37. Analytical techniques

37.4 Proton (1H) NMR spectroscopy

Paper 4

Marking Scheme

Q1.

(e)

	peaks
Dewar benzene	2
Ladenburg benzene	1
delocalised benzene	1

1

Q2.

(c)(i)

ester	number of peaks seen in proton (^{1}H) NMR	number of peaks seen in carbon-13 NMR
B	5	6
C	4	5

M1 row 1 correct
M2 row 2 correct

2

(c)(ii) A and B

1

Q3.

(c)(i) CHI_3 / triiodomethane

1

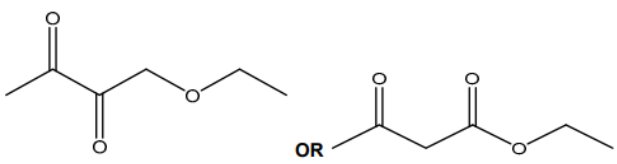
(c)(ii)

chemical shift (δ)	splitting pattern	number of ^{1}H atoms responsible for the peak	number of protons on adjacent carbon atoms
1.15	triplet	3	2
2.25	singlet	3	0
3.60	singlet	2	0
3.95	quartet / quad ruplet	2	3

mark as any three [1] any six [2] any nine [3] all twelve [4]

4

(c)(iii)



1

Q4.

(f)	CH_2 and CH only in column one [1] CH_2 gives a doublet, CH gives a triplet [1] doublet due to 1 proton on neighbouring carbons triplet due to 2 protons on neighbouring carbons [1]	3

Q5.

(e)(i)	<table><tr><th>chemical shift (δ)</th><th>splitting pattern</th><th>number of ^1H atoms responsible for the peak</th><th>number of protons on the adjacent carbon(s)</th></tr><tr><td>1.4</td><td>doublet</td><td>3</td><td>1</td></tr><tr><td>3.5</td><td>singlet</td><td>3</td><td>0</td></tr><tr><td>4.0</td><td>quartet</td><td>1</td><td>3</td></tr></table> Three correct for one mark, six correct for two marks, nine correct for three marks.	3
(e)(ii)	one extra peak for NH_2 group seen in $CDCl_3$, **AND** H exchanged for D in D_2O	1

Q6.

(c)(i)	(because solvent / D / $CDCl_3$) doesn't give a signal / peak / absorption **ORA**	1

(c)(ii)	<table><tr><th>chemical shift δ / ppm</th><th>environment of proton</th><th>splitting pattern</th><th>number of ^1H atoms responsible for the peak</th></tr><tr><td>1.2</td><td>alkyl / alkane / (R-)$CH_{(3)}$</td><td>triplet</td><td>3</td></tr><tr><td>2.8</td><td>alkyl next to C=O / $CH_{(2)}C=O$</td><td>triplet</td><td>2</td></tr><tr><td>3.7</td><td>alkyl next to electronegative atom / $CH_{(2)}$-Cl</td><td>triplet</td><td>2</td></tr><tr><td>3.9</td><td>alkyl next to electronegative atom / $CH_{(2)}$-O</td><td>quartet / quadruplet</td><td>2</td></tr></table> Any three [1], any six [2], any nine [3], all twelve [4]	4
(c)(iii)	(δ = 3.9) three H on neighbouring / adjacent C / it's next to a CH_3	1

Q7.

(d)(ii)		3

environment	δ	splitting pattern	explanation for SP
CH_3	0.9-1.7	doublet	1H on neighbouring C / next to CH / one vicinal proton
CH	2.2-3.0	multiplet / heptet / septet	6H on neighbouring C / next to 2 x (CH_3) / six vicinal protons
COOH	9.0-13.0	singlet	

[1] for δ values
[1] for splitting
[1] for explanations

Q8.

(b)(i)	d values: 12, 4.4 [1] 5.0, 1.6 [1] splitting patterns: singlet, quartet / quadruplet, singlet, doublet [1]	3
(b)(ii)	TMS / tetramethylsilane [1]	1
(b)(iii)	$CDCl_3$ will not give an absorption / peak **OR** $CHCl_3$ will give an absorption / peak [1]	1

Q9.

(b)		1

	carbon-13 NMR	proton NMR
number of peaks in $CDCl_3$	4	5

Q10.

(b)	6	1

Q11.

(a)	TMS reference **OR** standard **OR** to define d = 0 D_2O solvent **OR** identification of **O-H / N-H** protons / group	**1**

(b)(i)	<table><tr><th>ketone</th><th>number of peaks observed in proton NMR spectrum</th><th>number of peaks observed in carbon-13 NMR spectrum</th></tr><tr><td>pentan-2-one</td><td>4</td><td>5</td></tr><tr><td>pentan-3-one</td><td>2</td><td>3</td></tr><tr><td>3-methylbutanone</td><td>3</td><td>4</td></tr></table> three for one mark, six for two marks	**2**
(b)(ii)	**M1** 3-methylbutanone **M2** 3-methylbutanone **AND** pentan-2-one	**2**

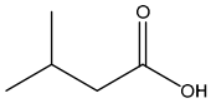
Q12.

(c)	4 [1] singlet, (two) triplet(s), multiplet (any order) [1]	
(d)(i)	**D** = $CH_3CH_2CO_2CH_2CH_3$ [1] **E** = $(CH_3)_2CHCO_2CH_3$	
(d)(ii)	O-CH_2 **labelled F** **AND** three protons on neighbouring **carbon** / adjacent CH_3	
(d)(iii)	**both CH_3 in** isopropyl group **labelled G** **AND** alkane / alkyl (protons)	

Q13.

(a)	C* marked on CH of T and nowhere else	**1**
(b)(i)	R – $C_6H_5CH_2COCH_2CH_3$ [1] 3.7 is $C_6H_5\mathbf{CH_2}COCH_2CH_3$ 2.5 is $C_6H_5CH_2CO\mathbf{CH_2}CH_3$ 1.0 is $C_6H_5CH_2COCH_2\mathbf{CH_3}$ [1]	**2**
(b)(ii)	singlet **and** no H on neighbouring C	**1**
(c)(i)	P and T	**1**
(c)(ii)	P	**1**
(d)	$CDCl_3$ or CCl_4	**1**
(e)	no difference **and** no protons that exchange with D	**1**

Q14.

(c)(i)		1

(c)(ii)	<table><tr><th>chemical shift (δ)</th><th>environment of proton</th><th>splitting pattern (words required)</th><th>number of ^1H atoms responsible for the peak</th></tr><tr><td>0.95</td><td>alkane / CH_3</td><td>doublet</td><td>6</td></tr><tr><td>1.90</td><td>alkane / CH **ALLOW** alkyne</td><td>multiplet</td><td>1</td></tr><tr><td>2.20</td><td>R / alkyl / CH_2 next to C=O / COOH</td><td>doublet</td><td>2</td></tr></table> mark as • • ✓ • • ✓ • • ✓	3

Q15.

(e)(i)	a [1]	1
(e)(iii)	d [1]	1
(e)(iii)	b, c, f [1]	1
(e)(iv)	f [1]	1

Q16.

(b)	alanine because glutamic acid would have more than two / three peaks / absorb^{ns} / proton environments [1] reason why alanine has a **doublet** given as one neighbouring proton [1] glutamic acid would have (two) **triplet**(s) **OR** a **multiplet** [1] reason why alanine has a **quartet / quadruplet** given as three neighbouring protons [1]	3

Q17.

(e) **3**

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3	alkane / CH / CH_3	triplet	3
2.2	CH_3CO **or** alkyl / CH next to C=O	singlet	3
4.0	CH_2O **or** alkyl / CH next to electronegative atom / C=O	quartet / quadruplet	2

Award one mark for every three correct responses.

(f) **2**

CH **AND** CH_3 **circled**

these protons do not exchange with D_2O
OR OH and NH protons exchange with D_2O

Q18.

(a) **1**

(because $CDCl_3$ / it) does not give a peak [1]
OR because $CHCl_3$ does give a peak

(b) **1**

as a **standard / reference** for (chemical shift measurements) [1]

(c) **1**

ester [1]

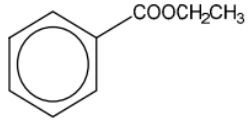
(d)(i) **2**

- (δ = 1.4) triplet
- (δ = 1.4) two H on neighbouring C atom
- (δ = 4.3) quartet / quadruplet
- (δ = 4.3) three H on neighbouring C atom
  mark as • ✓ • ✓ [2]

(d)(ii) **1**

aryl group / arene / phenyl [1]

(d)(iii) **1**



OR $C_6H_5CO_2C_2H_5$ [1]

Q19.

(d)(i) **1**

(because $CDCl_3$) doesn't give a signal / peak / absorption
OR because $CHCl_3$ does give a signal / peak / absorption [1]

(d)(ii) **2**

Clockwise from left:
absorption at σ = 1.9 to 2.1
absorption at σ = 6.5 to 7 [1]
absorption at σ = 3 to 3.5
absorption at σ = 1 to 1.5 [1]

(d)(iii) **2**

the peak at 6.6 to 6.8 / due to NH would disappear [1]
H exchanges with D [1]

Q20.

(c)(i)	**M1**: CH_3CO **M2**: CH_3CH_2O **M3**: $(CO)CH_2O$	**3**

(d)	$HCO_2C(CH_3)_3$	**1**

Q21.

(b)(i)	carbon-13 NMR = 5 peaks [1] proton NMR = 3 peaks [1]	**2**
(b)(ii)	**OH** proton had disappeared due to proton exchange with D / D_2O [1] **ALLOW** $OH + D_2O \rightarrow OD + HOD$	**1**

Q22.

(c)(i)	2 [1]	**1**
(c)(ii)	CH_2 next to ester **and** terminal CH_3 are circled [1]	**1**
(c)(iii)	• one less peak • the lost peak is NH_2 / aryl amine • protons exchange with D **OR** protons are labile **OR** valid equation •✓✓ for two marks [2]	**2**

Q23.

(f)	**M1:** most acidic: hexanoic acid > phenol > hexan-1-ol :least acidic • the other O atom in CO_2H group of hexanoic acid **either** – withdraws charge from OH group **or** is electronegative **and** weakens O–H bond **or** – stabilises resultant anion/negative ion / $–CO_2^-$ group/carboxylate ion • benzene / aromatic / C_6H_5 ring in phenol <u>delocalises</u> **either** – lone pair on O atom **and** weakens O–H bond **or** – lone pair on resultant anion/negative ion / phenoxide ion this stabilises resultant anion negative ion / $–CO_2^-$ group/carboxylate ion • the alkyl group in hexan-1-ol donates electrons this strengthens O–H bond Award 1 mark for each bullet point identified.	**3**
(g)(i)	**M1:** δ12.7 is COOH **M2:** δ3.3 is CH **and** δ1.1 is CH_3	**2**
(g)(ii)	quadruplet / quartet 3 H / protons on neighbouring / adjacent carbon / carbons / C	**1**
(g)(iii)	2 (butanedioic acid) and 3 (methylpropanedioic acid)	**1**

Q24.

(e)(i)	propanoic acid	**1**
(e)(ii)	propan-1-ol would have peak at 0.5–6.0 because of OH group	**1**
	propanal would have peak at 9.3–10.5 because of CHO / aldehyde	**1**