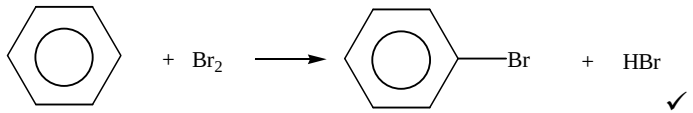
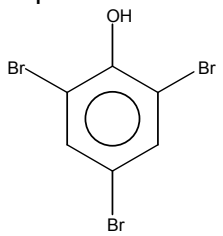
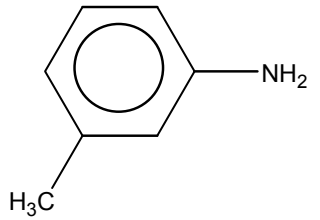
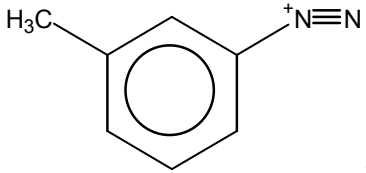
F324 Rings, Polymers and Analysis

Question			Expected Answers	Marks	Additional Guidance
1	(a)		 ✓	1	**ALLOW** $C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$ **DO NOT ALLOW** multiple substitution **DO NOT ALLOW** Br^+
	(b)	(i)	White precipitate **OR** white solid **OR** white crystals ✓  ✓	2	**DO NOT ALLOW** colourless **DO NOT ALLOW** white ppt and bubbles **DO NOT ALLOW** $Br_3C_6H_2OH$ **OR** 2,4,6-tribromophenol **OR** tribromophenol
		(ii)	1,2-Dibromocyclohexane ✓	1	**ALLOW** 1,2dibromocyclohexane **OR** 1-2dibromocyclohexane **OR** 12dibromocyclohexane **OR** cyclo-1,2-dibromohexane **DO NOT ALLOW** dibromocyclohexane **OR** $C_6H_{10}Br_2$ **OR** structures
		(iii)	**MUST** spell delocalised/delocalized or localised/localized correctly once in the answer to obtain all 5 marks **benzene** electrons or π-bonds are delocalised ✓ **phenol** a lone or non-bonded pair of electrons on the oxygen or the OH group is (partially) delocalised into the ring ✓ **cyclohexene** electrons are localised **OR** delocalised between two carbons ✓ benzene has a lower **electron density OR** phenol has a higher electron density **OR** cyclohexene has a higher electron density ✓ benzene cannot **polarise** or induce a dipole in Br_2 **OR** phenol can polarise the Br_2 **OR** cyclohexene can polarise Br_2 or the Br–Br bond ✓	5	**ALLOW** diagram to show overlap of all 6 p-orbitals for delocalisation **DO NOT ALLOW** benzene has delocalised structure or ring **ALLOW** diagram to show movement of lone pair into ring for phenol **ALLOW** diagram or description of overlap of 2 adjacent p-orbitals for bonding in cyclohexene **DO NOT ALLOW** cyclohexene has a C=C double bond **IGNORE** slip if cyclohexene is written as cyclohexane but π - bonding correctly described **DO NOT ALLOW** charge density **OR** electronegativity instead of electron density **ALLOW** $Br^{\delta+}$ **OR** electrophile Br^+ as alternate to polarise

(c)



✓



✓✓

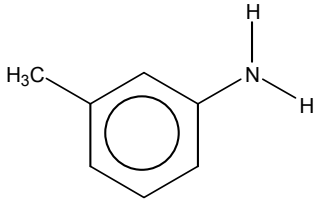
ALLOW ECF ✓✓ on incorrect amine

HNO_2 + HCl and temp < 10 °C **OR** $NaNO_2$ + HCl and temp < 10 °C ✓

alkaline **AND** phenol (if temperature stated must be below 10 °C) ✓

5

ALLOW

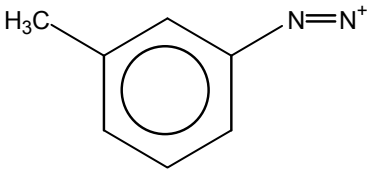


IGNORE Cl^- ion

DO NOT ALLOW if ring is connected to the N triple bond in the diazonium or if diazonium has a negative charge

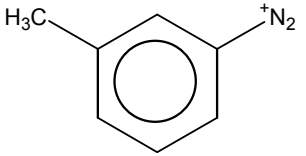
ALLOW one mark for correct displayed diazonium if alkyl group is not shown

ALLOW



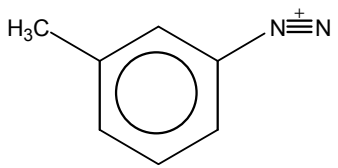
for both marks

ALLOW



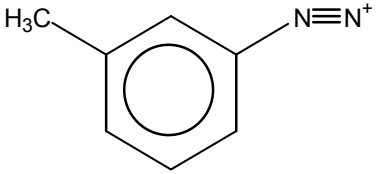
for one mark

ALLOW



for one mark

ALLOW



for one mark

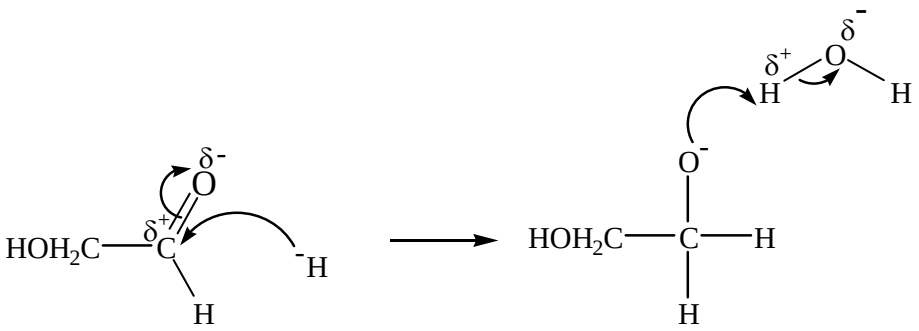
ALLOW NaOH **OR** KOH & C_6H_5OH **OR** phenoxide ion **OR** $C_6H_5O^-$

ALLOW reagents and conditions from the equations

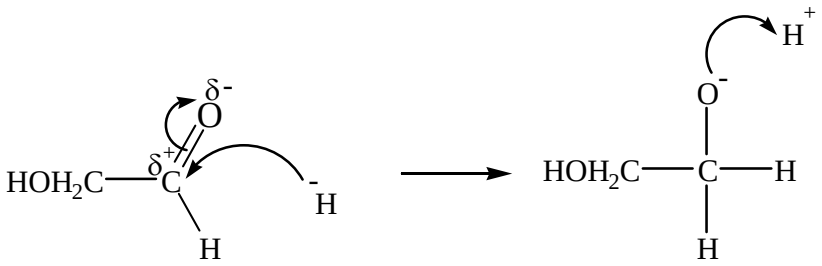
Total **14**

Question			Expected Answers	Marks	Additional Guidance
2	(a)	(i)	silver mirror ✓	1	**ALLOW** Ag(s) **OR** Ag mirror **OR** precipitate **OR** ppt **OR** solid **ALLOW** brown **OR** black **OR** grey
		(ii)	$HOCH_2COOH$ ✓	1	**ALLOW** $CH_2OHCOOH$ **OR** CH_2OHCO_2H **OR** $HOCH_2CO_2H$ **OR** displayed **OR** skeletal formula **OR** $HOCH_2COO^-$ **DO NOT ALLOW** C_2H_4O **OR** 2-hydroxyethanoic acid
	(b)		$HOCH_2CHO + 3[O] \rightarrow HOOCCOOH + H_2O$ reagents ✓ both products ✓	2	**ALLOW** displayed/skeletal formula/COOHCOOH ✓✓ if molecular formula used $C_2H_4O_2 + 3[O] \rightarrow C_2H_2O_4 + H_2O$ max = 1 ✓ **Any correctly balanced equation for partial oxidation** can score 1 mark ✓ $HOCH_2CHO + [O] \rightarrow HOCH_2COOH$ **OR** $HOCH_2CHO + 2[O] \rightarrow OHCCOOH + H_2O$ **OR** $HOCH_2CHO + [O] \rightarrow OHCCHO + H_2O$ **OR** $HOCH_2CHO + 2[O] \rightarrow HOOCCHO + H_2O$
	(c)	(i)	$HOCH_2CH_2OH$ ✓	1	**ALLOW** $HO(CH_2)_2OH$ **OR** $(CH_2OH)_2$ **OR** skeletal formula **OR** displayed formula **DO NOT ALLOW** molecular formula ($C_2H_6O_2$)
		(ii)	curly arrow from H^- to $C^{\delta+}$ ✓ dipoles and curly arrow from C=O bond to O ✓ intermediate ✓ curly arrow from intermediate to $H^{\delta+}$ in H_2O/ H^+ and if H_2O is used it must show the curly arrow from the O–H bond to the O ✓ *lone pairs are not essential*	4	**ALLOW** curly arrow to C even if dipole missing or incorrect **ALLOW** maximum of 3 marks if incorrect starting material is used See page 36 for detailed mechanisms – ***Alternative 3*** scores all 4 marks even though the intermediate is not shown

Alternative 1

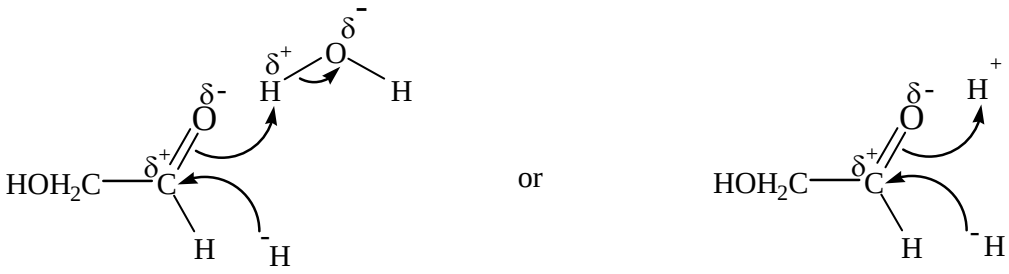


Alternative 2

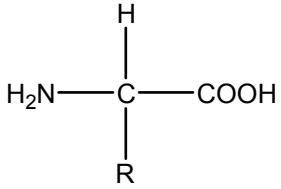
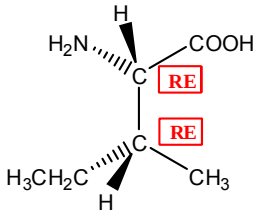
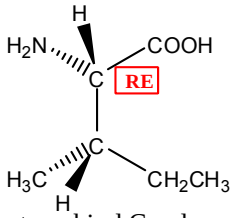
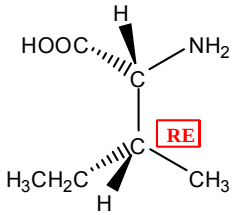


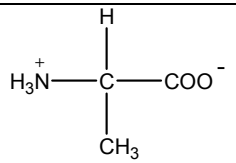
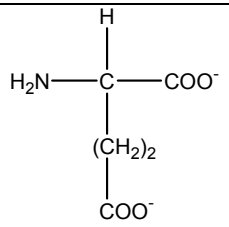
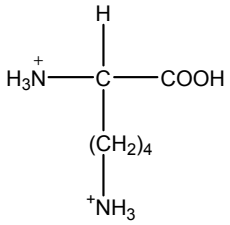
products are not required

Alternative 3

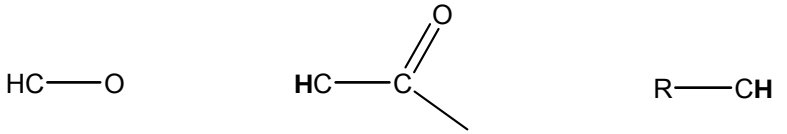


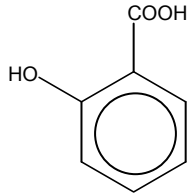
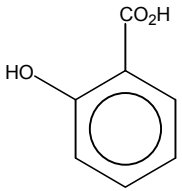
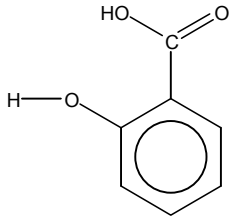
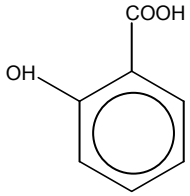
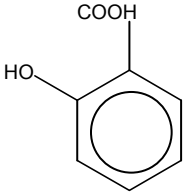
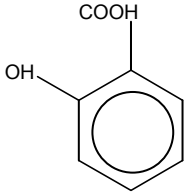
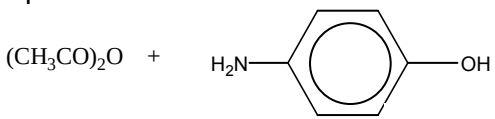
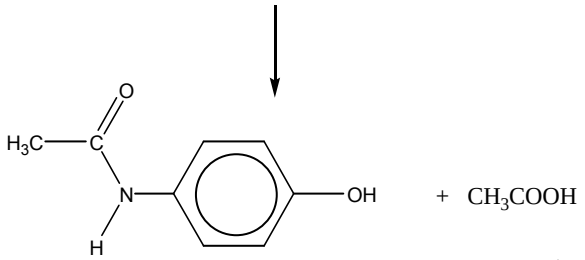
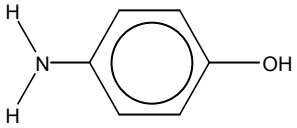
			Total	**9**	

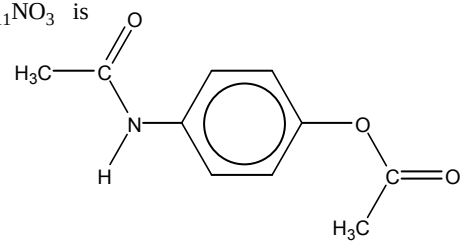
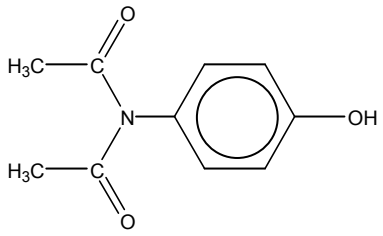
Question			Expected Answers	Marks	Additional Guidance
3	(a)	(i)	adsorption ✓	1	**ALLOW** partition **OR** adsorbtion **IGNORE** solubility **OR** desorption **DO NOT ALLOW** absorption
		(ii)	measure how far each spot travels relative to the solvent front or calculate the R_f value ✓ compare R_f values to those for known amino acids ✓	2	**ALLOW** compare R_f values to database **ALLOW** compare to known amino acids **DO NOT ALLOW** retention times for first mark, but the 2nd mark would be available as ✓ ECF **ALLOW** alternative approach: on the same plate compare position of spots ✓ with known amino acids ✓
		(iii)	(amino acids won't separate because) similar compounds have similar R_f (values) ✓	1	**ALLOW** spots often overlap **OR** don't (fully) separate **ALLOW** they have similar R_f (values) or similar adsoptions or similar retention times ECF to **a(ii)**
	(b)	(i)	 ✓	1	**ALLOW** $RCH(NH_2)COOH$ any order for R, NH_2 and COOH but C must be next to H 'CH' must be shown **ALLOW** CO_2H brackets around NH_2 are **not** essential **ALLOW** structure
		(ii)	must attempt 3D use **RE** symbol in the "tools" to denote whether or not each chiral C is a reflection of the one given in the question  both chiral Cs are mirror images  top chiral C only is a mirror image  bottom chiral C only is a mirror image	3	each chiral C must have 2 — bonds, 1 wedge bond (**IGNORE** shading) & 1 dash bond (**IGNORE** wedge) check the clockwise orientation of each C. For each C start with the H and if on the: • top C the H is followed by COOH it is not a mirror image. If it is a mirror image annotate using RE. • bottom C the H is followed by CH_3 it is not a mirror image. If it is a mirror image annotate using RE. the four groups can be attached in any order. If the molecule is drawn upside down – clockwise becomes anti-clockwise. **MUST** check that the drawn structure is non-superimposable irrespective of the orientation or the way it has been drawn. **IGNORE** bond linkage for all groups

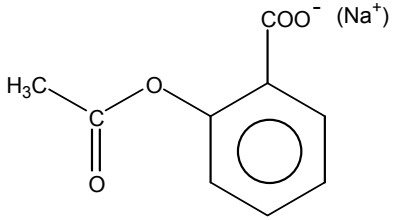
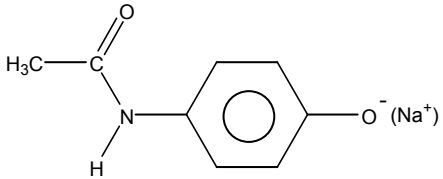
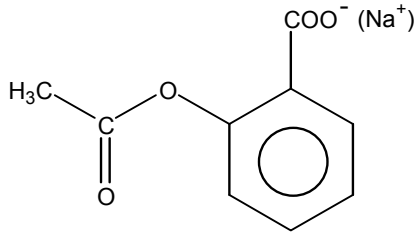
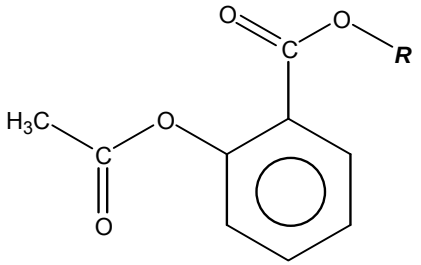
	(c)		 alanine at pH = 6.0 ✓  glutamic acid at pH =10 ✓  lysine at pH = 2.0 ✓		**ALLOW** CO_2^- **ALLOW** NH_3^+ If NH_3 fully displayed **ALLOW** + charge on N or H If COO fully displayed **ALLOW** $^-$ charge on O only
	(d)		valine–glycine–leucine ✓	**1**	**ALLOW** val–gly–leu **DO NOT ALLOW** structures
	(e)		$H_2N(CH_2)_6NH_2$ ✓ $HOOC(CH_2)_8COOH$ ✓	**2**	**ALLOW** $H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$ **ALLOW** $HOOCCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$ **ALLOW** CO_2H for COOH **ALLOW** acid chloride, $ClOC(CH_2)_8COCl$ **ALLOW** displayed formulae or skeletal formulae
			Total	**14**	

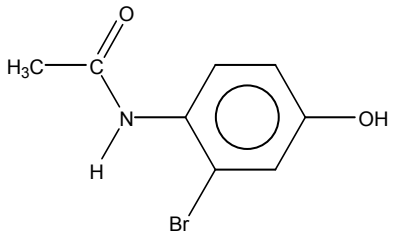
Question			Expected Answers	Marks	Additional Guidance
4	(a)		**infrared – 1 mark only** shows (very broad) peak between 2500–3300 (cm^{-1}) (due to O–H bond) ✓	3	**ALLOW** (very broad) peak around 3000 (cm^{-1}) **OR** any stated value between 2500 and 3300 (cm^{-1}) for O–H **DO NOT ALLOW** peak in range 3200–3550 (cm^{-1}) **IGNORE** any reference to C=O or C–O as both are also present in an ester **OR** to fingerprint region
			^{13}C NMR – 2 marks $(CH_3)_2CHCH_2COOH$ has 4 peaks (due to 4 different C environments) ✓ $(CH_3)_3CCOOH$ has 3 peaks (due to 3 different C environments) ✓		**ALLOW** '*^{13}C NMR detects the number of/different C environments*' for 1 ✓, suitable example for the 2nd mark
	(b)		**splitting pattern** explains any two in terms of '*n* + 1 rule' for two marks ✓✓ Explains any one peak for 1 mark ✓ • *singlet* therefore adjacent C (if any) has no Hs • *multiplet* **OR** split into 7 therefore adjacent Cs have lots of/6 Hs • *doublet* therefore adjacent C is bonded to 1H *must spell **one** of multiplet / heptet, singlet, doublet correctly* **max = 2 marks**	6	**1 mark** for correct ester if two splitting patterns are correctly analysed **ignore** the third **ALLOW** singlet because next or bonded to an O **ALLOW** multiplet/heptet because next to 2 CH_3s **ALLOW** doublet because next to a CH
			chemical shifts		**ALLOW** tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3

			two marks if any two absorptions are identified correctly ✓✓ one mark if any one absorption is identified correctly ✓ • peak ~3.7 (ppm) – bonded to an O • peak ~2.7 (ppm) – indicates it is next to a C=O • peak ~1.2 (ppm) – bonded to other Cs **OR** part of a chain **max = 2 marks** compound identified as $(CH_3)_2CHCOOCH_3$ ✓✓ **2 marks** compound identified as $CH_3COOCH(CH_3)_2$ ✓ **1 mark**		(ppm) **ALLOW** any two gets 2 marks, any one scores 1 mark  **ALLOW** peaks labelled on the spectrum **ALLOW** singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks if two chemical shifts are correctly identified **IGNORE** the third
			Total	**9**	

Question			Expected Answers	Marks	Additional Guidance
5	(a)		 ✓	1	**ALLOW**  or  **DO NOT ALLOW** incorrect bond linkage  or  or 
	(b)	(i)	equation  reactants ✓  products✓	2	**ALLOW** $(CH_3CO)_2O + H_2NC_6H_4OH \rightarrow CH_3CONHC_6H_4OH + CH_3COOH$ **ALLOW**  **DO NOT ALLOW** molecular formulae

		(ii)	$C_{10}H_{11}NO_3$ is  or  ✓	1	**ALLOW** amide shown as either $CH_3CONH–$ **OR** $H_3CCONH–$ **OR** $CH_3COHN–$ **OR** $H_3CCOHN–$ **ALLOW** ester shown as either $–OCOCH_3$ **OR** $–OOCCH_3$
		(iii)	to ensure that there are no (harmful) side effects ✓	1	**ALLOW** impurities reduce effectiveness (of drug) **OR** might be toxic **OR** avoids litigation **OR** harmful **OR** hazardous **ALLOW** to ensure that the drug/active component is safe **IGNORE** dangerous **OR** nasty **OR** can kill **OR** increased dosage
	(c)		(aspirin contains) ester **AND** carboxylic acid ✓ (paracetamol contains) amide **AND** phenol ✓	2	**IGNORE** arene or benzene or aromatic or phenyl or methyl but any other group loses the mark **ALLOW** carboxyl group **DO NOT ALLOW** acid **IGNORE** arene or benzene or aromatic or phenyl or methyl but any other group loses the mark **ALLOW** peptide **ALLOW** hydroxy(l) **DO NOT ALLOW** hydroxide or alcohol **DO NOT ALLOW** amine
	(d)	(i)	**Both**	3	**ALLOW** hydrolysis by $H^+(aq)$ or H^+ or HCl(aq) or HCl or $H_2SO_4(aq)$

			Na **OR** NaOH ✓  from aspirin ✓  from paracetamol ✓		or H_2SO_4 to give hydroxybenzoic acid + ethanoic acid with aspirin ✓ and ammonium salt of 4-aminophenol + ethanoic acid with paracetamol ✓ **ALLOW** hydrolysis by $OH^-(aq)$ or NaOH(aq) and other alkali leading to hydrolysis to give carboxylate salt and phenoxide salt on the ring + ethanoate with aspirin ✓ and 4-aminophenoxide ion + ethanoate ion with paracetamol ✓ **ALLOW** HNO_3 (and H_2SO_4) to give NO_2 in one or more positions on the ring in both aspirin and paracetamol ✓✓ **DO NOT ALLOW** NH_3 but correct ammonium salts can be awarded 2 marks ECF **DO NOT ALLOW** H_2O but correct products can be awarded 2 marks ECF if no reagent there cannot be any marks for the products If reagent selected is incorrect but would react with **either** aspirin or paracetamol **ALLOW** ✓ ECF for the correct organic product
		(ii)	**aspirin only** $NaHCO_3$ **OR** Na_2CO_3 **OR** metal oxide ✓  ✓	**2**	**ALLOW** Mg, carbonates, NH_3 **ALLOW** alcohols (***R***OH) to give ester if no reagent there cannot be any marks for the products  If reagent selected is incorrect but would react with **BOTH** aspirin and paracetamol **ALLOW** ✓ ECF for the correct organic product
		(iii)	**paracetamol only**		**ALLOW** Br_2 water

			Br_2 ✓  ✓	**2**	**ALLOW** one or more Br at **any** position on the ring **DO NOT ALLOW** Br substitution of OH **ALLOW** acyl chloride or acid anhydride and corresponding ester **ALLOW** $FeCl_3$ to form a purple <u>complex ion</u> (structure not required) **ALLOW** diazonium and structure showing azo group substituting one of the Hs in the ring if no reagent there cannot be any marks for the products If reagent selected is incorrect but would react with **BOTH** aspirin and paracetamol **ALLOW** ✓ ECF for the correct organic product
			Total	**14**	