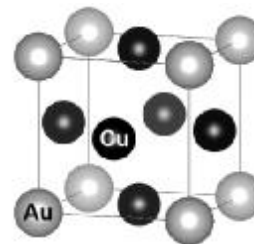


Section I. Inorganic chemistry

Problem 1

When we work with noble metal compounds, it is often need to extract them for later using. Thus, it was necessary to regenerate chemically pure metal **B** after synthesis of the intermetallic compound of the composition A_3B . For this, a sample of A_3B was dissolved in aqua regia (a mixture of nitric and hydrochloric acids). Ammonium nitrate solution was added to the solution, resulting in a yellow precipitate of **C** substance. The separation of this precipitate and following thermal decomposition at the air ($\sim 600^\circ\text{C}$) resulted in metal **B**.

1. Identify unknown substances **A** – **C** and write the mentioned chemical reactions if it is known that A_3B crystallizes in the Cu_3Au structure type (shown in the figure). In a cubic unit cell, Au atoms are located at the vertices of the cube, and Cu atoms – at the centers of all cube faces. The density of A_3B is $d = 14.674 \text{ g/cm}^3$, and the unit cell parameter is $a = 3.887 \text{ \AA}$.



2. Calculate the efficiency of **B** metal regeneration (percentage of regenerated metal) using the above method if 50 mL of a solution formed after dissolution of 1 g of A_3B in aqua regia. 50 mL of a 0.1 M solution of NH_4NO_3 was added to obtained solution. The solubility constant of **C** substance is $K_s = 9 \cdot 10^{-6}$.

The structure of binary substance **D** consists of isolated cluster particles – octahedra of **B** atoms with bridged chlorine atoms located above each edge of the octahedron. **D** dissolves in a cold HCl solution to form a dark red solution of substance **E**. When ammonia is rapidly added to **E**, a bright yellow complex substance **F** is formed, which has a molecular structure and turns into a yellow-green isomer under heating. The dark green substance **G** is precipitating under slowly (small portions) adding of ammonia to **E**.

3. Identify unknown substances **D** – **G** and write the mentioned chemical reactions.
4. Draw the structure of the isomers of the **F** compound.
5. Suggest the composition of the complex cationic and anionic parts of **G**, if it is known that molecular weight of **G** 2 times the molecular weight of **F**.
6. Specify the trivial name of the **G** substance among the options listed in the answer sheet.

Problem 2

A large number of borates are known with very different spatial structures, sometimes very exotic. This is due to the fact that boron and oxygen atoms can form fragments of BO_3 and BO_4 . These two types of fragments can be combined into spatial structures in the most bizarre combinations. In recent decades, much attention has been paid to the study of alkali metal borates due to the presence of some nonlinear optical properties in single crystals.

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In 2008 the article about synthesis and investigation of novel hydrated lithium borate **X** has been published. To synthesize **X** the mixture of 1.259 g monohydrate lithium hydroxide, 3.092 g orthoboric acid and 0.360 g water placed in stainless steel Teflon-line reactor (volume 40 cm³) and heated at 170°C during 3 days. After cooling the clear colorless crystals were separated from the mother liquor and dried at ambient temperature. It was obtained 2.103 g of product **X** (yield 82.0%).

From X-ray diffraction data the crystals of **X** contain lithium ions (mass fraction 6.77%), water of crystallization and large polyborate anion **A**, which is connected by six common oxygen atoms with neighboring anions to form two-dimensional network containing 13-membered anion cycles.

Anion **A** consists of two identical clusters **B**, linked through common oxygen atom. Each cluster **B** contains two structural fragments **C** with the same in composition and bonded through common oxygen atom too. The composition of each fragment **C** includes two groups BO₃ and two groups BO₄, moreover in one of them one terminal oxygen atom is protonated. The structure of each fragment **C** has two six-membered cycles with two common boron atoms. Included in the cluster **B** fragments **C** are connected through oxygen atom which is common for BO₃ and BO₄ groups (belonging to the different fragments **C**) and differ only in that hydroxo-groups in them are bonded to boron atoms in different hybrid states.

The thermal curve of **X** shows three endothermic peaks at 160°C, 291°C and 368°C. On heating from 35 to 245°C a weight loss of sample **X** comprise 8.77%. On heating in range from 326°C to 736°C a weight loss comprise 4.39% from weight of starting sample and formed substance **Y** melts.

1. Give stereochemical formulas of fragments BO₃ and BO₄ and specify hybrid state of boron atom in each of them.
2. What reagents were taken in excess on synthesis of **X**?
3. Specify molecular formula of **X** and the composition of anion **A**.
4. Give the reaction equation for synthesis of **X**.
5. Specify structure and give structural formulas of fragments **C** including in cluster **B** (oxygen atom which is common for two fragments **C** should be noted as O_c).
6. Draw structural formula of cluster **B** (oxygen atom which is common for two fragments **B** should be noted as O_b) and give its molecular formula.
7. Specify formula of **Y**. Give your calculations.
8. Write down the chemical reaction equation which takes place on thermal analysis of **X** in range from 245°C to 326°C.

Problem 3

Two of five oxides of element **X** (**X1** – **X5**) **X1** and **X2** are well studied; **X1**, **X2**, **X3**, **X4** are formed after acid dehydrations, and **X2**, **X3**, **X5** belong to structural formula X_mO_2 .

1. Decode oxides, if $M_{X3} - M_{X2} = M_{X5} - M_{X3} = 24$ g/mol; **X4** contains cycle X_6 and 6 fragments $XO_{1.5}$.
2. Draw the structural formulas of oxides, if they have bonds **X–X** (with distances 0.128; 0.139; 0.149 nm) and **X–O** (with distances 0.113; 0.117÷0.120; 0.140 nm).

In water, **X2** forms acid **A**, for which the reference constant is $K_1 = 4.45 \cdot 10^{-7}$, although, according to Pauling's prediction, it should be equal to $10^{-4} - 10^{-3}$ mol/L (K_a). Such inconsistency are explained by the fact that in the K_1 expression ($[A] + [X2]$) is in the denominator, not $[A]$.

3. Calculate K_a , if equilibrium constant for $X2 + H_2O \rightleftharpoons A$ $K = 1.67 \cdot 10^{-3}$.
4. Write the reaction equations of **X1** with OH^- and $[H_3C-Mn(CO)_5]$, and **X2** with $Zn-(CH_2CH_3)_2$ and OH^- (intruding fragments show as structure formulas).

Despite the difference in structure, **X1** and **X2** react similarly with OH^- and are built in the Me–C bond.

For a long time, it was considered that **X2**, unlike **X1**, cannot be a ligand in the complexes. In 1965, an attempt to substitute one ligand in $[Pt\{P(C_6H_5)_3\}_3]$ with **X2** turned out unsuccessful. Although 1/3 of phosphine was released, oxygen was involved in the reaction and it is found its amount associated with **X** to be more than in **X2**.

5. Decode the obtained complex **I**, if the mass fraction of oxygen is $W_O = 6.12\%$ in it.

Only in 1969 it was shown that complexes with **X2** can still be synthesized from solutions in benzene (toluene) in atmosphere of **X2**. Thus, the yellow solvated complex **II** ($W_O = 4.37\%$, $W_{C_6H_5CH_3} = 9.43\%$) was synthesized from the red $[Ni\{P(C_6H_{11})_3\}_4]$ in toluene at 25°C and $P_{X2} = 1$ atm. In 1992, **III** was synthesized with a different coordination of **X2**. For that, $[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]\{X1\}_3Re(X2)H$ was dissolved in THF and stirred for 24 hours with KOH up to red mixture coloring. The precipitate was separated, THF was removed from the filtrate on a rotary evaporator and brown crystals were obtained ($m_{III} = 6.143$ g; $v = 4.445 \cdot 10^{-3}$ mol).

6. Decode **II** and **III**, if to form 1 mol of **III**, in 1 mol of **X1** and an acid with the same oxidation state of element **X** as in **X1** is released and alkali is used to neutralize the latter.

7. Using X-ray diffraction data, draw structural formulas **I**, **II**, **III**.

Complex	Bond length, nm (number of bonds)			Valence angle, °		
	Me–X	Me–O	X–O	O–X–O	O–Me–O	O–Me–X
I	–	0.207	0.118; 0.128	143; 74	64	–
II	0.184(1)	0.199(1)	0.117; 0.122	133	–	37
III	0.186(5); 0.219(1)	0.220(2)	0.114(5); 0.124(2)	113	57	95

Section II. Analytical chemistry

Problem 1

1. a) In the middle of the 20th century the concentration of sulfhydryl groups was determined by using 4-chloromercuribenzoate 4-HOOC-C₆H₄-HgCl (BzHgCl). When analyzing a BzHgCl preparation, 5.00 mL of its 0.0375 M suspension was titrated with hydrocarbonate in the presence of bromothymol blue (BTB, transition range: pH 7.0–7.5), and 1.80 mL of 0.104 M hydrocarbonate was spent for this titration. Provide your calculations; write down the reaction equation.

b) In parallel, the same amount of BzHgCl was reacted with 0.375 mmol of cysteine, and the products of this interaction was titrated in the presence of BTB with the same hydrocarbonate solution, 3.60 mL of which was spent. Write the equation of the reaction of BzHgCl with cysteine. Provide your calculations.

2. A weighed portion (740 mg) of BzHgCl preparation was dissolved in 50 mL of acetate buffer. An aliquot (5.00 mL) was mixed with 5.00 mL of a standard 0.050 M solution of iodine in ethanol. For the titration of iodine excess, 5.00 mL of 0.0200 M thiosulfate solution were spent.

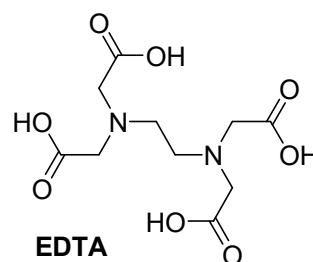
a) Write the equation of reaction of BzHgCl with iodine; b) find the percentage of impurities in the preparation.

3. Sulfhydryl groups are slowly oxidized by bromate, a mixture of two products being formed (bromate is often used as a dough improver to increase its elasticity). Suppose the nature of the functional groups of the oxidation products, find their amounts and write down the oxidation reaction schemes (indicate mercapto compounds as RSH), if a protein containing 1.00 mmol of SH groups reacted with 0.25 mmol of KBrO₃. Note that no sulfhydryl groups were left after this reaction. However, when an excess of sodium sulfite was added to the obtained oxidation products at pH 9.0 and titrated with a BzHgCl solution with amperometric indication, it required 0.90 mmol of the titrant, which confirmed the presence of sulfhydryl groups in the solution. Write down the reaction scheme of the sulfur-containing compound with sulfite. Show your calculations.

Problem 2

A young ecology chemist was examining the composition of local tap water. Following is the data that he obtained from an analytical laboratory. Unfortunately, some types were missed.

Ion	Concentration, mg/L
Cl ⁻	94.1
HCO ₃ ⁻	68.8
Ca ²⁺	---
X ⁺	14.2



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The chemist decided to measure calcium concentration on his own by means of titration. During titration of three analytes of 50 mL each with murexide as indicator measured volumes on burette were as follows: 7.75 mL, 15.45 mL, and 23.10 mL (the burette was not refilled between the titrations). The 0.01026 M solution of Complexone III (disodium EDTA salt) served as the titrant.

- Depict the structure of the complex of EDTA tetraanion with calcium.
 - Calculate the Ca concentration in water (mg/L).
- Determine **X** (assume that only components mentioned in the table are present in water).
 - Calculate the maximum weight of the precipitate that could be obtained if one adds an excess of silver fluoride to 100 mL of water with such composition. Write down corresponding chemical equations of precipitate formation.

6) *By what value* will change the weight of the precipitate if an excess of HCl is than added? (In the answer sheets put the '+' before the value if the weight of precipitate increases, and '-' if it decreases.)

The pH value of the water was found to be 8.0. Under these conditions $[Ca^{2+}][CO_3^{2-}]$ exceeds the solubility product ($K_{CaCO_3} = 4.76 \cdot 10^{-9}$) and after a while the precipitate of lime is formed.

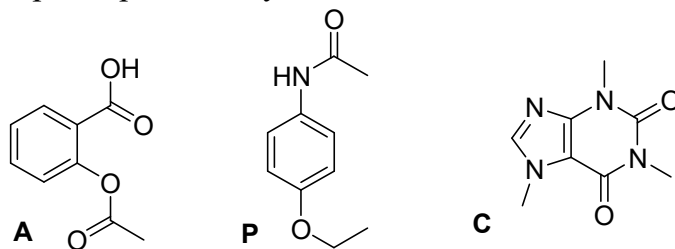
- Calculate the weight of the lime precipitate that is formed after ageing 1 m³ of water provided that the pH value finally decreases by 0.1.
 $K_a(H_2CO_3) = 4.0 \cdot 10^{-7}$, $K_a(HCO_3^-) = 4.7 \cdot 10^{-11}$.

To reduce water hardness one may use various reagents. A small amount of sodium orthophosphate was added to the initial water (see the beginning of the problem). After that, the Ca concentration decreased in 10 times.

- Write down the equation of the process described provided that the non-stoichiometric precipitate with the composition of $Ca_{10-x}(HPO_4)_y(PO_4)_{6-x}(OH)_{2-y}$ (x and y are to be calculated) and $Ca/P = 1.60$ is formed under the given conditions. Calculate the weight of the precipitate formed after the treatment of 1 tonne of hard water.

Problem 3

The pharmaceutical drug **APC** is a mixture of three medicinal agents: aspirin (**A**), phenacetin (**P**) and caffeine (**C**). For the quantitative analysis of this mixture the combination of methods: extraction, titrimetry and spectrophotometry is used.



500 mg tablet of the drug was powdered, dissolved in 100 mL of dichloromethane (CH₂Cl₂) and transferred to a separatory funnel. Aspirin (**A**) was quantitatively extracted from the organic

phase with 40 mL of 0.100 M NaOH. The distribution constant ($K_D = \frac{[A]_{org}}{[A]_{aq}}$) of aspirin is 10^5 and the acidity constant of aspirin is $pK_a=3.5$.

1. Why the aqueous solution of alkali is used for the extraction? Confirm your answer with the reaction equation.
2. Calculate the recovery (R , %) of aspirin from organic to an aqueous phase if it was extracted not with alkaline, but with a buffer solution at pH 7.
3. What is the minimum pH of the aqueous phase (40 mL) required to recover aspirin from 100 mL of dichloromethane by 99%?

The separated alkaline phase was boiled for 15 minutes, cooled and diluted in a volumetric flask to 100 mL. For the titration of 10.00 mL aliquot of the prepared solution in the presence of phenolphthalein 7.80 mL of 0.020 M HCl was used. Note that the pK_a of carboxylic acids is about 5 and of phenols is about 10.

4. Write the equations of the reactions taking place during the boiling of aspirin alkaline solution and titration of the prepared solution with hydrochloric acid.
5. Calculate the mass fraction (%) of aspirin in the sample of **APC** tablet.

The organic phase left after extraction was dried under anhydrous Na_2SO_4 and diluted with dichloromethane to a line in 250 mL volumetric flask. Then 1.00 mL aliquot was taken from the obtained solution and again diluted in a volumetric flask to 100 mL volume. The prepared solution of the mixture of phenacetin and caffeine was analysed spectrophotometrically at wavelengths (λ) 250 and 275 nm. The absorbances at these wavelengths were 0.465 and 0.160, respectively, for the cuvettes with 1 cm optical path length. The molar extinction coefficients ($\epsilon_\lambda, M^{-1}cm^{-1}$) of the compounds are given in the table:

Compound	$\epsilon_{250}, M^{-1}cm^{-1}$	$\epsilon_{275}, M^{-1}cm^{-1}$
Phenacetin (P)	12 566	2 846
Caffeine (C)	2 541	9 409

6. Calculate the mass fractions (%) of phenacetin and caffeine in the sample of **APC** tablet.

Section III. Life sciences and polymers

Problem 1

Technological contaminants are the substances that are not added to the foodstuff on purpose, rather appearing in the course of processing of raw materials. According to the WHO classification, some of these substances belong to the group of possible carcinogenic agents.

Contaminants **A**, **B**, and **C** are formed during processing of plant oils, of palm oil in particular. Being isomers, these compounds are mostly found in oil as residues at ester bonds.

1. Deduce the molecular formula corresponding to **A**, **B**, and **C**, if the substances contain 32.60% C and 6.38% H by mass and are composed of four elements.
2. Draw the structures of **A**, **B**, and **C**, if the molar ratio of **B** and **C** esters in the processed oil equals 1:1.
3. Propose the compound **X**, which is used for treatment of plant oils at high temperature and pressure. Note that this substance is directly involved in the formation of **A**, **B**, and **C** as well as their esters in the course of processing.

The presence of isomeric volatile acyclic compounds **D** and **E** in processed oil was demonstrated in a number of studies. These substances are composed of the same elements as **A**, the numbers of their atoms forming an arithmetic progression.

4. Deduce the structures of **D** and **E**, showing appropriate calculations and taking into account that **D** is free of chiral carbon atoms.

The compound **Y** is found in commercially available palm oil. **Y** is an ester of **A** with the molar ratio of O to C atoms of 1:7.

5. Draw all possible structural isomers of **Y** that are in agreement with the problem conditions, if the fatty acid(s) found in **Y** is(are) saturated and contain(s) an even number of carbon atoms (typical of fatty acids of plant origin).

Esters of the cyclic compound **F** containing 48.64% C and 8.16% H by mass are other contaminants formed in plant oil at temperatures above 180°C. The impact of these contaminants on human health is widely discussed now.

6. Deduce the structure of **F**, if it is a chiral compound containing atoms of three elements.
7. Explain the toxic effect of **F** on living things by writing down the schemes of its reactions with major biopolymers – nucleic acids and proteins (clearly show the reacting groups of the polymers).

The compound **G** is an ester of **F**. **G** is composed of four elements. It is found in man as a metabolite of a widely used drug **Z**.

8. Deduce the structures of **G** and **Z**, if the mass fractions of C and H differ by 26.03% in **G** (the molar ratio of 1.67:1, respectively). Calculations obligatory.

The polymer **H**, obtained on the basis of **G**, can be used as a rocket propellant. **G** is an unstable compound, its decomposition leading to a great number of various particles.

9. Mass spectrometry analysis of gaseous (under the experiment conditions) products of the decomposition of **H** has been reported. In particular, the authors proposed 4 variants of particles for the peak with $m/z = 44$. Give all the variants as molecular formulae.

Problem 2

Besides well-known lactose and fats, breast milk contains various sugars referred to as human milk oligosaccharides (HMO). As prebiotics, HMO contribute to protection from pathogens. Trisaccharide **A** is the major HMO. It is formed in man from disaccharide **B** ($M = 342.3 \text{ g/mol}$) and hexose **C**. In turn, the derivative of **C**, in which the first carbon atom is bound with guanine diphosphate (GDP), is also formed from **B** according to the following scheme:



ADP and ATP are adenosine di- and triphosphate, respectively, GTP is guanosine triphosphate, PP_i is inorganic phosphate, NADP^+ и NADPH are oxidized and reduced forms of nicotinamide adenine dinucleotide phosphate, respectively.

Only isomerization reactions of either interconversion between aldoses and ketoses or intermolecular transfer of the phosphate group (only one such step in the above scheme) are found on the way from **F** к **I**. The phosphate group is attached to either the first or the last carbon atom in the intermediates of the metabolic pathway under consideration. **F** and **H** are different compounds. Oxidation of **E** with concentrated nitric acid leads to an optically inactive compound **L** with hydroxyl groups oriented both sides in its Fischer projection. Similar reaction with the product of hydrolysis of **H** affords compound **M** with self-coinciding Fischer projection when rotated through 180° . **F** and **H** interact with the Tollens reagent, whereas **G** and **I** don't.

1. Write down the reaction of *D*-glucose with the Tollens' reagent.
2. Draw the structures of **D**, **E**, **F**, **G**, **H**, **I**, **L**, and **M**, if all these compounds (or their carbohydrate moieties) are *D*-isomers.

Each of **J** and **K** contain one keto group located at the 4th position. **GDP-J** transforms into **GDP-K** as a result of isomerization, which is neither interconversion between aldoses and ketoses, nor intermolecular transfer of phosphorylated fragments. This isomerization step affects both the 3rd and 5th carbon atoms.

Extensive oxidation by periodate is commonly used to analyze saccharides. Thus, oxidation of glucose by periodate leads to 1 equivalent of formaldehyde and 5 equivalents of formic acid, whereas that of fructose affords 2 equivalents of formaldehyde and 4 equivalents of formic acid. Oxidation of **C** with an excess of periodate leads to 1 equivalent of acetaldehyde and 4 equivalents of formic acid. **C**, **D**, and **L** belong to the same family.

3. Draw the structures of **J**, **K**, and **C**.

4. Write down the three-stage scheme of GDP-I transformation into GDP-J.

Methylation of **A** by MeI with subsequent complete hydrolysis leads to 1,2,3,6-tetra-*O*-methyl derivative of **D**, 3,4,6-tri-*O*-methyl derivative of **E**, and 2,3,4-tri-*O*-methyl derivative of **C**. Similar treatment of disaccharide **B** leads to 1,2,3,6-tetra-*O*-methyl derivative of **D** and 2,3,4,6-tetra-*O*-methyl derivative of **E**. Monosaccharide units are linked by the bond of β type in **B**, whereas the residue of **C** exists in the α -anomeric form.

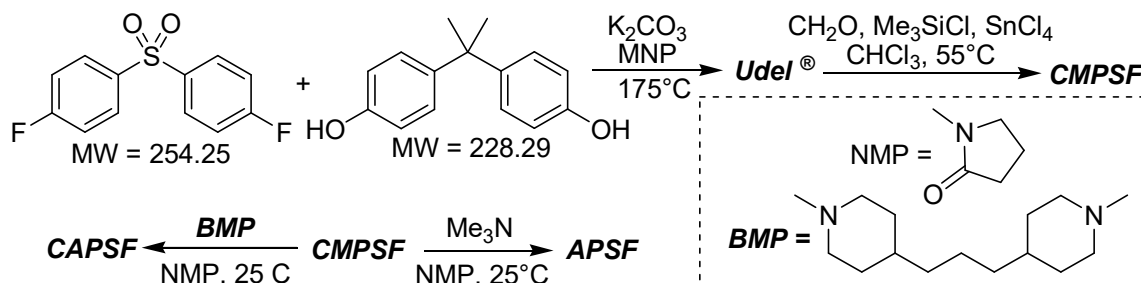
5. Draw the structures of **B** and **A**.

Another HMO **N** is an isomer of **A**. **N** affords the following products of methylation and hydrolysis: 1,2,6-tri-*O*-methyl derivative of **D**, 2,3,4,6-tetra-*O*-methyl derivative of **E**, and 2,3,4-tri-*O*-methyl derivative of **C**. There are no differences in the conformations of monosaccharide residues present in **A** and **N**.

6. Draw the structure of **N**.

Problem 3

Crosslinking (curing) of linear polymers is an important industrial process. The products are insoluble and cannot be molten, yet acquire valuable mechanical properties. Crosslinking can be readily performed, if the polymer bears suitable functional groups. For example, two polymers (**APSF** and **CAPSF**) were produced from **Udel**[®] polymer (Scheme 1).



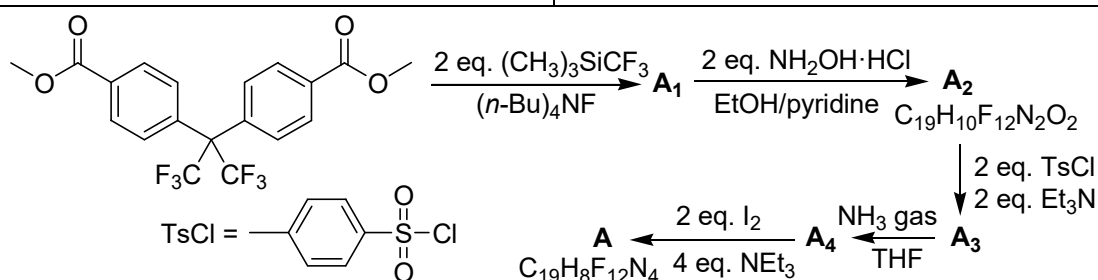
Scheme 1. Synthesis of polymers **APSF** and **CAPSF**.

1. Draw the structure of **Udel**[®] and calculate its degree of polymerization, if it was prepared from 50.85 g of the monomer with MW 254.25 and 45.66 g of the monomer with MW 228.29. Note that the reaction afforded 23.18 g of the inorganic product.

2. Draw the structures of **CMPSF**, **APSF**, and **CAPSF**, if **CMPSF** was synthesized from the entire portion of **Udel**[®] prepared as described in i. 1 and 6.0 g of paraform.

3. Correlate the polymer classes given in the Answer Sheet with **APSF** and **CAPSF**.

Curing of polymers containing no reactive functional groups is complicated. However, a recently developed agent **A** is capable of crosslinking virtually any polymers containing C-H bonds:



Scheme 2. Synthesis of the crosslinker **A**.

4. Draw the structures of **A**₁ – **A**₄ and **A**.

To determine the efficiency of the interaction of **A** with a C–H bond, the agent was subjected to heating at 110 °C in cyclohexane, which afforded compound **B** (C₃₁H₃₂F₁₂) as a mixture of two diastereomers with the total yield of 9.5%. Both diastereomers were characterized by 12 signals in the ¹³C NMR and 2 signals in the ¹⁹F NMR spectra.

5. Draw the structure of **B**. Determine the probability of the reaction of a single group in **A** with cyclohexane during the conversion of **A** into **B**. Note that the reactive fragments are completely consumed.

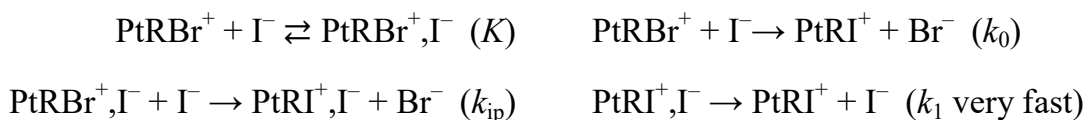
A melt of linear polyethylene (*M* 50000) was treated with **A** as described above in the case of cyclohexane. The reaction yielded a crosslinked polymer.

6. Estimate the minimal amount of **A** (in mass %) sufficient for complete loss of polyethylene solubility due to curing, considering that the probability of the reaction of **A** with aliphatic C–H bonds of cyclohexane and the polymer is the same.

Section IV. Physical chemistry

Problem 1

In non-aqueous solvents, nucleophilic substitution reactions often proceed with the formation of an ion pair. In 1965 an unusual mechanism was proposed for the reaction in methanol $\text{PtRBr}^+ + \Gamma^- \rightarrow \text{PtRI}^+ + \text{Br}^-$ (R – four dentate ligand tris-(o-diphenylarsinophenyl)arsin) with the formation of not one but two ion pairs:



1. Suggest the formulas for calculating the mole fractions PtRBr^+ и PtRBr^+, Γ^- in equilibrium with excess of Γ^- ($[\Gamma^-] \approx C_1$).
2. Derive the kinetic equation and the expression for the observed rate constant (k_{obs}) using the method of stationary approximations.
3. Take an approximation and suggest the linear kinetic equation and the expression for the k_{obs} at high C_1 concentration.

By processing the spectral data the following results were obtained for this reaction at 25°C and concentrations of PtRBr^+ $C_0 = 10^{-4}$ mol/L:

C_1 , mol/L	$2 \cdot 10^{-2}$	10^{-2}	$8 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	10^{-3}	$7 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
k_{obs} , s ⁻¹	0.674	0.384	0.326	0.199	0.0968	0.0813	0.0685	0.0513

4. Draw the plot $k_{\text{obs}} = f(C_1)$, indicate the linear section where $k_{\text{obs}} = k + k_{\text{ip}}C_1$ and calculate k_{ip} and k . Explain the dependence of k on the nature of the nucleophile.

Since it is impossible to calculate K from kinetic data, it was estimated independently by conductometric method from the values of specific conductivity L (Ohm⁻¹cm⁻¹): PtRBr^+ ($C_0 = 1.33 \cdot 10^{-4}$ mol/L, $L = 1.54 \cdot 10^{-5}$); Γ^- ($C_1 = 1.33 \cdot 10^{-4}$ mol/L, $L = 1.53 \cdot 10^{-5}$); ($\text{PtRBr}^+ + \Gamma^-$) ($C_0 = C_1 = 1.33 \cdot 10^{-4}$ mol/L of each in the mixture, $L = 2.35 \cdot 10^{-5}$).

5. Calculate molar conductivity Λ (Ohm⁻¹cm²mol⁻¹) for PtRBr^+ and Γ^- . Assuming that $[\text{PtRBr}^+] + [\Gamma^-] = 1000L/\Lambda_{\text{av}}$ (Λ_{av} – average molar conductivity of PtRBr^+ and Γ^-), estimate K and k_0 .
6. Calculate the ratio of contributions of the routes with k_0 and k_{ip} at $C_1 = 10^{-3}$ and 10^{-2} mol/L.

It turned out that the coordination of nucleophile in the first ion pair does not depend on its charge and is carried out due to the van der Waals forces.

7. Considering steric hindrances for the attack on Pt^{2+} by nucleophile, indicate the most probable atom for the attack and show the formation of ion pair with structural formulas.

Problem 2

Richard Zsigmondy, the first Hungarian Nobel Prize winner, is known for the studies of colloidal systems. He developed a method of gold nanoparticles preparation independently of Michael Faraday.

1. Write the equations of reactions occurring during the synthesis of gold nanoparticles in an aqueous solution of chloroauric acid (HAuCl₄) under the action of a) phosphorus (the Faraday method) and b) formaldehyde (the Zsigmondy method).

Using the so obtained gold nanoparticles, Zsigmondy demonstrated that a well-known substance used in the production of red glass was a mixture of two different nanoparticles, rather than an individual compound (as Jöns Berzelius suggested). The dye samples were produced either a) via the mixing of 348.7 mg of Au and 400.0 mg of compound **A** or b) via the reaction between 901.9 mg of HAuCl₄ and 754.9 mg of compound **B**. Compounds **A** and **B** contain 78.8 and 62.6% of element Z, respectively. The Au/Z ratio in the produced samples was found identical.

2. Determine element Z and compounds **A** and **B**; write the equation of the described reaction. Support the answer with calculations.

3. Which formula could be assigned by Berzelius to the product of the interaction between HAuCl₄ and **B**, having known its qualitative composition, Au/Z ratio and suggesting that it is a salt?

Special properties of nanoparticles are explained by the presence of a considerable fraction of the atoms at the surface, their valence state differing from that in bulk.

4. Considering that gold nanoparticle is a spherical crystalline particle with face-centered cubic lattice (the unit cell parameter 4.07 Å, particle diameter 5.00 nm), determine the number of gold atoms at the surface (those forming the outer shell of atoms) and their fraction with respect to total number of atoms.

Detailed mechanism of HAuCl₄ reduction during the nanoparticles preparation has remained unclear. Kinetics of the decreased in HAuCl₄ concentration under the action of formic acid (pH 3.0) has been recently studied. Reduction of HAuCl₄ does not occur in the absence of formic acid. The kinetics of Au(III) concentration decrease can be expressed as $c_{\text{Au(III)}} = c_{\text{Au(III),0}} e^{-kt}$. The table below shows the apparent rate constant k values at certain starting concentrations of the reactants.

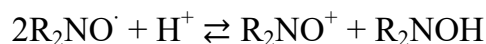
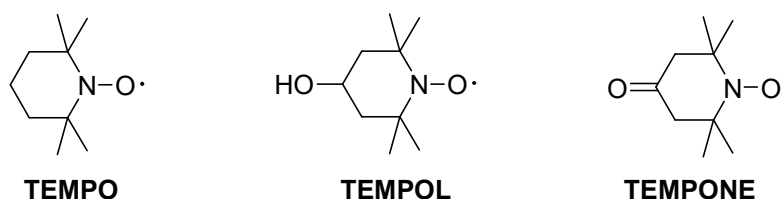
$c(\text{HAuCl}_4)_0$, mmol/L	$c(\text{HCOOH})_0$, mmol/L	k , s ⁻¹
0.0075	7.5	0.393
0.015	2.5	0.093
0.015	5	0.243
0.015	7.5	0.393
0.015	10	0.543
0.015	12.5	0.693
0.015	15	0.843

5. a) Write an equation expressing the dependence of k on the starting concentration of formic acid. b) Determine the rate order of the reaction between HAuCl₄ and HCOOH with respect to HCOOH.

6. Draw a stage-by-stage scheme of the formation of Au from HAuCl_4 during the interaction with HCOOH . Consider that the Au(0) nanoparticles are detected much later than a significant decrease in HAuCl_4 concentration is observed, and the addition of NaCl decelerates the formation of gold nanoparticles but does not affect the kinetics of Au(III) consumption.

Problem 3

Nitroxide radicals are stable radicals widely used in electron paramagnetic resonance spectroscopy (EPR) as spin labels and spin probes. However, in acid solutions they reversibly disproportionate via single electron transfer which turns them into non-radical species: oxoammonia cation and hydroxylamine derivative. The latter species cannot be detected by EPR technique.



A solution containing $1 \cdot 10^{-3}$ M of TEMPONE was acidified with hydrochloric acid up to pH 3.0 then sealed. At equilibrium point the amount of the radical species decreased by 22.5 times according to EPR.

1. Evaluate the equilibrium constant.

At high pH the following equilibrium predominates:



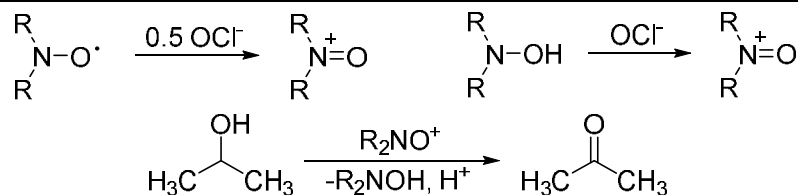
2. a) Calculate the equilibrium constant of this reaction; $\text{p}K_a(\text{R}_2\text{NOH}) = 8.0$; b) What percentage of initial concentration comprises the equilibrium concentration of the radical at high pH values?

3. a) Standard electrode potentials for $\text{R}_2\text{NO}^+/\text{R}_2\text{NO}$ system at 25°C is 0.946 V. Calculate the standard electrode potentials for $\text{R}_2\text{NO}\cdot/\text{H}^+/\text{R}_2\text{NOH}$ system; b) What is the equilibrium electrode potential for $\text{R}_2\text{NO}\cdot/\text{H}^+/\text{R}_2\text{NOH}$ system under conditions of question No. 1?

Hydroxylamine derivatives in acidic media may be *slowly* oxidized by ambient oxygen to oxoammonium salts. 10 mL of 0.025 M solution of TEMPOL-H were kept at pH 1.46 for 2 days and then neutralized to pH value of 8 (the volume change is negligible). A test portion of $7 \mu\text{L}$ was taken from this solution and the presence of nitroxyl radicals with an amount of $1.69 \cdot 10^{16}$ was found by means of EPR.

4. Calculate the average rate of oxidation of TEMPOL-H by ambient oxygen.

One can use nitroxyl radicals to oxidize primary and secondary alcohols to obtain aldehydes and ketones, respectively:



5. Consider 0.1 mole of an alcohol, 3.725 g of NaClO and 1.560 g of TEMPO. What amount of alcohol will be oxidized in this system?
6. Some times a catalytic amount of NaBr is added to speed up the oxidation. Suppose a mechanism explaining its catalytic activity.
7. The oxidation of benzyl alcohol was conducted with the help of TEMPOL radical. However, after the reaction is over and nitroxide is regenerated, TEMPOL was not found in the solution. Suppose structure of the new radical.

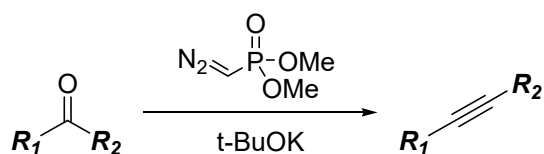
Additional data: Nernst equation: $E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$.

The relation of the Gibbs energy of reaction to its EMF: $\Delta_r G^0 = -nFE^0$, $F = 96500 \text{ C/mol}$

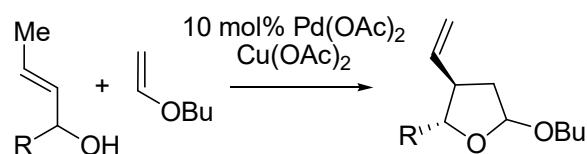
Section V. Organic chemistry

Problem 1

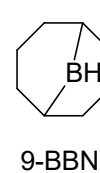
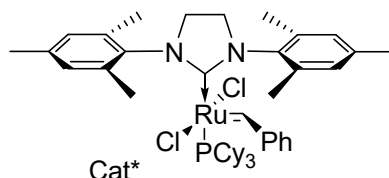
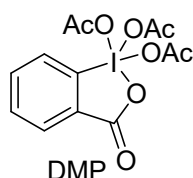
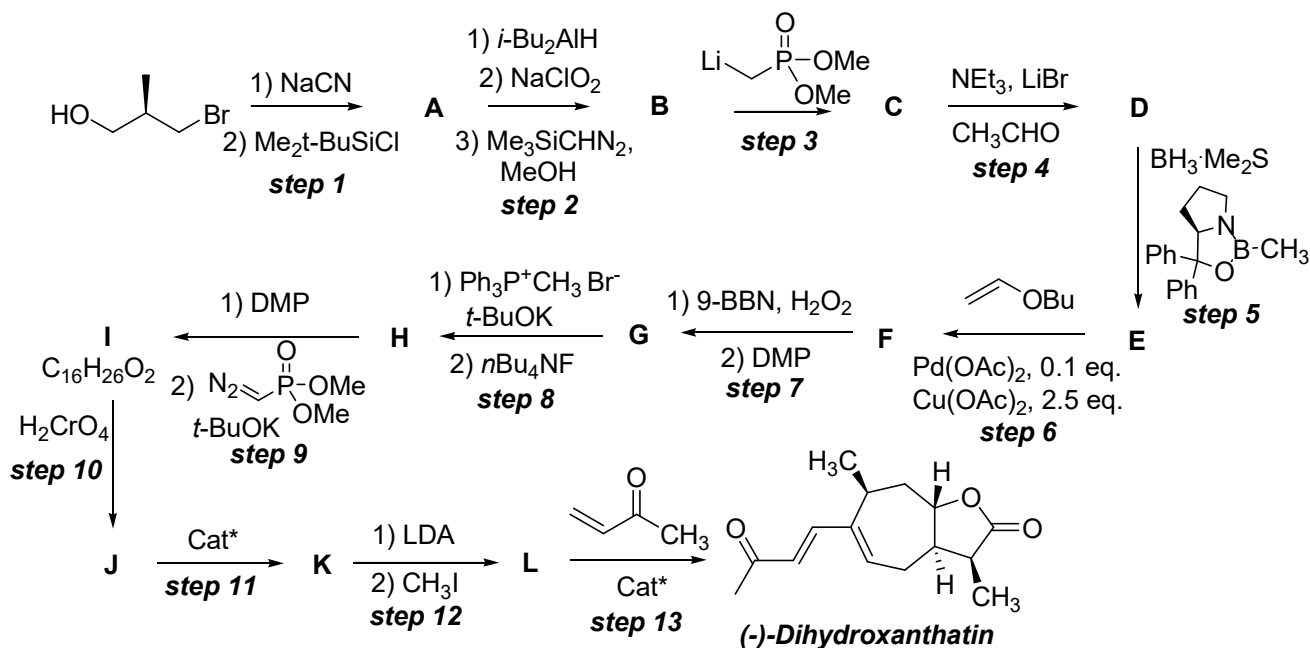
It is a tradition to call significant reactions and reagents in organic chemistry the names of their discoverers. This tradition is still in use. In the 1970-80s the homologation reaction of carbonyl compounds was discovered independently of each other by Dietmar Seyferth and John Gilbert (Scheme 1). In the late 1980s, a reaction of the formation of tetrahydrofuran derivatives from allyl alcohols and vinyl esters catalyzed by palladium salts was discovered by Japanese chemists Koichiro Oshima and Kiitiro Utimoto (Scheme 2). Nowadays, these name reactions were used by James Morcken to prepare natural compound *(-)*-Dihydroxanthatin (Scheme 3).



Scheme 1. Seyferth–Gilbert reaction



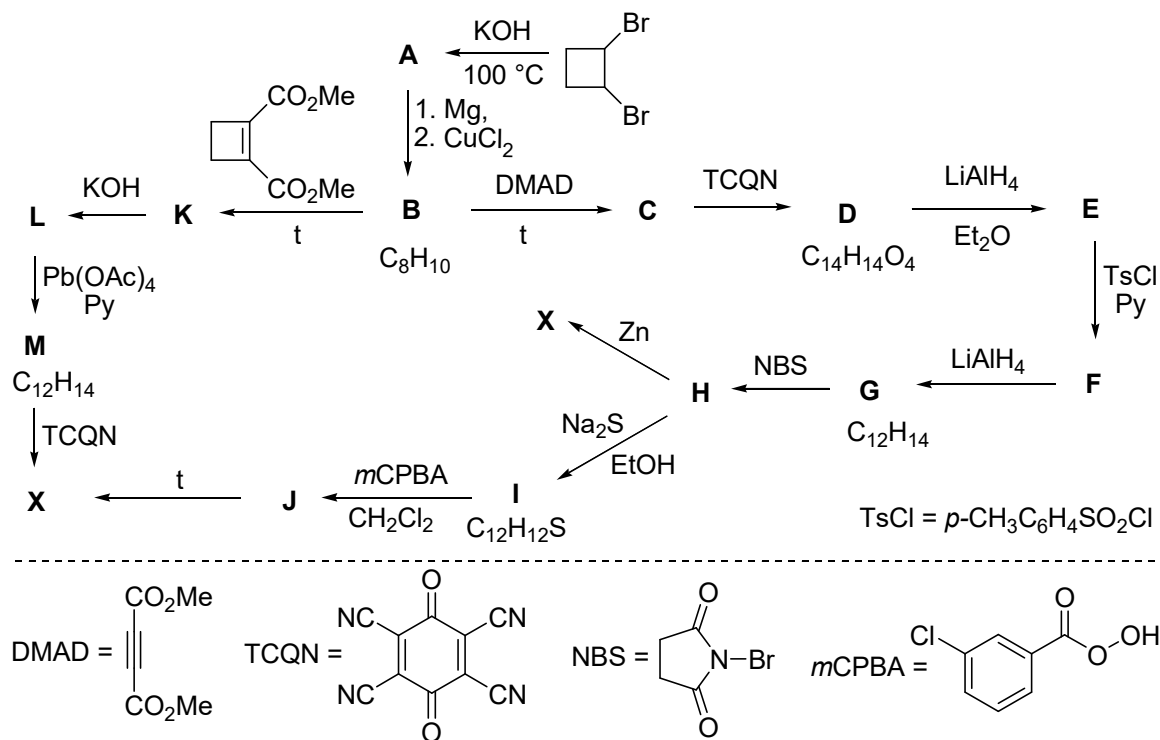
Scheme 2. Oshima-Utimoto reaction

Scheme 3. Total synthesis of *(-)*-Dihydroxanthatin

1. Give the structure of compounds A – L, taking into account stereochemistry, if:
 - Oshima-Utimoto reaction leads to the formation of the tetrahydrofuran ring, which is not affected in further transformations;
 - D – more thermodynamically stable stereoisomer.

Problem 2

In 1930, Mills and Nixon tried to explain the chemical behavior of condensed aromatic systems, taking into account that the tension energy could lead to the bond localization in these structures. This effect was named in honor of these two chemists and since that time a lot of experimental and theoretical chemists made great efforts to clarify if this effect exists in reality. In the framework of these studies, quite a lot of interesting model compounds was synthesized. Thus, substance **X** ($C_{12}H_{12}$) was obtained also in this scope. The schema below show how this compound **X** could be obtained from compound **A** which synthesises in one stage from 1,2-dibromocyclobutane:



Substance **X** has one signal in the ^1H NMR spectrum and 2 signals in the ^{13}C NMR spectrum. The compound **X** also has a 3rd order symmetry axis. The substance **C** in the ^{13}C NMR spectrum does not contain characteristic signals of sp -hybridized carbon atoms. The reactions $\text{B} \rightarrow \text{C}$ and $\text{B} \rightarrow \text{K}$ are the same type reactions.

1. Find all unknown substances **A** – **M** and **X**.

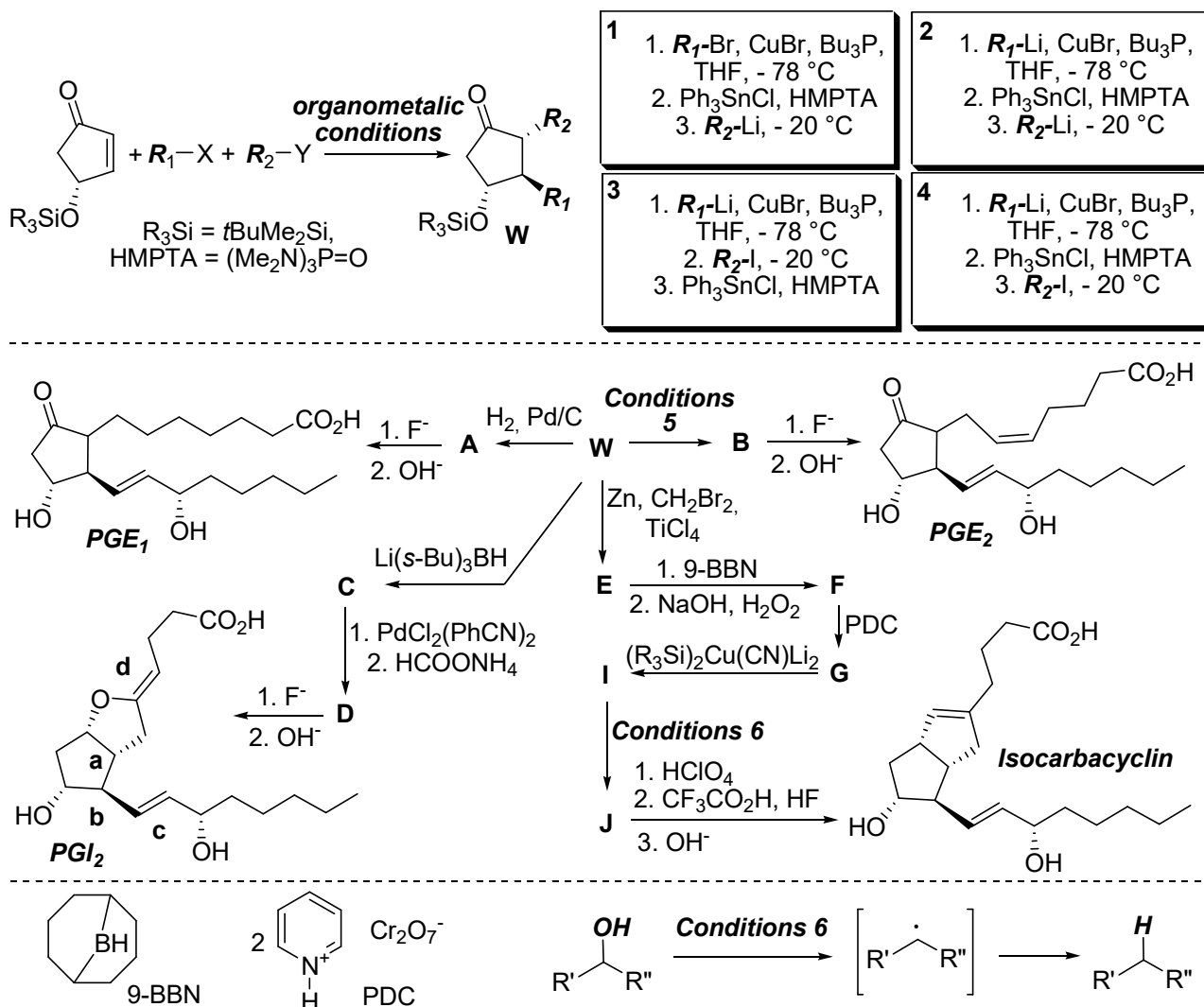
It was expected that the hydrocarbon **X** could be obtained in one step from an isomeric cyclic hydrocarbon **Y** that does not have sp^2 -hybridized carbon atoms, but the product was another hydrocarbon **Z**, the isomer of **X**. The compound **Z** has only sp^2 -hybridized carbon atoms and one signal in ^1H NMR spectrum.

2. Give the formula of hydrocarbons **Y** and **Z**.

3. Compound **X** has four types of carbon-carbon bonds with next distances: 1.384, 1.401, 1.517, and 1.569 Å; compound **Y** has three types of carbon – carbon bonds with distances of 1.213, 1.467, and 1.539 Å, while **Z** has only two different C–C lengths of 1.332 and 1.495 Å. Relate the lengths to the specific bonds with the given compounds.

Problem 3

Organic synthesis is pivotal in developing of interdisciplinary scientific research such as biochemistry, pharmacology and medicine. In this context, the synthesis of prostaglandins is one of the triumphs of synthetic organic chemistry. In the 1980s, the group of future Nobel laureate Ryoji Noori proposed a “three-component” synthesis of a series of prostaglandins and their synthetic analogues from the general intermediate **W**, which was synthesized according to the scheme below using one of the sequences of reagent addition.



- Select one box with correct conditions from proposed **1-4** and give (using the notation R_1 and R_2) the intermediates formed after the first and second addition of the reagents.
- Decipher **W** and R_1 -X и R_2 -Y, which were used for this synthesis. Write the structures of compounds **A** and **B**. Write the condition(s) converting **W** to **B** (Conditions 5 in the Scheme). Note that compound **W** is methyl ether and bearing the equal protective groups on alcohol oxygen.
- Decode the compounds **C** – **J**. Note that under the conditions of the transformation **I** → **J**, the alcohol group is formally removed through the radical intermediate. Also note that compound **J** is bicyclic and contain an allyl silane fragment.