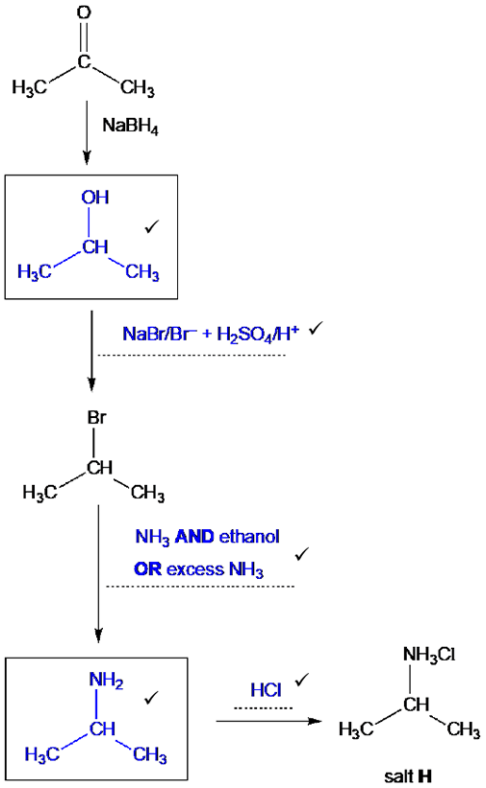
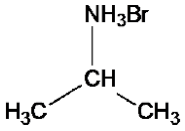
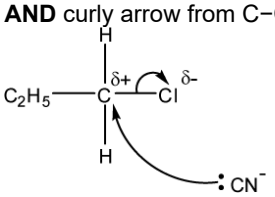
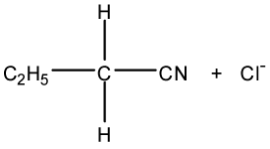
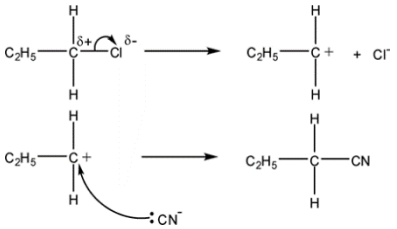
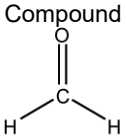
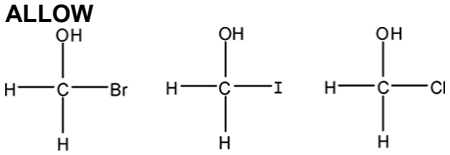
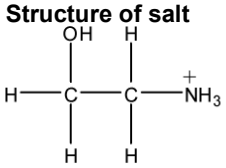
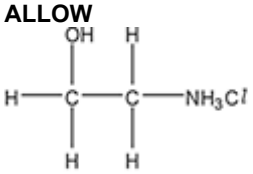
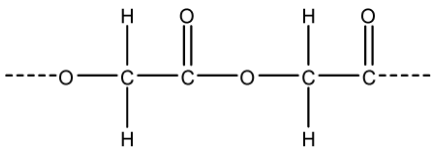
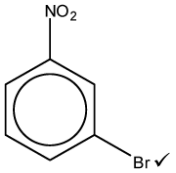
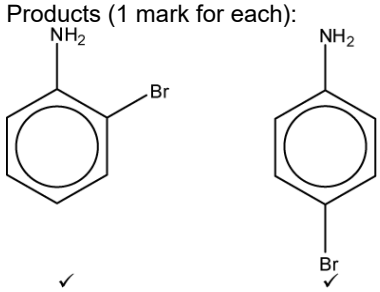
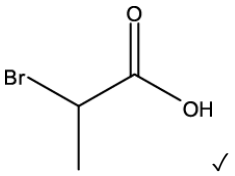
Mark scheme - Amines

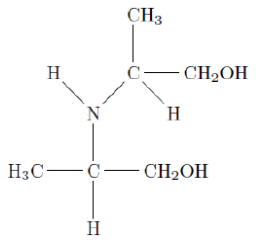
Question			Answer/Indicative content	Marks	Guidance
1				5 (AO2.5×5)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** HBr **ALLOW** for the bottom left structure 
			Total	**5**	
2		i	curly arrow from ⁻CN to carbon atom of C−Cl bond ✓ Dipole shown on C–Cl bond, $C^{\delta+}$ and $Cl^{\delta-}$, **AND** curly arrow from C−Cl bond to Cl atom ✓  correct organic product **AND** Cl⁻✓ 	**2**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** Curly arrow must come from lone pair on C of ⁻CN OR CN^- **OR** from minus sign on C of ⁻CN ion (then lone pair on CN^- does not need to be shown) **IGNORE** NaCl **ALLOW** S_N1 mechanism: Dipole shown on C–Cl bond, $C^{\delta+}$ and $Cl^{\delta-}$, **AND** curly arrow from C–Cl bond to Cl atom ✓ Correct carbocation **AND** curly arrow from ⁻CN to carbocation. Curly arrow must come from lone pair on C of ⁻CN **OR** CN^- **OR** from minus sign on C of ⁻CN ion (then lone pair on CN^- does not need to be shown) ✓ correct organic product **AND** Cl^- ✓

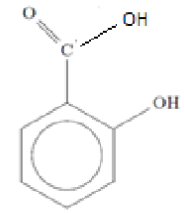
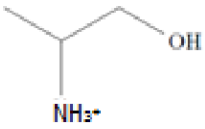
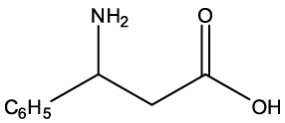
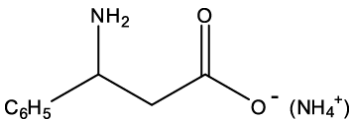
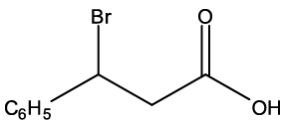
					 **Examiner Comments** The mechanism for the reaction of 1-chloropropane was well done with the majority of candidates scoring two or three of the marks. Marks were not awarded when candidates used a negative charge or a lone pair sited on the nitrogen as the starting point for a curly arrow in the first stage of the reaction mechanism. The final marking point was awarded for the production of a Cl^- ion. The placing of curly arrows, dipoles and lone pairs of electrons are important when communicating by mechanisms.
		ii	Compound **G**  ✓ **Reagents** **Reaction 2:** H_2 **AND** Ni ✓ **Reaction 3:** Correct formula of an aqueous acid e.g. HCl(aq)/H_2SO_4(aq) ✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** name(s) **ALLOW**  **ALLOW** any suitable metal catalyst e.g. Pt **ALLOW** $LiAlH_4$ for reagent in reaction 2 **DO NOT ALLOW** $NaBH_4$ for reagent in reaction 2 **IGNORE** names *(question asks for formulae)* **IGNORE** references to temperature and/or pressure **ALLOW** H^+(aq) **IGNORE** dilute **ALLOW** formula of an acid **AND** water e.g. HCl **AND** H_2O H_2SO_4 **AND** H_2O **Examiner Comments** Although many candidates were able to provide the structure of methanal as the starting material for this synthesis, the structures of chloromethanol, bromomethanol and iodomethanol were accepted as suitable alternatives. It should be noted that hydrolysis is carried out using aqueous acid and that dilute acid is not a suitable alternative.

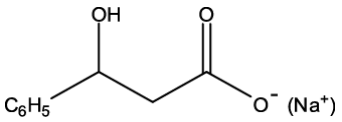
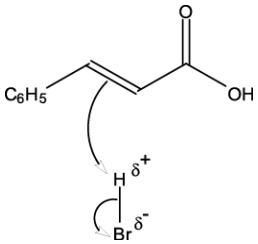
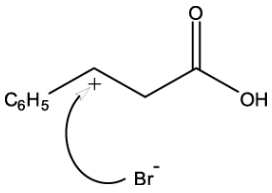
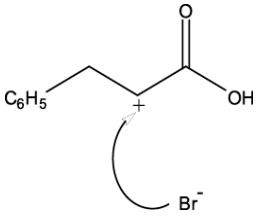
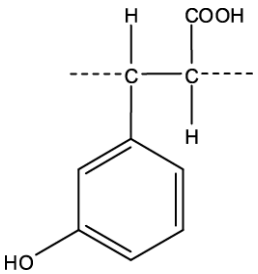
		iii	**Explanation** Nitrogen electron pair **OR** nitrogen lone pair **AND** accepts a proton / H^+✓ **Structure of salt**  **AND** Cl^- ✓	**2**	**IGNORE** NH_2 group donates electron pair **ALLOW** nitrogen donates an electron pair to H^+ **DO NOT ALLOW** nitrogen donates lone pair to acid **IGNORE** comments about the O in the –OH group Compound **H** is a base is **not sufficient** *(role of lone pair required)* **DO NOT ALLOW** nitrogen/N lone pair accepts hydrogen (*proton/H^+ required*) **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW**  *i.e.* charges **not** required **IF** charges are shown **both** need to be present **ALLOW** charge either on **N** atom or NH_3^+ **IF** displayed then + charge must be on the nitrogen **Examiner Comments** Only 20% of candidates were awarded both marks for this question. The commonest error was a failure to state that the N atom has a lone pair of electrons that can gain a proton. Answers stating that amines accept protons or that a salt is produced when an acid reacts with a base were not credited. Where a full displayed structure is given the positive charge must be shown on the nitrogen atom, although $-NH_3^+$ is acceptable. As the question required the formula of the salt, the Cl^- had to be included.
		iv	 Ester link ✓ Rest of structure✓ (polymer **J** is biodegradable because) the ester / ester bond / ester group / polyester can be hydrolysed✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** more than two repeat units for second marking point. 'End bonds' **MUST** be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** ***n*** Broken down by water is **not** sufficient

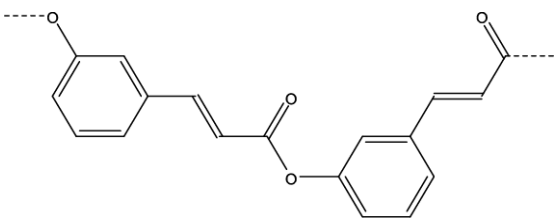
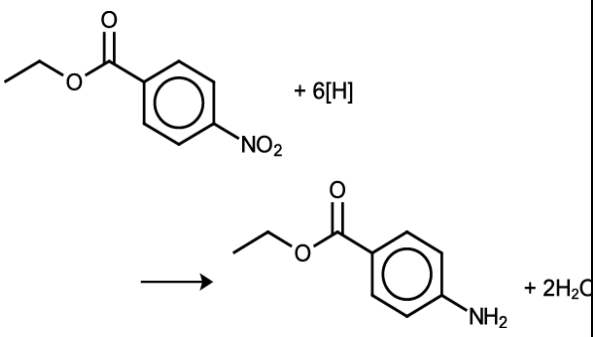
					IGNORE references to photodegradable **Examiner Comments** The most common mark for this question was two out of the three marks available, with candidates giving a correct structure of the polymer but failing to express that the polymer was biodegradable due the ability of the ester functional group to undergo hydrolysis.
			Total	**11**	
3		i	**Bromination:** Br_2 **AND** A/Br_3/$FeBr_3$/Fe ✓ **Intermediate**  **Reduction:** Sn **AND** (concentrated) HC*l* ✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** any suitable halogen carrier catalyst **ALLOW** Kekulé structure **IGNORE** names *(question asks for formulae)* **IGNORE** reaction conditions even if incorrect **IGNORE** 'dilute' for HC*l* **IGNORE** H_2 **IGNORE** NaOH if seen as a reagent to convert nitro group into amine e.g 'Sn/(concentrated) HC*l* then NaOH' scores the mark **Examiner Comments** Candidates were able, in the main, to provide the reagents for bromination and reduction. The structure of the intermediate compound in the preparation of 3-bromophenylamine proved to be straightforward, however common errors involved the omission of the halogen carrier catalyst for bromination or stating names rather than formulae as indicated in the question.
		ii	NH_2 is 2,4 directing ✓ Products (1 mark for each):  	**3**	**IGNORE** references to electron donating/withdrawing groups **ALLOW** –NH_2 activates the ring causing the new group to join at positions 2 and 4. **ALLOW** ortho and para directing for 2,4 directing **IGNORE** 6-directing **ALLOW** Kekulé structure **IGNORE** names **Examiner Comments** The most able candidates completed this question with a clear statement that the

					–NH_2 group was 2,4 directing and provided two clearly drawn structures of 2-bromophenylamine and 4-bromophenylamine. The most common errors observed included drawing two structures that were identical and explaining the two structures in terms of electron donation from the –NH_2 without any indication of positioning. Candidates using the terms ortho and para directing were awarded full marks for their answers.
			Total	**6**	
4			**Reagents for first stage** $NaBr/H_2SO_4$ ✓ **Compound H**  ✓ **Reagent for second stage** (excess ethanolic) NH_3 ✓	3	**ALLOW** any suitable halide salt/sulfuric acid combination **ALLOW** HC/ **OR** HBr **OR** HI **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Note:** the halogen in compound **H** can be C/, Br or I, but **must** be consistent with halide salt used
			Total	**3**	
5	a	i	**^{1}H NMR spectrum for 2-aminopropan-1-ol** **Chemical shift, δ/ppm** / **Relative peak area** / **Splitting pattern** 0.8 – 2.0 / 3 / doublet 2.3 – 3.0 / 1 / multiplet 3.3 – 4.2 / 2 / doublet ✓✓✓	3	One mark for each correct row **ALLOW** δ values as a range or a value within the specified range. **ALLOW** δ values +/− 0.2 ppm. **ALLOW** a response that implies a splitting into two for a doublet etc. **ALLOW** sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once **Examiner's Comments** Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.
		ii	M^+ peak at 75 (peak 1) $CH_3CH(NH_2)CH_2OH^+/C_3H_9NO^+$ ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as

			Fragment peak at 44 (peak 2) $CH_3CH(NH_2)^+/C_2H_6N^+$ ✓		long as unambiguous Positive charge is essential but **ALLOW** maximum of one mark if both formulae are correct **AND** neither species has a positive charge **Examiner's Comments** Although peak 2 was often correct, the species responsible for the M+ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.
	b	i	Ethanolic ammonia **OR** ammonia/NH_3 **AND** ethanol ✓	1	**ALLOW** ammonia in a sealed tube **ALLOW** dilute ethanolic ammonia/NH_3 **IGNORE** heat **ALLOW** alcohol for ethanol **DO NOT ALLOW** any reference to water or hydroxide ions **Examiner's Comments** A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
		ii	(compound D)  ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **Examiner's Comments** This question discriminated well. Although there were very few blank pages, many incorrect structures were seen.
	c	i	Alcohol **AND** Amide/peptide ✓	1	**IGNORE** phenol **IGNORE** hydroxyl/hydroxy **IGNORE** attempts to classify alcohol or amide as primary, secondary or tertiary **DO NOT ALLOW** hydroxide **Examiner's Comments** Generally well answered but incorrect functional groups included carbonyl and amine.

		ii	 	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** + on N or H i.e. $^{+}NH_3$ or NH_3 $^{+}$**ALLOW** $NH_3^{+}Cl^{-}$ **Examiner's Comments** Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH_2^{+}.
			Total	**10**	
6	a		**Product from NH_3/ethanol**  ……	3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW**  **ALLOW ECF** from 2-bromo compound as product from Reaction 1 …… ..
			Product from Reaction 1  ……		**DO NOT ALLOW** 2-bromo compound *(inconsistent with final product shown)* …… ..
			Product from NaOH(aq)		**DO NOT ALLOW ECF** from 2-bromo compound as product from Reaction 1 *(inconsistent with final product shown)*

					
	b				**ANNOTATE ANSWER WITH TICKS AND CROSSES**
			Curly arrow from C=C bond to H of H-Br		
					ALLOW any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Correct dipole shown on H–Br **AND** curly arrow showing the breaking of H-Br bond		
					**DO NOT ALLOW** partial charges shown on C=C double bond
			.....		**DO NOT ALLOW** δ+ on C of carbocation
			Correct carbocation **AND** curly arrow from Br^- to C^+ of carbocation		**ALLOW** formation of the 2-bromo isomer
					
			.....		Curly arrow must come from a lone pair on Br^- **OR** from the negative sign of Br^- ion (then lone pair on Br^- ion does not need to be shown)
			Electrophilic addition		
	c	i		1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** *n*

		ii	 Ester link Rest of structure	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown (do not have to be dotted)
			Total	**10**	
7		i	**step 1** = (conc.) H_2SO_4 **AND** CH_3CH_2OH	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous.
		ii	 **BOTH** organic structures balanced equation	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous.
			Total	**3**	