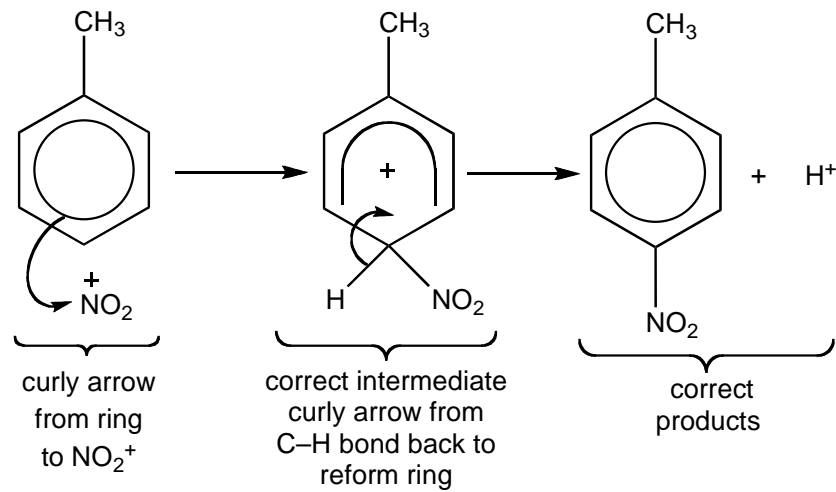
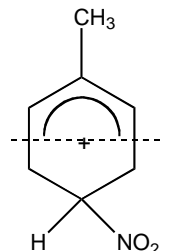
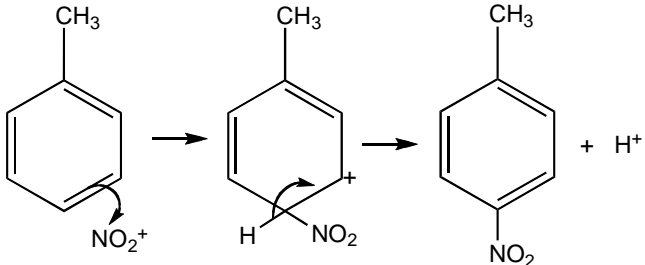
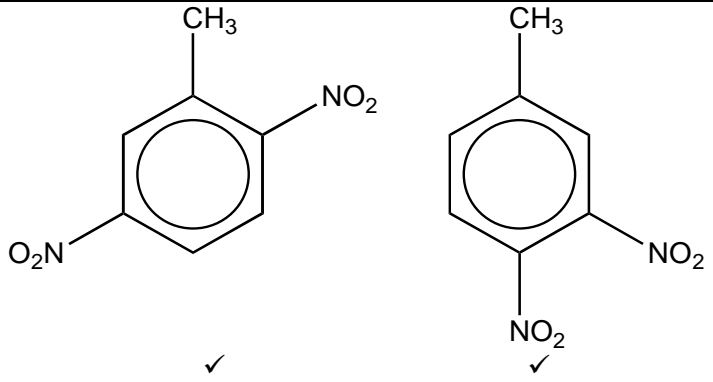
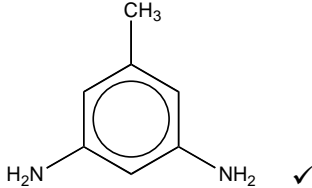
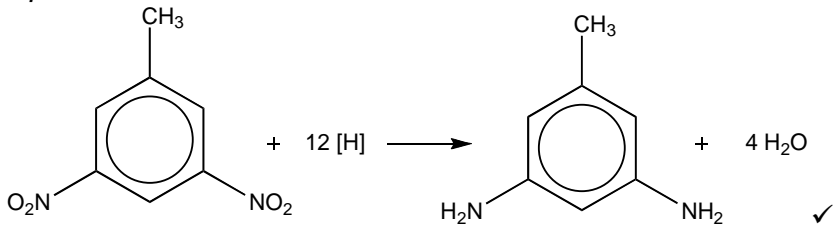
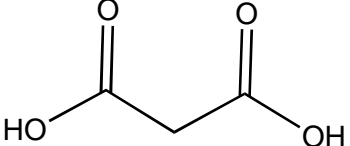
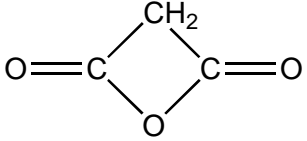
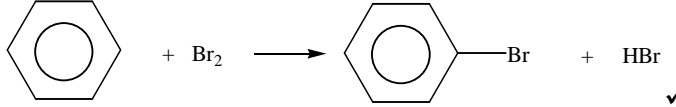
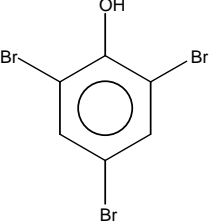


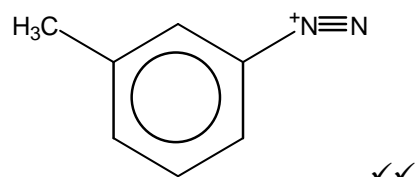
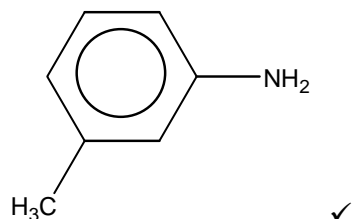
Question	Answer	Mark	Guidance
1 (a)	 <p>curly arrow from ring to <math>\text{NO}_2^+</math> ✓</p> <p>correct intermediate curly arrow from C-H bond back to reform ring ✓ ✓</p> <p>correct products ✓</p> <p>1 mark for intermediate</p> <p>1 mark for curly arrow</p>		<p><b>ANNOTATIONS MUST BE USED</b></p> <p><b>ALLOW</b> skeletal <math>\text{CH}_3</math></p> <p><b>ALLOW</b> <math>^+\text{NO}_2</math> OR <math>\text{NO}_2^+</math></p> <p><b>ALLOW</b> 1st curly arrow from the ring OR from within the ring to any part of the <math>\text{NO}_2^+</math> including the + charge</p> <p><b>DO NOT ALLOW</b> intermediate with broken ring less than halfway down:</p>  <p>Horseshoe must have open end towards <math>\text{NO}_2</math></p> <p>4</p> <p><b>ALLOW</b> Kekulé mechanism:</p>  <p><b>ALLOW</b> double bonds shown in other Kekulé arrangement</p> <p><b>IF</b> <math>\text{CH}_3</math> has been omitted completely (<i>ie</i> benzene shown), <b>DO NOT AWARD</b> intermediate mark <b>OR</b> products mark (<b>max 2</b>)</p> <p><b>IF</b> <math>\text{NO}_2</math> is shown in incorrect position in intermediate or product, <b>DO NOT AWARD</b> intermediate mark but award other marks (<b>max 3</b>)</p>

Question	er	Mark	Guidance
1 (b)		2	<p><b>ALLOW</b> any correct unambiguous structures</p> <p><b>ALLOW</b> NO<sub>2</sub><sup>-</sup></p> <p><b>Note:</b> connectivity is <b>NOT</b> being assessed in this part</p>
1 (c)	<p><b>1st stage</b> isomer: <b>isomer 3</b> ✓ product:</p>  <p>reagents: Sn <b>AND</b> (conc) HCl ✓</p> <p>equation:</p> 		<p><b>ANNOTATIONS MUST BE USED</b></p> <p><b>ALLOW</b> structure of <b>isomer 3</b> shown separately <b>OR</b> in equation</p> <p><b>ALLOW</b> structure of <b>product</b> shown separately <b>OR</b> in equation <b>ALLOW</b> correct name (3,5-diaminomethylbenzene) <b>IGNORE</b> incorrect name <b>DO NOT ALLOW</b> CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub></p> <p><b>ALLOW</b> Zn + HCl/H<sub>2</sub> + metal catalyst/LiAlH<sub>4</sub>/Na in ethanol <b>IGNORE</b> NaBH<sub>4</sub> <b>ALLOW</b> Sn and HCl followed by NaOH <b>DO NOT ALLOW</b> Sn and HCl and NaOH</p> <p><b>IF</b> isomer <b>3</b> <b>OR</b> 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><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula <b>ALLOW</b> combination of formulae as long as unambiguous</p>

Question	Answer	Mark	Guidance
(c) (i)	<p><b>2nd stage</b>  <i>organic compound:</i> <math>\text{HOOC-CH}_2\text{-COOH}</math> ✓</p>           <p><i>type of polymer:</i> polyamide ✓</p>	6	<div style="text-align: center;">  </div> <p><b>DO NOT ALLOW</b> molecular formula</p> <p><b>ALLOW</b> name of compound:  propanedioic acid <b>OR</b> propane-1,3-dioic acid  <b>ALLOW</b> absence of 'e' after 'propan'</p> <p><b>ALLOW</b> acyl dichloride: <math>\text{ClOC-CH}_2\text{-COCl}</math>  <b>ALLOW</b> cyclic acid anhydride of propanedioic acid:</p> <div style="text-align: center;">  </div> <p><b>ALLOW</b> Nylon or Kevlar  <b>DO NOT ALLOW</b> polypeptide  <b>DO NOT ALLOW</b> amide</p>
<b>Total</b>		12	

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

(c)

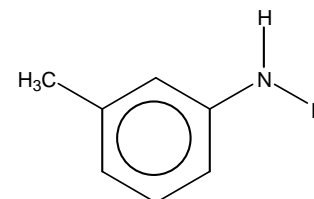


ALLOW ECF ✓✓ on incorrect amine

$\text{HNO}_2 + \text{HCl}$  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  $10^\circ\text{C}$ ) ✓

ALLOW



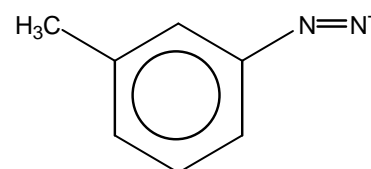
5

IGNORE  $\text{Cl}^-$  ion

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

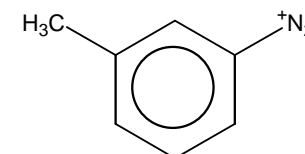
ALLOW one mark for correct displayed diazonium if alkyl group is not shown

ALLOW



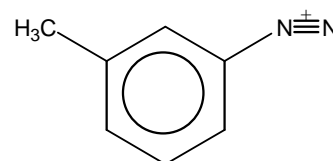
for both marks

ALLOW



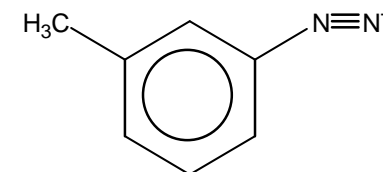
for one mark

ALLOW



for one mark

ALLOW





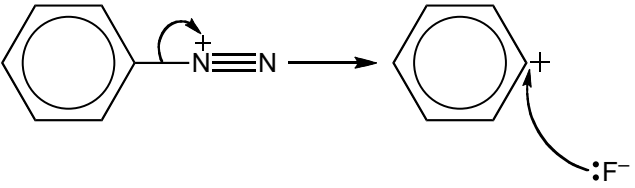
for one mark

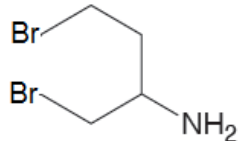
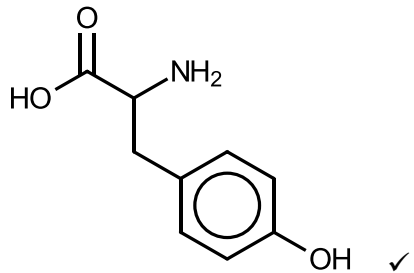
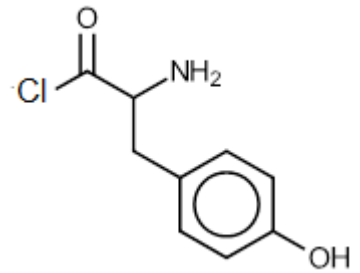
ALLOW NaOH OR KOH &  $\text{C}_6\text{H}_5\text{OH}$  OR phenoxide ion OR  $\text{C}_6\text{H}_5\text{O}^-$   
ALLOW reagents and conditions from the equations

Total

14

Question			Answer	Mark	Guidance
3	(a)	(i)	<p><b>M1</b> p-orbitals overlap (to form pi/<math>\pi</math>-bonds) ✓</p> <p><b>M2</b> <math>\pi</math>-bond(s) are <u>delocalised</u> in <b>structure B</b> ✓</p> <p><b>M3</b> <math>\pi</math>-bonds are localised/between two carbons in <b>structure A</b> ✓</p> <p><b>M4</b></p> <div style="text-align: center;">  <p>AND</p> </div> <p><b>Diagrams</b> show correct <b>position</b> of delocalised and localised <math>\pi</math>-bonds/<math>\pi</math>-electrons <b>OR</b> correct position of p-orbital overlap ✓</p> <p> <b>QWC</b> requires delocalised/delocalized <b>spelled correctly</b> and used in correct context</p>	4	<p><b>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</b></p> <p><b>IGNORE</b> p-orbitals overlap to form sigma bonds</p> <p><b>ALLOW</b> electrons are delocalised in structure B <b>IGNORE B</b> has delocalised structure or ring (must be electrons or <math>\pi</math>-bonds)</p> <p><b>ALLOW</b> <math>\pi</math>-electrons/p-orbital overlap localised/between two carbons in structure A <b>ALLOW</b> p-orbitals overlap with one other carbon <b>IGNORE</b> electrons are localised <b>OR structure A</b> has localised structure (must be <math>\pi</math>-bonds/<math>\pi</math>-electrons/p-orbital overlap) <b>ALLOW</b> labelled diagram showing overlap of p-orbitals between two carbon atoms <b>DO NOT ALLOW</b> C=C in this diagram</p> <p>Diagram for structure A must show the full ring for <b>M4</b> <b>IGNORE</b> C=C in <b>M4</b> diagram</p> <p><b>IGNORE</b> charge density <b>DO NOT ALLOW</b> 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><b>structure B</b>/delocalised structure is (more) stable ✓</p> <p><b>structure B</b> is a better because (enthalpy change of hydrogenation for benzene is) less (exothermic) than (-) 357 (kJ mol<sup>-1</sup>) ✓</p>	2	<p><b>ALLOW</b> structure <b>B</b> is low in energy</p> <p><b>IGNORE</b> structure <b>B</b> is less reactive</p> <p><b>ALLOW</b> enthalpy change/hydrogenation for benzene is less (negative) than <math>3 \times (-)119</math></p> <p><b>IGNORE</b> more positive than <math>(-)357 \text{ kJ mol}^{-1}</math></p> <p><b>ALLOW</b> enthalpy change is less than 3x enthalpy change for cyclohexene</p> <p><b>ALLOW</b> structure <b>B</b> is more stable by <math>149 \text{ kJ mol}^{-1}</math> (2 marks)</p> <p><b>DO NOT ALLOW</b> 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><b>IGNORE</b> <math>360 \text{ kJ mol}^{-1}</math></p> <p>No marks can be awarded if structure <b>A</b> is selected</p>
(b)	 <p>curly arrow from C–N bond to N<sup>+</sup> ✓</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><b>ALLOW</b> first curly arrow to nitrogen atom <b>OR</b> to positive charge on nitrogen atom</p> <p><b>ALLOW</b> second curly arrow from negative charge on fluoride ion</p> <p><b>ALLOW</b> 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	<b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formulae <b>OR</b> a combination of above as long as unambiguous <b>ALLOW</b> positive charge anywhere on the electrophile <b>IGNORE</b> $\text{AlCl}_3$ <b>OR</b> $\text{AlBr}_3$
	(d) (i)	First reactant = $\text{HNO}_2$ ✓  Second reactant =  ✓  Third reactant =  ✓	3	<b>ALLOW</b> $\text{NaNO}_2 + \text{HCl}$ <b>OR</b> $\text{HNO}_2 + \text{HCl}$ <b>IGNORE</b> conditions/concentration  <b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formulae <b>OR</b> a combination of above as long as unambiguous  <b>ALLOW</b> 



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