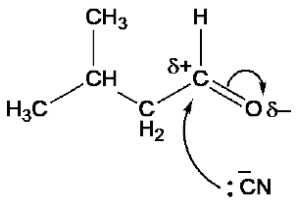
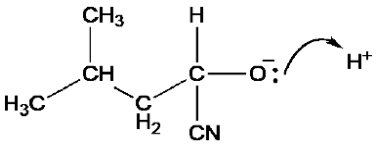
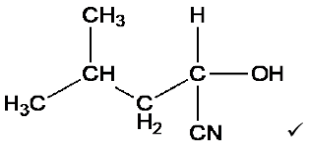
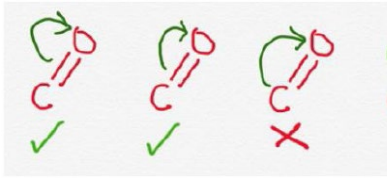
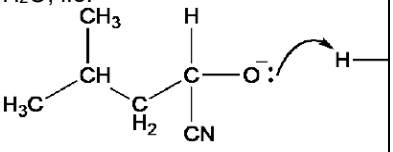
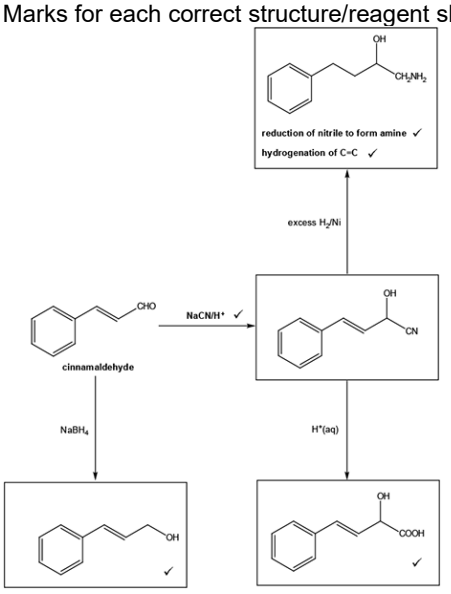
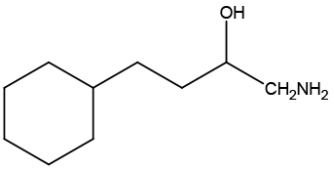
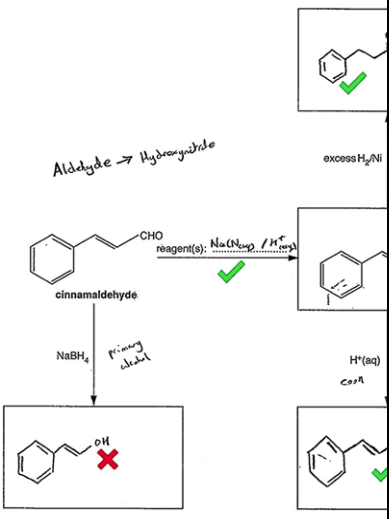
Mark scheme - Carbon-Carbon Bond Formation

Question			Answer/Indicative content	Marks	Guidance
1		i	**Mechanism** ***3 marks***  Curly arrow from ^{-}CN to C atom of C=O ✓ Dipole shown on C=O bond, $C^{\delta+}$ and $O^{\delta-}$, **AND** curly arrow from C=O bond to O atom ✓  Curly arrow from lone pair **OR** – charge on O^{-} of **correct** intermediate to H^{+} ✓ --- **Product** ***1 mark***  ✓ --- **Name of mechanism** ***1 mark*** Nucleophilic addition ✓	5 (AO1.2) (AO1.2) (AO2.5) (AO2.5) (AO2.5) (AO1.1)	**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) Curly arrow from C=O bond must start from, OR be traced back to, any part of C=O bond and go to O  --- **ALLOW** curly arrow to H atom of H_2O, i.e.  **IGNORE** attempt to draw curly arrow showing breaking of H–O in H_2O **IGNORE** lack of dipole on H_2O
		ii	**Heterolytic** One (bonded) atom/O receives both/2 electrons ✓ **Fission** Breaking of a **covalent** bond ✓	2 (AO1.2)	**ALLOW** 2 electrons go to one (bonded) atom/O **DO NOT ALLOW** both pairs of electrons go to O **IGNORE** formation of ions/radicals For O atom, **ALLOW** species **DO NOT ALLOW** element or molecule **ALLOW** π bond in C=O breaks

					IGNORE breaking of C=O bond (no reference to only one bond breaking) 'Bond breaking' is **not** sufficient *(no reference to covalent)* **Examiner's Comments** Candidates often referred to NaCN and HCN in their responses. Candidates who identified the correct bond breaking often then incorrectly wrote that the oxygen atom gained the lone pair of electrons.
			Total	**7**	
2			Marks for each correct structure/reagent shown below  	**5**	**ANNOTATE WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous For reaction with excess H_2/Ni **IGNORE** hydrogenation of benzene ring i.e. the following structure scores two marks  **ALLOW** KCN/H^+ **ALLOW** HCN **ALLOW** H_2SO_4 or HNO_3 or HCl for H^+ **Examiner's Comments** This question proved difficult and although the majority of candidates scored in some parts, only the very best responses secured all five marks. More detailed feedback is discussed with Exemplar 8.

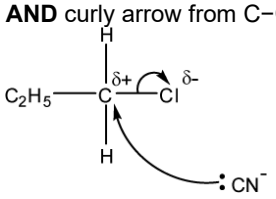
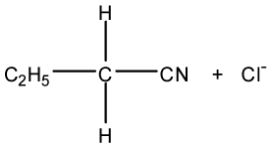
Exemplar 8

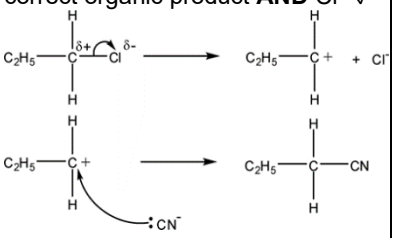
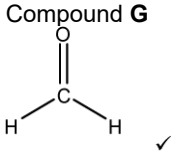
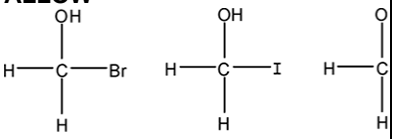


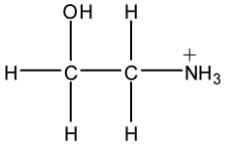
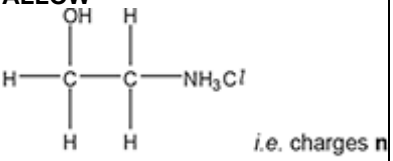
Cinnamaldehyde was the starting point for this flowchart of reactions.

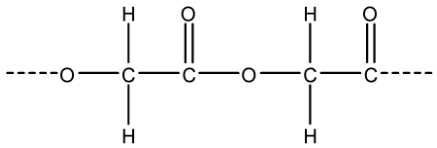
The most frequently scored mark was correct identification of the reagents required for the formation of the hydroxynitrile. This response uses NaCN/H^+. Other candidates used HCN which was also acceptable.

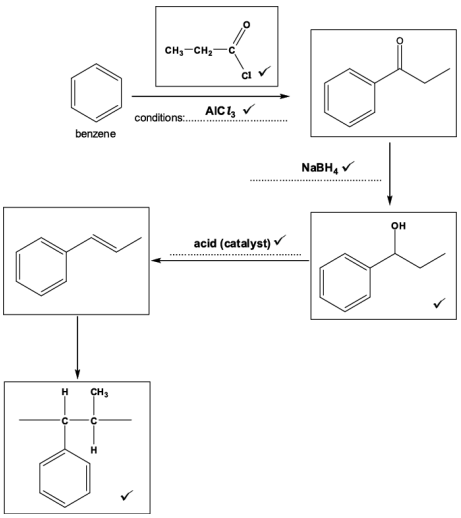
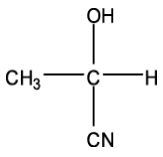
The flowchart shows two different reactions of this hydroxynitrile. The first is the reaction with excess hydrogen in the presence of Ni. Most candidates scored one mark for their product. As in this exemplar, the double bond was often reacted to form a saturated chain. Some candidates identified

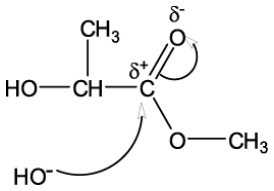
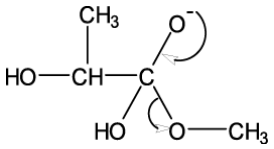
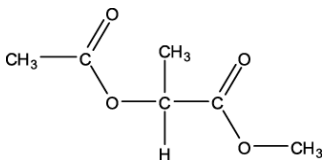
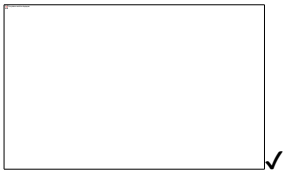
					that the CN group would also react but instead of writing CH_2NH_2 they replaced the CN group with just NH_2, effectivity removing a carbon atom from the chain. The second reaction of the hydroxynitrile is acid hydrolysis of the CN group. This response identifies the correct carboxylic acid. However, this reaction seemed unfamiliar to many candidates and a range of incorrect responses were frequently seen. The final reaction is the reduction of cinnamaldehyde with $NaBH_4$. Many candidates recognised this reaction, but as can be seen in this response the alcohol group is shown on the incorrect carbon atom. This was a common error. Candidates are advised to number carbon atoms present if provided with a complex structure, such as cinnamaldehyde. Numbering will ensure that each carbon is considered when drawing reaction products and would minimise errors, such as those demonstrated in the reduction product.
			Total	**5**	
3		i	curly arrow from ^-CN to carbon atom of C−C*l* bond ✓ Dipole shown on C–C*l* bond, $C^{\delta+}$ and $Cl^{\delta-}$, **AND** curly arrow from C−C*l* bond to C*l* atom ✓  correct organic product **AND** C*l*-✓  	**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–C*l* bond to C*l* atom ✓ Correct carbocation **AND** curly arrow from ^-CN to carbocation. Curly arrow

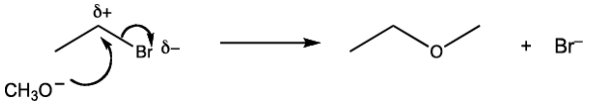
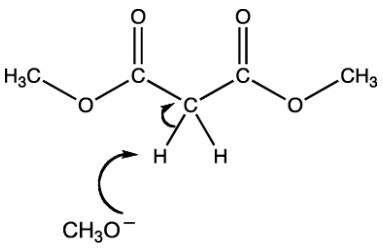
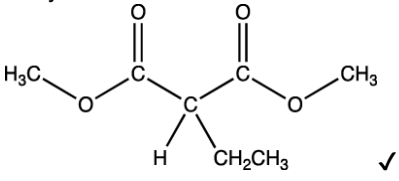
					must come from lone pair on C of $^{-}$CN **OR** CN^{-} **OR** from minus sign on C of $^{-}$CN ion (then lone pair on CN^{-} does not need to be shown) ✓ correct organic product **AND** Cl^{-} ✓  **Examiner Comments** The mechanism for the reaction of 1-chloropropane was well done with the majority 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 C*l*$^{-}$ 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. HC*l*(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

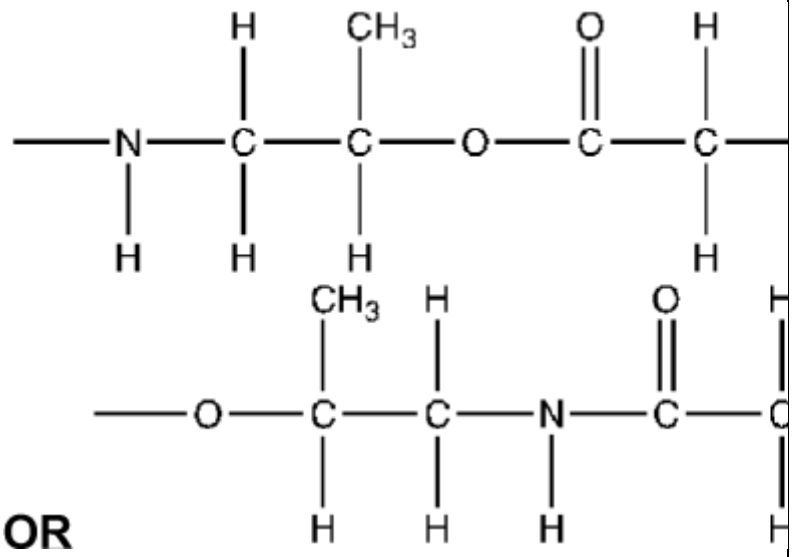
					e.g. HC*l* **AND** H_2O H_2SO_4 **AND** H_2O **Examiner Comments** Although many candidates were able to provide the structure of methanal as the starting material for this synthesis, the structures of chloromethanol, bromomethanol and iodomethanol were accepted as suitable alternatives. It should be noted that hydrolysis is carried out using aqueous acid and that dilute acid is not a suitable alternative.
		ii i	**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 n **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.
		i v	 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**	

4	a		One mark for each correct structure/reagent/condition as shown below  	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names of organic compounds *(question asks for structures)* **ALLOW** aluminium(III) chloride **OR** aluminium trichloride **ALLOW** $FeCl_3$ **OR** Fe as halogen carrier in first step. **ALLOW** sodium borohydride **OR** sodium tetrahydridoborate **IGNORE** [H] for reducing agent in second step **ALLOW** H^+ / H_2SO_4 / H_3PO_4 / named mineral acid for reagent in third step
	b		Use as an organic feedstock ✓ **OR** Combustion for energy production ✓	1	**ALLOW** the production of plastics or monomers or new polymers Combustion alone is **not** sufficient
			Total	**7**	
5	a	i	 	1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
		ii	**aqueous** acid **OR** H^+ / **H_2O**	1	**ALLOW** $H^+(aq)$ / $H_2SO_4(aq)$ / $HCl(aq)$

		ii i	Angle a = 109.5° Angle b = 104.5° Angle c = 120° **Two** correct All **three** correct	2	**ALLOW** 109–110° **ALLOW** 104–105°
	b	i	It is an electron pair donor **OR** donates a lone pair	1	
		ii	 Curly arrow from HO^- to carbon atom of C=O bond Correct dipole **AND** curly arrow from C=O bond to $O^{\delta-}$ ……  Curly arrow from negative charge on oxygen to C–O bond (to reform carbonyl π-bond) Curly arrow from C–O single bond to oxygen atom (to form methoxide ion)	4	Curly arrow must come from lone pair on O of HO^- **OR** OH^- **OR** from minus sign on HO^- ion (No need to show lone pair if curly arrow came from negative charge on O) **IGNORE** dipole on C–O single bond Curly arrow must come from lone pair on O **OR** from minus sign on O^- ion (No need to show lone pair if curly arrow came from negative charge on O)
		ii i	Correct organic product:  HC*l*	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Total	**11**	
6	a			1	

	b	i	$2Na + 2CH_3OH \rightarrow 2Na^+ + 2CH_3O^- + H_2$ ✓	1	**ALLOW** $2Na + 2CH_3OH \rightarrow 2CH_3ONa + H_2$
		ii	 Curly arrow from CH_3O^- to carbon atom of C-Br bond ✓ Dipole shown on C–Br bond, $C^{\delta+}$ and $Br^{\delta-}$ **AND** curly arrow from C–Br bond to the Br atom ✓ Products of reaction (must not be ambiguous) ✓	3	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous. The curly arrow must start from **O atom** of CH_3O^- **AND** must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. **ALLOW** S_N1 Dipole shown on C–Br bond, $C^{\delta+}$ and $Br^{\delta-}$, and curly arrow from C–Br bond to the Br atom. Correct carbocation drawn. **AND** curly arrow from CH_3O^- to carbocation. The curly arrow must start from the oxygen atom of the CH_3O^-, and must start either from a lone pair or from the negative charge.
		ii i	CH_3O^- donates an electron pair **AND** heterolytic fission ✓	1	**ASSUME** 'it' refers to CH_3O^-
	c		**Chemical shift, δ/ppm Relative peak area Splitting pattern** 0.5−1.9 3 Triplet ✓ 3.0−4.3 2 Quartet ✓ 0.5−1.9 6 Doublet ✓ 3.0−4.3 1 Heptet ✓	4	**ALLOW** δ values ± 0.2 ppm, as a range or a value within the range **ALLOW** multiplet for heptet
	d	i	 Curly arrow from CH_3O^- to H of CH_2 ✓ Curly arrow from C–H bond to C of CH_2 ✓  ✓	3	The curly arrow must start from **O atom** of CH_3O^- **AND** must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge.

					ALLOW any unambiguous structure, skeletal, displayed, structural or combination.
		ii	CH_3O^- accepted a proton ✓	1	**ASSUME** 'it' refers to CH_3O^-
			Total	**14**	
7		i	**Step 1**: add HCN **OR** H_2SO_4/KCN $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ **Step 2**: react with H_2/Ni $CH_3CH(OH)CN + 2H_2 \rightarrow CH_3CH(OH)CH_2NH_2$	4	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous first mark can be implicit from equation. third mark can be implicit from equation if Ni shown as catalyst (*e.g.* above the reaction arrow) **ALLOW** $CH_3CH(OH)CN + 4[H] \rightarrow CH_3CH(OH)CH_2NH_2$
		ii	because (compound **D**) forms hydrogen bonds form **with** water demonstrated through diagram showing: - dashed line between —OH and (:)OH_2 - dashed line between —NH_2 and (:)OH_2	3	dipole and lone pair are **not** required **IGNORE** bond angles Diagram does **not** need to show all of Compound **D** (and **IGNORE** if wrong)
		ii i	 **OR** ester **AND** amide link rest of structure	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous 'End bonds' **MUST** be shown (solid or dotted) **IGNORE** brackets and / or *n*
			Total	**9**	