5-2016

Synthesis of Two Monomers for Proton Exchange Membrane Fuel Cells (PEMFCs)

Abdulmajeed A. Alayyaf
East Tennessee State Universtiy

Synthesis of Two Monomers for Proton Exchange Membrane Fuel Cells (PEMFCs)

A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfilment

of the requirements for the degree

Master of Science in Chemistry

---

by

Abdulmajeed Alayyaf

May 2016

Dr. Hua Mei, Chair

Dr. Ismail Kady

Dr. Aleksey Vasiliev

Keywords: Diazonium, Proton Exchange Membrane (PEM) Fuel Cells, Nafion, Diazonium(perfluoroalkyl) arylsulfonylimide (PFSI) Monomer

ABSTRACT

Synthesis of Two Monomers for Proton Exchange Membrane Fuel Cells (PEMFCs)

by

Abdulmajeed Alayyaf

The overall goal of this research is to synthesize two different monomers for proton exchange membrane (PEM) Fuel Cells. Such monomers are proposed to be polymerized to improve the efficiency and compatibility of electrodes and electrolytes in PEM fuel cells.

The first target is to synthesize 4-diazonium-3-fluoro PFSI zwitterionic monomer. Three steps were carried out in the lab. First one was the ammonolysis of 3-fluoro-4-nitrobenzenesulfonyl chloride. Second reaction was the bromination of Nafion monomer. The next coupling reaction, between brominated Nafion monomer and the 3-fluoro-4-nitrobenzenesulfonamide, was failed. The obstacles involve the harsh reaction condition and troublesome purification procedure.

The second target is to synthesize 5-nitro-1, 3-benzenedisulfonamide. According to the literature, this synthesis was also designed as three steps: 1)nitration of sodium 1, 3-benzenedisulfonate salt; 2)chlorination of sodium 5-nitro-1, 3-benzenedisulfonate salt; and 3)ammonolysis of 5-nitro-1, 3-benzenedisulfonyl chloride. This monomer is expected to be copolymerized for membrane electrolyte in PEM fuel cells.

DEDICATION

This research work is dedicated to God Almighty, my parents, my wife, my siblings, and the department of chemistry at King Saud University.

ACKNOWLEDGEMENTS

I would like to really thank Dr. Hua Mei for her motivation and patience.

Thanks to Dr. Ismail Kady and Dr. Aleksey Vasiliev for serving as committee members.

I appreciate Drs. Reza Moheseni, Scott Kirkby, and Sandy Eagle's continuous support in the lab.

I would also like to really thank Dr. Mei's group for their help and assistance.

Finally, I would like to say a big thank you to the ETSU faculty, staff, and graduate students of the Chemistry department for their assistance and support throughout my time at ETSU.

TABLE OF CONTENTS

Page

ABSTRACT ……2

DEDICATION ……..3

ACKNOWLEDGEMENTS ……..4

Chapter

1. INTRODUCTION.....12

Preface.....12

Objectives.....12

Fuel Cells.....13

PEM Fuel Cells (PEMFCs).....14

Membrane Electrode Assembly (MEA)….....16

Polymer Electrolytes….....18

MEA Configuration.....….....20

Target Monomers…….…….…….22

4-Diazonium-3-Fluoro PFSI Zwitterionic Monomer……...……..……..…….23

5-Nitro-1, 3-Benzenedisulfonylamide Monomer……..……..……..26

2. RESEARCH AND DISCUSSION.....28

Summary……...……...…28

4-Diazonium-3-Fluoro PFSI Zwitterionic Monomer……..…28

Ammonolysis of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride 28

Bromination of Nafion Monomer 33

Coupling Reaction.....33

Debromination Reaction.....35

5-Nitro-1, 3-Benzenedisulfonylamide Monomer…….……36

Nitration of Sodium 1, 3-Benzenedisulfonate……...……36

Chlorination of Sodium 5-Nitro-1, 3-Benzenedisulfonate…..……..37

Ammonolysis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride ….……37

3. EXPERIMENTAL.....39

General Considerations.....39

NMR Spectroscopy.....39

Gas Chromatography-Mass Spectrometer.....39

Infra-red Spectroscopy.....39

Thin Layer Chromatography.....40

Glass Vacuum System.....40

Purification of Solvents and Experimental Practice.....41

Synthesis of 3-Fluoro-4-Nitrobenzenesulfonyl Amide **2** (Trial 1)……....41

Synthesis of 3-Fluoro-4-Nitrobenzenesulfonyl Amide **2** (Trial 2)……....43

Synthesis of $FSO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$ **4**….....44

Synthesis of 3-F-4-$NO_2PhSO_2N(Cs)SO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$ **5**..45

Synthesis of 3-F-4-$NO_2PhSO_2N(Cs)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$ **6**…...46

Synthesis of Sodium 5-Nitro-1, 3-Benzenedisulfonate **2'**……..…….47

Synthesis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride **3'**……...……..……48

Synthesis of 5-Nitro-1, 3-Benzenedisulfonyl Amide **4'**…..…….……48

4. CONCLUSION.....50

REFERENCES.....52

APPENDICES.....57

Appendix A1: GC-MS Chromatogram of Compound **2** (Trial 1).....57

Appendix A2: GC-MS Chromatogram of Compound **2** (Trial 2).....58

Appendix B1: ^{19}F NMR Spectrum of Compound **2** (Trial 1), 400MHZ, CD_3CN.....59

Appendix B2: ^{19}F NMR Spectrum of Compound **2** (Trial 2), 400MHZ, CD_3CN.....60

Appendix B3: ^{19}F NMR Spectrum of Compound **2** (Trial 2) After Column, 400MHZ,CD_3CN…….……..……..61

Appendix B4: ^{19}F NMR Spectrum of Compound **4**, 400MHZ, CD_3CN.....62

Appendix B5: Expanded ^{19}F NMR Spectrum of Compound **4**, 400MHZ, CD_3CN….....63

Appendix B6: ^{19}F NMR Spectrum of Compound **5**, 400MHZ, CD_3CN.....64

Appendix C1: ^{1}H NMR Spectrum of Compound **2** (Trial 1), 400MHZ, CD_3CN.....65

Appendix C2: Expanded ^{1}H NMR Spectrum of Compound **2** (Trial 1), 400MHZ, CD_3CN.66

Appendix C3: ^{1}H NMR Spectrum of Compound **2** (Trial 1) After Recrystallization, 400MHZ, CD_3CN.....67

Appendix C4: ^{1}H NMR Spectrum of Compound **2** (Trial 2), 400MHZ, CD_3CN.....68

Appendix C5: Expanded ^{1}H NMR Spectrum of Compound **2** (Trial 2), 400MHZ, CD_3CN.69

Appendix C6: ^{1}H NMR Spectrum of Compound **5**, 400MHZ, CD_3CN.....70

Appendix C7: ^{1}H NMR Spectrum of Compound **2'**, 400MHZ, D_2O.....71

Appendix C8: ^{1}H NMR Spectrum of Compound **3'**, 400MHZ, Acetone-d_6.....72

Appendix C9: ^{1}H NMR Spectrum of Compound **4'**, 400MHZ, Acetone-d_6.....73

Appendix D1: ^{13}C NMR Spectrum of Compound **2'**.....74

Appendix D2: ^{13}C NMR Spectrum of Compound **4'**.....75

Appendix E1: FTIR Spectrum of Compound **2** (Trial 1).....76

Appendix E2: FTIR Spectrum of Compound **2** (Trial 2).....77

Appendix E3: FTIR Spectrum of Compound **2'**.....78

Appendix E4: FTIR Spectrum of Compound **3'**.....79

Appendix E5: FTIR Spectrum of Compound **4'**.....80

VITA.....81

LIST OF FIGURES

Figure Page

1. 3-Fluoro-4-Diazonium Perfluoroalkyl Benzenesulfonylimide Monomer (I) and 5-Nitro -1, 3-Benzenedisulfonylamide Monomer (II) Structures……13

2. Proton Exchange Membrane Fuel Cell……16

3. Expanded MEA Structure at the Cathode Side……17

4. Overview Diagram of MEA Structure……18

5. Chemical Structure of Nafion® Polymers……19

6. Dense Carbon Electrode in PEM Fuel Cells……21

7. Proposed MEA in PEM Fuel Cells……22

8. Example of the Amino Acid at the Isoelectric Point……23

9. 4-Diazonium-3-Fluoro PFSI Monomers Structure ……24

10. The Hydrolysis Impurity from the Ammonolysis of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride……29

11. Possible Intermediate of the Solvolysis Reaction of 2-Fluoro-4-Nitroaromatics……31

12. X-ray Structure of 3-Fluoro-4-Nitrobenezenesulfonyl Amide 1st Trial……32

13. The Brominated Nafion Monomer Hydrolysis Impurity from Coupling Reaction……33

14. Ammonolysis Half Reaction Side Product……38

15. The Line Diagram of a Dual-manifolds Glass Vacuum Line……40

LIST OF SCHEMES

Scheme Page

1. The Reactions Occurred at PEM Fuel Cells……...15

2. Resonance Structure of PFSI Compounds' Conjugate Base (Rf=C_4F_9)……20

3. Grafting of Diazonium PFSI Compound on the Carbon Electrode (X= $CF_3SO_2N^-SO_2$)...22

4. The Overall Synthesis Scheme of 4-Diazonium-3-Fluoro PFSI Monomer…….....….25

5. The Overall Synthesis Scheme of 5-Nitro-1, 3-Benzenedisulfonylamide Monomer…....26

6. Copolymerization of 5-Nitro-1, 3-Benzenedisulfonylamide Monomer……...……..27

7. Ammonolysis reaction of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride…..……29

8. Ammolysis and Solvolysis of the 3-Fluoro-4-Nitrobenzenesulfonyl Chloride…….……31

9. Bromination Reaction of Nafion® Monomer……..…..…...…….33

10. Coupling Reaction of 3-Fluoro-4-Nitrobenzenesulfonyl Amide and Brominated Nafion Monomer…….……...34

11. Debromination Reaction of 3-Fluoro-4-Nitrobenzenesulfonyl Amide and Brominated Nafion Monomer……...……..……...35

12. Nitration of Sodium 1, 3-Benzenedisulfonate…….……..36

13. Chlorination of Sodium 5-Nitro-1, 3-Benzenedisulfonate……37

14. Ammonolysis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride……..38

LIST OF ABBREVATIONS

AFC	Alkaline Fuel Cell
DMF	Dimethylformamide
DMFC	Direct Methanol Fuel Cell
EW	Equivalent weight
FDZ	Functional Diazonium Zwitterion
FTIR	Fourier Transform Infra Red
GDL	Gas Diffusion Layer
Hz	Hertz
IEC	Ion Exchange Capacity
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
NMR	Nuclear Magnetic Resonance
PAFC	Phosphonic Acid Fuel Cell
PEM	Polymer Electrolyte Membrane
PFSA	Perflurosulfonic acid
PFSI	Perflurosulfonylimide
ppm	Parts per million
TPB	Triple-phase boundary
PTFE	Polytetrafluorethylene
SOFC	Solid Oxide Fuel Cell
TMS	Tetramethylsilane
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

Preface

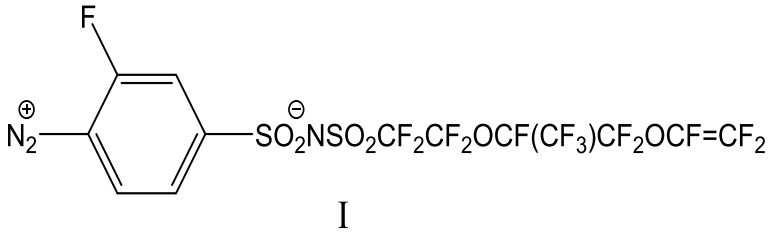
In my thesis, the attempts to prepare two functional monomers for PEMFC (Polymer Electrolyte Membrane Fuel Cell) will be discussed. The first one is 3-fluoro-4-diazonium perfluoroalkyl benzenesulfonylimide monomer, which originally comes from 3-fluoro-4-nitrobenezenesulfonyl amide and Nafion® monomer. The second one is 5-nitro-1, 3-benzenedisulfonylamide, which is prepared from sodium 1, 3-benzenedisulfonate. These two monomers are anticipated to be further polymerized for PEM fuel cells.

In this introduction, the background of the projects and why it is necessary to prepare such monomers will be discussed. The objectives of this research are first lay out. And then, the concepts and categories of fuel cells are described. Details of PEM fuel cells, including the basic structure, how they worked, and Membrane Electrode Assembly (MEA) modification plans are elaborated. Last, the two target monomers are introduced and the initiate ideas to design such monomers are explained.

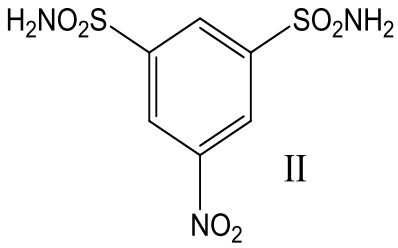
Objectives

The research objective is to synthesize two monomers (I) and (II), which could be further polymerized and grafted onto the electrode as the electrolytes in PEM fuel cell. The diazonium moiety in these monomers is expected to make the covalent grafting of the PFSI compounds with the carbon electrodes. The grafted PFSI polymers are proposed to replace the Nafion® as

electrolytes for PEM fuel cells because of their better thermal and mechanical stability compared to PFSA polymers [1, 2].



I



II

Figure 1: 3-Fluoro-4-Diazonium Perfluoroalkyl Benzenesulfonylimide Monomer (I) and 5-Nitro-1, 3-Benzenedisulfonylamide Monomer (II) Structures.

Fuel Cells

A fuel cell is an electro-chemical energy conversion device that produces electricity from a chemical reaction between an oxidant and a fuel. The byproducts produced from fuel cells are including heat, gases (CO_2 & CO), and water vapor [3-5]. Fuel cells work like batteries. However, the biggest difference is that fuel cells do not have to be charged provided the fuel is continuously supplied. With electrochemical reaction, the fuel cells generate energy in the form of heat and electricity, both of which can be utilized [6, 7]. Basically, fuel cells are alternative energy sources to fossil fuels with a comparatively good efficiency [3]. The fuel cells applications can be categorized into the following: portable power generation, stationary power generation, and power for transportation [8, 9].

Various types of fuel cells are used for different purposes, depending on the components, operating temperature, and the source of fuel supplied [10]. In summary, they are phosphoric acid fuel cell (PAFC), solid oxide fuel cell (SOFC), direct methanol fuel cell (DMFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and polymer electrolyte membrane fuel cell

(PEMFC). Table 1 gives a brief comparison of different types of fuel cells in operating temperature, fuel, mobile ion, and applications [11, 12].

Table 1: Types of Fuel Cells [9, 12, 13].

Fuel Cell Type	Operating Temperature [^{o}C]	Fuel	Mobile Ion	Applications
Polymer Electrolyte (PEMFC)	30-100	Hydrogen	H^+	Motive Small Utility Portable
Alkaline (AFC)	50 -200	Hydrogen	OH^-	Aerospace
Direct methanol (DMFC)	50–120 °C	Methanol	H^+	Utility Portable
Molten Carbonate (MCFC)	~650	Hydrogen	CO_3^{2-}	Utility
Phosphoric Acid (PAFC)	~220	Hydrogen	H^+	Small Utility
Solid Oxide (SOFC)	500 – 1000	Hydrogen Carbon monoxide	O^{2-}	Utility

Most of fuel cells are operated at high temperatures except PEM fuel cells and DMFCs. While PEM fuel cells use hydrogen gas, the DMFCs utilize liquid methanol as fuel [3, 7]. Compare to DMFC, PEM fuel cells are more environmental friendly since only water is produced from the chemical reaction.

PEM Fuel Cells

The PEM fuel cells were advanced for space exploration by NASA in the United States in the 1960s. In 1970, General Electric continued the work on PEM fuel cells for the US Navy [9, 14]. Since then, the technology related PEM fuel cells has been dramatically developed for different applications.

It is generally known that hydrogen and oxygen gases are the fuels of PEM fuel cells. Compare with other kinds of fuel cells, PEM fuel cells have many advantages, such as tight packing, lower operation temperature, and low waste emission. Moreover, they are the most versatile, produce the most power for a given weight or volume, lightweight, having high power density, and cold start capability. For example, the PEM fuel cells provide 40-60 % of electrical efficiency at 80 ^{o}C, compared to around 60 % electrical efficiency with solid oxide fuel cells at around 1000 ^{o}C. [3, 15-17]. More importantly, as a clear energy source, PEM fuel cells produce negligible amounts of CO_2 and no CO, HC, and NO_x [18, 19]. However, PEM fuel cells can be contaminated with small amounts of NO_x, SO_2, NH_3, H_2S, CO, CO_2. Additionally, there are some obstacles for commercialization of PEM fuel cells, such as expensive components (electrolyte & catalyst) and hydrogen gas storage [16, 20].

Basically, the PEM fuel cells consist of two basic components, gas-feeding channel and membrane electrode assembly (MEA). As figure 2 depicts, the fuel gases are transported inside the cell from the gas-feeding channel by pressure. At the anode, the hydrogen is oxidized at the surface of the catalyst layer to generate electrons and protons. The electrons are transported out of the anode to produce electricity through an external circuit before re-entering the cathode. Meanwhile, the protons pass through the polymer electrolyte membrane from the anode to the cathode, where they combined with electrons, and oxygen to produce water. The combination of the two half-cell reactions gives the overall reaction, which is shown as scheme 1 [21].

1- Anode: $2H_2 \longrightarrow 4H^+ + 4e^-$

2- Cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

3- Overall equation: $2H_2 + O_2 \longrightarrow 2H_2O$

Scheme 1: The Reactions Occurred at PEM Fuel Cells.

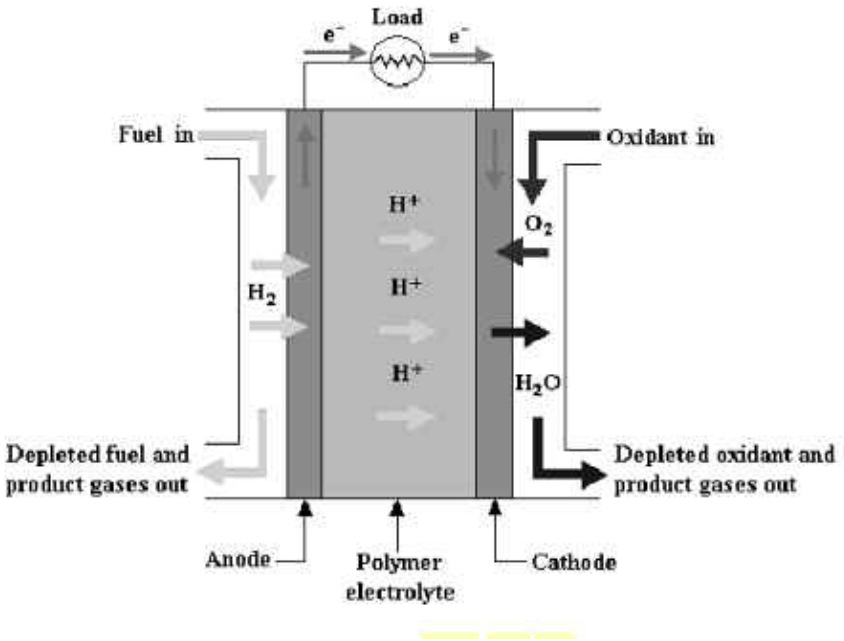


Figure 2: Proton Exchange Membrane Fuel Cell. Used with Permission [22].

Membrane Electrode Assembly (MEA)

As the heart of the fuel cells, MEA is made up of membrane electrolyte, the gas diffusion layer (GDL), and the catalyst layer (Figure 3)[9, 23]. In MEA, protons are transferred from the membrane to the catalyst layer. Also, the electrons reach the catalyst from the electrical circuit through GDL. And then, the reactant and product gases are shuttled between the catalyst layer and gas channels. The reactions occur in the triple phase boundary (TPB) of catalyst layer. The three phases are referred as protons, electrons, and gases. The TPB is the contact region between different phases [3, 14].

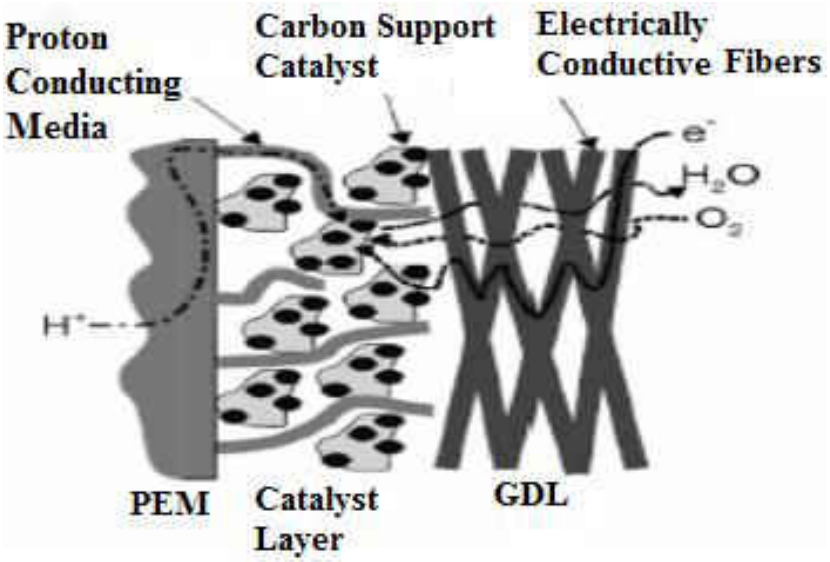


Figure 3: Expanded MEA Structure at the Cathode Side. Used with Permission [14].

In MEA, the catalyst layer is made of platinum nanoparticles and carbon material. The platinum nanoparticles are coated onto the porous carbon layer. Inside the pores of carbon layer, the electrolyte is fabricated to connect the protons to the platinum particles. Since the electrochemical oxidation and reduction reactions take place at the TPB interface of catalyst layer, it is critical to maintain the hydrophobic/ hydrophilic balance within it. Too much hydrophilic electrolyte results in the accumulation of water, which hinders the gases from getting to the TPB. But the extremely hydrophobic catalyst layer won't let protons reach to the TPB neither. So, the properties of TPB interface have the important impact on the catalyst performance [1, 24, 25].

In the GDL, the porous carbon is coated with hydrophobic polytetrafluoroethylene (PTFE), which allows gases to diffuse through the pores to the catalyst layer (Figure 4). If the carbon pores is congested with water, the gases will also have trouble to reach TPB. [26].

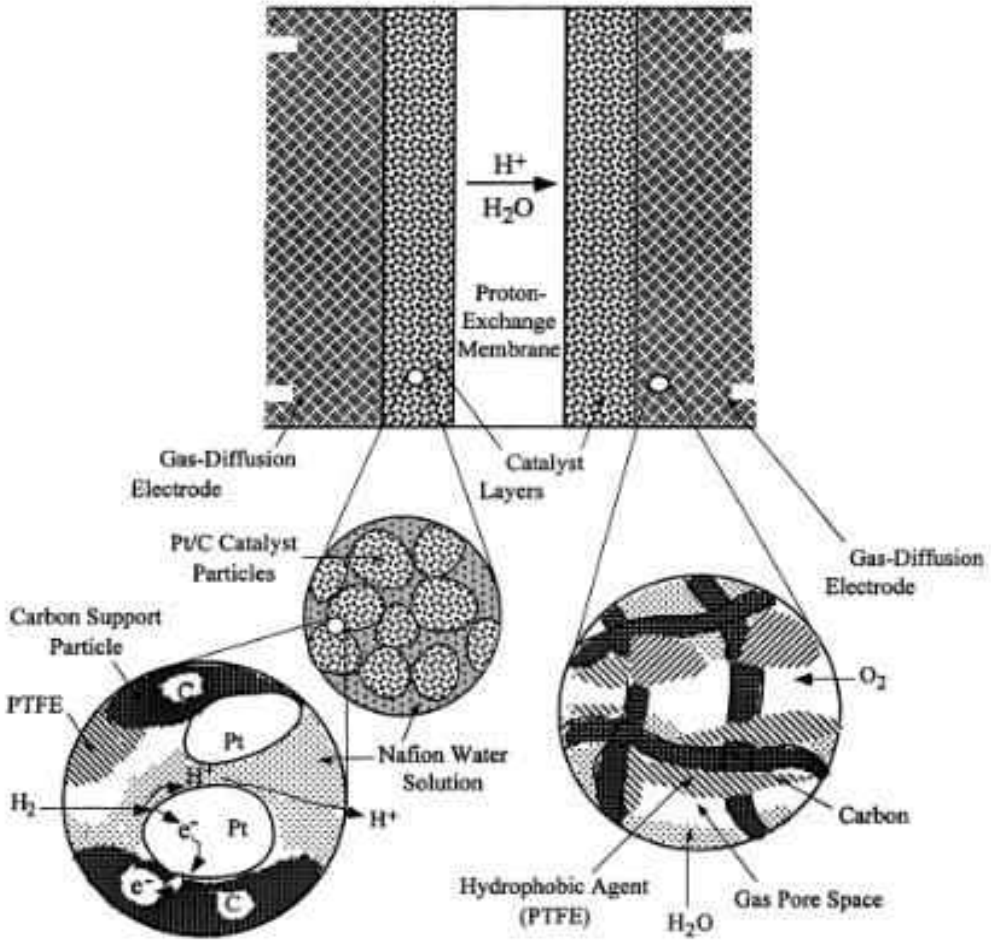


Figure 4: Overview Diagram of MEA Structure. Used with Permission [27].

Polymer Electrolytes

Another important component of MEA is the polymer membrane electrolyte. The most commonly used membrane electrolyte for PEM fuel cells are polyperfluorosulfonic acid (PFSA) polymers, such as Nafion® polymers [28]. The PFSA polymers in general present good chemical, thermal, and mechanical stabilities at low temperature [29, 30]. However, there are some disadvantages related to PFSA polymers, such as low protonic conductivity with a limited amount of water, high cost, and not stable at high temperatures. For example, at high

temperature, the sulfonic acid groups dehydrate to anhydrides ($-SO_2OSO_2-$). Thus, the loss of active sulfonic acid group of polymer electrolyte suffers the protonic conductivity [31-34].

Among the PFSA polymers, Nafion® polymers are the one well studied and commercialized electrolytes for PEM fuel cells applications. Nafion® polymers have high conductivity (>0.1 S cm^{-1} at high temperature), low dielectric constants, inertness toward chemical attacking, insolubility in alcohol & water, and good insulating ability in oxidation and reduction [35-38].

As shown in Figure 5, Nafion® polymers are random copolymers, which are prepared from Nafion monomer, perfluoro(4-methyl-3, 6-dioxaoct-7-ene)-sulfonic acid and tetrafluoroethylene (TFE) [28].

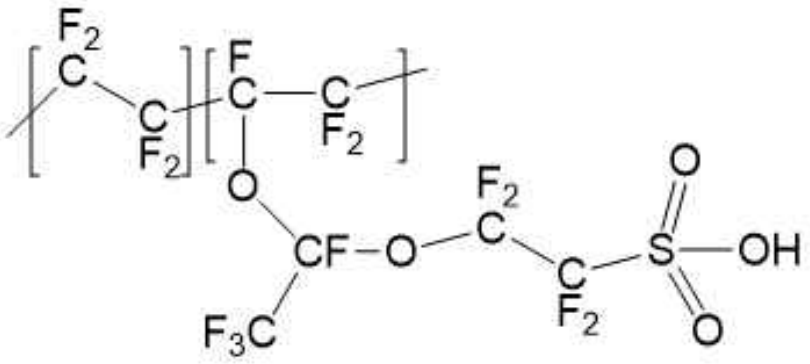
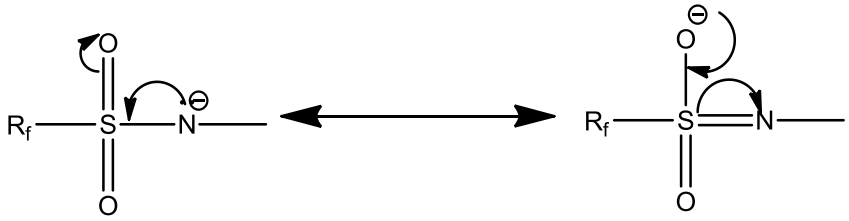


Figure 5: Chemical Structure of Nafion® Polymers.

In this project, the PFSI polymers are proposed to replace the traditional used PFSA polymers. Compared to PFSA polymers, the PFSI polymers not only can provide better protonic conductivity but also it can be more stable under high temperatures. For example, it is less susceptible to oxidative degradation and dehydration than fluorosufonic acid compounds at high temperature [39, 40]. It was reported that the PFSI compounds $(RfSO_2)_2NH$ were first prepared in the 1980s. Later, Zhang et al. established relative gas-phase acidities (GA) for a series of

Bronested strong acids, such as $(C_4F_9SO_2)_2NH$ at GA = 284.1-278.6 kcal/mol. The acidity of PFSIs are greater than the traditional mineral acids. For example, $(CF_3SO_2)_2NH$ has a pKa value = 7.8 in acetic acid compared with pKa value = 10.2 of HNO_3 in the same condition. The super acidity of such compounds comes from three basic factors. First one is the presence of the strong electron-withdrawing perfluoroalkyl group in the structure. Second, the polarizability effect which stabilizes the negative charge [41-43]. Third, the resonance stabilization of the conjugate bases of PFSI compounds, as shown in Scheme 2. Therefore, these factors all contribute to the strong acidity of PFSI compounds, which turns out to be high proton conductivity.



Scheme 2: Resonance Structure of PFSI Compounds' Conjugate Base (Rf=C_4F_9) [16].

MEA Configuration

The traditional MEA is made up from physically mixing PFSA polymers, metal catalysts and the carbon materials (Figure 6). There are several problems related such MEA configuration. First, the catalyst efficiency is only about 10-20% [28, 44]. The reason is that poor integration of interfaces of electrode/electrolyte. Second, PFSA polymers tend to form the large "rod-shaped" micelles inside the porous carbon. These micelles will be washed out overtime, which sacrifice proton conductivity of electrolytes. Therefore, it is necessary to investigate the three-phase interface for MEA configuration [16, 25, 45, 46].

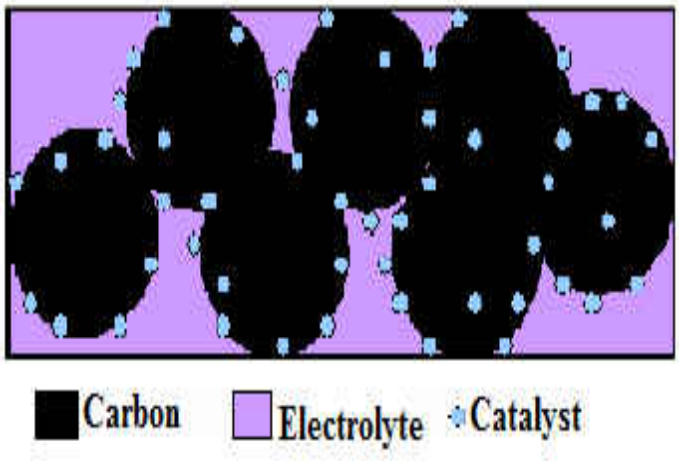
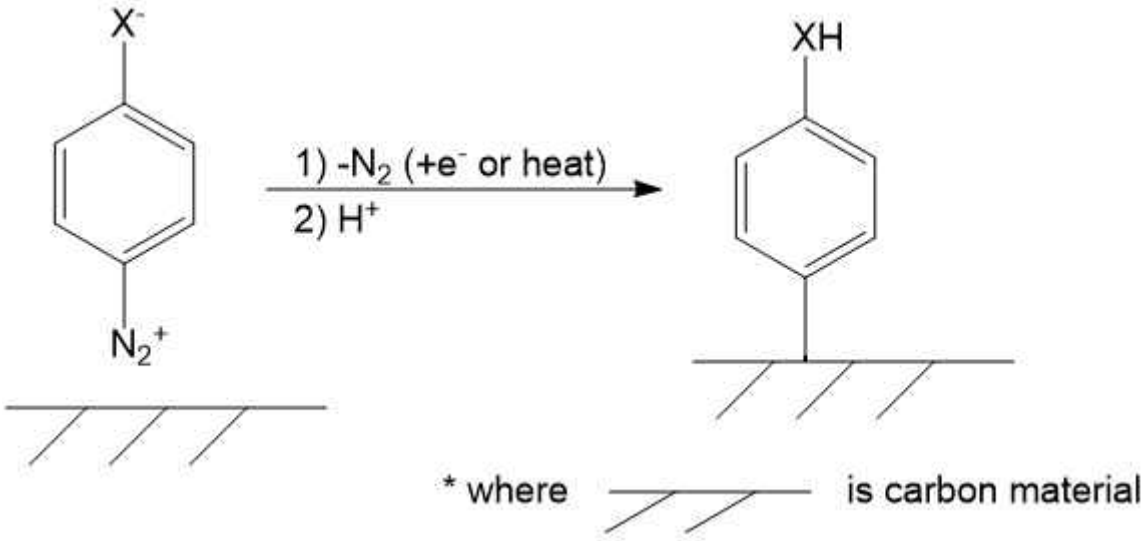


Figure 6: Dense Carbon Electrode in PEM Fuel Cells. Used with Permission [31].

The MEA structure, as illustrated in Figure 7, is proposed as a new configuration of MEA. The key of such configuration is to chemically graft PFSI polymers onto the carbon support. The diazonium chemistry is employed to form covalent bond between the carbon and PFSI compounds after losing the nitrogen gas [47]. Scheme 3 shows the one example of grafting of a simple functional diazonium PFSI zwitterions compound ($p\text{-}N_2^+PhSO_2N^-SO_2CF_3$) on the carbon electrode via the electronic or thermal reactions [48]. The new MEA structure is supposed to lower the amount of expensive electrolyte, increase the catalyst efficiency via the chemical connection between the thin carbon layer and the electrolyte and finally enhance the TBR sites [49-51].



Scheme 3: Grafting of Diazonium PFSI Compound on the Carbon Electrode (X= $CF_3SO_2N^-SO_2$) [16].

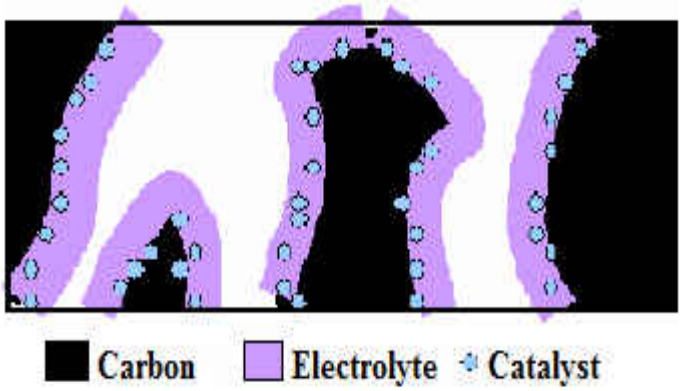


Figure 7: Proposed MEA in PEM Fuel Cells. Used with Permission [31].

Target Monomers

Therefore, the proposed target monomers contain at least three parts: the aromatic diazonium zwitterionic moiety, the polymerizable functional unit, such as perfluorovinyl ether, and the PFSI pendant [51]. The reasons for introduction of PFSI pendant to the target monomers are already elaborated as above described advantages of PFSI compounds. Besides, the monomers need to

be further polymerized before or after chemical attaching on to the carbon electrode via diazonium group. But the diazonium compounds are usually not stable at room temperature. So, the purpose to involve the zwitterionic structure for the target monomers is to stabilize the highly reactive diazonium moiety in monomers.

Zwitterions were first defined as neutral compounds that have both positive and negative ionic groups in the isoelectric point in 1943. One of zwitterionic inner salt examples is the amino acids at the isoelectric point (Figure 8). In zwitterionic compounds, the dipolar groups (semi-polar) with a significant charge are unattached between bonded atoms. These atoms can be described as one orbital filled and another orbital unfilled. Therefore, the atoms become distorted by the separate charges that are sometimes conjugated. The interactions minimize the polarity of semi-polar groups more than pure dipolar form. It is reported that generally the zwitterionic molecules display better stability than the non-zwitterionic salts [52, 53].

Figure 8: Example of the Amino Acid at the Isoelectric Point.

4-Diazonium-3-Fluoro PFSI Zwitterionic Monomer

The first target is to synthesis one analogue of diazonium PFSI monomers from Nafion monomer, which contains one fluorine atom in the aromatic ring. Such monomer's structure is shown in the Figure 9.

Two analogues diazonium PFSI monomers have already been previously prepared in our lab from Nafion monomer [58]. The purpose of introducing fluorine atom on the aromatic ring is of

twofold: First, the presence of fluorine on the aromatic ring provides a strong electron withdrawing inductive effect. Second, fluorine also has a donate resonance effect. Compared to the trifluoromethyl substituted benzene ring, which only has electron withdrawing effect, the target monomer, with the fluorine substituted benzene ring, is anticipated to have the differences in synthesis and reactivity [54].

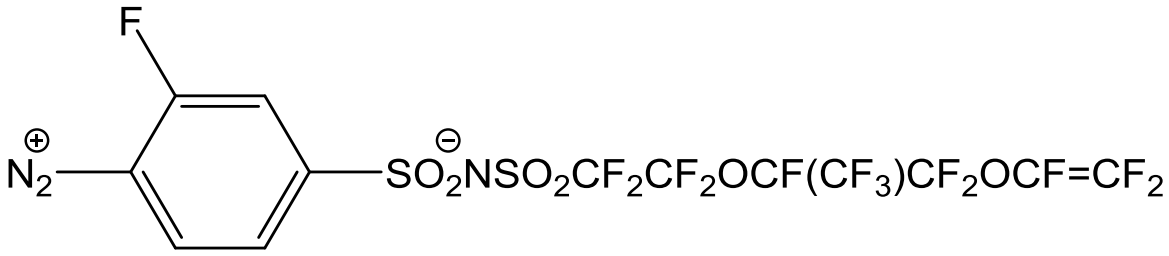
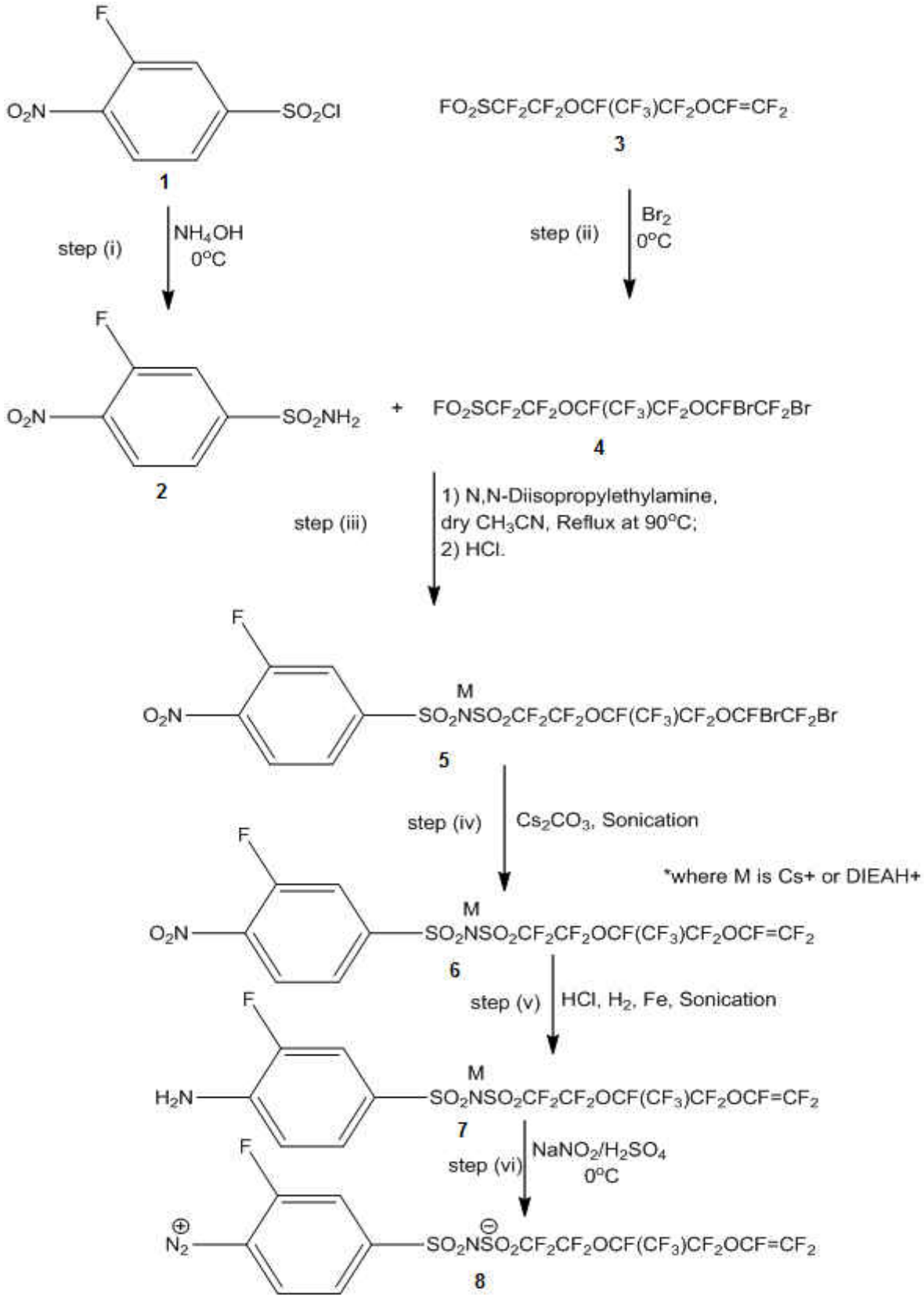


Figure 9: 4-Diazonium-3-Fluoro PFSI Monomers Structure.

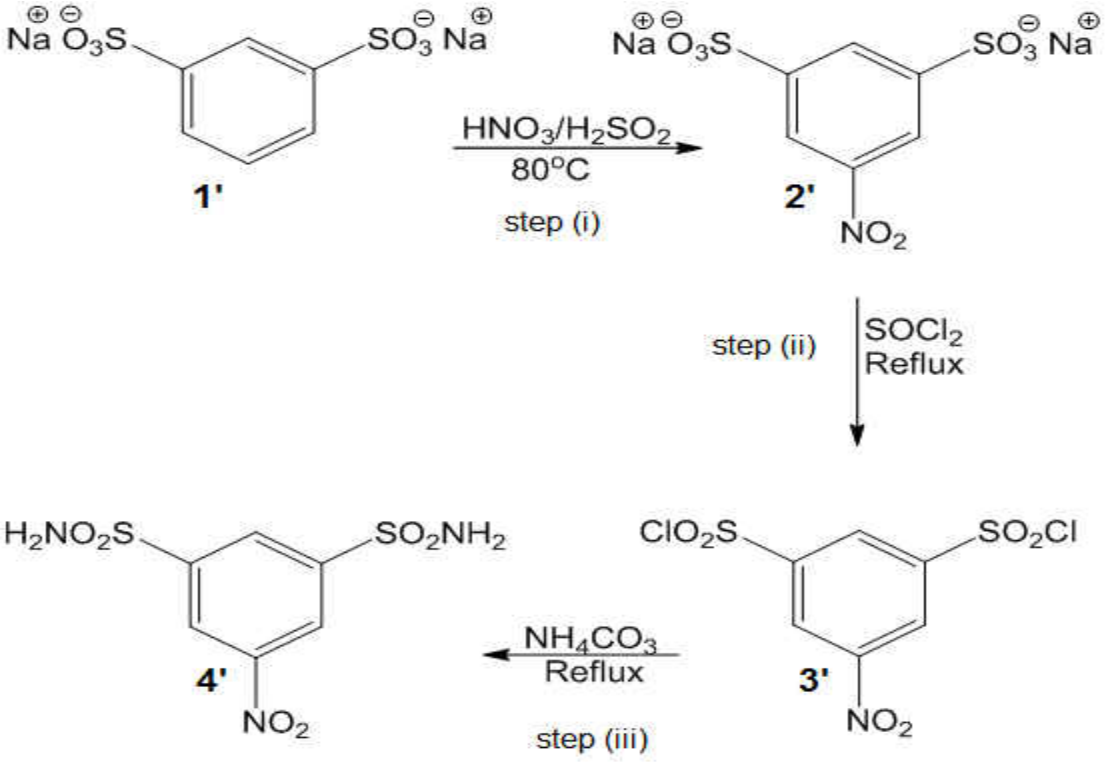
The proposed synthetic route of 4-diazonium-3-fluoro PFSI zwitterionic monomer is shown in Scheme 4 and it involves six steps: 1) ammonolysis of 4-nitro-3-fluorbenzenesulfonyl chloride, 2) bromination of Nafion® monomer, 3) coupling reaction between 3-fluoro-4-nitrobenezenesulfonyl amide and brominated Nafion® monomer, 4) debromination of 4-NO_2-3-F-$PhSO_2N(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$, 5) reduction of 4-$NO_2$-3-F-$PhSO_2N(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$, and 6) diazotization of 4-NH_2-3-F-$PhSO_2N(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$.



Scheme 4: The Overall Synthesis Scheme of 4-Diazonium-3-Fluoro PFSI Monomer.

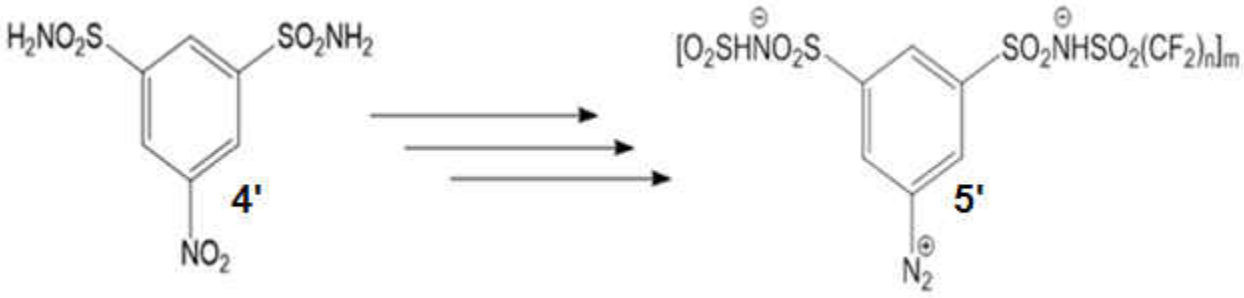
5-Nitro-1, 3-Benzenedisulfonylamide Monomer

Another target monomer is 5-nitro-1, 3-benzenedisulfonylamide **4'**, which was synthesized through a three-step procedure (Scheme 5). According to literature [55], the synthesis of 5-nitro-1, 3-benzenedisulfonylamide can be achieved first by nitration of disodium 1, 3-benzenedisulfonate, then chlorination of sodium 5-nitro-1, 3-benzenedisulfonate, followed by ammonolysis of 5-nitro-1, 3-benzenedisulfonyl chloride. The overall synthesis is shown in Scheme 5.



Scheme 5: The Overall Synthesis Scheme of 5-Nitro-1, 3-Benzenedisulfonylamide Monomer.

Such monomer is expected to make a cross-linked copolymer (**5'** in Scheme 6) with perfluoroalkyl disulfonyl fluoride monomers. The nitro group in **4'** is to be converted into diazonium moiety, prior to grafting onto carbon electrode for use in PEM fuel cells.



Scheme 6: Copolymerization of 5-Nitro-1, 3-Benzenedisulfonylamide Monomer.

CHAPTER 2

RESEARCH AND DISCUSSION

Summary

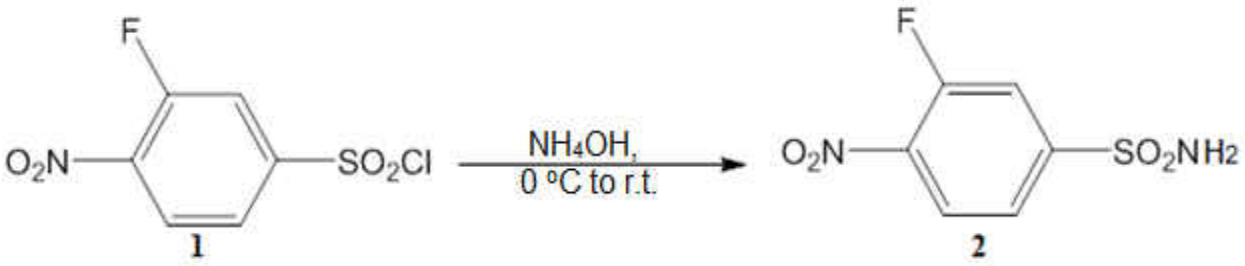
The two target PEM fuel cells monomers, 4-diazonium-3-fluoro PFSI zwitterionic monomer and 5-nitro-1, 3-benzenedisulfonylamide, were successfully synthesized and characterized. The following is a discussion of the synthesis strategies of these monomers.

4-Diazonium-3-Fluoro PFSI Zwitterionic Monomer

The diazonium PFSI monomer is prepared from two readily available starting materials, 3-fluoro-4-nitrobenezenesulfonyl amide and nafion monomer. This original synthesis plan involves six steps: Ammonolysis, bromination, coupling, debromination, reduction, and diazotation. However, this synthetic approach was abandoned because all attempts to purify the coupling product were not successful.

Ammonolysis of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride

3-Fluoro-4-nitrobenezenesulfonyl amide **2**, which is one of starting materials for the later coupling reaction, was synthesized by ammonolysis of 3-fluoro-4-nitrobenzenesulfonyl chloride **1**. Ammonolysis, an S_N2 reaction, is expected to be faster and more feasible than hydrolysis reaction due to the fact that NH_3 is a stronger nucleophile than H_2O. The side product of the ammonolysis reaction is NH_4Cl salt, which can be removed from the product upon washing with water [51, 56]. The reaction scheme is shown in Scheme 7 as bellow.



1 2

Scheme 7: Ammonolysis of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride.

Surprisingly, the hydrolysis impurity cannot be removed by filtration from water. The typical hydrolysis impurity as showed in Figure 10, aromatic sulfonate salts, usually can be removed from the water filtration due to the good solubility in water. However, the anticipated product 3-fluoro-4-nitrobenzenesulfonyl amide **2,** not like other aromatic sulfonyl amide, is slightly soluble in water as well. Thus, recrystallization is used to remove the hydrolysis impurities and other side products.

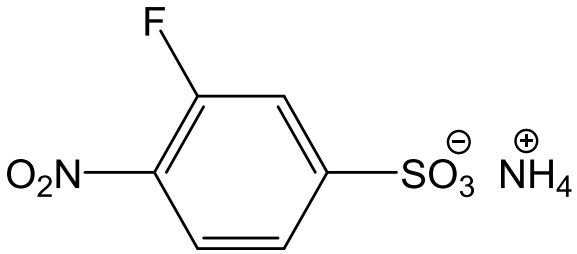


Figure 10: The Hydrolysis Impurity from the Ammonolysis of 3-Fluoro-4-Nitrobenzenesulfonyl Chloride.

Indeed, more than 10 trials are carried out for ammonolysis reaction. Among them, only two trials offer the possible desired product after purification. Results from these two trials are summarized in Table 2.

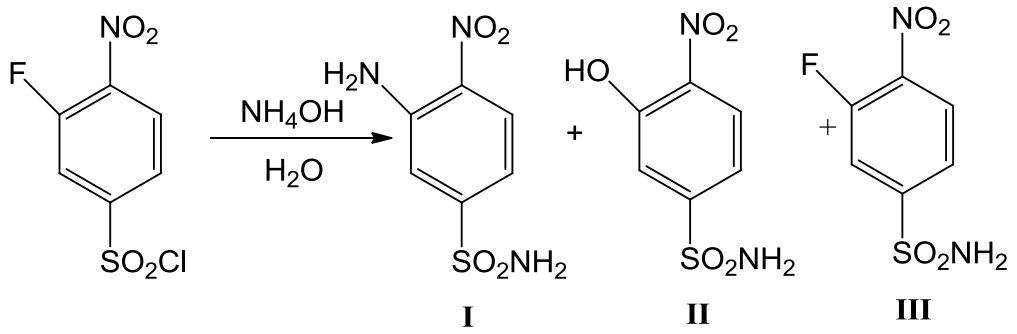
Table 2: Comparison of Ammonolysis Procedure and Products.

Entry	1st Trial	2nd Trial
Reactants	Ratio of sulfonyl chloride: ammonia = 1:23	Ratio of sulfonyl chloride: ammonia = 1:1.45
M.P.	205.9-206.3°C	132.8-133.4°C
Solubility (water)	Slightly soluble	Not soluble
^{19}F NMR	Singlet peak at -115.49 ppm	Singlet peak at -115.62 ppm
^{1}H NMR	δ_A 8.17 (1H, d), δ_B 7.52 (1H, s), δ_C 7.03 (1H, d), δ_D 6.48 (2H, s).	δ_A 8.26 (1H, t), δ_{B+C} 7.88 (2H, m), δ_D 6.72 (2H, s).
GC-MS	m/z: 220(M^+, 20%), 156, 140, 94, 64, 50.	m/z: 220(M^+, 20%), 156, 140, 94, 64, 50.
FTIR	3352.28w and 3263.56w (NH_2) stretch, 1606.7m (NH_2) bend	3358.07w and 3265.49w (NH_2) stretch, 1606.7m (NH_2) bend

According to the fluorine NMR spectra, the chemical shifts of products from both entries are not the same as the reactant, at -117.5 ppm. The FT-IR was further used to characterize the product. As shown in table 2, both IR spectra indicated successful functional group conversion from sulfonyl chloride to sulfonyl amide. Moreover, gas chromatograph (GC) showed only one peak for both entries with the molar mass of desired product. This indicates that the target products are obtained from both entries, 1 and 2.

However, entry 1 involved a tedious purification process because, surprisingly, both product and the hydrolysis impurity are soluble in water. Compare to entry 2, the product from entry 1 has a higher melting point. The reason is that the entry 1 product is obtained with a side product.

According to a report by Ji and coworkers [57], aromatic nucleophilic substitution may occur besides the desired S_N^2 ammonolysis reaction (Scheme 8).



Scheme 8: Ammolysis and Solvolysis of the 3-Fluoro-4-Nitrobenzenesulfonyl Chloride [58].

The nucleophilic aromatic substitution side reaction is attributed to its low activation energy due to the possibility of intermolecular hydrogen bonding between the ortho- amino (or hydroxy) group and the nitro substituent (Figure 11) [58]. The fact that the side products I & II have the same solubility properties as the desired product III made complicated the separation attempts. For that reason all purification attempts by chromatography and recrystallization were not satisfactory, recrystallization provided only limited amount of pure product. X-ray crystallography confirmed the structure of desired product, as shown in Figure 12.

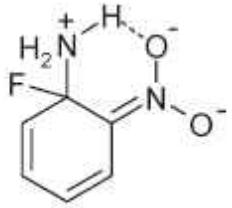


Figure 11: Possible Intermediate of the Solvolysis Reaction of 2-Fluoro-4-Nitroaromatics [58].

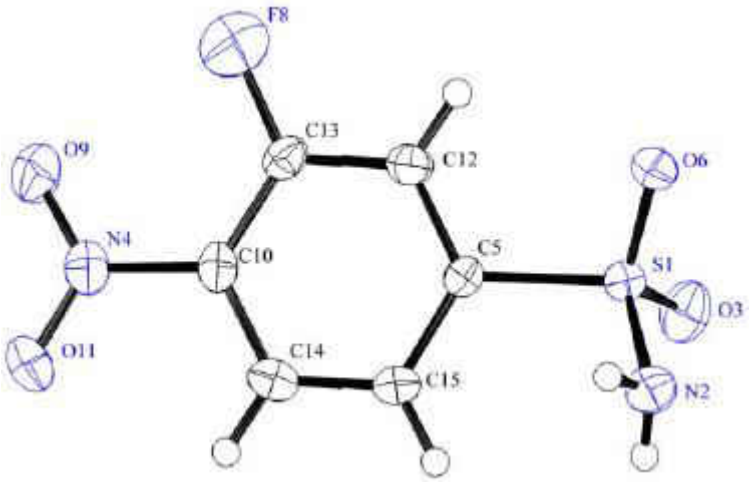


Figure 12: X-ray Structure of 3-Fluoro-4-Nitrobenezenesulfonyl Amide 1st Trial.

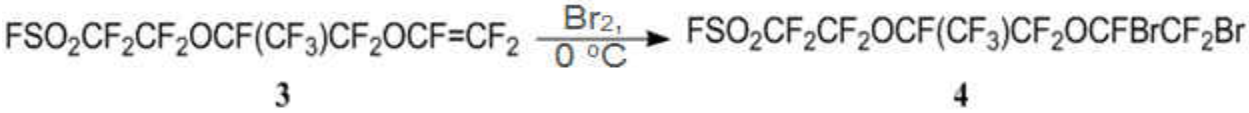
On the other hand, the product isolated from entry 2 shows a different ^{1}H-NMR spectrum, which is similar to the literature results [59]. However, X-ray chrystallography of this product was not successful.

Meanwhile, column chromatography was carried out to remove the starting material, aromatic sulfonyl amide, in entry 2. The TLC revealed two spots with R_f values of 0.32 (product) and 0.62 (starting material), in hexane: ethyl acetate (1:1). Unfortunatedly, none of the fractions collected from the column chromatography contains fluorine, according to the fluorine NMR spectroscopy. Further identification of these fractions was not attempted.

In summary, the preparation of ammonlysis product proved to be troublesome because of the tedious and unsuccessful purification procedure. The ammonlysis products from both entries, 1 and 2 needs to be further studied to minimize the formation of impurities. To overcome this problem, 3-fluoro-4-(N-acetyl)-benzenesulfonyl chloride is proposed to replace 3-fluoro-4-nitrobenzenesulfonyl chloride as the starting material. Although other starting materials with fluorine atom at different positions can be also used in order to avoid side reactions, unfortunately none of them are available commercially.

Bromination of Nafion Monomer

The double bond in Nafion® monomer **3** is very sensitive to nucleophiles at high temperature. The reason is that the electron-rich double bond becomes electron-deficient with the strong electron-withdrawing effect of perfluoroalkyl pendant. Thus, double bond of Nafion® can be protected by bromination, before the base catalyzed coupling step (Scheme 9). During the free radical bromination step, small amount of impurity is often formed from hydrolysis of sulfonyl fluoride group. Vacuum distillation is used to separate the pure product.



Scheme 9: Bromination Reaction of Nafion® Monomer.

Coupling Reaction

The reaction is carried out in a dry condition with nitrogen gas protection and extremely dried reagents to minimize hydrolysis impurity. Also, excess brominated nafion monomer **4** was used to consume the costly reactant, 3-fluoro-4-nitrobenzenesulfonyl amide [1, 16]. The viscous crude product **5** is obtained with hydrolyzed impurity, as seen in Figure 13.

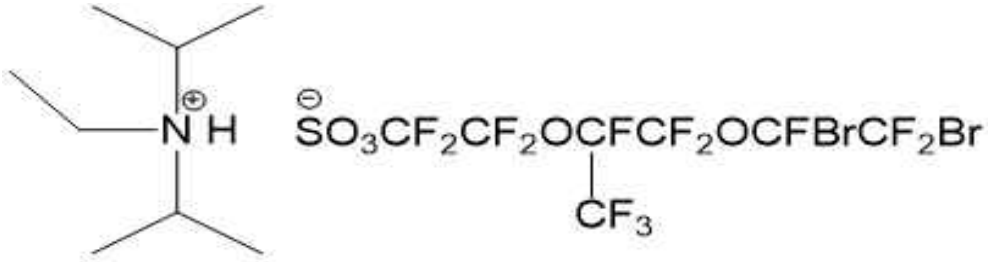
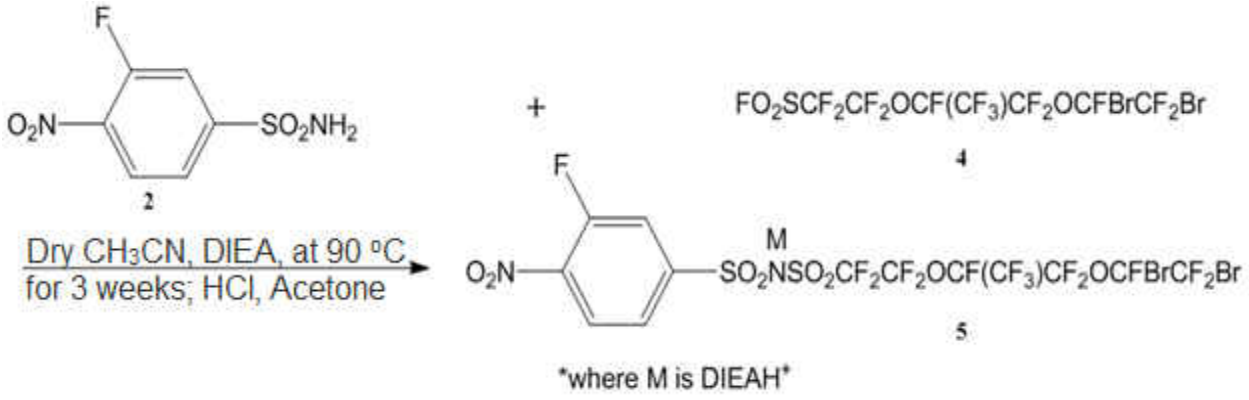


Figure 13: The Brominated Nafion Monomer Hydrolysis Impurity from Coupling Reaction [1].

The brominated nafion monomer **4** is relatively stable in acidic medium. For basic condition, it does not only react with 3-fluoro-4-nitrobenzenesulfonyl amide but also is attacked by a catalyzed weak nucleophile water to form hydrolyzed product at high temperature. Also as typical S_N^2 reaction, the nucleophilicity of aromatic sulfonyl amide is enhanced with a strong base catalyst N, N-diisopropylethylamine (DIEA) in the coupling reaction. Surprisingly, the reaction takes longer time than expected due to the poor reactivity of nucleophile, 3-fluoro-4-nitrobenzenesulfonyl amide. On the other hand, the brominated nafion monomer is consumed or hydrolyzed after one week and another equivalent amount of the brominated nafion monomer was added during the process. It took another two weeks to consume the extra brominated nafion monomer. The possible reason for sluggish reaction is the poor nucheophilicity of 3-fluoro-4-nitrobenezenesulfonyl amide [54, 58]. The aimed coupling reaction is shown in Scheme 10 below.



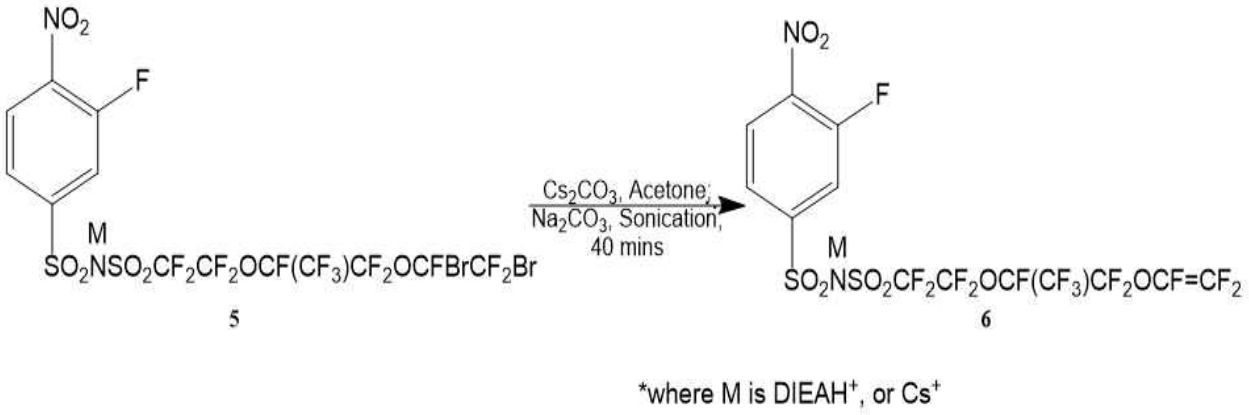
Scheme 10: Coupling Reaction of 3-Fluoro-4-Nitrobenzenesulfonyl Amide and Brominated Nafion Monomer.

The purification procedure involved acidification, neutralization, recrystallization, and column chromatography. The $DIEAH^+$ counterion is first removed by acidification the crude

product with concentrated HCl and extraction. Next, the inorganic base Cs_2CO_3 is used to convert the acidic crude product into a Cesium salt, which can be precipitated out from water. However, the ^{19}F-NMR spectrum indicated that a partial debromination happened during the recrystallization of Cesium salt.

Debromination Reaction

The debromination was completed after sonication with Na_2CO_3 for 40 minutes (Scheme 11). However, the product **6** was failed to purify by column chromatography. Extraction also was attempted many times with different solvent but failed. Eventually, the excess starting material still remains in the product and cannot be removed.



Scheme 11: Debromination Reaction of 3-Fluoro-4-Nitrobenzenesulfonyl Amide and Brominated Nafion Monomer.

In summary, the purification of crude coupling product failed because of the difficulty of separating it from starting material that is used in excess. Column chromatography may be tried for the separation purpose.

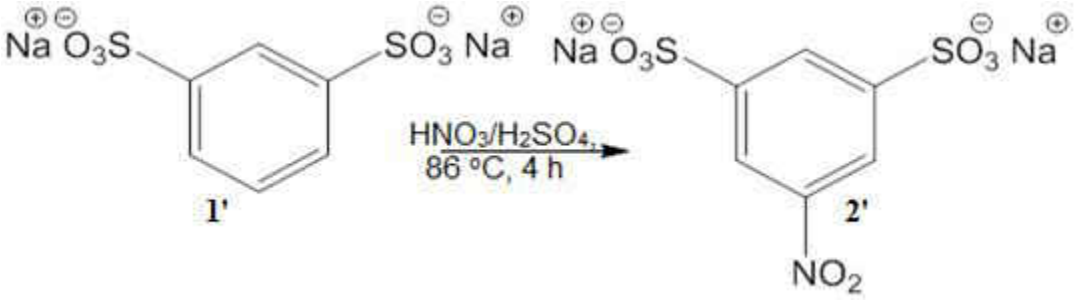
5-Nitro-1, 3-Benzenedisulfonamide Monomer

The purpose of this project is to synthesis 5-nitro-1, 3-benzenedisulfonamide monomer. The monomer is prepared from sodium 1, 3-benzenedisulfonate (starting material). Basically, the synthesis of such monomer is designed with three steps procedure: 1. the nitration reaction, 2. the chlorination reaction, 3. the ammonolysis reaction. The products obtained were characterized with ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy.

Nitration of Sodium 1, 3-Benzenedisulfonate

The conversion of sodium 1, 3-benzenedisulfonate **1'** to sodium 5-nitro-1, 3-benzenedisulfonate **2'** is carried out via refluxing with concentrated sulfuric acid and nitric acid for 4 hours. In the typical electrophilic aromatic substitution (EAS) reaction (Scheme 12), the electrophile (NO_2^+) is formed with the assistance of concentrated H_2SO_4. The reaction is slow due to the electron withdrawing ($-SO_3$) on the aromatic ring. Therefore, low yield is due to the poor electrophilicity of sodium 1, 3-benzenedisulfonate.

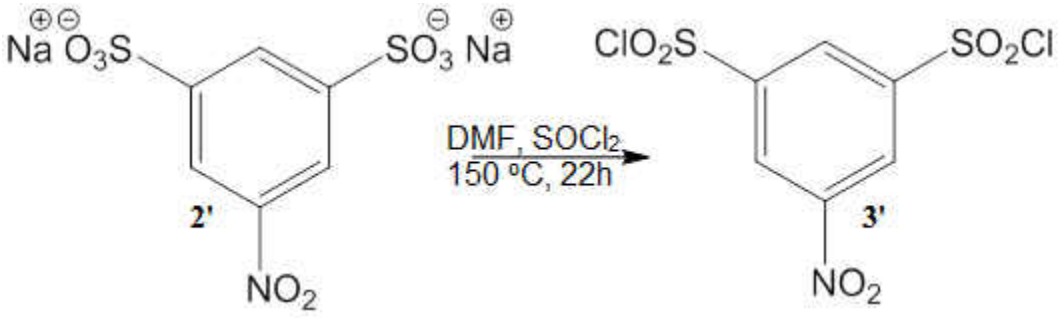
The purification process involves three steps that include neutralization, basification, and recrystallization to separate the product. The reaction is slow and takes longer time to complete; the product is obtained as a water-soluble salt, which has a high melting point (> 400 ^{o}C).



Scheme 12: Nitration of Sodium 1, 3-Benzenedisulfonate.

Chlorination of Sodium 5-Nitro-1, 3-Benzenedisulfonate

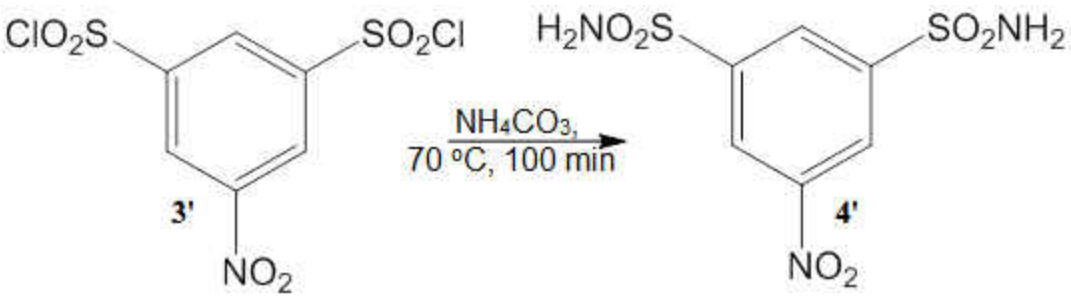
Synthesize 5-nitro-1, 3-benzenedisulfonyl chloride (**3'** in Scheme 13) was obtained by chlorination of sodium 5-nitro-1, 3-benzenedisulfonate **2'** upon refluxing in thionyl chloride and N,N-Dimethylformamide (DMF) solvent at 150 ^{o}C (Scheme 13). This chlorination reaction is believed to involve an addition/elimination mechanism, which results in the conversion of the sulfonate groups into sulfonyl chloride. The reaction involves treatment with excess calcium hydroxide from last step work-up process, which needs to be neutralized with the acidic thionyl chloride. Indeed, excess thionyl chloride is used to make sure the reactant (sodium 5-nitro-1, 3-benzenedisulfonate) reacts completely. Extraction (with chloroform and water) is applied to remove the excess starting material as well as any hydrolysis side products. After all, the product is obtained in low yield.



Scheme 13: Chlorination of Sodium 5-Nitro-1, 3-Benzenedisulfonate.

Ammonolysis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride

Ammonolysis of 5-nitro-1, 3-benzenedisulfonyl chloride **3'** is a typical S_N2 reaction (Scheme 14), which is accompanied with the undesirable hydrolysis as a competing reaction. The reason is that the ammonia is stronger nucleophile than water. Therefore, it is critical to carry out such reaction in dry conditions to prevent hydrolysis.



Scheme 14: Ammonolysis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride.

Hydrolysis impurity can be easily removed by extraction. Other impurity originated from incomplete amomonolysis of disulfonylchlorides, as seen in Figure 14, is removed via recrystallization. The pure product is finally obtained after recrystallization but with low yield, possibly due to insufficient reaction time.

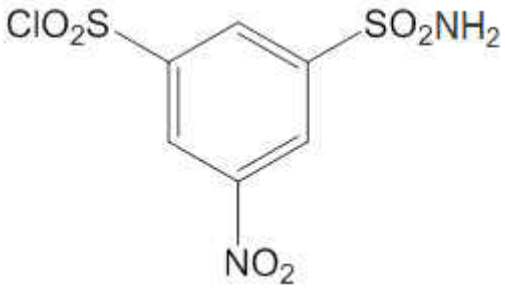


Figure 14: Ammonolysis Half Reaction Side Product.

CHAPTER 3

EXPERIMENTAL

General Considerations

NMR Spectroscopy

The ^{1}H & ^{19}F NMR spectroscopies were measured on a Joel JNM-ECP 400 MHz Fourier Transform NMR spectrometer. The chemical shifts stated in parts per million (ppm) via using high frequency; the coupling constant are reported as a 'J' value in Hz. The chemical shifts of ^{1}H-NMR spectra were referenced against tetramethyl silane (TMS) while the chemical shifts of ^{19}F-NMR spectra were referenced to $CFCl_3$ external standard.

The splitting patterns of resonance were characterized as in the following: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The NMR spectra were measured by using up 1-2 mmol/L concentrations of the solutions (unless indicated otherwise).

Gas Chromatography-Mass Spectrometer

GC-MS were recorded on Shimadzu GCMS-QP2010 Plus GC system spectrometer. The samples were prepared by dissolving 1 mg of the solid samples in 1 mL of acetone.

Infra-red Spectroscopy

The infrared spectra were recorded on the Shimadzu IR Prestige-21 FTIR spectrometers. The solid samples were prepared by adding around 1 mg of the compound on the spectrometer lens. IR spectra were scanned from 4000 cm-1 to 400 cm-1 and reported in wavenumbers (cm-1) with intensity abbreviations: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

Thin Layer Chromatography

Thin Layer Chromatography (TLC) was conducted with using UV active silica gel plates in suitable solvents. The readout was carried out under a (254 nm) UV lamp.

Glass Vacuum System

The usage of glass vacuum line as shown in Figure 15 was for drying, sublimation, purging, and vacuum distillation of compounds. This high-vacuum line was equipped with several stopcocks connected to a diffusion pump and Teflon® that consists of two manifolds where one manifold is for the vacuum, and the other is for the nitrogen gas.

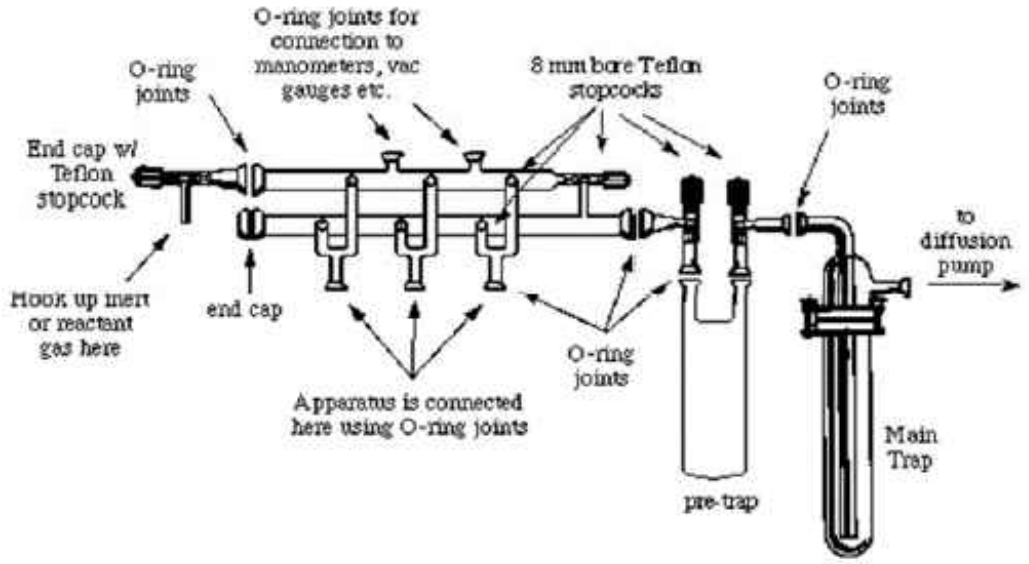


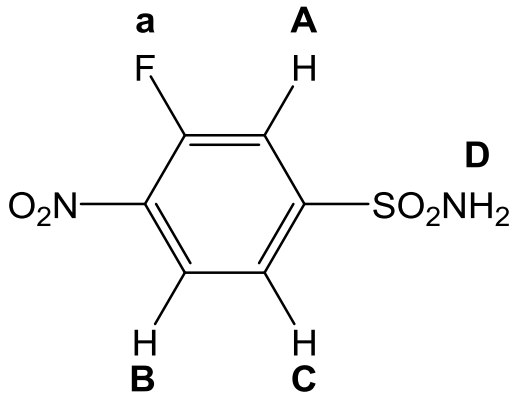
Figure 15: The Line Diagram of a Dual-manifolds Glass Vacuum Line. Used with Permission [60].

Purification of Solvents and Experimental Practice

The starting materials: 3-fluoro-4-nitrobenzenesulfonyl chloride and Nafion® monomer ($FSO_2CF_2CF_2OCF_2CF(CF_3)OCF=CF_2$) were commercially bought from Matrix Scientific and used as received unless otherwise stated. All the reactions were performed in glassware unless otherwise stated. Solvents were dried via activated molecular sieves.

Synthesis of 3-Fluoro-4-Nitrobenzenesulfonyl Amide **2** (Trial 1)

In a 50 ml round bottom flask with a stir bar, (2 grams, 8.3 mmoles) of 3-fluoro-4-nitrobenzenesulfonyl chloride and 10 ml of acetonitrile were added. After cooling down in an ice bath at 0 ºC, 15 ml of ammonium hydroxide (28-30%) was added dropwise to the solution. And then the solution returned to room temperature for 30 minutes. Rotate evaporator removed the organic solvent after that. Then, recrystallization was carried out at room temperature with 11.5 ml of acetone and 1 ml of water for 2 days. 054 g (29.51%) of the product was obtained as a yellow solid.



Entry 1: ^{19}F-NMR (400 MHz; CD_3CN; ppm) δ_a -115.49 (1F, s).

^{1}H-NMR before recrystallization (400 MHz; CD_3CN; ppm) δ_A 7.53 (1H, d), δ_B 8.16 (1H, d), δ_C 7.03 (1H, dd), J_{BC} = 8 Hz, δ_D 6.72 (2H, s), δ_b 8.23 (0.05H, m), δ_{a+c} 7.88 (H, m), δ_d 6.72 (2H, s), δ_e 7.12 (2H, s).

^{1}H-NMR after recrystallization (400 MHz; CD_3CN; ppm) δ_A 7.52 (1H, s), δ_B 8.17 (1H, d), δ_C 7.03 (1H, d), J_{BC} = 12 Hz, δ_D 6.48 (2H, s).

IR (ν_{MAX}/cm^{-1}): 3352.28w and 3263.56w (NH_2) stretch, 1517.98m (NO_2) stretch, 1344.38 (NO_2) bend, 1153.43 (SO_2) stretch.

m/z: 220(M^+, 20%), 156, 140, 94, 64, 50.

X-ray crystals were obtained. The structure is showed in Figure 2. The crystallographic data is given in Table 3.

Table 3: Crystallographic Data.

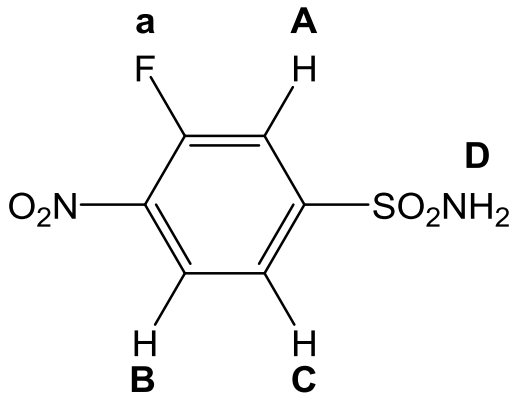
Empirical Formula	$C_6H_5FN_2O_4S$
Formula Weight	220.17
Crystal Color, Habit	yellow, platelet
Crystal Dimensions	0.210 X 0.100 X 0.060 mm
Crystal System	Monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.337(2) Å b = 6.139(1) Å c = 16.297(3) Å b = 94.793(7) º V = 831.1(3) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.759 g/cm^3
F_{000}	448.00
m(MoKa)	3.967 cm^{-1}

Table 3 (Continued)

Temperature	50.0ºC
Reflections collected / unique	7479 / 1897 (R_{int} = 0.1165)
Corrections	Lorentz-polarization Absorption
trans. Factors	0.692 - 0.976
Refinement	Full-matrix least-squares on F^2
Reflection/Parameter Ratio	14.26
Goodness of Fit Indicator	1.058
Residuals: R1 (I>2.00s(I))	0.0677
Residuals: R (All reflections)	0.1129
Residuals: wR2 (All reflections)	0.1703
Maximum peak in Final Diff. Map	0.54 e.A^-3
Minimum peak in Final Diff. Map	-0.70 e.A^-3

Synthesis of 3-Fluoro-4-Nitrobenzenesulfonyl Amide **2** (Trial 2)

In a 25 ml round bottom flask, (1 gram, 4 mmoles) of 3-fluoro-4-nitrobenzenesulfonyl chloride was added with a stir bar. 4 ml of acetonitrile was added subsequently. The solution cooled down in an ice bath at 0 ºC and then 0.9 ml of ammonium hydroxide (28-30%) was added dropwise to the solution. After finish dropping, the reaction was remaining at room temperature for another 30 minutes. The solvents were removed via rotary evaporator. Next, the solid was re-dissolved in 10 mL of water and followed by extraction with 2 x 10 ml of dichloromethane. The combined organic parts, was dried over $MgSO_4$ and then the solvent was removed by a rotary evaporator. Next, the recrystallization at room temperature for 2 days with 8 ml of acetone and 0.6 ml of water was used to purify the product. Finally, 0.27 g (29.38 %) of the crude product was obtained as a yellow solid. The column chromatography with 1:1 ethyl acetate: hexane was carried out to purify the product but failed.



Entry 2: ^{19}F-NMR (400 MHz; CD_3CN; ppm) δ_a -115.62 (1F, s).

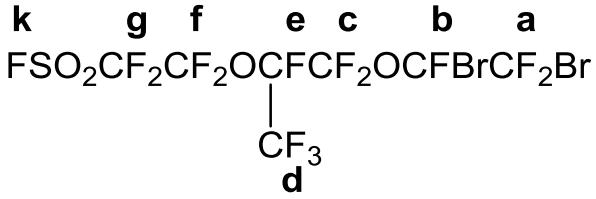
^{1}H-NMR (400 MHz; CD_3CN; ppm) δ_B 8.26 (1H, t), δ_{A+C} 7.88 (2H, m), J_{BC} = 8 Hz, δ_D 6.72 (2H, s).

IR (ν_{MAX}/cm^{-1}): 3358.07w and 3265.49w (NH_2) stretch, 1529.55m (NO_2) stretch, 1346.31s (NO_2) bend, 1161.15s (SO_2) stretch.

Synthesis of $FSO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$ **4**

In a 50 ml round bottom flask, (10.0 g, 22.4 mmol) of Nafion® monomer $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$ was added first. The bromine liquid (2 ml, 38.8 mmol) was then slowly added with a pressure equalizing for around 1 hour at 0 °C. As the reddish color stayed for another 30 minutes, it indicated that the bromine is excess. The reaction was allowed to continue overnight in the presence of light.

At the next day, the excess of bromine was removed by adding 5% $NaHSO_3$ solution 10 mL slowly until the reddish color disappeared. The crude product was extracted with 7×3 ml of distilled water and dried with small amount of Na_2SO_4. Finally, 8.19 g (61%) of pure product was finally obtained after distillation around 60 °C under a dynamic high vacuum.



^{19}F-NMR (400 MHz; CD_3CN; ppm) δ_a -65.64 (2F, s), δ_b -73.75 (1F, m), δ_c -86.5 (2F, m), δ_d -80.72 (3F, m), δ_e -145.9 (1F, s), δ_f -80.72 (2F, m), δ_g -113.11 (2F, s), δ_k 44.24 (1F, s).

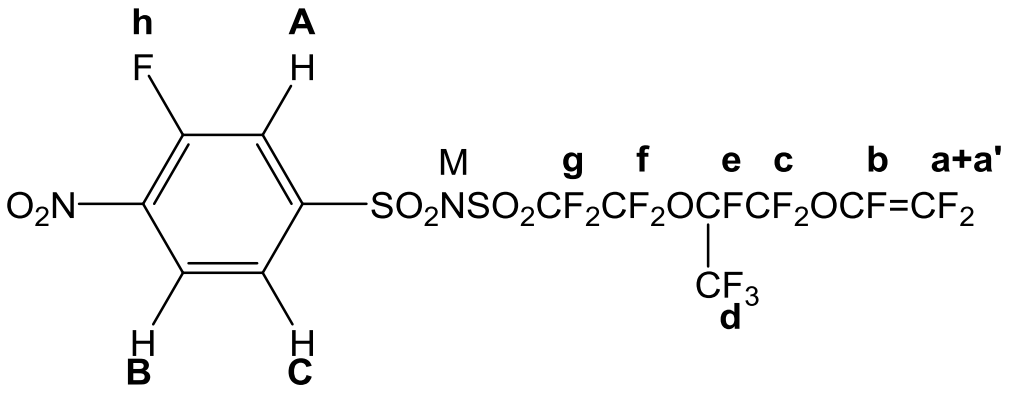
Synthesis of 3-F-4-NO_2PhSO_2N(Cs)SO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br **5**

3-Fluoro-4-nitrobenzenesulfonyl amide (0.48 grams 2.18 mmoles) was added to a 50 ml of three-necked round bottom flask equipped with a condenser, two rubber septa, and a stir bar inside the glove box. And then, the brominated Nafion monomer (1.35 grams, 2.23 mmoles, the ratio is 1:1.02), 15 ml of acetonitrile, and 2 ml diisopropyl ethyl amine (DIEA) were injected into the flask by syringe subsequently. With nitrogen gas protection, the solution was refluxed for two weeks at 90 ºC. The proton and fluorine NMR were used to monitor the reaction progress. After all the brominated nafion monomers was consumed, another 1 gram (1.65 mmoles) of brominated Nafion monomer was added to the reaction solution for refluxation ten more days until the fluorine peak in ^{19}F-NMR (-SO_2F) disappeared again. The solvent was removed via rotary evaporator after the mixture solution. And then the solid was redissolved in 35 ml acetone, and following acidification with 1 ml of (12 M) concentrated HCl. The solution was tested with PH paper till it turned to red. After drying again with a rotary evaporator, the crude product was dissolved again in 55 ml of ethyl acetate and extracted with 3 × 50 of brine water. 2.39 g (97.5 %) of the coupling product was obtained.

Next, the solvent was removed from the combined organic layer, and the product was converted to salt form with an aqueous solution of 1.06 gram 8 % of Cs_2CO_3 (3.25 mmoles) in 10 ml of acetone. 2.14 g (87.3 %) of the coupling product was obtained.

Synthesis of 3-F-4-$NO_2PhSO_2N(Cs)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$ **6**

2.14 g (2.28 mmoles) of coupling product was dissolved in 10 ml of acetone and 10 ml of 16 % of Na_2CO_3 in a 100 ml round bottom flask. At room temperature, the solution was sonicated for 40 minutes. Next, the solvent was evaporated from the solution, and the resulted solid was dried under dynamic high vacuum overnight. The product was dissolved in 20 ml of ethyl acetate and extracted with 3 × 20 ml of brine water. The organic layer was collected, and the solvent was removed via rotary evaporator. 1.96 g (80%) of black solid was obtained.

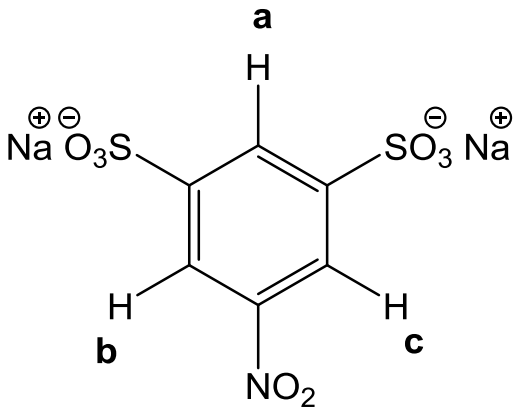


^{19}F-NMR (400 MHz; CD_3CN; ppm): δ_a -120.72 (1F, m), $\delta_{a'}$ -135.46 (1H, m), δ_b -112.55 (1H, d), δ_c -83.60 (2H, s), δ_d -78.31 (3H, m), δ_e -144.34 (1H, s), δ_f -78.31 (2H, m), δ_g -115.40 (2H, m), δ_h -116.69 (1H, s).

^{1}H-NMR (400 MHz; CD_3CN; ppm): δ_B 8.12 (1H, d), δ_A 7.51 (1H, s), δ_C 7.07 (1H, d), J_{BC} = 8 Hz, δ_b 8.18 (0.38H, m), δ_{a+c} 7.86 (0.61H, m), δ_d 6.82 (1.82H, s).

Synthesis of Sodium 5-Nitro-1, 3-Benzenedisulfonate **2'**

3.0 g (0.01 mole) of sodium 1, 3- benzenedisulfonate was added to 4 ml of sulfuric acid in a 25 ml three-neck round bottom flask with a stir bar that fitted with a condenser, thermometer, and dropping funnel. The mixture was heated at 80 ^{o}C for 30 minutes. Without heating, 2 ml of nitric acid was added dropwise. Then, the mixture was heated again around 80 ^{o}C for another 4 hours. The mixture was cooled overnight. After that, the mixture was slowly poured into ice-water bath. The solution was neutralized to pH = 5-6 by adding 2.0 g of $Ca(OH)_2$ and 6.7 g of KOH. The formed precipitate was filtered off. The filtrate was then basified with 0.6 g of Na_2CO_3 to pH = 10. The precipitate was again filtered off. The filtrate was concentrated to small volume. Then, it was dissolved in boiling water and recrystallized. 0.51 g (15 %) of the product was collected as a yellow solid.



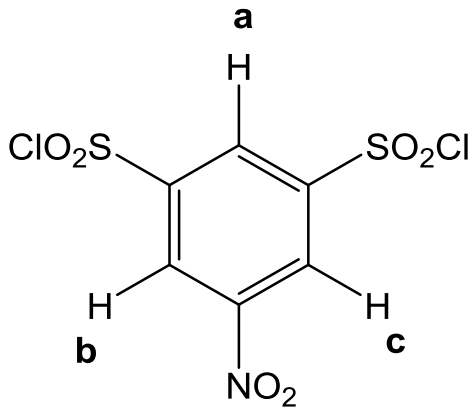
^{1}H-NMR (400MHz; D_2O; ppm): δ_a 8.57 (1H, s), δ_{b+c} 8.80 (2H, s).

^{13}C-NMR (400MHz; D_2O; ppm): δ_A 129.47, δ_{B+F} 146.27, δ_{C+E} 124.25, δ_D 149.19.

IR (ν_{MAX}/cm^{-1}): 1546.91m (NO_2) stretch, 1361.74m (NO_2) bend, 1043.49s (SO_2) stretch.

Synthesis of 5-Nitro-1, 3-Benzenedisulfonyl Chloride **3'**

3.0 g (9.2 mmoles) of sodium 5-nitro-1, 3-benzenedisulfonate, 20 ml of thionyl chloride, and 3 ml of N, N-dimethylformamide (DMF) were refluxed at 150 ^{o}C for 22 hours inside a 50 ml round bottom flask with a stir bar. After the reaction finished, the solid was filtered off. The filtrate was concentrated to an oil. The oil was dissolved in 6 ml of chloroform and extracted with 2 × 6 ml of brine water. The organic layer was collected and the solvent was removed via rotating evaporator. 0.96 g (33 %) of the product was obtained.



^{1}H-NMR (400MHz; Acetone-d_6; ppm): δ_a 9.14 (1H, s), δ_{b+c} 9.28 (2H, s).

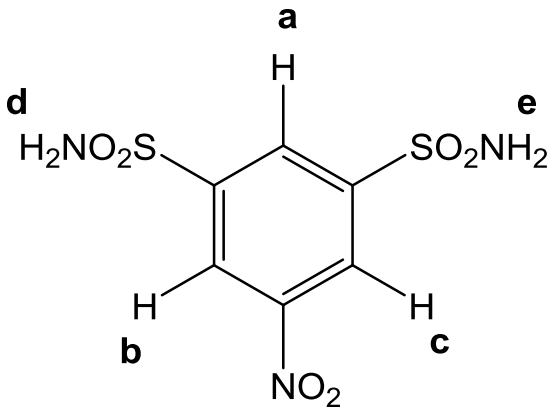
IR (ν_{MAX}/cm^{-1}): 1577.77m (NO_2) stretch, 1386.82m (NO_2) bend, 1097.5s (SO_2) stretch.

Melting Point = 93.7 - 94.6 ^{o}C.

Synthesis of 5-Nitro-1, 3-Benzenedisulfonyl Amide **4'**

0.77 g (2.4 mmoles) of 5-nitro-1, 3-benzenedisulfonyl chloride, 5.4 ml of dried tetrahydrofuran (THF), and 1.54 g of ammonium carbonate were added in a 25 ml round bottom flask inside the glove box. Under nitrogen gas protection, the mixture was refluxed for 100 minutes around 70 ^{o}C. Then, the mixture was filtered and the filtrate was evaporated to an oil. The oil was dissolved in 10 ml of ethyl acetate and extracted with 2 × 10 ml of brine water.

Then, the recrystallization was carried out with 4 ml of water and few drops of ethanol. Finally, 0.07 g (10.4 %) of the product was obtained as a white solid.



^{1}H-NMR (400MHz; Acetone-d_6; ppm): δ_a 8.67 (1H, s), δ_{b+c} 8.84 (2H, s), δ_{d+e} 7.23 (4H, s).

^{13}C-NMR (400MHz; Acetone-d_6; ppm): δ_A 129.82, δ_{B+F} 147.65, δ_{C+E} 124.86, δ_D 149.51.

IR (ν_{MAX}/cm^{-1}): 3361.93w and 3263.56w (NH_2) stretch, 1531.48m (NO_2) stretch, 1348.24s (NO_2) bend, 1147.65s (SO_2) stretch.

Melting Point = 219 – 220.1 ºC.

CHAPTER 4

CONCLUSION

Two new monomers for proton exchange membrane fuel cells are the synthesis target in this project. All the intermediates are purified and characterized by spectroscopy, such as NMR, IR, and GCMS.

The first attempt to synthesize diazonium perfluoroalkyl arylsulfonamide (PFSI) zwitterionic monomer is unsuccessful due to the difficulty to purify one of the intermediate from the coupling reaction of 3-fluoro-4-nitrobenzenesulfonylamide and brominated Nafion monomer. The undesired solvolysis reaction is almost unpreventable because of the fluorine atom in the ortho position of nitro group in the aromatic ring. Also, poor nucleophilicity of the 3-fluoro-4-nitrobenezenesulfonyl amide led to incomplete rxn for over one week. Thus, the preparation for such compound needs further exploration, specifically on the purification procedure. Furthermore, 3-fluoro-4-(N-acetyl)-benzenesulfonyl chloride could be a possible alternative starting material. Different starting materials with other than ortho positions of the nitro group in the aromatic ring will also be tried to avoid the solvolysis intermediate.

The second attempt to synthesize disulfonyl amide monomer is struggled but successful. The major problem is the purification in the first aromatic nitration reaction. For the chlorination, it is critical to run the reaction for a longer time to consume all the starting material. Last, the ammonolysis reaction only provides the product with low yield because of the incomplete reaction.

For future work, the target product will be copolymerized with perfluoroalkyl(aryl) disulfonyl fluoride. And then, the nitro group will be converted to diazonium group, which can help the chemical grafting of the polymer electrolyte onto carbon electrodes in PEM fuel cells.

REFERENCES

[1] Nworie, C. Synthesis of a 4-(Trifluoromethyl)-2-Diazonium Perfluoroalkyl Benzenesuflonylimide (PFSI) Zwitterionic Monomer for Proton Exchange Membrane Fuel Cell. Master. Dissertation, East Tennessee State University, Johnson City, Tennessee, 2014.

[2] Baker, R.; and Zhang, J. *Institute for fuel cell innovation*; National Research of Canada: 4250 Wesbrook Mall, Vancouver, British Columbia, Canada, 2011.

[3] Barber, F. *PEM Fuel Cells: Theory and Practice*; Academic Press: 225 Wyman Street, Waltham, Massachusetts, USA, 2nd ed., 2012.

[4] Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C. A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, *Applied Energy.* **2011,** *88,* 981–1007.

[5] Chen, H.; Cong, T. N.; Yang, W.; Tan, C.; Li, Y.; Ding, Y. Progress in electrical energy storage system: A critical review, *Progress in Natural Science.* **2009,** *19,* 291–312.

[6] Fuel Cell Markets. Advantages and Benefits of Hydrogen and Fuel Cell Technologies. http://www.fuelcellmarkets.com/fuel_cell_markets/5,1,1,663.html (accessed June 29, 2010).

[7] Srinivasan, S. *Fuel Cells: From Fundamentals to Applications*; Springer: New York, USA 2006.

[8] Yang, W. C.; Bates, B.; Fletcher, N.; Pow, R. Control challenges and methodologies in fuel cell vehicle development, *Proceedings of the SAE Conference*. **1998,** *328*, 363–70.

[9] Larminie, J.; Dicks, A. *Fuel Cell Systems explained*; J. Wiley: Chichester, West Sussex, 2003.

[10] Geiger, A. Characterization and Development of Direct Methanol Fuel Cells, Ph.D. Dissertation, Swiss Federl Institute of Technology, Zurich, Switzerland, 2002.

[11] Kordesch, K.; Simader, G. *Fuel Cells and Their Applications,* Wiley-VCH: Weinheim, 1996.

[12] Ledjeff, K. "Brennstoffzellen: Entwicklung, Technologie, Anwendung", CF Müller Verlag GmbH, Heidelberg, 1995.

[13] Gilchrist, T. Fuel Cells to the fore, *IEEE Spectrum.* **1998,** *35*, 35-40.

[14] Litster, S.; McLean, G. PEM fuel cell electrodes. *J. of power sources*. **2004,** *130*, 61-76.

[15] Zhang, J. *PEM Fuel Cell Electrocatalysts and catalyst layers*; Springer, 2008.

[16] Mei, H. Perfluoroalkyl (Aryl) Sulfonimide Zwitterions. Ph.D. Dissertation, Clemson University, Clemson, SC, 2006.

[17] Zhu, W.; Ignaszak, A.; Song, C.; Baker, R.; Hui, R.; Zhang, J.; Nan, F.; Botton, G.; Ye, S.; Campbell, S. Nanocrystalline tungsten carbide (WC) synthesis/characterization and its possible application as a PEM fuel cell catalyst support, *Electrochimica Acta.* **2012,** *61*, 198– 206.

[18] Pukrushpan, J. T.; Stefanopoulou, A. G.; Peng, H. *Control of Feul Cell Power Systems: Principles, Modeling Analysis, and Feedback Design,* AIC Press, 2004.

[19] Vasquez, L. O. Fuel Cell Research Trends, *Nova Publishers*, 2007, pp 34-65.

[20] Chen, H.; Cong, T. N.; Yang, W.; Tan, C.; Li, Y.; Ding, Y. Progress in electrical energy storage system: A critical review. *Progress in Natural Science*. **2009**, *19*, 291-312.

[21] Pu, H. *Polymers for PEM Fuel cells*, 2014.

[22] Zhang, J. *PEM Fuel Cell Electrocatalysts and catalyst layers*, 2008.

[23] Mehta, V.; Cooper, J. Review and analysis of PEM fuel cell design and manufacturing, *J. of power sources*. **2003,** *114*, 32-53.

[24] Qi, Z.; Kaufman, A. Low Pt Loading High Performance Cathodes for Fuel Cells. *J. Power Sources.* **2003,** *113*, 37.

[25] Jia, N.; Martin, R. B.; Qi, Z.; Lefebvre, M. C.; Pickup, P. G. Modification of Carbon Supported Catalysts to Improve Performance in Gas Diffusion Electrodes. *Electrochimica Acta.* **2001,** *46,* 2863-9.

[26] Wilson, M.S.; Valerio, J.A.; Gottesfeld, S. Low Platinum Loading Electrode for Polymer Electrolyte Fuel Cells Fabricated Using Thermoplastic Ionomers. *Electrochim. Acta.* **1995,** *40*, 355–363.

[27] Thampan, T.; Makhotra, S.; Zhang, J.; Datta, R. PEM Fuel Cell as a Membrane Reactor. *Catal. Today.* **2001,** *67*, 15-32.

[28] Zaidi, J.; Matsuura, T. *Polymer Membrane for Fuel cells,* 2009; p 550.

[29] Kang, M. S.; Kim, J. H.; Won, J.; S. H. Moon, S. H.; Kang, Y. S. Highly charged proton exchange membranes prepared by using water soluble polymer blends for fuel cells, *J. Membrane Science*. **2005,** *247,* 127-135.

[30] Kim, H.; Kang, M. S.; Lee, D. H.; Won, J.; Kim, J.; Kang, Y. S. Proton Exchange membranes with high cell performance based on Nafion/poly(p-phenylene vinylene) composite polymer electrolyte, *J. Membr.* **2007,** *304,* 60-64.

[31] Creager, S. E. Proposal for DOE project, 2006.

[32] Uchida, M.; Fukuoka, Y.; Sugwara, Y.; N. Eda, N.; Ohta, A. Effects of Microstructure on Carbon Support in the Catalyst Layer on the Performance of Polymer Electrolyte Fuel Cells *Journal of the Electrochemical Society*. **1996**, *143*, 2245-2252.

[33] Honma, I.; Nakajima, H.; Nishikawa, O.; Sugimoto, T.; Nomura, S. Family of High-Temperature Polymer-Electrolyte Membranes Synthesized from Amphiphilic Nanostructured Macromolecules, *J. Electrochem. Soc.* **2003**, 150, A616-A619.

[34] Gilchrist, T. Fuel Cells to the fore, *IEEE Spectrum.* **1998***, 11*, 35-40.

[35] Smitha, B.; Sridhar, S.; Khan. A. Solid Polymer Electrolyte Membrane for Fuel Cell. *J. Mebran. Sci.* **2005,** *259*, 10.

[36] Passalacqua, E.; Lufrano, F.; Squadrito, G.; Patti, A.; Giorgi, L. Nafion content in the catalyst layer of polymer electrolyte fuel cells: effects on structure and performance. *Electrochimica Acta.* **2001,** *46*, 799-805.

[37] Liu, D. *Engineering Particle Morphology and Assembly for Proton Conducting Fuel Cell Membrane Applications*; University of Rochester: Rochester, New York, 2009.

[38] Sahu, A.K.; Pitchumani, S, et al. Nafion and modified-Nafion membranes for polymer electrolyte fuel cells: An overview. *Bulletin Material Science.* **2009,** *32*, 285-294.

[39] Creager, S. E.; Liu, B.; Mei, H.; DesMarteau, D. Electrochemical Grafting of an Aryl Fluorosulfonimide Electrolyte onto Glassy Carbon, *Langmuir.* **2006,** 22, 10747-10753.

[40] Hampden-Smith, M. J.; Atanassova, P.; Napolitano, P.; Bhatia, Rice, G. I.; Caruso, J.; Brewster, J.; Gurau, B. *Modified Carbon Products, Their Use in Fluid/Gas Diffusion Layers and Similar Devices and Methods Relating to the Same WO2005/091416,* 2005.

[41] Olah, G. A.; Iyer, P. S.; G. K. Prakash, G. K. Perfluorinated Resinsulfonic Acid (Nafion-Hw) Catalysis on Synthesis., *Synthesis.* **1986,** *7*, 513.

[42] Nakajima, T.; Groult, H. *Fluorinated Materials for Energy Conversion*; ELSEVIER Ltd: The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK, 2005.

[43] Zhang, M.; Sonoda, T.; Mishima, M.; Honda, T.; Leito, I.; Koppel, I. A.; Bonrath, W.; Netscher, T. Gas-phase acidity of bis[(perfluoroalkyl) sulfonyl]imides. Effects of the perfluoroalkyl group on the acidity. *J. Phys. Org. Chem.* **2014,** *27*, 676-679.

[44] Wilson, M. S.; Gottesfeld, S. Thin-Film Catalyst Layers for Polymer Electrolyte Fuel Cell Electrodes. *J. Appl. Electrochem*. **1992,** *22*, 1.

[45] Yu, Y.; Kosbach, L. Modified Carbon Products Useful in Gas Diffusion Electrodes. US6399202, **2002,** June 4.

[46] Fowler, M.; Lam, A. *PEM Fuel-Cell Test Station and Laboratory Expermat*, University of Waterloo, Waterloo, Ontario, Canada, 2004.

[47] Kirsch, P. Modern Fluoroorganic Chemisty: Synthesis, Reactivities, Applications Wiley-VCH: *Weinheim,* 2004, pp 182-223.

[48] Creager, S. E.; Liu, B.; Mei, H.; DesMarteau, D.; Electrochemical Grafting of an Aryl Fluorosulfonimide Electrolyte onto Glassy Carbon. *Langmuir.* **2006,** *22,* 10747-10753.

[49] Kumar, G. S.; Raja, M.; Parthasarathy, S. High Performance Electrodes with Very Low Platinum Loading For Polymer Electrolyte Fuel Cells. *Electrochim. Acta.* **1995,** *40*, 285.

[50] Hayre, R.; Lee, S. J.; Cha, S. W.; Prinz, F. B. A Sharp Peak in The Performance of Sputtered Platinum Fuel Cells at Ultra-Low Platinum Loading, *J. of Power Sources.* **2002,** *109*, 483-493.

[51] Mei, H.; D'Andrea, D.; Nguyen, T.; Nworie, C. Synthesis of the diazonium (perfluoroalkyl) benzenesulfonimide monomer from Nafion monomer for proton exchange membrane fuel cells. *Journal of Power Sources.* **2014,** *248*, 1177-1180.

[52] Cohn, E. J.; Edsall, J. T. *Proteins, Amino Acids and Peptides as Dipolar Ions,* Rheinhold, New York, 1943; p 157.

[53] Laughin, R. G. HLB from a Thermodynamic Perspective *J. Soc. Cosmet. Chem.* **1981,** *32*, 371.

[54] Tomasz, S.; Wojciech, P. O.; Marcin, H.; Henryk, K.; Tadeusz, M. K. Toward a Physical Interpretation of Substituent Effects: The Case of Fluorine and Trifluorome- thyl Groups. *J. Org. Chem*. **2014**, *79*, 7321−7331.

[55] Conrow, R. B.; Bernstein, S. Substituted Aromatic Naphthalene Sulfonamides. US4117003, **1978,** September 26.

[56] Wynberg, N. A.; Leger, L. J.; Conrad, M. L.; Vogels, C. M.; Decken, A.; Duffy, S. J.; Westcott, S. A. Synthesis and catalysed hydroboration of styryl sulfonamides, *Can, J. Chem.* **2005**, 83, 661-667.

[57] Ji, P.; Atherton, J. H.; Page, M. I. The Kinetics and Mechanisms of Aromatic Nucleophilic Substitution Reactions in Liquid Ammonia, *J. Org. Chem.* **2011**, 76, 3286-3295.

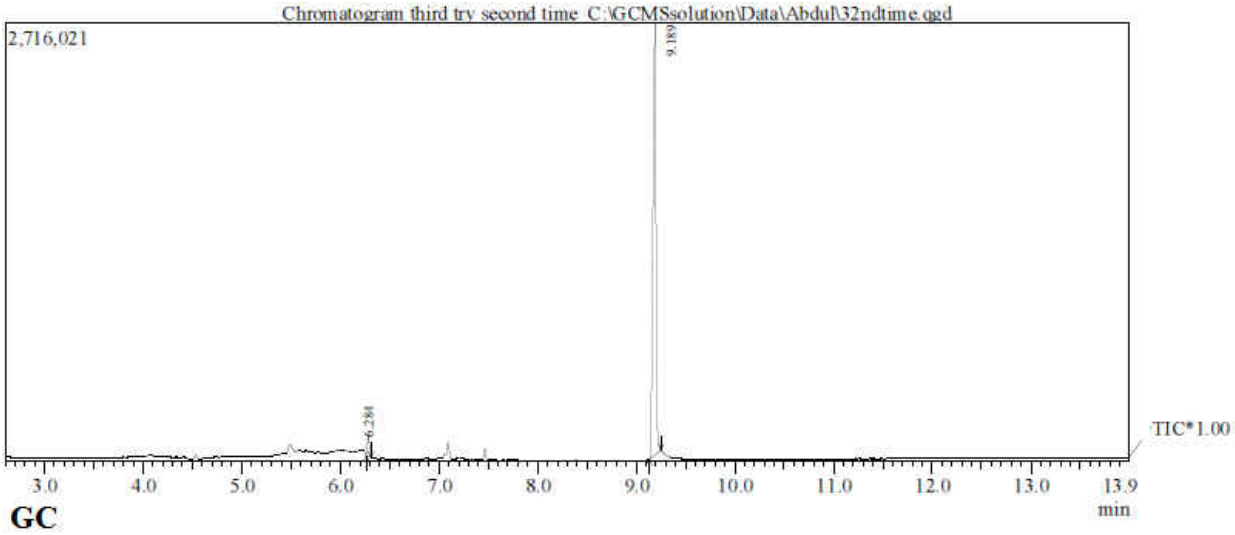
[58] Mei, H.; Nworie, C.; Abban, G.; Alayyaf, A.; McCloud, R. Diazonium (perfluoroalkyl) Arylsulfonylimide zwitterionic monomers analogues: Effective synthesis and thermal stability, *International journal of hydrogen energy*. **2016**, *XXX*, 1-10.

[59] Van Loevezijn, A.; et al. Arylsulfonyl pyrazoline carboxamidine derivatives as 5-HT6 antagonists and their preparation, pharmaceutical compositions and use in the treatment of diseases. PCT Int. Appl. Patent Number 2009115515, September 24, 2009.

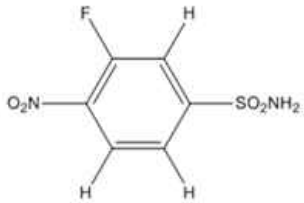
[60] Toreki, R. Interactive Learning Paradigms Incorporated, The Glassware Gallery: Schlenk Lines and Vacuum Lines [Online]. http://www.ilpi.com/inorganic/glassware/vacline.html (accessed Jul 1, 2015).

APPENDICES

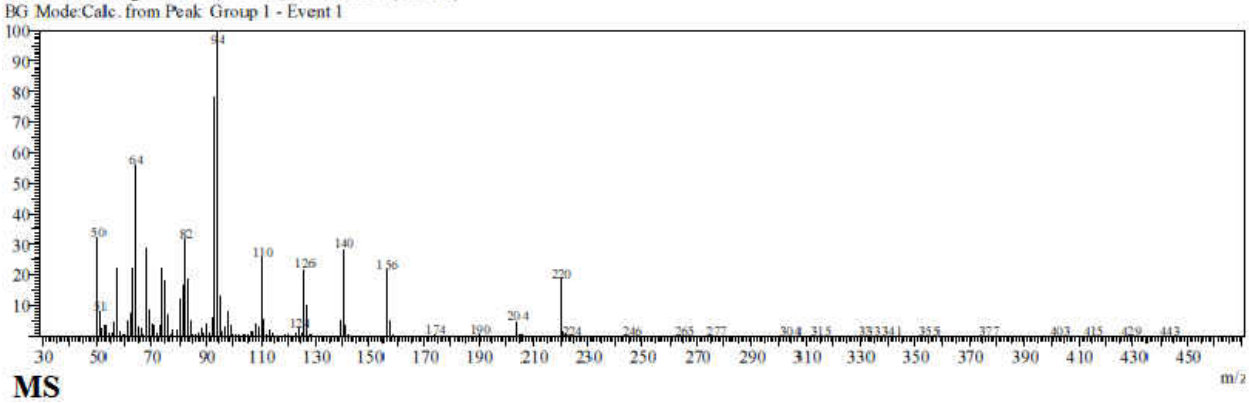
APPENDIX A1: GC-MS Chromatogram of Compound **2** (Trial 1)



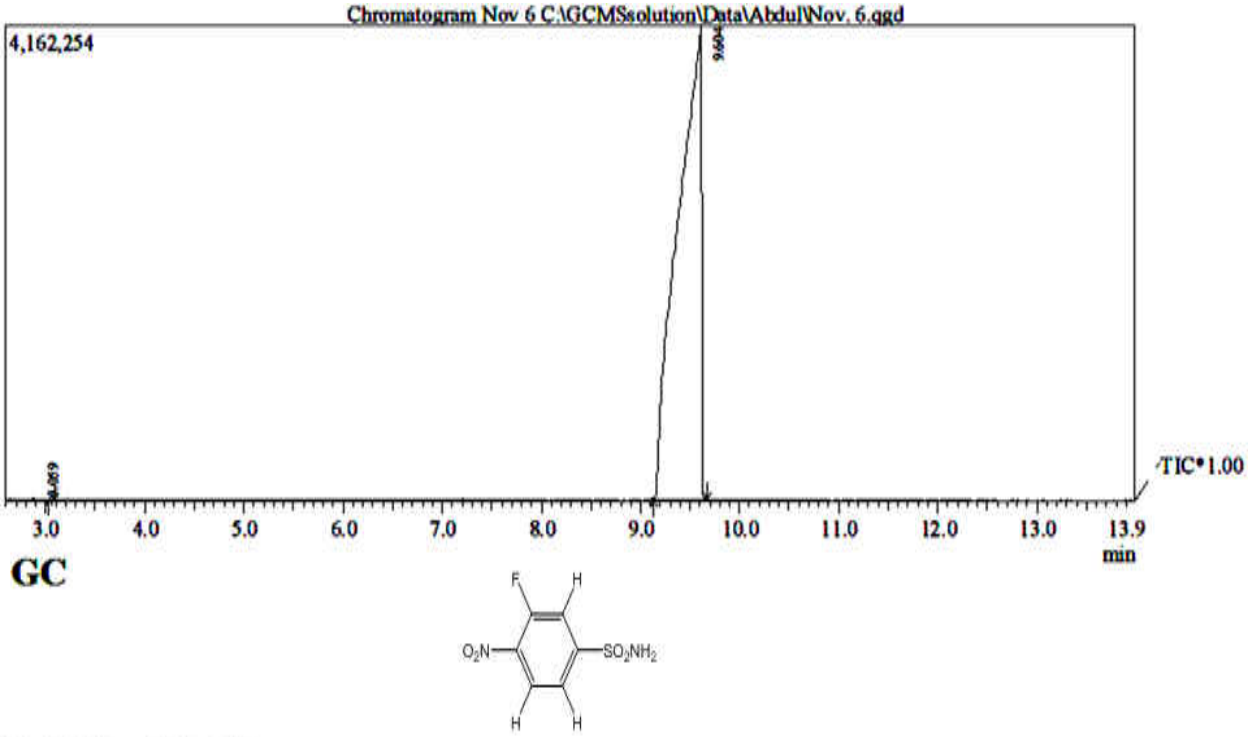
Spectrum

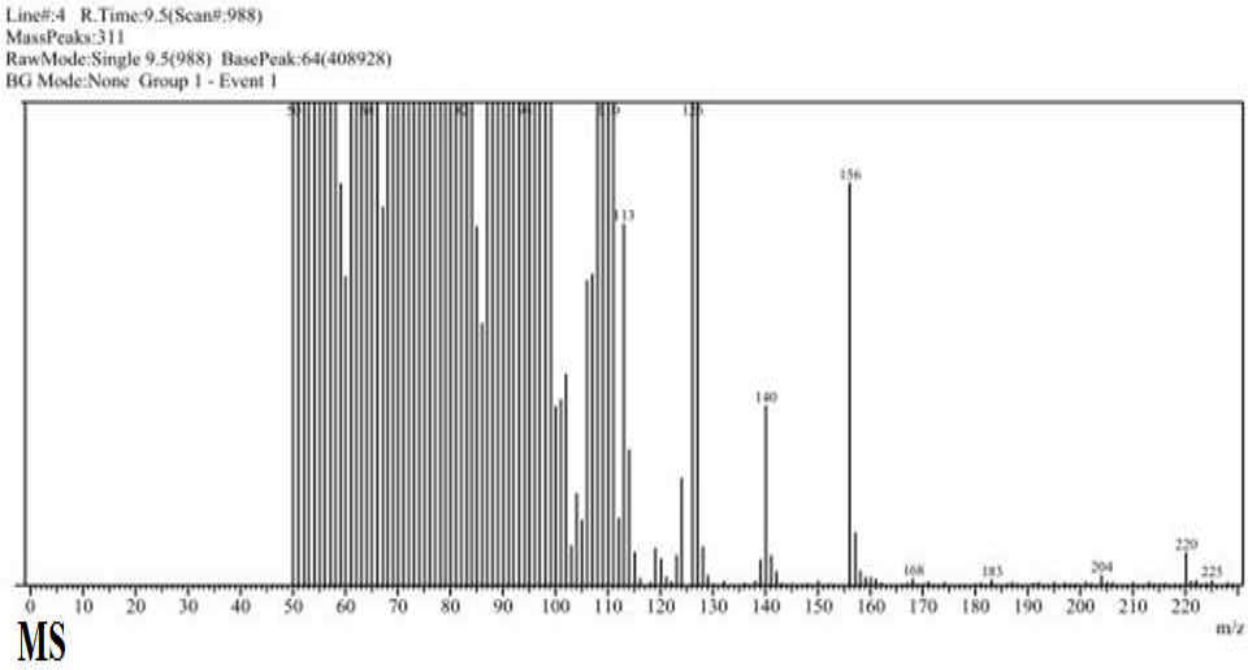


Line#:2 R.Time:9.2(Scan#:942)
MassPeaks:182
RawMode:Averaged 9.2-9.2(941-943) BasePeak:94(327321)
BG Mode:Calc. from Peak Group 1 - Event 1

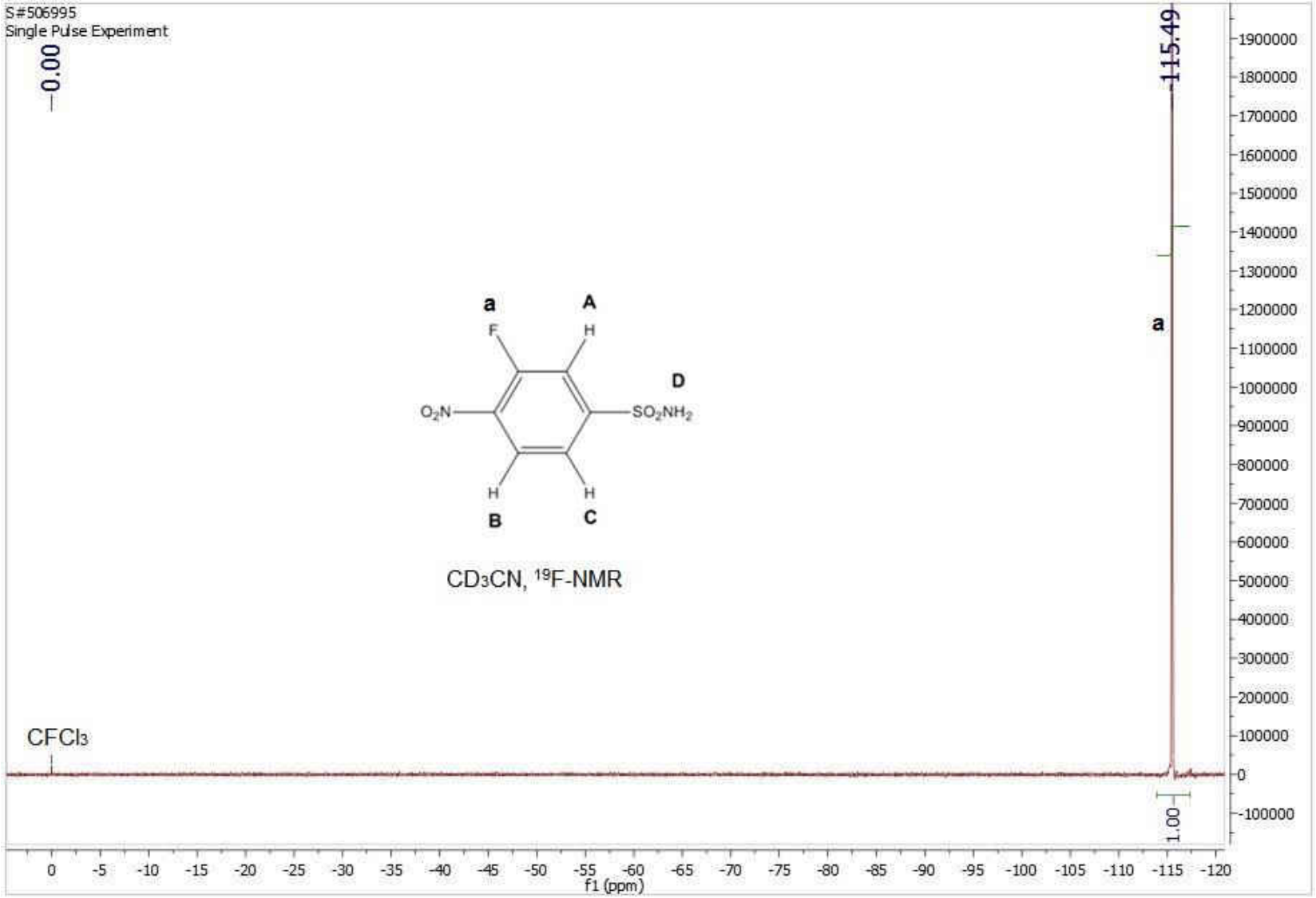


APPENDIX A2: GC-MS Chromatogram of Compound **2** (Trial 2)

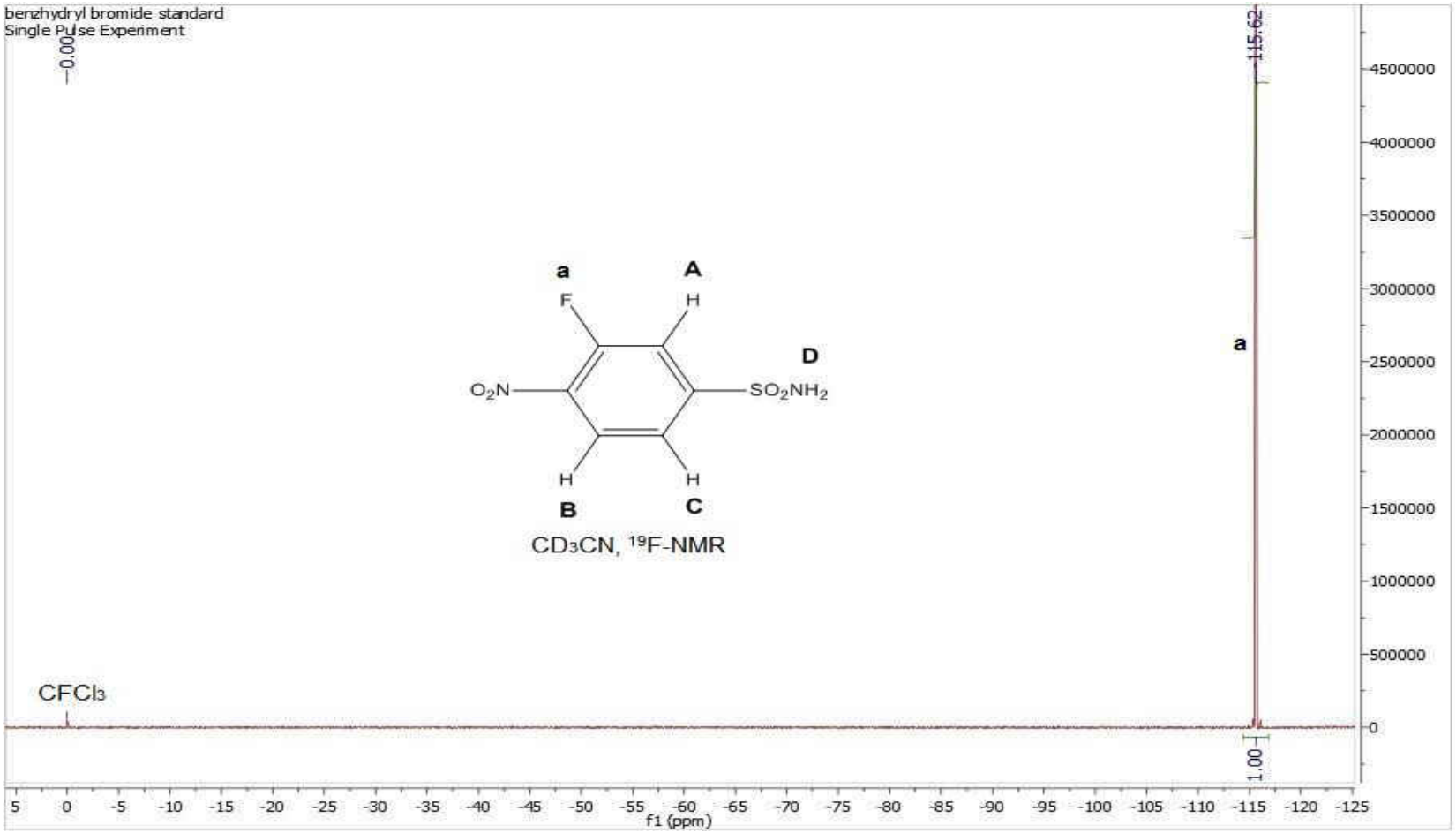




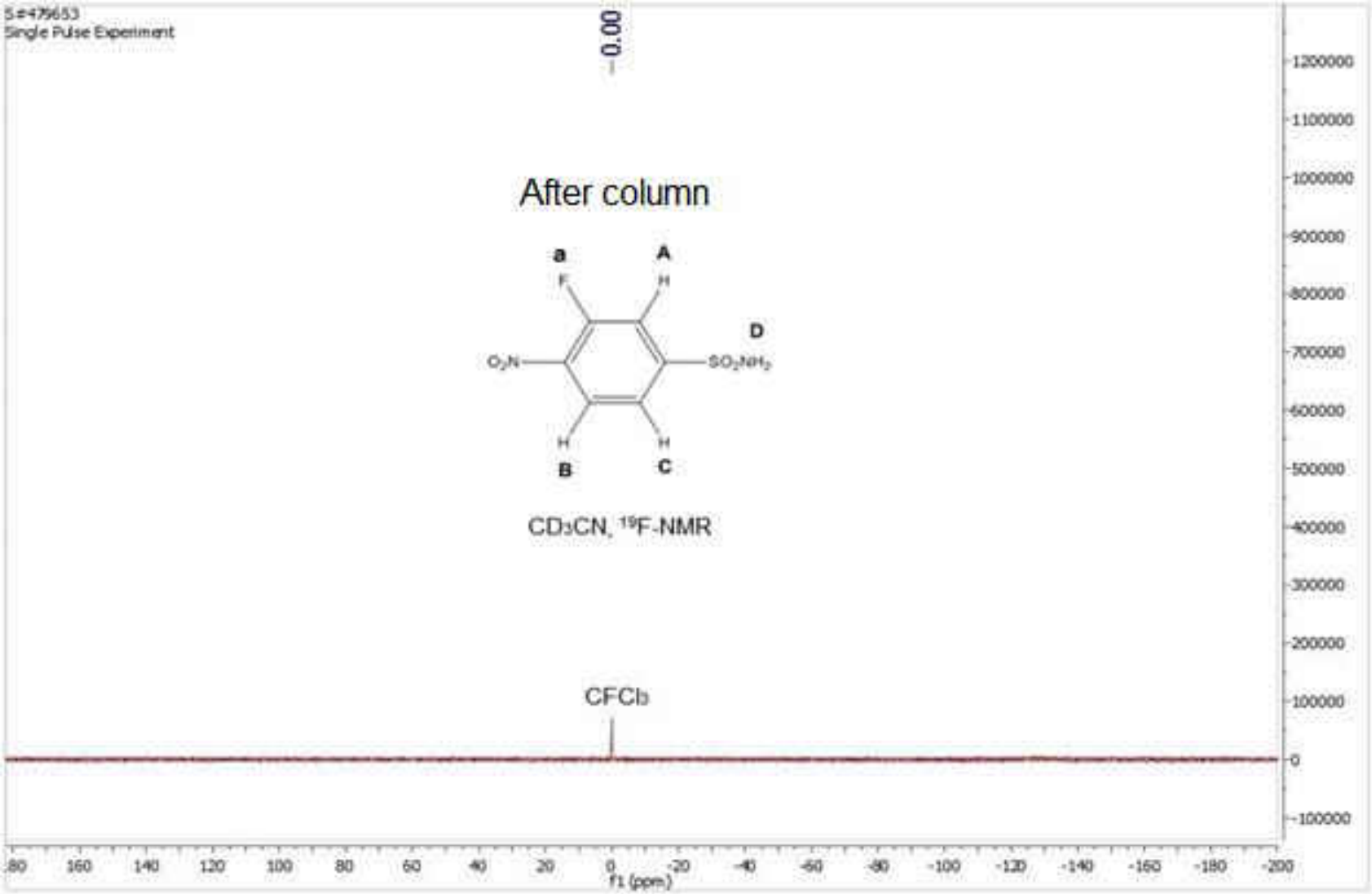
APPENDIX B1: ^{19}F-NMR Spectrum of Compound **2** (Trial 1)



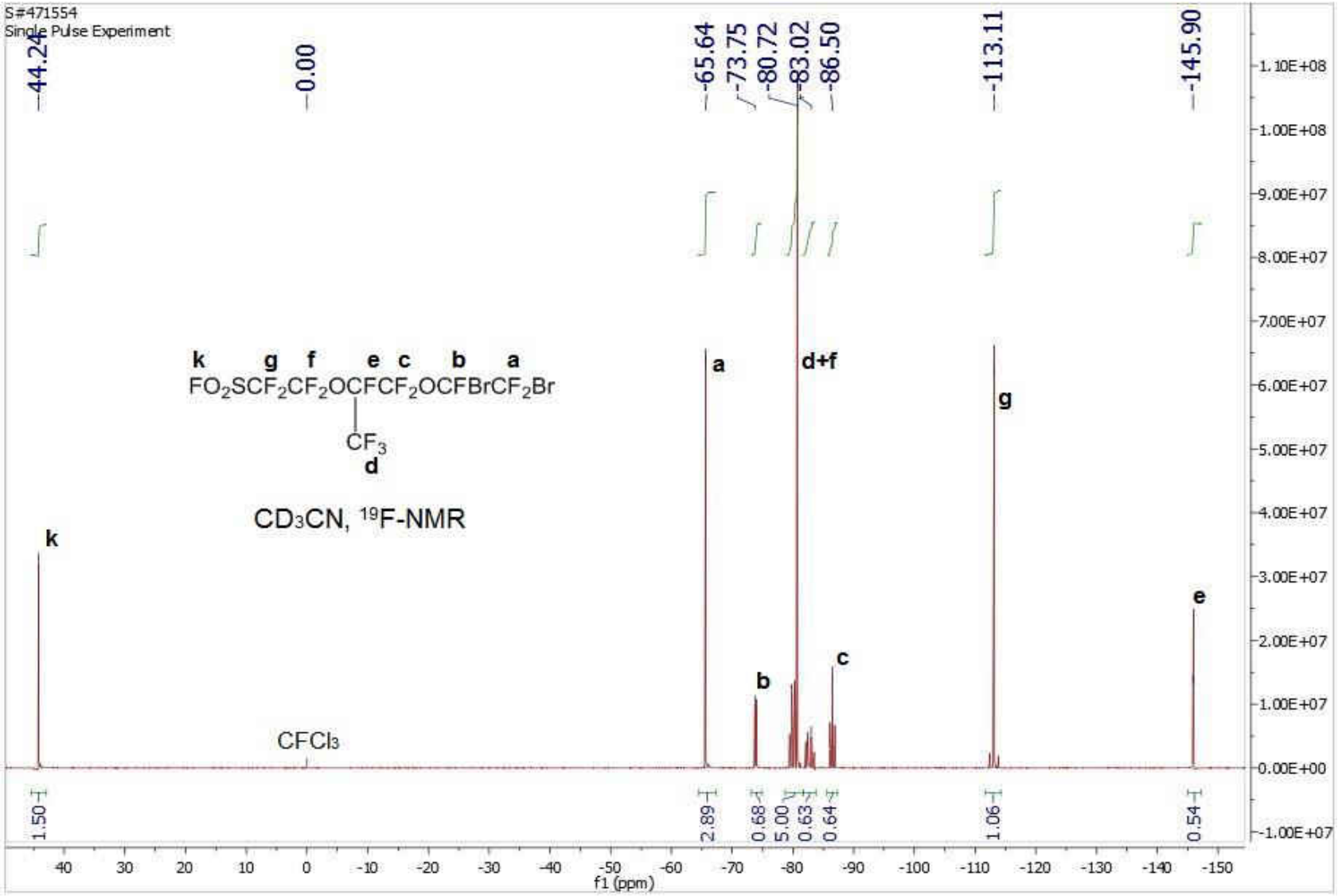
APPENDIX B2: ^{19}F-NMR Spectrum of Compound **2** (Trial 2)



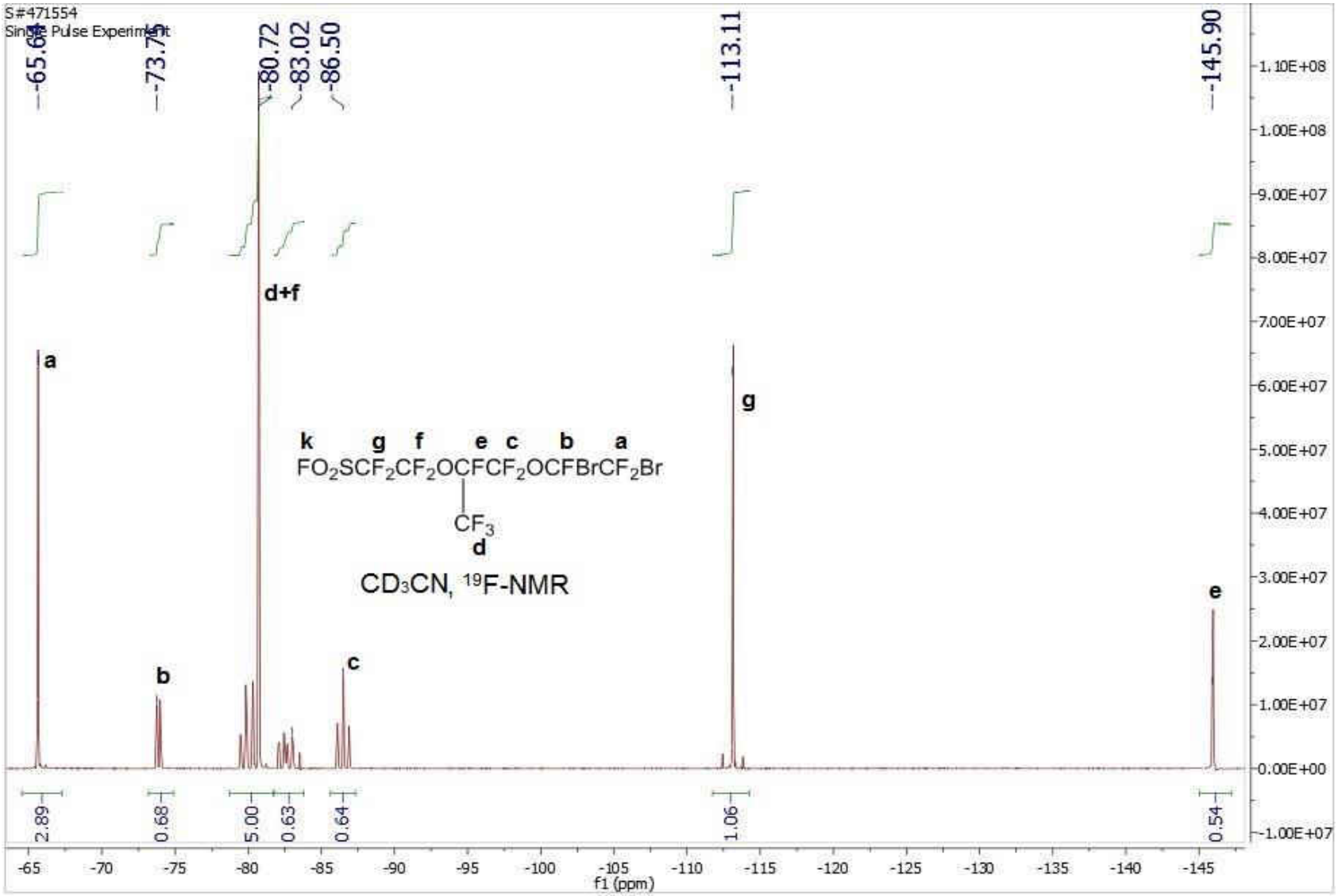
APPENDIX B3: ^{19}F-NMR Spectrum of Compound **2** (Trial 2) After Column



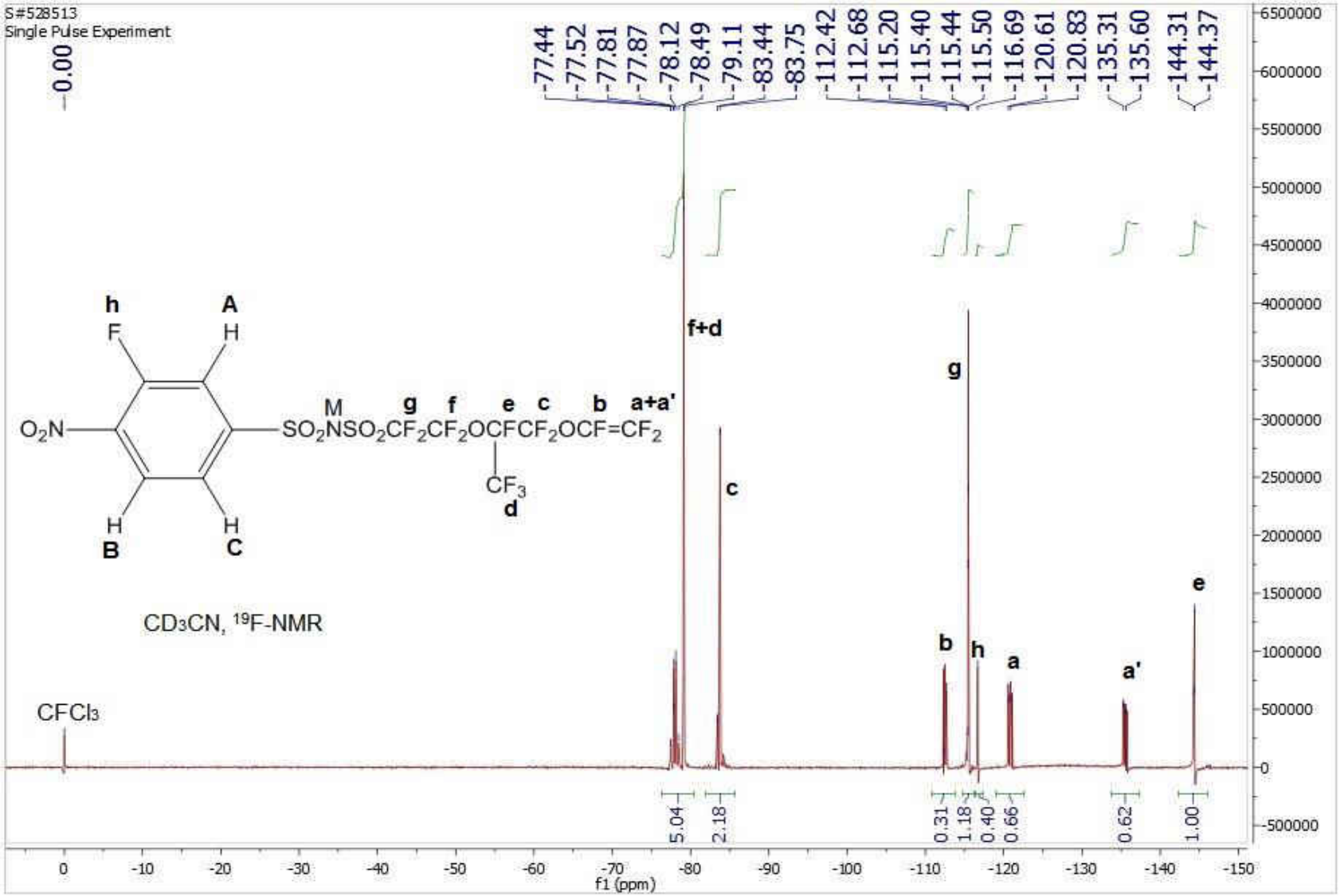
APPENDIX B4: ^{19}F-NMR Spectrum of Compound **4**



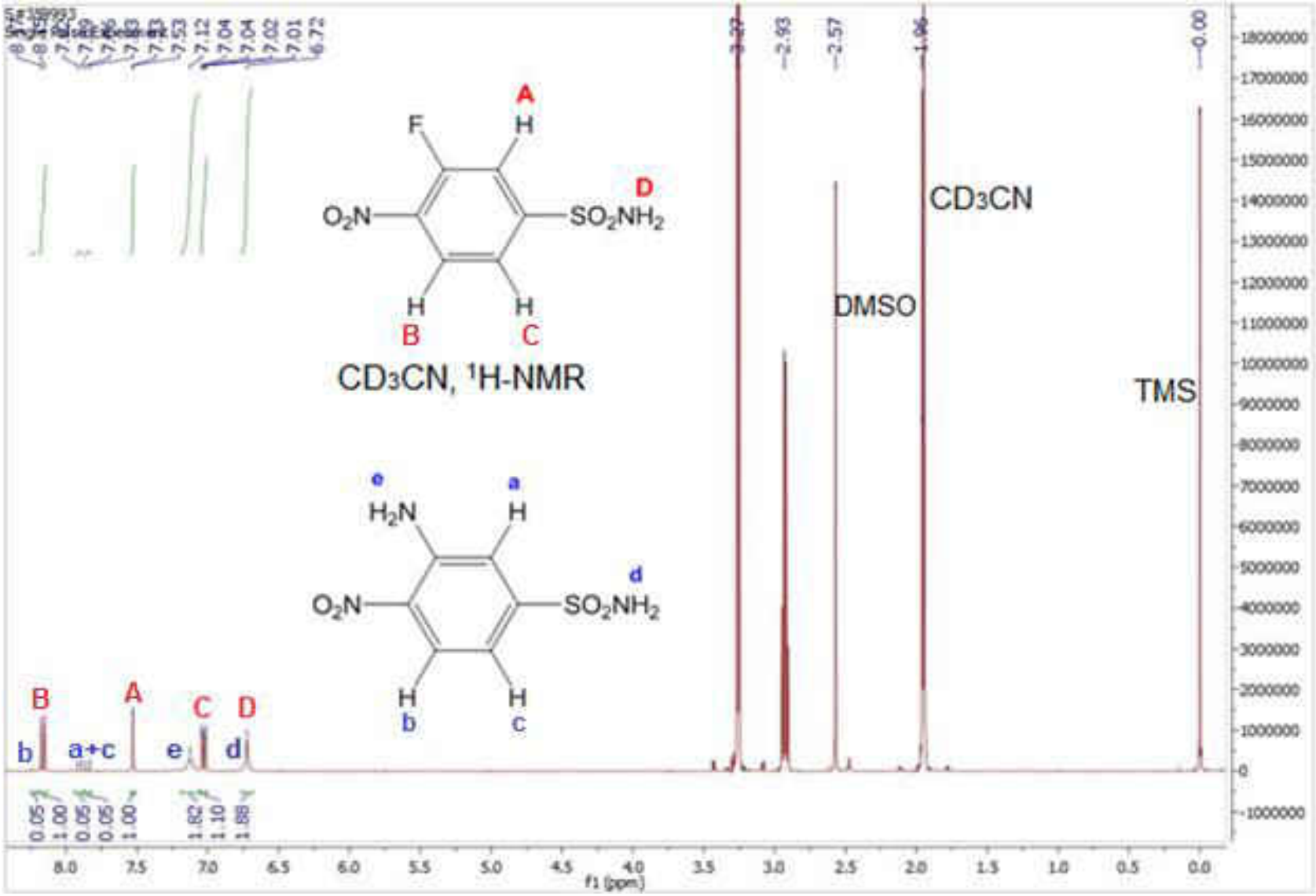
APPENDIX B5: Expanded ^{19}F-NMR Spectrum of Compound **4**



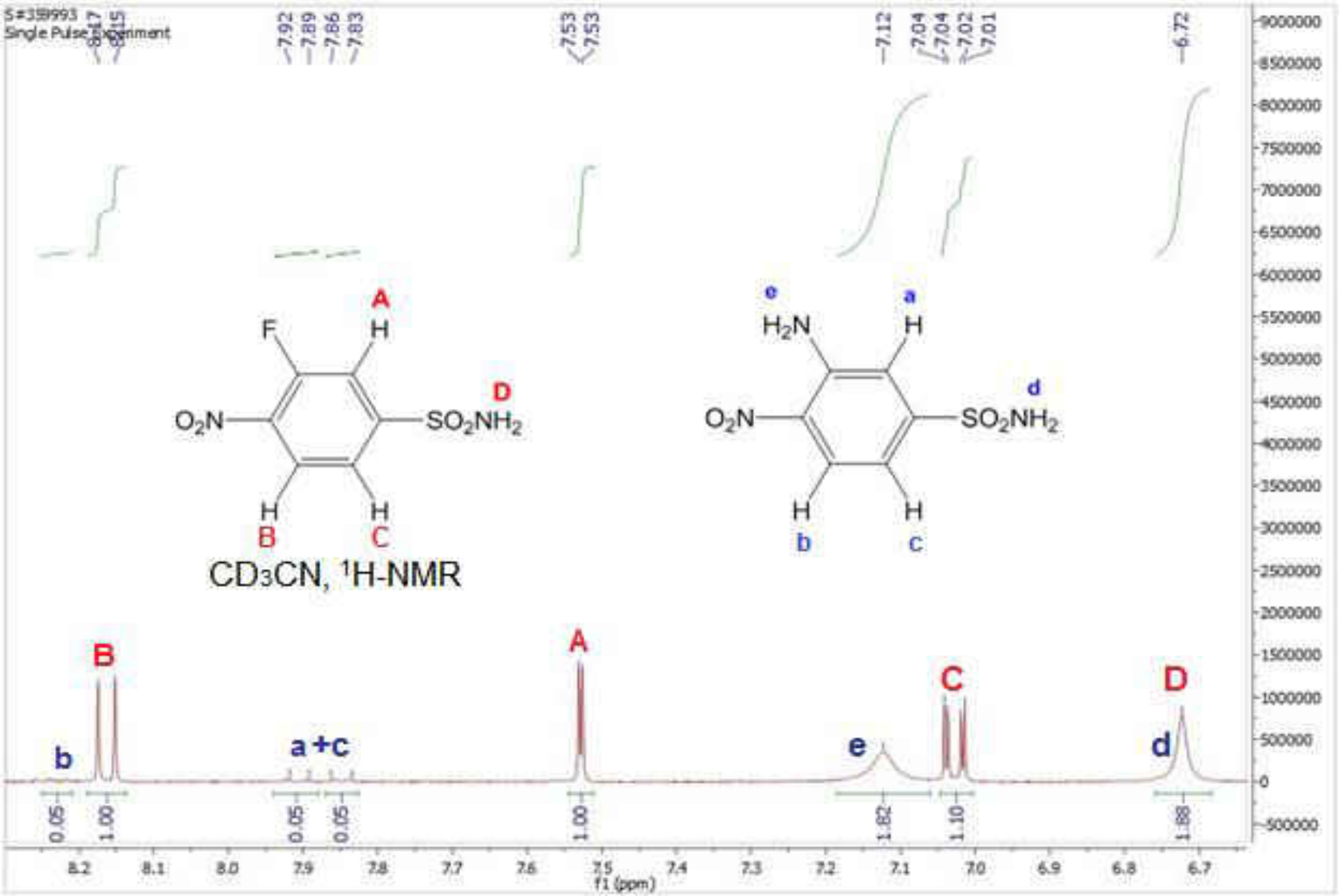
APPENDIX B6: ^{19}F-NMR Spectrum of Compound **5**



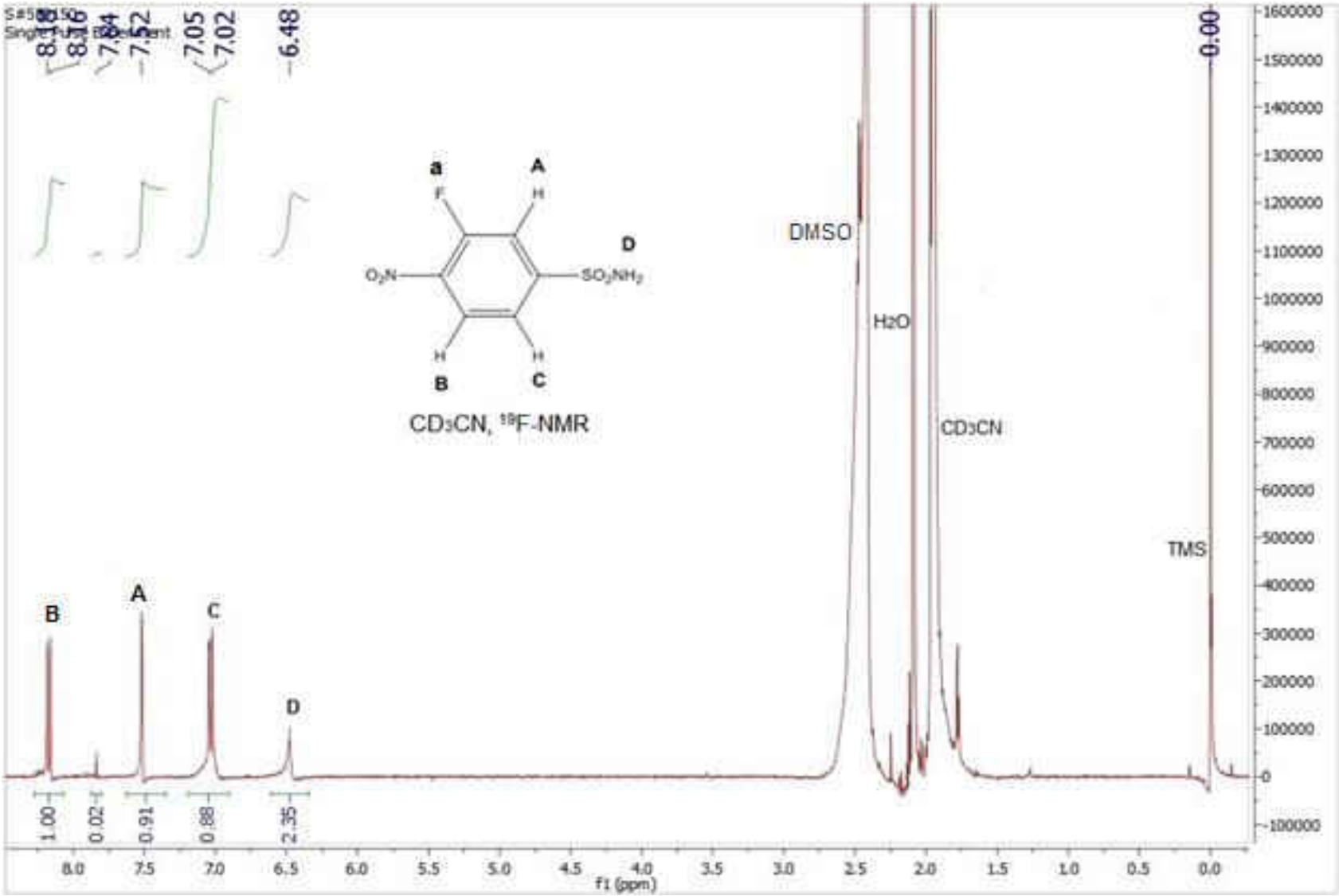
APPENDIX C1: ^{1}H-NMR Spectrum of Compound **2** Before Recrystallization (Trial 1)



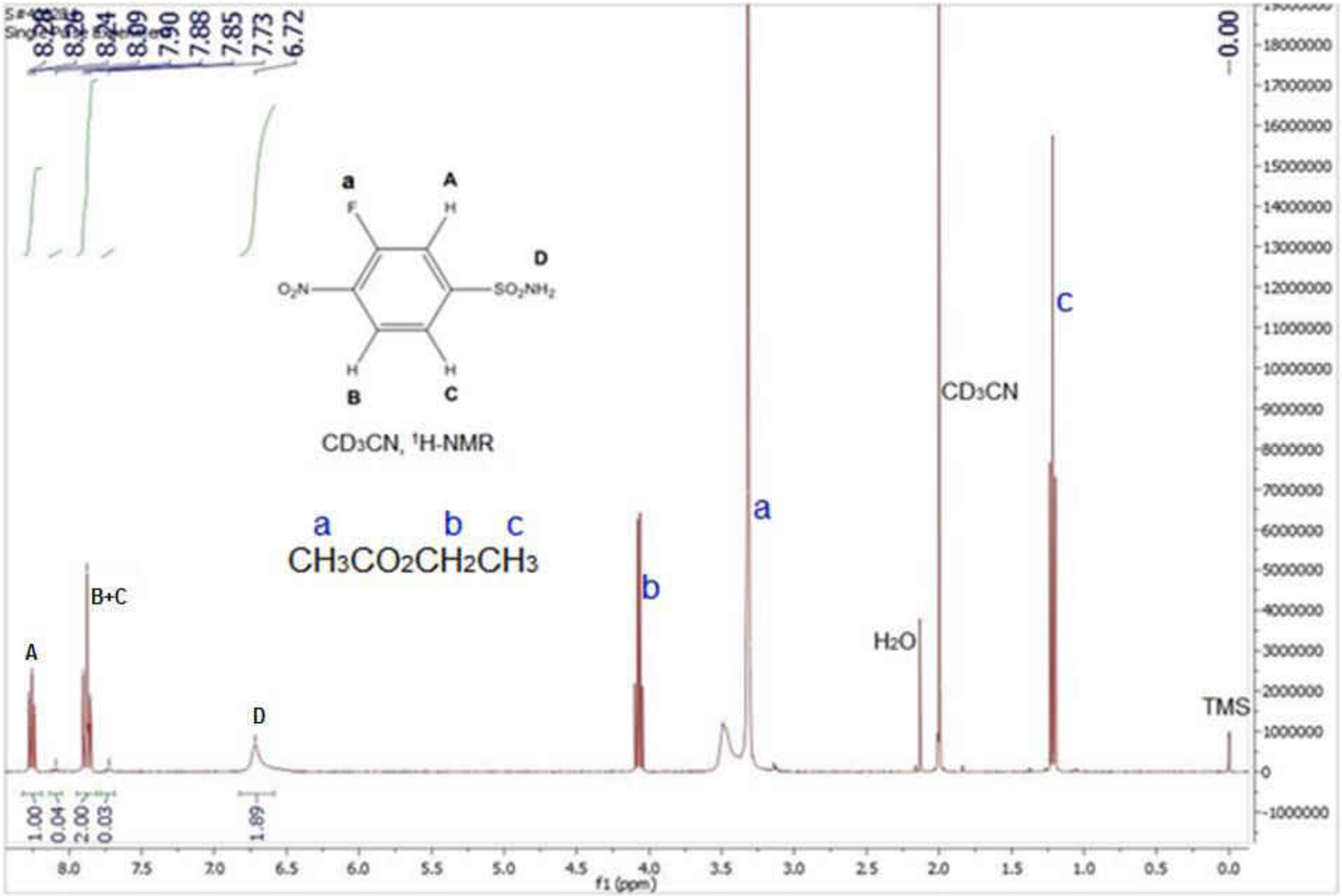
APPENDIX C2: Expanded ^{1}H-NMR Spectrum of Compound **2** Before Recrystallization (Trial 1)



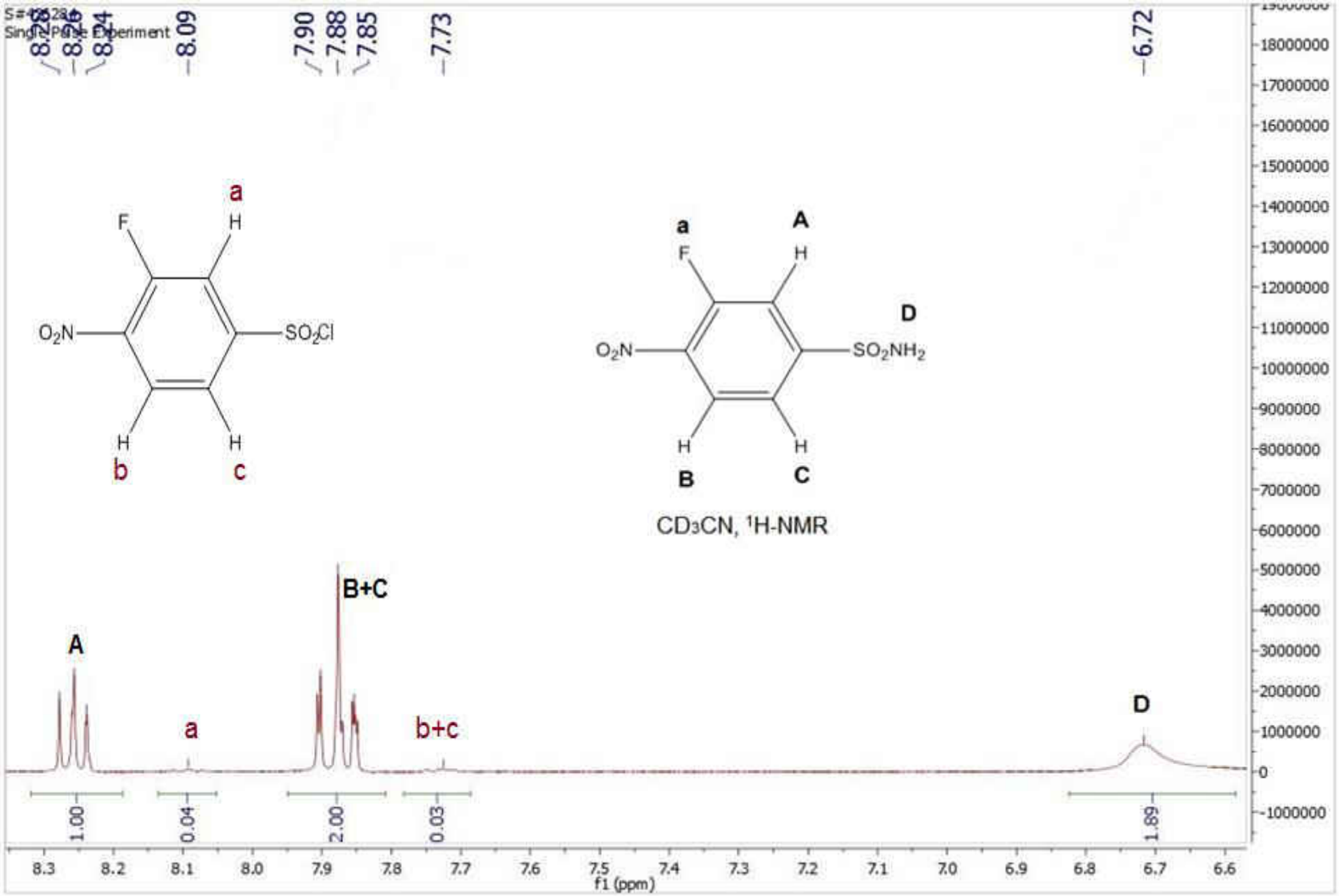
APPENDIX C3: ^{1}H-NMR Spectrum of Compound **2** After Recrystallization (Trial 1)



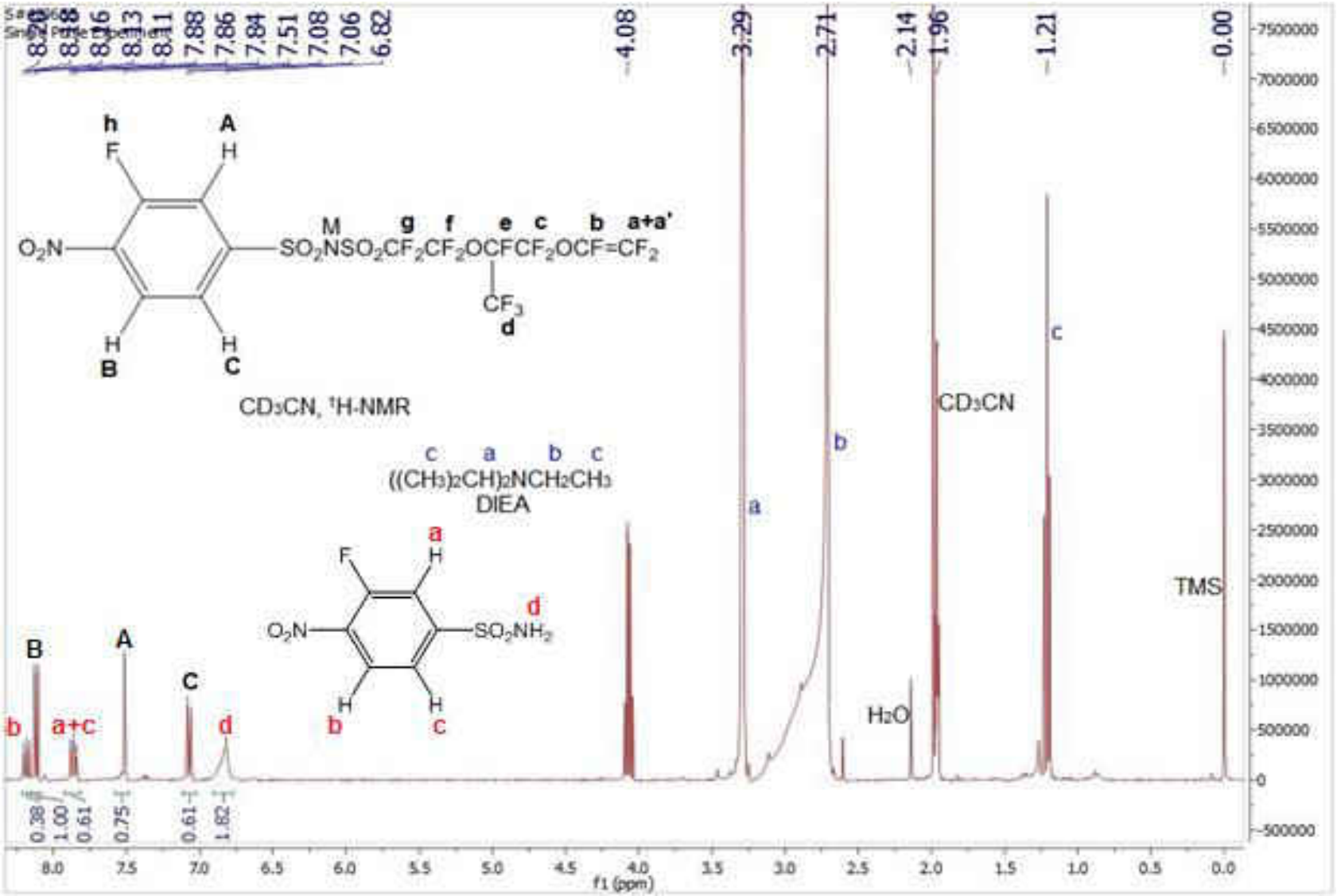
APPENDIX C4: ^{1}H-NMR Spectrum of Compound **2** (Trial 2)



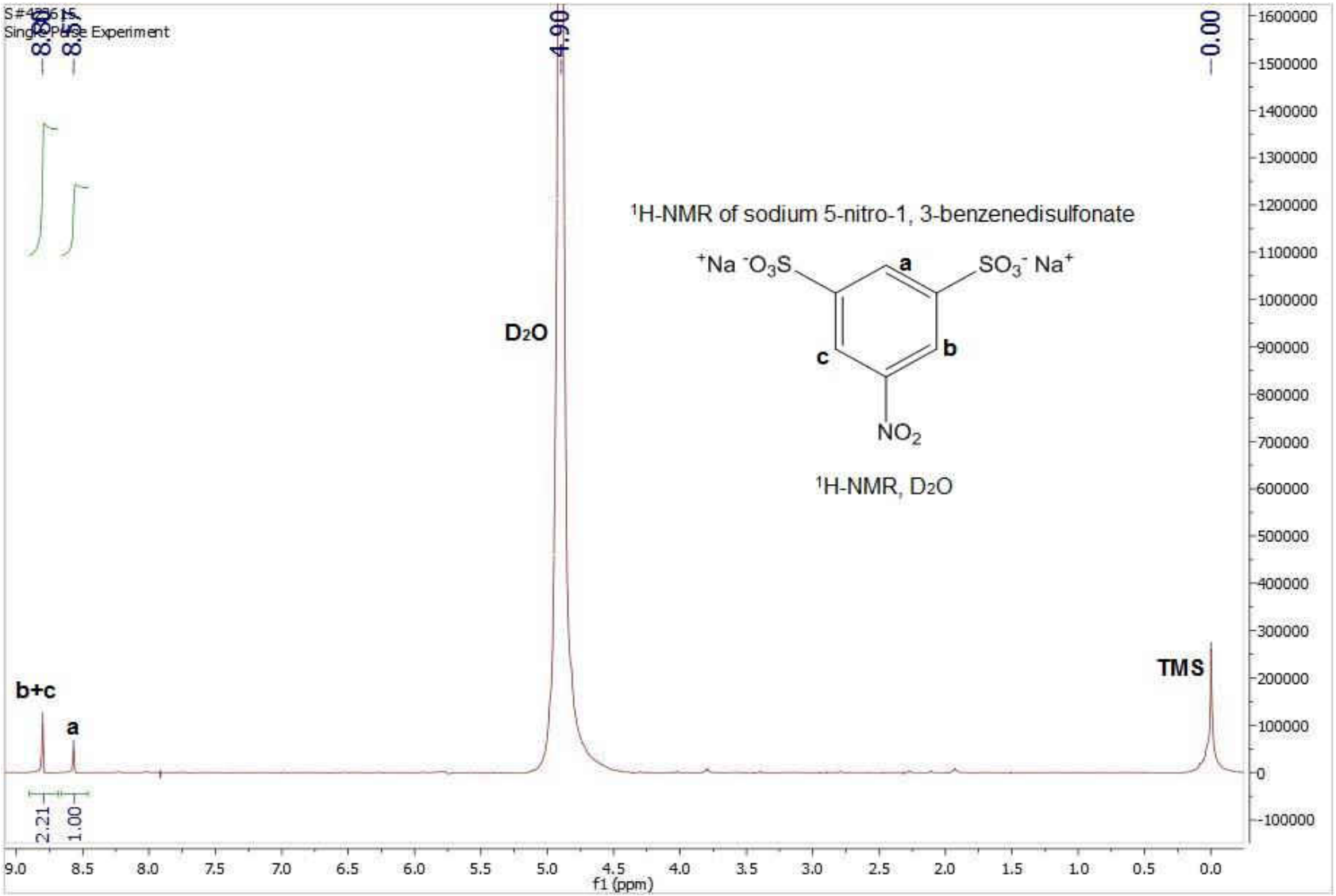
APPENDIX C5: Expanded ^{1}H-NMR Spectrum of Compound **2** (Trial 2)



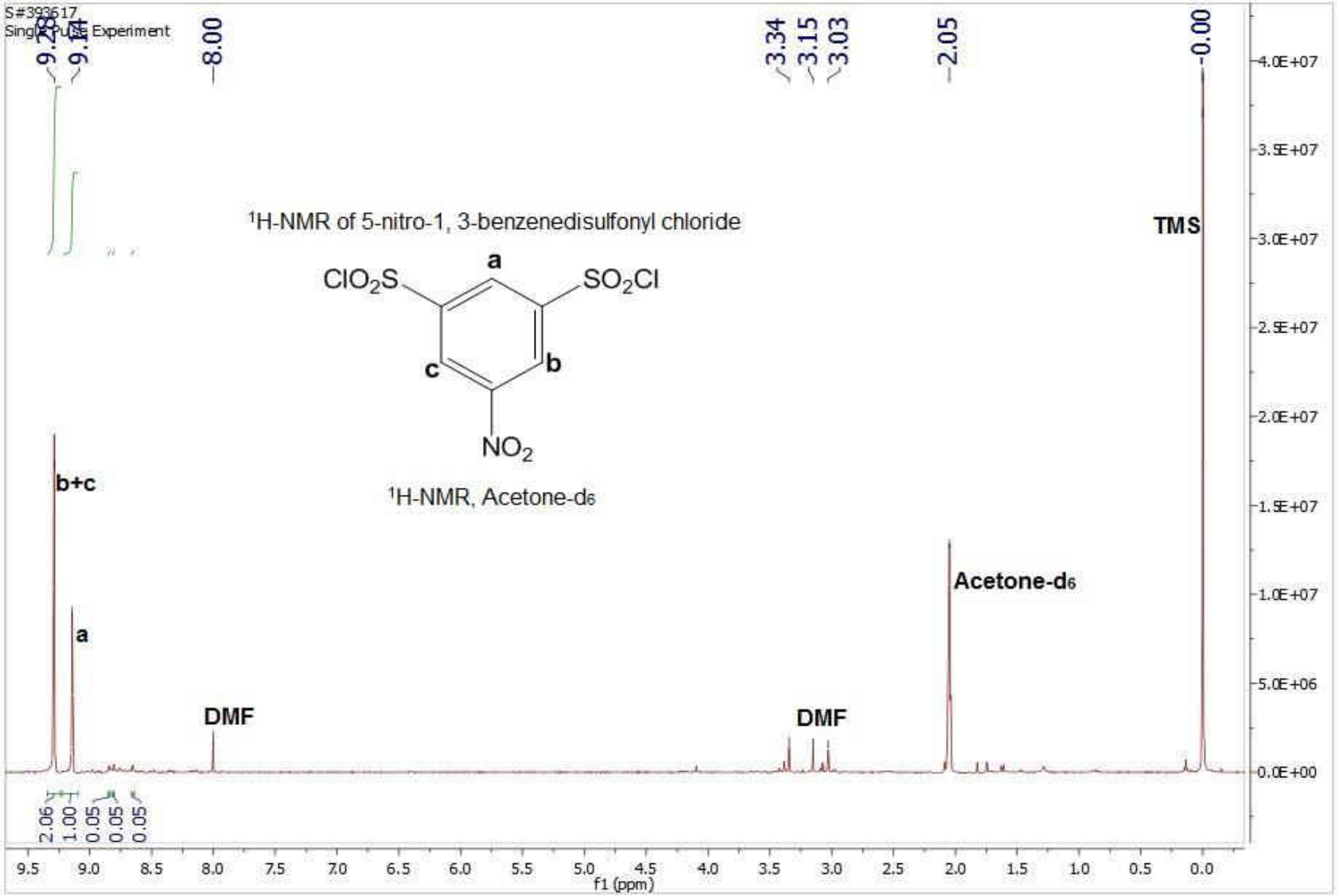
APPENDIX C6: ^{1}H-NMR Spectrum of Compound **5**



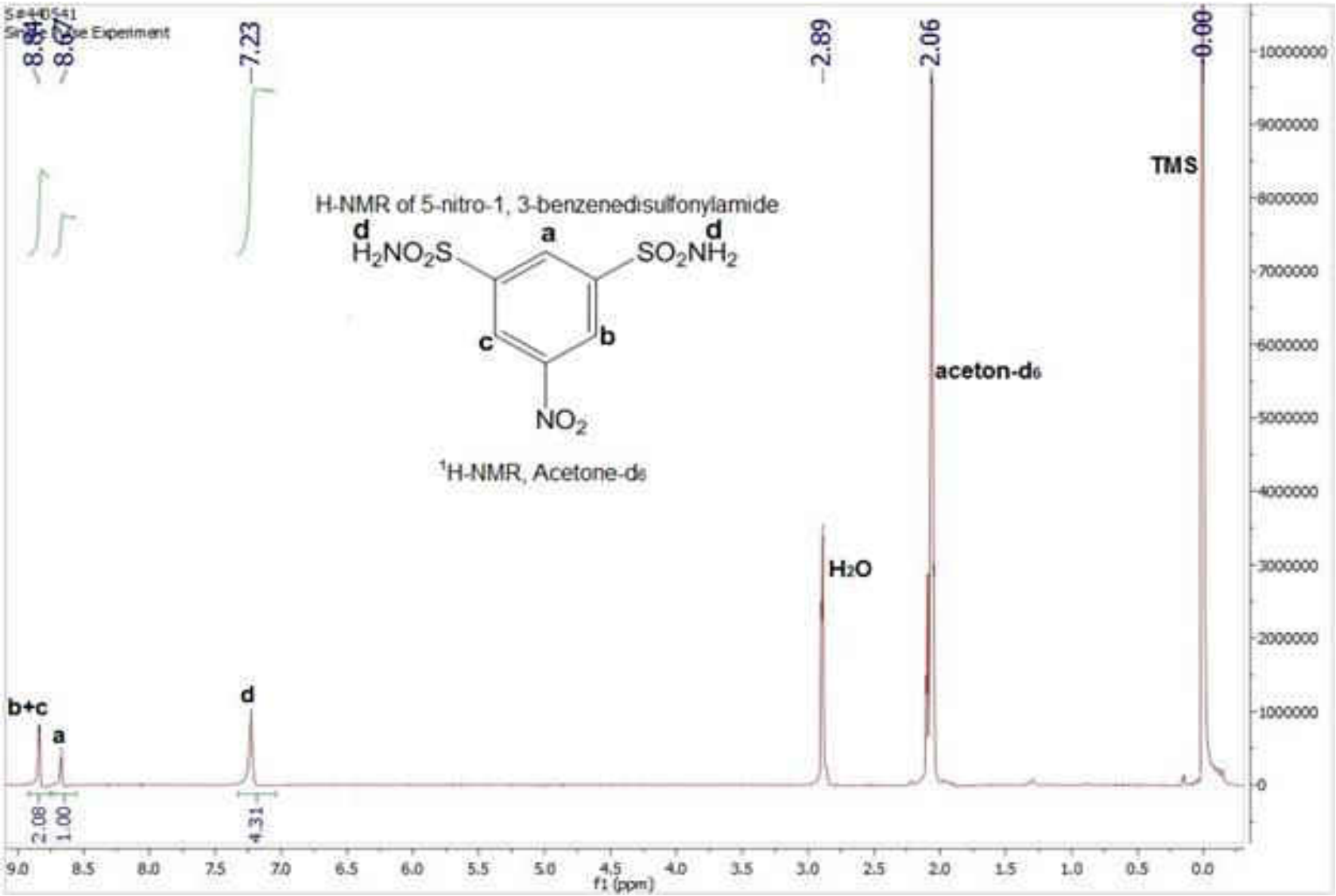
APPENDIX C7: ^{1}H-NMR Spectrum of Compound **2'**



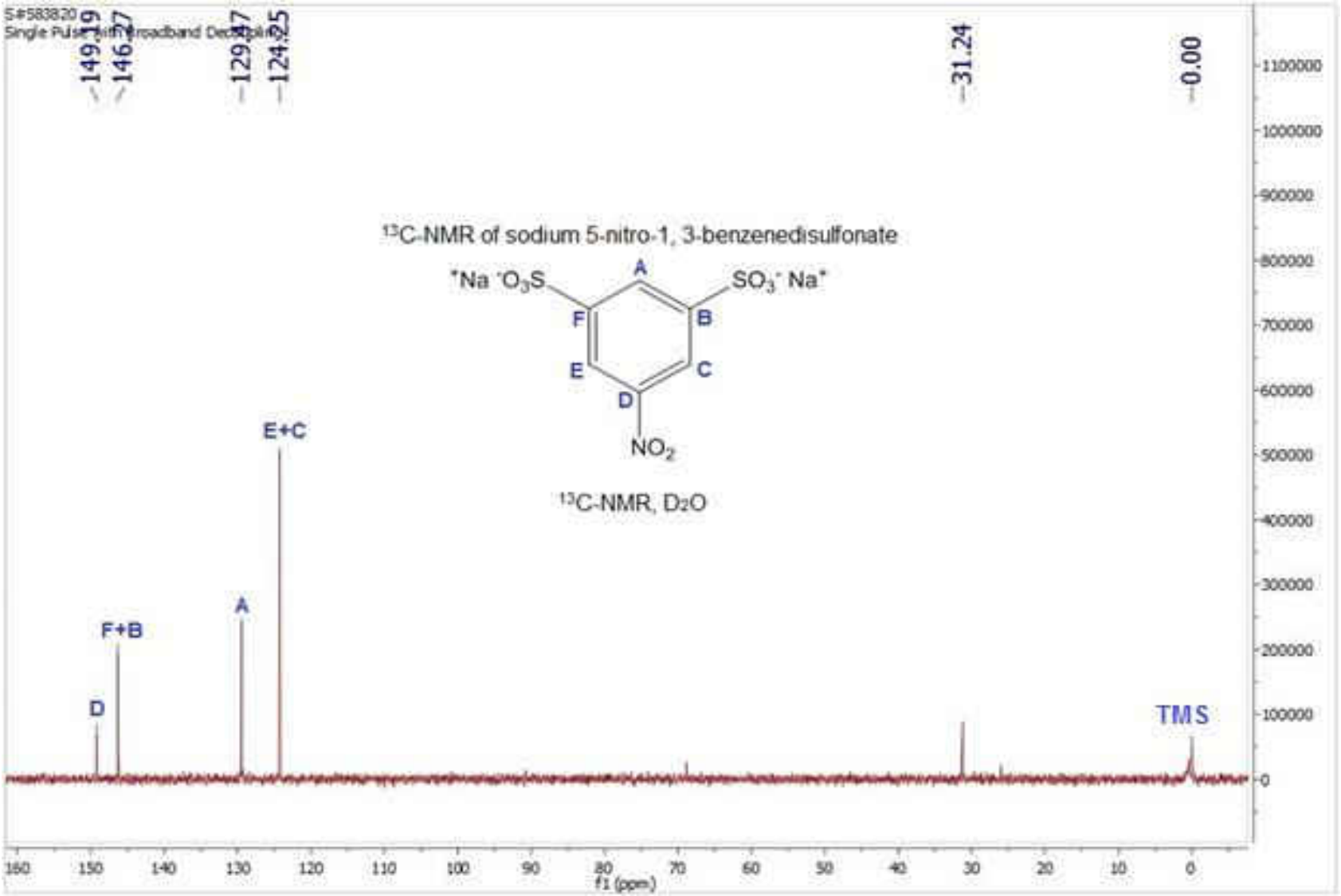
APPENDIX C8: ^{1}H-NMR Spectrum of Compound **3'**



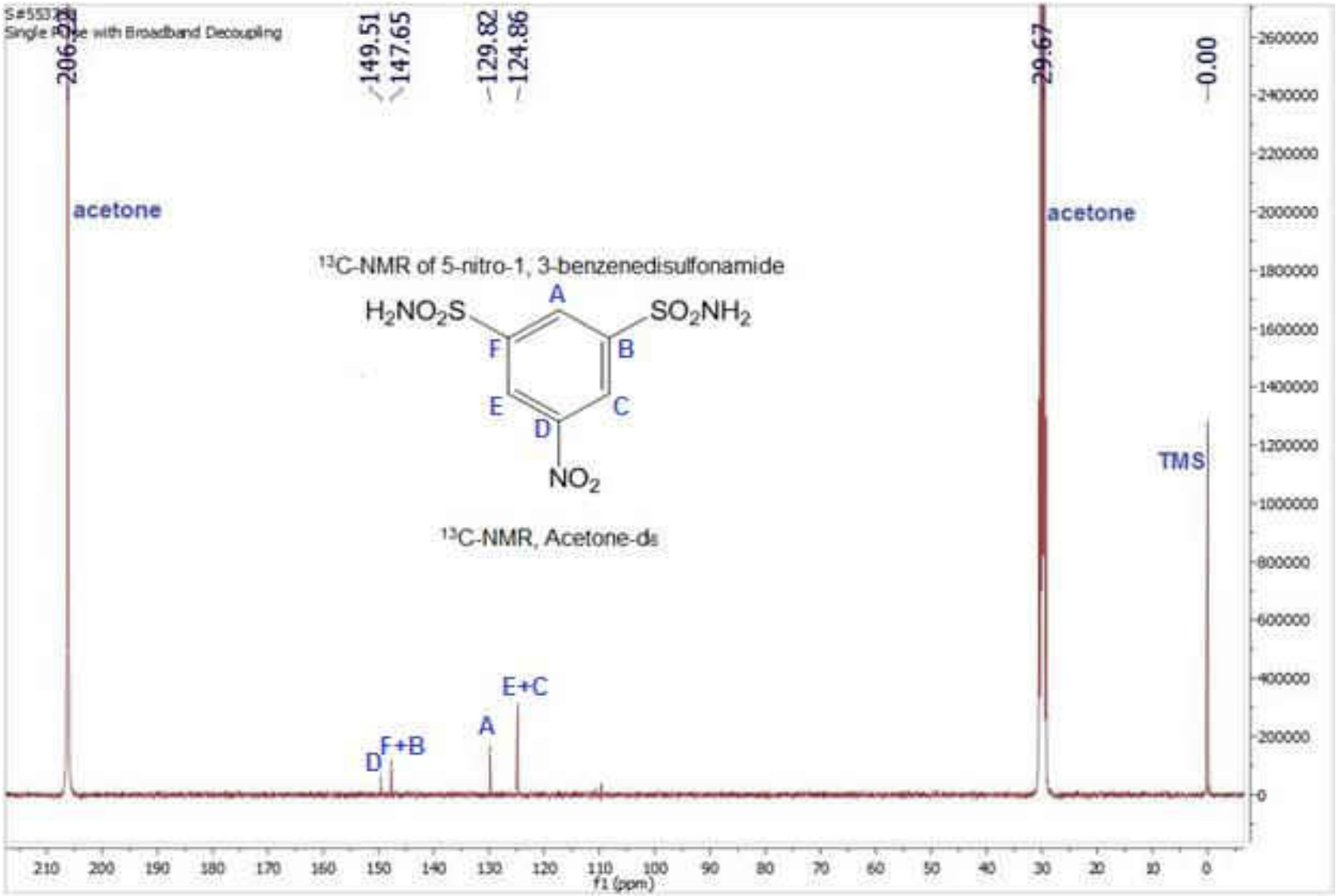
APPENDIX C9: ^{1}H-NMR Spectrum of Compound **4'**



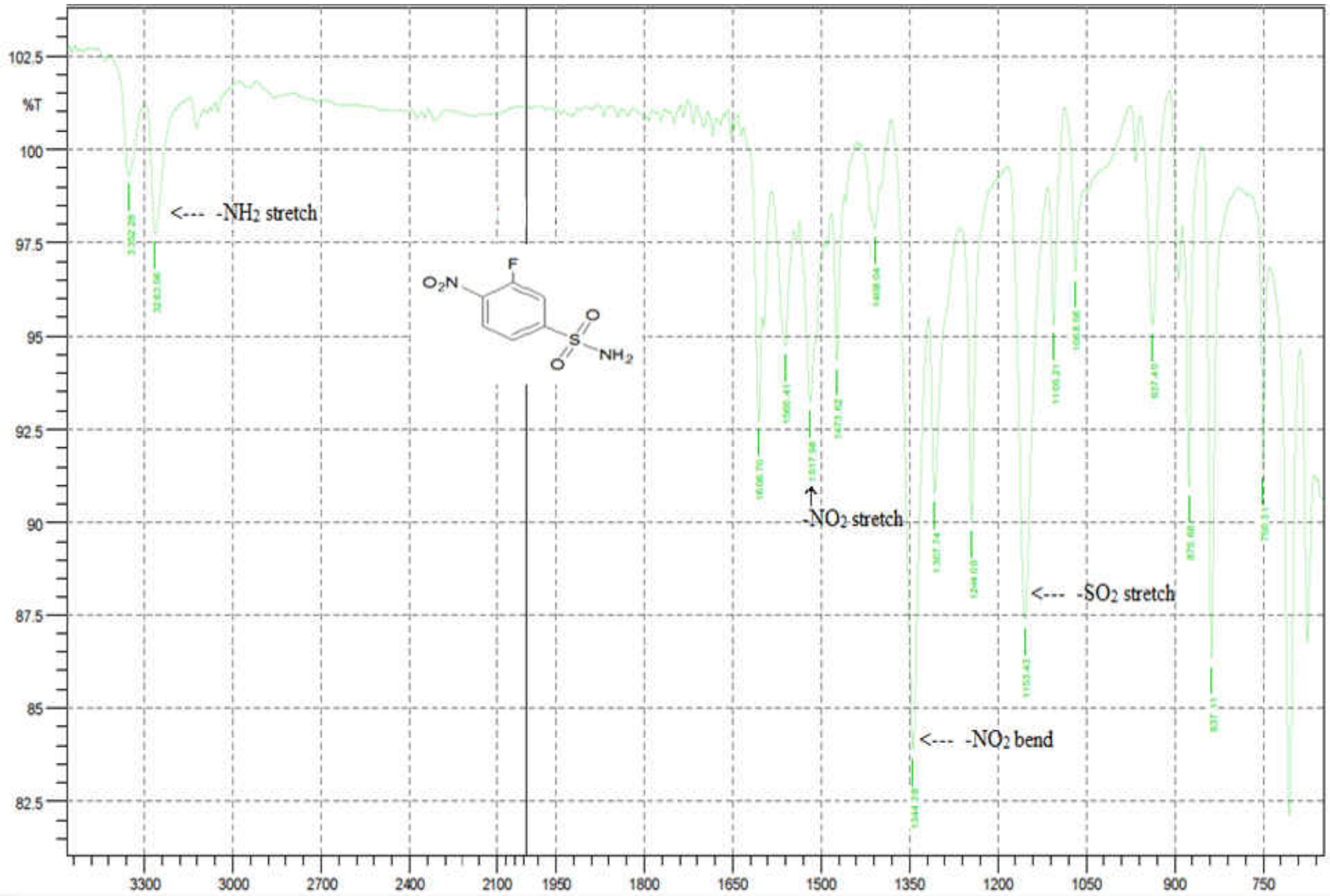
APPENDIX D1: ^{13}C-NMR Spectrum of Compound **2'**



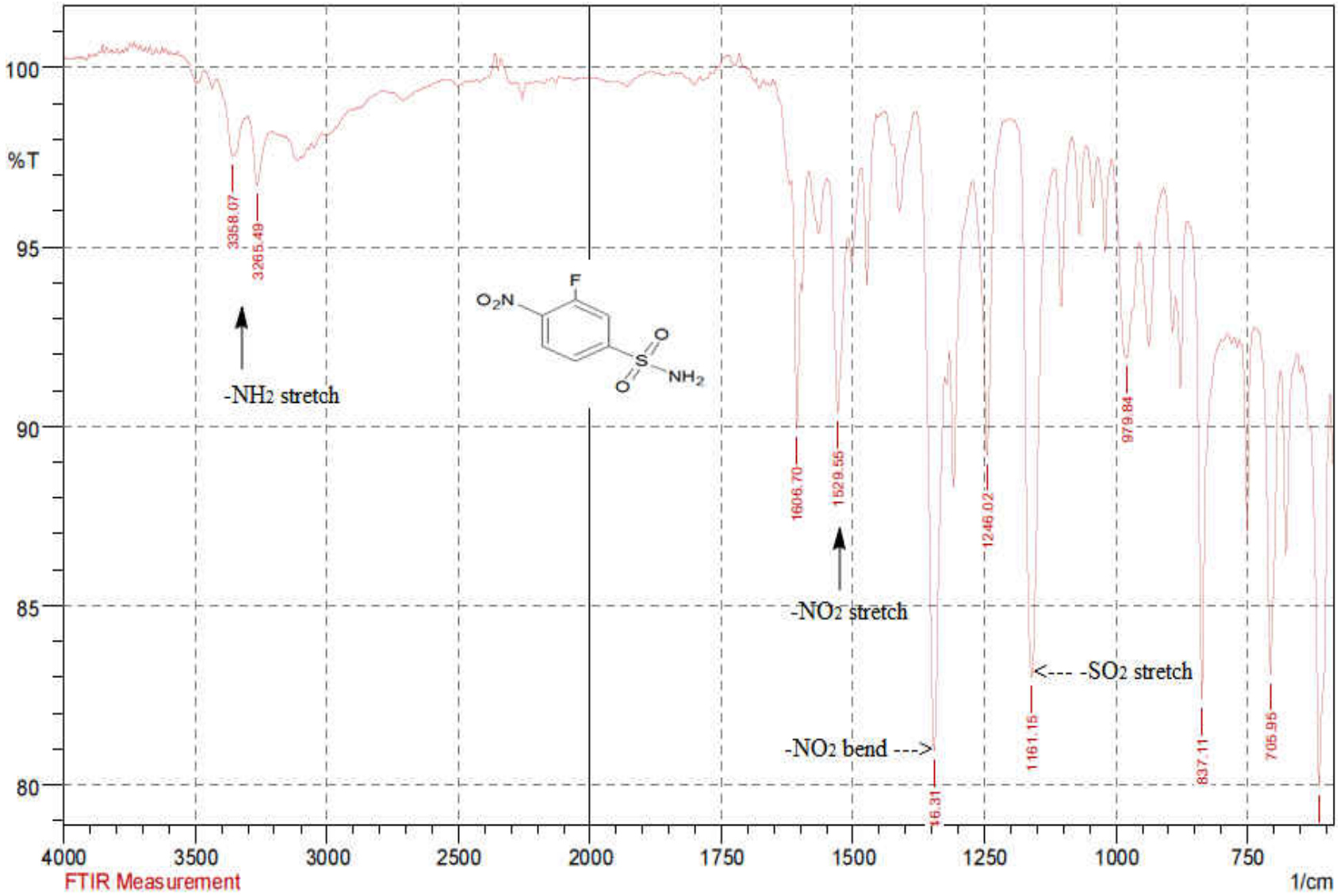
APPENDIX D2: ^{13}C-NMR Spectrum of Compound **4'**



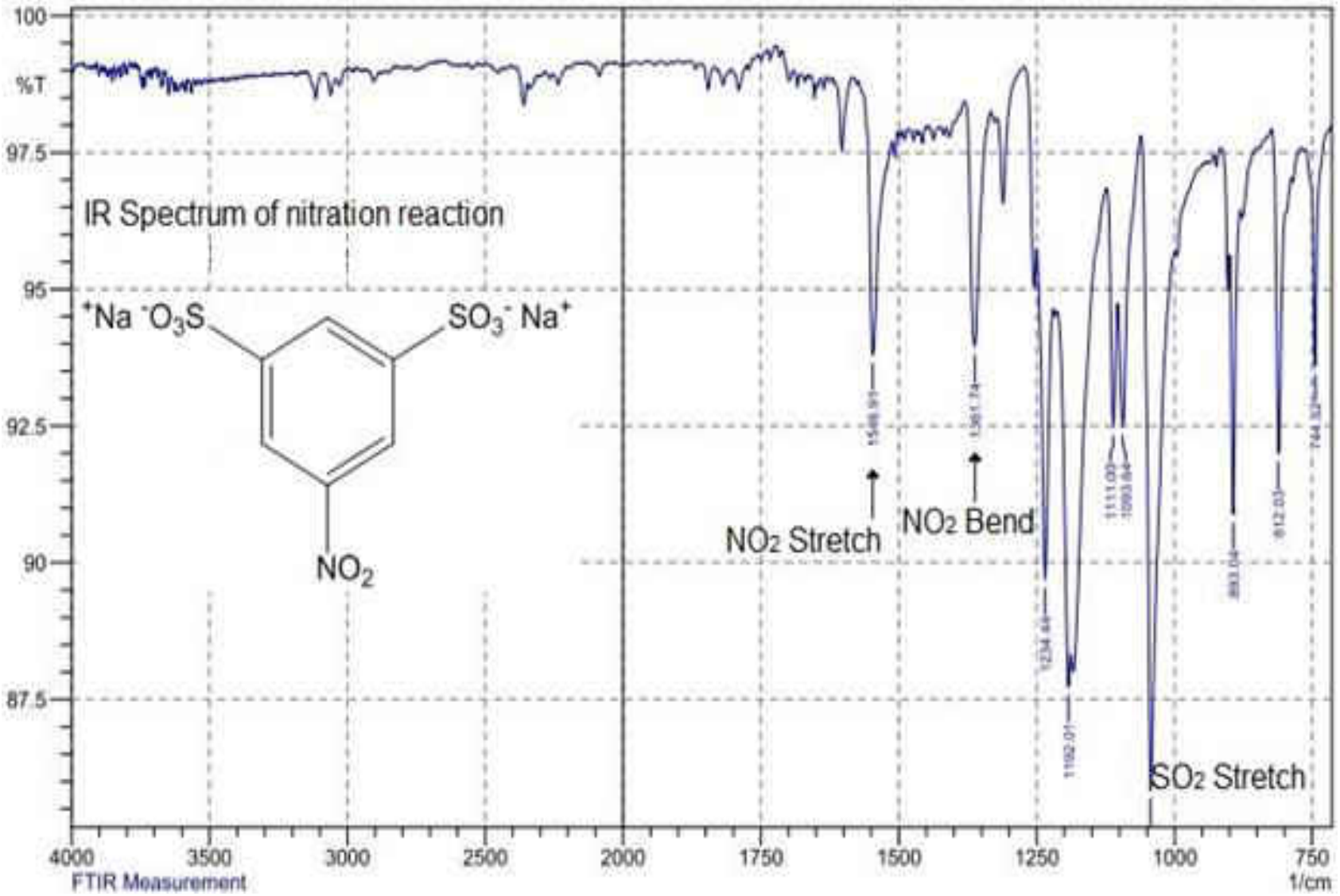
APPENDIX E1: FT-IR Spectrum of Compound **2** (Trial 1)



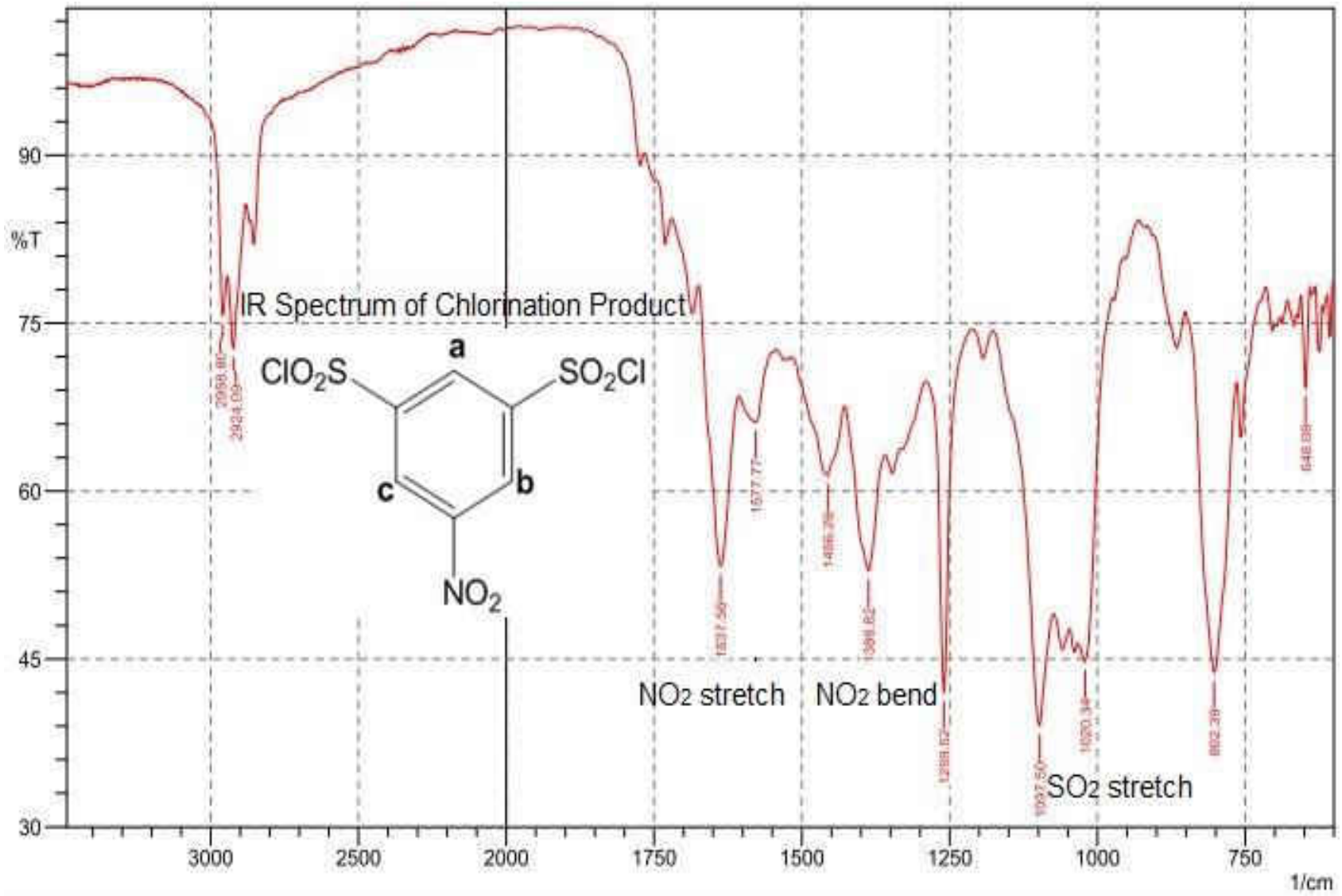
APPENDIX E2: FT-IR Spectrum of Compound **2** (Trial 2)



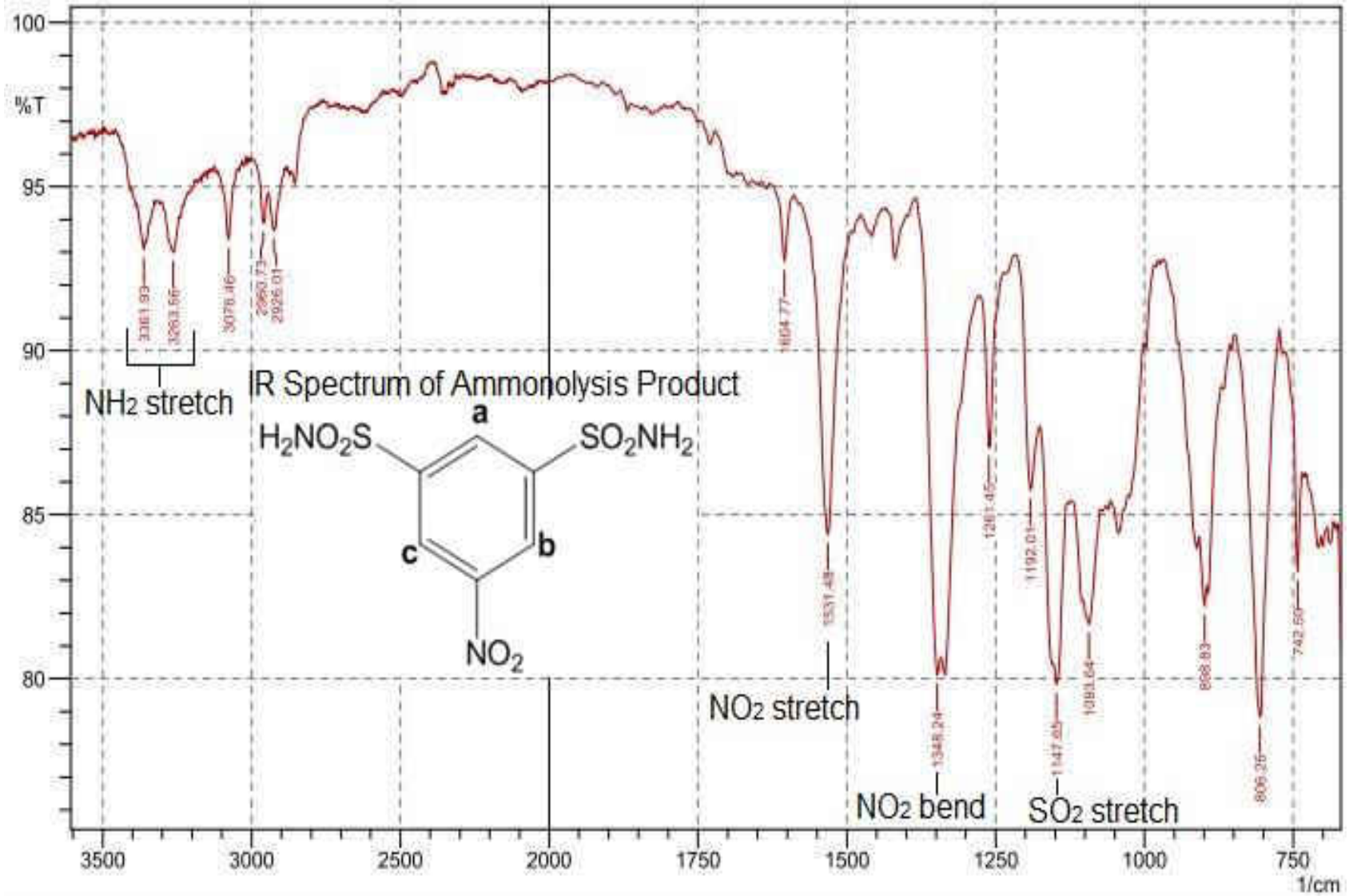
APPENDIX E3: FT-IR Spectrum of Compound **2'**



APPENDIX E4: FT-IR Spectrum of Compound **3'**



APPENDIX E5: FT-IR Spectrum of Compound **4'**



VITA

ABDULMAJEED ALAYYAF

Education: M.S. Chemistry, East Tennessee State University, Johnson City, Tennessee 2016

B.S. Chemistry, King Saud University, Riyadh, Kingdom of Saudi Arabia, 2010

Professional Experience: Teaching Assistant, King Saud University, Riyadh, Kingdom of Saudi Arabia, 2010-2011

Publications: Mei, H.; Nworie, C.; Abban, G.; Alayyaf, A.; McCloud, R. Diazonium (perfluoroalkyl) Arylsulfonylimide zwitterionic monomers analogues: Effective synthesis and thermal stability, *International journal of hydrogen energy*. **2016**, *XXX*, 1-10.

Honors and Awards: Most Outstanding Graduate Student Award, Chemistry, East Tennessee State University.