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PERFLUOROALKYL (ARYL) SULFONIMIDE ZWITTERIONS

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ABSTRACT

This research focuses on superacid perfluoroalkyl(aryl) sulfonimides and their derivatives as a source of stable zwitterionic salts. The strong resonance stabilization of sulfonimides imparts unexpected stability to the zwitterions.

Two types of zwitterions were investigated. The first are symmetrical diaryliodonium zwitterions (DZs) as potential photo acid generators (PAGs) for microlithography. Driven by the demand for smaller feature sizes in the microelectronics industry, microlithography using shorter wavelength light has evolved and new PAGs are of interest. New DZs are potentially useful because they have good thermal stability and may be structurally modified to alter their spectral absorption characteristics. As an extension of earlier research in our group, three new symmetric difunctional DZs (p-$PhI^{+}PhSO_2N^{-}SO_2R_f)_2$ ($R_f = C_4F_8$, or C_6F_{12}, or $C_2F_4OC_2F_4$) were synthesized. Similar to earlier monofunctional DZs, they have very good thermal stability and high extinction coefficients.

The second zwitterions were developed for electrochemical applications. In order to incorporate strong acid electrolytes into nanoporous carbon electrodes for Polymer Electrolyte Membrane (PEM) fuel cells, we have synthesized functional diazonium zwitterions (FDZs) based on fluorinated sulfonimides. FDZs provide a means to covalently attach the electrolyte to the carbon substrate as an alternative to physical deposition of an electrolyte from a solution. The typical electrolyte deposition for membrane electrode assembly using solubilized Nafion® cannot be used for nanoporous

carbons due to size exclusion. Most diazonium salts are unstable at room temperature and some are explosive. Three series of thermally stable FDZs were successively prepared. Monofunctional Diazonium Zwitterions (MFDZs) p-$N_2^+PhSO_2N^-SO_2R_f$ ($R_f = CF_3$ or C_4F_9) were the first example and were shown to have surprisingly high decomposition temperatures and good solubility in organic solvents. Then, Difunctional Diazonium Zwitterions (DFDZs) (p-$N_2^+PhSO_2N^-SO_2R_f)_2$ ($R_f = C_4F_8$ or C_6F_{12}) were synthesized from the experience of making DZs and MDZs. These salts only dissolve in more polar solvents such as DMSO and exhibited good thermal stability. Finally, Multifunctional Diazonium Zwitterions (MFDZs) p-$N_2^+PhSO_2N^-SO_2R_fSO_2N(H)SO_2CF_3$ ($R_f = C_4F_8$ or C_6F_{12}) were prepared with two acidic proton positions on grafting. These salts had good solubility in water and several organic solvents. In principle, all of these salts are composed of acidic protons upon grafting to carbon. The best carbon coating method is still under investigation.

An alternative route to higher ion exchange capacity after attachment to carbon was envisaged via two other types of FDZs. A trifluorvinyl ether (TFVE) of the type p-$N_2^+PhSO_2N^-SO_2PhOCF{=}CF_2$ was prepared and can in principle be used to prepare a multifunctional polymer using step-growth polymerization with an appropriate functional TFVE monomer. Similarly, the novel FDZs p-$N_2^+PhSO_2N^-SO_2R_fSO_2N(H)SO_2F$ ($R_f = C_4F_8$ or C_6F_{12}) can be used to grow or attach a polymer by condensation reaction with an appropriate amide.

DEDICATION

I dedicate this work to my Dad and my Mom. This dissertation exists because of their love and support.

ACKNOWLEDGMENTS

All of my work could not have been completed without the support of several special people. I am especially grateful to my advisor, Dr. Darryl. D. DesMarteau, whose advice, not only in research but also in personal development, has immeasurably contributed to my growth as a chemist and as a person. His incredible scientific capability and vast amount of knowledge have been an inspiration through my pursuit of this PHD degree.

I would also like to thank Dr. Stephen Creager for valuable creative discussions and advice on the fuel cell project. And gratitude goes to my committee members Dr. Dennis W. Smith, Jr. and Dr. Dev P. Arya for providing their beneficial insights regarding my research work. Special recognition goes to Dr. VanDerveer Don for helping me with X-ray structures of my compounds. Group members, Dr. Jie Zhang, Dr. Shuang Zhou, Dr. Monika Mujkic and Tom Hickeman, have enriched my work and life with their help in the laboratory, and simply with their encouragement, support, and friendship.

I dedicate this thesis to my parents, my mom Liming Cui and my dad Xiaolin Mei who passed away in March 2006, who provide me with the example of personal sacrifice that helps me believe anything is possible.

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CHAPTER I

INTRODUCTION

Preface

Two research projects that target industrial applications are the focus of this thesis: one is for microlithography, and the other is for Polymer Electrolyte Membrane (PEM) fuel cell. Novel functional zwitterions, which contain perfluoroalkyl sulfonimide groups, provide a common link between these disparate areas.

In this introduction, some background of each project is given along with the motivation for the research work. Details about synthesis and characterization of these novel zwitterionic salts are discussed in the succeeding chapters. Zwitterions are presented first, followed by a short overview about perfluoroalkyl sulfonimide compounds. Bringing this function to the zwitterionic compounds provides the potential to use them as PAGs and in PEM Fuel Cells. Background on how the diaryliodonium salts act as PAGs is presented, along with PEM Fuel Cell principles.

Zwitterions

Zwitterions are the inner salts formally possessing substituent groups with the anion and cation contained in the same molecule. This definition mostly appears in the amino acids, peptides, and proteins. The ionic species has both a positive and a negative charge, such as an amino acid at the isoelectric point. Cohn and Edsall defined "zwitterions" in 1943. For example, glycine contains both a basic amino group (NH_2) and an acidic carboxyl group (COOH); when these are both ionized in aqueous solution to a certain pH value, the acid group loses a proton to the amino group and the molecule is

positively charged at one end and negatively charged at the other, forming a zwitterionic form $NH_3^+CH_2COO^-$ [1, 2].

$$RCH(NH_2)COOH \longrightarrow RCH(NH_3^+)COO^-$$

Scheme 1.1 Example of Amino Acid at the Isoelectric Point

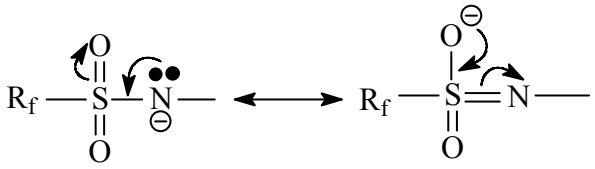
Occasionally the term "zwitterionic" is used to describe the dipolar form of groups such as aliphatic amine or phosphine oxides. It is preferable, however, to restrict "zwitterion" to molecules, which have substituent groups bearing formal charges. The term "semipolar" aptly describes functional groups within which significant charge separation between directly bonded atoms exists. In semipolar groups the filled orbital on one atom and the unfilled orbital on the other are inductively distorted by the charge separation, and may also be conjugated. Both interactions reduce the polarity of semipolar groups below that of the pure dipolar form[3]. There is a large difference between zwitterions and typical non-zwitterionic salts[4].

Super Acid Bis((Perfluoroalkyl) sulfonyl)imides and Their Derivatives

Because of fluorine atom's relatively small size (Van der Waals radius =1.47Å) and highest electronegativity (3.98), it has a profound effect on the neighboring chemical bonds[5]. The trifluoromethanesulfonyl group ($CF_3SO_2^-$) is reported as one of the strongest neutral electron-withdrawing groups[6, 7]. The large inductive effect of the same series perfluoroalkysulfonyl group provides all kinds of strong acids, such as CF_3SO_2OH, $(C_4F_9SO_2)_2NH$, and 1,3,5,-$(CF_3SO_2)_3PhOH$.

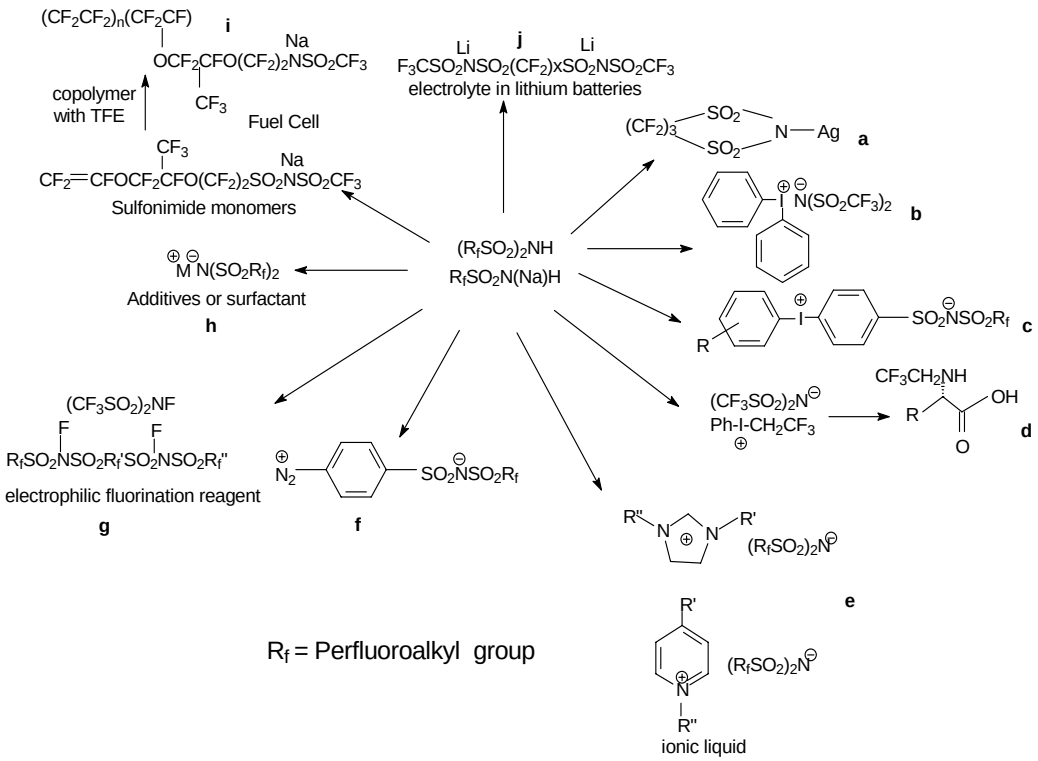
In the 1980s, while searching for additional nitrogen ligands to bond to Xenon, DesMarteau and coworkers synthesized a new acid series $(CF_3SO_2)_2NH$ [8, 9]. Based on

earlier work by Meussdoerffer and Niederprum[10], who prepared several $(R_fSO_2)_2NH$ compounds, ($R_f \neq CF_3$) solution acidity indicated that $(CF_3SO_2)_2NH$ was a very strong acid. Later gas phase acidity measurement indicated that all the relative acidity base on R_f in $(R_fSO_2)_2NH$ could be significantly different[11]. The most acidic of the very strong neutral acids is the $(C_4F_9SO_2)_2NH$ (pK_a=19.8) in gas phase[12]. The previous results provided evidence that three kinds of major substituent effects contribute to the increasing inherent acidity. They are: (i) correctly oriented dipolar substituent/anion interaction (F effect), (ii) polarizable substituent/anion interaction (P effect), and (iii) substituent/π-electron-acceptor interaction (R effect) which preferentially stabilizes the strong electron-pair donor anion forms compared to the corresponding weaker π-donor conjugate acid forms. Bis(perfluoroalkyl sulfonyl) imide has remarkable acidity not only because of the properties of R_f group but also due to the pronounced delocalization of charge over the O-S-N skeleton and its stabilized conjugate base of the acid.



Scheme 1.2 Delocalization of Perfluoroalkyl Sulfonyl Group

Derivatives of perfluoroalkyl sulfonimides provide a diverse reaction chemistry world[13]. A few examples of its main branches are show in **Scheme 1.3**.



Scheme 1.3 Perfluoroalkyl Sulfonimide Chemistry

The conjugate bases of these acids are extremely weak nucleophiles and thus their coordination with metals and other cations is weak. Metal derivatives of perfluoroalkyl sufonylimide acid **a** have the similar structure as other metal derivatives of many different acids[14, 15].

Diaryl iodonium salts, such as **b,** are effective but not very reactive arylating reagents in general. Novel iodonium salt **d** is a powerful alkylating agent which can be utilized in water and it was used in fluoroalkylation of amino acids and peptides[16, 17, 18, 19]. Diaryl iodonium salts also were found to absorb strongly in the short-wavelength (220-250nm) UV region and to function as efficient cationic photoinitiators for polymerization. Stable diaryl iodonium zwitterions **c** were envisaged to be used as photo

acid generators in microlithography. The difunctional symmetric diazonium zwitterions will be discussed in detail in Chapter II.

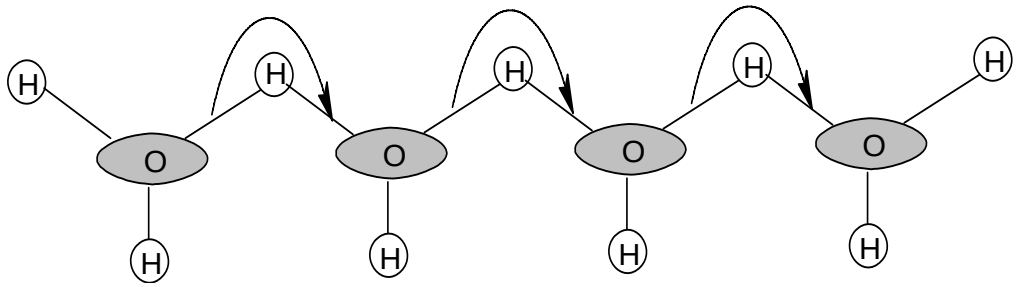
Functional diazonium zwitterions **f** were proposed for use in bonding electrolyte to carbon materials by loss of the active diazonium group. Details will be presented in Chapters III and IV.

With an NF bond, the compounds behave as the most powerful electrophilic fluorination reagents **g**. They are easily produced in high yield with excellent stability and desirable physical properties. The compounds are useful in variety of fluorination including aromatic rings[20]. The anion $(CF_3SO_2)_2N^-$ is an effective anion in producing low melting point. Preparation of bis(trifluoromethylsulfonyl)imide containing ionic liquids usually takes multiple steps and involves slow removal metal halide, which leads to low yield and purity problems. N-methyl bis(perfluoroalkylsulfonyl)imides were used as methylating agent to provide ionic liquids **e** [19] in a one step reaction.

Most hydrocarbon surfactants are either chemically or physically degraded under extreme environment. In patent US 6555510, bis((perfluoroalkyl) sulfonyl) imides salts such as **h** were synthesized with good stability, while providing outstanding surface activity under chemically harsh or extreme conditions [21].

The lithium ion or proton can move from one sulfonic acid to another by Grotthuss (hopping) mechanisms as **Scheme 1.4** shows [22]. Perfluoroalkyl sulfonimide acids are fascinating since they have the same electrochemical property as sulfonic acid [23, 24]. The high acidity associated with $(R_fSO_2)_2NH$ and the oxygen solubility in perfluorocarbon compounds led to excellent oxygen reduction kinetics in a typical

phosphoric acid fuel cell when used as additive[25]. Monomers **i** was successfully prepared and copolymerized with TFE to make new ionomer materials[26].



Scheme 1.4 Models of Grotthuss (hopping) Mechanism for H^+ Transportion within Perfluorosulfonated Ionomer Membranes in the Fully Hydrated State.

To prevent concentration polarization problems in lithium batteries, ideally lithium ions will be the only mobile ions in a single-ion conductor. Dimeric bis[(perfluoroalkyl)sulfonyl] imide anion **j** is attractive due to the possibility of limited anion motion (pure cationic conduction is desired in a lithium battery) and also greater delocalization of negative charge in dimeric anions, which can reduce ion pairing and increase conductivity[27]. Moreover, these salts can be dissolved in a polymer host or forming a solid polymer electrolyte in which ionic charges are chemically bonded to the polymer host backbone[28, 29].

Diaryliodonium Salts in Photo Acid Generators (PAGs)

PAGs are compounds that can generate acids upon irradiation with light. They can be divided into two groups, ionic and non-ionic compounds. Ionic PAGs involve onium salts such as aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts that contain weakly nucleophilic complex anions, such as SbF_6^-

and BF_4^- [30]. When they are irradated at wavelengths in the range of 200-300nm, they undergo photolysis to form a protic acid[31].

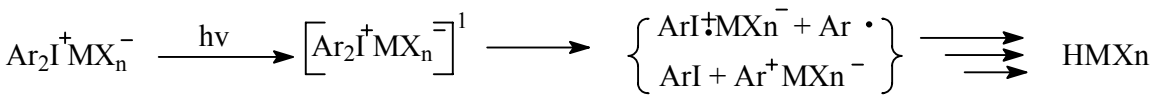
Many systems in the literature involve photo-induced generation of an acid from non-ionic compounds[32]. The generation of carboxylic acids, sulfonic acids, phosphoric acids and hydrogen halides are involved. Ionic and non-ionic PAGs are compared in **Table 1.1**.

Table 1.1. **Comparison Ionic and Non-ionic PAGs**

PAGs	Advantages	Disadvantages
Ionic Aryldiazonium Salts, Diarylhalonium Salts, Triarylsulfonium Salts, Such as $ArN_2^+X^-$, $[PhI^+Ph]\ X^-$, $[(CH_3OPh\text{-})_3\text{-}S^+]\ X^-$, Triphenylphosphonium Salts	Thermally stable and being structurally modified to alter spectral absorption characteristics	Limited solubility in common organic solvent
Non-ionic Notribenzyl Esters,Sulfones, Phosphates, N-Hydroxyimide Sulfonates, Sulfonic Acid Esters of Phenol, Diazonaphthoquinones, Halogen-Contaning Compounds, Imino Sulfonates, Such as 2-nitrobenzyl esters, N-hydrooxyphthalimide Methanesulfonate	Wider range of solubility in solvents and in polymer films	Thermally less stable

$X= BF_4^-, AsF_6^-, PF_6^-$

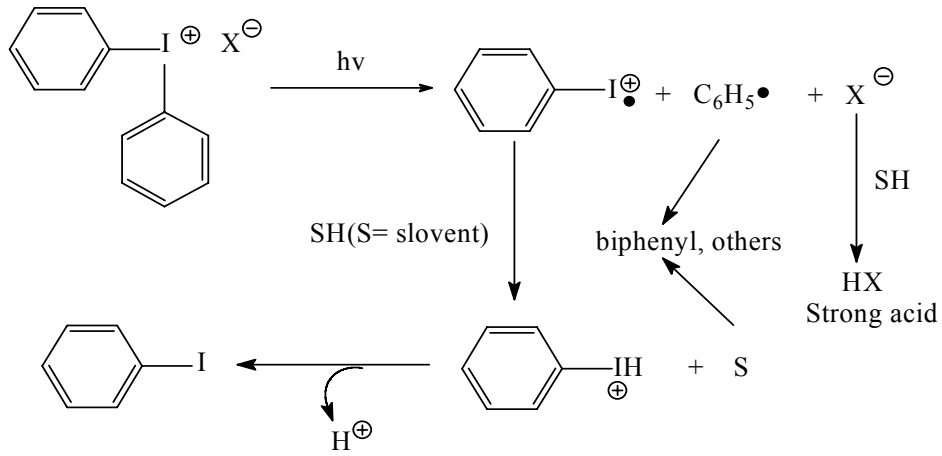
In contrast to other ionic PAGs, diaryliodonium salts exhibit high thermal stability, as well as hydrolytic reactivity[33]. **Scheme 1.5** shows the proposed mechanism involving the first photoexcitation of the diaryliodonium salt and then the decay of the resulting excited singlet state with both heterolytic and homolytic cleavage of the carbon-iodine bond [34].



MXn= BF_4^-, AsF_6^-, PF_6^- (M-metal)

Scheme 1.5 Mechanism of Photoexcitation of Diaryliodonium Salts

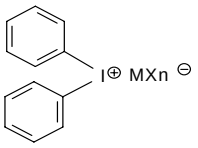
The aryl cations and aryliodine cation radicals generated during the photolysis are highly reactive species and react further with solvents, monomers or impurities to produce protonic acids, HMXn, which are the predominant initiators of the cationic polymerization photo resist monomers. The mechanism for the photolysis of diaryliodonium salts based on product analysis is shown in **Scheme 1.6**[35].



Scheme 1.6 Mechanism of Photolysis of Diaryliodonium Salts

The placement of various chromophores on the aromatic rings allows the manipulation of the wavelength and intensity of absorption of the diaryliodonium salt. As shown in **Scheme 1.6**, the cation is the light absorbing component and the basis of the photochemistry in these compounds. For this reason, the structure of the cation controls the UV absorption characteristics, the photosensitivity (quantum yield), whether the

compound can be photosensitized, and the ultimate thermal stability of the diaryliodonium salt. The absorption maximum of these compounds falls near 250nm, which is not significantly affected by the structure of aryl substituents and the anion. The nature of the anion determines the acid formed during photolysis and its corresponding initiation efficiency. Also, the anions can change the polarity of solvent to determine the character of the propagating ion pair. It would have direct impact on the kinetics (i.e. rate) of polymerization and whether termination may occur[36].



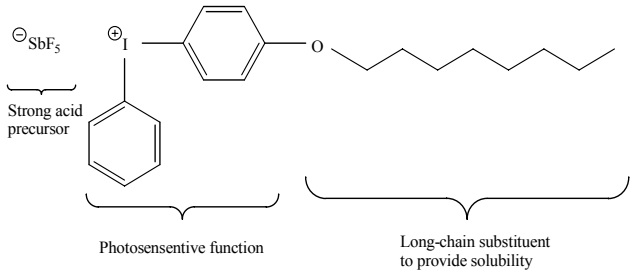
Cation	Anion
Determines Photochemistry	Determines Polymer Chemistry
Λ_{max}	Acid Strength
Molar Absorption Coefficient	Nucleophilicity (Ion Pairing)
Quantum Yield	Anion Stability
Photosensitization	Initiation Efficiency
Thermal Stability	Propagation Rate Constants

MXn= BF_4^-, AsF_6^-, PF_6^- (M-metal)

Scheme 1.7 Anatomy of an Onium Salt Photoinitiator

While diaryliodonium salts are good photo acid generators, there is considerable room for further improvements in these materials. First, diaryliodonium salts may be viewed as photoacid generators capable of producing acids of whatever strength desired depending on the starting anion. The high electronegativity and poor polarizablility of fluorine means that in both organic anions (e.g. $CF_3SO_3^-$, FSO_3^-, $(C_6F_5)_4B^-$, $(CF_3SO_2)_2N^-$ [37]) and inorganic complex anions (e.g. BF_4^-, AsF_6^- [38]), it can reduce basicity and nucleophilicity of these moieties. These inorganic complex anions, however, have several drawbacks. They are toxic heavy metals, and sensitive to humidity, especially when these

salts are stored for long periods of time[39]. Second, simple diaryliodonium salts have very limited solubility in non-polar solvents. The organic solubility can be improved by attaching the long alkyl groups to the phenyl rings[40], as shown in **Scheme 1.8**. Additional, toxicity is also a problem for diarylidonium salts. Dipenyliodonium hexafluoroantimonate has an oral LD_{50} of 40mg kg^{-1}(rats). Polymers containing diaryliodonium salt groups in their main chains were reported to be efficient photoacid generators[41].

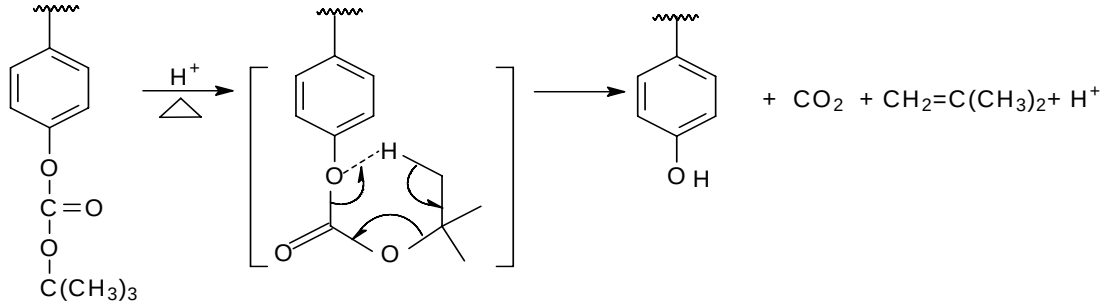


Scheme 1.8 Example of Improving Solubility

Diaryliodonium salt PAGs, which generate acids on UV irradiation, are utilized in the photoinitated cationic polymerization[42, 43]. Cation-induced polymerization is not sensitive to oxygen so that, by contrast to photochemically induced radical polymerization, the chain reaction continues in the dark even in the presence of air.

Starting in the early 1980s, PAGs were used in a new class of materials called "chemically amplified" microlithographic resists. Resists themselves are photosensitive polymeric resins which are applied in the manufacture of semiconductor devices, such as integrated circuit chips and read/write heads for magnetic media drives. There are typically four steps involved in the microlithographic process: a. depositing a layer of a photoresist material onto a device such as a silicon wafer; b. baking the device at a

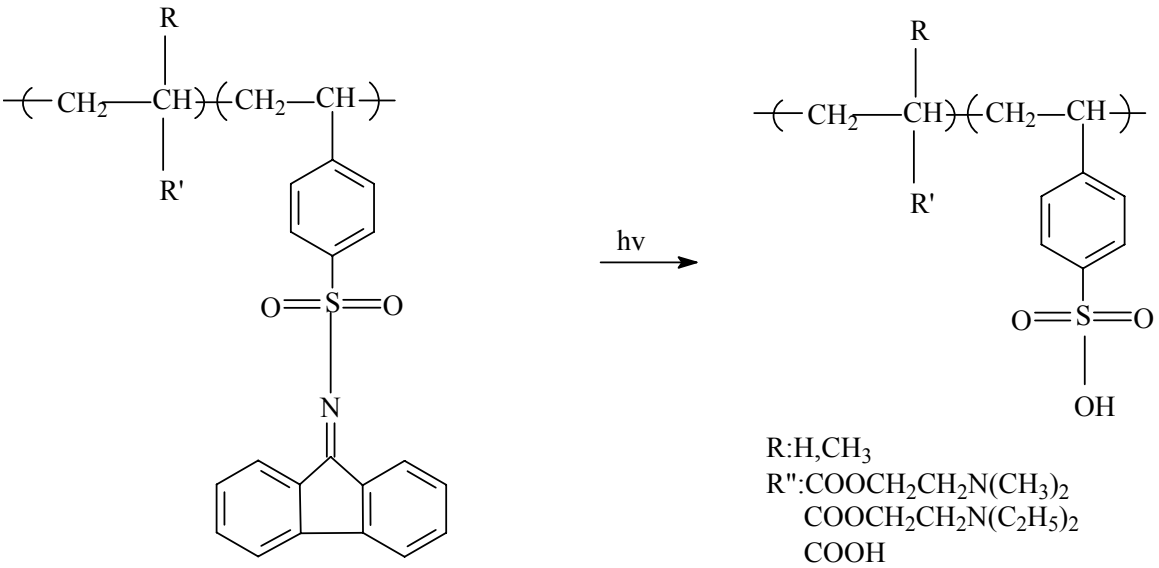
temperature of approximately 110ºC; c. selectively exposing portions of the photo resist layer to radiation; and d. developing the photo resist layer by washing with a basic developer solution[44]. Chemically amplified resists (CAMP) are formulated by dissolving an acid sensitive polymer and a photo acid generator in a casting solvent. Upon UV exposure, a catalytic amount of acid is generated and is subsequently used in the post exposure bake step to deprotect the acid sensitive polymer as shown in **Scheme 1.9** [45]. Deprotection transforms the acid labile polymer into a base soluble polymer and ultimately enables positive tone image development in the dilute aqueous base [46].



Scheme 1.9 Example of CAMP

Ionic PAGs typically are capable of producing acid by direct irradiation at 248nm or below. This is a particular advantage for ArF resists where nonaromatic resists, incapable of energy-transfer sensitization, are necessary in order to achieve sufficient transparency at 193nm[47].

To improve the efficiency, photoacid generating polymers were sometimes prepared as surface imaging resists directly. For example in **Scheme 1.10**, since polymers having pendant imino sulfonate units can be photochemically converted into styrenesulfonic acid units, and the irradiated polymers become soluble in aqueous and polar solvents [48, 49].



Scheme 1.10 Example of Polymer as a Surface Imaging Resist

PEM Fuel Cell

Fuel cell is a viable alternative for clean energy generation[50, 51]. Varieties of fuel cells for different applications are under development[52, 53, 54]. And they are: Solid Polymer Fuel Cells (SPFC), also known as proton exchange membrane fuel cells and Polymer Electrolyte Membrane Fuel Cells (PEMFC), operating at ~80^{o}C; Alkaline Fuel Cells (AFC) operating at ~100^{o}C; Phosphoric Acid Fuel Cells (PAFC) for ~200^{o}C operation; Molten Carbonate Fuel Cells (MCFC) at ~650^{o}C; and solid oxide fuel cells (SOFC) for high temperature operation, 800-1000^{o}C. PEM fuel cells possess a series of advantageous features that make them leading candidates for mobile power applications or for small stationary power units: low operating temperature, sustained operation at high current density, low weight, compactness, potential for low cost and volume conduction, long stack life, fast start-ups, and suitability to discontinuous operation.

PEM fuel cells were first applied in 1960s as an auxiliary power source in the Gemini space flight [55]. The advances in this technology were stagnant until the late 1980s when the fundamental design underwent significant reconfiguration. New fabrication methods, which have now become conventional, were adopted and optimized to a high degree [56]. PEMFC is about twice as fuel efficient as the internal combustion engine and produce virtually no CO, HC or NO_x, and along with a reduced level of CO_2. They operate on the basic principle of direct conversion of chemical energy into electrical energy, avoiding the mechanical steps and thermodynamic limitations of traditional combustion energy generation cycles. As **Figure 1.1** shows[57], a PEM fuel cell consists of two electrodes sandwiched around an electrolyte. Hydrogen fuel is electrochemically oxidized at the anode. Encouraged by a catalyst, the hydrogen atom splits into a proton and an electron that take different paths to the cathode. The proton passes through the electrolyte, and then combines with electrochemically reduced O_2 (from the air) at the cathode to produce H_2O. Since the membrane is not electrically conductive, the electrons flow through the external circuit creating a separate current that can be utilized before they return to the cathode.

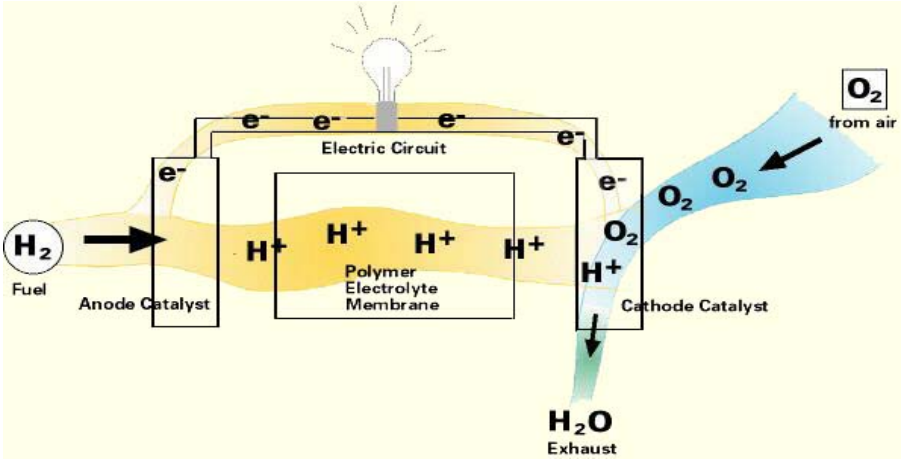


Figure 1.1 PEM Fuel Cell

At the heart of the PEM fuel cell is the membrane electrode assembly (MEA). Usually, carbon powders with Pt catalysts attached on membranes have been used as electrodes for oxygen reduction and hydrogen oxidation. This structure is called the MEA. The MEA is pictured in the schematic of a single PEM fuel cell shown in **Figure 1.2**[58]. The MEA consists of a proton exchange membrane, catalyst layers, and a gas diffusion layer (GDL). Fabrication of the MEA strongly influences electrochemical performance of the oxygen and hydrogen electrodes[59, 60, 61].

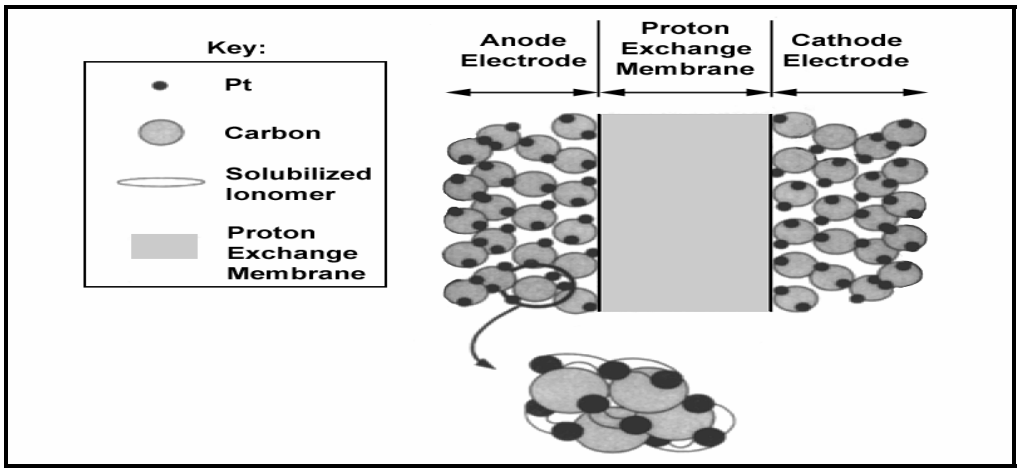


Figure 1.2 Components of the Membrane Electrode Assembly (MEA)

Common requirements critical to all high performance proton exchange membranes include (1) high protonic conductivity, (2) low electronic conductivity, (3) low permeability to fuel and oxidant, (4) low water transport through diffusion and electro-osmosis, (5) oxidative and hydrolytic stability, (6) good mechanical properties in both the dry and hydrated states, (7) cost, and (8) capability for fabrication into MEAs [61, 62, 63]. Nearly all existing membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce proton conductivity. Due to the large fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues. Proton conductivity, water uptake, ion content and other definitions were established to compare the different membrane material systems[64, 65].

Among potential membrane structures, the most widely used material for PEM cells is still the sulfonic acid based perfluoropolymer Nafion® (PFSA), which has an ionic conductivity higher than 0.1S cm^{-1} at $80^{o}C$ [66]. It was originally developed as a cation exchange membrane for the chloralkali industry in the late 1960s. Nafion® and other PFSAs possess many of the desirable qualities required for a successful PEM fuel

cell, namely, good thermal stability, inertness towards chemical attack, low dielectric constants, insolubility in water and alcohol, and insulating ability. However, they also possess certain limitations. One limitation is that the soluble form is not likely to work well with nanoporous electrodes. The large rod-shaped micelles formed on dissolution cannot enter the micropores and the ionomer coating of the carbon in the MEA catalyst layer since it tends to be "washed out" in fuel cell operation. At higher temperatures, the sulfonic acid groups further dehydrate forming an anhydride ($-SO_2OSO_2-$) which leads to decomposition; and most of the electrolyte-to-surface bonds cannot withstand for very long the highly acidic and oxidizing conditions expected inside the operating fuel cell [67]. Other kinds of new electrolyte membranes as shown in **Figure 1.3** have also been extensively developed [68, 69, 70, 71, 72], in affection to improve cost performance, ionic conductivity, and mechanical strength of the membrane.

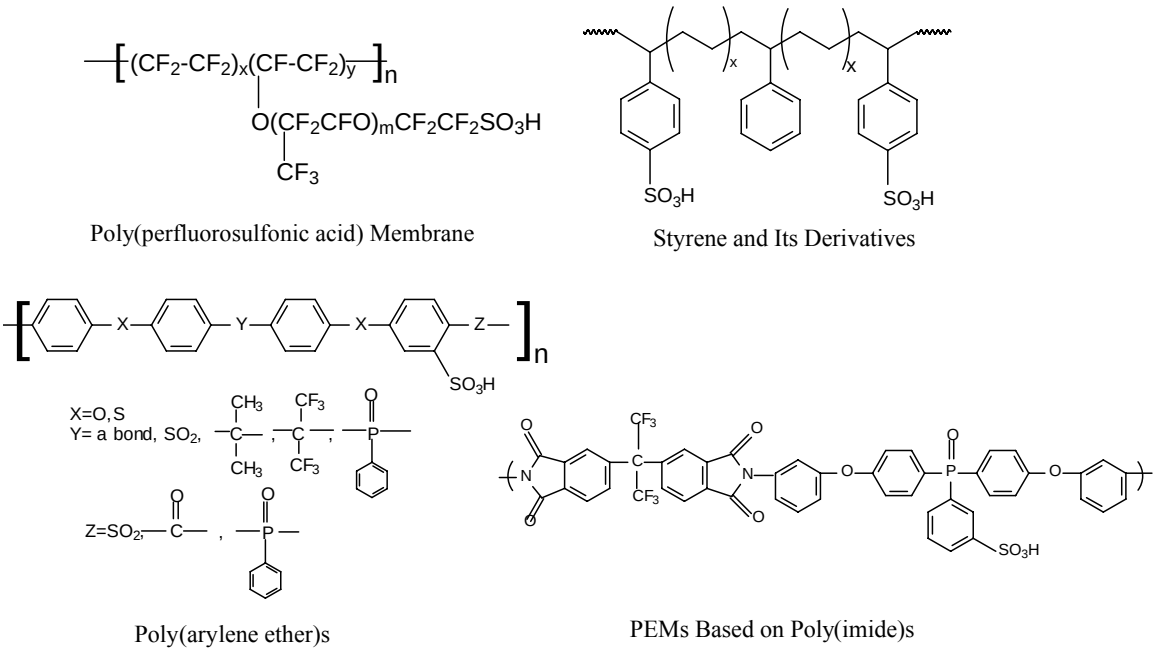


Figure 1.3 Other New Electrolyte Membranes

General Experimental Methods

NMR Spectroscopy

^{1}H and ^{19}F NMR spectroscopic studies were carried on a Bruker AC 200 (^{1}H—200.1 MHz and ^{19}F—188.3 MHz) or 50FL 300 (^{1}H—300.53 MHz and ^{19}F—282.78 MHz). All chemical shifts are quoted in ppm using the high-frequency position convention. ^{1}H NMR spectra were referenced to external trimethyl silane(TMS), ^{19}F chemical shifts were referenced to $CFCl_3$. The chemical shifts of residual H in CD_3CN, $CDCl_3$ and DMSO are 1.93ppm, 7.24ppm and 4.63 ppm, respectively, relative to TMS. Negative chemical shifts and positive chemical shifts indicate up field and down field from the reference correspondingly. The splitting patterns of resonance were described by the following: singlet (s), doublet (d), triplet (t), quartet, (q) and multiplet (m).

The NMR spectra were measured using solutions of 1–2 mmol/L concentrations (unless otherwise stated) and small amounts of $CFCl_3$ gas in an appropriate deuterated solvent. For moisture sensitive compounds, anhydrous deuterated solvents were used, which were prepared by drying them over appropriate drying reagents and then transferring into the one-piece-flask with molecular sieves for storage. Dry NMR samples were prepared in the 4 mm glass tubes fused to a joint. The sample tube containing the compound of the interest was connected to a vacuum system for transferring the dry solvent and the internal reference into the sample tube at $-196^{o}C$. The 4 mm tube was sealed by a torch and inserted into a normal 5mm NMR tube for analysis.

IR Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 1600 and 2000 series FTIR spectrometer. Solid samples were prepared in one of the three ways: 1) 1-5mg of sample were dissolved in 2mL volatile solvent acetone and one drop of the solution was added on KCl or KBr plates; 2) a mixture of 5-10mg of sample and one drop of Nujol were added on KCl or KBr plates. After the solvent was evaporated, the sample film is formed between two plates and can be analyzed in the instrument. Unless indicated otherwise, samples were a minimum of 99.5% pure by ^{19}F NMR. IR spectra were scanned from 4000cm^{-1} to 450 cm^{-1} and reported in wave numbers (cm^{-1}) with intensity abbreviations: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA was performed on a Perkin-Elmer TGA7 with a date system using Compaq computer. TGA samples were typically around 3.0mg and were run in a nitrogen environment with a platinum sample pan, with heating rates of 10°C/min.

DSC was performed on either a Perkin-Elmer DSC7 or a Mettler DSC821. The data were obtained in stainless steel pans for acidic and corrosive samples, or with aluminum pans, using around 10mg pure samples. The temperature change rate was around 10°C/minfor heating and cooling system

Temperatures reported from TGA data are the onset T_d as determined from the step tangent. Temperatures reported from DSC data are curve peaks, freezing points being exothermic upon cooling and melting points being endothermic upon heating.

pH Value Measurement

The pH values of aqueous solution were obtained on Fisher Accumet Model 925 pH meter, with the standard size glass body combination electrodes/calomel reference. At room temperature, the instrument was standardized at pH= 7 and 4 using two Fisher certified buffers. The concentrations of solutions for measurement were in the range of 0.1M to 0.4M.

Molar Absorptivity, ε

UV/Vis spectra were recorded on a Perkin-Elmer Lamda-19 Spectrophotometer in acetonitrile solution using 1cm path length quartz cells. The instrument was referenced against acetonitrile, and measurements were made in ambient air. Spectra were scanned at 240nm/min from 500 to 185nm. Extinction coefficients of samples at 193 and 248nm were calculated based on absorption at these two wavelengths and have estimated error limits of +/-10%. Sample concentration was adjusted so that the absorbance at the wavelength of interest was close to 2.5 in order to minimize effects of possible PAG photodecomposition on the measure ε values. Each sample was run in triplicate and the ε values reported are averages.

Purification of Solvents and Experimental Practice

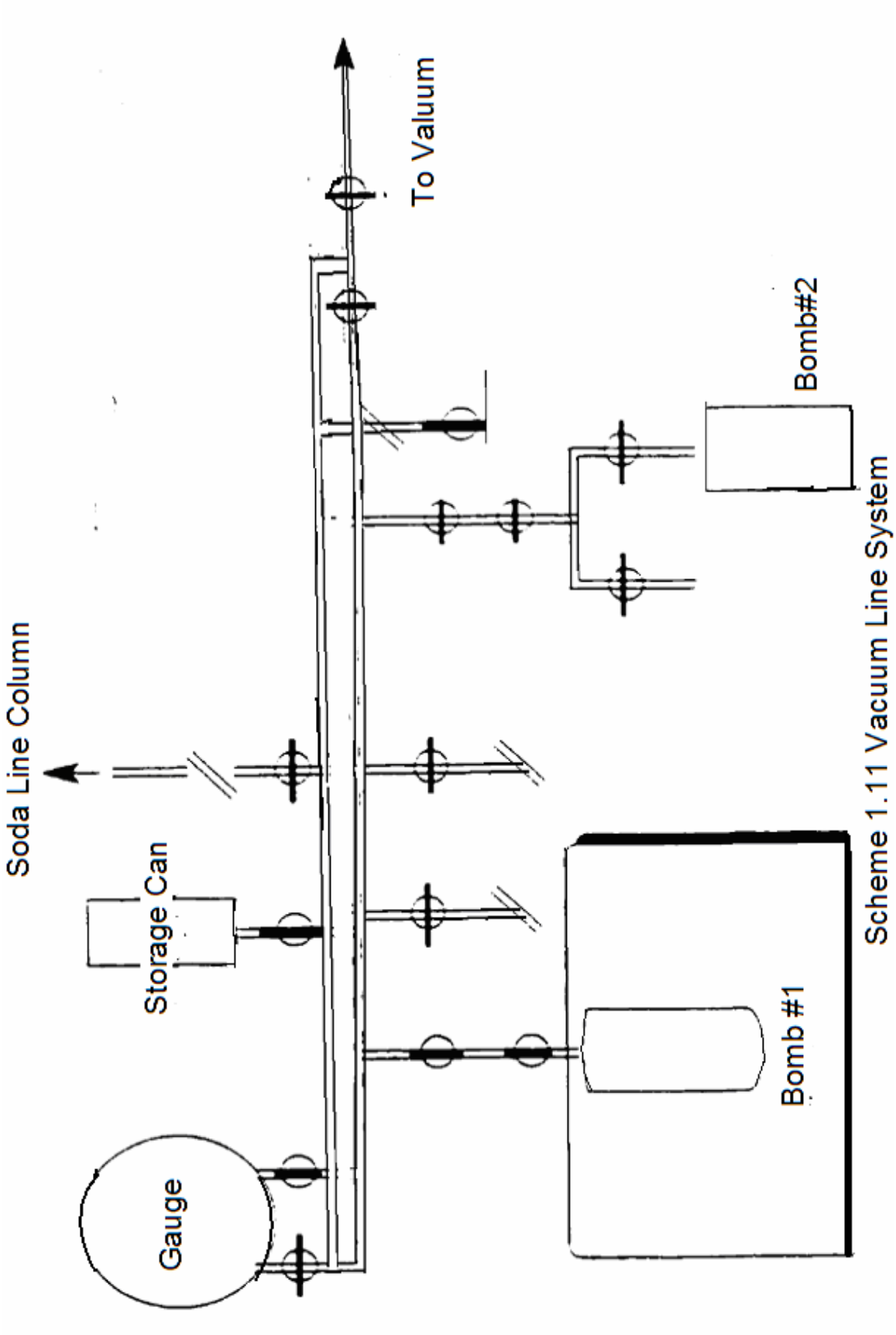
All starting materials were obtained from commercial sources and used as received unless otherwise stated. Dry CH_3CN solvent was prepared over CaH_2 and then distilled over P_4O_{10} before using. Diethyl ether and methanol were distilled over $CaSO_4$.

All the reactions were carried out in glass apparatus unless otherwise specified. Moisture or air sensitive compounds were handled in a dry box filled with nitrogen.

Handling any kinds of highly toxic and corrosive gases such hydrogen chloride was done through vacuum system transfer.

Glass Vacuum System

The glass vacuum line shown in **Scheme 1.11** was used for reduced pressure distillation, sublimation and trap-to-trap transfer of low boiling point compounds. The vacuum line was equipped with Kontes Teflon Valves and consisted of an upper manifold, a lower manifold with a built in trap-to-trap separation system, a liquid nitrogen trap, a diffusion pump and a mechanical Welch vacuum pump. An ultimate vacuum of 20μmHg could be achieved in the system.



Scheme 1.11 Vacuum Line System

CHAPTER II

IODONIUM ZWITTERIONS

Introduction

Polyfunctional Iodonum Zwitterions (IZs, also called polyfunctional zwitterionic compounds, ZICs) constitute an interesting class of hypervalent iodine compounds[73], which are valuable for a variety of applications.

Interestingly, the physical properties and reactivity of these IZs, which have two aromatic rings, change a lot. The discoveries of and the focus at Clemson are the IZs containing perfluoroalky sulfonimides substituents.

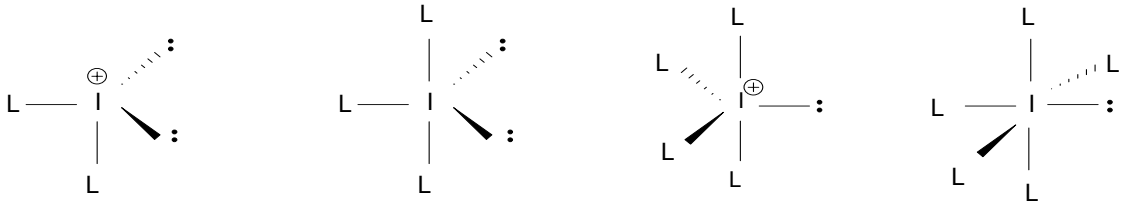
In microlithography, diaryl iodonium salts are potentially useful photoacid generators as they do not contain any of the contaminates (such as heavy element antimony) to the semiconductor materials during the lithography process. Using these salts, resists that operate at 193nm or even 157nm can be produced. Due to the trend of using shorter wavelength light to produce images for higher resolution in microelectronics [74, 75], and also the new technology of two-photon absorption (TPA) [76, 77], improved new PAGs were needed. V. Montanari introduced perfluoralky(aryl) sulfonimide anions as the substitutent group of some novel IZs, based on B. Thomas's successful preparation of iodophenyl perfluoroalkyl sulfonimides. Because the super acids of the type $\Phi SO_2NHSO_2R_f$ arising from these anions have lower volatility than acid such as $C_4F_9SO_2OH$, $(C_2F_5SO_2)_2NH$ [78, 79]. Highly volatile acid, like CF_3SO_3H, can evaporate from the surface layer of the resist during imagine and post-back steps leading to problems such as T-topping of image

profiles and contamination of optical elements. Therefore, PAGs that produce a photo-acid that is less volatile than triflic acid are preferred[80]. Subsequently, new ideas about novel PAGs as Difuctional Iodonium Zwitterions (DIZs) seemed reasonable.

Untill now, industrial application of these salts is unknown, but their probable properties make them good candidate for evaluation.

Diaryliodonium Salts

A wide variety of structural classes are known for iodine in oxidation state other than common –1. In terms of the Martin-Arduengo N-X-L designation, iodonium zwitterions belong to iodanes, and are considered as derivatives of trivalent iodine that has two ligands as **A** in **Scheme 2.1**[81]. They are usually stable at room temperature, but light sensitive, and should be stored in the dark[82, 83].



A **B** **C** **D**

Scheme 2.1 Polyvalent Iodine N-X-L Structure

One of the most important applications of diaryliodonium salts is their use in the arylation of organic and inorganic nucleophiles[84]. The best arylation yields of the nuclophilic bases are achieved by using diaryliodonium salts with substantially non-nucleophilic counterions, such as tosylates, triflates, hydrogensulfates, perchlorates, etc [85, 86].

Some of them also display biological activity and useful photochemical properties. They were found to absorb strongly in the short-wavelength (220-250nm) UV region and to function as efficient cationic photoinitiators[87] for polymerization.

In the 1950s, Beringer and Grindler developed several typical routes for the preparation of symmetric and unsymmetric diaryliodonium salts, $Ar_2I^+X^-$ and $Ar(Ar')I^+X$, and extensively explored their reaction chemistry [88, 89]. Those methods were summarized in **Scheme 2.2** [90].

Method A: Coupling of two aromatic compounds with iodyl sulfate in sulfuric acid

Example: $4ArH + 3H_2SO_4 + (IO)_2SO_4 \longrightarrow 2Ar_2I^+ + 2H_2O + 4HSO_4^-$

Method B: Coupling of two aromatic compounds with an iodate in acetic acid-acetic anhydride-sulfuric acid

Example: $IO_3^- + 2ArH + 2Ac_2O + 2H_2SO_4 \longrightarrow [(C_6H_5)_2I]^+HSO_4^- + 4AcOH + [O]$

Method C: Coupling of two aromatic compounds with iodine (III) acylate in the presence of an acid

Example: $2ArH + I(OCOCF_3)_2 + HX \longrightarrow Ar_2I^+X^- + 3RCOOH$

Method D: Condensation of an iodoso compound, an iodoso diacetate or an iodoxy compound with another aromatic compound in the presence of an acid

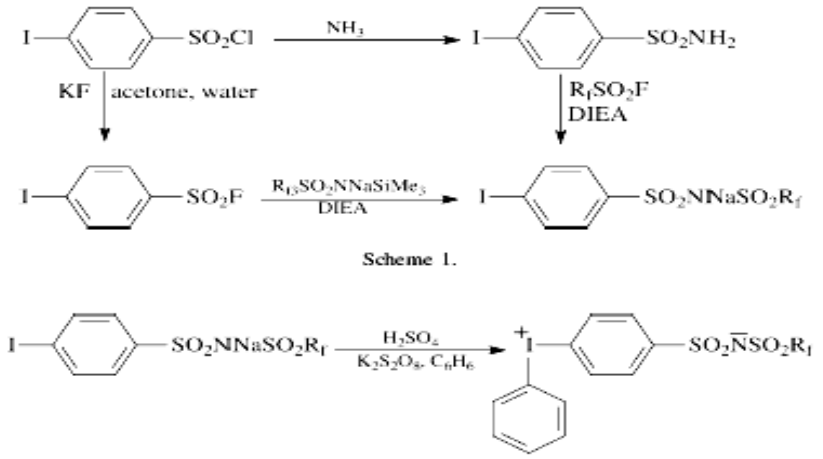
Example: $ArI{=}O + Ar'H + K_2S_2O_8/H_2SO_4 \longrightarrow [(4\text{-}HO_2C\text{-}C_6H_4\text{-}I)_2]^+HSO_4^-$

Scheme 2.2 Summary of Methods for the Preparation of Iodonium Zwitterions

Methods A, B and C were all involved in the symmetrical coupling of two aromatic compounds. Only method D was proposed for the synthesis of unsymmetrical diaryliodonium salts.

Preparation of IZs

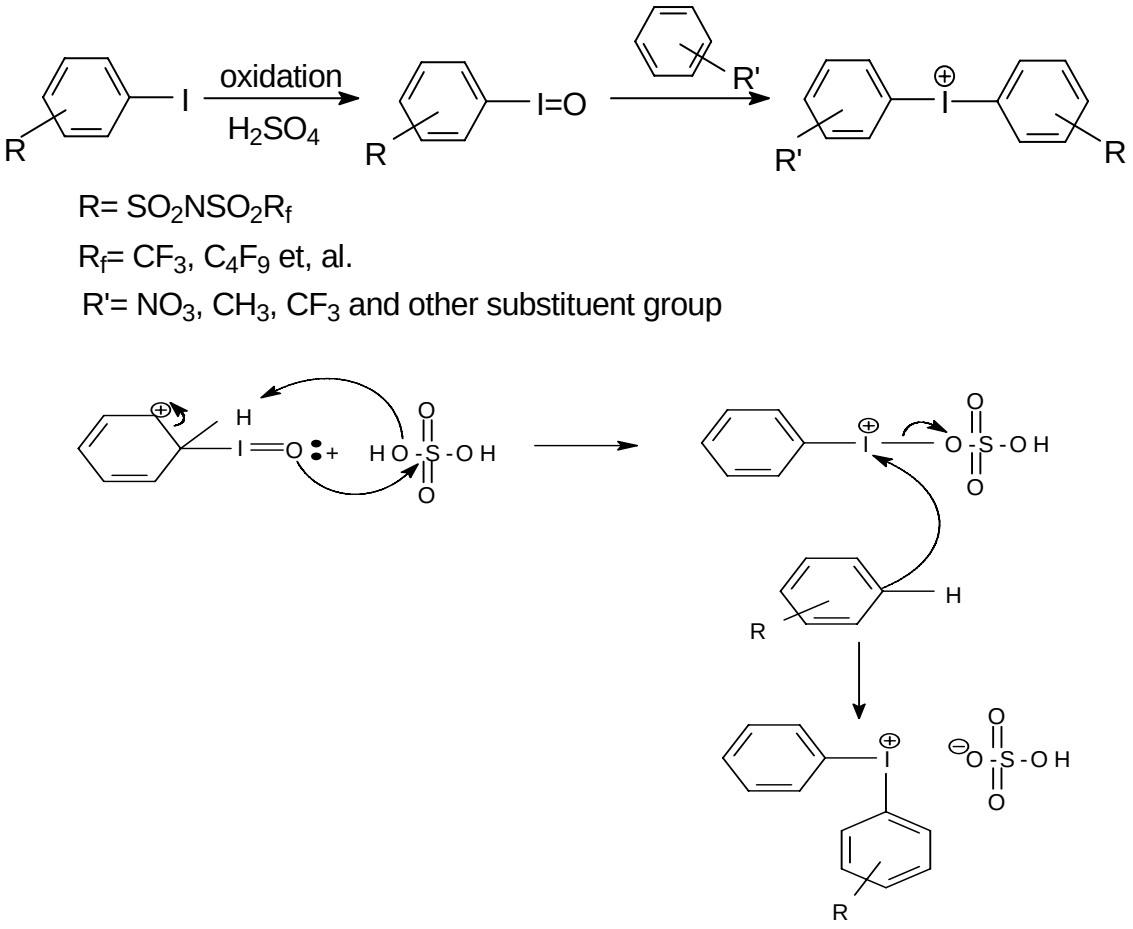
Base on method D, attempts were made to synthesize Monofunctional IZs (MIZs) from p-iodophenyl perfluoroalkyl sulfonamides (**Scheme 2.3**) [91, 92]. From the starting material pipsyl (p-iodobenzenesulfonyl) chloride, there are two ways to prepare the target compounds. Due to the electron donating character of the iodine, pipsyl chloride is a poor electrophile but pipsyl amide is good nuclophile. With DIEA, pipsyl amide coupling with R_fSO_2F to give p-$IPhSO_2R_f$ can be achieved. Alternatively, coupling reaction of pipsyl halides or fluoride with silyated perfluoroalkyl sulfonimide compounds can be used too. And finally Beringer's method **D** give a one step oxidation of p-$IPhSO_2R_f$ in sulfuric acid with potassium persulfate in the presence of benzene to provide the MIZs**.**



Scheme 2.3 Synthesis Routes for Iodonium Zwtterions (IZs)

The proposed mechanism **(Scheme 2.4)** for this reaction process is from oxidizing the substituted iodobenzene to forming a trivalent iodine intermediate. Then it reacts with

benzene followed as electrophilic reaction in acid. Because electron-donating group won't tolerate the oxidation, the benzene with strong electron withdrawing group such perfluoroalky sulfonimide would be oxidized in the mechanism.

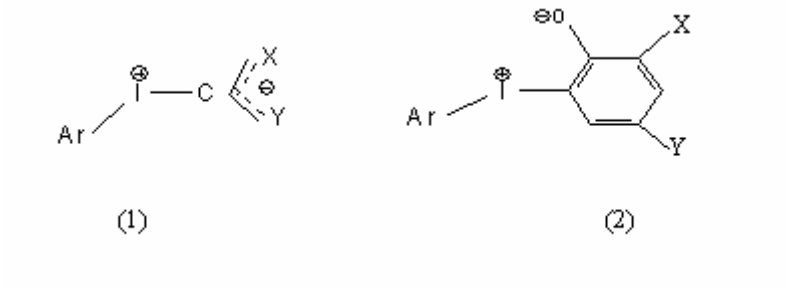


Scheme 2.4 Mechanism of Beringer's Method D

IZs in Literature

Some IZ's chemistry is reviewed in Koser's book [93]. According to Spyroudis and his group, the majority of IZs contains two C-I bonds and may be divided into (a) aryliodonium ylides of active methylene compounds (**Figure 2.1)**[94]: (1) where the

negative charge is dispersed over a system of neighbouring bonds usually belonging to keto groups or enolized 1,3-dicarbonyl heterocycles [95] and (2) aryl(oxidoaryl)-iodonium inner salts; (b) other compounds in which the negative charge is largely localized on the oxygen atom [96, 97].



(X, Y=COR, NO_2, CO-Het-CO) (X, Y= Cl, NO_2)

Figure 2.1 Spyroudis' ZICs

In the early 1960's, Beringer and his colleagues obtained some IZs, which they called diaryliodonium inner salts (**Figure 2.2**)[98]. These salts without a space between the aryl and ionic group were unstable.

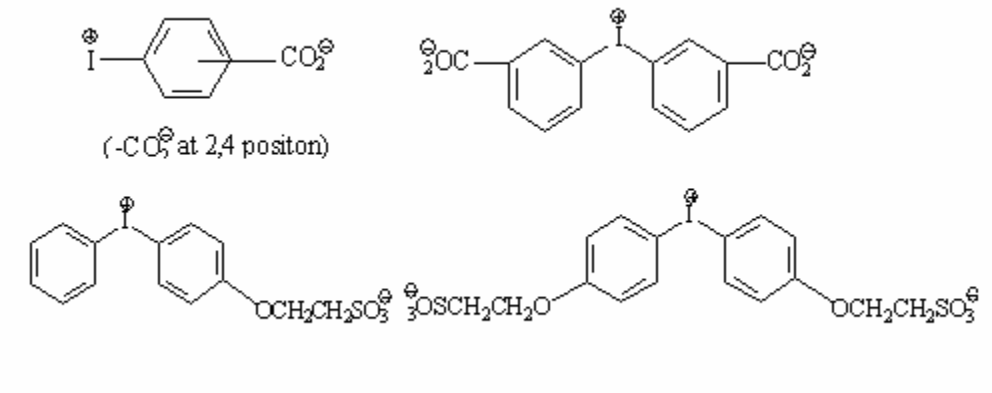


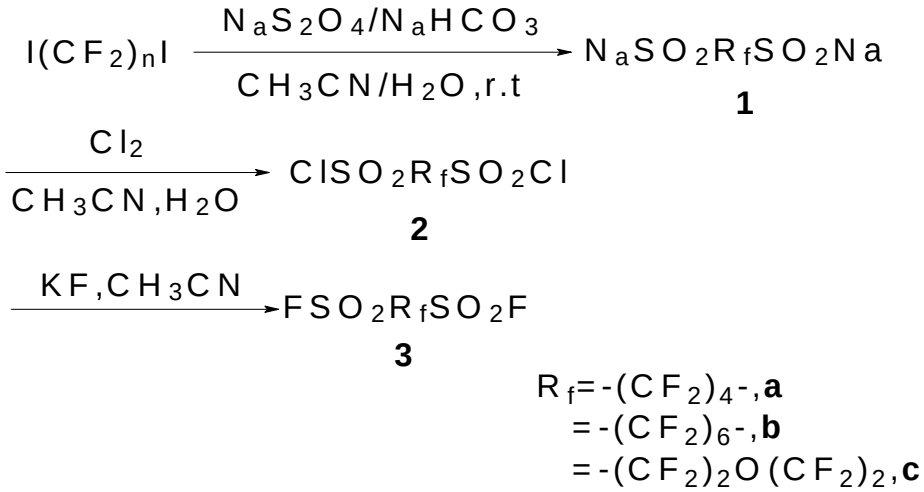
Figure 2.2 Beringer's IZs

Result and Discussion

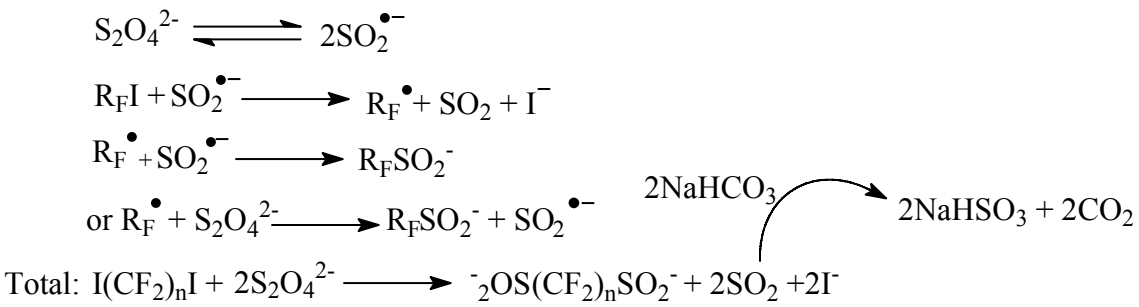
Preparation of Difunctional Iodonium Zwitterions (DIZs)

Perfluororalkyl disulfonic fluoride 3a-c

Different from IZ compounds, DIZs were used ($FSO_2R_f)_2$ (**3a, 3b** in **Scheme 2.5**) as starting materials. Perfluorinated haloalkanes can have sulfinatodehalogenation with sodium dithionite [99]. According to Huang and his coworkers in 1983, the possible radical reaction mechanism is shown in **Scheme 2.6**. Based on the equation, the ratio for the reactants should be $I(CF_2)_nI$: $Na_2S_2O_4$: $NaHCO_3$ = 1: 2: 2. Neutralizing SO_2 with excess $NaHCO_3$ can push the whole reaction forward. The reactivity of perfluorinated haloalkanes undergoing this dehalogensulfination reaction follows the order: R_fSO_2I> R_fSO_2Br> R_fCCl_3.

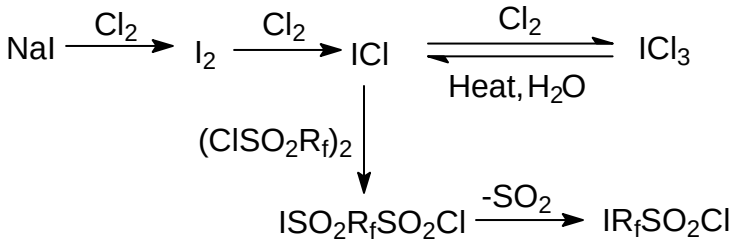


Scheme 2.5 Synthesis Perfluoroalkyl Disulfonic Fluoride



Scheme 2.6 Mechanism of Dehalogensulfination

The conversion of the perfluorosulfonate in **Scheme 2.5** to the chloride requires careful controlling of reaction temperature and bubbling excess Cl_2 gas, which converts ICl to ICl_3. The impurity iodo perfluoralkane sulfonyl chloride comes from ICl reacting with perfluorosulfinate as shown in **Scheme 2.7**.



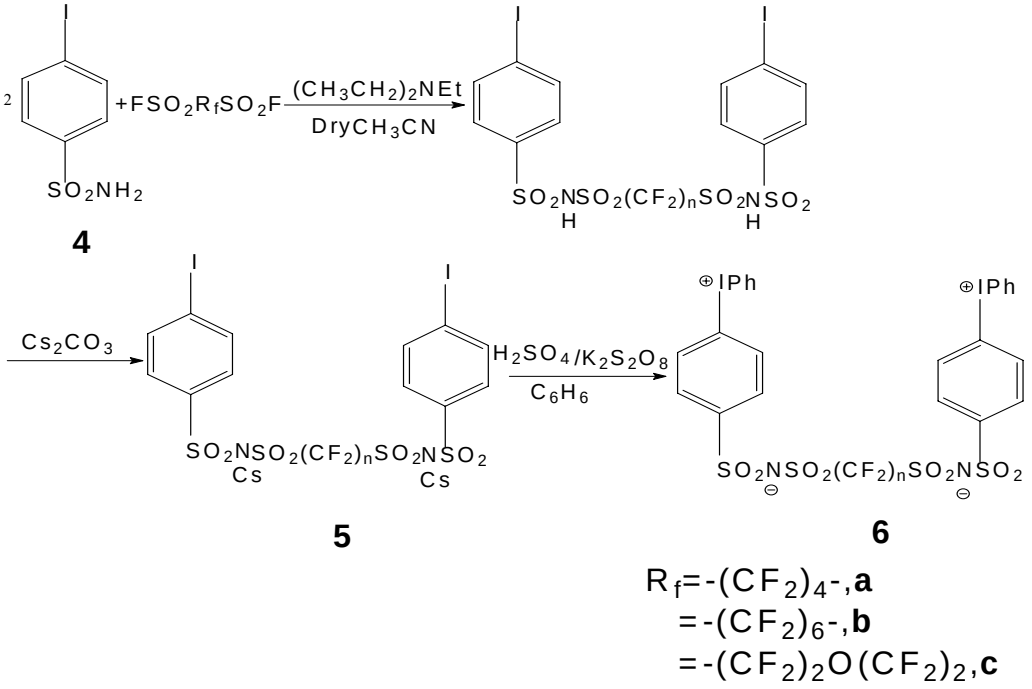
Scheme 2.7 By-product Iodo Perfluoralkane Sulfonyl Chloride

The final fluorinated step with KF in acetonitrile (**Scheme 2.5**) proceeds in high yield if the KF and acetonitrile are dry.

Difunctional Iodonium Zwitterions 6

The synthesis of DIZs is outlined in **Scheme 2.8**. Since difunctional perfluorosulfonic amides $(NH_2SO_2R_f)_2$ are very weak nucleophiles, they are not easy to couple with pipsyl fluoride p-$IPhSO_2F$ directly even using DIEA base. It takes longer time to prepare silylated difunctional perfluorosulfonic imide sodium salts

$(Me_3SiN(Na)SO_2R_f)_2$ than small molecule $CF_3SO_2N(Na)SiMe_3$. The reason is the long chains' steric lower the reactivity of $R_fSO_2N(Na)H$, probably due to solubility effects. Therefore, perflouroralkyl disulfonic fluoride **3** and pipsyl amide **4** were chosen for the coupling reaction promoted by dry DIEA in dry acetonitrile. However, with just a small amount of moisture, perflouroralkyl disulfonic fluoride will be easily hydrolyzed to $-SO_3^-$ in the basic condition. And those small amounts of impurities are difficult to remove. Conversion of the coupled cesium salt **5** to **6** was carried out using the same methodology as for IZs.



Scheme 2.8 Synthesis of DIZs

IZs and DIZs

A series of IZs with the sulfonimide moiety were described by V. Montanari [91]. **Table 2.1** supports the reaction mechanism we described earlier. Substituents such as fluorine, bromine, toluene and acetic acid that have p-p repulsion ($+I_\pi$ effect) or

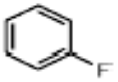
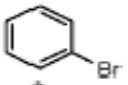
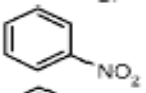
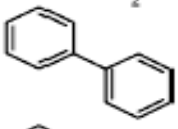
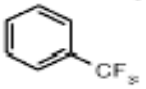
resonance effect (+R effect) enhance the formation of the IZs. At the same time, strong electron withdrawing groups such as trifluoromethyl group and nitro group retard the electrophilic reaction. Crystals of IZs as well were made from DMSO/water solvent free or DMSO co-crystals depending on the DMSO/water ratio. This gave two different conformations of the compounds, one open and one close respectively.

Using α, ω-difuntional perfluoroalkane, two new difunctional iodonium zwitterions (DIZs) were successfully prepared. Except the difference to make starting materials, the synthesis process was quite the same.

Table 2.1 Other Examples of Iodonium Zwitterions

Reaction: $Ar + p\text{-}IArSO_2NSO_2R_f \xrightarrow{H_2SO_4/K_2S_2O_8} Ar\text{-}\overset{\oplus}{I}\text{-}Ar\overset{\ominus}{S}O_2NSO_2R_f$

Other examples of iodonium zwitterions

Ar	R_f	Yield (%)
	CF_3, C_4F_9	84, 78
	CF_3, C_4F_9	80, 79
	CF_3, C_4F_9	84, 84
	CF_3, C_4F_9	0, 0
	CF_3	Decomposed by heat
	CF_3, C_4F_9	70 (90% meta), 65

The thermal stability of these compounds was similar to the monfunctional IZs, but is quite distinct in other characteristics. The polarity of these DIZs is much bigger

than MIZs because of their symmetric polar structures. As a result, they are much less soluble than IZs and DMSO is the best solvent. DIZs also exhibited much stronger light absorption, having ε (molar extinction coefficients) almost double that of IZs (**Table 2.2**).

Table 2.2 Comparison IZ and DIZs in UV-Vis

λ	Max: 248nm ε_1 ($cm^{-1}M$)	193nm ε_2 ($cm^{-1}M$)	254nm ε_3 ($cm^{-1}M$)
$PhI^{+}PhSO_2N^{-}SO_2CF_3$	22.62×10^3	14.03×10^3	2.206×10^3
$(PhI^{+}PhSO_2N^{-}SO_2C_2F_4)_2$ **6a**	57.91×10^3	29.47×10^4	39.11×10^3
$(PhI^{+}PhSO_2N^{-}SO_2C_3F_6)_2$ **6b**	47.92×10^3	21.75×10^4	35.85×10^3

Experimental

Preparation of $NaSO_2R_fSO_2Na$ (**1a-1c**)

In a typical reaction, 45.40g of $(IC_2F_4)_2$ (0.1mol) was dissolved in 100mL of acetonitrile and 200mL of water in a 500mL round bottom flask. The whole solution was made to basic with 30.00g of $NaHCO_3$ (0.36mol) first and then fresh 50.00g of $Na_2S_2O_4$ (0.28mmol, the ratio is 1:2.8) was slowly added in with good stirring at 22°C. After 20h, fluorine NMR indicated the peak of ICF_2 disappeared. The reaction was completed. The solution $(NaSO_2C_2F_4)_2$ **1a** and other byproducts were light yellow. Compound **1b**, **1c** was obtained by an exactly identical procedure.

$(NaSO_2CF_2^aCF_2^b)_2$ (**1a**) ^{19}F NMR (CD_3CN, ppm) δ_a –121.6(4F, m) , δ_b –129.6(4F,m).

$(NaSO_2CF_2^aCF_2^bCF_2^c)_2$ (**2a**) ^{19}F NMR (CD_3CN, ppm) δ_a –121.3(4F,m), δ_b –121.7(4F,m), δ_c –129.8(4F,m).

$(NaSO_2CF_2^aCF_2^b)_2O$ (**3a**) ^{19}F NMR (CD_3CN, ppm) δ_a –81.9(4F,m), δ_b –132.6(4F,m).

Preparation of $ClSO_2R_fSO_2Cl$ (**2a-2c**)

In a typical reaction, 100mL of water was added to the $(NaSO_2C_2F_4)_2$ **1a** solution. At 0°C, chlorine was bubbled into another 100mL of ice water in a 1000mL flask cooled with an ice bath. While continue bubbling Cl_2 gas, the $(NaSO_2C_2F_4)_2$ solution was slowly added from a dropping funnel. Each drop instantly gave a dark color in the solution, and then quickly turned back to light yellow. After the reaction was completed, the white solid was filtrated out and dissolved in CH_2Cl_2. Then, the resulting solution was washed with water and dried over anhydrous Na_2SO_4 for at least 48 hours. Finally 31.90g of white product $(ClSO_2C_2F_4)_2$ **2a** (the yield is 80%) was obtained after removing the Na_2SO_4 crystals by filtration, and followed by removal of organic solvent under vacuum. Compound **2b**, **2c** was obtained by an exactly identical procedure.

$(ClSO_2CF_2^aCF_2^b)_2$ (**2a**) ^{19}F NMR ($CDCl_3$, ppm) δ_a –103.9(4F, m) , δ_b –118.1(4F,m).

$(ClSO_2CF_2^aCF_2^bCF_2^c)_2$ (**2b**) The yield is 88%.

^{19}F NMR ($CDCl_3$, ppm) δ_a –104.7(4F, m), δ_b –119.6(4F,m), δ_c –121.6(4F,m).

$(ClSO_2CF_2^aCF_2^b)_2O$ (**2c**) The yield is 84%.

^{19}F NMR ($CDCl_3$, ppm) δ_a –78.8(4F, m), δ_b –108.5(4F,m).

Preparation of $FSO_2R_fSO_2F$ **(3a-3c)**

In a typical reaction, 31.00g of compound **2a** (77.69mmol), 15.00g of dry KF (0.259mol, 1: 3.33) were put into a 250mL round bottom flask in the dry box. The flask was evacuated and dry CH_3CN (50ml) was vacuum transferred into the flask. The mixture was stirred at 22°C for 24h. ^{19}F NMR monitored the reaction process. After reaction was completed, the crude product and CH_3CN were transferred to a trap at high vacuum. Water (30ml) was then added to the CH_3CN mixture. The lower layer was

separated and distilled over P_4O_{10}. Purified product 21.34g of $(FSO_2C_2F_4)_2$ **3a** (yield 75%) was collected in the flask. Compound **3b**, **3c** was obtained by an exactly identical procedure.

$(F^aSO_2CF_2{}^bCF_2{}^c)_2$ **(3a)** ^{19}F NMR (CD_3CN, ppm) δ_a 47.5(2F, s) , δ_b –106.9(4F,m), δ_c–119.0(4F,m), bp120^{o}C at room temperature, atmospheric pressure.

$(F^aSO_2CF_2{}^bCF_2{}^cCF_2{}^d)_2$**(3b)** (yield 79%)

^{19}F NMR (CD_3CN, ppm) δ_a 47.2(2F, s), δ_b –106.8(4F,m), δ_c–119.1(4F,m), δ_d – 120.3(4F,m), bp 140^{o}C at room temperature, atmospheric pressure.

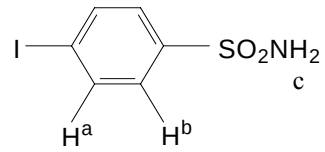
$(F^aSO_2CF_2{}^bCF_2{}^c)_2O$ **(3a)** (yield 73%)

^{19}F NMR (CD_3CN, ppm) δ_a 46.6(2F, s) , δ_b –80.9(4F,m), δ_c–111.2(4F,m), δ_d – 129.6(4F,m), bp 120 ^{o}C at room temperature, atmospheric pressure.

Preparation of p-$IPhSO_2NH_2$ **(4)**

15mL of ammonia was bubbled into 30mL of water in a 100mL round bottom flask. P-iodobenzenesulfonyl chloride (9.08g, 0.03mol) was added and the solution was refluxed for 8 hours. The solid product was extracted out with 40mL of dry CH_3CN after washing byproduct NH_4F out. The pure product 7.64g of p-iodobenzenesulfonyl amide **4** was obtained with a yield of 90% after drying under high vacuum for 2hours.

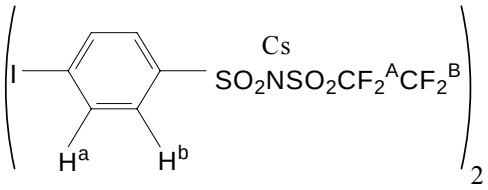
Alternatively, in a 250mL three-necked round bottom flask, 9.08g of pipsyl chloride (0.03mol) was added. And then 30ml ammonia was condensed into the flask at -60^{o}C and allowed to slowly warm to room temperature for 8 hours. The crude product was washed with 40mL water and dried under the vacuum, to give 8.07g purified amide **4** with a yield of 95%.

4 

^{1}H NMR (CD_3CN, ppm): ab, δ_a 7.89(2H, d) , δ_b 7.60(2H,d), J_{ab}= 10Hz, δ_c 5.70(2H,s)

Preparation of p-IPhSO_2N(Cs)$SO_2R_fSO_2$N(Cs)SO_2PhI-p (**5a-5c**)

In a typical reaction, 5.66g of dry p-iodobenzenesulfonyl amide **4** (0.02mol) and 3.66g of $(FSO_2C_2F_4)_2$ **3a** (0.01mol) (2:1) were put into a gas tight vessel with 10mL of dry $(CH_3CH_2)_2NCH_2CH_3$ (DIEA) and 20mL of dry CH_3CN. The solution was refluxed with good stirring at 80^{o}C for 2 days. According to ^{19}F NMR, the reaction was completed after –SO_2F group disappeared in the spectrum. All the volatile impurities were removed under the vacuum except the crude product R_3NH^+ salt and the inorganic impurities. The mixture was dissolved in 5mL of acetone and then acidified with 20mL of 15% dilute hydrochloric acid till pH paper turned red (pH= 2.5). **5a** (10.85g, 80%) was obtained after precipitation with 20mL of aqueous Cs_2CO_3 solutions (0.025mol). Compound **5b**, **5c** was obtained by an exactly identical procedure.

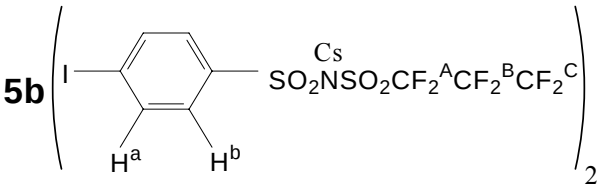
5a 

^{19}F NMR (CD_3CN, ppm): AB δ_A –112.2(4F, m), δ_B -119.3(4F,m);

^{1}H NMR (CD_3CN, ppm): ab ^{1}H NMR δ_a 7.83(4H, d), δ_b 7.60(4H,d, J=8Hz), J_{ab}= 10Hz;

^{13}C NMR (CD_3CN, ppm): δ207.1, δ145.7, δ137.7, δ128.6, δ99.0

IR (cm^{-1}) (KBr pellet, acetone) 2924(vs), 2855(vs), 1650(w), 1572(m), 1460(s), 1385(m), 1325(vs), 1294(s), 1270(m)1314(s), 1196(vs), 1142(vs), 1093(s), 1007(m), 818(m), 761 (m), 719(w).

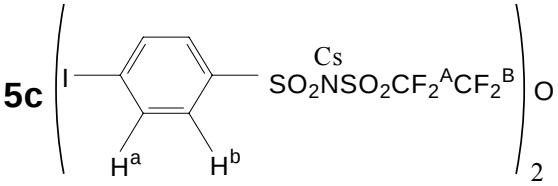
5b 

(yield 87%)

^{19}F NMR (CD_3CN, ppm): ABC δ_A –112.4(4F, m) , δ_B -119.7(4F,m), δ_C–121.1(4F,m);

^{1}H NMR (CD_3CN, ppm): ab, δ_a 7.86(4H, d) , δ_b 7.51(4H,d), J_{ab}= 10Hz;

IR (cm^{-1}) (KBr pellet, acetone) 2926(vs), 2855(vs), 1650(w), 1569(m), 1460(s), 1377(s), 1314(s), 1201(m), 1147(s), 1097(m), 1002(m), 767(m), 722 (m).

5c 

(yield 84%)

^{19}F NMR (CD_3CN, ppm): AB, δ_A –80.5(4F, m) , δ_B –115.3(4F,m);

^{1}H NMR (CD_3CN, ppm): aabb, δ_a 7.83(4H, d), δ_b 7.60(4H,d), J_{ab}= 10Hz;

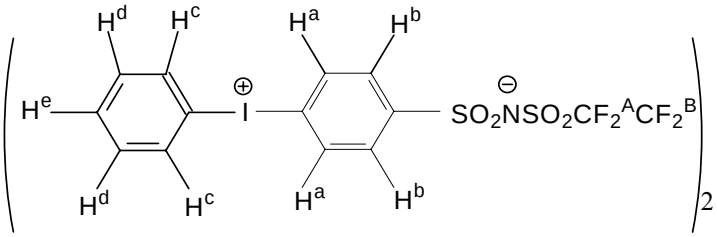
IR (cm^{-1}) (KBr pellet, acetone): 2926(vs), 2855(vs), 1650(m), 1572(m), 1460(s), 1383(s), 1326(s), 1226(s), 1142(vs), 1090(s), 1059(m), 1008(m), 986(m), 819(m), 765(s), 721(m).

Preparation of Diaryl Iodonium Zwitterions (**6a-6b**)

In a typical reaction, 2.33g of (I-$PhSO_2N(Cs)SO_2CF_2CF_2)_2$ **5a** (2.0mmol) in 30mL of sulfuric acid was cooled to -30°C in a 50mL round bottom flask. Potassium

persulfate (1.39g, 8.0mmol) was added in one portion and the reaction mixture was slowly warmed to -20°C in ice bath with good stirring. To the resulting suspension, 0.37mL benzene (4.2mmol, the ratio is 1:4:2.1) was added. The reaction mixture became a dark yellow solution and was warmed to 20°C over 8 hours. Pouring the mixture into the ice quenched the reaction. The resulting suspension was filtered and the solid was washed with 30ml of water on the filter. The 1.62g of dried solid **6a** (the yield is 65%) was obtained with the purity of 95%. The impurity was the hydrolyzed compound $PhI^{+}PhSO_2N^{-}SO_2CF_2CF_2CF_2CF_2SO_3H$ (or SO_3^{-}). Compound **6b**, **6c** was obtained by an exactly identical procedure.

6a

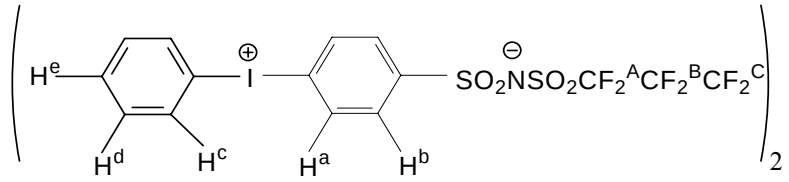


^{19}F NMR (DMSO, ppm): δ_A –112.3(4F, m), δ_B -119.6(4F,m);

^{1}H NMR (DMSO, ppm): aabb, δ_a 8.32(4H, d), δ_b 8.23(4H,d), J_{ab}=8Hz, δ_c 7.83(4H, d), δ_d 7.66(2H, t), δ_e 7.52(4H,t), J_{cd}=8Hz, J_{de}=7Hz;

^{13}C NMR (DMSO, ppm): δ207.1,148.9, 135.8, 135.8, 132.7, 132.4, 129.7, 128.7, 119.5, 117.2

IR (cm^{-1}) (KBr pellet, acetone) 2927(vs), 2855(vs), 1564(m), 1461(s), 1377(s), 1317(m), 1140(m), 1085(m), 987(m), 725 (m).

6b 

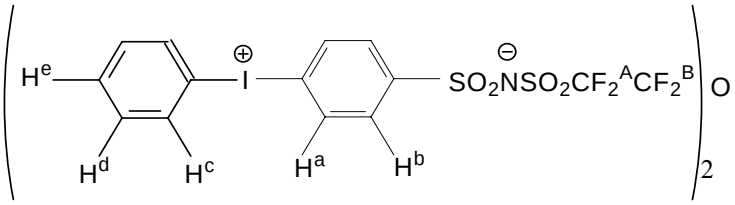
(yield 68%, purity is 98%)

^{19}F NMR (DMSO, ppm): δ_A –112.3(4F, m), δ_B -119.7(4F,m), δ_C–121.1(4F,m);

^{1}H NMR(DMSO, ppm): ab, δ_a 8.33(4H, d), δ_b 8.25(4H,d), J_{ab}=8Hz;

δ_c 7.84(4H, d), δ_e 7.66(2H, t), δ_d 7.53(4H,t), J_{cd}=8Hz, J_{de}=7Hz;

^{13}C NMR (DMSO, ppm): δ 148.7, 137.8, 135.8, 132.7, 132.4, 129.7, 128.6, 119.5, 119.4, 119.3, 117.1;IR (cm^{-1}) (KBr pellet, acetone) 2919(vs), 2855(vs), 1565(m), 1461(s), 1377(s), 1326(s), 1272(m), 1210(m), 1149(s), 1086(m), 987(m), 821(m), 767 (m), 740(m).

6c 

(yield 60%, purity 94%)

^{19}F NMR (CD_3CN, ppm): δ_A –112.3(4F, m), δ_B -119.6(4F,m);

^{1}H NMR (CD_3CN, ppm): ab, δ_a 8.32(4H, d), δ_b 8.23(4H,d), J_{ab}=8Hz, δ_c 7.85(4H, d), δ_d 7.67(2H, t), δ_e 7.50(4H,t), J_{cd}=8Hz, J_{de}=7Hz;

IR (cm^{-1}) (KBr pellet, acetone) 2927(vs), 2856(vs), 1565(m), 1461(s), 1378(s), 1318(s), 1194(s), 1157(s), 1114(m), 1086(m), 987(m), 822(m), 782(m), 735(m).

Conclusion

The synthesis of those symmetric diaryl iodonium zwitterionic compounds has been achieved through the oxidation reaction of the substituted iodobenzene sulfonimide cesium salt and benzene. Although monoaryliodonium zwitterions are easily dissolved in CH_3CN, these diaryl zwitterions are soluble in more polar solvents due to their greater polarity. With the knowledge of monoaryl salt synthesis and this work, a wide variety of IZs and DIZs can now be synthesized. The DIZs contain a small amount impurities caused by the hydrolysis of one of the $-SO_2F$ groups during the coupling reaction of the aryl sulfonamide. No satisfactory method was found to remove their impurities.

As photoacid generators, they have larger light absorption compared to the IZs. Applications as photoacids await further research.

CHAPTER III

FUNCTIONAL DIAZONIUM ZWITTERIONS

Introduction

PEM Fuel Cell are of high interests as efficient sources of alternative energy. As Chapter I mentioned, the MEA is the key to the whole PEM Fuel Cell structure. It is a three-phase reaction system including transport processes as shown in **Figure 3.1**[100]: a. protons from the membrane to the catalyst; b. electrons from the current collector to the catalyst through the gas diffusion layer; c. the reactant and product gases to and from the catalyst layer and the gas channel.

For the gas diffusion layer (GDL) in the electrode, polytetrafluoroethylene (PTFE) was coated on carbon particles surface to ensure that the pores of this layer do not become congested with water. PTFE does not dissolve in any solvents, so fabricate electrodes with it as liquid suspension, which is quite difficult to control the electrode structure and the porosity. In this layer, gas can easily diffuse through the pores towards the electroacitve layer, where the reaction takes place. GDL is also an electron conductor with carbon materials and an electrolyte barrier to prevent penetration of the electrolyte. The essential for catalyst layer keeps the balance of hydrophilic to hydrophobic ratio since it needs to permit electrolyte to enter from the membrane to wet the carbon material, and permit air to enter from GDL to contact the electrolyte in the this layer [101,

[102]. Thus, catalyst layer is the mixture of hydrophobic carbon powder and a hydrophilic fluorinated polymer resin such as Nafion®[103]. If this whole layer was flooded with electrolyte, it will restrict gas access; on the other hand, if it is too hydrophobic, the performance of the catalyst will be decreased[104]. Even with the optimal Nafion® content, the efficiency of utilization of the catalyst is low, only about 10-20% [105]. The reason is because a three dimensional reaction zone on an electrode in contact with the electrolyte is not created easily since the PEM electrolyte is a polymer solid [106].

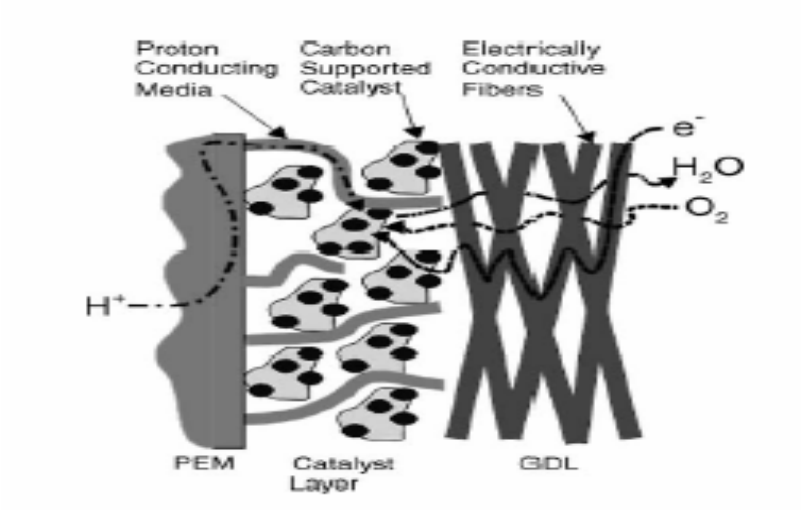


Figure 3.1 The Structure of Gas Diffusion Electrode

Attempts have been made to solve these problems by a. placing the catalyst particles in close proximity to the membrane; b. impregnating a small amount of electrolyte into the electrode structure; c. increasing proportion of active metal in the metal catalyst on the porous electrode surfaces [107, 108, 109]As potential route to improve their interface exploratory research to develop a new family of nanoscale materials was begun. The goal was to maximize the activity of catalyst particles in contact with PEM fuel cell electrodes. Figure 3.2 shows the overall structure that we envisaged for the proposed materials. The top one is conventional electrode fabricated using Pt-decorated

carbon powder and polymer electrolyte, such as Nafion®; the bottom one is proposed electrode based on carbon aerogel with interior pores decorated with Pt particles and grafted electrolyte [110].

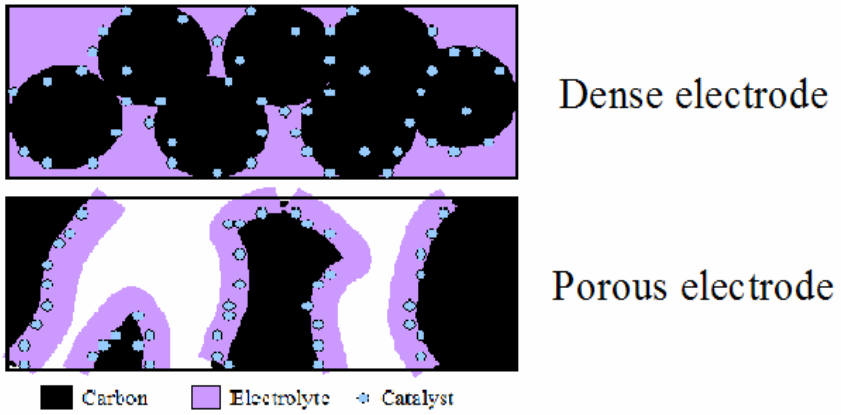
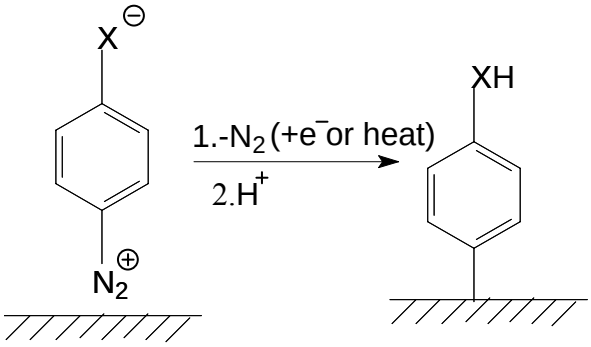


Figure 3.2 Nanoporous Carbon/Catalyst/Electrolyte Fuel-Cell Electrodes

A feature of the present research is to provide catalyst layer of a gas diffusion electrode primarily containing one or more modified carbon products with or without at least one binder. The amount of binder that usually is Nafion®[111] can be substantially reduced or eliminated entirely by using a modified carbon product. Thus, a modified carbon product used in the catalyst layer will serve the function of the fluoro-binder directly. The modified carbon product, which has an organic group acting as an electron conductor and proton conductor, permits the catalyst particles to be in close proximity to the proton-conducting group. This is not possible when a binder such as Nafion is used as the proton conductor[112, 113].

At this point, novel Functional Diazonium Zwitterions (FDZs) containing perfluoroalkyl sulfonimide groups were synthesized as proton conductors in order to graft onto modified carbon. To replace the fluorinated sulfonic acid base polymer such as Nafion® that was widely used in Fuel Cell PEM, these stable diazonium zwitterions can

integrate an electrolyte with a carbon electrode to obtain good contact between the carbon and electrolyte.As shown in **Scheme 3.1**, by easily losing N_2 in thermo- or electro-chemical reaction, the functional aryl group is directly grafted onto carbon electrodes with the formation of a covalent carbon-carbon bond [114]. The sulfonimide group can provide a basis for a variety of functionalities, which might form more useful electrolyte in PEM Fuel Cell. Methods for preparing various monofuctional, difunctional, and multifunctional diazonium zwitterions are presented in this chapter. Among them, p-$N_2^+PhSO_2N^-SO_2CF_3$ was already crystallized and grafted onto carbon successfully.



$X = SO_2N^-SO_2R_f$

Scheme 3.1 Graft FDZs on Carbon

Modified Carbon in Gas Diffusion Electrode

Many efforts have been made over the last several decades to modify the surface chemistry of carbon black. Some processes for chemically changing the surface of carbon black are known and already used commercially, such as sulfonation, halogenation [115], grafting polymers onto carbon black by heating [116], reaction with alkali or alkaline earth metal to form catalyst composition from [117]; hydrocarbon chemical attachment [118]; and azo pigment [119, 120, 121]. Gas diffusion electrodes are general category, which include air-

diffusion electrodes, wherein the air diffusion electrodes can be used in metal-air batteries and fuel cells and the like. This type of electrode is constructed to have a gas diffusion layer and a catalyst layer as **Figure 3.1** shows.

The active layer, referred to as the catalyst layer with the membrane[122], contains a modified carbon product that promotes hydrophilic and hydrophobic characteristics. The modified carbon products with hydrophilic organic group were applied as the active layer. They were obtained by dispersing the modified carbon products in aqueous solution such as water or methanol and the formation of a thin proton conducting catalyst layer directly. Since the carbon product has a tendency to be naturally hydrophobic, how to attain the hydrophilic characteristic of modified carbon is more important. Usually, the carbon product would rather attach directly with at least one type of hydrophilic organic group which can be an aromatic or alkyl group substituted with an ionic group, an ionizable group, an organic group that is a sulfonphenyl group, or a carboxyphenyl group, or salts, et. al[123].

Since the modified carbon product is a carbon black having attached small molecule groups, the equivalent weight (EW) of acid group will be much higher than Nafion® [124]. Therefore, it can have less material present in the catalyst layer. The thickness of catalyst layer can also be greatly reduced since the need for binder is reduced. Furthermore, it can undergo an ion exchange reaction with metal catalyst such as Pt. The cationic metal catalyst complex can be attached or absorbed onto the modified carbon products too. Organic groups on the modified carbon products are strongly acidic and thus function as superb proton conductors in a fuel cell. The ratio of micropore-free surface area to total surface area is significantly increased, which in turn reduces catalyst

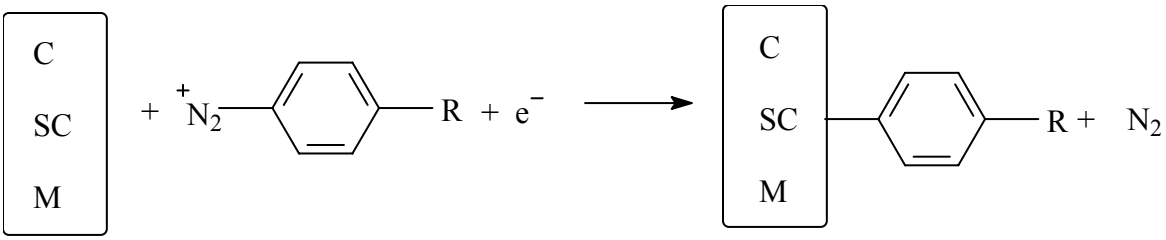
lost in micropores. Having the metal catalyst in very close proximity to the organic groups makes it quite possible to form an active layer with a catalyst, proton conductor, and electron conductor, which permits excellent catalyst utilization.

In addition, the membrane can contain modified carbon products that avoid loss in ionic conductivity. Hence, the incorporation of modified carbon products, such as carbon black with a high level of attached organic groups, onto a membrane reduces the extent of crossover and preferably permits the use of thinner membranes resulting in diminished ohmic losses in fuel cells[125].

For a preferred embodiment in GDL, the modified carbon product really needs to have an organic group covalently attached to the carbon surface. A native carbon surface is relatively inert to most organic reactions, and the attachment of specific organic groups at high coverage levels has been difficult. Diazonium salts with special organic function were generated to overcome this problem.

Grafting Diazonium Salts onto Carbon Black

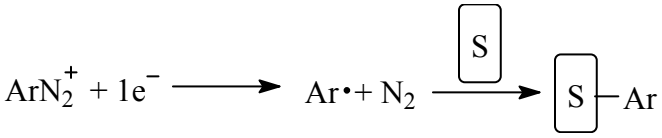
Saveant and Pinson [126] first demonstrated that the reduction of an aryl diazonium cation afforded the corresponding aryl radical, which can further react with a carbon atom of the carbon substrate to yield the covalent bonding of this aryl group. By electrochemical or thermodynamical reduction of diazonium salts, the surface modification can lead to aryl radicals grafting onto materials, such the metal and carbon surface as shown in **scheme 3.2** [127].



C: Carbon, SC: Semiconductor, M: Metal

Scheme 3.2 Electrochemical Graft Diazonium Salts on Substrate

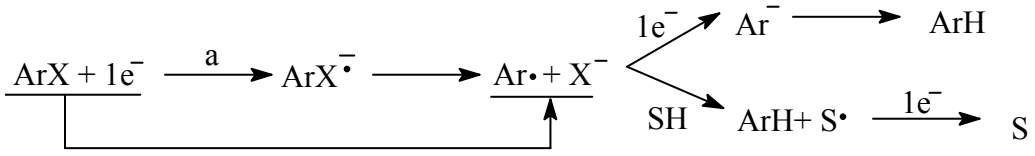
The electrochemical grafting mechanism (**Scheme 3.3)** is believed different with electrochemical reduction of aryl halide (**Scheme 3.4)**[128, 129]. The phenyl radical is produced directly "on the electrode" through an electron transfer concerted with the cleavage of dinitrogen to give the phenyl radical. In contrast to aryl halides, at the very low cathodic reduction potential of diazonium the phenyl radical is not reduced and can react with the surface.



S = Substrate: carbon, semiconductor or metal

Scheme 3.3 Mechanism of Electrochemical Grafting of Aryl

Diazonium Salts

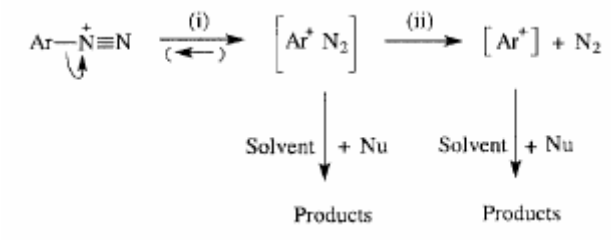


X=Halides

Scheme 3.4 Electrochemical Reduction of Aryl Halide

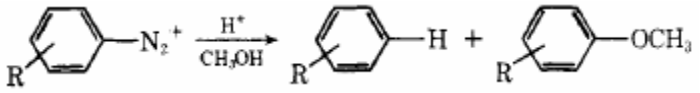
Those arendiazonium compounds were used in attachment of organic layers to conductive or semiconductive surface [130, 131, 132].

The mechanism of thermolysis of arenediazonium ions and attachment to carbon materials is still not very clear. In 1940, Hammet[133] postulated a slow unimolecular thermal heterolytic disscoatiation of arenediazonium ions into aryl cations and N_2. Following that, Lewis [134], Swain [135] and DeTar [136], Zollinger [137] and others provided experimental proofs. Canning [138] and coworkers concluded that for the simple arenediazonium ions in the polar solvents, most decomposed by the mechanism of **Scheme 3.5**.



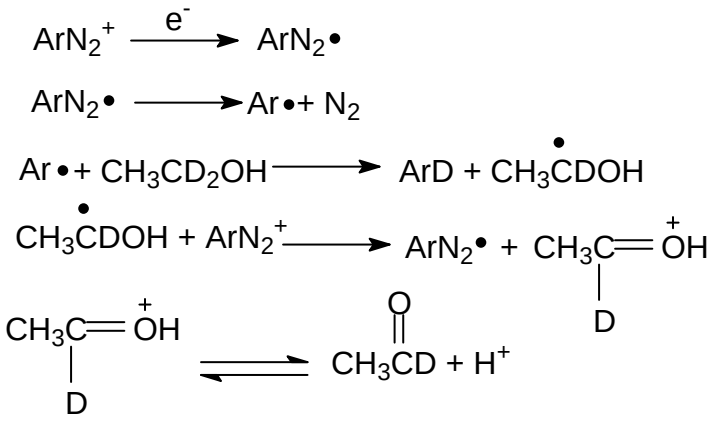
Scheme 3.5 Heterolytic Mechanism of Dediazoniation

But according to Bunnett and Yijima, there are competing radical chain and an ionic mechanism on thermolysis in acidic ethanol [139]. The radical mechanism leads principally to protodediazoniation products and the ionic mechanism to aryl methyl ethers [140] as shown in **Scheme 3.6**.



Scheme 3.6 Diazonium Salts Decomposition in Acidic Methanol

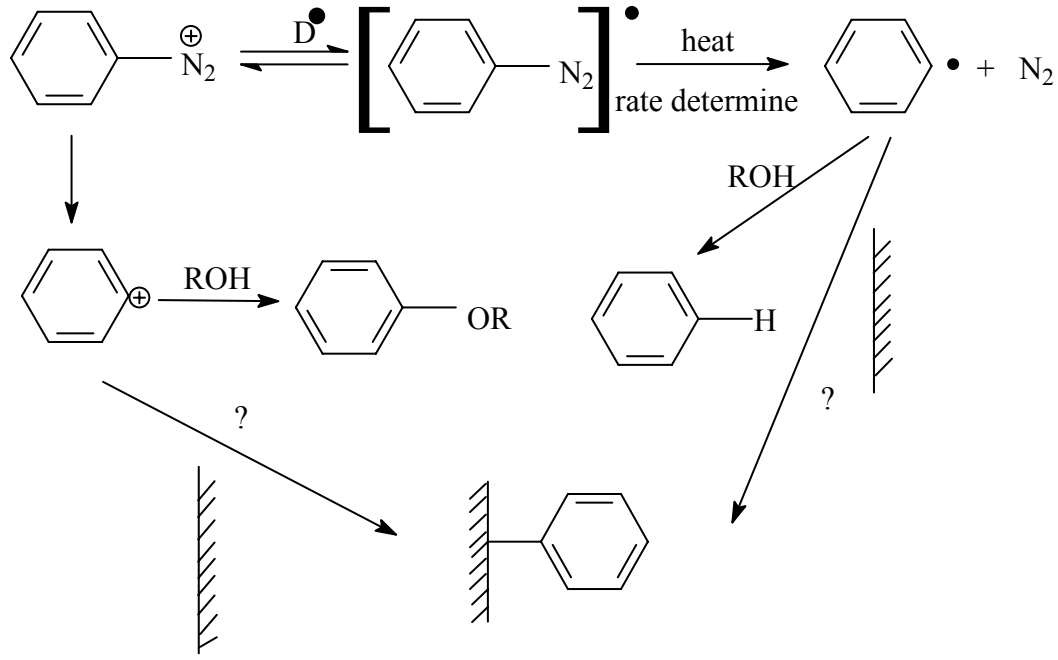
DeTar and others [141, 142] concluded a radical mechanism following much earlier suggestions by Hey and Waters for EtOH. The electron donor in **Scheme 3.7** is probably the solvent, ethanol.



Scheme 3.7 Radical Mechanisms for Reduction of Arenediazonium Ions by Ethanol

Zollinger [143] reported that increasing the nucleophilicity of the solvent itself, as well as introducing nucleophilic solutes, promotes homolysis of diazonium ions. It can be proved by adding pyridine to the dediazoniation of benzenediazonium tetrafluoroborate salt with an increased overall rate and yield of the products of the hemolytic decomposition.

Arenediazonium ions can acquire electrons by means of electrochemical generation, by photolytic dissociation or by transferring an electron from inorganic or organic compounds [144]. A large number of reducing agents can be used to generate aryl radicals [145, 146]. Thermal diazonium salt grafting mechanism is proposed as shown in **Scheme 3.8**.



Scheme 3.8 Proposed Thermal Mechanisms for Diazonium Salts Grafting onto Carbon

Belmont et al. in a patent disclose a process (referred to herein as the Belmont process) that significantly improves the ability to modify carbon surfaces with organic groups. Through thermally decomposing diazonium salts, organic groups can be covalently bonded to the carbon surface so that the groups are highly stable and do not readily desorb from the carbon surface [147, 148]. Different reaction conditions were tried in many patents. Although the overall mechanism of the reaction is not very clear, those attempts seem promising and worthy of explanation with the new diazonium compounds generated in this research.

Other Diazonium Zwitterions and Properties

Organic diazonium salts were first prepared as early as 1858 [149] and their reactions were among the first to be studied systematically by organic chemists. Aromatic diazonium salts have long been of interest principally because of their synthetic versatility [150, 151, 152, 153, 154]. They are important intermediates for the preparation of halides (Sandmeyer Reaction, Schiemann Reaction), and azo compounds. Since they can react as pseudohalide-type electrophiles, they are used in specific protocols for the Heck Reaction or Suzuki Coupling. Diazonium ions are also of interest in theoretical chemistry. In more recent theoretical works they are considered as electron-donor/acceptor complexes between a phenyl cation and a nitrogen molecule [155].

Few dizonium zwitterions are reported in the literature. By definition a zwitterionic diazonium compound is one except diazonium group, containing another substituent that functions as an anion. Common examples of such substitute in the dye art are the sulfonic acid group and the hydroxyl group such as in **Figure 3.3**[156, 157]. Most dry diazonium zwitterions were surprisingly thermal stable and won't decompose till 160^{o}C according to TGA[158]. But since they are small molecules, they are very explosive.

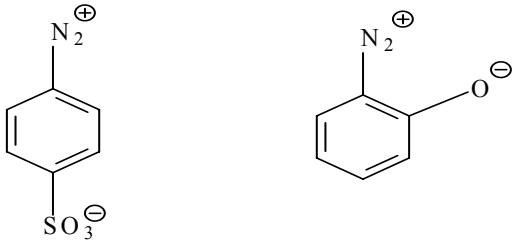
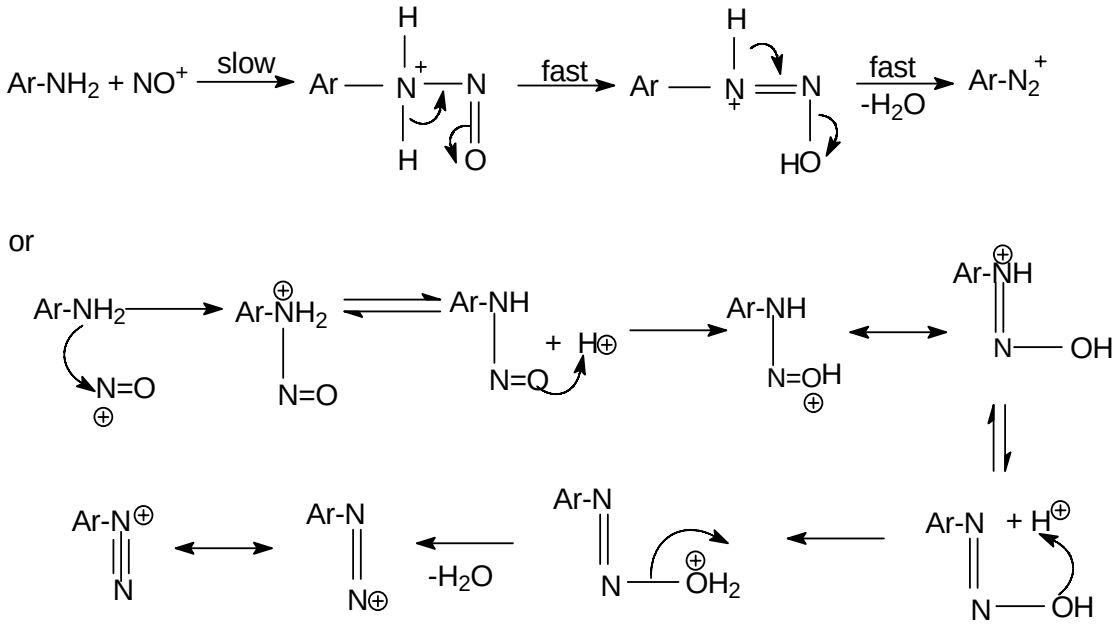


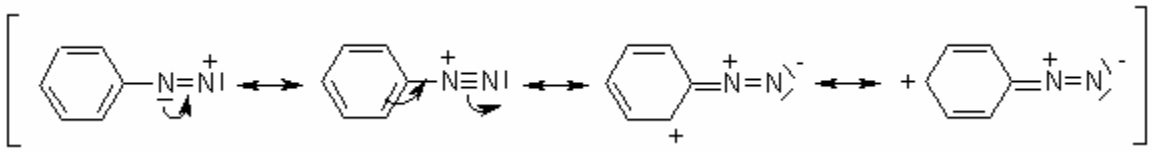
Figure 3.3 Common Diazonium Zwitterions

Diazotiazation of primary aromatic amines by NO^+-donors proceed mechanisms as shown in **Scheme 3.9** [159]:



Scheme 3.9 Mechanisms of diazotiaztion

The diazotiazations are normally performed in aqueous medium, concentrated acids and organic solvents. Reactivity decreases under normal conditions in the following sequence: $NO^+ > H_2O^+$-NO>NCS-NO>Br-NO>Cl-NO>O_2N-NO [160]. In consequence of the easy loss of molecular nitrogen, the simple arenediazonium salts are less explosive in the solid state because of their resonance structure as shown in **Scheme 3.10**, especially the most common diazonium chlorides. The explosive character is diminished by higher molecular weight and large complex anions [161].

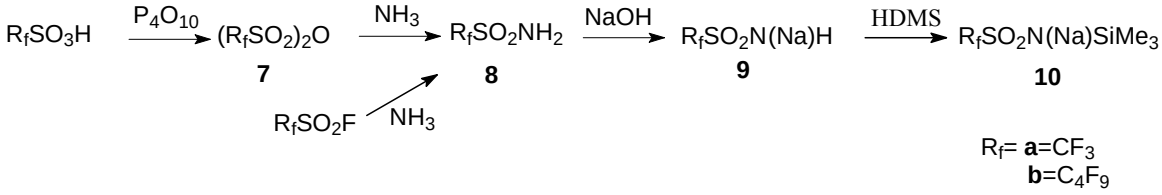


Scheme 3.10 Resonance Structures of Diazonium Salts

Research and Discussion

Preparation of Sodium N-trimethylsilyl Perfluoroalkane Sulfonimide Salts

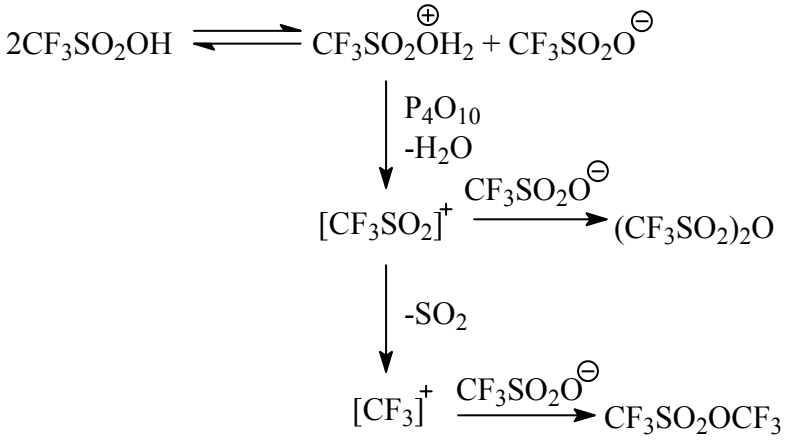
$R_fSO_2N(Na)SiMe_3$ is a very useful salt in our synthesis. It can be prepared from two methods [162, 163] as shown in **Scheme 3.11**. But since trifluoromethylsulfonyl fluoride is a gas at room temperature, sodium N-trimethylsilyl trimethylsulfonimide salt **10a** was preferred to be make from trifluoromethyl sulfonic acid or directly from trifluoromethyl sulfonic acid anhydride **7a,** which is already commercialized, but expensive. It is very easy to use perfluorobutyl sulfonyl fluoride as the starting material for **10b.**



Scheme 3.11 Synthesis Starting Materials

Often, trifluoromethyl sulfonic acid anhydride **7a** is prepared in the lab from the low cost of trifluoromethyl sulfonic acid, which has often been acclaimed as one of the strongest of all known monoprotic organic acids [164, 165, 166]. Before the dehydration, it is better to purify triflic acid by distillation to remove the varying amounts of water. This is because samples turned black after staying in the lab for a long time. The mechanism is

proposed [167, 168] as shown in **Scheme 3.12**. The reaction temperature has to be controlled around 0°C to avoid the decomposition of triflic anhydrides **7** at the high temperature and the formation of ester byproduct. The dehydration is exothermic so that care must be taken in the step to add P_4O_{10} slowly.



Scheme 3.12 Mechanism of Dehydride CF_3SO_2OH

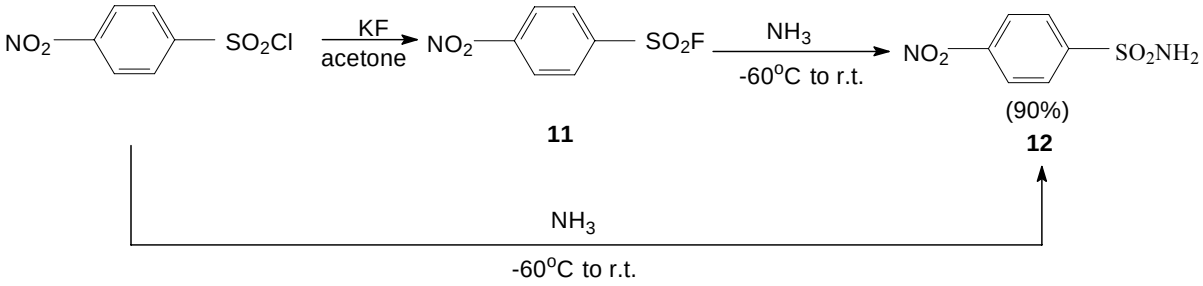
It is an easy reaction between anhydride and ammonia to give $CF_3SO_2NH_2$ **8a**. Keeping the reaction slow in a nitrogen atmosphere could prevent anhydride hydrolysis. The purified $R_fSO_2NH_2$ can be got by simple sublimation. **8b** can be prepared by ammonolysis of perflorobutyl sulfonic fluoride directly since it is not a gas.

The next step is to neutralize **9** with NaOH solution. Since $R_fSO_2NH_2$ are weak acids in the aqueous solution [169], titration really relies on their different acidity. Also the small amount excess base will bring problems in the following silated reaction by catalyzing the polymerization of HMDS and by hydrolyzing functional group $–SO_2Cl$ or $–SO_2F$ in the coupling reaction. Therefore, slightly less than the stoichimetric amount of NaOH will be good for neutralization. Excess reactant $R_fSO_2NH_2$ can be removed by sublimation. Finally silation step gives high yield of the product if handled under strictly

anhydrous condition. **10** is extremely moisture sensitive, and is required to be stored in a dry box.

P-nitrobenzenesulfonyl fluoride and amide

Scheme 3.13 shows the synthesis of compounds **11** and **12**.

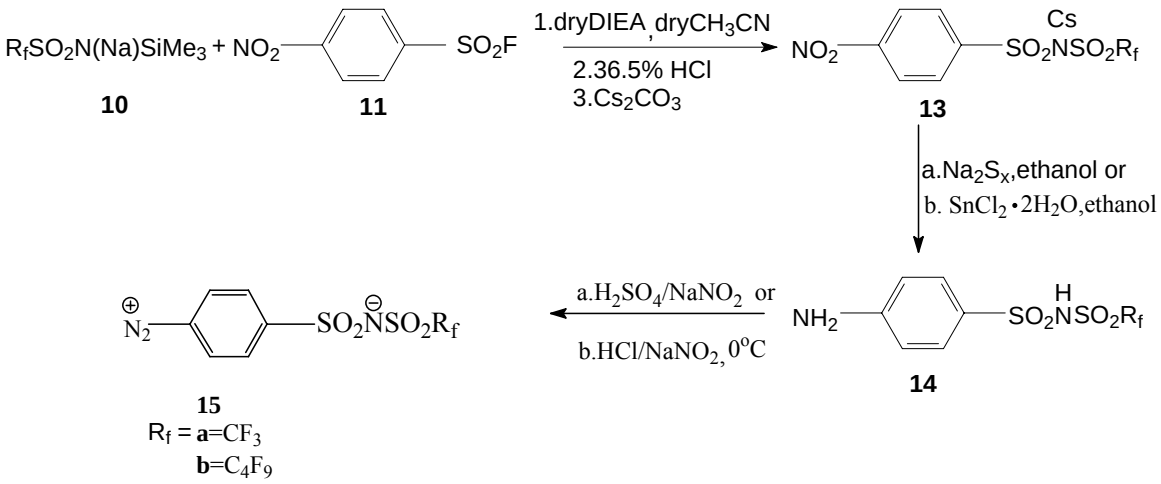


Scheme 3.13 Synthesis of P-Nitrobenzensulfonyl Fluoride and Amide

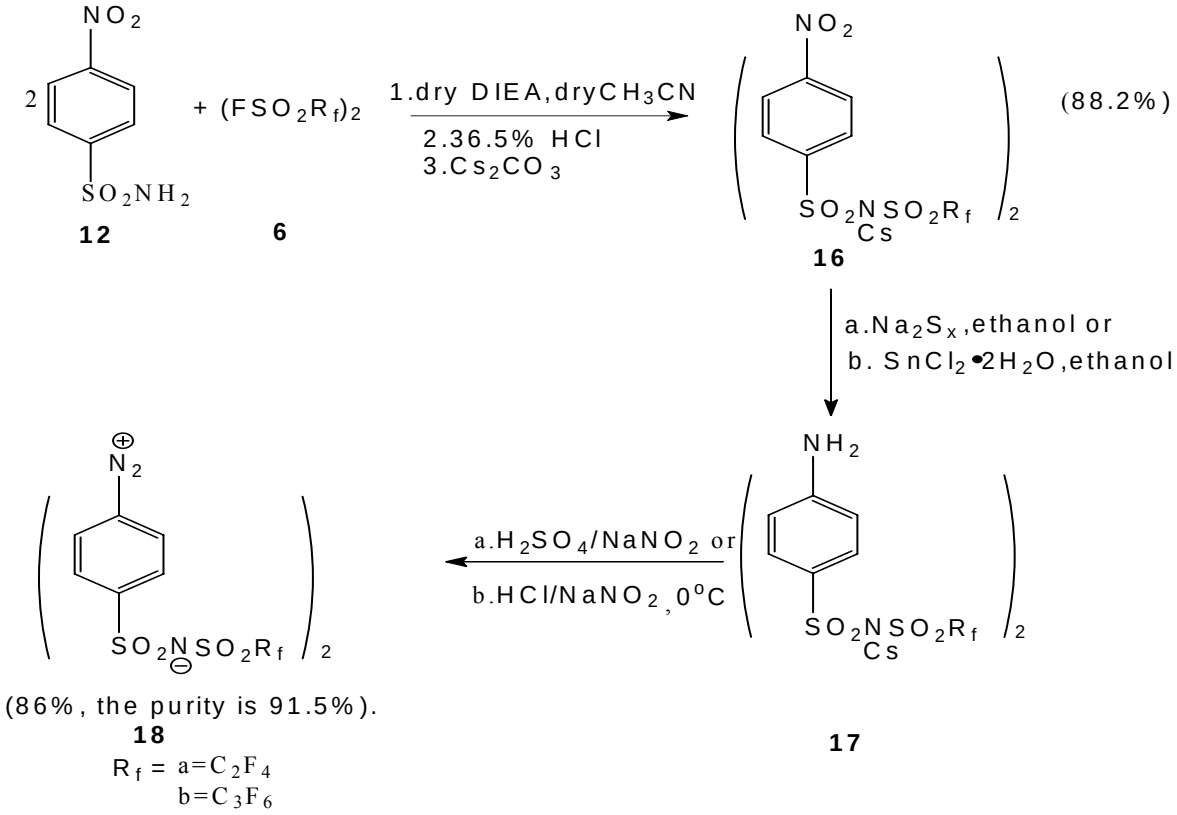
P-nitrobenzene sulfonyl chloride is very sensitive to water in basic conditions because of good leaving group –Cl, and fluorination or ammolysis need to be carried out with N_2 protection.

FDZs Preparation

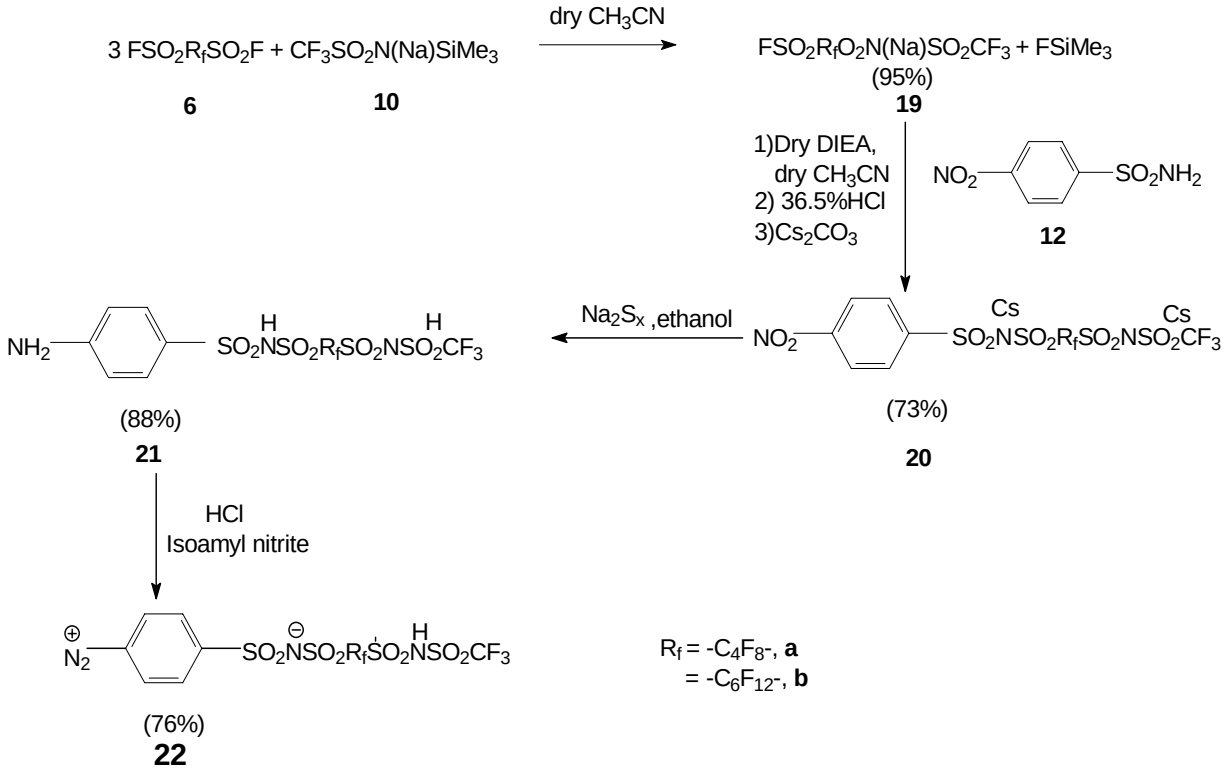
Although there are some differences in the synthesis process of the first three series of FDZs, the regular process is still as follows: (1) coupling reaction; (2) reduction reaction and (3) dizotiazation reaction. These steps are shown in **schemes 3.14, 3.15, and 3.16,** respectively**.**



Scheme 3.14 Synthesis of Monofuctional Diazonium Salts



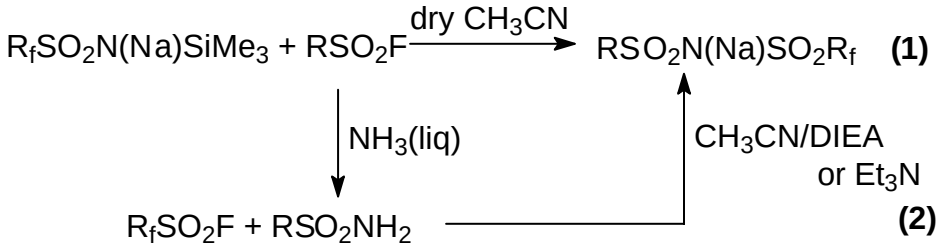
Scheme 3.15 Synthesis of Difunctional Diazonium Salts



Scheme 3.16 Synthesis of Multifuctional Diazonium Salts

Coupling reaction

There are two types of coupling reactions to make sulfonimide products as shown in **scheme 3.17**. Both of them were used in their research to target different goals.



Scheme 3.17 Coupling Reaction Routes

Under certain circumstances, reaction **(1)** is more feasible as **13** in **Scheme 3.14** and **19** in **Scheme 3.16**. The reaction is driven forward by the formation of $FSiMe_3$ that has stronger F-Si bond than S-F bond. When the R_f is a short chain, for example R_f=CF_3, C_4F_9, this reaction will be quite simple. And using $CF_3SO_2N(Na)SiMe_3$ is much more easier than handling the gas CF_3SO_2F in the synthesis,

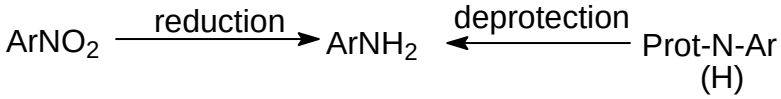
But if R_f is a big group, it takes more time to prepare sodium N-trimethylsilyl perfluoroalkane sulfonimide salt and to complete the coupling reaction. Recation **(2)** works fine by using sulfonyl fluorides directly, such as **16** in **Scheme 3.15** and **20** in **Scheme 3.16**. It is a nucleophilic substitution reaction, in which $–NH_2$ group was catalyzed with organic base such as diisopropylethylamine (DIEA) to increase its nucleophilicity.

Both typical coupling reactions **(1)** and **(2)** are used to synthesize **20** in **Scheme 3.16.** It is very important to notice that both reactions have to run in extremely dry conditions. Otherwise, silylated salts in reaction **(1)** will be hydrolyzed in the solution; and the sulfonyl fluoride group certainly will be hydrolyzed to $–SO_3^-$ at the basic condition in reaction **(2)**. After reaction **(2),** most of hydrolyzed impurities can be removed in the next step by precipitating out the pure product as Cs salt.

Aromatic Amine

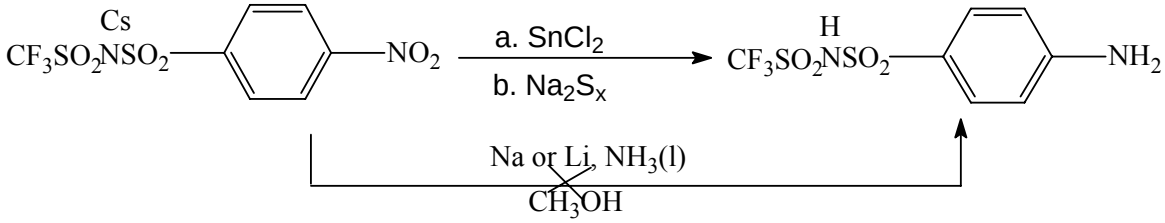
Aromatic amine compounds were very useful intermediates in the research to obtain the final diazonium zwitterions. The range of preparative methods for amines is large. Many reactions are old but have stood the test of the time. There are several

methods to prepare aromatic amines including reduction of corresponding nitro compounds and deprotection of functional groups as in **scheme 3.18**.



Scheme 3.18 Synthesis Routes to Aromatic Amide

A large number of reducing agents have been used for this purpose [170]. Procedures for the reduction of nitro compounds to amines are described precisely in the series of books: organic synthesis, namely, Fe + ArOH, Zn + NaOH, Fe + HCl, Sn + HCl, H_2-Raney Ni, H_2-PtO_2, H_2-Pd/C and N_2H_4-Pd/C, sodium sulfide and polysulfide, $NaBH_4$-Co(II), Cu(II), Ru(III) halides, and so on . Based on available compounds, some reducing agents were tried first. In a view of the fact that Cs salt and product amine don't have good solubility in protic solvents, how to remove the reducing agent after the required reactions become very critical.



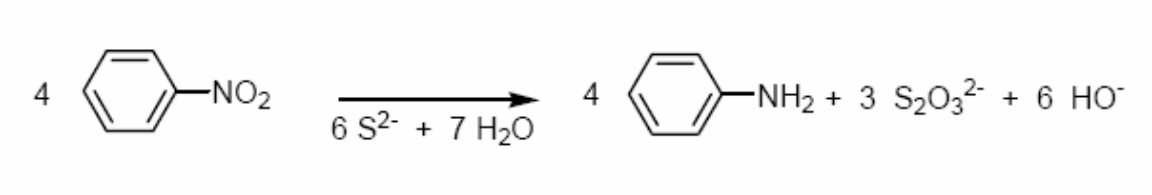
Scheme 3.19 Reduction Reaction

Use of $SnCl_2$•H_2O or Na_2S_x successfully give the reduce product, but isolating the pure product form the inorganic byproducts in the final product was not convenient. For tin (II), the halides readily dissolve in donor solvents such as acetone, pyridine, or DMSO, and pyramidal adducts, SnX_2L_2, are formed [171]. After reaction, the excess tin (II)

and by-product tin (IV) are left in the solution with the product. According to Bellamy[172], the inorganic product usually can be precipitated out with base and then the organic product can be extracted from ethyl acetate. However, extracting agent has to change to acetonitrile instead of ethyl acetate since any of aromatic amines **14, 17, 21** are soluble in ethyl acetate. Somehow, small trace of inorganic impurities always remains with the product from acetonitrile extraction. These impurities remain and contaminate the final diazonium product.

In order to prevent the heavy metal pollution in the final product, another reducing reagent Na_2S_x was used. This reduction is also called Zinin reduction. Zinin first used it in 1842 to prepare aniline from nitrobenzene [173]. The reaction mechanism is still not clear but some proposals are as shown in **scheme 3.20**. It was made fresh from hydrochloric acid reaction with sodium sulfide. The impurities, sodium salts and S, can be washed out by water and CS_2, respectively.

$$S_2^{2-} + H_2O \rightleftharpoons HS_2^- + OH^-$$



Scheme 3.20 Mechanism of Zinin Reaction Diazotization reaction

Three procedures can be carried out for diazotization, including in aqueous medium, in concentrated acids and in organic solvents[174]. Normal diazotization of aromatic amines with nitrous acid is performed in dilute aqueous mineral acids and yields the diazonium salts in solution. In this case, the amine with strongly acidic groups

therefore appears as sparingly soluble betains[175]. Weakly basic amines bearing strongly electron-attracting substituents on the aromatic nucleus are diazotized preferentially in concentrated acids, since hydrolysis of the generated diazonium compounds occurs in aqueous solution with rising dilution[176]. For most organic fluorine compounds, anhydrous hydrofluroic acid is a very good choice[177]. The disadvantages are undesired nitrations and oxidations as well as the enormously high danger of explosion of diazonium nitrates by using concentrated nitric acid[178]. In order to prepare specific diazonium salts, which may hydrolysis in aqueous solvent and explode in concentrated acid, the organic solvent would be best choice.

Diazotization of aromatic amines **14** and **17** were occured with sulfuric acid or hydrochloric acid with $NaNO_2$. When the same way was tried to synthesize MDZs **22**, they immediately decomposed in aqueous solution. This unusual phenomenon is comes for the fact that they can dissolve in water with more hydrophilic groups and hydrolysize immediately. Thus, isoamyl nitrate and HCl gas in anhydrous ethanol were applied to the synthesis of this type salts to obtain satisfactory results.

Property Comparison of FDZs

(1) Crystals

From CH_3CN solvent, very fine crystals of **15a** were obtained. The X-ray structure is shown in **Figure 3.4**. Though **15a** and **15b** were made by the same techniques, dry **15a** is quite stable at room temperature, whereas **15b** has to be kept in a dry box. It is believed that two molecules of **15a** are close to each other like a sheet, which makes it difficult to have a substitution reaction at $–N_2^+$. **15b** has more bulky

functional group $-C_4F_9$, which may give a different structural arrangement. Attempts to obtain X-ray crystals of **15b** were not successful due to its higher reactivity.

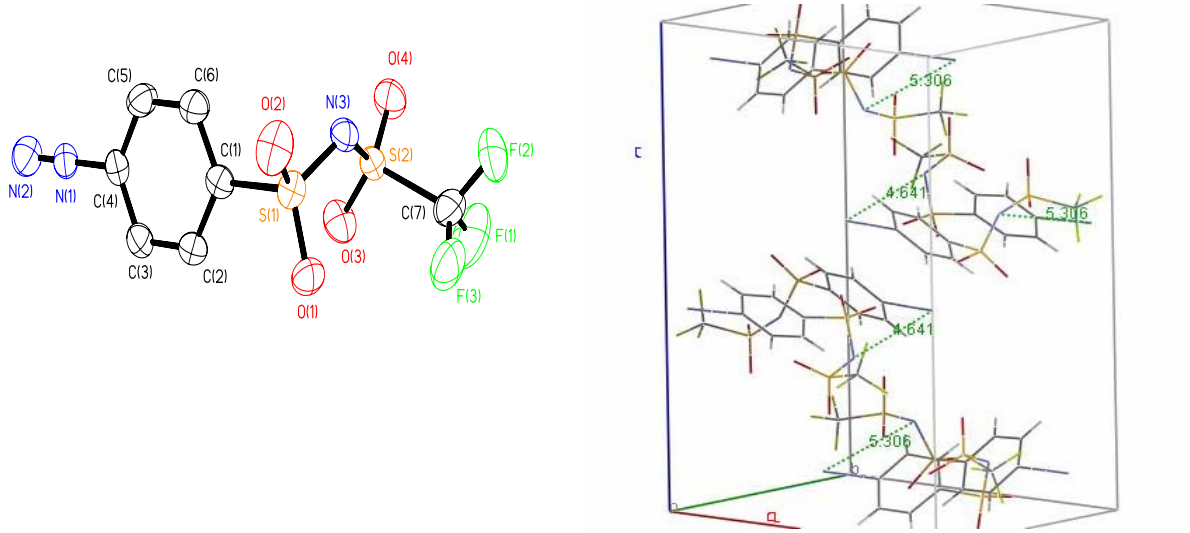


Figure 3.4 X-Ray Structure of p-$N_2^+PhSO_2N^-SO_2CF_3$

(2) Thermal Stability

Based on the TGA data in **Figure 3.5**, **3.6**, **3.7**, all the FDZs obtained have high thermal stability compared to other diazonium salts. The trend of decomposition temperature is shown as: MDZs > DDZs > MutiDZs. Among them, **15a** is the most stable one without of decomposition until 190°C. Even MutiDZ **22** has the lowest decomposition temperature around 80°C in **Figure 3.7**. The decomposition is the loss of N_2 and further decomposition does not occur until higher temperature around 200°C, suggesting that the aryl sulfonimide salts are quite stable as expected.

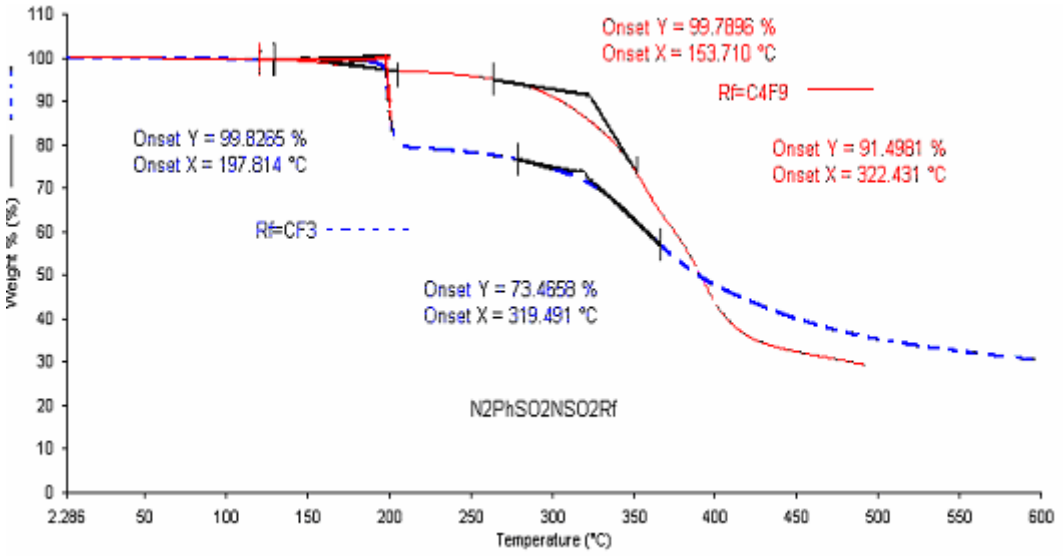


Figure 3.5 TGA of 15a and 15b

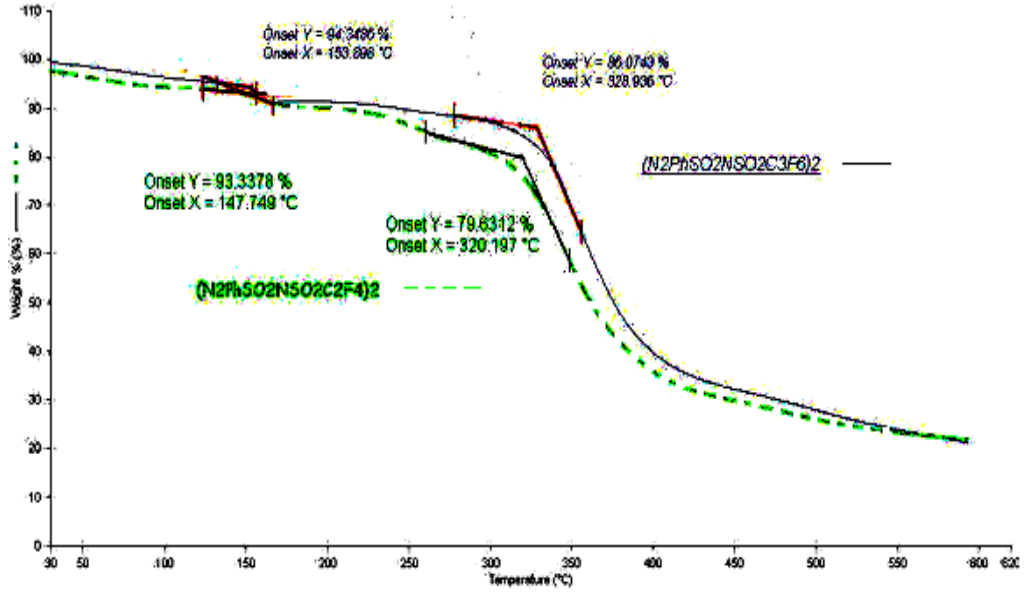


Figure 3.6 TGA of 18a and 18b

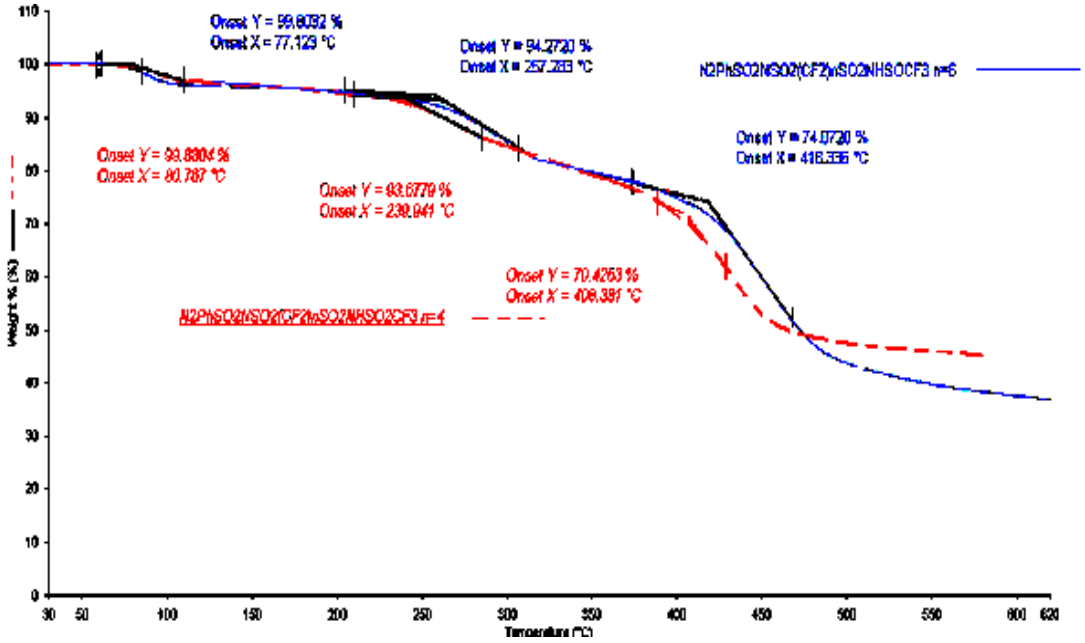


Figure 3.7 TGA of 22a and 22b

(3) Solubility

Solution casting of FDZs for thermolysis and grafting onto carbon is very important in this project. Compounds **15**, **18** and **22** are very polarized zwitterions, so all of them were checked in polar organic solvents. The different structures gave quite different solubilities. Clearly, DDZ **18** with symmetrical diaryl groups is more polar than MDZ **15** and has poor solubility in CH_3CN, but good solubility in DMSO. Compound multi FDZs **22** have high solubility in CH_3CN and water due to more hydrophilic groups.

Data for all compounds are summarized in **Table 3.1.**

Table 3.1 Summary of Properties of FDZ

FDZs	TGA	Solubility	Color
p-$N_2^+PhSO_2N^-SO_2CF_3$ **15a**	197.8°C	CH3CN	yellow
p-$N_2^+PhSO_2N^-SO_2C_4F_9$* **15b**	163.5°C	CH3CN	yellow
(p-$N_2^+PhSO_2N^-SO_2C_2F_4)_2$ **18a**	183.5°C	CH3CN<DMSO	yellow
(p-$N_2^+PhSO_2N^-SO_2C_3F_6)_2$ **18b**	153.9°C	CH3CN<DMSO	pink
p-$N_2^+PhSO_2N^-SO_2(CF_2CF_2)_2SO_2N(H)SO_2CF_3$	80.77°C	CH3CN, Water	brown
p-$N_2^+PhSO_2N^-SO_2(CF_2CF_2CF_2)_2SO_2N(H)SO_2CF_3$	77.12°C	CH3CN, Water	brown

Experimental

Preparation of trifluoromethyl anhydride **7a**

In a 250mL round bottom flask equipped with Teflon coated stir bar was placed 67.24g (0.489mol) of CF_3SO_3H. The flask was cooled in an ice bath and 48.6g (0.17mol) of P_4O_{10} was added into the flask four times with 15minutes between intervals (P_4O_{10}:CF_3SO_3H = 0.35: 1). After the last addition, the closed flask remained in the ice bath and slowly warmed to room temperature with good stirring for 8 hours.

After the reaction was completed, the flask was attached to the vacuum system consisting of three cold traps: the first at -30°C to collect any unreacted CF_3SO_3H, the second one at -90°C to collect the anhydride, and the third one at -196°C to collect the side product.

Then, the flask was evacuated at room temperature until full vacuum was reached, and subsequently heated to 80°C for 4-5 hours to vacuum transfer all anhydride, no reacted triflic acid and the side product. The yield was 50%. The flask was tilted until the NMR tube contained an amount of anhydride suitable for NMR analysis. The flask and the NMR tube were frozen and evacuated simultaneously. After vacuum transfer small amount of anhydride to NMR tube, it was sealed and used by inserting in a 5 mm NMR tube containing deuterated lock solvent and a reference (F^{11}).

$(CF_3SO_2)_2O$ (**7a**) ^{19}F NMR (CD_3CN, ppm) δ_a –73.5ppm(s).

Preparation of Perfluoroalkyl sulfonyl amide (**8a-8b**)

Approximately 50mL of liquid ammonia was condensed into a 250mL three-necked round bottom flask at -60°C. With vigorous stirring and N_2 protection, 31.54g (0.123mol) of **7a** was slowly added dropwise into the flask. The excess NH_3 was allowed to slowly distill out from –40°C to 22°C over 10h. The mixture was sublimed at 80°C under high vacuum. White product $CF_3SO_2NH_2$ **8a** 32.98g was obtained with the yield of 90%.

For **8b**, perfluorobutanesulfonyl fluoride $C_4F_9SO_2F$ was added to cooled liquid ammonia in the flask (yield 90%).

$CF_3SO_2NH_2$ (**8a**)

^{19}F NMR (CD_3CN): δ_a –79.3ppm(s);

^{1}H NMR (CD_3CN): δ 6.76ppm(s).

$CF_2^aCF_2^bCF_2^cCF_2^dSO_2NH_2$ (**8b**)

^{19}F NMR (CD_3CN): δ_a –80.3ppm(3F,t),

δ_b –113.2ppm(2F,m), δ_c –120.6ppm(2F,t), δ_d –125.2ppm(2F,t);

^{1}H NMR (CD_3CN): δ 5.31ppm(s).

Preparation of sodium perfluoroalkyl sulfonamide (**9a-9b**)

In a typical reaction, 25.00g (0.168mol) of compound **8a** was dissolved in water first. The solution was made basic with 40mL (0.04M) of NaOH till pH reached 7.5. It was refluxed at 110°C over 8 hours. Then the solution was evaporated, and the solid was sublimed under vacuum to remove the excess $CF_3SO_2NH_2$. White solid **9a** (28.69g, 92%) was obtained after drying at 80°C under high vacuum for 8 hours.

9b was obtained with the same process except pH reached 8.5.

$CF_3SO_2N(Na)H$ (**9a**)

^{19}F NMR (CD_3CN): δ_a –79.2ppm(s);

^{1}H NMR (CD_3CN): δ 2.95(s).

$CF_2^aCF_2^bCF_2^cCF_2^dSO_2N(Na)H$ (**9b**) (yield 95%)

^{19}F NMR (CD_3CN) δ_a –80.4ppm(3F,t), δ_b–114.0ppm(2F,m), δ_c –120.4ppm(2F,m), δ_d –125.2ppm(2F,t);

^{1}H NMR (CD_3CN): δ 2.46(s).

Preparation of sodium N-trimethylsilyl perfluoroalkylsulfonimide salts (**10a-10b**)

In a typical reaction, 28.96g (0.17mol) of compound **9a** and 50mL of dry HMDS were added into a 250mL round bottom flask. The mixture was refluxed at 110 °C for 8 hours. The excess HMDS was removed under vacuum using a rotary evaporator. And finally white product $CF_3SO_2N(Na)SiMe_3$ **10a** (38.69g, 94%) was obtained after drying at 100°C under high vacuum for 8h. Compound **10b** was obtained by an exactly identical procedure.

$CF_3SO_2N(Na)SiMe_3$ (**10a**)

^{19}F NMR (CD_3CN): δ_a –78.7ppm(s);

^{1}H NMR (CD_3CN): δ 0.02ppm (s).

$CF_2^aCF_2^bCF_2^cCF_2^dSO_2N(Na)SiMe_3$ (**10b**) (yield 94%)

^{19}F NMR (CD_3CN): δ_a –80.4ppm(3F,t), δ_b–113.2ppm(2F,m), –120.1ppm(2F,m), –125.2ppm(2F,t);

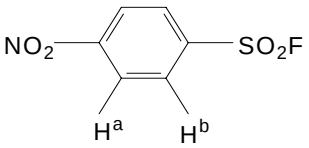
^{1}H NMR (CD_3CN): δ 0.02ppm (s).

Preparation of p-nitrobenzene sulfonyl fluoride (**11**) and amide (**12**)

P-nitrobenzene sulfonyl chloride (5.00g, 22.57mmol) and KF (3.39g, 67.8mmol) (1:3) were added into a 50 mL round bottom flask with 30mL of acetone. The mixture was refluxed at 60°C for 8 hours. Light green solid **11** (3.81g, 82%) was obtained after removing the solvent and sublimation under high vacuum at 80°C.

30mL of Ammonia was cooled in a 250mL round flask and then p-nitrobenzenesulfonyl fluoride **11** (20.00g, 90.29mmol) was added. The mixture was allowed to return to 22°C for 8 hours. The byproduct NH_4F was filtered out with 30mL of dry CH_3CN. Dry solid product **12** (15.11g, 81%) was obtained after evaporating the solvent and drying for 24 hours

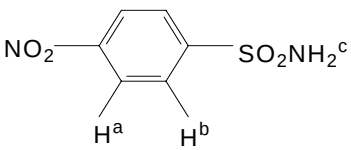
11



^{19}F NMR (CD_3CN) δ 65.7ppm(s);

^{1}H NMR (CD_3CN) δ_a 8.46ppm (2H, d), δ_b 8.27ppm (2H,d), J_{ab}= 8Hz.

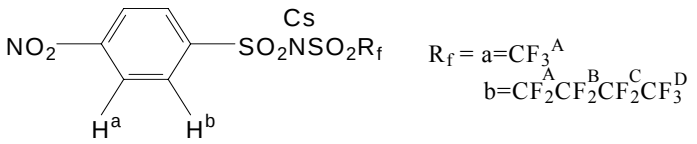
12



^{1}H NMR ab (CD_3CN) δ_a 8.34ppm (2H, d), δ_b 8.06ppm (2H,d), J_{ab}= 11Hz, δ_c 5.90ppm(2H,s).

Preparation of p-nitrobenzenesulfonyl perfluoroalkylsulfonylimide cesium salt (**13a-13b)**

In a typical reaction, 4.10g (0.02mol) of p-NO_2PhSO_2F **11** and 4.86g (0.02mmol) of $CF_3SO_2N(Na)SiMe_3$ **10a** (1:1) were added into a 50ml flask. Dry CH_3CN 20mL was vacuum transferred in an evacuated flask. With N_2 protection, 4.0mL(0.023mol) of dry DIEA was injected into the flask. The solution was kept refluxing at 80°C for 48 hours. After the starting material disappeared in the ^{19}F NMR spectrum, the reaction was completed. The mixture was acidified 20mL of 36.5% HCl till pH paper turned red (pH=2.5). The solvent was removed under high vacuum. The protonated compound was dissolved in 5mL of acetone, and 30mL (0.015mol) of Cs_2CO_3 solution was used to precipitate out the product. Finally, 7.65g of purified products 1**3a** was obtained after filtration and drying in vacuum for 8 hours at 22^{o}C (yield 82%). Compound **13b** was obtained by an exactly identical procedure.



13a-b

13a ^{19}F NMR (CD_3CN) δ-78.16(s);

^{1}H NMR (CD_3CN) ab δ_a 8.26(2H, d), δ_b 8.05(2H, d) J_{ab}=9Hz.

13b (yield 81%)

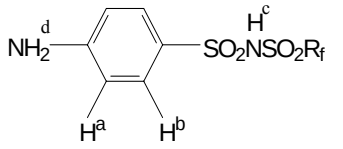
^{19}F NMR (CD_3CN) δ_D -80.32(3F,t), δ_C -112.47(2F,m), δ_B -120.46(2F,m), δ_A -125.26(2F,t);

^{1}H NMR (CD_3CN) ab δ_a 8.26(2H,d), δ_b 8.05(2H,d) J_{ab}=10Hz.

Preparation of p-$NH_2PhSO_2NHSO_2R_f$ (**14a-14b)**

In a typical reaction, the Zinin reducing agent was prepared as follows. $Na_2S{\cdot}9H_2O$ (4.80g, 0.02mol) was dissolved in 30mL of water in the ice bath with good stirring (mixture B). At the same time, 7.2g(0.03mol) $Na_2S{\cdot}9H_2O$ was added dropwise to 8mL (0.073mol) of 36.5% HCl solution as batch A. The gas product H_2S from batch A was bubbled rapidly into the mixture B. This mixture B was saved in refrigerator.

In a 250mL two necked flask, 20mL of ethanol dissolved 7.65g (16.42mmol) of p-$NO_2PhSO_2N(Cs)SO_2CF_3$ **13a**. The mixture B was added dropwise into this solution over one hour at 80°C, and then the mixture was refluxed for another 1.5 hours at this temperature. Next, the solvent was removed by rotary evaporation and the solid mixture was dried under high vacuum at 80°C for 8hours. The crude product was extracted with CS_2 in a soxhlet apparatus to remove element S. Purified product **14a** (4.63g, yield 92%) was obtained after drying under dynamic vacuum at 22^{o}C for 8 h. Compound **14b** was obtained by an exactly identical procedure.

14a-b 

$R_f = a{=}CF_3^A$
$b{=}CF_2^ACF_2^BCF_2^CCF_3^D$

(**14a**)^{19}F NMR (CD_3CN) A δ -77.69 (s);

^{1}H NMR (CD_3CN) ab δ_a 7.53(2H,d), δ_b 6.61(2H,d) J_{ab}=7Hz, $\delta_{c,d}$ 4.59(3H,s);

IR (cm^{-1}) (KBr pellets) 3403(m), 2921(vs), 2854(vs), 1631(m), 1600(m), 1505(m), 1460(vs), 1377(s), 1321(s), 1287(s), 1166(s), 1093(s), 1060(s), 827(m), 75(m), 741(m).

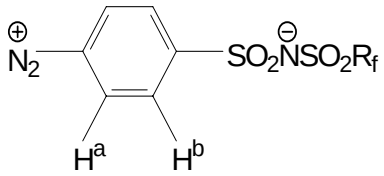
(**14b**) (yield 88%)

^{19}F NMR (CD_3CN): δ_D-80.33(3F,t), δ_C-112,49(2F,m), δ_B-120.48(2F,m), δ_A-125.20(2F,t);

^{1}H NMR (CD_3CN) ab δ_a 7.90(2H,d), δ_b 7.39(2H,d) J_{ab}=6Hz, $\delta_{c,d}$ 4.62(3H,s).

Preparation of p-$N_2^+PhSO_2N^-SO_2R_f$ **(15a-15b)**

In a typical reaction, 4.63g (15.23mmol) of p-$NH_2PhSO_2N(H)SO_2CF_3$ **14a** was dissolved in 10mL of 36.5% hydrochloric acid in a 50mL roundbottom flask with good stirring. In an ice bath, a mixture of cooled 3mL of 36.5% hydrochloric acid and 1.06g (15.36mmol) of sodium nitrite was added into the flask. The solution was stirred for 2 hours until diazotization was completed. Then the solution was poured onto the cracked ice. The product was filtered out from the water, and 4.14g of **15a** was obtained after drying the compound under dynamic vacuum at 22^{o}C for 8h (86%). Compound **15b** was obtained by an exactly identical procedure.

15a-b  R_f = a=CF_3^A b=$CF_2^ACF_2^BCF_2^CCF_3^D$

(15a) ^{19}F NMR (CD_3CN) A δ -78.24;

^{1}H NMR (CD_3CN) ab δ_a 8.50(2H,d), δ_b 8.33(2H,d) J_{ab}=9Hz;

IR (cm^{-1}) (KBr pellet) 2287 (m) for $-N_2^+$ group.

3101(s), 1568(s), 1410(s), 1332(vs), 1191(vs), 1136(vs), 1159(vs), 1056(vs), 1091(s), 841(m), 743(m).

(15b) (yield 80%)

^{19}F NMR (CD_3CN) δ_D -80.31(3F), δ_C -112.37(2F), δ_B -120.47(2F), δ_A -125.22(2F);

^{1}H NMR (CD_3CN) a δ_a 8.55(2H,d), δ_b 8.33(2H,d) J_{ab}=9Hz;

IR (cm^{-1}) (KBr pellet,nujor) 2287 (s) for $-N_2^+$group,

3100(s), 1566.9(s), 1458(s), 1408(s), 1332.6(vs), 1313.4(s), 1300.5(s), 1231.7(s), 1194.3(vs), 1144.7(vs),1090.4(s), 1073.8(s), 846.6(m), 817.3(m).

Crystals of **15a** for X-ray were obtained from CH_3CN. The crystallographic data is given in **Table 3.2**. The structure is shown in **Figure 3.4**.

Table 3.2 Crystallographic Data

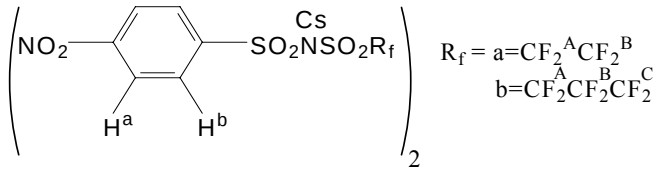
Empirical formula	C7 H4 F3 N3 O4 S2
Formula weight	315.25
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 12.539(3) A alpha = 90 deg. b = 9.6700(19) A beta = 90 deg. c = 18.927(4) A gamma = 90 deg.
Volume	2294.9(8) A^3
Z, Calculated density	8, 1.825 Mg/m^3
Absorption coefficient	0.520 mm^-1
F(000)	1264
Crystal size	0.46 x 0.12 x 0.07 mm
Theta range for data collection	2.15 to 25.10 deg.
Limiting indices	-14<=h<=14, -11<=k<=11, -22<=l<=20
Reflections collected / unique	18695 / 2040 [R(int) = 0.1071]
Completeness to theta = 25.10	99.8 %

Absorption correction	REQAB (multi-scan)
Max. and min. transmission	0.9645 and 0.7961
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2040 / 0 / 176
Goodness-of-fit on F^2	1.104
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1643
R indices (all data)	R1 = 0.1032, wR2 = 0.1876
Largest diff. peak and hole	0.440 and -0.331 e.A^-3
Largest diff. peak and hole	0.440 and -0.331 e.A^-3

Preparation of p-nitrobenzenesulfonyl sulfonylperfluoroalkyl cesium imide (**16a-16b**)

In a typical reaction, 4.04g (0.02mol) of dry p-nitrobenzenesulfonyl amide **12** and 3.66g (0.01mol) of $(FSO_2C_2F_4)_2$ **3a** (2:1) were added into a 50mL flask with an ace thread connection. Dry CH_3CN (25mL) was vacuum transferred into the evacuated flask, followed with injection of dry $(CH_3CH_2)_2NCH_2CH_3$ (DIEA) (4mL). The solution was refluxed at 80°C and monitored by NMR. According to ^{19}F NMR, the reaction was completed in 48 h after the starting material $(FSO_2C_2F_4)_2$ **3a** was invisible in the spectrum. The solution was acidified with 15mL of 20% HCl till pH paper turned red (pH= 2.5). The solvent was distilled out under high vacuum. Next, the protonated compound was dissolved in 5mL of acetone, and 30mL (0.025mol) of Cs_2CO_3 solution was added to precipitate out the product. The suspension was filtered and the solid was dried under high vacuum at 100°C. 8.45g of deep yellow product **16a** was obtained with

98% purity according to ^{19}F NMR (yield 85%). Compound **16b** was obtained by an exactly identical procedure.

16 

R_f = a=$CF_2^ACF_2^B$
b=$CF_2^ACF_2^BCF_2^C$

(**16a**) ^{19}F NMR (CD_3CN, ppm) δ_A –112.2ppm(4F,s), δ_B –119.4ppm(4F,s);

^1H NMR (CD_3CN) ab δ_a 8.26(2H,d), δ_b 8.16(2H,d) J_{ab}=9Hz,

(**16b**) (Yield 89%, purity 98%)

^{19}F NMR (CD_3CN, ppm) δ_A–112.2ppm(4F,s), δ_B –119.5ppm(4F,s), δ_C –120.9ppm(4F,s);

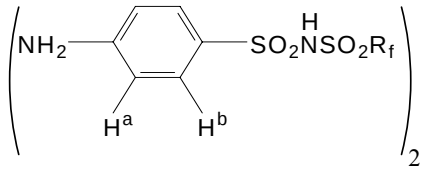
^1H NMR (CD_3CN) ab δ_a8.26(2H,d), δ_b8.06(2H,d) J_{ab}=9Hz,

Preparation of p-nitrobenzenesulfonyl sulfonylperfluoroalkyl amine (**17a-17b**)

In a typical reaction, 15g (0.0625mol) of $Na_2S{\cdot}9H_2O$ was dissolved in 400mL of water in the ice bath with good stirring (A). At the same time, 30g (0.125mol) of $Na_2S{\cdot}9H_2O$ was dropwised by 22mL of 20% HCl solution. The gas product H_2S was bubbled rapidly into A. This mixture 430mL of B (0.1563mol/L) was stored in a refrigerator.

. In a 500mL flask, 80mL of dry ethanol was added to dissolve 14.90g (24.19mmol) of (p-$NO_2PhSO_2N(Cs)SO_2C_4F_9)_2$ **16a.** 160mL (0.025mol) of mixture B was dropwised into this solution over 3 hours at 80°C, followed by refluxing for 2 hours. The crude product was extracted with CS_2 in a soxhlet apparatus to remove element S. Then the other inorganic impurities were filtered out with 30mL of dry CH_3CN. Finally 12.21g of product **17a** was obtained (yield 75.36%, purity 98%) after evaporating the solvent and

drying in the vacuum for 12 hours at 22°C. Compound **17b** was obtained by an exactly identical procedure.

17 

R_f = a=$CF_2^ACF_2^B$
b=$CF_2^ACF_2^BCF_2^C$

(**<u>17a</u>**) ^{19}F NMR (CD_3CN, ppm) δ_A –112.4ppm(4F,s), δ_B –119.4ppm(4F,s);

^1H NMR (CD_3CN) ab δ_a 7.93(2H,d), δ_b 7.52(2H,d) J_{ab}=9Hz, δ_{c+d} 3.13(6H,s).

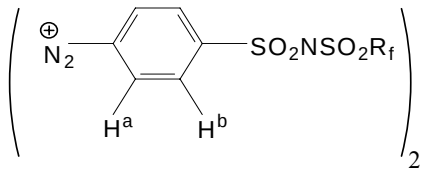
<u>(17b)</u> (yield 81%, purity 98%)

^{19}F NMR (CD_3CN, ppm) δ_A–112.3ppm(4F,s), δ_B –119.6ppm(4F,s), δ_C –121.0ppm(4F,s);

^1H NMR (CD_3CN) ab δ_a 7.61(2H,d), δ_b 6.96(2H,d) J_{ab}=9Hz, δ_{c+d} 4.35(6H,s)

<u>Preparation of ($p\text{-}N_2^+PhSO_2N^-SO_2(CF_2)_n$)$_2$ (**18a-18b**)</u>

In a typical reaction, the 6.78g of (10.12mmol) yellow compounds **17a** was dissolved in 15mL of concentrated sulfuric acid in a 100mL flask with good stirring. The solution was cooled in an ice bath. With stirring, a mixture of cooled 10mL of concentrated sulfuric acid and 0.069g (0.01mol) sodium nitrite was added. The mixture was stirred for 3 hours until diazotization was completed. At the end, the solution was poured onto cracked ice. Finally, 5.96g of yellow product **18a** was obtained with 95% purity according to ^{19}F NMR (yield 85%). Compound **18b** was obtained by an exactly identical procedure.

18 

⊖
R_f = a=$CF_2^ACF_2^B$
b=$CF_2^ACF_2^BCF_2^C$

(18a) ^{19}F NMR (CD_3CN, ppm) δ_A –112.1ppm(4F,s), δ_B–119.4ppm(4F,s);

^1H NMR (CD_3CN) ab δ_a 8.65(2H,d), δ_b 8.28(2H,d) J_{ab}=9Hz,

IR (cm^{-1}) (KBr pellet,nujor) 2294.3 (s) for $-N_2^+$group,

3100(s), 1568.9(s), 1519.9(s), 1336(vs), 1309.4(s), 1300.5(s), 1199.7(vs), 1146.9(vs), 1092.7(s), 1078.3(s), 1053.3(s), 1611(m), 1569.0(m), 1519.9(m), 1409(s), 854.8(m), 740.8(m).

(18b) (yield 88% , purity 98%)

^{19}F NMR (CD_3CN, ppm) δ_A –112.2ppm(4F,s), δ_B –119.6ppm(4F,s), δ_C –121.1ppm(4F,s);

^1H NMR (CD_3CN) ab δ_a8.55(2H,d), δ_b8.32(2H,d) J_{ab}=9Hz;

IR (cm^{-1}) (KBr pellet,nujor) 2287.5 (s) for $-N_2^+$group,

3100(s), 1568.6(m), 1458(vs),1465(vs), 1408(m), 1376.5(s), 1334.3(s), 1306.2(s) 1210(vs), 1150.2(vs), 1090.2(s), 1077(s), 840.1(m), 721.5(m).

Preparation of $CF_3SO_2N(Na)(CF_2)_nSO_2F$ (**19a-19b**)

In a typical reaction, a mixture of 10.98g(0.03mol) of $FSO_2(CF_2)_4SO_2F$ **3a** and 2.43g(0.01mol) of $CF_3SO_2N(Na)SiMe_3$ **10a** in 30mL of dry CH_3CN were added into a 100mL flask under a dry N_2 atmosphere,. The mixture was refluxed at 100°C for 48 hours. After cooling to room temperature, excess $FSO_2(CF_2)_4SO_2F$ **3a** and the solvent were distilled out under high vacuum through a trap cooled in liquid N_2 at –196°C. To the solution, 30mL of H_2O was added to recover the excess $FSO_2(CF_2)_4SO_2F$. 4.64g of white products **19a** was obtained after drying at 100°C under high vacuum over 4 h (yield 90%). Compound **19b** was obtained by an exactly identical procedure.

$CF_3{}^aSO_2N(Na)CF_2{}^bCF_2{}^{c'}CF_2{}^cCF_2{}^dSO_2F^e$ (**19a**)

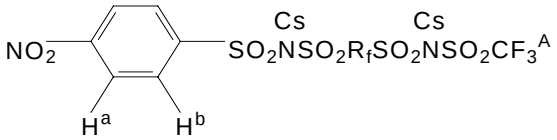
^{19}F NMR (CD_3CN, ppm) δ_e 46.7ppm(1F,s), δ_a –78.9ppm(3F,s), δ_b –106.6ppm(2F,t), $\delta_{c+c'}$ –119.0ppm(4F,m), δ_d –112.5ppm(2F,t);

$CF_3{}^aSO_2N(Na)CF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^gSO_2F^h$ (**19b**) (yield 92%)

^{19}F NMR (CD_3CN, ppm) δ_h 47.2ppm(1F,s), δ_a –78.9ppm(3F,s), δ_g –106.8ppm(2F,s), δ_b –112.5ppm(2F,s), δ_{f+c} –119.4ppm(4F,s), δ_{f+c} –120.3ppm(4F,s).

Preparation of $CF_3SO_2N(Cs)SO_2(CF_2)_nSO_2N(Cs)SO_2PhNO_2$-p (**20a-20b**)

In a typical reaction, 4.84g (9.36mmol) of **19a** and 3.80g (18.81mmol) of p-$NO_2PhSO_2NH_2$ **12** (1:2) were added into a 50mL flask. 15mL of dry CH_3CN and 2mL of dry DIEA was vacuum transferred into the evacuated flask. The solution was refluxed at 80°C for 48hours until starting material was invisible in F^{19} NMR spectrum. Then the solution was acidified with 20mL of 36.5% HCl till pH paper turn red (pH=2.5). The solvent and excess DIEA were removed with a rotary evaporator, followed by dissolving in 10mL of acetone and precipitation with 50ml (21.47mmol) of Cs_2CO_3 solution (1:2.29). Pure light yellow Cs salt **20a** (7.65g, 87%) was obtained after filtering out the Cs salt and drying under high vacuum over 4h. Compound **20b** was obtained by an exactly identical procedure.

20 

R_f = a=$CF_2{}^BCF_2{}^CCF_2{}^{C'}CF_2{}^{B'}$
b=$CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^G$

(**20a**) ^{19}F NMR (CD_3CN, ppm) δ_A –78.9ppm(3F,s), $\delta_{B+B'}$ –112.3ppm(4F,t), $\delta_{C+C'}$ –119.5ppm(4F,m)

^{1}H NMR (CD_3CN) ab δ_a8.26(2H,d), δ_b8.06(2H,d) J_{ab}=10Hz

(**20b**) (yield 88%)

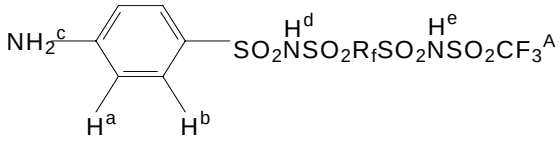
^{19}F NMR (CD_3CN, ppm) δ_A –79.2ppm(3F,s), δ_G, δ_B –112.2ppm,-112.5(4F,s), δ_{F+C} – 119.5ppm(4F,s), δ_{F+C} –120.8ppm(4F,s);

^{1}H NMR (CD_3CN) ab δ_a8.26(2H,d), δ_b8.06(2H,d) J_{ab}=10Hz.

Preparation of $CF_3SO_2NHSO_2(CF_2)_nSO_2NHSO_2PhNH_2$-p (**21a-21b**)

In a typical reaction, 3.50g (14.58mmol) of $Na_2S{\cdot}9H_2O$ was dissolved in 100mL of water in the ice bath with good stirring (mixture B). At the same time, 10.00g (40mmol) of $Na_2S{\cdot}9H_2O$ was dropwised by 20mL of 36.5% HCl solution as reaction A. The gas product H_2S from the reaction A was bubbled rapidly into the mixture of B. The mixture B was stored in a refrigerator.

In a 250mL three necked flask, 80mL of dry ethanol was added to dissolve 6.23g (7.10mmol) of p-$NO_2PhSO_2N(Cs)SO_2(CF_2)_4SO_2N(Cs)SO_2CF_3$ **20a.** The 100mL of mixture B was dropwised into this solution over one hour at 80°C. The reaction was completed after refluxing for 8 h. Then, the solution was acidified with 20mL of 36.5% HCl until the pH paper turned red (pH=2.5). The solvent was removed with rotary evaporation and dried under high vacuum. Yellow product **21a** (3.95g, 86%) was obtained after removing S with soxhlet apparatus. Compound **21b** was obtained by an exactly identical procedure.

21 

R_f = a=$CF_2{}^BCF_2{}^CCF_2{}^{C'}CF_2{}^{B'}$
b=$CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^G$

(21a) ^{19}F NMR (CD_3CN, ppm) δ_A –78.9ppm(3F,s), $\delta_{B+B'}$ –112.3ppm(4F,t), $\delta_{C+C'}$ – 119.4ppm(4F,m);

^{1}H NMR (CD_3CN) ab δ_a7.89(2H,d), δ_b7.33(2H,d) J_{ab}=10Hz, δ_{c+d+e}4.59(4H,s);

IR (cm^{-1}) (KBr pellet, acetone) 3389(m), 1708(s), 1629(s), 1600(s), 1504(m), 1437(w), 1320(vs), 1202(vs), 1147(vs), 1090(s), 1067(s), 831(m), 762 (m).

(21b) (yield 88%)

^{19}F NMR (CD_3CN, ppm) δ_A –78.9ppm(3F,s), δ_{B+G} –112.4ppm,(4F,s), δ_{F+C} – 119.5ppm(4F,s), δ_{D+E} –120.8ppm(4F,s);

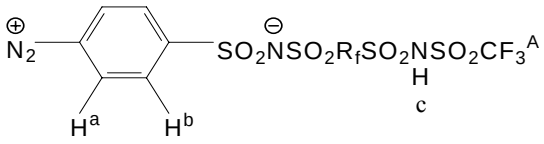
^1H NMR (CD_3CN) ab δ_a 7.53(2H,d), δ_b6.60(2H,d) J_{ab}=9Hz

δ_{c+d+e}4.56(4H,s);

IR (cm^{-1}) (KBr pellet, acetone) 3389(m), 1708(s), 1629(s), 1600(s), 1504(m), 1438(w), 1320(vs), 1202(vs), 1147(vs), 1090(s), 1067(s), 831(m), 762 (m).

Preparation of $CF_3SO_2NHSO_2(CF_2)_nSO_2N^-SO_2PhN^+$-p (**22a-22b**)

In a typical reaction, 2.00g (2.89mmol) of **21a** was mixed with 4mL of 100% ethanol first. The mixture were poured into 70mL of 100% alcohol containing dissolved hydrogen chloride (148Torr) and cooled to -5°C. 1.60mL of 7.45M (11.92mmol) isoamyl nitrite was injected into the mixture. After 10 minutes, 40ml of dry ether cooled to 0°C was added which caused a yellow solid to precipitate out. Product **22a (**1.42g, 76%) was obtained by filtration and drying under high vacuum for 8 h. Compound **22b** was obtained by an exactly identical procedure.

22 

R_f = a=$CF_2{}^BCF_2{}^CCF_2{}^{C'}CF_2{}^{B'}$
b=$CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^G$

(22a) ^{19}F NMR (CD_3CN, ppm) δ_A–78.9ppm(3F,s), $\delta_{B+B'}$ –112.3ppm(4F,d), $\delta_{C+C'}$ – 119.5ppm(4F,m);

^1H NMR (CD_3CN) ab δ_a 8.55(2H,d), δ_b 8.32(2H,d), J_{ab}=9Hz, δ_c 3.40 (1H,m);

IR (cm^{-1}) (KBr pellet, acetone) 2290.7 (s) for $–N_2^+$group,

3104(s), 1705.7(m), 1569.2(m), 1411.1(m), 1335(vs), 1196.2(vs), 1147.7(vs), 1092.5(s),

1059.6(s), 839.8(m), 786.6(m).

(22b) (yield 80%)

^{19}F NMR (CD_3CN, ppm) ^{19}F NMR (CD_3CN, ppm) δ_A –78.9ppm(3F,s), δ_{G+B} –

112.3ppm,(4F,d), δ_{F+C} –119.4ppm(4F,s), δ_{D+E} –120.9ppm(4F,s);

^{1}H NMR (CD_3CN) ab δ_a8.54(2H,d), δ_b8.31(2H,d) J_{ab}=9Hz, δ_c 3.51(1H,m);

IR (cm^{-1}) (KBr pellet, acetone) 2289.0 (s) for $–N_2^+$group,

3103(s), 1708.9(m), 1571.2(m), 1410.9(m), 1333.6(vs), 1203(vs), 1148.2(vs), 1092.7(s),

1068.2(s), 841.2(m), 784.5(m).

Conclusion

Three novel functional diazonium zwitterions containing the sulfonimide group were successfully synthesized to match the request for PEM Fuel Cell. Original preparation methods allowed us to explore them to more complex monomers. The thermal analysis data showed that they have strong thermal stability compare to other diazonium outer salts, especially after losing $-N_2$. This provides us opportunities to graft a thermal stable sulfonimide anion onto the surface of carbon electrodes by formation of a covalent carbon-carbon bond, either through electrochemical reduction or thermal decomposition. By comparing their different properties, appropriate methods need to be chosen to graft them onto carbon materials. Among them, p-$N_2^+PhSO_2N^-SO_2CF_3$ **15a** was already crystallized and grafted on carbon successfully.

More synthesis about novel diazonium monomer compounds will be discussed in Chapter IV.

CHAPTER IV

DIAZONIUM ZWITTERION MONOMERS

Introduction

In order to improve flexibility and ion exchange capacity for attachment of electrolyte to carbon, a functionalized polymer chain was desirable for fuel cell applications. The attachment of monomers capable of undergoing further reaction was envisaged as a way to accomplish this. Some new functional diazonium zwitterion monomers, such as shown in **Figure 4.1**, are based on previous research as discussed in chapter III. With an active diazonium group on one end and a polymerizable functional group on the other, possible synthetic routes to these novel compounds differ from the other diazonium zwitterions.

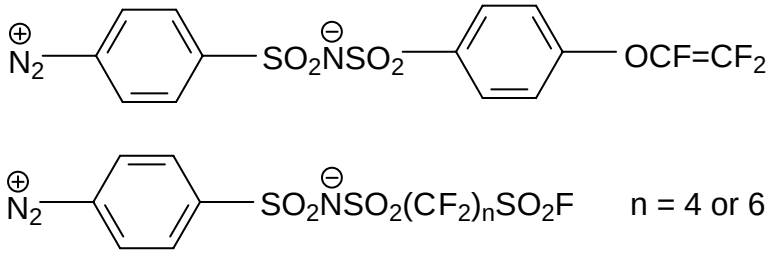


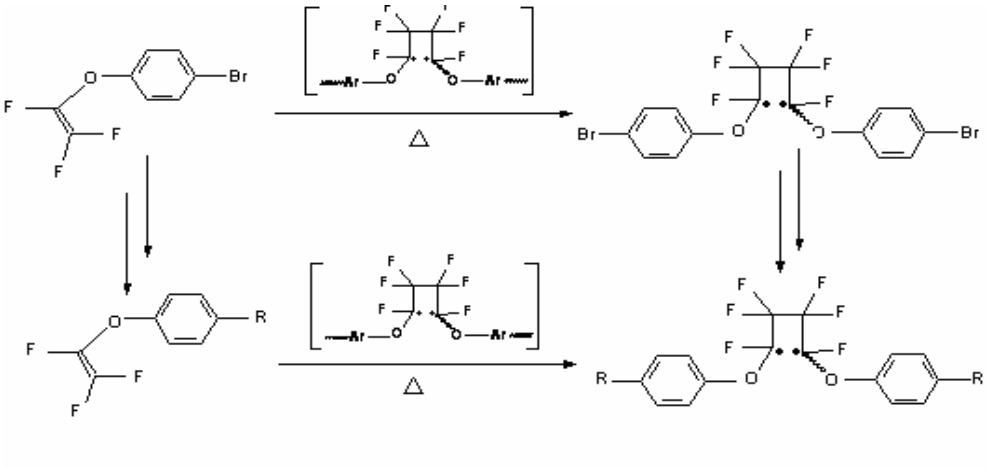
Figure 4.1 Structures of new FDZ monomers

Aromatic Trifluorovinyl Ethers (TFVE) Derivatives

Trifluorovinyl aryl ethers (TFVE) are versatile compounds with applications as intermediates and, most often, precursors to fluorinated condensation polymers[179, 180, 181].

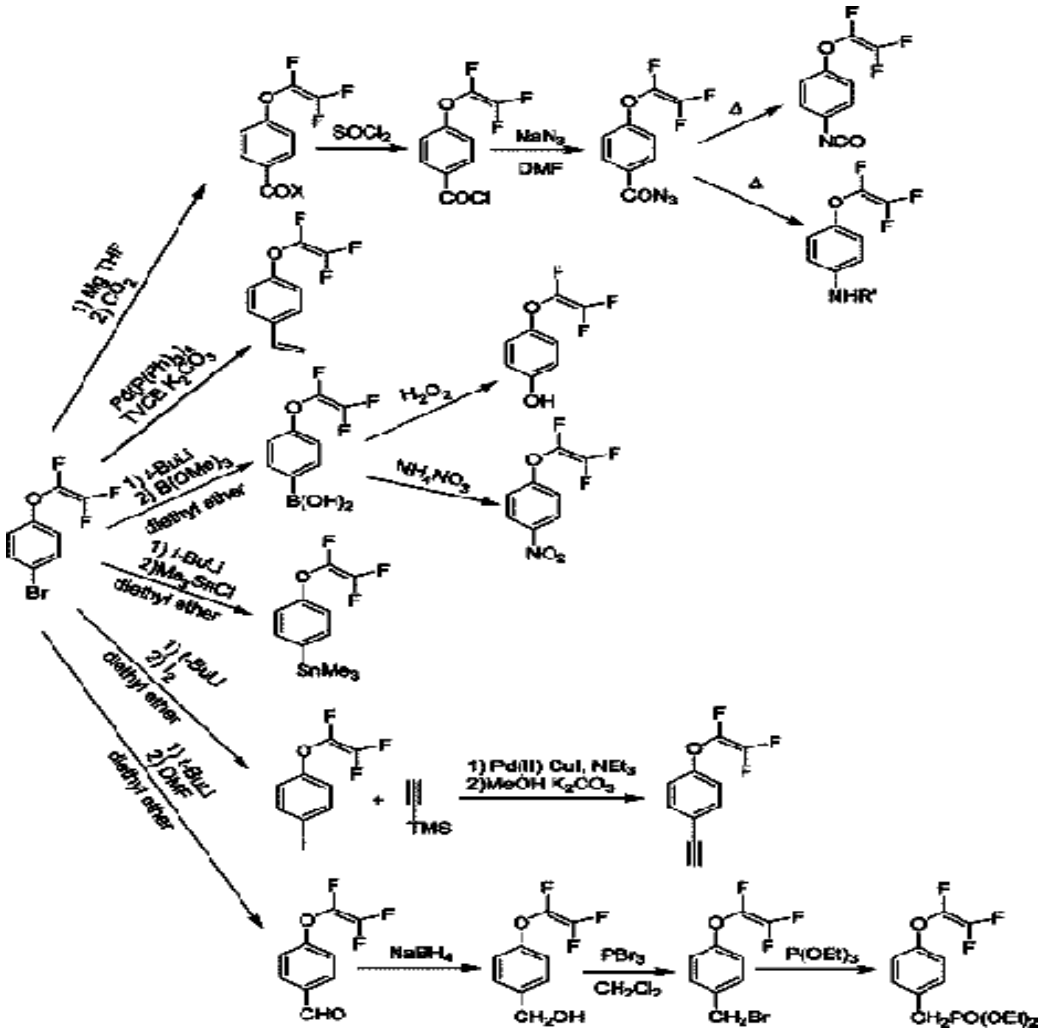
Multifunctional aromatic TFVE monomers are of interest for ion exchange resins [182], fuel cell membranes [183], microphotonics [184], optics [185], liquid crystals [186], interlayer dieletrics [187], and coating applications [188].

Aromatic TFVEs undergo thermal cyclopolymerisation [2π+2π] giving perfluorocyclobutane (PFCB) containing polymers[189, 190]. The thermodynamically favored [2π+2π] product is due to an increased double bond strain, lower π-bond energy[191], and the strength of the resulting fluorinated C-C single bond. As illustrated in **Scheme 4.1**, predominant head-to-head cycloaddition proceeds by rapid ring closure to give both cis- and trans- products in equal amounts [192].



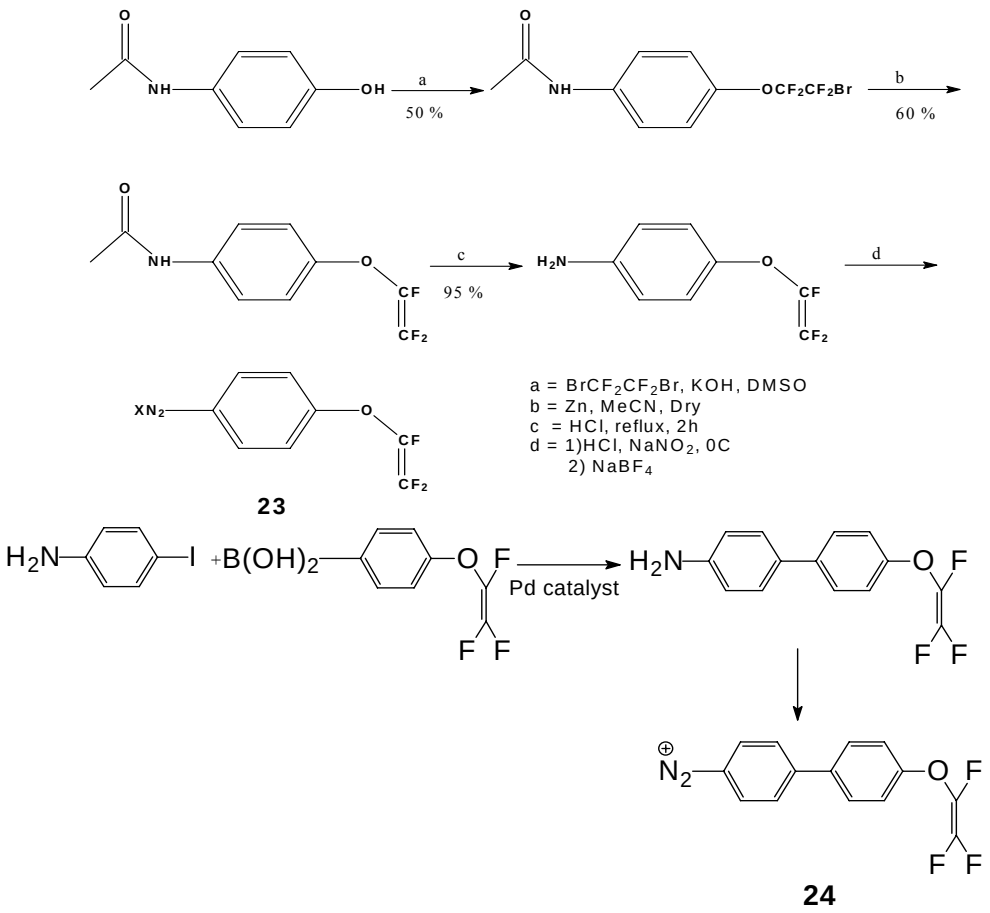
Scheme 4.1 Dimerization Strategy for Aromatic TFVE

Many of these aromatic TFVE derivatives originate from the versatile precursor 4-bromo (trifluorovinyloxy) benzene. According to Smith and coworkers[193], numerous functional compounds can be synthesized from 4-bromo(trifluorovinyloxy benzene) as shown in **Scheme 4.2**.



Scheme 4.2 Synthesis of Substituted Aromatic Trifluorovinyl Ethers from Bromo Intermediate

Based on end-capped imide oligormers[194, 195], the synthesis of the designed the trifluorovinylaryl (TFVE) diazonium salt **23** was invented out. **Scheme 4.3** also illustrates dizaonium salt **24**, which was synthesized by Qing, F.-L.[190] et. al incorporating two aromatic rings.



Scheme 4.3 Synthesis Process of TVE Diazonium

Perfluoroalkyl Sulfonyl Fluoride Polymers

Polymers with pendant fluoroalkylsulfonate groups have been of significant scientific and commercial interest for many years[196]. The perfluorinated backbone provides high chemical and thermal stability. The side chain $–SO_2F$ group can be hydrolyzed to a $–SO_3H$ group, which lets protons "hop" from one acid site to another in the polymers. Current and potential applications include membranes for chloroalkali cells, batteries, fuel cells, and strong solid acid catalysts[197]. The best known examples are Dupont's Nafion® polymer [198] and Dow's XUS PFSA shown in **Figure 4.2**[199], which are

used as proton exchange membranes (PEM) in the fuel cell industry. With other functional groups, some scientists can make use of them as new surfactants and ion-exchange resins [200, 201].

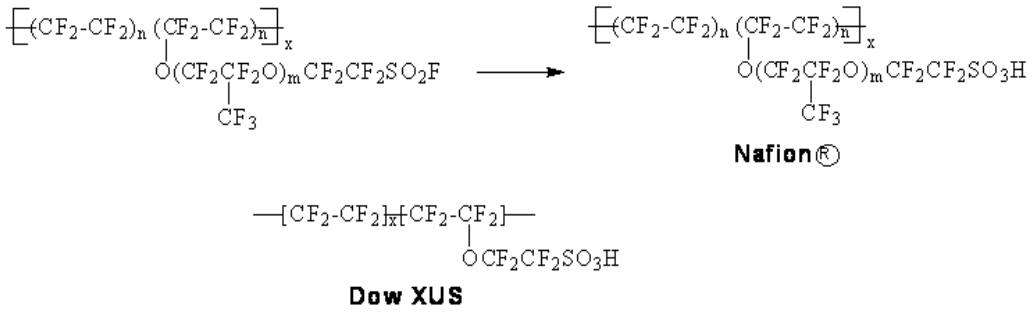
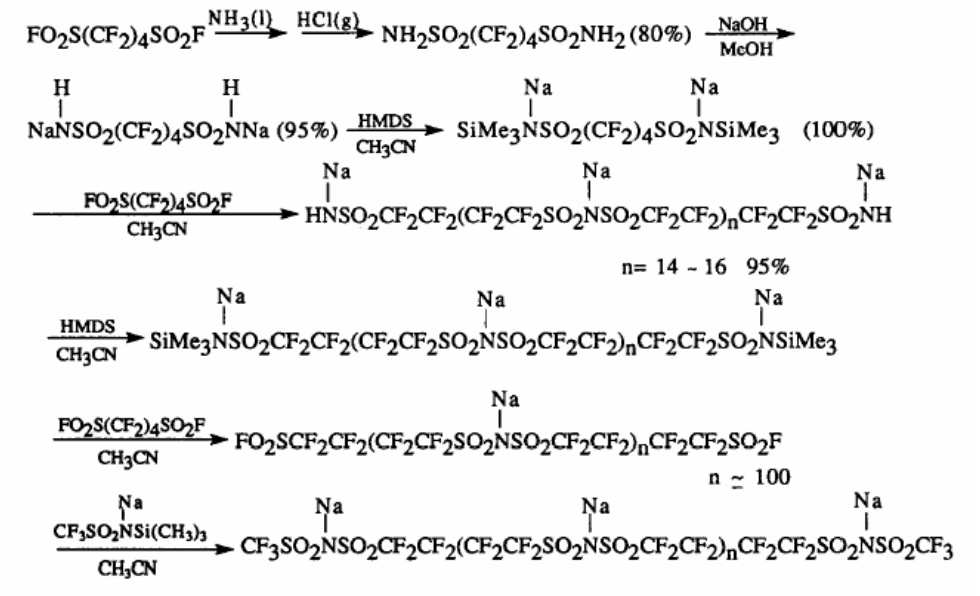


Figure 4.2 Ionomers Examples for PEMFC

DesMarteau and coworkers also studied perfluoroalkyl sulfonyl fluoride polymers containing the sulfonylimide groups. These polymers exhibit greater thermal stability than PFSAs in the acid form, excellent chemical electrochemical inertness and possible less susceptibility to dehydration, oxidative degradation reactions than PFSAs.

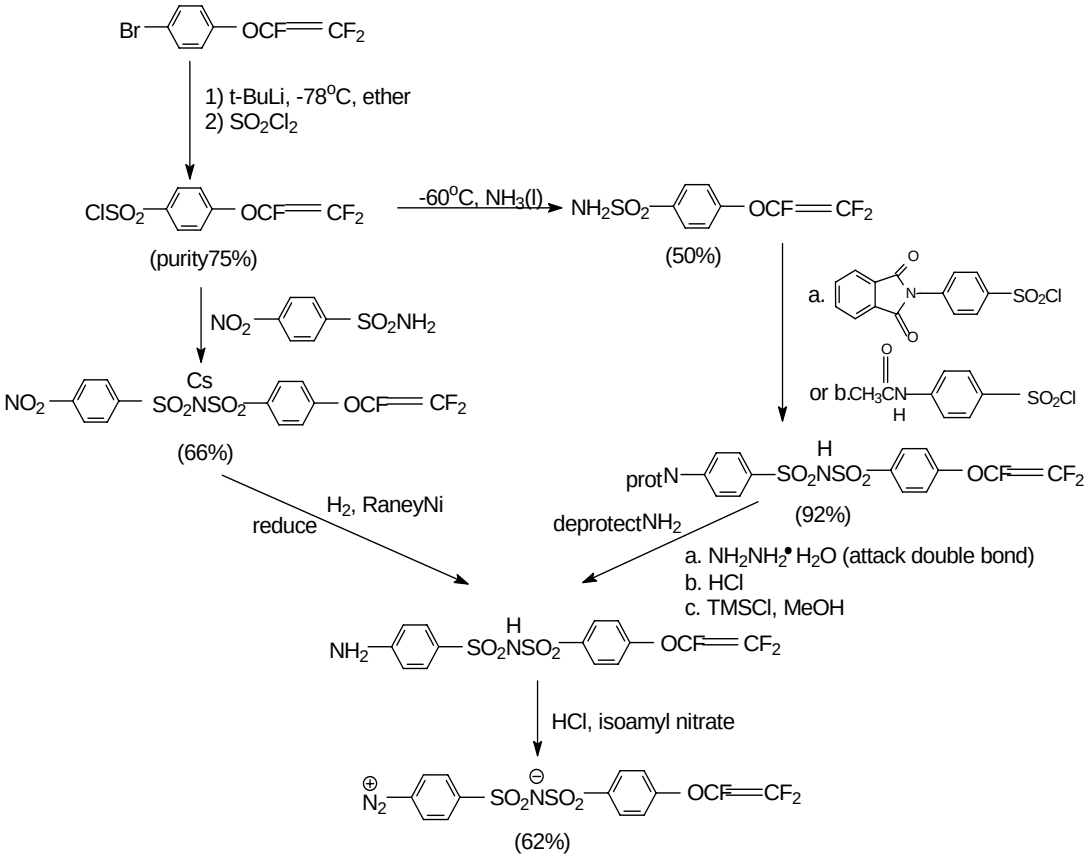
Another type of bis((perfluoroalkyl)sulfonyl) imide polymer is also possible with sulfonyl fluoride. These are termed ionomer and the synthesis is shown in **Scheme 4.4**[202]. These unique polymers and their methodology provide a potential route to surface modification of carbon with a fluorosulfonyl functionalized diazonium salt.



Scheme 4.4 Synthetic Routes for Ionomers in DesMarteau's Lab

Research and Discussion

Synthesis of TFVE Diazonium Zwitterion Monomer



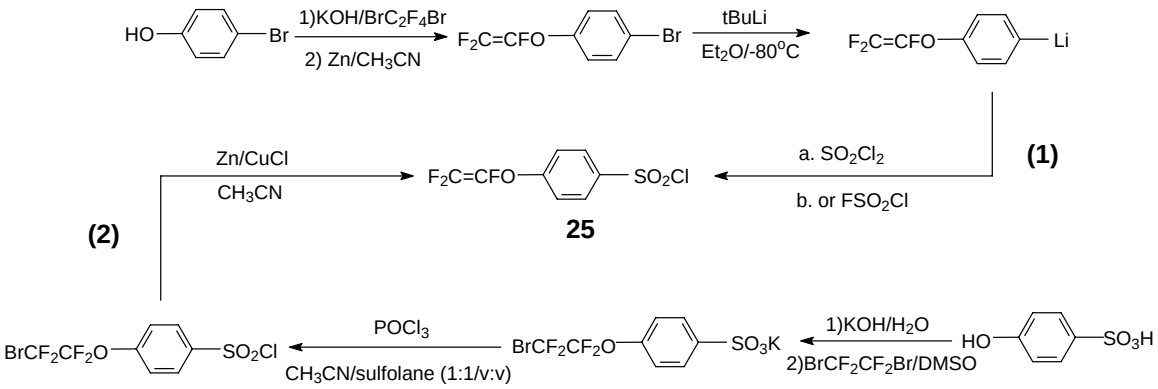
Scheme 4.5 Synthesis Designs of TFVE Aryl Diazonium Zwitterions

The syntheses of stable diazonium salts containing reactive trifluorovinyl aryl ether functions were challenging. The successful synthesis required a procedure, which did not attack the triflurovinyl function of the aryl ether and provided an amino group for diazotization in the final step. **Scheme 4.5** outlines the planned routes to the desired compound **30**.

(1) 4-sulfonylchloride (trifluorovinyloxy) benzene

The key intermediate 4-sulfonylchloride (trifluorovinyloxy) benzene **25** can be prepared through two routes as shown in **Scheme 4.6**[203, 204]. Both routes start from very

simple starting materials and were demonstrated by DesMarteau and coworkers. Route **(1)** is used here since it is more straightforward on a small scale than **(2)**. The organolithium intermediate requires extremely dry conditions, and reacts quickly. Using FSO_2Cl gas, prepared in advance with SO_2Cl_2 and KF, only gives around 65% yield for **25**. Interestingly, it is found that if the lithium intermediate reacted with SO_2Cl_2 directly, a somewhat better yield of **25** (72%) was obtained.



Scheme 4.6 Synthesis Routes for 4-sulfonylchloride TFVE Benzene

(2) Purification of compound 25

Compound **25** is a very sticky liquid and consequently purification is difficult. Ammonolysis of **25** is a convenient way to obtain amide product **26**, which is further purified by sublimation. Although the reaction is simple, the sublimation of **26** is slow and tedious. Another route is to carry out the coupling reaction directly, with 4-nitrobenzene sulfonyl chloride followed by converting to the cesium salt. Most of the impurities will stay in the Cs salt and are difficult to remove. Slightly less than the stoichimetric amount of Cs_2CO_3 was added to keep its pH value<7 and to precipitate out

the Cs salts. The key in this reaction is to keep the reaction slightly acidic because the trifluorovinyl ether double bond will be hydrolyzed by basic aqueous solution.

(3) Reduction of Cs Salt

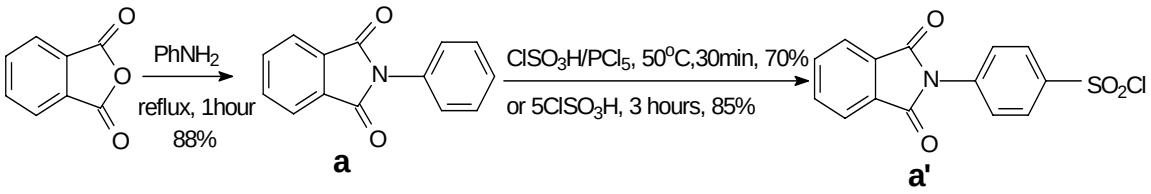
As mentioned before, Cs salt **27** can be obtained from the coupling reaction between **26** and p-nitrobenzenesulfonyl chloride or **25** with p-nitrobenzene sulfonylchloride. It cannot be reduced directly to **28** with usual Zinc reduction since pH of the solution is >7. For the same reason, hydrazine can't be used to deprotect the amine group. A mild non-basic reducing agent is required.

(4) Nitrogen protection and deprotection

The chemical manipulation of complex polyfunctional molecules often requires the sequential protection and deprotection of the various functional groups. There are several typical nitrogen protection groups for primary amines, such as carbamate groups, N-trifluoroacetyl groups, N-azidobenzyloxycarbonyl groups, and allyl groups [205, 206, 207, 208].

The challenges of designing nitrogen protection groups are that they need to be easily removed under mild reaction condition and also stable to a wide range of reaction conditions at the same time. The trifluorovinyl aryl ether function is normally react with mild acids and some strong bases.

The phthalimide function was first chosen as the protection group based on the synthetic of other aromatic TFVE derivatives and for economic reasons. But the first attempt to synthesize p-$NH_3^+PhSO_2Cl$ from aniline failed. However chlorosulfonated N-phenyl phthalimide **a** worked well[209, 210]. Subsequent coupling of p-phthalimido benzenesulfonyl chloride **a** with **25** gave a pure sulfonimide **28a** shown in **Scheme 4.7**.



Scheme 4.7 P-phthalimido Benzenesulfonyl Sulfonyl Chloride a' Synthesis

Cleavage of the phthalimide to deprotect the primary amine **29** is typically not difficult on laboratory scale. One method is to use acid hydrolysis, which generally requires 20-30% HCl reflux for 12 h with very high temperature and pressure [211, 212]. Another route is to use aqueous alkaline hydrolysis, followed with a mineral acid [213]. More often, hydrazine is commonly used in deprotection [214]. However, with the stronger electron withdrawing sulfonimide group para to the protected amine, the deprotection failed. This can be explained from the sulfonimide structure of the Cs salt shown in **Figure 4.3**.

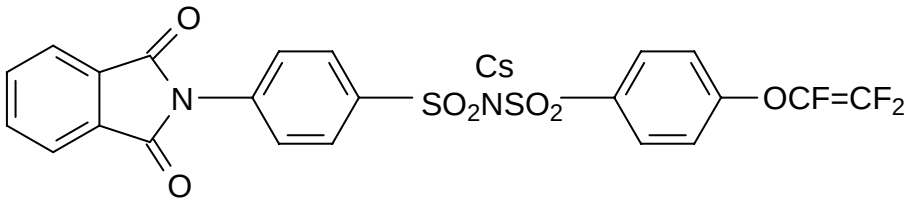
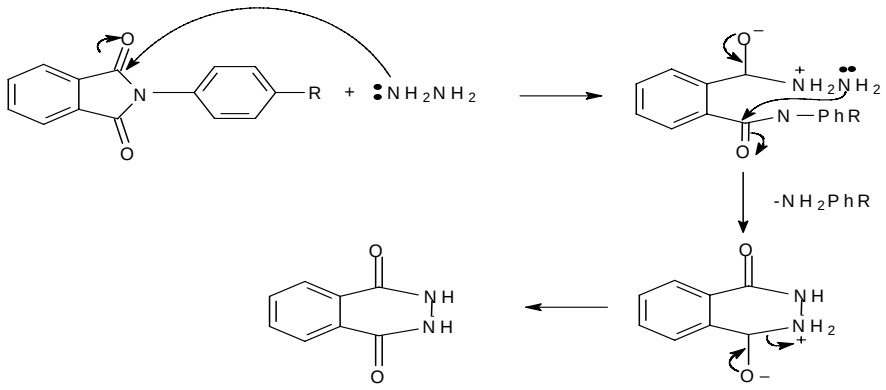


Figure 4.3 Structure of 28a

In the deprotection step, hydrazine acts as a nucleophile towards the carbonyl group as shown in **scheme 4.8**. Usually, the trifluorovinyloxyl ether is not attacked by hydrazine in spite of the fluorine on the vinyl group.



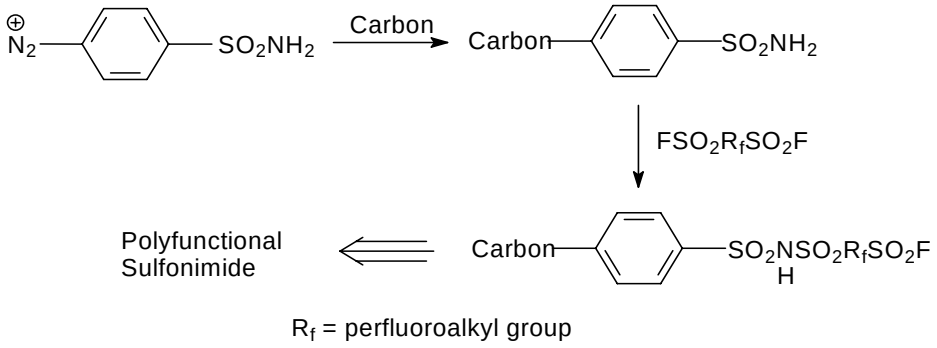
Scheme 4.8 Deprotection of Phthalimides with Hydrazine

However, the sulfonimide function decreases the electron density in double bond of TFVE, thus facilitating nucleophilic attack on the TFVE group by the mild protic base hydrazine [215]. With hydrochloric acid, deprotection of primary amine **29** can not be completed in 12 h. And longer reaction results in attacking the double bond of the trifluorovinyl ether group in **29**.

Therefore, a protection group must be chosen that can tolerate the organic base during the coupling reaction, and then can be easy deprotected with a mild acid. Another economical protecting group, N-acetylsulfanilyl chloride was considered as an alternative for the deprotection to give **29**.

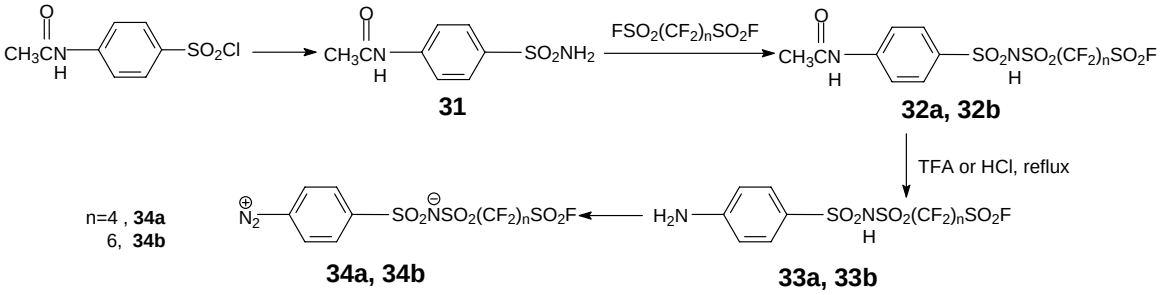
Synthesis of Perfluoroalkyl Sulfonyl Fluoride Diazonium Zwitterion Monomers

As mentioned in the introduction, another route to functionalizing an electrolyte after attachment to carbon via the diazonium salt is to use the reactivity of $–SO_2NH_2$ with $–SO_2F$. This could be done as shown in **Scheme 4.9**.



Scheme 4.9 Proposed Routes to Functionalize Electrolyte by Diazonium Aromatic Amine

Based on experience with aromatic TVFE diazonium zwitterion monomer syntheses, N-Acetylsulfanily chloride was chosen as the starting material because it can be easily deprotected with an acid. After the coupling reaction, maintaining acid conditions is the essential to obtaining the final product. Refluxing it in 25% hydrochloridic acid for a long time can remove the protection group but this also leads to hydrolysis of the suflonyl fluoride group. Strong organic acid anhydrous trifluoroacetic acid is a good alternative since it has no solubility problems. The synthesis process is shown as **Scheme 4.10**.



Scheme 4.10 Synthetic Route for Perfluoroalkyl Sulfonyl Fluoride Diazonium Zwitterion Monomers

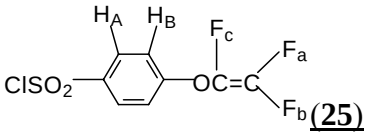
Experimental

Preparation of 4-sulfonylchloride (trifluorovinyloxy) benzene **25**

Under nitrogen atmosphere, 25mL of dry ether and 5.00g (20.1mmol) p-BrPhOCF=CF_2 was injected into an evacuated 250mL round bottom two-neck flask. This was cooled to a -80°C ethanol bath. Then 14.20mL 1.7M n-BuLi was injected four times every 15mins (24.12mmol) into the flask (A). After this mixture (A) stirred for 2 hours, 15mL of dry ether and 16.41 torr of FSO_2Cl (40.23mmol) (1:2.35) were transferred into another 100mL round bottom three-necked flask (B). Mixture B was cooled to -76°C first. And then the mixture (A) was vacuum transferred into this flask (B) by using a syringe needle inserted to (A). At -76°C, the reaction was maintained for another 30 mins and then 50mL of water was added. The organic layer was separated from the aqueous layer using a separatory funnel. The pink liquid product **25** was obtained in 50% yield and 60% purity after the ether was removed under vacuum.

Another method involved using SO_2Cl_2 in place of SO_2FCl. In a typical reaction, 15mL of dry ether and 5.12g of p-BrPhOCF=CF_2 (20.56mmol) were added into a 250mL two-necked round bottom flask. The mixture was cooled to –78^oC in an ethanol bath with N_2 protection. Then 14.51mL of 1.7M n-BuLi was injected four times every 15mins (24.67mmol) (1:1.2) into the flask. After this mixture (A) stirred for 1 hour, 15mL of dry ether and dry 2.1mL of SO_2Cl_2 (25.93mmol) (1:1.26) were transferred into another 100mL round bottom three-necked flask (B). Mixture B was cooled to -76°C, the mixture (A) was vacuum transferred into this flask (B) by using a syringe needle inserted to (A). At -76°C, the reaction was maintained for another 30 mins and then 50mL of

water was added. The organic layer was separated from water using a separation funnel. The pink liquid product was obtained in a yield 70% and 70% purity.



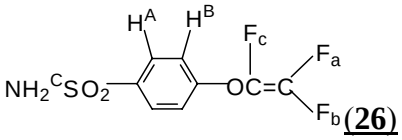
(25)

^{19}F NMR (CD_3CN, ppm) abc δ_a –107.1ppm(1F, d-d), J_{ab}= 96Hz, J_{ac}= 59Hz; δ_b –114.2ppm(1F,d-d), J_{ba}= 96Hz; J_{bc}= 107Hz, δ_c –136.0ppm(1F,d-d). J_{ca}= 59Hz, J_{cb}= 107Hz;

^{1}H NMR (CD_3CN) AB δ_A8.10 (2H,d), δ_B7.43 (2H,d), J_{AB}=9Hz.

Preparation of 4-sulfonylamide (trifluorovinyloxy) benzene **26**

Ammonia (30mL) was cooled to –60^{o}C in a 250ml round flask and then the liquid compound **25** 3.92g (90.29mmol, 70% purity) was added dropwise with the N_2 protection. The solution was allowed to return 22^{o}C over 8h. Dry ether (20mL) was used to wash the rest of **25** from the dropping funnel into the flask. After removing ether by rotary evaporation, NH_4Cl was washed out with dry acetonitrile. The product was dried under vacuum for 8 h. White product **26** (2.89g, 57%) of was obtained after sublimation at 50-60^{o}C under vacuum.



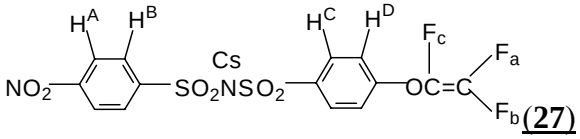
(26)

^{19}F NMR (CD_3CN, ppm) abc δ_a –107.1ppm(1F, d-d), J_{ab}= 96Hz, J_{ac}= 59Hz; δ_b –114.2ppm(1F, d-d), J_{ba}= 96Hz, J_{bc}= 107Hz; δ_c –136.0ppm(1F, d-d). J_{ca}= 59Hz, J_{cb}= 107Hz;

^{1}H NMR (CD_3CN) AB δ_A7.93 (2H, d), δ_B7.35 (2H, d), J_{AB}=6Hz, δ_C5.69 (2H, s).

Preparation of CF_2=CFOPhSO_2N(Cs)SO_2PhNO_2 **27**

Compound p-SO_2ClPhOCF=CF_2 **24** (2.62g, purity around 60%, 0.006mol) and 2.02g of p-NO_2PhSO_2NH_2 (0.01mol) (0.6:1) were added into a 50mL flask. Dry CH_3CN (15mL) was vacuum transferred into the evacuated flask. Then 2mL of dry DIEA was injected into the flask with the N_2 protection. The solution was kept at reflux at 80°C for 48 h. The reaction was completed when the starting material was no longer visible in the ^{19}F NMR spectrum. The solvent was removed on a rotary evaporator and then the resulting solid was acidified with 4mL of 36.5% HCl. The acid form of **27** was extracted into ether to separate it from water solution. The ether was removed under vacuum and the solid dried under vacuum at 22°C for 8 h. Then, 20mL of Cs_2CO_3 water solution (0.3M) was added to precipitate out the crude product. The 1.78g of compound **27** was obtained after filtration and removal of the excess p-nitrobenzenesulfonylamide under vacuum at 80°C (yield 50%).



(27)

^{19}F NMR (CD_3CN, ppm) abc δ_a

–118.8ppm(1F, d-d), J_{ab}= 99Hz, J_{ac}= 59Hz; δ_b –126.0ppm(1F,d-d), J_{ba}= 99Hz, J_{bc}= 110Hz

δ_c –134.4ppm(1F,d-d). J_{ca}= 59Hz, J_{cb}= 110Hz

^1H NMR (CD_3CN) AB δ_A8.12 (2H,d), δ_B7.86 (2H,d) J_{AB}=9Hz; CD δ_C7.72 (2H, d), δ_D7.10 (2H, d), J_{AB}=9Hz.

Preparation of CF_2=CFOPhSO_2N(Cs)SO_2PhNH_2 **29**

(1) Zinin reaction.

Zinin reducing agent was prepared as follows. The sulfide $Na_2S·9H_2O$ (10.00g, 0.042mol) was dissolved in 60mL of water in the ice bath with good stirring (mixture B). At the same time, in batch A, another 15.0g of $Na_2S·9H_2O$ (0.0625mol) was added dropwise to 16mL of 36.5% HCl solution (0.146mol) to produce H_2S, which was bubbled rapidly into mixture B. Mixture B was stored in the refrigerator.

In a 250mL two-necked flask, 30mL of ethanol solution of 1.78g of p-$NO_2PhSO_2N(Cs)SO_2PhOCF=CF_2$ **27** (0.003mol) was added. Then 50mL of the mixture B was added dropwise into this solution at 80°C and the solution was refluxed for 2 hours. The solvent was removed using a rotary evaporator. The resulting solid compound was dried under high vacuum at 80°C for 8 h. F^{19} NMR showed that the basic reducing agent destroyed the double bond in **27**.

(2) Raney-Ni as reducing agent.

In a 100mL two-necked flask, 0.554g of Cs salt **27** (0.93mmol), 15mL of DMF and around 0.06g of Raney-Ni were added. 200mL of H_2 was collected in a balloon. 200mL of H_2 was slowly vacuum transferred from the balloon into the evacuated flask. The reaction was completed in 2h. The solvent was removed by vacuum. Under these conditions, the nitro group did reduce to the amide without affecting the trifluorovinyl ether group according to NMR spectrum. But the catalyst could not be removed from the product.

<u>Preparation of p-phthalimido benzenesulfonyl chloride **a'**</u>

Method (1)

Chlorsulfonic acid (6.65mL, 0.1mol) and 30mL of dry ether were added into a 100mL three-necked round bottom flask. At room temperature, 9.10mL of aniline

(0.1mol) (1:1) was slowly added dropwise to the chlorosulfonic acid with good stirring over 4 hours. Dry ether (30mL) more added to precipitate the crude product. 14.71g of solid product sulfanilyl chloride was obtained after filtration and drying (yield 64%).

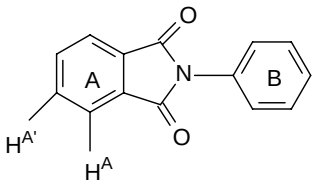
Sulfanilyl chloride (4.56g, 0.02mol) and 3.26g of phthalic anhydride (0.022mol) (1:1.10) were mixed in a three-necked 100mL flask. Then, the mixture was heated to 130°C with N_2 protection. The water bead on the wall of flask was wiped carefully with cotton ball to push the reaction forward. Then small amount of phthalic anhydride was removed using sublimator at 50°C. Finally 5.60g of solid was obtained. But 4-amino benzenesulfonic acid was obtained according to ^{1}H NMR instead of desired product p-phthalimido benzenesulfonyl chloride **a**.

Method (2)

Phthalic anhydride (5.00g, 33.81mmol) and 4mL of aniline (43.91mmol) (1:1.3) were added into a three-necked round bottom flask with good stirring. The solution was refluxed at 160 ^{o}C under a flow of nitrogen for two hours until the entire water bead on the wall of flask was dried away by the N_2 flow. White solids crystallized upon cooling the solution and were collected using a Büchner funnel with 20mL*4 of water washing. N-Phenyl phthalimide **a (**6.68g, 88.67%) was obtained after drying at 80^{o}C.

N-Phenyl phthalimide (3.00g, 13.43mmol) was combined with 7 equivalent of excess chlorosulfonic acid (8mL, 98.78mmol) at 60 ^{o}C for 2 hours. Then the solution was poured onto ice. The solid product was filtered from ice water and washed with 50mL of water twice. Finally p-phthalimido benzenesulfonyl chloride **a'** was obtained with 58.96% yield and 90% purity after drying under vacuum for 8h.

Compound **a'** also can be obtained as follows. To a solution of 2.20ml of chlorosulfonic acid (27.17mmol) and 2.80g of phosphorus pentachloride (13.43mmol) that had been stirred for 1 hour, N-Phenyl phthalimide **a** (3.00g, 13.43mmol) was slowly added. The solution was refluxed at 50^{o}C for 3.5 hours and the reaction mixture was poured to ice. The solid product was filtered from the ice water and washed with 50mL of water twice. Finally 4.02g of purified p-phthalimido benzenesulfonyl chloride **a'** was obtained after drying under vacuum for 8 h (yield 93%).

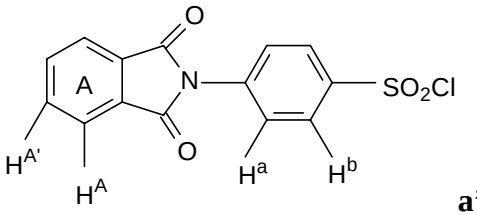


a

^{1}H NMR (CD_3CN) A δ_A 7.94 (2H,m), $\delta_{A'}$ 7.78(2H,d) $J_{AA'}$=3Hz,

BB'B" δ_A7.44 (5H,m);

^{13}C NMR (CD_3CN) δ 167.39(C_6,C_7), 134.50(C_5,C_8), 131.87(C_1,C_4), 131.70($C_{4'}$), 129.23($C_{2'}$,$C_{6'}$), 128.22($C_{1'}$), 126.68($C_{3'}$,$C_{5'}$), 123.86(C_2,C_3).



a'

^{1}H NMR (CD_3CN) AA' δ_A 7.96 (2H,m), $\delta_{A'}$ 7.89 (2H,d) $J_{AA'}$=3Hz,

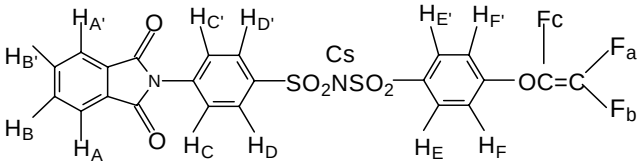
ab δ_a7.72 (2H,m), δ_b7.39(2H,m), J_{ab}=8Hz;

^{13}C NMR (CD_3CN) δ 167.39(C_6,C_7), 134.50(C_5,C_8), 131.87(C_1,C_4), 131.70($C_{4'}$), 129.23($C_{2'}$,$C_{6'}$), 128.22($C_{1'}$), 126.68($C_{3'}$,$C_{5'}$), 123.86(C_2,C_3).

Preparation of protected Cs salt **28a**

P-triperfluorovinyloxybenzene sulfuric amide (0.51g, 2.0mmol) and 0.64g of p-phthalimido benzenesulfonyl chloride **a'** (2.0mmol) (1.05:1) were added into a one-piece 50mL flask reactor. Under high vacuum, 15mL of dry CH_3CN and 0.4ml of dry DIEA (2.30mmol) were injected into the evacuated flask. The reaction was refluxed at 80 ^oC with N_2 protection for 24 h.

The mixture was acidified with 10mL of 4.38% hydrochloride solution (14.94mmol) till pH paper turned red (pH=2.5). The mixture was then refluxed at 50^oC for two hours. With 25ml of ether, the organic layer was separated out with separation funnel. The protonated form of **28a** crude product was dissolved in 5mL of acetone after removal of the ether under vacuum. The product was precipitated out by titration 0.01M Cs_2CO_3 solution till PH meter reached 7. Finally, 0.67g of purified product **28a** was obtained after filtration and drying (yield 50%).



28a

^{19}F NMR (CD_3CN, ppm) abc δ_a –118.9ppm(1F, d-d), J_{ab}= 99Hz, J_{ac}= 59Hz; δ_b – 126.1ppm(1F,d-d), J_{ba}= 99Hz, J_{bc}= 110Hz δ_c –134.8ppm(1F,d-d). J_{ca}= 59Hz, J_{cb}= 110Hz; ^1H NMR (CD_3CN) ABCDEF δ_A7.95(2H, m), δ_B7.86(2H,m) J_{AB}=3Hz; δ_C7.82(2H, d), δ_D7.75(2H,d) J_{CD}=9Hz; δ_E7.40(2H, d), δ_F7.13(2H,d) J_{EF}=7Hz.

Deprotection to amine **29**

Trial (1)

Cs salt **28a** (0.067g, 0.10mmol) was added into a 50mL flask. Then the air was evacuated and 15mL of $N_2H_4 \cdot H_2O$ (0.31mol) was added by vacuum suction. The mixture

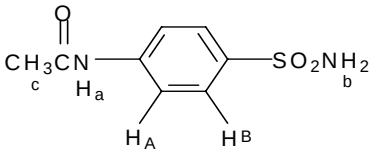
was allowed to stand at 22°C for 8h. F^{19}NMR indicated the compound's double bond was destroyed after removal of the solvent under vacuum.

Trial (2)

0.067g of Cs salt **28a** (0.1mmol) was dissolved in 15mL acetone and cooled to 0°C. 0.50g of Br_2 (3.13mmol) liquid was dropped into the flask. After 20 min, 20mL of 5% sodium bisulfite was poured in to destroy any excess Br_2. The solvent was removed by rotary evaporation. The brominated product was filtered out and washed 3 times with 20mL of water. According to NMR spectrum, Br_2 reacted with both aromatic ring and the trifluorovinyl ether double bond.

Preparation of N-acetylsulfanilyl amide **31**

In a 100mL three-necked flask, 11.67g of N-acetylsulfanilyl chloride (0.05mol) was added to 20ml liquid ammonia, which was collected by cooling in a ethanol-water slush bath at -65°C first. The mixture was allowed to return to room temperature for 8 h. And then the mixture was dissolved in the 100mL of ethanol and water co-solvent (1:1) at 80°C. Finally, the pure product was recrystallized in the solvent by cooling to room temperature. 8.5g of pure white crystal product was obtained by filtration (yield 84.92%).



31

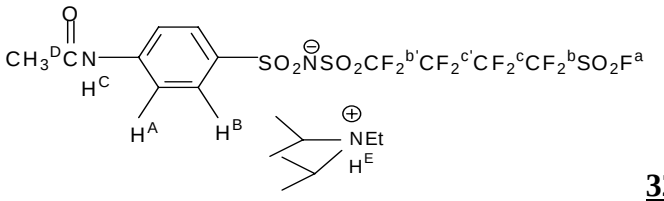
^{1}H NMR (CD_3CN) abc δ_a 9.70(1H, s), δ_b 6.61(2H,s), δ_c 2.69 (3H, s);

AB δ 7.75(4H,d) J_{AB}= 2Hz.

Preparation of $CH_3C(O)NHPhSO_2N^-SO_2(CF_2)_nSO_2F$ **32a, 32b**

In a typical reaction, 4.66g of $(FSO_2C_3F_6)_2$ (0.01mol) and 2.13g of N-acetylsulfanilyl amide (0.01mol) (1:1) were added into a 100mL round bottom flask.

10mL of dry acetonitrile and 0.58mL of dry DIEA were vacuum transferred into the evacuated flask. The solution was refluxed at 80^{o}C for 8 h. The reaction was completed after NH_2- peak no longer visible in ^{1}H NMR spectrum. The crude product **32a** was obtained after removing the solvent. Compound **32b** was obtained by an exactly identical procedure.

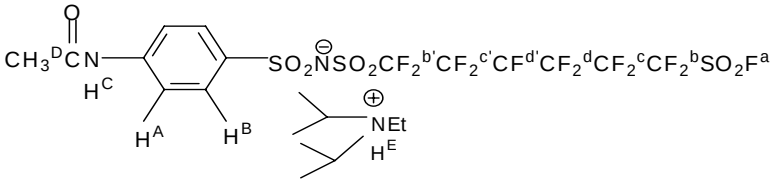


32a

^{19}F NMR (CD_3CN, ppm) δ_a 46.5ppm(1F, m), δ_b –106.5ppm(2F,s), $\delta_{b'}$ –112.3ppm(2F,s), $\delta_{c+c'}$ –119.1ppm(4F,m);

^{1}H NMR (CD_3CN) δ_C 8.50(1H, s), δ_E 6.26(1H, t); δ_D 2.05 (3H,s);

AB δ_A7.75(2H,d), δ_B7.62(2H,d) J_{AB}= 9Hz.



32b

^{19}F NMR (CD_3CN, ppm) δ_a 46.96ppm(1F, m), δ_b –106.7ppm(2F,t), $\delta_{b'}$ –112.3ppm(1F,d-d). $\delta_{c+c'}$ –119.3,-119.4ppm(4F,s-s), $\delta_{d+d'}$ –120.6ppm(4F,m);

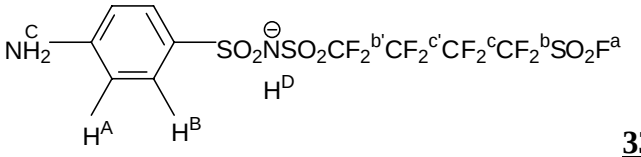
^{1}H NMR (CD_3CN) ab δ_a 8.57(1H, s), δ_b 2.05(3H, s);

AB δ_A7.75(2H,d), δ_B7.62(2H,d) J_{AB}= 9Hz.

Prepare $NH_2PhSO_2NHSO_2(CF_2)_nSO_2F$ **33a, 33b**

In a typical reaction, 0.30g of compound **32a** was acidified with 5mL of TFA at room temperature with good stirring for 30mins. The volatile components were removed using rotary evaporator. The yellow crude product **33a** with other inorganic salts were

obtained by separation the inorganic layer from the mixture of 36.5% HCl (10mL) and ether (15ml). Crude product **33b** was obtained by an exactly identical procedure.



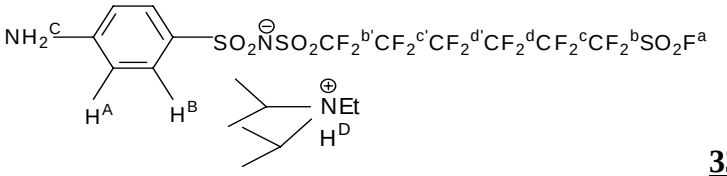
33a

^{19}F NMR (CD_3CN, ppm) δ_a 46.46ppm(1F, m), δ_b –106.51ppm(2F,s),

$\delta_{b'}$ –112.31ppm(2F,s), $\delta_{c+c'}$ –119.12ppm(4F,m);

^{1}H NMR (CD_3CN) δ_C 8.50(1H, s), δ_E 6.26(1H, t); δ_D 2.05 (3H,s),

AB δ_A7.96(2H,d), δ_B7.40(2H,d) J_{AB}= 9Hz.



33b

^{19}F NMR (CD_3CN, ppm) δ_a 46.96ppm(1F, m), δ_b –106.7ppm(2F,t),

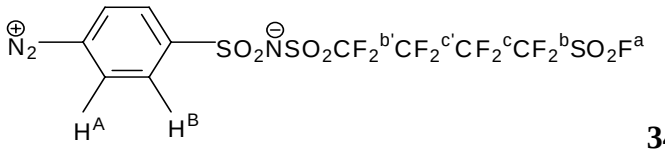
$\delta_{b'}$ –112.36ppm (1F,s). $\delta_{c+c'}$ –119.2, -119.4ppm(4F,s-s), $\delta_{d+d'}$ –120.6ppm(4F,m);

^{1}H NMR (CD_3CN) ab δ_a 8.57(1H, s), δ_b 2.05(3H, s),

AB δ_A 7.75(2H,d), δ_B 7.62(2H,d), J_{AB}= 9Hz.

Preparation of $N_2^+PhSO_2N^-SO_2(CF_2)_nSO_2F$ **34a, 34b**

In a typical reaction, the yellow acid solution of **33a** from previous step was placed in an ice bath (batch A). Another batch B was prepared by combining 0.07g of $NaNO_2$ (1.00mmol) and 5mL of 36.5% HCl in an ice bath for 5 minutes. Then the mixture of B was poured into A at 0^{o}C. The white solid was filtered out after stirring for half an hour. Finally, purified product **34a** (0.09g, 48% for three steps) was obtained. Compound **34b** was obtained by an exactly identical procedure.

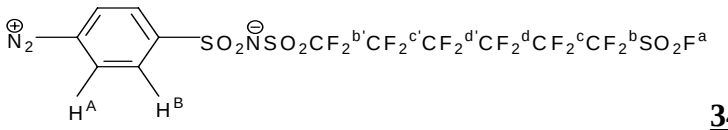


34a

^{19}F NMR (CD_3CN, ppm) δ_a 46.0ppm(1F, m), δ_b –106.54ppm(2F,s), $\delta_{b'}$ – 112.16ppm(2F,s), $\delta_{c+c'}$ –119.07ppm(4F,s);

^{1}H NMR (CD_3CN) AB δ_A 8.54(2H,d), δ_B 8.33(2H,d) J_{AB}= 9Hz;

IR (cm^{-1}) (KBr pellet, acetone) 2285.2 (s) for $-N_2^+$group, 3099.0(s), 1565.0(m), 1453.7(s), 1406.9(m), 1332.9(s), 1306.7(s), 1207.5.2(vs), 1145.8(vs), 1064.4(s), 938.3(m), 831.5(m).



34b (yield 51% for three steps)

^{19}F NMR (CD_3CN, ppm) δ_a 47.0ppm(1F, m), δ_b –106.67ppm(2F,s), $\delta_{b'}$ – 112.18ppm(2F,t), $\delta_{c+c'}$ –119.16ppm(2F,s), -119.39ppm(2F, m), $\delta_{d+d'}$ –120.53ppm(4F,m);

^{1}H NMR (CD_3CN) AB δ_A 8.54(2H,d), δ_B 8.34(2H,d), J_{AB}= 8Hz;

IR (cm^{-1}) (KBr pellet, nujor) 2286.7 (m) for $-N_2^+$group, 1565.7(m), 1459.2(s), 1376.9(m), 1333.3(m), 1209.8(vs), 1152.7(vs), 1069.0(m), 850.4(m).

Conclusion

Three new diazonium zwitterions monomers were obtained, which provide more avenues to other diazonium zwitterions synthesis or to further fictionalization of carbon after attachement of the monomers via the diazonium salt. The potential success of these approaches requires further research.

APPENDICES

Figure A ^{19}F NMR spectrum of Comound **5a**, 200MHz, CD_3CN

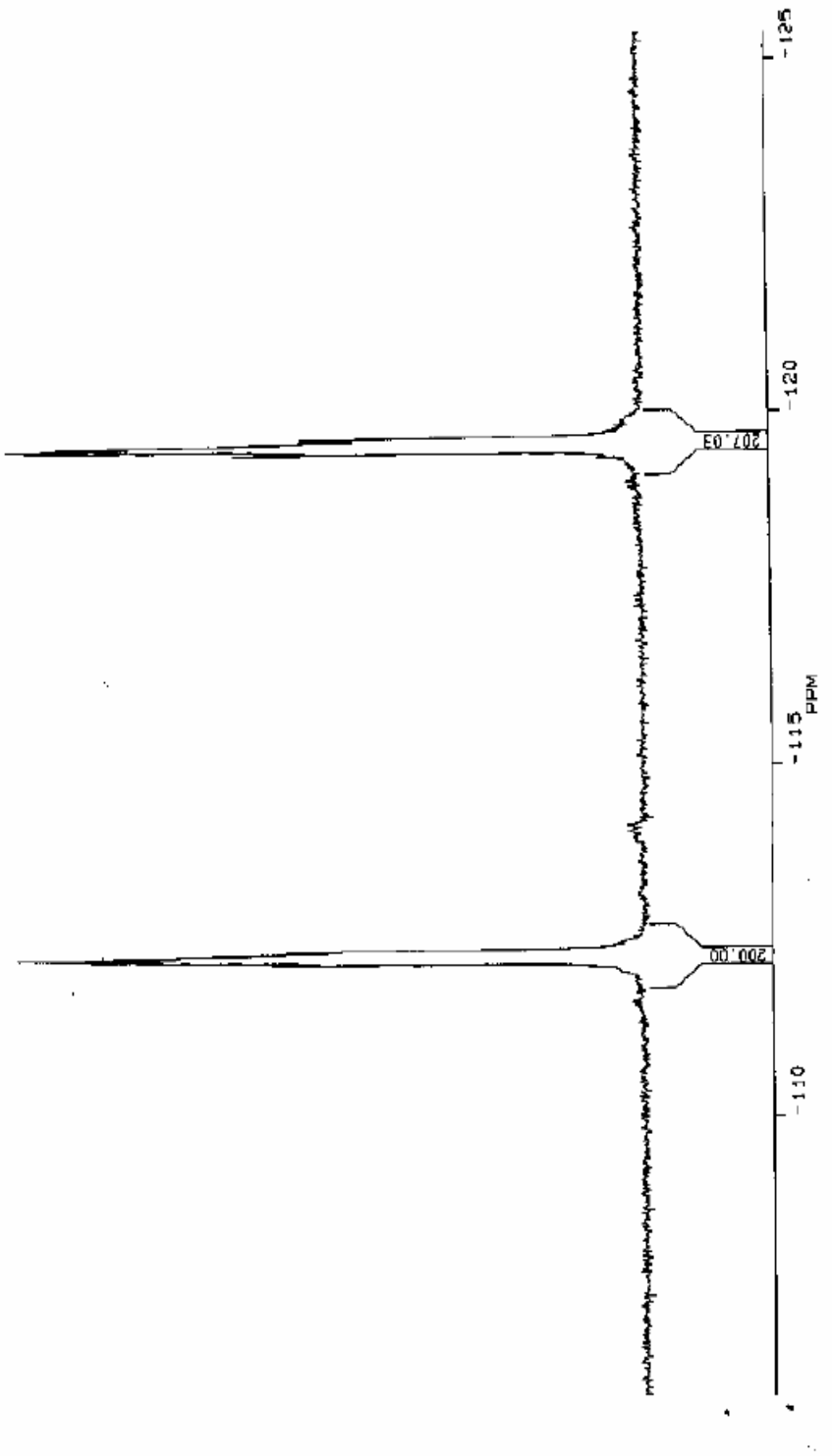


Figure A ^{1}H NMR spectrum of Comound **5a**, 500MHz, DMSO

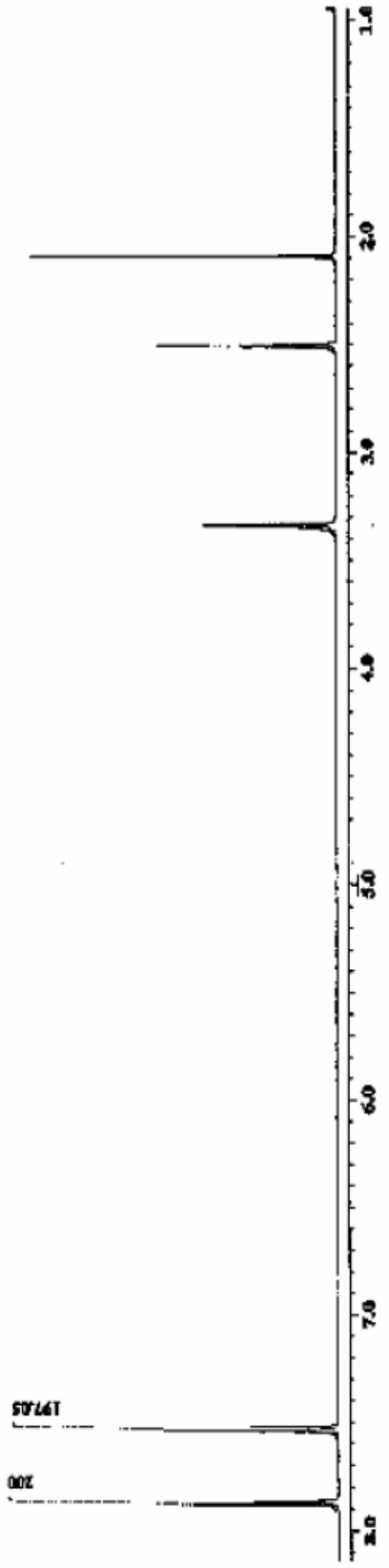
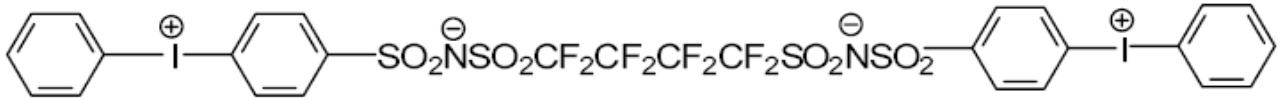


Figure A ^{19}F NMR spectrum of Comound **6a,** 200MHz, DMSO



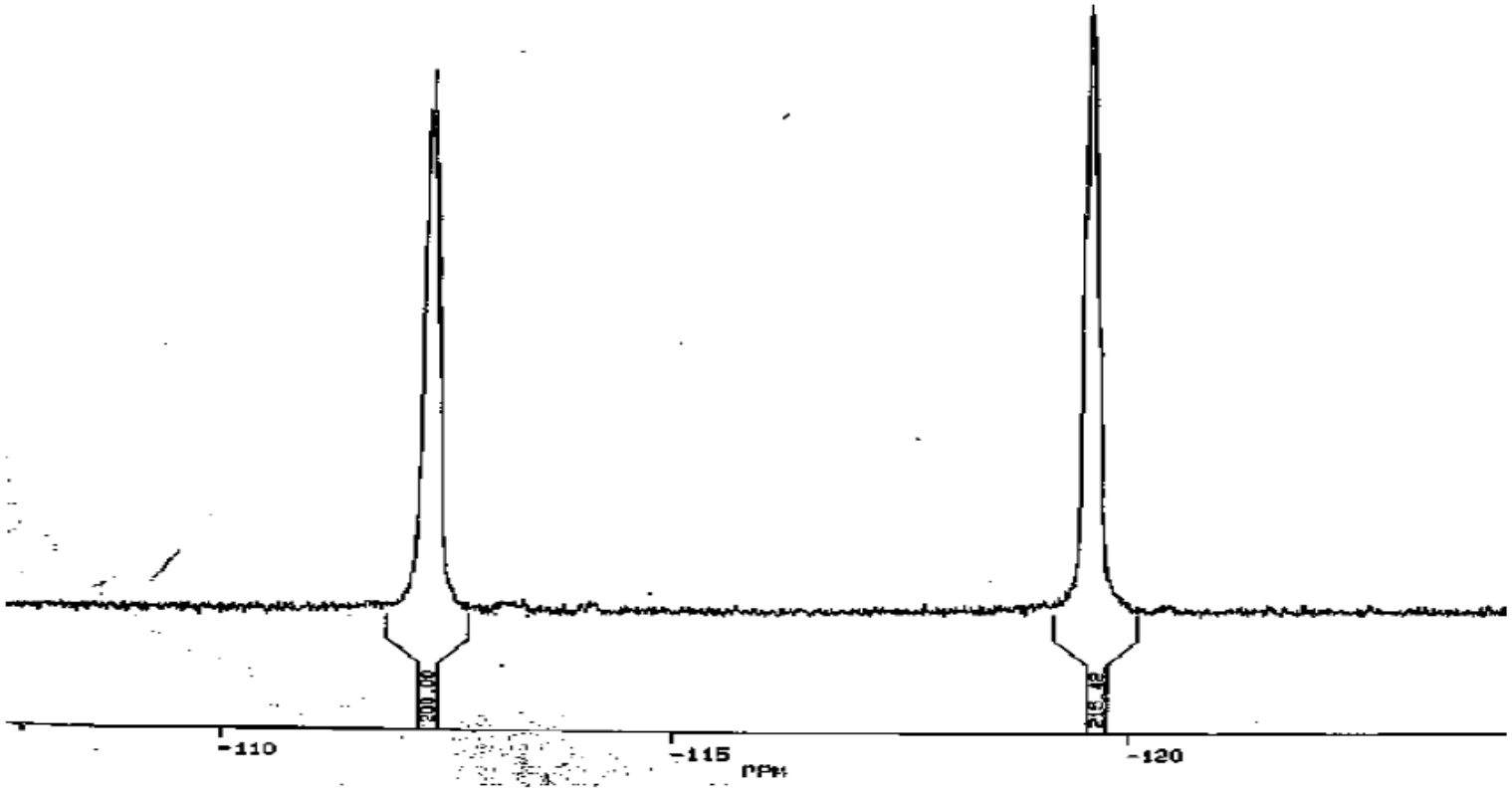


Figure A ^{1}H NMR spectrum of Comound **6a,** 200MHz, DMSO

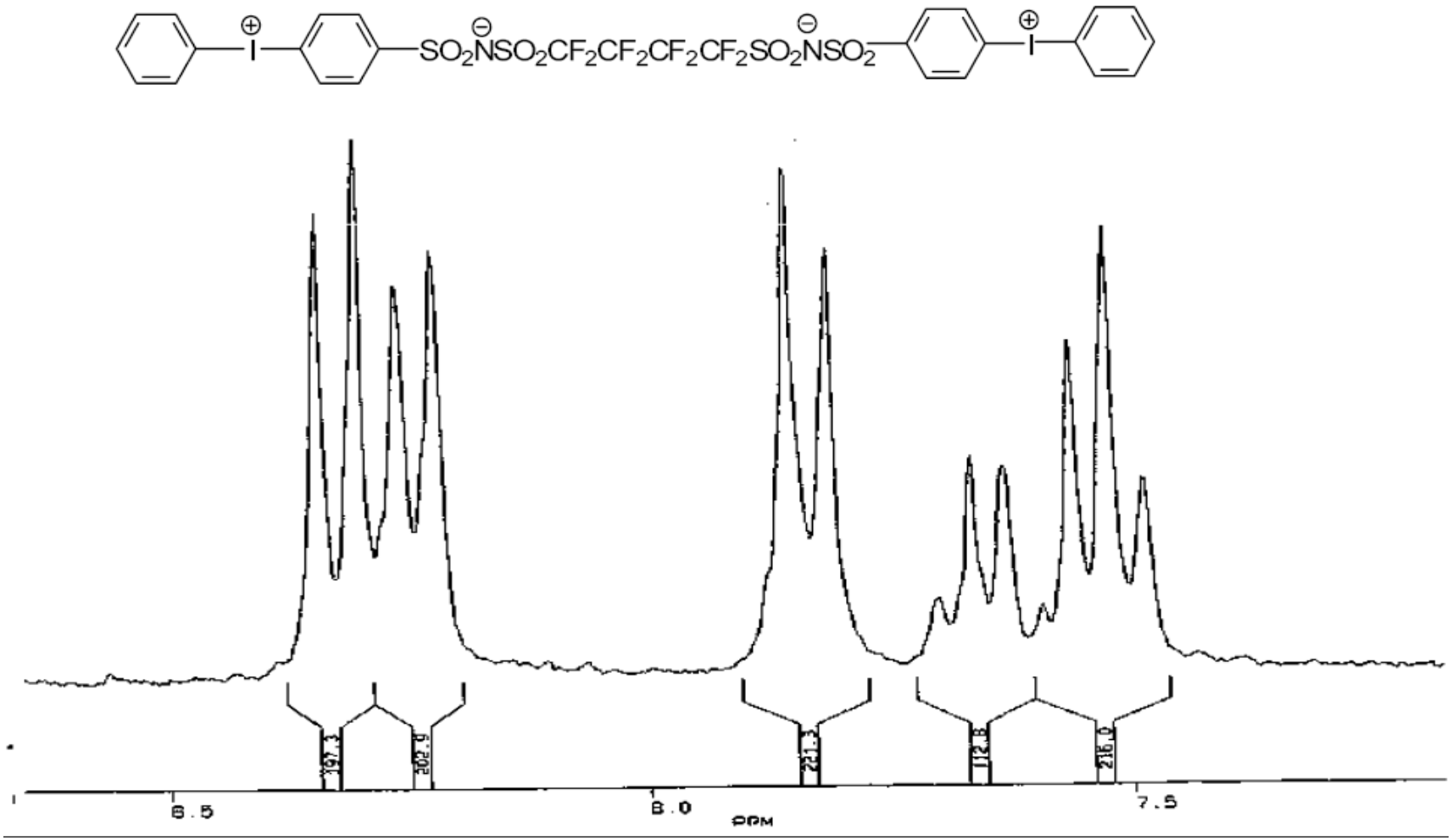
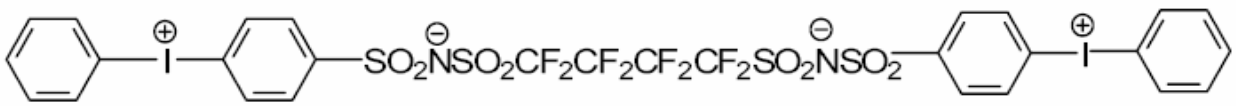


Figure A ^{13}C NMR spectrum of Comound **6a,** 500MHz, DMSO



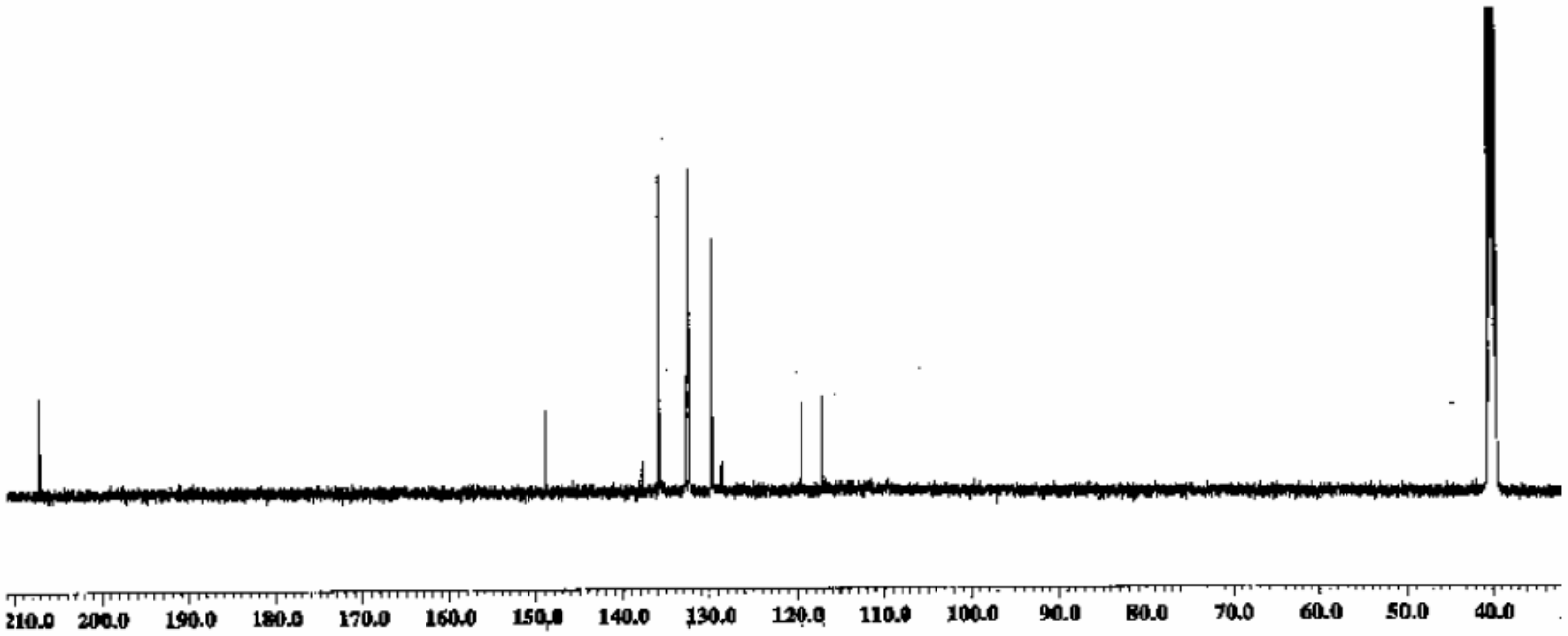
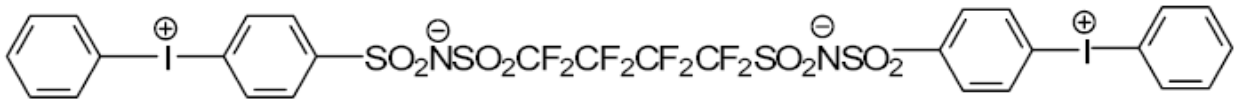


Figure A TGA spectrum of Comound **6a**



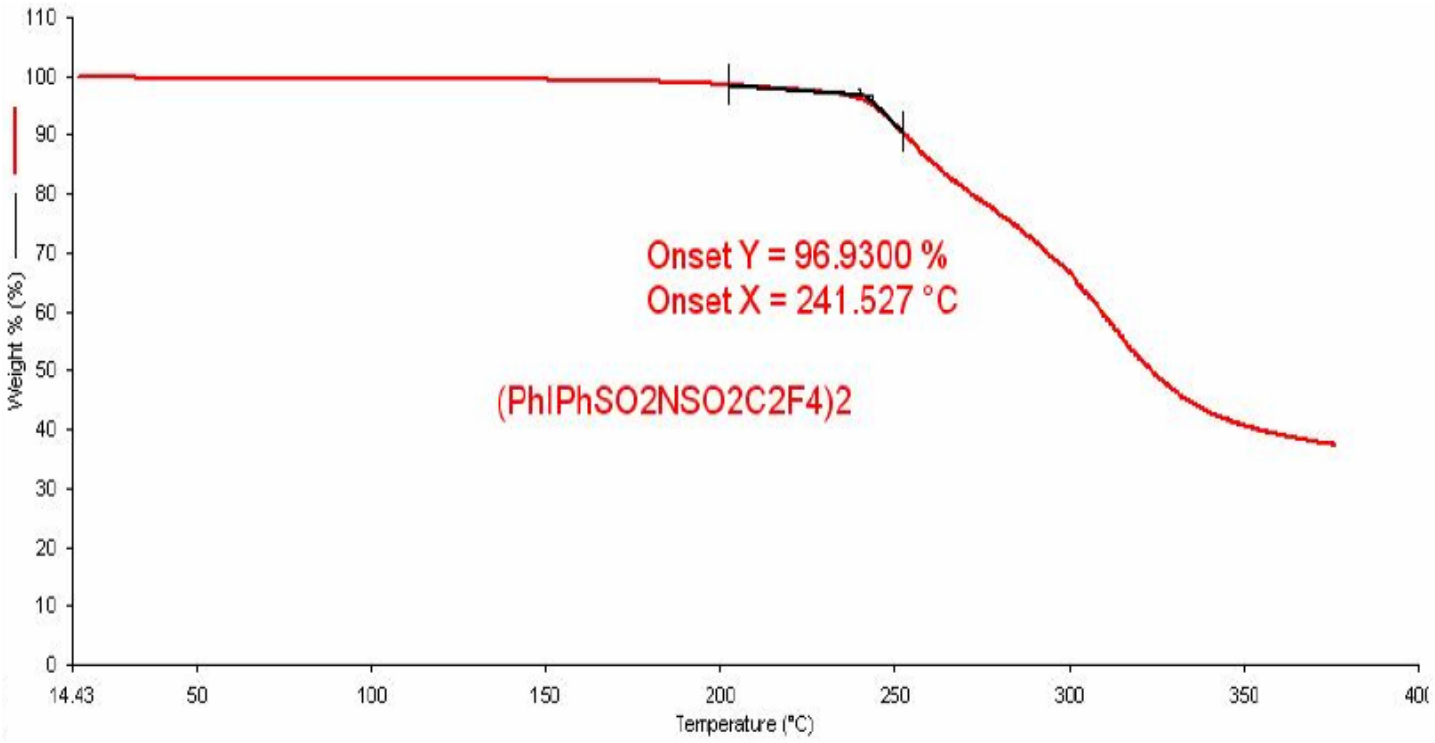


Figure A ^{19}F NMR spectrum of Comound **5b**, 200MHz, DMSO

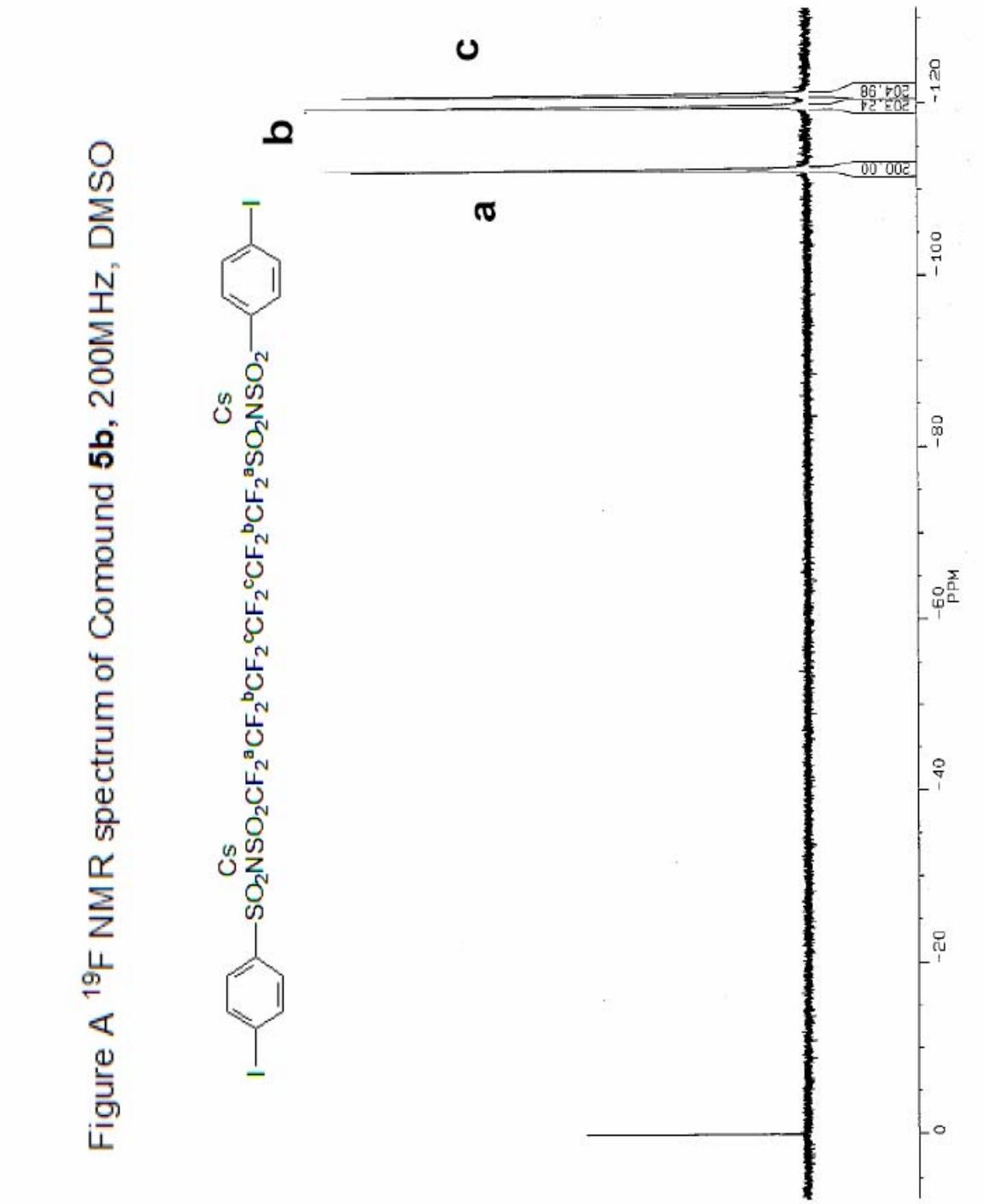


Figure A ^{1}H NMR spectrum of Comound **5b**, 200MHz, DMSO

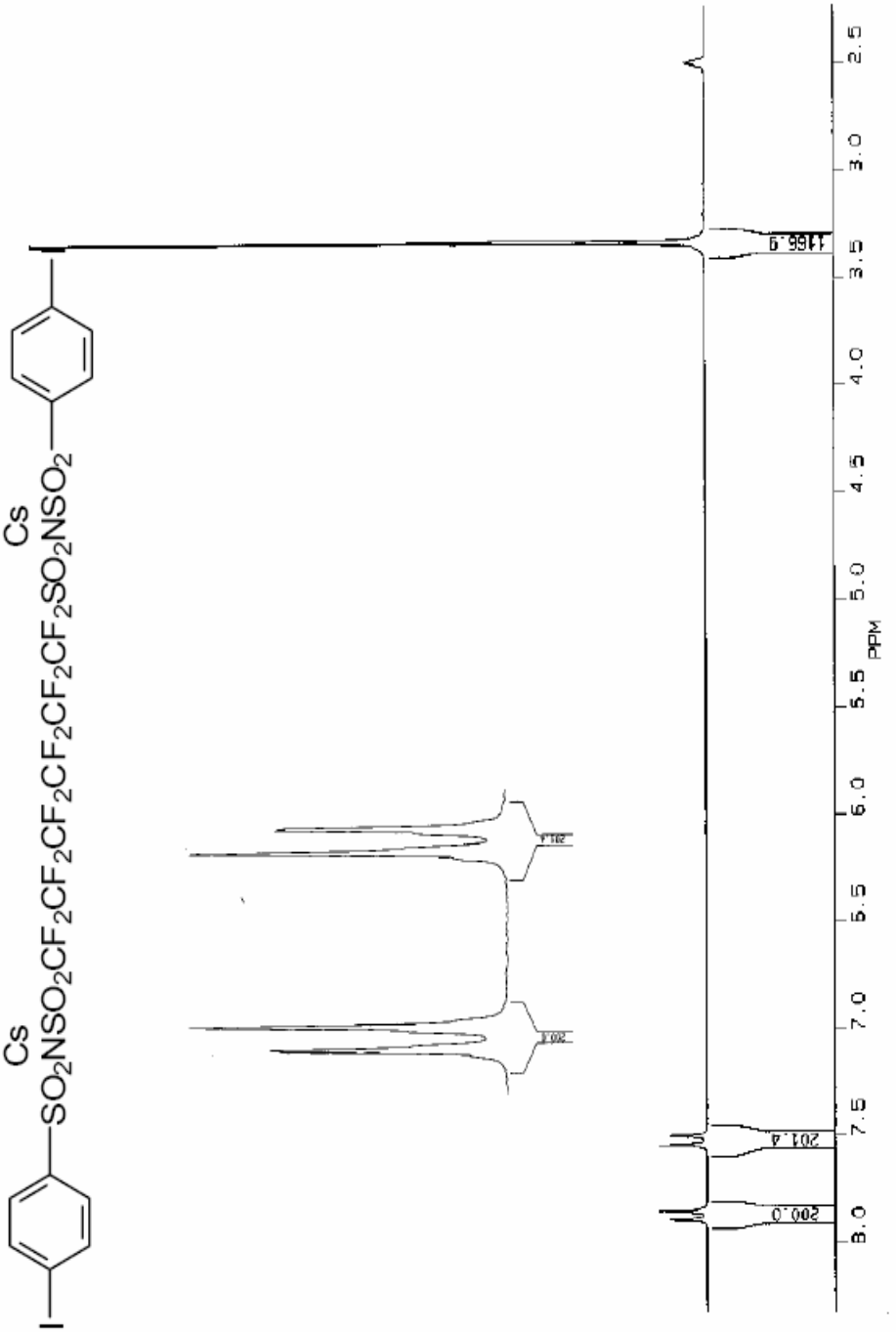


Figure A ^{19}F NMR spectrum of Comound **6b**, 200MHz, DMSO

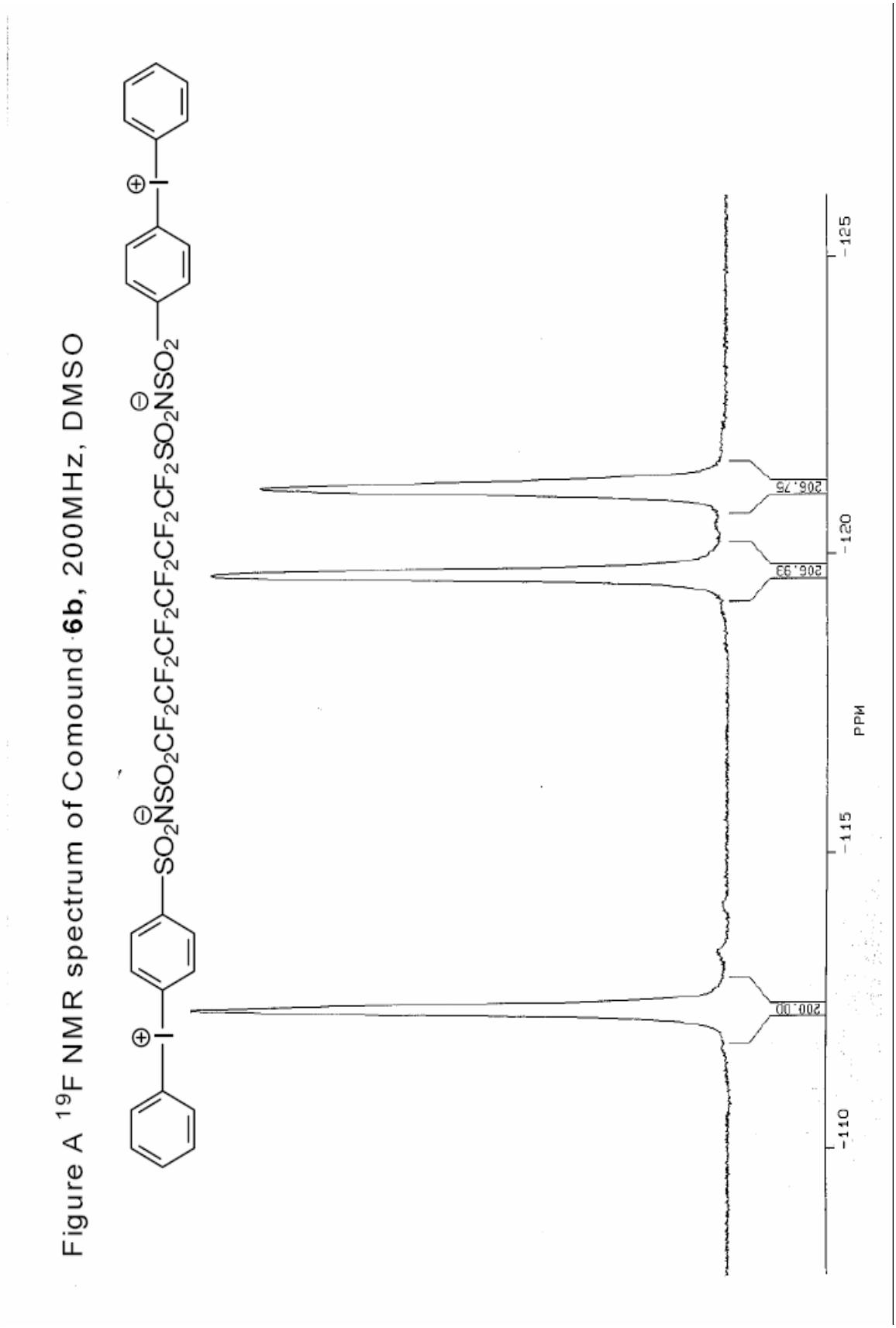


Figure A ^{1}H NMR spectrum of Comound **6b**, 500MHz, DMSO

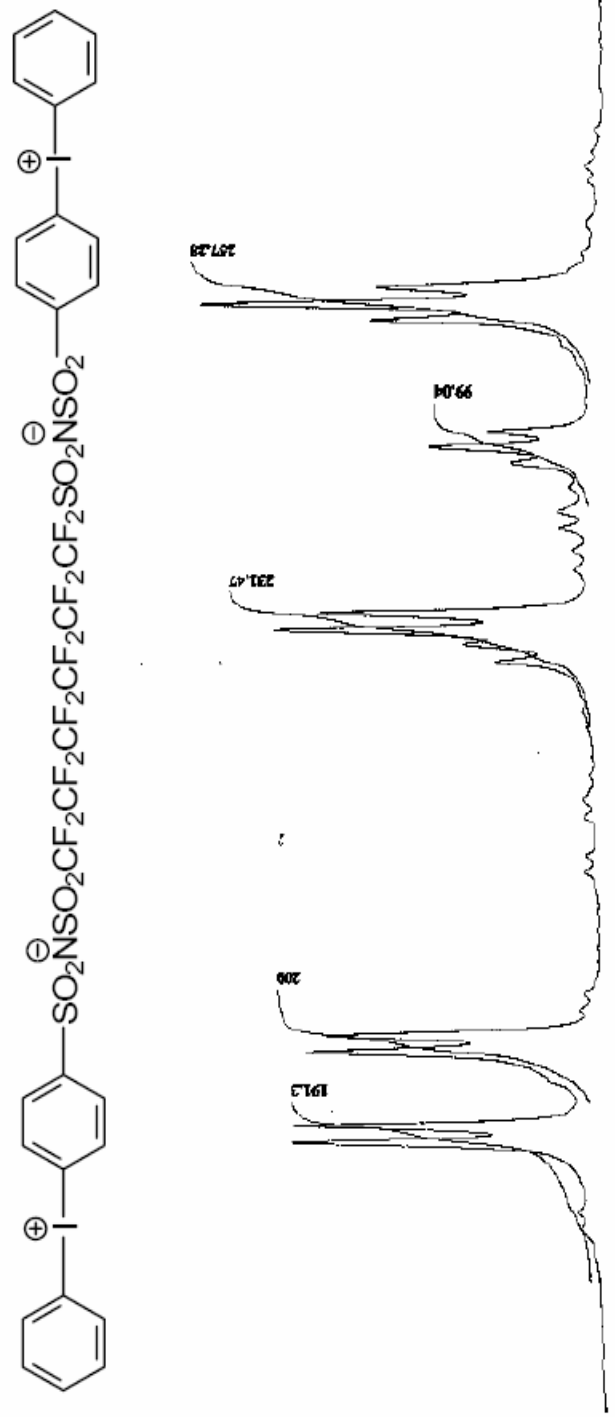


Figure A ^{19}F NMR spectrum of Comound **5c**, 200MHz, CD_3CN

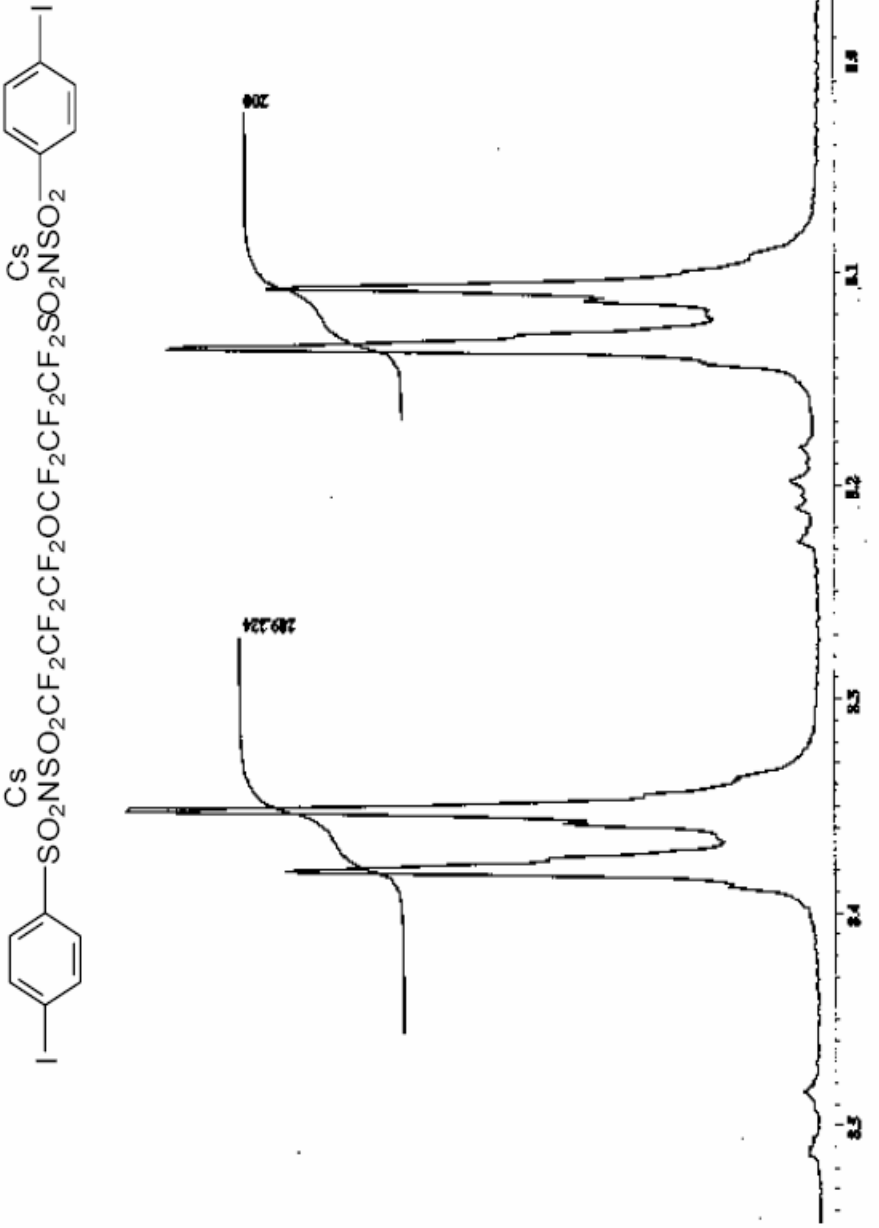


Figure A ^{19}F NMR spectrum of Comound **6c**, 200MHz, DMSO

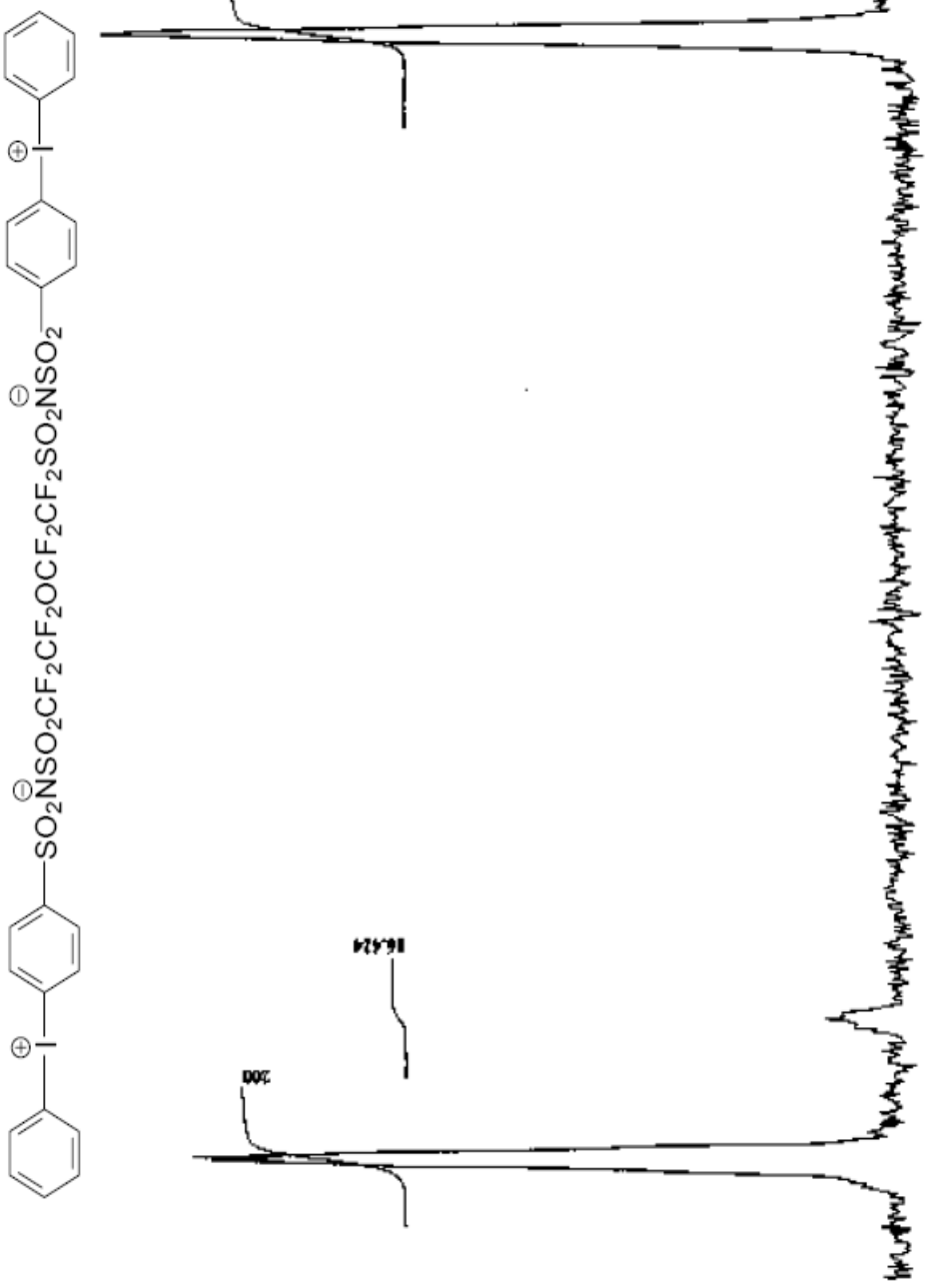


Figure A ^{1}H NMR spectrum of Comound **6c**, 200MHz, DMSO

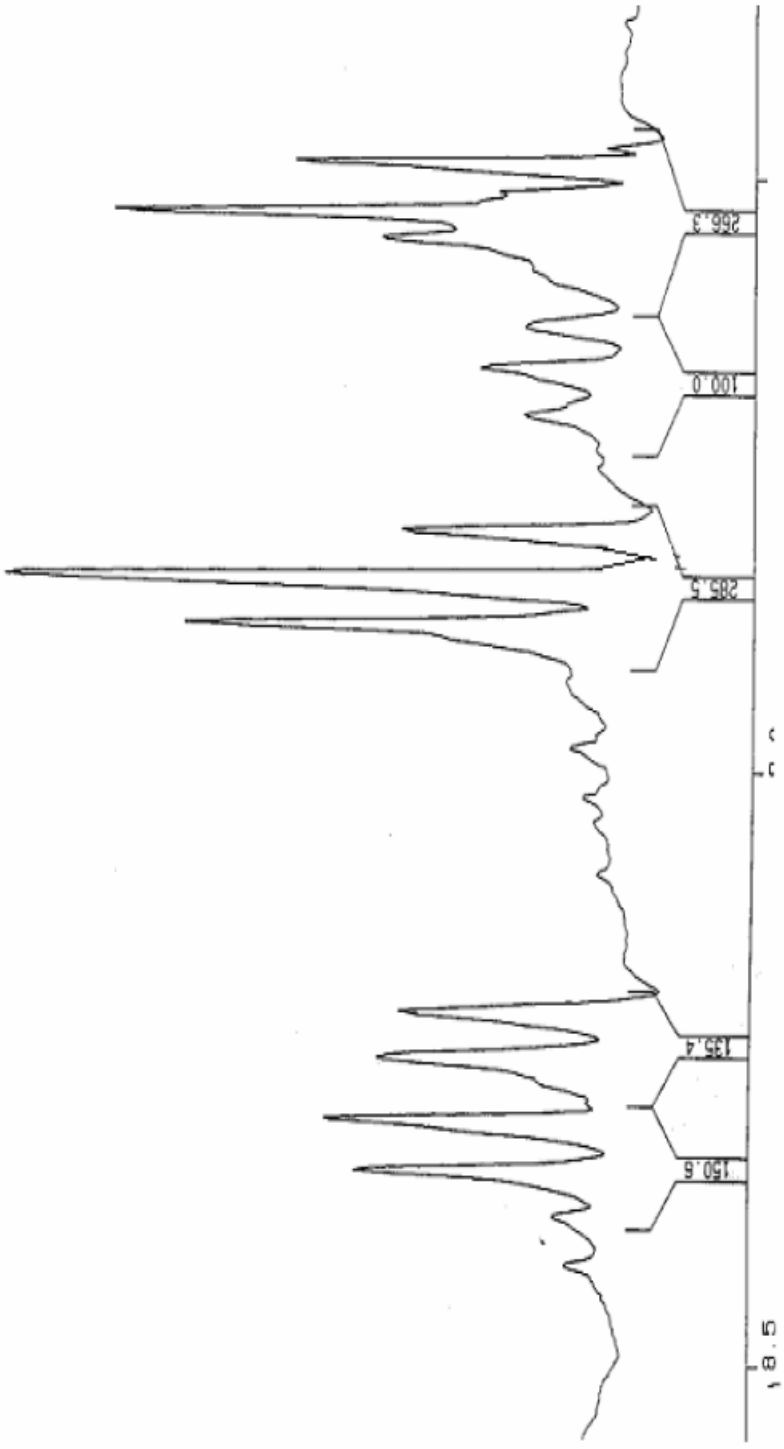


Figure A ^{19}F NMR spectrum of Comound **13a**, 200MHz, CD_3CN

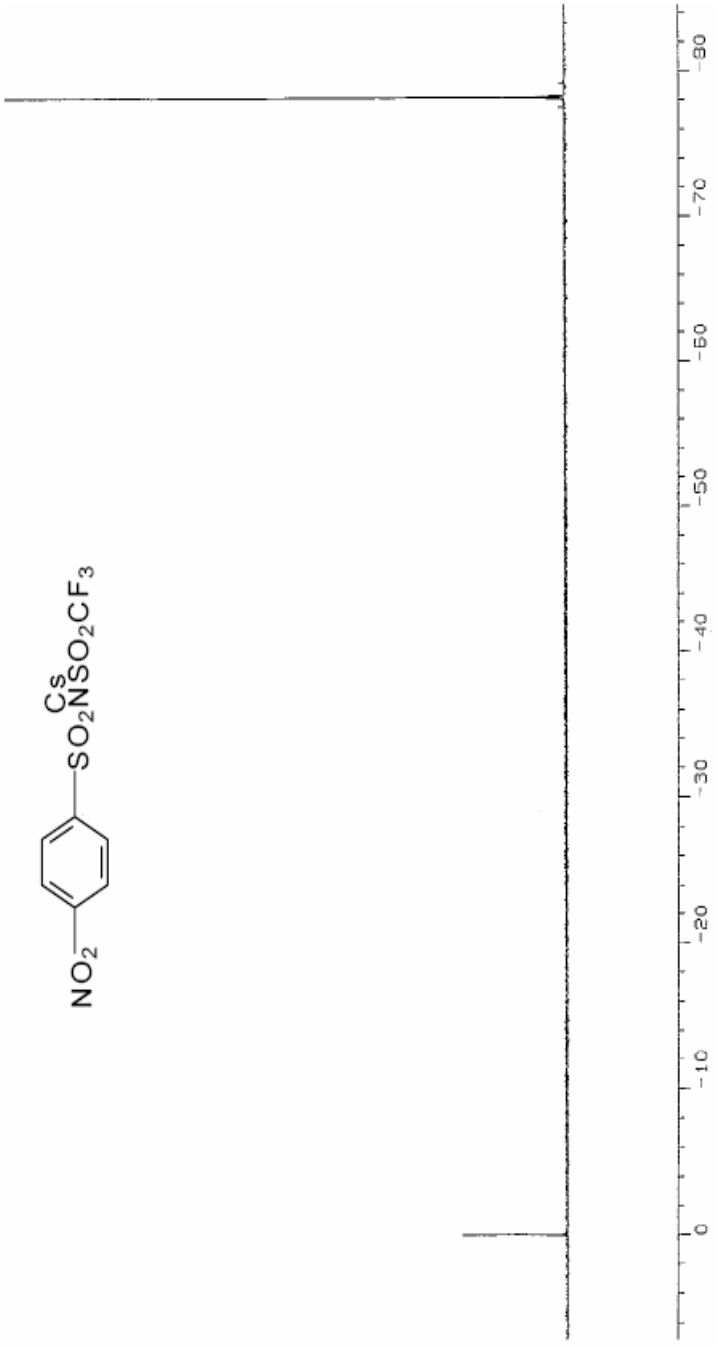


Figure A ^{1}H NMR spectrum of Comound **13a**, 200MHz, CD_3CN

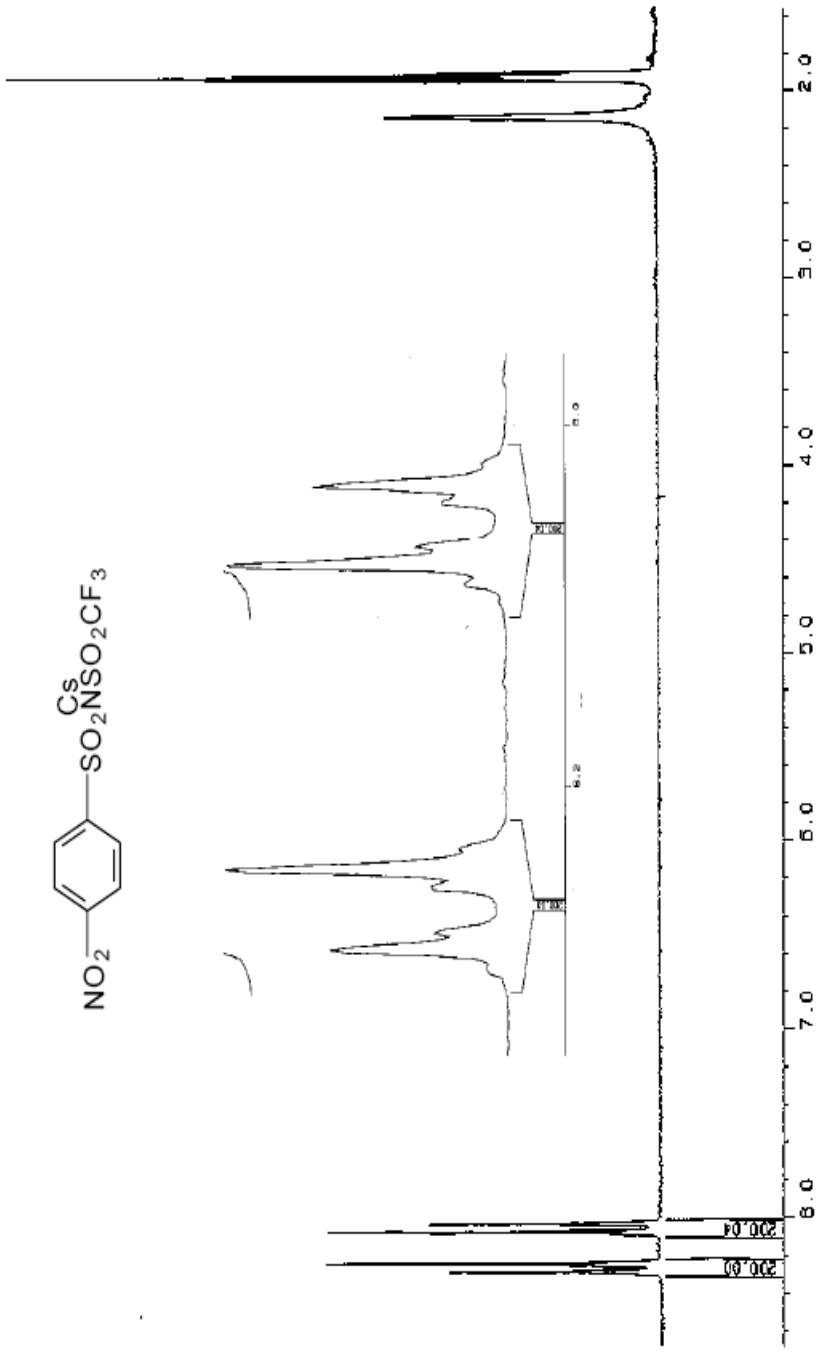


Figure A ^{19}F NMR spectrum of Comound **14a**, 200MHz, CD_3CN

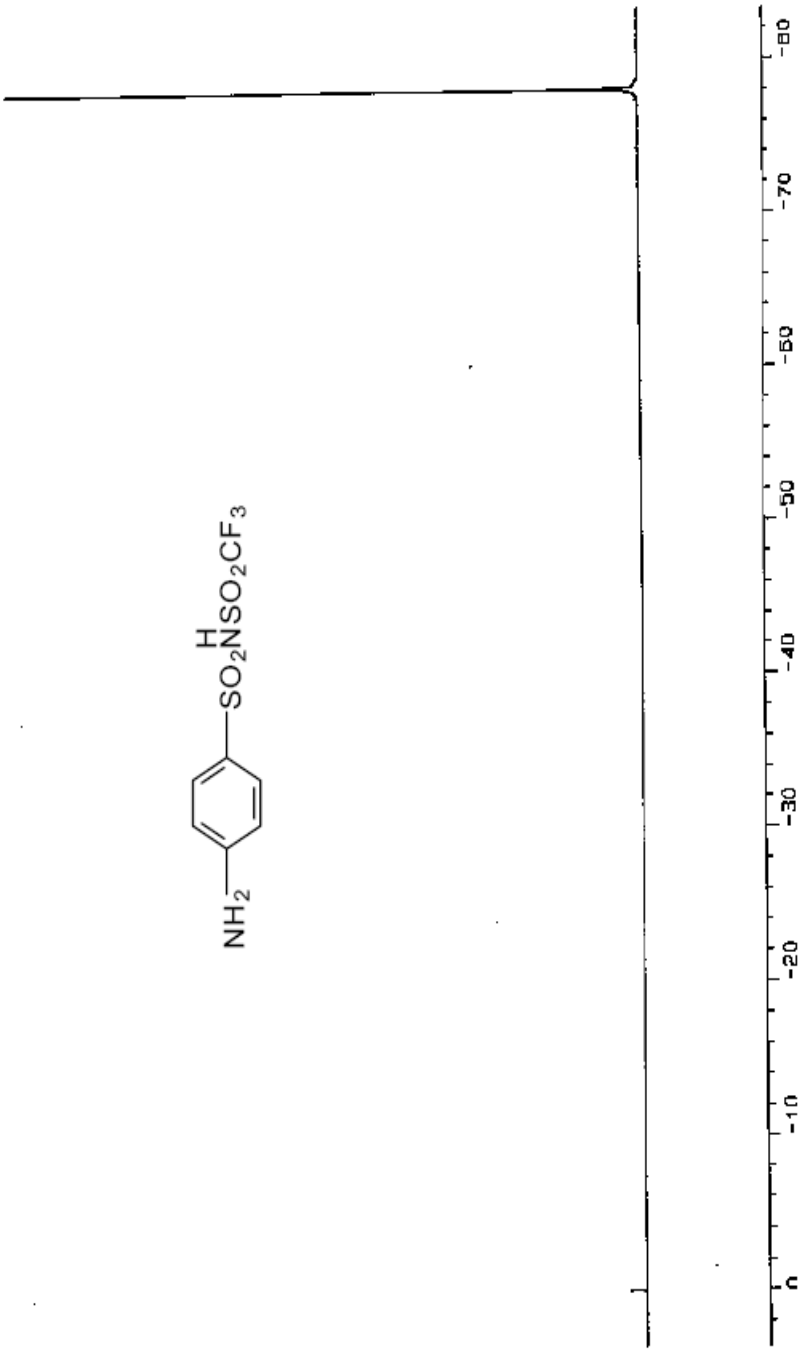


Figure A ^{1}H NMR spectrum of Comound **14a**, 200MHz, CD_3CN

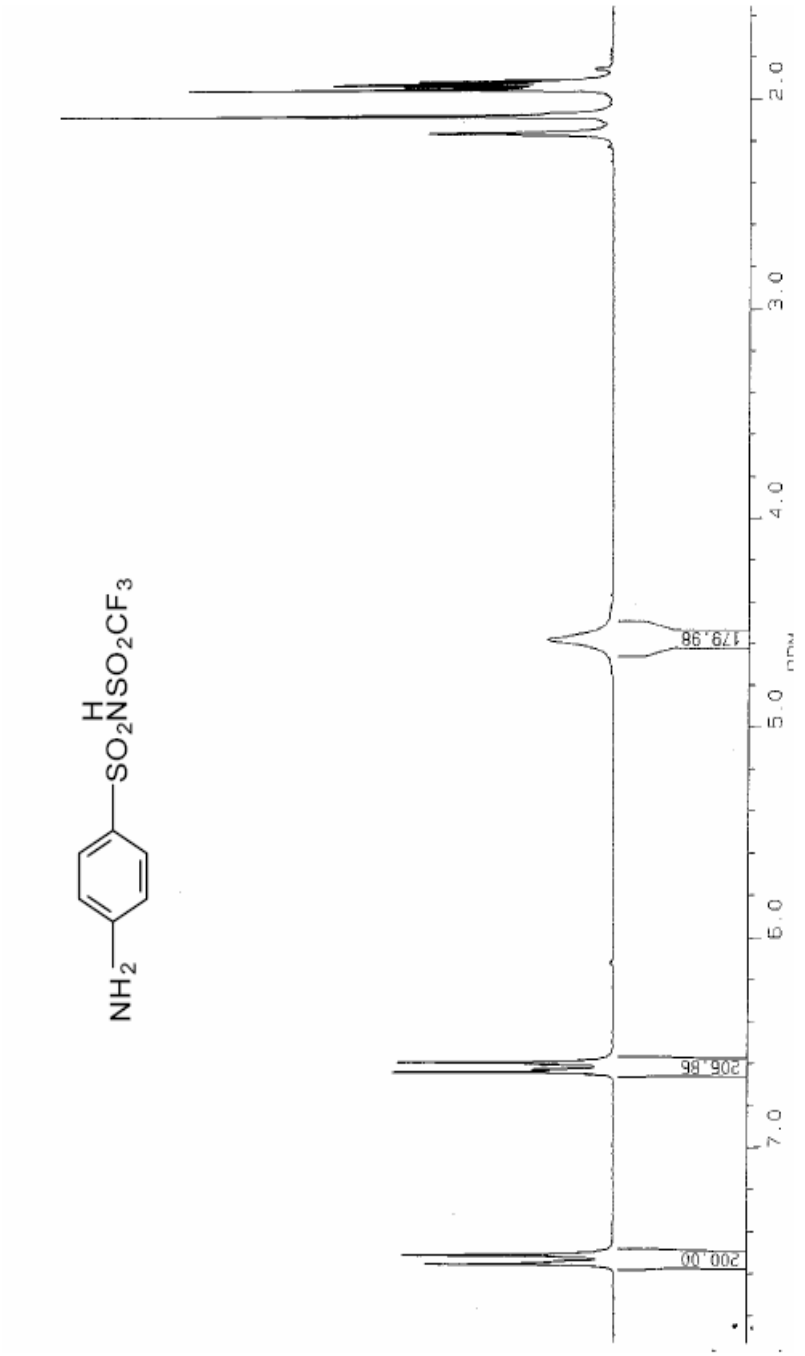


Figure A ^{1}H NMR spectrum of Comound **15a**, 200MHz, CD_3CN

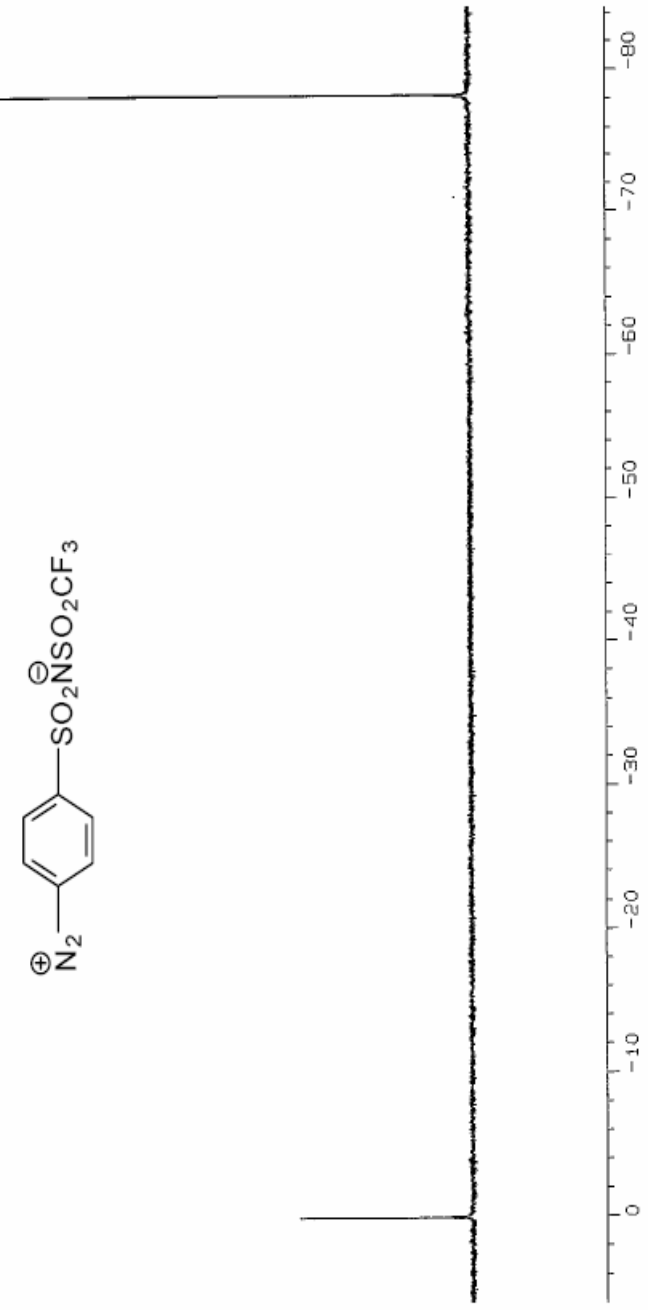


Figure A ^{1}H NMR spectrum of Comound **15a**, 200MHz, CD_3CN

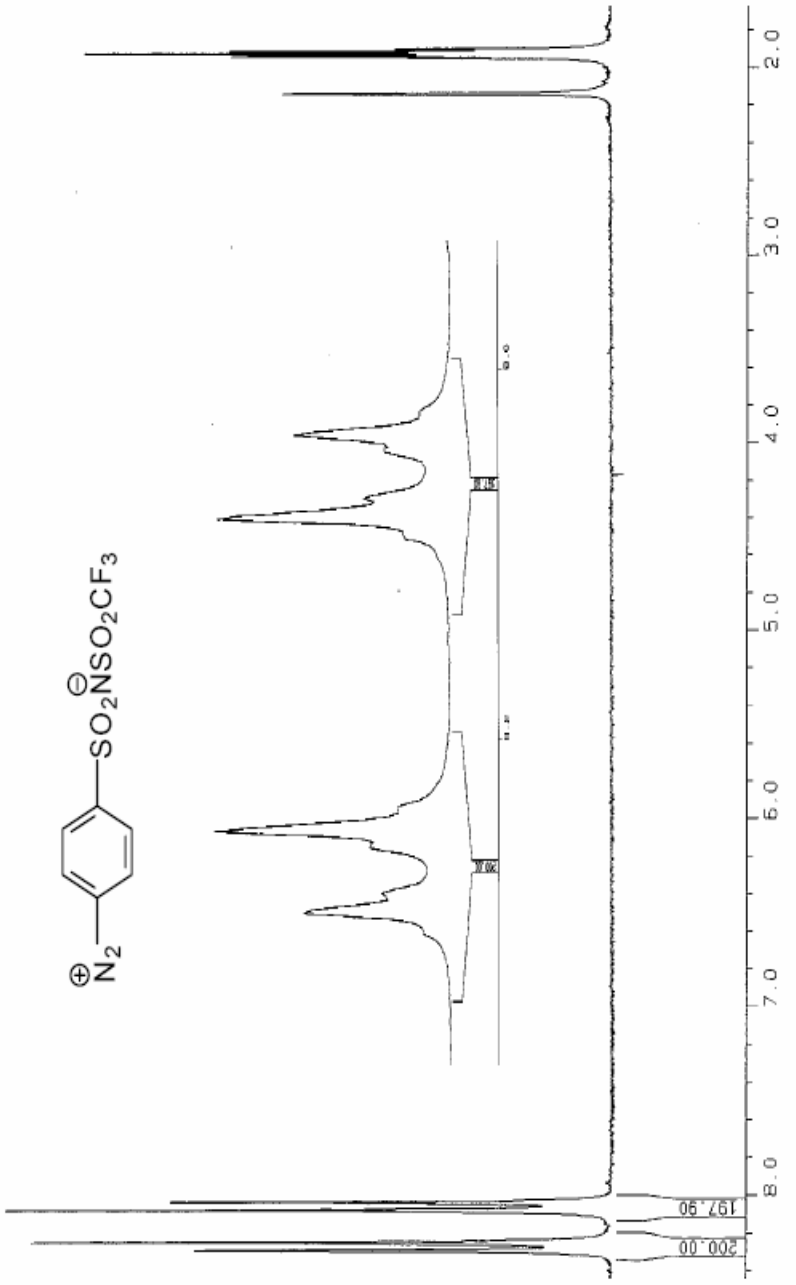


Figure A IR spectrum of Comound **15a**, 200MHz, CD_3CN

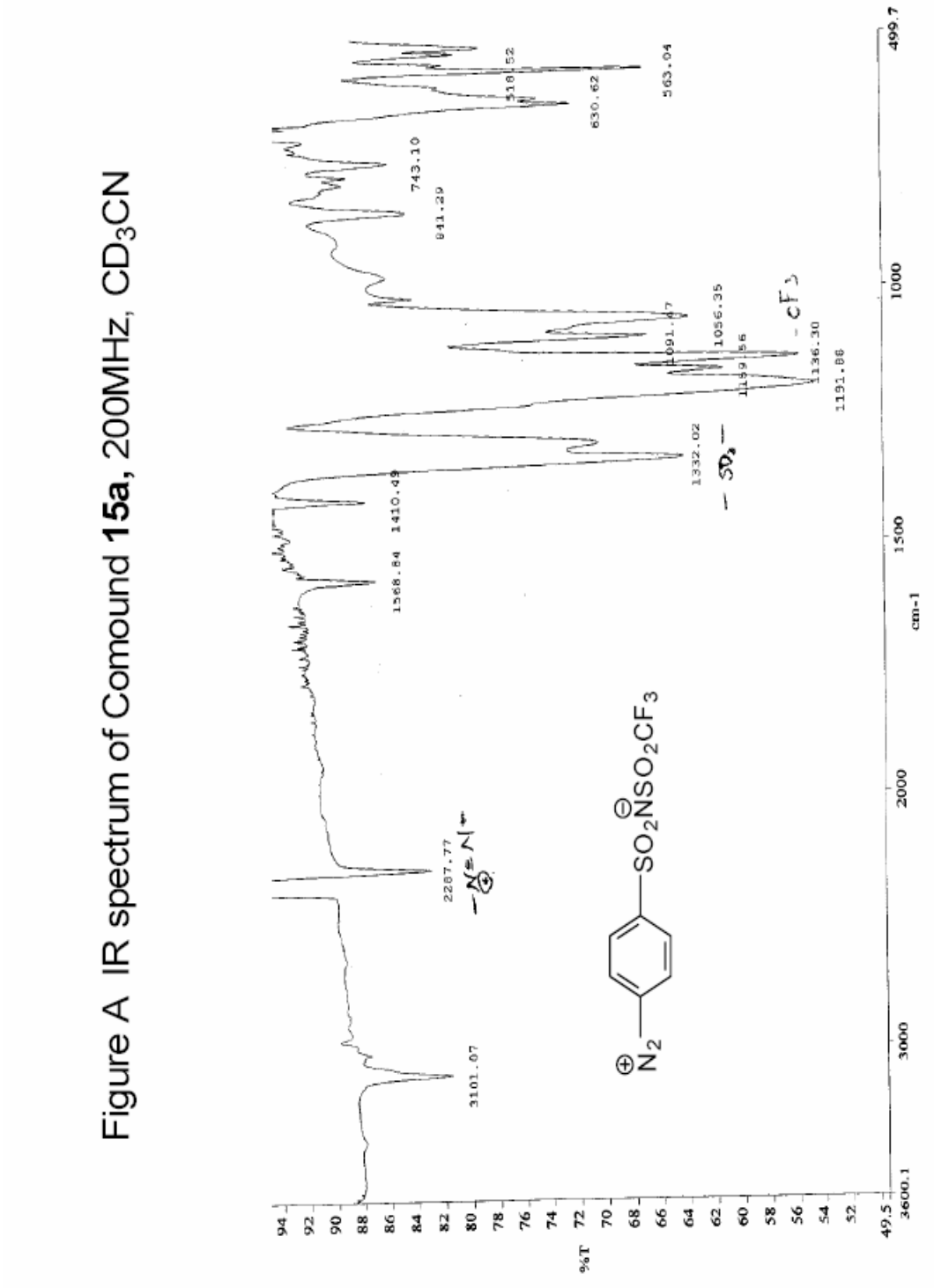


Figure A ^{19}F NMR spectrum of Comound **13b**, 200MHz, CD_3CN

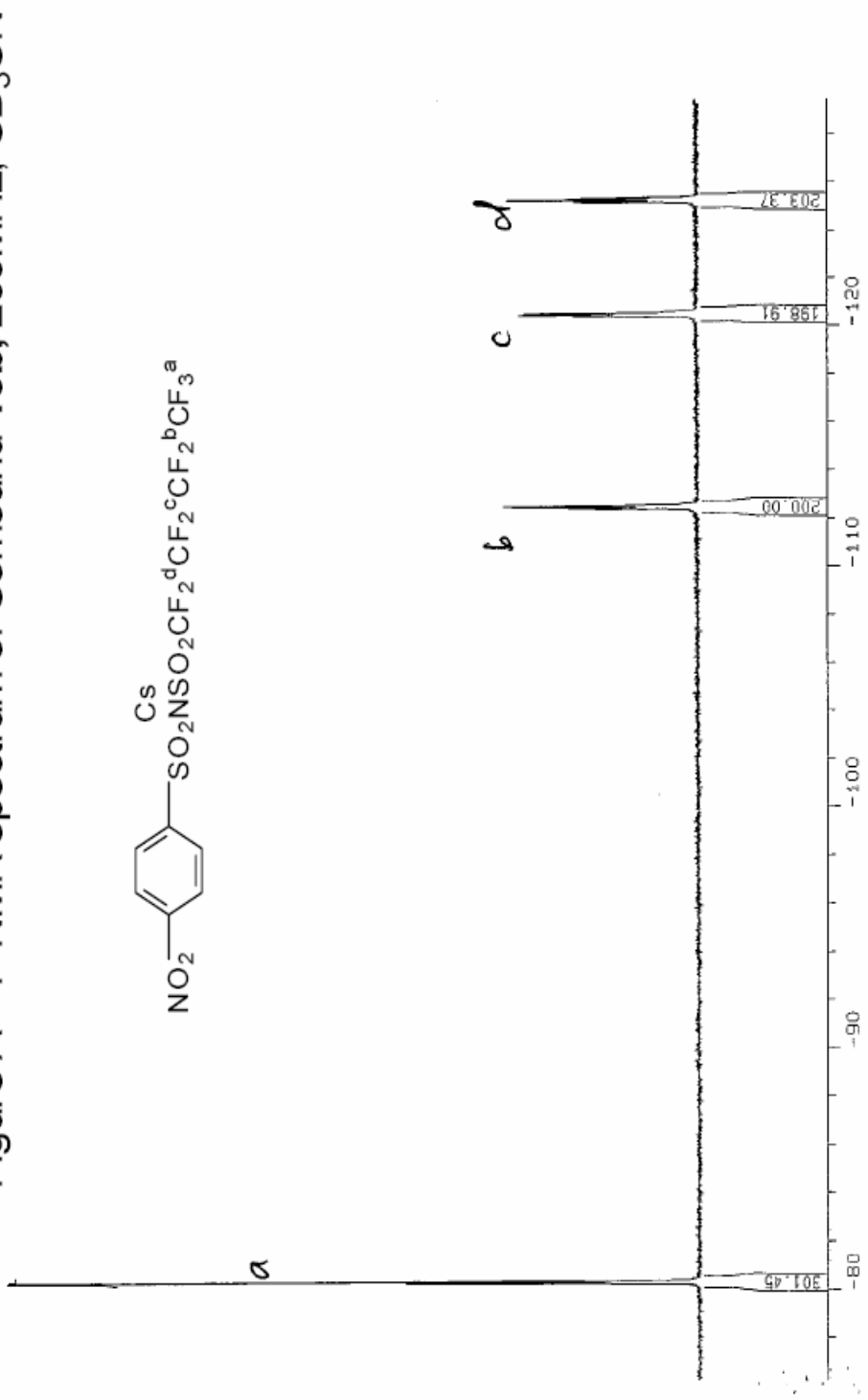


Figure A ^{1}H NMR spectrum of Comound **13b**, 200MHz, CD_3CN

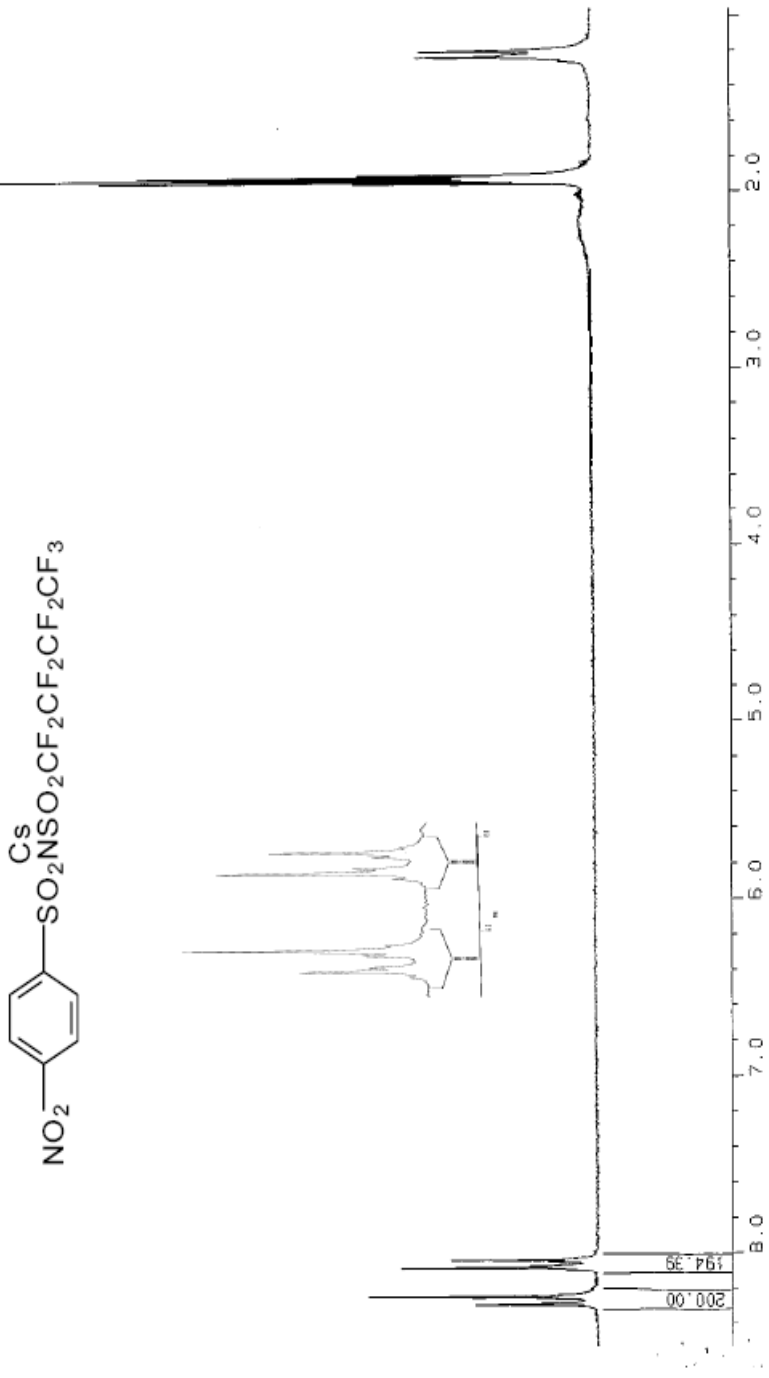


Figure A ^{19}F NMR spectrum of Comound **14b**, 200MHz, CD_3CN

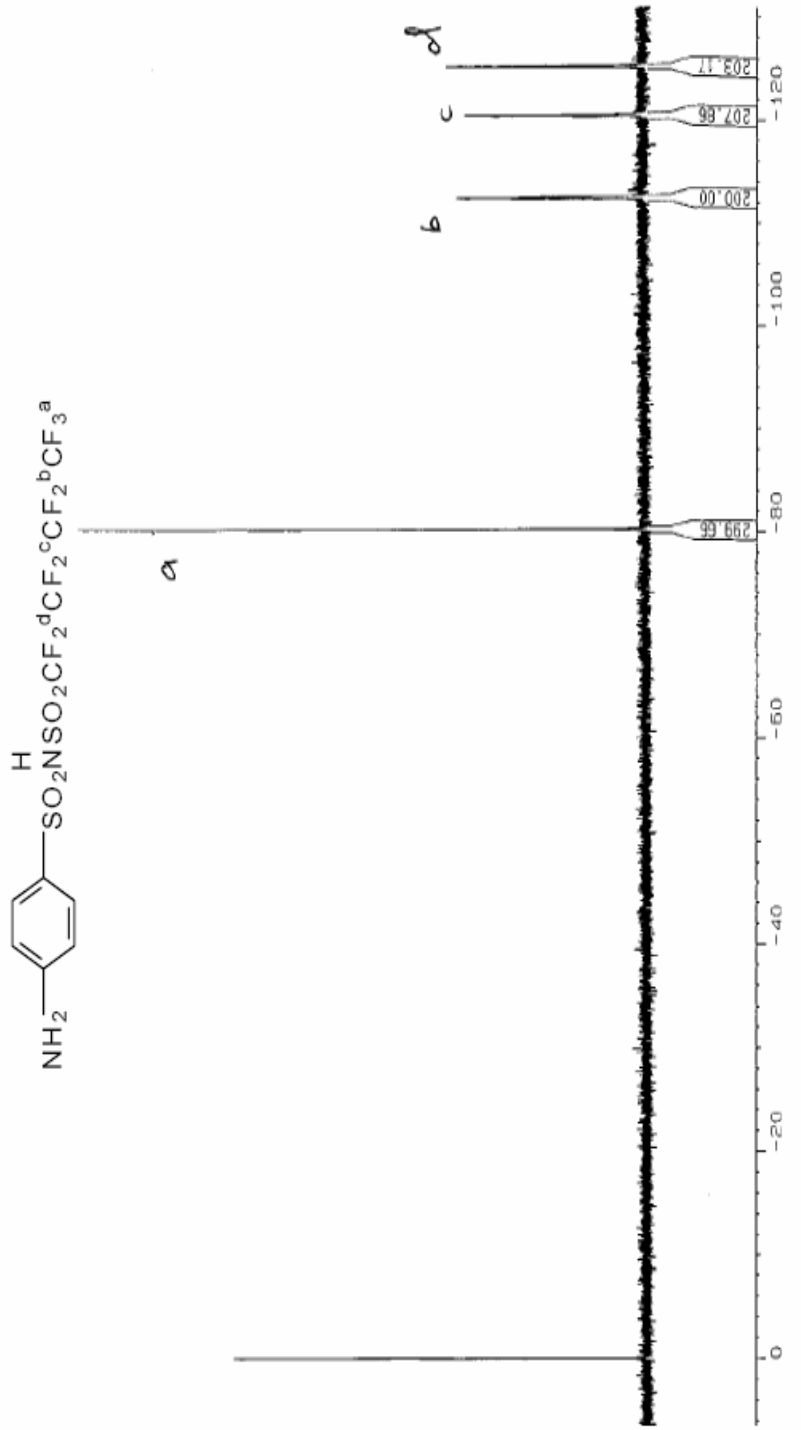


Figure A ^{1}H NMR spectrum of Comound **14b**, 200MHz, CD_3CN

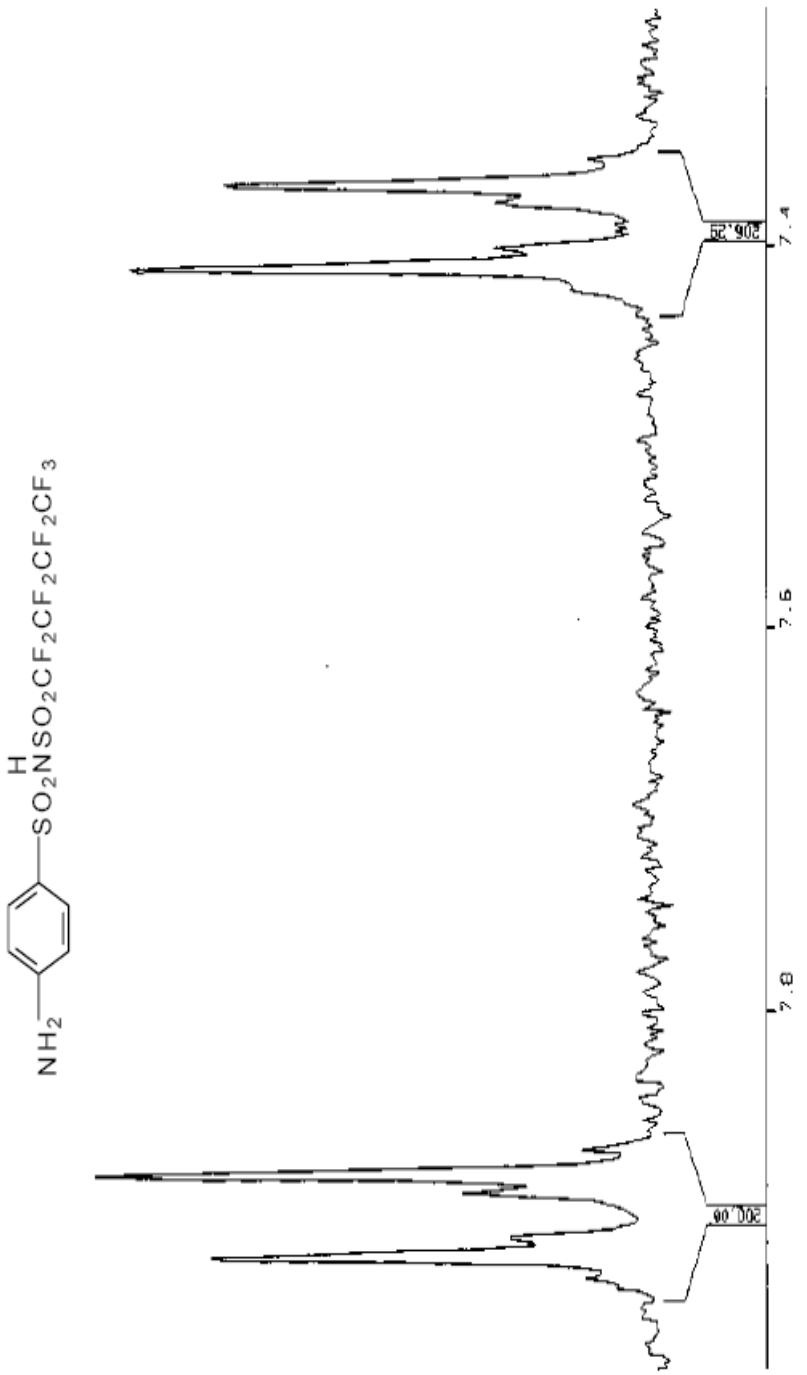


Figure A IR spectrum of Comound **14b**

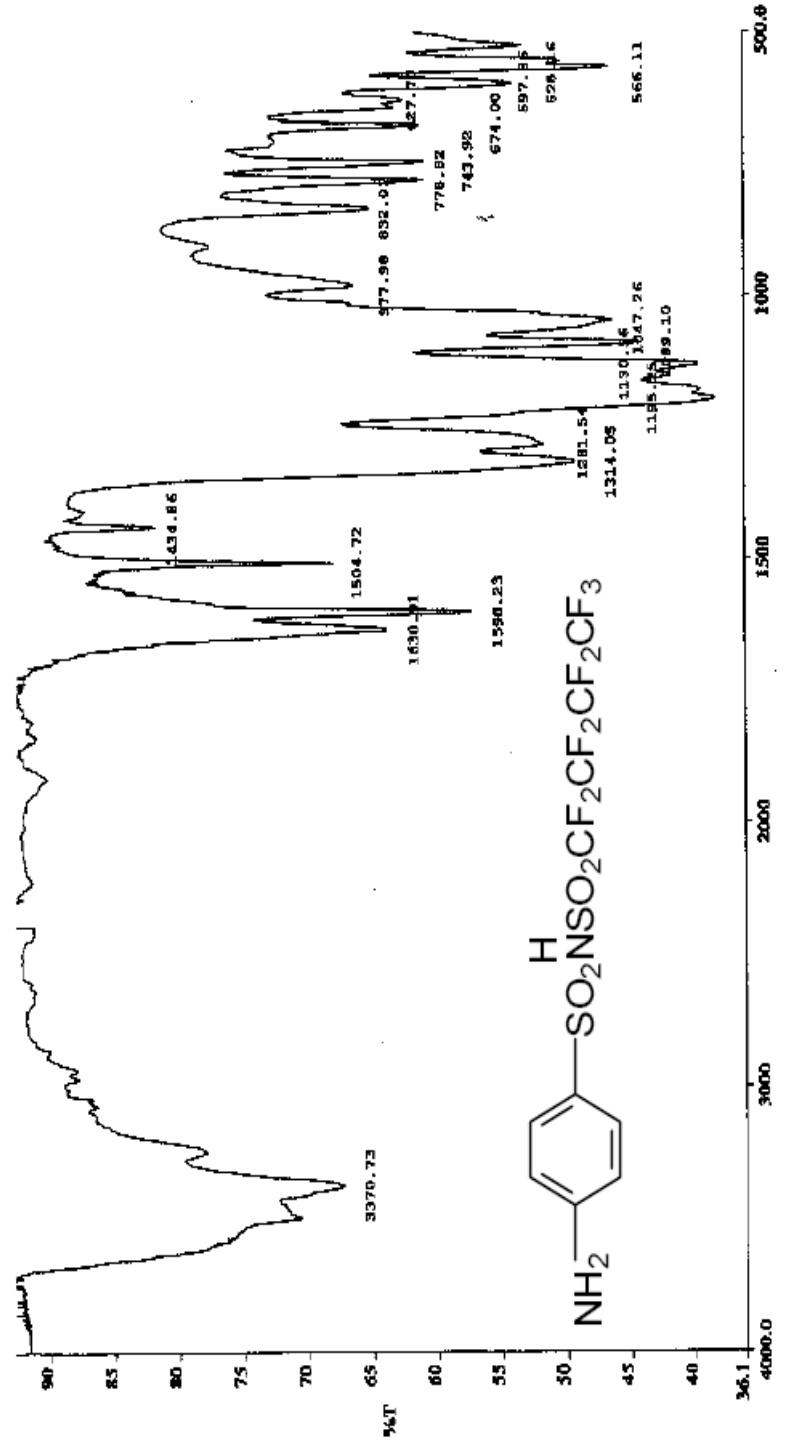


Figure A ^{19}F NMR spectrum of Comound **15b**, 200MHz, CD_3CN

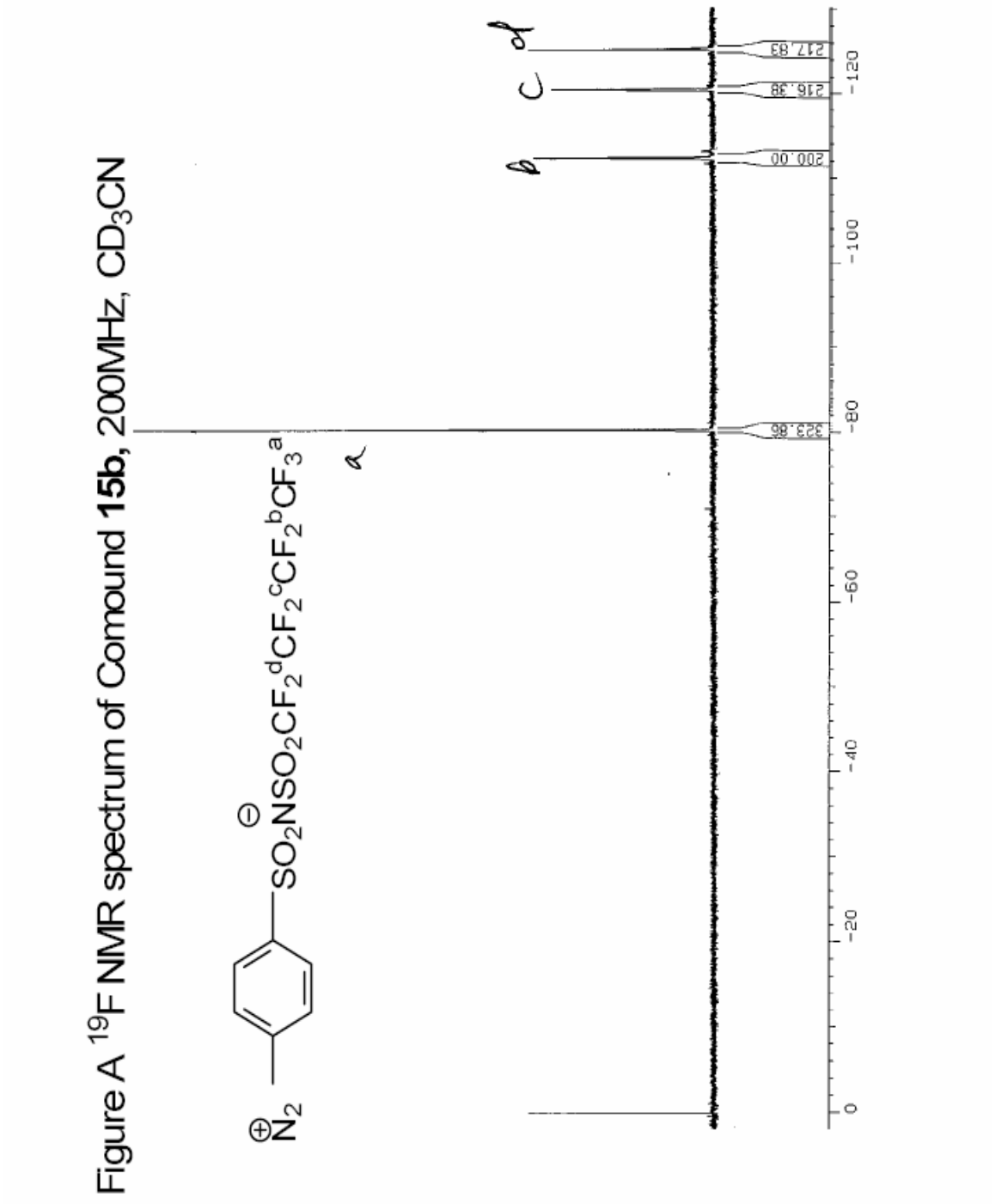
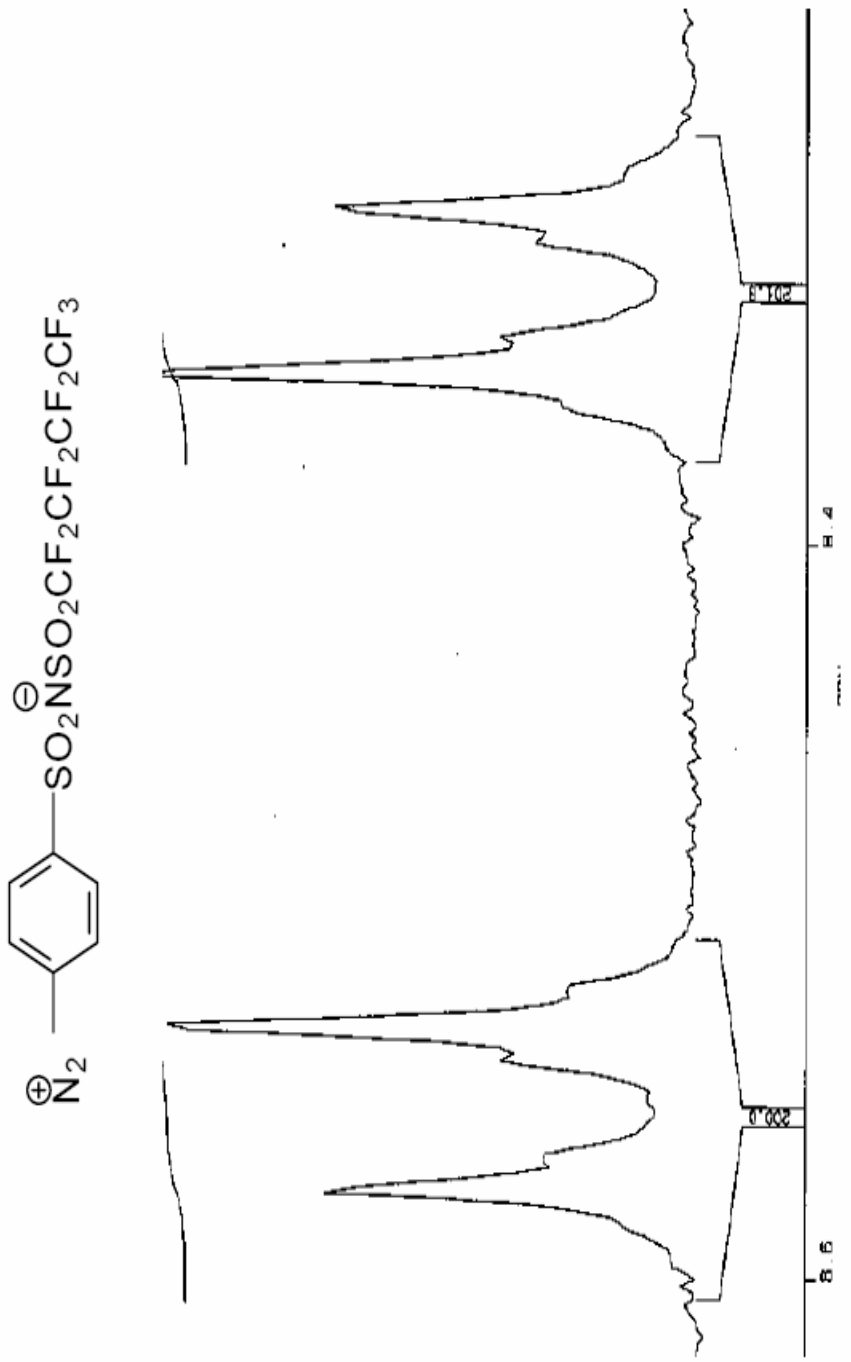


Figure A ^{1}H NMR spectrum of Comound **15b**, 200MHz, CD_3CN



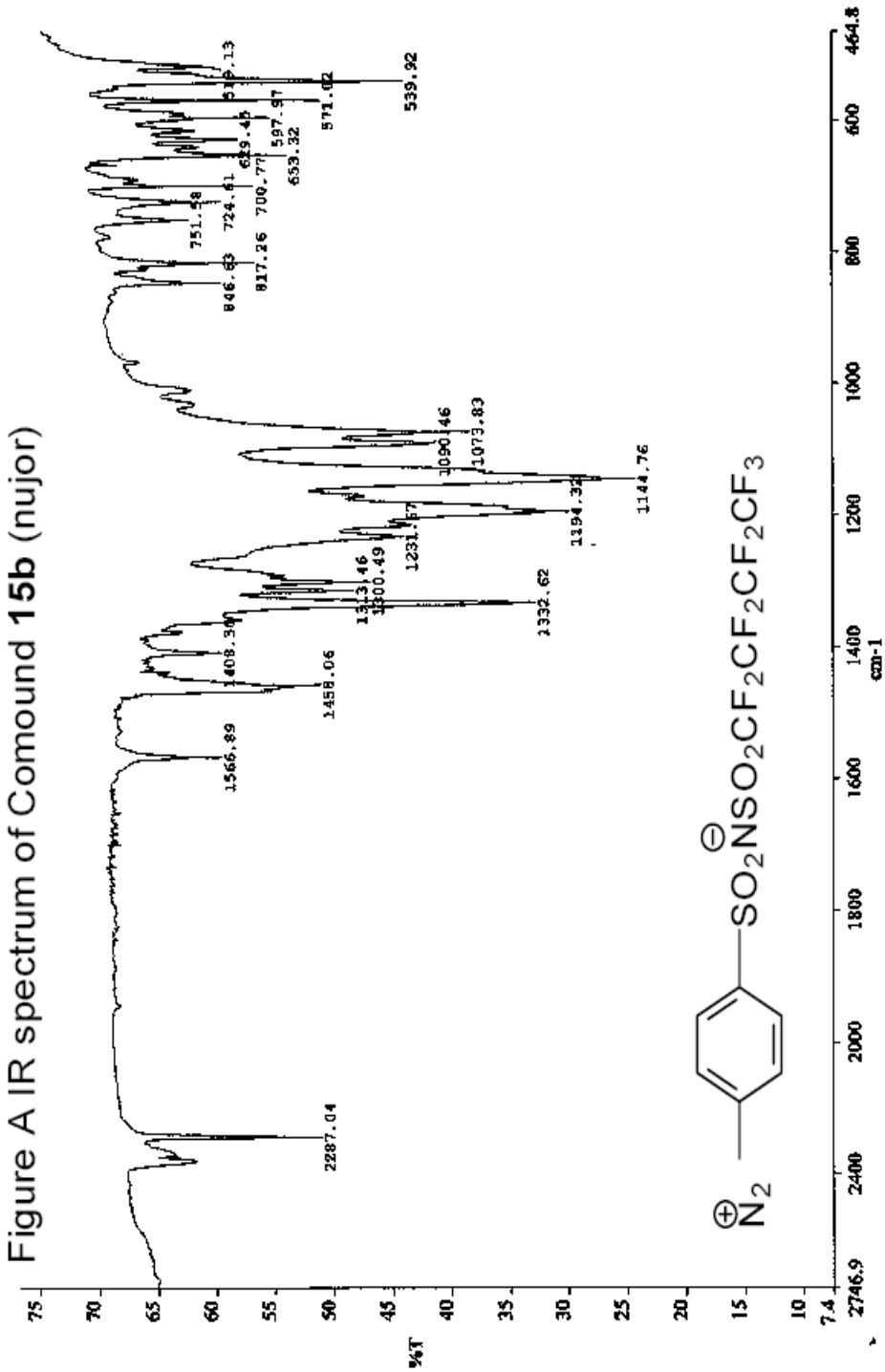


Figure A IR spectrum of Comound 15b (nujor)
2287.04
1566.89
1458.06
1408.38
1332.62
1231.67
1194.32
1144.76
1090.46
1073.83
846.63
817.26
751.48
724.61
700.77
653.32
597.97
571.62
539.92
%T
cm-1
$\oplus N_2$
$SO_2NSO_2CF_2CF_2CF_2CF_3$

Figure A ^{1}H NMR spectrum of Compound **17a**, 200MHz, CD_3CN

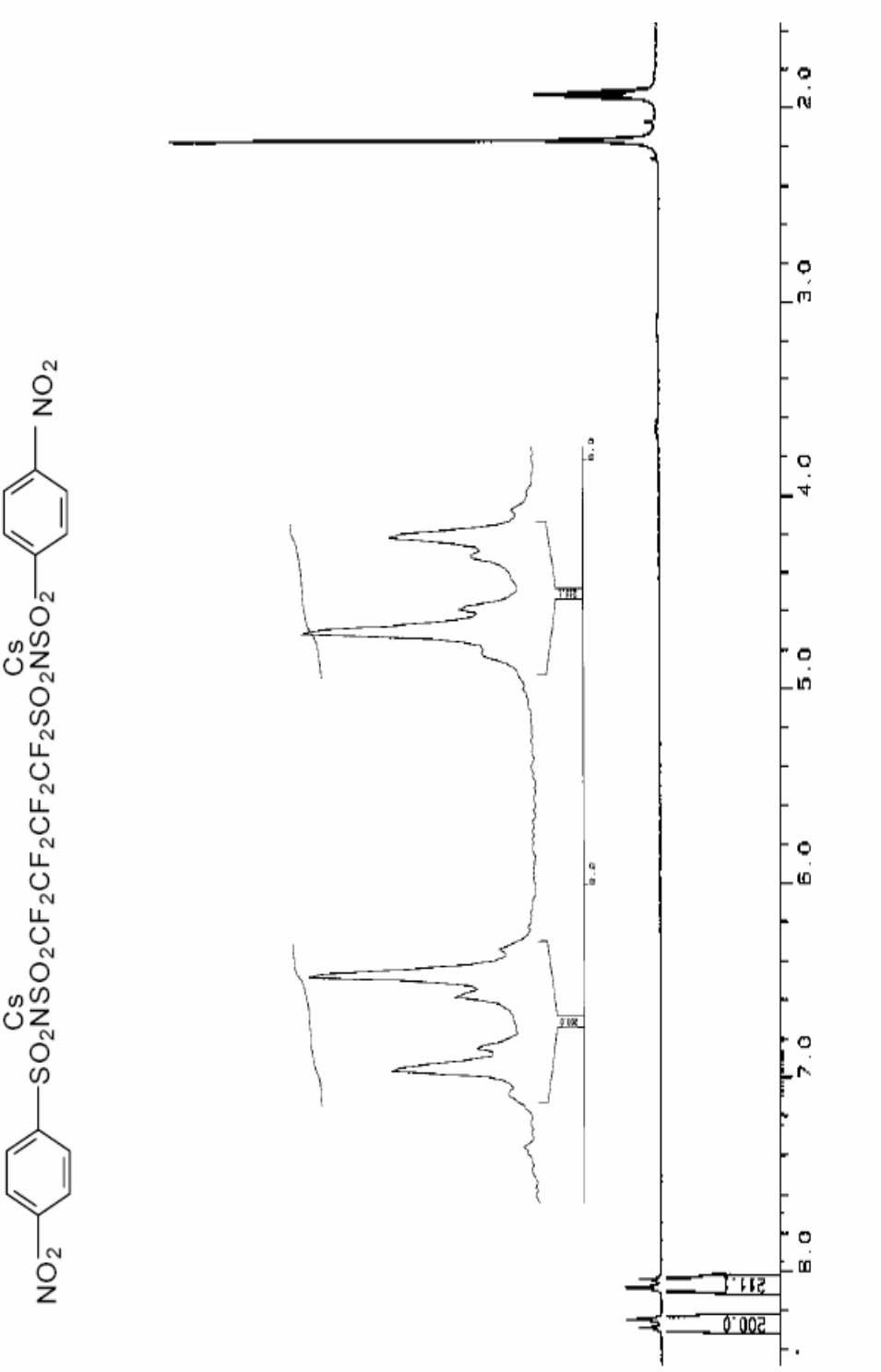


Figure A ^{19}F NMR spectrum of Comound **17a**, 200MHz, CD_3CN

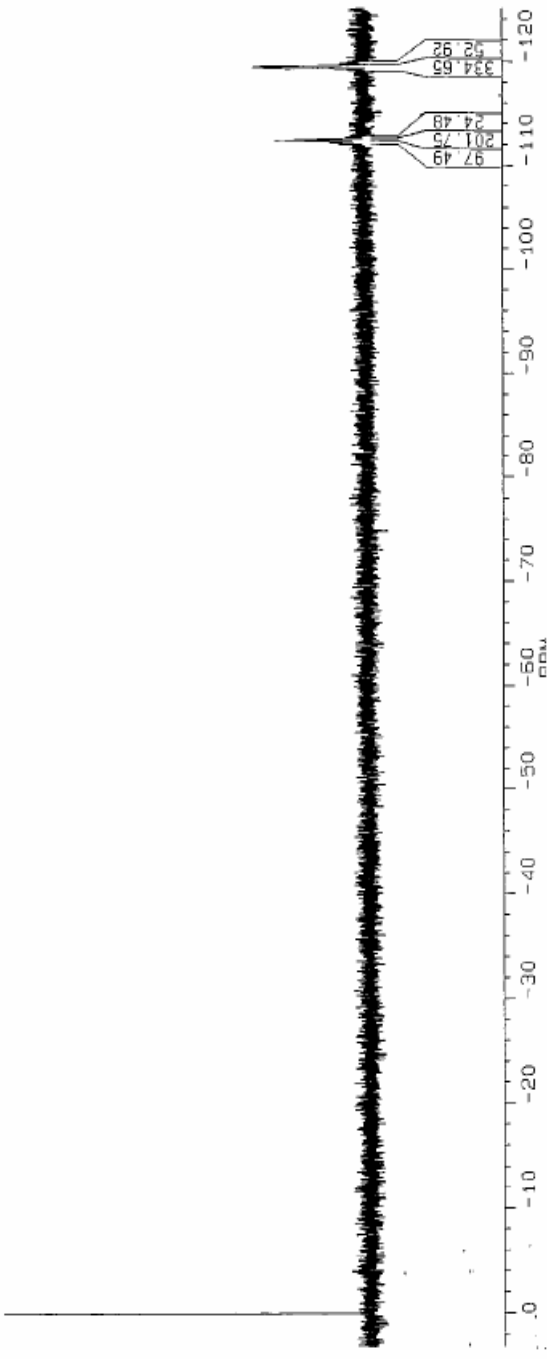


Figure A ^{1}H NMR spectrum of Compound **18a**, 200MHz, CD_3CN

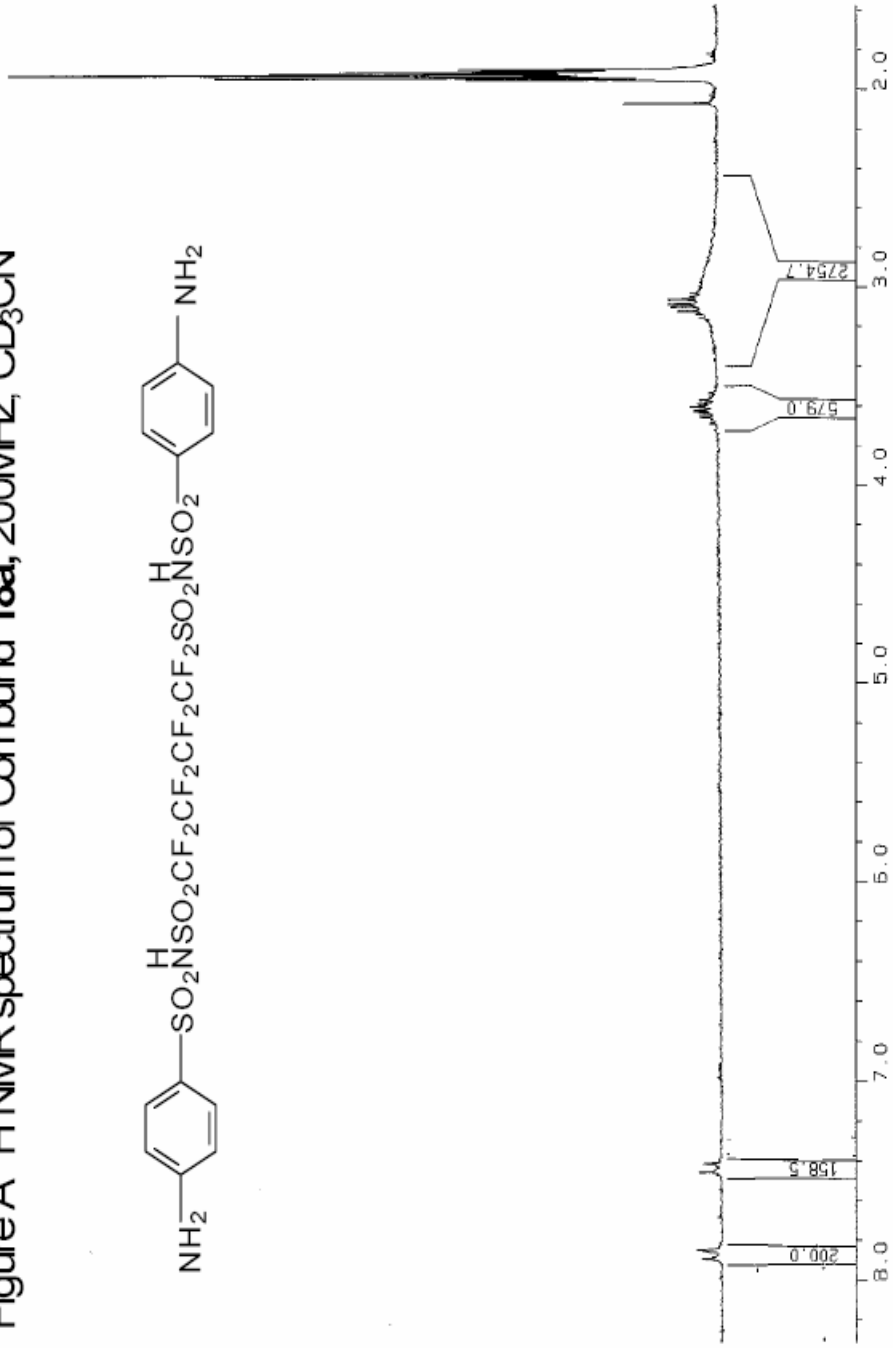


Figure A ^{19}F NMR spectrum of Comound **18a**, 200MHz, CD_3CN+DMSO

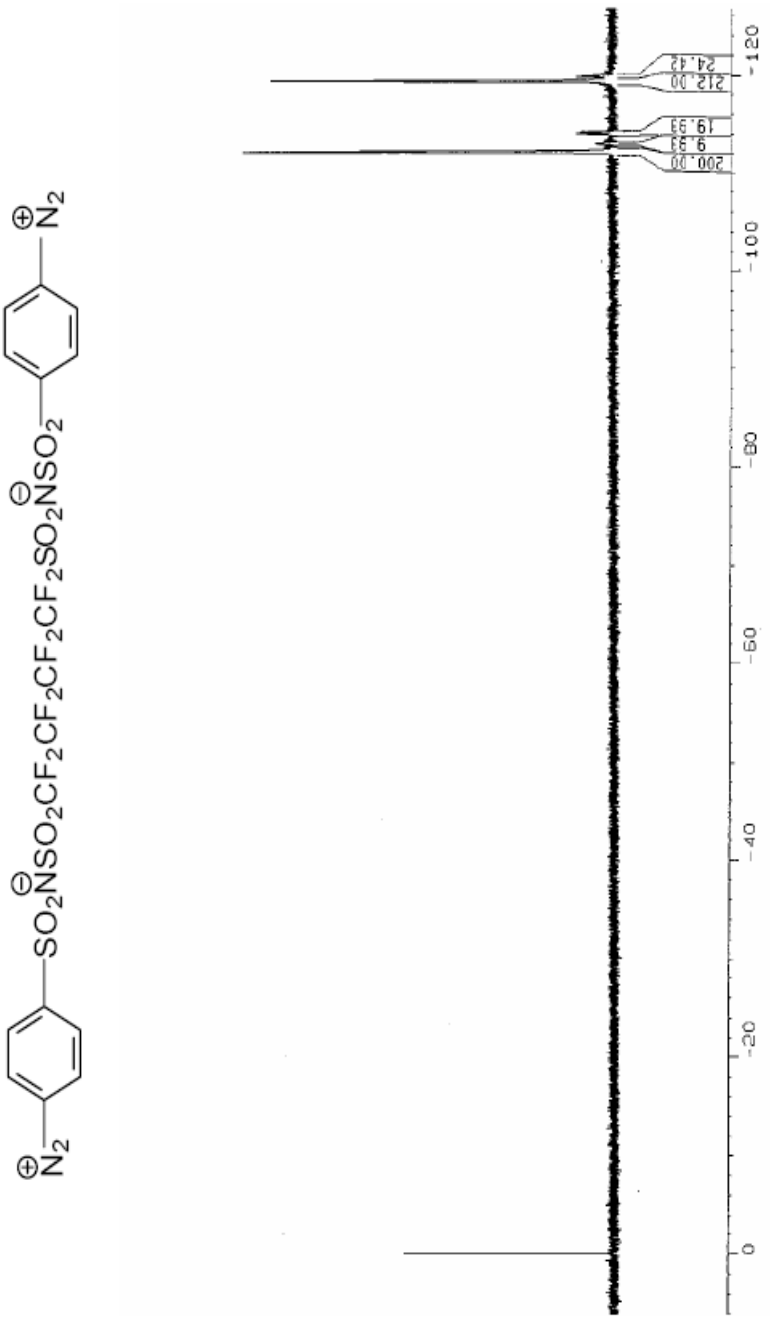


Figure A IR spectrum of Comound **18a**, 200MHz, CD_3CN

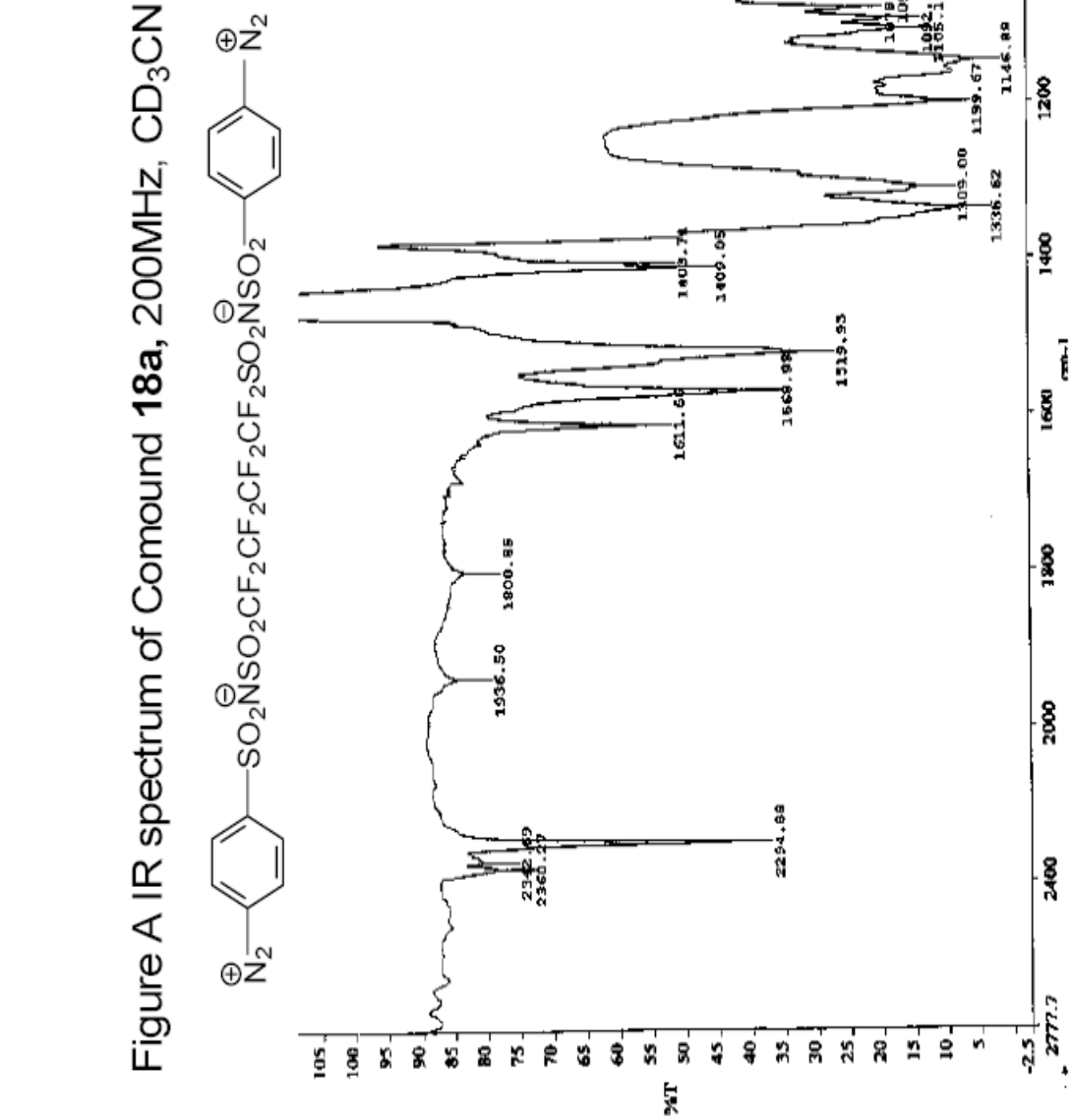


Figure A ^{19}F NMR spectrum of Comound **16b**, 200MHz, CD_3CN

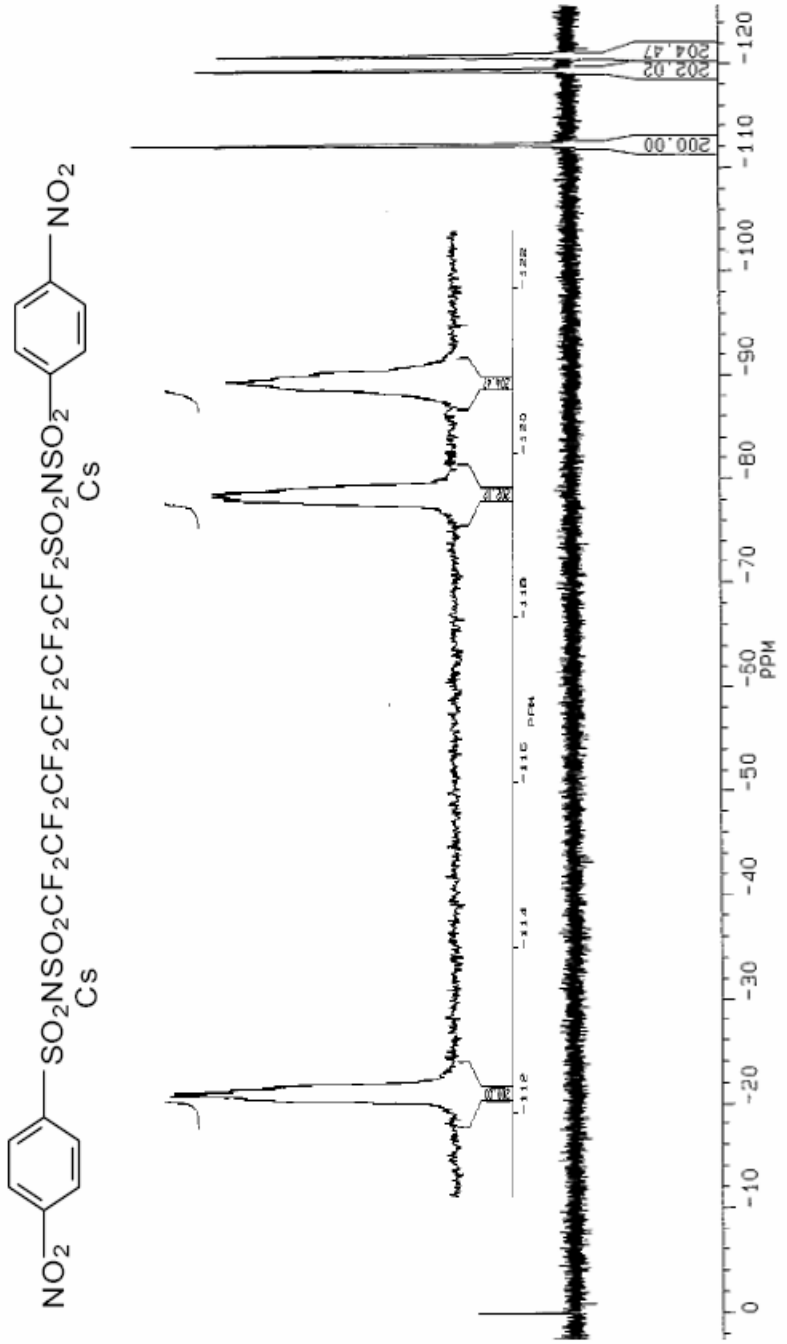


Figure A ^{19}F NMR spectrum of Comound **16b**, 200MHz, CD_3CN

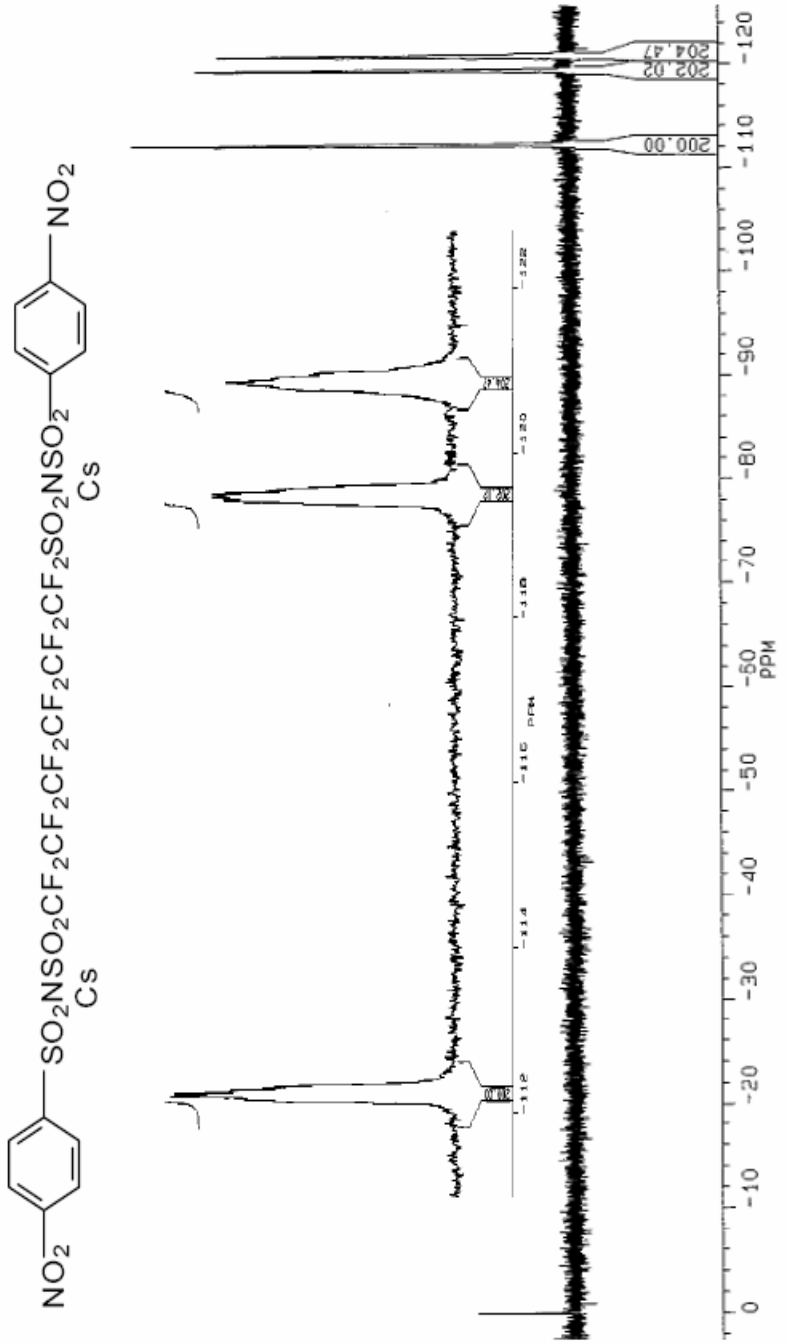


Figure A ^{19}F NMR spectrum of Comound **17b**, 200MHz, CD_3CN

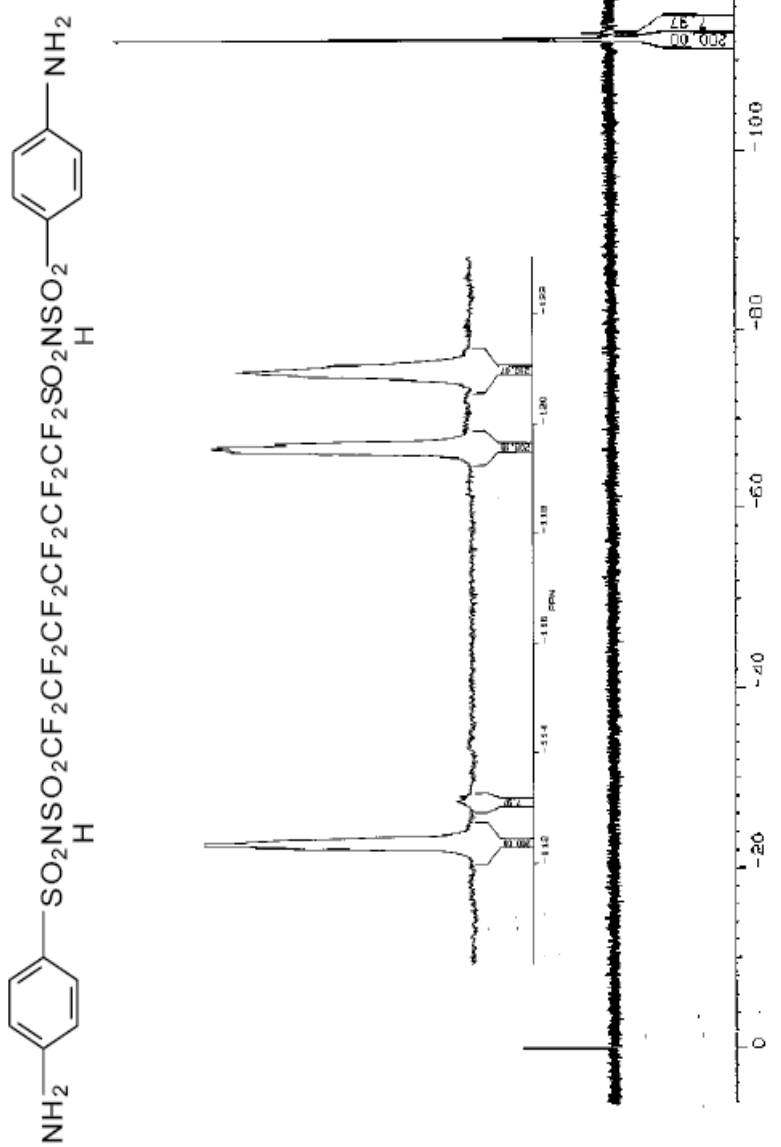


Figure A ^{1}H NMR spectrum of Comound **17b**, 200MHz, CD_3CN

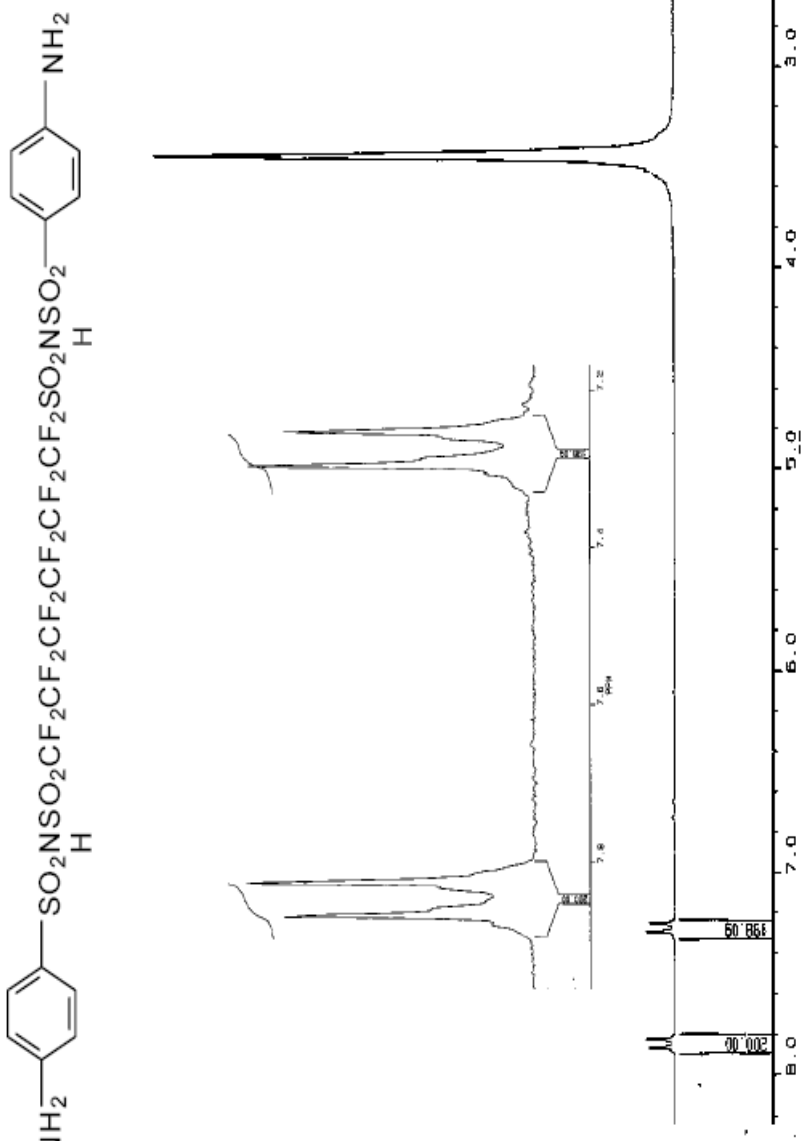
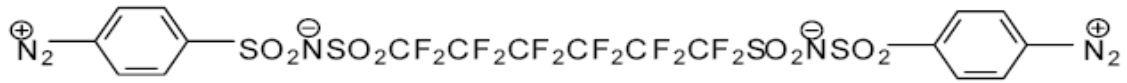


Figure A ^{19}F NMR spectrum of Comound **18b,** 200MHz, DMSO



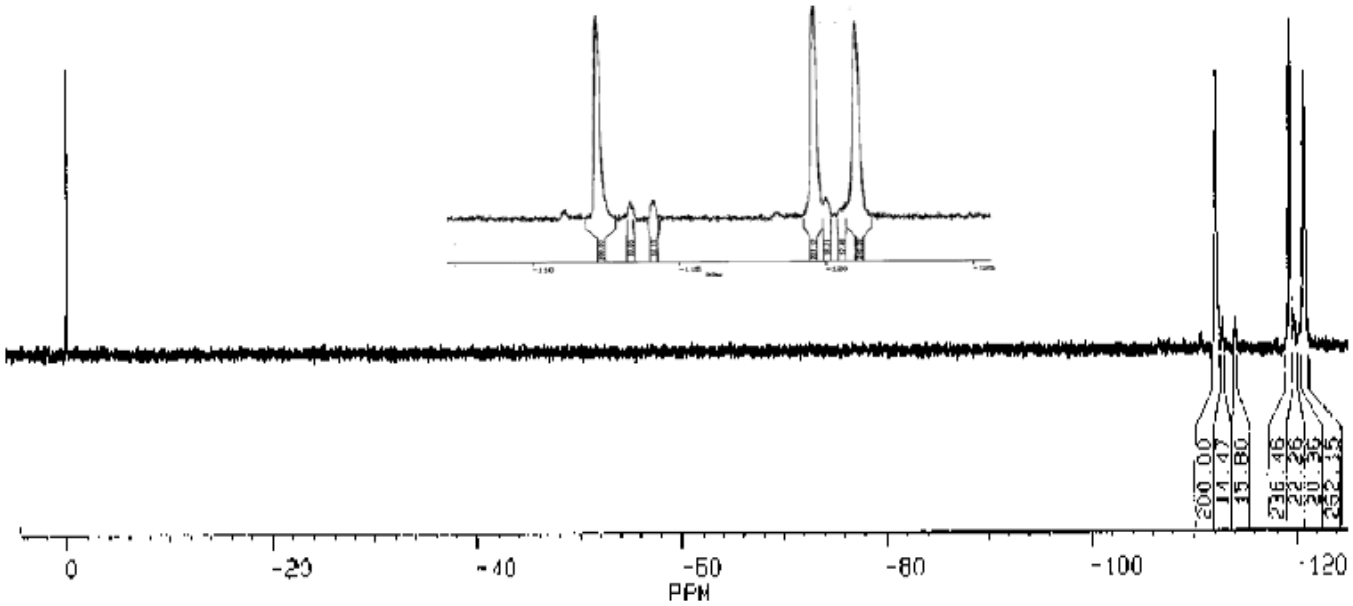


Figure A ^{1}H NMR spectrum of Comound **18b**, 200MHz, DMSO

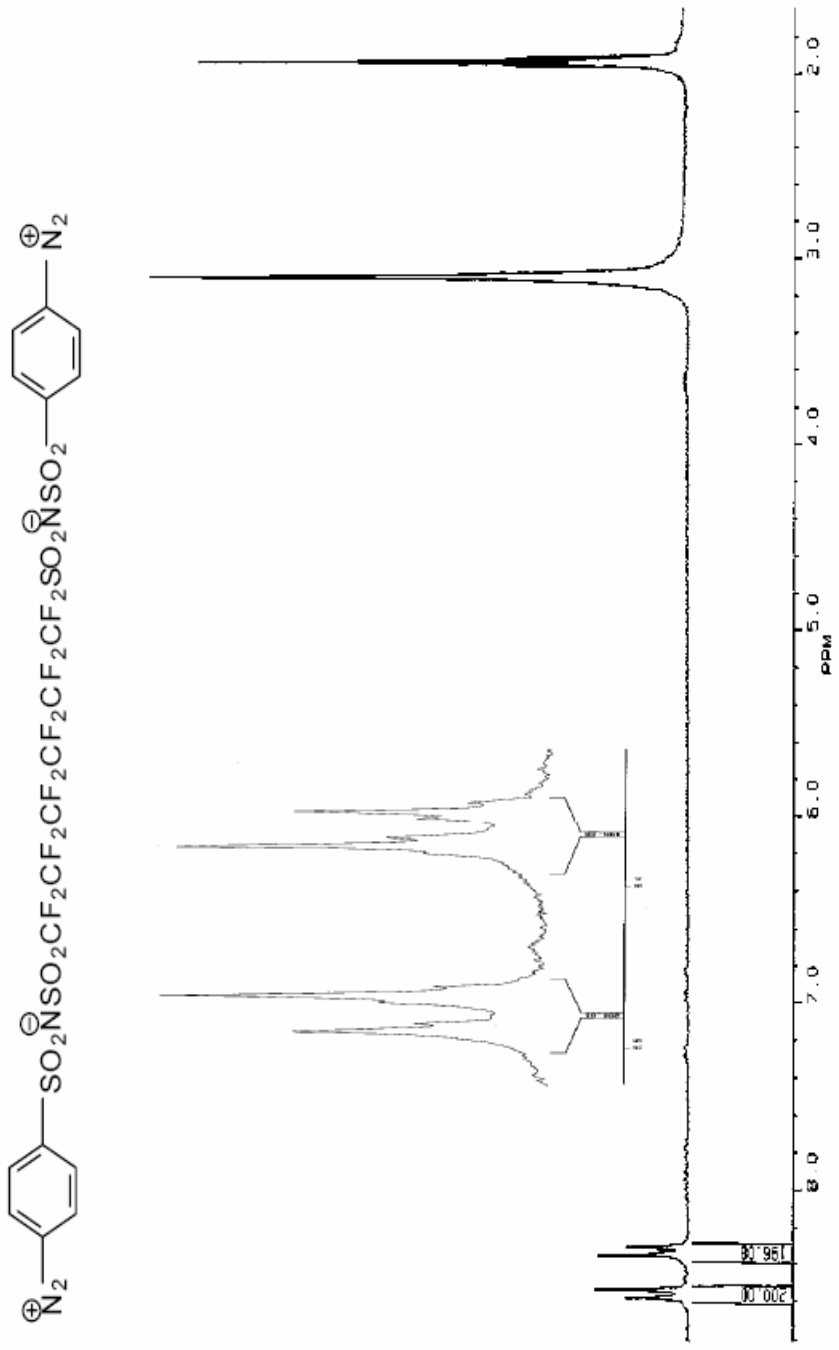


Figure A IR spectrum of Comound **18b** (nujor)

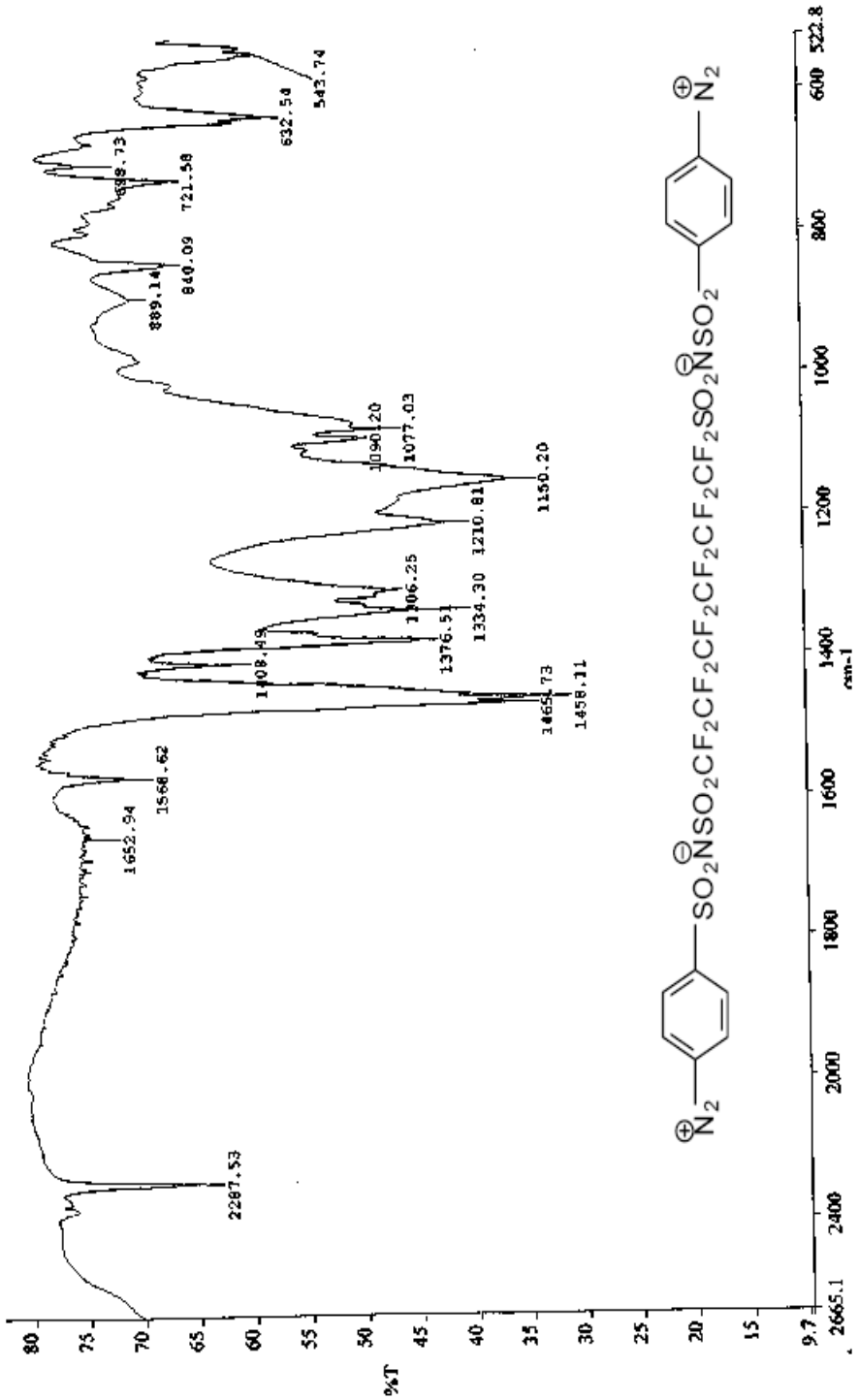


Figure A ^{19}F NMR spectrum of Comound **19a**, 200MHz, CD_3CN

$F^{e}SO_2CF_2{}^{d}CF_2{}^{c'}CF_2{}^{c}CF_2{}^{b}SO_2NSO_2CF_3{}^{a}$
Na

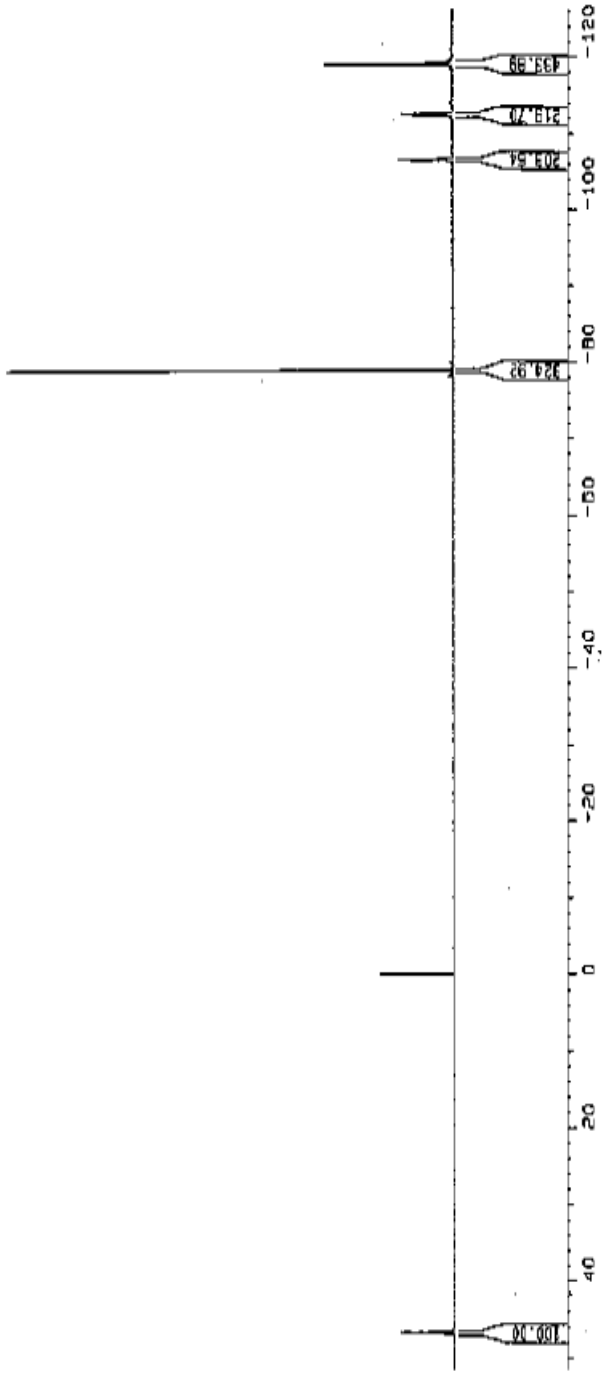
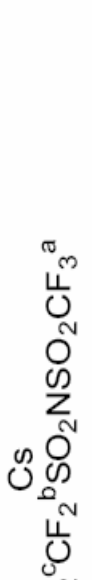


Figure A ^{19}F NMR spectrum of Comound **20a**, 200MHz, CD_3CN



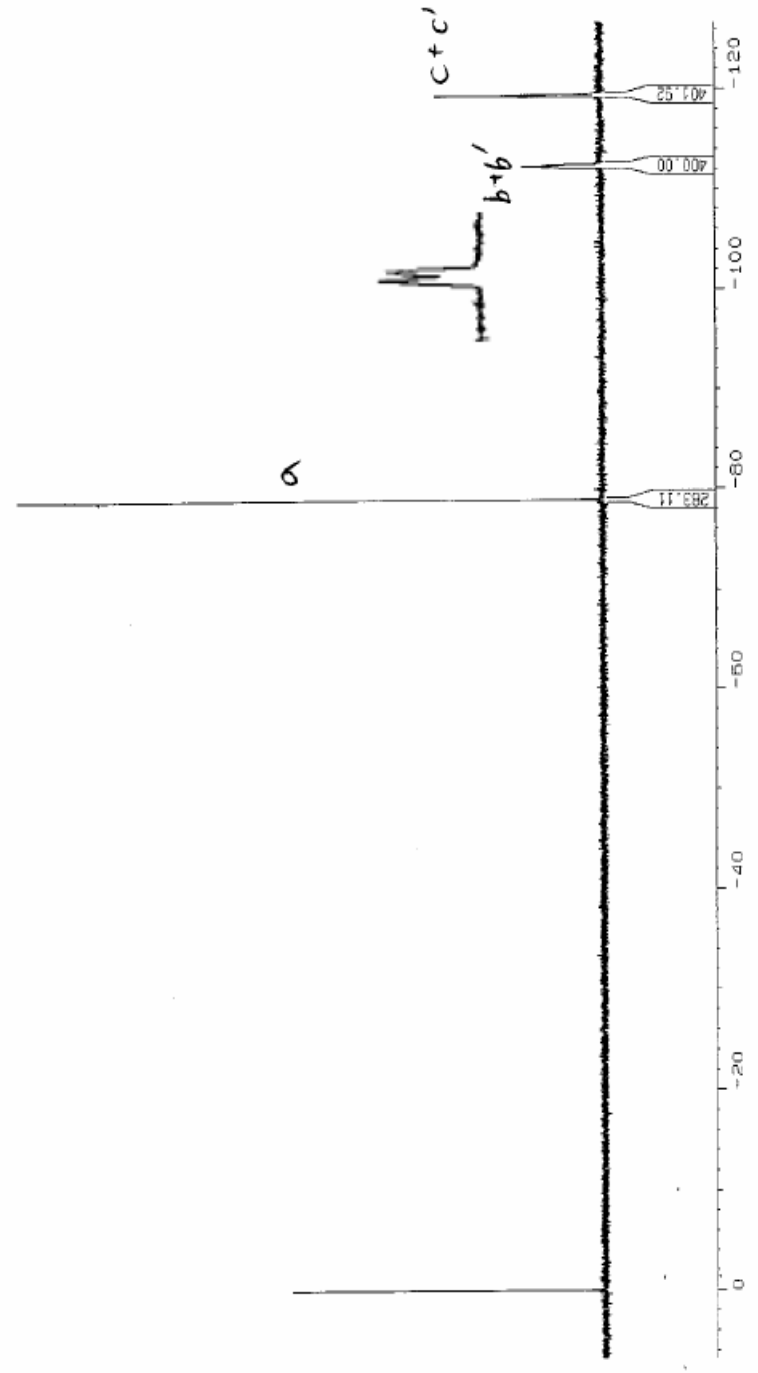


Figure A ^{1}H NMR spectrum of Comound **20a**, 200MHz, CD_3CN

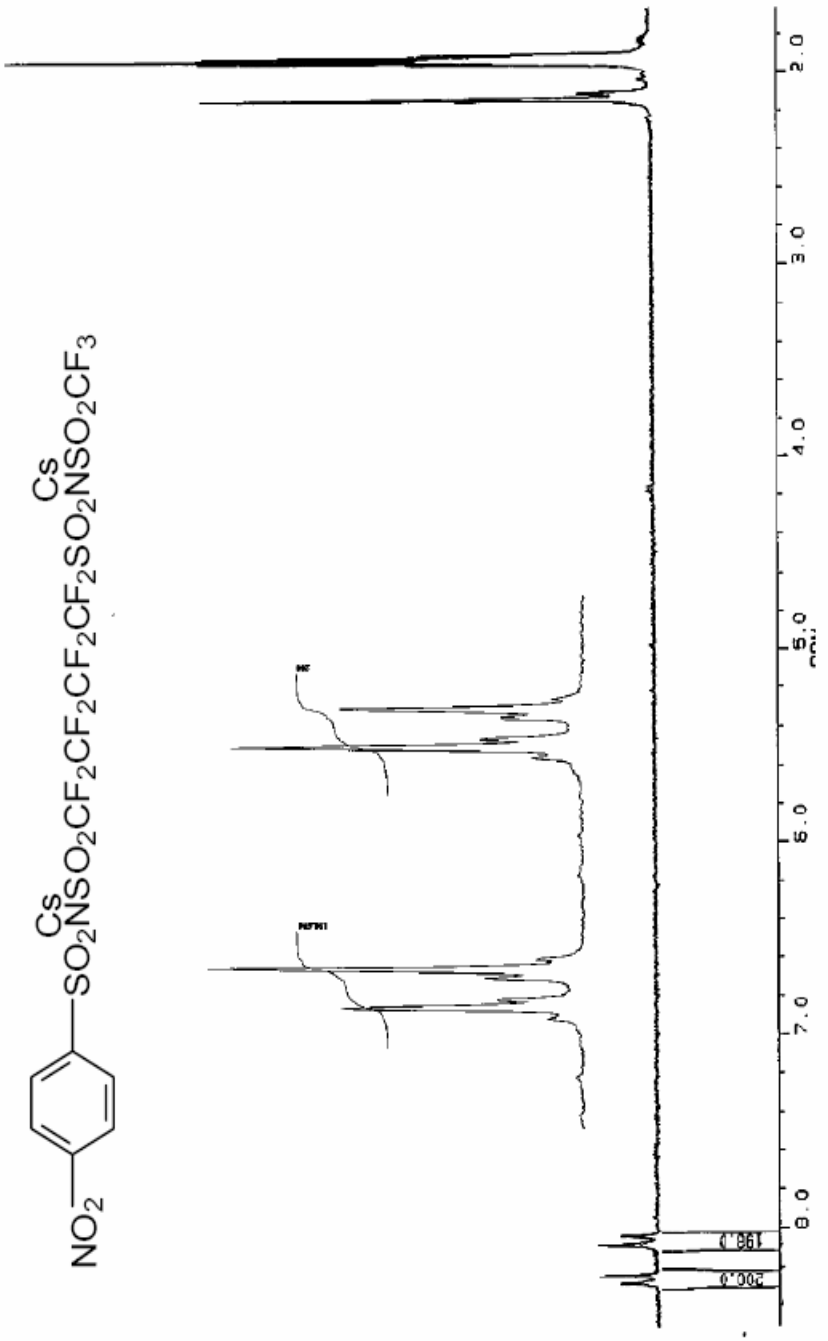


Figure A ^{19}F NMR spectrum of Comound **21a**, 200MHz, CD_3CN

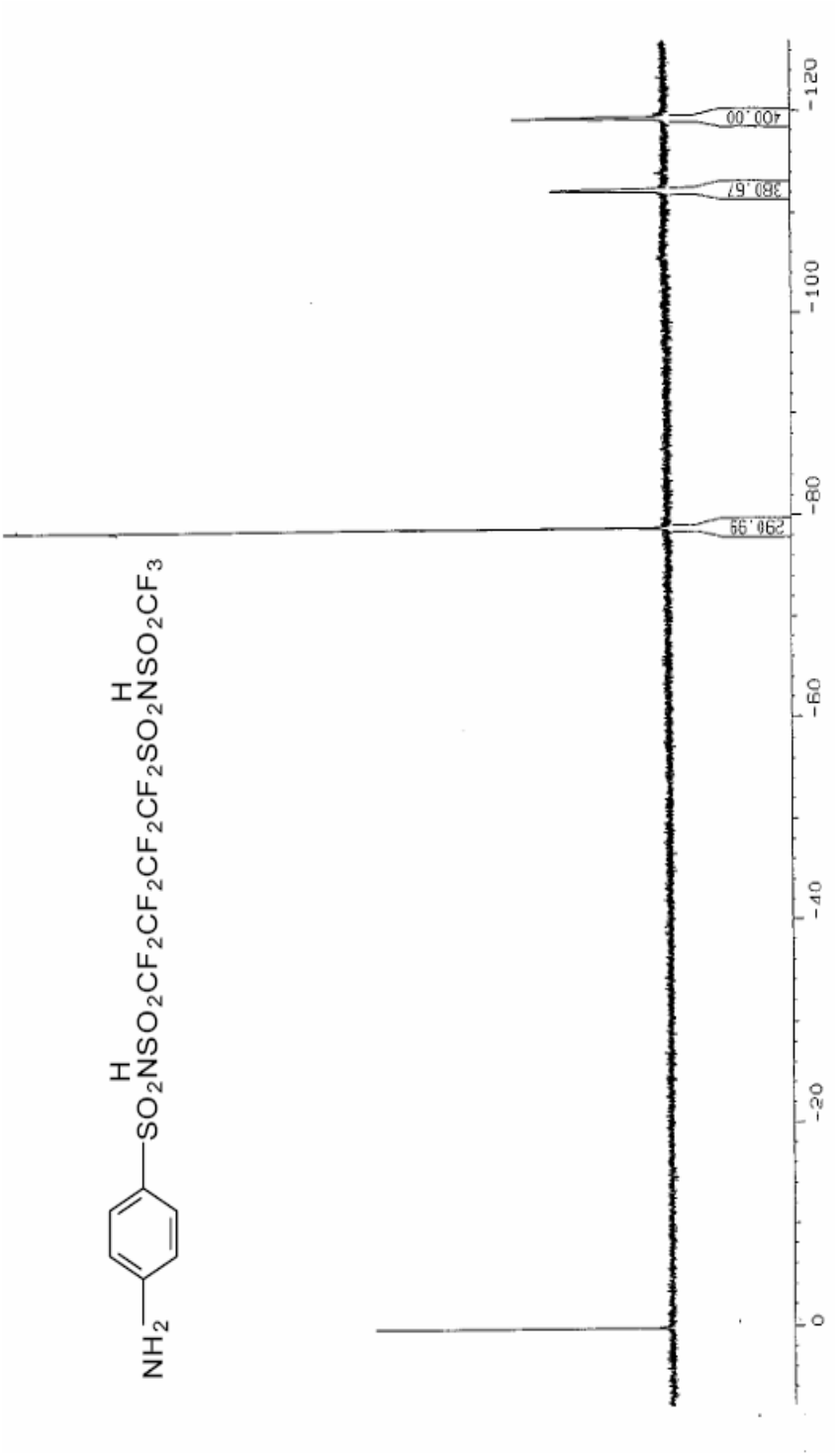


Figure A ^{1}H NMR spectrum of Comound **21a**, 200MHz, CD_3CN

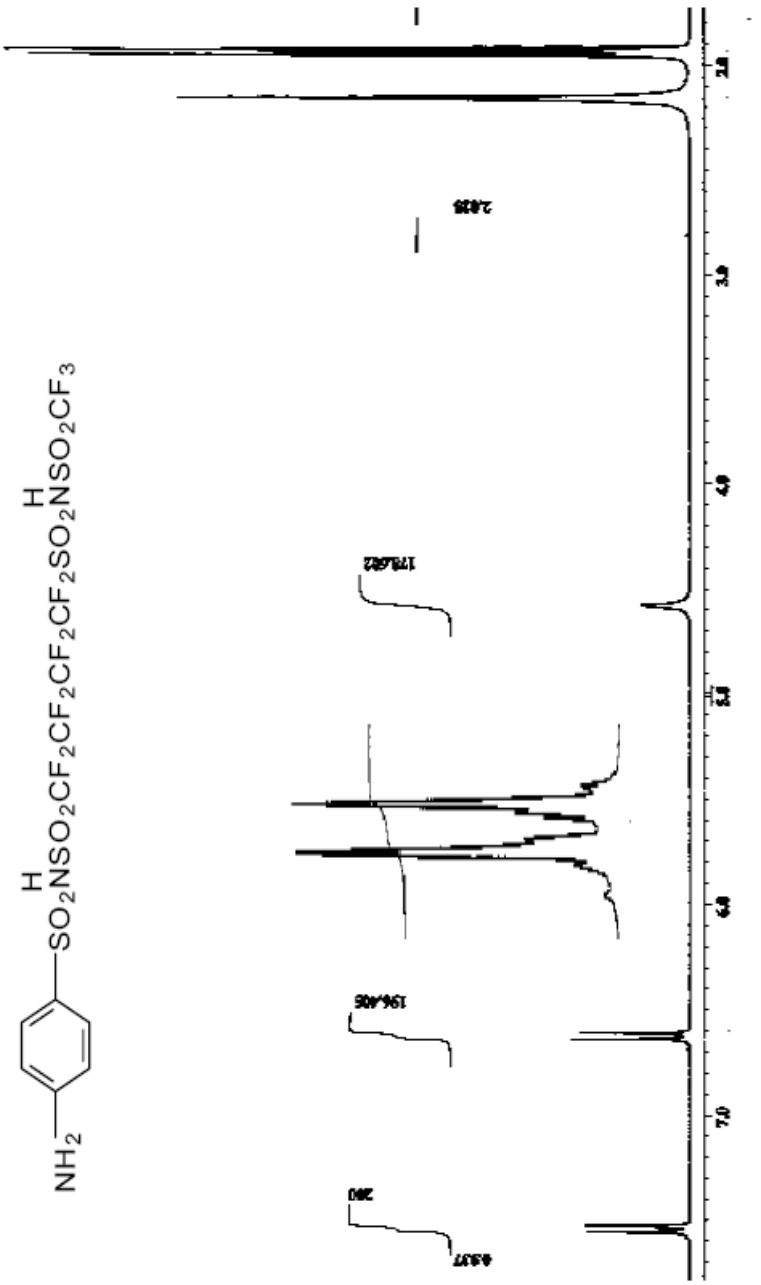


Figure A IR spectrum of Comound **21a**

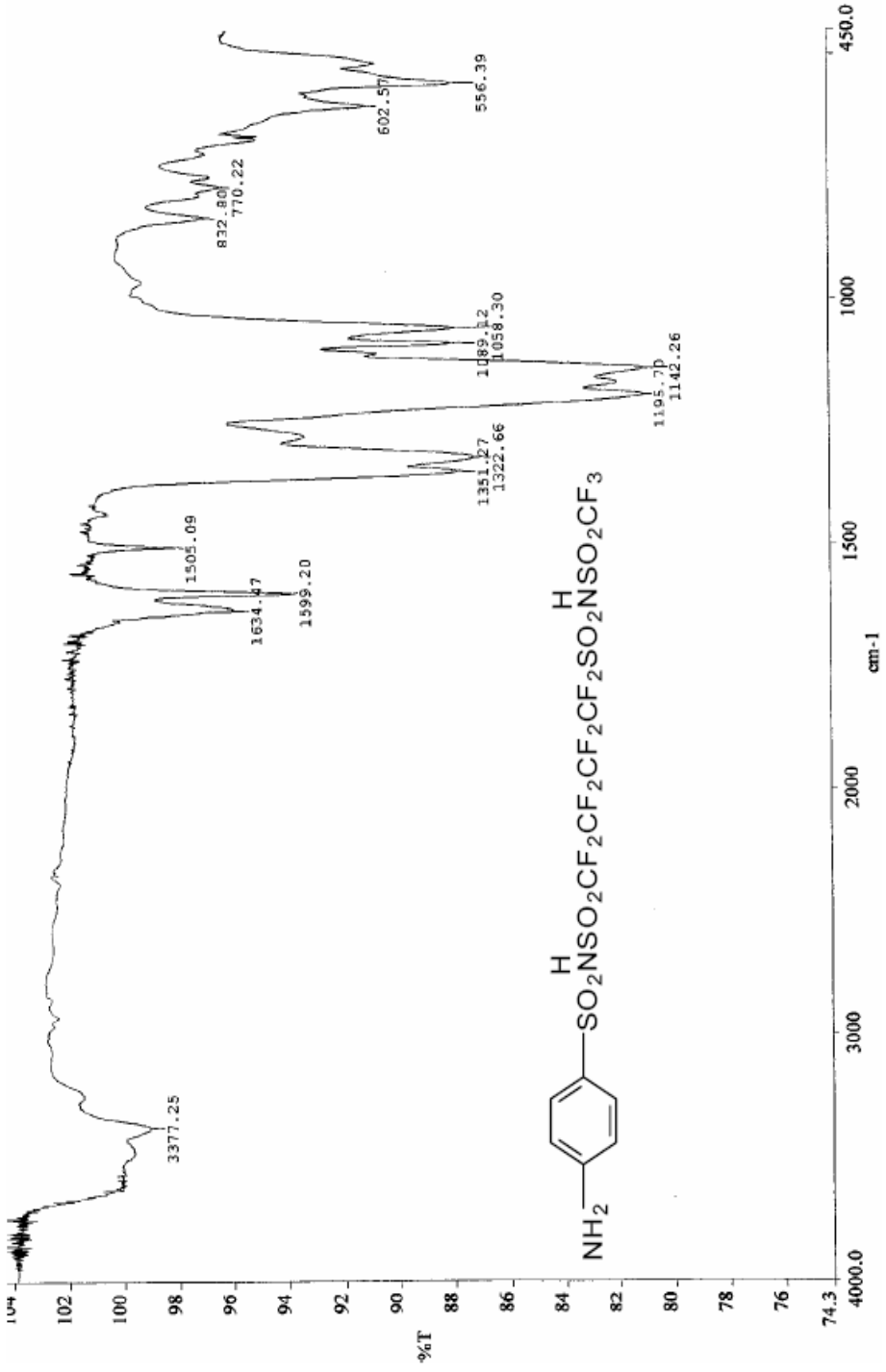


Figure A ^{19}F NMR spectrum of Comound **22a**, 300MHz, CD_3CN

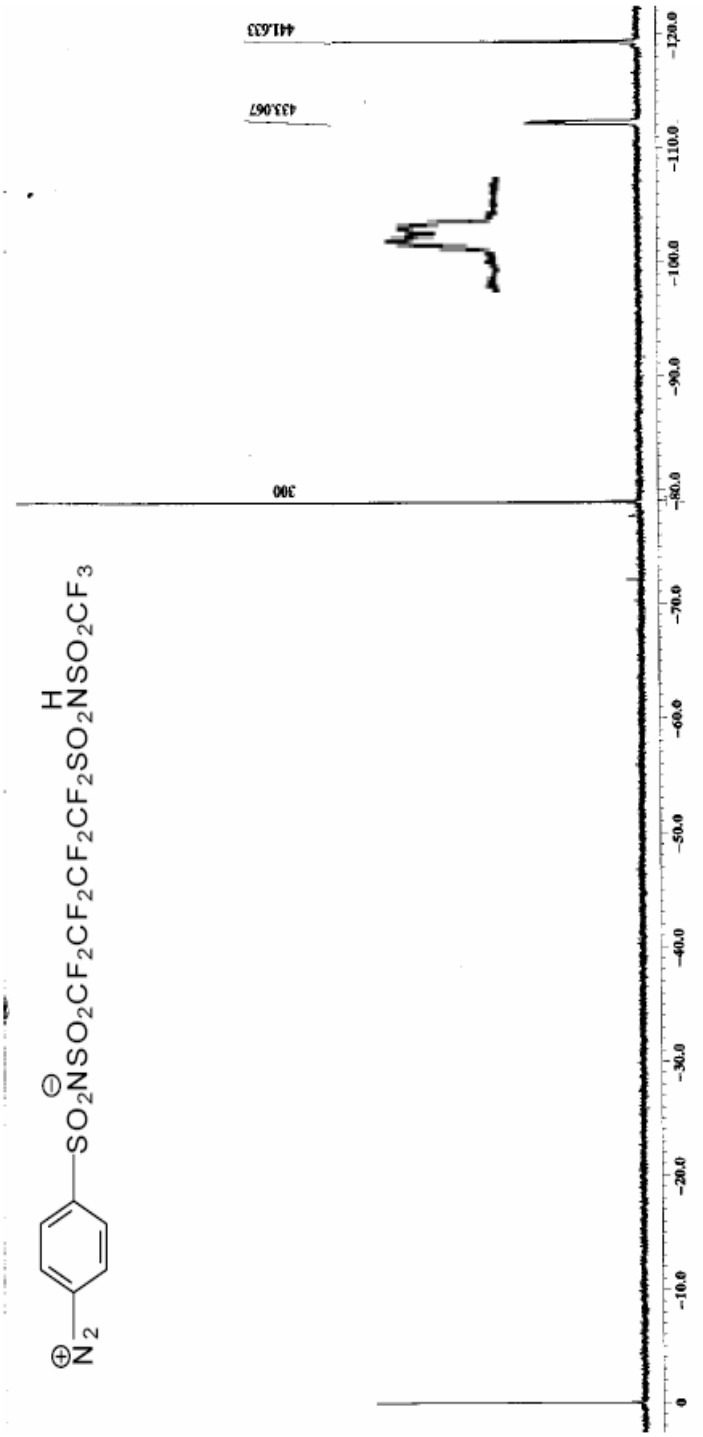
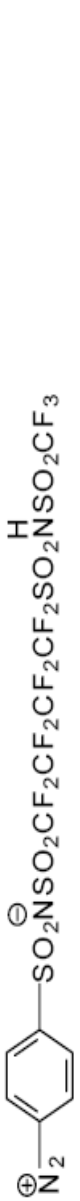


Figure A ^{1}H NMR spectrum of Comound **22a**, 300MHz, CD_3CN



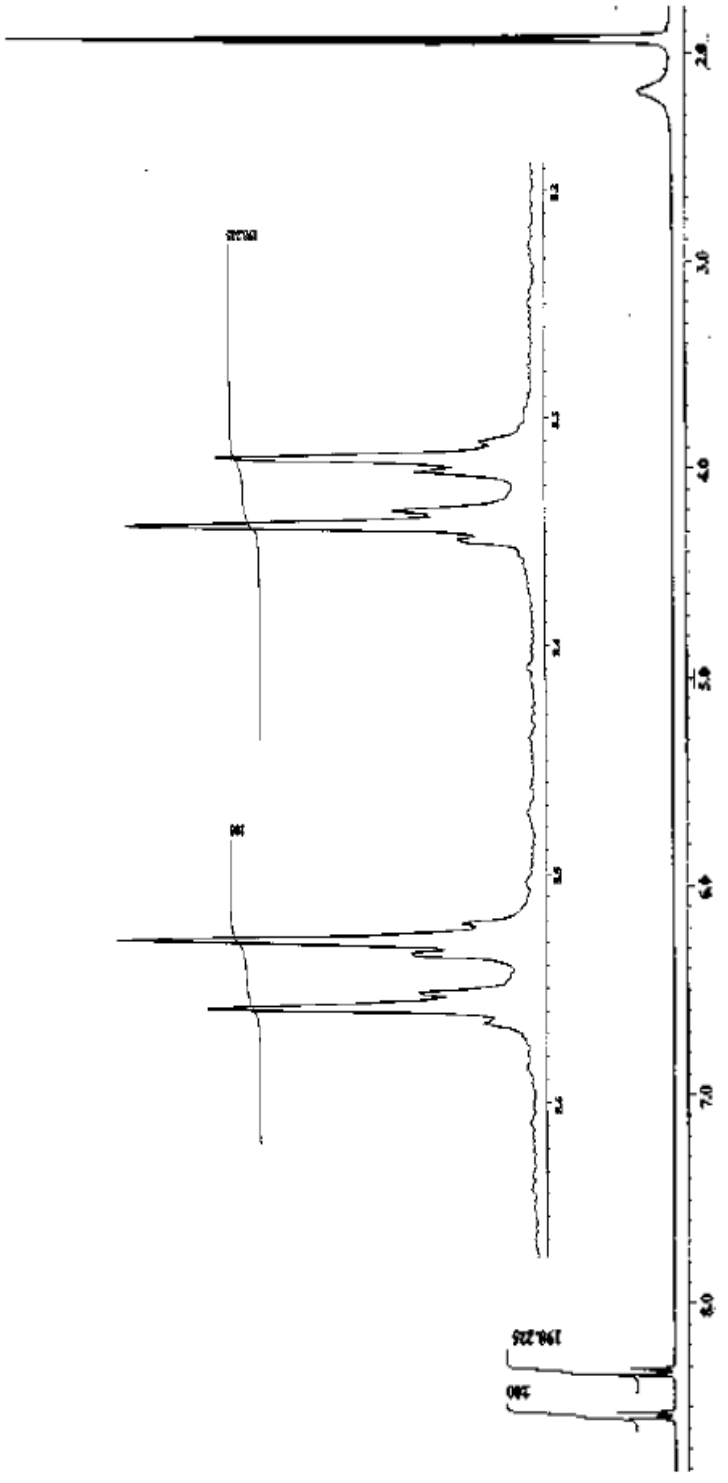


Figure A IR spectrum of Comound **22a**

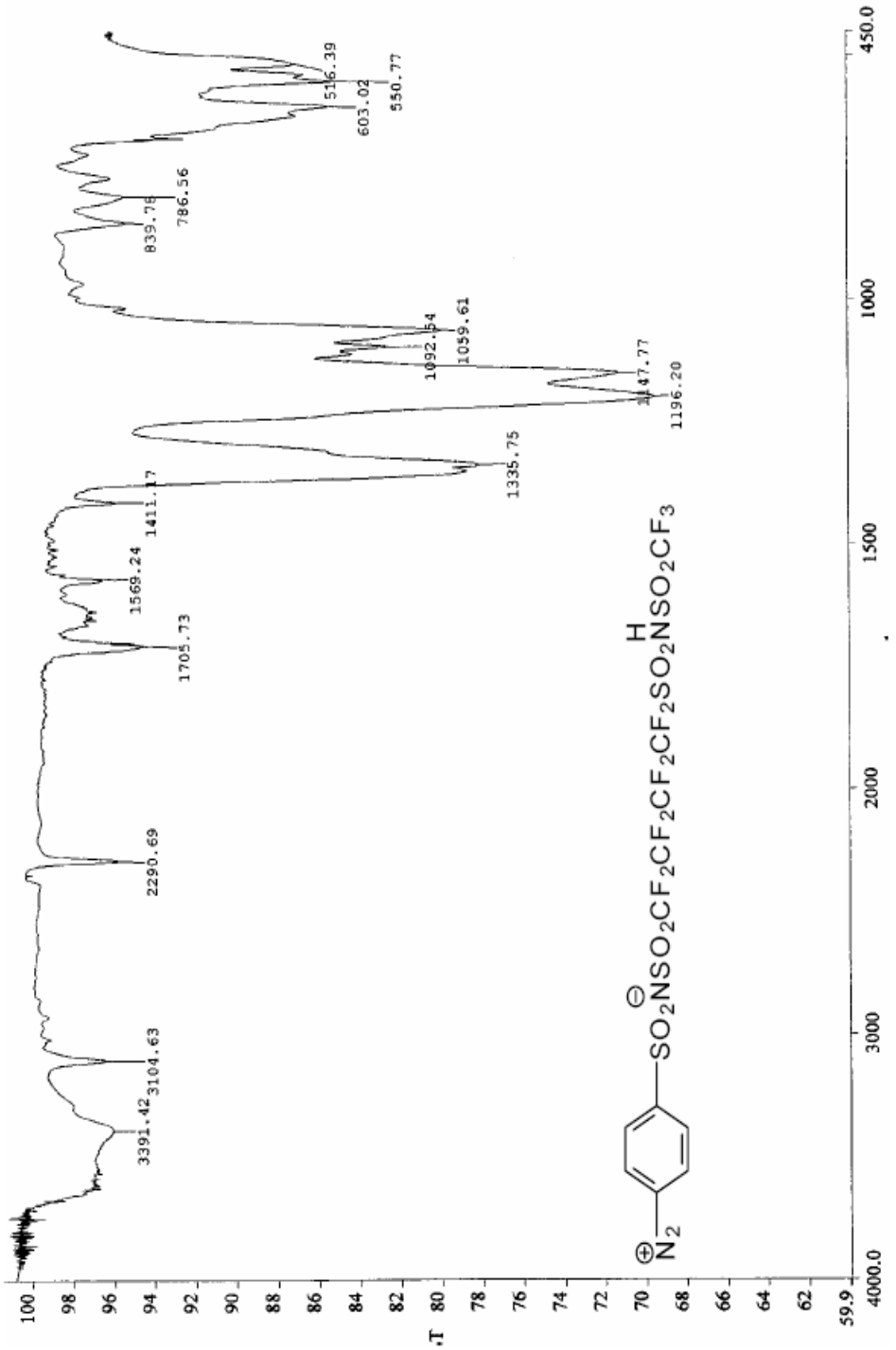


Figure A ^{19}F NMR spectrum of Comound **19b,** 300MHz, CD_3CN

$F^hSO_2CF_2{}^gCF_2{}^fCF_2{}^eCF_2{}^dCF_2{}^cCF_2{}^bSO_2NSO_2CF_3{}^a$

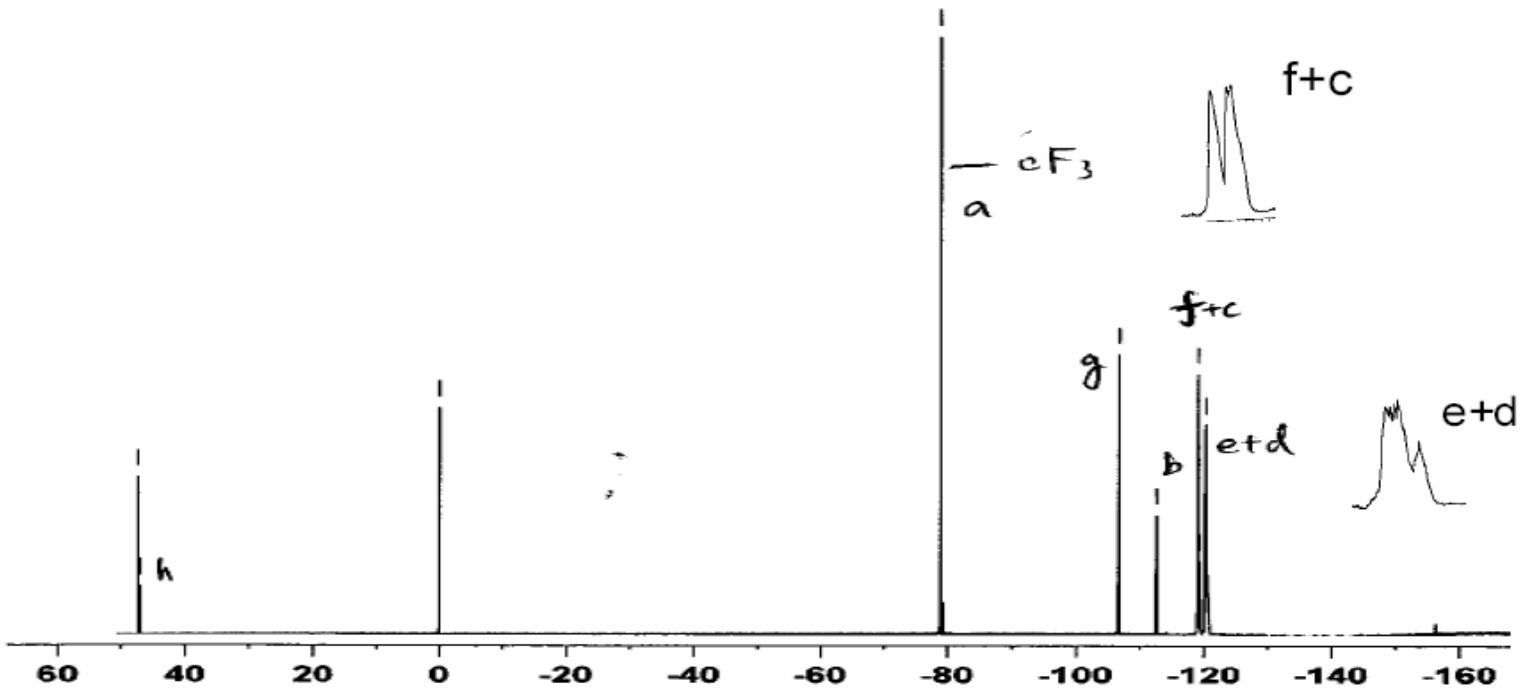


Figure A ^{19}F NMR spectrum of Comound **21b**, 300MHz, CD_3CN

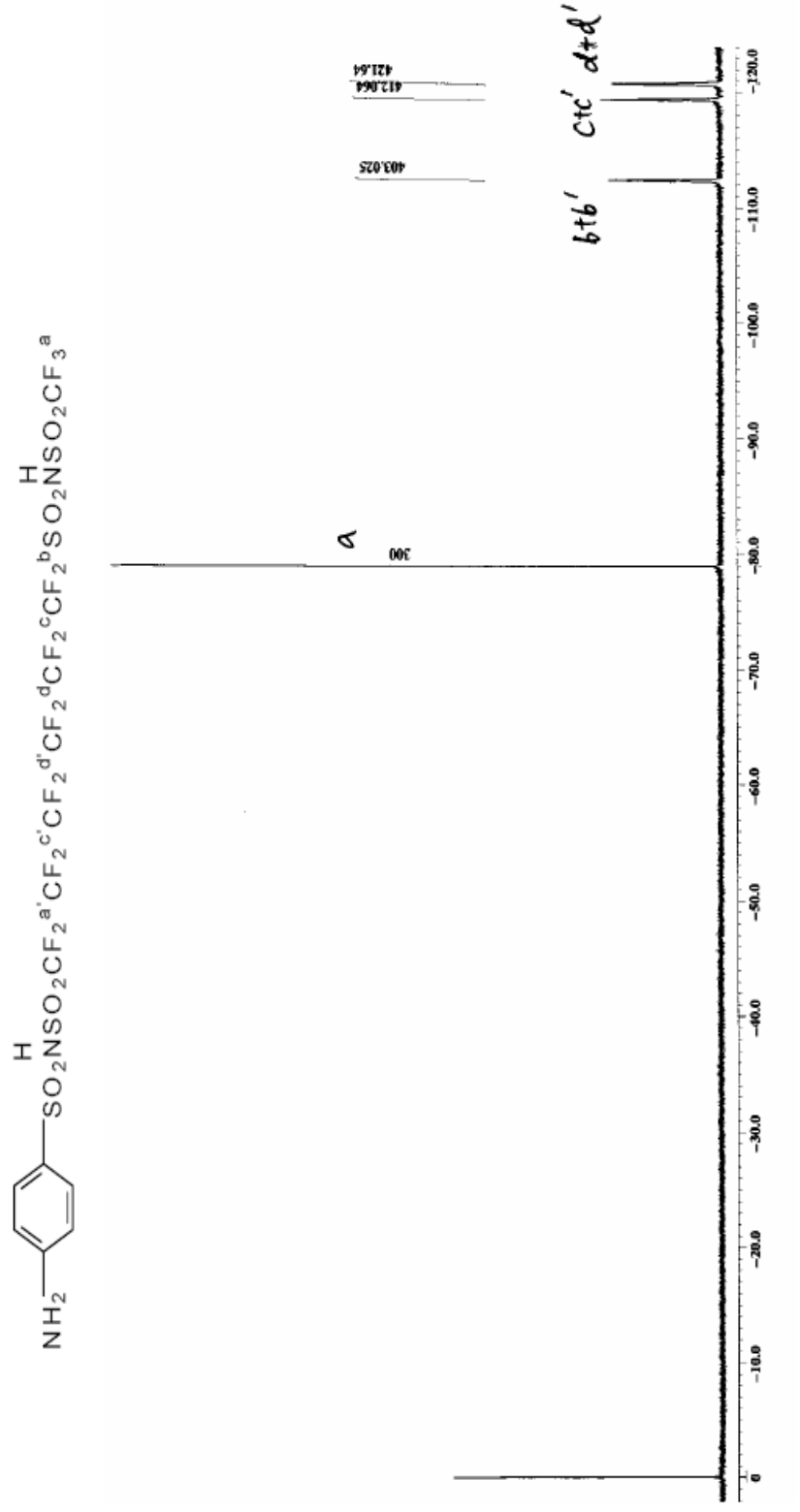


Figure A ^{1}H NMR spectrum of Comound **21b**, 300MHz, CD_3CN

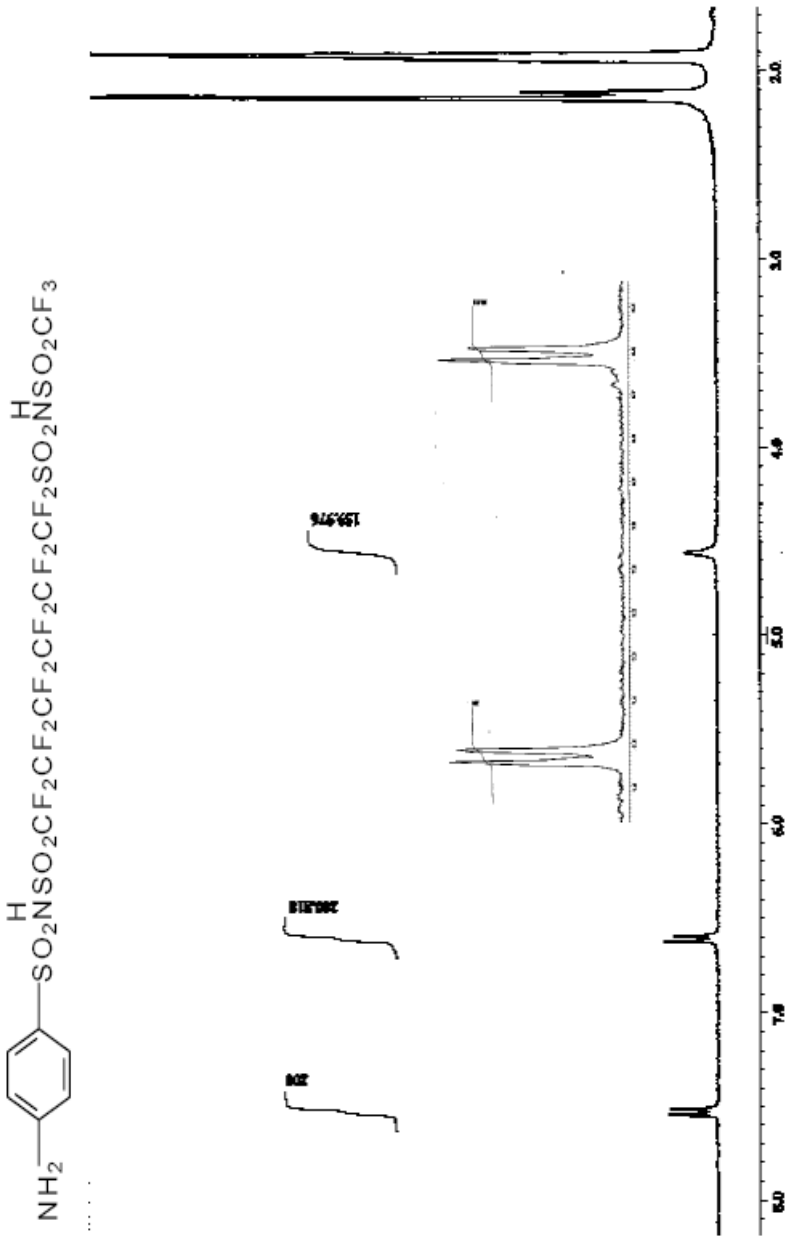


Figure A IR spectrum of Comound **21b**

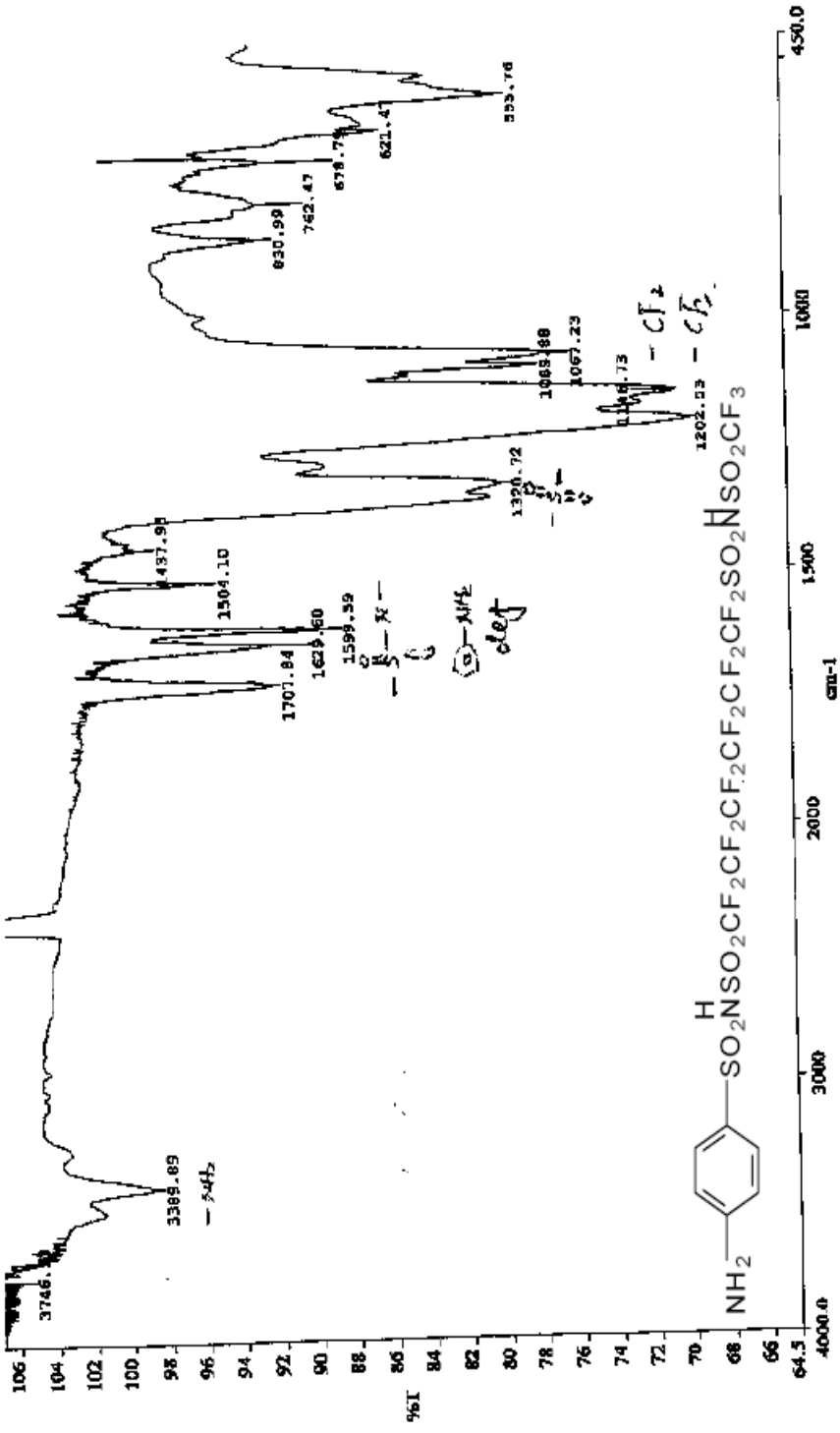


Figure A ^{19}F NMR spectrum of Comound **22b**, 300MHz, CD_3CN

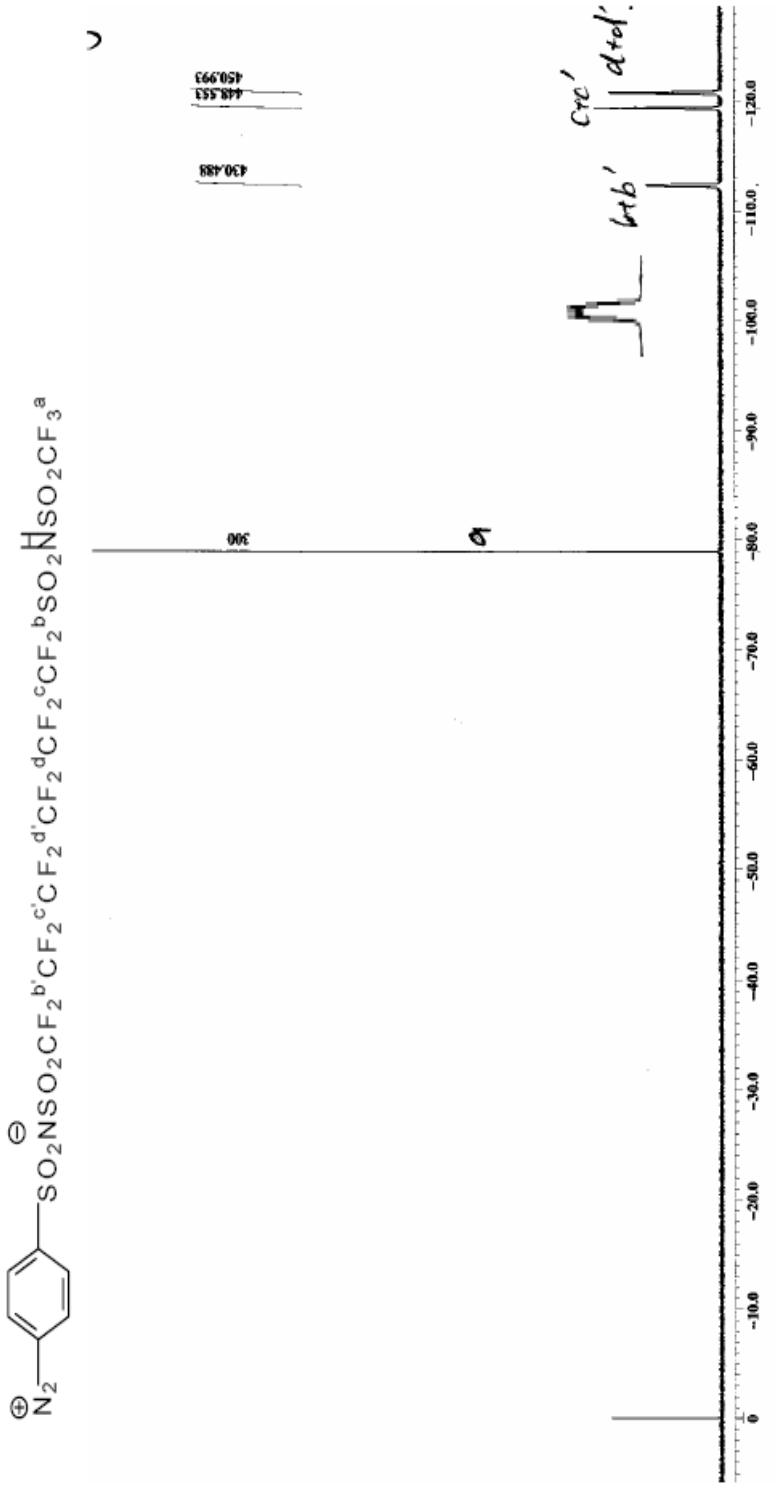


Figure A ^{1}H NMR spectrum of Comound **22b**, 300MHz, CD_3CN

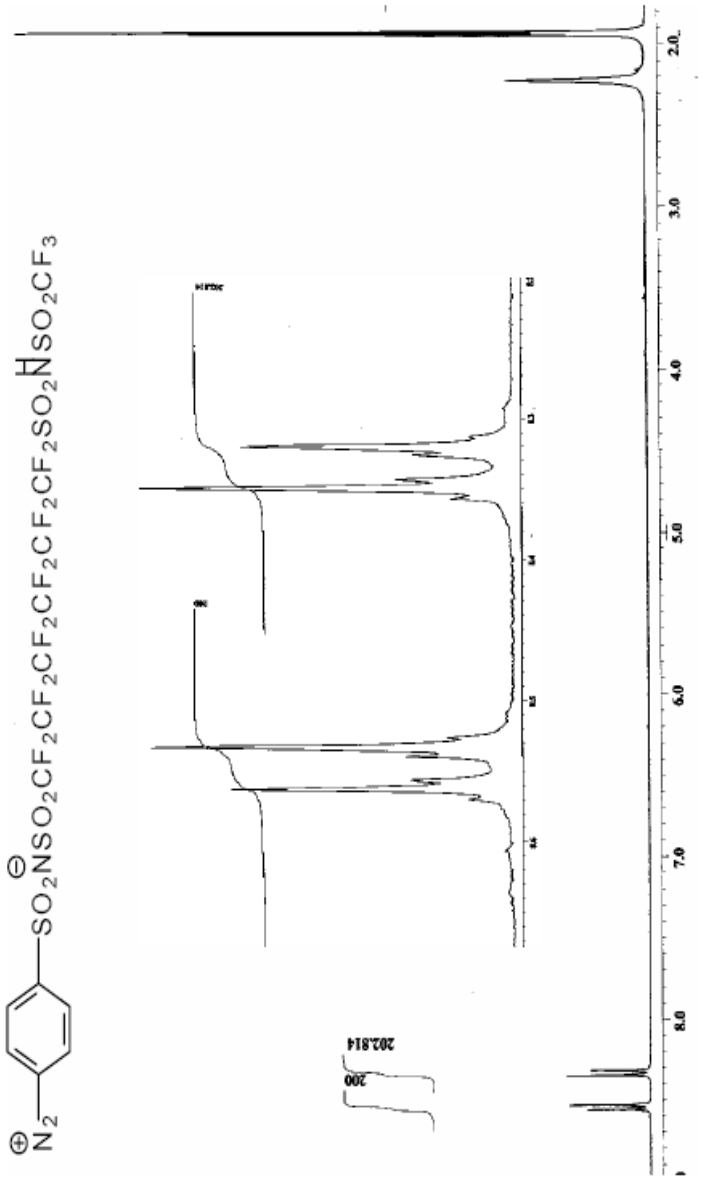


Figure A IR spectrum of Comound **22b**

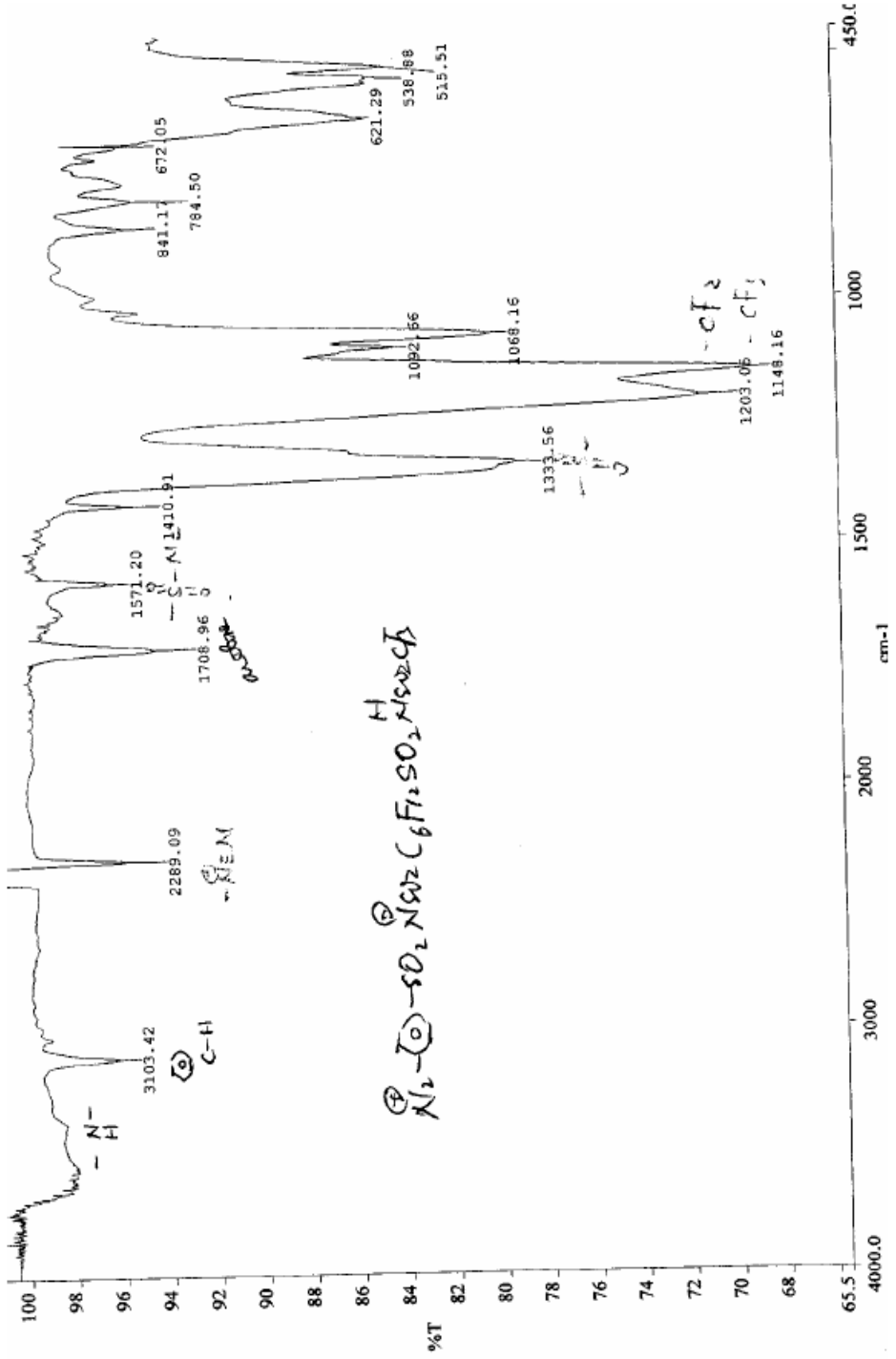


Figure A ^{19}F NMR spectrum of Comound **26**, 300MHz, CD_3CN

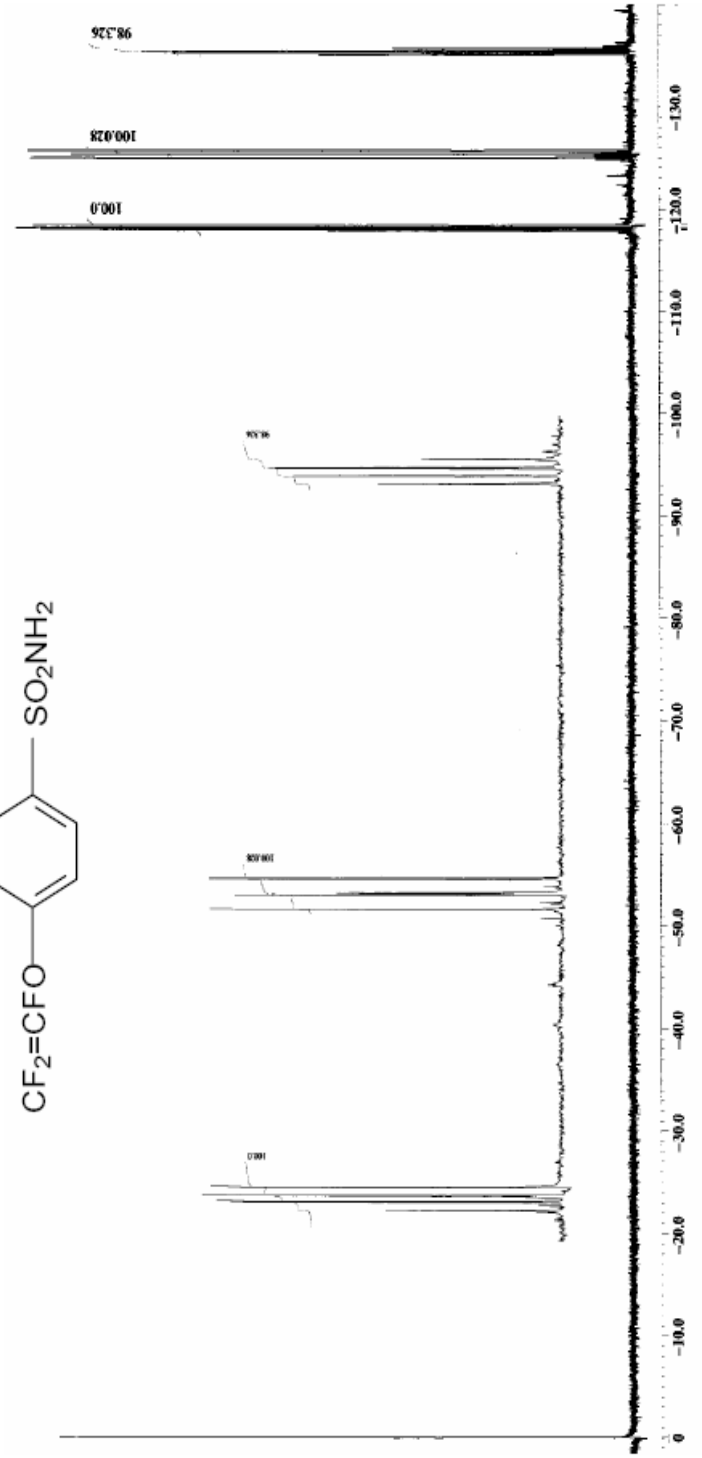


Figure A ^{1}H NMR spectrum of Comound **26**, 300MHz, CD_3CN

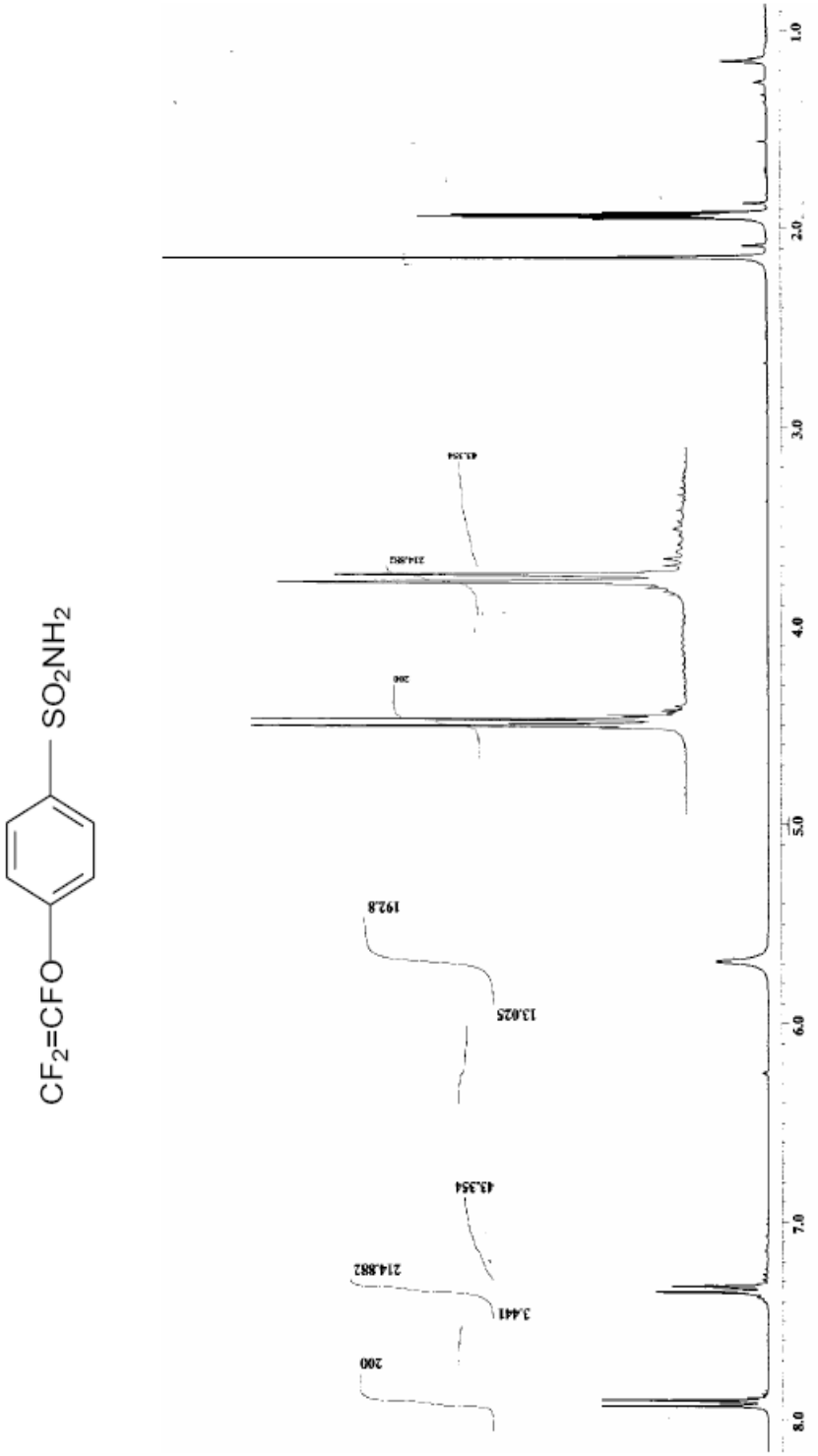


Figure A ^{19}F NMR spectrum of Comound **27**, 300MHz, $CD_3CN+CF_3SO_2H$

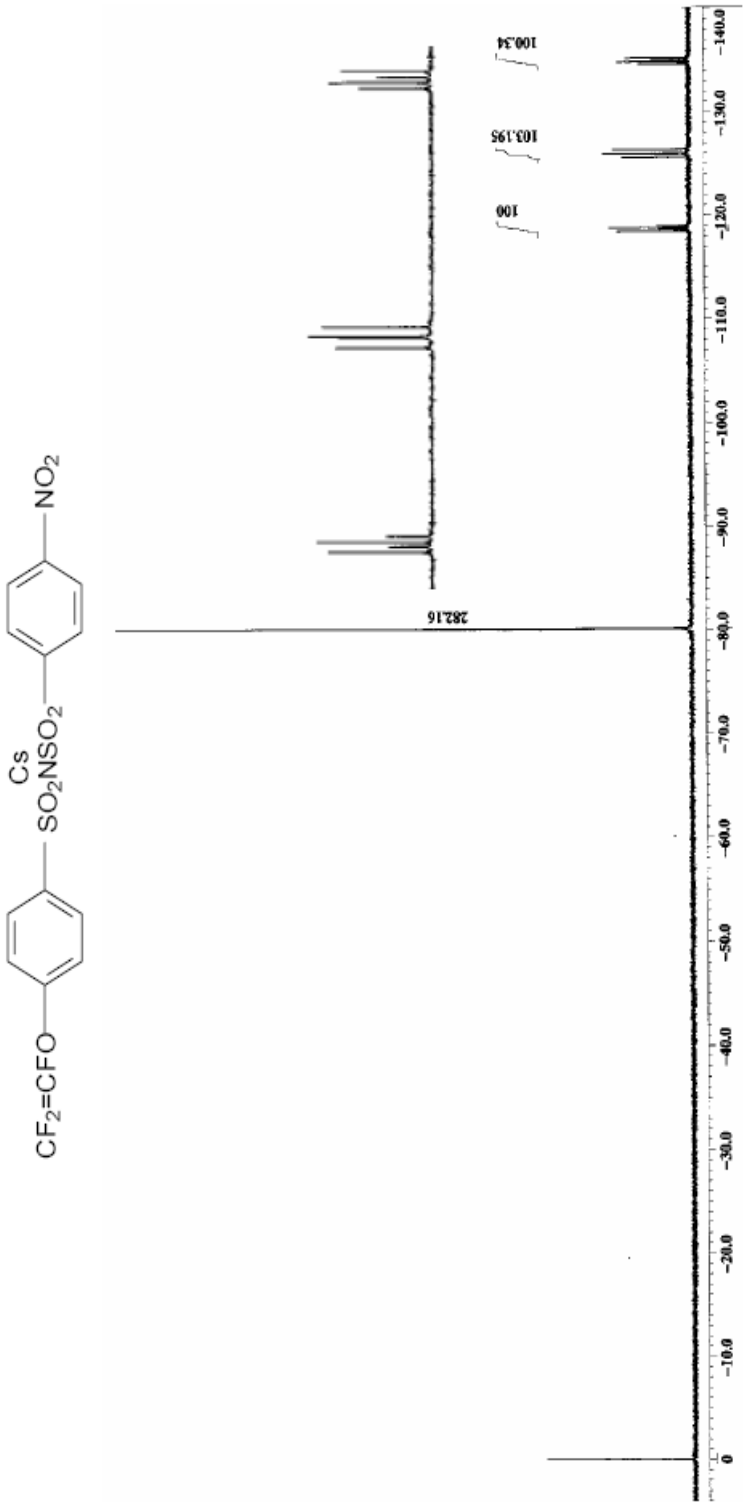


Figure A ^{1}H NMR spectrum of Comound **27**, 300MHz, $CD_3CN+CF_3SO_2H$

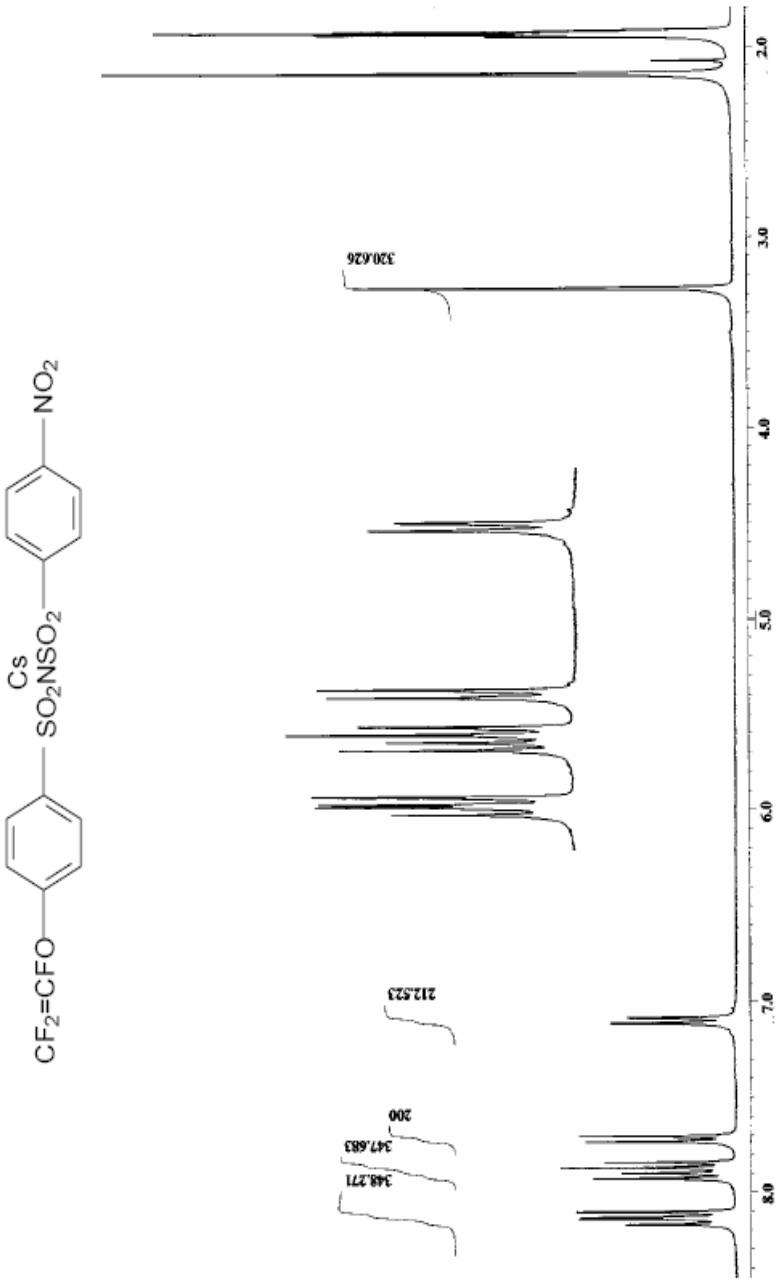


Figure A ^{1}H NMR spectrum of Comound **a**, 300MHz, $CDCl_3$

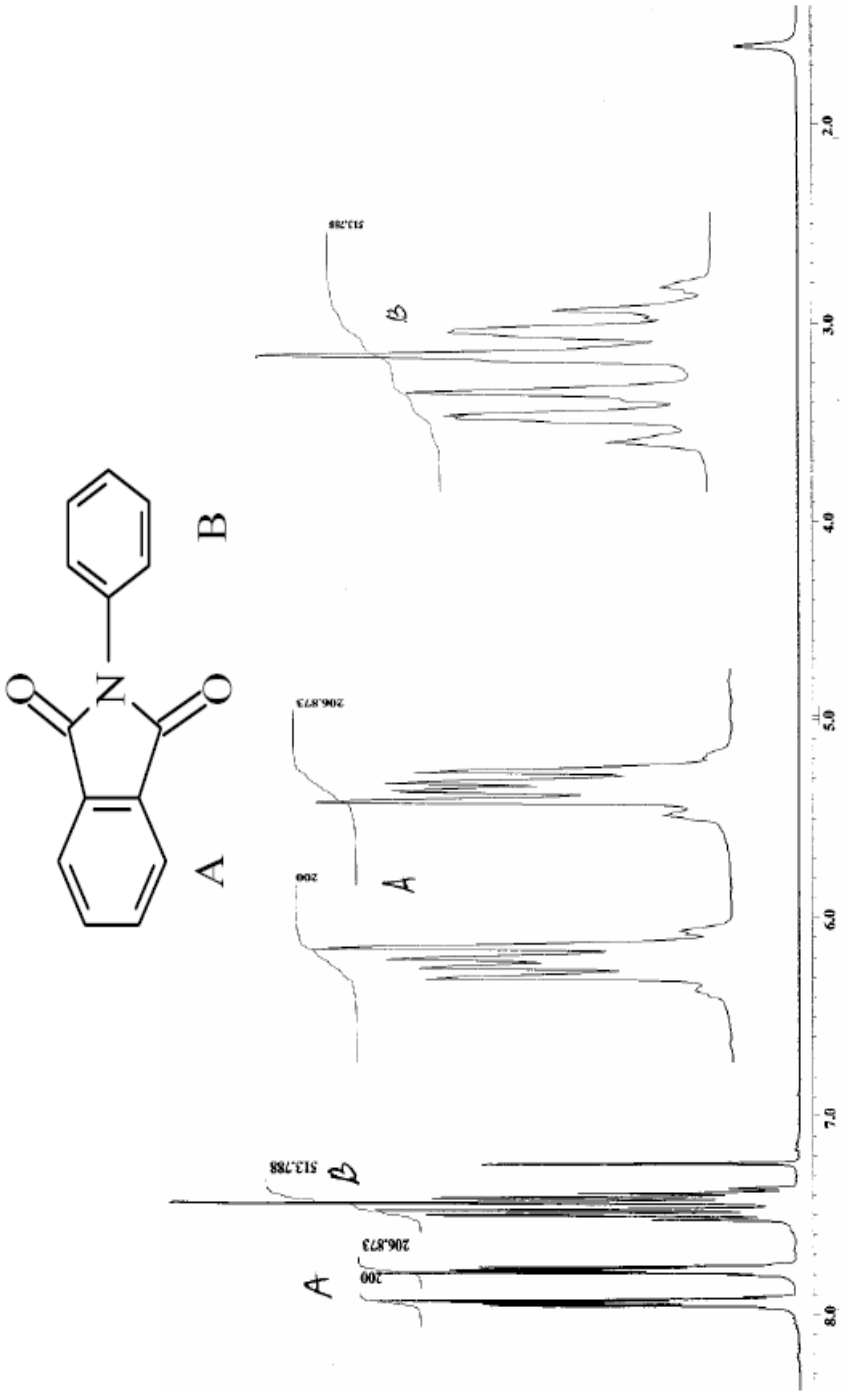


Figure A ^{13}C NMR spectrum of Comound **a**, 300MHz, $CDCl_3$

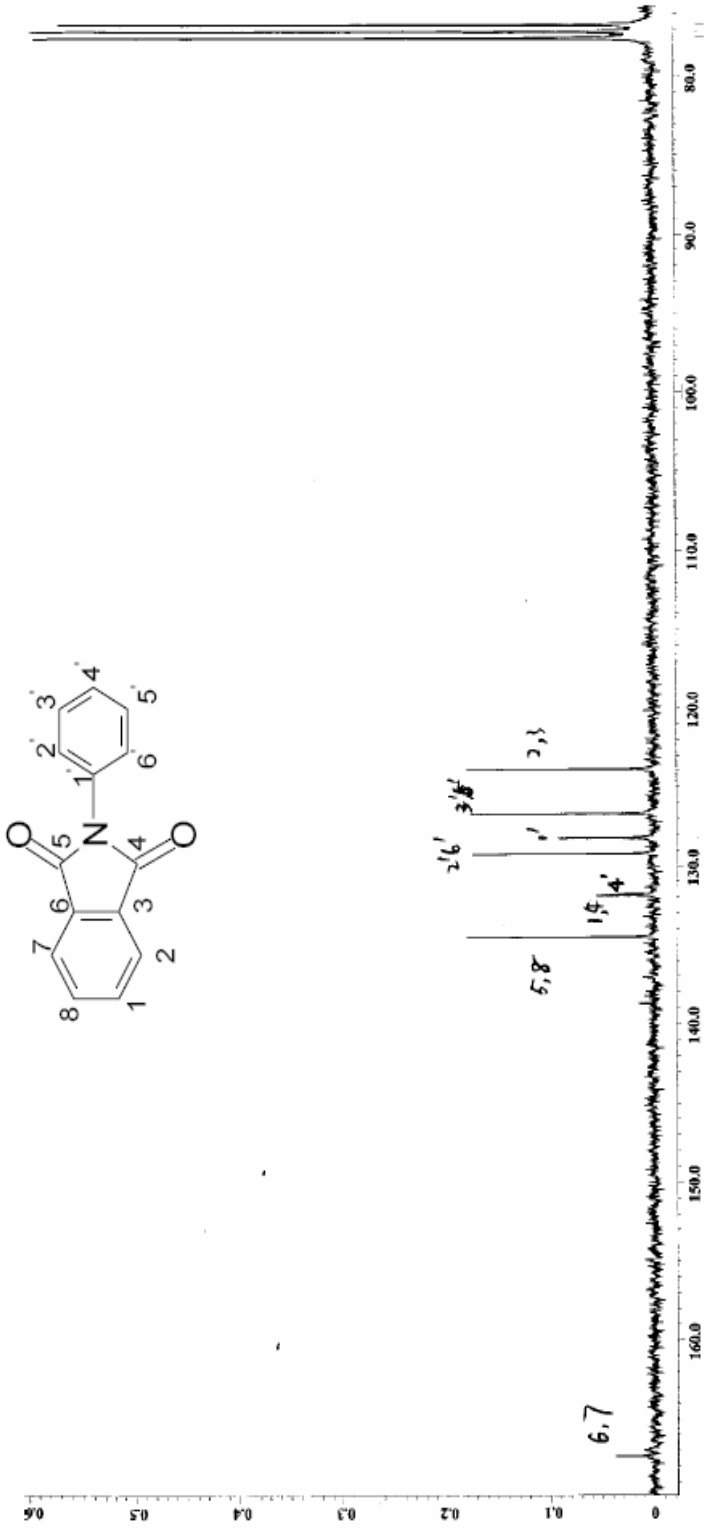


Figure A ^{1}H NMR spectrum of Comound **a'**, 300MHz, DMSO

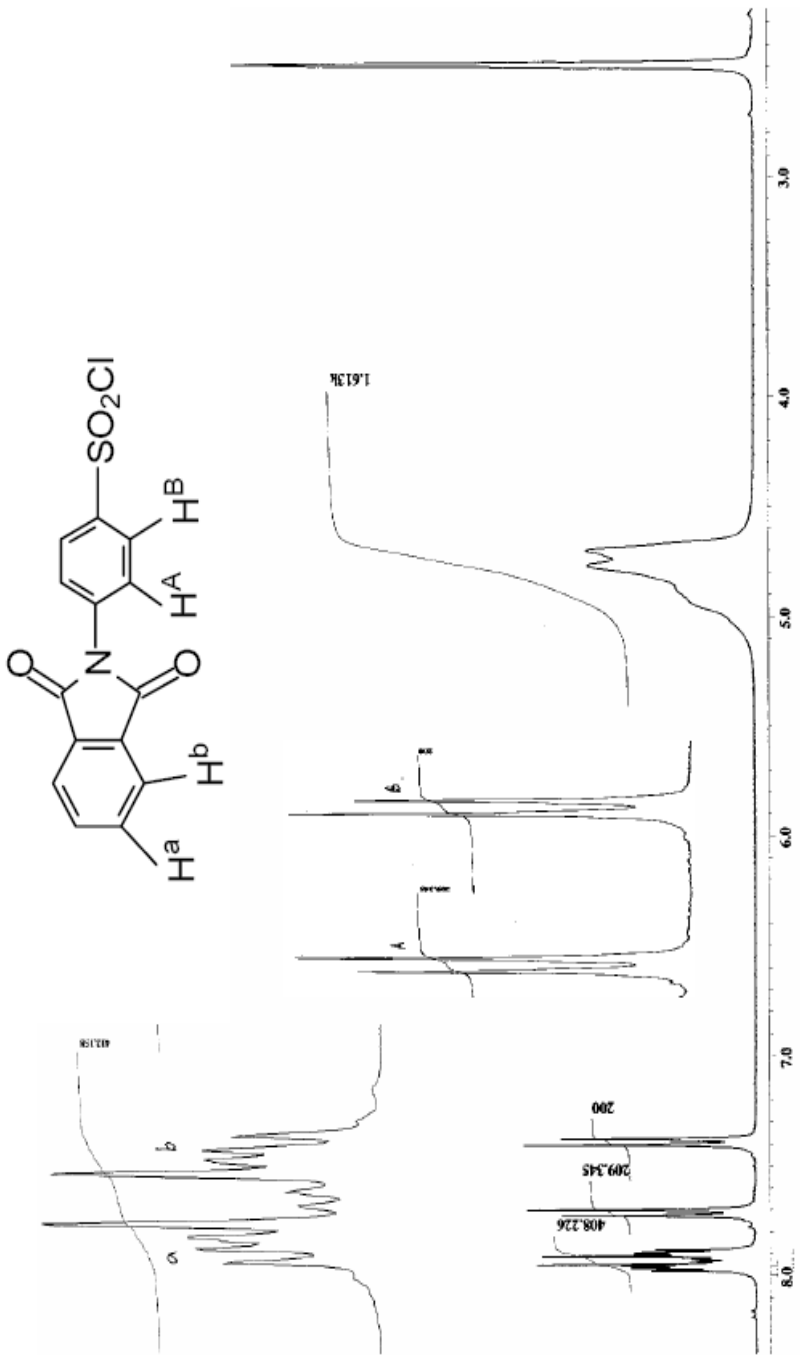


Figure A ^{13}C NMR spectrum of Comound **a'**, 300MHz, DMSO

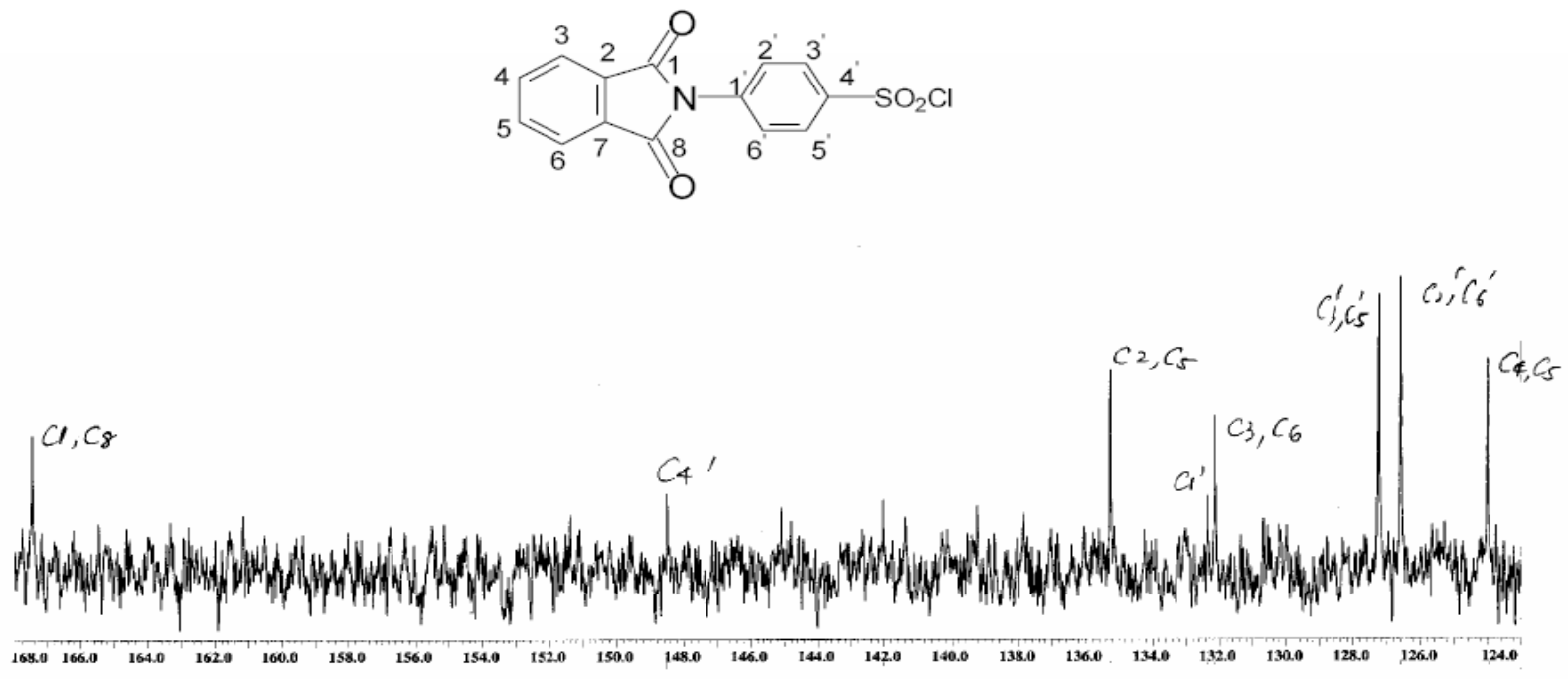


Figure A ^{19}F NMR spectrum of Comound **28a**, 300MHz, CD_3CN

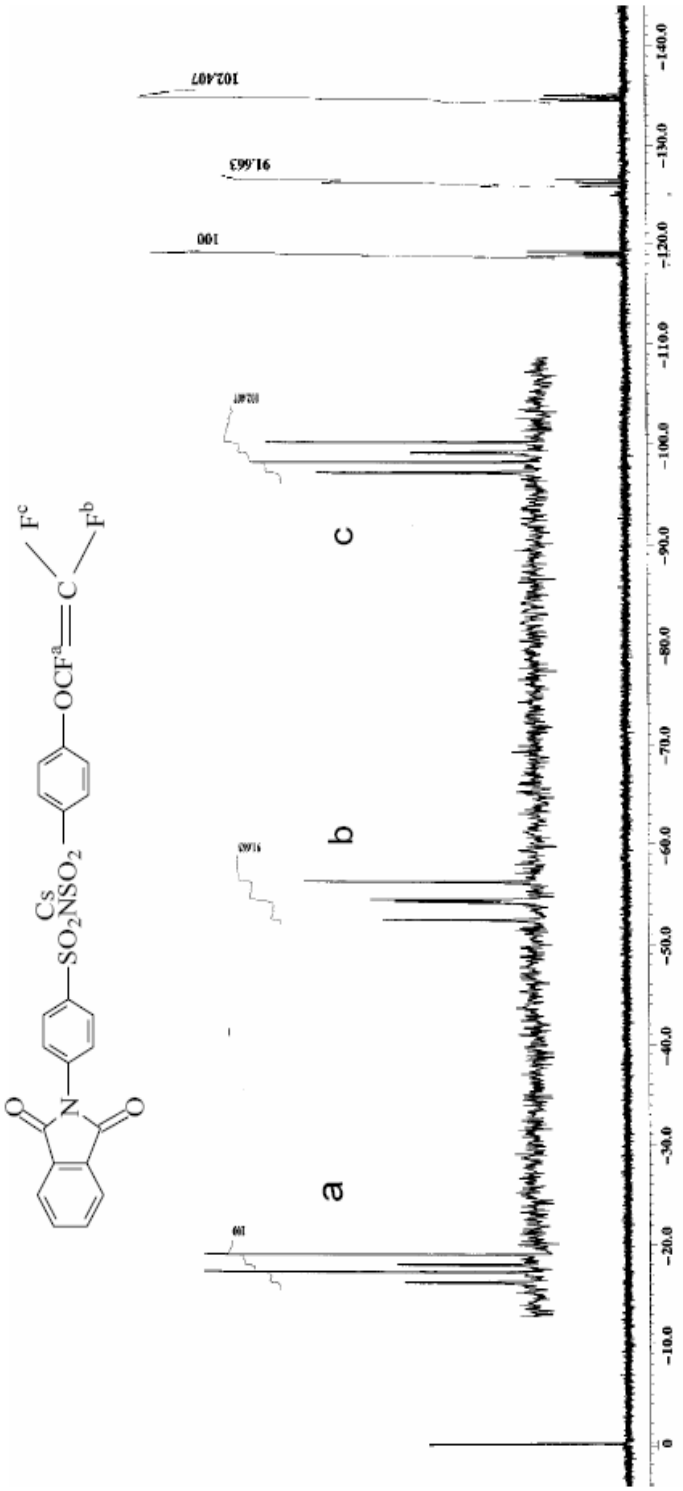


Figure A ^{1}H NMR spectrum of Comound **28a**, 300MHz, CD_3CN

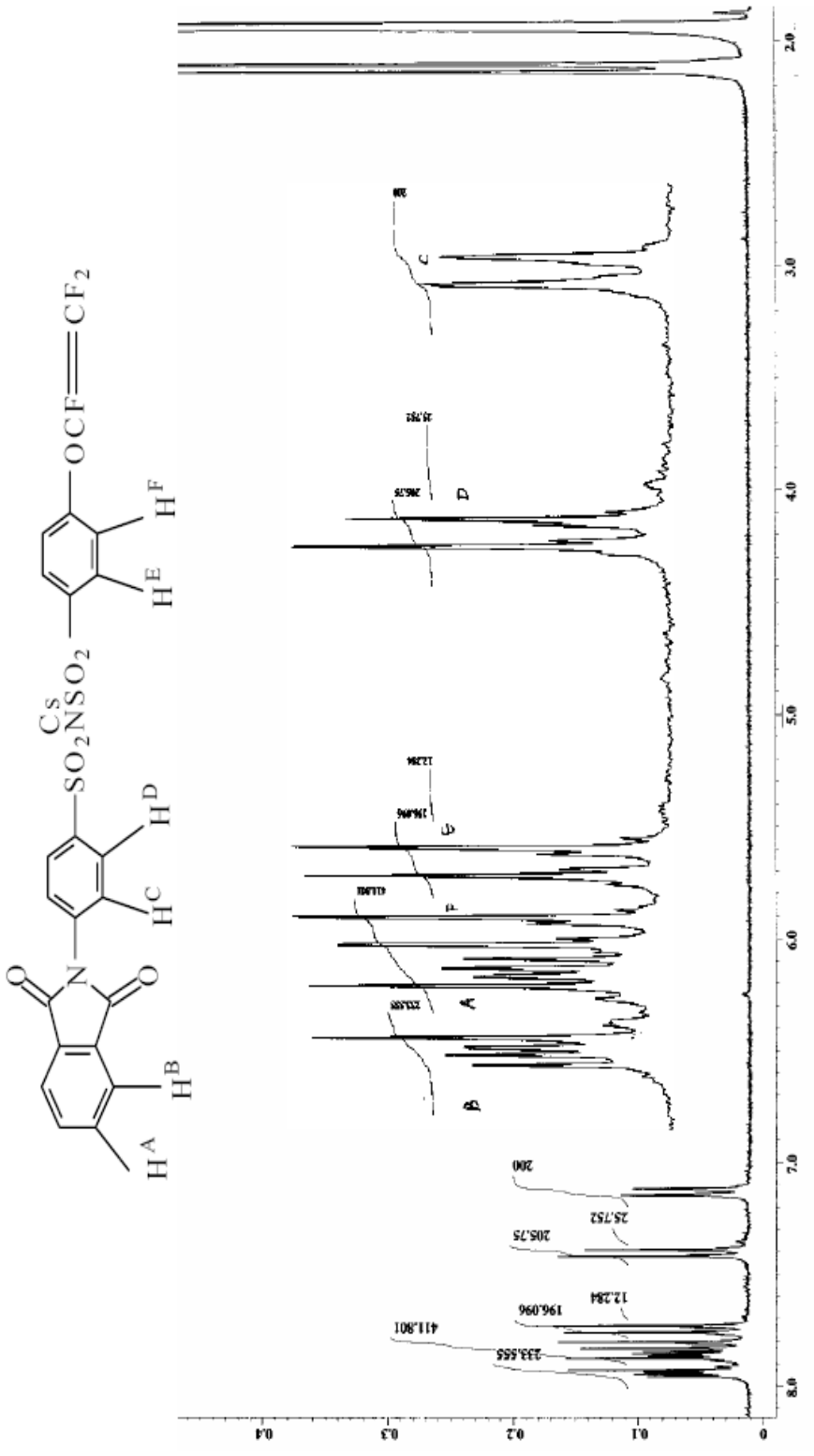


Figure A ^{1}H NMR Spectrum of Compound **31**, 300MHz, CD_3CN

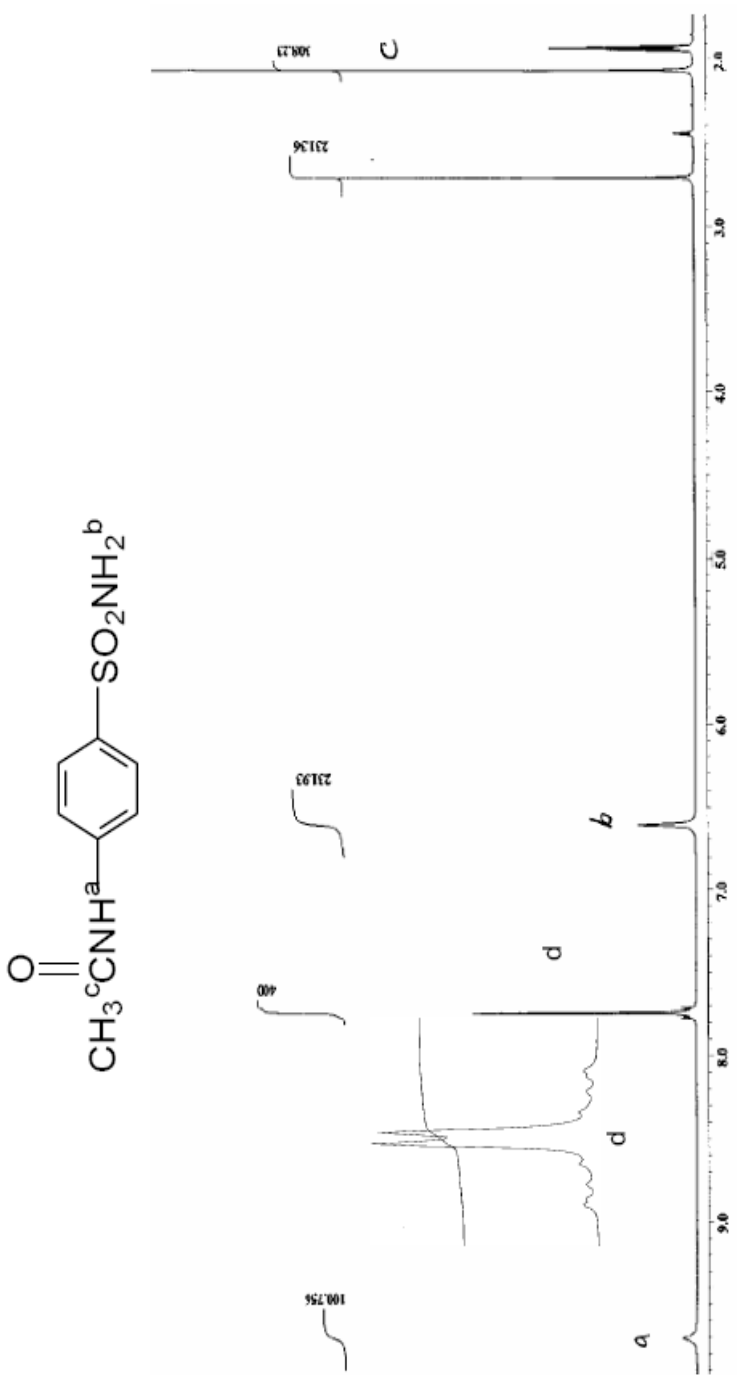


Figure A ^{19}F NMR spectrum of Comound **32a**, 300MHz, CD_3CN

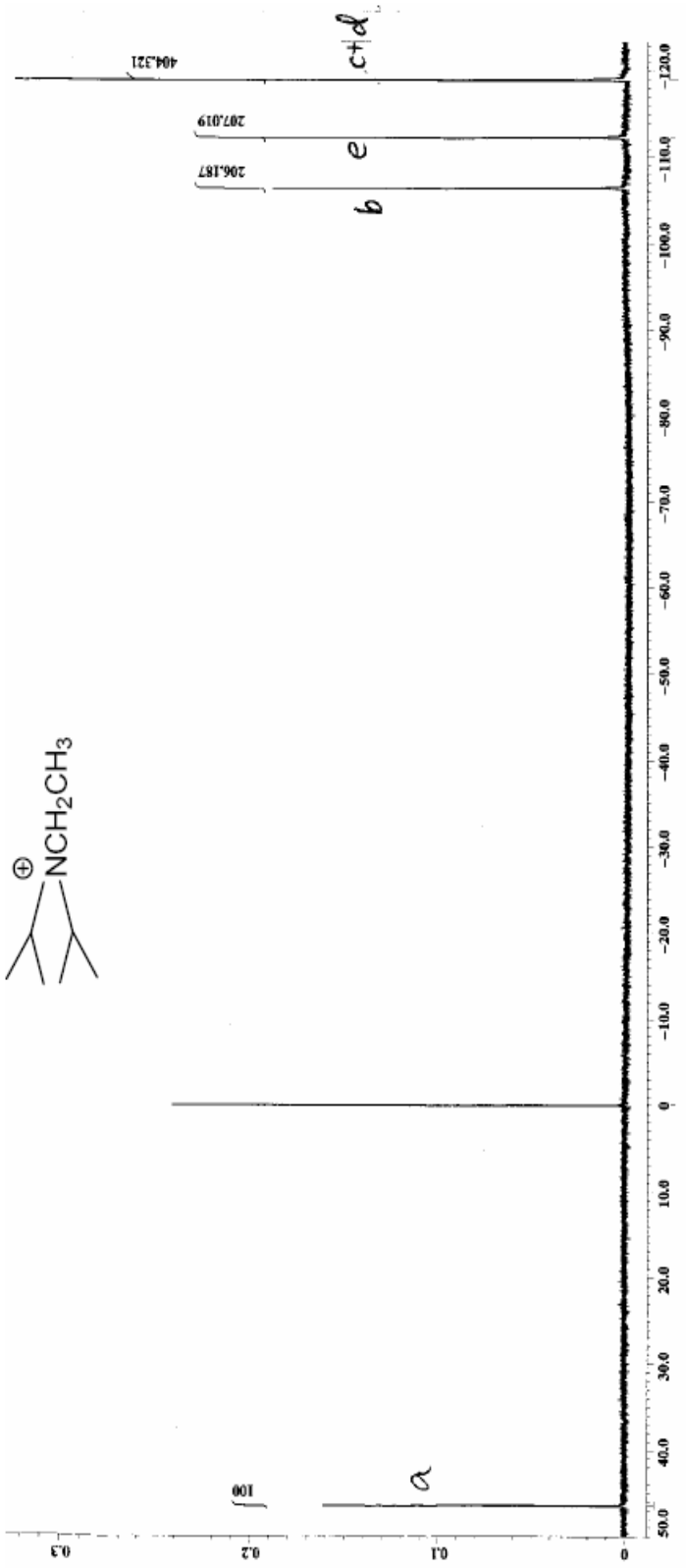


Figure A ^{1}H NMR Spectrum of Compound **32a**, 300MHz, CD_3CN

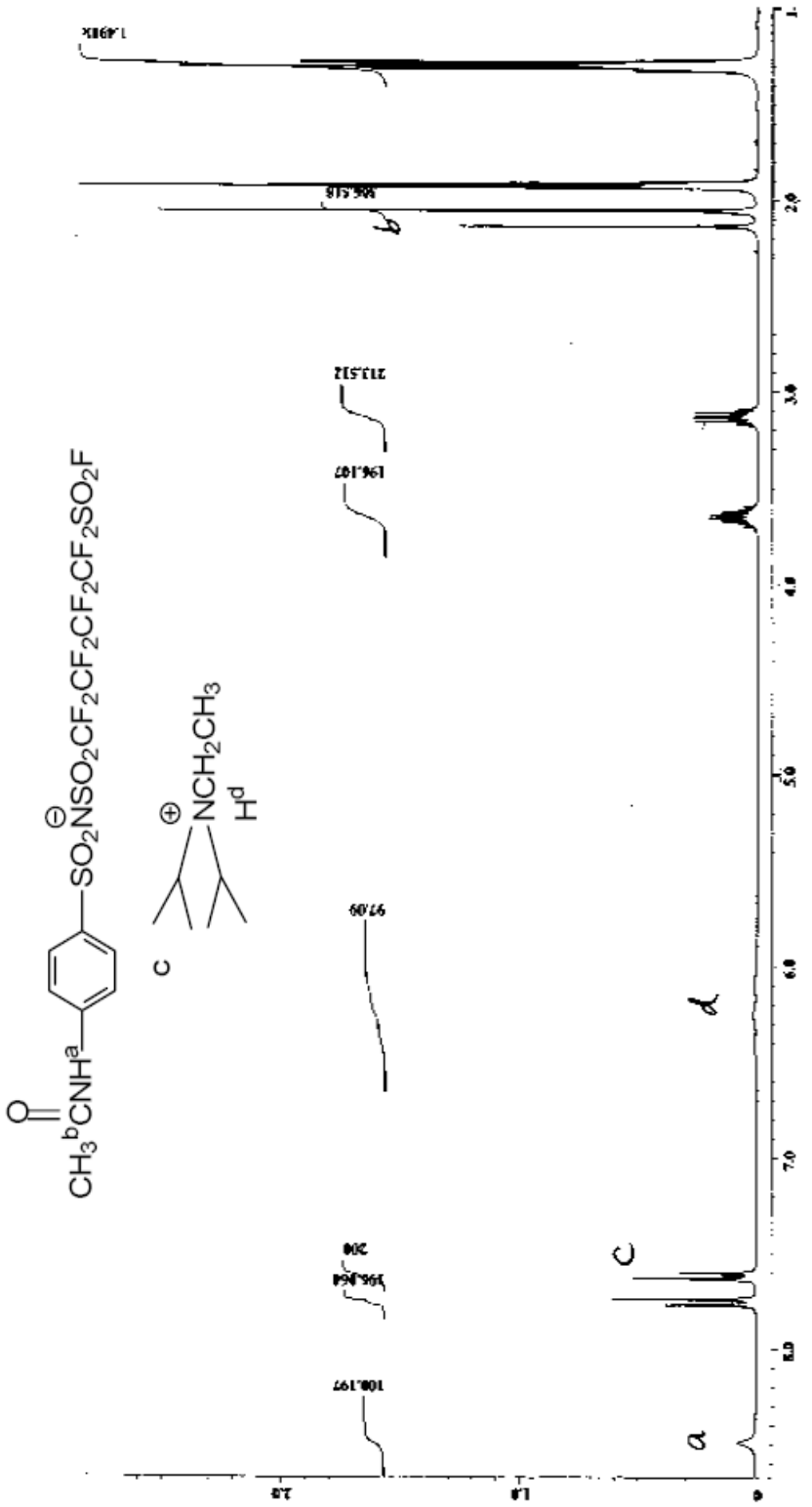


Figure A ^{19}F NMR Spectrum of crude compound **33a**, 300MHz, CD_3CN

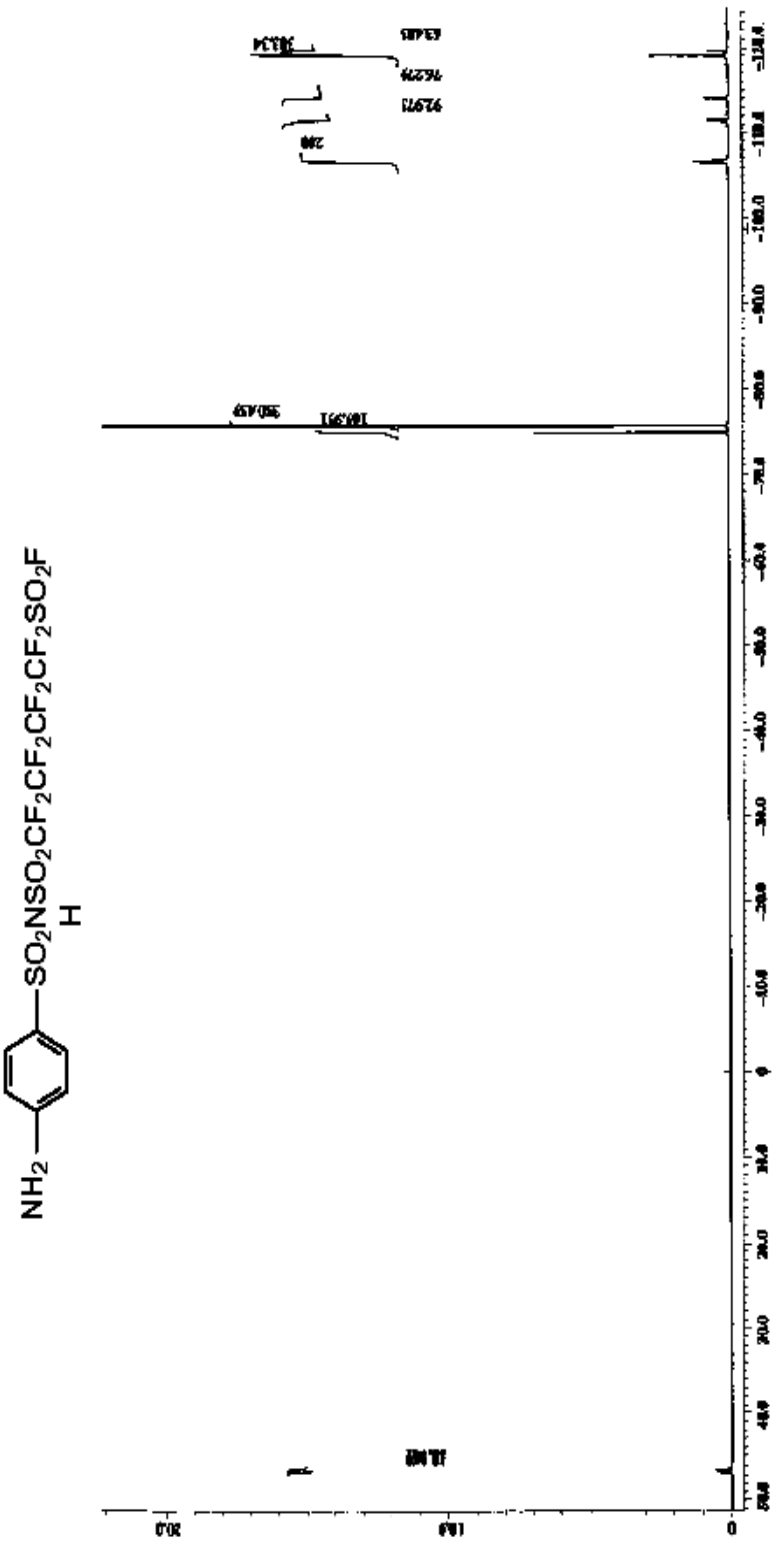


Figure A ^{1}H NMR Spectrum of Compound **33a**, 300MHz, CD_3CN

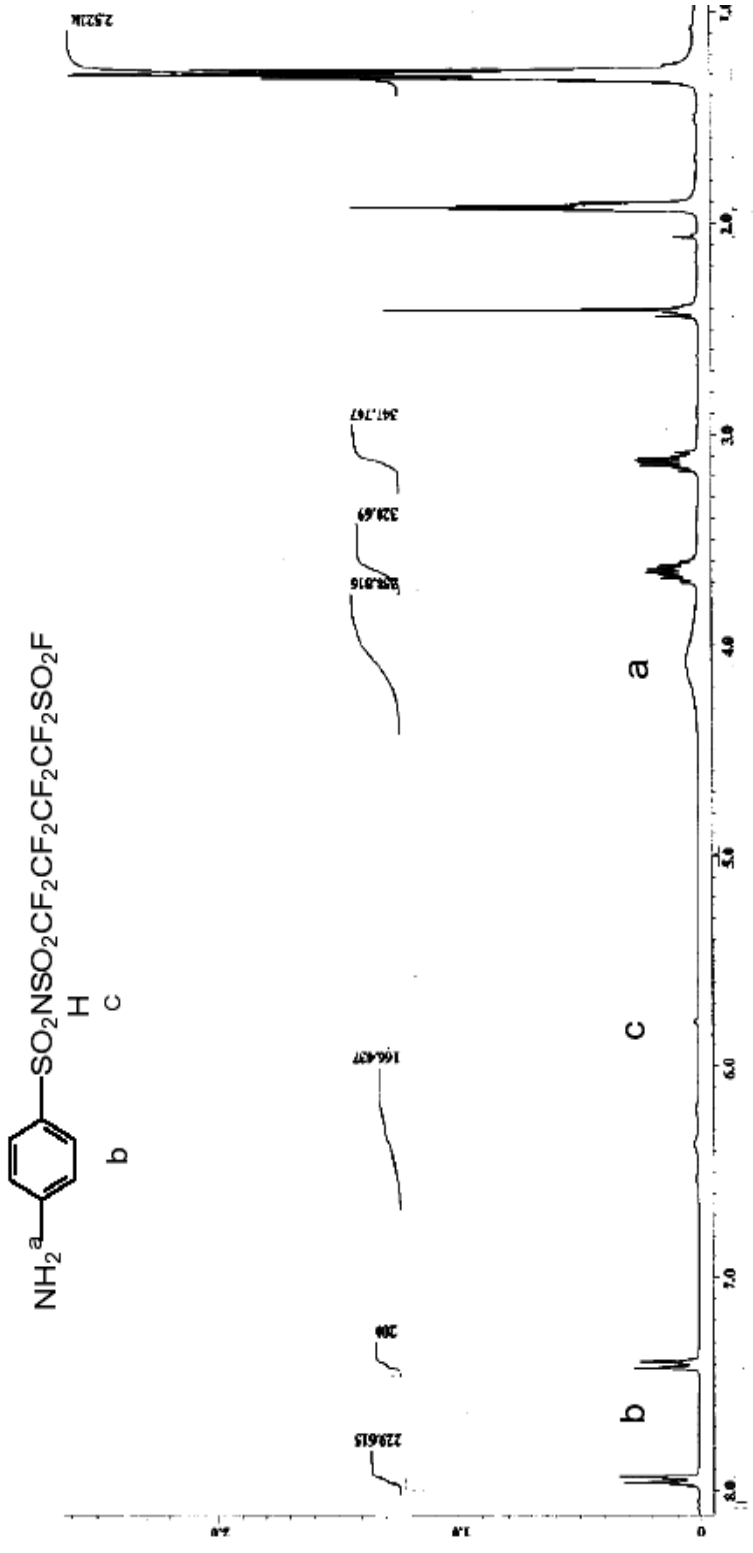


Figure A ^{19}F NMR spectrum of Comound **34a**, 300MHz, CD_3CN

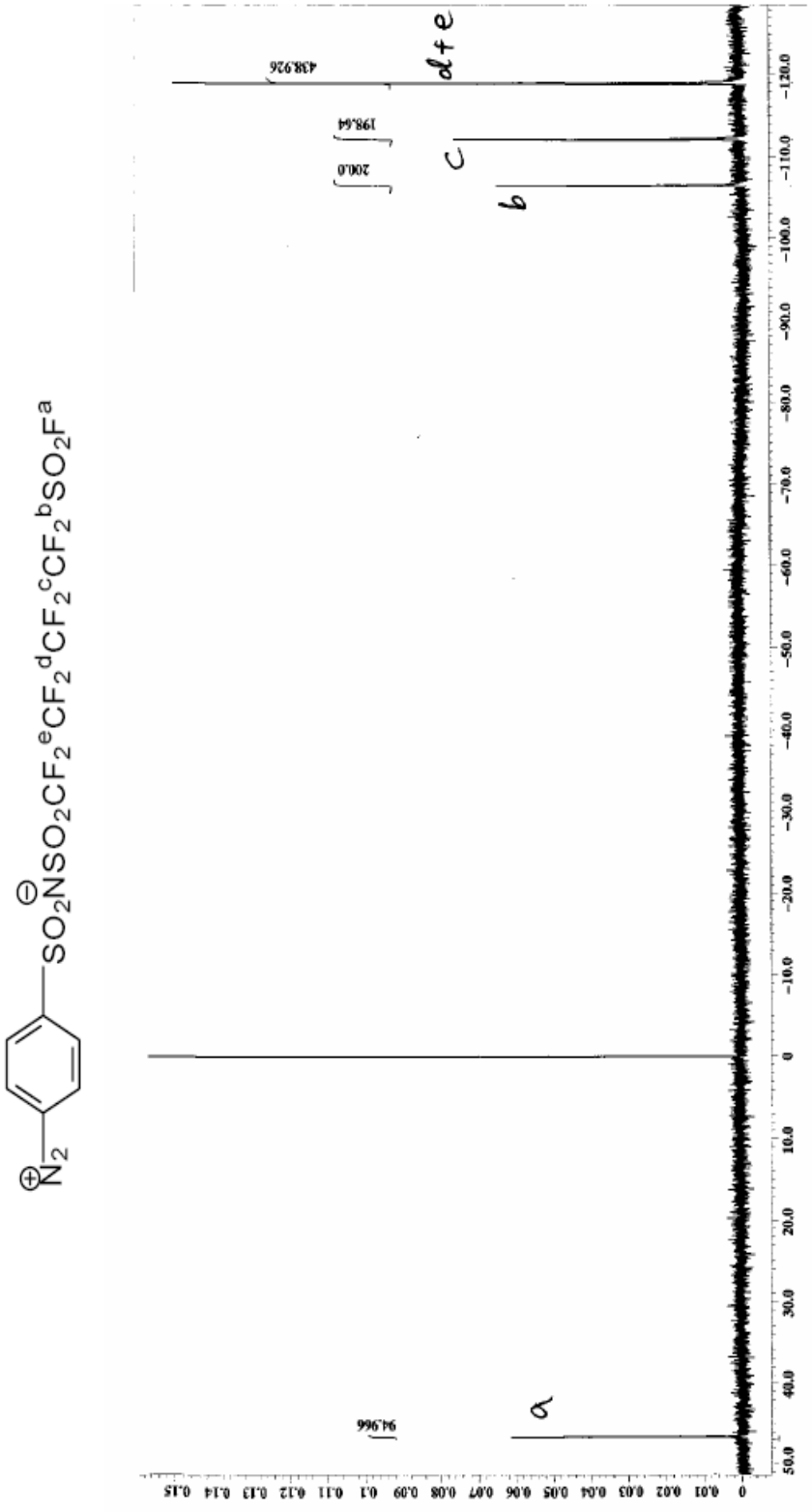


Figure A ^{1}H NMR spectrum of Comound **34a**, 300MHz, CD_3CN

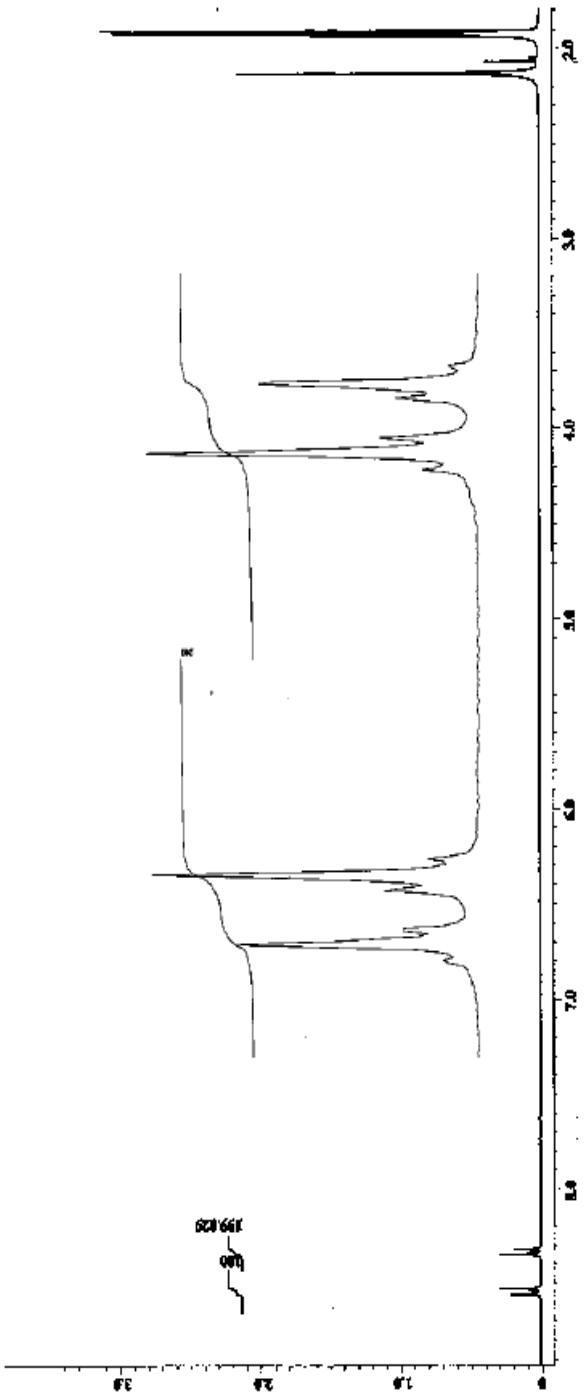


Figure A TGA spectrum of Comound **34a**

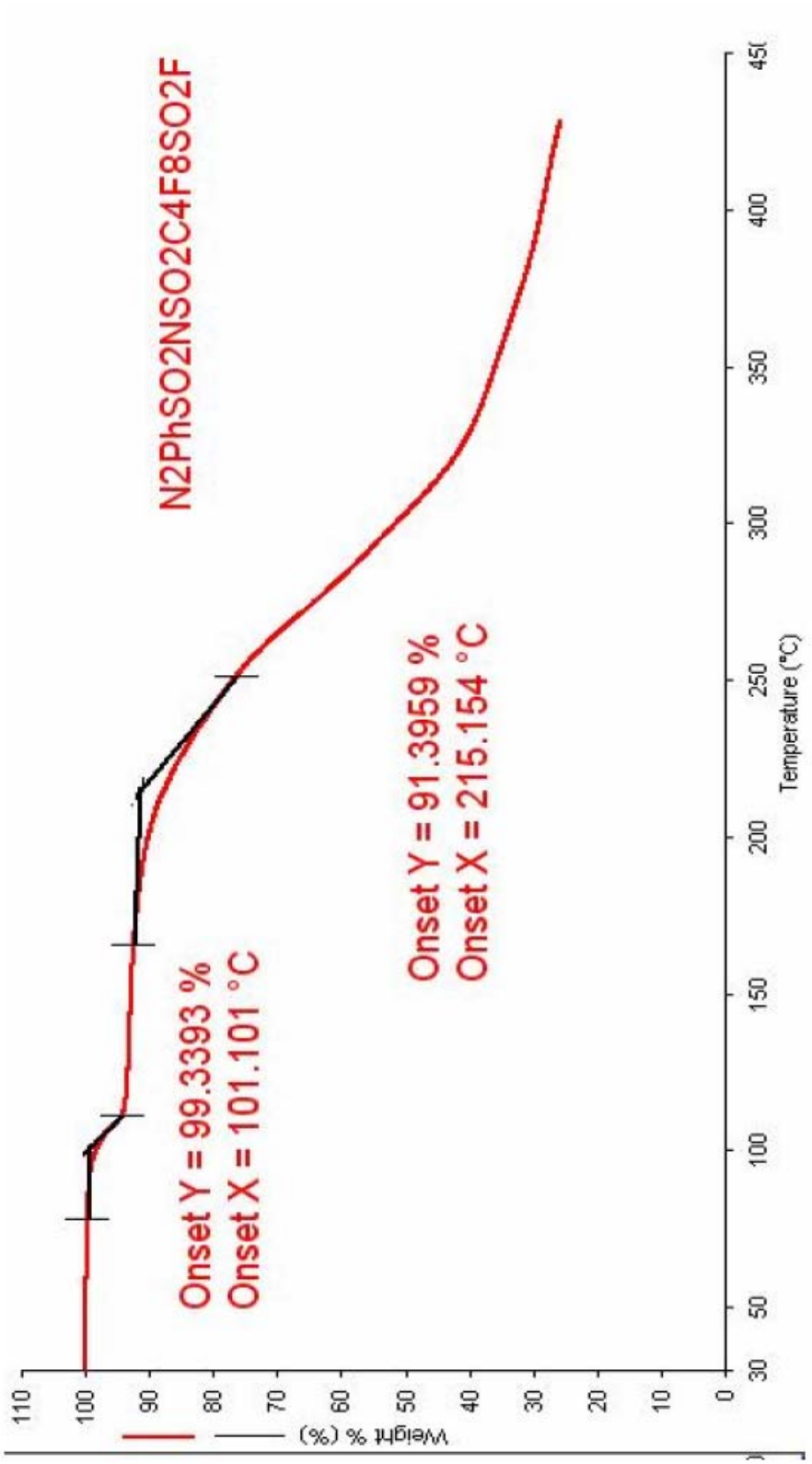


Figure A ^{19}F NMR Spectrum of crude compound **32b**, 300MHz, CD_3CN

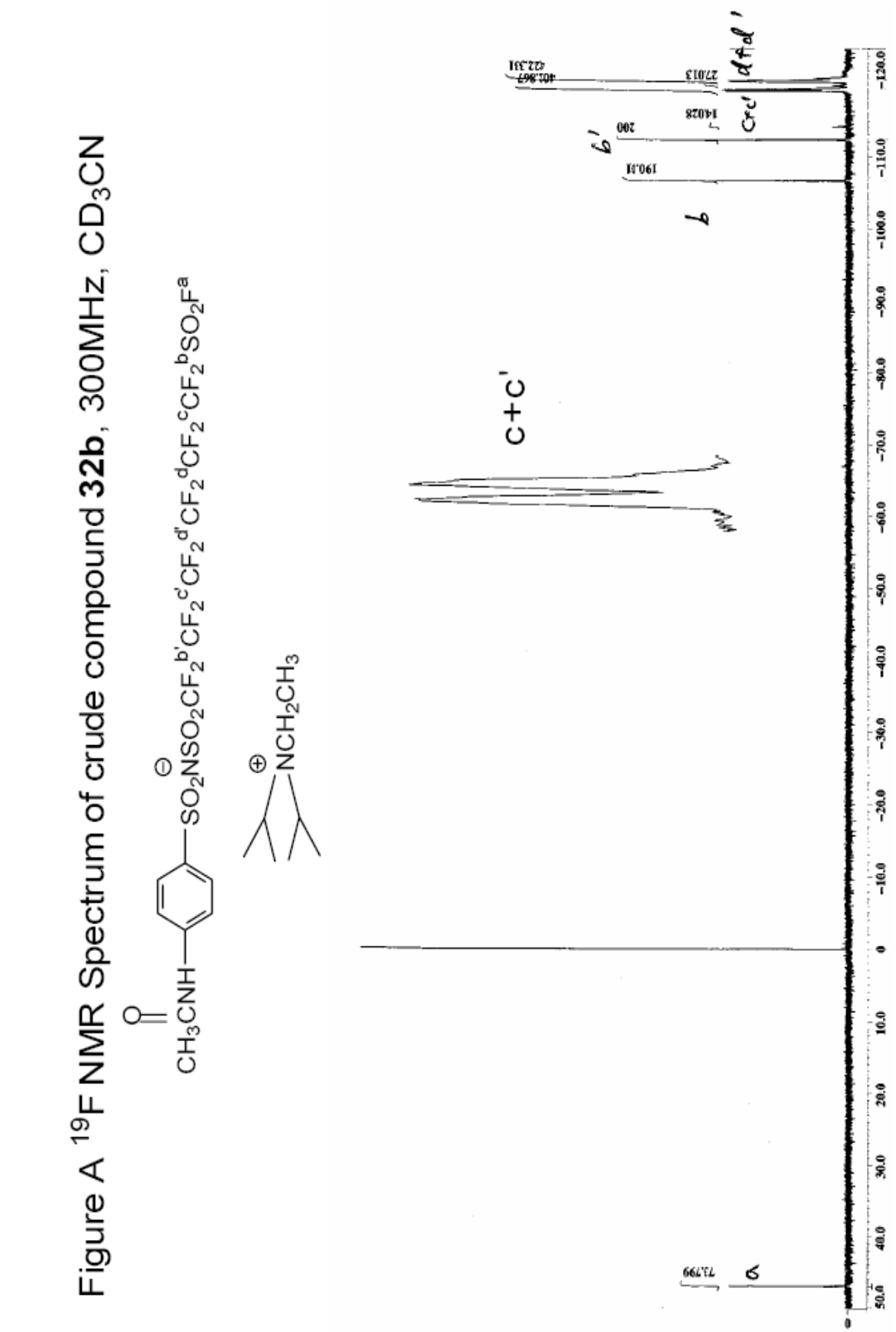


Figure A ^{1}H NMR Spectrum of crude compound **32b**, 300MHz, CD_3CN

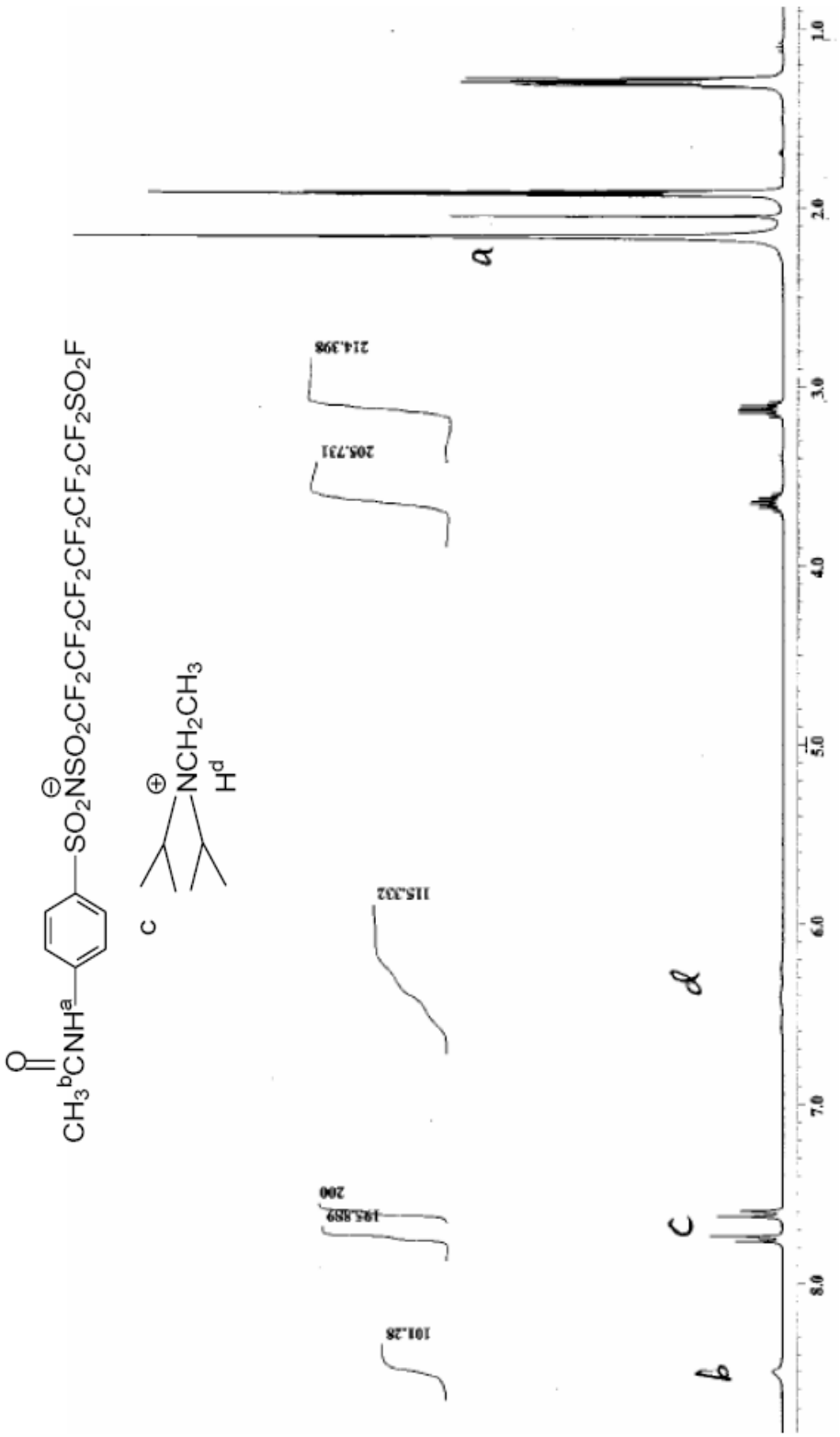


Figure A ^{19}F NMR Spectrum of crude compound **33b** in TFA, 300MHz, CD_3CN

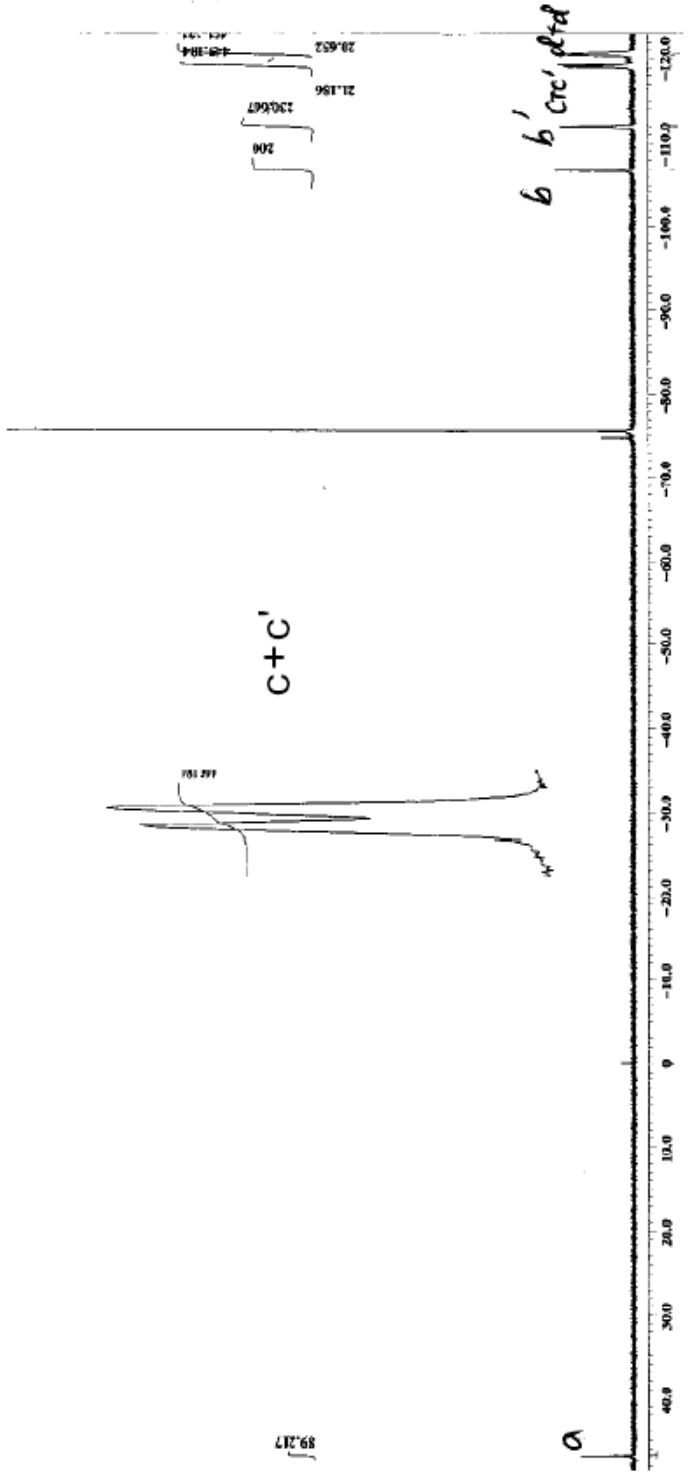


Figure A ^{1}H NMR Spectrum of crude compound **33b**, 300MHz, CD_3CN

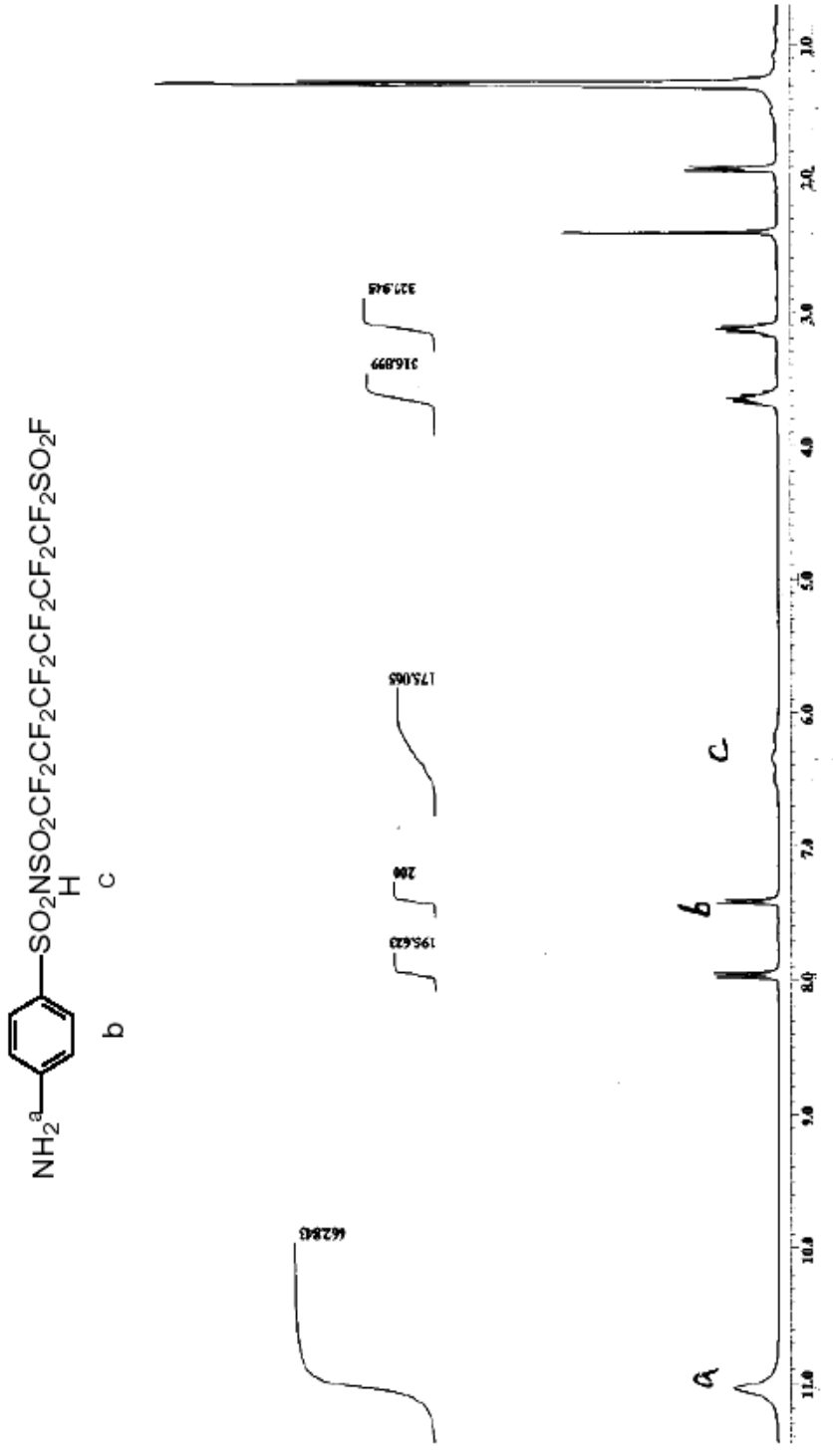


Figure A ^{19}F NMR Spectrum of compound **34b**, 300MHz, CD_3CN

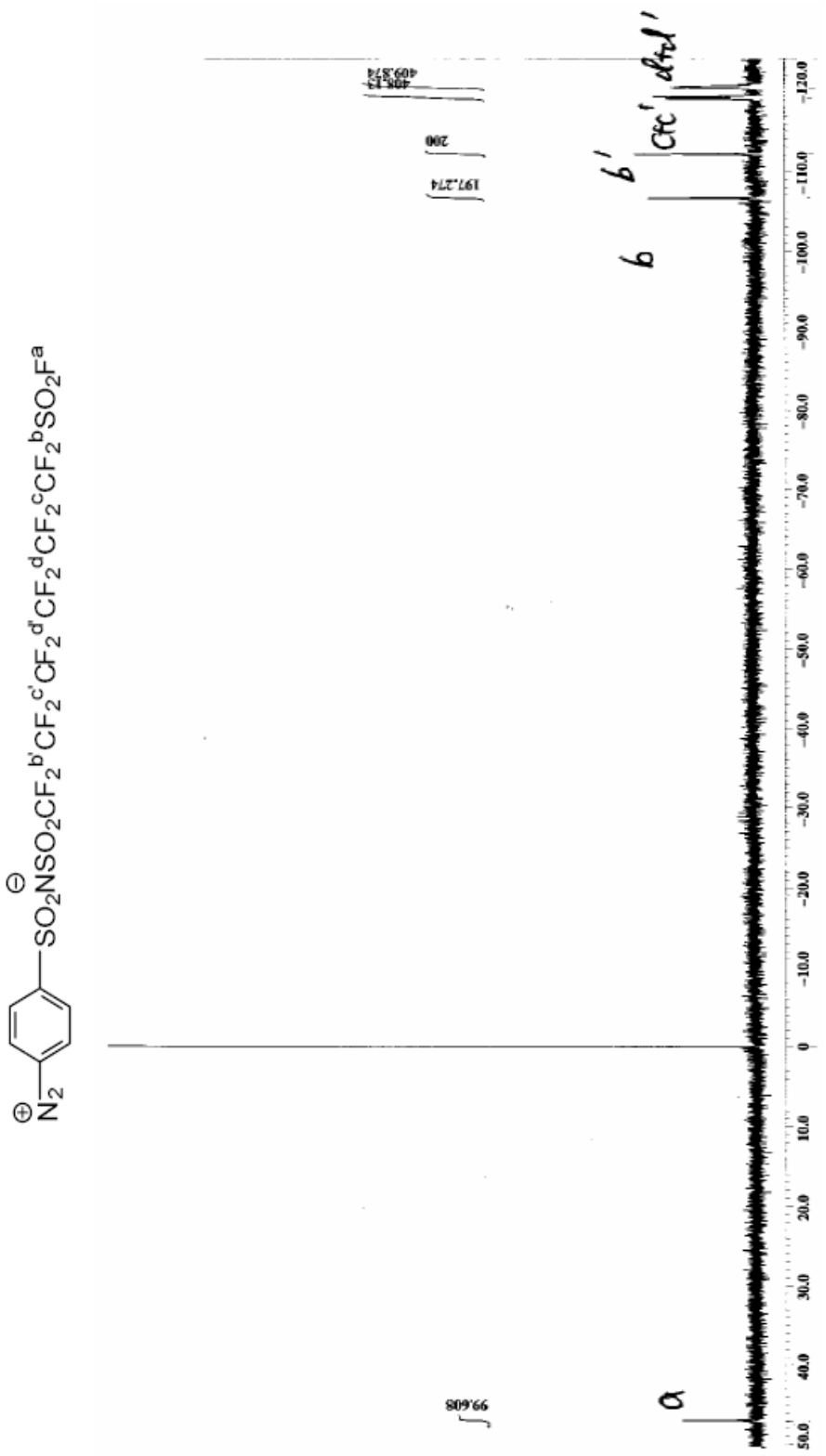


Figure A ^{1}H NMR Spectrum of compound **34b**, 300MHz, CD_3CN

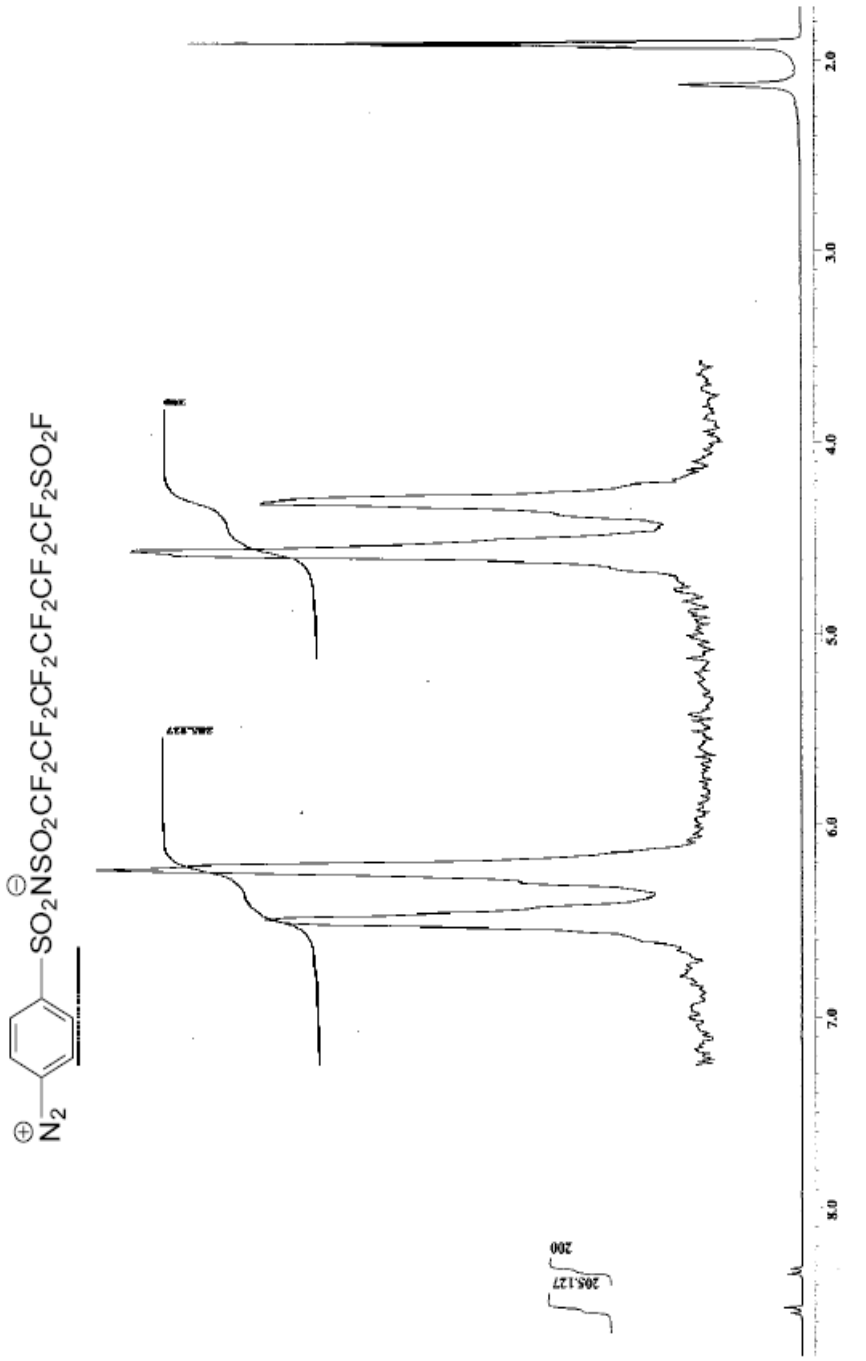


Figure A IR Spectrum of compound **34b**, 300MHz, CD_3CN

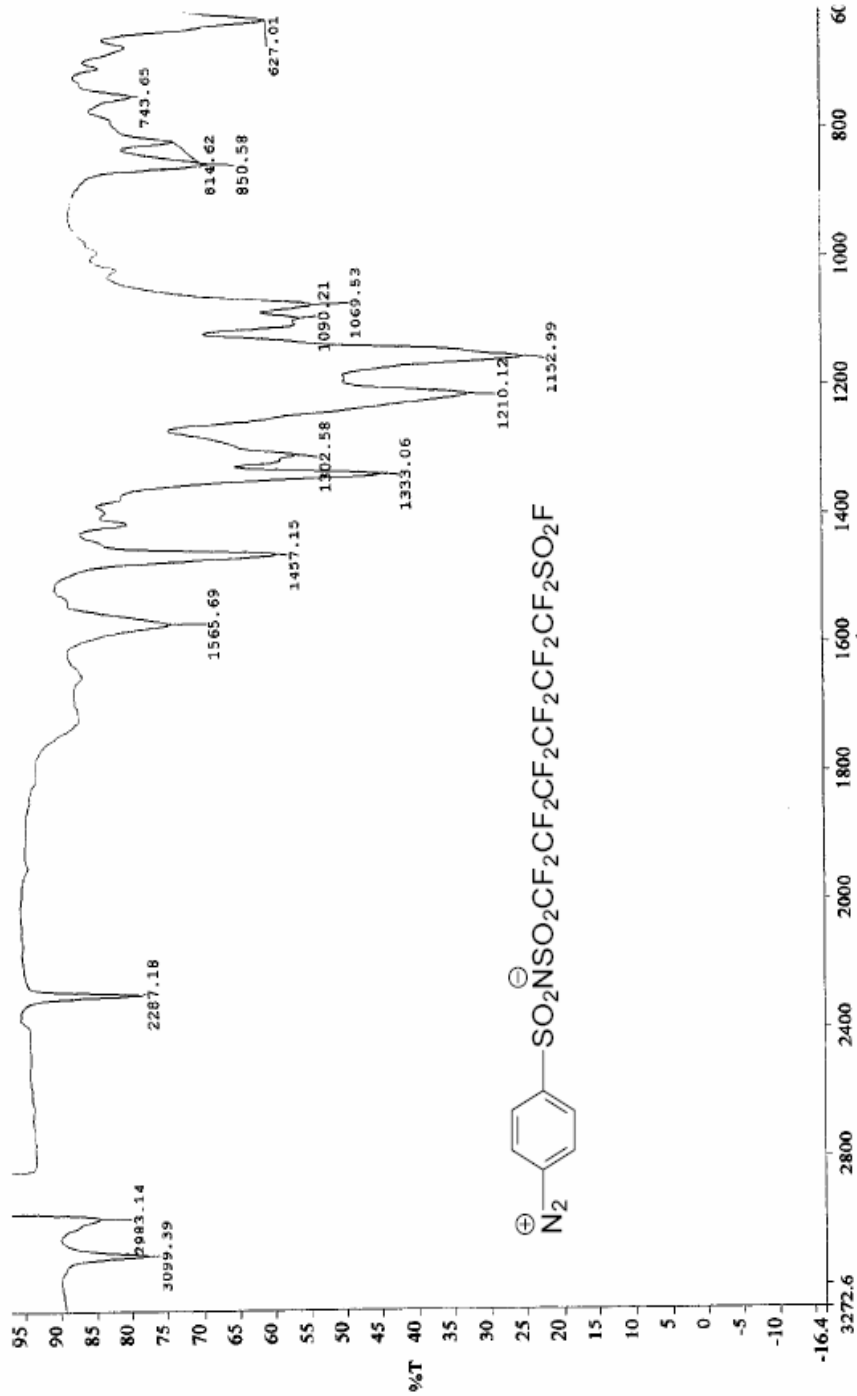
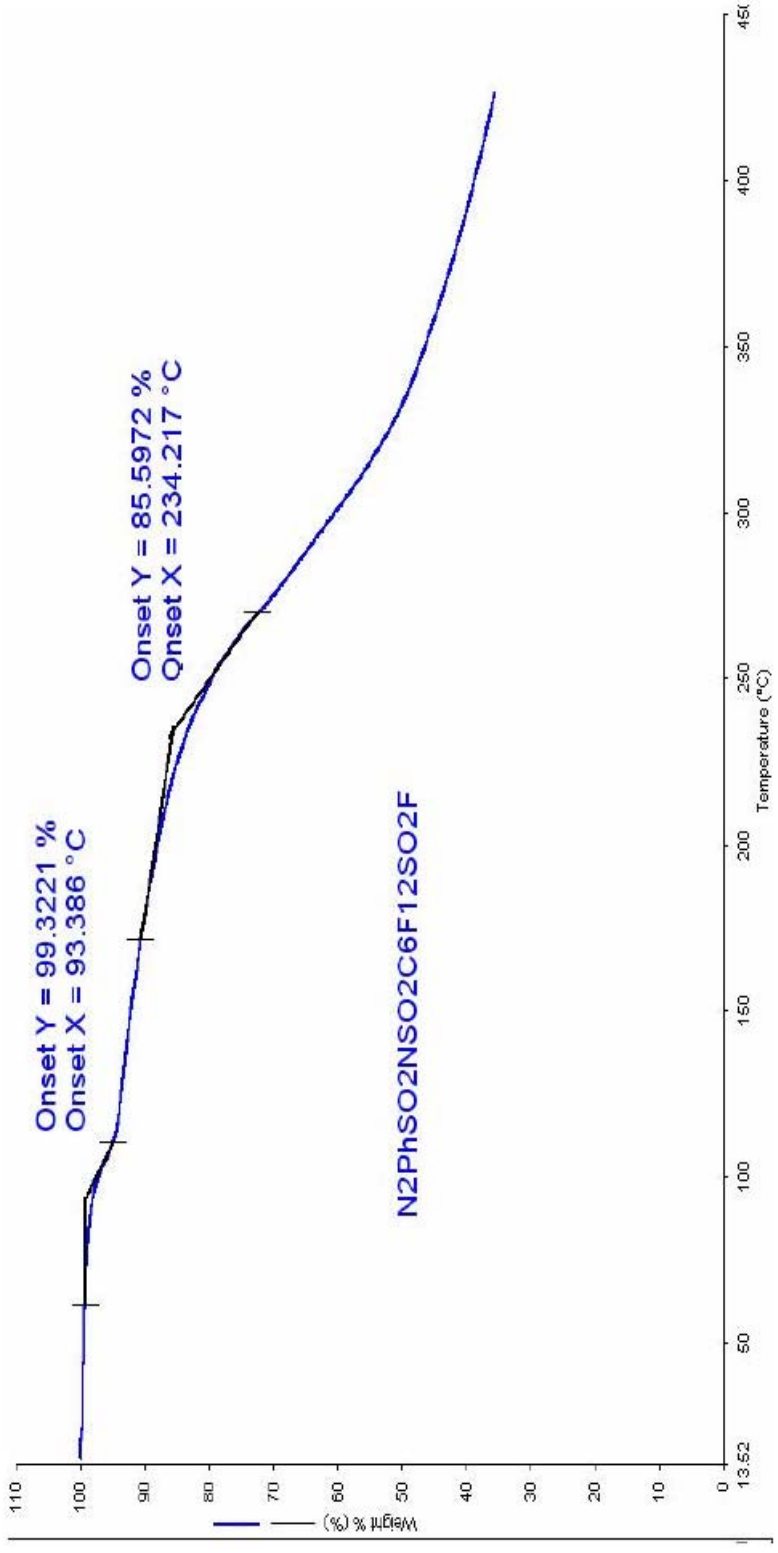


Figure A TGA spectrum of Comound **34b**



LITERATURE CITED

[1] Edsall, J. T. *In Proteins, Amino Acids, and Peptides*; Cohn, E. J., Edsall, J. T., Eds,; *American Chemical Soceity Monograph Series*, Hafner Publishing Co. New York, 1943.

[2] http://www.tiscali.co.uk/reference/encyclopaedia/hutchinson/m0031178.html.

[3] Laughin, R.G. *J. Soc Cosmet. Chem*. 32, 1981, 371.

[4] Laughin, R.G., *Langmuir*, 7, 1991, 842.

[5] Kirsch, P., *Modern Fluoroorganic Chemisty*, 2004.

[6] Gramstad, T.; Hazeldine, R. N., *J. Chem. Soc*., 1957, 4069.

[7] Bordwell, F. G.; Vanier, N. R.; Matthews, W. S.; Hendrickson, J. B.; Skipper, P. L., *J. Am. Chem. Soc*., 977, 1975, 160.

[8] Foropoulos, J. Jr.; DesMarteau, D. D., *J. Am. Chem. Soc*., 104, 1982, 4260.

[9] Foropoulos, J. Jr.; DesMarteau, D. D., *Inorg. Chem.,* 23, 1984, 3720.

[10] Harzdorf, C.; Meussdoerffer, J.; Niederprum, H.; Wechsberg, M., *Justus Liebigs Ann. Chem*., 33, 1973.

[11] Olah, G. A.; Prakash, G. K. S.; Sommer, J., *Superacids*, 1985.

[12] Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sun, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Vlasov, V. M.; Notario, R.; Maria, P. C., *J. Am. Chem. Soc*. 116, 1994, 3047.

[13] DesMarteau, D. D., *Journal of Fluorine Chemisty*, 72, 1995, 203.

[14] DesMarteau, D. D.; Zuberi, S. S.; Pennington, W. T.; Randolph, B. B., *J. Solid State Inorgan. Chem*., 58, 1992, 71.

[15] DesMarteau, D. D.; Pennington, W. T.; Sung K.-S.; Zhu, S.-Z., *Eur. J. Solid State Inorgan. Chem*., 28, 1991, 905.

[16] Saito, M.; Hayamizu, K.; Okada, T., *J. Phys. Chem*. B 109, 2005, 3112.

[17] DesMarteau, D. D.; Lu, C.-Q., 227th ACS National Meeting, March 28-April 1, 2004 (2004), *FLUO-011*. Publisher: (American Chemical Society, Washington, D. C)

[18] Zhang, J.; Martin, G. R.; DesMarteau, D. D., *Chemical Communication*, 10, 2003, 1039.

[19] DesMarteau, D. D.; Hickman, T. D.; Zhang, J.; Rajagopal, R.; Dukes, A., *231st ACS National Meeting*, Atlanta, GA, United States, March 26-30, 2006.

[20] Zhang, J.; DesMarteau, D. D.; Zuberi, S.; Ma, J.-J.; Xue, L.-X.; Gillette, S. M.; Blau, H.; Gehardt, R., *J. Fluor. Chem*., 116, 2002, 45.

[21] Lamanna, W. M.; Savu, P. M.; Parent, M. J.; Zazzera, L. A., *Patent, US6, 555,510*, Apr29, 2003.

[22] Singh, S.; DesMarteau, D. D.; Zuberi, S. S.; Witz, M.; Huang, H.-N., *J. Am. Chem. Soc.,* 109, 1987, 7194.

[23] Gray, F. M., *Solid Polymer Electrolytes-Fundamentals and Technological Applications*, VCH, New York, 1991.

[24] Kordesch, K.; Simader, G., *Fuel Cells and Their Applications*, VCH, New YORK, 1996.

[25] Razaq, J., *Electrochem. Soc*., Vol. 136, No. 2, 1989, 385.

[26] Thomas, B. H.; Shafer, G.; Ma, J.-J.; Tu, M.-H.; DesMarteau, J. Fluor. Chem., 125, 2004, 1231.

[27] a. Geiculescu, O. E.; Yang, J.; Bailey-Walsh, R.; Creager, S. E.; Pennington, W. T.; DesMarteau, D. D., *Solid State Ionics*, 148, 2002, 173.

b. Geiculescu, O. E.; Yang, J.; Zhou, S.; Shafer, G.; Xie, Y.; Albright, J.; Creager, S. E.; Pennington, W. T.; DesMarteau. D. D., *J. Electrochemical Soc*., V. 1512004, Part 9, A1363-A1368, 2004.

[28] Noda, A.; Susan, M. A. B. H.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M., *J. Phys. Chem*. B 107, 2003, 4024.

[29] Waddell, J. E.; Lamanna, W. M.; Krause, L. J.; Moore, G. G. I.; Hamrock, S. J., *US 5514493*, 1996.

[30] Fouassier, J. P.; Rabek, J. F., *Radiation Curing in Polymer Scince and Technology.* Vol. 2-Photoinitiating Systems, Elsevier Applied Science, London (1993).

[31] Ren, K.; Malpert, J. H.; Gu, H.-Y.; Li, H.-Y.; Neckers, D. C., *Tetrahedron*, 58, 2002, 5267.

[32] a. Morspool, W. M., *Synthetic Organic Photochemistry*, Plenum Press, New York, 1984.

b. Ruhimann, D.; Fouassier, J. P., *Eur. Polym. J.,* 29, 1993, 1079.

[33] Shirai, M.; Tsunooka, M., *Prog. Polym. Sci*., Vol. 21, 1996, 1.

[34] Stang, P. J.; Zhdankin, V. V., *Chem. Rev*., 96, 1996, 1123.

[35] Pappas, S. P.; Pappas, B. C.; Gatechair. L. R., *J. Polym. Chem.* Ed. 22, 1984, 69.

[36] Crivello, J. V., *J. Poly. Science: Part A:Polymer Chemistry*,Vol.37, 1999, 4241.

[37] Lamanna, W. M.; Kessel, C. R.; Savu, P. M.; Cheburkov, Y.; Brinduse, S.; Kestner, T.; Lillquist, G.; Parent, M.; Moorhouse, K. S.; Zhang, Y.; Birznieks, G.; Kruger, T.;

Parllazzotto, M., Fedynyshyn, T. (Ed.), *Proceeding of the Society Photo-Optical Instruments Engeering, Advances in Resist Technology and Processing*, Vol. 4690, 2002.

[38] Olah, G. A.; Surya Prakash, G. K.; *Sommer,J.Superacids; Wiley*: New York, 1985, 7.

[39] Ren, K.; Malpert, J. H.; Gu, H.; Li, H.; Neckers, D. C., *Tetrahedron* 58, 2002, 5267.

[40] Crivello, J. V.; Lam, J. H. W., *Macromolecules*, 10, 1977, 1307.

[41] Crivello, J. V.; Lam, J. H. W., *J. Polym. Sci*., *Polym. Chem. Ed*. 17, 1979, 3845.

[42] Neckers, D. C.; Abu-Abdoun, I. I., *Macormolecules*, 17, 1984, 2468.

[43] Komoto, K.; Ishidoya, M.; Ogawa, H.; Sawada, H.; Okuma, K.; Ohta. H. *Polymer,* 35, 1994, 217.

[44] Moreeau, W., *Semiconductor Lithography*, 1989.

[45] Reichmanis, E.; Nalamasu, O.; Houlihan, F. M., *Acc. Chem. Res.,* 32, 1999, 659.

[46] Ablaza, S. L.;Cameron, J. F.; Xu, G.-Y.; Yueh, W., *J.Vac.Sci.Technol. B*, Vol.18, No.5, Sep/Oct 2000.

[47] Lamamnna, W. M.; Kessel, C. R.; Savu, P. M.; Cheburkov, Y.; Brinduse, S.; Kestner, T.; Lillquist, G. J.; Parent, M. J.; Moorhouse, K.S.; Zhang, Y-F; Birzenieks, G.; Kruger, T.; Pallazzotto, M. C., *Advances in Resist Technology and Processing XIX, Proceeding of SPIE*, Vol. 4690, 2002, 817.

[48] Shirai, M.; Katsuta, N.; Tsunooka, M.; Tanaka, M.; Nishijima, K.; Ishikawa, K., *Chem. Express* 3, 1998, 439.

[49] Shirai, M.; Saito, T.; Tsunooka, M.; Tanaka, M., *J. Appl. Polym. Sci*. 41, 1990, 2527.

[50] Gary, P. G.; Petch, M. I., *Platinum Metals Rev.* 44(3), 2000, 108.

[51] Golunski, S., *Platinum Metals Rev.,* 42(1), 1998, 2.

[52] National Energy Technology Laboratory, *Science Applications International Coporation-US Department of Energy*, Parson, Fuel cells hand book, EG&G Services, Office of Fossil Energy, 5th ed, 2000.

[53] Acres, G. J. K.; Frost, J. C.; Hards, G. A; Potter, R. J.; Ralph, T. R.; Thompsett, D. et al. *Catal. Today,* 38, 1997, 393.

[54] Ralph, T. R.; Hards, G. A., *Fuel cells: clean energy production for the new millennium*. Chem Ind, Lond, 1998, 8, 334.

[55] Hyder, A. K.; Sabripour, S.; Flood, D. J.; Halpert, G.; Wiley, R. L., *Spacecraft Power Technologies,* Imperial College Press, World Scientific Publishing Co, Pte, Ltd, 2003, 224.

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

[57] http://www.fuelcells.org/whatis.htm.

[58] Cha, S. Y.; Lee, W. M., *Journal of the Electrochemical Society*, 146 (11), 1999, 4055.

[59] Ticianelli, E. A.; Derouin, C. R.; Redondo, A.; Srinivasan, S., *Journal of the Electrochemical Society*, 135, 1988, 2209.

[60] Wilson, M. S.; Gottesfeld, S., *J. Appl. Electrochem*., 22, 1992, 1.

[61] Uchida, M.; Fukuoka, Y.; Sugwara, Y.; Eda, N.; Ohta, A., *Journal of the Electrochemical Society*, 143 (11), 1996, 2545.

[62] Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; Mcgrath, J. E., *Chem. Rev*., 104, 2004, 4587.

[63] Zawodzinski,T. A.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. J. *Phys. Chem.,* 95, 1991, 6040.

[64] Alberti, G.; Casciola, M.; Palombari, R., *J. Membr. Sci*., 172, 2000, 233.

[65] Gottesfeld, S.; Zawodzinki. T., *Adv. Electrochem. Sci. Eng*., 5, 1997, 195.

[66] Fuel Cells 2000, Types of Fuel Cells, www. Fuelcells.Org/fuel/fctypes.html.

[67] Honma, I.; Nakajima, H.; Nishikawa, O.; Sugimoto, T.; Nomura, S., *J. Electrochem. Soc.*, 150, 2003, A616.

[68] Hobson, L. J.; Ozu, H.; Yamaguchi, M.; Hayase, S., *J. Electochem. Soc*., 148, 2001, A1185.

[69] Slade, S.; Campbell, S. A.; Ralph, T. R.; Walsh, F. C., *J. Electrochem. Soc*., 149, 2002, A1556.

[70] Savett, S. C.; Atkins, J. R.; Sides, C. R.; Harris, J. L.; Thomas, B. H.; Creager, S. E.; Pennington, W. T.; Desmarteau, D. D., *Journal of the Electrochemical Society*, 149 (12), 2002, 1527.

[71] Yamaguchi, T.; Ibe, M.; Nair, B. N.; Nakao, S., *J. Electochem. Soc*., 149, 2002, A1448.

[72] Smitha, B.; Sridhar, S.; Khan. A. A., *J. Mebran. Sci*., 259, 2005, 10.

[73] Montanari, V.; DesMarteau, D. D.; Pennington, W. T., *J. Mol. Struc*, 337, 2000, 550.

[74] Pohlers, G.; Suzuki, Y.; Chan, N.; Cameron, J. F., *Advances in Resist Technology and Processing XIX*, Vol. 4690, 2002, 178.

[75] Lee, D.-K.; Ma, X.; Lamanna, W. M.; Pawlowski, G., *Advances in Resist Technology and Processing XIX*, Vol. 4690, 2002, 169.

[76] Zhou, W.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R., *Science*, Vol.296, 5570, 2002, 1106.

[77] Kuebler, S. M.; Braun, K. L.; Zhou, W.; Cammack, J. K.; Yu, T.; Ober, C. K.; Marder, S. R.; Perry, J. W.; *J. Photochem. and Photobio. A: Chem.* 158, 2003, 163.

[78] Federal Register: *Perfluorooctyl Sulfonates*: Proposed Signifcant New Use Rule. Oct 18, (Vol.65, 202), 62319.

[79] Wafer News, V.8.04, Jan 29, 2001, 1.

[80] Lamanna, W. M.; Kessel, C. R.; Savu, P. M.; Cheburkov, Y.; Brinduse, S.; Kestener, T. A.; Lillquist, G. J.; Parent, M. J.; Moorhouse, K. S.; Zhang, Y.-F.; Birznieks, G.; Kruger, T.; Pallazzotto, Advances in Resist Technology and Processing XIX, Fedynyshyn, T. H., Editor, *Proceeding of SPIE*, 4690, 2002, 817.

[81] Perkins, C.W.; Martin, J. C.; Arduengo, A. J.,III; Law.W.;Alegria, A,; Kochi, J. K., *J. Am. Chem. Soc*. 102, 1980, 7753.

[82] Varvoglis, A., *Hypervalent Iodine in Organic Synthesis*, San Diego 1997.

[83] Varoglis, A., *The Organic Chemistry of Polycoordinated Iodine*, Weinheim, 1992.

[84] Stan, P. J.; Zhdankin, V. V., *Chem. Rev*., 96, 1996, 1123.

[85] Akiba, K., *Chemistry of hypervalent compounds*, New York, 1999, Chap.11 and12.

[86] Kitamura, T.; Matsuyuki, J.; Taniguchi, H., *Syntheis,* 1994, 147.

[87] Shirai, M.; Tsunooka, M., *Perog. Polym. Sci*. Vol. 21, 1996, 1.

[88] Beringer, F. M.; Falk, R. A.; *J. Am. Chem. Soc*. 81, 1959, 2997.

[89] Beringer, F. M.; Lillien, I.; *J. Am. Chem .Soc*., 83, 1960, 725 and 5141.

[90] Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E., *J. Am. Chem. Soc*. 81, 1959, 342.

[91] DesMarteau, D. D.; Montanari, V.; Pennington, W. T., *J. Fluor.Chem*., 2003, 57.

[92] Montanari, V.; DesMarteau, D. D.; Pennington, W. T.; *J. Molecular Sturcture*, 2000, 337.

[93] Koser, G. F. *The chemistry of Functional Groups,* Wiley: New York, 1983; Supplement D, Chapter 18, 774.

[94] Kappe, T.; Korbuly, G.; Stadlbauer, W.*Chem. Ber*. 111, 1978, 3857.

[95] Pongratz, E.; Kappe,T., *Monatsh.Chem*., 115, 1984, 231.

[96] Spyroudis, S.; Varvoglis, A., *J. Chem. Soc*., Perkin Trans.1, 1984, 135.

[97] Hubbard. C. R.; Himes, V.; Mighell, A. D. *,Acta. Cryst*., B36, 1980, 2819.

[98] a. Beringer, F. M.; Lillien, I., *J .Am. Chem. Soc*., 82, 1960, 725.

b. Bachofner, H. E.; Beringer, F. M.; Meites, L., *J. Am. Chem. Soc*. 80, 1957, 4274.

c. Beringer, F. M.; Falk, R. A., *J. Am. Chem. Soc*., 81, 1959, 2997.

[99] Huang, W-Y, *J. Fluorine Chem*, 54, 1991, 1.

[100] Litster, S.; Mclean, G., *J. Power. Source*, 130, 2004, 61.

[101] Yu, Y.; Kosbach, L., US6399202, June 4, 2002.

[102] Belmont, J.A.; Amici, R. M.; Galloway, C. P., US6042643, Mar 28, 2004

[103] Qi, Z.; Kaufman, A., *J. Power Sources*, 113, 2003, 37.

[104] Jia, N.; Martin, R. B.; Qi, Z.; Lefebvre, M. C.; Pickup, P. G., *Electrochimica Acta.,* 46, 2001, 2863.

[105] Wilson, M. S.; Valerio, J. A.; Gotttesfeld, S., *Electrochim. Acta.,* 40, 1995, 355.

[106] Tosco, P.; Kosbach, L.; Yu, Y.; Orecchia, C., US 6881511, 2003.

[107] Kumar, G. S.; Raja, M.; Parthasarathy, S., *Electrochim. Acta.,* 40, 1995, 285.

[108] Cha, S.Y.; Lee, W. M., *J. Electrochem. Soc*., 146, 1999, 4055.

[109] O'Hayre, R.; Lee, S. J.; Cha, S. W.; Prinz, F. B., *J. Power Source,* 109, 2002, 483.

[110] Creager, S. E., proposal for DOE project, 2006.

[111] Lee, S. J.; Mukerje, S.; McBreen, J.; Rho, Y. W.; Kho, Y. T.; Lee, T. H., Electochim. Acta., 43, 1998, 3693.

[112] Gebel, G.; Benoit, L., *Journal of Molecular Strucuture*, 383, 1996, 43.

[113] Loppinet, B.; Gebel G.; Williams, C. E., *Journal of Physical Chemistry B*, 101(10), 1997, 1884.

[114] Hampden-smith, M. J.; Atanassova, P.; Napolitano, P.; Bhatia, R.; Rice, G.I.; Caruso, J.; Brewster, J.; Gurau, B., WO2005/091416, 2005.

[115] Tsubakowa, I., *Polym. Sci.*,Vol. 17, 1992, 417,.

[116] Vidal, A.; Riess, G.; Donnet, J. B. US 4014844, 1971.

[117] Rivin, D.; Aron, J., US 3479300, 1969.

[118] Watson, J. W.; Kendall, C. E.; Jervis, R., U.S.3043708, 1962.

[119] Van, A.; Johannes, J. A. P., U.S.2502540, 1950.

[120] Glassman, J., U.S 2514236, 1950.

[121] Pinson, J.; Saveant, J. M.; Hitmi, R., WO 92/13983, 1992.

[122] Litster, S.; McLean, G., *Journal of Power Science*, 130, 2004, 61.

[123] Baranton, S.; Belanger, D., *J. Phys. Chem.B*, 109, 2005, 24401.

[124] Jameel, M., US20030017379, 2003.

[125] Hitchcoci, M. K.; Suh, K. W.; Bartz, A. M.; Paquet, A. N.; Stobby, W. G., US 5571847, 1996.

[126] Pinson, J.; Podvorica, F., *Chem. Soc. Rev*., 34, 2005, 429.

[127] Liu, G.; Liu, J.; Bocking, T.; Eggers, P. K.; Gooding, J. J., *Chemical Physics*, 319, 2005, 136.

[128] Adenier, A.; Bernard, M.-C.; Chehimi, M. M.; Cabet-Deliry, E.; Desbat, B.; Fagebaume, O.; Pinson, J.; Podvorica, F., *J. Am. Chem. Soc*., 123, 2001, 4541.

[129] Villeneuve, C. H.; Pinson, J.; Bernard. M.-C.; Allongue, P., *J. Phys. Chem.B*, 101, 1997, 2415.

[130] Combellas, C.; Delamar, M.; Kanoufi, F.; Pinson, J.; Podvorica, F. I., *Chem, Mater*., 17, 2005, 3968.

[131] Radi, A. E.; Montornes, J. M.; O'Sullivan, C. K.; *J. Electoanalytcal Chem*., 587, 2006, 140.

[132] Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski,M. J.; Smalley, R. E.; Tour, J. M., *J. Am. Chem. Soc*., 123, 2001, 6536.

[133] Hammett, L. P., *Physical Organic Chemistry*, McGraw Hill, New York, 1940, 295.

[134] a. Insole, J. M.; Lewis, E. S., *J. Am. Chem. Soc*., 85, 1963, 122.

b. Lewis, E. S.; Hinds, W. H., *J. Am. Chem. Soc*., 74, 1952, 304.

c. Lewis, E. S.; Holliday, R. E., *J. Am. Chem. Soc.,* 91, 1969, 426

[135] a. Swain, C. G.; Sheats, J. E.; Gorenstein, D. G.; Harbison, K. B., *J. Am. Chem. Soc*., 97, 1975, 791.

b. Swain, C.G.; Sheats, J. E.; Harbison, K. B., *J. Am. Chem. Soc*., 97, 1975, 783.

[136] a. DeTar, D. F.; Kwong, S., *J. Am. Chem. Soc*., 78, 1956, 3921.

b. DeTar, D. F.; Ballentine, A. R., *J. Am. Chem. Soc*., 78, 1956, 3916.

[137] a. Gloor, B.; Kaul B. L.; Zollinger, H., *Helv. Chim. Acta*, 1972, 55,1596.

b. Zollinger, H., *Acc. Chem. Res*., 6, 1973, 335.

c. Ravenscroft, M. D.; Skrabai, P.; Weiss B.; Zollinger, H., *Helv. Chim. Acta*, 71, 1988, 515.

[138] Canning, P. S;. McCrudden, J. K.; Maskill, H.; Sexton, B., *J. Chem. Soc*., Perkin Trans. 2, 1999, 2735.

[139] Bunnett, J. F.; Yijima, C., *J. Org. Chem*., Proceeding Paper in this issue.

[140] Broxton, T. J.; Bunnett, J. F.; Paik, C. H., J. *Org. Chem*., Vol.42, No.4, 1977, 643.

[141] a. DeTar, D. F.; Osuge, T. K., J. Am. Chem. Soc., 80,1958, 6072.

b. DeTar, D. F.; Turetzky, M. N., *J. Am. Chem. Soc*. ,1956, 78,3925.

[142] a. Melander, L., *Ark. Kemi*, 3, 1951, 525.

b. Kumar, R.; Singh, P. R., *Tetrahedron Lett*., 1972, 613.

c. Wassmundt, F. W.; Kiesman, W. F., *J. Org. Chem*., 62, 1997, 8304.

[143] a. Burri, P.; Loewenschuss, H.; Zollinger, H.; Zwolinski, G. K., *Helv. Chim. Acta*, 57, 1974, 395.

b. Szele I.; H.Zollinger, Helv.Chim.Acta, 1978,61,1721.

[144] Pazo-Llorente, R.; Bravo-Diaz, C.; Gonzalez-Romero, E., *J. Anal. Chem*., 2001, 582.

[145] Zollinger, H., *Diazo Chemistry I, Aromatic and Heteroaromatic Compounds*, VCH: Weinheim, New York, 1994.

[146] Saunders, K. H.; Allen, R. L., *Aromatic Diazo Compounds*, 3th edn, Edward Arnold: Baltimore, 1985.

[147] Belmont, J. A.; Amici, R. M.; Galloway, C. P., U.S.5900029, 1998.

[148] Belmont, J. A.; Amici, R. M.; Galloway, C. P., U.S.6042643, 1998.

[149] Griess, J. P.; *Justus Liebigs Ann.Chem*. 106, 1858, 123; 120, 1861, 125.

[150] Hanson, P.; Jones, J. R.; Taylor A. B.; Walton P. H.; Timms, A. W., *J. Chem. Soc*., Perkin Trans. 2, 2002, 1135.

[151] Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Paolillo, R.; Taccardi, N., *Eur. J. Inorg. Chem*., 2005, 582.

[152] Mella, M.; Coppo, P.; Guizzardi, B.; Fagnoni, M.; Freccero, M.; Albini, A., *J. Org. Chem*., 66, 2001, 6344.

[153] Meerwein, H.; Buchner, E.; Emster, K.van, *J. Prakt. Chem*., 152, 1939, 237.

[154] Balz G.; Schiemann, G., Ber., 60, 1927, 1186.

[155] Glaser,R.; Horan, C. J., *J. Org. Chem*., 60, 1995, 7518.

[156] Svyentoslavskii, V.; Manoszon, A., *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva,* 45, 1914, 1765.

[157] Greenberg, B.; Okaya, Y., *Acta. Cryst*., B25, 1969, 2101.

[158] Siegrist, U.; Rapold, T.; Blaser, H-U., *Organic Process Research & Development* 7, 2003, 429.

[159] Schank, K., *Methodicum Chimicum*, Vol.6 (Ed.F.Zymalkowski), Academic Press, New York, San Francisco, London, 1975, p.159; Georg Thieme Publishers, Stuttgart, 1975.

[160] Wilcox, D. H. Jr, *Amer. Dyest. Rept*., 55, 1966, 891.

[161] Shaw, R., *The Chemistry of Dizonium and Diazo Groups*,(Ed. S. Patai), Stonebridge Press, Chichester, New York, Brisbane, Toronto, 1978, John Wiley & Sons Publishers.

[162] DesMarteau, D. D.; Witz, M., *J. Fluor. Chem*., 1991, 52, 7.

[163] Adenier, A.; Bernard, M.-C.; Chehimi, M. M.; Cabet-Deliry, E.; Desbat, B.; Fagebaume, O.; Pinson J.; Podvorica, F., *J. Am. Chem. Soc*., 123, 2001, 4541.

[164] Howells, R. D.; McCown, J. D., *Chem. Review*, No.1, 1977, 69.

[165] Senning, A., *Chem. Reviews*, 65, NO.4, 1965, 385.

[166] Hendrickson, J. B.; Sternbach, D. D.; Bair, K.W., *Acc. Chem. Res*., 1976, 306.

[167] Varfolomeev, L. I.; Grodetskii, S. A.; Dudkin, V. V.; Kat'yanova, V. R.; Strushlyak, A. I.; Shinkarkin, N. L.; Yurochkin, V. M. *Russ*., 5 pp. RU 2177940, 2002.

[168] Bernard, C. F.; Casey, M.; Chen, F-X.; Grogan, D. C.; Poirier, M.; Williams, R. P.; Wong, Y-S.; Wu, G. G., *Synthesis of intermediates useful in preparing tricyclic compounds*., U.S. 6372909, 2002 ,

[169] Klumpp, D. A; Rendy R.; Zhang, Y.; Gomez A.; McElrea, A., *Organic letters*, 6(11), 2004, 1789.

[170] Sir Derek Barton, F. R. S.; Davidollis, W. F. R. S., *Comprehensive Organic Chemistry*, 1979.

[171] Carruthers, W., *Some Modern Methods of Organic Synthesis*, 1986.

[172] Bellamy, F. D.; Ou, K., *Tetrahedron Letters*, Vol.25, 8, 1984, 839.

[173] Zinin, N., *J. Prakt. Chem*., [1] 27, 149, 1842.

[174] Patai, S., *The Chemistry of Diazonium and Diazo Groups* (II), John Wiley & Sons, Chichester, New York, Brisbane, Toronto, An Interscience Publication, 1978, 647.

[175] Schank, K., *Methodicum Chimicum,* Vol. 6 (Ed. F. Zymalkowski), Academic Press, New York, San Francisco, London, Georg Thieme Publishers, Stuttgart, 1975, 164.

[176] Pütter, R., *Methoden der Organischen Chemie* (Houben-Weyl-Müller), Vol. X, Part 3, 4th ed., Georg Thieme Verlag, Stuttgart, 1965, 22.

[177] Refernce [74], 165.

[178] Refernce [75], 28.

[179] Sheppard, W.A., *J. Org. Chem*. 29, 1964, 1.

[180] Feiring, A. E.; Auman, B. C.; Wonchoba, E. R., *Macromoleules,* 26, 1993, 2779.

[181] Feiring, A. E.; Auman, B. C.; *Polym. Prepr. (Am. Chem. Soc. Div. Polym.Chem.*) 35, 1994, 751.

[182] DesMarteau, D. D.; Martin, C. W.; Ford, L. A.; Xie, Y., *US 6268532*, July31, 2001.

[183] Creager, S. E.; Summer, J. J.; Baily, R. D.; Ma, J. J.; Pennington, W. T.; DesMarteau, D. D., *Electrochem. Solid State Lett*. 2 (9), 1999, 434.

[184] Smith, D. W. Jr.; Chen, S.; Kumar, S.; Ballato, J.; Shah, H.; Topping, C.; Foulger, S., *Adv. Mater*., 14 (21), 2002, 1585.

[185] a. Foulger, S. H.; Jiang, P.; Lattam, A.; Smith, D. W. Jr.; Ballato, J., *Langmuir,* 17, 2001, 6023.

b. Luo, J.; Liu, S.; Haller, M.; Liu, L.; Ma, H., Jen, A. K. Y., *Adv. Mater*., 14 (23), 2002, 1763.

[186] Traiphol, R.; Shah, H. V.; Smith, D. W. Jr.; Perahia, D., *Macromolecules,* 34 (12), 2001, 3954.

[187] Fishbeck, G.; Moosburger, R.; Kostrzewa, C.; Achen, A.; Petermann, K., *Electron. Lett*., 33(6), 1997, 518.

[188] Tumolillo, T. A. Jr.; Thomas, A.; Ashley, P. R., *Appl. Phys. Lett*., 62 (24), 1993, 3068.

[189] Souzy, R.; Ameduri, B.; Boutevin, B.; Virieux, D., *J. Fluorine Chem*., 125, 2004, 1317.

[190] Qing, F-l.; Wang, R-w.; LI, B-h.; Zheng, X.; Meng, W-d., *J. Fluorine Chem*., 120, 2003, 21.

[191] Wang, S.Y.; Borden, W. T., *J. Am. Chem. Soc*., 111, 18, 1989, 7282.

[192] Spraul, B. K.; Suresh, S.; Jin, J-y.; Smith, D. W. Jr., *J. Amer.Chem.Soc*., 126, 2006, 7055.

[193] a. Smith, D. W. Jr.; Babb, D. A.; Shah, H. V.; Hoeglund, A.; Traiphol, R.; Perahia, D.; Boone, H. W.; Langhoff, C.; Radler, M., *Journal of Fluorine Chemistry*, 104, 2000, 109.

b. Ligon, S. C. Jr; Krawiec, M.; Kitaygorodskiy, A.; Smith, D. W. Jr., *Journal of Fluorine Chemistry*, 123, 2003, 139.

c. Perpall, M. W.; Smith, D. W.; DesMarteau, D. D.; Creager, S. E., *Polymer Reviews*, 46, 2006, 297.

[194] Woon-Seop C., Harris, F. W., *Polymer* 41, 2000, 6213.

[195] Perpall, M. W.; Shaban, I. S.; Mei, H.; Creager, S. E.; DesMarteau, D. D.; Smith, D. W., *Functionalized nanostructured carbons for fuel cell electrodes.*, Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22-26, 2004.

[196] Yamabe, M.; Miyake, H., Organofluorine Chemistry. Principles and Commerical Applications, Banks, R. E.; Smart, B. E.; Tatlow, J. C.,(Eds.), Plenum Press, NY, 1994, 403-411.

[197] a. Meyer, W. H., *Adv. Mater*. 10, 1998, 439.

b. Savadogo, O., *J. New Mater. Electrochem. Sys*. 1, 1998, 47.

[198] www. Fuelcells. Org/fuel/fctypes, html.

[199] Connoly, D. J.; Gresham, W. F.; *US. 3,282,875*, 1996.

[200] Olah, G. A.; Iyer, P. S.; Sura, P., *Synthesis,* 1986, 513.

[201] Terjeson, R. J.; Mohtasham, J.; Sheet, R. M.; Gard. G. L.; *J. Fluorone Chem*. 38, 1988, 3.

[202] DesMarteau, D. D.; *J. Fluor. Chem*., 72, 1995, 203.

[203] DesMarteau, D. D.; Marin, C. W.; Ford, L. A.; Xie, X., *US 6268532*, assigned to 3M Innovative Properties Company, 2001.

[204] Ford, L. A.; Smith, D.W. Jr., DesMarteau, D. D., *Polym. Mater. Sci. Eng*., *(Am. Chem. Soc., Div. PMSE*), 83, 2000, 10.

[205] Theodoridis, G., *Tetrahedron*, 56, 2000, 2339.

[206] Jarowicki, K.; Kocieński, P., *J. Chem. Soc*., Perkin Trans. 1, 2001, 2109.

[207] O'Sullivan, M. C.; Dalarylmple, D. M.; *Tetrahedron Lett*. 36, 1995, 3451.

[208] Admczyk, M.; Fishpaugh, J. R.; Heuser, K.; *J. Org. Prep. Proced. Int*., 30(3), 1998, 339.

[209] Lima, L. M.; Castro, P.; Machado, A. L.; Fraga, C. A. M.; Lugnier, C.; Moraes, V. L. G.; Barreiro, E. J., *Bioorganic&Medicinal Chemistry*, 10, 2002, 3067.

[210] Cremlyn, R. J., *Chlorosulfonic Acid (A Versatile Reagent)*, Athenaeum Press Ltd, Gateshead, Tyne and Wear, UK, 2002.

[211] *Liebig Ann.Chem*. 1949, 22

[212] *Chem.Ber*., 20, 1887, 2224.

[213] *Chem. Ber*., 37, 1904, 1038.

[214] Halberstadt, E. S.; Hughes, E. D.; Ingold, C. K., *Nature*, 158, 1946, 514.

[215] Rappoport, *Z*.; Peled, P., *J. Amer. Chem. Soc*., 101, 10, 1979, 2682.