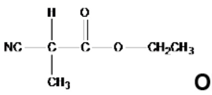
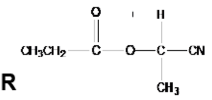
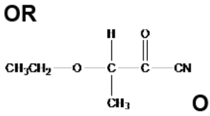
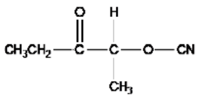
Mark scheme - Spectroscopy

Question			Answer/Indicative content	Marks	Guidance
1	a		*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 **I** has a viable chemical structure of $C_6H_9NO_2$ which has the key features consistent with spectral data **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)** Compound **I** has a viable chemical structure of C6H9NO2 with most of the 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 (AO3.1× 4) (AO3.2× 2)	**Indicative scientific points:** **Empirical and Molecular Formulae** $\begin{array}{lccccccc} & C & : & H & : & N & : & O \\ = & \frac{56.69}{12.0} & : & \frac{7.09}{1.0} & : & \frac{11.02}{14.0} & : & \frac{25.20}{16.0} \\ \textbf{OR} & 4.72 & : & 7.09 & : & 0.787 & : & 1.575 \\ = & 6 & : & 9 & : & 1 & : & 2 \end{array}$ - Empirical formula = $C_6H_9NO_2$ - *m/z* = 127.0 and empirical formula mass (127) used to determine molecular formula as $C_6H_9NO_2$ **Structures of compound I**  **OR**  **OR**  **OR**  **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Key features** - C ≡N - C=O in aldehyde, ketone, ester, amide, acid anhydride - CH_3 group that would give a doublet - CH_3 group that would give a triplet - CH_2 group that would give a quartet **^{1}H NMR and IR analysis** ^{1}H NMR spectrum - δ = 4.2 ppm, quartet, 2H CH3–**CH2**–O - δ = 2.9 ppm, quartet, 1H CO–**CH**–CH3 - δ = 1.7 ppm, doublet, 3H CO–CH–**CH3** - δ = 1.3 ppm, triplet, 3H **CH3**–CH2 IR spectrum - peak at 1750 (cm^{-1}) is C=O - peak at 2280 (cm^{-1}) is C ≡N **ALLOW** ranges from *Data Sheet* **IGNORE** references to C–O peaks **Examiner's Comments** Candidates achieving Level 2 had most of the key features, e.g. CN,

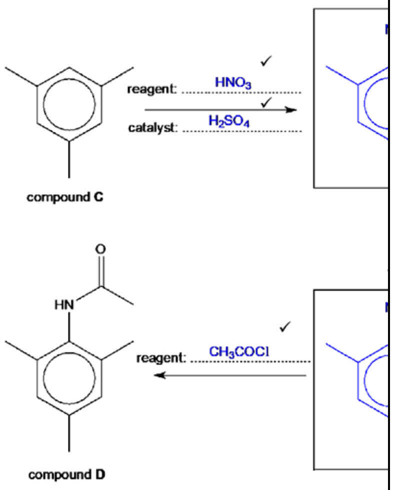
<table>
<tr><td></td><td></td><td></td><td></td><td></td><td>C=O bond and a methyl group but did not consider the splitting patterns seen in the NMR. Most candidates could correctly work out the empirical and molecular formula but then did not use their analysis of the NMR and IR data to suggest a structure. This limited their response to Level 1. The IR spectrum had no O-H peak from an alcohol or carboxylic acid, but candidates often included these groups in their suggested structures.</td></tr>
<tr><td></td><td>b</td><td></td><td>$CDCl_3$ used as a solvent ✓

D_2O used to identify OH OR NH protons ✓</td><td>2
(AO1.1×2)</td><td>Example and use required for each mark

ALLOW for 1 mark, D_2O as a solvent

<u>Examiner's Comments</u>

? Misconception

The use of deuterated compounds in NMR analysis was often explained the use in terms of lack of spin but did not give examples (e.g. CDCl3 as a solvent or D2O as for identifying OH/NH protons)</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>8</td><td></td></tr>
<tr><td>2</td><td></td><td>i</td><td><table><tr><td></td><td>Compound C</td><td>Compound D</td></tr><tr><td>Number of peaks</td><td>3 ✓</td><td>8 ✓</td></tr></table></td><td>2
(AO3.2)</td><td></td></tr>
<tr><td></td><td></td><td>ii</td><td> </td><td>5
(AO3.2×5)</td><td>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous

IGNORE names for organic intermediates (question asks for structures

ALLOW names of reagents and catalyst

Around top arrow, ALLOW 1 of 2 marks if HNO_3 and H_2SO_4 swapped.
i.e.
reagent: ....H_2SO_4........
$\longrightarrow$
catalyst: ....HNO_3........

IGNORE references to concentration

ALLOW $(CH_3CO)_2O$ for left arrow

IGNORE CH_3COOH
IGNORE acyl chloride

DO NOT ALLOW $AlCl_3/FeCl_3/Fe4$</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>7</td><td></td></tr>
<tr><td>3</td><td></td><td>i</td><td></td><td>5 → 4 max</td><td>ANNOTATE WITH TICKS AND CROSSES, etc.
-- ALLOW ORA throughout</td></tr>
</table>

			Comparison of branching and points of contact e.g. $CH_3CH_2CH_2NH_2$ has longer chain / straight chain / no branches **AND** e.g. $CH_3CH_2CH_2NH_2$ has more points of contact / more surface interaction (between molecules) ✓ ***Relative strength of force*** e.g. $CH_3CH_2CH_2NH_2$ has stronger/more induced dipole(–dipole) interactions **OR** London forces ✓ -- ***Hydrogen bonds*** $CH_3CH_2CH_2NH_2$ **OR** $(CH_3)_2CHNH_2$ have hydrogen/H bonds **OR** $(CH_3)_3N$ has no hydrogen/H bonds ✓ ***Relative strength of force*** Hydrogen bonds are stronger than London forces /permanent dipole interactions ✓ --- ***Comparison of energy required to break force*** e.g. More energy to break/overcome London forces/intermolecular forces in $CH_3CH_2CH_2NH_2$ **OR** More energy is needed to break H bonds (than London forces) ✓	(AO 1.2) (AO 2.1) (AO 1.2) (AO 2.1)	**ALLOW** 'The straighter the chain, the more points of contact ….' **IGNORE** comparison using 'primary', 'secondary' and 'tertiary'. *Comparison of branching is required.* For London forces, • **ALLOW** induced dipole(–dipole) interactions • **IGNORE** IDID **OR** van der Waals' forces/VDW **DO NOT ALLOW** $CH_3CH_2CH_2NH_2$ has more electrons *(number of electrons are the same)* **DO NOT ALLOW** 'more energy to break covalent bonds **ALLOW** little energy is required to break London forces (compared with H bonds) **<u>Examiner's Comments</u>** Candidates were expected to explain the different boiling points of three amines. Most candidates linked increased branching with less surface contact between molecules, leading to weaker induced dipole interactions (London forces). Fewer candidates linked the decreasing boiling points to less energy being required to break the intermolecular bonds. The highest performing candidates recognised the large difference between the boiling points of the primary and tertiary amines. They then identified the cause: primary amines form hydrogen bonds but tertiary amines do not. This question was answered reasonably well with fewer candidates than in the past describing relative strengths of covalent bonds, a common misconception.
		ii	**FIRST CHECK MOLECULAR FORMULA and STRUCTURE** **IF** molecular formula = C_5H_{13}**N** **AND** correct structure **AND** evidence of ideal gas equation → **6 marks** Correct up to 87 **AND** $C_5H_{13}N$ → **5 marks** Correct up to 87 → **4 marks** --	6 (AO 2.2×4	**IF** $n = \frac{pV}{RT}$ is omitted, **ALLOW** when values are substituted into rearranged ideal gas equation.

Rearranging ideal gas equation

$n = \frac{pV}{RT}$ ✓

Unit conversion AND substitution into

$n = \frac{\boldsymbol{pV}}{\boldsymbol{RT}}$ **:**

- *R* = 8.314 **OR** 8.31
- *V* = 72(.0) × 10^{-6}
- *T* in K: 373 K

e.g.

$$\frac{1.00 \times 10^5 \times 72.0 \times 10^{-6}}{8.314 \times 373} ✓$$

Calculation of n

n = 2.32 × 10^{-3} (mol) ✓

Calculation of M

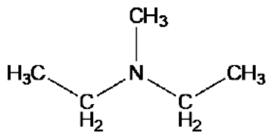
$$M = \frac{0.202}{2.32 \times 10^{-3}} = 87 ✓$$

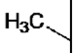
Molecular formula

$C_5H_{13}N$ ✓

Molecular formula required

Structure of amine A from $C_5H_{13}N$ ✓





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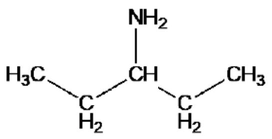

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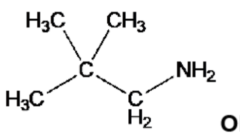

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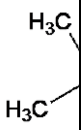


OR

Use of 24000

3 marks max possible for use of 72.0 cm^3 **OR** 0.720 dm^3 by **ECF**

Calculation

e.g. $n = \frac{72.0}{24000} = 3.00 \times$ **No mark** *(calculati*

)

(AO 3.2)

(AO 3.2)

Calculator: *n* = 2.321740325 × 10^{-3} from 8.314

From 8.31, n = 2.322857889 × 10^{-3}

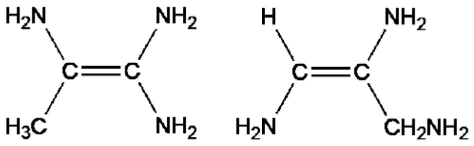
ALLOW elements in any order

ALLOW molecular formula = $C_3H_9N_3$

ALLOW other molecular formulae of an amine that has *M* = 87, e.g. C_4H_9NO

ALLOW any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

ALLOW structures below from molecular formula = $C_3H_9N_3$



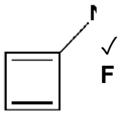
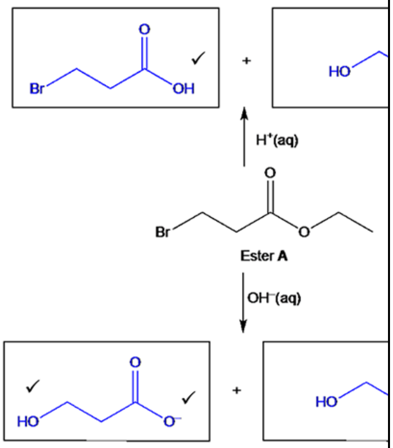
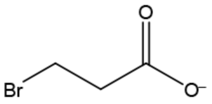
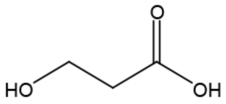
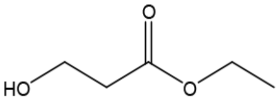
ALLOW ECF but only if structure has calculated M_r **AND** has 3 peaks in ^{13}C NMR spectrum.

__**Examiner's Comments**__

Most candidates rearranged the ideal gas equation correctly to make *n* the subject. They then substituted correct values for *p*, *V*, *R* and *T* into the equation, with correct unit conversions. Most candidates then calculated *n* correctly as 2.32 × 10^{-3} and combined this value with the mass of 0.202 g to derive the molecular formula as 87.

Lower-attaining candidates often made an error in their conversion of cm^3 into m^3, by multiplying by 10^{-3} rather than 10^{-6}. This error resulted in a value of *n* as 2.32 and the unrealistic molecular mass of 8.7 × 10^{-3}, from which a molecular formula is impossible. Candidates in this position are advised to check back at the unit conversions in the working. Very few candidates did not convert 100°C into 373 K.

Candidates with the correct molecular formula of 87 usually suggested

			on much simpler) $M = \frac{0.202}{3.00 \times 10^{-3}} = 67.3$ (✓ **ECF** **Molecular formula** = C_4H_5N ✓ **ECF** **Structure**  ✓ **ECF**		C5H13N as the molecular formula. A significant number quoted $C_5H_{11}NH_2$. This response was not credited as it is not a 'molecular' formula. There are several possible structures of $C_5H_{13}N$ with three ^{13}C NMR peaks and any were credited. Error carried forward was applied from a different molecular mass for both the molecular formula and a structure. This emphasises the importance of working within calculation; credit will always be given for a correct method. Instead of using the ideal gas equation, some candidates used the molar gas constant at room temperature and pressure, 24.0 dm3, which gives a molecular mass of 67. This simplified approach could only gain the final 2 marks for this question: a molecular formula (with an error carried forward value of 67, e.g. C_4H_5N) and a structure of an amine with this molecular formula and 3 peaks in the ^{13}C NMR spectrum.
			Total	**10**	
4	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 **<u>Examiner's Comments</u>** 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**  **OR**  **DO NOT ALLOW** OH– **ALLOW** in either order For reaction with OH⁻, **ALLOW** one mark for  **OR**  **OR** 

<table>
<tr><td></td><td></td><td></td><td></td><td></td><td><u>Examiner’s Comments</u>

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.</td></tr>
<tr><td></td><td></td><td>iii</td><td>hydrolysis ✓</td><td>1(AO 1.1)</td><td>IGNORE ‘acid’ and ‘alkaline’’
IGNORE nucleophilic substitution</td></tr>
<tr><td></td><td>b</td><td></td><td>
<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 ✓</td><td>4(AO 3.1 × 4)</td><td>ALLOW δ values ± 0.2 ppm, as a range or a value within the range

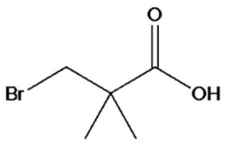
ALLOW integers for δ values
e.g. 2 is equivalent to 2.0

ALLOW quadruplet for quartet

ALLOW diagrams to show splitting pattern
e.g.
 for triplet
 for quartet

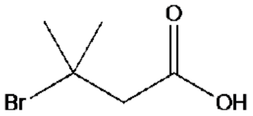
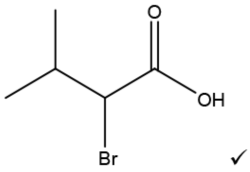
ALLOW splitting patterns shown as numbers
i.e. ‘3’ for triplet, ‘4’ for quartet

<u>Examiner’s Comments</u>

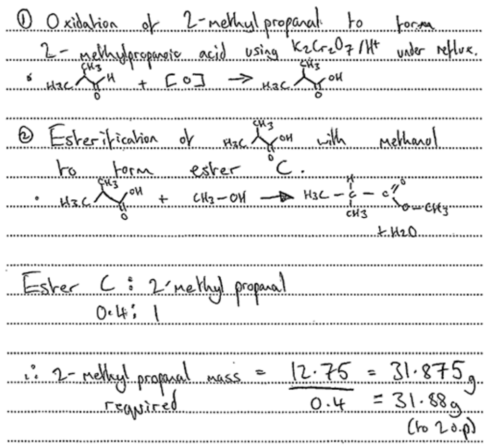
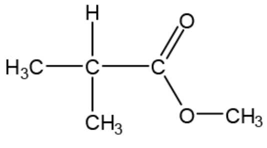
This question was answered well and most candidates scored full marks. A common error was the chemical shift of environment 2, which was sometimes shown as 9.0-10.0. Some candidates gave incorrect splitting patterns for environment 2, stating it would give a singlet, rather than a triplet. This is presumably 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.</td></tr>
<tr><td></td><td>c</td><td></td><td>
OR</td><td>1(AO 3.1)</td><td>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous

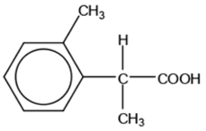
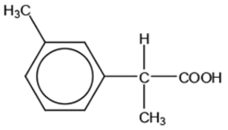
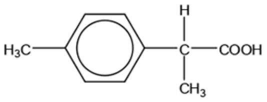
<u>Examiner’s Comments</u>

This question required candidates to use both pieces of information to deduce that B was a carboxylic acid with two equivalent carbon atoms.</td></tr>
</table>

			 **OR**  ✓		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.* **Level 2 (3-4 marks)** Calculation of the mass of (CH3)2CHCHO is partly correct **AND** Planned synthesis includes	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) • Theoretical $n((CH_3)_2CHCHO) = \frac{31.875}{102}$ = 0.3125 (mol) • Mass of $(CH_3)_2CHCHO$ = 72.0 × 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 $0.125 \times \frac{40}{100} \times 72$

			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.		*(% 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**

					 ① Oxidation of 2-methylpropanal to form 2-methylpropanoic acid using $K_2Cr_2O_7/H^+$ under reflux. + [O] → ② Esterification of ... with methanol to form ester C. + CH_3-OH → + H_2O Ester C : 2-methyl propanal 0.4 : 1 ∴ 2-methyl propanal mass required = $\frac{12.75}{0.4}$ = 31.875 g = 31.88 g (to 2 d.p) 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 **<u>Examiner's Comments</u>** 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**	
5			_* 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.  **OR**  **OR**  **<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 $C_6\mathbf{H}_4$– **ALLOW** approximate values for chemical shifts. **IR:**

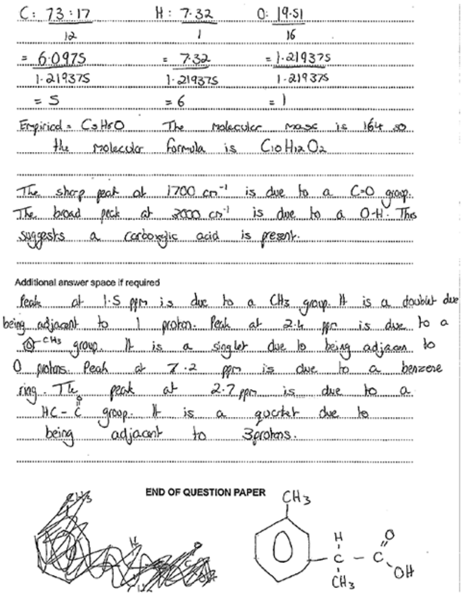
- peak at 2300–3700 (cm^{-1}) is O–H
- peak at ~1720 (cm^{-1}) is C=O
- unknown is a carboxylic acid

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: $\frac{73.17}{12}$ H: $\frac{7.32}{1}$ O: $\frac{19.51}{16}$

$= \frac{6.0975}{1.219375}$ $= \frac{7.32}{1.219375}$ $= \frac{1.219375}{1.219375}$

= 5 = 6 = 1

Empirical = C_5H_6O The molecular mass is 164 so the molecular formula is $C_{10}H_{12}O_2$

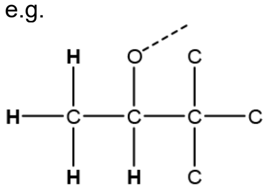
The sharp peak at 1700 cm^{-1} is due to a C=O group. The broad peak at 3000 cm^{-1} is due to a O-H. This suggests a carboxylic acid is present.

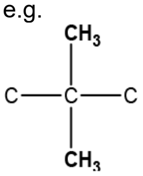
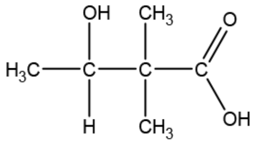
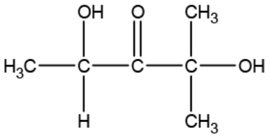
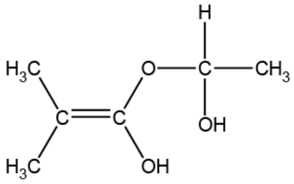
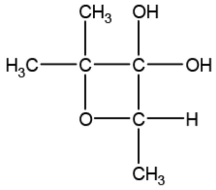
Additional answer space if required

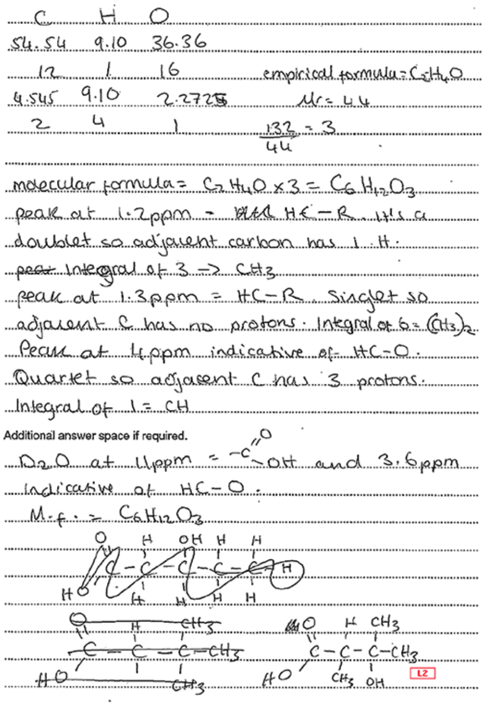
Peak at 1.5 ppm is due to a CH_3 group. It is a doublet due to being adjacent to 1 proton. Peak at 2.4 ppm is due to a ⌬-CH_3 group. It is a singlet due to being adjacen to 0 protons. Peak at 7.2 ppm is due to a benzene ring. The peak at 2.7 ppm is due to a HC-C(=O) group. It is a quartet due to being adjacent to 3protons.

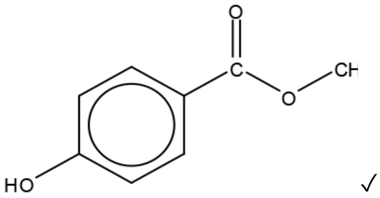
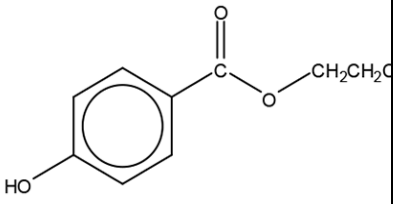
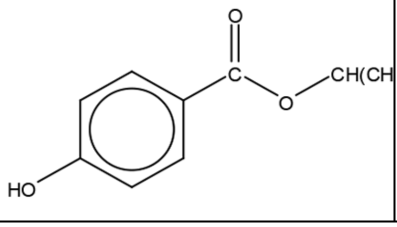
END OF QUESTION PAPER

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**	
6			*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.	**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

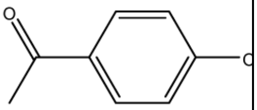
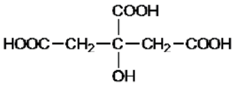
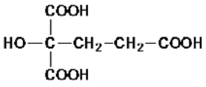
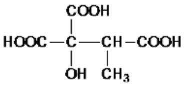
			There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. **0 marks** No response or no response worthy of credit.		e.g.  Examples of structures consistent with splitting and chemical shift in NMR     **Note:** there may be other possible structures 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  C H O 54.54 9.10 36.36 12 1 16 empirical formula = C_2H_4O 4.545 9.10 2.2725 Mr = 44 2 4 1 $\frac{132}{44} = 3$ molecular formula = $C_2H_4O \times 3 = C_6H_{12}O_3$ peak at 1.2ppm = ~~[illegible]~~ HC−R. It's a doublet so adjacent carbon has 1 H. ~~peak~~ Integral of 3 => CH_3 peak at 1.3ppm = HC−R. Singlet so adjacent C has no protons. Integral of 6 = $(CH_3)_2$ Peak at 4ppm indicative of HC−O. Quartet so adjacent C has 3 protons. Integral of 1 = CH Additional answer space if required. D_2O at 11ppm = −COOH and 3.6ppm indicative of HC−O. M.f. = $C_6H_{12}O_3$ L2 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**	
7		i	**FIRST CHECK ANSWER ON ANSWER LINE IF answer = 7.5 × 10^{-4} award 2 marks** -- **[K] in mol dm^{-3}** $\frac{9.13 \times 10^{-2}}{166} = 5.50 \times 10^{-4}$ (mol dm^{-3} **[L] from peak areas**	**2**	**If there is an alternative answer, Apply ECF** **Alternative method** **[K] in g dm^{-3} with peak area of 5.9** $9.13 \times 10^{-2} \times \frac{5.9}{4.3}$ **OR** $9.13 \times 10^{-2} \times 1.37$ = 0.125 **OR** 0.13 (g dm^{-3}) ✓ Calculator: 0.125272093 **[L] in mol dm^{-3}**

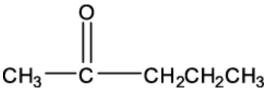
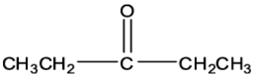
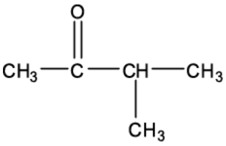
			$5.50 \times 10^{-4} \times \frac{5.9}{4.3}$ **OR** $5.50 \times 10^{-4} \times 1.37.....$ $= 7.5 \times 10^{-4}$ (mol dm^{-3}) ✓ ***2 SF Required***		**OR** $\frac{0.125}{166}$ = $\mathbf{7.5 \times 10^{-4}}$ $\frac{0.13}{166}$ = $\mathbf{7.8 \times 10^{-4}}$ (mol dm^{-3}) ✓ --- **Common errors:** **Common errors:** **Award 1 mark for:** • 0.099(from $\frac{9.13 \times 10^{-2}}{166} \times 180$) • 6.9×10^{-4} (from $\frac{0.125}{180}$) • 7.2×10^{-4} (from $\frac{0.13}{180}$) • 7.0×10^{-4} (from $\frac{0.25272093}{180}$) **<u>Examiner's Comments</u>** This question required candidates to apply their knowledge of gas chromatography and the mole to solve this problem. Most candidates recognised the need to use the relative peak areas to determine the relative proportion of **M**. Many also realised that division by the molar mass was required to ensure the final answer was given in mol dm^{-3}. However, some used molar mass of **M** rather than **K** in this step, leading to an answer of 7.0×10^{-4} mol dm^{-3}. Answer = 7.5×10^{-4} mol dm^{-3}
		ii	**ester J**  ✓ **esters L and M**  	3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **L** and **M** can be identified either way round **IGNORE** 'C_3H_7' in **L** and/or **M** as ambiguous *(question requires structures)* **IGNORE** connectivity of phenol OH group *(marks are for structures of alkyl groups)* **<u>Examiner's Comments</u>** Examiners were encouraged by the number of good responses to this problem solving question. Most candidates achieved at least one mark in this part, often from a correct structure of **J**. Although many candidates deduced that the R group for both **L** and **M** consisted of 3 C atoms and 7 H atoms, only the highest ability candidates were able to join these correctly. A small but significant number of responses showed R groups

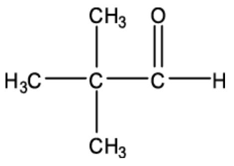
					that involved O atoms, despite the prompt that the R represented an alkyl group. Candidates are advised to read questions carefully.
			Total	**5**	
8		i	**Number of peaks 2 marks** 2-nitrophenol **AND** 3-nitrophenol have **six** peaks/environments/types of carbon ✓ 4-nitrophenol has **four** peaks/environments/types of carbon ✓ **Statement 1 mark** 4-nitrophenol can be distinguished **OR** 2-nitrophenol and 3-nitrophenol cannot be distinguished ✓	**3**	**IGNORE** any numbers shown on structures **ALLOW** 1 mark only **IF** a response identifies that all the compounds have 6 peaks/environments/types of C **OR** all the compounds have 4 peaks/environments/types of carbon **IGNORE** chemical shifts **DO NOT ALLOW ECF** from an incorrect number of peaks/environments/types of carbon **Examiner's Comments** This question required candidates to apply their knowledge of ^{13}C NMR spectroscopy to deduce the number of different carbon environments in each of the nitrophenols shown. The best responses were succinct, stating that it is possible to distinguish 4-ntirophenol from the other two after deducing the correct number of carbon environments for each compound. Lower ability candidates' responses did not identify the symmetry in 4-nitrophenol and suggested all three compounds would produce six peaks, therefore making it impossible to distinguish between them.
		ii	(In phenol) a (lone) pair of electrons on O is(partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ **ORA** (phenol) is more susceptible to electrophilic attack **OR** (phenol) attracts/accepts electrophile/HNO_3 more **OR** (phenol) polarises electrophile/HNO_3 more ✓ **ORA**	**3**	**ALLOW** the electron pair in the p-orbitals of the O atom becomes part of the π-system / ring **ALLOW** diagram to show movement of lone pair into ring **ALLOW** lone pair of electrons on O is (partially) drawn/attracted/pulled/ into π-system / ring **IGNORE** activating **IGNORE** charge density **IGNORE** electronegativity **IGNORE** phenol reacts more readily *(no reference to electrophile)* **ALLOW** NO_2^+ for electrophile **Examiner's Comments** The relative reactivity of phenol is well known by candidates at this level and the majority scored two or three marks. Candidates who did not score full marks gave imprecise or vague explanations. This included reference to 'higher charge density' or 'higher electronegativity' of the phenol ring, rather than 'higher electron density'.

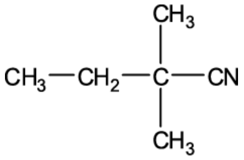
			Total	**6**	
9	a		**Empirical formula** Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓ Empirical formula = C_4H_4O ✓ **Molecular formula** Molecular formula = $C_8H_8O_2$ **AND** Evidence of 136 in working or from labelled peak in spectrum ✓	**3**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$ **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** 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 –	**3**	**ALLOW** peaks to be identified by: • 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

			30 ppm ✓ **Structure** 		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**	
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)** 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.	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** • $M(\mathbf{C}) = \frac{2.323}{1.21 \times 10^{-2}} = 192$ (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.  $HOOC{-}CH_2{-}\underset{OH}{\overset{COOH}{C}}{-}CH_2{-}COOH$ **NOTE**: Structure below match all evidence except for ^{13}C NMR. See Level 3 criteria.  $HO{-}\underset{COOH}{\overset{COOH}{C}}{-}CH_2{-}CH_2{-}COOH$  $HOOC{-}\underset{OH}{\overset{COOH}{C}}{-}\underset{CH_3}{CH}{-}COOH$

			Total	**6**	
11	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** $RCHO + [O] \rightarrow RCOOH$ ✓	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** $(CH_3)_3CCOOCH_3 + NaOH \rightarrow (CH_3)_3CCOONa + CH_3OH$ $(CH_3)_3CCOONa$ ✓ Rest of equation correct ✓	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)*
		ii	**Reagent and observation** $H^+/Cr_2O_7^{2-}$ **OR** acidified (potassium/sodium) dichromate **AND** Orange to green (with CH_3OH) ✓ **Equation**	2	

			$CH_3OH + [O] \rightarrow HCHO + H_2O$ **OR** $CH_3OH + 2[O] \rightarrow HCOOH + H_2O$ ✓		**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)*
		iii	**^{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) ✓ **^1H NMR (2 marks)** (It is) possible to identify (the esters) with ^1H NMR (^1H NMR spectrum of) $CH_3COOC(CH_3)_3$ has a singlet/peak between 2.0−3.0 (ppm) (^1H 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		<u>**Possible structures for ketone (2 marks)**</u>  $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$  $CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$  $CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{\|}}{CH}-CH_3$ All **three** correct ✓✓ Any **two** correct ✓	5	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names of ketones

			Aldehyde (3 marks) 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**	
12			**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*	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, $\mathbf{CH_3}$ $-CH_2-(C-)$ • δ = 1.4 ppm, singlet, $\mathbf{(CH_3)_2}$ C^- • δ = 1.6 ppm, quartet, $CH_3-\mathbf{CH_2}^-$ (C₋) **IR Spectrum and Structure of J** ○ peak at 2220−2260 (cm^{-1}) is C≡N

<table>
<tr>
<td></td><td></td><td></td>
<td>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.
0 marks
No response or no response worthy of credit.</td>
<td></td>
<td>○ Correct structure of J

$CH_3-CH_2-C(CH_3)_2-CN$
ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</td>
</tr>
<tr>
<td></td><td></td><td></td>
<td>Total</td>
<td>6</td>
<td></td>
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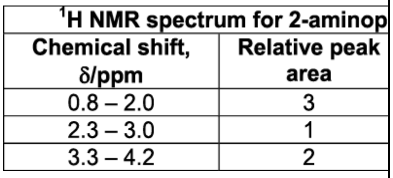
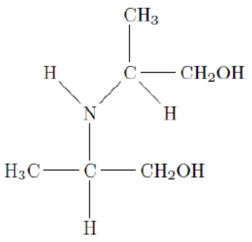
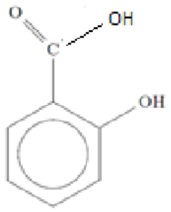
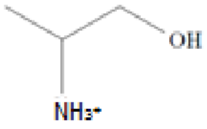
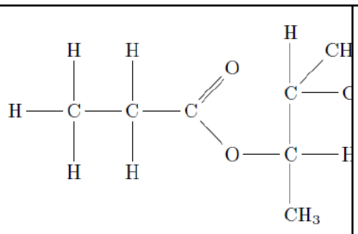
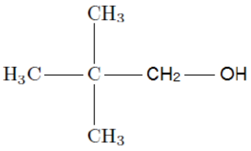
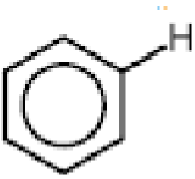
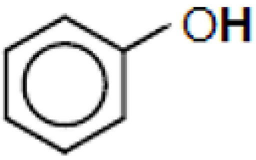
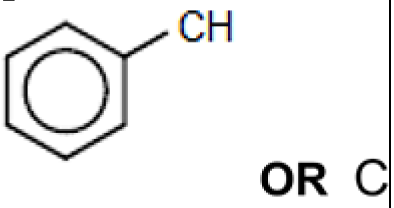
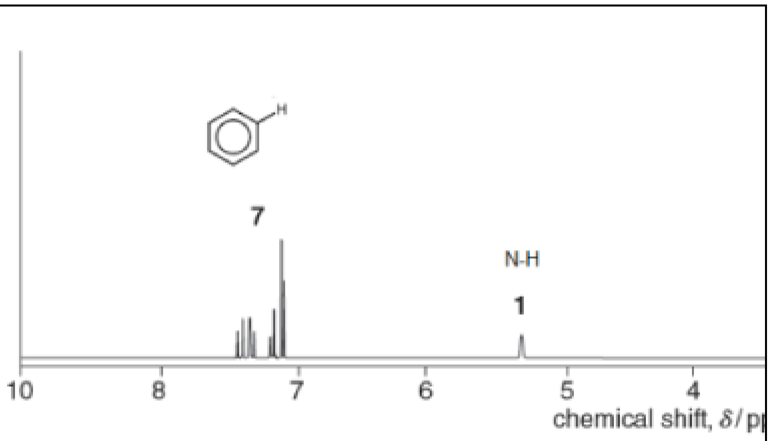
<tr>
<td>13</td><td>a</td><td>i</td>
<td>
<table>
<tr><th colspan="2">^{1}H NMR spectrum for 2-aminop</th></tr>
<tr><th>Chemical shift, δ/ppm</th><th>Relative peak area</th></tr>
<tr><td>0.8 – 2.0</td><td>3</td></tr>
<tr><td>2.3 – 3.0</td><td>1</td></tr>
<tr><td>3.3 – 4.2</td><td>2</td></tr>
</table>
✓✓✓</td>
<td>3</td>
<td>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.</td>
</tr>
<tr>
<td></td><td></td><td>ii</td>
<td><u>M$^+$ peak at 75</u> (peak 1)
$CH_3CH(NH_2)CH_2OH^+$/$C_3H_9NO^+$
✓
<u>Fragment peak at 44</u> (peak 2)
$CH_3CH(NH_2)^+$/$C_2H_6N^+$
✓</td>
<td>2</td>
<td>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.</td>
</tr>
</table>

	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**	
14	a		<u>Reducing agent</u> $NaBH_4$ / sodium tetrahydridoborate(III) / sodium borohydride✓ <u>Equation</u>	1	**ALLOW** $LiAlH_4$/lithium tetrahydridoaluminate(III)/lithium aluminium hydride **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above

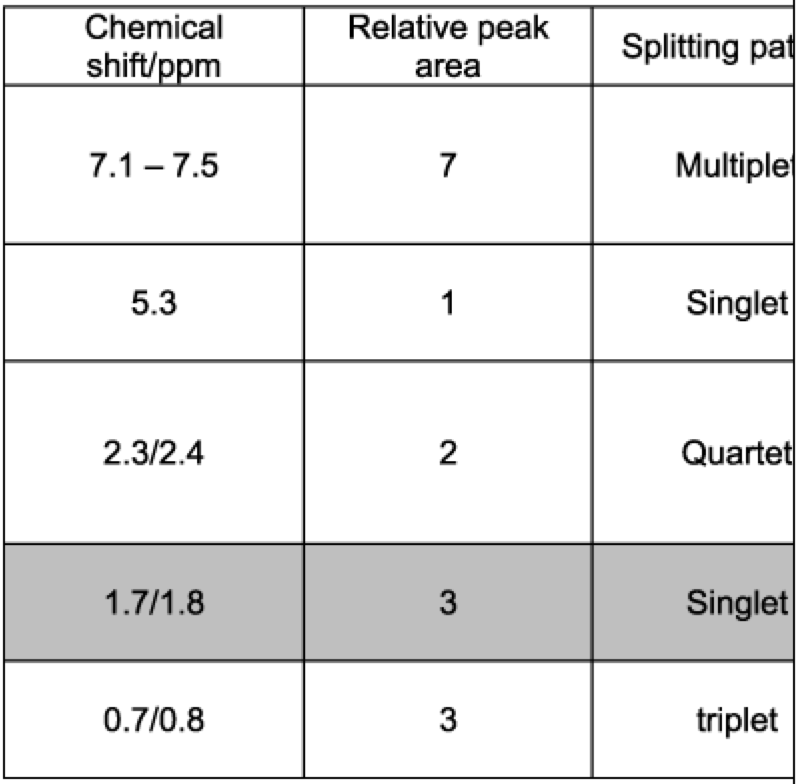
			$CH_3(CH_2)3CHO + 2[H] \rightarrow$ $CH_3(CH_2)3CH_2OH$ ✓		**ALLOW** $C_4H_9CHO + 2[H]$ $\rightarrow C_5H_{11}OH$ **ALLOW** molecular formulae: $C_5H_{10}O + 2[H] \rightarrow C_5H_{12}O$ **DO NOT ALLOW** –COH for aldehyde **Examiner's Comments** Very well answered. The most common error was an incorrect formula for the aldehyde.
	b		**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** =	7	**ANNOTATE WITH TICKS AND CROSSES ETC** **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	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.
	b		14 ✓	1	**Examiner's Comments** Almost all candidates scored this mark for counting the peaks in the ^{13}C NMR spectrum.
	c		**NMR analysis** (5 marks) **M1**	7	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** IGNORE analysis of ^{13}C spectrum

			Peaks between (δ) 7.1 and 7.5 (ppm) **OR** Relative peak area of 7 **OR** Multiplet =  ✓		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** 
			M2 Peak at 5.2/5.3 **OR** Relative peak area of 1 = N–**H** ✓		**IGNORE** O–**H** , CON**H** **AND** C=C**H**
			M3 Peak at 2.3/2.4 **OR** Relative peak area of 2 **OR** Quartet =  ✓		**ALLOW** quadruplet **IGNORE** C**H**C=O **AND** **H**C–N **DO NOT ALLOW** triplet = CH_3 **OR** CH_2CH_3
			M4 Peak at 0.7/0.8 **OR** Triplet = R–CH **OR** R–CH_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 **OR** —CH_2– and 3 adjacent H The information can be presented on the spectrum or in a table.
			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 ✓		



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



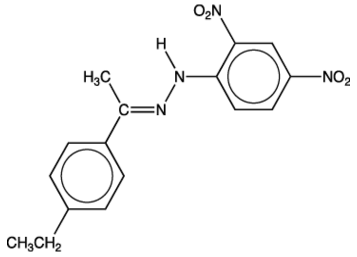
Chemical shift/ppm	Relative peak area	Splitting pat
7.1 – 7.5	7	Multiple
5.3	1	Singlet
2.3/2.4	2	Quartet
1.7/1.8	3	Singlet
0.7/0.8	3	triplet

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 **R¹** or **R²** (see below)

Identification of R¹ and R² (2 marks)

Orange precipitate L

Correct structure scores 2 marks



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

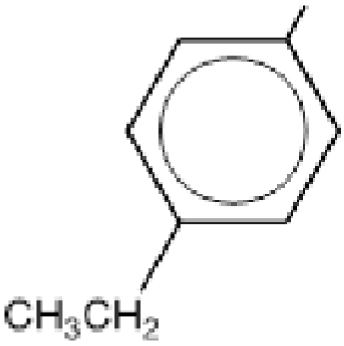
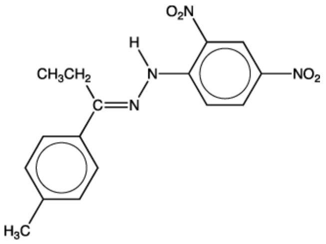
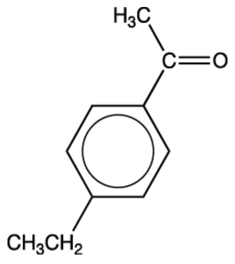
R¹ or **R²** = −CH_3 ✓

R₁ or **R₂** =

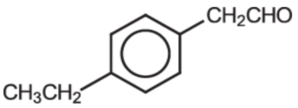
Marks are for structure of R^1 and R^2

IGNORE errors in the rest of the structure

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

					 **ALLOW** H_3C–C=N– **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 ^{1}H 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 ^{1}H NMR spectrum. The second identification mark required careful analysis of both the ^{1}H 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.
	d		**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.
			Total	**11**	

16	a		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.
	b		**NMR analysis = 5 marks**	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
			M1: Peak(s) at (δ) 9.7 = CHO ✓		**ALLOW** CH_2CHO / aldehyde **IGNORE** reference to phenol
			M2: Peak(s) at (δ) 7.1 = C_6H_4 ✓		**ALLOW** (four) benzene ring proton(s) **IGNORE** reference to phenol
			M3: Triplet at (δ) 1.3 / peak at 1.3 **AND** quartet (at δ 2.6) / peak at 2.6 = CH_2CH_3 ✓		**M3** and **M4** Look for a clear link (using words or diagrams) between the two peaks
			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 ○ triplet at (δ) 1.3 shows (C with) 2 adjacent Hs / protons **OR** adjacent CH_2 *(because of splitting: so triplet)*		**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

			○ 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		**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

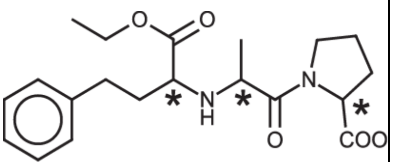
<table>
<tr><td></td><td></td><td></td><td></td><td></td><td>benzene ring protons. Many gave a good explanation of a splitting pattern to score the fifth marking point. These marks were often achieved by the construction of a clearly labelled and well organised table.

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.</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>10</td><td></td></tr>
<tr><td>17</td><td></td><td></td><td><table><tr><td>Compound</td><td>C</td><td>D</td></tr><tr><td>Number of peaks</td><td>5</td><td>5</td></tr></table>
all correct ✓</td><td>1</td><td>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.</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>1</td><td></td></tr>
<tr><td>18</td><td>a</td><td></td><td><table><tr><td colspan="2">^{1}H NMR spectrum for se</td></tr><tr><td>chemical shift, δ /ppm</td><td>relative peak area</td></tr><tr><td>2.0 to 3.0</td><td>1</td></tr><tr><td>3.3 to 4.2</td><td>2</td></tr></table>
One mark for each correct row ✓✓</td><td>2</td><td>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.</td></tr>
<tr><td></td><td>b</td><td>i</td><td> </td><td>1</td><td>ALL correct for one mark

Examiner's Comments

This part was answered well by many candidates. Some missed the chiral centre on the proline moiety or added an asterisk to a carbonyl carbon.</td></tr>
<tr><td></td><td></td><td>ii</td><td><i>any two from:</i>

no / fewer side effects

increases the (pharmacological) activity / effectiveness

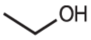
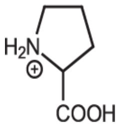
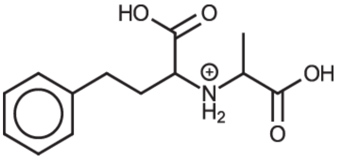
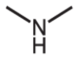
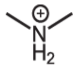
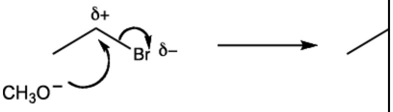
Reduces / stops the need for / cost / difficulty in separating stereoisomers / optical isomers ✓✓</td><td>2</td><td>IGNORE toxic / harmful

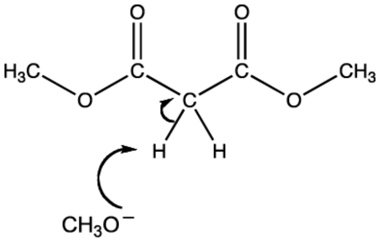
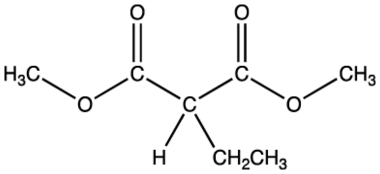
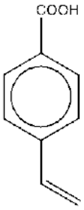
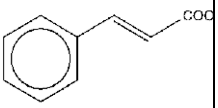
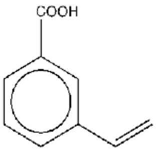
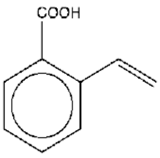
IGNORE a response that implies a reduced dose

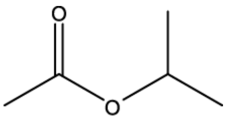
IGNORE “it takes (less) time to separate”

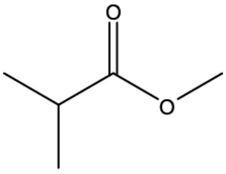
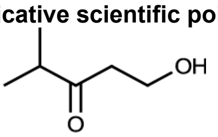
Examiner's Comments

Most candidates gained this mark by stating that the use of a single stereoisomer results in fewer side effects and increased pharmacological activity. Vague answers and comments about a reduced dose did not score marks.</td></tr>
</table>

		iii	 ✓ one mark for ethanol  ✓ one mark for proline with NH **OR** NH_2^+  ✓ one mark for remaining fragment with  or  ✓ **Fourth** mark for structure of **both** ions shown correctly with NH_2^+	4	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** + charge on H of NH_2 groups, *i.e.* NH_2^+ **IGNORE** negative (counter) ions **Examiner's Comments** This question discriminated well. Most candidates were able to score one mark for the formula of ethanol. Only a small number of able candidates scored full marks for including the correct formulae for the protonated amine groups formed during acid hydrolysis.
		iv	idea of separating (the components / compounds) **AND** idea of (identifying compounds by) comparison with a (spectral) database ✓	1	**ALLOW** (identifies compounds) using fragmentation (patterns) / fragment ions (but **IGNORE** molecular ions) **IGNORE** retention times **Examiner's Comments** To get the mark for this question candidates had to include points about the separation of the mixture and identification of the compounds. Answers based on identification using retention times or measurement of molar mass did not score the mark.
			Total	**10**	
19	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 ✓	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.

			Products of reaction (must not be ambiguous) ✓		**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.
		iii	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**	
20			Electrophilic substitution means benzene ring Electrophilic addition means alkene / C=C Isomer of $C_9H_8O_2$ containing C=C, benzene ring **AND** COOH Correct isomer:  **OR** 	5	Concluded using data provided and conclusions from 1st two marks. **ALLOW** 1 mark for:  **OR**  (does not gain final justification mark)

<table>
<tr><td></td><td></td><td></td><td>justification in terms of number of carbon environments</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>5</td><td></td></tr>
<tr><td rowspan="2">21</td><td rowspan="2"></td><td rowspan="2"></td><td rowspan="2">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:

Allow one mark for</td><td rowspan="2">8</td><td>ANNOTATE ANSWER WITH TICKS AND CROSSES
<table>
<tr><td>C : H : O</td><td>=</td><td>58.80 / 12</td><td>:</td><td>9.87 / 1</td><td>:</td><td>31.33 / 16</td></tr>
<tr><td></td><td></td><td>4.90</td><td>:</td><td>9.87</td><td>:</td><td>1.96</td></tr>
<tr><td></td><td></td><td>2.5</td><td>:</td><td>5.04</td><td>:</td><td>1</td></tr>
<tr><td></td><td></td><td>5</td><td>:</td><td>10</td><td>:</td><td>2</td></tr>
</table>
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 <i>e.g.</i> ‘the peak between 1.3−1.4’
• its relative peak area
• its splitting
• labelling on spectrum</td></tr>
<tr><td>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
DO NOT ALLOW ECF from incorrect molecular formula</td></tr>
</table>

					
			Total	**8**	
22			** 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.* **0 marks** No response or no response worthy of credit.	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 → $C_6H_{12}O_2$
			Total	**6**	