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BIRCH-TYPE REDUCTION OF ANTHRACENE BY FIELD EMISSION OF ELECTRONS IN MICROREACTORS

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Abstract

A microreactor system for performing the Birch-type reduction of polycyclic aromatic hydrocarbons (PAHs), of which anthracene is used as a model compound, is investigated. The microreactor contains two electrodes separated by a microfluidic channel. The cathode is a silicon nanowire (SiNW) field emitter array for generating solvated electrons in the solution flowing through the channel, which are used for the reduction of anthracene.

Experiments were performed in order to investigate the formation of various side products with different solvents and anode materials. No consistent conversion towards the desired product (9,10-dihydroanthracene) was observed, presumably because of a malformation of the field emitter array. Many different side products were detected. Indirect evidence for the role of the alcohol (used as solvent / proton donor) as reducing agent was obtained. It was demonstrated that tert-butanol in acetone as solvent can still produce side products. One experiment with a microreactor chip with indium tin oxide (ITO) anode resulted in production of side products, however, the other experiments with ITO chips resulted in no products at all. The fact that side products still form in a chip with ITO anode suggests that the hypothesis about the formation of these side products is incorrect.

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1 Introduction

The synthesis of some pharmaceuticals requires partial reduction of an aromatic ring [1, 2]. Conventionally, this is done by means of the Birch reduction [2, 3, 4]: an organic reaction that partially reduces aromatic rings in liquid ammonia with an alkali metal like lithium, sodium, or potassium. The reaction is based on the generation of solvated electrons (commonly denoted e^-_{sol}), which are recognisable by their characteristic deep blue colour. In several steps, the solvated electrons can transfer to the aromatic ring, thereby transforming it into a radical anion. The radical anion in turn reacts with H^+ donated by a proton donor (usually an alcohol) to form the hydrogenated product. The reaction works well, but leaves a lot to be desired in terms of reaction conditions: the need for liquid ammonia and alkali metals is a severe disadvantage. Apart from the fact that these materials are hazardous, the sub-zero temperatures needed to keep ammonia in its liquid phase makes the process energy inefficient.

An alternative to the Birch reduction would be a device that generates solvated electrons by some other means. This device, a microreactor that uses nanowires to 'inject' electrons into solution by cold field emission, is the subject of this assignment.

1.1 Preliminary findings

Previous research done by Morassutto with such a microreactor containing silicon nanowires (SiNW) (see figure 1) has shown that it is possible to reduce polycyclic aromatic hydrocarbons (PAHs) such as naphtalene and anthracene (which are used as a model compounds) by this method [5]. The reaction results in the desired hydrogenated product.

Slotboom did further research on the same set-up as part of his bachelor assignment, focusing on reaction mechanisms and maximising yield of the desired product [6].

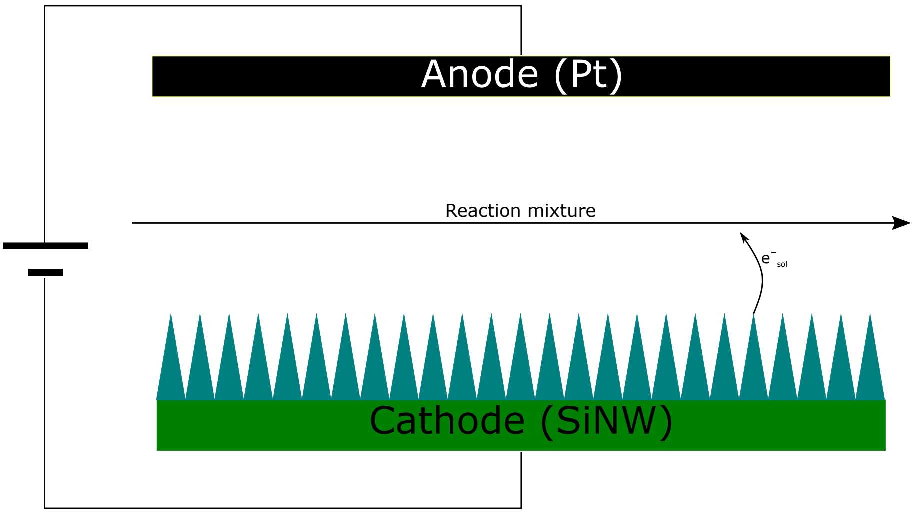

Figure 1: *Schematic view of the microreactor. An electrical potential is applied between the electrodes, causing field emission of electrons from the silicon nanowires into the reaction mixture.*

1.2 Challenges

The main problem with this set-up is that some unexpected side products, such as alkyl-substituted and/or oxidation products of anthracene, are formed. Slotboom hypothesised that these side products are formed by a surface adsorption reaction on the platinum anode [6]. However, this can only be evidenced by testing with alternative anodes.

It is not clear what is happening at the oxidising part of the reactor (the anode) in the case that no side products are formed. While the reactant is reduced, some other chemical species must be oxidised to balance the redox reaction; if only the reducing half reaction took place, the reaction mixture would be left containing alkoxide ions and thus the the effluent would be electrically charged. This is not a realistic scenario.

Another problem identified by Slotboom was the breakage of the nanowires due to fluid pressure and shear stresses, causing short-circuits. These problems are thought to be easily solved by making some slight adjustments to the microreactor design, which will be implemented in this assignment.

1.3 Aim

The aim of this assignment is to further investigate the mechanism of the desired reaction and side reactions, and try to improve the process by taking into account the recommendations given by Slotboom.

Main research questions, along with methods to investigate these questions are:

- Which species are acting as the reducing agent in the redox reaction?
  - Perform analysis (IR, GC-MS, H-NMR) on the effluent
- What is the origin of the side products?
  - Study the effect of an anode other than platinum (glassy carbon, gold, ITO) on the side product formation
  - Study the effect of addition of radical scavengers on (side) product formation
- How can the microreactor be improved?
  - Slight modifications to the design, such as inclusion of a barrier in front of the SiNWs and wider flow channels

If time allows, an additional opportunity would be to do experiments with pharmaceutically-relevant precursors instead of anthracene.

2 | Theoretical aspects

2.1 Birch reduction

The Birch reduction is a reaction used for selectively hydrogenating aromatic rings. Unlike catalytic hydrogenation which fully hydrogenates unsaturated bonds, the Birch reduction is selective. It yields a 1,4-dihydro derivative of the reactant [2].

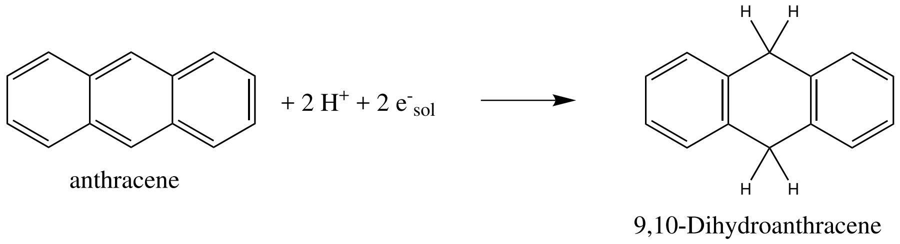

Figure 2: *The reaction equation for the Birch reduction of anthracene to (9,10)-dihydroanthracene.*

By dissolving an alkali metal such as Li, Na, K (in order of decreasing reactivity) in ammonia, an alkali cation and a solvated electron (e^-_{sol}) are formed. This solvated electron is a powerful reducing agent. As ammonia is not acidic enough to act as a proton donor for the reaction, a (stoichiometric amount of) alcohol is added to the reaction mixture.

The mechanism is outlined in figure 3. First, an electron adds to the antibonding π^* orbital of the aromatic ring, creating a radical anion. The radical anion is then protonated by an alcohol to form a cyclohexadienyl radical, which again immediately adds an electron to form an anion. Again, the cyclohexadienyl anion is protonated by the alcohol to form the final 1,4-dihydrogenated product. [2, 3]

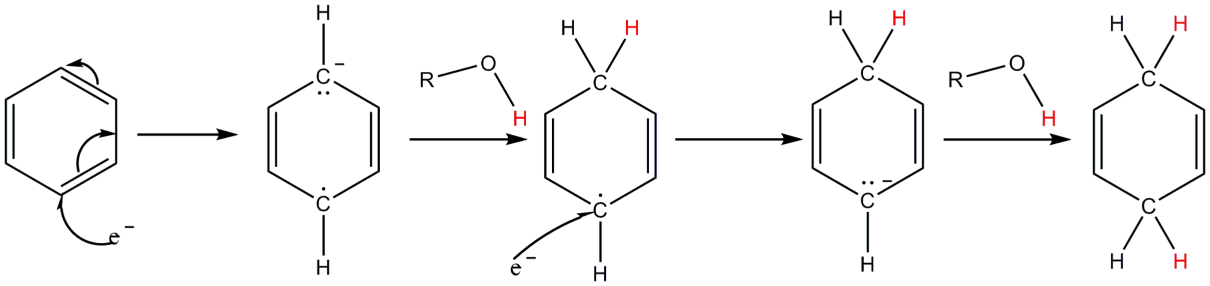

Figure 3: *The mechanism of the Birch reduction for benzene. After: [7]*

If the ring is substituted, the regioselectivity of the reaction is determined by the substituents. As a rule, the compound formed is the one with the most electron-donating substituents at the remaining double bonds. Electron-withdrawing substituents facilitate the formation of an anion (and thus, hydrogenation) at the carbon bearing this substituent, resulting in para-addition of hydrogen. Similarly, electron-donating substituents facilitate meta-addition. In the case of polycyclic aromatic systems, the ring with the most fusions to other rings is most likely to undergo reduction [4].

A competing reaction is the reduction of protons to H_2 in a reaction known as the hydrogen reaction (equation 1). In this case, two protons donated by the alcohol directly accept two electrons and combine to form H_2 [4], similarly to the reaction of alkali metals with water. The extent of this side reaction is generally limited by the low (stoichiometric) concentration of the alcohol.

$$2\,\mathrm{ROH} + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{RO}^- + \mathrm{H}_2 \tag{1}$$

2.2 Solvated electrons

Both dissolving an alkali metal in ammonia and cold field emission result in the generation of solvated electrons: unbound electrons that exist as a solute in a liquid medium. In essence, a solvated electron can be viewed as the smallest possible anion [8].

Lithium in liquid ammonia is the best- and first-known case of solvated electrons. When lithium is dissolved in ammonia, it donates an electron to the solvent to become Li^+. The lithium ion gets coordinated by four ammonia molecules. The resulting solution absorbs light in the red/infrared region of the spectrum (giving it a blue colour), is paramagnetic and electrically conductive [8, 9, 10].

Aside from ammonia, solvated electrons are also known to be able to exist in other polar solvents such as water, amines, and alcohols [9]. Solvated electrons in water and ammonia are also more specifically referred to as "hydrated electrons" and "ammoniated electrons" respectively.

The dynamics and structure of solvated electrons are still not completely understood. Several models aiming to explain this phenomenon have been constructed. Most models view the electron as occupying a cavity with solvent molecules surrounding it. Alternative models regard the ammoniated electron as a system where most of the excess electron density is shared between the nitrogen atoms of the ammonia molecules, which form a solvation cavity due to electrostatic repulsion [9, 11]. A similar model has been developed for the hydrated electron [12].

Electrochemical methods for generating solvated electrons and using them to perform Birch-type reduction reactions have existed for a long time, but these methods involve the use of an alkali salt (usually LiCl) dissolved in amine as electrolyte. It is claimed that the alkali cation is reduced to the alkali metal, following immediate solvation of the metal [13, 14]. Another method involves tetrabutylammonium salts instead of alkali salts [15]. Not much is known in literature about the generation of solvated electrons directly into alcohols by cold field emission.

Cold field emission

Cold field emission (CFE) refers to the emission of electrons from an electrode under the influence of an electrostatic field. A high electric field is required to emit electrons from a metal surface into a vacuum or dielectric, but the required voltage to generate a locally high electric field can be significantly decreased by using a field emitter array consisting of sharp tips which locally enhance the electric field [5].

As a method to generate solvated electrons, CFE is much more mild and convenient than alternatives, such as radiolysis or photolysis.

Morassutto developed a microreactor with an integrated SiNW field emitter array that is able to effectively inject solvated electrons in alcohols by cold field emission at a potential of 25 V (at a gap size of 5 µm, corresponding to an electric field of $5\,\mathrm{MV\,m^{-1}}$). At lower potentials, formation of charge carriers (ions) is favoured instead [5].

2.3 Birch-type reaction at study

The mechanism of the electricity-driven reaction in the microreactor is assumed to be identical to that of the conventional Birch reduction outlined in section 2.1, only the source of the solvated electrons is different, as well as the solvent (no ammonia is used).

The reaction is performed in a microreactor (see section 3.1) utilizing SiNWs as cathode to inject electrons into the reaction mixture by CFE. The anode is platinum. As a solvent and proton donor, alcohols such as ethanol or propanol can be used in pure form or dissolved in another solvent (see section 2.3.3).

The focus is on the reduction of anthracene, which is used as a model compound for this reaction. Morassutto and Slotboom showed that anthracene can be successfully reduced to 9,10-dihydroanthracene, but not without some side products (see section 2.3.2) [5, 6].

Electrochemistry

Even though the electricity-driven reduction is distinct from a conventional electrolysis (the reaction does not take place at the electrode), it is an electricity-driven redox reaction and, as such, falls under the field of electrochemistry.

As briefly explained in section 1.2, there must be an oxidation half-reaction to balance the redox reaction. The reduction reaction adds two electrons from the cathode together with two protons from the alcohol to the reactant, resulting in the 1,4-dihydro derivative of the reactant and two alkoxide ions:

$$\mathrm{C_6H_6 + 2\,e^- + 2\,ROH \longrightarrow C_6H_8 + 2\,RO^-} \tag{2}$$

Overall, in terms of electron balance, this amounts to the addition of two electrons to the reaction mixture. Hence, the reactor effluent would be electrically charged if this was the only reaction that took place, because the solution contains alkoxide ($\mathrm{RO^-}$) ions without cations.

Therefore, it is postulated that there is an oxidation reaction happening at the anode, which allows the reduction reaction to occur. A plausible candidate is the (platinum-catalysed) oxidation of the alcohol to the corresponding aldehyde (for a primary alcohol) or ketone (for a secondary alcohol) (equation 3). If water is present, the aldehyde can further oxidise to a carboxylic acid (equation 4).

$$\mathrm{RCH_2OH \longrightarrow RCHO + 2\,e^- + 2\,H^+} \tag{3}$$

$$\mathrm{RCHO + H_2O \longrightarrow RCOOH + 2\,e^- + 2\,H^+} \tag{4}$$

It has been reported that this reaction can occur at the platinum surface in the presence of oxygen, or electrochemically without oxygen, with the electrons collected by the anode [16, 17]. For ethanol, 1-propanol, and 2-propanol it has been reported that both reactions occur competitively, but when oxygen is not available and/or at high alcohol concentrations, the pathway towards the aldehyde/ketone is dominant [18, 19, 20, 21]. The electro-oxidation of ethanol can also occur on other platinum-group metals, such as gold and palladium [22, 23].

The presence of aldehydes or carboxylic acids was not reported by Morassutto or Slotboom [5, 6], but it is possible that these side products were missed in analysis because the used GC-MS instrument did not analyse effluent with a retention time below 8 minutes. However, Slotboom did find propyl propanoate on one occasion as a product of the reaction of pure 1-propanol [6]. This indicates that the above mentioned oxidations might occur.

Side reactions

The yield is hindered by a couple of side products, such as alkyl-substituted derivatives and oxidation products of anthracene. It is thought that the origin of the side reactions is the platinum anode; platinum is known to be catalytically active in many organic reactions [6].

Table 1: *(Side-)products reported by Morassutto and Slotboom [5, 6]*

Product	Reported by	Solvent	Voltage
9,10-dihydroanthracene	Morassutto	1-propanol	25 V
		Ethanol	10 V
	Slotboom	2-propanol	25 V
10-propyl-9-anthranol	Morassutto	1-propanol	10 V to 25 V
10-(2-propyl)-10*H*-9-anthranone	Slotboom	2-propanol	< 10 V
Anthraquinone	Morassutto	Ethanol	10 V
	Slotboom	2-propanol	< 10 V
9-ethyl-2-methyl-9,10-dihydroanthracene 9-ethyl-3-methyl-9,10-dihydroanthracene	Morassutto	Ethanol	10 V
9-methyl-10-(2-propyl)-9,10-dihydroanthracene	Slotboom	2-propanol	< 10 V

Products reported by Morassutto and Slotboom are listed in table 1. Morassutto found 10-propyl-9-anthranol and Slotboom found 10-(2-propyl)-10*H*-9-anthranone. They are probably referring to the same compound (the isomer of the propyl group aside) because they are each other's keto-enol tautomers (figure 4), which are in rapid equilibrium. The tautomeric equilibrium favours the keto form (10-propyl-10*H*-9-anthranone) [24, 25]. This is also supported by Slotboom's mass spectrum, which is in good agreement with fragmentation patterns for anthranone found in literature [6, 26].

In order to explain the formation of 10-alkyl-10*H*-9-anthranones, the alcohol used as proton donor has to break its $\mathrm{C-O}$ bond. Morassutto hypothesised that the anthracene radical anion intermediate (formed by addition of e^-_{sol} to anthracene, see figure 3) reacts with an alkyl cation, which presumably originates from some ionisation process taking place at the anode (instead of with a proton) followed by anodic oxidation [5].

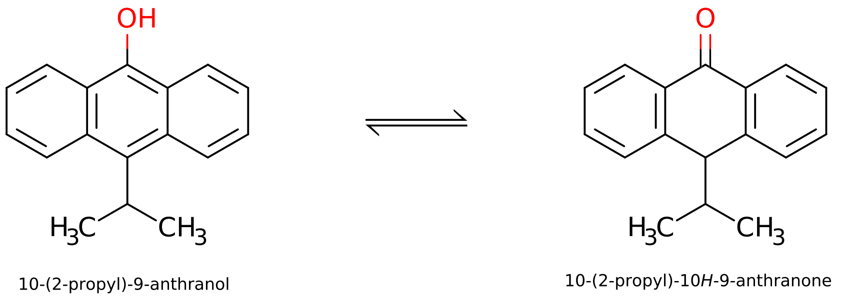

Figure 4: *Keto-enol tautomerism between 10-(2-propyl)-9-anthranol and 10-(2-propyl)-10H-9-anthranone*

On the other hand, Slotboom proposed a radical-based mechanism where the alcohol homolytically cleaves its C−O bond on the platinum anode, resulting in an (adsorbed) hydroxyl ($HO\cdot$) radical and a alkyl ($RCH_2\cdot$) radical [27]. These then add to the central ring of anthracene on the 9 and 10 positions, forming an 10-alkyl-9,10-dihydro-9-anthranol. The last step to 10-alkyl-10*H*-9-anthranone is the oxidation of the alcohol to the ketone (figure 5). Considering that the oxidation of alcohols to ketones is known to happen on platinum for simple alcohols like ethanol, it seems plausible that the dihydroanthranol can oxidise to anthranone this way [16, 17]. Slotboom suggested that the entire reaction happens as a Langmuir-Hinshelwood adsorption reaction on the platinum surface [6].

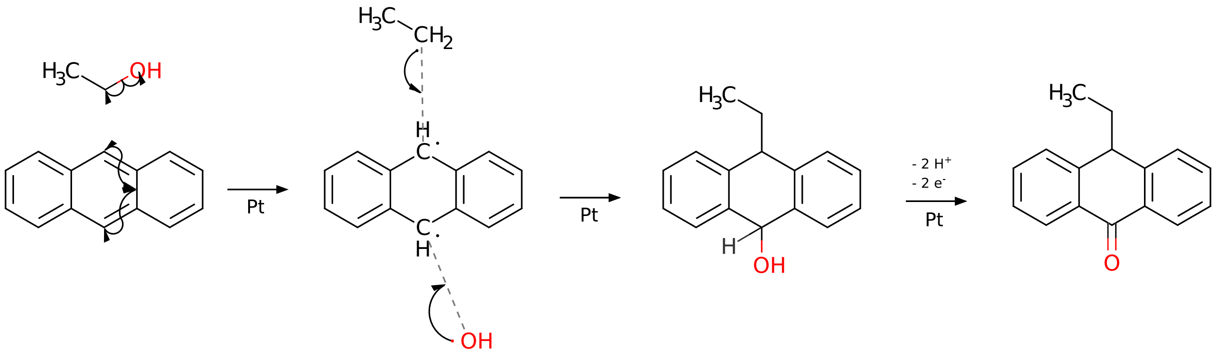

Figure 5: *Proposed pathway for the reaction of anthracene with 2-propanol to 10-(2-propyl)-10H-9-anthranone on the platinum surface.*

The fact that formation of 10-alkyl-10*H*-9-anthranones still happens even when no solvated electrons are generated due to insufficient voltage (< 10 V) strongly suggests that the radical-based pathway on the platinum surface is the correct one.

Traces of anthracene with two alkyl chains attached (such as 9-ethyl-3-methyl-9,10-dihydroanthracene and 9-methyl-10-(2-propyl)-9,10-dihydroanthracene) were also found. The reaction mechanism for the formation is probably similar to that described above, except two alkyl radicals add to the anthracene instead of an hydroxyl radical. The presence of a methyl group with ethanol and propanol as solvents means that a C−C bond has to be cleaved, which is known to be able to occur when ethanol adsorbs on a platinum surface [28].

For the formation of anthraquinone again a similar approach can be formulated, where two hydroxyl radicals add to the anthracene, followed by anodic oxidation (figure 6).

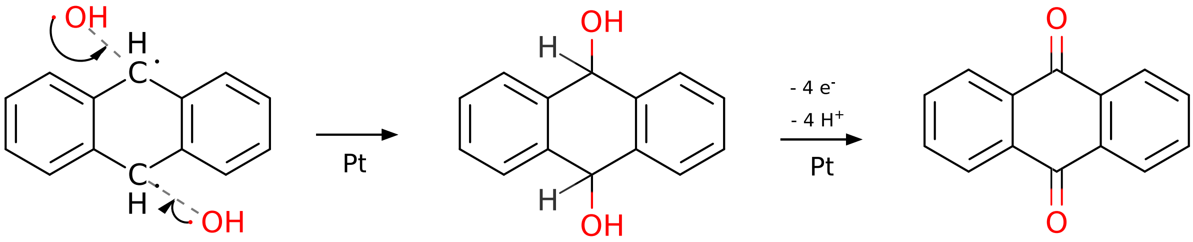

Figure 6: *Proposed pathway for the reaction of anthracene to anthraquinone on the platinum surface.*

Solvents

A number of solvents can be used in the microreactor. Obvious choices are protic solvents like alcohols; these double as proton donor. However, it is also possible to use a solution of an proton donor in an aprotic solvent, such as hexane or acetone.

In selection of a solvent, attention must be paid to properties such as polarity, vapour pressure, and viscosity. Much higher currents are observed for polar solvents than for apolar solvents, which suggests that polar solvents are better able to support solvated electrons [5]. High vapour pressures are inconvenient because they can cause crystallisation of anthracene when the solvent evaporates at the outlet. Very viscous solvents are unsuitable for use in the microreactor because the flow channels are very small, and thus viscous solvents cause high pressure drops over the microreactor, which means that high pressures are needed to attain a sufficient flow. This in turn can result into leaks and damage to the chip [6].

Morassutto and Slotboom did not accomplish reduction of anthracene to 9,10-dihydroanthracene with n-hexane as solvent (with added ethanol), although side products were produced [5, 6]. Morassutto achieved conversion to 9,10-dihydroanthracene with 1-propanol and ethanol, and Slotboom with 2-propanol.

The chemical properties of the proton donor are also important. Obviously the proton donor must be acidic to be able to donate protons, but only slightly so (the carbanion intermediates formed by electron addition are very basic). Alcohols seem to work well in this regard.

Some potential solvents are listed in table 2. Clogging of the chip seemed to be a major problem according to Slotboom, so out of protic solvents, ethanol and 1-propanol seem to be the best options [6]. 2-propanol is already too viscous. t-butanol is interesting since it is not expected to form side products because of its steric hindrance and the inability of the carbonyl to undergo dehydrogenation, but it is solid at room temperature and still far too viscous to be used when liquid. However, dissolved in a solvent of low viscosity such as acetone, it might be a viable option. Anthracene is more soluble in acetone than in n-hexane, and a higher current is observed with acetone than with n-hexane [6].

Table 2: *Physical properties of solvents at* 20 °C *and* 100 kPa. *Data obtained from [29, 30]*

Solvent	Dynamic viscosity (mPa s)	Vapour pressure (kPa)	$\mathrm{p}K_\mathrm{a}$	Relative permittivity
Ethanol	1.199	5.87	15.9	24.6
1-propanol	2.199	1.99	16	20.1
2-propanol	2.405	4.18	16.5	18.3
t-butanol (30 °C)	3.391	7.57	16.54	12.5
Acetone	0.322	24.50	19.2	21.0
n-hexane	0.312	16.08	~50	1.89

On the other hand, it has been reported that acetone can act as a scavenger of solvated electrons in the context of pulse radiolysis [31, 32]. More specifically, acetone as a solute in alcohol can capture solvated electrons, yielding acetone ketyl radicals (equation 5). However, the electron is loosely bound to the acetone and can relatively easily be transferred to another compound. In other words, acetone can act as an electron carrier. Alternatively, it is possible for the acetone ketyl radical to be protonated to form an 2-propanol radical (equation 6) [33]. It is unclear what consequences this has on the Birch-type reaction when using acetone as solvent.

$$(CH_3)_2CO + e^-_{sol} \longrightarrow (CH_3)_2CO\cdot^- \tag{5}$$

$$(CH_3)_2CO\cdot^- + H^+ \longrightarrow (CH_3)_2COH\cdot \tag{6}$$

It is peculiar that the "hydrogen reaction", i.e. the direct reduction of protons to hydrogen gas (equation 1), does not occur in the microreactor to the extent one would expect when a protic solvent such as an alcohol is used. Both for the conventional Birch reduction as well as for electrochemical methods of reducing PAHs it is widely mentioned that high alcohol concentration results in evolution of hydrogen gas [4, 9, 10, 34]. However, this does not seem to be the case in the CFE microreactor. Morassutto reported the presence of bubbles at the outlet of the microreactor, but it was unclear whether this was H_2, injected air, dissolved ambient gas, or vaporised solvent [5].

Research plan

With the aforementioned results from Morassutto and Slotboom as basis, experiments will be conducted to gain further insight in this reaction.

Reactions in several solvents, including solutions of alcohols in acetone (per Slotboom's recommendation) will be performed and the yields will be measured to confirm and compliment existing data. Acetone with t-butanol as proton donor will be tested to see if the reaction is able to proceed with tertiary alcohols (which are resistant to oxidation). In order to test Slotboom's hypothesis concerning the formation of side products on the platinum anode, experiments will be done with microreactors with alternative anode materials (gold and indium tin oxide). Besides GC-MS, IR spectroscopy will be performed on samples (both with and without anthracene) to try to detect aldehydes, as evidence of the oxidation of the alcohol. Viscous solvents (2-propanol and t-butanol) will not be used in pure form since this proved very problematic.

Detailed experimental methods are described in section 3.3.

3 | Experimental aspects

3.1 Microreactor set-up

The reaction is performed in a microreactor (figure 9). The microreactor consists of two electrodes with a microfluidic flow channel (12 mm long, 1 mm wide and 5 µm high) in between. The cathode consists of a SiNW field emitter array for injecting solvated electrons into the reaction mixture. Opposite to the cathode is the (flat) anode (figure 7).

The volume of the microreactor is 60 nL. Hence, for a desired residence time of 1 s, the flow rate is 3.6 µL min^{-1}.

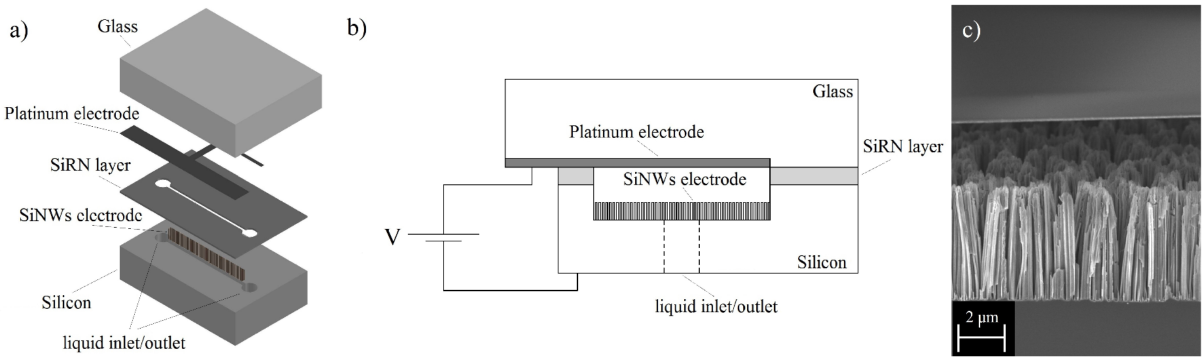

Figure 7: The microreactor set-up. a) the 3D concept drawing. b) cross-section schematic. c) SEM image of the flow channel showing the SiNW field emitter array. After Morassutto [5]

Compared to the microreactors Morassutto and Slotboom used, the microreactors used here have a wider flow channel (5x as wide) to try to alleviate the high pressure drop observed and thereby permit the use of moderately viscous solvents and/or higher flow rates. Another modification is the inclusion of a barrier, in the form of a solid silicon block of the same height as the SiNWs, at the inlet of the microreactor (figure 8). The idea is that this will guide the liquid *over* the SiNWs instead of against them, to try to reduce the shear forces of the liquid on the SiNWs resulting into damage to the SiNWs.

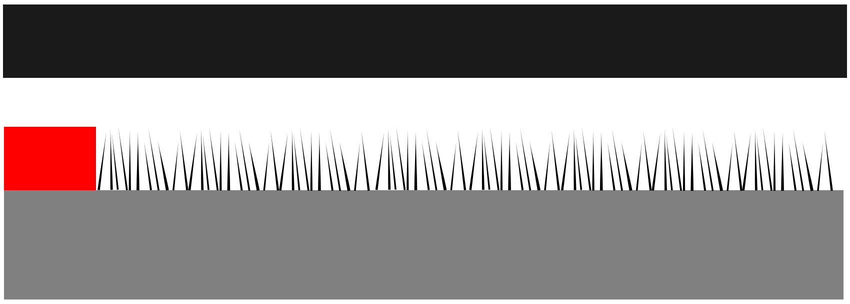

Figure 8: Schematic drawing of the barrier (shown in red) at the inlet of the channel.

In addition to platinum, additional designs of microreactors will be used with gold and indium tin oxide (ITO) as anodic material.

Altogether, 6 different versions of the microreactor are considered: 3 different anodes, of which one half of the chips with barrier at the inlet, and the other half without (table 3).

Table 3: *All types of the microreactor chips with their designations*

	Platinum	Gold	Indium tin oxide
Barrier	Pt-b	Au-b	ITO-b
No barrier	Pt-nb	Au-nb	ITO-nb

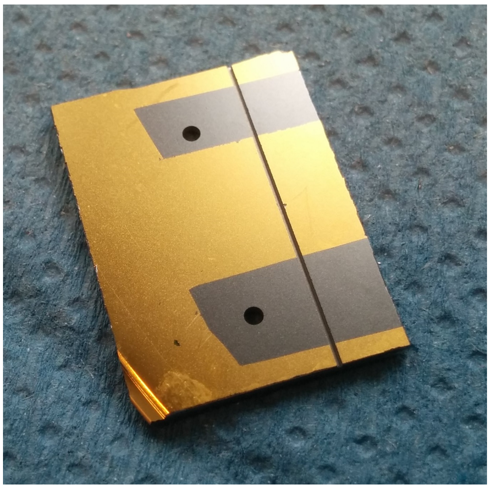

Figure 9: *Picture of a microreactor chip (top side). The two circular holes are the fluid in- and outlet.*

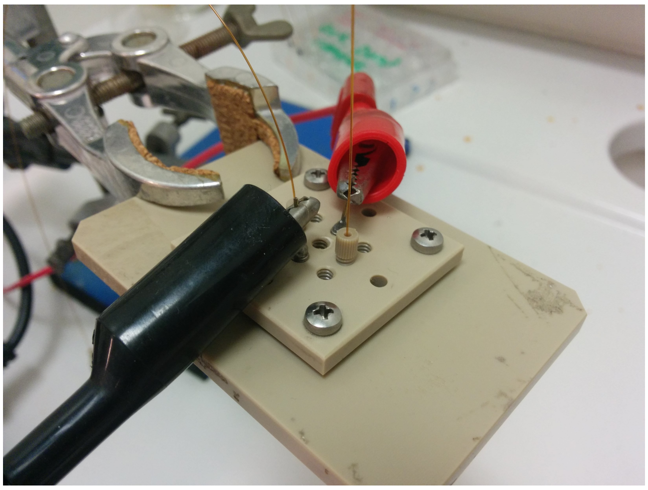

Figure 10: *Picture of the fully assembled chip holder with the capillaries and electrodes connected.*

3.2 Experimental set-up

The microreactor chip is placed into a holder with predefined screw holes that fit on the microreactor in- and outlet (figure 10). The inlet is connected via a fused silica capillary (Polymicro, 250 µm inner diameter, 360 µm outer diameter) to a glass syringe (Hamilton Gastight 5 mL and 10 mL) in a volumetric syringe pump (Harvard Apparatus PHD 2000). Another capillary is connected to the outlet and put into a vial.

A source measure unit (Keithley 2410) is connected to the electrodes and used to provide the electric potential. Voltage and current are measured by the source measure unit and logged using a LabVIEW program.

The sample collected at the outlet is analysed by GC-MS (Agilent Technologies 7890A 5975C) and ATR-FTIR (Thermo Scientific Nicolet 6700).

3.3 Methods

In order to investigate the questions raised in section 1.3, several experiments were performed, which are explained in detail below.

Preparation

Around 8.9 mg of anthracene is dissolved in 10 mL of the respective solvent in a volumetric flask to give a solution of 5 mmol L^{-1}. When an alcohol is used as proton donor in acetone, 1 mL of the alcohol is transferred to the volumetric flask with the anthracene solution using a micropipette, after which the volumetric flask is filled with acetone to 10 mL to give a solution of 5 mmol L^{-1} anthracene in 10% (by volume) alcohol in acetone.

Reaction

The solution is pumped through the microreactor at a constant rate of 3 µL $\min^{-1}$ for several hours, to collect several milliliters of sample. A constant potential of 25 V is applied between the two electrodes, and the resulting current is measured continuously, with a period of 0.5 s. The compliance (current limit) of the source measure unit is set at 1 mA.

It was made sure the chip was fully flushed with the new solution by discarding the first few drops of liquid coming out of the outlet before starting the measurement and collecting the sample.

Analysis

The primary characterisation method is GC-MS. Additionally, IR spectroscopy (ATR-FTIR) will be performed for select samples for the detection of volatile components such as aldehydes, which cannot be detected by GC-MS due to the too low retention time.

H-NMR was also considered, but was not deemed a viable option because the samples are dilute solutions of the analyte(s) in alcohol/aceton. The signals from the analytes would get completely drown out by the signal from the solvent.

3.4 Results and discussion

An overview of all performed experiments is attached in Appendix A.

Current behaviour

Current-time diagrams taken during the reaction are attached in Appendix B.

The current drawn by the microreactor is in the order of several hundred µA in the case of the platinum anode. This is higher than what Morassutto and Slotboom reported, but this is expected since the chips used in this study have a 4x as large electrode surface area. The lowest current (100 µA to 200 µA) was observed for ethanol in acetone, and the highest current (600 µA) for t-butanol in acetone.

In many cases the current fluctuates or has anomalies such as peaks or dips (see Appendix B). It is not possible to say with certainty what the cause for these fluctuations and anomalies is; no clear patterns are visible in these deviations. Possible explanations include concentration gradients in the reaction mixture, air bubbles, degradation of the electrodes, or inconsistent flow rate due to leaks.

For the microreactors with ITO anode, a much lower current (around 1 µA) was observed. This can either be because of a chemical effect (lack of electrocatalytic effect of the anode resulting in lower current) or as a result of the high resistance of the ITO leads themselves. In the latter case, this means that the effective potential over the channel is lower than 25 V because of the current drop over the ITO lead to the actual electrode.

Effect of solvent on yields

Several solvents (alcohols and solutions of alcohols in acetone) were tested in order to compare the yields towards the main product and side products. Samples obtained by flowing solutions of anthracene in these solvents through the microreactor were analysed by GC-MS.

The yields towards the various products are reported in table 4. Identification of products was done by interpretation of mass spectra, in some cases with the aid of online mass spectral databases [35]; compounds for which a mass spectrum was available could be highly accurately identified by this means. Other compounds were correlated with mass spectra reported by Morassutto and Slotboom. New compounds were identified on basis of general fragmentation patterns specific for the respective functional groups, such as ethers [36]. Quantitative measures were calculated from the ratios of chromatogram peak areas. However, it must be noted that these are not guaranteed to be accurate because of the high number of distinct products; in some cases, separation was insufficient and peaks overlapped. Also note that it is not always possible to determine the constitutional isomer of a compound by mass spectrometry. In these cases it has therefore been assumed that anthracene is substituted on the 9 and/or 10 positions.

Table 4: *Yields of anthracene towards several products for various solvents. All experiments were performed using a Pt chip. Supportive information can be found in Appendix D and E.*

Solvent	Proton donor	Conversion (%)	Yields
Ethanol		90.7	3.8% 10-ethyl-9-methyl-9,10-dihydroanthracene 0.2% 9-methyl-9,10-dihydroanthracene 34.3% anthraquinone 51.2% 10-ethyl-10*H*-9-anthranone 1.2% 9,10-diethoxyanthracene
Acetone	10% ethanol	60.5-64.6	60.5-64.6% 10-ethyl-10*H*-9-anthranone
Acetone	10% t-butanol	75.3	2.5% 9-methoxyanthracene 52.7% anthraquinone 20.0% 10-methyl-9-methoxyanthracene[1]
Acetone	10% 2-propanol	44.8	3.6% 9-methyl-10-(2-propyl)-anthracene 12.7% 10-methyl-10*H*-9-anthranone[1] 28.5% 10-(2-propyl)-10*H*-9-anthranone
1-propanol		52.1	3.0% 9,10-dihydroanthracene 5.6% anthraquinone 43.5% 10-propyl-10*H*-9-anthranone

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[1] Most likely. These peaks overlapped with anthraquinone ($RT \approx 65.8$ s) and where thus difficult to identify with certainty.

Only in a single case was 9,10-dihydroanthracene detected in the samples: with 1-propanol as solvent. The (small) peak was found at a retention time of 53.3 min and the yield was only 3%. This was unanticipated because Morassutto and Slotboom managed to successfully perform the reaction with both ethanol and 1-propanol in much higher yields, with the same microreactor (design) and conditions.

However, many side products (substituted anthracenes) were detected, including some products not reported by Morassutto or Slotboom. Ethanol as solvent produced the highest number of products, although 10% ethanol in acetone produced only one product. In most cases the major products are anthraquinone and 10-ethyl-10*H*-9-anthranone. 10% t-butanol in acetone produced no 10-ethyl-10*H*-9-anthranone, but contained 10-methyl-9-methoxyanthracene as second largest product.

t-butanol seems to favour the formation of anthracene ethers. The mechanism for this is unclear, but it is unlikely to proceed via a mechanism analog to the ones drawn out in figure 5/6, because the O−H bond is unlikely to homolytically cleave on the platinum surface, like is suspected to happen for C−C and C−O bonds. Neither do any of the well-known syntheses for (aromatic) ethers apply in this specific situation.

Effect of anodic material

In order to investigate the effect of the material used as the anode, microreactor chips with indium tin oxide (ITO) anodes were tested alongside the chips with platinum anodes. The yields for the ITO chips are reported in table 5.

Table 5: *Yields of anthracene towards several products for various solvents. All experiments were performed using a ITO chip.*

Solvent	Proton donor	Conversion (%)	Yields
Ethanol[1]		29.2	2.5% anthraquinone 26.6% 10-ethyl-10*H*-9-anthranone
Acetone	t-butanol	0	
Acetone	2-propanol	0	

Considering the hypothesis given in section 2.3.2, it is surprising that side products still form in one case (ethanol) with the ITO chip. The other two experiments did not result into any conversion at all, though. This observation correlates with the measured current (see Appendix B), which is around 10 µV for the ethanol experiment, and around 1 µV for the later two measurements. In all three cases, the same chip was used. Because all experiments were done with the same chip, the chip itself cannot be excluded; because the observed currents were so low (and declining over time), it is possible that there was some (electrical) degradation occurring at the chip.

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[1] The GC-MS analysis for the experiment indicated acetone contamination through the presence of 2,2-diethoxypropane. Possibly the syringe was not rinsed or dried properly before use. The microreactor chip used in this experiment was new.

The fact that anthraquinone and 10-ethyl-10*H*-9-anthranone still form with the ITO anode has considerable consequences to the hypothesis about the formation of these compounds. It either means that ITO has the same electrocatalytic effects as platinum (which is unlikely), or that this reaction is happening in the bulk fluid instead. In the latter case, the reaction mechanism remains unexplained.

Oxidation of alcohols

Samples obtained by flowing pure 1-propanol (#9), 1-propanol with anthracene (#10), and ethanol with anthracene (#11) through the microreactor were analysed by ATR-FTIR in order to try to detect evidence of alcohol oxidation to aldehydes. Pure 1-propanol (not passed through the microreactor) was also analysed as a negative control.

While running the experiments, the samples were collected in a vial with rubber septum to prevent the sample from evaporating. Samples #9 and #10 were also cooled using an ice bath for the duration of the experiment.

The captured IR spectra did not indicate the presence of aldehydes in any of the samples. The IR spectra closely resemble those of the pure solvent used (propanol/ethanol), without the (for an aldehyde) expected C=O stretch peak around $1700\,\mathrm{cm}^{-1}$. There is a small peak at $1650\,\mathrm{cm}^{-1}$, but this peak is also present in the control and is probably from water. The spectra can be found in Appendix C.

This can either mean that the alcohols do not oxidise, or that the concentration of aldehydes in the sample is too low for the spectrometer to detect. It is possible that the aldehydes still evaporated despite the measures taken to prevent this (vial with septum and ice bath).

However, on one occasion (experiment #4) 1,1-diethoxyethane was detected by GC-MS. 1,1-diethoxyethane is the acetal formed by condensation of ethanal and ethanol. This indirectly indicates the presence of ethanal. Similarly, for experiment #10, propyl propanoate (the propanol ester of propanoic acid) and 1,1-dipropoxypropane (the acetal of 1-propanol and propanal) was detected.

Deterioration of the chip

No deterioration of the SiNWs, like what was reported by Slotboom, was noticed. Currents fluctuated somewhat (on a short time scale) and had anomalies at times, but (for the chips with platinum electrode) no consistent decline in current over time was found, nor did the chip short out. There was also no noticeable difference between chips with barrier at the inlet and chips without.

The use of viscous solvents (in pure form) possibly contributed to damage to the SiNWs in Slotboom's study. Another reason is the difference in channel width; the wider channels may have prevented high pressure drops that happened in Slotboom's case.

Inspection of field emitter array

The failure to achieve conversion from anthracene to 9,10-dihydroanthracene in significant yields was unanticipated, given the positive outcome of this same reaction in the same system by Morassutto and Slotboom. The microreactors are manufactured based on Morassutto's procedures and reaction conditions (concentration, residence time, voltage) have been kept identical. Only one relevant aspect of the microreactor design is different, namely the size of the channel and the electrodes. The chips used here have wider (and somewhat shorter) channels. The net surface area of the electrodes is 4x as large. However this is not expected to have any intrinsic influence on the reactions happening. If anything, this should result in more generation of solvated electrons and thus higher yields.

To investigate the reason behind the lack of reduction, SEM images were taken of a unbonded wafer containing SiNW field emitter arrays.

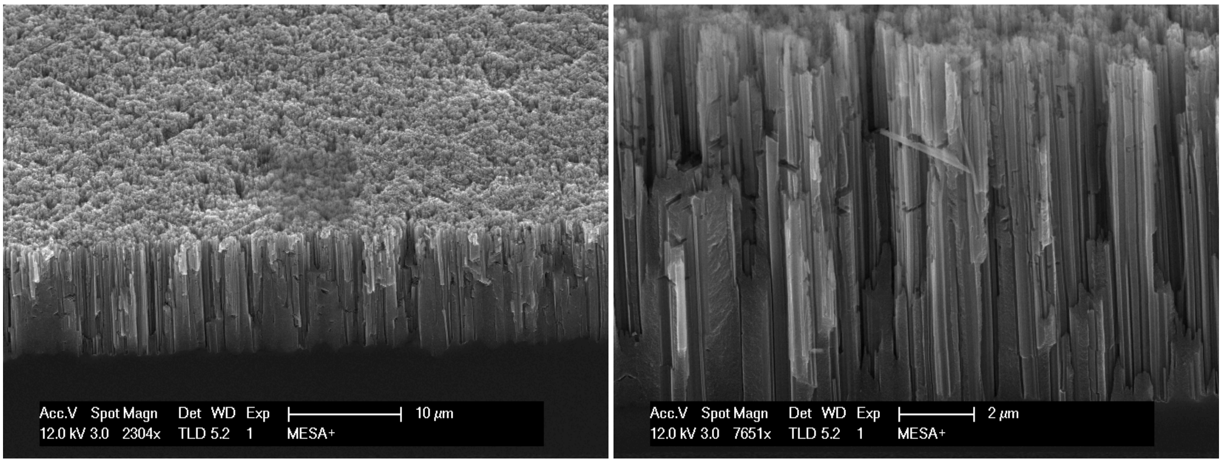

Figure 11: *Cross-section SEM pictures of the field emitter array (from an unused chip).*

The pictures (figure 11) show a brush-like appearance. This is expected, though when the pictures are compared to similar pictures from Morassutto and Slotboom, it becomes clear that the field emitter array is packed more dense than was the case for Morassutto's chips. A denser array means more emission points, but the exact shape of the individual SiNWs and the structure of the array as a whole may be critical for the function. In more concrete terms, it may be the case that the field emitter array is not working as intended because it was not etched far enough and the individual wires are packed too close to each other, thereby not exhibiting the desired local amplification of the electric field required for field emission of electrons. This is possibly the culprit behind the lack of reduction of anthracene; if little to no solvated electrons are generated, this reaction cannot occur.

One possible reason for the malformation of the field emitter array is a discrepancy in the amount of light during etching. The reaction used to make the SiNWs is sensitive to light, and a difference in handling (brightness of the environment, use of opaque glassware) could be the cause for deviating results.

4 | Evaluation

4.1 Experimental complications

When starting out with the experiments, it was initially thought that the microreactor chips were shorting out. When the voltage was applied directly after assembling the chip in the chip holder, the current was very low (but non-zero). However, after connecting the capillaries and applying the voltage again, the current was all of a sudden much higher, exceeding the current compliance of 105 µA. This happened without starting the pump; simply the act of connecting the capillaries appeared to cause a current rise. This strange effect was confirmed multiple times.

Afterwards it was realised that the compliance was simply set too low; the chip was not shorting out, the current was just higher than initially expected. After setting the compliance to 1 mA, these issues were solved and no further effort was put into investigating the above-mentioned effect.

During the experiments, some fluidic complications arose: leaking couplings, solvent evaporation, and clogging of the chips.

During the first experiments, the coupling between the syringe needle and the capillary leaked. The leak was not immediately noticed because the flow rates used are low, and the solvents are volatile, which meant that any leaked fluid evaporated quickly. The leak was fixed by using a tighter sleeve on the needle tip. After this modification, much more solution was collected in the sample vial; it was only then that it was fully realised how much fluid leaked before. In some cases the leaking caused too little sample to be collected for GC-MS analysis.

After finishing an experiment and trying to set-up a new one, it sometimes occurred that the chip was clogged and no fluid could be pumped through. It was found that washing the chip in an acetone bath worked very easily and reliably to clean the chips. After this treatment, the liquid was again very easily pumped through the chips.

4.2 Time constraints

Unfortunately, due to delays in both fabrication of microreactor chips and analysis of samples, not all planned experiments could be performed. Only chips with platinum and ITO anodes were tested; at the time of writing, the chips with gold anodes were not finished.

It was also not possible to conduct any further experiments after receiving and interpreting the results from the first analyses because of the waiting time for GC-MS. In other words, all the experiments were conducted *before* any results about previous experiments were known, which hindered the capability to choose new experiments on basis of new information gained from results of previous ones.

5 | Conclusion

Unfortunately, due to time constraints, not all questions were answered.

Only in one experiment conversion to the desired product, 9,10-dihydroanthracene, was achieved, and only in small amounts. Nevertheless, many side products were detected and identified. In contrast with Slotboom's results, it was demonstrated that a wide range of side products are produced when using acetone as a solvent. It was also shown that tert-butanol as a proton-donor still can produce side products. No conclusion can be drawn about influences on the yield towards the desired product, because it was not consistently produced.

One experiment with a chip with ITO anode still resulted in side products (anthraquinone and 10-ethyl-10*H*-9-anthranone). If this result can be reproduced, it means that the hypothesis that these side products are formed as a Langmuir-Hinshelwood adsorption reaction on the platinum surface is incorrect (unless ITO sustains the exact same adsorption reaction). The experiments with chips with ITO anodes are considered problematic because only one experiment managed to convert any anthracene; the other two experiments did not yield any (side) products.

The reason for the lack of conversion to 9,10-dihydroanthracene is thought to be a malformation of the field emitter array. SEM pictures showed that the SiNWs were packed much closer than was the case with Morassutto's chips.

No direct evidence of oxidation of the alcohol used as solvent and/or proton donor was observed, but there was some indirect evidence in the form of the acetal of ethanol and ethanal (1,1-diethoxyethane), the acetal of propanol and propanal (1,1-diproproxypropane), and the propanol ester of propanoic acid (propyl propanoate), which were detected by GC-MS in significant quantities. The latter compound was also reported by Slotboom. These observations together suggest that the electrocatalytic oxidation of alcohols indeed occurs in the microreactor.

6 | Outlook

To answer the questions left unanswered, further research needs to be conducted. New microreactor chips with an improved field emitter array should be fabricated and tested. It is recommended to look into tuning the field emitter array density/shape to maximise solvated electron generation.

When a working microreactor is achieved, the experiments done in this study should be repeated to obtain data about yields to 9,10-dihydroanthracene.

Furthermore, it is specifically recommended to repeat the experiments done with chips with ITO anodes, and also test microreactors with a gold anode. Gold is probably a better anode material than ITO, because the chips with ITO anodes suffer from ITO's low conductivity. If possible, other promising materials (such as glassy carbon, which is very inert) would also be interesting to test.

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A | List of experiments

Table 6: *List of experiments and conditions. The first few experiments (which did not yield sample due to setup problems) are not shown.*

#	Chip type	Reaction mixture	Typical current (µA)	Flowrate (µL min^{-1})	Sample collection method
2_7[1]	Pt-nb	1-propanol + 4.8 mM anthracene	400	2	Open vial
3[2]	Pt-b	1-propanol + 4.8 mM anthracene	500	3	Sealed vial
4	Pt-nb	Ethanol + 4.9 mM anthracene	400	3	Sealed vial
5[3]	Pt-nb	10% ethanol in acetone + 4.8 mM anthracene	100	3	Sealed vial
6[4]	Pt-b	10% t-butanol in acetone + 4.8 mM anthracene	600	2.13	Sealed vial
7[4]	Pt-b	10% ethanol in acetone + 4.8 mM anthracene	250	2.13	Sealed vial
8[4]	Pt-b	10% 2-propanol in acetone + 5.0 mM anthracene	400	2.13	Sealed vial
9	Pt-b	1-propanol	300	3	Vial+septum in ice
10[5]	Pt-nb	1-propanol + 4.8 mM anthracene		3	Vial+septum in ice
11	ITO-b	Ethanol + 4.9 mM anthracene	10	3	Vial+septum
12	ITO-b	10% t-butanol in acetone + 4.8 mM anthracene	1	3	Vial+septum
13	ITO-b	10% 2-propanol in acetone + 5.0 mM anthracene	1	3	Vial+septum
14	ITO-nb	1-propanol + 5.0 mM anthracene	1	3	Vial+septum

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[1] Compliance set at 500 µA, current limited by compliance at end of measurement

[2] Chip broke in half after measurement

[3] Interrupted pump momentarily in middle of measurement to tighten connection between syringe needle and capillary, which caused a strange peak in the current

[4] Pump was set at the wrong syringe diameter, which caused the flowrate to be 2.13 µL min^{-1} instead of 3 µL min^{-1}

[5] Very strange current behaviour (see figure 20)

B | Current-time diagrams

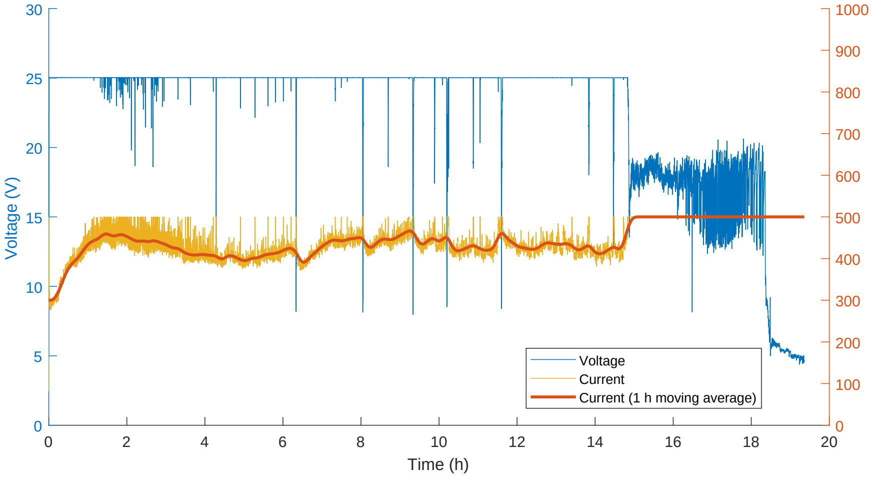

Figure 12: *Experiment #2_7 (Pt-nb, 1-propanol)*

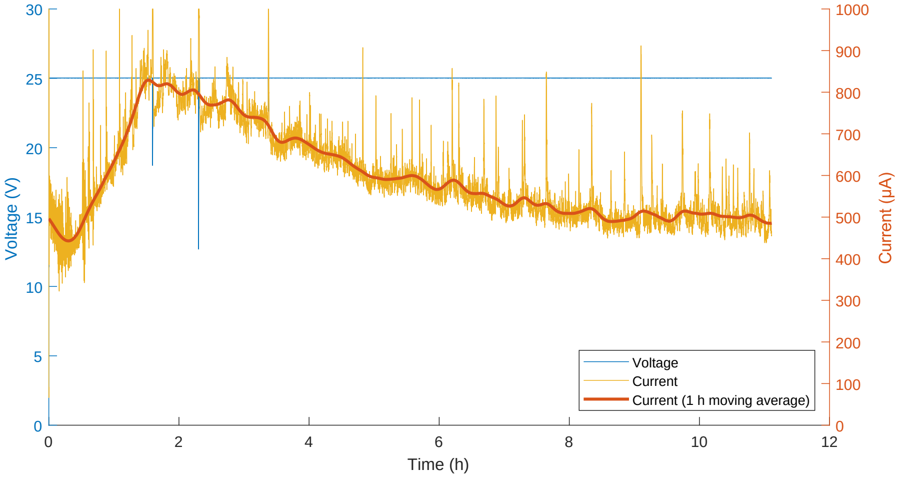

Figure 13: *Experiment #3 (Pt-b, 1-propanol)*

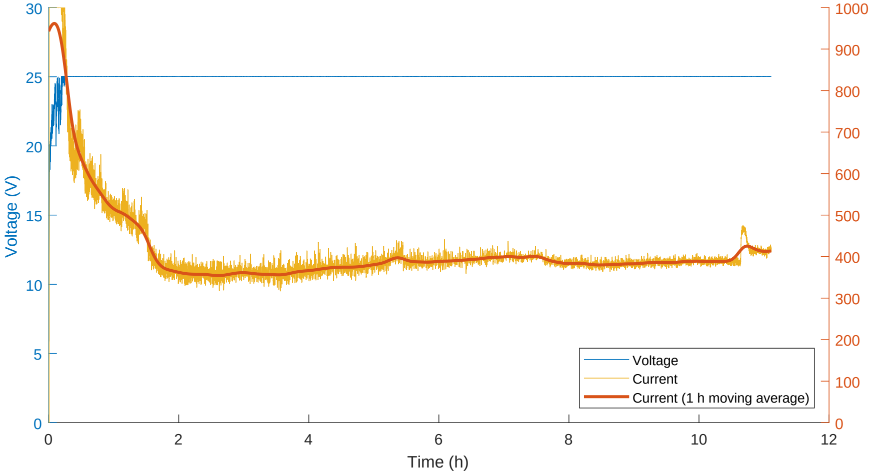

Figure 14: *Experiment #4 (Pt-nb, ethanol)*

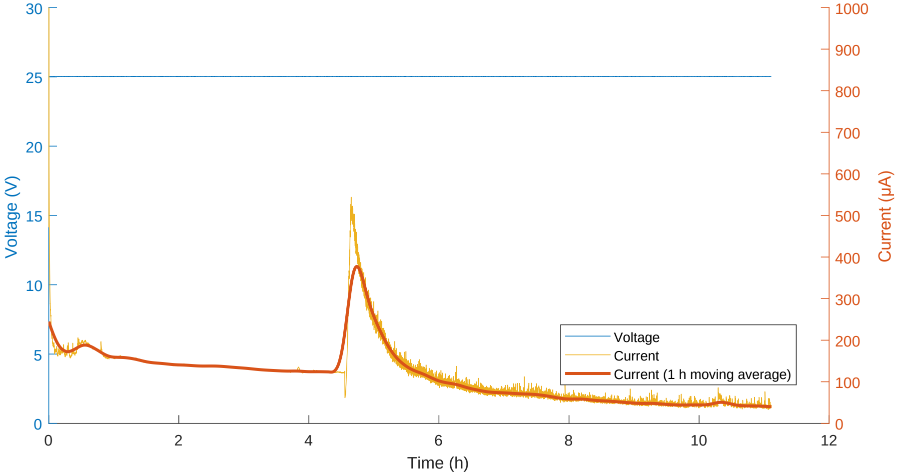

Figure 15: *Experiment #5 (Pt-nb, ethanol in acetone)*

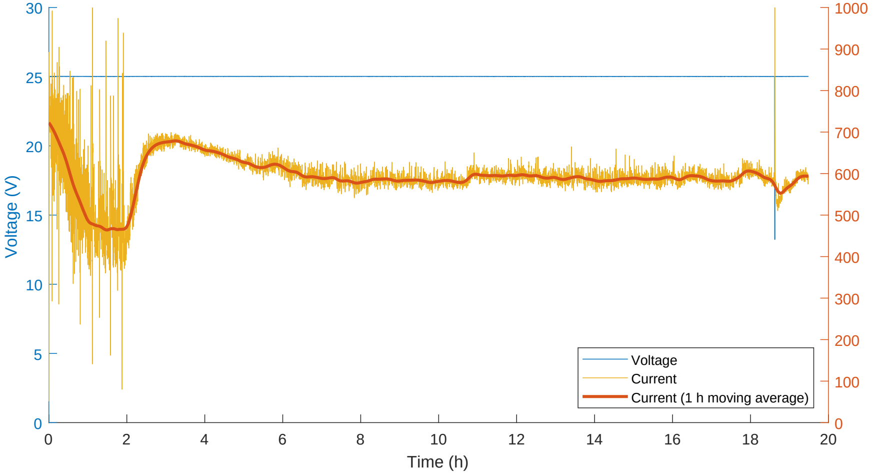

Figure 16: *Experiment #6 (Pt-b, t-butanol in acetone)*

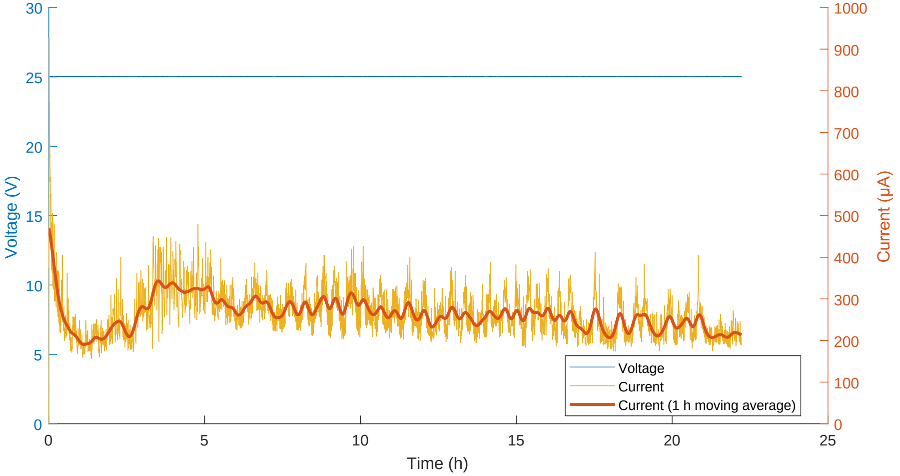

Figure 17: *Experiment #7 (Pt-b, ethanol in acetone)*

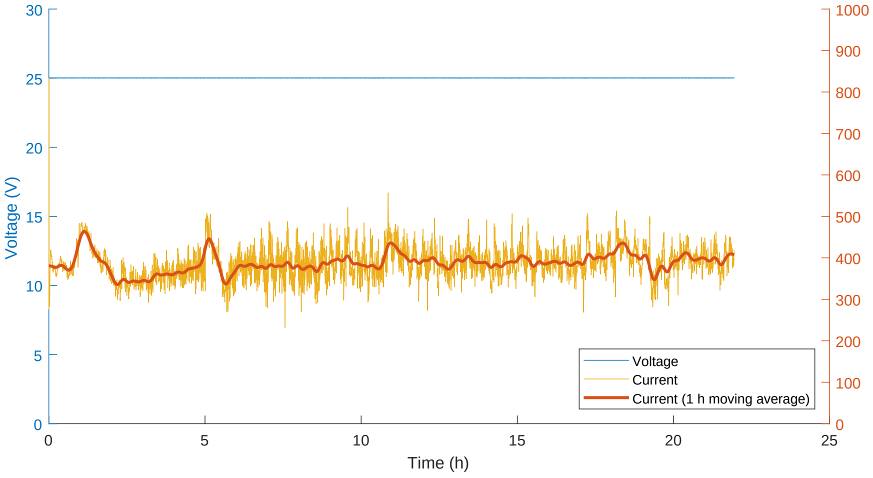

Figure 18: *Experiment #8 (Pt-b, 2-propanol in acetone)*

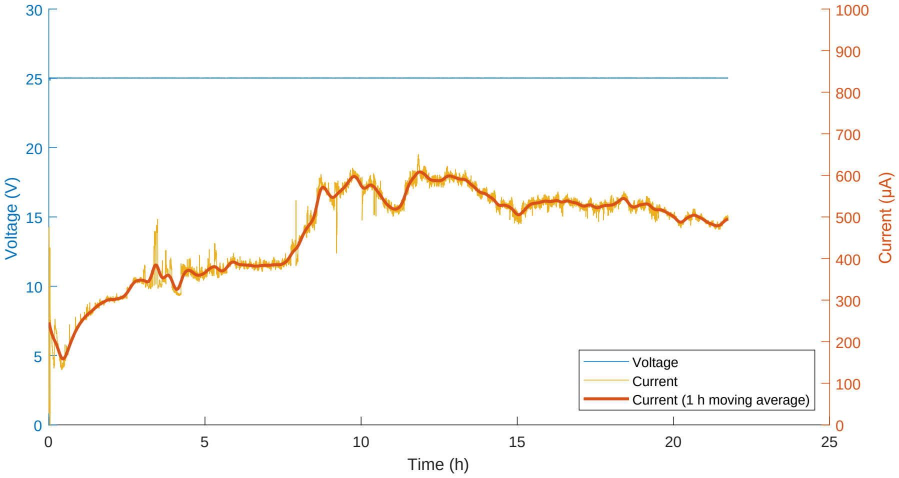

Figure 19: *Experiment #9 (Pt-b, pure 1-propanol)*

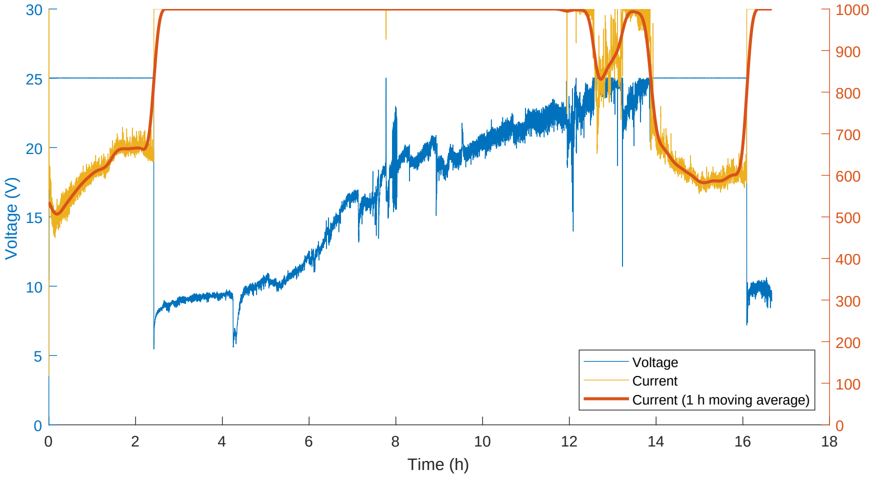

Figure 20: *Experiment #10 (Pt-nb, 1-propanol)*

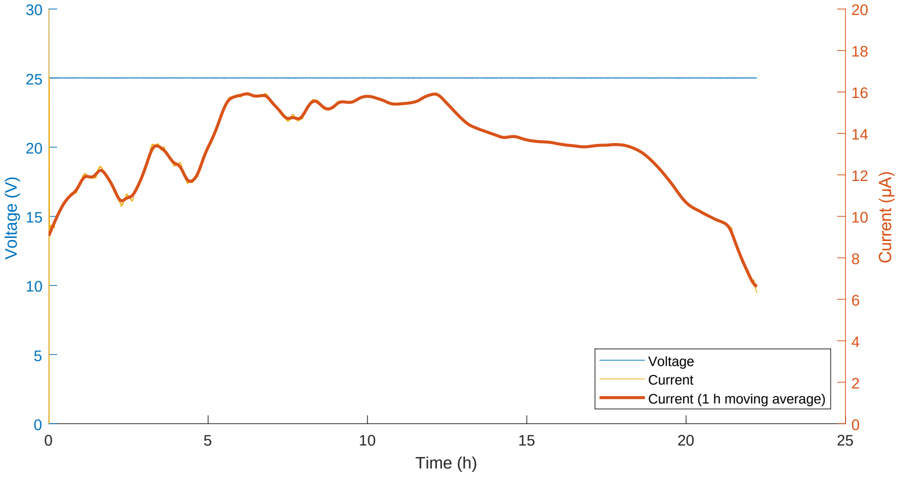

Figure 21: *Experiment #11 (ITO-b, ethanol)*

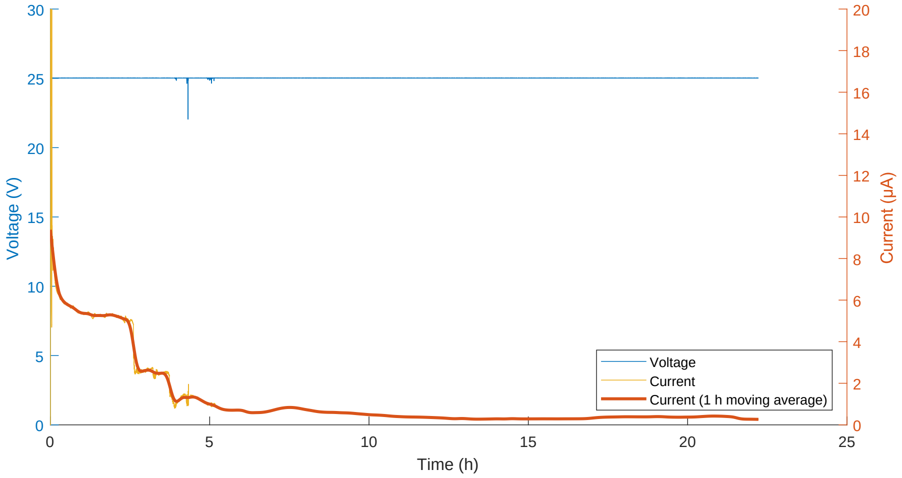

Figure 22: *Experiment #12 (ITO-b, t-butanol in acetone)*

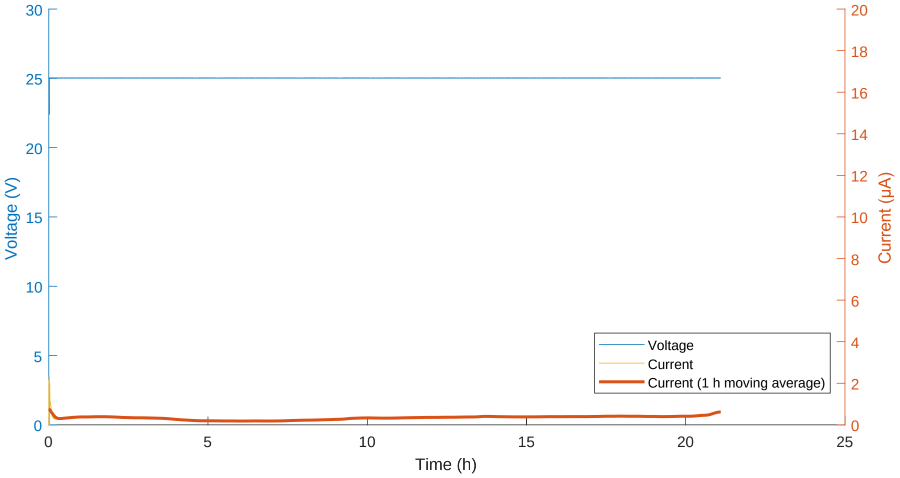

Figure 23: *Experiment #13 (ITO-b, 2-propanol in acetone)*

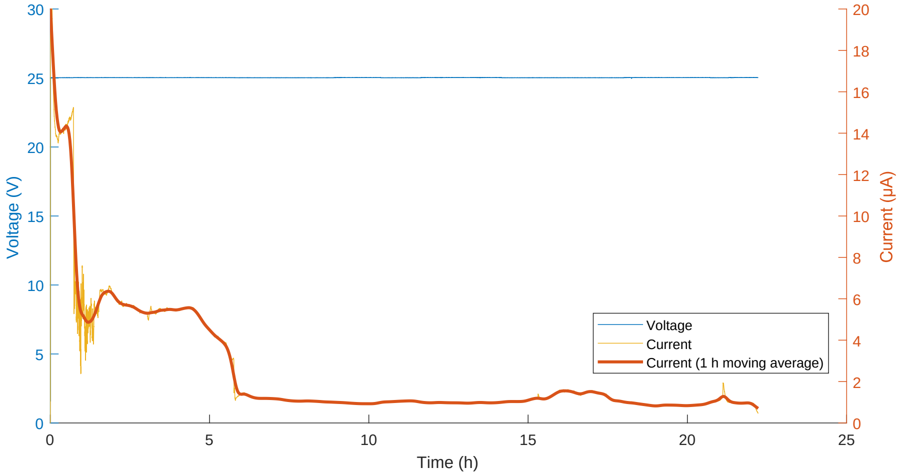

Figure 24: *Experiment #14 (ITO-nb, 1-propanol in acetone)*

C IR spectra

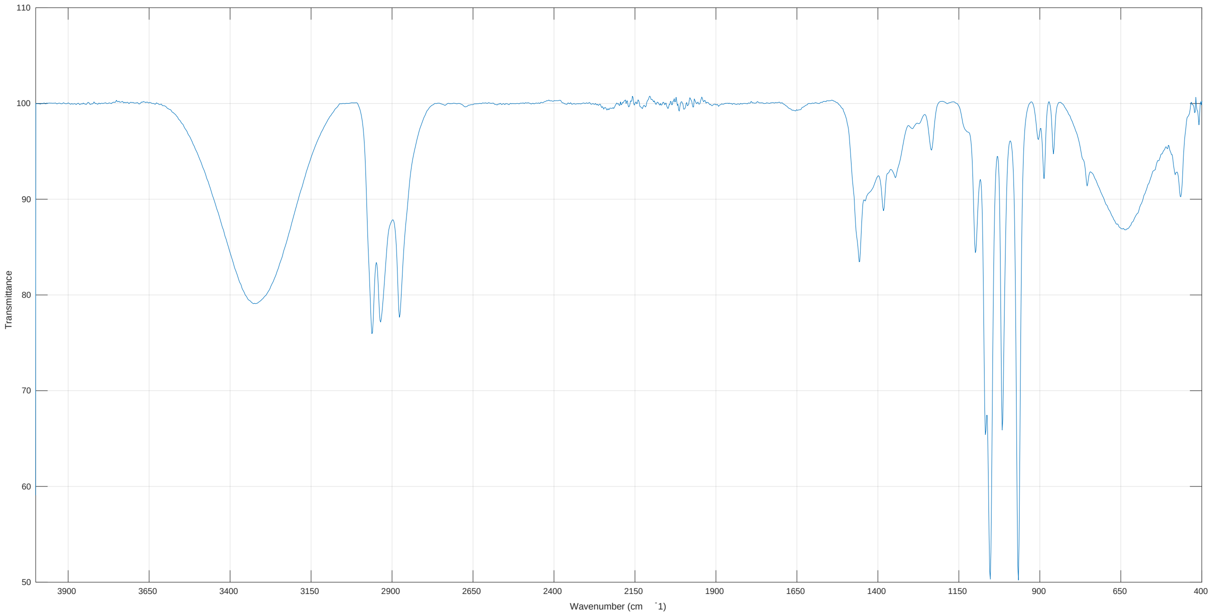

Figure 25: *Experiment #9 (pure 1-propanol)*

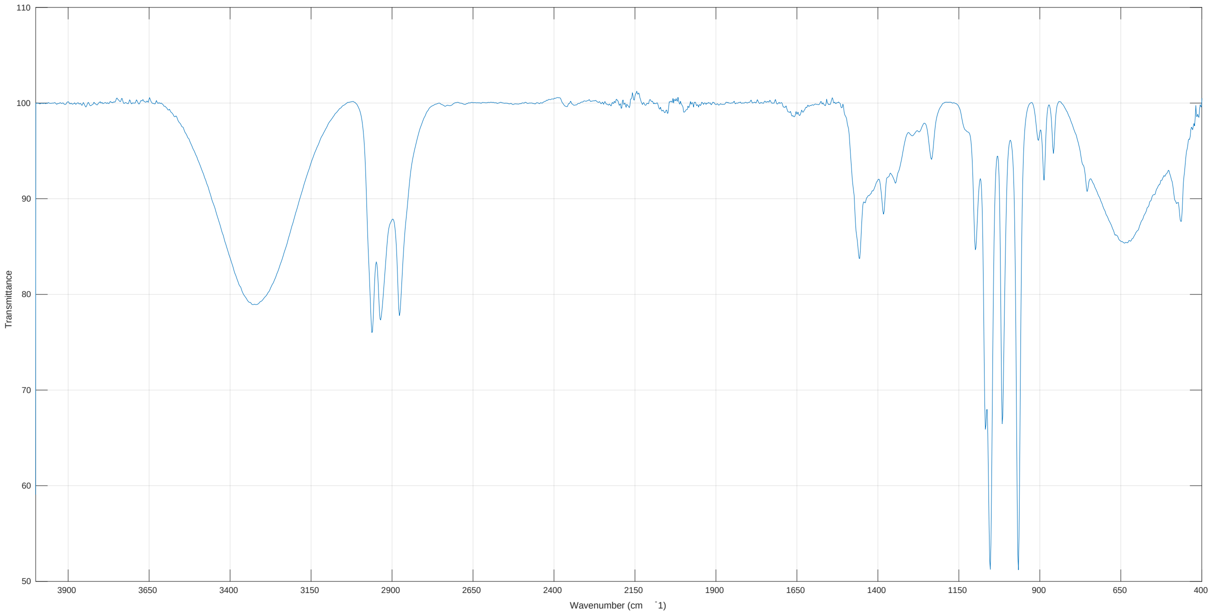

Figure 26: *Experiment #10 (1-propanol with anthracene)*

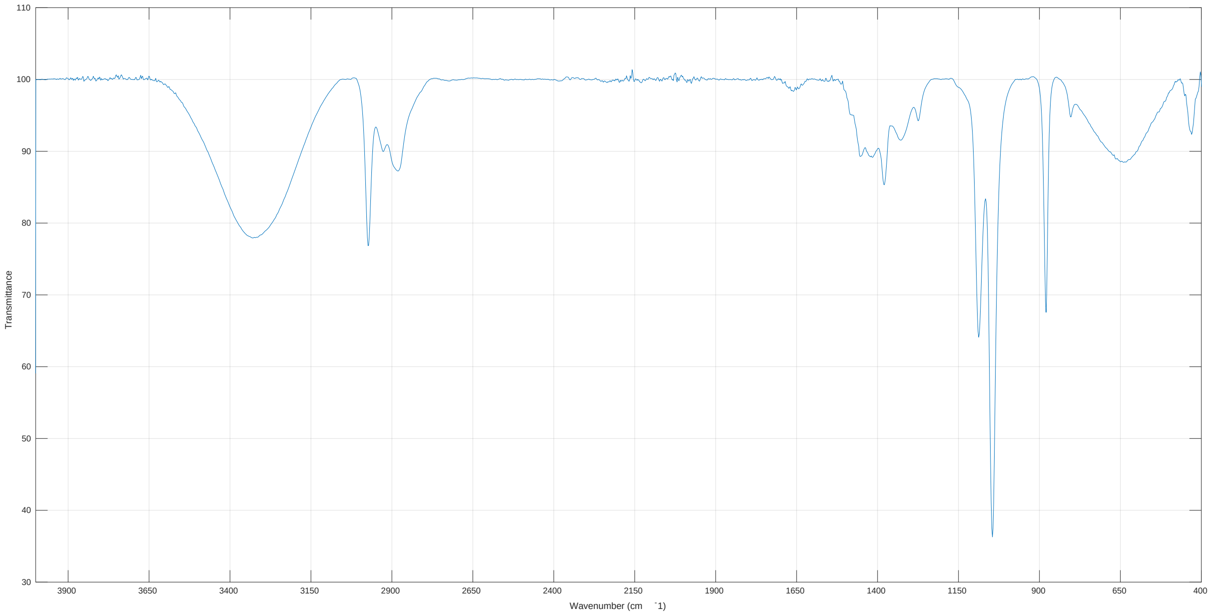

Figure 27: *Experiment #11 (ethanol with anthracene)*

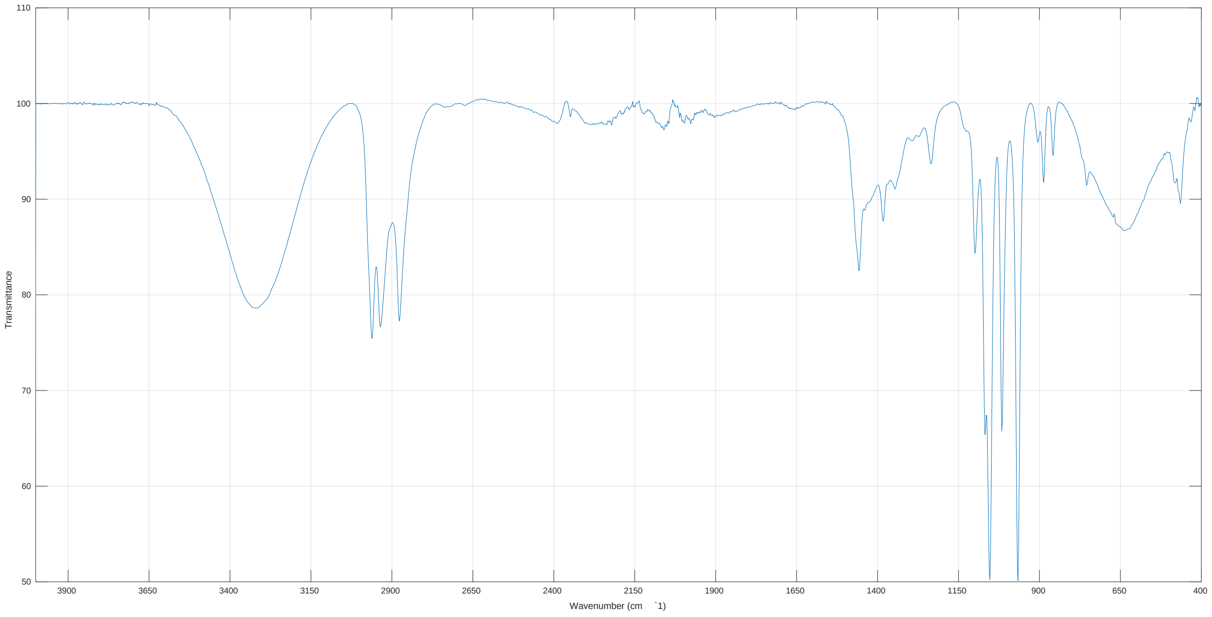

Figure 28: *Negative control (unreacted 1-propanol)*

D Chromatograms

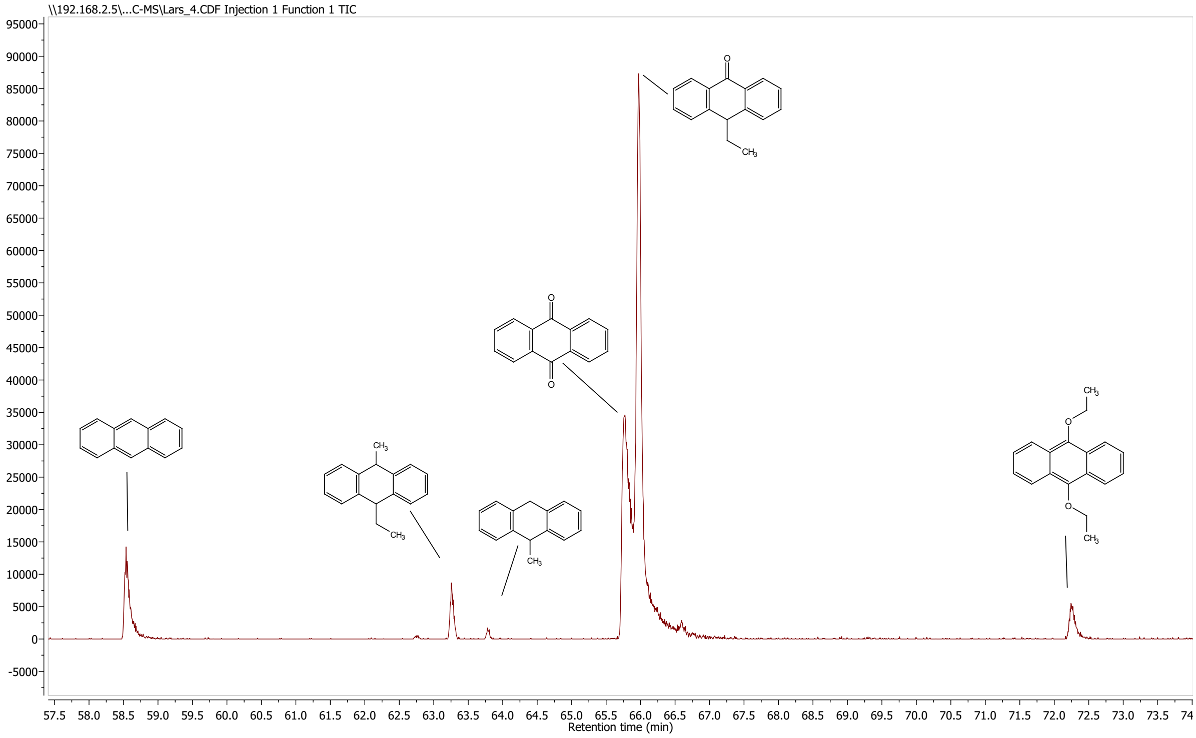

Figure 29: *Experiment #4 (Pt-nb, ethanol)*

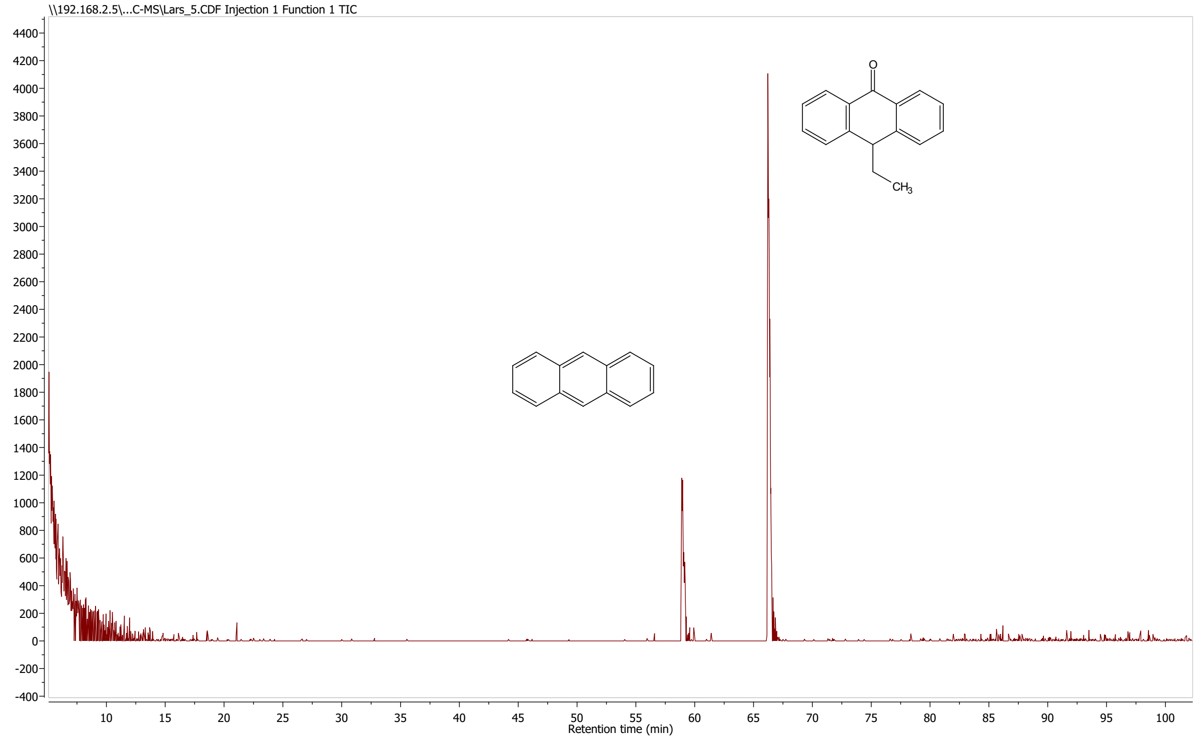

Figure 30: *Experiment #5 (Pt-nb, ethanol in acetone)*

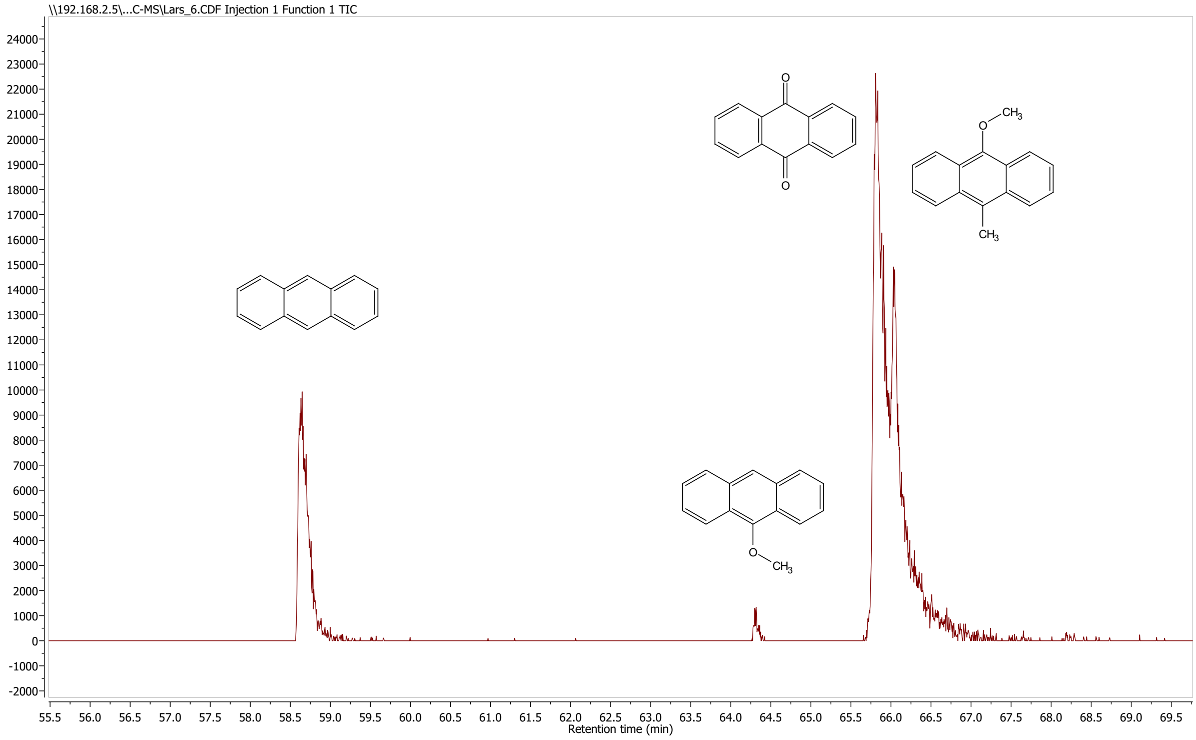

__Figure 31:__ Experiment #6 (Pt-b, t-butanol in acetone)

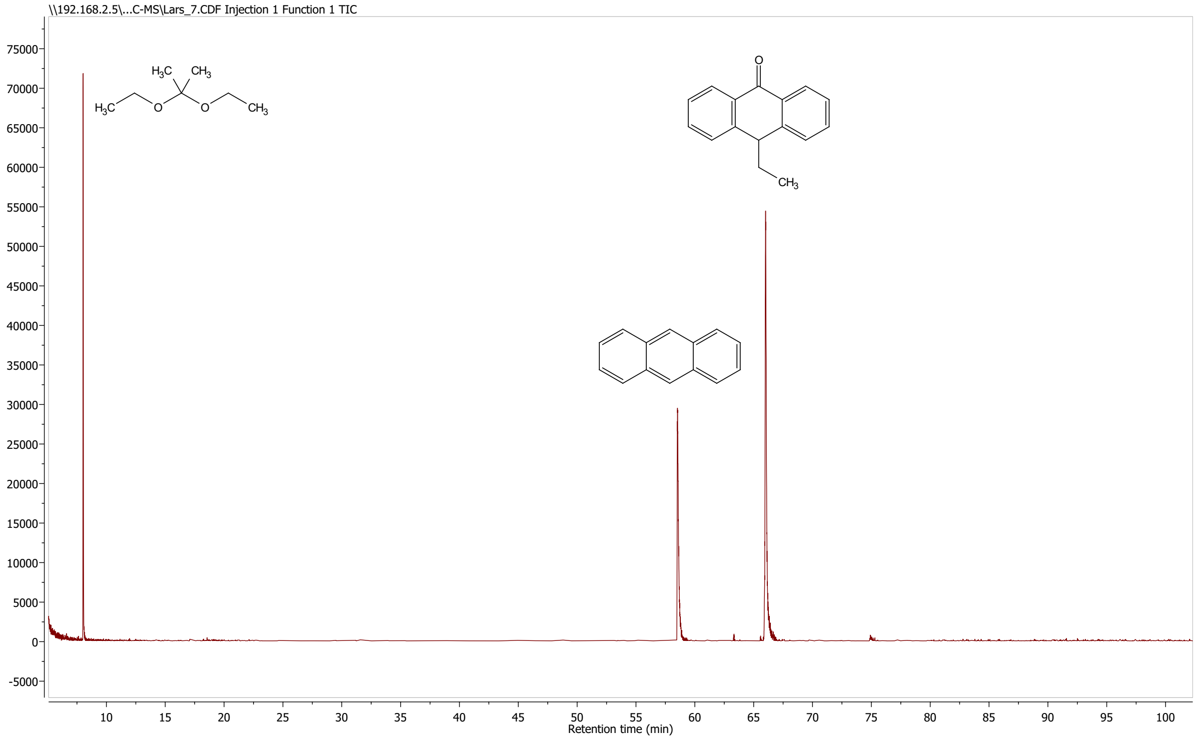

__Figure 32:__ Experiment #7 (Pt-b, ethanol in acetone)

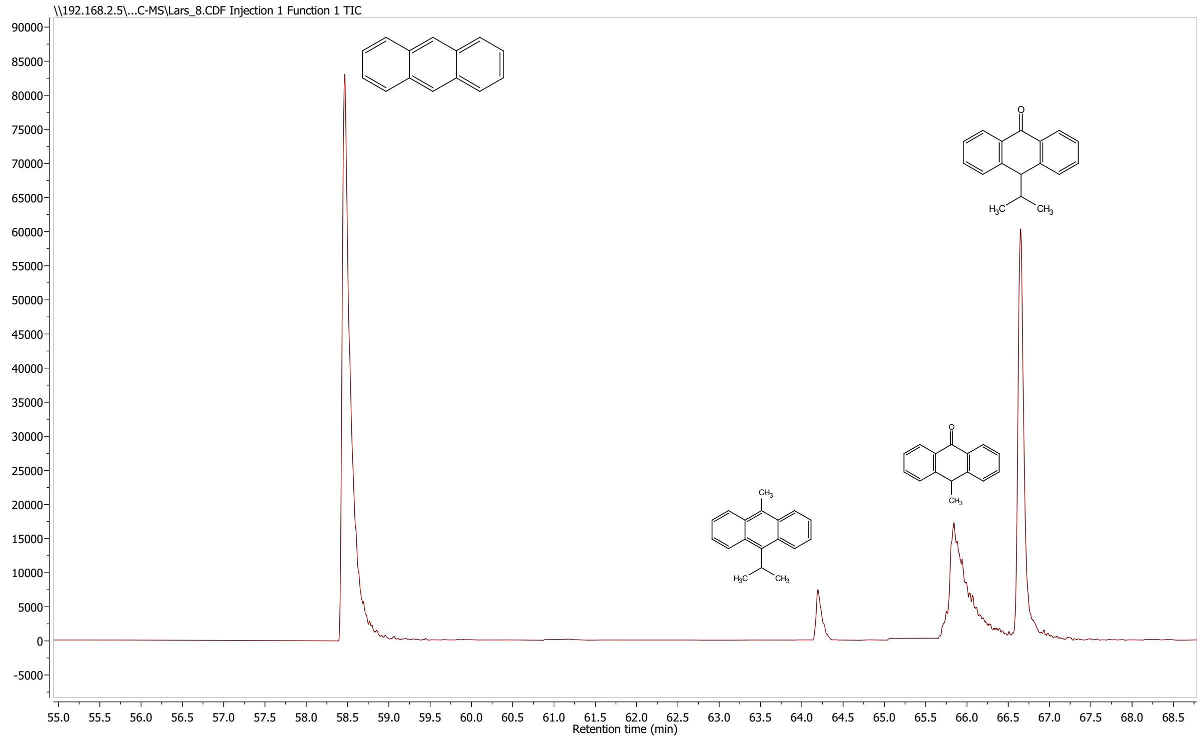

Figure 33: *Experiment #8 (Pt-b, 2-propanol in acetone)*

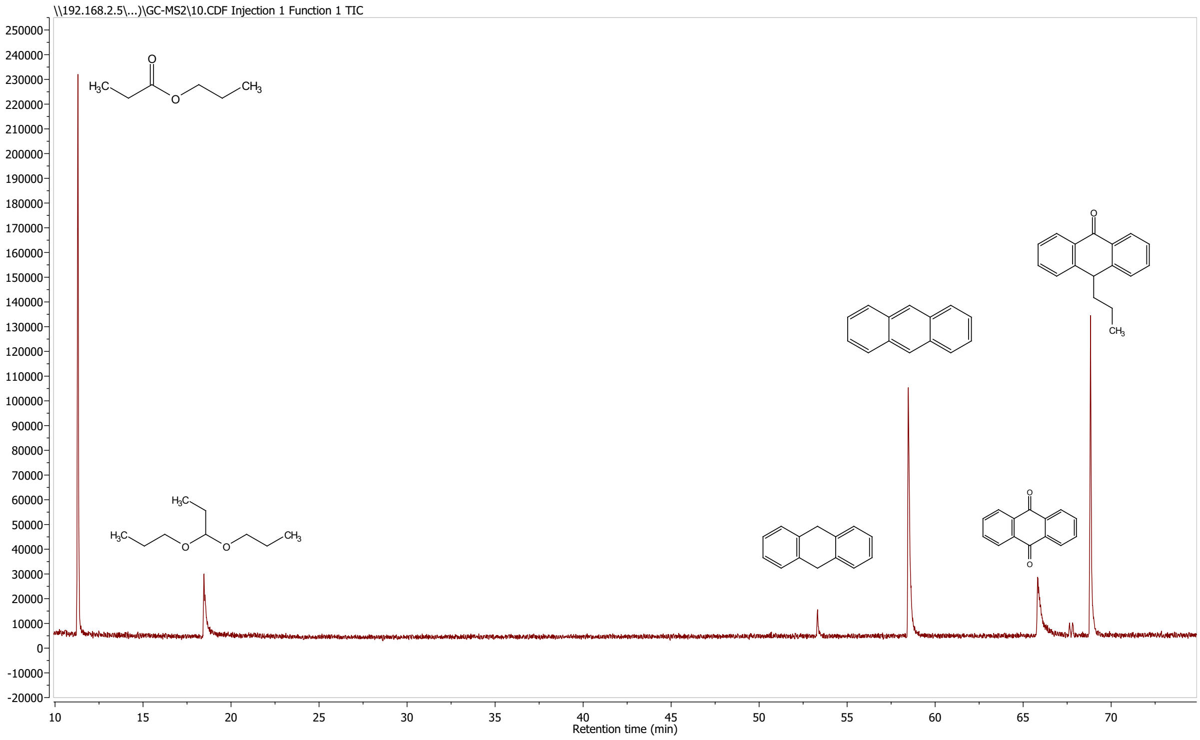

Figure 34: *Experiment #10 (Pt-nb, 1-propanol)*

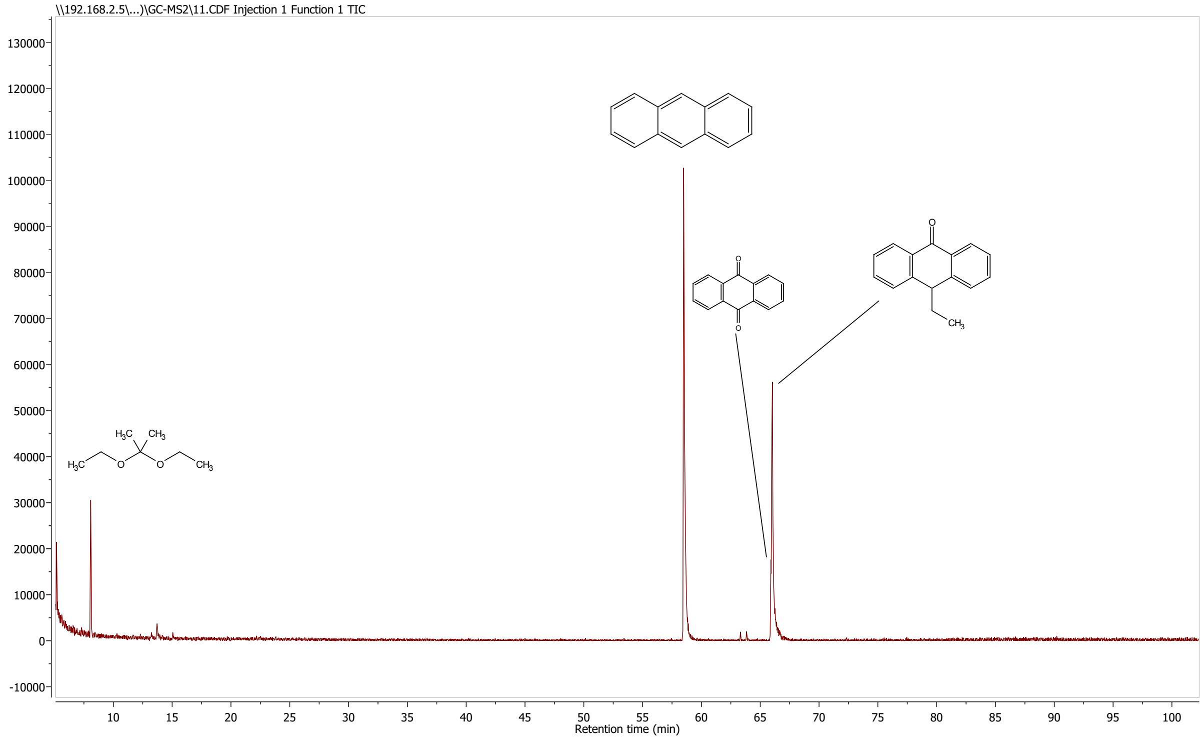

__Figure 35:__ Experiment #11 (ITO-b, ethanol)

E | Mass spectra

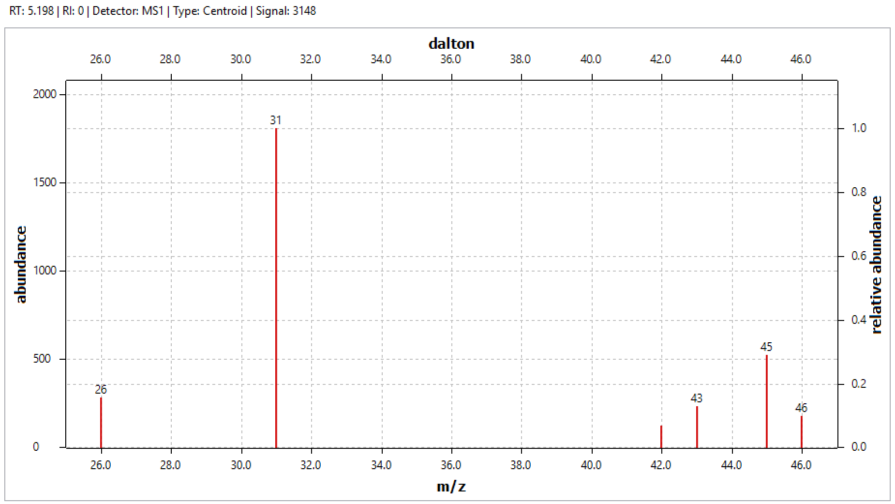

Figure 36: *Ethanol*

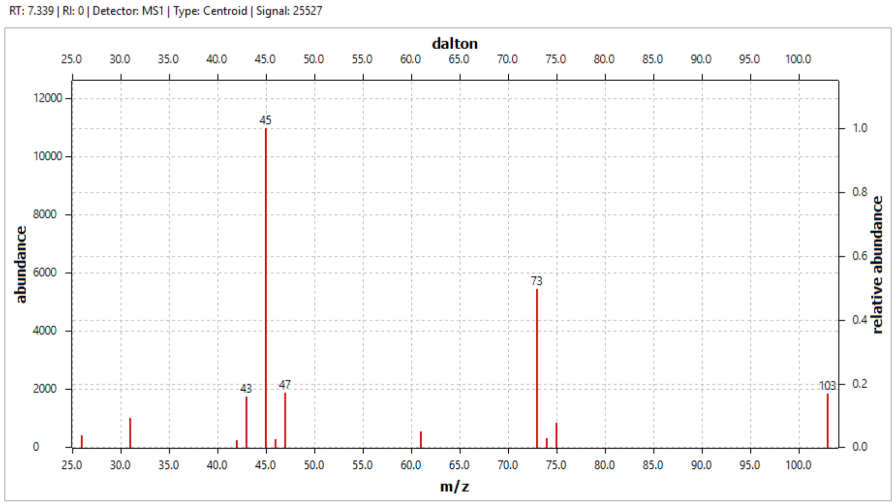

Figure 37: *1,1-diethoxyethane*

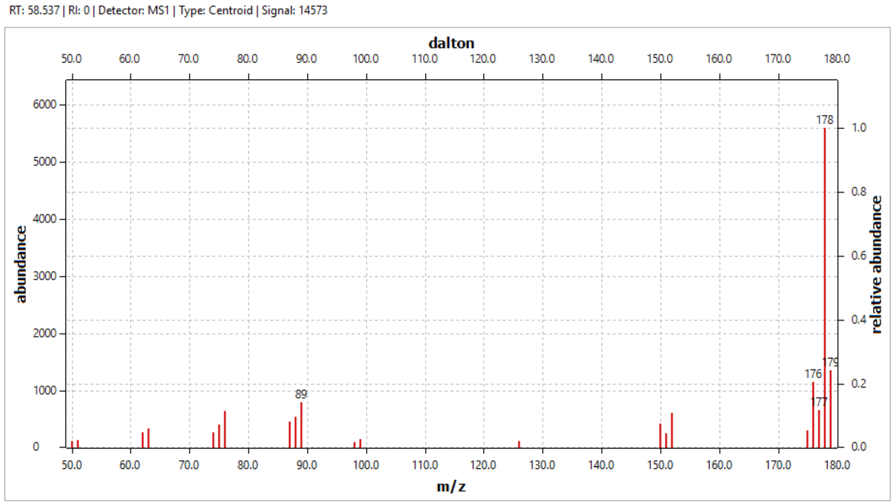

Figure 38: Anthracene

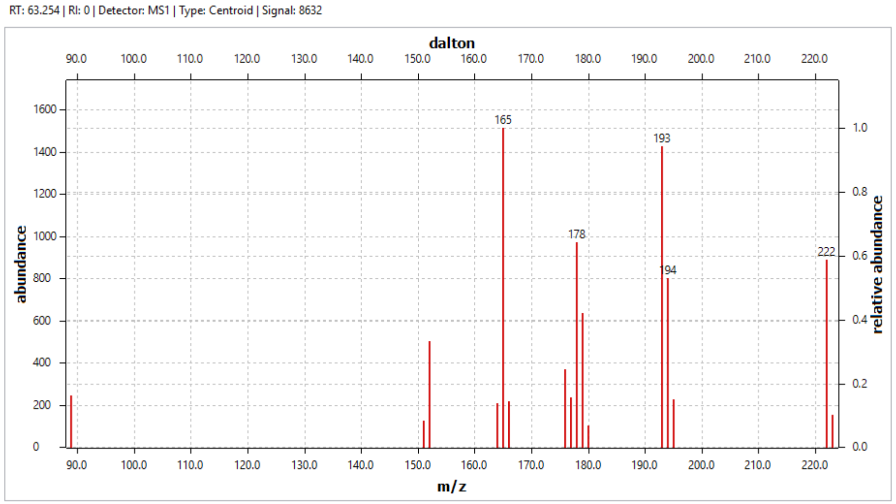

Figure 39: 10-ethyl-9-methyl-9,10-dihydroanthracene

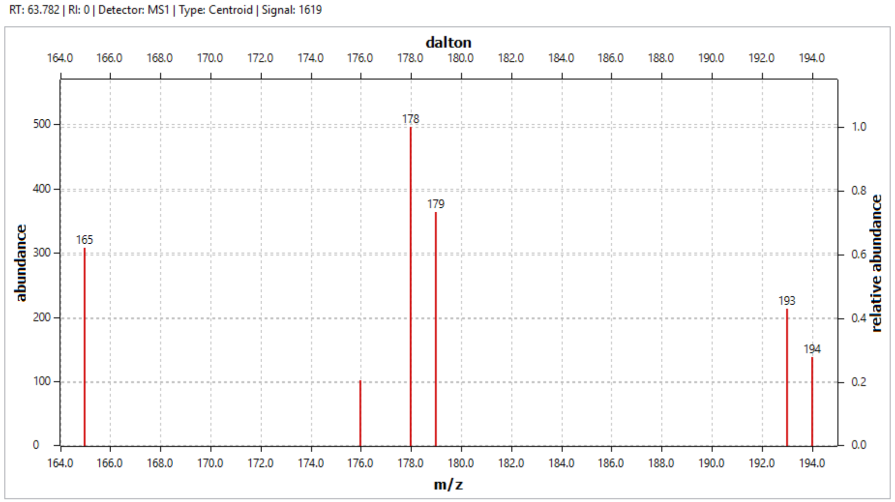

Figure 40: 9-methyl-9,10-dihydroanthracene

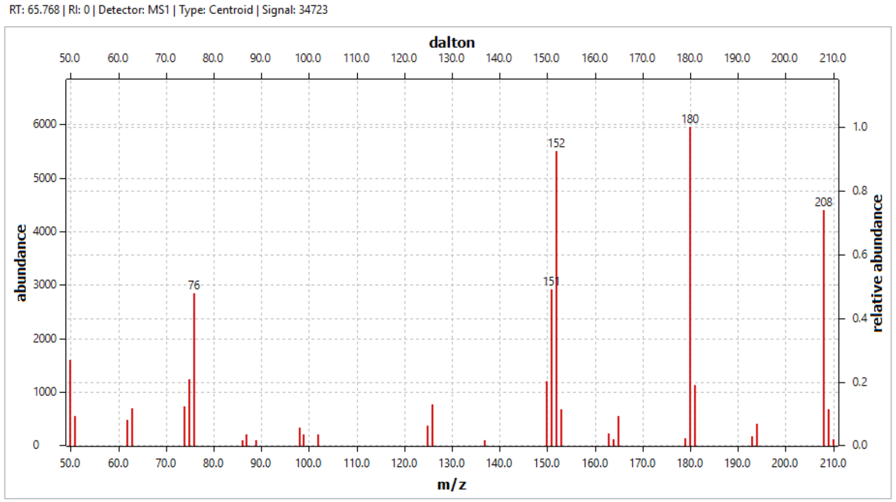

Figure 41: Anthraquinone

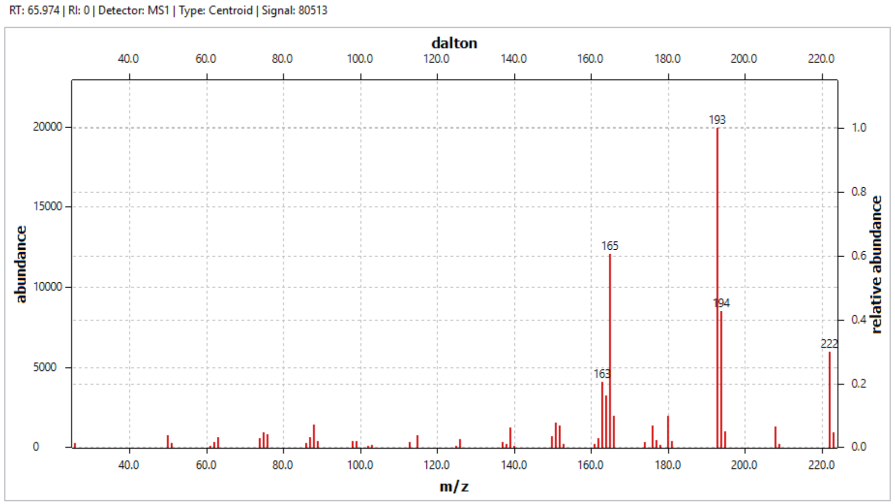

Figure 42: *10-ethyl-10H-9-anthranone*

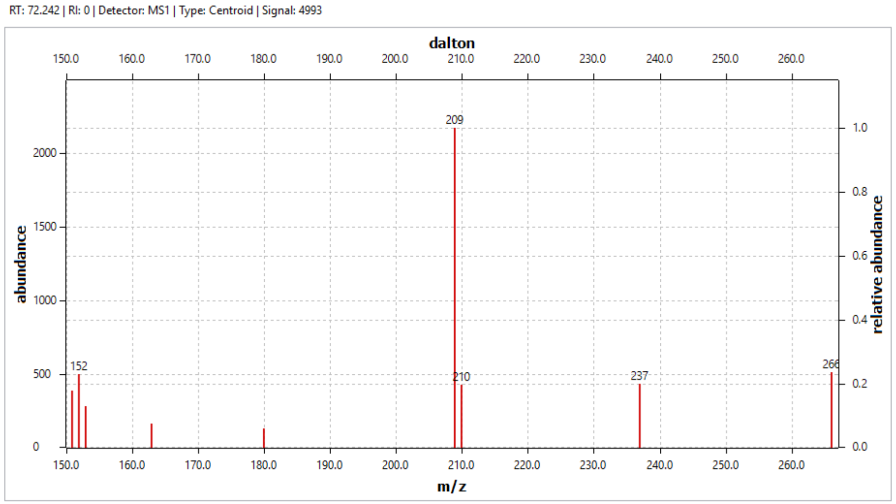

Figure 43: *9,10-diethoxyanthracene*

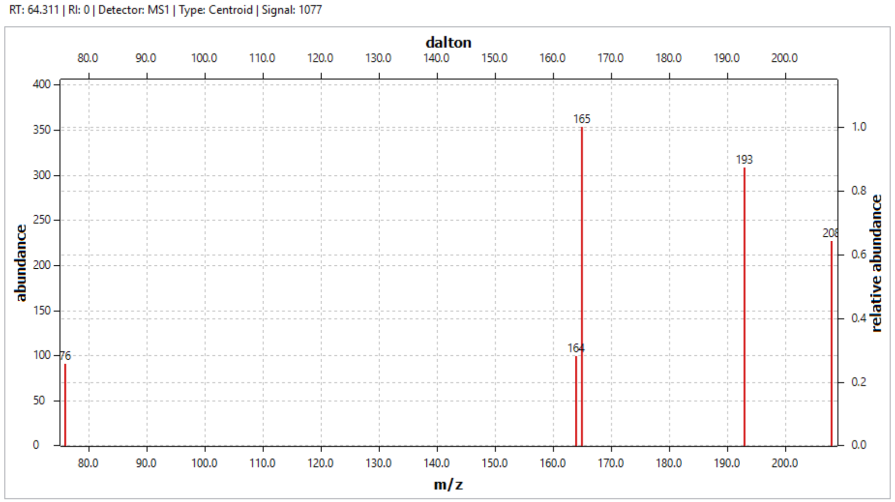

Figure 44: *9-methoxyanthracene*

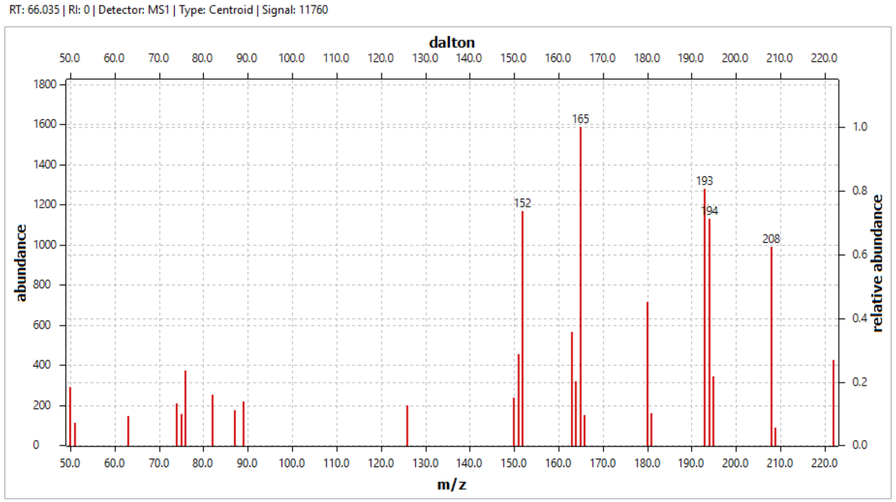

Figure 45: *10-methyl-9-methoxyanthracene*

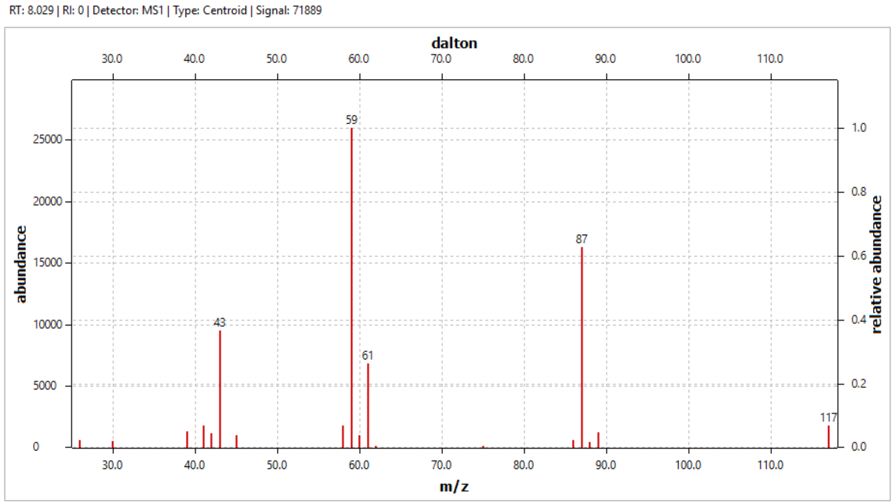

Figure 46: *2,2-diethoxypropane*

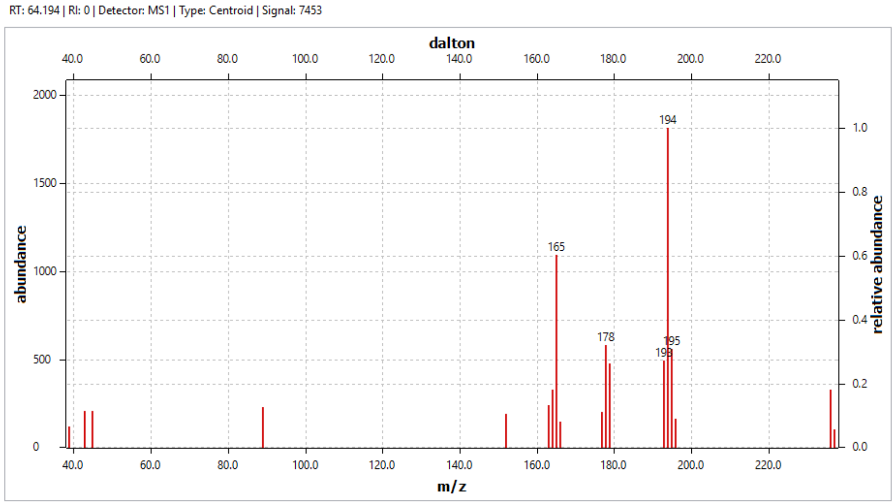

Figure 47: *9-methyl-10-(2-propyl)-anthracene*

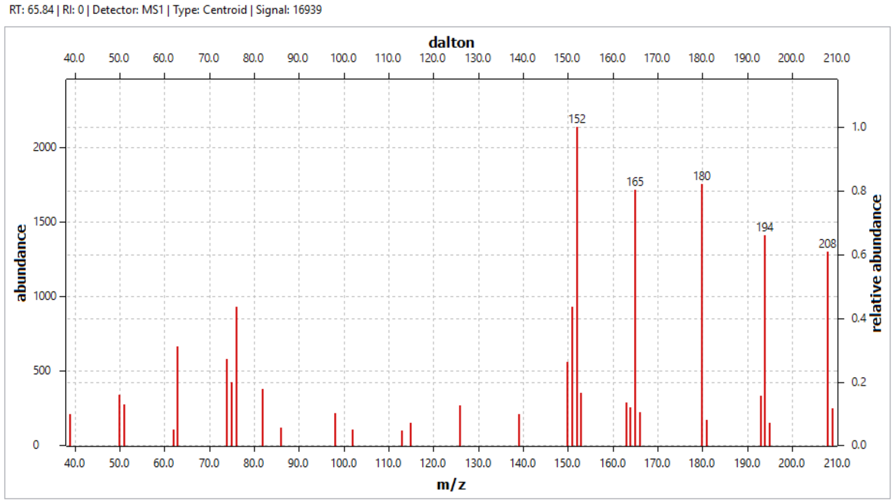

Figure 48: *10-methyl-10H-9-anthranone*

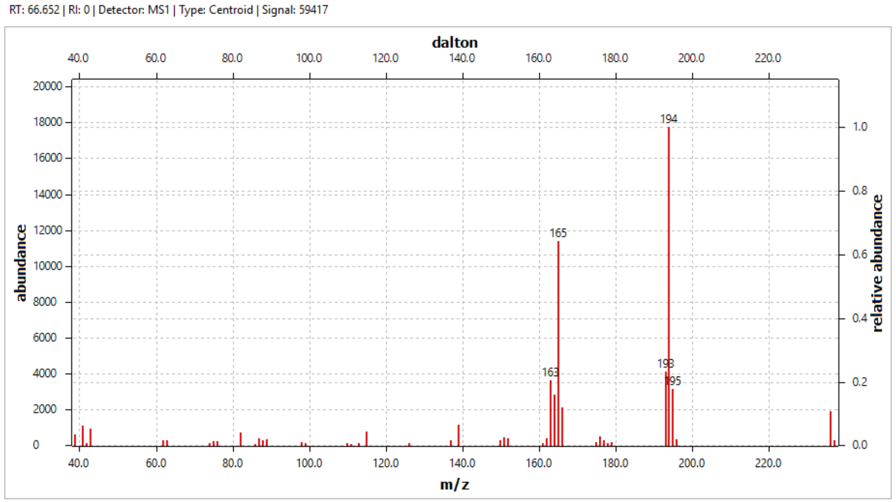

Figure 49: *10-(2-propyl)-10H-9-anthranone*

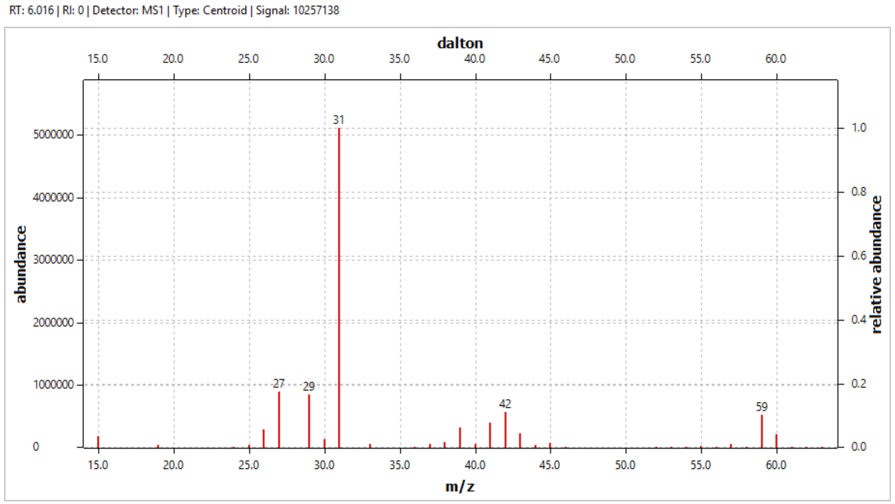

__Figure 50:__ 1-propanol

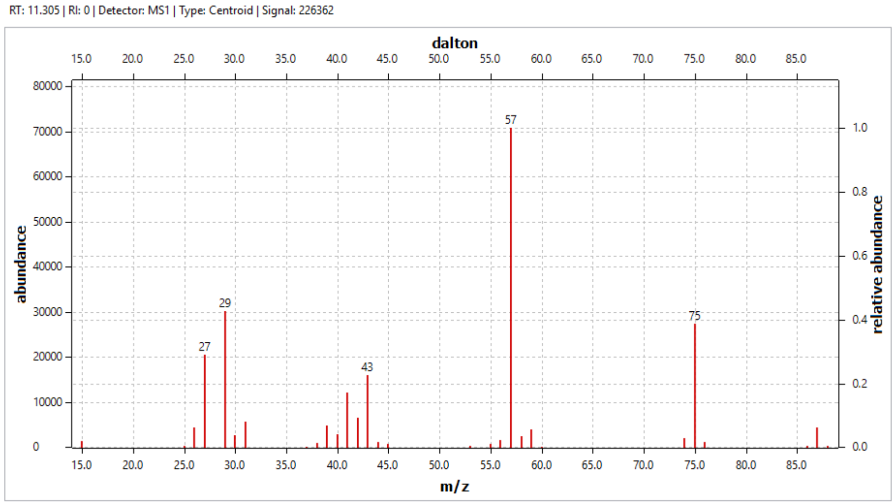

__Figure 51:__ propyl propanoate

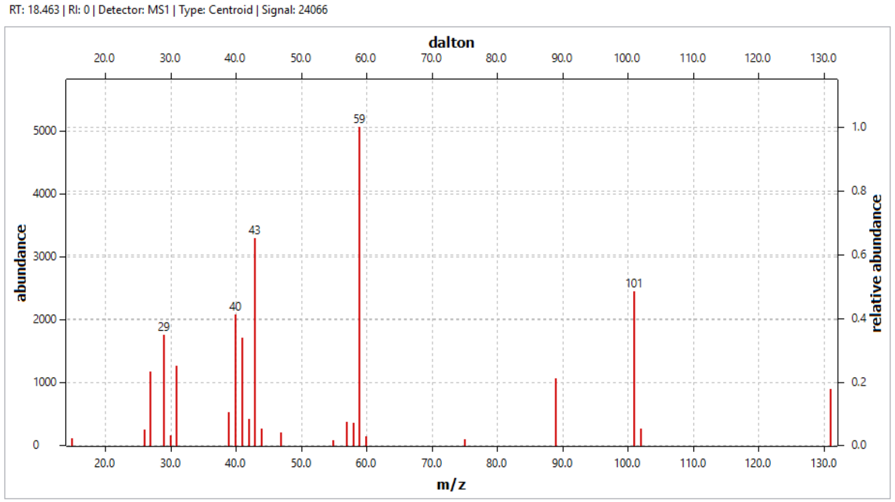

__Figure 52:__ 1,1-dipropoxypropane

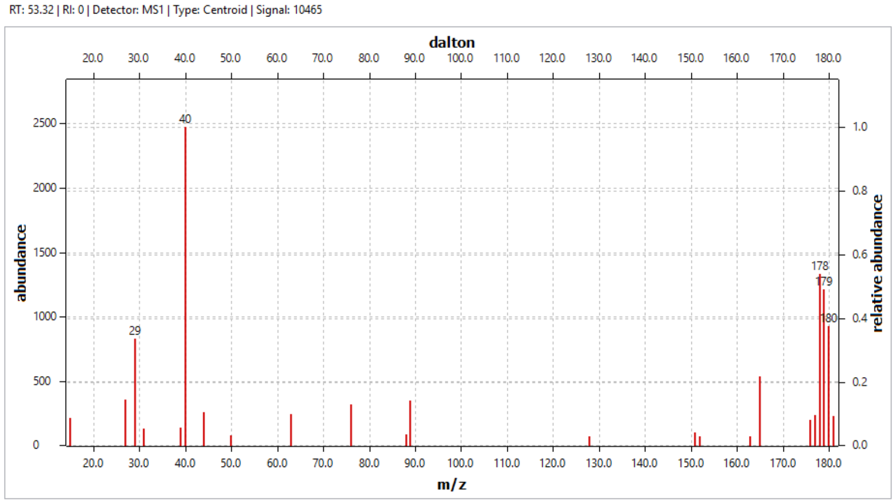

__Figure 53:__ 9,10-dihydroanthracene