Problems of the 2024/25 National Chemistry Olympiad
11th and 12th grade

1. From Ores to Clusters (10 p)

Tungsten is usually found in nature in the form of tungstate minerals with the general chemical formula **M**WO_4 (**M** = a certain metal). The main minerals are wolframite and scheelite ($CaWO_4$). Wolframite is a mixture of the tungstates of two metals $\mathbf{M}_1$ and $\mathbf{M}_2$.

a) It is known that in a 1.000 g sample of wolframite, the mass percentage of $\mathbf{M}_1WO_4$ is exactly 30.0%. The same amount of sample also contains 0.6058 g of tungsten and 0.1832 g of the metals $\mathbf{M}_1$ and $\mathbf{M}_2$. Identify the metals $\mathbf{M_1}$ and $\mathbf{M_2}$, show calculations! (2)

When tungsten reacts with fluorine, it forms the only known gaseous *d*-metal compound **X** at room temperature, which is 10.27 times heavier than air (M = 29 g·mol^{-1}). Compound **X** is sensitive to moisture in air and reacts with water vapor to form a yellow oxide **Y** (w_{oxygen} = 20.71%).

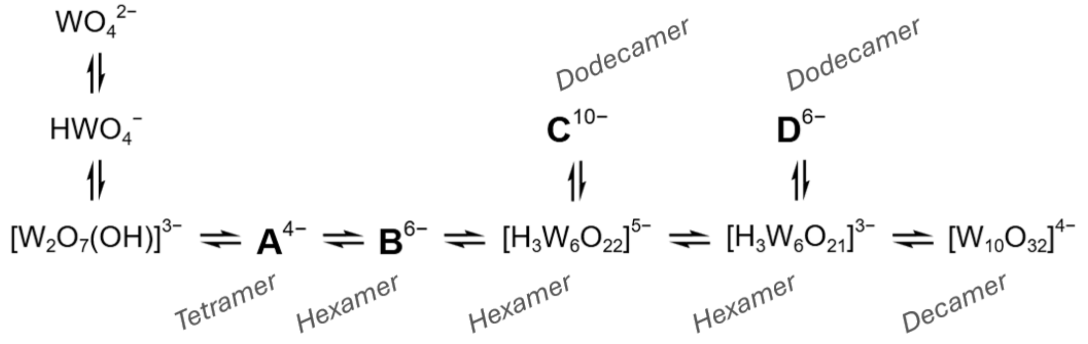
b) **i)** Determine the formulas of **X** and **Y**, showing the corresponding calculations! (1)

ii) Calculate the density of gas **X** (g·cm^{-3}) under the standard conditions (T = 298 K and p = 10^5 Pa). The universal gas constant R = 8.314 m^3·Pa·K^{-1}·mol^{-1}. (1)

When scheelite is treated with a concentrated nitric acid solution, a yellow precipitate of tungstic acid, which is poorly soluble in water, is formed. Tungstate anions present in solution have a tendency to polymerize at low pH, which is represented by the following general reaction equation:

$$n\,WO_4^{2-} + m\,H^+ \rightarrow H_xW_nO_{4n-\frac{(m-x)}{2}}^{(2n-m)-} + \frac{(m-x)}{2}\,H_2O$$

During the condensation reactions, the coordination number of tungsten atoms increases from four to six. Subsequent aggregation then leads to the formation of higher polyoxotungstate clusters, whose structural units are connected to each other through W–O–W bridging bonds.



Vihjed:

- *In anion A^{4-}, the mole ratio of hydrogen to oxygen is 1 : 4.*
- *In anion B^{6-}, there are two times fewer hydrogen atoms than in anion A^{4-}.*
- *In anions C^{10-} and D^{6-}, the number of tungsten atoms is six times greater than the number of hydrogen atoms.*

c) Draw the planar structural formulas of **i)** HWO_4^- and **ii)** $[W_2O_7(OH)]^{3-}$. (1)

d) Identify the chemical formulas of anions **A**–**D**. (2)

e) Write and balance the following reaction equations, using the previously given general reaction representation: (1)

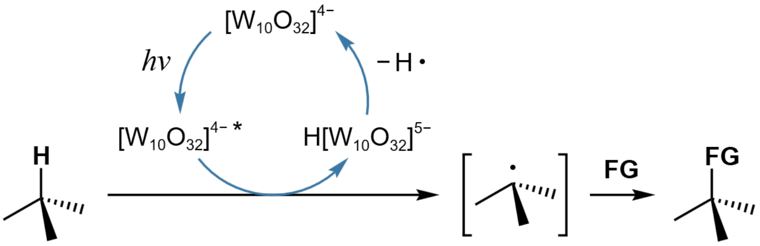
i) the formation of $[H_3W_6O_{22}]^{5-}$;

ii) the single-step reaction equation for the transformation $[H_3W_6O_{22}]^{5-} \rightarrow [W_{10}O_{32}]^{4-}$.

Tungsten oxopolymetallates have historically also been described stoichiometrically through the content of tungstate and the metal oxide **Y**, at a time when the actual structures of the corresponding anions were not yet known.

f) Express the formulas of **i)** D^{6-} ja **ii)** $[W_{10}O_{32}]^{4-}$ in the form of $x WO_4^{2-} \cdot y\mathbf{Y} \cdot zH_2O$. (1)

TBADT, i.e. (n-$Bu_4N)_4[W_{10}O_{32}]$ is the ammonium salt of decatungstate, which is used as a catalyst in organic synthesis. TBADT mediates photocatalytic HAT hydrogen atom transfer reactions, enabling the functionalisation of C(sp^3)−H bonds. FG = functional group.



g) Answer the questions by choosing the appropriate answer. (1)

i) What type of reaction occurs in the transformation $[W_{10}O_{32}]^{4-} \rightarrow H[W_{10}O_{32}]^{5-}$?

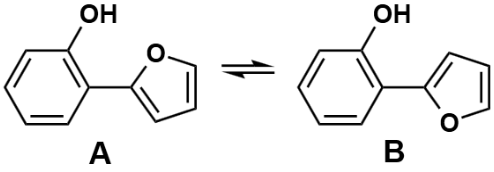
☐ Oxidation
☐ Reduction
☐ Comproportionation
☐ Disproportionation

ii) With which C(sp^3)−H bond does the HAT reaction occur the fastest in the catalytic cycle?

☐ 1° primary C−H
☐ 2° secondary C−H
☐ 3° tertiary C−H
☐ The HAT reaction occurs equally fast in all of the above mentioned cases

2. Conformer Puzzle (10 p)

Conformers are different 3D shapes of molecules that are in dynamic equilibrium with each other. Unlike isomers, whose interconversion requires breaking covalent bonds, conformational transitions occur through rotation of molecular groups around single bonds. In different solution environments, the stability (and thus the proportion) of conformers can vary. Below are two conformers of 2-(furan-2-yl)phenol (for simplicity, we can ignore the rotation of the OH group around the C–O bond). The proportion of conformer **A** is 80% in chloroform, 1% in tetrahydrofuran, and 5% in benzyl alcohol.



a) Determine which conformer (**A** or **B**) predominates in each of the following solvents. (2)

Solvent	**Preferred conformer**
Acetone	
Dimethyl sulfoxide	
Dodecane	
Isopropyl acetate	
White spirit	
Methanol	
Toluene	
Triethylamine	

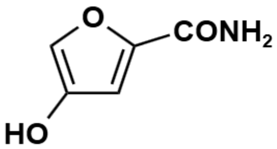
b) The Gibbs free energy change of the transition shown in the scheme in a certain solvent at 20 °C is −0.66 kcal·mol^{-1} (1 cal = 4.184 J). Calculate the percentages of conformers **A** and **B** under these conditions. Universal gas constant R = 8.314 J·mol^{-1}·K^{-1}. (2)

c) The Gibbs free energy of a particle in a liquid is the sum of its energy in the gas phase and its solvation energy. The fraction of conformer **A** in the gas phase at 28 °C is 93%. Calculate by how many kcal·mol^{-1} conformer **B** must be more strongly solvated than conformer **A** in order to become the predominant conformer in solution at the same temperature. (2)

d) Place the following substances in the table according to their properties: albumin (protein), benzene, diethyl ether, dichloromethane, phenolphthalein, tetrabutylammonium, cyclohexane. Each substance must be used at least once, and the same substance may appear in multiple cells. (2)

Property	**Substances**
The spatial structure of the molecule changes when the pH of the solution decreases 7 → 3	
The spatial structure of the molecule changes when the pH of the solution increases 7 → 10	
The relative stabilities of multiple conformers of the substance practically do not depend on the pH of the environment	
The substance has only one conformer	

e) Determine how many possible conformers 4-hydroxyfuran-2-carboxamide has, given that all conformers are planar. Consider rotation around C–O and C–N bonds. (1)



f) The lifetimes of 1,3-propanediol conformers in aqueous solution at room temperature are a few picoseconds (ps) to a few tens of ps. Mark one or more correct statements. (1)

☐ The conformer mixture of this substance can be separated chromatographically and the amount of each conformer measured this way.

☐ To study conformers present in a dilute solution, the solution can be evaporated and the conformers examined in the precipitated crystals.

☐ At lower temperature, the lifetime of conformers increases.

☐ Conformers with higher Gibbs free energy have longer lifetimes.

3. Acid Strength in Aqueous and Non-Aqueous Solutions (9 p)

The strength of an acid HA in a solvent S is characterized by the value of the equilibrium constant K_a of the acid dissociation reaction:

$$HA + S \rightleftharpoons SH^+ + A^-$$

The acid dissociation reaction can be described through the standard Gibbs free energy change:

$$\Delta_{diss}G° = -RT\ln K_a$$

K_a ja pK_a values depend significantly on the solvent's ability to solvate/stabilize ions (and neutral molecules) and thereby promote ion formation. Water is a highly polar protic solvent that strongly solvates both cations and anions. Consequently, acids dissociate more extensively in water than in most non-aqueous solvents. Accordingly, since ionic species are on the right side of the acid dissociation equation, K_a values for acids are usually higher in water than in non-aqueous solvents of lower polarity. The effect of the solvent on the $\Delta_{diss}G^\circ$ value (and thus on K_a and pK_a) can be expressed (somewhat simplified) as follows:

$$\Delta_{diss}G^\circ(\text{HA, S}) = \Delta_{diss}G^\circ(\text{HA, gas phase}) + \Delta_{solv}G^\circ(\text{H}^+\text{, S}) + \Delta_{solv}G^\circ(\text{A}^-\text{, S}) - \Delta_{solv}G^\circ(\text{HA, S})$$

$\Delta_{diss}G^\circ$(HA, S) and $\Delta_{diss}G^\circ$(HA, gas phase) are the standard Gibbs energy changes of the acid dissociation reaction in solvent **S** and the gas phase, respectively. $\Delta_{solv}G^\circ$(X, S) is the standard Gibbs energy of solvation of species **X** in solvent **S** (the Gibbs energy change when moving species **X** from the gas phase into solvent **S**). Since solvation always stabilizes the respective species, $\Delta_{solv}G^\circ$(X, S) values are always negative.

Dimethyl sulfoxide (DMSO), $(CH_3)_2S{=}O$, is a polar aprotic solvent widely used in the study of acid-base equilibria due to its excellent dissolving power and high polarity. DMSO differs significantly from water in its ability to solvate ions, as reflected in **Table 1**.

Table 1. Estimated $\Delta_{solv}G^\circ$ values for the hydrogen ion, acetate anion, and acetic acid molecule in water and DMSO.

Species X	**$\Delta_{solv}G^\circ$(HA, H_2O), kJ·mol^{-1}**	**$\Delta_{solv}G^\circ$(HA, DMSO), kJ·mol^{-1}**
H^+	−1105	−1124
CH_3COO^-	−325	−270
CH_3COOH	−28	−35

Table 1. Estimated $\Delta_{solv}G^\circ$ values for the hydrogen ion, acetate anion, and acetic acid molecule in water and DMSO.

a) The pK_a of acetic acid in aqueous solution is **4.76**. Based on this value and the data provided in Table 1, calculate the estimated pK_a of acetic acid in DMSO. R = 8,314 J·mol^{-1}·K^{-1} ja T = 298 K.
(4)

b) A 1.00 millimolar (mM) solution of acetic acid in both water and DMSO is studied. Calculate for both solutions: **i)** The dissociation constant K_a, **ii)** The hydrogen ion concentration [H^+] and **iii)** the degree of dissociation α (%) (i.e., what fraction of the acetic acid molecules in the solution have dissociated). (4)

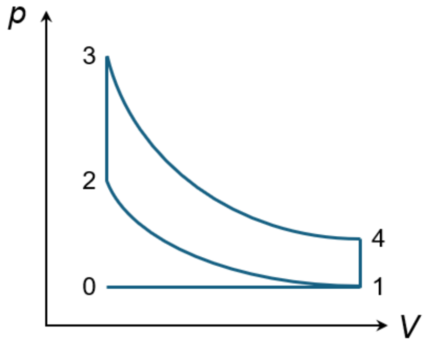
CH_3COOH	**H_2O**	**DMSO**
i) K_a		
ii) [H^+]		
iii) α		

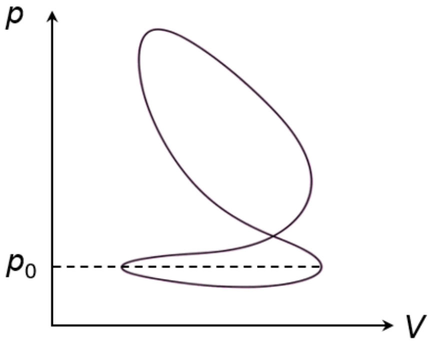
c) **i)** In which solvent (water or DMSO) does acetic acid behave as a stronger acid? **ii)** Briefly justify why. (1)

4. The Otto Cycle (11 p)

In 1876, the German engineer Nikolaus Otto invented the four-stroke internal combustion engine, which used as fuel a mixture of air and gas produced from coal. Later, the company Daimler improved the engine so that it could be used in automobiles. Modern gasoline engines operate according to the same principle. The pressure–volume diagram of the process occurring in the engine is shown in the right-hand figure below. The left-hand figure shows the idealized version of the same process. During the process **0** → **1**, a mixture of air and fuel is drawn into the engine. During **1** → **2**, the gas is compressed, and at point **2** the mixture is ignited by a spark plug. During **3** → **4**, the gas produced pushes the piston and performs work. During **4** → **1**, excess heat is released, and during **1** → **0** the combustion products leave the engine. **1** → **0** käigus põlemisproduktid. In the ideal cycle, there is no heat exchange with the surroundings during the processes **1** → **2** and **3** → **4**, and these processes are reversible. When solving the problem, the ideal gas equation may be needed:

$$pV = nRT\text{, where } R = 8.314\ \text{J·mol}^{-1}\text{·K}^{-1}.$$





a) Indicate in the table what type of processes they ideally represent. (1.5)

	0 → 1	**1 → 2**	**2 → 3**	**3 → 4**	**4 → 1**
Isochoric					
Isobaric					
Isothermal					
Isentropic					
Isenthalpic					
Adiabatic					

If the Gibbs free energy (G) describes the maximum useful work of processes at constant pressure and temperature, then the Helmholtz free energy (F) describes the maximum useful work at constant volume and temperature.

The definition of Helmholtz free energy is:

$$F = H - TS - pV$$

b) How does the following change during the cycle: **i)** internal energy, **ii)** Helmholtz free energy? Determine **i)** ΔU and **ii)** ΔF. (1)

To derive the relationships between temperature, pressure, and volume (state parameters) for the process **1** → **2**, one can start from the first law of thermodynamics.

c) Below is shown a fragment of an important intermediate result in deriving the relationships between the state parameters for the process **1** → **2**. Derive this result, starting from the first law of thermodynamics. The dotted lines represent different variables and constants. (2.5)

$$\ldots \frac{\Delta V}{V} = \ldots \frac{\Delta T}{T}$$

For the previous result to be useful, one must consider infinitesimally small changes in volume and temperature, and then sum all the obtained results together. The result is (the dotted lines contain exactly the same terms as in part **c)**):

$$\ldots \ln \frac{V_{final}}{V_{initial}} = \ldots \ln \frac{T_{final}}{T_{initial}}$$

Assume that the engine uses as fuel a mixture of butane and neopentane (the chain isomer of pentane) and that the fuel mixture is compressed 10 times. At point **1**, 1 mole of the mixture enters at a temperature of 25 °C, in which the volume ratios of butane, neopentane, and air are 2 : 1 : 107. The ratio of heat capacities of the mixture is $\gamma = 1.363$. Assume that air is a mixture of oxygen and nitrogen with a volume ratio of 1 : 4, and that enthalpy values do not depend on temperature.

d) Find the temperature (K) at point **2**. (1)

	$\Delta_c H_{298}$ (kJ·mol^{-1})	Boiling point (°C)
Butane	−2877	−0.5
Neopentane	−3514	9.5

	O_2	N_2	H_2O (g)	CO_2
C_V (J·mol^{-1}·K^{-1})	21.0	20.8	29.2	41.3

e) Calculate how much energy (kJ) is released when 1 mole of **i)** butane and **ii)** neopentane burns in a constant-volume reactor at 298 K. Use the obtained results in the subsequent calculations. (1.5)

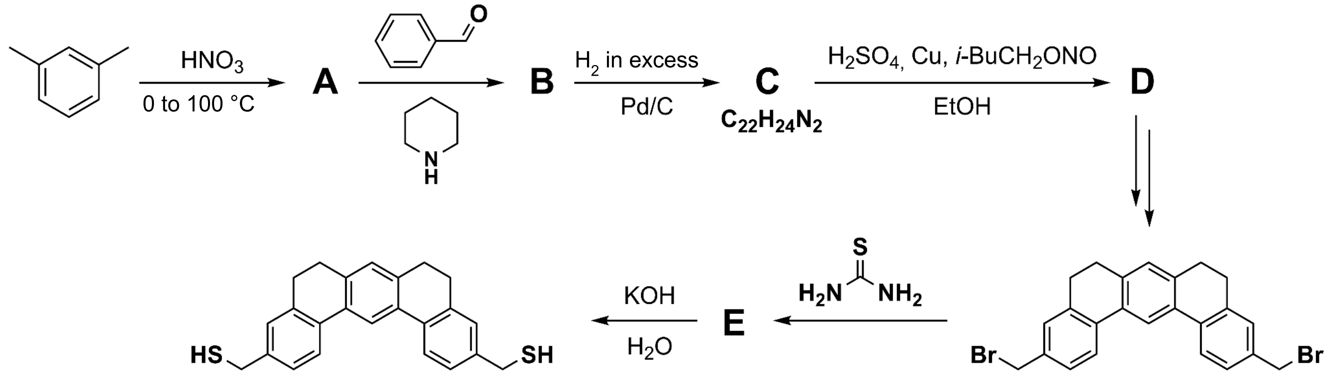
f) At point **3** the temperature is the highest. Calculate the temperature (K) at point **3**. (3.5)

5. The More Rings, the Better (10 p)

August Kekulé is often considered the scientist who discovered the structure of benzene. As the legend goes, Kekulé arrived at the idea of benzene's structure in 1865 after dreaming of a snake biting its own tail. In reality, debates about the exact structure of the molecule continued for decades. The cyclic structure of benzene was finally confirmed only in 1928 by the crystallographer Kathleen Lonsdale, more than a century after the compound was first isolated in 1825 by Michael Faraday.

The polycyclic aromatic hydrocarbon **kekulene** ($C_{48}H_{24}$), synthesized in 1978, was named after August Kekulé. The two-part laboratory synthesis of kekulene is shown in the following reaction schemes.

Part 1



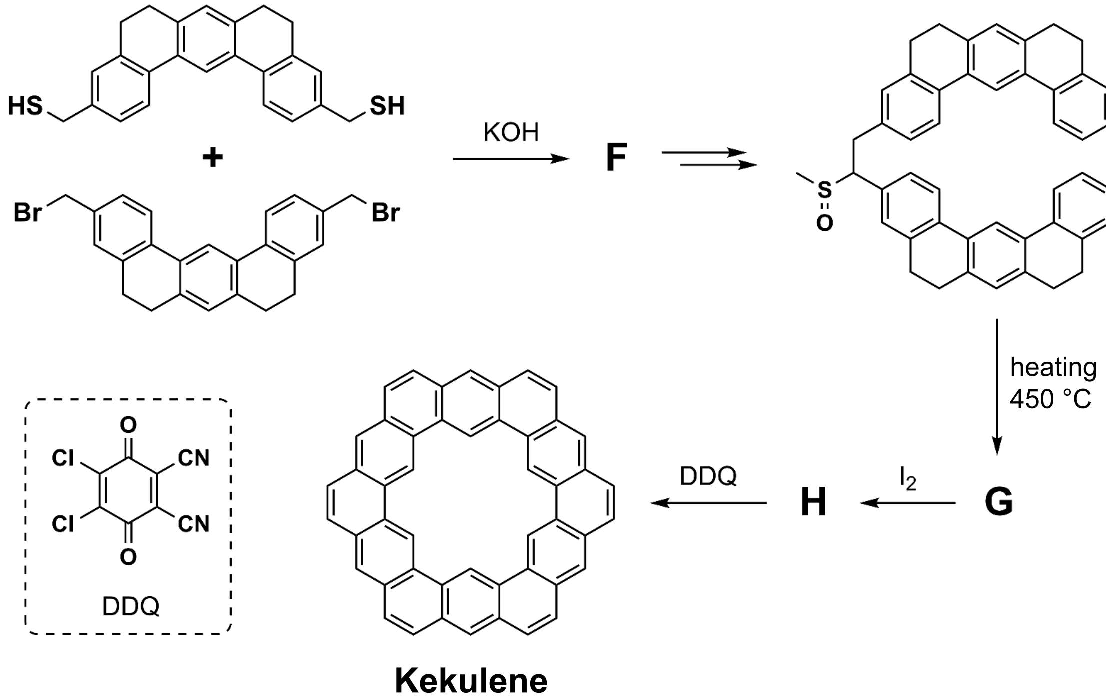
Hints:

- *In the step **A** → **B**, the piperidine molecule acts as a moderately strong base.*
- *In the step **C** → **D**, a diazonium salt (R–N_2^+) is first formed, after which intramolecular cyclization occurs in the presence of a copper catalyst, with the release of two N_2 molecules.*
- *The final step is basic hydrolysis.*

a) Draw the structural formulas of compounds **A**–**E**. (2.5)

The products and intermediates obtained in the first part are used for the synthesis of the final product:

Part 2



Vihjed:

- *In the first step, a nucleophilic substitution reaction (S_N2) takes place.*
- ***G** is a hydrocarbon.*
- *DDQ is a strong oxidizing agent.*

b) Draw the structural formulas of compounds **F**–**H**. (1.5)

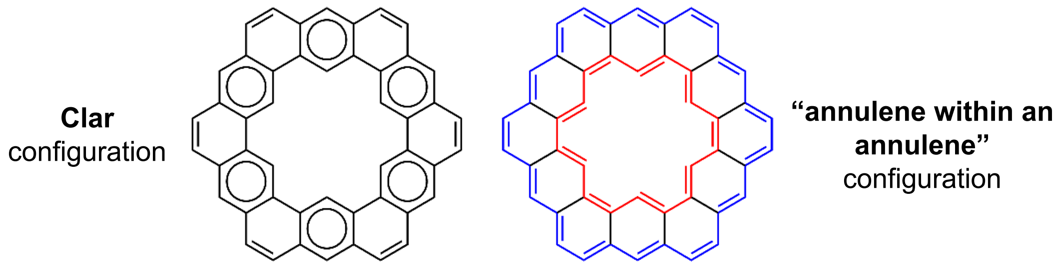
Kekulene is classified as a [**12**]-circulene, where the integer 12 describes how many benzene rings surround the polygon formed in the central cavity of the molecule. In addition to kekulene, other stable circulenes include [**5**]-, [**6**]- and [**7**]-circulenes.

c) Draw the structural formulas of [**5**]-, [**6**]- and [**7**]-circulenes. (1.5)

d) Considering the structures of the circulenes drawn in part **c)**, indicate their geometry in the table.
(1.5)

Geometry	**[5]-circulene**	**[6]-circulene**	**[7]-circulene**
Planar			
Bowl- or saddle-shaped			

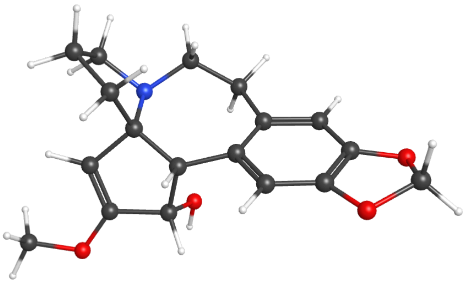
Aromatic systems and molecules follow the **Hückel rule**, according to which their π-orbital systems must contain **4*n* + 2** electrons (integer ***n*** = 0, 1, 2, 3, ...). In contrast, **antiaromatic** systems contain **4*n*** electrons. The π-orbital system of kekulene contains 48 π-electrons, which means that according to the aforementioned rule it should be antiaromatic. However, it has been experimentally proven that kekulene behaves like an aromatic compound. To describe this phenomenon, there are two possible explanations and resonance structures. In the **Clar** configuration of the kekulene molecule, the benzene rings and C=C double bonds are arranged alternately. Another possible explanation is the so-called "**annulene within an annulene**" configuration, which represents the kekulene molecule as two rings: an 18 π-electron inner ring (red) and a 30 π-electron outer ring (blue).



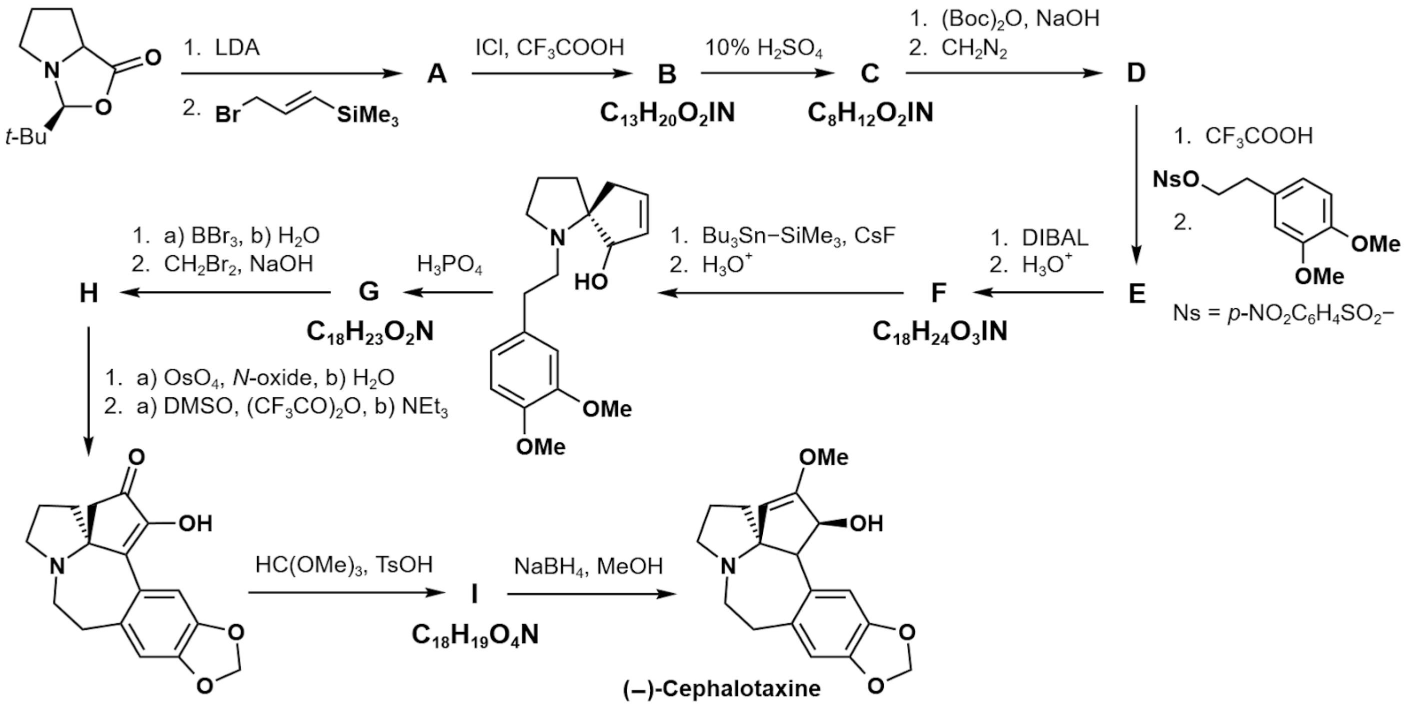
e) The aromaticity of [**5**]-, [**6**]- ja [**7**]-circulenes has been experimentally proven. Draw the **Clar** and/or “**annulene within an annulene**” configuration for the corresponding circulenes that explains their aromaticity. (3)

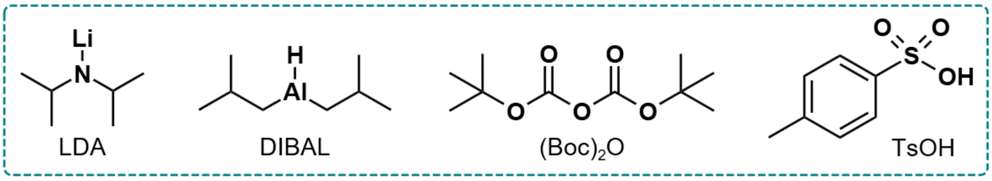
6. Let’s Synthesize Cephalotaxine! (10 p)

Cephalotaxine is a polycyclic alkaloid whose structure contains an azaspiro motif within a tetracyclic carbon skeleton. Cephalotaxine-type alkaloids are bioactive compounds with anticancer activity that inhibit protein synthesis, thereby promoting apoptosis (“programmed” cell death) in tumor cells.



The synthesis of optically active (−)-cephalotaxine begins with the alkylation of a lactone derivative of the amino acid *D*-(+)-proline, giving compound **A**, which is converted through an electrophilic substitution reaction into vinyl iodide **B**. Subsequent acid-catalyzed hydrolysis, followed by introduction of a protecting group and methylation (introduction of a methyl group), yields compound **D**. After removal of the protecting group, another alkylation is carried out, forming compound **E**, which upon further treatment with DIBAL gives compound **F**. The azaspiro tetracyclic carbon skeleton in compound **G** forms through two consecutive intramolecular cyclization reactions (ring-forming reactions). When **F** reacts with $Bu_3SnSiMe_3$, a *Stille-type silylation reaction* first produces a nucleophilic silyl species (a silicon compound), which then forms an alcohol via an addition reaction (see figure). This alcohol participates in the next step in a *Friedel–Crafts alkylation reaction*. Compound **G** is then derivatized over several steps into the enol ether **I**, and reduction of **I** finally yields the desired end product.





Hints:

- *(Boc)$_2$O, which is acid-labile, is used to protect an amino group (R–Boc).*
- *CH_2N_2 (diazomethane) and $HC(OMe)_3$ are reagents used to methylate functional groups.*
- *In the step **G** → **H** demethylation occurs first, producing catechol (1,2-dihydroxybenzene).*

a) Determine which term ***best describes*** the role of the following compounds in the corresponding reactions in the synthesis scheme. (1)

	Electrophile	Nucleophile	Strong base	Oxidizing agent	Reducing agent
LDA					
$BrCH_2CH{=}CHSiMe_3$					
ICl					
DIBAL					
OsO_4					

b) Draw the structural formulas of compounds **A**–**I**. When drawing the structural formulas, you do not need to indicate the stereochemistry of the chemical bonds. (9)