30. Hydrocarbons

30.1 Arenes

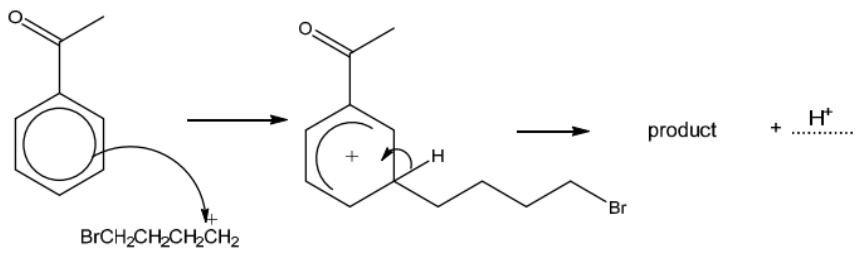
Paper 4

Marking Scheme

Q1.

(f)(i)	$BrCH_2CH_2CH_2CH_2Br + FeBr_3 \rightarrow BrCH_2CH_2CH_2CH_2^+ + FeBr_4^-$	1

(f)(ii)

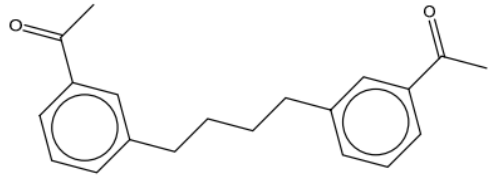


M1 curly arrow from inside the hexagon towards C^+
M2 structure of the intermediate
M3 curly arrow from C–H bond into the ring **AND** H^+

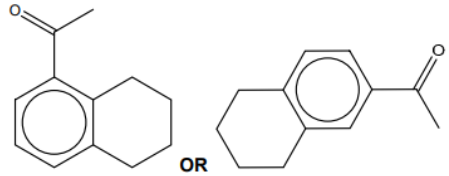
3

(f)(iii)

M1 **Y**



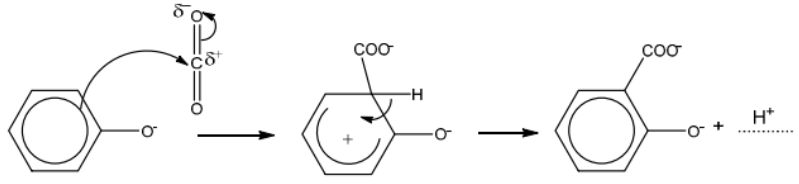
M2 **Z**



2

Q2.

(b)



M1 correct dipole **AND** curly arrow from inside the hexagon to the carbon atom
M2 structure of the intermediate
M3 curly arrow from C-H bond into the ring **AND** H^+

3

Q3.

(a)(i)	2-nitrobenzoic acid **OR** 2-nitrobenzenecarboxylic acid	**1**
(a)(ii)	hot / reflux / heat **AND** (alkaline / acidified / neutral) MnO_4^- / $KMnO_4$	**1**
(a)(iii)	COOH / carboxyl group is electron-withdrawing / electronegative **AND** 3- and 5- / meta- directing	**1**

Q4.

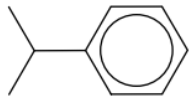
(d)(i)	 [1]	**1**
(d)(ii)	step 1: $CH_3Cl + AlCl_3$ [1] step 2: hot alkaline $KMnO_4$ [1]	**2**

Q5.

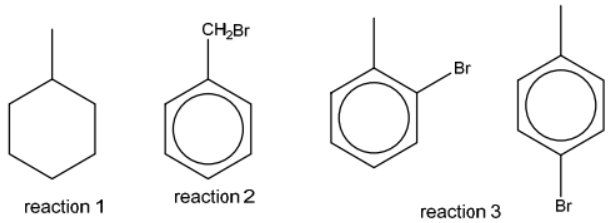
(a)	aluminium chloride **OR** $AlCl_3$ [1]	**1**
(b)(i)	delocalised system / delocalised ring / pi system / pi ring [1] C–Cl bond [1]	**2**
(b)(ii)	C–H bond [1] delocalised system / delocalised ring / pi system / pi ring [1]	**2**

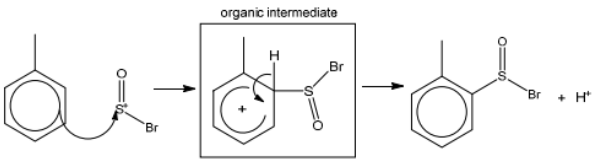
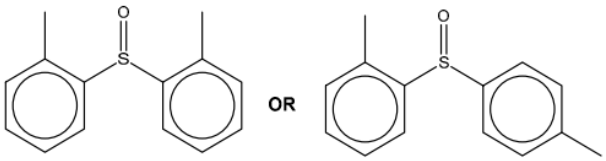
(d)	$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ [1]	**1**
(e)	Cl^+ hydrogen / H chlorine / Cl [1]	**1**

Q6.

(b)(i)	**X**  [1] **Y**  [1]	**2**
(b)(ii)	**M1** step 1 $(CH_3)_2CHBr$ and $FeBr_3$ / $AlBr_3$ **M2** step 2 conc HNO_3 and conc H_2SO_4 **M3** step 3 Sn and conc HCl	**3**

Q7.

(a)(i)	 reaction 1 reaction 2 reaction 3 **M1** **M2** **M3 BOTH**	**3**
(a)(ii)	**M1** reaction 1: hydrogenation / reduction **M2** mechanism 2: (free) radical substitution	**2**
(b)	the substitution product is stabilised by delocalization of π-electrons / by π-electrons in the ring **OR** the addition product is **not** stabilised by delocalisation (of π-)electrons **ALLOW** addition product will remove π-electron delocalised system	**1**

(c)(i)	 **M1** curly arrow from inside the hexagon to S atom **M2** structure of the intermediate **M3** curly arrow from C-H bond into the ring **AND** formation/loss of H^+	**3**
(c)(ii)		**1**

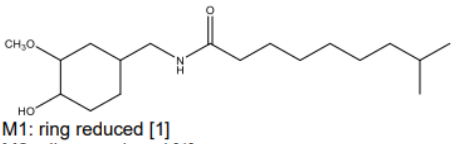
Q8.

(b)(i)	carboxylic acid/carboxyl, ester, amide, amine Any two [1], all four [2]	**2**

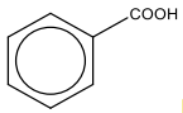
Q9.

(b)	iodobenzene **AND** as Br is more electronegative (than I / $I^{\delta+}$/I^+ in the electrophile)	**1**

Q10.

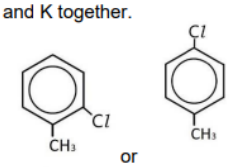
(c)	 M1: ring reduced [1] M2: alkene reduced [1]	2
(d)(i)	hot AND concentrated acidified AND MnO_4^- / $KMnO_4$ all [1]	1

Q11.

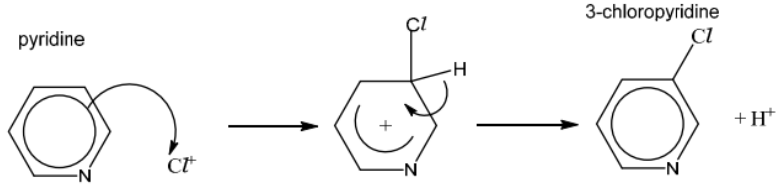
(a)(i)	**M**  [1]	1
(a)(ii)	hot (alkaline) $KMnO_4$ / MnO_4^- [1] $SOCl_2$ OR PCl_5 OR PCl_3 + heat[1]	2
(a)(iii)	oxidation [1] (nucleophilic) substitution	2

Q12.

(a)	CH_3Cl + $AlCl_3$ [1] hot alkaline) MnO_4^- [1]	2

(c)(i)	Mark J and K together.  either or J or K [1]  J or K [1] for the ring substituted product – $AlCl_3$ [1] for the side-chain substituted product – uv [1]	4

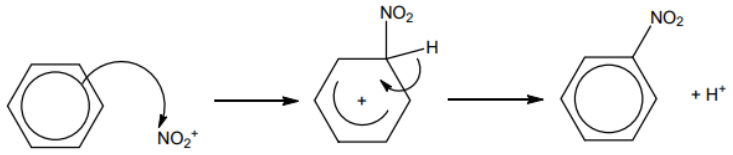
Q13.

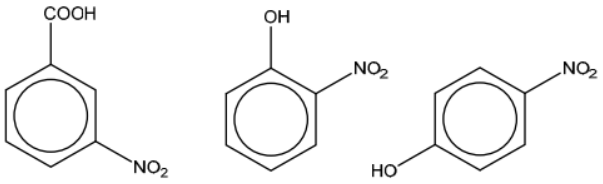
(e)	 **M1** first curly arrow to Cl^+ **M2** correct intermediate **M3** second curly arrow **AND** H^+ formed / lost	**3**

Q14.

(d)(i)		**1**
(d)(ii)	step 1 **M1** concentrated HNO_3 and H_2SO_4 step 2 **M2** hot (alkaline) $KMnO_4$ (followed by addition of H^+)	**2**

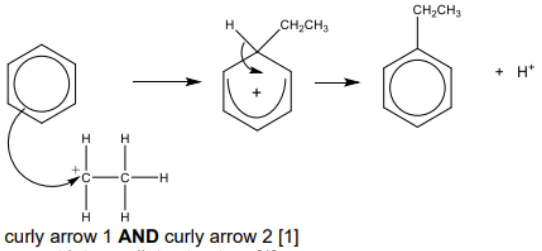
Q15.

(a)(i)	 **M1** first curly arrow from within hexagon to N of the NO_2^+ **M2** correct intermediate **M3** second curly arrow from C-H bond into the ring **AND** H^+ formed / lost	**3**
(a)(ii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$	**1**

(b)	**M1** *benzoic acid* **M2** *phenol*  **OR**	**2**
(c)	**M1** phenol > benzene > benzoic acid **M2 / M3** phenol: • lone pair / p-orbital on oxygen delocalises into the ring / overlaps with π-delocalised ring • accepts / attracts / polarises NO_2^+ / electrophiles better benzoic acid: • COOH / C=O is an electron-withdrawing / positive inductive effect two for one mark, three for two marks **M4** (phenol-oxygen) increases electron density in the ring *(as compared to benzene as a result of the OH group)* **OR** (benzoic acid–COOH) decreases electron density in the ring *(as compared to benzene as a result of the COOH group)*	**4**

Q16.

(b)(i)	$C_2H_5Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$	**1**

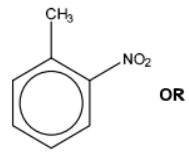
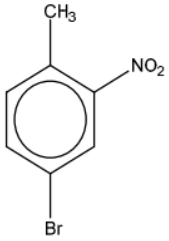
(b)(ii)	 curly arrow 1 **AND** curly arrow 2 [1] correct intermediate structure [1] $C_6H_5C_2H_5$ **AND** H^+ [1]	**3**

Q17.

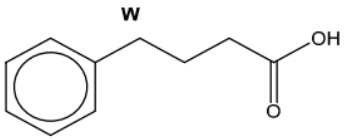
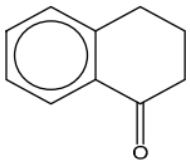
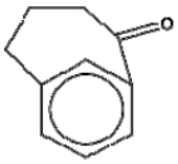
(b)(i)	chloromethane aluminium chloride	1
(b)(ii)	$CH_3Cl + AlCl_3 \rightarrow AlCl_4^- + CH_3^+$	1
(b)(iii)	curly arrow from within benzene to CH_3^+ [1] positively charged intermediate [1] curly arrow from C–H bond into ring, $C_6H_5CH_3$, H^+ [1]	3
(b)(iv)	hot alkaline $KMnO_4$ [1] $C_6H_5CH_3 + 3[O] \rightarrow C_6H_5CO_2H + H_2O$ **OR** $C_6H_5CH_3 + 3[O] + OH^- \rightarrow C_6H_5CO_2^- + 2H_2O$ [1]	2

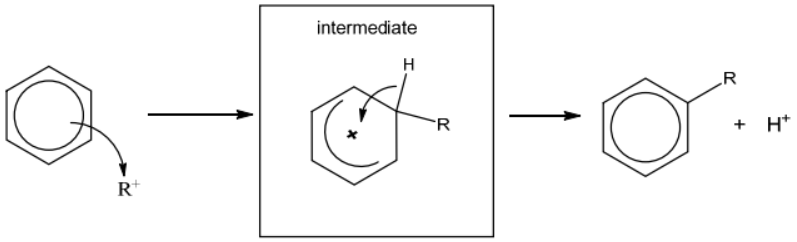
Q18.

(c)(i)	4-bromo-2-nitrobenzoic acid **OR** 4-bromo-2-nitro(-1-)benzenecarboxylic acid	1

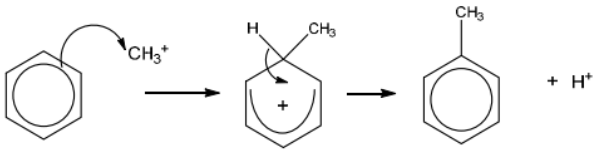
(c)(ii)	**E =**  **OR**  **F =** 	2
(c)(iii)	**M1:** step 1 conc. H_2SO_4 and conc. HNO_3 **M2:** step 2 Br_2 and $AlBr_3$ **M3:** step 3 hot (alkaline / acidified) MnO_4^- / $KMnO_4$	3

Q19.

(b)(i)	$RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$ **OR** $Cl(CH_2)_3COOH + AlCl_3 \rightarrow {}^+(CH_2)_3COOH + AlCl_4^-$	1
(b)(ii)	**W**  **X** $C_{10}H_{10}O$  **OR** 	2

(b)(iii)	$SOCl_2$ **OR** PCl_5 **ALLOW** PCl_3 **AND** heat	1
(b)(iv)	 **M1:** arrow to R^+ **OR** arrow to positive carbon of ${}^+(CH_2)_3COOH$ **M2:** correct structure of intermediate **M3:** arrow from C-H bond into the ring **AND** H^+	3

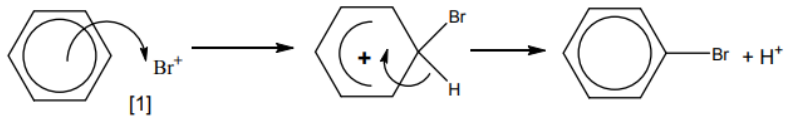
Q20.

(c)(i)	$CH_3Cl + AlCl_3 \rightarrow {}^+CH_3 + AlCl_4^-$ [1]	1
(c)(ii)	 M1: arrow to CH_3^+ (arrow must come from inside the hexagon) [1] M2: correct structure of intermediate [1] M3: arrow <u>from</u> C-H bond into the ring **AND** H^+ seen [1]	3

Q21.

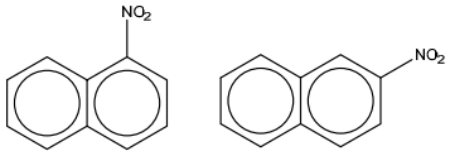
(c)(i)	benzoic acid [1]	**1**
(c)(ii)	COOH directs 3 position [1]	**1**
(c)(iii)	electrophilic substitution [1]	**1**
(c)(iv)	M1 curly arrow from within hexagon towards $CH_3C^+=O$ [1] M2 correct intermediate [1] M3 curly arrow from C–H bond into hexagon and correct product Q [1]	**3**
(c)(v)	MnO_4^- / $KMnO_4$ / manganate**VII** / permanganate aq / H^+ / acidified / OH^- then acid / alkaline then acid heat / boil / reflux / T>50° **OR** alkaline iodine followed by acidification [1]	**1**

Q22.

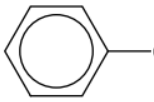
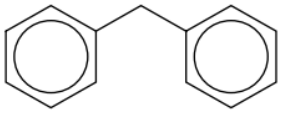
(a)(i)	The substitution product is stabilised by delocalisation of (6)π-electrons **OR** The addition product is not stabilised by delocalisation of (6)π-electrons [1]	**1**
(a)(ii)	 [1] intermediate [1] curly arrow + H^+ lost [1] • first curly arrow • intermediate • 2nd curly arrow, product **and** H^+ formed / lost	**3**
(a)(iii)	$AlBr_4^-$ + H^+ → $AlBr_3$ + HBr	**1**
(b)	lone pair of oxygen is delocalised into the ring any one from: • phenol has a higher electron density in the ring • phenol can polarise/induce a dipole in Br_2	**2**
(c)(i)	$CH_3CH_2CH^+CH_3$ $(CH_3)_2CHCH_2^+$ $(CH_3)_3C^+$ Each correct structure = 1 mark	**3**

Q23.

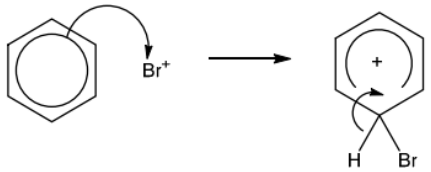
(a)(i)	• trigonal planar • tetrahedral. • trigonal planar Award one mark for two correct statements, award two marks for three correct statements	**2**

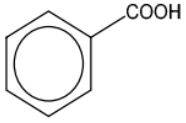
(a)(ii)	 Both structures required	**1**
(b)	$C_{10}H_8 + 9[O] \rightarrow C_8H_4O_3 + 2CO_2 + 2H_2O$	**1**

Q24.

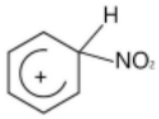
(c)(i)	J =  K =  Award one mark for each correct structure	**2**
(c)(ii)	step 1 PCl_5 **OR** $SOCl_2$ **OR** PCl_3 + heat	**1**
(d)(i)		**1**
(d)(ii)	**M1** step 3 electrophilic substitution **M2** step 3 benzene and $AlCl_3$ (and heat)	**2**
(d)(iii)	step 4 oxidation	**1**

Q25.

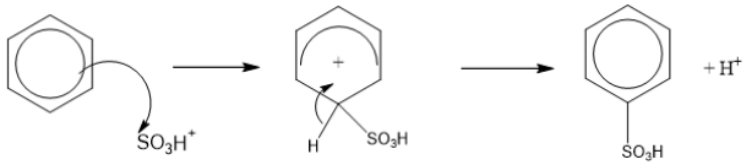
(a)(i)	HBr / hydrogen bromide [1]	1
(a)(ii)	 **M1** curly arrow to Br^+ **AND** curly arrow from C–H bond as shown [1] **M2** correct intermediate [1]	2
(a)(iii)	**electrophilic substitution** [1]	1
(b)(i)	reagent: chloroethane / bromoethane / iodoethane **OR** formula [1] catalyst: $FeCl_3$ / $AlCl_3$ etc. [1]	2

(b)(ii)	 [1] **ALLOW** C_6H_5COONa	1
(b)(iii)	step 3 = $LiAlH_4$ [1] step 4 = Pt **AND** H_2 [1]	2
(b)(iv)	5 / five [1]	1

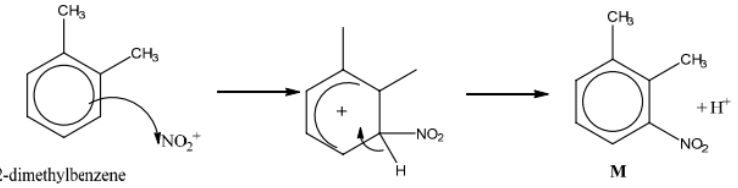
Q26.

(b)(i)	curly arrow from within hexagon towards NO_2+ **AND** curly arrow from C–H bond to within hexagon [1]  intermediate [1]	2
(b)(ii)	electrophilic substitution [1]	1
(b)(iii)	conc nitric acid and sulfuric acid [1] $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ **OR** [1] $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + SO_4^{2-}$ $2HNO_3 + H_2SO_4 \rightarrow 2NO_2^+ + H_2O + SO_4^{2-}$ $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$	2

Q27.

(a)(i)	**M1**: reduction / hydrogenation **M2**: H_2 + Ni / Pt catalyst	**2**
(a)(ii)	**M1**: benzene (**120°**) and cyclohexane (**109.5°**) **M2**: as π-bonds are transformed into σ-bonds	**2**
(b)(i)	 **M1**: first curly arrow to the sulfur atom **M2**: intermediate shown **M3**: 2nd curly arrow and H^+ formed / lost	**3**
(b)(ii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$	**1**
(c)	**M1**: $C_{12}H_{25}Br$ **and** halogen carrier e.g. $AlBr_3$ (+ heat) **M2**: electrophilic substitution	**2**

Q28.

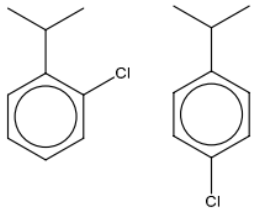
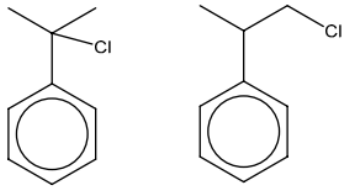
(b)(i)	$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2O + NO_2^+$ ***or*** $HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ [1]	**1**
(b)(ii)	 1,2-dimethylbenzene first curly arrow to N of NO_2^+ [1] correct intermediate [1] 2nd curly arrow **and** H^+ formed / lost [1]	**3**
(b)(iii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$ [1]	**1**
(b)(iv)	Sn + conc. HCl (+ heat) [1] reduction [1] **IGNORE** redox	**2**

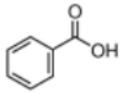
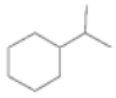
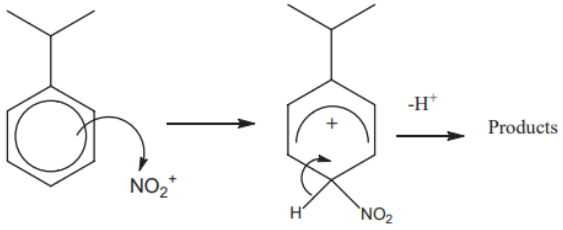
(d)	**3°** carbocations are more stable than **2°** carbocations [1] due to the methyl group acting as an electron donating group (leading to an increase in electron density on the cation stabilising it) [1]	**2**

Q29.

(a)	**M1:** CH_3COCl or ethanoyl chloride **M2:** $AlCl_3$ catalyst	**2**

Q30.

(a)(i)	**D** 2-chloropropane	**1**
	E hydrogen chloride	**1**
(a)(ii)	(Friedel-Crafts) alkylation	**1**
(b)(i)	$AlCl_3$ or $FeCl_3$	**1**
(b)(ii)		**1**
(b)(iii)	sunlight or UV **OR** T>100 °C	**1**
(b)(iv)		**1**

(c)	reaction with hot $KMnO_4$(aq) 	**1**
	reaction with H_2 + Ni, high pressure 	**1**
(d)		
	attacking species is NO_2^+	**1**
	curly arrow starting within hexagon and going to NO_2^+	**1**
	correct intermediate	**1**
	2nd curly arrow from C-H bond into ring	**1**