PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 4: SPECTROSCOPY AND CHROMATOGRAPHY

SCORE	PERCENTAGE
/150	%

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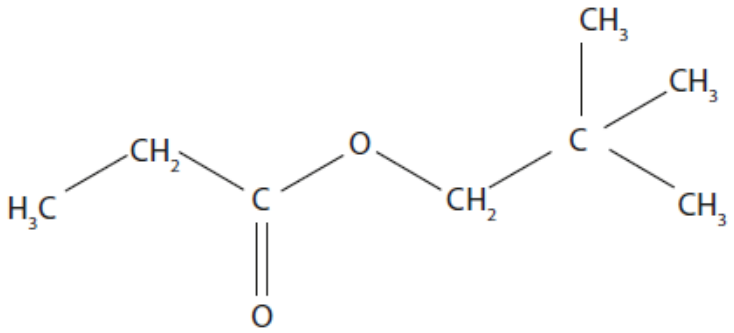
Q1.

This question is about an ester, **Y**, with the molecular formula $C_8H_{16}O_2$.

(a) **Y** contains 66.7 % carbon, 11.1 % hydrogen and 22.2 % oxygen by mass. Show that these data are consistent with its molecular formula.

(2)

(b) The structure of compound **Y** is



(i) Give the IUPAC name of **Y**.

(2)

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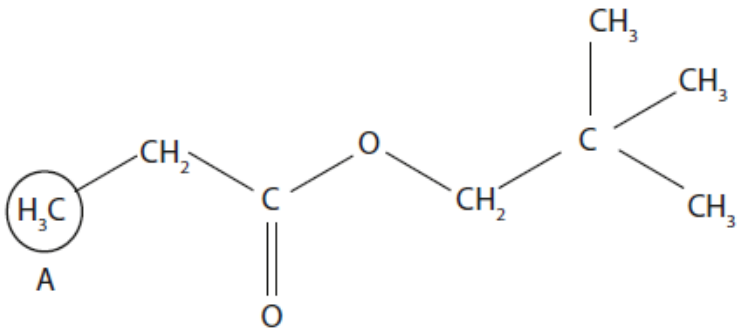
(ii) Draw the structures of two organic compounds that would react together to form **Y**.

(1)

(c) The high resolution proton NMR spectrum of compound **Y** was obtained.

(i) Label the three remaining hydrogen environments B, C and D on the structure.

(1)



(ii) Complete the table.

(3)

Hydrogen environment	Splitting pattern of peak	Relative peak area
A	triplet	3
B		
C		
D		

(Total for question = 9 marks)

Q2.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

This question is about chromatography.

(a) A spot caused by an amino acid has moved 42 mm from the baseline of a paper chromatogram.
The R_f value for the amino acid under these conditions is 0.62.

What is the distance moved by the solvent?

(1)

☐ **A** 680 mm

☐ **B** 68 mm

☐ **C** 42 mm

☐ **D** 26 mm

(b) In gas chromatography, GC, which of these would be the most suitable carrier gas?

(1)

☐ **A** argon

☐ **B** hydrogen

☐ **C** methane

☐

D oxygen

(Total for question = 2 marks)

Q3.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

A mixture of organic compounds was analysed using thin-layer chromatography.

The R_f value was 0.92 for one of the components in the mixture.

What can be deduced about the attractions between that component and the stationary and mobile phases?

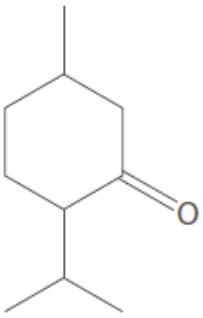
		Attraction between component and stationary phase	Attraction between component and mobile phase
☒	**A**	strong	strong
☒	**B**	strong	weak
☒	**C**	weak	weak
☒	**D**	weak	strong

(Total for question = 1 mark)

Q4.

This question is about carbonyl compounds.

(a) The skeletal formula of menthone is shown.



Give the molecular formula of menthone.

(1)

.....

(b) Ethanal, CH_3CHO , reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxypropanenitrile.

Draw the mechanism for this reaction.
Include curly arrows, and any relevant lone pairs and dipoles.

(4)

(c) A carbonyl compound, **F**, has the molecular formula $C_6H_{12}O$.

(i) **F** reacts with iodine in an alkaline solution to give a pale yellow precipitate.

Give the name or formula of the group in **F** identified by this test.

(1)

.....

(ii) Draw the **skeletal** formulae of the four possible structures of carbonyl compound **F**.

(2)

(iii) The carbon-13 (^{13}C) NMR spectrum of **F** has four peaks.

Identify **F** by drawing its **displayed** formula.
Justify your answer by labelling the carbon atoms or groups of carbon atoms responsible for the four peaks in the spectrum.

(2)

*(d) Explain, in terms of all the intermolecular forces involved, why butanal has a higher boiling temperature than pentane but a lower boiling temperature than propanoic acid.

Substance	Boiling temperature / °C
butanal	76
pentane	36
propanoic acid	141

(6)

(Total for question = 16 marks)

Q5.

This question is about carbonyl compounds.

(a) Three carbonyl compounds, **A**, **B** and **C**, are **straight-chain** structural isomers, with the formula $C_5H_{10}O$.

Only isomer **A** reacts with Tollens' reagent to give a silver mirror.
Only isomer **B** reacts with iodine in the presence of alkali to produce pale yellow crystals.

Draw the **displayed** structures of these three isomers.

(3)

A	
B	
C	

(b) Another carbonyl compound, propanal, reacts with HCN in the presence of KCN to form a racemic mixture of two optical isomers of $CH_3CH_2CH(OH)CN$.

(i) Give the IUPAC name for $CH_3CH_2CH(OH)CN$.

(1)

.....

(ii) Describe how you could distinguish between pure samples of the two optical isomers.

(1)

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(iii) Explain, with reference to the reaction mechanism, why this reaction produces a racemic mixture.

(2)

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(c) (i) Propanone, an isomer of propanal, also reacts with HCN in the presence of KCN.

Draw the **skeletal** formula of the product of this reaction.

(1)

(ii) State why the product formed in (c)(i) does **not** show optical isomerism.

(1)

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.....

(d) ^{13}C NMR spectroscopy provides information about the structures of propanal and propanone.

(i) Identify the chemical shift range and carbon environment of **one** peak you would expect to see in **both** spectra.

(1)

Chemical shift range	Carbon environment

(ii) State the number of peaks you would expect to see in each ^{13}C NMR spectrum.

(1)

Propanal .....

Propanone .....

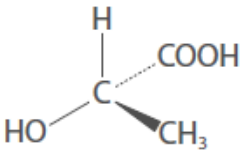
(Total for question = 11 marks)

Q6.

This question is about carboxylic acids and their derivatives.

(a) Lactic acid, $CH_3CH(OH)COOH$, is produced in muscles as a result of anaerobic respiration.

(i) The structure of lactic acid is



Give a reason why lactic acid shows optical isomerism.

(1)

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(ii) A laboratory sample of lactic acid does **not** rotate the plane of plane-polarised monochromatic light.

Give a reason for this observation.

(1)

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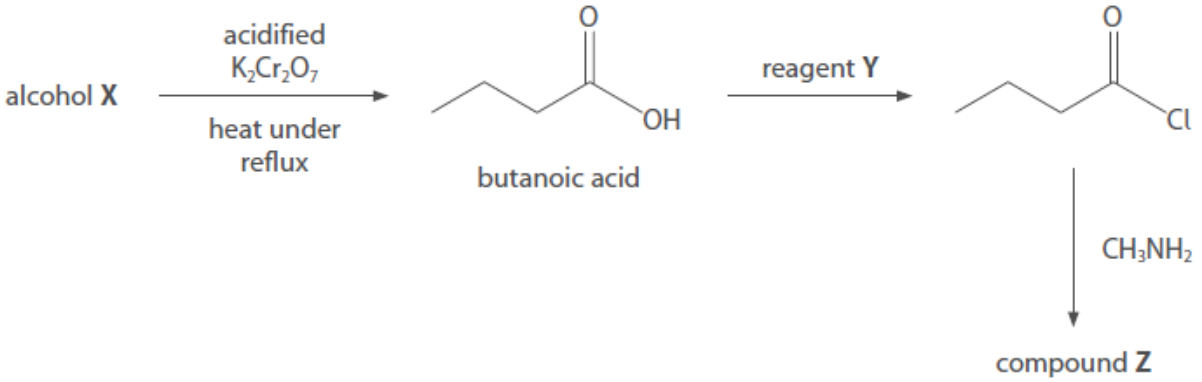
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(iii) Give the structure of the organic product formed when lactic acid reacts with concentrated phosphoric(V) acid, H_3PO_4 .

(1)

(b) A reaction scheme involving butanoic acid is shown.

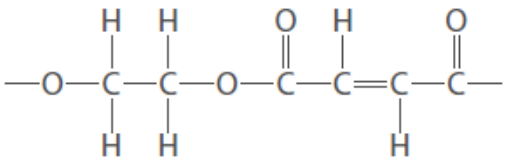


Identify **X**, **Y** and **Z** by name or formula.

(3)

Alcohol **X**
Reagent **Y**
Compound **Z**

(c) The repeat unit of a polyester is shown.



Give the structures of the two monomers that could form this polyester.

(2)

Monomer 1	Monomer 2

(d) An organic compound **E** contains carbon, hydrogen and oxygen only.

(i) The accurate relative atomic masses, A_r , of the three elements in **E** are shown in the table.

Element	A_r
hydrogen	1.0078
carbon	12.0000
oxygen	15.9949

E contains five carbon atoms and gives a molecular ion peak at $m / z = 102.0678$ in its mass spectrum.

Deduce the molecular formula of **E**.

(1)

(ii) Aqueous sodium hydrogencarbonate is added to a sample of **E**.
No effervescence occurs.

State what can be deduced by this observation.

(1)

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.....

(iii) The infrared spectrum of **E** has an absorption in the range 1750 – 1735 cm^{-1}.

Name the functional group in **E**.

(1)

.....

(iv) Data from the high resolution proton NMR spectrum of **E** is shown.

Peak	Chemical shift, δ / ppm for TMS	Splitting pattern	Relative peak area
A	4.02	triplet	2
B	2.05	singlet	3
C	1.65	sextet	2
D	0.95	triplet	3

Deduce the structure of **E**.
Justify your answer by labelling the protons responsible for each peak.

(3)

(Total for question = 14 marks)

Q7.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

In gas chromatography, a gas containing a mixture is passed over a liquid stationary phase. The main reason a mixture is separated into its components is because they have different.

☒ **A** boiling temperatures

☒ **B** forces of attraction to the liquid

☒ **C** relative molecular masses

☒ **d** volatilities

(Total for question = 1 mark)

Q8.

This question is about compounds with the molecular formula $C_6H_{12}O_2$.

(a) Hexanoic acid, $C_5H_{11}COOH$, is a weak acid.

(i) Write the equation for the acid dissociation constant, K_a, of hexanoic acid.

(1)

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of hexanoic acid.

[pK_a of hexanoic acid = 4.88]

(4)

(iii) The solubility of hexanoic acid in water is 1.08 g per 100 g of water.

The isomer of hexanoic acid, butyl ethanoate, $CH_3CO_2C_4H_9$, has a solubility of 0.68 g per 100 g of water.

Explain the differences in these data in terms of the hydrogen bonding between hexanoic acid and water, and between butyl ethanoate and water.

(3)

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(b)(i) Compound **A** is thought to be another isomer of hexanoic acid.

10 g of compound **A** is found to contain 6.21 g of carbon and 1.03 g of hydrogen, with the remainder being oxygen.

Use the data to calculate the empirical formula of compound **A**.

You must show **all** your working.

(3)

(ii) State how you might use your answer to (b)(i) and a mass spectrum of compound **A** to prove that compound **A** is an isomer of hexanoic acid.

(1)

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*(iii) A series of tests was performed on compound **A**.

	Test	Observation
1	addition of phosphorus(V) chloride	misty fumes
2	addition of 2,4-dinitrophenylhydrazine	orange precipitate
3	addition of Benedict's or Fehling's reagent	solution remains blue with no precipitate
4	addition of acidified potassium dichromate(VI)	solution remains orange
5	test using polarimetry	plane of plane polarised light is rotated

Deduce the structure for compound **A**.
Justify your answer by using all the test results.

(6)

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(c) Compound **B**, another isomer with the molecular formula $C_6H_{12}O_2$, contains a ring of six carbon atoms.

The carbon-13 NMR spectrum has only two peaks, one of which is at 69 ppm.

Draw the structure of compound **B**.

(2)

(Total for question = 20 marks)

Q9.

A high performance liquid chromatography (HPLC) system used a column with a non-polar stationary phase and a solvent of methanol and water.

A mixture of octane, octanal and octan-1-ol was placed into the HPLC column.

What is the order of retention times?

	Shortest retention time	Intermediate retention time	Longest retention time
☒ **A**	octane	octanal	octan-1-ol
☒ **B**	octanal	octan-1-ol	octane
☒ **C**	octane	octan-1-ol	octanal
☒ **D**	octan-1-ol	octanal	octane

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 1 mark)

Q10.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

In HPLC, the mobile and stationary phases are

		Mobile phase	Stationary phase
☒	**A**	gas	liquid
☒	**B**	gas	solid
☒	**C**	liquid	gas
☒	**D**	liquid	solid

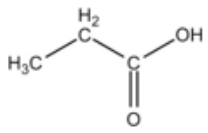
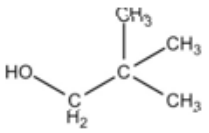
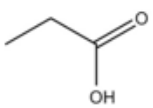
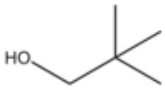
(Total for question = 1 mark)

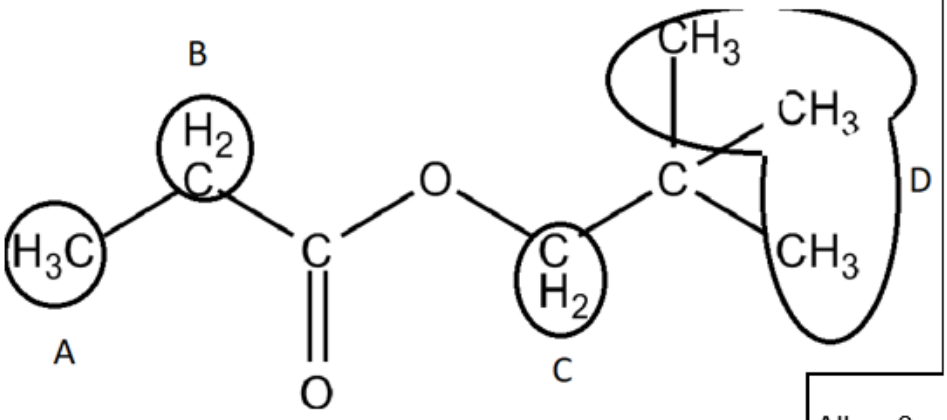
Mark Scheme

Q1.

Q	Acceptable Answers	Additional Guidance	Mark
(a)	• calculation of moles of C, H and O **(1)** • calculation of ratio **and** identify that ratio matches molecular formula **(1)** OR • calculate molar mass of **Y** **(1)** • calculate % of each element **(1)**	element / moles / ratio C / 66.7○12 =5.56 / 5.56○1.3875 = 4 H / 11.1○1 = 11.1 / 11.1○1.3875 = 8 O / 22.2○16 =1.3875 / 1.3875○1.3875 = 1 Ratio C_4H_8O matches $C_8H_{16}O_2$ Molar mass = 144 (g mol^{-1}) C=96○144x100 = 66.7% H=16○144x100 = 11.1% O=32○144x100 = 22.2%	**2**

Q	Acceptable Answers	Additional Guidance	Mark
(b)(i)	2,2-dimethylpropyl propanoate **(2)**	Any name with '-propyl propanoate' scores 1 propyl-2,2-dimethyl propanoate scores 1 2,2-dimethylpropylethanoate scores 1	**2**

Q	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	  **OR**  	Both structures required for mark Allow structures of propanoyl chloride / propanoic anhydride Allow any combination of correct skeletal, structural or displayed formulae. Ignore names even if incorrect Do not award connectivity to hydroxyl group via H atom	**1**

Q	Acceptable Answers	Additional Guidance	Mark
(c)(i)		Labels B C and D can be used interchangeably as long as the three proton environments are identified correctly. Allow 3 methyl groups to be circled individually but with a single label / labels pointing to all 3	1

Q	Acceptable Answers	Additional Guidance	Mark
(c)(ii)	<table><tr><th>Hydrogen environment</th><th>Splitting pattern of peak</th><th>Relative peak area</th></tr><tr><td>(A)</td><td>(triplet)</td><td>(3)</td></tr><tr><td>B</td><td>quartet</td><td>2</td></tr><tr><td>C</td><td>singlet</td><td>2</td></tr><tr><td>D</td><td>singlet</td><td>9</td></tr></table> Note : allow 'quadruplet' as alternative for quartet / 'single' as alternative for singlet Do not award 'quadrat'	1 mark for each row. But If two or more rows are incorrect then award whichever of these alternatives is higher Allow 2 marks for 3 correct splitting patterns. OR Allow 1 mark for 3 correct peak areas. OR Allow 1 mark for correct row marked consequentially on the labelling in 17(c)(i)	3
(Total for Question = 9 marks			

Q2.

Q	Correct Answer	Mark
(a)	**The only correct answer is B** (68 mm) *A is incorrect as it is a factor of 10 to large* *C is incorrect as it is the distance moved by the amino acids* *D is incorrect as it is the expression for R_f has been inverted*	1

Q	Correct Answer	Mark
(b)	**The only correct answer is A** (argon) *B is incorrect as the carrier gas must be inert* *C is incorrect as the carrier gas must be inert* *D is incorrect as the carrier gas must be inert*	1

Q3.

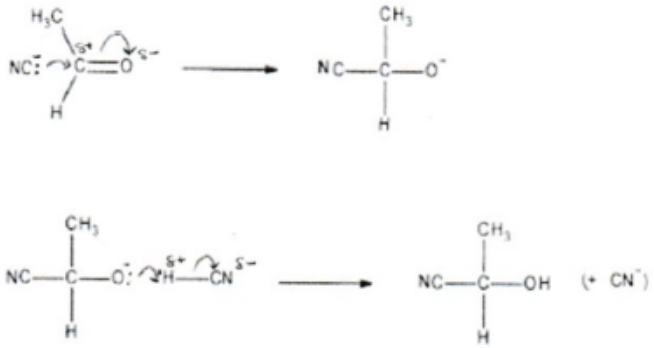
Question Number	Answer	Mark
	The only correct answer is D (weak attraction to stationary phase, strong attraction to mobile phase) *A is not correct because if there was a strong attraction to the stationary phase the component would not move very far and would have a low R_f value* *B is not correct because if there was a weak attraction to the mobile phase the component would not move very far and would have a low R_f value* *C is not correct because if there was a weak attraction to the mobile phase the component would not move very far and would have a low R_f value*	(1)

Q4.

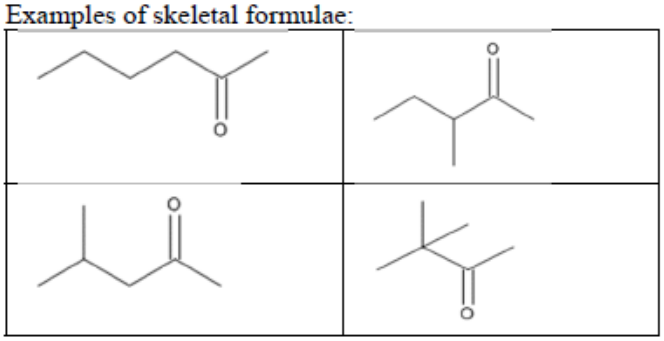
Question Number	Answer	Additional Guidance	Mark
(a)	• $C_{10}H_{18}O$	Allow symbols in any order i.e. $C_{10}OH_{18}$ / $H_{18}C_{10}O$ / $H_{18}OC_{10}$ / $OC_{10}H_{18}$ / $OH_{18}C_{10}$ Allow large numbers e.g. C10H18O Do not award superscripts e.g. $C^{10}H^{18}O$	(1)

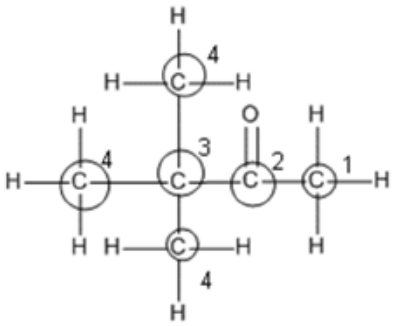
Question Number	Answer	Additional Guidance	Mark
(b)	An answer that makes reference to the following points: • curly arrow from lone pair on C of CN^- towards C of aldehyde group (1) • curly arrow from C=O to, or just beyond, O **and** dipole on C=O (1) • intermediate (1) • curly arrow from lone pair on O^- to H **and** curly arrow from H-CN bond to anywhere on CN **and** final organic product (1)	Penalise an incorrect dipole in M1 and M4 once only Penalise curly arrow not starting from lone pair once only in M1 and M4 Penalise half arrow-heads once only Allow CN^- to attack C=O from any angle Allow CN bond displayed If M1 lost as curly arrow from N of CN^-, allow CN joined to carbon through N Ignore connectivity for vertical CN groups Allow curly arrow from lone pair on O^- to H^+ Ignore missing dipole in HCN	(4)

Example of mechanism:



Question Number	Answer	Additional Guidance	Mark
(c)(i)	• CH_3CO- / $-COCH_3$ / methyl ketone	Allow any combination of structural / displayed formula or skeletal formula Allow methyl next to ketone / methyl and ketone / methylcarbonyl Allow CH_3COR / $RCOCH_3$ Ignore missing continuation bond from structures Do not award ethanal / methyl secondary alcohol / a specific compound	(1)

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	• any 2 skeletal formulae (1) • remaining 2 skeletal formulae (1)	Examples of skeletal formulae:  Ignore bond lengths and bond angles Allow (1) for 4 correct displayed / structural formulae	(2)

Question Number	Answer	Additional Guidance	Mark
(c)(iii)	• displayed formula of **F** (1) • carbon atoms labelled (1)	Example of displayed formula:  Allow CH_3 Allow other unambiguous labels for the carbon atoms Allow M2 for labels on structural / skeletal formulae, including labels on formulae in (c)(ii) Ignore reference to singlet / splitting patterns	(2)

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>(d)*</td>
<td>This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.

Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5–4</td><td>3</td></tr>
<tr><td>3–2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>
The following table shows how the marks should be awarded for structure and lines of reasoning.</td>
<td>Guidance on how the mark scheme should be applied:
The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).
If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).</td>
<td>(6)</td>
</tr>
</table>

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	Number of marks awarded for structure of answer and sustained line of reasoning
Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.	2
Answer is partially structured with some linkages and lines of reasoning.	1
Answer has no linkages between points and is unstructured.	0

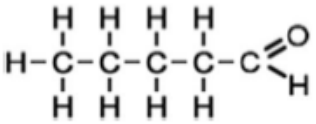
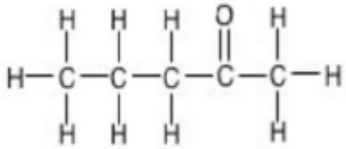
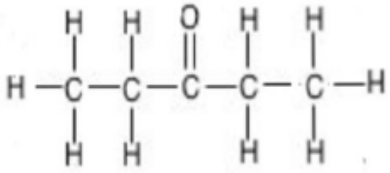
Comment:
Look for the indicative marking points first, then consider the mark for structure of answer and sustained line of reasoning

In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning.

Additional incorrect chemistry loses a structure and lines of reasoning mark (if 1 or 2 have been awarded).

	Indicative content • **IP1 London forces** Pentane (only) has London forces / all have London forces • **IP2 Butanal** Butanal (also) has (permanent) dipole-dipole interactions • **IP3 Propanoic acid** Propanoic acid (also) has (dipole-dipole and) hydrogen bonding • **IP4 Intermolecular forces** The London forces have about the same strength as they have a similar number of electrons / pentane has 42, butanal has 40 (and propanoic acid has 40 electrons) **or** butanal has dipole-dipole interactions because it is polar / has a dipole on C=O **or** propanoic acid has hydrogen bonding because it contains OH / COOH group • **IP5 Butanal and pentane** Dipole-dipole interactions are stronger than London forces **or** more energy is needed to overcome the dipole-dipole interactions than London forces • **IP6 Butanal and propanoic acid** Hydrogen bonding is stronger than dipole-dipole interactions **or** more energy is needed to overcome hydrogen bonding than dipole-dipole interactions	Allow dispersion forces / van der Waals' forces / forces between an instantaneous dipole and an induced dipole for London forces throughout answer Do not award IP1 if any other forces mentioned Allow dipole-dipole forces / attractions / bonds Do not award IP2 if hydrogen bonding included Allow similar relative molecular masses (butanal 72, pentane 72, propanoic acid 74) Do not award incorrect numbers of electrons / relative molecular masses Allow dipole-dipole interactions linked to C=O Allow diagram of hydrogen bond between two molecules Ignore formation of dimer Allow London forces are the weakest (intermolecular force) Do not award if covalent bonds broken or explanation is about intermolecular forces with water Allow hydrogen bonding is the strongest (intermolecular force) Do not award if covalent bonds broken or explanation is about intermolecular forces with water	**(6)**

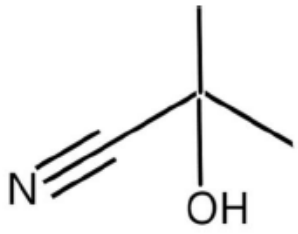
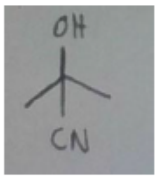
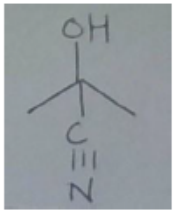
Q5.

Question Number	Answer	Additional Guidance	Mark
(a)	An answer that makes reference to the following points: • A  (1) • B  (1) • C  (1)	Allow structural or skeletal formulae for max 2 marks Ignore any names even if incorrect Ignore bond angles/lengths Penalise missing Hs only once	(3)

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• 2-hydroxybutanenitrile	Allow 2-hydroxy(l)buta(n)nitrile Allow 2-hydroxy(l)butane-1-nitrile Do not award 2-hydroxobutanenitrile Do not award 2-oxobutanenitrile Do not award cyanides or other non IUPAC names Ignore any extra hyphens, commas and spaces	(1)

Question Number	Answer	Additional Guidance	Mark
(b)(ii)	• one isomer rotates (the plane of monochromatic) plane-polarised light in one direction and the other in the opposite direction/ the isomers rotate (the plane of) plane-polarised light in opposite directions/clockwise and anticlockwise	Do not award bends Allow different directions Allow PPL for plane polarised light Allow the direction of rotation of plane polarised light Allow see which way the sample rotates PPL	(1)

Question Number	Answer	Additional Guidance	Mark
(b)(iii)	An answer that makes reference to the following points: • propanal is planar around the CHO/reaction site/C=O/carbonyl **(1)** • CN^-/nucleophile can attack on either side/both sides/above and below (giving a racemic/equimolar/ 50/50 mixture) **(1)**	Do not award just propanal is planar Do not award planar intermediate/carbocation Do not award any reference to nucleophilic substitution (S_N1/S_N2)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(c)(i)		Ignore displayed or structural formulae Ignore bond lengths and bond angles Allow   Ignore connectivity if vertical bond	**(1)**

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	• no carbon atom has 4 different groups or (central) carbon atom is bonded to two CH_3/same groups or no asymmetric/chiral carbon atom or the compound is superimposable on its mirror image or it does not have a chiral centre	Ignore symmetrical Do not award 2 of the same molecules/compounds attached to the carbon atom Do not award racemic mixture	**(1)**

Question Number	Answer	Additional Guidance	Mark
(d)(i)	• correct chemical shift **and** carbon environment	<table><tr><th>Chemical shift range</th><th>Carbon environment</th></tr><tr><td>190-225 (ppm)</td><td>C=O</td></tr><tr><td colspan="2">**OR**</td></tr><tr><td>0-60 (ppm)</td><td>C—C</td></tr></table> Both range **and** carbon environment required. Allow the full range or a number/ smaller range within the range. Allow for carbon environment C-**C**=O **and** C-**C**=O | | C H Ignore any splitting patterns	(1)

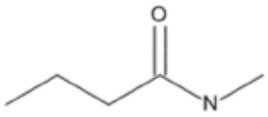
Question Number	Answer	Additional Guidance	Mark
(d)(ii)	• Propanal: 3/three **and** • Propanone: 2/two		(1)

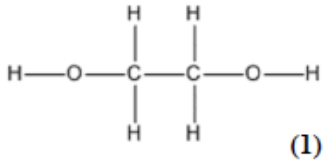
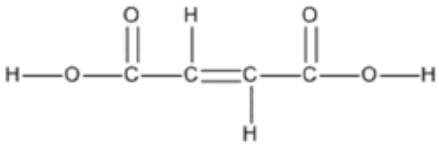
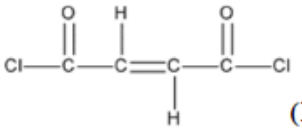
Q6.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following point: • it / lactic acid is non-superimposable on its mirror image	Allow there are four different atoms / groups attached to a carbon (atom) Allow it is chiral / has a chiral centre / has a chiral carbon (atom) / has an asymmetric carbon (atom) Ignore rotates the plane of plane-polarised light Do not award four different molecules attached to a carbon (atom)	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	An answer that makes reference to the following point: • it is a racemic mixture or contains equal amounts of the two enantiomers / (optical) isomers	Allow rotations caused by both enantiomers / isomers cancel Ignore just contains two enantiomers / isomers Do not award plane-polarised light cannot pass through the solution	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	• CH_2=CHCOOH	Allow any combination of structural or displayed formulae or skeletal formulae / $COOHCH=CH_2$	(1)

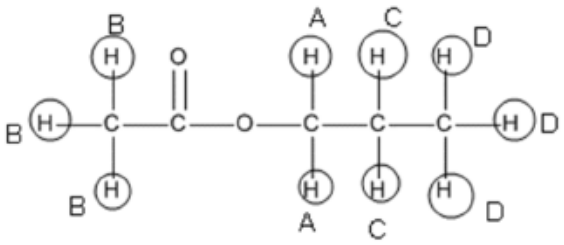
Question Number	Answer	Additional Guidance	Mark
(b)	• **X**: butan-1-ol or  or $CH_3CH_2CH_2CH_2OH$ / $CH_3(CH_2)_2CH_2OH$ (1) • **Y**: phosphorus(V) chloride / phosphorus pentachloride / PCl_5 (1) • **Z**: *N*-methylbutanamide or  or $CH_3CH_2CH_2CONHCH_3$ / $CH_3(CH_2)_2CONHCH_3$ (1)	Mark independently If names and formulae are given, both must be correct but penalise missing H from carbon chain displayed formulae once only Allow any combination of skeletal, structural or displayed formulae Ignore molecular formulae for **X**, **Y** and **Z** Ignore butanol / C_4H_9OH Do not award $CH_3CH_2CH_2CH_2O$ Do not award butanal Allow phosphorus(III) chloride / PCl_3 / thionyl chloride / $SOCl_2$ Do not award hydrochloric acid / HCl Ignore methylbutanamide / butanamide in addition to a correct structure Allow NH in skeletal formula Do not award $CH_3CH_2CH_2COHNCH_3$ / $CH_3CH_2CH_2COCH_3NH$	(3)

Question Number	Answer	Additional Guidance	Mark
(c)	• Monomer 1  (1) • Monomer 2  or  (1)	Allow monomers in either order Allow any combination of structural or displayed formulae / skeletal formulae Allow OH Ignore bond lengths and bond angles Penalise OH-C on left of molecules once only Penalise missing H from carbon chain displayed formulae once only Accept cis isomers	(2)

Question Number	Answer	Additional Guidance	Mark
(d)(i)	• $C_5H_{10}O_2$	Allow symbols in any order Ignore any working Ignore + charge	(1)

Question Number	Answer	Additional Guidance	Mark
(d)(ii)	• **E** is not a carboxylic acid or does not contain COOH (group)	If name and formula are given, both must be correct Allow **E** is not an acid Do not award additional functional groups	(1)

Question Number	Answer	Additional Guidance	Mark
(d)(iii)	• **E** is an ester	Ignore saturated / -COO- / C=O Do not award additional functional groups	(1)

Question Number	Answer	Additional Guidance	Mark
(d)(iv)	• structure of **E** (1) • 2 or 3 proton environments correct (1) • 4th proton environment correct (1)	Example of structure:  Protons can be circled and labelled or just labelled Allow labels using data from the table Only 1 proton from each group needs to be labelled Allow whole groups to be labelled, including the carbon atom	(3)

Q7.

Question Number	Correct Answer	Mark
	The only correct answer is B (forces of attraction to the liquid) ***A*** *is incorrect because these do not affect passage through the stationary phase* ***C*** *is incorrect because this is not the main reason and does not directly affect passage through the stationary phase* ***D*** *is incorrect because these do not affect passage through the stationary phase*	(1)

Q8.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following points: • $K_a = \frac{[C_5H_{11}COO^-][H^+]}{[C_5H_{11}COOH]}$	Accept $[CH_3CH_2CH_2CH_2CH_2CO_2^-]$ and $[CH_3CH_2CH_2CH_2CH_2CO_2H]$ Accept $[H_3O^+]$ instead of $[H^+]$ Accept other representations of the chain of hexanoic acid / hexanoate ion, such as $[CH_3(CH_2)_4COO^-]$ Ignore equation for dissociation Do not award $[H^+]^2/[C_5H_{11}COOH]$ Do not award brackets that are not square brackets Do not award molecular formulae	**(1)**

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• uses expression for pK_a **(1)** • use of K_a expression **(1)** • rearrange and solve for H^+ **(1)** • find pH	Example calculation $K_a = 10^{-pK_a}$ / $K_a = 10^{-4.88}$ / $pK_a = -\log_{10}K_a$ / $4.88 = -\log_{10}K_a$ / $K_a = 0.000013183$ / 1.3183×10^{-5} $10^{-4.88} / 1.3183 \times 10^{-5}$ / $0.000013183 = \frac{[H^+]^2}{0.1}$ $[H^+] = \sqrt{0.000013183 \times 0.1}$ = 0.0011482 / 0.00115 / 1.1482×10^{-3} / 1.15×10^{-3} (mol dm^{-3}) $pH = -\log_{10}[H^+] = 2.94$ / 2.9400 Do not award M4 with units Final correct answer with no working scores (4) Final correct answer scores (4) Allow TE at each stage Omitting the square root gives 5.88 scores (3) Use of 4.88 for K_a gives 0.1558 scores (3) Ignore SF except 1 SF	**(4)**

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • hexanoic acid forms more hydrogen bonds (per molecule) with water than butyl ethanoate does **(1)** **(1)** • hexanoic acid has an -OH group which forms hydrogen bonds (with water) **(1)** • butyl ethanoate / hexanoic acid has a C=O group which forms hydrogen bonds (with water)	All marks may be scored with a diagram or diagrams Allow hexanoic forms two hydrogen bonds per molecule but butyl ethanoate forms only one Ignore references to the strength of the hydrogen bonds Ignore all references to other intermolecular forces	**(3)**

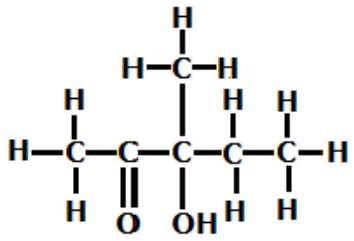
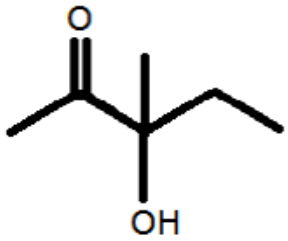
Question Number	Answer	Additional Guidance	Mark
(b)(i)	• calculate mass of oxygen **(1)** **(1)** • divides masses by atomic mass • divides by smallest to find the simplest ratio **(1)** **and** correct empirical formula	Example calculation Mass of O = 10 - 6.21 - 1.03 = 2.76(g) Element / Mass / Mass / Atomic Mass / Ratio C: 6.21 / 6.21 / 12 = 0.5175 / 3 H: 1.03 / 1.03 / 1 = 1.03 / 6 O: 2.76 / 2.76 / 16 = 0.1725 / 1 C_3H_6O Correct answer with mass/atomic mass ratios calculated scores (3) Do not award $C_6H_{12}O_2$ stated as empirical formula Ignore SF Ignore reference to $C_6H_{12}O_2$ after finding empirical formula Allow 1 mark for CH_2 deduced without finding the mass of oxygen Allow max 1 mark for incorrect masses of oxygen divided correctly by atomic mass Correct answer with no working scores (1)	**(3)**

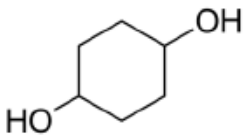
Question Number	Answer	Additional Guidance	Mark
(b)(ii)	An answer that makes reference to the following points: • molecular ion peak / peak at highest mass will be at twice the mass of the empirical formula / will be at 116	Ignore references to n.m.r or i.r.	**(1)**

Question Number	Answer	Additional guidance	Mark
(b)(iii)	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5–4 / 3 3–2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning.	Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). In general, an answer with 5 or 6 IPs would score 2 reasoning marks, 3 or 4 IPs would score 1 reasoning mark, 0, 1 or 2 IPs would score 0 reasoning marks.	**(6)**

	<table><tr><td></td><td>Number of marks awarded for structure of answer and sustained line of reasoning</td></tr><tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.</td><td>2</td></tr><tr><td>Answer is partially structured with some linkages and lines of reasoning.</td><td>1</td></tr><tr><td>Answer has no linkages between points and is unstructured.</td><td>0</td></tr></table>	If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s). Candidates may treat each test separately or may build on each test. Accept statements in any order.

	Indicative content • **IP1** Misty fumes suggest OH group present • **IP2** Orange precipitate suggests a carbonyl group is present (so no carboxylic acid, must be alcohol) • **IP3** (Negative) Benedict's / Fehling's reagent suggests no aldehyde group present / a ketone is present	Accept alcohol or carboxylic acid group present (must state both) Accept ketone or aldehyde present (must state both Ignore C=O is present Accept just 'no oxidisable groups present / cannot be oxidised' in either IP3 or IP4 but not both Allow tertiary alcohol is present	

	• **IP4** Acidified potassium dichromate(VI) suggests not a primary, a secondary alcohol or an aldehyde present	Accept just no primary or secondary alcohol present Ignore references to ketone and carboxylic acid giving no result	
	• **IP5** Polarimetry indicates a chiral centre is present / it is a chiral molecule	Ignore S_N2 Allow 4 different groups on a carbon Allow optically active Allow contains a single enantiomer	
	• **IP6** Structure of 3-hydroxy-3-methylpentan-2-one  	Allow the correct name Allow displayed or structural formula or combinations Allow contractions such as CH_3- C_2H_5-	

Question Number	Answer	Additional Guidance	Mark
(c)	An answer that makes reference to the following points: • a structure containing **two** –OH groups **(1)** • correct structure **(1)**	Do not award an –OH group and a -COOH group Award this mark even if the structure does not contain a ring of six atoms.  Structure may be skeletal or displayed or a mixture, as long as it is clear. Allow, for example, a displayed formula with condensed CH_2. Ignore connectivity of -OH	**(2)**

Q9.

Question Number	Answer	Mark
	The only correct answer is D (octan-1-ol, octanal, octane,) *A is not correct because octan-1-ol is the most polar so would have the shortest retention time* *B is not correct because octan-1-ol is more polar than octanal and so would have a shorter retention time* *C is not correct because octane is non-polar so would have the longest retention time*	(1)

Q10.

Question Number	Correct Answer	Mark
	The only correct answer is D (Liquid Solid) ***A** is incorrect because high performance liquid chromatography has a liquid mobile phase* ***B** is incorrect because high performance liquid chromatography has a liquid mobile phase* ***C** is incorrect because high performance liquid chromatography has a solid stationary phase*	(1)

Q1.

This question concerns six isomers each with the molecular formula $C_5H_{10}O_2$.

(a) Isomers **A**, **B**, **C** and **D** are structural isomers that all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **A** is a straight-chain compound.

Isomer **B** has only two peaks in its high resolution proton NMR spectrum, both of which are singlets.

Isomer **C** contains a chiral centre but isomer **D** does not.

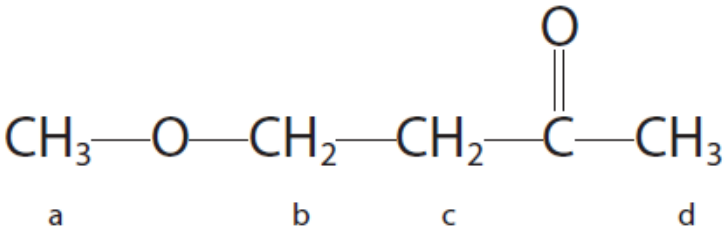
Give the structures of these **four** isomers.

(4)

A	B

C	D

(b) (i) Isomer **E** contains an ether functional group (R-O-R) and a ketone functional group. The **low** resolution proton NMR spectrum of isomer **E** has four peaks. The displayed formula of isomer **E** is



The four hydrogen environments responsible for the four peaks are labelled. Complete the table of information regarding these peaks including the splitting pattern in the **high** resolution spectrum.

(3)

Peak	a	b	c	d
Relative peak area	3			
Chemical shift range, δ / ppm	2.9 – 4.2			
Splitting	singlet			

(ii) State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of **E**.

(1)

.....

(c) Isomer **F** is a neutral compound that smells of pears.

It can be formed by the reaction between compounds **V** and **W** in the presence of concentrated sulfuric acid.

Compound **V** has an absorption in its infrared spectrum at 1720 cm^{-1} and a broad absorption around 3050 cm^{-1}.

Compound **W** can be formed directly from propanal.

(i) Identify, by name or formula, compounds **V**, **W** and **F**.

Justify your answer by using **all** the available information.

(4)

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(ii) State the conditions required and the reagent needed to form compound **W** from propanal.

(1)

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(iii) State the role of sulfuric acid in the formation of **F**.

(1)

.....

(d) State which one of the isomers **A**, **E** and **F** has the highest boiling temperature.

Justify your answer.

(3)

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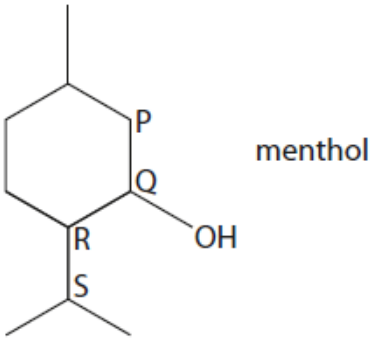
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(Total for question = 17 marks)

Q2.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

The compound menthol has the structure shown.
Some of the carbon atoms are labelled P, Q, R and S.



menthol

(a) What is the number of chiral centres in a molecule of menthol?

(1)

☒ **A** 1

☒ **B** 2

☒ **C** 3

☒ **D** 4

(b) Which of the carbon atoms is responsible for a peak at 72 ppm in the ^{13}C NMR spectrum of menthol?

(1)

☒ **A** P

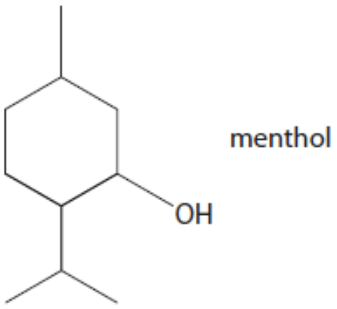
☒ **B** Q

☒ **C** R

☒ **D** S

(c) Four groups of students warmed samples of menthol with sodium dichromate(VI) in acid. They purified the reaction mixture and carried out a series of qualitative tests on the organic product.

The findings of each group in the class are shown in the table.



menthol

	Qualitative test		
Group	Add 2,4-dinitrophenylhydrazine	Warm with Fehling's solution	Add PCl_5
One	✓	×	✓
Two	✓	×	×
Three	✓	✓	×
Four	×	×	✓

A tick (✓) shows a positive result, a cross (×) shows a negative result.
Which group recorded the results you would expect?

(1)

☒ **A** One

☒ **B** Two

☒ **C** Three

☒ **D** Four

(Total for question = 3 marks)

Q3.

Answer the questions with a cross in the boxes you think are correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

This question is about proton NMR spectroscopy.

(a) How many peaks are there in the **low** resolution proton NMR spectrum of 2-methylpropan-2-ol?

(1)

☒ **A** one

☒ **B** two

☒ **C** three

☒ **D** four

(b) Which compound has **three** peaks with relative peak areas of 3 : 2 : 1 in its **low** resolution proton NMR spectrum?

(1)

☒ **A** propanal

☒ **B** propane

☒ **C** propan-1-ol

☒ **D** propan-2-ol

(c) Which compound does **not** have a singlet peak in its **high** resolution proton NMR spectrum?

(1)

☒ **A** butanoic acid

☒ **B** butanone

☒ **C** butanal

☒ **D** butan-1-ol

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 3 marks)

Q4.

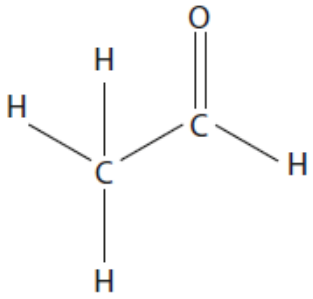
Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

The high resolution mass spectrum of a compound X has a molecular ion peak at m / z = 44.0632. Accurate relative atomic masses are given in the table.

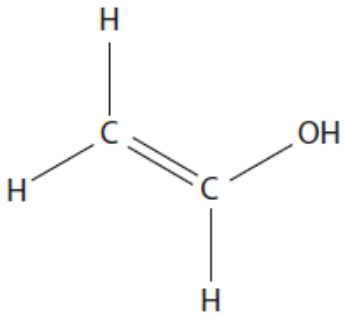
Element	Relative atomic mass
Hydrogen	1.0079
Carbon	12.0000
Oxygen	15.9949

Which of these compounds, with a relative molecular mass of 44, gives rise to this peak?

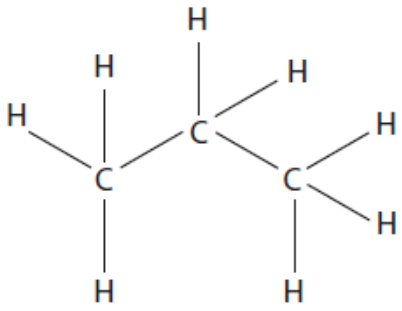
☒ **A**

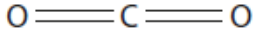


☒ **B**



☒ **C**



☒ **D** 

(Total for question = 1 mark)

Q5.

In gas chromatography (GC), which one of the following would **increase** the retention time for an alcohol?

(1)

☒ **A** increasing the flow rate of the mobile phase

☒ **B** increasing the polarity of the stationary phase

☒ **C** decreasing the polarity of the stationary phase

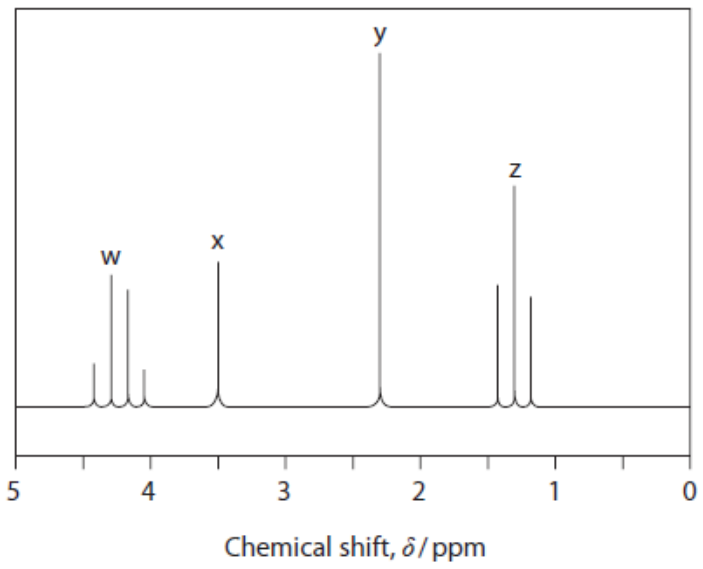
☒ **D** increasing the polarity of the mobile phase

(Total for question = 1 mark)

Q6.

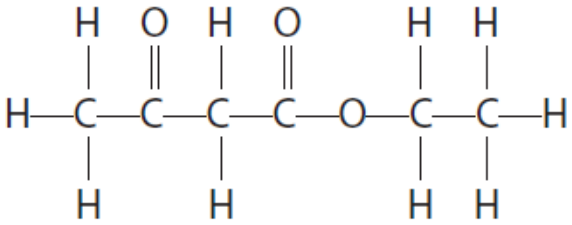
The compound ethyl 3-oxobutanoate, which is used in food flavouring, has the formula $CH_3COCH_2COOCH_2CH_3$.

The high resolution proton (^1H) NMR spectrum of this compound is



(a) (i) Identify which groups of hydrogen atoms are responsible for each peak in the spectrum by adding the labels w, x, y and z to the appropriate parts of this displayed formula to match the letters on the spectrum.

(2)



(ii) Explain the splitting patterns of the peaks at 4.2 ppm and 1.3 ppm.

(2)

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(iii) The carbon-13 (^{13}C) NMR spectrum of ethyl 3-oxobutanoate has six peaks.

Draw the structure of an **isomer** of ethyl 3-oxobutanoate that contains a carboxylic acid group and a ketone functional group, but only has four peaks in its carbon-13 NMR spectrum.

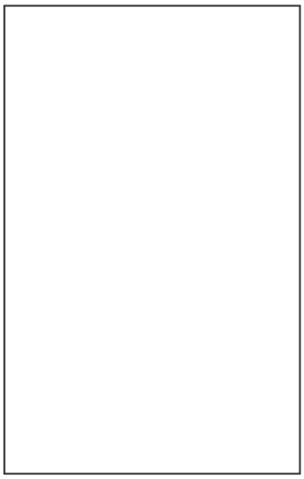
(1)

(b) A chemist synthesising ethyl 3-oxobutanoate looked for its presence in the reaction mixture using thin-layer chromatography. The solvent used was a mixture of ethoxyethane, $C_2H_5OC_2H_5$, which is polar, and hexane.

Under these conditions, the R_f value for ethyl 3-oxobutanoate was 0.45.

(i) Complete the diagram below, showing a chromatogram for ethyl 3-oxobutanoate, including appropriate labels.

(3)



(ii) Suggest why the R_f value for ethyl 3-oxobutanoate is significantly lower than 0.45 when just hexane is used as the solvent.

(2)

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(Total for question = 10 marks)

Q7.

The standard enthalpy change of solution for ammonium nitrate, NH_4NO_3 , is +25.7 kJ mol^{-1}.

(a) Calculate the value for the standard entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, when ammonium nitrate dissolves in water at 298 K. Include a sign and units with your answer.

(2)

(b) Explain what can be deduced from your answer in (a) about the sign and the value of the standard entropy change in the system, $\Delta S^{\ominus}_{system}$, when NH_4NO_3 dissolves.

(3)

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(Total for question = 5 marks)

Q8.

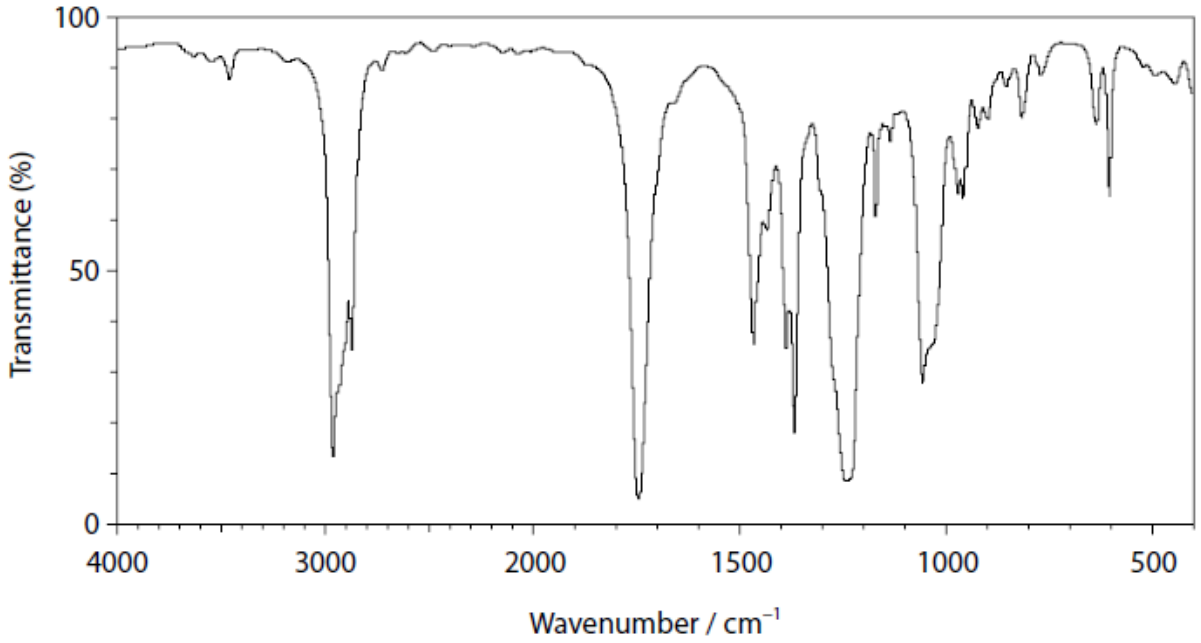
One of the compounds responsible for the characteristic smell of bananas is 3-methylbutyl ethanoate.
The structural formula of this compound is:

$$CH_3COOCH_2CH_2CH(CH_3)_2$$

(a) Draw the **skeletal** formula for 3-methylbutyl ethanoate.

(1)

(b) The infrared spectrum of a sample of 3-methylbutyl ethanoate is shown below.



(i) Use this spectrum to identify one peak resulting from a bond in the ester group of 3-methylbutyl ethanoate. Include the relevant bond and its wavenumber range.

(1)

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(ii) 3-methylbutyl ethanoate was synthesised by reacting a suitable carboxylic acid with an alcohol.

Show that its infrared spectrum confirms there is no alcohol remaining in the sample.

(1)

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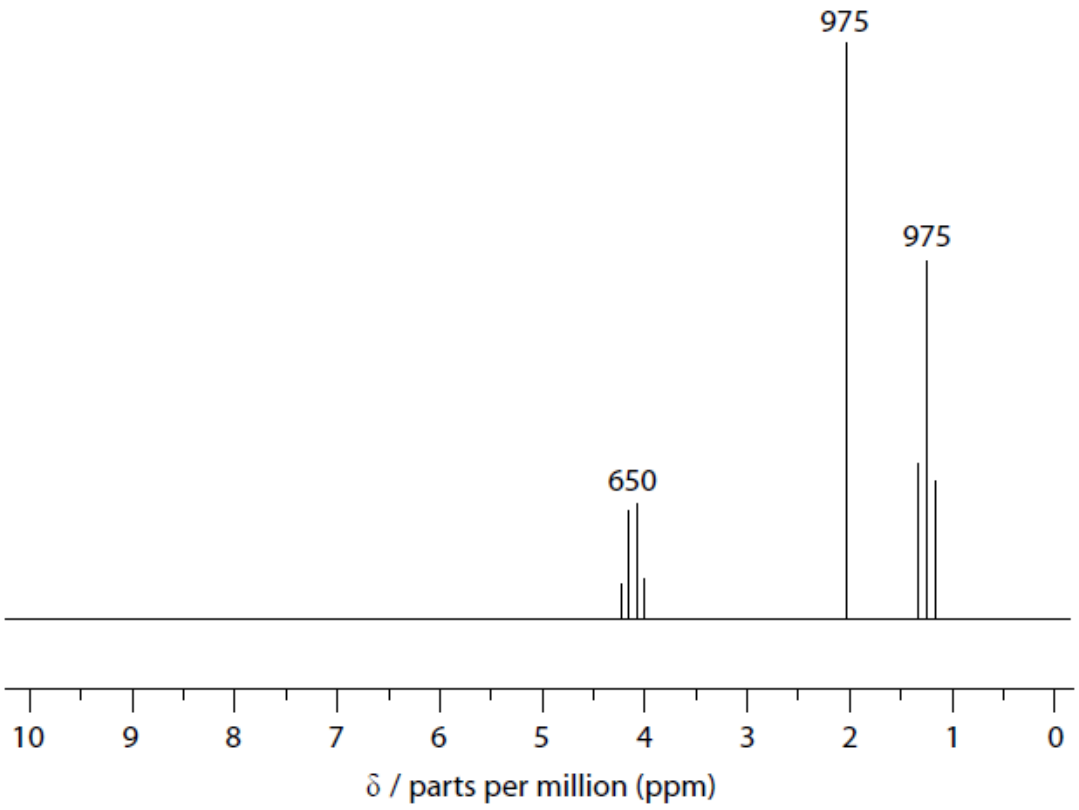
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*(c) The high resolution proton nuclear magnetic resonance (NMR) spectrum of a different ester, ethyl ethanoate, $CH_3COOCH_2CH_3$, is shown.

The numbers over each peak represent their approximate relative areas.



Show that the structure of ethyl ethanoate is consistent with this NMR spectrum, using all the

data in the spectrum.

(6)

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(d) Ethyl ethanoate has three isomers which are also esters.

(i) Draw the structures of these three isomers.

(2)

(ii) Explain to what extent it is possible to distinguish between the three isomers using carbon-13 NMR spectroscopy.

(2)

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(Total for question = 13 marks)

Q9.

Compound **X** is used by mammals as an alternative energy source to sugars.
X is a compound of carbon, hydrogen and oxygen only.

(a) Complete combustion of a 2.50 g sample of **X** in dry oxygen produced 4.31 g of carbon dioxide and 1.32 g of water as the only products.

(i) Give a reason why the oxygen used must be dry.

(1)

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(ii) Show that the empirical formula of **X** is $C_4H_6O_3$. You **must** show your working.

(5)

(b) Compound **X** gave an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine) but no reaction with Tollens' reagent.

When **X** was added to a solution of sodium hydrogencarbonate, effervescence occurred and the gas evolved turned limewater cloudy.

The carbon-13 NMR spectrum of **X** had only four peaks.

(i) Deduce the **two** possible structures of **X**, showing how this information supports your answer.

(6)

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(ii) Give a **chemical** test which would allow you to distinguish between the two compounds you have given in (b)(i). Include the reagents required and the result for each of the compounds.

(3)

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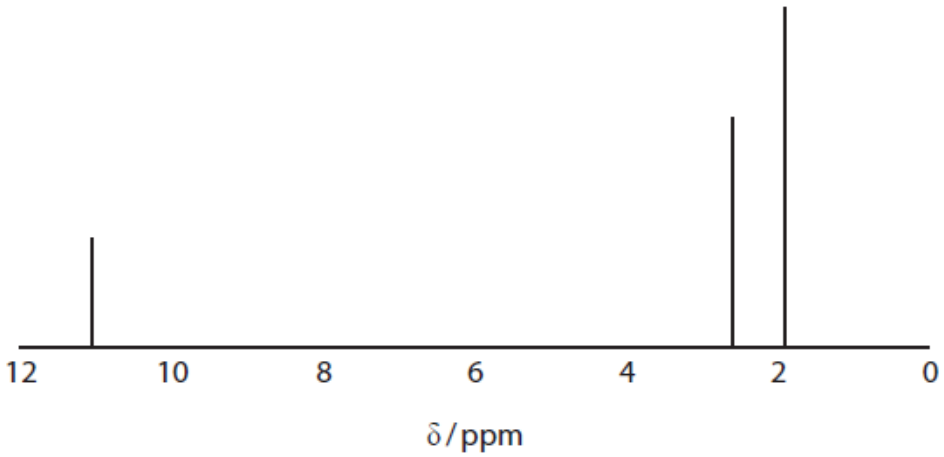
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(c) A simplified **high** resolution proton (^{1}H) NMR spectrum of compound **X** is shown.



Explain how the number of peaks in the ^{1}H NMR spectrum, together with their relative heights, their chemical shifts and their splitting patterns, may be used to confirm the structure of **X**. Use the chemical shifts given in your Data Booklet.

(5)

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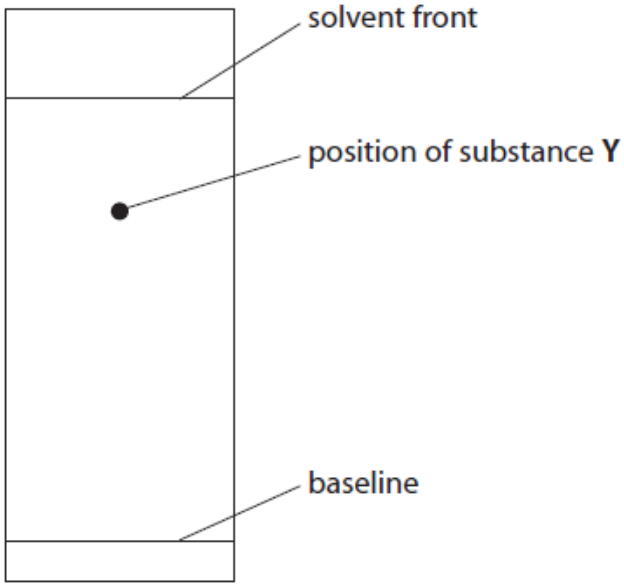
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(Total for question = 20 marks)

Q10.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

A diagram of a thin layer chromatogram of substance **Y** is shown.



What is the R_f value of substance **Y**?

☒ **A** 0.25

☒ **B** 0.60

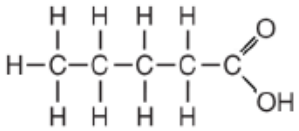
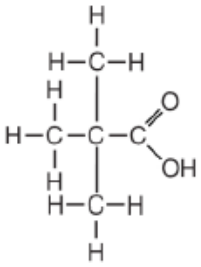
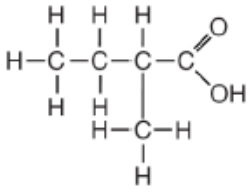
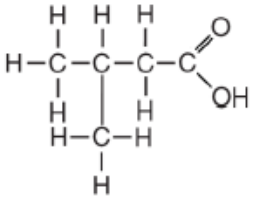
☒ **C** 0.75

☒ **D** 1.33

(Total for question = 1 mark)

Mark Scheme

Q1.

Question Number	Answer	Additional guidance	Mark
(a)	• Structure A (1) • Structure B (1) • Structure C (1) • Structure D (1)	A:  B:  C:  D:  Allow condensed or skeletal formulae If Structure B has not been scored allow this structure as a correct answer for Structure D Penalise OH−C connectivity once only to horizontal bonds Ignore connectivity on vertical bonds to OH and all bonds to CH_3 groups. Penalise incorrect names also given once only	(4)

Question Number	Answer	Additional guidance	Mark
(b)(i)	• 3, 4 or 5 correct boxes (1) • 6, 7 or 8 correct boxes (2) • Nine correct boxes (3)	<table><tr><td>b</td><td>c</td><td>d</td></tr><tr><td>2</td><td>2</td><td>3</td></tr><tr><td>2.7 – 4.2</td><td>1.5 – 2.9</td><td>1.5 – 2.9</td></tr><tr><td>triplet</td><td>triplet</td><td>singlet</td></tr></table> Allow a value or range within the range Allow triple / single 3lines / 1 line	(3)

Question Number	Answer	Additional guidance	Mark
(b)(ii)	• Five / 5 (peaks)		(1)

Question Number	Answer	Additional guidance	Mark
(c)(i)	• Identifies isomer **F** (1) • Identifies compound **V** and compound **W** (1) • Two points of justification for identification of isomer **F**, compound **V** and compound **W** (2)	Penalise use of C_3H_7 for formulae once only **F** is propyl ethanoate / $CH_3COOCH_2CH_2CH_3$ Allow TE on incorrect alcohol or carboxylic acid for V and W If name and formula is given both must be correct Compound **V** is ethanoic acid / CH_3COOH and Compound **W** is propan-1-ol / $CH_3CH_2CH_2OH$ Ignore just 'propanol' Any two from: Compound **V** is a carboxylic acid justified by infra-red Award for correct identification of the bond responsible for either peak? Compound **W** is propan-1-ol / an alcohol / propanol justified by reduction of propanal Allow propanol here but not in M2 Compound **V** or **W** justified by reaction with the other to form an ester Compound **F** is an ester justified by smell / neutral compound	(4)

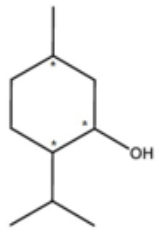
Question Number	Answer	Additional guidance	Mark
(c)(ii)	• (Lithium tetrahydridoalumate(III) / lithium aluminium hydride) / $LiAlH_4$ **AND** in dry ether / diethyl ether / ethoxyethane (solvent)	ALLOW Lithal ALLOW Sodium tetrahydridoborate / sodium borohydride AND Water / ethanol solvent	(1)

Question Number	Answer	Additional guidance	Mark
(c)(iii)	• Catalyst	Ignore mention of acid / homogeneous / proton donor Ignore additional words Do not award just 'proton donor' or donates hydrogen ions	(1)

Question Number	Answer	Additional guidance	Mark
(d)	An explanation that makes reference to the following points: • Isomer A (has the highest boiling temperature) (1) • (Isomer A has the) **only** molecules held together by hydrogen bonding / Isomer A forms hydrogen bonds but E and F do not (1) • Hydrogen bonds are the strongest intermolecular forces (1)	In general ignore reference to other intermolecular forces (but see below) Allow it forms hydrogen bonds Ignore it forms hydrogen bonds with other compounds/substances Ignore comments about straight chain so stronger London forces Allow hydrogen bonding is stronger than London forces and/or permanent dipoles Allow just 'forms strong hydrogen bonds'	(3)

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Q2.

Q	Correct Answer	Mark
(a)	**The only correct answer is C** (3)  ***A*** *is incorrect as menthol has 3 chiral carbon atoms* ***B*** *is incorrect as menthol has 3 chiral carbon atoms* ***D*** *is incorrect as menthol has 3 chiral carbon atoms*	1

Q	Correct Answer	Mark
(b)	**The only correct answer is B** (Q) ***A*** *is incorrect as this carbon would produce a peak between 0 and 60 ppm* ***C*** *is incorrect as this carbon would produce a peak between 0 and 60 ppm* ***D*** *is incorrect as this carbon would produce a peak between 0 and 60 ppm*	1

Q	Correct Answer	Mark
(c)	**The only correct answer is B** (Two) ***A*** *is incorrect as the oxidation product is a ketone, so would not react with* PCl_5 ***C*** *is incorrect as the oxidation product is a ketone, so would not react with Fehling's solution* ***D*** *is incorrect as the oxidation product is a ketone, so would not react with* PCl_5 *but would react with 2,4- dinitrophenylhydrazine*	1

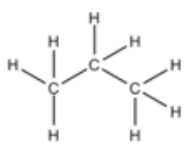
Q3.

Question Number	Answer	Mark
(a)	**The only correct answer is B** (two) *A is not correct because 2-methylpropan-2-ol has a peak for the 3 CH_3 groups and one for the OH group making 2 in total* *C is not correct because 2-methylpropan-2-ol has a peak for the 3 CH_3 groups and one for the OH group making 2 in total* *D is not correct because 2-methylpropan-2-ol has a peak for the 3 CH_3 groups and one for the OH group making 2 in total*	(1)

Question Number	Answer	Mark
(b)	**The only correct answer is A** (propanal) *B is not correct because propane has 2 peaks in the ratio 3:1* *C is not correct because propan-1-ol has 4 peaks in the ratio 3:2:2:1* *D is not correct because propan-2-ol has 3 peaks in the ratio is 6:1:1*	(1)

Question Number	Answer	Mark
(c)	**The only correct answer is C** (butanal) *A is not correct because butanoic acid has a singlet due to the COOH* *B is not correct because butanone has a singlet due to the CH_3 adjacent to the C=O* *D is not correct because butan-1-ol has a singlet due to the OH*	(1)

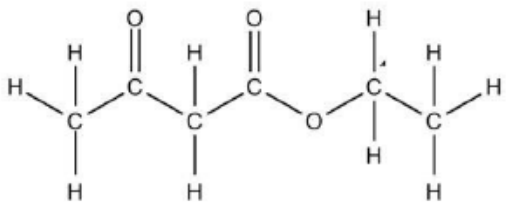
Q4.

Q	Correct Answer	Mark
	The only correct answer is C  *A is incorrect as the molar mass to 4 dp is 44.0265* *B is incorrect as the molar mass to 4 dp is 44.0265* *D is incorrect as the molar mass to 4 dp is 43.9898*	1

Q5.

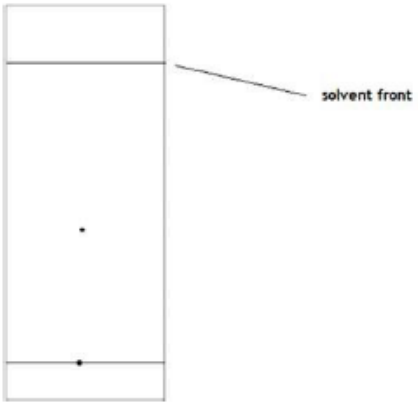
Question number	Answer	Mark
	B increasing the polarity of the stationary phase	1

Q6.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	y x w z  (2) All 4 peaks correctly matched scores both marks 2 or 3 peaks correctly matched scores 1 mark 0 or 1 peak correctly matched scores 0 marks	NOTE Allow labels to/near to carbon of correct group	2

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	4.2 ppm quartet due to 3 hydrogen (atoms) on adjacent carbon (1) 1.3 ppm triplet due to 2 hydrogen (atoms) on adjacent carbon (1)	Allow 'due to adjacent CH_3' Allow 'due to adjacent CH_2' If neither mark awarded can score 1 for correct reference to n+1 rule If no reference to splitting patterns then allow 1 for correctly identifying both sets of adjacent hydrogens	2

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	$C(CH_3)_3COCOOH$	Allow skeletal or displayed formulae If more than 1 structure type given, both must be correct.	1

Question Number	Answer	Additional Guidance	Mark
(b)(i)	Origin/start line shown above bottom of paper (1) Straight line for solvent front added and labelled (1) **Spot** due to ethyl-3-oxobutanoate in position consistent with *R*f between 0.4 and 0.5 (1)	Ignore omission of initial spot, but if shown must be on baseline Allow 'distance travelled by solvent' Do not award wavy lines Do not award the top of the paper as the solvent front 	3

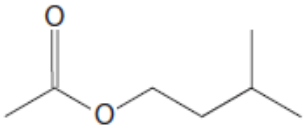
Question Number	Answer	Additional Guidance	Mark
(b)(ii)	**M1** As only London forces form between them (so spot moves a shorter distance) / ethyl-3-oxobutanoate is polar, hexane is non-polar / (1) **M2** Weaker interaction between hexane and ethyl-3- oxobutanoate / ethyl-3-oxobutanoate is less soluble in hexane (1)	Allow reverse arguments Do not award M1 if reference to hydrogen bonds Allow solvent / mobile phase for hexane Allow ethyl-3-oxobutanoate does not dissolve in hexane	2

Q7.

Q	Acceptable Answers	Additional Guidance	Mark
(a)	• correct expression for $\Delta S_{surroundings}$ **(1)** • correct evaluation **and** correct units **and** correct sign **(1)**	Example of calculation $-\Delta H \circ T = -25.7 \circ 298$ -0.086242 kJ K^{-1} mol^{-1} / -86.242 J K^{-1} mol^{-1} Ignore SF except 1 SF Correct answer with no working scores (2) Allow TE in M2 for use of $\Delta H \circ T$ Comment Mark value first – if correct, with units and sign award 2 marks For units allow kJ K^{-} mol^{-} / J K^{-} mol^{-}	**2**

Q	Acceptable Answers	Additional Guidance	Mark
(b)	An explanation that makes reference to: • ΔS_{system} must be positive **(1)** • $\Delta S_{system} > 86.24$ J mol^{-1} / answer to (a) **(1)** • (as compound does dissolve) ΔS_{total} is > 0 / positive **(1)**	Allow 'ΔS_{system} is more positive' Allow $T\Delta S_{system}$ is greater in magnitude / more negative than ΔH ΔG is negative If answer to (a) is positive , then M1 and M2 will be • ΔS_{system} could be positive or negative • ΔS_{system} smaller in magnitude than answer to (a) / $T\Delta S_{system}$ is greater than ΔH	**3**
			(Total for Question = 5 marks)

Q8.

Question number	Answer	Additional guidance	Mark
(a)	• 	Must be skeletal formula	1

Question number	Answer	Additional guidance	Mark
(b)(i)	• C=O peak identified **and** range 1750 - 1735 cm^{-1}	Allow C-O peak identified **and** range 1250 - 1230 cm^{-1}	1

Question number	Answer	Additional guidance	Mark
(b)(ii)	• Absence of a peak in the range 3750 - 3200 cm^{-1}	Absence of alcoholic O-H peak	1

Question number	Answer	Additional guidance	Mark
(c)	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5-4 / 3 3-2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning. Number of marks awarded for structure and sustained lines of reasoning	Guidance on how the mark scheme should be applied. The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s). Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of	6

	Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.	2	reasoning. Some or all the information may be shown on a diagram of the molecule.	
	Answer is partially structured with some linkages and lines of reasoning.	1		
	Answer has no linkages between points and is unstructured.	0		
	Indicative points: • three groups of peaks indicates three hydrogen environments • one or two shifts identified (by number) **and** linked to alkanes • three shifts correctly identified **and** linked to alkanes • two (or more) splitting patterns correctly identified		2.1 (±0.2) = CH_3 next to C=O 4.1 (±0.2) = CH_2 next to C-O- 1.2 (±0.2) = CH_3 next to CH_2 singlet, triplet, quartet	

	• use of n + 1 rule to explain splitting for one (or more) group(s) of protons • areas under peaks/integration numbers linked to numbers of protons in each group.	ratio of areas = 3:2:3	

Question number	Answer	Additional guidance	Mark
(d)(i)	An answer that makes reference to the following points: • $HCOOCH_2CH_2CH_3$ • $HCOOCH(CH_3)_2$ • $CH_3CH_2COOCH_3$ All three correct scores two marks, any two correct scores one mark	Allow displayed/skeletal formulae	2

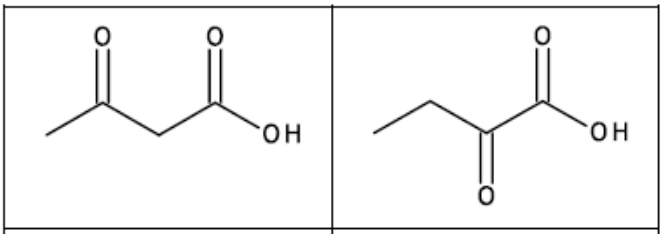
Question number	Answer	Additional guidance	Mark
(d)(ii)	An explanation that makes reference to the following points: • $HCOOCH(CH_3)_2$ has three carbon enviornments (1) whereas • $HCOOCH_2CH_2CH_3$ **and** $CH_3CH_2COOCH_3$ both have four carbon environments. (1)		2

Q9.

Question number	Answer	Additional guidance	Mark
(a)(i)	• otherwise the mass of water from the combustion cannot be measured	Allow any indication that the measurement of water is affected Allow indication that the values of H and O obtained will be affected Ignore just reference to 'the products' Do not award (presence of water) affects the reaction of O_2 with X Do not award water reacts with X Do not award water dissolves CO_2	1

Question number	Answer	Additional guidance	Mark
(a)(ii)	• moles of CO_2 **and** H_2O (1) • masses of C and H (1) • mass of O (1) • moles of C, H and O (1) • **ratio** (1.33:2:1), (integer ratio) **and** empirical formula (1) Allow inductive calculation • balanced equation (1)	Example of calculation mol CO_2 = 4.31 ÷ 44 = 0.097955 mol H_2O = 1.32 ÷ 18 = 0.073333 mass of C = 0.097955 x 12 = 1.1755 g mass of H = 0.073333 x 2 = 0.1467 g mass of O = 2.50 – (1.1755 + 0.1467) = 1.1778 g C: mol 0.0980 x 1 = 0.0980; ratio 1.33; integers 4 H: mol 0.0733 x 2 = 0.147; ratio 2; integers 6 O: mol 1.178/16 = 0.0736; ratio 1; integers 3 $C_4H_6O_3$ No TE if oxygen mass not calculated In M1 and M2 mol CO_2 and mass of carbon scores (1) mol H_2O and mass of hydrogen scores (1) Example of inductive calculation $C_4H_6O_3 + 4O_2 \rightarrow 4CO_2 + 3H_2O$ Formula mass (4x12 + 6 + 3 x 16) = 102 (g) CO_2 = 4 x 44 = 176 (g) and H_2O = 3 x 18 = 54 (g) 2.5 x 176 ÷ 102 = 2.5 (g)	5

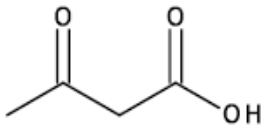
	• Formula mass ($C_4H_6O_3$) **(1)** • Product masses from equation **(1)** • Mass of CO_2 from 2.5 g of X **(1)** • Mass of H_2O from 2.5 g of X **(1)**	2.5 x 54 ÷ 102 = 1.32 (g) Correct answer with any correct method scores (5) Correct answer with no working scores (0) TE at each stage Ignore SF except 1 SF	

Question number	Answer	Additional guidance	Mark
(b)(i)	An answer that makes reference to the following • two structures **(2)** • ^{13}C spectrum shows four different (types of) carbon atom (so molecular formula same as empirical formula) **(1)** • reaction with Brady's reagent indicates a carbonyl compound **(1)**	 A B Allow displayed or structural formulae or any combination of skeletal, displayed and structural Penalise incorrect horizontal –OH connectivity once Ignore names even if incorrect Accept X has four carbon environments Allow ^{13}C spectrum shows X has four types of carbon atom Ignore just 'X has four carbon atoms' Ignore just 'X is a ketone' / C=O present Do not award 'acyl' Accept COOH (group)	6

	• no reaction with Tollens' reagent indicates a ketone (group) / not an aldehyde **(1)** • reaction with $NaHCO_3$ (forming CO_2) indicates (carboxylic) **acid** **(1)**		

Question number	Answer	Additional guidance	Mark
(b)(ii)	An answer that makes reference to the following • reagents for iodoform test **(1)** • result for methyl ketone **(1)** • result for ethyl ketone **(1)**	iodine / I_2 **and** sodium hydroxide /NaOH / potassium hydroxide KOH Accept NaI / KI **and** NaOCl Allow iodine **and** OH^- / alkali Ignore 'iodoform test' (pale) yellow precipitate Allow yellow solid / ppt /ppte /antiseptic smell No change / precipitate Allow no reaction / (pale) yellow precipitate does not form M2 and M3 dependent on M1 or a near miss or just 'iodoform test' If result not linked to structure max (2) e.g NaOH and I_2 give yellow ppt (positive) and no reaction (negative) scores (2) If no reagent or an incorrect reagent given then both observation marks correct scores (1)	**3**

		Do not award use of physical methods	

Question number	Answer	Additional guidance	Mark
(c)	An answer that makes reference to the following • structure of **X** **(1)** • (three) peaks indicate three proton environments **(1)** • peak heights / areas indicate environments contain 3, 2 and 1 protons **(1)** • all singlets / no splitting so no adjacent proton environments **(1)** • identification of proton environments from chemical shifts **(1)**	 Answers may refer to the diagram Allow number of peaks shows number of proton environments Allow if the protons in each environment are clearly labelled e.g. each set circled Ignore just 'peak areas are 3:2:1' peak at δ about 11.1 is COO**H** peak at δ about1.9 is C**H**$_3$CO peak at δ about 2.5 is -OCC**H**$_2$COOH Allow 'alkane proton' / **H**-C-C Allow both 1.9 and 2.5 identified as **H**-C-C=O Do not award reference to the functional group rather than the proton M2, M3 and M5 may be awarded without referring to the structure M2 and M3 are standalone	**5**

Q10.

Question Number	Answer	Mark
	The only correct answer is C (0.75) ***A*** *is not correct because the calculation has used the distance from the solvent front to the sample not the baseline* ***B*** *is not correct because the calculation has used the length of the plate, not the distance the solvent travelled* ***D*** *is not correct because the calculation has been inverted*	**(1)**