



GCE

Chemistry A

Advanced GCE F324

Mark Scheme for June 2010

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All Examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the Report on the Examination.

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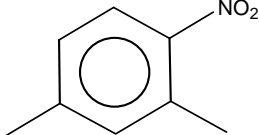
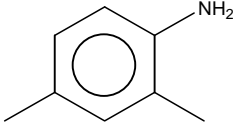
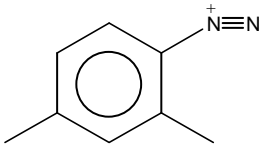
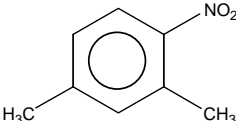
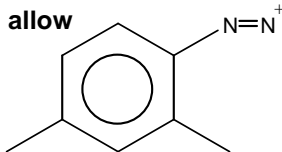
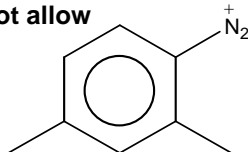
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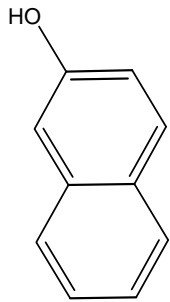
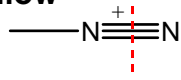
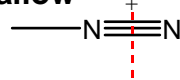
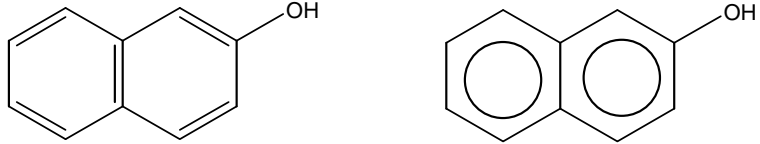
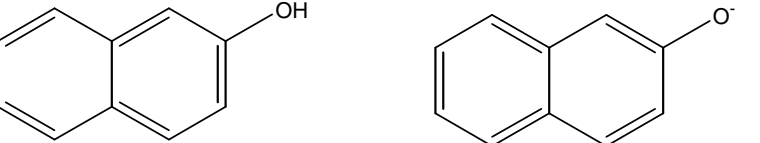
Allow Kekulé structures throughout

Question		Expected Answers	Marks	Additional Guidance
1	a	<p>Bond length intermediate between/different from (short) C=C and (long) C–C ✓</p> <p>ΔH hydrogenation less exothermic than expected (when compared to ΔH hydrogenation for cyclohexene) ✓</p> <p>Only reacts with Br₂ at high temp or in presence of a halogen carrier / resistant to electrophilic attack ✓</p> <p>Please annotate, use ticks to show where marks are awarded</p>	3	<p>ALLOW all carbon–carbon bonds the same length</p> <p>ALLOW ΔH hydrogenation less (negative) than expected</p> <p>ALLOW ΔH hydrogenation different from that expected</p> <p>DO NOT ALLOW ΔH halogenation/hydration</p> <p>ALLOW doesn't decolourise/react with/polarise Br₂</p> <p>ALLOW doesn't undergo addition reactions (with Br₂)</p>
	b	<p>i</p> <p>compound A</p>  <div style="border: 1px solid black; padding: 5px; display: inline-block; margin-left: 20px;"> <p>if NO₂ in wrong position penalise here and ECF for rest of b(i) and b(ii)</p> </div> <p style="text-align: right;">✓</p> <p>compound B</p>  <p style="text-align: right;">✓</p> <p>compound C</p>  <p style="text-align: right;">✓</p>	4	<p>ALLOW any 4-nitro-1,3-dimethylbenzene drawn in any orientation</p> <p>ALLOW</p>  <p>drawn in any orientation</p> <p>ALLOW any 4-amino-1,3-dimethylbenzene drawn in any orientation</p> <p>ECF amine of incorrect compound A (e.g. position of NO₂ or lack of methyl sticks/groups)</p> <p>ALLOW diazonium chloride salt of 1,3-dimethylbenzene</p> <p>ECF diazonium salt/compound of incorrect compound B</p> <p>IGNORE Cl[–] ion</p> <p>allow</p>  <p>not allow</p> 

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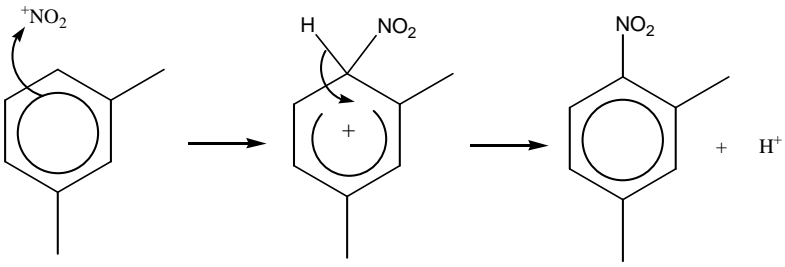
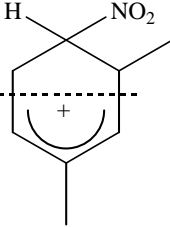
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Question	Expected Answers	Marks	Additional Guidance
	<p>compound D</p> 	<p>✓</p>	<p>ALLOW if + charge is floating between the two Ns only if it is closer to the correct N</p> <p>allow </p> <p>not allow </p> <p>ALLOW any of</p>   <p>ALLOW O⁻ in place of OH</p>

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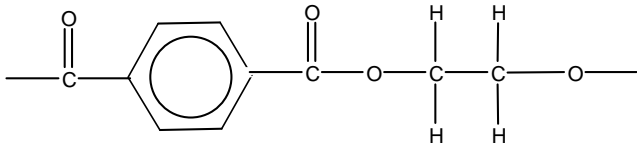
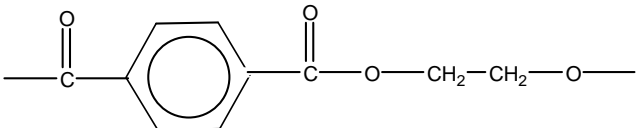
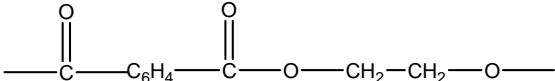
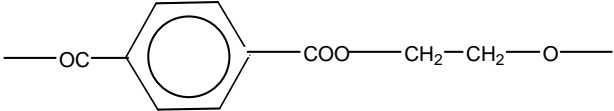
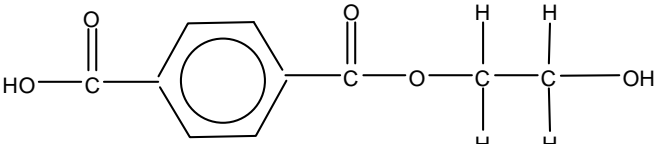
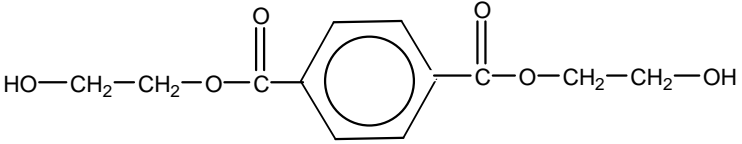
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Question	Expected Answers	Marks	Additional Guidance
<p>ii</p> <div data-bbox="69 360 309 627" style="border: 1px solid black; padding: 5px; width: fit-content;"> If NO₂ is in correct position do not penalise even if compound A in b(i) is not in correct position </div>	<p>mark 1 $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+ \checkmark$</p> <p>mark 2 – curly arrow from π ring to $^+\text{NO}_2 \checkmark$</p> <p>mark 3 – intermediate with π ring broken in the correct place \checkmark</p> <p>mark 4 – curly arrow from C–H bond back to reform π ring AND correct products \checkmark</p> <p>mark 5 - $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4 \checkmark$</p> <div data-bbox="846 699 1155 940" style="border: 1px solid black; padding: 5px; width: fit-content;"> Link to compound A in part (i) – cannot score full marks [in b(i) & b(ii)] if NO₂ is not adjacent to a methyl </div> 	<p>5</p>	<p>Equation to show formation of NO₂⁺ ion \checkmark ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+$ $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$</p> <p>ALLOW mark 2 curly arrow must be from 1,3-dimethylbenzene to NO₂⁺ and ECF for marks 3 and 4</p> <p>DO NOT ALLOW intermediate</p> <p>π-ring must be more than $\frac{1}{2}$ way up</p>  <p>ALLOW CH₃s shown</p> <p>ALLOW $\text{H}_3\text{O}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4$</p>
<p>iii</p>	<p>2 \checkmark</p>	<p>1</p>	<p>No other correct response</p>
Total		<p>13</p>	

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Question	Expected Answers	Marks	Additional Guidance
2 a i	 <p>✓✓ Ester group must be displayed to get both marks and must contain 4 Os</p>	2	<p>ALLOW for both marks</p>  <p>ALLOW for one mark</p>  <p>ALLOW for one mark</p>  <p>ALLOW Kekulé structure / (CH₂)₂ ALLOW one mark if end bonds missing ALLOW 1 mark if the CH₂CH₂ is drawn skeletally ALLOW for</p>  <p>ALLOW <u>1 mark</u> if repeat unit shows a displayed ester group and contains a benzene ring and two other carbons</p> <p>DO NOT ALLOW -OCC₆H₄COOCH₂CH₂O-</p>
	 <p>✓</p>	1	<p>ALLOW Kekulé structure/ (CH₂)₂ CO₂ for ester groups C₆H₄ if already penalised in a(i)</p>

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Question		Expected Answers	Marks	Additional Guidance
	b i	$C_7H_5O_2$	1	ALLOW any order of elements ALLOW $C_{14}H_{10}O_4 \rightarrow C_7H_5O_2$ or $C_{14}H_{10}O_4 = C_7H_5O_2$
	ii	<p>Penalise incorrect bond linkage in 2b(ii) only. Do not penalise elsewhere on the paper</p>	2	ALLOW COOH/CO ₂ H ALLOW ALLOW HO(CH ₂) ₂ OH
	c i		2	ALLOW any of the following for 1 mark DO NOT ALLOW any other response
	ii	(PGA is) (bio)degradable OR photodegradable OR hydrolysed (but hydrocarbon based polymers are non-biodegradable) ✓ One of (bio)degradable OR photodegradable OR hydrolysed must be spelt correctly – if one spelt correctly and another incorrectly spelt – ALLOW mark	1	ALLOW broken down by <u>bacteria</u> (must be spelt correctly) ALLOW degrade as alternative to degradable ALLOW undergoes hydrolysis as alternative to hydrolysed IGNORE any additional information if the additional information is correct e.g. biodegradable and doesn't produce toxic gases DO NOT ALLOW any additional information if the additional information is incorrect e.g. biodegradable and can be recycled
Total			9	

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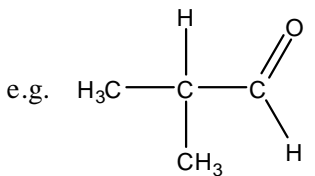
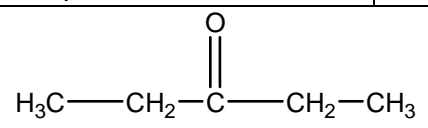
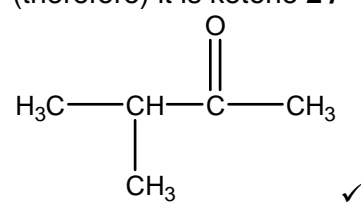
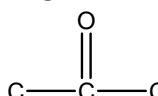
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Question		Expected Answers		Marks	Additional Guidance
3	a	Alternative approaches		4	<p>ALLOW ammoniacal AgNO_3 / $\text{Ag}^+(\text{NH}_3)_2$ / $\text{Ag}^+(\text{NH}_3)$</p> <p>ALLOW acidified dichromate OR Fehlings as an alternative to Tollens – observation ‘turn green’ OR ‘red precipitate’ respectively</p> <p>ALLOW acidified manganate(VII) and observation as either brown precipitate/decolourised/pale pink</p> <p>ALLOW Brady’s (reagent)</p> <p>ALLOW orange/red/yellow for colour of the 2,4-DNP(H) precipitate</p> <p>ALLOW solid/crystals in place of precipitate</p> <p>IGNORE any reference to melting points</p> <p>ALLOW PCl_5 as a test for the acid – observation would be ‘white fumes (of HCl)’</p> <p>ALLOW detection of (carboxylic) acid by reacting with an alcohol to make an ester but no mark for the observation.</p> <p>DO NOT ALLOW detection of (carboxylic) acid by pH or indicator</p> <p>Please annotate, use ticks to show where marks are awarded</p>
		<p>Tollens’ test AND ‘silver precipitate/mirror’ ✓ is the aldehyde ✓</p> <p>react with 2,4-DNP(H) and ‘orange precipitate’ ✓</p> <p>must be the ketone ✓</p>	<p>Tollens’ test AND ‘silver precipitate/mirror’ ✓ is the aldehyde ✓</p> <p>react with carbonate/hydrogencarbonate/Na/Mg and ‘fizzes/bubbles/ effervesces/ gas evolved’ ✓</p> <p>must be the (carboxylic) acid ✓</p>		
	b	<p>2,4-DNP(H) AND orange precipitate ✓ is either aldehyde OR ketone ALLOW carbonyl OR $\text{C}=\text{O}$ ✓</p> <p>Tollens’ test & ‘silver ppt/mirror’ ✓ is the aldehyde ✓</p>	<p>2,4-DNP(H) and no orange precipitate ✓ is the (carboxylic) acid ✓</p> <p>Tollens’ test & ‘silver ppt/mirror’ ✓ is the aldehyde ✓</p>	1	<p>DO NOT ALLOW single peak quoted within range 2500–3300 other than 3000 (cm^{-1}) for OH</p> <p>DO NOT ALLOW range 3200–3550 (cm^{-1})</p> <p>IGNORE any reference to C-O or C=O</p>

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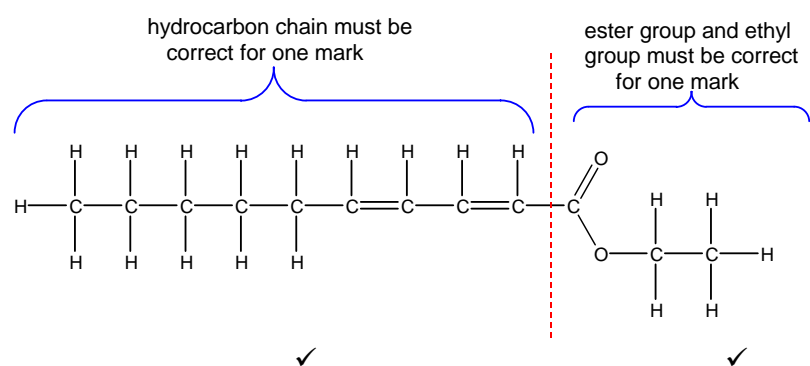
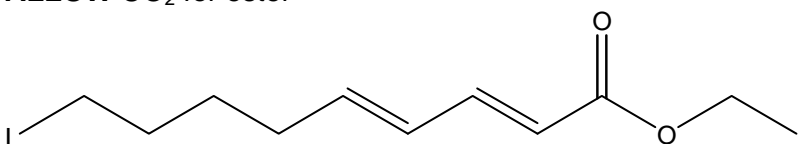
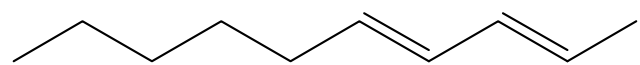
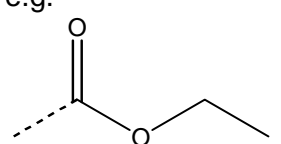
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Question		Expected Answers	Marks	Additional Guidance						
	c	<p>Alternative approaches depending on whether or not the aldehyde is correct</p> <table border="0"> <tr> <td> Doublet indicates adjacent C is bonded to only 1H OR (relative) peak area indicates 2 x CH₃ (in the same environment) ✓ </td> <td> Doublet indicates adjacent C is bonded to only 1H ✓ AND (relative) peak area indicates 2 x CH₃ (in the same environment) ✓ </td> </tr> <tr> <td> If aldehyde is correct (CH₃)₂CH—CH₂—CHO ✓ ✓ </td> <td> If aldehyde identified is incorrect ✗ </td> </tr> <tr> <td> <i>If aldehyde is correct only need to explain doublet OR peak areas</i> </td> <td> <i>if aldehyde is incorrect must explain both doublet or peak areas</i> </td> </tr> </table>	Doublet indicates adjacent C is bonded to only 1H OR (relative) peak area indicates 2 x CH ₃ (in the same environment) ✓	Doublet indicates adjacent C is bonded to only 1H ✓ AND (relative) peak area indicates 2 x CH ₃ (in the same environment) ✓	If aldehyde is correct (CH ₃) ₂ CH—CH ₂ —CHO ✓ ✓	If aldehyde identified is incorrect ✗	<i>If aldehyde is correct only need to explain doublet OR peak areas</i>	<i>if aldehyde is incorrect must explain both doublet or peak areas</i>		<p>ALLOW 3-methylbutanal, any correct unambiguous structure ALLOW two marks for correct aldehyde with no explanation</p> <p>ALLOW doublet/peak at 0.9ppm due to R—CH ALLOW the splitting shows adjacent to CH/environment that contains 1 H/proton</p> <p>ALLOW 6 Hs/ protons in same environment DO NOT ALLOW 6 Hs in same environment next to CHO</p> <p>e.g. </p> <p>would score two marks if the doublet and the peak areas were correctly explained</p>
Doublet indicates adjacent C is bonded to only 1H OR (relative) peak area indicates 2 x CH ₃ (in the same environment) ✓	Doublet indicates adjacent C is bonded to only 1H ✓ AND (relative) peak area indicates 2 x CH ₃ (in the same environment) ✓									
If aldehyde is correct (CH ₃) ₂ CH—CH ₂ —CHO ✓ ✓	If aldehyde identified is incorrect ✗									
<i>If aldehyde is correct only need to explain doublet OR peak areas</i>	<i>if aldehyde is incorrect must explain both doublet or peak areas</i>									
	d i	 ✓ ketone 3	1	ALLOW displayed/skeletal formulae						
	ii	There are 4 (different C) environments ✓ (therefore) it is ketone 2 /  ✓ (C responsible for peak at δ = 210 ppm) is C=O/carbonyl carbon ✓	3	<p>ALLOW 2 Cs are in same environment/equivalent</p> <p>ALLOW 3-methylbutan(-2-)one/ any correct unambiguous structure</p> <p>ALLOW 2-methylbutan-3-one</p> <p>ALLOW</p> 						
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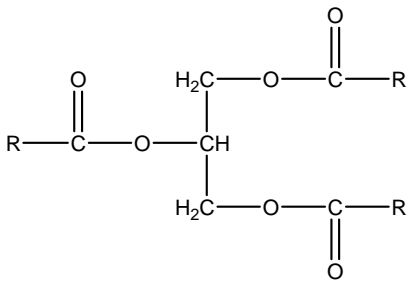
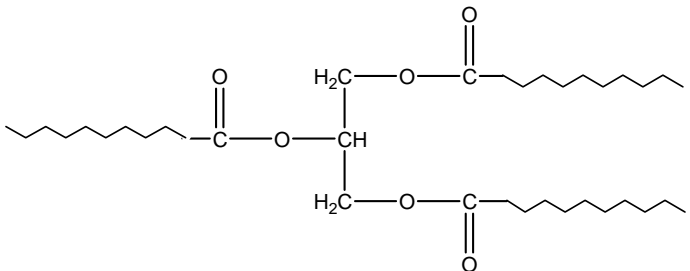
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4 a i	The time (from the injection of the sample) for the component to leave the column ✓	1	ALLOW time from injection to detection ALLOW time spent in column ALLOW time taken to reach detector
	ii They have similar retention times ✓	1	ALLOW both are esters therefore partition/adsorption/retention times will be very similar ALLOW ECF if they describe R_f values in part a(i) ALLOW same retention times
	iii Butylbutanoate ✓	1	ALLOW butyl butanoate ALLOW but-1-yl butanoate DO NOT ALLOW butanyl butanoate
b i	<p>hydrocarbon chain must be correct for one mark</p> <p>ester group and ethyl group must be correct for one mark</p> 	2	<p>ALLOW any correct unambiguous structure/ $\text{CH}_3(\text{CH}_2)_4\text{CHCHCHCHCOOCH}_2\text{CH}_3$ / $\text{CH}_3(\text{CH}_2)_4\text{CHCHCHCHCOOC}_2\text{H}_5$ $\text{CH}_3(\text{CH}_2)_4(\text{CH})_4\text{COOCH}_2\text{CH}_3$ DO NOT ALLOW $\text{C}_5\text{H}_{11}\text{CHCHCHCHCOOCH}_2\text{CH}_3$ etc ALLOW CO_2 for ester</p>  <p>ALLOW 1 mark for correct 2,4-decadiene structure e.g.</p>  <p>ALLOW 1 mark for correct ethyl ... oate structure e.g.</p>  <p>or $-\text{CO}_2\text{C}_2\text{H}_5$ or $-\text{COOC}_2\text{H}_5$</p>

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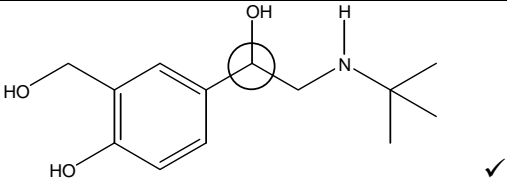
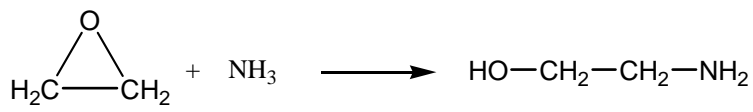
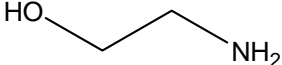
Question	Expected Answers	Marks	Additional Guidance
ii		1	<p>ALLOW</p>  <p>any orientation of the three fatty acids</p>
c	<p>1. react phenylethanal with $\text{H}_2\text{SO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ ✓</p> <p>2. to get phenylethanoic acid/$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ✓</p> <p>mark 2 can be scored if dichromate is used without being acidified</p> <p>3. react phenylethanal with NaBH_4 ✓</p> <p>4. to get 2-phenylethanol/$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ ✓</p> <p>mark 3 must be correct to score mark 4</p> <p>5. react phenylethanoic acid with 2-phenylethanol. If both already correctly named ALLOW acid and alcohol ✓</p> <p>6. H_2SO_4 if linked to the reaction of an alcohol and acid ✓</p> <p>7. reflux in either (1) or (5) or catalyst used in (5) ✓</p> <p>QWC must spell catalyst or reflux correctly</p>	7	<p>ALLOW H^+ & $\text{Cr}_2\text{O}_7^{2-}$ or $\text{H}_2\text{SO}_4/\text{Na}_2\text{Cr}_2\text{O}_7$ - any other oxidising agent or other named acid – please consult with TL</p> <p>ALLOW LiAlH_4 as alternative to NaBH_4</p> <p>phenylethanoic acid & phenylethanol must be unambiguously identified by either name or formula</p> <p>DO NOT ALLOW or oxidised to form (a carboxylic) acid or reduced to form alcohol for marks 2 and 4</p> <p>ALLOW conc H_2SO_4 DO NOT ALLOW dilute or $\text{H}_2\text{SO}_4(\text{aq})$ DO NOT ALLOW just acid catalyst DO NOT ALLOW HCl, HNO_3</p> <p>Please annotate, use ticks to show where marks are awarded</p>
Total		13	

if either phenylethanoic acid or 2-phenylethanol not prepared – automatically lose two marks

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Question		Expected Answers	Marks	Additional Guidance			
5	a i		1	ALLOW * in place of circle ALLOW if circle extends to include OH			
	ii	<p>Mark 1 – production of a single isomer is more expensive/difficult OR separation of the single isomer is expensive/difficult ✓</p> <p>Mark 2 – one of the isomers is more (pharmacologically) active or one of the isomers might have adverse/harmful/nasty side effects ✓</p> <p>Marks 3 and 4 – problems are overcome by using:</p> <table style="border: none;"> <tr> <td style="border: none;"> Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool </td> <td style="border: none; vertical-align: middle;"> } } } } </td> <td style="border: none; vertical-align: middle;"> ✓✓ any </td> </tr> </table>	Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool	} } } }	✓✓ any	4	IGNORE any reference to dosage ALLOW one is more effective/works (better) DO NOT ALLOW use naturally occurring isomer unless stated that it is a chiral compound DO NOT ALLOW transition metal ion DO NOT ALLOW pool synthesis Chiral pool synthesis scores 1 (not 2) marks
Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool	} } } }	✓✓ any					
	b i		1	ALLOW  ALLOW epoxy ethane as C ₂ H ₄ O, (CH ₂) ₂ O, CH ₂ OCH ₂ ALLOW product as HO(CH ₂) ₂ NH ₂ DO NOT ALLOW product as C ₂ H ₇ NO			
	ii	HO—CH ₂ —CH ₂ —NH—CH ₂ —CH ₂ —OH ✓	1	ALLOW (CH ₂) ₂ ALLOW displayed/skeletal formula DO NOT ALLOW molecular formula			

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Question		Expected Answers	Marks	Additional Guidance
	c i	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+ \text{Cl}^-$ Must show Cl^- ion ✓	1	ALLOW $\text{HOCH}_2\text{CH}_2\text{NH}_3\text{Cl}$ if formula is correct and both charges not shown ALLOW $(\text{CH}_2)_2/$ any correct unambiguous structure DO NOT ALLOW ions joined by covalent bonds
	ii	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+ \text{HS}^-$ Must show HS^- ion ✓	1	ALLOW if formula is correct and both charges not shown ALLOW $(\text{CH}_2)_2/$ any correct unambiguous structure ALLOW $\left(\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+\right)_2 \text{S}^{2-}$
	d i	Both NH_2 and COOH are joined to the same C ✓	1	ALLOW $\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{R} \end{array}$ or $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$ The 4 groups/atoms attached to the C can be in any order but CH must be adjacent. () not essential
	ii	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 2[\text{O}] \longrightarrow \text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{NH}_2 + \text{H}_2\text{O}$ ✓	1	ALLOW $(\text{CH}_2)_2$ DO NOT ALLOW molecular formula
	e i	Question 5e is followed by two blank lined pages (15 and 16) which candidates can use instead of requesting additional paper. Please check to see whether or not pages 15 or 16 have been used		

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Question		Expected Answers	Marks	Additional Guidance
e	i	<p>Isomer F</p> $ \begin{array}{cccc} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{HO} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{NH}_2 \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} \end{array} $ <p style="text-align: right;">✓</p> <p>Isomer G</p> $ \begin{array}{cccc} & \text{H} & \text{OH} & \text{H} & \text{H} \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & & \\ & \text{H} & \text{H} & \text{NH}_2 & \text{H} \end{array} $ <p style="text-align: center;">* not required</p> <p style="text-align: right;">✓</p>	2	<p>ALLOW HO(CH₂)₄NH₂/ ALLOW any correct unambiguous structure of 1-aminobutan-4-ol</p> <p>ALLOW CH₃CH(OH)CH(NH₂)CH₃ ALLOW any correct unambiguous structure of 2-aminobutan-3-ol.</p>
Total			13	

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