Mark Scheme

Question	Key	Marks	Guidance
1	D	**1**	

Mark Scheme

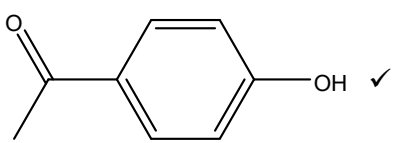
Question			Answer	Marks	Guidance
2	(a)*		*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Correctly labelled diagram of apparatus that works, with no safety problems **AND** Full appreciation of further two steps required to gain pure sample *There is a well-developed diagram which is clear and structured. The information on further purification is detailed and relevant.* **Level 2 (3–4 marks)** Labelled diagram of apparatus but with safety/procedural problems **OR** clear diagram of functional apparatus without labelling **AND** Some details of further purification steps *The diagram presents apparatus that is in the most-part relevant with some correct labelling, and supported by some details of further purification steps.* **Level 1 (1–2 marks)** Diagram of apparatus drawn with no labelling **OR** labelled diagram with significant safety/procedural problems **AND** Few or imprecise details about further purification stages *The diagram is basic and unstructured. Any mention of purification steps is limited to generic term, e.g. 'drying', without relevant detail.*	**6**	**Indicative scientific points may include:** **Diagram** <u>Includes following components:</u> distillation flask heat source thermometer at outlet (bulb **level** with outlet) still-head water condenser (**correct direction** of water flow) receiving vessel **open** system. **Further purification** Shake and leave to settle in a separating funnel Separate layers by tapping off Add (a small amount of) anhydrous magnesium sulfate/anhydrous calcium chloride to organic layer (in a dry conical flask) (Re)distil the organic layer Collect fraction distilling at (between 150 °C and) 156 °C.

Mark Scheme

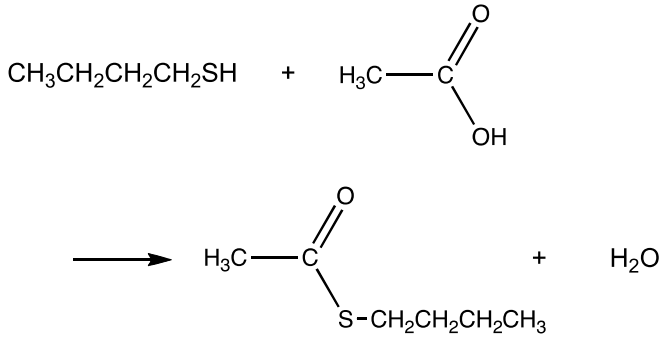
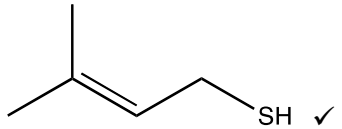
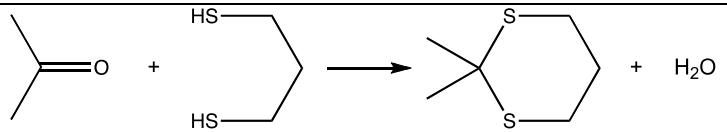
Question			Answer	Marks	Guidance
			0 marks No response or no response worthy of credit.		
	(b)		Lack of (further) effervescence ✓	**1**	**ALLOW** fizzing/bubbling stops
	(c)		Take samples from reaction mixture at regular intervals ✓ Spot/run on a TLC plate, alongside cyclohexanol (and cyclohexanone) controls ✓	**2**	**ALLOW** "frequent" for "regular" **ALLOW** measure/compare R_f value to cyclohexanol **IGNORE** reference to solvent or visualising chemicals/UV
	(d)		React (sample of distillate) with 2,4-dinitrophenylhydrazine ✓ recrystallise **AND** determine the melting point ✓ Compare melting point to known/library value for cyclohexanone (derivative) ✓	**3**	**ALLOW** (2,4-)DNPH/Brady's reagent
			Total	**12**	

Question			Answer	Marks	Guidance
3	(a)		**Empirical formula** Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓ Empirical formula = C_4H_4O ✓ **Molecular formula** Molecular formula = $C_8H_8O_2$ **AND** Evidence of 136 in working or from labelled peak in spectrum ✓	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$ **ALLOW** 4:4:1 if linked to C:H:O Alternative method for 3 marks: C: $\frac{136 \times 70.58/100}{12.0} = 8$ H: $\frac{136 \times 5.92/100}{1.0} = 8$ O: $\frac{136 \times 23.50/100}{16.0} = 2$
	(b)		**Functional groups** Phenol **AND** ketone ✓ **Explanation**	3	**DO NOT ALLOW** any other functional groups for first marking point.

Mark Scheme

Question			Answer	Marks	Guidance
			Links phenol to (weak) acidity **AND** no reaction with Na_2CO_3 (so not carboxylic acid) ✓ Links 2,4-DNP(H) or Brady's reagent observation to carbonyl **AND** Tollens' reagent observation (so not an aldehyde) ✓		**ALLOW** identity of functional groups in the explanation if not stated on functional group prompt line. **ALLOW** "aldehyde or ketone" in place of carbonyl
	(c)		**Carbon NMR analysis** Peaks between 110–160 ppm are the (four) aromatic (carbon environments) ✓ Compound contains a C=O between 190 - 200 ppm **AND** Compound contains a C-C at 20-30 ppm ✓ **Structure**  ✓	**3**	**ALLOW** peaks to be identified by: • Peaks labelled on spectrum • Peaks indicated on a chemical structure • Peaks indicated from within text **Note:** If identifying aromatic peaks from the spectrum all four peaks should be indicated. **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Total	**9**	

Mark Scheme

Question			Answer	Marks		Guidance
			For 5a(i)–(iv) IGNORE poor connectivity to SH groups	*Given in question*		
4	**(a)**	**(i)**	$K_a = \frac{[H^+]\,[C_4H_9S^-]}{[C_4H_9SH]}$ ✓ *Square brackets required*	**1**		**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous
	(a)	**(ii)**	 Structure of thioester ✓ Complete equation ✓	**2**		**ALLOW** correct skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous **ALLOW** C_4H_9SH **ALLOW** CH_3COOH Thioester functional group **must** be fully displayed, **OR** as a skeletal formula but allow SC_4H_9 in thioester
	(a)	**(iii)**	 ✓	**1**		**IF** correct **skeletal** formula is shown, **IGNORE** displayed formula in a second structure
	(a)	**(iv)**	 Reactants ✓ Products **AND** balanced equation ✓	**2**		**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous

Mark Scheme

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th></th><th>Guidance</th></tr>
<tr><td></td><td>(b)*</td><td></td><td>Refer to the marking instructions on page 5 of the mark scheme for guidance on marking this question.

Level 3 (5–6 marks)
Develops a plan that identifies all compounds by a process of elimination
AND
includes essential detail for all required tests and observations

There is a well-developed line of reasoning which is clear and logically structured

Level 2 (3–4 marks)
Develops a plan that identifies at least half of the compounds OR identifies the functional groups in most of the compounds
AND
includes detail of the required tests and observations

There is a line of reasoning with some structure. The information is mostly relevant and supported by some evidence.

Level 1 (1–2 marks)
Develops a plan that attempts to identify the compounds OR functional groups
AND
includes detail of the required tests and observations
There is a line of reasoning using information that is mostly relevant.

0 marks – No response or no response worthy of credit with no compounds identified</td><td>6</td><td></td><td>Indicative scientific points may include:

<u>Functional groups</u>
• B alkene and tertiary alcohol
• C alkene and aldehyde
• D alkene and primary alcohol
• E ketone
• F secondary alcohol
• G alkene and ketone

<u>Tests</u>
• B, C, D and G → Bromine decolourises
• C, D and F → (H^+/)$Cr_2O_7^{2-}$ green
• C, E and G → 2,4-DNP orange precipitate
• C → Tollens silver mirror

For Tollens’ ALLOW alternative: Fehling’s solution produces a ‘brown/brick red/orange precipitate

For 2,4-DNP, ALLOW 2,4-DNPH and Brady’s

<table>
<tr><th></th><th>B</th><th>C</th><th>D</th><th>E</th><th>F</th><th>G</th></tr>
<tr><td>Bromine</td><td>✓</td><td>✓</td><td>✓</td><td></td><td></td><td>✓</td></tr>
<tr><td>(H^+/)$Cr_2O_7^{2-}$</td><td></td><td>✓</td><td>✓</td><td></td><td>✓</td><td></td></tr>
<tr><td>2,4-DNP</td><td></td><td>✓</td><td></td><td>✓</td><td></td><td>✓</td></tr>
<tr><td>Tollens’</td><td></td><td>✓</td><td></td><td></td><td></td><td></td></tr>
</table>

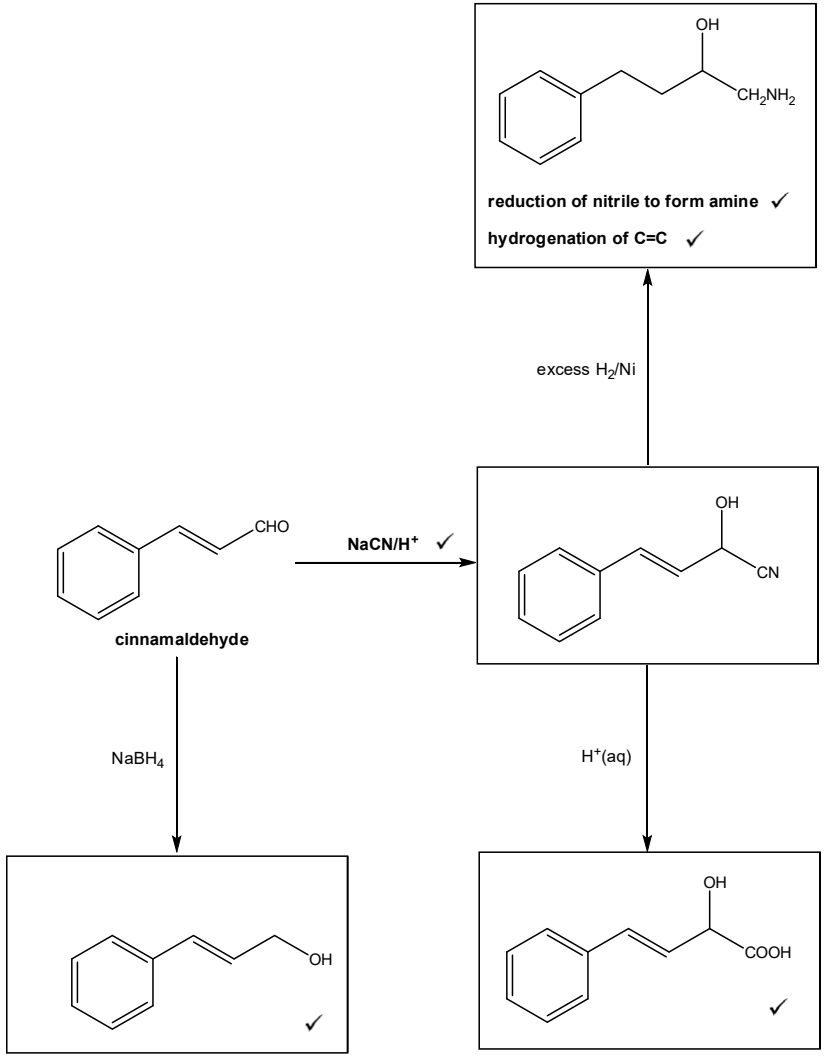
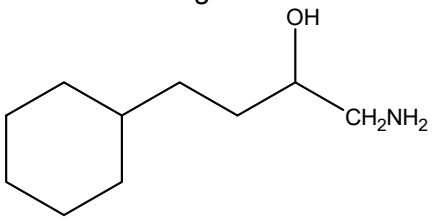
No credit for tests on products of tests, melting points, spectra, etc.
For other tests seen, contact TL for advice</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>12</td><td></td><td></td></tr>
</table>

Mark Scheme

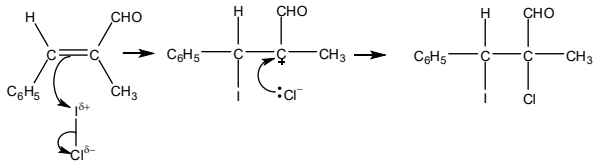
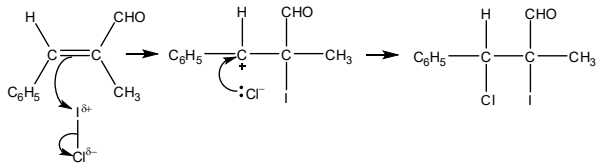
Question			Answer	Marks	Guidance
5	(a)		priority groups/atoms are on different/opposite sides ✓ High(est) priority groups are C_6H_5 **AND** CHO **OR** Lowest priority groups are H and CH_3 ✓	2	**ALLOW** suitable alternatives to 'priority' e.g. groups with highest atomic number or more important groups etc. **ALLOW** high priority groups are diagonal(ly across) **IGNORE** references to relative mass of groups, A_r, M_r, **ALLOW** identification by name e.g aldehyde for CHO phenyl/benzene group for C_6H_5 alkyl for CH_3 **ALLOW** response in terms that O has higher priority than H in context of $–CH_3$ and –CHO **IF** 'priority' is not mentioned **ALLOW** 1 mark for 'C_6H_5 and CHO are on different sides' **OR** H and CH_3 are on different sides
	(b)	(i)	Bromine/ Br_2 **AND** goes colourless/decolourised ✓	1	**Note:** both reagent and observation are required **ALLOW** bromine water/ Br_2(aq)
		(ii)	Tollens' (reagent) **AND** Silver (mirror/precipitate/ppt/solid) ✓	1	**Note:** both reagent and observation are required for the mark. **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt

Question			Answer	Marks	Guidance
		(iii)	(Add) 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate✓ Take melting point (of crystals) ✓ Compare to known values/database ✓	3	**ALLOW** errors in spelling **ALLOW** 2,4(-)DNP **OR** 2,4(-)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate **Mark second and third points independently of response for first marking point** **DO NOT ALLOW** 2nd and 3rd marks for taking and comparing boiling points **OR** chromatograms

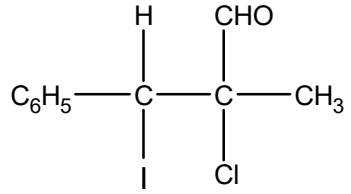
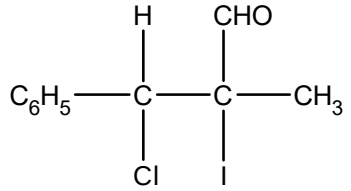
Mark Scheme

Question	Answer	Marks	Guidance
(c)	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 HC*l* for H^+

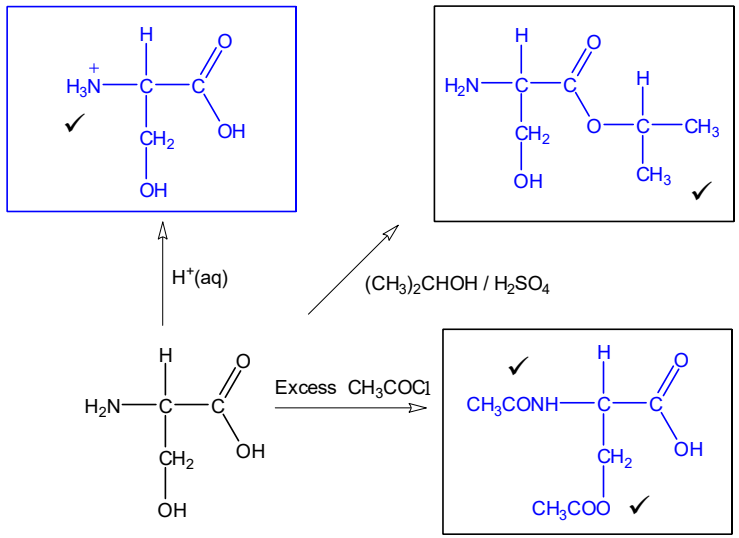
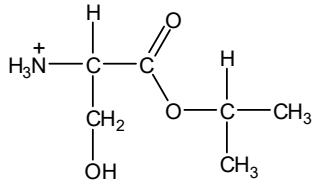
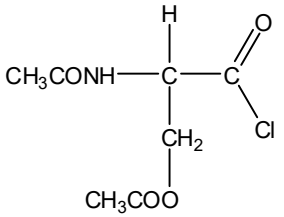
Mark Scheme

Question	Answer	Marks	Guidance
(d)*	*Please refer to marking instructions on page 5 of mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** An outline of the mechanism for the formation of either product which is mostly correct. **AND** Major and minor products identified with a correct explanation of which product is most/least likely to be formed. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** An outline of the mechanism for the formation of either product but with a few omissions/errors. **AND** Identifies major/minor product correctly **OR** Explanation of which product is most/least likely to be formed. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** A basic outline of the mechanism for the formation of either product is attempted. **OR** Basic explanation of which of the products is most/least likely to be formed. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.*	6	**Please check all of page 23 which is included with this response. If this page is blank please annotate with SEEN** Throughout: **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above if unambiguous **Indicative scientific points:** **<u>Mechanism for formation of either product.</u>** • Curly arrow from C=C to attack the I atom of the I-Cl • Correct dipole on I-Cl • Curly arrow from I-Cl bond to Cl • Carbocation with full positive charge on carbon atom • Curly arrow from negative charge on Cl^- or lone pair on Cl^- to carbon atom with positive charge  **OR** 

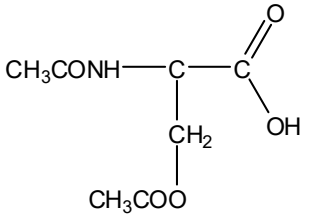
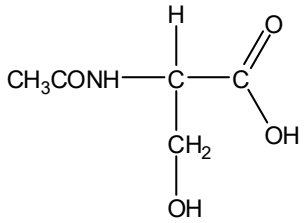
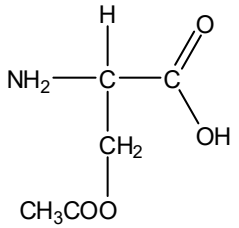
Mark Scheme

Question			Answer	Marks	Guidance
			0 marks *No response or no response worthy of credit.*		**Organic products** • Major/most likely product  • Minor/least likely product  • Major/most likely product is formed from the most stable carbocation intermediate **OR** – C*l* is attached to carbon atom with the least hydrogens attached **OR** the carbon with the most –C atoms attached **OR** the – I is attached to the carbon atom with most hydrogens attached
			Total	**18**	

Mark Scheme

Question			Answer	Marks	AO element	Guidance
6	(a)	(i)		4	AO2.5 ×4	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** protonation of NH_2 group in reaction with $(CH_3)_2CHOH$ i.e.  **ALL** structures must be based on serine For reaction with excess CH_3COCl, **IGNORE** reaction of COOH to form an acid anhydride --- **ALLOW** 1 mark for  *(both NH and OH groups reacted but acyl chloride instead of COOH)* **OR**

Mark Scheme

Question			Answer	Marks	AO element	Guidance
						 *(both NH and OH groups reacted but H missing from α C atom)* **OR**  *(NH group reacted correctly but rest of serine unchanged)* **OR**  *(OH group reacted correctly but rest of serine unchanged)*
		(ii)	**IF M_r(amino acid) = 131 from titration analysis AWARD**	**4**		

Mark Scheme

Question			Answer	Marks	AO element	Guidance
			first 3 marks **ALLOW 3SF** or more throughout **IGNORE** trailing zeroes, e.g. **ALLOW** 0.044 for 0.0440 --- n(HCl) $= 0.150 \times \frac{25.0}{1000}$ **OR** 3.75×10^{-3} (mol) ✓ n(**amino acid**) in 250 cm^3 $= 3.75 \times 10^{-3} \times \frac{250.0}{21.30}$ **OR** 0.0440 (mol) ✓ M(**amino acid**) $= \frac{5.766}{0.0440} = 131$ (g mol^{-1}) ✓ Amino acid = $(CH_3)_2CHCH_2CH(NH_2)COOH$/leucine **AND** working to show R = 57 to justify choice **OR** evidence to show M_r leucine = 131 to justify choice ✓		AO2.8 AO2.8 AO2.8 AO3.2	**ALLOW** alternative approaches **Calculator:** 0.04401408451 **ALLOW ECF** from incorrect n(HCl) **ALLOW ECF** from incorrect n(**amino acid**) **ALLOW ECF** from incorrect M(**amino acid)** **i.e. ECF** for alkyl group closest to calculated M(alkyl group), e.g. for M(alkyl group) = 15, **ALLOW** $CH_3CH(NH_2)COOH$ **Note:** evidence may be shown with table
	(b)	**(i)**	R_f value in range 0.33 – 0.35 ✓	**1**	AO1.1	**ALLOW** 2 SF or more. But ignore digits after second sig fig **ALLOW** $0.\dot{3}$ for 0.33…..
		(ii)	gly(cine) ✓ Amino acid matches (leu(cine) and) glycine in Solvent **W** **AND** Amino acid matches (ala(nine) and) glycine in Solvent **X** ✓	**2**	AO2.3 ×2	 **ALLOW** glycine has the same/similar R_f as the unknown in both solvents/chromatograms **ALLOW** suitable alternatives for R_f e.g. moves same distance
			Total	**11**		

Mark Scheme

Question	Answer	Marks	AO element	Guidance
7	A	1	1.1	