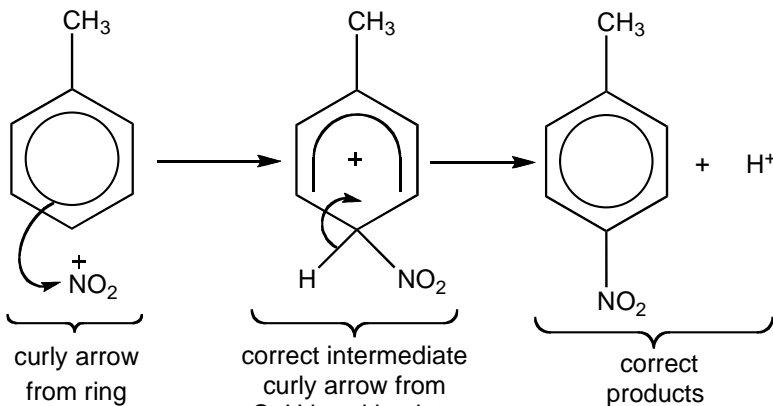
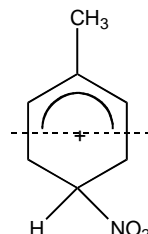
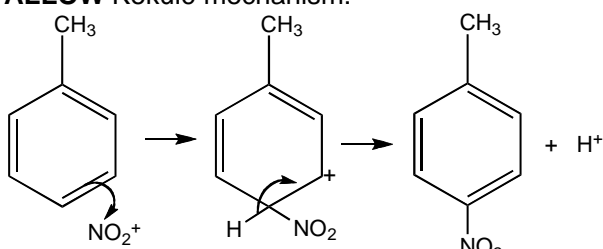
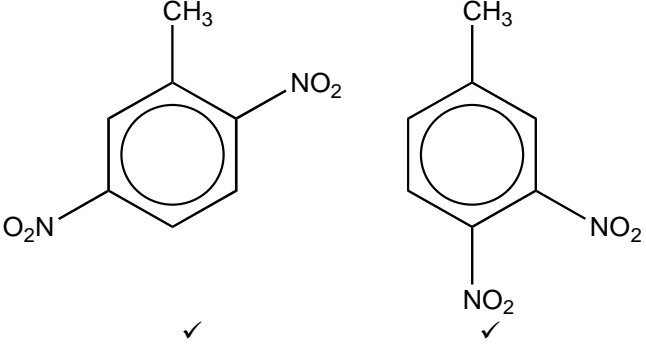
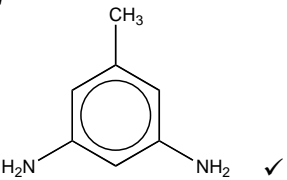
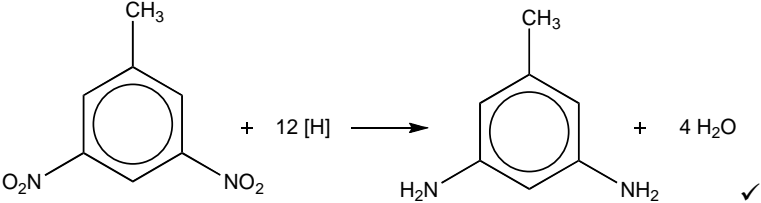
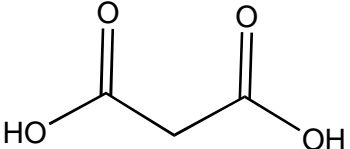
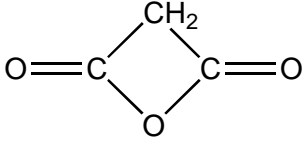
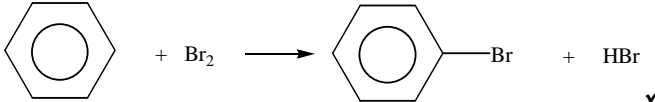
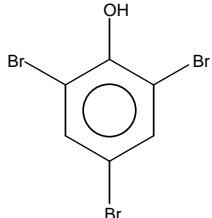


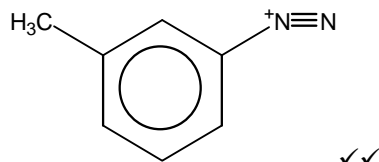
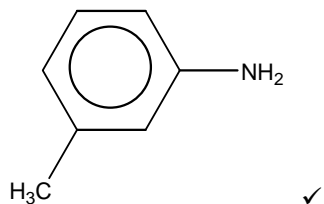
Question	Answer	Mark	Guidance
1 (a)	 <p>curly arrow from ring to NO_2^+ ✓</p> <p>correct intermediate curly arrow from C-H bond back to reform ring ✓ ✓</p> <p>correct products ✓</p> <p>1 mark for intermediate</p> <p>1 mark for curly arrow</p>	4	<p>ANNOTATIONS MUST BE USED</p> <p>ALLOW skeletal CH_3</p> <p>ALLOW $^+\text{NO}_2$ OR NO_2^+</p> <p>ALLOW 1st curly arrow from the ring OR from within the ring to any part of the NO_2^+ including the + charge</p> <p>DO NOT ALLOW intermediate with broken ring less than halfway down:</p>  <p>Horseshoe must have open end towards NO_2</p> <p>ALLOW Kekulé mechanism:</p>  <p>ALLOW double bonds shown in other Kekulé arrangement</p> <p>IF CH_3 has been omitted completely (<i>ie</i> benzene shown), DO NOT AWARD intermediate mark OR products mark (max 2)</p> <p>IF NO_2 is shown in incorrect position in intermediate or product, DO NOT AWARD intermediate mark but award other marks (max 3)</p>

Question	er	Mark	Guidance
1 (b)		2	<p>ALLOW any correct unambiguous structures</p> <p>ALLOW NO₂⁻</p> <p>Note: connectivity is NOT being assessed in this part</p>
1 (c)	<p>1st stage isomer: isomer 3 ✓ product.</p>  <p>reagents: Sn AND (conc) HCl ✓</p> <p>equation:</p> 		<p>ANNOTATIONS MUST BE USED</p> <p>ALLOW structure of isomer 3 shown separately OR in equation</p> <p>ALLOW structure of product shown separately OR in equation ALLOW correct name (3,5-diaminomethylbenzene) IGNORE incorrect name DO NOT ALLOW CH₃C₆H₃(NH₂)₂</p> <p>ALLOW Zn + HCl/H₂ + metal catalyst/LiAlH₄/Na in ethanol IGNORE NaBH₄ ALLOW Sn and HCl followed by NaOH DO NOT ALLOW Sn and HCl and NaOH</p> <p>IF isomer 3 OR product are given in equation but not shown previously then credit here</p> <p>Also credit reagents here if shown (eg above arrow)</p> <p>ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous</p>

Question	Answer	Mark	Guidance
(c) (i)	<p>2nd stage <i>organic compound:</i> HOOC-CH₂-COOH ✓</p> <p><i>type of polymer:</i> polyamide ✓</p>	6	<div style="text-align: center;">  </div> <p>DO NOT ALLOW molecular formula</p> <p>ALLOW name of compound: propanedioic acid OR propane-1,3-dioic acid ALLOW absence of 'e' after 'propan'</p> <p>ALLOW acyl dichloride: ClOC-CH₂-COCl ALLOW cyclic acid anhydride of propanedioic acid:</p> <div style="text-align: center;">  </div> <p>ALLOW Nylon or Kevlar DO NOT ALLOW polypeptide DO NOT ALLOW amide</p>
	Total	12	

Question	Expected Answers	Marks	Additional Guidance
2 (a)		1	<p>ALLOW $C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$</p> <p>DO NOT ALLOW multiple substitution DO NOT ALLOW Br^+</p>
(b) (i)	<p>White precipitate OR white solid OR white crystals ✓</p> 	2	<p>DO NOT ALLOW colourless DO NOT ALLOW white ppt <u>and</u> bubbles</p> <p>DO NOT ALLOW $Br_3C_6H_2OH$ OR 2,4,6-tribromophenol OR tribromophenol</p>
(ii)	1,2-Dibromocyclohexane ✓	1	<p>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</p>
(ii)	<p>MUST spell <u>delocalised/delocalized</u> or <u>localised/localized</u> correctly once in the answer to obtain all 5 marks</p> <p>benzene <u>electrons</u> or <u>π-bonds</u> are delocalised ✓</p> <p>phenol a <u>lone</u> or <u>non-bonded</u> pair of electrons on the oxygen or the OH group is (partially) delocalised into the ring ✓</p> <p>cyclohexene electrons are localised OR delocalised between two carbons ✓</p> <p>benzene has a lower electron density OR phenol has a higher electron density OR cyclohexene has a higher electron density ✓</p> <p>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 ✓</p>	5	<p>ALLOW diagram to show overlap of all 6 p-orbitals for delocalisation DO NOT ALLOW benzene has delocalised structure or ring</p> <p>ALLOW diagram to show movement of lone pair into ring for phenol</p> <p>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</p> <p>DO NOT ALLOW charge density OR electronegativity instead of electron density ALLOW $Br^{\delta+}$ OR electrophile Br^+ as alternate to polarise</p>

(c)



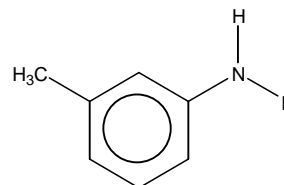
ALLOW ECF ✓✓ on incorrect amine

$\text{HNO}_2 + \text{HCl}$ and temp $< 10^\circ\text{C}$ OR $\text{NaNO}_2 + \text{HCl}$ and temp $< 10^\circ\text{C}$ ✓

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

Total 14

ALLOW



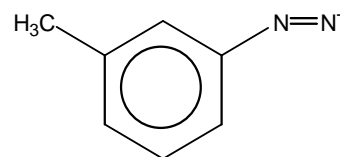
5

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

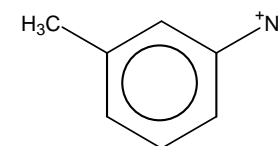
ALLOW one mark for correct displayed diazonium if alkyl group is not shown

ALLOW



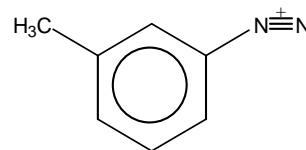
for both marks

ALLOW



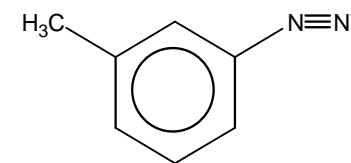
for one mark

ALLOW



for one mark



ALLOW

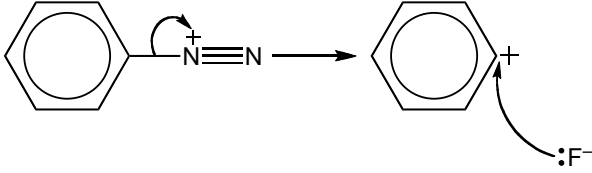


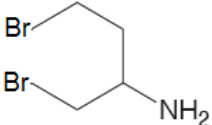
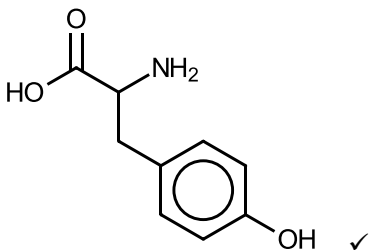
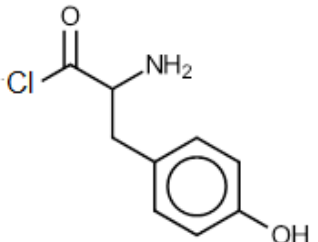
for one mark

ALLOW NaOH OR KOH & $\text{C}_6\text{H}_5\text{OH}$ OR phenoxide ion OR $\text{C}_6\text{H}_5\text{O}^-$

ALLOW reagents and conditions from the equations

Question			Answer	Mark	Guidance
3	(a)	(i)	<p>M1 p-orbitals overlap (to form pi/π-bonds) ✓</p> <p>M2 π-bond(s) are <u>delocalised</u> in structure B ✓</p> <p>M3 π-bonds are localised/between two carbons in structure A ✓</p> <p>M4</p> <div style="text-align: center;">  <p>AND</p> </div> <p>Diagrams show correct position of delocalised and localised π-bonds/π-electrons OR correct position of p-orbital overlap ✓</p> <p> QWC requires delocalised/delocalized spelled correctly and used in correct context</p>	4	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>IGNORE p-orbitals overlap to form sigma bonds</p> <p>ALLOW electrons are delocalised in structure B IGNORE B has delocalised structure or ring (must be electrons or π-bonds)</p> <p>ALLOW π-electrons/p-orbital overlap localised/between two carbons in structure A ALLOW p-orbitals overlap with one other carbon IGNORE electrons are localised OR structure A has localised structure (must be π-bonds/π-electrons/p-orbital overlap) ALLOW labelled diagram showing overlap of p-orbitals between two carbon atoms DO NOT ALLOW C=C in this diagram</p> <p>Diagram for structure A must show the full ring for M4 IGNORE C=C in M4 diagram</p> <p>IGNORE charge density DO NOT ALLOW electronegativity</p> <p>Structures do not need to be labelled A and B if the description matches the structure</p>

Question	Answer	Mark	Guidance
(ii)	<p>structure B/delocalised structure is (more) stable ✓</p> <p>structure B is a better because (enthalpy change of hydrogenation for benzene is) less (exothermic) than (-) 357 (kJ mol⁻¹) ✓</p>	2	<p>ALLOW structure B is low in energy</p> <p>IGNORE structure B is less reactive</p> <p>ALLOW enthalpy change/hydrogenation for benzene is less (negative) than 3 × (-)119</p> <p>IGNORE more positive than (-)357 kJ mol⁻¹</p> <p>ALLOW enthalpy change is less than 3x enthalpy change for cyclohexene</p> <p>ALLOW structure B is more stable by 149 kJ mol⁻¹ (2 marks)</p> <p>DO NOT ALLOW more/less energy needed for the reaction</p> <p>Answer must refer to data given in the question and must be a comparison</p> <p>IGNORE 360 kJ mol⁻¹</p> <p>No marks can be awarded if structure A is selected</p>
(b)	 <p>curly arrow from C–N bond to N⁺ ✓</p> <p>curly arrow from lone pair on fluoride ion to positive charge on benzene ring ✓</p>	2	<p>First curly arrow must come from bond not from C atom</p> <p>ALLOW first curly arrow to nitrogen atom OR to positive charge on nitrogen atom</p> <p>ALLOW second curly arrow from negative charge on fluoride ion</p> <p>ALLOW second curly arrow to carbon atom with positive charge</p>

Question		Answer	Mark	Guidance
	(c)	$(\text{CH}_3)_2\text{CHBr} + \text{FeBr}_3 \longrightarrow (\text{CH}_3)_2\text{CH}^+ + \text{FeBr}_4^-$	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW positive charge anywhere on the electrophile IGNORE AlCl_3 OR AlBr_3
	(d) (i)	First reactant = HNO_2 ✓ Second reactant =  ✓ Third reactant =  ✓	3	ALLOW $\text{NaNO}_2 + \text{HCl}$ OR $\text{HNO}_2 + \text{HCl}$ IGNORE conditions/concentration ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW 

Question		Answer	Mark	Guidance
	(ii)	<p>FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 1.35 (g) award 3 marks IF answer = 0.54 (g) award 2 marks (no scale-up) IF answer = 0.216 (g) award 2 marks (incorrect scale-up)</p> <p>$n(\text{compound D}) = 1.73/346 = 0.00500 \text{ mol}$ ✓ $n(1,3\text{-diaminobenzene}) \text{ required} = 100/40 \times 0.005$ $= 0.0125 \text{ mol}$ ✓ Molar mass of 1,3-diaminobenzene = $108 \text{ (g mol}^{-1}\text{)}$ AND Mass of 1,3-diaminobenzene = $(108)(0.0125) = 1.35 \text{ g}$ ✓</p>	3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC If there is an alternative answer, check to see if there is any ECF credit possible</p> <p>ALLOW ECF from incorrect amount, scale-up or molar mass</p> <p>Alternative 1 $n(\text{compound D}) = 1.73/346 = 0.00500 \text{ mol}$ Molar mass of 1,3-diaminobenzene = $108 \text{ (g mol}^{-1}\text{)}$ AND Mass of 1,3-diaminobenzene = $(0.00500)(108) = 0.540 \text{ g}$ Mass of 1,3-diaminobenzene required = $(0.540)(100/40) = 1.35 \text{ g}$</p> <p>Alternative 2 346 g gives 108 g 1.73 g gives $108/364 \times 1.73 = 0.54 \text{ g}$ $0.54/40 \times 100 = 1.35 \text{ g}$</p>
	(iii)	<p>(compound D has) two chiral centres ✓</p> <p>Four optical isomers exist ✓</p> <p>(Synthesis could) use enzymes OR bacteria OR use (chemical) chiral synthesis OR <u>chiral</u> catalysts OR use natural chiral molecules OR single isomers (as starting materials)</p> <p>✓</p>	3	<p>ALLOW (Compound D) has two asymmetric carbons OR has two stereocentres</p> <p>ALLOW four enantiomers OR two pairs of enantiomers</p> <p>INDEPENDENT MARK ALLOW biological catalysts ALLOW <u>chiral</u> transition metal complex/catalyst OR <u>stereoselective</u> transition metal complex/catalyst ALLOW '<u>chiral</u> pool'/chiral auxiliary</p>
Total			18	