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RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for January 2011

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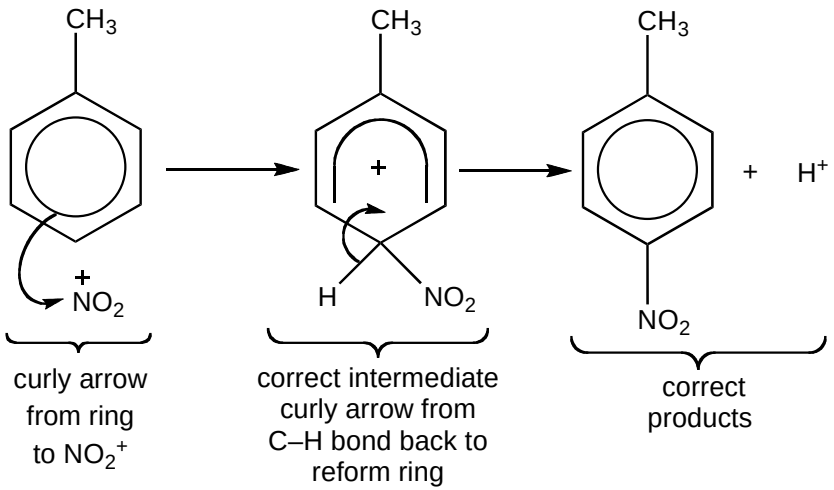
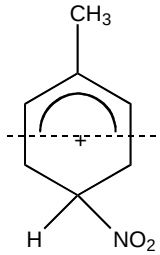
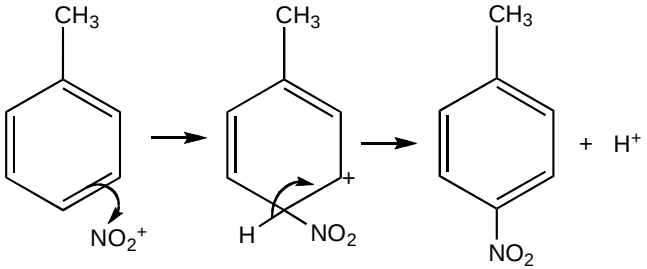
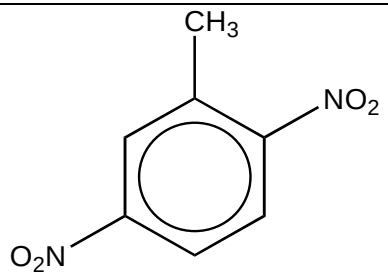
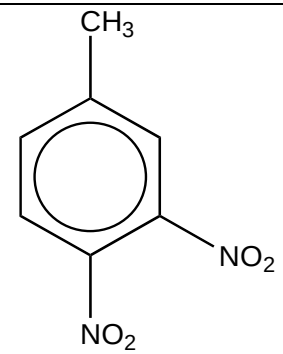
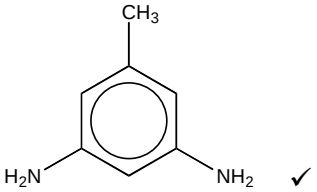
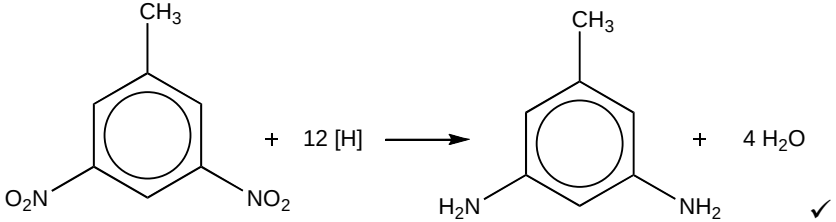
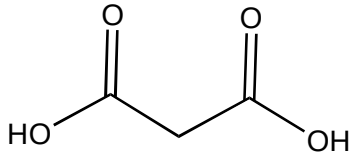
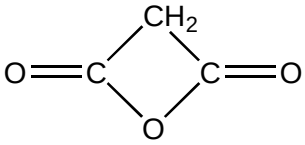
ALLOW Kekulé structures throughout

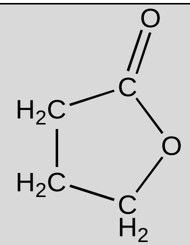
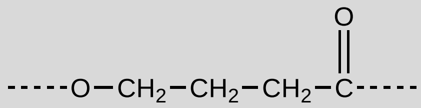
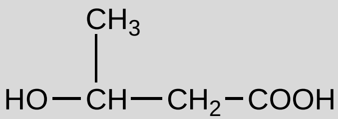
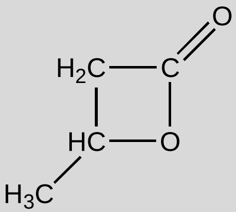
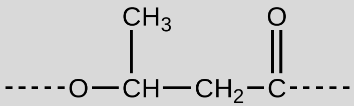
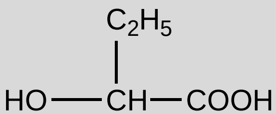
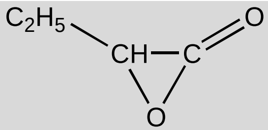
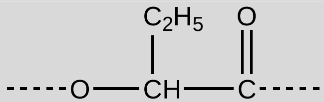
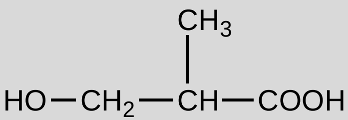
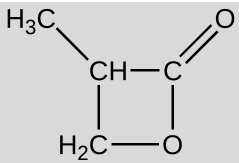
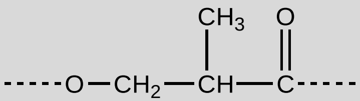
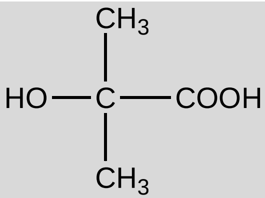
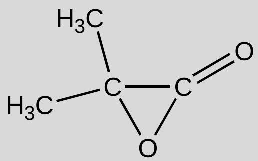
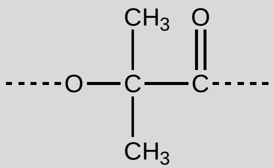
Question	Answer	Mark	Guidance
1 (a)	 curly arrow from ring to NO_2^+ correct intermediate curly arrow from C–H bond back to reform ring correct products ✓ ✓ ✓ ✓ 1 mark for intermediate 1 mark for curly arrow	4	***ANNOTATIONS MUST BE USED*** **ALLOW** skeletal CH_3 **ALLOW** $^+NO_2$ **OR** NO_2^+ **ALLOW** 1st curly arrow from the ring OR from within the ring to any part of the NO_2^+ including the + charge **DO NOT ALLOW** intermediate with broken ring less than halfway down:  Horseshoe must have open end towards NO_2 **ALLOW** Kekulé mechanism:  **ALLOW** double bonds shown in other Kekulé arrangement **IF** CH_3 has been omitted completely (*ie* benzene shown), **DO NOT AWARD** intermediate mark **OR** products mark **(max 2)** **IF** NO_2 is shown in incorrect position in intermediate or product, **DO NOT AWARD** intermediate mark but award other marks **(max 3)**

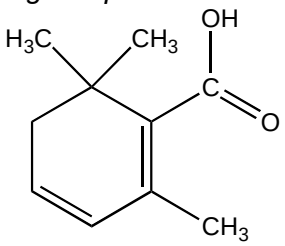
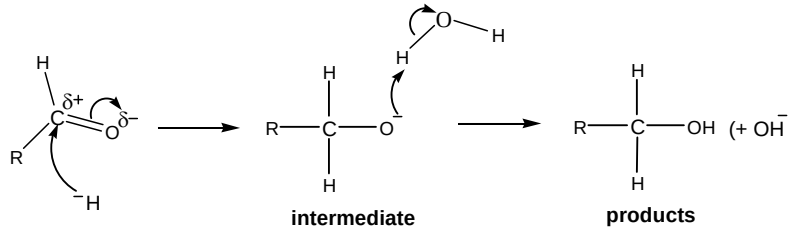
Question			Answer	Mark	Guidance
1	(b)		 ✓  ✓	2	**ALLOW** any correct unambiguous structures **ALLOW** NO_2– **Note**: connectivity is **NOT** being assessed in this part
1	(c)		**1st stage** *isomer*: **isomer 3** ✓ *product*:  ✓ *reagents*: Sn **AND** (conc) HCl ✓ *equation*:  ✓		***ANNOTATIONS MUST BE USED*** **ALLOW** structure of **isomer 3** shown separately **OR** in equation **ALLOW** structure of **product** shown separately **OR** in equation **ALLOW** correct name (3,5-diaminomethylbenzene) **IGNORE** incorrect name **DO NOT ALLOW** $CH_3C_6H_3(NH_2)_2$ **ALLOW** Zn + HCl/H_2 + metal catalyst/$LiAlH_4$/Na in ethanol **IGNORE** $NaBH_4$ **ALLOW** Sn and HCl followed by NaOH **DO NOT ALLOW** Sn and HCl and NaOH **IF** isomer **3 OR** product are given in equation but not shown previously then credit here Also credit reagents here if shown (*eg* above arrow) **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous

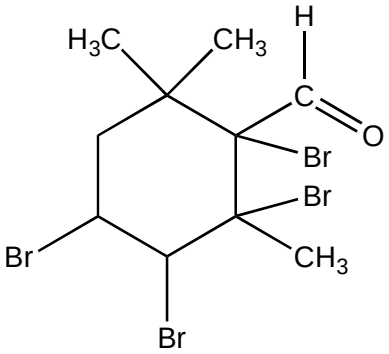
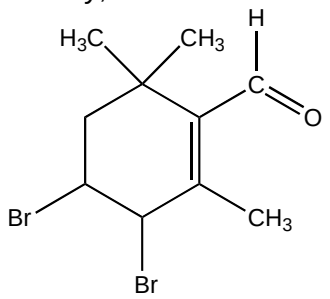
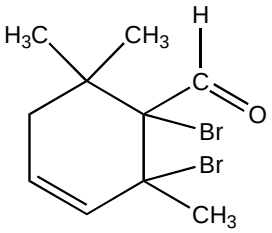
Question			Answer	Mark	Guidance
	(c)	(i)	**2nd stage** *organic compound*: $HOOC–CH_2–COOH$ ✓	6	 **DO NOT ALLOW** molecular formula **ALLOW** name of compound: propanedioic acid **OR** propane-1,3-dioic acid **ALLOW** absence of 'e' after 'propan' **ALLOW** acyl dichloride: $ClOC–CH_2–COCl$ **ALLOW** cyclic acid anhydride of propanedioic acid: 
			type of polymer: polyamide ✓		**ALLOW** Nylon or Kevlar **DO NOT ALLOW** polypeptide **DO NOT ALLOW** amide
			Total	**12**	

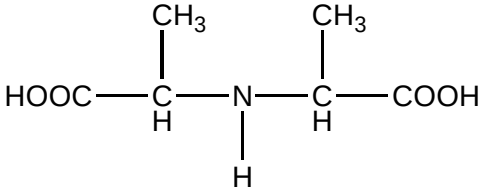
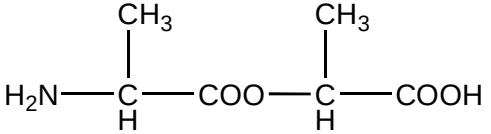
Question			Answer	Mark	Guidance
2	(a)		propane-1,2,3-triol ✓	1	**ALLOW** absence of 'e' after 'propan' **ALLOW** 1,2,3-propanetriol **ALLOW** absence of hyphens 1, 2 and 3 must be clearly separated: **ALLOW** full stops: 1.2.3 **OR** spaces: 1 2 3 **DO NOT ALLOW** 123
2	(b)	(i)	methanol **OR** ethanol **AND** renewable ✓	 1	**BOTH points required for the mark** **ALLOW** correct structural **OR** displayed **OR** skeletal formula **DO NOT ALLOW** molecular formulae **ALLOW** easy/cheap to manufacture/produce as alternative for renewable/from plants/from fermentation/burns more easily/efficiently
	(b)	(ii)	equilibrium shifts to right ✓	1	**ALLOW** equilibrium shifts in forward direction **ALLOW** more products form **ALLOW** greater yield **OR** fully reacts **OR** goes to completion **DO NOT ALLOW** improves atom economy

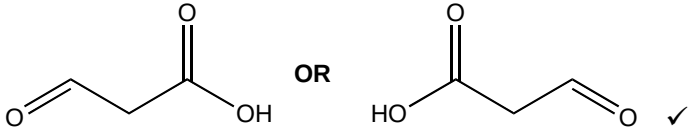
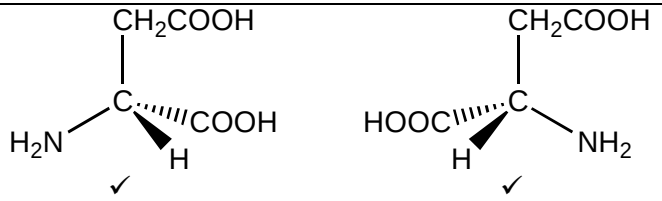
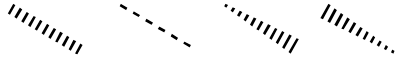
Question			Answer	Mark	Guidance
2	(c)		$CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$ ✓ $(CH_3CH_2CO)_2O + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + CH_3CH_2COOH$ ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** further esterification, *ie* $(CH_3CH_2CO)_2O + 2CH_3CH_2OH \rightarrow 2CH_3CH_2COOCH_2CH_3 + H_2O$ ***ALLOW*** *linear formula for anhydride,* ie $CH_3CH_2COOCOCH_2CH_3$ If incorrect carboxylic acid/anhydride/alcohol is used, **ALLOW ECF** for second equation

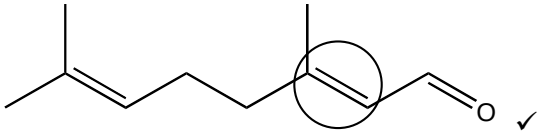
Question			Answer A	Answer B	Answer C	Mark	Guidance
2	(d)		**A**	**B**	**C**	3	Mark **A**, **B** and **C** independently ie • **A** can be **any** of the alternatives in the 1st column • **B** can be **any** of the alternatives in the 2nd column • **C** can be **any** of the alternatives in the 3rd column **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** correct names for **A**, **B** and **C** **For B** accept diester **For C**, **IGNORE** ‘*n*’ **OR** brackets (even if wrong); **ALLOW** solid side bonds Minimum is **one** correct repeat unit. Polymer must be open at both ends
			$HO-CH_2-CH_2-CH_2-COOH$				
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
					Total	**8**	

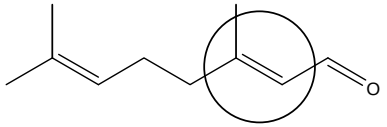
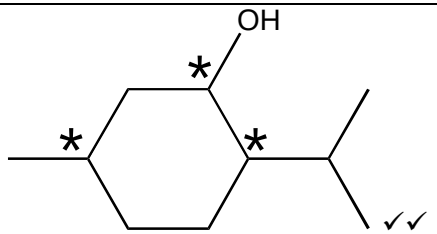
Question			Answer	Mark	Guidance
3	(a)		*observation*: silver **OR** Ag ✓ *type of reaction*: oxidation✓ *organic product*:  ✓	3	**ALLOW** black **OR** grey **ALLOW** redox **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** carboxylate, $–COO^-$
3	(b)		 1 mark for curly arrow from H^- to C of C=O ✓ 1 mark for correct dipole on C=O **AND** curly arrow from double bond to $O^{\delta-}$ ✓ 1 mark for correct intermediate with negative charge on O **AND** curly arrow from O^- to H of H–O–H **AND** curly arrow from H–O to O of H–O–H ✓ 1 mark for correct **organic** product ✓	4	***ANNOTATIONS MUST BE USED*** **ALLOW** mechanism showing curly arrows from lone pair on H^- and O^- of intermediate Dipole not required on H–O–H **DO NOT ALLOW** incorrect dipole on H–O–H **ALLOW** 1 mark for correct intermediate with '–' charge on O **AND** curly arrow from O^- to H^+ **IGNORE** missing OH^- **DO NOT ALLOW** incorrect second product

Question			Answer	Mark	Guidance
3	(c)		*reagent*: Br_2 ✓ *observation*: decolourised **OR** orange to colourless ✓ *organic product*: ✓  	3	**DO NOT ALLOW ECF** from incorrect reagent, eg 2,4-DNP **DO NOT ALLOW** goes clear **ALLOW** red/orange/yellow/brown in any combination **ALLOW** organic product from reaction of one of the double bonds only, ie  **OR**  **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae ***ALTERNATIVE reagents*** **For 1st mark,** **ALLOW** H_2 **OR** Cl_2 **OR** I_2 **OR** HCl **OR** HBr **OR** HI **OR** H_2O **For 2nd mark**, there **must** be a statement of no change **OR** no observation or similar that implies there is no visible change **EXCEPT** for I_2 which has an observation of 'decolourised' **OR** brown to colourless **For 3rd mark,** correct organic product must be shown that could be from reaction of both or one of the double bonds.
			Total	**10**	

Question			Answer	Mark	Guidance
4	(a)	(i)	$ClCH(CH_3)COOH + 3NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + NH_4Cl$ ✓	1	**ALLOW** use of **two** NH_3: $ClCH(CH_3)COOH + 2NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + HCl$ **ALLOW** products as above **OR** $H_2NCH(CH_3)COOH + NH_4Cl$ **ALLOW** use of **one** NH_3: $ClCH(CH_3)COOH + NH_3 \rightarrow H_2NCH(CH_3)COO^- + H^+ + HCl$ **ALLOW** products as above **OR** $H_2NCH(CH_3)COOH + HCl$ For alternatives below, for NH_4Cl, **ALLOW** $NH_4^+Cl^-$ **OR** $NH_4^+ + Cl^-$ for HCl, **ALLOW** H^+Cl^- **OR** $H^+ + Cl^-$ for $H_2NCH(CH_3)COO^- + NH_4^+$ **ALLOW** $H_2NCH(CH_3)COO^-NH_4^+$ **OR** $H_2NCH(CH_3)COONH_4$ **ALLOW** R in equation in place of CH_3 (either or both sides) **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae
	(a)	(ii)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **ALLOW** product from carboxylate ion as nucleophile: 

Question			Answer	Mark	Guidance
4	(b)	(i)	 OR ✓	1	**DO NOT ALLOW** any structure containing C **OR** H (except in OH)
	(b)	(ii)	 ✓ ✓	2	**ALL** bond linkages must be correct, eg the chiral C must be linked to the C of the COOH, the C of the CH_2COOH and the N of the NH_2 (connectivity is being tested) The 2nd mark is for the mirror image of an amino acid. This could be any amino acid **EXCEPT** glycine **DO NOT** penalise connectivity more than once **ALLOW** R in equation in place of CH_2COOH (either or both sides) Each structure **must** have four central bonds, with at least two wedges, one in; one out For bond into paper, accept: 
4	(c)		***Disadvantages*** *Any **two** from:* • (one stereoisomer might have harmful) side effects✓ • reduces the (pharmacological) activity/effectiveness ✓ • cost **OR** difficulty in separating stereoisomers ✓ ***Synthesis of a single optical isomer*** *Any **two** from:* • using enzymes or bacteria ✓ • using a chiral catalyst **OR** transition metal complex/transition metal catalyst ✓ • using chiral synthesis **OR** chiral starting material **OR** natural amino acid ✓	2 max 2 max	***ANNOTATIONS MUST BE USED*** **ALLOW** optical isomer **OR** enantiomers as alternative for stereoisomers **ALLOW** a response that implies an increased dose **ALLOW** biological catalyst **ALLOW** 'chiral pool' **OR** L-amino acids **OR** D-sugars
			Total	**8**	

Question			Answer	Mark	Guidance
5	(a)	(i)	Adsorption ✓(onto the stationary phase) ***Quality of Written Communication*** 'Adsorption' must be spelled correctly	1	**ALLOW** adsorbtion or adsorb(s) or adsorbed spelled correctly at least once **DO NOT ALLOW** anything that begins with ab...
	(a)	(ii)	0.2 ✓	1	**ALLOW** any value in the range 0.1 – 0.3 **IGNORE** significant figures **DO NOT ALLOW** fraction/percent as final answer
	(a)	(iii)	Spot may contain more than one compound/component ✓	1	**ALLOW** compounds have similar R_f values/adsorptions **OR** compounds have not (fully) separated **OR B** is spread over a large region **OR** compounds are similar **IGNORE** retention times
5	(b)	(i)	GC separates the components/compounds **AND** MS is compared to a database/reference ✓	1	**ALLOW** chromatography for GC **ALLOW** they have different retention times **ALLOW** MS analyses compounds/gives structural information/gives different mass spectra **ALLOW** (uses) fragmentation patterns/fragments/peaks/parts of the compound **DO NOT ALLOW** MS identifies compounds (in question) **DO NOT ALLOW** molecular ion alone/M_r etc.
		(ii)	nerol and geraniol **AND** they are stereoisomers **OR** primary alcohols ✓	1	Compounds **AND** reason required for the mark **ALLOW** they are *E*/*Z* isomers **OR** *cis*-*trans* isomers **ALLOW** straight-chain alcohols **OR** unsaturated alcohols
		(iii)	stereoisomers have the same structural formula **AND** different 3D arrangements ✓	1	**BOTH** points required for the mark **ALLOW** different arrangements in space
		(iv)	 ✓	1	Circle must include the correct C=C double bond **AND** must not extend further than the adjacent atoms in the main chain, ie limit is:

Question			Answer	Mark	Guidance
					
	(b)	(v)	 ✓✓	2	**ALL THREE** chiral centres required for 2 marks **ANY TWO** chiral centres required for 1 mark If more than three asterisks are shown, mark incorrect asterisk(s) first
5	(c)		Correctly calculates amount of myrcene = 34/136 **OR** 0.25 (mol) ✓ Correctly calculates 60% yield of menthol = 0.25 × 60/100 **OR** 0.15 (mol) ✓ Correctly calculates mass of menthol = 0.15 × 156 = 23.4 (g) ✓	3	***ANNOTATIONS MUST BE USED*** **ALLOW** amount of myrcene × 60/100 **ALLOW** amount of menthol × 156 **ALLOW** alternative approach based on reacting masses (using same **ECF** principles as above): correctly calculates mass of myrcene that could be obtained from 34 g myrcene: mass = 34 × 156/136 = 39 (g) × 156 ✓; ÷ 136 ✓ 60% of 39 g = 39 × 60/100 = 23.4 (g) ✓ **ALLOW** final answer to 2 or more significant figures correctly rounded Correct answer of 23.4 (g) with no working scores all 3 marks
			Total	**12**	

Question			Answer	Mark	Guidance
6	(a)		a **singlet** for position 2 **OR** a **singlet** because it has no adjacent H's✓ A **triplet** for positions 4 and 6 ***OR** a **triplet** because it has 2 adjacent H's* ✓ A **quintet** for position 5 **OR** a **quintet** because it has four adjacent H's ✓ ***Quality of Written Communication*** singlet **OR** triplet **OR** quintet **OR** pentet **OR** multiplet (see Guidance) must be spelled correctly at least once	3	***ANNOTATIONS MUST BE USED*** **ALLOW** a response that implies a single peak **OR** 'no splitting' **ALLOW** a response that implies a splitting into three **DO NOT ALLOW** implications of more than one triplet **ALLOW** 'pentet' **OR** a response that implies a splitting into five **OR** multiplet **ALLOW** 1 mark for singlet and triplet and quintet/pentet/multiplet with no identification of protons Any suggestion that the oxygens cause a splitting scores a maximum of 2 marks. • All 3 remaining splitting patterns correct 2 marks. • Any 2 correct 1 mark. **IF** number labels for protons in diagram are **not** identified, **ALLOW** identification by chemical shifts for 2 marks max: • singlet at 3.3–4.2 **AND** a triplet at 3.3–4.2 ✓ • quintet/pentet/multiplet at 0.7–2.0 ✓ Clear and unambiguous identification of the protons other than by position number should be credited, *ie* 'CH_2 between two oxygens'

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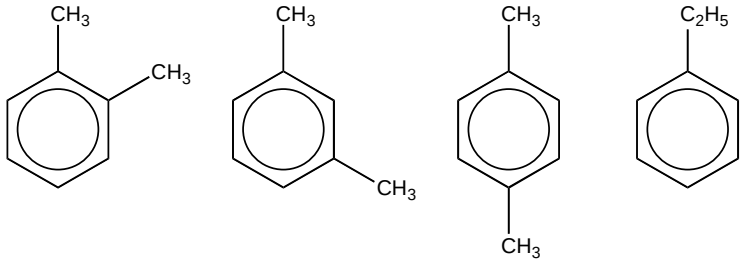
Question			Answer	Mark	Guidance
6	(b)		***ANY 5 marks plus correct structure (in box)***		***ANNOTATIONS MUST BE USED***
			Molecular ion/M^+ peak at (*m*/*z* of) 106 ✓		**ALLOW** molecular mass **OR** relative molecular mass
			Fragment peak at 91 is $C_6H_4–CH_3^+$/$C_6H_5–CH_2^+$ ✓		**ALLOW** $C_6H_4–CH_3$/$C_6H_5–CH_2$ **ALLOW** peak at 91 represents loss of CH_3
			Molecular formula is C_8H_{10} (or implied, *ie* any one of the structures below) ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **ALLOW** a correct name eg a dimethylbenzene
			 ✓		**ALL FOUR** structures needed for 1 mark **ALLOW** correct names
			^{13}C NMR spectrum shows 5 C environments ✓		**ALLOW** NMR spectrum shows five different types of carbon **DO NOT ALLOW** 'NMR spectrum has five peaks' – the mark is for realising what the peaks show, not for just describing the spectrum
			Peak near 20 is a C attached at another carbon, **C**–C **OR** peaks at ~125–140 for aromatic **C**s ✓		

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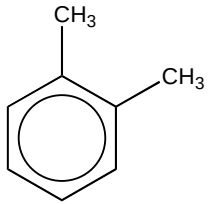
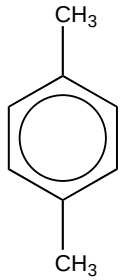
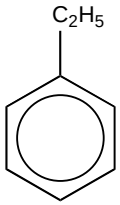
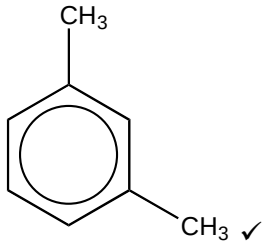
Question			Answer	Mark	Guidance
6	(b)		Number of peaks for other three isomers matched to structures: *Any 2 correct for 2 marks* ✓✓ *1 correct for 1 mark* ✓  4 peaks  3 peaks  6 peaks Correct structure shown: 	6	**ALLOW** 'carbon environments' for peaks
			Total	**9**	

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