



## General Instructions

This examination has 9 problems and is 5 hours long.

The question paper is viewable on your screen. You are also provided with a "Theory Schemes Booklet" which contains important reaction schemes from the question paper. You may use any part of this booklet for rough work. **Nothing written in this booklet will be assessed.**

The printed answer booklet has 42 pages and is on your desk.

The answer booklet contains boxes with numbers corresponding to the questions. **Write** your answer in the designated box for that question. If you must write outside of the designated box, make a note in the box and write your answer somewhere else **on the same page**.

Do not write on the reverse side of the answer booklet. Markers will only see the printed sides of the answer booklet. Do not separate the pages of the stapled answer booklet.

**Write** relevant calculations where needed. **Full marks will only be given for correct answers showing working.**

For multiple choice questions, if you want to change your answer, completely **scribble out** the box you have ticked and **draw** a new box next to it.



Start working when the "**START**" command is given. The supervisors will announce a "**30 MINUTE WARNING**" 30 minutes before the end of the exam. At the end of the exam, a "**STOP**" command will be given and you must stop working immediately. If you do not stop working, you may be given a score of zero for the examination.

**Write only** with the pen provided. **Use only** the calculator provided.

The Official English version of this examination is available for clarification purposes only. This can be viewed on your screen.

If you need a toilet break or any assistance, **raise** the appropriate card.



 BATHROOM	If you need a toilet break
 Questions	If you have any questions

At the end of the exam, **put** your answer booklet back into the envelope. **Do not seal** the envelope.



(Good Luck)



## Periodic table and data sheet

### Physical constants and formulae

Avogadro constant	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
molar gas constant	$R$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F$	$96485 \text{ C mol}^{-1}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$
speed of light in vacuum	$c$	$2.998 \times 10^8 \text{ m s}^{-1}$
mass of electron	$m_e$	$9.109 \times 10^{-31} \text{ kg}$
charge of electron	$e$	$1.602 \times 10^{-19} \text{ C}$
atmospheric pressure	$p_{atm}$	$101325 \text{ Pa}$
ionic product of water at 298 K	$K_W$	$10^{-14}$

$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$
$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$
$0 \text{ °C} = 273.15 \text{ K}$
$1 \text{ kWh} = 3600 \text{ kJ}$
$1 \text{ W} = 1 \text{ J s}^{-1}$
$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
$1 \text{ bar} = 10^5 \text{ Pa}$



area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$
surface area of sphere	$S = 4\pi r^2$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$E = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon cd$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)} \text{ BM}$
Henderson-Hasselbalch equation	$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
0 <sup>th</sup> order integrated rate law	$[\text{A}] = [\text{A}]_0 - kt$
1 <sup>st</sup> order integrated rate law	$\ln[\text{A}] = \ln[\text{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$
Clausius-Clapeyron equation	$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
specific heat	$Q = mC_p \Delta T$
boiling point elevation	$\Delta T = iK_b m_i$
freezing point depression	$\Delta T = iK_f m_i$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of 1 mol dm<sup>-3</sup>.



## IR absorption data

### Bond stretching frequencies

Bond type		Wavenumber (cm <sup>-1</sup> )
C-H	Alkane	3000-2850
	Alkene	3100-3000
	Aromatic	3150-3050
	Alkyne	~3300
	Aldehyde	2900-2700
C=C	Alkene	1680-1600
	Aromatic	1600-1400
C≡C	Alkyne	2250-2100
C=O	Aldehyde	1740-1720
	Ketone	1725-1705
	Carboxylic acid	1725-1700
	Ester	1750-1720
	Amide	1670-1640
	Anhydride	1810, 1760
C-O	Alcohol, ether, ester, carboxylic acid, anhydride	1300-800
O-H	Alcohol, phenol, free	3600-3200
	Hydrogen bonded	3500-3200
	Carboxylic acid	3400-2500
N-H	Primary and secondary amine and amide	3500-3100
C-N	Amine	1350-1000
C=N	Imine and oxime	1690-1640
C≡N	Nitrile	2260-2240
N=O	Nitro (R-NO <sub>2</sub> )	1600-1500, 1400-1300
S=O	Sulfoxide	1050
	Sulfate, sulfonamide	1200-1140



### Characteristic bond stretching frequencies of anionic species

Anion	Wavenumber (cm <sup>-1</sup> )
SO <sub>4</sub> <sup>2-</sup>	1100-1200 (ν <sub>as</sub> )
ClO <sub>4</sub> <sup>-</sup>	1050-1170 (ν <sub>as</sub> )
NO <sub>3</sub> <sup>-</sup>	1370 (ν <sub>as</sub> )
CN <sup>-</sup>	2089
SCN <sup>-</sup>	2053 (ν <sub>C-N</sub> ), 748 (ν <sub>C-S</sub> )
N <sub>3</sub> <sup>-</sup>	2042 (ν <sub>as</sub> ), 1343 (ν <sub>s</sub> )
CNO <sup>-</sup>	2052 (ν <sub>C-N</sub> ), 1057 (ν <sub>N-O</sub> )

### Number of CO stretching bands in the IR spectra of metal carbonyl complexes

Complex	Number of bands
M(CO) <sub>6</sub>	1
M(CO) <sub>5</sub> X	3
<i>cis</i> -M(CO) <sub>4</sub> X <sub>2</sub>	4
<i>trans</i> -M(CO) <sub>4</sub> X <sub>2</sub>	1
<i>fac</i> -M(CO) <sub>3</sub> X <sub>3</sub>	2
<i>mer</i> -M(CO) <sub>3</sub> X <sub>3</sub>	3
<i>fac</i> -M(CO) <sub>3</sub> X <sub>2</sub> Y	3
<i>cis</i> -M(CO) <sub>2</sub> X <sub>4</sub>	2
<i>trans</i> -M(CO) <sub>2</sub> X <sub>4</sub>	1



## Periodic table

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

	Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
	Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



Number	Question	Weighting
1	Isocaryophyllene, clovene, and humulene	6%
2	Rapamycin - A molecular glue	6.5%
3	Lanterns and the Burj Khalifa	7.5%
4	The life of tennis balls	6%
5	Solar-powered multi-stage flash desalination	6.5%
6	Solar energy conversion by CO <sub>2</sub> reduction	6%
7	Dubai crude oil	7%
8	Carbon monoxide: deadly poison or promising therapeutic agent?	7.5%
9	Enzymes and cofactors	7%
<b>Total</b>		<b>60%</b>





## 1. Isocaryophyllene, clovene, and humulene

6% of the total

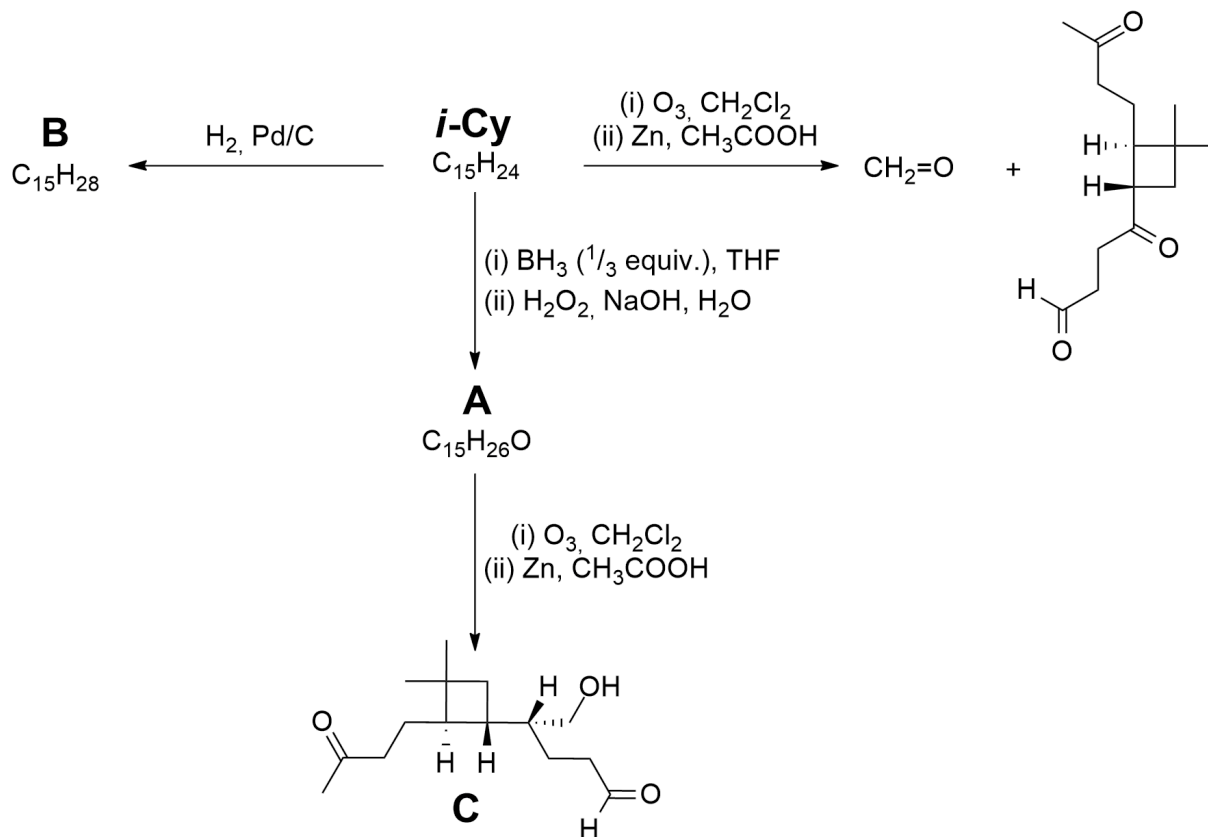
1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	Total
7	3	6	2	2	8	2	2	2	34



Sesquiterpenes have the formula  $C_{15}H_{24}$ . They are secondary metabolites in plants and both deter insects which eat plants and attract animals which eat the insects.

Isocaryophyllene (***i*-Cy**) is a sesquiterpene found in oregano, rosemary, pepper, and cloves.

The structural formula of ***i*-Cy** can be determined by performing various reactions and analysing the products as shown in the figure.

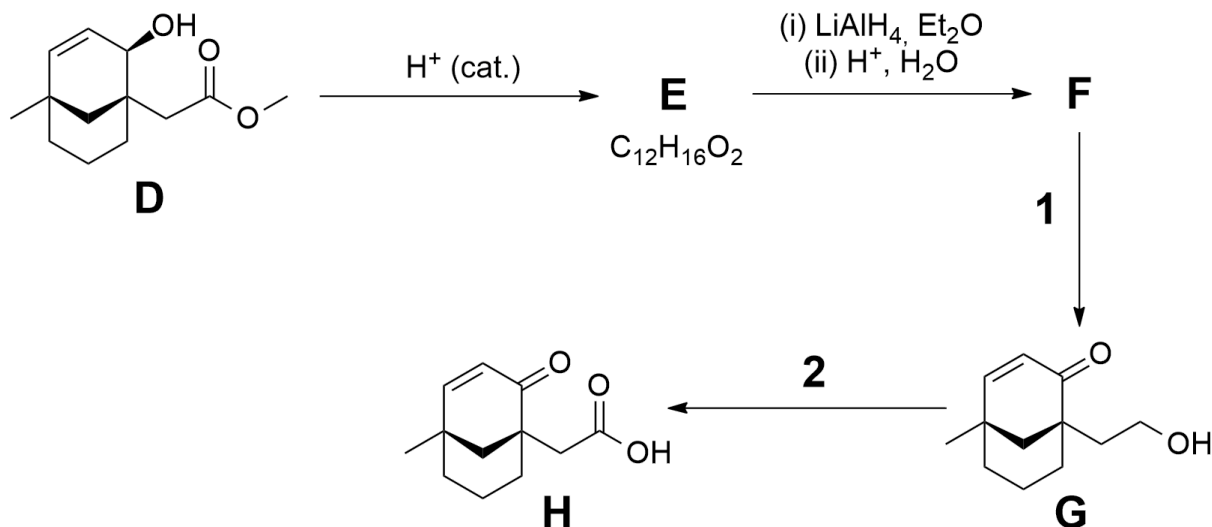


equiv. = translation 'equiv.'

**1.1 Draw** the structures of ***i*-Cy**, **A**, and **B**. Stereochemistry is not required.

**1.2 Circle** the stereocentres in compound **C** and **assign** them as *R* or *S*.

Clovene (**Cv**) can be synthesised from ***i*-Cy** under acid catalysis. The synthesis of **Cv** starts from compound **D**.

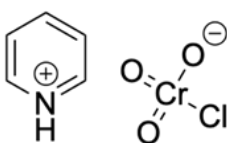


$\text{H}^+$  (cat.)="translation  $\text{H}^+$  (cat.)"

**1.3 Draw** the structures of compounds **E** and **F**. Stereochemistry is not required.

For steps '**1**' and '**2**' several reagents could be considered. For example:

- ☐ PCC
- ☐  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$
- ☐  $\text{MnO}_2$
- ☐ (i)  $\text{OsO}_4$ , (ii)  $\text{KHSO}_3$

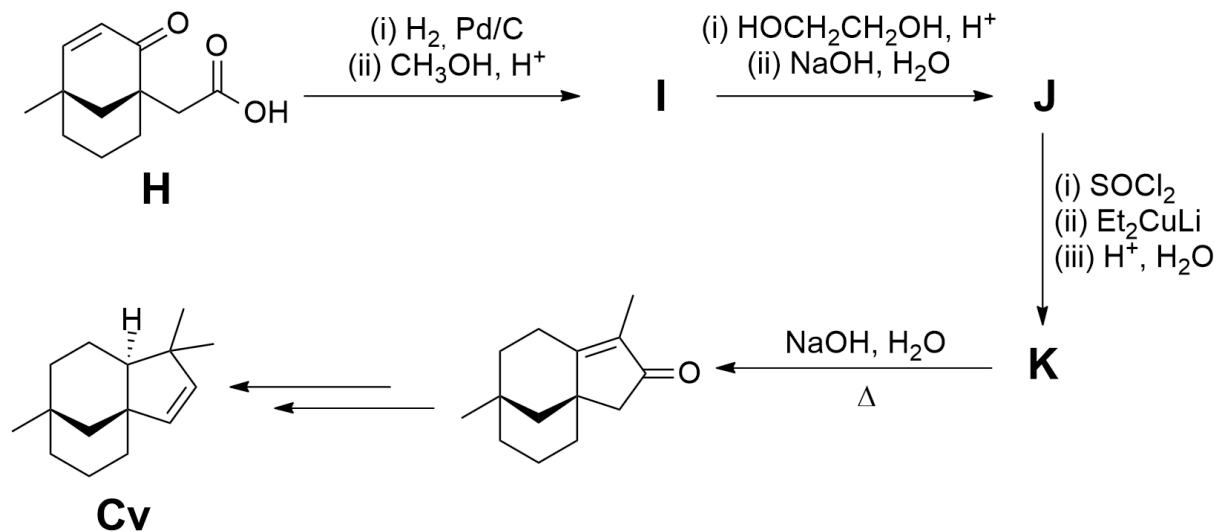


PCC

**1.4** From the reagents above, **tick** which one(s) would be suitable for step '**1**'.

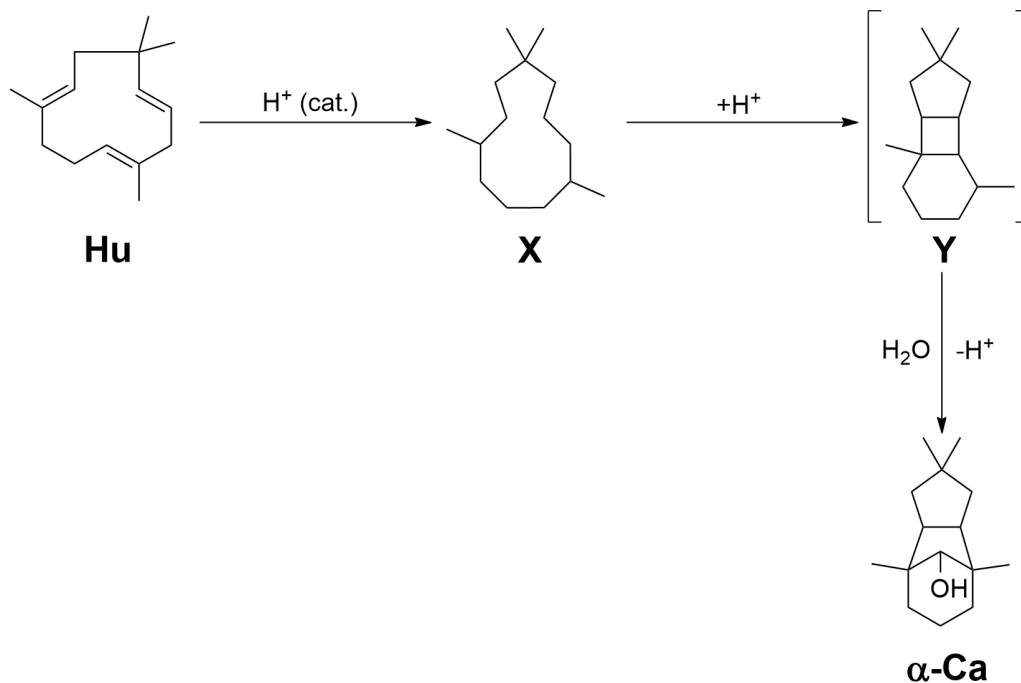
**1.5** From the reagents above, **tick** which one(s) would be suitable for step '**2**'.

The final part of the synthesis is shown.



**1.6 Draw** the structures of compounds **I**, **J**, and **K**. Stereochemistry is not required.

Humulene (**Hu**) is another sesquiterpene. It can be converted to  $\alpha$ -caryophyllene alcohol ( **$\alpha$ -Ca**), which is similar in structure to **Cv**. This conversion is an acid-catalysed hydration reaction which takes place via multiple intermediate structures. Incomplete structures of some intermediates, **X** and **Y**, are shown.



$H^+$  (cat.)="translation  $H^+$  (cat.)"

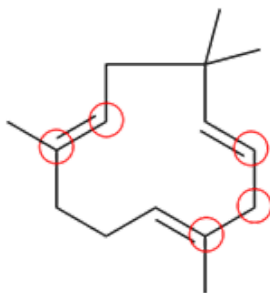
The transformation from **Hu** to **X** is an acid-catalysed isomerisation reaction.  
Intermediate **Y** is charged.



**1.7 Complete** the structure of intermediate **X** by adding double bonds in the correct places.

**1.8 Complete** the structure of intermediate **Y** by adding a positive charge in the correct place.

Five carbon atoms are circled in **Hu**. Through understanding the mechanism we can determine where these five carbon atoms end up in  **$\alpha$ -Ca**.



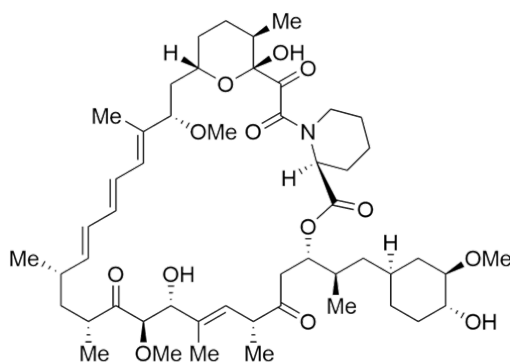
**1.9 Circle** the five corresponding carbon atoms in  **$\alpha$ -Ca** which are circled in **Hu**.



## 2. Rapamycin - A molecular glue

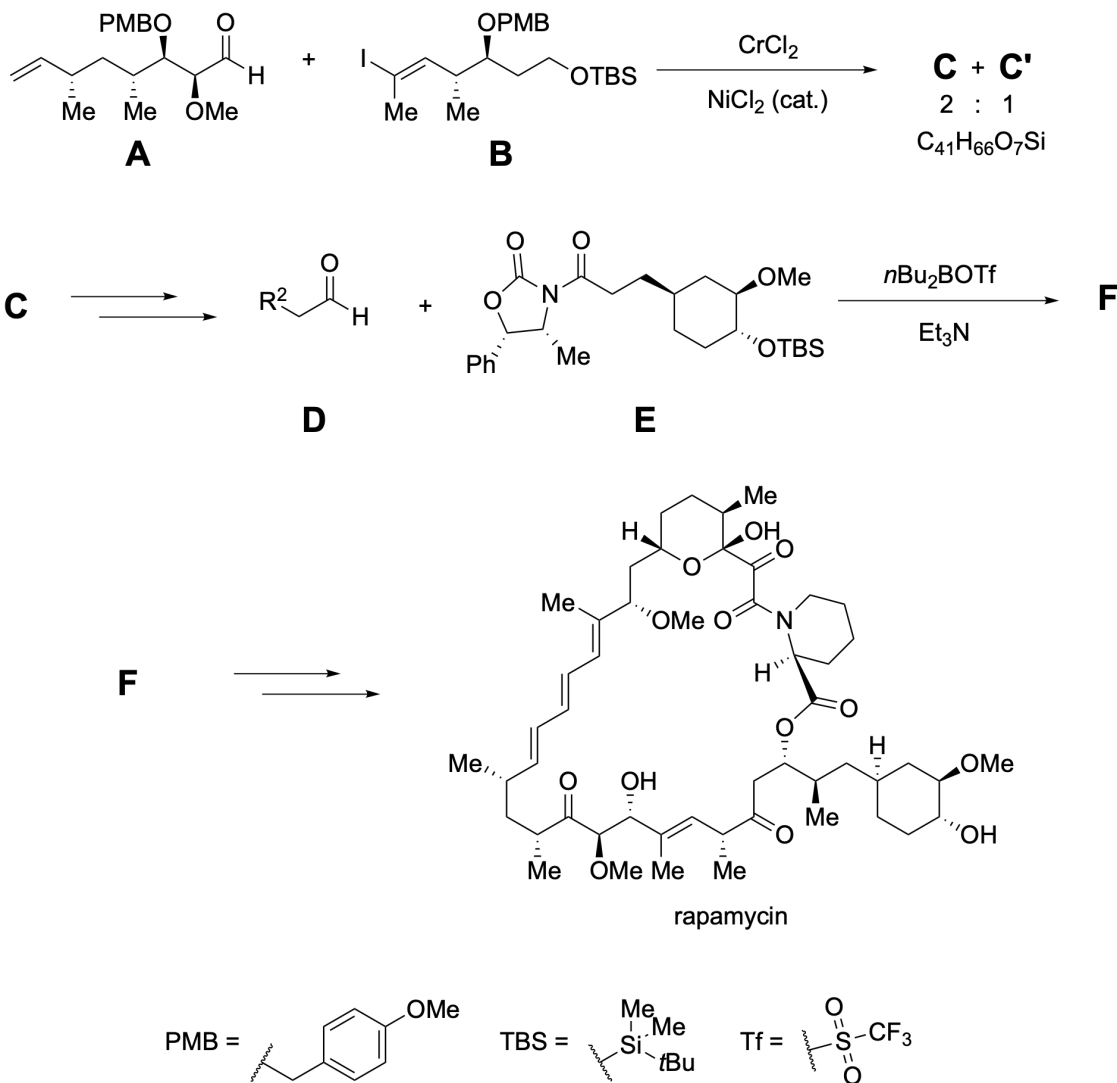
6.5% of the total

2.1	2.2	2.3	2.4	Total
12	19	18	18	67



rapamycin

Rapamycin was isolated from the bacterium *Streptomyces hygroscopicus* in 1972. It acts as a “molecular glue” and inhibits the activity of the protein mTOR through binding to another protein. It has been used to treat various diseases. The stereochemical complexity of rapamycin makes its total synthesis challenging. The figure shows part of the first total synthesis by the Nicolaou group.



The major stereoisomer (**C**) is formed from the chromium-mediated coupling reaction of aldehyde **A** and vinyl iodide **B** and can be predicted using the Felkin-Anh model without chelation.

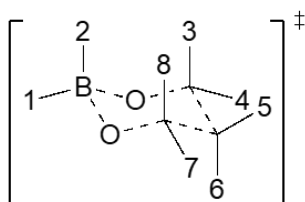
**2.1a Draw** a Newman projection showing the best approach of the nucleophile in this reaction. Use the labels =O, -H,  $-\text{R}^1$ , -OMe, and Nu.

**2.1b Draw** the full structure of the major diastereomer **C** showing all stereochemistry.

After a few transformations, **C** can be converted into an aldehyde **D** which reacts with **E** to form **F**. **F** can be further transformed into rapamycin.



**2.2a** Using the Zimmerman-Traxler model, **predict** the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **F**. **Draw** the substituents at positions labelled with numbers. If a position does not have a substituent, put an "X" in the box. Boxes 1 and 2 have been filled in as an example. You may use the abbreviation  $R^2$  as given in the scheme above.



**2.2b Draw** the structure of **F** showing all stereochemistry. You may use the abbreviation  $R^2$  as given in the scheme above.

Whilst stereochemical control is challenging synthetically, the biological synthesis controls stereochemistry elegantly through an assembly line of various enzymes.

The carbon chain is built up through the addition of monomers. These units are connected via a thioester to Coenzyme A (CoA).

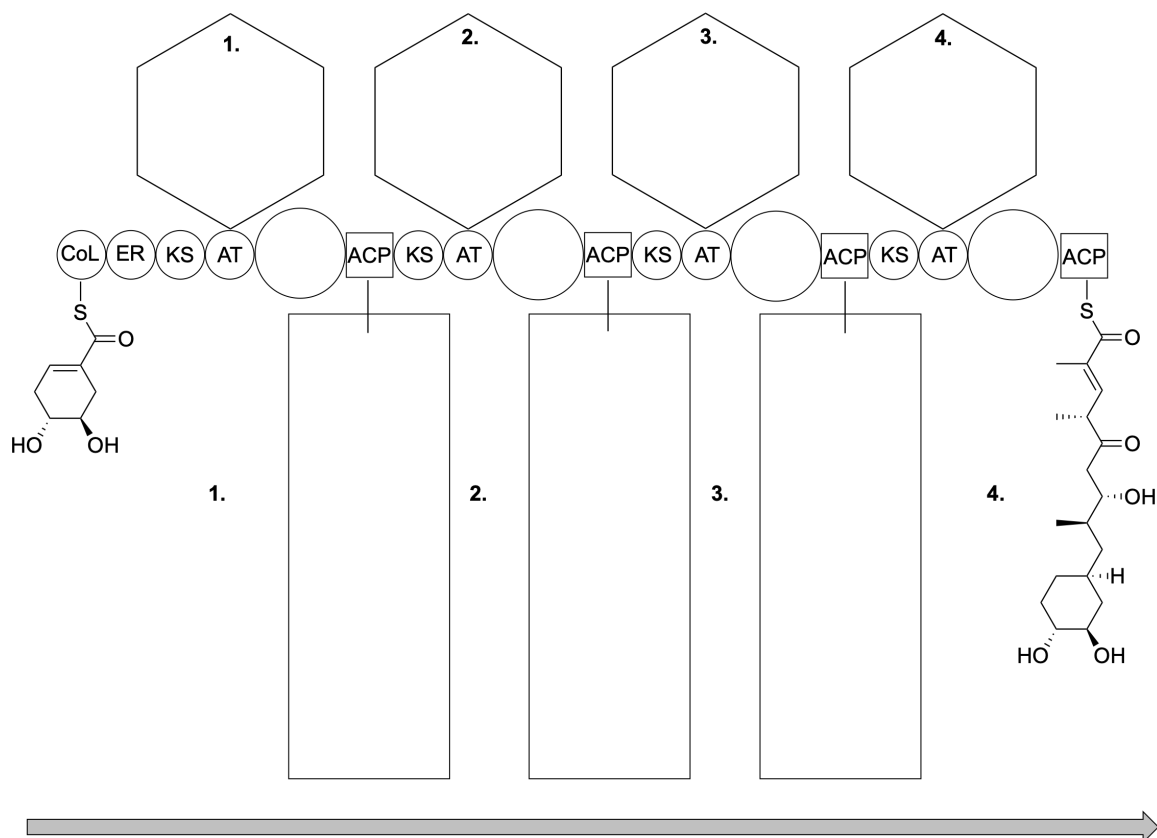
The functions of the various enzymes and proteins are shown in the table.

Abbreviation	Name	Function
ACP	Acyl-carrier protein	Carries growing chain between domains
CoL	CoA-Ligase	Activates a carboxylic acid substrate to be loaded onto the ACP
AT	Acyltransferase	Selects monomer and transfers to ACP
KS	Ketosynthase	Accepts growing chain from previous ACP and activates it for Claisen condensation with next monomer-loaded ACP
KR	Ketoreductase	Reduces carbonyl of a previous monomer to a hydroxyl
DH	Dehydratase	Forms $\alpha$ , $\beta$ -unsaturated thioester via elimination on the previous monomer
ER	Enoylreductase	Reduces $\alpha$ , $\beta$ -unsaturated thioester to saturated chain on the previous monomer

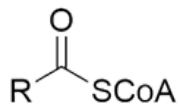




The first part of the assembly line is shown with blanks. The enzymes are shown in circles and act in the order of the arrow.



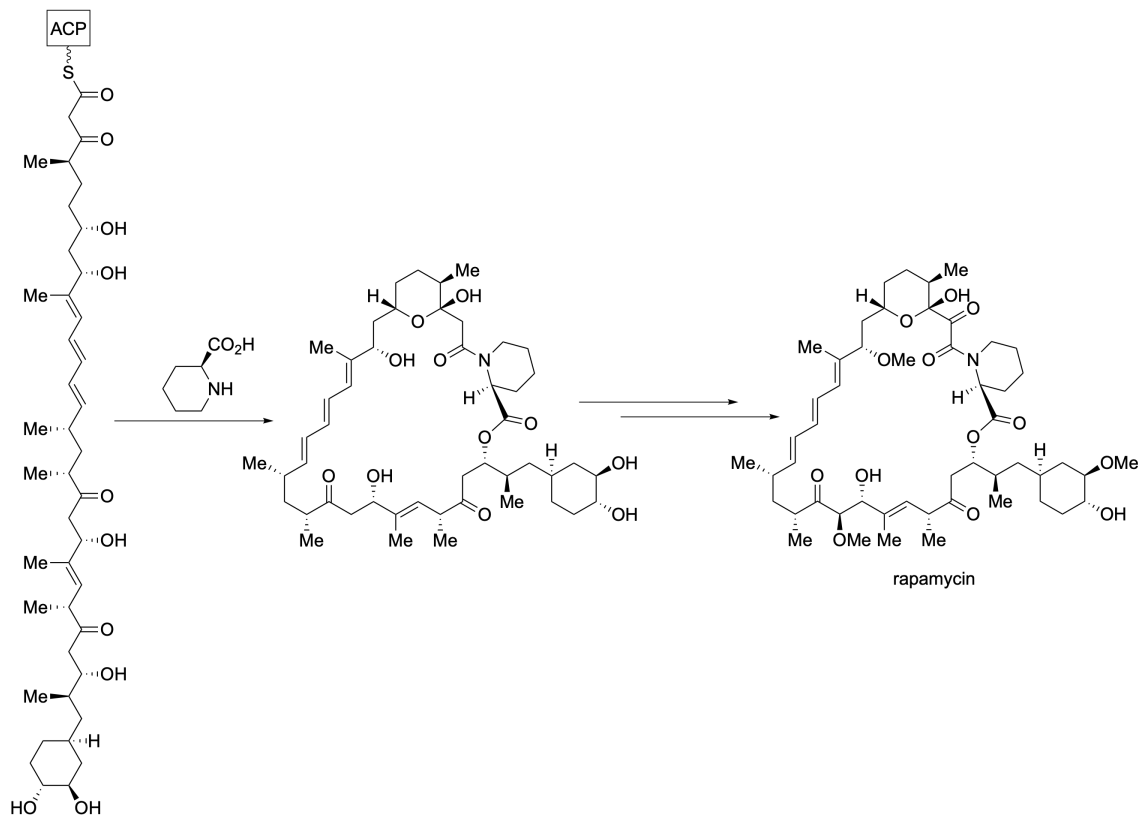
**2.3a Draw** in the hexagons the structure of the monomer needed by the enzyme AT at each of the points numbered **1-4**. Carbon dioxide is released when the monomers are incorporated. The monomers have the following general structure where the R group is anionic:



**2.3b Fill in** each circle with the abbreviations of enzyme(s) needed. Write "X" if no additional enzyme is needed.

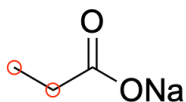
**2.3c Complete** the rectangles with the structure of the growing molecule attached to the enzyme.

The final steps of the enzymatic synthesis are shown below.

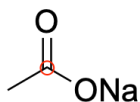


The building blocks involved were determined by feeding the bacterium with three different  $^{13}\text{C}$ -labelled starting materials which are incorporated into the monomers ( $^{13}\text{C}$  are circled as shown below):

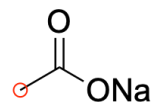
**a.**



**b.**



**c.**

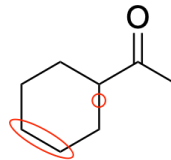
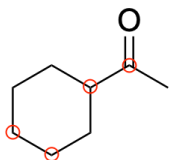


**2.4 Circle** the carbons in rapamycin that will be  $^{13}\text{C}$ -labelled when the bacterium is fed with each of the three starting materials **a-c** in turn, following the guidelines on the next page. Incorrect circles will be penalised but there is no negative scoring.

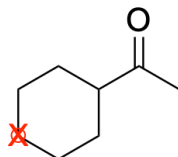


### Guidelines for circling carbon atoms:

- Each circle should clearly surround one carbon atom
- Do not include multiple carbon atoms in the same circle
- Do not circle any bonds



- If you would like to change your answer and cross-out a circle, put an "X" over the circle.





### 3. Lanterns and the Burj Khalifa

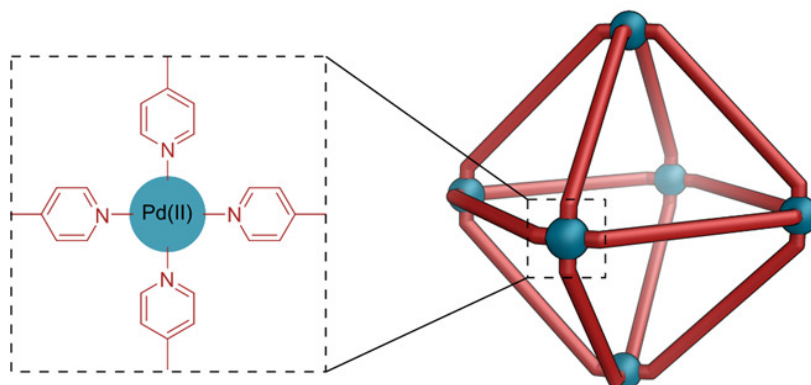
7.5% of the total

3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
6	4	4	5	40	20	32	111



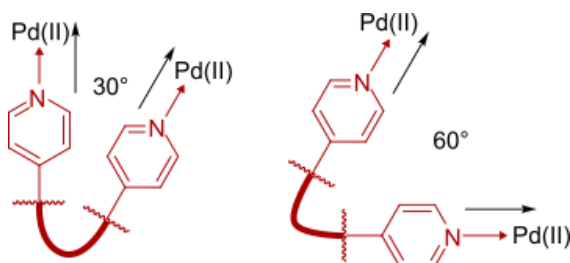
At 829.8 m, Dubai's Burj Khalifa is the world's tallest structure. To simplify construction, many floors were made from similar pieces. Some artificial "molecular skyscrapers" can be made through coordination chemistry of just two pieces: metal ions and organic ligands.

In these 3D structures, every vertex contains a square planar Pd(II) ion coordinated to four pyridine ligands. Along each edge is a bent organic ligand consisting of two pyridines linked together.



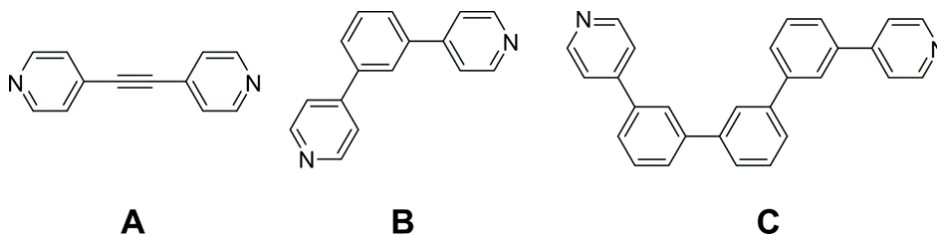


The angle between the two N → Pd bonds from the same ligand controls which structure forms. Larger angles give larger structures.

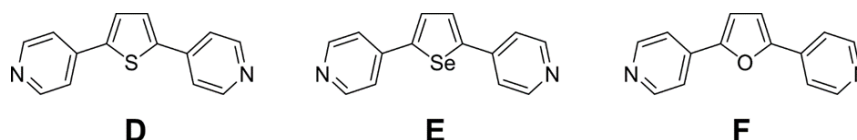


Where free rotation around a bond is possible, the ligand adopts a conformation to form a structure with the smallest possible angle.

**3.1 Tick** the smallest angle (approximately) between the N → Pd bonds which could be achieved by ligands **A**, **B**, and **C**.



**3.2** Using “<”, **rank** ligands **D**, **E**, and **F**, from smallest angle to largest angle between the N → Pd bonds that they could form.

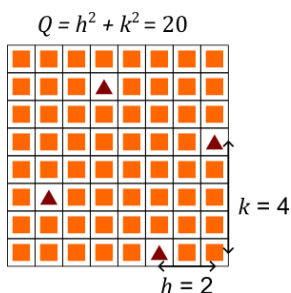


One series of structures can be modelled as polyhedra with tetracoordinated Pd(II) ions at the vertices. All structures have eight triangular faces ( $F_3$ ), with various numbers of square faces ( $F_4$ ).

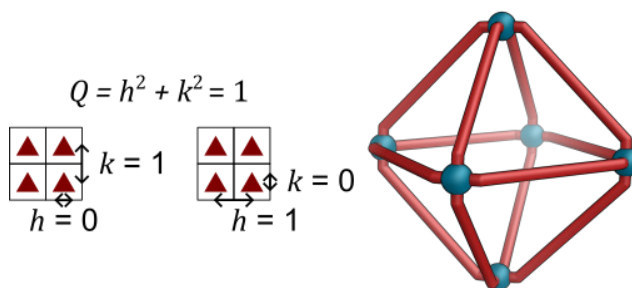
The triangular and square faces can be placed onto a square grid, where the relative position of two nearest triangles is described with integer coordinates  $h$  and  $k$ .  $Q$  is then given by the equation:

$$Q = h^2 + k^2$$

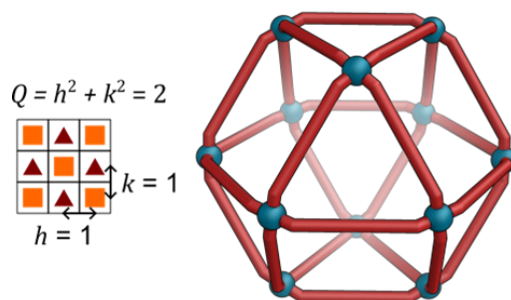
Part of the grid for a structure with  $h = 2$  and  $k = 4$  is shown below.



The smallest possible structure in this series is an octahedron, where  $Q = 1$ , and  $(h, k) = (0, 1)$  or  $(1, 0)$ . It has six vertices, eight triangular faces, and 12 edges. Nearest triangles are a move of one face in one direction apart.



The second smallest structure is a cuboctahedron, where  $Q = 2$ . Nearest triangles are a move of one face in each direction apart.



**3.3 Complete** the column in the table for  $Q = 2$ , describing the number of vertices,  $V$ , number of edges  $E$ , the total number of faces,  $F$ , and the number of square faces,  $F_4$ .



$Q$	1	2
$(h, k)$	(0, 1) or (1, 0)	(1, 1)
$V$	6	
$E$	12	
$F$	8	
$F_3$	8	8
$F_4$	0	

All structures obey the following rules:

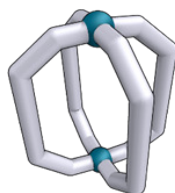
$$V - E + F = 2$$

$$V = 6Q$$

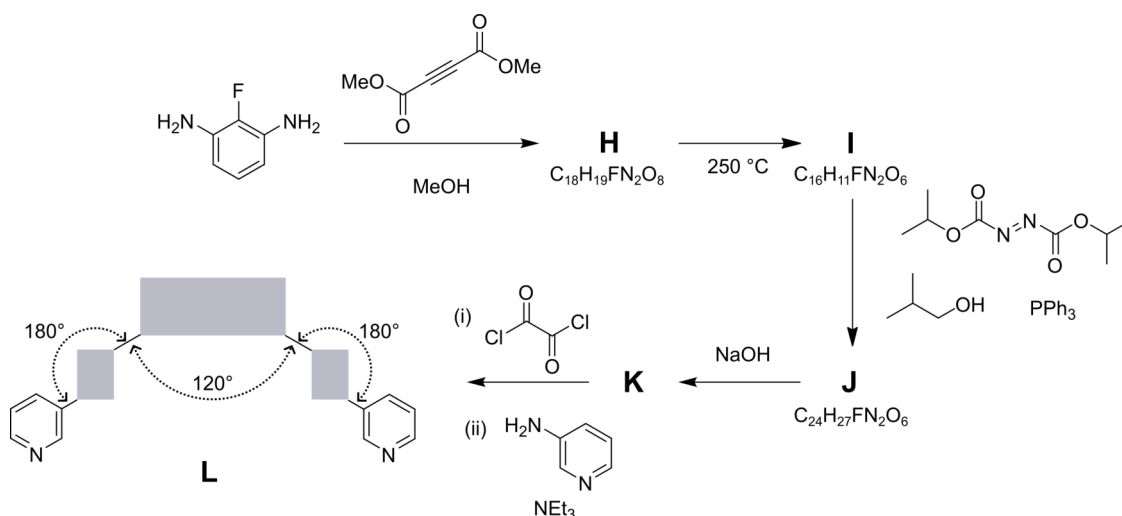
$$F - V = 2$$

**3.4 Complete** the table for the third smallest structure, where  $Q = 4$ .

$Q$	4
$(h, k)$	
$V$	
$E$	
$F$	
$F_3$	8
$F_4$	



In contrast to these large structures, the smallest structures contain two metals and four ligands and are called lanterns. They are similar in shape to the traditional lanterns seen at the Dubai light festival. Lanterns are formed by ligands such as **L**, which make two parallel  $N \rightarrow Pd$  bonds. Ligand **L** has two planes of symmetry and can adopt a planar conformation with the angles shown.

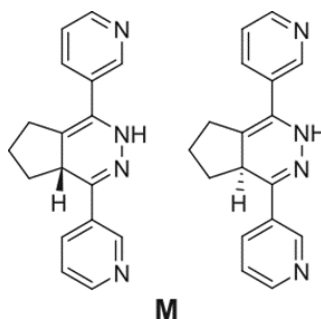


Hint:

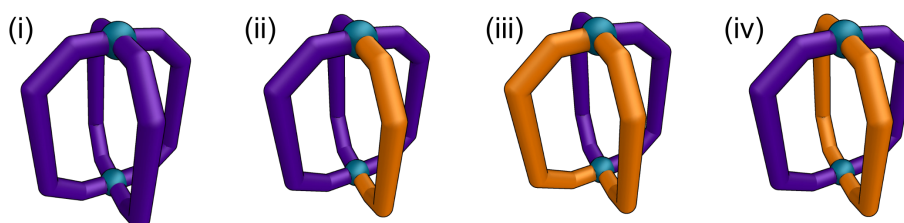
- The transformation from **H** to **I** could also be achieved by Lewis acid catalysis.

**3.5 Draw** the structures of compounds **H**, **I**, **J**, **K**, and ligand **L**.

Unlike symmetrical ligand **L**, chiral ligand **M** lacks symmetry and exists as a pair of *R* and *S* enantiomers.

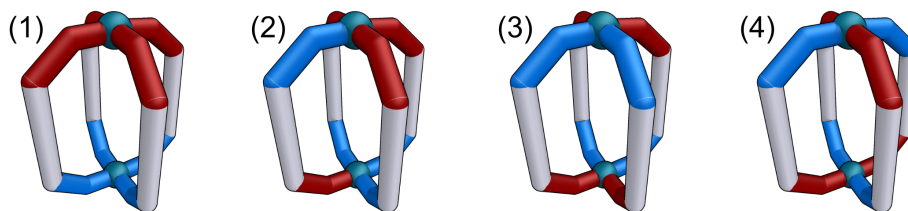


Multiple lantern isomers can be formed from ligand **M**. We can group these isomers in two ways. Firstly we categorise by the number of each type of ligand in the lantern: (i) all the same (*RRRR* or *SSSS*), (ii) one different (*RRRS* or *SSSR*), (iii) *cis*-*RRSS*, and (iv) *trans*-*RSRS*.



Secondly, the two ends of ligand **M** are not the same; the ligand has a head (H) and a tail (T). There are four categories of structure considering head-to-tail orientation: (1) all up (HHHH), (2) three up (HHHT), (3) *cis*-HHTT, and (4) *trans*-HTHT.

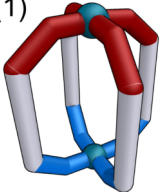
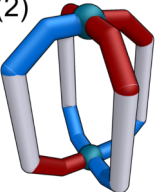
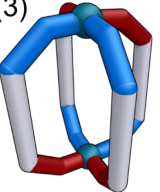
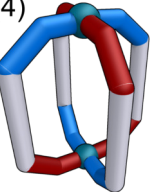
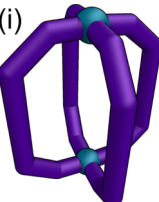
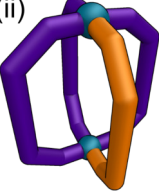
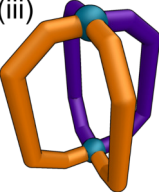
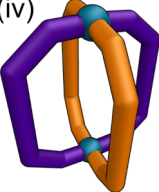




The 16 possible combinations of these categories are represented by empty cells in the table. Some combinations have only one possible isomer, whereas others have multiple possible isomers. In any one combination, all possible isomers are either chiral or achiral.

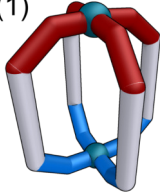
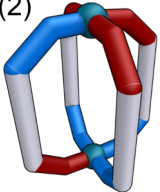
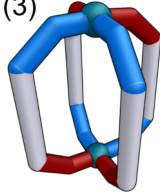
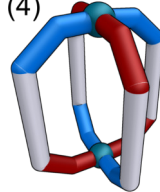
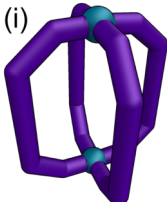
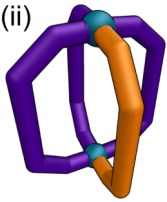
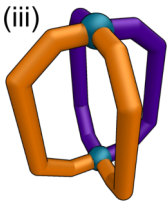
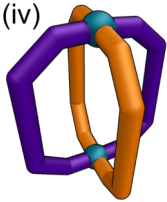


**3.6 Complete** the table by **writing "C"** for chiral and **"A"** for achiral. **Note**, in this part you will be awarded points for each correct answer but deducted points for each incorrect answer down to a minimum of zero. There is no penalty for empty cells.

	(1) 	(2) 	(3) 	(4) 
(i) 				
(ii) 				
(iii) 				
(iv) 				



3.7 **Complete** the table with the number of possible isomers of each combination.

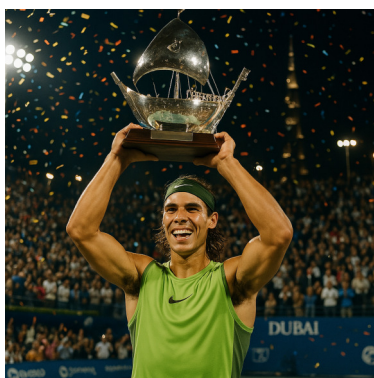
	(1) 	(2) 	(3) 	(4) 
(i) 		2		
(ii) 			4	
(iii) 				
(iv) 				



## 4. The life of tennis balls

6% of the total

4.1	4.2	4.3	4.4	Total
3	16	5	16	40



*This problem honours the incredible Rafael Nadal, a true tennis icon who concluded his remarkable career in 2024.*

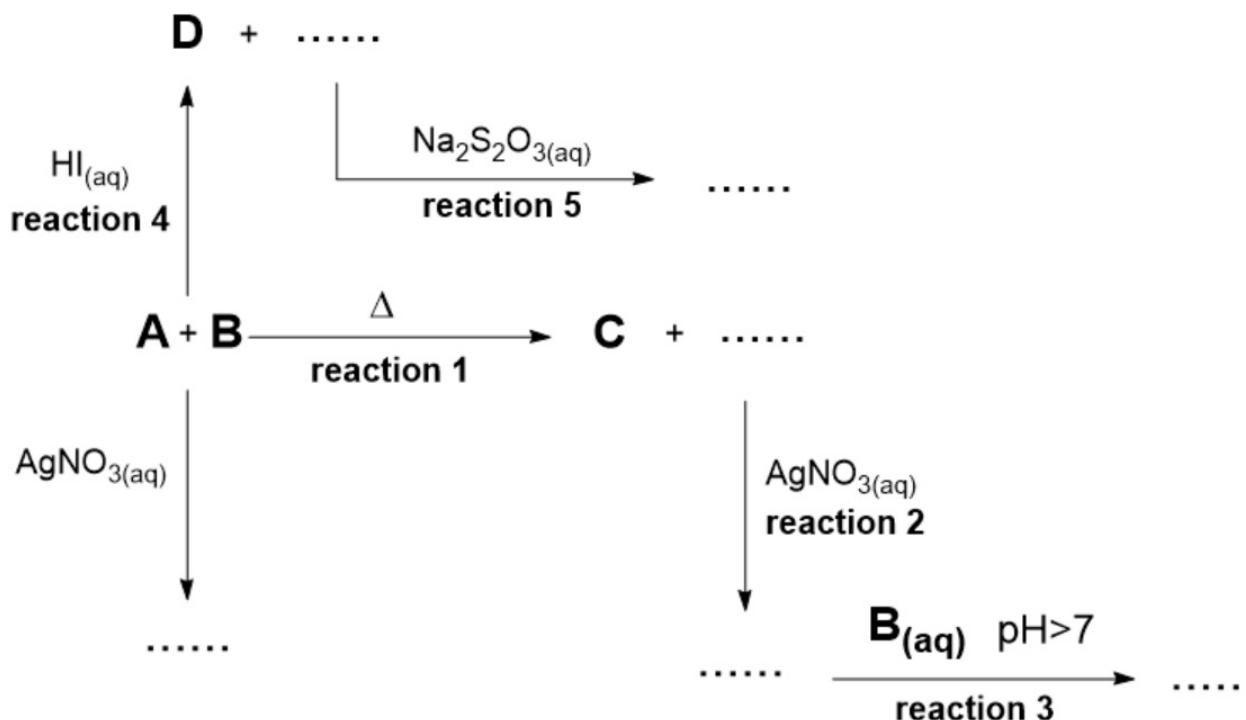
The Dubai Tennis Championships is a prestigious tournament held annually in UAE. Many of the world's top players, including Rafael Nadal, Roger Federer, Novak Djokovic, and Andy Murray have won titles there.

The composition of tennis balls has evolved over hundreds of years. To ensure a good bounce, the inside of modern tennis balls is pressurised above atmospheric pressure. However, old hollow tennis balls just contained air at atmospheric pressure.

In this problem, assume tennis balls have an inner radius of  $R = 3.0$  cm that remains constant throughout the pressurisation process. Assume that the composition of air is 20%  $O_2$  and 80%  $N_2$  by volume. Consider that overpressure does not expand the ball.

**4.1 Calculate** the mass  $m$  (in g) of air inside an old tennis ball at  $T_0 = 25$  °C.

Chemists then discovered how to pressurise a ball above atmospheric pressure using a reaction between compounds **A** and **B**, which forms gas **C** (to create additional inner pressure) plus other non-gaseous products.



A capsule with a quantity  $m_{\text{mix}} = 0.3389 \text{ g}$  of a stoichiometric mixture of two white inorganic compounds **A** and **B** was placed inside a ball filled with air at atmospheric pressure. They reacted completely inside the ball upon heating to form gas **C** and other products (**reaction 1**) to produce an overall pressure inside the ball of  $p = 1.600 \text{ atm}$  (at  $25^\circ \text{C}$ ). Once this ball was opened, all residue inside was collected and dissolved in water. The dropping of silver nitrate in that solution gave a white precipitate (**reaction 2**). This collected precipitate could be partially dissolved in a concentrated aqueous solution of **B**. By increasing the pH of this mixture, the precipitate dissolved completely (**reaction 3**). If the same initial capsule of **A+B** is dissolved in water and concentrated solution of silver nitrate added,  $m_{\text{precipitate}} = 0.8224 \text{ g}$  of white precipitate formed which was approximately twice the mass of precipitate formed in **reaction 2**.

When the capsule of **A+B** dissolved in a solution of HI the formation of gas **D** started, and the solution turned brown (**reaction 4**). Upon further addition of sodium thiosulfate this colour disappeared (**reaction 5**).

The densities of gases **C** and **D** differ by no more than 10%.

**4.2 Write** the chemical formulae of compounds **A-D**.

**4.3 Write** equations for **reactions 1-5**.



The pressure inside modern tennis balls is  $p_0 = 1.80$  atm. They are sold in a pressurised can, with the same pressure in the can as in the ball to stop gas coming out during storage.

Standard balls contain air and premium balls contain pure  $N_2$ . Once the can is opened, depressurisation begins, and the gas diffuses out of the balls until the internal pressure reaches atmospheric pressure. Assume there is no diffusion of gas into the balls at any point. The activation energy for the depressurisation of a premium ball is  $E_A = 50.0$  kJ mol<sup>-1</sup>.

The rate of ball depressurisation (pressure/time) could be described by similar equations of those used in chemical kinetics. At  $T_0 = 25.0$  °C, once the can is opened, the premium balls depressurise to  $p_1 = 1.40$  atm after  $t_1 = 241$  h and to  $p_2 = 1.19$  atm after about  $t_2 = 21$  days. The initial depressurisation rate of regular balls is 10% faster than premium balls.

**4.4a Demonstrate** that the depressurisation process follows the first kinetic order by **calculating** the depressurisation rate constant  $k_{N_2}$  for  $N_2$  in h<sup>-1</sup>.

*Note: If you couldn't calculate the answer, use  $k_{N_2} = 10^{-3}$  h<sup>-1</sup> in further calculations.*

**4.4b Calculate** the (depressurisation) rate constant  $k_{O_2}$  for  $O_2$  in h<sup>-1</sup>, **assuming** the rates for both gases are additive.

As well as today being the IChO 2025 theory paper, it is also (perhaps less importantly) the Semi-Finals day at Wimbledon. Amanda Anisimova will start a match in  $t_{\text{match}} = 12.0$  h from now. The weather today in Wimbledon is predicted to be a constant  $T_W = 30.0$  °C. Assume a new set of **premium balls**, which were manufactured and placed in the can at  $T_0 = 25.0$  °C, are opened now and quickly change to  $T_W = 30.0$  °C.

**4.4c Calculate** the pressure  $p_{\text{start}}$  (in atm) of the balls at the start of the match.



## 5. Solar-powered multi-stage flash desalination

### 6.5% of the total

5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
2	2	3	2	2	2	1	2	16

Freshwater is scarce in the arid climate of the UAE. The country relies on solar-powered desalination plants to produce freshwater. A Dubai desalination plant uses a multi-stage flash (MSF) desalination process. In MSF desalination, seawater is heated by passing through a series of heat exchangers to raise its temperature, reaching its saturation temperature at a high pressure. When pressure is reduced, this superheated seawater gives off pure water vapour to become saturated again, a process known as flashing.



Assume seawater in Dubai is at  $T_0 = 25.00\text{ }^{\circ}\text{C}$  and is an aqueous solution of 3.45 % mass NaCl. Assume complete ionisation of NaCl in water.

The boiling point of seawater is higher than pure water. The boiling point elevation constant,  $K_b = 0.5120\text{ K kg mol}^{-1}$ .

**5.1 Calculate** the boiling point,  $T$ , (in  $^{\circ}\text{C}$ ) of Dubai seawater at atmospheric pressure. *If you couldn't calculate the answer, use a temperature of **373.50 K** for further calculations.*

**5.2 Calculate** the percentage mass of NaCl,  $w_{\text{NaCl}}$ , in water that has a boiling point,  $T_b = 378.00\text{ K}$ .

**5.3** The boiling point of seawater also increases as pressure increases. **Calculate** the boiling point,  $T$ , (in  $^{\circ}\text{C}$ ) of the **initial Dubai seawater** at a pressure,  $p = 2.50\text{ atm}$ . The latent heat of vaporisation of water,  $E_{\text{vap}} = 2260\text{ kJ kg}^{-1}$  (40.716 kJ/mol). Assume this is the same for seawater.

In the plant, a flash chamber (of volume,  $V = 100\text{ L}$ ) contains a mass of 1.00 kg of seawater (l) at  $T_1 = 90.0\text{ }^{\circ}\text{C}$ .



Another mass of 1.00 kg of seawater is then overheated to  $T_2 = 110.0\text{ }^{\circ}\text{C}$  at high pressure before being added to this chamber, where a reduction in pressure causes some water to turn into steam.

After equilibrium was established, the temperature in the chamber was  $T_f = 97.0\text{ }^{\circ}\text{C}$ . Assume there was no loss of energy, and that the latent heat of vaporisation is independent of temperature.

The specific heat capacity of seawater,  $C_p = 3.85\text{ kJ kg}^{-1}\text{ K}^{-1}$ , assumed to be independent of temperature. The density of seawater,  $d = 1025\text{ kg m}^{-3}$ .

**5.4 Calculate** the amount,  $n$ , (in mol) of water that vapourised, assuming that the latent heat of vaporization does not depend on pressure, and that the heat capacity of water vapor in the chamber is negligible.

*If you couldn't calculate the answer, use **0.56 mol** for further calculations.*

**5.5** Assuming the **initial** vapour pressure before addition of the overheated water in the chamber was  $p_i = 0.690\text{ atm}$ , **calculate** the final vapour pressure,  $p_f$ , (in atm) in the chamber assuming the water vapour behaves as an ideal gas.

**5.6 Calculate** the thermal energy,  $E$ , (in kWh) required to heat a mass of 1.00 kg of seawater from  $T_1 = 25.0\text{ }^{\circ}\text{C}$  to  $T_2 = 110.0\text{ }^{\circ}\text{C}$ .

*If you couldn't calculate the answer, use **0.1 kWh** for further calculations.*

**5.7** A plant produces  $50,000\text{ m}^3$  of pure water per day. The plant passes Dubai seawater through 30 flash cycles and overall can extract 85% of the water present. **Calculate** the mass,  $m$ , (in kg) of Dubai seawater needed per day.

*If you couldn't calculate the answer, use  **$6.0 \times 10^7\text{ kg}$**  for further calculations.*

Plants make efficient use of heat exchangers to save energy. We can assume the total energy required by the plant is the same as the energy needed to heat all the seawater from  $T_1 = 25.0\text{ }^{\circ}\text{C}$  to  $T_2 = 110.0\text{ }^{\circ}\text{C}$ .

**5.8** Assuming a  $10\text{ m}^2$  solar panel has a power of 2.00 kW averaged during the 12 operational hours every day and the efficiency of using energy is 67%, **calculate** the number of panels,  $N$ , required for the plant.





## 6. Solar energy conversion by CO<sub>2</sub> reduction

6% of the total

6.1	6.2	6.3	6.4	6.5	6.6	6.7	Total
5	2	3	3	3	2	4	22

Use the following data to solve this problem. Assume enthalpy and entropy changes of reactions do not depend on temperature.

	CO <sub>2</sub> (g)	CO(g)	O <sub>2</sub> (g)	Zn(s)	Zn(l)	Zn(g)	ZnO(s)
$\Delta_f H^\circ_{298} / \text{kJ mol}^{-1}$	-393.5	-110.5			6.5	130.4	-350.5
$S^\circ_{298} / \text{J mol}^{-1} \text{K}^{-1}$	213.8	197.7	205.1	41.7	50.8	161.0	43.7
Melting Point / K				692.7			2247
Boiling Point / K					1180		

Photochemical reduction of carbon dioxide is a promising approach both for solar energy conversion and for reduction of CO<sub>2</sub> content in the atmosphere. There are several ways to convert CO<sub>2</sub> to CO and other useful substances.

### Direct decomposition

Direct decomposition of CO<sub>2</sub> to CO and O<sub>2</sub> is a highly endothermic process which requires a large amount of energy – from heat or from light.

**6.1 Estimate** the temperature (in K) at which half of CO<sub>2</sub> decomposes at equilibrium at a total pressure of 1 bar.

### Catalytic decomposition

The use of metal/metal oxide catalytic systems allows the temperature of CO<sub>2</sub> decomposition to be significantly reduced and eases the separation of the gaseous products by using thermochemical cycles.



Consider a catalytic cycle based on the Zn/ZnO system and containing two reactions. The net reaction is CO<sub>2</sub> decomposition into CO and O<sub>2</sub>. **Reaction 1** is exothermic, while **Reaction 2** is highly endothermic – the reactants should be heated to the required temperature.

**6.2 Write** equations for **Reaction 1** and **Reaction 2**.

The operating temperature for **Reaction 1** is 1073 K.

**6.3 Calculate** the equilibrium constant,  $K$ , for **Reaction 1** and **find** the degree of CO<sub>2</sub> conversion,  $x$ , at this temperature.

**Reaction 2** is performed at the much higher temperature of 2000 K.

**6.4 Calculate** the equilibrium pressure of oxygen,  $p(\text{O}_2)$ , in bar, at this temperature.

### Photocatalytic reduction

Photocatalytic reduction of CO<sub>2</sub> with water is akin to natural photosynthesis. Plants convert CO<sub>2</sub> to carbohydrates as an energy source, but human civilisation needs hydrocarbons to produce energy. On the way from CO<sub>2</sub> to C<sub>x</sub>H<sub>y</sub> there are many possible intermediate products of CO<sub>2</sub> reduction.

**6.5 Complete the table** with the formulae of the **one-carbon** species from CO<sub>2</sub> reduction, containing only H and/or O atoms in addition to the **one C**. The oxidation number of the carbon in each species is shown. For the oxidation state +2 give the formulae of both an anion "**anion**" and a neutral molecule "**neutral molecule**". **Indicate** only one species in each box.

+3	+2 (anion)	+2 (neutral molecule)	0	-2	-4

Visible light ( $400 \text{ nm} < \lambda < 700 \text{ nm}$ ) makes up >40% of the total solar radiation reaching Earth. Light can be absorbed by semiconductors or dyes, leading to electronic excitation which can promote redox reactions. The band gaps of some common semiconductors are listed.

Semiconductor	CdS	Ge	Si	SiC	WO <sub>3</sub>	ZrO <sub>2</sub>
Band gap / eV	2.4	0.67	1.1	3.2	2.8	5.0



**6.6 Tick** which semiconductor(s) can be excited by visible light to serve as a potential photocatalyst(s). **Support** your answer with calculations.

In an early photocatalysis experiment, SiC semiconductor was suspended in  $V = 100$  mL of water, and  $\text{CO}_2$  was bubbled through at a rate of  $v = 3.0 \text{ L min}^{-1}$  ( $T = 25^\circ\text{C}$ ,  $p = 1 \text{ atm}$ ). The suspension was irradiated by a  $P = 500 \text{ W}$  lamp ( $\lambda = 365 \text{ nm}$ ) for  $t = 7 \text{ h}$ . After irradiation, the solution contained  $c(\text{HCHO}) = 1.0 \times 10^{-3} \text{ M}$  and  $c(\text{CH}_3\text{OH}) = 5.4 \times 10^{-3} \text{ M}$ .

The apparent quantum yield  $\phi$  is defined as:

$$\phi = \frac{N_e}{N_i},$$

where  $N_e$  is the number of electrons transferred and  $N_i$  is the number of incident photons.

**6.7 Calculate** the total degree of  $\text{CO}_2$  conversion,  $\eta$ , and the apparent quantum yield of photocatalytic reduction,  $\phi$ .



## 7. Dubai crude oil

### 7% of the total

7.1	7.2	7.3	7.4	7.5	Total
8	2	3	1	8	22

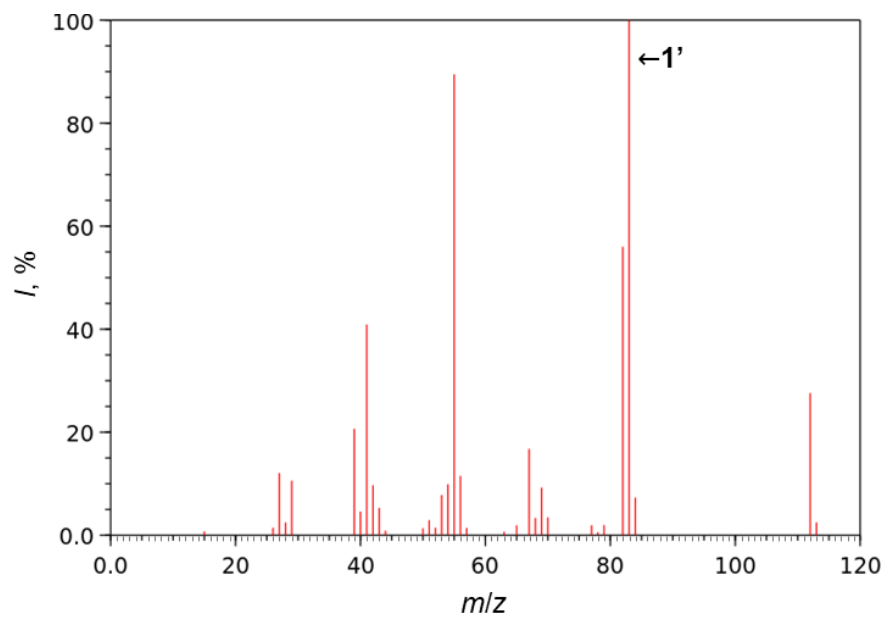
The petroleum industry plays an important role in the UAE economy. The oil called “Dubai Crude” is a benchmark for global oil prices. Crude oil is a complex mixture of organic compounds, mainly hydrocarbons, along with smaller amounts of S, N, and O-containing compounds.

The hydrocarbon composition of oil is characterised by the PONA number. The abbreviation stands for *P* – paraffins (alkanes), *O* – olefins (alkenes), *N* – naphthenes (cycloalkanes), and *A* – aromatics (arenes). One method to determine the composition of oil is gas chromatography–mass spectrometry (GC–MS).

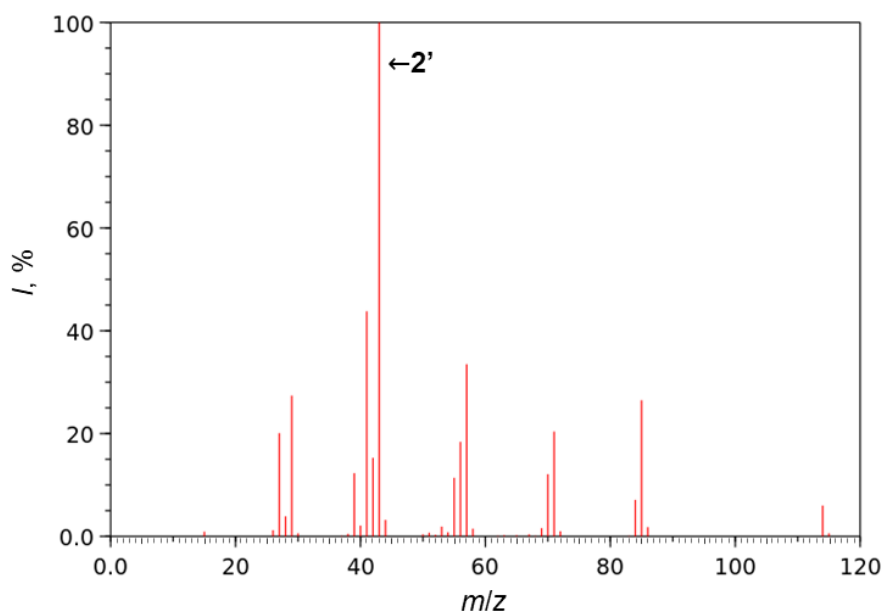
Below are mass spectra (electron impact ionisation, *I* – relative intensity) of four hydrocarbons **1–4** of Dubai Crude oil. They include **linear** alkane **P**, **linear** alkene **O**, **monosubstituted** cycloalkane **N**, and arene **A**. Alkene **O** does **not** have *cis-trans* isomers. **1'–4'** are selected fragmentation products.



**Compound 1**

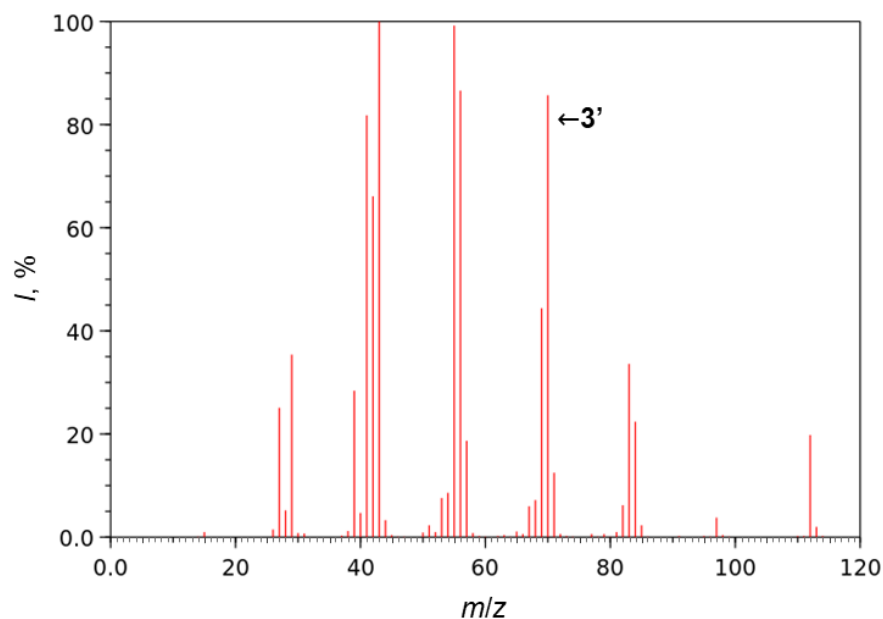


**Compound 2**

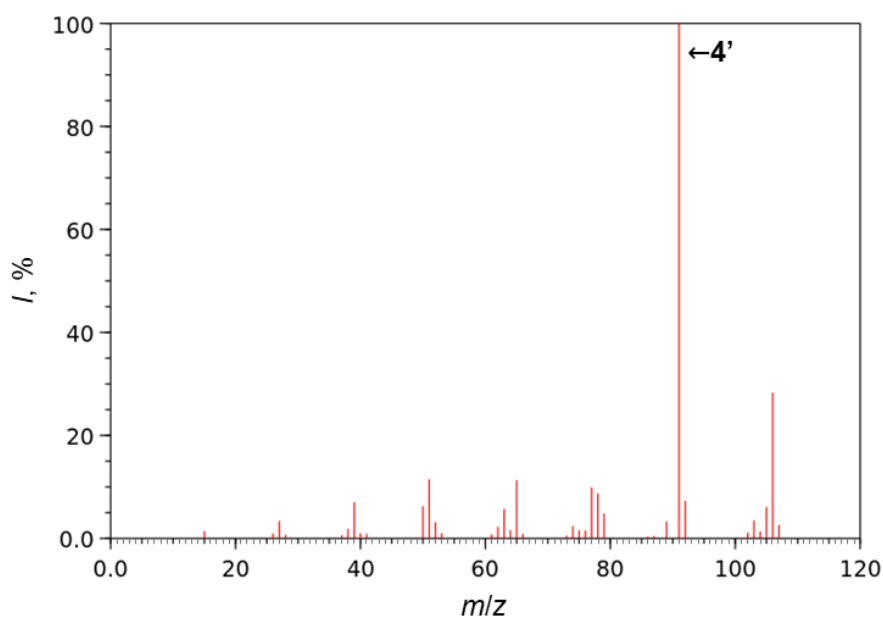




Compound 3



Compound 4



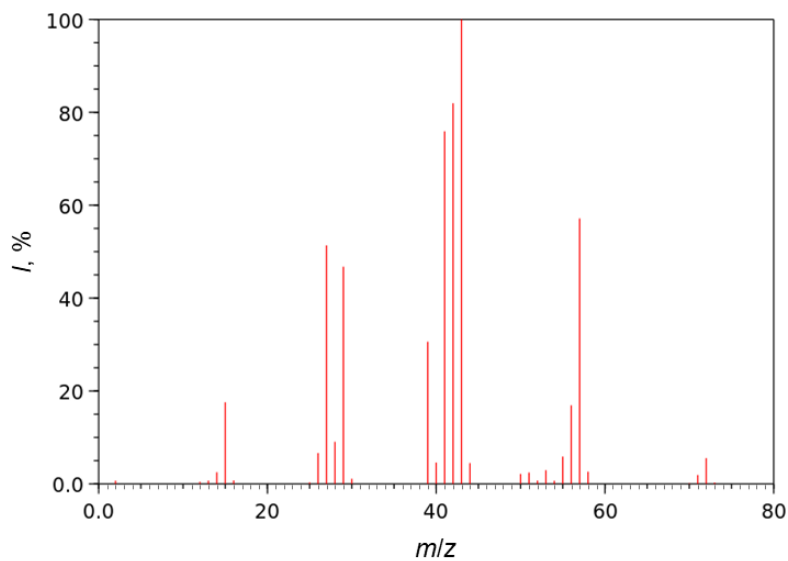
**7.1 Draw** the structures of **1–4** and **1'–4'**. If you cannot determine the structure(s) of **1–4**, **write** the corresponding letter code (**P/O/N/A**) and the molecular formula.

*Hint: Species **3'** is formed by a rearrangement of the molecular ion by the McLafferty mechanism.*

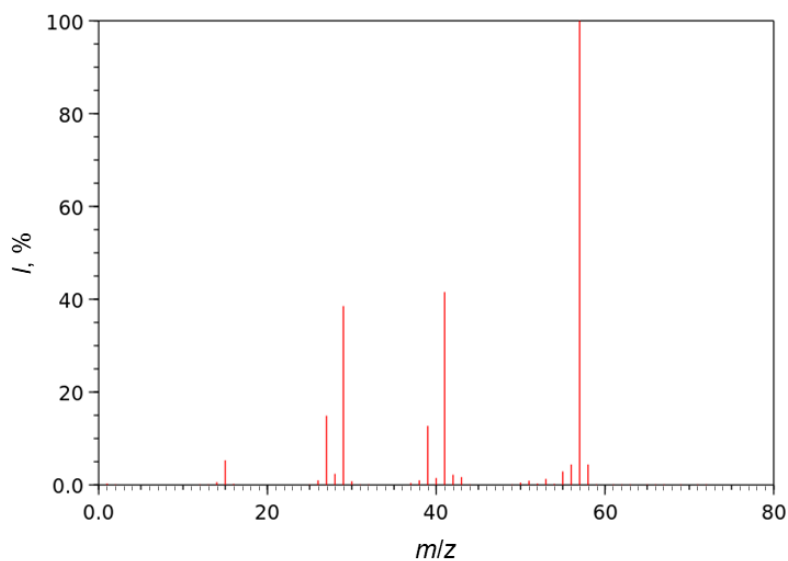
To differentiate isoparaffins (isoalkanes, *I*) from *n*-alkanes, the *PIONA* number may be used for a more precise description of crude oil composition. Below are two mass spectra of branched alkanes **5** and **6**. In the mass spectrum of **6**, the  $[M+1]^+$  peak has an intensity of *ca.* 5.4% relative to the intensity of the  $[M]^+$  peak of the molecular ion.



**Compound 5**



**Compound 6**



**7.2 Draw** the structures of compounds **5** and **6**.

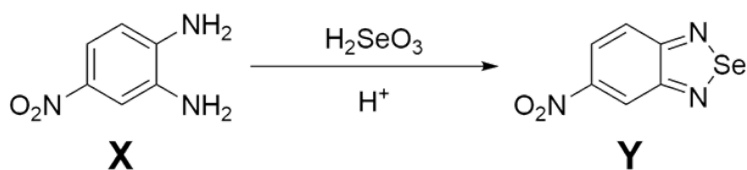


Crude oil is classified by the sulfur content as either sweet ( $<0.5$  wt%) or sour ( $>0.5$  wt%). A  $V = 115\ \mu\text{L}$  sample of Dubai Crude oil ( $\rho = 871\ \text{g dm}^{-3}$ ) was completely burnt. The resulting gas mixture was passed through a  $\text{H}_2\text{O}_2$  solution containing an excess of  $\text{Ba}(\text{OH})_2$ , leading to the formation of  $m = 1.395\ \text{g}$  of white precipitate. Upon acidification with  $\text{HNO}_3$ , the precipitate's mass decreased by 98.95%.

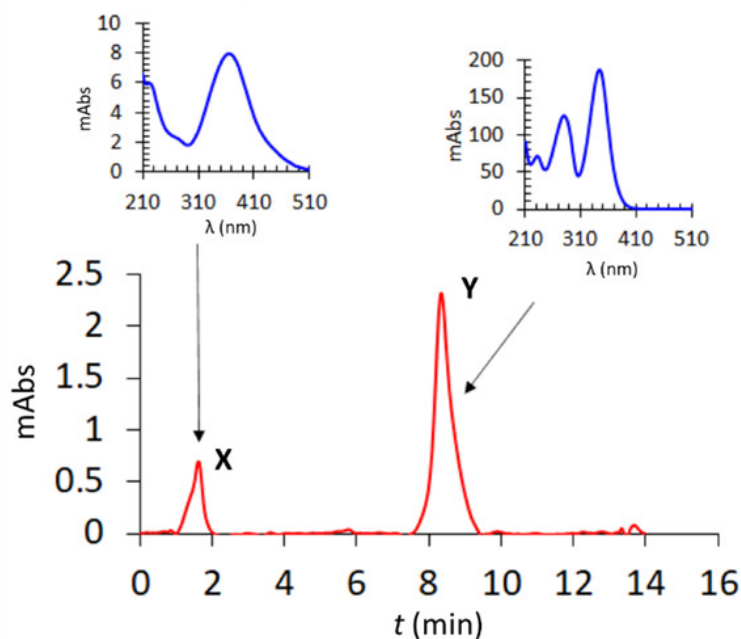
**7.3 Calculate** the sulfur content ( $w(\text{S})$ , wt%) of Dubai Crude oil.

In addition to sulfur, crude oil contains trace amounts of selenium, which transfers into the water used during refining. In aqueous solutions, selenium exists as  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$ .

The concentration of  $\text{SeO}_3^{2-}$  can be determined chromatographically by its selective reaction with diamine **X** under acidic conditions, forming piazoselenol **Y**. This reaction is complete only at the right pH range.



**X** and **Y** elute at different times ( $t$ ) on the chromatogram shown below. The absorption spectra (1 mAbs corresponds to absorbance  $A = 0.001$ ) of **X** and **Y** are also provided.







**7.4 Tick** the optimal wavelength ( $\lambda$ ) for the absorbance measurements in the chromatogram.

☐ 270 nm    ☐ 300 nm    ☐ 350 nm    ☐ 510 nm

Acidified water from the refining process, containing  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  (**solution 1**), was analysed as follows. A 9.50 mL sample was mixed with 0.50 mL of an aqueous solution of **X** (300  $\mu\text{M}$ , excess) to form **solution 2**.

The area,  $S$ , under each chromatogram peak was measured. These areas are proportional to the amount of the respective species in the peak. In a blank experiment under the same conditions with Se-free water, the peak area of **X**,  $S(\text{X})$  from the free diamine, was 0.825 mAbs·min. Running identical measurements with known amounts of  $\text{SeO}_3^{2-}$  showed that the peak area for **Y** (mAbs·min) depends on Se concentration ( $\mu\text{M}$ ) as follows:  $S(\text{Y}) = 1.21 \cdot c(\text{Se})$ .

The measurements for the Se-containing sample (**solution 2**) were carried out at different pH values, adjusted by adding four different strong acids. The ratios  $S(\text{X})/S(\text{Y})$  of the area under peak **X** to the area under peak **Y** for these measurements are shown in the **table below**. Assume all reactions have reached equilibrium.

**Table.**  $S(\text{X})/S(\text{Y})$  measured at different pH values with four strong acids

pH	3.0	2.0	1.5	1.0	0	-0.50
$\text{HNO}_3$	1.523	3.334	5.454	7.783	10.232	13.450
HCl	0.634	0.538	0.523	0.523	0.581	0.782
HBr	0.523	0.377	0.368	0.368	0.399	0.546
HI	1.722	2.223	5.114	8.123	11.736	15.780

*Hint: You need only two values from the table to solve this question.*

**7.5 Calculate** the concentrations of selenium species ( $c_0(\text{SeO}_3^{2-})$ ,  $c_0(\text{SeO}_4^{2-})$ , in  $\mu\text{M}$ ) in **solution 1**.



## 8. Carbon monoxide: deadly poison or promising therapeutic agent?

7.5% of the total

8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	Total
4	1	6	3	2	2	4	8	5	35

Carbon monoxide is a toxic gas because it binds to haemoglobin and blocks oxygen binding. A major source of CO is incomplete combustion of engine fuel. Therefore, many exhausts are fitted with catalytic converters which remove CO and other hazardous compounds including unburnt hydrocarbons and nitrogen oxides (NO<sub>x</sub>), forming mainly water vapour, carbon dioxide, and nitrogen.

**8.1 Write** the equations for the reactions of the following in a converter. **Tick** the box to indicate whether the carbon or nitrogen atom(s) have been oxidised by oxygen, "**Ox**", been reduced "**Red**", or stayed at the same oxidation state "**Same**". Please ignore any reactions between the exhaust gases.

- (a) CO
- (b) Unburnt hydrocarbon C<sub>x</sub>H<sub>y</sub>
- (c) Nitrogen oxides NO<sub>x</sub>

Catalytic converters contain nanoparticles of noble metals which act as catalysts, immobilised on a cheap high surface area material such as Al<sub>2</sub>O<sub>3</sub>.

In one experiment,  $m(\text{cat.}) = 0.10$  g of catalyst containing  $w(\text{Pd}) = 10$  wt% was used in a tube reactor. Gases were passed over the catalyst under continuous flow. The flow rate of CO gas was  $v(\text{CO}) = 10$  mL min<sup>-1</sup>, which was mixed with a second flow of air (assume 20% O<sub>2</sub>, 80% N<sub>2</sub>), at  $T = 273.15$  K and  $p = 1.00$  atm, before entering the reactor.

**8.2 Calculate** the flow rate  $v$  (in mL min<sup>-1</sup>) of air required for the reactants to be present in a stoichiometric ratio.

Assume 10% of the Pd atoms in the nanoparticles are exposed on the surface. Assume the conversion of CO to CO<sub>2</sub> was  $\eta = 70\%$ .

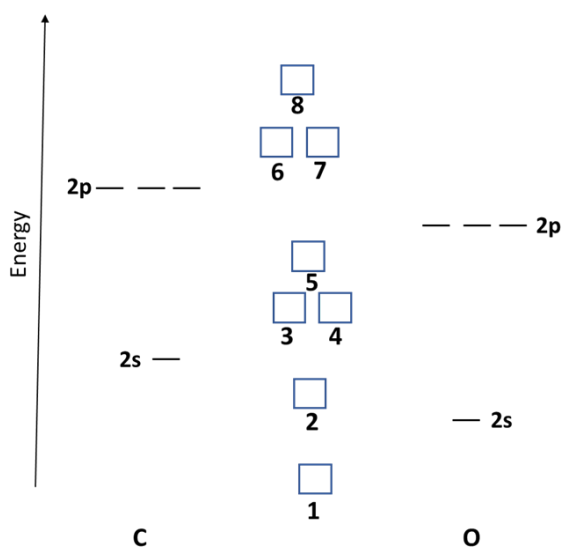
**8.3 Calculate** the number of CO<sub>2</sub> molecules,  $N$ , formed after  $t = 1$  h per surface Pd atom.



Ruthenium nanoparticles are efficient catalysts for CO combustion. The bonding interactions between CO molecules and the surface Ru atoms are of two types:

1.  $\sigma$ -bonding through a lone pair on the carbon atom;
2.  $\pi$ -interaction through an overlap between the Ru valence d-orbitals and CO molecular orbitals.

**8.4 Complete** the MO diagram for CO with electrons and the following table with the type ( $\sigma/\pi$ ) of overlap for forming each MO.



MO	1	2	3	4	5	6	7	8
Type of overlap								

**8.5** What is the effect of the Ru-CO  $\pi$ -interaction on the Ru-CO and the C-O bond strengths? **Tick** the correct answer.

(i) Ru-CO bond strength:

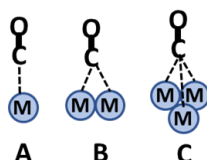
- ☐ increases "**in**"
- ☐ decreases "**dec**"
- ☐ no change "**nc**"

(ii) C-O bond strength:

- ☐ increases "**in**"
- ☐ decreases "**dec**"
- ☐ no change "**nc**"



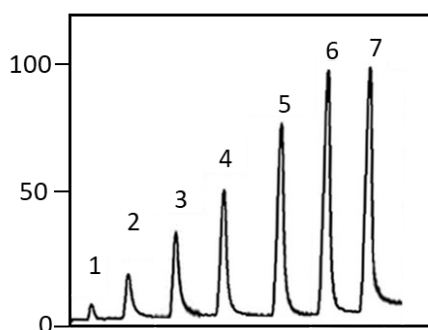
Adsorbed CO molecules have strong IR absorptions due to C–O stretching vibrations. Three binding modes for CO adsorbed on a metal surface are shown, where CO can interact with one or more metal atoms. IR peaks in the spectra of free CO and the three binding modes of adsorbed CO were observed at values of 1850, 1930, 2100, and 2143  $\text{cm}^{-1}$ .



**8.6 Tick** which wavenumber corresponds to each adsorption mode (**A**, **B**, and **C**) and to free CO.

Dispersion of a metal catalyst refers to the percentage of its atoms exposed on the surface. Dispersion can be determined by pulse chemisorption of CO since it adsorbs selectively onto surface atoms. Equal pulses of known amounts of CO are injected and a certain amount is adsorbed from each pulse. The amount remaining is measured by a detector and a peak, the area under which correlates with the amount of unadsorbed CO from each pulse, is plotted as shown below. Injections continue until no more CO adsorbs.

One experiment used 50  $\mu\text{L}$  pulses consisting of 10% vol CO in He, at 25  $^{\circ}\text{C}$  and 100 kPa. 15 mg catalyst was used, composed of 10 wt% Ni on an  $\text{Al}_2\text{O}_3$  support. Assume one CO molecule adsorbs on each surface Ni atom.



Pulse # (x axis)	1	2	3	4	5	6	7
% of pulse unadsorbed (y axis)	4	10	20	50	80	100	100

**8.7 Calculate** the percentage of Ni atoms exposed on the surface, %<sub>Ni</sub>.



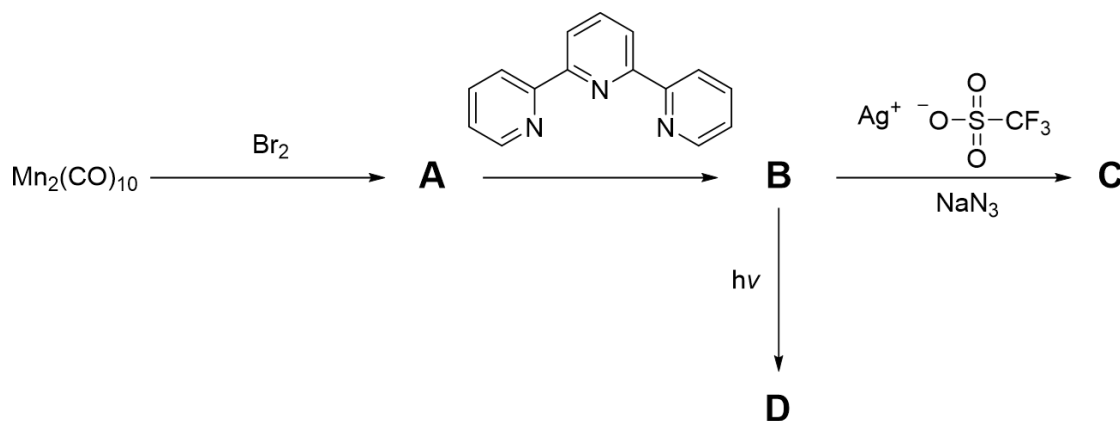
Despite being toxic at higher concentrations, at a concentration of 10-250 ppm, CO shows anti-inflammatory properties. Prodrugs known as CO releasing molecules (CORMs) target the delivery of effective dosages of CO to tissues in response to a trigger. Mn(I) carbonyl complexes have shown promise as PhotoCORMs as they can release CO when exposed to light.

Compounds **A-D** are all neutral Mn(I) carbonyl complexes.

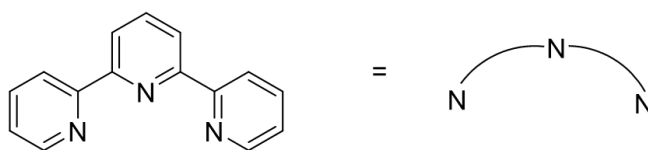
**B**, **C**, and **D** do not contain two CO ligands in a *trans* arrangement.

The IR spectrum of **C** contains a band at  $2042\text{ cm}^{-1}$  in addition to the CO stretching bands. The table with the number of CO stretching bands in the IR spectra of metal carbonyl complexes is given in the data sheet section at the beginning of the exam.

Compound	%Mn by mass	Number of CO stretching bands
<b>A</b>	19.98	3
<b>B</b>	12.15	3
<b>C</b>	13.26	3
<b>D</b>	12.95	2



For simplicity, the ligand can be drawn as:



**8.8 Draw** the structures of compounds **A-D**, ensuring the three-dimensional shape is clear. If the compound is chiral, only one enantiomer needs to be drawn.



Compound **C** reacts with alkynes and this can be used to tag proteins. This is known as an Inorganic Click (iClick) reaction.



During the conversion of **C** to **E**, the  $2042\text{ cm}^{-1}$  band in the IR spectrum of **C** disappears. The IR spectrum of **E** has two new C=O bands in the range of  $1735\text{--}1725\text{ cm}^{-1}$ . After a further 6 h, compound **E** converts to compound **F** which only has one C=O band in the range of  $1735\text{--}1725\text{ cm}^{-1}$ . Compound **G** does not contain manganese and has two planes of symmetry.

**8.9 Draw** the structures of compounds **E**, **F**, and **G**, ensuring the three-dimensional shape is clear. If the compound is chiral, only one enantiomer needs to be drawn.



## 9. Enzymes and cofactors

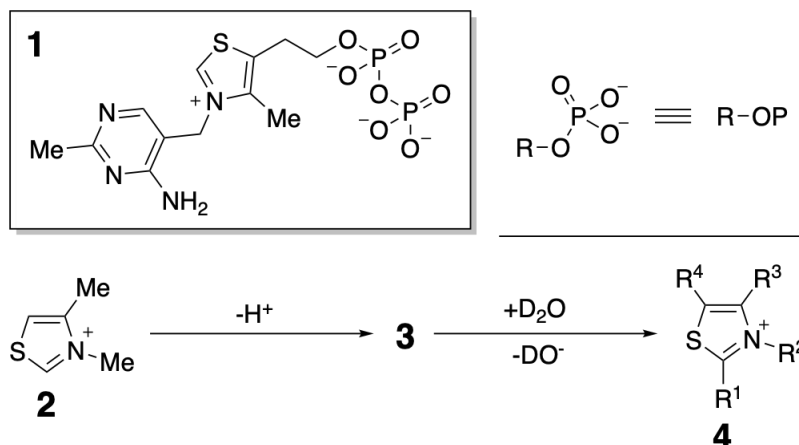
7% of the total

9.1	9.2	9.3	9.4	9.5	9.6	Total
2	6	2	6	10	10	36

In any answer for this task, **stereochemistry** is **not required** and the **phosphate group** can be abbreviated as "OP" (see the scheme below).

Transketolase (TK) and transaldolase (TA) are enzymes that catalyse C–C bond cleavage. TK contains the cofactor thiamine pyrophosphate **1**, a derivative of vitamin B1, in the active site.

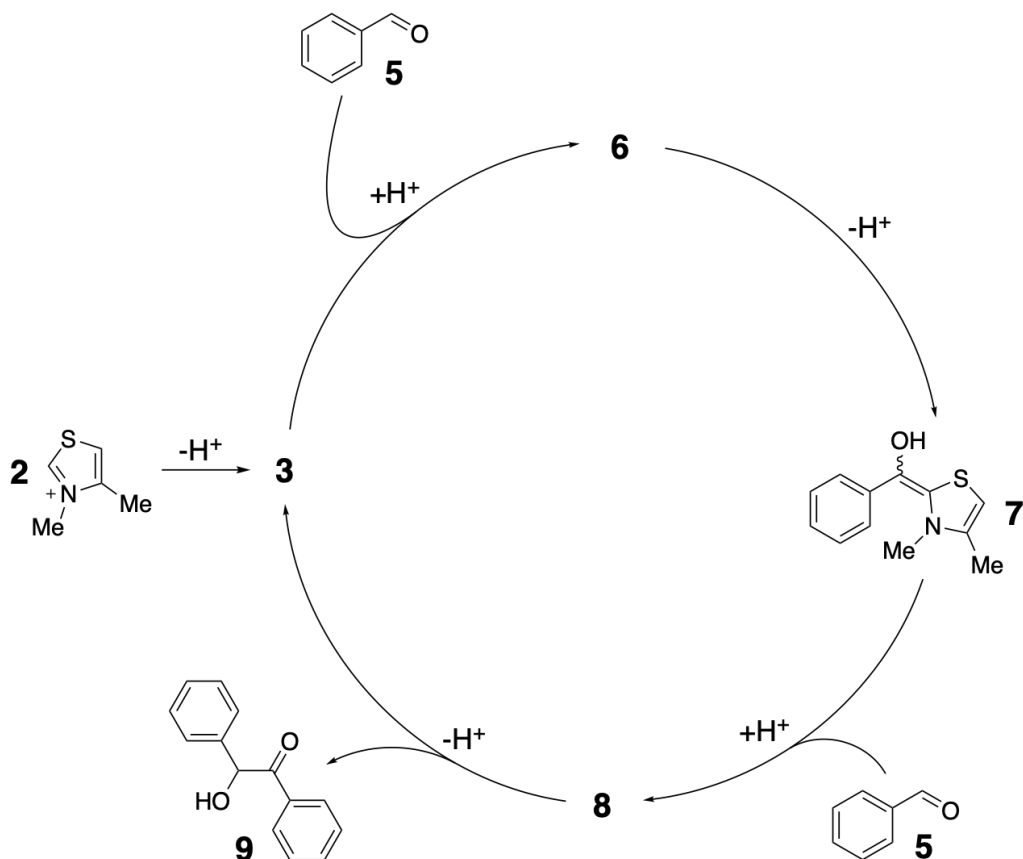
Breslow and coworkers studied cation **2**, a model of cofactor **1**, to demonstrate the relatively acidic properties of thiamine. Cation **2** underwent a **single** H/D exchange in D<sub>2</sub>O, which yielded **4** via intermediate **3**.



9.1 From the structures in the answer sheet, **choose** the one that corresponds to compound **4**.



Compounds such as **3** have many applications in organocatalysis. When a catalytic amount of **3** is generated in a solution of benzaldehyde **5**, a condensation reaction leads to product **9** via the catalytic cycle shown.

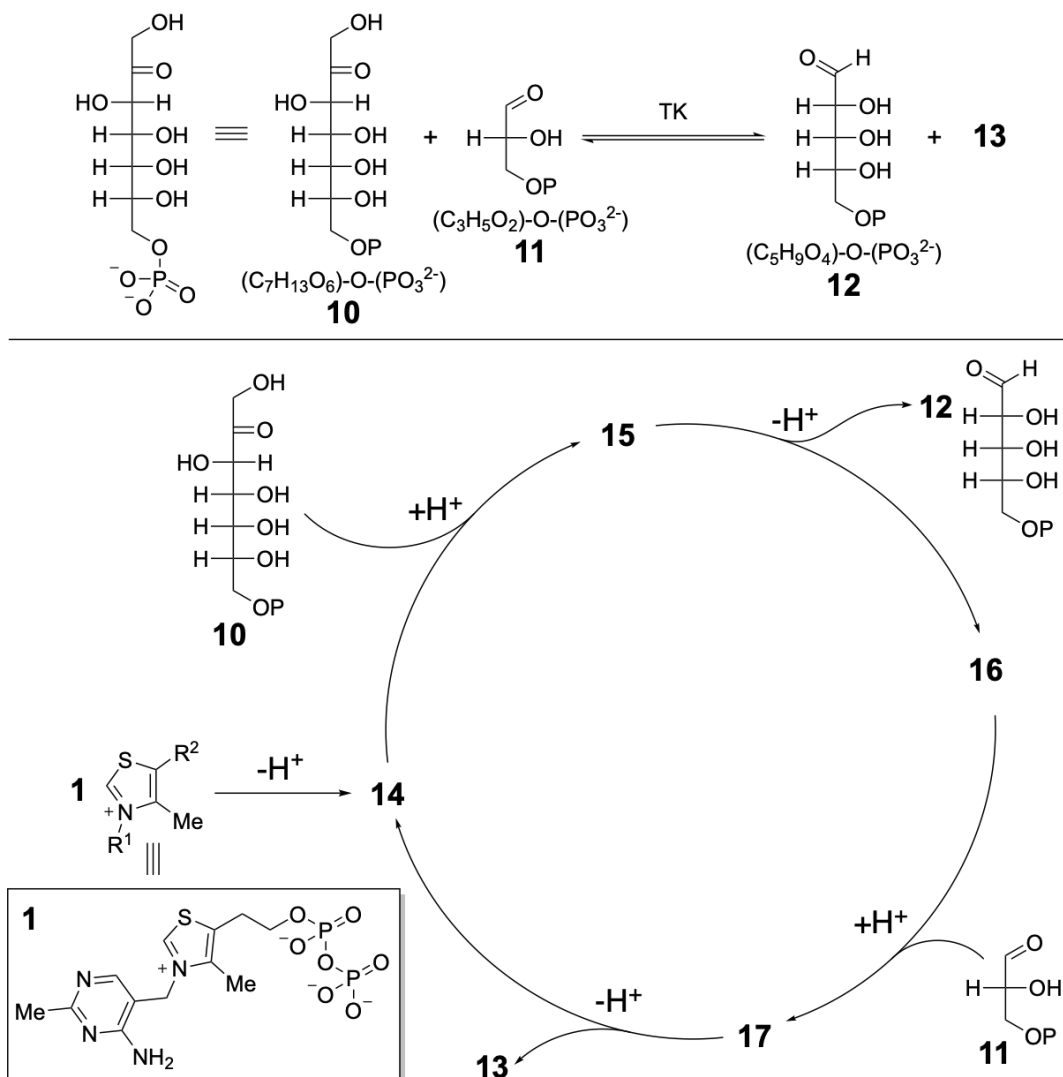


**9.2 Draw** the structures of compounds **3**, **6**, and **8**. Intermediates **6** and **8** are cations. There is no rearrangement in this catalytic cycle.





An aldose is a sugar containing an aldehyde. A ketose is a sugar containing a ketone. Enzyme TK contains **1** as a cofactor which catalyses the transfer of a two-carbon fragment from a ketose to an aldose by the catalytic cycle presented below.

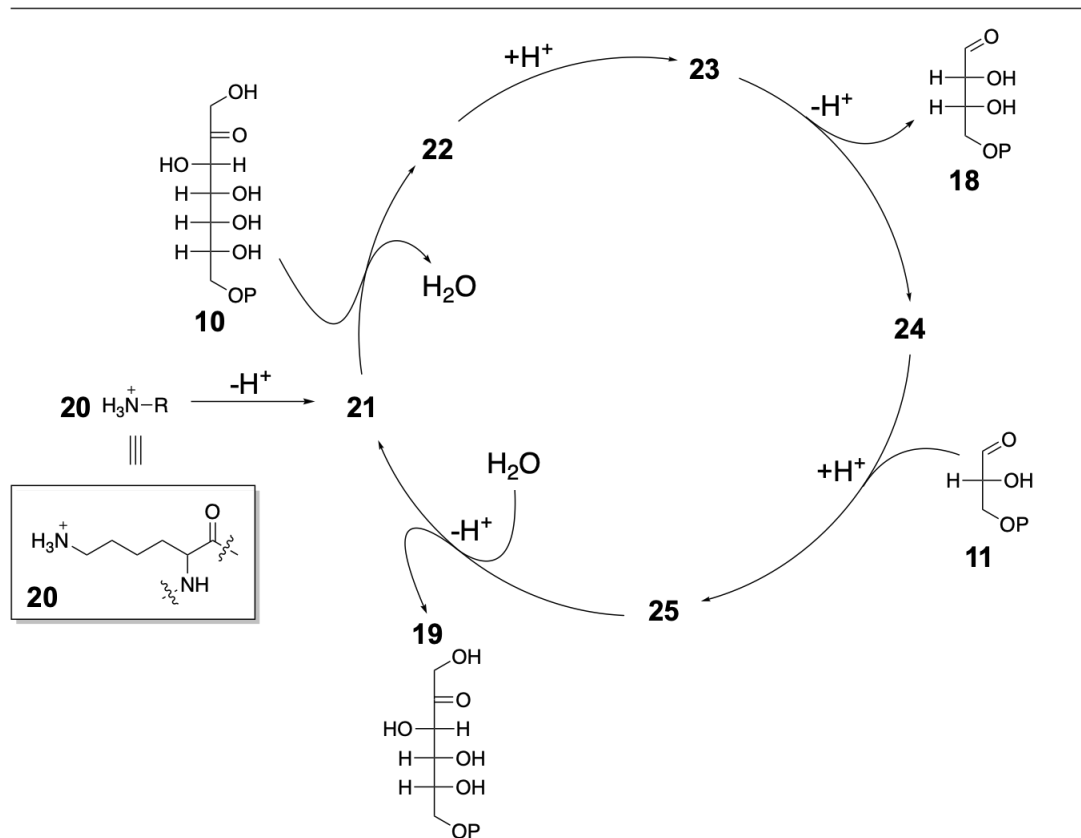
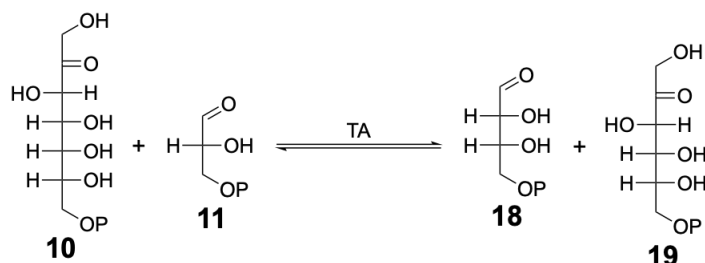


**9.3 Draw** the structure of **13**.

**9.4 Draw** the structures of intermediates **15-17**.



Enzyme TA catalyses the transfer of a three-carbon fragment from a ketose to an aldose. The residue of amino acid lysine **20** in the active site of TA is responsible for the enzyme activity.



**9.5 Draw** the structures of intermediates **21-25**. **23** and **25** have the same functional groups.

TK and TA are used in some organisms to transform **five molecules of three-carbon** sugars into **three molecules of a five-carbon** sugars.

**9.6 Propose a reaction sequence** for this transformation. **Label** all sugars with a letter followed by a number. **Use** the letter **A** for any aldose and the letter **K** for any ketose. **Use** the number corresponding to the number of carbon atoms in the sugar; see the example below (e.g., present structure **10** as **K7**; using full structural formulae is not required). The



number of carbon atoms in the sugar intermediates is **between 3 and 7**. There are **no non-enzymatic steps** in the pathway.

**Write** either TA or TK as the catalyst for each step. **Ignore** any phosphorylation, dephosphorylation, and isomerisation reactions. Beside transaldolase activity, TA exhibits aldolase activity resulting in only one product. Any five-carbon sugar (A5 or K5) is an acceptable product. **Use** the same style as shown in the figure below.

