
CHEMISTRY**9701/42**

Paper 4 A Level Structured Questions

October/November 2016

MARK SCHEME

Maximum Mark: 100

Published

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

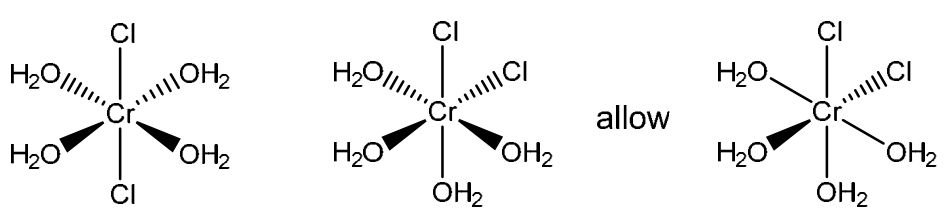
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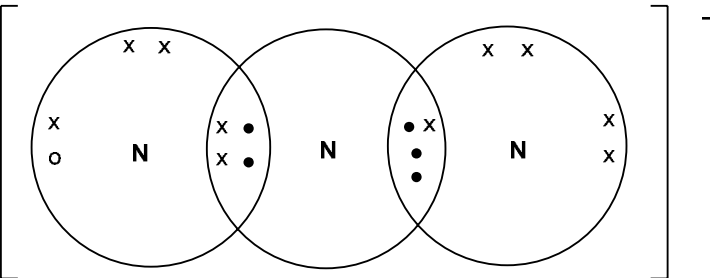
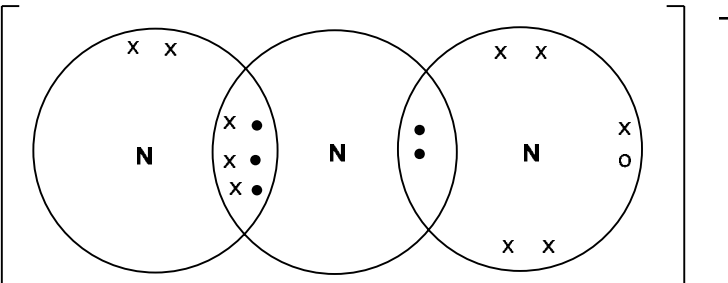
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| Page 2 | Mark Scheme | Syllabus | Paper |
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| Question | Answer | Marks | | | | | | | | | |
|---|--|------------------|----------------------|------------------|---|---|----|---|---|----|---|
| 1(a) | (an element) forming (one or more stable) ions with incomplete d subshell [1] | 1 1 | | | | | | | | | |
| 1(b)(i) | <table border="1"> <thead> <tr> <th></th> <th>co-ordination number</th> <th>oxidation number</th> </tr> </thead> <tbody> <tr> <td>$[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$</td> <td>4</td> <td>+2</td> </tr> <tr> <td>$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$</td> <td>6</td> <td>+3</td> </tr> </tbody> </table> | | co-ordination number | oxidation number | $[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$ | 4 | +2 | $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ | 6 | +3 | 2 |
| | co-ordination number | oxidation number | | | | | | | | | |
| $[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$ | 4 | +2 | | | | | | | | | |
| $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ | 6 | +3 | | | | | | | | | |
| 1(b)(ii) | dative (covalent)/co-ordinate | 1 1 | | | | | | | | | |
| 1(b)(iii) | <p>correct diagram of $[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$</p> <p>square planar or tetrahedral</p> | 1 1 2 | | | | | | | | | |
| 1(c)(i) | (concentrated) hydrochloric acid / soluble chloride ion | 1 1 | | | | | | | | | |
| 1(c)(ii) | ligand exchange / substitution | 1 1 | | | | | | | | | |
| 1(d)(i) | cis-trans (isomerism) / geometric(al) | 1 1 | | | | | | | | | |

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| Question | Answer | Marks |
|----------|---|---|
| 1(d)(ii) | <p>one 3D isomer one correct isomer other isomer correct in 3D</p>  | <p>1 1 1</p> <p style="text-align: right;">3</p> |
| | Total: | 12 |

| | | | |
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| Question | Answer | Marks |
|----------|---|-------------------------|
| 2(a) | $\text{NaN}_3 \rightarrow \text{Na} + 1.5\text{N}_2$ | 1 1 |
| 2(b) |  <p>all atoms must have 8 outer electrons coding for electrons correct = $16 (10 \times 5 + 1 \square)$ central N must have 8 bonding electrons (inc. 5 • and no non-bonded electrons) allow</p>  | 1 1 1 3 |
| 2(c)(i) | (energy change) when 1 mole of an (ionic) compound is formed or (energy change) when 1 mole of an <u>ionic</u> solid/lattice/crystal is formed (from) gas (phase) ions / gaseous ions (under standard conditions) | 1 1 2 |
| 2(c)(ii) | forming an (ionic) bond | 1 1 |

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| Question | Answer | Marks |
|-----------|---|-------------------------|
| 2(c)(iii) | use of ΔH_{f1} 494 (kJ mol ⁻¹) $\Delta H_f^\ominus = +107+494+142-732$ $\Delta H_f^\ominus = +11$ (kJ mol ⁻¹) | 1 1 1 3 |
| 2(c)(iv) | (ionic) radius/size of Na ⁺ is smaller (so stronger attraction to azide ion) OR ionic radius increases down the group | 1 1 |
| | Total: | 11 |

| Question | Answer | Mark |
|-----------|--|--------------------|
| 3(a) | Fe [Ar] 3d ⁶ 4s ² Fe ³⁺ [Ar] 3d ⁵ | 1 1 2 |
| 3(b)(i) | (catalyst is in) the same phase / state as the reactants | 1 1 |
| 3(b)(ii) | $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ | 1 1 |
| 3(b)(iii) | (two) negatively-charged species repel each other | 1 1 |
| 3(b)(iv) | Equation 1: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Equation 2: $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$ | 1 1 2 |

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| Question | Answer | Marks |
|-----------------|---|--------------------|
| 3(c)(i) | (entropy is a measure/degree of the) disorder of a system/substance | 1 1 |
| 3(c)(ii) | $\Delta S^\ominus = (2 \times 27) + (3 \times 214) - (90) - (3 \times 198)$ OR $696 - 684$ $\Delta S^\ominus = (+) 12 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$ | 1 1 2 |
| 3(c)(iii) | $\Delta G^\ominus = -43.6 - (298 \times 12 / 1000)$ $\Delta G^\ominus = -47.2 \text{ (kJ mol}^{-1}\text{)}$ | 1 1 2 |
| 3(c)(iv) | high E_a and to speed up the rate | 1 1 |
| | Total: | 13 |

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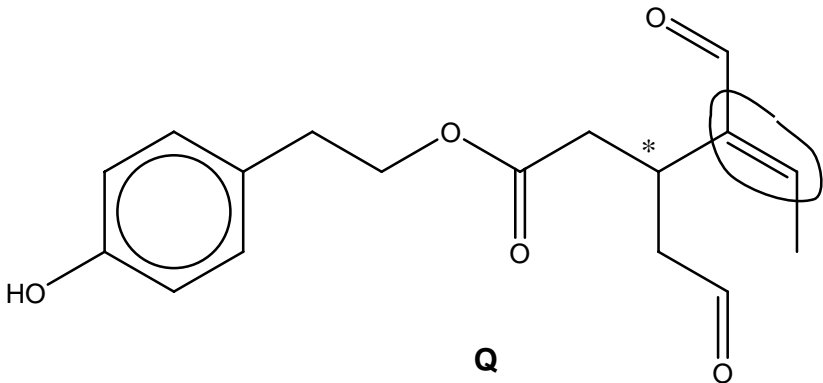
| Question | Answer | Marks |
|-----------------|---|---|
| 4(a) | <p>d orbitals split into lower and upper orbitals</p> <p>light/photon absorbed</p> <p>electron(s) promoted/excited/jumps up to (higher) (d-) orbital or electron(s) moves/jumps (from lower (d-)) to higher (d-) orbital</p> | <p>1</p> <p>1</p> <p>1</p> <p>3</p> |
| 4(b)(i) | <p>$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$</p> <p>or ionic $\text{Cu} + 4\text{H}^+ + 2\text{NO}_3^- \rightarrow \text{Cu}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O}$</p> <p>correct species correct balancing</p> | <p>1</p> <p>1</p> <p>2</p> |
| 4(b)(ii) | <p>moles $\text{S}_2\text{O}_3^{2-} = 0.1 \times 22.4 / 1000 = \mathbf{2.24 \times 10^{-3}}$</p> <p>moles of Cu^{2+} in $25 \text{ cm}^3 = \mathbf{2.24 \times 10^{-3}}$</p> <p>moles of Cu^{2+} in $250 \text{ cm}^3 = 2.24 \times 10^{-2}$</p> <p>mass of $\text{Cu} = 2.24 \times 10^{-2} \times 63.5 = 1.4224 \text{ g}$</p> <p>$\% \text{ Cu} = 1.42 / 1.75 \times 100 = \mathbf{81.1}$ or $\mathbf{81.3\%}$</p> | <p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>4</p> |
| | Total: | 9 |

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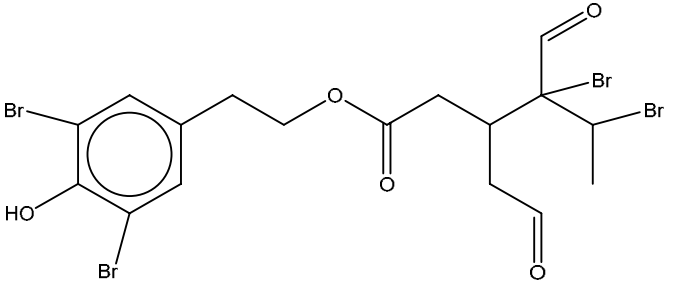
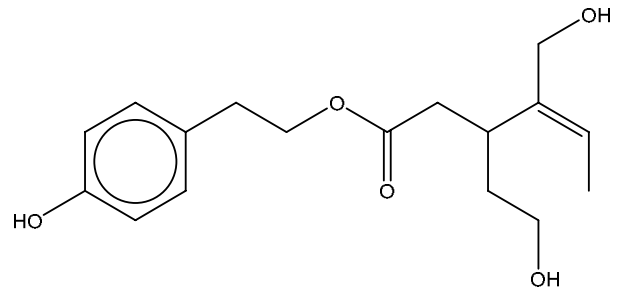
| Question | Answer | Marks |
|-----------------|--|-------------------------------------|
| 5(a) | $K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$ | 1 1 |
| 5(b)(i) | a solution that resists changes in pH when small amounts of acid and base / alkali are added | 1 1 2 |
| 5(b)(ii) | addition of acid: $\text{H}^+ + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{PO}_4^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ addition of base: $\text{HO}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$ OR $\text{OH}^- + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{O} + \text{PO}_4^{3-}$ | 1 1 2 |
| 5(c) | $[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8}$ $[\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = K_a / [\text{H}^+]$ $([\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]) = 6.31 \times 10^{-8} / 3.98 \times 10^{-8} = \mathbf{1.58-1.6}$ | 1 1 1 3 |
| 5(d)(i) | $\text{HCl} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{Cl}^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ OR $\text{H}_2\text{O} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{OH}^-$ | 1 1 |

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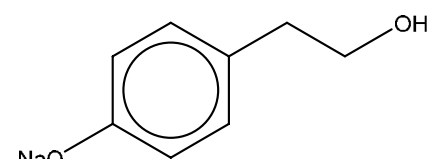
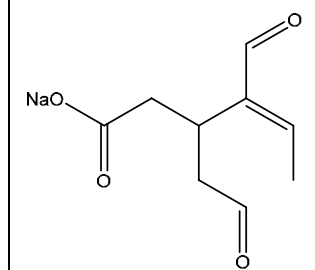
| Question | Answer | Marks |
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| 5(d)(ii) | $\text{NaOH} + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O} + \text{Na}^+$ OR $\text{OH}^- + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$ OR $\text{H}_2\text{O} + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_3\text{O}^+$ | 1 1 |
| | Total: | 10 |

| Question | Answer | Marks |
|----------|---|--------------------|
| 6(a) |  <p style="text-align: center;">Q</p> | 1 |
| 6(b)(i) | ratio of the concentration of a solute in the (two immiscible) solvents/liquids at equilibrium | 1 1 2 |
| 6(b)(ii) | $K_{\text{partition}} = (0.06/40)/(0.25-0.06/10)$ or reversed ratio: $K_{\text{partition}} = (0.25-0.06/10)/(0.06/40)$ $K_{\text{partition}} = \mathbf{0.079}$ (0.0789) $K_{\text{partition}} = 12.7/13.0$ | 1 1 2 |

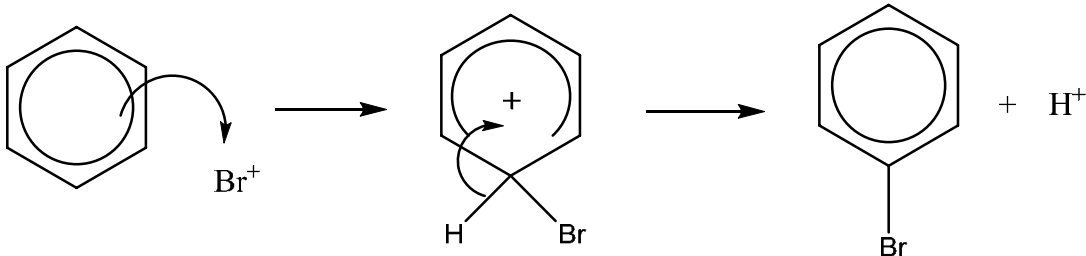
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| Question | Answer | | | Marks |
|-----------------|---|---|--|--------|
| 6(c) | reagent | structure of product(s) | type of reaction | 1 1 |
| | excess $\text{Br}_2(\text{aq})$ |  <p>addition of bromine to alkene 2xBr substituted in phenol at positions 2 and 6</p> | (electrophilic) substitution or (electrophilic) addition | |
| NaBH_4 |  | reduction (allow nucleophilic addition) | 1 | |

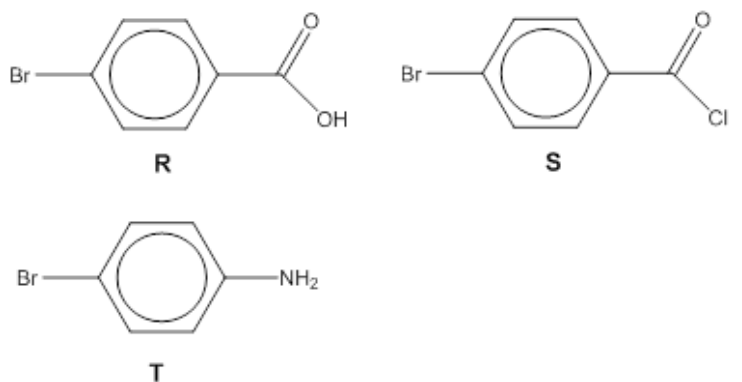
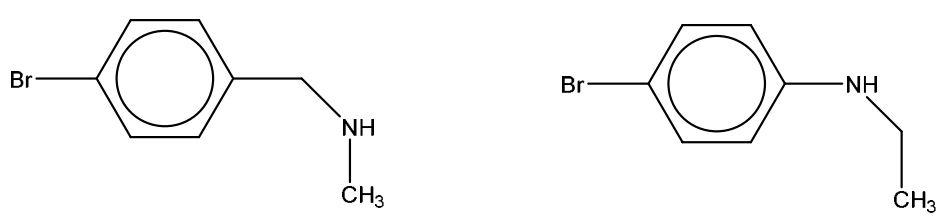
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| Question | Answer | | | Marks |
|----------|---|---|-------------------|------------|
| | <p>excess hot NaOH(aq)</p>  |  | <p>hydrolysis</p> | <p>1+1</p> |
| | all three reaction types | | | 1 |
| 6(d) | mixture of (two) optical/stereo isomers formed | | | 1 |
| | Total: | | | 12 |

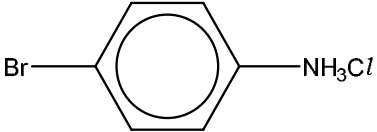
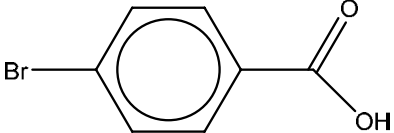
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| Question | Answer | Marks |
|----------|--|------------------------------|
| 7(a)(i) | electrophilic substitution | 1 1 |
| 7(a)(ii) | $(\text{Br}_2 + \text{A}/\text{Br}_3) \rightarrow \text{Br}^+ + \text{A}/\text{Br}_4^-$  <p>curly arrow from ring system to Br^+ correct intermediate curly arrow from C–H bond into ring and loss of H^+</p> | 1 1 1 4 |
| 7(b) | both amide | 1 1 |
| 7(c)(i) | step 1, A/Br_3 and CH_3Br OR other suitable halogen instead of Br step 2, KMnO_4 or potassium manganate(VII) step 3, conc. H_2SO_4 and conc. HNO_3 step 4. Sn and (conc.) HCl (heat) | 1 1 1 1 4 |

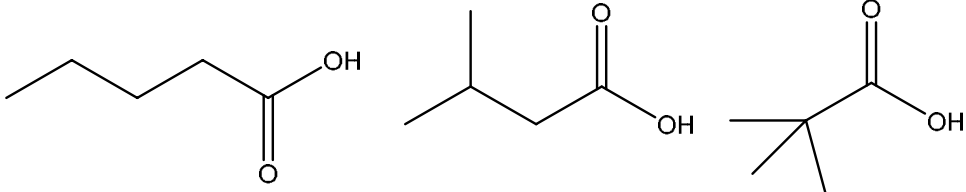
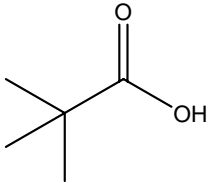
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|----------|---|--|
| 7(c)(ii) |  <p>R</p> <p>S</p> <p>T</p> | <p>1 mark for each correct structure</p> <p>3</p> |
| 7(d)(i) |  | <p>1 mark for each correct structure</p> <p>2</p> |
| 7(d)(ii) | reduction | <p>1</p> <p>1</p> |

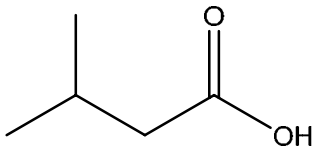
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| Question | Answer | Marks |
|-----------|---|---|
| 7(e)(i) |  CH_3COOH (or ionic) | 1 mark for each correct structure 2 |
| 7(e)(ii) |  | 1 1 |
| 7(e)(iii) | (precipitate) compound is less polar / more non-polar / non-ionic resulting in less hydrogen bonding to water | 1 1 |
| | Total: | 20 |

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| Question | Answer | Marks | | | | | | | | | | | | |
|---------------------|--|----------------------------------|--------------------------------|----------------------------------|----|----------------------|---------------|----|---|---------------|-----|---------------------------------|---------------|----------|
| 8(a) | $102 \times 0.314 = 32$ (32.028) ($102 - 32 = 70$) and $(12 \times 5) + (1 \times 10) = 70$ OR F contains $\text{CO}_2\text{H} = 45$ so $102 - 45 = 57$ so C_4H_9 | 1 1 | | | | | | | | | | | | |
| 8(b)(i) |  <p>2 correct = 1 mark 3 correct = 2 marks</p> | 2 | | | | | | | | | | | | |
| 8(b)(ii) | 2-methyl butanoic acid | 1 1 | | | | | | | | | | | | |
| 8(c)(i) |  | 1 1 | | | | | | | | | | | | |
| 8(c)(ii) | <table border="1"> <thead> <tr> <th>δ/ppm</th> <th>environment of the carbon atom</th> <th>hybridisation of the carbon atom</th> </tr> </thead> <tbody> <tr> <td>27</td> <td>alkyl/CH_3</td> <td>sp^3</td> </tr> <tr> <td>41</td> <td>next to carboxyl/$(\text{CH}_3)_3\text{C}$</td> <td>sp^3</td> </tr> <tr> <td>179</td> <td>carboxyl/CO_2H</td> <td>sp^2</td> </tr> </tbody> </table> | δ/ppm | environment of the carbon atom | hybridisation of the carbon atom | 27 | alkyl/ CH_3 | sp^3 | 41 | next to carboxyl/ $(\text{CH}_3)_3\text{C}$ | sp^3 | 179 | carboxyl/ CO_2H | sp^2 | 2 |
| δ/ppm | environment of the carbon atom | hybridisation of the carbon atom | | | | | | | | | | | | |
| 27 | alkyl/ CH_3 | sp^3 | | | | | | | | | | | | |
| 41 | next to carboxyl/ $(\text{CH}_3)_3\text{C}$ | sp^3 | | | | | | | | | | | | |
| 179 | carboxyl/ CO_2H | sp^2 | | | | | | | | | | | | |

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| Question | Answer | | | | Marks |
|----------|---|---|-------------------|--------------------|-----------|
| 8(d)(i) | δ/ppm | type of proton | number of protons | splitting | 4 |
| | 0.9 | alkane/CH/CH ₃ | 6 | doublet | |
| | 1.6 | alkane/CH | 1 | [multiplet] | |
| | 2.4 | alkyl next to C=O/CH ₂ CO/CH | 2 | doublet | |
| | 11.5 | OH/CO ₂ H/carboxylic acid | 1 | singlet | |
| 8(d)(ii) |  | | | | 1 |
| 8(e) | CDCl ₃ OR D ₂ O, DMSO, CD ₂ Cl ₂ , CCl ₄ | | | | 1 |
| | Total | | | | 13 |