

Chemistry A

Advanced GCE

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

Mark Scheme for June 2011

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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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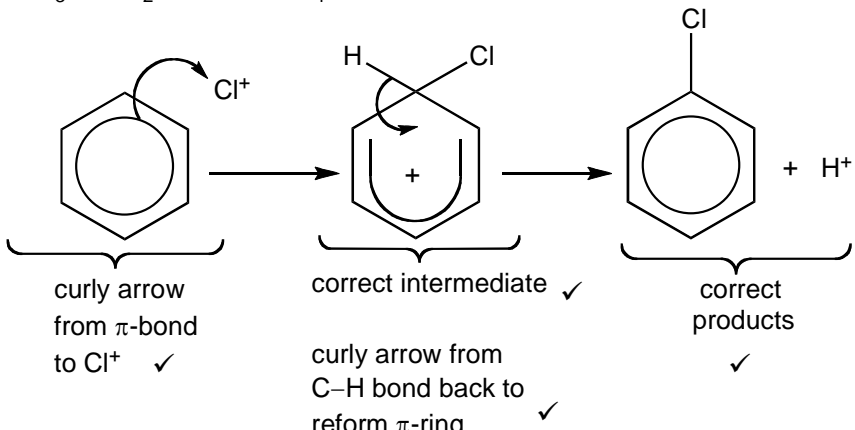
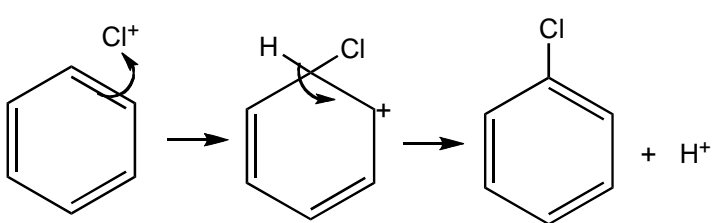
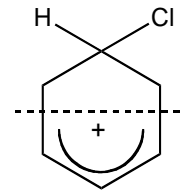
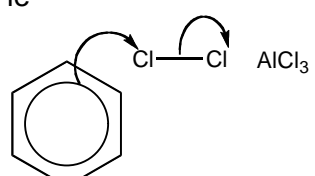
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ALLOW Kekulé structures throughout

Question	Answer	Mark	Guidance
1 (a)	<p>$\text{AlCl}_3 + \text{Cl}_2 \longrightarrow \text{AlCl}_4^- + \text{Cl}^+ \checkmark$</p>  <p>curly arrow from π-bond to $\text{Cl}^+ \checkmark$</p> <p>correct intermediate \checkmark</p> <p>curly arrow from C-H bond back to reform π-ring \checkmark</p> <p>correct products \checkmark</p> <p>$\text{H}^+ + \text{AlCl}_4^- \longrightarrow \text{AlCl}_3 + \text{HCl} \checkmark$</p> <p>Note: 1st curly arrow should start within the ring or on the ring</p> <hr/> <p>Note: ALLOW mechanism using Kekulé structures:</p> 	6	<p>ANNOTATIONS MUST BE USED</p> <p>DO NOT ALLOW the following intermediate:</p>  <p>π-ring must be more than 1/2 way up AND 'horseshoe' the right way up, <i>ie</i> gap towards C with Cl</p> <p>ALLOW + sign anywhere inside the 'hexagon' of intermediate</p> <p>ALLOW 1st curly arrow starting within the hexagon</p> <p>ALLOW mechanism with $\text{Cl}-\text{Cl} \cdots \text{AlCl}_3$ for 1st 2 marks, <i>ie</i></p>  <p>Second curly arrow to either $-\text{Cl}$ or AlCl_3</p> <p>Note: If Br^+ is used, DO NOT ALLOW 1st mechanism mark but all other marks available by ECF</p>

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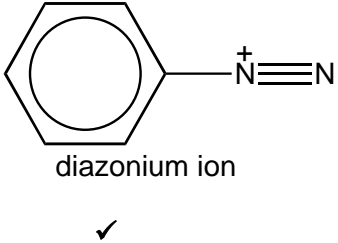
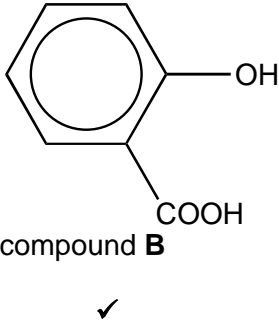
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Question			Answer	Mark	Guidance
1	(b)	(i)	<p>2 <chem>c1ccc(Cl)cc1</chem> + <chem>ClC(Cl)(Cl)C=O</chem></p> <p>↓</p> <p>2 <chem>c1ccc(Cl)cc1</chem> + <chem>O</chem></p> <p>1st mark: reactants, correctly balanced, ✓ ie 2 C₆H₅Cl + Cl₃CCHO</p> <p>2nd mark: product, (correctly balanced) ✓ ie H₂O</p>	2	<p>Each mark is independent of the other</p> <p>ALLOW C₆H₅Cl for chlorobenzene</p> <p>ALLOW any unambiguous structure for Cl₃CCHO, e.g. CCl₃CHO BUT DO NOT ALLOW CCl₃COH</p> <p>Standalone mark</p> <p>Standalone mark</p>
		(ii)	6 ✓	1	
	(c)		<p>substitution/nitration/NO₂ at different positions (on the ring) OR forms different isomers OR multiple substitution/nitration ✓</p>	1	<p>ALLOW examples, e.g. 1-chloro-2-nitrobenzene and 1-chloro-3-nitrobenzene ALLOW 'it' for nitro group</p> <p>ALLOW examples, e.g. 1-chloro-2,3-dinitrobenzene IGNORE nitrate/NO₃</p>
	(d)		<p>In phenol, (lone) pair of electrons on O is (partially) delocalised into the ring ✓ QWC: delocalised/delocalized/delocalise, etc must be spelt correctly in the correct context for benzene OR phenol at least once</p> <p>electron density increases/is high ✓ ORA</p> <p>Cl₂/electrophile is (more) polarised ✓ ORA</p>	3	<p>ANNOTATIONS MUST BE USED</p> <p>ALLOW diagram to show movement of lone pair into ring but delocalised ring must be mentioned ALLOW lone pair of electrons on O is (partially) drawn/ attracted/pulled into delocalised ring IGNORE 'activates the ring'</p> <p>DO NOT ALLOW charge density or electronegativity</p> <p>ALLOW Cl₂ is (more) attracted OR Cl₂ is not polarised by benzene OR induces dipoles (in chlorine/electrophile)</p>
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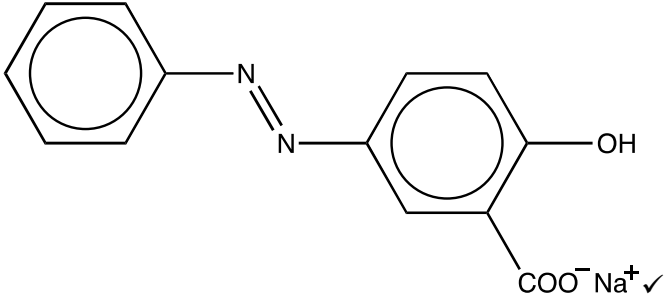
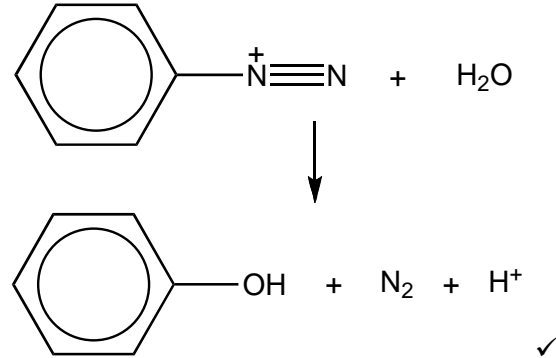
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Question		Answer	Mark	Guidance
2	(a)	(i)		
		donates a lone pair (on N) OR accepts a proton/H ⁺ ✓	1	IGNORE 'forms a dative covalent bond' (no direction of lone pair) ALLOW 'forms a dative covalent bond with/to H ⁺ ' ALLOW mark for N:→H ⁺ (can be from correct equation)
		(ii)		
		(C ₂ H ₅ NH ₃ ⁺) ₂ SO ₄ ²⁻ ✓ C ₂ H ₅ NH ₃ ⁺ CH ₃ COO ⁻ ✓	2	ALLOW (C ₂ H ₅ NH ₃) ₂ SO ₄ DO NOT ALLOW (C ₂ H ₅ NH ₃) HSO ₄ OR (C ₂ H ₅ NH ₃ ⁺) HSO ₄ ⁻ <i>brackets not required</i> ALLOW (C ₂ H ₅ NH ₃) (CH ₃ COO) OR (C ₂ H ₅ NH ₃ ⁺) (CH ₃ COO ⁻) <i>brackets not required</i> ALLOW separate ions with or without a '+' sign between them, e.g. C ₂ H ₅ NH ₃ ⁺ + CH ₃ COO ⁻
	(b)	(i)		
		 	2	In diazonium ion, IGNORE Cl ⁻ ALLOW '+' sign up to halfway along triple bond from left-hand N In compound B , ALLOW -OH ionised as -O ⁻ ALLOW -COOH ionised as COO ⁻
		(ii)		
		conditions = alkaline /OH ⁻ AND use = dye/pigment/colouring ✓	1	BOTH responses required for one mark ALLOW named alkali, e.g. NaOH/KOH ALLOW base IGNORE references to temperature ALLOW use = indicator

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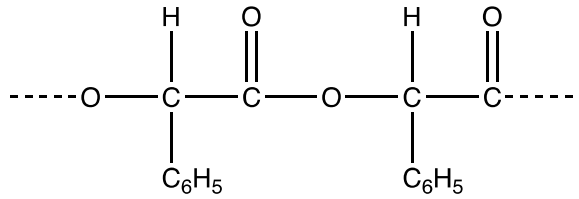
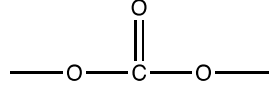
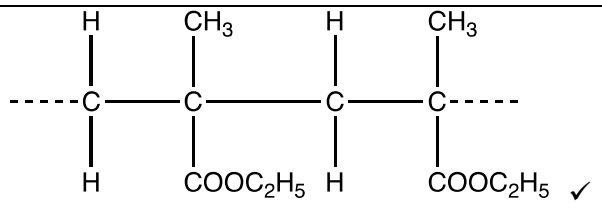
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Question		Answer	Mark	Guidance
2	(b) (iii)	Organic product:  Other products: CO ₂ AND H ₂ O ✓	2	IGNORE phenoxide: O ⁻ OR O ⁻ Na ⁺ ALLOW COO ⁻ OR COONa ALLOW H ₂ CO ₃ Note: must be formulae and not names (in question)
	(c)		1	ALLOW N ₂ ⁺ on structural formula ALLOW C ₆ H ₅ N ₂ ⁺ + H ₂ O → C ₆ H ₅ OH + N ₂ + H ⁺ ALLOW C ₆ H ₅ N ₂ Cl + H ₂ O → C ₆ H ₅ OH + N ₂ + HCl If + charge shown, IGNORE its position
Total			9	

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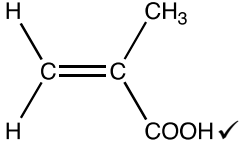
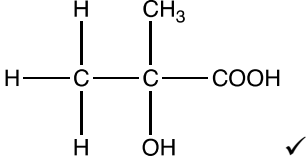
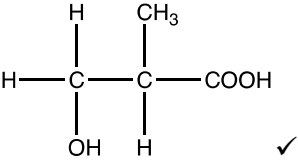
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Question		Answer	Mark	Guidance
3	(a)	<p>monomers join/bond/add/react/form polymer/form chain AND another product/small molecule e.g. H₂O/HCl ✓</p> <p>QWC must spell AND use 'monomer(s)' correctly throughout</p>	1	<p>IGNORE 'two' when referring to monomers, ie (two) monomers</p>
	(b) (i)	 <p>ester link ✓ Note: Any ester link shown must be correct rest of the structure ✓</p>	2	<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>ALLOW benzene ring for C₆H₅</p> <p>'End bonds' MUST be shown (do not have to be dotted)</p> <p>ALLOW one or more repeat units but has to have a whole number of repeat units (<i>ie</i> does not have to be two)</p> <p>For ester, DO NOT ALLOW </p> <p>ALLOW structure with no O at left end and COO at right end</p> <p>IGNORE brackets IGNORE <i>n</i></p>
	(ii)		1	<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>ALLOW one or more repeat units but has to have a whole number of repeat units (<i>ie</i> does not have to be two)</p> <p>'End bonds' MUST be shown (do not have to be dotted)</p> <p>IGNORE brackets IGNORE <i>n</i></p>

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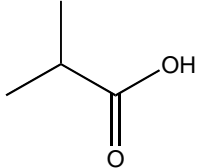
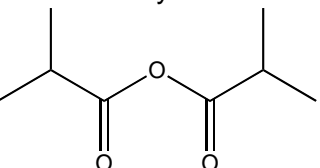
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Question		Answer	Mark	Guidance
3	(c)	<p>compound C</p>  <p>compound D and compound E</p>  	3	<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous) ALLOW CH₂C(CH₃)COOH</p> <p>ALLOW D and E by ECF from an incorrect structure of C provided that C contains a double bond and molecular formulae of D and E is C₄H₈O₃ with H₂O added across double bond</p>
	(d)	(i)		<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous) e.g. (CH₃)₂CHOH</p> <p>DO NOT ALLOW –HO</p> <p>IGNORE working (<i>ie</i> other structures) provided correct structure of propan-2-ol is shown</p> <p>IGNORE name (even if wrong)</p>

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Question			Answer	Mark	Guidance
3	(d)	(ii)	 OR acid anhydride: 	1	<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous) OR (2-)methylpropanoic acid</p> <p>DO NOT ALLOW incorrect name (will CON a correct structure)</p> <p>ALLOW acyl chloride: $(\text{CH}_3)_2\text{CHCOCl}$</p> <p>IGNORE working provided correct structure of propan-2-ol is shown</p>
		(iii)	<p>Hydrogen bonds form with water ✓ Note: Can be shown in diagram as dashed line, <i>ie</i> ---- (no label required)</p> <p>DO NOT CON 'hydrogen bond' from an incorrect hydrogen bond in diagram</p> <p>Mandelic acid forms more hydrogen bonds (with water) ✓ ORA</p> <p>Mandelic acid has an extra OH OR 2 OH groups OR has a COOH group ✓ ORA</p>	3	<p>ANNOTATIONS MUST BE USED</p> <p>ALLOW a diagram showing hydrogen bonds with water, dipole and lone pair are not required ALLOW a hydrogen bond to C=O, <i>ie</i> C=O---H-O IGNORE bond angles Diagram does not need to show all of mandelic acid (IGNORE if wrong)</p> <p>ALLOW any comparison of numbers of hydrogen bonds provided that mandelic acid has more hydrogen bonds</p> <p>DO NOT ALLOW 'No -OH groups in ester (as there are)' DO NOT ALLOW reference to -OH^- / hydroxide</p> <p>IGNORE reference to carbon chain and van der Waals' forces</p> <p>Note: If a response compares Ester 1 with Ester 2 rather than with mandelic acid, maximum of 2 marks: 1st mark hydrogen bonds 2nd mark Ester 2 has more Os/oxygens OR Ester 2 forms more hydrogen bonds</p>

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Question			Answer	Mark	Guidance
3	(d)	(iv)	To test for (adverse) side effects OR to test toxicity OR to test for irritation ✓	1	ALLOW a stated adverse side effect, eg allergy, carcinogenic, etc IGNORE references to optical isomers, chirality, etc IGNORE vague statements such as harmful to skin, dangerous to skin, corrosive to skin, reacts with skin ALLOW company liable to litigation/damages
			Total	13	

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Question	Answer	Mark	Guidance
4	<p>Equations $\text{CH}_3\text{COCHO} + 4[\text{H}] \longrightarrow \text{CH}_3\text{CHOHCH}_2\text{OH} \checkmark$ $\text{CH}_3\text{COCHO} + [\text{O}] \longrightarrow \text{CH}_3\text{COCOOH} \checkmark$</p> <p>Reduction reagents and observation Methylglyoxal is reduced by $\text{NaBH}_4 \checkmark$</p> <p>Oxidation reagents and observation Methylglyoxal is oxidised by H_2SO_4 AND $\text{K}_2\text{Cr}_2\text{O}_7 \checkmark$ Observation: turns green OR blue \checkmark</p> <p>OR Methylglyoxal is oxidised by Tollens' reagent \checkmark Observation: Silver (mirror) \checkmark</p>	<p>1</p> <p>1</p> <p>1</p> <p>2</p>	<p>ANNOTATIONS MUST BE USED Throughout question, ALLOW correct structural OR displayed OR skeletal formula DO NOT ALLOW molecular formulae</p> <p>ALLOW partial reduction (ie reduction of either C=O group) [H] implies reduction [O] implies oxidation</p> <p>reduced AND reagent are both required for the mark ALLOW link to equation with [H] for reduction ALLOW LiAlH_4 as alternative for NaBH_4 ALLOW any recognisable attempt at name IGNORE any reference to acids</p> <p>oxidised AND reagent are both required for the mark ALLOW link to equation with [O] for oxidation ALLOW $\text{Na}_2\text{Cr}_2\text{O}_7$ instead of $\text{K}_2\text{Cr}_2\text{O}_7$ ALLOW H^+ AND $\text{Cr}_2\text{O}_7^{2-}$ OR H^+ AND CrO_4^{2-}</p> <p>If name given, ALLOW dichromate OR dichromate(VI) ALLOW acidified dichromate ALLOW any strong acid If formulae used, formulae must be correct</p> <p>ALLOW AgNO_3 in ammonia OR ammoniacal AgNO_3</p> <p>ALLOW oxidised by manganate Observation: decolourised</p> <p>Note: If one reaction is identified as oxidation, assume the other is reduction (and vice versa)</p>
	Total	5	

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Question		Answer	Mark	Guidance
5	(a)	idea of separating (the components/compounds) ✓ idea of (identifying compounds) by comparison with a (spectral) database ✓	2	ALLOW (identifies compounds) using fragmentation (patterns)/fragment ions (but IGNORE molecular ions) ✓ Note: Each marking point does not need to be linked to GC or MS (The question asks about GC–MS as a combined technique)
	(b)	(i) 54.2% of 118 OR $54.2/118 \times 100 = 64/63.96$ (hence there are 4 oxygens) ✓ $118 - 64 = 54$ hence 4 carbon (48) and 6 hydrogen (6) ✓	2	IGNORE calculation that proves that $C_4H_6O_4$ has a molar mass of 118 (ie $12 \times 4 + 6 \times 1 + 16 \times 4$) ALLOW $64/118 \times 100 = 54.2\%$ for 1st mark IGNORE method using empirical formula ALLOW any reasonable working leading to 4C Note: $54.2(\%) \div 16$ would not get the 1st mark but the answer could be used to get the 2nd mark
		(ii) carboxyl group OR carboxylic acid ✓ must be name (in question)	1	IGNORE working, e.g. O–H, C=O, C–O on IR spectrum

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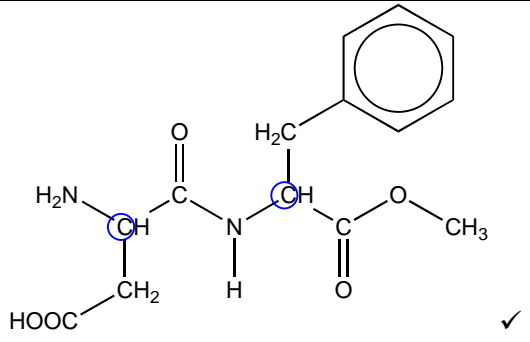
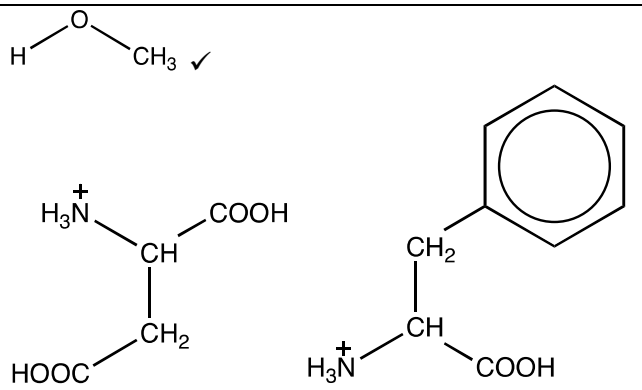
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Question		Answer	Mark	Guidance
5	(c) (i)	<p>Chemical shifts Any two peaks identified for 1 mark ✓ peak at $\delta = 0.8$ ppm due to R-CH / CH₃CH peak at $\delta = 3.4$ ppm due to HC-C=O peak at $\delta = 11$ ppm due to COOH / carboxylic acid</p> <p>Splitting quartet shows adjacent CH₃ OR 3 adjacent Hs ✓ doublet shows adjacent CH OR 1 adjacent H ✓</p> <p>Identification</p> $\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{CH}_3}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \quad \checkmark$	1	<p>ANNOTATIONS MUST BE USED CHECK SPECTRUM for responses ANNOTATE with '^'</p> <p>For peak at ($\delta =$) 0.8 (ppm), ALLOW doublet and vice versa For peak at ($\delta =$) 3.4 (ppm), ALLOW quartet ' and vice versa For peak at ($\delta =$) 11 (ppm), ALLOW singlet and vice versa</p> <p>ALLOW peak at $\delta = 2.4$ ppm for peak at $\delta = 3.4$ ppm ALLOW tolerance on δ values: ± 1 ppm</p> <p>For quartet, ALLOW quadruplet</p>
	(ii)	(CD ₃) ₂ SO / D / It does not absorb OR does not give a peak ✓	1	<p>ALLOW (CD₃)₂SO / does not contain H ALLOW undeuterated solvents would absorb OR give peaks</p> <p>ALLOW responses in terms of (CH₃)₂SO producing peaks but IGNORE number of peaks</p>
	(iii)	TMS is the standard (for chemical shift measurements) ✓	1	<p>ALLOW TMS is the reference OR TMS has $\delta = 0$ (ppm) OR for calibration</p> <p>IGNORE unreactive, volatile, it gives a sharp peak</p>
	(iv)	peak at $\delta = 11.0$ (ppm) disappears ✓	1	<p>ALLOW COOH (peak) disappears</p> <p>ALLOW OH (peak) disappears</p>
Total			12	

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Question		Answer	Mark	Guidance
6	(a) (i)		1	<p>Circles can be around C OR CH atoms but must not include other atoms</p> <p>ALLOW any suitable way of highlighting chiral carbons, e.g. asterisk, *</p> <p>Note: Mark the circles and ignore other working on diagram</p>
	(ii)	<p>carboxyl OR carboxylic acid, amine, amide, ester must be names</p> <p>2 marks for 4 correct functional groups ✓✓ 1 mark for 3 correct functional groups ✓</p>	2	<p>ALLOW peptide for amide</p>
	(b)	 <p>1 mark for left-hand amino acid with NH₃⁺ OR NH₂ ✓ 1 mark for right-hand amino acid with NH₃⁺ OR NH₂ ✓ 1 mark for both amino acids shown with NH₃⁺ ✓</p>	4	<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>ALLOW + charge on H of NH₃ groups, ie NH₃⁺</p> <p>Note: If there are more than three structures shown, credit any correct structures and ignore incorrect structures</p>

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Question		Answer	Mark	Guidance
6	(c)	(adverse) side effects OR toxicity OR irritation ✓	1	<p>ALLOW a stated adverse side effect, eg allergy, carcinogenic, hyperactivity etc</p> <p>IGNORE references to optical isomers, chirality, etc</p> <p>IGNORE vague statements such as harmful to body, dangerous to body</p> <p>DO NOT ALLOW obesity, corrosive to body</p> <p>ALLOW company liable to litigation/damages</p> <p>Note: Scroll down to bottom of page to check for any further writing</p>
			Total	8

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