Safety rules in the practical exam

Students must obey the following safety rules. Any student who breaks these rules will have to leave the practical exam and may receive a score of zero for the practical part.

Whilst in the practical exam hall, students must:

• **wear** full length trousers or other clothing covering their whole legs;
• **wear** closed and flat shoes;
• **wear** a lab coat with long sleeves;
• **wear** safety goggles that fit well;
• **wear** gloves when handling solutions and substances;
• **tie** back any long hair and/or beards.

Note: Contact lenses are prohibited during the practical exam. Students needing vision correction must wear glasses covered by safety goggles.

Students must not eat or drink at their bench. Chewing gum is not allowed.

Students must work only in their designated area. Common work areas must be kept tidy.

Electrical Hazard! Be aware you are working with aqueous solutions close to electrical equipment.

No unauthorised experiments or modification of the experiments is allowed.

Inform your lab assistant about any accident, spills, or broken glassware immediately.

All waste must be properly discarded to prevent contamination or injury. **Dispose** of the solutions in the containers with the correct labels. If any container is full inform your lab assistant.

GHS Statements

Hazard Code	Hazard Statement
H225	Highly flammable liquid and vapour
H226	Flammable liquid and vapour
H260	In contact with water releases flammable gases which may ignite spontaneously
H272	May intensify fire; oxidiser
H290	May be corrosive to metals
H301	Toxic if swallowed
H302	Harmful if swallowed
H304	May be fatal if swallowed and enters airways
H311	Toxic in contact with skin
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H331	Toxic if inhaled
H332	Harmful if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H341	Suspected of causing genetic defects
H351	Suspected of causing cancer
H361d	Suspected of damaging the unborn child
H361f	Suspected of damaging fertility
H361fd	Suspected of damaging fertility. Suspected of damaging the unborn child
H371	May cause damage to organs
H373	May cause damage to organs through prolonged or repeated exposure
H400	Very toxic to aquatic life
H410	Very toxic to aquatic life with long lasting effects
H411	Toxic to aquatic life with long lasting effects
H412	Harmful to aquatic life with long lasting effects

Chemicals:	
1-Nitroso-2-naphthol	H225, H302, H315, H317, H319, H341
Acetate buffer pH 5	H226, H314
Alizarin Red S indicator	Non-hazardous
Anisaldehyde stain	H225, H290, H314, H319, H361fd, H412
Carbonate buffer pH 10	H319
Copper(II) acetate	H302, H314, H410
Ehrlich's Reagent	H225, H290, H314, H317, H319
Eluent	H225, H319, H336
Eluent EtOAc/hexane	H225, H304, H315, H319, H336, H361f, H373, H411
Ethanol	H225, H319
Ethylenediaminetetraacetic acid disodium salt	H332, H373
EtOAc	H225, H319, H336
Iron(III) chloride in ethanol	H225, H302, H315, H318, H319
Murexide indicator	Non-hazardous
α-Naphthol	H225, H302, H311, H315, H317, H318, H319, H335, H371, H410
Ninhydrin stain	H302, H315, H319
Nitric acid	H272, H290, H314, H331
Potassium permanganate stain	H272, H302, H314, H315, H319, H335, H361d, H373, H410
Salen ligand	H315, H319, H335
Salen ligand in ethanol	H225, H315, H319, H335
Sodium carbonate	H319
Sodium hydroxide	H290, H314
Sodium hypochlorite	H290, H314, H410
Sodium nitrite	H272, H301, H319, H400
Sodium nitroprusside	H301
Sulfanilic acid	H290, H314, H315, H317, H319, H335
Sulfuric acid	H290, H314
Unknown amino acid sample	Non-hazardous
Unknown mixtures of amino acids	Non-hazardous

Unknown samples **A**-**D**	H302, H317, H319, H332, H335, H411
Unknown samples **E**-**H**	H225, H260, H290, H301, H302, H311, H312, H315, H317, H319, H331, H336, H351, H373, H410, H412
Urea	Non-hazardous

General instructions

This examination has 3 problems and is 5 hours long. There is 20 minutes reading time before the examination starts. **During the reading time you are not allowed to touch the equipment nor open the answer booklet.**

The question paper is viewable on your screen. The printed answer booklet has 11 stapled pages and 4 separate sheets for TLC plates 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 your answers 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.

You **must not leave** your workspace unless with a lab assistant. If you need assistance during the exam, **raise** the appropriate card.

 BATHROOM	If you need a toilet break
 ANALYSIS	When you want to submit your 96 well plate
 UV	When you need to visualise a TLC plate
 CAM	When you want the assistant to take a picture of your TLC plate
 Questions	If you need a refill or replacement item, or have any other questions

The switches to turn on the "**Hot plate**" and "**Vacuum**" are behind your computer screen. If you are unsure how to turn on the equipment, **ask** your lab assistant.

Gloves, distilled water, and paper tissues are available for free refill as needed. If you need a replacement or refill of any other item both you and the assistant need to **sign the table** on the answer sheet. One extra TLC plate (either for Q2 or for Q3 non-UV) and one other replacement of any item are given without penalty. Each further replacement will result in the deduction of 1 point from your 40 practical exam points.

Keep all items within the marked out area of your bench.

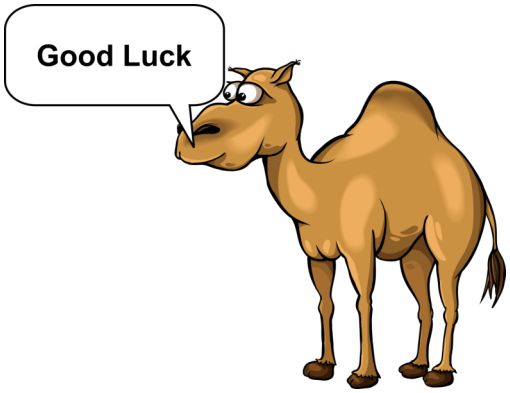
The following abbreviations are used for state: solid = s; liquid = l; aqueous solution = aq; solution containing organic solvent = sol.

Write only with the pen provided in the answer booklet. Do not use the permanent marker or the pencil for your answers. The permanent marker is only for labelling lab equipment. The pencil is only for labelling TLC plates. **Use only** the calculator provided.

The Official English version of this examination is available on your computer.

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

Do not take anything out of the lab when you leave.



(Good Luck)

Periodic table and data sheet

Formulae

Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c d$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)}\ \mathrm{BM}$

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	A complex problem	10%
2	Exploring the AminOasis	15%
3	R_f you ready to spot the answers?	15%
Total		**40%**

Common equipment and chemicals

Equipment

Item	Quantity	Label
Shared on the table of common use:		
Nitrile gloves (S, M, L)	as needed	
Paper tissues refill	as needed	
Ice box with ice and cold ethanol	as needed	
UV-lamp		
Wash bottles with distilled water	as needed	
Trays to deliver the TLC plates		
TLC photography station		
Shared in the hall central area:		
Distilled water refill tanks	as needed	
For each student:		
Hot plate covered with foil and 2 clamps	1	
Crystallisation dish (water bath)	1	**Q1/Q3 Water Bath**
Permanent marker	1	
Ruler	1	
Tweezers	1	
Pencil	1	
Pen	1	
Rubber	1	
Sharpener	1	
Pack of paper tissues	1	
Container for disposal of sharps	1	**Sharp waste**
Container for disposal of general waste	1	**General waste**

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
For each student:					
Distilled water	l	-	500 cm^3	Wash bottle, 500 cm^3	**H_2O dist.**
Ethanol	l	-	50 cm^3	Bottle, 100 cm^3	**Ethanol**

1. A complex problem

Equipment

Item	Quantity	Label
Part A		
In a labelled bag:		
Magnetic stirring bar	1	**Q1**
Plastic Pasteur pipette	1	
Steel spatula	1	
Tweezers	1	
Weighing paper	2	
On/under the desk:		
Sintered funnel	1	
Buchner flask with rubber sleeve	1	
Vacuum pump with hose	1	
Glass vial with cap for product	1	**Fe-salen + student code**
Thermometer	1	
125 mL plastic bottle	1	**Q1 waste**
In the box:		**Q1**
10 mL measuring cylinder	1	
50 mL glass beaker	2	
96 Well plate	1	**Student Code**
Glass rod	1	
Micropipette	1	**Student Code**
Micropipette tips	1 box	

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Part A					
Iron(III) chloride in ethanol	sol	0.1264 M	5 mL	10 mL bottle	**$FeCl_3$**
Salen ligand	s	-	200 mg	10 mL bottle	**Salen**
For Part B					
Iron(III) chloride in ethanol	sol	0.00045 M	4 mL	10 mL bottle	**Fe-Stock**
Salen ligand in ethanol	sol	0.00045 M	4 mL	10 mL bottle	**Salen-Stock**

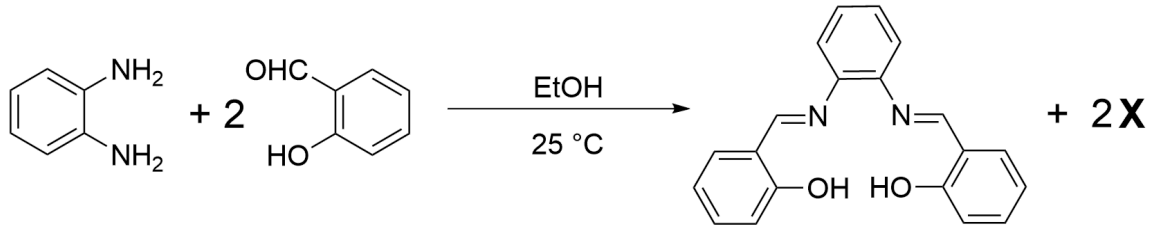
10% of the total

1.1	1.2	1.3	1.4	1.5	1.6	1.7	Total
1	20	0	18	3	2	3	47

Schiff base ligands are a class of organic compounds characterised by the presence of an imine group (-C=N-). They can easily be prepared by condensation reactions between aldehydes/ketones and amines. These ligands form many complexes, including salen complexes, which are efficient oxidation catalysts for organic molecules.

This task has two parts. In **Part A**, using a pre-synthesised sample of the salen ligand (*N*,*N*'-Bis(salicylidene)-1,2-phenylenediamine) you will make an iron salen complex, which you will then characterise in **Part B** using UV-Vis absorption.

The synthesis of this salen ligand from *o*-phenylenediamine and salicylaldehyde is shown below.



Q1.1 **Identify** by-product **X** formed in the ligand synthesis.

PART A: Synthesis of the iron salen complex

The switches for the vacuum and the hot plate are behind the computer.

1. **Transfer** all the salen ligand sample "**Salen**" (200 mg, 0.632 mmol) into a 50 mL beaker.

2. **Add** 15 mL of ethanol and a magnetic stirrer bar.

3. **Fill** approximately half of the water bath on the hot plate with distilled water.

4. **Clamp** the beaker in the water bath. **Insert** the thermometer into the water bath using the thermometer clamp.

5. **Gently heat** the beaker containing the suspension, while stirring, until the water bath reaches around 60 °C (position **VI** on the dial). **Warning: Electrical hazard!!**

6. Using a Pasteur pipette, **add slowly** all the ethanolic $FeCl_3$ solution "**$FeCl_3$**". An immediate colour change from orange to dark brown occurs.

7. **Continue stirring** for 20 min while keeping the temperature at around 60 °C, during which time a fine dark precipitate forms. You can work on other tasks during this time.

8. **Turn off** the heating and continue stirring for an additional 10 min. Then **remove** the beaker from the hot plate and let it cool to room temperature.

Using the tweezers provided, remove the magnetic stirrer bar from the beaker.

9. **Filter** the reaction mixture using the vacuum filtration setup.

10. **Raise** the "**Questions**" card. A lab assistant will bring you some ice-cold ethanol. **Wash** the precipitate once with 2 mL of ice-cold ethanol.

11. **Let air pass through** the product for about 3 min to dry it.

12. **Carefully transfer** your product to the vial labelled "**Fe-salen + student code**". You **may use** weighing paper. **Do not scrape too hard** as this may lead to some of the frit coming off.

Q1.2 **Keep** the vial. At the end of the exam, a lab assistant will **collect** your vial and both you and the lab assistant should **sign** on your answer sheet.

PART B: Characterisation of the iron salen complex

The iron salen complex can decompose over time, so the following things are important:

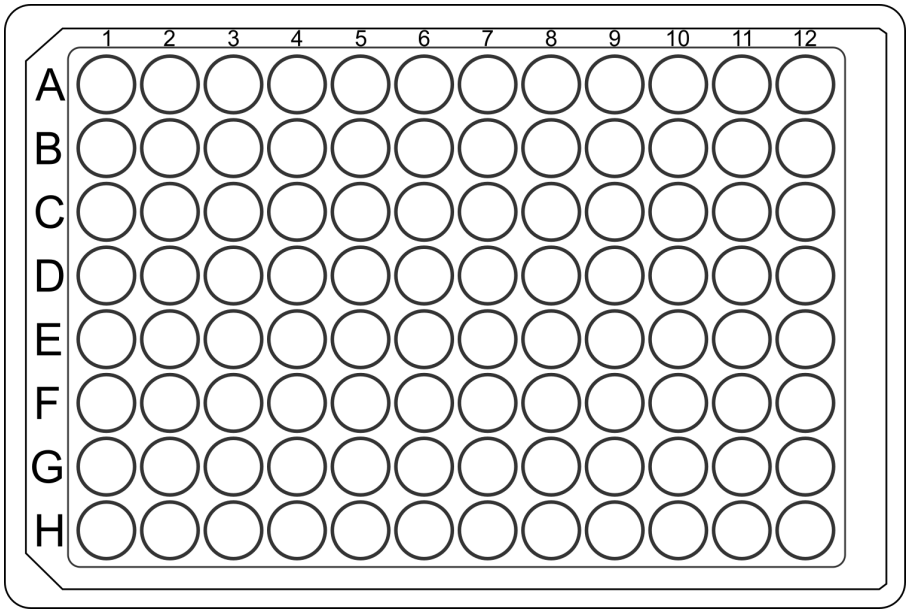
- **Complete** all of your pipetting in one go.
- You **don't need to mix** as this will be done by the spectrometer **with an in built linear shaker function.**
- First **add** "**Salen-Stock**" to all the wells you intend to use; then **add** ethanol, finally **add** "**Fe-Stock**". You **should finish** adding the first reagent to the plate before adding the second. Added volumes are mentioned in the table below.
- **Submit** your plate as soon as you have finished pipetting. The time you submit your plate will be noted.

- **Note you will only be able to submit a plate once and your plate will not be returned**.

- **Measuring the absorbance values may take some time, during which you should do other tasks.**

You have been provided with stock solutions of the salen ligand and iron(III) chloride, both of which have a concentration of 4.50×10^{-4} M.

Using a micropipette, you will prepare solutions with nine different ratios of metal to ligand, according to the table below. These solutions should be made in the 96 well plate. **Ensure** the plate is the same way around as in the figure.



The columns are labelled with numbers 1-12. Columns 1-9 will contain each of these solutions. The last three columns (Columns 10-12) should be left empty. **The solution number must be in the correct column of the plate with the same number to gain credit.**

The plate has eight rows labelled A-H. One set of the solutions can fit in each row. It is recommended that you make three sets. When the list of absorbance values is returned, you will be asked to tick which row(s) you would like to choose for your accepted absorbance values. You will also be able to exclude individual wells in a row from being taken into account if you think there has been an error in that well.

Solution/Column No.	1	2	3	4	5	6	7	8	9
Salen-Stock / µL	90	80	70	60	50	40	30	20	10
Ethanol / µL	100	100	100	100	100	100	100	100	100
Fe-Stock / µL	10	20	30	40	50	60	70	80	90
Total Volume / µL	200	200	200	200	200	200	200	200	200

Transfer the solutions to the appropriate wells using the micropipette.

Q1.3 As soon as you have filled all the wells that you want to, **raise** the "ANALYSIS" card. A lab assistant will collect your plate. Both you and the assistant should **sign** on the answer sheet. The lab assistant will write the time collected on the answer

sheet. The lab assistant will run your plate in the spectrometer, and return a printed list of absorbance values for all wells. They will write the time the plate was run on the spectrometer on the answer sheet.

We will measure samples in the order they are submitted and will do so as quickly as possible. The grading scheme accounts for the time between submission of the plate and running of the plate.

Q1.4 On the picture of the plate, **tick** the letter(s) of the row(s) you have selected to determine your accepted absorbance values. If you choose multiple rows, we will take an average of these for your accepted values. If you have made a mistake in a well, **draw** a cross over that individual well, and it will not be graded.

Q1.5 Determine the metal-to-salen ratio, Fe:salen, of the iron salen complex. By refering to the printed list of absorbance values, you may wish to draw a graph of absorbance, *A*, versus mole fraction of Fe, *x*(Fe), on the plot provided. The graph will not be graded.

The spin-only magnetic moment of a complex, μ_{B}, in Bohr magnetons (BM), can be calculated from the following formula, where *n* is the number of unpaired electrons.

$$\mu_B = \sqrt{n(n+2)}\ BM$$

The iron salen complex was measured to have μ_{B} = 5.89 BM.

Q1.6 Determine the number of unpaired electrons, *n*, in this complex and the oxidation state, *z*, of the Fe centre.

The obtained Fe-salen complex contains chloride and no coordinated solvent. Adding a few drops of an aqueous $AgNO_3$ solution to a solution of Fe-salen complex does not produce a precipitate.

Q1.7 Draw the structure of the complex based on your data and this information. **Do not use** any abbreviation for the structure of the ligand.

2. Exploring the AminOasis

Equipment

Item	Quantity	Label
Part A		
In labelled bags:		
pH indicator paper	5 strips	**Q2**
pH scale	1	
Filter paper	1	
TLC plate	1	**Q2 TLC**
On the desk:		
Test tube rack	1	
Glass test tube, 30 mL	25	
Glass beaker for water bath, 250 mL	1	**Q2 Water bath**
Test tube holder	1	
TLC capillary (in a centrifuge tube)	5	**Q2 Capillaries**
TLC chamber with a filter paper	1	**Q2 TLC chamber**
Glass Petri dish	1	

Item	Quantity	Label
Part B		
On/under the desk:		
Laboratory stand with a double burette clamp	1	
Burette, 25.00 mL	2	
Funnel	2	**Q2**
Graduated pipette, 10.00 mL	1	
Graduated pipette, 5.00 mL	1	
Three-valve pipette bulb	1	
Erlenmeyer flask, 100 mL	3	
Measuring cylinder, 10.0 mL	1	
Glass beaker, 50 mL	3	

Item	Quantity	Label
Parts A and B		
In a labelled bag:		
Plastic Pasteur pipette	5 + 2 extra	**Q2**
On the desk:		
Plastic bottle for liquid waste, 1 L	1	**Q2 Waste**

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Part A					
5 unknown mixtures of amino acids	aq	0.05–0.5% (each amino acid)	10 mL	Centrifuge tubes, 15 mL	**Mix 1, Mix 2, Mix 3, Mix 4, Mix 5**
Eluent	l	75 vol.% propan-2-ol, 25 vol.% H_2O	10 mL	Bottle, 25 mL	**1. *i*PrOH:H_2O**
Ninhydrin stain	sol	0.5%	10 mL	Dropping bottle, 30 mL	**2. Ninhydrin**
Ehrlich's reagent	sol	0.2 g 4-dimethylamino-benzaldehyde in 5 mL ethanol and 5 mL 20% H_2SO_4	10 mL	Dropping bottle, 30 mL	**3. Ehrlich's reagent**
Sulfuric acid	aq	50%	10 mL	Dropping bottle, 30 mL	**4. H_2SO_4**
Sodium nitroprusside	aq	10%	10 mL	Dropping bottle, 30 mL	**5. $Na_2[Fe(CN)_5NO]$**
Sodium hydroxide	aq	5 M	10 mL	Dropping bottle, 30 mL	**6. NaOH**
α-Naphthol	sol	1%	10 mL	Dropping bottle, 30 mL	**7. α-Naphthol**
Urea	aq	5%	10 mL	Dropping bottle, 30 mL	**8. Urea**
Sodium hypochlorite	aq	5% active chlorine	10 mL	Dropping bottle, 30 mL	**9. NaClO**
Sulfanilic acid	aq	1% in 0.1 M HCl	10 mL	Dropping bottle, 30 mL	**10. Sulfanilic acid**
Sodium nitrite	aq	5%	10 mL	Dropping bottle, 30 mL	**11. $NaNO_2$**

Name	State	Concentration	Quantity	Placed in	Label
Sodium carbonate	aq	10%	10 mL	Dropping bottle, 30 mL	**12. Na_2CO_3**
1-Nitroso-2-naphthol	sol	0.1%	10 mL	Dropping bottle, 30 mL	**13. 1-Nitroso-2-naphthol**
Nitric acid	aq	2 M	10 mL	Dropping bottle, 30 mL	**14. HNO_3**
Part B					
Alizarin Red S indicator	aq	0.2%	10 mL	Dropping bottle, 30 mL	**15. Alizarin Red S**
Murexide indicator	s	1% in NaCl	0.21 g	Amber dropping bottle, 30 mL	**16. Murexide**
Copper(II) acetate	aq	To be determined	150 mL	Bottle, 250 mL	**17. $Cu(CH_3COO)_2$**
Ethylene-diamine-tetraacetic acid disodium salt	aq	0.0200 M	100 mL	Bottle, 100 mL	**18. Na_2H_2EDTA**
Acetate buffer (pH 5.5)	aq	0.25 M (CH_3COONa + CH_3COOH)	30 mL	Bottle, 50 mL	**19. Acetate buffer**
Carbonate buffer (pH 10)	aq	0.1 M (Na_2CO_3 + $NaHCO_3$)	100 mL	Bottle, 100 mL	**20. Carbonate buffer**
Unknown amino acid sample	aq	1%	25.00 mL	Volumetric flask, 100 mL	**21. Sample X**

15% of the total

2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	2.10	Total
14	11.5	6.5	0	10	3	0	15	1	4	65

Part A: Qualitative analysis of mixtures

Five aqueous solutions **Mix 1**–**Mix 5** each contain two of the following ten amino acids:

Arginine (**Arg**), Cysteine (**Cys**), Glutamic acid (**Glu**), Histidine (**His**), Lysine (**Lys**), Phenylalanine (**Phe**), Proline (**Pro**), Serine (**Ser**), Tryptophan (**Trp**), Tyrosine (**Tyr**).

Each amino acid is present only once. The structures of these amino acids are given on the answer sheet. Your task is to **identify** the amino acids present in each solution **Mix 1**–**Mix 5**, using TLC, pH measurement and qualitative tests.

TLC and ninhydrin test:
- **Mark** the starting line on the TLC plate ("**Q2 TLC**") at least 1 cm from the bottom.
- **Mark** positions **1**-**5** on the starting line and **spot** solutions **Mix 1**–**Mix 5** 1-2 times on their respective positions.
- **Develop** the TLC plate using the "**1. *i*PrOH:H_2O**" solution as the eluent, keeping the filter paper in the chamber. Bear in mind that this step is time-consuming, so you should proceed with the problem.
- Once finished, **mark** the solvent front and **let** the TLC plate dry in the air.
- **Make sure to wear** gloves for further operations when handling the ninhydrin stain solution.
- **Fill** the Petri dish with the "**2. Ninhydrin**" stain solution using a dropper until the bottom of the dish is just covered.
- **Dip** the TLC plate in the ninhydrin stain solution using the tweezers, **let** the excess stain drip off the plate onto the paper wipes.
- **Heat** the TLC plate on the hot plate covered with aluminium foil (**set** the dial at **VI**). The test distinguishes between amino acids with a primary α-amino group (brown to purple colour) and a secondary α-amino group (yellow colour). Overheating may turn the spots brown.
- **Circle** all spots with a pencil.

Q2.1 **Label** the TLC plate with your student code using the pencil and **put** it on the separate answer sheet for question **2.1**. **Raise** the "**CAM**" card. You and the lab assistant **must sign** the answer sheet. The lab assistant will take a picture of it and return it to you. **Put** the TLC plate in the box in the zip bag labelled with your code.

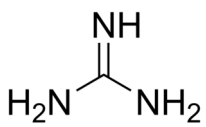
Q2.2 **Complete** the table with your results as follows:
(a) **Report** the approximate pH value of each solution using the pH indicator paper strips;
(b) **Report** if the qualitative tests described below were positive (use the plus sign "+") or negative (use the minus sign "–"). **Only "+" and "–" signs will be graded.**

For some tests, you will need a water bath:
- **Fill** the beaker "**Q2 Water bath**" with 50 mL of water and **put** it on the hot plate.
- **Set** the dial of the hot plate to **X**.
- When the water starts boiling, **decrease** the heating so it boils gently (**set** the dial between **VI** and **X**).

Ehrlich test ("**Ehrlich**" on the answer sheet):
- **Add** 10 drops of "**4. H_2SO_4**" to *ca.* 0.5 mL of the unknown solution.
- **Add** 10 drops of "**3. Ehrlich's reagent**" and **mix** thoroughly.
- **Heat** the solution using the water bath.
- The appearance of a **violet** colour indicates the presence of indole (bicyclic heterocycle) derivatives in the solution.

Nitroprusside test ("**Nitroprusside**" on the answer sheet):
- **Add** 5 drops of "**6. NaOH**" to *ca.* 1 mL of the unknown solution.
- **Add** 5 drops of "**5. $Na_2[Fe(CN)_5NO]$**" and **mix** thoroughly.
- The appearance of **red colour** indicates the formation of the $Na_4[Fe(CN)_5(NOS)]$ complex. **Note** that this colour disappears over time.

Sakaguchi test ("**Sakaguchi**" on the answer sheet):
- **Add** 5 drops of "**6. NaOH**" to *ca.* 1 mL of the unknown solution.
- **Add** 5 drops of "**7. α-Naphthol**" and **mix** thoroughly.
- **Add** 3 drops of "**8. Urea**" and then 5 drops of "**9. NaClO**" solution while **mixing**.
- Only a **stable red colour** indicates the presence of guanidine derivatives in the solution. The structure of guanidine is given below:



Pauly's test ("**Pauly**" on the answer sheet):
- **Mix** 3 drops of "**11. $NaNO_2$**" with 5 drops of "**10. Sulfanilic acid**" (4-aminobenzenesulfonic acid).
- **Quickly** after mixing the first two reagents, **add** 3 drops of the unknown solution and **mix** thoroughly.
- **Add** 5 drops of "**12. Na_2CO_3**".
- The appearance of a **red or red-orange** colour indicates coupling of an amino acid with a diazonium salt.

Gerngross test ("**Gerngross**" on the answer sheet):
- **Add** 3 drops of "**13. 1-Nitroso-2-naphthol**" to *ca.* 1 mL of the unknown solution.
- **Add** 5 drops of "**4. H_2SO_4**" and 5 drops of "**14. HNO_3**".
- **Heat** the solution using the water bath.
- The appearance of a **red colour** indicates the presence of a phenol group. **Note** that this colour disappears over time.

Q2.3 (a) **Write** the three-letter codes of the amino acids (the row "**AA**" on the answer sheet) you identified in each solution;
(b) For each pair of amino acids identified in each solution, **tick** the box for the amino acid with a higher R_f value (the row "**Higher R_f**" on the answer sheet).

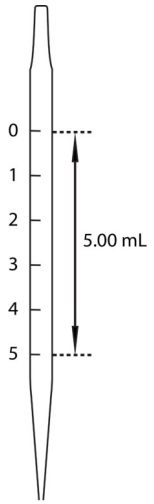
Part B: Titrimetric analysis

Step 1. Standardisation of copper(II) acetate solution

1. **Fill** a burette with 0.0200 M "**18. Na_2H_2EDTA**" solution.

2. To an Erlenmeyer flask, **add**:
   - 3 mL of "**19. Acetate buffer**" using a plastic Pasteur pipette;
   - 3 drops of the "**15. Alizarin Red S**" indicator solution using a dropper;
   - 5.00 mL of "**17. $Cu(CH_3COO)_2$**" solution using a graduated pipette.

Note that the 5.00 mL pipette is graduated as shown below:



3. **Titrate** until the solution changes colour from pink to a steady bright green.

4. **Repeat** steps 1-3 if necessary.

Q2.4 Record the observed volumes (V_0, mL – initial burette reading; V_f, mL – final burette reading; T, mL – titre).

Q2.5 Record your accepted final titre of Na_2H_2EDTA ($V_{Na_2H_2EDTA}$, mL).

Q2.6 Calculate the concentration of the copper(II) acetate solution ($c_{Cu(CH_3COO)_2}$, M).

Step 2. Titration of a sample of an unknown natural amino acid

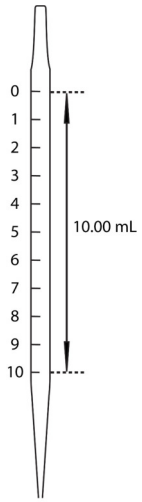
5. **Fill** the volumetric flask containing "**21. Sample X**" (250 mg of an unknown amino acid) to the mark with distilled water.

6. **Fill** a new burette with the standardised "**17. $Cu(CH_3COO)_2$**" solution.

7. **Add** 15 mL of "**20. Carbonate buffer**" to the amber bottle with the "**16. Murexide**" indicator. **Mix** until the indicator is fully dissolved. **Proceed** with the titration immediately after preparation of the indicator solution.

8. To an Erlenmeyer flask, **add**:
   - 10 mL of "**20. Carbonate buffer**" using the measuring cylinder;
   - 2 mL of prepared murexide solution using the dropper;
   - 10.00 mL of **Sample X** solution using a graduated pipette.

Note that the 10.00 mL pipette is graduated as shown below:



9. **Titrate** from pink until the complete disappearance of the intermediate violet colour. **Observe** the colour change against a **white background** and **out of direct sunlight**.

10. **Repeat** steps 8-9 if necessary.

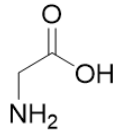
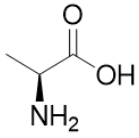
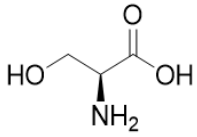
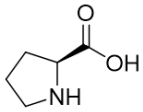
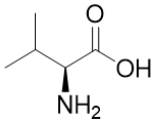
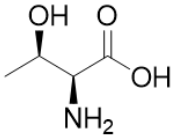
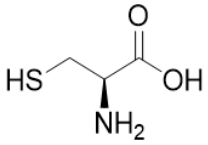
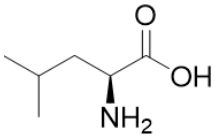
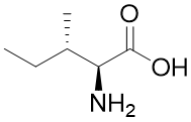
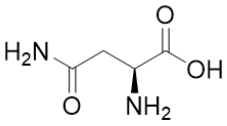
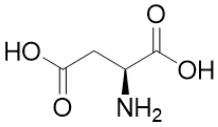
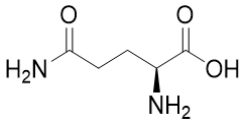
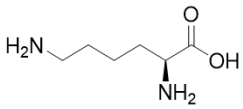
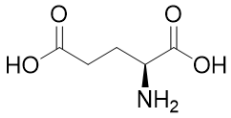
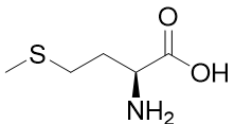
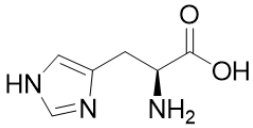
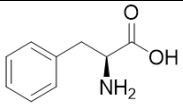
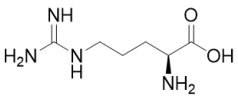
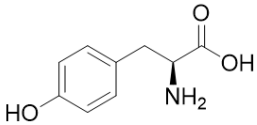
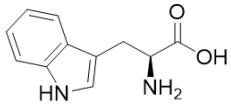
Q2.7 Record the observed volumes (V_0, mL – initial burette reading; V_f, mL – final burette reading; T, mL – titre).

Q2.8 Write your accepted final titre of $Cu(CH_3COO)_2$ ($V_{Cu(CH_3COO)_2}$, mL).

Q2.9 Copper(II) acetate reacts with the titrated amino acid in 1:2 ratio. **Draw** a reasonable structure of the product of this reaction (use "R" to indicate the amino acid side chain).

Q2.10 Calculate the molecular weight (M_r) of the amino acid in **Sample X** based on the titration results.

Note: The M_r values of natural amino acids and their structures are presented on the next page for your reference.

 Glycine (Gly) $C_2H_5NO_2$ M_r = 75.07	 L-Alanine (Ala) $C_3H_7NO_2$ M_r = 89.09	 L-Serine (Ser) $C_3H_7NO_3$ M_r = 105.1	 L-Proline (Pro) $C_5H_9NO_2$ M_r = 115.1
 L-Valine (Val) $C_5H_{11}NO_2$ M_r = 117.1	 L-Threonine (Thr) $C_4H_9NO_3$ M_r = 119.1	 L-Cysteine (Cys) $C_3H_7NO_2S$ M_r = 121.2	 L-Leucine (Leu) $C_6H_{13}NO_2$ M_r = 131.2
 L-Isoleucine (Ile) $C_6H_{13}NO_2$ M_r = 131.2	 L-Asparagine (Asn) $C_4H_8N_2O_3$ M_r = 132.1	 L-Aspartic acid (Asp) $C_4H_7NO_4$ M_r = 133.1	 L-Glutamine (Gln) $C_5H_{10}N_2O_3$ M_r = 146.1
 L-Lysine (Lys) $C_6H_{14}N_2O_2$ M_r = 146.2	 L-Glutamic acid (Glu) $C_5H_9NO_4$ M_r = 147.1	 L-Methionine (Met) $C_5H_{11}NO_2S$ M_r = 149.2	 L-Histidine (His) $C_6H_9N_3O_2$ M_r = 155.2
 L-Phenylalanine (Phe) $C_9H_{11}NO_2$ M_r = 165.2	 L-Arginine (Arg) $C_6H_{14}N_4O_2$ M_r = 174.2	 L-Tyrosine (Tyr) $C_9H_{11}NO_3$ M_r = 181.2	 L-Tryptophan (Trp) $C_{11}H_{12}N_2O_2$ M_r = 204.2

3. R_f you ready to spot the answers?

Equipment

Item	Quantity	Label(s)
PS stain chamber	1	**PS**
AS stain chamber	1	**AS**
TLC chamber, 250 mL with filter paper	2	**Q3 TLC**
Petri dish	2	**1:3** and **1:6**
Bottle, 250 mL	1	**Q3 waste**
Eppendorf tubes (2 mL)	8 + 2 extra	**E, F, G, H, EF, EG, FH, GH**
Vial stand (for Eppendorfs)	1	–
Floating rack	1	In the box labelled **Q3**
In labelled bags:		
Non-UV TLC plate	2	**Q3 TLC A + Student Code**
UV TLC plate	1	**Q3 TLC UV A + Student Code**
Non-UV TLC plate	5 + 4 extra	**TLC B + Student Code**
Plastic spatula	4 + 1 extra	In the box labelled **Q3**
Plastic Pasteur pipette	10 + 10 extra	In the box labelled **Q3**
Capillaries in a centrifuge tube	15 + 15 extra	**Q3 capillaries**

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
$KMnO_4$ stain	aq	-	40 mL	50 mL bottle	**PS**
Anisaldehyde stain	sol	-	40 mL	50 mL bottle	**AS**
Eluent EtOAc:hexane	l	1:6	20 mL	50 mL bottle	**1:6**
Eluent EtOAc:hexane	l	1:3	40 mL	50 mL bottle	**1:3**
Ethyl acetate	l	-	20 mL	50 mL bottle	**EtOAc**
1 in EtOAc	sol	0.1 M	0.3 mL	2 mL vial	**A, B, C, D**
2 in EtOAc	sol	0.1 M	0.3 mL	2 mL vial	
3 in EtOAc	sol	0.1 M	0.3 mL	2 mL vial	
4 in EtOAc	sol	0.1 M	0.3 mL	2 mL vial	
5	-	Pure	200 mg	2 mL vial	**E, F, G, H**
6	-	Pure	200 mg	2 mL vial	
7	-	Pure	200 mg	2 mL vial	
8	-	Pure	200 mg	2 mL vial	
9	-	Pure	200 mg	2 mL vial	
10	-	Pure	200 mg	2 mL vial	
11	-	Pure	200 mg	2 mL vial	

15% of the total

3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	3.11	3.12
1	1	1	1	1	1	1	1	1	1	5.8	2

3.13	3.14	3.15	3.16	3.17	3.18	3.19	3.20	3.21	3.22	Total
1.2	4	1	2	1	0	4	15	4	12	62

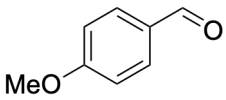
Thin Layer Chromatography (TLC) is a powerful analytical technique in organic chemistry. This task explores some of its many purposes.

In Part A, you will use three types of visualisation to identify unknown solutions **A**-**D**.

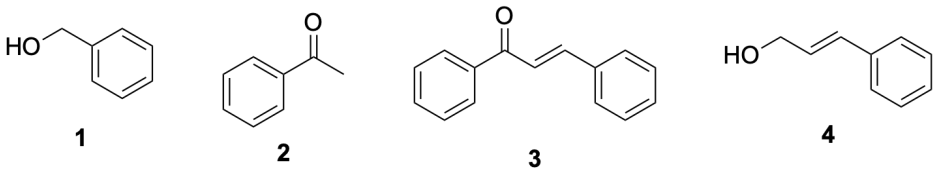
In Part B, you will identify unknown chemicals **E**-**H** by their pairwise reactions and subsequent TLC analysis of the reaction mixtures.

Part A: TLC visualisation

You are provided with alkaline $KMnO_4$ stain (**PS**), acidic *p*-anisaldehyde stain (**AS**), and four unknown samples **A**-**D**. The structure of *p*-anisaldehyde is given below.



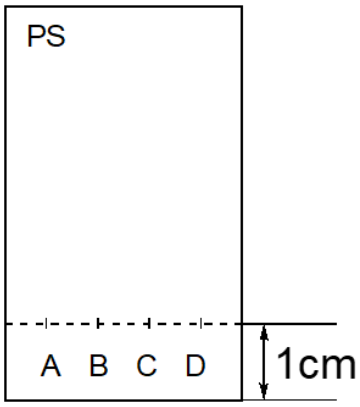
Each sample contains a different one of the compounds **1**-**4**. You must identify which sample contains each compound by running TLC plates and using the stains and UV light visualisation.



1. **Turn on** the heating on the hot plate (**turn** the dial to **between VI and X**) and slow stirring. The stirring is required as it cools the hot plate electronics.

2. For this part, you need two TLC plates from zip bag "**Q3 TLC A**" and one from zip bag "**Q3 TLC UV A**". **Prepare** the plates as shown in the figure below: **mark** the starting line and four spots labelled (**A**-**D**) at equal distance apart.

Example of TLC plate for **PS**



3. **Label** the two TLC plates at the top with "**AS**" and "**PS**". **Label** the UV plate in the separate bag as "UV". **Do not stain or heat this plate**, it will be used for UV visualisation.

4. **Prepare** the TLC chamber marked as "**1:6**" using the eluent EtOAc:Hexane = 1:6. The eluent level should be ~0.5 cm. Discard any excess eluent into the bottle labelled "**Q3 waste**".

5. **Load** the three TLC plates with unknowns **A-D** using the glass capillary. Do not overload the plates; the spot **diameter** should be **below 4 mm**.

6. **Use** the tweezers to place the TLC plates in the chamber and **run** the TLC plates. More than one TLC plate can be run in the same chamber at once. We recommend to run at least 5 cm of the TLC plate. The chamber should **always be closed**.

7. Once the plates have run, **remove** them from the chamber and **mark** the solvent front with a line.

8. **Dry** the plates in the air until all visible solvent has evaporated.

PS TLC Plate

9. **Have** a paper tissues ready. **Put** the stain in chamber labelled as **PS**. **Take** the **PS** TLC plate with tweezers. **Dip** the **PS** TLC plate in the **PS** stain. **Ensure** the stain reaches up to the solvent front line.

10. **Take** the plate out and **let** the excess stain drip off the plate onto the paper tissues. **Wipe** the back of the plate with a paper tissues.

Q3.1 **Report** any spots that appear before heating. **Tick** the appropriate box/boxes if there is a spot for that sample; **tick** the box "N" if no spot appears.

Q3.2 **Draw** a sketch of the **PS** TLC plate before heating.

11. **Heat** the TLC plate on the hot plate (use tweezers to place and remove the TLC plate) until the spots have developed (~5-60 s).

Q3.3 **Report** only **additional spot(s)** that appear after heating by ticking the appropriate box/boxes; **tick** the box "N" if no additional spot appears.

12. **Circle** all the spots on the TLC plate with a pencil.

Q3.4 **Draw** a sketch of the **PS** TLC plate after heating.

AS TLC Plate

13. **Stain** the **AS** TLC plate in the **AS** stain using the same procedure as for the **PS** stain. **Close** the stain chamber.

Q3.5 **Report** any spots that appear before heating. **Tick** the appropriate box/boxes if there is a spot for that sample; **tick** the box "N" if no spot appears.

Q3.6 **Draw** a sketch of the **AS** TLC plate before heating.

14. **Heat** the plate.

Q3.7 **Report** only **additional spot(s)** that appear after heating by **ticking** the appropriate box/boxes; **tick** the box "N" if no additional spot appears.

15. **Circle** all the spots on the plate with a pencil.

Q3.8 **Draw** a sketch of the **AS** TLC plate after heating.

UV TLC Plate

The UV TLC plate is used to compare detection with stains and UV. **Do NOT heat this plate.**

16. **Raise** the "**UV**" card. The lab assistant will take you to the UV lamp to visualise this plate.

17. **Circle** any spots visible under UV light.

Q3.9 **Mark** the lane with the compound with the **lowest** absorption of UV light.

Q3.10 **Draw** a sketch of the UV TLC plate.

Q3.11 **Put** all three TLC plates on the separate answer sheet. **Raise** the "**CAM**" card. From this point on, both you and the lab assistant **must sign** the answer sheet. The lab assistant will take the TLCs for a picture with your answer sheet and return it to you. **Place** the three TLC plates in their respective bags (labelled as "**Q3 TLC A**" and "**Q3 TLC UV A**"). Both the picture and the submitted plates will be used for grading.

Q3.12 According to the TLC:

(a) **Tick** the most polar compound(s) of **A-D**.
(b) **Tick** the least polar compound(s) of **A-D**.

Q3.13 Based solely on your experimental observations during this test, **tick** the box(es) corresponding to the statements you found to be correct. Do not rely on prior theoretical knowledge or assumptions.

(a) **PS** does not visualise alkenes.
(b) **PS** visualises alkenes without heating.
(c) **PS** visualises alkenes only with heating.
(d) **AS** visualises alkenes without heating.
(e) **AS** does not visualise carbonyl compounds with α-CH bonds.
(f) **AS** visualises carbonyl compounds with α-CH bonds without heating.
(g) **AS** visualises carbonyl compounds with α-CH bonds only with heating.
(h) UV does not visualise compounds that absorb UV light of the lamp used.
(i) UV visualises compounds that absorb UV light of the lamp used.

Q3.14 **Assign** compounds **1-4** to the samples **A-D**.

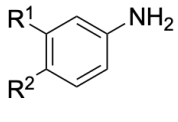
Part B: Identification of unknown compounds by their reactions

Reagent concentration affects the rate of most chemical reactions. This often makes solventless reactions (reactions performed with little or no solvent) more robust than reactions performed in solvents. In this task you will perform a set of almost solventless reactions on a small scale to identify unknown compounds. This solventless technique allows these reactions to occur in 10 min, compared to 1-10 h in solvent.

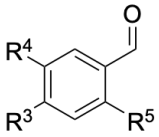
You have four unknown samples: **E**, **F**, **G**, and **H**. Each sample is different and contains one of the seven compounds listed below (**5**-**11**).

Reaction progress will be monitored using TLC visualised with PS.

Do NOT smell any compounds as they may be toxic if substantially inhaled!



5



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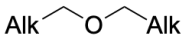

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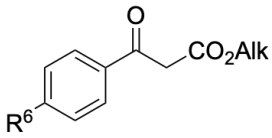

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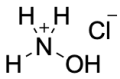


10

11

Do not rely on smell or physical state of any compound for identification. The substituents have not been given to prevent this. "Alk" is an alkyl substituent. The substituents R^1-R^6 are inert in reactions you will perform. We recommend relying on the experimental tests performed to identify the samples.

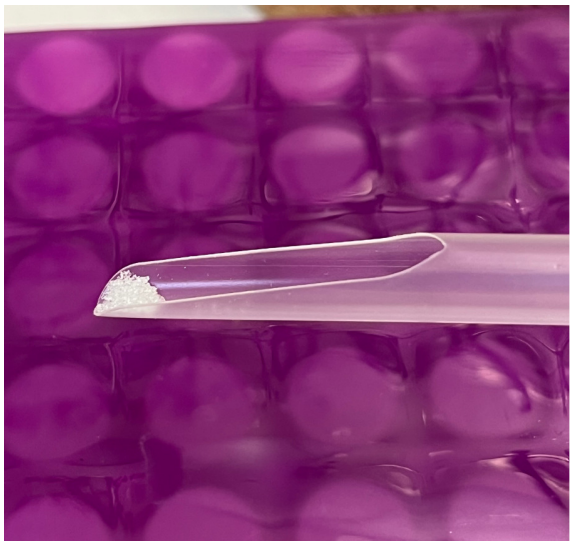
Solubility/miscibility test

Perform solubility/miscibility tests in EtOAc for unknowns **E**-**H** as follows:

1. **Take a labelled** Eppendorf tube with the letters **E**-**H**.

2. **Add** one drop (if a liquid) or one small spatula (if a solid, see the picture below) of the appropriate unknown sample.

One small spatula looks like this



3. **Add** ~1 mL of EtOAc.

Q3.15 Tick your observations for each compound ("Y" for dissolved/miscible, or "N" for not dissolved/not miscible).

4. **Keep** the vials as the samples will be used as a reference for the subsequent TLC analysis.

TLC analysis of pure unknowns

5. **Prepare** a TLC plate; **use** the plates from the ziplock bag labelled as "**Q3 TLC B**". **Mark** the starting line and spots labelled **E**-**H**. **Label** the plate **UNK**.

6. **Prepare** a new chamber with eluent EtOAc:Hexane = 1:3. **Run** the TLC of **E**-**H**. **Mark** the solvent front.

7. **Stain** the TLC plate with **PS**. **Heat** the plate. **Circle** all the developed spots.

Q3.16 Put this plate on the separate answer sheet. **Raise** the "**CAM**" card. The lab assistant will come and take the plates for a photo. At the end of the task, **put** the TLC plate back in the bag labelled "**Q3 TLC B**". Both the picture and the submitted plate will be used for grading at the end of the exam.

Q3.17 **Tick** your observations after PS visualisation ("Y" – visualised, "N" – not visualised) in the table.

If a compound is not visualised with **PS**, you do not need to make a reference spot of this compound on TLCs in the remainder of this experiment.

Pairwise reactions

Perform pairwise reactions between unknown samples **E**-**H** as follows.

All reaction products **should be visible** by TLC analysis if run correctly.

No reaction occurs between pairs E+H and F+G, so you **do not need** to perform them.

8. **Preheat** the water bath to a gentle boil: **place** the dial at **X**, when the bath reaches boiling, **decrease** the heating so it boils gently (dial between **VI** and **X**).

9. **Use** the four Eppendorf tubes labelled for the four pairwise reactions you need to perform, for example, the reaction between **E** and **F** is performed in the Eppendorf labelled "**EF**".

10. **Add** the first reagent (**two drops** of liquid or **two small spatula portions** of solid).

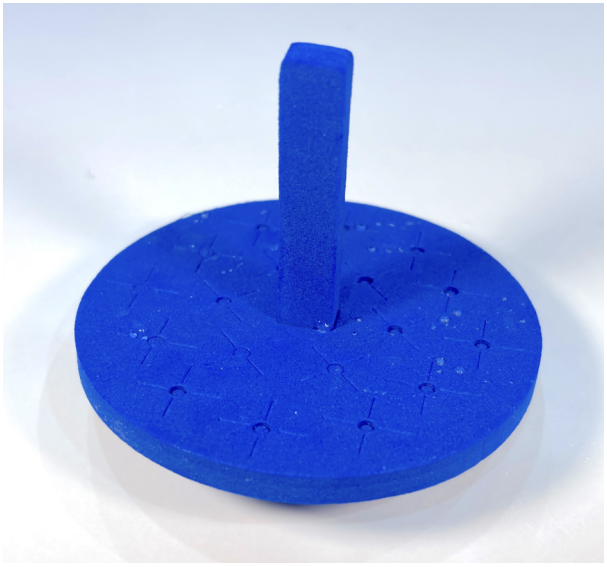
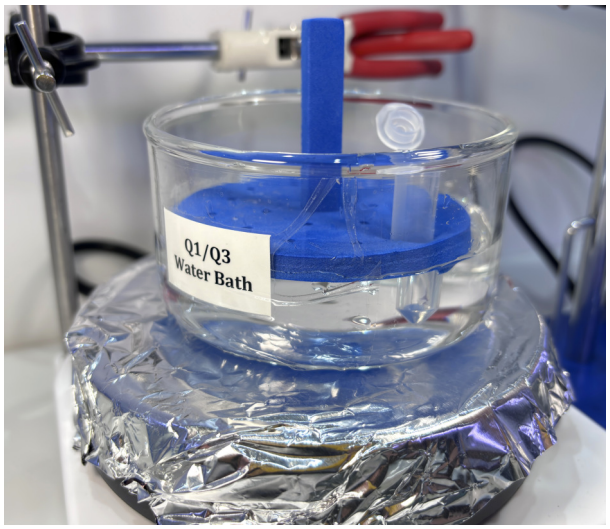
11. **Add only one drop** of EtOH as a solvent.

12. **Add** the second reagent (**two drops of liquid** or **two small spatula portions** of solid).

13. **Do not close** the reaction vessel.

Q3.18 You can **note** your observations (if any) in the table. This table is for your convenience, it will not be graded!

14. **Heat** the reaction mixture for 10 min, by putting the vial in the floating rack and putting the rack in the preheated water bath (see the picture below).

Floating rack	Reaction set-up
	

15. After 10 min **remove** the reaction mixture and **let it cool** to room temperature.

16. **Add** EtOAc (~1.5-1.8 mL), **close** the reaction vessel, and **mix** it cautiously.

17. **Perform** TLC analysis of the reaction mixture, staining with **PS** and heating the plate afterwards. First, **label** the TLC plate with the combination, for example **EF**. **Mark** three spots: **E** – for compound **E**, **R** – for reaction mixture, **F** – for compound **F**. **Use** the EtOAc:Hexane = 1:3 eluent for all TLCs **except the reaction between F and H** for which you need to use EtOAc:Hexane = 1:6 eluent. **Mark** the solvent front line. Ensure you **circle all spots** on the TLC plate.

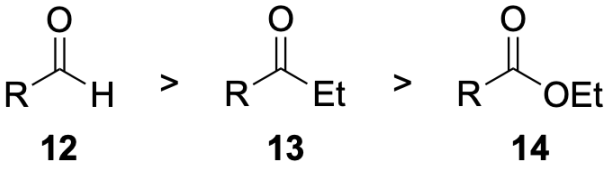
Q3.19 **Tick** the reaction outcome ("Y" = reaction proceeds; "N" = no reaction) according to the TLC for each reaction pair on the answer sheet.

Q3.20 **Identify** the unknown chemicals according to your experimental observations. **Write** the appropriate letter **E**-**H** below the chemicals **5**-**11** or **tick** "N" if a chemical is absent from all vials **E**-**H**.

Q3.21 For each reaction pair, **draw** the product structures of the reactions according to the reactants **E**-**H** used; **tick** the box "N" in case of no product.

Hints:
One reaction pair gives two organic products; another reaction pair gives a cyclic product.

The carbonyl compounds are listed below in order of decreasing reactivity with a certain nucleophile.



12 **13** **14**

Q3.22 **Put** each TLC plate in the appropriate place on the separate answer sheet. **Raise** the "**CAM**" card. The lab assistant will take the plates for a picture. **Place** all the TLC plates from this part in the bag labelled "**Q3 TLC B**". Both the picture and the submitted plate will be used for grading at the end of the exam.

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.

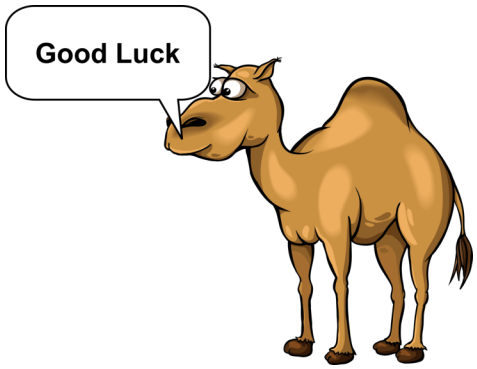
Write only with the pen provided. **Use only** the calculator provided.

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

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

area of triangle	$A = \frac{1}{2}ab \cdot sinC$
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	$\mathrm{E} = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon cd$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)}\,\mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
0th order integrated rate law	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
1st order integrated rate law	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\mathrm{o} = -RT\ln K = -nFE^o_{cell}$
Clausius-Clapeyron equation	$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
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^{-3}.

IR absorption data

Bond stretching frequencies

Bond type		Wavenumber (cm^{-1})
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_2)	1600-1500, 1400-1300
S=O	Sulfoxide	1050
	Sulfate, sulfonamide	1200-1140

Characteristic bond stretching frequencies of anionic species

Anion	Wavenumber (cm^{-1})
SO_4^{2-}	1100-1200 (ν_{as})
ClO_4^-	1050-1170 (ν_{as})
NO_3^-	1370 (ν_{as})
CN^-	2089
SCN^-	2053 (ν_{C-N}), 748 (ν_{C-S})
N_3^-	2042 (ν_{as}), 1343 (ν_s)
CNO^-	2052 (ν_{C-N}), 1057 (ν_{N-O})

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

Complex	Number of bands
$M(CO)_6$	1
$M(CO)_5X$	3
cis-$M(CO)_4X_2$	4
trans-$M(CO)_4X_2$	1
fac-$M(CO)_3X_3$	2
mer-$M(CO)_3X_3$	3
fac-$M(CO)_3X_2Y$	3
cis-$M(CO)_2X_4$	2
trans-$M(CO)_2X_4$	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_2 reduction	6%
7	Dubai crude oil	7%
8	Carbon monoxide: deadly poison or promising therapeutic agent?	7.5%
9	Enzymes and cofactors	7%
Total		**60%**

1. Isocaryophyllene, clovene, and humulene

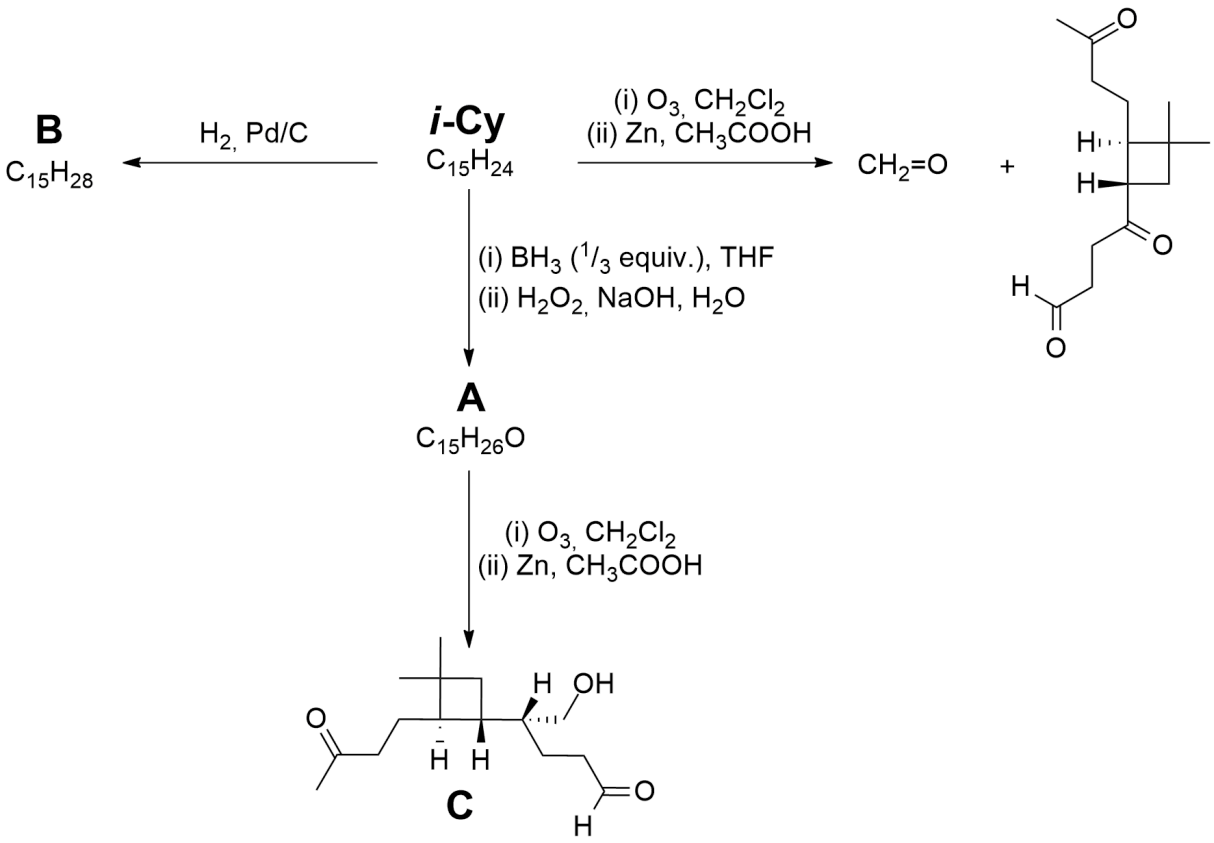
6% of the total

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.

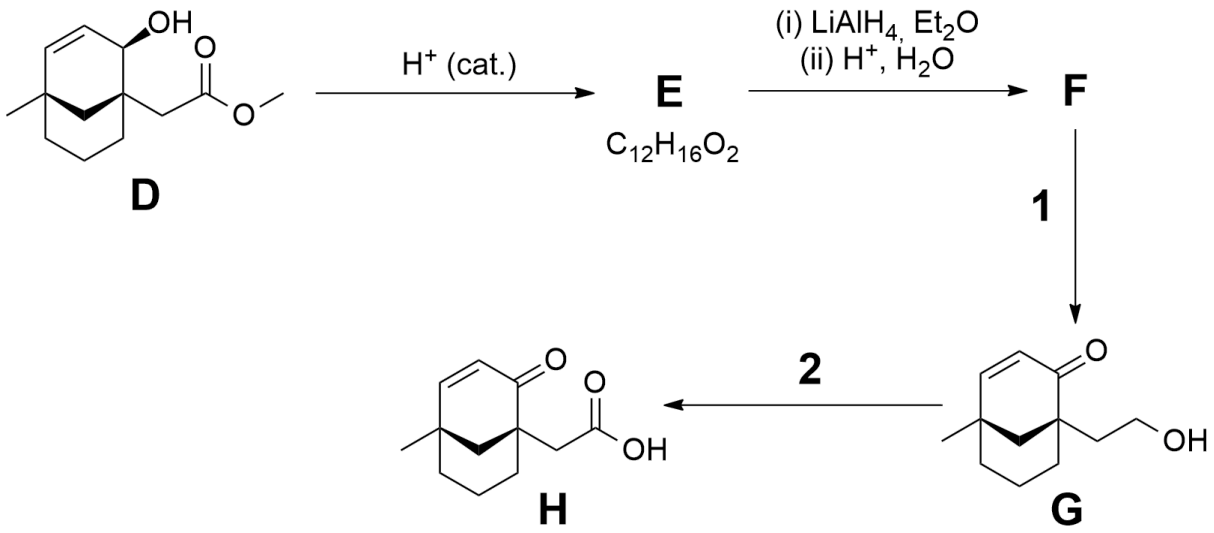


equiv. = translation 'equiv.'

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**.



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

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

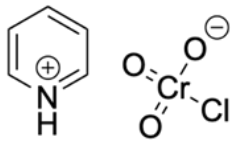
For steps **'1'** and **'2'** several reagents could be considered. For example:

□ PCC

□ $K_2Cr_2O_7$, H_2SO_4, H_2O

□ MnO_2

□ (i) OsO_4, (ii) $KHSO_3$

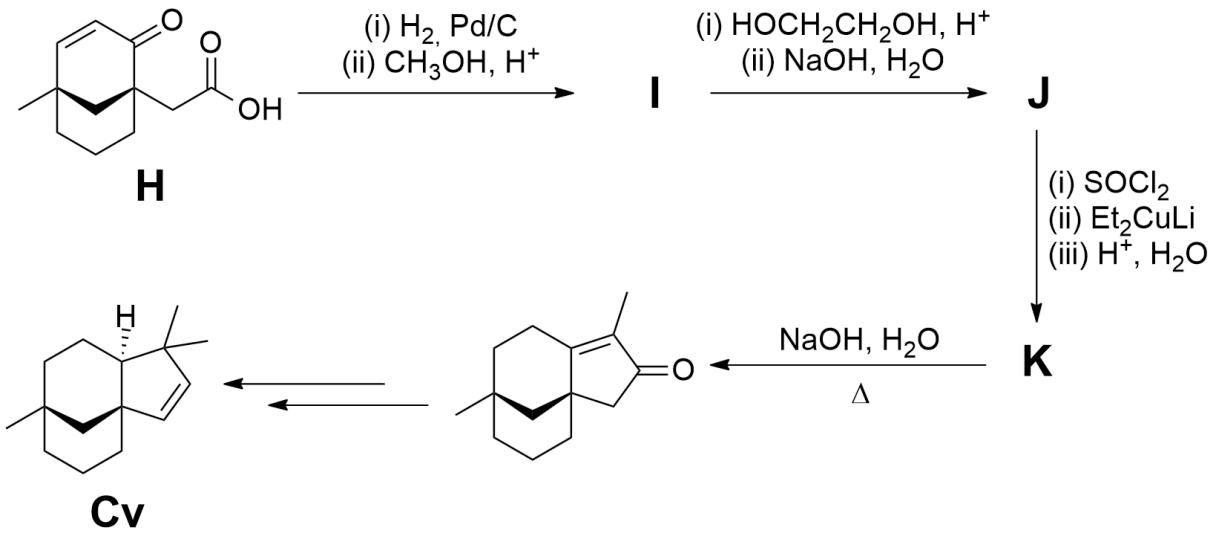


PCC

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

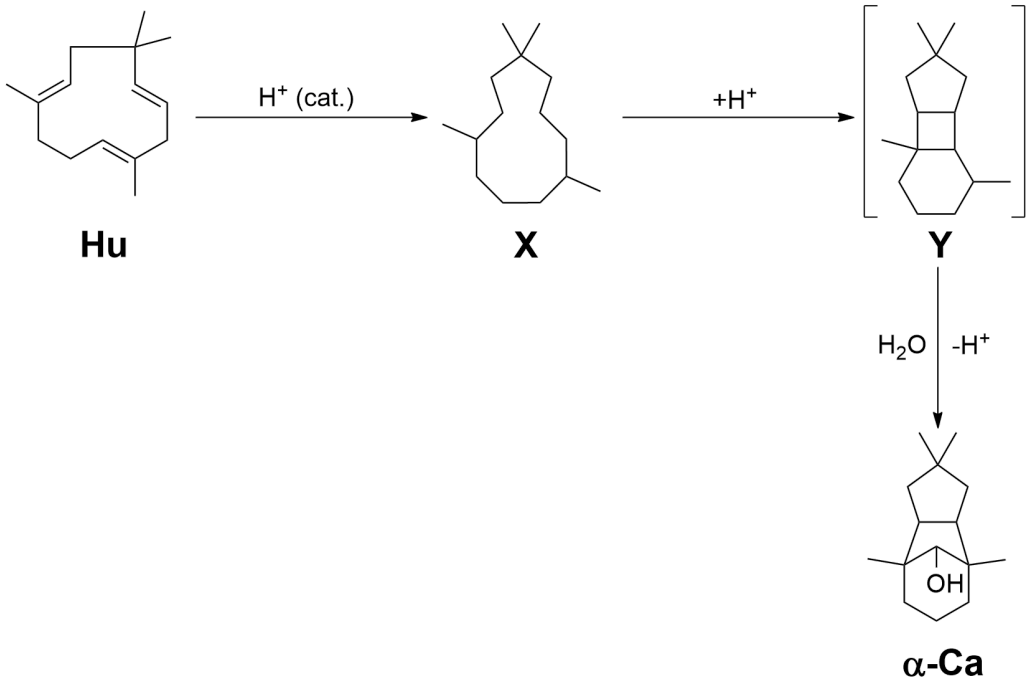
1.5 From the reagents above, **tick** which one(s) would be suitable for step **'2'**.

The final part of the synthesis is shown.



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

Humulene (**Hu**) is another sesquiterpene. It can be converted to α-caryophyllene alcohol (**α-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.



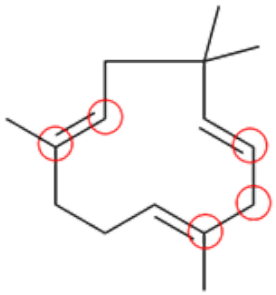
H^+ (cat.)="translation H^+ (cat.)"

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 **α-Ca**.

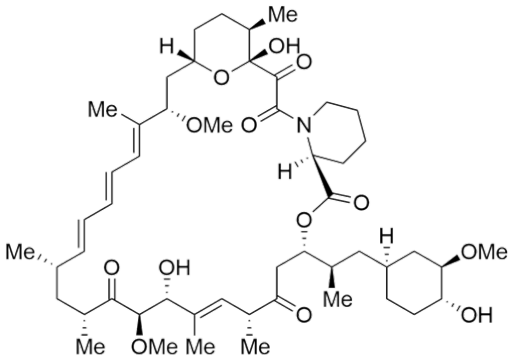


1.9 Circle the five corresponding carbon atoms in **α-Ca** which are circled in **Hu**.

2. Rapamycin - A molecular glue

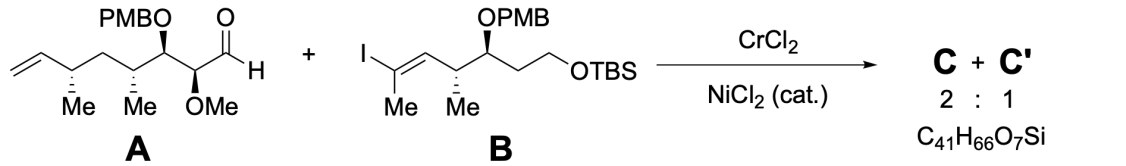
6.5% of the total

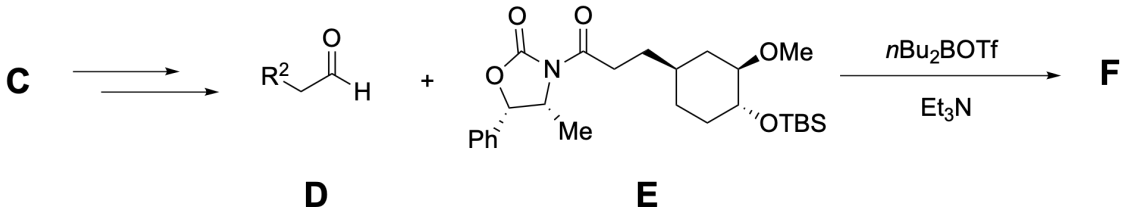
2.1	2.2	2.3	2.4	Total
12	19	18	18	67

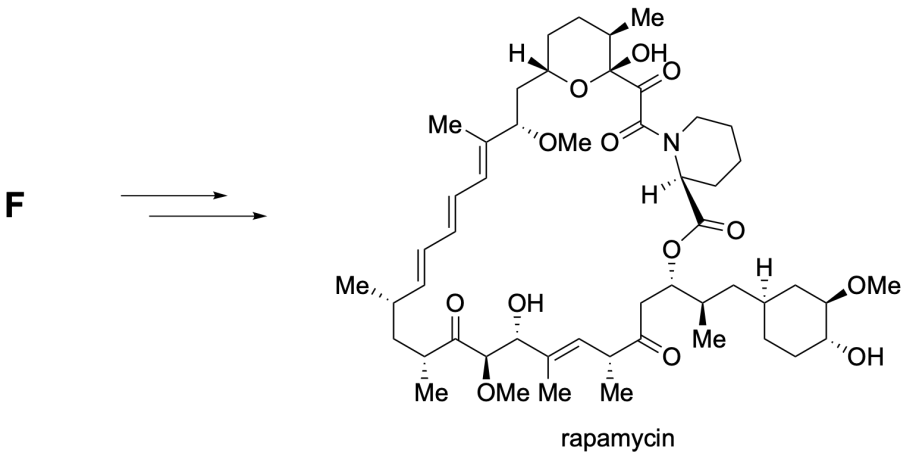


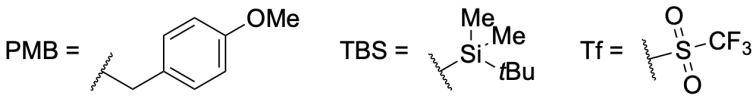
rapamycin

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.









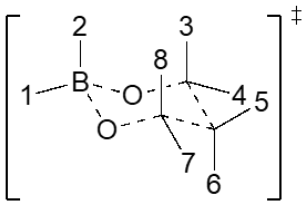
The major stereoisomer (**C**) is formed from the chromium-mediated coupling reaction of aldehyde **A** and vinyl iodide **B** and can be predicted using the Felkin-Anh model without chelation.

2.1a **Draw** a Newman projection showing the best approach of the nucleophile in this reaction. Use the labels =O, –H, –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.

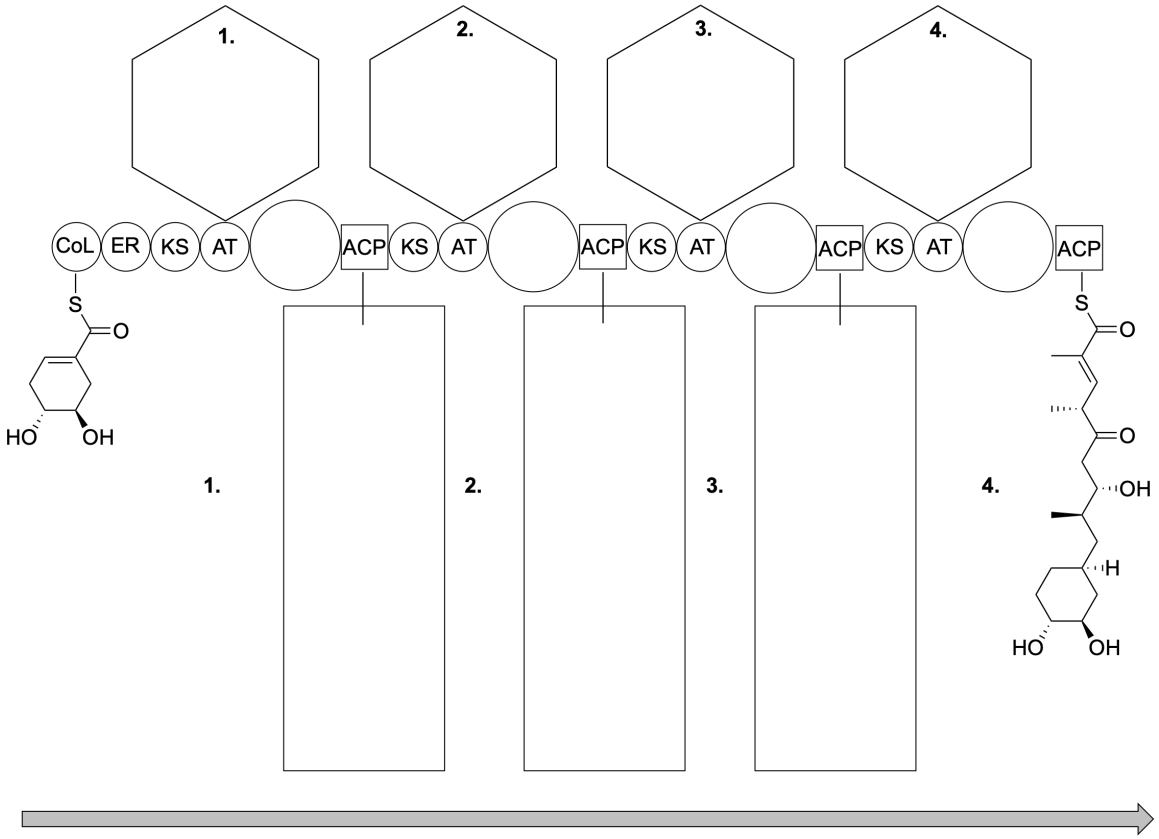
Whilst stereochemical control is challenging synthetically, the biological synthesis controls stereochemistry elegantly through an assembly line of various enzymes.

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

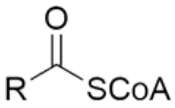
The functions of the various enzymes and proteins are shown in the table.

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 α, β-unsaturated thioester via elimination on the previous monomer
ER	Enoylreductase	Reduces α, β-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.



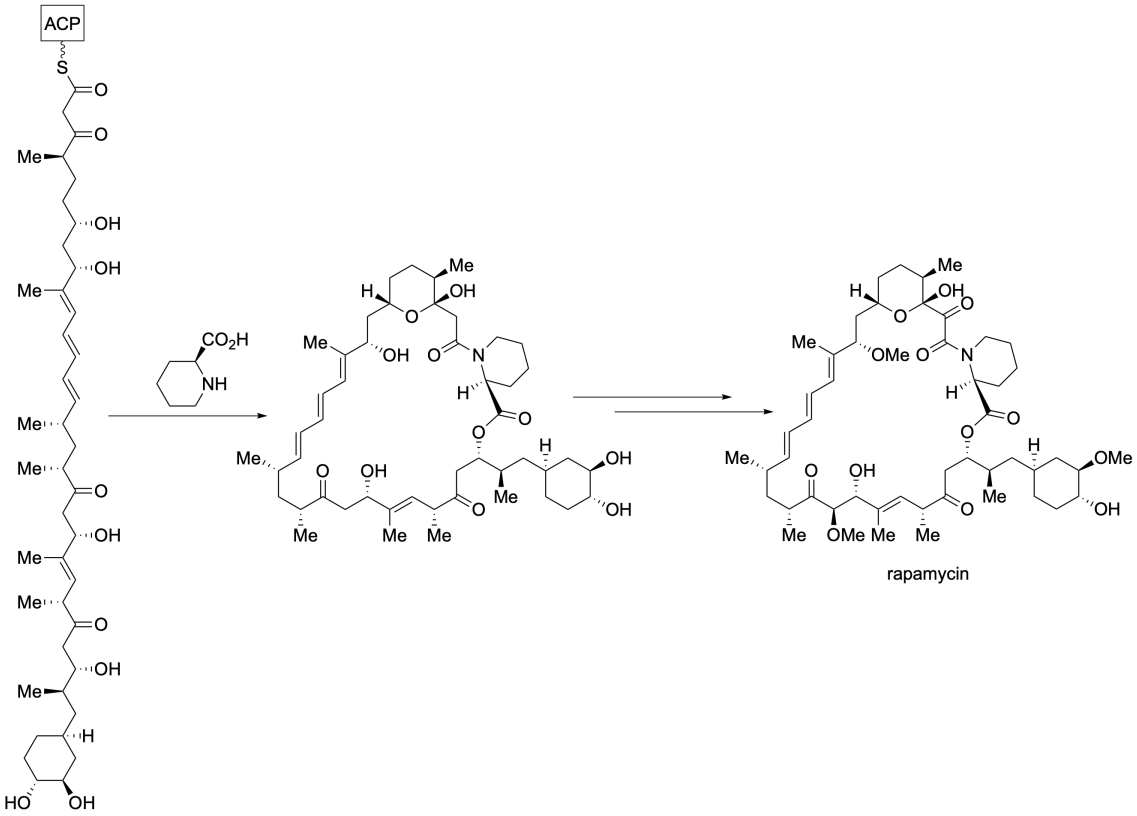
2.3a **Draw** in the hexagons the structure of the monomer needed by the enzyme AT at each of the points numbered **1**-**4**. Carbon dioxide is released when the monomers are incorporated. The monomers have the following general structure where the R group is anionic:



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

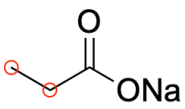
2.3c **Complete** the rectangles with the structure of the growing molecule attached to the enzyme.

The final steps of the enzymatic synthesis are shown below.

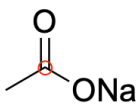


The building blocks involved were determined by feeding the bacterium with three different ^{13}C-labelled starting materials which are incorporated into the monomers (^{13}C are circled as shown below):

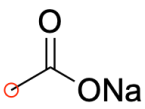
a.



b.



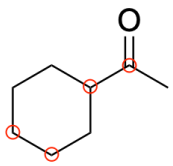
c.



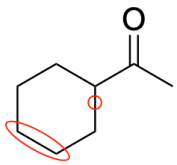
2.4 <u>Circle</u> the carbons in rapamycin that will be ^{13}C-labelled when the bacterium is fed with each of the three starting materials **a**-**c** in turn, following the guidelines on the next page. Incorrect circles will be penalised but there is no negative scoring.

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

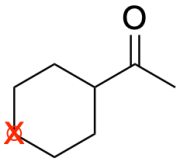


✅



❌

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



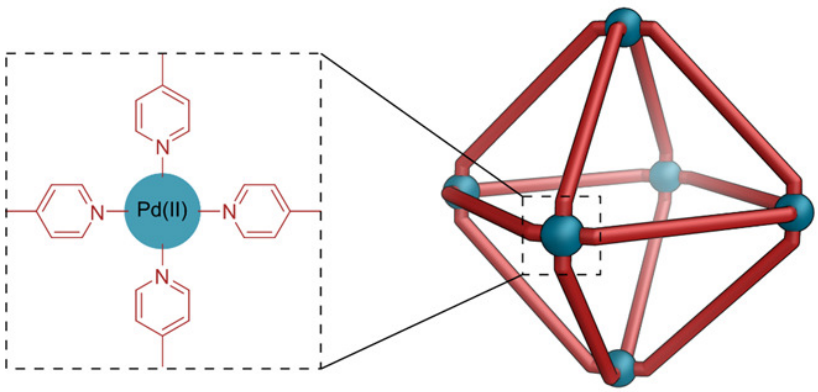
3. Lanterns and the Burj Khalifa

7.5% of the total

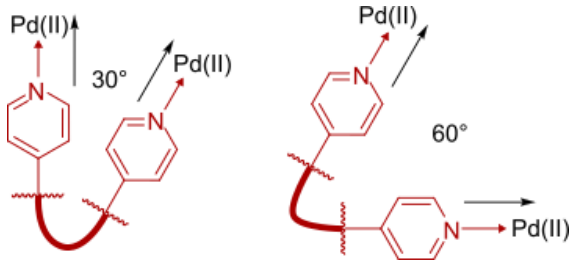
3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
6	4	4	5	40	20	32	111

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.

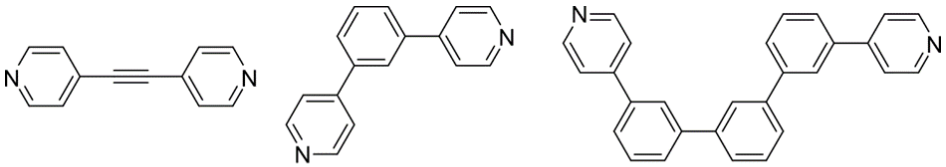


The angle between the two N→Pd bonds from the same ligand controls which structure forms. Larger angles give larger structures.



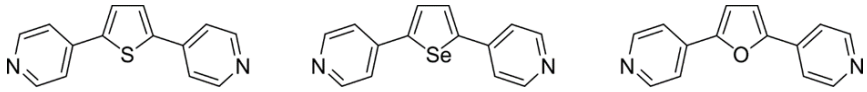
Where free rotation around a bond is possible, the ligand adopts a conformation to form a structure with the smallest possible angle.

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



A **B** **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.



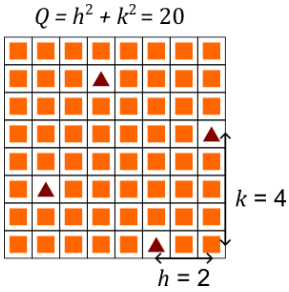
D **E** **F**

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).

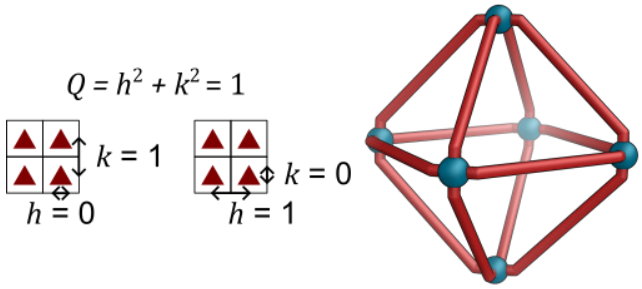
The triangular and square faces can be placed onto a square grid, where the relative position of two nearest triangles is described with integer coordinates *h* and *k*. *Q* is then given by the equation:

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

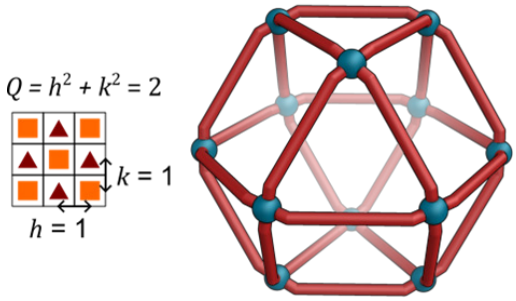
Part of the grid for a structure with *h* = 2 and *k* = 4 is shown below.



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 <u>Complete</u> 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:

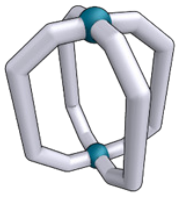
$$V - E + F = 2$$

$$V = 6Q$$

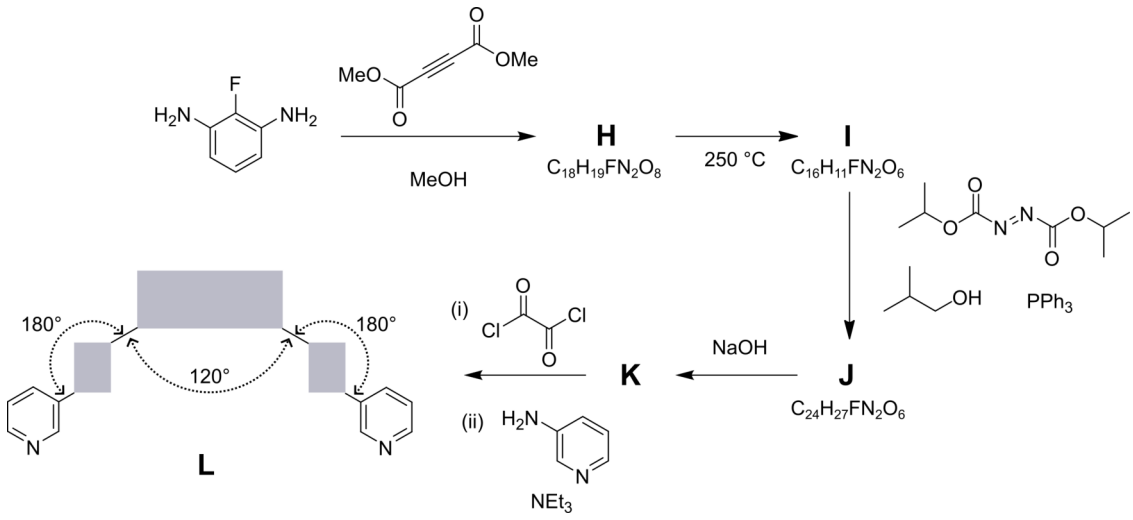
$$F - V = 2$$

3.4 <u>Complete</u> 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→Pd bonds. Ligand **L** has two planes of symmetry and can adopt a planar conformation with the angles shown.

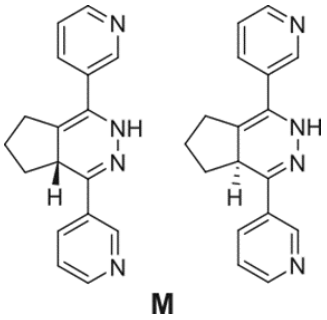


Hint:

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

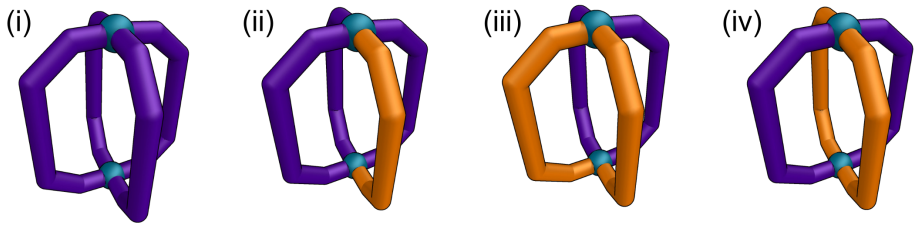
3.5 <u>Draw</u> the structures of compounds **H**, **I**, **J**, **K**, and ligand **L**.

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

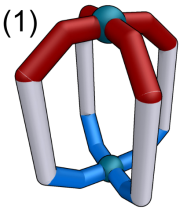
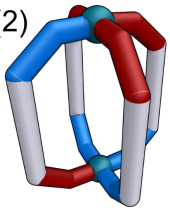
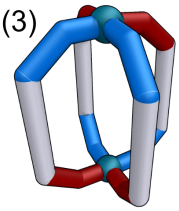
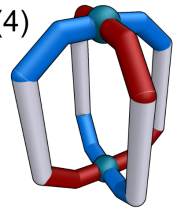


M

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*.

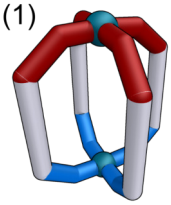
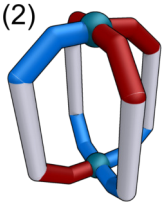
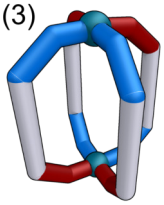
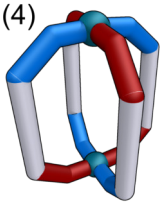
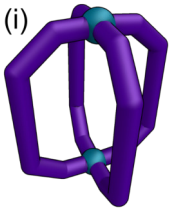
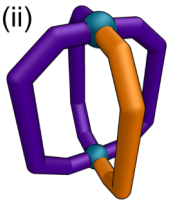
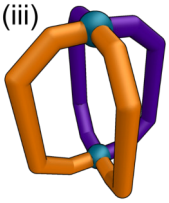
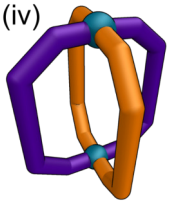


Secondly, the two ends of ligand **M** are not the same; the ligand has a head (H) and a tail (T). There are four categories of structure considering head-to-tail orientation: (1) all up (HHHH), (2) three up (HHHT), (3) *cis*-HHTT, and (4) *trans*-HTHT.

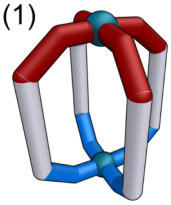
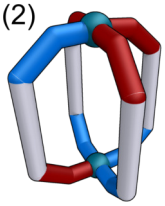
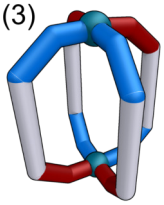
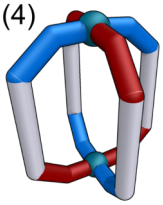
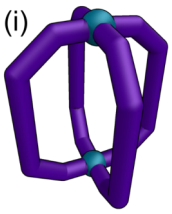
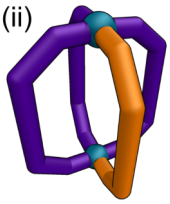
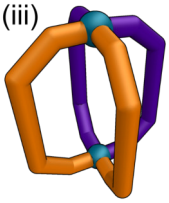
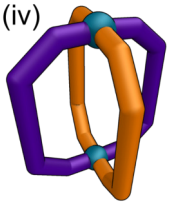
(1)  (2)  (3)  (4) 

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 <u>Complete</u> the table by **<u>writing</u> "C"** for chiral and "**A**" for achiral. **<u>Note</u>**, 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 <u>Complete</u> 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.

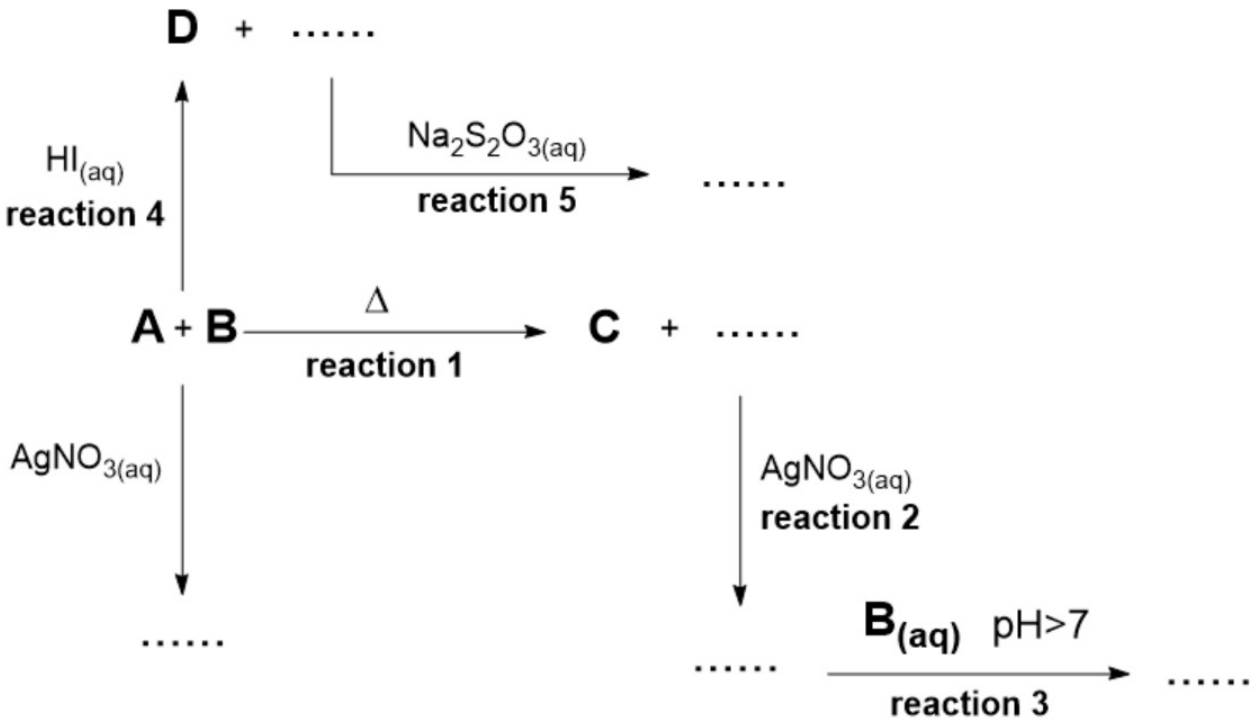
The Dubai Tennis Championships is a prestigious tournament held annually in UAE. Many of the world's top players, including Rafael Nadal, Roger Federer, Novak Djokovic, and Andy Murray have won titles there.

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_{mix} = 0.3389 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 atm (at 25° 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, $m_{precipitate}$ = 0.8224 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^{-1}.

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^{-1}.

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

4.4b **Calculate** the (depressurisation) rate constant k_{O_2} for O_2 in h^{-1}, **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_{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_{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 °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 K kg mol^{-1}.

5.1 **Calculate** the boiling point, T, (in °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_{NaCl}, in water that has a boiling point, T_b = 378.00 K.

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

In the plant, a flash chamber (of volume, V = 100 L) contains a mass of 1.00 kg of seawater (l) at T_1 = 90.0 °C.

Another mass of 1.00 kg of seawater is then overheated to T_2 = 110.0 °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 °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 kJ kg^{-1} K^{-1}, assumed to be independent of temperature. The density of seawater, d = 1025 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 negligble.
*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 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 ^{o}C to T_2 = 110.0 ^{o}C.
*If you couldn't calculate the answer, use **0.1 kWh** for further calculations.*

5.7 A plant produces 50,000 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 **6.0×10^7 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 ^{o}C to T_2 = 110.0 ^{o}C.

5.8 Assuming a 10 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_2 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_2(g)	CO(g)	O_2(g)	Zn(s)	Zn(l)	Zn(g)	ZnO(s)
$\Delta_f H°_{298}$ / kJ mol^{-1}	-393.5	-110.5			6.5	130.4	-350.5
$S°_{298}$ / J mol^{-1} 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_2 content in the atmosphere. There are several ways to convert CO_2 to CO and other useful substances.

Direct decomposition

Direct decomposition of CO_2 to CO and O_2 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_2 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_2 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_2 decomposition into CO and O_2. **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_2 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, $p(O_2)$, in bar, at this temperature.

Photocatalytic reduction

Photocatalytic reduction of CO_2 with water is akin to natural photosynthesis. Plants convert CO_2 to carbohydrates as an energy source, but human civilisation needs hydrocarbons to produce energy. On the way from CO_2 to C_xH_y there are many possible intermediate products of CO_2 reduction.

6.5 Complete the table with the formulae of the **one-carbon** species from CO_2 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 nm < λ < 700 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_3	ZrO_2
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 CO_2 was bubbled through at a rate of v = 3.0 L min^{-1} (T = 25 ^{o}C, p = 1 atm). The suspension was irradiated by a P = 500 W lamp (λ = 365 nm) for t = 7 h. After irradiation, the solution contained c(HCHO) = 1.0 × 10^{-3} M and c(CH_3OH) = 5.4 × 10^{-3} M.

The apparent quantum yield ϕ 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 CO_2 conversion, η, and the apparent quantum yield of photocatalytic reduction, ϕ.

7. Dubai crude oil

7% of the total

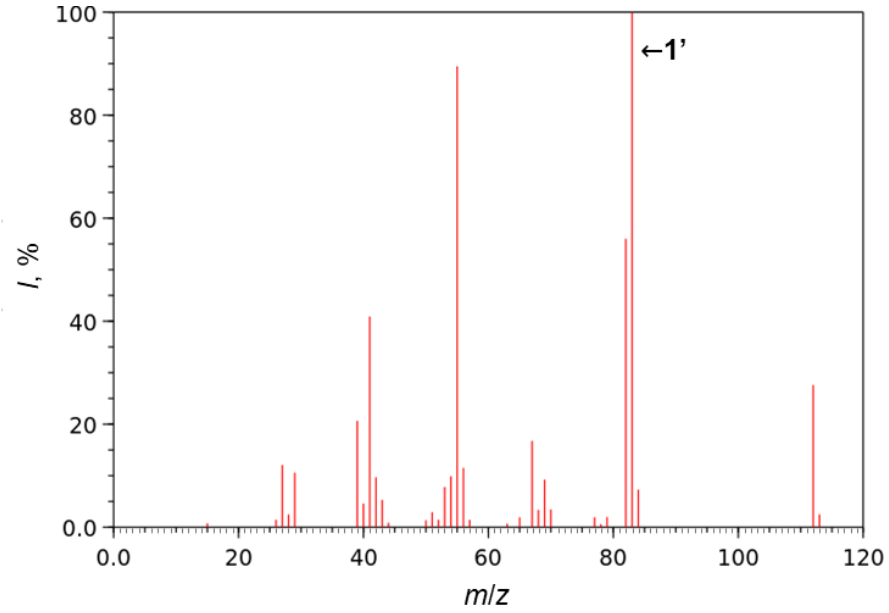
7.1	7.2	7.3	7.4	7.5	Total
8	2	3	1	8	22

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.

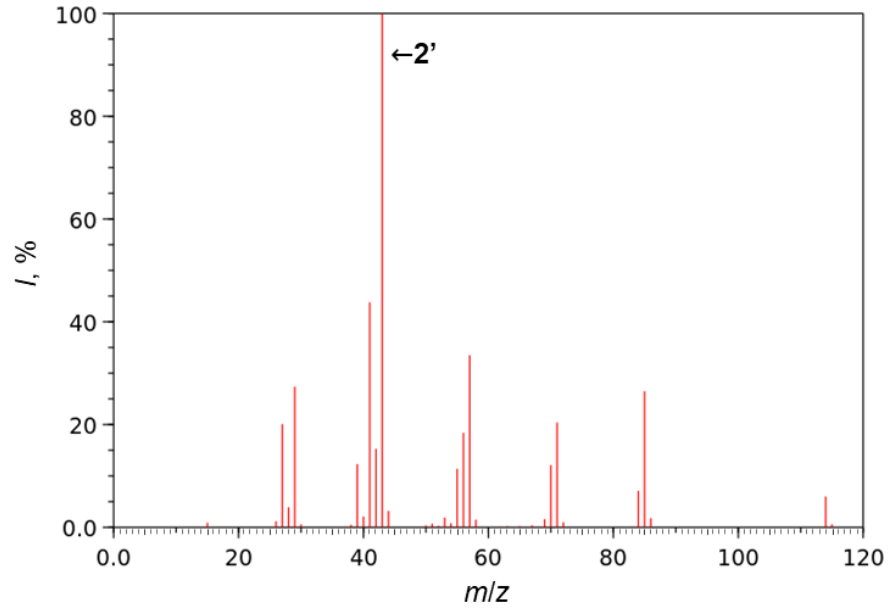
The hydrocarbon composition of oil is characterised by the PONA number. The abbreviation stands for *P* – paraffins (alkanes), *O* – olefins (alkenes), *N* – naphthenes (cycloalkanes), and *A* – aromatics (arenes). One method to determine the composition of oil is gas chromatography–mass spectrometry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

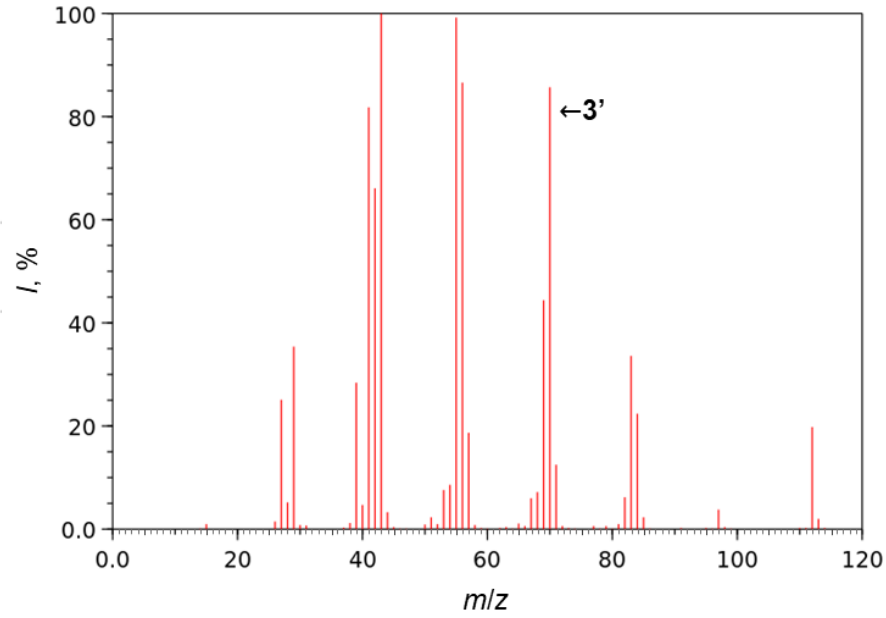
Compound 1



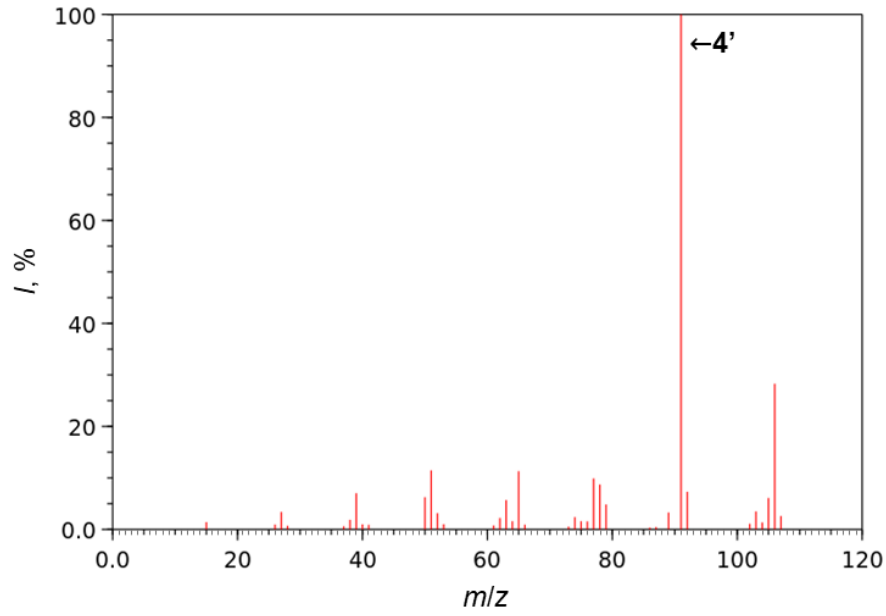
Compound 2



Compound 3



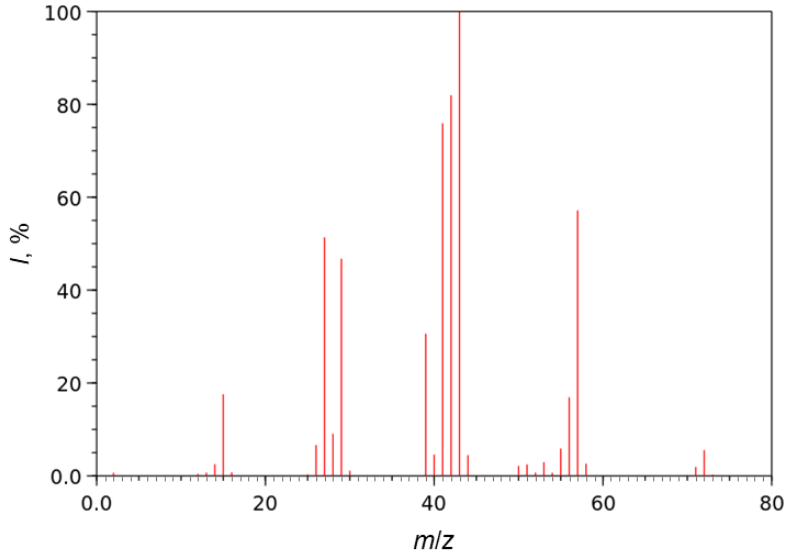
Compound 4



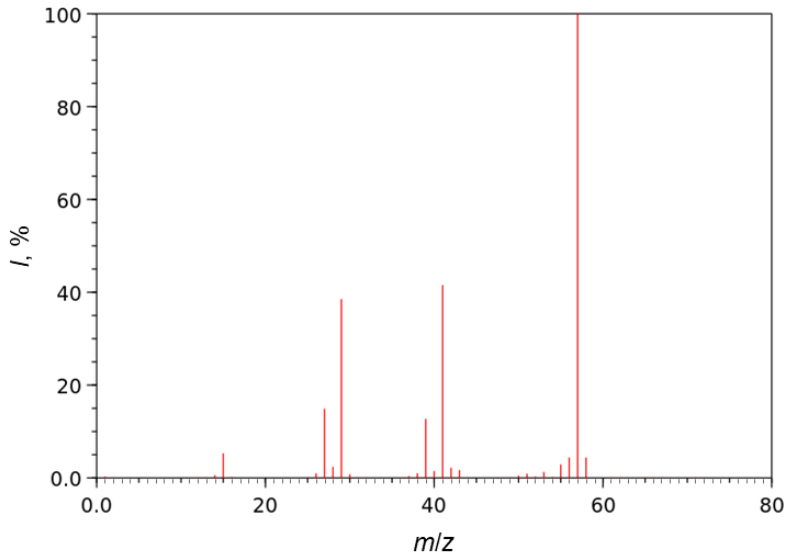
7.1 **Draw** the structures of **1**–**4** and **1'**–**4'**. If you cannot determine the structure(s) of **1**–**4**, **write** the corresponding letter code (**P**/**O**/**N**/**A**) and the molecular formula.
*Hint: Species **3'** is formed by a rearrangement of the molecular ion by the McLafferty 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



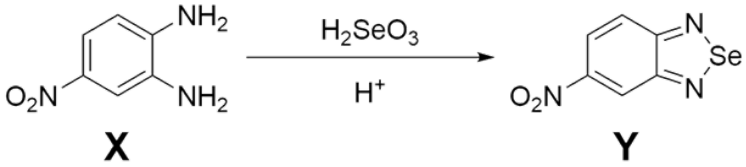
7.2 <u>Draw</u> the structures of compounds **5** and **6**.

Crude oil is classified by the sulfur content as either sweet (<0.5 wt%) or sour (>0.5 wt%). A V = 115 µL sample of Dubai Crude oil (ρ = 871 g dm^{-3}) was completely burnt. The resulting gas mixture was passed through a H_2O_2 solution containing an excess of $Ba(OH)_2$, leading to the formation of m = 1.395 g of white precipitate. Upon acidification with HNO_3, the precipitate's mass decreased by 98.95%.

7.3 <u>Calculate</u> the sulfur content (w(S), wt%) of Dubai Crude oil.

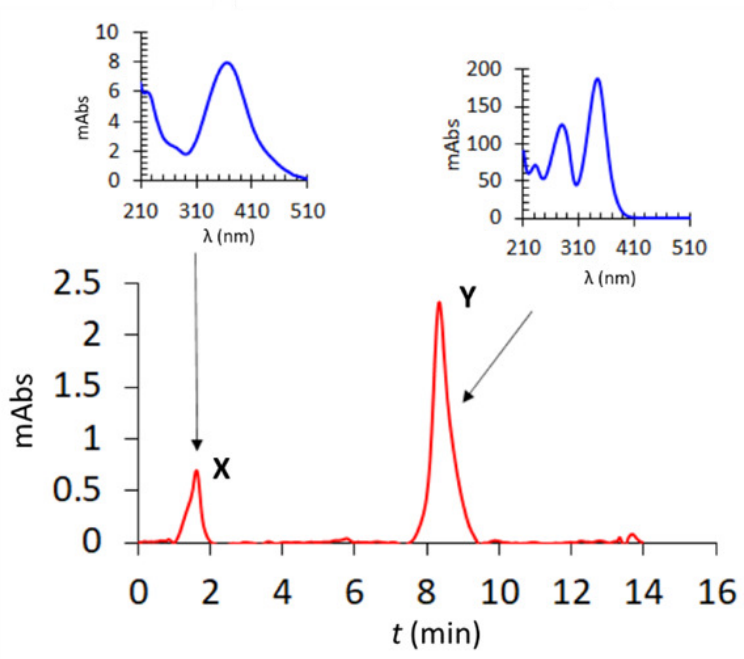
In addition to sulfur, crude oil contains trace amounts of selenium, which transfers into the water used during refining. In aqueous solutions, selenium exists as SeO_3^{2-} and SeO_4^{2-}.

The concentration of 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 **Y**

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 (λ) for the absorbance measurements in the chromatogram.

☐ 270 nm ☐ 300 nm ☐ 350 nm ☐ 510 nm

Acidified water from the refining process, containing SeO_3^{2-} and 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 µM, 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*(**X**) from the free diamine, was 0.825 mAbs·min. Running identical measurements with known amounts of SeO_3^{2-} showed that the peak area for **Y** (mAbs·min) depends on Se concentration (µM) as follows: *S*(**Y**) = 1.21·*c*(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*(**X**)/*S*(**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*(**X**)/*S*(**Y**) measured at different pH values with four strong acids

pH	3.0	2.0	1.5	1.0	0	−0.50
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 ($c_0(SeO_3^{2-})$, $c_0(SeO_4^{2-})$, in µM) 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_x), 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_xH_y
(c) Nitrogen oxides NO_x

Catalytic converters contain nanoparticles of noble metals which act as catalysts, immobilised on a cheap high surface area material such as Al_2O_3.

In one experiment, m(cat.) = 0.10 g of catalyst containing w(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(CO) = 10 mL min^{-1}, which was mixed with a second flow of air (assume 20% O_2, 80% N_2), at T = 273.15 K and p = 1.00 atm, before entering the reactor.

8.2 **Calculate** the flow rate v (in mL min^{-1}) of air required for the reactants to be present in a stoichiometric ratio.

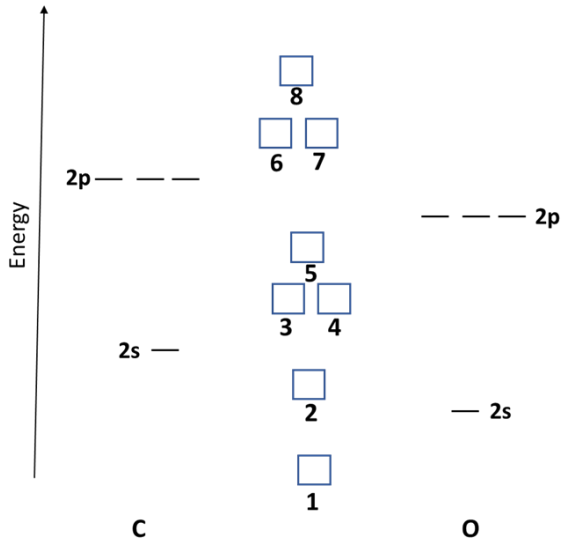
Assume 10% of the Pd atoms in the nanoparticles are exposed on the surface. Assume the conversion of CO to CO_2 was η = 70%.

8.3 **Calculate** the number of CO_2 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. σ-bonding through a lone pair on the carbon atom;
2. π-interaction through an overlap between the Ru valence d-orbitals and CO molecular orbitals.

8.4 <u>Complete</u> the MO diagram for CO with electrons and the following table with the type (σ/π) 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 π-interaction on the Ru−CO and the C−O bond strengths? **<u>Tick</u>** the correct answer.

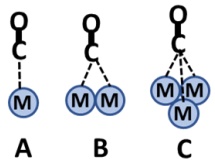
(i) Ru−CO bond strength:

□ increases "**in**"
□ decreases "**dec**"
□ no change "**nc**"

(ii) C−O bond strength:

□ increases "**in**"
□ decreases "**dec**"
□ no change "**nc**"

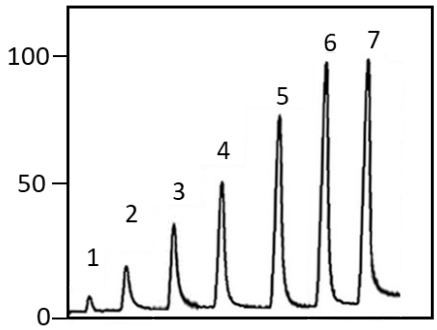
Adsorbed CO molecules have strong IR absorptions due to C–O stretching vibrations. Three binding modes for CO adsorbed on a metal surface are shown, where CO can interact with one or more metal atoms. IR peaks in the spectra of free CO and the three binding modes of adsorbed CO were observed at values of 1850, 1930, 2100, and 2143 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 μL pulses consisting of 10% vol CO in He, at 25 °C and 100 kPa. 15 mg catalyst was used, composed of 10 wt% Ni on an Al_2O_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, $\%_{Ni}$.

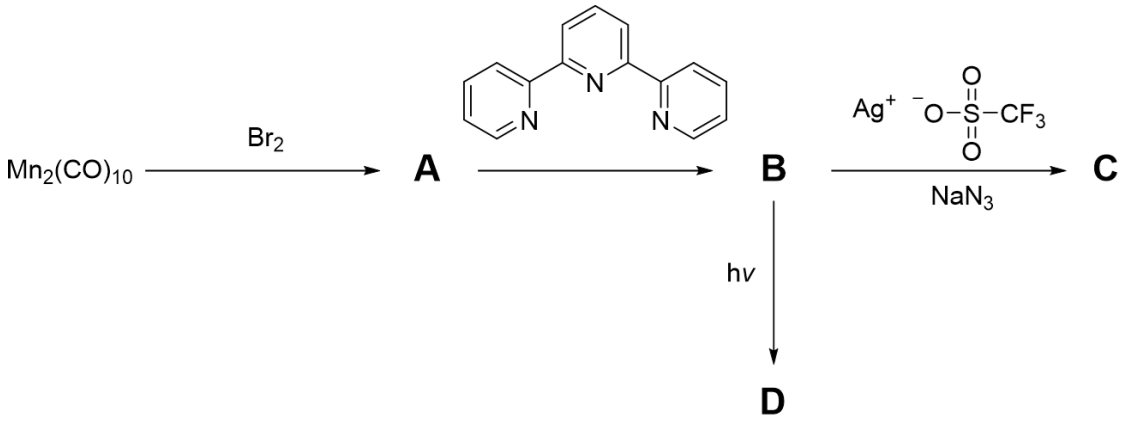
Despite being toxic at higher concentrations, at a concentration of 10-250 ppm, CO shows anti-inflammatory properties. Prodrugs known as CO releasing molecules (CORMs) target the delivery of effective dosages of CO to tissues in response to a trigger. Mn(I) carbonyl complexes have shown promise as PhotoCORMs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

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

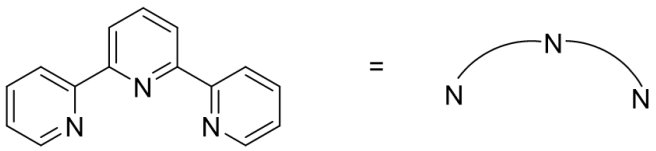
B, **C**, and **D** do not contain two CO ligands in a *trans* arrangement.

The IR spectrum of **C** contains a band at 2042 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
A	19.98	3
B	12.15	3
C	13.26	3
D	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 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 1735-1725 cm^{-1}. After a further 6 h, compound **E** converts to compound **F** which only has one C=O band in the range of 1735-1725 cm^{-1}. Compound **G** does not contain manganese and has two planes of symmetry.

8.9 <u>Draw</u> 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

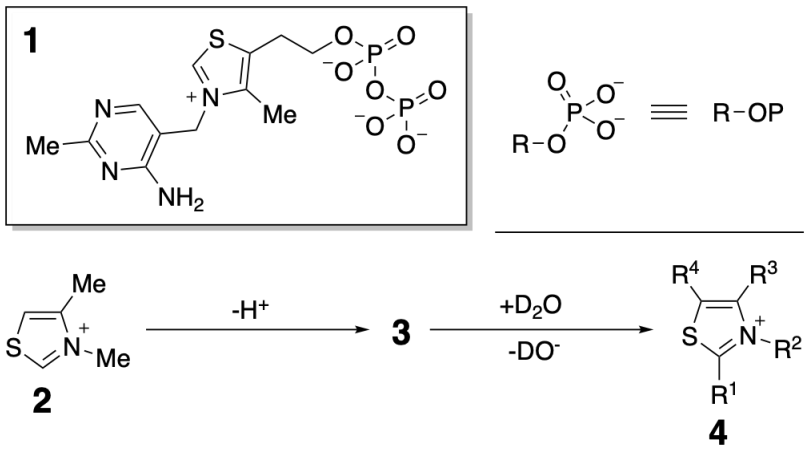
7% of the total

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 abbriviated as "OP" (see the scheme below).

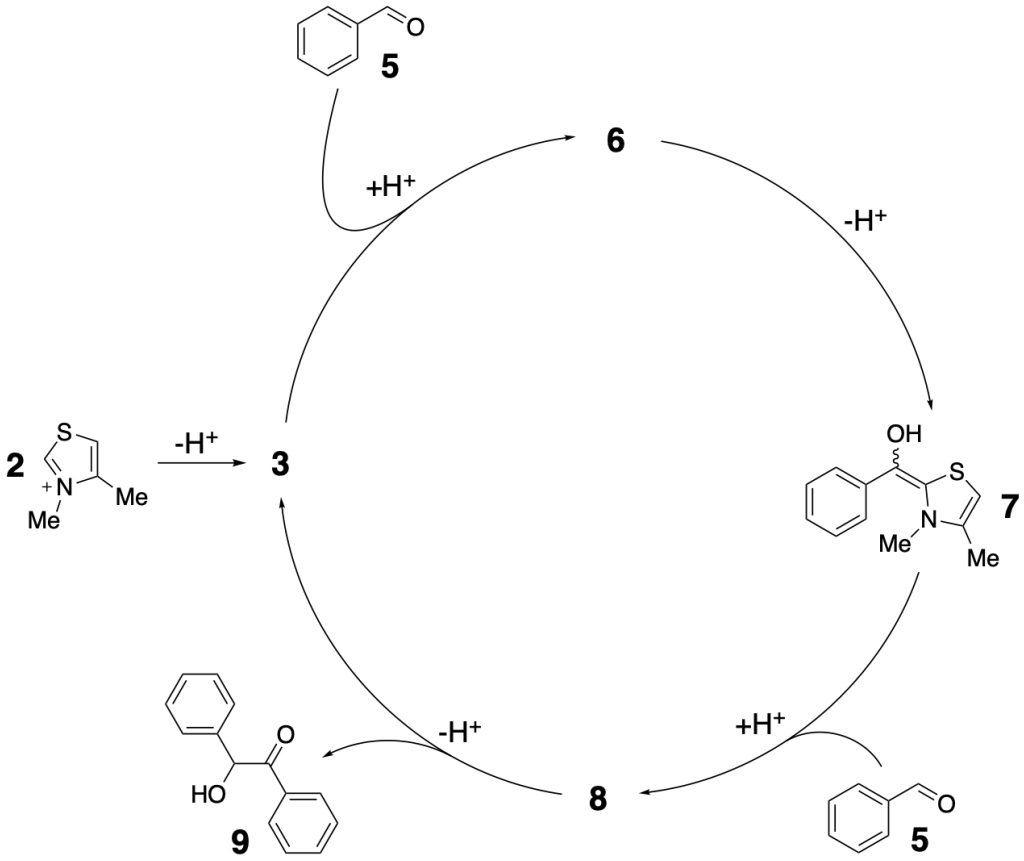
Transketolase (TK) and transaldolase (TA) are enzymes that catalyse C–C bond cleavage. TK contains the cofactor thiamine pyrophosphate **1**, a derivative of vitamin B1, in the active site.

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_2O, which yielded **4** via intermediate **3**.



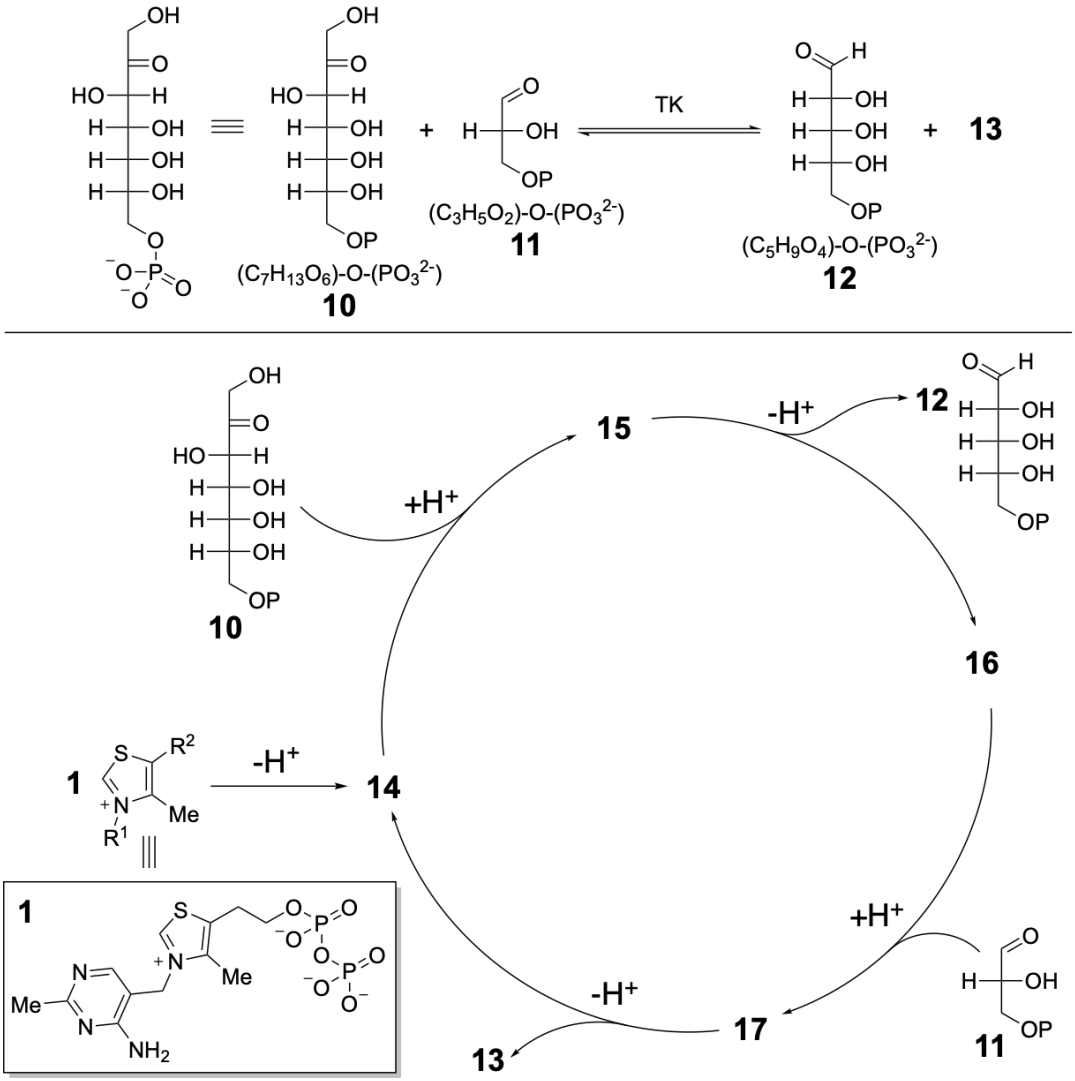
9.1 From the structures in the answer sheet, **choose** the one that corresponds to compound **4**.

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

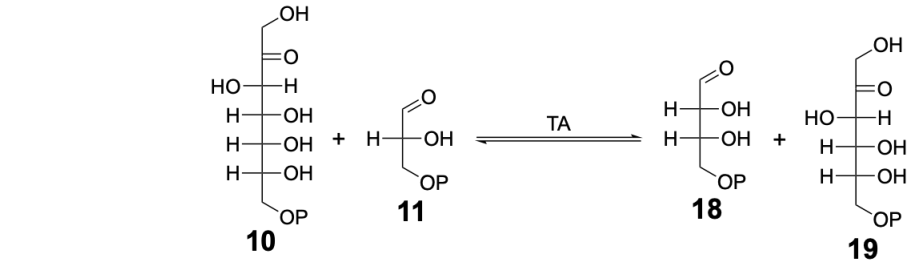
An aldose is a sugar containing an aldehyde. A ketose is a sugar containing a ketone. Enzyme TK contains **1** as a cofactor which catalyses the transfer of a two-carbon fragment from a ketose to an aldose by the catalytic cycle presented below.

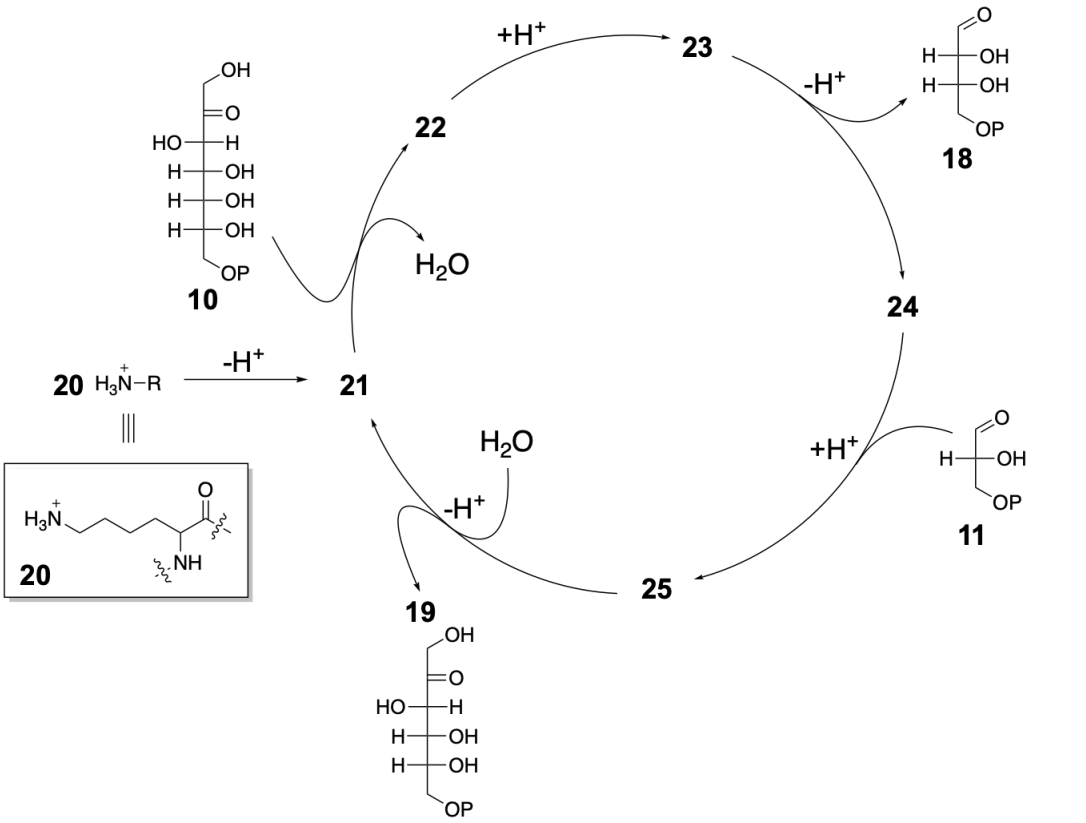


9.3 **Draw** the structure of **13**.

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.