

27th BChO 2019, Tartu, Estonia

Problem 1 – STRUCT – Iron complexes

Iron is an element that makes up the greatest part of Earth by mass (34.6%), constituting 4.65% of Earth's crust. It has been used in the production of various tools. Also, iron complex compounds have been used as pigments. Depending on the pH of the aqueous solution, Fe^{3+} ions can form octahedral complexes, which differ in color. Iron(III) ion-containing salt was dissolved in concentrated acid, and the pH of the solution was slowly increased by adding NaOH solution dropwise. During the addition of NaOH solution, there was a gradual change in the color of the solutions, as shown in the table below:

pH	The color of the solution	Complex
Increase ↓	Pale violet	A
	Yellow	B
	Green	C

- Write the chemical formulas of the complexes **A–C**. If any isomers exist for **A–C**, draw their structural formulas.
- Provide the equations of formation of **B** from complex **A** and **C** from complex **B**.
- At high pH values, Fe^{3+} ions almost could not be found in solution because brown solid substance **D** is formed. Write the chemical formula of substance **D**.

According to the magnetic measurements, it was stated that $[\text{Fe}(\text{CN})_6]^{3-}$ ion has one unpaired electron, while $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has more than one.

- Draw the crystal field diagrams for both complexes.
- Are $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions paramagnetic or diamagnetic?

It is very common for iron ions to interfere with the analysis of other ions. In order to prevent interference of Fe^{2+} ions, sodium oxalate is added to the solution. Fe^{2+} , combined with oxalate ions, make a very stable octahedral complex (stability constant $K = 1.7 \cdot 10^5$). Equal volumes of solution, where the concentration of Fe^{2+} ions is 0.20 g dm^{-3} and solution of $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$, were mixed.

- Calculate the pH of the $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$ (oxalic acid's $\text{p}K_{a1} = 1.27$ and $\text{p}K_{a2} = 4.27$).
- Calculate the percentage of free Fe^{2+} ions remaining in the solution after mixing equal volumes of $0.20 \text{ g dm}^{-3} \text{ Fe}^{2+}$ and $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$ solutions. *Hint: because $\text{C}_2\text{O}_4^{2-}$ concentration is relatively high, you can assume that complex formation does not affect it.*

$[\text{Fe}(\text{SCN})_6]^{3-}$ solution shows strong absorbance at $\lambda = 490 \text{ nm}$. This characteristic is used for iron concentration determination by absorption spectrophotometry in white wine. H_2O_2 , HNO_3 , and KSCN are added to wine. Then absorption is measured.

- Draw Lewis dot structures for all SCN^- resonance structures.
- Determine the color of $[\text{Fe}(\text{SCN})_6]^{3-}$ solution.
- Why are H_2O_2 and HNO_3 added to wine? Answer by writing the net ionic equation/equations for appropriate reaction/reactions.

It was determined that 100.0 g of compound $\text{X}_y[\text{Fe}(\text{CN})_6]_z$ contains 45.50 g of iron.

- Identify the element **X** and write the formula of the compound. Show your calculation.

Problem 2 – EQUIL, THERMO – CaCO₃ in nature and laboratory

When solving this problem, you will need thermodynamic data from the table below. Assume that all gases and solutions are ideal and enthalpy change of all reactions is temperature-independent. Thermodynamic data at 298 K temperature and 10⁵ Pa pressure.

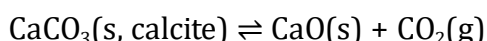
	ΔH_f° [kJ mol ⁻¹]	ΔG_f° [kJ mol ⁻¹]	S° [J mol ⁻¹ K ⁻¹]
CaO (s)	-635.1	-604.0	39.7
Ca ²⁺ (aq)	-542.8	-553.6	-53.1
Ca(OH) ₂ (s)	-986.1	-898.5	83.4
CaCO ₃ (s, calcite)	-1206.9	-1128.8	92.9
CaCO ₃ (s, aragonite)	-1207.1	-1127.7	88.7
CO ₂ (g)	-393.5	-394.4	213.7
H ₂ O (l)	-285.8	-237.2	69.9
OH ⁻ (aq)	-230.0	-157.2	-10.7

Calcium carbonate is found in nature in the form of several polymorphs: calcite, aragonite, vaterite, and ikaite. The first three polymorphs are anhydrous calcium carbonate. Ikaite is a hydrated calcium carbonate – a mineral that is found in the cold waters of Ikka Fjord in Greenland. When heated, ikaite CaCO₃·xH₂O readily loses approximately 52% of its initial mass. Under strong heating (1000 °C), it additionally loses approximately 21% of its initial mass.

- Determine number x in CaCO₃·xH₂O. Show your calculations.
- Predict which polymorph (calcite or aragonite) is more stable at 298 K and 10⁵ Pa.

Calcium carbonate minerals are abundant in nature and cause the formation of hard water.

- Write the chemical equation depicting calcium carbonate forming hard water.
- Calculate equilibrium constant of the following reaction at **i)** 25 °C and **ii)** 1070 K:



In the laboratory, a special tightly closed reactor with the possibility to heat substance samples was constructed. This reactor was equipped with a special mechanism that gives the possibility to input samples of solid without any gas leakage. The volume of the reactor is 5.0 dm³. Initially, the reactor was filled with argon (25 °C, 1.0·10⁵ Pa).

- Calculate the pressure (Pa) in the reactor when the temperature was increased to 1070 K. Then, five samples of calcite in consecutive order were introduced into the reactor. The mass of each sample was 1.0 g. Temperature all the time remains at 1070 K. A new sample of calcite was introduced only after constant pressure in the reactor was established.
- Calculate the final total gas pressure in the reactor after the introduction of each sample of calcite.

Finally, the reactor was quickly cooled down to 25 °C and flushed with argon gas to expel all carbon dioxide. A mixture of solid compounds from the reactor was transferred into the water. The final volume of the solution is 0.60 dm³.

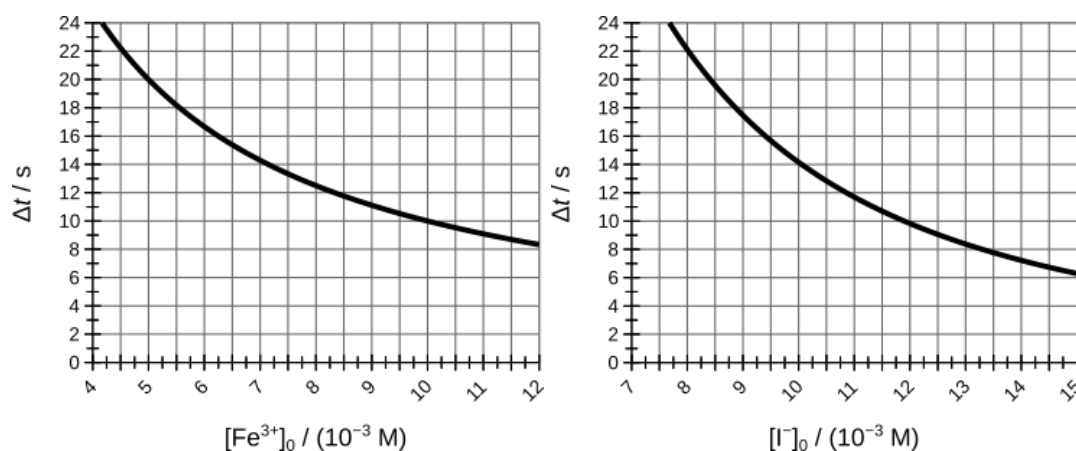
- Calculate the pH of this solution (at 25 °C). Show your calculations.

Problem 3 – ELECTRO, KINETICS – Colorful kinetics

Reactions between iodide ions and iron(III) ions as well as iodine and thiosulfate ions in an aqueous solution are known to occur spontaneously.

- a) Examine the given standard potentials and predict the products of the reactions **i)** between Fe^{3+} and I^- as well as **ii)** between I_2 and $\text{S}_2\text{O}_3^{2-}$. Show your calculations. Write equations of the feasible reactions. $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V}$; $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$; $E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) = +2.20 \text{ V}$; $E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.54 \text{ V}$; $E^\circ(\text{IO}_3^-/\frac{1}{2}\text{I}_2) = +1.20 \text{ V}$; $E^\circ(\text{HIO}/\frac{1}{2}\text{I}_2) = +1.44 \text{ V}$; $E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) = +0.08 \text{ V}$.

Oxidation of iodide by iron(III) ions in the presence of $\text{S}_2\text{O}_3^{2-}$ ions and starch can run like a clock reaction. The reaction is started by mixing a solution of iron(III) nitrate with a solution containing thiosulfate, iodide, and starch. The solution immediately turns purple due to the formation of $\text{Fe}(\text{S}_2\text{O}_3)^+$ complex. The color gradually fades until the solution becomes colorless and then suddenly turns dark blue due to the formation of the starch–pentaiodide complex. The kinetics of the reaction between iodide and iron(III) can be studied by the initial rates method by measuring the time (Δt) elapsed from the mixing of the two solutions to a sudden color change. Under certain conditions, the initial reaction rate is inversely proportional to the measured time: $v_0 = [\text{S}_2\text{O}_3^{2-}]_0/\Delta t$. Two graphs given below were obtained measuring Δt after mixing solutions with different initial $[\text{Fe}^{3+}]_0$ or $[\text{I}^-]_0$ concentrations while keeping the concentration of all other components constant.



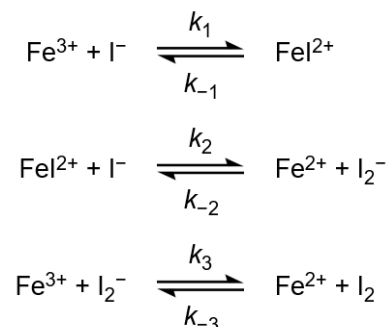
- b) Show how to determine the reaction order with respect to **i)** Fe^{3+} and **ii)** I^- ions, then calculate the half-life of $[\text{Fe}^{3+}]$ in solution at experimental conditions.

Some experimental results are summarized in the table below:

#	$[\text{Fe}^{3+}]_0$	$[\text{I}^-]_0$	$v_0 [\text{M s}^{-1}]$
1	0.09900	0.0744	0.008836
2	0.09900	0.0431	0.002978
3	0.04945	0.0960	0.007319
4	0.00118	0.0960	0.000175
5	0.00118	0.0607	0.000070
6	0.00118	0.0431	0.000035

- c) Calculate the rate constant of the reaction.

The following reaction scheme was proposed to explain the mechanism of Fe^{3+} reduction by I^- :



- d) Derive a rate equation for consumption of Fe^{3+} ($-\text{d}[\text{Fe}^{3+}]/\text{d}t$) from the provided scheme, stating any reasonable assumptions made.
- e) Explain whether the provided experimental data confirms the proposed mechanism or not.

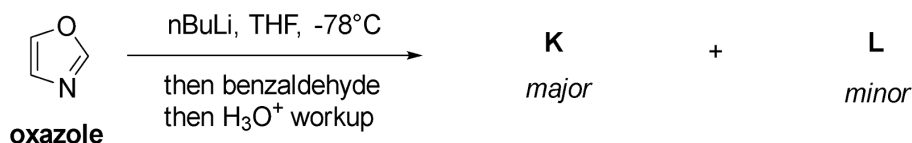
Problem 4 – EQUIL – Some penguin chemistry

While in the rookery, Antarctic Adélie penguins may encounter intense solar radiation. Panting during severe heat stress can result in alternations of gas composition and acid–base balance in the blood of brooding adults. Let us examine how the temperature influences the pH by altering the $\text{HCO}_3^-/\text{CO}_2(\text{aq})/\text{CO}_2(\text{g})$ equilibrium, in which the level of CO_2 is adjusted by respiration. The following data is available: $\text{p}K_{\text{a}1} = 6.35$ (25 °C), $\text{p}K_{\text{a}1} = 6.07$ (38.5 °C), $\Delta H_{\text{vap}}(\text{CO}_2, \text{blood}) = 19.95 \text{ kJ mol}^{-1}$, $K_{\text{H}}(\text{CO}_2, 38.5 \text{ °C}) = 2.2 \cdot 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$.

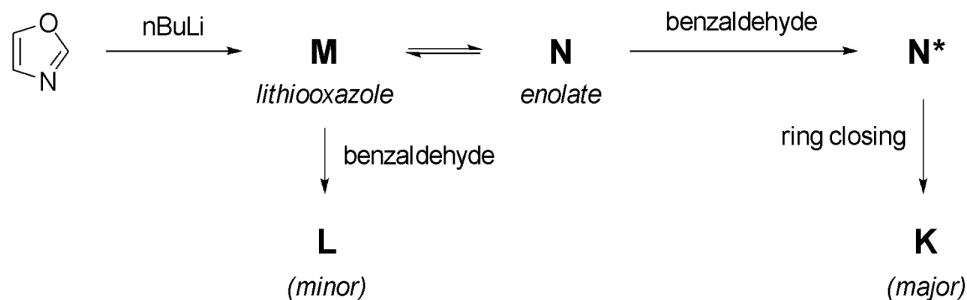
- a) Calculate the pH of the Adélie penguin blood at a normal body temperature of 38.5 °C if $[\text{HCO}_3^-] = 29.4 \text{ mM}$ and $p(\text{CO}_2) = 4.9 \text{ kPa}$.
- b) Calculate the values of $\text{p}K_{\text{a}1}$ (40.7 °C) and $K_{\text{H}}(\text{CO}_2, 40.7 \text{ °C})$.
- c) Estimate the pH of the Adélie penguin blood at a critical body temperature of 40.7 °C assuming that the CO_2 pressure remains the same and the concentration of HCO_3^- depends on the pH as $[\text{HCO}_3^-] = (302.4 - 36.4 \cdot \text{pH}) \text{ mM}$.
- d) Estimate the pH of the Adélie penguin blood at a critical body temperature of 40.7 °C taking into account that due to hyperventilation $p(\text{CO}_2)$ decreases to 1.5 kPa.
- e) Would you expect the described overheating to cause some of the following conditions: **i)** alkalosis; **ii)** acidosis; **iii)** hypocarbia; **iv)** hypercarbia? “Hypo” and “hyper” originate from the Greek words meaning “below” and “above”, respectively.

Problem 5 – MECH, SYNTH – Lithiation gone wrong

One of the most popular methods for introducing substituents in heterocyclic compounds is lithiation and then subsequential alkylations, acylations, additions etc. The lithiation of oxazole is harder and produces two regioisomers after the addition of benzaldehyde and sequential aqueous workup, where the minor isomer is needed.



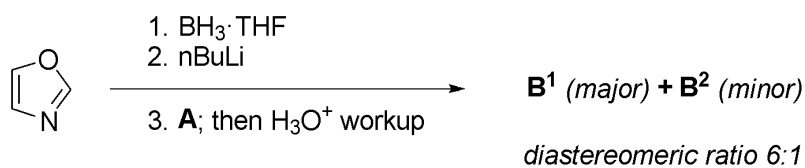
The reason for that is when the oxazole has been lithiated in the most acidic position, the obtained lithiooxazole **M** is not stable and is in equilibrium with enolate **N**. Enolate **N** can attack benzaldehyde and, after closing the ring, create the major addition product **K**.



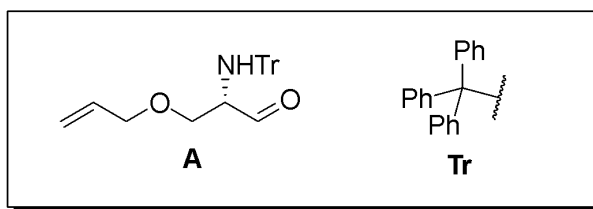
a) Draw the structural formula of compounds **K–N***.

To overcome the unwanted selectivity, 1 equivalent of BH_3 is added before lithiation.

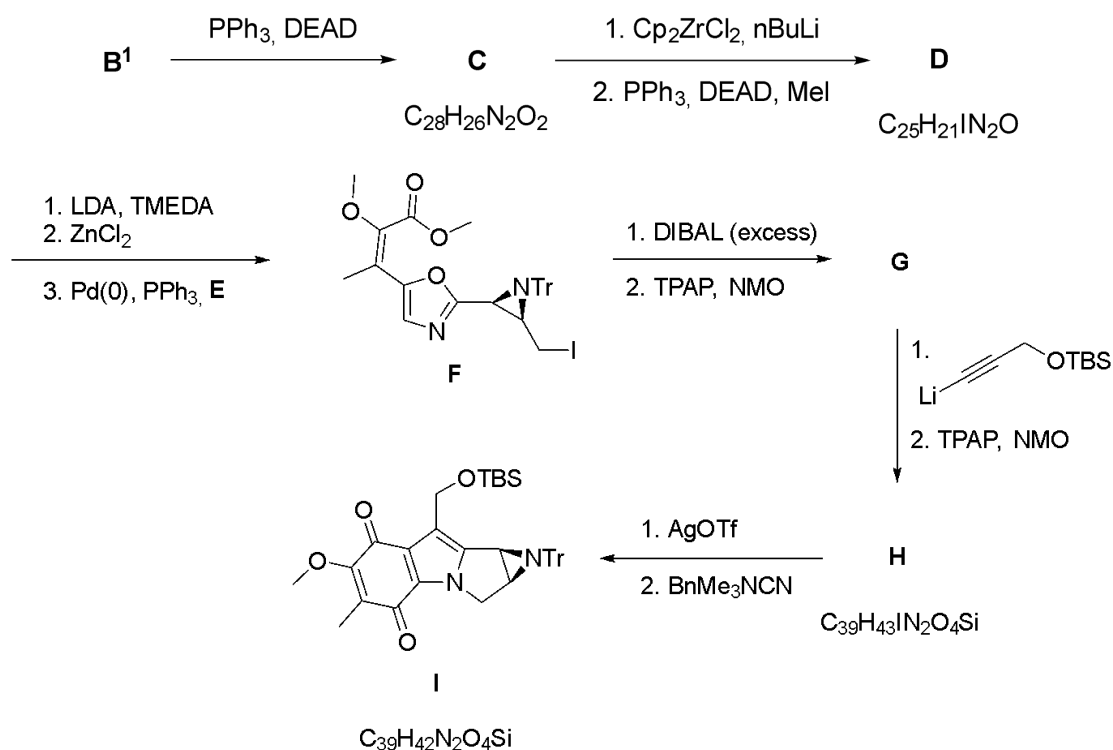
b) Show how BH_3 might change the selectivity by drawing mechanisms or structures.

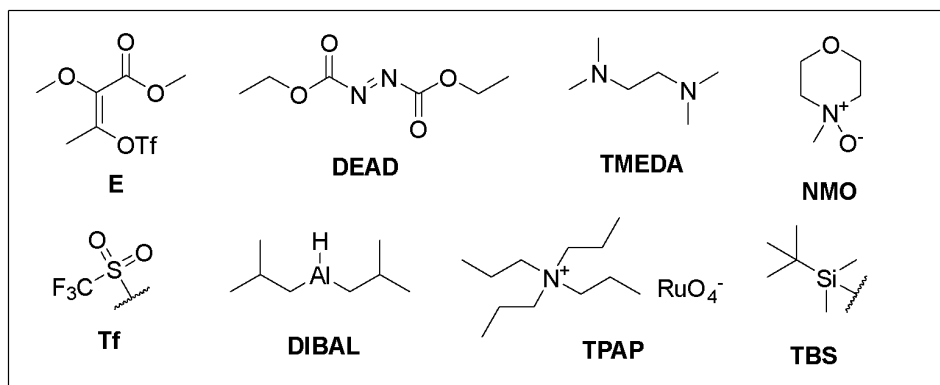


This method was used in an attempted synthesis of a synthetic product Aziridinomitosenone **A**, which has the same core structure as Mytomycins. These natural compounds possess interesting structure and antitumor activity.



The synthesis starts with selective oxazole lithiation.



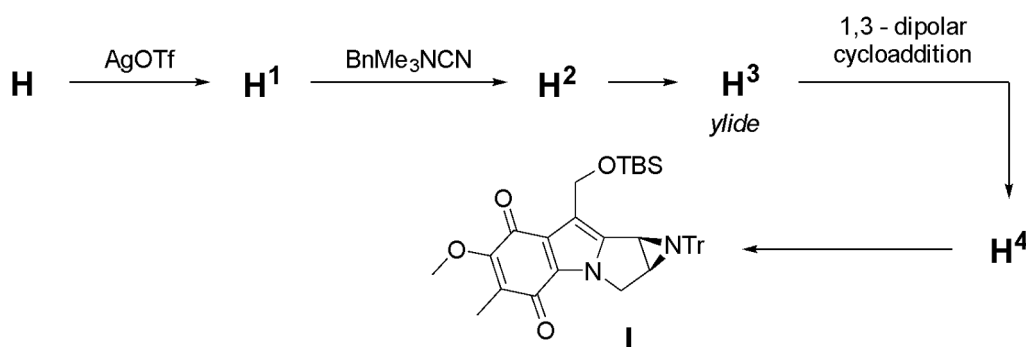


Note: Cp_2ZrCl_2 , BuLi are allyl group deprotection conditions.

c) Draw structures **B**¹, **B**², **C**, **D**, **G**, **H** and indicate the stereochemistry.

d) Draw the mechanism for the transformation **B**¹ → **C**.

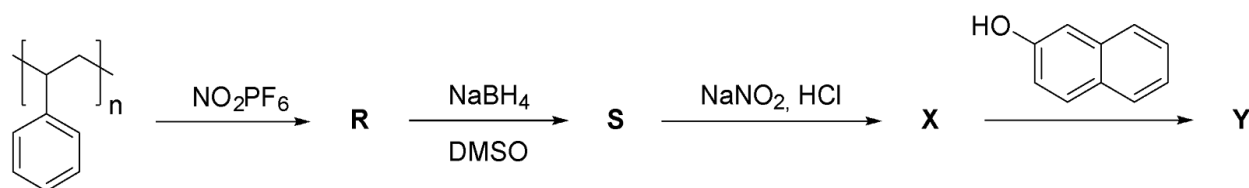
The reaction **H** → **I** is a complex multi-step transformation. First, AgOTf is added to **H**, which creates an ionic compound **H**¹ and a yellow salt. To **H**¹, BnMe_3NCN is added, which is a source of cyanide anions, and additional product **H**² is obtained, which reorganizes to azomethine ylide **H**³. Ylide **H**³ undergoes an intramolecular 1,3-dipolar cycloaddition reaction, forming **H**⁴, which subsequently gives **I**.



e) Draw all the missing structures of **H** and **H**¹–**H**⁴.

Problem 6 – SPECTRA, SYNTH – Deformed polymers

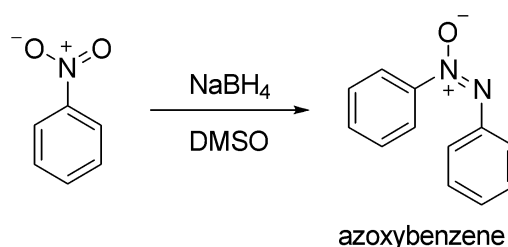
In order to change the color of polystyrene, one may use so-called polymer-analogous reactions that alter only functional groups but leave alkyl chains unaffected. These sorts of reactions may also be useful in the synthesis of polymers that are impossible to make from monomers. Let us look at one of the modifications that could be made with the polymer.



a) Identify product **R** considering that not all benzenes are nitrated.

NaBH_4 is not good for the reduction of aromatic nitro compounds because of the formation of various side products, such as azoxybenzene.

Side products form due to the fact that reduction happens stepwise.



d) Identify product **S** and four other possible intermediates (**S**¹, **S**², **S**³ and **S**⁴), knowing that **S** is fully reduced.

c) Which two intermediates **S**¹–**S**⁴ lead to the formation of azoxybenzene?

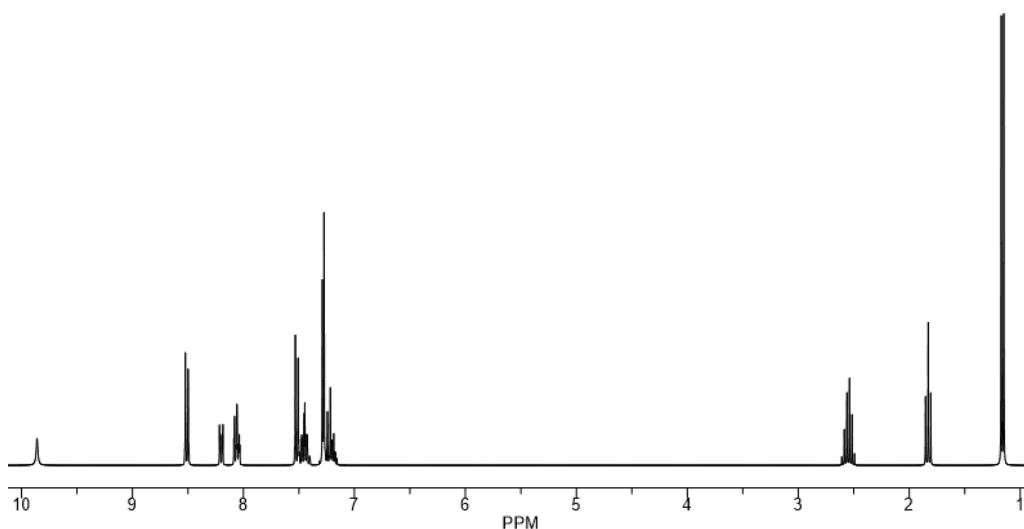
d) What product is also formed in the reaction of azoxybenzene formation?

e) Is azoxy-product forming at **i)** low or **ii)** high polystyrene concentrations?

In the case of a more convenient reduction of **R** (with hydrogen), polymer **P** was obtained. Titration of 1.000 g of **P** required 1.920 cm³ of 0.2000 M HCl.

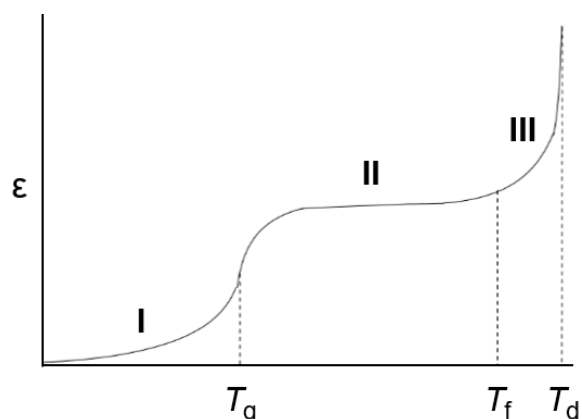
f) Calculate the percentage of nitrated benzene rings, considering that all reactions are quantitative.

g) Draw the structural formulas of **X** and **Y**, considering the ¹H NMR spectrum of **Y**:



Y: ¹H NMR (300 MHz, CDCl₃): δ 9.86 ppm (s), 8.51 (d), 8.20–8.05 (m), 7.52–7.43 (m), 7.27–7.19 (m), 2.58–2.53 (m), 1.89–1.83 (m), 1.16 (d).

An important characteristic of the mechanical properties of polymers is the dependence of equilibrium deformation ϵ on temperature T . ϵ describes the straightening of polymer chains under calibrated stress. If polymer chains are mobile, then the sample has more developed equilibrium deformations. On the left, you can see the thermomechanical curve for polystyrene. At low temperatures, the polymer has small deformations (**I**). At temperatures higher than T_g , the polymer becomes highly elastic, in which deformations are determined by the movement of segments of macromolecules (**II**); higher than T_f , the polymer becomes liquid, and at T_d , it decomposes.



h) Sketch thermomechanical curves and denote temperature for phase change on the same graph: **i)** For nitrated polystyrene, reduced with excess NaBH₄ at low polymer concentration (nitrated/non-nitrated = 5%); **ii)** For nitrated polystyrene, reduced with excess NaBH₄ at high polymer concentration (nitrated/non-nitrated = 5%); **iii)** For nitrated polystyrene, reduced with excess NaBH₄ at high polymer concentration (nitrated/non-nitrated = 15%).