

GCE

Chemistry A

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

Advanced GCE

Mark Scheme for June 2015

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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.

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Annotations available in Scoris.

Annotation	Meaning
	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

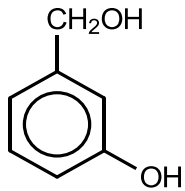
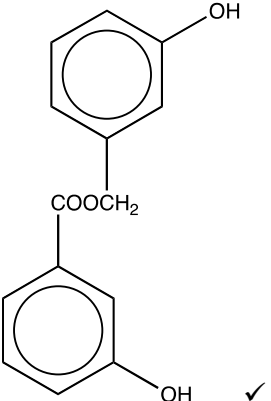
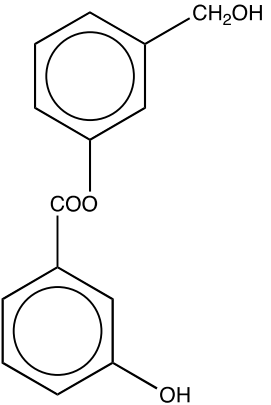
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

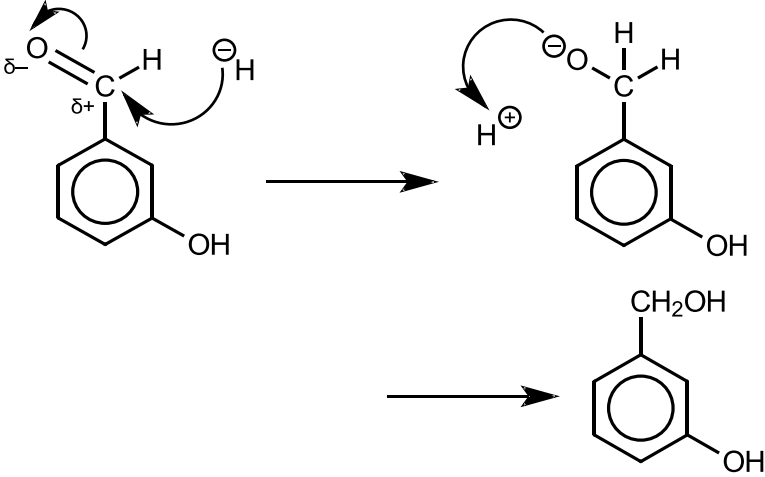
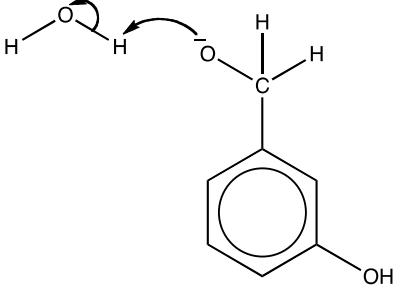
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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



1(c)(ii), 2(a)(i), 2(d)(ii), 3(b) and 4(d)

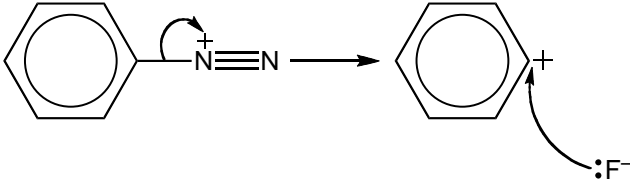
Question		Answer	Mark	Guidance
1	(a)	(Relative) solubility (in stationary phase) ✓	1	ALLOW how well the compound dissolves IGNORE retention time AND partition DO NOT ALLOW adsorption OR absorption
	(b)	(i) Compound B AND M ⁺ /molecular ion peak (at m/z) = 124 ✓	1	ALLOW Mr = 124 IGNORE compound B because m/z = 124 ALLOW C ₇ H ₈ O ₂ ⁺ = 124 OR C ₇ H ₈ O ₂ = 124 ALLOW peak at (m/z =) 109 due to HOC ₆ H ₄ O ⁺ ALLOW peak at (m/z =) 109 due to loss of CH ₃ IGNORE reference to other peaks in the spectrum
		(ii) Compound (B) is less soluble in the stationary phase/ liquid	1	ORA Answer refers to the first compound to emerge from the column ALLOW compound (B) is more soluble in mobile phase/gas ALLOW compound interacts less with stationary phase/liquid OR compound interacts more with mobile phase/gas IGNORE compound adsorbs less IGNORE compound is not very soluble (comparison needed) IGNORE volatility OR reactivity

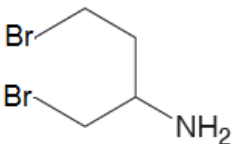
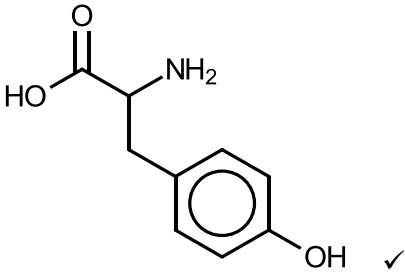
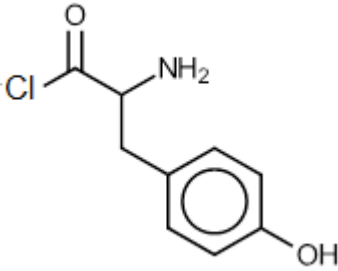
Question	Answer	Mark	Guidance
(c) (i)	<p>reagent = $K_2Cr_2O_7$ AND H_2SO_4 ✓</p> <p>compound C =  ✓</p> <p>ester =  ✓</p>	3	<p>ALLOW acidified dichromate</p> <p>ALLOW H^+/any acid</p> <p>IGNORE concentration of acid</p> <p>ALLOW $Na_2Cr_2O_7 / Cr_2O_7^{2-}$ / (potassium OR sodium) dichromate((VI))</p> <p>ALLOW acidified MnO_4^-</p> <p>ALLOW Tollens' reagent/ammoniacal silver nitrate</p> <p>IGNORE conditions</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>ALLOW ECF from incorrect compound C Check positions of OH groups</p> <p>ALLOW esterification of phenol group</p> 

Question	Answer	Mark	Guidance
(ii)	<p>curly arrow from H^- to $\text{C}^{\delta+}$ ✓</p> <p>dipole AND curly arrow from $\text{C}=\text{O}$ bond to O ✓</p> <p>correct intermediate AND curly arrow to H^+ ✓</p> 	3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC curly arrow must come from lone pair on H or negative charge on H</p> <p>curly arrow must come from the bond, not the carbon atom</p> <p>curly arrow must come from lone pair on O or negative charge on O and go to H or positive charge on H</p> <p>Where circles have been placed round charges, this is for clarity only and does not indicate a requirement</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>ALLOW for second stage</p>  <p>IF H_2O is used it MUST show the curly arrow from the negative charge or lone pair on the oxygen atom of the intermediate to H in H_2O AND from the $\text{O}-\text{H}$ bond to the O in H_2O. Dipole not required on water molecule</p> <p>Penalise missing $-\text{OH}$ on intermediate only</p> <p>IGNORE product – already given credit in part (i)</p>

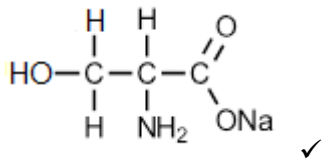
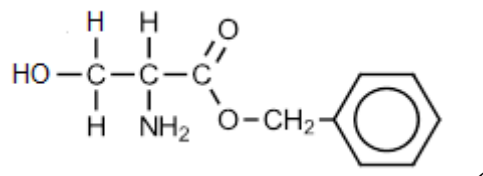
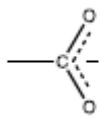
Question		Answer	Mark	Guidance
	(d)	<p><chem>COc1cccc(O)c1.BrBr.BrBr>>COc1c(Br)cccc(O)c1.BrBr</chem></p>	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW disubstitution at any positions on benzene ring
		Total	10	

Question			Answer	Mark	Guidance
2	(a)	(i)	<p>M1 p-orbitals overlap (to form pi/π-bonds) ✓</p> <p>M2 π-bond(s) are <u>delocalised</u> in structure B ✓</p> <p>M3 π-bonds are localised/between two carbons in structure A ✓</p> <p>M4</p> <div style="text-align: center;">  <p>AND</p> </div> <p>Diagrams show correct position of delocalised and localised π-bonds/π-electrons</p> <p>OR correct position of p-orbital overlap ✓</p> <p> QWC requires delocalised/delocalized spelled correctly and used in correct context</p>	4	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>IGNORE p-orbitals overlap to form sigma bonds</p> <p>ALLOW electrons are delocalised in structure B IGNORE B has delocalised structure or ring (must be electrons or π-bonds)</p> <p>ALLOW π-electrons/p-orbital overlap localised/between two carbons in structure A ALLOW p-orbitals overlap with one other carbon IGNORE electrons are localised OR structure A has localised structure (must be π-bonds/π-electrons/p-orbital overlap) ALLOW labelled diagram showing overlap of p-orbitals between two carbon atoms DO NOT ALLOW C=C in this diagram</p> <p>Diagram for structure A must show the full ring for M4 IGNORE C=C in M4 diagram</p> <p>IGNORE charge density</p> <p>DO NOT ALLOW electronegativity</p> <p>Structures do not need to be labelled A and B if the description matches the structure</p>

Question	Answer	Mark	Guidance
(ii)	<p>structure B/delocalised structure is (more) stable ✓</p> <p>structure B is a better because (enthalpy change of hydrogenation for benzene is) less (exothermic) than (-) 357 (kJ mol⁻¹) ✓</p>	2	<p>ALLOW structure B is low in energy</p> <p>IGNORE structure B is less reactive</p> <p>ALLOW enthalpy change/hydrogenation for benzene is less (negative) than 3 × (-)119</p> <p>IGNORE more positive than (-)357 kJ mol⁻¹</p> <p>ALLOW enthalpy change is less than 3x enthalpy change for cyclohexene</p> <p>ALLOW structure B is more stable by 149 kJ mol⁻¹ (2 marks)</p> <p>DO NOT ALLOW more/less energy needed for the reaction</p> <p>Answer must refer to data given in the question and must be a comparison</p> <p>IGNORE 360 kJ mol⁻¹</p> <p>No marks can be awarded if structure A is selected</p>
(b)	 <p>curly arrow from C–N bond to N⁺ ✓</p> <p>curly arrow from lone pair on fluoride ion to positive charge on benzene ring ✓</p>	2	<p>First curly arrow must come from bond not from C atom</p> <p>ALLOW first curly arrow to nitrogen atom OR to positive charge on nitrogen atom</p> <p>ALLOW second curly arrow from negative charge on fluoride ion</p> <p>ALLOW second curly arrow to carbon atom with positive charge</p>

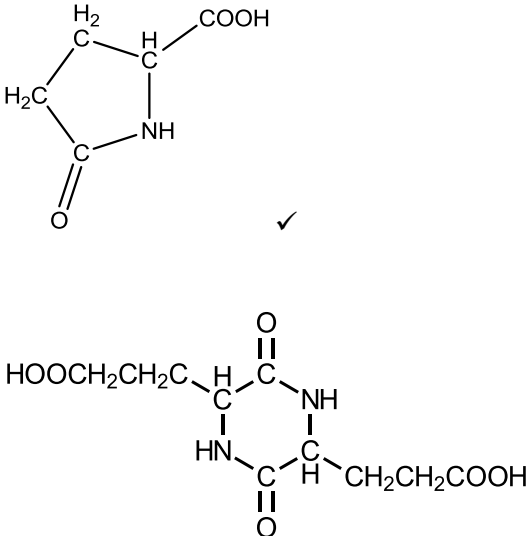
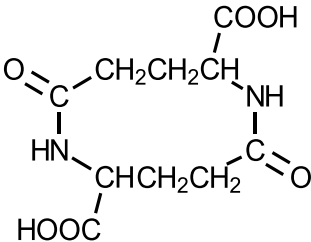
Question	Answer	Mark	Guidance
(c)	$(\text{CH}_3)_2\text{CHBr} + \text{FeBr}_3 \longrightarrow (\text{CH}_3)_2\text{CH}^+ + \text{FeBr}_4^-$	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW positive charge anywhere on the electrophile IGNORE AlCl_3 OR AlBr_3
(d)	<p>(i) First reactant = HNO_2 ✓</p> <p>Second reactant =</p>  <p style="text-align: right;">✓</p> <p>Third reactant =</p>  <p style="text-align: right;">✓</p>	3	ALLOW $\text{NaNO}_2 + \text{HCl}$ OR $\text{HNO}_2 + \text{HCl}$ IGNORE conditions/concentration ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW 

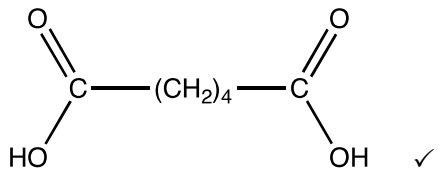
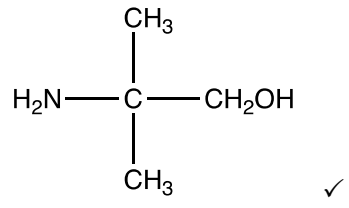
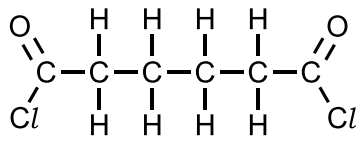
Question	Answer	Mark	Guidance
(ii)	<p>FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 1.35 (g) award 3 marks IF answer = 0.54 (g) award 2 marks (no scale-up) IF answer = 0.216 (g) award 2 marks (incorrect scale-up)</p> <p>$n(\text{compound D}) = 1.73/346 = 0.00500 \text{ mol} \quad \checkmark$ $n(1,3\text{-diaminobenzene}) \text{ required} = 100/40 \times 0.005$ $= 0.0125 \text{ mol} \quad \checkmark$ Molar mass of 1,3-diaminobenzene = 108 (g mol⁻¹) AND Mass of 1,3-diaminobenzene = (108)(0.0125) = 1.35 g \checkmark</p>	3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC If there is an alternative answer, check to see if there is any ECF credit possible ALLOW ECF from incorrect amount, scale-up or molar mass</p> <p>Alternative 1 $n(\text{compound D}) = 1.73/346 = 0.00500 \text{ mol}$ Molar mass of 1,3-diaminobenzene = 108 (g mol⁻¹) AND Mass of 1,3-diaminobenzene = (0.00500)(108) = 0.540 g Mass of 1,3-diaminobenzene required = (0.540)(100/40) = 1.35 g</p> <p>Alternative 2 346 g gives 108 g 1.73 g gives $108/364 \times 1.73 = 0.54 \text{ g}$ $0.54/40 \times 100 = 1.35 \text{ g}$</p>
(iii)	<p>(compound D has) two chiral centres \checkmark</p> <p>Four optical isomers exist \checkmark</p> <p>(Synthesis could) use enzymes OR bacteria OR use (chemical) chiral synthesis OR <u>chiral</u> catalysts OR use natural chiral molecules OR single isomers (as starting materials)</p> <p>\checkmark</p>	3	<p>ALLOW (Compound D) has two asymmetric carbons OR has two stereocentres</p> <p>ALLOW four enantiomers OR two pairs of enantiomers</p> <p>INDEPENDENT MARK ALLOW biological catalysts ALLOW <u>chiral</u> transition metal complex/catalyst OR <u>stereoselective</u> transition metal complex/catalyst ALLOW '<u>chiral</u> pool'/chiral auxiliary</p>
	Total	18	

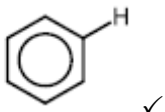
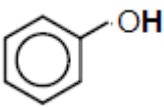
Question			Answer	Mark	Guidance
3	(a)	(i)	  —NH ₃ ⁺ in second product ✓	3	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW —O ⁻ Na ⁺ OR —O ⁻ (cation not required) DO NOT ALLOW —O—Na (covalent bond) DO NOT ALLOW —O (without the sodium) ALLOW delocalised carboxylate 
		(ii)	perfume/fragrance/flavouring ✓	1	IGNORE solvent OR food additive
		(iii)	Reaction 3: (hot) ethanolic ammonia ✓ Reaction 4: oxidation ✓ Reaction 5: hydrolysis ✓	3	ALLOW NH ₃ (dissolved) in ethanol IGNORE other conditions ALLOW oxidisation/oxidised DO NOT ALLOW redox ALLOW nucleophilic addition-elimination DO NOT ALLOW nucleophilic substitution IGNORE acid/base

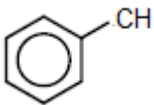
Question	Answer	Mark	Guidance
(b)	<p>M1 Compound E</p> $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}-\text{CHO} \\ \\ \text{NH}_2 \end{array}$	6	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>Labels are not required for compound E, F, G or H</p> <p>IGNORE labels for M1, M2, M3 and M4</p> <p>CH₂=CH must be shown in E</p>
	<p>M2 Compound F</p> $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}-\text{COOH} \\ \\ \text{NH}_2 \end{array}$	✓	<p>ALLOW C₂H₃ OR CHCH₂ for CH=CH₂ in F</p>
	<p>M3 Compound G</p> $\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---} \text{C} - \text{C} \text{---} \\ \quad \\ \text{H} \quad \text{CHNH}_2 \\ \quad \quad \\ \quad \quad \text{COOH} \end{array} \right]$	✓	<p>ALLOW multiple repeat units but must be full repeat units</p> <p>ALLOW end bonds shown as</p> <p>DO NOT ALLOW if structures have no end bonds</p> <p>IGNORE brackets unless they are used to pick out the repeat unit from a polymer chain</p> <p>IGNORE n</p>
	<p>M4 Compound H</p> $\left[\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{---} \text{N} - \text{C} - \text{C} \text{---} \\ \quad \\ \text{H} \quad \text{CH}=\text{CH}_2 \end{array} \right]$	✓	<p>ALLOW C₂H₄NO₂ for CH(NH₂)COOH in polymer G</p> <p>ALLOW C₂H₃ OR CHCH₂ for CH=CH₂ in polymer H</p> <p>ALLOW ECF from NH₂CH₂CH=CHCOOH for the formation of compound G or compound H</p>


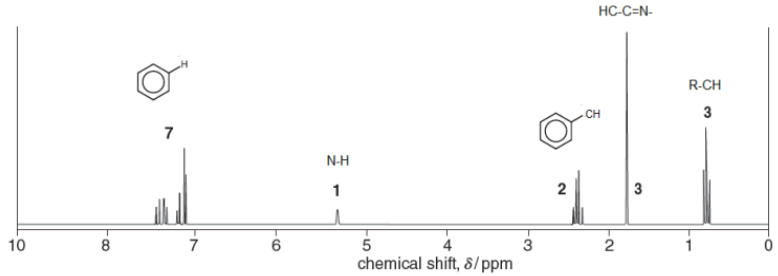
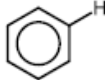
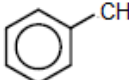
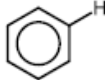
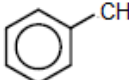
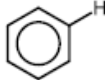
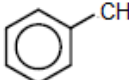
Question	Answer	Mark	Guidance
	<p>M5 Compound G OR</p> $\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{CHNH}_2 \\ \quad \quad \\ \quad \quad \text{COOH} \end{array} \right]$ <p>Is an addition polymer ✓</p> <p>M6 Compound H OR</p> $\left[\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{---N---C---C---} \\ \quad \\ \text{H} \quad \text{CH=CH}_2 \end{array} \right]$ <p>is a condensation polymer ✓</p>		<p>ALLOW alkene forms addition polymer/polymer with same empirical formula as monomer</p> <p>ALLOW equation for reaction</p> $n \text{ H}_2\text{C}=\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} \quad \text{C} \\ \quad \\ \text{NH}_2 \quad \text{COOH} \end{array} \longrightarrow \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{CHNH}_2 \\ \quad \quad \\ \quad \quad \text{COOH} \end{array} \right]_n$ <p>ALLOW amino acid forms condensation polymer</p> <p>OR (molecules of) compound F join/bond/add/react/form polymer and water/small molecule</p> <p>ALLOW equation for reaction</p> $n \text{ H}_2\text{C}=\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} \quad \text{C} \\ \quad \\ \text{NH}_2 \quad \text{COOH} \end{array} \longrightarrow \left[\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{---N---C---C---} \\ \quad \\ \text{H} \quad \text{CH=CH}_2 \end{array} \right]_n + \text{H}_2\text{O}$
(c) (i)	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{O} & \\ & & & & & & \\ \text{H} & \text{---N---} & \text{C---} & \text{C---} & \text{C---} & \text{C---} & \text{OH} \\ & & & & & & \\ & & \text{HOOC} & \text{H} & \text{H} & & \end{array}$ <p style="text-align: right;">✓</p>	1	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR a combination of above as long as unambiguous</p>

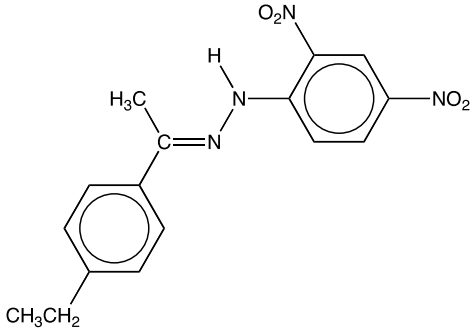
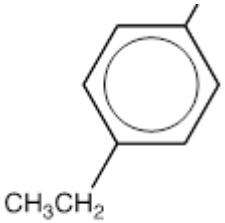
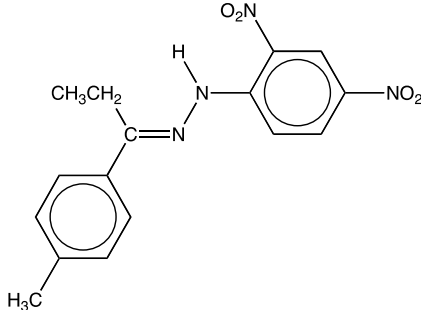
Question	Answer	Mark	Guidance
(ii)	 <p>The first structure is a 3-membered cyclic amide (beta-lactam) with a methyl group and a carboxylic acid group. The second structure is a cyclic amide with two propyl chains attached to the ring carbons.</p>	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>ALLOW a cyclic amide with a 3 membered ring</p> <p>ALLOW</p>  <p>OR a structure obtained by condensation of a glutamic acid molecule with the first cyclic amide</p>

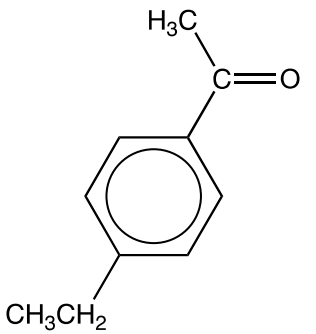
Question		Answer	Mark	Guidance
(d)	(i)	Ester AND amide ✓	1	ALLOW peptide for amide
	(ii)	 	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>Functional groups do not need to be fully displayed</p> <p>ALLOW structures as shown; the O-H bond and the N-H bonds in the functional groups do not need to be displayed</p> <p>DO NOT ALLOW -COOH</p> <p>ALLOW</p>  <p>Penalise incorrect connectivity to OH once in this question</p>
	(iii)	(The molecule/amide/ester) can be <u>hydrolysed</u> ✓	1	<p>ALLOW (the molecule/amide/ester) can form hydrogen/H-bonds <u>with water</u></p> <p>IGNORE acid/base</p>
Total			20	

Question		Answer	Mark	Guidance
4	(a)	magnetic resonance imaging/providing diagnostic information/body scanners. ✓	1	ALLOW MRI/scanning internal structures e.g. brain ALLOW detection of tumours/cancer/haemorrhage/aneurysm IGNORE reference to drugs, chemicals or functional groups IGNORE analysis of blood DO NOT ALLOW CT scan/CAT scan
	(b)	(i) Radio (waves) ✓	1	ALLOW a value in the range 60 – 900 MHz
		(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
4	(c)	14 ✓	1	
	(d)	NMR analysis (5 marks) M1 Peaks between (δ) 7.1 and 7.5 (ppm) OR Relative peak area of 7 OR Multiplet =  M2 Peak at 5.2/5.3	7	ANNOTATE ANSWER WITH TICKS AND CROSSES ETC IGNORE analysis of ¹³ C spectrum Each peak can be identified from its δ value \pm 0.2 ppm ALLOW (seven) benzene ring protons OR aromatic protons DO NOT ALLOW benzene ring without reference to protons ALLOW C ₆ H ₆ IGNORE 

Question	Answer	Mark	Guidance
	<p>OR Relative peak area of 1 = N-H ✓</p> <p>M3 Peak at 2.3/2.4 OR Relative peak area of 2 OR Quartet =  OR C₆H₅CH₂ ✓</p> <p>M4 Peak at 0.7/0.8 OR Triplet = R-CH OR R-CH₃ ✓</p> <p>M5 Triplet (at δ 0.7) AND quartet (at δ 2.3) = CH₂CH₃ OR triplet at (δ) 0.7 shows (C with) 2 adjacent Hs/protons = CH₂CH₃ OR quartet (at δ 2.3) shows (C with) 3 adjacent Hs/protons = CH₂CH₃ ✓</p>		<p>IGNORE O-H , CONH AND C=CH</p> <p>ALLOW quadruplet IGNORE CHC=O AND HC-N</p> <p>DO NOT ALLOW triplet = CH₃ OR CH₂CH₃</p> <p>This also scores M4 if triplet is linked to R-CH₃</p> <p>ALLOW CH₃CH₂ described as R-CH₃ and 2 adjacent H OR -CH₂- and 3 adjacent H</p> <p>The information can be presented on the spectrum or in a table.</p>

Question	Answer	Mark	Guidance																								
	<p> QWC: triplet or quartet spelled correctly in the correct context for M5</p>		 <table border="1" data-bbox="1279 576 2085 1074"> <thead> <tr> <th>Chemical shift/ppm</th> <th>Relative peak area</th> <th>Splitting pattern</th> <th>Type of proton</th> </tr> </thead> <tbody> <tr> <td>7.1 – 7.5</td> <td>7</td> <td>Multiplet</td> <td></td> </tr> <tr> <td>5.3</td> <td>1</td> <td>Singlet</td> <td>N-H</td> </tr> <tr> <td>2.3/2.4</td> <td>2</td> <td>Quartet</td> <td></td> </tr> <tr> <td>1.7/1.8</td> <td>3</td> <td>Singlet</td> <td>HC-C=N-</td> </tr> <tr> <td>0.7/0.8</td> <td>3</td> <td>triplet</td> <td>R-CH/R-CH₃</td> </tr> </tbody> </table> <p>IGNORE peak in the range 1.6–2.2 = HC–C=N– because this information is given in the question. H₃C–C=N– scores one mark for the identification of R¹ or R² (see below)</p>	Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton	7.1 – 7.5	7	Multiplet		5.3	1	Singlet	N-H	2.3/2.4	2	Quartet		1.7/1.8	3	Singlet	HC-C=N-	0.7/0.8	3	triplet	R-CH/R-CH ₃
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Question	Answer	Mark	Guidance
	<p>Identification of R¹ and R² (2 marks)</p> <p>Orange precipitate L Correct structure scores 2 marks</p>  <p>R¹ or R² = -CH₃ ✓</p> <p>R¹ or R² =</p>  <p>✓</p>		<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>Marks are for structure of R¹ and R²</p> <p>IGNORE errors in the rest of the structure</p> <p>ALLOW 1 mark for CH₃ and CH₃CH₂ swapped, i.e. the following structure</p>  <p>ALLOW H₃C-C=N-</p> <p>MUST BE 1,4-disubstituted (14 carbon environments in the ¹³C NMR spectrum)</p>

Question	Answer	Mark	Guidance
(e)	<p>Carbonyl compound K</p>  <p style="text-align: right;">✓</p>	1	ALLOW ECF from incorrect compound L Must be a correct carbonyl structure
	Total	12	

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