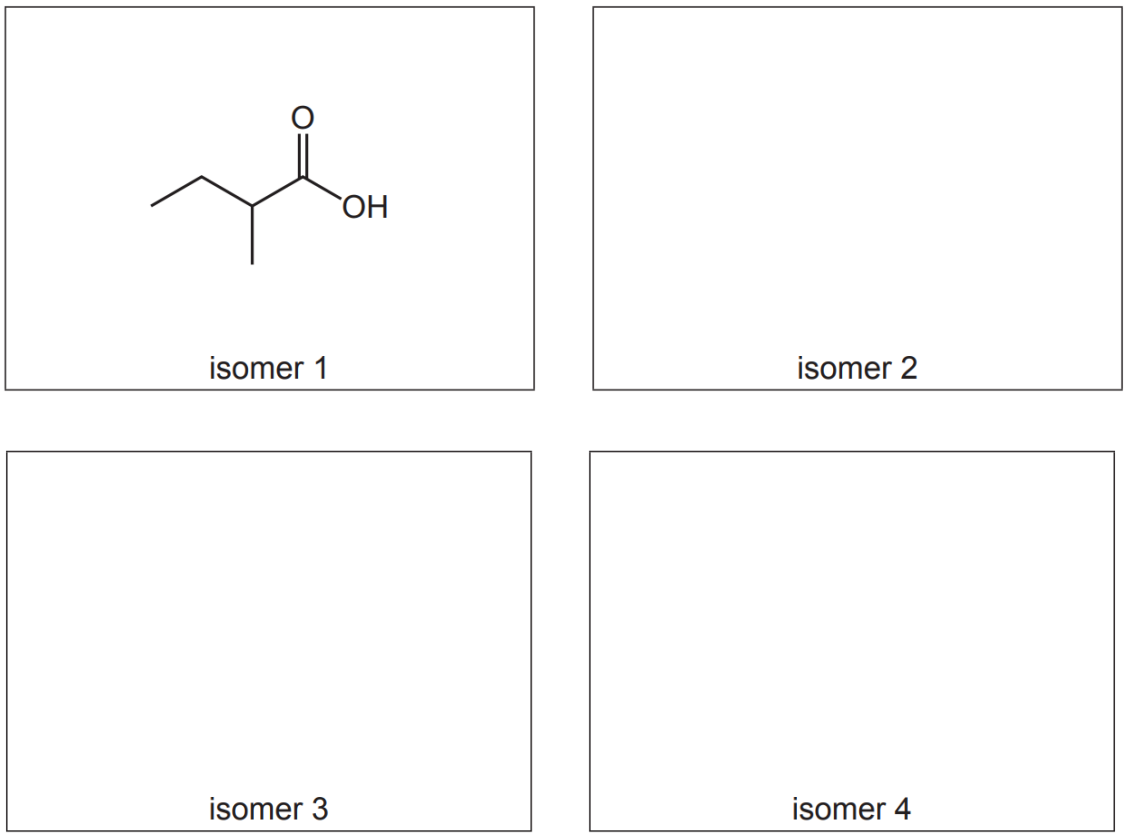
1. 9701/42/O/N/16 Q8b

(b) There are **four** possible structural isomers of $C_5H_{10}O_2$ that are carboxylic acids.

(i) The first isomer has been drawn.

Draw the skeletal formulae of the three **other** structural isomers.

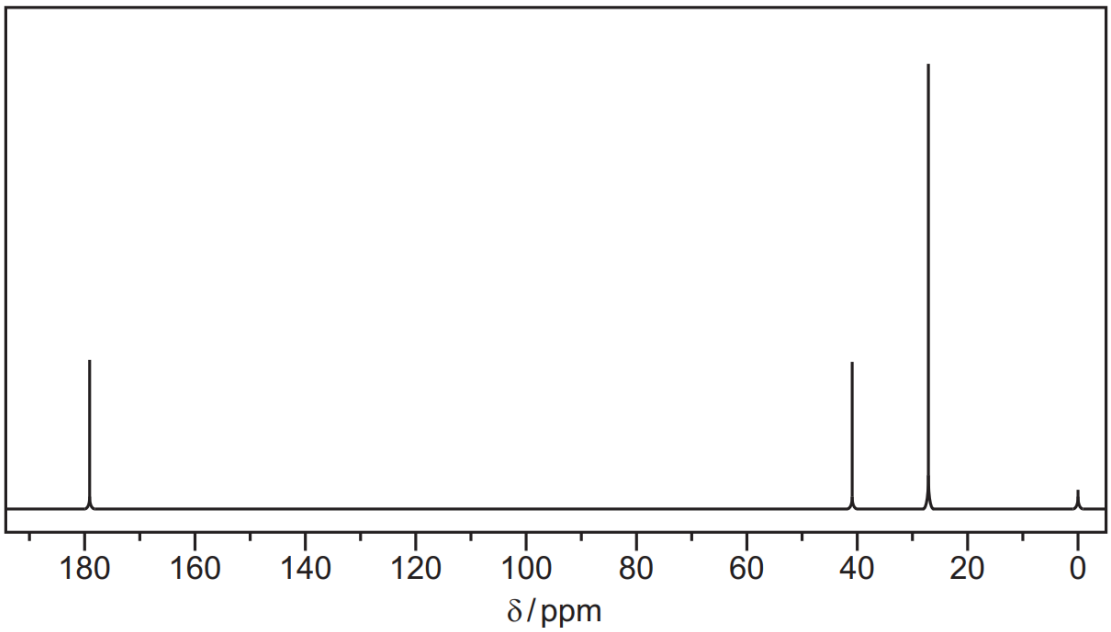


[2]

(ii) State the systematic name of isomer 1.

..... [1]

(c) **F** is one of the four structural isomers in **(b)(i)**. A carbon-13 NMR spectrum of **F** is shown.



(i) Use the spectrum to identify isomer **F**. Draw its structure in the box below.

F

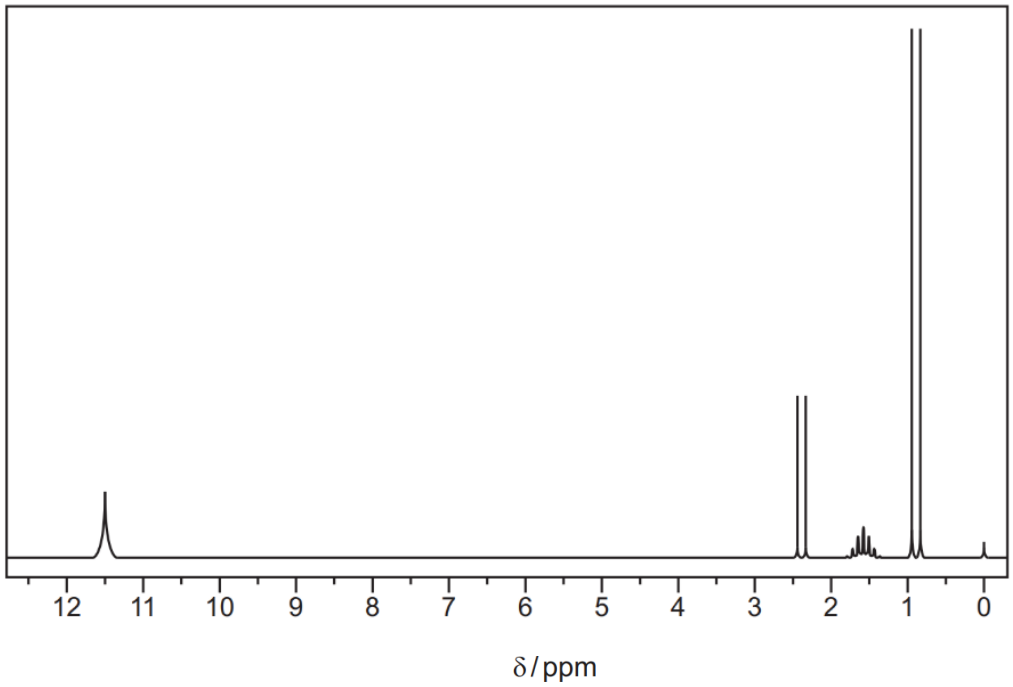
[1]

(ii) Use the *Data Booklet* and your knowledge of carbon-13 NMR spectroscopy to identify the environments and hybridisations of the carbon atoms responsible for each of the three absorptions.

δ / ppm	environment of the carbon atom	hybridisation of the carbon atom
27		
41		
179		

[2]

(d) **G** is another of the four structural isomers in **(b)(i)**. The proton NMR spectrum of **G** is shown.



(i) Use the *Data Booklet* and the spectrum to complete the table below.

The actual chemical shifts for the four absorptions in **G** and the splitting pattern at δ = 1.6 ppm have been added for you.

δ / ppm	type of proton	number of protons	splitting pattern
0.9			
1.6			multiplet
2.4			
11.5			

[4]

(ii) Deduce which isomer is **G** and draw its structure in the box.

G

[1]

(e) Name or give the formula of a suitable solvent for obtaining a proton NMR spectrum.

..... [1]

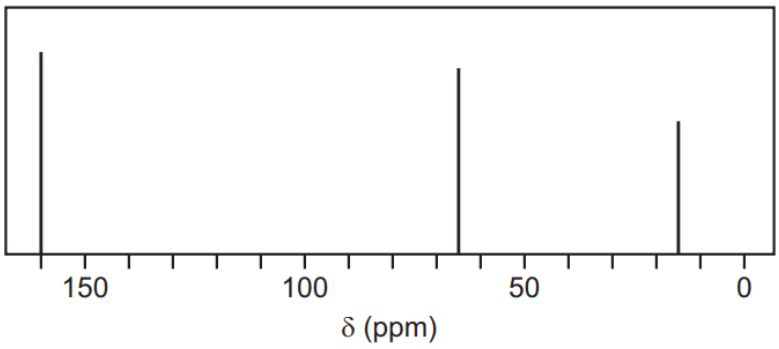
2. 9701/41/M/J/16 Q2c

Ethanedioic acid can be converted into ethanedioyl chloride:

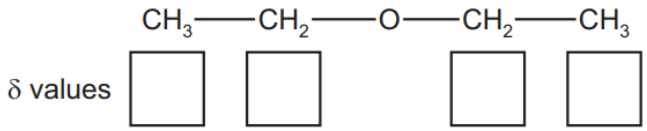
$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(c) When ethanedioyl chloride is reacted with silver ethanedioate, AgO_2CCO_2Ag, in ethoxyethane at –30 °C, an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6.

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $CH_3CH_2OCH_2CH_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.



[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

..... [1]

(d) When pure **L** is reacted with an excess of CH_3OH, a mixture of three compounds is formed.

$$\underset{(C_4O_6)}{\mathbf{L}} \text{ and } CH_3OH \rightarrow \underset{(C_2H_2O_4)}{\mathbf{M}} \text{ and } \underset{(C_3H_4O_4)}{\mathbf{N}} \text{ and } \underset{(C_4H_6O_4)}{\mathbf{O}}$$

M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.

M, $(C_2H_2O_4)$

N, $(C_3H_4O_4)$

O, $(C_4H_6O_4)$

[3]

(ii) Suggest a structure for **L** that fits all the data given in **(c)** and **(d)**.

L, (C_4O_6)

[1]

3. 9701/42/M/J/16 Q6b

Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $CH_3CO_2C_6H_5$, but not its isomer methyl benzoate, $C_6H_5CO_2CH_3$.

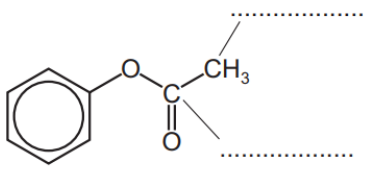
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer **A** and isomer **B**.

(i) The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

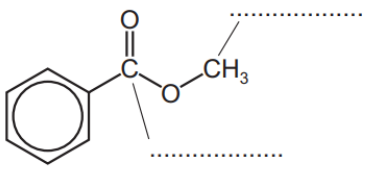
isomer **A**	isomer **B**
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomer .....



methyl benzoate is isomer .....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.
You should state the reagents and conditions for each step, and any observations you would make.

step 1 .....

.....

.....

step 2 .....

.....

.....

[3]

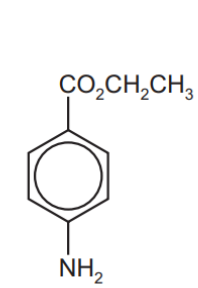
4. 9701/41/O/N/17 Q6d

(d) A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

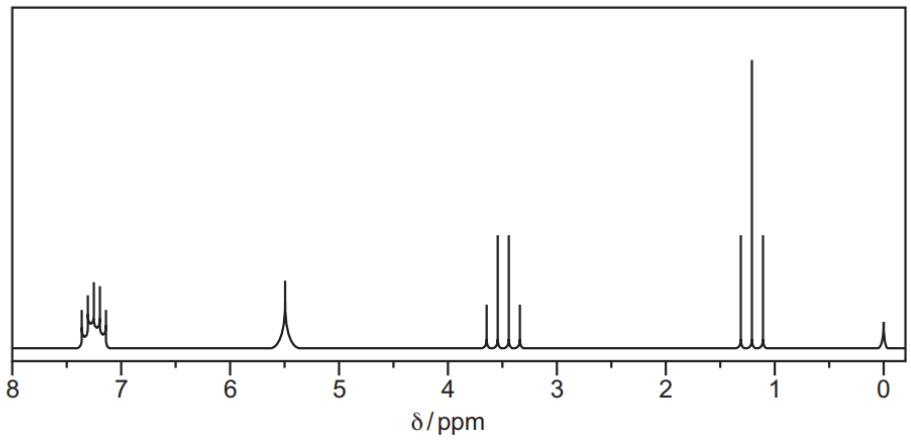
(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

(ii) Benzocaine was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded.



benzocaine



Suggest why $CDCl_3$ and not $CHCl_3$ is used as the solvent when obtaining a proton NMR spectrum.

.....

..... [1]

(iii) Use the *Data Booklet* and the spectrum in **(d)(ii)** to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ, for the four absorptions have been added.

δ / ppm	group responsible for the peak	number of ^1H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at δ1.2 ppm.

.....

..... [1]

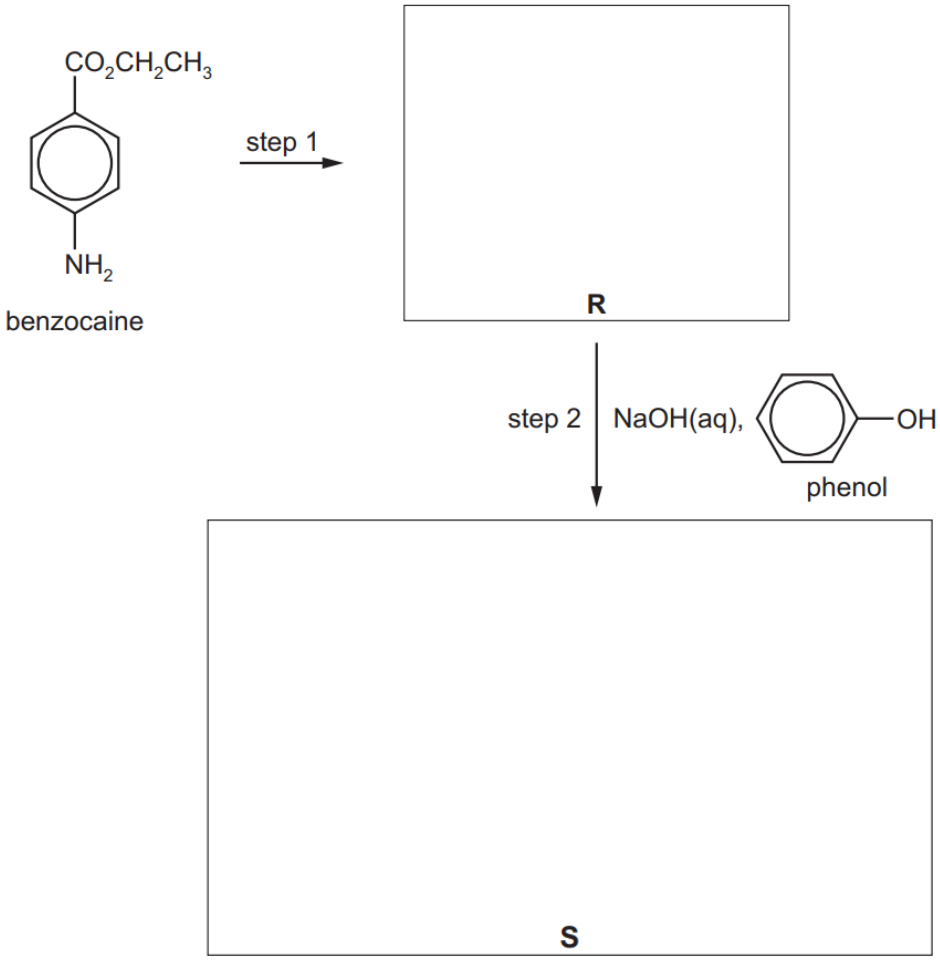
(v) The proton NMR spectrum of benzocaine dissolved in D_2O was recorded.

Suggest how this spectrum would differ from the spectrum in **(d)(ii)**.
Explain your answer.

.....

..... [1]

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



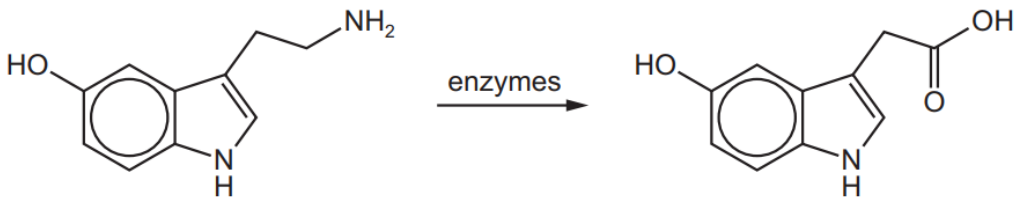
(i) Suggest the reagents used for step 1.

..... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

5. 9701/42/O/N/17 Q3c

Serotonin is converted by enzymes in the liver to compound **M**.



serotonin **M**

(ii) The proton NMR spectrum of **M** dissolved in $CDCl_3$ shows eight peaks due to the eight different types of proton present in the molecule.

The proton NMR spectrum of **M** dissolved in D_2O was recorded.

Predict the number of peaks that would be seen in the proton NMR spectrum of **M** in D_2O. Explain your answer.

number of peaks .....

explanation .....

.....

[2]

6. 9701/41/M/J/17 Q6d

(d) The proton NMR spectrum of a sample of 1-phenylethanol shows four peaks: a multiplet for the C_6H_5 protons and three other peaks as shown in the table. When the sample is shaken with D_2O and the proton NMR spectrum recorded, **fewer** peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, $C_6H_5CH(OH)CH_3$.
Use of the *Data Booklet* might be helpful.

δ/ppm	number of ^1H atoms responsible for the peak	group responsible for the peak	splitting pattern	result on shaking with D_2O
1.4				
2.7				
4.0				
7.2-7.4	5	C_6H_5	multiplet	peak remains

[4]

7. 9701/42/M/J/17 Q2e

(e) (i) State the number of peaks that would be seen in the carbon-13 NMR spectrum of $CH_3CH_2CHClCH_3$.

..... [1]

(ii) There are two isomers of $CH_3CH_2CHClCH_3$ that have **fewer** peaks in their carbon-13 NMR spectra than $CH_3CH_2CHClCH_3$.

Draw the structures of the isomers and state the number of peaks for each isomer.

isomer 1

number of peaks = ...

isomer 2

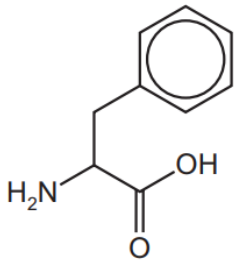
number of peaks = ...

[3]

8. 9701/42/F/M/17 Q7e

(e) Use the *Data Booklet* to help you answer this question.

The carbon-13 NMR spectrum of **K** was recorded.



K

(i) State how many different carbon environments are present in **K**.

..... [1]

(ii) The chemical shifts, δ, due to two of the carbon atoms x and y present in **K** are given in the table.

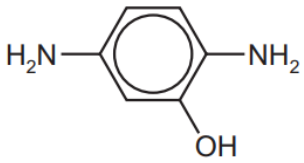
carbon atom	δ/ppm
x	130
y	170

On the structure of **K**, circle **and** label **two** carbon atoms which could correspond to x and y. [1]

9. 9701/41/O/N/18 Q5a(i)

(a) Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.

F



G

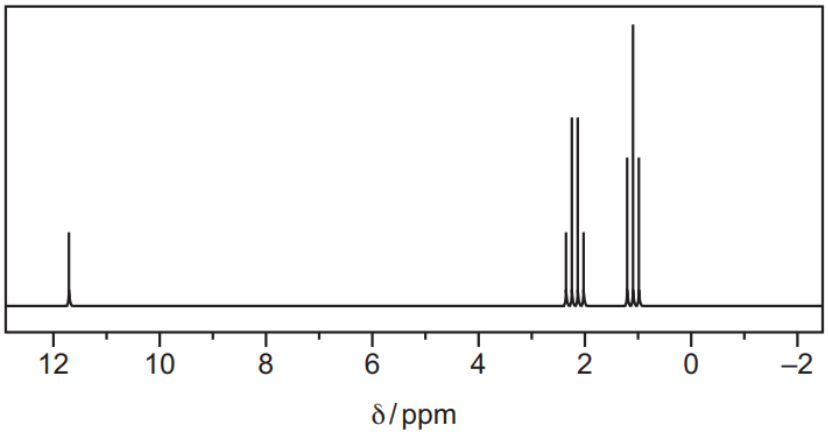
(i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.

	number of peaks
F	
G	

[2]

10. 9701/41/M/J/18 Q7e

(e) An unknown compound, **Z**, is propan-1-ol, propanal or propanoic acid. The proton NMR spectrum of **Z** dissolved in $CDCl_3$ is shown.



(i) From the proton NMR spectrum, identify **Z**.

..... [1]

(ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

.....

.....

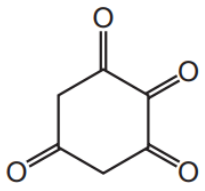
.....

..... [2]

11. 9701/42/M/J/18 Q8d

(d) A sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII). There are three different carbon-containing products of this reaction.

One of these three products, **X**, is shown.



X

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **X**.

..... [1]

(ii) For the carbon-13 NMR spectrum of **X**, state the expected chemical shift ranges (δ) of the peaks predicted in **(i)** and the number of peaks in each range.

.....

.....

.....

..... [3]

(iii) Predict the number of peaks this compound would show in its proton NMR spectrum.

..... [1]

(iv) For each of the peaks in the proton NMR spectrum you have identified in **(iii)** give the expected splitting pattern. Explain your reasoning.

.....

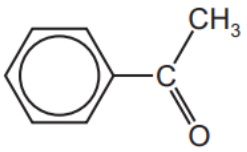
.....

..... [2]

12. 9701/41/O/N/19 Q4d

Phenylethanone is an important chemical with many uses.

phenylethanone



(iv) State the number of peaks in the C-13 NMR spectrum of **phenylethene**.

..... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

.....

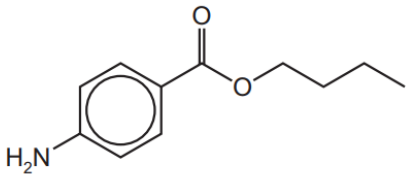
.....

..... [2]

13. 9701/41/O/N/19 Q9c

The structure of butamben is shown.

butamben

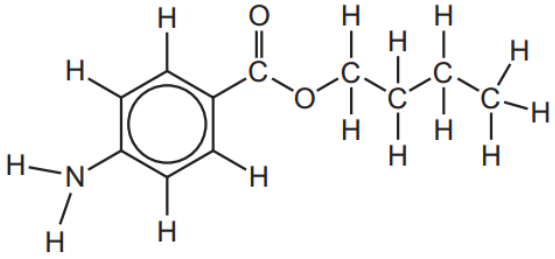


(c) The proton NMR spectrum of butamben in $CDCl_3$ contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

..... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in **(c)(i)**.



[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in $CDCl_3$.

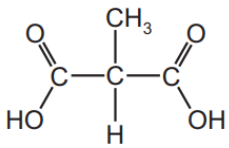
.....

..... [2]

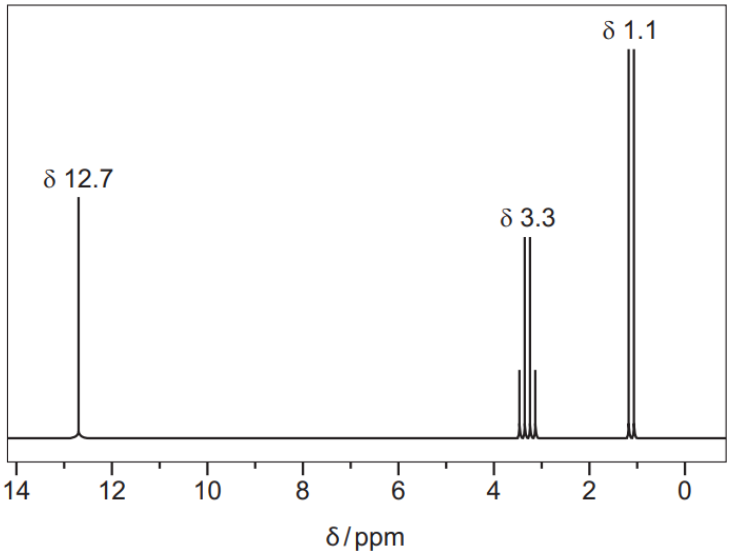
14. 9701/42/O/N/19 Q8g

(g) Methylpropanedioic acid is an isomer of butanedioic acid.

methylpropanedioic acid



The proton NMR spectrum of methylpropanedioic acid in CCl_4 is shown.



(i) Identify the protons in the methylpropanedioic acid molecule that are responsible for each area of the proton NMR spectrum.

δ 12.7 .....

δ 3.3 .....

δ 1.1 .....

[2]

(ii) Name the splitting pattern shown at δ 3.3 and explain how it arises.

.....

..... [1]

The carbon-13 NMR spectra of butanedioic acid, $HO_2CCH_2CH_2CO_2H$, and methylpropanedioic acid, $HO_2CCH(CH_3)CO_2H$ are different.

(iii) State the number of peaks

- in the carbon-13 NMR spectrum of butanedioic acid

.....

- in the carbon-13 NMR spectrum of methylpropanedioic acid.

.....

[1]

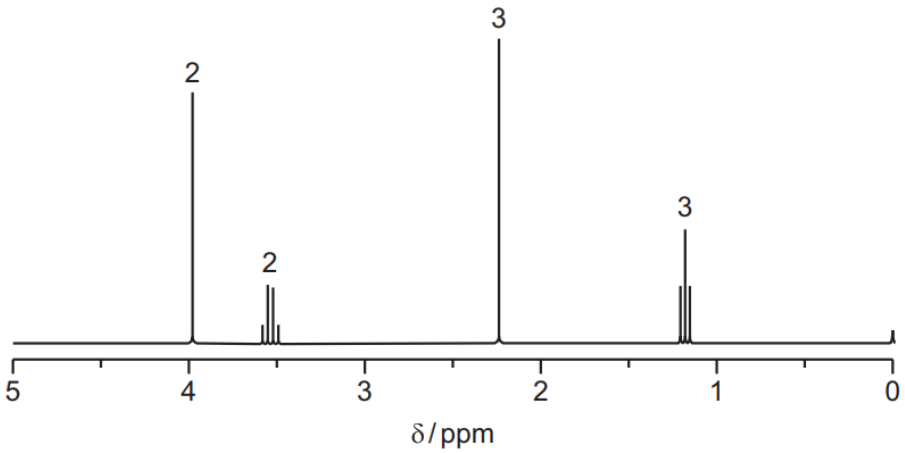
15. 9701/41/M/J/19 Q8b

(b) State the use of TMS and $CDCl_3$ in NMR spectroscopy.

- TMS .....
- $CDCl_3$ .....

[1]

(c) The proton NMR spectrum of compound **X**, $C_5H_{10}O_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at δ2.2,

.....

- deduce the part of the molecule that produces the peaks at δ1.2 and δ3.5,

.....

- deduce the part of the molecule that produces the peak at δ4.0.

.....

[3]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

.....

..... [1]

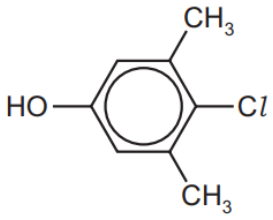
(ii) Suggest a structure for **V**.

[1]

16. 9701/42/M/J/19 Q8

Compound **R** is shown.

R



(a) State the systematic name of compound **R**.

..... [1]

(b) (i) **R** is dissolved in $CDCl_3$ and analysed using carbon-13 and proton NMR spectroscopy.

- Predict the number of peaks that are seen in the carbon-13 NMR spectrum of **R**.

.....

- Predict the number of peaks that are seen in the proton NMR spectrum of **R**.

.....

[2]

(ii) A separate sample of **R** is dissolved in D_2O. The proton NMR spectrum of this solution shows **one less** peak than is obtained in $CDCl_3$.

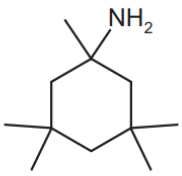
Explain why.

.....

..... [1]

17. 9701/42/F/M/19 Q6c

(c) Neramexane is another drug.



neramexane

(i) Suggest the number of peaks in the carbon-13 NMR spectrum of neramexane.

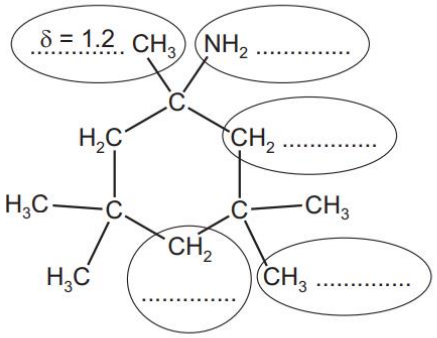
..... [1]

The proton (^{1}H) NMR spectrum of neramexane in $CDCl_3$ shows five peaks with the following chemical shifts (δ).

δ/ppm	number of protons responsible	splitting pattern (singlet, doublet, triplet, quartet or multiplet)
0.9		singlet
1.2	3	
1.4	2	
1.7	4	
2.2		broad singlet

(ii) Complete the table. [4]

(iii) Use the *Data Booklet* and the table in **(c)(ii)** to complete the assignment of the correct δ values to each of the circled hydrogen atoms on the structure of neramexane.



[2]

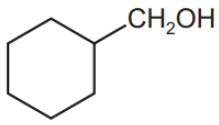
(iv) One of the peaks in the proton (^{1}H) NMR spectrum disappears when the sample is shaken with D_2O.

Identify the peak and explain why it disappears.

.....

..... [1]

18. 9701/41/O/N/20 Q8b(iv)



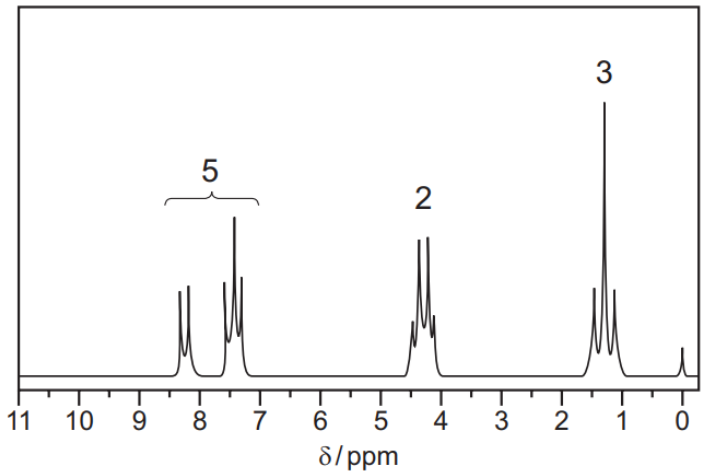
cyclohexylmethanol

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

..... [1]

19. 9701/41/O/N/20 Q9

The proton NMR spectrum of compound **E** in the solvent $CDCl_3$ is shown. The molecular formula of compound **E** is $C_9H_{10}O_2$.



(a) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

..... [1]

(b) Explain why TMS is added to give the small peak at chemical shift $\delta = 0$.

..... [1]

(c) Compound **E** is hydrolysed by hot NaOH(aq), giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq).

..... [1]

(d) (i) Describe and explain the splitting patterns of the peaks at $\delta = 1.4$ and $\delta = 4.3$.

splitting pattern at $\delta = 1.4$ .....

reason for splitting pattern at $\delta = 1.4$ .....

splitting pattern at $\delta = 4.3$ .....

reason for splitting pattern at $\delta = 4.3$ .....

[2]

(ii) Each molecule of compound **E** contains five protons which give rise to the peaks between $\delta = 7.0$ and $\delta = 8.5$.

Identify the functional group in compound **E** which contains these protons.

..... [1]

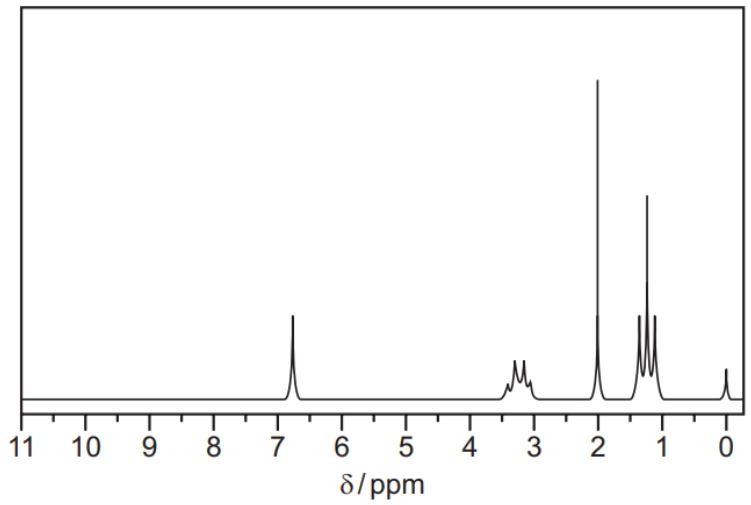
(iii) Give the structural formula of compound **E**.

[1]

20. 9701/42/O/N/20 Q6d

(d) Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.

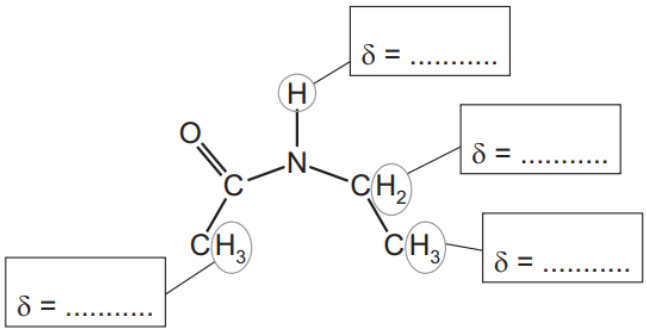
The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(i) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

..... [1]

(ii) Complete the diagram with the chemical shifts, δ, of the protons labelled in the $CH_3CONHC_2H_5$ molecule.



[2]

(iii) State and explain how the proton NMR spectrum of the amide $CH_3CONHC_2H_5$ differs when dissolved in D_2O rather than $CDCl_3$.

.....

.....

..... [2]

(f) The amide undergoes the following reaction to produce diethylamine.

$$CH_3CONHC_2H_5 \xrightarrow{\text{reagent } \mathbf{B}} \underset{\text{diethylamine}}{C_2H_5NHC_2H_5}$$

(i) Identify reagent **B**.

..... [1]

(ii) State the number of different absorptions in the carbon-13 NMR spectrum of diethylamine.

..... [1]

21. 9701/41/M/J/20 Q6c

(c) (i) There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

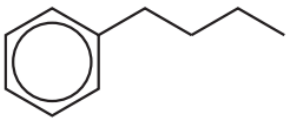
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.
In each reaction an organic compound with formula $C_{10}H_{14}$ is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

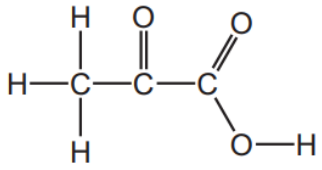
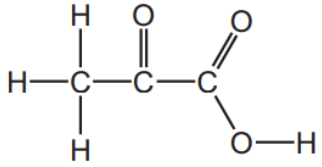
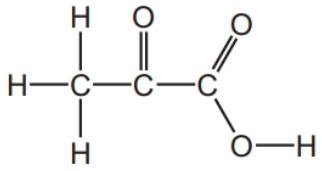
[4]

22. 9701/41/M/J/20 Q6d

(d) A sample of pyruvic acid, CH_3COCO_2H, is analysed by carbon-13 NMR spectroscopy. Three peaks are observed.

Complete the table by:
- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

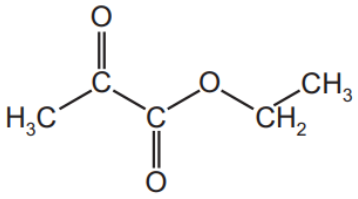
Complete the table by:
- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

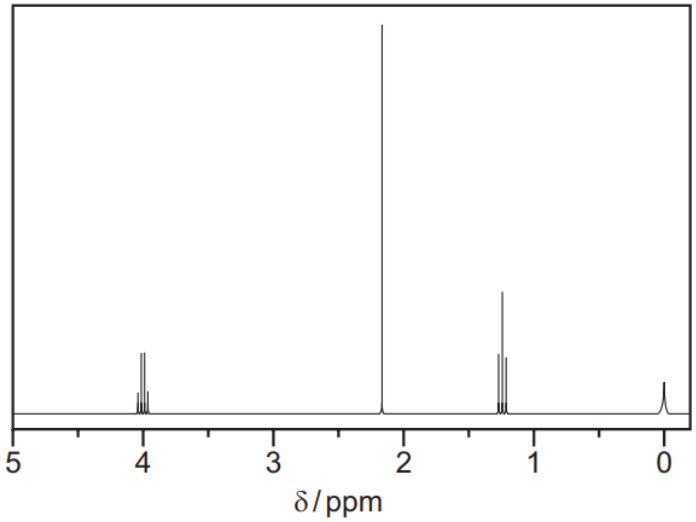
[2]

(e) An ester of pyruvic acid, **F**, is dissolved in $CDCl_3$ and analysed by proton NMR spectroscopy.

F



The proton NMR spectrum of **F** is shown.



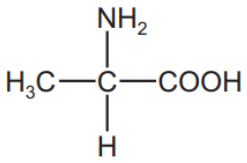
Use the proton NMR spectrum of **F** to complete the table.

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3			
2.2			
4.0			

[3]

(f) Deuterium oxide, D_2O, where D is ^2H, can be used as a solvent in proton NMR spectroscopy.
The proton NMR spectrum of alanine in $CDCl_3$ has 4 peaks.
The proton NMR spectrum of alanine in D_2O has 2 peaks.

alanine



On the diagram of alanine, circle the protons that show peaks in **both** NMR spectra.
Explain your answer.

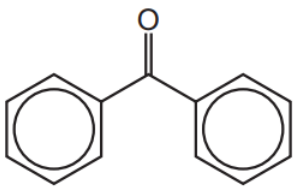
.....

.....

..... [2]

23. 9701/42/M/J/20 Q5e

benzophenone



(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks ..... [1]

(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

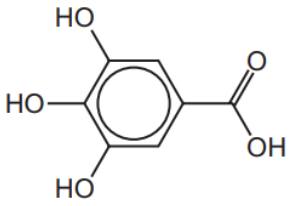
environment of carbon atom	chemical shift range (δ)

[2]

24. 9701/42/F/M/20 Q5d

(d) (i) State the number of peaks that would be observed in the ^{13}C NMR spectrum of gallic acid.

gallic acid



..... [1]

(ii) The proton NMR spectrum of gallic acid dissolved in D_2O is recorded.

- Predict the number of peaks observed and any expected splitting pattern.
- State the expected chemical shift range (δ) of each peak predicted.

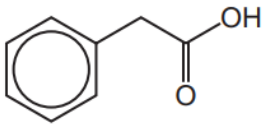
.....

.....

..... [2]

25. 9701/41/O/N/21 Q7a

The structure of phenylethanoic acid is shown.

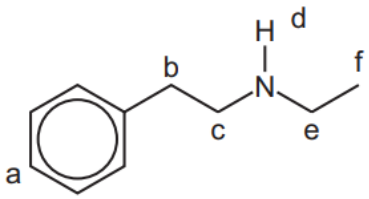


(a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

26. 9701/41/O/N/21 Q9e

(e) The proton (^{1}H) NMR spectrum of compound **T** shows hydrogen atoms in different environments. Six of these environments are shown on the structure using letters a, b, c, d, e and f.



Use the letters a, b, c, d, e and f to answer the questions that follow. The questions relate to the proton (^{1}H) NMR spectrum of **T**.

Proton d does not cause splitting of the peaks for protons c or e under the conditions used.

Each answer may be one, or more than one, of the letters a, b, c, d, e and f.

(i) Identify the proton or protons with a chemical shift (δ) in the range 6.0 to 9.0.

..... [1]

(ii) Identify the proton or protons whose peak will disappear if D_2O is added.

..... [1]

(iii) Identify the proton or protons whose peak is a triplet.

..... [1]

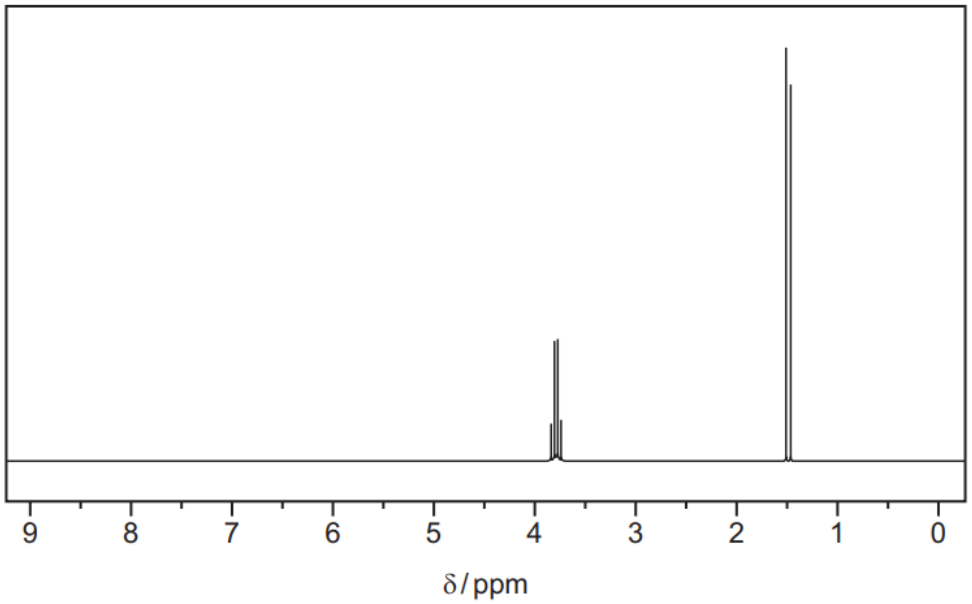
(iv) Identify the proton or protons with the lowest chemical shift (δ).

..... [1]

27. 9701/42/O/N/21 Q8b

Alanine, $H_2NCH(CH_3)CO_2H$, and glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, are two naturally occurring amino acids.

(b) The proton (^1H) NMR spectrum of **either** alanine in D_2O or glutamic acid in D_2O is shown.



State whether this is the spectrum of alanine in D_2O or the spectrum of glutamic acid in D_2O. Explain your answer by reference to the number of peaks and splitting patterns.

.....

.....

.....

..... [3]

28. 9701/41/M/J/21 Q6b

(ii) Each compound, HCO_2H, HO_2CCO_2H and $HO_2CCH_2CH_2CO_2H$, is dissolved seperately in $CDCl_3$. Proton (^1H) NMR and carbon-13 (^{13}C) NMR spectra are then obtained.

Complete the table.

compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR
HCO_2H		
HO_2CCO_2H		
$HO_2CCH_2CH_2CO_2H$		

[2]

(iii) The proton NMR spectrum of HCO_2H in D_2O is obtained.

Describe and explain the difference observed between this spectrum and the proton NMR spectrum of HCO_2H in **(b)(ii)**.

.....

.....

..... [1]

29. 9701/42/M/J/21 Q6

(a) There are four possible structural isomers of C_8H_{10} that contain a benzene ring.

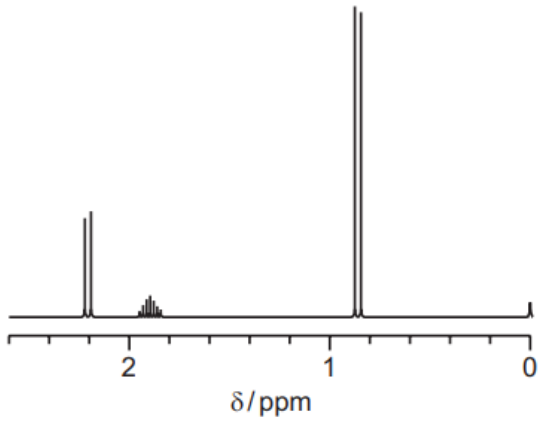
Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

isomer 1 three peaks in ^{13}C NMR	isomer 2 four peaks in ^{13}C NMR
isomer 3 five peaks in ^{13}C NMR	isomer 4 six peaks in ^{13}C NMR

[4]

30. 9701/42/M/J/21 Q8c

(c) Compound **Y**, $C_5H_{10}O_2$, reacts with $Na_2CO_3(aq)$ to evolve bubbles of gas. The proton (^1H) NMR spectrum of compound **Y** in D_2O is shown.



(i) Use this information to suggest a structure for **Y**.

[1]

(ii) Use the *Data Booklet*, the proton (^1H) NMR spectrum and your answer to **(c)(i)** to complete the table.

chemical shift (δ)	environment of proton	splitting pattern	number of ^1H atoms responsible for the peak
0.95			
1.90			
2.20			

[3]

31. 9701/41/O/N/22 Q9b

(b) Complete Table 9.1 to give the number of peaks in the carbon-13 NMR spectrum of each of the five isomers of $C_5H_{10}O_2$ that has an ester group.

Table 9.1

structural formula	number of peaks
$CH_3CH_2CH_2CO_2CH_3$	
$CH_3CH_2CO_2CH_2CH_3$	
$CH_3CO_2CH_2CH_2CH_3$	
$(CH_3)_2CHCO_2CH_3$	
$CH_3CO_2CH(CH_3)_2$	

[2]

(c) State the number of peaks that would be seen in the proton (^1H) NMR spectrum of methyl butanoate, $CH_3CH_2CH_2CO_2CH_3$. Name all the splitting patterns seen in this spectrum.

number of peaks .....

splitting patterns .....

[2]

(d) **D** and **E** are both esters with the molecular formula $C_5H_{10}O_2$. Their proton (^1H) NMR spectra are shown in Fig. 9.2 and Fig. 9.3.

D

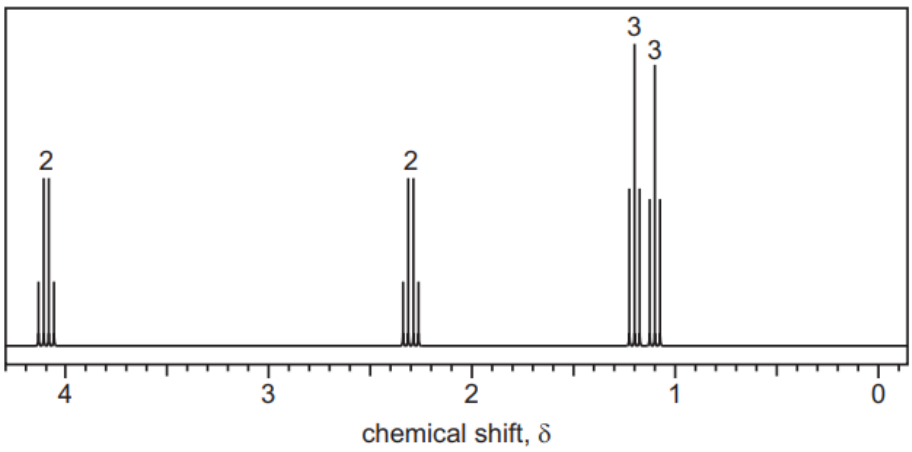
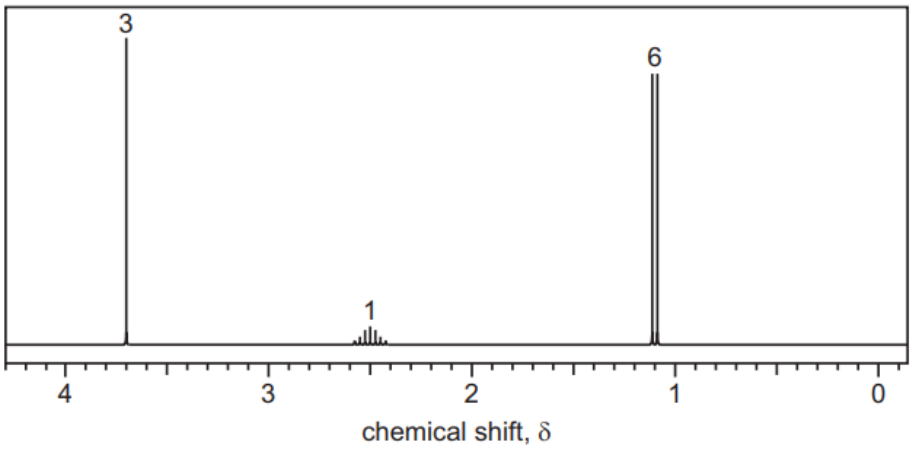


Fig. 9.2

E



environment of proton	example	typical chemical shift range, δ/ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	=CHR	4.5–6.0

(i) Deduce the structures of the two esters **D** and **E** and draw their displayed formulae in the boxes below.

D $C_5H_{10}O_2$	**E** $C_5H_{10}O_2$

[2]

(ii) The spectrum of **D** includes a quartet at δ 4.1.

Identify the protons responsible for this quartet on your structure in **(i)** by labelling these protons with the letter **F**.

Explain why this peak is split into a quartet.

.....

.....

[1]

(iii) The spectrum of **E** has a doublet at δ 1.1.

Identify the protons responsible for this doublet on your structure in **(i)** by labelling these protons with the letter **G**.

Explain why this peak has a chemical shift of 1.1.

.....

.....

[1]

32. 9701/42/O/N/22 Q8

When answering this question it should be assumed that together all the hydrogen atoms in a benzene ring result in a single unsplit peak at δ = 7.2 in a proton (^{1}H) NMR spectrum.
The structures of five isomeric ketones, **P**, **Q**, **R**, **S** and **T** are given.

P $C_6H_5COCH(CH_3)_2$

Q $C_6H_5COCH_2CH_2CH_3$

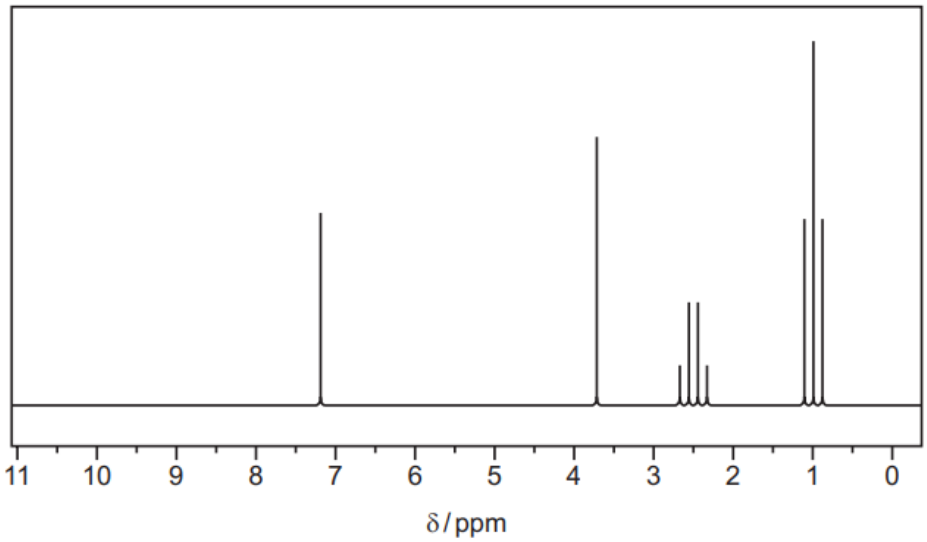
R $C_6H_5CH_2COCH_2CH_3$

S $C_6H_5CH_2CH_2COCH_3$

T $C_6H_5CH(CH_3)COCH_3$

(a) Identify all the chiral carbon atoms on the structures above. Label each chiral carbon atom with an asterisk (*). [1]

(b) The proton (^{1}H) NMR spectrum of one of the five isomers, **P**, **Q**, **R**, **S** or **T**, is shown in Fig. 8.1.



(i) Identify which of the compounds **P**, **Q**, **R**, **S** or **T** gives this spectrum.
Draw the displayed formula of the compound you have identified. Identify the protons responsible for the peaks at δ = 3.7, δ = 2.5 and δ = 1.0 on the structure you have drawn.

[2]

(ii) Name the splitting pattern of the peak at δ = 3.7. Explain why it has this splitting pattern.

.....

..... [1]

(c) Choose from the letters **P**, **Q**, **R**, **S** and **T** to identify:

(i) the **two** compounds that each have a doublet peak in the proton (^{1}H) NMR spectrum

..... [1]

(ii) the compound with only three peaks in its proton (^{1}H) NMR spectrum.

..... [1]

(d) Suggest a suitable solvent that should be used for obtaining the spectrum shown in Fig. 8.1.

..... [1]

(e) The proton (^{1}H) NMR spectrum of compound **T** is compared in the presence of D_2O and in the absence of D_2O.

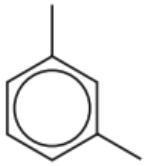
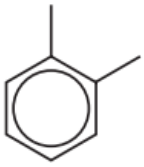
Describe any difference between the two spectra. Explain your answer.

.....

..... [1]

(f) Complete Table 8.1 below to give the number of peaks in the carbon-13 NMR spectrum of each compound.

Table 8.1

compound	number of peaks	compound	number of peaks
			
			

[2]

33. 9701/41/M/J/22 Q6b

(b) Asparagine is an amino acid that contains a chiral carbon atom and displays stereoisomerism.

Separate samples of asparagine are dissolved in $CDCl_3$ and analysed using carbon-13 and proton (^1H) NMR spectroscopy.

asparagine

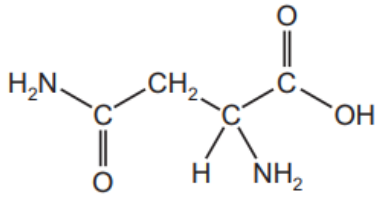


Fig. 6.1

Predict the number of peaks seen in the carbon-13 and proton (^1H) NMR spectra of asparagine.

	carbon-13 NMR	proton (^1H) NMR
number of peaks		

[1]

34. 9701/42/M/J/22 Q7

(a) State the uses of TMS and D_2O in NMR spectroscopy.

TMS .....

D_2O .....

[1]

(b) The three isomeric ketones with molecular formula $C_5H_{10}O$ are:

- pentan-2-one
- pentan-3-one
- 3-methylbutanone.

(i) Complete Table 7.1 to show the number of peaks observed in the proton (^1H) NMR spectrum and in the carbon-13 NMR spectrum for each compound listed.

Table 7.1

ketone	number of peaks observed in the proton (^1H) NMR spectrum	number of peaks observed in the carbon-13 NMR spectrum
pentan-2-one		
pentan-3-one		
3-methylbutanone		

[2]

(ii) State **all** the ketones with molecular formula $C_5H_{10}O$ that have:

a doublet in their proton (^1H) NMR spectrum

.....

a singlet in their proton (^1H) NMR spectrum.

.....

[2]