IONIC LIQUIDS: SYNTHESES, CHARACTERIZATION AND APPLICATIONS IN ANALYTICAL CHEMISTRY

By

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ABSTRACT

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Multifunctional ionic liquids (especially dicationic and dianionic) have been shown to have a greater range of physical properties than most traditional, singly charged ionic liquids (ILs). In this work, 28 novel tricationic ILs with specific structural variations have been synthesized in order to investigate the effect on their physicochemical properties. It was observed that the physicochemical properties can be varied to a greater extent in tricationic ILs than in traditional ILs. The central core of the tricationic IL itself can have different degrees of flexibility and these moieties can be altered as can the charge carrying groups to produce ILs with the desired physicochemical properties. These ILs have a greater range of viscosities and higher

thermal stabilities than typical imidazolium based singly charged ionic liquids. Anion effects are also prominent with these highly tunable ionic liquids.

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CHAPTER 1

TRIGONAL TRICATIONIC IONIC LIQUIDS: MOLECULAR ENGINEERING OF TRICATIONS TO CONTROL PHYSICOCHEMICAL PROPERTIES

1.1 Introduction

1.1.1 General description of ionic liquids

Room temperature ionic liquids (RTILs), salts that are liquids at ambient temperatures have attracted the attention of many investigators leading to a number of studies. They resemble a classical liquid, but they do not contain any neutral molecules. They are made out of only ions. Like any other salts, these materials therefore have negligible vapor-pressure.

There are many synonyms used for ionic liquids. “Molten salts” is the most common and most broadly applied term for ionic compounds in the liquid state. RTIL is applied to all salts having melting temperatures at or below ambient temperatures. On the other hand ionic liquids (ILs) applied to any other salts, which have a melting temperature below 100 ^{o}C. Other names in literature for materials that meet the working definition of ionic liquids are: “room temperature molten salt”, “low temperature molten salt”, “ambient-temperature molten salt”, and ”liquid organic molten salt”. The first RTIL, ethyl ammonium nitrate with a melting point of 12 ^{o}C was reported in 1914, during World War I.[1] However it is during the last two and half decades or so that

extensive research on ILs was carried out with the advent of imidazolium containing ILs.

The cations of most common ILs consist of imidazolium, pyrrolidinium, pyridinium, tetraalkylphosphonium, and tetraalkylammonium ions. On the other hand the anions of common ILs include h alides (X^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), trifluoromethylsulfonate (TfO^-), nitrate (NO_3^-), acetate (OAc^-), and most commonly used bis(trifluoromethanesulfonyl)imide (NTf_2^-). The combinations of such cations and anions can lead to a large number of ionic liquids that can provide considerable flexibility in the selection of the most suitable pair for a specific chemical application. Some of the common cations and anions are depicted in **Figure 1.1**.

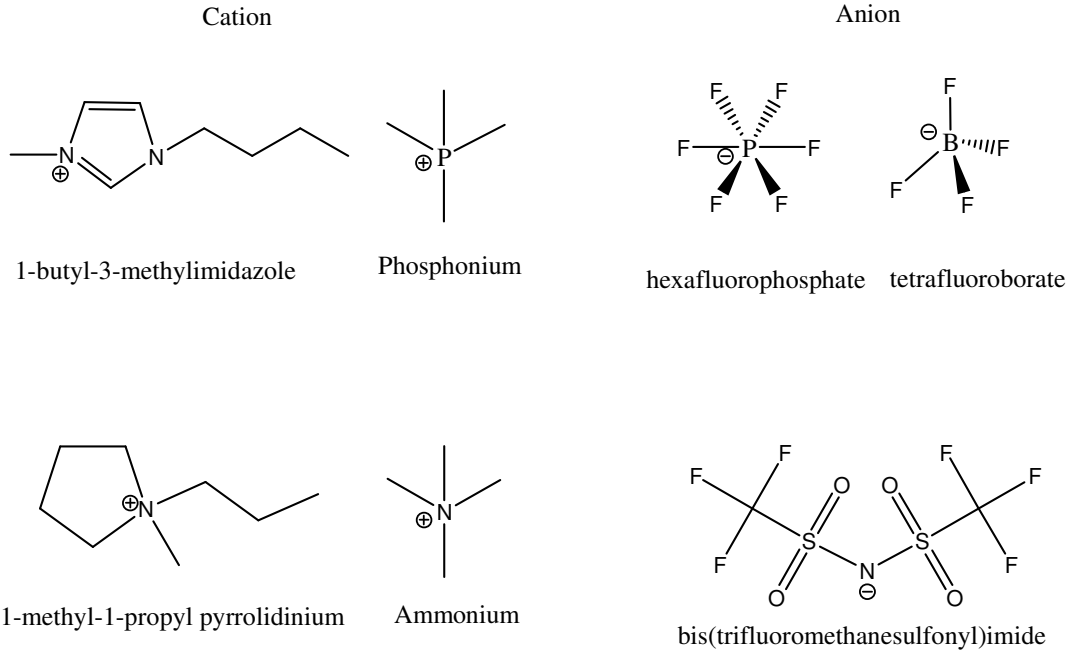


Figure 1.1 Common anions and cations used in Ionic Liquids

1.1.2 Applications of ionic liquids

The absence of vapors is the central factor that resulted in the gain of the popularity for these materials in the scientific community. This is because these materials are capable of replacing the standard volatile organic solvents that are frequently used in organic syntheses. Simple modification of traditional ionic liquids (ILs) by varying their cations and anions can produce ILs with variable or tunable physicochemical properties that make them much more versatile and useful for a variety of applications. Their uses traverse many areas of chemistry and biochemistry, including novel solvent systems in organic syntheses and catalysis,[2-9] enzyme-catalyzed reactions,[10-13] electrochemical studies,[14-17] electrolyte materials for double-layer capacitors, dye-sensitized solar cells, liquid-liquid extractions,[18-22] liquid matrices for matrix-assisted laser desorption/ionization mass spectrometry,[23-26] additives in HPLC and capillary electrophoresis, and stationary phases in GC.[27-33]

1.1.3 Physicochemical properties of ionic liquids

RTILs are said to be "tunable", "tailored", "task-specific" or "designer" liquids because cation-anion combinations can be molecularly tailored for specific applications to fulfill desired tasks with optimal performances.

Applications of ILs have expanded tremendously over the past few years due to their variable physicochemical properties. The main attractive physicochemical properties of RTILs are: (1) negligible vapor pressure;[2] (2) wide liquid-range over a temperature range of 200 to 300 ^{o}C; (3) can be custom synthesized for miscibility

and/or immiscibility with other liquid solvents;[34] (4) wide electrochemical stability window;[14-16] (5) capability to undergo multiple solvation interactions with many types of molecues;[35] and(6) wide range of viscosities.

Multifunctional ionic liquids (especially dicationic and dianionic ILs) have been shown to have a greater range of tunable physical properties than most traditional, singly charged ILs.[35, 36] Consequently, they have been shown to have exceptional high temperature stable and selective gas chromatographic stationary phases[35, 37] and have been prepared as a new class of high temperature lubricants.[38, 39] They often have greater thermal stability, lower volatility, and more flexibility in tuning/varying their physicochemical properties. In particular, varying the cationic or anionic moieties to produce unsymmetrical dicationic (or dianionic) moieties allows greater variety and control of virtually all IL properties.[36]

The question arises, can ever more complex multifunctional ILs (tricationic, trianionic, tetracationic, etc.) be beneficial? As the number of charged groups and the molecular weight of these multifunctional salts increases it becomes increasingly difficult to produce them in liquid forms (at ambient temperature). In addition, the synthetic/manufacturing process can become increasingly complex which raises their production cost. Hence it is possible to reach a point of diminishing returns in the quest for ever larger and more complicated multifunctional ionic liquids.

However, unsymmetrical tricationic ionic liquids reported to date have shown good thermal stabilities and were tested for antimicrobial activity.[40] In this work, we present a much extended study to demonstrate that symmetrical, trigonal tricationic

ionic liquids can be molecularly tailored to a greater extent than traditional ILs. This is achieved by synthesizing novel symmetrical tricationic ionic liquids using four major types of central cores having five or more different cationic moieties for each center. We also demonstrate that this sort of molecular structure alterations could be used to further tune their physical properties such as melting point, viscosity, density, thermal stability, hydrophilicity/lipophilicity, refractive index and miscibility with water and organic solvents. A final important consideration is the fact that there have been no prior IL studies involving these symmetrical tri-cations.

1.2 Results and Discussion

The four main symmetrical tricationic core moieties, **A, B, C and D** are shown in **Figure 1.2**. These central structures were selected to range from the more rigid mesitylene core (**A**) to the more flexible tri(2-hexanamido)ethylamine core (**D**). Application of tricationic liquids can be obtained by attributing any of five different

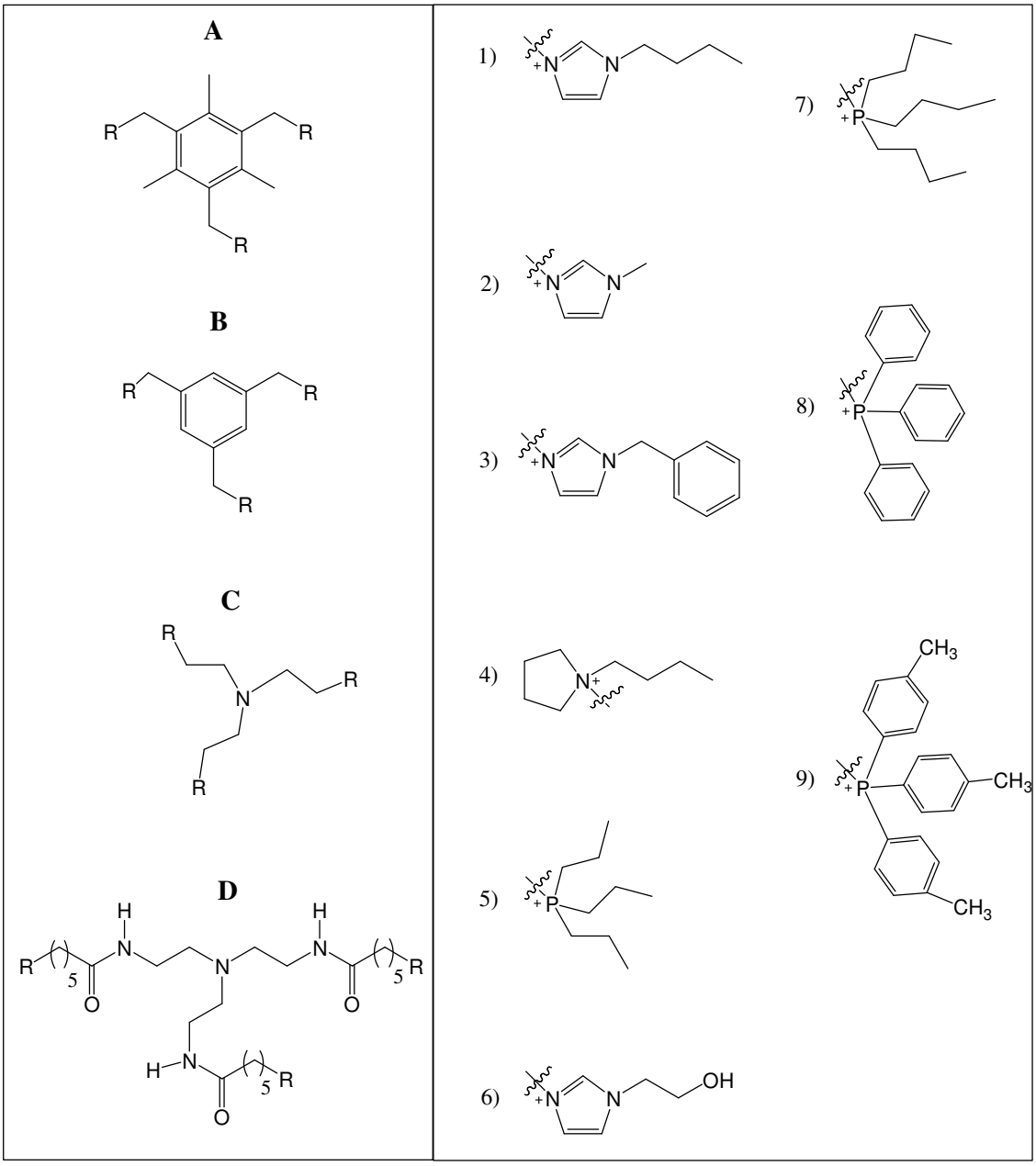


Figure 1.2 Structures of trications examined

charge carrying groups (**R1, R2, R3, R4** and **R5**) to the desired core. This allows study of the molecular structure dependence of the trication salts to their physicochemical

properties. Several other tricationic ILs were also synthesized using a central core-**C** with **R6**, **R7, R8 and R9** charge carrying moieties. The counter anions studied include bis(trifluoromethylsulfonyl)imide (NTf_2^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and trifluoromethanesulfonate (TfO^-)

All four synthesized NTf_2^- salts with the flexible central-tri(2-hexanamido)ethylamine core (**D1** to **D4**) provided melting temperatures below 0 ^oC (see Chapter 3). The more rigid mesitylene core (**A**) provided all NTf_2^- salts that were solids at ambient temperatures. The melting temperatures of the NTf_2^- salts having **B** and **C** cores, with intermediate flexibilities, were dependent on the nature of the charge carrying moieties **1**, **2**, **3**, **4** and **5**. Except for **C2**-NTf_2 all tricationic NTf_2^- salts having the **B** and **C** cores with their charge carrying moieties having imidazolium systems, provided melting temperatures below 0 ^oC. The phosphonium charge carrying moiety provided an RTIL only with the most flexible central core (**D)**. With central core structures: **A**, **B** and **C,** all salts are solids at room temperature (compare ILs-**B5**, **A5** and **C5)**

Tricationic salts with PF_6^-, BF_4^- and TfO^- counter ions and the moderately rigid central core (**B)** and moderately flexible core (**C)** associated with butylimidazolium charge carrying moiety were evaluated. Melting temperature of these along with the NTf_2^- salts were compared. A general trend of melting temperatures for the tricationic ILs with same tri-cation with varying anions is observed as follows: $NTf_2^- < TfO^- < BF_4^- < PF_6^-$. The melting point trends observed for these tricationic ILs is similar to that

observed for previously reported imidazolium based dicationic ILs.[35] However, the trend is different to that observed in traditional imidazolium based monocationic ILs.[34] The densities of the synthesized tricationic ILs range from 1.20 to 1.69 g/cm^3. The highest density is observed for IL-A2 having three methylimidazolium cationic moieties associated with mesitylene core (**A**) having NTf_2^- counter anions (1.69 g/cm^3, IL-A2). The lowest density was observed for compound IL-**C5** which has nitrogen core(**C**) with three tripropylphosphinium cationic moieties (**5**) and NTf_2^- anions (1.20 g/cm^3, IL-C5). For similar cationic moieties with NTf_2^- anions, ionic liquids having mesitylene cores are more dense than those with the other three types of cores. The general trend that can be discerned from the data in **Table 1.1**, is that the densities of imidazolium based ionic liquids decreases with increasing length of the hydrocarbon chain at the no.3-position of imidazole (compare 1.53 g/cm^3 for IL-**B1** to 1.56 g/cm^3 for IL-**B2**, 1.55 g/cm^3 for IL-**A1** to 1.69 g/cm^3 for IL-**A2**, 1.41 g/cm^3 for IL-**C1** to 1.56 g/cm^3 for IL-**C2**, 1.49 g/cm^3 for IL-**D1** to 1.59 g/cm^3 for IL-**D2**). Similar trends have been previously reported for a large series of mono and dicationic ionic liquids.[35, 41, 42] Furthermore, it is clear from the data obtained given in **Table 1.1** that for ionic liquids with similar cationic moieties, densities are also affected by the nature of the counter anions in the order: $NTf_2^- > PF_6^- > TfO^- > BF_4^-$. This trend is similar to that observed for both di- and mono-cationic ILs.[34, 35]

Table 1.1 Physicochemical Properties of Tricationic ILs Synthesized

Ionic Liquid	MW (g/mol)	Melting Point (^{0} C)	D[b] (g/cm^3)	Refractive index	Viscosity[c] (cSt)	Thermal Stability[d] (^{0}C)		Miscibility with heptane[e]	Miscibility with water[e]
						99% w	95% w		
A1- NTf2	1372.3	66-69	1.546	-	-	300	359	I	I
A2- NTf2	1246.0	82-85	1.686	-	-	338	370	I	I
A3- NTf2	1474.3	60-62	1.588	-	-	339	365	I	I
A5- NTf2	1480.4	123-126	1.314	-	-	288	398	I	I
B1- NTf2	1330.2	-24.6*	1.533	1.467	2320	344	401	I	I
B2- NTf2	1203.9	-38.6*	1.564	1.467	1280	364	414	I	I
B3- NTf2	1432.2	-87.4*	1.548	1.588	20000-25000	262	361	I	I
B4- NTf2	1339.3	62-64	1.442	-	-	344	371	I	I
B5- NTf2	1438.3	89-91	1.243	-	-	397	430	I	I
C1- NTf2	1311.2	-47.5*	1.409	1.451	1580	308	363	I	I
C2- NTf2	1184.9	36-37	1.556	-	-	338	393	I	I
C3- NTf2	1413.2	-6.7*	1.514	1.493	25000-30000	348	381	I	I
C4- NTf2	1320.3	57-58	1.473	-	-	297	337	I	I
C5- NTf2	1419.3	103-104	1.204	-	-	260	385	I	I
C6- NTf2	1275.0	-38.5	1.638	1.460	7980	344	392	I	I
C7- NTf2	1545.5	133-135	1.261	-	-	361	406	I	I
C8- NTf2	1725.5	82-84	1.534	-	-	235	269	I	I
C9- NTf2	1851.7	17.1	1.369	-	-	396	398	I	I

Table 1.1 continued

D1- NTf2	1650.6	-54.1*	1.49	1.466	10200	262	335	I	I
D2- NTf2	1524.4	-16.4*	1.59	1.465	7760	279	351	I	I
D3- NTf2	1752.7	-15.6*	1.54	1.495	40000-45000	210	280	I	I
D5- NTf2	1758.8	-31.4*	1.48	1.466	35000-40000	284	388	I	I
A1- Pf6	924.6	141-143	1.49	-	-	246	320	I	I
A1- Tfo	937.0	63-65	1.47	-	-	316	380	I	M
A1- Bf4	750.1	130-133	1.41	-	-	302	357	I	M
C1- Pf6	905.6	195-197	1.33	-	-	309	344	I	I
C1- Tfo	917.9	64.2*[a]	1.33	-	-	253	349	I	M
C1- Bf4	731.1	101-104	1.21	-	-	274	297	I	M

[*] Phase transition temperature determined by using differential scanning calorimetry (DSC). [a] Amorphous solid. [b] Measured using pycnometer. [c] Measured using a capillary viscometer. [d] Thermogravimetric analysis (TGA), 99% w = temperature at 1% mass decrease of sample, 95% w = temperature at 5% mass decrease of sample. [e] I = immiscible, M = miscible.

The kinematic viscosities of the nine room temperature ionic liquids (IL-**B1**, IL-**B2**, IL-**B3**, IL-**C1**, IL-**C3**, IL-**D1**, IL-**D2**, IL-**D3**, IL-**D4**,) were measured at 30 ^{o}C and are given in **Table 1.1**. The tricationic ionic liquids are much more viscous than traditional monocationic ionic liquids and dicationic ionic liquids.[34] The viscosities are remarkably high for ILs containing charged benzylimidazolium charge moieties (20000-45000 cSt for IL-**B3**, IL-**C3**, IL-**D3**). This may be due to the presence of additional aromatic moieties compared to the other cationic groups.[36] Ionic liquids with higher viscosities are preferred for some applications, such as stationary phases for gas-liquid chromatography.[10, 11] Viscosities of ionic liquids with imidazolium based moieties and NTf_2^- anions show increasing in viscosities with increasing alkyl chain at the 3-position of imidazole (compare 2320 cSt for IL-**B1** to 1280 cSt for IL-**B2**, 10200 cSt for IL-**D1** to 7760 cSt for IL-**D2**). An analogous trend has been observed with traditional monocationic and dicationic ionic liquids.[18, 34, 35, 42]

Thermal stabilities of all 28 tricationic salts were measured by thermogravimetric analysis (TGA) and are given in **Table 1.1**. Thermal stabilities (5% weight loss) of 16 tricationic ionic liquids with NTf_2^- counter anion range from 355 ^{o}C to 430 ^{o}C which is higher than monocationic ionic liquids and similar to dicationic ionic liquids. All central cores carrying phosphonium cationic moieties show the highest thermal stabilities compared to the others (430 ^{o}C for IL-**B5**, 398 ^{o}C for IL-**A5**, 385 ^{o}C for IL-**C5** and 405 ^{o}C for IL-**D5)** followed by

methylimidazolium cationic moieties (414 ^{o}C for IL-**B3**, 370 ^{o}C for IL-**A3**, 430 ^{o}C for IL-**C3** and 430 ^{o}C for IL-**D3**). Furthermore the data shows that ILs with NTf_2^- anion possess highest thermal stabilities followed by ILs with TfO^- as counter anion.

The miscibility of all ionic liquids with both water (polar) and heptane (non-polar) as solvents was evaluated (**Table 1.1**). Tricationic ionic liquids exhibit similar solubility behavior as monocationic and dicationic ionic liquids.[2, 36, 43-46] None of the ionic liquids were soluble in heptane. Refractive index values were recorded for those samples that were liquids at room temperature. All values are in the general region observed for monocationic and dicationic ionic liquids[36, 43] and lie between 1.451 and 1.588.

In summary, we have demonstrated the effect of molecular structure modifications on the physicochemical properties of a series of 28 new symmetrical tricationic ILs. We observed that the physicochemical properties of tricationic ILs often can be varied and controlled to a greater extent than simple, more conventional ILs. For bis(trifluoromethylsulfonyl)-imide tricationic ionic liquids, the viscosity generally increased to 4 to 5 fold higher than those reported earlier, when benzylimidazolium is used as the cationic moiety. The thermal stabilities of most of the tricationic ionic liquids (often > 400 ^{o}C) are greater than that of traditional monocationic ionic liquids. It is also clear that melting point of tricationic ILs are contingent by the flexibility of the central core system; e.g. ILs

(Core **D**) with more flexible structure have low melting points compared to ILs (Core **A**) having more rigid structures. The solubility of tricationic ionic liquids in water and heptane appears very similar to that of the traditional monocationic and dicationic ionic liquids and depends largely on the selected anion.

CHAPTER 2

APPLICATION OF IONIC IQUIDS IN ANALYTICAL CHEMISTRY

2.1 Introduction

Room temperature ionic liquids (ILs) are gaining wide recognition in analytical chemistry. This is due to their unique properties such as negligible vapor pressure, variable viscosity, high thermal stability and good extractability of various organic compounds and metal ions. Moreover, they can be custom-synthesized to be miscible or immiscible in water and can undergo multiple solvation interactions with various types of molecules. ILs are most often said to be 'tunable' or 'tailored'.

The analytical of applications of ILs have covered many areas of chemistry and even biochemistry. Several selected applications of ILs are as follows.

I. Ionic liquids as stationary phases for gas chromatography (GC)
II. Ionic liquids in mass spectrometry
III. Ionic liquids as additives for capillary electrophoresis (CE)
IV. Ionic liquids in liquid chromatography (LC)
V. Ionic liquids as solvents for extractions

2.1.1 Ionic liquids as stationary phases for GC

ILs possess many favorable properties such as high thermal stability, high viscosity, non-volatility and non-flammability, which makes possible their use as GC stationary phases. Moreover, they are: (1) capable of providing highly selective, high-efficiency separations; (2) easy to immobilize on the capillary wall; and (3) able to undergo multiple solvation interactions with molecules. These properties make them excellent candidates for GC stationary phases.[35]

The first application of molten metals stearates as gas chromatographic stationary phase was reported by Barber *et al*.[47] Poole and co-workers have also published a series of papers on using ionic liquids as molten salts as GC stationary phases.[48-52] The initial alkylammonium and alkylphosphonium based ionic liquid stationary phases had limitations such as thermal instability, relatively narrow liquid ranges, and poor wetability toward the surface of fused silica. Later novel ionic liquids containing alkylimidazolium and alkylpyridinium cations possessed improved physicochemical properties and were more suitable for GC stationary phases.[27, 30] Armstrong *et al*. showed that RTILs possess "dual nature" properties. They separate non-polar compound such as linear alkanes as if they are a non-polar stationary phase and separate a polar compounds with somewhat acidic or basic functional group as if they are polar stationary phase.[27]

RTILs were also examined as solvents for headspace GC and it was shown that all analytes could be determined with detection and quantitation limit in the

low-parts-per-million range.[53] This work demonstrated that ILs had remarkable potential for the quantitation of compounds with low vapor pressure, an area in which traditional headspace GC is limited. IL-based GC stationary phases also were used to determine activity coefficients at infinite dilution for several solutes in the ILs.[54, 55, 56]

2.1.2. Ionic liquids in mass spectrometry.

As ILs can produce a much more homogeneous sample solution and have a greater vacuum stability than most solid MALDI matrices, the use of ILs as matrices could enhance reproducibility and sensitivity. In one of the first reports of its kind, application of RTILs as matrices for matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) was established by Armstrong's group.[23] Many RTIL-based matrices tested showed excellent solubilizing properties and vacuum stability compared to other frequently employed solid and liquid matrices. ILs were also used as matrices in MALDI time-of-flight mass spectrometry to determine DNA oligomer masses directly.[33] These studies demonstrated that some ILs do produce greater peak intensities and lower limits of detection. In another application, IL-matrices were used for analysis of phospholipids by MALDI-MS to produce higher signal intensities, smaller spot sizes, improved spot homogeneity, better signal reproducibility, and better detection limits than with crystalline matrices.[57]

2.1.3. Ionic liquids as additives for CE

Vaher *et al.* first reported use of RTIL-buffer electrolytes in non-aqueous capillary electrophoresis for separation of water-insoluble dyes in acetonitrile that were previously not accessible using conventional CE methodology.[58] The miscibility of ILs with acetonitrile makes it easy to use them for adjustment of analyte mobility and separation in non-aqueous CE. It was also reported that anionic part of the RTIL changed the general electrophoretic mobility of the system. Stalcup *et al*. reported use of 1-alkyl-3-methylimidazolium as running electrolytes in CE to resolved phenolic compound found in grape seed extracts.[59] The same ionic liquid were also used as running buffer electrolytes to separate basic proteins such as, lysozyme, cytochrome c, trypsinogen, and α-chymotypsinogen A.[60] In this study baseline separation, high efficiencies, and symmetrical peaks were obtained during separation of the four proteins.

ILs were also used in order to reverse the electroosmotic (EOF) flow of the silica capillary, in which they were covalently bound to the internal capillary surface by static coating. This approach was applied to separate positively charged drugs, DNA, and metal ions.[61, 62, 63] They also reported that this covalently IL-coated capillary could be used for at least 80 h with relatively stable EOF.

2.1.4. Ionic liquids in LC

Imidazolium based RTILs were used as mobile phase additives in HPLC to separate amines.[64] It was reported that the structure of the IL, especially the length

of the alkyl chain, and the concentration in the mobile phase influenced selectivity and efficiency, respectively. In another application, chromatographic behavior of ephedrine on a C18 column was investigated with different concentrations of BMIM-BF_4 as the eluent.[65] Addition of an IL resulted in decreased band tailing, improved resolution, and reduced band broadening. In another application of BMIM-PF_6 as a novel solvent in countercurrent chromatography (CCC) was reviewed by Berthod and Carda-Broach.[66] They investigated the partitioning of 38 aromatic derivatives possessing acidic, basic, or neutral moieties between BMIM-PF_6 and water. They found that the viscosity of pure RTILs is too high for direct use as a liquid phase in CCC and addition of third solvent was needed to decrease viscosity. In a later investigation the same authors utilized a different concentration of water:acetonitrile:BMIM-PF_6 biphasic liquid system in CCC and again demonstrated the drawback of using RTIL was its high viscosity.[67]

2.1.5 Ionic liquids as solvent for extractions

In liquid-liquid extraction, two immiscible or partially miscible solvents are used. RTILs possess the unique property that they can be custom synthesized to be either water- or hexane-immiscible, making them useful for liquid-liquid extraction. Miscibility of ionic liquids in water can be altered by changing anions. Dai *et al.* first reported a very highly efficient procedure for extraction of Sr^{2+} from aqueous phase by dissolving dicyclohexyl-18-crown-6 in 1-alkyl-3-methylimidazolium hexafluorophosphate.[68] In the presence of crown ethers in

RTIL-based liquid-liquid separations, the resulting metal ion partitioning depended on the hydrophobicity of the crown ether and the composition of the aqueous phase. Later, Visser *et al*. studied extraction of Na^+, Cs^+, and Sr^{2+} from aqueous solution by dissolving crown ether in ionic liquid[69], [70] and extraction of Hg^{2+} and Cd^{2+} from water by task-specific ILs.[71]

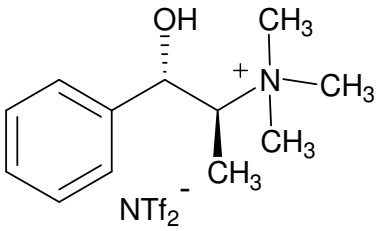
Fadeev and Meagher reported the potential of RTILs as extractants in the recovery of butyl alcohol from fermentation broth.[72] Abraham *et al.* showed that an increase in solute hydrogen bond basicity and solute volume led to a decrease and increase in log *P,* respectively.[73] The IL 1-octyl-3-methylimidazolium PF_6 was used as a disposable liquid absorbent for solid-phase microextraction (SPME) studies of xylenes, benzene, ethyl benzene, and toluene from paints[74] IL-SPME fibers provided a much lower cost per determination, similar reproducibility, and no detectable carryover compare to commercially available SPME fibers. Brennecke *et al*. have shown that liquid-liquid extraction with water resulted in the loss of some ionic liquid, whereas a variety of solutes could be extracted from ionic liquids with supercritical carbon dioxide without cross contamination.[75]

2.2 Testing of Different Chiral Ionic Liquids as Stationary Phases for GC Enantiomeric Separations.

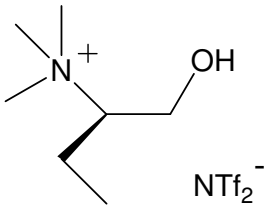
2.2.1 Introduction

Room-temperature ionic liquids are a class of non-molecular ionic solvents with low melting points. Their properties have the potential to be especially useful

as stationary phases in gas-liquid chromatography. The initial alkylammonium and alkylphosphonium based ionic liquids stationary phases had limitations such as thermal instability, relatively narrow liquid ranges, and poor ability to wet the surface of fused silica. Later novel ionic liquids containing alkylimidazolium and alkylpyridinium cations possessed improved properties and were more suitable for GC stationary phases. Even though there have been many publications on ionic liquids, only few examples of chiral ionic liquids have been reported. Howarth and co-workers described the use of the chiral imidazolium cation in Diels-Alder reactions.[76] Seddon *et al.* also investigated Diels-Alder reactions in ionic liquids having *N*-butyl-*N*-methylimidazolium cation with lactate as a counter anion.[77] These lactate-based ILs are relatively inexpensive because its anion was readily available as sodium salts. Wassercheid and co-workers synthesized three different groups of chiral ionic liquids and they have studied the positive diastereomeric interactions between racemic substrates and chiral ionic liquids by NMR.[78] Bao *et al.* reported the first synthesis of chiral imidazolium ionic liquids derived from natural amino acids.[79] Later, Thanh *et al.* designed an efficient method for the preparation of ephedrinium-based chiral ionic liquids under microwave activation.[80] The application of chiral ionic liquids as stationary phases in GC was first reported by Armstrong *et al.* [28, 81]



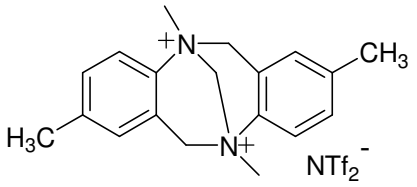
(a)



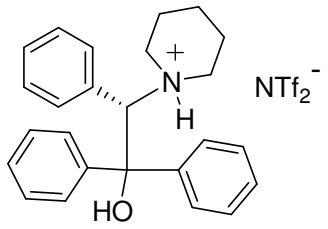
(b)

Figure 2.1 Chiral ionic liquids. (a) and (b) are NTf_2 salts of chiral cations

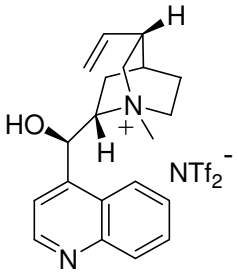
Separation of enantiomers is a very important area of study in both research and industry, mostly in the pharmaceutical industry. The search for novel chiral selectors is an open field for researchers all over the world. In GC, chiral separations using chiral ionic liquids can be carried out in two ways, (1) by dissolving the chiral selector in an achiral ionic liquid[28] or (2) by directly using enantiomeric ionic liquids as stationary phases.[81, 82] The first method was reported in 1999 by Armstrong *et al.* where permethylated-β-cyclodextrin (BPM) and dimethylated-β-cyclodextrin (BDM) were dissolved in RTILs and used as stationary phases for GC enantiomeric separations. Armstrong *et al.* (2004) then reported for the first time enantiomeric separations using a chiral IL stationary phase in gas chromatography. The compounds that have been separated include alcohols, diols, sulfoxides, epoxides and acetylated amines. The molecular structure of this chiral IL is given in **Figure 2.1(a)**. The other ionic liquid that has given GC-chiral separations reported which has a similar functionality is shown in **Figure 2.1(b)**.



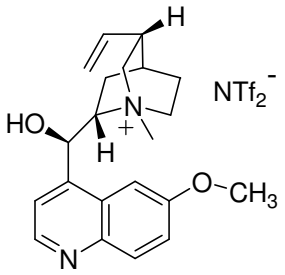
(a)



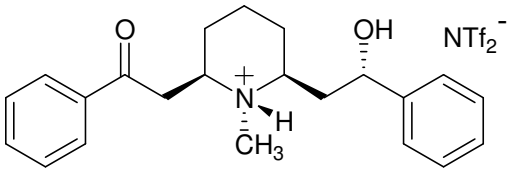
(b)



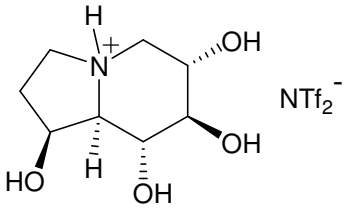
(c)



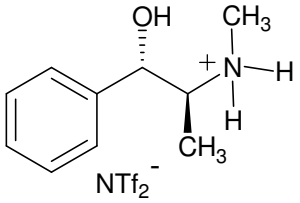
(d)



(e)



(f)



(g)

Figure 2.2 Chiral ionic liquids. (a), (b), (c), (d), (e), (f) and (g) are NTf_2 salts of chiral cations

2.2.2 Results and Discussion

Seven chiral ionic liquids shown in **Figure 2.2 (a), (b), (c), (d), (e), (f)** and **(g)** were tested for enantiomeric GC-separations. These compounds were synthesized by other group members. No successful enantiomeric separations were observed with any of the ionic liquids tested. Compounds that have been tried to separate using these ionic liquid chiral selectors include alcohols, diols, sulfoxides, epoxides, and acetylated amine.

The ionic liquid shown in **Figure 2.2 (a)** is based on Troger's base, which exhibits chirality due to the presence of two bridgehead stereogenic nitrogen atoms in its structure. The molecule can be considered a molecular tweezer because the bicyclic skeleton forces the molecule in a locked conformation with the aromatic rings in close proximity. The melting point of this ionic liquid was above room temperature and vinyl silicone (OV-1701) was used as a solubilizing medium. The chiral-IL (**Figure 2.2 (e)**) was synthesized from lobeline. Lobeline was arbitrarily selected to make a chiral-IL expecting chiral separations as a GC-stationary phase.

Chiral ionic liquid (**Figure 2.2 (g)**) having similar structures to N,N-dimethyl ephedrinium having one less methyl group (Figure-D) was tested to check whether it would give the same types of separations or better ones. But the separations observed were not like the former. So it was confirmed that presence of three methyl groups on the N-atom matters for enantiomeric separations.

In conclusion we have tested several new chiral ionic liquids for chiral separations but as of yet our attempts have failed to produce any separation. Further studies are needed to find an adequate ionic liquid chiral selector as a GC stationary phase.

2.3 Evaluating the Use of Tricationic Reagents for the Detection Of Divalent Anions in the Positive Mode by ESI-MS

2.3.1 Introduction

Mass spectrometry is growing in popularity as a universal detector for anions and it can be used alone[83, 84] or in combination with a separation method.[85-88] The negative ion mode is the most common way of detecting anions using ESI-MS. However, operating in negative ion mode with standard solvents used in chromatography (primarily water and methanol) can lead to corona discharge, poor spray stability, and a propensity for arcing.[89, 90] These effects can be suppressed by using electron scavenging gases[91] or halogenated solvents.[92-94] The substitution of isopropanol or butanol[95] for methanol has also been recommended for operation in the negative ion mode. However, these solvents are less commonly used in liquid chromatography (LC) methods involving water and result in higher operating pressures. Recently, we successfully used dicationic reagents to detect singly charged anions in the positive mode by ESI-MS.[96, 97] The dicationic reagent paired with the anion in the solution phase and enabled detection in the positive mode using common LC solvents. Additional benefits include: (a) moving anions to a higher mass range out of the low mass region dominated by chemical noise; (b)

increasing sensitivity for anions with masses near the low mass cutoff of quadrupole instruments (e.g. traps); and (c) help discriminate against interferences with the same mass to charge ratio. This approach has also been used with ion chromatography to determine the levels of perchlorate anions in human urine,[98] milk,[99] and seawater.[100] The success of dicationic reagents to detect singly charged anions in the positive mode has encouraged us to use a similar approach for the detection of doubly charged anions. The mass spectrometry study was done by other group members.

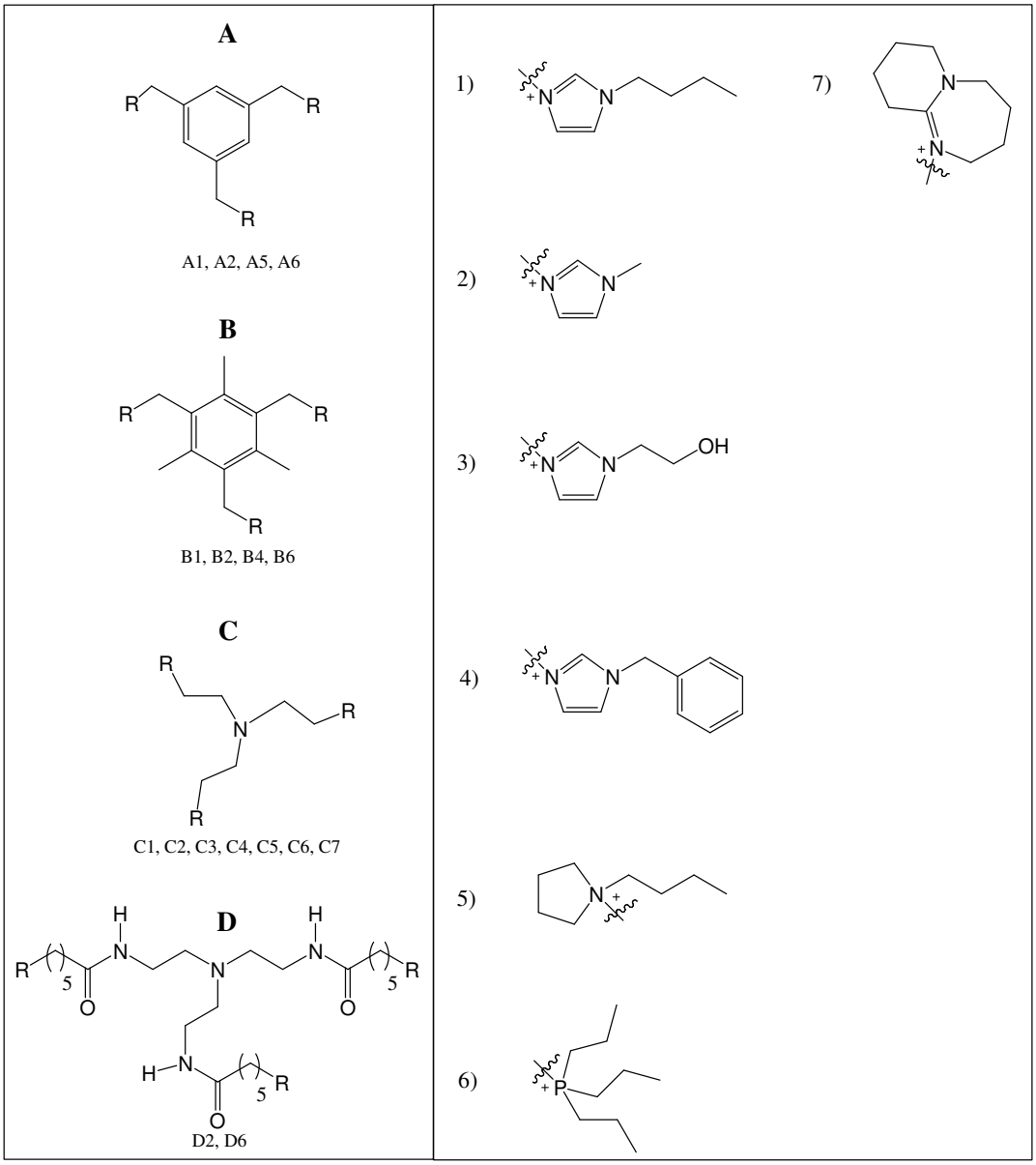


Figure 2.3 Structure and numbering system for the 17 tricationic reagents synthesized and evaluated in this study

2.3.2 Results and Discussion

Eleven divalent anions were used to evaluate seventeen different tricationic reagents (**Figure 2.3**). Trications A6 and B1 provide good sensitivity for a broad

range of the representative divalent anions. A6 (1,3,5-tris-(tripropylphosphonium) methylbenzene trifluoride) performs the best overall since it ranks as one of the top three trication reagents for all of the anions except sulfate and oxalate. Even then, it ranks as the fifth best tricationic reagent for detecting oxalate. Trication B1 (1,3,5-tris-(1-(3-butylimidazolium)) methyl-2,4,6-trimethylbenzene trifluoride) also does well, but is in the top three less consistently than A6. Structural features of the tricationic reagents including the terminal charged groups and the core structure influenced the detection limits for the doubly charged anions. The nature of the optimal charged groups for the tricationic reagents were often different from that found in a previous study for dicationic reagents.

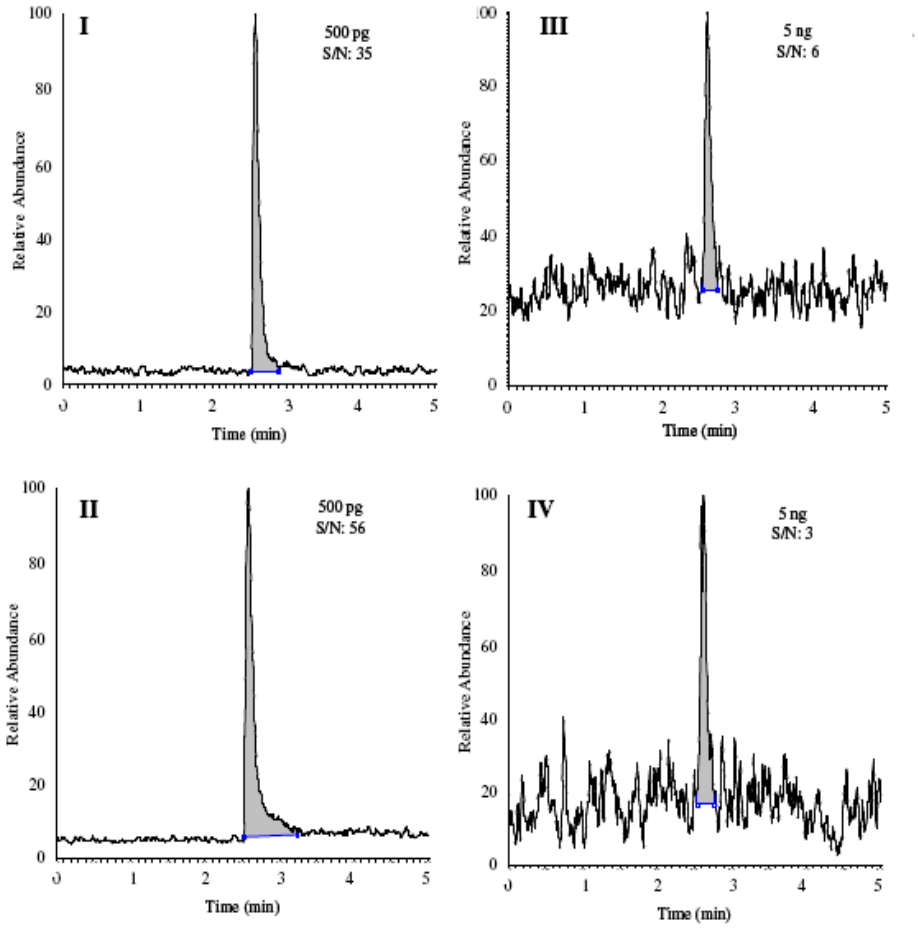


Figure 2.4 A comparison of positive (I,II) and negative modes (III. IV) for hexachloroplatinate (I, II) and o-benzenedisulfonate (II, IV). Tricationic reagents A6 (I) and B1 (II) in water were introduced into the carrier flow after anion injection in positive ion mode while only water was used in negative ion mode (III, IV).

In both cases, using a tricationic reagent in the positive mode produced superior signal to noise ratios even though ten times less sample was injected. By detecting divalent anions in the positive ionization mode as a complex, the sensitivity for the two anions increases by almost two order of magnitude. This

demonstrates the ability of tricationic reagents to improve the sensitivity of mass spectrometry for divalent anions.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 Instrumental Information

Melting Point:

DSC measurements were carried out on a Perkin Elmer Diamond DSC calibrated using an indium primary standard, with solid-solid transitions for cyclohexane and ethyl benzene as supplementary low temperature standards. Ionic liquid samples were sealed in aluminium pans and an empty aluminium pan was used as reference. The measurements were carried out in the temperature range -120 °C to a predetermined temperature. All DSC data presented were measured on 7-15 mg samples then heated and cooled at scan rate of 5 °C min^{-1} under a flow of nitrogen. Melting points could not be easily determined for all compounds. For solid compounds, the melting points were verified using a capillary melting point apparatus.

Density:

The densities of the ionic liquids were determined at 23 °C with Kimble Glass Specific Gravity Pycnometer (Vineland, NJ). The pycnometer also called specific gravity bottle, is traditionally a glass flask with a close-fitting ground glass

stopper with a capillary tube (fine hole) through it, so that a given volume can be accurately obtained. This enables the density of a fluid to be measured accurately, by reference to an appropriate working fluid such as water or mercury, using an analytical balance.

Refractive Index:

The refractive index of a medium is the ratio of speed of light in a vacuum to its speed in the medium, and is the square root of the relative permittivity of the medium at that frequency. Refractive index measurements were conducted at 23 °C using a Bausch & Lomb Abbe-3L refractometer.

Viscosity:

Kinematic viscosities were determined at 30 °C using Cannon-Manning Semi-Micro capillary viscometer (State College, PA).

Thermal stability:

Thermogravimetric analysis (TGA) measurements were made using a TGA 2050 (TA Instruments Inc., Thermal Analysis & Rheology, New Castle, DE, USA). Samples (ca. 60 mg) were placed in the platinum pans, and heated at 10 °C min^{-1} from room temperature to 600°C in a dynamic nitrogen atmosphere. The decomposition temperature were determined at 1% weight loss was observed from

the sample which corresponds to 99% w value and 5% weight loss from the sample which corresponds to 95% w value.

Miscibility:

All compounds synthesized in this study were tested for miscibility with water and heptane. This was simply done by placing different volumes/amounts of the compound of the interest in the respective solvent. Compounds were classified miscible if they were observed to completely dissolve in resulting compositions with test solvents: 25%, 50%, 75% (V/V) at room temperature.

Mass spectrometry:

ESI-MS analysis was carried out on a LXQ (Thermo Fisher Scientific San Jose, CA, USA) linear ion trap. A Surveyor MS pump (Thermo Fisher Scientific) with a vacuum degasser provided the carrier flow (67% MeOH/ 33%Water) at 300 μL/min. The tricationic reagent was introduced to carrier flow using a Y-type tee and a Shimadzu 6A LC pump operated at 100 μL/min was used for this purpose. For analysis in negative mode water replaced the aqueous tricationic reagent solution. The test anions were introduced into the carrier solvent using a sixport injection valve located between the Surveyor MS pump and the Y-type tee. ESI ionization conditions for positive mode were as follows: spray voltage: 3 kV; capillary temperature: 350ºC; capillary voltage: 11 V; tube lens: 105 V; Sheath gas 37 arbitrary units (AU); Auxiliary gas: 6 AU. Optimized conditions for detecting

fluorophosphate with cation D6 were spray voltage: 5 kV; capillary temperature: 250ºC; capillary voltage: 28 V; tube lens: 95 V; Sheath gas 37 arbitrary units (AU); Auxiliary gas: 6 AU. In negative mode the conditions were: spray voltage: 4.7 kV; capillary temperature: 350ºC; capillary voltage: -21 V; tube lens: -96 V; Sheath gas 37 arbitrary units (AU); Auxiliary gas: 6 AU. Detection limits (defined as S/N=3) for the eleven anions were determined by five replicate injections. The mass spectrometer was operated in single ion monitoring mode for the determination of all limits of detection (LODs).

Gas chromatography:

A Hewlett-Packed model 6890N gas chromatograph was used for all GC-analyses performed. Helium gas was used as the mobile phase with a flow rate of 1.0 mL/min. Split injection and flame ionization detection were utilized with injector and detector temperatures of 250 ^{o}C.

Chiral ionic liquids and coated on untreated fused-silica capillary columns having 250 μm internal diameter. Coating is carried out using the static method which is frequently practiced method for coating GC-columns. Static method involves first dissolving the IL in a desired solvent to give 0.25% (w/v). The column is then kept in an insulated water bath at 40 ^{o}C. IL-solution (e.g. IL dissolved in CH_2Cl_2) is injected from one end to completely fill the capillary. Then the capillary is sealed from one end and from the other end the solvent is removed

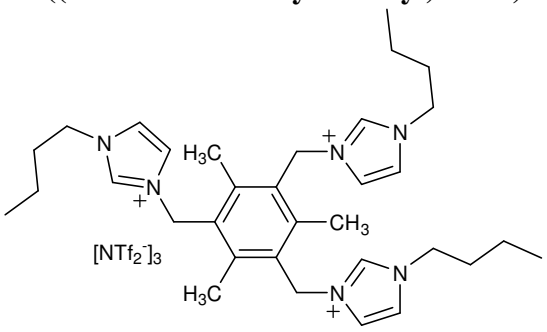
using a vacuum pump. The columns are coated with a 0.15 μm layer of thickness. Coated columns are flushed with dry helium gas and conditioned overnight from 35 to 110 ^{o}C at 1 ^{o}C/min. Column tested by naphthalene at 100 ^{o}C. Columns having efficiency above 2200 plates/m are generally tested for chiral separations.

General Procedure:

Commercial reagents were used as received, unless otherwise noted. All ILs synthesized were characterized using ^{1}H NMR spectrometry and mass spectrometry. The NMR spectra were recorded in (methyl sulfoxide)-d6 (unless otherwise stated) on JEOL ECX spectrometers (300 and 500 MHz) at ambient temperature. The coupling constants, J, are reported in Hz. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as m (multiplet) or br (broad).

3.2 Synthesis Information

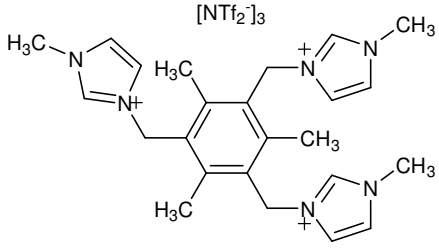
1. ILA1-NTf2:1,3,5-{tris(3-n-butylimidazolium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide)



Synthesis of compound **A1** involved refluxing 8.0 g (0.020 mol) of 1,3,5-tris(bromomethyl)mesitylene with 13.0 ml (0.100 mol) of 1-butylimidazole in 150.0 ml isopropanol for 6 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. In metathesis process 1 molar equivalents of bromide salt dissolved in water and treated with 4.5 molar equivalents of lithium NTf_2^-. The resulting solution was stirred at room temperature for 24 hrs. After that, dichloromethane was added to the solution to dissolve the tricationic NTf_2^- salt that has phase separated from the water. The lithium bromide and excess lithium NTf_2^- were removed from the dichloromethane phase with successive washing with water. Removal of dichloromethane through rotoevaportaiton followed by vacuum

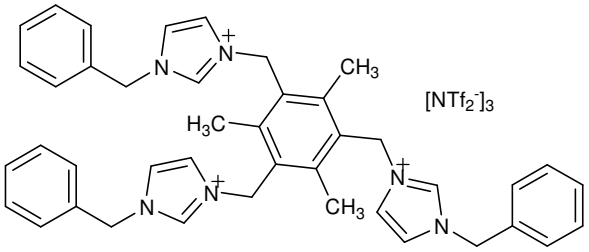
drying over phosphorous pentoxide at 80 ^{0}C for 24hrs resulted in the pure tricationic ILs with NTf_2^- counter ions. ^{1}H-NMR (300 MHz): δ (ppm) = 9.36 (s, 3H), 7.84 (t, 3H, *J* = 1.7 Hz), 7.80 (t, 3H, *J* = 1.8 Hz), 5.52 (s, 6H), 4.21 (t, 6H, *J* = 7.1 Hz), 2.22 (s, 9H), 1.71 (p, 6H, *J* = 7.5 Hz), 1.17 (sextet, 6H, *J* = 7.4 Hz), 0.82 (t, 9H, *J* = 7.4 Hz). ESI-MS (*m/z*): 177.18 (M^{3+}), found 177.18.

2. ILA2-NTf2:1,3,5-{tris(3-n-methylimidazolium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide)



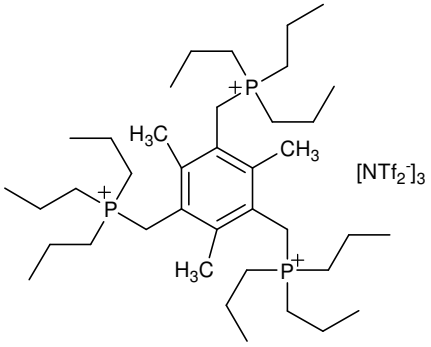
Compound **A2** synthesized by refluxing 5.0 g (0.013 mol) of 1,3,5-tris(bromomethyl)mesitylene with 5.0 ml (0.063 mol) of 1-methylimidazole in 150.0 ml isopropanol for 6 days. After removal of isopropanol, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (300 MHz): δ (ppm) = 8.84 (s, 3H), 7.80 (t, 3H, *J* = 1.7 Hz), 7.67 (t, 3H, *J* = 1.7 Hz), 5.59 (s, 6H), 3.87 (s, 9H), 2.36 (s, 9H). ESI-MS (*m/z*): 135.09 (M^{3+}), found 135.09.

3. ILA3-NTf2:1,3,5-{tris(3-n-benzylimidazolium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide)



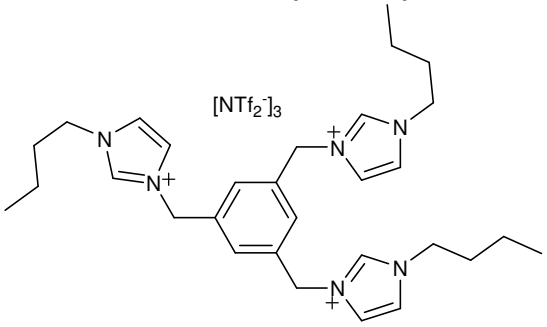
Compound **A3** synthesized by refluxing 6.0 g (0.015 mol) of 1,3,5-tris(bromomethyl)mesitylene with 12.0 g (0.075 mol) of 1- benzylimidazole in 125.0 ml toluene for 6 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (500 MHz): δ (ppm) = 9.62 (s, 3H), 7.92 (t, 3H, J = 1.7 Hz), 7.87 (t, 3H, J = 1.7 Hz), 7.49 (q, 6H, J = 3.5 Hz), 7.43 (t, 9H, J = 3.5 Hz), 5.65 (s, 6H), 5.56 (s, 6H), 2.34 (s, 9H). ESI-MS (*m/z*): 211.12 (M^{3+}), found 211.12.

4. ILA4-NTf2:1,3,5-{tris(tripropylphosphonium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide)



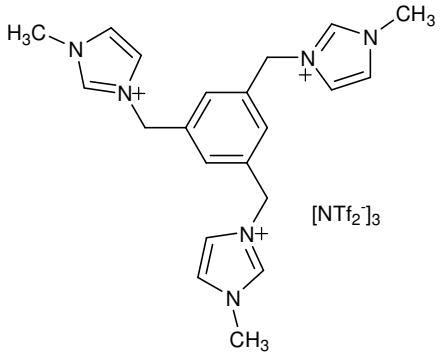
Synthesis of compound **A5** involve refluxing 5.0 g (0.013 mol) of 1,3,5-tris(bromomethyl)mesitylene with 12.5 ml (0.063 mol) of tripropylphosphine in 150.0 ml isopropanol for 7 days. After removing isopropanol, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (500 MHz): δ (ppm) = 3.98 (d, 6H, J = 15.4 Hz), 2.39 (s, 9H), 2.27 (m, 18H), 1.50 (sextet, 18H, J = 7.5 Hz), 1.00 (m, 27H). ESI-MS (*m/z*): 213.32 (M^{3+}), found 213.32.

5. ILB1-NTf2:1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide)



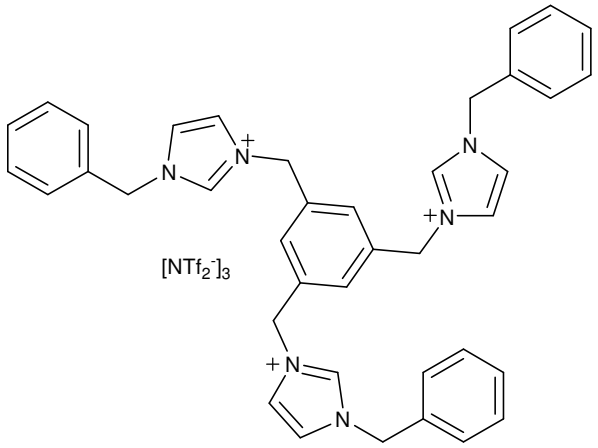
Compound **B1** was synthesized by refluxing 10.0 g (0.028 mol) of 1,3,5-tris(bromomethyl)benzene with 16.5 ml (0.126 mol) of 1-butylimidazole in 150.0 ml isopropanol for 7 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (300 MHz): δ (ppm) = 9.50 (s, 3H), 7.83 (t, 6H, J = 1.7 Hz), 7.54 (s, 3H), 5.44 (s, 6H), 4.18 (t, 6H, J = 7.2 Hz), 1.76 (p, 6H, J = 7.4 Hz), 1.24 (sextet, 6H, J = 7.6 Hz), 0.87 (t, 9H, J = 7.2 Hz). ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

6. ILB2-NTf2:1,3,5-{tris(3-n-methylimidazolium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide)



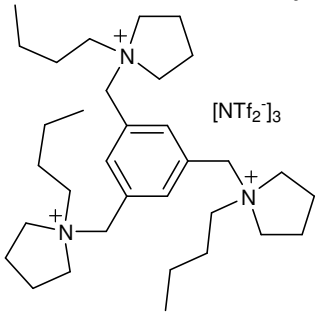
Synthesis of compound **B2** carried out by refluxing 8.0 g (0.022 mol) of 1,3,5-tris(bromomethyl)benzene with 8.0 ml (0.101 mol) of 1-methylimidazole in 150.0 ml isopropanol for 6 days. The bromide salt was purified by first extraction with ether and then with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (500 MHz): δ (ppm) = 9.40 (s, 3H), 7.83 (t, 3H, J = 1.8 Hz), 7.76 (t, 3H, J = 1.7 Hz) 5.47 (s, 6H), 3.90 (s, 9H). ESI-MS (*m/z*): 121.08 (M^{3+}), found 121.08.

7. ILB3-NTf2:1,3,5-{tris(3-n-benzylimidazolium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide)



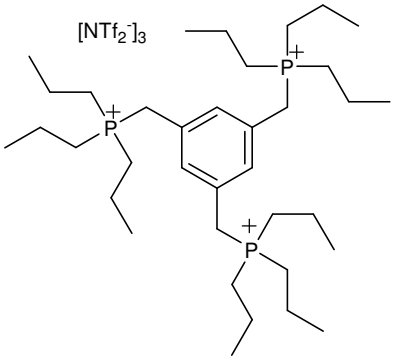
Compound **B3** was synthesized by refluxing 5.0 g (0.014 mol) of 1,3,5-tris(bromomethyl)benzene with 10.0 g (0.063 mol) of 1-benzylimidazole in 150.0 ml isopropanol for 6 days. After removal of isopropanol, the bromide salt was dissolved in water and purified by extraction with ethyl acetate and ether. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (300 MHz): δ (ppm) = 9.33 (d, 3H, J = 11.6 Hz), 7.79 (m, 3H), 7.69 (m, 3H), 7.39 (m, 18H), 3.90 (s, 9H). ESI-MS (*m/z*): 197.26 (M^{3+}), found 197.26.

8. ILB4-NTf2:1,3,5-{tris(butypyrrolidinium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide)



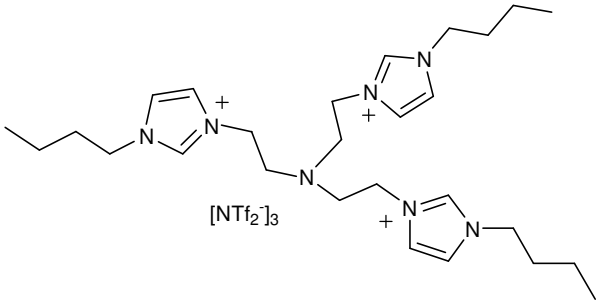
Compound **B4** was synthesized by refluxing 6.5 g (0.018 mol) of 1,3,5-tris(bromomethyl)benzene with 13.0 ml (0.082 mol) of 1-butylpyrrolidine in 150.0 ml isopropanol for 4 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (500 MHz): δ (ppm) = 7.92 (s, 3H), 4.65 (s, 6H), 3.63 (m, 6H), 3.56 (m, 6H), 3.24 (t, 6H, J = 8.4 Hz), 2.11 (m, 12H), 1.85 (m, 6H), 1.30 (sextet, 6H, J = 7.4 Hz). ESI-MS (*m/z*): 166.28 (M^{3+}), found 166.28.

9. ILB5-NTf2:1,3,5-{tris(tripropylphosphonium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide)



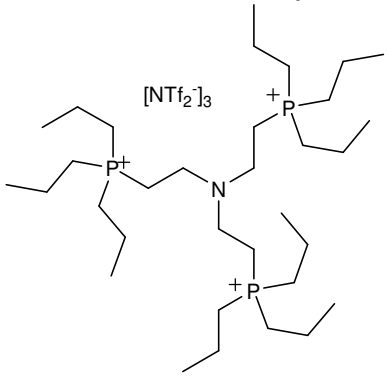
Compound **B5** was synthesized by refluxing 3.0 g (0.011 mol) of 1,3,5-tris(bromomethyl)benzene with 10.0 ml (0.051 mol) of tripropylphosphine in 150.0 ml isopropanol for 7 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum. Final products were synthesized through a metathesis reaction of the bromide salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (500 MHz): δ (ppm) = 7.33 (d, 3H, *J* = 2.1 Hz), 3.93 (d, 6H, *J* = 15.8 Hz), 2.29 (m, 18H), 1.56 (d, 6H, *J* = 15.8 Hz), 2.29 (m, 18H), 1.56 (septet, 18H, *J* = 7.8 Hz), 1.03 (t, 27H, *J* = 7.2 Hz). ESI-MS (*m/z*): 199.16 (M^{3+}), found 199.16.

10. ILC1-NTf2:Tris(2-(3-n-butylimidazolium)ethyl)amine tris((bistrifluoromethylsulfonyl)imide)



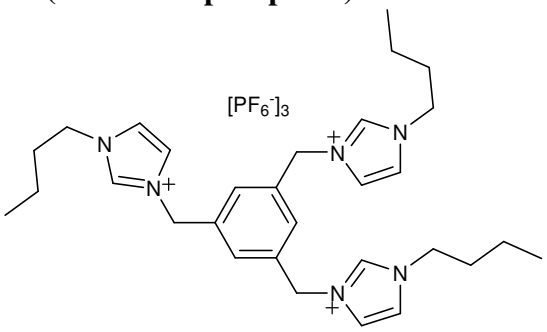
Compound **C1**, was synthesized by refluxing 1 molar equivalent of Tris(2-chloroethyl)amine hydrochloride (8.0 g, 0.033 mol) in 150.0 ml isopropanol with 6 molar equivalents of 1-butylimidazole (26.2 ml, 0.199 mol). Rotoevaporation of the solvent yielded the crude hydrochloride salt. This was then dissolved in water with 2 molar equivalents of NaOH. Sodium hydroxide is used to neutralize the hydrochloride salt. The excess starting material was extracted with ethyl acetate. Final products were synthesized through a metathesis reaction of the chloride salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (300 MHz): δ (ppm) = 9.02 (s, 3H), 7.75 (t, 3H, J = 1.5 Hz), 7.60 (t, 3H, J = 1.7 Hz), 4.15 (q, 12H, J = 6.5 Hz), 2.94 (t, 6H, J = 6.4 Hz), 1.73 (p, 6H, J = 7.4 Hz), 1.22 (sextet, 6H, J = 7.4 Hz), 0.88 (t, 9H, J = 7.2 Hz). ESI-MS (*m/z*): 156.80 (M^{3+}), found 156.80.

11. ILC5-NTf2:Tris(2-(tripropylphosphoniummethyl)ethyl)amine tris((bistrifluoromethylsulfonyl)imide)



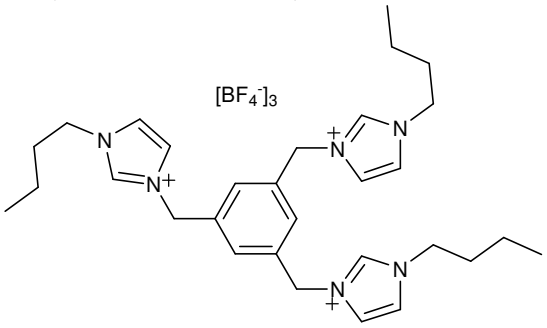
Compound **C5**, was synthesized by refluxing 1 molar equivalent of tris(2-chloroethyl)amine hydrochloride (6.0 g, 0.025 mol) in 150.0 ml isopropanol with 6 molar equivalents of tripropylphosphine (29.9 ml, 0.149 mol). Rotoevaporation of the solvent yielded the crude hydrochloride salt. This was then dissolved in water with 2 molar equivalents of NaOH. The excess starting material was extracted with ethyl acetate. The final products was synthesized through a metathesis reaction of the chloride salts with lithium bistrifluoromethanesulfonimidate. ^{1}H-NMR (300 MHz): δ (ppm) = 2.74 (q, 6H, J = 7.9 Hz), 2.31 (p, 6H, J = 7.2 Hz), 2.17 (m, 18H), 1.52 (m, 18H), 1.02 (tt, 27H, J = 7.2 Hz). ESI-MS (*m/z*): 192.84 (M^{3+}), found 192.84.

12. ILB1-PF_6:1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(hexafluorophosphate)



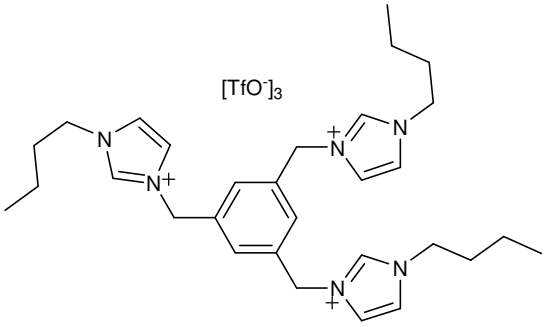
The PF_6^- salt for compound B1 was synthesized directly from its bromide salt. In this method 1 molar equivalent of bromide salt was first dissolved in water and 4 molar equivalents of hexafluorophosphoric acid added slowly to it with constant stirring. Hexafluorophosphoric acid is toxic and corrosive and must be handled with care. The remaining ionic liquid was washed with water until all washings were no longer acidic and no trace of silver bromide was observed using silver nitrate. The solid compound was filtered under vacuum and allowed to dry in an oven and then placed under a P_2O_5 vacuum. ^{1}H-NMR (300 MHz): δ (ppm) = 9.19 (s, 3H), 7.80 (t, 3H, *J* = 1.7 Hz), 7.68 (t, 3H, *J* = 1.7 Hz), 7.39 (s, 3H), 5.39 (s, 6H), 4.14 (t, 6H, *J* = 7.3 Hz), 1.75 (p, 6H, *J* = 7.4 Hz), 1.24 (sextet, 6H, *J* = 7.6 Hz), 0.88 (t, 9H, *J* = 7.4 Hz). ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

13. ILB1-BF_4:1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(tetrafluoroborate)



The BF_4^- salt for compound **B1** was synthesized directly from its bromide salt. Bromide salt for compound **A1** first dissolved in water and passed through anion exchange resin - Amberlite IRA-400(Cl) saturated with OH^- anion to obtain the hydroxide salt of the trication. The eluent was then titrated with tetrafluoroboric acid until pH 7. Evaporation of water under vacuum and drying under phosphorous pentoxide at 80 ^oC yield the pure TIL2 as the BF_4^- salt. ^{1}H-NMR (500 MHz): δ (ppm) = 9.20 (s, 3H), 7.43 (t, 3H, J = 1.8 Hz), 7.71 (t, 3H, J = 1.7 Hz), 7.42 (s, 3H), 5.42 (s, 6H), 4.15 (t, 6H, J = 7.2 Hz), 1.78 (p, 6H, J = 7.4 Hz), 1.24 (sextet, 6H, J = 7.4 Hz), 0.91 (t, 9H, J = 7.4 Hz). ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

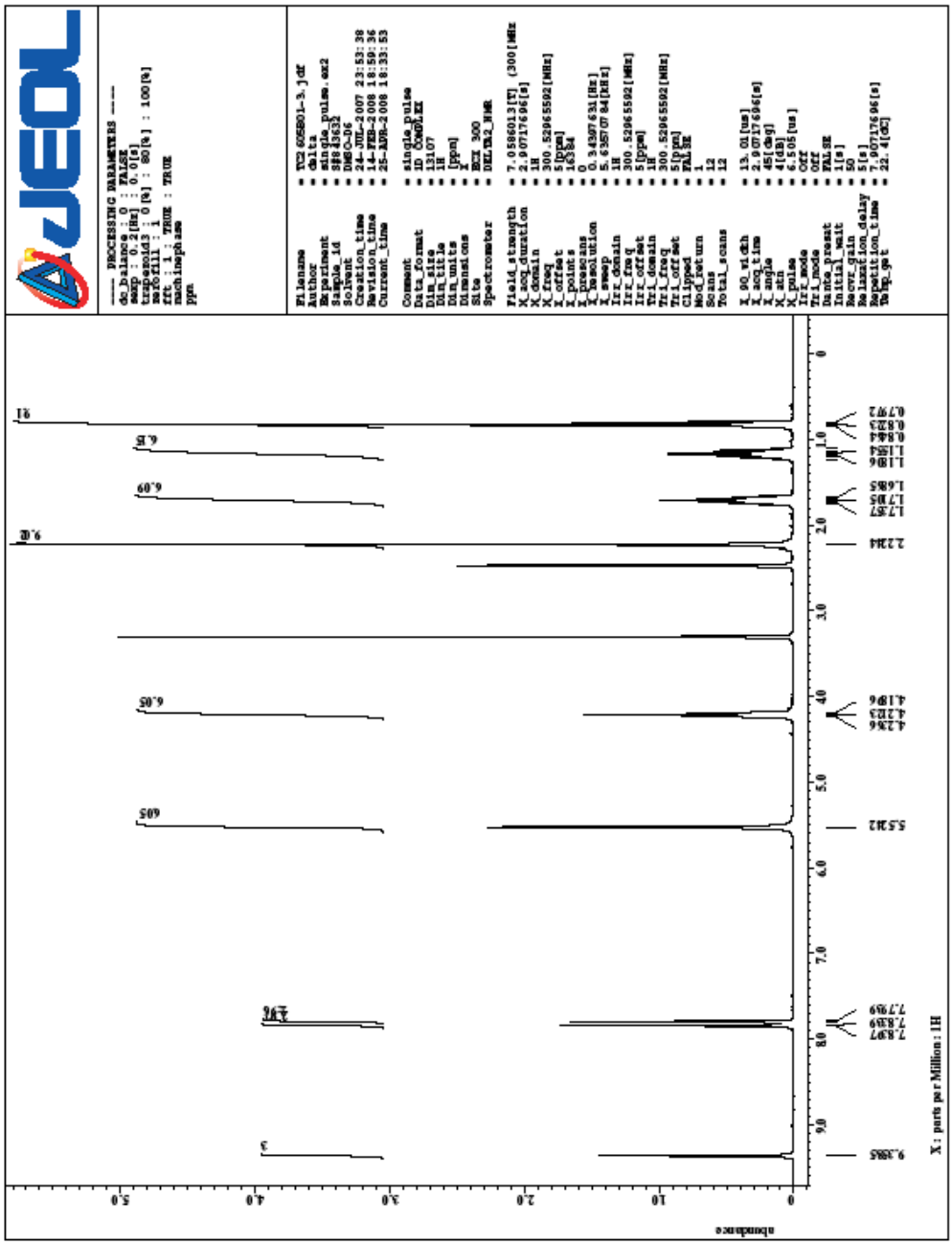
14. ILB1-TfO:1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(trifluoromethanesulfonate)

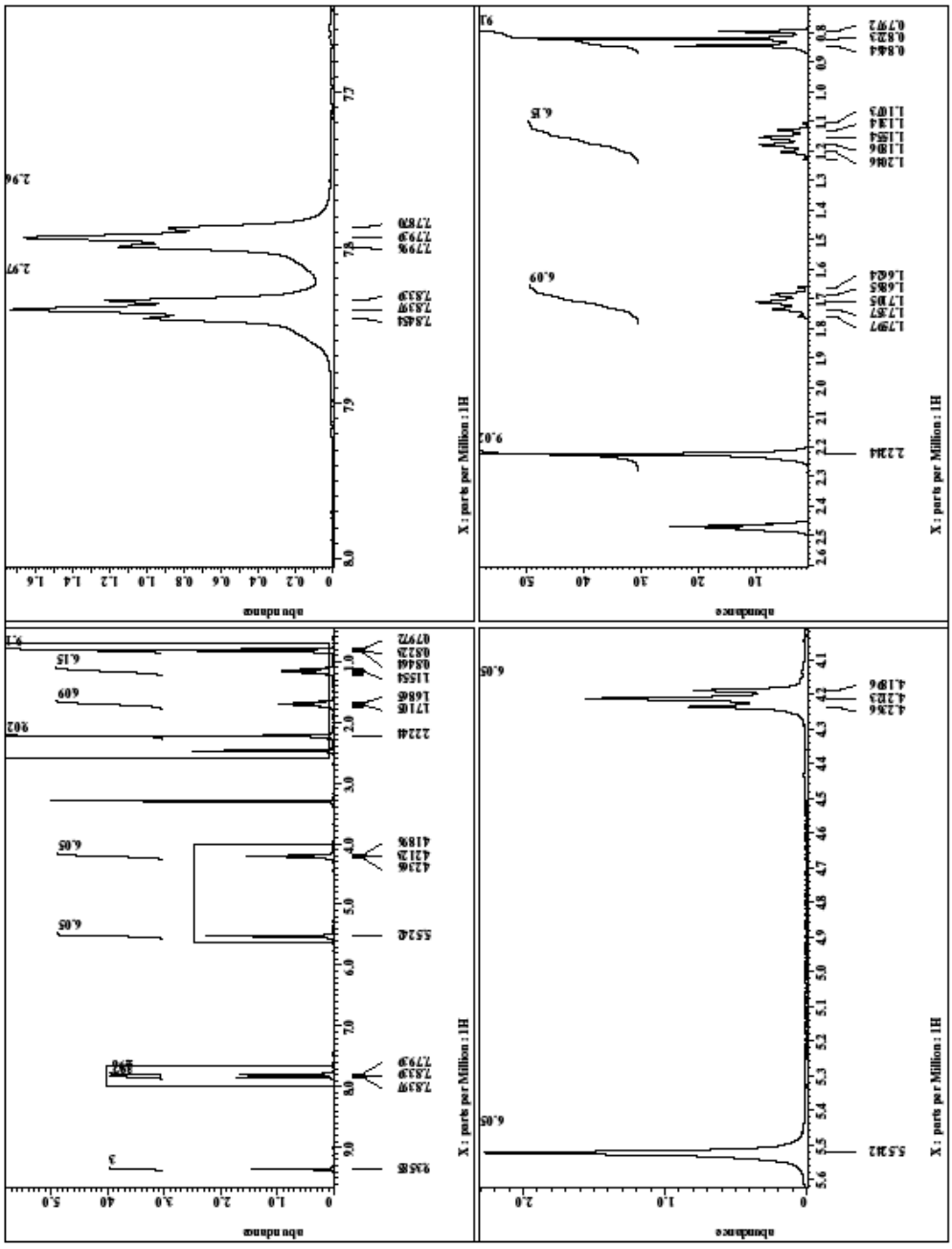


The TfO^- salt for compound B1 was synthesized directly from its bromide salt. Bromide salt of A1 first dissolved in water and passed through anion exchange resin - Amberlite IRA-400(Cl) saturated with OH^- anion to obtain the hydroxide salt of the trication. The eluent was then titrated with trifluoromethanesulfonic acid until pH 7. Evaporation of water under vacuum and drying under phosphorous pentoxide at 80 ^oC yield the pure TIL2 as the TfO^- salt. ^{1}H-NMR (300 MHz): δ (ppm) = 9.18 (s, 3H), 7.82 (t, 3H, *J* = 1.7 Hz), 7.69 (t, 3H, *J* = 1.7 Hz), 7.40 (s, 3H), 5.39 (s, 6H), 4.15 (t, 6H, *J* = 7.2 Hz), 1.75 (p, 6H, *J* = 7.4 Hz), 1.24 (sextet, 6H, *J* = 7.4 Hz), 0.88 (t, 9H, *J* = 7.4 Hz). ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

APPENDIX 1

^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-butylimidazolium)methyl}mesitylene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6

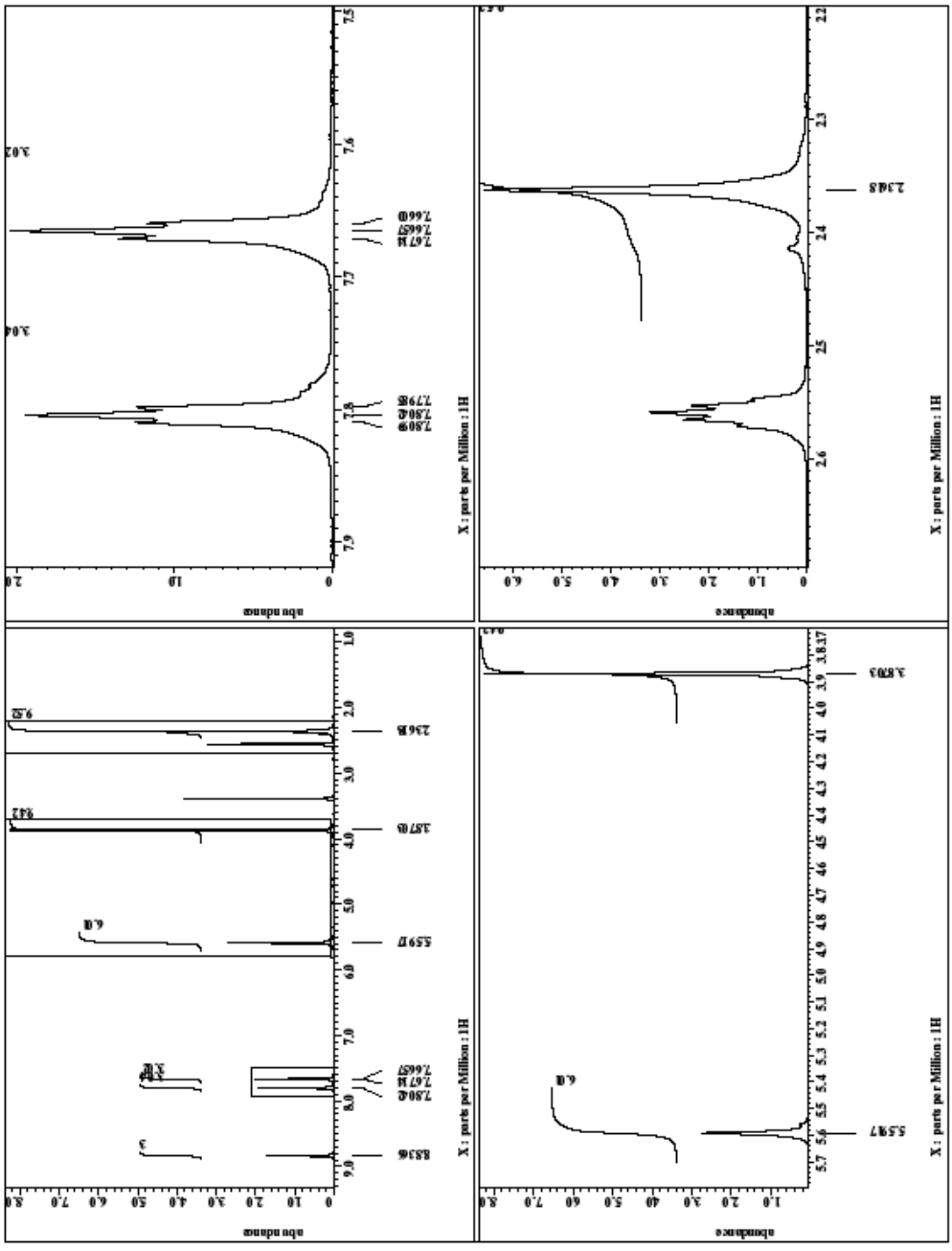

JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_0 [Hz] : 0.0[Hz]
threshold3 : 0 [%] : 80[%] : 100[%]
autofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename : TC2605801-3.jdf
Author : delta
Experiment : single_pulse.ex2
Sample_id : DMSO-D6
Solvent : DMSO-D6
Creation_time : 24-JUL-2007 23:53:38
Revision_time : 14-FEB-2008 18:59:36
Current_time : 25-AUG-2008 18:33:53
Comment : single_pulse
Data_format : 1D COMPLEX
Dim_title : H1 07
Dim_title : H
Dim_units : [ppm]
Dimensions : 1
Site : Ex2 300
Spectrometer : DELTA2_NMR
Field_strength : 7.0560913[T] (300[MHz
X_acquisition : 2.907176961[s]
X_domain : H
X_freq : 300.52965502[MHz]
X_offset : 5[ppm]
X_points : 16384
X_prescans : 0
X_resolution : 0.343976311[Hz]
X_sweep : 5.638707841[kHz]
Y_domain : H
Irr_freq : 300.52965502[MHz]
Irr_offset : 5[ppm]
Tri_domain : H
Tri_freq : 300.52965502[MHz]
Tri_offset : 5[ppm]
Clipped : FALSE
Mod_factorn : 1
Scans : 12
Total_scans : 12
X_90_width : 13.01[us]
X_acq_time : 2.907176961[s]
X_angle : 45[deg]
X_atn : 4[dB]
X_pulse : 6.505[us]
Irr_mode : Off
Tri_mode : Off
Data_format : FALSE
Initial_wait : 1[s]
Recyc_gain : 50
Relaxation_delay : 5[s]
Repetition_time : 7.907176961[s]
Pulse_pi : 22.4[deg]
9.00
6.75
6.09
9.00
6.05
6.05
4.96
5
9.3885
7.8997
7.8589
7.7989
5.5342
4.2364
4.2265
4.1896
2.2344
1.7597
1.7385
1.6885
1.1886
1.1554
0.8844
0.8525
0.7972
Absorbance
X : parts per Million : 1H



APPENDIX 2

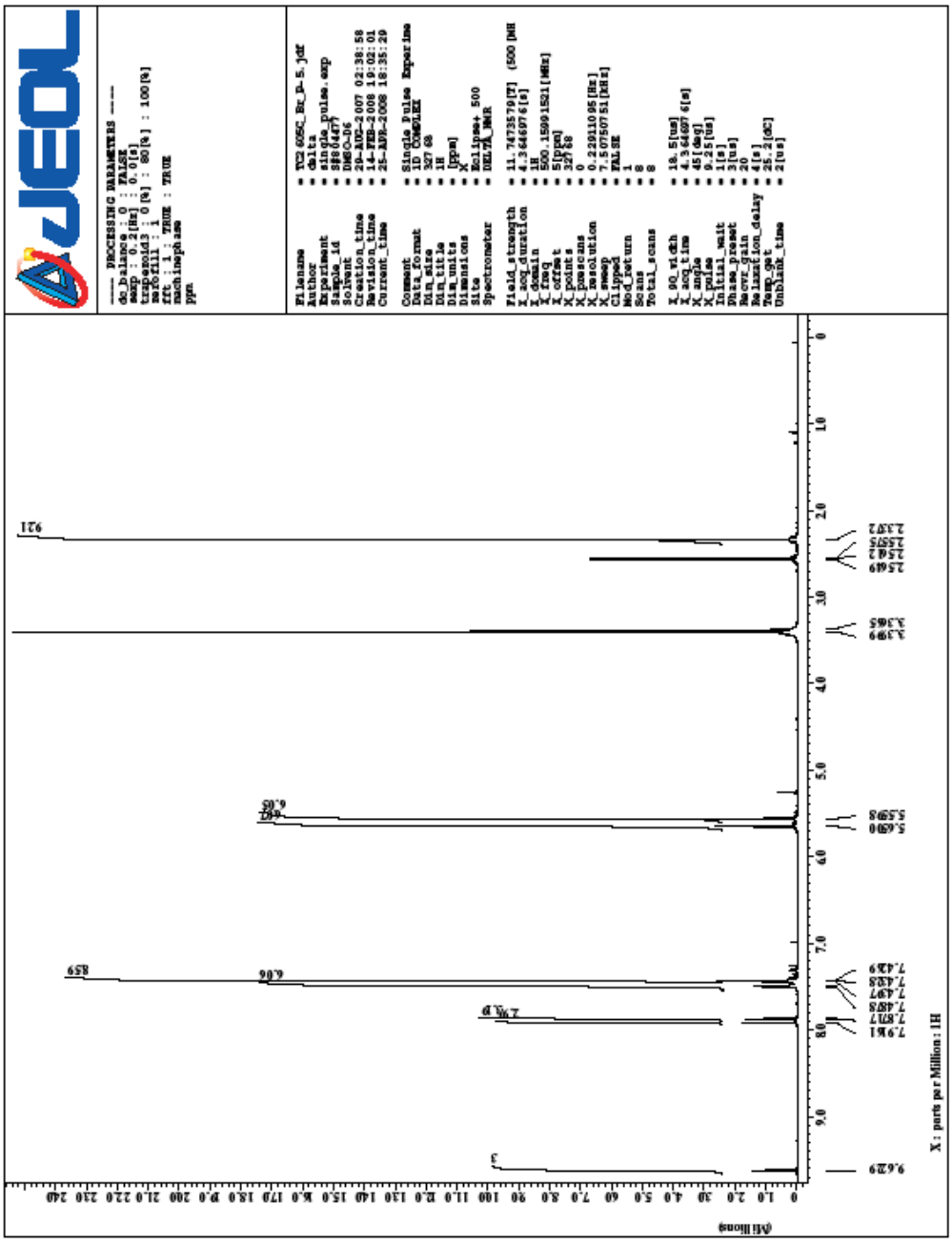
^{1}H NMR SPECTRA OF
3,5-{tris(3-n-methylimidazolium)methyl}mesitylene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6

JEOL
9.52
9.42
6.01
3.84
3.82
8.856
7.802
7.674
7.667
5.597
3.805
2.348
X : parts per Million : 1H
abundance



APPENDIX 3

^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-benzylimidazolium)methyl}mesitylene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_no : 0 [0]
threshold[%] : 0 [%] : 100[%]
unfold1 : 1
fft : 1 : TRUE : TRUE
mathsphase
ppm
Filename : TC2605C_Rx_P-5.jdf
Author : delta
Experiment : single_pulse.exp
Sample_id : SB0447
Solvent : DMSO-D6
Creation_time : 24-AUG-2007 02:38:58
Revision_time : 14-FEB-2008 19:02:01
Current_time : 25-APR-2008 18:35:29
Comment : Single Pulse Experime
Data_format : 1D COMPLEX
Dim_size : 32768
Dim_title : H
Dim_units : [ppm]
Dimensions : X
Site : Eclipse+ 500
Spectrometer : DELTA_NMR
Field_strength : 11.7473579[T] (500 MH
X_acq_duration : 4.3446976[s]
X_domain : H
X_freq : 500.1599152l[MHz]
X_offset : 5[ppm]
X_points : 32768
X_prescans : 0
X_resolution : 0.2291109[Hz]
X_sweep : 7.5075075l[kHz]
Clipped : FALSE
Mod_return : 1
Scans : 8
Total_scans : 8
X_90_width : 18.5[us]
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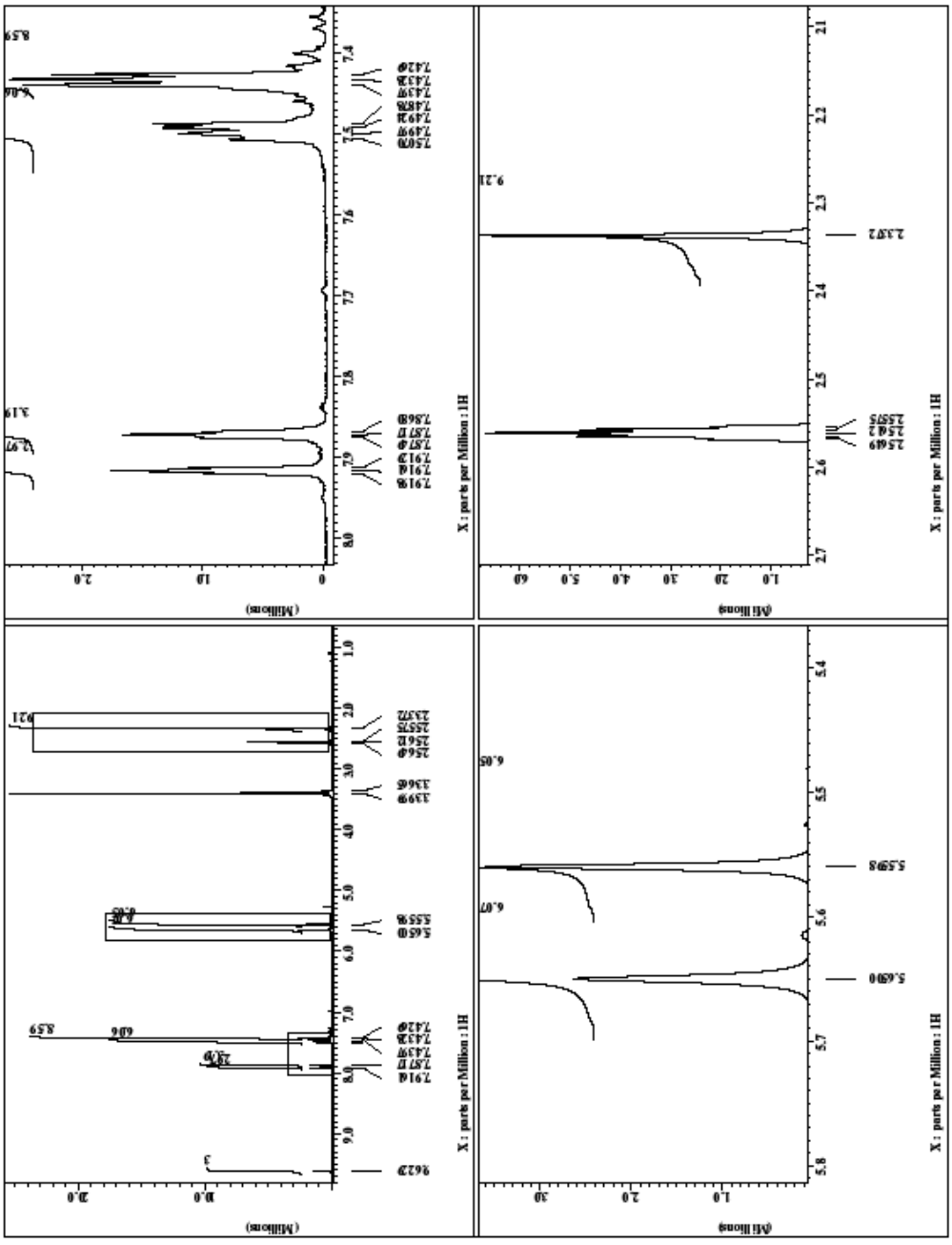
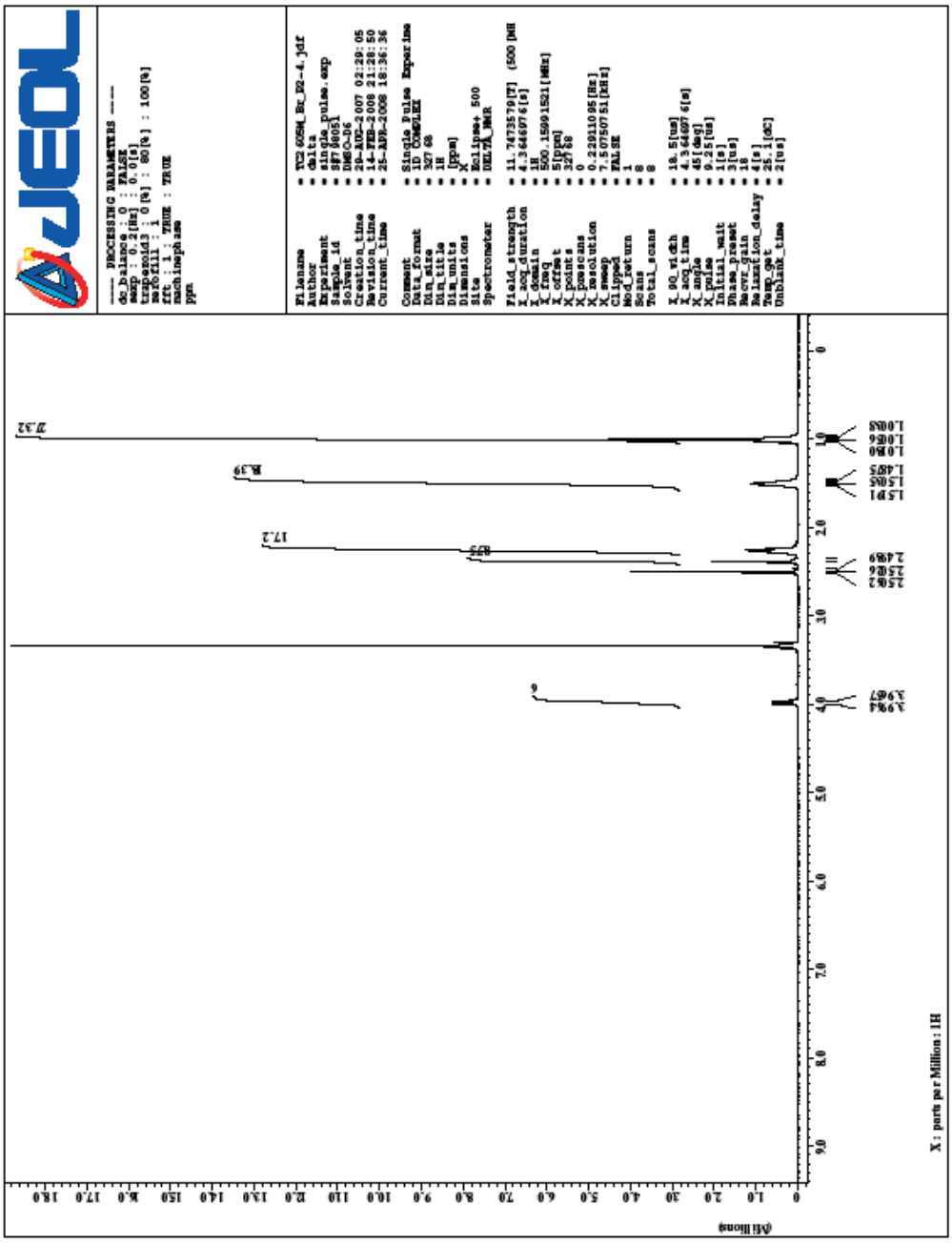
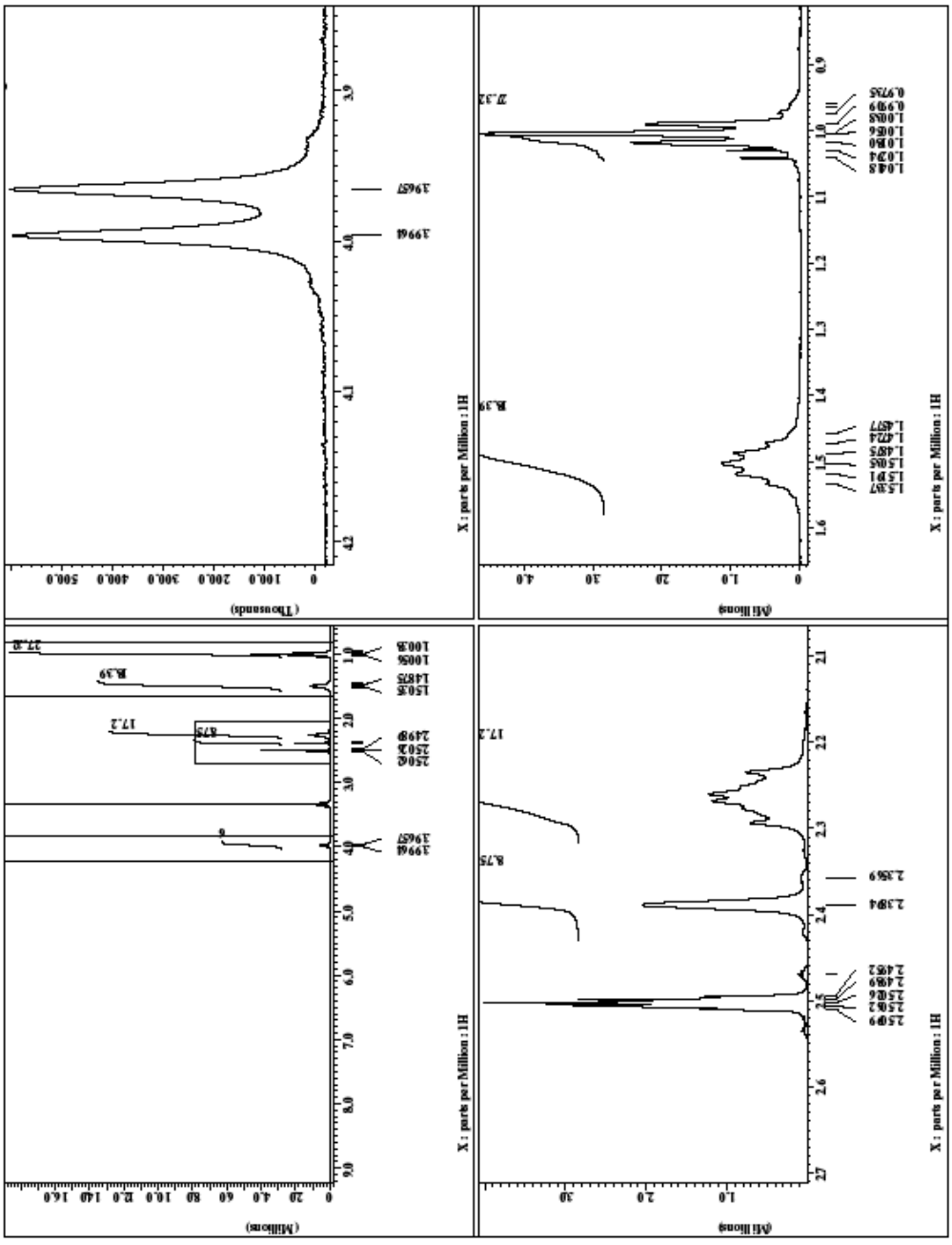
X_angle : 45[deg]
X_pulse : 9.25[us]
X_pulse_wait : 1[s]
Phase_preset : 1[s]
Recvr_gain : 20
Relaxation_delay : 4[s]
Temp_get : 25.2[dC]
Unblank_time : 2[us]
9.629
7.961
7.817
7.487
7.458
7.439
6.06
5.598
5.690
3.199
3.165
2.572
2.565
2.549
921
859
6.06
5
(Million)
X : parts per Million : 1H



APPENDIX 4

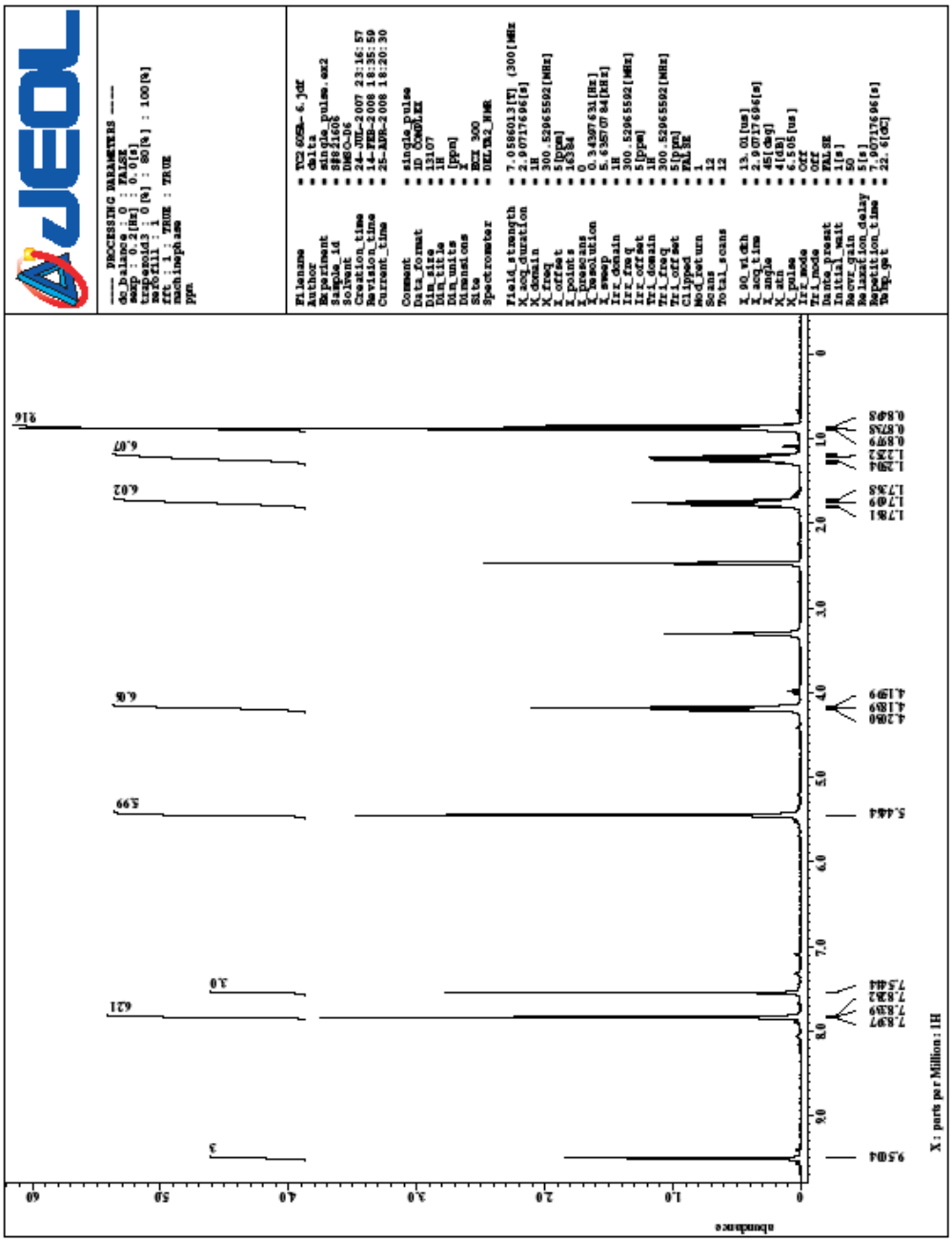
^{1}H NMR SPECTRA OF
1,3,5-{tris(tripropylphosphonium)methyl}mesitylene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6





APPENDIX 5

^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-butylimidazolium)methyl}benzene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_type : 0 [0]
threshold[%] : 0 [%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
manipulate
ppm
Filename * TC2 60SA-6.jdf
Author * delta
Experiment * single_pulse.ex2
Sample_id * SB21608
Solvent * DMSO-d6
Creation_time * 24-DEC-2007 23:16:57
Revision_time * 14-FEB-2008 18:35:59
Current_time * 25-APR-2008 18:20:30
Comment * single_pulse
Data_format * 1D COMPLEX
Dim_size * 13107
Dim_title * 1H
Dim_units * [ppm]
Dimensions * 1
Site * ECX 300
Spectrometer * DELTA2_NMR
Field_strength * 7.0586013[T] (300[MHz
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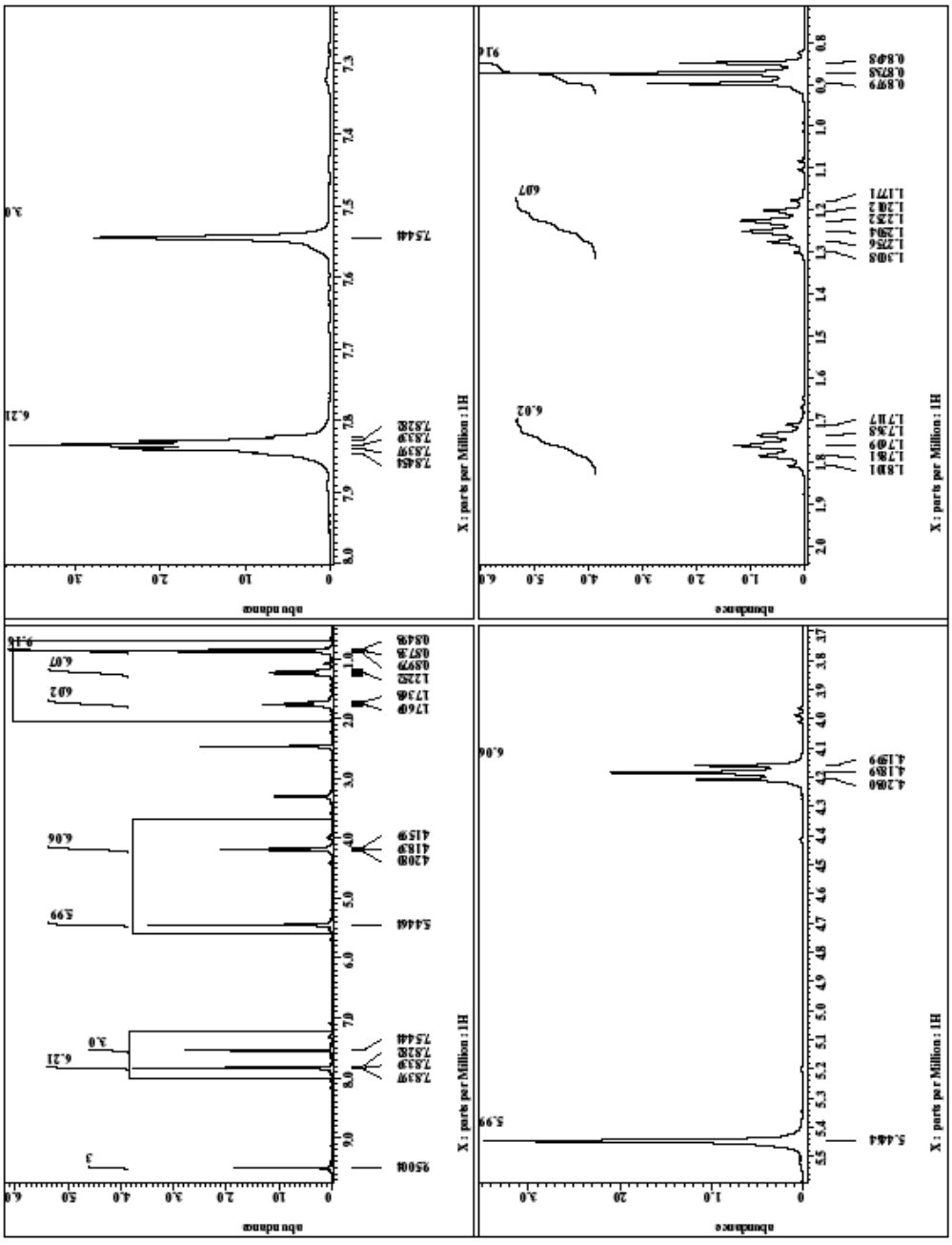
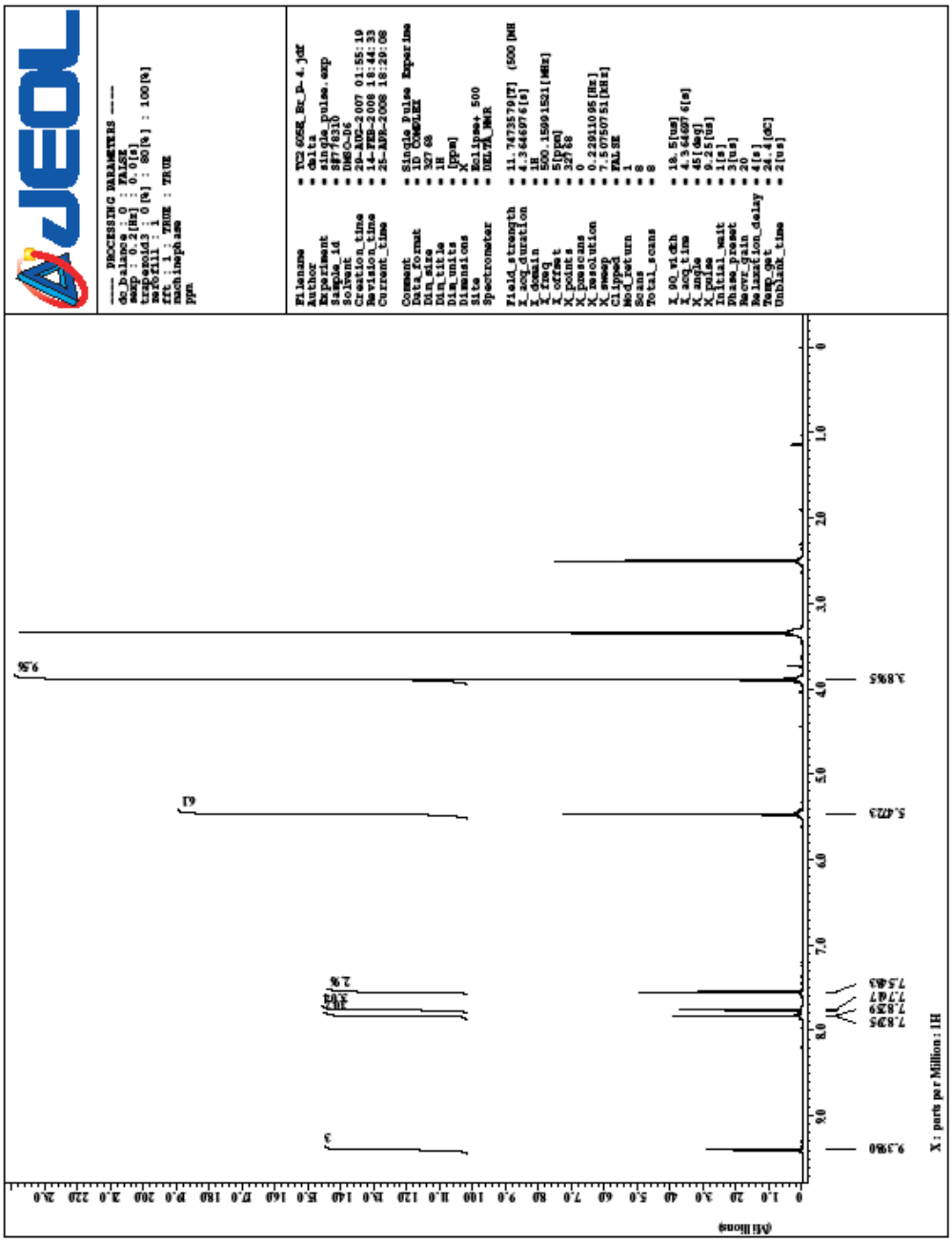
X_domain * 1H
X_freq * 300.52965502[MHz]
X_offset * 5[ppm]
X_points * 16384
X_prescans * 0
X_resolution * 0.34307631[Hz]
X_sweep * 5.63507084[kHz]
Irr_domain * 1H
Irr_freq * 300.52965502[MHz]
Irr_offset * 5[ppm]
Irr_power * 1W
Tri_freq * 300.52965502[MHz]
Tri_offset * 5[ppm]
Clipped * FALSE
Mod_Return * 1
Scans * 12
Total_scans * 12
X_90_width * 13.01[us]
X_acq_time * 2.9071696[s]
X_angle * 45[deg]
X_atn * 4[dB]
X_pulse * 6.505[us]
Irr_mode * Off
Tri_mode * FALSE
Decpl_mount * 1[s]
Delta1_wait * 50
Recvr_gain * 5[s]
Relaxation_delay * 7.9071696[s]
Repetition_time * 22.6[SC]
Temp_get
9.504
8.897
7.899
7.883
7.544
3.0
6.21
3
5.99
6.08
4.280
4.189
4.189
5.444
6.02
6.07
8.16
1.781
1.769
1.735
1.284
1.273
0.899
0.875
0.849
abundance
X : parts per Million : 1H



APPENDIX 6

^{1}H NMR SPECTRA OF
3,5-{tris(3-n-methylimidazolium)methyl}benzene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6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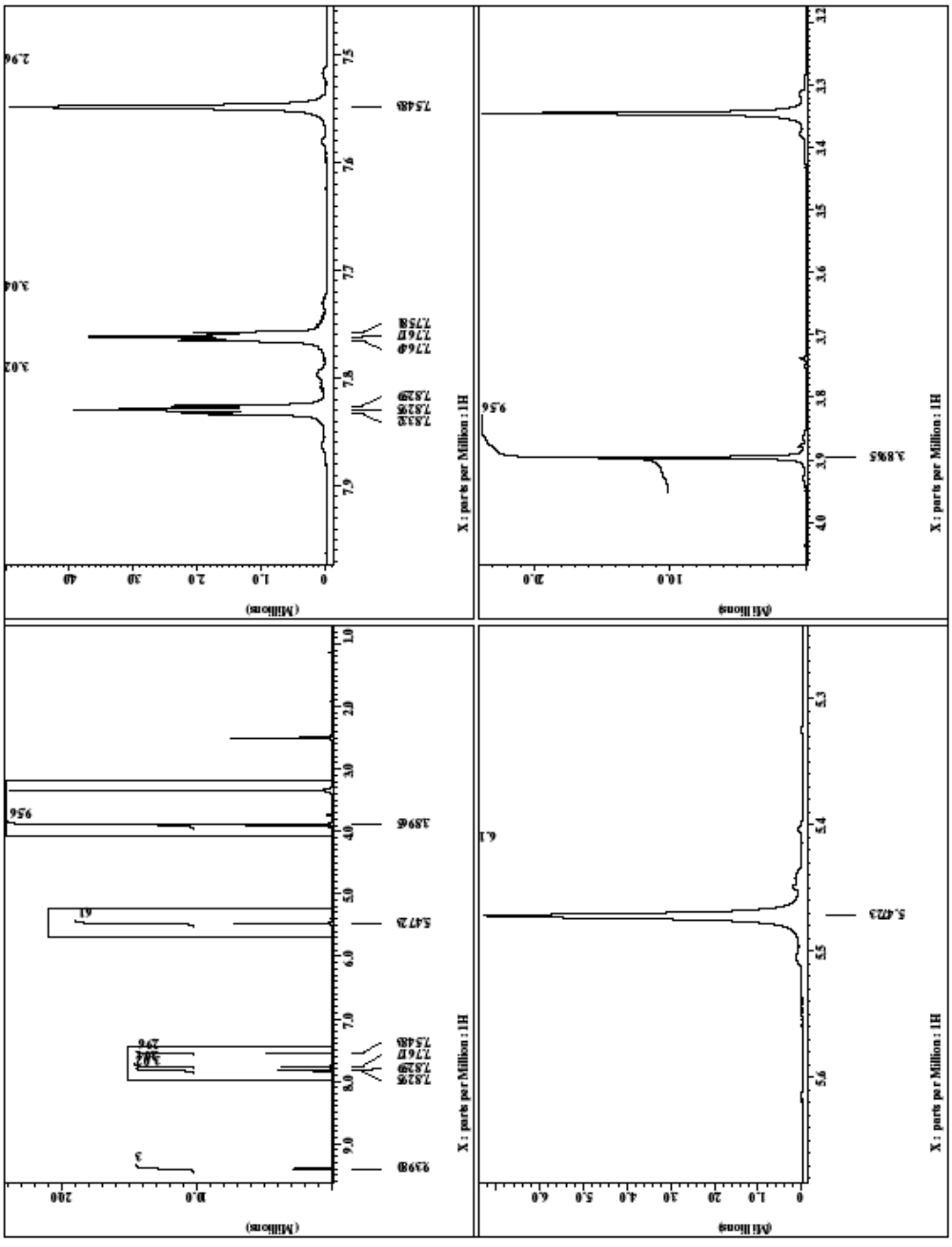
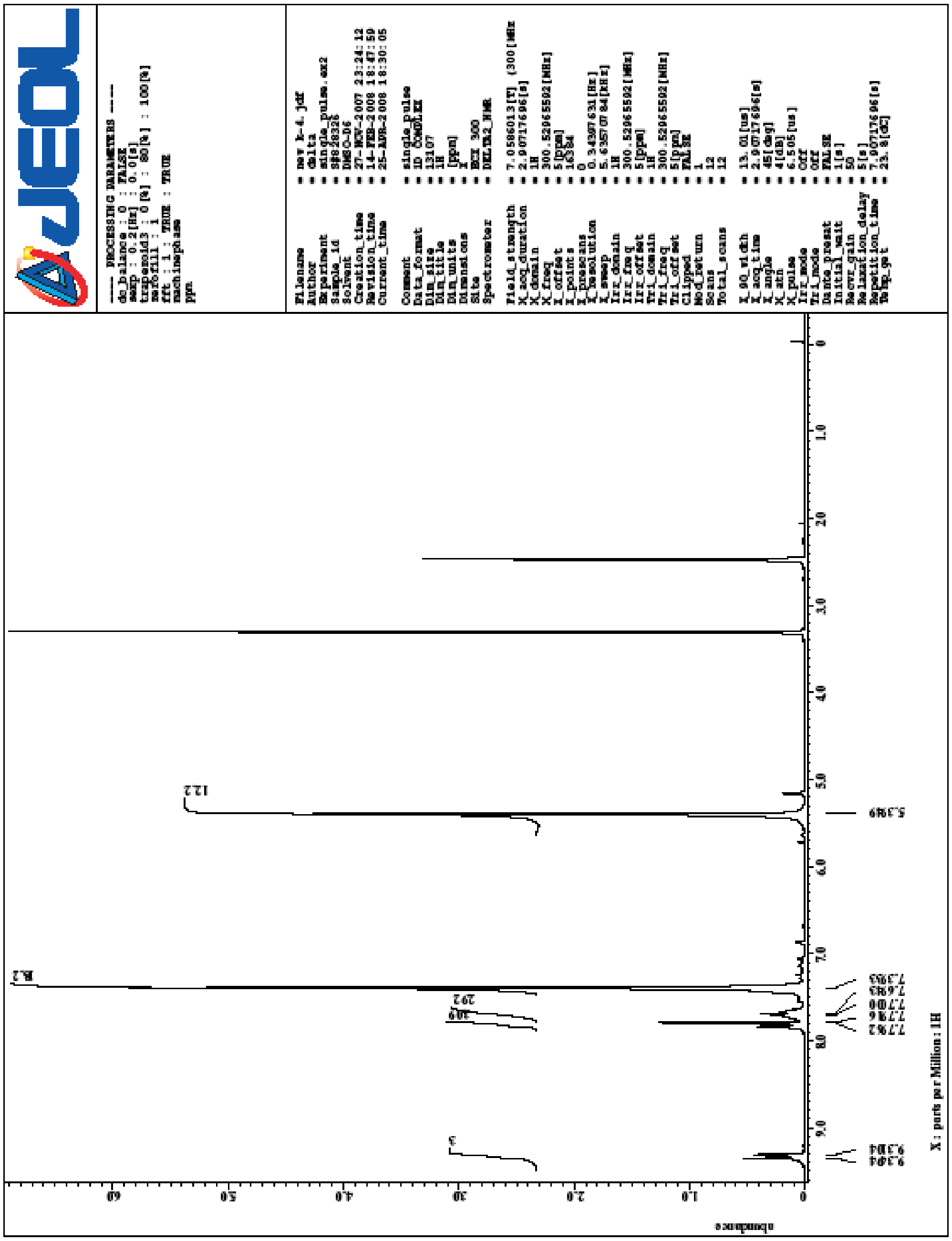
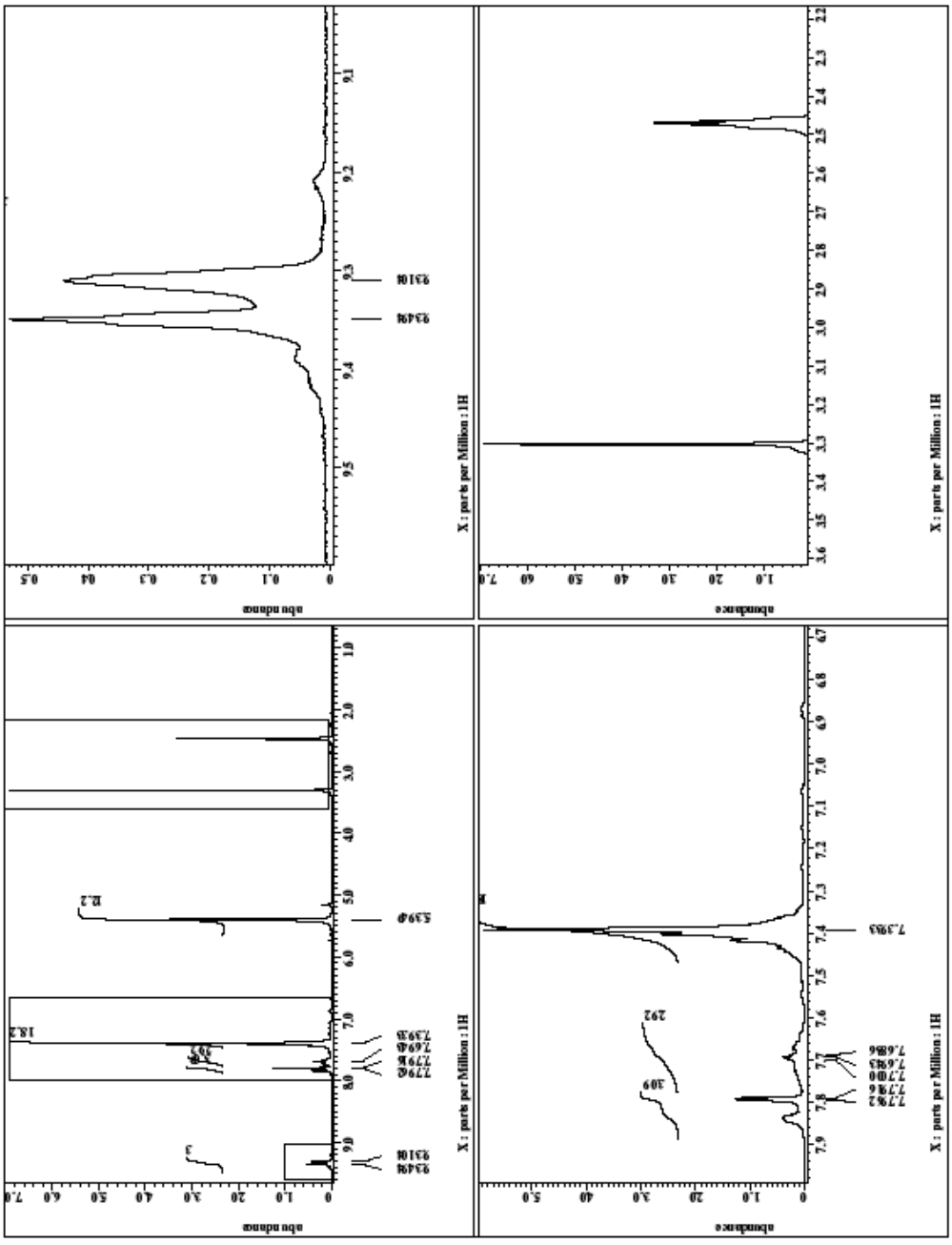
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_no : 0 [0]
threshold[%] : 0 [%] : 100[%]
zerofill : 1 : TRUE
fft : 1 : TRUE
machinephase
ppm
Filename : TC2605R_Rc_P-4.jdf
Author : delta
Experiment : single_pulse.exp
Sample_id : SF76310
Solvent : DMSO-D6
Creation_time : 24-Dec-2007 01:55:19
Revision_time : 14-FEB-2008 18:44:33
Current_time : 25-APR-2008 18:29:08
Comment : Single Pulse Experime
Data_format : 1D COMPLEX
Dim_size : 327 68
Dim_title : H
Dim_units : [ppm]
Dimensions : X
Site : Eclipse+ 500
Spectrometer : DELTA_NMR
Field_strength : 11.7473579[T] (500 [MH
X_acq_duration : 4.3446977[s]
X_domain : H
X_freq : 500.1599182l[MHz]
X_offset : 5[ppm]
X_points : 32768
X_prescans : 0
X_resolution : 0.22911095[Hz]
X_sweep : 7.5075075l[kHz]
Clipped : FALSE
Mod_return : 1
Scans : 8
Total_scans : 8
X_90_width : 18.5[us]
X_acq_time : 4.3646807[s]
X_angle : 45[deg]
X_pulse : 9.25[us]
Dimensions : 1[-]
Pulse_sequ : 1[-]
Recvr_gain : 20
Relaxation_delay : 4[s]
Temp_get : 24.4[dC]
Unblank_time : 2[us]
9.5%
61
2.%
5
9.3580
7.8375
7.8359
7.7847
7.5845
5.4725
3.8965
X : parts per Million : 1H



APPENDIX 7

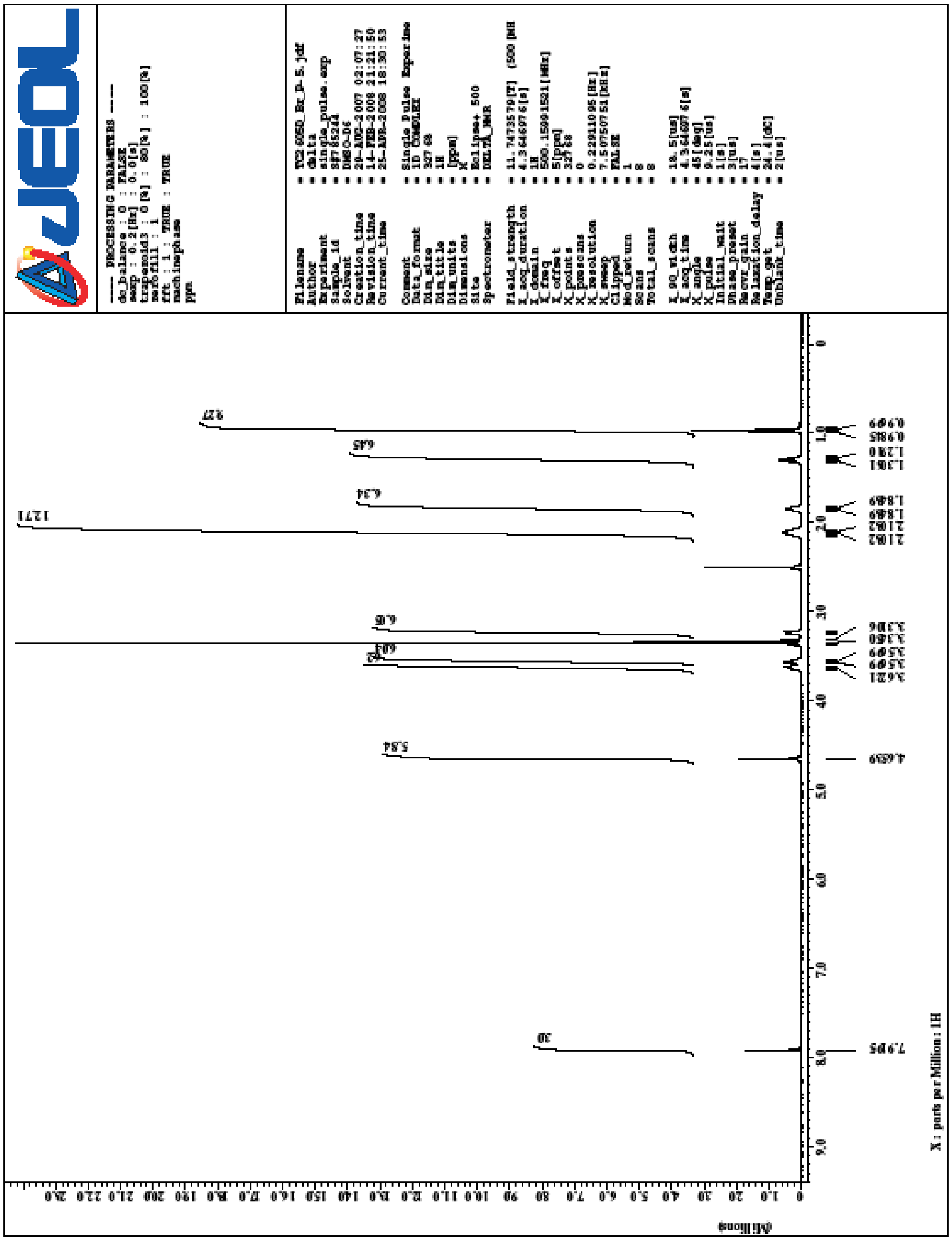
^{1}H NMR SPECTRA OF
3,5-{tris(3-n-benzylimidazolium)methyl}benzene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6


JEOL
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = new k-4.jdf
Author = delta
Experiment = single_pulse.ex2
Solvent = DMSO-D6
Creation_time = 27-NOV-2007 23:24:12
Revision_time = 14-FEB-2008 18:47:59
Current_time = 25-APR-2008 18:30:05
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.8[dC]
9.3494
9.3104
7.7962
7.7946
7.7700
7.6983
7.3955
5.3969
X : parts per Million : 1H
abundance

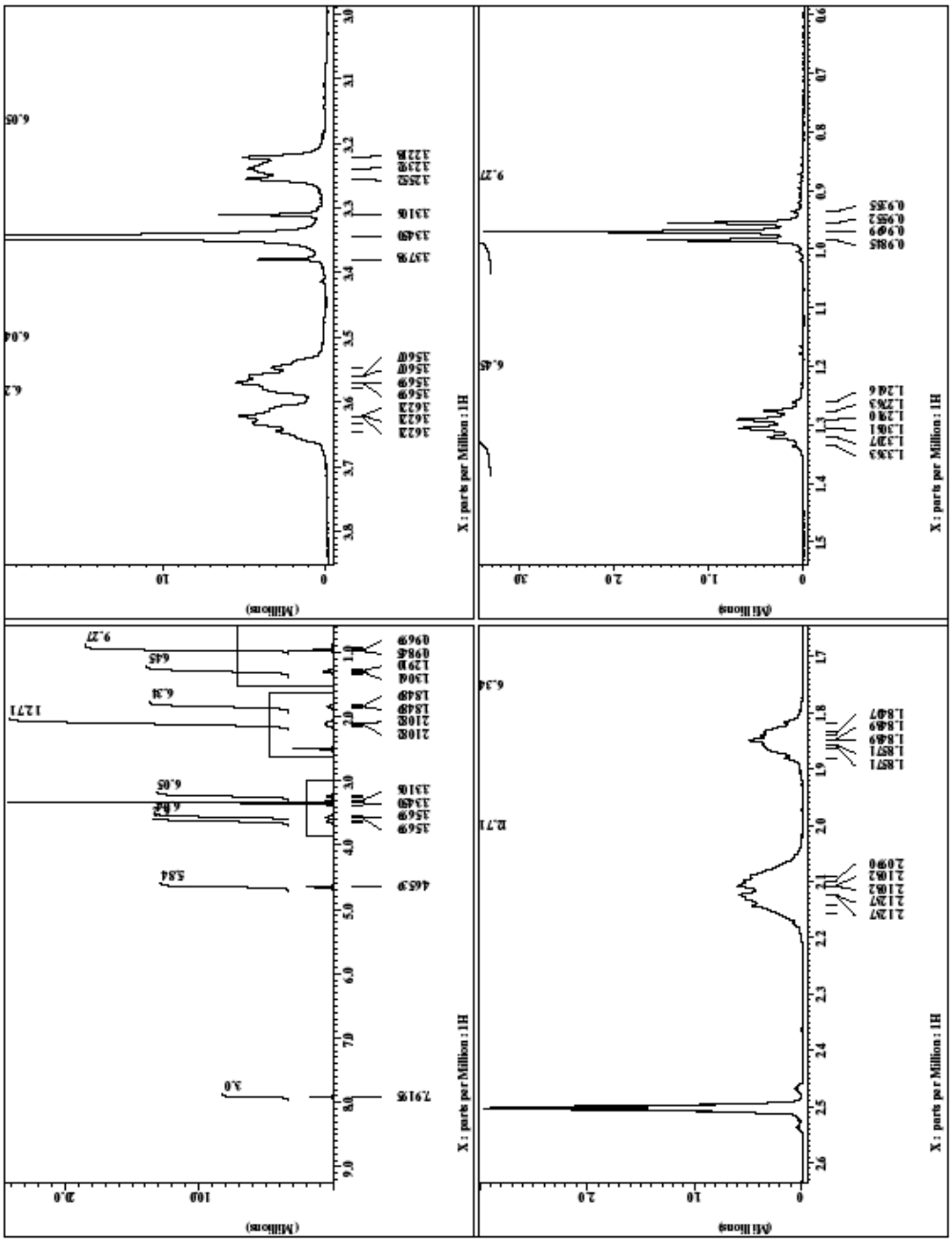


APPENDIX 8

^{1}H NMR SPECTRA OF
1,3,5-{tris(butypyrrolidinium)methyl}benzene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6

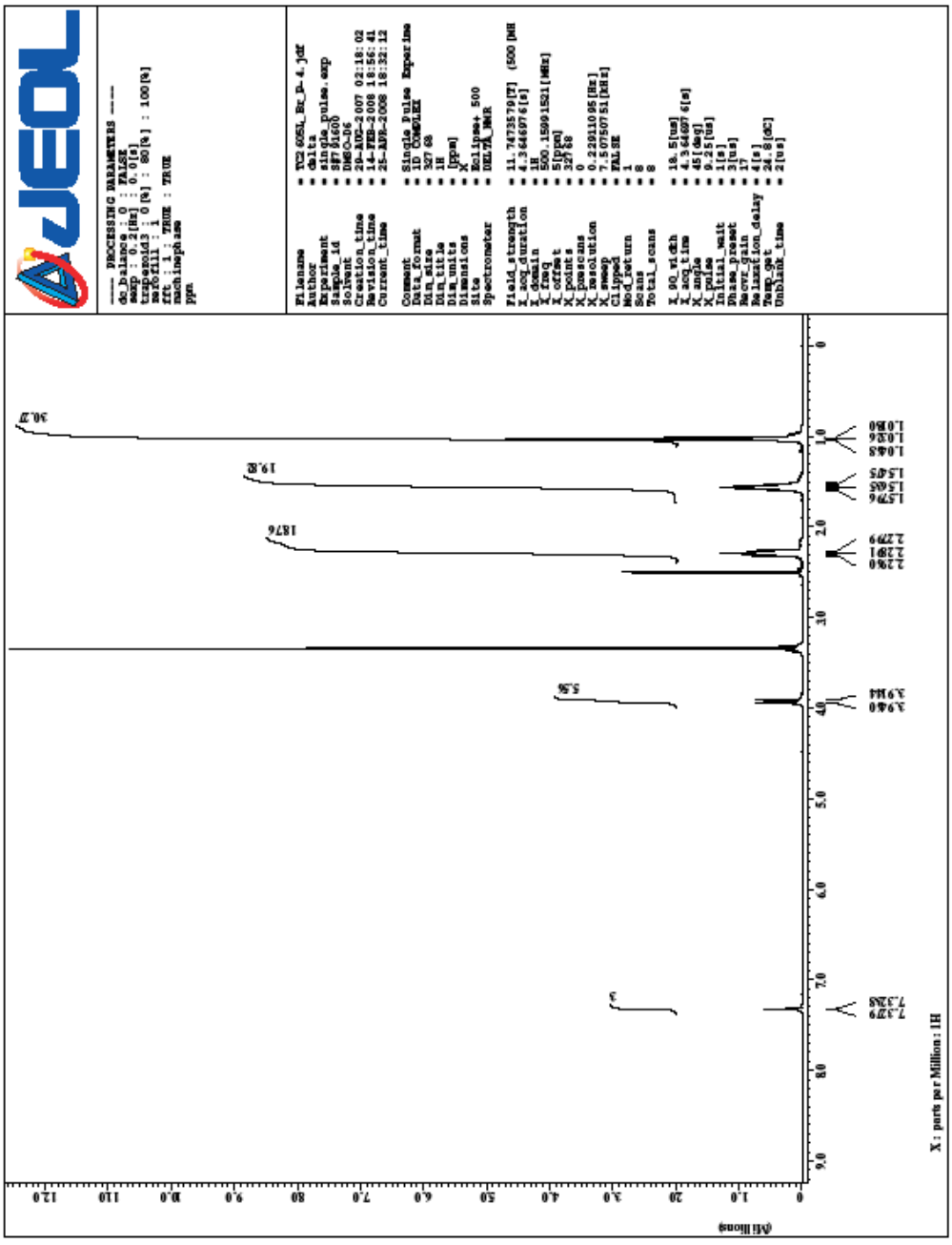


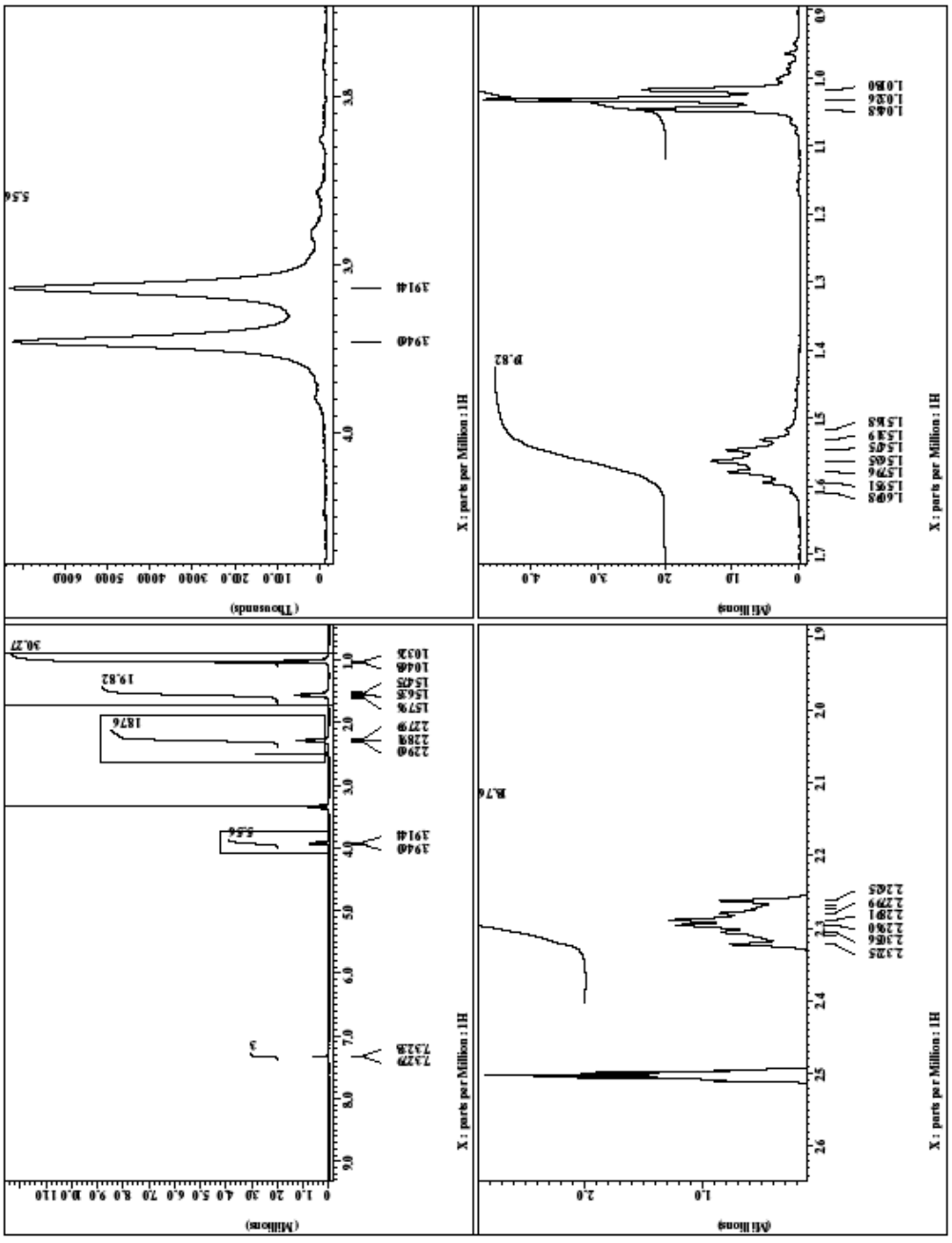
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = TC2 605D_Br_D-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#785244
Solvent = DMSO-D6
Creation_time = 29-AUG-2007 02:07:27
Revision_time = 14-FEB-2008 21:21:50
Current_time = 25-APR-2008 18:30:53
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500 [MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 4[s]
Temp_get = 24.4[dC]
Unblank_time = 2[us]
X : parts per Million : 1H
7.995
4.6539
3.6221
3.5699
3.5699
3.3450
3.3106
2.1082
2.1082
1.8489
1.8489
1.3061
1.2910
0.9835
0.9699



APPENDIX 9

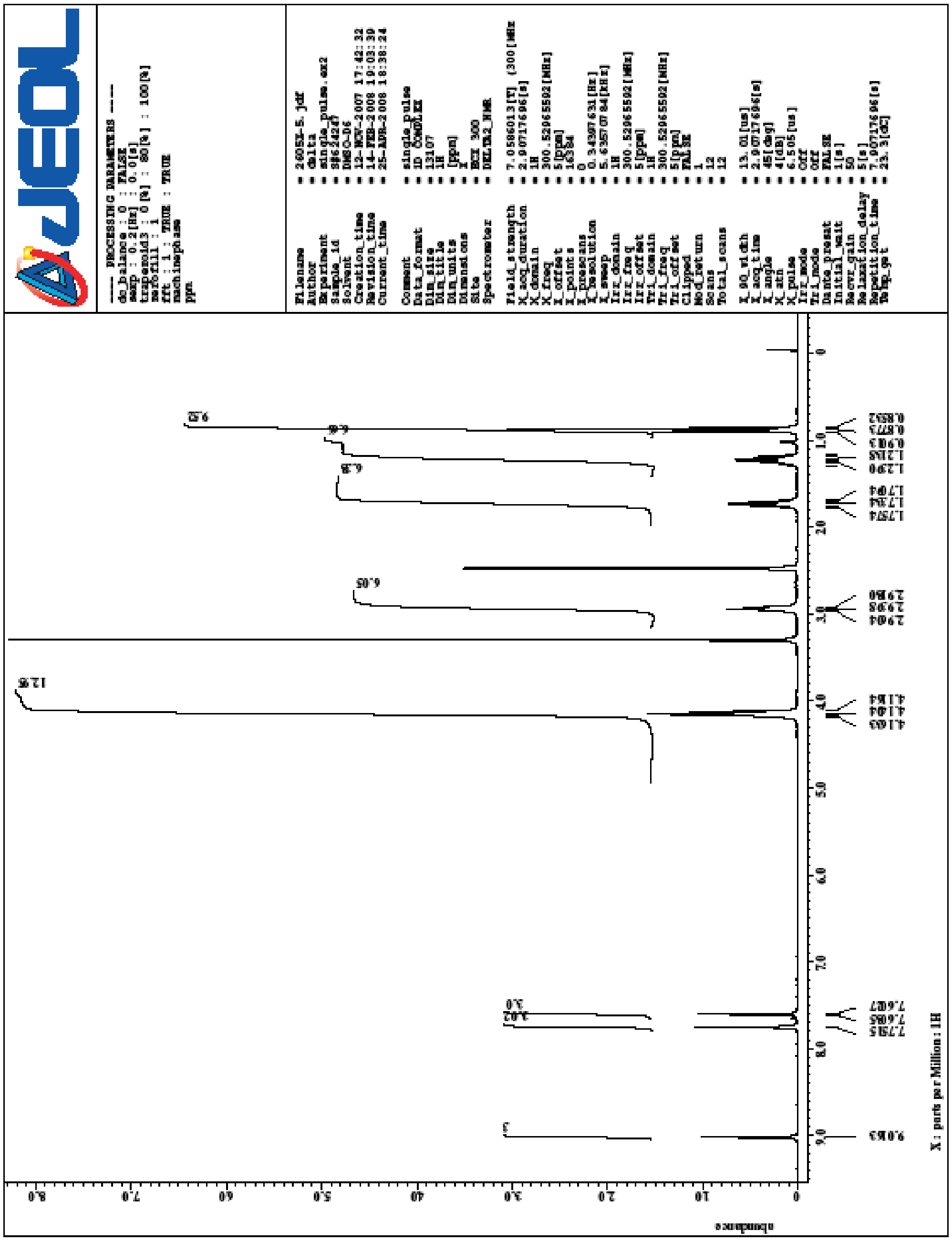
^{1}H NMR SPECTRA OF
1,3,5-{tris(tripropylphosphonium)methyl}benzene
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_no : 0 [0]
threshold[%] : 0 [%] : 100[%]
unfold1 : 1
fft : 1 : TRUE : TRUE
mathsphase
ppm
Filename : TC2605L_Rr_P-4.jdf
Author : delta
Experiment : single_pulse.exp
Sample_id : SF1600
Solvent : DMSO-D6
Creation_time : 24-DEC-2007 02:18:02
Revision_time : 14-FEB-2008 18:56:41
Current_time : 25-APR-2008 18:32:12
Comment : Single Pulse Experime
Data_format : 1D COMPLEX
Dim_size : 327 68
Dim_title : H
Dim_units : [ppm]
Dimensions : X
Site : Eclipse+ 500
Spectrometer : DELTA_NMR
Field_strength : 11.7473579[T] (500 MH
X_acq_duration : 4.3446977[s]
X_domain : H
X_freq : 500.1599152l[MHz]
X_offset : 5[ppm]
X_points : 32768
X_prescans : 0
X_resolution : 0.2291109[Hz]
X_sweep : 7.5075075l[kHz]
Clipped : FALSE
Mod_return : 1
Scans : 8
Total_scans : 8
X_90_width : 18.5[us]
X_acq_time : 4.3446977[s]
X_angle : 45[deg]
X_pulse : 9.25[us]
X_pulse_mult : 1[s]
Dimtitl_wait : 1[s]
Phase_preset : 17
Recvr_gain : 17
Relaxation_delay : 4[s]
Temp_get : 24.8[dC]
Unblank_time : 2[us]
30.37
19.88
18.76
5.56
3
7.329
7.328
3.960
3.944
2.780
2.761
2.739
1.577
1.565
1.545
1.048
1.026
1.010
(Million)
X : parts per Million : 1H

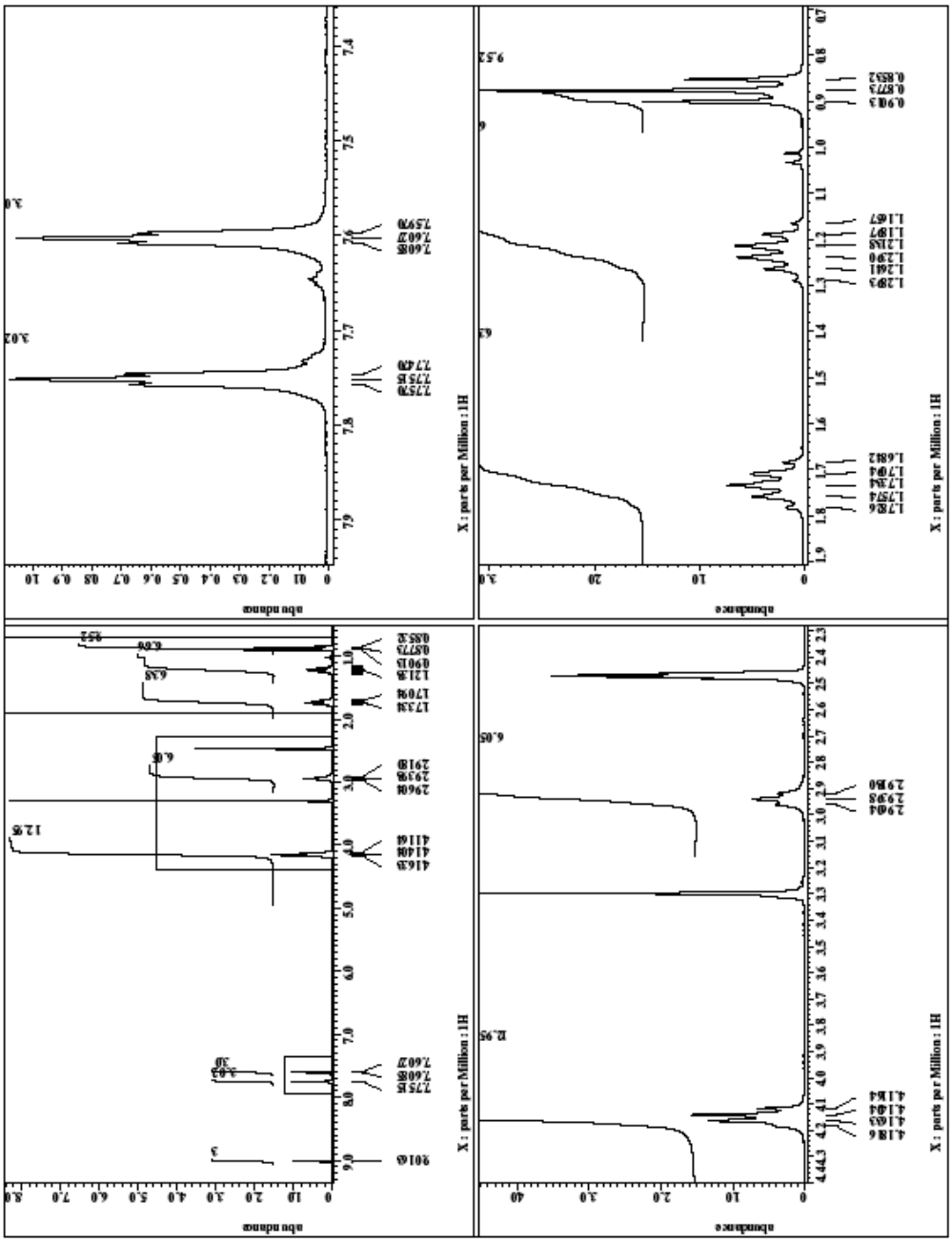


APPENDIX 10

^{1}H NMR SPECTRA OF
Tris(2-(3-n-butylimidazolium)ethyl)amine
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6

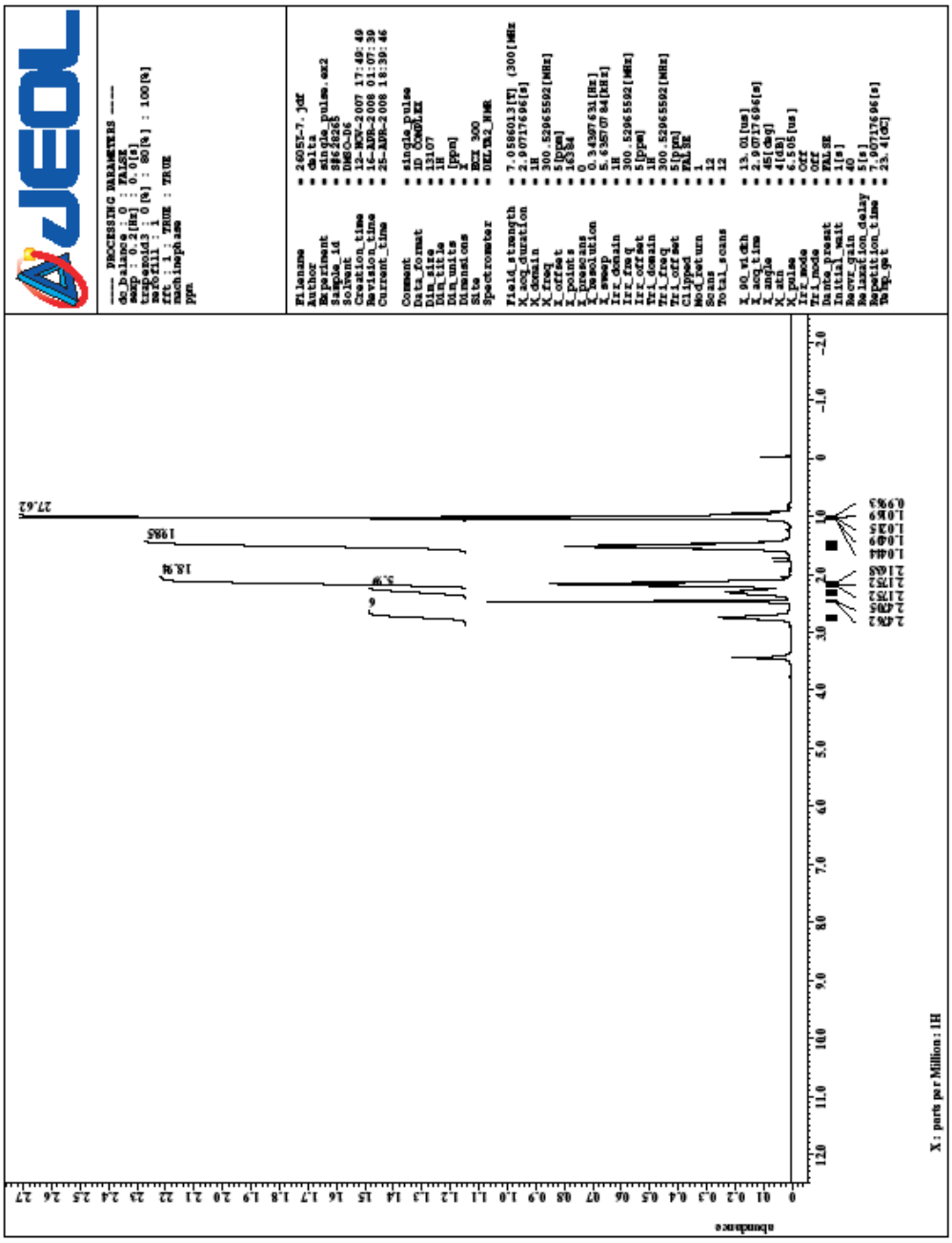


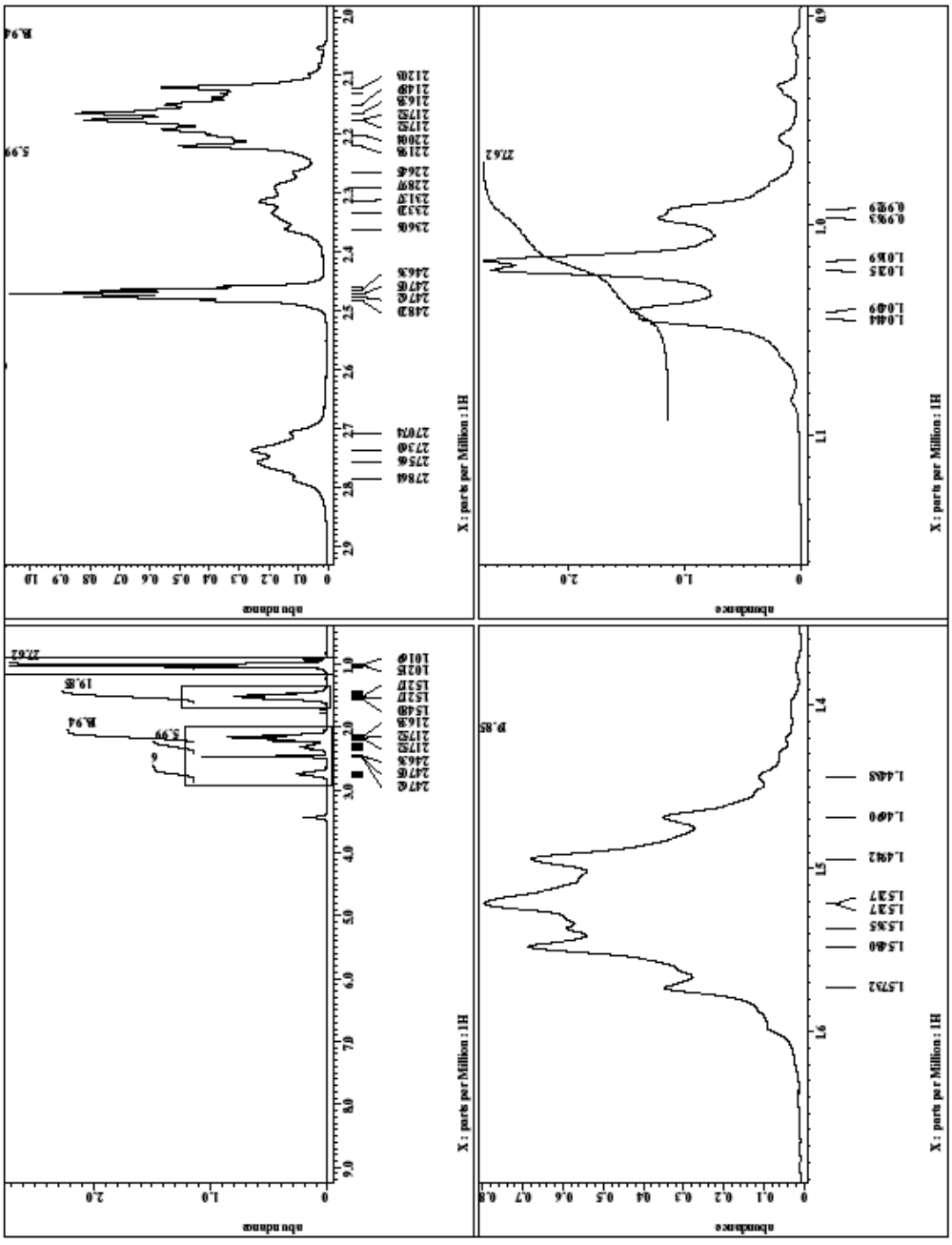
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = 2605X-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S8624247
Solvent = DMSO-D6
Creation_time = 12-NOV-2007 17:42:32
Revision_time = 14-FEB-2008 19:03:39
Current_time = 25-APR-2008 18:38:24
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.3[dC]
abundance
X : parts per Million : 1H
9.0163
7.7515
7.6085
7.6027
4.1633
4.1404
4.1164
2.9604
2.9398
2.9180
1.7574
1.7334
1.7094
1.2390
1.2155
0.9013
0.8773
0.8532
3
3.02
3.0
12.95
6.05
6.38
6.46
9.52



APPENDIX 11

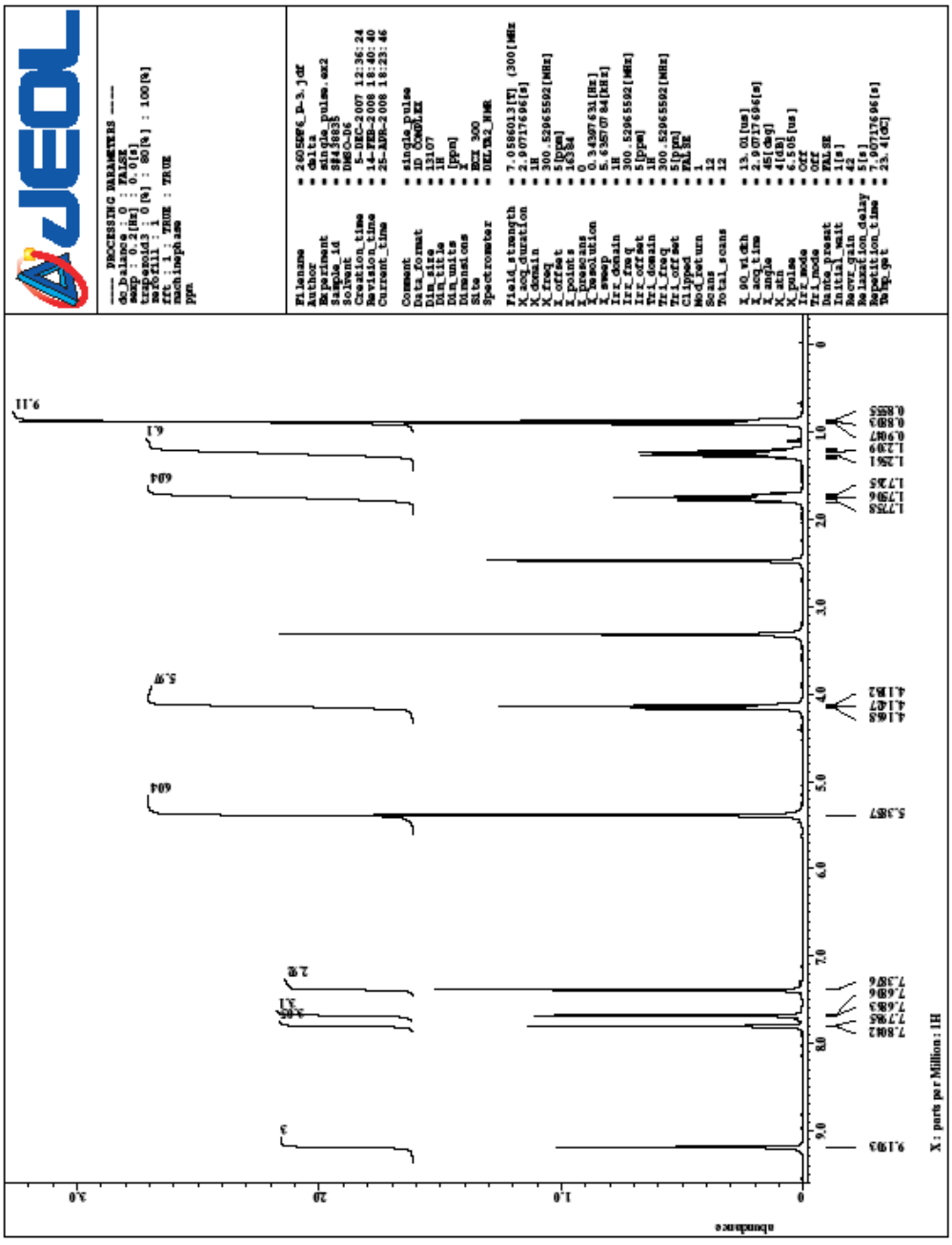
^{1}H NMR SPECTRA OF
Tris(2-(tripropylphosphoniummethyl)ethyl)amine
tris((bistrifluoromethylsulfonyl)imide)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6

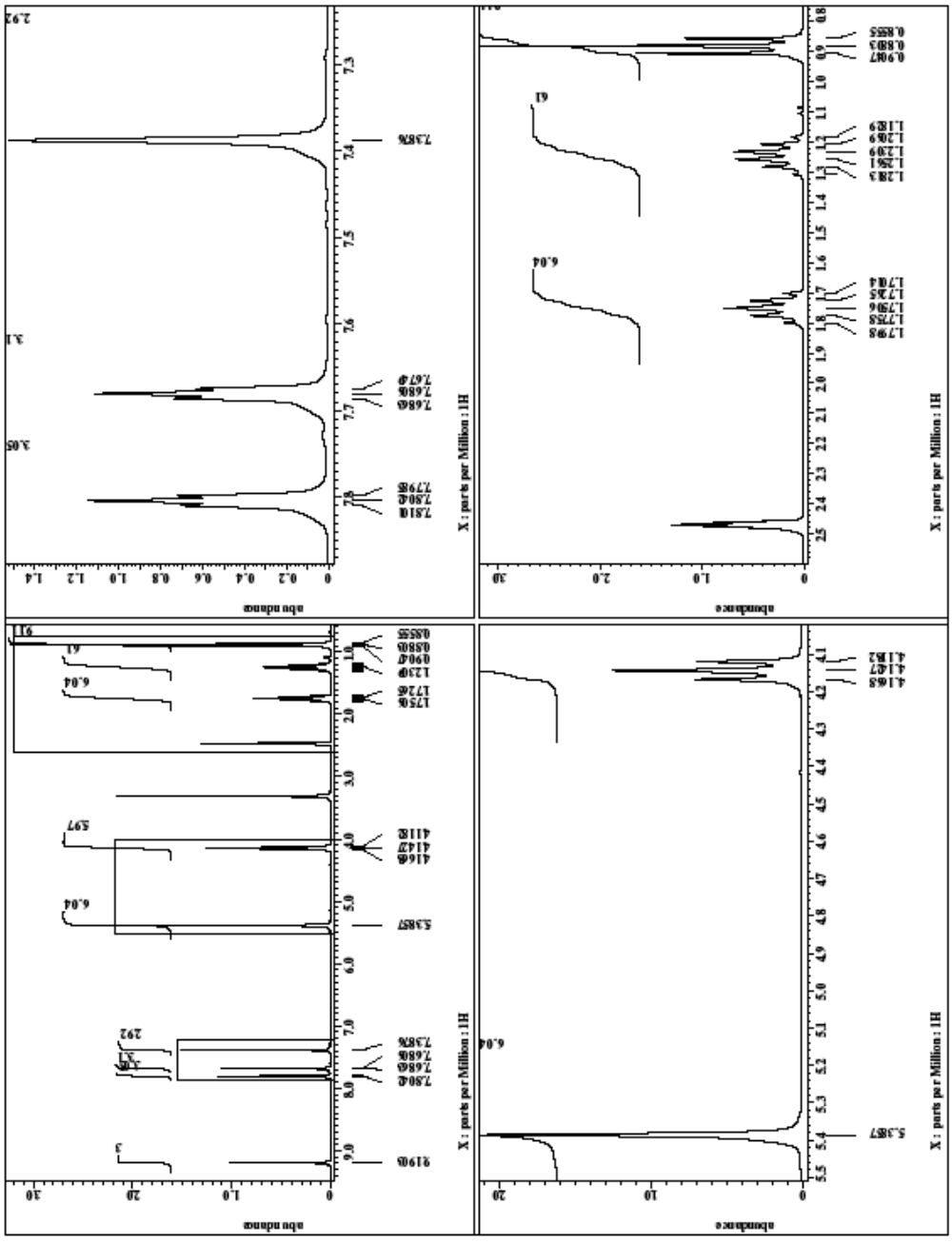

JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_no : 0 [%]
magnoid3[0] : 0 [%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename : 26057-7.jdf
Author : delta
Experiment : single_pulse.ex2
Sample_id : SH62525
Solvent : DMSO-D6
Creation_time : 13-NOV-2007 17:49:49
Revision_time : 16-AUG-2008 01:07:39
Current_time : 25-AUG-2008 18:39:46
Comment : single_pulse
Data_format : 1D COMPLEX
Dim_size : 13107
Dim_title : 1H
Dim_units : [ppm]
Dimensions : 1
Site : ECX 300
Spectrometer : DELTA2_NMR
Field_strength : 7.0586013[T] (300[MHz
X_acq_duration : 2.9071769[s]
X_domain : 1H
X_freq : 300.52965502[MHz]
X_offset : 5[ppm]
X_points : 16384
X_prescans : 0
X_resolution : 0.34307631[Hz]
X_sweep : 5.63507084[kHz]
Irr_domain : 1H
Irr_freq : 300.52965502[MHz]
Irr_offset : 5[ppm]
Irr_domain : 1H
Tri_freq : 300.52965502[MHz]
Tri_offset : 5[ppm]
Clipped : FALSE
Mod_Return : 1
Scans : 12
Total_scans : 12
X_90_width : 13.01[us]
X_acq_time : 2.9071769[s]
X_angle : 45[deg]
X_atn : 4[db]
X_pulse : 6.505[us]
Irr_mode : Off
Tri_mode : PFG_SE
Delta_wait : 1[s]
Recvr_gain : 40
Relaxation_delay : 5[s]
Repetition_time : 7.9071769[s]
Temp_get : 23.4[dC]
27.62
18.98
19.85
5.99
6
X : parts per Million : 1H
Abundance



APPENDIX 12

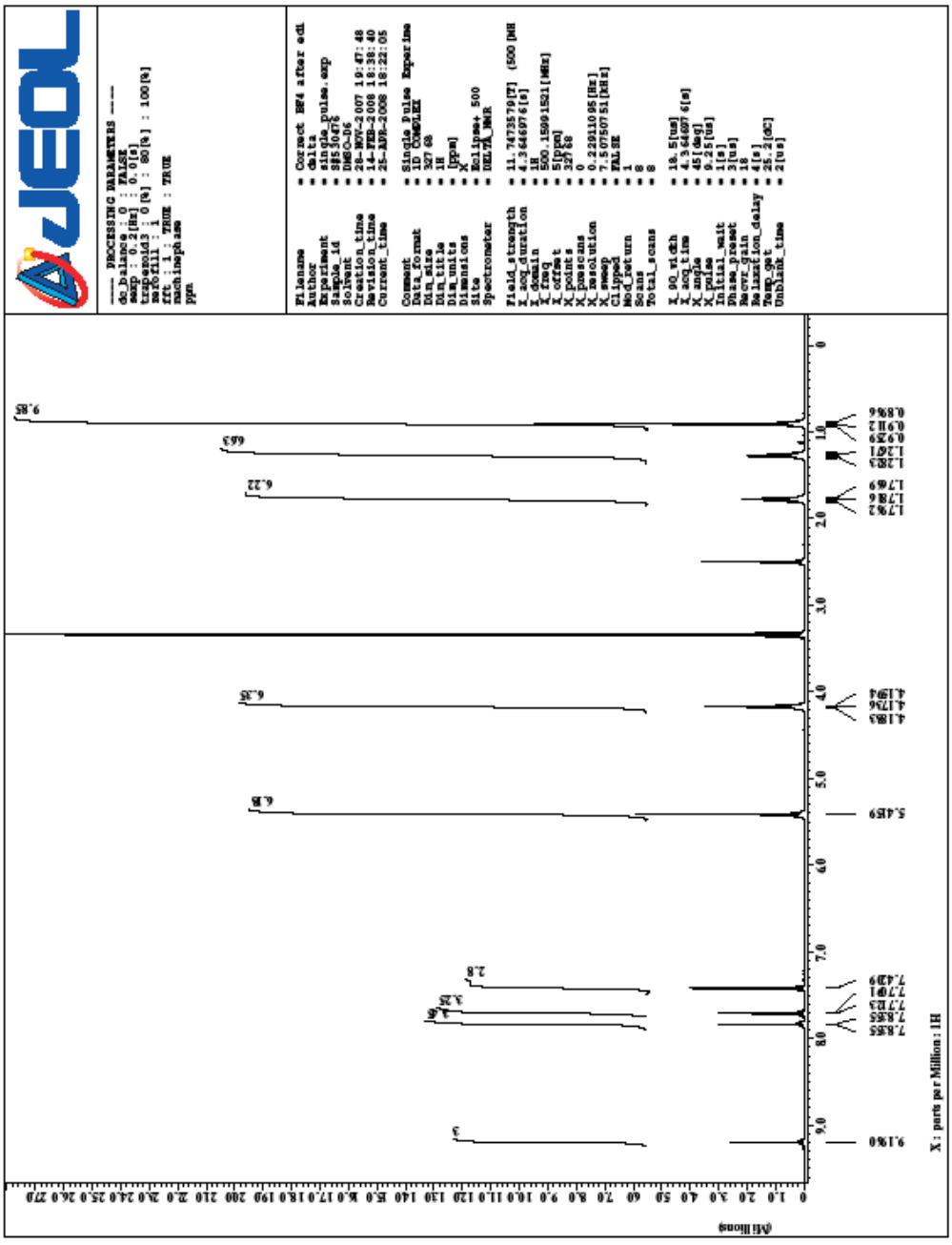
^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(hexafluorophosphate)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6

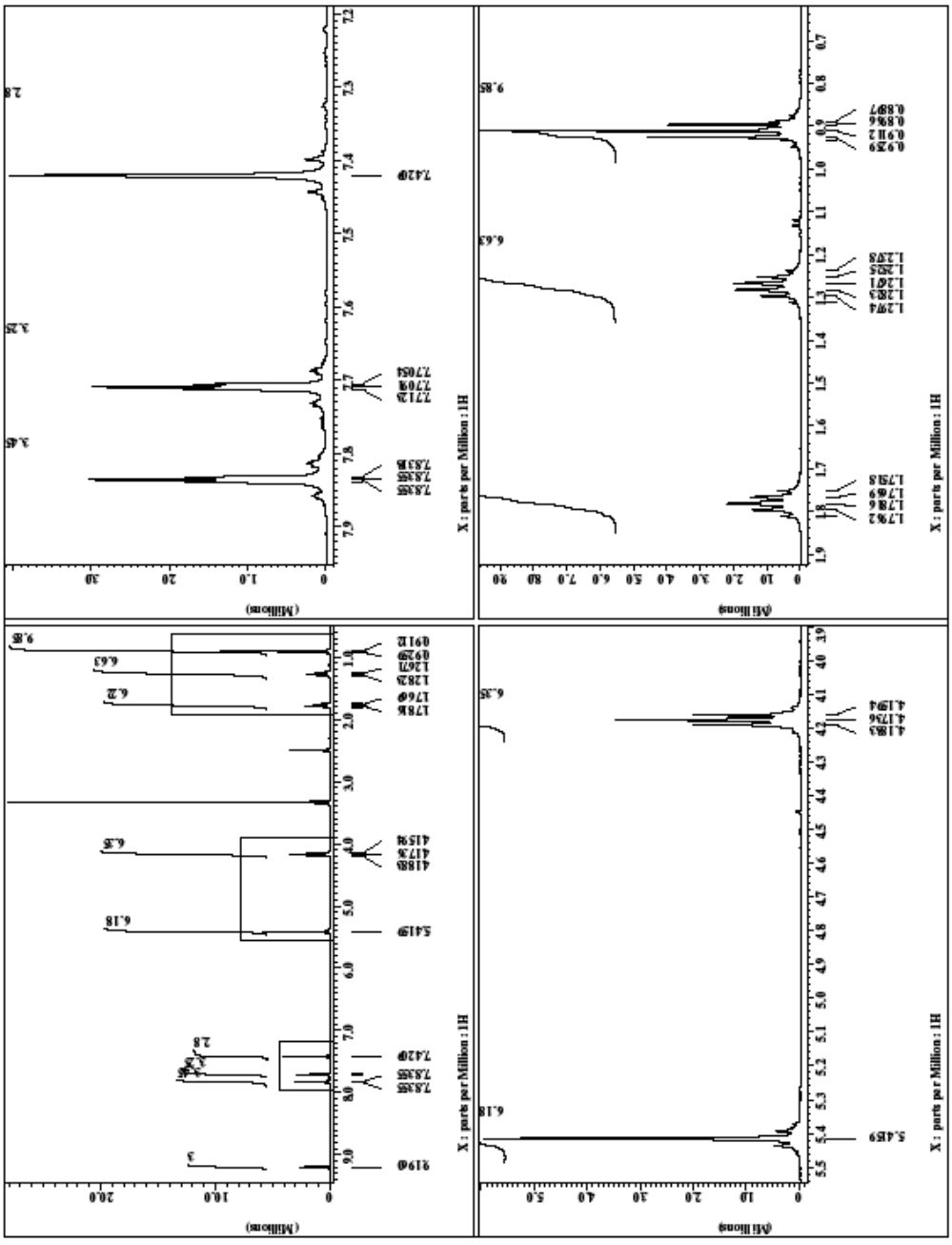




APPENDIX 13

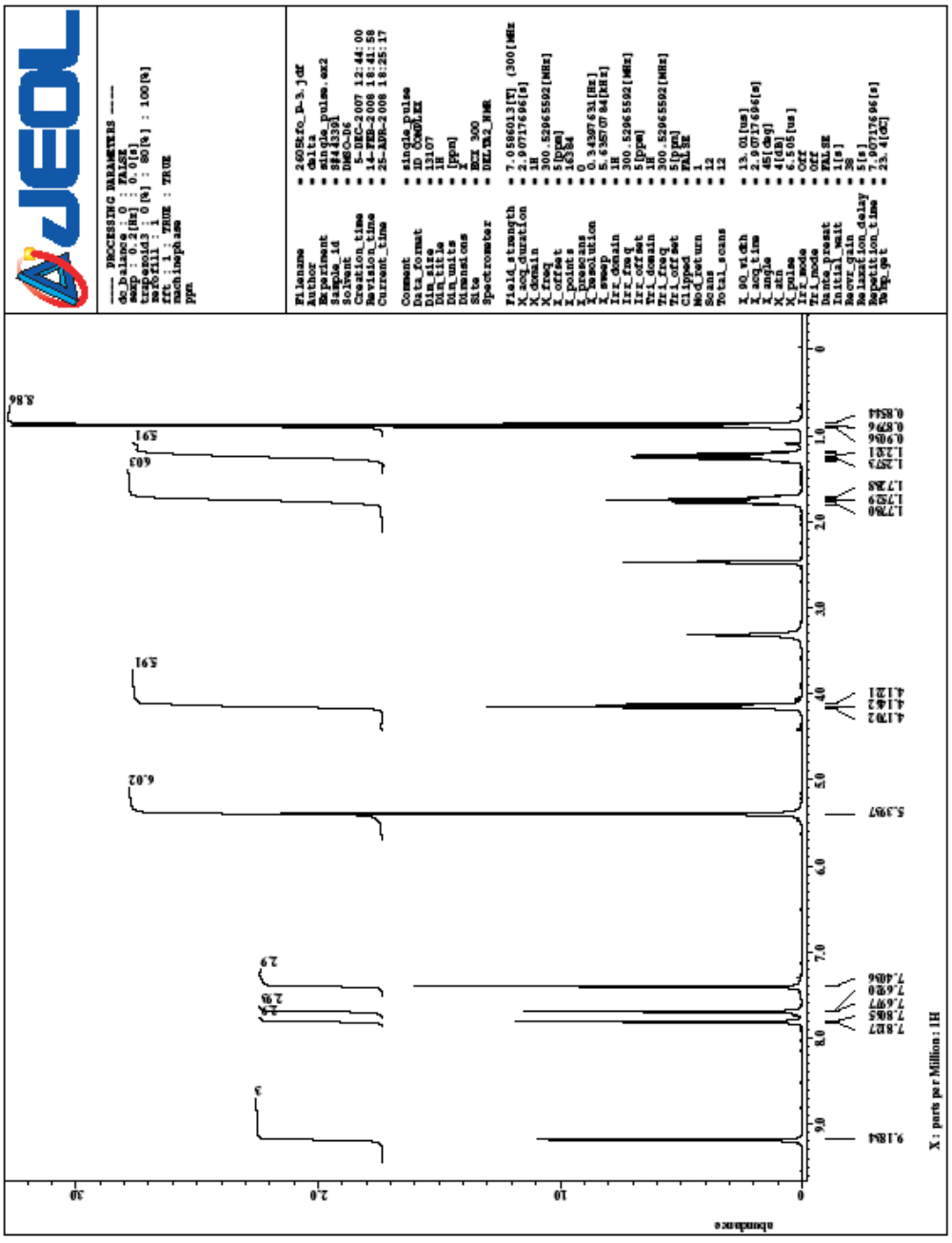
^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(tetrafluoroborate)
MEASURED ON A JEOL ECLIPSE 500+ SPECTROMETER IN DMSO-d6

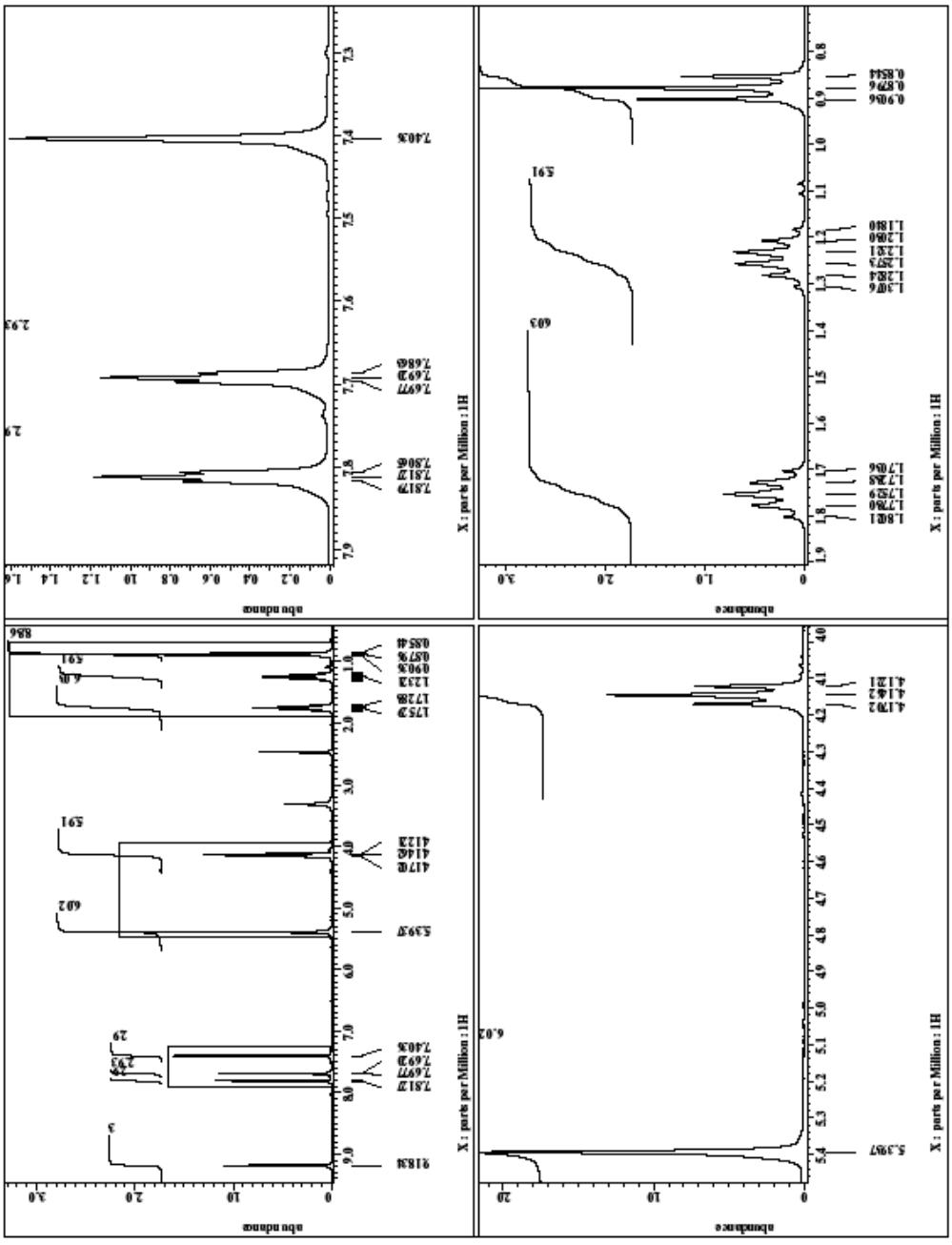




APPENDIX 14

^{1}H NMR SPECTRA OF
1,3,5-{tris(3-n-butylimidazolium)methyl}benzene
tris(trifluoromethanesulfonate)
MEASURED ON A JEOL ECLIPSE 300+ SPECTROMETER IN DMSO-d6


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
exp_no : 0 [No]
threshold[%] : 0 [%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
mach1sepbase
ppm
Filename : 2605kfo_p-3.jdf
Author : delta
Experiment : single_pulse.ex2
Sample_id : SH43391
Solvent : DMSO-D6
Creation_time : 14-DEC-2007 12:44:00
Revision_time : 14-FEB-2008 16:41:58
Current_time : 25-AUG-2008 18:25:17
Comment : single_pulse
Data_format : 1D COMPLEX
Dim_size : 13107
Dim_title : 1H
Dim_units : [ppm]
Dimensions : 1
Site : ECX 300
Spectrometer : DELTA2_NMR
Field_strength : 7.0586013[T] (300[MHz
X_acq_duration : 2.9071769[s]
X_domain : 1H
X_freq : 300.52965502[MHz]
X_offset : 5[ppm]
X_points : 16384
X_prescans : 0
X_resolution : 0.34307631[Hz]
X_sweep : 5.6357084[kHz]
Irr_domain : 1H
Irr_freq : 300.52965502[MHz]
Irr_offset : 5[ppm]
Tri_domain : 1H
Tri_freq : 300.52965502[MHz]
Tri_offset : 5[ppm]
Clipped : FALSE
Mod_Return : 1
Scans : 12
Total_scans : 12
X_90_width : 13.01[us]
X_acq_time : 2.9071769[s]
X_angle : 45[deg]
X_atn : 4[db]
X_pulse : 6.505[us]
Irr_mode : Off
Tri_mode : Off
Delay_forever : PULSE
Init_wait : 1[s]
Recyc_gain : 38
Relaxation_delay : 5[s]
Repetition_time : 7.9071769[s]
Temp_get : 23.4[dC]
abundance
X : parts per Million : 1H
8.86
2.91
6.03
2.91
6.02
2.9
2.8
9.1844
7.8127
7.8065
7.4977
7.4820
7.4686
5.3987
4.1781
4.1621
4.1463
4.1303
1.7780
1.7659
1.7345
1.2979
1.2821
0.9896
0.8796
0.8544



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