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SYNTHESIS AND CHARACTERIZATION OF 4,4'-BIPYRIDINE BASED IONIC LIQUIDS (ILs)

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A GRADUATE PROJECT SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADDIS ABABA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OFSCIENCE IN CHEMISTRY

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DECLARATION

I, the undersigned confirm that this is my original work obtained by research carried out by me under the supervision of my advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2009-2010. No part of this work shall be published in any scientific journals or presented at conferences without the knowledge and consent of my advisor, who is the principal scientist for my publication. Furthermore if the work is published, the international address given should be that of the Chemistry Department of AAU. Finally this work has not been submitted for a degree in any other University and all sources used for the study have been duly acknowledged.

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This project work has been submitted for examination with my approval as University advisor:

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List of abbreviations and symbols

ILs – ionic liquids

VOCs – volatile organic compounds

NTf_2 – bis(trifluoromethylsulfonyl)imide

bPy – bipyridine

C_1bPyI/NTf_2 – methyl-4,4'-bipyridinium (iodide)/ bis(trifluoromethylsulfonyl)imide –1A/1B

C_2bPyI/NTf_2 – ethyl-4,4'-bipyridinium (iodide)/ bis(trifluoromethylsulfonyl)imide –2A/2B

C_3bPyBr/NTf_2 – propyl-4,4'-bipyridinium (bromide)/ bis(trifluoromethylsulfonyl)imide –3A/3B

C_4bPyBr/NTf_2 – butyl-4,4'-bipyridinium (bromide)/ bis(trifluoromethylsulfonyl)imide –4A/4B

C_5bPyBr/NTf_2 – pentyl-4,4'-bipyridinium (bromide)/ bis(trifluoromethylsulfonyl)imide –5A/5B

NMR – Nuclear magnetic resonance

DMSO – dimethyl sulfoxide

$CHCl_3$ – chloroform

δ – Chemical shift

J – Coupling constant

S – Singlet

d – Doublet

t – Triplet

q – Quartet

quin– quintet

sex– sextet

dd – doublet of doublet

td – triplet of double

Abstract

Ionic liquids are salts with low melting points (<100 ^{0}C). Since ionic liquids exhibit extremely low vapor pressures, they do not release VOCs to the environment; and have positive impact on ecological and environmental effect during synthesis and processing of chemicals. They provide good solubility for a wide range of reactions, their design for use as solvents can serve both for immobilization and coordinating ligands for the catalyst in processes involving homogeneous catalysis. This can be addressed by synthesizing ionic liquids with functional groups that can complex the metal centers. To this effect, they are called designer and eco-friendly solvents.

These interesting compounds are achieved either by incorporating a bulky, asymmetric N-heterocyclic cation into the structure through quaternization process in order to preclude good crystal packing and/or by selecting an anion in which there is considerable delocalization of the electron cloud over the molecular backbone that tends to decrease interionic interaction, example-bis(trifluoromethylsulfonyl)amide.

Therefore the main objective of this project is to synthesize such important ionic liquids based on 4,4'-bipyridine heterocycles through quaternization with alkyl halides which are applicable in homogeneous catalysis as solvents, solvent and ligand, and electrochemical uses in electrodeposition.

As a result of this quaternization reaction monoalkylation has been successfully done in which the products were confirmed by Spectroscopic techniques, analytical data (elemental analysis) and different physical techniques having melting point of almost higher than 200^{0}C. After metathesis process the melting point of the prepared ILs have <80^{0}C which fulfills the first criteria to be true ILs with melting point of <100^{0}C.

Synthesis and characterization of 4,4'-bipyridine based ionic liquids

1. Introduction

The use of a large excess of conventional volatile solvents and energy source required to conduct a chemical reaction creates an ecological and economic concerns. As a result the term green chemistry was a counter attack against the bad reputation of chemists and chemicals. Response to this, it is imperative that chemicals should be produced in a sustainable way and that they are safe to use. Green chemistry is defined as the "Approach to synthesis, processing and use of chemicals that reduces risks to humans and the environment".

Green chemistry has been one of the keywords when ionic liquids have been introduced. It is misleading to state ionic liquids are "green chemistry" by themselves. Ionic liquids have an overall positive environmental effect on the synthesis and processing of chemicals. As a result they are attracting attention as eco-friendly solvents for organic reactions as they are relatively non-toxic substance because of their negligible vapor pressure, less volatility, workable viscosity, low melting point, wide liquidus range, thermal and chemical stabilities. [1, 2, 3]

1.1 Ionic liquids (ILs)

Recently, the growing awareness of environmental issues has focused attention on the need for greener and more sustainable technologies in the chemical industry. As environmental concerns have increased in order to provide a safer environment by reducing harmful effects of chemicals, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment.

One of these approaches is the green chemistry movement having around twelve principles which are helpful to minimize and prevent environmental pollution. Of these principles one is concerned with the use of auxiliary substances in order to reduce or eliminate solvent waste in the chemical industry. Because solvents are often necessary in chemical reactions, alternative solvents have been developed. The ideal solvent should have very negligible vapor pressure, low

volatility, low melting point, and it should be chemically and physically stable, recyclable, reusable and easy to handle. One such candidate is an ionic liquid. [2, 4, 5]

By the term "Ionic liquid" is usually meant liquids that are comprised of entirely cationic and anionic species.[6] They are again considered to be salts. Ions in salt consist of small symmetric species which have high charge density and thus they can be effectively packed in to a crystal lattice. As a result they have high melting point. When ionic liquid is constructed, the size of ion/ions is changed. For example NaCl has melting point above 800^0C, but when Na is changed to 1-butyl-3-methylimidazolium ([BMIM]) the melting point decreases to about 60^0C. This is because when Na is changed to [BMIM] the size of the cation is increased from 102pm (6-coordinate ionic radius of Na) to 350pm (distance of imidazolium rings face to face in crystal lattice). As a result charge density of the ionic liquid decreases dramatically. Crystal lattice packing is affected, since Na is symmetrical ion (spherical) and imidazolium is a bulky asymmetrical ion. The crystal packing energy with [BMIM] is much higher and thus the melting point is lower. Similar changes occur on the anion part of the ionic liquids. 1-ethyl-3-methylimidazolium chloride ([EMIM] [Cl]) has a melting point of 89^0C and [EMIM] bis (trifluoromethylsulfonyl) imide ([NTf_2]) has a melting point of -15^0C.

The same explanation of the melting point shift is valid for the anions as for the cations. Increasing size of the anion lowers the charge density. A bulkier anion also decreases the attractive forces between anions and cations and this lowers the melting point. [6] One of the physical properties of ionic liquids is that they have melting point lower than 100^0C. The melting point of large, unsymmetrical ions, whose charge can be distributed over a large bulky volume, is low and hence the melting point of the ionic liquid can be far below 0^0C. Furthermore, ionic liquids do not evaporate like organic compounds do emit VOCs, [7] that's why they are termed as environmental eco-friendly solvents, but they will decompose at high temperatures.[5,8] Generally most ionic liquids are non-flammable, recyclable, thermally stable, electric conductor and have workable viscosity etc. In addition to these properties, these amazing liquids have essentially no vapor pressure and provide good solubility for a wide range of organic, inorganic, and organometallic compounds and, as a result, are suitable as reaction media. Since these liquids are salts, the cations and anions may interact with solutes and therefore have dramatic effects on any reactions attempted. Indeed, there are a number of reports citing great improvements in reaction yields and rates when ionic liquids are used as solvents.

An ionic liquid is formed from organic cations and inorganic or organic anions. Commonly used cations are usually large and unsymmetrical, example, derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium (see figure 1 below).

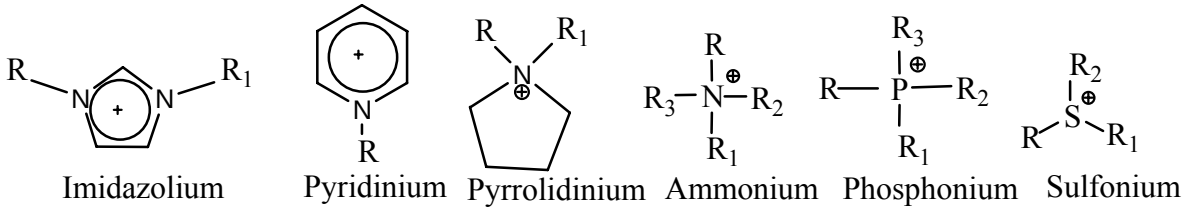


Figure 1 commonly used cations in ionic liquids

Typical inorganic anions are example, halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate, bis (trifluoromethylsulfonyl) imide and typical organic anions are alkyl sulfate, alkylsulfonate, tosylate and trifluoroacetate (see figure 2 below).

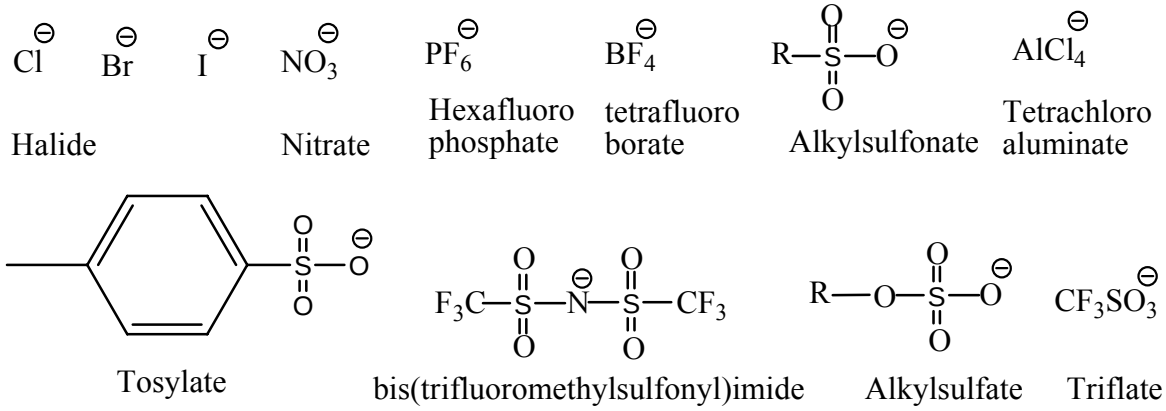


Figure 2 commonly used anions in ionic liquids

1.2 Quality of ionic liquids

Purity of an ionic liquid has paramount importance, since impurities influence its physico-chemical properties. The possible impurities in the preparation of alky N-heterocyclic halides are unreacted organic starting materials, N-heterocyclic compounds, alkyl halides, water and different solvents. Volatile compounds, such as alkyl halides in this process, are easily removed by distillation. Impurities sometimes affect the color of ionic liquids. The chemical nature of coloring impurities is not clear, but they are assumed to be oxidation products or thermal

degradation products of starting materials. Such all impurities affect both the thermal and chemical stability of ionic liquids.

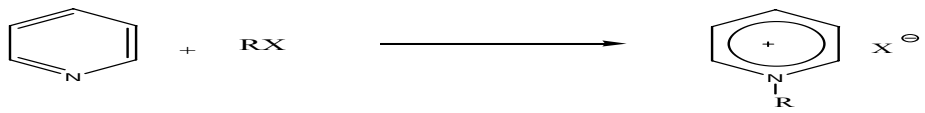
1.3 Synthesis of ionic liquids

The general synthesis of ionic liquids based on nitrogen-containing heterocycles is an easiest process. That is, to say ionic liquids are green solvents their preparation methods should be as simple as possible. This involves:

1.3.1 Quaternization /nucleophilic substitution reaction:

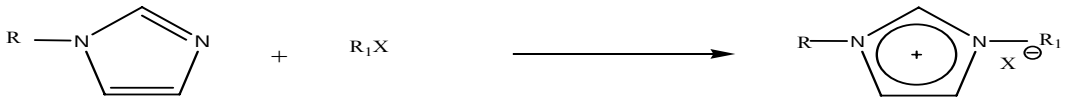
Consecutive quaternization or alkylation reactions with alkylating agents afford an alkylated halide precursor. This universal method of preparing ionic liquids is nucleophilic type of alkylation of a suitable heteroatom aromatic molecule, such as nitrogen atom containing compounds, capable of becoming positively charged species (a cation) like imidazolium, pyridinium, bipyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium derivatives where the nitrogen in the ring is substituted with alkyl halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate, bis(trifluoromethylsulfonyl)imide, alkyl sulfate, alkylsulfonate, tosylate and trifluoroacetate. Alkyl halides are the most common alkylating agents used, because they are readily available in all sizes and shapes and they are inexpensive. The reaction temperature and the reaction time depend on the reactivity of the alkyl halide. In principle, reactivity decreases as a function of increasing alkyl chain length, methyl > ethyl > propyl > butyl > pentyl. The nature of the halide also influences the reactivity of the alkyl halide. Iodine is most reactive, followed by bromine and chlorine, as is expected for a nucleophilic substitution reaction, S_N2.[9]

One of the first aromatic heterocyclic cation used in preparation of ionic liquids was ethyl pyridinium with aluminum chloride anion. Alkyl pyridinium chlorides are made by the alkylation of pyridine and aluminum trichloride (see scheme 1 below).

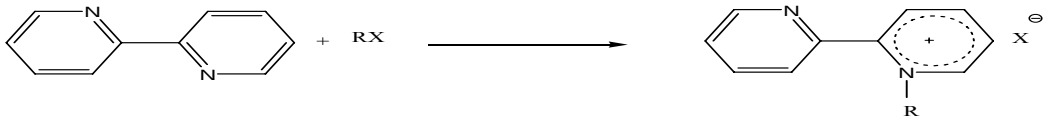


Scheme 1 Preparation of alkyl pyridinium ionic liquid by alkylation (R= alkyl chain, X = halide)

Imidazolium is the most popular synthesized ionic liquids. The reason for popularity of imidazolium as ionic liquid cation is due to the features which can be achieved. It is easy to modify, stable under acidic conditions, low charge density due to aromatic system and it has easily accessible electrons. Actually there is one problem associated with imidazolium derivatives; the protons found on the ring are acidic and tend to come loose when imidazolium is used under basic conditions. It follows the some preparation steps as pyridinium cation, 1-alkylimidazole, 2,2'-bipyridine and 4,4'-bipyridine are used as starting materials and wide variety of alkyl halides can be used as alkylating agents(see schemes 2 &3 below)



Scheme 2 Preparation of dialkyl imidazolium ionic liquid by nucleophilic alkylation

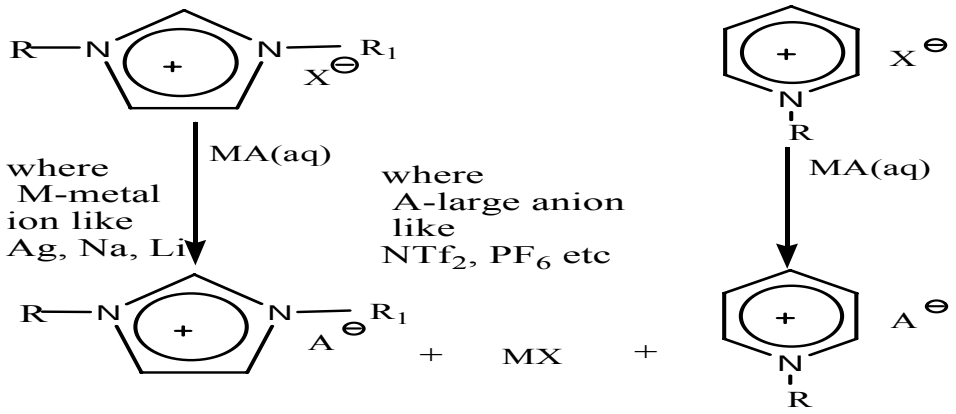


Scheme 3 preparation of bipyridinium based ionic liquids

When N-heterocyclic aromatic molecules like imidazolium, pyridinium and 2,2'-bipyridinium are mono alkylated with alkyl halides and other types of alkylating agents, asymmetry of the cation increases. As a result melting point of the salt starts to decrease. In the case of dialkylation, chain length has dual effect on the melting point of the ionic liquid. Even though the charge density of substituted pyridinium cation is smaller than imidazolium, melting point of pyridinium is larger than imidazolium due to an increase in symmetry in pyridinium with the same alkyl tail.[1]

1.3.2 Metathesis/anion exchange reaction:

Metathesis procedure is second step in ionic liquid syntheses from an alkylated halide precursor, which upon metathesis with a metal salt produces metal halide (MX) (see scheme 4 below). The ionic liquid formed is now with a different anion and relatively pure having lower melting point. This anion exchange step has its own limitation. That is, there is stoicheiometric amount of halide wastes (MX).



Scheme 4 metathesis reaction of ionic precursors of imidazolium and pyridinium halides [10]

1.4 Characterization of ionic liquids

Preparations of ionic liquids should be monitored with characterizing techniques to check their purity. Prior to use, ionic liquids should be carefully characterized with several methods, such as melting point, NMR (^{1}H &^{13}C), elemental analysis, solubility, conductivity, halide test and IR.

1.4.1 Melting point:

Melting point is one of the most important physical characterizing techniques of ionic liquids. According that ionic liquids are classified in to room temprature and not. Of course this technique is very sensitive to impurities like the starting materials and solvents. Based on this fluorinated monoquaternary products of 4,4'-bipyridine which were synthesized before are not room temperature ILs although they are relatively low melting salts ranging, 52-109 °C.[11] In most cases halide based ionic liquids follow the trend shown in the figure below.

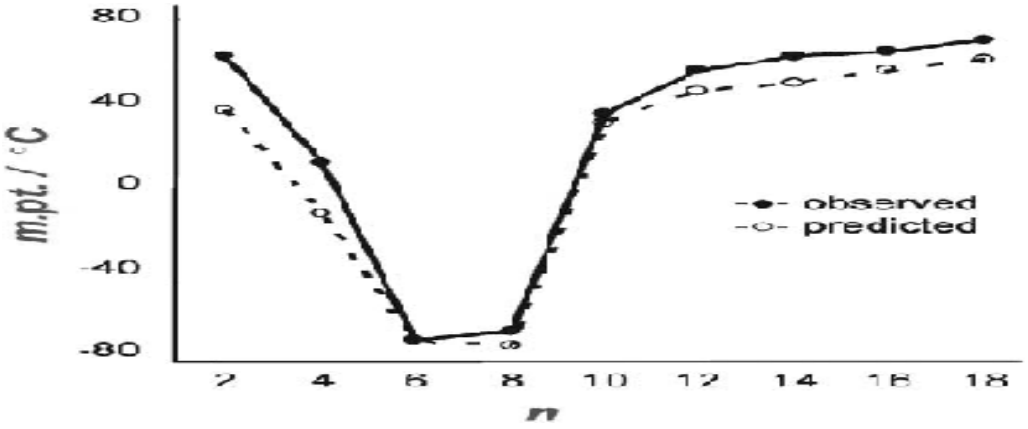


Figure 3 predicted and observed melting point of halide based ILs

Even though alkyl chain is one of the factors that change melting point of ILs, its size and symmetry determines the type of interaction and in turn influences melting point of the IL.

1.4.2 Halide test:

The easiest way, which is used to check the presence of halides as counter ions, is to undertake the halide test done by mixing already separately prepared clear solutions of $AgNO_3$ and reaction intermediates halides dissolved in H_2O or other solvents like methanol. Confirmation to the presence of halides, the combined solution gives white precipitate like suspension which is AgX.

1.4.3 ^{1}H & ^{13}C NMR (DEPT):

^{1}H & ^{13}C NMR proved to be generally the most efficient method for monitoring alkylation reaction. Both the reagents and the resulting ionic liquid could be detected from the ^{1}H & ^{13}C NMR spectrum by measuring the chemical shifts of hydrogen and carbon. ILs do not evaporate, and hence the only compounds expected to be detected were the starting components, the N-heterocyclic aromatic molecule and the alkylating reagent. The biggest difference in the NMR spectra of such ionic liquids is the chemical shift of the most acidic proton, H and carbon found on the different cations on different environments. [5, 12]

1.5 Application of ionic liquids

Aromatic nitrogen-containing heterocycles such as pyridine, 2,2'-bipyridine, 1,10'-phenanthroline [13] and related molecules are widely employed as ligands in coordination and organometallic chemistry.[14] At this time one of the predominant research areas involving ionic liquids as solvents of such compounds focus on homogeneous catalysis because ionic liquids have been demonstrated to be ideal immobilizing agents for various classical transition metal catalyst precursors. Since the coordinating abilities of ordinary ionic liquids are often very poor, the design of ionic liquids for use as solvents that can serve both for immobilization and as coordinating ligands for the catalyst in processes involving homogeneous catalysis is a worthwhile objective.

In those molecules with multiple centers available for quaternization, such as 4,4'-bipyridine, a coordination center could remain available after alkylation of only one of the two basic nitrogens to give the monoquaternary salt.[11]This way the IL could be both solvent and ligand.

Extension to this, transition metal clusters or colloidal suspensions have received increasing interest because of their unique properties and have found applications in catalysis. Nevertheless, metallic nanoparticles are thermodynamically unstable and must be stabilized by various protective agents to prevent their agglomeration. Among the different protective agents, ionic liquids (ILs) have proved to be interesting because they could play the dual role of a solvent and a stabilizing agent.[15]

To date, some efforts have been made to address this by synthesizing ionic liquids with functional groups that can complex the metal centers.[16] The excellent donor properties of these molecules, which are usually viewed as a-diimines, stem from the presence of sp^2-hybridized N atoms become efficient alkylating agent due to the presence of unbonded electrons on nitrogen atom fused in the ring system.[14] Even though there is no an exclusive study on 4,4'-bipyridine ionic liquids, fluorinated diquaternary salts of 4,4'-bipyridine has special application in electrochemistry as electrodeposition, electron carriers, model systems in photosynthesis, herbicides, cardiovascular agents, hypotensive, and neuromuscular agents in addition to its catalytic use.[17]

In general ionic liquids have wide range of applications including Friedel-Crafts alkylation reaction, Heck reaction, enzyme catalyzed reaction; hydrogenations, benzoylation, Fischer-synthesis, phase transfer catalysis etc are being looked up as future commercial solvents.

Therefore, the main focus of this project is to synthesize new alkyl bipyridinium based ionic liquids which could find diversified uses as environmentally eco-friendly alternative to VOC solvents for homogeneous catalysis in two ways: as solvents and/ or as both solvents and ligands(L-M-L). Also due to their wide electrochemical window they have promising application in electrodeposition of metals with extremely negative reduction potential like Al, Si, Ga, V, Sn, Mg, Nb, Ta, Ti, Cr which is absent in common solvents.

2. Experimental

2.1 Chemicals

The chemicals used in this project are 4,4'-bipyridine from Aldrich, iodo and bromo alkanes all from B.D.H, LiNTf2 obtained from Nottingham University, Department of Chemical Engineering and 1,4-dioxane, extra pure and other organic solvents from Scharlau.

2.2 Instrumentation

All melting points were determined on a ***Stuart SMP3*** melting point apparatus. Conductivities were measured on **EC214** Bench type conductivity meter (Hanna instrument) in deionized water. Elemental analyses were performed on a **Flash EA 1112** elemental analyzer. ^{1}H, ^{13}C NMR spectra were recorded on a ***BRUKER 400 Ultra shielded NMR*** instrument working at 400 MHz, using the solvent tetramethylsilane as the internal standard. Deuterated solvents of H_2O and chloroform were used as solvents. Chemical shifts are given in ppm (δ) and *J*-values in Hertz (Hz).

2.3 Syntheses of alkyl-4,4'-bipyridinium based ionic liquids

A round bottom reaction flask containing a magnetic stirring bar was charged with4,4'-bipyridine 1.8 gm(11.5 mmol) and ethyl iodide 1.9 ml in 1:2molar ratio, immersed in an oil bath in dioxane as reaction solvent and heated to 50°C during a period of 48 hours reflux. Upon formation of new product from the reaction, pale yellow product was formed which is insoluble in dioxane. This crystalline product was collected; the solvent removed through filtration and the alkylated product was dried for about two days in desiccator. The rest ionic liquids were synthesized in similar ways as the ethyl procedures. 4,4'-bipyridine,1.8 gm (11.5 mmol) and methyl iodide, 3.0 ml heated to 40°C during a period of 24 hours and pale yellow product formed; primary propyl bromide, 2.2 ml heated to 60°C during a period of 56 hours, primary butyl bromide, 2.5 ml heated to 65°C during a period of 60 hours, primary pentyl bromide, 2.9 ml heated to 70 °C during a period of 72 hours all cloudy product formed.

2.4 Metathesis/anion exchange reaction

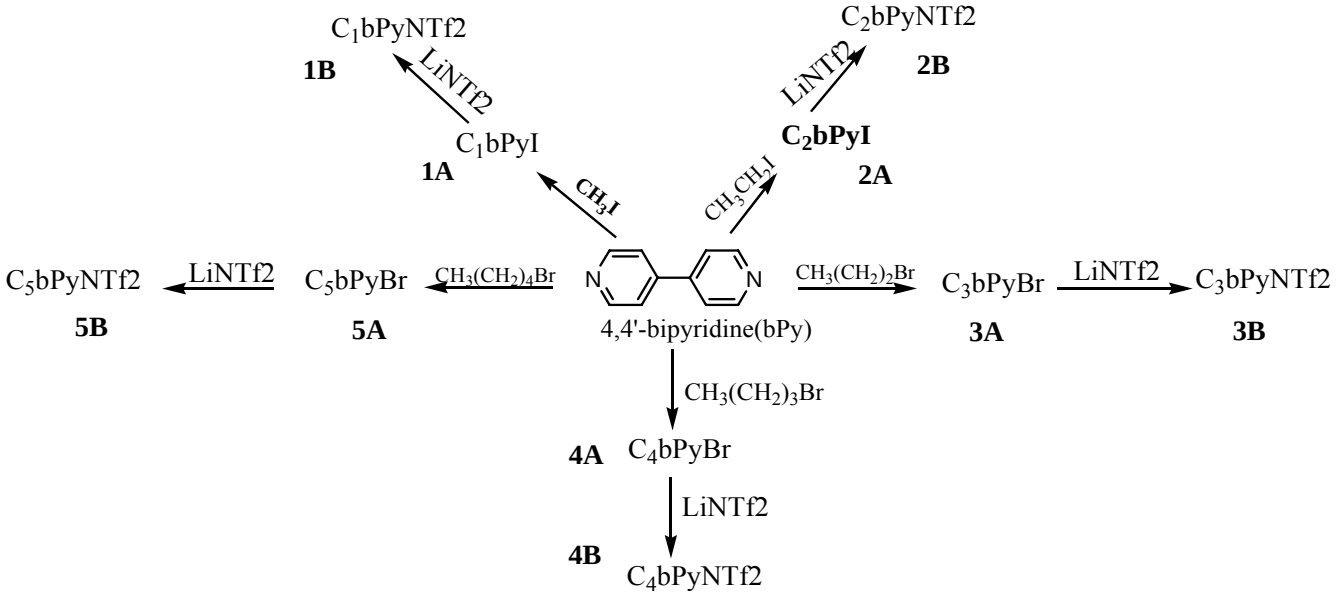
Preparation of true ionic liquids involve metathesis reaction between alkyl-4,4'-bipyridinium halide and a salt of lithium bis(trifluoromethylsulfonyl)imide in aqueous solution. In general terms, the reaction of a quaternary halide salt of alkyl-4,4'-bipyridiniumhalide(halide, X = iodide, bromide), Q^+X^-(aq) lithium bis(trifluoromethylsulfonyl)imide salt, M^+Y^-(aq) results in the formation of precipitate, QY(↓).This process has been done through drop wise titration in order to avoid and minimize the coagulation of the halide inside the precipitated crystalline form of the ionic liquid. The product is easily separated from the solution by filtration.

All the above products(the precursors and their respective ionic liquids) were characterized by spectroscopic techniques ^{1}H NMR, ^{13}C NMR, DEPT under solvent D_2O and chloroform, elemental analysis, as well as by physical techniques like melting point /Mp/ ^{0}C, solubility, halide test and conductivity.

3. Results and Discussion

3.1 Results

The route to 1-alkyl-4,4'-bipyridinium bis(trifluoromethylsulfonyl)imide is depicted in the following scheme.



Scheme 5 Synthesis of monoquaternized alkyl-4,4'-bipyridinium halide and alkyl-4,4'-bipyridinium bis(trifluoromethylsulfonyl)imide where the alkyl ranges from methyl to pentyl and halide is iodide /bromide

All the alkyl-bipyridinium halide intermediates in scheme 5 (**1A**, **2A**, **3A**, **4A** and **5A**) are soluble in deionized water and DMSO forming clear solutions. They are again all insoluble in 1,4-dioxane, which is the reaction solvent. The true ionic liquids listed in scheme 5 (**1B**, **2B**, **3B**, **4B** and **5B**), which are the result of metathesis separated by filtration, are insoluble in water and all these are soluble in 1,4-dioxane, acetone, chloroform, DMSO and methanol. Physical properties

of these products seen in the above scheme (scheme a) like melting point, conductivity and solubility are summarized as follows in the table below (table1).

Entry	Compound Precursors	T^0 (^{0}C)	Time (hr)	Solvent	M.P (^{0}C)	Conductivity (mS/23OC, deionized H2O)	Solubility test H2O	DMSO	CHCl3	acetone	dioxane
1A	C_1bPyI	40	24	dioxane	244-246	1.4	✓	✓	X	X	X
2A	C_2bPyI	50	48	"	217-219	0.5	✓	✓	X	X	X
3A	C_3bPyBr	60	56	"	186	1.7	✓	✓	✓	X	X
4A	C_4bPyBr	65	60	"	220	1.5	✓	✓	✓	✓	X
5A	C_5bPyBr	70	72	"	226-227	0.9	✓	✓	✓	X	X
Anion exchanged ionic liquids					CH_3OH						
1B	C_1bPyNTf2	r.t		H_2O	57	0.2	X	✓	✓	✓	✓
2B	C_2bPyNTf2	"		"	72	0.1	X	✓	✓	✓	✓
3B	C_3bPyNTf2	"		"	76	0.2	X	✓	✓	✓	✓
4B	C_4bPyNTf2	"		"	_	_	X	✓	✓	✓	✓
5B	C_5bPyNTf2	"		"	65	0.4	X	✓	✓	✓	✓

Table 1 Physical properties of the alkyl-4,4'-bipyridinium precursors and their ionic liquids

The spectroscopic measurements of ^{1}H NMR, ^{13}C NMR and DEPT of the reaction intermediates and products of **2A** (97% purity), **5A** (97 % purity), **2B** (77% purity), **3B**(96% purity), **4B**(97% purity) and **5B**(98% purity) (see appendix) give the chemical shift of hydrogen and carbon found as labeled in the predicted structure in figure 4 & 5 below respectively. In addition to this it gives the value of coupling constants and coupling pattern of the protons. Such all data are summarized in the tables below (table 2 &3).

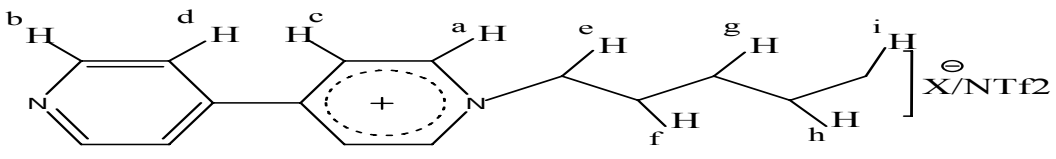


Figure 4 assignment of protons for ^{1}H NMR in the alkyl-bipyridinium halide/NTf2 exchanged ionic liquids, where the alkyl ranges from methyl to pentyl and halide is iodide/bromide

Entry	Compound	Chemical shifts(δ) and coupling pattern & No of Hydrogen									Coupling constant(j-Hz)					
		a-H	b-H	c-H	d-H	e-H	f-H	g-H	h-H	i-H	$J_{a,c}$	$J_{b,d}$	$J_{e,f}$	$J_{f,g}$	$J_{g,h}$	$J_{h,i}$
1A	C_1bPyI	8.83 **d 2H**	8.58 **d 2H**	8.26 **d 2H**	7.75 **d 2H**	4.35 **s 3H**	_	_	_	_	6.8	6.3	_	_	_	_
2A	C_2bPyI	8.89 **d 2H**	8.59 **d 2H**	8.26 **d 2H**	7.75 **d 2H**	4.6 **q 2H**	1.6 **t 3H**	_	_	_	6.8	6.3	7.4	7.4	_	_
5A	C_5bPyBr	9.56 **d 2H**	8.67 **d 2H**	8.39 **d 2H**	7.65 **d 2H**	4.8 **t 2H**	1.94 **qui 2H**	1.21 **qui 2H**	1.21 **td 2H**	0.68 **t 3H**	6.8	6.3	7.6	7.8, 14.8	14.8 , 6.8	6.8
2B	C_2bPyNTf2	8.94 **d 2H**	8.93 **d 2H**	8.28 **d 2H**	7.69 **d 2H**	4.73 **q 2H**	1.74 **s 3H**	_	_	_	6.7	6.1	7.4	7.4	_	_
3B	C_3bPyNTf2	8.92 **d 2H**	8.87 **d 2H**	8.29 **d 2H**	7.70 **d 2H**	4.59 **t 2H**	2.1 **td 2H**	1.04 **t 3H**	_	_	6.8	6.1	7.5	7.3, 14.8	7.4	_
4B	C_4bPyNTf2	8.86 **d 2H**	8.76 **d 2H**	8.25 **d 2H**	7.67 **d 2H**	4.55 **t 2H**	1.95 **qui 2H**	1.35 **sep 2H**	0.88 **t 3H**		6.8	4.7	7.5	7.4, 15.1	15.1 ,7.5	7.5
5B	C_5bPyNTf2	8.93 **d 2H**	8.85 **d 2H**	8.30 **d 2H**	7.71 **d 2H**	4.6 **t 2H**	2.05 **qui 2H**	1.37 **qui 2H**	1.35 **td 2H**	0.89 **t 3H**	6.7	6.1	7.6	7.6, 14.6	14.6 ,6.8	6.8

Table 2 [1]H NMR spectral data of alkyl-4,4'-bipyridinium precursors and their ionic liquids

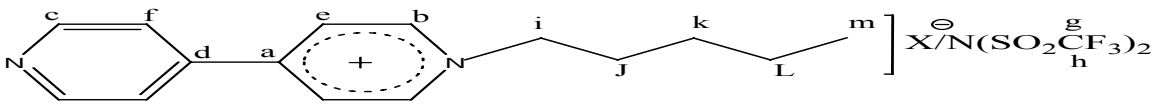


Figure 5 assignment of carbons for C-13 in the alkyl-bipyridinium halide/NTf2 exchanged ionic liquids, where the alkyl ranges from methyl to pentyl and halide is iodide /bromide

Entry	Compound	Chemical shifts, δ of C-13												
		Ca	Cb	Cc	Cd	Ce	Cf	Cg	Ch	Ci	Cj	Ck	Cl	C_m
1A	C_1bPyI	153.02	149.96	145.70	142.24	125.73	122.46	_	_	48.10	_	_	_	_
2A	C_2bPyI	153.24	149.94	144.53	142.34	125.99	122.45	_	_	57.11	15.73	_	_	_
5A	C_5bPyBr	153.34	151.17	145.76	140.87	125.95	121.59	_	_	61.47	31.41	27.93	21.98	13.71
2B	C_2bPyNTf2	154.05	151.54	144.59	141.15	126.29	121.46	121.69	118.17	57.30	16.08	_	_	_
3B	C_3bPyNTf2	154.64	151.48	144.95	140.87	126.14	121. 48	121.40	118.21	63.47	24.76	10.27	_	_
4B	C_4bPyNTf2	154.31	151.20	144.88	140.99	126.07	121.63	121.34	118.14	61.81	33.09	19.14	13.05	
5B	C_5bPyNTf2	154.45	151.37	144.94	140.95	126.15	121.55	121.38	118.19	62.15	31.08	27.93	21.90	13.57

Table 3 ^{13}C NMR spectral data of alkyl-4,4'-bipyridinium precursors and their ionic liquids

In addition to the information found from spectroscopic and physical characterizing techniques it is possible to judge the structure and chemical composition of the reaction product from analytical techniques explicitly the elemental analysis. The elemental compositions of the products from their predicted structures are summarized in table below (table 4).

Entry	Compound	Experimental(theoretical)percentage of C, H, N and S in the compounds						
		C%	H%	N%	S%	O%	F%	Br %
5A	C_5bPyBr	58.13 (58.63)	5.98(6.18)	8.97(9.12)	-	-	-	- (26.05)
5B	C_5bPyNTf2	40.24 (40.29)	3.94(3.75)	8.35(8.28)	13.38(12.62)	- (12.62)	- (22.48)	-

Table 4 analytical data of alkyl-4,4'-bipyridinium precursors and their ionic liquids

3.2 Discussion

3.2.1 Melting point

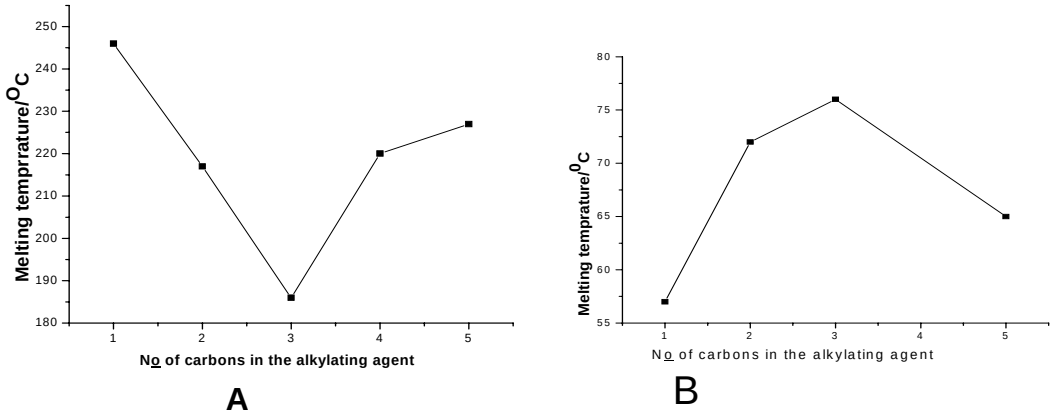


Figure 5 melting point curves of ionic liquids and their intermediates against size of alkyl chain

Like all molten salts, ILs are highly structured materials; much of the crystal lattice of the solid state is retained on melting. The strong ion-ion interactions present in ILs lead to highly-ordered three-dimensional polymeric networks of anions and cations linked by Coulombic interactions.

Melting temperatures of **1A**, **2A**, **3A**, **4A** and **5A** salts have a melting point higher than 100^0C. All of these salts deviate from the IL class since their melting points are above 100^0C.The correlation between melting points and alkyl substituents of cations is clearly observed in table1. As the alkyl groups are changed from$C_1$to C_2 to C_3 the melting points vary from 245 to 218 to 186^0C. Lower melting point characterizes IL C_3, although an increasing trend can be observed comparing the melting points of ILs bearing alkyl groups changing from C_3 to C_4 to C_5 as can be seen in figure 5. This behavior suggests that for relatively short alkyl chains result in higher melting point salts, probably a consequence of a stronger packing into the crystal lattice, smaller volume, higher symmetry and Coulombic interaction between the ion-ion pairs. In the presence of long alkyl chains, however, stronger van der Waals forces in addition to the Coulombic interactions favor the formation of compounds having higher melting point.[18]On the other hand melting point of the true ionic liquids, **1B**, **2B**, **3B** and **5B** increases with increasing alkyl chain until C_3 but falls down in C_5 (see the above graph B). Their values range from 57 - 76^0C. This is in agreement within the range cited by literatures. But it is unable to measure melting point of butyl. This is because during the anion exchange butyl could not get dried. Even if it forms crystalline solid but get melted at room temprature.

Even though there is no clear statistical analysis of the factors that affect the melting points of alkyl-bipyridinium NTf_2 based ionic liquids the most important parameters found to be influential are coordination ability of the cation, electrostatic interactions, conformational or rotational degrees of freedom, and Vander Waals interaction. Common rationalizations for the unusually low melting points of ionic liquids compared to the halide intermediate often refer to symmetry and ion size (Madelung constant), charge magnitude, and intercharge distance (coulombic stabilization), as well as molecular interactions such as H-bonding, van der Waals forces, and π–π stacking. The presence of non-charged groups, asymmetric ions, or rotational and vibrational freedom can break up the lattice structure and increase inter-charge distances, thereby lowering the stability of the crystalline phase and lowering the melting point. These rationalizations are couched in general terms; however we are unable to provide explicit conforming evidence in the form of energies and structures that allow a more specific 'picture' of these factors that influence melting point of ionic liquid structure to emerge. As a result this needs further investigation. Generally melting point of anion exchanged ionic liquids is smaller than that of the halide precursors in all cases. This is because of the ionic strength of interaction predicted from ion-pair dissociation energies decreases as $C_nNTf_2 < C_nBF4 < C_nX$.[19]

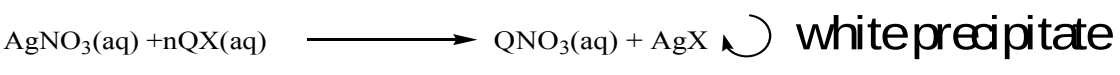
3.2.2 Conductivity

Modern ionic liquids have moderate specific conductivities, usually in the same range as those of aqueous electrolytes. Unfortunately, there were reports of new "ionic liquids" without data on conductivities, which would establish that they are dissociated to some extent at least into ions. Parts of this, these ionic liquid intermediates understudy are weak electrolytes. Their specific conductivity is far small which is in the miliSiemens level. Thus these ionic liquid intermediates for one thing might consist of more of ion pairs (undissociated molecules). Another case can be because of the cationic charge is not localized due to resonating nature.[20]The variation of alkyl chain length exerts reductive effect on the ionic conductivity. For the present salts, there is a pronounced decrease in conductivity with elongating of the alkyl chain in the cations, even though there is an irregularity to **2A**. Conductivity of the true ionic liquids is fur smaller than these intermediates. Conductivity values for **1B**, **2B**, **3B** and **5B** are almost the same.[21]

3.2.3 Halide test

From the halide test white suspension/precipitate was formed which is AgX as can be seen from

the possible reaction below.



where nQX, ionic liquid intermediates
= **1A**, **2A**, **3A**, **4A**, **5A**

This signifies the preplanned quaternization/alkylation reaction was taken place. Had it not been taken the quaternization reaction the halide test would have given simply a clear solution.

The easiest way to check presence of halide impurities is to undertake the halide test done by mixing separately prepared solutions of $AgNO_3$ and ionic liquids, **1B, 2B, 3B, 4B** and **5B** (all dissolved in methanol) prepared from metathesis reaction. Reputation to this process, no white precipitate formed indicating that there is almost no halide impurity in the already synthesized ionic liquids. Unfortunately, there is no general method for obtaining halide-free ionic liquids from the alkylation reaction of heteroatom and alkyl halides. As a result this **1B** and **2B** ionic liquids which are the methyl and ethyl iodide derivatives that white precipitate was formed on addition of $AgNO_3$ solution indicating that the iodide counter anion of **1A** and **2A** is partially exchanged. This might be due to both the iodide and NTf2 anions are soft. So a sort of equilibrium could be formed. The best way to avoid such halide impurities is to prepare ionic liquid intermediates from a metathesis reaction by using alkylation reagents other than alkyl halides e.g. alkylsulfonate.[5]

3.2.4 Solubility

The ionic liquid intermediates of **1A**, **2A**, **3A**, **4A** and **5A** have different solubility to different solvents. All are highly soluble in H_2O and DMSO but all are insoluble in the reaction solvent dioxane. Except **5A** all are again insoluble in acetone. After subsequent metathesis of these intermediates with lithium bis(trifluoromethylsulfonyl)imide (LiNTf2) in 1:1.2molar quantities, afforded the corresponding NTf2 exchanged products of **1B**, **2B**, **3B**, **4B** and **5B**.These are the true ionic liquids under investigation which are completely miscible with various polar solvents, such as dioxane, DMSO, acetone, chloroform and methanol. Solubility of these ionic liquids in dioxane indicates that there are new products due to the metathesis reaction. As a result of this such salt may be used as a solvent, a solvent additive, an electrolyte, a heat carrier, a charge carrier, a heat carrier additive, a charge career additive, homogeneous catalyst, or a phase transfer catalyst.[20] Furthermore, these ionic liquids have very low solubility in water and other

polar organic solvents. The difference in solubility of the halide based ionic liquids and NTf2 exchanged ILs might depend on the higher hydration energy of the halide. Utilization of this property enables recovery and reuse of ionic liquids, after extracting the product with an appropriate organic solvent. This can help to reduce the waste of traditional solvents which are rarely reused.[21]

3.2.5 NMR spectroscopy

3.2.5.1 NMR of the ionic liquid intermediates

In the ^{1}H NMR spectra of appendix A, B and C for compounds **1A, 2A** and **5A** (table 2 & 3), one can observe four groups of protons of the bipyridine ring in aromatic region, and one, two and five groups of *N*-methyl, N-ethyl and N-pentyl protons as well. Specifically this discussion focuses more on compounds **2A** and **5A** because of their complete data. Taking these spectroscopic results into consideration with elemental analysis, the above compounds (**2A and 5A)** could be assigned as ethyl-4,4'-bipyridinium iodide and pentyl-4,4'-bipyridinium bromide having ethyl and pentyl groups as substituents at position N-4. It is easy to check the occurrence of the quaternization reaction by looking at the number of peaks as well chemical shifts of bipyridine protons and carbons. If really the reaction does not take place it is expected that there will be two groups of protons and three groups of carbons due to presence of symmetry from 4,4'-bipyridine. As a result of the alkylation at the electronegative nitrogen atom the chemical shift of H**e** in ^{1}H NMR spectrum B of compound **2A** goes down field and it was observed at δ4.62 (q, 2H**e,** $J_{e\,f}$ 7.4Hz) compared to the chemical shift of it found from Aldrich is δ3.15(q, 2H). C-13 NMR of this N-ethyl CH_2 substituent is found atδ57.11ppm which goes much to down field than ethyl iodide does which is δ23.3.[22]he lower-field signals in such a ring system of **2A** for 1H NMR were observed at δ8.83(**d,** 2H**a,** $J_{a\,c}$ 6.8Hz) 8.58(**d,** 2H**b,** $J_{b\,d}$ 6.3Hz) 8.26(**d,** 2H**c,** $J_{c\,a}$ 6.8Hz) 7.75(**d,** 2H**d,** $J_{d\,b}$ 6.3Hz). Chemical shifts for C-13 NMR of similar compound looks like δ153.24(C**a**,-)149.53(C**b**,**149.94**)144.53(C**c**,**144.54**)142.34(C**d**,-) 125.99(C**e**, **125.98**)122.45(C**f**, **122.45**)57.11(C**i**, **57.11**)15.73(C**k**, **15.73**).

In addition to this, it is clear that the chemical shift of H**a** of compound **2A** is deemed to be too high compared to that of H**b** in the same compound and in the same chemical environment for the bipyridine case indicating that there happens quaternization reaction on position N-4 which is nearest to H**a** and C**b** in this assignment. As a result there is chemical shift difference in both ^{1}H

and C-13 NMR spectroscopy which goes much to down field due to the presence of electronegative N nearest to it.

If one looks at the spectrum C (table 2 &3)of compound **5A** the chemical shift for ^{1}H NMR of H**e** is δ 4.82 (**t,** 2H**e,** $J_{e\,f}$ 7.6) and the 1-CH_2 in1- pentyl bromide taken from Aldrich was found at δ 3.3. The chemical shift C**i** in C-13 NMR is at δ 61.47(**61.47**) and its equivalent 1-CH_2 from similar compound taken from Aldrich is at δ 37. From the chemical shift data of H**e** and C**i** it is possible to say that there happens quaternization reaction. Reputation to this reaction their chemical shifts go much to down field. Signals for aromatic protons of 5**A** for ^{1}H NMR were observed δ 9.56(**d,** 2H**a,** $J_{a\,c}$ 6.8)8.67(**d,** 2H**b,** $J_{b\,d}$ 6.3**)**8.39(**d,** 2H**c,** $J_{c\,a}$ 6.8)7.65(**d,** 2H**d,** $J_{d\,b}$ 6.3)4.82(**t,** 2H**e,** $J_{e\,f}$ 7.6)1.94(**quin,** 2H**f,** $J_{f\,e}$7.8, $J_{f\,g}$ 14.8)1.21(**quin,** 2H**g,** $J_{g\,f}$ 14.8, $J_{g\,h}$ 14.8**)**1.21 (**td,** 2H**h,** $J_{h\,g}$ 14.8, $J_{h\,i}$ 6.8) 0.68 (**t,** 3H**i,** $J_{i\,h}$ 6.8). Chemical shifts for C-13 NMR of similar compound looks like δ 153.34(C**a**,-) 151.17(C**b**, **151.17**)145.76(C**c, 145.76)**140.87(C**d**,-) 125.95(C**e**, **125.95**) 121.59(C**f**, **121.59**)61.47(C**i**, **61.47**)31.41(C**j**, **31.41**)27.93(C**k**, **27.93**) 21.98(C**L**, **21.98**)13.71(C**m**, **13.71**). Similar trend works for the rest compounds synthesized in this study.

When one gives a bit attention on the ^{1}H NMR spectra B and C of compounds **2A** and **5A** chemical shift generally goes down field for the **5A** (bromide derivative) than **2A** (iodide derivative). Formations of hydrogen bonding with the halide anions cause the proton chemical shift move to lower field. This is because increasing anion basicity increases the strength of hydrogen bonding and this increases chemical shifts of protons.[23]This phenomenon is in line with the theoretical considerations saying that electron withdrawing nature of bromine is more than iodine because of its larger electronegativity which in turn supports the chemical shifts from the spectra.

3.2.5.2 NMR of the ionic liquids

In the ^{1}H NMR spectrum E of **3B** (table 2 & 3), one can observe four groups of protons from bipyridine ring, and three groups of propyl protons as well. Its chemical shifts from **1**H NMR spectrum E was reported as δ 8.92(**d,** 2H**a,** $J_{a\,c}$ 6.8)8.87(**d,** 2H**b,** $J_{b\,d}$ 6.1**)**8.29(**d,** 2H**c,** $J_{c\,a}$ 6.8)7.70(**d,** 2H**d,** $J_{d\,b}$ 6.1)4.59(**q,** 2H**e,** $J_{e\,f}$ 7.5)2.1(**qui,** 2H**f,** $J_{f\,e}$7.3, $J_{f\,g}$ 14.8)1.04(**t,** 3H**g,** $J_{g\,f}$ 7.4**)**.

Chemical shifts for C-13 NMR of similar compound looks like δ 154.64(C**a**,-) 151.48(C**b**, **151.48**)144.95(C**c, 144.96**)140.87(C**d**,-) 126.14(C**e**, **126.14**) 121.48(C**f**, **121.49**)121.40(C**g,**-)

118.21(C**h,-)** 63.47(C**i**, **63.47**)24.76(C**j**, **24.78**)10.27(C**k**, **10.29**)

In the ^{1}H NMR spectrum G of **5B** (table 2 & 3), one can observe four groups of protons from bipyridine ring, and three groups of pentyl protons as well. Chemical shifts from ^{1}H NMR of spectrum G was reported as δ 8.93(**d,** 2H**a,** $J_{a\ c}$ 6.7)8.85(**d,** 2H**b,** $J_{b\ d}$ 6.1)8.30(**d,** 2H**c,** $J_{c\ a}$ 6.7)7.71(**d,** 2H**d,** $J_{d\ b}$ 6.1)4.60(**t,** 2H**e,** $J_{e\ f}$ 6.1)2.05(**qui,** 2H**f,** $J_{f\ e}$ 6.1, $J_{f\ g}$ 7.6)1.37(**qui,** 2H**g,** $J_{g\ f}$ 7.6, $J_{g\ h}$ 14.6 **)**1.35(**td,** 2H**h,** $J_{h\ g}$14.6, $J_{h\ i}$ 6.8 **)** 0.89**(t,** 2H**i,** $J_{i\ h}$ 6.8 **)**. Chemical shifts for C-13 NMR of similar compound looks like δ 154.45(C**a**,-) 151.37(C**b**, **151.34**)144.94(C**c, 144.95***)*

140.95(C**d**,-) 126.15(C**e**, **126.15**)121.55(C**f**, **121.56**)121.38(C**g,**-) 118.19(C**h,-)** 62.15(C**i**, **62.15**) 31.08(C**j**, **31.08**)27.93(C**k**, **27.93**) 21.90(C**L**, **21.91**) 13.57(C**m**, **13.57**).

From the C -13NMR spectra there is another supportive data concerning the metathesis reaction. There are four new peaks appeared at~124.56, ~121.39, ~118.20 and ~114.49 seeming like quartets splited by fluorine which go much to down field because of the presence of most electronegative environment from the NTf2. Taking the DEPT of such spectra confirmed that these peaks disappeared showing they are quaternary carbons.

Taking these results into consideration with elemental analysis, compound **3B** and **5B** could be assigned as propyl-4,4'-bipyridinium bis(trifluoromethylsulfonyl)imide pentyl-4,4'-bipyridinium bis(trifluoromethylsulfonyl)imide having propyl and pentyl groups as substituent and $^{-}$NTf2 as counter anion. Their quaternization processes were easily justified already from the elemental analysis data which fit to the number and mass of atoms found in **3B** and **5B** respectively.

On the other hand, in the ^{1}H NMR spectra of compounds **2A** and **2B** (see appendix for all spectra) (table 2), one can observe chemical shifts of NTf2 in spectra **2B** are greater than that of iodide in spectra **2A.** In the ^{1}H NMR spectra of compounds **5A** and **5B**, one can observe chemical shifts of ring H's for Br in spectra **5B** are larger than that of NTf2 in spectra **2A**. But chemical NTf2 in spectra **2B** are greater than that of I in spectra **2A.** In the ^{13}**C** NMR spectra of compounds **5A** and **5B**, one can observe chemical shifts of ring C's for NTf2 are larger than that of Br. But chemical shifts of aliphatic C's for Br are larger than NTf2. In all cases there are few irregularities to this generalization which might be resulted from concentration, alkyl chain

length, difference in hydrophobicity, formation of hydrogen bonding and environmental conditions.

One thing which was a strange in the iodide derivatives is the impurities observed in the metathesis process with NTf2, as it was expressed in the halide confirmation test, it again appears in the ^{1}H NMR spectra as the chemical shift of peaks appeared in the intermediates as side bands indicating that there is an intrinsic property of the iodide with NTf2.

3.2.6 Elemental analysis

As it was displayed in the result part (table 4) the experimental value exactly fits to the theoretical data for the pentyl derivatives (**5A** and **5B**) indicating that there is almost no impurity as it is confirmed by the NMR spectra. The maximum deviation observed here is +0.76% for the sulfur atom and this is not actually impurity of the intermediate. Because this element does not exist in the intermediate instead it is found in the LiNTf2.

4. Conclusion

To our delight, the ionic liquids, containing bis(trifluoromethanesulfonyl)imide as an anion, produced (**1B**, **2B**, **3B**, **4B**, **5B**) are at the range of definition of ionic liquids having melting point $<100^0$C. They have high liquidus range and thermal stability up to 280^0C. Of course the iodide derivatized ionic liquids (**1B** and **2B**) have impurities checked by halide test and shown from the ^{1}H NMR spectra.

Even though the use of an excess of alkyl halide, or high temperatures, is expected to favor formation of the diquaternization product in one pot synthesis,[18]in this reaction, only monoquaternary products were formed in all cases at the specified reaction conditions. From chemical shifts and number of peaks in all the ^{1}H, ^{13}C NMR spectra and data of elemental analysis, no diquaternary salt was formed even upon the addition of more alkyl halide with concomitant heating at higher temperature (90^0C). This is not surprising since the formed monoquaternary salt is insoluble in the alkyl halide and in the reaction solvent. Thus due to its insolubility it is unable to be dialkylated further in one pot synthesis.[16] To do that solvent selection is vital and that solvent should solubilise the already synthesized monoquaternary salt and the alkyl halide under reaction.

As a future work it is important to synthesize similar ILs with different alkyl chain lengths and taking purity issues to check the melting point trend. By this end testing the application of these ILs as homogeneous catalysts and their use in electrodeposition with in specific reaction is very important and they are the major future works.

5. References

[1] Janne Asikkala, Application of ionic liquids and microwave activation in selected organic reactions, Acta Univ. Oulu. A 502, 2008

[2] S. Mallakpour and M.Taghavi, Organic polymer chemistry research laboratory, Isfahan University of technology, Islamic republic of Iran, 2008

[3] R. S. Varma and V. V. Namboodiri, Pure Appl. Chem., Vol. 73, No. 8, pp. 1309–1313, 2001.

[4] Peter Wasserscheid and Tom Welton, Ionic liquids in synthesis, 2nd edition, 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[5] Johanna Karkkainen, Acta University Oulu A 480, 2007

[6] Preparation and use of ionic liquids in microwave-assisted chemical transformations, European patent, International publication number WO 2000/072956(07-12-2000 Gazette 2000/49)

[7] Peter Wasserscheid, Tom Welton. Ionic Liquids in Synthesis, First Edition, November 2002, pages 240-275, Wiley-VCH Verlag GmbH & Co. KGaA

[8] Keith E. Johnson, The Electrochemical Society Interface, spring 2007

[9] Alan R.Katritzky, Advances in Heterocyclic Chemistry, v-35, pages 325- 369, 1984, Academic Press, INC.

[10] Maggel Deetlefs and Kenneth R. Seddon, Green Chemistry, 2003, 5, 181–186

[11] Ji-Chang Xiao, Brendan Twamley, and Jean'ne M. Shreeve, Organic letters 2004, V-6, No.21, 3845-3847

[12] Alexander Wulf,[a] Koichi Fumino,[a] Dirk Michalik,[b] and Ralf Ludwig, ChemPhysChem 2007, 8, 2265 – 2269

[13] Theophil Eicher, Siegfried Hauptmann, The Chemistry of Heterocycles, Strauss Offsetdruck GmbH, Mörlenbach

[14] Salvador Conejero, Patricia Lara, Angew. Chem. Int. Ed. 2008, 47, 4380 –4383

[15] Bastien Leger, Audrey Denicourt-Nowicki, He´le`ne Olivier-Bourbigou, and Alain Roucoux, Inorg. Chem. 2008, 47, 9090-9096

[16] Ji-Chang Xiao, Chengfeng Ye, and Jean'ne M. Shreeve, Organic letters 2005, v-7,

No.10, 1963-1965

[17] Marinela Irimia, a, Gabriela Lisa, a Ramona Danac, b Neculai Aelenei, a and Ioan Drutãb, Croatia Chemica Acta, 77 (4) 587-591 (2004)

[18] Cinzia Chiappe, Bernardo Melai, Angelo Sanzone, Giulia Valentini, Pure and Applied Chemistry, Nov, 2009

[19] Patricia A. Hunt, Ian R. Gould, and Barbara Kirchner, Aust. J. Chem. **2007**, 60, 9–14

[20] Subbiah Sowmiah, Venkatesan Srinivasadesikan, Ming-Chung Tseng and Yen-Ho Chu, Molecules 2009, 14, 3780-3813

[21] Ayyaz Muhammad, M.I. Abdul Mutalib, C.D. Wilfred, T. Murugesan, Amir Shafeeq, Journal of Chemical Thermodynamics 40 (2008) 1433–1438

[22] J.Label, Compd Radiopharm 2004; 47: 723–731.

[23] P. Bonhote, Ana Paula Dias, N. Papageorgiou, Inorganic chemistry 1996, 35, 1168-1178

[24] Brittany L.Hayes, Ph.D., Microwave synthesis: chemistry at the speed of light CEM publishing

[25] J.Fraga-Dubreuil, M. Famelart, and J. P. Bazureau, Organic Process Research & Development **2002**, *6,* 374-378

[26] G. Cravotto, E. C. Gaudino, L. Boffa, J.M. Leveque, J. Estager and W. Bonrath, Molecules 2008, 13, 149-156

[27] B.M.Khadilkar and G. L.Rebeiro, applied organic chemistry laboratories, University dept. of chemical technology, University of Mumbai

[28] R. Corberán, E. Mas-Marzá, and E.Peris, European Journal of Inorganic Chem. 2009, 1700–1716

[29] Jie Ding and Daniel W. Armstrong, Chirality 17:281–292 (2005)

[30] J.Hoffmann, M.Nuchter, B.Ondruschka, Friedrich-Schiller-University Jena, Institute of Technical and Environmental Chemistry

[31] Vasudevan V. Namboodiri and Rajender S. Varma, Tetrahedron Letters 43 (2002) 5381–5383

[32] Qing Hai CAI, Yong Kui SHAN, Li Yi DAI, Bi Xia SU, Ming Yuan HE, Chinese Chemical Letters, Vol. 14, No. 5, pp 523. 524, 2003

[33] Rita Annunziata, Maurizio Benaglia and Alberto Bologna, Magnetic Resonance Chemistry 2002; 40: 461–466

[34] Gwan-Hong Min, Taeeun Yim, Hyun Yeong Lee, Dal Ho Huh, Eunjoo Lee, Junyoung Mun, Seung M. Oh, and Young Gyu Kim, Bull. Korean Chem. Soc. 2006, Vol. 27, No. 6 847-851

[35] Ruben Maidan, Zafrir Goren, James Y. Becker, and Itamar Willner, Journal of American Chemical Society 1984, 106, 6217-6222

[36] Hong Xue[a] and Jean'ne M. Shreeve, European Journal of Inorganic Chemistry 2005, 2573–2580

[37] Kenji Sasaki, Akifumi Tsurumori and Takashi Hirota, Journal of Chemical Society, Perkin Trans. 1, 1998, 3851–3856

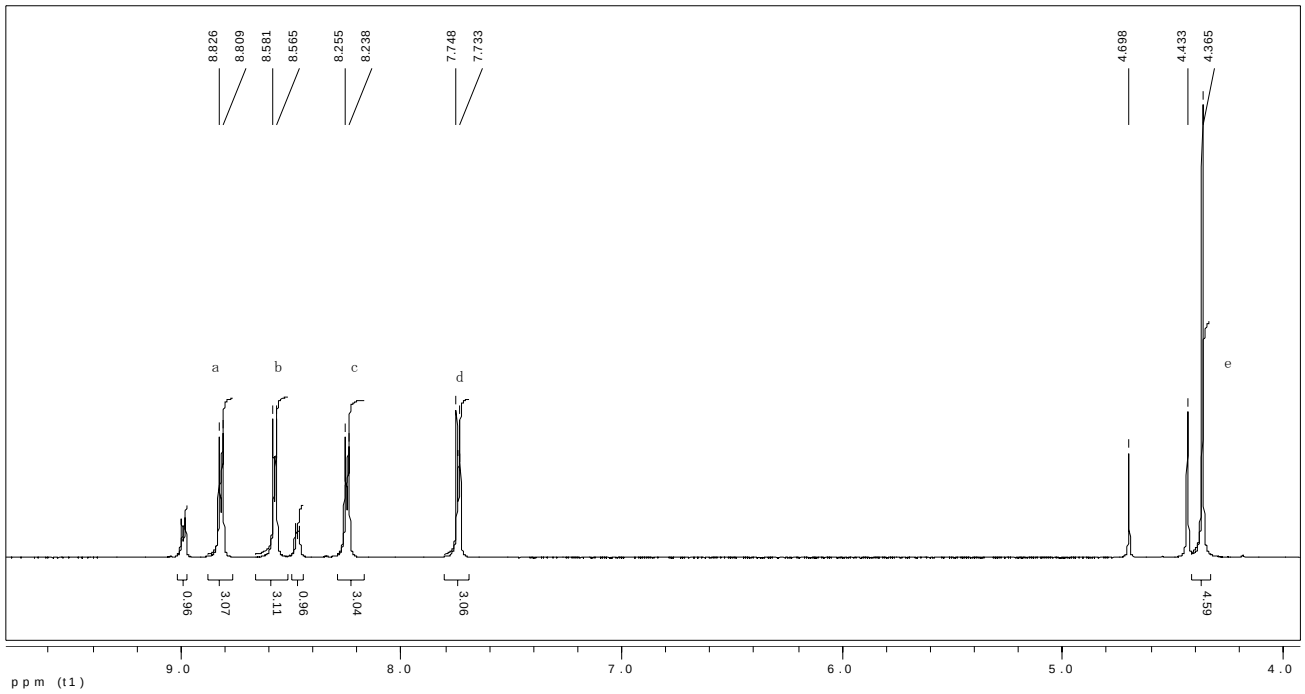
[38] Seda Keskin, Defne Kayrak-Talay, Ugur Akman, Oner Hortacsu, J. of Supercritical Fluids 43 (2007) 150–180

[39] Natalia V.plechkova and Kenneth R.Seddon, Chemical society Review, 2008, 37, 123-150

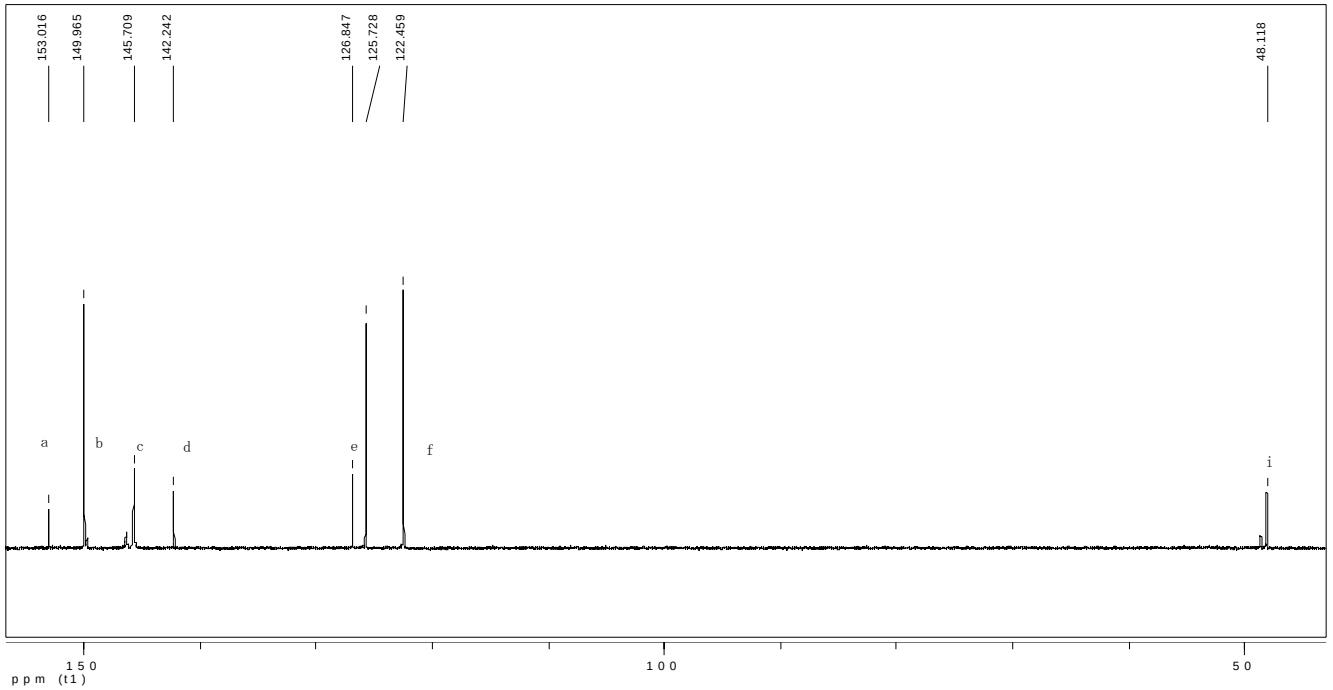
[40] Kenneth R.Seddon, J.Chemical society, Dalton Trans, 1999, 37, 2133-2139

6. Appendices NMR spectra of 1A, 2A, 5A and 2B, 3B, 4B and 5B

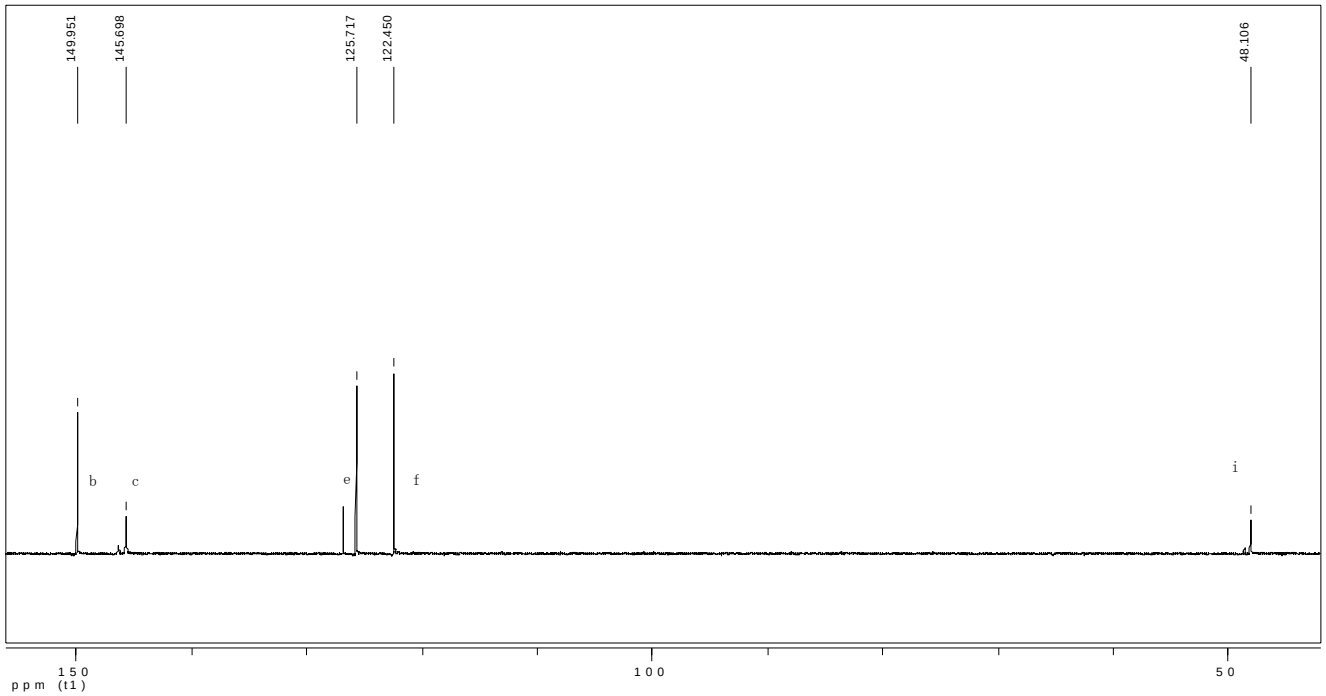
A. NMR spectra of C_1bPyI (1A)



^{1}H NMR spectrum of methyl-bipyridinium iodide

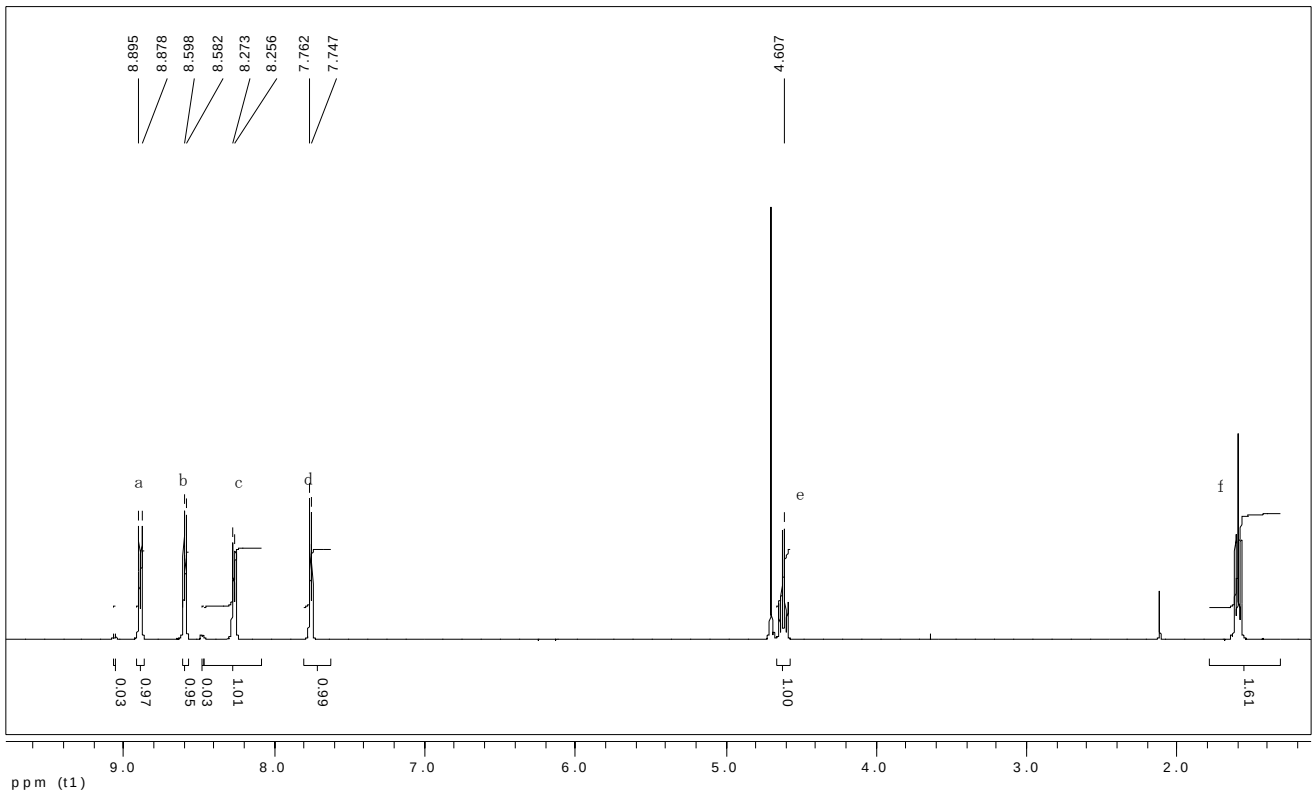


^{13}C NMR spectrum of methyl-bipyridinium iodide

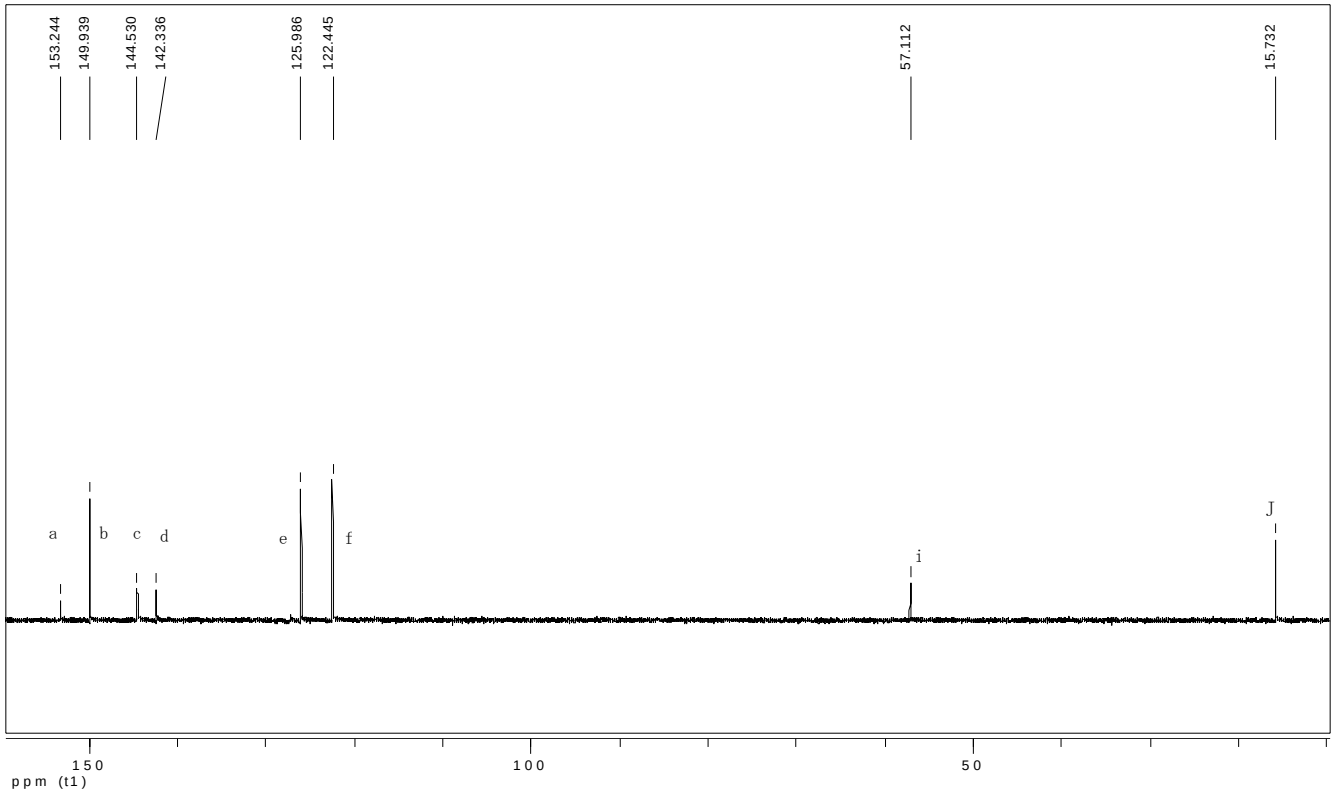


DEPT spectrum of methyl-bipyridinium iodide

B. NMR spectra of C_2bPyI (2A)



^{1}H NMR spectrum of ethyl-bipyridinium iodide



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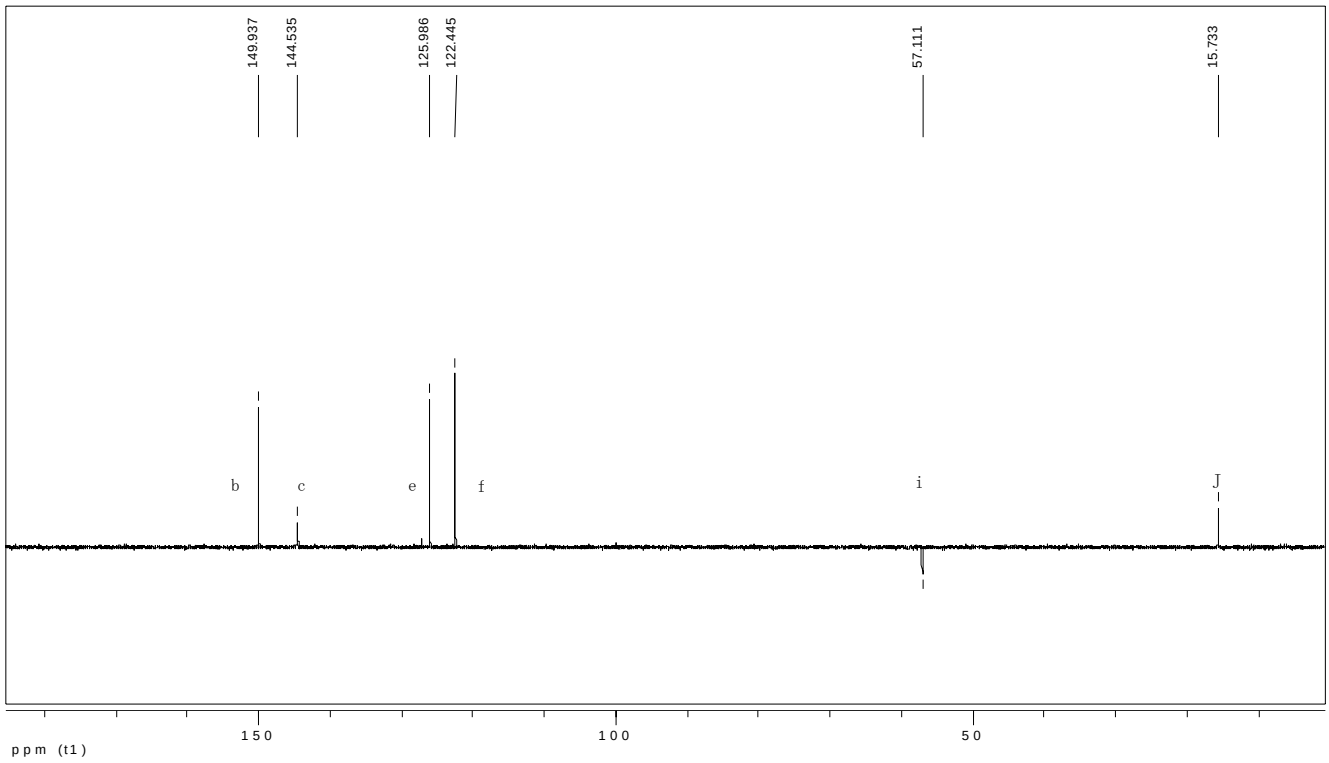
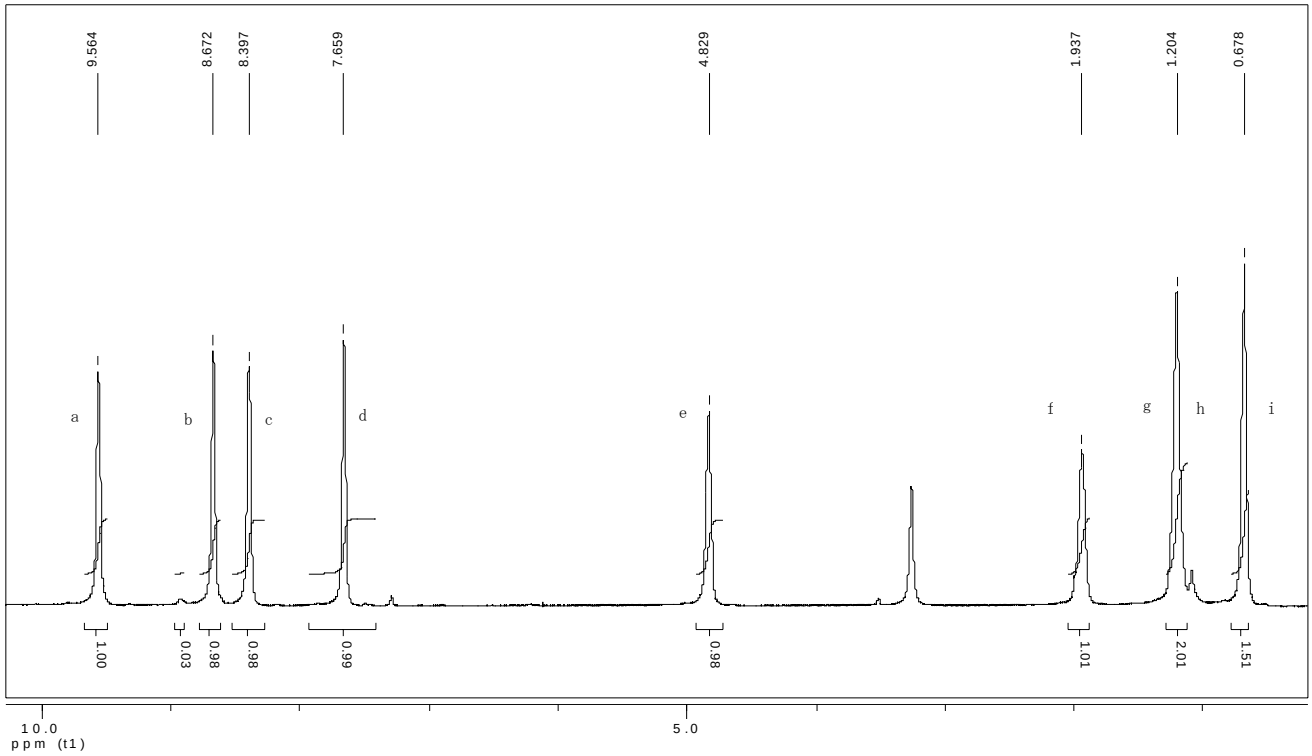
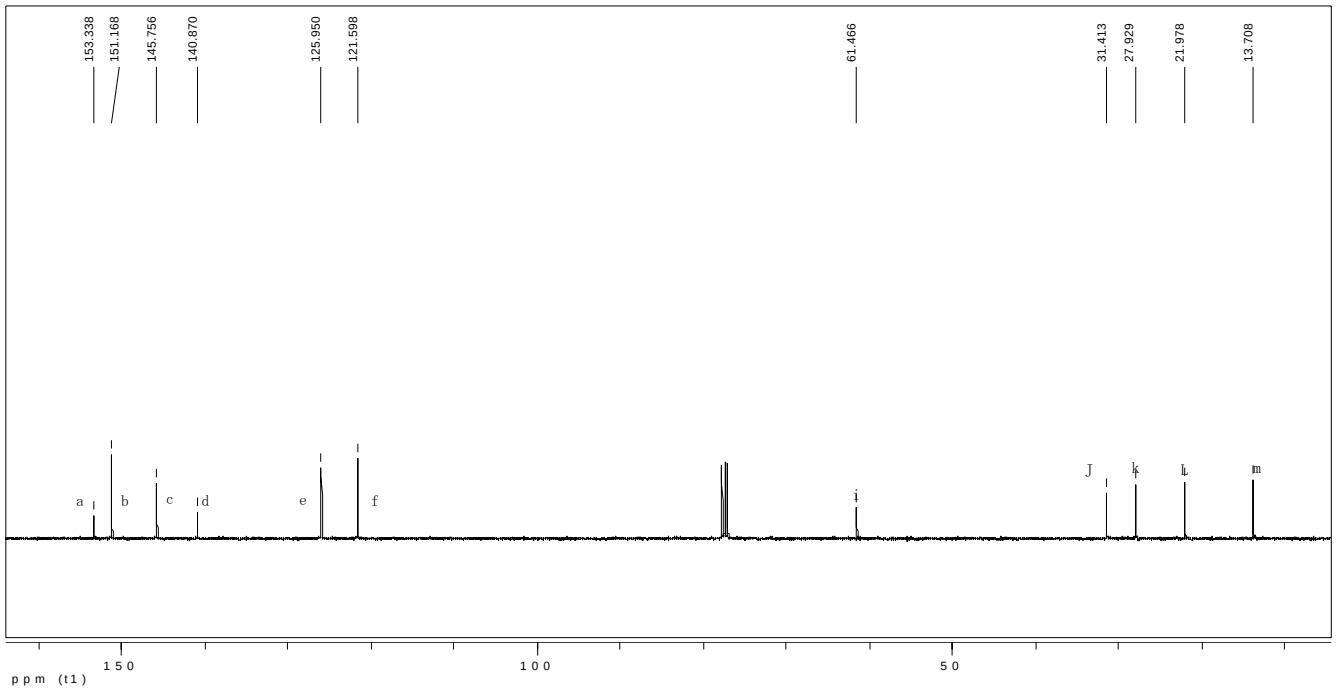


DEPT spectrum of ethyl-bipyridinium iodide

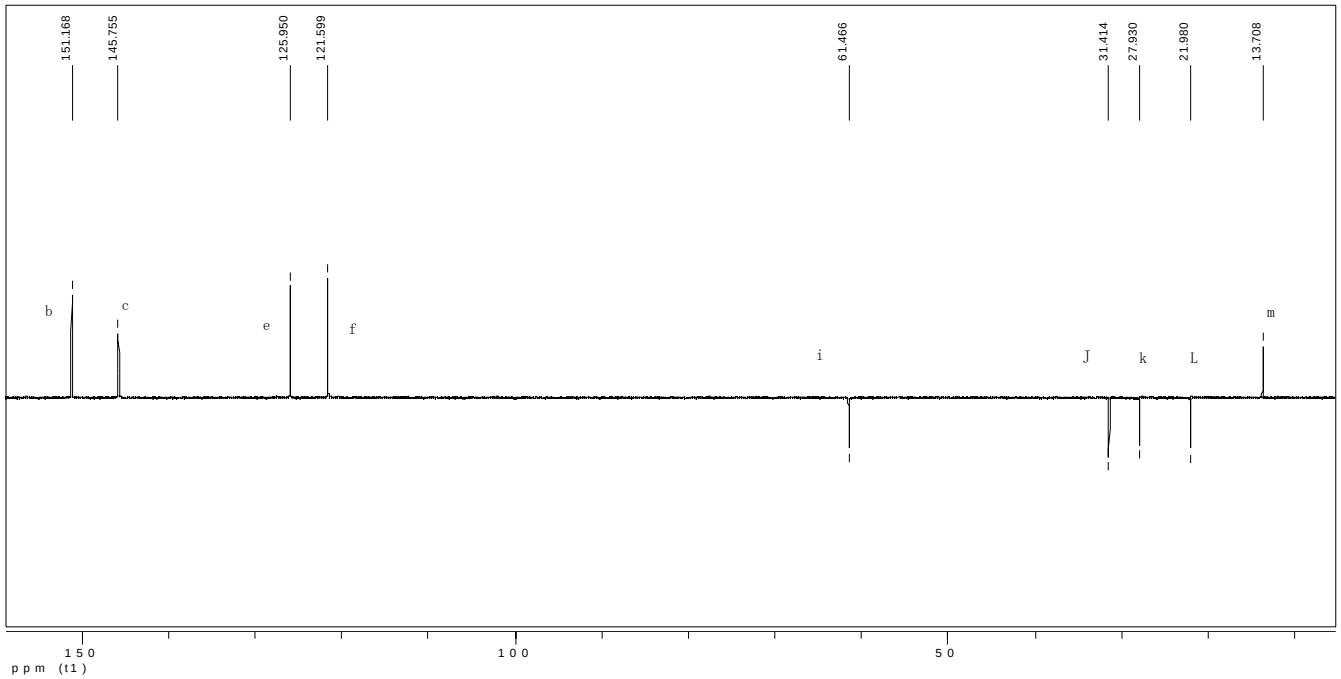
C. NMR spectra of C_5bPyBr(5A)



^{1}H NMR spectrum of pentyl-bipyridinium bromide

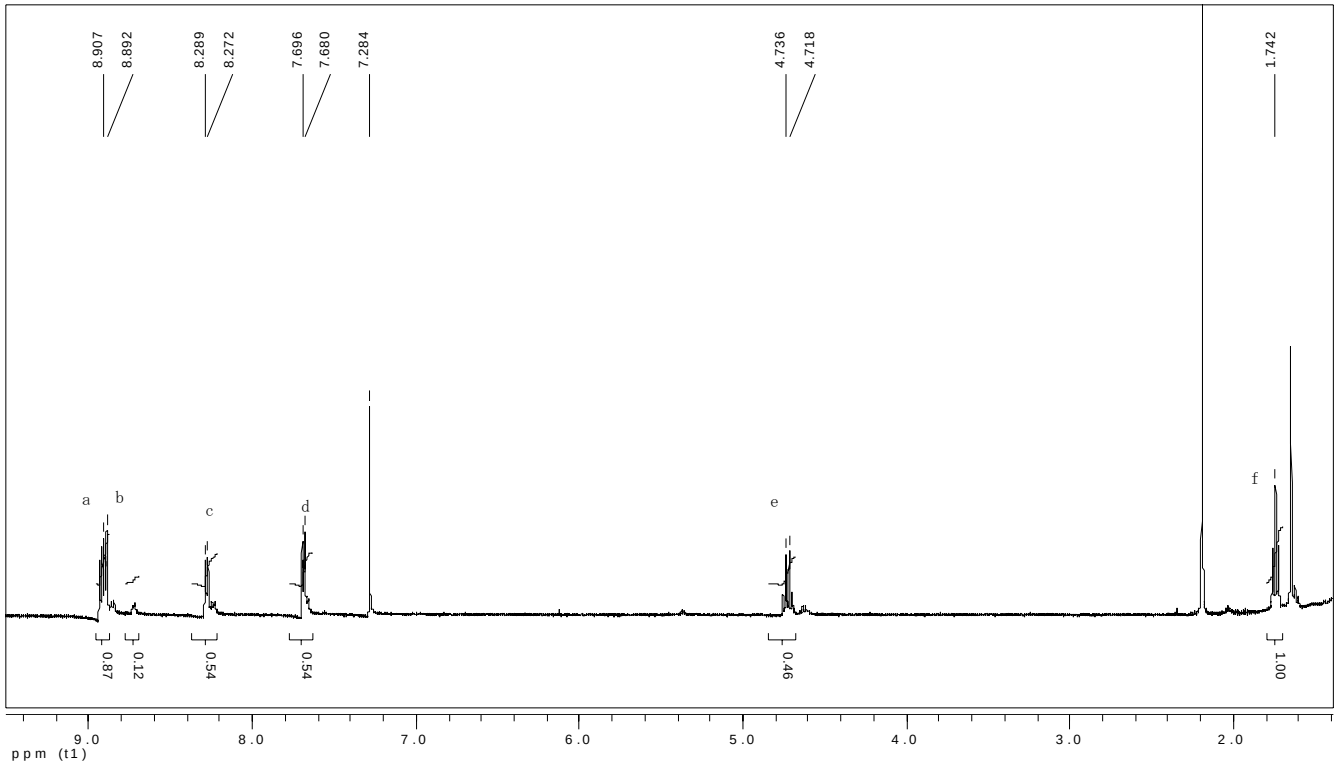


^{13}C NMR spectrum of pentyl-bipyridinium bromide

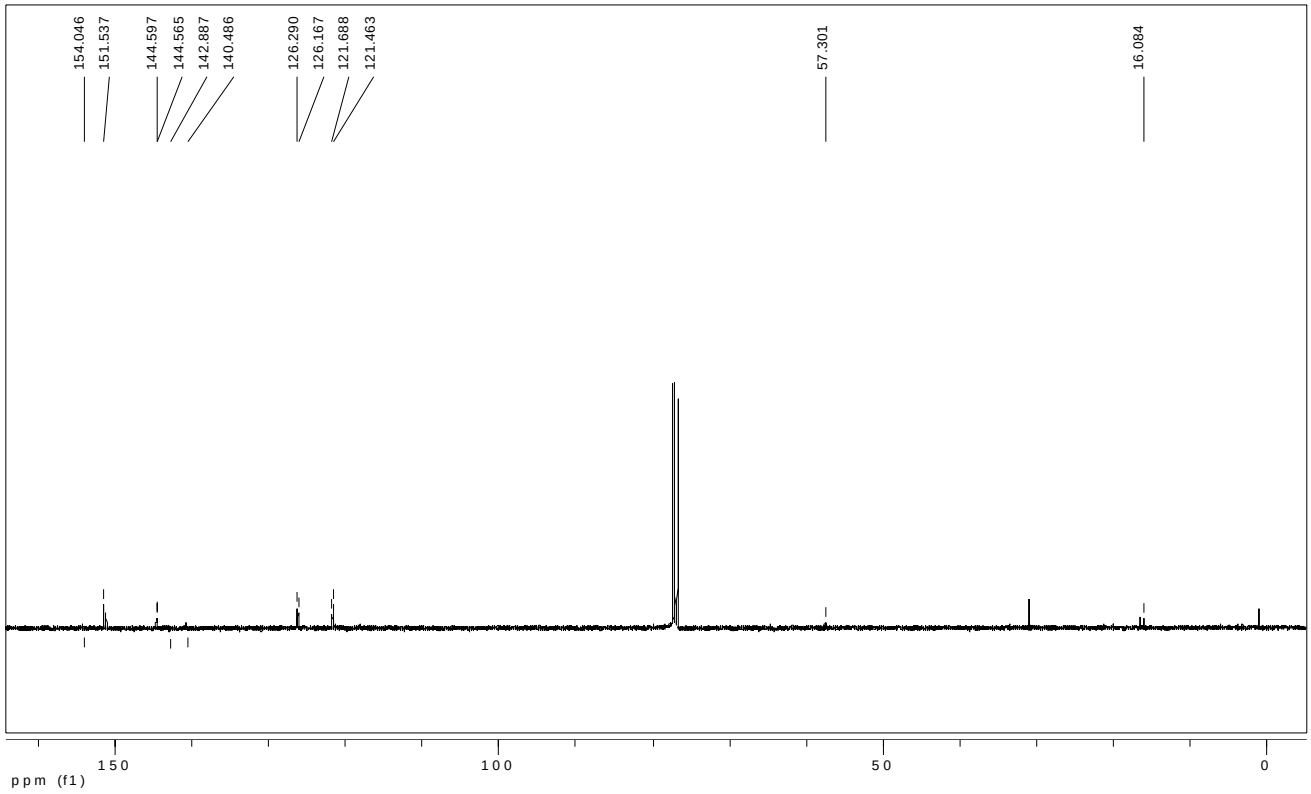


DEPT spectrum of pentyl-bipyridinium bromide

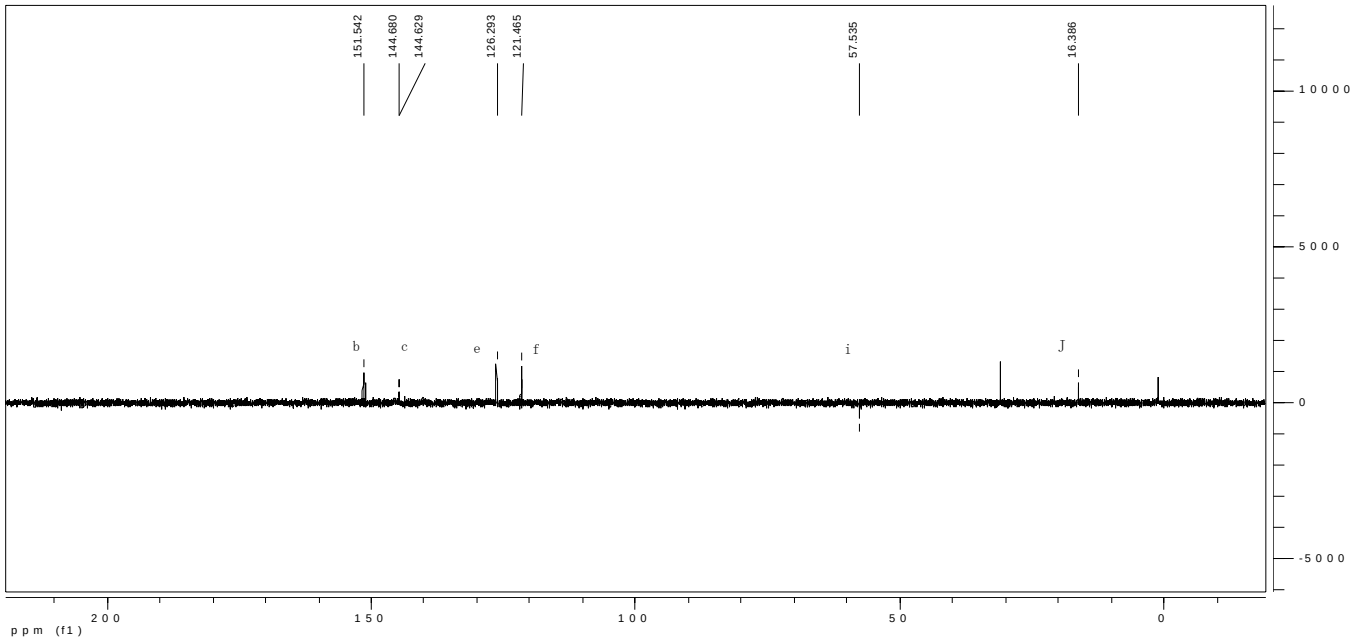
D. NMR spectra of C_2bPyNTf2 (2B)



^{1}H NMR of spectrum of ethyl-bipyridinium bis(trifluoromethylsulfonyl)imide

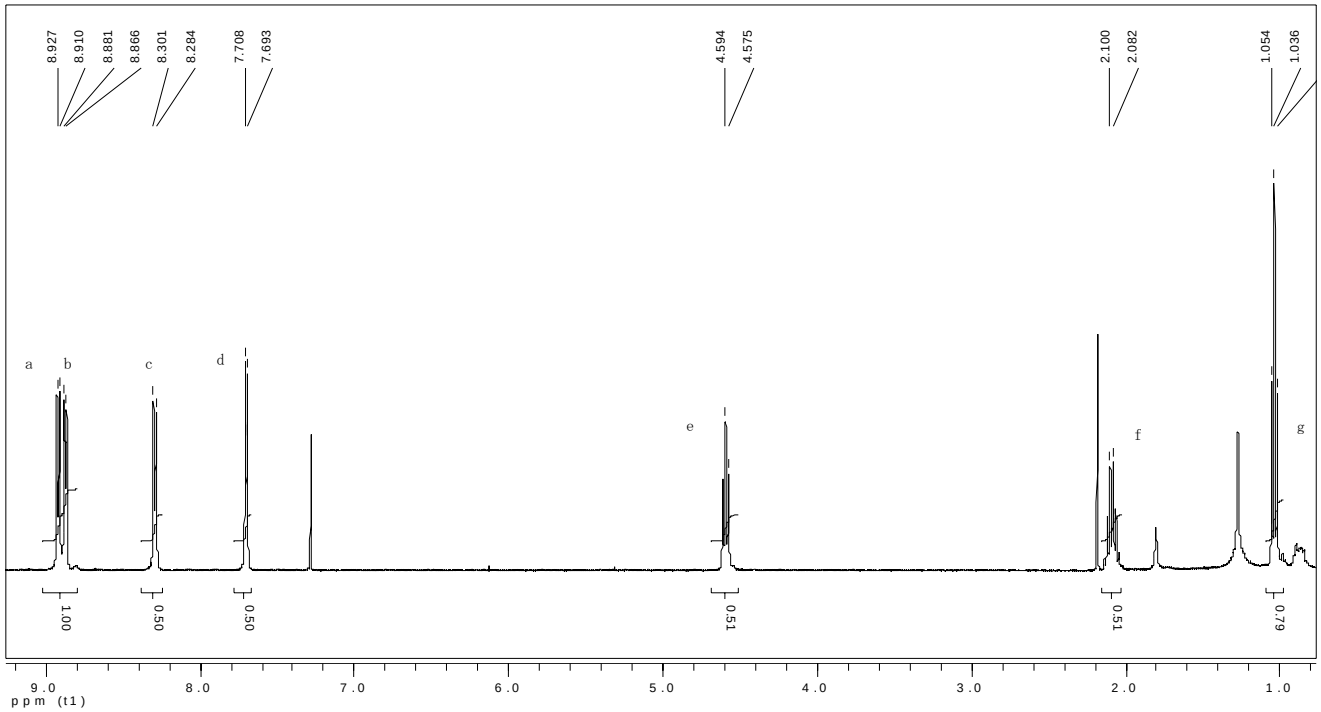


^{13}C NMR of spectrum of ethyl-bipyridinium bis(trifluoromethylsulfonyl)imide

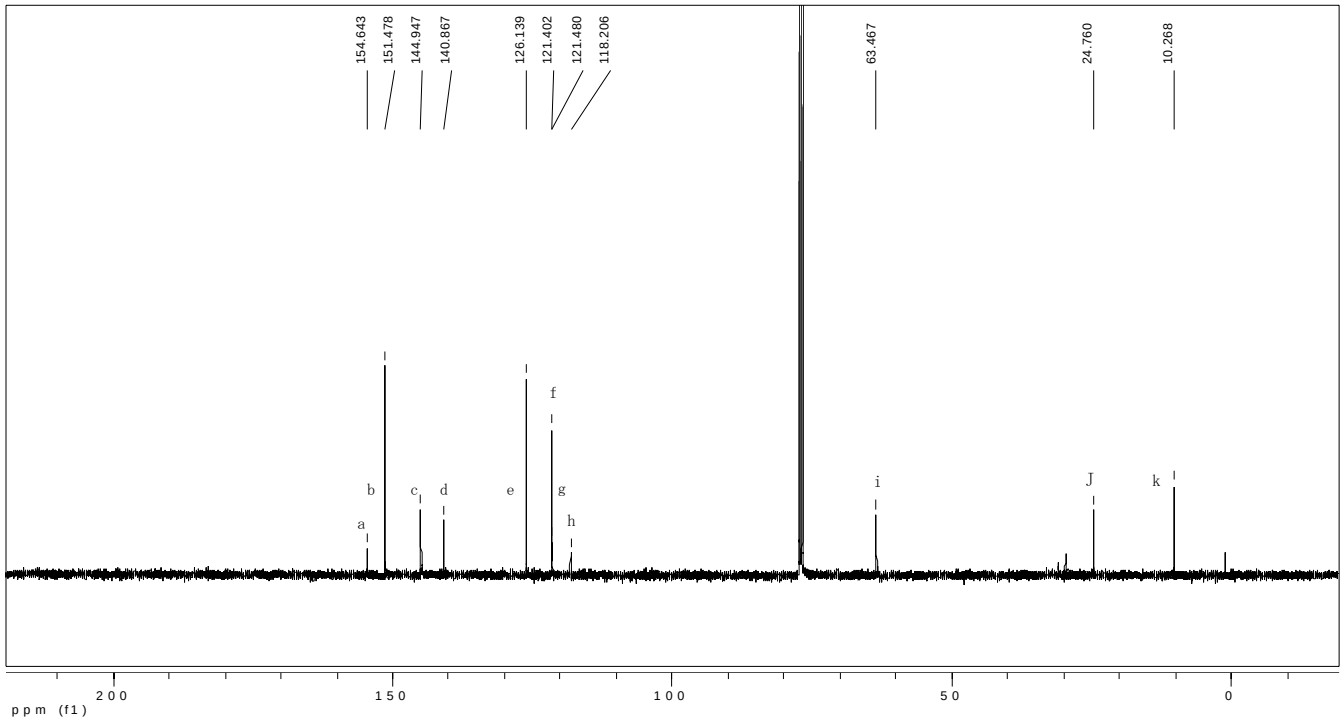


DEPT spectrum of ethyl-bipyridinium bis(trifluoromethylsulfonyl)imide

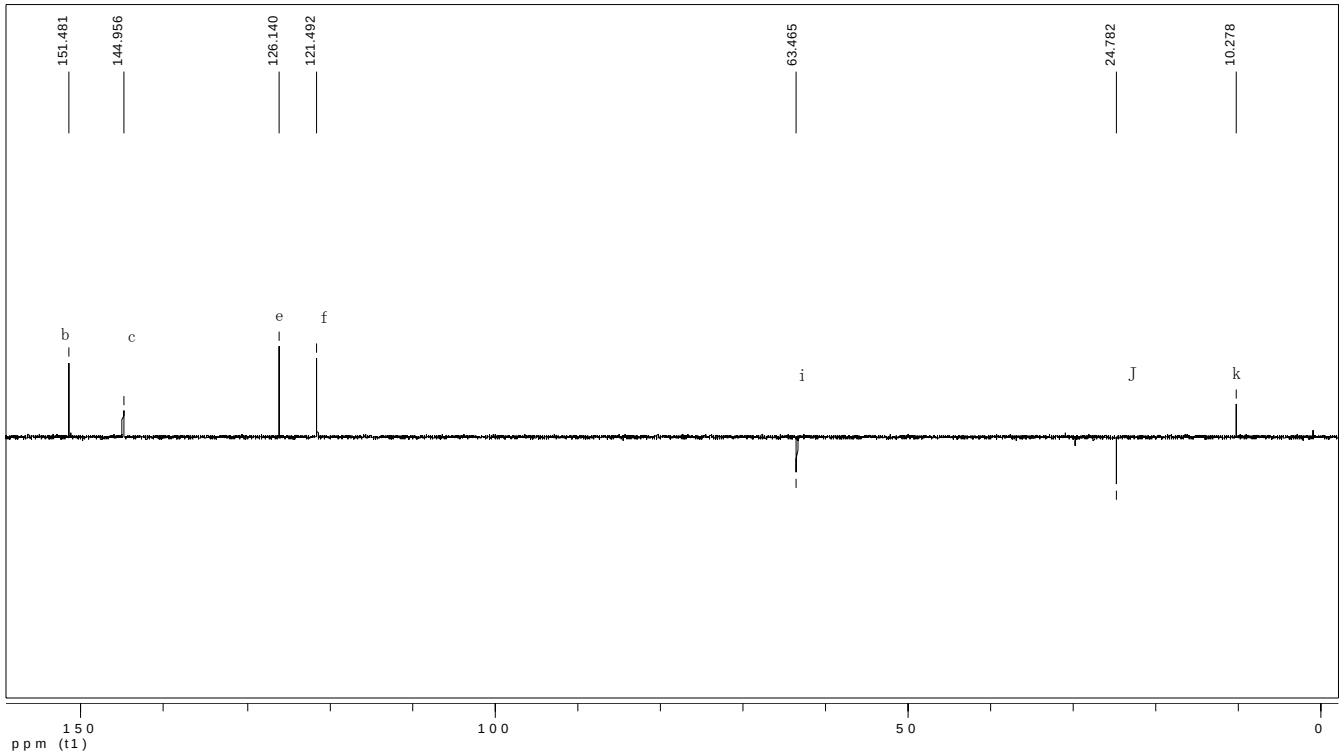
E. NMR spectra of C_3bPyNTf2 (3B)



^{1}H NMR spectrum of propyl-bipyridinium bis(trifluoromethylsulfonyl)imide

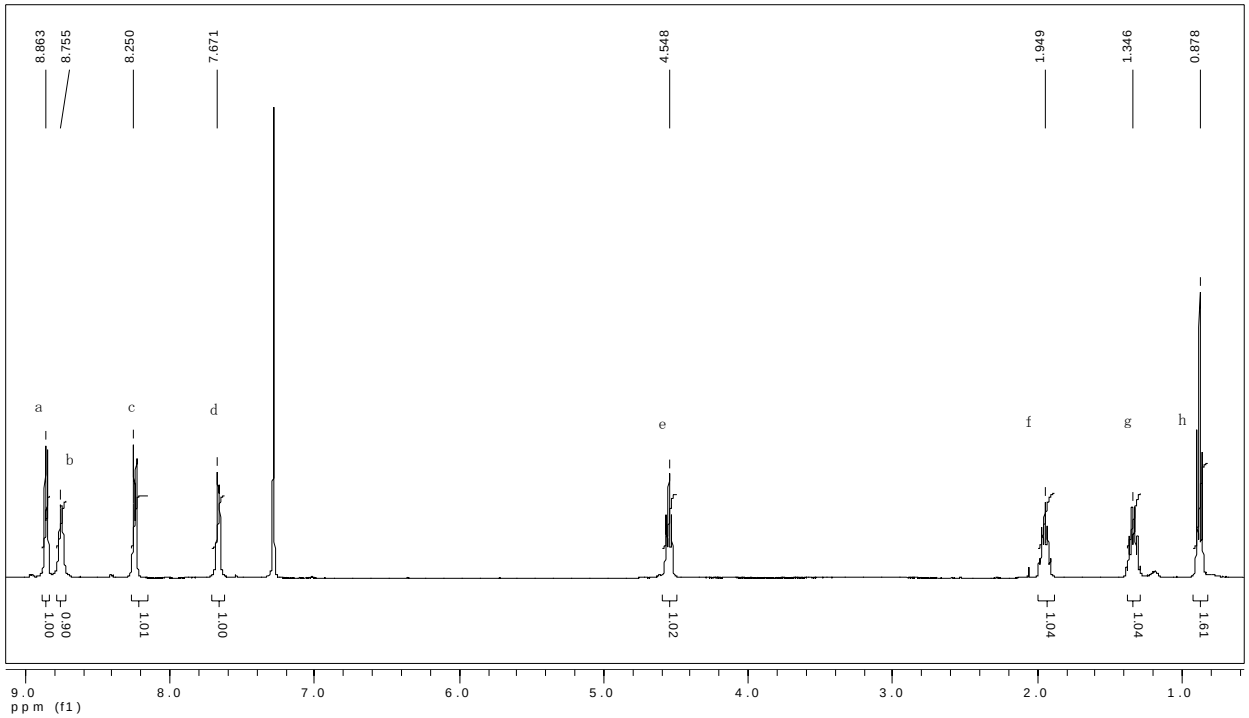


^{13}C NMR spectrum of propyl-bipyridinium bis(trifluoromethylsulfonyl)imide

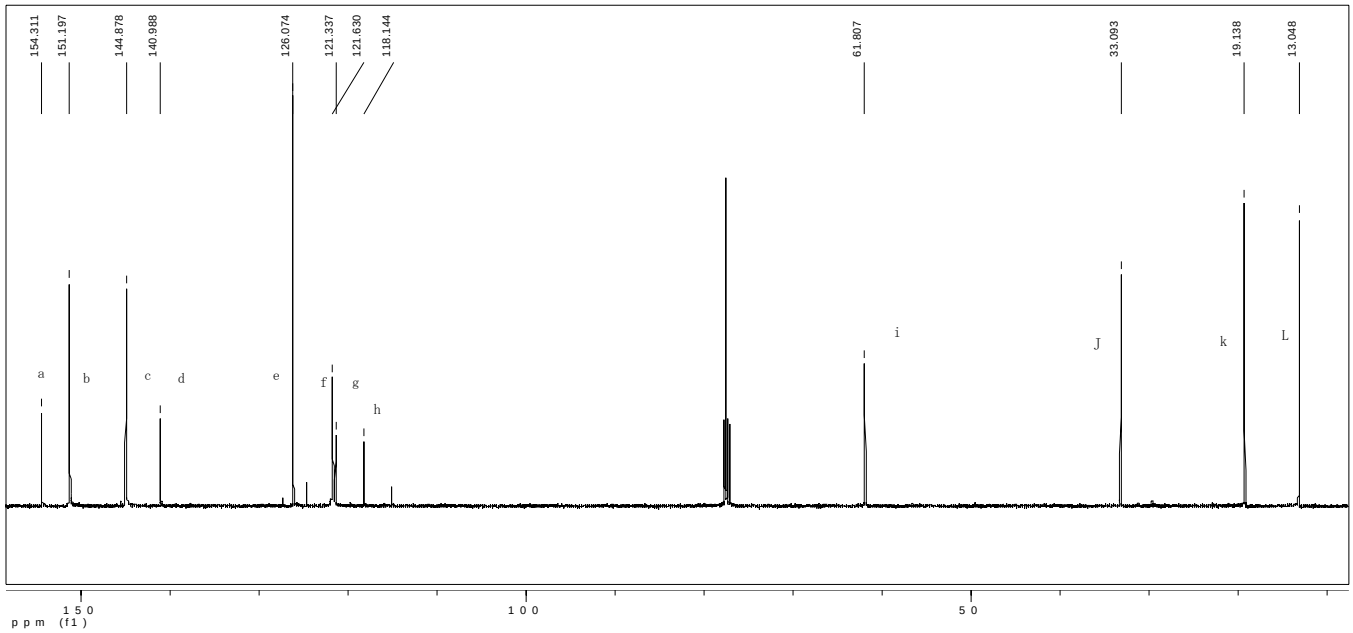


DEPT spectrum of propyl-bipyridinium bis(trifluoromethylsulfonyl)imide

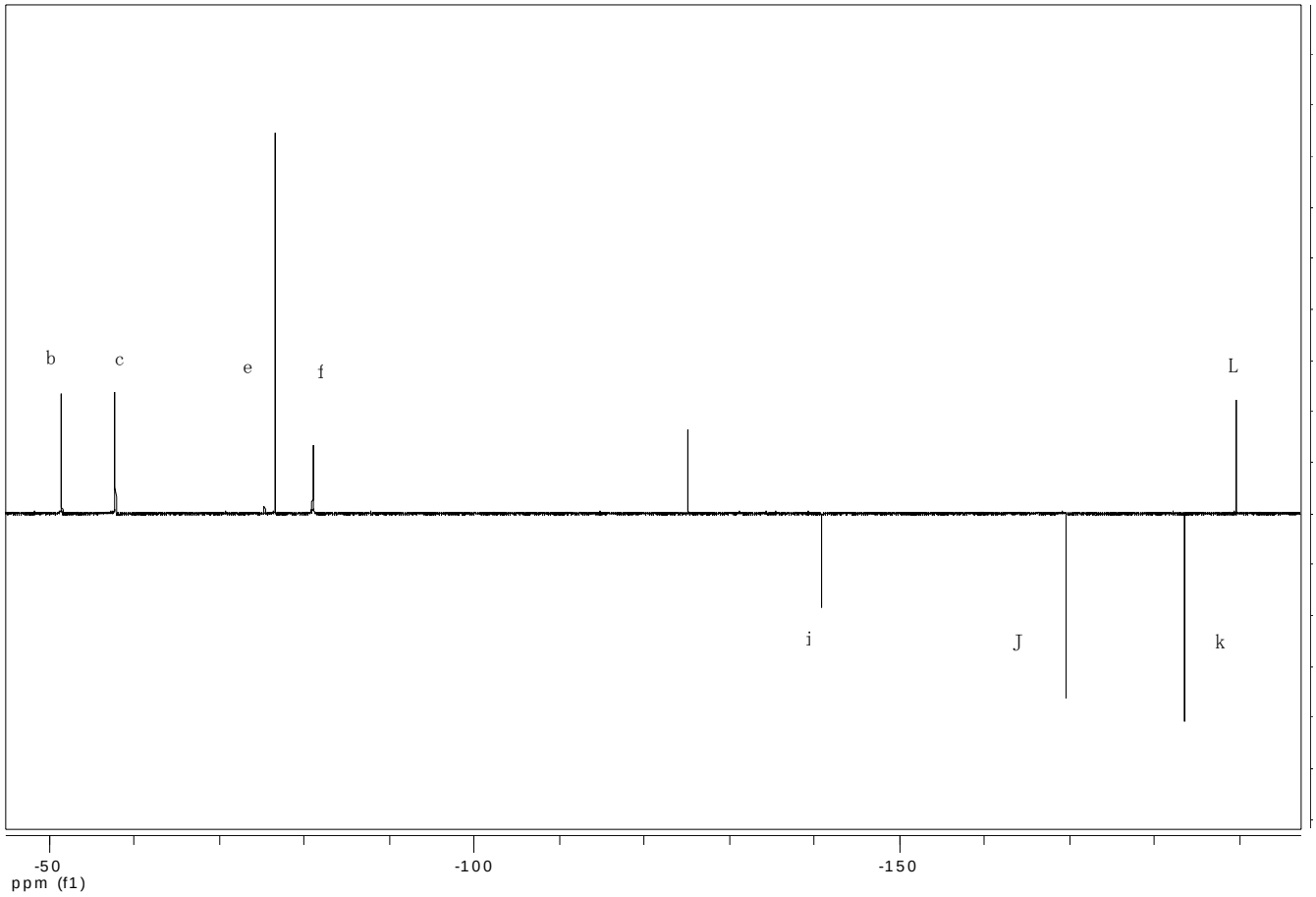
F. NMR spectra of C_4bPyNTf2 (4B)



^{1}H NMR spectrum of butyl-bipyridinium bis(trifluoromethylsulfonyl)imide

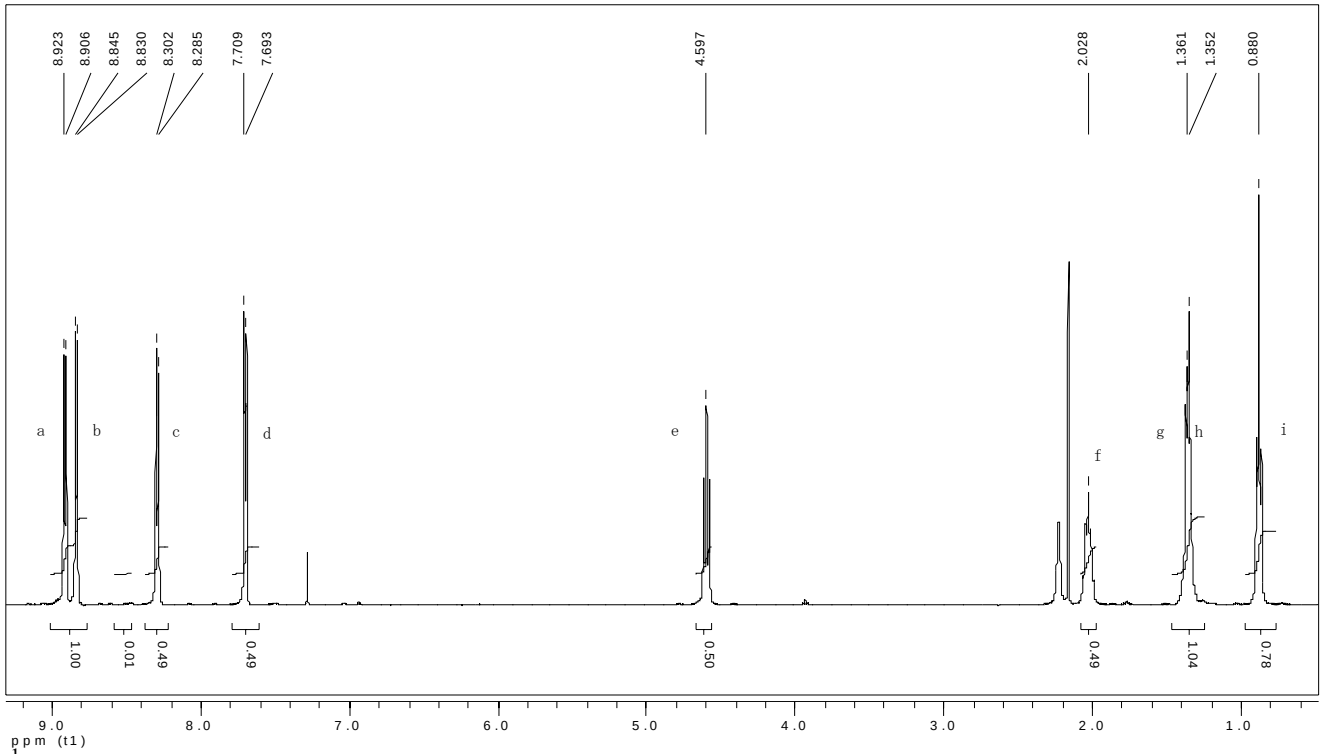


^{13}C NMR spectrum of butyl-bipyridinium bis(trifluoromethylsulfonyl)imide



DEPT spectrum of butyl-bipyridinium bis(trifluoromethylsulfonyl)imide

G. NMR spectra of C_5bPyNTf2 (5B)



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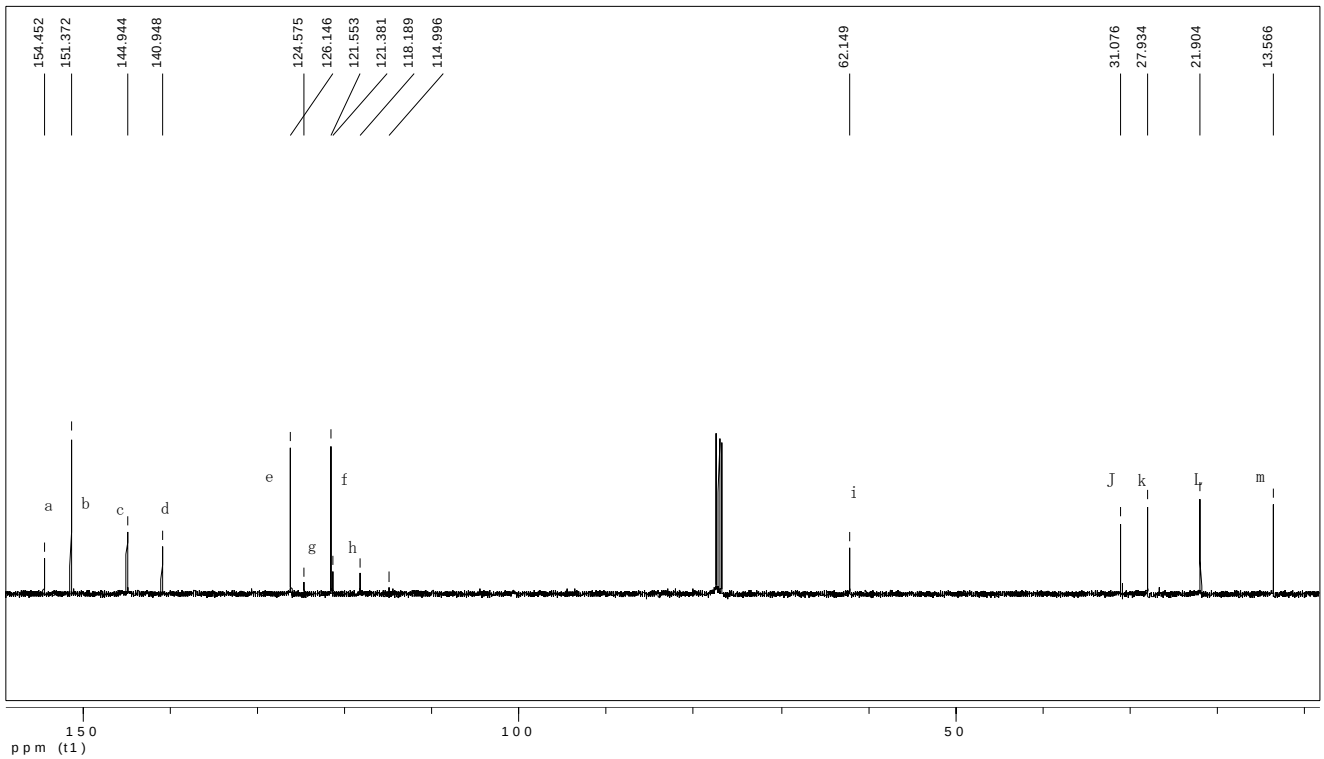

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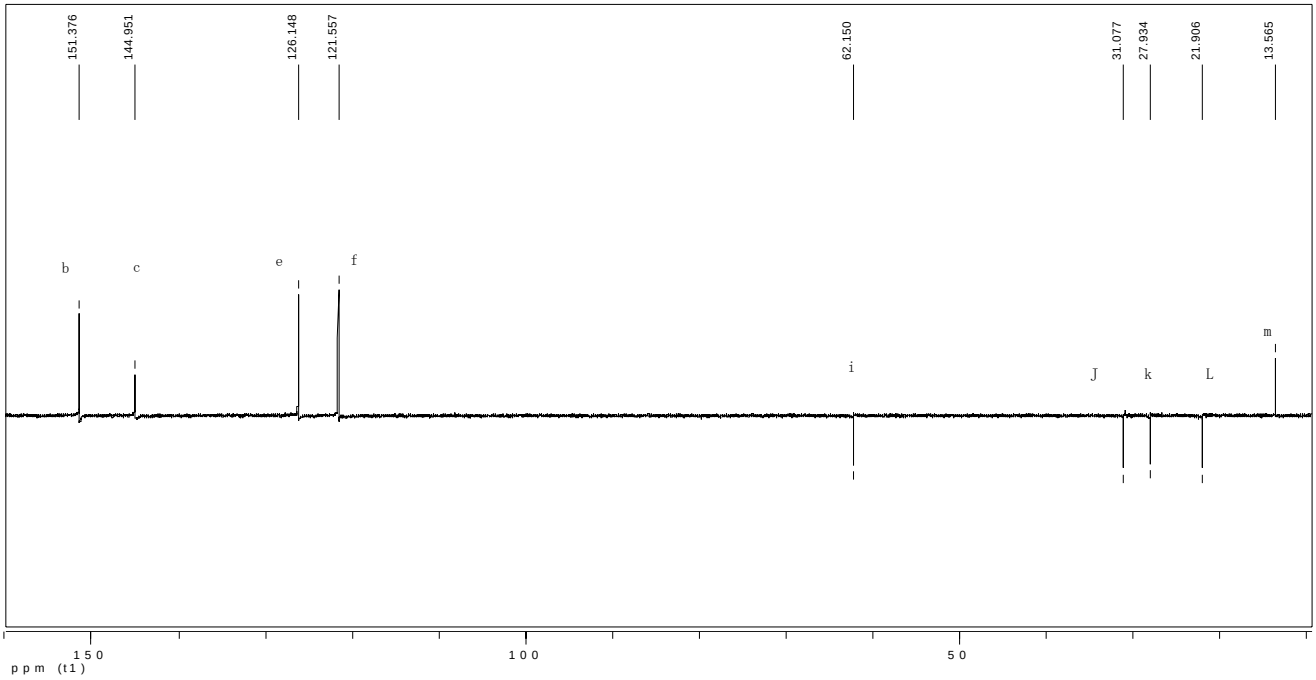

DEPT spectrum of pentyl-bipyridinium bis(trifluoromethylsulfonyl)imide