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Synthesis of monovinyl isosorbide and its polymerization

Bachelor Thesis

12 EAP

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INFOLEHT

Pealkiri: Monovinüül isosorbiidi süntees ja selle polümeerisatsioon.

Kokkuvõte: Selle uurimistöö eesmärgiks oli uurida isosorbiidi omadusi eesmärgiga kasutada seda biopäritolu polümeeride sünteesiks. Uurimistöö käigus õnnestus sünteesida monovinüülisosorbiidi, mida tulevikus on võimalik kasutada uute polümeeride sünteesiks. Töö käigus õnnestus sünteesida ka uudne vinüülisosorbiidi oligomeer, seega uurimistöö eesmärk sai täidetud.

Marksõnad: isosorbiid, polümeerisatsioon, vinüülimine, biopäritolu polümeerid

CERCS kood: P390 Orgaaniline keemia T390 Polümeeride tehnoloogia, biopolümeerid

Title: Synthesis of monovinyl isosorbide and its polymerization

Summary: In this thesis properties of isosorbide, that is as a precursor for the synthesis of new biobased polymers were studied. Synthetic methods for obtaining of vinylated compounds were obtained from the literature and tested on isosorbide. During this research monovinyl isosorbide was synthesized. Further, different polymerization methods we investigated and the new polymer (oligomer) was synthesized. In addition, the advantages and disadvantages of methods for isosorbide vinylation and polymerization were analyzed. The next goals and prospects were defined.

Consequently, new isosorbide based polymer was synthesized, that can replace fossil based polymers in the future..

Keywords: isosorbide, polymerization, vinylation, biobased polymers

CERCS code: P390 Organic chemistry , T390 Polymer technology, biopolymers

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ABBREVIATIONS

AIBN - Azobisisobutyronitrile

Ar - argon

CDCl₃ - deuterated chloroform

DCM - dichloromethane

DMSO - dimethyl sulfoxide, solvent

DPP - 4,7-diphenyl,10-phenanthroline

HPLC - high-performance liquid chromatography

[IrCl(cod)]₂ - 1,5-cyclooctadiene-iridium(I) chloride dimer

NMR - nuclear magnetic resonance

Pd(DBA)₂ - Palladium(0) bis(dibenzylideneacetone)

PDI - polydispersity index

THF - tetrahydrofuran

TLC - thin-layer chromatography

TMCS - Trimethylsilyl chloride

V-601 - Dimethyl 2,2'-azobis(2-methylpropionate)

INTRODUCTION

In our modern world the main source for chemicals, and fuel is fossil feedstock (Dapsens *et al.*, 2012). Furthermore, plastic materials, household chemicals goods, synthetic clothes, etc. are also mostly made of fossil raw materials.

However, accelerated use of finite fossil resources is not a sustainable solution. Considering also acute environmental problems like rapidly increasing CO₂ emissions (Dapsens *et al.*, 2012), alternative and sustainable carbon source is desperately needed. One alternative carbon source is a renewable and non-edible lignocellulosic biomass.

Right now oil and gas resources belong only to a very limited number of world countries, but biomass is distributed more evenly.

The use of lignocellulosic biomass also eliminates the feared competition with food (Dapsens *et al.*, 2012).

Our research group explores isosorbide properties in the context of novel biobased polymeric materials. More specifically, in this thesis the potential of monovinyl isosorbide as a novel monomer for polymers, is evaluated. The ultimate goal is to replace fossil based polymers with biobased ones in various plastics.

To achieve this goal, the following tasks will be undertaken in this thesis:

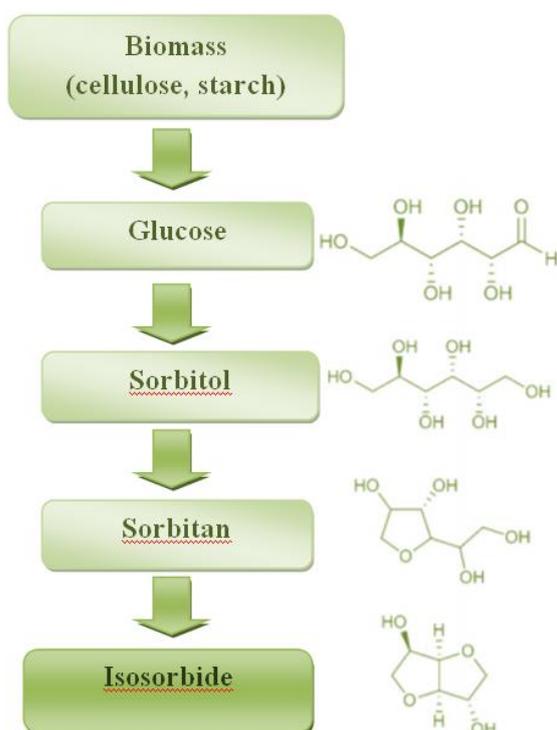
1. Search and analysis of possible methods to obtain monovinyl isosorbide in one step from commercial isosorbide
2. Testing different methods for vinyl isosorbide synthesis in practice
3. Evaluate possible ways to polymerize the monovinyl isosorbide
4. Realization of polymeric reactions and analysis of the polymers obtained
5. Conclusions and the future perspectives for our research

1. LITERATURE OVERVIEW

1.1. Isosorbide and its characteristics

Isosorbide is very valuable material that could substitute the finite fossil resources in many applications.

Synthesis of isosorbide (1,4:3,6-dianhydrohexitol) is well established. It is obtained from glucose portion of biomass by hydrogenation to sorbitol followed by twofold dehydration (Scheme 1, Rose, M. and Palkovits, R., 2012).



Scheme 1. Production of isosorbide from biomass

By physical characteristics, isosorbide is white, crystalline solid with high hygroscopic features (in one liter of water can be dissolved roughly in eight kilograms of isosorbide). Its melting point is 63°C and the boiling point is 160°C.

Isosorbide is stable compound and contains two hydroxyl groups in 2- and 5- positions, that give opportunities for further reactions and modifications because hydroxyl groups can be transformed to other functional groups.

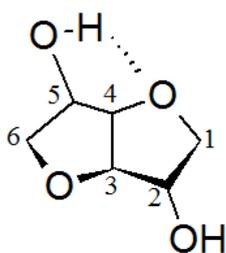


Figure 1. Molecular structure of isosorbide

It has a rigid V-shaped structure (Figure 1), with two *cis*-connected tetrahydrofuran rings (Rose, M. and Palkovits, R., 2012). This rigidity makes isosorbide particularly appealing for polymer science, because there aren't many biobased rigid building blocks available. Hydroxyl group in 2-position has *exo*-configuration, while in 5-position it has *endo*-configuration. Reactivity of these groups is rather different. Hydroxyl oxygen atom in 5-position has more nucleophilic character because of the hydrogen bond, so it is more reactive compared to hydroxy in position 2. However, at the same time, it is sterically less accessible compared to *exo*-OH in position 2. (Rose, M. and Palkovits, R., 2012).

Nowadays, nontoxic isosorbide is used in cosmetics and pharmaceutical products and as a plasticizer in some polymers. It is an object of an intense research. Currently, it is produced in more than 20 000 tons per year.

1.2 Monovinyl isosorbide

Monovinyl isosorbide is a novel vinyl ether compound where vinyl functionality is attached to one hydroxyl group (Figure 2).

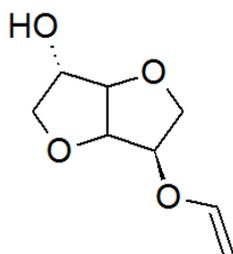


Figure 2. Molecular structure of vinyl isosorbide.

This material could be used as a monomer for the synthesis of novel polymeric

structures. From the application point of view, the use of monovinyl is more interesting than bivinyl, since bivinyl isosorbide monomer would give cross-linked polymers, which would be very difficult to process.

1.3. Methods for the synthesis of vinyl ethers

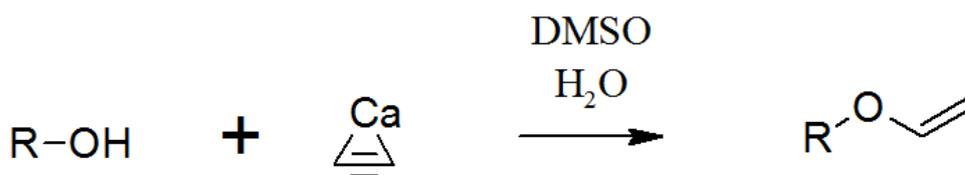
Some methods for the synthesis of vinyl ethers have been reported.

Favorski-Reppe reaction between acetylene and alcohol in the presence of KOH as a catalyst is known. Also alcohol elimination reactions and mercury-catalyzed synthesis have been reported (Okimoto *et al.*, 2002).

However, such methods have several disadvantages: use of toxic catalysts, harsh reaction conditions (high temperature and pressure), difficult to scale up, etc.

In this thesis we wanted to explore new methods of vinylation that are more safe, environmental friendly and also have higher product yield.

1.3.1. Synthesis of vinyl ethers with calcium carbide reagent



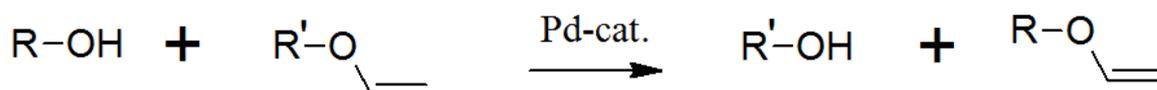
Scheme 2. General reaction mechanism between alcoholic compound and calcium carbide

Calcium carbide (CaC_2) is well known, easy-to-handle and inexpensive compound used in organic synthesis and elsewhere. In the presence of water, calcium carbide releases acetylene which vinylates alcohol and this is well-known process (Scheme 2). In recent years, this reagent has been successfully used for the vinylation of benzylic alcohols, phenols, various thiols, indoles and sugar alcohols (Teong *et al.*, 2017). The use of controlled amount of water is important. Water disrupts the polymeric structure of CaC_2 and forms calcium acetylide, which is more reactive than acetylene. So the addition of bigger amount of water improves the

product yield. DMSO is the solvent of choice for this type of reactions because it forms superbases in the medium. Selectivity of this method is decreased with increasing number of hydroxyl groups because the side reactions take place in the basic medium. (Teong *et al.*, 2017)

Employment of this method is more ecological and safe than using heavy metal mixtures. Therefore we want to explore this method by conducting the reaction between CaC_2 and isosorbide.

1.3.2. Synthesis of vinyl ethers with palladium catalyst ($\text{Pd}(\text{OOCF}_3)_2$)



Scheme 3. General reaction scheme between alcoholic compound and vinyl ether with palladium catalyst.

The complex $(\text{DPP})\text{Pd}(\text{OOCF}_3)_2$ (where DPP is 4,7-diphenyl-1,10-phenanthroline) is used as optimized catalyst for the equilibrium transfer vinylation of various alcohols with butyl vinyl ether. Earlier in this method acetate was used as the initiator but reaction was very slow (4-7 days). Later it was changed to trifluoro acetate, which is more catalytically active. Butyl vinyl ether has double role in this transformation: it is used both as a solvent and a vinyl source.

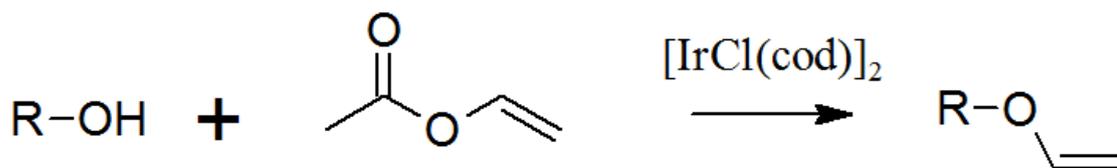
The Et_3N is an additional base in this reaction (Bosch, M. and Schlaf, M., 2003).

This method has been already tested for vinylation of primary, secondary and tertiary alcohols, also used for vinylation of primary and secondary allyl alcohols (Bosch, M. and Schlaf, M., 2003).

Such complex system is steady for external effects. During this reaction acetal side products are not formed because they are suppressed by Et_3N (Bosch, M. and Schlaf, M., 2003).

The advantages of this method are: one step reaction, cheap and available reagents, no need to use gaseous acetylene.

1.3.3. Synthesis of vinyl ethers with $[\text{IrCl}(\text{cod})]_2$ catalyst

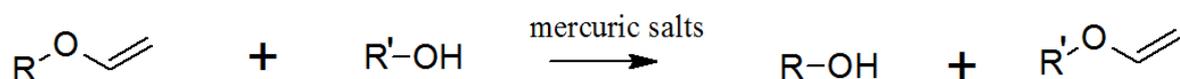


Scheme 4. General reaction mechanism between alcoholic compound and vinyl acetate using iridium complex catalyst.

$[\text{IrCl}(\text{cod})]_2$ complex has been used previously to catalyze coupling of imines with alkynes, hydrogenation of enones with alcohols, and rearrangement of allyl homoallyl ethers. Later this complex has been proposed also as a catalyst for vinyl ethers synthesis of alcohols or phenols (Scheme 4, Okimoto *et al.*, 2002). This method has been reported to afford good yields at low catalyst loadings. It has high catalytic activity and is available commercially. Compared with other described methods this method has higher reaction rate and it takes about two hours to complete the reaction. Also it does not need high pressure and reaction occurs at 100°C (Okimoto *et al.*, 2002).

These characteristics favorably mark out this method against several others.

1.3.4. Mercury catalyzed vinyl ethers synthesis



Scheme 5. General reaction mechanism between alcohol and vinyl ether using mercury salt catalyst.

In the 50s of the last century it was discovered that mercuric salts of weak acids could be used as catalysts for vinyl ethers synthesis from alcohols (Scheme 5). Comparing with other methods at that time, it demonstrated high rate and efficiency. Also, at the same time the reactions with salts of cobalt, cadmium, copper, iron, lead, silver, nickel and zinc were tested. Some of these metals resulted the formation of some desired product, however, more often high-boiling byproducts were obtained (Watanabe, W.H. and Conlon, L.E., 1957). Moreover, mercuric salts of strong acids were suggested to use as the catalysts. In this way the formation of vinyl ethers occurred at low temperatures (-10°C or lower). But using mercuric acetate and mercuric benzoate instead, the formation of side products was

suppressed and higher reaction temperatures could be used (Watanabe, W.H. and Conlon, L.E., 1957).

However, the use of mercuric salts is very dangerous for both humans and for the environment, these are highly toxic compounds. Right now mercuric salts are not used at the industrial scale, and the use in laboratories is very limited.

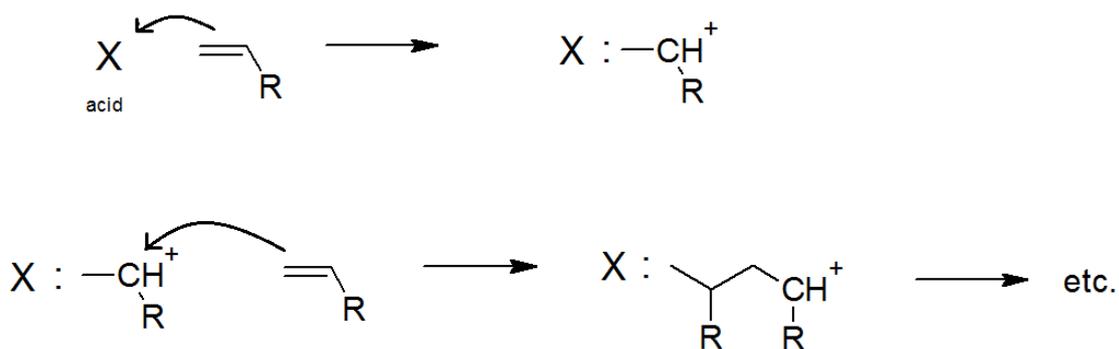
1.4. Methods of vinyl ethers polymerization.

Chain growth polymerization is a process where monomers add into active site of the polymer one at a time. (Jenkins *et al.*, 1996).

Vinyl ether could in principle be polymerized via three types of polymerizations: radical, cationic and anionic polymerization.

In these types of the reactions the kinetic-chain carriers are radicals, cations and anions, respectively (Jenkins *et al.*, 1996).

1.4.1. Cationic polymerization of vinyl ethers



Scheme 6. General scheme of cationic polymerization.

Cationic polymerization is the type of polymerization where the cation is initiator and attacks the double bond to form a new cation which can continue the polymerization.

In cationic polymerization Lewis acids are used as catalysts. Metal halides are suitable catalysts for the polymerization of vinyl ethers (Kanazawa *et al.*, 2010). Equilibrium in cationic polymerization can be shifted towards the polymers in various ways: control by nucleophilic counteranions, added weak Lewis bases such as esters or ethers, or added salts

including quaternary ammonium salts (Kanazawa *et al.*, 2010).

Cationic polymerization is interesting for our project because of its high activity, high tolerance and selectivity.

1.4.1.1. Cationic polymerization of vinyl ethers with FeCl₃

For cationic polymerization iron(III) halides (FeX₃) are often employed Lewis acids because of their various advantages for industrial use: they are easy to handle, have low toxicity and are readily available at low price (Kanazawa *et al.*, 2006). FeCl₃ is Lewis acid because it is an electron pairs' acceptor. In these reactions cyclic ethers are used as solvents. These are also weak bases and help to initiate the living polymerization more efficiently. For example, dioxane is a cyclic ether and also a weak Lewis base because oxygen has a lone pair and acts as an electron donor.

This method has high reaction rate and it takes about just few seconds to complete the reaction (only in few cases longer reaction times were needed). Polymerizations occur at 0°C (Kanazawa *et al.*, 2006).

1.4.1.2. Cationic polymerization of vinyl ethers with BF₃•OEt₂

Using of BF₃•Et₂O/ROH system leads to cationic polymerization in the presence of water with free hydroxyl groups (Satoh *et al.*, 2000).

BF₃•Et₂O acts as Lewis acid in this system, whereas alcohol is a Lewis base. Cation compound is formed after their interaction and an attack to the double bound in vinyl ether initiates the polymerization.

This reaction tolerates free hydroxyl groups in the monomer.

The time of the reaction can vary from 3 to 20 hours. It depends on the substituents in the monomer. Polymerization occurs at 0°C (Satoh *et al.*, 2000).

BF₃•Et₂O is commercially available and relatively easy to handle.

1.4.2. Radical polymerization of vinyl ethers with V-601 or AIBN

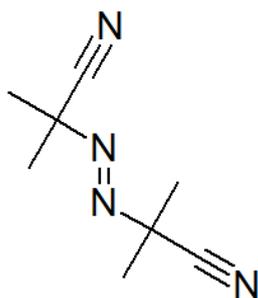


Figure 3. Structure of AIBN

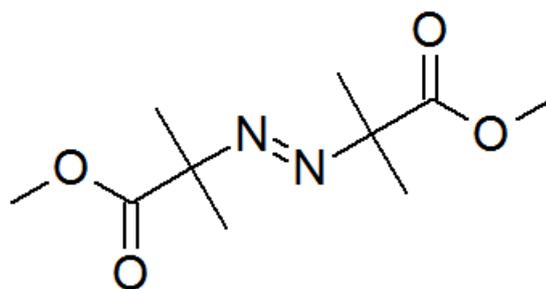
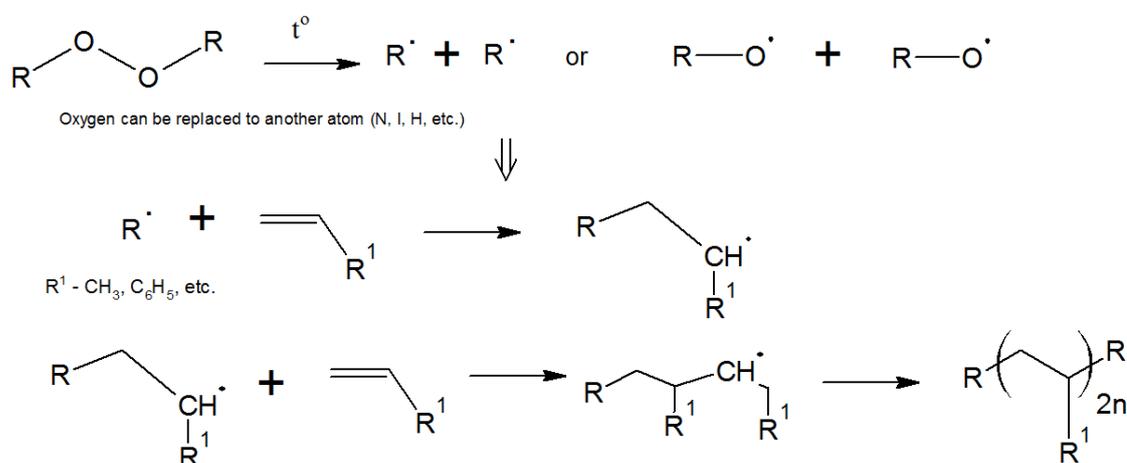


Figure 4. Structure of V-601

During the last years radical polymerization has gained popularity because of simple setup and tolerance towards various functional groups (Hirao *et al.*, 2014).

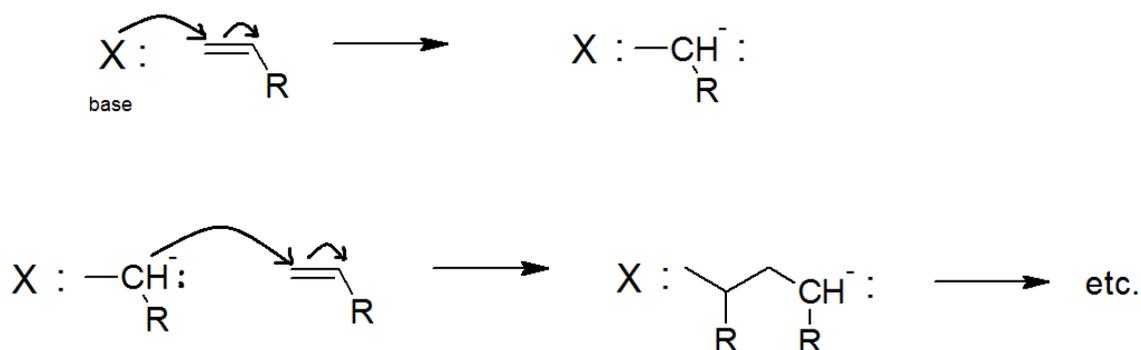
V-601 is well-known as azo-initiator for radical polymerization reactions (Figure 4). Its efficiency is increased in alcoholic solvents (Sugihara *et al.*, 2016). AIBN (Figure 3) is an alternative initiator to V-601. In the context of this thesis we want to polymerize vinyl ether compound with AIBN. AIBN is widely used in radical polymerization reactions, specially in the laboratory scale.



Scheme 7. General scheme of radical polymerization.

AIBN decomposes into isobutoronitrile radicals at the temperatures above 60°C. (Paquette, 1999). Polymerization as the chain reaction occurs via new C-C bond formation. For this method only small amount of AIBN initiator is required. Such reaction occur typically at temperatures 60-70°C and lasts ca 1 day (Sugihara *et al.*, 2016).

1.4.3. Anionic polymerization of vinyl ethers.



Scheme 8. General scheme of anionic polymerization.

R₂Li reagents are used as the initiator for the anionic polymerization. These reagents have normally high reactivity (Hirao *et al.*, 2014). In this thesis we want to polymerize vinyl ether compound with OH-functional group that includes active hydrogen. In common conditions anionic polymerization does not occur with free hydroxyl groups because an anionic initiator are not compatible with active hydrogen. Therefore, the free hydroxy group should be protected first (Hirao *et al.*, 2014). One obvious way to protect alcohol is using TMCSCl which is widely used reagent to protect alcohols. Functional groups of alcohols and amines react with TMCSCl and form trimethylsilyl amines and ethers. After polymerization the protection groups can be removed.

These polymerization reactions need the following conditions: use of polar solvents (like THF) and low temperature (usually: -78°C) (Hirao *et al.*, 2014).

2. EXPERIMENTAL PART

2.1 Methods and equipment

Synthesis of organic compounds were conducted in accordance with standard methods of organic chemistry.

Commercially available solvents and chemicals were used as received. Argon atmosphere was used for performing air- and water-sensitive reactions.

Solvents or liquid reagent were added to the reaction mixture using plastic syringes or syringes for gas chromatography.

Products of reactions were purified by the column chromatography.

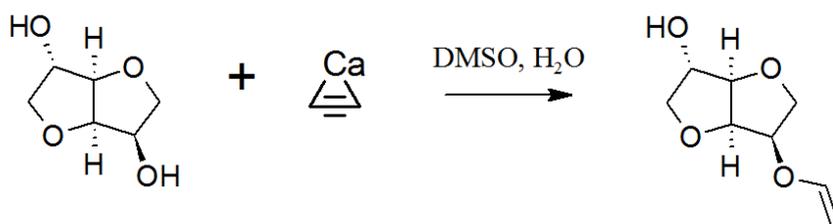
Solvents were removed by the rotary evaporator.

Obtained products were analyzed by NMR, TLC and HPLC methods.

2.2. Obtaining of vinyl isosorbide

One of the aims in our work is a synthesis of vinyl isosorbide which can be used as monomer in polymerization reactions. Different methods were tested to achieve this goal.

2.2.1. Obtaining of vinyl isosorbide by calcium carbide reagent (with isosorbide)



Scheme 9. The vinylation reaction between isosorbide and calcium carbide.

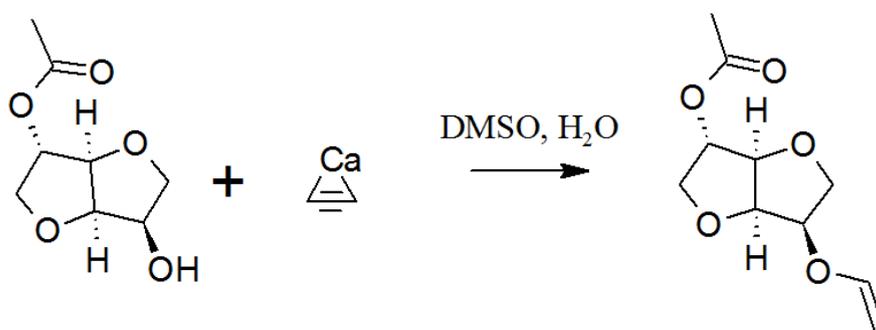
To a solution of isosorbide (98 %, 1,4912 g; 10,204 mmol) in DMSO (50 mL) CaC₂ (1,923 g; 30 mmol) and Cs₂CO₃ (1,6291 g; 5 mmol) were added. The flask (100 mL) that was equipped with a magnetic stir bar and was evacuated using high-vacuum pump and backfilled with

argon. After this water (3,5 mL; 7 % in relation to DMSO) was added under Ar atmosphere. Then the reaction flask was placed to the preheated oil bath (100 °C) and stirred for 3 h. Then the reaction mixture was diluted with EtOAc (250 mL) and the precipitate was separated. The liquid part transferred to the separation funnel and solution of NaCl (50 mL) was added. Additionally, water (20 mL) was added because of formation of precipitate. The precipitate was treated with EtOAc (200 mL) and NH₄Cl (100 mL). Two layers were formed. Precipitate did not dissolve, thus 10 % HCl (30 mL) was added. After water layer was extracted with EtOAc (2 x 100 mL). Both organic phases were combined, evaporated and weighed to give 5,1679 g of crude product. The product was purified by column chromatography (length 15cm, silica gel, 50 % EtOAc/petroleum). Three fractions were formed: F1(0,103 g), F2(0,1349 g), F3(0,1433 g).

Derived fractions were analyzed by NMR (see supplemental materials: №1, №2, №3, №4, №5, №6).

Fraction F2 is monovinyl isosorbide.

2.2.1.1. Obtaining of vinyl isosorbide by calcium carbide reagent (with isosorbide-2-acetate)



Scheme 10. The vinylation reaction between isosorbide-2-acetate and calcium carbide.

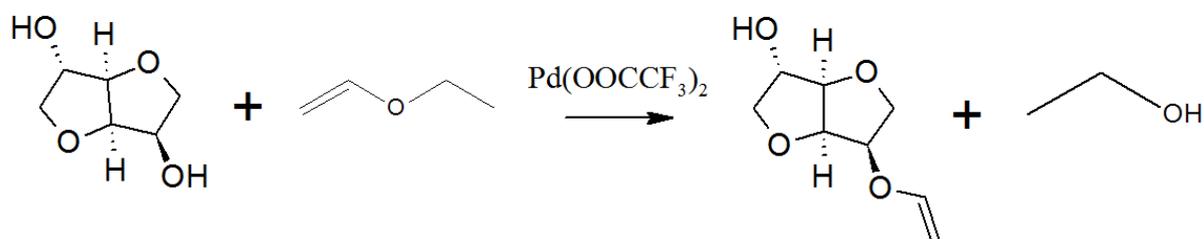
To solution of isosorbide-2-acetate (0,188 g; 1 mmol) in DMSO(5 mL) CaC₂ (0,2564 g; 4 mmol) and Cs₂CO₃ (0,1629 g; 0,5 mmol) were added. The flask (25 mL) was equipped with a magnetic stir bar and evacuated using high-vacuum pump and backfilled with argon. After this H₂O (0,35 mL; 7 % in relation to DMSO) was added under Ar atmosphere. Then the reaction flask was placed in the preheated oil bath (100 °C) and stirred for 3 h.

The reaction mixture after that was extracted with Et₂O (3x15 mL) and H₂O (3x15 mL). Ether layer was dried by MgSO₄, evaporated and dried under high vacuum. The product

weight was 0,0149 g.

Water layer was double extracted: with DCM (3x) and then with EtOAc (3x). Two new fractions (F1-after DCM extaction; F2- after EtOAc extraction) were dried with MgSO₄, evaporated and dried under high vacuum. Both fractions were weighed(F1-0,4461 g; F2-0,1344 g) Then received products were analyzed by NMR.

2.2.2. Obtaining of vinyl isosorbide with palladium catalyst (Pd(OOCCF₃)₂)



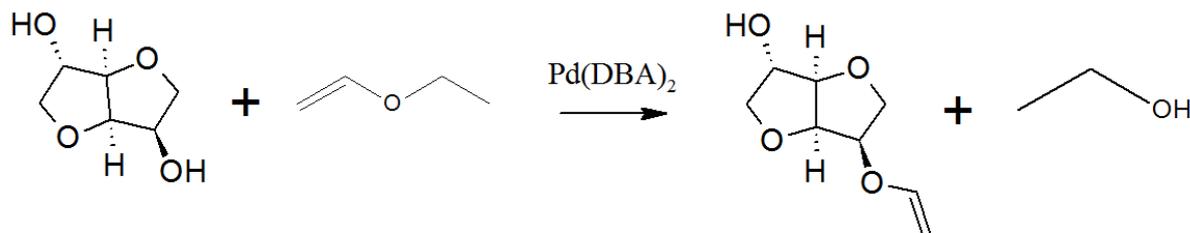
Scheme 11. The vinylation reaction between isosorbide and ethyl vinyl ether with Pd(OOCCF₃)₂.

In 50mL flask PdCl₂ (6,2 mg; 0,035 mmol) was dissolved in ethyl vinyl ether (5 mL). Et₃N (73 μg; 0,525 mmol), CF₃COOH (5,3 μg; 1,4 mmol) were added after that. Then in reaction mixture phenantroline (6,3 mg; 0,035 mmol) and isosorbide (1,0438 g; 7 mmol) were added. Ethyl vinyl ether (10 mL) was added again.

Dioxane (4 mL) and few drops of ethanol were added to improve solubility.

Flask was equipped with Liebig condenser, filled with Ar, placed in the preheated oil bath (50 °C) and was stirred for 1 day. Sample from reaction mixture was taken for NMR (see supplemental materials: №7).

2.2.3. Obtaining of vinyl isorbide with palladium catalyst (Pd(DBA)₂)



Scheme 12. The vinylation reaction between isorbide and ethyl vinyl ether with Pd(DBA)₂.

This reaction is analogous to the reaction that was described above.

(DPP)Pd(OOCCF₃)₂ has poor solubility in THF, therefore a better soluble complex was used instead – Pd(DBA)₂.

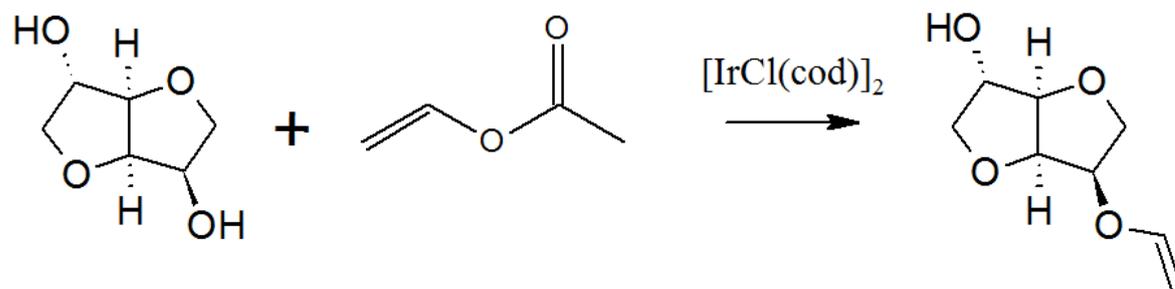
To the solution of Pd(DBA)₂ (0,1207 g; 0,21 mmol) in THF (5 mL) Et₃N (0,439 μl; 3,15 mmol), CF₃COOH (0,0324 μl; 0,42 mmol) and phenantroline (0,0382 g; 0,21 mmol) were added.

In another flask isorbide (1,0438 g; 7 mmol) was dissolved in THF (10 mL) and then transferred to the main reaction mixture. After this dioxane (5 mL) and vinyl ether (5 mL) were added.

Flask was equipped with Liebig condenser, filled with Ar, placed in the preheated oil bath (60 °C) and was stirred for 1 day.

Sample from reaction mixture was taken for NMR (see supplemental materials: №8).

2.2.4. Obtaining of vinyl isorbide with [IrCl(cod)]₂ catalyst



Scheme 13. The vinylation reaction between isorbide and vinyl acetate with [IrCl(cod)]₂.

Na₂CO₃ (0,04496 g; 4,2 mmol), isorbide (1,0438 g; 7 mmol) and [IrCl(cod)]₂ (0,0484; 0,07

mmol) were added in the flask (50 mL) that was equipped with a magnetic stir bar. Then dry components were stirred and air was removed with high vacuum.

Flask was equipped with Liebig condenser, filled with Ar. Toluene (7 mL) and vinyl acetate (1,3034 ml; 14 mmol) were added in the reaction mixture under Ar atmosphere. Then the reaction was stirred for 2 at 100 °C.

After that the solution and precipitate were separated. The solution was evaporated and weighed (0,6871 g).

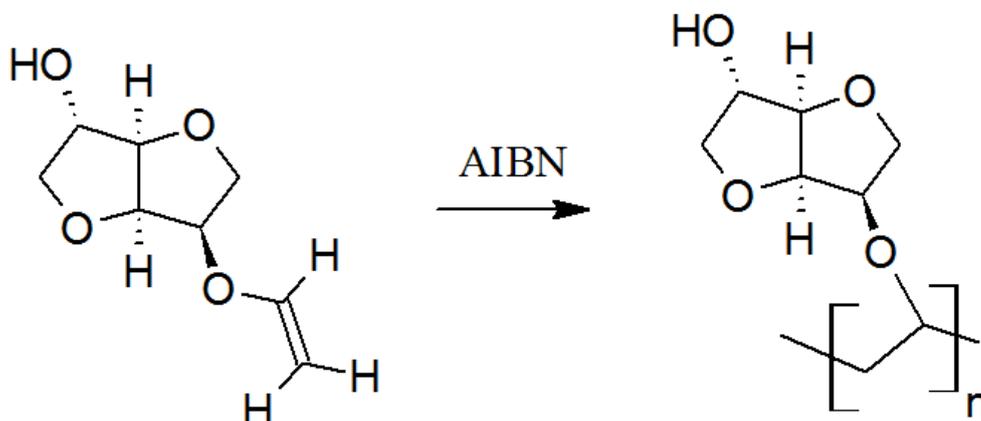
Precipitate was extracted 3 times with EtOAc and H₂O (1st time: 20 ml and 20 ml; 2nd, 3rd: 10 ml and 10 ml respectively). Then precipitate was dried with MgSO₄, evaporated and weighed (0,2443 g).

Products from solution and from residue were combined. The product was isolated by column chromatography (length 15 cm, silica gel, 50 % EtOAc/petroleum). Two fractions were formed: F1 (0,1982 g) and F2 (0,2378 g). Then fractions were analyzed by NMR (see supplemental materials: №9, №10, №11).

Later reaction was repeated again for using in another polymerization reactions. Reaction conditions were the same but amount of all components was doubled. After isolating by column chromatography (15 cm, silica gel, 50 % EtOAc/petroleum) three fractions were formed: F1 (0,061 g), F2 (0,3028 g), F3 (0,6504 g) and analyzed by NMR (see supplemental materials: №12, №13, №14).

Fraction F3 is monovinyl isosorbide.

2.3. Reaction of polymerization of vinyl isosorbide with AIBN



Scheme 14. Polymerization reaction of vinyl isosorbide by AIBN catalyst.

Vinyl isosorbide (0,106 g; 0,62 mmol) was added to the microwave reaction vial that was equipped with a magnetic stir bar.

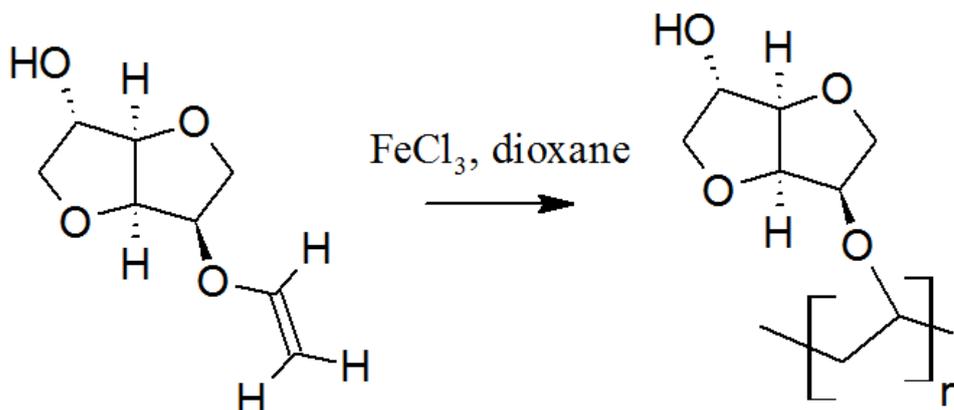
For this reaction AIBN was needed in small amount: 1,0168 mg or 6,192 μmol . So AIBN (5,4 mg) was dissolved in EtOAc (0,5 mL) and then was added (0,1 mL) to reaction mixture.

The mixture of vinyl isosorbide, EtOAc (1,5 mL) and AIBN was stirred for 30 min under Ar atmosphere. After that EtOAc (2 mL) was added and reaction mixture let to run additional 30 min.

Flask was placed in the preheated oil bath (70 $^{\circ}\text{C}$) and stirred for 1 day. After that the reaction mixture was analyzed by NMR (see supplemental materials: №15).

Later, reaction was repeated under the same conditions but the amount of AIBN was doubled. For that AIBN (9 mg) was dissolved in EtOAc (0,5 mL). This solution (0,1 mL) was added to the reaction mixture.

2.4. Cationic polymerization of vinyl isosorbide with FeCl_3



Scheme 15. Polymerization reaction of vinyl isosorbide by FeCl_3 and dioxane.

The flask containing vinyl isosorbide (0,2378 g; 1,38 mmol) was evacuated under high vacuum and backfilled with argon, then dioxane (0,14685 g) and toluene (1,5 mL) were added to the reaction mixture. Reaction mixture was placed into the ice bath. A solution of FeCl_3 was prepared as follows: First, anhydrous FeCl_3 (0,036 g, 8,23 μmol) was dissolved in E_2O (1 mL). Then a portion of this solution (0,13 mL) was transferred to another vial and diluted

with toluene (0,38 mL). After this a portion of the obtained mixture (0,17 mL) was added to the main reaction. Reaction was placed in an ice bath for 15 min. Then ice bath was removed and reaction mixture was stirred at room temperature for 1 h. Then volatiles were removed to give

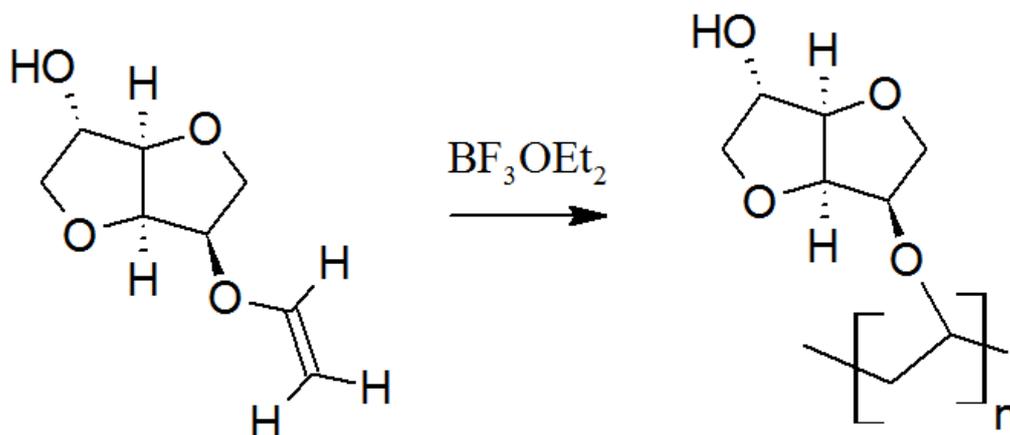
(0,1482 g) of product. Obtained product was insoluble in toluene. The residue was dissolved in DCM (5 mL) and solution of NaCl (few drops) was added.

Water layer was removed and the organic layer was dried with $MgSO_4$. Obtained solution was filtered filtered and evaporated to give (0,1006 g) of product. A sample was taken for NMR analysis (see supplemental materials: №16).

The crude product was dissolved in EtOAc (1 mL) and after addition of Et_2O oily precipitate started to form. Then liquid was removed and oily precipitate was again dissolved in EtOAc and precipitated with Et_2O

This time precipitate was not oily. Ether was decanted and precipitate was evacuated with vacuum. White precipitate (0,0464 g) was then analyzed by NMR (see supplemental materials: №17).

2.5. Cationic polymerization of vinyl isosorbide with $BF_3 \cdot OEt_2$



Scheme 16. Polymerization reaction of vinyl isosorbide with $BF_3 \cdot OEt_2$.

Vinyl isosorbide (0,2g, 1,16 mmol) was placed to the flask that was equipped with a magnetic stir bar. DCM (1,2mL), CH_3CN (4,4mL) and H_2O (21 μ l, 0,2 mmol) were added under Ar atmosphere.

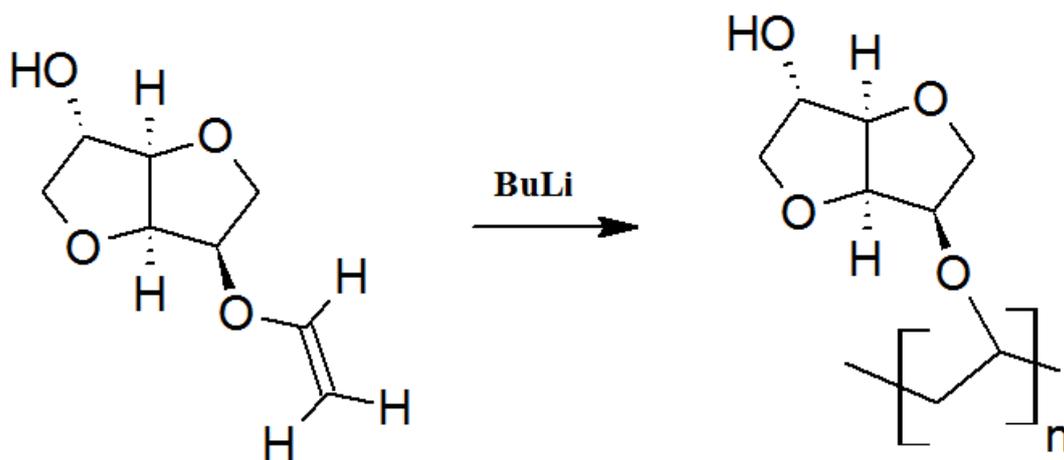
Benzyl alcohol (23,9 μ l, 0,2 mmol) was dissolved with CH_3CN (1 mL) and then a portion (0,1 mL) of this solution was transferred to the reaction mixture.

$BF_3 \cdot Et_2O$ (14,8 μ l, 0,002 mmol) was dissolved in CH_3CN (1 mL) and then a portion of this

solution(0,1 mL) was added to the reaction mixture to the reaction.

Reaction was placed in an ice bath for 2 hours. Sample was taken for NMR analysis (see supplemental materials: №19).

2.6. Anionic polymerization of vinyl isosorbide with butyllithium.



Scheme 17. Polymerization reaction of vinyl isosorbide with butyllithium.

The flask was charged with vinyl isosorbide (0,2g, 1,16 mmol), then THF (5mL) was added, followed by TMSCl (0.147mL, 1,16 mmol). The reaction mixture was stirred for 1 hour under Ar atmosphere.

After this the reaction mixture was evaporated (to remove HCl) and the residue was dissolved again in THF (5 mL) under Ar atmosphere. Then the reaction mixture was cooled to -78°C and butyllithium was added (10 mol %; 46,4 μl). The the reaction was stirred for 30min. After that HCl (10 %, 1mL) was added and reaction was stirred for 1 hour. A sample was taken for NMR analysis (see supplemental materials: №20).

3.RESULTS AND DISCUSSION

One of the tasks during our research was the obtaining of monovinyl isosorbide in one step from commercial isosorbide. To achieve this goal, different methods of vinyl isosorbide synthesis were tested.

Firstly we tried to synthesize monovinyl isosorbide using calcium carbide. This reaction is interesting because of relatively cheap and eco-friendly reagents are used (Teong *et al.*, 2017). In the literature a good product yield was reported (ca 70 %) for this reaction, but in our case the product yield was very small (10 %). One of the difficulties is reaction selectivity. Teong *et al.*, has described methods for synthesis of vinyl ether from compounds with one free OH-group. Isosorbide has two OH-groups, thus reaction can occur in three ways: vinylation of one OH-group, vinylation of the other OH-group, and the vinylation of the both groups to give divinyl isosorbide(see supplemental materials: №1, №2, №3, №4, №5, №6). Vinyl isosorbide is polar compound and therefore it has a good solubility in H₂O and may present difficulties for purification using a column chromatography. The part of product may be lost during extraction. DMSO (the reaction solvent) is a very polar that mixes with water, thus presenting the difficulties for the extraction. One of the possible ways for improving the yield is the replacement the reaction solvent with a less polar one..

In the result of this experiment three fractions were received (see supplemental materials: №1, №2, №3, №4, №5, №6). The second fraction was monovinyl isosorbide. It was analyzed by NMR (№3, №4):

¹H NMR (400,1 MHz, CDCl₃): δ 6,34-6,28 (dd, 1H); 4,59-4,56 (t, 1H); 4,47-4,42 (dd, 2H); 4,27-4,20 (m, 2H); 4,10-4,06 (m, 2H); 3,94-3,89 (d, 1H); 3,84-3,79 (dd, 1H); 3,56-3,51 (dd, 1H); 2,61-2,58 (d, 1H) ppm.

¹³C NMR (100,6 MHz, CDCl₃): δ 149,49; 89,28; 85,43; 81,91; 81,82; 73,60; 73,18; 72,25 ppm.

Then the vinylation reaction of isosorbide-2-acetate using calcium carbide was performed. The use of isosorbide-2-acetate theoretically could solve the problem of free OH-group that was mentioned above, but the product has not formed in this reaction. The sample was analyzed by NMR. Strong signal of acetate ion was the only one registered. It shows that isosorbide-2-acetate was hydrolyzed by Ca(OH)₂.

After that we tried another method for synthesis of vinyl ethers: reaction between isosorbide

and ethyl vinyl ether with Pd(OOCCF₃)₂ catalyst. Bosch, M. and Schlaf, M. reported a high product yield (ca 90%) for vinylation reactions. (Bosch, M. and Schlaf, M., 2003) However for isosorbide this method did not work, probably because of bad solubility of isosorbide and palladium catalyst in the reaction medium. Sample was taken for NMR analysis (see supplemental materials: №7).

To overcome problem of solubility we have changed the solvent to THF and used Pd(DBA)₂ as catalyst. Pd(DBA)₂ has good solubility in THF. NMR spectrometry showed only traces of product (see supplemental materials: №8). From this observation can conclude that using of palladium catalysts is not suitable for synthesis of monovinyl isosorbide.

Because previous methods didn't give positive results, we tested the method of vinylation using [IrCl(cod)]₂ as catalyst. In the article (Okimoto *et al.*, 2002) a high product yield was reported (ca 67-97 %) for vinylation reactions. The yield of the target product was 20 % , what is somewhat higher than in the reaction with calcium carbide. In this reaction the selectivity also was not high. Reaction optimization is needed to achieve greater yield. We used this method again on greater scale (product yield was 23 %) for getting monovinyl isosorbide for the subsequent polymerization. NMR spectrometry results were analogous for calcium carbide reaction and were described above (see supplemental materials: №14).

When monovinyl isosorbide was obtained, we tried to polymerize it.

Synthesis method that uses V-601 as initiator was reported in literature (Sugihara *et al.*, 2016). In our method V-601 was changed for analogous and more common initiator - AIBN. The two performed experiments showed no significant polymerization, and only unchanged starting material could be seen (see supplemental materials: №15).

Later we tried cationic polymerization method. Only small part of polymerization methods is suitable for the compounds with free OH-group. Thus method of choice was polymerization with FeCl₃ as catalyst because of its high reaction rate ca 15 sek (Kanazawa *et al.*, 2006). During this reaction oligomer was obtained and analyzed by NMR spectrometry and HPLC(see supplemental materials: №17, №18).

¹H NMR (400,1 MHz, CDCl₃): δ 5,02-4,72 (m, 1H); 4,60-4,11 (m, 4H); 4,04-3,73 (m, 3H); 3,62-3,36 (m, 1H); 1,39-1,12 (m, 3H).

M_n=1062

M_w=1694

PDI =1,67

Molecular masses of obtained compound are comparable to the results that reported in literature (Kanazawa *et al.*, 2006). The precipitation of catalyst (forming of dark, solid crystals at the flask bottom) was spotted after first minutes of the polymerization reaction, it could be the reason for low degree of polymerization.

Another method of polymerization was used that can be applied for compounds with free OH-groups was also investigated. In this method $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was used as initiator. During this reaction polymer was not obtained, however NMR spectrometry (see supplemental materials: №19) showed the absence of vinyl group signals. It can be explained by vinyl group hydrolysis by the action of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and H_2O .

Anionic polymerization with protecting of OH-groups was tested (Hirao *et al.*, 2014). Protection was performed using TMSCl and butyllithium was used as the initiator. NMR spectrometry (see supplemental materials: №20) showed the absence of vinyl group signals and possible formation of polymer. However, the interpretation of crude product spectrum was difficult. In future, the methods for removing protection of OH-groups and the polymer extraction should be developed.

4.SUMMARY

In this thesis properties of isosorbide as a precursor for the synthesis of new biopolymers were studied. Synthetic methods for obtaining of vinylated compounds were obtained from the literature and tested on isosorbide. During this research monovinyl isosorbide that can be used later as a monomer for the creation of new biopolymer was synthesized. Further different polymerization methods we investigated and the new polymer (oligomer) was synthesized. In addition, the advantages and disadvantages of methods for isosorbide vinylation and polymerization were analyzed. The next goals and prospects were defined.

Consequently, one more step for new biobased polymers synthesis, that can replace fossil based polymers, was done.

5.RESÜMEE

Monovinüül isosorbiidi süntees ja selle polümerisatsioon.

Daria Eremenko

Tänapäeval on peamine kemikaalide allikas naftatööstus. Kuna fossiilsed ressursid on kas taastumatud või taastuvad aeglaselt, on vaja otsida uusi allikad. Arvestades ka sellega, mis koormuse on tekitanud klassikaline keemiatööstus keskkonnale, on vaja leida uus ja säästlik süsiniku allikas. Lignotselluloosilise biomassi kasutamine toorainena ja sellest kemikaalide ning polümeeride saamine on üks ning võimalus.

Selle uurimistöö eesmärgiks oli uurida isosorbiidi omadusi selleks, et kasutada seda biopäritolu polümeeride sünteesiks. Uurimistöö käigus õnnestus sünteesida uudne monovinüülisosorbiid, mida tulevikus on võimalik kasutada uute polümeeride sünteesiks. Töö käigus õnnestus ka sünteesida vinüülisosorbiidi oligomeer, seega uurimistöö eesmärk sai täidetud.

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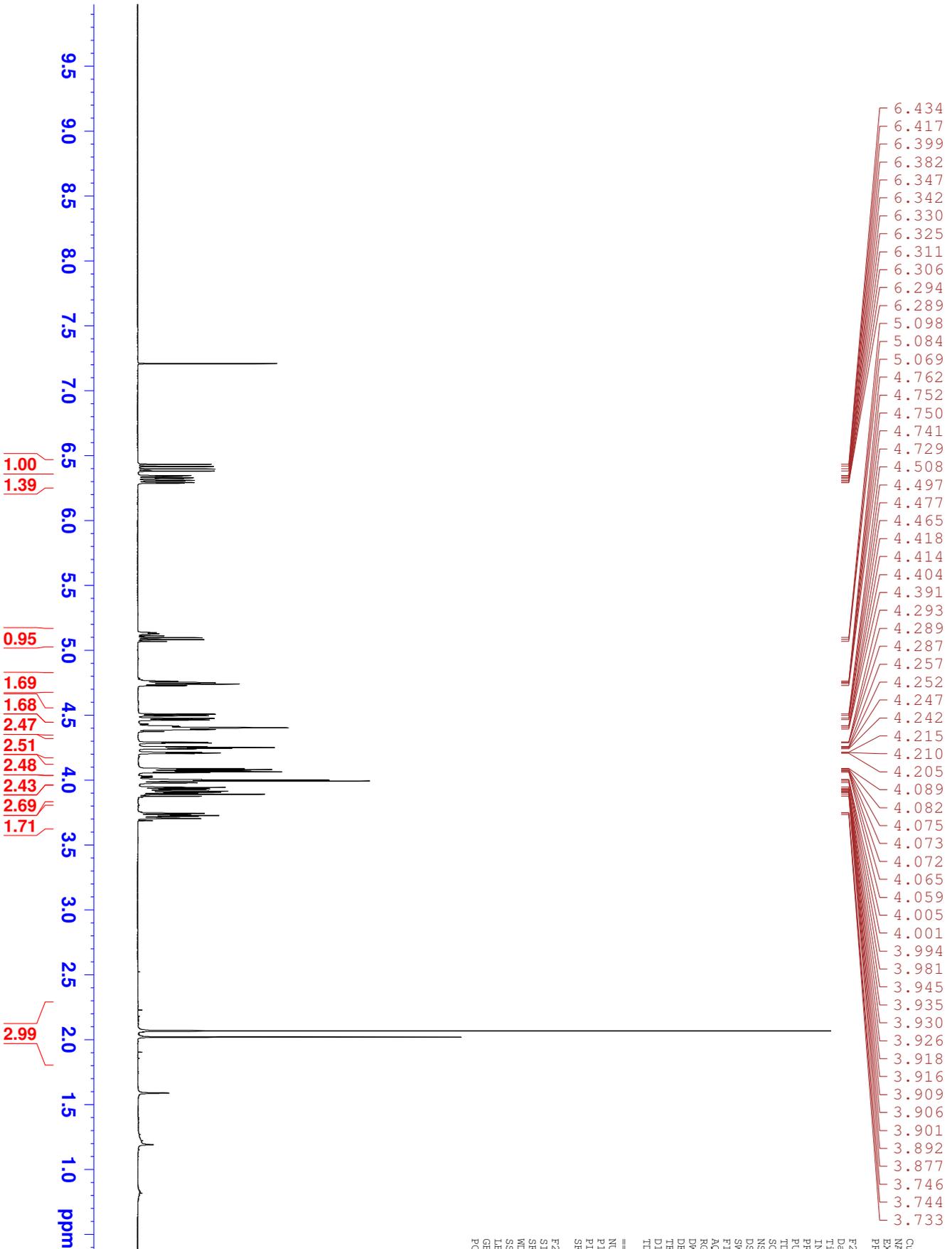
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7. SUPPLEMENTAL MATERIALS



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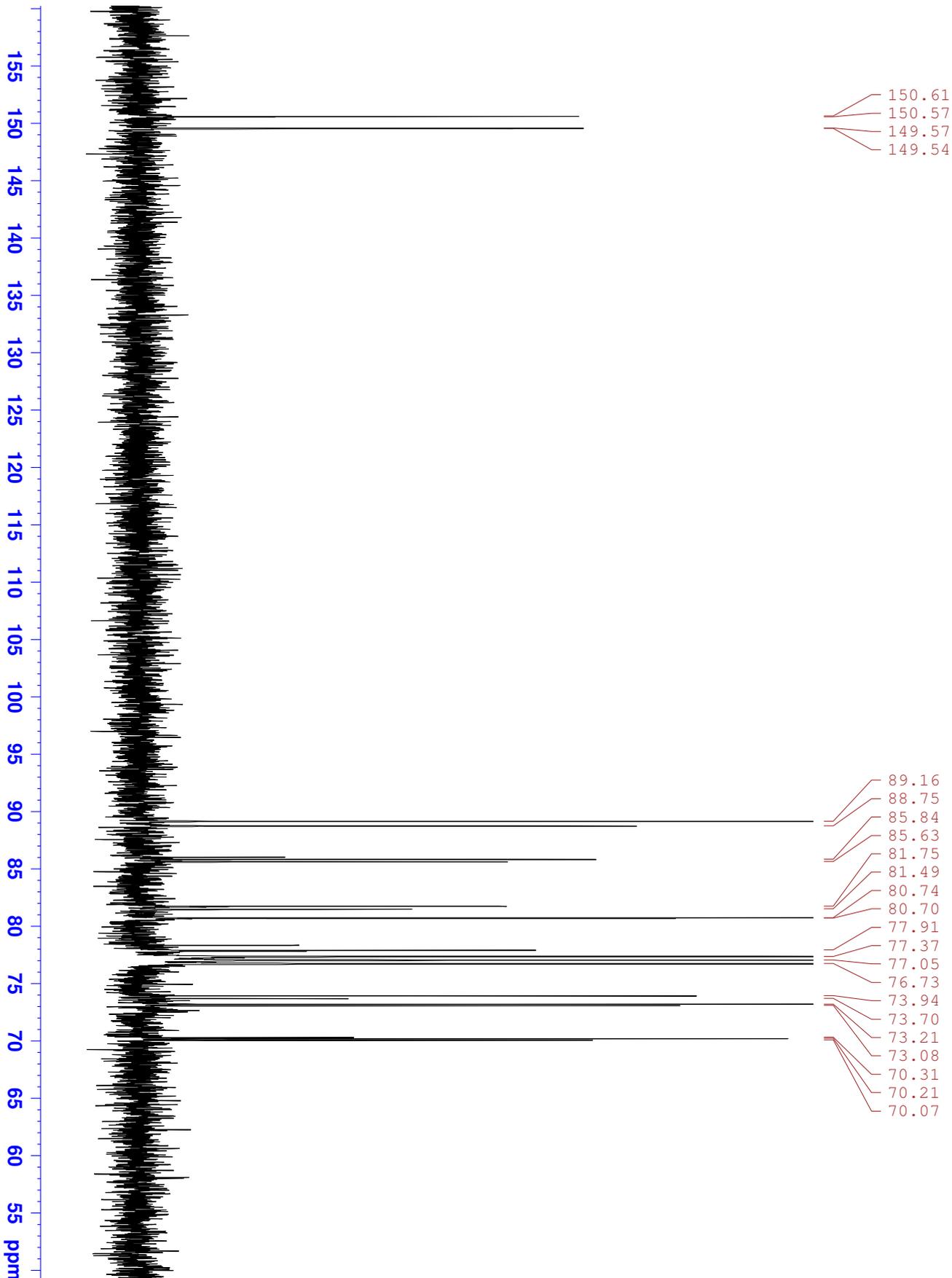
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№2, F1 The vinylation reaction between isosorbide and calcium carbide



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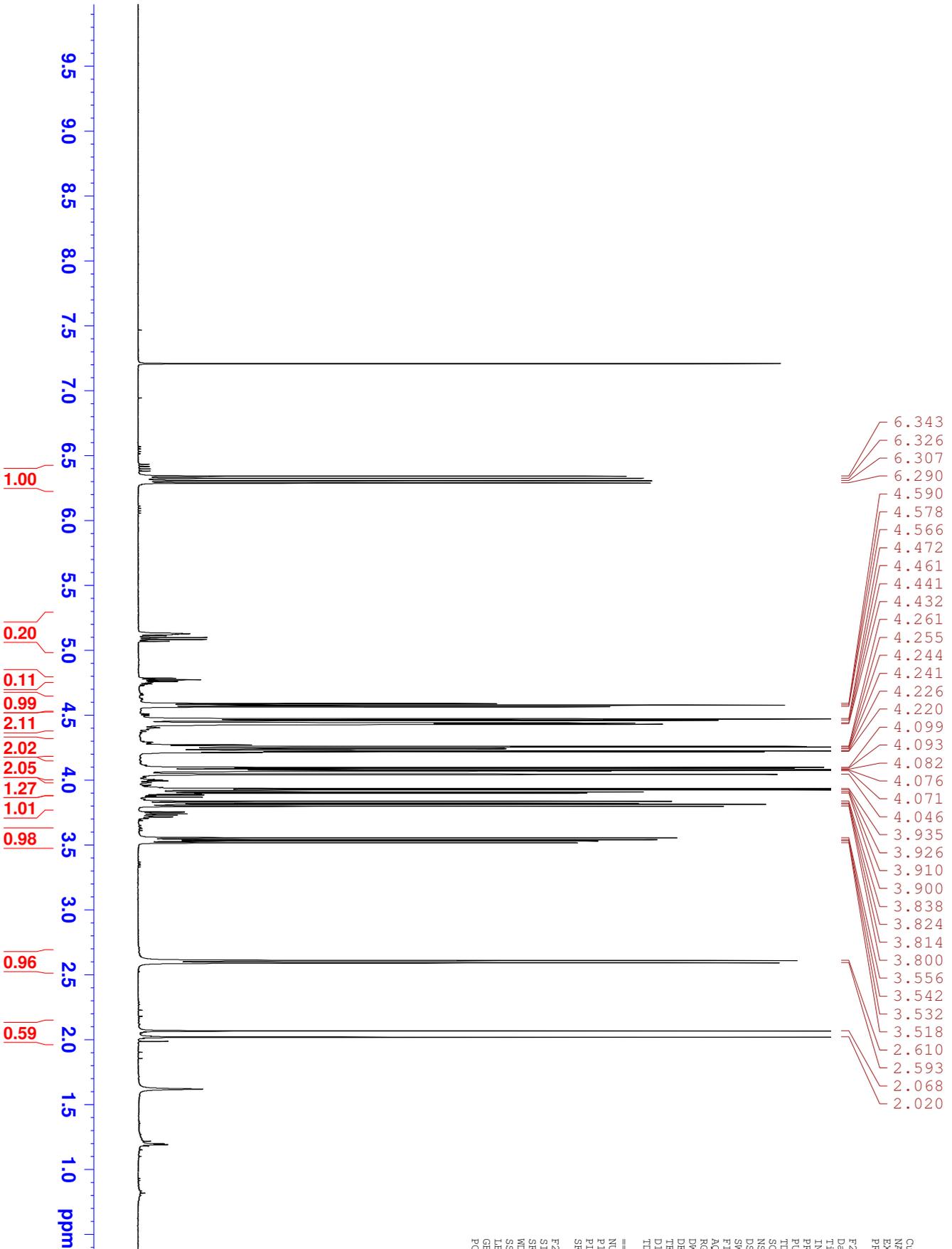
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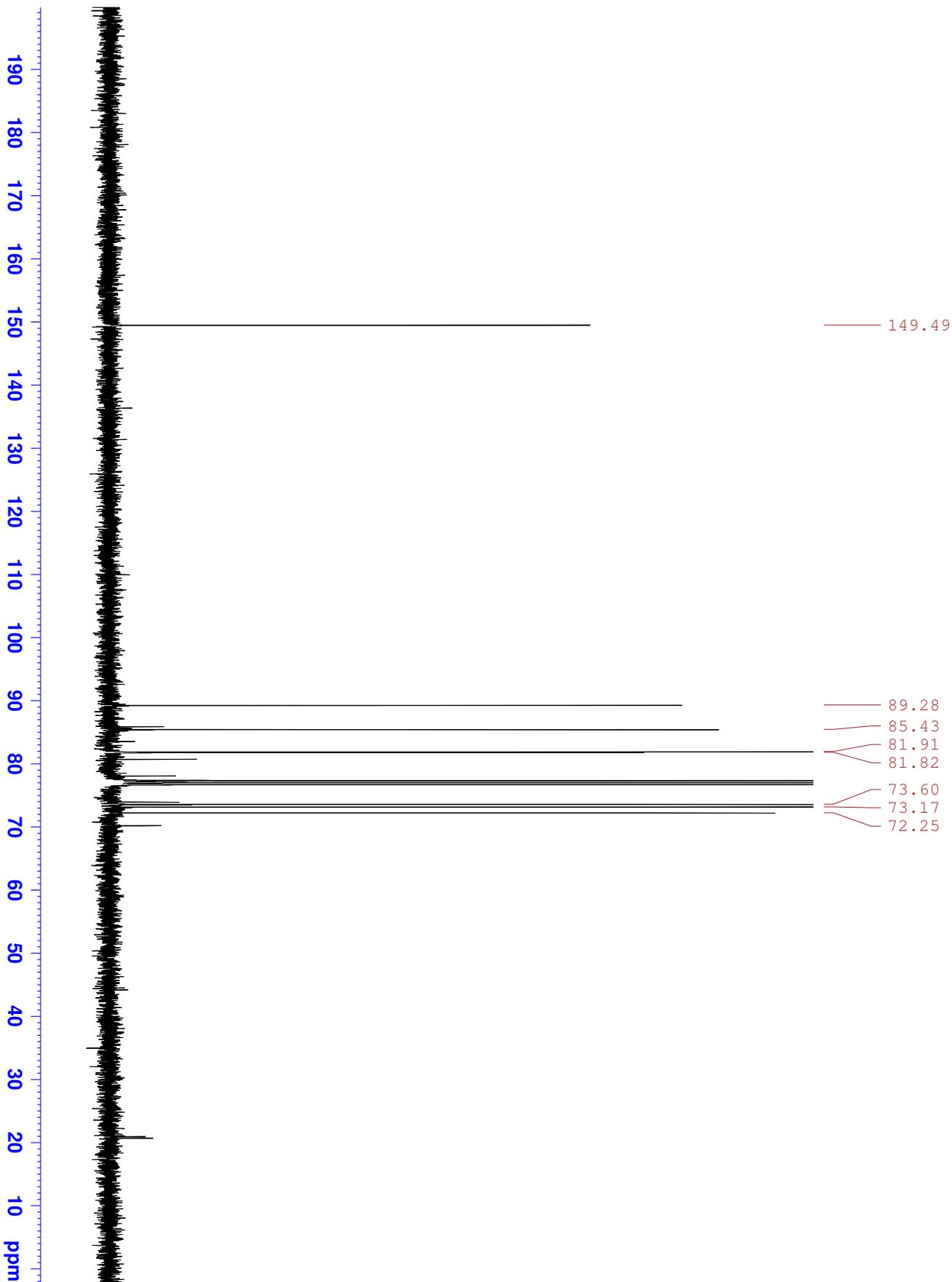
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№4 F2 The vinylation reaction between isosorbide and calcium carbide



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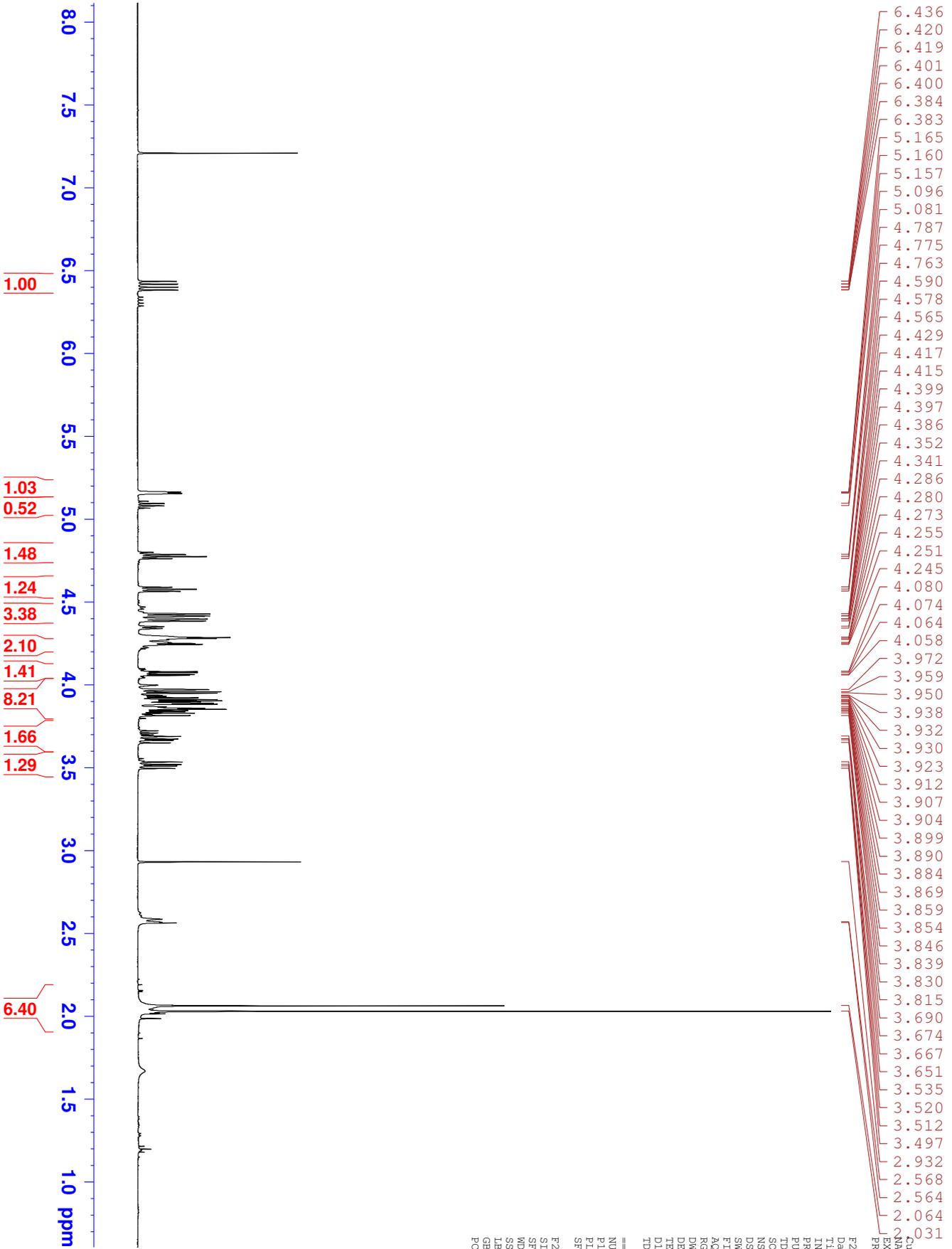
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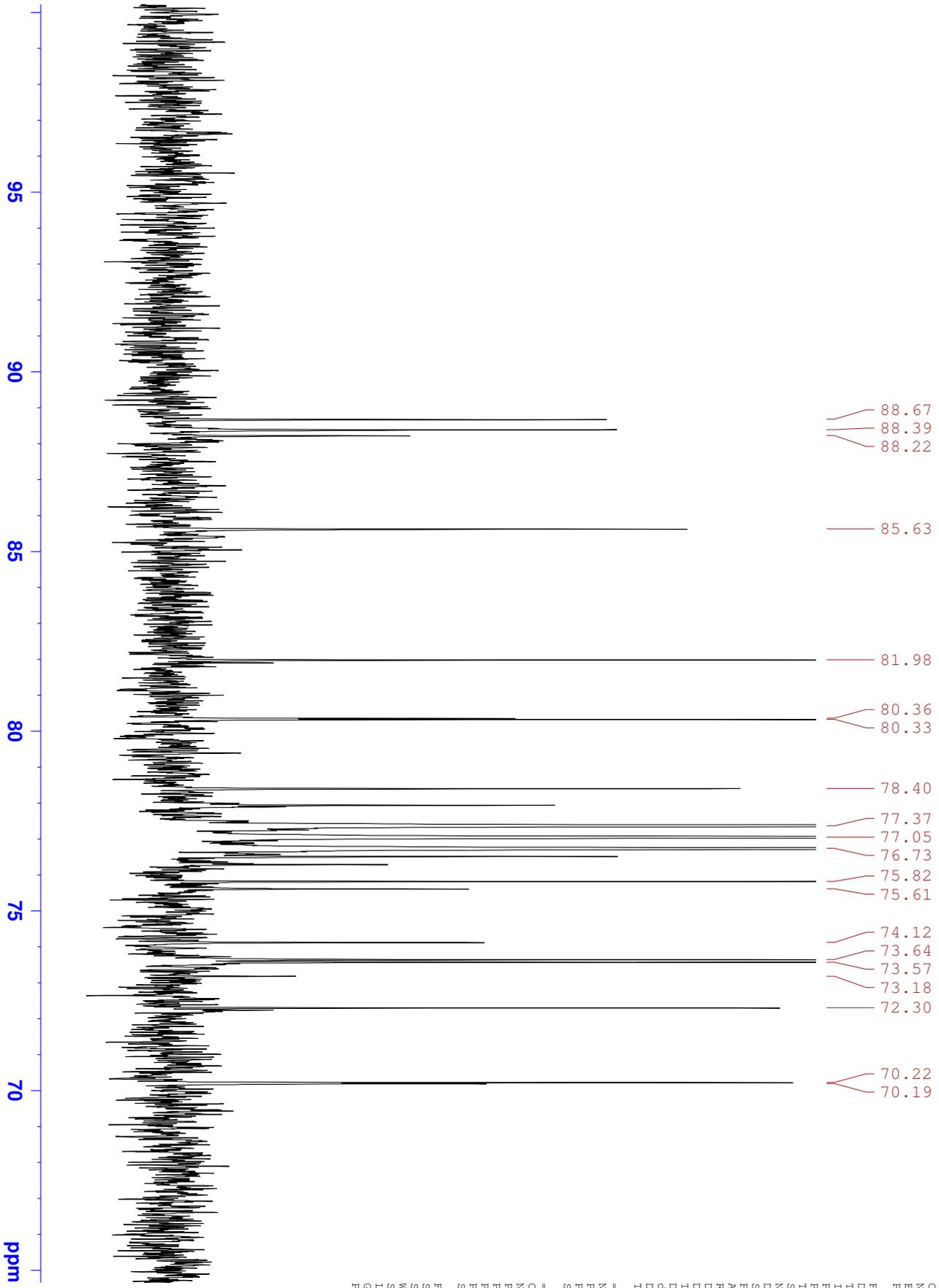
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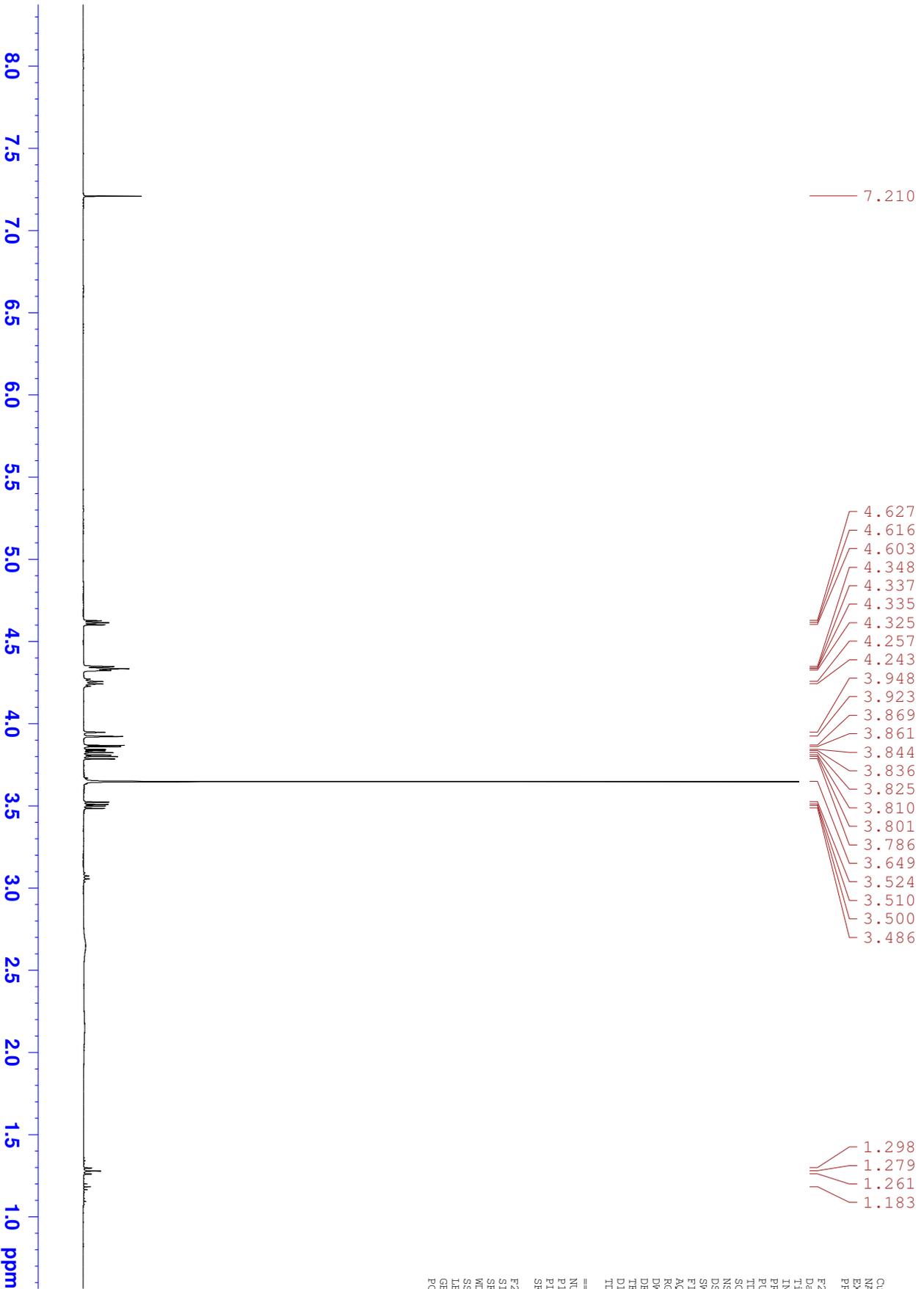
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```

Pd



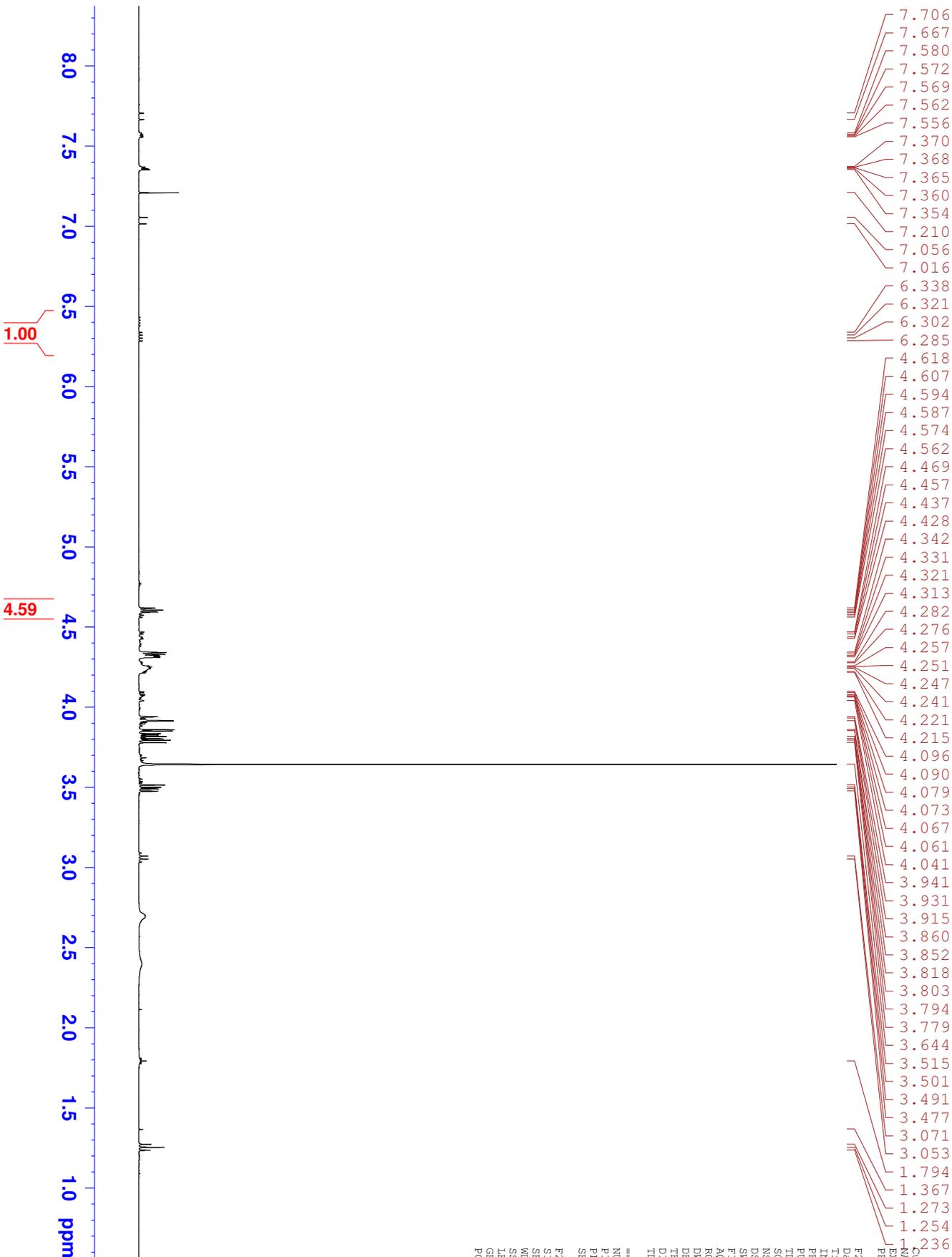
```

Current Data Parameters
NAME          DE12
EXPNO         1
PROCNO        1
F2 - Acquisition Parameters
Date_         20180206
Time          13.51
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            46
DS            0
SWH           6087.662 Hz
FIDRES       0.092890 Hz
AQ           5.3827400 sec
RG           144
DW           82.133 usec
DE           6.00 usec
TE           292.2 K
D1           2.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1           14.35 usec
PL1          0.00 dB
SFO1         400.1328028 MHz

F2 - Processing parameters
SI           65536
SF           400.1300380 MHz
WDW          EM
SSB          0
GB           0
PC           1.00
    
```

Pd(DBA)₂ 2



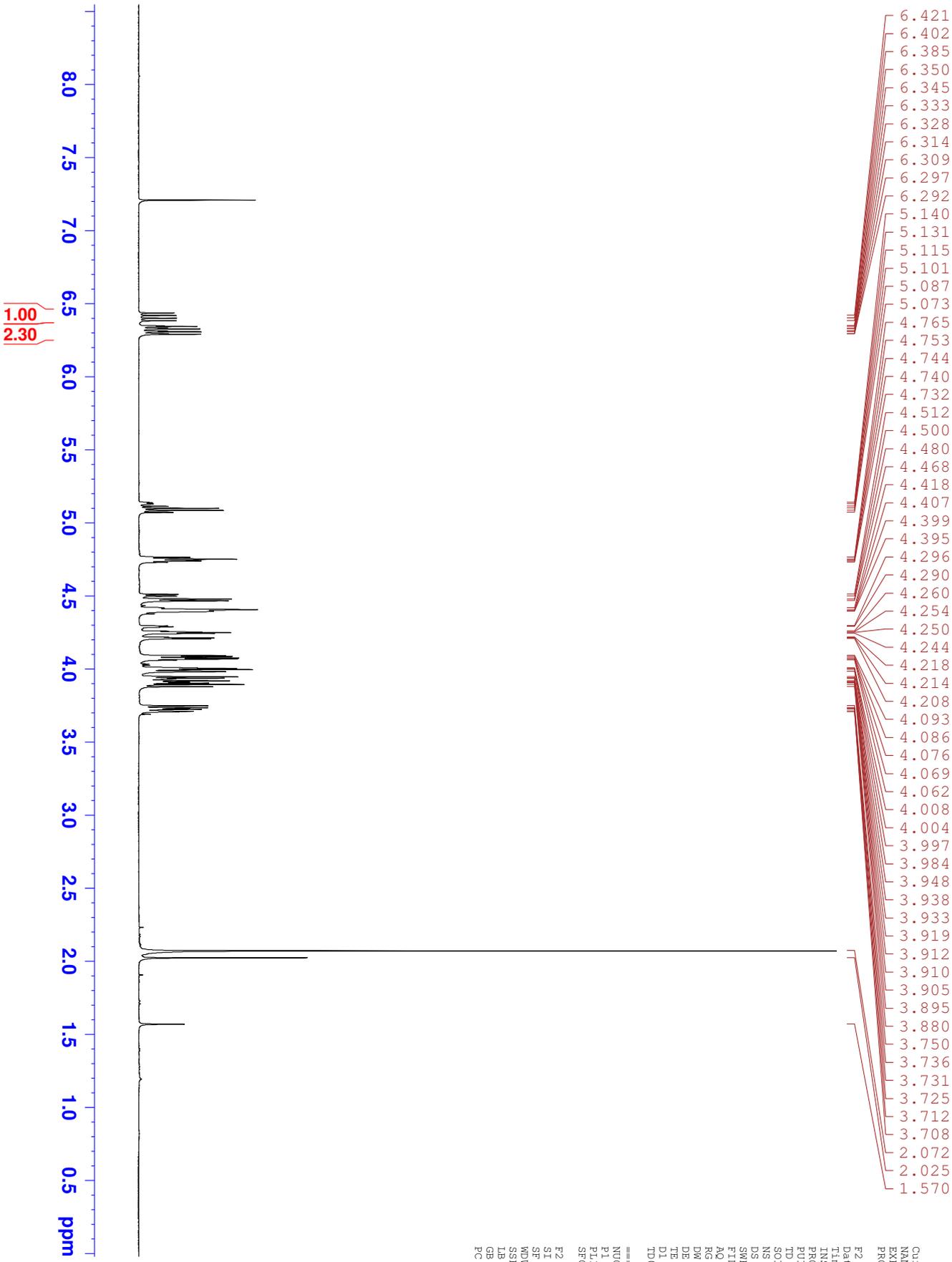
```

Current Data Parameters
NAME          DE13
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20180216
Time          12.36
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zg30
TD            65536
SOLVENT      CDCl3
NS            64
DS            0
SWH           6087.662 Hz
FIDRES       0.092890 Hz
AQ            5.3827400 sec
RG            144
DW            82.133 usec
DE            6.00 usec
TE            292.0 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            14.35 usec
PL1           0.00 dB
SFO1          400.1328028 MHz

F2 - Processing parameters
SI            65536
SF            400.1300380 MHz
WDW           EM
SSB           0
GB            0
PC            1.00
    
```



Current Data Parameters
 NAME DEL17
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20180308
 Time 14.20

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30

TD 65536
 SOLVENT CDCl3
 NS 64

DS 0
 SWH 6087.662 Hz
 FIDRES 0.092890 Hz

RG 5.3827400 sec
 AO 144

DW 82.133 usec
 DE 6.00 usec

TE 292.1 K
 D1 2.00000000 sec

TD0 1

==== CHANNEL f1 =====
 NUCL1 1H

PI 14.35 usec
 PL1 0.00 dB

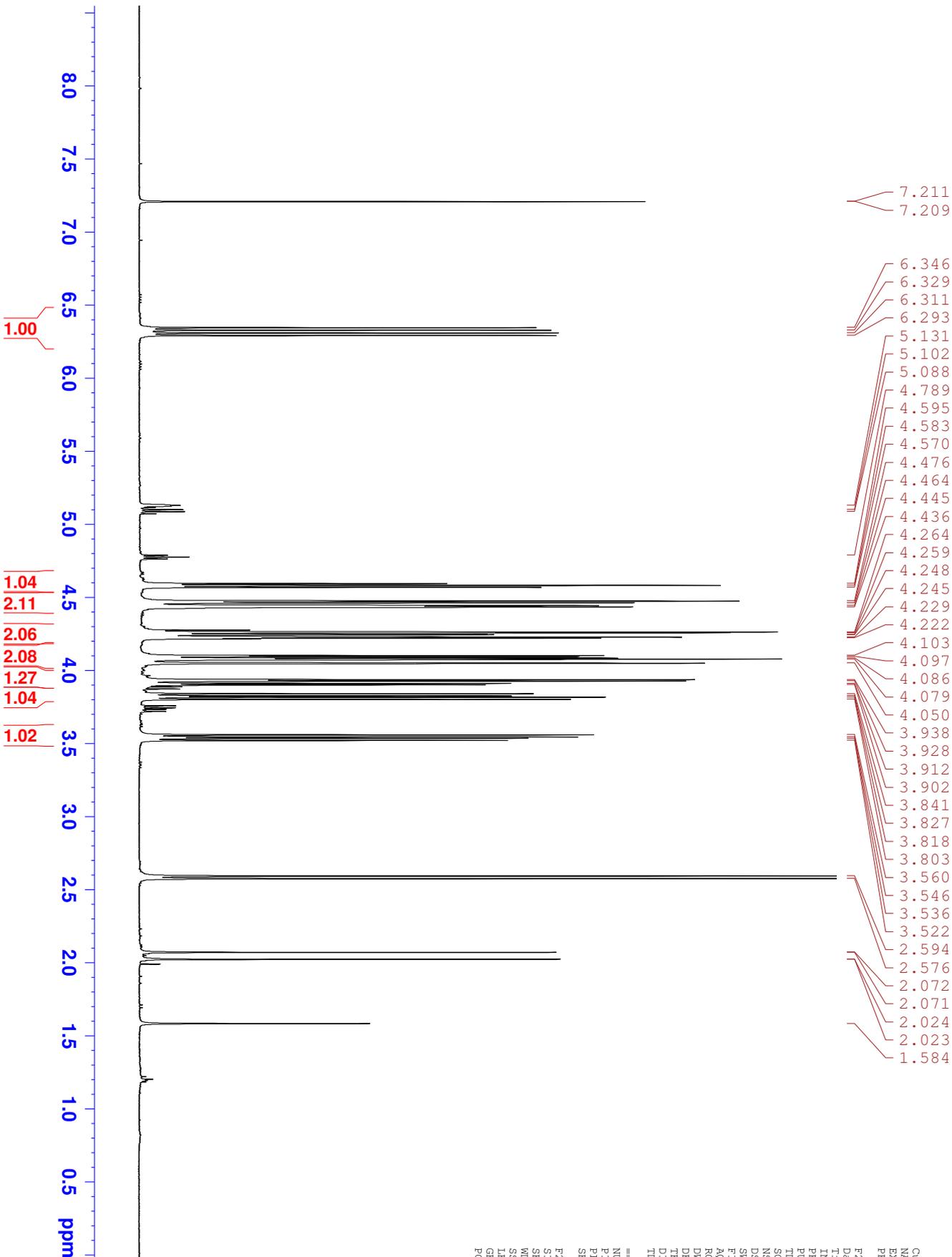
SFO1 400.1328028 MHz

F2 - Processing parameters
 SI 65536

SF 400.1300380 MHz
 WDW EM

SSB 0
 IB 0.10 Hz

GB 0
 PC 1.00



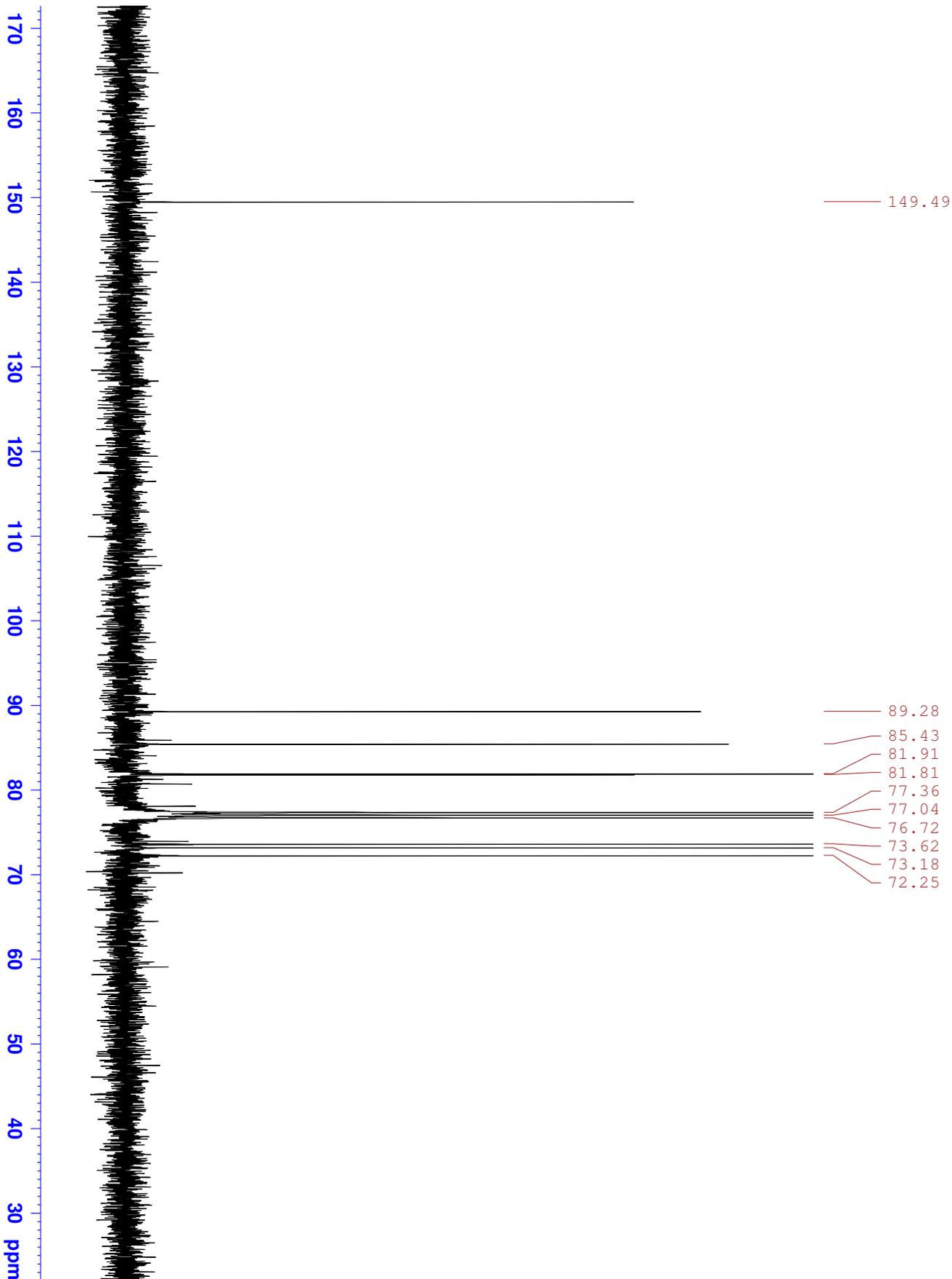
```

Current Data Parameters
NAME          DE17
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20180308
Time          13.27
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           64
DS           0
SWH          6087.662 Hz
FIDRES      0.092890 Hz
AQ          5.3827400 sec
RG          144
DW          82.133 usec
DE          6.00 usec
TE          291.8 K
D1          2.00000000 sec
TD0         1

===== CHANNEL f1 =====
NUC1         1H
P1          14.35 usec
PL1         0.00 dB
SFO1        400.1328028 MHz

F2 - Processing parameters
SI          65536
SF          400.1300380 MHz
WDW         EM
SSB         0
GB          0
PC          1.00
    
```



```

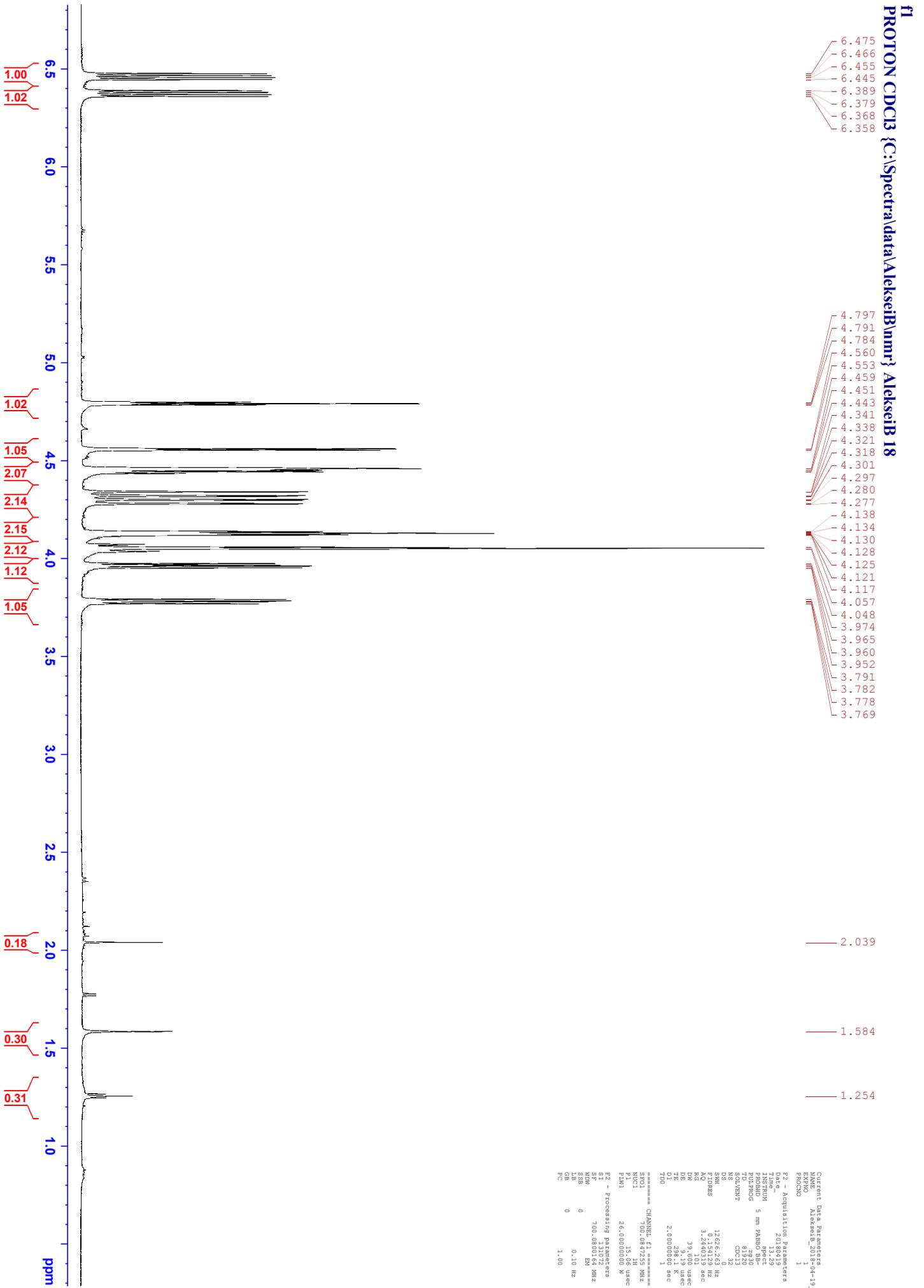
Current Data Parameters
NAME          DEL17
EXPNO         2
PROCNO        1

F2 - Acquisition Parameters
Date_         20180308
Time_        13.59
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           512
DS           0
SWH          24038.461 Hz
FIDRES       0.366798 Hz
AQ           1.3631988 sec
RG           32800
DW           20.800 usec
DE           6.00 usec
TE           293.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0          1

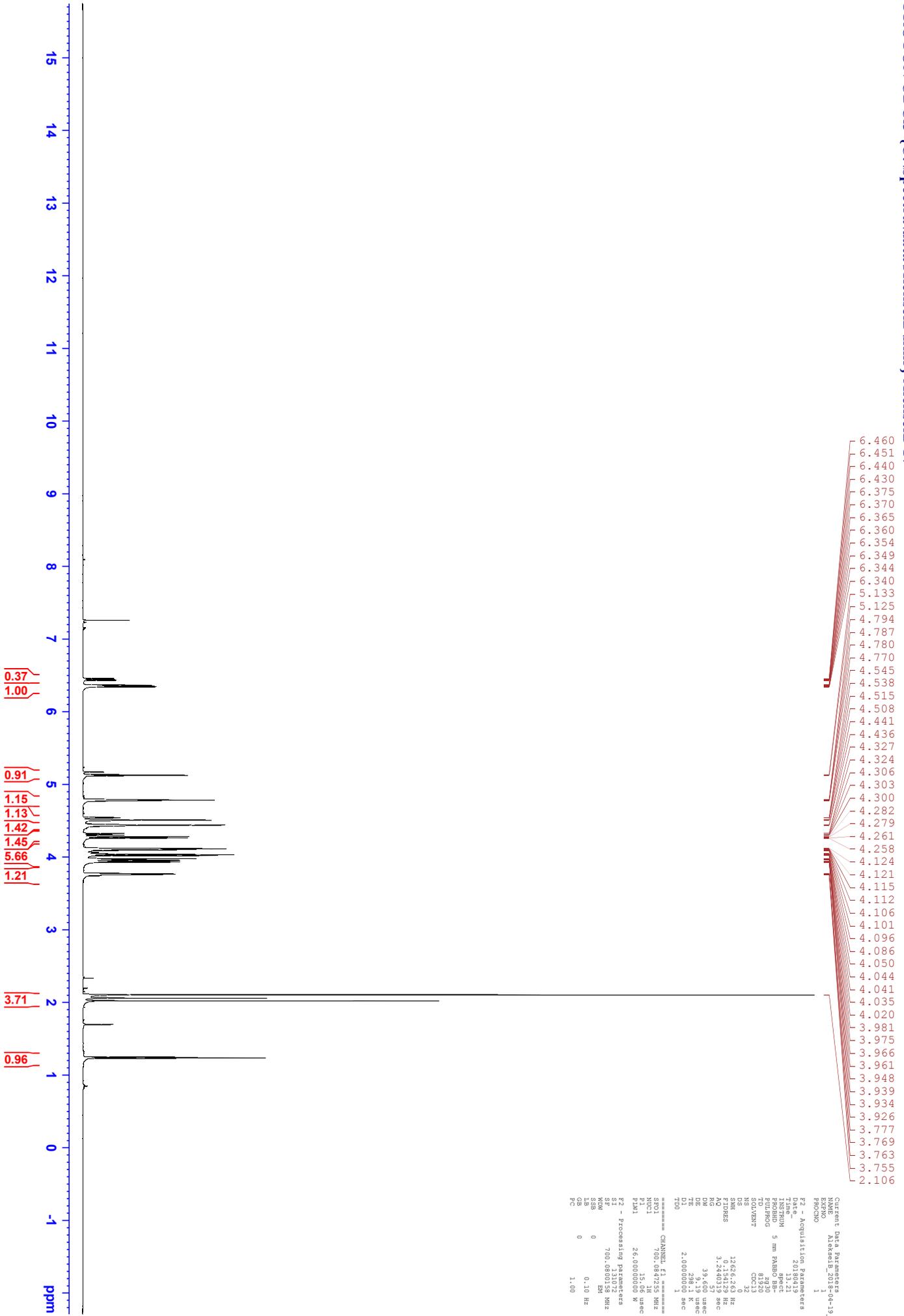
===== CHANNEL f1 =====
NUC1          13C
P1            9.90 usec
PL1          -2.00 dB
SFO1         100.6238364 MHz

===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        70.00 usec
PL12         13.78 dB
PL13         14.00 dB
PL14         0.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI            32768
SF           100.6127697 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40
    
```

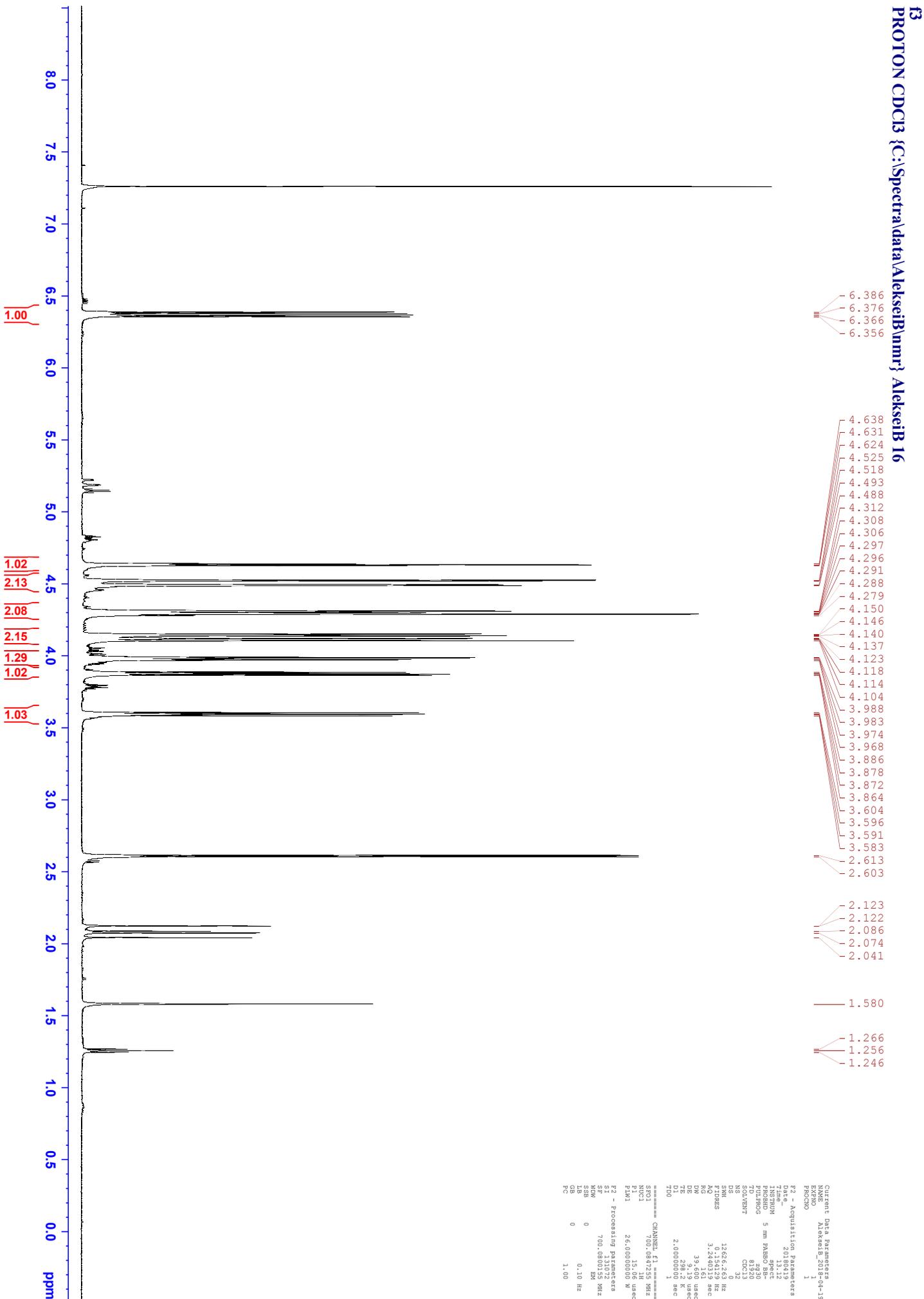


F2
PROTON CDCl₃ {C:\Spectra\data\Alekseib\mnr} Alekseib 17

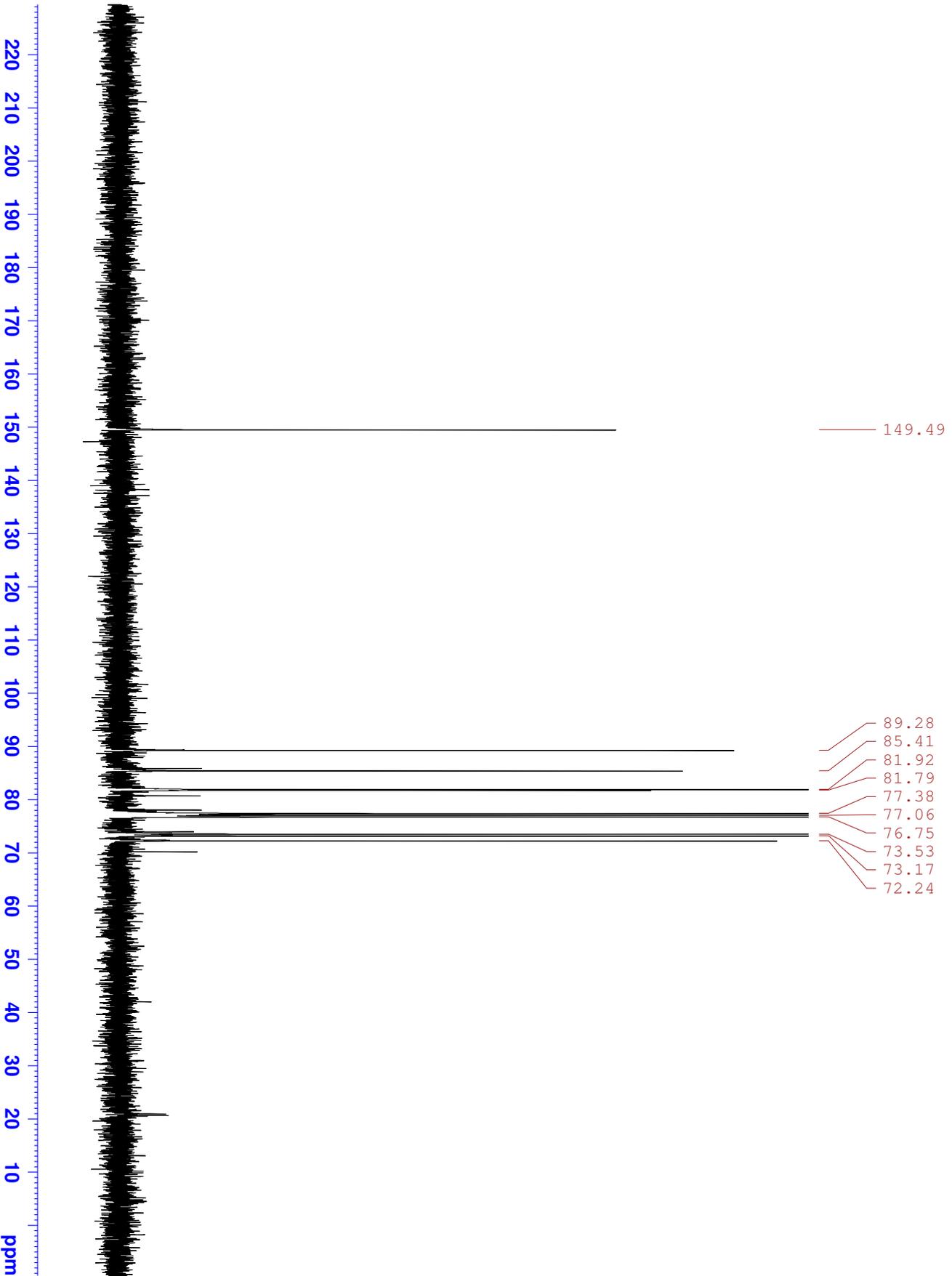


6.460
6.451
6.440
6.430
6.375
6.370
6.365
6.360
6.354
6.349
6.344
6.340
5.133
5.125
4.794
4.787
4.780
4.770
4.545
4.538
4.515
4.508
4.441
4.436
4.327
4.324
4.306
4.303
4.300
4.282
4.279
4.261
4.258
4.124
4.121
4.115
4.112
4.106
4.101
4.096
4.086
4.050
4.044
4.041
4.035
4.020
3.981
3.975
3.966
3.961
3.948
3.939
3.934
3.926
3.777
3.769
3.763
3.755
2.106

Current Data Parameters
NAME: Alekseib_2018-04-19_17
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Time: 2013.21
INSTRUM: spect
PROBHD: 5 mm BBO
PULPROG: zgpg30
TD: 65536
SFO: 700.146300 MHz
FIDRES: 0.13429 Hz
AQ: 3.2440319 sec
RG: 312.5
DE: 2.19 usec
D1: 2.0000000 sec
T1: 1.00
===== CHANNEL f1 =====
SFO1: 700.08417255 MHz
P1: 15.06 usec
PL1: 26.0000000 W
F2 - Processing parameters
SI: 33072
WDW: EM
SSB: 0
GB: 0
PC: 1.00



№15 Polymerization reaction of vinyl isosorbide by AIBN catalyst



89.28
85.41
81.92
81.79
77.38
77.06
76.75
73.53
73.17
72.24

Current Data Parameters
NAME DE10
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters

Date_ 20171215
Time 13.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 406
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 32800
DW 20.800 usec
DE 6.00 usec
TE 293.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

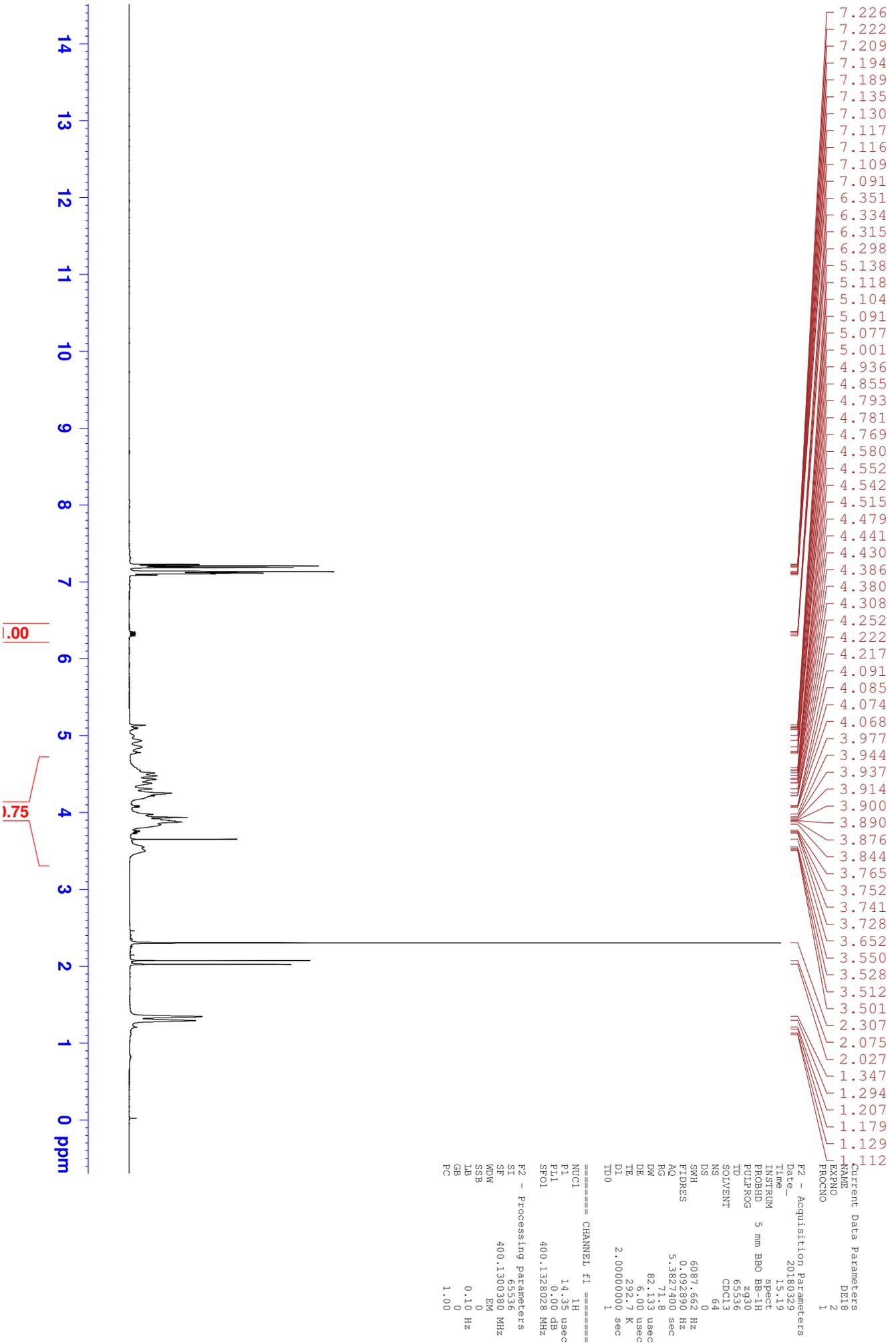
==== CHANNEL F1 =====
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
SFO1 100.6238364 MHz

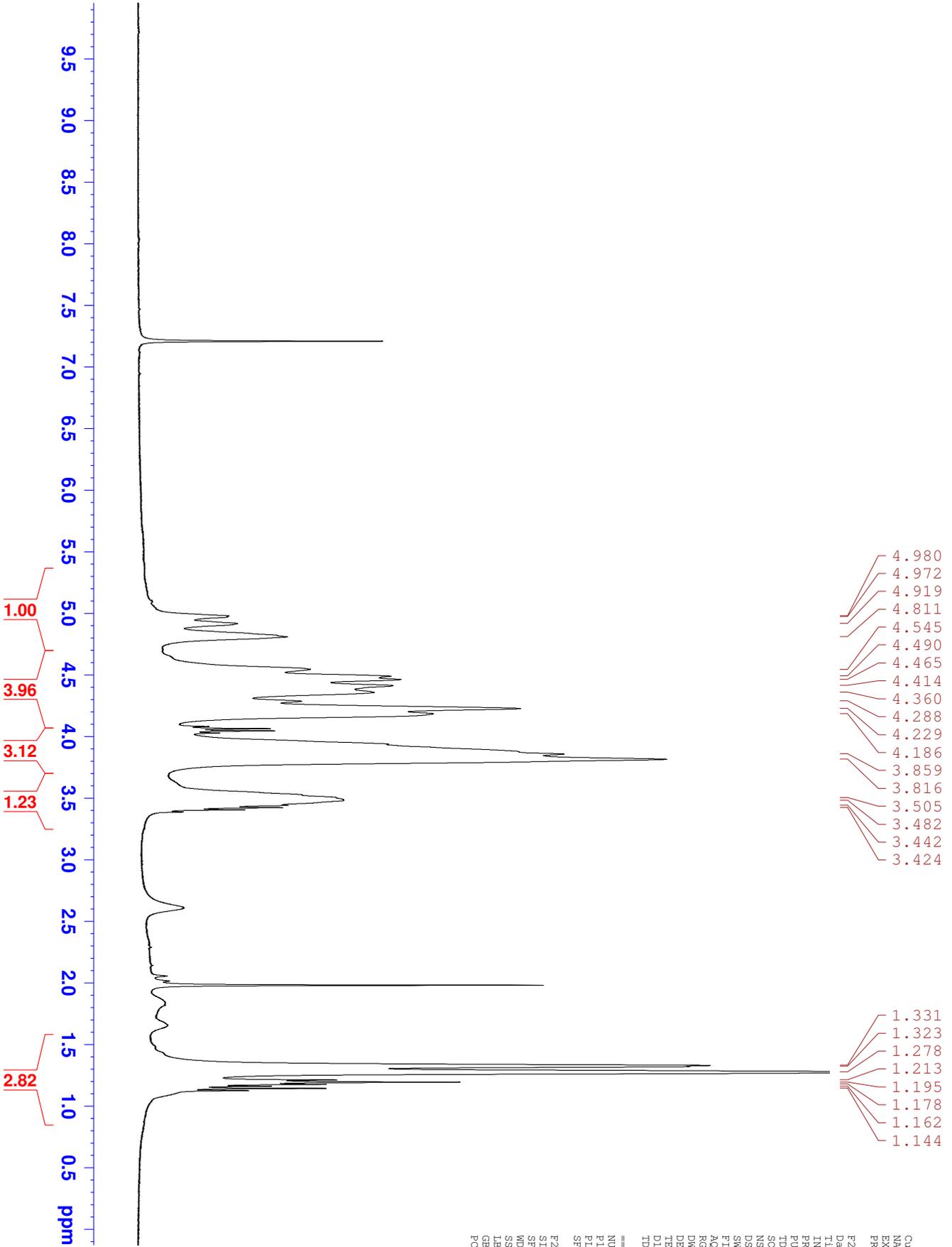
==== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 13C
PCPD2 70.00 usec
PL12 13.76 dB
PL13 14.00 dB
PL2 0.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127697 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
FC 1.40

№16 Polymerization reaction of vinyl isosorbide by FeCl₃ and dioxane

polimerisatsioon, mitte ekstrageeritud





- 4.980
- 4.972
- 4.919
- 4.811
- 4.545
- 4.490
- 4.465
- 4.414
- 4.360
- 4.288
- 4.229
- 4.186
- 3.859
- 3.816
- 3.505
- 3.482
- 3.442
- 3.424

- 1.331
- 1.323
- 1.278
- 1.213
- 1.195
- 1.178
- 1.162
- 1.144

```

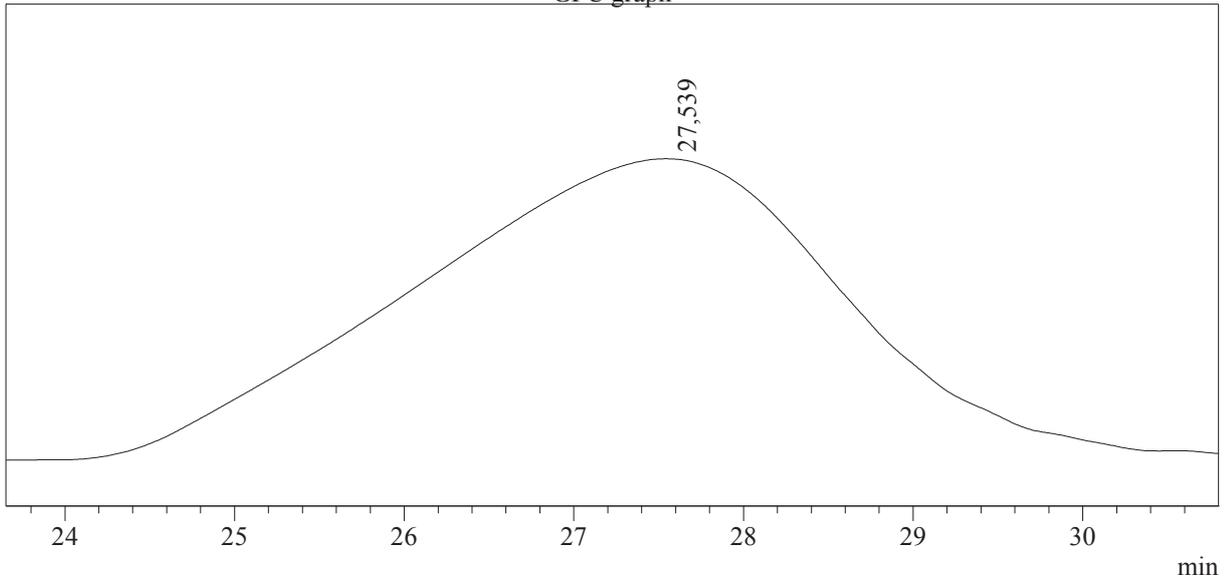
Current Data Parameters
NAME          DE22
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20180525
Time          13.40
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           64
DS           0
SWH          6087.662 Hz
FIDRES      0.092890 Hz
AQ          5.3827400 sec
RG          114
DW          82.133 usec
DE          6.00 usec
TE          294.4 K
D1          2.00000000 sec
TD0         1

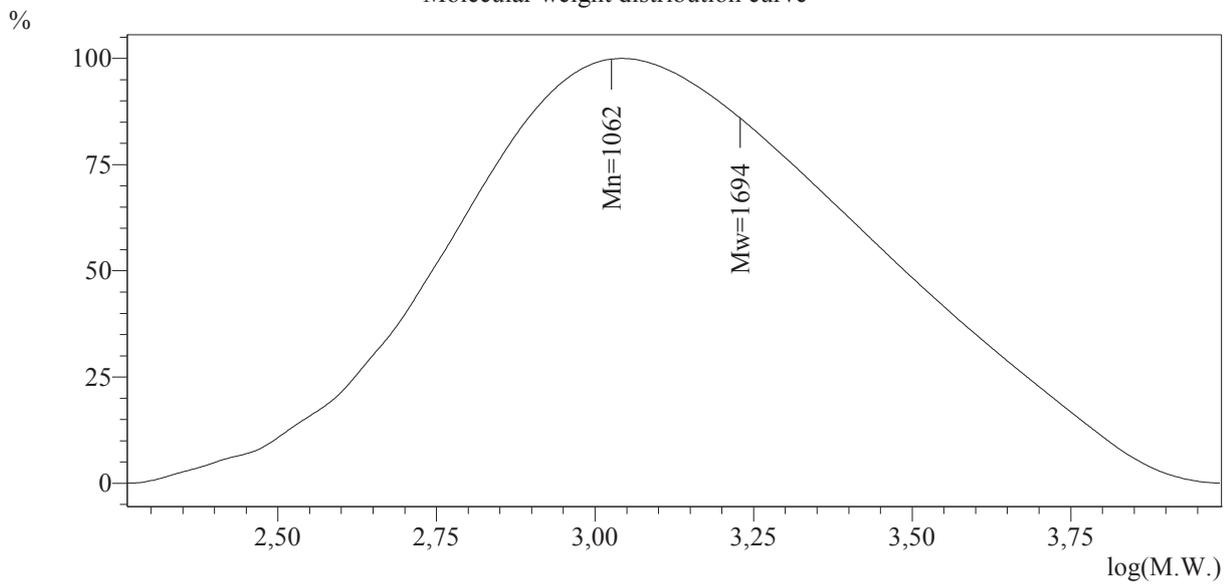
===== CHANNEL f1 =====
NUC1         1H
P1          14.35 usec
PL1         0.00 dB
SFO1        400.1328028 MHz

F2 - Processing parameters
SI          65536
SF          400.1300380 MHz
WDW         EM
SSB         0
GB          0.10 Hz
PC          1.00
    
```

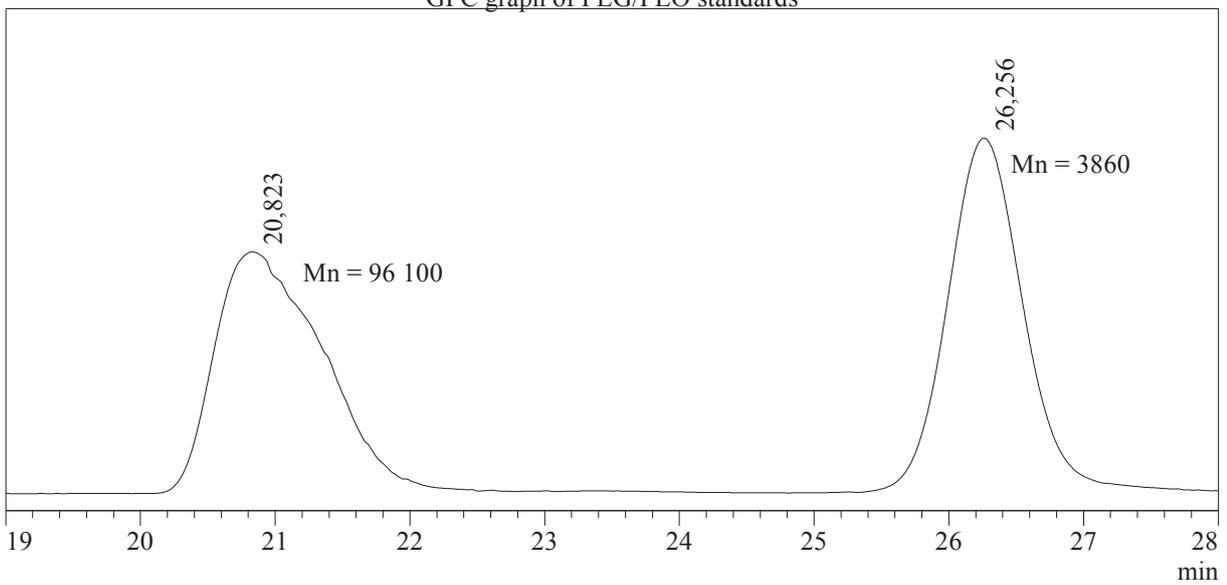
GPC graph

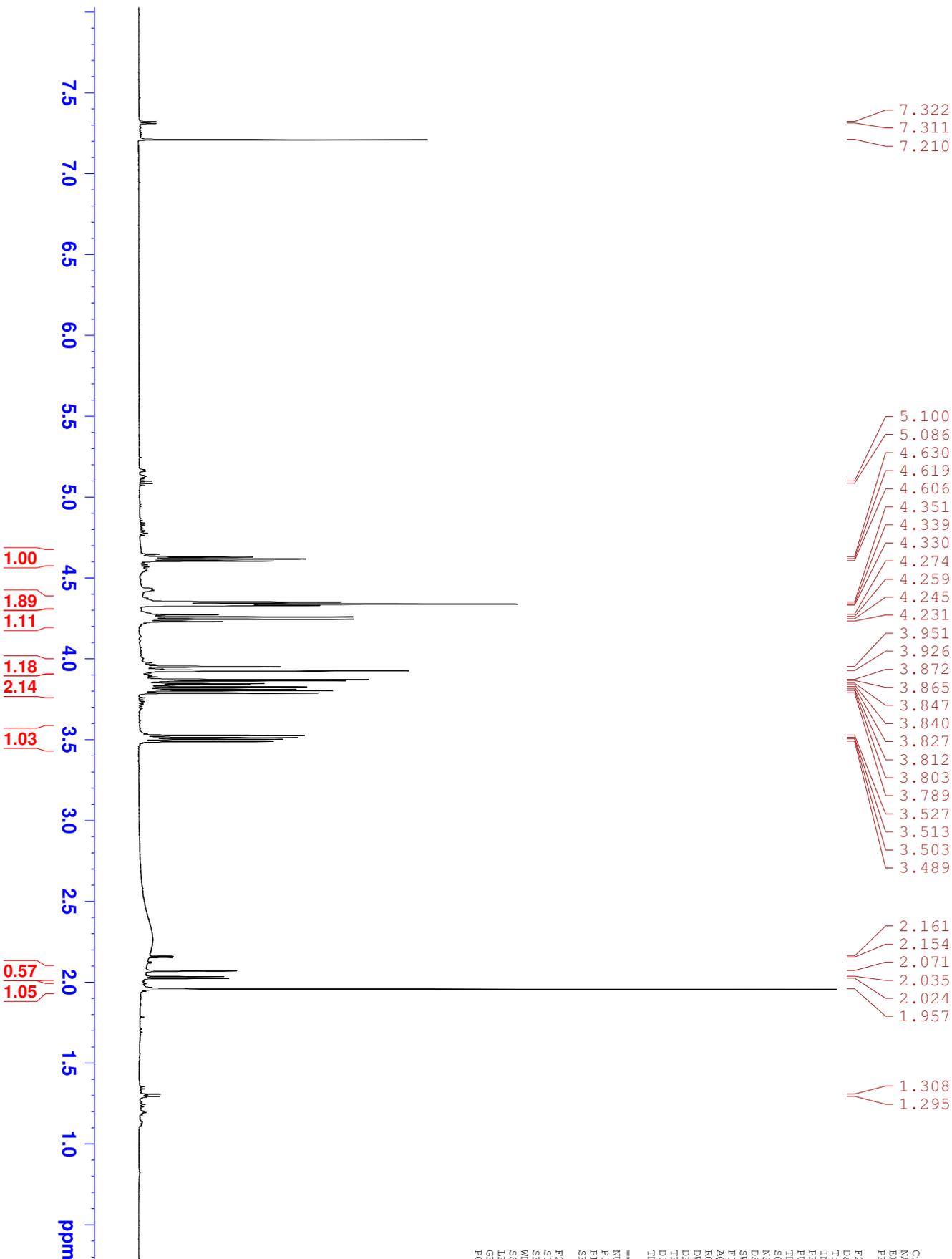


Molecular weight distribution curve



GPC graph of PEG/PEO standards





```

Current Data Parameters
NAME          DE19
EXPNO        1
PROCNO       1

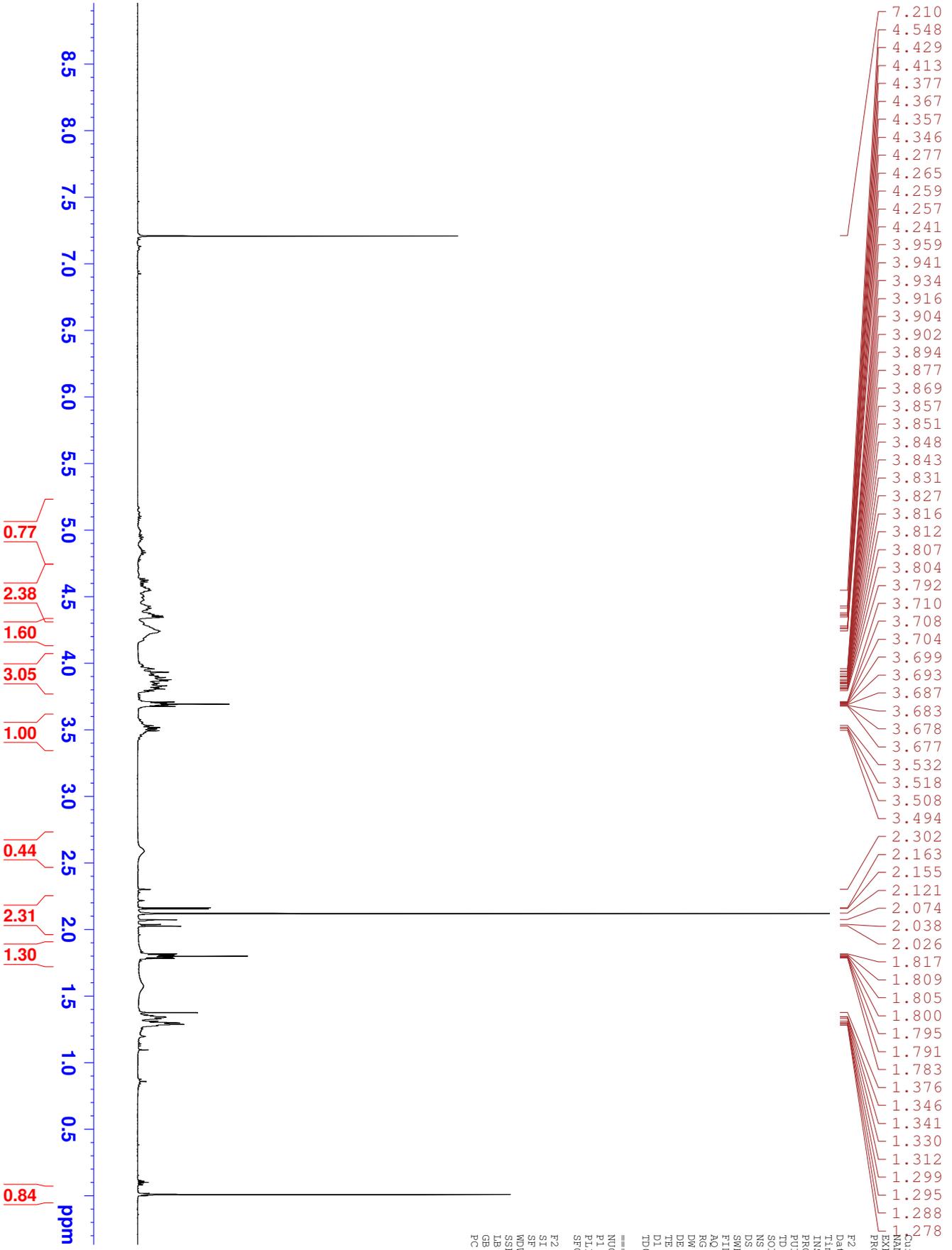
F2 - Acquisition Parameters
Date_        20180420
Time         15.51
INSTRUM     spect
PROBHD      5 mm BBO BB-1H
PULPROG     zg30
TD          65536
SOLVENT     CDCl3
NS          64
DS          0
SWH         6087.662 Hz
FIDRES     0.092890 Hz
AQ         5.3827400 sec
RG         228
DW         82.133 usec
DE         6.00 usec
TE         293.1 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1        1H
P1          14.35 usec
PL1         0.00 dB
SFO1       400.1328028 MHz

F2 - Processing parameters
SI          65536
SF         400.1300380 MHz
WDW         EM
SSB         0
GB         0.10 Hz
PC         1.00
    
```

№20 Polymerization reaction of vinyl isosorbide with butyllithium

an.poliomerisatsioon



- 7.210
- 4.548
- 4.429
- 4.413
- 4.377
- 4.367
- 4.357
- 4.346
- 4.277
- 4.265
- 4.259
- 4.257
- 4.241
- 3.959
- 3.941
- 3.934
- 3.916
- 3.904
- 3.902
- 3.894
- 3.877
- 3.869
- 3.857
- 3.851
- 3.848
- 3.843
- 3.831
- 3.827
- 3.816
- 3.812
- 3.807
- 3.804
- 3.792
- 3.710
- 3.708
- 3.704
- 3.699
- 3.693
- 3.687
- 3.683
- 3.678
- 3.677
- 3.532
- 3.518
- 3.508
- 3.494
- 2.302
- 2.163
- 2.155
- 2.121
- 2.074
- 2.038
- 2.026
- 1.817
- 1.809
- 1.805
- 1.800
- 1.795
- 1.791
- 1.783
- 1.376
- 1.346
- 1.341
- 1.330
- 1.312
- 1.299
- 1.295
- 1.288
- 1.278

- 0.77
- 2.38
- 1.60
- 3.05
- 1.00
- 0.44
- 2.31
- 1.30
- 0.84

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

```

Current Data Parameters
NAME          DE20
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20180425
Time          15.24
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            64
DS            0
SWH           6087.662 Hz
FIDRES       0.092890 Hz
AQ           5.3827400 sec
RG           228
DE           82.133 usec
TE           292.8 K
D1           2.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1            14.35 usec
PL1           0.00 dB
SFO1         400.1328028 MHz

F2 - Processing parameters
SI            65536
SF           400.1300380 MHz
WDW           EM
SSB           0
IB            0.10 Hz
GB            0
PC            1.00
    
```

Lihlitsents lõputöö reprodutseerimiseks ja lõputöö üldsusele kättesaadavaks tegemiseks

Mina (*autori nimi*) Daria Eremenko

(sünnikuupäev: 23.01.1996)

1. annan Tartu Ülikoolile tasuta loa (lihlitsentsi) enda loodud teose (*lõputöö pealkiri*),
Synthesis of monovinyl isosorbide and its polymerization

mille juhendajad on Lauri Vares ja Aleksei Bredihhin.

1.1.reprodutseerimiseks säilitamise ja üldsusele kättesaadavaks tegemise eesmärgil, sealhulgas digitaalarhiivi DSpace-is lisamise eesmärgil kuni autoriõiguse kehtivuse tähtaja lõppemiseni;

1.2.üldsusele kättesaadavaks tegemiseks Tartu Ülikooli veebikeskkonna kaudu, sealhulgas digitaalarhiivi DSpace'i kaudu alates **28.05.2018** kuni autoriõiguse kehtivuse tähtaja lõppemiseni.

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