

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.

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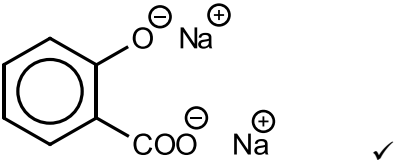
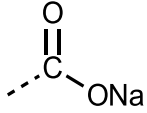
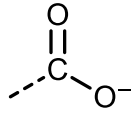
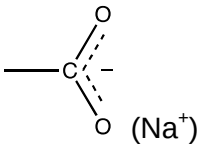
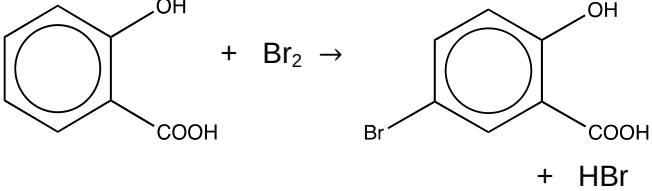
Annotations available in Scoris.

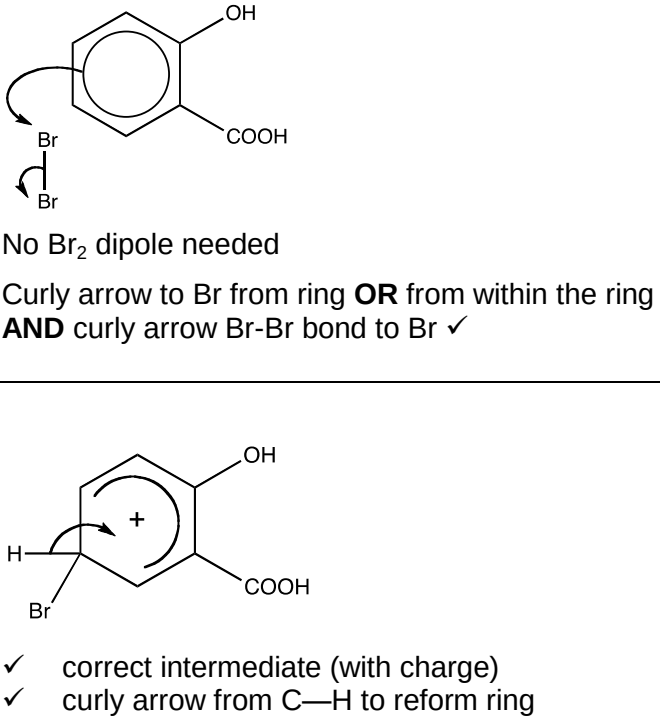
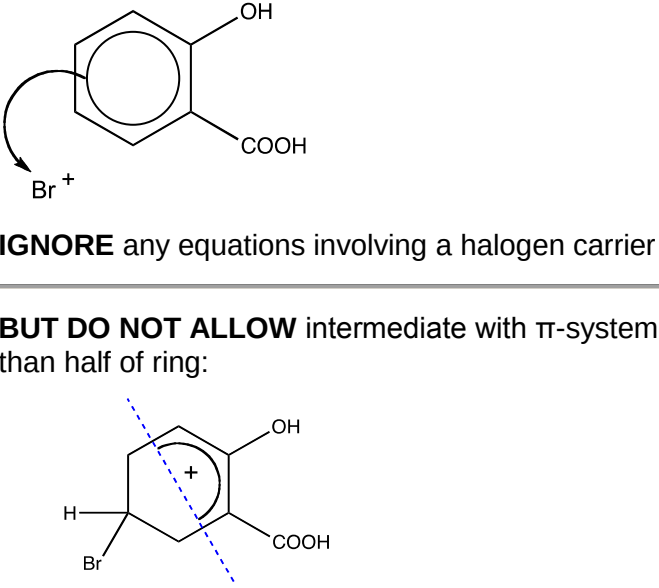
Annotation	Meaning
	Blank Page – this annotation must be used on all blank pages within an answer booklet (structured or unstructured) and on each page of an additional object where there is no candidate response.
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore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

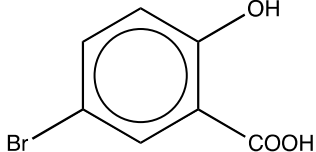
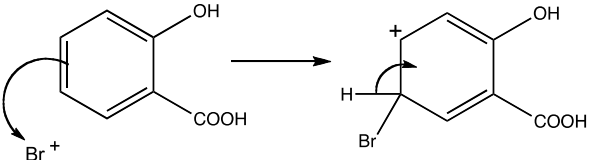
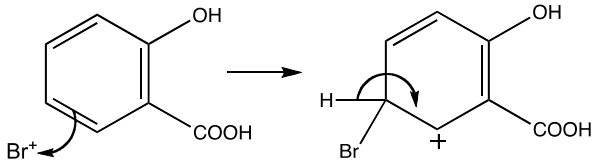
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

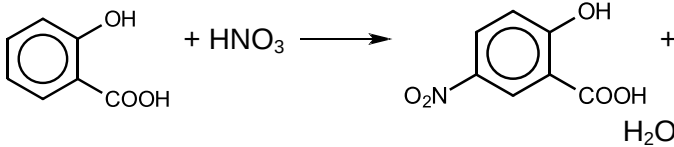
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

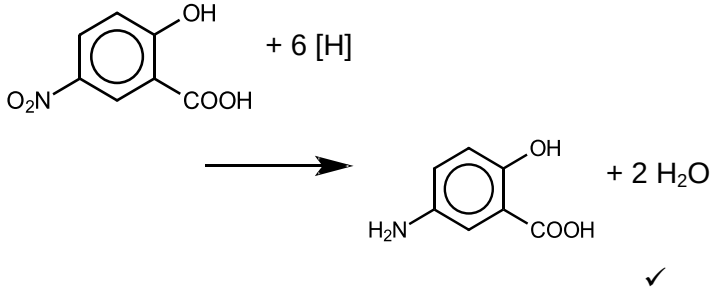
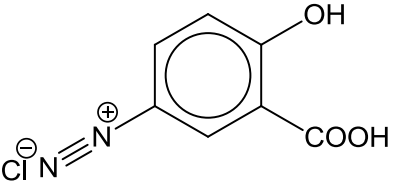
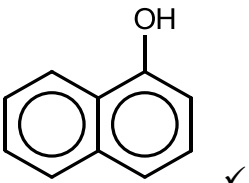
The following questions should be annotated with ticks to show where marks have been awarded in the body of the text:

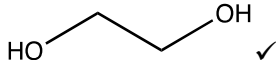
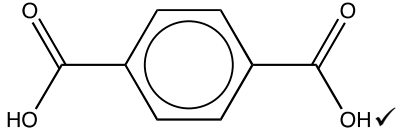
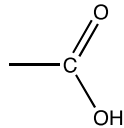
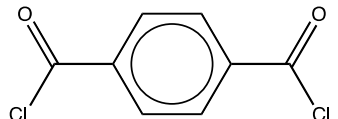
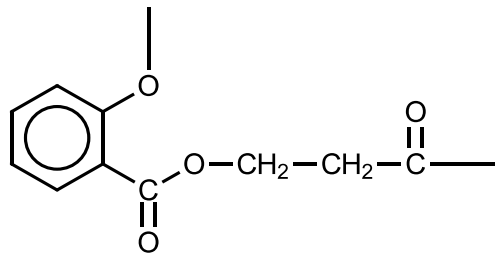
Question	Answer	Mark	Guidance
Where circles have been placed round charges, this is for clarity only and does not indicate a requirement			
1 (a) (i)		1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous DO NOT ALLOW —O—Na OR -COO-Na (covalent bond) ALLOW —O⁻ ALLOW —ONa ALLOW —COONa OR  OR  ALLOW delocalised carboxylate  (Na⁺)
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. $\text{C}_7\text{H}_6\text{O}_3 + \text{Br}_2 \rightarrow \text{C}_7\text{H}_5\text{O}_3\text{Br} + \text{HBr}$

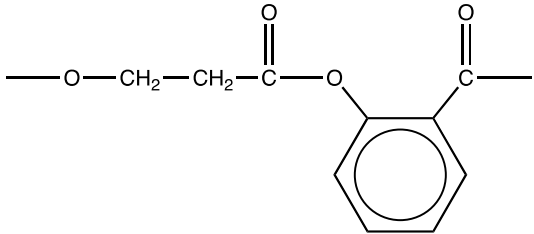
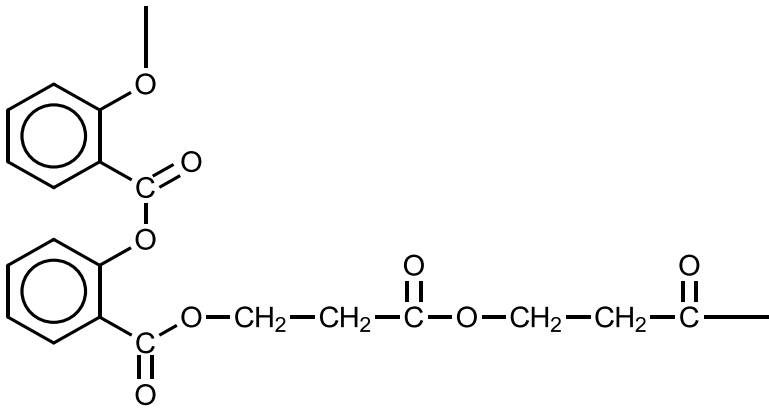
Question	Answer	Mark	Guidance
1 (a) (iv)	$(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{CH}(\text{OH})\text{CH}_3/\text{propan(-)2(-)ol}$ AND acid/ $\text{H}^+/\text{H}_2\text{SO}_4$ (catalyst) ✓	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW 2-propanol DO NOT ACCEPT incorrect name or incorrect formula of alcohol IGNORE reflux/concentrated (acid)
1 (b) (i)		4	ALLOW mechanism with Br^+ electrophile (Maximum 3 marks) 

Question	Answer	Mark	Guidance
	 $+ \text{HBr} / \text{H}^+ + \text{Br}^-$ ✓ 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 

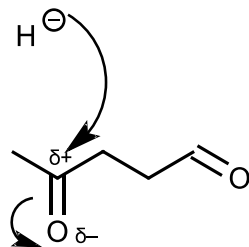
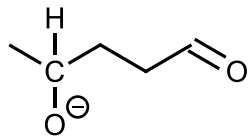
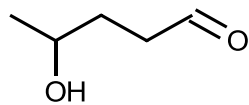
Question	Answer	Mark	Guidance
1 (b) (ii)	(In salicylic acid) lone pair/pair of electrons on O(H)/phenol is ~ (partially) delocalised into the ring ✓ electron density increases/is high ORA ✓ Br₂/electrophile is (more) polarised ORA ✓  QWC: delocalised/delocalized/delocalise etc. must be spelled correctly 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 Br₂ is (more) attracted OR Br₂ 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 HNO₃ ✓  ✓	4	ALLOW reagent mark if HNO₃ in equation IGNORE H₂SO₄ (NOTE: H₂SO₄ 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

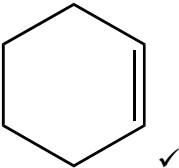
Question			Answer	Mark	Guidance
			Step 2 Tin AND concentrated HCl ✓ 		DO NOT ALLOW 3H ₂
1	(c)	(ii)	Nitrogen electron pair OR nitrogen lone pair accepts a proton/H⁺ ✓	1	DO NOT ALLOW nitrogen/N lone pair accepts hydrogen (proton/H⁺ required) ALLOW nitrogen donates an electron pair/lone pair to H⁺ IGNORE NH₂ 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 —N₂Cl OR —N₂⁺Cl⁻ DO NOT ALLOW —N≡N⁺ OR —N≡N⁺ Cl⁻ DO NOT ALLOW —N₂-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 ₂ O/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

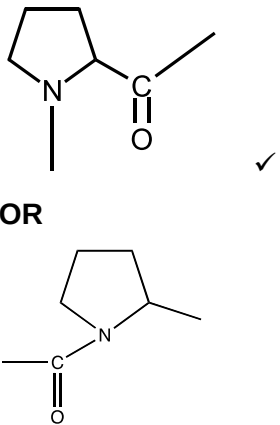
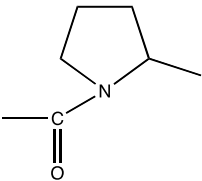
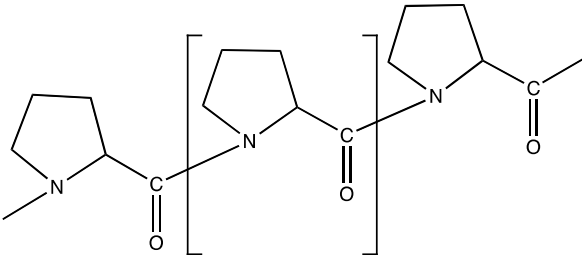
Question	Answer	Mark	Guidance
			ALLOW  IGNORE bond angles DO NOT ALLOW more than one repeat unit unless correct repeat unit is indicated IGNORE brackets with <i>n</i> ALLOW any correct repeat unit ALLOW end bonds shown as - - - - DO NOT ALLOW if structure has no end bonds
	Total	22	

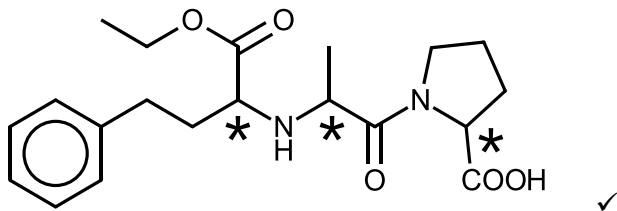
Question	Answer	Mark	Guidance
2 (a)	FIRST react all with Tollens' reagent AND silver mirror/ppt/solid (formed) with compound D OR with Fehling's/Benedict's solutions AND (brick-red/orange) solid/precipitate (formed) with compound D ✓ NOTE: eliminates D ✓ THEN react C and E with $\text{H}_2\text{SO}_4/\text{H}^+$ AND $\text{K}_2\text{Cr}_2\text{O}_7/$ $\text{Cr}_2\text{O}_7^{2-}/\text{Na}_2\text{Cr}_2\text{O}_7$ AND colour change OR green colour with compound C OR <u>no</u> change OR <u>no</u> reaction OR no green colour with compound E ✓ ✓	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 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

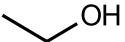
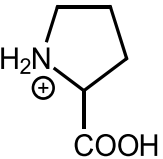
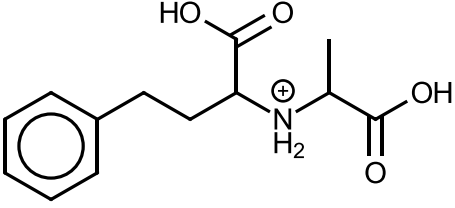
Question	Answer	Mark	Guidance
			ALLOW alternative sequences e.g. FIRST react all with H_2SO_4 AND $\text{K}_2\text{Cr}_2\text{O}_7$ colour change with C and D <i>eliminates E</i> At least one correct equation and structure of one product from either reaction required for the second mark. NB several possible products for the oxidation of D THEN react C and D with Tollens' <i>distinguishes between C and D</i>
2 (b)	 curly arrow from H^- to $\text{C}^{(\delta+)}$ of correct $\text{C}=\text{O}$ group ✓ dipole correct AND curly arrow from $\text{C}=\text{O}$ bond to $\text{O}^{(\delta-)}$ ✓  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 $\text{C}-\text{H}$ if entirely skeletal IGNORE curly arrows in second stage Apply ecf to error in structure e.g. CH_2 missing from the chain or $-\text{COOH}/-\text{COH}$ instead of $-\text{CHO}$ IGNORE other products

Question			Answer	Mark	Guidance								
2	(c)		<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 ✓	Compound	C	D	E	Number of peaks	5	5	4	1	
Compound	C	D	E										
Number of peaks	5	5	4										
2	(d)	(i)	- pent-2-ene - hexa-2,4-diene H₃C C=O H AND O=C H CH₂CH₃ ✓ H₃C C=O H ✓ O=C C=O H H ✓	3	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW C₂H₅CHO and CH₃CHO								
2	(d)	(ii)		1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous								
			Total	13									

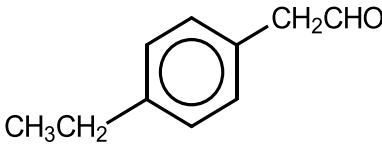
Question			Answer	Mark	Guidance
3	(a)	(i)	$ \begin{array}{c} \text{H} \quad \text{O} \quad \text{CH}_2\text{OH} \\ \quad \quad \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \\ \quad \quad \\ \text{CH}_3 \quad \text{H} \quad \text{H} \end{array} $ $ \begin{array}{c} \text{H} \quad \text{O} \quad \text{CH}_3 \\ \quad \quad \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \\ \quad \quad \\ \text{HOH}_2\text{C} \quad \text{H} \quad \text{H} \end{array} $ ✓	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 $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}_3\text{N}^+-\text{C}-\text{C}-\text{O}^- \\ \\ \text{CH}_3 \end{array}$ ✓ serine at pH 10.0 $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{O}^- \\ \\ \text{CH}_2\text{OH} \end{array}$ ✓	2	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + charge on N or H: <i>i.e.</i> $^+\text{NH}_3$ or NH_3^+ DO NOT ALLOW '–' charge on C <i>i.e.</i> ^-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 

Question			Answer	Mark	Guidance												
3	(b)		<table border="1"><thead><tr><th colspan="3">¹H NMR spectrum for serine</th></tr><tr><th>chemical shift, δ /ppm</th><th>relative peak area</th><th>splitting pattern</th></tr></thead><tbody><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></tbody></table> One mark for each correct row ✓✓	¹ H NMR spectrum for serine			chemical shift, δ /ppm	relative peak area	splitting pattern	2.0 to 3.0	1	triplet	3.3 to 4.2	2	doublet	2	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW a response that implies a splitting into three for a triplet/into two for a doublet
¹ H NMR spectrum for serine																	
chemical shift, δ /ppm	relative peak area	splitting pattern															
2.0 to 3.0	1	triplet															
3.3 to 4.2	2	doublet															
3	(c)	(i)		1	ALL correct for one mark												
3	(c)	(ii)	any two from: no/fewer side effects increases the (pharmacological) activity/effectiveness Reduces/stops the need for/cost/difficulty in separating stereoisomers/optical isomers ✓✓	2	IGNORE toxic/harmful IGNORE a response that implies a reduced dose IGNORE “it takes (less) time to separate”												

Question	Answer	Mark	Guidance
3 (c) (iii)	 ✓ one mark for ethanol  ✓ one mark for proline with NH OR NH₂⁺  ✓ one mark for remaining fragment with  or  ✓ Fourth mark for structure of both ions shown correctly with NH₂⁺	4	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + charge on H of NH₂ groups, <i>i.e.</i> NH₂⁺ 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) ₄ Si ALLOW TMS is the reference OR TMS has $\delta = 0$ (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 = C₆H₄ ✓ M3: Triplet at (δ) 1.3/peak at 1.3 AND quartet (at δ 2.6)/ peak at 2.6 = CH₂CH₃ ✓ M4: Triplet at (δ) 9.7/peak at 9.7 AND doublet (at δ 3.7)/peak at 3.7 = CH₂CHO ✓	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 CH₂CHO/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 CH₂ (because of splitting: so triplet) • quartet at (δ) 2.6 shows (C with) 3 adjacent Hs/protons OR adjacent CH₃ • triplet at (δ) 9.7 shows (C with) 2 adjacent Hs/protons OR adjacent CH₂ • 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 C₆H₄ ✓ IF structure contains C₆H₄ AND the organic structure contains CH₃CH₂ directly attached to the benzene ring OR contains CH₂CHO directly attached to the benzene ring ✓✓ IF structure has formula C₁₀H₁₂O AND structure contains C₆H₄ AND the structure contains CH₃CH₂ AND contains CH₂CHO 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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