

Chemistry A

Advanced GCE

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

Mark Scheme for June 2012

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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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Annotations

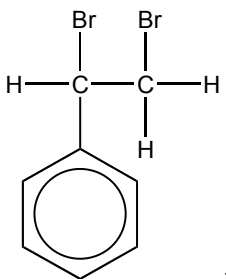
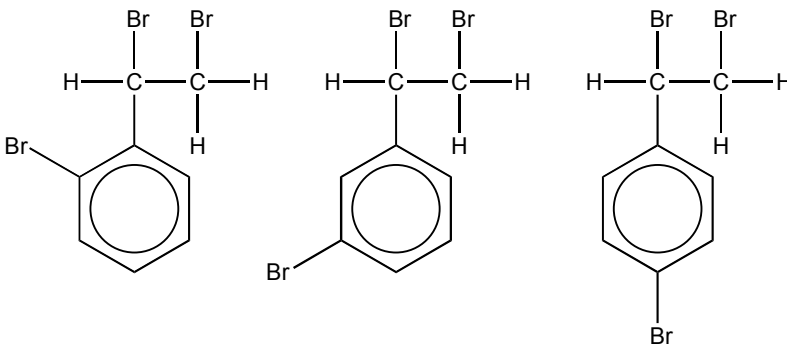
Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

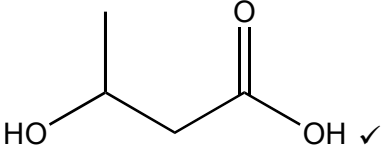
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

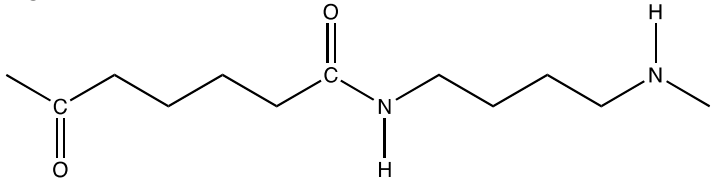
The following questions should be annotated with ticks, etc. to show where marks have been awarded in the body of the text:

Q1(a), Q3(c)(iii), Q4(a), Q4(d)(i), Q5(b).

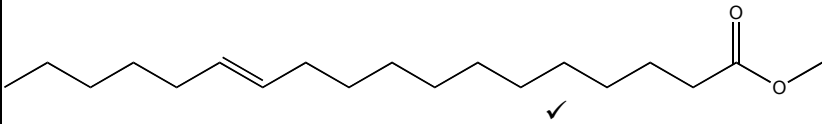
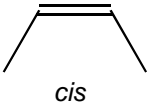
Question	Answer	Marks	Guidance
1 (a)	<p>In benzene, electrons OR π-bond(s) are delocalised ✓</p> <p>QWC requires delocalised/delocalized spelled correctly and used in correct context</p> <p>In alkenes, π-electrons are OR π-bond is AND localised OR between two carbons ✓</p> <p>benzene has a lower electron density OR alkene/C=C has a higher electron density ✓ <i>Comparison essential</i></p> <p>benzene polarises bromine / Br₂ LESS</p> <p>OR benzene attracts bromine / Br₂ LESS</p> <p>OR benzene induces a weaker dipole in bromine / Br₂ ✓</p>	4	<p>ANNOTATIONS MUST BE USED</p> <p>ALLOW diagram with (π-bond) electrons AND delocalised labelled</p> <p>IGNORE benzene has delocalised structure or ring</p> <p>ALLOW diagram with π-bond labelled ALLOW pi bond for π-bond</p> <p>π-bond OR π-electrons essential for this mark</p> <p>IGNORE charge density DO NOT ALLOW electronegativity</p> <p>ALLOW Br–Br for Br₂ ALLOW electrophile for Br₂</p> <p>ALLOW benzene does NOT polarise bromine / Br₂ OR alkene/C=C polarises Br₂</p> <p>ALLOW benzene does NOT attract bromine / Br₂ OR alkene/C=C attracts Br₂</p> <p>ALLOW benzene does NOT induce dipole in bromine / Br₂ OR alkene/C=C induces dipole in Br₂</p>

Question			Answer	Marks	Guidance
1	(b)	(i)	 ✓	1	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous
		(ii)	6 ✓	1	NO ECF from (i)
		(iii)	Two of the three structures below with 1 mark for each correct structure ✓✓ 	2	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous Structures must clearly show position of Br on benzene ring in relation to side chain ALLOW ECF from (i) if BOTH Br atoms on same carbon on side chain DO NOT ALLOW ECF from (i) if EITHER bromine has been substituted onto the benzene ring
		(iv)	reaction 1: electrophilic addition ✓ reaction 2: electrophilic substitution ✓	2	ALLOW electrophile addition ALLOW electrophile substitution ALLOW other phonetic spellings for electrophilic, e.g. electrophylic, etc.
Total				10	

Question			Answer	Marks	Guidance
2	(a)	(i)	photodegradable OR light/sunlight/UV ✓	1	IGNORE IR/heat IGNORE bacteria DO NOT ALLOW burn/combustion
		(ii)	 ✓	1	DO NOT ALLOW structure with any C shown (especially as part of C=O) DO NOT ALLOW OH—
	(b)	(i)	ammonia/NH ₃ AND ethanol OR ethanolic ammonia ✓	1	ALLOW ammonia in a sealed tube IGNORE heat ALLOW dilute ethanolic ammonia /NH ₃ DO NOT ALLOW any reference to water or hydroxide ions, e.g. DO NOT ALLOW dilute ethanolic NH ₃ (aq) e.g. DO NOT ALLOW ethanolic NH ₃ + NaOH
		(ii)	Nitrogen electron pair/lone pair accepts a proton/H ⁺ ✓ <i>Requires position of electron pair on N</i> Cl ⁻ H ₃ N ⁺ (CH ₂) ₄ N ⁺ H ₃ Cl ⁻ OR ClH ₃ N(CH ₂) ₄ NH ₃ Cl ✓	2	DO NOT ALLOW Nitrogen/N lone pair accepts hydrogen proton/H ⁺ required ALLOW nitrogen donates an electron pair IGNORE NH ₂ group donates electron pair ALLOW + charge (if shown) on N or H of NH ₃ e.g. Cl ⁻ H ₃ N ⁺ (CH ₂) ₄ NH ₃ ⁺ Cl ⁻ DO NOT ALLOW just H ₃ N ⁺ (CH ₂) ₄ NH ₃ ⁺ i.e. 2 x Cl⁻ MUST be included

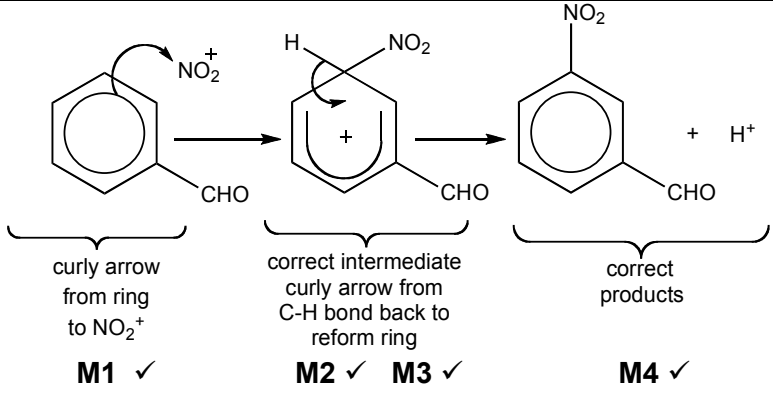
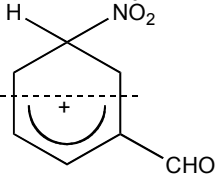
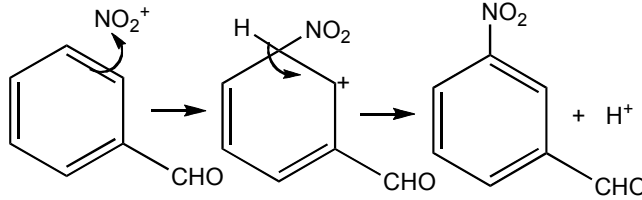
Question	Answer	Marks	Guidance
2	<p>(iii)</p> <p>1 mark for amide/peptide link correctly displayed within an attempted repeat unit ✓</p> <p>1 mark for rest of structure correct including side links ✓</p> $\text{---C(=O)---(CH}_2\text{)}_4\text{---C(=O)---N(H)---(CH}_2\text{)}_4\text{---N(H)---}$	2	<p>Minimum requirement is each end of a displayed amide group attached to a carbon atom (could be skeletal)</p> <p>Brackets not required</p> <p>IF more than one repeat unit has been drawn a single repeat unit MUST be identified by brackets or clear label</p> <p>DO NOT ALLOW 2nd mark if amide/peptide link wrong <i>1st mark requires amide group fully displayed</i> <i>For 2nd mark, ALLOW –CONH– in correct structure</i></p> <p>ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous e.g.</p> 

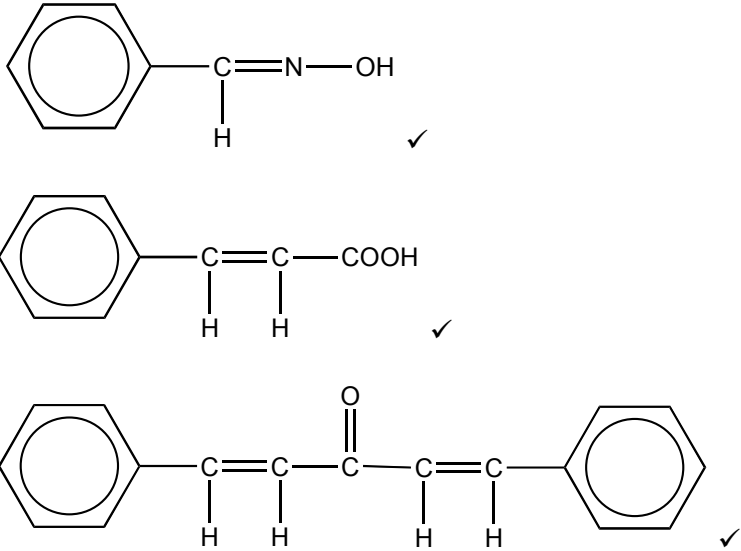
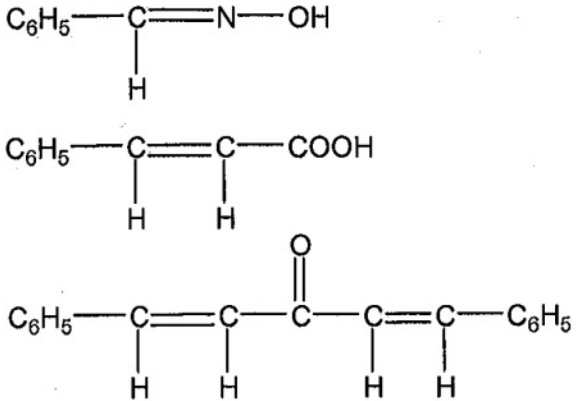
Question			Answer	Marks	Guidance
2	(c)	(i)	<p>One mark for each correct structure</p> $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{N}^+ - \text{CH} - \text{C} - \text{O}^- \\ \\ \text{CHOH} \\ \\ \text{CH}_3 \end{array} \quad \checkmark$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{N}^+ - \text{CH} - \text{C} - \text{O}^- \\ \\ (\text{CH}_2)_4 \\ \\ \text{NH}_2 \end{array} \quad \text{OR} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N} - \text{CH} - \text{C} - \text{O}^- \\ \\ (\text{CH}_2)_4 \\ \\ \text{NH}_3^+ \end{array} \quad \checkmark$	2	<p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p> <p>ALLOW COO⁻</p> <p>'-' charge must be on O of COO⁻ but</p> <p>ALLOW + sign shown as ⁺NH₃ OR NH₃⁺</p> <p>BUT only one NH₂ can be protonated in zwitterion</p>
		(ii)	<p>Zwitterion at pH 9.60/higher pH has one NH₂ group</p> <p>OR</p> <p>Zwitterion OR amino acid at pH 9.60/higher pH has a side chain with an NH₂ group ✓</p> <p>Note:</p> <p>ASSUME that 'it' refers to zwitterion</p>	1	<p>ALLOW amino acid at 9.60/higher pH has two NH₂ groups</p> <p>ALLOW amino acid at 9.60/higher pH has more NH₂ groups</p> <p>ALLOW amine OR amino for NH₂</p> <p>IGNORE CHOH slightly acidic</p>
Total				10	

Question			Answer	Marks	Guidance
3	(a)	(i)	 <p> <i>cis</i>-isomer has Hs on same side OR <i>cis</i>-isomer has branches on same side OR <i>cis</i>-isomer has same groups on same side OR <i>cis</i>-isomer has lowest priority groups on same side OR <i>cis</i>-isomer has highest priority groups on same side ✓ </p>	2	<p> ALLOW <i>trans</i>-isomer has Hs on opposite sides OR <i>trans</i>-isomer has branches on opposite sides OR <i>trans</i>-isomer has same groups on opposite sides DO NOT ALLOW 'similar groups' for 'same groups' OR <i>trans</i>-isomer has lowest priority groups on opposite sides OR <i>trans</i>-isomer has highest priority groups on opposite sides ✓ </p> <p>For explanation, ALLOW a clear diagram, <i>ie</i>:</p>  <p> ALLOW response in terms of packing, e.g. molecules/chains of <i>trans</i>-isomer pack close together OR molecules/chains of <i>cis</i>-isomer do not pack closely together DO NOT ALLOW 'carbon atoms' for 'molecules/chains' </p>
		(ii)	heart disease/strokes ✓	1	<p> ALLOW any named heart/circulatory complaint e.g. atheroma, atherosclerosis ALLOW increase in bad cholesterol/LDL ALLOW high in LDLs ALLOW fat lining arteries ALLOW high blood pressure ALLOW hypertension IGNORE reference to HDLs and cholesterol on its own </p>

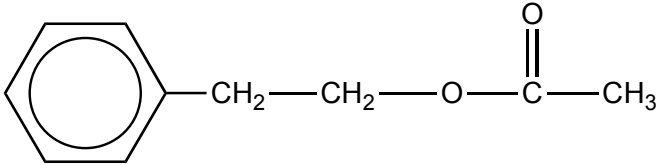
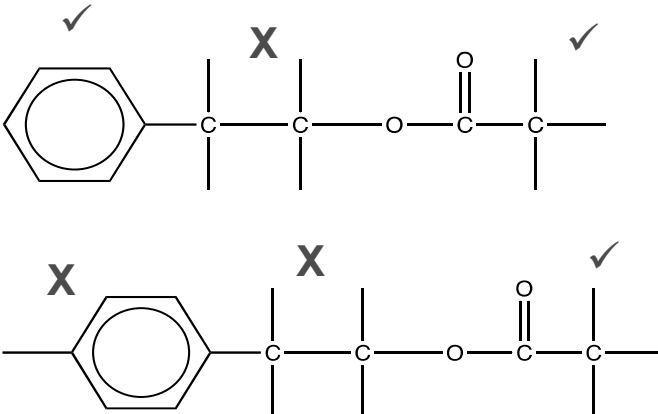
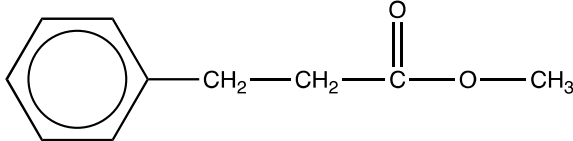
Question			Answer	Marks	Guidance
3	(b)	(i)	27	1	
		(ii)	8	1	
	(c)	(i)	alcohol ✓ ester ✓	2	<p>IGNORE OH OR hydroxyl OR hydroxy</p> <p>DO NOT ALLOW phenol OR hydroxide</p> <p>IGNORE COOR</p> <p>IF there is a list with more than two responses, mark wrong responses first, e.g. alcohol, ketone X, ether X zero marks alcohol ✓, ester, methyl X 1 mark ester, hydroxide X, ketone X zero marks ester ✓, hydroxyl I, ketone X 1 mark</p>
		(ii)	ensures correct chirality ✓	1	<p>ALLOW enantiomer for optical isomer</p> <p>ALLOW produces only one optical isomer</p> <p>ALLOW stops need/cost/difficulty of separating optical isomers</p> <p>ALLOW stops formation of the optical isomer which may have (harmful) side effects</p> <p>DO NOT ALLOW lower doses/dosage needed</p> <p>DO NOT ALLOW forms one stereoisomer (could be <i>E/Z</i>)</p> <p>DO NOT ALLOW stereoselectivity</p>

Question		Answer	Marks	Guidance
3	(iii)	<p>1st step</p> <p><i>reagent:</i> NaBH₄ ✓</p> <p><i>functional groups:</i> aldehyde forms an alcohol ✓ <i>names required</i></p> <p>2nd step Marks ONLY available from correct hydroxycarboxylic acid formed in 1st step</p> <p><i>reagent:</i> Acid OR H⁺ (catalyst) ✓</p> <p><i>functional groups:</i> alcohol and carboxylic acid / carboxyl group form an ester ✓ <i>names required</i></p>	4	<p>ANNOTATIONS MUST BE USED</p> <hr/> <p>ALLOW H₂/Ni (catalyst) DO NOT ALLOW LiAlH₄ (<i>because LiAlH₄ reduces COOH</i>)</p> <p>IGNORE type of reaction or conditions IGNORE CHO OR OH IGNORE carbonyl OR hydroxyl OR hydroxy DO NOT ALLOW phenol OR hydroxide</p> <p>ALLOW named acid/correct formula IGNORE dilute/concentrated</p> <p>IGNORE OH, COOH, COO, IGNORE hydroxyl OR hydroxy DO NOT ALLOW phenol OR hydroxide</p>
Total			12	

Question	Answer	Marks	Guidance
4 (a)	 <p>curly arrow from ring to NO_2^+ M1 ✓</p> <p>correct intermediate curly arrow from C-H bond back to reform ring M2 ✓ M3 ✓</p> <p>correct products M4 ✓</p> <p>Note: ALLOW M1, M2 AND M3 for benzene OR ANY substituted benzene compound For M4, credit ONLY the correct products</p> <hr/> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^- \checkmark$ $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$ <p>OR</p> $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^- \checkmark$ $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$ <p>OR</p> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ <p>AND $\text{H}_2\text{NO}_3^+ \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O} \checkmark$</p> $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$	6	<p>ANNOTATIONS MUST BE USED</p> <hr/> <p>Mark 1 (M1) ALLOW curly arrow from the ring OR from within the ring</p> <hr/> <p>Mark 2 (M2) – intermediate showing delocalisation over less than 6 carbons with the correct orientation BUT DO NOT ALLOW intermediate with π system less than halfway up:</p>  <hr/> <p>Mark 3 (M3) curly arrow from C–H bond reforming π-delocalised ring in benzene</p> <p>ALLOW Kekulé mechanism:</p>  <hr/> <p>ALLOW double bonds shown in other Kekulé arrangement</p> <hr/> <p>Mark 4 (M4) BOTH correct products: 3-nitrobenzaldehyde AND H+</p>

Question	Answer	Marks	Guidance
4 (b)	$2 \text{C}_6\text{H}_5\text{CHO} + \text{KOH} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COOK}$ OR $2 \text{C}_6\text{H}_5\text{CHO} + \text{OH}^- \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COO}^-$ <p>1 mark for $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ✓</p> <p>1 mark for $\text{C}_6\text{H}_5\text{COOK}$ OR $\text{C}_6\text{H}_5\text{COOH}$ OR $\text{C}_6\text{H}_5\text{COO}^-$ ✓</p> <p>1 mark for complete fully correct balanced equation (i.e. as above) ✓</p>	3	<p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p> <p>ALLOW use of NaOH instead of KOH throughout, i.e. $2 \text{C}_6\text{H}_5\text{CHO} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COONa}$</p> <p>ALLOW $\text{C}_6\text{H}_5\text{COO}^-\text{K}^+$</p>
(c)		3	<p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p> <p>e.g. ALLOW</p> 

Question			Answer	Marks	Guidance
4	(d)	(i)	<p>1 mark for curly arrow from R^- to C of $C=O$ (lone pair not necessary) ✓</p> <p>1 mark for correct dipoles on $C=O$ AND curly arrow from double bond to $O^{\delta-}$ ✓</p> <p>1 mark for correct intermediate with $-$ charge on O ✓</p> <p>1 mark for correct product ✓</p>	4	<p>ANNOTATIONS MUST BE USED</p> <p>IGNORE connectivity on OH of product</p> <p>Curly arrow MUST start from $-$ sign of R^- OR from lone pair on R^- lone pair does not need to be shown on R^-</p> <p>IGNORE any curly arrows shown for stage 2 i.e. in intermediate</p>
		(ii)	<p>OR</p>	1	<p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p> <p>IGNORE C_4H_9Li OR $C_4H_9^-Li^-$</p>
Total				17	

Question			Answer	Marks	Guidance
5	(a)	(i)	(number of esters) from number of peaks/retention times AND (proportions) from (relative) peak areas ✓	1	BOTH points for 1 mark ALLOW peak heights OR sizes of peaks
		(ii)	(Some esters may have) same retention time ✓	1	ALLOW (very) similar retention times ALLOW some esters come out at same time
	(b)	<p>Ester structure 3 marks</p>  <p style="text-align: right;">✓✓✓</p> <hr/> <p>STICKS IF there are sticks are shown in CH₂CH₂ OR in CH₃ DO NOT AWARD when first seen</p> <p>DO NOT ALLOW sticks on the benzene ring, <i>Sticks on benzene ring must be interpreted as methyl groups</i></p> <p>e.g.</p> 	3	<p>ANNOTATIONS MUST BE USED</p> <p>-----</p> <p>ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous NO ECF for structure</p> <p>-----</p> <p>IF the structure is NOT fully correct, award the following marks:</p> <p>IF ESTER shown AND contains ONE of the following: C₆H₅ OR CH₃C=O OR CH₂CH₂ 1 mark ✓</p> <p>IF ESTER shown AND contains TWO of the following: C₆H₅ OR CH₃C=O OR CH₂CH₂ 2 marks ✓✓</p> <p>IF ESTER contains C₆H₅ AND CH₂CH₂ BUT ester link is reversed 2 marks ✓✓</p>  <p>DO NOT ALLOW CH₂CH₂ with H on any adjacent Cs e.g. DO NOT ALLOW CH₂CH₂CH₃, CH₂CH₂CH₂, etc.</p> <p>IGNORE any name</p>	

Question	Answer	Marks	Guidance
	<p>Mass spectrum</p> <p>164 linked directly to molecular formula of $C_{10}H_{12}O_2$ OR an ester structure with formula $C_{10}H_{12}O_2$ ✓ <i>This direct link could be seen anywhere in the response</i> e.g. 164 is $C_{10}H_{12}O_2$ e.g. $C_{10}H_{12}O_2 = 120 + 12 + 32 = 164$ e.g. $(164 - 44/COO) = 120$; $120 = C_9H_{12}$</p> <hr/> <p>NMR analysis</p> <p>QWC Triplet must be spelled correctly and used in correct context Triplet at 2.8 ppm shows an adjacent CH_2 AND Triplet at 4.4 ppm shows an adjacent CH_2 ✓</p> <p>Peak at 2.2 shows $CH_3-C=O$ OR Peak at 2.2 shows $HC-C=O$ AND 3 Hs of this type OR Peak at 2.2 shows $HC-C=O$ AND adjacent to (C with) no Hs ✓</p> <p>Peak at 7.3 shows 5 aromatic Hs OR shows C_6H_5 ✓ <i>5Hs required</i></p> <p>Peak at 2.8 shows C_6H_5-CH OR $C_6H_5-CH_2$ ✓ <i>Just require C_6H_5-CH as testing environment here</i></p> <p>Peak at 4.4 due to $HC-O$ OR H_2C-O ✓ <i>Just require $HC-O$ as testing environment here</i></p>	<p>1</p> <hr/> <p>5</p>	<p>Check back for any responses added to spectrum</p> <p>Credit responses throughout provided that it is clear which peaks are being referred to</p> <hr/> <p>ALLOW tolerance on δ values: ± 0.2 ppm Throughout, ALLOW for H: proton OR H^+</p> <p>For adjacent CH_2, ALLOW (C) adjacent to 2 Hs</p> <p>ALLOW There are 2 triplets AND triplet shows an adjacent CH_2</p> <p>For peak at ($\delta =$) 2.2 ALLOW singlet OR peak labelled 3</p> <p>For peak at ($\delta =$) 7.3 ALLOW peak labelled 5 OR multiplet OR quintet OR hextet OR heptet</p> <p>For peak at ($\delta =$) 2.8 ALLOW triplet at 2.8</p> <p>For peak at ($\delta =$) 4.4 ALLOW triplet at 4.4</p>
	Total	11	

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