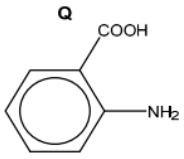
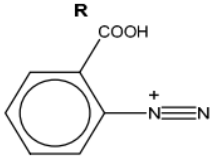
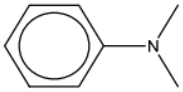
34. Nitrogen compounds

34.2 Phenylamine and azo compounds

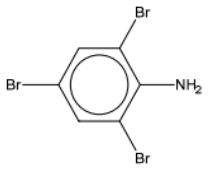
Paper 4

Marking Scheme

Q1.

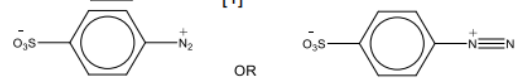
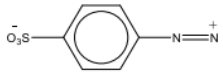
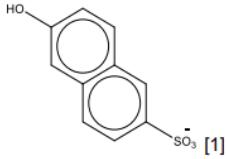
(b)(i)	**Q**  **R**  **S** 	3
(b)(ii)	**M1** step 1: Fe / Sn, conc. HC*l* **M2** step 2: HNO_2 **OR** $NaNO_2$ **AND** HC*l* **M3** step 1: heat / reflux / hot **AND** step 2: ⩽10 °C	3

Q2.

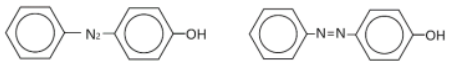
(b)(i)	**M1** white ppt. **M2** structure 	2
(b)(ii)	**M1** lone pair / p-orbital / electrons on the nitrogen / NH_2 **AND** overlap / delocalised / incorporated **AND** with the (π–electrons) ring / π system **M2** increasing its electron density (of the ring) **OR** it can polarise the electrophile / Br_2 better	2

Q3.

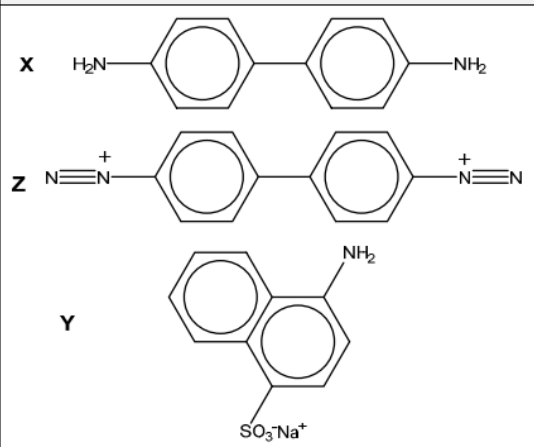
(a)	$C_{16}H_{10}N_2O_7S_2^{2-}$ OR $C_{16}H_{10}N_2O_7S_2$ [1]	1

(b)	E:  [1] F:  OR  [1] ECF from E G  [1]	3
(c)	M1 step 1: HNO_2 OR $NaNO_2$ + HC*l* [1] M2 step 1: T ⩽ 10 °C [1] M3 step 2: NaOH(aq) / alkaline conditions [1]	3

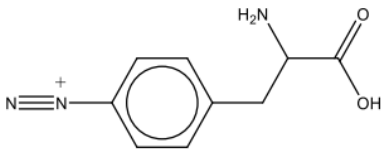
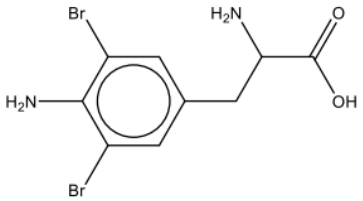
Q4.

(b)	phenylamine, ammonia, diethylamine [1] • Availability of lone pair on N to receive H^+ • phenylamine – LP, delocalised / overlaps into ring [1] • diethylamine – ethyl are electron donating [1] Two bullet points for one mark, three bullet points for two marks.	3
(c)	 Q or [1] N_2 or N=N circled **AND** dye / colouring[1]	2

Q5.

(d)(i)		3
(d)(ii)	step 1 **M1** Sn and hydrochloric acid / HC*l* **M2** concentrated (HC*l*) + heat / reflux (followed by NaOH) step 2 **M3** HNO_2 and (HC*l*) $\leqslant$10°C **OR** $NaNO_2$, HC*l* and $\leqslant$10°C	3

Q6.

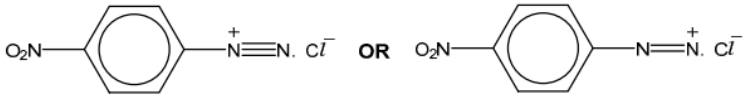
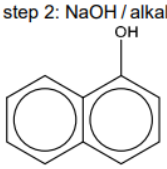
(c)(ii)	 NH_2 on ring gives diazonium ion [1]  dibromo compound with Br atoms 2,6 to amine group [1]	2

Q7.

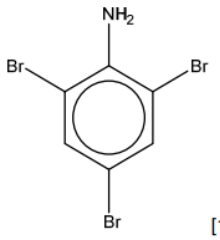
(c)(i)	HNO_2, T between 0° and 10°C	1
(c)(ii)	warm / T>10°C **and** H_2O	1

(c)(iii)	$CH_3C_6H_4–N=N–C_6H_3(CH_3)OH$ [1] T between 0° and 10°C **and** NaOH(aq) [1]	2

Q8.

(a)	**M1:** ethylamine phenylamine 4-nitrophenylamine most basic least basic **M2 / 3 / 4:** *explanation two correct for one mark, three correct for two marks, four correct for three marks* • (basicity linked to) lone pair / p orbital on N **AND** being able accept / donate to / coordinate to a proton / H^+ • ethyl / alkyl group is electron donating / has a positive inductive effect (so lone pair on N is more able to accept a proton) • (phenylamines are less basic than ethylamine as) p orbital / lone pair on N is delocalised (into the ring so less able to accept a proton) • (4-nitrophenylamine is less basic than phenylamine as) nitro / NO_2 group is electron withdrawing (so lone pair on N is less able to accept a proton)	**4**
(b)(i)	 **OR**	**1**
(b)(ii)	**M1:** step 1: HNO_2, ⩽ 10°C **OR** $NaNO_2$, HCl(aq), ⩽ 10°C **M2:** step 2: NaOH / alkaline **AND** 1-naphthol / α-naphthol / structure below 	**2**

Q9.

(a)	bromine decolourised **OR** orange / brown to colourless [1] white precipitate [1]	**2**
(b)	no change [1]	**1**
(c)	 [1]	**1**
(d)	2,4,6-tribromophenylamine [1] **ECF** 8(c) for a bromophenylamine	**1**

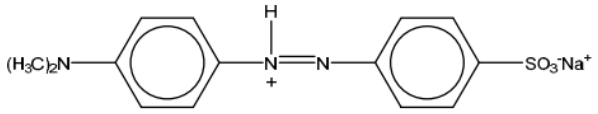
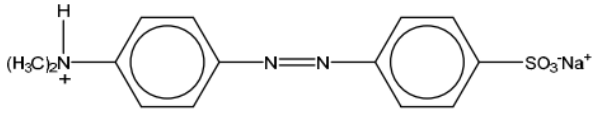
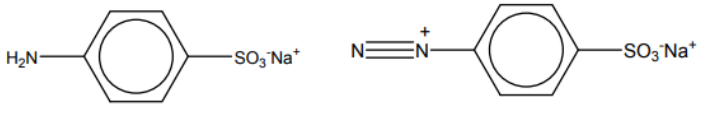
Q10.

(b)	M1 butylamine > ammonia > phenylamine [1] M2 basicity related to ability of **lp** to accept proton / H^+ [1] M3 butylamine is stronger because of positive inductive effect of **alkyl** group / C_4H_9 [1] M4 phenylamine is weaker because **lp on N** is delocalised into ring [1]	**4**

Q11.

(a)	**M1** phenylmethanamine / **U** > phenylamine / **T** > benzamide / **S** [1] any two from: • alkyl group is electron donating so lone pair more able to accept a proton • lone pair on N overlaps with delocalised system so less able to accept a proton • presence of electron-withdrawing oxygen / carbonyl group means lone pair is not available to accept a proton **OR** amides are neutral	**3**

Q12.

(f)(i)	bond circled between the two Ns, or N=N or –N=N–	**1**
(f)(ii)	 **or** 	**1**
(g)(i)	 **R** **S** Award one mark for each correct structure	**2**
(g)(ii)	**M1** step 1 Sn and HC*l* conc. and heat **M2** step 2 $NaNO_2$ and HC*l* and 0-10 °C	**3**

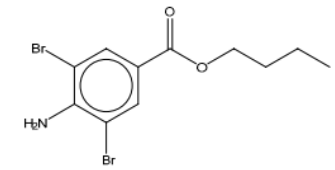
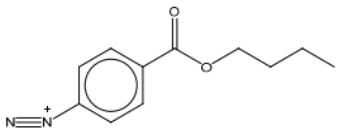
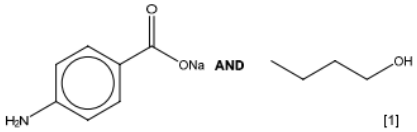
Q13.

(c)(i)	$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3HBr$ [1]	1
(c)(ii)	2,4,6-tribromophenylamine [1]	1
(c)(iii)	decolourisation of bromine **AND** white precipitate [1]	1

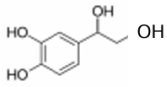
(d)	phenylamine < ammonia < ethylamine [1] • lp on nitrogen of phenylamine delocalised into ring • alkyl group of ethylamine electron donating / has positive inductive effect [1] • correct statement about availability of lone pair to accept proton once [1]	3

Q14.

(a)(i)	$RNH_2 + H^+ \rightarrow RNH_3^+$ **OR** $RNH_2 + HCl \rightarrow RNH_3Cl$ [1]	1
(a)(ii)	weaker **AND** lone pair of N delocalised into benzene ring [1]	1

(b)	 [1]  [1]  **AND** [1]	3

Q15.

(c)(i)	(phenyldiazonium ion is stabilised because) positive charge is delocalised by ring / positive charge is spread over ring	1
(c)(ii)		1
	N_2	1