Mark Scheme

Q1.

Question Number	Answer	Additional Guidance		Mark
	• correct formula (phenol) **(1)** • balanced equation **(1)**	Example of equation $C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$ Allow C_6H_6O Do not award [O] Ignore state symbols even if incorrect		**(2)**

Q2.

Question Number	Answer	Additional Guidance	Mark
(i)	• mass of carbon in both substances **(1)** • molar masses of both substances **(1)** • calculation of percentages by mass of carbon **(1)**	Example of calculation (12 x 7 =) 84 Phenylmethanol 108 and Benzoic acid 122 Phenylmethanol (84 ÷ 108) x100 = 78%/ 77.8%/ 77.78% / 77.7 % Benzoic acid (84 ÷ 122) x 100 = 68.85%/ 68.9%/69% Ignore sf except 1 Allow TE on incorrect M_r values Allow (2) for 11.1% and 9.8% calculated using 12 not 84 Allow 'rescue' (1) for one substance completely correct	**(3)**

Question Number	Answer	Additional Guidance	Mark
(ii)	A description that makes reference to: • black smoke	Allow Black fumes/soot/(yellow) smoky flame / grey smoke Ignore carbon particulates Do not award carbon monoxide/yellow flame	**(1)**

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to • Alkenes	Allow Cycloalkenes/cycloalkanes/alkynes/ carbon-carbon double bonds Ignore Ethene/named alkenes/named alkynes Do not award benzene/arenes	(1)

Question Number	Answer	Additional Guidance	Mark
(iv)	An explanation that makes reference to • (window) above the safety line means the exhaust system is not strong enough to draw in the fumes **(1)** • so the toxic fumes will escape (into the laboratory) **(1)**	Allow reverse argument Allow reference to exhaust/fan not able to prevent gas escaping Allow poisonous/harmful/irritant/ carbon monoxide/soot for 'toxic fumes' Ignore reference to protection from splashing etc	(2)

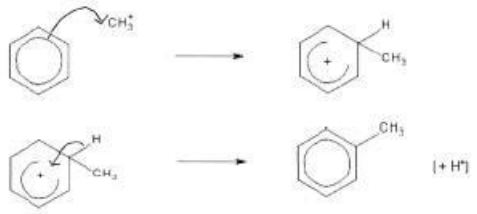
Q3.

Question Number	Answer	Additional Guidance	Mark
	An explanation that makes reference to the following points: • **lone pair** (of electrons) from the **oxygen** **and** will interact with the delocalised ring of electrons / increase the (pi/π) electron density of the benzene ring **(1)** • which increases the reactivity toward electrophiles (such as bromine)/ which means that the bromine is more easily polarised **(1)**	Allow reference to the **lone pair** (of electrons) from the **nitrogen** Ignore activation of ring Do not award charge density Allow $Br^+/Br^{\delta+}$ for electrophile Allow reference to benzene as being a stronger nucleophile Do not award references to electrophilic addition	(2)

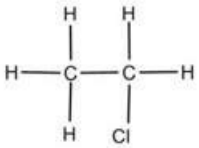
Q4.

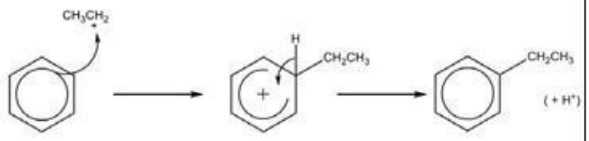
Question Number	Answer	Additional Guidance	Mark
(i)	• dot-and-cross diagram	Example of diagram  Allow electrons in overlapping circles Allow all dots / all crosses Ignore inner shell electrons, even if incorrect Ignore lines as bonds e.g. x • Do not award diagram with lone pair on Al	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following points: • shape – trigonal planar (1) • bond angle - 120° (1)	Mark independently Both words needed Allow triangular for trigonal – but not just tri Allow marks for labelled diagram **Note** If shape is pyramidal, no mark for M1 but allow (1) for 107° No TE for any other shape	(2)

Question Number	Answer	Additional Guidance	Mark
(iii)	• equation for the formation of the electrophile (1) • curly arrow from on or within the circle to CH_3^+ (1) • structure of intermediate including charge with some part of the charge within the horseshoe **and** horseshoe covering at least 3 carbon atoms **and** facing the tetrahedral carbon (1) • curly arrow from C-H bond to anywhere in the hexagon reforming the delocalised structure (1)	Example of mechanism $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + [AlCl_4]^-$  Allow $AlCl_4^-$ / $^{\delta+}CH_3\text{-}AlCl_4^{\delta-}$ Allow curly arrow from anywhere within the hexagon Allow curly arrow to any part of CH_3^+, including the + charge Do not award curly arrow from outside the hexagon Allow dotted / dashed lines for horseshoe Do not award dotted bonds to H and CH_3 unless clearly part of a 3D structure Ignore any involvement of $AlCl_4^-$ in the final step /HCl **Note** Correct Kekulé structures score full marks	(4)

Q5.

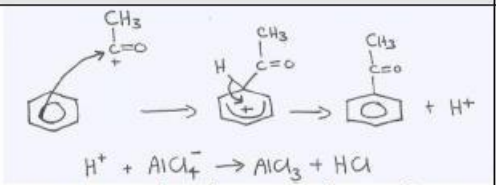
Question Number	Answer	Additional Guidance	Mark
(i)		Do not award skeletal or structural formulae	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	• **M1 equation** to show formation of electrophile (1) • **M2** curly arrow from anywhere on the central ring to positive carbon (1) • **M3** structure of intermediate (1) • **M4** curly arrow from C-H bond to reform the ring (1) • **M5 equation** showing regeneration of catalyst (1)	Example of mechanism Penalise incorrect halogenoalkane in (a)(i) only $CH_3CH_2Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$ Ignore any curly arrows given in the equation Allow curly arrow from anywhere within the hexagon Do not award if curly arrow to CH_3 carbon in $CH_3CH_2^+$ Do not award if curly arrow to $C_2H_5^+$ Horseshoe facing the tetrahedral carbon and covering at least three carbon atoms Some part of the positive charge in the horseshoe Do not award dotted lines unless clearly part of a 3D structure $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ Ignore regeneration step if part of the mechanism **Mechanism**  Allow TE from (a)(i)	(5)

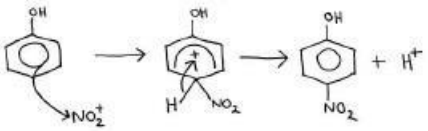
Question Number	Answer	Additional Guidance	Mark
(iii)	An explanation that makes reference to the following points: Phenol is likely to be more reactive because • **M1 lone pair** on **oxygen** (atom of –OH group) delocalises / is incorporated into the (benzene) ring / donated to the ring (1) • **M2** which increases the electron density (of the ring) (1) • **M3** making the ring / phenol more susceptible to electrophilic attack (1)	Do not award M2 if mention of "charge density" / "electronegativity" Ignore references to "the ring becomes more negative" Award "making the ring more nucleophilic" / "making the ring more susceptible to attack by a positive ion" Ignore references to "activation of the ring"	(3)

Q6.

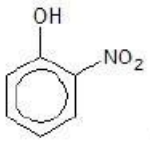
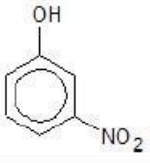
Question Number	Answer	Additional Guidance	Mark
(i)	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	Accept use of $FeCl_3/Fe + Cl_2$ Allow displayed formulae Do not award C_2H_3OCl Ignore state symbols even if incorrect	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	 $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ • electron pair movement from ring to electrophile **(1)** • formula of intermediate ion **(1)** • curly arrow from C–H bond to reform delocalised ring **(1)** • correct product and equation to show regeneration of catalyst and HCl **(1)**	Do not award curly arrow that ends at the CH_3 Allow arrow starting anywhere within the hexagon 'Horseshoe' to cover at least three carbon atoms and face the tetrahedral carbon and with some part of the plus sign inside 'horseshoe' Allow Kekulé diagrams Do not award dotted bonds unless part of a 3D structure Could be shown in reaction mechanism Ignore curly arrows	**(4)**

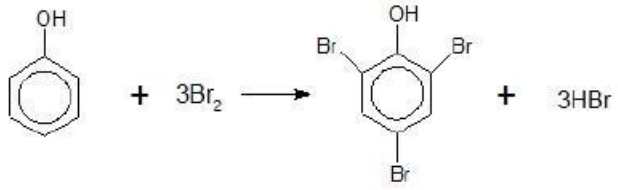
Q7.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	An answer that makes reference to • Electron pair movement from ring to electrophile **(1)** • Formula of intermediate ion **(1)** • Curly arrow from C-H bond to reform delocalised ring and correct final structure with H^+ also formed **(1)**	Allow arrow that starts from anywhere within the hexagon but it must go to the nitrogen of the ion 'Horseshoe' to cover at least three carbon atoms, facing the tetrahedral carbon and part of the + sign to be inside the 'horseshoe' Do not award '+' charge on the tetrahedral carbon Do not award dotted bonds unless part of a 3D structure Curly arrow to go from the bond to anywhere inside the ring Accept the drawing of HSO_4^- to remove the H from the ring as long as H_2SO_4 is given as the product instead of H^+ Exemplar mechanism  Do not penalise attachment of OH/NO_2 to benzene ring Penalise incorrect product: 1 mark	(3)

Question Number	Acceptable Answer	Mark
(ii)	The only correct answer is **B** ***A*** *is incorrect because this is 15% of the mass of the starting material* ***C*** *is incorrect because this is the percentage of the starting mass over the max mass of product* ***D*** *is incorrect because this is 100% yield and not 15%*	(1)

Question Number		Additional Guidance	Mark
(iii)	 **and** 	Ignore connectivity of OH/NO_2	(1)

Q8.

Question Number		Additional Guidance	Mark
(i)	 • Structure of 2,4,6-tribromophenol **(1)** • Balanced equation **(1)**	Ignore state symbols even if incorrect Do not award $C_6H_3OBr_3$ M2 dependent on M1	**(2)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following: Similarity • Both electrophilic substitution **(1)** Any two from: Contrast • No need of a halogen carrier with phenol **(1)** • oxygen's lone pair of electrons interacts with the benzene ring of delocalised electrons so electrophilic attack more likely **(1)** • Tri-substitution of phenol compared to mono for benzene **(1)** • Bromination of phenol requires bromine in aqueous solution but benzene requires liquid bromine **(1)** • Bromination of phenol requires room temperature but benzene requires heating (under reflux) / reflux **(1)**	Ignore comments of ease of reaction Should be stated clearly as a similarity Accept reverse argument Allow $Fe/FeBr_3/AlBr_3$ with benzene Do not award just 'catalyst' Allow reference to OH group Allow 'bromine' for 'electrophilic' Do not award for nucleophilic attack Allow "multiple-" for "tri-"	**(3)**

Q9.

Question Number	Answer	Additional Guidance	Mark
(i)	An explanation that makes reference to the following points: • the electron density of the (benzene) ring is greater in phenol (than in benzene) (1) • because the lone pair (of electrons) on oxygen **and** (1) overlaps with the pi cloud / delocalised electrons / delocalised system	Allow lone pair (of electrons) on oxygen feeds into / donates into / interacts with the delocalised electrons / system Ignore electron pushing effect of OH	(2)

Question Number	Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: • they both form hydrogen bonds (1)	Allow M1 and M2 shown in diagrams Ignore reference to other specific types of intermolecular forces	(2)
	• in 4-nitrophenol the hydrogen bonds join molecules in a straight chain / at both ends / at opposite ends (of the molecule so are stronger) **or** (1) 2-nitrophenol forms intramolecular hydrogen bonds / forces / interactions (so fewer intermolecular hydrogen bonds)	Allow 4-nitrophenol forms stronger intermolecular hydrogen bonds / forces / interactions Allow in 2-nitrophenol the hydrogen bonds join 2 molecules together / form a dimer (so there are fewer / weaker hydrogen bonds) Allow in 2-nitrophenol the hydrogen bonds are on the same side (of the molecule)	

Q10.

Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to • **(M1)** (similarity) all have arene C–H absorptions Either 3030 (cm^{-1}) **or** 750 and/or 700 (cm^{-1}) **(1)** • **(M2)** only phenol and phenylmethanol have O–H 3750 - 3200 (cm^{-1}) **(1)** • **(M3)** only benzoic acid has O–H 3300 - 2500 (cm^{-1}) **(1)** • **(M4)** only benzoic acid has C=O 1700 - 1680 (cm^{-1}) **(1)** • **(M5)** only phenylmethanol has alkane C–H absorptions either 2962 - 2853 (cm^{-1}) or 1485 - 1365 (cm^{-1}) **(1)**	Bond and wavenumber ranges necessary for each mark Do not award 880/830/780 (cm^{-1}) Do not award –OH / C–OH by penalising once only in M2 and M3 All 5 correct bonds with no wavenumber ranges scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) All 5 correct wavenumber ranges with no bonds or incorrect bonds scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) Penalise any additional peaks once only Ignore references to different fingerprint regions	**(5)**

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to • five peaks (in the ^{13}C NMR spectrum) **(1)** • (four) aromatic peaks within the chemical shift range of 165 - 105 (ppm) **(1)** • (one) peak (for the C-OH) within the chemical shift range of 75 - 55 (ppm) **(1)**	Allow any range within the stated ranges Penalise single values as opposed to ranges once only Accept annotations on diagram Penalise additional peaks once only when three or more types of peak are stated	**(3)**

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to • suitable formula of fragment ion **(1)** • matching *m*/*z* value **(1)**	Example of a suitable formula $C_6H_5COO^+$ or $C_6H_5CO^+$ Do not award $C_7H_5O_2^+$ or $C_7H_5O^+$ *m*/*z* = 121 or 105 Allow $COOH^+$ (1) Do not award bond to the fragment, e.g. $-COOH^+$ *m*/*z* = 45 (1) No TE on incorrect fragment ions such as CH_3^+	**(2)**

Q11.

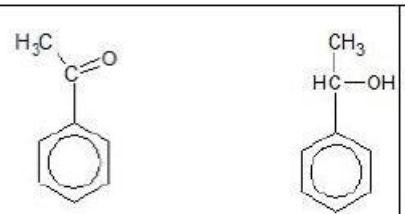
Question Number	Acceptable Answers	Additional Guidance	Mark
*	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5–4 / 3 3–2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning.	Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 5 marks (3 marks for indicative content and 2 marks for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).	**(6)**

		Number of marks awarded for structure of answer and sustained line of reasoning		In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. **General points to note** If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).	
		Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.	2		
		Answer is partially structured with some linkages and lines of reasoning.	1		
		Answer has no linkages between points and is unstructured.	0		

	Comment: Look for the indicative marking points first, then consider the mark for structure of answer and sustained line of reasoning		

	Indicative content • **IP1 Type of reaction** **Both** reactions are (examples of) electrophilic substitution • **IP2 Products** Benzene forms bromobenzene **and** phenol forms 2,4,6-tribromophenol • **IP3 Comparison of reactivity** Benzene is less reactive (than phenol) / phenol is more reactive (than benzene) • **IP4 Conditions** Benzene requires (a catalyst of) $FeBr_3$ **and** phenol does not require a catalyst / can react with just bromine water • **IP5 Lone pair** (Phenol is more susceptible to electrophilic attack) because the lone pair on the oxygen (atom in phenol) delocalises into the ring / π system • **IP6 Electron density** Increasing the electron density of the ring / π system	If names and formulae are given, both must be correct Do not award addition-elimination for substitution Allow these products shown as structures in equations, even if equations are not fully correct Allow any feasible dibromophenol / tribromophenol Ignore dibromobenzene / tribromobenzene Allow Fe / $FeCl_3$ / $AlBr_3$ / $AlCl_3$ / Lewis Acid catalyst Allow Friedel-Crafts catalyst / halogen carrier Can be shown in equation Allow phenol reacts at room temperature Ignore reference to heat / mechanism Allow IP4 if stated that only benzene requires a catalyst Allow lone pair on oxygen is donated into the ring Allow OH for oxygen Allow activates the ring Do not award increases the electronegativity / charge density of the ring Penalise omission of 'the ring / π system' once only in IP5 and 6	

Q12.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An answer that makes reference to the following: synthetic pathway that consists of: (Step 1) • (acylation of benzene) using ethanoyl chloride **(1)** • use of aluminium chloride (and heat) **(1)** (Step 2) • (reduction of) **A** with $LiAlH_4$ in ether (dry) **(1)** (Step 3) • (dehydration of) **B** with (conc.) phosphoric acid/H_3PO_4 **(1)** (Intermediates) • identification of **A** as phenylethanone and **B** as (1-)phenylethanol	The compounds used can be stated or given within equations. Only award if part of a Friedel-Crafts reaction Only award if given to reduce an aromatic carbonyl or carboxylic acid Allow (conc.) sulfuric acid/ H_2SO_4 Only award if given to dehydrate an aromatic alcohol Accept formulae for names, but if both given, then both must be correct This also applies to reagents	**(5)**
	 **(1)**	Do not award use of other reagents not in the table.	