| Question |  |  | Answer | Mark | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | (a) | (i) | M1 <br> p-orbitals overlap (to form pi/ד-bonds) <br> M2 <br> m-bond(s) are delocalised in structure B <br> M3 <br> m-bonds are localised/between two carbons in structure A <br> M4 <br> AND <br> Diagrams show correct position of delocalised and localised m-bonds/m-electrons <br> OR correct position of p-orbital overlap <br> QWC <br> requires delocalised/delocalized spelled correctly and used in correct context | 4 | ANNOTATE ANSWER WITH TICKS AND CROSSES ETC <br> IGNORE p-orbitals overlap to form sigma bonds <br> ALLOW electrons are delocalised in structure $B$ IGNORE B has delocalised structure or ring (must be electrons or m-bonds) <br> ALLOW $\pi$-electrons/p-orbital overlap localised/between two carbons in structure A <br> ALLOW p-orbitals overlap with one other carbon IGNORE electrons are localised OR structure A has localised structure (must be $\pi$-bonds/ $\pi$-electrons/p-orbital overlap) <br> ALLOW labelled diagram showing overlap of p-orbitals between two carbon atoms DO NOT ALLOW C=C in this diagram <br> Diagram for structure A must show the full ring for M4 IGNORE C=C in M4 diagram <br> IGNORE charge density <br> DO NOT ALLOW electronegativity <br> Structures do not need to be labelled $A$ and $B$ if the description matches the structure |


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


| Question |  | Answer | Mark | Guidance |
| :---: | :---: | :---: | :---: | :---: |
| (c) |  | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHBr}+\mathrm{FeBr}_{3} \longrightarrow\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}^{+}+\mathrm{FeBr}_{4}^{-}$ | 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 $\mathrm{AlCl}_{3}$ OR $\mathrm{AlBr}_{3}$ |
| (d) | (i) | First reactant $=\mathrm{HNO}_{2} \checkmark$ <br> Second reactant $=$ <br> Third reactant $=$ | 3 | ALLOW $\mathrm{NaNO}_{2}+\mathrm{HCl}$ OR $\mathrm{HNO}_{2}+\mathrm{HCl}$ <br> IGNORE conditions/concentration <br> ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous <br> ALLOW |


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


| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | (a) |  | Nitrogen lone pair accepts a proton/ $/ \mathrm{H}^{+} \checkmark$ Requires position of lone pair on N | 1 | DO NOT ALLOW Nitrogen/N lone pair accepts hydrogen Proton $/ \mathrm{H}^{+}$is required ALLOW nitrogen donates a lone pair IGNORE $\mathrm{NH}_{2}$ group donates a lone pair |
|  | (b) |  |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> DO NOT ALLOW |
|  | (c) |  |  | 4 | ALLOW ${ }^{+} \mathrm{NO}_{2}$ OR $\mathrm{NO}_{2}{ }^{+}$ <br> ALLOW first curly arrow from the ring OR from within the ring to any part of the $\mathrm{NO}_{2}{ }^{+}$including the + charge <br> DO NOT ALLOW intermediate with broken ring covering less than half the ring or incorrect orientation of broken ring + must be within the br ken ring <br> ALLOW non-delocalized (Kekulé) structures with carbocation on either side of $\mathrm{Br} / \mathrm{NO}_{2}$ substituents <br> DO NOT ALLOW M1 if a second arrow used on the diagram DO NOT ALLOW M3 ecf if arrow does not come from $\mathrm{C}-\mathrm{Br}$ bond <br> If OH missing on intermediate do not award M 2 . If OH missing on final product do not award M4 |
|  | (d) | (i) | hydrochloric acid/HCl $\checkmark$ | 1 | ALLOW conc / dilute HCl |


| Question |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: |
|  | (ii) | 4-amino-3,5-dibromophenol $\checkmark$ | 1 | ALLOW 3,5-dibromo-4-aminophenol ALLOW 2,6-dibromo-4-hydroxyphenylamine ALLOW 2,6-dibromo-4-hydroxy(-1-)aminobenzene OR (1-)amino-2,6-dibromo-4-hydroxybenzene ALLOW absence of hyphens numbers must be clearly separated ALLOW full stops OR spaces |
|  | (iii) |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous |
|  | (iv) |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW $-\mathrm{O}^{-} \mathrm{Na}^{+} \mathrm{OR}-\mathrm{O}^{-}$ DO NOT ALLOW -O-Na |
| (e) | (i) | dyes/dyestuffs/pigments/food colourings $\checkmark$ | 1 | ALLOW indicators / biological stains DO NOT ALLOW unqualified paint or food |


| Question | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: |
| (ii) | reaction $1 \mathrm{HNO}_{2}$ (with or without HCl ) $\mathrm{OR} \mathrm{NaNO}_{2}+\mathrm{HCl} \checkmark$ <br> temp $<10^{\circ} \mathrm{C}$ <br> reaction 2 CuI <br> reaction 3 alkali(ne) | 5 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous No alternative pathway possible <br> ALLOW dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ but NOT conc $\mathrm{H}_{2} \mathrm{SO}_{4}$ ALLOW conc HCl |
|  | Total | 16 |  |


| Question |  |  | Answer | Mark | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | (a) | (i) | donates a lone pair (on N) OR <br> accepts a proton/ $/ \mathrm{H}^{+} \checkmark$ | 1 | IGNORE 'forms a dative covalent bond' (no direction of lone pair) ALLOW 'forms a dative covalent bond with/to $\mathbf{H}^{+}$ ALLOW mark for $\mathrm{N}: \rightarrow \mathrm{H}^{+}$(can be from correct equation) |
|  |  | (ii) | $\begin{aligned} & \left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}\right)_{2} \mathrm{SO}_{4}{ }^{2-} \checkmark \\ & \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+} \mathrm{CH}_{3} \mathrm{COO}^{-} \checkmark \end{aligned}$ | 2 | ALLOW $\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}\right)_{2} \mathrm{SO}_{4}$ DO NOT ALLOW $\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}\right) \mathrm{HSO}_{4} \mathrm{OR}\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}\right) \mathrm{HSO}_{4}^{-}$ brackets not required <br> ALLOW $\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}\right)\left(\mathrm{CH}_{3} \mathrm{COO}\right) \mathrm{OR}\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}\right)\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$ brackets not required ALLOW separate ions with or without a ' + ' sign between them, e.g. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-}$ |
|  | (b) | (i) |   <br> compound B | 2 | In diazonium ion, IGNORE Cl ${ }^{-}$ <br> ALLOW ' + ' sign up to halfway along triple bond from left-hand N <br> In compound B, <br> ALLOW -OH ionised as - $\mathrm{O}^{-}$ <br> ALLOW - COOH ionised as $\mathrm{COO}^{-}$ |
|  |  | (ii) | conditions = alkaline $/ \mathrm{OH}^{-}$ <br> AND <br> use $=$ dye/pigment/colouring $\checkmark$ | 1 | BOTH responses required for one mark <br> ALLOW named alkali, e.g. $\mathrm{NaOH} / \mathrm{KOH}$ ALLOW base <br> IGNORE references to temperature <br> ALLOW use = indicator |


| Question |  | Answer | Mark | Guidance |
| :---: | :---: | :---: | :---: | :---: |
| (b) | (iii) | Organic product: <br> Other products: $\mathrm{CO}_{2}$ AND $\mathrm{H}_{2} \mathrm{O} \checkmark$ | 2 | IGNORE phenoxide: $\mathrm{O}^{-} \mathrm{OR} \mathrm{O}^{-} \mathrm{Na}^{+}$ <br> ALLOW COO ${ }^{-}$OR COONa <br> ALLOW $\mathrm{H}_{2} \mathrm{CO}_{3}$ <br> Note: must be formulae and not names (in question) |
| (c) |  |  | 1 | ALLOW $\mathrm{N}_{2}{ }^{+}$on structural formula <br> ALLOW $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}_{2}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}+\mathrm{N}_{2}+\mathrm{H}^{+}$ <br> ALLOW $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}_{2} \mathrm{Cl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}+\mathrm{N}_{2}+\mathrm{HCl}$ <br> If + charge shown, IGNORE its position |
|  |  | Total | 9 |  |


| Question |  |  | Expected Answers | Marks | Additional Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | a |  |  | 1 | ALLOW * in place of circle ALLOW if circle extends to include OH |
|  |  | ii | Mark 1 - production of a single isomer is more expensive/difficult OR separation of the single isomer is expensive/difficult $\checkmark$ <br> Mark 2 - one of the isomers is more (pharmacologically) active or one of the isomers might have adverse/harmful/nasty side effects $\checkmark$ <br> Marks 3 and 4 - problems are overcome by using: Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool any | 4 | IGNORE any reference to dosage ALLOW one is more effective/works (better) <br> DO NOT ALLOW use naturally occurring isomer unless stated that it is a chiral compound DO NOT ALLOW transition metal ion DO NOT ALLOW pool synthesis <br> Chiral pool synthesis scores 1 (not 2) marks |
|  | b | i |  | 1 |  <br> ALLOW epoxy ethane as $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O},\left(\mathrm{CH}_{2}\right)_{2} \mathrm{O}$, $\mathrm{CH}_{2} \mathrm{OCH}_{2}$ <br> ALLOW product as $\mathrm{HO}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{NH}_{2}$ DO NOT ALLOW product as $\mathrm{C}_{2} \mathrm{H}_{7} \mathrm{NO}$ |
|  |  | ii | $\mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{OH}$ | 1 | ALLOW $\left(\mathrm{CH}_{2}\right)_{2}$ <br> ALLOW displayed/skeletal formula DO NOT ALLOW molecular formula |


| Question |  | Expected Answers | Marks | Additional Guidance |
| :---: | :---: | :---: | :---: | :---: |
| c | i | $\mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}_{3}{ }^{+} \mathrm{Cl}^{-}$ <br> Must show $\mathrm{Cl}^{-}$ion | 1 | ALLOW $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl}$ if formula is correct and both charges not shown ALLOW $\left(\mathrm{CH}_{2}\right)_{2}$ / any correct unambiguous structure DO NOT ALLOW ions joined by covalent bonds |
|  | ii | $\mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}_{3}{ }^{+} \mathrm{HS}^{-}$ <br> Must show $\mathrm{HS}^{-}$ion | 1 | ALLOW if formula is correct and both charges not shown <br> ALLOW $\left(\mathrm{CH}_{2}\right)_{2}$ any correct unambiguous structure ALLOW $\left(\mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}_{3}^{+}\right)_{2} \mathrm{~S}^{2-}$ |
| d | i | Both $\mathrm{NH}_{2}$ and COOH are joined to the same $\mathrm{C} \downarrow$ | 1 |  <br> The 4 groups/atoms attached to the C can be in any order but CH must be adjacent. ( ) not essential |
|  | ii |  | 1 | $\text { ALLOW }\left(\mathrm{CH}_{2}\right)_{2}$ <br> DO NOT ALLOW molecular formula |
| e | i | Question 5e is followed by two blank lined pages (15 and 16) which ca Please check to see whether or not pages 15 or 16 have been used | didate | can use instead of requesting additional paper. |


| Question |  | Expected Answers |  | Marks | Additional Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| e | i |  <br> Isomer G <br> * not required |  | 2 | ALLOW HO(CH2 $)_{4} \mathrm{NH}_{2} /$ <br> ALLOW any correct unambiguous structure of 1-aminobutan-4-ol <br> ALLOW CH3 $\mathrm{CH}(\mathrm{OH}) \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{CH}_{3}$ <br> ALLOW any correct unambiguous structure of 2-aminobutan-3-0 |
|  |  |  | Total | 13 |  |

