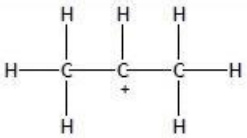
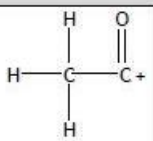
Mark Scheme

Q1.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	(identify the peak at the) highest/largest *m/z* value	Allow Peak (furthest) to the right/last peak on the spectrum Do not award the mark for "largest peak" / "highest peak" Ignore "parent ion" / molecular ion peak / References to *m/z* = 86	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	 (1)  (1)	Allow positive charge anywhere on structure Ignore open bonds Penalise non-displayed formulae once only Ignore brackets around the structure Penalise missing charge once only	(2)

Q2.

Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to the following points: • chlorine / Cl_2 **and** ultraviolet / uv (light)	Allow sunlight Ignore chlorine radicals Ignore temperatures Do not award presence of an additional catalyst Do not award hydrogen chloride / HCl / hydrochloric acid / HCl(aq)	(1)

Question Number	Answer	Mark
(ii)	The only correct answer is **C** (free radical substitution) ***A*** *is not correct because as ethane is saturated the reaction is a substitution* ***B*** *is not correct because as ethane is saturated the reaction is a substitution* ***D*** *is not correct because as ethane has no bonds with significant polarity the reaction is not nucleophilic*	**(1)**

Question Number	Answer	Additional Guidance	Mark
(iii)		Allow radical dots anywhere on the radical species throughout	**(3)**
	• chloroethane reacts with a chlorine radical OR	$CH_3CH_2Cl + Cl\bullet \rightarrow \bullet CH_2CH_2Cl + HCl$ or $CH_3CH_2Cl + Cl\bullet \rightarrow CH_3CHCl\bullet + HCl$ Allow $C_2H_5Cl + Cl\bullet \rightarrow C_2H_4Cl\bullet + HCl$	
	both correct structure formulae of the products **including** identification of which is which **(1)**	CH_3CHCl_2 1,1-dichloroethane CH_2ClCH_2Cl 1,2-dichloroethane	
	• formation of 1,1-dichloroethane via radical mechanism OR	$CH_3CHCl\bullet + Cl\bullet \rightarrow CH_3CHCl_2$ or $CH_3CHCl\bullet + Cl_2 \rightarrow CH_3CHCl_2 + Cl\bullet$ Ignore reactions of $C_2H_4Cl\bullet$	

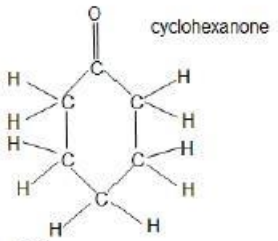
	overall equation for the formation of 1,1-dichloroethane **(1)**	$CH_3CH_2Cl + Cl_2 \rightarrow CH_3CH_2Cl_2 + HCl$	
	• formation of 1,2-dichloroethane via radical mechanism OR	•CH_2CH_2Cl + Cl• → CH_2ClCH_2Cl or •CH_2CH_2Cl + Cl_2 → CH_2ClCH_2Cl + Cl• Ignore reactions of C_2H_4Cl•	
	equation for the formation of 1,2-dichloroethane **(1)**	$CH_3CH_2Cl + Cl_2 \rightarrow CH_2ClCH_2Cl + HCl$ If M2 and M3 are not scored allow (1) for a balanced equation for the reaction of C_2H_4Cl• with Cl• or Cl_2 to form $C_2H_4Cl_2$ (examples shown) C_2H_4Cl• + Cl• → $C_2H_4Cl_2$ or C_2H_4Cl• + Cl_2 → $C_2H_4Cl_2$ + Cl•	

Question Number	Answer	Additional Guidance	Mark
(iv)	An answer that makes reference to the following points: • 98 peak is due to $C_2H_4{}^{35}Cl_2^+$ **and** 102 peak is due to $C_2H_4{}^{37}Cl_2^+$ **(1)** • 100 peak is due to $C_2H_4{}^{35}Cl^{37}Cl^+$ **(1)**	Allow $C_2H_4{}^{35}Cl^{35}Cl^+$ Allow $C_2H_4{}^{37}Cl^{37}Cl^+$ Allow structural formulae of the molecular ions of either 1,1- or 1,2-dichloroethane or both Allow structures with the positive charge anywhere including outside of brackets of any type. Penalise omission of + once only	**(2)**

Question Number	Answer	Additional Guidance	Mark
(v)	An answer that makes reference to the following point • ^{35}Cl and ^{37}Cl atoms are in a 3:1 ratio	Answer must refer to the isotopes of chlorine. Ignore comments about isotopes of carbon or hydrogen or just isotopes Allow a larger proportion of chlorine atoms are chlorine-35 than chlorine-37 Allow the ratio of the peak heights to be 9:6:1 Allow the abundance of chlorine- 35 and chlorine-37 are different Allow there are two isotopes of chlorine	(1)

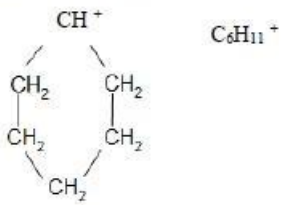
Question Number	Answer	Additional Guidance	Mark
(vi)	An answer that makes reference to the following points: Either • the peaks are formed by fragments containing both chlorine atoms attached to one carbon atom or the fragments are $CH^{35}Cl^{37}Cl^{+}$, $CH^{35}Cl_2^{+}$ and $CH^{37}Cl_2^{+}$ **(1)** • this fragmentation / configuration is only possible from 1,1-dichloroethane / is not possible from 1,2-dichloroethane **(1)** Or • the peaks at 83, 85 and 87 represent the loss of a CH_3 group **(1)** • only 1,1-dichloroethane has a methyl group **(1)**	Allow a diagram showing the fragmentation of 1,1- dichloromethane to form a fragment containing one carbon and two chlorine atoms Allow the use of molecule instead of fragment Do not award fragments where the number of hydrogens on the carbon changes Allow just $CHCl_2^{+}$ Do not penalise the absence of the positive charge Do not award fragments where the number of hydrogens changes to allow for the different masses Allow only 1,1-dichloroethane has two chlorines on the same carbon / 1,2-dichlorethane does not have two chlorines on the same carbon Allow the peaks are 15 below the molecular ion values so they represent the loss of a CH_3 group	**(2)**

Q3.

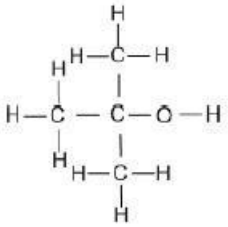
Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to the following points: • name (1) • displayed formula (1)	Example of displayed formula  Allow CH_2 groups Allow skeletal formula Do not award molecular formula	(2)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following points: • O-H bond (stretching) 3750 – 3200 cm^{-1} in cyclohexanol is not present in cyclohexanone /disappears (when cyclohexanol reacts). (1) • C=O bond (stretching) 1720 – 1700 cm^{-1} appears in cyclohexanone (1)	Allow a range within the specified range Allow 1725 – 1700 cm^{-1} Do not allow 1740 – 1720 cm^{-1} (aldehyde)	(2)

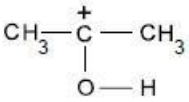
Question Number	Answer	Additional Guidance	Mark
(iii)	• highest $m/z = M_r = 98$	Check, answer may be shown on mass spectrum Do not accept just '98' with no supporting evidence Allow peak furthest to the right / molecular ion peak is 98	(1)

Question Number	Answer	Additional Guidance	Mark
(iv)	• fragment (1) • charge (1)	Examples of fragment structure  Allow charge anywhere on fragment, including outside brackets around the fragment Allow straight chain fragment provided it has the correct number of C and H atoms	(2)

Q4.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)		display all three methyl groups allow –OH do not award C-H-O	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
(b)(i)	An answer that makes reference to one of the following: molecular ion/molecule fragments/is unstable		(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)		allow + charge on any part of the ion/outside the structure but + must be shown allow displayed/structural/skeletal/ molecular formulae or any combination of these.	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
(c)(i)	• calculation for bonds broken in the alcohol (*) **(1)** • calculation for bonds broken in oxygen **and** total energy for bonds broken(**) **(1)** • calculation for bonds made(***) **(1)** • calculation of $\Delta_c H$ (2-methylpropan-2-ol) with sign **(1)**	Example of calculation 3(C-C) + 9(C-H) + (C-O) + (O-H) =(3x347) + (9x413) + 358 + 464 = (+)5580 (kJ mol^{-1}) 6(O=O) = (6 x 498) = (+)2988 (kJ mol^{-1}) total = + 5580 + 2988 = (+)8568 (kJ mol^{-1}) TE from ans * M1 + 2988 = 8(C=O) + 10(O-H) = (8x805) + (10x464) = -11080 (kJ mol^{-1}) = +8568 – 11080 = -2512 (kJ mol^{-1}) allow TE for answer(**) + answer(***) units not required but if given they must be correct correct final answer with no working scores 4 marks	**(4)**

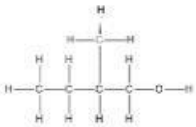
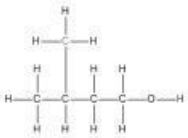
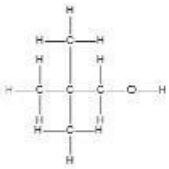
Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: • incomplete combustion **(1)** • $\Delta_c H$ (2-methylpropan-2-ol) will be less negative /less exothermic than data book value **(1)**	mark independently do not award just lower/smaller/decreases/ more positive allow reduce the magnitude (of the value)	**(2)**

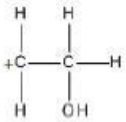
Question Number	Acceptable Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to the following points: $\Delta_c H$ figures are at 298 K /data book bond energies refer to gaseous state and water and/or 2-methylpropan-2-ol are/is (both) liquid(s) (at 298 K)	allow just liquid involved do not award data book bond energies are mean (values)/not specific to 2-methylpropan-2-ol	(1)

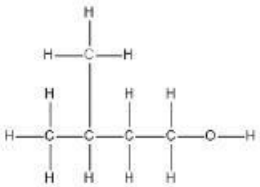
Q5.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)	• calculation of empirical formula (1) • uses molecular ion to prove molecular formula (1) or • calculation of percentage of each element in compound all 3 correct scores (2) any 2 correct scores (1) or • calculation of the number of atoms of each element directly all 3 correct scores (2) any 2 correct scores (1)	Example of calculation C : H : O $\frac{68.2}{12}$ $\frac{13.6}{1}$ $\frac{18.2}{16}$ = 5.68 13.6 1.14 = 5 12 1 Use of 88 to show molecular formula is $C_5H_{12}O$ e.g. M_r is (5x12) + (12x1) + 16 = 88 or states that M_r of empirical formula is 88 or % C = $\frac{5 \times 12 \times 100}{88}$ = 68.2 % H = $\frac{12 \times 1 \times 100}{88}$ = 13.6 % O = $\frac{1 \times 16 \times 100}{88}$ = 18.2 or C atoms = $\frac{68.2 \times 88}{100 \times 12}$ = 5 H atoms = $\frac{13.6 \times 88}{100 \times 1}$ = 12 O atoms = $\frac{18.2 \times 88}{100 \times 16}$ = 1	(2)

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	• (**X** is a) primary/ 1° (alcohol)		(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	   	Allow alcohols in any order Allow CH_3 / OH Allow slip of 1 H missing from 1 alcohol / 1 C-C bond missing Ignore names, even if incorrect Penalise O-H-C- / -C-H-O at end of molecule once only If no other mark is given, allow (2) for 4 correct skeletal / structural formulae or any combination of these or (1) for 3 correct Allow (2) for displayed formulae of pentan-2-ol, pentan-3-ol and 3-methylbutan-2-ol if secondary alcohol in (b)(i), or (1) for any two of those	(3)
	• 4 correct (3) • 3 correct (2) • 2 correct (1)	If no other mark awarded and if (b)(i) is blank or incorrect, allow (2) for any 4 different alcohols with formula $C_5H_{12}O$, (1) for 3 alcohols	

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iii)	• 	Allow structural formula or any combination of displayed and structural formula Allow + anywhere on structure or outside of a formula in a bracket Do not allow $C_2H_5O^+$/$C_2H_4OH^+$ Do not allow missing charge Allow CH_3C^+HOH if secondary alcohol identified in (b)(i)	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iv)	•  (1) • because this is the **only** alcohol with a branched chain <u>and</u> forms $CH_2OHCH_2^+$ / $C_2H_4OH^+$ / peak at 45 / fragment identified in (b)(iii) (1)	Allow any type of identification, including name 3-methylbutan-1-ol Ignore incorrect name with correct structure Conditional on correct identification Ignore missing charge on fragment Allow reasons why the others are not correct e.g. not pentan-1-ol as it is not branched <u>and</u> not 2-methylbutan-1-ol or 2,2-dimethylpropan-1-ol as they do not form $CH_2OHCH_2^+$ If secondary alcohol identified in (b)(i): Allow 3-methylbutan-2-ol (1) as it is the only alcohol with a branched chain that forms CH_3C^+HOH (1)	(2)

Q6.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	furthest peak to right/ highest *m / z* = 154	Ignore just ' highest peak' may be shown on spectrum alone provided 154 stated Allow parent ion/molecular ion/last peak at 154 Must see the figure 154 in text or on graph	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	$C_5H_9^+$ / $[C_5H_9]^+$	+ charge is essential, allow charge anywhere on the ion/ outside / inside brackets Allow displayed/structural/skeletal formula or any combination of these. Ignore name of ion even if incorrect (Correct name: 2-methylbut-2-ene ion)	(1)

Q7.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• molecular ion is at m/z = 168 **or** 168 is equal to the M_r of **D** / twice the empirical formula / 2 x 84 / 168 ÷ 2 = 84 / M_r of empirical formula is 84 **(1)** • (so the molecular formula is) $C_6H_4N_2O_4$ **(1)**	Allow 168 shown on spectrum along with the rest of the explanation Do not award M1 for any other value Stand alone mark Ignore structural / displayed / skeletal formula Do not award $C_6H_4N_2O_4^+$	**(2)**

Q8.

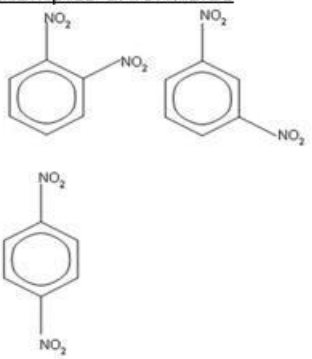
Question Number	Answer	Additional Guidance	Mark
(i)	• calculate percentage of carbon **(1)** • division of all percentages by atomic mass **(1)** • find simplest ratio and give empirical formula **(1)**	Example of calculation: 100 – (34.0 + 54.5) = 11.5% Cl 34.0 / 35.5 = 0.95775 F 54.5 / 19.0 = 2.8684 C 11.5 / 12.0 = 0.95833 Cl (0.95775 / 0.95775 = 2.9949) = 1 F (2.8684 / 0.95775 = 2.9949) = 3 C (0.95833 / 0.95775 = 2.9949) = 1 So CF_3Cl / $CClF_3$ Allow any order Correct answer with no working scores (3) Ignore significant figures throughout.	**(3)**

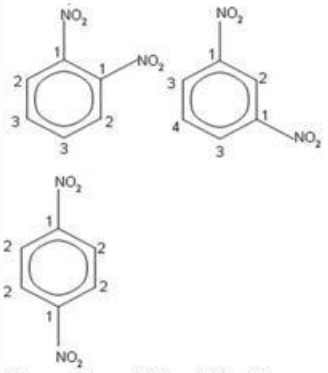
Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following points: • molecular ion peak at 104 / 106 (which matches the mass of the empirical formula)	Do not award statements stating that the molecular ion peak is at 105 or at 104.5, unless this is a calculated average.	(1)

Question Number	Answer	Additional Guidance	Mark
(iii)	• correct ion	CF_3^+ Do not award CF_3 with no plus.	(1)

Q9.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	$C_6H_4^+$	Allow $H_4C_6^+$ Do not award just C_6H_4	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	• 3 correct formulae **(2)**	Examples of formulae  Allow (1) for any 2 correct formulae Allow (2) for three disubstituted benzenes with incorrect substituents / (1) for any two disubstituted benzenes with incorrect substituents Allow incorrectly displayed formulae of NO_2 groups **In (c)(ii) and (iii):** Allow Kekule structures Allow hydrogen atoms shown on benzene Ignore connectivity of NO_2 groups Penalise missing circle in benzene once only	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(iii)	• **D** identified as 1,3-dinitrobenzene **and** 4 different carbon environments labelled **(1)** • 3 different carbon environments labelled on 1,2-dinitrobenzene **(1)** • 2 different carbon environments labelled on 1,4-dinitrobenzene **(1)**	 Examples of identification These labels may be shown on the structures in (c)(ii) The identification of **D** can be assumed if it is the only structure with 4 carbon environments labelled Allow any form of identification of the carbon environments e.g. numbers, letters, equivalent carbon environments circled TE on disubstituted benzene substituents in (ii) Penalise only half the carbon environments labelled once only	(3)

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 Answer	Additional Guidance	Mark
(i)	• relative molecular mass	170 May be shown on graph Do not award peak at 171	**(1)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	• $C_{12}H_{26}$	Allow TE from (i) provided H/C could exist eg DNA 57 = C_4H_9 Allow $C_{13}H_{14}$	**(1)**