

## 10: Analysis – Topic questions

The questions in this document have been compiled from a number of past papers, as indicated in the table below.

Use these questions to formatively assess your learners' understanding of this topic.

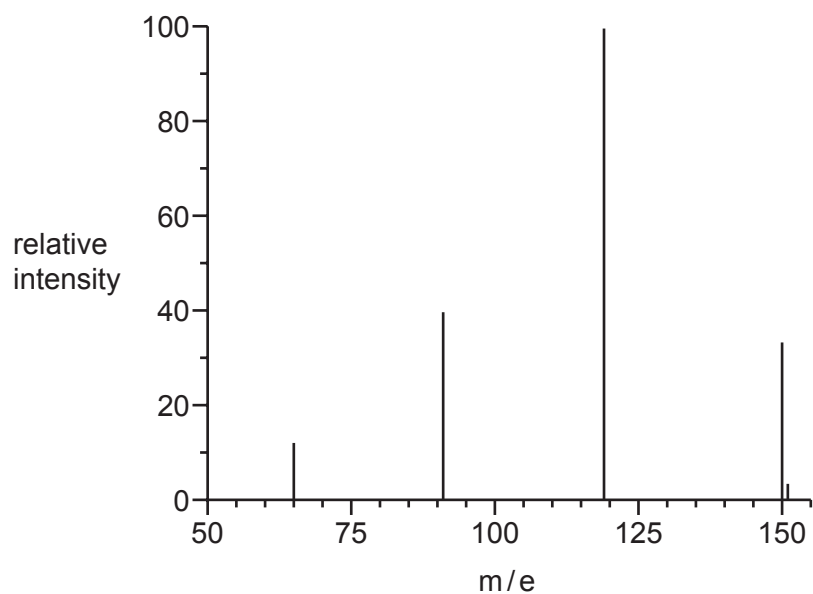
Question	Year	Series	Paper number
9	2017	March	42
6	2017	November	43
8	2017	November	42

The mark scheme for each question is provided at the end of the document.

9 This question is about compound **T**,  $C_xH_yO_z$ .

(a) Part of the mass spectrum of **T** is shown.

The peak heights of the  $M$  and  $M+1$  peaks are 33.9 and 3.4 respectively.



(i) Calculate  $x$ , the number of carbon atoms present in **T**.

$x = \dots\dots\dots$  [2]

(ii) Deduce the molecular formula of **T**.

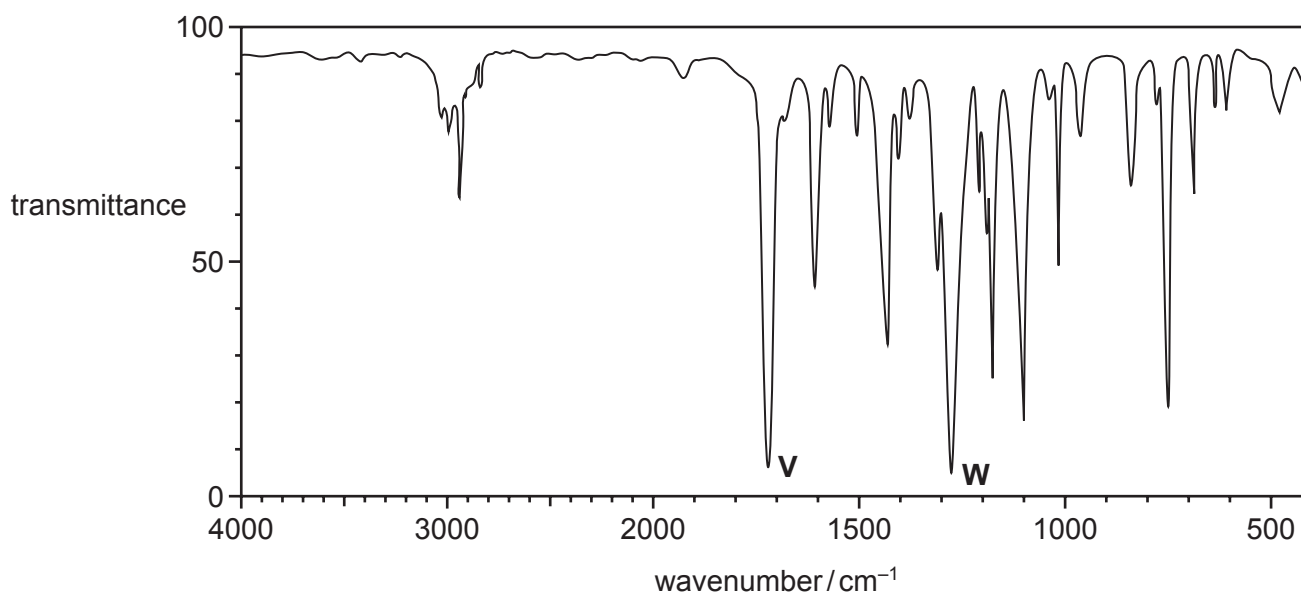
$\dots\dots\dots$  [1]

(iii) The mass spectrum has a peak at  $m/e = 119$ .

Identify the fragment lost from **T** to produce this peak.

$\dots\dots\dots$  [1]

(b) The infra-red spectrum of **T** is shown.

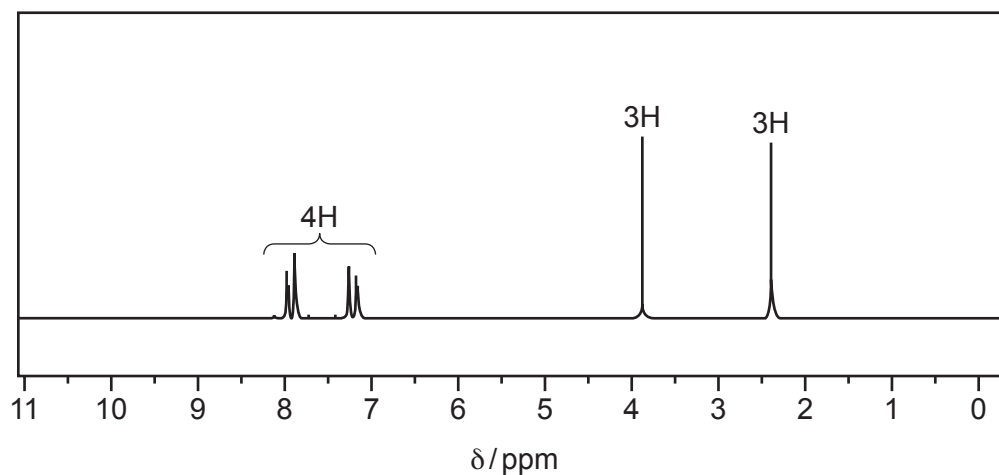


Identify the type of bond responsible for each of the peaks **V** and **W**.  
Use the *Data Booklet* to help you.

**V** ..... **W** .....

[1]

(c) The proton NMR spectrum of **T** in  $\text{CDCl}_3$  is shown.



(i) Complete the table for the proton NMR spectrum of **T**.  
Use the *Data Booklet* to help you.

$\delta$ / ppm	type of proton
3.9	
7.2–7.9	

[1]

(ii) The peak at  $\delta = 2.4$  ppm is due to a proton attached to a saturated carbon atom.

State the **two** possible types of proton.

1. ....

2. ....

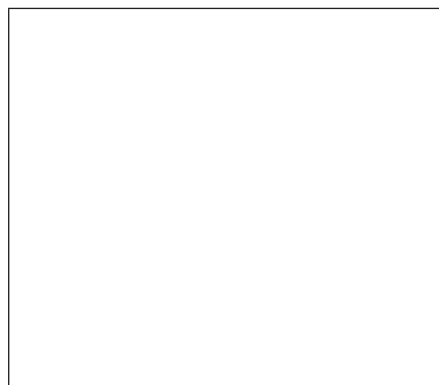
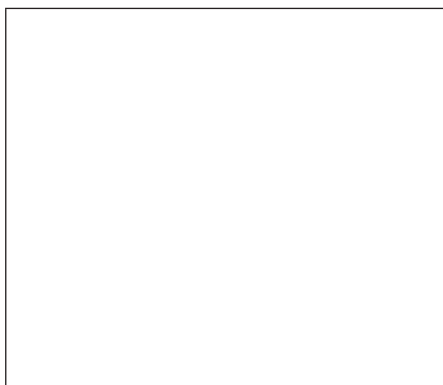
[1]

(iii) Adding  $D_2O$  to **T** does **not** change its proton NMR spectrum.

What does this tell you about the functional groups present in **T**?

..... [1]

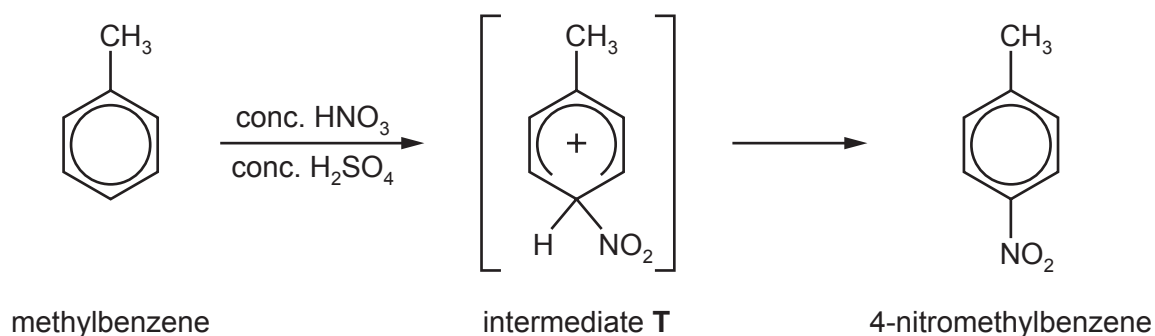
(d) Use the information to draw **two** possible structures of **T** which are functional group isomers of each other.



[2]

[Total: 10]

- 6 (a) 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



- (i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

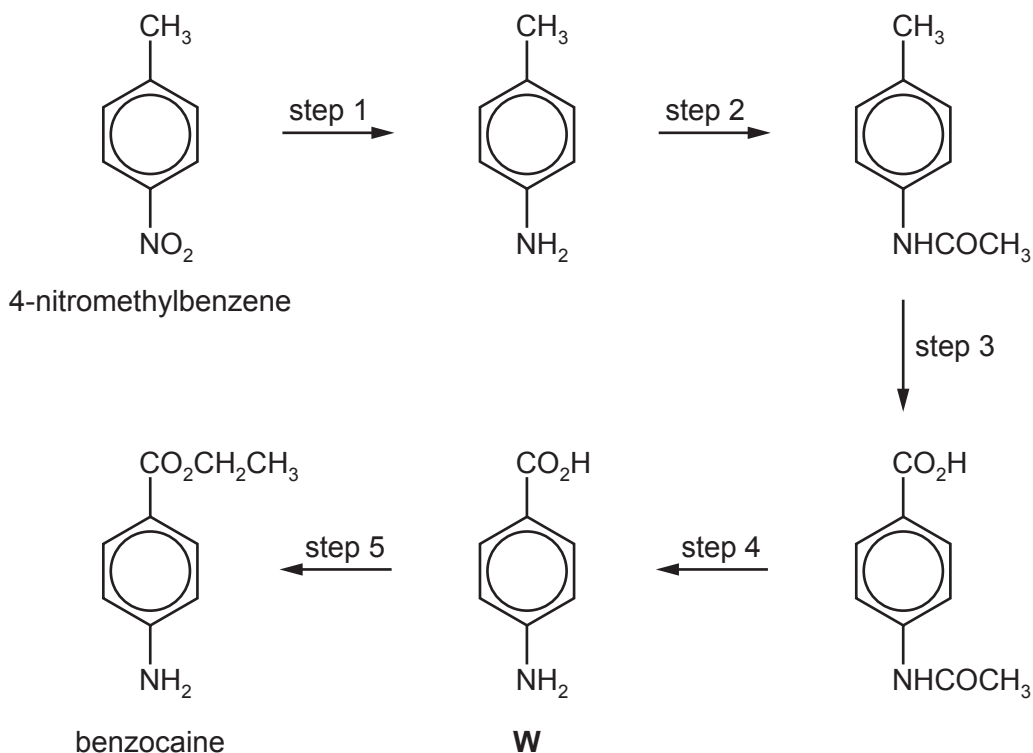
- (ii) Write an equation for the reaction between  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  that forms the electrophile for this reaction.

..... [1]

- (iii) Describe how the **structure and bonding** of the six-membered ring in intermediate T differs from that in methylbenzene.

.....  
.....  
.....  
..... [3]

- (b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



- (i) Give the systematic name of compound **W**.

..... [1]

- (ii) Suggest the reagents and conditions for steps 1–5.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

[6]

- (c) Suggest how the basicity of benzocaine would compare to that of ethylamine. Explain your answer.

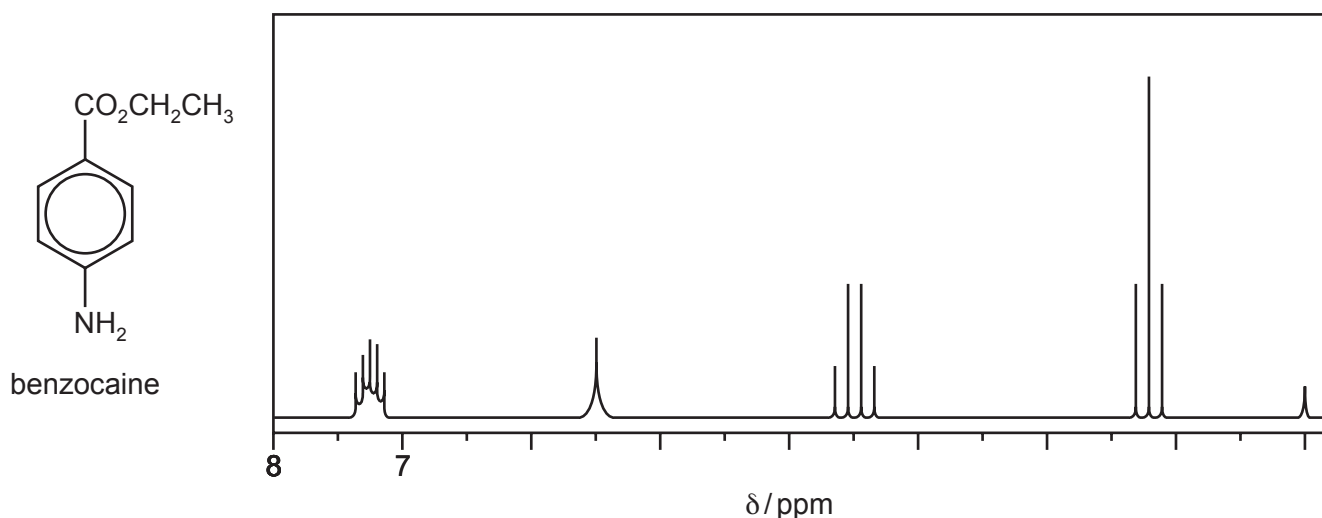
.....  
 .....  
 ..... [2]

(d) A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

(ii) Benzocaine was dissolved in  $\text{CDCl}_3$  and the proton NMR spectrum of this solution was recorded.



Suggest why  $\text{CDCl}_3$  and not  $\text{CHCl}_3$  is used as the solvent when obtaining a proton NMR spectrum.

..... [1]

(iii) Use the *Data Booklet* and the spectrum in (d)(ii) to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts,  $\delta$ , for the four absorptions have been added.

$\delta/\text{ppm}$	group responsible for the peak	number of $^1\text{H}$ atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at  $\delta 1.2\text{ppm}$ .

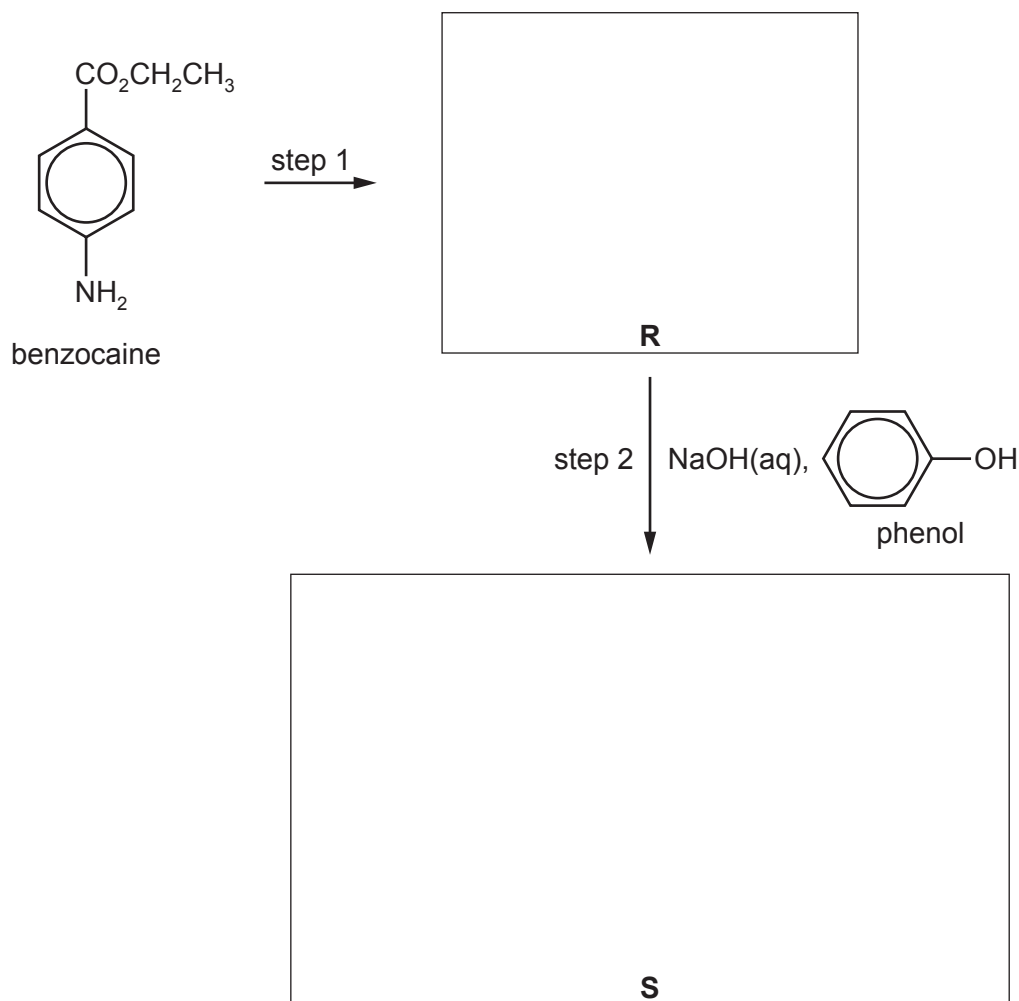
..... [1]

- (v) The proton NMR spectrum of benzocaine dissolved in  $D_2O$  was recorded.

Suggest how this spectrum would differ from the spectrum in (d)(ii).  
Explain your answer.

.....  
..... [1]

- (e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



- (i) Suggest the reagents used for step 1.

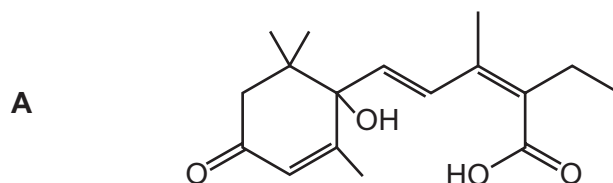
..... [1]

- (ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

[Total: 25]



- 8 (a) Compound **A** can be produced from a plant hormone.



- (i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,

- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

- (ii) Give the **names** of four functional groups present in **A**.

.....

..... [2]

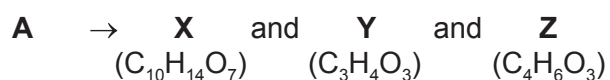
- (iii) A molecule of **A** has 17 carbon atoms.

State the number of carbon atoms that are  $sp$ ,  $sp^2$  and  $sp^3$  hybridised in **A**.

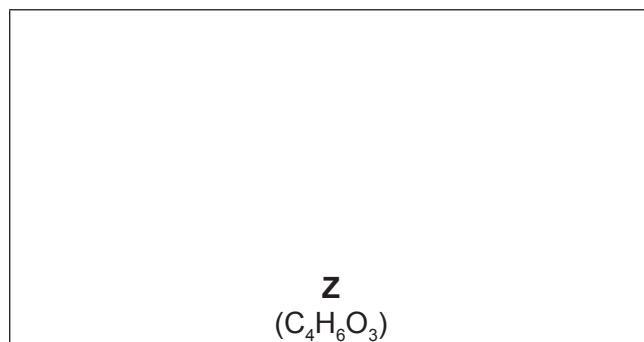
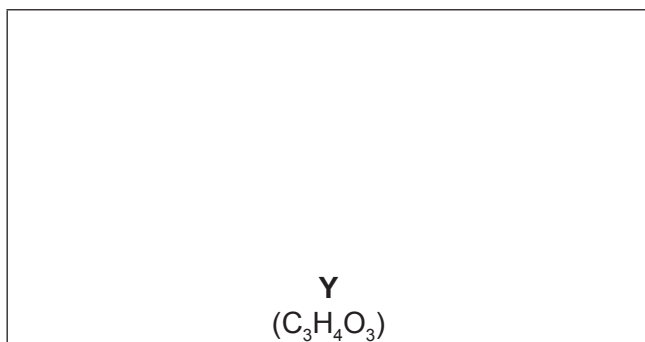
$sp$  carbons = .....  $sp^2$  carbons = .....  $sp^3$  carbons = .....

[1]

- (iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

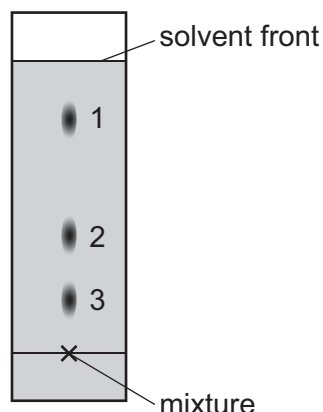


Suggest the structures of **Y** and **Z**.



[2]

- (b) A mixture of three different compounds, **J**, **K** and **L**, was analysed by thin layer chromatography using a polar stationary phase and a non-polar mobile phase. The three compounds all have similar molecular masses. The resulting chromatogram is shown.



- (i) Identify which spot corresponds to each compound.

compound	spot
<b>J</b> $\text{CH}_3\text{COCO}_2\text{H}$	
<b>K</b> $\text{HO}_2\text{CCO}_2\text{H}$	
<b>L</b> $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	

[1]

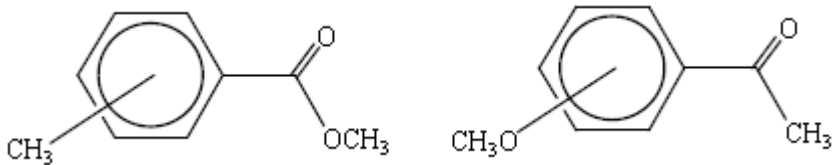
- (ii) Explain your answers to (b)(i).

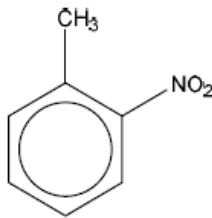
.....  
 ..... [1]

- (iii) What is meant by the term  $R_f$  value?

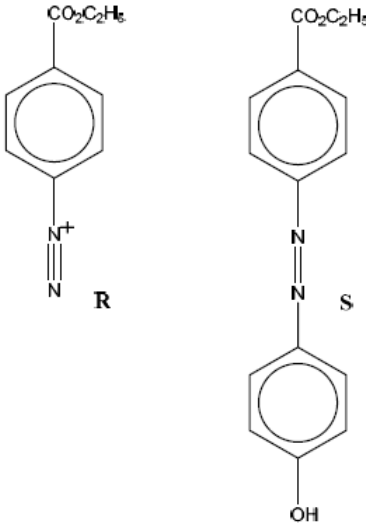
.....  
 ..... [1]

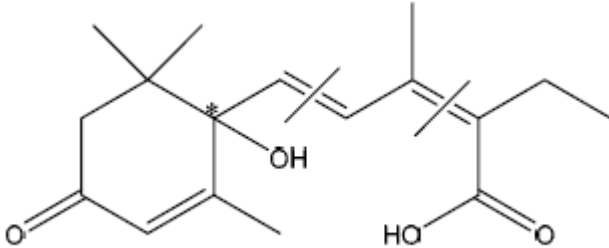
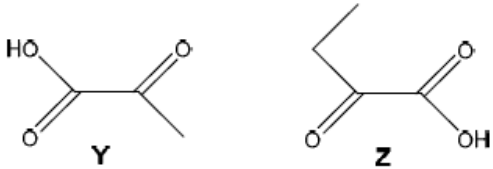
[Total: 10]

Question	Answer	Marks
9 (a) (i)	$n = 100 \times (M+1)/(1.1 \times M) = 100 \times 3.4/(1.1 \times 33.9) = 9.1$	1
	hence <b>9</b> carbons atoms	1
9 (a) (ii)	$C_9H_{10}O_2$	1
9 (a) (iii)	(150 – 119 = 31), hence fragment is $CH_3O$	1
9 (b)	<b>V</b> is $C=O$ <b>AND</b> <b>W</b> is $C-O$	1
9 (c) (i)	$\delta$ 3.9 is CH or alkyl / $CH_3$ next to oxygen <b>AND</b> $\delta$ 7.2–7.9 is CH / aryl hydrogens	1
9 (c) (ii)	alkyl H next to $C=O$ <b>AND</b> alkyl H next to aryl ring	1
9 (c) (iii)	none of the functional groups in <b>T</b> contains a labile proton / <b>T</b> does not contain $-OH$ or $-NH$ groups.	1
9 (d)		2
Total: 10		

Question	Answer	Marks
6 (a) (i)		1
6 (a) (ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	1
6 (a) (iii)	<b>any three</b> from: Point 1: bonds / electrons are <b>partially</b> delocalised in <b>T</b> <b>or</b> delocalised / $\pi$ system / $\pi$ bonding extends over only five carbons Point 2: four $\pi$ -electrons in the (delocalised system of <b>T</b> ) <b>or</b> methylbenzene has (two) more $\pi$ -electrons / (two) more delocalised electrons Point 3: contains a carbon that is $sp^3$ hybridised in <b>T</b> <b>or</b> (all the) carbons are $sp^2$ hybridised in methylbenzene Point 4: one carbon has a bond angle of $109.5^\circ$ / tetrahedral (in <b>T</b> ) <b>or</b> (C-C) bond strengths / lengths are not all the same <b>or</b> not all the bond angles are $120^\circ$ (in <b>T</b> )	3
6 (b) (i)	4-aminobenzoic acid	1
	step 5 substitution / hydrolysis	1

Question	Answer	Marks																				
4 (b) (iii)	step 1 $\text{Sn} + \text{HCl}$	1																				
	concentrated / reflux / heat	1																				
	step 2 $\text{CH}_3\text{COCl}$	1																				
	step 3 $\text{KMnO}_4$ / manganate(VII) / $\text{MnO}_4^-$ (acidified / alkaline) <b>and</b> heat	1																				
	step 4 aqueous $\text{HCl}$ <b>and</b> heat	1																				
	step 5 ethanol, $\text{H}_2\text{SO}_4$ , concentrated / reflux / heat	1																				
6 (c)	(benzocaine) is less (basic than ethylamine) <b>AND</b> <b>lone pair</b> (on N) is less available to <b>accept</b> a proton / $\text{H}^+$  since (lone pair on N) is delocalised over the ring <b>or</b> phenyl ring is electron withdrawing group  <b>OR</b> ethylamine is more basic (than benzocaine) <b>AND</b> <b>lone pair</b> (on N) is more available to <b>accept</b> a proton / $\text{H}^+$  since ethyl / alkyl group is electron-donating group	2																				
6 (d) (i)	7 peaks	1																				
6 (d) (ii)	$\text{CDCl}_3$ will produce no signal in the spectrum <b>or</b> $\text{CHCl}_3$ would produce a signal / would be detected	1																				
6 (d) (iii)	<table><tr><th><math>\delta/\text{ppm}</math></th><th>group responsible for the peak</th><th>number of H atoms responsible for the peak</th><th>splitting pattern</th></tr><tr><td>1.2</td><td><math>\text{CH}(3)</math></td><td>3</td><td>triplet</td></tr><tr><td>3.5</td><td><math>\text{CH}(2)\text{O}</math></td><td>2</td><td>quartet</td></tr><tr><td>5.5</td><td><math>\text{NH}_2</math></td><td>2</td><td>singlet (broad)</td></tr><tr><td>7.1–7.4</td><td>H attached to aromatic / benzene ring</td><td>4</td><td><i>multiplet</i></td></tr></table>	$\delta/\text{ppm}$	group responsible for the peak	number of H atoms responsible for the peak	splitting pattern	1.2	$\text{CH}(3)$	3	triplet	3.5	$\text{CH}(2)\text{O}$	2	quartet	5.5	$\text{NH}_2$	2	singlet (broad)	7.1–7.4	H attached to aromatic / benzene ring	4	<i>multiplet</i>	4
$\delta/\text{ppm}$	group responsible for the peak	number of H atoms responsible for the peak	splitting pattern																			
1.2	$\text{CH}(3)$	3	triplet																			
3.5	$\text{CH}(2)\text{O}$	2	quartet																			
5.5	$\text{NH}_2$	2	singlet (broad)																			
7.1–7.4	H attached to aromatic / benzene ring	4	<i>multiplet</i>																			
6 (d) (iv)	neighbouring / adjacent carbon <b>atom</b> has two protons / H (attached to it) <b>or</b> there is an adjacent $\text{CH}_2(\text{O})$ group	1																				
6 (d) (v)	peak at 5.5 / $\text{NH}_2$ peak will disappear <b>and</b> $\text{NH}_2$ / protons exchange / swap with deuterium	1																				
6 (e) (i)	$\text{NaNO}_2 + \text{HCl}$ <b>or</b> $\text{HNO}_2$	1																				

Question	Answer	Marks
6 (e) (i)	 <p>structure of diazonium salt <b>R</b></p> <p>structure of azo dye <b>S</b></p>	<p>1</p> <p>1</p>
Total: 25		

Question	Answer	Marks
8 (a) (i)	 <p>circle or asterisk on correct C atom only [1] lines through the two correct bonds only [1]</p>	2
8 (a) (ii)	ketone, (tertiary) alcohol, alkene, carboxylic acid two for each mark	2
8 (a) (iii)	sp carbons = 0 sp <sup>2</sup> carbons = 8 sp <sup>3</sup> carbons = 9	1
8 (a) (iv)	 <p><b>Y</b>                      <b>Z</b></p>	2

Question	Answer	Marks								
8 (b) (i)	<table><tr><th>compound</th><th>spot</th></tr><tr><td>J</td><td>2</td></tr><tr><td>K</td><td>3</td></tr><tr><td>L</td><td>1</td></tr></table>	compound	spot	J	2	K	3	L	1	1
compound	spot									
J	2									
K	3									
L	1									
8 (b) (ii)	The more polar the compound <b>and</b> stronger attractive forces to the (polar) stationary phase ora: less polar compound <b>and</b> weaker attractive forces to the (polar) stationary phase	1								
8 (b) (iii)	$R_f$ = retardation factor <b>or</b> retention factor <b>or</b> $R_f$ = distance moved by compound from baseline over distance travelled by solvent front	1								
Total: 10										

Notes about the mark scheme are available separately.