OCR
Oxford Cambridge and RSA

GCE

Chemistry A

Unit **F324:** Rings, Polymers and Analysis

Advanced GCE

Mark Scheme for June 2014

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

OCR will not enter into any discussion or correspondence in connection with this mark scheme.

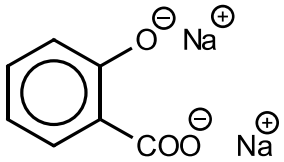
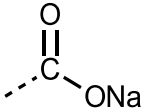
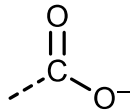
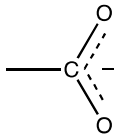
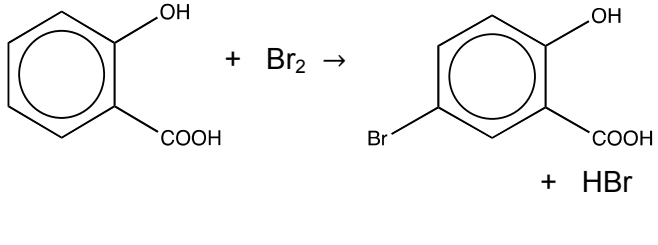
Annotations available in Scoris.

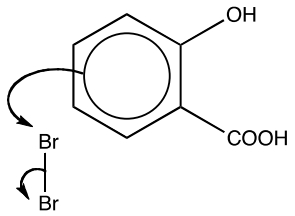
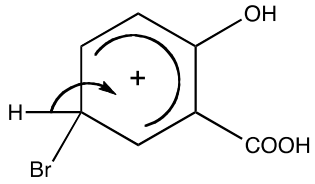
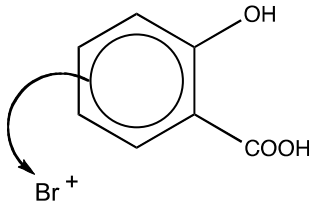
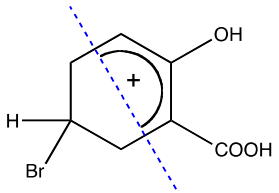
Annotation	Meaning
	Blank Page – this annotation must be used on all blank pages within an answer booklet (structured or unstructured) and on each page of an additional object where there is no candidate response.
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

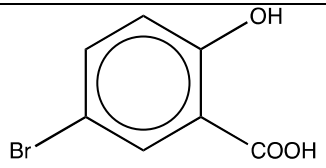
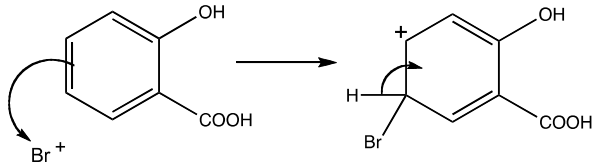
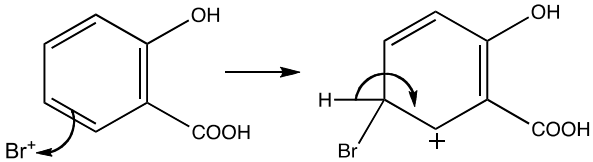
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

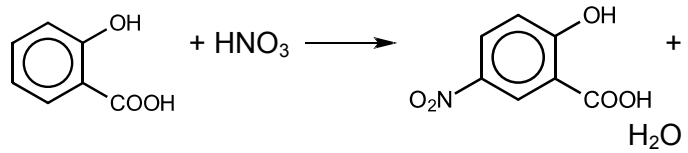
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

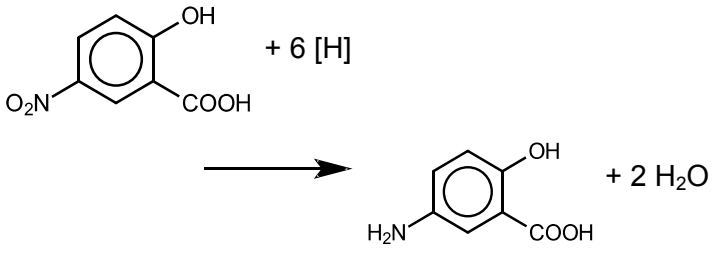
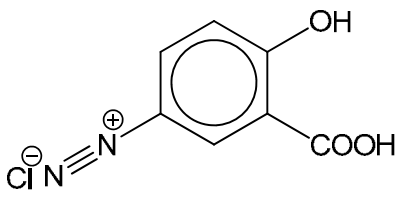
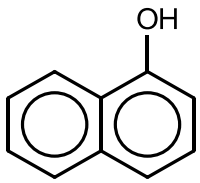
The following questions should be annotated with ticks to show where marks have been awarded in the body of the text:

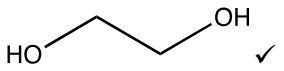
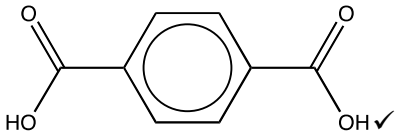
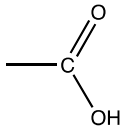
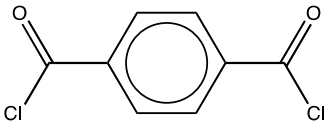
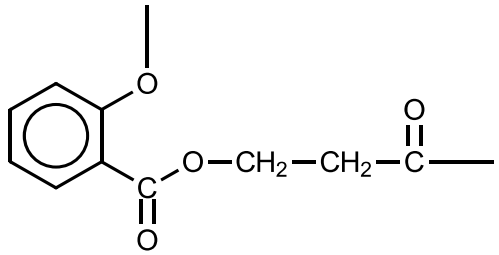
Question			Answer	Mark	Guidance
Where circles have been placed round charges, this is for clarity only and does not indicate a requirement					
1	(a)	(i)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **DO NOT ALLOW** —O—Na **OR** -COO-Na (covalent bond) **ALLOW** $-O^-$ **ALLOW** —ONa **ALLOW** —COONa **OR**  **OR**  **ALLOW** delocalised carboxylate 
1	(a)	(ii)	(Bromine) would be decolourised/turn (from orange/red/yellow/brown) to colourless **OR** white precipitate/solid/emulsion (formed) ✓	1	**IGNORE** goes clear **DO NOT ALLOW** other colours for bromine **IGNORE** cream precipitate **DO NOT ALLOW** salicylic acid turns colourless/decolourised **IGNORE** temperature/fumes
1	(a)	(iii)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **MUST** be all correct to score mark **ALLOW** molecular formulae, i.e. $C_7H_6O_3 + Br_2 \rightarrow C_7H_5O_3Br + HBr$

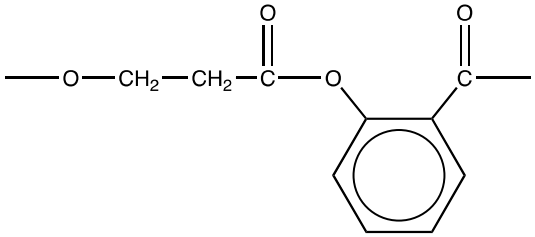
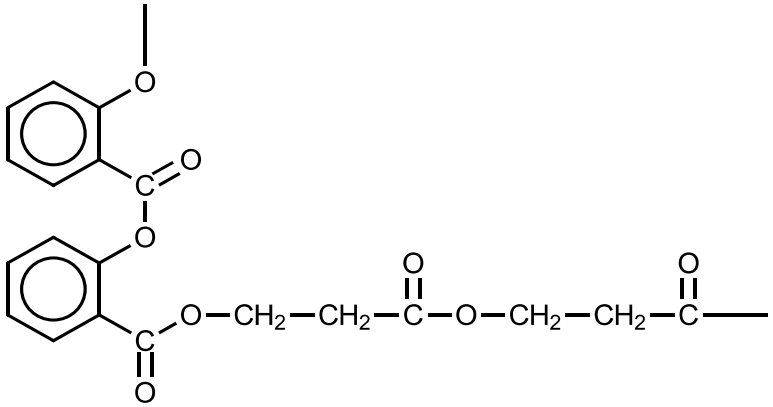
Question			Answer	Mark	Guidance
1	(a)	(iv)	$(CH_3)_2CHOH/CH_3CH(OH)CH_3$/propan(-)2(-)ol **AND** acid/H^+/H_2SO_4 (catalyst) ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** 2-propanol **DO NOT ACCEPT** incorrect name or incorrect formula of alcohol **IGNORE** reflux/concentrated (acid)
1	(b)	(i)	 No Br_2 dipole needed Curly arrow to Br from ring **OR** from within the ring **AND** curly arrow Br-Br bond to Br ✓  ✓ correct intermediate (with charge) ✓ curly arrow from C—H to reform ring	4	**ALLOW** mechanism with Br^+ electrophile (Maximum 3 marks)  **IGNORE** any equations involving a halogen carrier **BUT DO NOT ALLOW** intermediate with π-system covering less than half of ring:  **ALLOW** + charge anywhere inside the 'horseshoe' Horseshoe must have open end towards Br Apply ecf to error in structure of intermediate (M2)

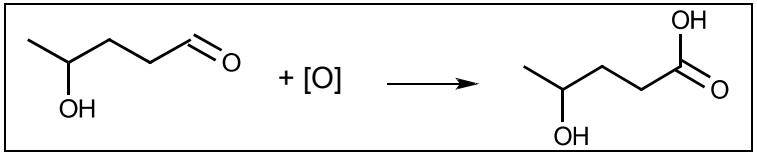
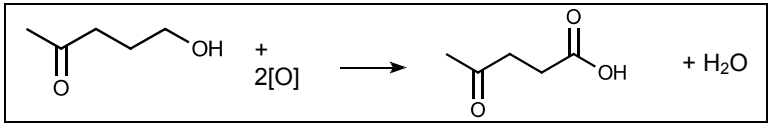
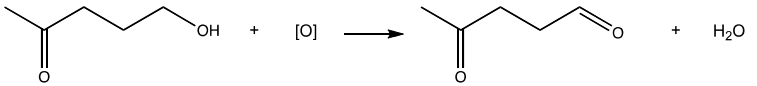
Question	Answer	Mark	Guidance
	 + HBr /H^++ Br^- ✓ Correct products (Br^- may be shown in the first step)		**ALLOW** Kekulé mechanism as shown (Maximum 3 marks if Br^+ is the electrophile)  **ALLOW** double bonds in alternate arrangement 

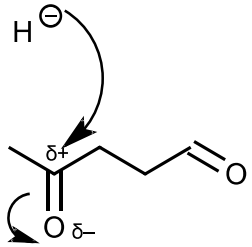
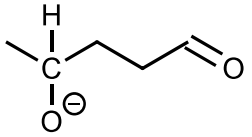
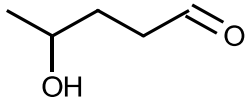
Question			Answer	Mark	Guidance
1	(b)	(ii)	(In salicylic acid) lone pair/pair of electrons on O(H)/phenol is ~ (partially) **delocalised** into the ring ✓ electron density increases/is high **ORA** ✓ Br_2/electrophile is (more) polarised **ORA** ✓ ✎ **QWC**: delocalised/delocalized/delocalise *etc*. must be spelled correctly in the correct context at least once	**3**	**ALLOW** diagram to show movement of lone pair into ring but delocalised ring must be mentioned **ALLOW** lone pair/pair of electrons on O(H)/phenol is (partially) drawn/attracted/pulled into **delocalised** ring **IGNORE** 'activates the ring' **ALLOW** more electron rich **DO NOT ALLOW** charge density or electronegativity **ALLOW** (salicylic acid) attracts electrophiles more/more susceptible to electrophilic attack **ALLOW** Br_2 is (more) attracted **OR** Br_2 is not polarised by benzene **OR** induces dipoles (in bromine/electrophile) Delocalise(d) needed to score the first marking point
1	(c)	(i)	**Step 1** Add HNO_3 ✓  ✓	**4**	**ALLOW** reagent mark if HNO_3 in equation **IGNORE** H_2SO_4 (**NOTE**: H_2SO_4 not required with phenols) **IGNORE** concentrations of acids/temperature **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous Equations **MUST** be completely correct for **one** mark each

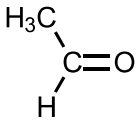
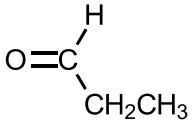
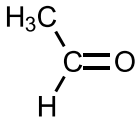
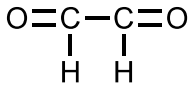
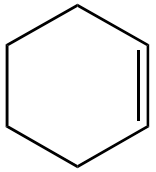
Question			Answer	Mark	Guidance
			Step 2 Tin **AND concentrated** HC*l* ✓  ✓		**DO NOT ALLOW** $3H_2$
1	**(c)**	**(ii)**	Nitrogen electron pair **OR** nitrogen lone pair accepts a proton/H^+ ✓	**1**	**DO NOT ALLOW** nitrogen/N lone pair accepts hydrogen (proton/H^+ required) **ALLOW** nitrogen donates an electron pair/lone pair to H^+ **IGNORE** NH_2 group donates electron pair
1	**(c)**	**(iii)**	compound **A** ✓  compound **B**  ✓	**2**	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** —N_2Cl **OR** —$N_2^+Cl^-$ **DO NOT ALLOW** —N≡N^+ **OR** —N≡N^+ Cl^- **DO NOT ALLOW** –N_2-Cl (covalent bond)

Question			Answer	Mark	Guidance
1	(d)	(i)	**monomers** join/bond/add/react/form polymer/form chain **AND** another product/small molecule/H_2O/HCl ✓	1	**IGNORE** specific reference to number of molecules
1	(d)	(ii)	 ✓  ✓ Connectivity is penalised only in this question	2	**DO NOT ALLOW** –HO (penalise connectivity once only) Both structures must be skeletal **DO NOT ALLOW** stray sticks (skeletal means CH_3 attached) **DO NOT ALLOW** structure with a C shown, e.g.  **ALLOW** 
1	(d)	(iii)	 ester link **MUST** be fully displayed ✓ **OR**	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous

Question	Answer	Mark	Guidance
			**ALLOW**  **IGNORE** bond angles **DO NOT ALLOW** more than one repeat unit unless correct repeat unit is indicated **IGNORE** brackets with *n* **ALLOW** any correct repeat unit **ALLOW** end bonds shown as - - - - - **DO NOT ALLOW** if structure has no end bonds
	Total	**22**	

Question			Answer	Mark	Guidance
2	(a)		**FIRST** react **all** with Tollens' reagent **AND** silver mirror/ppt/solid (formed) with compound **D** **OR** with Fehling's/Benedict's solutions **AND** (brick-red/orange) solid/precipitate (formed) with compound **D** ✓ ***NOTE**: eliminates **D***	4	**ALLOW** ammonia + silver nitrate for reagent **ALLOW** black solid/ppt **ALLOW** 'the aldehyde gives a silver mirror' **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous
			 ✓		**DO NOT ALLOW** molecular formulae for organic structures
			THEN react **C** and **E** with H_2SO_4/H^+ **AND** $K_2Cr_2O_7$/ $Cr_2O_7^{2-}$/$Na_2Cr_2O_7$ **AND** colour change **OR** green colour with compound **C** **OR** no change **OR** no reaction **OR** no green colour with compound **E** ✓		**IGNORE** all references to 2,4-dinitrophenylhydrazine/Brady's **ACCEPT** acidified dichromate **ALLOW** blue/green blue **IGNORE** equation for oxidation of **D**
			 ✓		**ALLOW** equation for partial oxidation 

Question			Answer	Mark	Guidance
					ALLOW alternative sequences e.g. **FIRST** react **all** with H_2SO_4 **AND** $K_2Cr_2O_7$ colour change with **C** and **D** *eliminates **E*** At least one correct equation and structure of one product from either reaction required for the second mark. **NB** several possible products for the oxidation of **D** **THEN** react **C** and **D** with Tollens' …… *distinguishes between **C** and **D***
2	**(b)**		 curly arrow from H^- to $C^{(\delta+)}$ of correct C=O group ✓ dipole correct **AND** curly arrow from C=O bond to $O^{(\delta-)}$ ✓  correct intermediate with negative charge on O ✓  correct product ✓	**4**	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous First curly arrow must come from either a lone pair on H or negative charge on H **IF** aldehyde reduced **OR** both carbonyls reduced **DO NOT AWARD** first mark (second, third and fourth marks can be awarded **ECF**) **IGNORE** lack of C—H if entirely skeletal **IGNORE** curly arrows in second stage Apply ecf to error in structure e.g. CH_2 missing from the chain or –COOH/-COH instead of –CHO **IGNORE** other products

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Mark</th><th>Guidance</th></tr>
<tr><td>2</td><td>(c)</td><td></td><td>
<table>
<tr><td>Compound</td><td>C</td><td>D</td><td>E</td></tr>
<tr><td>Number of peaks</td><td>5</td><td>5</td><td>4</td></tr>
</table>
all correct ✓</td><td>1</td><td></td></tr>
<tr><td>2</td><td>(d)</td><td>(i)</td><td>• pent-2-ene  AND  ✓
• hexa-2,4-diene  ✓  ✓</td><td>3</td><td>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous
ALLOW C_2H_5CHO and CH_3CHO</td></tr>
<tr><td>2</td><td>(d)</td><td>(ii)</td><td>  ✓</td><td>1</td><td>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>13</td><td></td></tr>
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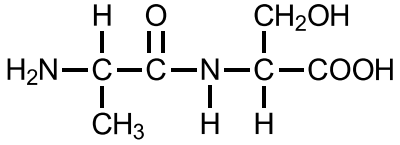
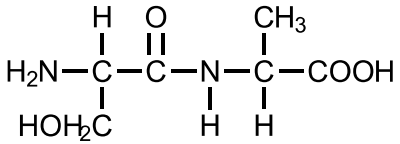
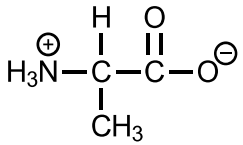
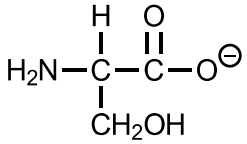
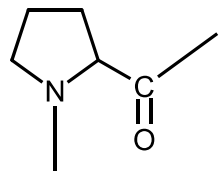
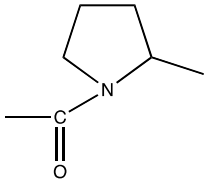
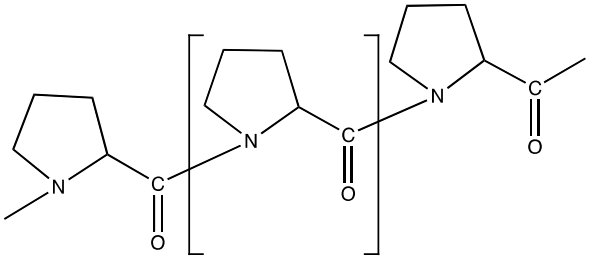
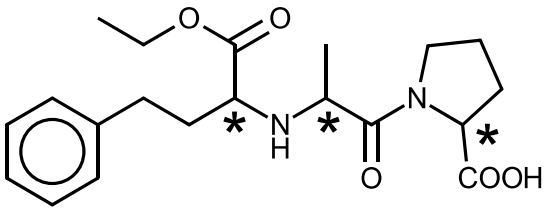
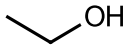
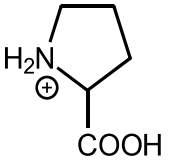
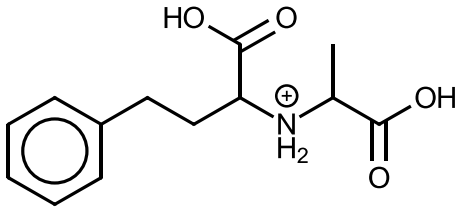
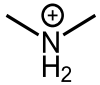
Question			Answer	Mark	Guidance
3	(a)	(i)	 ✓  ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **DO NOT ALLOW** peptide chains
3	(a)	(ii)	 alanine at pH 6.0 ✓  serine at pH 10.0 ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** + charge on N or H: *i.e.* $^{+}NH_3$ or NH_3^{+} **DO NOT ALLOW** '–' charge on C *i.e.* ^{-}COO **DO NOT ALLOW** if structure is incomplete

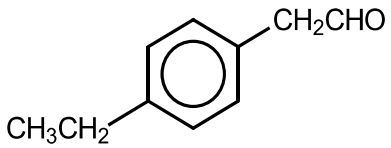
Question			Answer	Mark	Guidance
3	(a)	(iii)	 ✓ **OR** 	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **IGNORE** bond angles **DO NOT ALLOW** more than one repeat unit **ALLOW** end bonds shown as - - - - - **DO NOT ALLOW** if structure has no end bonds **IGNORE** brackets unless they are used to pick out the repeat unit from a polymer chain **IGNORE** *n* 

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Mark</th><th>Guidance</th></tr>
<tr><td>3</td><td>(b)</td><td></td><td>
<table>
<tr><td colspan="3">^{1}H NMR spectrum for serine</td></tr>
<tr><th>chemical shift, δ /ppm</th><th>relative peak area</th><th>splitting pattern</th></tr>
<tr><td>2.0 to 3.0</td><td>1</td><td>triplet</td></tr>
<tr><td>3.3 to 4.2</td><td>2</td><td>doublet</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</td></tr>
<tr><td>3</td><td>(c)</td><td>(i)</td><td>  ✓</td><td>1</td><td>ALL correct for one mark</td></tr>
<tr><td>3</td><td>(c)</td><td>(ii)</td><td>any two from:
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”</td></tr>
</table>

Question			Answer	Mark	Guidance
3	(c)	(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
3	(c)	(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
			Total	15	

Question			Answer	Mark	Guidance
4	(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
4	(b)		**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 ✓	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

Question	Answer	Mark	Guidance
	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)* • 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 ✓✓✓

Question			Answer	Mark	Guidance
					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)
			Total	**10**	

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