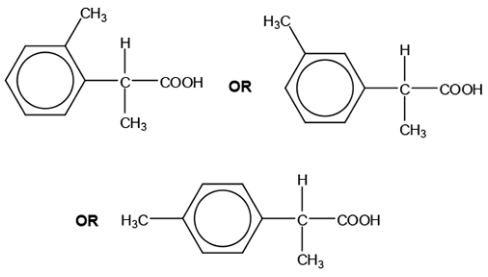
Mark scheme

Question	Answer/Indicative content	Marks	Guidance
1	** Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Structure is $CH_3C_6H_4CH(CH_3)COOH$ **AND** Most of the data analysed. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** A viable aromatic structure of $C_{10}H_{12}O_2$ that contains C=O **AND** most key features consistent with spectral data **AND** Some of the spectral data analysed *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** Correct determination of empirical formula and/or molecular formula. **OR** Analyses some of the IR and NMR data. **OR** Analyses most of the NMR data. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** No response or no response worthy of credit.	6(AO 1.2 × 2)(AO 3.1 × 2)(AO 3.2 × 2)	**Indicative scientific points:** **<u>Empirical and Molecular Formulae</u>** • C : H : O $= \frac{73.17}{12.0} : \frac{7.32}{1.0} : \frac{19.51}{16.0}$ $= 6.10 : 7.32 : 1.22$ $= 5 : 6 : 1$ • Empirical formula = C_5H_6O • uses *m/z* = 164.0 to determine molecular formula as $C_{10}H_{12}O_2$ Structure **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Key features of an aromatic structure consistent with spectral data** • COOH group • 4 aromatic H atoms • single H atom that would give a quartet • CH_3 group that would give a doublet • CH_3 group that would give a singlet **Correct Structure** • $CH_3C_6H4CH(CH_3)COOH$ **ALLOW** 2-, 3- **OR** 4- substitution of ring i.e.  **<u>Spectral analysis</u>** **^{1}H NMR** • δ = 1.6 ppm, doublet, 3H **CH_3**–CH– • δ = 2.3 ppm, singlet, 3H Ar-C**H_3**

- δ = 2.7 ppm, quartet, 1H CO–**CH**–CH_3
  OR Ar–**CH**–CH_3 / C_6H_5–**CH**–CH_3
- δ = 7.1–7.5 ppm, multiplet, 4H C_6**H**$_4$–

ALLOW approximate values for chemical shifts.

IR:

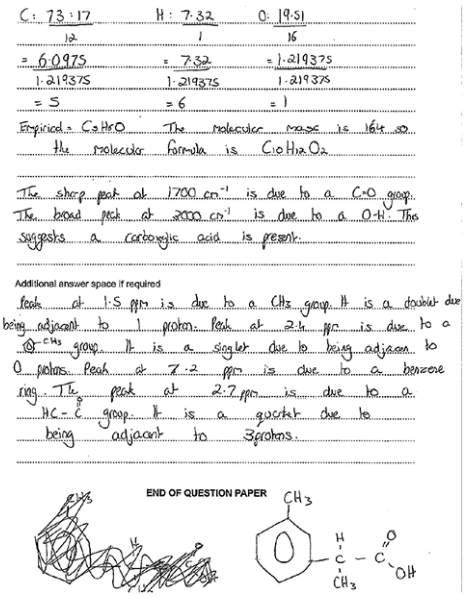
- peak at 2300–3700 (cm^{-1}) is O–H
- peak at ~1720 (cm^{-1}) is C=O
- unknown is a carboxylic acid

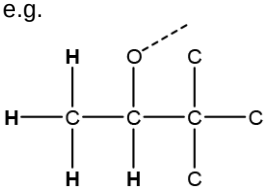
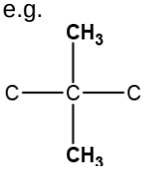
ALLOW ranges from *Data Sheet*
IGNORE references to C–O peaks

Examiner's Comments

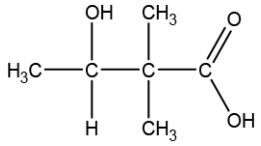
Candidates are confident in tackling questions requiring spectral analysis. Most candidates were able to determine the empirical and molecular formula of the unknown compound and analyse the IR and NMR data. A number of excellent responses were seen which included interpretation of the peak splitting in the NMR spectrum. However, many candidates were unable to suggest a structure that matched their spectral analysis. The majority of structures seen were aromatic but not all contained the carboxylic acid group. Some candidates focused on the NMR data and suggested a structure that was consistent with some of these peaks and included a two substituents of the ring or a degree of chain branching. Lower ability responses often showed a simpler structure of a monosubstituted ring with a straight chain. Stronger responses were able to use all the data to suggest a correct structure as demonstrated in Exemplar 9. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were given six marks.

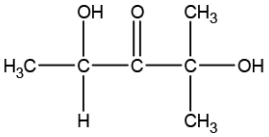
Exemplar 8

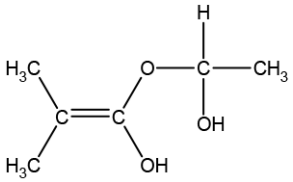
					 C: 73.17 / 12 = 6.0975 / 1.219375 = 5 H: 7.32 / 1 = 7.32 / 1.219375 = 6 O: 19.51 / 16 = 1.219375 / 1.219375 = 1 Empirical = C_5H_6O The molecular mass is 164 so the molecular formula is $C_{10}H_{12}O_2$ The sharp peak at 1700 cm^{-1} is due to a C=O group. The broad peak at 3000 cm^{-1} is due to a O-H. This suggests a carboxylic acid is present. Additional answer space if required Peak at 1.5 ppm is due to a CH_3 group. It is a doublet due to being adjacent to 1 proton. Peak at 2.4 ppm is due to a CH_3 group. It is a singlet due to being adjacen to 0 protons. Peak at 7.2 ppm is due to a benzene ring. The peak at 2.7 ppm is due to a $HC-C$ group. It is a quartet due to being adjacent to 3 protons. END OF QUESTION PAPER This candidate starts their analysis by determining the empirical and molecular formula of the unknown compound. Next the IR and NMR data is analysed in a clear, logical fashion. Although not shown in this report, the candidate had annotated the spectra, a good strategy. At the end of the response the candidate has determined a possible structure. Notice how the candidate has crossed out the first attempt at a structure. This is much better than rubbing out a pencil diagram and re-drawing over the space as this often leads to unclear images that are difficult for examiners to read. This candidate received full marks in this question.
			Total	**6**	
2			**C**	1 (AO 2.5)	**Examiner's Comments** Many candidates identified that 2-methylpropan-1-ol (C) produced the ^{13}C NMR spectrum show. The majority of successful responses included diagrams showing the structures of the compounds to choose from. The most frequently seen incorrect response was D.
			Total	**1**	
3			**B**	1 (AO 2.5)	**Examiner's Comments** Most candidates correctly selected B as the compound that would show four peaks in the ^{13}C NMR spectrum. Many candidates annotated the structures, indicating the different carbon environments with a circle. This proved a good strategy. Common incorrect responses included C and D which were seen in roughly equal proportions.
			Total	**1**	

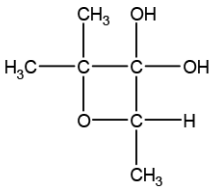
4			*Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Compound is a structure of $C_6H_{12}O_3$ that is consistent with splitting pattern and **chemical shifts** in NMR spectrum. **AND** Comprehensive reasoning with most of the data analysed. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** Compound has a feasible chemical structure that is consistent with the **splitting** pattern in NMR spectrum but may have incorrect molecular formula. **AND** Reasoning provided with some of the data analysed. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** Correct determination of empirical formula and/or molecular formula. **OR** Analyses most of the NMR data. **OR** Attempts to determine empirical and/or molecular formula **AND** analyses some of the NMR data. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** No response or no response worthy of credit.	**6**	**Indicative scientific points:** **Empirical and Molecular Formula** • C : H : O = 54.54/12 : 9.10/1 : 36.36/16 4.545 : 9.10 : 2.273 2 : 4 : 1 • Empirical formula = C_2H_4O • uses *m/z* = 132.0 to determine molecular formula as $C_6H_{12}O_3$ **^{1}H NMR analysis** **Spectrum:** • δ = 4.0 ppm, quartet, 1H, CH_3–**CH**–O • δ = 1.3 ppm, singlet, 6H, **$(CH_3)_2$**–C • δ = 1.2 ppm, doublet, 3H, **CH_3**–CH– **Without D_2O:** • Peak at 11.0 ppm COO**H or OH** • peak at 3.6 ppm O**H** **Note:** Data Sheet shows O-H chemical shift can occur around 11.0 ppm **Structure** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous Contains • region that gives doublet and quartet e.g.  • region that gives singlet e.g. 

Examples of structures consistent with splitting and chemical shift in NMR







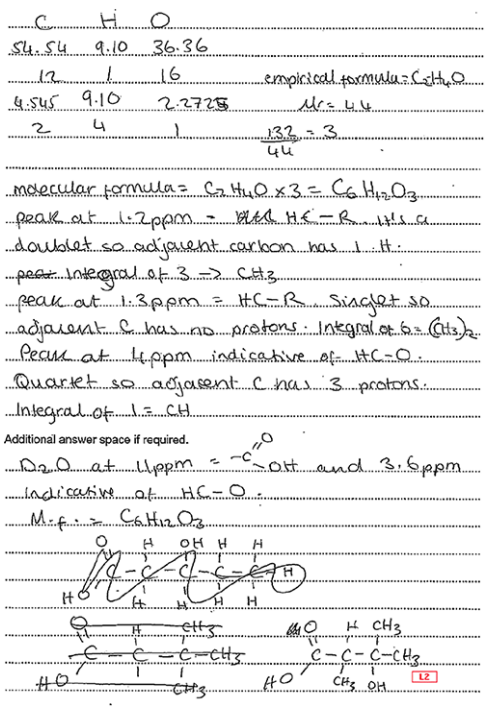


Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader

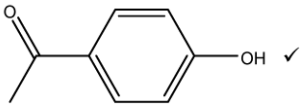
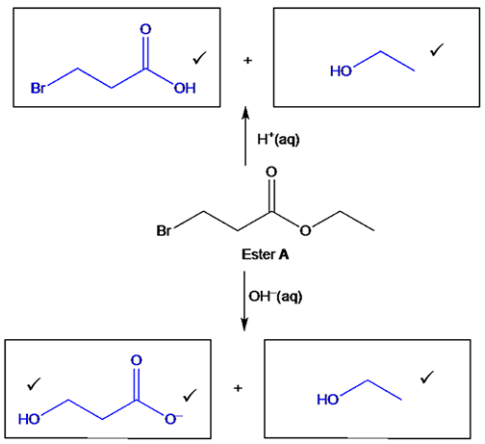
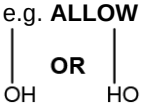
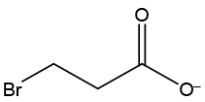
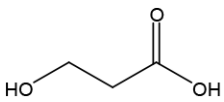
Examiner's Comments

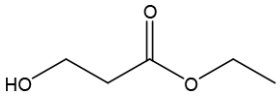
Most candidates were able to determine the empirical and molecular formula of the unknown compound. A number of excellent and clear response were seen, where the NMR data was explained, including interpretation of the additional peaks observed without D_2O. However many candidates were unable to suggest a structure that matched their NMR interpretation. Some candidates used the quartet, doublet and singlet to suggest a structure that would give rise to this splitting pattern, but which was not consistent with the chemical shifts, see Exemplar 12. Such responses received a level 2 mark (3-4). Stronger responses were able to use all the data to suggest a correct structure. The most common was $CH_3CH(OH)C(CH_3)_2COOH$ although other viable structures, including $CH_3CH(OH)COC(CH_3)_2OH$, were also seen. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were credited six marks.

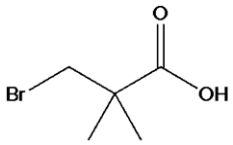
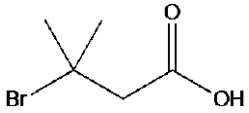
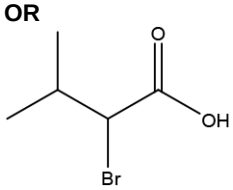
Exemplar 12

					 This logically presented Level 2 response uses the elemental analysis and mass spectrum data to determine the correct empirical and molecular formula of the unknown compound. The peaks in the NMR spectrum are analysed in detail, with a clear explanation of the splitting patterns. A comment about the two additional peaks observed when the spectrum is run without D_2O is also provided. The response concludes with a structure of $C_6H_{12}O_3$ that would show a singlet, doublet and quartet in its ^1H NMR spectrum. However, this structure is not consistent with the chemical shift values shown in the spectrum provided. In particular this structure would produce a quartet between 2.0–2.9 ppm, rather than at 4.0 as in the spectrum shown. Consequentially this response does not achieve Level 3. When tackling questions of this type candidates are advised to check that a proposed structure would produce peaks in the correct region of the NMR spectrum to ensure it is totally consistent with the data analysed.
			Total	**6**	
5			**B**	**1**	**ALLOW** 4 (This is the number of peaks in the NMR spectrum) **<u>Examiner's Comments</u>** Many candidates correctly identified that the ^1H NMR spectrum would contain 4 peaks and selected B. In most cases candidates arrived at this answer by drawing out the structure and labelling the environments. A common distractor was A (3 peaks) which presumably arose from candidates assuming that the C–H and O–H protons in the centre of the structure were equivalent.
			Total	**1**	

6			**A**	**1**	**Examiner's Comments** Candidates found this question more challenging than anticipated. While many correctly chose A, a significant proportion of candidates selected C.
			Total	**1**	
7	a		**Empirical formula** Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓ Empirical formula = C_4H_4O ✓ **Molecular formula** Molecular formula = $C_8H_8O_2$ **AND** Evidence of 136 in working or from labelled peak in spectrum ✓	**3**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$ **ALLOW** 4:4:1 if linked to C:H:O Alternative method for 3 marks: C: $\frac{136 \times 70.58/100}{12.0} = 8$ H: $\frac{136 \times 5.92/100}{1.0} = 8$ O: $\frac{136 \times 23.50/100}{16.0} = 2$ **Examiner Comments** The empirical formula was correctly calculated by all but the weakest candidates. The final mark was more difficult to obtain as it required evidence that the molar mass had been determined from the mass spectrum and used in establishing the molecular formula.
	b		**Functional groups** Phenol **AND** ketone ✓ **Explanation** Links phenol to (weak) acidity **AND** no reaction with Na_2CO_3 (so not carboxylic acid) ✓ Links 2,4-DNP(H) or Brady's reagent observation to carbonyl **AND** Tollens' reagent observation (so not an aldehyde) ✓	**3**	**DO NOT ALLOW** any other functional groups for first marking point. **ALLOW** identity of functional groups in the explanation if not stated on functional group prompt line. **ALLOW** "aldehyde or ketone" in place of carbonyl **Examiner Comments** Many candidates were able to suggest that the compound contained a ketone but found it more difficult to indicate the presence of phenol. Approximately 20% of the entry obtained all three marks. When explaining the presence of the ketone some failed to indicate that the 2,4-DNP test indicated that the compound must contain a carbonyl and just focused on the lack of reactivity with Tollens'. Answers suggesting the molecule contained a ketone as no reaction was observed with Tollens' did not gain credit when no reference to carbonyl was seen. Those who recognised the presence of a phenol explained that the only acidic functional group that does not react with sodium carbonate is a phenol.
	c		**Carbon NMR analysis**	**3**	**ALLOW** peaks to be identified by:

			Peaks between 110–160 ppm are the (four) aromatic (carbon environments) ✓ Compound contains a C=O between 190 – 200 ppm **AND** Compound contains a C-C at 20 – 30 ppm ✓ **Structure**  ✓		• Peaks labelled on spectrum • Peaks indicated on a chemical structure • Peaks indicated from within text **Note:** If identifying aromatic peaks from the spectrum all four peaks should be indicated. **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Examiner Comments** When interpreting a carbon-13 NMR spectrum, candidates should be advised to fully label any peaks. Many candidates failed to indicate the presence of four aromatic peaks yet produced a structure containing a benzene ring. In some cases candidates did not link their answer to part (a) of the question giving structures that did not match their molecular formula.
			Total	**9**	
8	a	i	ethyl 3-bromopropanoate ✓	1(AO 1.2)	**ALLOW** one word: ethyl3-bromopropanoate **OR** more words, e.g. ethyl 3-bromo propanoate **IGNORE** lack of hyphens, or addition of commas **Examiner's Comments** This demanding question discriminated well. The most able candidates were able to apply the nomenclature rules to name ester A correctly as ethyl 3-bromopropanoate. Common incorrect responses included ethyl 1-bromopropanote and ethyl 4-bromopropanoate.
		ii	 	5(AO 2.5 ×5)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** in either order **ALLOW** any vertical bond to the OH group e.g. **ALLOW**  **DO NOT ALLOW** OH– **ALLOW** in either order For reaction with OH^-, **ALLOW** one mark for  **OR** 

					OR  **Examiner's Comments** This question required candidates to apply their knowledge of hydrolysis reactions to ester A. The majority of candidates were able to show 3-bromopropanoic acid and ethanol in the top two boxes to secure two marks. The organic products from the alkaline hydrolysis proved more difficult. Many candidates identified ethanol as a product in one of the lower boxes but lower ability responses showed the ethoxide ion. Some candidates drew the 3-bromopropanoate ion as the other product. Higher ability candidates realised that the Br atom would be replaced by an OH group and the best responses showed the correct carboxylate ion. Examiners were encouraged by the number of excellent responses seen and the majority of candidates scored 4 or 5 marks.
		ii i	hydrolysis ✓	1(AO 1.1)	**IGNORE** 'acid' and 'alkaline'' **IGNORE** nucleophilic substitution
	b		<table><tr><th>Proton environment</th><th>Chemical shift</th><th>Splitting pattern</th></tr><tr><td>1</td><td>3.0–4.3</td><td>Triplet</td></tr><tr><td>2</td><td>2.0–3.0</td><td>Triplet</td></tr><tr><td>3</td><td>3.0–4.3</td><td>Quartet</td></tr><tr><td>4</td><td>0.5–1.9</td><td>Triplet</td></tr></table> **Mark by column** **Chemical shift:** all 4 correct ✓✓ 3 correct ✓ **Splitting pattern: all** 4 correct ✓✓ 3 correct ✓	4(AO 3.1 × 4)	**ALLOW** δ values ± 0.2 ppm, as a range or a value within the range **ALLOW** integers for δ values e.g. 2 is equivalent to 2.0 **ALLOW** quadruplet for quartet **ALLOW** diagrams to show splitting pattern e.g.  for triplet  for quartet **ALLOW** splitting patterns shown as numbers i.e. '3' for triplet, '4' for quartet **Examiner's Comments** This question was answered well and most candidates scored full marks. A common error was the chemical shift of environment **2**, which was sometimes shown as 9.0-10.0. Some candidates gave incorrect splitting patterns for environment **2**, stating it would give a singlet, rather than a triplet. This is presumably the result of focusing on the carbon atom to the right of the environment with no H atoms. Candidates should be reminded to consider adjacent carbon atoms on both sides of a particular environment, rather the just looking in one direction.

	c		 **OR**  **OR**  ✓	1(AO 3.1)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Examiner's Comments** This question required candidates to use both pieces of information to deduce that **B** was a carboxylic acid with two equivalent carbon atoms. Many candidates were able to suggest a suitable structure. However some candidates did not use all the information and it was common to see responses that showed an ester or a straight chain carboxylic acid.
	d		**IF** answer on answer line = 24018, **AWARD** 2 marks **IF** answer on answer line = 27600, **AWARD** 1 mark --- Relative mass of 200 molecules = 200 × 138 = 27600 ✓ M_r of polyester = 27600 – 199 × 18 = 24018 ✓	2(AO 2.2 ×2)	**ALLOW ECF** from incorrect M_r Alternative method based on repeat unit: M_r of 200 repeat units = 200 x 120 = 24000 ✓ M_r of polymer = 24000 + 1 + 17 = 24018 ✓ **Examiner's Comments** A variety of responses was seen in this demanding question. In general candidates adopted one of two approaches. The most common was to multiply the Mr of 2-hydroxybenzoic acid by 200 and then subtract the mass of the 199 water molecules removed during polymerisation. The other approach used the Mr of the repeat unit. This was multiplied by 200 and the mass of H and OH at each end of the polymer was added to give the final answer. Many candidates were successful with the first step of their approach, but the best responses included the second step taking into account the Mr of water. A significant number of candidates used an incorrect value for the Mr in their first step. Candidates are advised to draw out the structure of a compound before determining the Mr. This is particularly important when only a name is given in the question.
	e	i	** Refer to marking instructions on page 4 of mark scheme for guidance on marking this question.* **Level 3 (5-6 marks)** Correct calculation of the mass of $(CH_3)_2CHCHO$. **AND** Planned synthesis includes oxidation of aldehyde and formation of ester **C** with most of the reagents and conditions identified and equations are mostly correct. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.*	6 (AO 3.3 ×6)	**Indicative scientific points may include:** **Calculation of mass of $(CH_3)_2CHCHO$** **Using moles** • $n(\text{ester}) = \frac{12.75}{102.0}$ = 0.125 (mol) • $n((CH_3)_2CHCHO) = 0.125 \times \frac{100}{40}$ = 0.3125 (mol) • Mass of $(CH_3)_2CHCHO$ = 72.0 × 0.3125 = 22.5 g **Using mass** • Theoretical mass of ester $= 12.75 \times \frac{100}{40}$ = 31.875 (g)

Level 2 (3-4 marks)
Calculation of the mass of (CH3)2CHCHO is partly correct
AND
Planned synthesis includes oxidation of aldehyde and formation of ester **C** with some of the reagents and conditions identified
OR
Attempts to calculate mass of (CH3)2CHCHO but makes little progress
AND
Planned synthesis includes oxidation of aldehyde and formation of ester **C** with most of the reagents and conditions identified and equations for each step are mostly correct

There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.

Level 1 (1-2 marks)
Calculation of the mass of $(CH_3)_2CHCHO$ is partly correct
OR
Planned synthesis includes both steps with some of the reagents and conditions identified
OR
Attempts equations for both steps but these may contain errors
OR
Describes one step of the synthesis with reagents, conditions and equation mostly correct

There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks
No response or no response worthy of credit.

- Theoretical $n((CH_3)_2CHCHO) = \frac{31.875}{102}$
  $= 0.3125$ (mol)
- Mass of $(CH_3)_2CHCHO = 72.0 \times 0.3125 = 22.5$ g

ALLOW small slip/rounding errors such as errors in *Mr* e.g. use of 71 instead of 72 for $(CH_3)_2CHCHO$

Examples of partly correct calculations

Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$

(% yield inverted)

Mass = 9.00 g from 0.125×72

(% yield omitted)

Synthesis: reagents and conditions

Step 1: Oxidation of aldehyde $(CH_3)_2CHCHO$

- Reagents: $Cr_2O_7^{2-}/H^+$
- Conditions: reflux
- Equation:
  $(CH_3)_2CHCHO + [O] \rightarrow (CH_3)_2CHCOOH$

Step 2: Formation of ester C

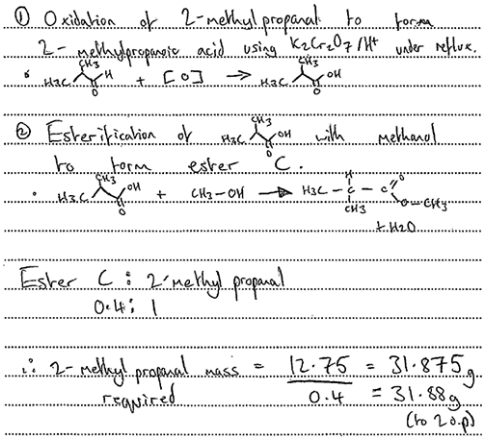
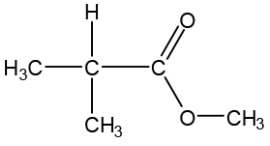
- Reagents: methylpropanoic acid/$(CH_3)_2CHCOOH$ and methanol/CH_3OH
- Conditions: acid (catalyst) reflux/heat
- Equation:

$(CH_3)_2CHCOOH + CH_3OH \rightarrow (CH_3)_2CHCOOCH_3 + H_2O$

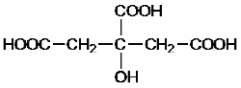
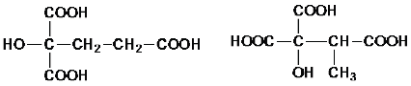
IGNORE attempts to form methanol in synthesis

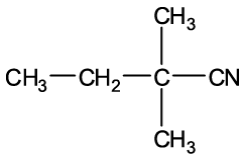
Examiner's Comments

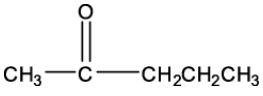
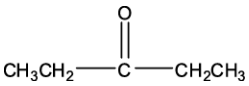
This question was marked using a level of response mark scheme. Most candidates gave a response worthy of at least Level 2 (3-4 marks) by either providing the synthetic steps with reagents and/or equations for the synthesis of ester **C** as well as calculating the mass of 2-methylpropanal required. Exemplar 3, below, shows a frequently seen Level 2 response. The best performing candidates determined the mass correctly and showed the synthesis efficiently, using equations to communicate the preparation of ester **C** and received Level 3 (5-6 marks). Some responses focused solely on the 2-methylpropanal and suggested it would be both oxidised and reduced with each of the products being used to form an ester. Others omitted the mass calculation or gave only a partial synthesis. Such responses received Level 1 (1-2 marks).

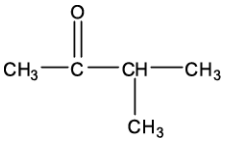
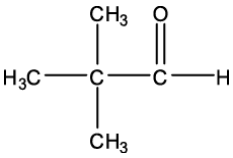
					Exemplar 3  This response includes an excellent description of the synthesis of ester **C**. Each step is labelled clearly with the most of the reagents and conditions stated and correct equations. The candidate makes little progress with the calculation of the mass of 2-methylpropanal required, completing only the first step. This response satisfies the Level 2 criteria. The information is provided is relevant and presented with a clear logical structure and was therefore given the upper mark within the level and achieved four marks. The presentation of the synthesis by equations rather than words is an excellent strategy. Candidates are advised to adopt such an approach in questions like this as it allows them develop and clear line of reasoning without the need to write lots of unnecessary text.
		ii	**Y** (43) = $(CH_3)_2CH^+$ ✓ **Z** (71) $(CH_3)_2CHCO^+$ ✓ *If '+' charge is missing/incorrect but the structures of **both** fragments are correct, award one mark*	2(AO 2.7 × 2)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** positive charge to be anywhere on the structure For **Y** and **Z**, **ALLOW** structure of a feasible fragment ion formed from ester **C**  **Ester C** e.g. **Y** (43) = CH_3OC^+ **Z** (71) = $^+CCOOCH_3$ **ALLOW** 1 mark if both correct **ions** are shown but in the incorrect

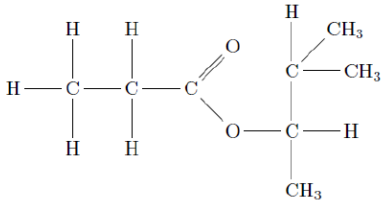
					columns **ALLOW** 1 mark for both correct **ions** if one or both have an 'end bond' **ALLOW** 1 mark if both **ions** are shown using correct molecular formulae **Examiner's Comments** Most candidates were able to provide a correct structure for each of the ions responsible for the peaks labelled **Y** and **Z**. Some candidates omitted the charge, or included 'end bonds'. These responses were able to achieve one mark if both fragments were correct. So the majority of candidates scored one or two marks in this part.
			Total	**22**	
9			C	1	**ALLOW** 3 (This is the number of peaks in the NMR spectrum) **Examiner Comments** This was well answered on the whole, with some candidates failing to include the peak associated with the −COOH part of the molecule. The common incorrect answer was D.
			Total	**1**	
10			*Please refer to marking instructions on page 4 of mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** A comprehensive analysis of the information available with through explanations linked to the evidence. Acid **C** identified as a tricarboxylic acid with a tertiary −OH group and the correct molecular formula of $C_6H_8O_7$. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated* **Level 2 (3–4 marks)** Analysis of the information available but explanations may be incomplete or there may be mistakes in calculations, although the method may be sound. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)**	6	**Indicative scientific points may include Identification of functional groups** • Tribasic acid → three −COOH groups *From 1 mol **C** requires 3 mol NaOH* • Tertiary alcohol *From no colour change with hot acidified dichromate(VI)* **Determination of molecular formula of C** • M(**C**) = $\frac{2.323}{1.21 \times 10^{-2}}$ = 192 (g mol^{-1}) *From 1.21 × 10^{-2} mol **C** has a mass of 2.323 g.* • 192 − 3 × 45 (3 × COOH) − 16 (O) = 41 41 → C_3H_5*(or evidence of working)* • Molecular formula = $C_6H_8O_7$ **Structure of citric acid** • 4 peaks in ^{13}C NMR → 4 types of carbon • Correct structure of **C** matching evidence.

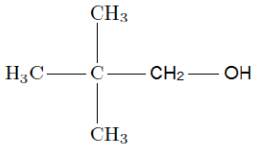
			A simple analysis of the information available and limited explanations which may or may not be explicitly linked to the evidence. *The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.* **0 marks** − No response worthy of credit.		 **NOTE**: Structure below match all evidence except for ^{13}C NMR. See Level 3 criteria. 
			Total	**6**	
1 1			**Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Structure of **J** identified as $CH_3CH_2C(CH_3)_2CN$ **AND/OR** A comprehensive analysis with most of the spectral data analysed and few omissions. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** Analysis may be incomplete and structure of **J** identified. **OR** Thorough analysis of one aspect of the information given in question and structure of **J** may be incorrectly identified. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** An attempt at a simple analysis. **OR** Explains one scientific point thoroughly with a few omissions. *The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.*	6	**LOOK ON THE SPECTRA for labelled peaks.** **Indicative scientific points may include:** **Empirical and Molecular Formula of J** C : H : N = 74.17/12 : 11.41/1 : 14.42/14 6.18 : 11.41 : 1.03 ○ 6 : 11 : 1 ○ Empirical formula of **J** = $C_6H_{11}N$ • uses *m/z* = 97.0 and empirical formula to determine molecular formula of **J** as C_6H_{11}**N** **^{1}H NMR spectrum** • δ = 0.9 ppm, triplet, **CH_3** $-CH_2-(C-)$ • δ = 1.4 ppm, singlet, **$(CH_3)_2$** C^- • δ = 1.6 ppm, quartet, CH_3-**CH_2^-** $(C-)$ **IR Spectrum and Structure of J** ○ peak at 2220−2260 (cm^{-1}) is C≡N ○ Correct structure of **J**

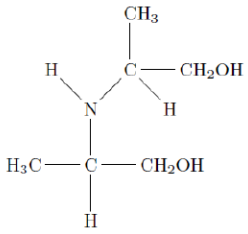
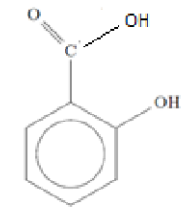
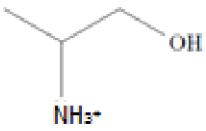
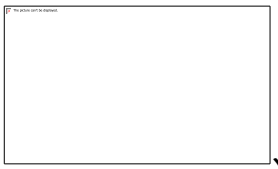
			0 marks No response or no response worthy of credit.		 **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Total	**6**	
12	a	i	**Reagent and observation** sodium carbonate **AND** Fizzing/effervescence/bubbling ✓ **Equation** Correctly balanced equation ✓ e.g. $2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + CO_2 + H_2O$	2	**Note:** both reagent and observation are required for first mark **ALLOW** name or formula for any suitable carbonate e.g $NaHCO_3$, potassium carbonate etc. **ALLOW** reagent from equation if not stated elsewhere
		ii	**Reagent and observation** Tollens' (reagent) **AND** Silver (mirror) ✓ **Equation** RCHO + [O] → RCOOH ✓	2	**Note:** both reagent and observation are required for first mark **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** $H^+/Cr_2O_7^{2-}$ **OR** acidified (potassium/sodium) dichromate **AND** Orange to green *(this would identify the aldehyde from the carboxylic acid, ketone and esters)*
	b		2,4−dinitrophenylhydrazine **AND** Orange/yellow/red precipitate ✓	1	**ALLOW** errors in spelling **ALLOW** 2,4(−)DNP **OR** 2,4(−)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate
	c	i	$CH_3COOC(CH_3)_3 + NaOH \rightarrow CH_3COONa + (CH_3)_3COH$ CH_3COONa ✓ Rest of equation correct ✓ **OR** $(CH_3)_3CCOOCH_3 + NaOH \rightarrow (CH_3)_3CCOONa + CH_3OH$	2	**Note:** the hydrolysis of either ester may be given **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** molecular formulae of products *(question requires structures of products to be shown)*

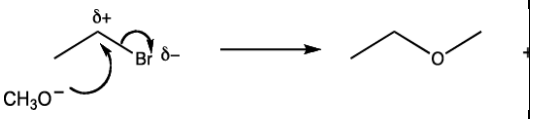
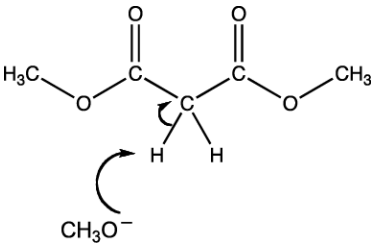
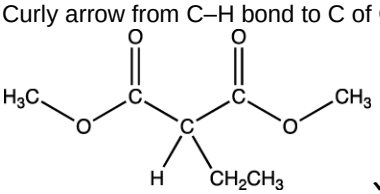
			$(CH_3)_3CCOONa$ ✓ Rest of equation correct ✓		
		ii	**Reagent and observation** $H^+/Cr_2O_7^{2-}$ **OR** acidified (potassium/sodium) dichromate **AND** Orange to green (with CH_3OH) ✓ **Equation** $CH_3OH + [O] \rightarrow HCHO + H_2O$ **OR** $CH_3OH + 2[O] \rightarrow HCOOH + H_2O$ ✓	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** molecular formulae *(question requires structures of organic compounds to be shown)*
		ii i	**^{13}C NMR (1 mark)** (It is) not possible to identify (the esters) with ^{13}C NMR **AND** (both) spectra would contain four peaks (with similar chemical shifts) ✓ **^{1}H NMR (2 marks)** (It is) possible to identify (the esters) with ^{1}H NMR (^{1}H NMR spectrum of) $CH_3COOC(CH_3)_3$ has a singlet/peak between 2.0−3.0 (ppm) (^{1}H NMR spectrum of) $(CH_3)_3CCOOCH_3$ has a singlet/peak between 3.0−4.3 (ppm) All **three** correct statements✓✓ Any **two** correct statements ✓	3	**ALLOW** 'same number of peaks' in place of 'four peaks' **ALLOW** any value or range of values within 2.0−3.0 **ALLOW** any value or range of values within 3.0−4.3
	d		**Possible structures for ketone (2 marks)**  	5	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names of ketones

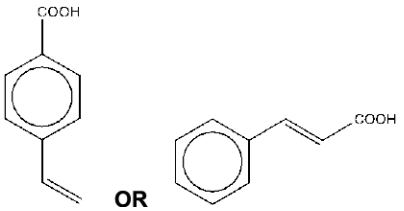
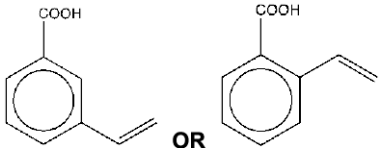
			 All **three** correct ✓✓ Any **two** correct ✓ **<u>Aldehyde (3 marks)</u>** Peak at (δ) 1.2 shows HC–R **AND** No H on adjacent C atom as peak is singlet ✓ Peak at (δ) 9.6 shows H–C=O **AND** No H on adjacent C atom as peak is singlet ✓  **OR** (2,2−)dimethylpropanal ✓		
			Total	**17**	
13			**C**	1	
			Total	**1**	
14	a		<u>Reducing agent</u> $NaBH_4$ / sodium tetrahydridoborate(III) / sodium borohydride✓ <u>Equation</u> $CH_3(CH_2)3CHO + 2[H] \rightarrow CH_3(CH_2)3CH_2OH$ ✓	1	**ALLOW** $LiAlH_4$/lithium tetrahydridoaluminate(III)/lithium aluminium hydride **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above **ALLOW** $C_4H_9CHO + 2[H] \rightarrow C_5H_{11}OH$ **ALLOW** molecular formulae: $C_5H_{10}O + 2[H] \rightarrow C_5H_{12}O$ **DO NOT ALLOW** –COH for aldehyde **Examiner's Comments** Very well answered. The most common error was an incorrect formula for the aldehyde.
	b			7	**ANNOTATE WITH TICKS AND CROSSES ETC**

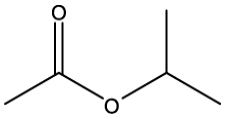
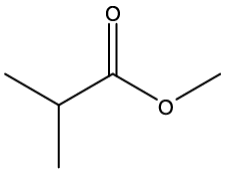
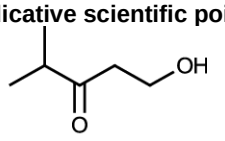
			M1 Compound **F** structure is a secondary alcohol with the formula $C_5H_{11}OH$ ✓ **M2** Compound **F** = $CH_3CH(OH)CH(CH_3)CH_3$ ✓ **M3** Compound **G** = $CH_3COCH(CH_3)CH_3$ ✓ **M4** n(NaOH) = (0.125 x 22.8/1000) = 0.00285 (mol) ✓ **M5** M(compound H) = (0.211/0.00285 =) 74(.0) (g mol^{-1}) ✓ **M6** Compound **H** = / CH_3CH_2COOH ✓ **M7** Compound **I** =  ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **IGNORE** names if structures are given **ALLOW** 3-methylbutan-2-ol if structure not given **ALLOW ECF** from an incorrect secondary alcohol for **M3** e.g. pentan-2-ol → pentan-2-one e.g. pentan-3-ol → pentan-3-one **ALLOW** (3-)methylbutanone if structure not given **IGNORE** any discussion of the reactions of compound **G** with 2,4-dinitrophenylhydrazine and/or Tollens' reagent. **ALLOW 3 SF** up to calculator value correctly rounded **IF** M(compound H) = 74 award 2 marks (M4 + M5) **ALLOW ECF** from incorrect calculation of amount of NaOH **ALLOW** propanoic acid if structure not given **ALLOW ECF** from incorrect compound **F** (alcohol) and/or incorrect compound **H** (carboxylic acid) to form compound **I** (ester). Compounds **F**, **G**, **H** and **I** must be placed in the correct box or correctly labelled for **M2**. **M3**, **M6** and **M7** **Examiner's Comments** A high scoring question with many candidates gaining full marks. Although most realised that Compound F was a secondary alcohol, fewer candidates combined this knowledge with the information provided by carbon-13 NMR to deduce the correct structure of the secondary alcohol.
	c		The structural isomer is:	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous

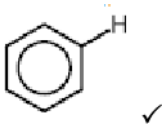
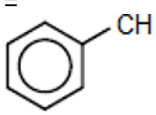
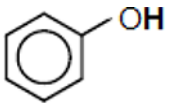
			 ✓		**ALLOW** 2,2-dimethylpropan-1-ol **Examiner's Comments** A good discriminator but many correct structures were seen.
			Total	**10**	
15	a	i	**^{1}H NMR spectrum for 2-aminopropan-1-ol** **Chemical shift, δ/ppm** / **Relative peak area** / **Splitting pattern** 0.8 – 2.0 / 3 / doublet 2.3 – 3.0 / 1 / multiplet 3.3 – 4.2 / 2 / doublet ✓✓✓	3	One mark for each correct row **ALLOW** δ values as a range or a value within the specified range. **ALLOW** δ values +/− 0.2 ppm. **ALLOW** a response that implies a splitting into two for a doublet etc. **ALLOW** sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once **Examiner's Comments** Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.
		ii	M^+ peak at 75 (peak 1) $CH_3CH(NH_2)CH_2OH^+/C_3H_9NO^+$ ✓ Fragment peak at 44 (peak 2) $CH_3CH(NH_2)^+/C_2H_6N^+$ ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous Positive charge is essential but **ALLOW** maximum of one mark if both formulae are correct **AND** neither species has a positive charge **Examiner's Comments** Although peak 2 was often correct, the species responsible for the M+ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.
	b	i	Ethanolic ammonia **OR** ammonia/NH_3 **AND** ethanol ✓	1	**ALLOW** ammonia in a sealed tube **ALLOW** dilute ethanolic ammonia/NH_3 **IGNORE** heat **ALLOW** alcohol for ethanol **DO NOT ALLOW** any reference to water or hydroxide ions **Examiner's Comments**

					A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
		ii	(compound D)  ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **Examiner's Comments** This question discriminated well. Although there were very few blank pages, many incorrect structures were seen.
	c	i	Alcohol **AND** Amide/peptide ✓	1	**IGNORE** phenol **IGNORE** hydroxyl/hydroxy **IGNORE** attempts to classify alcohol or amide as primary, secondary or tertiary **DO NOT ALLOW** hydroxide **Examiner's Comments** Generally well answered but incorrect functional groups included carbonyl and amine.
		ii	 	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** + on N or H i.e. $^{+}NH_3$ or NH_3^{+}**ALLOW** $NH_3^{+}Cl^{-}$ **Examiner's Comments** Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH_2^{+}.
			Total	**10**	
16	a		 ✓	1	
	b	i	$2Na + 2CH_3OH \rightarrow 2Na^{+} + 2CH_3O^{-} + H_2$ ✓	1	**ALLOW** $2Na + 2CH_3OH \rightarrow 2CH_3ONa + H_2$

		ii	 Curly arrow from CH_3O^- to carbon atom of C-Br bond ✓ Dipole shown on C–Br bond, $C^{\delta+}$ and $Br^{\delta-}$ **AND** curly arrow from C–Br bond to the Br atom ✓ Products of reaction (must not be ambiguous) ✓	3	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous. The curly arrow must start from **O atom** of CH_3O^- **AND** must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. **ALLOW** S_N1 Dipole shown on C–Br bond, $C^{\delta+}$ and $Br^{\delta-}$, and curly arrow from C–Br bond to the Br atom. Correct carbocation drawn. **AND** curly arrow from CH_3O^- to carbocation. The curly arrow must start from the oxygen atom of the CH_3O^-, and must start either from a lone pair or from the negative charge.
		ii i	CH_3O^- donates an electron pair **AND** heterolytic fission ✓	1	**ASSUME** 'it' refers to CH_3O^-
	c		**Chemical shift, δ/ppm** / **Relative peak area** / **Splitting pattern** 0.5−1.9 / 3 / Triplet ✓ 3.0−4.3 / 2 / Quartet ✓ 0.5−1.9 / 6 / Doublet ✓ 3.0−4.3 / 1 / Heptet ✓	4	**ALLOW** δ values ± 0.2 ppm, as a range or a value within the range **ALLOW** multiplet for heptet
	d	i	 Curly arrow from CH_3O^- to H of CH_2 ✓ Curly arrow from C–H bond to C of CH_2 ✓  ✓	3	The curly arrow must start from **O atom** of CH_3O^- **AND** must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. **ALLOW** any unambiguous structure, skeletal, displayed, structural or combination.
		ii	CH_3O^- accepted a proton ✓	1	**ASSUME** 'it' refers to CH_3O^-
			Total	**14**	
17			Electrophilic substitution means benzene ring	5	

			Electrophilic addition means alkene / C=C Isomer of $C_9H_8O_2$ containing C=C, benzene ring **AND** COOH Correct isomer:  **OR** justification in terms of number of carbon environments		Concluded using data provided and conclusions from 1st two marks. **ALLOW** 1 mark for:  **OR** (does not gain final justification mark)
			Total	**5**	
18			**Elemental analysis and molecular formula** Use of percentages to give empirical formula $C_5H_{10}O_2$ Evidence of using empirical formula **AND** 102 to give molecular formula = $C_5H_{10}O_2$ **IR Spectrum** Peak at ~1750 **OR** 1630–1820 (cm^{-1}) **AND** C=O **NMR analysis** Peak(s) at (δ) 4.9 shows HC–O **AND** 1 H in environment (peak area) **OR** 6H on adjacent C as peak is multiplet / heptet / septet Peak at (δ) 2.2 shows HC–C=O **AND** 3 H in environment (peak area) **OR** No H on adjacent C as peak is singlet Peak(s) at (δ) 1.3 shows HC–R **AND** 6 H (or 2 × CH_3) in environment (peak area) **OR** 1H on adjacent C as peak is doublet **Structure** Correct structure:	8	**ANNOTATE ANSWER WITH TICKS AND CROSSES** C : H : O = 58.80 / 12 : 9.87 / 1 : 31.33 / 16 = 4.90 : 9.87 : 1.96 = 2.5 : 5.04 : 1 = 5 : 10 : 2 Alternative method: carbon: (102 × 58.80 / 100)/12 = 5 hydrogen: (102 × 9.87 / 100)/1 = 10 oxygen: (102 × 31.33 / 100)/16 = 2 **ALLOW** C=O peak labelled on spectrum **IGNORE** reference to C–O peak **NOTE** each peak can be identified from: • its δ value • a range *e.g.* 'the peak between 1.3−1.4' • its relative peak area • its splitting • labelling on spectrum **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

			 Allow one mark for 		**DO NOT ALLOW ECF** from incorrect molecular formula
			Total	**8**	
19			B	1	
			Total	**1**	
20			** Please refer to the marking instruction point 10 for guidance on how to mark this question.* **Level 3 (5–6 marks)** Structure correct **AND** Analysed all ^{1}H NMR signals with at least two supporting statements made. *The analysis is clear and logically structured. The supporting statements are relevant to the correct structure drawn.* **Level 2 (3–4 marks)** Structure has correct molecular formula **AND** C=O **AND** OH but in incorrect positions **AND** Analysed at least three ^{1}H NMR signals with one or two supporting statements made. *The analysis is presented with some structure. The supporting statements are in the most-part relevant to the structure drawn.* **Level 1 (1–2 marks)** Structure has correct molecular formula **AND** C=O **OR** OH but in incorrect positions. **AND** Analysed at least two ^{1}H NMR signals with no or one supporting statements made. *The analysis is basic and communicated in an unstructured way. The relationship of the supporting evidence to the structure may not be clear.*	6	**Indicative scientific points may be included: Structure** **L** =  **^{1}H NMR spectrum** δ = 3.8 ppm, triplet, 2H — CH_2—**CH_2—O** δ = 3.7 ppm, singlet, 1H — O—**H** δ = 3.1 ppm, triplet, 2H — CH_2—**CH_2C=O** δ = 2.7 ppm, septet, 1H — $(CH_3)_2$C**HC=O** δ = 1.0 ppm, doublet, 6H — **$(CH_3)_2$**CH **Supporting statements** δ = 3.7 ppm lost after D_2O, indicating —O**H** δ = 213 ppm in ^{13}C NMR but no δ = 9–10 ppm in ^{1}H NMR so ketone, **not** aldehyde $M_r(C_3H_6O) = 58$ 116/58 = 2 → $C_6H_{12}O_2$

			0 marks No response or no response worthy of credit.		
			Total	**6**	
21			A	1	
			Total	**1**	
22	a		14 ✓	1	**Examiner's Comments** Almost all candidates scored this mark for counting the peaks in the ^{13}C NMR spectrum.
	b		**NMR analysis** (5 marks) **M1** Peaks between (δ) 7.1 and 7.5 (ppm) **OR** Relative peak area of 7 **OR** Multiplet =  ✓ **M2** Peak at 5.2/5.3 **OR** Relative peak area of 1 = N–**H** ✓ **M3** Peak at 2.3/2.4 **OR** Relative peak area of 2 **OR** Quartet =  **OR** $C_6H_5CH_2$✓ **M4** Peak at 0.7/0.8 **OR** Triplet = R–CH **OR** R–CH_3 ✓	7	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** IGNORE analysis of ^{13}C spectrum Each peak can be identified from its δ value ± 0.2 ppm **ALLOW** (seven) benzene ring protons **OR** aromatic protons **DO NOT ALLOW** benzene ring without reference to protons **ALLOW** C_6H_6 **IGNORE**  **IGNORE** O–**H** , CON**H AND** C=C**H** **ALLOW** quadruplet **IGNORE** C**H**C=O **AND H**C–N **DO NOT ALLOW** triplet = CH_3**OR** CH_2CH_3 This also scores **M4** if triplet is linked to R–CH_3 **ALLOW** CH_3CH_2 described as R–CH_3 and 2 adjacent H

M5

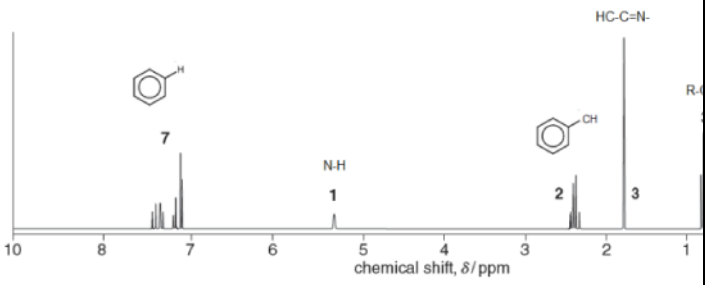
Triplet (at δ 0.7) **AND** quartet (at δ 2.3) = CH_2CH_3

OR triplet at (δ) 0.7 shows (C with) 2 adjacent Hs / protons = CH_2CH_3

OR quartet (at δ 2.3) shows (C with) 3 adjacent Hs / protons = CH_2CH_3 ✓

OR —CH_2– and 3 adjacent H

The information can be presented on the spectrum or in a table.



Chemical shift/ppm	Relative peak area	Splitting pattern	Type of pr
7.1 – 7.5	7	Multiplet	
5.3	1	Singlet	N-H
2.3/2.4	2	Quartet	
1.7/1.8	3	Singlet	HC-C=N
0.7/0.8	3	triplet	R-CH/R-C

QWC: **triplet** or **quartet** spelled correctly in the correct context for **M5**

IGNORE peak in the range 1.6–2.2 = HC–C=N– because this information is given in the question.

H_3C-C=N- scores one mark for the identification of **R^1** or **R^2** (see below)

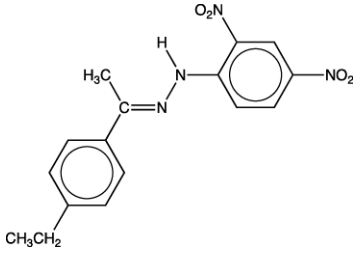
Identification of R^1 and R^2 (2 marks)

Orange precipitate L

ALLOW correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous

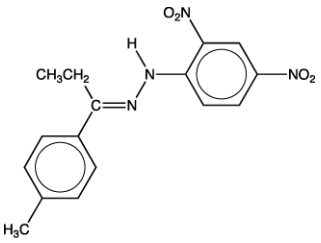
Marks are for structure of R^1 and R^2

Correct structure scores 2 marks



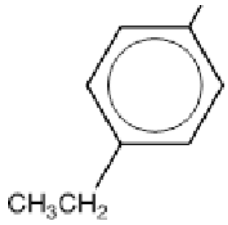
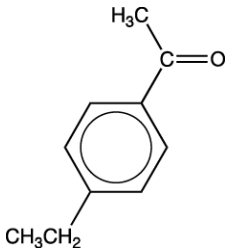
IGNORE errors in the rest of the structure

ALLOW 1 mark for CH_3 and CH_3CH_2 swapped, i.e. the following structure

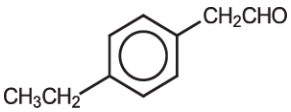


R^1 or **R^2** = $-CH_3$ ✓

ALLOW H_3C–C=N–

			R_1 or **R_2** =  ✓		**MUST BE** 1,4-disubstituted (14 carbon environments in the ^{13}C NMR spectrum **Examiner's Comments** Although the use of 2,4-dinitrophenylhydrazine to detect the presence of a carbonyl group in an organic compound and to identify a carbonyl compound from the melting point of the derivative is required in the specification, the equation for this reaction and the structure of the derivative was not required in the question. The equation for the reaction and the structure of the derivative, with R^1 and R^2 groups from the original carbonyl compound, was given in the question. The structure of carbonyl **K** was similar in complexity to structures featured in previous papers. The mark scheme was constructed so that at least two of the first five marks awarded for the analysis were easily accessible by comparing the chemical shifts in the ^1H NMR spectrum with those displayed in the data sheet. These marks were often achieved by the construction of a clearly labelled and well organised table or by annotating the spectrum. Splitting patterns were well understood but one problem for candidates was the difficulty in associating the peak at δ = 2.3/2.4 ppm with a benzylic hydrogen; many candidates focused more on coupling than on chemical shifts and missed a chance to solve the structure. Of the two marks available for identifying R^1 and R^2, one could be derived quickly by linking information given in the question with one of the peaks in the ^1H NMR spectrum. The second identification mark required careful analysis of both the ^1H NMR and ^{13}C NMR data. Overall, most candidates were able to score marks on this question and completely correct answers were achieved by the most able candidates.
	c		**Carbonyl compound K**  ✓	1	**ALLOW ECF** from incorrect compound **L** Must be a correct carbonyl structure **Examiner's Comments** It was not possible to score a mark for this question unless a structure had been drawn for compound **L**. However, many candidates were able to score this mark as error carried forward from structures that had failed to gain any credit in the previous question were allowable.
	d	i	Radio (waves) ✓	1	**ALLOW** a value in the range 60 – 900 MHz **Examiner's Comments** The interaction of materials with the low-energy radio wave region of the electromagnetic spectrum is described in the specification but this question was surprisingly poorly answered. Infrared, ultraviolet, X-rays and gamma rays were all commonly seen

					answers in addition to ranges of chemical shift quoted from the data sheet.
		ii	The solvent does not have any hydrogen / H / protons ✓	1	**ALLOW** to prevent (^{1}H nuclei from) the solvent from interfering with the NMR spectrum **ALLOW** does not show on the spectrum **ALLOW** no peak / signal (from solvent) **IGNORE** volatility **Examiner's Comments** The need for deuterated solvents was well known but some candidates confused the use of this solvent with the use of TMS as the standard for chemical shift measurements or the identification of O—H and N—H protons by proton exchange using D2O.
			Total	**11**	
23	a		**NMR analysis = 5 marks** **M1:** Peak(s) at (δ) 9.7 = CHO ✓ **M2:** Peak(s) at (δ) 7.1 = C_6H_4 ✓ **M3:** Triplet at (δ) 1.3 / peak at 1.3 **AND** quartet (at δ 2.6) / peak at 2.6 = CH_2CH_3 ✓ **M4:** Triplet at (δ) 9.7 / peak at 9.7 **AND** doublet (at δ 3.7) / peak at 3.7 = CH_2CHO ✓ **M5:** (n+1 rule) Any one of the following	9	**NOTE**: Each peak can be identified from: • its δ value • a range, e.g. “the peak between 0.8 and 2.0” • its relative peak area (beware two peaks with 2 protons) • its splitting (beware two triplets) • labelling on the spectrum **ALLOW** CH_2CHO / aldehyde **IGNORE** reference to phenol **ALLOW** (four) benzene ring proton(s) **IGNORE** reference to phenol **M3** and **M4** Look for a clear link (using words or diagrams) between the two peaks

			○ triplet at (δ) 1.3 shows (C with) 2 adjacent Hs / protons **OR** adjacent CH_2 *(because of splitting: so triplet)* ○ quartet at (δ 2.6 shows) (C with) 3 adjacent Hs / protons **OR** adjacent CH_3 ○ triplet at (δ) 9.7 shows (C with) 2 adjacent Hs / protons **OR** adjacent CH_2 • doublet at (δ 3.7 shows) (C with) 1 adjacent H / proton **OR** adjacent CH ✓ ✎**QWC**: **triplet** spelled correctly in the correct context once		**ALLOW** a response that implies a splitting into three for a triplet / into two for a doublet etc. **ALLOW** "neighbouring" Hs for "adjacent to" Hs **IGNORE** other comments about splitting once **M5** has been awarded **DO NOT ALLOW** one of **M3** or **M4** or **M5** if triplet not seen
			Aldehyde structure = 4 marks  ✓✓✓✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **IF** structure contains C_6H_4 ✓ **IF** structure contains C_6H_4 **AND** the organic structure contains CH_3CH_2 directly attached to the benzene ring **OR** contains CH_2CHO directly attached to the benzene ring ✓✓ **IF** structure has formula $C_{10}H_{12}O$ **AND** structure contains C_6H_4 **AND** the structure contains CH_3CH_2 **AND** contains CH_2CHO **AND** 1,2 **OR** 1,3 substituted ✓✓✓ **IF** structure has formula $C_{10}H_{12}O$ **AND** structure contains C_6H_4 **AND** the structure contains CH_3CH_2 **AND** contains CH_2CHO **AND** 1,4 substituted ✓✓✓✓ (use of ^{13}C data) **Examiner's Comments**

					Good discrimination was achieved in this question. Nearly all could score at least one mark from the first two marking points by identifying the peak associated with the proton in the aldehyde group, or the peak given by benzene ring protons. Many gave a good explanation of a splitting pattern to score the fifth marking point. These marks were often achieved by the construction of a clearly labelled and well organised table. Many were able to suggest a structure for compound **H**. The best candidates included a 1,4 substituted benzene ring after correctly interpreting the information from the carbon-13 NMR spectrum. Candidates should avoid drawing several different structures and not indicating which one they wish to have marked.
	b		TMS / tetramethylsilane (which is the) standard (for chemical shift measurements) ✓	1	**ALLOW** $(CH_3)_4Si$ **ALLOW** TMS is the reference **OR** TMS has δ = 0 (ppm) **OR** for calibration **OR** for comparison **IGNORE** solvent, unreactive, volatile, it gives a sharp peak **Examiner's Comments** This was well answered by the majority of candidates.
			Total	**10**	
24			^{1}H NMR spectrum for serine **chemical shift, δ /ppm** | **relative peak area** | **splitting patt** 2.0 to 3.0 | 1 | triplet 3.3 to 4.2 | 2 | doublet One mark for each correct **row** ✓✓	2	**ALLOW** δ values ± 0.2 ppm, as a range or a value within the range **ALLOW** a response that implies a splitting into three for a triplet / into two for a doublet **Examiner's Comments** Many candidates did not have the skills required to score marks on this question. Errors were made in all three columns and most often in assigning appropriate shift values from the data sheet.
			Total	**2**	
25			**Compound** | **C** | **D** | **E** **Number of peaks** | 5 | 5 | 4 **all** correct ✓	1	**Examiner's Comments** The interpretation of carbon-13 NMR spectra seems to be very well understood and the vast majority of candidates were able to correctly predict the number of peaks for all three compounds.
			Total	**1**	