CODS
SUMMER CHEMISTRY OLYMPIAD
Gold Tier

NAME			
DATE		PROCTOR'S NAME	
CIN			
TIER	**GOLD**		

For Proctor's Use	
Time start:	
Time end:	

INSTRUCTIONS:
Fill in your team name, date, proctor's name, team captain's CIN and tier above.

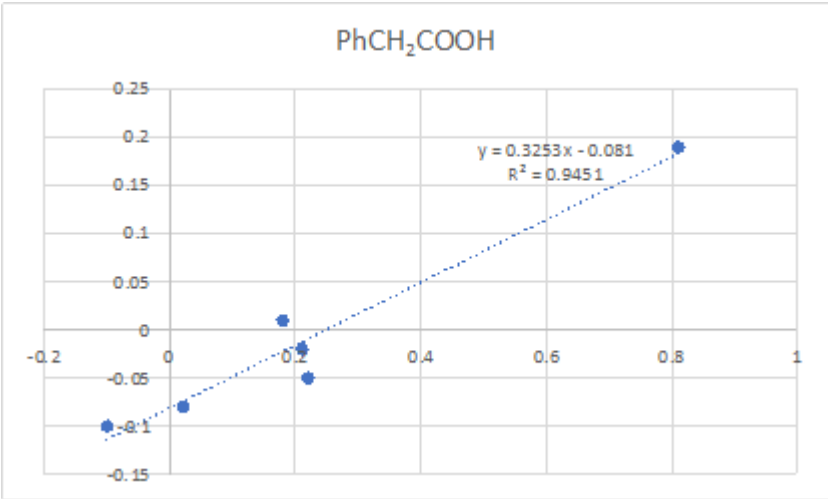
All results must be written in the appropriate answer boxes with pen or pencil on the answer sheets.

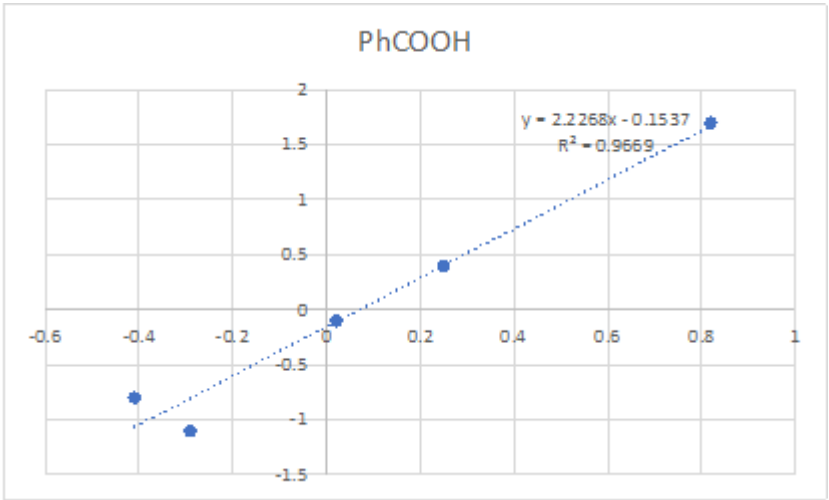
The number of marks is given in the table at the top of each question.

This document consists of **37** printed pages.

Problem 1 11.1% of total	Question	1.1	1.2	1.3	1.4	1.5	1.6	1.7	Total
	Points	5	10	8	10	5	5	5	48

1.1)





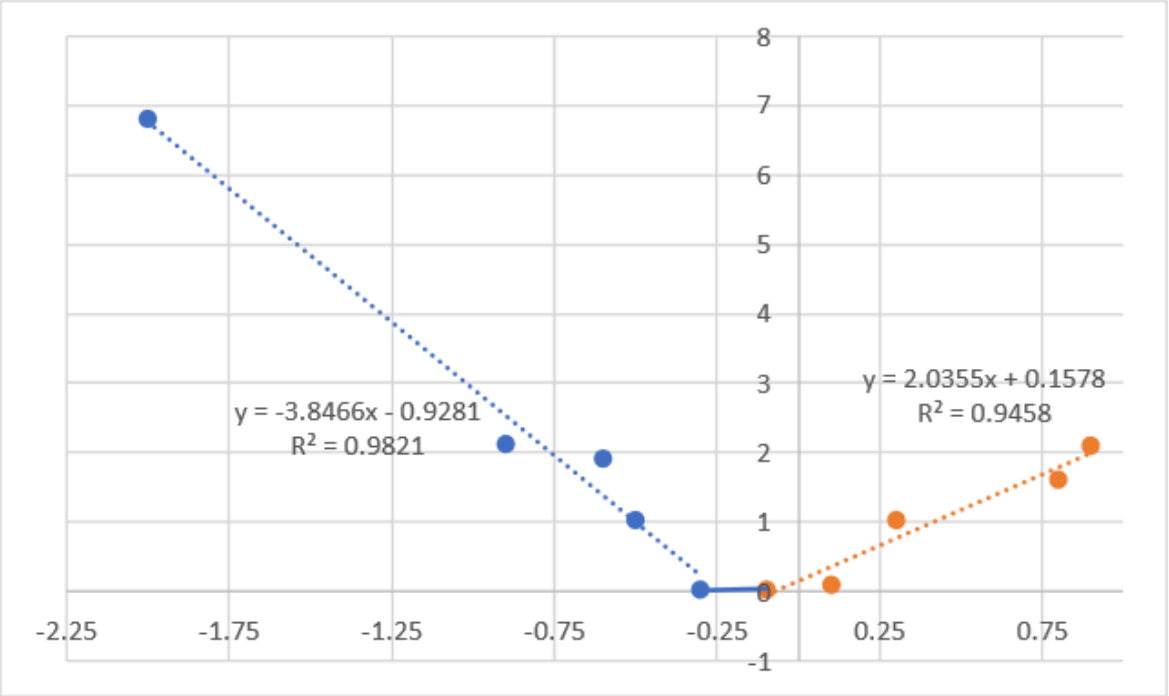
2.5 points for each correct regression line (BOTH coefficients must be in the acceptable range (5%)):
For PhCH2COOH: slope = [0.309, 0.342], y-intercept = [-0.00851, -0.00769]
For PhCOOH: slope = [2.11, 2.34], y-intercept = [-0.162, -0.14]
1 point each if coefficients are close to the acceptable range (within 10%)

1.2)

Phenylacetic acids have a smaller rho value than benzoic acids. **[2 points]**
The rho values indicate lower and higher sensitivities of the acidities to the substituent effects. The smaller rho for the phenylacetic acids derives from the more remote position of the substituents relative to the carboxyl group, which leads to decreased stabilization of the carboxylate anion, as compared to that in the benzoic acids. Hence, the substituents in benzoic acids are more important in stabilizing/destabilizing of the negative charge in the carboxylates. **[8 points]**

1.3)

Breaking point occurs at p-CH3 and p-F. [3 pts]



2.5 points for each correct regression line (BOTH coefficients must be in the acceptable range (5%)).
If the breaking point is determined incorrectly, the acceptable range is ±5% from the coefficients of least squares regression on the regions determined by the students (no double penalty).
Before the break: slope = [-4.04, -3.66], y-intercept = [-0.975, -0.881]
After the break: slope = [1.93, 2.14], y-intercept = [0.149, 0.166]
1 point each if coefficients are close to the acceptable range (within 10%)

[Turn Over]

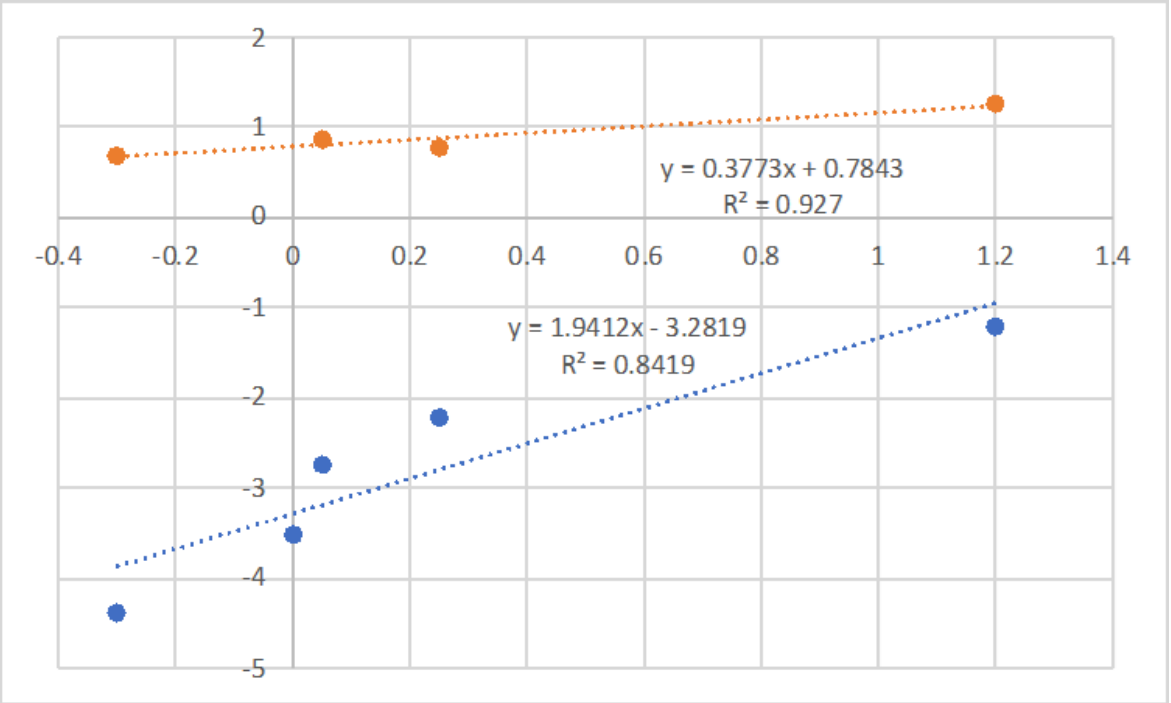
1.4)

[See the plot from the previous part]

2 points for a V-shaped plot.

The shape of the LFER plot suggests a mechanism change from SN1 to SN2, which occurs due to the decrease in stability of the phenylethyl carbocation. **[5 points]** The electron-donating substituents, i.e. with negative sigma values, stabilize the resulting carbocation, which makes the SN1 pathway more favourable, and the leftmost substituents on the LFER plot show best selectivity to azide, which is a better nucleophile. **[3 points]** On the other hand, electron-withdrawing groups do not exhibit such stabilization, which leads to SN2 mechanism being favoured and worse selectivity for stronger nucleophiles.**[2 points]**

1.5)



2.5 points for each correct regression line (BOTH coefficients must be in the acceptable range):
For uncatalyzed reactions: slope = [0.358, 0.397], y-intercept = [0.745, 0.823]
For catalyzed reactions: slope = [1.84, 2.04], y-intercept = [-3.45, -3.11]
1 point each if coefficients are close to the acceptable range (within 10%)

1.6)

There is a change in dominating mechanism: from E1cB to BAc2 [2 points] as evidenced by the decrease of rho values. **[3 points]**

1.7)

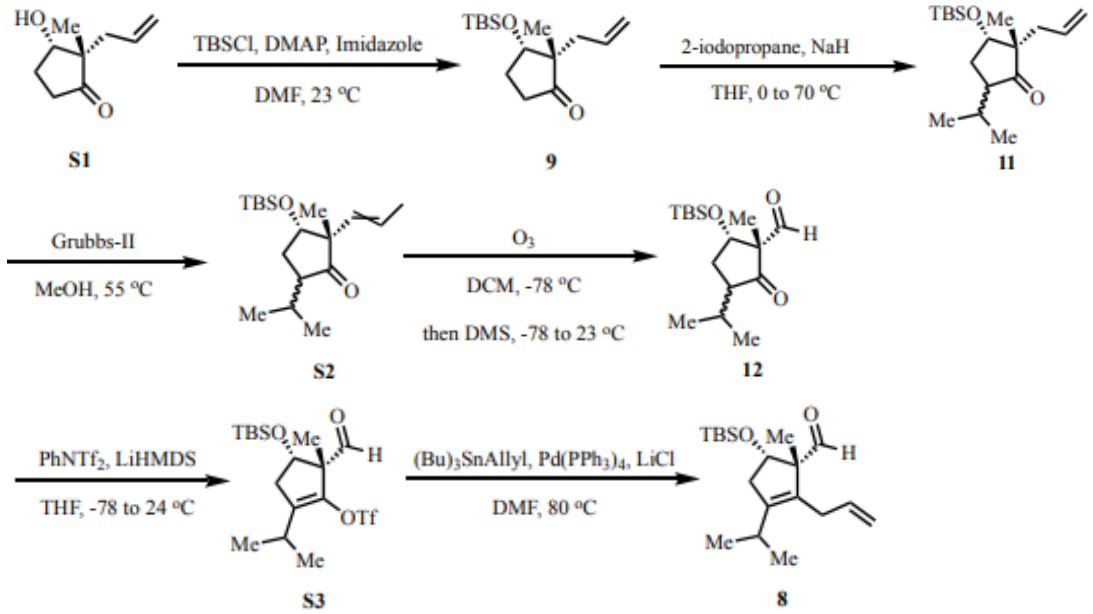
The antibody binds to the anionic intermediate to stabilize it, lowering the energy barrier for the BAc2 pathway, making it energetically favored, and hence, dominating.

[Turn Over]

Problem 2 11.1% of total	Question	2.1	2.2	2.3	2.4	Total
	Points	7	21	2	5	35

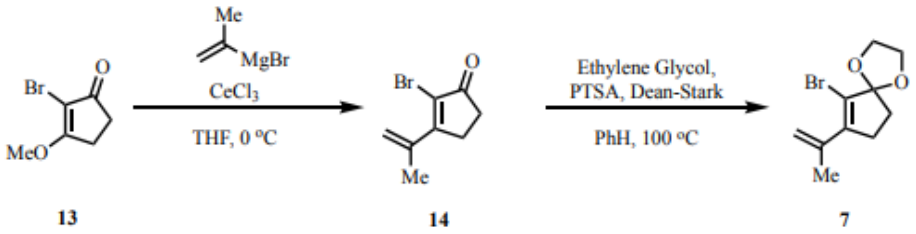
2.1)

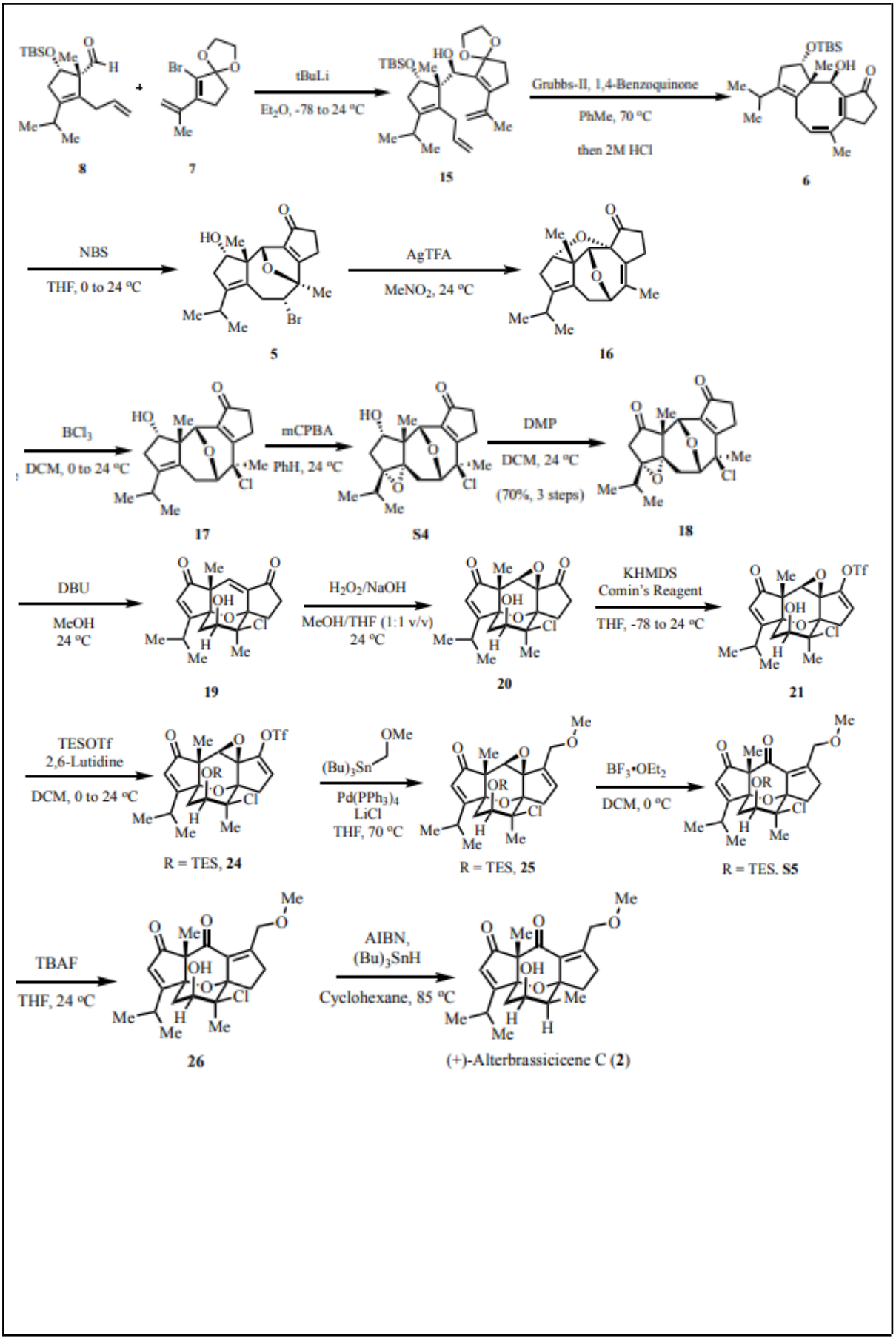
8, 9, 11, 12, S3 – 1 point, S2 – 2 points.



2.2)

5, 6, 15, 16, 17, 18, 19, 20, 21, 24, 25, 26, S5, S4 – 1.5 points

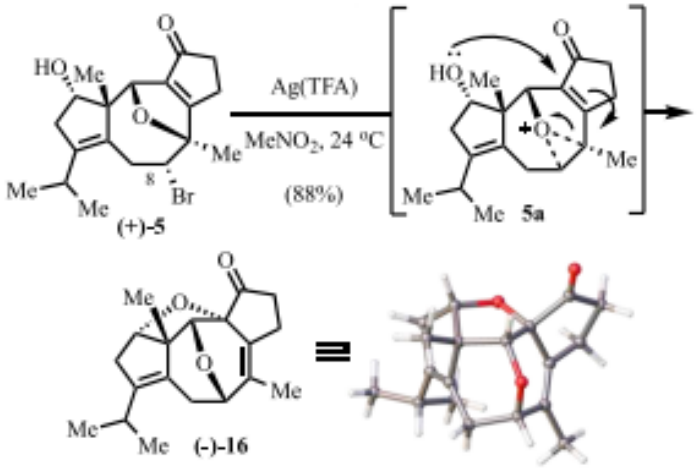



8
7
tBuLi
Et2O, -78 to 24 °C
15
Grubbs-II, 1,4-Benzoquinone
PhMe, 70 °C
then 2M HCl
6
NBS
THF, 0 to 24 °C
5
AgTFA
MeNO2, 24 °C
16
BCl3
DCM, 0 to 24 °C
17
mCPBA
PhH, 24 °C
S4
DMP
DCM, 24 °C
(70%, 3 steps)
18
DBU
MeOH
24 °C
19
H2O2/NaOH
MeOH/THF (1:1 v/v)
24 °C
20
KHMDS
Comin's Reagent
THF, -78 to 24 °C
21
TESOTf
2,6-Lutidine
DCM, 0 to 24 °C
R = TES, 24
(Bu)3Sn
Pd(PPh3)4
LiCl
THF, 70 °C
R = TES, 25
BF3•OEt2
DCM, 0 °C
R = TES, S5
TBAF
THF, 24 °C
26
AIBN,
(Bu)3SnH
Cyclohexane, 85 °C
(+)-Alterbrassicicene C (2)

[Turn Over]

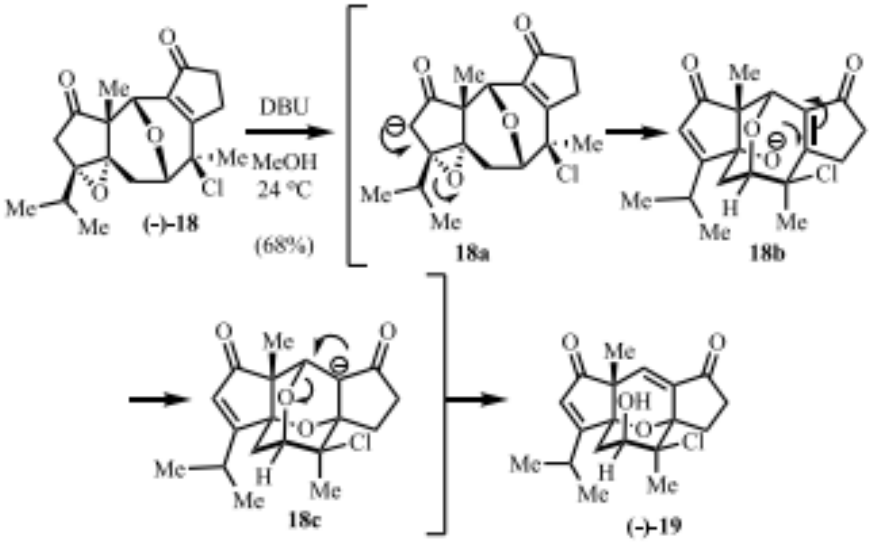
2.3)

Mechanism with intermediate – 2 points



2.4)

Mechanism – 5 points

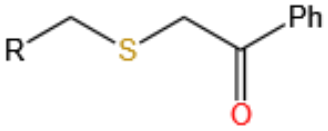


Problem 3 11.1% of total	Question	Ingredient #1			Ingredient #2					Ingredient #3		Total
		3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	80
	Points	9	12	9	4	5	2	10	4	17	8	

3.1)

1

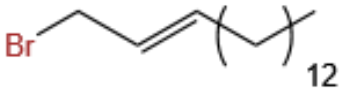
2



3

3.2)

5



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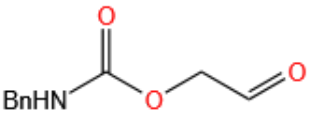

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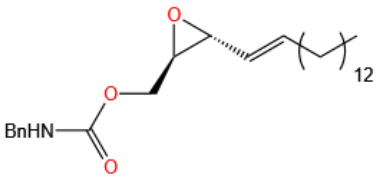

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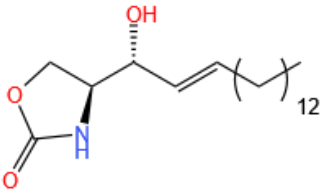
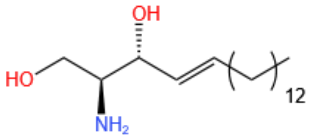
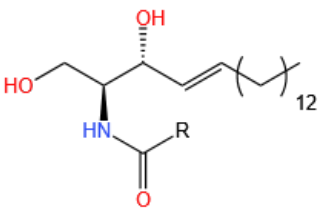


3.3)

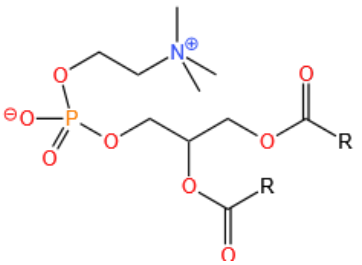
10



11



9



[Turn Over]

3.4)

Let us start with the Michaelis-Menten equation. Using the following substitutions:

$$y = 1/v \text{ AND } x = 1/[S],$$

We obtain the linearised form **(1.5m)**

$$1/v = \frac{K_m}{V_{max}}\frac{1}{[S]} + \frac{1}{V_{max}}$$

$1/V_{max}$ is the y-intercept (1m). By substituting y = 0 to yield the x-intercept, we obtain **$1/[S] = -1/K_m$. (1.5m)**

3.5)

I expect a low degree of accuracy for this question because… the image in the original paper is pretty grainy LOL. I am more interested in the **proof of concept**. The candidate should be able to do the following for EACH graph:

- Locate each x-intercept
- Take their inverse to find K_m for each reading
- For each graph, take the average among the K_m.

For reference, here are my readings:
Varying [SAM], intercepts are -0.083, -0.1085 and -0.1300. Average K_m is 9.7 μM ± 1.5 μM **(3m)**
Varying [DBA], intercepts are -0.1096 and -0.1344. Average K_m is 8.3 mM ± 1.0 mM **(2m)**

3.6)

Non-competitive inhibition (2m)

3.7)

Mass balance for [E] **(2m)**

$$[E]^\circ = [E] + [ES] + [EI] + [ESI]$$

We then **substitute** with K_m and K_i; by definition, K_i does NOT change when the enzyme is bound to the substrate. Else this would be **mixed inhibition**.

$$[E]^\circ = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_i} + \frac{[EI][S]}{K_i}$$

Sub for [EI] again and factorise [E]: **(2m)**

$$\frac{[E]^\circ}{[E]} = 1 + \frac{[S]}{K_M} + \frac{[I]}{K_i} + \frac{[S][I]}{K_M K_i}$$

Factorise RHS, which is in the form 1 + a + b + ab: **(1m)**

$$\frac{[E]^\circ}{[E]} = \left[1 + \frac{[S]}{K_M}\right]\left[1 + \frac{[I]}{K_i}\right]$$

Now let's introduce V_{max} into the equation and manipulate the LHS: **(2m)**

$$V_{max} = k[E]^\circ$$

$$v = k[ES] = \frac{k[E][S]}{K_M}$$

$$\frac{[E]^\circ}{[E]} = \frac{V_{max}[S]}{vK_M}$$

Multiply both sides by K_M, **(1m)**

$$\frac{V_{max}[S]}{v} = (K_M + [S])\left[1 + \frac{[I]}{K_i}\right]$$

Final step to make v the subject **(2m)**

$$v = \frac{V_{max}[S]}{(K_M + [S])\left[1 + \frac{[I]}{K_i}\right]}$$

[Turn Over]

3.8)

By definition, when [I] = IC_{50}, v is half that of v_0 when [I] = 0M. When [I] = 0M, the inhibition equation simplifies to the original Michaelis-Menten equation. Let's call the rate without inhibition v_0. **(2m)**

$$2 = \frac{v_0}{v} = \frac{\cancel{V_{max}}[S]}{\cancel{K_M + [S]}} \div \frac{\cancel{V_{max}}[S]}{\cancel{(K_M + [S])}\left[1 + \frac{[I]}{K_i}\right]}$$

This equation simplifies VERY quickly **(1m)**

$$2 = 1 + \frac{[I]}{[K_i]}$$

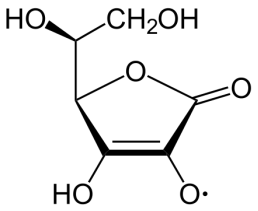
Hence, we can arrive at [I] = IC_{50} = K_i. (1m) A pretty elegant solution if you ask me, because the IC_{50} here is **independent of [S]** (non-competitive inhibition).

3.9)

1
O_2 (2m)

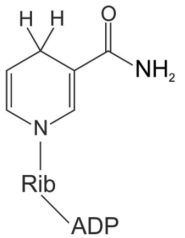
2
H_2O (2m)

3



(3m)
Full credit if radical is on other reductone hydroxy group.

4

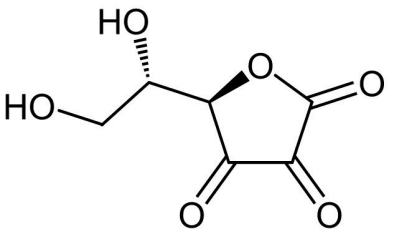


(3m)
Riboside can be shown as "R"

5

H^+ (2m)

6



(3m)

7 **GSSG (2m)**
3.10)
W $NADH + H^+ + 2C_6H_7O_6 \rightarrow NAD^+ + 2C_6H_8O_6$
X $2C_6H_8O_6 + H_2O_2 \rightarrow 2C_6H_7O_6 + 2H_2O$
Y $C_6H_6O_6 + 2GSH \rightarrow C_6H_8O_6 + GSSG$
Z $NADH + H^+ + GSSG \rightarrow NAD^+ + RSH$

[Turn Over]

Problem 4 11.1% of total	Question	4.1	4.2	4.3	4.4	4.5	Total
	Points	4	4	6	6	6	26

4.1)

2 Points per correct structure

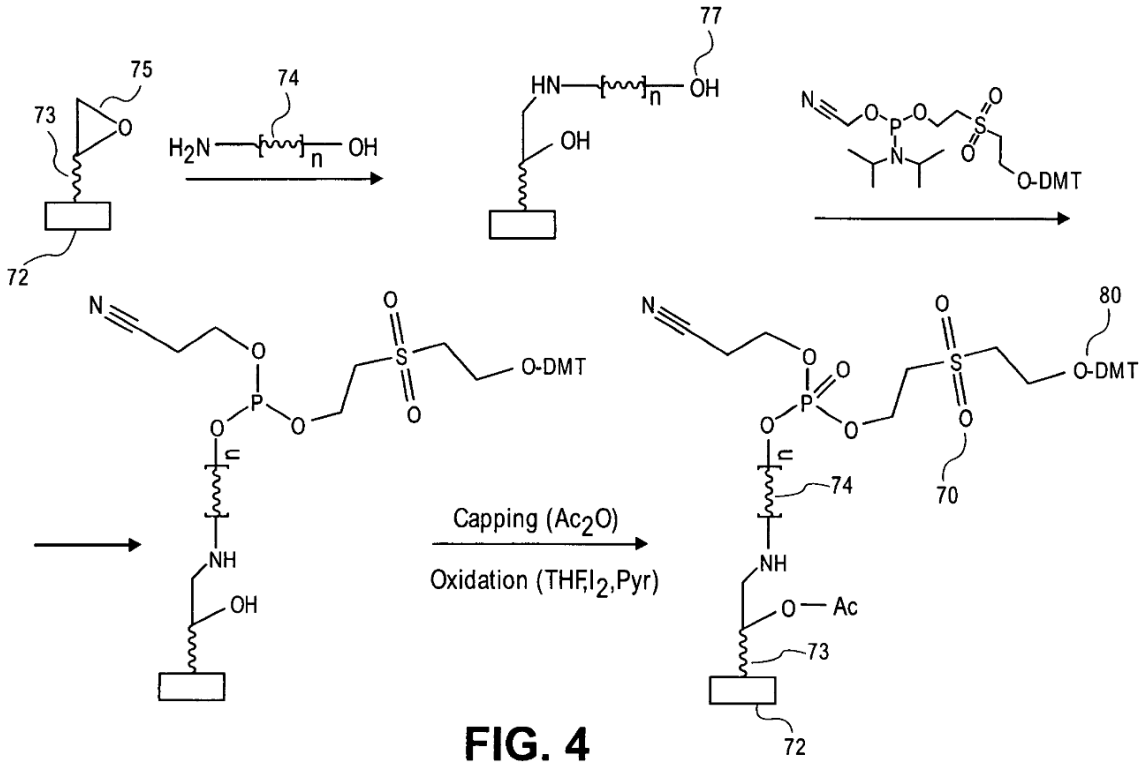


FIG. 4

4.2)

2 Points per correct structure

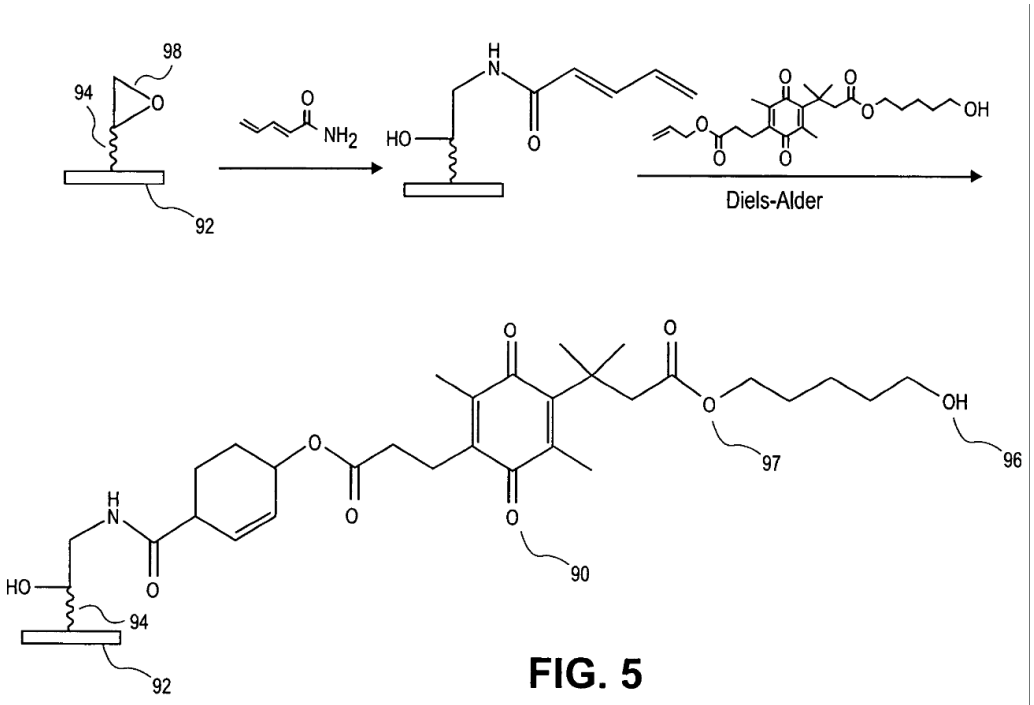
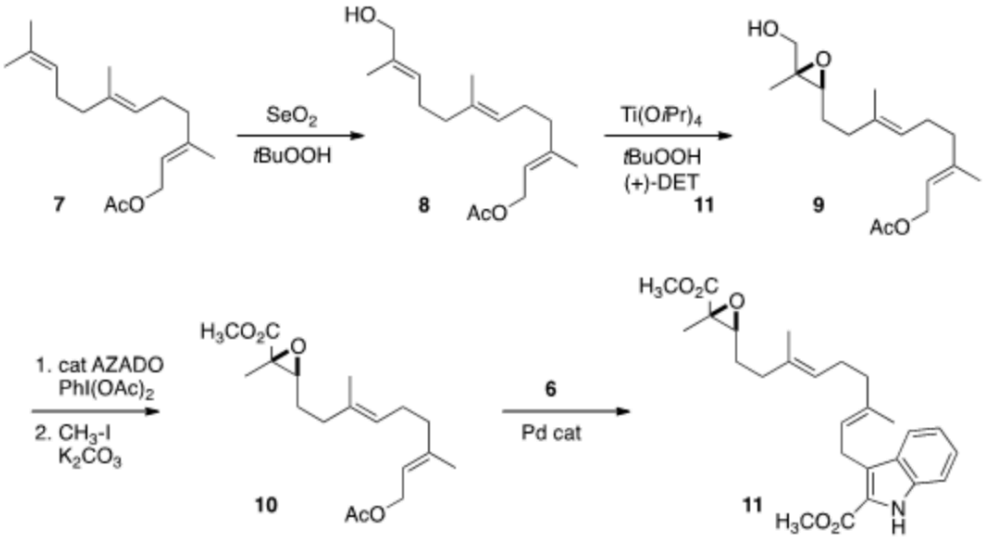


FIG. 5

4.3)

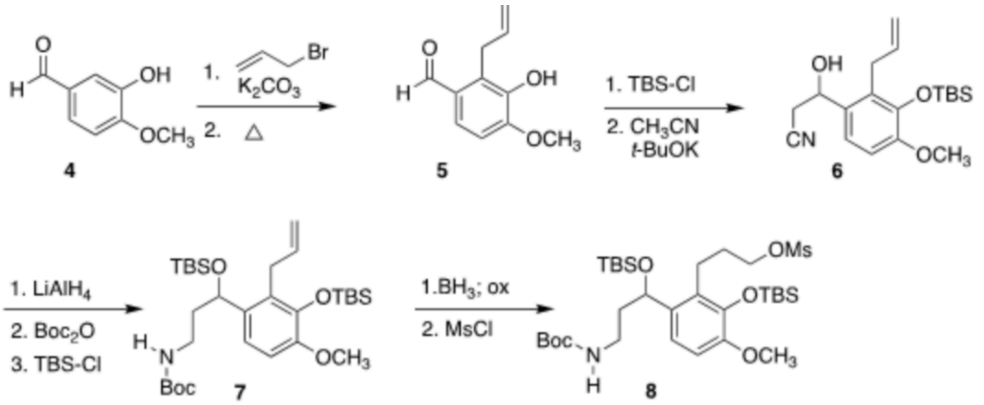
2 Points per correct structure



[Turn Over]

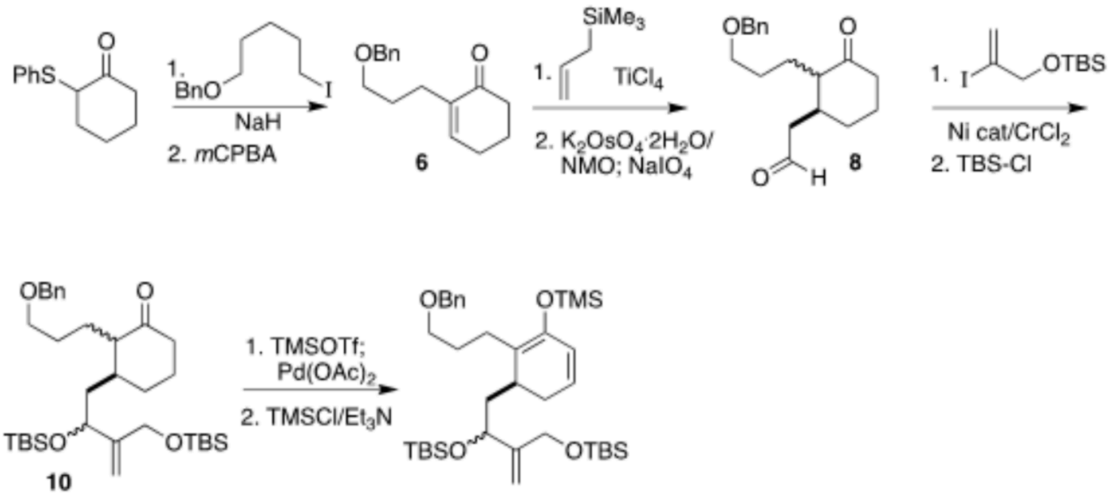
4.4)

2 Points per correct structure



4.5)

2 Points per correct structure



Problem 5
11.1% of total

Question	5.1	5.2	5.3	5.4	5.5	Total
Points	4	2	3	4	4	40
Question	5.6	5.7	5.8	5.9	5.10	
Points	5	4	3	9	2	

5.1)

Conserving total moles, we have $n = n^\alpha + n^\beta$. Furthermore, conserving total moles of component 2, we get $n^\alpha X_2^\alpha + n^\beta X_2^\beta = nX_2^0$. We substitute $n^\beta = n - n^\alpha$ and get:

$$n^\alpha X_2^\alpha + (n - n^\alpha)X_2^\beta = nX_2^0$$

Rearranging to isolate $f^\alpha = n^\alpha/n$, we get $f^\alpha = \frac{X_2^\beta - X_2^0}{X_2^\beta - X_2^\alpha}$.

+0.5 for total mole conservation, +0.5 for total X_2 conservation. +3 correct answer; half credit may be given if n^α is isolated. Out of 4 possible pts.

5.2)

Observe that $f^\beta = 1 - f^\alpha$. Simplifying, we get $f^\beta = \frac{X_2^0 - X_2^\alpha}{X_2^\beta - X_2^\alpha}$.

+2 all or nothing.

5.3)

Given chemical potentials in J/mol, then we can express G_i as $G_i = n_1 G_1^0 + n_2 G_2^0$.

+3 all or nothing.

[Turn Over]

5.4)

Similar to part 3, we express G_f as $G_f = n_1 G_1 + n_2 G_2$. We plug in $G = G^0 + RT \ln \frac{p}{P}$ for both components and get:

$$G_f = n_1 \left(G_1^0 + RT \ln \tfrac{p_1}{P}\right) + n_2 \left(G_2^0 + RT \ln \tfrac{p_2}{P}\right)$$

Recall that, according to Raoult's law, $p_i = X_i P \rightarrow X_i = p_i / P$ and $X_1 = 1 - X_2$, and we get:

$$G_f = n_1 \left(G_1^0 + RT \ln(1 - X_2)\right) + n_2 \left(G_2^0 + RT \ln X_2\right)$$

+1.5 correct expression of G_f in terms of pressures. +0.5 substituting pressure for mole fraction using Raoult's law. +2 correct final answer. Out of 4 possible pts.

5.5)

Recall that $\Delta G_{mix} = G_f - G_i$. Observe that the $n_1 G_1^0 + n_2 G_2^0$ terms cancel out, resulting in:

$$\Delta G_{mix} = n_1 RT \ln(1 - X_2) + n_2 RT \ln X_2$$

Observe that $X_i = n_i / n \rightarrow n_i = X_i n$ for some component i. As such:

$$\Delta G_{mix} = X_1 nRT \ln(1 - X_2) + X_2 nRT \ln X_2$$

which simplifies to $\Delta G_{mix} = nRT(X_2 \ln X_2 + (1 - X_2) \ln(1 - X_2))$.

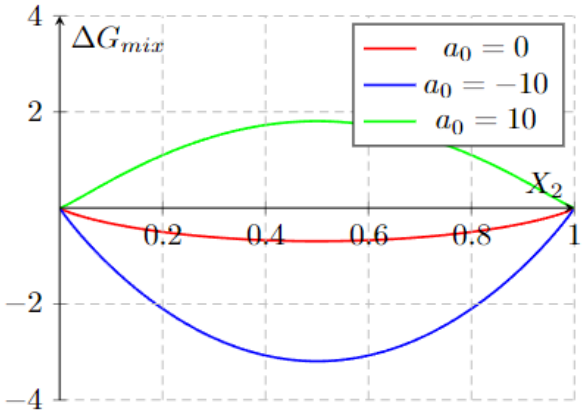
+0.5 correct definition of $\Delta G_{mix} = G_f - G_i$. +1 correct substitution of $n_i = X_i n$. +2.5 correct final answer. Out of 4 possible pts.

5.6)

Given conditions (1) and (2), we can conclude that $\Delta H_{mix} \propto X_2(1 - X_2)$. The maxima of a quadratic is the midpoint between the two zeroes, or $X_2 = 0.5$. Then $\Delta H_{mix} = a_0 nRT/4 = CX_2(1 - X_2) = C/4$, then $C = a_0 nRT$. As a result, $\Delta H_{mix} = a_0 nRTX_2(1 - X_2)$.

+2 correct quadratic form. +3 correct logic in obtaining the constant factor. Out of 5 possible pts.

5.7)



As seen from the plot, we can see that large, positive a_0 results in a positive Gibbs free energy of mixing, and the opposite for large, negative a_0. As such, $a_0 >> 0$ signifies a positive enthalpy of mixing and repulsive interactions between components, while $a_0 << 0$ signifies a negative enthalpy of mixing and attractive interactions between components.

+1 for each correct plot. +1 for a reasonable explanation of a_0. Out of 4 possible pts.

5.8)

This question is similar to part 3; we can express $G_{sep}(X_2)$ as $G_{sep}(X_2) = f^{\alpha}G(X_2^{\alpha}) + f^{\beta}G(X_2^{\beta})$.

+3 all or nothing.

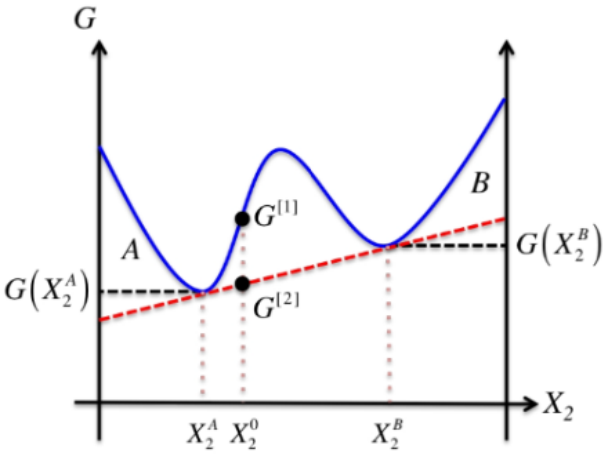
[Turn Over]

5.9)

Starting from part 8, we plug in our expressions for f^α, f^β derived from parts 1 and 2, and simplify as follows:

$$\begin{aligned} G_{sep}(X_2) &= \frac{X_2^\beta - X_2}{X_2^\beta - X_2^\alpha} \cdot G(X_2^\alpha) + \frac{X_2 - X_2^\alpha}{X_2^\beta - X_2^\alpha} \cdot G(X_2^\beta) \\ &= \frac{(X_2^\beta - X_2) \cdot G(X_2^\alpha) + (X_2 - X_2^\alpha) \cdot G(X_2^\beta)}{X_2^\beta - X_2^\alpha} \\ &= \frac{(X_2^\beta - X_2^\alpha) \cdot G(X_2^\alpha) + (X_2 - X_2^\alpha) \cdot (G(X_2^\beta) - G(X_2^\alpha))}{X_2^\beta - X_2^\alpha} \\ &= G(X_2^\alpha) + \frac{(X_2 - X_2^\alpha) \cdot (G(X_2^\beta) - G(X_2^\alpha))}{X_2^\beta - X_2^\alpha} \end{aligned}$$

Observe that (1) $G_{sep}(X_2)$ is linear w.r.t. X_2, and (2) that $G_{sep}(X_2)$ goes through points $(X_2^\alpha, G(X_2^\alpha))$ and $(X_2^\beta, G(X_2^\beta))$. From our derived model in part 6, observe that at the two phase compositions, the Gibbs free energy of mixing is minimized, meaning the Gibbs free energy of the total system is also locally minimized (since chemical potentials are linear wrt. to X_2). A labeled plot of some $G(X_2)$ and $G_{sep}(X_2)$ is shown below to assist in the intuition:



As such, we can conclude that $G_{sep}(X_2)$ is the tangent line to $G(X_2)$ at both of the minima, which means that $G_{sep}(X_2)$ must be $\leq G(X_2)$ (otherwise the points of tangency are not minima). As such, $G_{sep}(X_2) \leq G(X_2)$ for the domain of $G(X_2)$, which is $X_2 \in [0, 1]$.

+1 plugged in phase mole fractions into part 8. +2 adequate simplification of $G_{sep}(X_2)$. +1 addressed linearity of $G_{sep}(X_2)$. +2 notes that $G_{sep}(X_2)$ intersects with

$G(X_2)$ **at the mole fraction of the two phases. +3 concludes that** $G_{sep}(X_2)$ **is tangent to** $G(X_2)$ **and** $G_{sep}(X_2) \leq G(X_2)$**,** $\forall X_2 \in [0,1]$ **using the minima. Out of 9 possible pts.**

5.10)

As seen from part 9, $G_{sep}(X_2)$ is the tangent line of $G(X_2)$ at the mole fraction of the two phases. As such, $G_{sep}(X_2) = G(X_2)$ when $X_2 = \{X_2^{\alpha}, X_2^{\beta}\}$.

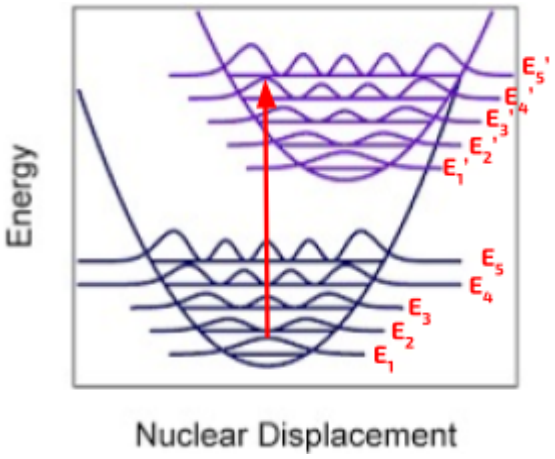
+**1 for each answer. Out of 2 possible pts.**

[Turn Over]

Problem 6 11.1% of total	Question	6.1	6.2	6.3	6.4	6.5	6.6	Total
	Points	2	1	9	1	6	4	54
	Question	6.7	6.8	6.9	6.10	6.11	6.12	
	Points	2	2	7	2	9	9	

6.1)

Given the assumption, the electronic transition may be represented by a straight, ascending arrow. For the greatest overlap in vibrational wavefunctions, start the arrow from the nuclear displacement value at the highest amplitude of the vibrational wavefunction and extend vertically upwards. Upon contacting another vibrational wavefunction in the excited state potential curve with maximal overlap, stop the arrow. This corresponds to the energy gap of the electronic transition with the highest intensity (highest probability).



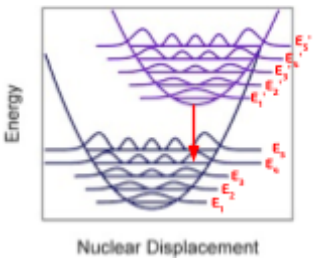
Using the Planck-Einstein equation, $E_4' = hc/\lambda_{max}$. Hence, $\boldsymbol{\lambda_{max} = hc/(E_4' - E_1)}$.

1 point for applying the Planck-Einstein equation.
1 point for correct final answer.

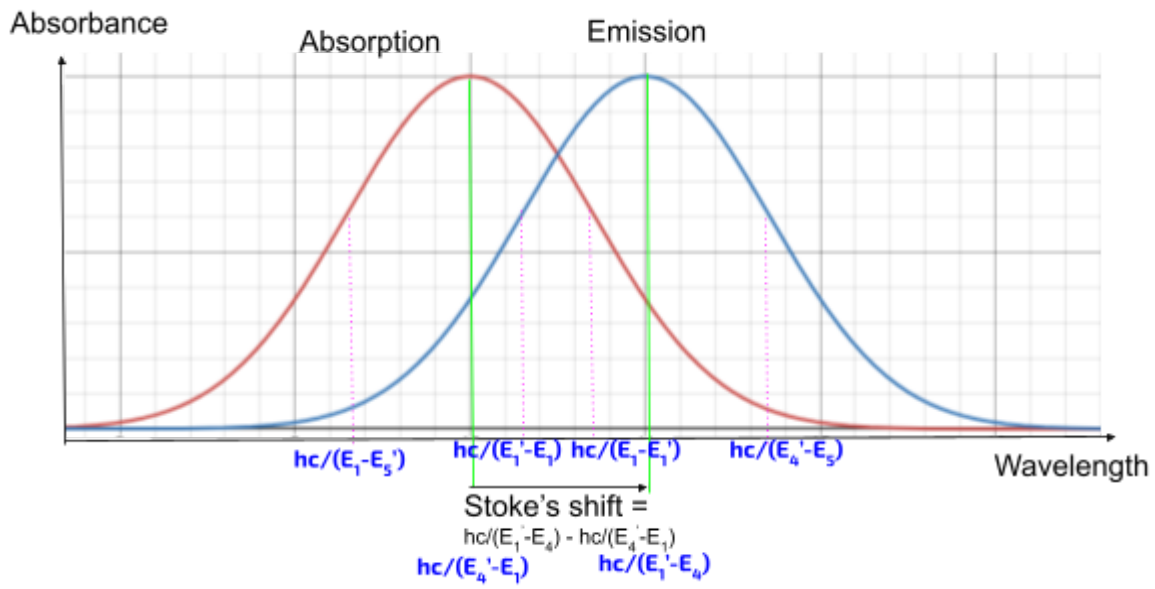
6.2)

$E_1' \rightarrow E_4$.

1 point for stating the correct electronic transition.



6.3)



1 point for a visible plane of symmetry between the absorption and emission graphs.
1 point for the correct bell-shaped curve.
1 point for the correct labelling of axes (ignore units).
1 point for correct labelling of λ_{max}.
1 point for correct labelling of at least 1 of the 2 other points.
1 point for correct relative positions with respect to the *x*-axis of the 2 other points.
1 point for writing down the energy differences (penalise –2 points if not shown)
1 point for correct conversions of all energy differences to wavelength.
1 point for correct Stoke's shift (direction of arrow is not important) and calculation.

6.4)

Applying the beer-lambert law (A = εlc),

Wavelength (nm)	**300**	**450**	**510**
pH = 12	***a* = 266.7**	400.0	293.3
pH = 7	533.3	***b* = 666.7**	440.0
pH = 2	800.0	933.3	***c* = 586.7**

1 point for correct final answers (units not required).
Penalise –0.5 points if answers were not given to 4 sf.

[Turn Over]

6.5)

Set up a system of 3 simultaneous equations at the 3 pH values to solve for a, b and c, using Beer-Lambert's Law. Let $x = [H_2A]$, $y = [HA^-]$, $z = [A^{2-}]$.

At 300nm, $1200x + 799.5y + 400.05z = 0.99496$
At 450nm, $1399.95x + 1000.05y + 600z = 1.24181$
At 510nm, $880.05x + 660y + 439.95z = 0.81872$

Solving, $x = 0.00024232$, $y = 0.00076885$, $z = 0.00022281$.

If we use the values of x and y, and set up the Henderson-Hasselbach equation, as well as $K_{a,1}$, we get the first value of pH to be 7.501452.

If we use the values of y and z, and set up the Henderson-Hasselbach equation, as well as $K_{a,2}$, we get the second value of pH to be 7.562093.

Averaging them out to minimise any errors from precision of the machine, we get pH = 7.53.

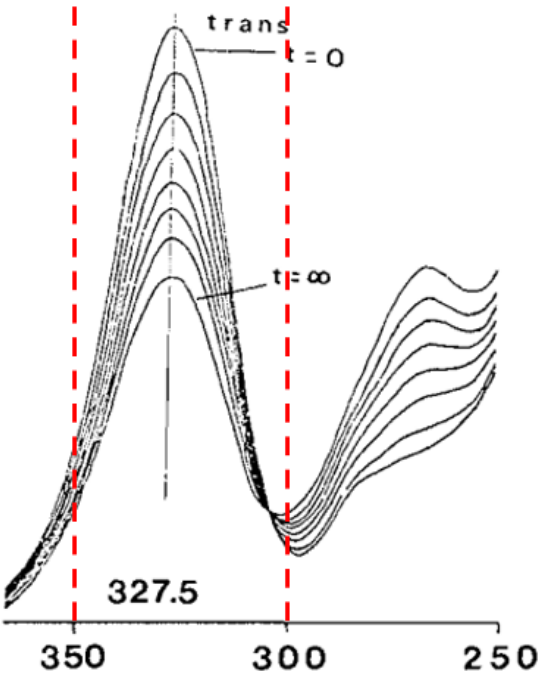
1 point for setting up the correct system of equations.
1 point for solving the system of equations correctly.
1 point for solving for one set of pH values using the Henderson-Hasselbach equation and the pH being in the range of 7.50 to 7.57, inclusive.

6.6)

A sample answer is given on the right. Only the region between the red dotted lines need to be drawn.

Marking points:

- The intensity of the absorption peak generally decreases from $t = 0$ to $t = \infty$.
- $t = 0$ should have a larger absorbance than $t = \infty$.
- At least 5 curves are drawn, with similar shapes.
- The absorption peak is drawn slightly to the right of the centre of the region. That is, it should be to-scale, since participants are expected to have a ruler with them.



1 point for each correctly drawn feature of the spectrum as identified above.
(Total 4 points)

6.7)

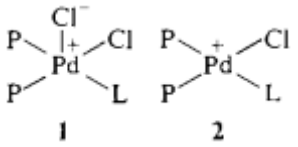
Since Beer-Lambert's Law is given by A = ε[complex]l, and the initial rate of reaction is:

$$k = -\frac{d[\text{complex}]}{dt}$$

We can deduce that: $k = -\frac{A'(0)}{\varepsilon l}$, where *A*'(0) is the first derivative of *A* with respect to *t* when *t* = 0, or equivalently, $k = -\frac{1}{\varepsilon l}\frac{dA}{dt}\Big|_{t=0}$.

1 point for correct derivation of answer through Beer-Lambert's Law and the definition of the initial rate of reaction.
1 point for the correct expression.
–0.5 points if the condition of *t* = 0 is not stated.

6.8)



These structures can be deduced from the fact that an addition-elimination reaction seems to appear as **2** has Cl^- as a side product.

1 point for each correct structure. (Total 2 points)

6.9)

<u>For the cis-to-trans isomerisation,</u>

$$\text{Rate} = \frac{d[\mathbf{4}]}{dt} = k_3[\mathbf{1}] - k_{-3}[\mathbf{4}][\mathbf{L}]$$

Assuming the pre-equilibria approximation, and since $[\mathbf{2}] = [Cl^-] \approx [\mathbf{L}_0]$,

$$K_2 = \frac{[\mathbf{2}][Cl^-]}{[\mathbf{1}]} = \frac{[\mathbf{L}_0]^2}{[\mathbf{1}]}$$

Substituting this into the first equation, and since initially, $[\mathbf{4}] = 0$,

$$\text{Rate} = \frac{k_3[\mathbf{L}_0]^2}{K_2} = k_0[\mathbf{L}_0]^2,$$

k_0 is the observable second-order rate constant.

<u>For the trans-to-cis isomerisation,</u>

$$\text{Rate} = \frac{d[\mathbf{3}]}{dt} = k_{-1}[\mathbf{1}]$$

As equilibria K_1 and K_2 are rapidly established,

$$\frac{d[\mathbf{1}]}{dt} = k_1[\mathbf{3}][\mathbf{L}] + k_{-2}[\mathbf{2}][Cl^-] + k_{-3}[\mathbf{4}][\mathbf{L}] - (k_{-1} + k_2 + k_3)[\mathbf{1}] \approx 0$$

It is clear that at steady-state, $[\mathbf{L}] \approx 0$.

$$\text{Hence, } [\mathbf{1}] = \frac{k_{-2}[\mathbf{L}_0]^2}{k_{-1} + k_2 + k_3}.$$

Substituting this into the first equation,

$$\text{Rate} = \frac{k_{-1}k_{-2}[\mathbf{L}_0]^2}{k_{-1} + k_2 + k_3} = k_0'[\mathbf{L}_0]^2,$$

k_0' is the observable second-order rate constant.

[Turn Over]

Hence, both isomerisations obey second-order kinetics with respect to $\mathbf{L}_0$.

1 point for correct use of pre-equilibrium approximation.
1 point for correct rate equation for cis-to-trans isomerization.
1 point for correct use of SSA.
1 point for correct approximations being stated.
1 point for correct deduction of [1] expression.
1 point for correct rate equation.
1 point for correct showing of second-order kinetics.

6.10)

$$\text{Absorbance, } A = 0.59\mathrm{e}^{-x^2+1104-304704}$$

$$\frac{\mathrm{d}A}{\mathrm{d}x} = 0.59\left(-2x+1104\right)\mathrm{e}^{-x^2+1104-304704}$$

$$\text{At } \lambda_{\max},\ \frac{\mathrm{d}A}{\mathrm{d}x} = 0.$$

$$0.59\left(-2x+1104\right)\mathrm{e}^{-x^2+1104-304704} = 0$$

$$\because \mathrm{e}^{-x^2+1104-304704} > 0\ \forall\ x \in \mathbb{R},$$

$$0.59\left(-2x+1104\right) = 0$$

$$2x = 1104$$

$$x = 502, \text{ i.e. } \lambda_{\max} = 502 \text{ nm}$$

1 point for correct differentiation.
1 point for correct λ_{max}.

6.11)

Substituting the values into the equation, $(0.20105)(10) = 0.5(K_2)(0.5/100^2)(200^2)$.
$K_2 = 2.0105$ G Oe^{-1}, i.e. $\chi_m = 2.0105M$.

Due to FCC structure,
Cell length = 2/sqrt(2) × 249.28 pm = 352.5351568 pm,
Volume = $(352.5351568 \text{ pm})^3 = 4.38134348 \times 10^{-23}$ cm^3;
Mass of 1 unit cell = $4.38134348 \times 10^{-23}$ cm^3 × 8.9 g cm^{-3} = $3.899395697 \times 10^{-22}$g
No. of atoms in 1 FCC unit cell = 4
Mass per MOLE of atom = $(6.022 \times 10^{23}) \times (3.899395697 \times 10^{-22}) / 4 = 58.70540 \sim 58.69$
Therefore ion **Y** is nickel with $M_r = M = 58.69$.

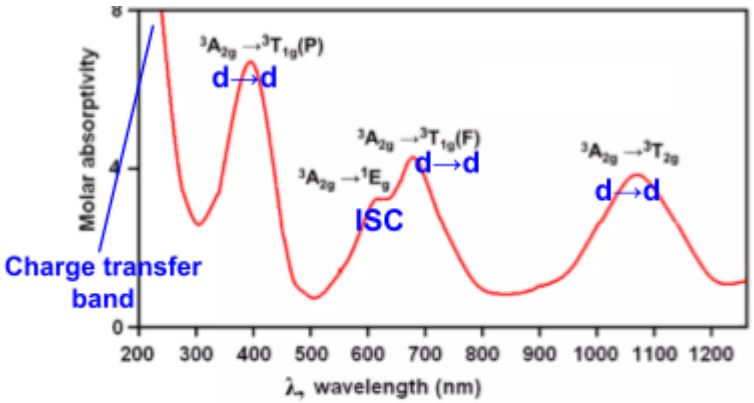
$\chi_m = MK_2 = 2.0105 \times 58.69 = 117.996245$, i.e. $\mu_{eff} = 2.992603382$
Solving, n = 2.155 ~ 2.

This implies that the Ni ion contains 2 lone pairs.
There are only a few possibilities: d^8, d^7 high-spin, d^6 high-spin, and d^2.
These correspond to Ni^{2+}, Ni^{3+}, Ni^{4+} and Ni^{8+} ions.

The UV-vis data provides a clue that the ion should exist as a greenish colour in solution as most of the light at wavelength corresponding to green is unabsorbed. Therefore the ion is Ni^{2+}, i.e. it has an oxidation state of +2.

1 point for correctly calculating K_2.
2 points for determining mass of 1 unit cell.
2 points for deducing that Y is Ni.
1 point for determining that n = 2.
1 point for stating the possible oxidation states of Ni (seen or implied).
2 points for using the UV-vis data given to deduce that Ni^{2+} is present.

6.12)



The first band (charge transfer band) is neither spin-forbidden nor Laporte-forbidden due to the huge absorption.

The d ⟶ d bands are Laporte forbidden but spin-allowed as $[Ni(H_2O)_6]^{2+}$ is centrosymmetric. However, in spite of the Laporte-forbidden nature of d ⟶ d transitions in **Y**, vibronic coupling can transiently break symmetry and allow for electronic transitions. Similarly, spin–forbidden transitions can be allowed due to the phenomenon of spin-orbit coupling.

The shoulder peak with the lowest absorbance corresponds to intersystem crossing (ISC) which is both spin-forbidden and Laporte-forbidden. *This can be illustrated on a Jablonski diagram.*

Identification of all correct peaks: 4 points (≥ 2 correct peaks: 2 points)
Identifying charge transfer as not being subject to restriction by any spin selection rules: 1 point
Explanation of d ⟶ d transitions being Laporte forbidden: 1 point
Mentioning vibronic coupling/spin-orbit coupling: 1 point
Explanation of ISC being spin-forbidden AND Laporte forbidden : 2 points

[Turn Over]

Problem 7 11.1% of total	Question	7.1	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.9	Total
	Points	7	2	15	5	7	1	3	2	5	47

7.1)

Since the sample of **A** contains only one isotope of the metal, the presence of the M + 2 and M + 4 peaks are likely due to the presence of two halogen atoms. We can hence deduce the identity of the halogen atoms based on the ratio of the relative abundances of the M, M + 2 and M + 4 peaks.

***Note**: For ^{35}Cl : ^{37}Cl, this ratio is approximately 3 : 1; for ^{79}Br : ^{81}Br, this ratio is approximately 1 : 1; for iodine, virtually only ^{127}I will be present (i.e. we can presume I is absent, especially since the molecular ion peak is only at m/e of 291).*

Notice that if two Cl atoms are present, the relative abundances of the M, M + 2 and M + 4 peaks are as such:

Isotopes present	Relative abundance	Ratio of peaks
^{35}Cl, ^{35}Cl	(3/4)(3/4) = 9/16	9
^{35}Cl, ^{37}Cl	2(1/4)(3/4) = 6/16	6
^{37}Cl, ^{37}Cl	(1/4)(1/4) = 1/16	1

Hence **A** contains 2 Cl atoms.

Additionally, we can obtain the approximate number of carbon atoms in **A**, based on the abundance of ^{12}C : ^{13}C, which is approximately 100 : 1.1.

Number of carbon atoms = (100/1.1) × 0.11 = 10 (i.e. 10 carbon atoms)

Notice that the mass spectrum of **A** shows a peak at M – 65 (226) and M – 130 (161). This implies that **A** likely has two identical ligands, i.e. each ligand has 5 carbon atoms. Then,

Total mass of remaining atoms in one of the ligands = 65 – 5(12) = 5,

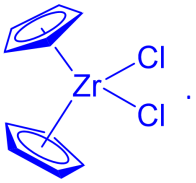
which indicates the presence of 5 hydrogen atoms, i.e. the chemical formula of the ligand is C_5H_5. This corresponds to the well-known cyclopentadienyl anion ligand, which is confirmed by the fact that **A** demonstrates hapticity. Since **A** is a quaternary compound with only one metal centre, we can probably deduce the identity of the metal centre.

***Note**: this implies that the Cl atoms are directly bonded to the metal centre in compound **A**.*

Then, to figure out the identity of the metal centre, we can simply deduct the masses of the ligands from the molecular ion peak value.

$$\text{Mass of metal isotope} = 291 - 2(65) - 2(35) = 91,$$

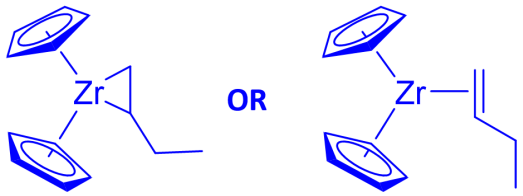
which best corresponds to ^{91}Zr.

Hence, compound **A** is zirconocene dichloride, 

.

[1] for deducing that A contains 2 Cl atoms.
[1] for deducing that A contains 10 C atoms.
[1] for deducing that A contains two identical ligands of formula C_5H_5.
[1] for deducing that the identity of the C_5H_5 ligand is Cp.
[1] for deducing the identity of the metal present in A.
[2] for correct final structure drawn (accept the use of the abbreviation Cp).

7.2)



Note: *The hygroscopic salt is LiCl, and the flammable gas is butane which is obtained via reductive elimination.*

[2] for correct structure drawn.

7.3)

From the molecular formula of **B**, we can deduce that there are 4 DBEs here. One of the DBEs can be attributed to the terminal alkene functional group, as given by the hint. One of them can also be attributed to a C=O bond, as noted in the ^{13}C spectrum (δ = 221.0). In the absence of other sp^2 hybridised carbon atoms (inferred from the ^{13}C NMR spectrum), this suggests that the remaining 2 DBEs are due to rings. Indeed, the hint tells us there is a six-membered ring, so another ring will account for the final DBE.

Let us first list out some deductions based on each individual peak.

^{1}H NMR Spectrum:

[Turn Over]

δ / ppm	Integral	Multiplicity/ Coupling	Deductions
1.03, 1.13	3, 3	s	2 chemically similar terminal methyl groups present
1.75, 2.04	1, 1	d, J = 11 Hz	2 geminal hydrogens coupling with each other ($R_2CH_aH_b$)
4.92, 5.16	1, 1	m	Presence of 2 terminal alkene protons, multiplets likely arose from allylic coupling.

^{13}C NMR Spectrum:

δ / ppm	Deductions
23.6, 25.5	2 chemically similar terminal methyl groups present
26.0	RCH_2R
26.1	RCH_2R
40.7	$R^1R^2R^3CH$
48.2	$R^1R^2R^3CH$
48.7	$R^1R^2R^3CH$
107.2	Fully substituted sp^2 alkene carbon (R^1R^2**C**=CH_2) present.
151.0	Terminal sp^2 alkene carbon (R^1R^2C=**C**H_2) present. Note the large difference in chemical shifts between the two alkene carbons, where one is highly shielded while the other is highly deshielded. This strongly suggests the presence of a terminal alkene.
221.0	C=O bond, indicating presence of ketone functional group.

Next, we shall attempt to deduce the structure of the other ring in **B**.

Since the oxygen is part of a ketone function group, the only possible atom forming the rings is carbon, implying that there are 6 carbons in the six-membered ring. There is a terminal alkene functional group, implying that one carbon is used to form the terminal alkene. Furthermore, there are 2 terminal methyl groups, which correspond to 2 carbons. Then,

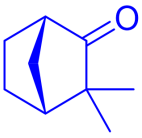
$$\text{number of remaining carbons} = 10 - 6 - 1 - 2 = 1,$$

which heavily implies that the other ring arises from bridging within the 6-membered ring by the last carbon atom. There are 3 possible bridged backbone structures: norbornane (1,4-bridging), norpinane (1,3-bridging) and norcanane (1,2-"bridging"). However, the other two possibilities can be ruled out: as compared to norbornane,

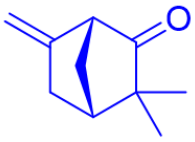
norcanane and norpinane are highly unlikely to be the main product of the reaction (as mentioned in the question) due to greater ring strain.

Hence, we can set up the backbone of **B**:

From the NMR spectrums, we can infer that the 2 methyl groups are still bonded to a single carbon. Based on the structure of filfolone, we can infer that the carbonyl carbon and the carbon bonded to the 2 methyl groups are still adjacent to each other in compound **B**:



Similarly, to determine the position of the remaining terminal alkene functional group, we can refer to the structure of filfolone. The terminal alkene functional group most likely originated from the methyl group on the alkene in filfolone, which is on the carbon furthest away from the carbon bonded to the other two methyl groups. Hence, we can finally deduce the structure of **B**, and we are done.

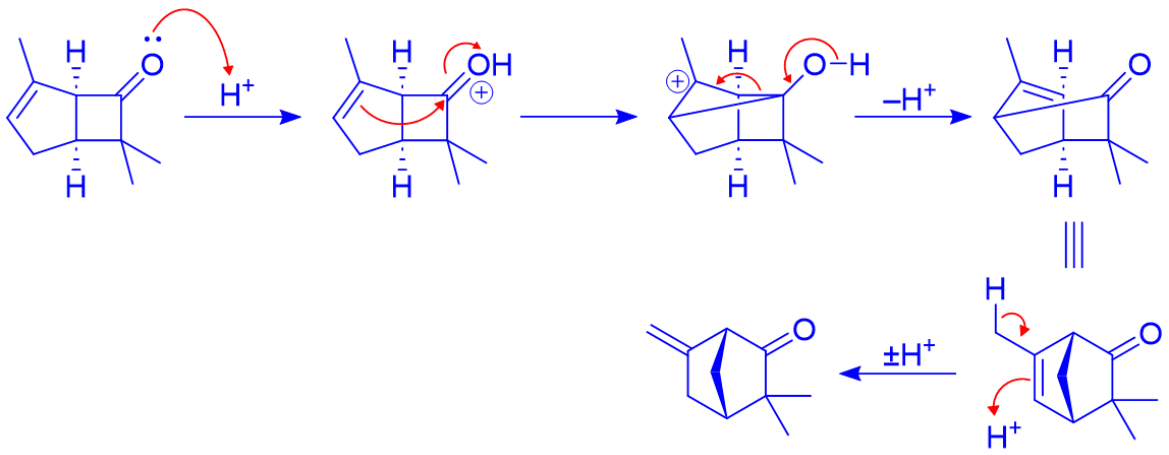


[2] for deducing that B is bicyclic.
[1] for deducing that the 2 methyl groups are still bonded to the same carbon.
[1] for deducing that there are 2 geminal hydrogens.
[1] for assigning the δ = 4.92 and 5.16 peaks of the ^{1}H NMR spectrum to the terminal alkene protons (not required to state that the multiplets are due to allylic coupling).
[1] for deducing that there are 2 di-substituted carbons and 3 tri-substituted carbons based on the ^{13}C NMR spectrum given.
[1] for deducing the presence of a terminal alkene based on the ^{13}C NMR spectrum.
[1] for assigning the carbonyl carbon to the δ = 221.0 peak in the ^{13}C NMR spectrum.
[3] for deducing and explaining the bridged backbone structure of B (process of elimination – [1]; correct backbone structure – [2]).
[1] for correct positioning of the ketone and 2 methyl functional groups.
[1] for explaining the position of the alkene functional group.
[2] for the correct structure of B.

Sources:
^{1}H NMR spectrum: https://doi.org/10.1021/jo01023a056
^{13}C NMR spectrum: predicted using https://www.nmrdb.org and slightly modified

[Turn Over]

7.4)



[2] for formation of tricyclic carbocation intermediate.
[2] for the formation of the 6-membered Zaitsev product.
[1] for isomerisation to form compound B.

7.5)

Compound **C** has the following NMR data: 4.35 (BB'm, 12H), 4.32 (AA'm, 12H), 3.99 (s, 30H)

We can compute the total number of hydrogens as 54. Since the original benzene ring was already hexasubstituted, we can guess that the final compound **C** is also hexasubstituted. Hence, each of the substituents must contribute 54/6 = 9 hydrogen atoms.

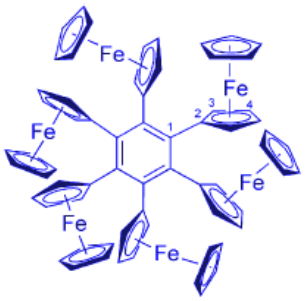
Next, we know that 30 H atoms are equivalent, that is, 5 of the hydrogen atoms in each of the substituents are equal. This corresponds nicely to a cyclopentadienyl ring.

The AA'm and BB'm pattern corresponds nicely to another cyclopentadienyl ring, as observed from the structures of AA'BB' systems given in the introduction to such naming conventions, and one of the carbon atoms are bonded to the benzene ring. We also note that the protons with δ = 4.35 ppm are H_4 (further from the benzene ring), while the protons with δ = 4.32 ppm are H_3 (closer to the benzene ring). We will examine this in a later part.

Hence, we have two cyclopentadienyl rings as part of the substituents. Let us then determine what the counterion is.

Based on the molar mass of 1181.436 g mol^{-1}, we can compute the atomic mass of the counterion. Since there are 6 carbon atoms in the benzene ring, and 10 carbon atoms per substituent, there are a total of 66 carbon atoms. There are 54 hydrogen atoms. Hence, the average atomic mass of the counterion is (1181.436 - 66 × 11.999 - 54 × 1.008)/6 = 55.845 g mol^{-1}, which corresponds nicely to Fe.

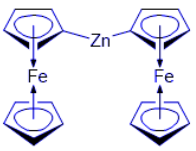
Hence, we can deduce that the structure of compound **C** is as follows:



1 point for determination of number of hydrogen atoms per ligand.
1 point for deduction of C being hexasubstituted, and thus likely being fully symmetrical.
2 points for determination of nature of ligands (cyclopentadienyl) with the AA'BB' system.
1 point for determination of correct metal ion (Fe).
2 points for correct structure of compound C.

7.6)

Reagent **D** is diferrocenylzinc, which structure is shown on the right:



1 point for correct answer.

7.7)

The steric hindrance of the bis-cyclopentadienyl iron rings causes the benzene ring to assume a chair conformation to relieve steric strain. This causes the dihedral angles to differ from the expected 0°.

1 point for correctly pointing out the relieving of steric strain.
1 point for pointing out a chair conformation of benzene.
1 point for highlighting the expected dihedral angle of 0°.

[Turn Over]

7.8)

The bond lengths will alternate with bond lengths being longer or shorter than the C–C bonds in benzene. The enthalpy change of hydrogenation of the benzene ring will thus be more exothermic due to the loss of aromaticity / relieving steric strain upon hydrogenation.

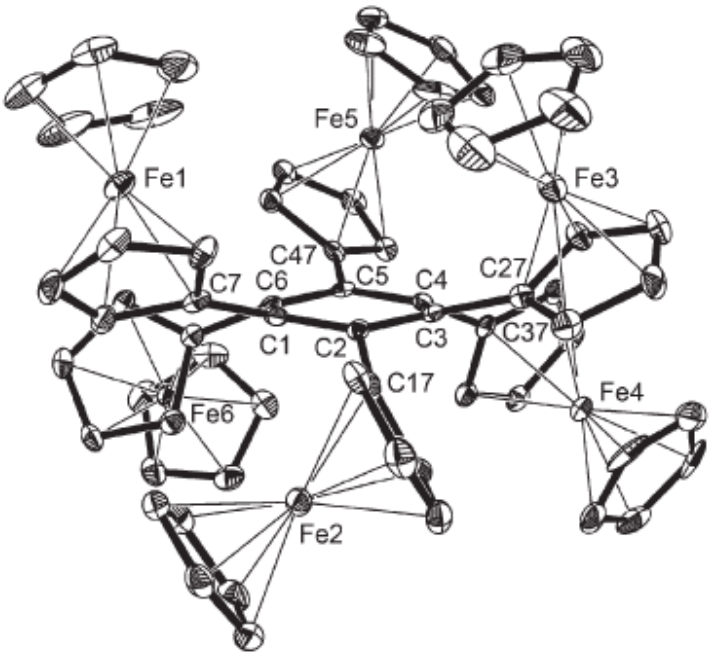
1 point for alternating bond lengths.
1 point for more exothermic heat of hydrogenation.

7.9)

This can be attributed to the anisotropic effect. The benzene ring in hexaferrocenylbenzene has a delocalized π-system, generating a ring current. This ring current induces a magnetic field that opposes the applied external magnetic field in the plane of the benzene ring.

The protons in the Cp ring experience the influence of this ring current. The protons closer to the benzene ring are shielded from the applied magnetic field due to the ring current, resulting in a lower chemical shift.

However, we realise that the difference in chemical shifts is very small – the reason for this is due to the fact that the benzene ring is not entirely planar, and in a chair conformation, the π-electron delocalization in the benzene ring is perturbed, and the ring current may be weakened or distorted. This leads to a smaller anisotropic effect than expected, and thus a smaller-than-expected difference in the chemical shifts.



Note: *From the XRD above, we see that the benzene ring is only very slightly*

non-planar, and this is why some degree of the anisotropic effect is still observed.

1 point for identification of anisotropic effect.
1 point for explanation of shielding by benzene ring.
1 point for identification of non-planar benzene.
1 point for explanation of perturbation of ring current.
1 point for explanation of smaller-than-expected anisotropic effect.

[Turn Over]

Problem 8
11.1% of total

Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	Total
Points	4	4	3	2	2	1	11	5	54
Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16	
Points	4	2	2	5	1	1	2	5	

8.1)

B2 is likely ionic from the information in the question.
The peak at 2361.1 cm^{-1} is likely to be a C-O stretch of CO_2.
The peak at 1448.8 cm^{-1} is likely to be the C-O stretch of CO_3^{2-}.
The peak at 866.8 cm^{-1} is likely to be the C-O bending modes of CO_3^{2-}.

Hence, **B2** is likely a carbonate.

Let **B2** be M_xCO_3. Let $A_r(M) = m$.
Thus,

$$0.41 \leq \frac{xm}{xm+12+16\times3} \leq 0.45 \Rightarrow 0.41xm + 24.6 \leq xm \text{ and } xm \leq 0.45xm + 27$$

We can further rearrange this to:

$$\frac{24.6}{1-0.41} \leq xm \leq \frac{27}{1-0.45} \Rightarrow 41.69 \leq xm \leq 49.09$$

If $x = 1$, $41.69 \leq m \leq 49.09$. The only element corresponding to this is Ti, and the compound is $TiCO_3$. Ti^{2+} is not very common, so unlikely to be Ti.
If $x = 2$, $20.85 \leq m \leq 24.55$. The only element corresponding to this is Na, and the compound is Na_2CO_3. Hence, it is likely to be Na.

B2 is Na_2CO_3.

1 point for determining CO_3^{2-} anion using IR data.
1 point for justifying Na^+ cation using mass data.
2 points for correct B2.

8.2)

For **B3**, let **M** be the metal. Let the A_r(**M**) = m.

79.3% is likely to be the metal, which judging from the percent mass, is likely to be very heavy. Then, we consider various common counterions, like O^{2-}, Cl^- and so on.

Let **B3** be **M**O_x. Then $\frac{m}{m+16x} = 0.793 \Rightarrow m = 61.29x$.

x	*m*	Possible metals
1	61.29	No metals correspond
2	122.58	No metals correspond
3	183.87	Likely W, and WO_3 makes sense

Beyond this, masses are too high to be likely.

Let **B3** be **M**F_x. Then $\frac{m}{m+19x} = 0.793 \Rightarrow m = 72.787x$.

x	*m*	Possible metals
1	72.787	Ge, but GeF is very unlikely to exist
2	145.574	Maybe Pm, but it only shows one stable oxidation state of +3

Beyond this, masses are too high to be likely.

Let **B3** be **M**Cl_x. Then $\frac{m}{m+35.5x} = 0.793 \Rightarrow m = 136x$.

x	*m*	Possible metals
1	135.997	No metals correspond
2	271.994	No metals correspond

Beyond this, masses are too high to be likely.

For halides beyond Cl, notice that written in the form $m = ax$, a will only get larger and larger. For Br, a = 306.1 and so on, so it cannot be a bromide, iodide, etc.

Hence, **B3** is WO_3.

[Turn Over]

Since **B4** is strongly basic, it is likely a metal oxide.

It has a molar mass between 355 and 365 g mol^{-1}.
Let it be $\mathbf{M}_x O_y$.

If $y = 1$, x $A_r(\mathbf{M})$ = 339 to 349 g mol^{-1}. If $x = 1$, we do not have any plausible candidates. If $x = 2$, we get some of the *f*-block metals, unlikely in this case to exhibit the +1 oxidation state.

If $y = 2$, x $A_r(\mathbf{M})$ = 323 to 333 g mol^{-1}. If $x = 1$, we again do not have any plausible candidates. If $x = 2$, it reduces to the case of $\mathbf{M}_2O_2$, which is simply **M**O, so not possible.

If $y = 3$, x $A_r(\mathbf{M})$ = 307 to 317 g mol^{-1}. If $x = 1$, we again do not have any plausible candidates. If $x = 2$, we find that the only possible **M** is Gd. Gd_2O_3 is possible.

Hence, **B4** is Gd_2O_3.

1 point for considering a few anions for B3, and deducing that oxide must be the anion.
1 point for deducing B3 as WO_3.
1 point for trying out various values of *y* as shown above.
1 point for deducing B4 as Gd_2O_3.

8.3)

By considering the organic reactions, compound **A1** is likely SmI_2.
Hence, element **A** is Sm.
Burning Sm in air is likely to give Sm_2O_3, which is compound **B5**.

1 point for each correct compound and element.

8.4)

We know that phosphor **B1** has the form $\mathbf{PQ}_{1-x}\mathbf{R}_x\mathbf{S}_y$. **P** is Na, **Q** is Gd, **R** is Sm.
Gd and Sm have oxidation state 3+, so $\mathbf{S}_y$ should have an overall charge of 4-.
Since **S** is associated with WO_3, the corresponding anion should be WO_4^{2-}.
Thus, **B1** should be $NaGd_{1-x}Sm_x(WO_4)_2$.

1 point for identifying the correct anion, 1 point for correct B1.

8.5)

At such low temperatures, it is likely to be water of crystallisation, as seen in the IR spectrum of Na_2CO_3 at the very start. Hence, the molecule is likely to be H_2O.

The DTA shows a dip, corresponding to an endothermic process. Loss of water of crystallisation is an endothermic process.

1 point for identifying the correct molecule, 1 point for correct identification of the endothermic process.

8.6)

475°C, where the sharp peak was shown, corresponding to a very exothermic reaction which was phosphor formation (bond forming is an exothermic process).

1 point for any temperature between 450°C to 500°C, justifying using the peak.

8.7)

*Compound **C2** is often used for desilylation, and has the same cation as compound **B2**.*
Hence, compound **C2** has a fluoride anion, so **C2** is NaF.

*Compound **C3** exhibits a characteristic green flame, and turns blue litmus paper red.*
Compound **C3** is clearly H_3BO_3.

*Compound **C4** is often used as a base in organic chemistry due to its solubility in certain organic solvents like alcohols and DMF. Compound **C4** is often used in reactions like the Suzuki and Heck reactions. Compound **C4** has the same anion as compound **B2**.*
Compound **C4** is Cs_2CO_3.

*Compound **C6** reacts with $HgCl_2$ to form a highly insoluble solid in the Calomel Reaction, which upon addition of KOH, yielded Millon's Base.*
Compound **C6** must be NH_3, because $HgCl_2 + NH_3 \rightarrow HgCl(NH)_2$ (highly insoluble) + NH_4Cl.
Upon addition of base, it forms $Hg_2(OH)N{\cdot}xH_2O$, which is Millon's Base.

*Compound **C7** is a triprotic acid that readily undergoes condensation with the elimination of water when concentrated, forming a reagent that is often used in organic chemistry for the cyclisation or acylations of compounds, with the alternative being Eaton's reagent.*
The reagent mentioned in the end of the question is polyphosphoric acid (PPA). Hence, compound **C7** must be H_3PO_4.

[Turn Over]

*Compound **C5** consists of 2 polyatomic ions. Compound **C5** can be synthesised by the reaction of a binary compound **C6** and ternary compound **C7**, with compound **C6** deprotonating compound **C7** only once.*
H_3PO_4 reacting with NH_3 in the correct stoichiometric ratio yields **C5** being $\underline{NH_4H_2PO_4}$.

Reaction **I**: $NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$.
Reaction **II**: $HgCl_2 + 2NH_3 \rightarrow HgCl(NH)_2 + NH_4Cl$.
Reaction **III**: $n\ H_3PO_4 \rightarrow HO(-P(O)(OH)-O-)_nH + (n\text{-}1)\ H_2O$.

1 point for each correct answer.
1 point for reaction I, 2 points for reactions II and III.
If unbalanced, deduct 0.5 points.
If wrong products, 0 points.
For reaction I, if $(NH_4)_2HPO_4$ or $(NH_4)_3PO_4$ is given, give 0.5 points.
For reaction III, if lower polyphosphoric acids like $H_4P_2O_7$, give 0.5 points.

8.8)

Since $b - (c + d) = 0$ and $cd = 0.0784$, and we know that **A** must be Cs, and since c and d are fractional, we know that **B** must be Na. Correspondingly, **C** and **D** should correspond to Gd and Sm as in part 1.

Hence, we can guess that **E** and **F** must correspond to H_3BO_3 and $NH_4H_2PO_4$. It is likely that these give rise to anions. **E** likely gives rise to BO_3^{3-} and **F** therefore gives rise to PO_4^{3-}, since both **E** and **F** have the same charge.

Thus, we know that $a + b + 3(c+d) - 3e - mf = 0$.
Since $b = c + d$, this simplifies to $a + 4b - 3e - mf = 0$.
Since $ab = 2$, we can guess that either $a = 1$, $b = 2$ or $a = 2$, $b = 1$.

If $a = 2$, $b = 1$, that means that $cd = 0.0784$, $c + d = 1$. Solving this system of equations, we realise that c and d have surds in them, and are hence not rational.
Thus, $a = 1$, $b = 2$, and $(c, d) = (1.96, 0.04)$. We know that Sm is doped, hence Sm corresponds to d while Gd corresponds to c.

Hence, $1 + 4 \times 2 - 3e - 3f = 0$.

If $e = 1$, $3f = 6$, $f = 2$.
If $e = 2$, $3f = 3$. Knowing that $e < f$, this cannot be the case.

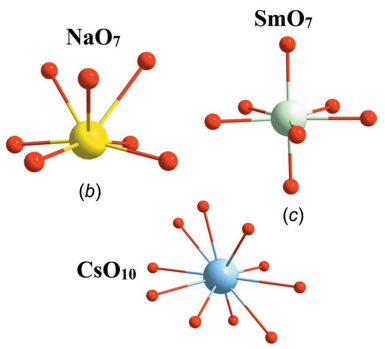
Hence, **C1** must be $CsNa_2Gd_{1.96}Sm_{0.04}(BO_3)(PO_4)_2$.

1 point for all correct elements and ions.
1 point for correct subscripts for Cs, Na.
1 point for correct subscripts for Gd, Sm.
1 point for correct subscripts for BO_3^{3-} and PO_4^{3-}.
1 point for the correct formula for C1

8.9)

Consider the following environments on the right:

- NaO_7 forms a truncated square pyramid.
- Each Sm^{3+} cation is also coordinated by seven O atoms to form an SmO_7 pentagonal bipyramid.
- Cs^+ connects to 10 O atoms to form a polyhedra.



2 points for correct geometry of SmO_7 environments.
1 point each for the correct number of atoms of NaO_7 and CsO_{10} environments.

8.10)

$$\frac{I}{x} = k\left[1 + \beta x^{\frac{\theta}{3}}\right]^{-1} \Rightarrow \frac{I}{x} = k\beta^{-1}x^{-\frac{\theta}{3}}$$

$$\Rightarrow \lg\left(\frac{I}{x}\right) = \lg k - \lg\beta - \frac{\theta}{3}\lg x$$

$$\Rightarrow \lg\left(\frac{I}{x}\right) = K - \frac{\theta}{3}\lg x \ \ (K = \lg k - \lg\beta)$$

0.5 points for the approximation (step 1).
0.5 points for usage of logarithm rules (step 2).
1 point for correct linearisation, with the statement of *K*.

8.11)

Since slope = -1.5, θ = -3(slope) = 4.5. This is closest to 6, implying that the quenching mechanism originates from d–d interactions between Sm^{3+} cations.

1 point for computation of θ.
1 point for the correct conclusion that the quenching mechanism originates from d-d interactions.

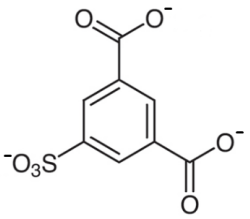
[Turn Over]

8.12)

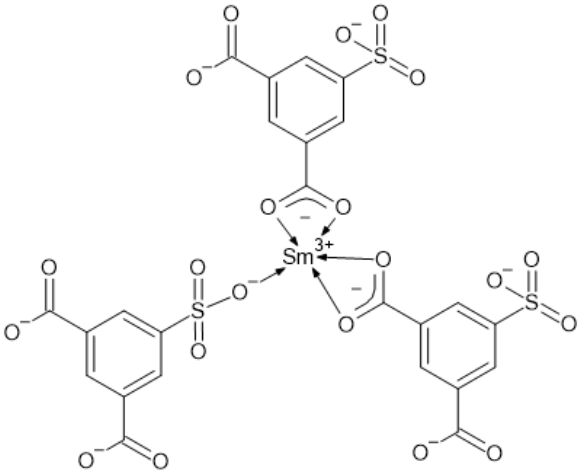
Since ligand **G** can be formed from m-xylene, it is clear that ligand **G** should most likely contain a benzene ring.

Subtracting away the mass of the benzene ring, the remaining molecular mass is 246.197 - 6 × 12.011 - 6 × 1.008 = 108.083. Since ligand **G** is a μ_3 ligand, and two are bidentate, we can guess that two of them are carboxylate groups. The remaining mass is 108.083 - 2 × (12.011 + 15.999 × 2 + 1.008) = 78.049. Trying out various common groups, we find that the last group is most likely a SO_3H group, accounting for the 3 H atoms that were substituted.

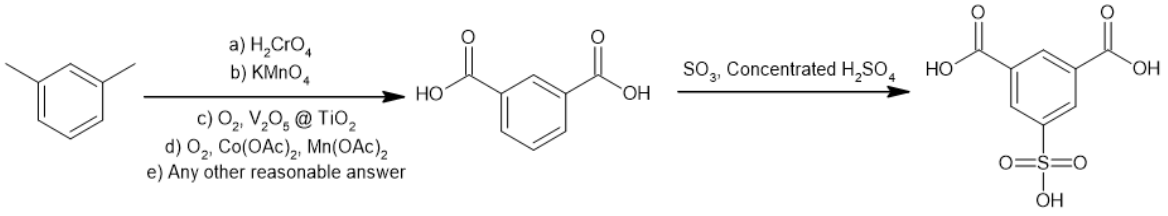
Hence, ligand **G** is the anionic form of 5-sulfoisophthalic acid, or as shown below:



Hence, the monomer will look as follows:



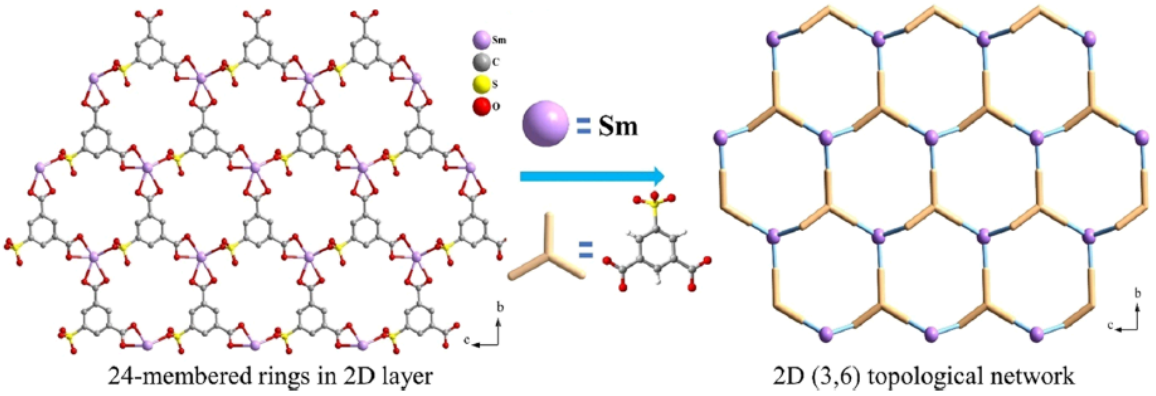
Any reasonable synthesis will be accepted (any condition from a to e will be accepted):



1 point for deducing the carboxylate anion as a ligand of the MOF.
1 point for deducing the structure of G.
1 point for correct structure of the monomer.
1 point for a reasonable first step for the conversion of m-xylene to isophthalic acid.
1 point for a reasonable second step for the conversion of isophthalic acid to G.

8.13)

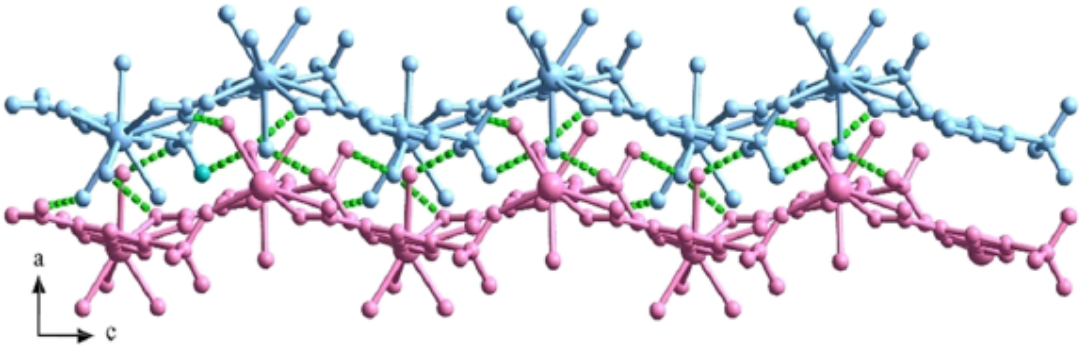
n = 24 atoms. See the picture below for a better understanding of why the answer is 24.



1 point for the correct answer.

8.14)

Hydrogen bonding. The green bonds below are the hydrogen bonds.



1 point for the correct answer.

[Turn Over]

8.15)

Quinolinic acid competes with the SIP^{3-} ligand (5-sulfoisophthalate ion ligand) and blocks the ligand to metal charge-transfer energy transferring path from SIP^{3-} to Sm(III), thus quenching the $^4G_{5/2} \rightarrow {}^4H_j$ transitions. This causes a decrease in the intensity of emission, causing I to decrease, and thus I_0/I to increase.

1 point for identifying quinolinic acid competing with the ligand, blocking the LMCT energy transfer and quenching the associated transitions. The specific transition ($^4G_{5/2} \rightarrow {}^4H_j$) need not be identified.
1 point for identifying that this causes a decrease in the intensity of emission, and the ratio is inversely proportional to the intensity of emission.

8.16)

Since the normal quinolinic acid level in human urine is 49 μM, we shall compute the quinolinic acid levels in each of the urine samples.

We already have each of the absorbances, and recall that absorbance = $\log_{10}(I_0/I)$. We can hence compute the ratio $I_0/I = 10^{\text{absorbance}}$, and by using the linear regression formula, we can compute the concentration of quinolinic acid in the sample **after the MOF was added**. We can use [quinolinic acid] = $201.6129(I_0/I) - 226.7621$.

Patient number	**1**	**2**	**3**	**4**	**5**
Volume of urine / mm^3	21754	530	2150	38128	170
Absorbance recorded / Abs	0.124	0.118	0.083	0.129	0.056
I_0/I	1.330	1.312	1.211	1.346	1.138
Concentration of quinolinic acid after MOF added / μM	41.4747	37.7943	17.3101	44.5807	2.5982

Now, all the concentrations look normal, but we need to consider that the sample was **diluted** when we added in the MOF sample. We notice that in the preparation of the final sample, we added 3 mL of the MOF sample. We can therefore obtain the original concentration of quinolinic acid, C_0 from the concentration of quinolinic acid after MOF was added, C_1 through the following relationship: $C_0 = (C_1 \times (V_{urine} \times 10^{-6} + 3 \times 10^{-3}))/(V_{urine} \times 10^{-6})$. Now, calculating the original concentration of quinolinic acid for each patient, we obtain:

Patient number	1	2	3	4	5
Volume of urine / mm^3	21754	530	2150	38128	170
Concentration of quinolinic acid after MOF added / µM	41.4747	37.7943	17.3101	44.5807	2.5982
Original concentration of quinolinic acid / µM	47.1943	251.7245	41.4637	48.0884	48.4495

Hence, we see that the only patient with an elevated quinolinic acid level is patient **2**, with a quinolinic acid concentration of 251.7245 µmol dm^{-3} in their urine.

1 point for computing the ratio I_0/I using the definition of absorbance for all patients.
1 point for computing the concentration of quinolinic acid using the calibration curve.
1 point for factoring in dilution, and computing the original concentration of quinolinic acid in their urine.
1 point for coming to the conclusion that patient 2 is most likely to have RCC due to elevated quinolinic acid levels.
1 point for correct concentration of quinolinic acid in patient 2's urine.

[Turn Over]

Problem 9 11.1% of total	Question	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	Total
	Points	3	3	3	1	1	1	4	2	6	24

9.1)

$$Molar\ mass\ (Sm) = \frac{\sum_i \left(Abundance_i \times Molar\ mass_i\right)}{100}$$

$$M\_Sm =$$
$$[\ (3.07\% \times 143.91\ amu) + (14.99\% \times 146.92\ amu) + (11.24\% \times 147.91\ amu) +$$
$$(13.82\% \times 148.91\ amu) + (7.38\% \times 149.92\ amu) + (26.75\% \times 151.92\ amu) +$$
$$(22.75\% \times 153.92\ amu)\ ] / 100$$

$$M_{Sm} = \frac{(3.07\% \times 143.91\ amu) + [..] + (22.75\% \times 153.92\ amu)}{100} = 150.36\ amu$$ **(3 p.)**

9.2)

$$m_{Sm} = \rho V w_{Sm} = \rho \frac{4\pi}{3} R^3 w_{Sm} = 5500 \cdot \frac{4\pi}{3}((6.4 \cdot 10^3)^3 \cdot 10^9) \cdot 6 \cdot 10^{-6}$$ **(2 p.)**

$$m_{Sm} = 3.622 \cdot 10^{19}\ (kg)$$ **(1 p.)**

9.3)

H; O_2; Mn; W; $TiCl_3$; $V(CO)_6$ **(3 p., 0.5p for every correct -0.5 p for every incorrect, no less than 0 p. total)**

9.4)

$^{15653}Eu + \beta-$ **(1 p.)**

9.5)

3+ **(1 p.)**

9.6)

4+ **(1 p.)**

9.7)

$k = \frac{ln2}{t_{1/2}}; ln\frac{[^{153}Sm_t]}{[^{153}Sm_0]} = -kt; ln\frac{[^{153}Sm_t]}{[^{153}Sm_0]} = -\frac{ln2}{t_{1/2}}t;$ **(2 p.)**

$\frac{[^{153}Sm_t]}{[^{153}Sm_0]} = e^{-\frac{ln2}{t_{1/2}}t} = e^{-\frac{ln2}{46.3}56} = 0.432 = 43.2\,\%$ **(2 p.)**

9.8)

$CeO_{2-\delta} + \frac{\delta}{2}\,CO_2 + \frac{\delta}{2}\,H_2O \rightarrow CeO_2 + \frac{\delta}{2}\,CO + \frac{\delta}{2}\,H_2$ **(2 p.)**

9.9)

Multiplying the samarium equation by A and the cerium equation by B and adding them together we obtain **(2 p.)**

$A\ Sm_2O_{3-\delta}$ + B $CeO_{2-\delta}$ + (A $\frac{\delta}{3}$ + $B\frac{\delta}{2}$) CO_2 +($\frac{2\delta}{3}$ A +$\frac{\delta}{2}$ B) $H_2O \rightarrow$

A Sm_2O_3 + B CeO_2 + (A $\frac{\delta}{3}$ + $B\frac{\delta}{2}$) CO + ($\frac{2\delta}{3}$ A + $\frac{\delta}{2}$ B) H_2

A Sm_2O_3 + B CeO_2 or $Ce_BSm_{2A}O_{3A+2B}$ needs to be expressed as $Ce_xSm_{1-x}O_{1.5+0.5x}$, **(2 p.)** which means that B = x and A = (1-x)/2, inserting them back in we get:

$Ce_xSm_{1-x}O_{1.5+0.5x-\frac{x+1}{2}\delta}$ + $\frac{2x+1}{6}$ δ CO_2 + $\frac{x+2}{6}$ δ $H_2O \rightarrow$

$Ce_xSm_{1-x}O_{1.5+0.5x}$ + $\frac{2x+1}{6}$ δ CO + $\frac{x+2}{6}$ δ H_2 **(2 p.)**

Alternative solutions are worth full 6 p. as well