Theoretical Exam Solutions

For marking:

Student name:			code:			
Problem #						
1	2	3	4	5	6	

April 22, 2022
Vilnius, Lithuania

Problem 1. Some chemistry of element X

9 points

References
- https://www.sciencedirect.com/science/article/pii/B9780124186880000010
- https://www.sciencedirect.com/science/article/abs/pii/S0304386X16307095

a) $\rho = \frac{MZ}{N_A a^3} \Rightarrow M = \frac{\rho N_A a^3}{Z} = 1479.06 \ g \ mol^{-1}$ (1 point)

Tennantite = $Cu_a X_b Y_c$, hence $a = \frac{1479.06 \times 0.5165}{63.55} = 12$

$M(X_b) = 1479.06 \times 0.2026 = 299.66 \ g \ mol^{-1}$

b	$M(X)$ / g mol^{-1}
1	299.66
2	149.83
3	99.89
4	**74.91** (As)
5	59.93
6	49.94
7	42.81
8	37.46

Hence, the only sensible possibility is $b = 4$, meaning that **X** = As. (2 points)

$M(Y_c) = 1479.06 \times 0.2818 = 416.80 \ g \ mol^{-1}$

We know that **Y** must be from the group 16 in the periodic table, so possible candidates are – O, S, Se, Te. **Y** = S (2 points), since we know that the most abundant minerals of arsenic are sulfides – orpiment (As_2S_3), realgar (As_4S_4) and enargite (Cu_3AsS_4). Meaning that, $c = 13$.

Tennantite = $Cu_{12}As_4S_{13}$ (1 point)

b) i)

A - As_4S_4 (realgar)

B - As_2O_3 or As_4O_6

C - AsF_3

D - $[AsF_2^+][SbF_6^-]$

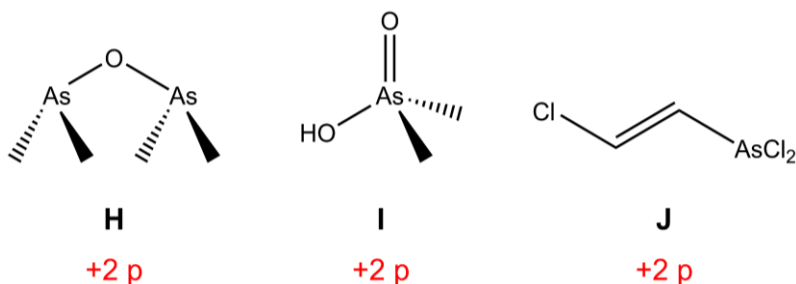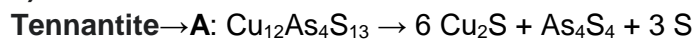**E** - $[Cs^+][AsF_4^-]$

F - $AsCl_3$

G - AsH_3

K - GaAs

*Marking: 2 points for compound **A**, 1 point for compounds **B-G, K**.*

ii)

H	**I**	**J**
+2 p	+2 p	+2 p

c)

Tennantite→A: $Cu_{12}As_4S_{13} \rightarrow 6\ Cu_2S + As_4S_4 + 3\ S$

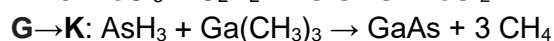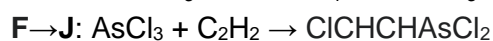Actually, disulfur S_2 is formed under these conditions: $2\ Cu_{12}As_4S_{13} \rightarrow 12\ Cu_2S + 2\ As_4S_4 + 3\ S_2$

A→B: $As_4S_4 + 7\ O_2 \rightarrow 2\ As_2O_3 + 4\ SO_2$

B→C: $As_2O_3 + 6\ HF \rightarrow 2\ AsF_3 + 3\ H_2O$

C→D: $AsF_3 + SbF_5 \rightarrow [AsF_2][SbF_6]$

C→E: $AsF_3 + CsF \rightarrow Cs[AsF_4]$

B→F: $As_2O_3 + 6\ HCl \rightarrow 2\ AsCl_3 + 3\ H_2O$

F→G: $4\ AsCl_3 + 3\ NaBH_4 \rightarrow 4\ AsH_3 + 3\ NaCl + 3\ BCl_3$

F→J: $AsCl_3 + C_2H_2 \rightarrow ClCHCHAsCl_2$

G→K: $AsH_3 + Ga(CH_3)_3 \rightarrow GaAs + 3\ CH_4$

B→H: $As_2O_3 + 4\ CH_3CO_2K \rightarrow [(CH_3)_2As]_2O + 2\ K_2CO_3 + 2\ CO_2$
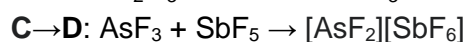
H→I: $[(CH_3)_2As]_2O + 2\ HgO + H_2O \rightarrow 2\ (CH_3)_2As(=O)OH + 2\ Hg$
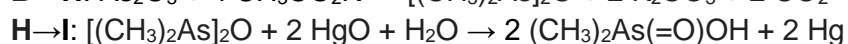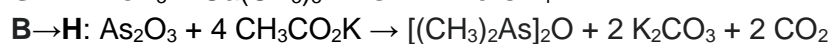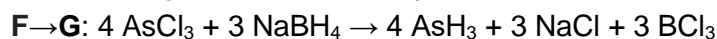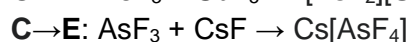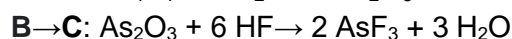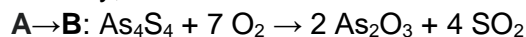
Marking: 1 point for every correct reaction (0.5 p for correct species, 0.5 p for correct coefficients). Give full credit for the first reaction if students provide a correctly balanced equation using S_8. Full marks are also awarded if As_4O_6 is used instead of As_2O_3.

d)

BAL	**product**
+1 p	+2 p
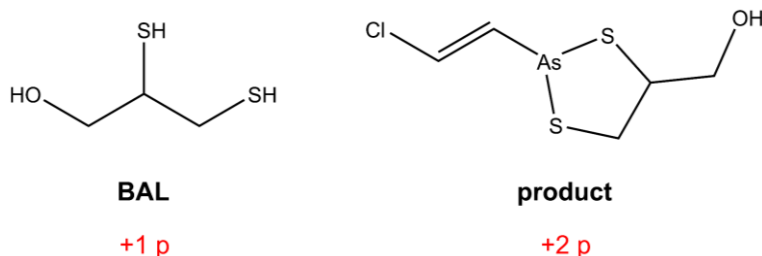
e) AsF_2^+ - bent linear or just bent (**1 point**), SbF_6^- - octahedral (**1 point**)

f)

^{19}**F NMR**: 3 resonances
- quartet (1:1:1:1)
- overlapping sextet (1:1:1:1:1:1) and octet (1:1:1:1:1:1:1:1) in a rough 1.34:1 ratio of intensities

^{75}**As NMR**: 1 resonance - triplet (1:2:1)

^{121}**Sb NMR**: 1 resonance - septet (1:6:15:20:15:6:1)

Marking: 1 point for every correct number of resonances (3 points total), 0.5 points for determining every splitting pattern (2.5 points total) and 0.5 points for every correct ratio of intensities (2.5 points total). 0.5 bonus points for calculating the ratio of ^{121}Sb- and ^{123}Sb-coupled ^{19}F signals and another 0.5 bonus points for mentioning the overlap.

Problem 2. Thermodynamics of electrochemical CO_2 capture

10 points

1. Using the Nernst equation **write** an expression for the reduction half-cell potential E.

$E = E^0 - RT/mF \ln([A^{m-}]/[A])$ *- 1 pt*

2. **Write** an expression for the equilibrium constant K for the given reaction, assuming the reference pressure P_0 to be 1.

$K = [A(CO_2)_m{}^{m-}]/([A^{m-}]\cdot P_{CO2}{}^m)$ *- 1 pt*

3. **Find** expressions for $f_1(x_{A'})$ and $f_2(KP_{CO2}{}^m)$.

Starting from $E = E^0 - RT/mF \ln([A^{m-}]/[A])$,   *- 1 pt*
let's consider $[A^{m-}]/[A]$ part, while also remembering that:

$$A_0 = [A] + [A^{m-}] + [A(CO_2)_m{}^{m-}] \qquad (1)$$
$$x_{A'} = ([A^{m-}] + [A(CO_2)_m{}^{m-}])/A_0 \qquad (2)$$
$$K = [A(CO_2)_m{}^{m-}]/([A^{m-}]\cdot P_{CO2}{}^m) \qquad (3)$$

From (2): $([A^{m-}] + [A(CO_2)_m{}^{m-}]) = x_{A'} A_0$
Insert in (1): $A_0 = [A] + x_{A'} A_0$
Solve for $[A]$: $[A] = A_0(1-x_{A'})$ *- 1 pt*

Also from (2): $A_0 = ([A^{m-}] + [A(CO_2)_m{}^{m-}])/x_{A'}$
So $[A] = (1-x_{A'})/x_{A'} \cdot ([A^{m-}] + [A(CO_2)_m{}^{m-}])$ *- 1 pt*
And hence: $[A^{m-}]/[A] = x_{A'}/(1-x_{A'}) \cdot [A^{m-}]/([A^{m-}] + [A(CO_2)_m{}^{m-}])$

Now in second term divide through $[A^{m-}]$:
$[A^{m-}]/[A] = x_{A'}/(1-x_{A'}) \cdot 1/(1 + [A(CO_2)_m{}^{m-}]/[A^{m-}])$
But from (3): $[A(CO_2)_m{}^{m-}]/[A^{m-}] = KP_{CO2}{}^m$ *- 1 pt*
And hence: $[A^{m-}]/[A] = x_{A'}/(1-x_{A'}) \cdot 1/(1 + KP_{CO2}{}^m)$

So we can rewrite equation for E:
$$E = E^0 - RT/mF \ln(x_{A'}/(1-x_{A'}) \cdot 1/(1 + KP_{CO2}{}^m))$$
$$E = E^0 - RT/mF \ln(x_{A'}/(1-x_{A'})) - RT/mF \ln(1/(1 + KP_{CO2}{}^m))$$
$$E = E^0 + RT/mF \ln((1-x_{A'})/x_{A'}) + RT/mF \ln(1 + KP_{CO2}{}^m) \qquad \textit{- 1 pt}$$
And so:

$f_1(x_{A'}) = \ln[(1-x_{A'})/x_{A'}]$ $f_2(KP_{CO2}) = \ln(1 + KP_{CO2}{}^m)$ *- 1 pt*

Overall - 6 pts

4. **Write** an expression for E^{dev} in this case.
(*In case you could not do the previous question, provide the answer using $f_1(x_{A'})$ and $f_2(KP_{CO2}{}^m)$*)

$E^{dev} = RT/mF \cdot f_2(KP_{CO2}{}^m)$ or

$E^{dev} = RT/mF \ln(1 + KP_{CO2}{}^m)$ *- 1 pt*

Part II - Thermodynamical analysis (9 pts)

5. **Calculate** the total CO_2 content x_{CO2} for cases α=0.25 and α=0.75.

$x_{CO2} = 0.25 \cdot 500 \cdot 1/(1+500 \cdot 1) + 0.05 \cdot 1 = 0.2995$ *- 1 pt*
$x_{CO2} = 0.75 \cdot 500 \cdot 1/(1+500 \cdot 1) + 0.05 \cdot 1 = 0.7985$ *- 1 pt*

6. **Calculate** the partial pressure P_{CO2} at point C.
(In case you could not calculate x_{CO2} in the previous question, use a value $x_{CO2} = 0.35$)

$0.2995 = 0.75 \cdot 500 \cdot x/(1+500 \cdot x) + 0.05 \cdot x$ *- 1 pt*
$x = 0.00133$ bar   *- 1 pt*

For alternative value:
$0.35 = 0.75 \cdot 500 \cdot x/(1+500 \cdot x) + 0.05 \cdot x$
$x = 0.00175$ bar

7. **Assign** all the described steps with points shown in the E^{dev} vs. α diagram.
(*In the form:* 1. X to Y)

Four-stage system:
      1. A to C   0.5 pt
      2. C to D   0.5 pt
      3. D to F   0.5 pt
      4. F to A   0.5 pt
Two-stage system:
      1. A to B to D   1 pt
      2. D to E to A   1 pt

The work required to perform the capture-release cycle is described as the area enclosed by the cycle in the E^{dev} vs. α diagram.

8. **Tick** the correct answer, consistent with your answer to the previous part.

☐ - Four-stage system requires less work.
☑ - Two-stage system requires less work.
1 pt

References:

      https://www.sciencedirect.com/science/article/abs/pii/S175058361930427X

Problem 3. Solution ≠ liquid

1. Assuming that the cubic cell given in Fig. 1 corresponds to the composition of whole material, calculate the x value in empirical formula Fe_xCr_{1-x}.

Solution:
12 Fe atoms are centered at the edges and one atom – in the center of the cube. Therefore, the count of Fe atoms that reside in the cubic cell is **(1 point)**:

$$12 \cdot \frac{1}{4} + 1 = 4$$

8 Cr atoms are centered at the vertices, 6 – at the face centers and 8 atoms are inside the cell (at z = 0.25 and z = 0.75 planes). Therefore, the count of Cr atoms that reside in the cubic cell is **(1 point)**:

$$8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} + 8 = 12$$

The ratio is:

$$\frac{n(Fe)}{n(Cr)} = \frac{4}{12} = \frac{x}{1-x}$$

Solution of the equation is $x = 0.25$ **(1 point)**

2. The lattice parameter of the cell given in Fig. 1 is 576 picometers. Calculate the density of ferrochrome. Express the answer in g·cm^{-3} dimensions.

Solution:
The mass of the cubic cell is (1 point):

$$m_{cell} = m_{Fe} + m_{Cr} = \frac{N_{Fe}}{N_A} \cdot M(Fe) + \frac{N_{Cr}}{N_A} \cdot M(Cr) = \frac{4M(Fe) + 12M(Cr)}{N_A}$$

Then the density of ferrochrome, using the assumption that one cell represents overall composition, is equal to (1 point):

$$\rho_{cell} = \frac{m_{cell}}{V_{cell}} = \frac{4M(Fe) + 12M(Cr)}{N_A a^3}$$

Calculation (1 point):

$$\rho_{cell} = \frac{4 \cdot 55.85 \frac{g}{mol} + 12 \cdot 52.00 \frac{g}{mol}}{6.0221 \cdot 10^{23} \ mol^{-1} \cdot (5.76 \cdot 10^{-8} \ cm)^3} = 7.36 \ g \cdot cm^{-3}$$

3. The experimental ferrochrome density value differs by 5 % compared with the result you've calculated in question 2. Which of the following statements can explain such a difference? ***Circle correct answer letter(s)***

a)	Additional Fe or Cr atoms can be intercalated in octahedral or tetrahedral voids of the lattice (incorrect option, Fe and Cr atoms have similar radii so they cannot fit into the voids)
b)	Formation of vacancies in nodes of crystal lattice **(1 point)**
c)	Because of random distribution of Fe and Cr atoms in the lattice one cubic cell does not ideally correspond to the actual composition of material **(1 point)**
d)	Chemical interactions between Fe and Cr cause the significant change of metallic radii of Fe and Cr atoms (incorrect option, their chemical interactions are very similar to the interaction in pure iron or chromium crystals so we would not expect a significant change of radii)
e)	In solid solutions lattice parameter values fluctuates significantly (incorrect option, Fe and Cr atoms have similar radii so lattice parameter remains around the same value)

4. Write chemical formula of byproduct.

Answer: MgO (1 point)
Explanation: La atoms can substitute only Mg atoms in forsterite and there is oxygen excess from the La_2O_3, that means that byproduct is a material, consisting of magnesium and oxygen.

5. Express index y as a function of x.

Solution:
Forsterite must remain neutral during the exchange of Mg^{2+} and La^{3+} ions. Thus every three Mg^{2+} ions are substituted by two La^{3+} ions (condition of electric charge balance) **(1 point)**

If x mol La^{3+} are introduced into 1 mol of Mg_2SiO_4, that means that $\frac{3x}{2}$ mol Mg^{2+} must be excluded from the material. The total amount of magnesium was 2 mol, therefore **(1 point)**:

$$y = 2 - \frac{3x}{2}$$

The empirical formula can be written as $La_xMg_{2-1.5x}SiO_4$

6. When La^{3+} ions substitute Mg^{2+} ions, a certain concentration of vacancies are formed. Vacancies influence electrical conductivity of ionic solid solution. Which electric charge transfer mechanism occurs in $La_xMg_ySiO_4$ solid solution? *Circle one correct answer letter.*

a)	Mg^{2+} migrates to the vacancy, a new vacancy is formed in Mg^{2+} node
b)	La^{3+} migrates to the vacancy, a new vacancy is formed in La^{3+} node
c)	Si^{4+} migrates to the vacancy, a new vacancy is formed in Si^{4+} node
d)	O^{2-} migrates to the vacancy, a new vacancy is formed in O^{2-} node
e)	Mg^{2+} or La^{3+} migrates to the vacancy, a new vacancy is formed in Mg^{2+} or La^{3+} node **(1 point)** (explanation: Mg^{2+} and La^{3+} share the same nodal positions, and SiO_4^{4-} tetrahedral ions both electrostatically and sterically cannot move to cation nodal positions)
f)	Mg^{2+}, La^{3+} or Si^{4+} migrates to the vacancy, a new vacancy is formed in Mg^{2+}, La^{3+} or Si^{4+} node

g)	Mg^{2+}, La^{3+}, Si^{4+} or O^{2-} migrates to the vacancy, a new vacancy is formed in Mg^{2+}, La^{3+}, Si^{4+} or O^{2-} node
h)	Free electrons migrate from vacancy to vacancy

7. By performing electrical conductivity measurements it was calculated that concentration of vacancies in lanthanum-doped forsterite is $6.2 \cdot 10^{17}$ cm^{-3}. Density of the material is 3.223 $g \cdot cm^{-3}$. One unit cell contains one silicon and four oxygen atoms. Calculate index x in formula $La_xMg_ySiO_4$ by assuming that all vacancies are formed because of La^{3+}–Mg^{2+} exchange.

Solution:

Because one silicon and four oxygen atoms are in one unit cell, one formula unit belongs to one unit cell. Then the mass of one unit cell is **(1 point)**:

$$m_{cell} = m(La_xMg_ySiO_4) = \frac{N}{N_A} \cdot M(La_xMg_ySiO_4) = \frac{M(La_xMg_ySiO_4)}{N_A}$$

Then the volume of unit cell can be calculated from density:

$$V_{cell} = \frac{m_{cell}}{\rho} = \frac{M(La_xMg_ySiO_4)}{\rho N_A}$$

There is one vacancy per $V = (6.2 \cdot 10^{17}\ cm^{-3})^{-1} = 1.6 \cdot 10^{-18}\ cm^3$ volume **(1 point)**.

We introduce N_{cell} – amount of unit cells in volume V, and N_{vac} – a fraction of vacancy per unit cell. Then we can deduce that **(1 point)**:

$$N_{cell} = \frac{V}{V_{cell}} \quad \Rightarrow \quad N_{vac} = \frac{1}{N_{cell}} = \frac{V_{cell}}{V}$$

We expect a small fraction of vacancies and a small fraction of lanthanum atoms, so we can approximate that $M(La_xMg_ySiO_4) \approx M(Mg_2SiO_4)$ and calculate N_{vac} **(1 point)**:

$$N_{vac} \approx \frac{M(Mg_2SiO_4)}{V\rho N_A} = \frac{(2 \cdot 24.31 + 28.09 + 4 \cdot 16.00)\ \frac{g}{mol}}{1.6 \cdot 10^{-18}\ cm^3 \cdot 3.223\ \frac{g}{cm^3} \cdot 6.0221 \cdot 10^{23}\ mol^{-1}} = 4.53 \cdot 10^{-5}$$

When three Mg^{2+} ions are exchanged by two La^{3+} ions, one nodal position becomes a vacancy. That means that lanthanum amount in the formula unit is $x = 2N_{vac} = 9.06 \cdot 10^{-5}$ **(1 point).**

8. Calculate values a and b.

Solution:
We can separate +2 oxidation state and +3 oxidation state iron in the empirical formula like this:
$$Li_x Fe_y^{II} Fe_{1-x-y}^{III} O$$
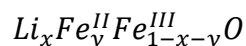
And now we apply electric charge neutrality condition – the sum of all amounts (empirical formula indices) and oxidation states must be equal to 0 **(1 point).**
$$x \cdot (+1) + y \cdot (+2) + (1 - x - y) \cdot (+3) + 1 \cdot (-2) = 0$$

We can solve for y **(1 point):**
$$x + 2y + 3 - 3x - 3y - 2 = 0 \qquad \Rightarrow \qquad y = 1 - 2x$$

Then molar amounts $n(Fe^{3+})$ ir $n(Fe^{2+})$ are proportional to their indices, so the ratio is **(1 point):**
$$r = \frac{n(Fe^{3+})}{n(Fe^{2+})} = \frac{1 - x - y}{y} = \frac{x}{1 - 2x}$$

We can raise both sides of the equation to the –1 power and extract the reciprocal of x:
$$\frac{1}{r} = \frac{1 - 2x}{x} = \frac{1}{x} - 2 \qquad \Rightarrow \qquad \frac{1}{x} = \frac{1}{r} + 2$$

That shows that $a = 1$ and $b = 2$ **(1 point).**

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9. Calculate the ratio r and index x from electrochemical measurement data.

Solution:

If $[Fe(CN)_6]^{4-}$ concentration increases, then $[Fe(CN)_6]^{3-}$ participates in a reduction to $[Fe(CN)_6]^{4-}$ and oxidation process occurs in the reference electrode. It means that we can calculate potential difference by substracting reference electrode potential from reduction process potential **(1 point).**

$$\Delta E = E_{reduction} - E_{reference}$$

We know that $E_{reference} = +0.197\ V$. Reduction potential can be calculated using Nernst equation **(1 point).**

$$E_{reduction} = E° - \frac{RT}{zF} \ln \ln \frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]} = E° - \frac{RT}{F} \ln \ln \frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}$$

$[Fe(CN)_6]^{4-}$ concentration represents the amount of Fe^{2+} in the analyzed material and $[Fe(CN)_6]^{3-}$ represents the amount of Fe^{3+} in the analyzed material. That implies **(1 point).**

$$E_{reduction} = E° - \frac{RT}{F} \ln \ln \frac{n(Fe^{2+})}{n(Fe^{3+})} = E° - \frac{RT}{F} \ln \ln \frac{1}{r} = E° + \frac{RT}{F} \ln \ln r$$

Now we can derive r **(1 point):**

$$\frac{RT}{F} \ln \ln r = E_{reduction} - E° = \Delta E + E_{reference} - E°$$

$$r = \exp \exp \left(\frac{F}{RT} \cdot \left(\Delta E + E_{reference} - E° \right) \right)$$

Calculation **(1 point):**

$$r = \exp \exp \left(\frac{96485.3 \frac{C}{mol}}{8.3145 \frac{J}{K \cdot mol} \cdot 298\ K} \cdot (0.092\ V + 0.197\ V - 0.370\ V) \right) = 0.0427$$

And using the relationship derived in question 8 we can calculate x value **(1 point):**

$$x = \left(\frac{1}{r} + 2 \right)^{-1} = \left(\frac{1}{0.0427} + 2 \right)^{-1} = 0.0393$$

10. Show that for orthorhombic lattice with different unit cell lengths a, b, c phosphorescence intensity can be calculated using formula below.

$$I = \frac{9 \cdot CN \cdot k_{ph}}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot CN^2 \cdot (a^2 + b^2 + c^2)}$$

Solution:

No matter which node we select, the first coordination shell comprises of six nodal positions: two at distance a, two at distance b and two at distance c from the selected molecule (figure in the right) **(1 point).**

Maximum possible CN value is 6. But in solid solutions $CN < 6$ (not every nodal position is occupied by **A** molecule). But because probability to occupy site at distance a, or distance b, or distance c, is exactly 1/3, we can deduce **(1 point):**

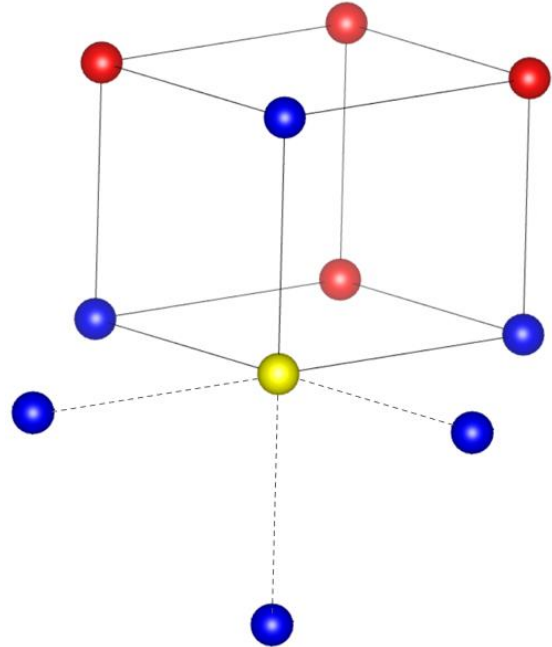$$CN_a = CN_b = CN_b = \frac{CN}{3}$$

Now we expand the sum in the denominator of the model equation into three parts **(1 point):**

$$I = \frac{CN \cdot k_{ph}}{k_{ph} \cdot r_0^2 + k_{vib}(CN_a^2 \cdot a^2 + CN_b^2 \cdot b^2 + CN_c^2 \cdot c^2)}$$

We change CN_a, CN_b and CN_c values to CN and derive the final expression **(1 point):**

$$I = \frac{CN \cdot k_{ph}}{k_{ph} \cdot r_0^2 + k_{vib}\left(\frac{CN^2}{9} \cdot a^2 + \frac{CN^2}{9} \cdot b^2 + \frac{CN^2}{9} \cdot c^2\right)}$$

$$I = \frac{CN \cdot k_{ph}}{k_{ph} \cdot r_0^2 + \frac{1}{9} k_{vib} \cdot CN^2(a^2 + b^2 + c^2)} = \frac{9 \cdot CN \cdot k_{ph}}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot CN^2(a^2 + b^2 + c^2)}$$

11. Solid solution **X** is prepared by co-crystallising **A** and **B** in ratio $n(A){:}n(B) = 1{:}1$. Solid solution **Y** is prepared by co-crystallising **A** and **B** in ratio $n(A){:}n(B) = 2{:}1$. **X** phosphoresce 1.25 times more intensely than **Y**. Calculate the length of the diagonal of orthorhombic unit cell, if $\frac{k_{ph}}{k_{vib}} \approx 10^{-4}$ and $r_0 \approx 710$ Å.

Solution:

In solid solution **X**, 50 % of nodal positions are occupied by molecules A. Therefore, in average coordination number of A molecules around A molecule is $CN_X = 0.50 \cdot 6 = 3$ **(1 point).**

Similarly, in solid solution **Y**, 2/3 = 66.7 % of nodal positions are occupied by molecules A. That implies $CN_Y = 2/3 \cdot 6 = 4$ **(1 point).**

By Pythagorean theorem, diagonal length of the unit cell d can be expressed as **(1 point):**
$$d^2 = a^2 + b^2 + c^2$$

Now we know that **(1 point):**
$$\frac{I_X}{I_Y} = \frac{\dfrac{\cancel{9 \cdot} CN_X \cdot \cancel{k_{ph}}}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot CN_X^2 \left(a^2 + b^2 + c^2\right)}}{\dfrac{\cancel{9 \cdot} CN_Y \cdot \cancel{k_{ph}}}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot CN_Y^2 \left(a^2 + b^2 + c^2\right)}} = \frac{\dfrac{3}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 9d^2}}{\dfrac{4}{9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 16d^2}} = 1.25$$

We can derive d from the ratio above and calculate its value **(2 points):**
$$9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 16d^2 = 1.25 \cdot \frac{4}{3} \cdot \left(9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 9d^2\right)$$
$$9 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 16d^2 = 15 \cdot k_{ph} \cdot r_0^2 + k_{vib} \cdot 15d^2$$
$$k_{vib} d^2 = 6 \cdot k_{ph} \cdot r_0^2$$
$$d = r_0 \sqrt{6 \cdot \frac{k_{ph}}{k_{vib}}} = 710 \text{ Å} \sqrt{6 \cdot 10^{-4}} = 17.4 \text{ Å}$$

Total: 37 points.

Problem 4. Kinetics

9 points

1. 1. <u>Select</u> ALL appropriate mechanisms which are consistent with the assumption given in **1.**

☐ Mechanism (a)

☒ **Mechanism (b)**

☐ Mechanism (c)

☒ **Mechanism (d)**

> *1 point for each correct answer*
>
> *-1 point for each incorrect answer*
>
> *No negative points in total*

<u>2 points</u> in total for **1. 1.**

1. 2. <u>Select</u> ALL graphs that could depict the relationship between $[B]$ and both t, time, or r, rate of reaction (0), and are consistent with the condition given in **1.** Assume a constant state for $[A]$.

☒ **Graph (a)**	☒ **Graph (d)**
☒ **Graph (b)**	☐ Graph (e)
☐ Graph (c)	☐ Graph (f)

> *1 point for each correct answer*
>
> *-1 point for each incorrect answer*
>
> *No negative points in total*

<u>3 points</u> in total for **1. 2.**

2. For each condition listed below, <u>**determine**</u> whether the rate-limiting step of the mechanism presented above is step (1), step (2) or neither. Assume that $[A]$ and $[B]$ are much greater than $[AB]$ and $[AB_2]$.

2. 1. $k_1 \gg k_{-1}$; $k_2 \gg k_1$

2. 2. $k_1 \gg k_{-1}$; $k_2 \ll k_1$

2. 3. $k_1 \gg k_{-1}$; $k_2 \cong k_1$

2. 4. $k_1 \cong k_{-1}$; $k_2 \ll k_1$

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Condition **2. 1.**	**Step (1)** ☒	Step (2) ☐	Neither ☐
Condition **2. 2.**	Step (1) ☐	**Step (2)** ☒	Neither ☐
Condition **2. 3.**	Step (1) ☐	Step (2) ☐	**Neither** ☒
Condition **2. 4.**	Step (1) ☐	**Step (2)** ☒	Neither ☐

1 point for each correct answer

0 points for each incorrect answer

<u>*4 points*</u> *total for* **2.**

3. At time $t = t_1$, the concentration of intermediate AB has become constant, i.e. $[AB] = [AB]_{const}$, and the concentration of reagent A has reached a certain value, i.e. $[A] = [A]_1$.

3. 1. <u>**Express**</u> the ratio of the rate constants, namely $\frac{k_1}{k_2}$, using terms $[A]_1$ and $[AB]_{const}$. Assume that $k_1, k_2 \gg k_{-1}$.

The rate of production of AB_2 can be expressed as follows:

$$\frac{d[AB_2]}{dt} = k_2[B][AB]$$

Since $[AB]$ is given to be constant, we can assume a steady-state for this compound:

$$\frac{d[AB]}{dt} = k_1[A][B] - k_{-1}[AB] - k_2[AB][B] = 0$$

$$[AB] = \frac{k_1[A][B]}{k_{-1} + k_2[B]}$$

Taking into account that $k_1, k_2 \gg k_{-1}$, we can simplify the equation above as follows:

$$[AB] = \frac{k_1[A][B]}{k_{-1} + k_2[B]} \cong \frac{k_1[A][B]}{k_2[B]} = \frac{k_1[A]}{k_2}$$

Using this expression of $[AB]$, we can express the rate of reaction (2) as follows:

$$\frac{d[AB_2]}{dt} = k_2[B][AB] = \frac{k_1 k_2[A][B]}{k_2} = k_1[A][B]$$

$$k_1[A][B] = k_2[B][AB] \Rightarrow \frac{k_1}{k_2} = \frac{[AB]}{[A]}$$

At time $t = t_1$:

$$\frac{k_1}{k_2} = \frac{[AB]_{const}}{[A]_1}$$

1 point for showing $\frac{d[AB_2]}{dt} = k_2[B][AB]$

2 points for correctly applying the steady-state intermediate law for $[AB]$

1 point for simplifying the initial expression of $[AB]$

2 points for deriving the equality $k_1[A][B] = k_2[B][AB]$

1 point for finding the ratio of the rate constants

*7 points in total for **3.1.***

4.

4. 1.   Assuming that under given conditions steps (1) and (2) proceed much slower than step (3), **show** that the observed rate constant, k_{obs}, is approximately equal to rate constant k_1.

$$\frac{d[ABC]}{dt} = k_3[C][AB]$$

Assuming the steady-state intermediate law for compound AB:

$$\frac{d[AB]}{dt} = k_1[A][B] - k_{-1}[AB] - k_2[AB][B] - k_3[AB][C] = 0$$

$$[AB] = \frac{k_1[A][B]}{k_{-1} + k_2[B] + k_3[C]}$$

Given that step (2) proceeds much slower than step (3), their reaction rates can be compared as follows:

$$k_2[AB][B] \ll k_3[C][AB]$$

$$k_2[B] \ll k_3[C]$$

We can therefore simplify the expression of $[AB]$:

$$[AB] = \frac{k_1[A][B]}{k_{-1} + k_2[B] + k_3[C]} \cong \frac{k_1[A][B]}{k_3[C]}$$

Thus, the rate of production of $[ABC]$ becomes:

$$\frac{d[ABC]}{dt} = k_3[C]\frac{k_1[A][B]}{k_3[C]} = k_1[A][B]$$

Therefore $k_{obs} \cong k_1$.

---

1 point for showing $\frac{d[ABC]}{dt} = k_3[C][AB]$

2 points for correctly applying the steady-state intermediate law for $[AB]$

3 points for simplifying the initial expression of $[AB]$

1 point for obtaining $k_{obs} \cong k_1$

7 points total for **4. 1.**

4. 2. Using signs $>$, $<$ and/or $\cong$, **denote** the relationship between reactions' (2) and (3) Arrhenius pre-factors, A_2 and A_3, and activation energies, E_{a2} and E_{a3}, respectively. Assume that Arrhenius pre-factors and activation energies of these reactions are independent of temperature.

At lower temperature, $k_2 < k_3 \Rightarrow A_2 \cdot exp\left(\frac{-E_{a2}}{RT}\right) < A_3 \cdot exp\left(\frac{-E_{a3}}{RT}\right)$

As the temperature increases, k_2 increases at a faster rate than k_3, meaning $\frac{E_{a2}}{T}$ decreases at a faster rate than $\frac{E_{a3}}{T}$. Therefore $E_{a2} > E_{a3}$ and $exp\left(\frac{-E_{a2}}{RT}\right) < exp\left(\frac{-E_{a3}}{RT}\right)$.

If $k_2 = k_3$ and $exp\left(\frac{-E_{a3}}{RT}\right) < exp\left(\frac{-E_{a4}}{RT}\right)$, then the following must be true: $A_2 > A_3$.

$$A_2 > A_3 \qquad\qquad\qquad\qquad E_{a2} > E_{a3}$$

5. Certain amounts of B, C and AB were added to a container under conditions that favor <u>only</u> reactions (2) and (3). Assume, that the initial concentration of AB, $[AB]_0$, is much greater than initial concentrations of both B, $[B]_0$, and C, $[C]_0$.

At time $t = t_3$, concentrations of compounds AB_2 and ABC were measured and their values were found to be equal.

5. 1. **<u>Express</u>** the ratio of initial concentrations of B and C, namely $\frac{[B]_0}{[C]_0}$, in terms of $[AB]_0$, k_2, k_3 and t_3.

Concentrations of compounds AB_2 and ABC at time $t = t_3$ can be expressed as follows:

$[AB_2] = [B]_0 - [B]_t$ (5)

$[ABC] = [C]_0 - [C]_t,$ (6)

where $[B]_t$ and $[C]_t$ are concentrations of their respective compounds at time $t = t_3$.

Given that $[AB] \gg [B], [C]$, we can assume $[AB]$ stays constant throughout the remainder of the reaction and can be denoted as $[AB]_0$.

$$\frac{d[B]}{dt} = -k_2[AB][B] = -k_2[AB]_0[B] \Rightarrow [B]_t = [B]_0 \cdot exp\left(-k_2[AB]_0t_3\right) \quad (7)$$

$$\frac{d[C]}{dt} = -k_3[AB][C] = -k_2[AB]_0[C] \Rightarrow [C]_t = [C]_0 \cdot exp\left(-k_3[AB]_0t_3\right) \quad (8)$$

Plugging in these values into (5) and (6), we obtain:

$[AB_2] = [B]_0 \cdot (1 - exp(-k_2[AB]_0t_3))$

$$[ABC] = [C]_0 \cdot (1 - exp(k_3[AB]_0t_3))$$

Given that $[AB_2]$ and $[ABC]$ are equal, we derive the following equation:

$[B]_0 \cdot (1 - exp(-k_2[AB]_0t_3)) = [C]_0 \cdot (1 - exp(k_3[AB]_0t_3))$ (9)

$$\frac{[B]_0}{[C]_0} = \frac{1 - exp(-k_3[AB]_0t_3)}{1 - exp\left(-k_2[AB]_0t_3\right)}$$

---

1 points each for obtaining (5) and (6)

2 points each for obtaining (7) and (8)

2 points for deriving equation (9)

1 point for finding the ratio of initial concentrations

*9 points in total for **5. 1.***

5. 2. <u>**Calculate**</u> the ratio of the rates of reactions (2) and (3), namely $\frac{r_2}{r_3}$, at time $t = t_3$, when $[AB]_0 = 1.20 \cdot 10^{-3} \, mol \cdot L^{-1}$, $k_2 = 1.40 \cdot 10^{-3} \, L \cdot mol^{-1} \cdot s^{-1}$, $k_3 = 5.60 \cdot 10^{-4} \, L \cdot mol^{-1} \cdot s^{-1}$ and $t_3 = 2.50 \cdot 10^3 \, s$.

At time $t = t_3$:

$$\frac{r_2}{r_3} = \frac{k_2[B]_t[AB]}{k_3[C]_t[AB]} = \frac{k_2[B]_t}{k_3[C]_t}$$

Plugging in values from (7) and (8) we obtain:

$$\frac{r_2}{r_3} = \frac{k_2[B]_0 \cdot exp\left(-k_2[AB]_0 t_3\right)}{k_3[C]_0 \cdot exp\left(-k_3[AB]_0 t_3\right)} = \frac{k_2}{k_3} \cdot \frac{[B]_0}{[C]_0} \cdot \frac{exp\left(-k_2[AB]_0 t_3\right)}{exp\left(-k_3[AB]_0 t_3\right)}$$

Using the derived expression of $\frac{[B]_0}{[C]_0}$ in **5. 1.**:

$$\frac{r_2}{r_3} = \frac{k_2}{k_3} \cdot \frac{1 - exp(-k_3[AB]_0 t_3)}{1 - exp(-k_2[AB]_0 t_3)} \cdot \frac{exp\left(-k_2[AB]_0 t_3\right)}{exp\left(-k_3[AB]_0 t_3\right)}$$

Using values given in **5. 2.** we obtain a numerical expression of $\frac{r_3}{r_4}$:

$\frac{r_2}{r_3}$

$$= \frac{1.40 \cdot 10^{-3}\, s^{-1} \cdot exp\left(-1.40 \cdot 10^{-3}\, s^{-1} \cdot 1.20 \cdot 10^{-3}\, mol \cdot L^{-1} \cdot 2.50 \cdot 10^3\, s\right)\left(1 - exp(-5.60 \cdot 10^{-4}\, s^{-1} \cdot 1.20 \cdot 10^{-3}\, mol \cdot L^{-1} \cdot 2.50 \cdot 10\right.}{5.60 \cdot 10^{-4}\, s^{-1} \cdot exp\left(-5.60 \cdot 10^{-4}\, s^{-1} \cdot 1.20 \cdot 10^{-3}\, mol \cdot L^{-1} \cdot 2.50 \cdot 10^3\, s\right)\left(1 - exp(-1.40 \cdot 10^{-3}\, s^{-1} \cdot 1.20 \cdot 10^{-3}\, mol \cdot L^{-1} \cdot 2.50 \cdot\right.}$$

$$\frac{r_2}{r_3} = 0.9987$$

2 points for showing $\frac{r_2}{r_3} = \frac{k_2[B]_t}{k_3[C]_t}$

*2 points for using the answer obtained in **5. 1.***

2 points for obtaining the correct numerical expression of $\frac{r_2}{r_3}$

<u>*6 points*</u> *in total for **5. 2.***
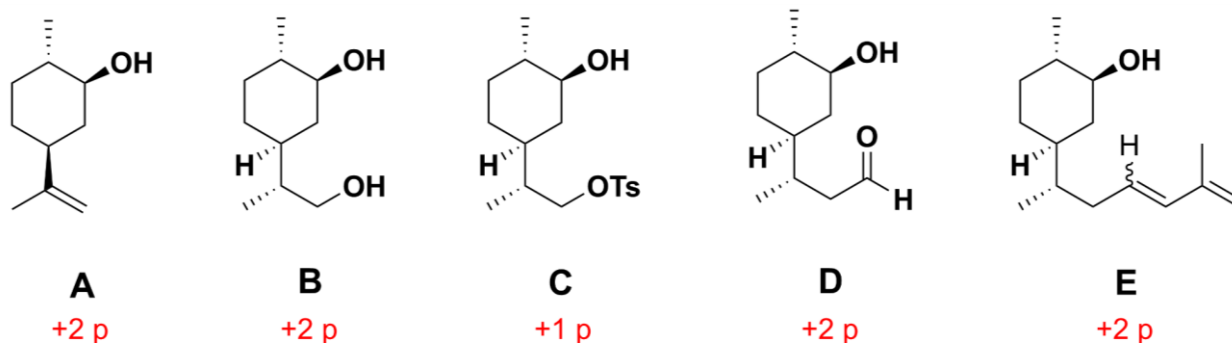
46 points in total

Problem 5. Total synthesis of (–)-Colombiasin A

10 points

References:

- https://onlinelibrary.wiley.com/doi/epdf/10.1002/anie.200601872?saml_referrer
- https://onlinelibrary.wiley.com/doi/epdf/10.1002/ange.200462268
- https://pubmed.ncbi.nlm.nih.gov/11822436/
- Squarate **X** spectroscopic data - suppmat, article

1)

A	B	C	D	E
+2 p	+2 p	+1 p	+2 p	+2 p

One-time penalty of –1 p for every incorrect assignment of stereochemistry, including geometry about the double bond in **E**.

2) DMSO (best for solvating Na⁺) (2 points)

3) The reaction mechanism is that of the Julia-Kocienski olefination, a refined version of the well-known Julia olefination. The aldehyde is abbreviated as RCHO for the sake of clarity.

+1 p

+2 p

+2 p

+1 p

+1 p total for by-products
+0,5 p total if 1/3 incorrect or missing

+ SO₂
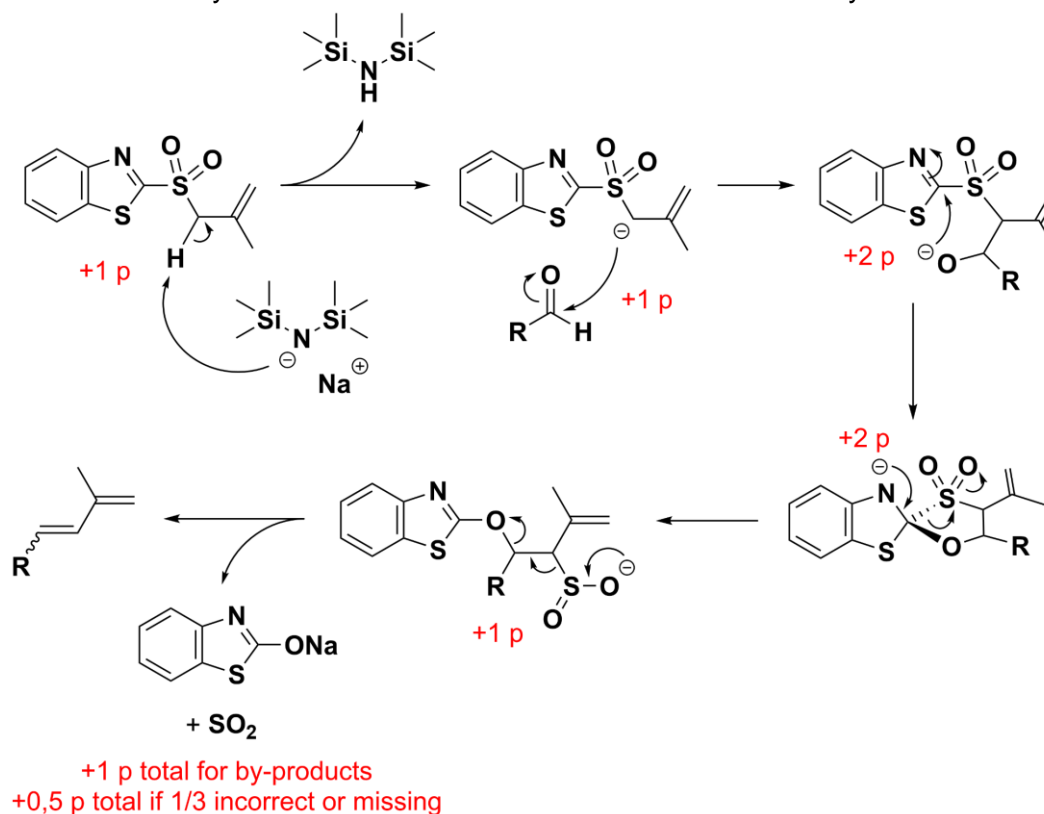
4) Assuming the relevant ^{1}H NMR resonances do not overlap significantly with other resonances, the ratio of *E/Z* isomers can be qualitatively approximated by the ratio of integrals of corresponding ^{1}H resonances (1 point). The alkene protons of *E*-**E** and *Z*-**E** can be distinguished based on the values of $^3J_{H-H}$ coupling constants (1 point). While *cis*-alkene protons usually have a $^3J_{H-H}$ value in the range 7-12

Hz, the coupling constants of *trans*-alkene protons usually come in the range 12-18 Hz (1 point even if it has been simply stated that generally $^3J_{H\text{-}H,cis} < \,^3J_{H\text{-}H,trans}$).
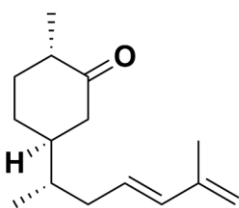
5) CO, CO_2, Me_2S and Et_3NHCl. (4x 0.5 points, HCl accepted in place of ammonium salt)
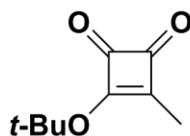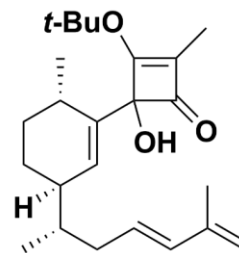
6)
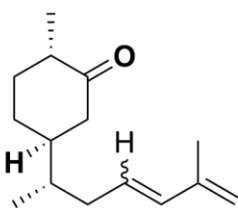
F	G	X	H
+1 p	+2 p	+2 p	+3 p

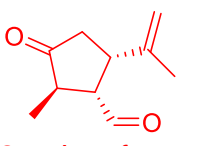*Marking: no marks for writing the chemical formula of **X** ($C_9H_{12}O_3$).*

7)

H

4π *electrocyclic ring opening* | 110 °C, μwave irradiation
THF

ketene **I**   +2 p

6π *electrocyclisation, then tautomerisation*

correct tautomers accepted

J   +2 p

oxidation   air, r.t.

+1 p total if any other PG than *t*-Bu ether depicted (1-time award)

−1 p for incorrect stereochemistry

L   +2 p

toluene, 150 °C
[4+2] cycloaddition

quinone **K**   +2 p

BF₃·OEt₂
0 °C
deprotection

(−)-Colombiasin A

22
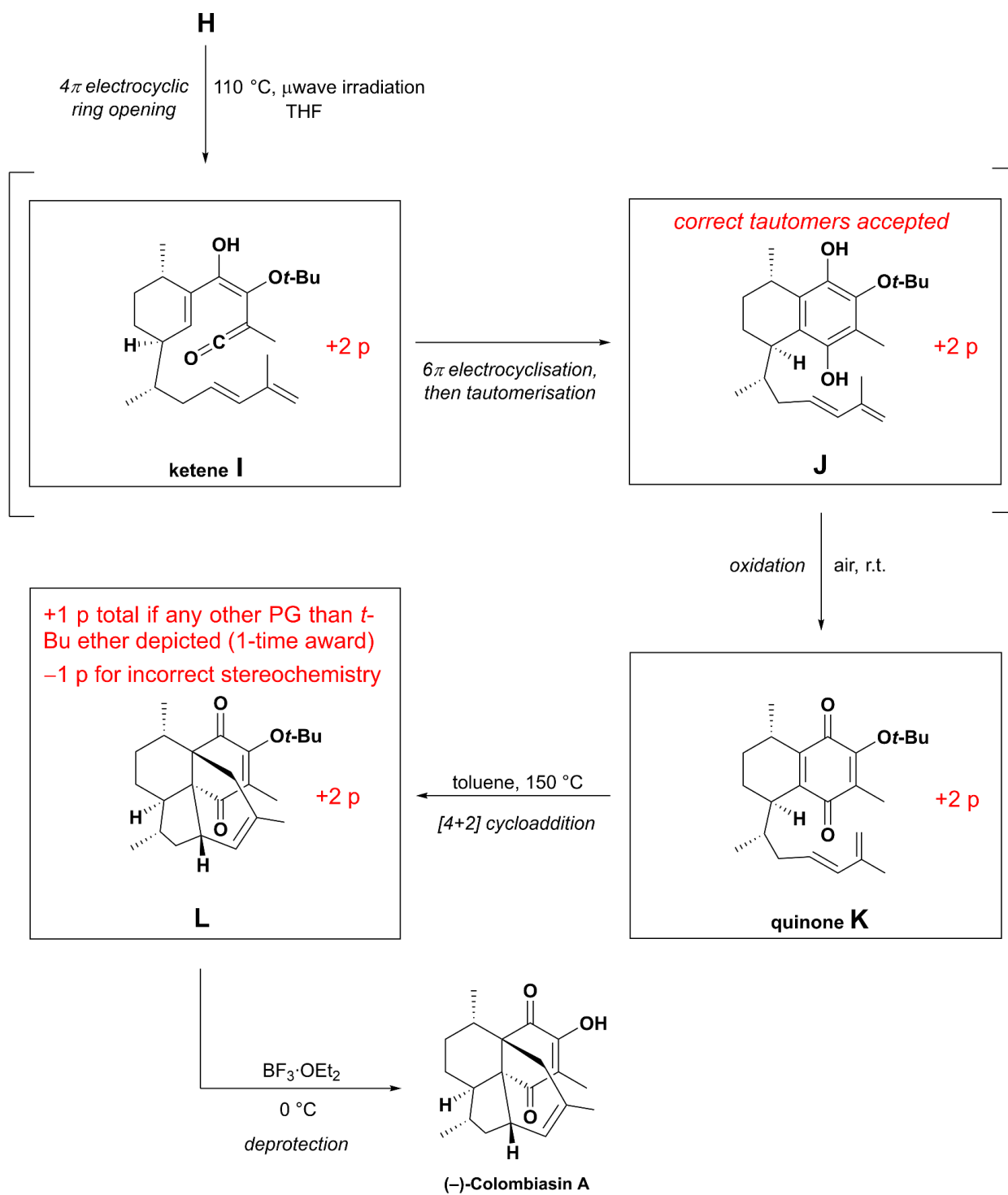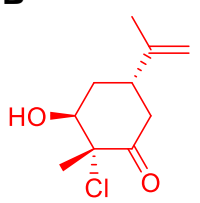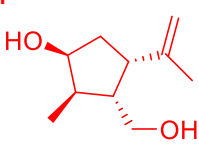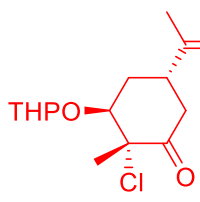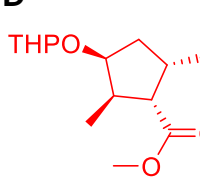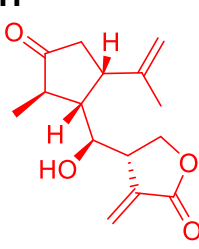
Problem 6. Chiral Pool

10 points

1.Determine the structures of compounds **B** – **D**, **F** – **H**. (15 points)
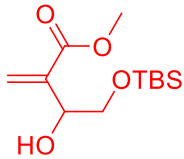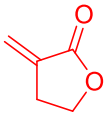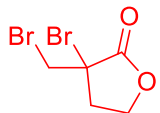
B	**F**
2 points for correct skeleton/regioselectivity +0.5 points for trans OH/Cl + 0.5 points for correct diastereomer	2 points for correct structure 1 point if reduced till aldehyde
C	**G**
2 points for correct structure 1 point if ketone was protected (through enol form instead of alcohol)	2 points for correct structure 1 point if only one of the alcohols were oxidized
D	**H**
2 points for correct skeleton/regioselectivity +1 point for ester and methyl trans	2 points for correct skeleton/regioselectivity +0.5 points for trans OH/lactone + 0.5 points for correct diastereomer

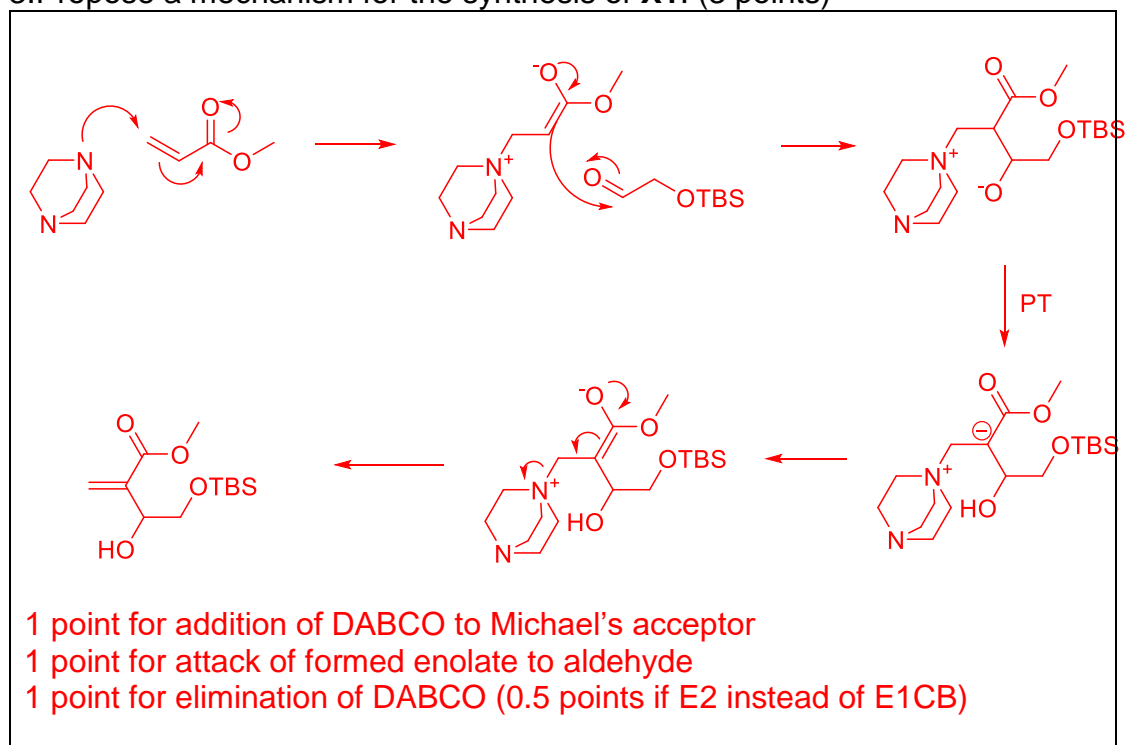The reagent **X** could be obtained in many ways. In the scheme below, two of the most popular routes are shown.

23
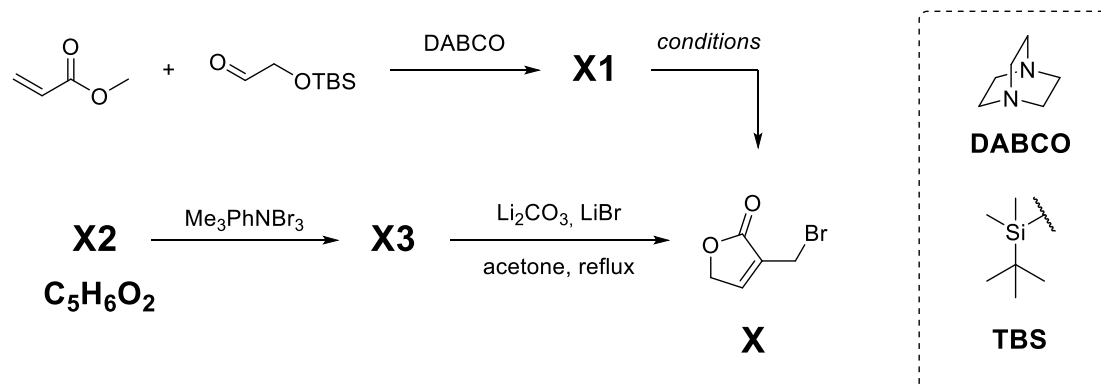
^{1}H NMR spectra of **X2**: 6.08 (t, J = 3 Hz, 1H), 5.63 (t, J = 3 Hz, 1H), 4.30 (t, J = 7 Hz, 2H), 2.97 (m, 2H).

2.Determine the structures of compounds **X1**, **X2** and **X3**. (6 points)

X1	**X2**
  2 points for correct structure 1 point if elimination on endo double bond	 2 points for correct structure 1 point for six-membered lactone
X3 2 points for structure 1 point if different dibromide isomer formed	*You can draw something nice here*

3.Propose a mechanism for the synthesis of **X1**. (3 points)

1 point for addition of DABCO to Michael's acceptor
1 point for attack of formed enolate to aldehyde
1 point for elimination of DABCO (0.5 points if E2 instead of E1CB)

4.Propose a reagent(-s) to obtain **X** from **X1** in **<u>one step</u>**. (2 points)

HBr (2 points)
1 point if proposed reagent can 1) remove TBS or 2) substitute OH to Br

The endgame of the synthesis was planned through a Swern oxidation followed by cyclization

to obtain the 8-epigosheimin (**K**). During the oxidation, an isomer **J1** was formed instead of the necessary **J2**. Although the endgame was quite short, in order to prove the absolute configuration, a different route was taken (through **L**).
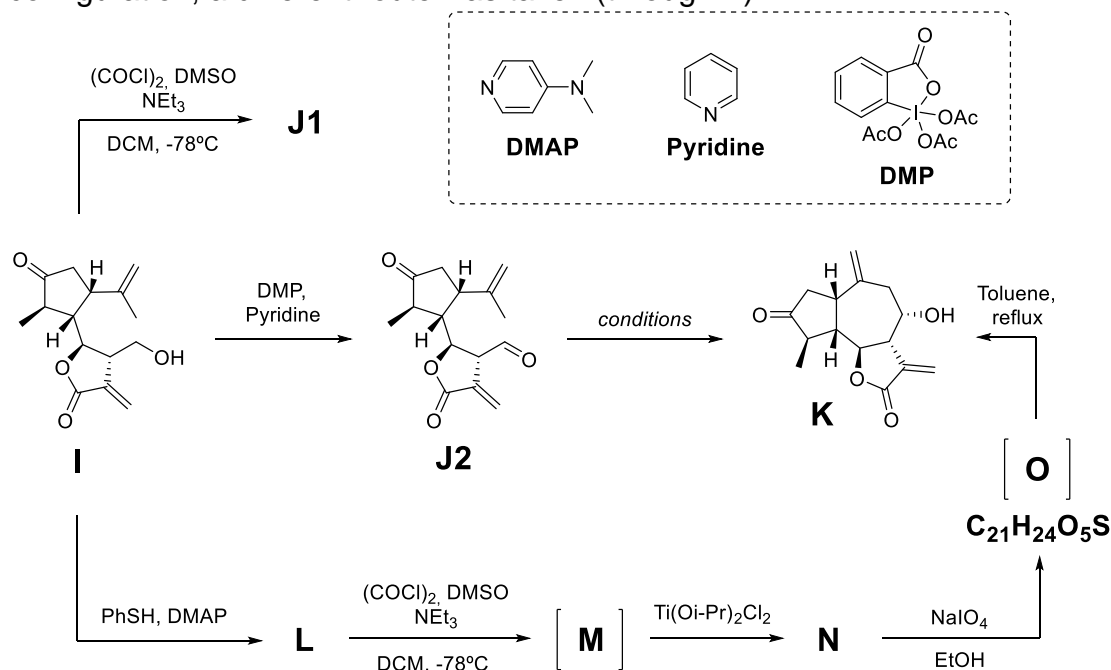
Note, that Ti(IV) salts are strong, oxophilic Lewis acids.

5. Determine the structures of compounds **J1**, **L** – **O**. (10 points)

J1	N
2 points for correct structure 1 point if epimerized any one of carbonyl's alpha positions	2 points for correct structure
L	**[O]**
2 points for correct structure (stereochemistry on new center not important)	2 points for correct structure 1 point if diol/epoxide formed instead
[M]	*Space for corrections*

  2 points for correct structure	26

6.Choose (from the set of conditions below) the appropriate conditions for the transformation of **J2** to **K**. (2 points)

☐ nBuLi, diethylamine
☐ MgSO$_4$, toluene, reflux
☐ BF$_3$·Et$_2$O
☐ NaOH, H$_2$O$_2$
☐ NaClO$_2$, NaH$_2$PO$_4$, tBuOH/H$_2$O
  2 points for correct one (minus 1 point for every additional conditions chosen)