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Isaac D. Addo

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Diazonium 4-(trifluorovinyloxy) Perfluorobutanesulfonyl Benzenesulfonimide Zwitterionic
Monomer Synthesis

A thesis

Presented to

The faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

by

Isaac Darko Addo

December 2016

Dr. Hua Mei, Chair

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Dr. Greg Bishop

Keywords: Diazonium, Proton Exchange Membrane Fuel Cells (PEMFC), Nafion,
Perfluoroalkyl (aryl) sulfonimide (PFSI), Perfluorocyclobutane (PFCB), Trifluorovinyl ether
(TFVE)

ABSTRACT

Diazonium- 4-(trifluorovinyloxy) - Perfluorobutanesulfonyl Benzenesulfonimide Zwitterionic

Monomer Synthesis

by

Isaac Darko Addo

3-Diazonium- 4-(trifluorovinyloxy) - perfluorobutanesulfonyl benzenesulfonimide zwitterionic monomer (see figure 1) is proposed to be polymerized and further act as a new electrolyte for Polymer exchange membrane fuel cells (PEMFCs). One reason is that, the aromatic trifluorovinyl aryl ether (TFVE) group can easily be homopolymerized to aromatic perfluorocyclobutane (PFCB) polymer. Furthermore, the diazonium moiety in the monomer is expected to covalently attach the electrolyte to the carbon electrodes support. The perfluoroalkyl(aryl) sulfonimide (PFSI) pendant provides good chemical and mechanical stability as well as better proton conductivity. Several multi-step synthetic schemes are designed to obtain such monomer from perfluoroalkyl(aryl) sulfonimide (PFSI). Among them, the purified coupling product 4-OCF₂CF₂Br-3-NO₂-PhSO₂(M) SO₂C₄F₉ from the first approach was successfully completed. The next stages of the work will involve dehalogenation, reduction, and diazotization to achieve the targeting monomer. All the intermediates were characterized by ¹H and ¹⁹F NMR and FT-IR spectroscopy.

DEDICATION

I dedicated this research work to my late dad (Alex Ben Addo) and my mother (Joyce Addo) for their precious love, support, and words of wisdom. Also, to my siblings, Eric, Wendy, Faustina and Joseph for their words of encouragement. A very special thanks go to my lovely and indefatigable wife Abigail Addo and my adorable children Josiah Adom Darko Addo (JADA) and Lois Adubea Addo (LADO) for their unflinching support love and understanding during this stressful moments.

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LIST OF ABBREVIATIONS

AFC	Alkaline Fuel Cell
DIEA	N, N-Diisopropylethylamine
DMFC	Direct Methanol Fuel Cell
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
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFCB	Perfluorocyclobutane
PFSA	Perflurosulfonic acid
PFSI	Perflurosulfonylimide
ppm	Parts per million
TPB	Triple-phase boundary
PTFE	Polytetrafluorethylene
SOFC	Solid Oxide Fuel Cell
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

Preface

In this introduction, the background and the motivation for carrying out this work will be extensively discussed. The objectives of this research are first introduced followed by the discussion of the various types of fuel cell available. Particular elaboration involves the PEMFC's basic operation, Membrane Electrode Assembly (MEA) and its modification. Lastly, the reasons to propose the targeting monomer and design the synthetic routes to obtain this monomer are explained.

Research Aim

The research aim focuses on synthesizing a novel functionalized diazonium zwitterionic (FDZ) Monomer (Figure 1) which contains: the diazonium moiety, the trifluorovinyl (TFVE) pendant and PFSI functionality. The diazonium moiety in this monomer is expected to be chemically grafted onto the carbon electrodes. The TFVE pendant can be further polymerized as the PFCB polymer. The PFCB polymers are proposed to replace the Nafion[®] as electrolytes for PEM fuel cells because of its ease of preparation and improved flexibility [1, 2]. Also, the perfluoroalkylsulfonimide functionality provides the chemical and thermal stability for the targeting monomer and polymers.

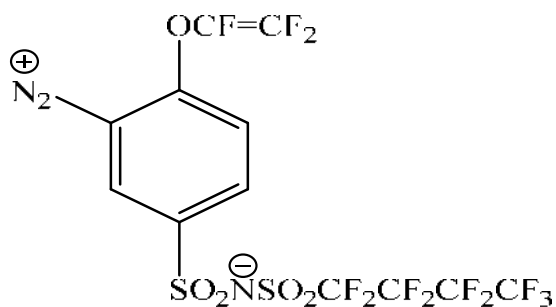


Figure 1: 3-Diazonium- 4-(Trifluorovinyl)oxy - Perfluorobutanesulfonyl Benzenesulfonimide
Zwitterionic Monomer

Fuel Cells

A fuel cell is a device that directly converts the chemical energy stored in gaseous molecules of fuel and oxidant into electrical energy. Hydrogen fuel, methanol and other hydrocarbons like natural gasses are commonly used as fuels for various kinds of fuel cells. These fuel cells offer higher efficiencies and lower emissions than the conventional technologies such as internal combustion engines. [3-5]. A fuel cell is comparable to a battery in the generation of electricity from an electrical reaction. However, the main difference is that fuel cells do not need to be recharged as long as fuel is continuously supplied. [6, 7].

As renewable energy sources, fuel cells have gained much attention over the years for their potential diverse applications which are broadly classified as portable power generation, stationary power generation, and power for transportation [8, 9].

Basically, fuel cells are made up of two electrodes, a negative electrode called anode and a positive electrode called cathode which is sandwiched around an electrolyte, gas diffusion layers (GDL) and the bipolar plates (BP). Based on the electrolytes, type of fuel and the operational temperature, fuel cells are classified into 1) polymer electrolyte membrane fuel cell

(PEMFC), also called as the proton exchange membrane fuel cell, 2) alkaline fuel cell (AFC), 3) direct methanol fuel cell 4) phosphoric acid fuel cell (PAFC), 5) molten carbonate fuel cell (MCFC) and 6) solid oxide fuel cell (SOFC). The classification determines the type of electrochemical reaction, the catalyst, the temperature range in which the cell operates and the fuel required [10- 12]. Table 1 gives a summary of the different types of fuel cells.

Table 1: Different Types of Fuel Cells

Fuel Cell Type	Operating Temperature [° 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

It can be seen from the table that direct methanol fuel cells (DMFC) shares some similarities with the PEMFC but the major difference is the unrefined methanol fuel used rather than the hydrogen fuel. For this reason, the product given off in DMFC is carbon dioxide and carbon monoxide while that of the PEMFC is only water [3, 5, 7]. Another difference will be that the DMFC operates at slightly higher temperatures than PEMFCs (between 60 and 130 °C).

This research work will focus primarily on the PEMFC due to its advantageous features over other type's fuel cells. These features include low operating temperature, high energy density, fast start-ups, low weight compactness, quiet operations and low-to-zero emissions. [13].

Polymer Electrolyte Membrane Fuel Cells (PEMFCs)

In the early 1830's, Sir William Grove (often referred to as the "Father of the Fuel Cell") discovered the possibility to generate electricity by reversing the electrolysis of water [14, 15]. Despite the earlier discovery, it was not until 1960 that General Electric Motors developed PEMFCs as an auxiliary power supply in the Gemini space flights. Thus, PEMFCs has since attracted worldwide attention as viable and clean energy sources. Due to their environmentally friendly energy sources, PEMFCs have mainly been used in the transportation sector. Other areas of application such as portable power and stationary generations are extensively explored.

The reaction occurring in the PEMFC generally involves two fuels namely hydrogen and oxygen gasses. The electrochemical reaction occurring inside the PEMFC is oxidation – reduction reaction.

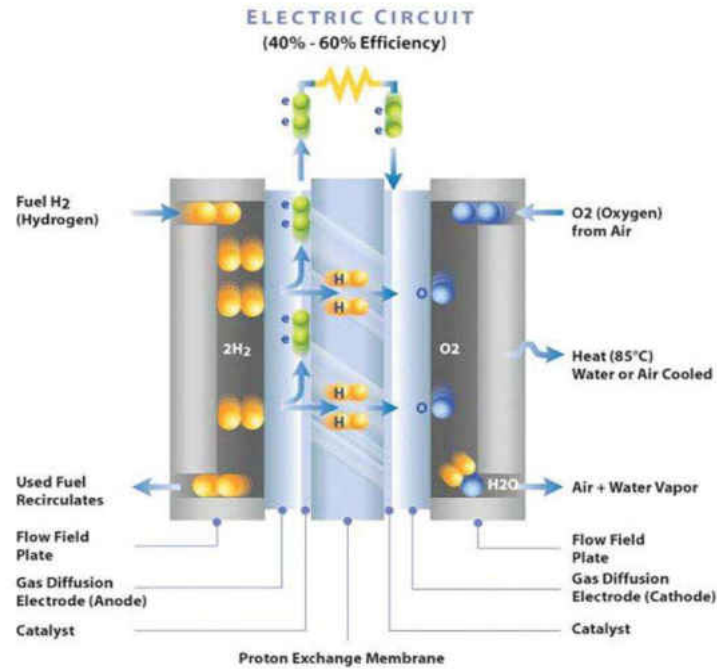
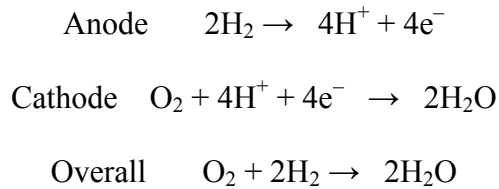


Figure 2: Schematic Diagram of a PEMFC. Used with Permission [16]

In the PEMFC, hydrogen fuel is channeled through the field flow plates to the anode while at the same time, oxygen normally from the air is channeled to the cathode on the other side of the cell. The platinum catalyst at the anode causes the hydrogen to split into protons and electrons. The proton exchange membrane is only proton conductive so ensures the transport of only protons. The electrons then travel along the external circuit where they create the electrical current. While at the cathode, the electrons and the protons combine with oxygen from the air to form the byproduct water. [17]. The electrochemical reaction occurring inside the cell is shown below in scheme 1. For better performance of the PEMFCs, the hydrogen fuel used must be clean and devoid of any contaminants such as NO_x or SO_x, CO or CO₂ (x = 2 or 3).



Scheme 1: The Chemical Reaction Occurring Within the PEMFC

Membrane Electrode Assembly (MEA)

The Membrane Electrode Assembly (MEA) is the core component of the fuel cell. A typical MEA basically comprises a polymer electrolyte membrane (PEM), a catalyst layer (CL) and gas diffusion layer (GDL) as shown in Figure 3 [14]. The membrane transports protons from the anode to the catalyst layer. The membrane must possess certain features such as high proton conductivity, low electronic conductivity, low gas permeability and good chemical and mechanical stability. [18, 19].

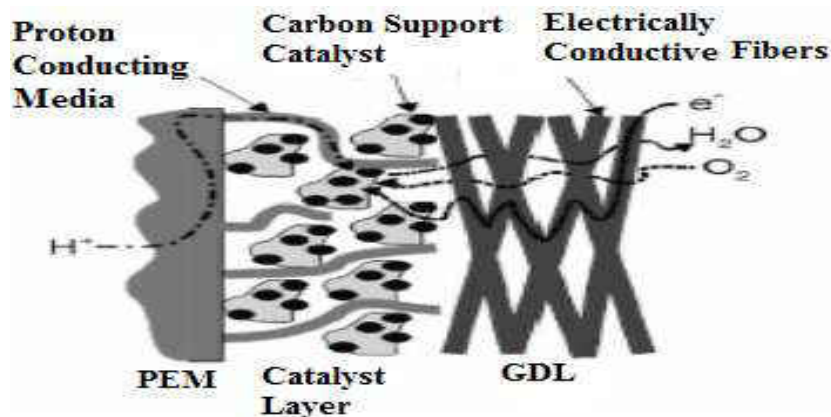


Figure 3: Expanded MEA Structure at the Cathode side. Used with Permission [14].

Inside the MEA, the CL, commonly called as active layers are where the half reaction occurs. The CL is made of carbon material, platinum nanoparticles, and fluorinated polymer resin. The reactions occur at the triple phase boundary (TPB) in the CL where the electrons, protons, and gasses meet each other. Among the three phases, the protons migrate from the membrane to the catalyst layer. The electrons move from the current collector to the catalyst through the GDL. Finally, the reactant and product gasses transport between the catalyst layer and gas channel and then flow out of the cell. Thus, how to maintain the balance of hydrophobic and hydrophilic ratio of the CL is critical for PEMFC performance. If the catalyst layer is too hydrophilic, it will limit gasses transport. Also, if the catalyst layer is too hydrophobic, the performance of the catalyst will be compromised.

Inside the GDL, the carbon material is coated with polytetrafluoroethylene (PTFE) which allows the transport of gasses through the pores of the active catalyst layer. Water management is also a key issue. The reason is that if the carbon pores are congested with too much water, it will be troublesome for gasses pass through [20].

The catalyst plays a very important role in the overall performance of the fuel cell. The commonly used catalysts in the CL are platinum or platinum alloys. Figure 4 shows the traditional MEA where the efficiency of the platinum catalyst employed is around 60 % due to the random deposition of the platinum catalyst onto the dense carbon electrode. [21]

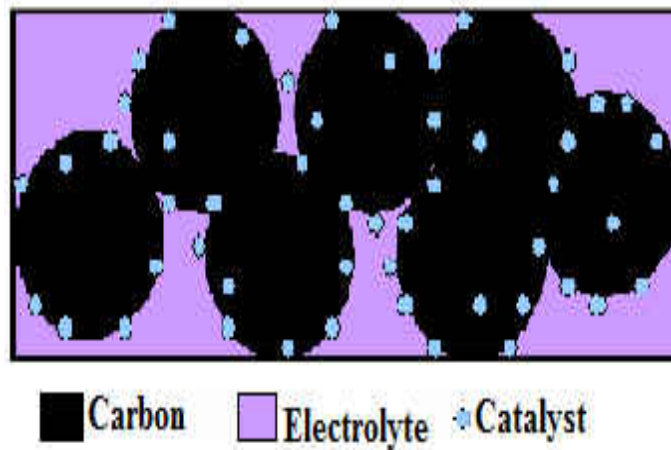


Figure 4: Traditional Dense Carbon Electrode in PEMFC. Used with Permission [21].

Proposed MEA system

Thus a new porous electrode is proposed to replace the traditional dense electrode (Figure 5). The idea is to chemically graft the PFCB polymers onto the carbon support. Diazonium chemistry provides the avenue to covalent bond the PFCB polymer and carbon electrode [22]. It is expected that the cost of PEM fuel cells will be reduced since the platinum catalyst can be utilized more efficiently and the less amount of expensive electrolyte is needed [23-24]. Scheme 2 shows the grafting of a functionalized diazonium zwitterion on the carbon electrode via either the electronic or the thermal reaction [25].

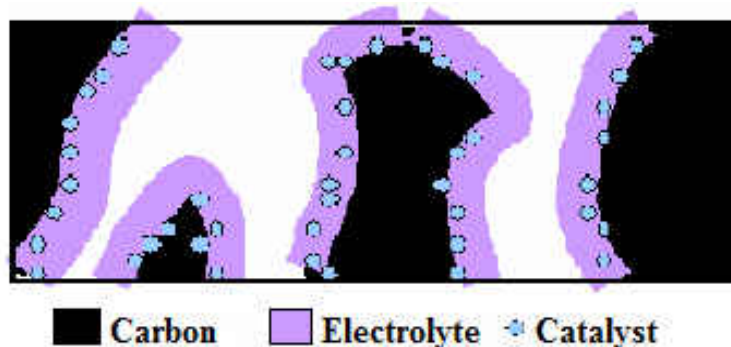
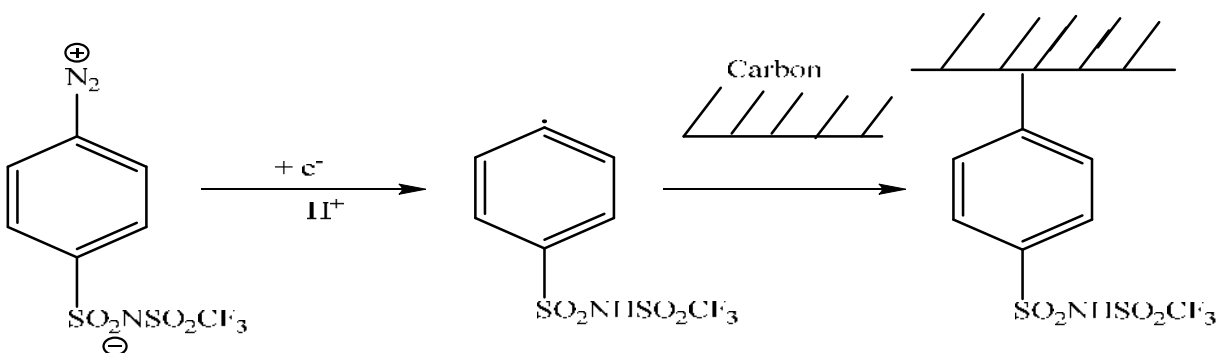


Figure 5: Proposed MEA in PEMFC. Used with Permission [21].



Scheme 2: The Grafting of Functionalized Diazonium Zwitterion onto a Carbon Electrode [25].

Polymer Electrolyte Membrane

One of the key components of MEA is the polymer membrane electrolyte. The widely used or well-known membrane electrolyte is the perfluorosulfonic acid (PFSA) polymers. Its stability in oxidation and reduction conditions comes from the polytetrafluoroethylene (PTFE) backbone [26]. One example of PFSA polymers is Nafion® polymers [27]. They possess strong chemical and thermal stability, high conductivity ($>0.1 \text{ Scm}^{-1}$) at high temperatures, and low

dielectric constant. [28-29]. Figure 6 shows the chemical structure of the Nafion® polymer which is prepared from nafion monomer, perfluoro (4-methyl-3, 6-dioxaoct-7-ene)-sulfonic acid and tetrafluoroethylene (TFE) [30].

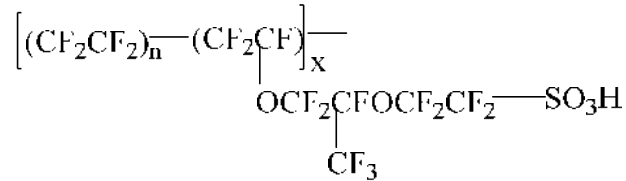


Figure 6: Chemical Structure of Nafion® Polymer [30]

In spite of the advantageous features of Nafion® polymer, there are certain drawbacks that limit the performance of PEMFC. For example, the Nafion® polymers tend to form large rod-shaped like micelles which then blocks the microporous carbon electrode. Thus the membrane is washed out after some time leading to poor ion conductivity. Also, at higher temperatures, the sulfonic acid component dehydrates into anhydride (-SO₂OSO₂-) leading to lower protonic conductivity. [31]. Also, the cost of the fabrication process of Nafion® limits the commercialization of PEMFCs. [32, 33].

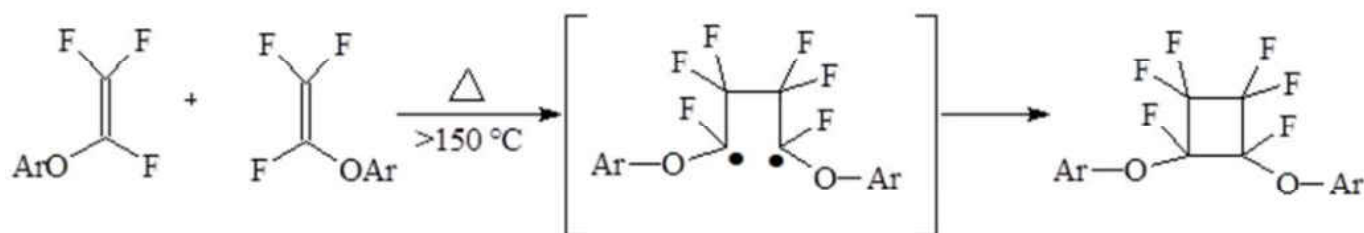
Apart from the conventional PFSA polymers, there are other polymers designed as electrolytes for PEMFCs [34]. A summary is shown in table 2.

Table 2: Categories of Membranes [34].

Membrane Category	Structure	Example	Physical properties
Perfluorinated polymer	1. Fluorinated backbone like PTFE 2. Fluorocarbon side chain 3. Ionic clusters consisting of sulfonic acid ions attached to the side chains	1. PFCA 2. PFSA 3. PFSI	Membranes are strong and stable in both oxidative and reductive environments
Partially perfluorinated polymer	1. Fluorocarbon base 2. Hydrocarbon or aromatic side chain grafted onto the backbone, which can be modified	1. PTFE-g-TFS 2. PVDF-g-PSSA	Membranes are relatively strong in comparison to pf but degrade fast
Non-perfluorinated hydrocarbon polymer	Hydrocarbon base, typically modified with polar groups	1. NPI 2. BAM3G	1. Membrane possesses good mechanical strength 2. Poor chemical and thermal stability

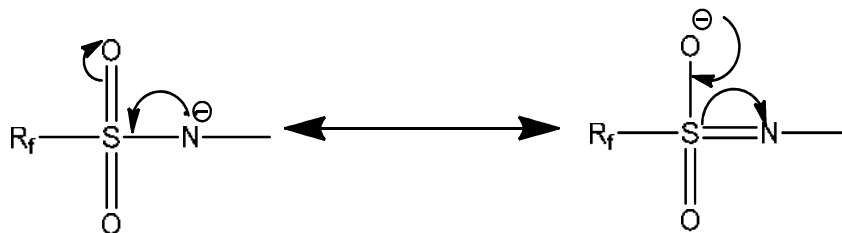
The functionalized perfluorocyclobutane (PFCB) polymers are proposed to replace the traditional PFSA polymers. The main distinguishable feature about PFCB polymers is that they

are safe and facile to prepare to compare to traditional PFSA polymers. They also show excellent solubility and processability, good thermal and mechanical stability and low dielectric constant [35-37]. PFCB polymers can be prepared by the thermal $[2\pi + 2\pi]$ cycloaddition of aryl trifluorovinyl ethers. Such cycloaddition is thermodynamically favored for fluoro olefin due to increased double-bond strain, lower C=C π bond energy and the strength of the C-C single bond formation. [38-40]. It was reported that the cycloaddition of fluoro olefin was first discovered by Lewis and Naylor at Dupont from research on pyrolysis of Polytetrafluoroethylene (PTFE).



Scheme 3: Perfluorocyclobutane (PFCB) Aromatic Ether Formation

The PFSI pendants are anticipated to give better ionic conductivity (higher than 0.1 S cm^{-1} at $80\text{ }^\circ\text{C}$), higher thermal stability in acidic medium and resistance towards oxidative degradation. There are two main factors that contribute to the acidity of PFSI side groups. First, the delocalization of charge over the O-S-N skeleton (Scheme 4) greatly increases the stability of its conjugate base, $(\text{R}_f\text{SO}_2)_2\text{N}^-$ [41-43]. Secondly, the presence of the strong electron withdrawing perfluoroalkyl group also increases the compounds' acidity.



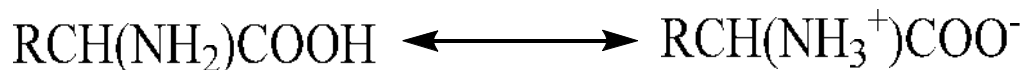
Scheme 4: Delocalization of Perfluoroalkylsulfonimide Group

Target Monomer

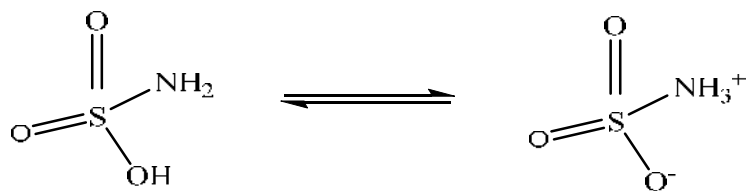
Diazonium PFCB zwitterionic monomers (Figure 1) is proposed as the targeting monomer which is further polymerized to replace the PFSA polymers as electrolytes in PEMFC. The diazonium PFCB zwitterionic monomers contain three main functionalities: namely the trifluorovinyl ether group, aromatic diazonium zwitterion moiety and the PFSI group. The trifluorovinyl ether group can provide a means to polymerize the monomer before or after grafting onto the carbon electrode. The perfluoroalkylsulfonimide group (strongly electron-withdrawing) offers super acidity, which corresponds to high proton conductivity. The diazonium moiety in the monomer is expected to be grafted onto the carbon electrode support for PEMFCs.

Zwitterions were introduced here since it can increase the stability of diazonium compounds. They are defined as the neutral compounds that possess groups with the anion and cation attached in the same molecule. A typical example of zwitterions is an amino acid at the iso-electric point shown in Scheme 5. Another example is sulfamic acid which contains both acidic and basic groups and can tautomerize to the zwitterionic forms as shown in scheme 6. Also, zwitterions are described as semipolar compounds due to their significant charge

separation between the directly bonded atoms. In semipolar groups, a filled orbital on one atom and an unfilled orbital on the other are inductively distorted by the charge separation [44, 45].



Scheme 5: Amino Acid at the Isoelectric Point (R= alkyl group)

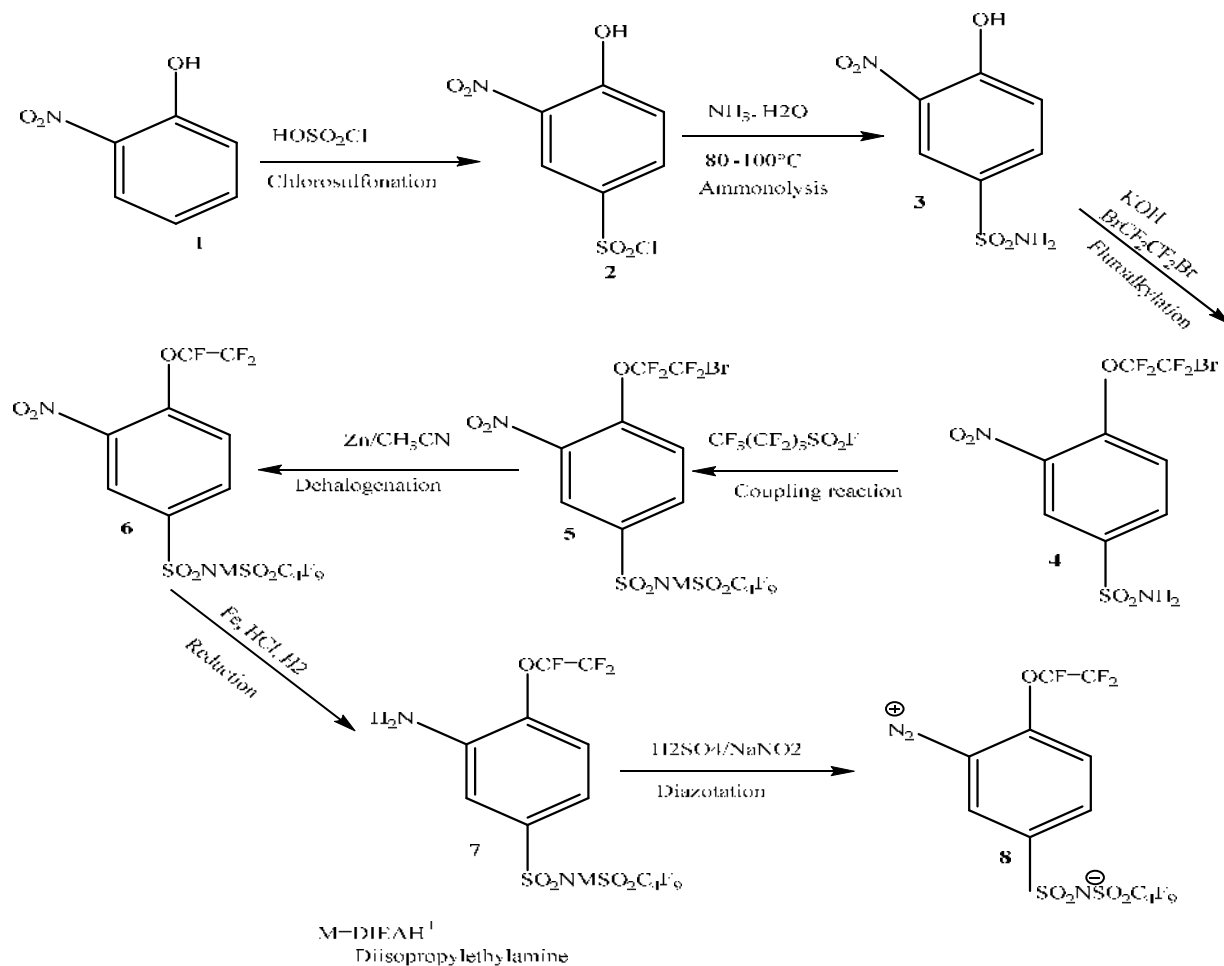


Scheme 6: The Sulfamic Acid in Zwitterionic Form

Synthesis of the targeting monomer (Figure 1) is very challenging. Three different starting materials with different routes were designed to obtain the targeting monomer. One of the three routes was successful and promising. All of these three routes are briefly elaborated as following.

2-Nitrophenol Starting Material (Approach 1)

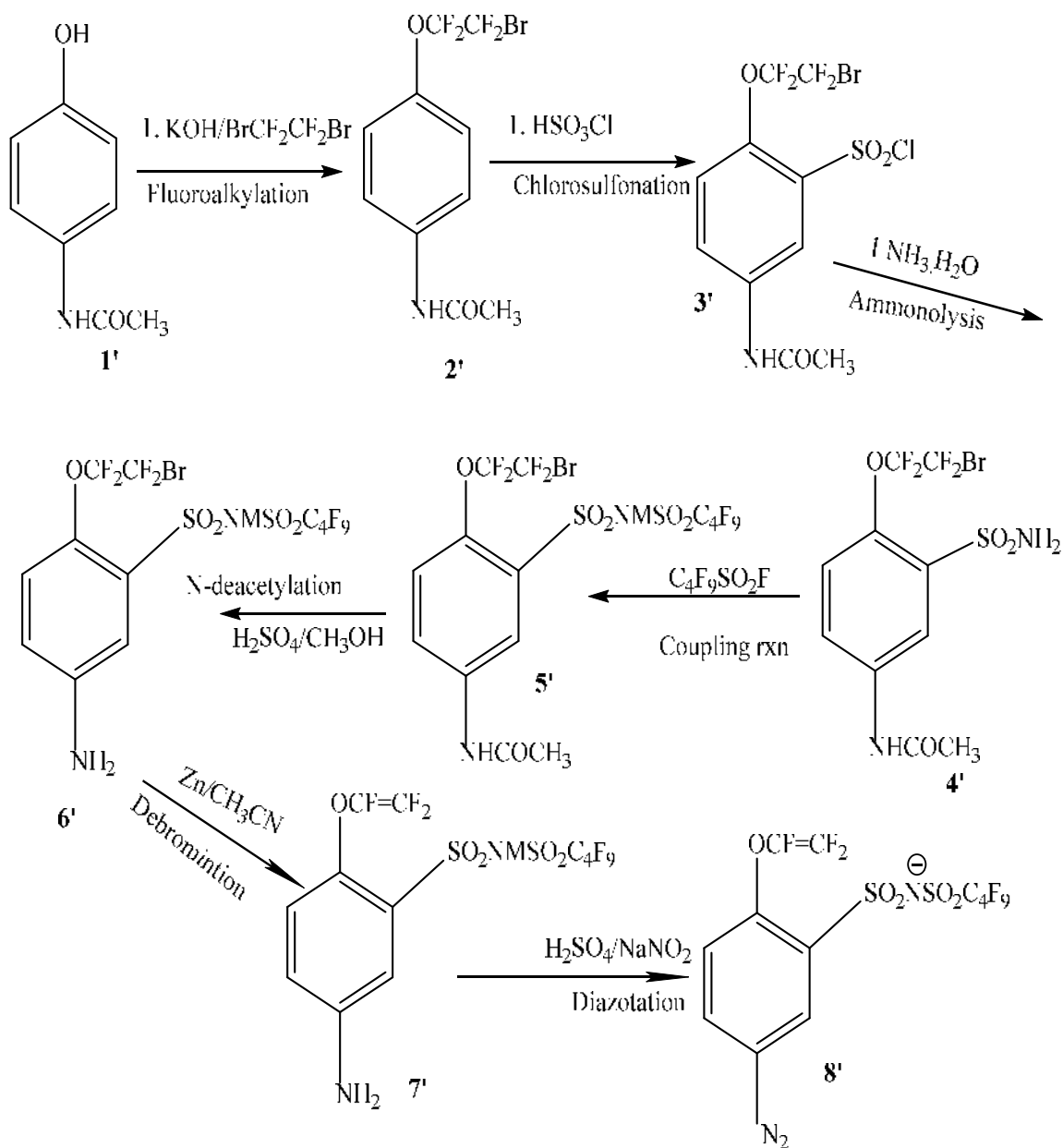
The first synthesis route (scheme 5) involved 2-nitrophenol as the starting material. A seven-step synthesis is designed to obtain the targeting monomer, including 1) chlorosulfonation reaction, 2) ammonolysis reaction, 3) fluoroalkylation reaction, 4) coupling reaction 5) dehalogenation reaction 6) reduction reaction, and 7) diazotization reaction. The first four steps were successfully carried out in the lab so far.



Scheme 7: Overall Synthesis Scheme of the Target Monomer. (Approach 1)

4-Acetamidophenol (Approach 2)

The second approach involved 4-acetamidophenol as the starting material. It is supposed to overcome the difficulties in the fluoroalkylation step in approach 1. The synthesis design is involved 7 steps and they are: 1) fluoroalkylation reaction, 2) chlorosulfonation reaction, 3) ammonolysis reaction, 4) coupling reaction, 5) N-deacetylation reaction, 6) dehalogenation reaction, and 7) diazotization reaction. Though the fluoroalkylation reaction was successful in this approach, the subsequent chlorosulfonation was very problematic.

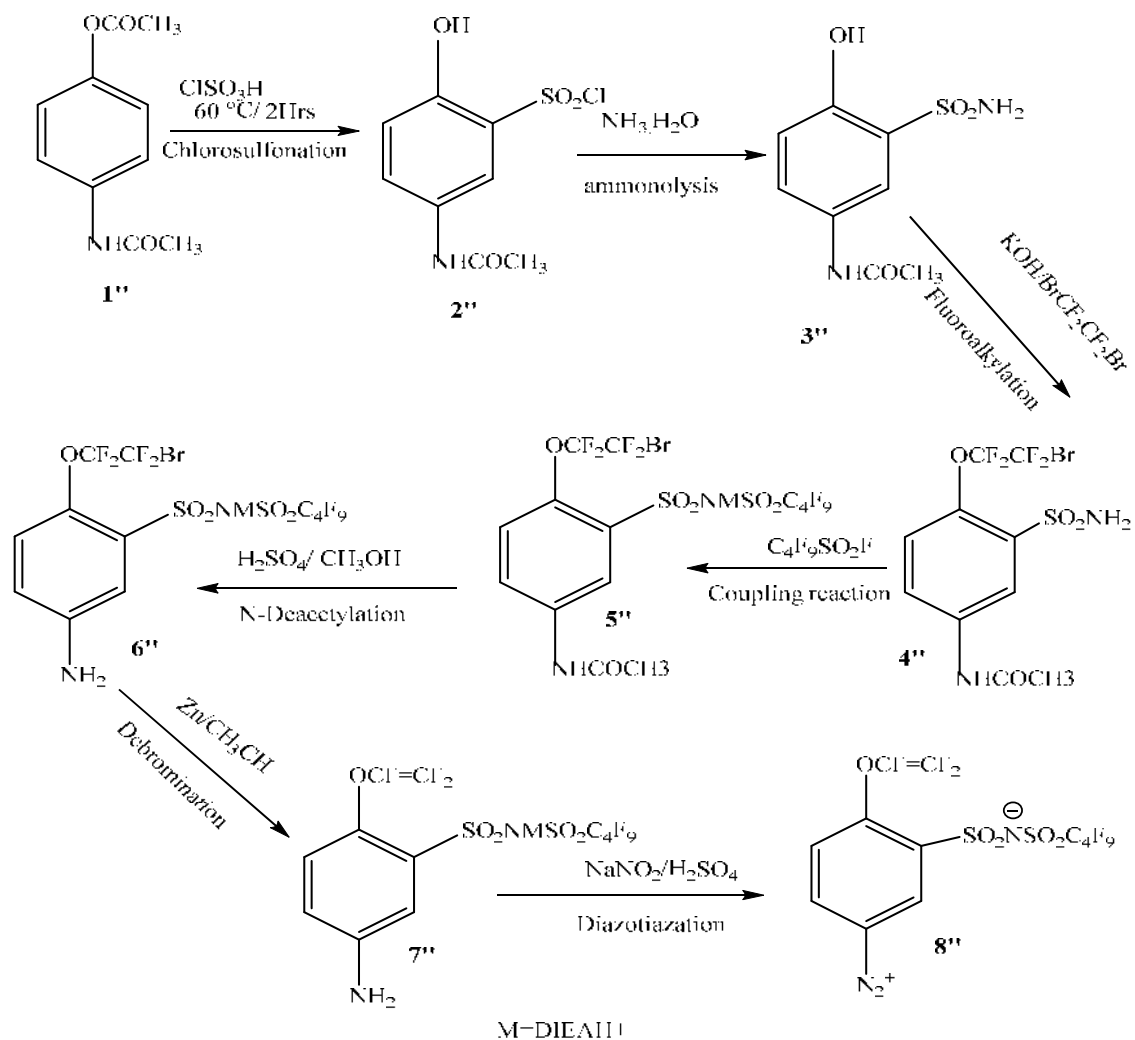


Scheme 8: Overall Synthetic Scheme for the Target Monomer (Approach 2)

4-Acetoxyacetanilide (Approach 3)

Another preparation route is expected to start with 4-acetoxyacetanilide. It is supposed to overcome the difficulties in the fluoroalkylation step in approach 1. The eight steps involved this approach are 1) chlorosulfonation reaction, 2) ammonolysis reaction, 3) fluoroalkylation, 4)

coupling reaction, 5) N-deacetylation reaction, 6) nitration reaction, 7) dehalogenation reaction, and 8) diazotization reaction. The attempts for this preparation route were given up since some side reactions occur in chlorosulfonation step.



Scheme 9: Overall Synthetic Scheme for the Target Monomer (Approach 3)

CHAPTER 2

RESEARCH AND DISCUSSION

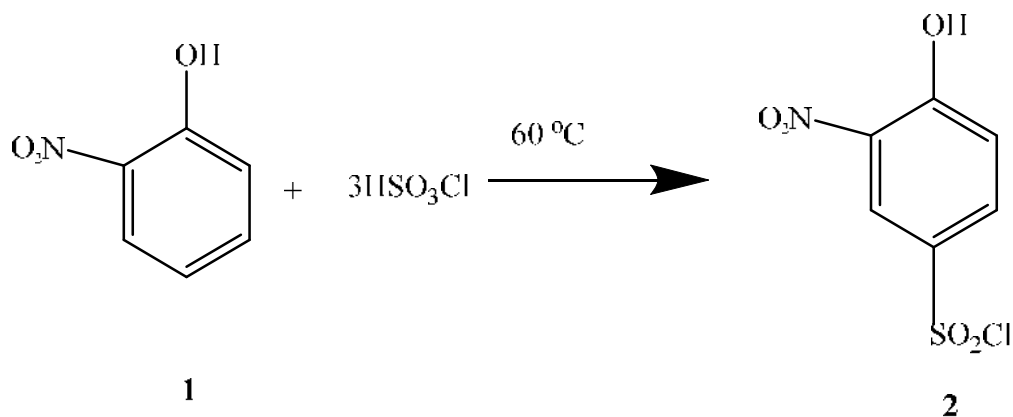
Three different routes were attempted in order to obtain the targeting monomer, diazonium 4-(trifluorovinyl)oxy) perfluorobutanesulfonyl benzenesulfonamide zwitterionic monomer. The three different starting materials that were used are 2-nitrophenol, 4-acetamidophenol, and 4-acetoxyacetanilide.

Approach 1: The Synthesis Route is Starting from 2-Nitrophenol

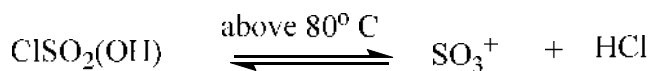
The seven-step synthetic route is designed for the targeting monomer. And they are chlorosulfonation, ammonolysis, fluoroalkylation, coupling, dehalogenation, reduction and diazotization reaction.

Chlorosulfonation of 2-Nitrophenol

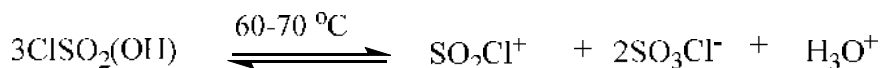
The synthesis of 4-hydroxy-3-nitrobenzenesulfonyl chloride **2**, was carried out in the presence of chlorosulfonic acid at around 60 °C (scheme 10). This reaction is a typical electrophilic aromatic substitution (EAS) reaction in which the electrophile replaces one proton on the aromatic ring. Excess of chlorosulfonic acid (at least more than 3 equivalent to the starting materials) and controlled temperature (about 60 °C) are the two principal factors, to determine whether or not the desired product will be obtained [46]. Otherwise, SO₃ will be generated as the electrophile (Scheme 11) instead of the needed electrophile SO₂Cl⁺ (Scheme 12)



Scheme 10: Chlorosulfonation of 2-Nitrophenol.



Scheme 11: The Unwanted Electrophile Generated with Less Chlorosulfonic acid/ at High Temperature.

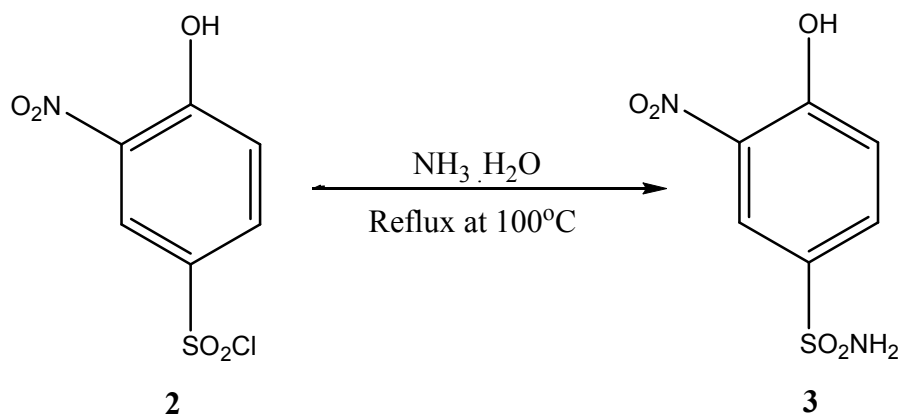


Scheme 12: The Desired Electrophile Generation Reaction.

The substituents on the aromatic ring play a key role in directing the position of the incoming electrophile. The strongly activating hydroxyl group takes precedence over the deactivating nitro group and directs the SO_2Cl^+ to the para position of the aromatic ring. Due to the steric hindrance, the hydrogen at the ortho position of the hydroxyl group is less likely to be replaced by electrophile, SO_2Cl^+ . The reaction was fairly easy and there were no impurities after purification. The relative low yield may be due to the purification process.

Ammonolysis of 4-Hydroxy-3-Nitrobenzenesulfonyl Chloride

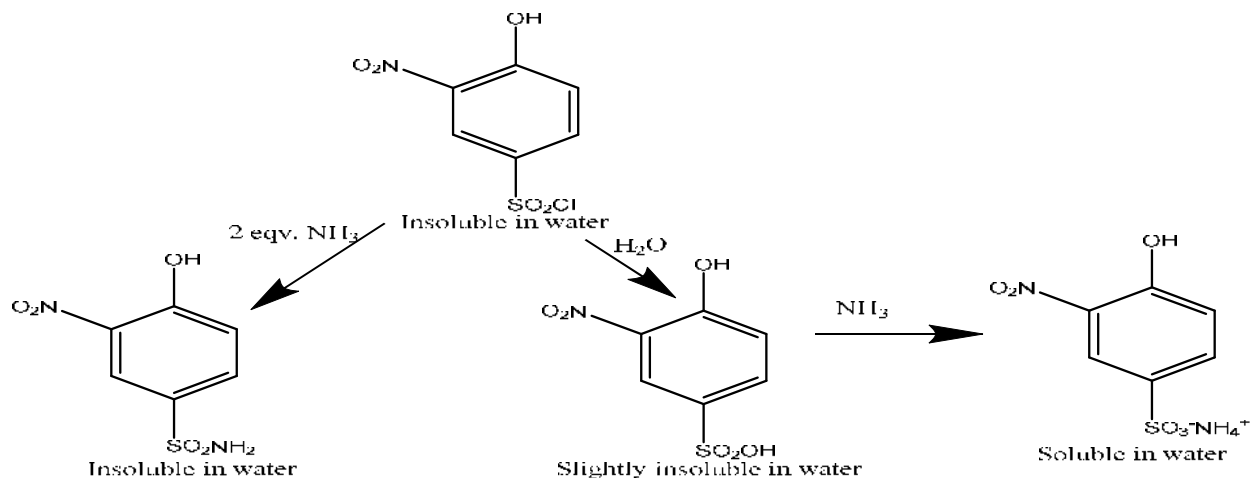
The synthesis of 4-hydroxy-3-nitrobenzenesulfonyl amide **3**, was completed by refluxing the 4-hydroxy-3-nitrobenzenesulfonyl chloride **2**, in the presence of ammonia water and acetonitrile as shown in scheme 13.



Scheme 13: Ammonolysis of 4-Hydroxy-3-Nitrobenzenesulfonyl Chloride

It is a S_N2 reaction where the chloride ion Cl⁻ is substituted by -NH₂. The ammonolysis reaction predominates the hydrolysis reaction because the NH₃ is a stronger nucleophile than H₂O. Since oxygen in H₂O is more electronegative than nitrogen in NH₃, ammonia is expected to be a stronger nucleophile than water [47]. The usual hydrolysis by-product associated with this

reaction is normally removed by washing with water. [56].



Scheme 14: Possible Hydrolysis Side Product Produced during the Ammonolysis Reaction.

As the disappearance of the OH peak around 10 ppm is observed in the proton NMR, a by-product of NH₄Cl⁺ salt (Figure 7) needed to be further converted back to phenol form by acidification.

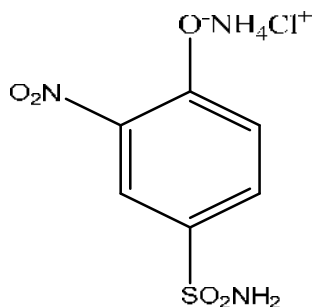


Figure 7: The Ammonium Salt By-product [48].

Fluoroalkylation of 4-Hydroxy-3-Nitrobenzenesulfonyl Amide

The most challenging part of this synthetic design was the synthesis of 4-(2-Bromotetrafluoroethoxy)-3-nitro-benzenesulfonyl amide **4**, from 4-hydroxy-3-nitrobenzenesulfonyl amide **3**. It is a two-step process. First, the substituted phenol is

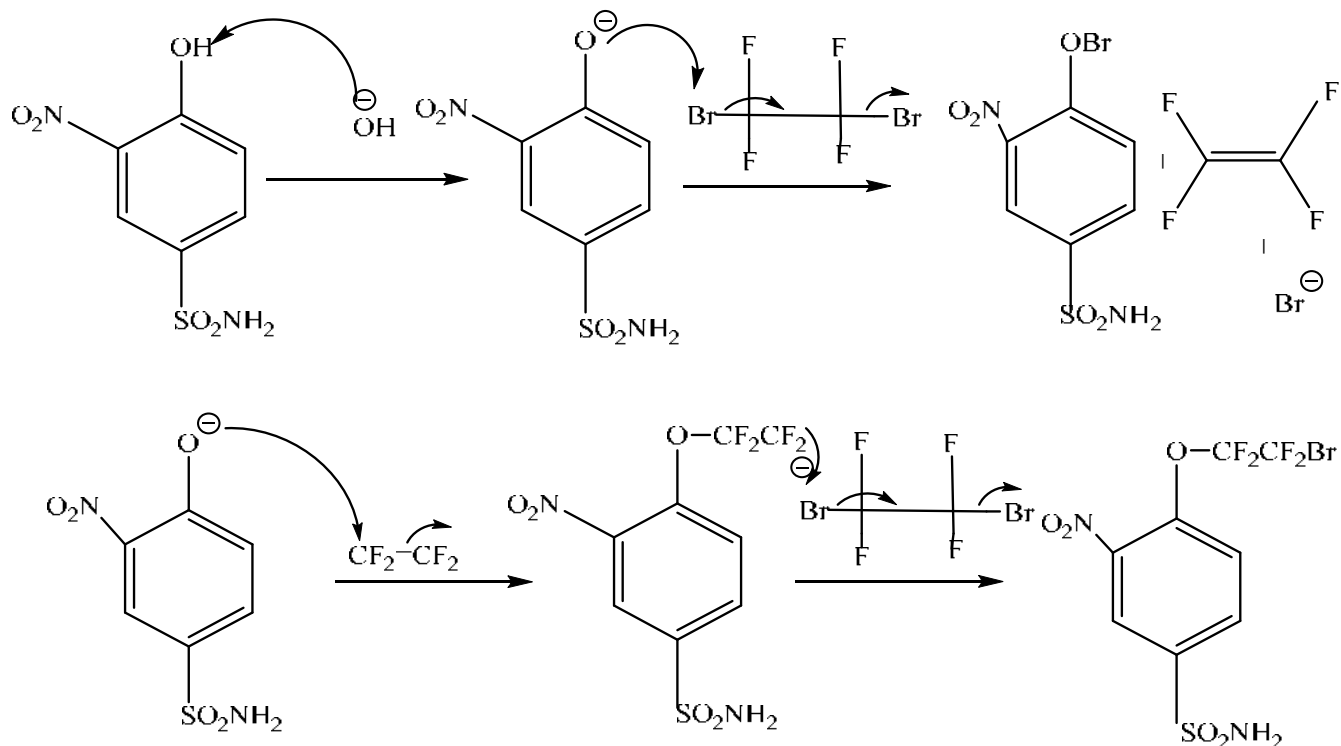
deprotonated by the base (KOH). Second, the obtained phenoxide anion subsequently attacks the fluoroalkylation agent, BrCF₂CF₂Br. Several trials were carried out before finally obtaining the desired purified product. For example, other bases, Na₂CO₃ and CaCO₃, were used to replace KOH. The organic solvents other than DMSO, such as acetonitrile, were also used since DMSO is very difficult to be removed after. But none of them offered the desired product.



Scheme 15: Fluoroalkylation Reaction with 1, 2-Dibromotetrafluoroethane.

Two general methods were reported for preparing the aryl trifluorovinyl ethers. One is the reaction of an alkali metal phenoxide (PhONa or PhOK) with tetrafluoroethylene [49]. According to Wall and Pummer, the reaction yield is low due to many side reactions. These reactions were carried out in a Parr digestion bombs (a chemical reactor) under very high temperature and pressure and introduce many impurities [50]. Babb et al reported a more efficient and clean way of producing aryl trifluorovinyl ethers [51]. Compared to the well-known alkylation, such as S_N1 and S_N2, the fluoroalkylation is rationalized as an unusual ionic chain mechanism according to Wakselman et al [52]. As shown in scheme 16, the reaction is initiated when the phenoxide ion attacks the electron-positive bromine (δ^+) on the BrCF₂CF₂Br. Tetrafluoroethylene (CF₂=CF₂) is generated in-situ after the loss of the bromide ion. The phenoxide then attacks the CF₂=CF₂ to form the reactive fluorocarbanion, which then attacks the positive bromide ion to form 4-(2-Bromotetrafluoroethoxy)-3-nitro-benzensulfonyl amide. The

reactive fluorocarbanion will also react with the proton from water and give a byproduct ($\text{NO}_2\text{SO}_2\text{NH}_2\text{PhOCF}_2\text{CF}_2\text{H}$) as shown in figure 8. [51]. Therefore, the extremely dry condition and the excess of $\text{BrCF}_2\text{CF}_2\text{Br}$ are essential to minimize hydrolysis byproduct.



Scheme 16: Proposed Fluoroalkylation Mechanism [52].

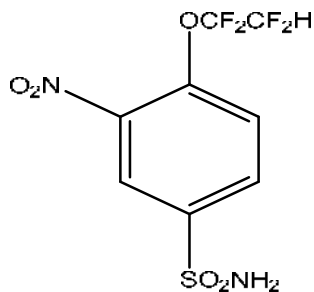


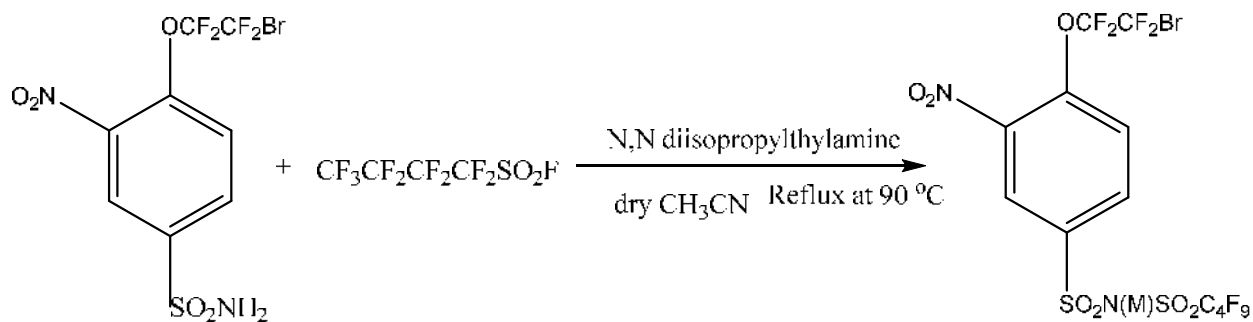
Figure 8: Possible Hydrolysis Impurity from Fluoroalkylation Reactions. [51].

Several techniques are essential to obtain the pure product. For example, the dean-stark distillation apparatus is used to remove the water-xylene azeotrope in-situ. The reason is that 1) the reaction can be pushed forward to the right by removing the by-product water, 2) it will lessen the hydrolysis impurity. The non-volatile solvent DMSO solvent is removed by evaporating the solvent at high temperature and extraction with water and methylene chloride (the ratio is 1:5). At last, the pure product was obtained by column chromatography by the three solvents system of DCM: methanol: diethyl ether (1:1:1).

The fluoroalkylation of the 3-nitro-4-hydroxybenzenesulfonyl amide is quite challenging. The first reason is the presence of the strongly electron withdrawing nitro group on the aromatic ring. It reduces the nucleophilicity of the phenoxide anion initially formed. Second, the inaccurate amount of water-xylene azeotrope was removed by the poor vacuum pump. The last but the most difficult is the removal of DMSO and hydrolysis impurity from the product.

Coupling Reaction of 4-(2-Bromotetrafluoroethoxy)-3-Nitrobenzenesulfonyl Amide

It is a typical S_N2 reaction which is carried out under extremely dry conditions to minimize possible hydrolysis impurity. This is because the sulfonyl fluoride group (-SO₂F) has the tendency to be hydrolyzed to -SO₃ anion. The nucleophilicity of aryl sulfonimide is increased by the addition of a base catalyst N, N-diisopropylethylamine (DIEA) (Scheme 17). Excess DIEA after the reaction can be removed by acidification with HCl (acid-base reaction) followed by extraction with ethyl acetate. Also, the excess amount of nonafluorobutane sulfonyl fluoride, C₄F₉SO₂F, is used to ensure enough for the reaction after hydrolysis.



Scheme 17: Coupling Reaction of Amide with Nonafluorobutanesulfonyl Fluoride

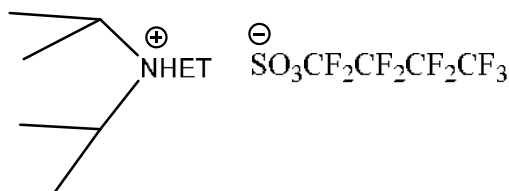


Figure 9: Possible Hydrolysis By-Product from Coupling Reaction

After purification, the NMR and IR spectra indicated the desired pure product was obtained. The proton NMR showed a successful coupling reaction by the disappearance of the NH_2 peak. Also, the fluorine NMR showed the disappearance of the SO_2F peak. The unusual movement in one of the fluorine peaks, labeled “A” in compound **5**, is still under consideration. This peak was expected to move downfield but instead moved further upfield.

Further steps are needed to be carried out to achieve target monomer.

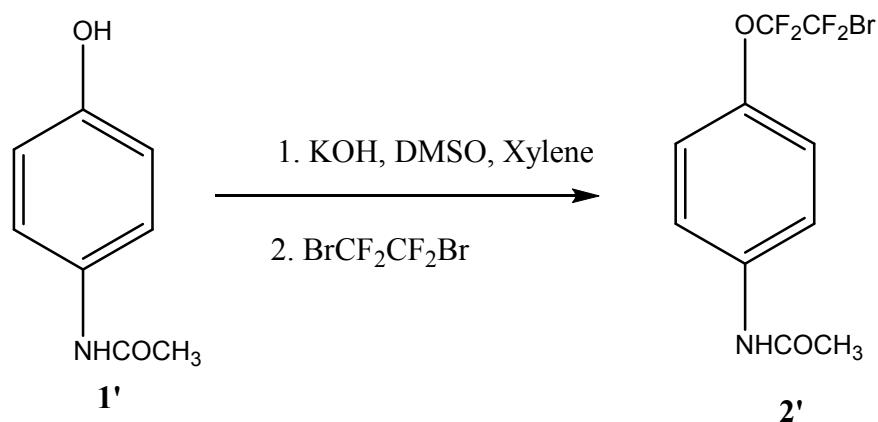
Approach 2: The Synthesis Route is Starting from 4-Acetamidophenol

Meanwhile, due to the difficulty with the fluoroalkylation reaction in the first approach, a different route was attempted for the targeting monomer. The various steps envisaged for this

reaction are 1. Fluoroalkylation 2. Chlorosulfonation 3. Ammonolysis 4. Coupling reaction 5. N-deacetylation 6. Dehalogenation reaction 7. Diazotization reaction.

Fluoroalkylation Reaction of 4-Acetamidophenol

In the first approach, the nitro group on the aromatic ring reduces the nucleophilicity of the phenoxide ion and leads to relatively lower yield and longer reaction time. Hence, 4-acetamidophenol was used as the new starting material to increase electron density on the aromatic ring since the acetamido group is moderately electron donating. The fluoroalkylation reaction was carried out with the similar procedure as in the first approach.

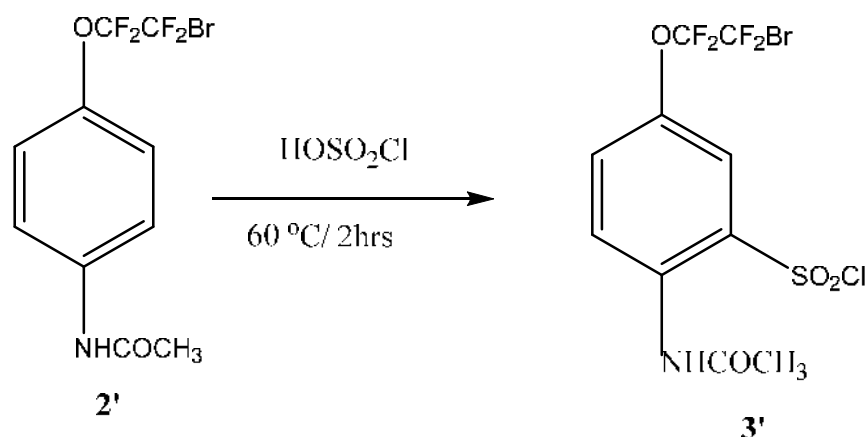


Scheme 18: Fluoroalkylation of 4-Acetamidophenol

The yield was relatively higher than the fluoroalkylation in the first approach. It is believed that the presence of the acetamido group on the aromatic ring act as the moderately activating group promote such reaction. The minor impurities associated with this reaction are easier to be removed by column chromatography (DCM: methanol 1:1). Thus, the purification process was less tedious since the product is easier to be dissolved in a volatile organic solvent.

Chlorosulfonation of 4-(2-bromotetrafluoroethoxy) Acetanilide

The synthesis of 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride was carried out in the presence of chlorosulfonic acid. As explained before, the chlorosulfonic acid was used in excess (3 molar equivalent) and at 60 °C temperature to generate the electrophile, SO_2Cl^+ .



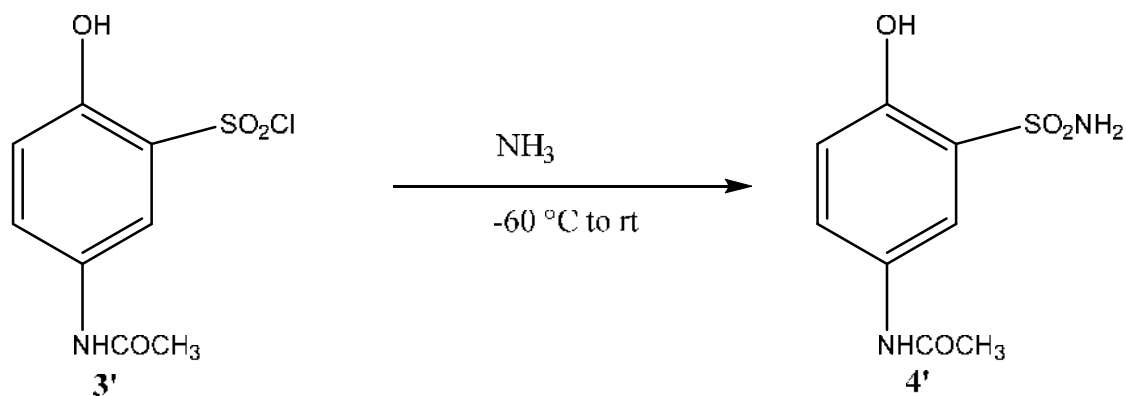
Scheme 19: Chlorosulfonation of 4-(2-Bromotetrafluoroethoxy) Acetanilide

The reaction was fairly facile and the proton NMR indicated that a pure product was obtained. However, the solubility of the synthesized product is poor in most organic solvents, except DMSO, which brings a challenge in the subsequent ammonolysis reaction.

Ammonolysis of 2-Acetamido-5-(2-Bromotetrafluoroethoxy) Benzenesulfonyl Chloride

This step involves converting the 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride **3** to 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl amide

4.



Scheme 20: Ammonolysis of 2-Acetamido-5-(2-bromotetrafluoroethoxy) Benzenesulfonyl Chloride

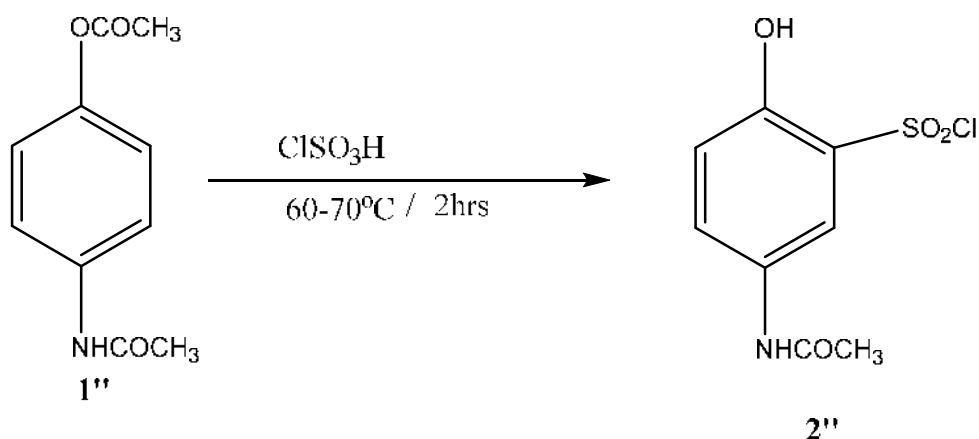
Two different trials were attempted for this reaction. The first trial involved refluxing in the presence of ammonium hydroxide and acetonitrile. Even at elevated temperatures, the starting material was partially soluble in the solvent. Some side products were accompanied and further purification was not successful. In the second trial, instead of ammonium hydroxide aqueous liquid, the reaction was running in the ammonia liquid from -60 °C to room temperature. It also didn't give the predictable product because of the compound 3's solubility issues. The further purification such as recrystallization was still troublesome. Therefore, this somehow less efficient approach was terminated.

Approach 3: The Synthesis Route is Starting from 4-Acetoxyacetanilide

Also, due to the difficulty with the ammonolysis reaction in the second approach, a different route was attempted for the targeting monomer.

Chlorosulfonation of 4-Acetoxyacetanilide

The synthesis of 5-acetamido-2-hydroxybenzenesulfonyl chloride **2''**, was carried out in the presence of chlorosulfonic acid. As described earlier, the chlorosulfonic acid was used in excess to generate the SO_2Cl^+ .

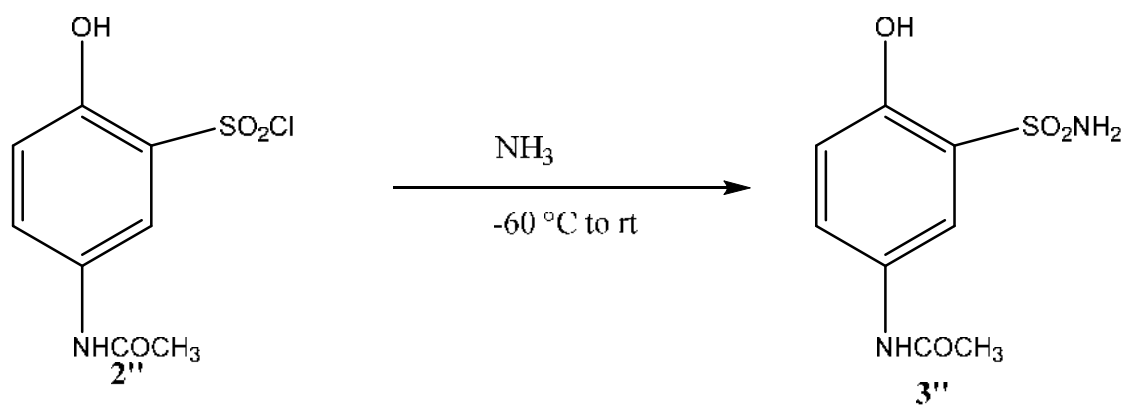


Scheme 21: Chlorosulfonation of 4-Acetoxyacetanilide

The reaction time was relatively short and a pure product also was obtained according to NMR and IR. The same problem occurs with the synthesized product, which only can dissolve in DMSO. This also brings the challenge for the next step.

Ammonolysis of 5-Acetamido-2-Hydroxybenzenesulfonyl Chloride

This step involves converting the 5-acetamido-2-hydroxybenzenesulfonyl chloride **2''** to 5-acetamido-2-hydroxybenzenesulfonyl amide **3''**.



Scheme 22: Ammonolysis of 5-Acetamido-2-Hydroxybenzenesulfonyl Chloride

The similar reaction condition was tried as in approach 2 and none of them provide the fully ammonolysis product.

CHAPTER 3

EXPERIMENTAL

General Consideration

NMR Spectroscopy

The ^1H & ^{19}F NMR spectroscopies were done on a Joel JNM-ECP 400 MHz Fourier Transform NMR spectrometer. The chemical shifts are stated in parts per million (ppm) using high-frequency position conversion; the coupling constant reported as a 'J' value in Hz. The chemical shifts of ^1H -NMR spectra were referenced with trimethyl silane (TMS) whereas that of ^{19}F -NMR spectra were referenced with CFCl_3 external standard. The splitting patterns of resonance were stated in the following ways: singlet (s), doublet (d), triplet (t), the quartet (q), and multiplet (m). The NMR spectra were measured by using 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 around 10 mg of solid in 1 mL of acetone.

Infrared Spectroscopy

The infrared spectra were recorded on a Shimadzu IR Prestige-21 FTIR spectrometers. The samples were prepared by placing about 2 mg of solid 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 (TLC)

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

Glass Vacuum System

Figure 10 shows a diagram of the glass Schlenk line which was used in several experiments, such as drying, purging, sublimation and vacuum distillation. This dynamic high vacuum line is connected with Teflon® and comprises of two manifolds, one manifold for the vacuum and the other one for nitrogen gas.

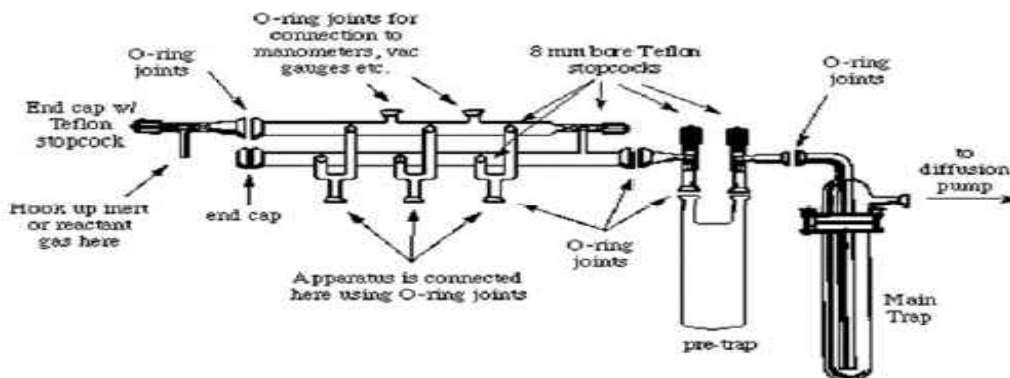


Figure 10: The line diagram of a dual-manifolds glass vacuum line Used with Permission [53].

pH Value Measurement

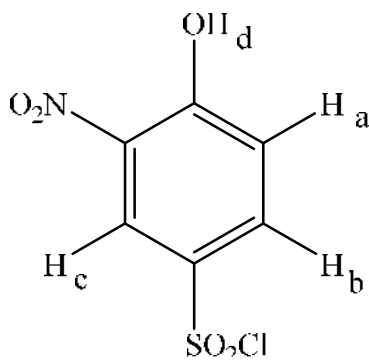
The pH values of aqueous solution were determined on Fisher Accumet Model A150 pH meter, with the standard size glass body combination electrodes/calomel reference. The instrument was standardized at pH= 4, 7 and 10 using three Fisher certified buffers at room temperature.

Purification of Solvents and Experimental Practice

The starting materials: 2-nitrophenol and nonafluorobutanesulfonyl fluoride ($C_4F_9SO_2F$) were bought commercially from SyQuest laboratories and used as received unless otherwise stated. All the reactions were performed in glassware unless otherwise stated. Moisture sensitive compounds were kept in a dry box under nitrogen gas. Solvents were dried using activated molecular sieves.

Approach 1: Synthesis of 4-hydroxy-3-nitrobenzenesulfonyl chloride, 2

In a typical procedure, 2-nitrophenol (5.0 grams, 35.9 mmol) was dissolved in 8 mL of chlorosulfonic acid (107.8 mmoles, the ratio of 1:3) in small portions over 20 minutes in a clean 50-ml round-bottom flask equipped with a stir bar at 0 °C. The reaction was then heated to 60 °C for 20 minutes and allowed to stir for another 18 h at 25 °C. The reaction solution then was quenched by pouring into 20 g of ice. Next, the organic part was extracted with dichloromethane (3 X 20 mL) and washed with cold water (2 X 50 mL). The combined organic extract was later dried over $MgSO_4$. Finally, the filtrate was concentrated by rotary evaporation and a dark sticky product (5.1 g, 60 %) 4-hydroxy-3-nitrobenzenesulfonyl chloride was obtained.



1H NMR (400 MHz; CD_3CN ; ppm): δ_a 7.45 (1H, d), δ_b 8.24 (1H, d), J_{ab} = 8 Hz; δ_c 8.71 (1H, s),

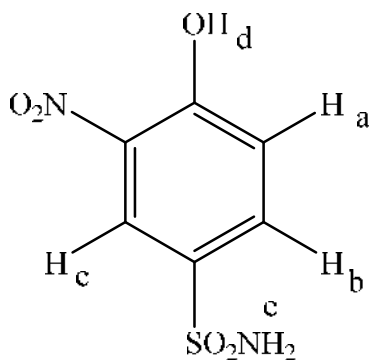
δ_d 10.76 (1H, s),

IR ($\nu_{\max}/\text{cm}^{-1}$): 3253 s (OH), 1614 s (C=C), 1519 m and 1328 s (NO) and 1163 m (S=O).

m/z: 202 (M^+ , 100%), 237, 154, 107, 91 and 63.

Synthesis of 4-hydroxy-3-nitrobenzenesulfonyl Amide, 3

In a typical procedure, 4-hydroxy-3-nitrobenzenesulfonyl chloride (3.5 grams, 21.1 mmoles) was added to a 100-mL round-bottom flask equipped with a stir bar. Next, 30 mL of ammonia hydroxide (30%) and 20 mL of acetonitrile were added subsequently to the round bottom flask. The solution was refluxed at around 100 °C overnight. The solvent was then removed by rotary evaporator. The crude product was vacuum filtered with 3 X 5 mL of water. Finally, the product was then vacuum dried overnight and a yellow product (2.45 g, 76.3 %) was obtained.



$^1\text{H NMR}$ (400 MHz; CD_3CN ; ppm): δ_a 7.33 (1H, d), δ_b 8.06 (1H, d), $J_{ab} = 8$ Hz, δ_c 8.53 (1H, s),

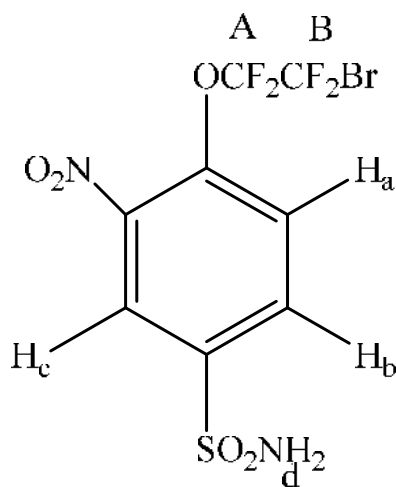
δ_d 10.52 (1H, s), δ_e 5.81 (2H, s),

IR ($\nu_{\max}/\text{cm}^{-1}$): 3356 s (OH), 3263 m (N-H), 1620 m (C=C), 1537 m and 1357 s (NO) and 1170 m (S=O).

m/z: 218 (M^+ , 100%), 202, 144, 120, 91, 80 and 63.

Synthesis of 4-(2-bromotetrafluoroethoxy)-3-nitro-benzensulfonyl amide, 4

In a typical procedure, 4-hydroxy-3-nitrobenzene sulfonylamide (2.0 grammes, 9.2 mmol), KOH (0.6 g, 9.2 mmol, the ratio is 1:1), 10 mL of DMSO and 1 mL of Xylene were added into a 25- mL three- necked round bottom flask equipped with a stir bar fitted with Dean-stark azeotropic distillation assembly. The mixture was heated to 60 °C at a reduced pressure of 4 torrs for 10 h to remove xylene and water (around 1.2 mL). The solution was then cooled to 25 °C and BrCF₂CF₂Br (2.4 g, 10.1 mmol, 1:1.1 ratio) was added under nitrogen protection. The solution was allowed to stir for another 12 h at 25 °C and 10 h at 35 °C. After the reaction, most of the solvents were removed by rotavapor at a bath temperature of 60 °C for 4 h. The crude product was then diluted with 20 ml of water and extracted with methylene chloride (3X 100 mL). The combined organic portion was washed with water (2 X 30 mL), dried over MgSO₄, and then concentrated with a rotary evaporator to give the crude product. And then, the co-solvent with 1:1:1 ratio of methylene chloride: methanol: diethyl ether was used to run the column chromatography to remove the hydrolysis by-product. The final purified product (1.30 g, 66.7 %) was obtained after filtration and drying under vacuum.



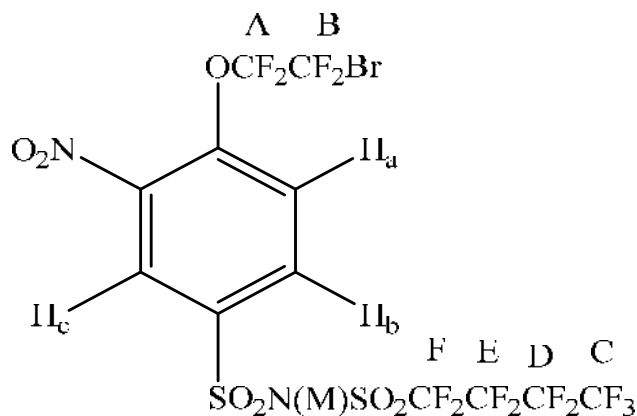
^{19}F -NMR (400 MHz; CD_3CN ; ppm) δ_{A} -69.5 (2F, s) δ_{B} -86.6 (2F,s)

^1H NMR (400 MHz; CD_3CN ; ppm): δ_{a} 7.36 (1H, d), δ_{b} 6.48 (1H, d), $J_{\text{ab}} = 8$ Hz, δ_{c} 8.23 (1H, s), δ_{d} 6.30 (2H, s),

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3369 m (N-H), 1631 m (C=C), 1504 m and 1315 s (NO) and 1143 m (S=O), 1087 vs (C-F).

Synthesis of 4-OCF₂CF₂Br-3-NO₂-PhSO₂(M) SO₂C₄F₉, **5**

In a typical procedure, the nonafluorobutanesulfonyl fluoride (0.36 g, 1.18 mmol) and 4-(2-Bromotetrafluoroethoxy)-3-nitro-benzensulfonyl amide (0.4 g, 1.13 mmol, 1: 1.04) were added into a 100 ml three-necked round bottom flask equipped with a stir bar and two rubber septa in a dry box. Then 20 mL of acetonitrile and 3 ml of the diisopropyl ethylamine (DIEA) were injected into the closed flask subsequently. The solution was refluxed for 5 days at 90 °C under nitrogen gas protection. ^{19}F NMR spectroscopy was used to monitor reaction progress. All of the volatile solvents were then removed by rotavapor and dried under dynamic vacuum for 12 hrs. The excess DIEA was removed by acidifying the crude product to a pH of 1 with 6M HCl and extracting with ethyl acetate (3x15 mL) from the aqueous layer. The purified final product (0.62 g, 67.7 %) was obtained after removing the solvent and drying under vacuum.



^{19}F -NMR (400 MHz; CD_3CN ; ppm) δ_{A} -138.3 (2F, s) δ_{B} -89.1 (2F, s), δ_{C} -81.6 (3F, s) δ_{D} -115.5 (2F, s), δ_{E} -122.1 (2F, s) and δ_{F} -126.5 (2F, s)

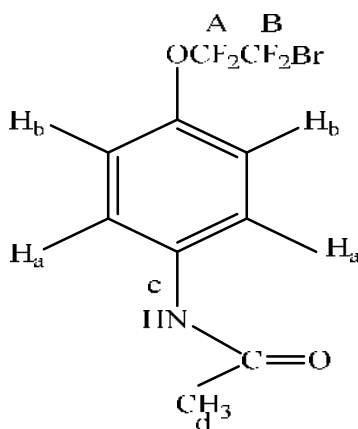
^1H NMR (400 MHz; CD_3CN ; ppm): δ_{a} 8.20 (1H, d), δ_{b} 7.43 (1H, d), $J_{\text{ab}} = 8$ Hz, δ_{c} 8.64 (1H, s),

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1625 m (C=C), 1508 s (NO stretch), 1327 m (NO bend), 1190 s (S=O) and 1095 vs (C-F).

Approach 2: Synthesis of 4-(2-bromotetrafluoroethoxy) acetanilide, 2'

In a typical procedure, 4-acetamidophenol (3.0 grammes, 19.8 mmol) , KOH (1.1 g, 19.8 mmol, the ratio is 1:1), 7 mL of DMSO and 1 mL of xylene were added into a 25- mL three- necked round bottom flask equipped with a stir bar fitted with Dean-stark azeotropic distillation assembly. The mixture was heated to 60 °C at a reduced pressure of 4 torrs for 10 hrs to remove xylene and water (1.4 mL). The solution was then cooled to 25 °C and $\text{BrCF}_2\text{CF}_2\text{Br}$ (5.7 g, 21.8 mmols, 1:1.1 ratio) was added under nitrogen protection. The solution was allowed to stir for another 12 h at 25 °C and 10 h at 35 °C. After the reaction, the DMSO was removed using the rotavapor at a bath temperature of 60 °C for 4 h. The crude product was then diluted

with 20 ml of water and extracted with methylene chloride (3 X 100 ml). The combined organic portion was washed with water (2 X 30 ml), dried over MgSO₄, and then concentrated with a rotary evaporator to give the crude product. And then, the co-solvent of acetone and hexane (1:1) was used to run the column chromatography to remove the hydrolysis by-product. The final purified product (2.36 g, 78.6 %) was obtained after filtration and drying under vacuum.



¹⁹F-NMR (400 MHz; CD₃CN; ppm) δ_A -69.5 (2F, s) δ_B -86.6 (2F, s)

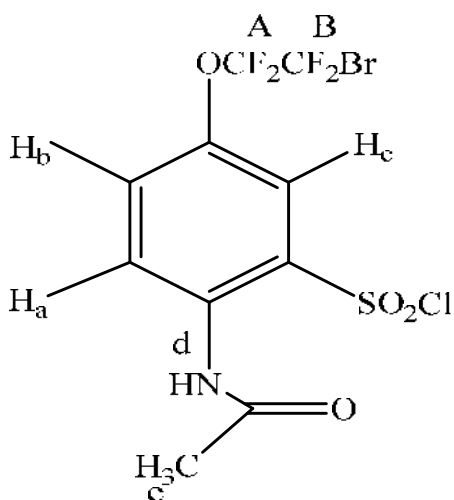
¹H NMR (400 MHz; CD₃CN; ppm): δ_a 7.22 (2H, d), δ_b 7.64 (2H, d), J_{ab} = 8 Hz, δ_c 8.48 (1H, s), δ_d 2.06 (3H, s)

IR (ν_{max}/cm⁻¹): 3460 m (N-H), 1739 s (C=O), 1602 m (C=C) and 1001 vs (C-F) stretch.

Synthesis of 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride, 3'

In a typical procedure, 4-(2-bromotetrafluoroethoxy) acetanilide (2.0 grams, 6 mmol) was added to 10 ml of chlorosulfonic acid (150 mmol) in a clean 50-ml round-bottom flask equipped

with a stir bar at 0 °C. The reaction was then heated at 60 °C for 2 h. The reaction was then quenched by pouring onto 20 g of ice, which was then extracted with dichloromethane (3X 20 mL). The combined organic extract was washed with brine water (2X 20 mL). The extract was dried over MgSO₄, filtered and the filtrate concentrated by rotary evaporation. A sticky brown product (1.05 g, 52.6 %) of 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride was obtained.



¹⁹F-NMR (400 MHz; CD₃CN; ppm) δ_A -70.1 (2F, s) δ_B -86.5 (2F,s)

¹H NMR (400 MHz; CD₃CN; ppm): δ_a 7.12 (1H, d), δ_b 7.62 (1H, d), J_{ab}= 12 Hz; δ_c 8.20 (1H, s), δ_d 8.75 (1H, s), δ_e 2.07 (3H, s)

IR (ν_{max}/cm⁻¹): 3466m (N-H), 1737 s (C=O), 1653 m (C=C), 1228 m (S-O), 1010 vs (C-F).

Synthesis of 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl Amide, 4' (Trial 1)

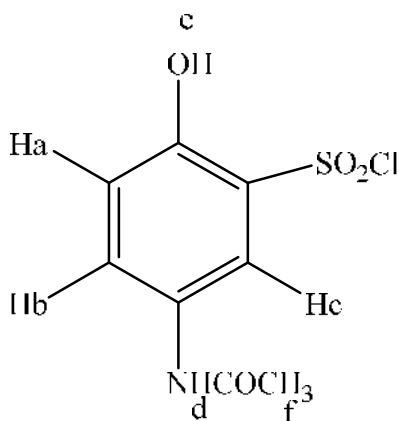
In a typical procedure, 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride (0.50 g, 1.17 mmol) was placed in a 250 mL three neck round bottom flask equipped with a stir bar. The reaction was carried out at - 60 °C under N₂ protection. Approximately 20 ml of ammonia gas was condensed into the flask and the reaction was carried on for 1 h. The excess NH₃ was slowly distilled out from - 40 °C to r.t. over 12 h. A brown impure product was obtained with a yield of 86.9 %.

Synthesis of 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl Amide, 4' (Trial 2)

In a typical procedure, 2-acetamido-5-(2-bromotetrafluoroethoxy) benzenesulfonyl chloride (0.50 g, 1.17 mmol) was added to a 100-mL round-bottom flask equipped with a stir bar. Next, 20 mL of ammonia hydroxide (30%) and 15mL of acetonitrile were added subsequently to the round bottom flask. The solution was refluxed at around 100 °C overnight. The solvent was then removed by rotary evaporator. The crude product was vacuum filtered with 3 X 5 mL of water. The product was then vacuum dried overnight and a brown impure product (0.26 g, 52.0 %) was obtained.

Approach 3: Synthesis of 5-acetamido-2-hydroxybenzenesulfonyl chloride, 2''

In a typical reaction, (3.0 g, 15.5 mmol) of 4-acetoxyacetanilide was heated with chlorosulfonic acid (9.0 g, 77.5 mmol, 1:5) at 60 °C for 2h. The reaction was quenched by pouring it into a mixture of ice-water and petroleum ether. The product (2.06 g, 68.8 %) precipitated out and was vacuum filtered as a fawn powder.



^1H NMR (400 MHz; CD_3CN ; ppm): δ_a 7.08 (1H, d), δ_b 7.87 (1H, d), J_{ab} = 8 Hz; δ_c 8.37 (1H, s), δ_d 10.31 (1H, s), δ_e 11.56 (3H, s) δ_f 3.09 (3H, s)

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3458 s (OH), 3216 m (N-H), 1737 s (C=O), 1616 m (C=C), 1217 m (S=O).

Melting point = 275 °C

Synthesis of 5-acetamido-2-hydroxybenzenesulfonyl amide, 3'' (Trial 1)

In a typical procedure, 5-acetamido-2-hydroxybenzenesulfonyl chloride (1.0 g, 4.0 mmoles) was added to a 100-mL round-bottom flask equipped with a stir bar. Next, 20 mL of ammonia hydroxide (30%) and 12 mL of acetonitrile were added subsequently to the round bottom flask. The solution was refluxed at around 100 °C overnight. The solvent was then removed by rotary evaporator. The crude product was vacuum filtered with 3 X 10 mL of water. The product was then vacuum dried overnight and a white impure product (0.46 g, 46 %) was obtained.

Synthesis of 5-acetamido-2-hydroxybenzenesulfonyl amide, **3''** (Trial 2)

In a typical procedure, 5-acetamido-2-hydroxybenzenesulfonyl chloride (1.0 g, 4.0 mmoles) was placed in a 250 ml three neck round bottom flask equipped with a stir bar. The reaction was carried out at -60 °C under N₂ protection. Approximately 30 ml of ammonia gas was condensed into the flask and the reaction was carried on for 1hr. The excess NH₃ was allowed to slowly distilled out from -40 °C to r.t. over 12hr. A white impure product (0.50 g, 50.1 %) was obtained.

CHAPTER 4

CONCLUSION

In conclusion, three different synthetic routes were attempted to obtain the targeting monomer, diazonium 4-(trifluorovinyl)oxy) perfluorobutanesulfonyl benzenesulfonimide zwitterionic monomer. Among them, only the first approach with 2-nitrophenol as the starting material is promising.

For the first approach, the chlorosulfonation and ammonolysis reactions are fairly facile and efficient. The fluoroalkylation step is rather difficult in the whole procedure. This is due to the inefficiency of the pump to remove the by-product water. Also, the presence of the nitro group on the aromatic ring reduces the nucleophilicity of the intermediate phenoxide ion formed, which slow down the next fluoroalkylation. Moreover, the solvent DMSO and impurity are hard to remove. Several purification techniques were tried, such as recrystallization, filtration, and extraction with different solvents. Finally, the pure fluoroalkylated product was obtained with column chromatography from the three-solvent system (DCM: methanol: diethyl ether 1:1:1). Although the obtained pure coupling product was identified, the unexpected details in ^{19}F NMR need further investigation.

For the second preparation route with 4-acetamidiphenol, the fluoroalkylation reaction was comparably easier with good yield. However, the ammonolysis reaction could not be completed because of the poor solubility of chlorosulfonation product.

For the third synthesis method with 4-acetoxyacetanilide, the similar solubility problem happened again with the ammonolysis of the chlorosulfonation product. None of the purification methods was successful for the ammonolysis product.

Overall, a pure couple product, 4-OCF₂CF₂Br-3-NO₂-PhSO₂(M) SO₂C₄F₉, has been successfully synthesized and characterized. For future work, dehalogenation, reduction, and diazotization will be carried out to obtain the targeting monomer. This monomer will further be polymerized and act as an electrolyte for chemical grafting onto the carbon electrodes in PEMFC.

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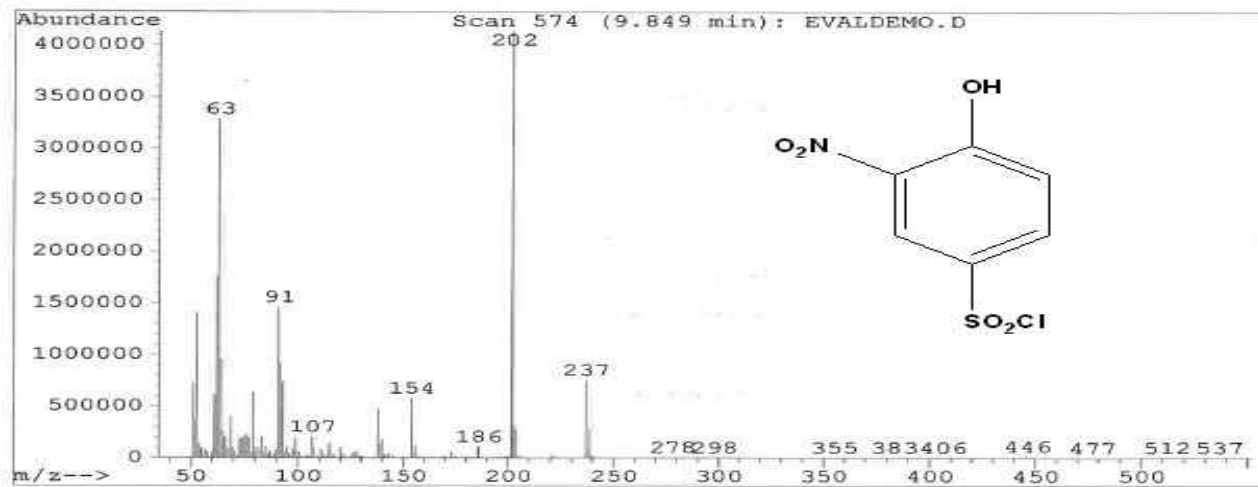
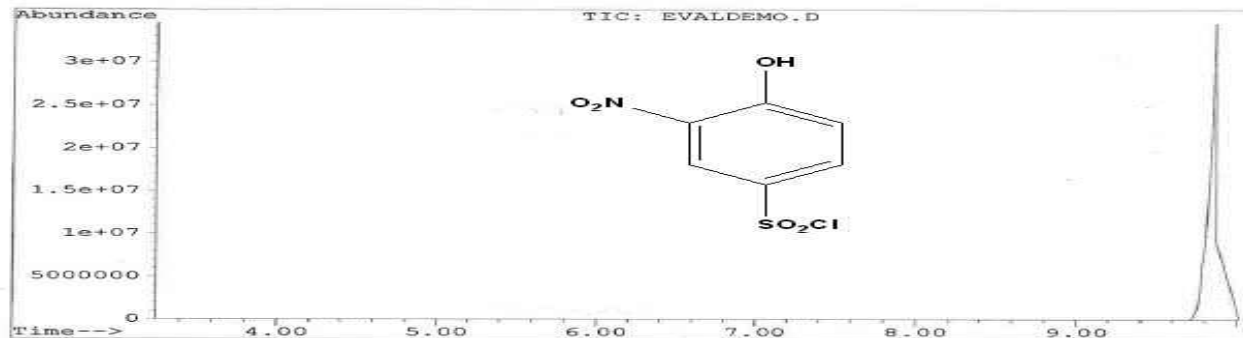
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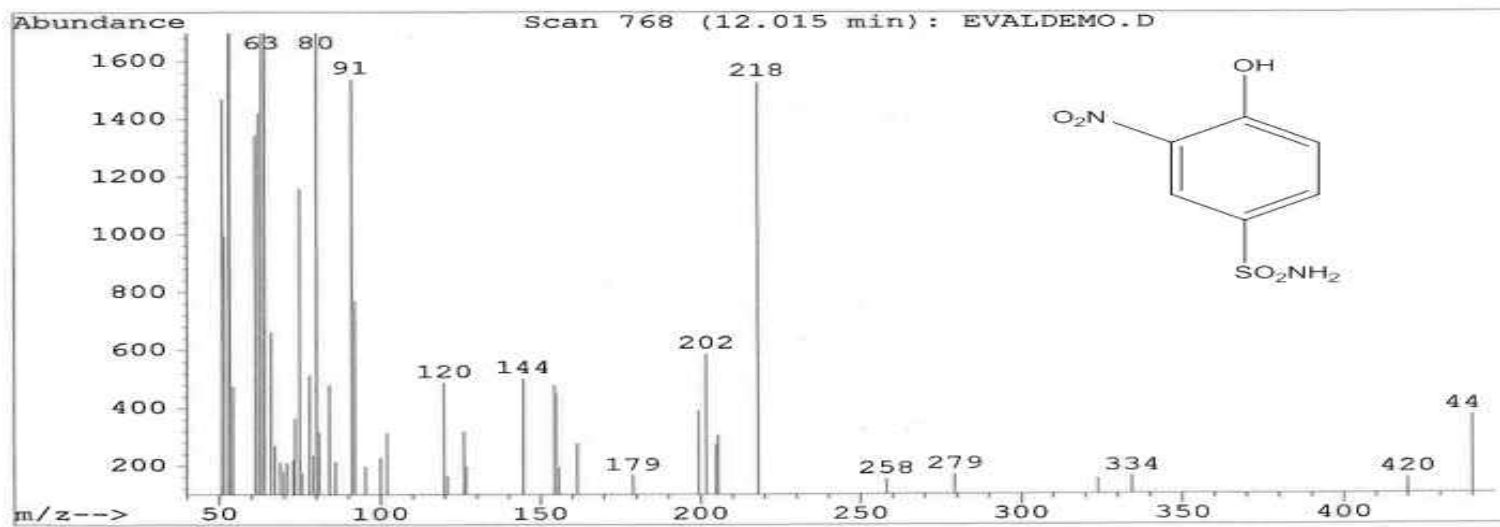
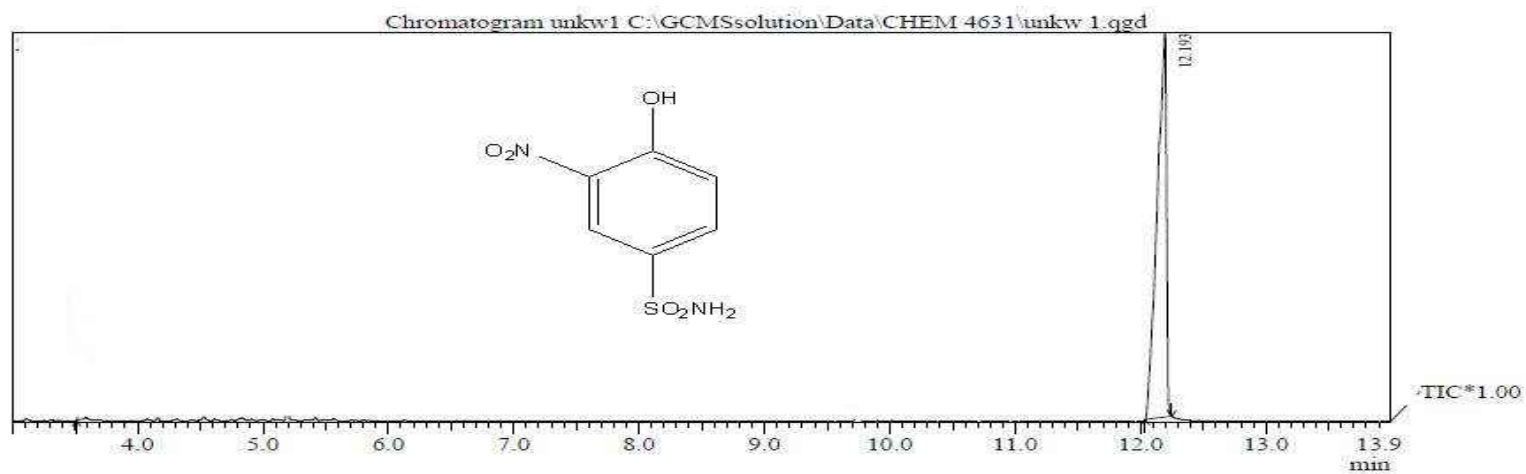
APPENDICES

APPENDIX A1: GC-MS Chromatogram of Compound 2

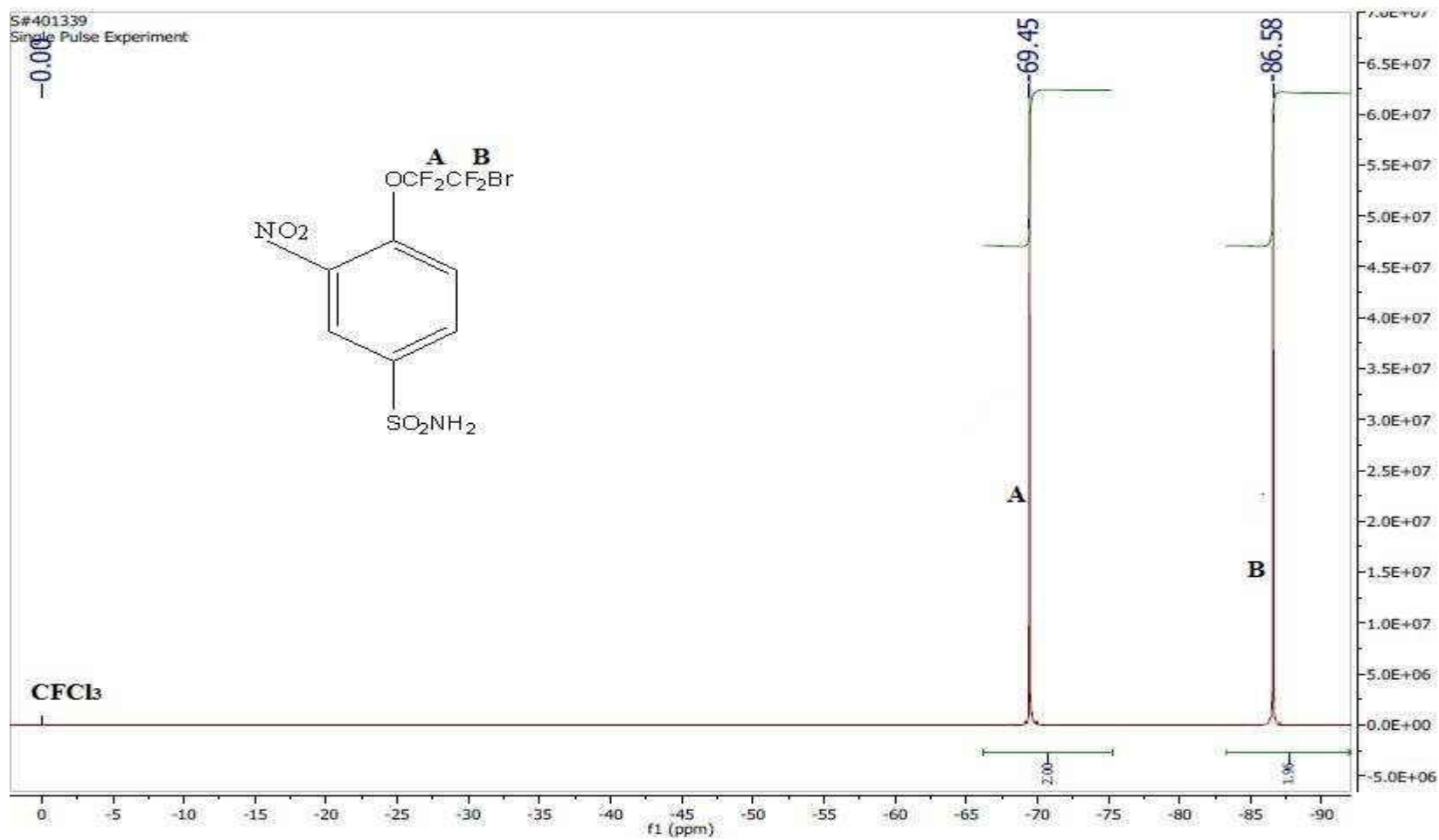
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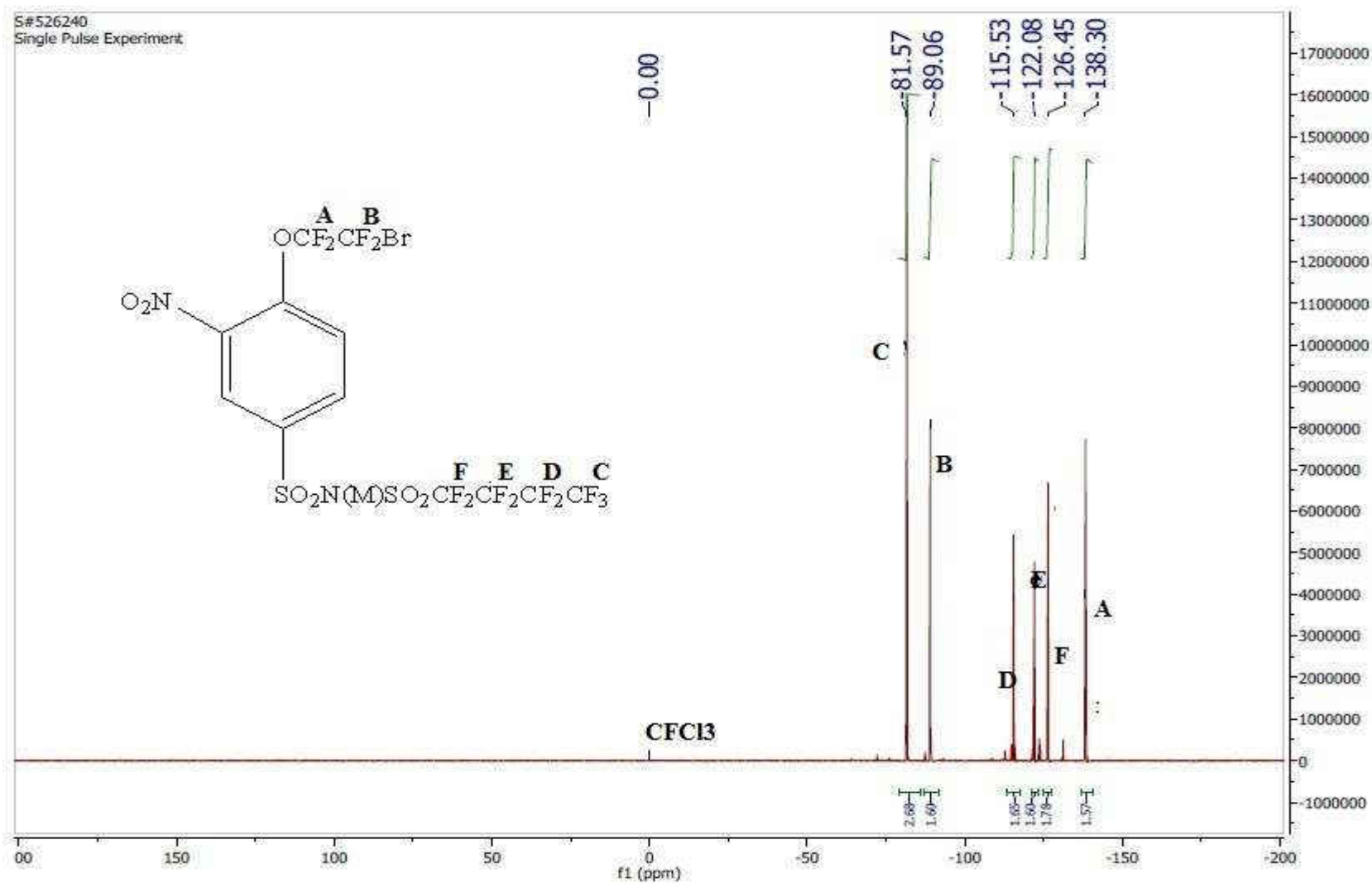
APPENDIX A2: GC-MS Chromatogram of Compound 3



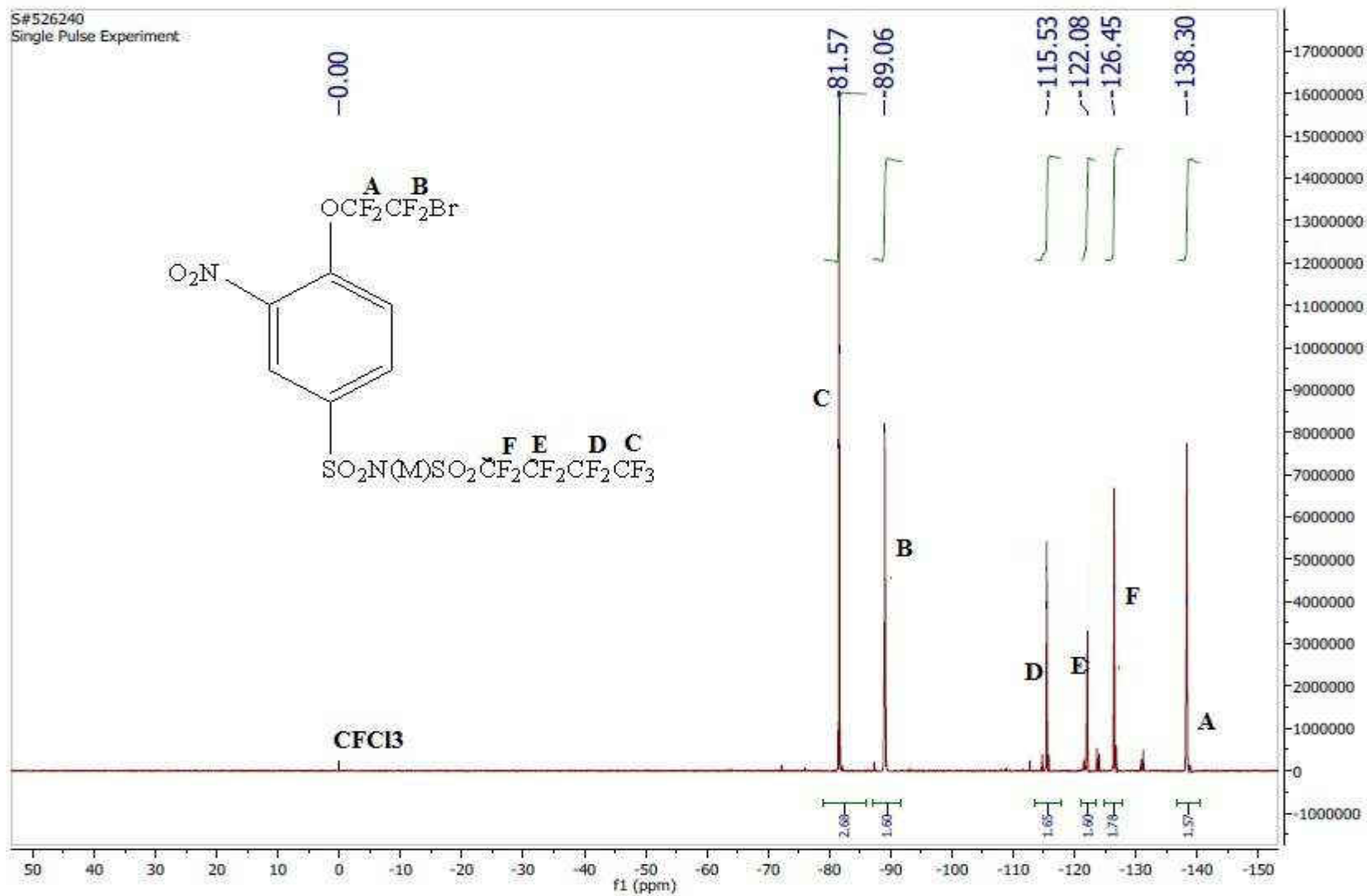
APPENDIX B1: ^{19}F NMR Spectrum of Compound 4



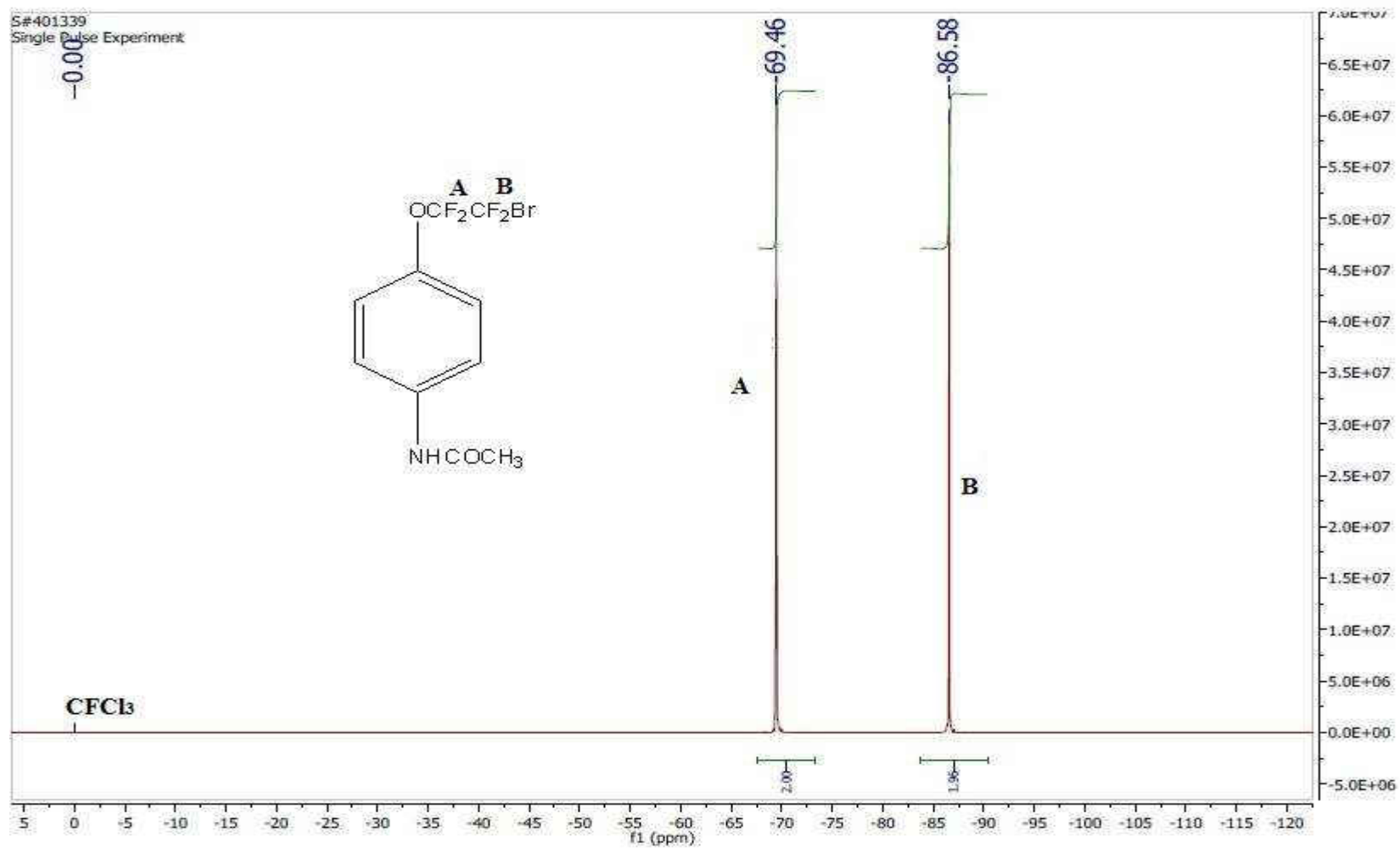
APPENDIX B2: ^{19}F NMR Spectrum of Compound 5



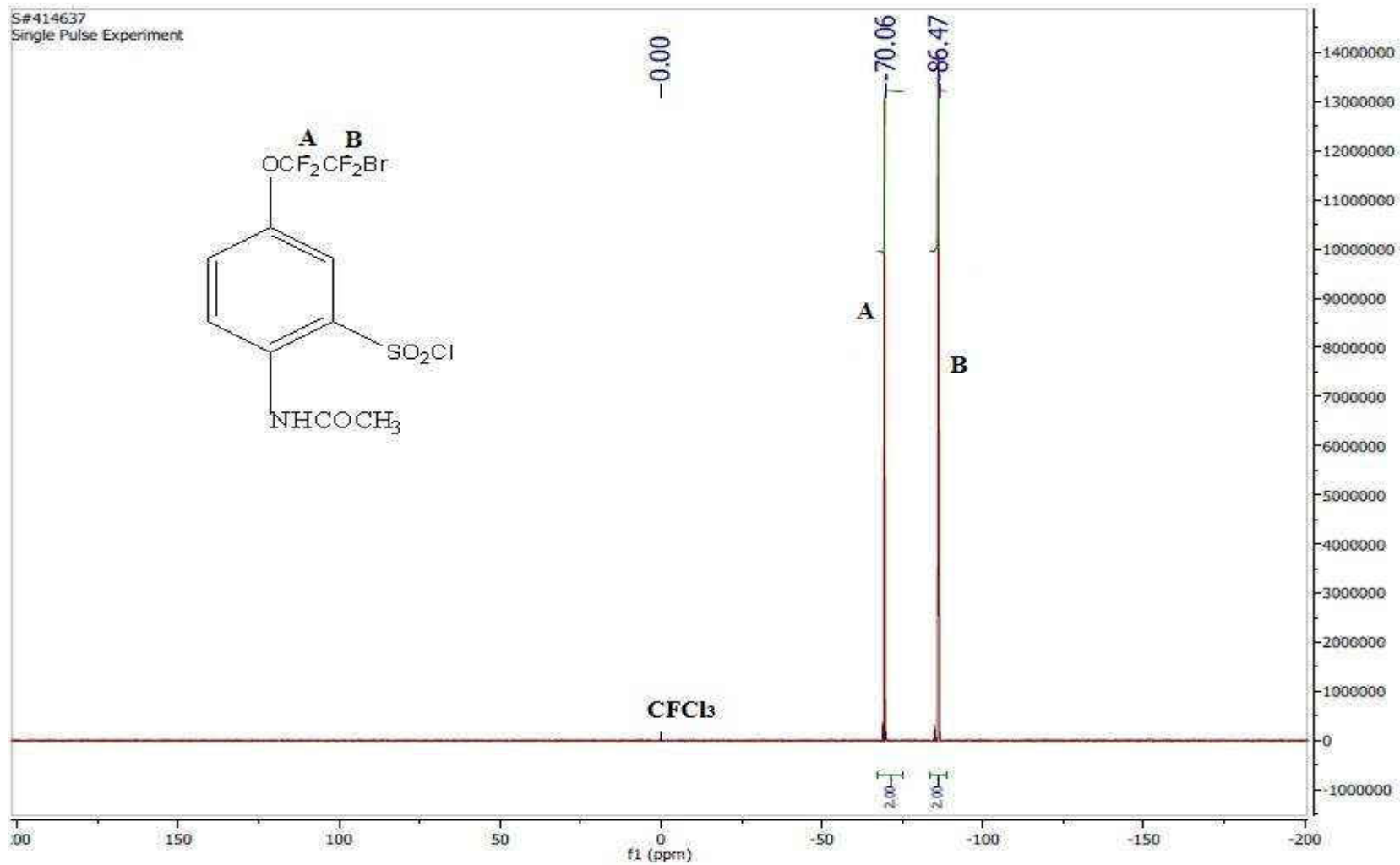
APPENDIX B3: Expanded ^{19}F NMR Spectrum of Compound 5



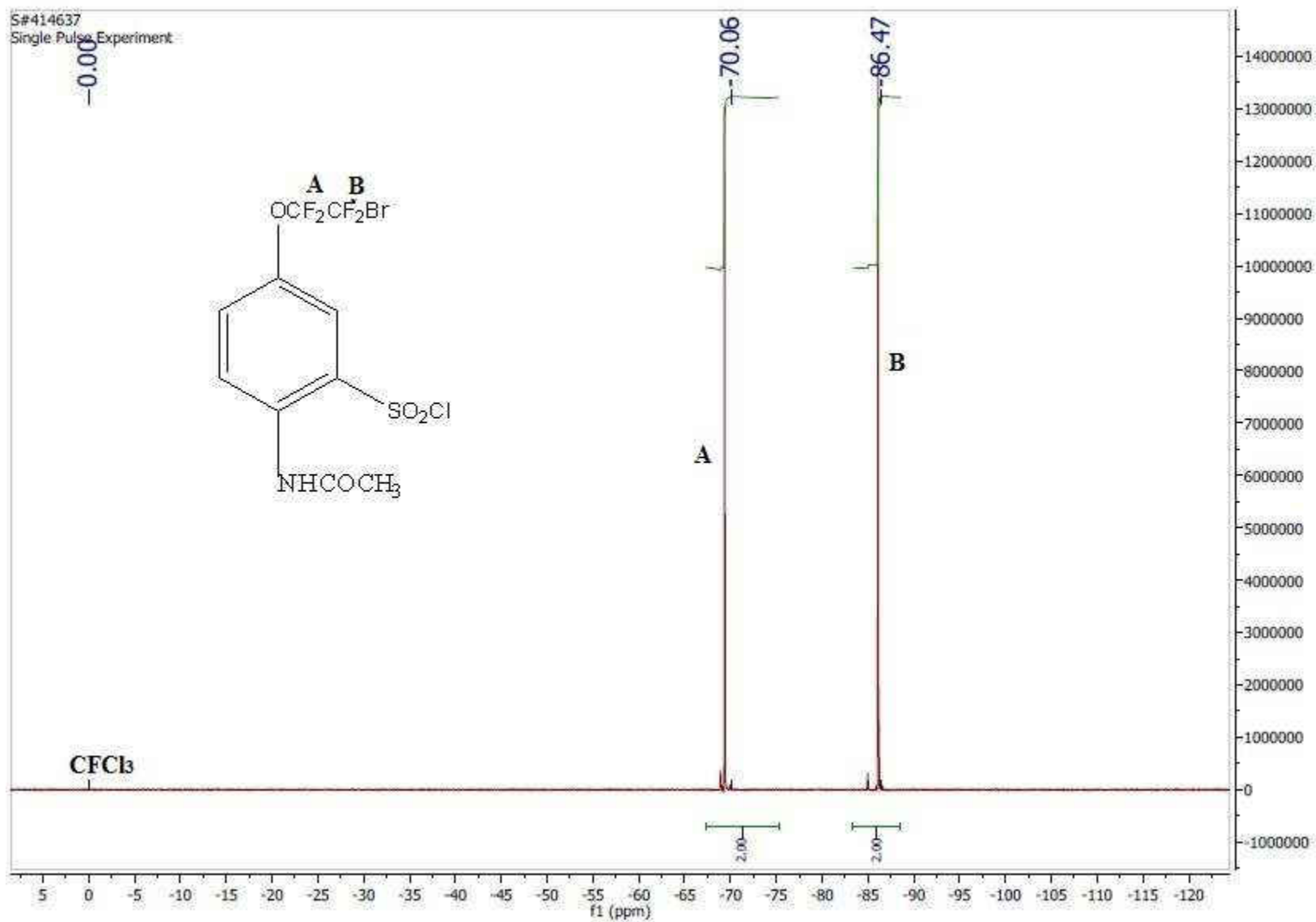
APPENDIX B4: Expanded ^{19}F NMR Spectrum of Compound **2'**



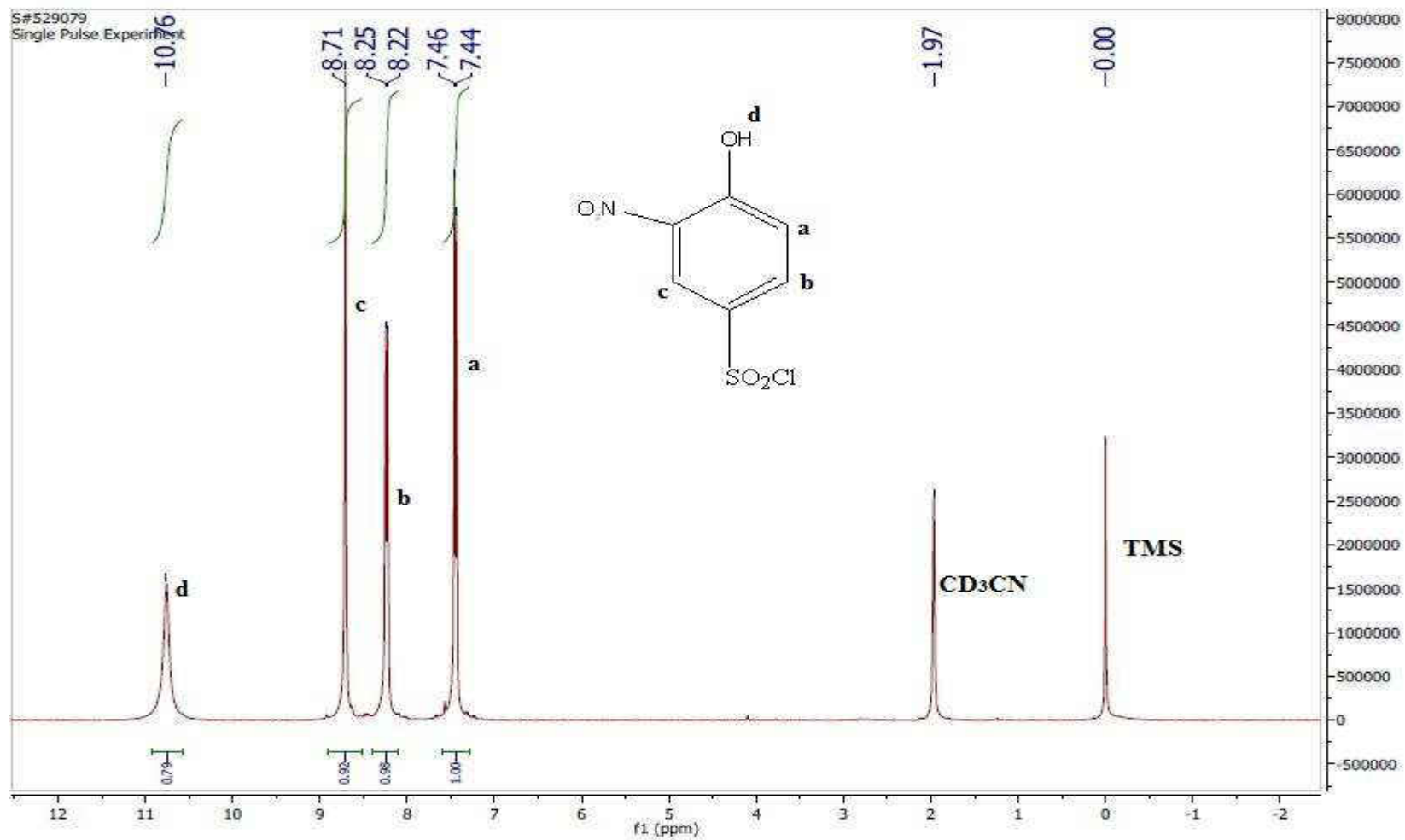
APPENDIX B5: ^{19}F NMR Spectrum of Compound 3'



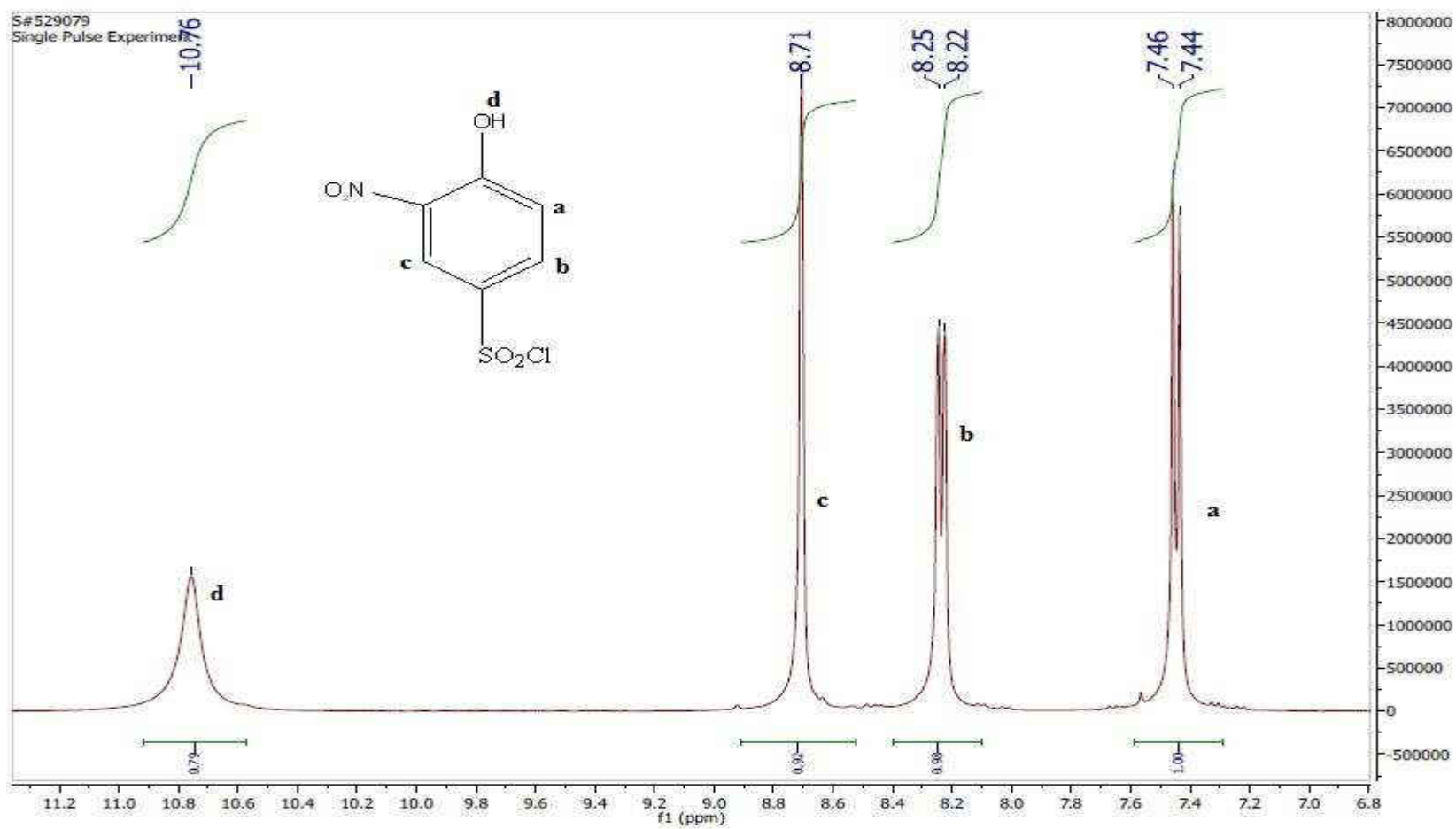
APPENDIX B6: Expanded ^{19}F NMR Spectrum of Compound 3'



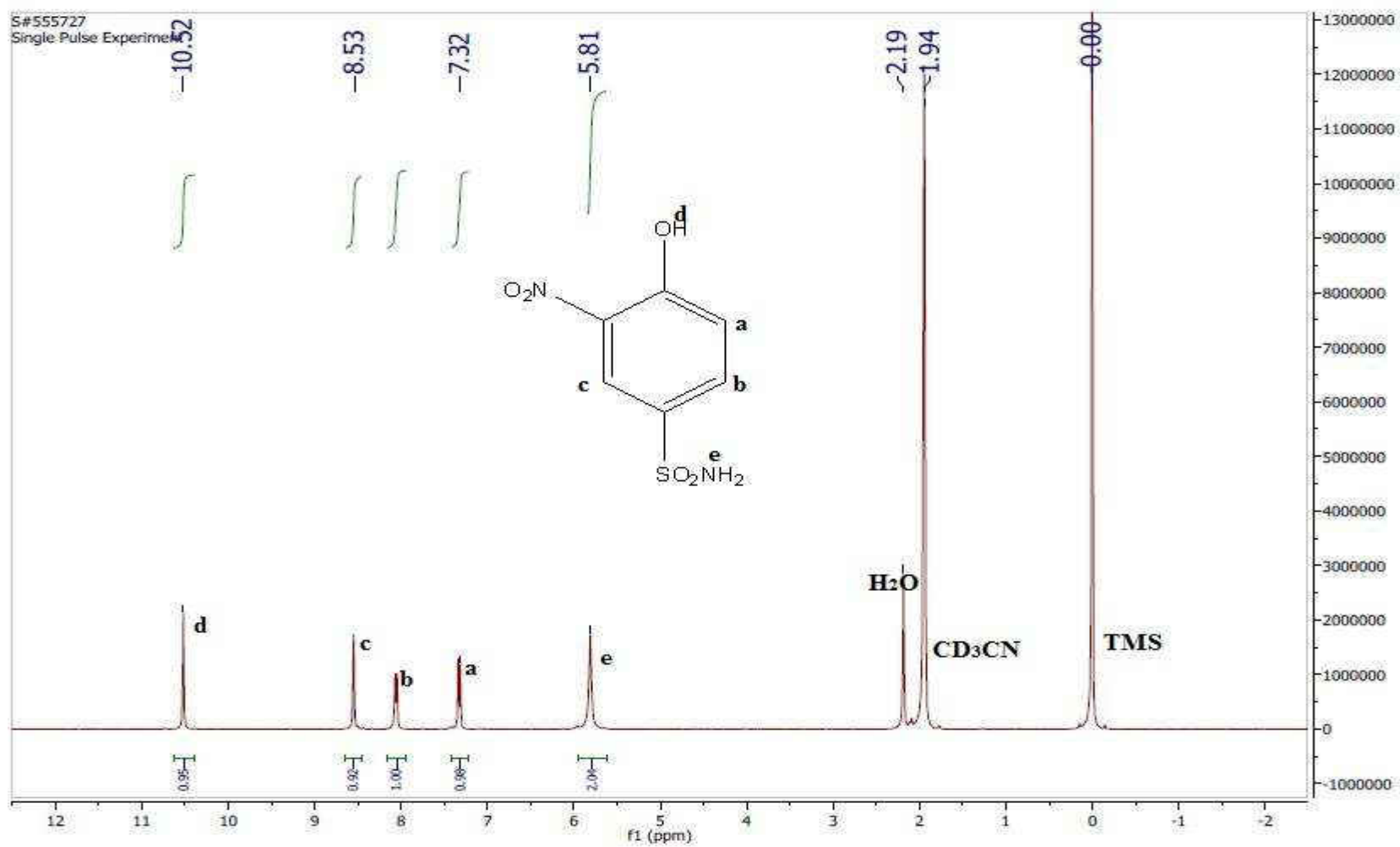
APPENDIX C1: ^1H NMR Spectrum of Compound 2



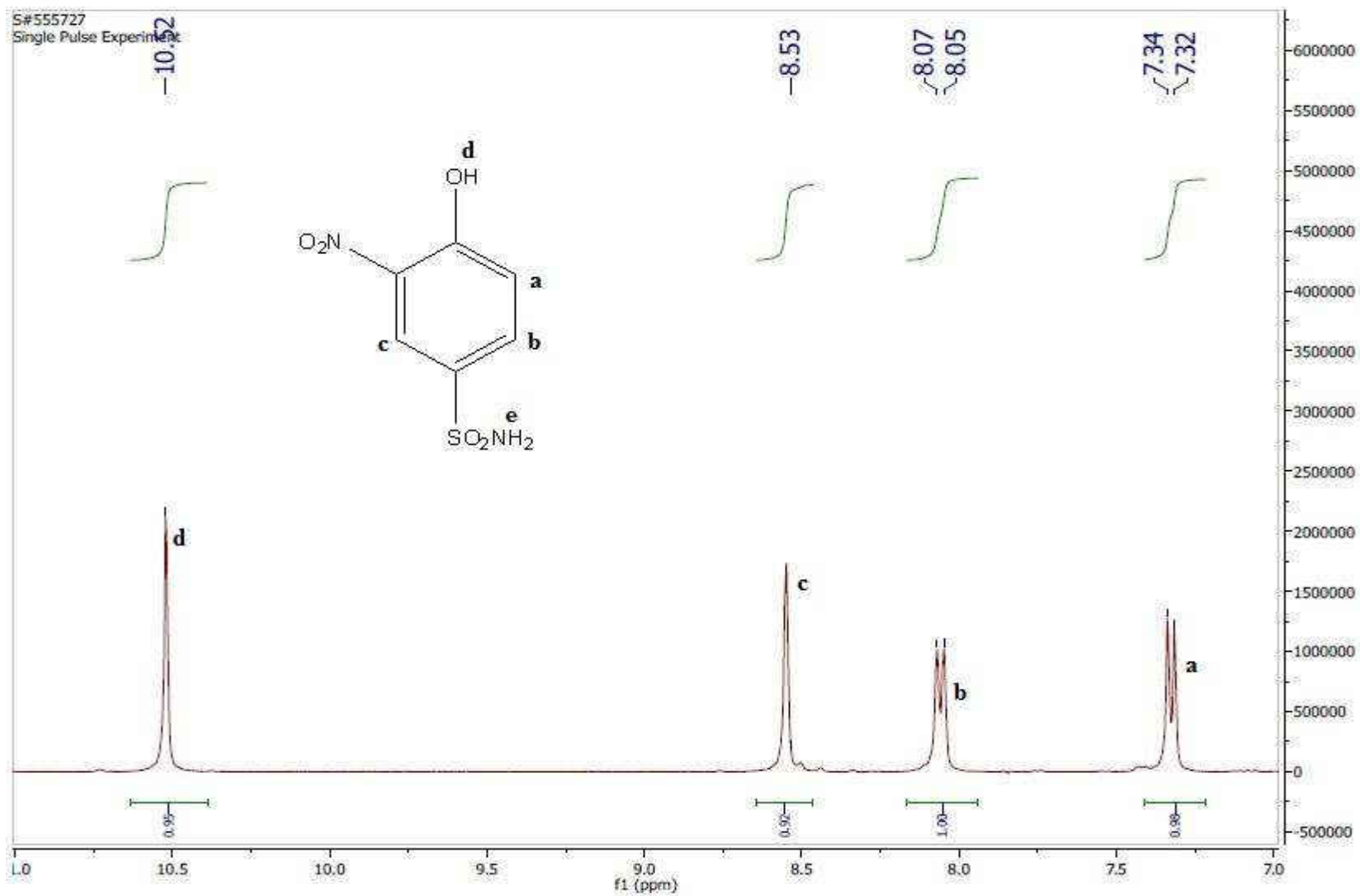
APPENDIX C2: Expanded ^1H NMR Spectrum of Compound 2



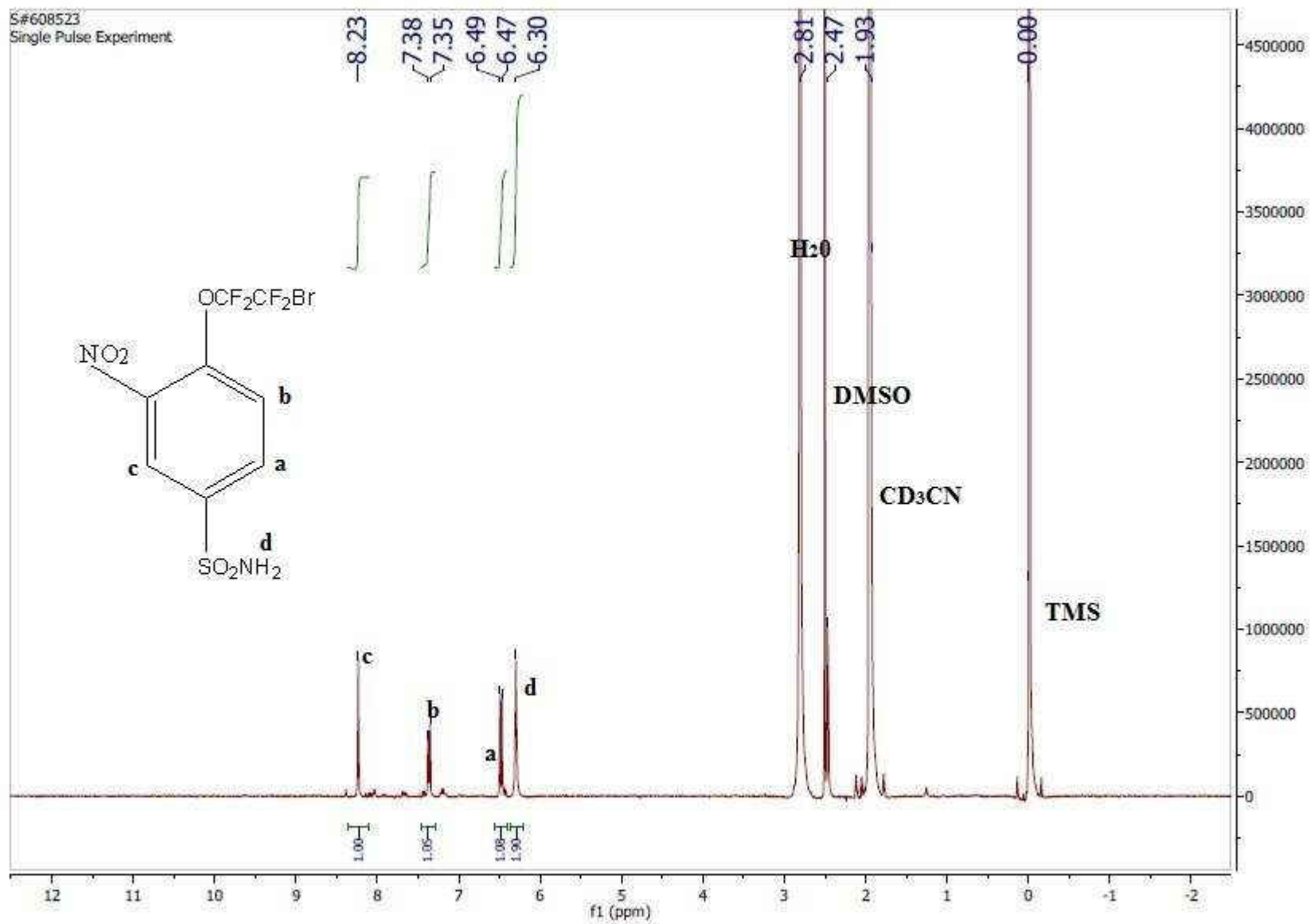
APPENDIX C3: ^1H NMR Spectrum of Compound 3



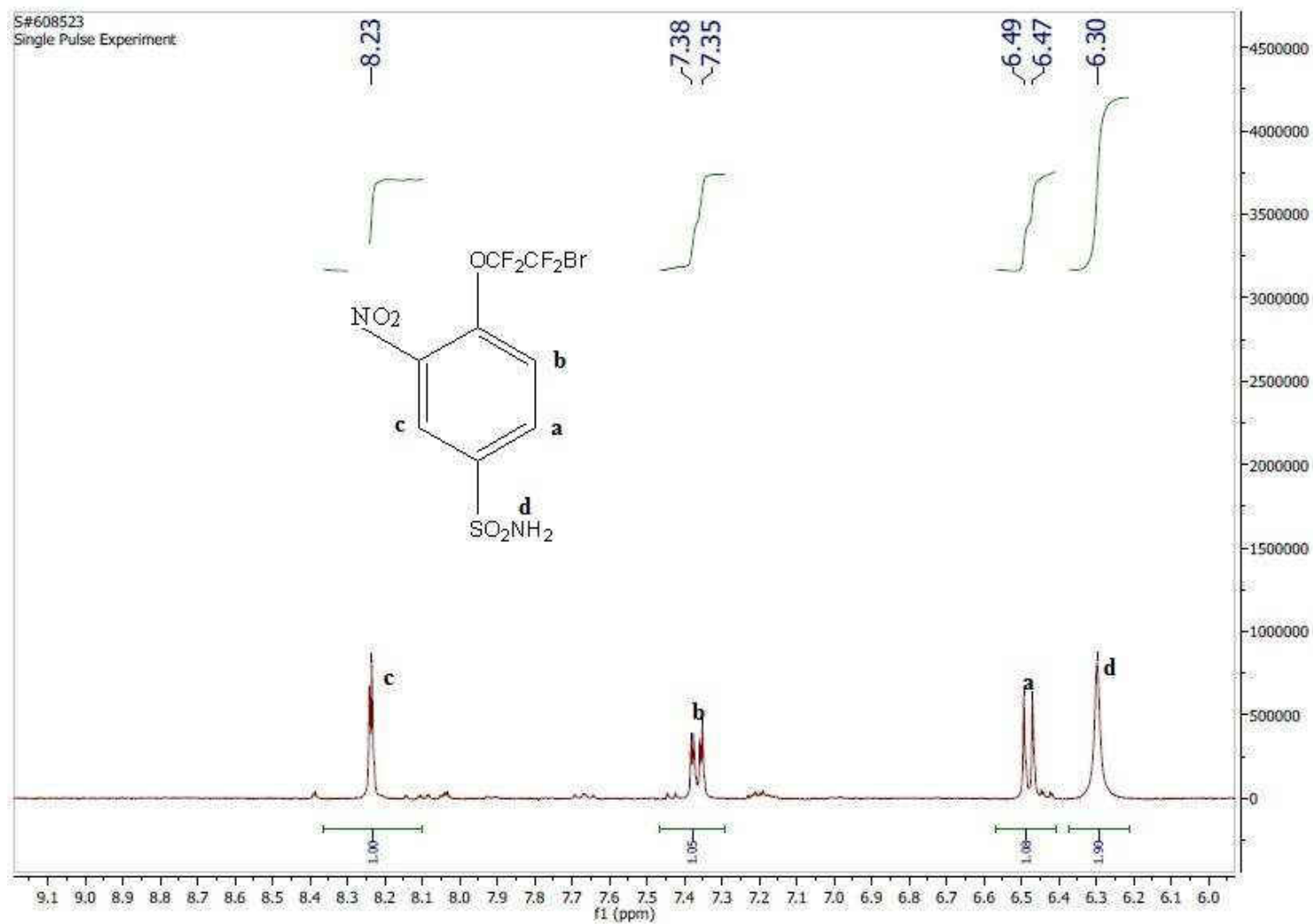
APPENDIX C4: Expanded ^1H NMR Spectrum of Compound 3



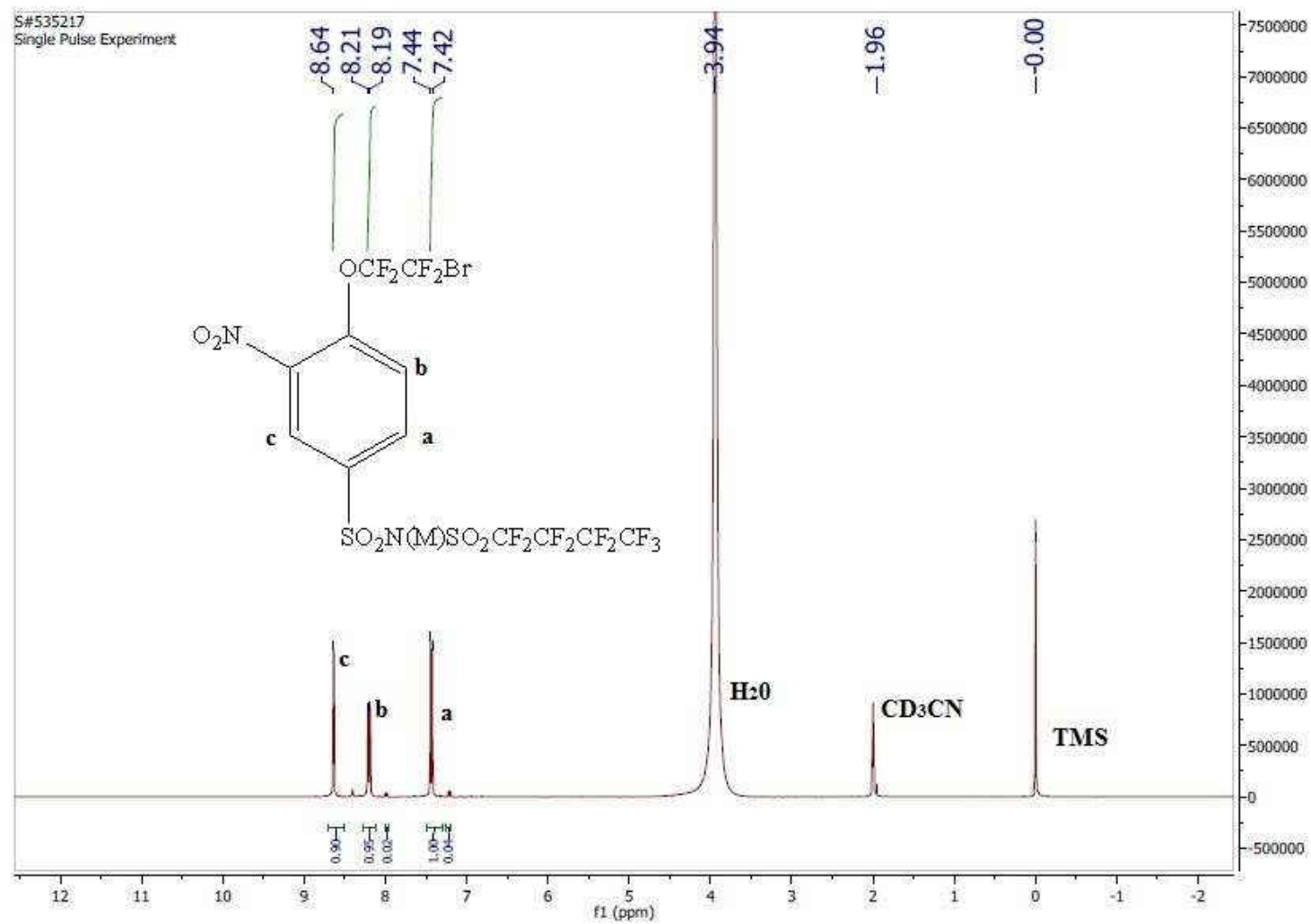
APPENDIX C5: ¹H NMR Spectrum of Compound 4



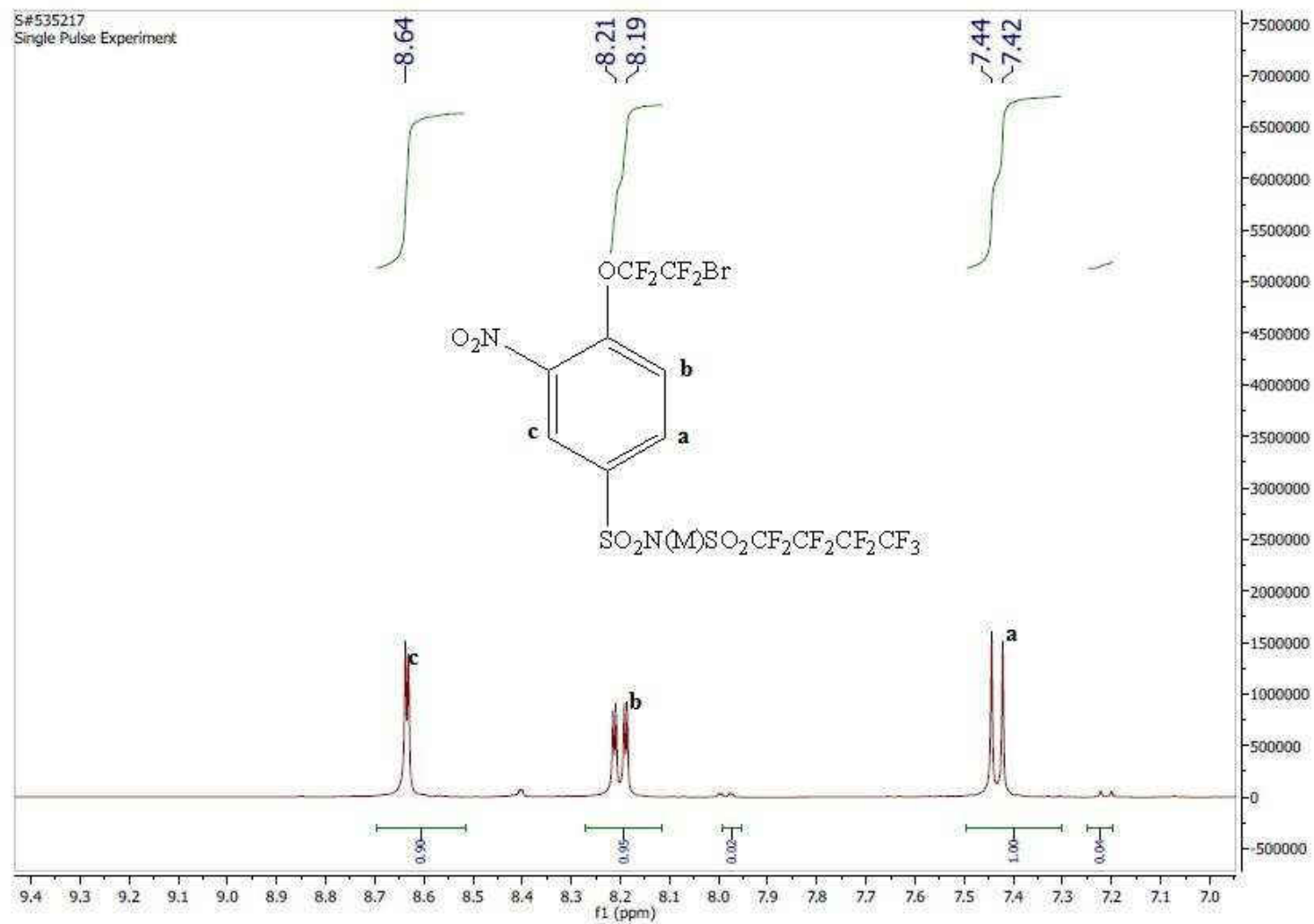
APPENDIX C6: Expanded ^1H NMR Spectrum of Compound 4



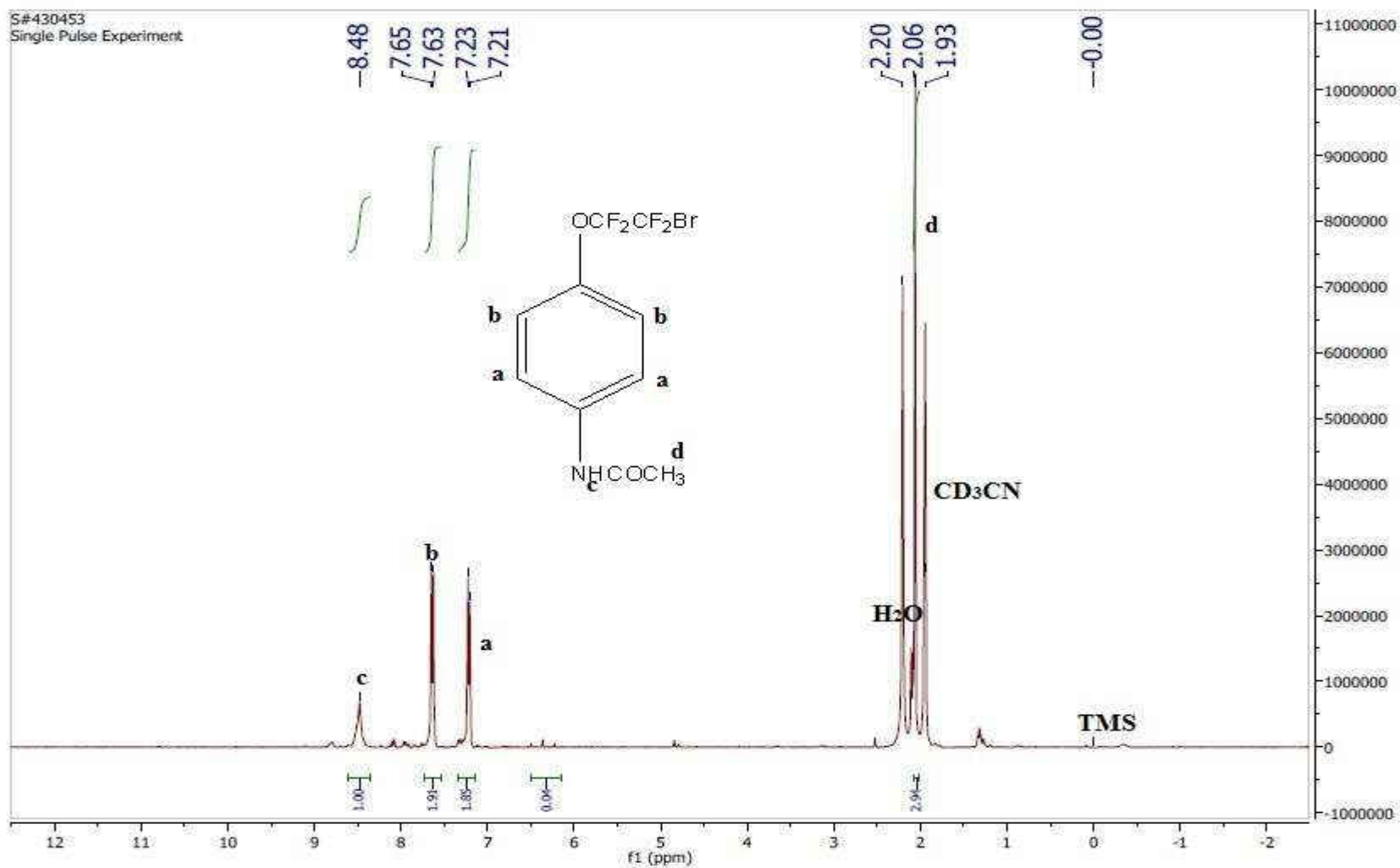
APPENDIX C7: ^1H NMR Spectrum of Compound 5



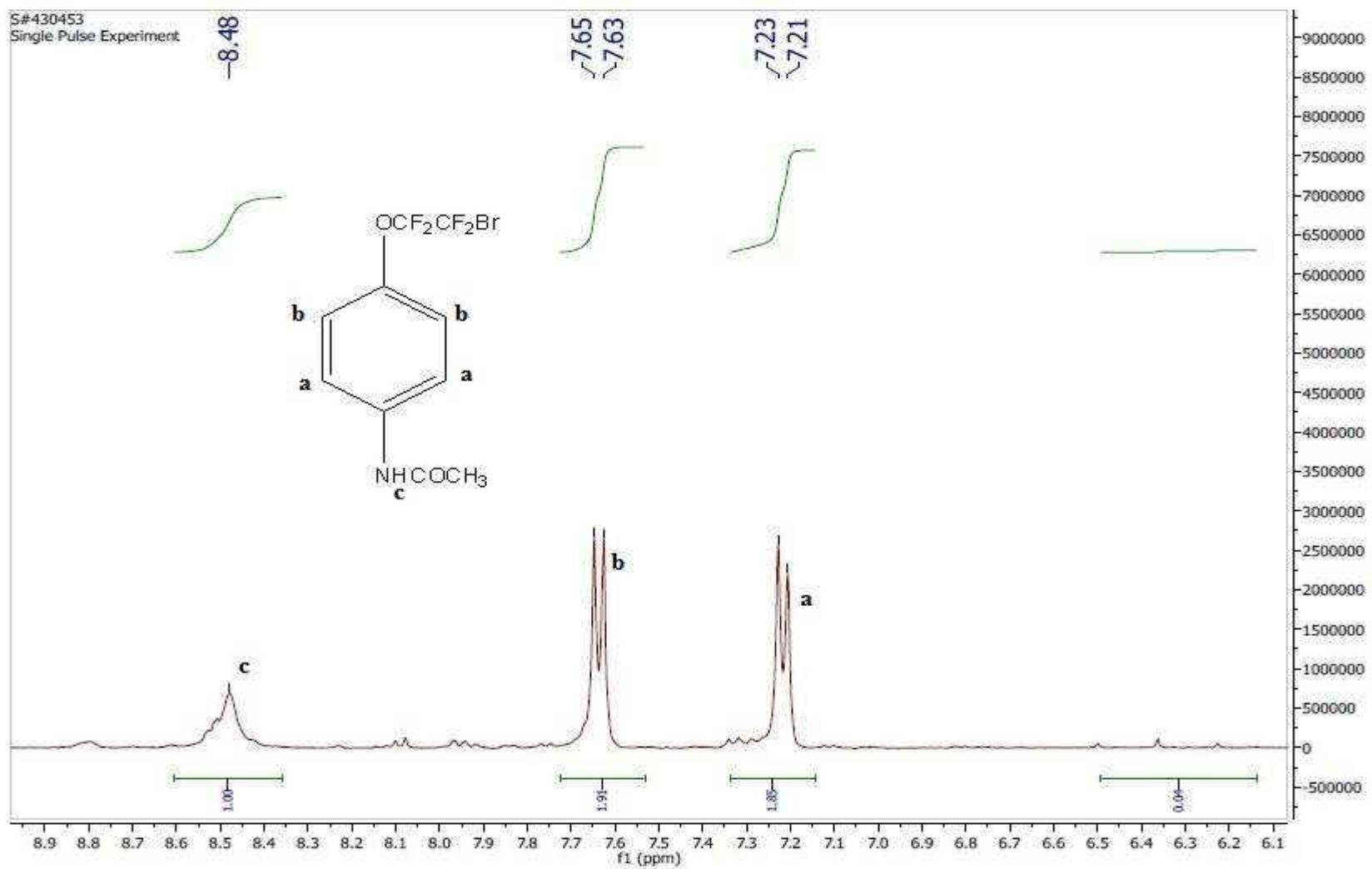
APPENDIX C8: Expanded ^1H NMR Spectrum of Compound 5



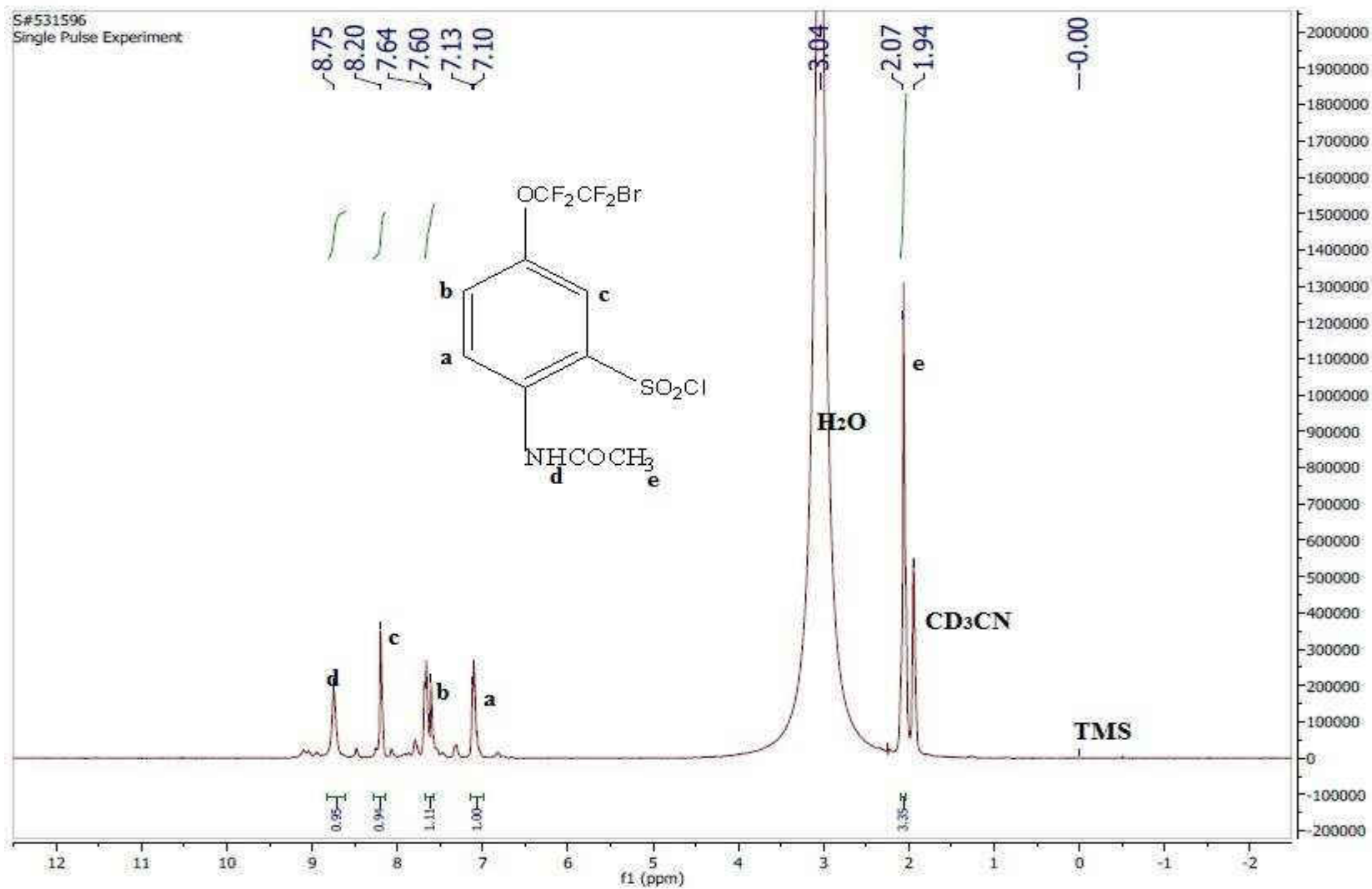
APPENDIX C9: ^1H NMR Spectrum of Compound 2'



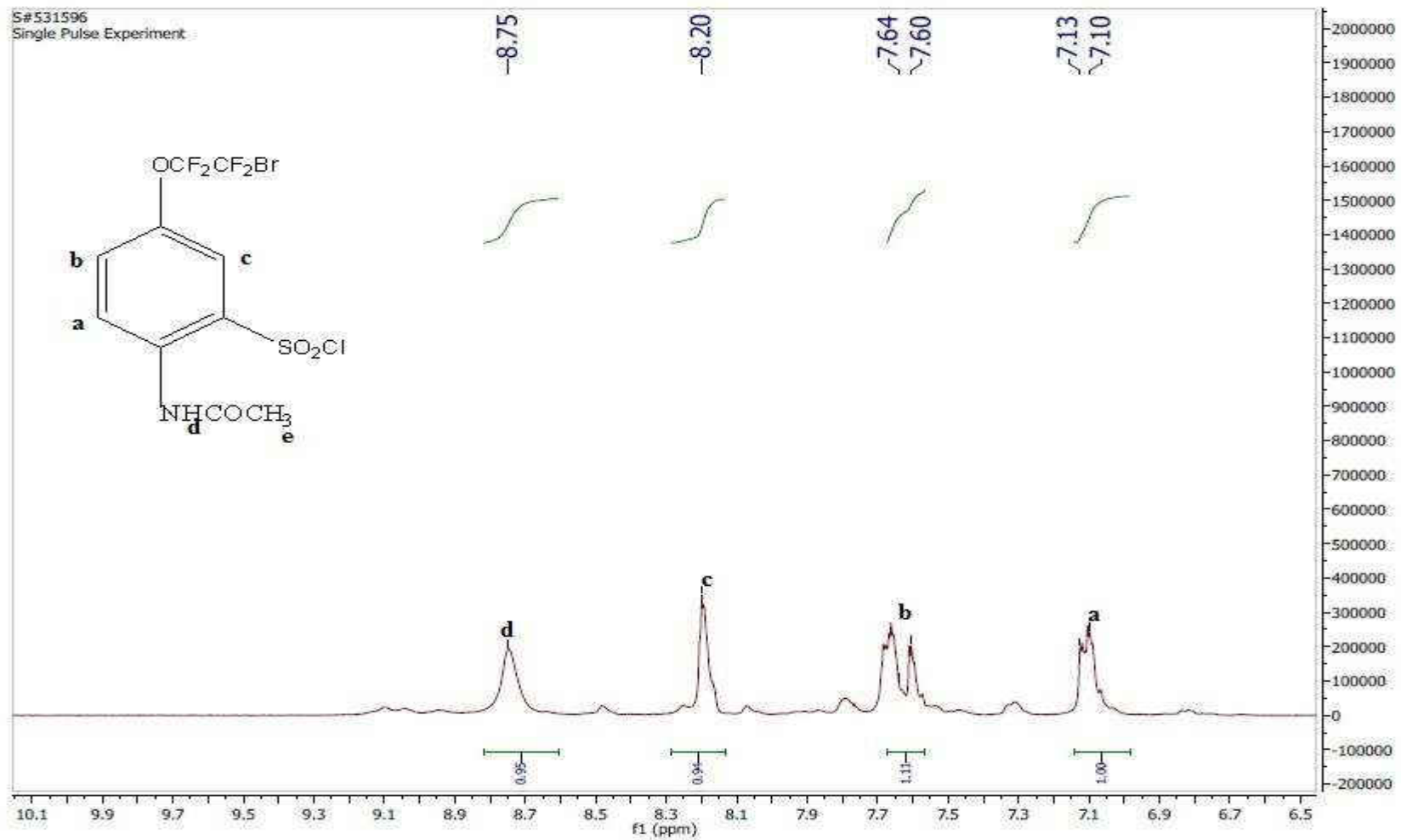
APPENDIX C10: Expanded ^1H NMR Spectrum of Compound 2'



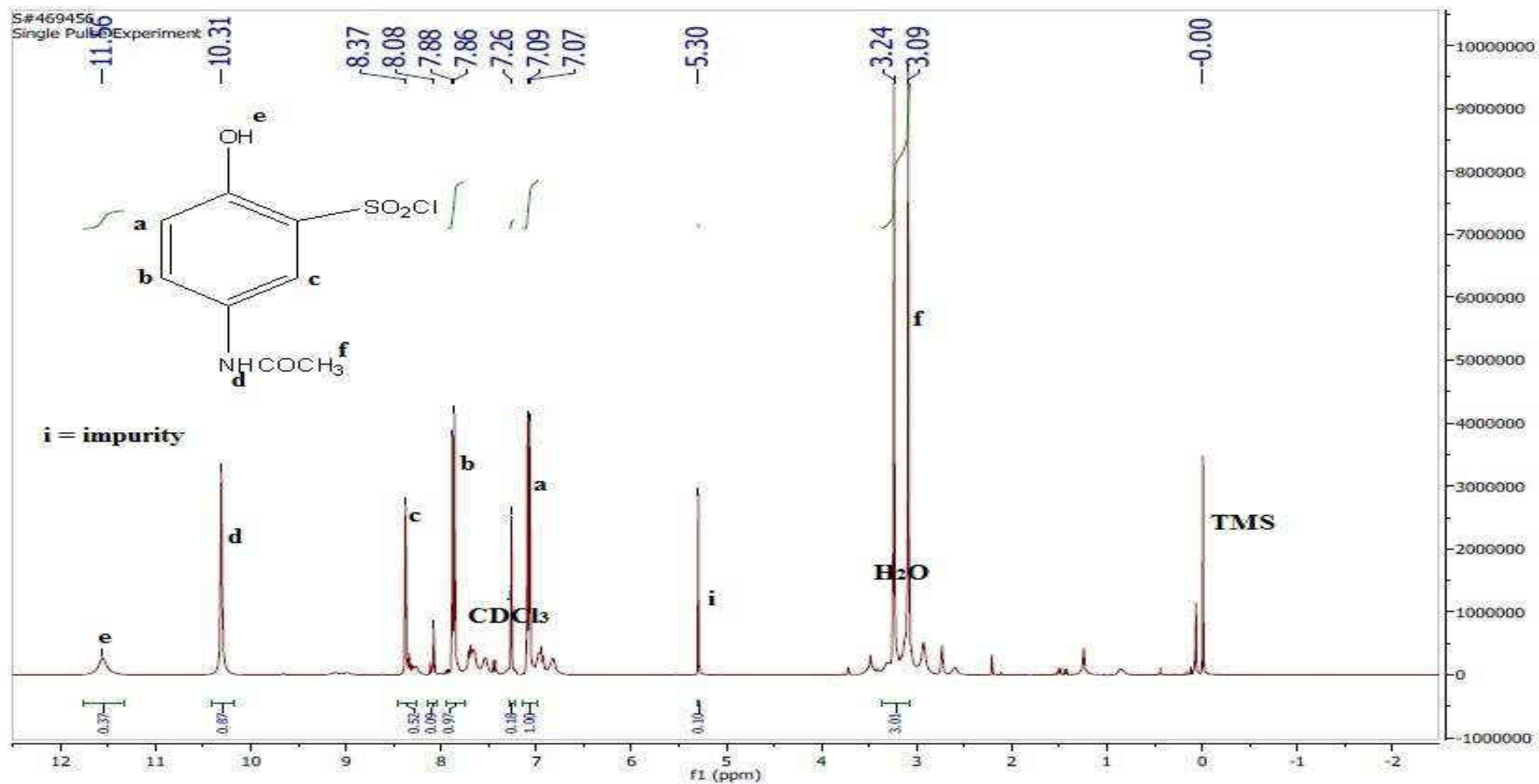
APPENDIX C11: ^1H NMR Spectrum of Compound 3'



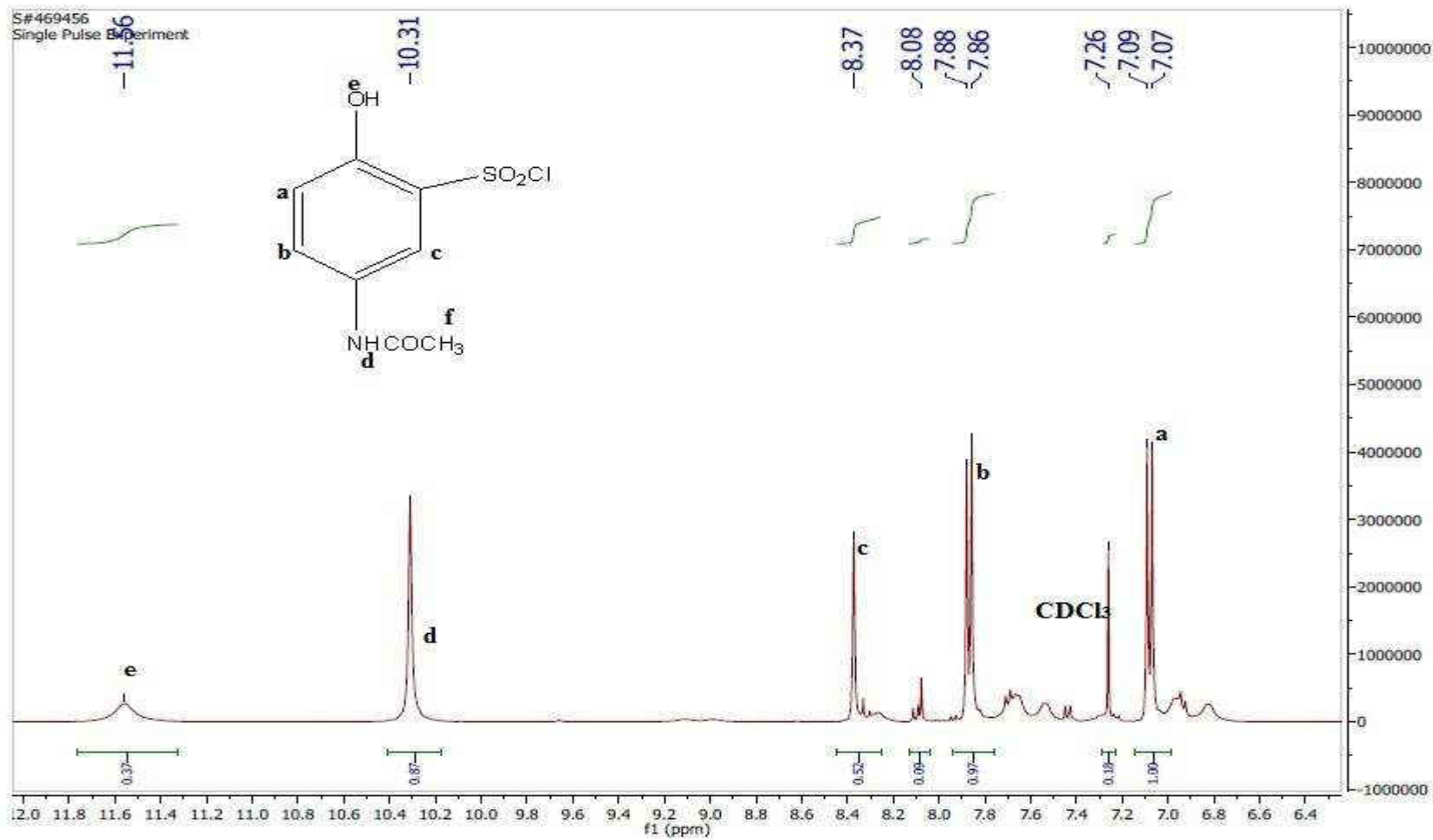
APPENDIX C12: Expanded ^1H NMR Spectrum of Compound 3'



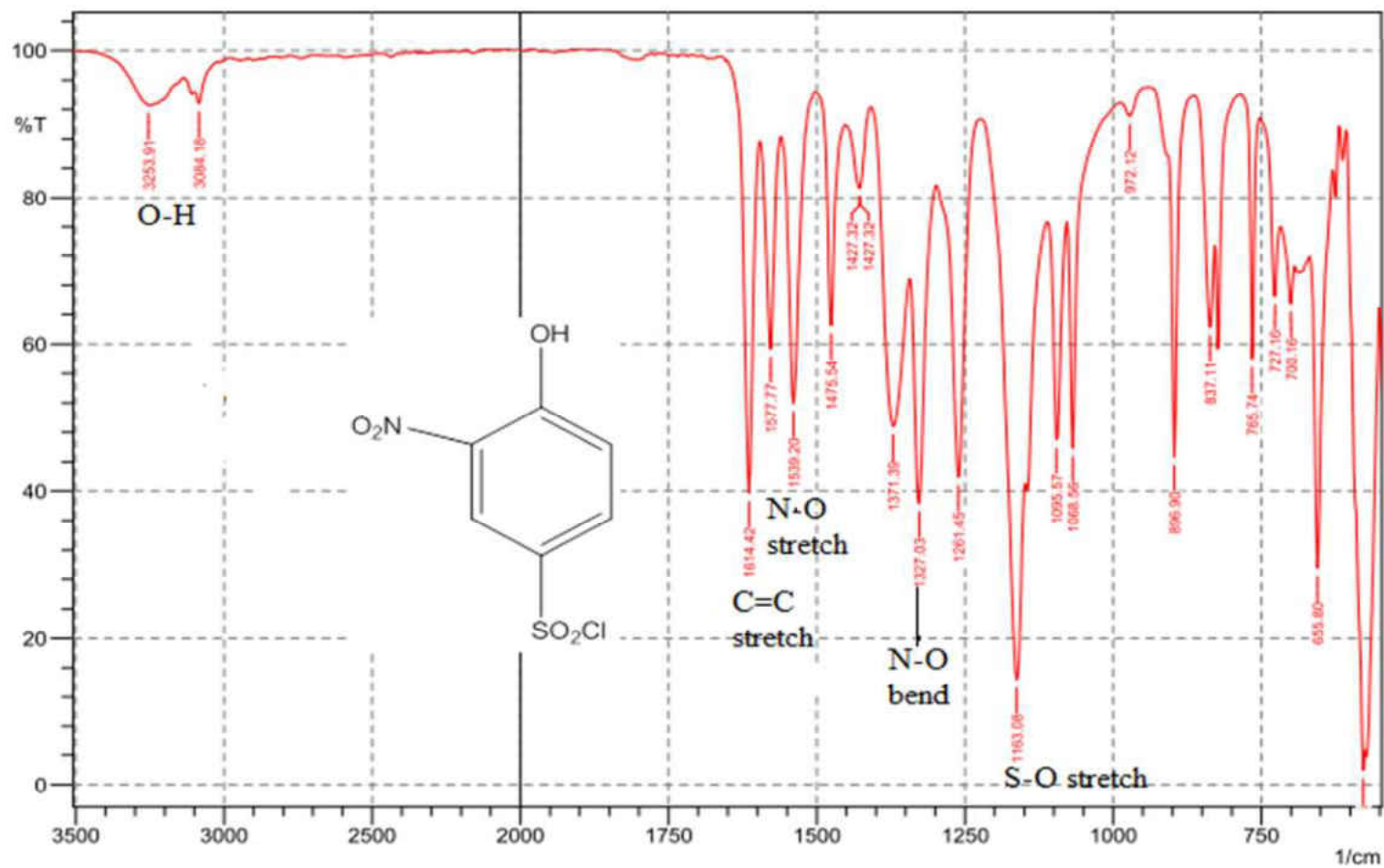
APPENDIX C13: ¹H NMR Spectrum of Compound 2''



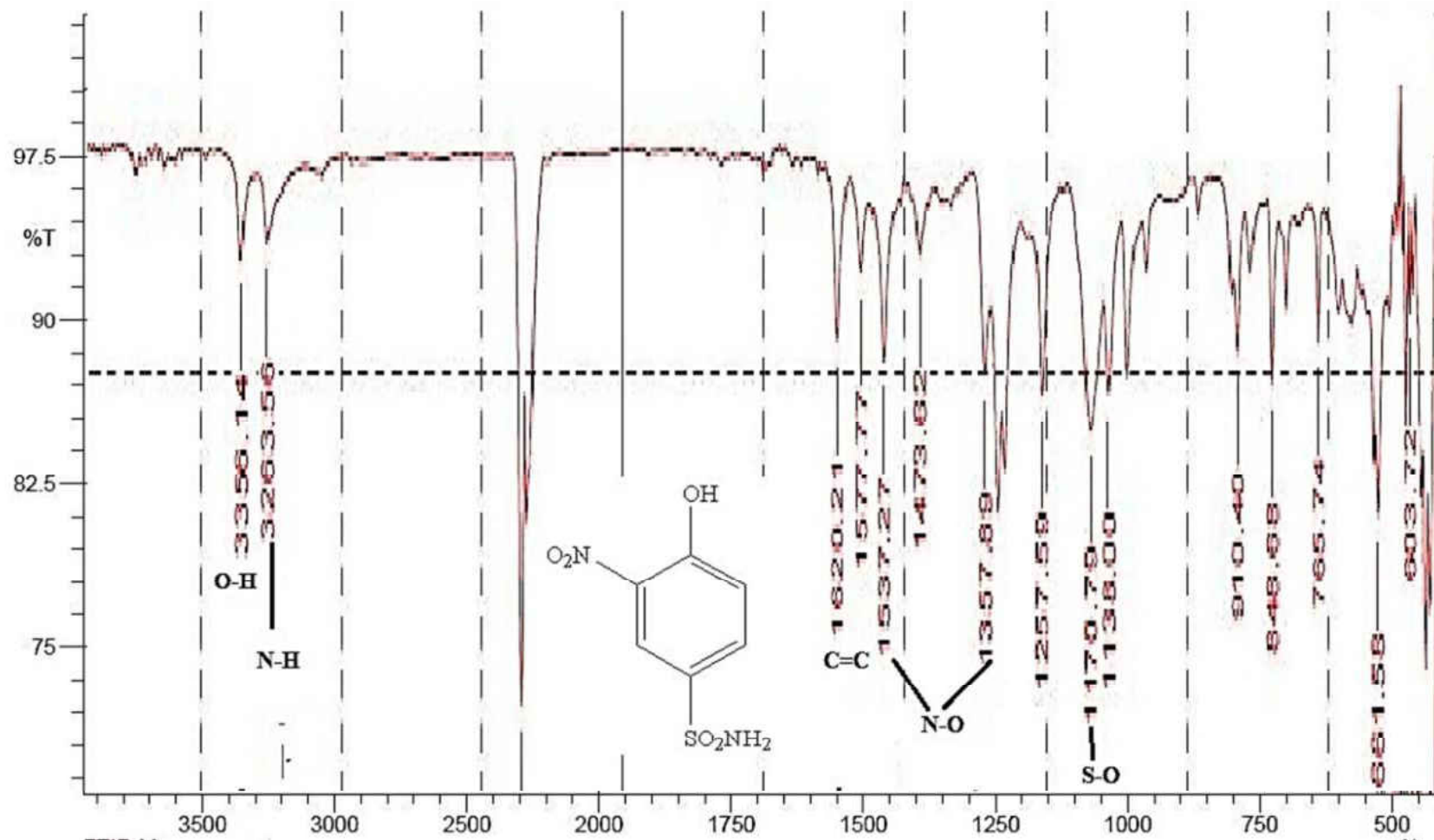
APPENDIX C14: Expanded ^1H NMR Spectrum of Compound 2''



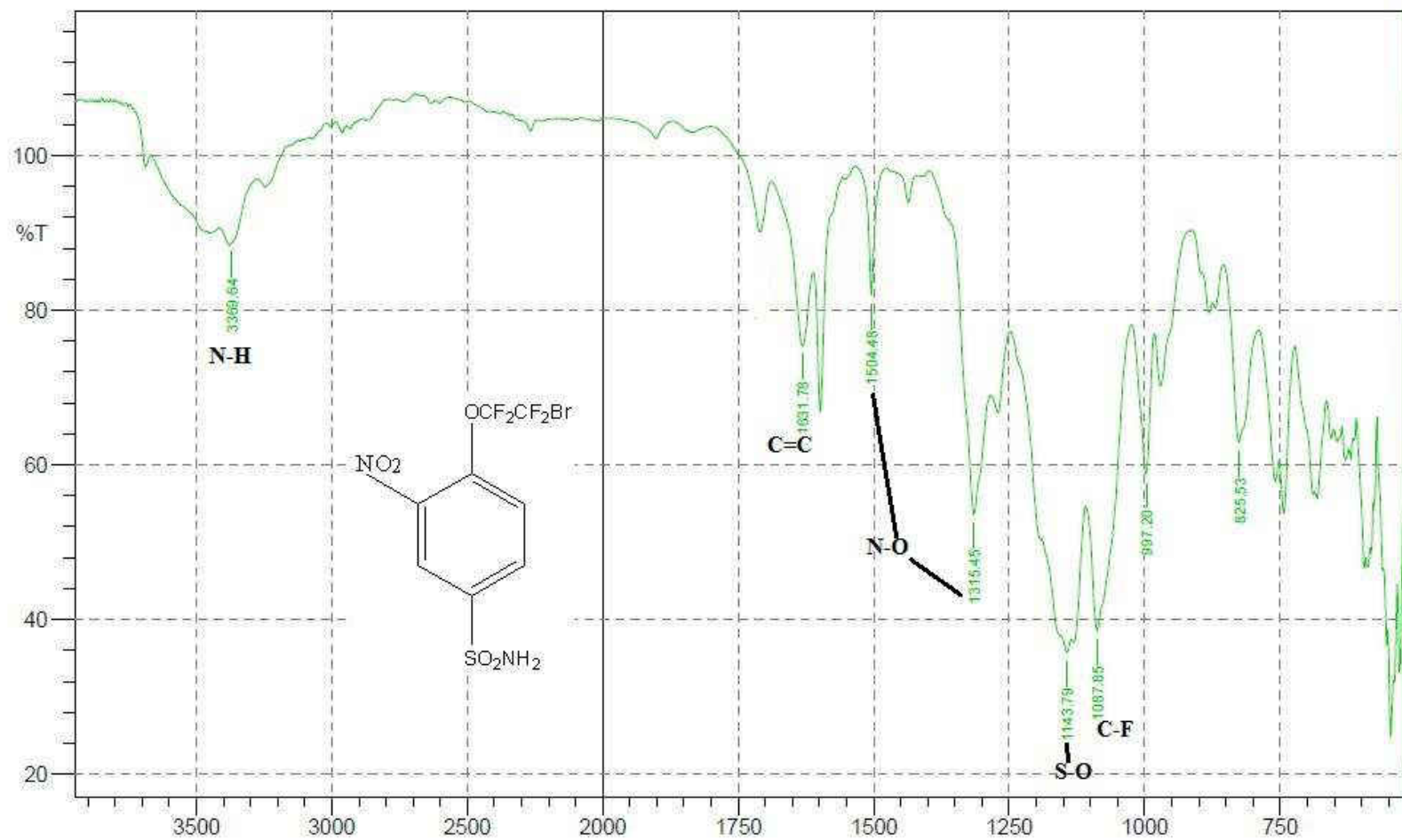
APPENDIX D1: FT-IR Spectrum of Compound 2



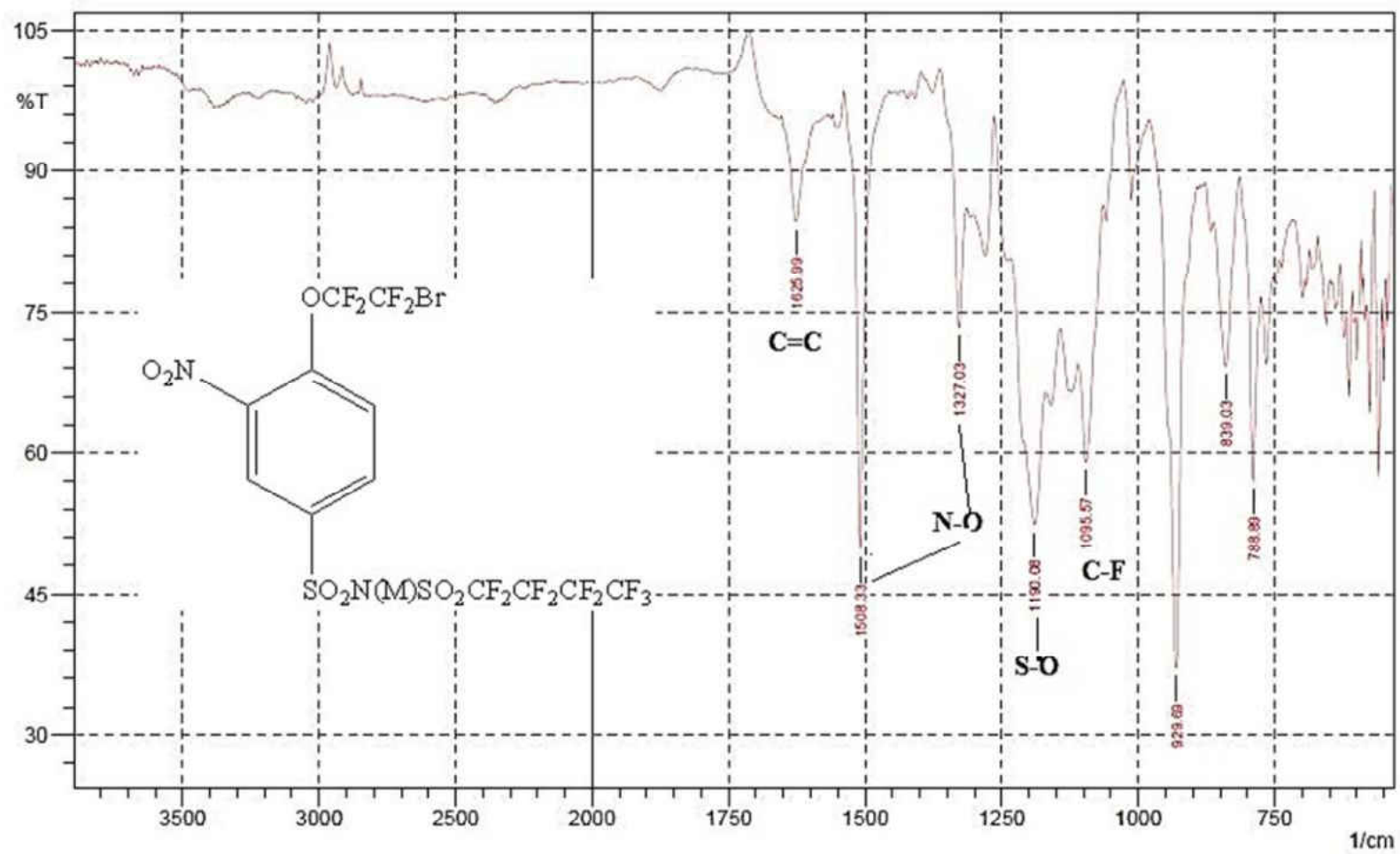
APPENDIX D2: FT-IR Spectrum of Compound 3



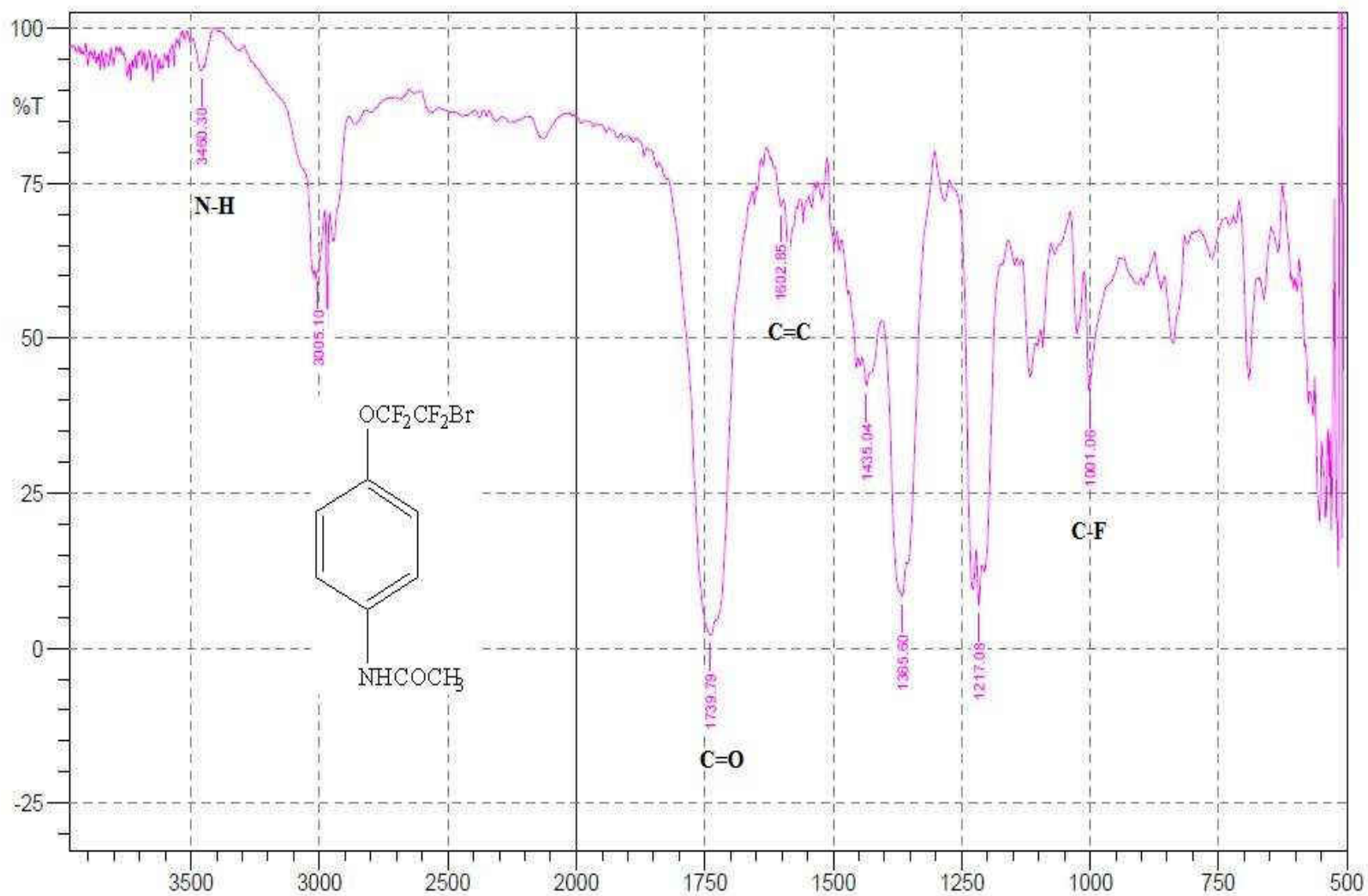
APPENDIX D3: FT-IR Spectrum of Compound 4



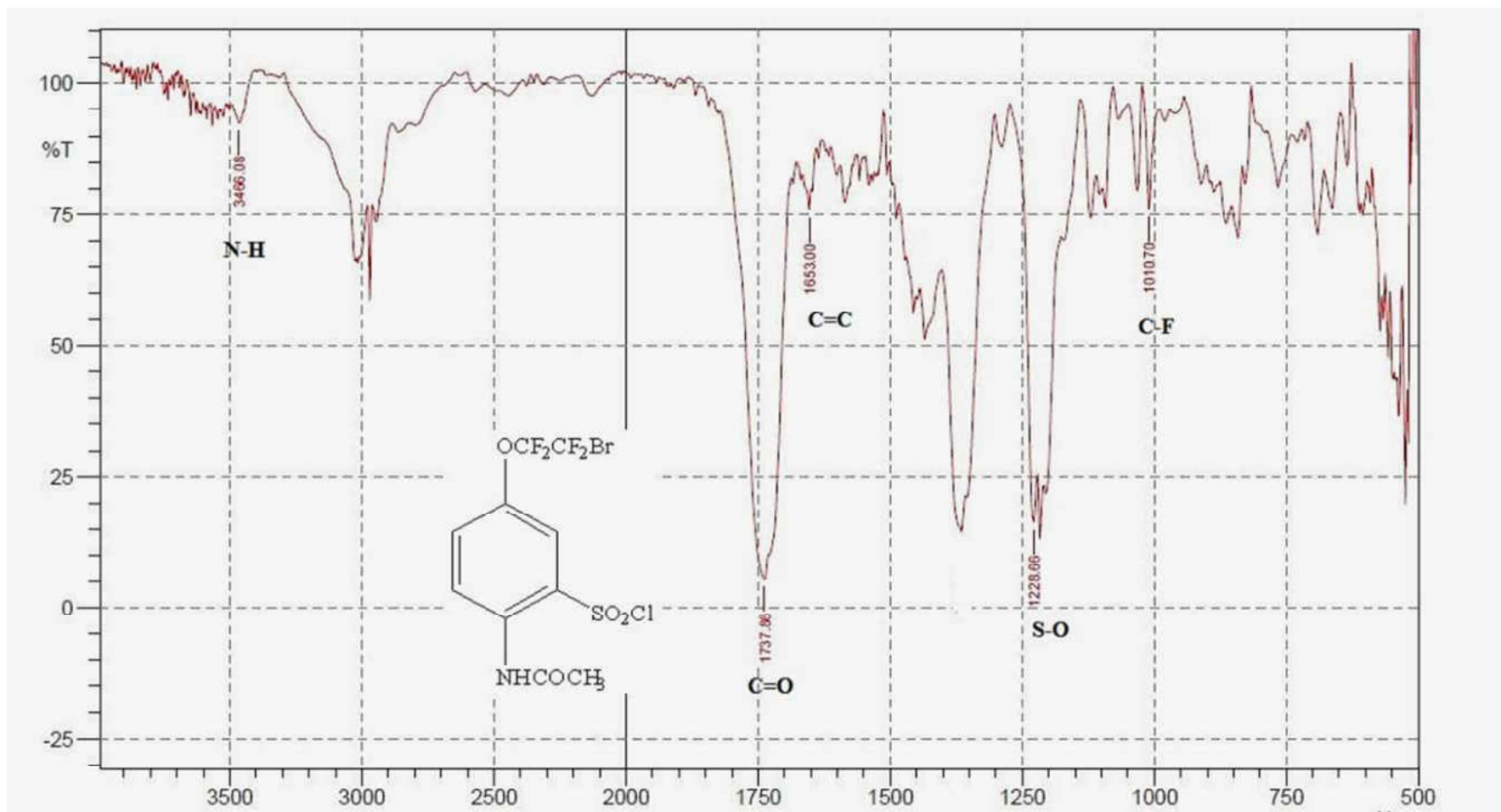
APPENDIX D4: FT-IR Spectrum of Compound 5



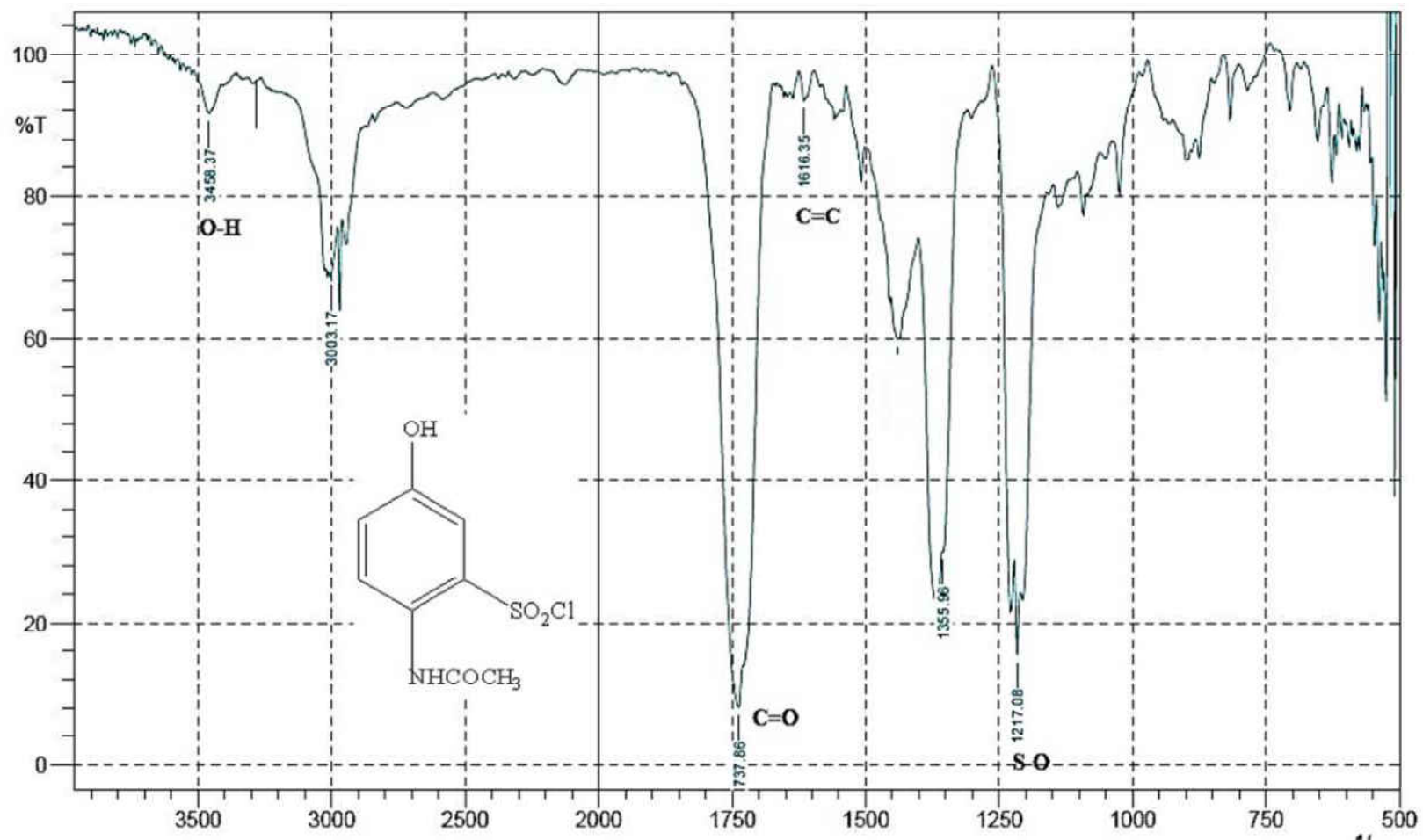
APPENDIX D5: FT-IR Spectrum of Compound 2'



APPENDIX D6: FT-IR Spectrum of Compound 3'



APPENDIX D7: FT-IR Spectrum of Compound 2''



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