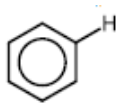
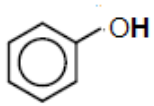
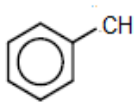
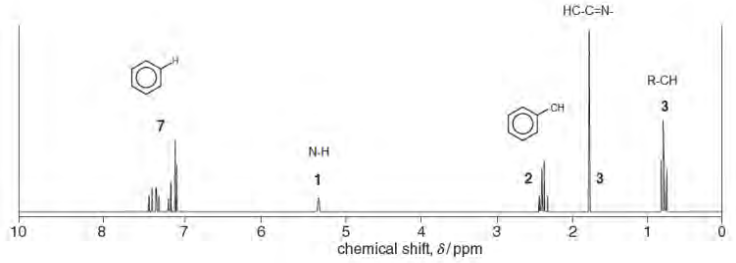
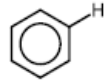
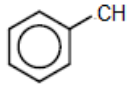
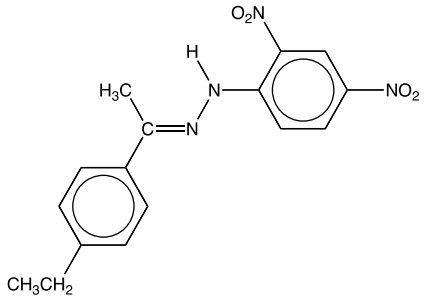
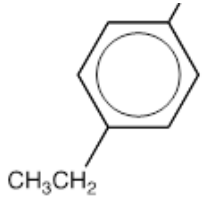
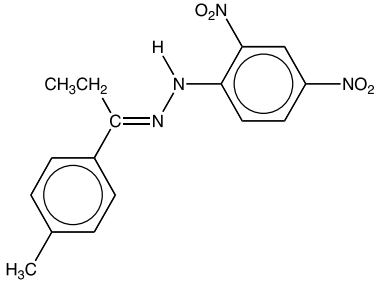
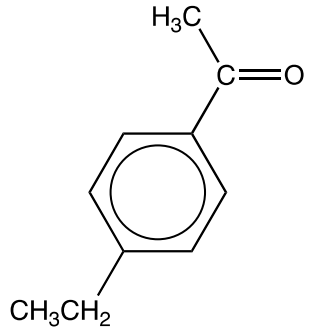
Question			Answer	Mark	Guidance
1	(a)		magnetic resonance imaging/providing diagnostic information/body scanners. ✓	1	**ALLOW** MRI/scanning internal structures e.g. brain **ALLOW** detection of tumours/cancer/haemorrhage/aneurysm **IGNORE** reference to drugs, chemicals or functional groups **IGNORE** analysis of blood **DO NOT ALLOW** CT scan/CAT scan
	(b)	(i)	Radio (waves) ✓	1	**ALLOW** a value in the range 60 – 900 MHz
		(ii)	The solvent does not have any hydrogen/H/protons ✓	1	**ALLOW** to prevent (^{1}H nuclei from) the solvent from interfering with the NMR spectrum **ALLOW** does not show on the spectrum **ALLOW** no peak/signal (from solvent) **IGNORE** volatility
4	(c)		14 ✓	1	
	(d)		**NMR analysis** (5 marks) **M1** Peaks between (δ) 7.1 and 7.5 (ppm) **OR** Relative peak area of 7 **OR** Multiplet =  ✓ **M2** Peak at 5.2/5.3	7	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **IGNORE** analysis of ^{13}C spectrum Each peak can be identified from its δ value ± 0.2 ppm **ALLOW** (seven) benzene ring protons **OR** aromatic protons **DO NOT ALLOW** benzene ring without reference to protons **ALLOW** C_6H_6 **IGNORE** 

Question			Answer	Mark	Guidance
			OR Relative peak area of 1 = N-**H** ✓		**IGNORE** O-**H** , CON**H** **AND** C=C**H**
			M3 Peak at 2.3/2.4 **OR** Relative peak area of 2 **OR** Quartet =  **OR** $C_6H_5CH_2$ ✓		**ALLOW** quadruplet **IGNORE** C**H**C=O **AND** **H**C-N
			M4 Peak at 0.7/0.8 **OR** Triplet = R-CH **OR** R-CH_3 ✓		**DO NOT ALLOW** triplet = CH_3 **OR** CH_2CH_3
			M5 Triplet (at δ 0.7) **AND** quartet (at δ 2.3) = CH_2CH_3 **OR** triplet at (δ) 0.7 shows (C with) 2 adjacent Hs/protons = CH_2CH_3 **OR** quartet (at δ 2.3) shows (C with) 3 adjacent Hs/protons = CH_2CH_3 ✓		This also scores **M4** if triplet is linked to R-CH_3 **ALLOW** CH_3CH_2 described as R-CH_3 and 2 adjacent H **OR** –CH_2- and 3 adjacent H The information can be presented on the spectrum or in a table.

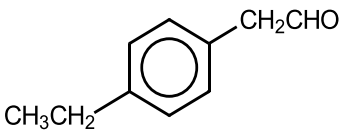
Question	Answer	Mark	Guidance
	✎ **QWC**: **triplet** or **quartet** spelled correctly in the correct context for **M5**		 **IGNORE** peak in the range 1.6–2.2 = HC–C=N– because this information is given in the question. H_3C-C=N- scores one mark for the identification of **R^1** or **R^2** (see below)

Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton
7.1 – 7.5	7	Multiplet	
5.3	1	Singlet	N-H
2.3/2.4	2	Quartet	
1.7/1.8	3	Singlet	HC-C=N-
0.7/0.8	3	triplet	R-CH/R-CH_3

Question	Answer	Mark	Guidance
	Identification of R^1 and R^2 (2 marks) **Orange precipitate L** Correct structure scores 2 marks  **R^1** or **R^2** = **-CH_3** ✓ **R^1** or **R^2** =  ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous Marks are for structure of R^1 and R^2 **IGNORE** errors in the rest of the structure **ALLOW** 1 mark for CH_3 and CH_3CH_2 swapped, i.e. the following structure  **ALLOW** H_3C-C=N- **MUST BE** 1,4-disubstituted (14 carbon environments in the ^{13}C NMR spectrum

Question			Answer	Mark	Guidance
	(e)		**Carbonyl compound K**  ✓	1	**ALLOW ECF** from incorrect compound **L** Must be a correct carbonyl structure
			Total	**12**	

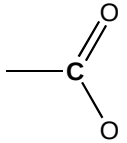
Question			Answer	Mark	Guidance
2	(a)		TMS/tetramethylsilane (which is the) standard (for chemical shift measurements) ✓	1	**ALLOW** $(CH_3)_4Si$ **ALLOW** TMS is the reference **OR** TMS has δ = 0 (ppm) **OR** for calibration **OR** for comparison **IGNORE** solvent, unreactive, volatile, it gives a sharp peak
	(b)		**NMR analysis = 5 marks** **M1:** Peak(s) at (δ) 9.7 = CHO ✓ **M2:** Peak(s) at (δ) 7.1 = C_6H_4 ✓ **M3:** Triplet at (δ) 1.3/peak at 1.3 **AND** quartet (at δ 2.6)/ peak at 2.6 = CH_2CH_3 ✓ **M4:** Triplet at (δ) 9.7/peak at 9.7 **AND** doublet (at δ 3.7)/peak at 3.7 = CH_2CHO ✓	9	**NOTE**: Each peak can be identified from: • its δ value • a range, *e.g.* "the peak between 0.8 and 2.0" • its relative peak area (beware two peaks with 2 protons) • its splitting (beware two triplets) • labelling on the spectrum **ALLOW** CH_2CHO/aldehyde **IGNORE** reference to phenol **ALLOW** (four) benzene ring proton(s) **IGNORE** reference to phenol **M3** and **M4** Look for a clear link (using words or diagrams) between the two peaks

Question			Answer	Mark	Guidance
			M5: **(**n+1 rule) Any one of the following • triplet at (δ) 1.3 shows (C with) 2 adjacent Hs/protons **OR** adjacent CH_2 *(because of splitting: so triplet)* • quartet at (δ 2.6 shows) (C with) 3 adjacent Hs/protons **OR** adjacent CH_3 • triplet at (δ) 9.7 shows (C with) 2 adjacent Hs/protons **OR** adjacent CH_2 • doublet at (δ 3.7 shows) (C with) 1 adjacent H/proton **OR** adjacent CH ✓ ✎ **QWC**: **triplet** spelled correctly in the correct context once		**ALLOW** a response that implies a splitting into three for a triplet/into two for a doublet etc. **ALLOW** "neighbouring" Hs for "adjacent to" Hs **IGNORE** other comments about splitting once **M5** has been awarded **DO NOT ALLOW** one of **M3** or **M4 or M5** if triplet not seen
			Aldehyde structure = 4 marks  ✓✓✓✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **IF** structure contains C_6H_4 ✓ **IF** structure contains C_6H_4 **AND** the organic structure contains CH_3CH_2 directly attached to the benzene ring **OR** contains CH_2CHO directly attached to the benzene ring ✓✓ **IF** structure has formula $C_{10}H_{12}O$ **AND** structure contains C_6H_4 **AND** the structure contains CH_3CH_2 **AND** contains CH_2CHO **AND** 1,2 **OR** 1,3 substituted ✓✓✓

Question			Answer	Mark	Guidance
					IF structure has formula $C_{10}H_{12}O$ **AND** structure contains C_6H_4 **AND** the structure contains CH_3CH_2 **AND** contains CH_2CHO **AND** 1,4 substituted ✓✓✓✓ (use of ^{13}C data)
			Total	**10**	

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td>3</td><td>(a)</td><td></td><td>
<table>
<tr><td></td><td>C</td><td></td><td>O</td></tr>
<tr><td>%</td><td>73.15%</td><td></td><td>19.48%</td></tr>
<tr><td>mol</td><td>6.10</td><td></td><td>1.22</td></tr>
<tr><td>ratio</td><td>5</td><td></td><td>1</td></tr>
</table>
molar ratio (C:H:O) = 6.10 : 7.37 : 1.22 OR = 5:6:1
OR empirical formula = C_5H_6O ✓
M_r is 164 so molecular formula = $C_{10}H_{12}O_2$ ✓
</td><td>2</td><td>ALLOW alternative method
73.15% × 164 = 120 } ratio = 10 OR 5
7.37% × 164 = 12.1 } 12 OR 6
19.48% × 164 = 31.9 } 2 OR 1
✓ ✓

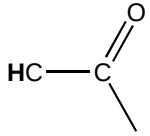
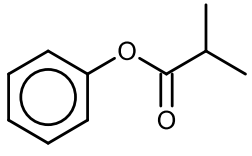
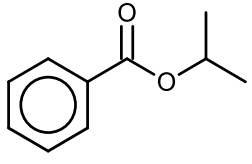
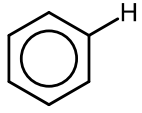
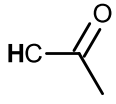
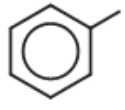
This mark is for some evidence of using M_r, which is twice the value that you would obtain from the empirical formula</td></tr>
<tr><td></td><td>(b)</td><td></td><td>seven ✓</td><td>1</td><td></td></tr>
<tr><td></td><td>(c)</td><td>(i)</td><td>TMS is the standard (for chemical shift measurements) ✓</td><td>1</td><td>ALLOW TMS is the reference OR for calibration
IGNORE unreactive / volatile / it gives a sharp peak
ALLOW TMS = 0 ppm / TMS is used for comparison</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>(relative) number of protons/hydrogens in each environment / peak / region
OR three proton environments with protons in ratio 5:1:6 ✓</td><td>1</td><td>ALLOW (relative) number of each type of proton/hydrogen
IGNORE number of protons in the compound</td></tr>
<tr><td></td><td></td><td>(iii)</td><td>^{13}C NMR Analysis (1 mark)

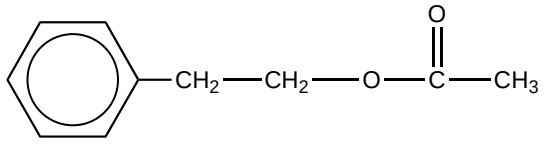
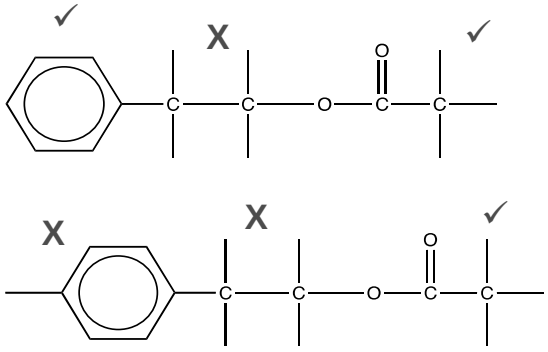
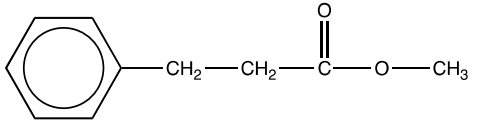
The peak at 185ppm suggests an ester group /
 

AND one of the following:

The peaks between 120ppm and 160ppm indicate a benzene ring
OR the peaks at 18ppm AND 36ppm suggest C-C ✓</td><td>7</td><td>FULL ANNOTATIONS WITH TICKS, CROSSES,CON ETC MUST BE USED

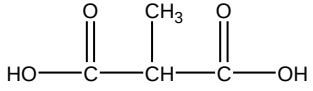
Inclusion of an incorrectly assigned ^{13}C peak CONS M1</td></tr>
</table>

Question	Answer	Marks	Guidance
	^{1}H ANALYSIS (4 marks) Doublet / peak at 1.2 shows R-C**H AND** 6 H's / 2 CH_3 (in this environment) ✓ Multiplet / septet / heptet / peak split into 7 / peak at 2.7ppm indicates  ✓ The doublet suggests that two CH_3 groups are attached to a CH **OR** the multiplet / septet / heptet suggests that the CH group is attached to two CH_3 groups ✓ ✎ **QWC** must spell **one** of *multiplet*, *septet*, *heptet* **OR** *doublet correctly* Peak at 7.3ppm indicates a benzene ring **AND** 5 H's ✓ **Compound identification (2 marks)** **IF** identified as  then **two** marks ✓✓ **IF** identified as  then **one** mark ✓		Candidates may quote δ values as ranges taken from Data Sheet, so **ALLOW** tolerance (ppm) eg  6.5–8 aromatic  2.0–2.9 carboxyl 0.7–2.0 alkyl R—C**H** **ALLOW** peaks labelled on the spectrum If **QWC** word is not used, MAX 3 for proton NMR **ALLOW** C_6H_5 **IGNORE** reference to phenol Allow  as C_6H_5 if they state that the benzene ring has 5 H's
	Total	**12**	

Question			er	Marks	Guidance
4	(a)	(i)	(number of esters) from number of peaks/retention times **AND** (proportions) from (relative) peak areas ✓	1	**BOTH** points for 1 mark **ALLOW** peak heights **OR** sizes of peaks
		(ii)	(Some esters may have) same retention time ✓	1	**ALLOW** (very) similar retention times **ALLOW** some esters come out at same time
	(b)		**Ester structure 3 marks**  ✓✓ **STICKS** IF there are sticks are shown in CH_2CH_2 **OR** in CH_3 **DO NOT AWARD** when first seen **DO NOT ALLOW** sticks on the benzene ring, *Sticks on benzene ring **must** be interpreted as methyl groups* e. 	3	***ANNOTATIONS MUST BE USED*** --- **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **NO ECF** for structure --- **IF** the structure is **NOT** fully correct, award the following marks: **IF ESTER** shown **AND** contains **ONE** of the following: C_6H_5 **OR** $CH_3C{=}O$ **OR** CH_2CH_2 1 mark ✓ **IF ESTER** shown **AND** contains **TWO** of the following: C_6H_5 **OR** $CH_3C{=}O$ **OR** CH_2CH_2 2 marks ✓✓ **IF ESTER** contains **C_6H_5 AND** CH_2CH_2 **BUT** ester link is reversed 2 marks ✓✓  **DO NOT ALLOW** CH_2CH_2 with H on any adjacent Cs e.g. **DO NOT ALLOW** $CH_2CH_2CH_3$, $CH_2CH_2CH_2$, etc. **IGNORE** any name

Question			er	Marks	Guidance
			Mass spectrum 164 linked directly to molecular formula of $C_{10}H_{12}O_2$ **OR** an ester structure with formula $C_{10}H_{12}O_2$ ✓ *This direct link could be seen anywhere in the response* e.g. 164 is $C_{10}H_{12}O_2$ e.g. $C_{10}H_{12}O_2$ = 120 + 12 + 32 = 164 e.g. (164 – 44/COO) = 120; 120 = C_9H_{12} --- **NMR analysis** **QWC** *Triplet must be spelled correctly and used in correct context* Triplet at 2.8 ppm shows an adjacent CH_2 **AND** Triplet at 4.4 ppm shows an adjacent CH_2 ✓ Peak at 2.2 shows C**H$_3$**–C=O **OR** Peak at 2.2 shows HC–C=O **AND 3** Hs of this type **OR** Peak at 2.2 shows HC–C=O **AND** adjacent to (C with) no Hs✓ Peak at 7.3 shows **5 aromatic Hs OR** shows C_6**H$_5$** ✓ *5Hs required* Peak at 2.8 shows C_6H_5–C**H OR** C_6H_5–C**H$_2$** ✓ *Just require* C_6H_5*–CH as testing environment here* Peak at 4.4 due to **H**C–O **OR H$_2$**C–O ✓ *Just require HC–O as testing environment here*	1 --- 5	***Check back for any responses added to spectrum*** ***Credit responses throughout provided that it is clear which peaks are being referred to*** --- **ALLOW** tolerance on δ values: ± 0.2 ppm Throughout**, ALLOW** for H: proton **OR** H^+ For adjacent CH_2, **ALLOW** (C) adjacent to 2 Hs **ALLOW** There are 2 triplets **AND** triplet shows an adjacent CH_2 For peak at (δ =) 2.2 **ALLOW** singlet **OR** peak labelled 3 For peak at (δ =) 7.3 **ALLOW** peak labelled 5 **OR** multiplet **OR** quintet **OR** hextet **OR** heptet For peak at (δ =) 2.8 **ALLOW** triplet at 2.8 For peak at (δ =) 4.4 **ALLOW** triplet at 4.4
			Total	**11**	

Question			Answer	Mark	Guidance
5	(a)		idea of separating (the components/compounds) ✓ idea of (identifying compounds) by comparison with a (spectral) database ✓	2	**ALLOW** (identifies compounds) using fragmentation (patterns)/fragment ions (but **IGNORE** molecular ions) ✓ **Note**: Each marking point does **not** need to be linked to GC or MS (The question asks about GC–MS as a combined technique)
	(b)	(i)	54.2% of 118 **OR** 54.2/118 x 100 = 64/63.96 (hence there are 4 oxygens) ✓ 118 – 64 = 54 hence 4 carbon (48) and 6 hydrogen (6) ✓	2	**IGNORE** calculation that proves that $C_4H_6O_4$ has a molar mass of 118 (ie 12 x 4 + 6 x 1 + 16 x 4) **ALLOW** 64/118 x 100 = 54.2% for 1st mark **IGNORE** method using empirical formula **ALLOW** any reasonable working leading to 4C **Note**: 54.2(%) ÷ 16 would **not** get the 1st mark but the answer could be used to get the 2nd mark
		(ii)	carboxyl group **OR** carboxylic acid ✓ must be **name** (in question)	1	**IGNORE** working, e.g. O–H, C=O, C–O on IR spectrum

Question			er	Mark	Guidance
5	(c)	(i)	***Chemical shifts*** Any **two** peaks identified for **1 mark** ✓ peak at δ = 0.8 ppm due to R–C**H** / CH_3CH peak at δ = 3.4 ppm due to **H**C–C=O peak at δ = 11 ppm due to COO**H** / carboxylic acid ***Splitting*** quartet shows adjacent CH_3 **OR** 3 adjacent Hs ✓ doublet shows adjacent CH **OR** 1 adjacent H ✓ ***Identification***  ✓	**1** **2** **1**	***ANNOTATIONS MUST BE USED*** **CHECK SPECTRUM** for responses **ANNOTATE** with '^' For peak at (δ =) 0.8 (ppm), **ALLOW** doublet and vice versa For peak at (δ =) 3.4 (ppm), **ALLOW** quartet ' and vice versa For peak at (δ =) 11 (ppm), **ALLOW** singlet and vice versa **ALLOW** peak at δ = 2.4 ppm for peak at δ = 3.4 ppm **ALLOW** tolerance on δ values: ± 1 ppm For quartet, **ALLOW** quadruplet **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous)
		(ii)	$(CD_3)_2SO$ / D / It does **not** absorb **OR** does not give a peak ✓	**1**	**ALLOW** $(CD_3)_2SO$ / does **not** contain H **ALLOW** undeuterated solvents would absorb **OR** give peaks **ALLOW** responses in terms of $(CH_3)_2SO$ producing peaks …… **but IGNORE** number of peaks
		(iii)	TMS is the standard (for chemical shift measurements) ✓	**1**	**ALLOW** TMS is the reference **OR** TMS has δ = 0 (ppm) **OR** for calibration **IGNORE** unreactive, volatile, it gives a sharp peak
		(iv)	peak at δ = 11.0 (ppm) disappears ✓	**1**	**ALLOW** COOH (peak) disappears **ALLOW** OH (peak) disappears
			Total	**12**	