

Cambridge International AS & A Level

CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2024

MARK SCHEME

Maximum Mark: 100

Published

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

Cambridge International will not enter into discussions about these mark schemes.

Cambridge International is publishing the mark schemes for the May/June 2024 series for most Cambridge IGCSE, Cambridge International A and AS Level and Cambridge Pre-U components, and some Cambridge O Level components.

This document consists of **15** printed pages.

PUBLISHED**Generic Marking Principles**

These general marking principles must be applied by all examiners when marking candidate answers. They should be applied alongside the specific content of the mark scheme or generic level descriptions for a question. Each question paper and mark scheme will also comply with these marking principles.

GENERIC MARKING PRINCIPLE 1:

Marks must be awarded in line with:

- the specific content of the mark scheme or the generic level descriptors for the question
- the specific skills defined in the mark scheme or in the generic level descriptors for the question
- the standard of response required by a candidate as exemplified by the standardisation scripts.

GENERIC MARKING PRINCIPLE 2:

Marks awarded are always **whole marks** (not half marks, or other fractions).

GENERIC MARKING PRINCIPLE 3:

Marks must be awarded **positively**:

- marks are awarded for correct/valid answers, as defined in the mark scheme. However, credit is given for valid answers which go beyond the scope of the syllabus and mark scheme, referring to your Team Leader as appropriate
- marks are awarded when candidates clearly demonstrate what they know and can do
- marks are not deducted for errors
- marks are not deducted for omissions
- answers should only be judged on the quality of spelling, punctuation and grammar when these features are specifically assessed by the question as indicated by the mark scheme. The meaning, however, should be unambiguous.

GENERIC MARKING PRINCIPLE 4:

Rules must be applied consistently, e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

GENERIC MARKING PRINCIPLE 5:

Marks should be awarded using the full range of marks defined in the mark scheme for the question (however; the use of the full mark range may be limited according to the quality of the candidate responses seen).

GENERIC MARKING PRINCIPLE 6:

Marks awarded are based solely on the requirements as defined in the mark scheme. Marks should not be awarded with grade thresholds or grade descriptors in mind.

Science-Specific Marking Principles

1 Examiners should consider the context and scientific use of any keywords when awarding marks. Although keywords may be present, marks should not be awarded if the keywords are used incorrectly.

2 The examiner should not choose between contradictory statements given in the same question part, and credit should not be awarded for any correct statement that is contradicted within the same question part. Wrong science that is irrelevant to the question should be ignored.

3 Although spellings do not have to be correct, spellings of syllabus terms must allow for clear and unambiguous separation from other syllabus terms with which they may be confused (e.g. ethane / ethene, glucagon / glycogen, refraction / reflection).

4 The error carried forward (ecf) principle should be applied, where appropriate. If an incorrect answer is subsequently used in a scientifically correct way, the candidate should be awarded these subsequent marking points. Further guidance will be included in the mark scheme where necessary and any exceptions to this general principle will be noted.

5 'List rule' guidance

For questions that require *n* responses (e.g. State **two** reasons ...):

- The response should be read as continuous prose, even when numbered answer spaces are provided.
- Any response marked *ignore* in the mark scheme should not count towards *n*.
- Incorrect responses should not be awarded credit but will still count towards *n*.
- Read the entire response to check for any responses that contradict those that would otherwise be credited. Credit should **not** be awarded for any responses that are contradicted within the rest of the response. Where two responses contradict one another, this should be treated as a single incorrect response.
- Non-contradictory responses after the first *n* responses may be ignored even if they include incorrect science.

6 Calculation specific guidance

Correct answers to calculations should be given full credit even if there is no working or incorrect working, **unless** the question states 'show your working'.

For questions in which the number of significant figures required is not stated, credit should be awarded for correct answers when rounded by the examiner to the number of significant figures given in the mark scheme. This may not apply to measured values.

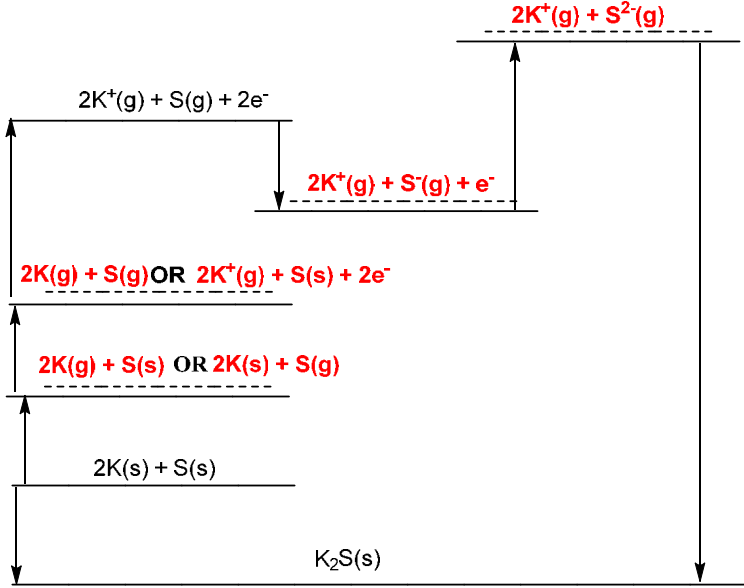
For answers given in standard form (e.g. $a \times 10^n$) in which the convention of restricting the value of the coefficient (a) to a value between 1 and 10 is not followed, credit may still be awarded if the answer can be converted to the answer given in the mark scheme.

Unless a separate mark is given for a unit, a missing or incorrect unit will normally mean that the final calculation mark is not awarded. Exceptions to this general principle will be noted in the mark scheme.

7 Guidance for chemical equations

Multiples / fractions of coefficients used in chemical equations are acceptable unless stated otherwise in the mark scheme.

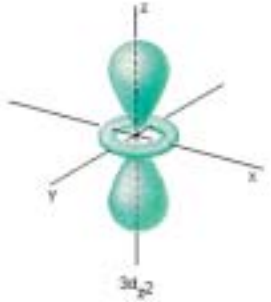
State symbols given in an equation should be ignored unless asked for in the question or stated otherwise in the mark scheme.

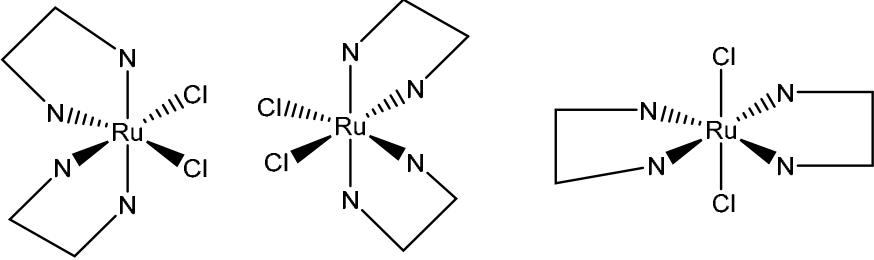
Question	Answer	Marks
1(a)	M1 magnesium > calcium > strontium M2 ΔH_{latt} and ΔH_{hyd} both become less exothermic / less negative M3 ΔH_{latt} changes less OR ΔH_{hyd} is dominant factor M4 ΔH_{sol} becomes less exothermic / less negative / more positive / more endothermic	4
1(b)	M1 ΔH / energy change when 1 mole of an ionic solid / compound is formed M2 from gaseous ions (under standard conditions)	2
1(c)	M1 as ionic radii increases AND ΔH_{latt} less exothermic M2 as ionic charge increases AND ΔH_{latt} increases/more exothermic	2
1(d)(i)	 <p>any two [1] any three [2] all four [3]</p>	3

Question	Answer	Marks
1(d)(ii)	<p>M1 selection of ONLY six correct values (–381, 89, 419, 279, –200, 640) AND use of $\times 2$ as only multiplier with K</p> <p>M2 correct evaluation of data used ecf</p> $-381 = (89 \times 2) + (419 \times 2) + 279 + (-200) + 640 + \Delta H_{\text{latt}}^{\ominus}$ $\Delta H_{\text{latt}}^{\ominus} = -2116 \text{ (kJ mol}^{-1}\text{)}$	2

Question	Answer	Marks
2(a)(i)	$2\text{LiNO}_3 \rightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$	1
2(a)(ii)	<p>M1 radius / size of cation / M^+ increases OR charge density of ion decreases</p> <p>M2 less polarisation / distortion of anion / nitrate ion / NO_3^- / less weakening of NO bond</p>	2
2(b)	<p>M1 M2 any two for one mark or all four for two marks:</p> <ul style="list-style-type: none"> mol total $\text{MnO}_4^- = 0.125 \times 0.0500 = 6.25 \times 10^{-3}$ mol $\text{Fe}^{2+} = 0.0400 \times 0.0225 = 9.00 \times 10^{-4}$ mol unreacted $\text{MnO}_4^- = 9.00 \times 10^{-4} \div 5 = 1.80 \times 10^{-4}$ ecf mol reacted $\text{MnO}_4^- = 6.25 \times 10^{-3} - 1.80 \times 10^{-4} = 6.07 \times 10^{-3}$ ecf <p>M3</p> <p>mol $\text{NO}_2^- = 2.5 \times 6.07 \times 10^{-3} = 1.5175 \times 10^{-2}$</p> <p>conc $\text{NaNO}_2 = 4 \times 1.5175 \times 10^{-2} = 6.07\text{-}6.08 \times 10^{-2} \text{ mol dm}^{-3}$ ecf min 2sf</p>	3
2(c)(i)	<p>$3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$</p> <p>M1 MnO_4^{2-} as a reactant and $\text{MnO}_4^- + \text{MnO}_2$ products identified</p> <p>M2 correct equation</p>	2
2(c)(ii)	<p>(E_{cell}) decreases / becomes less positive AND as $[\text{H}^+]$ decreases AND equilibrium shifts to the left</p> <p>OR in alkali the $E_{\text{cell}} = 0.60 - 0.56 = 0.04 \text{ V}$ (working required)</p>	1

Question	Answer	Marks
3(a)	<p>M1 $\Delta S^\circ = (213.8 + 2 \times 248.2) - (237.8 + 3 \times 205.2)$ $\Delta S^\circ = -143.2 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$</p> <p>M2 $\Delta H^\circ = (-393.5 + 2 \times -296.8) - (116.7)$ $\Delta H^\circ = -1103.8 \text{ (kJ mol}^{-1}\text{)}$</p> <p>M3 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta G^\circ = -1103.8 - (298 \times -0.1432) = -1061.1 \text{ to } -1061.4 \text{ (kJ mol}^{-1}\text{) ecf min 3sf}$</p>	3
3(b)	<p>M1 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ AND $\Delta G^\circ = 0$ OR $T = \Delta H^\circ / \Delta S^\circ$ [1]</p> <p>M2 $T = 261.6 \div 0.3655 = 715.7 / 716 / 715 \text{ K min 3sf}$</p>	2

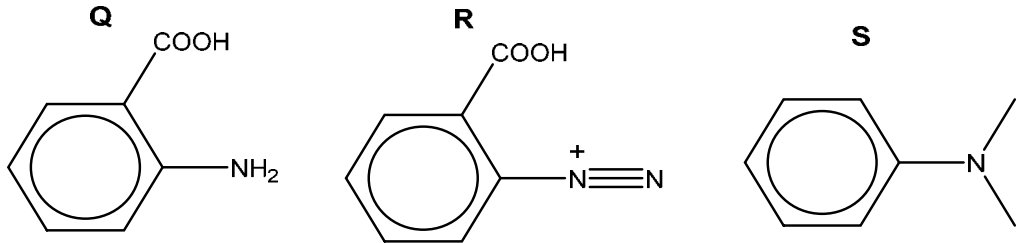
Question	Answer	Marks
4(a)(i)	the (3)d and (4)s (sub-shells/orbitals) are close/similar in energy	1
4(a)(ii)		1

Question	Answer	Marks
4(b)	<ul style="list-style-type: none"> • precipitation solution A: e.g. NaOH / OH⁻ • observations: (pale) blue ppt. / solid • product: Cu(OH)₂ OR [Cu(OH)₂(H₂O)₄] ecf from A • ligand substitution solution B: e.g. HCl / Cl⁻, NH₃ • observations: dark/deep blue solution (with NH₃) OR yellow solution (with Cl⁻) • product: [Cu(NH₃)₄(H₂O)₂]²⁺ OR [CuCl₄]²⁻ <p>any two [1] any four [2] all six [3]</p>	3
4(c)	<p>M1 (Ag⁺) d-subshell is full / complete OR d¹⁰ OR d-orbitals are full</p> <p>M2 no d-d(*) transition OR no d electrons promoted/excited</p>	2
4(d)	<p>M1 species with two lone pairs (of electrons)</p> <p>M2 that form dative (covalent) / co-ordinate bond(s) to a (central) metal atom / ion</p>	2
4(e)(i)		3
4(e)(ii)	optical AND cis-trans / geometrical	1
4(e)(iii)	trans isomer / trans isomer correctly identified AND dipoles cancel / partial charges cancel / ion dipoles cancel	1

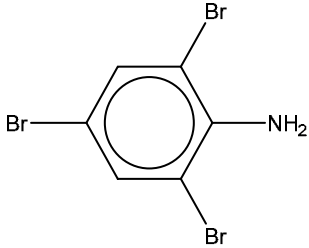
Question	Answer	Marks
5(a)(i)	<p>M1 (using exp 1 and 2) $[\text{NO}] \times 3$, rate $\times 9$ so 2nd order to NO</p> <p>M2 (using exp 1 and 3) $[\text{NO}] \times 2$, $[\text{Cl}_2] \times 4$, rate $\times 16$ so 1st order to Cl_2</p> <p>OR (using exp 2 and 3) $[\text{NO}] \times 2/3$, $[\text{Cl}_2] \times 4$, rate $\times 1.8$ so 1st order to Cl_2</p> <p>M3 (rate =) $k [\text{NO}]^2 [\text{Cl}_2]$ ecf</p>	3
5(a)(ii)	<p>M1 rate = $k [\text{NO}]^2 [\text{Cl}_2]$</p> <p>$k = (3.68 \times 10^{-2}) \div (0.025^2 \times 0.015) = 3925.33$ ecf (a)(i) min 2sf</p> <p>M2 $\text{dm}^6 \text{mol}^{-2} \text{min}^{-1}$ ecf (a)(i)</p>	2
5(b)	<p>initiation $\text{NO}_2\text{Cl} \rightarrow \text{Cl}\cdot + \text{NO}_2\cdot$</p> <p>step 1 $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$</p> <p>step 2 $\text{ClO}\cdot + \text{O}_3 \rightarrow \text{Cl}\cdot + 2\text{O}_2$</p> <p>Any two [1] all three [2]</p>	2
5(c)	<p>M1 $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$ ALLOW $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_5$</p> <p>M2 $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$ ALLOW $\text{NO}_5 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$</p>	2

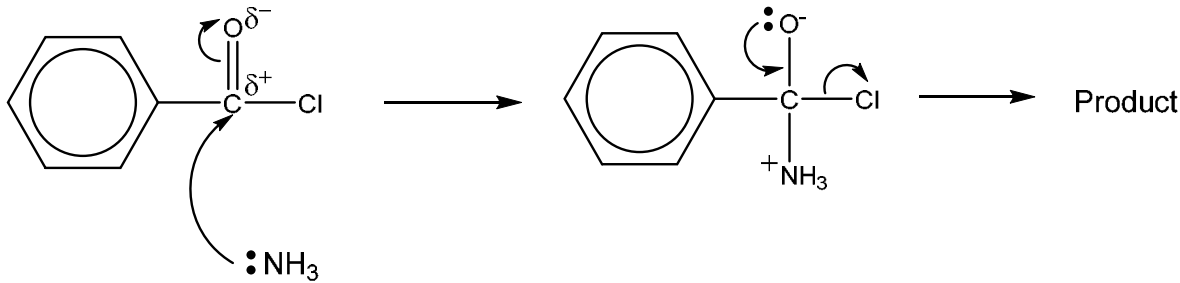
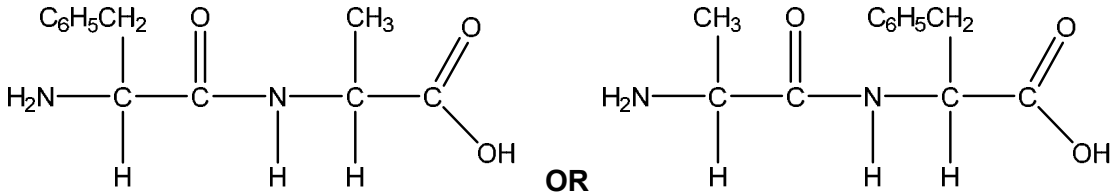
Question	Answer	Marks
6(a)(i)	species / molecules / pair that differ (by the presence or absence) of a H^+ ion / proton	1
6(a)(ii)	$\text{HCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCOO}^-$	1
6(b)(i)	$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]}$	1

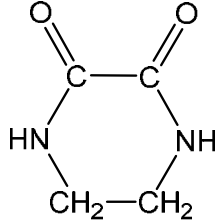
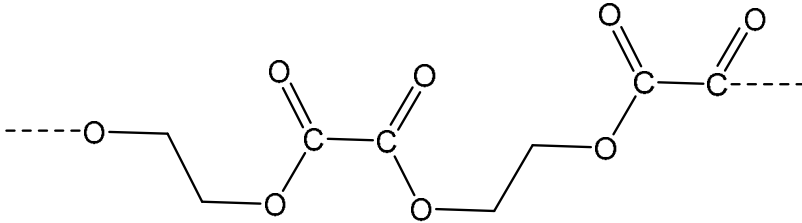
Question	Answer	Marks
6(b)(ii)	M1 $K_a = 10^{-4.82} = 1.51 \times 10^{-5}$ OR $[H^+] = 10^{-3.25} = 5.62 \times 10^{-4}$ M2 $[HA] = (10^{-3.25})^2 \div 1.51 \times 10^{-5} = 0.021 / 0.0209 / 0.02089$ (mol dm ⁻³) ecf min 2sf	2
6(c)(i)	M1 a solution that resists / opposes / minimises changes in pH M2 when small amounts of acid / H ⁺ and base / alkali / OH ⁻ are added to it	2
6(c)(ii)	<u>Method 1</u> M1 $[H^+] = 10^{-5.70}$ OR 2.00×10^{-6} OR 1.99526×10^{-6} M2 moles CH ₃ COONa = $0.400 \times 0.125 = 5.00 \times 10^{-2}$ moles CH ₃ COOH _{eqm} = $(5.00 \times 10^{-2} \times 2.00 \times 10^{-6}) \div 1.78 \times 10^{-5}$ OR 5.60×10^{-3} M3 $[CH_3COOH]_{initial} = 5.60 \times 10^{-3} \times 1000 / 600$ $[CH_3COOH]_{initial} = 0.00933-0.00936$ (mol dm ⁻³) ecf min 2sf <u>Method 2</u> M1 $pK_a = -\log(1.78 \times 10^{-5})$ OR 4.75 M2 $pH = pK_a + \log[B^-] / [HA]$ $5.7 = 4.75 + \log(0.05 / (0.6x))$ $0.95 = \log(0.05 / (0.6x))$ M3 $10^{0.95} = (0.05 / (0.6x))$ $5.348x = 0.05$ $x = 0.00935-0.00937$ (mol dm ⁻³) ecf min 2sf	3
6(d)(i)	$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$	1
6(d)(ii)	M1 $Q = 3.75 \times 40 \times 60$ OR 9000 C AND use of 96500 OR $1.6 \times 10^{-19} \times 6.02 \times 10^{23}$ M2 moles of oxygen = $9000 \div 386000 = 0.0233$ volume of O ₂ = $0.0233 \times 24000 = 559.6 / 559.8 / 560$ cm ³ ecf min 2sf ALLOW [use of $Q \div (1.6 \times 10^{-19} \times 6.02 \times 10^{23}) = 560.6$ cm ³]	2

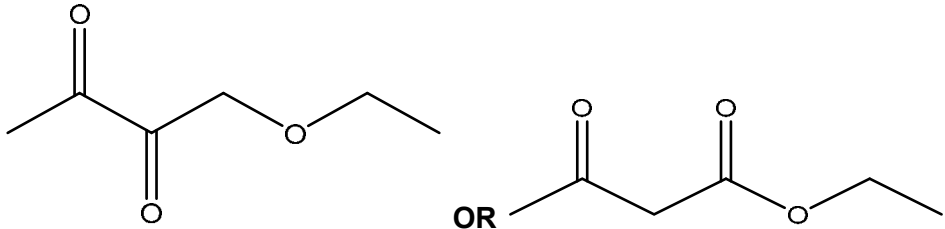
Question	Answer	Marks
7(a)(i)	2-nitrobenzoic acid OR 2-nitrobenzenecarboxylic acid	1
7(a)(ii)	hot / reflux / heat AND (alkaline / acidified / neutral) MnO_4^- / KMnO_4	1
7(a)(iii)	COOH / carboxyl group is electron-withdrawing / electronegative AND 3- and 5- / meta- directing	1
7(b)(i)		3
7(b)(ii)	M1 step 1: Fe / Sn, conc. HCl M2 step 2: HNO_2 OR NaNO_2 AND HCl M3 step 1: heat / reflux / hot AND step 2: $\leq 10^\circ\text{C}$	3

Question	Answer	Marks
8(a)	M1 benzylamine > ammonia > phenylamine M1 M2 Any two for one mark, all three for two marks: <ul style="list-style-type: none"> (basicity linked to) p orbital of N / lone pair on N AND being able to bond / accept / donate to / coordinate to a proton / H^+ (benzylamine) R / alkyl / CH_2 group AND is electron donating / positive inductive effect / has + I effect (phenylamine) p orbital of N / lone pair on N is overlaps / incorporated / delocalised in the ring / π-bond system 	3

Question	Answer	Marks
8(b)(i)	M1 white ppt. M2 structure 	2
8(b)(ii)	M1 lone pair / p-orbital / electrons on the nitrogen / NH ₂ AND overlap / delocalised / incorporated AND with the (π -electrons) ring / π system M2 increasing its electron density (of the ring) OR it can polarise the electrophile / Br ₂ better	2
8(c)	lone pair / p-orbital on N is delocalised AND into C=O group / across the two electronegative O and N	1

Question	Answer	Marks
8(d)	 <p>M1 / M2 any two for one mark, all four for two marks:</p> <ul style="list-style-type: none"> • lone pair on N • correct arrow from lone pair N to C (of C=O) • correct dipole on C=O • correct arrow from the C=O bond to O atom <p>M3 correct intermediate</p> <p>M4 arrow from O⁻ to C–O bond AND arrow from C–Cl bond to Cl ALLOW arrow from anywhere on O⁻ to C–O bond</p>	4
8(e)(i)	pH at which a molecule has no overall charge / is neutral / exist as a zwitterion	1
8(e)(ii)	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-$	1
8(f)	 <p>M1 correct peptide bond displayed (there must be a saturated carbon attached to either side of the peptide group) M2 rest of the dipeptide correct</p>	2

Question	Answer	Marks
9(a)	due to the electron-withdrawing effect/electronegative / –I effect of chlorine AND stabilising the anion / carboxylate ion OR weakening the O-H bond	1
9(b)(i)	$(\text{COOH})_2 + 2\text{SOCl}_2 \rightarrow (\text{COCl})_2 + 2\text{HCl} + 2\text{SO}_2$	1
9(b)(ii)	<p>CO₂ [1]</p>  <p>[1]</p>	2
9(b)(iii)	 <p>M1 one correct repeat unit (within their structure) M2 the rest of the structure correct ecf on one incorrect monomer used [If structure partly or fully skeletal: continuation bonds must be dashed / wavy / different or have through brackets]</p>	2
9(c)(i)	CHI ₃ / triiodomethane	1

Question	Answer				Marks																				
9(c)(ii)	<table border="1" data-bbox="338 217 1458 616"> <thead> <tr> <th data-bbox="338 217 557 317">chemical shift (δ)</th> <th data-bbox="557 217 766 317">splitting pattern</th> <th data-bbox="766 217 1120 317">number of ^1H atoms responsible for the peak</th> <th data-bbox="1120 217 1458 317">number of protons on adjacent carbon atoms</th> </tr> </thead> <tbody> <tr> <td data-bbox="338 317 557 384">1.15</td> <td data-bbox="557 317 766 384">triplet</td> <td data-bbox="766 317 1120 384">3</td> <td data-bbox="1120 317 1458 384">2</td> </tr> <tr> <td data-bbox="338 384 557 451">2.25</td> <td data-bbox="557 384 766 451">singlet</td> <td data-bbox="766 384 1120 451">3</td> <td data-bbox="1120 384 1458 451">0</td> </tr> <tr> <td data-bbox="338 451 557 518">3.60</td> <td data-bbox="557 451 766 518">singlet</td> <td data-bbox="766 451 1120 518">2</td> <td data-bbox="1120 451 1458 518">0</td> </tr> <tr> <td data-bbox="338 518 557 616">3.95</td> <td data-bbox="557 518 766 616">quartet / quadruplet</td> <td data-bbox="766 518 1120 616">2</td> <td data-bbox="1120 518 1458 616">3</td> </tr> </tbody> </table> <p data-bbox="338 651 1084 687">mark as any three [1] any six [2] any nine [3] all twelve [4]</p>				chemical shift (δ)	splitting pattern	number of ^1H atoms responsible for the peak	number of protons on adjacent carbon atoms	1.15	triplet	3	2	2.25	singlet	3	0	3.60	singlet	2	0	3.95	quartet / quadruplet	2	3	4
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