OCR
Oxford Cambridge and RSA

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.

Annotations available in Scoris.

Annotation	Meaning
BOD	Benefit of doubt given
CON	Contradiction
	Incorrect response
ECF	Error carried forward
I	Ignore
NAQ	Not answered question
NBOD	Benefit of doubt not given
POT	Power of 10 error
^	Omission mark
RE	Rounding error
SF	Error in number of significant figures
	Correct response

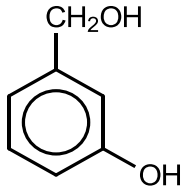
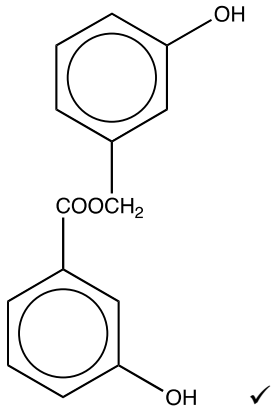
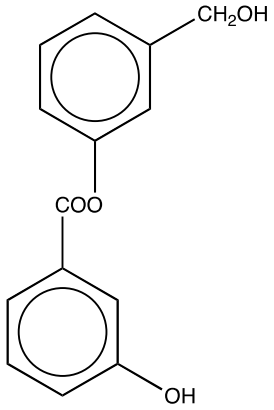
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

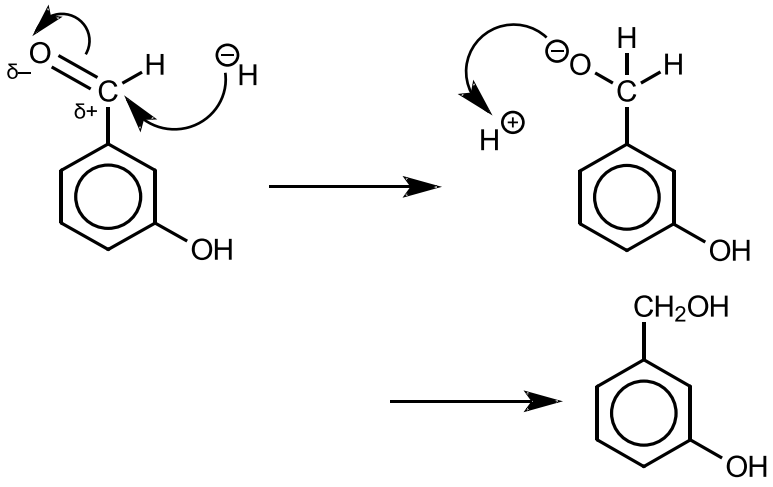
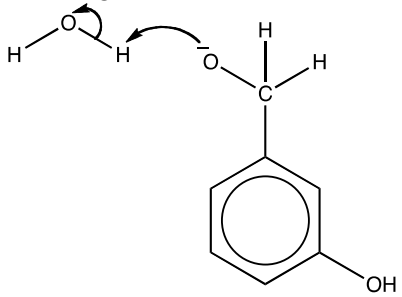
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

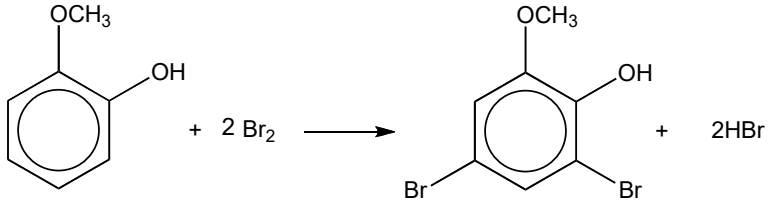
The following questions should be annotated with ticks to show where marks have been awarded in the body of the text:

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

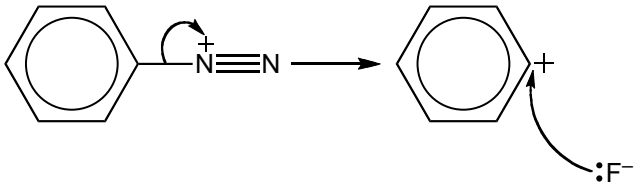
Question			Answer	Mark	Guidance
1	(a)		(Relative) solubility (in stationary phase) ✓	1	**ALLOW** how well the compound dissolves **IGNORE** retention time **AND** partition **DO NOT ALLOW** adsorption **OR** absorption
	(b)	(i)	Compound **B** **AND** M^+/molecular ion peak (at *m*/*z*) = 124 ✓	1	**ALLOW** Mr = 124 **IGNORE** compound B because *m*/*z* = 124 **ALLOW** $C_7H_8O_2^+$ = 124 **OR** $C_7H_8O_2$ = 124 **ALLOW** peak at (m/z =) 109 due to $HOC_6H_4O^+$ **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

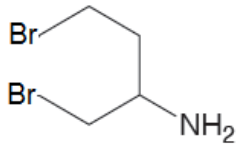
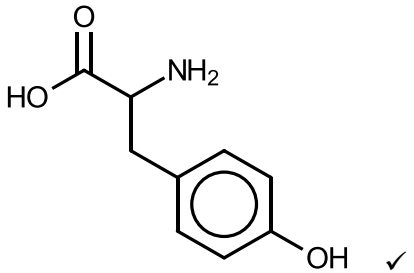
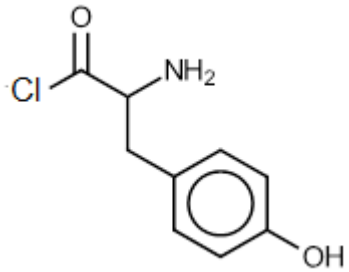
Question			Answer	Mark	Guidance
	(c)	(i)	reagent = $K_2Cr_2O_7$ **AND** H_2SO_4 ✓	3	**ALLOW** acidified dichromate **ALLOW** H^+/any acid **IGNORE** concentration of acid **ALLOW** $Na_2Cr_2O_7$ /$Cr_2O_7^{2-}$ **/**(potassium **OR** sodium) dichromate((VI)) **ALLOW** acidified MnO_4^- **ALLOW** Tollens'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

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

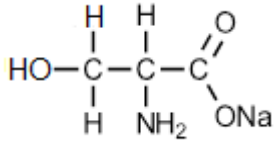
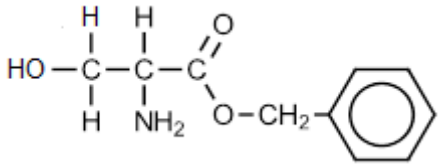
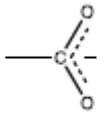
Question			Answer	Mark	Guidance
	(d)		 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** disubstitution at any positions on benzene ring
			Total	**10**	

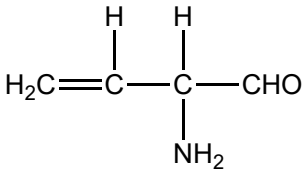
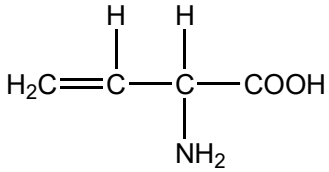
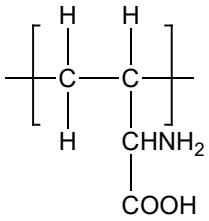
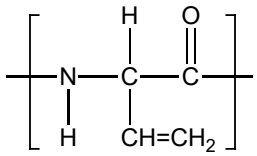
Question			Answer	Mark	Guidance
2	(a)	(i)	**M1** p-orbitals overlap (to form pi/π-bonds) ✓ **M2** π-bond(s) are <u>delocalised</u> in **structure B** ✓ **M3** π-bonds are localised/between two carbons in **structure A** ✓ **M4**  **AND** **Diagrams** show correct **position** of delocalised and localised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

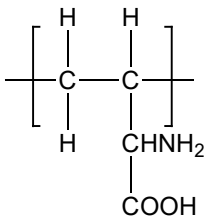
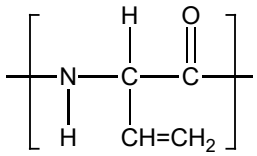
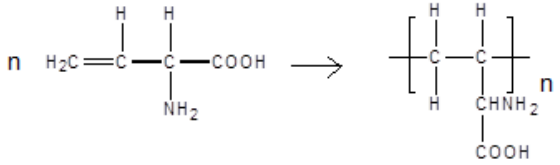
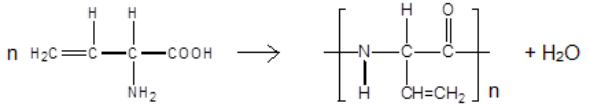
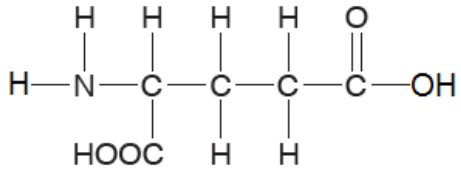
Question			Answer	Mark	Guidance
		(ii)	**structure B/**delocalised structure is (more) stable ✓ **structure B** is a better because (enthalpy change of hydrogenation for benzene is) less (exothermic) than (-) 357 (kJ mol^{-1}) ✓	2	**ALLOW** structure **B** is low in energy **IGNORE** structure **B**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

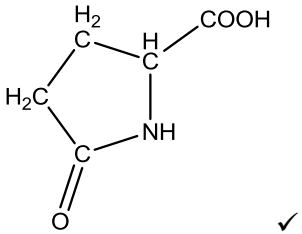
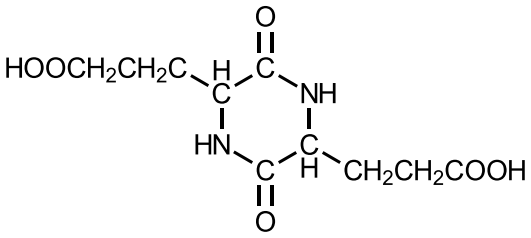
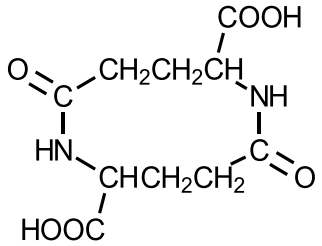
Question			Answer	Mark	Guidance
	(c)		$(CH_3)_2CHBr + FeBr_3 \rightarrow (CH_3)_2CH^+ + FeBr_4^-$	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** positive charge anywhere on the electrophile **IGNORE** $AlCl_3$ **OR** $AlBr_3$
	(d)	(i)	First reactant = HNO_2 ✓ Second reactant =  ✓ Third reactant =  ✓	3	**ALLOW** $NaNO_2$ + HCl **OR** HNO_2 + HCl **IGNORE** conditions/concentration **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** 

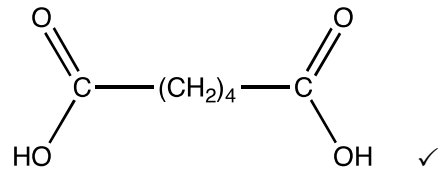
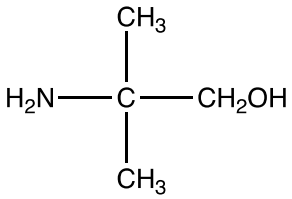
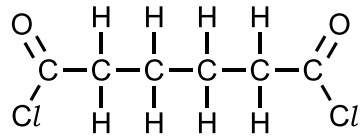
Question			Answer	Mark	Guidance
		(ii)	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 1.35 (g) award 3 marks **IF** answer = 0.54 (g) award 2 marks (no scale-up) **IF** answer = 0.216 (g) award 2 marks (incorrect scale-up) *n*(compound D) = 1.73/346 = 0.00500 mol ✓ *n*(1,3-diaminobenzene) required = 100/40 x 0.005 = 0.0125 mol ✓ Molar mass of 1,3-diaminobenzene = 108 (g mol^{-1}) **AND** Mass of 1,3-diaminobenzene = (108)(0.0125) = 1.35 g ✓	3	**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 **Alternative 1** n(compound D) = 1.73/346 = 0.00500 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 **Alternative 2** 346 g gives 108 g 1.73 g gives 108/364 x 1.73 = 0.54 g 0.54/40 x100 = 1.35 g
		(iii)	(compound D has) **two** chiral centres ✓ Four optical isomers exist ✓ (Synthesis could) use enzymes **OR** bacteria **OR** use (chemical) chiral synthesis **OR** chiral catalysts **OR** use natural chiral molecules **OR** single isomers (as starting materials) ✓	3	**ALLOW** (Compound **D**) has two asymmetric carbons **OR** has two stereocentres **ALLOW** four enantiomers **OR** two pairs of enantiomers **INDEPENDENT MARK** **ALLOW** biological catalysts **ALLOW** chiral transition metal complex/catalyst **OR** stereoselective transition metal complex/catalyst **ALLOW** 'chiral pool'/chiral auxiliary
			Total	**18**	

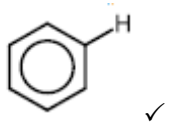
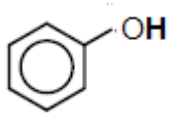
Question			Answer	Mark	Guidance
3	(a)	(i)	 ✓  ✓ $—NH_3^+$ in second product ✓	3	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** $—O^-Na^+$ **OR** $—O^-$ (cation not required) **DO NOT ALLOW** —O—Na (covalent bond) **DO 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

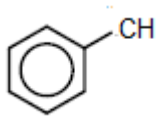
Question	Answer	Mark	Guidance
(b)	**M1** Compound **E**  ✓ **M2** Compound **F**  ✓ **M3** Compound **G**  ✓ **M4** Compound **H**  ✓	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous Labels are not required for compound E, F, G or H **IGNORE** labels for **M1**, **M2**, **M3** and **M4** CH_2=CH must be shown in **E** **ALLOW** C_2H_3 **OR** $CHCH_2$ for $CH=CH_2$ in **F** **ALLOW ECF** from error in structure of <u>aldehyde</u> E **ALLOW** multiple repeat units but must be full repeat units **ALLOW** end bonds shown as ..... **DO NOT ALLOW** if structures have no end bonds **IGNORE** brackets unless they are used to pick out the repeat unit from a polymer chain **IGNORE** n **ALLOW** $C_2H_4NO_2$ for $CH(NH_2)COOH$ in polymer **G** **ALLOW** C_2H_3 **OR** $CHCH_2$ for $CH=CH_2$ in polymer **H** **ALLOW ECF** from $NH_2CH_2CH=CHCOOH$ for the formation of compound G or compound H

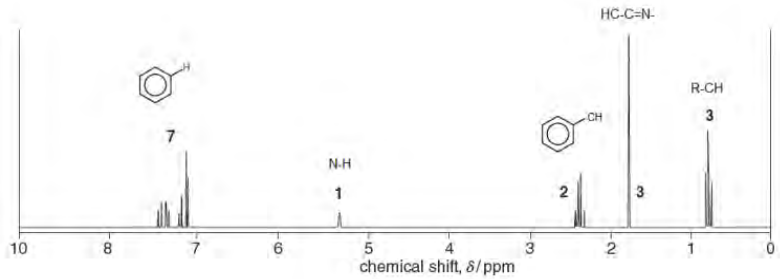
Question			Answer	Mark	Guidance
			M5 Compound **G** **OR**  Is an addition polymer ✓ **M6** Compound **H** **OR**  is a condensation polymer ✓		**ALLOW** alkene forms addition polymer/polymer with same empirical formula as monomer **ALLOW** equation for reaction  **ALLOW** amino acid forms condensation polymer **OR** (molecules of) compound **F** join/bond/add/react/form polymer and water/small molecule **ALLOW** equation for reaction 
	(c)	**(i)**	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous

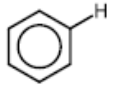
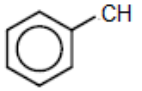
Question			Answer	Mark	Guidance
		(ii)	 ✓  ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** a cyclic amide with a 3 membered ring **ALLOW**  **OR** a structure obtained by condensation of a glutamic acid molecule with the first cyclic amide

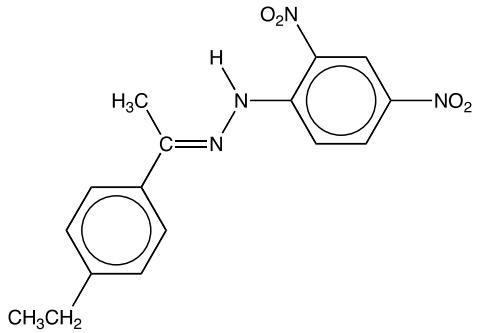
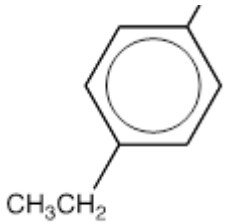
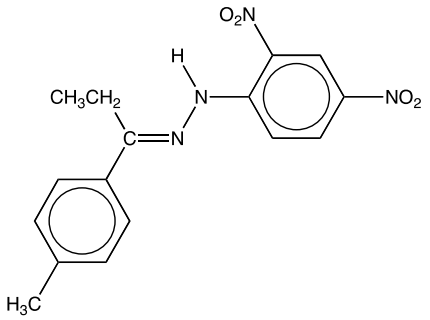
Question			Answer	Mark	Guidance
	(d)	(i)	Ester **AND** amide ✓	1	**ALLOW** peptide for amide
		(ii)	 ✓  ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous Functional groups do not need to be fully displayed **ALLOW** structures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

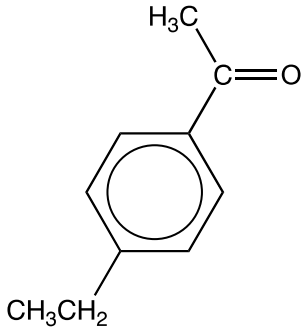
Question			Answer	Mark	Guidance
4	(a)		magnetic resonance imaging/providing diagnostic information/body scanners. ✓	1	**ALLOW** MRI/scanning internal structures e.g. brain **ALLOW** detection of tumours/cancer/haemorrhage/aneurysm **IGNORE** reference to drugs, chemicals or functional groups **IGNORE** 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 ± 0.2 ppm **ALLOW** (seven) benzene ring protons **OR** aromatic protons **DO NOT ALLOW** benzene ring without reference to protons **ALLOW** C_6H_6 **IGNORE** 

Question	Answer	Mark	Guidance
	OR Relative peak area of 1 = N-**H** ✓		**IGNORE** O-**H** , CON**H** **AND** C=C**H**
	M3 Peak at 2.3/2.4 **OR** Relative peak area of 2 **OR** Quartet =  **OR** $C_6H_5CH_2$ ✓		**ALLOW** quadruplet **IGNORE** C**H**C=O **AND** **H**C-N
	M4 Peak at 0.7/0.8 **OR** Triplet = R-CH **OR** R-CH_3 ✓		**DO NOT ALLOW** triplet = CH_3 **OR** CH_2CH_3
	M5 Triplet (at δ 0.7) **AND** quartet (at δ 2.3) = CH_2CH_3 **OR** triplet at (δ) 0.7 shows (C with) 2 adjacent Hs/protons = CH_2CH_3 **OR** quartet (at δ 2.3) shows (C with) 3 adjacent Hs/protons = CH_2CH_3 ✓		This also scores **M4** if triplet is linked to R-CH_3 **ALLOW** CH_3CH_2 described as R-CH_3 and 2 adjacent H **OR** –CH_2- and 3 adjacent H The information can be presented on the spectrum or in a table.

Question	Answer	Mark	Guidance
	✎ **QWC**: **triplet** or **quartet** spelled correctly in the correct context for **M5**		 **IGNORE** peak in the range 1.6–2.2 = HC–C=N– because this information is given in the question. H_3C-C=N- scores one mark for the identification of $\mathbf{R^1}$ or $\mathbf{R^2}$ (see below)

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

Question	Answer	Mark	Guidance
	Identification of R^1 and R^2 (2 marks) **Orange precipitate L** Correct structure scores 2 marks  R^1 or R^2 = $-CH_3$ ✓ R^1 or R^2 =  ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous Marks are for structure of R^1 and R^2 **IGNORE** errors in the rest of the structure **ALLOW** 1 mark for CH_3 and CH_3CH_2 swapped, i.e. the following structure  **ALLOW** H_3C-C=N- **MUST BE** 1,4-disubstituted (14 carbon environments in the ^{13}C NMR spectrum

Question			Answer	Mark	Guidance
	(e)		**Carbonyl compound K**  ✓	1	**ALLOW ECF** from incorrect compound **L** Must be a correct carbonyl structure
			Total	**12**	

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