CHEMISTRY

Paper 9813/01
Paper 1

This answer key is published as an aid to students, to indicate the requirements of the examination. It shows the basis on which the markers award marks. It does not indicate the details of the discussions that took place before marking began, which would have considered the acceptability of alternative answers.

Note:

1. If the candidate's answer has the same "meaning" or can be clearly interpreted as being of equivalent significance, detail and validity as that in the markscheme then award the mark. Where this point is considered to be particularly relevant in a question it is emphasized by ***OWTTE*** (or words to that effect).

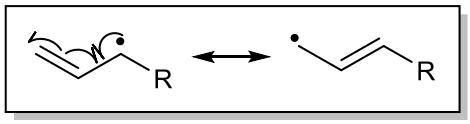
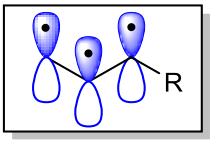
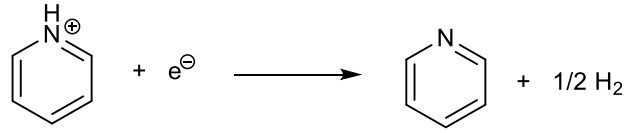
2. Occasionally, a part of a question may require an answer that is required for subsequent marking points. If an error is made in the first marking point then it should be penalized. However, if the incorrect answer is used correctly in subsequent marking points then **follow through** marks should be awarded. When marking, indicate this by adding **ECF** (error carried forward) on the script.

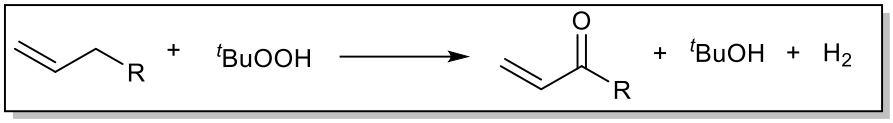
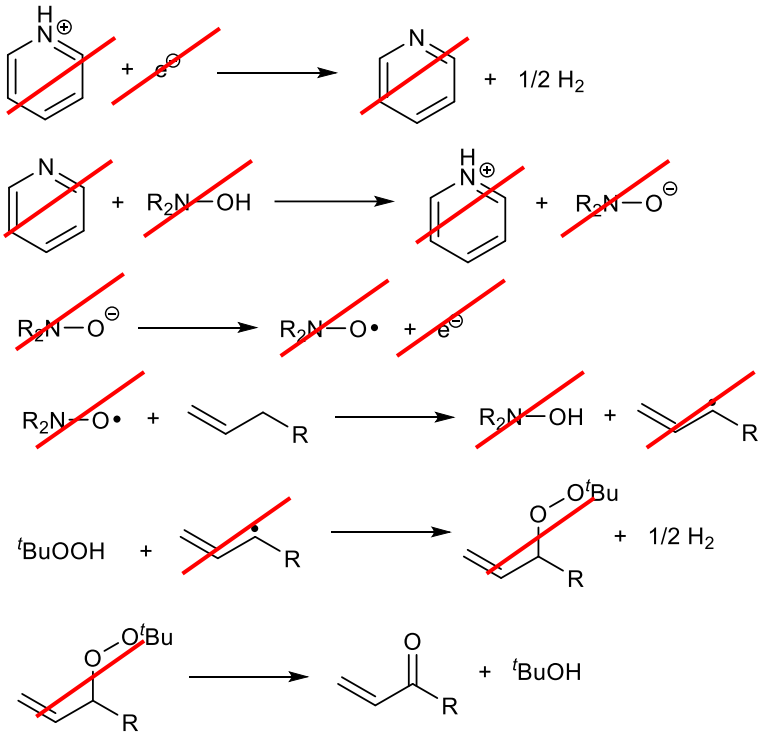
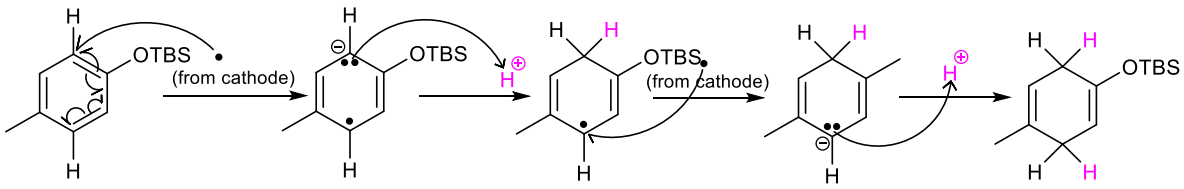
3. Do **not** penalize candidates for errors in units or significant figures, **unless** it is specifically referred to in the answer key.

4. If a question specifically asks for the name of a substance, do not award a mark for a correct formula unless directed otherwise in the answer key. Similarly, if the formula is specifically asked for, unless directed otherwise in the answer key, do not award a mark for a correct name.

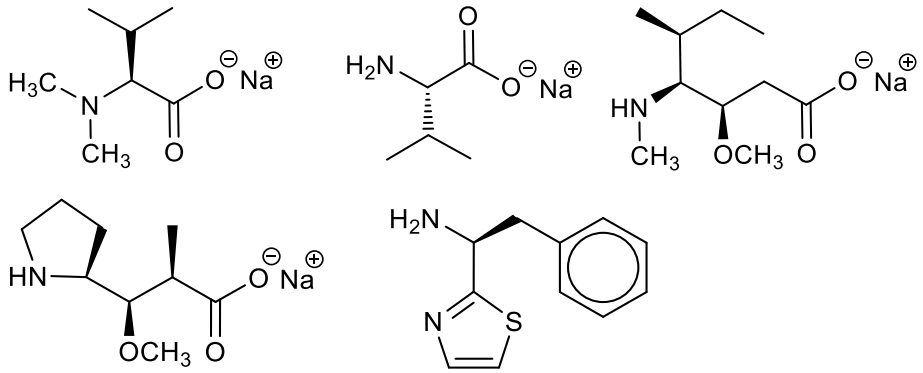
5. If a question asks for an equation for a reaction, a balanced symbol equation is usually expected, do not award a mark for a word equation or an unbalanced equation unless directed otherwise in the answer key.

6. Ignore missing or incorrect state symbols in an equation unless directed otherwise in the answer key.

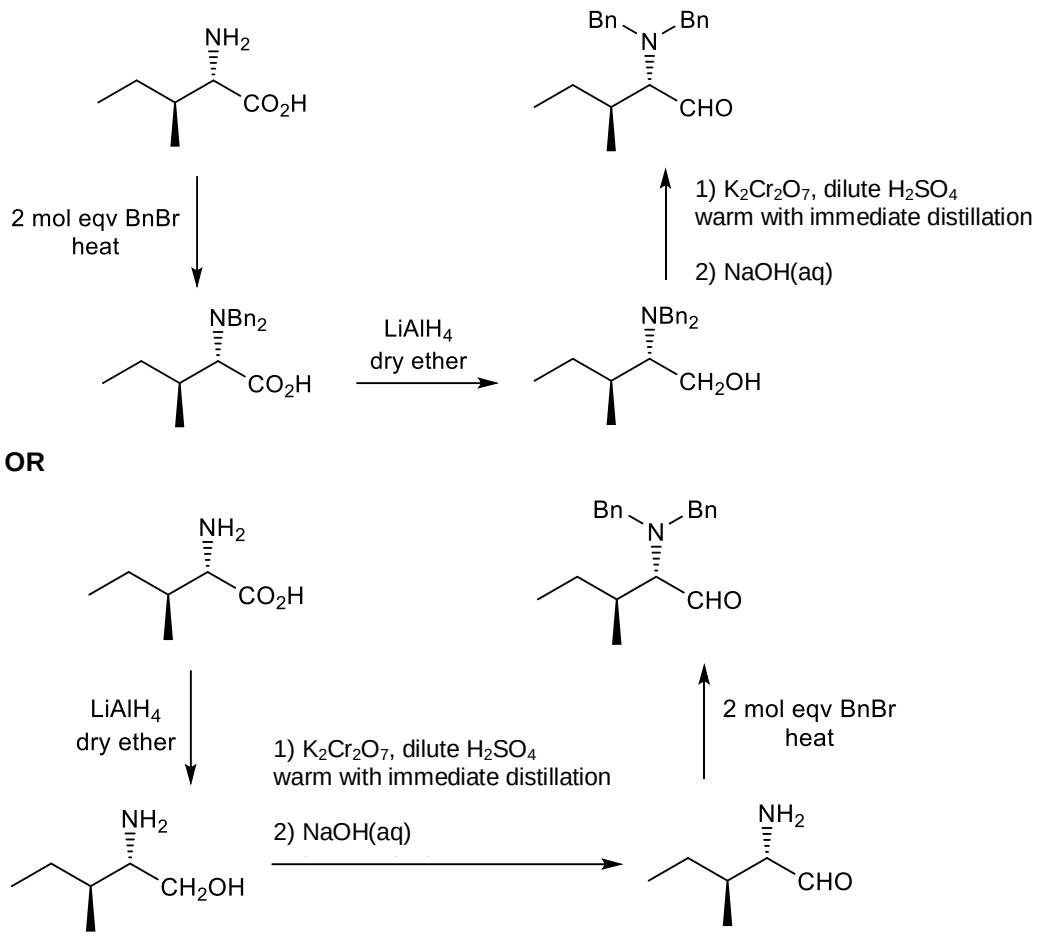
Question	Answer	Marks
1(a)	Chromium- and selenium-based reagents are toxic; large scale production will generate a lot of wasteful by-products. Getting these by-products removed will add to the cost of production, which is not sustainable.	**1**
	Palladium- and rhodium-based catalyst are expensive and will add to the cost of production.	**1**
	Removing the above-mentioned elements entirely from the product cannot be guaranteed – this is a problem especially when the products are used in medicines. The syntheses thus have no industrial application. (Allow other valid reasons)	
1(b)	 or  Electronic effect: Use the above and highlight that the radical is resonance stabilised (the lone electron on the 2° carbon is delocalised into the adjacent π system).	**1**
	Hammond postulate: Homolytic cleavage of C–H is endothermic and hence has a late transition state (TS resembles the radical intermediate). The activation barrier leading to the allylic radical is likely to be lower than that leading to the 1° radical.	**1**
1(c)(i)	cathode 	**1**
	anode $R_2N-O^{\ominus} \longrightarrow R_2N-O\bullet + e^{\ominus}$	**1**
1(c)(ii)	The allylic substrate does not get oxidised at the anode directly; instead it is being oxidised to the allylic radical by R_2N–O● which is produced when the conjugate base of R_2N-OH gets oxidised. Hence the role of the mediator is to function like a 'middleman' / electron shuttle between the anode and the substrate. (OWTTE)	**1**
	^{t}BuOOH works in synergy with R_2N–OH, helping to complete the oxidation by playing the role of an oxidant after the allylic radical is being formed.	**1**

Question	Answer	Marks
1(c)(iii)	 Working (not required to score the mark): 	**1**
1(d)(i)		
	1st step correct (accept SET to the meta C followed by full curly arrows towards the ortho C to give the negative charge)	**1**
	2nd & 4th steps correct	**1**
	3rd step correct	**1**
1(d)(ii)	$Mg \rightarrow Mg^{2+} + 2e^-$	**1**
1(d)(iii)	The reduced product will be re-oxidise back to TBS-cresol (accept bromide will be oxidised to bromine)	**1**

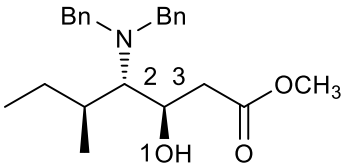
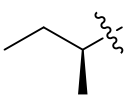
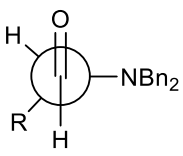
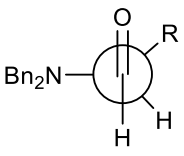
Question	Answer	Marks
1(e)	RDS of Pathway **A**: **D1** to **D2**; E_a = 52 kJ mol^{-1}	**1**
	RDS of Pathway **B**: **D3$_{ads}$** to **E$_{ads}$**; E_a = 41 kJ mol^{-1} (the correct RDS must be identified and E_a corrected computed to score the credit) The reduction of **D** to **E** undergoes the Pathway **B**. (ECF if students chose the wrong RDS but conclude the pathway with a lower E_a)	**1**
1(f)	(equipment) • Specialised equipment is required for maintaining the temperature of the reaction at –35 ^oC and this is especially so for large scale production. Expensive to build, maintain and operate. • The systematic removal of NH_3 and H_2 is challenging after the reaction is completed.	**1** **1**
	(risk) • If the equipment breaks down in the process, it will result in the vapourisation of 5 dm^3 of liquid NH_3 and this will translate to an enormous volume of gaseous NH_3. This might risk explosion/ compromise the health of scientist. (Allow other valid reasons)	**1**
1(g)(i)	Assuming the rate of reduction is constant, η(TBS-cresol) reduced after 16 hours = 7.1 / 222.1 = 3.1967 $\times$ 10^{-2} mol η(TBS-cresol) reduced per second = 3.1967 $\times$ 10^{-2} / (16 $\times$ 60 $\times$ 60) = 5.5499 $\times$ 10^{-7} mol A = 10.0 $\times$ 4.0 = 40.0 cm^3 $[R]_{surface}$ = 5.5499 $\times$ 10^{-7} / 40.0 = 1.39 $\times$ 10^{-8} mol cm^{-2}	**1**
1(g)(ii)	k_{red} = 0.75 / (96500 $\times$ 40.0 x 1.39 $\times$ 10^{-8}) = 13.9 s^{-1} (units not required)	**1**

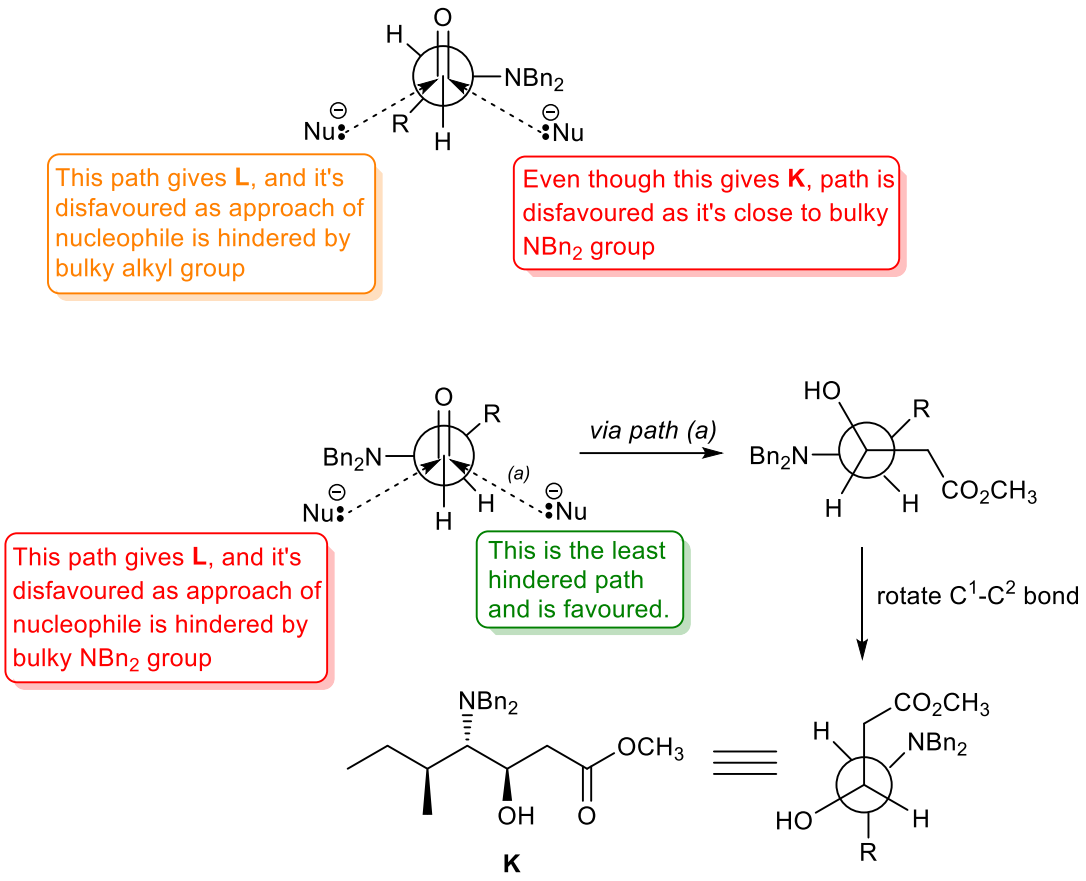
Question	Answer	Marks
2(a)	 1 – 2 correct structures [1] 3 – 4 correct structures [2] All 5 correct structures [3] (Award [2 max] if Na^+ is not included in the structure)	**3**

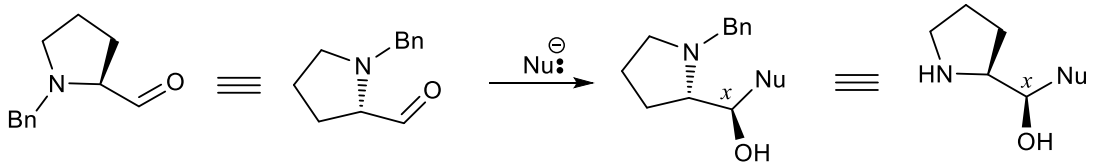
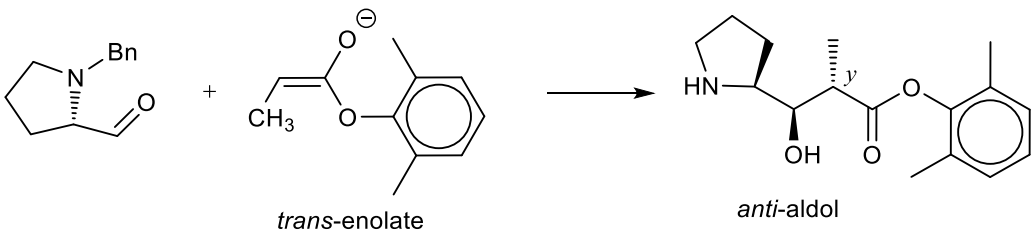
2(b)(i)



Correct reagents and conditions for the 1st step + intermediate	**1**
Correct reagents and conditions for the 2nd step + intermediate	**1**
Correct reagents and conditions for the 3rd step	**1**

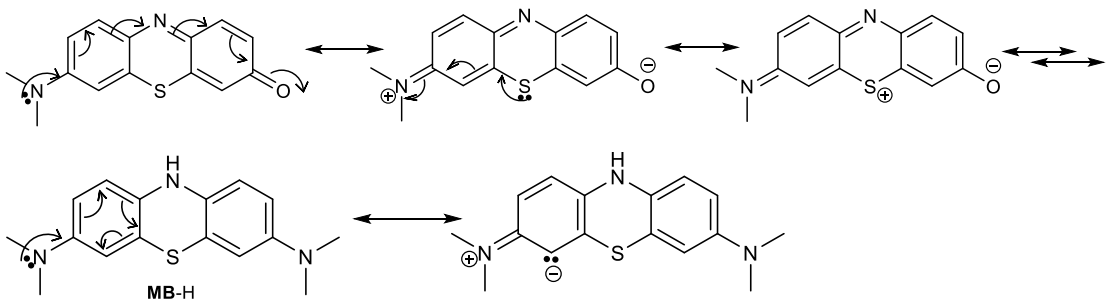
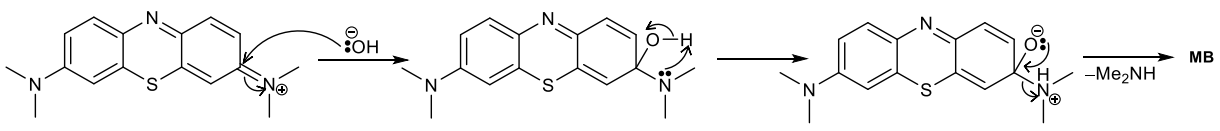
Question	Answer	Marks
2(b)(ii)	 With the fourth priority group (H atom) pointing into the plane, the top three priority groups are arranged clockwise, hence configuration is *R*. working is needed for the mark (Working is required for the credit)	**1**
2(c)(i)	Let R =   **and** 	

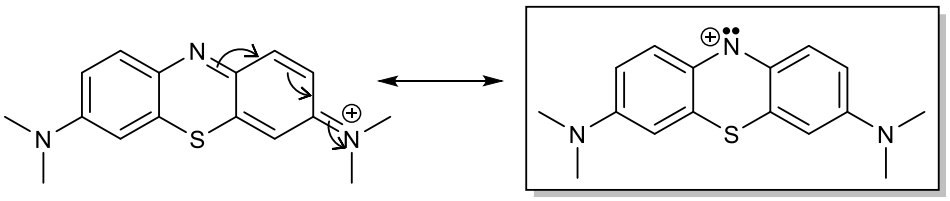
	Largest substituent (-NBn_2) perpendicular to the plane of C=O (marks awarded regardless of configuration)	**1**
	Two correct Newman projections drawn (check configuration before awarding marks)	**1**
2(c)(ii)		
	Correct explanations for the two paths of the first conformation (2 x [0.5])	**1**
	Correct explanations for the two paths of the second conformation (2 x [0.5])	**1**
	Show via a Newman projection (or otherwise) that the least hindered path gives **K**	**1**

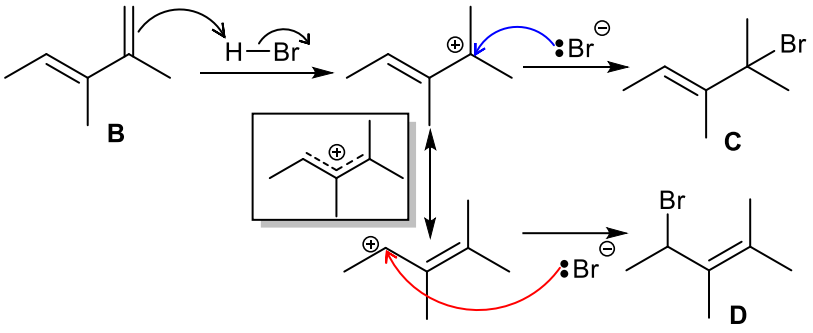
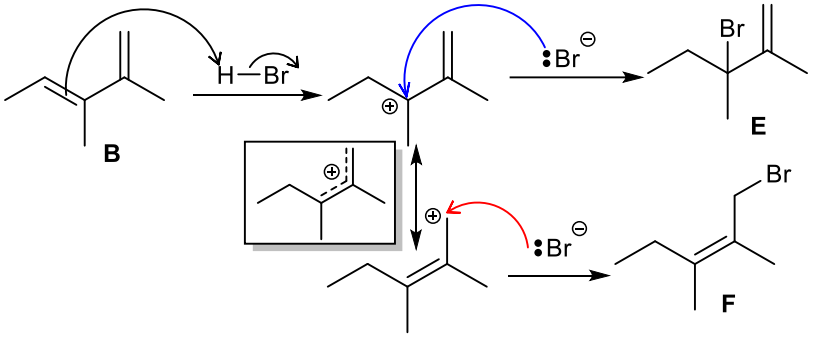
Question	**Answer**	**Marks**
2(c)(iii)	 Hence, the configuration of chiral centre *x* matches that in dolaproline.	**1**
	 *trans*-enolate *anti*-aldol	**1**

	Hence, the configuration of chiral centre *y* does not match that in dolaproline.	

Question	Answer	Marks
3(a)(i)	When radiation in the IR region is being absorbed, it is associated with the vibrational energy levels within the molecule. Different vibrational energy levels arise due to the different modes of vibrations in a molecule, which can either be stretching vibrations (changes in bond length) or bending vibrations (changes in bond angle).	**1**
	For any vibrational mode to be active in the IR region, it must lead to a net change in dipole moment when the vibration occurs. Energy is absorbed when the frequency of the radiation matches the frequency of the vibration.	**1**
3(a)(ii)	**P1**: sp^3 C–H stretch **P2**: C=N stretch **P3**: aromatic C=C stretch Any two correctly identified [1] All three correctly identified [2]	**2**
3(b)	$\eta_{\mathbf{MB}}$ in 250 cm^3 = 0.095 / 319.6 = 2.9725×10^{-4} mol $\eta_{\mathbf{MB}}$ in 100 cm^3 of the diluted solution = $2.9725 \times 10^{-4} \times 1.0 / 250 = 1.189 \times 10^{-6}$ mol	**1**
	$[\mathbf{MB}]_{\text{diluted solution}} = 1.189 \times 10^{-6} \times 1000/100 = 1.189 \times 10^{-5}$ mol dm^{-3} Using 'A = εcl', ε = 0.88 / ($1.189 \times 10^{-5} \times 1.0$) = 74013	**1**

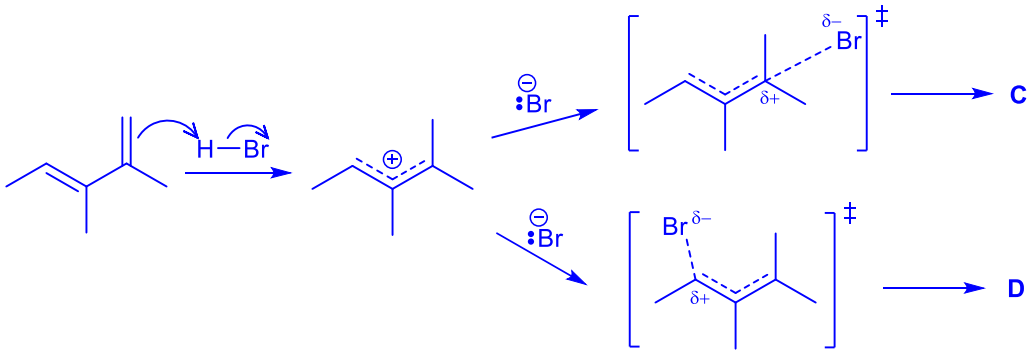
Question	Answer	Marks
3(c)(i)		**1**
	MVB has a greater extent of conjugation / delocalisation of π electron densities over the three fused rings; **MB**-H has a smaller extent of conjugation / delocalisation of π electron densities over one ring only.	**1**
3(c)(ii)	Addition-elimination **and** dimethylamine	**1**
	For reference: 	

3(d)(i)	 The resonance structure being boxed-up is the said resonance structure. However, this resonance structure is likely to be a very minor contributor as the nitrogen bearing the positive charge has only 6 electrons around it, making the structure highly unstable (and reactive).	**1**
3(d)(ii)	**MB**-OH is structurally similar to **MB**-H; therefore it has a much less extensive chromophore (than **MVB** or **MB**) causing its λ_{max} to fall within the UV region.	**1**

Question	Answer	Marks
4(a)(i)	 **B** **C** **D**	**1**
	 **B** **E** **F**	**1**
4(a)(ii)	The transition states leading to products **C** and **E** have a developing positive charge at the 3° carbon whereas the transition states leading to products **D** and **F** have a developing positive charge at the 2° and 1° carbon respectively. Hence the activation barrier for the former is likely to be lower and **C** and **E** are obtained as the dominant products at a lower temperature.	**1**
	Products **D** and **F** are thermodynamically more stable than **C** and **E** as they are tetrasubstituted. Although the activation barriers to **D** and **F** are higher, the products are lower in energy. They are likely to be obtained at a slower rate (due to higher E_a); they are termed as the *thermodynamic products* (they are more stable than **C** and **E**).	**1**
	Products **C** and **E** are thermodynamically less stable than **D** and **F** as they are disubstituted. Although the activation barriers to **D** and **F** are lower, the products are higher in energy. They are likely to obtain at a faster rate (due to lower E_a); they are termed as the *kinetic products*.	**1**

Thought processes & comments

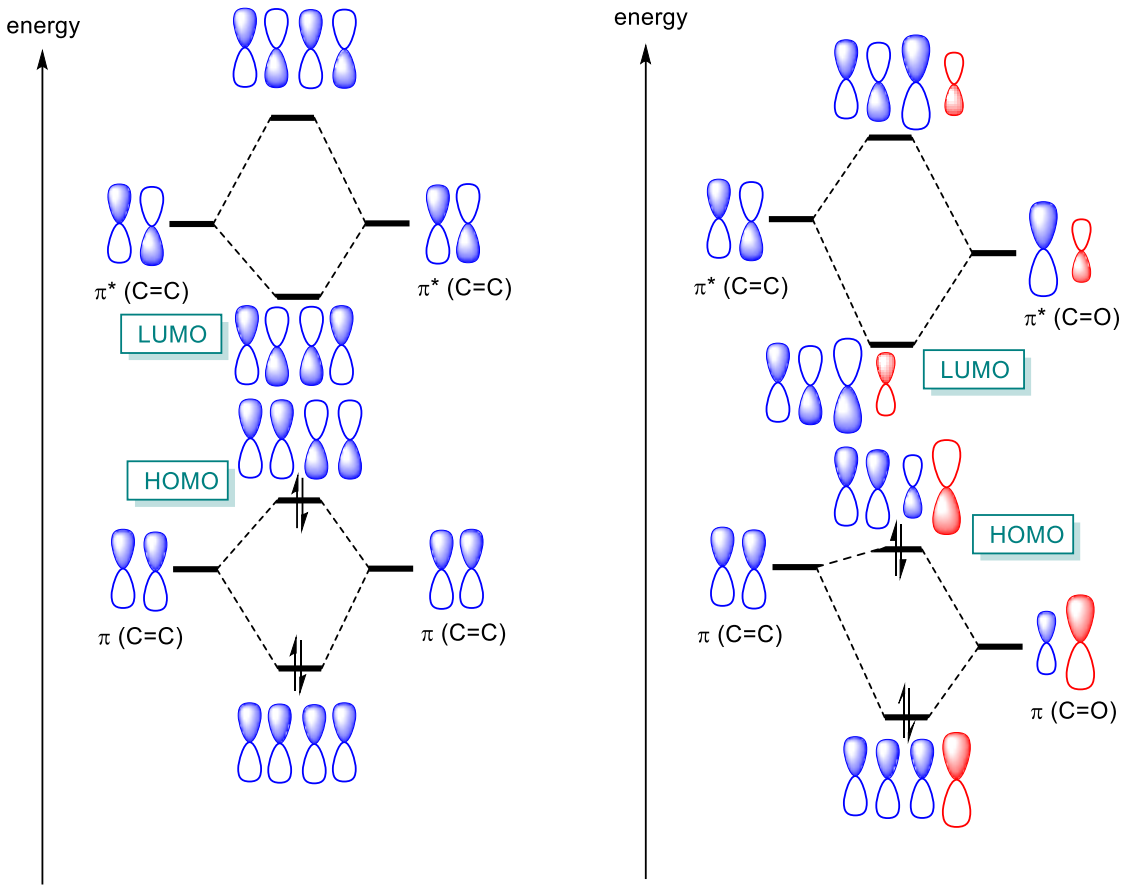
Many students made the first mistake by not recognising that the carbocation formed is resonance stabilised. Take for example, in the formation of **C** and **D**:



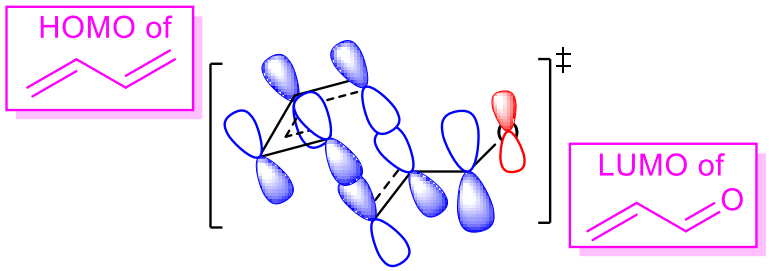
In the fast step, the bromide nucleophile is attacking the same carbocation, albeit at different sites, resulting in two possible transition states – the one leading to **C** has a developing positive charge at a 3° carbon whereas the one leading to **D** has a developing positive charge at a 2° carbon. It is therefore likely that the former transition state will be lower in energy as compared to the latter and hence at a lower temperature, the probability of overcoming the activation barrier leading to **C** is higher and hence it is formed as the predominant product at a lower temperature and at a *faster rate*.

However, **C** is thermodynamically less stable than **D** and hence at a higher temperature and with an increased in time frame, the position of equilibrium will shift towards the thermodynamic product and hence **D** is formed at a greater proportion at a higher temperature, albeit it takes a *longer time*.

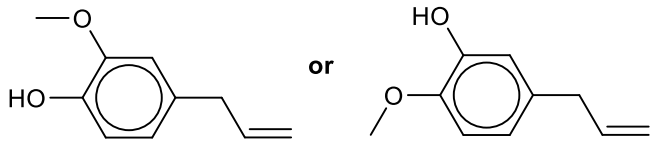
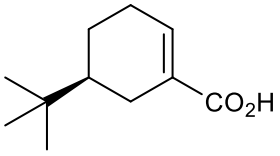
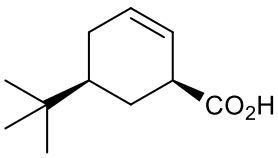
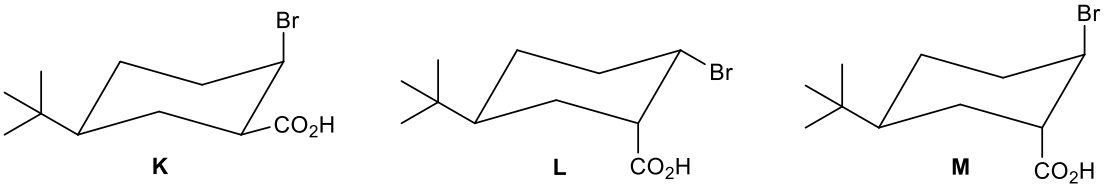
4(b)(i)

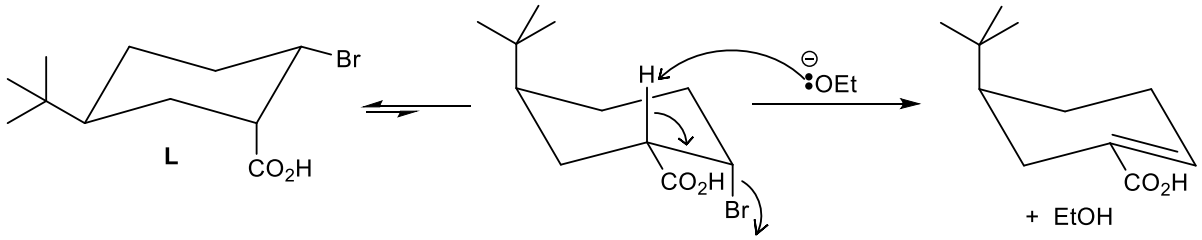
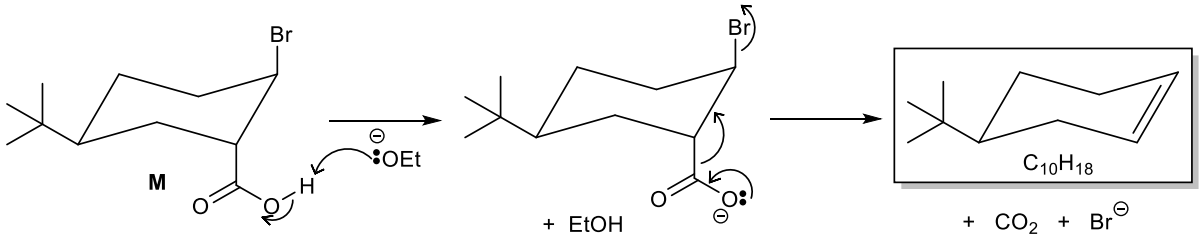


	Correct drawing of orbitals on buta-1,3-diene and propenal (size is not important)	**1**
	Correct (approximate) energy levels of MOs of propenal	**1**
	Correct label of HOMO and LUMO + populating the first 2 MOs with electron pairs	**1**

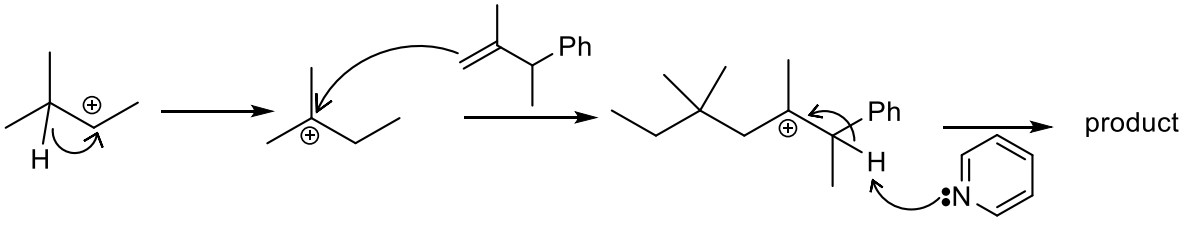
Question	Answer	Marks
4(b)(ii)		**1**
	Constructive interference occurs when the HOMO of buta-1,3-diene interacted with the LUMO of propenal, leading to the formation of two new σ bonds.	**1**
4(c)(i)	Electronic effect alone favours θ = 0° and 180° as the co-planar arrangement of the two phenyl rings allows the π electron cloud to overlap continuously (delocalisation of electron densities between the 2 phenyl rings). However, this conformation results in unfavourable steric repulsion between the alkyl groups.	**1**
	Steric effect alone favours θ = 90° as the two phenyl rings are orthogonal to one another, preventing unfavourable steric repulsion between the alkyl groups. However, electronic effect is lost entirely over here and delocalisation is not possible when the p orbitals in the two phenyl rings are orthogonal to each other.	**1**
	The local minimum points were instead found to be at θ = 45° and 135° as this is the conformation when a compromised is achieved between electronic and steric effect – some steric repulsion is present but at the same time, partial overlap between the π orbitals of the two phenyl rings.	**1**
4(c)(ii)	Enantiomeric **or** Both conformations are enantiomers of one another	**1**

Question	Answer	Marks
5(a)(i)	Number of carbon = (100/1.1)(6/54) = 10 Since there are 12 H atoms, let its molecular formula be $C_{10}H_{12}O_y$. 10(12.0) + 12(1.0) + y(16.0) = 164 ∴ y = 2	**1**
	Molecular formula of **Q** is $C_{10}H_{12}O_2$	**1**
5(a)(ii)	TMS has 4 equivalent methyl groups bonded to Si. Si is less electronegative than C and hence its signal will be well away from that of most compounds. TMS is hence suitable as an internal reference and it is assigned a chemical shift value of 0 ppm.	**1**

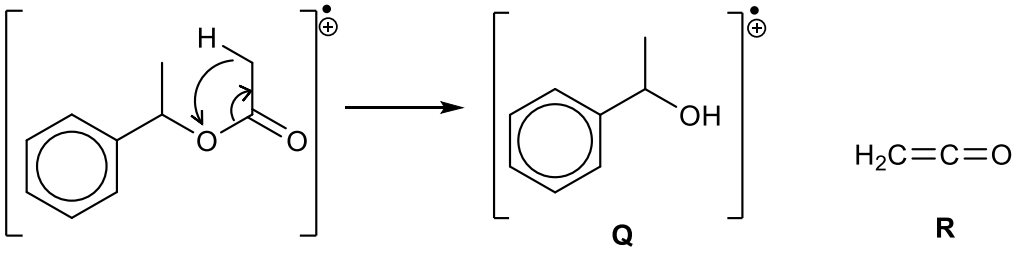
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>5(a)(iii)</td><td>The deduction is summarized in the table below.
<table>
<tr><th>chemical shift δ / ppm</th><th>integration</th><th>multiplicity</th><th>deduction</th></tr>
<tr><td>3.29</td><td>2</td><td>doublet</td><td>Highly dehielded; likely to be the 2 benzylic protons. This benzylic group is flank by the phenyl ring and –CH=C. The signal is a doublet due to the vinylic proton.</td></tr>
<tr><td>3.81</td><td>3</td><td>singlet</td><td>Highly deshielded; likely due to CH_3 bonded directly to highly electronegative O with no neighbouring protons.</td></tr>
<tr><td>5.04</td><td>2</td><td>multiplet</td><td>Highly deshielded due to magnetic anisotropic efffect; likely to be the 2 vinylic protons in the terminal alkene.</td></tr>
<tr><td>5.53</td><td>1</td><td>broad singlet</td><td>Due to the labile proton in –OH.</td></tr>
<tr><td>5.91</td><td>1</td><td>multiplet</td><td>Highly deshielded due to magnetic anisotropic efffect; likely to be the vinylic protons in –CH=C.</td></tr>
<tr><td>6.66</td><td>1</td><td>singlet</td><td rowspan="3">Aromatic protons; Q is likely to contain a tri-substituted phenyl ring. The multiplicity implies that the substituents are at the 1-, 2- and 4-position.</td></tr>
<tr><td>6.67</td><td>1</td><td>doublet</td></tr>
<tr><td>6.82</td><td>1</td><td>doublet</td></tr>
</table>
6 deductions in total; each [0.5]</td><td>3</td></tr>
<tr><td></td><td>  or </td><td>1</td></tr>
<tr><td>5(a)(iv)</td><td>A lower chemical shift would mean that the labile proton has a <u>higher electron density</u> and is <u>less deshielded</u>. Therefore, <u>intramolecular hydrogen bonding</u> is likely to be absent and hence the –OH and –OCH_3 groups in R are not likely to be adjacent to each other.</td><td>1</td></tr>
<tr><td>5(b)(i)</td><td>  and 
alkene K1 alkene K2
(Accept if student leave their answers as carboxylate anion)</td><td>1</td></tr>
<tr><td></td><td>The <u>more substituted</u>/ the conjugated alkene K1 is <u>more stable and will be formed as the major product</u> (Zaitsev product).</td><td>1</td></tr>
<tr><td>5(b)(ii)</td><td> 
K L M
All 3 conformations correctly drawn [2]
Any 2 conformations correctly drawn [1]</td><td>2</td></tr>
</table>

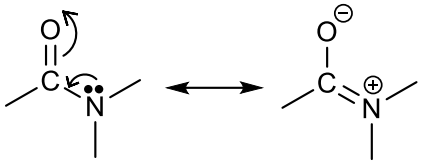
Question	Answer	Marks
5(b)(iii)		
	Correct configuration of the 3 substituents and curly arrows showing trans elimination. (Accept deprotonation of the other axial H)	**1**
	Slower rate for E2 for **L** as compared to **K** since **L** has to undergo ring flip to an unstable chair conformation which forces *tert*-butyl and H groups to be axial, resulting in unfavourable 1,3-diaxial interaction.	**1**
5(b)(iv)		
	Curly arrows showing decarboxylation (Accept mechanism without chair conformation)	**1**
	Correct structure of $C_{10}H_{18}$	**1**
5(b)(v)	M $[C_{11}H_{18}O^{79}Br^{35}Cl]^+$ M+2 $[C_{11}H_{18}O^{79}Br^{37}Cl$ and $C_{11}H_{18}O^{81}Br^{35}Cl]^+$ M+4 $[C_{11}H_{18}O^{81}Br^{37}Cl]^+$	**1**
	M : M+2 : M+4 0.5×0.75 : $0.5 \times 0.25 + 0.5 \times 75$: 0.5×0.25 0.375 : 0.50 : 0.125 3 : 4 : 1	**1**
5(c)(i)	*Either* Mass spectrometry, the M^+ for **P** will be one mass unit higher than that of **N**. *or* ^{1}H NMR, **N** will show two vinylic protons whereas **P** will show one.	**1**
5(c)(ii)	The bridge makes it difficult for norbornyl bromide to ring flip to the required chair conformation, hence syn elimination is predominant.	**1**

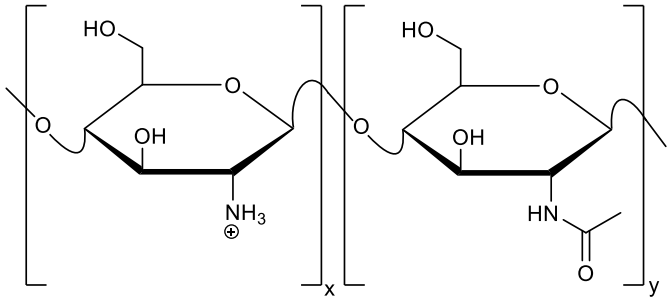
Question	Answer	Marks
6(a)(i)	PhS^- is a stronger nucleophile than PhO^- as the lone pair electron on S is more available for donation to an electron deficient C as it is less electronegative than O **or**	**1**

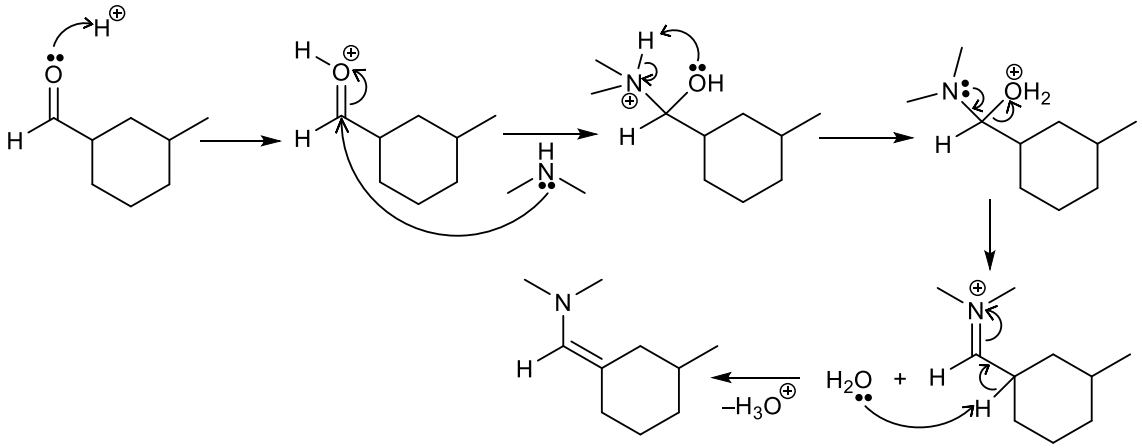
	PhS^- has a more polarisable electron cloud than PhO^- resulting in a more effective orbital overlap in the TS, hence reaction involving PhS^- has a lower activation barrier than that involving PhO^- resulting in a faster reaction.	
6(a)(ii)	Bromomethane undergoes S_N2 as the relative rate of reaction increases with increasing strength of the nucleophile. Therefore, both bromomethane and the nucleophile are involved in the rate determining step.	**1**
6(a)(iii)	$CH_3CO_2^-$, Cl^- and PhO^- undergo S_N1 reaction with **Y** as the relative rate of reactions are approximately the same implying all 3 ions are weak nucleophiles. So changing the nucleophiles has no effect on the rate of reaction.	**1**
	HO^- and PhS^- undergo S_N2 reaction with **Y** as both their relative rates are much greater than that of $CH_3CO_2^-$, Cl^- and PhO^-. This implies that the rate of reaction is related to their nucleophilicity and both are strong nucleophiles which favour S_N2.	**1**
6(a)(iv)	No S_N2 reaction as **X** is too sterically hindered for nucleophiles to approach from the opposite of the C–Br bond.	**1**
	No S_N1 reaction as **X** is unable to form a planar carbocation; the carbocation, if formed will take on an unfavourable tetrahedral geometry (due to the presence of the rigid bridging head).	**1**
6(b)(i)	The 2° carbocation formed will be stabilized via ion-dipole interaction with H_2O (a polar protic solvent). The helps to lower the energy of the TS and the intermediate.	**1**
	Diphosphate anion is a very good leaving group as the negative charge on oxygen can delocalised into P=O. Moreover, it forms an insoluble salt with Mg^{2+} which helps to drive the reaction forward.	**1**
6(b)(ii)	Both N_a and N_b are sp^2 hybridised. However, the lone pair of electrons on N_a and N_b are residing in the p and sp^2 hybrid orbital respectively.	**1**
	The lone pair of electrons on N_a delocalised into the imdazole ring (part of the aromatic sextet) and hence it is less available to coordinate to proton as compared to the lone pair of electrons on N_b which resides in the sp^2 hybrid orbital. Hence N_b is more basic than N_a and it reacts similarly as the N atom in pyridine.	**1**
6(b)(iii)		
	Correct curly arrows for the first step + intermediate	**1**
	Correct curly arrows for the second step + intermediate	**1**
	Correct curly arrows for the third step	**1**

Question	Answer	Marks
6(c)(i)	In reaction **I**, the hydroxyl group in (*R*)-1-phenylethan-1-ol is the nucleophile which attacks the carbonyl carbon in acyl chloride to form the ester. So the stereochemistry of the chiral center in the original alcohol remains unchanged.	**1**

6(c)(ii)	In reaction **II**, the hydroxyl group in (*R*)-1-phenylethan-1-ol undergoes condensation with TsC*l* to produce -OTs, which is a good leaving group.	**1**
	The resulting intermediate then undergoes a S_N2 reaction where the $CH_3CO_2^-$ nucleophile attacks from rear of -OTs bond, resulting in an inversion of the configuration of the original chiral centre.	**1**
6(c)(iii)	**P** = $[CH_3CO]^+$  **Q** **R**	
	P, **Q** and **R** ([1] each)	**3**
	Correct curly arrows from the molecular ion to **Q** and **R** (accept single electron transfer via fish-hook arrows)	**1**

Question	Answer	Marks
7(a)	$8C(s) + 15/2H_2(g) + 1/2N_2(g) + 3O_2(g) \rightarrow C_8H_{15}NO_6(s)$	**1**
	ΔH_f = (717 × 8 + 436 × 15/2 + 944 × 1/2 + 496 × 3) – (350 × 6 + 360 × 6 + 740 + 410 × 10 + 460 × 4 + 390 + 305 × 2) = 10966 – 11940 = –974 kJ mol^{-1}	**1**
7(b)(i)		**1**
	The delocalisation of the lone pair of electrons into C=O give it a partial single-bond character. This reduces the force constant and thus reduces the absorption frequency.	**1**
7(b)(ii)	(IR) The single peak of strong C=O amide stretching absorption at around 1650 cm^{-1} will reduce in intensity. The double peak of weak/ N-H amine stretching absorption at around 3400 cm^{-1} will appear.	**2**
	(NMR) The signal for acetyl group at around δ2.2, singlet, 3H will have reduced area under the signal. The signal for proton at amide group at around δ5 – 12 (any values), singlet, 1H will have reduced area under the signal. The signal for proton at amine group at around δ1 – 5 (any values), singlet, 2H, will appear. Any two points identified [2]	**2**

7(c)(i)		**1**
	In pure water, the polymer strands will interact via favourable hydrogen bonding, causing it to be insoluble in water as no favorable interaction with water can be formed.	**1**
	In the acidic medium, the amine group is protonated and takes on a permanent positive charge. The polymer strands will thus repel one other. This enables the hydrogen bonding / ion-dipole interaction to be formed with water, and hence soluble.	**1**

Question	Answer	Marks
7(c)(ii)	At the beginning the conductivity is high due to the ions from the excess of acid in the solution. The gradient of the graph is negative at first, which means conductivity decreases as more NaOH(aq) is added. This is due to neutralization of H^+ ion in the solution. Even though Na^+ ion is introduced, it is not as mobile as H^+.	**1**
	Next, the gradient of the graph is positive, which means conductivity increases as NaOH is added. This is due to the net increase in $[Na^+]$ ions as the neutralization of the $–NH_3^+$ groups present in chitosan occurs.	**1**
	Finally, the gradient of the graph becomes larger, means the increase in conductivity is greater as more NaOH is added. This is due to an increased in excess Na^+ and OH^- ions after all primary amine groups of chitosan are neutralised.	**1**
7(c)(iii)	η(glucosamine) = (14-6) × 0.1 /1000 = 8.0×10^{-4} mol	**1**
	mass of N-acetylglucosamine = $0.2 – 8.0 \times 10^{-4} \times 161 = 0.0712$ g η(N-acetylglucosamine) = 0.0712 / 203 = 3.51×10^{-4} mol DD = 8.0×10^{-4} / ($8.0 \times 10^{-4} + 3.51 \times 10^{-4}$) = 69.5%	**1**
7(d)(i)		
	Correct curly arrows for the first two steps + intermediates	**1**

	Correct curly arrows for the next two steps + intermediates	**1**
7(d)(ii)	The amine has higher priority as atomic number of N > H. The part of the ring with methyl group has higher priority as atomic number of C > H.	**1**
	Since the higher priority groups are on the same side of the C=C bond, it is *Z* isomer.	**1**