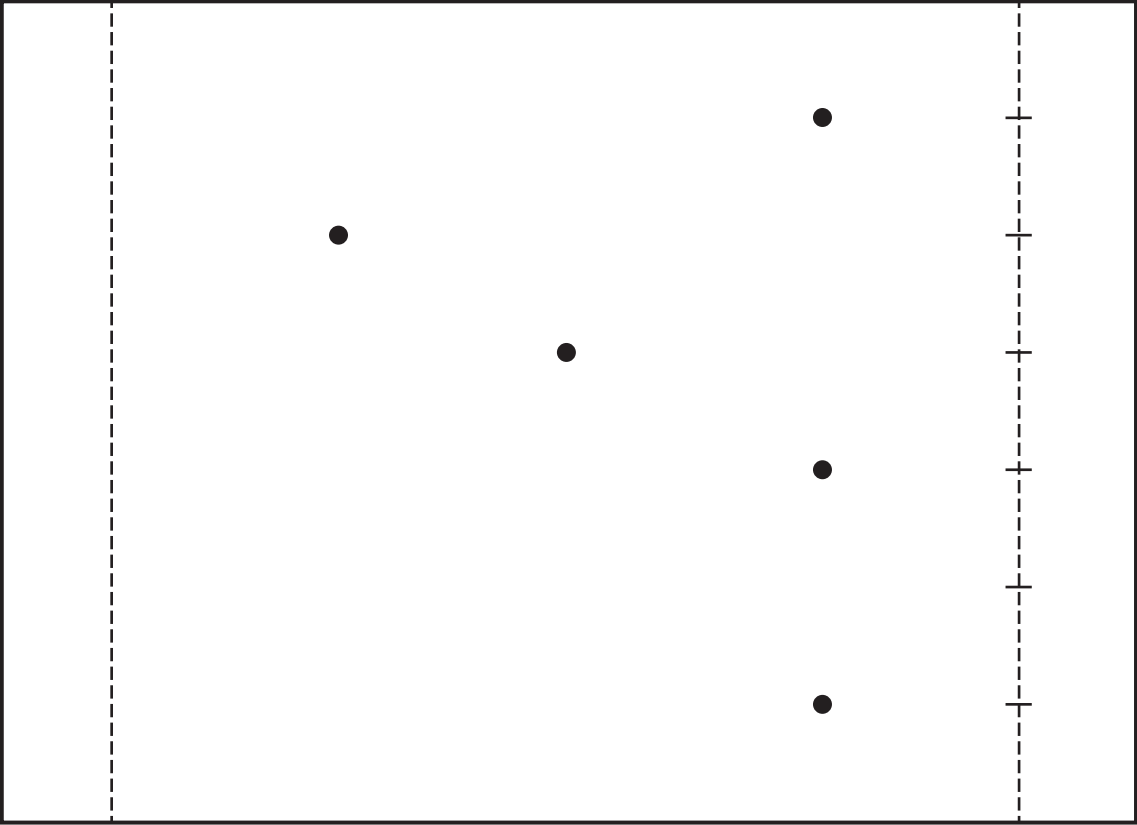
Explanation _____

_____ **[2]**

Solvent W



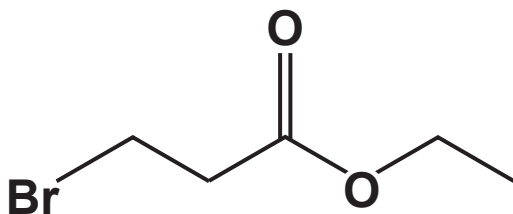
Solvent X



18 This question is about esters.

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

ESTER A

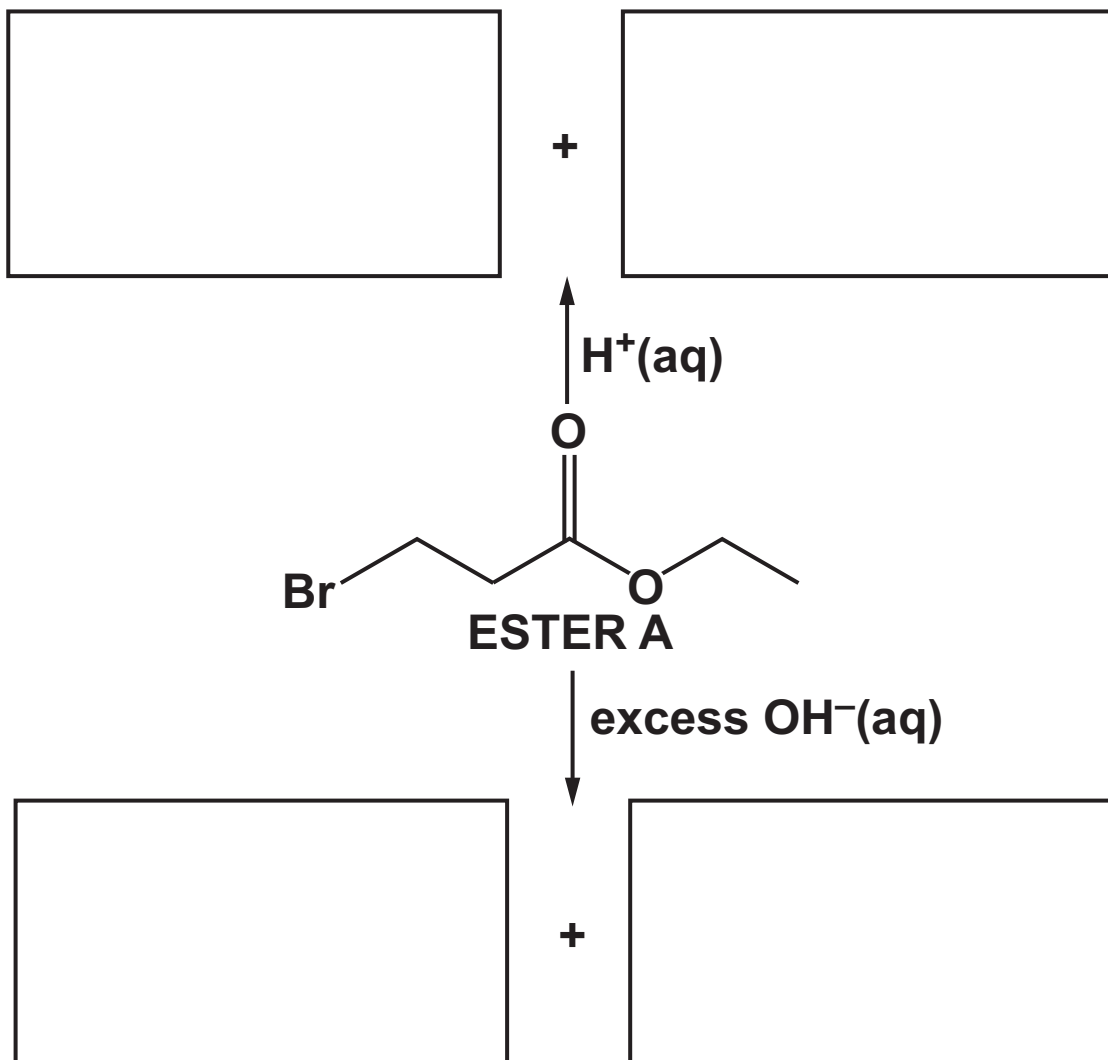


(i) What is the systematic name of ester A?

_____ [1]

- (ii) In the boxes, draw the organic products for the reactions of the functional groups in ester A shown below.

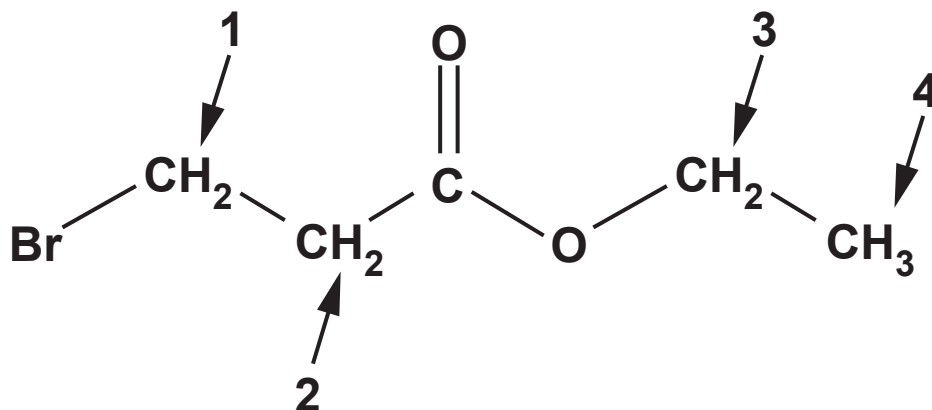
Each reaction forms two organic products. [5]



- (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. [4]

Proton environment	Chemical shift	Splitting pattern
1		
2		
3		
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. Use the space below. [1]

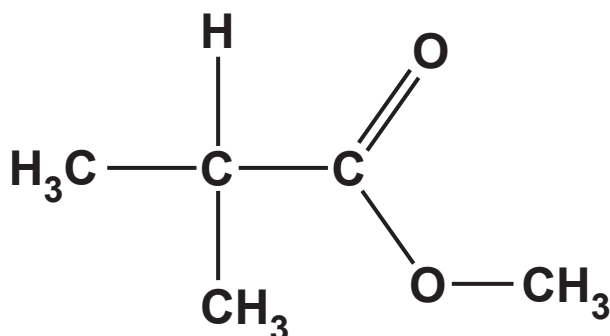
(d) A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.

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

$M_r = \text{_____} \text{ g mol}^{-1}$ [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, $(\text{CH}_3)_2\text{CHCHO}$. 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.

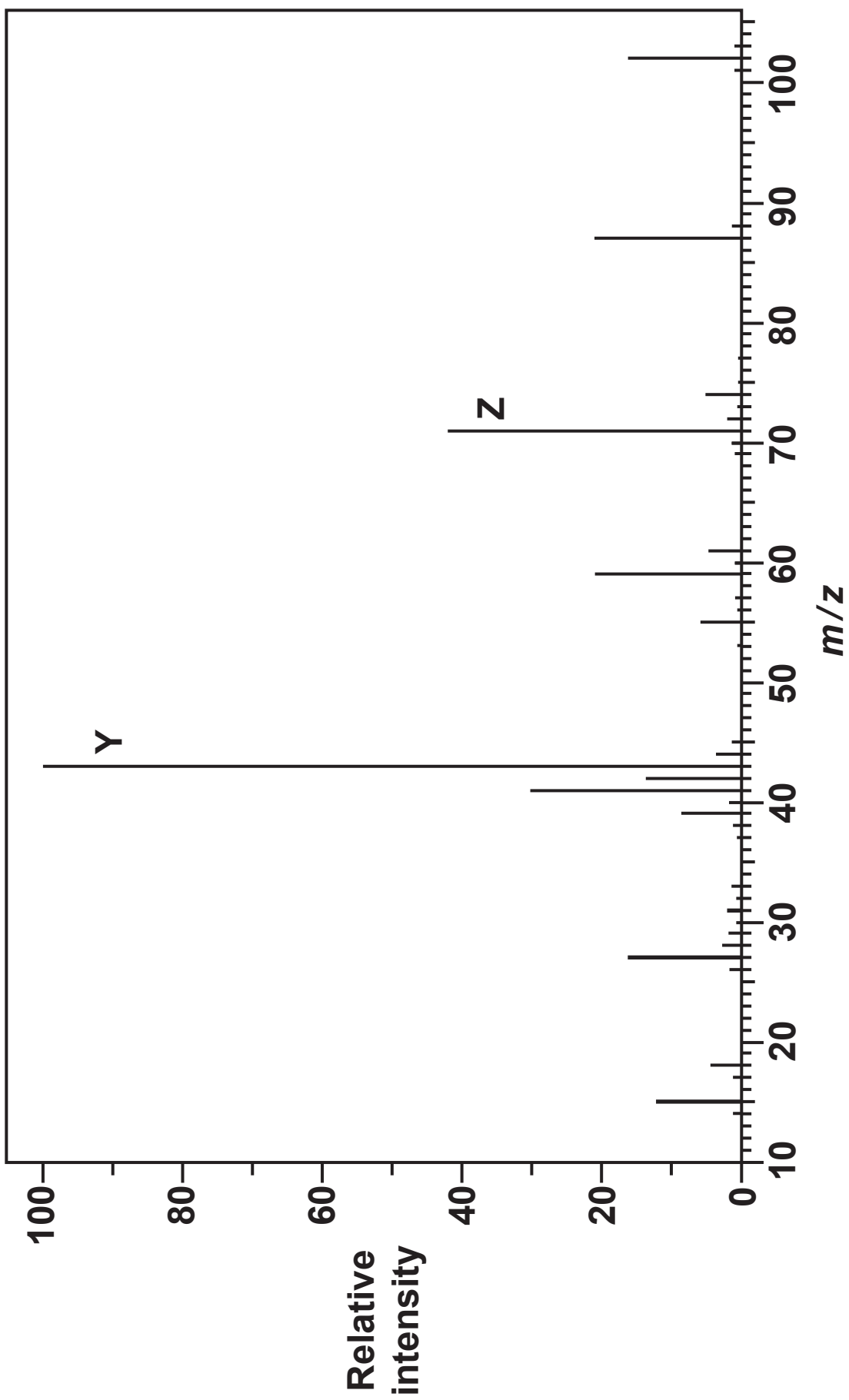
Purification details are NOT required. [6]

Additional answer space if required

- (ii) The mass spectrum of ester C is shown on the opposite page.

Suggest possible structures for the species responsible for peaks Y and Z in the mass spectrum. [2]

Y	Z



19 This question is about benzene.

(a) Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.

(i) Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

[3]

- (ii) Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

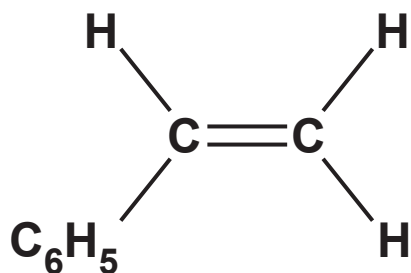
Describe TWO pieces of evidence to support the delocalised model of benzene.

[2]

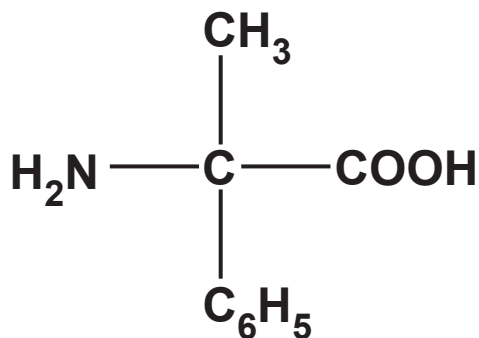
(b) Benzene can be used as the starting material for the synthesis of compounds D and E, shown below.

In the diagrams C_6H_5 is a phenyl group.

COMPOUND D



COMPOUND E



Compounds D and E can be converted into polymers.

(i) Draw TWO repeat units of these polymers. [3]

TWO repeat units of polymer formed from D

TWO repeat units of polymer formed from E

(ii) State the TYPE of polymer formed from compounds D and E.

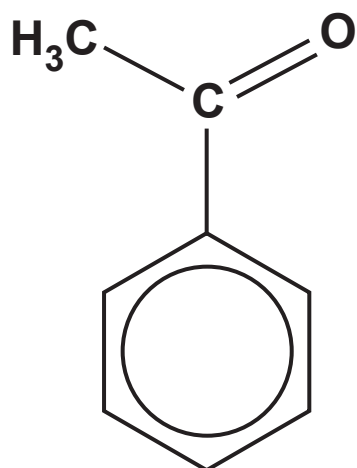
From compound D _____

From compound E _____

[1]

- (iii) In the synthesis of compounds D and E, benzene is first reacted with ethanoyl chloride, CH_3COCl , to form phenylethanone, shown below.

PHENYLETHANONE



The reaction takes place in the presence of aluminium chloride, AlCl_3 , which acts as a catalyst.

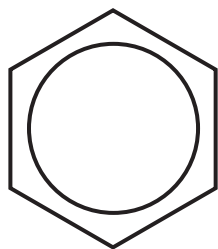
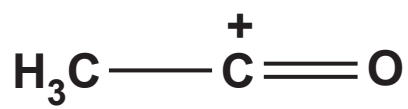
In the mechanism for this reaction, ethanoyl chloride first reacts with aluminium chloride to form the $\text{CH}_3\text{—C}^+=\text{O}$ cation

the $\text{CH}_3\text{—C}^+=\text{O}$ cation then behaves as an electrophile.

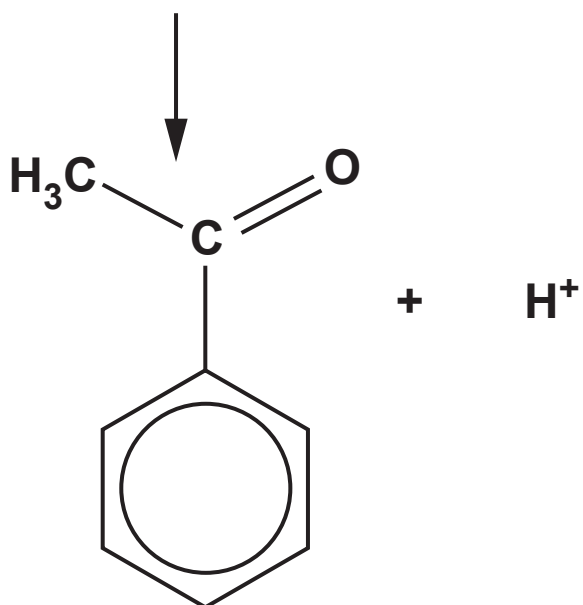
Complete the mechanism for the reaction.

Include equations to show the role of the AlCl_3 catalyst, relevant curly arrows and the structure of the intermediate.

Formation of electrophile _____



INTERMEDIATE

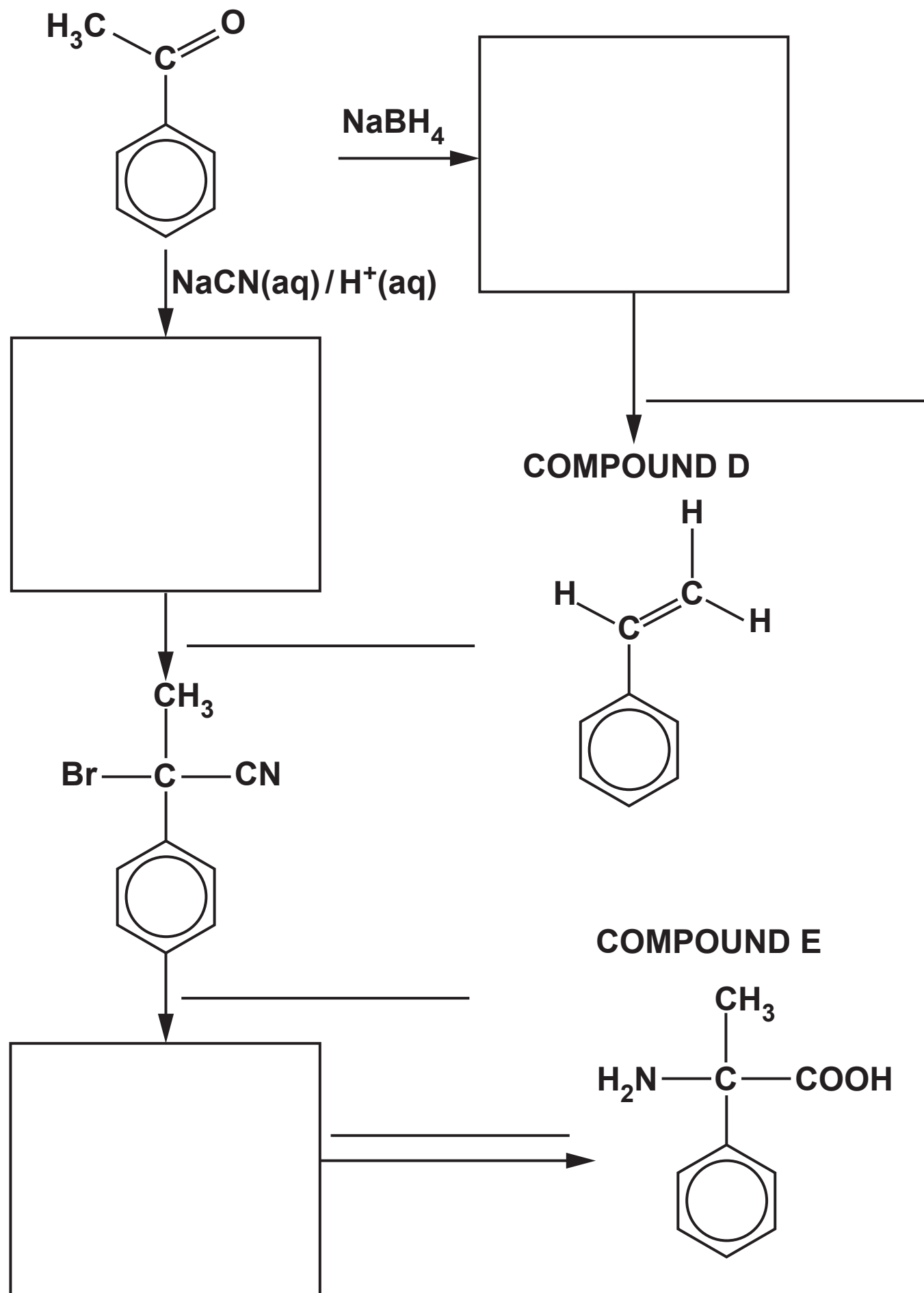


Regeneration of catalyst _____

[5]

- (iv) Complete the flowchart opposite for the synthesis of compounds D and E from phenylethanone. [7]**

PHENYLETHANONE



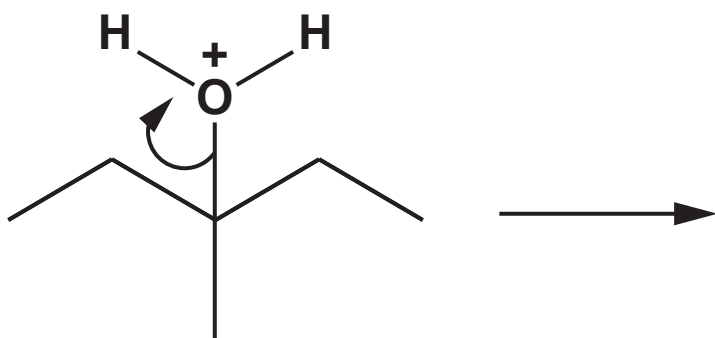
20 This question is about reaction mechanisms.

(a) Chemists use curly arrows in reaction mechanisms.

(i) What does a curly arrow show in a reaction mechanism?

_____ [1]

(ii) Draw structures to show the products in the reaction mechanism below. [2]

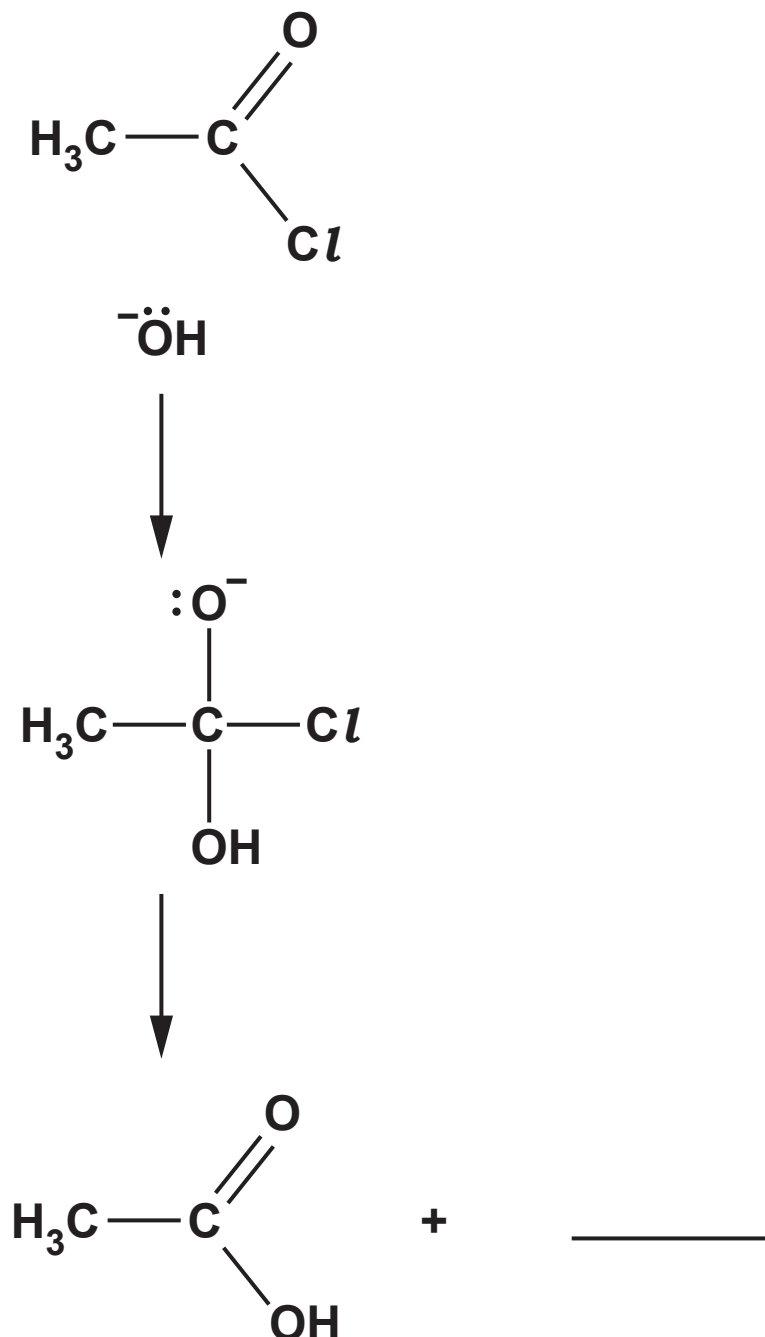


(iii) Use the mechanism in (ii) to explain what is meant by HETEROLYTIC FISSION.

_____ [2]

(b) An incomplete reaction mechanism is shown below.

(i) Complete the mechanism by adding curly arrows and any missing species. [4]



(ii) What is the role of OH^- in this mechanism?

_____ [1]

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21* Analysis of an unknown organic compound produced the following results shown on the spectrum diagrams on pages 52 and 53.

Elemental analysis by mass

C: 73.17%; H: 7.32%; O: 19.51%

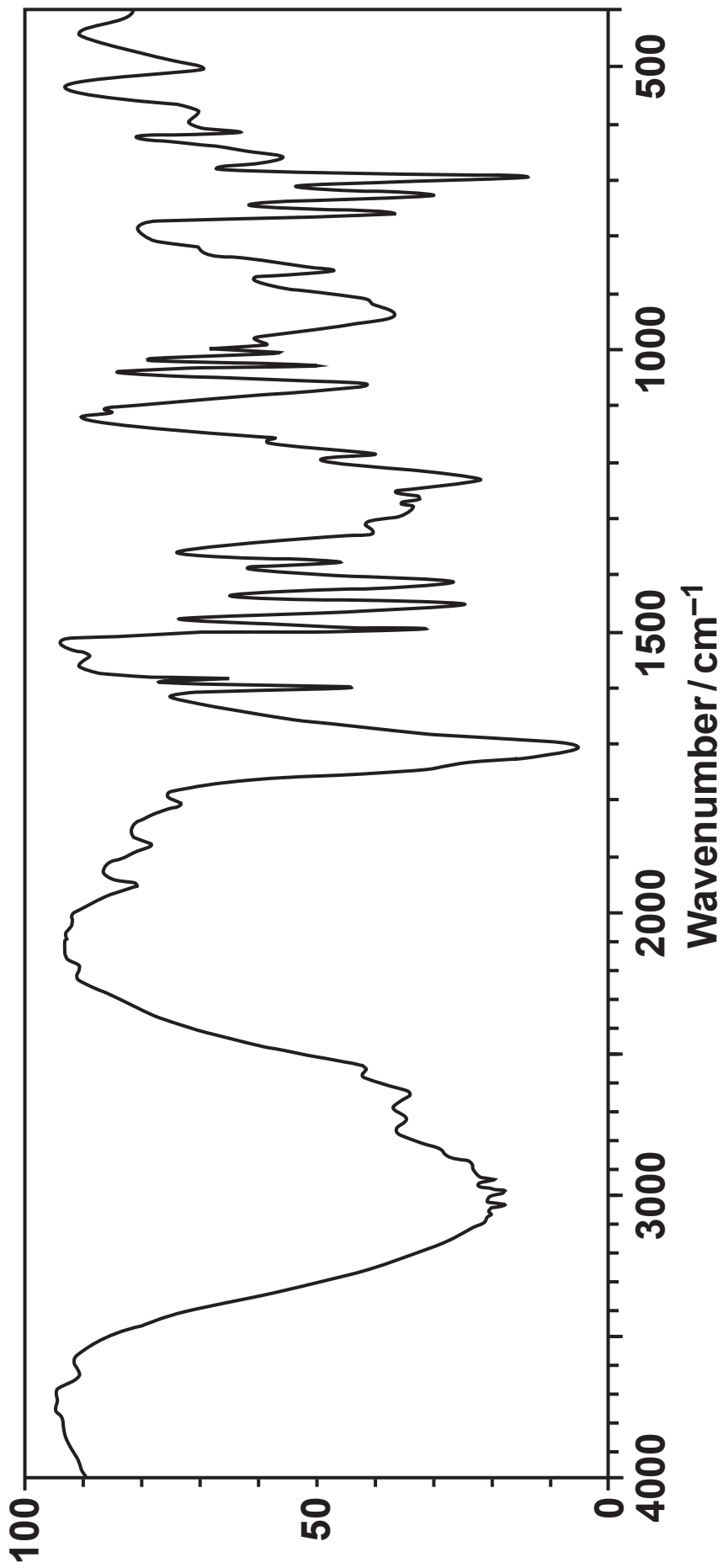
Mass spectrum

Molecular ion peak at $m/z = 164.0$

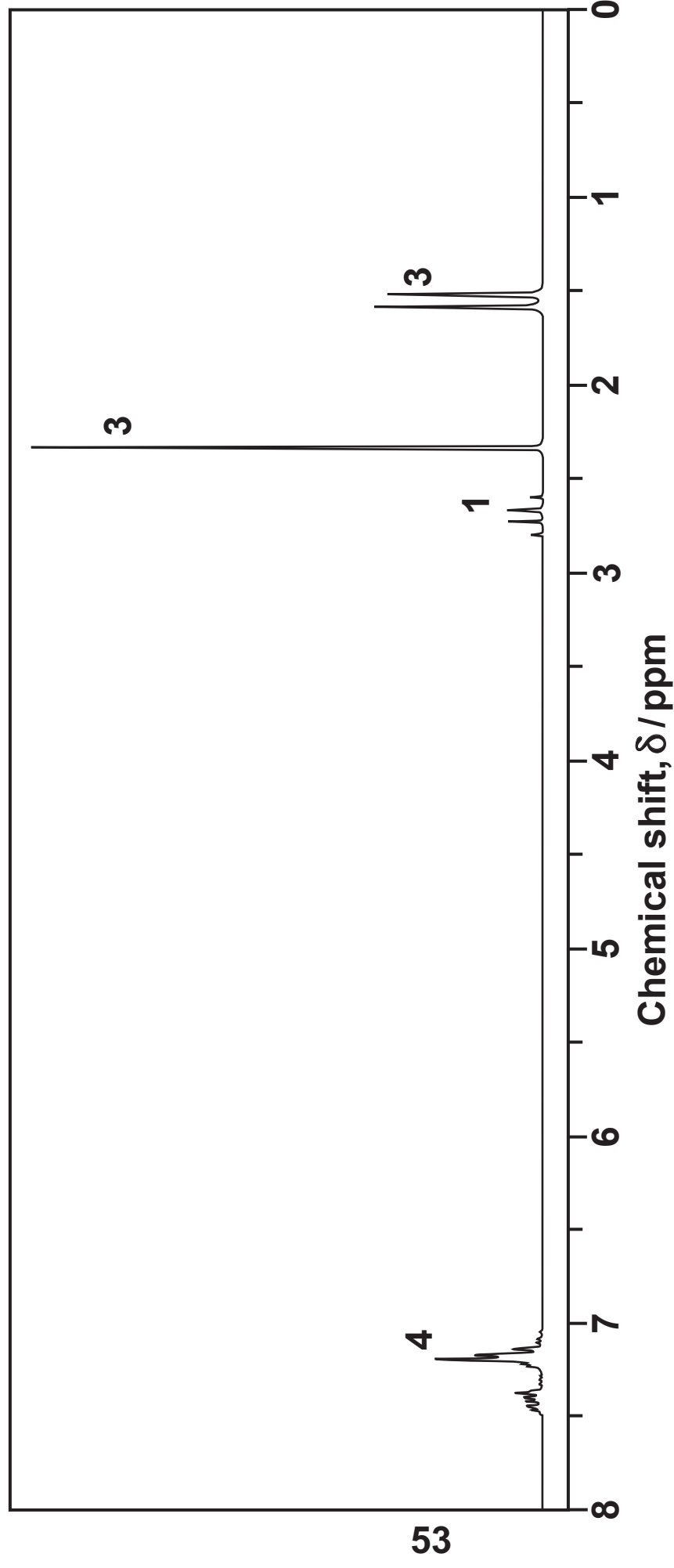
Infrared spectrum

Transmittance

(%)



¹H NMR spectrum in D₂O



The numbers by the peaks are the relative peak areas.

Show ALL your reasoning. [6]

This image shows a single sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

Additional answer space if required

END OF QUESTION PAPER

ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

[illegible]

