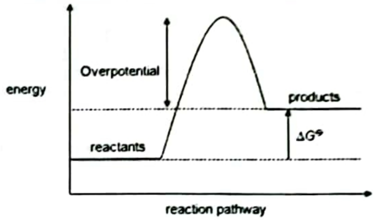
2022 Y6 H3 Chemistry Preliminary Exams – Suggested Solutions

<table>
<tr><td>1(a)(i)</td><td>$CH_4 + H_2O \longrightarrow CO + 3H_2$
$CO + H_2O \rightleftharpoons CO_2 + H_2$
For every 1 mole of CH_4, 4 moles of H_2 is produced.
Amount of $CH_4 = \frac{1 \times 10^6}{12.0 + 4(1.0)} = 62500$ mol
Amount of $H_2 = 4 \times 62500 = 250000$ mol
Mass of $H_2 = 250000 \times 2(1.0) = 500000$ g = 0.5 tonnes</td></tr>
<tr><td>1(a)(ii)</td><td>The calculation performed in (a)(i) assumed 100% yield of H_2, which is not achievable, as water-gas shift is reversible.</td></tr>
<tr><td>1(b)</td><td>As the product gases pass through the membrane with high permselectivity, it allows H_2 to leave the reaction chamber. This reduces the concentration of H_2 in the mixture.

According to Le Chatelier's Principle, when concentration of H_2 decreases, the position of water-gas shift equilibrium will shift right to favour the forward reaction producing H_2. Hence, it increases the yield.</td></tr>
<tr><td>1(c)</td><td>$\Delta G = \Delta H - T\Delta S$
ΔS is positive as there is an increase in the number of gaseous products in the equation.
Since ΔH is positive, the reaction is only feasible at high temperatures, when $|T\Delta S| > |\Delta H|$.</td></tr>
<tr><td>1(d)(i)</td><td>Anode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$
Cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$</td></tr>
<tr><td>1(d)(ii)</td><td>$E^{\ominus}_{cell} = -0.83 - (+0.40) = -1.23$ V
Minimum voltage required = +1.23 V</td></tr>
<tr><td>1(d)(iii)</td><td>When the electrolysis rate is very high, the reactants are rapidly converted to the products near the electrode surface. Thus, reactant concentration at electrode surface falls significantly below the rest of the electrolyte, while the product concentration increases. This shifts the POE and E_{cell} value to be more –ve. Hence a greater minimum voltage is required.

Rotation of the electrode increases rate of diffusion and equilibrates the electrode surface concentrations with the rest of the electrolytes, mitigating the increase in voltage required.</td></tr>
<tr><td>1(d)(iv)</td><td>$E_{reaction}$ corresponds to $\Delta G^{\ominus}$ of reaction. However more energy is needed to overcome E_a. Hence total potential(actual voltage) is higher than $E_{reaction}$.</td></tr>
<tr><td></td><td>

(Diagram not required)</td></tr>
<tr><td>1(d)(v)</td><td>$E_{cell}^{\ominus} = (-0.83) - (-0.81) = -0.02$ V

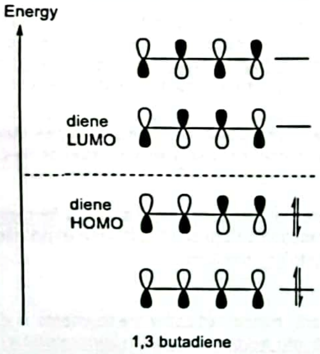
Since the $E_{cell}^{\ominus}$ for the electrolysis of methanol less negative than −1.23 V, a smaller voltage is required for the reaction to occur.</td></tr>
<tr><td>1(e)</td><td>The main difference between on-site storage of hydrogen and transport be vehicles is the ease of maintaining conditions of high pressure and low temperature.

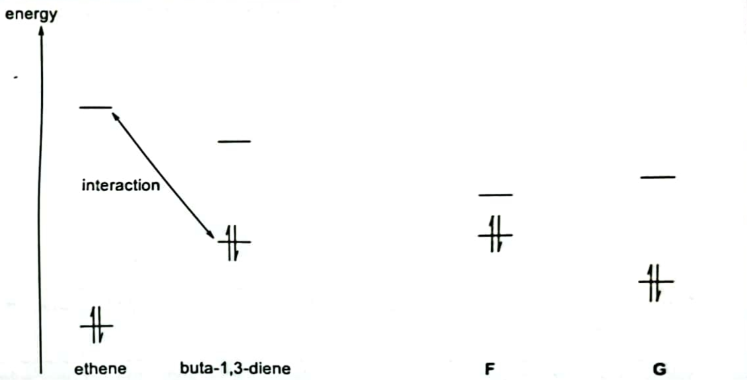
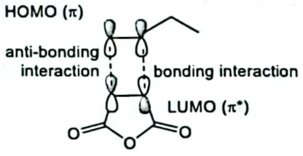
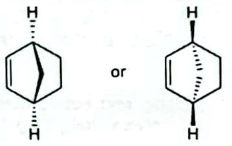
For on-site storage:
Storing H_2 as cryogenic liquid. Since the storage method is localised, it is easier to maintain low temperatures. With high volumetric density, it allows for more H_2 to be stored within a smaller space.
For transport:
High pressure gaseous H_2. It is easier/more practical to transport H_2 at ambient conditions instead of ultra-low temperatures like those in cryogenic liquid/carbon nanotubes, since bulky equipment or high energy consumption will not be required. In addition, the gravimetric density is higher than that of the other techniques, which allow for efficient transport.</td></tr>
<tr><td>1(f)(i)</td><td>A higher AE means that a greater proportion of the mass of the starting material is converted into the desired product, and less material is wasted as by-products.</td></tr>
<tr><td>1(f)(ii)</td><td>Advantages:
Atom Economy is a theoretical calculation, and it allows for rapid determination of the "greenness" of a reaction before conducting the experiment.
Simple and easy to apply to any reaction
Limitations:
Since Atom Economy is only concerned about the reactants and products in the equation, it does not take into account the waste generated by the process.
The Atom Economy assumes 100% yield in the reaction. This leads to an overestimation of the "greenness" of the reaction.</td></tr>
<tr><td>1(f)(iii)</td><td>Atom Economy of the reactions:
<table>
<tr><th>Steam Methane Reforming</th><th>Pyrolysis</th><th>Electrolysis</th></tr>
<tr><td>Reforming:
$\frac{3(2.0)}{12.0 + 4(1.0) + 2(1.0) + 16.0}$
$= 0.176$</td><td>$\frac{2(2.0)}{12.0 + 4(1.0)} = 0.25$</td><td>$2H_2O \longrightarrow 2H_2 + O_2$
$\frac{2(2.0)}{2[2(1.0) + 16.0]} = 0.11$</td></tr>
</table></td></tr>
</table>

Water-gas shift: $\frac{2(1.0)}{12.0 + 16.0 + 2(1.0) + 16.0}$ = 0.04		

From the Atom Economy calculation, pyrolysis has the highest atom economy.
Since the carbon produced by pyrolysis is in the solid state and is non-volatile, the process does not emit greenhouse gases.

Alternative responses:
Pyrolysis is not good because large amounts of energy required.
If CO_2 can be captured, the steam-reforming reaction can be a viable option too since 1 mole of CH_4 can produce 4 moles of H_2.
Ease of extraction/separation of product.

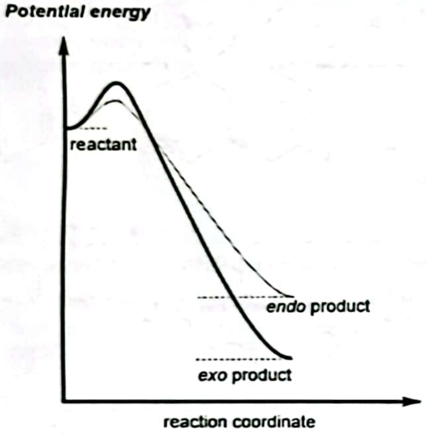
2(a)(i)	$\pi \rightarrow \pi^*$
(ii)	Since buta-1,3-diene has increased conjugation, there is more than one possible $\pi \rightarrow \pi^*$ transition, hence multiple absorption bands will be observed in its UV spectrum. Since conjugated π systems will reduce energy gap, buta-1,3-diene will absorb at longer wavelengths.
(iii)	

(b)(i)	
(ii)	A smaller energy gap between the HOMO of **F** and LUMO of **G** results in a better overlap/interactions of orbitall in the transition state, stabilising the transition state, lowering the E_a and increasing the rate of reaction between **F** and **G**.
(iii)	 The combination of orbitals is bonding on the right(in-phase overlap) but anti-bonding on the left(out-of-phase overlap), hence no reaction occurs.
(iv)	No, the 2 C=C bonds must be *cis* to each other along the C-C single bond so that interaction between diene HOMO and dienophile LUMO is possible.
(c)(i)	 (same molecule)
(ii)	The bonding interaction stabilises the transition state, lowering activation energy. The product is therefore formed faster.
(iii)	The exo product is more thermodynamically stable due to less steric hindrance between the anhydride and the one-atom bridge.

(iv) Diels-Alder reaction only involved changes on atoms 1 to 6. There are 3 C=C and 1 C–C bonds in the reactants, while the product has 1 C=C and 5 C–C bonds on atoms 1 to 6.

Enthalpy change = −4(350) + 2(610) = −180 kJ mol^{-1}

(v)

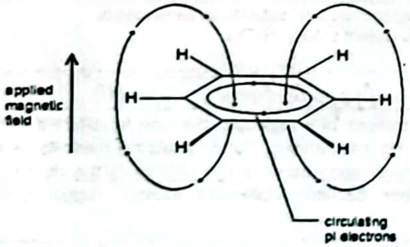


(vi) The reactants are insoluble in water due to their intermolecular instantaneous dipole-induced dipole interactions being incompatible with the hydrogen bonds between water molecules. Hence, when water is used as solvent, the reagents are "clumped together" and forced into close proximity.

Ratio is 96:4 (accept any ratio higher than 85:15 but lower than 100:0)

Water as a solvent favours a faster rate of reaction and hence the kinetic product to a greater extent than the organic solvent. Hence, a higher proportion of the endo product is formed.

3(a)

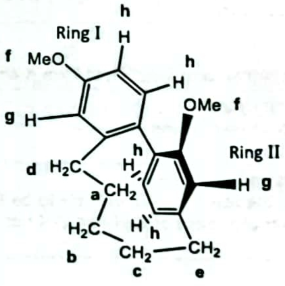


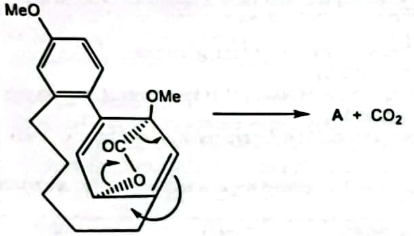
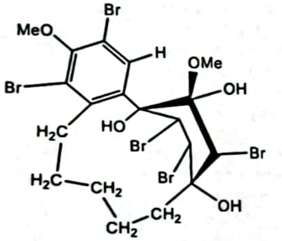
When a magnetic field is applied, the circulating π electrons of benzene generate a secondary magnetic field.
The H$_a$ protons are located near the centre of the benzene ring where the secondary magnetic field opposes the applied field . The H$_a$ protons experience a lower magnetic field hence greater shielding and thus have a negative chemical shift.

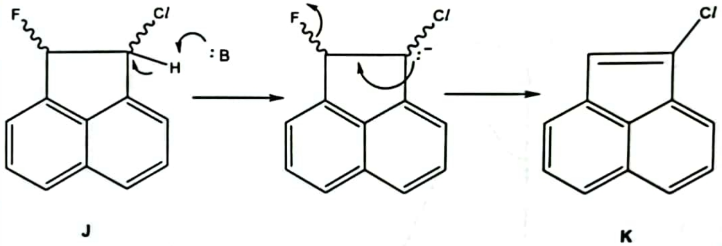
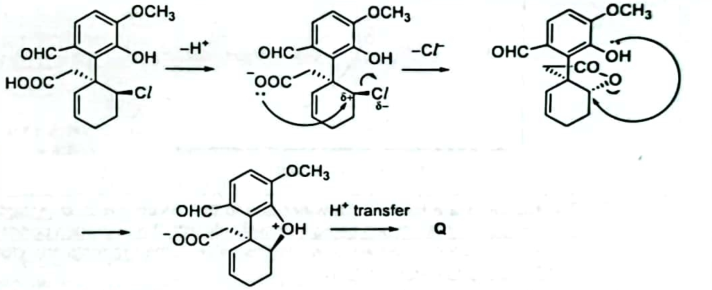
3(b)(i) $C_{19}H_{22}O_2$
At least one of the following reasons should be included:
- (m+1) C13 calculation (19 C)
- m/e value + counting H from ^{1}H NMR (11 H for empirical formula, 22H for molecular formula, 2O for making up Mr)
- figuring out the reaction should be decarboxylation and proposing MF from structure.

3(b)(ii) Index of unsaturation = 9. Two phenyl rings, and a 3rd ring for cyclophane bridge.

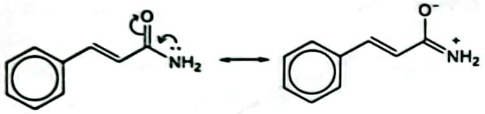
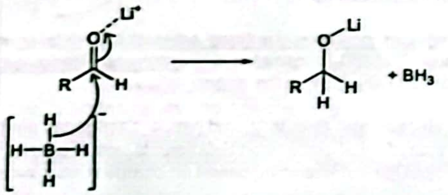
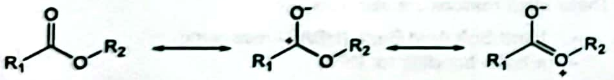
δ /ppm	splitting pattern	groups	label
−0.5	quintet	-CH$_2$- in bridge, over a benzene ring, with 2 CH$_2$ neighbours	a
0.9	quintet	-CH$_2$- in bridge, furthest position from phenyl with 2 CH$_2$ neighbours	b
1.2	quintet	-CH$_2$- in bridge with 2 CH$_2$ neighbours	c
2.1	triplet	-CH$_2$- in bridge, with only one CH$_2$ neighbour	d
2.3	triplet	-CH$_2$- in bridge, with only one CH$_2$ neighbour	e
3.7	singlet	-OCH$_3$	f
6.9 – 7.5	multiplet	phenyl	g-h

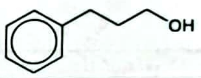
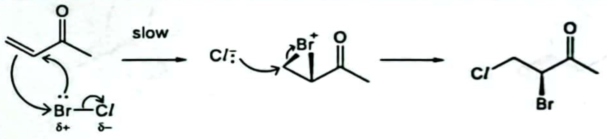


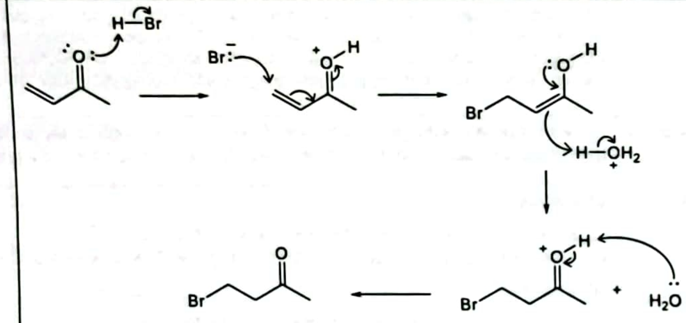
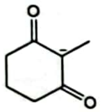
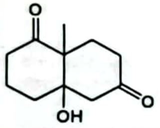
	The inclusion of ring I as part of the 7 member bridge over the 2-5 positions of ring II forces the plane of ring I to be locked perpendicularly to the plane of ring II. **A** thus has no plane of symmetry and will give a non-superimposable mirror image. Thus, it is chiral.
3(b)(iii)	
3(b)(iv)	**B** is product from the electrophilic substitution on anisole Ring I and electrophilic addition on Ring II. Electrophilic addition on Ring II removes the planar aromatic ring and relieves strain from the bridge structure. 
3(c)(i)	Considering C-X bond broken for elimination, BE(C-Cl) = 340 kJ mol^{-1} BE(C-F) = 485 kJ mol^{-1} More energy required to break C-F bond Hence E$_a$ for formation of K should be higher, and reaction to form K should be slower.
3(c)(ii)	When [J] doubled, rate doubled, 1st order w.r.t. J When [base] halved, rate halved, 1st order w.r.t. base Rate = k[J][base]
3(c)(iii)	Since it has second order kinetics, it is unlikely to be E1 Since stereochemistry does not affect the reaction, it is unlikely to be E2 (also, for cis isomers bond rotation to achieve planar alignment of C-H and C-X not possible due to cage structure)

	C-X bond breaking is not part of RDS (break C-Cl would be faster in both E1 or E2 and should give **L**). So it is not E2. The H$^+$ is extracted by the base, and the C-F bond breaks in a separate step. (This is E1cB) 
3(d)(i)	 Also possible/valid to deprotonate phenol group before second S$_N$2 takes place. S$_N$1 mechanism also acceptable, need to include neighbouring group for induction/ion-pair formation to explain stereochemistry.
3(d)(ii)	Step 4: condensation/nucleophilic addition-elimination Step 5: reduction + nucleophilic acyl substitution/aminolysis Step 5 reagent: NaBH$_4$ (reject LiAlH$_4$, H$_2$/Pt)

4(a)(i)	Different modes of vibrations in a molecule give rise to different vibrational energy levels, such as stretching and bending. For a vibrational mode to be active in the IR region, the vibration must bring about a net change in the dipole moment of the molecule. The transition between vibrational energy modes corresponds to IR frequency absorbed.

4(a)(ii)	Cinnamamide compared to cinnamaldehyde: The infra-red C=O stretching frequency in cinnamamide is lower than in cinnamaldehyde is because the C=O bond in cinnamamide is weaker. A weaker bond results in a smaller force constant which leads to lower IR absorption frequency. The lone pair of electrons on the N atom in cinnamamide can delocalize into the π electron cloud of the C=O, resulting in greater single bond character in C=O. In cinnamaldehyde, this delocalisation does not occur. Hence, the C=O bond is stronger in cinnamaldehyde than in cinnamamide.  (diagram not required) Cinnamaldehyde compared to cinnamoyl chloride: Presence of electron withdrawing Cl in the cinnamoyl chloride makes the C=O carbon more electron deficient, and increase polarity of C=O bond. C=O bond is thus strengthened and the infra-red C=O stretching frequency in cinnamoyl chloride is higher. Note: for Cl the inductive effect outweighs resonance effect in influencing C=O electron density.
4(b)(i)	
4(b)(ii)	 

	The carbonyl carbon in aldehydes are more electrophilic as one out of two of its resonance structures carries a positive charge. The carbonyl carbon in esters are less electrophilic as one out of three of its resonance structures carries the positive charge. Hence, aldehydes are more susceptible to the nucleophilic attack by the BH_4^-.
4(b)(iii)	Li^+, with a greater charge density, coordinates more strongly to the carbonyl oxygen atom than Na^+, activating the carbonyl towards nucleophilic attack to a larger extent.
4(c)	IR analysis: • absence of strong band ~1700 cm⁻¹ → no C=O group • presence of strong, broad band ~3200 – 3600 cm⁻¹ → presence of O–H group MS analysis: • *m/e* ratio of 136 corresponds to the molecular formula $C_9H_{12}O$ 
4(d)(i)	
4(d)(ii)	The $[M]^+$, $[M+2]^+$ and $[M+4]^+$ values are 184, 186 and 188 and corresponds to the ions with $^{35}Cl\ ^{79}Br$; $^{35}Cl\ ^{81}Br$ & $^{37}Cl\ ^{79}Br$; and $^{37}Cl\ ^{81}Br$ respectively. The abundances of the molecular ion peaks of $[M]^+$: $[M+2]^+$: $[M+4]^+$ would be: 0.75 x 0.5 : 0.75 x 0.5 + 0.25 x 0.5: 0.25 x 0.5 = 3 : 4 : 1
4(e)(i)	 The terminal vinylic carbon is electrophilic.

4(e)(ii)	
4(f)(i)	$(CH_3CH_2)_3N$ is a poor nucleophile as it has 3 alkyl groups which increase steric hindrance about the N atom.
4(f)(ii)	
4(f)(iii)	

5(a)(i)	OH^- ligands donate more electron density to Fe(III) metal center than H_2O ligands. Thus the Fe(III) metal center has higher electron density/is more stabilised, and less easily reduced in $Fe(OH)_3$. **OR** answer based on charge

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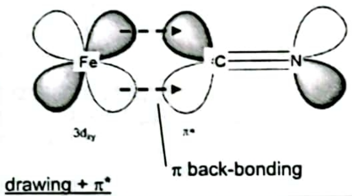
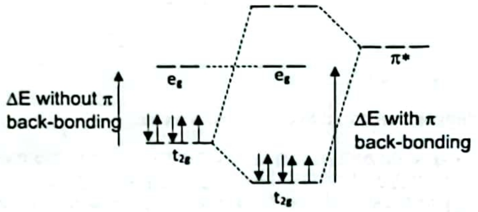
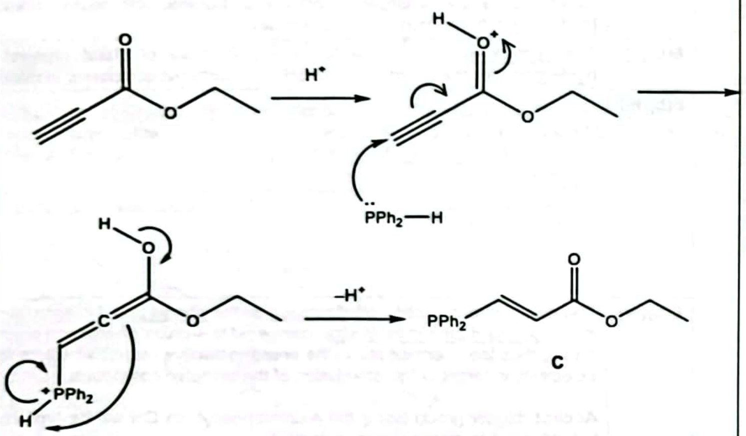
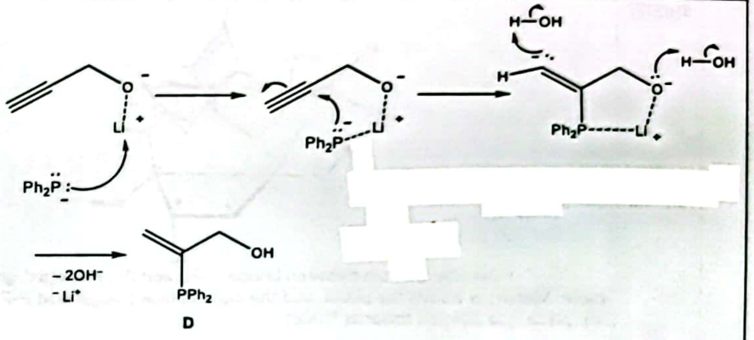
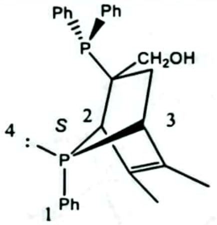
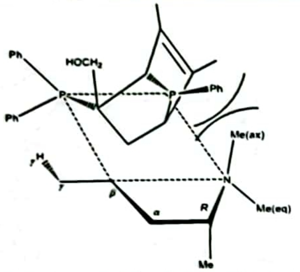
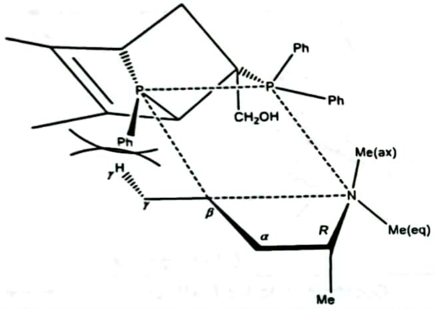
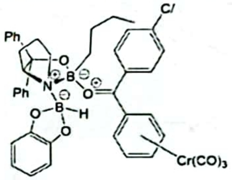
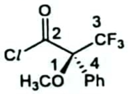
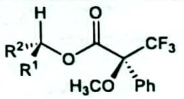
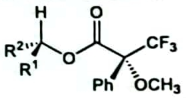
5(a)(ii)	$3d_{xy}$, $3d_{yz}$, and $3d_{xz}$. Any 1.  drawing + π*
5(a)(iii)	 Must conserve total number of contributing and resulting MOs. The empty π* orbital is used to accept electron density from the t_{2g} orbitals, resulting in lowered t_{2g} orbital energy and a larger ΔE. (labelling of resultant t_{2g} orbitals not required) This π back-bonding also increases the bond order of the metal-ligand bonds, and hence a more stable $[Fe(CN)_6]^{3-}$ complex with strongest ligand-metal bonds than $Fe(OH)_3(H_2O)_3$ and $[Fe(H_2O)_6]^{3+}$, with the largest $\lg K_{stab}$. The C atom is less electronegative than O, and hence ^-CN ligands are better σ donors of electron density to the Fe(III) center than H_2O ligands, with $[Fe(CN)_6]^{3-}$ having a less positive $E^\ominus$ than $[Fe(H_2O)_6]^{3+}$. (Reasoning based on charge is also accepted) This effect is offset partially by π back-bonding, as the Fe(III) center releases electron density to the CN^- ligand π* orbitals, and with a lower electron density, $[Fe(CN)_6]^{3-}$ has more positive $E^\ominus$ than $Fe(OH)_3$.
5(b)	P is below N in group 15 and has higher energy HOMO. Thus P HOMO has less energy gap with the Au LUMO. These other reasons are also accepted: - Hard Soft Acid Base (HSAB) reasoning. - π back-bonding for PPh_3

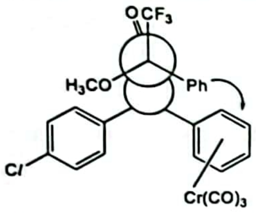
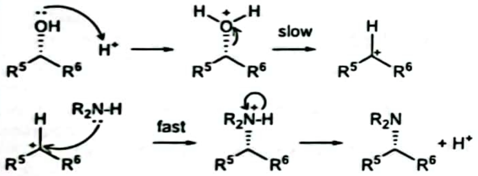
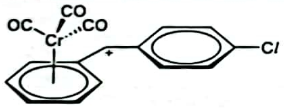
5(c)(i)	**H-PPh$_2$ is a poor electrophile as P is not so electronegative and the P-H bond is insufficiently polarised. Hence electrophilic addition to give B does not take place, instead, nucleophilic conjugate addition to give C can take place when the C=O is conjugated to the alkyne.** **OR vinylic cation formed from electrophilic attack not stable.** **OR nucleophilic attack not possible since the alkyne is not conjugated to C=O** 
5(c)(ii)	**Normally, we would expect the Ph_2P^- and CH_2O^- groups to repel.** **(Steric hindrance also accepted as reason)**
5(c)(iii)	**The product regiochemistry indicates the two groups associate instead, and that is probably through coordinating to a metal ion, such as Li^+.**

	
5(d)(i)	 F *S*-7-phosphorus
5(d)(ii)	- Coordination to the Pd(II) center reduces electron density of **D** and makes it more susceptible to receive electrons from the diene. - Coordination to the Pd(II) center takes away the lone pair electron from P in the cyclic phosphole and reduced its aromaticity. This increases the electron density in the double bonds and made the diene more able to donate electron density. - Coordination to the Pd(II) center places the two reactants in close proximity and alignment for reaction, increasing reactivity/decreasing activation energy required.

5(d)(iii)	 P2-A steric strain between bridge P-Ph and the N-Me(ax) group. (note: Me(ax) is above the plane, and the diphosphine bridgehead P-Ph is also above the plane and pointed towards N-Me)  P2-B steric strain between bridge P-Ph and the C-Hγ. (note because of *R* config on chiral auxiliary, the naphthalene ring is slightly tilted, and the Hγ is slightly below the plane, and pointed towards the diphosphine. The bridgehead P-Ph is pointed towards the Hγ and also below the plane.) Both complexes in set P2 are less stable due to steric strain, and are not formed. Thus, only the set P1 complexes form, which give rise to **F**

6(a)(i)	0
6(a)(ii)	The $Cr(CO)_3$ group is electron-withdrawing/Due to donation of π electron density for coordination to Cr thus reducing the negative charge and stabilising the conjugate base of compound **C**.
6(a)(iii)	$^{-}M{-}C{\equiv}O^{+} \leftrightarrow M{=}C{=}O$

	The resonance structure shows that the carbon monoxide ligands in compound **C** have a partial double bond character, hence the C≡O bond is weaker than that in free carbon monoxide resulting in a lower infra-red absorption frequency.
6(b)(i)	The orbital containing the lone pair of electrons on oxygen atom overlaps with the p-orbital of B in catecholborane, delocalizing the O electrons to B, thus reducing its lewis acidity/electrophilicity, thus the N atom in chiral catalyst B will react faster with BH_3 than catecholborane. Catecholborane is a larger molecule than borane, and causes greater steric strain hindrance in the formation of the complex.
6(b)(ii)	The convex exterior of the fused ring structure of chiral catalyst B poses less hinderance for the coordination of BH_3 and carbonyl compound in intermediate **F**.
6(b)(iii)	
6(b)(iv)	The enantiomeric excess will decrease as the phenyl and 4-chlorophenyl substituents in compound **H** are similar in size, compared to 4-chlorophenyl and phenyl with $Cr(CO)_3$ group, thus the intermediate in the enantioselective reduction will be formed with less selectivity in terms of the orientation of the carbonyl compound. **Accept** :bigger group being the 4-chlorophenyl, so OH will be "up" instead of "down" but still need to discuss lower selectivity.
6(c)(i)	Anisotropic effect
6(c)(ii)	 *R* configuration Priority assignment: OCH_3 > COC*l* > CF_3 > Ph
6(c)(iii)	 *S* Moscher ester  *R* Moscher ester *R* and *S* Moscher esters of compound **E** are diastereomers as they are stereoisomers which are not mirror images of each other.

6(c)(iv)	 shielding effect leads to smaller chemical shift of the signal for the protons here *S* Moscher ester of compound **E** Since the chemical shift of the signal due to the proton on the phenyl ring that is coordinated to the $Cr(CO)_3$ group in the *S* Moscher ester of compound **E** is smaller than that in *R* Moscher ester of compound **E**, Δδ of this signal will be negative.
6(d)(i)	Nucleophilic substitution, S_N1 
6(e)(ii)	 The loss of water as a leaving group anti to the $Cr(CO)_3$ group generates a carbocation with the $Cr(CO)_3$ group on one face, causing nucleophiles to preferentially approach from the other face, resulting in retention of configuration and no loss in enantiomeric excess. Partial double character in C-C single bonds between the positively charged carbon and phenyl increases the rotation energy barrier.
6(e)(iii)	The BF_4^- is non-nucleophilic (due to absence of lone pair on boron and highly electronegative fluorine) and will not interfere with the nucleophilic substitution reaction, unlike Cl^- which is nucleophilic as it is able to donate an electron pair.