Q9.

Isomers **X** and **Y** have the molecular formula C_5H_8O

Isomer **X**

Isomer **Y**

(a) Give the IUPAC name for isomer **X**.

_____

(1)

(b) Explain how and why isomers **X** and **Y** can be distinguished by comparing **each** of their

- boiling points
- ^{13}C NMR spectra
- infrared spectra.

Use data from Tables **A** and **C** in the Data Booklet in your answer.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

(6)

(Total 7 marks)

Q10.

Some compounds with different molecular formulas have the same relative molecular mass to the nearest whole number.

(a) A dicarboxylic acid has a relative molecular mass of 118, to the nearest whole number.

Deduce the molecular formula of the acid.

Molecular formula _____

(3)

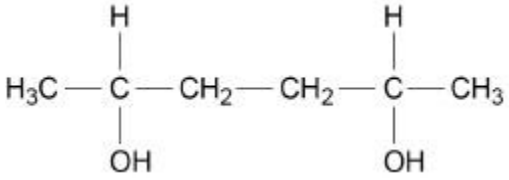
(b) A student dissolved some of the dicarboxylic acid from part (a) in water and made up the solution to 250 cm^3 in a volumetric flask.
In a titration, a 25.0 cm^3 sample of the acid solution needed 21.60 cm^3 of 0.109 mol dm^{-3} sodium hydroxide solution for neutralisation.

Calculate the mass, in g, of the dicarboxylic acid used.
Give your answer to the appropriate number of significant figures.

Mass _____ g

(4)

(c) Compounds with molecular formula $C_6H_{14}O_2$ also have a relative molecular mass of 118 to the nearest whole number. These include the diol shown.



Deduce the number of peaks in the ^1H NMR spectrum of this diol.

_____

(1)

(d) Draw the structure of a different diol also with molecular formula $C_6H_{14}O_2$ that has a ^1H NMR spectrum that consists of two singlet peaks.

(1)

(e) The dicarboxylic acid in part **(a)** and the isomers of $C_6H_{14}O_2$ in parts **(c)** and **(d)** all have a relative molecular mass of 118

State why the dicarboxylic acid can be distinguished from the two diols by high resolution mass spectrometry using electrospray ionisation.

_____

_____

_____

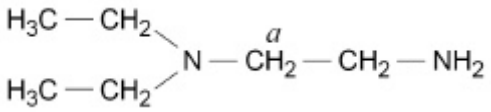
(1)

(Total 10 marks)

Q11.

There are several isomers with the molecular formula $C_6H_{16}N_2$

(a) One isomer is shown.



Give the number of peaks in the ^{13}C NMR spectrum of this isomer.

State and explain the splitting pattern of the peak for the hydrogens labelled *a* in its ^{1}H NMR spectrum.

Number of ^{13}C peaks _____

Splitting pattern _____

Explanation _____

_____

_____

_____

(3)

(b) Draw the structure of the isomer of $C_6H_{16}N_2$ used to make nylon 6,6

(1)

(c) Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **primary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

(1)

(d) Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **tertiary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

(1)

(Total 6 marks)

Q12.

How many peaks are there in the ^{13}C NMR spectrum of 1,4-dimethylbenzene?

A 8 ⬭

B 4 ⬭

C 3 ⬭

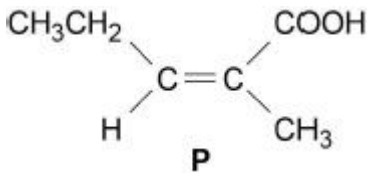
D 2 ⬭

(Total 1 mark)

Q13.

This question is about six isomers of $C_6H_{10}O_2$

(a) Give the full IUPAC name of isomer **P**.



P

_____

(1)

(b) A sample of P was mixed with an excess of oxygen and the mixture ignited. After cooling to the original temperature, the total volume of gas remaining was 335 cm^3

When this gas mixture was passed through aqueous sodium hydroxide, the carbon dioxide reacted and the volume of gas decreased to 155 cm^3

Both gas volumes were measured at 25 °C and 105 kPa

Write an equation for the combustion of **P** in an excess of oxygen and calculate the mass, in mg, of **P** used.

The gas constant R = 8.31 $J\,K^{-1}\,mol^{-1}$

Mass of **P** used _____ mg

(5)

(c) Isomer Q ($C_6H_{10}O_2$) is a cyclic compound. The infrared spectrum of **Q** is shown in **Figure 1** and the ^{13}C NMR spectrum of **Q** is shown in **Figure 2**.

Figure 1

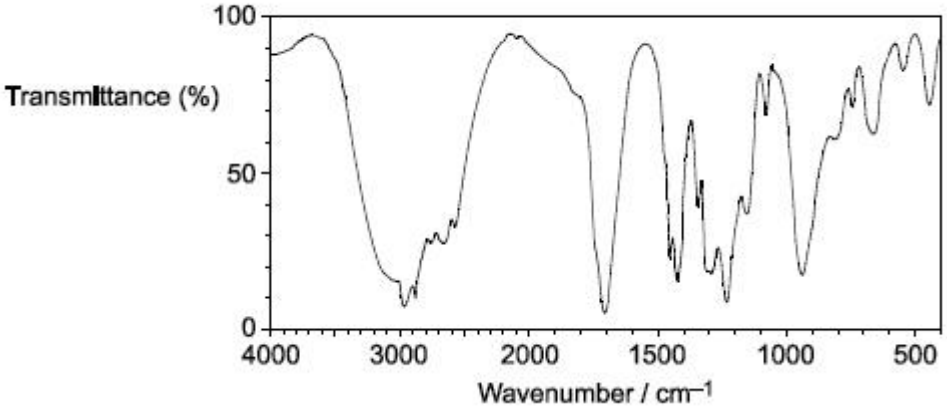
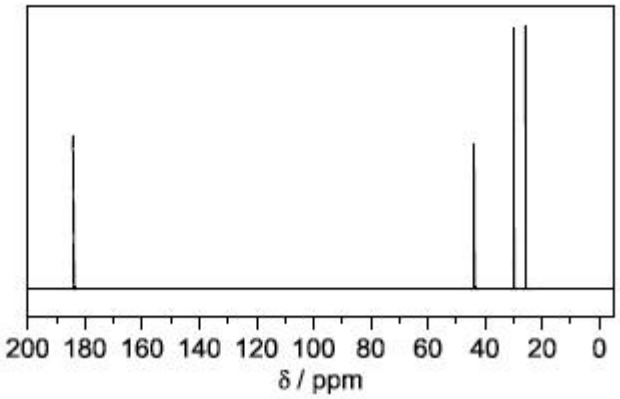


Figure 2



Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.

In your answer, state one piece of evidence you have used from each spectrum.

Structure of **Q**.

Evidence from **Figure 1**

_____

_____

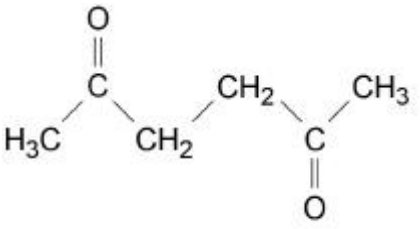
Evidence from **Figure 2**

_____

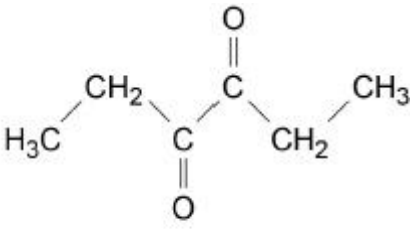
_____

(3)

(d) Isomers **R** and **S** are shown.



R



S

Although the ^{13}C spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using Table **C** from the Data Booklet.

Give the number of peaks for each isomer.

Justification

_____

_____

_____

_____

Number of peaks _____

(3)

(e) Although the ^{1}H spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using the splitting patterns of the peaks.

Give the number of peaks for each isomer.

Justification

_____

_____

_____

_____

Number of peaks _____

(3)

(f) The action of heat on 5-hydroxyhexanoic acid can lead to two different products.

On gentle heating, 5-hydroxyhexanoic acid loses water to form a cyclic compound, **T** ($C_6H_{10}O_2$).

Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

Draw the structure of **T**.

Draw the repeating unit of the polyester and name the type of polymerisation.

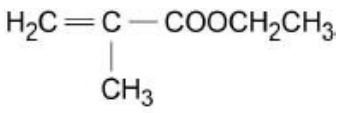
Structure of **T**

Repeating unit of polyester

Type of polymerisation _____

(3)

(g) Isomer **U** is shown.



U

The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in part (f) both contain ester groups that can be hydrolysed.

Draw the repeating unit of the polymer formed by **U**.

Justify the statement that, although both polymer structures contain ester groups, the polymer formed by **U** is not biodegradable.

Repeating unit of polymer formed by **U**.

Justification

_____

_____

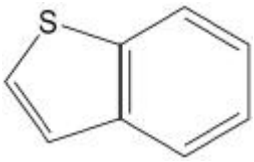
_____

(3)

(Total 21 marks)

Q14.

How many peaks does this compound have in its ^{13}C spectrum?



A 5 ⬭

B 6 ⬭

C 7 ⬭

D 8 ⬭

(Total 1 mark)

Q15.

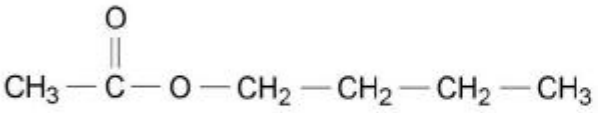
^{1}H NMR, ^{13}C NMR and infrared spectroscopy are used in organic chemistry to distinguish between compounds and to identify them.

(a) Give the skeletal formula of the compound that is used as the standard when recording a ^{13}C NMR spectrum.

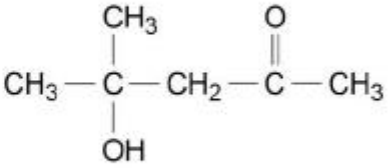
(1)

(b) Four isomers of $C_6H_{12}O_2$, **P**, **Q**, **R** and **S**, shown in **Figure 1**, were analysed by ^{13}C NMR spectrometry.

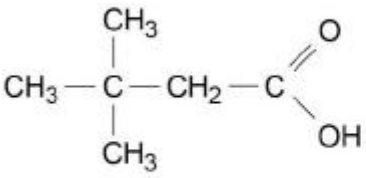
Figure 1



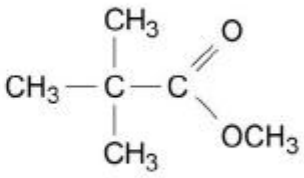
P



Q



R



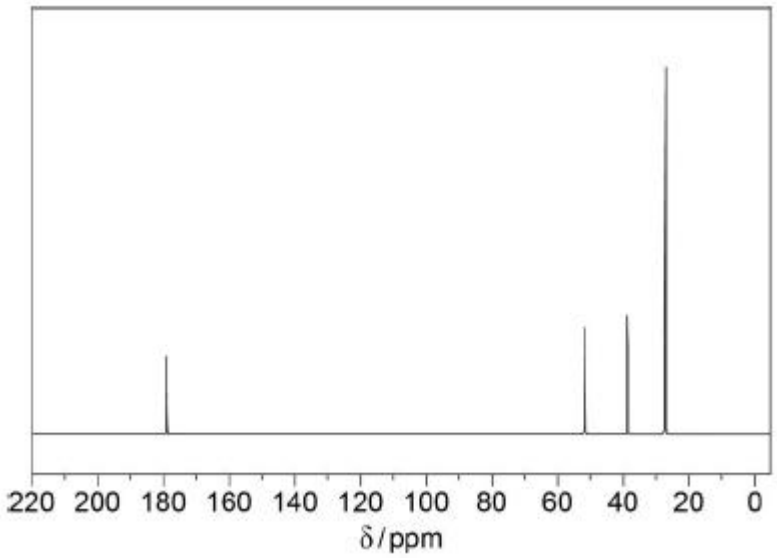
S

The ^{13}C NMR spectra of three of these isomers are shown in **Figure 2**.

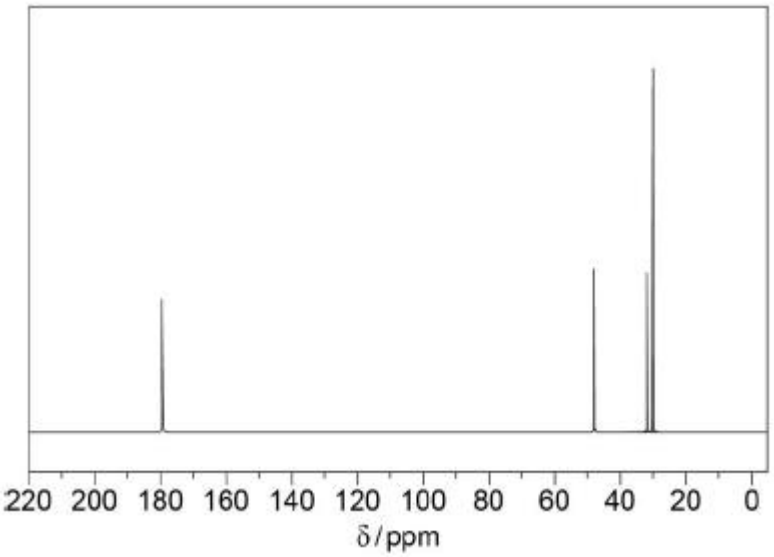
Use **Table C** in the Data Booklet to help you to identify which isomer produces each spectrum.

Write the letter of each isomer opposite its spectrum in **Figure 2**.

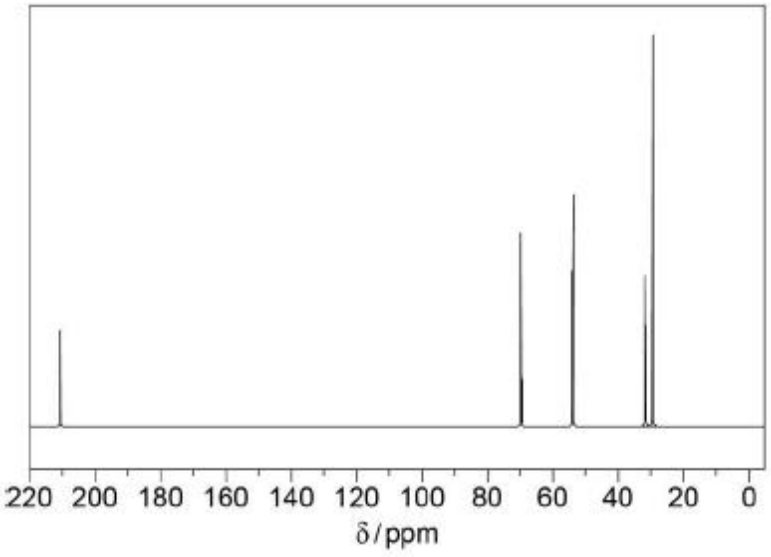
Figure 2


220 200 180 160 140 120 100 80 60 40 20 0
δ/ppm

☐


220 200 180 160 140 120 100 80 60 40 20 0
δ/ppm

☐

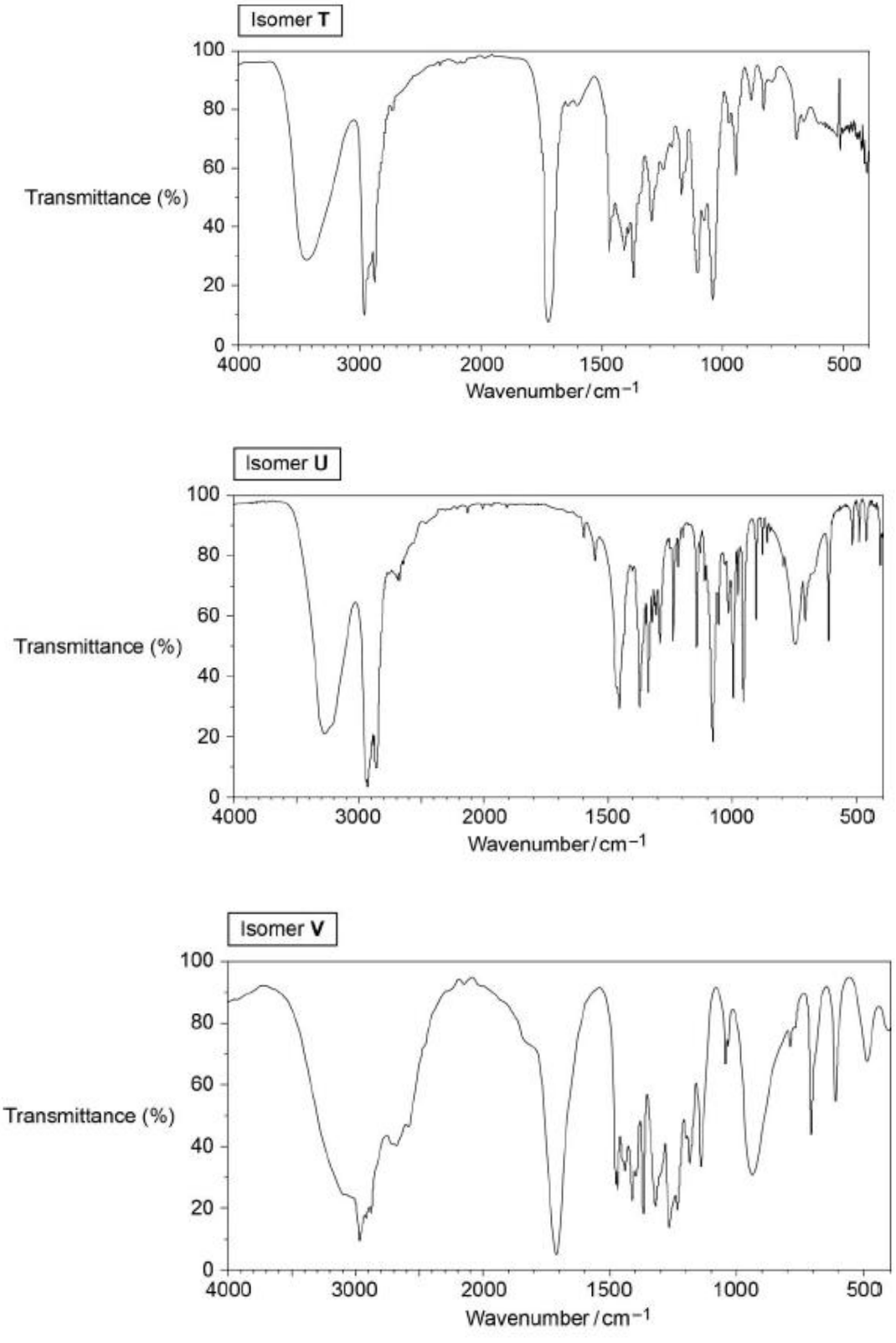

220 200 180 160 140 120 100 80 60 40 20 0
δ/ppm

☐

(3)

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

Figure 3



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

Explain your answer.

(6)

(d) The integration values for the peaks in the ^{1}H NMR spectrum of **X**, a different isomer of $C_6H_{12}O_2$, are given in the table below.

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

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

(1)

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

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

Explain the splitting patterns of these peaks.

Signal at δ= 3.5 _____

_____

_____

_____

Signal at δ= 2.2 _____

_____

_____

_____

(4)

(f) Deduce the structure of compound **X**, $C_6H_{12}O_2$

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

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

_____

_____

_____

_____

(2)

(Total 17 marks)

Mark Scheme

Q9.

(a) Cyclopentanone

Allow cyclopentan -1-one but no other numbers

Ignore spaces, commas and hyphens

1

(b)

This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.	
Level 3 **5-6 marks**	**All stages are covered and each stage is generally correct and virtually complete.** Answer is well structured with no repetition or irrelevant points. Accurate and clear expression of ideas with no errors in use of technical terms.
Level 2 **3-4 marks**	**All stages are covered but stage(s) may be incomplete or may contain inaccuracies OR two stages are covered and are generally correct and virtually complete.** Answer shows some attempt at structure Ideas are expressed with reasonable clarity with, perhaps, some repetition or some irrelevant points. Some minor errors in use of technical terms
Level 1 **1-2 marks**	**Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.** Answer includes isolated statements and these are presented in a logical order. Answer may contain valid points which are not clearly linked. Errors in the use of technical terms.
0 marks	Insufficient correct chemistry to gain a mark.

Indicative Chemistry content

Stage 1: boiling points
1a) **Y** has a higher bp
1b) **Y** has H-bonds between molecules and **X** has dip-dip imf
1c) More energy required to overcome H-bonds

Mention of covalent bond breaking loses 1c

Stage 2: ^{13}C NMR
2a) Both have 3 peaks/absorptions in their ^{13}C NMR
2b) **X** has peaks at 20-50 **OR** 190-220ppm
2c) **Y** has peaks at 50-90 **OR** 90-150ppm

(Ignore peaks at 5-40ppm - present in both)

Stage 3: ir
3a) **X** has a peak (for C=O) at 1680-1750 cm^{-1}
3b) **Y** has peak (for O−H) at 3230-3550 cm^{-1}
OR peak (for C=C) at 1620-1680 cm^{-1}
3c) They would have different fingerprint regions (below 1500 cm^{-1})

6

[7]

Q10.

(a) $(COOH)_2 = C_2H_2O_4 = 90$

M1

118 - 90 = 28 OR C_2H_4

M2

$C_4H_6O_4$

M3

Must be molecular formula
*Structural formula can score **M1** & **M2***

(b) Amount NaOH = $(21.60 \times 10^{-3}) \times 0.109$

$= 2.3544 \times 10^{-3}$ mol
***M1** for answer (to 3sfs min)*

M1

Amount H_2A in 25 cm^{-3} = 1.177×10^{-3} mol
M2** = 0.5 × **M1

M2

Amount H_2A in 250 cm^{-3} = 1.177×10^{-2} mol
***M3** = **M2** × 10*

M3

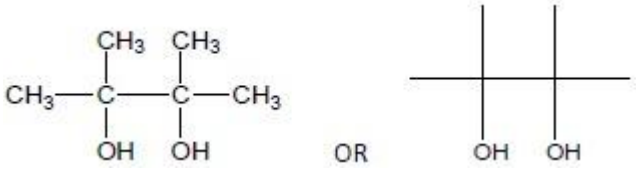
Mass = 1.39 g (Must be 3sf)
***M4** = answer to (**M3** × 118) and must be 3sf*

M4

(c) 4 or four

1

(d)



1

(e) The precise (relative molecular) masses are <u>different</u> or wtte
Allow M_r are different to 2 or more or several dp
Ignore different molecular formula

Ignore accuracy
Penalise fragments

1

[10]

Q11.

(a) 4 peaks

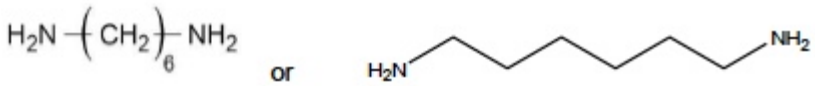
1

Triplet

1

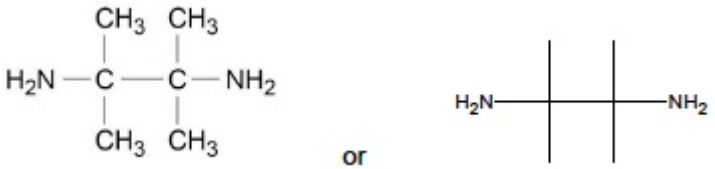
Two H on adjacent C
M3 dependent on correct M2

1

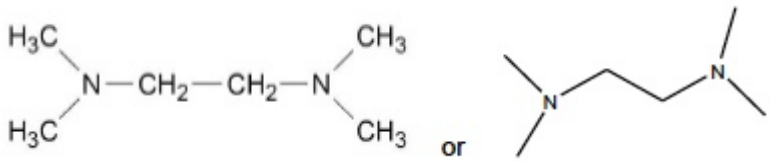
(b) 

Not –C_6H_{12}–

1

(c) 

1

(d) 

Not –C_2H_4–

1

[6]

Q12.

C

[1]

Q13.

(a) Z-2-methylpent-2-en (-1-) oic acid
Ignore missing hyphens or extra commas, spaces, hyphens

1

(b) $C_6H_{10}O_2 + 7½\ O_2 \longrightarrow 6CO_2 + 5H_2O$
Allow multiple

M1

Volume of CO_2 formed = 180 cm^3

If incorrect volume:155 gives 125mg / 335 gives 270mg could score M1,M3,M4 – max 3

If incorrect volume from AE then penalise M2 and mark on

(Final answer is 0.806 × their volume)

M2

Mol carbon dioxide = pV/RT = $\frac{105000 \times (180 \times 10^{-6})}{8.31 \times 298}$

$= 7.632 \times 10^{-3}$

If unit error in p, V or T lose M3 and M5

If incorrect rearrangement lose M3 and M5

If both errors seen then no further marks

M3

Mol **P**, $C_6H_{10}O_2$ used $= 7.632 \times 10^{-3} / 6 = 1.272 \times 10^{-3}$

M3 divided by 6 If wrong no further marks

M4

Mass **P** used $= 1.272 \times 10^{-3} \times 114(.0)$ g

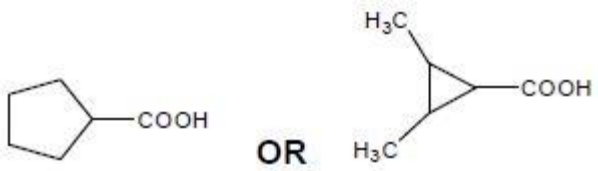
$= 145$ mg

Mark for answer (allow ans to 2 sf)

Check chemical equation before awarding final mark

M5

(c)



Mark independently

Apply the list principle

M1

Fig 4: <u>IR OH (acid)</u> peak (2500-3000cm^{-1}) present

Ignore C=O signal at 1750 cm^{-1}

M2

Fig 5: ^{13}C NMR 4 peaks so 4 (non-equivalent) environments
Or Peak at 160-185 (show C=O) in (esters or) acids
Or Peak at 40-50 (show R-CO-<u>C</u>H) presence of carbonyl

M3

Both M2 & M3 can be awarded on the spectra

Allow correct Fig 4 answers in Fig 5 and converse

(d) **R** has 4 C next to C=O **S** has 2 C next to C=O

M1 for structural point

M1

in range δ = 20-50
R has two peaks and **S** only one peak in this range
Or **R** has more peaks (allowed if no numbers given)

M2 for resulting peak in spectra

M2

OR

S has a -C(H_2)-C(H_3) **R** does not

M1

S has one peak in range δ = 5-40 **R** does not
/ lowest peak for **S** is lower than lowest for **R**

M2

(Both have) three peaks

M3

(e) **R** Both singlets

M1

S has triplet and a quartet

M2

OR

R CH_3/peak at 2.1-2.6 is a singlet

M1

S CH_3/peak at 0.7-1.2 is a triplet

M2

OR

R CH_2/peak at 2.1-2.6 is a singlet

M1

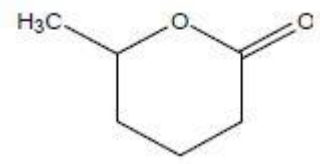
S CH_2/peak at 2.1-2.6 is a quartet

M2

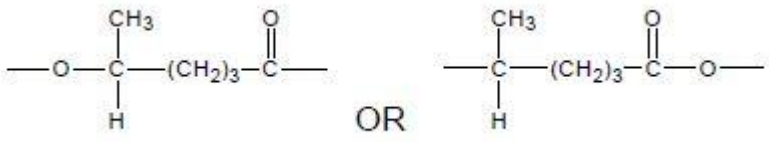
(Both have) two peaks

M3

(f)



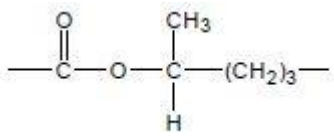
1



Must have trailing bonds

Ignore brackets and n

1



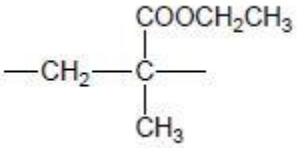
OR

condensation

Ignore esterification

1

(g)



Must have trailing bonds

Ignore brackets and n

M1

Strong / non-polar C-C bonds (in the chain)

M2

cannot be attacked by nucleophiles / acids / cannot be hydrolysed.

M3

OR

Only polar ester group

M2

Can be attacked by nucleophiles / acids / can be hydrolysed

M3

M3 dependent on correct or close M2

Allow 1 mark for in (polar) ester link in side chain/not in main chain therefore polymer chain not broken

[21]

Q14.

D

[1]

Q15.

(a)

1×AO1

1

(b) **S**

1

R

1

Q

1

(c) (Isomer **T**)

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

1

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

Allow not a carboxylic acid.

1

(Isomer U)

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

1

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

Allow OH but not C=O.

1

(Isomer V)

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

carboxylic acid group / −COOH present.

1
1

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

Any order.

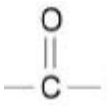
1

(e) (The quartet at δ=3.5 is for a CH_2 group) next to −**O**−**CH_2** **OR** shifted significantly downfield by electronegative O

1

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

1

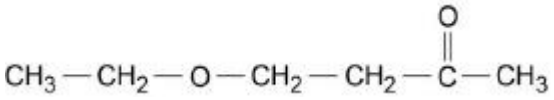
(singlet at δ=2.2 is for a CH_3 group) attached to  C**H_3** **OR** shifted downfield by electronegative C=O

1

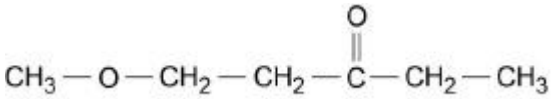
(is a singlet) because there are no adjacent protons / no coupling.

1

(f)



Allow 1 mark for:



2

[17]