SYNTHESIS AND EVALUATION OF MULTICATIONIC IONIC LIQUIDS AS GAS CHROMATOGRAPHIC STATIONARY PHASES AND SYNTHETIC POLYMERS AS CHIRAL HPLC STATIONARY PHASES

by

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This dissertation is dedicated to the man who taught me the most valuable lessons in life leading by example and never gave me a chance to stray even though I can't remember him saying 'no/don't' a whole lot; my father
And to the woman who trusts me wholeheartedly and thinks I can never do wrong; my mother.

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ABSTRACT

SYNTHESIS AND EVALUATION OF MULTICATIONIC IONIC LIQUIDS AS GAS CHROMATOGRAPHIC STATIONARY PHASES AND SYNTHETIC POLYMERS AS CHIRAL HPLC STATIONARY PHASES

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Due to the characteristics unique to ionic liquids (ILs), they are found in a plethora of applications from simple liquid-liquid extractions to a proposed liquid medium for a lunar telescope. These applications require a thorough knowledge of the physical and chemical properties of ionic liquids and the knowledge to tune the structure to obtain the desired properties. In this dissertation I have described the systematical design and synthesis of a large number of dicationic, trigonal tricationic and linear tricationic ionic liquids. Their physicochemical properties have been characterized and a comprehensive study on the structural variations attributing to changes in properties such as melting point, thermal stability, viscosity, density and miscibility has been carried out.

In the next section, application of trigonal tricationic ionic liquids (TTILs) as gas chromatographic stationary phases is discussed. Solvation parameters of these TTILs obtained through Abraham solvation parameter model were different from other ILs. Some of these TTILs were found to be highly polar stationary phases similar to the commercial SP-2331 (a cyanopropyl phase commercialized by Supelco-Sigma-Aldrich) but with better peak shapes for highly polar analytes, higher thermal stabilities and in some cases unique selectivities.

In the last section, the development of three polymeric chiral stationary phases for high performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) is discussed. These were found to be exceptional stationary phases for target chiral analytes in both normal phase HPLC as well as SFC. They showed faster separations and good sample loading capacity with promising preparative LC capability.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction to Ionic Liquids

Ionic liquids (ILs) are defined salts that exist as liquids below 100 °C. Those that are liquids at ambient temperatures are called room temperature ionic liquids (RTILs).[1] In earlier years names such as liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses have been used to identify ILs but now 'ionic liquid' is the widely accepted term in the scientific community. The first 'designed' synthesis of a room temperature ionic liquid dates back to 1914.[2] Paul Walden synthesized ethylammonium nitrate which had a melting point of 12 °C to study the electrical conductivity. He observed that this anhydrous organic salt demonstrated phenomena (conductivity) observed with fused inorganic salts at higher temperatures while physical appearance (density, viscosity) resembled ordinary aqueous and non aqueous solvents. This very fact has led ILs to attract lot of attention in many different areas of science today.

Even though Walden discovered the unique characteristics of ILs at the beginning of the century, it was not until 1980's that ILs garnered the attention of the scientific community. John Wilkes at United States Air Force Academy was conducting research for alternate electrolytes in batteries and synthesized alkyl substituted imidazolium chloroaluminates ($R\text{-}Im^+ AlCl_4^-$, R = Me, Et, Pr, Bu) and alkylpyridinium chloroaluminates. These showed wider liquid temperature ranges and electrochemical

windows than any electrolytes they had synthesized before.[3] However the air and moisture sensitivity of these ILs limited their practical use. In 1992 Wilkes *et al.* overcame this problem by switching the anion to tetrafluoroborate and acetate anions.[4] The first air and water stable ionic liquid was 1-ethyl-3-methylimidazolium tetrafluoroborate denoted as [EtMeIm]BF_4. Since then many different cation and anion combinations have been used to synthesize ionic liquids. The most common types used today are shown in Figure 1.1 and the physical difference between an inorganic salt and an ionic liquid is shown in Figure 1.2.

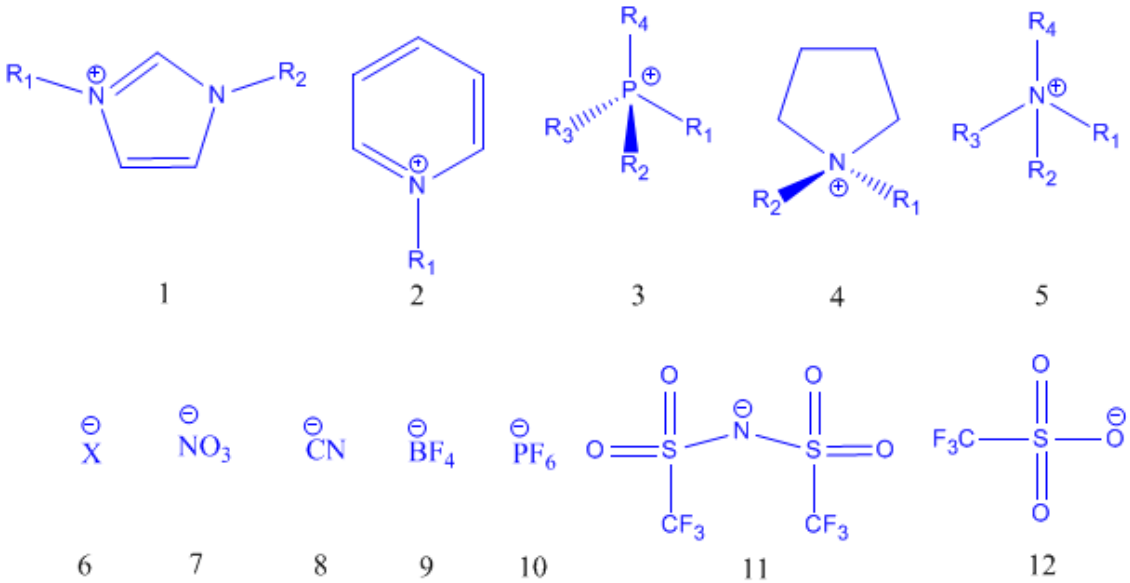


Figure 1.1 Common cations and anions used in ionic liquids synthesis.
Cations: 1. Imidazolium, 2. Pyridinium, 3. Phosphonium, 4. Pyrrolidinium, 5. Tetraalkyl ammonium, Anions: 6. Halides (Chloride, Bromide, Iodide), 7. Nitrate, 8. Cyanide, 9. Tetrafluoroborate, 10. Hexafluorophosphate, 11. Bis(trifluoromethanesulfonyl)imide, 12. Trifluoromethanesulfonate.

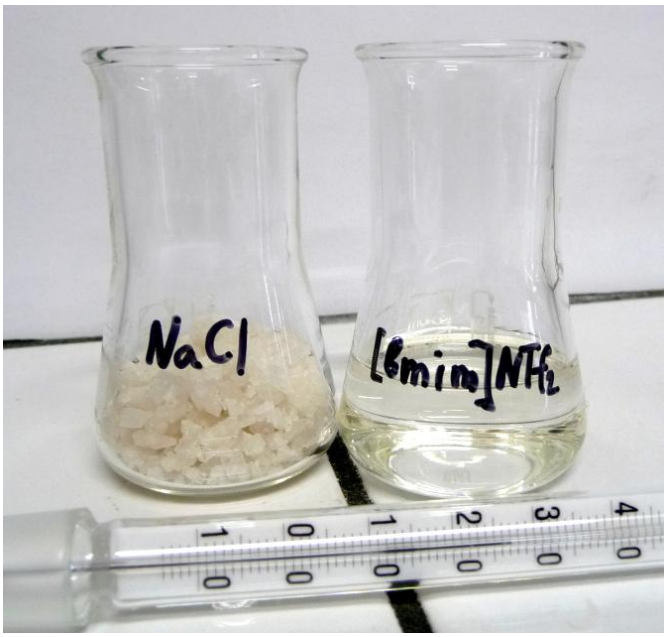


Figure 1.2 Rock salt (m.p. 801 °C) and an ionic liquid (m.p. 2 °C).
(Image source: http://en.wikipedia.org/wiki/Ionic_liquid)

As can be seen from Figure 1.1 the cations used for IL synthesis are large organic cations. Because of the size, asymmetry and charge distribution of the cation the electrostatic attraction between cation and anion (lattice energy in inorganic salts) is weakened giving rise to low melting salts.[5, 6] By delocalizing the charge in the anion the melting point can be further lowered. For this reason bis(trifloromethane sulfonyl)imide anion (11 in Figure 1.1) first used by Michael Graetzel in 1996 [7] is the most popular anion to produce the lowest melting ILs today.

Ionic liquids have unique properties such as negligible vapor pressures at room temperature, wide temperature ranges for liquid phase (~300 °C), good thermal stability over a wide temperature range, wide range of viscosities, resistance to decomposition for an extended period of time, high ionic conductivities (>10^{-4} S/cm) compared to molecular solvents, large electrochemical windows (>1V) and can undergo multiple

solvation interactions that enable them to be excellent solvents for many types of analytes.[8, 9] Because of these features ILs have found applications in many areas of research from liquid – liquid extractions,[10, 11] replacement of volatile organic solvents in organic/organometallic synthesis and catalysis,[1, 12-14] solvents for high temperature reactions,[15] as chromatographic stationary phases and additives,[16, 17] electrolytes in photovoltaic cells and fuel cells,[7] to the proposed fluid component of an extremely large diameter spinning liquid mirror telescope placed on the moon.[18] In the following section some of these applications are discussed in detail. In the remainder of the dissertation I will discuss my contribution to enhance the understanding of ILs and their properties as applied to separation science.

1.2 Ionic Liquids in Analytical Chemistry

1.2.1 ILs in Extraction

Extraction remains one of the most popular sample pretreatment methods for chemical analysis. The technique requires two immiscible phases into which the desired sample and impurities partition with unequal partition coefficients. This enriches one over the other and leads to isolation of the desired product. Ionic liquids are ideal for this application by virtue of their tunability to be soluble or insoluble in a particular solvent through the adjustment of accompanying anion.[19, 20] Since the late 1990's researchers have experimented with ionic liquids as replacements for volatile organic solvents. The types of analytes that can be extracted with the use of ILs vary from metal ions and small molecules to large biomolecules such as DNA. A brief description of such applications is given in the following section.

1.2.1.1 Direct use of ILs for Extraction

In 1998 Rogers *et al.* found that a group of benzene compounds show partitioning behavior in BMIM BF_4 and PF_6 /water system similar to that of the 1-Octanol/water system.[10] Since then, many types of analytes such as acids,[21] aromatic amines,[22] phenolic alkaloids,[23] aliphatic and aromatic hydrocarbons,[24] and polycyclic aromatic hydrocarbons (PAHs),[25] have been extracted directly to ionic liquids. Another important application is desulfurization of diesel fuel using 1-alkyl-3-methylimidazolium chloride ionic liquids.[26, 27] In 2001 Wasserscheid *et al.* first discovered the exceptional extraction capability for dibenzothiphene in diesel fuel using these ionic liquids.[11] Later pyridinium based ILs were used for this purpose. [28]

1.2.1.2 ILs and Chelating Agents

Ionic liquids can also be used in conjunction with chelating agents such as crown ethers or calixarenes to extract analytes of interest such as metal ions. Some examples for these are; extraction of Sr^{2+} into imidazolium ILs in the presence of dicyclohexyl-18-crown-6-ether,[29] extraction of Ag^{+} with pyridinocalix[4]arene in 1-alkyl-3-methylimidazolium PF_6,[30] extraction of La^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+} with thenoyltrifluoroacetone in 1-alkyl-3-methylimidazolium [C_nMIM] NTf_2,[31, 32] and extraction of gold nano particles and nanorods with thiols and amines in BMIM PF_6.[33]

1.2.1.3 Liquid Phase Microextraction (LPME)

Microextraction is a popular technique that can be used when the sample sizes are limited. Ionic liquids are ideal as the extraction solvent because of their non-volatility, ability to form multiple solvation interactions, high viscosity, and immiscibility with water. These can be used in both direct-immersion and headspace (HS) LPME.[34]

For example in 2003 Liu *et al.* determined that in a drop-based LPME experiment, polycyclic aromatic hydrocarbons (PAHs) showed higher extraction enrichment in the $[C_nMIM][PF_6]$ ionic liquid due to its ability to form a larger drop volume in the microsyringe needle compared to 1-octanol.[35] Similarly BMIM PF_6 was used in HS-LPME and HS-SDME (headspace-single-drop microextraction) in conjunction with HPLC to extract phenols[36] and chlorobenzenes[37, 38] from environmental water samples

1.2.1.4 Solid Phase Microextraction (SPME)

Because of the non-volatility of ionic liquids, drop-based LPME is incompatible with gas chromatography (GC). Instead in SPME ionic liquid coated fibers are used to extract analytes that can later be desorbed in the GC inlet at higher temperatures (see Figure 1.3).

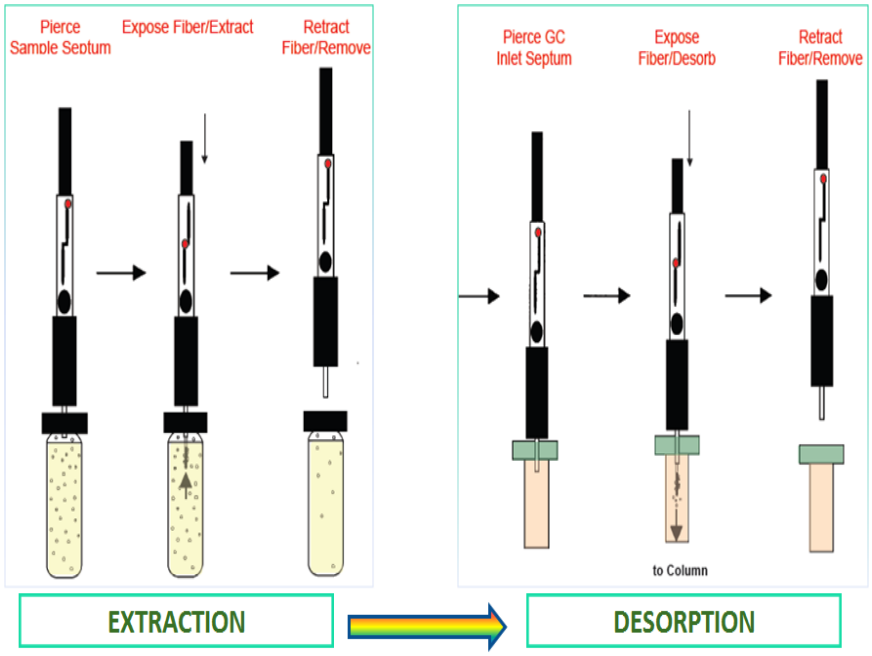


Figure 1.3 Extraction and desorption procedure for a SPME-GC system.
(Image source: http://www.sigmaaldrich.com/etc/medialib/docs/promo/Bulletin/1/basic-spme-sept-09.Par.0001.File.tmp/basic-spme-sept-09.pdf, Accessed: 02-02-2011)

The first application of ILs as SPME fiber coating material was reported by Liu *et al.* in 2004. They used a 1-octyl-3-methylimidazolium PF_6 coated fiber for headspace extraction of benzene, toluene, ethylbenzene, and xylene (BTEX) of paint.[39] Later Anderson *et al.* used a polymerized ionic liquid coating to extract fatty acid methyl esters (FAMEs) and other esters.[40] In both these examples the ionic liquid was physically coated on the solid support of the fiber. In 2010 Wanigasekara *et al.* developed the first bonded ionic liquid polymer coating for SPME.[41] These fibers show better mechanical strength and durability and were more stable for direct immersion applications than the previous physically coated IL fibers.

1.2.2 ILs in Mass Spectrometry

1.2.2.1 MALDI Matrices

MALDI (matrix-assisted laser desorption ionization) is a soft ionization technique that is usually employed to detect large and often labile molecules such as biomolecules and polymers.[42-44] The matrix facilitates ionization of the analyte by absorbing laser light. Ideal matrices must be non-volatile under high vacuum conditions, should dissolve (liquid matrix) or cocrystalize (solid matrix) analyte and must minimize analyte decomposition.[45] Commonly used matrices such as α-cyano-hydroxycinnamic acid are solids and such matrices may not be ideal for quantitative analysis due to sample heterogeneity problems. The signal may not be reproducible due to the presence/absence of hot-spots. In 2001 Armstrong *et al.* first investigated the possibility of using ionic liquids as MALDI matrices for the analysis of bradykinin, human insulin, horse skeletal apomyoglobin, and polyethylene glycol (PEG-2000).[45] In this study it was found that ILs produce much more homogeneous sample solutions with greater vacuum stability than most solid matrices. However, most traditional ionic

liquids failed to produce detectable signals. It was also noticed that some salts of CHCA and sinapinic acid (ionic liquids) produce higher signal intensities and lower limits of detection than their solid analogues (solid CHCA and sinapinic acid). Figure 1.4 shows a comparison of solid matrix and ionic liquid matrix used for analysis of insulin. A significant enhancement in the intensity of the molecular ion is observed in the IL matrix. A MALDI plate of CHCA (**A**) contains cracks, crystals, and numerous incongruities often found in solid matrices while the IL matrix (**B**) is homogeneous throughout. Therefore it was concluded that the choice of cation and anion in IL is critical for application as MALDI matrices. They must not only homogenously solubilize the analytes but also must facilitate ionization and volatilization of the sample.

In 2003 Armstrong group demonstrated the usefulness of ionic matrices to detect the molecular weight of DNA oligomers.[46] Subsequently, Tholey *et al.* used salts made from equimolar combinations of sinapinic acid, α-cyano-4-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid with organic bases as matrices to detect amino acids, sugars and vitamins.[47] They reported ionic matrices had better linearity, smaller standard deviations, and decreased analysis times compared to the molecular matrices. In the years that followed different research groups have used IL MALDI matrices for analysis various types of samples such as proteins and peptides,[48-50] Oligosaccharides and glycopeptides,[51-53] synthetic polymers,[54] and lipids.[55, 56]

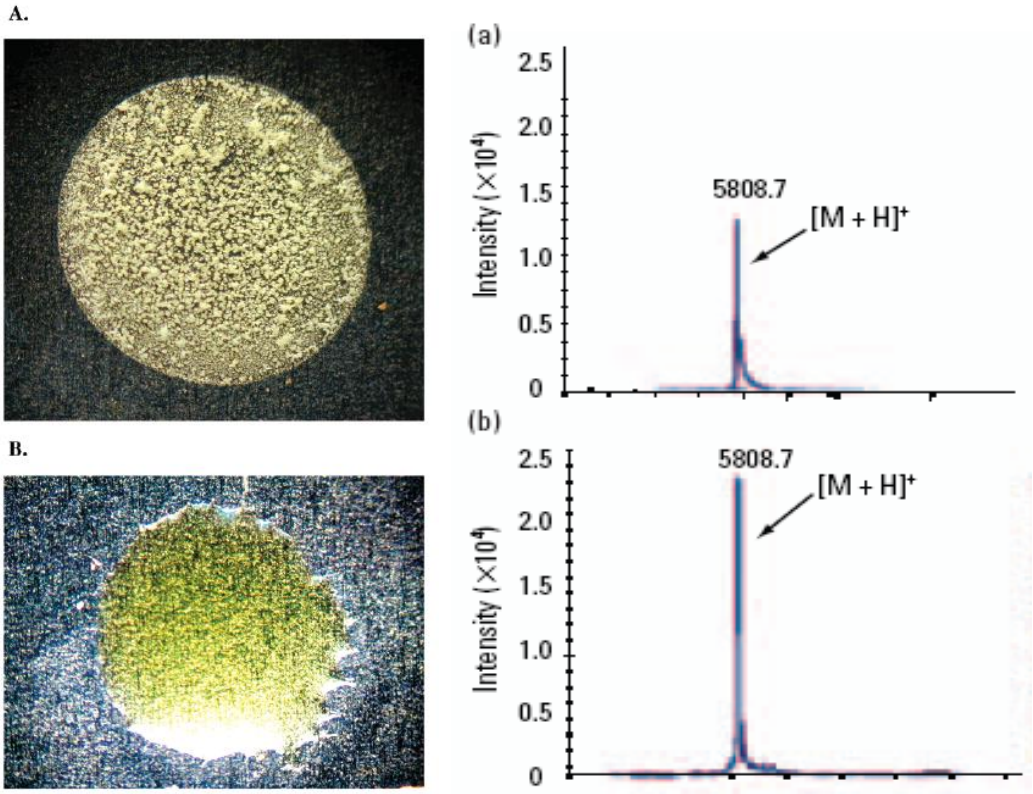


Figure 1.4 MALDI–MS spectra of insulin in the matrices (a) CHCA and (b) an IL. **A** and **B** images were reprinted from reference 45.

1.2.3 ILs in Capillary Electrophoresis

Capillary electrophoresis is a powerful separation technique that utilizes very small samples and solvents. The high peak efficiency is obtained because of the electroosmotic flow (EOF) that produces a flat flow profile (as opposed to parabolic flow profile generated in pressure driven processes). EOF is generated by the ionized silanol groups of the inner capillary wall. By modifying the surface charge of the capillary wall the EOF could be altered. For example, the separation of proteins in CE has always been problematic due to their surface adsorption resulting from the electrostatic attraction between negative capillary surface silanols and positively charged sites of the proteins. In 2003 Jiang *et al.* added an imidazolium based ionic liquid to the run buffer which dynamically coated the capillary surface and resulted in a reversal of surface charges. This improved the separation efficiency and repeatability of the proteins in CE.[57]

Ionic liquids can also be chemically bonded to the surface of the capillary (static coating) to reverse the EOF. Since the ionic liquids are immobilized on the silica capillary wall through covalent bonding, the static coated CE system is MS compatible whereas the dynamic coated system is not. Qin *et al.* bonded 1,3-dialkylimidazolium bases ionic liquid on the silica wall and baseline separated K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, and Ba^{2+} ions from the NH_4^+ matrix of urine.[58] Similar approaches were used to separate the positively charged drug Sildenafil (SL) and its metabolite,[59] and DNA.[60]

Ionic liquids are also used as buffer additives in non-aqueous CE. They dissolve in acetonitrile which is the most widely used solvent in non-aqueous CE and can be used to modify the analyte mobility and separation. Adding ionic liquids to non-

ionizable solvents increases the solubility of ionizable water-insoluble analytes such as dyes, aromatic acids, and polyphenols.[61, 62]

1.2.4 ILs in Liquid Chromatography

Adding ionic liquids in to the mobile phase solvent is shown to increase peak efficiency. The mechanism is similar to that of CE where the underivatized silanol groups of the stationary phase will be coated with the ionic liquid cations in a process similar to endcapping. It is found that imidazolium trifluoroborate ionic liquids were more effective than traditional mobile phase additives such as triethylamine, dimethyloctylamine and ammonia. This IL improves peak shapes and reduces retention times of polar analytes. An example for this is the separation of four basic compounds; norephedrine, ephedrine, pseudoehidrine, and methylephedrine on a C18 column with 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid.[63]

Furthermore, bonded ionic liquids are used as stationary phases for LC. Liu *et al.* used bonded imidazolium ILs as aion-exchange stationary phases to effectively and reproducibly separate ephedrines,[64] and common anions. [65, 66]

1.2.5 ILs in Gas Chromatography

Choices of available stationary phases for gas chromatography (GC) have been fairly constant for many years. The same basic types of columns that do analogous separations can be obtained from any of a large number of sources, world-wide. Recent research has indicated that unique new substances have been developed that will play an important role in GC column technology. These substances are ionic liquids (ILs). When used as GC stationary phases, melting points in the range of ~ - 40 °C to 50 °C are preferable. Ionic liquids have a number of properties that make them

exceptional stationary phases. For example: their viscosity can be varied over a broad range, they can have high thermal stabilities, they can be coated on fused silica capillaries with high efficiencies, they have unique solvent properties and they can be immobilized and crosslinked.[17, 20, 67-70] Indeed it was noted early on that ionic liquid stationary phases had a dual nature in that they separated nonpolar analytes as if they were nonpolar stationary phases and simultaneously separated polar analytes as if they were polar stationary phases.[71]

Another very important aspect of ionic liquid stationary phases is that their physico-chemical properties are almost infinitely tunable. That is a characteristic that is unavailable to all other classes of GC-stationary phases. With relatively simple synthetic modifications or changes to the IL's, cation, anion, the substituents thereon and their linkage chains, one can impact whatever solvent/selectivity characteristics are desired.

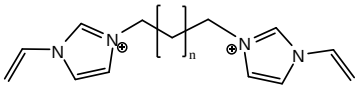
1.2.5.1 Types of ILs for GC

Figure 1.5 shows the structures of typical "tunable", high stability cations and anions that have been shown to be particularly useful as GC stationary phase components. Figure 1.6 shows the structure of two of the more common anions used in IL – GC formulations. The NTf_2^- anion tends to produce ionic liquids with lower melting points and somewhat lower polarities than the triflate anion. Also it provides excellent peak shapes for nonhydrogen bonding or weakly hydrogen bonding analytes, but tends to produce tailing peaks for alcohols, carboxylic acids and amines. The tailing peaks of these strong hydrogen bonding analytes can be minimized or eliminated by masking the effect of the NTf_2^- anion by using a cation containing an

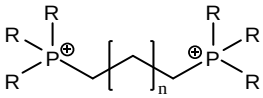
amide moiety (see trigonal cation in Figure 1.5 E or by utilizing the triflate anion. Examples of these behaviors will be shown throughout this monograph. The cations, (Figure 1.5) can be further selected and varied to emphasize or deemphasize any known solvation interactions including: n/π, dipolar, H-bond acidity, H-bond basicity and dispersion interactions. Clearly, the hydrocarbon linkage chains (connecting the charged moieties) produce less polar stationary phases than polyethylene glycol types. Shorter linkage chains result in more polar stationary phase than analogous longer chains. Imidazolium cations have a delocalized positive charge in contrast to phosphonium and pyrrolidinium cations (Figure 1.5 B and C). The NTf_2^- has a more delocalized charge and is more hydrophobic than the triflate anion.

While it is difficult to predict the future, it is clear that IL stationary phases will have a direct impact on specific areas of gas chromatography. Four representative areas are listed in Table 1.1. Examples of IL-based separations involving each of these “impact areas” will presented and discussed.

(A)

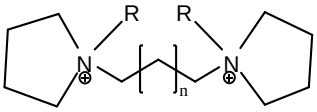


(B)



(R = alkyl or aryl)

(C)



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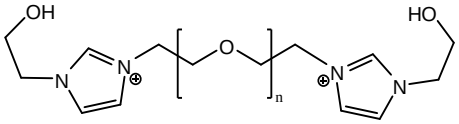
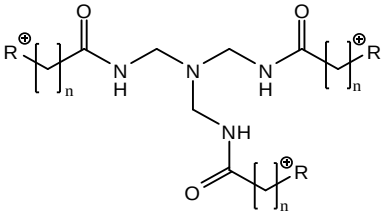
(D)



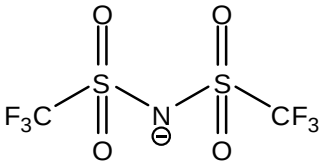
(E)



(R = substituted imidazoliums, phosphoniums, pyrrolidiniums, etc.)

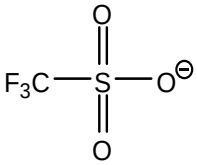
Figure 1.5 A – E are examples of some of the more useful IL cations for GC stationary phases.

(A)



NTf_2^-

(B)



TfO^-

Figure 1.6 Examples of some of the more useful anions for GC. (A) NTf_2^- is the abbreviation for Bis(trifluoromethanesulfonyl)imide anion, (B) TfO^- is the abbreviation for the triflate anion.

Table 1.1 Areas where ionic liquid stationary phases will impact GC
Reprinted with permission from reference 72.

I	New IL stationary phases will be introduced that are engineered to produce identical separations to current, often flawed commercial stationary phases. **Example:** The commercial polar stationary phase (TCEP) does some unique separations, but it has an upper temperature of only 140 ^{o}C and a sensitivity to oxygen and water vapor.
II	New IL stationary phases will be introduced that will have completely unique selectivities compared to any/all commercial columns. **Example:** The trigonal, amide-type of tricationic liquids and the hydroxyimidazolium(PEG)triflate IL.(see Figure 1.5)
III	New IL stationary phases of very high thermal stability are at hand.
IV	IL stationary phases should play a significant role in multidimensional separations because of their unique group selectivity and their natural or engineered orthogonality to existing stationary phases.

1.2.5.2 Polar IL Stationary Phases with Low Bleeds and High Thermal Stability

Polyethylene glycol/PEG/wax-type coatings are popular and ubiquitous polar stationary phases in GC. The “bleed temperature” can vary somewhat with the molecular weight of the polymers used and possibly pretreatment procedures used on the fused silica capillary. Typically the upper temperature limits for these columns are in the 240 °C to 280 °C range depending on the manufacturer. The figure 1.7 shows a comparison in the thermal stability/bleed profiles between a typical PEG GC column and a phosphonium ionic liquid-based column of approximately the same polarity (see structure in Figure 1.5 B). The “wax” stationary phase starts to show significant bleed at 280 °C and by 350 °C this stationary phase has been completely stripped from the fused silica capillary. At the same temperature (350 °C) the phosphonium IL column is just beginning to have detectable bleed. Figure 1.8 shows that there are minimal changes in the retention times of a rapeseed oil fatty acid methyl ester (FAME) mixture

on the phosphonium ionic liquid column after 80 hours of conditioning at 300 °C.[72]

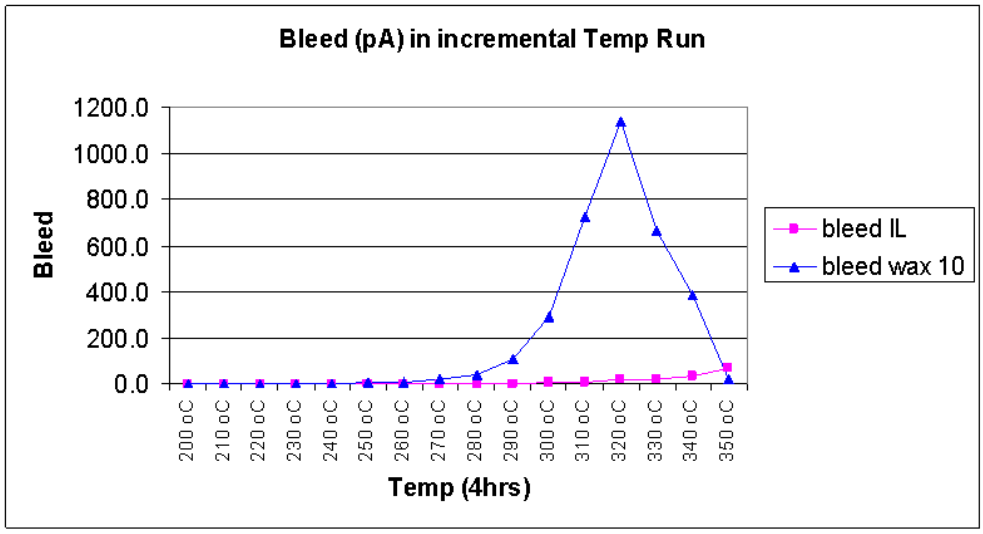


Figure 1.7 Comparison of column bleeding temperature between Supelcowax-10 column and the phosphonium NTf_2 IL column (see Figure 1.5 B for IL structure). Note that the columns were held at each temperature for four hours. Reprinted from reference 72.

1.2.5.3 Polar IL Stationary Phase with Same Selectivity and Higher Stability

One of the most polar GC stationary phases available today is 1,2,3 – tris (2-cyanoethoxy) propane (Figure 1.9). It has a maximum operating temperature of 140 °C and is moisture and oxygen sensitive. However, a divinylimidazolium NTf_2^- ionic liquid has been engineered to give the same selectivity (Figure 1.10) and it is both oxygen and moisture stable and has a thermal stability of ~240 °C. In addition the ionic liquid column (SBIL-100, Supelco, Bellefonte, Pennsylvania) shows unique selectivities for many other types of compounds. This is shown by the differences in the retention order of PCB congeners on the IL column (Figure 1.11) versus a commercial cyanopropylsilane column (SP-2331 Supelco, Bellefonte, Pennsylvania). Also note the faster elution times on the IL column. This was also seen for a different standard mixture versus the TCEP column (Figure 1.10).

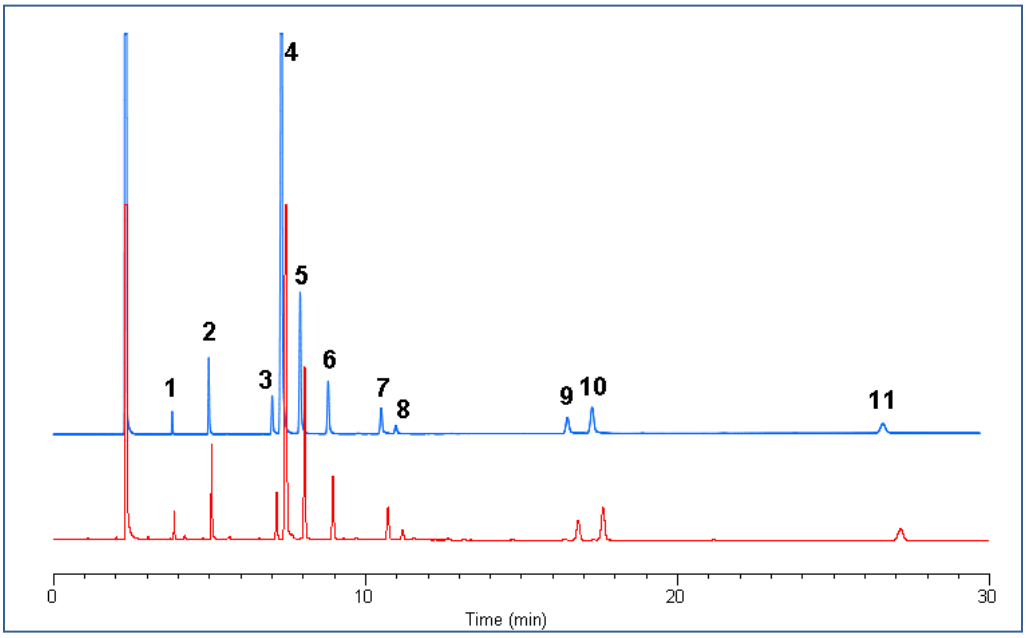


Figure 1.8 Comparison of retention behavior of Rapeseed oil FAMEs on the phosphonium IL (see Figure 1.5 B for structure) column before and after thermal treatment at 300 ^{o}C for 80 hours. 1 Myristic (C14:0), 2 Palmitic (C16:0), 3 Stearic (C18:0), 4 Oleic (C18:1n9c) 5 Linoleic (C18:2), 6 Linolenic (C18:3), 7 Arachidic (C20:0), 8 cis-11-Eicosenoic (C20:1), 9 Behenic (C22:1), 10 Erucic (C22:1), 11 Lignoceric (C24:0). Column dimensions: 30 m x 250 µm i.d., d_f 0.20 µm. Separation conditions: 300 °C isothermal. Reprinted with permission from reference 72.

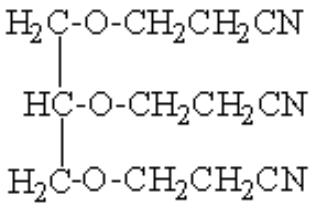


Figure 1.9 Structure of the polar GC stationary phase TCEP; (1,2,3-Tris(2-CyanoEthoxy)Propane which is oxygen and moisture sensitive, and has an upper temperature limit of 140 °C. Reprinted with permission from reference 72.

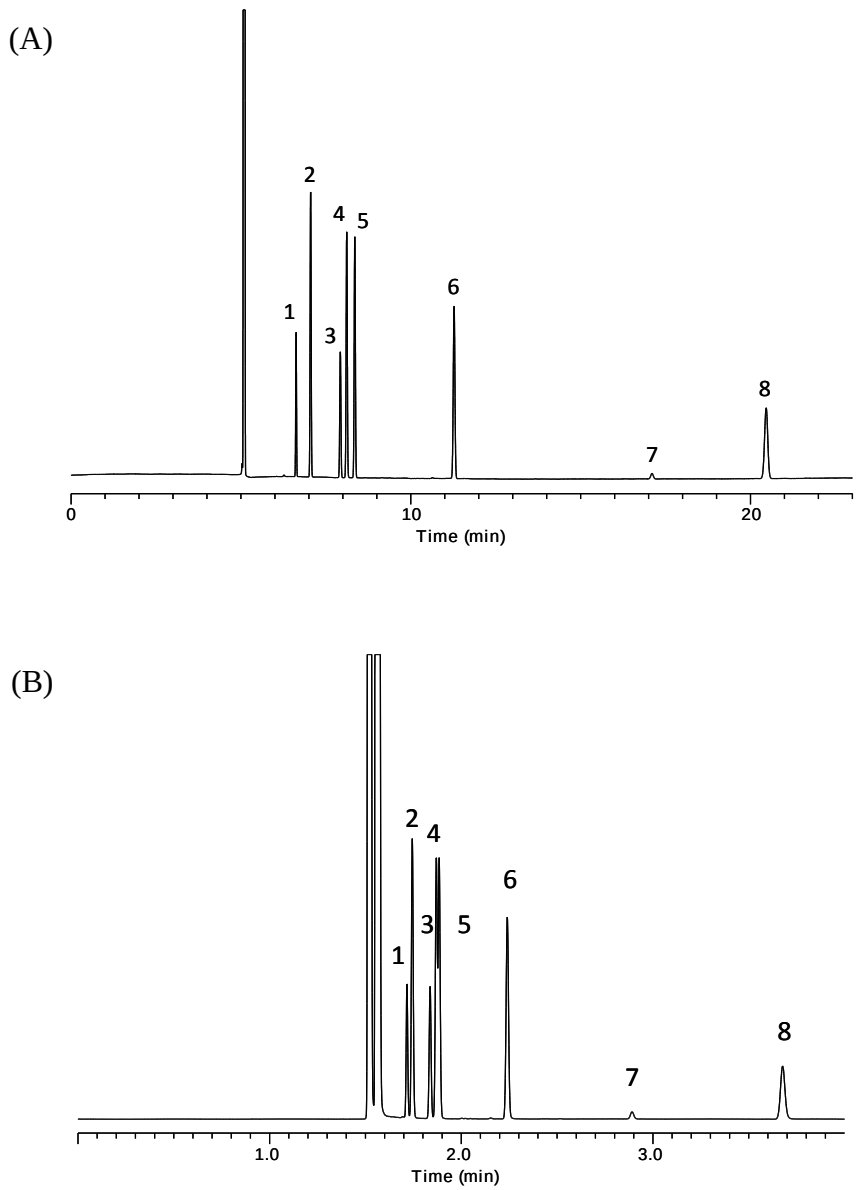


Figure 1.10 Separation of test analytes on (A) a 60 m x 250 µm i.d. TCEP Column at 110 °C and on (B) a 30 m x 250 µm i.d. SLB-IL100 (see Figure 1.5 A for IL structure) at 110 °C.

Compounds:1. n-Tridecane, 2. Toluene 3.Ethylbenzene 4.p-Xylene 5.Isopropylbenzene (Cumene) 6.1,2,4-Trimethylbenzene7.1,2,4,5-Tetramethylbenzene (Durene) 8.Cyclohexanone Reprinted with permission from reference 72.

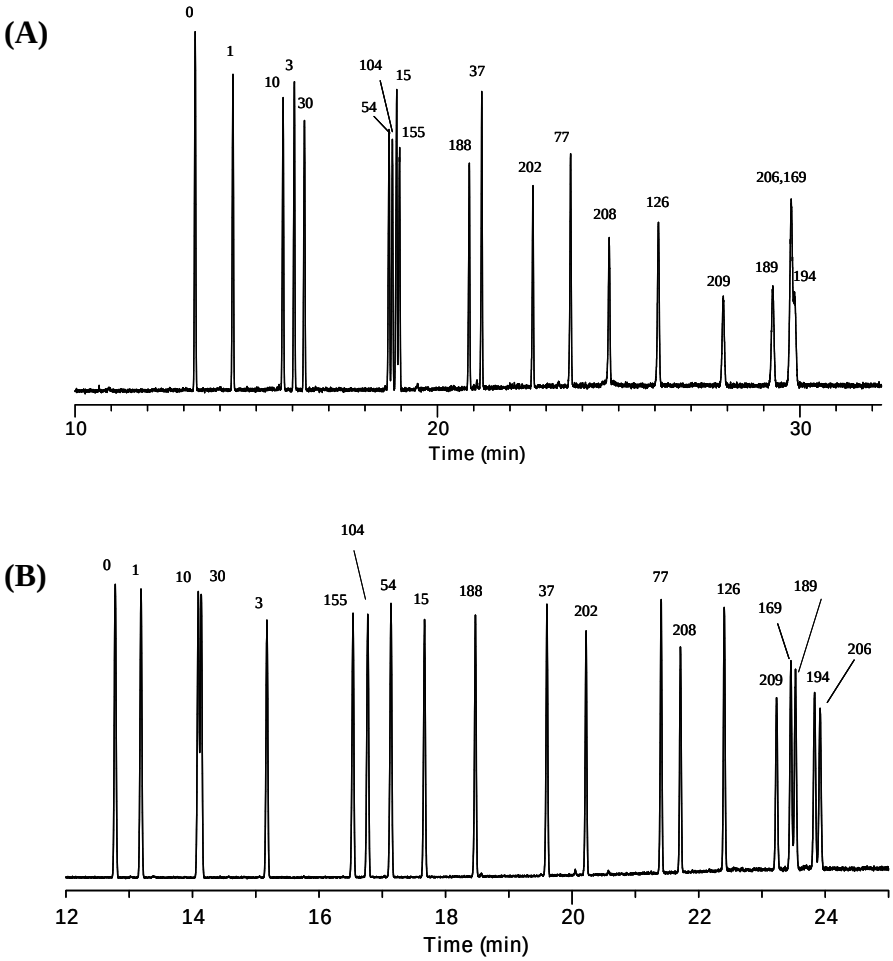


Figure 1.11 Comparison of the selectivity for polychlorinated biphenyls (PCB) congener standards, biphenyl through decachlorobiphenyl, on the (A) SP-2331 column (a highly polar cyanosilicone stationary phase) and (B) SLB-IL100 ionic liquid column (see Figure 1.5 A for IL structure).

Column dimensions: 30 m x 250 µm i.d., d_f 0.20 µm. Separation conditions: 60 °C (1 min.), 8 °C/min. to 230 °C. Compounds in the mix:- 0: Biphenyl, 1: 2-monochlorobiphenyl, 3: 4-monochlorobiphenyl, 10: 2,6-dichlorobiphenyl, 15: 4,4'-dichlorobiphenyl, 30: 2,4,6-trichlorobiphenyl, 37: 3,4,4'-trichlorobiphenyl, 54: 2,2',6,6'-tetrachlorobiphenyl, 77: 3,3',4,4'-tetrachlorobiphenyl, 104: 2,2',4,6,6'-pentachlorobiphenyl, 126: 3,3',4,4',5-pentachlorobiphenyl, 155: 2,2',4,4',6,6'-hexachlorobiphenyl, 169: 3,3',4,4',5,5'-hexachlorobiphenyl, 188: 2,2',3,4',5,6,6'-heptachlorobiphenyl, 189: 2,3,3',4,4',5,5'-heptachlorobiphenyl, 202: 2,2',3,3',5,5',6,6'-octachlorobiphenyl, 194: 2,2',3,3',4,4',5,5'-octachlorobiphenyl, 208: 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl, 206: 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl, 209: Decachlorobiphenyl. Reprinted with permission from reference 72.

1.2.5.4 IL Stationary Phases with New Selectivities

Ionic liquid stationary phases also appear to have excellent selectivity for cis-trans isomers of FAMEs, as shown in Figure 1.12. Positional geometric FAME isomers typically are resolved using 100 m × 0.25 mm highly polar cyanosilicone stationary phases. Figure 1.12 shows that a 60 m × 0.25 mm SLB-IL100 column is capable of providing resolution of a number of the monoene, diene and triene fractions of the C18 FAME isomers. Better resolution is seen of the triene compared with that provided by the longer cyanosilicone column.[73]

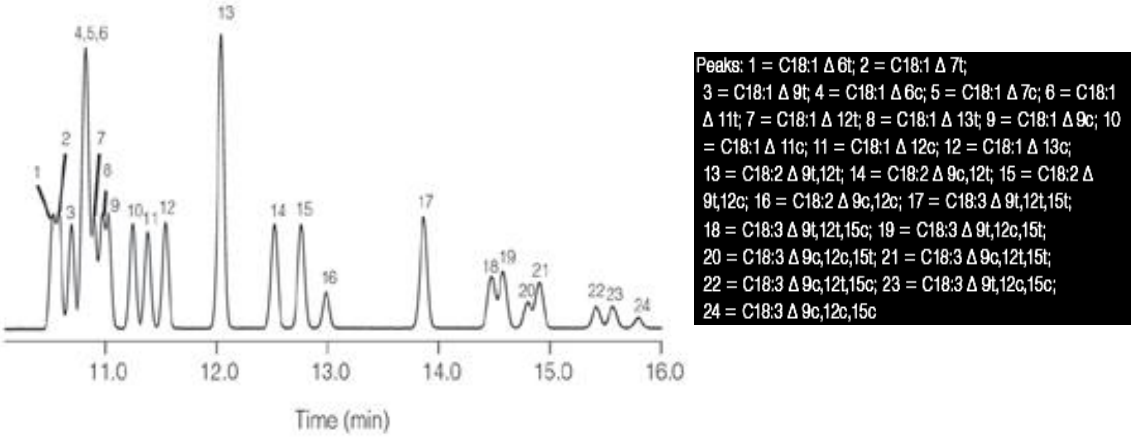


Figure 1.12 Separation of cis-trans C18 FAME isomers on a 60 m SLB-IL100 column. GC separation condition: 170 °C, isothermjal; 30 cm/s He carrier gas; flame ionization detection. Reproduced with the permission of reference 72.

Perhaps the most polar ionic liquid stationary phases yet tested are based on hydroxyimidazolium (PEG) triflate (Figure 1.5 D). In addition to being highly polar and possessing unique selectivities, the triflate anion gives excellent peak shapes for analytes with strong hydrogen bonding groups (esp. alcohols, diols, carboxylic acids

and amines). This is illustrated in Figures 1.13 and 1.14. A chromatogram for a mixture of n-alkanes and alcohols is shown in Figure 1.13. Note how much the hydrocarbons are shifted to lower retention values relative to the alcohols. Also note the excellent peak shapes for both groups of analytes on this relatively short 10m column. The Grob mix is separated on the same 10m column as shown in Figure 1.14. Because of the triflate anion, the acidic and basic analytes (6, 7, 11, and 12) have good peak shapes. Also note that peak 8 (methyl decanoate) elutes before peaks 4 and 3 (i.e., 1-octanol and 1-nonanal). This is quite unusual and is indicative of the high polarity of this IL stationary phase.

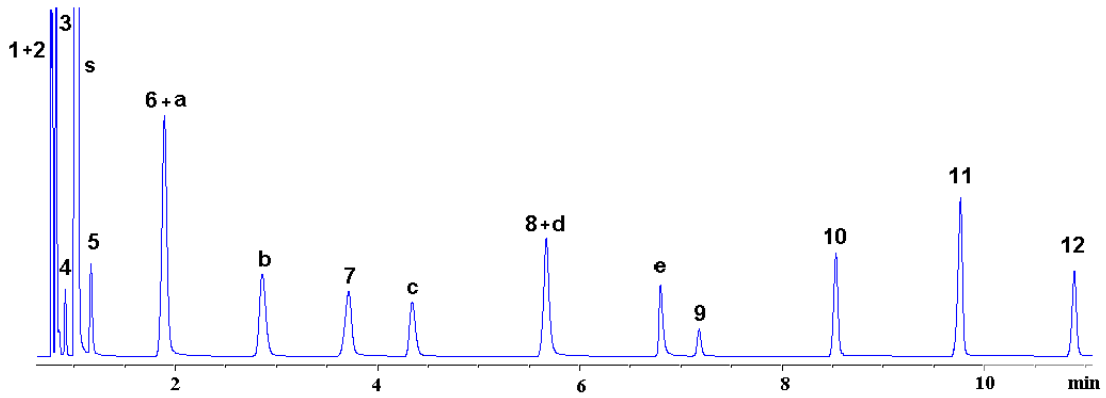


Figure 1.13 Separation of homologous alkane and alcohol mixture in $HyIm_2PEG_3TfO_2$ column. Compounds: **1** pentane, **2** hexane, **3** heptane, **4** octane, **5** nonane, **6** decane, **7** undecane, **8** dodecane, **9** tridecane,**10** tetradecane, **11** pentadecane, **12** hexadecane, **a** ethanol, **b**1-propanol, **c** 1-butanol, **d** 1-pentanol, **e** 1-hexanol, **s** dichloromethane,. GC separation conditions: 26 °C for 3 min,10 °C min^{-1} to 160 °C; 1 mL min^{-1} He; FID. Chromatogram was obtained using 10 m x .25 mm x 0.15 µm d_f column. Reprinted with permission from reference 72.

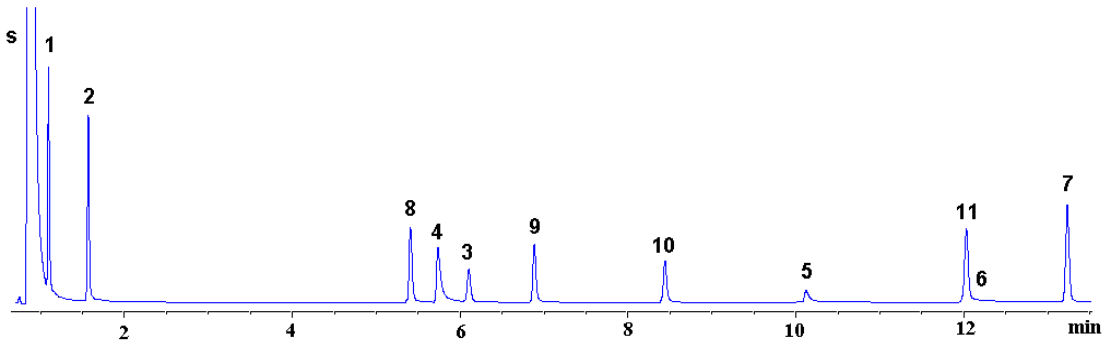


Figure 1.14 Separation of Grob test mixture in $HyIm_2PEG_3TfO_2$. Compounds: **1** n-decan, **2** n-undecane, **3** 1-nonanal, **4** 1-octanol, **5** 2,3-butanediol, **6** 2-ethylhexanoic acid, **7** 2,6-dimethylphenol, **8** methyl decanoate, **9** methyl undecanoate, **10** methyl dodecanoate, **11** 2,6-dimethylaniline, **12** dicyclohexylamine (eluted at 19 min.), **s** dichloromethane,. GC separation conditions: 40 °C to 190 °C at 6 °C min^{-1};1 mL min^{-1} He; FID. Chromatogram was obtained using 10 m x .25 mm x 0.15 µm d_f column. Reprinted with permission from reference 72.

1.2.5.5 IL Stationary Phases for Comprehensive GC

Given the unique characteristics of ionic liquid/stationary phases it is apparent that they will be quite useful for comprehensive multidimensional separations. Recent reports[74, 75] involving GCxGC indicate that ionic liquid columns used in conjunction with conventional columns (in either the first or second dimension) show unique group selectivities. For example when analyzing diesel fuel by GC x GC, the best group separation of saturated hydrocarbons vs. monoaromatic vs. diaromatic compounds was obtained when using a phosphonium NTf_2^- IL in the first dimension and a nonpolar HP-5 column in the second dimension.[74]

In other work, a GC x GC separation (which used a divinylimidazolium triflate IL in the second dimension) was the only combination able to completely isolate compounds containing phosphorous-oxygen (P-O) moieties from all other compounds.[75] This type of group selectivity is particularly important when analyzing

pesticides, nerve agents and residues thereof. Tunable dual column GC with a divinylimidazolium NTf_2^- stationary phase was used in conjunction with headspace sampling to characterize US currency and other complex samples.[76]

Figure 1.15 is a comparison of the GC x GC/ TOF-MS profiles of a petroleum distillate using two different column sets.[77] Figure 1.15 B utilized a phosphonium NTf_2^- column in the second dimension rather than the conventional PEG/wax column (Figure 1.15 A). As can be seen the important toxic compound, diphenylmethane, is only resolved when using the IL column (Figure1.15 B). In addition it appears that the group separations are more definitive in the column set that utilizes the ionic liquid stationary phase.

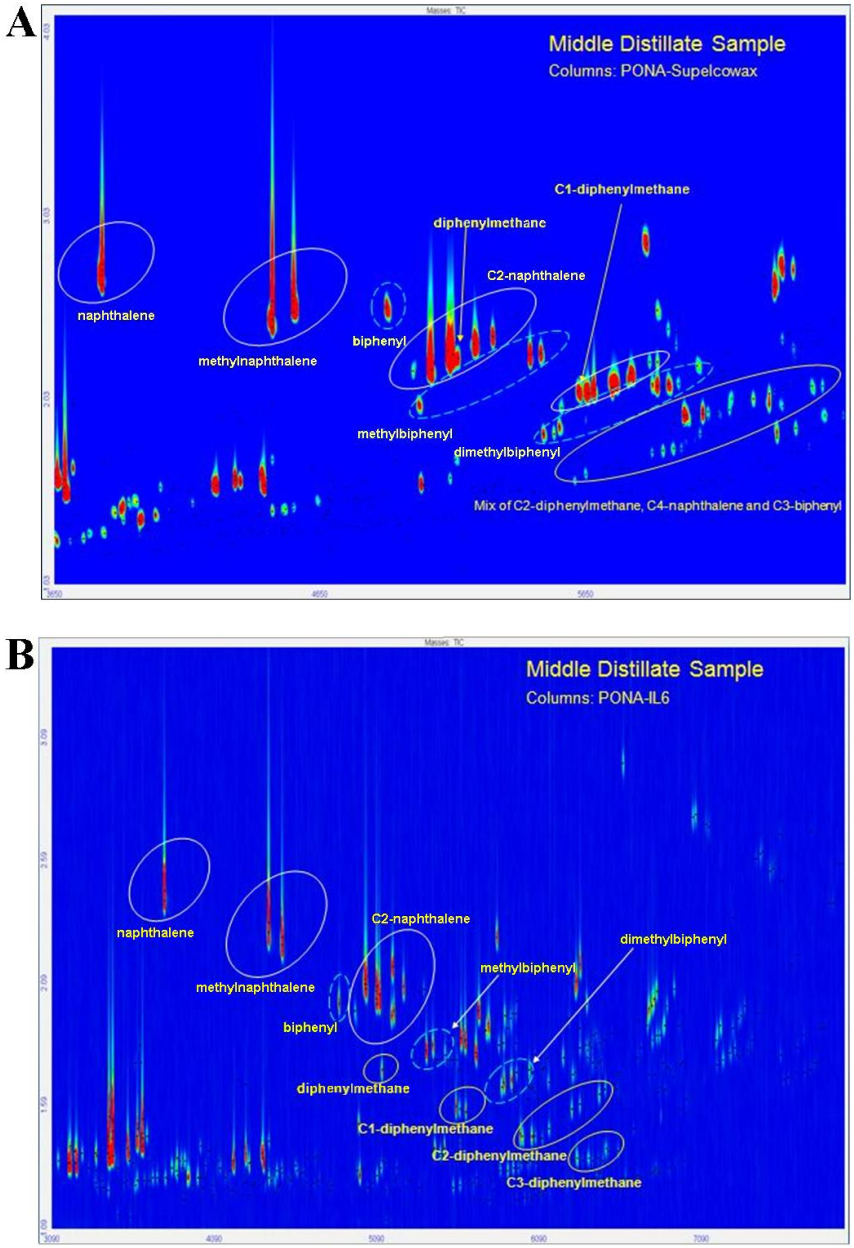


Figure 1.15 GCxGC/TOF MS characterization of petroleum distillate sample analyzed by column set 1: PONA (Crossbond 100% dimethyl polysiloxane-optimized for hydrocarbon analysis) /WAX (A) and column set 2: PONA/Ionic Liquid (see Figure 1.15 B for IL structure) column (B).Reprinted with permission from reference 77.

1.2.5.6 Conclusions

Undoubtedly the past two years have been a “benchmark” period for ionic liquids in gas chromatography. They have become widely available to both academic and industrial scientists for the first time. Although ionic liquids will continue to be the focus of cutting edge research in separation science in the foreseeable future, the current IL materials are about to be thoroughly examined and tested by every-day users of GC. They will be doing things to and with these columns that were not the focus of academics. Through this coming harsh reality we will learn considerably more about the uses and limitations of ionic liquid stationary phases. These lessons will then lead to another generation of ILs; after all they are almost infinitely tunable.

1.3 Organization of the Dissertation

In chapter 2 of this dissertation the synthesis and physico-chemical properties of geminal dicationic ILs are discussed. The changes of physical properties compared to the traditional monocationic ILs are also discussed. Also, methods of altering the physical properties by manipulating the cationic moieties, linkage chain length of the two cations, and by changing the anion are also demonstrated. These are distinctive advantages of multi-cationic ionic liquids compared to common ILs.

In chapter 3, the above discussion is extended to trigonal tricationic ILs having three identical cationic moieties attached to a core structure. The change of physico-chemical properties with the rigidity/flexibility of the core structure and the type of cation and anion is also discussed.

In chapter 4, the first ever synthesis of linear tricationic ionic liquids is discussed. The difference between the trigonal tricationic ILs and linear tricationic ILs

in terms of physical properties is explored. Furthermore, the electrowetting properties of these ionic liquids were also examined.

In chapter 5, the applicability of trigonal tricationic ILs as gas chromatographic stationary phases was explored. The structural features corresponding to very unique analyte selectivities and retention behaviors were also discussed. The separation capabilities of these new stationary phases are compared to the commercial phases with similar polarities.

In chapter 6, synthesis and evaluation of new chiral stationary phases for HPLC and SFC (supercritical fluid chromatography) based on derivatives of commercially available phase P-CAP-DP is discussed. The performance of these new phases are compared to the commercial phase and found to show complementary selectivities.

CHAPTER 2

UNSYMMETRICAL DICATIONIC IONIC LIQUIDS: MANIPULATION OF PHYSICOCHEMICAL PROPERTIES USING SPECIFIC STRUCTURAL ARCHITECTURES

2.1 Abstract

Geminal dicationic ionic liquids (ILs) have been proposed as novel ultra stable separation phases for gas chromatography in recent years due to their superior physical properties such as high thermal stability and low volatility. However due to increased charge density, dicationic ILs tend to exhibit higher melting points compared to traditional ILs. In this work, 21 new structurally related dicationic ILs were synthesized in order to investigate their structure-property relationships. We have found that the melting point and other physical properties can be altered and engineered by manipulating the cationic moieties with respect to each other, thereby forming unsymmetrical dicationic liquids. By this method we were able to manipulate the melting point between – 65 °C and 156 °C. Viscosity is manipulated between 101 cSt and 1217 cSt. These ILs can be modified to be miscible or immiscible with H_2O.

2.2 Introduction

Geminal dicationic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ionic liquids (ILs).[78] Consequently they have been proposed as novel high temperature lubricants,[79] solvents in high temperature reactions,[15, 80, 81] ultra-stable separations phases,[67, 76, 82]

and have potential in extractions similar to monocationic liquids[10] and mass spectrometry where ordinary ILs fail.[45, 46, 83] However, they possess the same desirable solvation properties as the more common singly charged ionic liquids.[9] They are able to dissolve all manner of polar and non-polar molecules including some proteins, peptides, polymers and simple organic molecules. In some instances geminal dicationic liquids exhibited higher melting points than their monocationic analogues, sometimes even extending beyond the accepted IL region of 100 ^{0}C.[84] The most common methodology applied to lower the melting point is changing the counter anion. But this alters the solvation properties of the IL, and even in cases where optimal anions (e.g. NTf_2^-, PF_6^-, BF_4^-, etc.) are used, some dicationic salts remained solids. We have found that the melting point and other physical properties can be altered and engineered by manipulating the cationic moieties thereby forming unsymmetrical dicationic liquids. The "tunability" of ILs (i.e. the ability to alter, control and tailor their structure as desired) had been touted as one of their virtues.

In this publication we demonstrate that dicationic liquids and their properties can be "tuned", controlled or altered to a greater extent than more conventional ILs. This approach is exclusive to dicationic liquids or other multi functional ions. In fact it appears that an advantage of dicationic ionic liquids over monocationic ionic liquids is that they provide more opportunities to fine tune their physical and chemical properties. Each structure contains two cationic moieties and two anionic moieties that can be varied with respect to each other. To understand the structural change that corresponds to a particular physical property, a series of related compounds with systematic structural variations were synthesized and investigated (see Figure 2.1). The structural variations investigated include the effect of symmetry of the cationic

fragment (i.e. having identical or dissimilar cationic moieties), the length of the alkyl chain substituted at the third position of the imidazole ring, and the type of accompanying anions. The anions studied include bis(trifluoromethylsulfonyl)imide, bromide, hexafluro-phosphate, tetrafluoroborate, and trifluoromethanesulfonate (NTf_2^-, Br^-, PF_6^-, BF_4^-, and TfO^- respectively). The spacer alkyl chain length between the two cationic moieties was set to be five carbons. This value was chosen based on previous research in our group.[78] It has been shown that if chain length was short (~3), ILs tend to be solids at room temperature irrespective of their other structural features. Similarly, when longer chain lengths were chosen (9,12), most ILs tend to be liquids at room temperature due to high conformational degrees of freedom. Therefore 5 is the best chain length for this study because of the melting point's sensitivity to the changes in the rest of the structure. The physicochemical data obtained for each ionic liquid is summarized in Table 2.1.

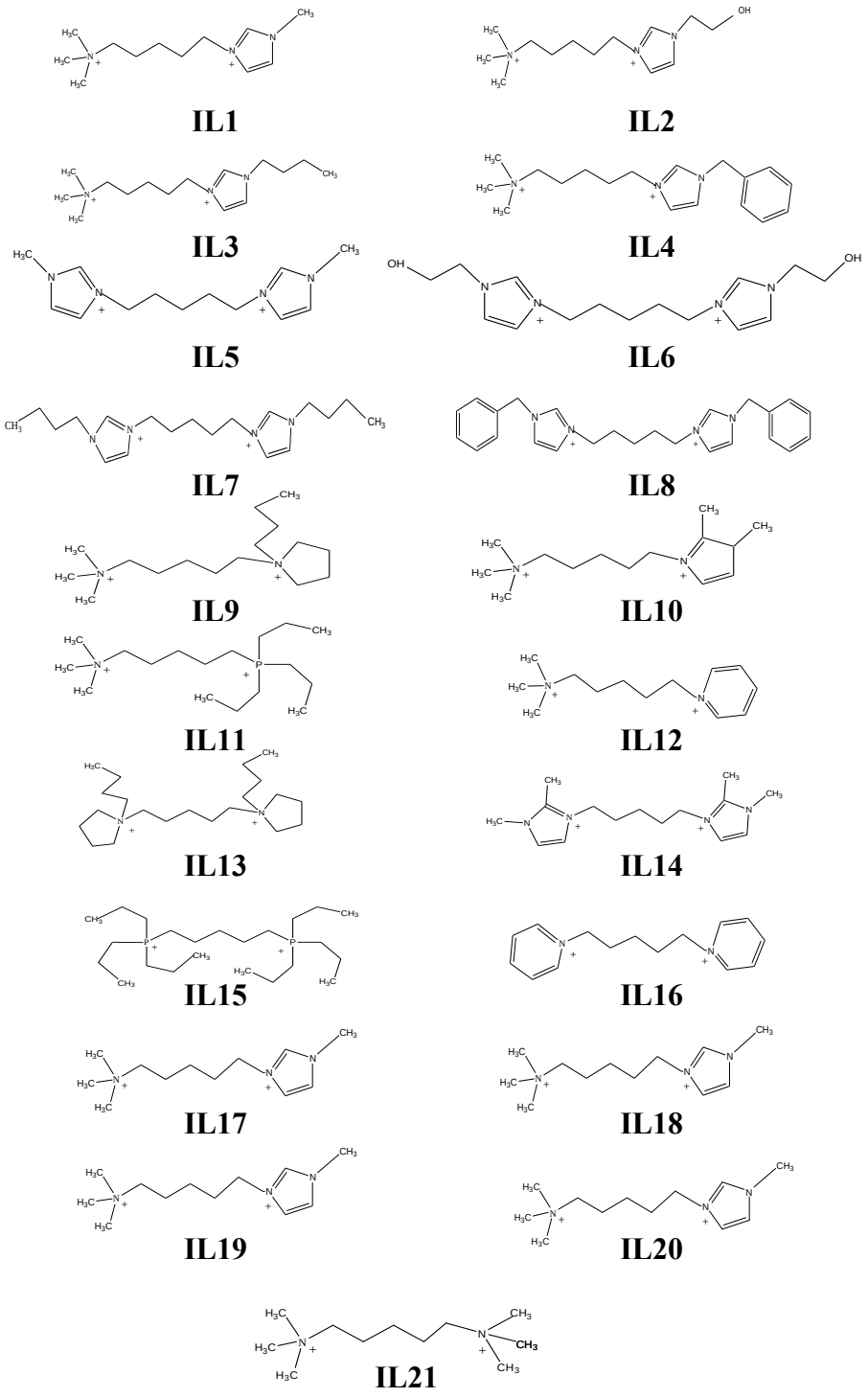


Figure 2.1 Structures of dicationic ionic liquids synthesized.

2.3 Experimental

2.3.1 Materials

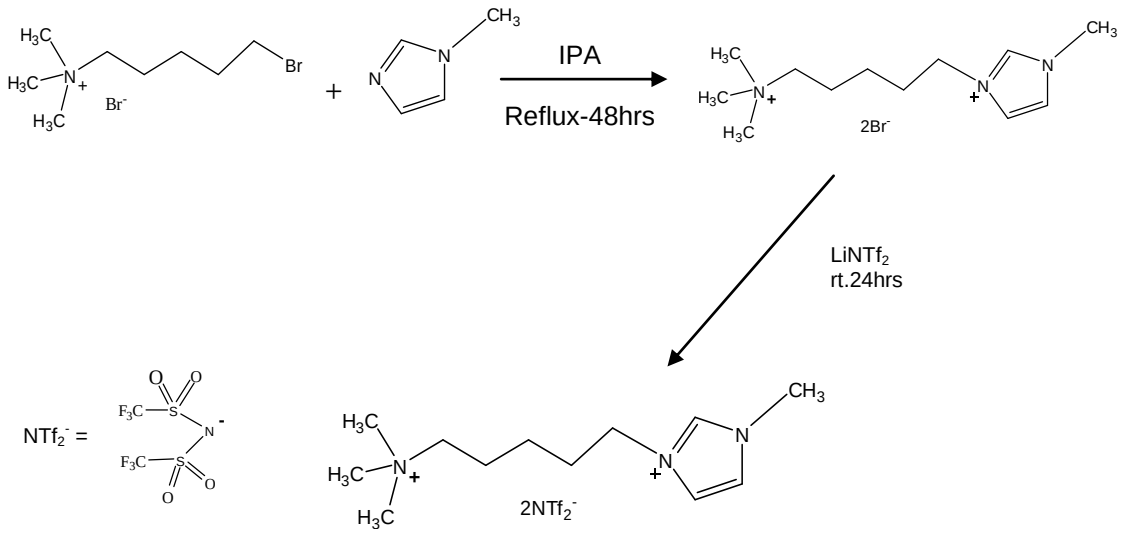
Commercial reagents were used as received from Sigma-Aldrich (St. Louise, MO), unless otherwise noted. All ILs synthesized were characterized by ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectrometry and Mass spectrometry. The NMR spectra were recorded in (methyl sulfoxide)-d6 (unless otherwise stated) on JEOL ECX spectrometers (300 and 500 MHz) at ambient temperature. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F, 85% H_3PO_4 for ^{31}P, and TMS for ^{1}H and ^{13}C NMR spectra. 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, hep = heptet, 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).

2.3.2 Methods

2.3.2.1 Syntheses

Prodecure1: As shown in Scheme 2.1 compounds IL1, IL2, IL3, IL4, IL9, IL10, IL11, and IL12 were synthesized by refluxing 1 molar equivalent of (5-bromopentyl)-trimethylammonium bromide in isopropyl alcohol with 3 molar equivalents of 1-methylimidazole,1-(2-hydroxyethyl)-imidazole,1-butylimidizole, 1- benzylimidazole, 1-butylpyrrolidine, 1,2-dimethylimidazole, tripropylphosphine and pyridine respectively. Rotoevaporation of the solvent yielded the crude di-bromide salt. This was then dissolved in water and the excess starting material was extracted with ethyl acetate.

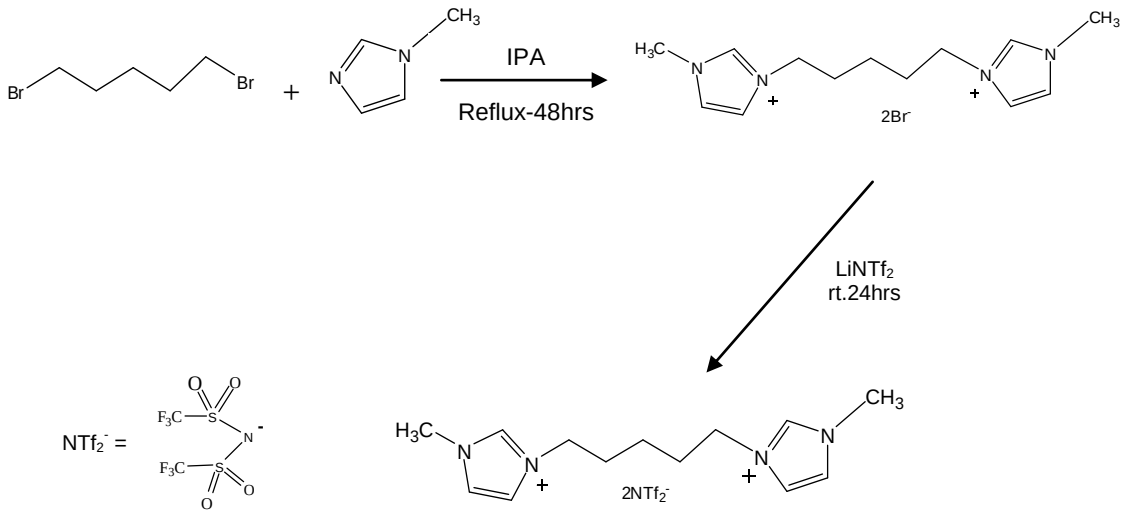
Removal of water through rotoevaporation followed by vacuum drying over phosphorous pentoxide resulted in the pure dication with bromide counter ions. (IL17 is the bromide salt of IL1 and was isolated after this step) Final products were synthesized through a metathesis reaction of the bromide salts with lithium trifluorlmethanesulfonimide (NTf_2^-). Specifically, 1 molar equivalent of the bromide salt was dissolved in water and treated with 3 molar equivalents of the 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 NTf_2^- salt that had phase separated from the water. The lithium bromide and excess lithium was removed from the dichloromethane phase with successive extractions with water. Removal of dichloromethane through rotoevaporation followed by vacuum drying over phosphorous pentoxide at 80 ^{0}C for 24hrs resulted in the pure dication with NTf_2^- counter ions.



Scheme 2.1 Synthesis of unsymmetrical dicationic ionic liquids (IL1)

Procedure 2: Compounds IL5, IL6, IL7, IL8, IL13, IL14, IL15, IL 16 and IL21 were synthesized similar to Procedure 1 except in this series 1,5-dibromopentane was used instead of (5-bromopentyl)-trimethylammonium bromide and to get IL21 trimethylamine was reacted with 1,5-dibromopentane. This is illustrated in Scheme 2.2

Procedure 3: Compound IL18 was synthesized by metathesis reaction of 1 molar equivalent of IL17 and 3 molar equivalent of sodium hexafluorophosphate in water. The sodium bromide and excess $NaPF_6$ were removed from the dichloromethane phase with successive extractions with water. Removal of dichloromethane through rotoevaporation followed by vacuum drying over phosphorous pentoxide at 80 °C for 24hrs resulted in the pure dication with PF_6^- counter ions.



Scheme 2.2 Synthesis of symmetrical dicationic ionic liquids (IL5)

Procedure 4: IL19 and IL20 were synthesized in Acetone medium by reacting l molar equivalent of IL17 and 3.5 molar equivalents of sodium tetrafluoroborate or potassium trifluoromethanesulfonate respectively. The precipitated out sodium bromide and potassium bromide were removed by filtration and the solvent was removed by rotoevaporation. Next the samples were dissolved in water and run through a cation exchange column (Sigma Aldrich, DOWEX 50WX2-400) and an anion exchange column (Sigma Aldrich, DOWEX 1X2-400) to get the pure product by replacing any existing trace amounts of Na^+, K^+ and Br^- by the desired cation and anions. Finally, water was evaporated and products were vacuum dried similar to above procedure.

2.3.2.2 Characterization

Melting Point

The thermal measurements were performed with a differential scanning calorimeter (DSC 2010, TA Instruments Inc., Thermal Analysis & Rheology, New Castle, DE, USA) calibrated using an indium primary standard, with solid-solid transitions for cyclohexane and ethylbenzene 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. The samples were sealed in aluminium pans, and then heated and cooled at scan rate of 5 °C min^{-1} under a flow of nitrogen. All DSC data presented were measured on 7-15 mg samples. 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).

Refractive Index

Refractive index measurements were conducted at 23 °C using a Bausch & Lomb Abbe-3L refractometer

Viscosity

Kinematic viscosities were determined at two different temperatures 30 °C and 50 °C using Cannon-Manning Semi-Micro capillary viscometer (State College, PA).

Thermal stability analysis

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.

Solubility

All compounds synthesized in this study were tested for solubility with water and heptane. This was simply done by placing a small amount (50-100 mg) of the compound in the solvent (15 mL) and through observation of whether the solute was miscible or immiscible in the solvent.

IL1, 1-(1-trimethylammonium-yl-pentyl)-3-methylimidazolium di[bis(trifluoro-methanesulfonyl)imide], m.p.: - 51.5 °C. ^{1}H NMR (300 MHz): δ 1.23 (p, 2H, J = 7.6), 1.70 (m, 2H), 1.83 (p, 2H, J = 7.3), 3.03 (s, 9H), 3.24 (m, 2H), 3.85 (s, 3H), 4.18 (t, 2H, J= 7.1), 7.69 (t, 1H, J = 1.8), 7.73 (t, 1H, J = 1.7), 9.09 (s, 1H). ^{13}C NMR (75 MHz): δ 22.0, 22.8, 29.3, 49.0, 52.7, 65.5, 120.0 (q, J = 319.3), 122.7, 124.2, 137.1. ^{19}F NMR (282 MHz): δ-78.8

IL2, **1-(1-trimethylammonium-yl-pentyl)-3-(2-hydroxyethyl)imidazolium di[bis(tri-fluoromethanesulfonyl)imide],** m.p. – 54.2 °C. ^{1}H NMR (300 MHz): δ 1.26 (p, 2H, J = 7.6), 1.71, (m, 2H), 1.87 (p, 2H, J = 7.4), 3.04 (s, 9H), 3.26 (m, 2H), 3.74 (br, 2H), 4.22 (t, 4H, J = 5.2), 5.17 (br, 1H), 7.34 (s, 2H), 9.14 (s, 1H). ^{13}C NMR (75 MHz): δ 22.0, 22.8, 29.3, 48.9, 52.5, 52.7, 59.7, 65.6, 120.0 (q, J = 319.3), 122.6, 123.3, 136.9. ^{19}F NMR (282 MHz): δ -78.6

IL3, **1-(1-trimethylammonium-yl-pentyl)-3-butylimidazolium di[bis(trifluoro-methanesulfonyl)imide],** m.p. -53.0 °C. ^{1}H NMR (500 MHz): δ 0.91 (t, 3H, J = 7.3), 1.27-1.32 (m, 2H), 1.73 (m, 2H), 1.79 (p, 2H, J = 7.4), 1.87 (p, 2H, J = 7.5), 3.05 (s, 9H), 3.27 (m, 2H), 4.17 (t, 2H, J = 7.2), 4.20 (t, 2H, J = 7.2), 7.76 (t, 1H, J = 1.6), 7.77 (t, 1H, J = 1.6), 9.17 (t, 1H, J = 1.6). ^{13}C NMR (125 MHz): δ 13.7, 19.4, 22.1, 23.0, 29.4, 31.9, 49.2, 49.4, 52.8, 65.7, 120.2 (q, J = 322.0), 123.0, 123.1, 136.6. ^{19}F NMR (470 MHz): δ –78.8.

IL4, 1-(1-trimethylammonium-yl-pentyl)-3-benzylimidazolium di[bis(trifluoro-methanesulfonyl)imide], m.p.-36.2 °C. ^{1}H NMR (300 MHz): δ 1.28 (p, 2H, J = 7.6), 1.74 (m, 2H), 1.88 (p, 2H, J = 7.4), 3.06 (s, 9H), 3.28 (m, 2H), 4.22 (t, 2H, J = 7.2), 5.43 (s, 2H), 7.43 (m, 5H), 7.78 (t, 1H, J = 1.6), 7.81 (t, 1H, J = 1.6), 9.29 (s, 1H). ^{13}C

NMR (75 MHz): δ 22.0, 22.8, 29.3, 30.9, 49.2, 52.6, 65.6, 120.0 (q, J = 319.3), 123.2, 128.8, 129.3, 129.5, 135.2, 136.7 . ^{19}F NMR (282 MHz): δ - 78.8

IL5, 1,1'-(pentane-1,5-diyl)-bis(3-methylimidazolium) di[bis(trifluoromethane-sulfonyl)imide], m.p. – 61.0 °C, ^{1}H NMR (300 MHz): δ 1.22 (p, 2H, J = 7.6), 1.81 (p, 4H, J = 7.4), 3.85 (s, 6H), 4.15 (t, 4H, J = 7.2), 7.69 (t, 1H, J = 1.5), 7.73 (t, 1H, J = 1.5), 9.07 (s, 1H). ^{13}C NMR (75 MHz): δ 22.5, 29.2, 36.2, 48.9, 120.0 (q, J = 319.3), 122.7, 124.1, 137.0. ^{19}F NMR (282 MHz): δ -78.7

IL6, 1,1'-(pentane-1,5-diyl)-bis[3-(2-hydroxyethyl)imidazolium] di[bis(trifluoro-methanesulfonyl)imide], m.p. -65.0 °C. ^{1}H NMR (300 MHz): δ 1.37 (p, 2H, J = 7.6), 1.83 (m, 4H), 3.73 (m, 4H), 4.19 (m, 8H), 5.17 (t, 2H, J = 4.5), 7.75 (s, 4H), 9.12 (s, 2H). ^{13}C NMR (75 MHz): δ 29.0, 31.9, 49.0, 52.2, 59.7, 120.0 (q, J = 319.3), 122.6, 123.3, 136.8. ^{19}F NMR (282 MHz): δ - 78.7.

IL7, 1,1'-(pentane-1,5-diyl)-bis(3-butylimidazolium) di[bis(trifluoromethane-sulfonyl)imide], m.p. -62.0 °C. ^{1}H NMR (500 MHz): δ 0.91 (t, 6H, J = 7.6), 1.26 (m, 6H), 1.81 (m, 8H), 4.16 (t, 8H, J = 7.3), 7.76 (t, 2H, J = 1.8), 7.78 (t, 2H, J = 1.8), 9.16 (s, 2H). ^{13}C NMR (125 MHz): δ 13.7, 19.4, 22.7, 29.2, 31.9, 49.1, 49.26, 120.0 (q, J = 320.0),123.0, 123.1, 136.5. ^{19}F NMR (470 MHz): δ – 78.7.

IL8, 1,1'-(pentane-1,5-diyl)-bis(3-benzyllimidazolium) di[bis(trifluoro-methanesulfonyl) imide], m.p. 34.5 °C. ^{1}H NMR (300 MHz): δ 1.23 (m, 2H), 1.83 (p, 4H, J = 7.4), 4.17 (t, 4H, J = 7.2), 5.42 (s, 4H), 7.42 (s, 10H), 7.79 (t,2H, J = 1.6), 7.81 (t, 2H, J = 1.6), 9.27 (s, 2H). ^{13}C NMR (75 MHz): δ 22.7, 29.1, 49.2, 52.6, 120.0 (q, J = 319.3), 123.2, 123.3, 128.8, 129.3, 129.5, 135.3, 136.7. ^{19}F NMR (282 MHz): δ -78.7

IL9, 1-(1-trimethylammonium-yl-pentyl)-1-butylpyrrolidinium di[bis(trifluoro-

methanesulfonyl)imide], m.p.: 30-32 °C. ^{1}H NMR (500 MHz): δ 0.94 (t, 3H, J = 7.4), 1.27-1.37 (m, 4H), 1.58-1.77 (m, 6H), 2.07 (br, 4H), 3.05 (s, 9H), 3.18-3.29 (m, 6H), 3.47 (br, 4H). ^{13}C NMR (125 MHz): δ 13.8, 19.7, 21.9, 22.2, 22.6, 23.2, 24.9, 52.7, 59.0, 59.3, 62.7, 65.6, 120.0 (q, J = 322.6). ^{19}F NMR (470 MHz): δ –78.7.

IL10, 1-(1-trimethylammonium-yl-pentyl)-2,3-dimethylimidazolium[bis(trifluoro-methanesulfonyl)imide], m.p.: 42-45 °C. ^{1}H NMR (300 MHz): δ 1.26 (p, 2H, J = 7.5), 1.73 (m, 4H), 2.58 (s, 3H), 3.03 (s, 9H), 3.24 (m, 2H), 3.75 (s, 3H), 4.12 (t, 2H, J = 7.4), 7.62 (s, 2H). ^{13}C NMR (75 MHz): δ 9.6, 22.1, 22.9, 29.1, 35.2, 47.6, 52.7, 65.5, 120.0 (q, J = 319.3), 121.3, 122.9, 144.8. ^{19}F NMR (282 MHz): δ -78.6

IL11, (1-trimethylammonium-yl-pentyl)-tripropylphosphoniumdi[bis(trifluoro-methanesulfonyl)imide], N[111]C5P[333]-NTf2, m.p.: 33 – 35 °C. ^{1}H NMR (500 MHz): δ 1.03 (td, 9H, $3J_{HH}$ = 7.3, $4J_{PH}$ = 1.4), 1.40 (p, 2H, J = 7.6), 1.48-1.58 (m, 8H), 1.73 (m, 2H), 2.12-2.23 (m, 8H), 3.05 (s, 9H), 3.28 (m, 2H). ^{13}C NMR (125 MHz): δ 15.2, 15.5 (d, J = 16.8), 18.1 (d, J = 48.0), 20.2 (d, J = 47.0), 20.9, 22.1, 27.4 (q, J = 15.8), 52.7, 65.7, 120.0 (q, J = 322.0). ^{19}F NMR (470 MHz): δ –78.8. ^{31}P NMR (202 MHz): δ 33.2.

IL12, 1-(1-trimethylammonium-yl-pentyl)pyridiniumdi[bis(trifluoromethanesul-fonyl)imide], m.p.: 39-40 °C. 1H NMR (500 MHz): δ 1.27 (p, 2H, J = 7.6), 1.72 (m, 2H), 1.98 (p, 2H, J = 7.6), 3.03 (s, 9H), 3.25 (m, 2H), 4.62 (t, 2H, J = 7.3), 8.18 (td, 2H, J = 7.4, J = 1.3), 8.62 (tt, 2H, J = 7.8, J = 1.4), 9.07 (dd, 4H, J = 7.5, J = 1.4). ^{13}C NMR (125 MHz): δ 22.0, 22.7, 30.6, 52.7, 61.0, 65.5, 120.0 (q, J = 322.4), 128.6, 145.2, 146.1. ^{19}F NMR (470 MHz): δ –78.6.

IL13, 1,1'-(pentane-1,5-diyl)-bis(1-butylpyrrolidinium) di[bis(trifluoromethane-sulfonyl)imide], m.p.: 36-38 °C. ^{1}H NMR (500 MHz): δ 0.94 (t, 6H, J = 7.6), 1.27-1.36 (m, 6H), 1.58-1.72 (m, 8H), 2.06 (br, 8H), 3.20 (m, 8H), 3.47 (br, 8H). ^{13}C NMR (125

MHz): δ 13.8, 19.6, 21.9, 22.6, 23.3, 24.9, 58.9, 59.2, 62.6, 120.0 (q, J = 322.4). ^{19}F NMR (470 MHz): δ –78.7.

IL14, 1,1'-(pentane-1,5-diyl)-bis(2-methyl-3-methyl-imidazolium)di[bis(trifluoro-methanesulfonyl)imide], MMImC5MMIm-NTf2, m.p.: 62-63 °C. ^{1}H NMR (500 MHz): δ 1.30 (p, 2H, J = 7.6), 1.76 (p, 4H, J = 7.6), 2.58 (s, 6H), 3.75 (s, 6H), 4.10 (t, 4H, J = 7.3), 7.61([AB]q, 4H). ^{13}C NMR (125 MHz): δ 9.6, 22.8, 29.1, 35.2, 47.8, 120.1 (q, J = 322.0), 121.4, 122.9, 144.8. ^{19}F NMR (470 MHz): δ –78.7.

IL15, 1,1'-(pentane-1,5-diyl)-bis(tripropylphosphonium) di[bis(trifluoro-methanesulfonyl)imide], P[333]C5P[333]-NTf2, m.p.: 71-72 °C. ^{1}H NMR (500 MHz): δ 1.02 (td, 18H, $3J_{HH}$ = 7.3, $4J_{PH}$ = 1.35), 1.48-1.56 (m, 18H), 2.12-2.19 (m, 16H). ^{13}C NMR (125 MHz): δ 15.2, 15.7 (br), 18.2 (d, J = 47.5), 20.2 (d, J = 47.0), 20.8, 120.1 (q, J = 322.0). ^{19}F NMR (470 MHz): δ –78.6. ^{31}P NMR (202 MHz): δ 33.2.

IL16, 1,1'-(pentane-1,5-diyl)-bis(pyridinium)di[bis(trifluoromethanesulfonyl) imide], m.p.: 53-54 °C. ^{1}H NMR (500 MHz): δ 1.30 (p, 2H, J = 7.5), 1.98 (p, 4H, J = 7.4), 4.60 (t, 4H, J = 7.4), 8.17 (t, 4H, J = 7.1), 8.61 (t, 2H, J= 7.8), 9.07 (d, 4H, J = 7.5). ^{13}C NMR (125 MHz): δ 22.4, 30.5, 61.0, 120.0 (q, J = 322.4), 128.7, 145.3, 146.1. ^{19}F NMR (470 MHz): δ –78.7.

IL17, 1-(1-trimethylammonium-yl-pentyl)-3-methylimidazolium dibromide. m.p.: 115 -116 °C. ^{1}H NMR (300 MHz): δ 1.23 (p, 2H, J = 7.5), 1.72 (m, 2H), 1.85 (p, 2H, J = 7.4), 3.10 (s, 9H), 3.38 (m, 2H), 3.87 (s, 3H), 4.24 (t, 2H, J = 7.1), 7.7 (t, 1H, J = 1.6), 7.89 (t, 1H, J = 1.6), 9.36 (s, 1H). ^{13}C NMR (75 MHz): δ 21.9, 22.7, 29.3, 36.4, 48.8, 52.7, 65.3, 122.8, 124.1, 137.1.

IL18, 1-(1-trimethylammonium-yl-pentyl)-3-methylimidazolium bis(hexafluoro-phosphate). m.p.: 86-88 °C. ^{1}H NMR (300 MHz): δ 1.24 (p, 2H, J = 7.4), 1.70 (m, 2H),

1.83 (p, 2H, J = 7.3), 3.02 (s, 9H), 3.23 (m, 2H), 3.83 (s, 3H), 4.17 (t, 2H, J = 6.8), 7.65 (s, 1H), 7.69 (s, 1H), 9.02 (s, 1H). ^{13}C NMR (75 MHz): δ 21.9, 22.7, 29.3, 36.2, 48.9, 52.7, 65.6, 122.7, 124.1, 136.9. ^{19}F NMR (282 MHz): δ -69.95 (d, J = 708.9) ^{31}P NMR (121 MHz): δ -143.6 (hep, J = 708.8)

IL19, 1-(1-trimethylammonium-yl-pentyl)-3-methylimidazolium bis(trifluoro-borate). m.p.: >50, <80 °C, ^{1}H NMR (300 MHz): δ 1.24 (p, 2H, J = 7.4), 1.70 (m,2H), 1.83 (p, 2H, J = 7.4), 3.02, (s, 9H), 3.24 (m, 2H), 3.83 (s, 3H), 4.17 (t, 2H, J = 7.0), 7.65 (s, 1H), 7.70 (s, 1H), 9.00 (s, 1H). ^{13}C NMR (75 MHz): δ 21.0, 22.7, 29.3, 36.2, 48.9, 52.6, 65.5, 122.7, 124.1, 137.0. ^{19}F NMR (282 MHz): δ -148.1

IL20, 1-(1-trimethylammonium-yl-pentyl)-3-methylimidazolium bis(trifluoro-methanesulfonate). m.p.: 153-156 °C. ^{1}H NMR (300 MHz): δ 1.23 (p, 2H, J = 7.3), 1.79 (m.4H), 3.02 (s, 9H), 3.25 (m, 2H), 3.84 (s, 3H), 4.18 (t, 2H, J = 6.6), 7.68 (s, 1H), 7.73 (s, 1H), 9.04 (s, 1H). ^{13}C NMR (75 MHz): δ 22.0, 22.8, 29.3, 36.3, 48.9, 52.7, 65.5, 120.0 (q, J = 319.7), 122.7, 124.2, 137.9. ^{19}F NMR (282 MHz): δ – 77.7

IL21, 1,1'-(pentane-1,5-diyl)-bis(trimethylammonium) di[bis(trifluoromethane-sulfonyl)imide], $N_{[111]}C_5N_{[111]}$-NTf_2, m.p.: 86-88 °C. ^{1}H NMR (500 MHz): δ 1.28 (p, 2H, J = 7.6), 1.73 (m, 4H), 3.04 (s, 18H), 3.27 (m, 4H). ^{13}C NMR (125 MHz): δ 22.1, 23.1, 52.7, 65.4, 120.0 (q, J = 322.0). ^{19}F NMR (470 MHz): δ –78.6.

2.4 Results and Discussion

2.4.1 Melting Point

The melting point of an ionic compound is determined by the crystal lattice energy between the cation and the anion. This lattice energy is controlled by 3 main factors: 1. intermolecular forces 2. molecular symmetry and 3. conformational degrees

of freedom.[5, 6, 85] Comparing IL1 to IL3 and IL5 to IL7, the chain length of the substituent group at the 3-position of the imidazole ring increases. The accompanying melting point decrease can be attributed to the added conformational degrees of freedom of IL3 and IL7. IL4 and IL8 have somewhat higher melting points compared to the comparable structures (IL1-IL8). This may be attributed to the added π-π interactions of the aromatic ring substituent. Of the seventeen NTf_2^- salts synthesized, IL21 with bis(trimethylammonium) groups has the highest melting point. This is a result of 2 main factors. High intermolecular attraction due to localized charged density on quaternary amine nitrogen and the inherent symmetry of the dicationic moiety. When the symmetry component is removed in IL1-IL4 the melting point decreases by about 140 °C compared to IL21. When the bis(trimethylamino) moieties are removed, thereby removing the high intermolecular attraction component, as in IL5-IL8, remarkably lower melting points are obtained despite the symmetry of the cationic fragments. Symmetry effects are more apparent in IL9-IL16. In this series, symmetrical ILs (IL13-IL16) have higher melting points than their unsymmetrical analogs (IL9-IL12). The extent to which this effect is observed depends on the type of cationic moieties utilized. If the two cationic moieties forming the unsymmetrical dication are comparable in size and charge distribution, the melting point change compared to their symmetrical analogs is smaller (compare 30 °C for IL9 to 36 °C for IL13).

When the two cationic moieties are dissimilar, there is a substantial drop in melting points compared to the corresponding symmetrical ILs (compare 33 °C for IL11 and 71 °C for IL15). Substitution of a methyl group at the 2- position of the imidazolium ring (IL5 vs. IL14) has a profound effect on the melting points of dicationic ILs. The melting point increased by about 123 ^{0}C (from – 61 °C for IL5 to 62 °C for IL14) with

this methyl substitution. Comparison of IL5,13,14,15,16 and 21 shows that the melting points of symmetrical dicationic salts are strongly affected by the type of cation moiety in the order: trimethylammonium > tripropylphosphonium > 2,3-dimethylimidazolium > pyridinium > *N*-butylpyrrolidinium >3-methylimidazolium (86 °C, 71 °C, 62 °C, 53 °C, 36 °C and -61 °C respectively). Furthermore it is apparent from the data obtained for IL1 and IL17-20 that for the same cation, the melting point decreases based on the anion in the order: TfO^- >Br^- > PF_6^- > BF_4^- > NTF_2^- (153 °C, 115 °C, 86 °C, 50-80 °C and -51.5 °C respectively).

2.4.2 Density

The densities of ILs range from 1.02 g/cm^3 to 1.62 g/cm^3 for this series. The lowest density is observed for an unsymmetrical cationic ionic liquid with tri-propylphosphonium and trimethylammonium cationic moieties (IL9) while a symmetrical ionic liquid with bispyridinium cationic moieties (IL16) has the highest density. The general trend that can be observed for the ILs listed in Table 2.1 is that the symmetrical cationic ILs tend to have higher densities than their corresponding unsymmetrical analogues (compare 1.54 g/cm^3 for IL1 to 1.57 g/cm^3 for IL5, 1.53 g/cm^3 for IL10 to 1.60 g/cm^3 for IL14, etc.). Furthermore, when the alkyl chain length of the substituent at the 3- position of the imidazole increases, the density decreases. For instance, the density decreases from 1.54 g/cm^3 for methyl substitution in IL1 to 1.47 g/cm^3 for butyl substitution in IL3, and also from 1.57 g/cm^3 for methyl substitution in IL5 to 1.44 g/cm^3 for the butyl substituted IL7. Similar observations are reported in previous literature for monocationic haloaluminate ILs and non-haloaluminate ILs.[3, 7, 86]

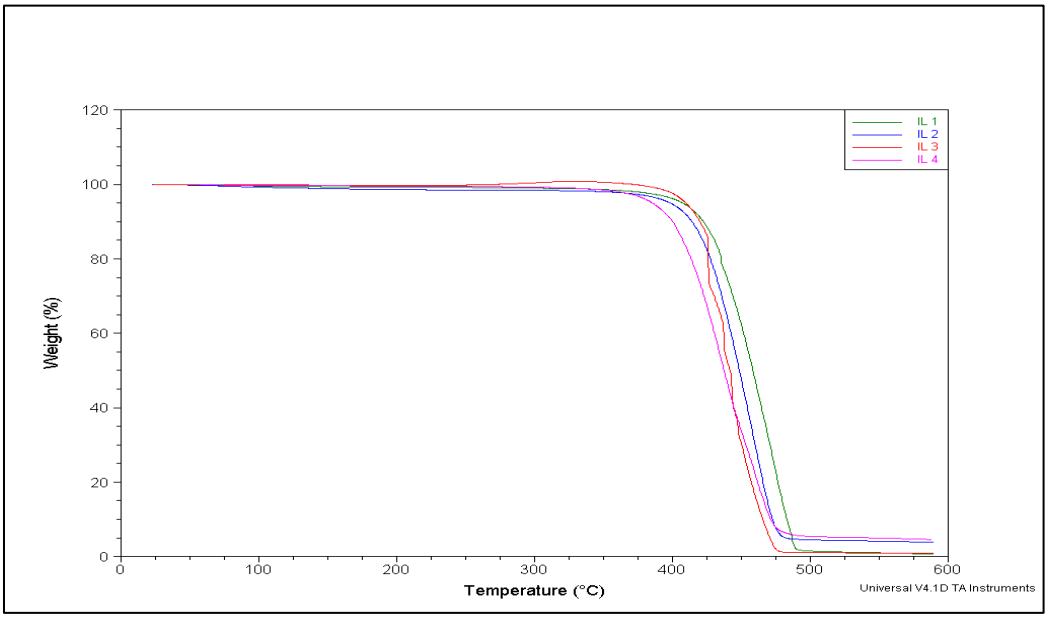


Figure 2.2 TGA curves for unsymmetrical dicationic ionic liquids IL1, IL2, IL3, and IL4.

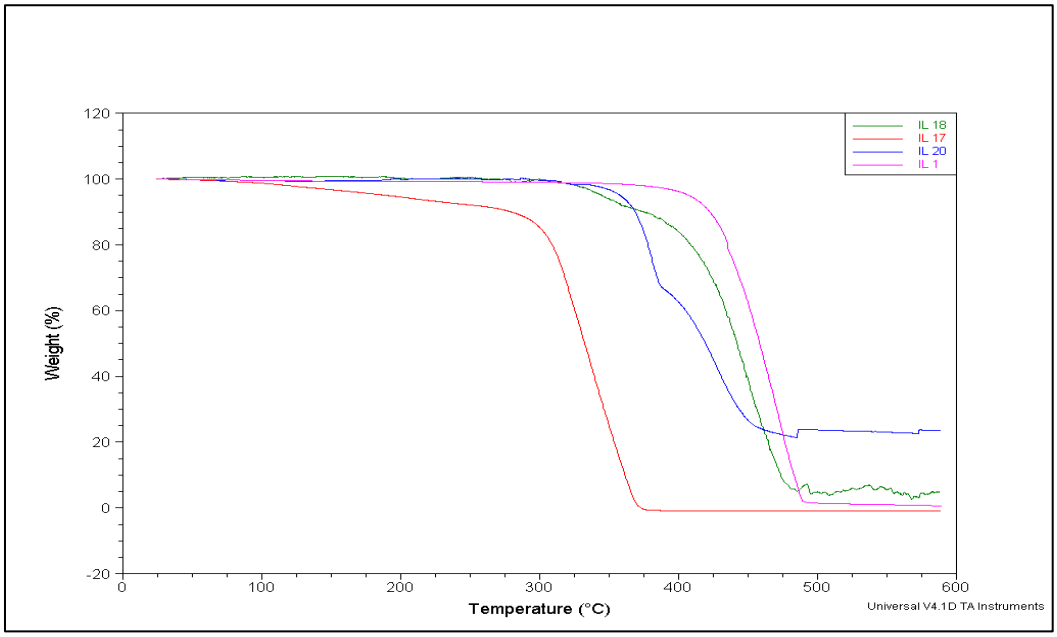


Figure 2.3 Effect of anion on thermal stability of dicationic ionic liquids IL1, IL17, IL18, and IL20.

Table 2.1 Physicochemical properties of dicationic ILs synthesized.

Ionic Liquid	MW (g/mol)	Melting Point (°C)	D [c] (g/cm^3)	Refractive index	Viscosity [e] (cSt)		Thermal Stability [f] (°C)		Miscibility with heptane [g]	Miscibility with water [g]
					30 °C	50 °C	99% w	95% w		
IL1	771.7	-51.5[a]	1.54	1.431	357	190	301.5	407.6	I	I
IL2	801.2	-54.2[a]	1.54	1.435	398	225	132.9	398.6	I	I
IL3	813.2	-53.0[a]	1.47	1.433	527	192	389.0	409.8	I	I
IL4	847.1	-36.2[a]	1.50	1.458	1217	352	328.0	385.5	I	I
IL5	794.3	-61.0[a]	1.57	1.441	251	119	365.2	431.1	I	I
IL6	854.2	-65.0[a]	1.58	1.456	241	106	257.4	322.2	I	I
IL7	878.3	-62.0[a]	1.44	1.433	355	101	375.8	421.3	I	I
IL8	946.1	-34.5[a]	1.55	1.486	1209	372	291.1	379.2	I	I
IL9	816.3	30-32	1.46	-	-	357	356.8	396.7	I	I
IL10	785.2	42-45	1.53	-	-	236	297.9	389.8	I	I
IL11	849.3	33-35	1.02[d]	1.435[d]	373[d]	144	177.0	380.0	I	I
IL12	768.2	39-40	1.56	-	-	218	335.0	384.0	I	I
IL13	884.4	36-38	1.47	-	-	337	309.5	379.5	I	I
IL14	822.2	62-63	1.60	-	-	-	392.1	440.4	I	I
IL15	919.2	71-72	1.30	-	-	-	391.4	421.7	I	I
IL16	788.2	53-54	1.62	-	-	-	332.7	374.8	I	I
IL17	371.6	115-116	1.37	-	-	-	90.5	190.7	I	M
IL18	501.3	86-88	1.57	-	-	-	312.4	345.2	I	I
IL19	385.0	>50 ,< 80[b]	-	-	-	-	336.9	355.0	I	M
IL20	510.3	153-156	1.50	-	-	-	315.9	358.2	I	M
IL21	748.2	86-88	1.33	-	-	-	363.7	399.6	I	I

[a] Determined by the peak position in DSC. [b] Amorphous solid – does not show a sharp melting point. [c] Measured using pycnometer. [d] Measured at a supercooled state. [e] Measured using capillary viscometer. [f] Thermo gravimetric analysis (TGA), 99% w = temperature at 1% weight loss of the sample. [g] I = immiscible, M = miscible.

2.4.3 Viscosity

The kinematic viscosities of this series of ILs range from 241 to 1217 cSt at 30^0C. Some dicationic liquid viscosities lie within the general monocationic ionic liquid range (IL1,2,5,6,7 and IL11 with viscosities <400 cSt) and some extend beyond the commonly observed values.[3, 7, 85, 86] The viscosities are exceptionally high for ILs containing benzyl groups (1217 cSt for IL4 and 1209 cSt for IL8 at 30 ^{0}C) probably due to the added intermolecular π-π interactions. Furthermore the viscosities were strongly dependant on the temperature. All ILs showed more than a 43 % decrease in viscosity with a 20 ^{0}C increase in temperature.

2.4.4 Thermal Stability

Thermal stabilities for the 21 ILs as measured by thermogravimetric analysis (TGA) are reported in Table 2.1 and TGA curves obtained for some unsymmetrical dicationic ionic liquids are shown in Figure 2.2. It is apparent that dicationic ILs show much higher thermal stabilities than monocationic ILs.[78] Out of the 21 salts, 18 were stable up to 350 °C with only a 5% thermal degradation. IL14 carrying bis(2,3-dimethylimidazolium) cation has the highest thermal stability with only 5% thermal degradation at 440.4 °C. More than the structure of the cation, the accompanying anion had the most influence on the thermal stability. Figure 2.3 shows the TGA curves for four dicationic ionic liquids with identical cation and 4 different anions; IL1 – NTf_2^-, IL17 – Br^-, IL18 – PF_6^-,and IL20 – TfO^-. It is evident that the bromide anion shows the lowest thermal stability and NTf_2^- shows the highest thermal stability. In the order of increasing thermal stability the anions could be arranged in the following order: $Br^- < PF_6^- < TfO^- < NTf_2^-$

2.4.5 Refractive Index

The refractive indices of the 21 dicationic ILs are in the general region observed for monocationic ILs[7] and lies between 1.431 to 1.486. The solubility behavior of this set of dicationic ILs parallels that of monocationic ILs[87-89] in that all Br^-, BF_4^- and TfO^- salts synthesized were soluble in water while all NTf_2^- and PF_6^- salts were insoluble in water. None of the ILs were soluble in heptane.

2.5 Conclusions

In conclusion, we have demonstrated the effect of symmetry on the melting points and other physical properties of dicationic ionic liquids. The effect on melting point is substantial for ionic liquids containing non-imidazolium based cationic moieties combined with trimethylammonium cationic moiety. Imidazolium based ionic liquids have the lowest melting points within the 21 ILs synthesized. The ability to control and "tune" the properties of an ionic liquid to this extent is exclusive to dicationic liquids. Furthermore, using this method the melting point can be lowered without affecting the desirable solvation properties and thermal stabilities.

CHAPTER 3

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

3.1 Abstract

Multicationic ionic liquids are shown to have unique advantages such as better thermal stability and tunability of physical parameters including melting point, viscosity, density, hydrophilicity/lipophilicity, refractive index, and miscibility with water and organic solvents, compared to traditional monocationic ionic liquids. In this study we explore a new class of multicationic ionic liquids; trigonal tricationic ionic liquids. For this study 28 new ionic liquids have been synthesized. Four types of trigonal core structures were synthesized with varying degrees of flexibility: mesitylene core, benzene core, triethyl amine core and tri(2-hexanamide)ethylamine core. Nine different cationic moieties were incorporated. Each ionic liquid contains three identical cationic moieties. Changes in properties such as melting point and viscosity showed direct correlation to the rigidity/flexibility of the central trigonal core structure.

3.2 Introduction

Simple modification of traditional ionic liquids (ILs) by varying their cations and anions can produce ILs with variable and tunable physicochemical properties that make them much more versatile and useful for a variety of applications.[82] Their uses traverse in many areas of chemistry and biochemistry, including novel solvent systems in organic syntheses and catalysis,[1, 8, 90-94] enzyme-catalyzed reactions,[95-98]

electrochemical studies,[99-102] electrolyte materials for double-layer capacitors, dye-sensitized solar cells, liquid-liquid extractions,[103-106] liquid matrixes for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry,[45, 46, 53] additives in HPLC and capillary electrophoresis, and stationary phases in GC.[9, 16, 71, 107-110] The tunable properties include but are not limited to melting point, viscosity, density, thermal stability, hydrophilicity/ lipophilicity and miscibility with water and organic solvents, as well as extractability for various organic compounds and metal ions.

Multifunctional ionic liquids (especially dicationic and dianionic ILs) have been shown to have a greater range of physical properties than most traditional, singly charged ILs.[19, 78] Consequently, they have been shown to be exceptional high temperature, selective gas chromatographic stationary phases[67, 78] and have been prepared as a new class of high temperature lubricants.[79, 111] They often have greater thermal stability, lower volatility, and more flexibility in tuning/varying their physiochemical 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.[19]

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, tricationic ionic liquids reported have been shown good thermal stabilities and were tested for antimicrobial activity.[112] The tricationic moieties were not symmetrical and were made only using 1,2,3-tri(chloromethoxy)propane to react with alkylimidazoles and alkylpyridines. 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 the traditional ILs. This is achieved by synthesizing novel symmetrical tricationic ionic liquids using four major types of central cores having five 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.

3.3 Experimental

3.3.1 Materials

Commercial reagents were used as received from Sigma-Aldrich (St. Louise, MO), unless otherwise noted. All ILs synthesized were characterized using 1H, 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).

3.3.2 Methods

3.3.2.1 Synthesis

Synthesis of compounds A1, A3 and A5 involve refluxing 1 molar equivalents of 2,4,6-tris(bromomethyl)mesitylene with 4 molar equivalents of 1-butylimidazole, 1-benzylimidazole, or tripropylphosphine respectively in isopropanol for 7 days. After the reaction, the products were all purified by extraction with ethyl acetate and dried under vacuum. Synthesis of compound A2 also involves similar procedure using 1 molar equivalents of 2,4,6-tris(bromomethyl)mesitylene with 4 molar equivalents of 1-methylimidazole but using toluene as the solvent. Final products were synthesized through a metathesis reaction of the bromide salts with lithium NTf_2^-. 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.

Compounds B1, B2,B3, B4, and B5 were synthesized by refluxing 1 molar equivalents of 1,3,5-tris(bromomethyl)benzene with 4 molar equivalents of 1-butylimidazole, 1-methylimidazole, 1- benzylimidazole, 1-butylpyrrolidine, or

tripropylphosphine respectively in 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 trifluorlmethanesulfonimide (NTf_2^-). In metathesis process 1 molar equivalents of bromide salt dissolved in water and treated with 4.5 molar equivalents of lithium trifluorlmethanesulfonimide. 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 °C for 24hrs resulted in the pure tricationic ILs with NTf_2^- counter ions.

Compounds C1, C2, C3, C4, C5, C6, C7, C8 and C5 were synthesized by refluxing 1 molar equivalent of Tris(2-chloroethyl)amine hydrochloride in isopropyl alcohol with 6 molar equivalents of 1-butylimidazole, 1-methylimidazole, 1-benzylimidazole, 1-butylpyrrolidine, tripropylphosphine, 1-hydroxyethylimidazole, tributylphosphine, triphenylphosphine or tritoylphosphine respectively for 7 days. Rotoevaporation of the solvent yielded the crude hydrochloride salt. This was then dissolved in water with 2 molar equivalents of NaOH. NaOH 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 NTf_2^-. Specifically, 1 molar equivalent of the chloride salt was dissolved in water

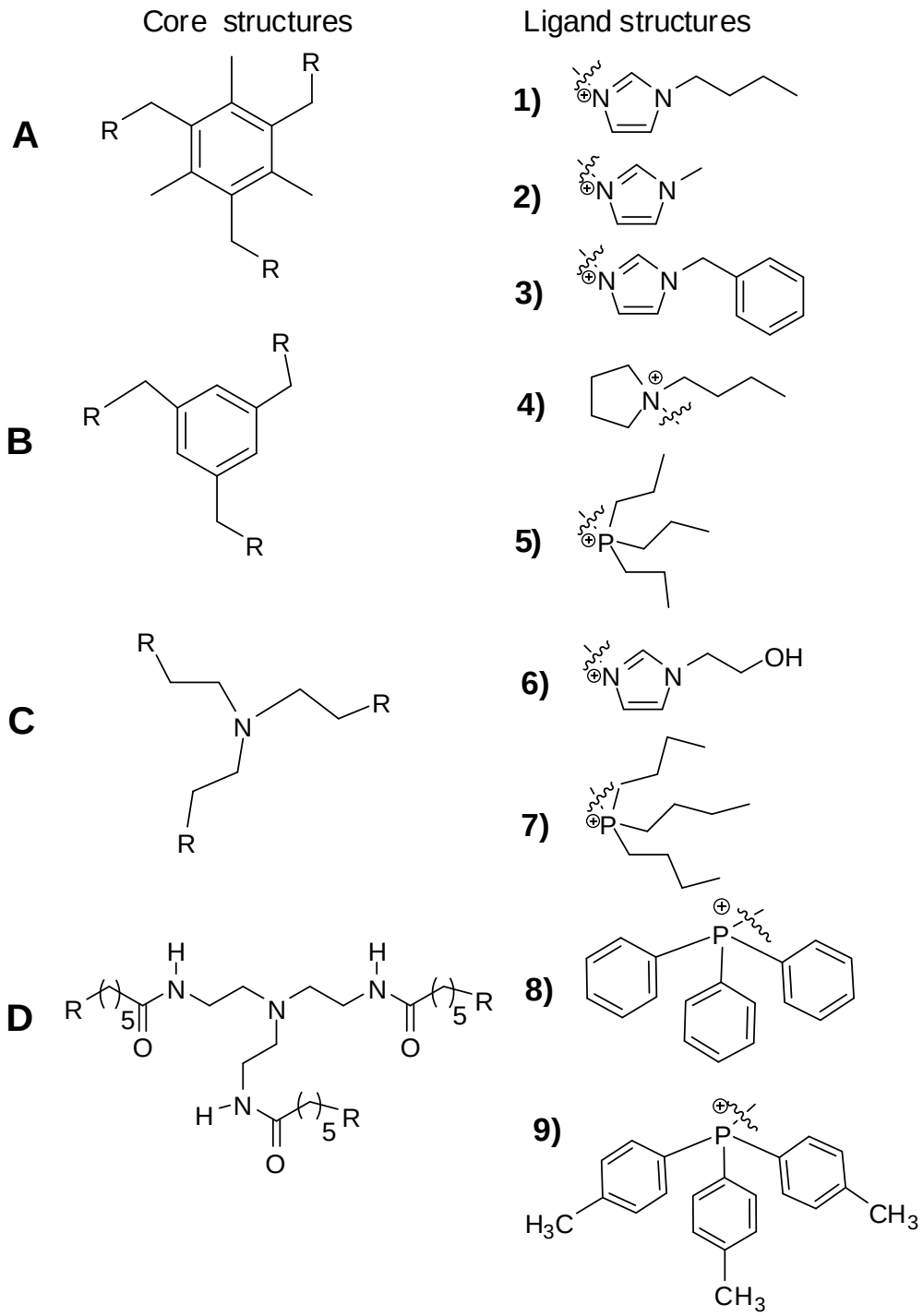


Figure 3.1 Structures of trigonal tricationic ionic liquids synthesized.

and treated with 4.5 molar equivalents of the 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 chloride, sodium chloride, excess sodium hydroxide 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 °C for 24hrs resulted in the pure tricationic ILs with NTf_2^- counter ions.

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 then 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.

PF_6^- salt for compound C1 was synthesized directly from its chloride salt. In this method 1 molar equivalent of chloride salt was first dissolved in water and 2 molar equivalent of NaOH was added to neutralize the hydrochloride salt. The excess starting material was removed by ethyl acetate. Metathesis reaction with 4 molar equivalents $NaPF_6$ resulted the final product. This was washed with water to remove excess $NaPF_6$ and other water soluble impurities. The solid compound was vacuum dried over P_2O_5 at 80 °C for 24 hours to get the pure ionic

BF_4^- salt for both compounds B1 and C1 was synthesized directly from their halide salt. Halide salts for both compounds 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 °C yield the pure TIL2 as the BF_4^- salt.

TfO^- salt for both compounds B1 and C1 was also synthesized directly from their halide salt. Halide salts for both compounds 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 °C yield the pure C1 as the TfO^- salt.

Core D was not commercially available and therefore had to be synthesized. To a solution of 1 mol of tris(2-aminoethyl)amine and 5 mol of triethylamine in CH_2Cl_2 at -78 °C was added 3.5 mol of 6-bromohexanoylchloride through a syringe under a vigorous stream of N_2. The reaction mixture was stirred for 3h at -78 °C and allowed to stir at temperature for 12 hour. Then the reaction mixture was poured in to 100 ml of cold water and the aqueous layer was extracted 3 times with 50 ml of CH_2Cl_2 and the combined organic layer was concentrated in vacuo to give a pale yellow liquid. This was further dried under high vacuum over P_2O_5 to give core D as orange color solid.

For synthesis of D1, D2, D3 and D5, 1-butylimidazole, 1-methylimidazole 1-benzylimidazole, or tripropylphosphine was added to a solution of core D in dry THF and refluxed for 36 hr under N_2. Then the solvent was evaporated under vacuum and resulted thick liquid was dissolved in 100 ml of water and washed the aqueous layer

with ethyl acetate (6 × 100 ml). The aqueous layer was evaporated to dryness and resulted ionic liquid was dried under vacuum for 24 hr to get bromide form of tricationic salt.

Final products were synthesized through a metathesis reaction of the bromide salts with lithium trifluorlmethanesulfonimide (NTf_2^-). In metathesis process 1 molar equivalents of bromide salt dissolved in water and treated with 4.5 molar equivalents of lithium trifluorlmethanesulfonimide. 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 °C for 24hrs resulted in the pure tricationic ILs with NTf_2^- counter ions.

IL A1-NTf2: 1,3,5-{tris(3-n-butylimidazolium)methyl}mesitylene tris((bistrifluoro-methylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{39}H_{51}F_{18}N_9O_{12}S_6$: C 34.14, H 3.75, N 9.19, . Found: C 34.60, H 3.91, N 8.93,. ESI-MS (*m/z*): 177.18 (M^{3+}), found 177.18.

IL A2-NTf2: 1,3,5-{tris(3-n-methylimidazolium)methyl}mesitylene tris((bistrifluoro-methylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal.

Calcd. for $C_{30}H_{33}F_{18}N_9O_{12}S_6$: C 28.92, H 2.67, N 10.12, . Found: C 28.92, H 2.97, N 9.81,. ESI-MS (*m/z*): 135.09 (M^{3+}), found 135.09.

IL A3-NTf2: 1,3,5-{tris(3-n-benzylimidazolium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{48}H_{45}F_{18}N_9O_{12}S_6$: C 39.10, H 3.08, N 8.55, . Found: C 39.65, H 3.38, N 8.54,. ESI-MS (*m/z*): 211.12 (M^{3+}), found 211.12.

IL A5-NTf2: 1,3,5-{tris(tripropylphosphonium)methyl}mesitylene tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{45}H_{78}F_{18}N_3O_{12}P_3S_6$: C 36.51, H 5.31, N 2.84, . Found: C 36.82, H 5.43, N 2.80,. ESI-MS (*m/z*): 213.32 (M^{3+}), found 213.32.

IL B1-NTf2: 1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{36}H_{45}F_{18}N_9O_{12}S_6$: C 32.51, H 3.41, N 9.48, . Found: C 32.51, H 3.63, N 9.32,. ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

IL B1-TfO: 1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(trifluoromethanesulfonate), ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd.

for $C_{33}H_{45}F_9N_6O_9S_3$: C 42.30, H 4.84, N 8.97, . Found: C 42.22, H 4.96, N 8.75,. ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

IL B1-BF_4: 1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(tetrafluoroborate) ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{30}H_{45}B_3F_{12}N_6$: C 48.03, H 6.05, N 11.20, . Found: C 48.35, H 6.19, N 10.98,. ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

IL B1-PF6: 1,3,5-{tris(3-n-butylimidazolium)methyl}benzene tris(hexafluoro-phosphate) ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{30}H_{45}F_{18}N_6P_3$: C 38.97, H 4.91, N 9.09, . Found: C 37.93, H 4.91, N 8.83,. ESI-MS (*m/z*): 163.12 (M^{3+}), found 163.12.

IL B2-NTf2: **1,3,5-{tris(3-n-methylimidazolium)methyl}benzene tris((bistrifluoro-methylsulfonyl)imide),** ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{27}H_{27}F_{18}N_9O_{12}S_6$: C 26.94, H 2.26, N 10.47, . Found: C 27.17, H 2.51, N 10.23,. ESI-MS (*m/z*): 121.08 (M^{3+}), found 121.08.

IL B3-NTf2: 1,3,5-{tris(3-n-benzylimidazolium)methyl}benzene tris((bistrifluoro-methylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 9.33 (d, 3H, *J* = 11.55 Hz), 7.79 (m, 3H), 7.69 (M, 3H), 7.39 (M, 18H), 3.90 (S, 9H). Anal. Calcd. for $C_{45}H_{39}F_{18}N_9O_{12}S_6$: C 37.74, H 2.74, N 8.80, . Found: C 38.10, H 3.09, N 8.71,. ESI-MS (*m/z*): 197.26 (M^{3+}), found 197.26.

IL B4-NTf2: 1,3,5-{tris(butypyrrolidinium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{39}H_{60}F_{18}N_6O_{12}S_6$: C 34.98, H 4.52, N 6.27, . Found: C 34.98, H 4.64, N 6.21,. ESI-MS (*m/z*): 166.28 (M^{3+}), found 166.26.

IL B5-NTf2: 1,3,5-{tris(tripropylphosphonium)methyl}benzene tris((bistrifluoromethylsulfonyl)imide) ^{1}H-NMR (500 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{42}H_{72}F_{18}N_3O_{12}P_3S_6$: C 35.07, H 5.05, N 2.92, . Found: C 35.23, H 4.98, N 2.84,. ESI-MS (*m/z*): 199.16 (M^{3+}), found 199.16.

IL C1-NTf2: **Tris(2-(3-n-butylimidazolium)ethyl)amine tris((bistrifluoromethylsulfonyl)imide),** ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{33}H_{48}F_{18}N_{10}O_{12}S_6$: C 30.23, H 3.69, N 10.68, . Found: C 30.77, H 3.94, N 10.59,. ESI-MS (*m/z*): 156.80 (M^{3+}), found 156.80.

IL C1-BF4: Tris(2-(3-n-butylimidazolium)ethyl)amine tris(tetrafluoroborate), ^{1}H-NMR (300 MHz, DMSO): δppm) = 9.12 (s, 3H), 7.77 (t, 3H, *J* = 1.6 Hz), 7.66 (t, 3H, *J* = 1.6 Hz), 4.15 (m, 12H), 2.99 (t, 6H, *J* = 6.6 Hz), 1.77 (p, 6H, *J* = 7.5 Hz), 1.22 (sextet, 6H, *J* = 7.4 Hz), 0.88 (t, 9H, *J* = 7.5 Hz). Anal. Calcd. for CHN: C 44.35, H 6.62, N 13.41, . Found: C 44.72, H 6.72, N 13.36,. ESI-MS (*m/z*): 158.80 (M^{3+}), found 158.80.

IL C1-PF6: Tris(2-(3-n-butylimidazolium)ethyl)amine tris(hexafluorophosphate), ^{1}H-NMR (500 MHz, DMSO): δppm) = 9.03 (s, 3H), 7.77 (t, 3H, *J* = 1.7 Hz), 7.63 (t, 3H,

J = 1.7 Hz), 4.18 (m, 12H), 2.99 (t, 6H, *J* = 6.7 Hz), 1.77 (p, 6H, *J* = 7.4 Hz), 1.26 (sextet, 6H, *J* = 7.4 Hz), 0.91 (t, 9H, *J* = 7.3 Hz). Anal. Calcd. for CHN: C 35.91, H 5.34, N 10.83, . Found: C 35.97, H 5.49, N 10.63,. ESI-MS (*m/z*): 158.80 (M^{3+}), found 158.80.

IL C1-TFO: Tris(2-(3-n-butylimidazolium)ethyl)amine tris(trifluoromethane-sulfonate), ^{1}H-NMR (500 MHz, DMSO): δppm) = 9.07 (s, 3H), 7.76 (t, 3H, *J* = 1.7 Hz), 7.64 (t, 3H, *J* = 1.7 Hz), 4.18 (m, 12H), 3.00 (t, 6H, *J* = 6.7 Hz), 1.77 (p, 6H, *J* = 7.4 Hz), 1.25 (sextet, 6H, *J* = 7.4 Hz), 0.90 (t, 9H, *J* = 7.4 Hz). Anal. Calcd. for CHN: C 39.25, H 5.27, N 10.68, . Found: C 39.00, H 5.03, N 10.26,. ESI-MS (*m/z*): 158.80 (M^{3+}), found 158.80.

IL C2-NTf2: Tris(2-(3-n-methylimidazolium)ethyl)amine tris((bistrifluoromethyl-sulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 8.94 (s, 3H), 7.64 (t, 3H, *J* = 1.7 Hz), 7.58 (t, 3H, *J* = 1.7 Hz), 7.58 (t, 3H, *J* = 1.7 Hz), 4.22 (t, 6H, *J* = 6.4 Hz), 3.86 (s, 9H), 2.99 (t, 6H, *J* = 6.5 Hz). Anal. Calcd. for CHN: C 24.33, H 2.55, N 11.82, . Found: C 24.51, H 2.77, N 11.59,. ESI-MS (*m/z*): 114.75 (M^{3+}), found 114.75.

IL C3-NTf2: Tris(2-(3-n-benzylimidazolium)ethyl)amine tris((bistrifluoromethyl-sulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 9.12 (s, 3H), 7.76 (t, 3H, *J* = 1.7 Hz), 7.61 (t, 3H, *J* = 1.7 Hz), 7.41 (m, 15H), 5.42 (s, 6H), 4.15 (t, 6H, *J* = 6.5 Hz), 2.96 (t, 6H, *J* = 6.6 Hz). Anal. Calcd. for CHN: C 35.70, H 3.00, N 9.91, . Found: C 35.76, H 3.29, N 9.62,. ESI-MS (*m/z*): 190.78 (M^{3+}), found 190.78.

IL C4-NTf2: Tris(2-(butypyrrolidiniummethyl)ethyl)amine tris((bistrifluoromethyl-sulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 3.51 (m, 12H), 3.33 (t, 6H, *J* = 7.3 Hz), 3.20 (m, 6H), 2.89 (t, 6H, *J* = 7.5 Hz), 2.10 (d, 12H, *J* = 5.3 Hz), 1.63 (m, 6H),

1.34 (sextet, 6H, *J* = 7.4 Hz), 0.95 (m, 9H). Anal. Calcd. for CHN: C 32.75, H 4.81, N 7.43, . Found: C 33.00, H 5.02, N 7.35,. ESI-MS (*m/z*): 159.83 (M^{3+}), found 159.83.

IL C5-NTf2: Tris(2-(tripropylphosphoniummethyl)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 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). Anal. Calcd. for $C_{39}H_{75}F_{18}N_4O_{12}P_3S_6$: C 33.00, H 5.33, N 3.95, . Found: C 33.42, H 5.49, N 3.83,. ESI-MS (*m/z*): 192.84 (M^{3+}), found 192.84.

IL C6-NTf2: Tris(2-(3-n-hydroxyethylimidazolium)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δ(ppm) = 8.99 (s, 3H), 7.71 (t, 3H, J = 1.7 Hz), 7.06 (t, 3H, J = 1.7 Hz), 5.21 (t, 3H, J = 5.0 Hz), 4.21 (m, 12H), 3.75 (t, 6H, J = 5.0), 2.97 (t, 6H, J = 6.5 Hz). Anal. Calcd. for CHN: C 25.43, H 2.85, N 10.99, . Found: C 25.65, H 3.00, N 10.82,. ESI-MS (*m/z*): 144.76 (M^{3+}), found 144.76.

IL C7-NTf2: Tris(2-(tributylphosphoniummethyl)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δ(ppm) = 2.50 (m, 12H), 2.23 (m, 18H), 1.46 (m, 36H), 0.94 (t, 27H, J = 7.1 Hz). Anal. Calcd. for CHN: C 37.30, H 6.07, N 3.63, . Found: C 37.64, H 6.23, N 3.56,. ESI-MS (*m/z*): 234.88 (M^{3+}), found 234.88.

IL C8-NTf2: **Tris(2-(triphenylphosphoniummethyl)ethyl)amine tris((bistrifluoromethylsulfonyl)imide)** ^{1}H-NMR (500 MHz, DMSO): δ(ppm) = 7.74 (m, 45H), 3.63 (m, 6H), 2.84 (m, 6H). Anal. Calcd. for CHN: C 45.94, H 3.33, N 3.25, . Found: C 45.81, H 3.04, N 3.50,. ESI-MS (*m/z*): 294.79 (M^{3+}), found 294.79.

IL C9-NTf2: **Tris(2-(tritolysphosphoniummethyl)ethyl)amine tris((bistrifluoromethylsulfonyl)imide)** ^{1}H-NMR (500 MHz, DMSO): δ(ppm) = 7.55 (m, 36H), 3.38 (s, 27H), 2.44 (m, 12H). Anal. Calcd. for CHN: C 48.65, H 4.08, N 3.03, . Found: C 48.98, H 4.30, N 3.02,. ESI-MS (*m/z*): 336.84 (M^{3+}), found 336.84

IL D1-NTf2: Tris(2-(6-(3-butylimidazolium)hexaamido)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (500 MHz, DMSO): δppm) = 9.14 (s, 3H), 7.75 (d, 6H, *J* = 7.22), 4.11 (m, 12H), 3.08 (s, 3H), 2.04 (t, 6H, *J* = 7.22 Hz), 1.76 (m, 12), 1.48 (m, 6H), 1.18 (m, 12H), 0.86 (t, 9H, *J* = 7.22 Hz). Anal. Calcd. for CHN: C 37.11, H 4.95, N 11.07, . Found: C 37.40, H 4.85, N 11.20. ESI-MS (*m/z*): 270.06 (M^{3+}), found 270.06.

IL D2-NTf2: Tris(2-(6-(3-methylimidazolium)hexaamido)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 9.05 (s, 3H), 7.67 (d, 6H, *J* = 7.22 Hz), 4.11 (t, 6H, *J* = 7.22 Hz), 3.81 (s, 9H), 3.06 (br S, 3H), 2.02 (t, 6H, *J* = 7.22 Hz), 1.74 (m, 6H), 1.48 (m, 6H), 1.18 (m, 6H). Anal. Calcd. for CHN: C 33.09, H 4.17, N 11.94, . Found: C 32.95, H 4.09, N 11.94. ESI-MS (*m/z*): 227.98 (M^{3+}), found 227.98.

IL D3-NTf2: Tris(2-(6-(3-benzylimidazolium)hexaamido)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 9.25 (s, 3H), 7.76 (d, 6H, *J* = 7.22 Hz), 7.38 (m, 15H), 5.39 (s, 8H), 4.12 (t, 6H, *J* = 7.22 Hz), 3.04 (br s, 3H), 2.05 (t, 6H, *J* = 7.22 Hz), 1.76 (m, 6H), 1.48 (m, 6H), 1.20 (m, 6H). Anal. Calcd. for CHN: C 41.10, H 4.31, N 10.39, . Found: C 41.50, H 4.25, N 10.21. ESI-MS (*m/z*): 304.00 (M^{3+}), found 304.00.

IL D5-NTf2: Tris(2-(6-tripropylphosphoniumhexaamido)ethyl)amine tris((bistrifluoromethylsulfonyl)imide), ^{1}H-NMR (300 MHz, DMSO): δppm) = 3.06 (br s, 3H), 2.11 (m, 30H), 1.48-1.35 (m 36H), 0.98 (t, 27H, *J* = 7.22 Hz). Anal. Calcd. for CHN: C 38.93, H 6.19, N 5.57. Found: C 38.80, H 6.22, N 5.28. ESI-MS (*m/z*): 306.08 (M^{3+}), found 306.08.

3.3.2.2 Characterization

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 ethylbenzene 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. The samples were sealed in aluminium pans, and then heated and cooled at scan rate of 5 °C min^{-1} under a flow of nitrogen. All DSC data presented were measured on 7-15 mg samples. 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.

Refractive Index:

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 analysis:

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.

Solubility:

All compounds synthesized in this study were tested for solubility with polar (water) and non-polar (heptane) solvent. This was simply done by placing a small amount (60-90 mg) of the compound in the solvent (15 mL) and through observation of whether the solute was miscible or immiscible in the solvent.

Table 3.1 Physicochemical properties of tricationic ILs synthesized.

ionic liquid	MW (g/mol)	melting point (°C)	D^a (g/cm^3)	refractive index	viscosity[b] (cSt)	thermal stability[c] (°C)		miscibility with heptane[d]	miscibility with water[d]
						99% w	95% w		
A1-NTf2	1372.3	66−69	1.55			300	359	I	I
A2-NTf2	1246.0	82−85	1.69			338	370	I	I
A3-NTf2	1474.3	60−62	1.59			339	365	I	I
A5-NTf2	1480.4	123−126	1.31			288	398	I	I
B1-NTf2	1330.2	−24.6[e]	1.53	1.467	2320	344	401	I	I
B2-NTf2	1203.9	−38.6[e]	1.56	1.467	1280	364	414	I	I
B3-NTf2	1432.2	−87.4[e]	1.55	1.588	20000−25000	262	361	I	I
B4-NTf2	1339.3	62−64	1.44			344	371	I	I
B5-NTf2	1438.3	89−91	1.24			397	430	I	I
C1-NTf2	1311.2	−47.5[e]	1.41	1.451	1580	308	363	I	I
C2-NTf2	1184.9	36−37[e]	1.56			338	393	I	I
C3-NTf2	1413.2	−6.7[e]	1.51	1.493	25000−30000	348	381	I	I
C4-NTf2	1320.3	57−58[e]	1.47			297	337	I	I
C5-NTf2	1419.3	103−104	1.20			310	395	I	I
C6-NTf2	1275.0	−38.5[e]	1.64	1.460	7980	344	392	I	I
C7-NTf2	1545.5	133−135	1.26			361	406	I	I
C8-NTf2	1725.5	82−84[e]	1.53			235	269	I	I
C9-NTf2	1851.7	17.1[e]	1.37			396	398	I	I
D1-NTf2	1650.6	−54.1[e]	1.49	1.466	10200	262	335	I	I
D2-NTf2	1524.4	−16.4[e]	1.59	1.465	7760	279	351	I	I
D3-NTf2	1752.7	−15.6[e]	1.54	1.495	40000−45000	212	337	I	I
D5-NTf2	1758.8	−31.4[e]	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[e,f]	1.33			253	349	I	M
C1-Bf4	731.1	101−104	1.21			274	297	I	M

[a] Measured using pycnometer. [b] Measured using a capillary viscometer at 30 °C. [c] Thermogravimetric analysis (TGA), 99% *w*) temperature at 1% mass decrease of sample, 95% *w*) temperature at 5% mass decrease of sample. [d] I) immiscible, M) miscible [e] Phase transition temperature determined by using differential scanning calorimetry(DSC). [f] Amorphous solid.

3.4 Results and Discussion

The four main symmetrical tricationic cores, A, B, C and D are shown in Figure 3.1. These central cores were selected to range from the more rigid mesitylene core (A) to more flexible tri(2-hexanamido)ethylamine (D). Further modifications of the central cores were carried out by incorporating five different charge carrying groups (R1, R2, R3, R4 and R5). This allows a much extended study of molecular structure dependence of trications 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^-)

3.4.1 Melting Point

All four NTf_2^- salts synthesized with the flexible central tri(2-hexanamido)ethylamine core (D1 to D4) provided melting temperatures below 0 °C. 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 °C. 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^- counteranions and the moderately rigid central core (B) and moderately flexible core (C) associated with butylimidazolium charge carrying moiety were evaluated. Melting temperatures of these along with the NTf_2^- salts were compared. A general trend of melting temperatures for the tricationic ILs with same trication 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.[78] However, the trend is different to that observed in traditional imidazolium based monocationic ILs.[82]

3.4.2 Density

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^- counteranions (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 denser than those with the other three types of cores. The general trend that can be discerned from the data in Table 3.1 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, and 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.[78, 113, 114] Furthermore, it is clear from the data obtained given in Table 3.1 that for ionic liquids with similar cationic

moieties, densities are also affected by the nature of the counteranions in the order NTf_2^- > PF_6^- > TfO^- > BF_4^-.This trend is similar to that observed for both di- and mono-cationic ILs.[78, 82]

3.4.3 Viscosity

The kinematic viscosities of the 9 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 ^oC and are given in Table 3.1. The tricationic ionic liquids are much more viscous than traditional monocationic ionic liquids and dicationic ionic liquids. Some extended beyond the commonly observed values.[82] The viscosities are remarkably high for ILs containing benzylimidazolium charge carrying moiety (20000-45000 cSt for IL-B3, IL-C3, IL-D3). This may be due to the presence of additional aromatic moieties compared to other charge carrying moieties.[19] Ionic liquids with higher viscosities are preferred for some applications, such as stationary phases for gas-liquid chromatography.[9, 16] Viscosities of ionic liquids with imidazolium based moieties with NTf_2^- anion show increase in viscosity 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). This has previously been observed and/or discussed with traditional monocationic and dicationic ionic liquids.[19, 78, 103, 114]

3.4.4 Thermal Stability

Thermal stabilities of the 28 tricationic liquids were measured by thermogravimetric analysis (TGA) and are given in Table 3.1. Thermal stabilities (5% weight loss) of 17 tricationic ionic liquids with NTf_2^- counter anion range from 355 ^oC to 430 ^oC 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, 395 ^{o}C for IL-C5 and 405 ^{o}C for IL-D5 at 5% thermal degradation) followed by methylimidazolium cationic moieties (414 ^{o}C for IL-B2, 370 ^{o}C for IL-A2, 393 ^{o}C for IL-C2 and 351 ^{o}C for IL-D2 at 5% thermal degradation). Furthermore the data show that ILs with NTf_2^- anion possess highest thermal stabilities followed by ILs with TfO^- as counter anion.

3.4.5 Miscibility

The miscibility of all ionic liquids in both water (polar) and heptane (non-polar) solvent were evaluated (Table 3.1). Tricationic ionic liquids illustrate similar solubility behavior as monocationic and dicationic ionic liquids.[1, 7, 19, 87-89] None of the ionic liquids were soluble in heptane. However all compounds with BF_4^-, and TfO^- as anions were soluble in water, whereas all compounds with PF_6^- and NTf_2^- anions were insoluble in water. 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[7, 19] and lie between 1.451 and 1.588.

3.5 Conclusions

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 °C) are greater than that of traditional monocationic ionic liquids. It is also clear that the melting point of tricationic ILs are contingent on the flexibility of the central core system; for example, 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 4

LINEAR TRICATIONIC ROOM TEMPERATURE IONIC LIQUIDS: SYNTHESIS, PHYSIOCHEMICAL PROPERTIES AND ELECTROWETTING PROPERTIES

4.1 Abstract

Efficient and facile synthesis of novel linear tricationic room temperature ionic liquids was performed and their physiochemical properties were determined. Different physiochemical properties were observed according to the structural variations such as the cationic moiety and the counter anion of the ionic liquid. The electrowetting properties of these ionic liquids were also investigated and linear tricationic ionic liquids were shown to be advantageous as effective electrowetting materials due to their high structural flexibility.

4.2 Introduction

Room temperature ionic liquids (RTILs) are a class of salts that are liquids at or near room temperature.[1] Recently RTILs have attracted much attention in academic research and industry since they have shown profound advantages in the context of green chemistry and have great technological potential.[84, 115] Recently monocationic, dicationic and tricationic ionic liquids have been used extensively in the field of analytical chemistry as ion pairing reagents for the ultra trace detection of anions in the positive mode of electrospray ionization mass spectrometry (ESI-MS),[83, 116] high thermal stability gas chromatographic (GC) stationary phases,[17, 67, 82, 117] capillary

electrophoresis (CE),[62] and electrowetting applications.[118-120] Payagala *et al*. recently reported the synthesis and physiochemical properties of a series of dicationic and tricationic ionic liquids.[19, 78, 121] These reported ILs possessed good thermal stabilities and higher viscosities with compare to monocationic ILs.[7, 85] Moreover, it was shown by Payagala *et.al*. that physicochemical properties such as viscosity, density, thermal stability, melting point and solubility behaviors can be varied (tuned) to a greater extent in multi-cationic ILs than in the conventional ILs by changing the cation type, linkage chain length, etc.[19, 78, 121] However, the tuning capability for trigonal tricationic ILs[121] was lower than that of linear dicationic ILs.[19] This was because in most of the trigonal ILs synthesized, there were only two methylene moieties between the rigid trigonal core and the three pendant cationic moieties. The rigid trigonal geometry and the existence of three charge carrying moieties in the close proximity resulted in high apparent polarity and relatively high melting salts. Based on these observations, it was concluded that for multi-cationic ILs, the linear geometry would give the best tunability in terms of physicochemical properties and the highest probability of forming RTILs.

The interesting physicochemical properties of the ILs have led to their use in applications involving electrowetting on dielectric-based microfluidic devices.[118-120] Electrowetting (EW) is the decrease in contact angle when an external voltage is applied across the solid/liquid interface. Simple EW which utilizes a metal base to hold the droplet is often associated with the drawback of droplet instability with change of the voltage whereas electrowetting on dielectric solid (e.g., Teflon) produces stable and reversible droplet shape with changes in the voltage.[122] Since reversibility of the droplet shape with the change in voltage is an important factor in microfluidic devices, electrowetting on dielectric (EWOD) has shown greater success in applications such as

fluid lens systems, electrowetting displays, optical filters, paint drying, micromotors, electronic microreactors, and in controlling fluids in multichannel structures.[122-126] Water or aqueous electrolytes are used in nearly all EWOD devices. Water-based systems were known to create complications due to their evaporation, low thermal stability and tendency to contribute to corrosion in integrated electronics.[122] The unique properties of RTILs including negligible vapor pressure, ultra high stability over a wide temperature range, and large electrochemical windows[1] make them ideal in EWOD applications over traditional aqueous or electrolyte solutions. Recently a detailed study was carried out to find electrowetting properties of traditional and multifunctional ILs.[118, 119] These EWOD-based microreactors and microextraction devices have been used in various scientific areas. Dubois *et al*. demonstrated the use of IL droplets as electronic microreactors on an open digital microfluidic chips.[127] Also, Chatterjee *et al.* recently demonstrated that ILs can be used in digital microfluidic devices.[128] Moon *et al.* used ILs in EWOD-based micro-heat transfer device and Kunchala *et al*. used an IL in a EWOD-based liquid-liquid extraction device.[129, 130]

The contact angle θ, between the dielectric surface and the ionic liquid droplet under an external voltage of V is derived from a combination of Young's and Lippmann's equations (eq 4.1).[118, 119]

$$\cos\theta = \cos\theta_0 + \frac{c}{2\gamma}V^2 = \cos\theta_0 + \frac{\varepsilon\varepsilon_0}{2\gamma t}V^2 \text{.....}(4.1)$$

Here, c is the capacitance per unit area (specific capacitance), ε is the relative permittivity of the dielectric layer (dielectric constant), ε_0 is the permittivity of a vacuum,

γ is the surface tension of the liquid, t is the thickness of the dielectric layer, θ is the contact angle at the designated voltage across a dielectric layer, and θ_0 is the contact angle at zero voltage. As the voltage increases, the contact angle also increases according to eq 4.1. After a certain point, the contact angle starts to deviate from the regular behavior with increasing voltage. The voltage and corresponding contact angle where this occurs is referred to as the saturation voltage and saturation angle, respectively. According to eq 4.1, a plot of contact angle versus applied voltage should give a parabolic graph as shown in Figure 4.1.

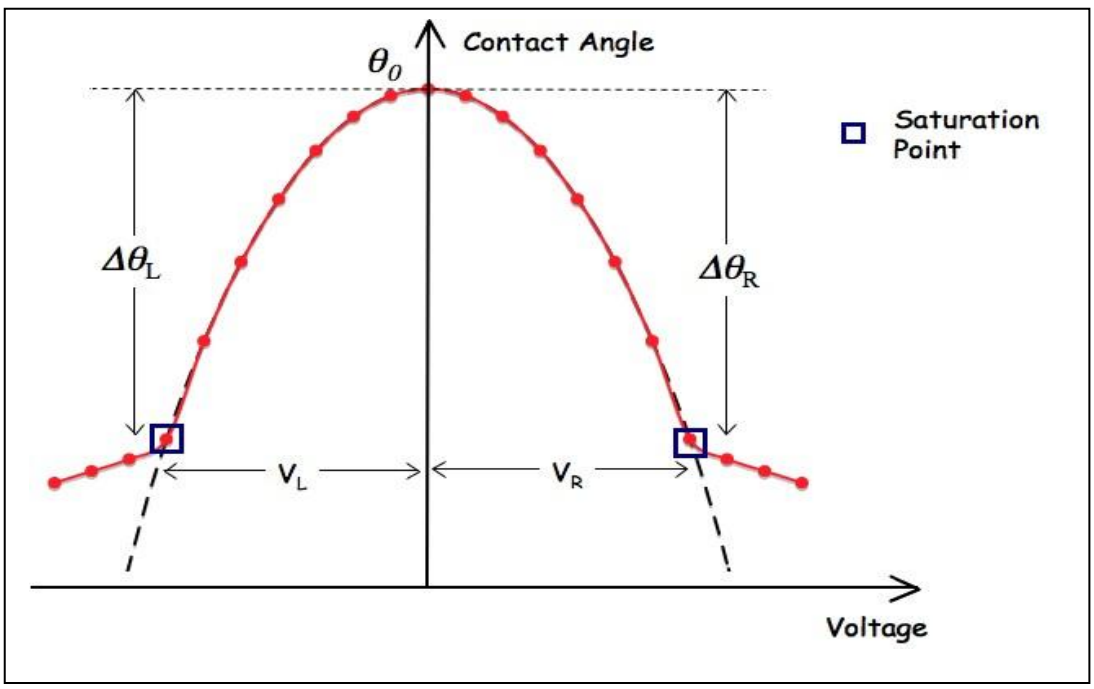


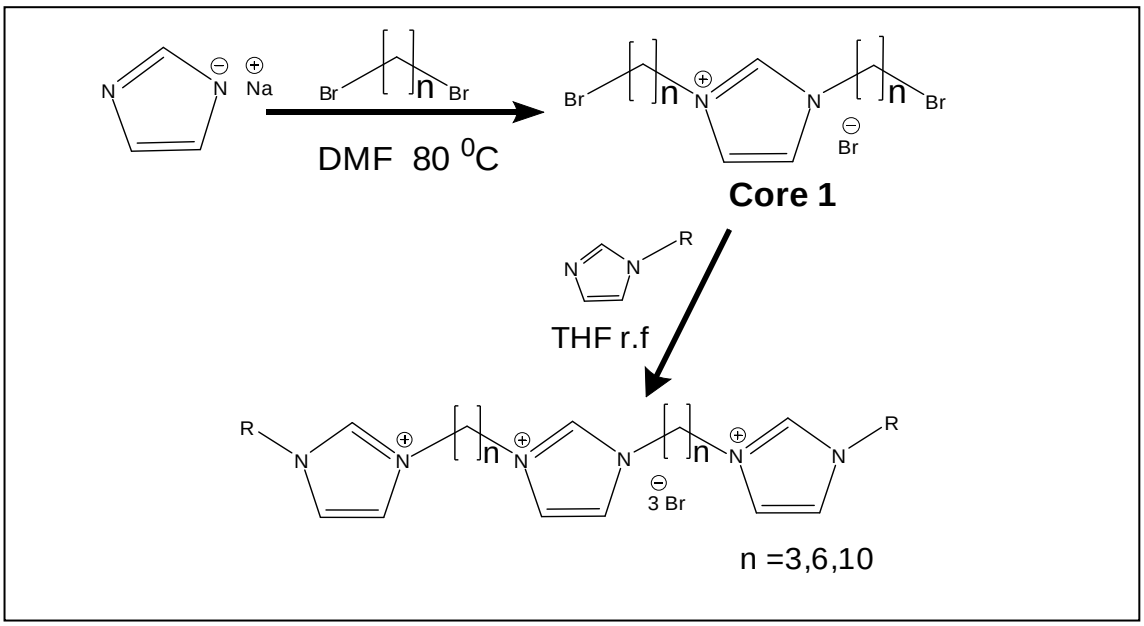
Figure 4.1 Plot of contact angle vs. voltage according to Young's and Lippmann's equation.

Our previous studies have shown the use of a series of RTILs in EW experiments and a correlation between contact angle variation with the structure of the ionic liquid (IL). Monocationic, dicationic and tricationic ILs were used in those experiments. The trigonal tricationic ILs in our previous study were of trigonal geometry hence had relatively rigid structure.[121]

In this study, we report the synthesis and physiochemical properties and electrowetting properties of linear tricationic ionic liquids (LTILs) for the first time. Furthermore, we explore the electrowetting properties and their correlation with structural flexibility.

4.3 Experimental

Structures of the LTILs synthesized are illustrated in Figure 4.2 and Scheme 4.1 illustrates the synthesis of the core structure.



Scheme 4.1 Synthesis of LTIL with R-substituted methyl imidazole as the charge carrying moiety.

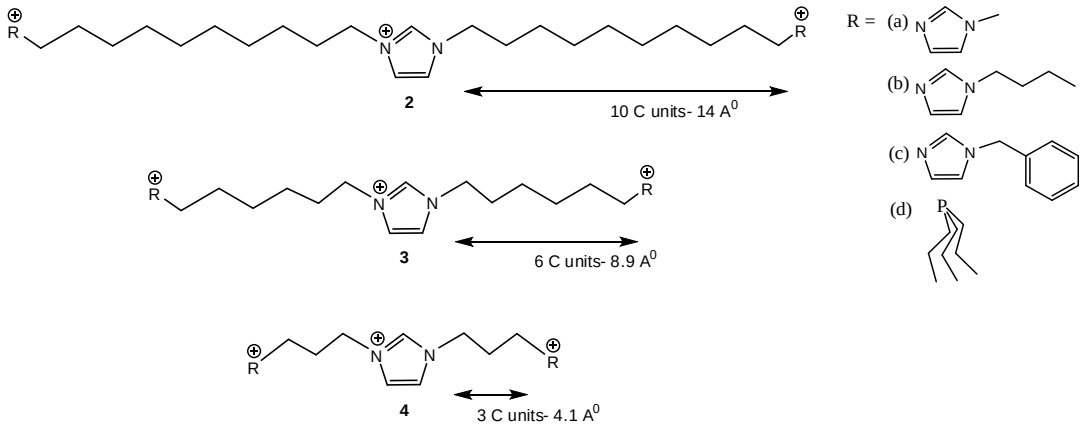


Figure 4.2 Structures of linear tricationic ionic liquids.

4.3.1 General Methods

All ^{1}H NMR, ^{13}C NMR (data reported are for bromide salts), and ^{31}P NMR spectra were recorded at 295 ± 1 K on JEOL Eclipse 300 MHz spectrometer. All NMR spectra were recorded in deuterated dimethylsulfoxide and the chemical shifts were measured relative to residual nondeuterated solvent resonances. Electrowetting experiments were conducted by using a slightly modified contact angle goniometer (www.ksvltd.com, Monroe, CT). Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen or argon atmosphere.

Caution 1: Tripropylphosphine is a pyrophoric substance and should be handled carefully under a stream of nitrogen or argon.

Caution 2: Toxicity data for the synthesized ionic liquids are unavailable hence should be handled carefully.

4.3.1.1 Glass transition temperature / melting point

The thermal measurements were performed with a differential scanning calorimeter (DSC, PerkinElmer Diamond DSC, 710 Bridgeport Av, Shelton, CT, USA). Diamond DSC was calibrated using an indium primary standard, with solid-solid transitions for cyclohexane and ethylbenzene as supplementary low temperature standards. IL samples (5-10 mg) 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. The samples were sealed in aluminium pans, and then heated and cooled at scan rate of 10 °C min^{-1} under a flow of nitrogen. For solid compounds, the melting points were verified using a capillary melting point apparatus (MEL-TEMP, 68 Cambridge, MA, USA).

4.3.1.2 Density

The densities of the ionic liquids were determined at 23 ±1 °C with Kimble Glass Specific Gravity Pycnometer (Vineland, NJ).

4.3.1.3 Refractive Index

Refractive index measurements were conducted at 23 ±1 °C using a Bausch & Lomb Abbe-3L refractometer.

4.3.1.4 Viscosity

Kinematic viscosities were determined at 30 ±1 °C using Cannon-Manning Semi-Micro capillary viscometer (State College, PA).

4.3.1.5 Thermal stability analysis

Thermogravimetric analysis (TGA) was done using a TGA 2050 (TA Instruments Inc., Thermal Analysis & Rheology, New Castle, DE, USA). Samples (ca.

20 mg) were placed on the platinum pans, and heated at 10 °C min^{-1} from room temperature to 600 °C in a dynamic nitrogen atmosphere. The decomposition temperatures were reported as the temperatures of 1%, 5% and 50 % weight loss of the sample.

4.3.1.6 Electrowetting experiments

Electrowetting experiments were conducted by using a slightly modified contact angle goniometer (www.ksvltd.com, Monroe, CT). Figure 4.3 shows the arrangement for the electrowetting experiment. Indium-tin-oxide (ITO, 30 nm thickness) pre-coated unpolished float glass slides (www.delta-technologies.com, Stillwater, MN) were used as purchased. They were dip-coated in a 4% (w/v) of Teflon AF1600 (www2.dupont.com, Wilmington, DE) in Fluoroinert FC75 solvent (www.fishersci.com Barrington, IL) solution. The dipping speed was approximately 0.78 ± 0.03 mm/s in a custom made dipcoater. Only 3/4 of the slide was dipped in the solution, then it was stopped for 5 seconds and after that the slide was raised at the same speed. The coated slides were kept in an oven at 112 ºC for 6 min, at 165 ºC 5 min and at 328 ºC for 15 min. Once Teflon coated glass slides were taken out from the oven, they were allowed to cool to room temperature. Then they were washed thoroughly with acetone and deionized water followed by air-drying.

A capillary tube was used to place a drop of IL on top of the Teflon layer. CAM 200 software (www.ksvltd.com, Monroe, CT) was used to calculate drop volume, it was between 5 ± 2 μL for all experiments. Keithley 2400 SourceMeter (www.keithley.com, Cleveland, OH) was used to apply voltage in 5 V increments starting from 0 to + 70 V.

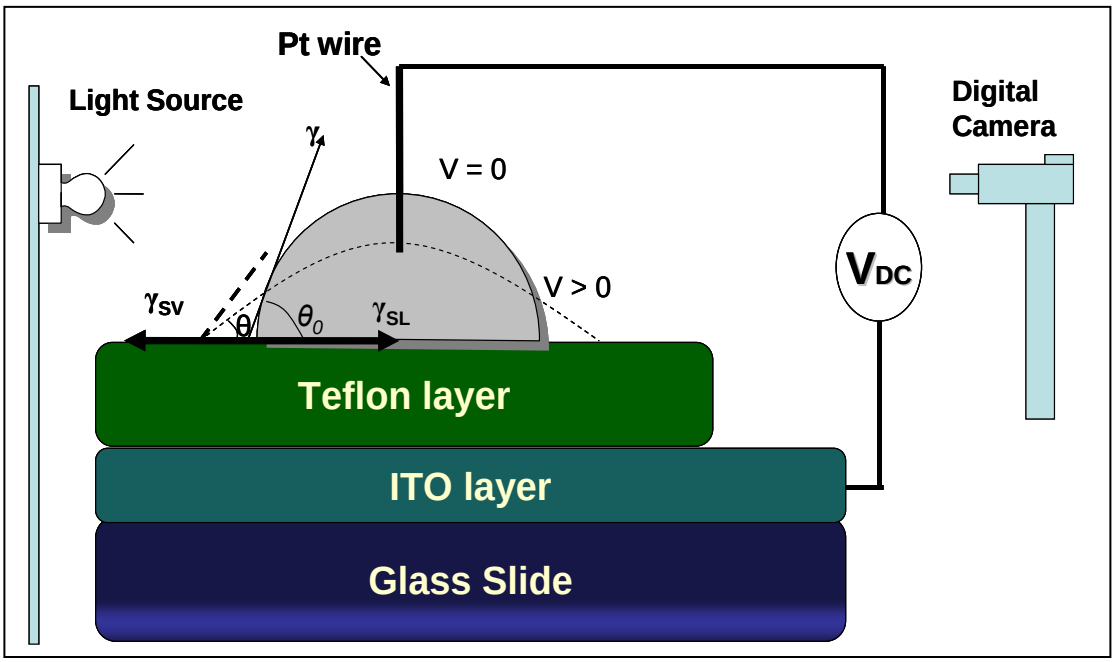


Figure 4.3 The electrowetting experimental setup.
Here, γ, γSV, and γSL are the interfacial tensions associated with the liquid/vapor, solid/vapor, and solid/liquid interfaces.

The positive probe was connected to the Pt wire and negative probe was connected to the ITO layer (see Figure 4.3). Afterwards, the above procedure was repeated for 0 to – 70 V for a fresh drop of IL placing at a different position on the surface. At each voltage increment a picture was taken and then CAM 200 software was used to measure corresponding contact angles. Finally, the contact angles versus voltage curves were plotted.

4.3.2 Materials

The reagents required for synthesis included anhydrous dimethylformamide, anhydrous acetonitrile, anhydrous tetrahydrouran, sodium imidazole, 1,3-dibromoproapne, 1,6-dibromohexane, 1,10-dibromodecane, methylimidazole,

butylimidazole, benzylimidazole, benzyl imidazole and tripropylphosphine which were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All chemicals were of reagent grade and were used without further purification. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200-425 mesh) was used.

Procedure for the synthesis of the core structure **(1-bromodecyl-3-bromodecyl imidazolium bromide salt (1a):** Sodium imidazole (1.0 g,12.1 mmol) in anhydrous 20 ml of DMF was added slowly in to a solution of dibromodecane (18.2 g 60.5 mmol) in 100 ml of anhydrous DMF by using a syringe pump over a period of 3 hr at room temperature. After completion of the addition, the reaction mixture was heated up to 70 ^{0}C for 12 hr. Then DMF was evaporated under vacuum and the resulting crude material was washed with hexane (5 ×100ml) to remove excess dibromoalkane. Then the crude product was subjected to column chromatography using CH_3OH:CH_2Cl_2 1:9 as the eluent system. The purified product was then dried under vacuum overnight to yield the desired product in 55% (3.8 g) .^{1}H NMR: δ 9.21 (s, 1H), 7.80 (d, J = 1.7 Hz, 2H), 4.15 (t, J = 7.0 Hz, 4H), 3.51 (t, J = 7.0 Hz, 4H), 1.77 (m, 8H), 1.33 (m, 4H), 1.24 (br s, 20H); ^{13}C NMR: δ 136.4, 123.0, 49.4, 35.8, 32.7, 29.7, 29.2, 28.8, 28.6, 28.0, 25.9. Anal Calcd for $C_{23}H_{43}N_2$: C, 47.04; H, 7.38; Br, 40.82; N, 4.77; Found: C, 47.1; H, 7.9; N, 4.8. ESI-MS (*m/z*): 507.4 (M^+), found 507.2.

Procedure for the synthesis of the core structure **(1-bromohexyl-3-bromohexyl imidazolium bromide salt (1b):** This compound was prepared by a similar procedure as described above for **1a**. Sodium imidazole (1.0 g, 12.1 mmol) in 20 ml anhydrous DMF was added slowly in to a solution of dibromodecane (14.8 g, 60.5 mmol) 100 ml of anhydrous DMF by using a syringe pump over a period of 3 hr at room temperature. After completion of the addition, the solution was stirred for

additional 12 hr. Then DMF was evaporated under vacuum and the resulting crude material was washed with hexane (5 ×100ml) to remove excess dibromoalkane. Then the resulting crude product was subjected to column chromatography using CH_3OH:CH_2Cl_2 1:9 as the eluent system. The purified product was then dried under vacuum overnight to yield the desired product in 62 % (2.9 g).^{1}H NMR: δ 9.38 (s, 1H), 7.84 (s, 2H), 4.18-4.13 (t, *J* = 7.2, 4H), 3.50-3.46 (t, *J* = 6.5, 4H), 1.81-1.70 (m, 8H), 1.41-1.31 (m, 4H), 1.25-1.15 (m, 4H); ^{13}C NMR: δ 136.5, 122.9, 60.9, 49.2, 32.6, 29.8, 25.8, 25.3; Anal Calcd for $C_{15}H_{27}N_2$: C, 37.92; H, 5.73; N, 5.90; Found: C, 37.9; H, 5.8; N, 5.9. ESI-MS (*m/z*): 475.10 (M^+), found 475.1.

Procedure for the synthesis of the core structure **(1-brompropyl-3-bromopropyl imidazolium bromide salt (1c):** This compound was prepared in a similar procedure to **1b** (Yield 70 %, 3.3 g). ^{1}H NMR: *δ* 9.27 (s, 1H), 7.83 (d, *J* = 1.4 Hz, 2H), 4.28 (t, *J* = 7.0 Hz, 4H), 3.54 (t, *J* = 7.0 Hz, 4H), 2.37 (m, 4H); ^{13}C NMR: *δ* 136.4, 122.9, 49.3, 29.9, 29.2, 28.9, 20.4, 19.8, 15.9, 15.2. Anal Calcd for $C_9H_{15}N_2$: C, 27.65; H, 3.87; Br, 61.32; N, 7.17; Found: C, 27.6; H, 3.9; N, 7.2. ESI-MS (*m/z*): 311.0 (M^+), found 311.0.

Procedure for the synthesis of LTILs **(2a-d, 3a-d, 4a-d):** All the reactions were carried out in tetrahydrofuran (THF) except for **4a-d** in which acetonitrile (ACN) was used as the reaction solvent. Linear core structures **1a, b** or **c** 1eq in THF (or ACN) were reacted with 2.5 eq of methyl imidazole, butyl imidazole, benzyl imidazole or tripropyl phosphine under reflux over 36-48 hrs. (Phosphonium ILs need to be reacted for 48 hrs). Then the solvent was removed in vacuo and resulting thick liquid or solid was dissolved in 5-10 ml of deionized water. The aqueous layer was then washed with

ethyl acetate (6 × 100 ml) and water was removed in vacuo. The final product as the bromide salt was then dried in high vacuum (75-85 % yield).

Final products were synthesized through a metathesis reaction of the bromide salts with lithium trifluorlmethanesulfonimide ($LiNTf_2$), sodium tetrafluoroborate ($NaBF_4$) and lithium trifluoromethansulfonate (LiTfO) according to the previously published procedure.

1-(1'-methyl-3'-decylimidazolium)-3-(1''-methyl-3''-decylimidazolium) imidazolium tri [bis(trifluoromethanesulfonyl)imide] (2a). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.15 (s, 1H), 9.08 (s, 2H), 7.78 (d, J = 1.4 Hz, 2H), 7.75 (t, J = 1.4 Hz, 2H), 7.69 (t, J = 1.4 Hz , 2H), 4.14 (t, J = 7.2 Hz, 8H), 3.84 (s, 6H), 1.65-1.80 (m, 8H), 1.24 (br s, 26H); ^{13}C NMR: δ 137.2, 136.4, 124.1, 122.9, 122.8, 49.3,49.2,36.3, 29.9, 29.3, 28.9, 26.1; ^{19}F NMR: -78.6. Anal. Calcd for $C_{37}H_{55}N_9$: C, 32.86; H, 4.10; N, 9.32; Found: C, 32.8; H, 4.3; N, 9.3. ESI-MS (*m/z*): 170.4 (M^{3+}), found 170.5.

1-(1'-butyl-3'-decylimidazolium)-3-(1''-butyl-3''-decylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (2b). ^{1}H NMR: δ 9.17 (s, 1H), 9.15 (s, 2H), 7.80-7.77 (m, 6H), 4.18 (q, J = 6.8 Hz, 12H), 1.81-1.74 (m, 12H), 1.30-1.18 (br s, 28H), 0.89 (t, J = 7.5 Hz, 6H); ^{13}C NMR: δ 136.5, 122.9, 122.8, 49.3, 49.0, 31.8, 29.8, 29.2, 28.8, 26.0, 19.3, 13.8; ^{19}F NMR: -78.6. Anal. Calcd for $C_{43}H_{67}N_9$: C, 35.95; H, 4.70; N, 8.78; Found: C, 35.5; H, 4.8; N, 8.8. ESI-MS (*m/z*): 198.51 (M^{3+}), found 198.5.

1-(1'-benzyl-3'-decylimidazolium)-3-(1''-benzyl-3''-decylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (2c) ^{1}H NMR: δ 9.25 (s, 2H), 9.12 (s, 1H), 7.79-7.75 (m, 6H), 7.38 (m, 10H) 5.38 (s, 2H), 4.14 (q, J = 7.0 Hz, 8H), 1.79-1.72 (m, 8H), 1.20 (br s, 24H); ^{13}C NMR: δ 136.6, 136.4, 135.4, 129.5, 129.3, 128.7, 123.3, 123.1, 122.9, 52.4, 49.5, 29.8, 29.3 28.8, 26.1; ^{19}F NMR: -78.6. Anal. Calcd for

$C_{49}H_{63}N_9$: C, 39.12; H, 4.22;N, 8.38; Found: C, 39.2; H, 4.3; N, 8.4. ESI-MS (*m/z*): 221.1 (M^{3+}), found 221.2.

1-decyltripropylphosphonium-3-decyltripropylphosphonium imidazolium tri [bis(trifluoromethanesulfonyl)imide] (2d). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.33 (s, 1 H), 7.83 (d, J = 1.4, 2H), 4.18 (t, J = 7.2, 4H), 2.17-2.10 (m, 18H), 1.77-1.73 (m, 18 H), 1.37-1.22 (m, 20H), 0.98 (t, J = 7.0, 18H); ^{13}C NMR: δ 136.4, 122.9, 49.3, 29.9, 29.3, 28.8, 26.1, 21.24, 20.4, 19.8, 18.5, 17.9, 15.9, 15.2; ^{19}F NMR: -78.6. Anal. Calcd for $C_{47}H_{85}N_5$: C, 37.42; H, 5.68; N, 4.64; Found: C, 37.7; H, 5.7; N, 4.6. ESI-MS (*m/z*): 222.5 (M^{3+}), found 222.5.

1-(1'-methyl-3'-hexylimidazolium)-3-(1''-methyl-3''-hexylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (3a). ^{1}H NMR: δ 9.50 (s, 1H), 9.35 (s, 2H), 7.86 (s, 2H), 7.84 (s, 2H), 7.73 (s, 2H), 4.17 (m, 8H), 3.84 (s, 6 H), 1.77 (m, 8H), 1.24 (m, 8H); ^{13}C NMR: δ 137.1, 136.5, 124.1, 122.9, 122.8, 49.1, 49.1, 36.3, 29.6, 29.5, 25.3; ^{19}F NMR: -78.6. Anal. Calcd for $C_{29}H_{39}N_9$: C, 28.09; H, 3.17; N, 10.17; Found: C, 28.1; H, 3.2; N, 10.2. ESI-MS (*m/z*): 133.1 (M^{3+}), found 133.1.

1-(1'-butyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide]) (3b). ^{1}H NMR: δ 9.47 (s, 1H), 9.43 (s, 2H), 7.86 (s, 4H), 7.84 (s, 2H), 4.17 (t, J = 7.2 Hz, 12H), 1.79-1.72 (m, 12H), 1.24-1.17 (m, 12H), 0.85 (t, J = 7.2 Hz, 6H); ^{13}C NMR: δ 136.5, 122.9, 49.1, 49.0, 31.8, 29.5, 25.3, 19.3, 13.8; ^{19}F NMR: -78.6. Anal. Calcd for $C_{35}H_{51}N_9$: C, 31.75; H, 3.88; N, 9.52; Found: C, 31.7; H, 3.9; N, 9.5. ESI-MS (*m/z*): 161.1 (M^{3+}), found 161.1.

1-(1'-benzyl-3'-hexylimidazolium)-3-(1''-methyl-3''-hexylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (3c). ^{1}H NMR: δ 9.52 (s, 1H), 9.44 (s, 2H), 7.85 (s, 6H), 7.44-7.34 (M, 10H), 5.45 (s, 4H), 4.19-4.15 (m,8 H), 1.77 (s, 8H), 1.24 (m,

8H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 136.6, 135.4, 129.5, 129.4, 128.8, 123.3, 123.0, 122.9, 52.3, 49.3, 49.1, 29.6, 29.5, 25.3; ^{19}F NMR: -78.6. Anal. Calcd for $C_{41}H_{47}N_9$: C, 35.37; H, 3.40; N, 9.05; Found: C, 35.3; H, 3.4; N, 9.1. ESI-MS (*m/z*): 183.7 (M^{3+}), found 183.8.

1-(hexyltripropylphosphonium)-3-(hexyltripropylphosphonium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (3d). ^{1}H NMR: δ 9.55 (s, 1H), 7.87 (s, 2H), 4.21 (t, *J* = 6.9 Hz, 4H), 2.24-2.12 (m, 16H), 1.85-1.75 (m, 4H), 1.56-1.26 (m, 24H) 1.00-0.95 (t, *J* = 6.8 Hz, 18H); ^{13}C NMR: δ 136.6, 122.9, 49.2, 29.5, 25.3, 21.0, 20.5, 19.9, 15.9, 15.7, 15.3; ^{19}F NMR: -78.6. Anal. Calcd for $C_{39}H_{69}N_5$: C, 33.55; H, 4.98; N, 5.02; Found: C, 33.6; H, 5.0; N, 5.0. ESI-MS (*m/z*): 185.1 (M^{3+}), found 185.2.

(1'-methyl-3'-propylmidazolium)-3-(1''-methyl-3''-propylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (4a). ^{1}H NMR: δ 9.50 (s, 1H), 9.32 (s, 2H), 4.31-4.25(m, 8H), 3.87 (s, 6H), 2.46-2.42 (m, 4H); ^{13}C NMR: δ 137.1, 123.0, 49.6, 26.0, 22.1, 20.4, 19.8, 15.9, 15.7, 15.3, ^{19}F NMR: -78.6. Anal. Calcd for $C_{23}H_{27}N_9$: C, 23.90; H, 2.3; N, 10.9; Found: C, 23.9; H, 2.40; N, 10.97. ESI-MS (*m/z*): 105.0 (M^{3+}), found 105.1.

1-(1'-butyl-3'-propylmidazolium)-3-(1''-butyl-3''-propylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (4b). ^{1}H NMR: δ 9.50 (s, 1H), 9.43 (s, 2H), 7.90-7.84 (m, 6H), 4.32-4.29 (m, 8H), 4.19 (t, *J* = 7.2 Hz, 4H), 2.48-2.43 (m, 4H), 1.81-1.76(m ,4H), 1.31-1.23 (m, 4H), 0.90 (t, *J* = 7.2, 6H); ^{13}C NMR: δ 137.1, 136.8, 49.2, 46.4, 31.7, 29.9, 19.3, 13.8; ^{19}F NMR: -78.6. Anal. Calcd for $C_{29}H_{39}N_9$: C, 28.09; H, 3.17; F, 27.58; N, 10.17; Found: C, 28.0; H, 3.2; N, 10.2. ESI-MS (*m/z*): 133.1 (M^{3+}), found 133.1.

1-(1'-benzyl-3'-propylmidazolium)-3-(1''-benzyl-3''-propylimidazolium)imidazolium tri [bis(trifluoromethanesulfonyl)imide] (4c). ^{1}H NMR: δ 9.52 (s, 2H), 9.48 (s, 1H), 7.48-7.38 (m, 10H), 5.47 (s, 4H), 4.29 (q, J = 5.8 Hz, 8H), 2.45 (m, 4H); ^{13}C NMR: δ 137.2, 123.0, 62.5, 49.4, 26.0, 22.1, 20.5, 19.9, 16.1, 15.9, 15.3; ^{19}F NMR: δ -78.6. Anal. Calcd for $C_{35}H_{35}N_9$: C, 32.14; H, 2.70; N, 9.64; Found: C, 32.1; H, 2.7; N, 9.6. ESI-MS (*m/z*): 155.7 (M^{3+}), found 155.7.

1-propyltripropylphosphonium-3-propyltripropylphosphonium imidazolium tri[bis(trifluoromethanesulfonyl)imide] (4d). ^{1}H NMR: δ 9.12 (s, 1H), 7.84 (s, 2H), 4.24 (t, J = 6.8, 4H), 2.23-2.21 (m, 20H), .57-1.47 (m, 12H), 1.04-1.00 (m, 12H), 1.04 (t, J = 7.2 Hz, 18H); ^{13}C NMR: δ 137.9, 123.0, 62.5, 49.6, 26.0, 22.1, 20.4, 19.8, 15.9, 15.3, ^{19}F NMR (282 MHz): -78.6 Anal. Calcd for $C_{33}H_{57}N_5$: C, 30.21; H, 4.38; N, 5.34; Found: C, 30.2; H, 4.4; N, 5.3. ESI-MS (*m/z*): 157.1 (M^{3+}), found 157.1.

4.4 Results and Discussion

4.4.1 Synthesis of Core Structures and Linear ILs

The synthetic strategy involved in these linear tricationic ILs was different from previously reported ionic liquids for the following reasons: 1. **Core 1** (Scheme 4.1) was designed and synthesized in-house. It was separated and isolated from the dicationic and polycationic impurities that were formed during the reaction, by running through flash chromatographic column (SiO_2 60 Å, CH_2Cl_2:CH_3OH 1:9). 2. Reaction solvent. In previous dicationic and trigonal tricationic IL syntheses, isopropyl alcohol was used as the reaction solvent in most cases.[19, 78, 121] However, when alcohols are used, the basic imidazole tends to deprotonate the alcohol enabling unwanted nucleophilic substitution reactions.[131] This complicated the separation of the pure LTILs from the reaction

mixture. Therefore the solvent used in the synthesis of **Core 1** was dimethylformamide (DMF). This was because DMF dissolved sodium imidazole (NaIM) and it minimized the side reactions that take place with protic solvents. Other reaction solvents for the synthesis of ILs involving imidazolium moieties were found to be acetonitrile (ACN) and tetrahydrofuran (THF). However IPA can be used as the solvent in reactions involving tripropyl phosphonium which has a weak basic character compared to imidazole.

4.4.2 Physicochemical Properties of Linear Tricationic Ionic Liquids

In this study, 14 linear tricationic ionic liquids were synthesized and their physicochemical properties were investigated. The results are listed in Table 4.1.

4.4.2.1 Phase transitions

Phase transition temperatures, including glass transition temperatures (Tg), were determined using differential scanning calorimetry (DSC). LTILs show significantly lower glass transition temperatures (except for **4d**) compared to many other types of ILs in the literature, such as symmetrical dicationic ILs.[19] It has been shown for most dicationic ILs that when the chain length is smaller than 3 methylene units, the IL becomes solid regardless of other structural changes.[78] However we found that LTILs with C-3 linkage chains (**4a**, **4b**, **4c)** (see Figure 4.1) do exist as RTILs when the counter anion is bis(trifluromethylsulfonyl)imide (NTf_2^-).

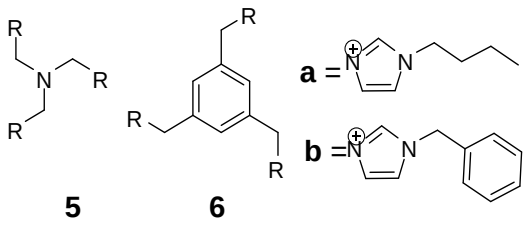


Figure 4.4 Structures of ILs 5a-6b.

Table 4.1 Physicochemical properties of linear tricationic ionic liquids.

Ionic Liquid	MW g/mol	melting	Density[b]	Refractive	Viscosity[c]	Thermal stability [d]			Miscibility [e]	
		point [a] (°C)	gcm-3	index	(cSt)	99 %w	95%w	50%w	Heptane	Water
2a-NTf2	1352.25	-53	1.65	1.45	1800	334	400	444	I	I
2b-NTf2	1435.29	-53	1.54	1.44	2400	350	390	430	I	I
2c-NTf2	1504.44	-36	1.36	1.48	4200	320	390	450	I	I
2d-NTf2	1507.37	-41	1.46	1.45	2100	360	410	440	I	I
2b-BF4	856.55	-18	1.33	-	-	191	308	369	I	M
2b-TfO	1043.18	-42	1.28	-	-	290	376	430	I	M
3a-NTf2	1240.03	-57	1.57	1.44	372	320	380	480	I	I
3b-NTf2	1324.19	-51	1.41	1.49	429	330	380	470	I	I
3c-NTf2	1391.14	-36	1.43	1.47	840	340	370	470	I	I
3d-NTf2	1396.3	-45	1.38	1.45	770	355	400	440	I	I
4a-NTf2	1155.88	-24	1.54	1.46	1200	290	360	410	I	I
4b-NTf2	1240.04	-44	1.48	1.49	600	310	370	470	I	I
4c-NTf2	1308.07	-27	1.41	1.48	4080	300	350	470	I	I
4d-NTf2	1312.14	71-72	1.59	-	-	320	390	480	I	I

[a] Determined by using Differential Scanning Calorimeter upon heating cycle and melting points are reported as the onset temperature of melting endotherm. [b] Determined by using a pycnometer, [c], Measured using capillary viscometer at 30 °C, [d] Decomposition temperature was determined by using TGA, 99% w = at 1% mass decrease of sample, 95% w = temperature at 5% mass decrease of the sample, 50% w = temperature at 50% mass decrease of sample [e] I = immiscible, M = miscible, [f] amorphous solid.

This can be explained by the relative flexibility of the LTILs. Unlike trigonal tricationic ILs, the LTILs have greater conformational degrees of freedom which help to minimize charge repulsion interactions.[5, 6] The Tg values are mainly governed by the size and charge distribution of the anion and or cation.[132] According to the literature, most ILs containing NTf_2^- are observed to be liquids at room temperature.[19, 78, 87-89, 121, 132] When the negative charge carrying moiety is a halide, X^- (X^- = F^-, Cl^-, Br^-, I^-), BF_4^-, TfO^- (trifluoromethanesulfonate) or PF_6^- the ILs tend to have higher melting points.[19, 121]

The LTILs with methylimidazolium charge carrying moieties **2a, 3a** and **4a** showed the lowest melting temperatures of the series. According to the melting point data in Table 4.1, the butylimidazole cationic moiety produces ILs with higher melting points compared to the methylimidazole moiety. This is probably because of the butyl group's greater van der Waals interactions. Relatively higher melting temperatures were observed when the IL incorporated the benzyl imidazole moiety, mainly because of the additional π-π stacking introduced by the phenyl groups.[19, 121]

4.4.2.2 Viscosities

The kinematic viscosities of these LTILs range from 372 to 4200 cSt at 303 K. LTILs with the C6 linkage chain generally showed lower viscosities ranging from 60-840 cSt. Typically monocationic ILs have lower kinematic viscosities.[7, 85] The viscosities are markedly higher in ILs with benzyl groups (see Table 4.1). The same phenomenon was observed in dicationic and trigonal tricationic ILs.[19, 121] It is interesting to note that ILs with a C3 linkage chain have higher viscosities compared to ILs with C6 linkage chain and lower viscosities when compared to those with C10 linkage chains.

According to these results, ILs having C3 linkage chains seem to possess greater ionic nature owing to closeness of the charged groups. When the distance between charged groups is increased to six methylene units (~ 8.9 Å) as in ILs with C6 linkage chain, the ionic nature is reduced resulting a lower viscosity. However when the linkage chain is further increased up to ten methylene units (~ 14 Å), higher viscosities are observed again due to the increase of intermolecular van der Waals interactions over ionic interactions.[132]

4.4.2.3 Densities

The densities of LTILs accompanying NTf_2^-anion range from 1.36 to 1.65 g cm^{-3}. The lowest density was observed for **2c** which has benzyl imidazolium cation and C10 linkage chains. The higher density values are obtained for LTILs with methylimidazolium groups. Moreover, when the chain length of the substituent at the 3-position of the imidazole increases from methyl imidazolium to butylimidazolium, the density decreases (**2a-2b, 3a-3b, and 4a-4b**). Similar observations have been reported for monocationic and dicationic ILs as well.[19, 78, 121]

4.4.2.4 Refractive indices and solubilities

The refractive indices of the LTILs range from 1.44 to 1.49 and lies in between the general range observed for monocationic ILs.[87-89] The solubility of these LTILs parallels that of monocationic ILs[87, 88, 133] in which all Br^-, BF_4^-, and TfO^- (trifluoromethane sulfonate) salts synthesized were soluble in water while all NTf_2^- salts were insoluble in water. All of the LTILs synthesized were insoluble in n-heptane.

4.4.2.5 Thermal Stability

For RTILs to be used in applications such as high temperature organic reactions[15, 134] and as GC stationery phases; they should posses a good thermal stability. Generally, phosphonium cation-based ILs show higher thermal stabilities compared to nitrogen cation-based ILs such as imidazolium and pyrolidinium ILs.[19, 78, 121, 133] This trend was clearly seen in this study as well. LTIL **2d** which accompanies two tripropyl phosphonium cations has the highest thermal stability with only 5% thermal degradation at 410 °C.

4.4.3 Electrowetting Properties

Electrowetting properties of ILs are listed in Table 4.2. Figure 4.5 shows the electrowetting curves of linear tricationic ionic liquids with C6 linkage chain and Figure 4.7 shows the electrowetting curves of benzylimidazolium substituted tricationic ionic liquids with different linkage chains lengths and core structures.

4.4.3.1 θ_0 values

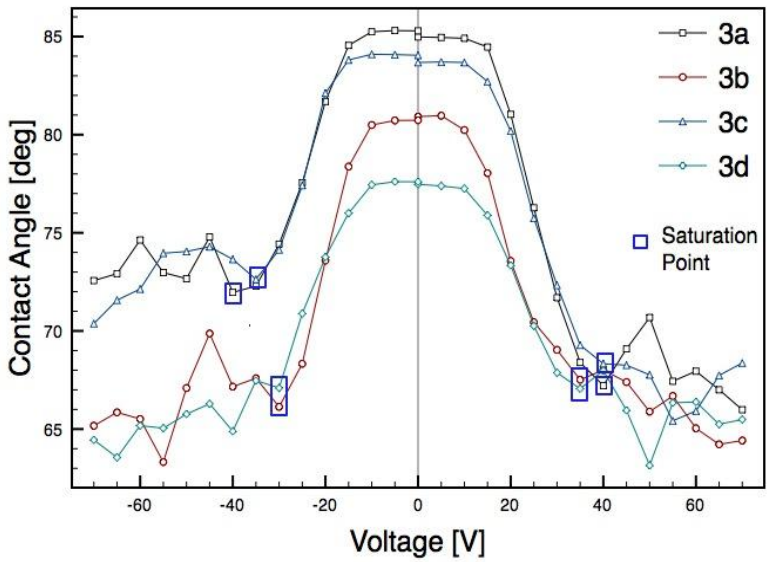
Since there is no external voltage at θ_0, only the three interfacial tensions [solid/liquid, liquid/air and air/solid] govern the θ_0 value. However solid (Teflon) is common in all experiments, therefore only the surface tension of the IL governs the θ_0 value.[118] The higher the surface tension value of the IL, the higher the θ_0 value obtained. Therefore from the observed θ_0 values the relative surface tension of these ILs can be deduced. This is a good indirect method to evaluate the relative surface tensions of this new class of ILs. According to Figure 4.5 and Table 4.2, ionic liquids **3a**, **3b**, **3c** and **3d** which have the same anion i.e. NTf_2^- and the same linkage chain

length i.e. C6, the θ_0 values decrease in the order of **3a**>**3c**>**3b**>**3d**. This decrease is solely due to the end cationic moieties. The θ_0 value directly correlates with the surface tension. Therefore the surface tension of these ILs decrease based on the cation in the order; methyl imidazolium> benzyl imidazolium> butyl imidazolium> tripropyl phosphonium. According to Figure 4.6 and Table 4.2, by considering θ_0 , surface tension values of benzyl substituted ILs are decreasing in the order of **IL 5b >4c>3c>2c>6b**. Surface tension values of liquids tend to increase with increase in hydrophilicity.[135] **IL 5b** with a nitrogen core (see Figure 4.6) has more hydrophilic character compared to IL **6b** with a benzene core. Therefore **IL 5b** has higher surface tension than **IL 6b** which is reflected by the θ_0 value. Similarly when the alkyl chain length of the LTILs increases from C3 to C10 as in **4c** to **2c**, the hydrophobic character increases and therefore surface tension decreases.

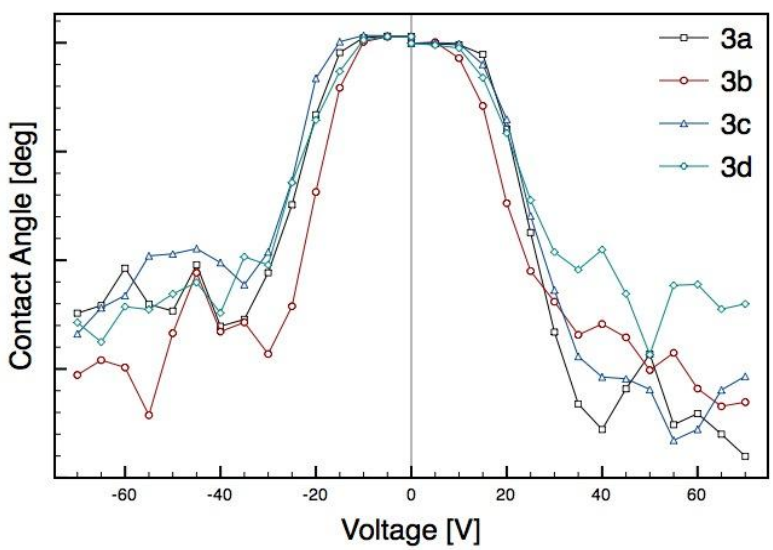
Table 4.2 Electrowetting properties of linear tricationic ionic liquids.

Ionic Liquid	θ_o	$\Delta\theta_L$	$\Delta\theta_R$	V_L	V_R
2a	83	16	18	-40	50
2b	80	14	15	-35	30
2c	83	17	18	-50	40
2d	80	16	16	-60	40
3a	85	13	18	-40	40
3b	81	15	14	-30	35
3c	84	12	16	-35	40
3d	78	11	11	-30	35
4a	82	21	16	-35	40
4b	88	19	14	-40	50
4c	86	23	16	-60	55
4d	-	-	-	-	-
5a*	77	>25	>20	<-70	>70
5b*	88	18	18	-65	60
6a*	77	20	25	-55	60
6b*	82	>15	>14	<-70	>70

θ_o-Contact angle at zero voltage, $\Delta\theta_L$- Change in contact angle at negative voltages, $\Delta\theta_R$- Analogous contact angle change at positive voltages, V_L- Saturation voltage in the negative voltage realm, V_R-Analogous saturation voltage in the positive voltage realm. Structures of 5a-6b are shown in Figure 4.5. * Data taken from reference 118.

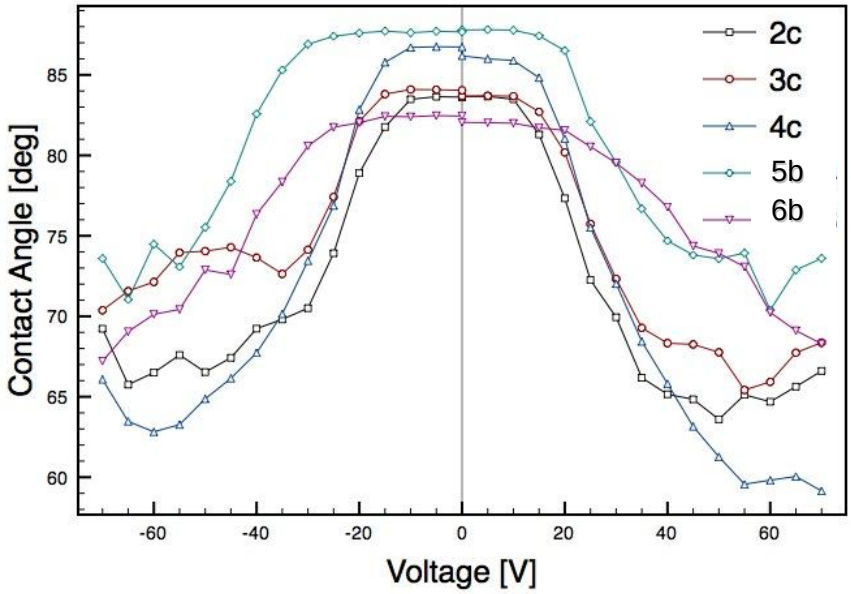


(a)

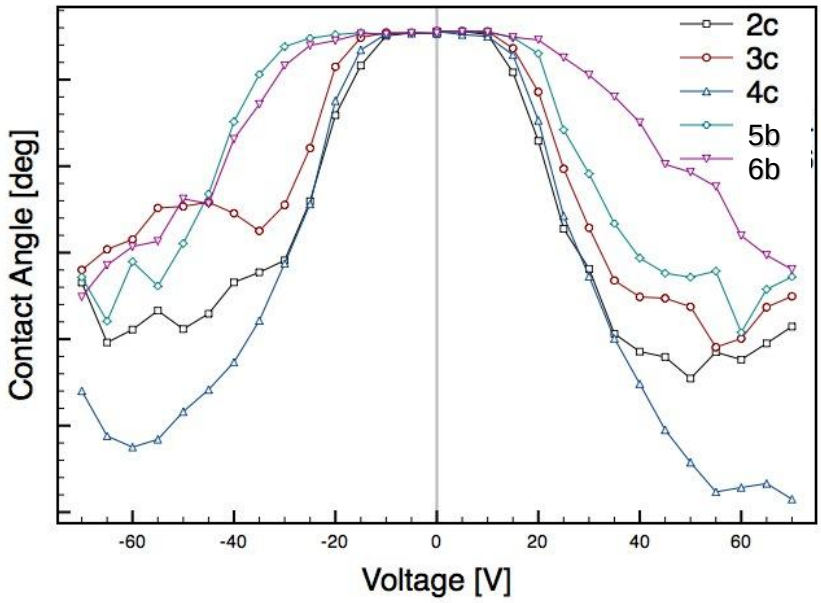


(b)

Figure 4.5 Electrowetting curves of linear tricationic ionic liquids with C6 linkage chains. Electrowetting curves of linear tricationic ionic liquids with C6 linkage chains (a) were overlaid normal to the maximum θ_0 value (b).



(a)



(b)

Figure 4.6 Electrowetting curves of benzyl substituted linear and rigid type tricationic ionic liquids. Electrowetting curves of benzyl substituted linear and rigid type tricationic ionic liquids (a) were overlaid normal to the maximum θ_0 value (b).

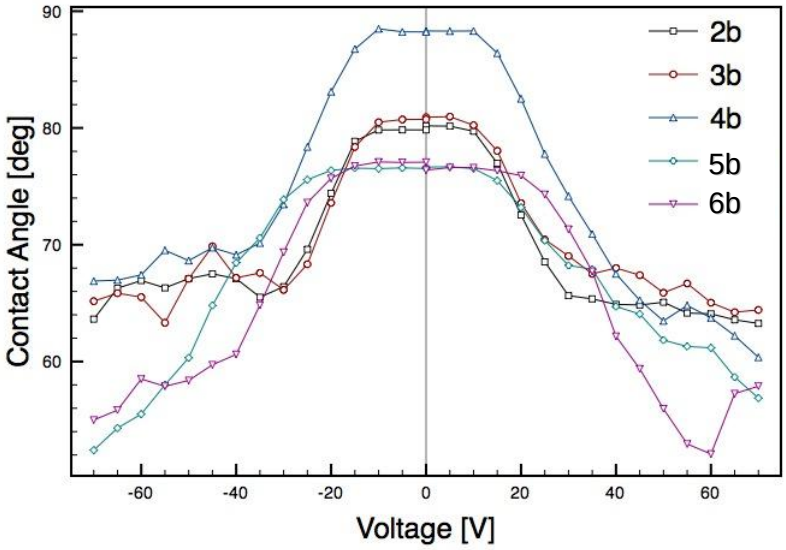
4.4.3.2 Rigid Core Structure vs. Flexible Core Structure

Figure 4.6(a) shows the electrowetting curves of benzylimidazole substituted ILs, both rigid core (**5b, 6b**) and flexible core (**2c, 3c, 4c**) ILs. In Figure 4.6(b) curves are overlaid normal to maximum θ_0 value. According to Figure 4.6(b) and Table 4.2, it can be clearly observed that rigid core ILs (**5a** and **5b**) have wider V_L and V_R values than those of flexible core ILs (**2c, 3c, 4c**). However, flexible core ILs produced much smoother curves than rigid core ILs. This means their electrowetting properties are much closer to the ideal behavior expected according to Young's and Lippmann's equations. Similar observations can be seen in butylimidazolium substituted rigid ILs (**5a, 6a)** and flexible ILs (**2b**, **3b**, **4b**) as well (see Figure 4.7).

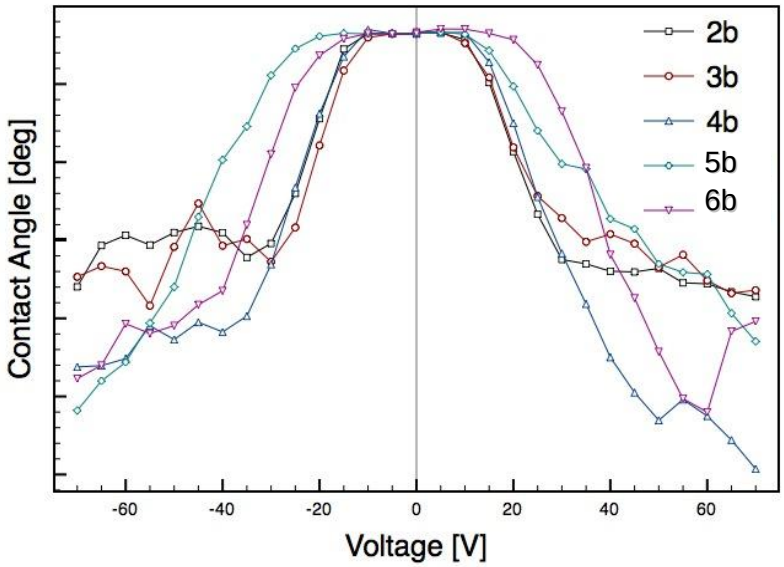
4.4.3.3 Effect of End groups

Electrowetting curves of linear tricationic ILs with C6 linkage chain each with four different end substituted groups were plotted in Figure 4.5(a). In Figure 4.5(b) they were overlaid normal to maximum θ_0 value. There are no significant differences in electrowetting properties by changing the end substituted groups, except θ_0 values. θ_0 values are different from one IL to the other due to their surface tension differences which was explained previously. It is interesting to note that the electrowetting properties of these ILs are fairly similar regardless of their different physicochemical properties. This unique situation enables one to choose an ionic liquid with the desired physical property from a large library of ionic liquids that have the same electrowetting properties. For example, if fast changes in contact angles are required in an electrowetting application, ILs with lower viscosities can be used. LTIL **3a** has significantly lower viscosity than **3c**, but their electrowetting properties are

approximately the same (Table 4.2). These observations are valid for the other C3 linkage chain and C10 linkage chain ILs as well (see Figures 4.8 and 4.9).

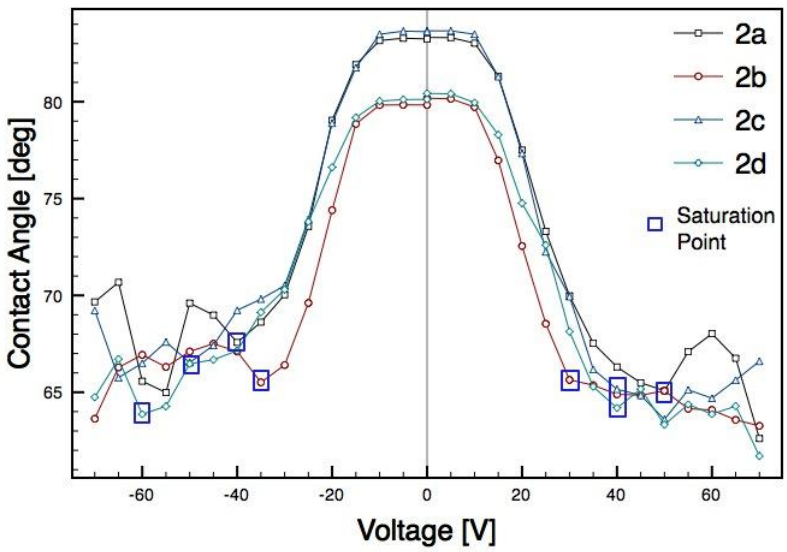


(a)

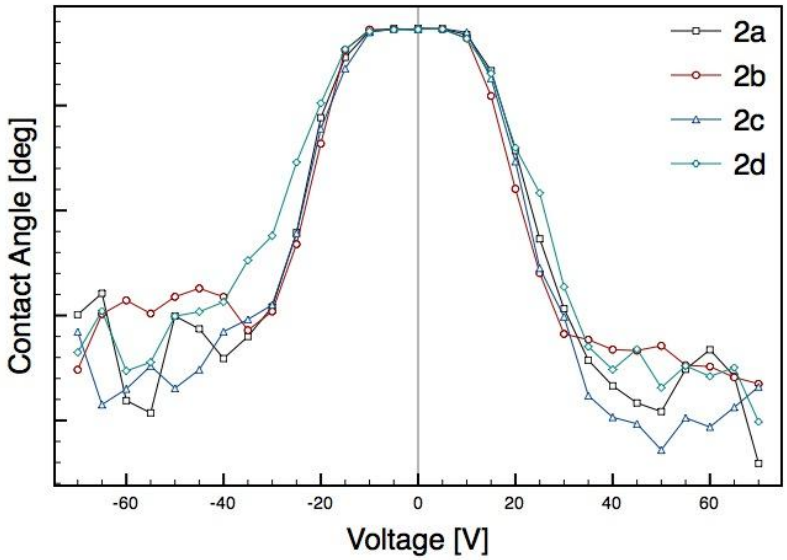


(b)

Figure 4.7 Electrowetting curves of butyl substituted tricationic ionic liquids. Electrowetting curves of butyl substituted tricationic ionic liquids (a) were overlaid normal to the maximum θ_0 value (b).

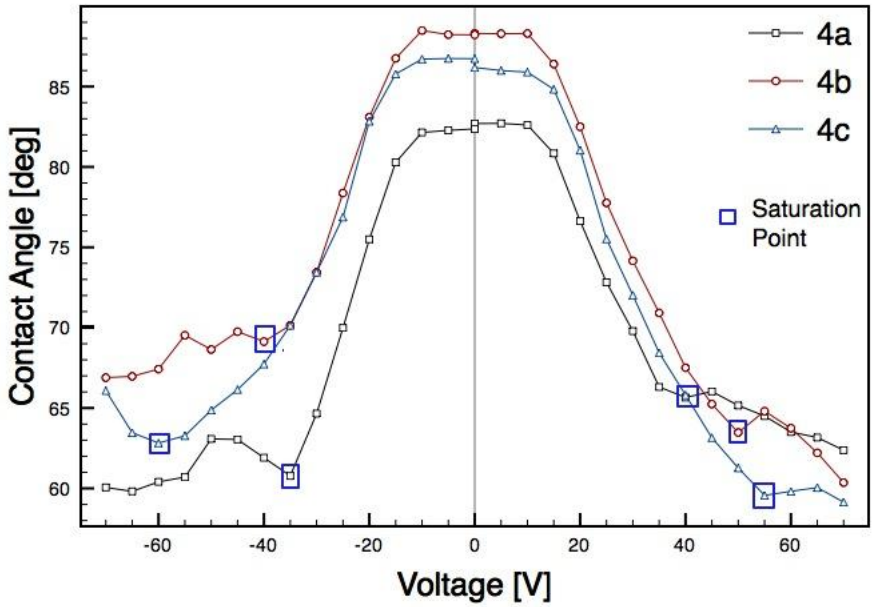


(a)

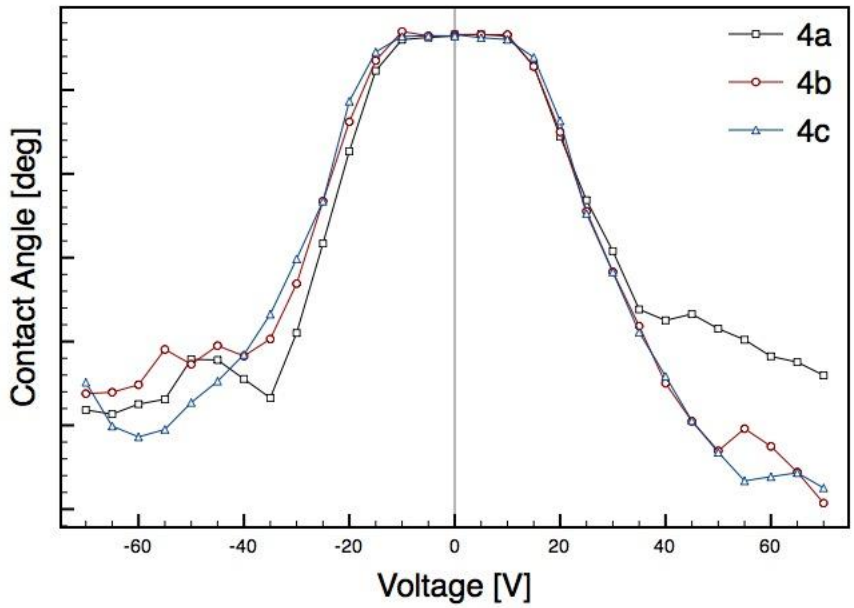


(b)

Figure 4.8 Electrowetting curves of C10 core linear tricationic ionic liquids. Electrowetting curves of C10 core linear tricationic ionic liquids (a) were overlaid normal to the maximum θ_0 value (b).



(a)



(b)

Figure 4.9 Electrowetting curves of C3 core linear tricationic ionic liquids. Electrowetting curves of C3 core linear tricationic ionic liquids (a) were overlaid normal to the maximum θ_0 value (b).

Examining electrowetting properties and physical properties of the relevant ILs listed here, one can find a suitable replacement for aqueous electrowetting in traditional EWOD-based devices.

4.5 Conclusions

Synthesis and physiochemical properties of 14 linear tricationic ionic liquids were reported and these have been explored as potential electrowetting liquids. These LTILs have shown high thermal stabilities and considerably high viscosities compared to traditional monocationic and dicationic ionic liquids. Most of the LTILs synthesized were room temperature ILs due to their higher structural flexibilities. This structural flexibility was advantageous in electrowetting applications as LTILs were observed to be much closer to the ideal behavior described in Young's and Lippmann's equation than any other ionic liquids reported in the literature.

CHAPTER 5

TRIGONAL TRICATIONIC IONIC LIQUIDS: A NEW GENERATION OF GAS CHROMATOGRAPHIC STATIONARY PHASES

5.1 Abstract

Trigonal tricationic ionic liquids (ILs) are a new class of ILs that appear to be unique when used as gas chromatographic stationary phases. They consist of four core structures; 1. **A =** mesitylene core, 2. **B =** benzene core, 3. **C =** triethylamine core, and 4. **D =** tri(2-hexanamido)ethylamine core; to which three identical imidazolium or phosphonium cationic moieties were attached. These were coated on fused silica capillaries and their gas chromatographic properties were evaluated. They were characterized using a linear solvation parameter model and a number of test mixtures. Based on the literature, it is known that both monocationic and dicationic ionic liquids possess almost identical polarities, solvation characteristics, and chromatographic selectivities. However some of the trigonal tricationic ILs were quite different. The different solvation parameters and higher apparent polarities appear to generate from the more rigid trigonal geometry of these ILs as well as their ability to retain the positive charges in relatively close proximity to one another in some cases. Their unique selectivities, retention behaviors and separation efficiencies were demonstrated using the Grob mixture, a flavor and fragrance test mixture, alcohols/alkanes test, and FAME isomer separations. Two ionic liquids **C1** (methylimidazolium substitution) and **C4** (2-hydroxyethylimidazolium substitution) had higher apparent polarities than any know

ionic liquid (mono, di and tricationic ILs) or commercial stationary phases. The tri(2-hexanamido)ethylamine core IL series proved to be very interesting in that it not only showed the highest separation efficiency for all test mixtures, but it also is the first IL stationary phase (containing Ntf_2^- anions) that eliminates peak tailing for alcohols and other H–bonding analytes. The thermal stabilities were investigated using 3 methods: thermogravimetric analysis (TGA) method, temperature programmed gas chromatographic method (TPGC) and isothermal gas chromatographic method. The **D** core series had a high working temperature range, exceptional selectivities and higher separation efficiencies than comparable polarity commercial columns. It appears that this specific type of multifunctional ILs may have the most promising future as a new generation of gas chromatographic stationary phases.

5.2 Introduction

New types of stationary phases are explored constantly in order to come up with entities that have better physico-chemical properties in order to provide better stabilities, selectivities, resolutions and separation efficiencies for qualitative and quantitative determination of increasingly complex analyte systems. Ionic liquids have attracted much attention recently as stationary phases in gas-liquid chromatography (GLC) due to the unique properties these compounds seem to possess. These characteristics include negligible vapor pressure at room temperature, a wide liquid phase temperature range, good thermal stability, non-flammability, resistance to decomposition, ability to undergo multiple solvation interactions, ionic conductivity ($>10^{-4}$ S/cm), and large electrochemical windows (>2V). These properties are highly desirable for many applications in areas of chemistry, physics, and engineering. Some

of these applications include replacement for volatile organic solvents in organic synthesis,[1, 4, 8, 90-94, 136-139] solvents for high temperature reactions,[15] solvents for enzyme catalyzed reactions,[95-98] electrochemical applications in photovoltaic cells and fuel cells,[99-102, 140] high temperature lubricants,[141, 142] liquid – liquid extractions,[29, 103-106] and mass spectrometric applications.[45, 46, 53, 143] The thermal stability, ability to form multiple solvation interactions, and low volatility makes them ideal candidates for use in gas chromatography as stationary phases. In the recent past, ultra stable stationary phases based on ionic liquids were the focus of many important publications.[9, 16, 67, 71, 78, 82, 107-110, 144-146] Based on the literature it is evident that multifunctional ionic liquids can show greater thermal stability than most common monocationic ionic liquids in GC applications but have almost identical solvent propeties.[78]

However, when multiple cationic moieties are present the ionic liquid tends to be a solid at room temperature. For the best performance as a gas chromatographic stationary phase, it is necessary that the ionic liquid be a room temperature ionic liquid (RTIL). These are defined as ionic liquids that are liquids at ambient temperatures.[1] Literature indicates that the highest probability for a multi-functional ionic liquid to be a room temperature ionic liquid is by incorporating the bis(trifluoromethane sulphonyl)imide (NTf_2^-) anion.[7, 19, 78, 112, 121] This anion not only gives low melting ionic liquids but also shows high thermal stability.[7, 19, 121] These two characteristics make the NTf_2^- anion ideal for ILs in GC applications. However, there is a distinct disadvantage of using this anion. That is, NTf_2^- produces peak tailing for alcohols and sometimes for other H-bonding analytes. Many different types of cation combinations have been tested in order to come up with a solution for this peak tailing and so far these attempts

have failed. In this work we introduce another class of ionic liquids that not only solves this problem but also provides unique properties and selectivities not found in previously reported ILs. These are trigonal tricationic ionic liquids and they are comprised of three positively charged moieties linked to a central core.

Since trigonal tricationic ILs are a new class of ionic liquids, it is necessary to characterize them based on their solvation properties and relative polarity compared to the general monocationic, dicationic ionic liquids and other common organic solvents. Many methods developed over the years have been adapted for the characterization of ionic liquid solvation properties.[147, 148] Some of the earliest developments include an empirical solvent polarity scale derived from either by a solvent dependent reaction rate constant or by the shift in maxima of an absorption or emission band of a solvatochromic dye or a fluorescent probe dissolved in a particular solvent.[7, 147-151] However, these methods have failed to provide a comprehensive picture of the polarity of ionic liquids due to the fact that these are single parameter polarity scales and therefore specific solvent-solute interactions are not taken into account. Ionic liquids can undergo multiple solvation interactions simultaneously such as ionic, dispersive, dipole-dipole, dipole-induced dipole, H-bond donating, H-bond accepting, π-π interactions and π-nonbonding interactions. Furthermore, ionic liquids may have complex extended three-dimensional liquid structures and possibly a supramolecular structure depicted by hydrogen bonding.[149] Hence, single parameter polarity does not correlate with the actual chemical environment of the ionic liquid. The next major development in this field comes with the inverse GLC application of Rohrschneider-McReynolds process.[71] In this method, specific solute-solvent interactions are evaluated by utilizing 5 probe molecules which are assumed to undergo only specific

types of interactions.[71, 152-154] However, due to the use of only one probe molecule per interaction, statistically the reliability of the values obtained is low.

The method used for the evaluation trigonal tricationic ILs is the Abraham solvation parameter model and it is the most comprehensive method available today.[155-161] This is based on a linear free energy relationship. The principle is similar to Rohrschneider-McReynolds method in that different types of solvent-solute interactions are evaluated separately. However, instead of one probe molecule, several probe molecules are used to characterize one interaction parameter increasing the reliability of the parameter coefficients obtained. The linear solvation energy relationship is given by equation 5.1:

$$\log k = c + eE + sS + aA + bB + lL \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.1)$$

Here, the higher case letters *E, S, A, B* and *L* are solute descriptors. *E* represents excess molar refraction of the solute at 20 ^{0}C, *S* is solute dipolarity and polarizability, *A* is Hydrogen bond acidity, *B* is Hydrogen bond basicity and *L* is gas-hexadecane partition coefficient at 25 ºC. Solute descriptor values are evaluated and published in the literature for a number of solutes.[158] The lower case letters are assigned to characterize different types of interactions between the solutes and the solvent. In this case the solvent is the ionic liquid acting as the stationary phase. The value of these coefficients depicts the strength of the interaction. Here *e* is π and non-bonding electron interactions, *s* is the ability of the phase to interact with dipolar/polarizable solutes, *a* is H–bond donating (H–bond basicity) interactions, *b* is H–bond accepting (H–bond acidity) interactions, *l* coefficient is composed of dispersion forces (positive contribution) and cavity term (negative contribution) and *c* is the system

constant. For all the solutes the retention factor *k* can be calculated chromatographically. These values can then be subjected to multiple linear regression analysis (MLRA) to find the five coefficients and system constant.

5.3 Experimental Procedures

5.3.1. Materials

Figure 5.1 gives the structures of all the trigonal tricationic ionic liquids synthesized. The reagents 1-methylimidazole, 1-butylimidazole, 1-benzylimidazole, 1-(2-hydroxyethyl)imidazole, tripropylphosphine, 2,4,6-tris(bromomethyl)mesitylene, 1,3,5-tris(bromomethyl)benzene, tris(2-chloroethyl)amine hydrochloride, tris(2-aminoethyl)amine, 6-bromohexanoyl chloride and all the probe molecules in Table 5.1 were purchased from Sigma Aldrich. Detailed synthesis procedure is given else where.[121] Grob test mixture, flavor and fragrance mixture and alcohols and alkanes mixture were also purchased from Sigma Aldrich. The GC capillaries (250 μm internal diameter) were purchased from Supelco. The FAME isomer mixture and the commercial columns Equity-1701, SUPELCOWAX, and SP-2331 were graciously donated by Supelco.

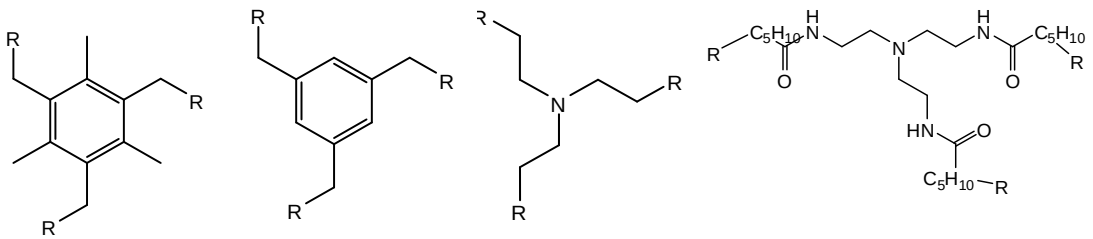
5.3.2. Methods

For the determination of solvation parameter the ionic liquids were coated using static coating technique on salt treated fused silica capillary (5m x .25mm). In this method, the IL was dissolved in dichloromethane to obtain 0.25% (w/v) coating solution and this was injected from one end of the capillary. The capillary tube was kept inside a water bath at 40 ºC. After that, one end of the capillary was sealed while the solvent was evaporated from the other end under high vacuum conditions. Finally the coated

columns were flushed with helium gas and conditioned overnight from 30 ºC to 120 ºC at 3 ºC/min. Efficiencies of the 12 IL columns were determined by using naphthalene at 100 ºC and were higher than 2000 plates m^{-1}.For the determination of solvation parameters, 30 probe molecules were used.

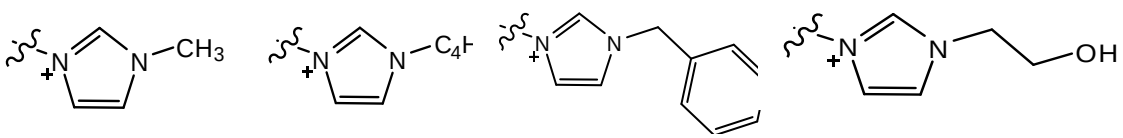
Core structures:

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

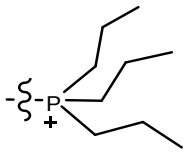


Ligand (R) structures:

1. **2.** **3.** **4.**



5.



Accompanying anion: Ntf_2^- =

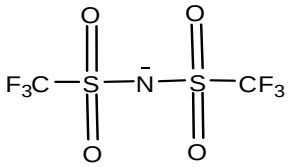


Figure 5.1 Structures of trigonal tricationic ionic liquids used in this analysis.

Table 5.1 Solute descriptor values for all the probe molecules used in this analysis.

Probe molecule	E	S	A	B	L
1,2-Dichlorobenzene	0.872	0.78	0	0.04	4.518
Phenol	0.805	0.89	0.6	0.31	3.766
Octylaldehyde	0.16	0.65	0	0.45	4.36
Valeradehyde	0.163	0.65	0	0.45	2.851
o-Xylene	0.663	0.56	0	0.16	3.939
p-Xylene	0.613	0.52	0	0.16	3.839
m-Xylene	0.623	0.52	0	0.16	3.839
Cyclohexanol	0.46	0.54	0.32	0.57	3.758
Nitrobenzene	0.871	1.11	0	0.28	4.511
N,N-Dimethylformamide	0.367	1.31	0	0.74	3.173
2-Pentanone	0.143	0.68	0	0.51	2.755
1-Nitropropane	0.242	0.95	0	0.31	2.894
Toluene	0.601	0.52	0	0.14	3.325
Benzaldehyde	0.82	1	0	0.39	4.008
Pyridine	0.794	0.87	0	0.62	3.003
Aniline	0.955	0.96	0.26	0.53	3.993
Butanol	0.224	0.42	0.37	0.48	2.601
Acetic acid	0.265	0.65	0.61	0.44	1.75
1-Octanol	0.199	0.42	0.37	0.48	4.619
Acetophenone	0.818	1.01	0	0.49	4.501
2-Choloraniline	1.033	0.92	0.25	0.31	4.674
Pyrrole	0.613	0.73	0.41	0.29	2.865
Benzonitrile	0.742	1.11	0	0.33	4.039
Propionitrile	0.162	0.9	0.02	0.36	2.082
1-Chlorohexane	0.201	0.4	0	0.1	3.777
p-Cresol	0.82	0.87	0.57	0.31	4.312
Ethylphenyl ether	0.681	0.7	0	0.32	4.242
Naphthalene	1.34	0.92	0	0.2	5.161
2-propanol	0.212	0.36	0.3	0.14	2.786
Cyclohexanone	0.403	0.86	0	0.56	3.792

The solute descriptors for the 30 probe molecules are listed in Table 5.1. For the determination of each parameter, more than 4 probe molecules having significant range of solute descriptor values were used in order to meet the statistical requirement to obtain meaningful results for the parameters.[161] The solvation parameters were determined using inverse GC method at 2 different temperatures, 70 ºC and 100 ºC. Probe molecules were injected and retention times were measured in triplicate. Methane was used to measure the column hold-up time. For the trigonal tricationic IL columns the three retention factors calculated for each probe molecule were identical within the experimental error. The log of average retention factor from triplicate measurement (log *k*) and solute descriptors (*E, S, A, B, L*) were then subjected to a multi parameter linear least squares fit on Analyse-it for Microsoft Excel software to determine the coefficients. Helium carrier gas flow rate was set at 1 mL min^{-1} for all the analysis with split ratio 100:1. Inlet and detector temperatures were kept at 250 ºC. The values obtained for the solvation coefficients using inverse GC approach are listed in Table 5**.**2**.** The value *n* represents the maximum number of probe molecules that could be used for MLRA. The value is less than 30 because some compounds co-eluted with the solvent peak especially at the higher temperature. Also, some of the data points had to be removed in order to obtain higher correlation coefficients ($R^2 \geq 0.98$). It was noted that highly peak tailing analytes such as acetic acid and N,N-dimethylformamide were common among the analytes that were removed from the data set.

Separations of Grob test mixture, flavor and fragrance mixture, alcohols and alkanes mixture, and FAME isomers were carried out in Agilent Technologies 6890N Network GC system equipped with Agilent Technologies 5975 inert mass selective detector.

Colum dimensions: 30 m x .25 mm x 0.20 µm. Separation conditions for Grob test mixture: 40 – 190 ºC at 6 ºC/min. Flavor and fragrance mixture: 40 ºC for 3 min, 10 ºC/min to 150 ºC. Alcohols and alkanes mixture: 30 ºC for 3 min, 10 ºC/min to 160 ºC. FAME isomers: 165 ºC isothermal.

Thermal stability of ionic liquids was evaluated using three methods. The first method involves thermogravimetric analysis (TGA) of the pure ionic liquid at 10 ºC/min heating rate. The decomposition temperature of 5% weight loss of the sample is reported in Table 5.2. The second approach is a temperature programmed GC (TPGC) method where the ionic liquid is coated in a 5 m x .25mm capillary and a temperature ramp of 3 ºC/min was applied from 100 ºC until decomposition is observed (see Figure 5.2). Third method is carried out for D core ionic liquids only. In this method, the ionic liquid is coated on a NaCl treated fused silica capillary of 5m x .25mm x .15 µm film thickness. The retention factor of naphthalene was determined at 100 ºC isothermally. It was then subjected to conditioning at higher temperatures for 12 hours (see Table 5.3) and the naphthalene retention factor was determined again at 100 ºC after each conditioning step. This method yields the most relevant thermal decomposition temperature of the IL stationary phases.

Table 5.2 Physical properties of the trigonal tricationic ILs used as stationary phases. (Adopted from reference121)

IL	M.W.	Melting Point (ºC)	Density [a] (g/cm^3)	Refractive index	Viscosity [b] (cSt)	Thermal Stability [c] (ºC)
A3	1474.3	60-62	1.59	-	-	365
B1	1203.9	-38*	1.56	1.467	1280	414
B2	1330.2	-24*	1.53	1.467	2320	401
B3	1432.2	-87*	1.55	1.588	20,000-25,000	361
C1	1184.9	36-37	1.56	-	-	393
C2	1311.2	-47*	1.41	1.451	1580	363
C3	1413.2	-6*	1.51	1.493	25,000-30,000	381
C4	1275	-38*	1.64	1.460	7980	392
D1	1524.4	-16*	1.59	1.465	7760	351
D2	1650.6	-54*	1.49	1.466	10,200	335
D3	1752.7	-15*	1.54	1.495	40,000-45,000	337
D5	1758.8	-31*	1.48	1.466	35,000-40,000	388
BMIM-Cl [d]	174.7	65	1.10	-	-	145 [e]
BMIM-TfO [d]	322.3	27	1.30	1.438	69.8	175 [e]
BMIM-NTf_2 [d]	419.4	-4	1.43	1.427	36.4	185 [e]

* Phase transition temperature determined by using differential scanning calorimetry (DSC). [a] Measured using pycnometer. [b] Kinematic viscosity determined using capillary viscometer at 30 ^{0}C. [c] Temperature of 5% thermal degradation determined by thermogravimetric analysis (TGA). [d] Values taken from the references 7, 16, 162. [e] Thermal stability determined by TPGC method in reference 78.

5.4 Results and Discussion

Four types of central cores were investigated in this study (see Figure 5.1) and in the order of increasing flexibility they are; **A** mesitylene core, **B** benzene core , **C** triethylamine core, and **D** tri(2-hexanamido)ethylamine core. These core structures also vary in their ability to form hydrogen bonds with the NTf_2^- anion and other solutes. The **A** and **B** cores do not have any intrinsic H–bonding capabilities. In the case of **C** core, the central nitrogen can be H–bond basic and in **D** core, the central nitrogen and amide oxygen both can be H–bond basic and the amide hydrogen can be H–bond acidic. It is important to note that to the best of our knowledge this is the first time an amide group is introduced in to the cationic fragment of an ionic liquid. Detailed information of synthesis and impurities present in these ionic liquids were discussed elsewhere.[121] In summary, the purities of these ILs were checked using NMR methods, Mass spectroscopy and elemental analysis. The only detectable contamination found was H_2O which can be removed by drying in vacuum oven at 80 ^{0}C under P_2O_5.

5.4.1 Physical Properties of Trigonal Tricationic Ionic Liquids

The physical properties of this series of multifunctional ILs are summarized in Table 5.2**.** Ionic liquid **A3** and **C1** were solids at room temperature with melting points 62 and 37 ºC respectively. The remaining 10 ionic liquids were room temperature ILs with melting points below 20 ºC. The RTILs were viscous liquids that did not show any air or moisture sensitivity that leads to decomposition at laboratory atmosphere. Densities of these tricationic ILs lie in the range observed for common monocationic and dicationic ILs[19] and are between 1.41 g/cm^3 and 1.64 g/cm^3. Refractive indices

range from 1.451 to 1.588. However viscosities of trigonal tricationic ILs are at least one or two orders of magnitude higher than those observed for typical monocationic ILs and dicationic ILs. In fact these are the highest viscosities reported for any ionic liquids. Ionic liquids **D3** and **D5** have the highest viscosities which range between 40,000-45,000 cSt and 35,000-40,000 cSt respectively. High viscosities are preferable for ILs that are to be used as stationary phases in GC.[9, 16] Furthermore when the benzyl imidazolium moiety is present the viscosities are markedly higher than other imidazolium cationic moieties. This trend was observed for symmetrical and unsymmetrical dicationic ILs as well.[19] This may be attributed to the added π-π stacking of the aromatic ring. Thermal stabilities of the trigonal tricationic ILs were measured using three methods (see **Experimental Section**) and a detailed discussion follows.

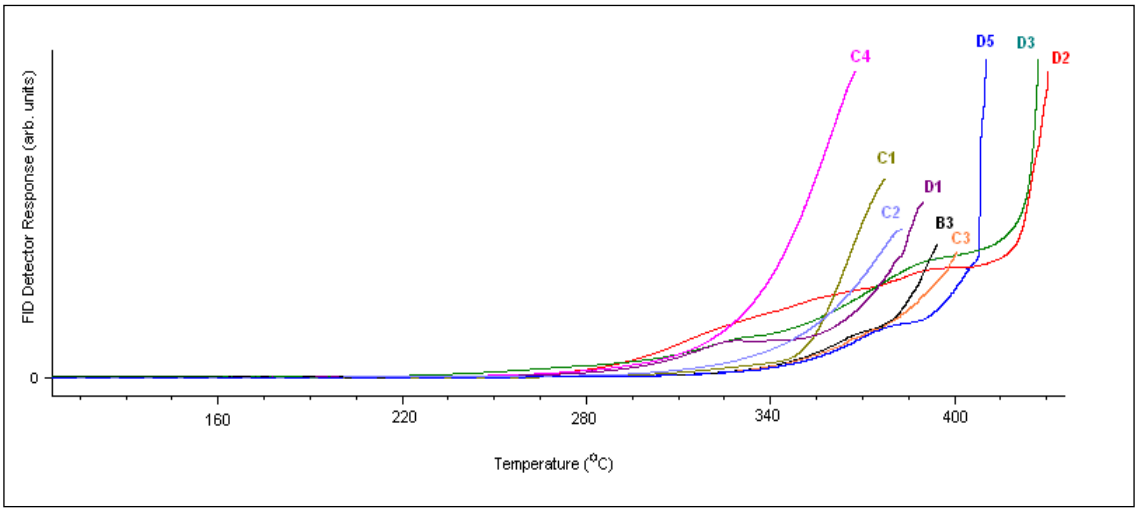


Figure 5.2 Temperature profile for column bleeding in gas chromatography. Temperature profile for column bleeding in gas chromatography due to thermal decomposition or volatilization of trigonal tricationic ionic liquids **B3, C1, C2, C3, C4, D1, D2, D3,** and **D3**.

5.4.2 Thermal Stability

The thermal stability of ionic liquids is important as it defines the upper limit of the temperature range where the column can be used as a separation medium. Three methods were used to evaluate thermal stability: First two methods, TGA method and temperature programmed GC method were used to obtain a general idea of the thermal stability. Using the TGA method, the temperatures of 5% thermal degradation of the trigonal tricationic IL samples are reported as the decomposition temperature in Table 5.2. All ionic liquids were thermally stable to at least 335 ºC in the TGA method. In the TPGC method, the baseline rise at the beginning of the decomposition event can be due to two reasons (see Figure 5.2). It can be due to the volatilization of the ionic liquid or it can be due to the actual decomposition. Either way, this region cannot be used for chromatographic separations due to the increasing baseline from column bleed. At the end of Table 5.2, the thermal stability of some common monocationic ionic liquids (determined by the TP GC method) is listed for comparison purposes.[16]

It is important to note that the thermal stability values reported in Table 5.2 for monocationic ionic liquids can be directly compared to the values obtained for trigonal tricationic ionic liquids by the TPGC method in Figure 5.2 as both experiments employed identical procedures. It is evident that the tricationic ionic liquids are much more thermally stable than the common monocationic ionic liquids. All 3 monocationic ILs start to decompose or volatilize before 185 ºC while for the trigonal tricationic ILs, no appreciable bleed is observed before 280 ºC. There is at least a 90 degree advantage of workable temperature range for tricationic ILs over the common monocationic IL stationary phases in gas chromatography.

Table 5.3 Variation of retention factors (k_{naph}) with thermal treatment of D core trigonal tricationic IL columns.[a]

Thermal treatment [b] (ºC)	k_{naph} in **D1**	k_{naph} in **D3**	k_{naph} in **D5**
100	3.2	8.1	7.2
130	3.1	6.9	7.0
150	3.0	6.5	6.8
200	2.9	5.2	6.5
230	2.9	4.6	6.4
250	2.8	4.3	6.3
270	2.5	3.2	6.2
290	2.1	2.3	6.0
300	3.0[c]	2.3[c]	6.7[c]
310	–[d]	–[d]	–[d]

[a] Measured isothermally for naphthalene, column temperature 100 ºC, He flow rate 1 ml/min. [b] Thermally treated for 12 hours under He 1 ml/min. [c] Peak tailing was observed. [d] No retention was observed for naphthalene.

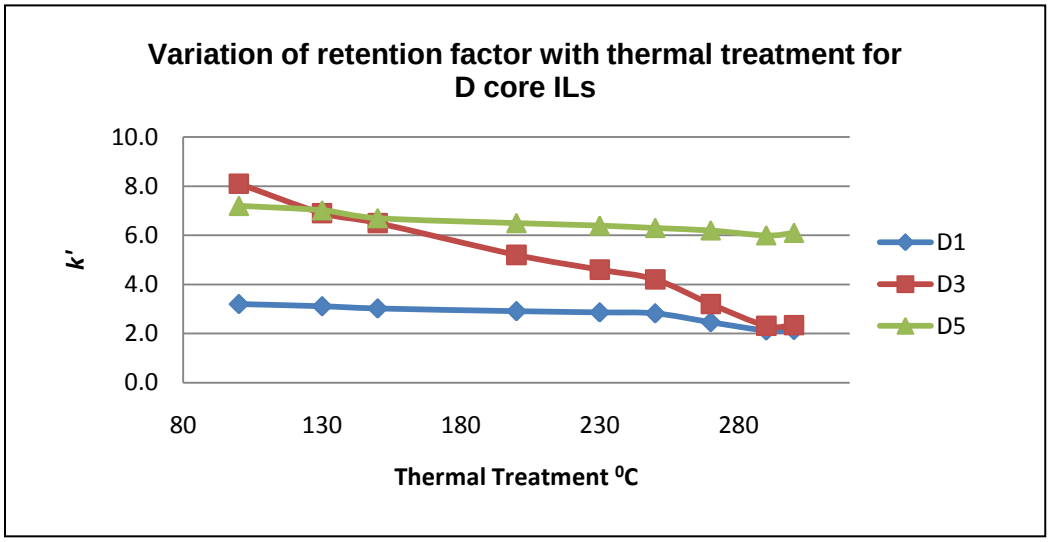


Figure 5.3 Graphical representation of changes in retention factor with the temperature treatment on **D1**, **D2**, **D3** IL phases.

Within the tricationic series since all the ionic liquids have the same anion, the thermal stability variation are solely due to variations in the cationic fragment. IL **C4** with hydroxytheylimidazolium cationic moiety and nitrogen core seems to decompose at somewhat lower temperature whereas IL **D5** with propylphosphonium cationic moiety and amide linkage shows the highest onset temperature of decomposition. In fact it appears that for **D5** the base line does not start to rise appreciably until the temperature exceeds 315 ºC. The above mentioned two methods were used to present general thermal stability comparison between the trigonal tricationic ILs and other ionic liquid based stationary phases since these are the most common methods used in the literature. The third method, an isothermal GC method, is probably the most relevant method for the determination of actual upper limit of temperature for the use of ionic liquids as stationary phases. The retention factor of naphthalene after each thermal treatment is listed in Table 5.3 and illustrated in Figure 5.3**.** For all the **D** core ILs listed, symmetrical sharp peaks were obtained up to 290 ºC conditioning. At 300 ºC thermal treatment the columns show reasonable retention for naphthalene. However the peaks show some tailing. After 310 ºC, there was no retention which indicates column bleed of the ionic liquid stationary phase.

These results confirm that the **D** core IL series is thermally stable up to 300 ºC as a GC stationary phase. In previous work it was shown that the phosphonium cationic moiety is more resistant to thermal degradation than most other N-based cations such as imidazolium and ammonium.[161] This implies that from this set of tricationic ionic liquids, **D5** has the largest workable temperature range as a stationary phase in gas chromatography. It exists as a liquid for a range of 331 ºC from – 31.4 ºC to at least 300 ºC. This in itself is quite impressive compared to the monocationic ionic

liquids which generally have a liquid temperature range of about 200 ºC or less. It is important to note that the commercial stationary phase SP-2331 which has similar polarity to **D5** ionic liquid has an upper temperature limit of 275 ºC. Therefore, IL **D5** has at least 25 ºC advantage over the comparable commercial stationary phase which in gas chromatographic terms leads to better separation efficiencies for heavy and highly polar compounds.

5.4.3 Ionic Liquid Solvation Parameters

The solvation parameters obtained for the trigonal tricationic ionic liquids are listed in Table 5.4. In Table 5.5 these values are compared with the same parameters found for common monocationic and dicationic ionic liquids.[9, 78] By comparison, nearly all interaction parameters obtained for monocationic and dicationic ILs are similar to each other whereas those obtained for some of the new tricationic ILs are quite unique. These unique parameters give rise to different behaviors in terms of retention, selectivity and separation efficiency.

Three of the five interaction parameter coefficients i.e., *s* = dipole–type interactions, *a* = H–bond donating interactions, and *l* = dispersion and cavity formation interactions have the greatest magnitude. This implies that solute retention is mainly due to these three types of interactions. Similar observations were made for monocationic and dicationic IL stationary phases.[9, 16, 67] Ionic liquid **C4** (with hydroxyethylimidazole charge carrying moieties and a “N” core) had the lowest *s* and *a* terms ever reported for any ionic liquid stationary phases carrying NTf_2^- anion. Hence the **C4** IL column exhibited the lowest retention for all the test mixtures investigated (Grob test, flavor and fragrance mixture, alcohols and alkanes, see Figures 5.5, 5.6

and 5.8.) The *e* term which corresponds to π- and nonbonding electron interactions is essentially negligible in this series of trigonal tricationic ionic liquids.

Table 5.4 Interaction parameters obtained for trigonal tricationic IL stationary phases.

Temperature (^{0}C)	**c**	**e**	**s**	**a**	**b**	**l**	**n**	**R^2**
A3 (BzIM)Mst								
70 (std. err.)	-3.34 (.10)	0.07 (.08)	2.02 (.09)	1.86 (.08)	0.72 (.11)	0.47 (.02)	29	0.99
100 (std. err.)	-3.37 (.09)	0.10 (.07)	1.87 (.08)	1.61 (.07)	0.58 (.10)	0.39 (.02)	29	0.99
B1 (MIM)Ph								
70 (std. err.)	-2.94 (.12)	0.14 (.10)	1.67 (.11)	1.68 (.10)	0.05 (.14)	0.50 (.03)	29	0.98
100 (std. err.)	-3.00 (.11)	0.18 (.08)	1.51 (.09)	1.42 (.08)	0.02 (.12)	0.42 (.03)	29	0.99
B2 (BuIM)Ph								
70 (std. err.)	-3.18 (.08)	0.07 (.07)	1.72 (.08)	1.80 (.07)	0.23 (.10)	0.56 (.02)	29	0.99
100 (std. err.)	-3.26 (.08)	0.09 (.07)	1.56 (.08)	1.57 (.07)	0.15 (.10)	0.48 (.02)	29	0.99
B3 (BzIM)Ph								
70 (std. err.)	-3.49 (.10)	0.04 (.07)	2.11 (.08)	2.09 (.08)	0.46 (.10)	0.51 (.03)	28	0.99
100 (std. err.)	-3.55 (.09)	0.06 (.07)	1.97 (.07)	1.78 (.07)	0.39 (.10)	0.43 (.02)	28	0.99
C1 (MIM)N								
70 (std. err.)	-3.53 (.11)	0.05 (.08)	1.55 (.10)	1.81 (.08)	0.35 (.11)	0.53 (.03)	28	0.99
100 (std. err.)	-3.70 (.12)	0.04 (.08)	1.58 (.08)	1.51 (.08)	0.31 (.11)	0.45 (.03)	25	0.98
C2 (BuIM)N								
70 (std. err.)	-2.92 (.09)	0.05 (.07)	1.57 (.08)	1.55 (.07)	0.14 (.10)	0.55 (.02)	27	0.99
100 (std. err.)	-2.98 (.09)	0.06 (.07)	1.43 (.08)	1.29 (.06)	0.16 (.10)	0.46 (.02)	27	0.99

Table 5.4 - *Continued*

Temperature (^{0}C)	c	e	s	a	b	l	n	R^2
C3 (BzIM)N								
70 (std. err.)	-3.23 (.09)	-0.03 (.07)	1.85 (.08)	1.62 (.07)	0.37 (.10)	0.54 (.02)	28	0.99
100 (std. err.)	-3.29 (.08)	-0.02 (.06)	1.10 (.07)	1.37 (.07)	0.30 (.09)	0.46 (.02)	28	0.99
C4 (HyIM)N								
70 (std. err.)	-3.18 (.10)	0.22 (.09)	0.66 (.10)	0.95 (.09)	0.09 (.12)	0.67 (.03)	29	0.99
100 (std. err.)	-3.05 (.09)	0.22 (.06)	0.45 (.07)	0.70 (.06)	0.03 (.08)	0.57 (.02)	25	0.99
D1 (MIM)NAmid								
70 (std. err.)	-3.42 (.12)	0.23 (.09)	2.15 (.11)	2.82 (.11)	0.31 (.14)	0.43 (.03)	28	0.99
100 (std. err.)	-3.58 (.12)	0.16 (.09)	2.10 (.10)	2.50 (.10)	0.17 (.14)	0.37 (.03)	26	0.99
D2 (BuIM)NAmid								
70 (std. err.)	-2.89 (.13)	0.11 (.11)	1.59 (.12)	2.23 (.10)	0.05 (.15)	0.52 (.03)	28	0.99
100 (std. err.)	-2.94 (.11)	0.10 (.09)	1.45 (.10)	1.84 (.09)	0.01 (.13)	0.45 (.03)	28	0.98
D3 (BzIM)NAmid								
70 (std. err.)	-3.10 (.12)	0.07 (.10)	1.85 (.11)	2.29 (.10)	0.15 (.14)	0.50 (.03)	29	0.99
100 (std. err.)	-3.16 (.10)	0.08 (.08)	1.69 (.09)	1.93 (.08)	0.10 (.11)	0.42 (.02)	29	0.99
D5 (PrP)NAmid								
70 (std. err.)	-3.30 (.10)	0.13 (.08)	1.91 (.09)	2.72 (.08)	0.03 (.11)	0.52 (.03)	29	0.99
100 (std. err.)	-3.34 (.10)	0.14 (.08)	1.72 (.09)	2.17 (.08)	0.07 (.11)	0.44 (.02)	29	0.99

Table 5.5 Comparison of the interaction parameters of monocationic and dicationic RTILs with trigonal tricationic ionic liquids.

Temperature (^{0}C)	**c**	**e**	**s**	**a**	**b**	**l**	**n**	**R^2**
BMIM-NTf_2 [a]								
70 (std. err.)	-3.03 (.09)	0 (.08)	1.67 (.09)	1.75 (.09)	0.38 (.11)	0.56 (.02)	35	0.99
100 (std. err.)	-3.13 (.12)	0 (.09)	1.60 (.10)	1.55 (.10)	0.24 (.12)	0.49 (.03)	32	0.98
C9(mim)2-NTf_2 [b]								
70 (std. err.)	-2.95 (.14)	0.11 (.07)	1.76 (.08)	1.75 (.07)	0.20 (.10)	0.51 (.02)	33	0.99
100 (std. err.)	-3.06 (.08)	0.11 (.06)	1.64 (.07)	1.50 (.06)	0.15 (.09)	0.43 (.02)	32	0.99
D1 (MIM)NAmid								
70 (std. err.)	-3.42 (.12)	0.23 (.09)	2.15 (.11)	2.82 (.11)	0.31 (.14)	0.43 (.03)	28	0.99
100 (std. err.)	-3.58 (.12)	0.16 (.09)	2.10 (.10)	2.50 (.10)	0.17 (.14)	0.37 (.03)	26	0.99

[a] values taken from reference 16. [b] values taken from 78.

It was observed that the *s, a, b,* and *l* coefficients decrease with increasing temperature. The most substantial decrease in magnitude is observed for the *s* and *a* values (dipole–type interactions and H–bond basicity). This is mainly due to the fact that these interactions result from directional bonds and therefore depend largely on the orientation of the solute molecules and the interacting stationary phase molecules. As the temperature increases, translational and rotational energy of the molecules increase. This disrupts the intermolecular interactions between the solute and stationary phase and leads to lower retention and coefficients.[161] When benzylimidazole is the ionic liquid's charge carrying moiety, the H–bond acidity term (*b*) is increased compared to the other cationic moieties (with the exception of the **D** core ionic liquids in which the methylimidazole cationic moiety shows a higher *b* value).

This is observed in symmetrical dicationic ionic liquids as well.[78] This may be due to the increased H–bond acidity of the bridging methylene hydrogens of the benzyl group**.** This contention is supported by previously published results (illustrated in Figure 5.4 which is a packing diagram of a symmetrical dicationic ionic liquid, C_3(methylimidazolium)$_2$ 2Br$^-$). This crystal structure shows H–bonding between the acidic hydrogens and the bromide anion.[78] The hydrogens that are marked with a red arrow are from the methyl group substituted at the 3 position of the imidazole ring. If the methyl group is substituted by a benzyl group, these would be the bridging methylene hydrogens. In that case due to the presence of the benzene ring in the adjacent carbon these hydrogens would be even more acidic giving rise to a larger *b* term. The **D** core series of tricationic ILs has the highest *a* values (i.e., hydrogen bond basicities). This is due to the three amide groups present in each ionic liquid. Both

amide nitrogen and carbonyl oxygen can participate in H–bonding. The central core nitrogen may be sterically hindered for effective hydrogen bonding.

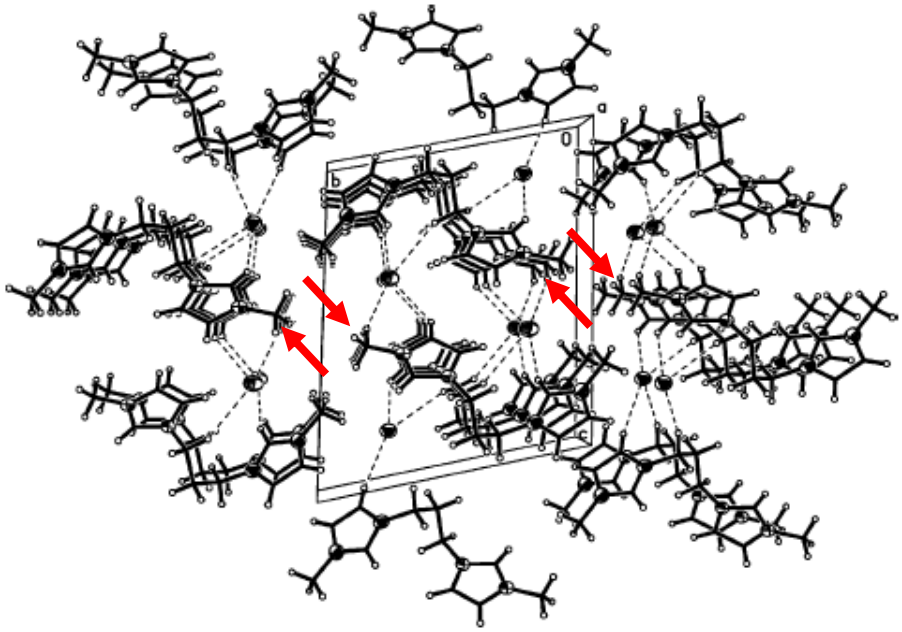


Figure 5.4 X-ray crystallographic data of $C_3(mim)_2\,2Br^-$ showing stacks along short a – axis and H-bonding. (Reproduced with the permission of the authors of reference 78)

The *e* term is probably the least significant coefficient for most of the tricationic ILs investigated. It implies that the interaction between solute and IL stationary phase through π-π and non-bonding electrons is minimal compared to other types of interactions. One would expect the benzylimidazole cationic moiety to introduce some π – bonding interactions but that is not what is observed. The only statistically significant *e* terms are observed for the **C4** ionic liquid, with the hydroxyethylimidazole charge carrying moiety; and for the **D1** ionic liquid with methylimidazole charge carrying moiety. It is expected that **C**–core series has the lowest *e* term, as there are no core π – bonding electrons and only one relatively inaccessible non-bonding

electron pair on the central nitrogen. However, **C4** with hydroxyethylimidazole as the cationic moiety shows the highest π-π and n-π interactions among the trigonal tricationic IL series. Furthermore this ionic liquid has a very low H–bond acidity (*b* coefficient). This implies that the hydroxyl group interacts with solutes through the non-bonding electrons of oxygen and not as much through H–bonding. Dispersion forces are one of the prominent type of interaction that contributes to analyte retention in these IL stationary phases. However, interaction of tricationic ILs through dispersion forces (*l* coefficient) seems to be similar since there is not much variation in the *l* value from one trigonal tricationic ionic liquid to another. The magnitude of *l* ranges from 0.43 to 0.67 and this falls within the range observed for symmetrical dicationic and monocationic ionic liquids.[9, 16, 78]

5.4.4 The Grob Test Mixture

This is a single test mixture that is used to evaluate a capillary column chromatographically.[163, 164] This mixture can be used to evaluate separation efficiency, acid/base characteristics, adsorptive activity and relative polarity of the column. The mixture contains 12 components and each peak gives information about the column. 1. n-decane and 2. n-undecane represents 100% recovery marker. Symmetrical sharp peaks are expected for properly produced and installed columns. 3. 1-nonanal is used to identify adsorption unique to aldehydes independent of H-bonding. 4. 1-octanol and 5. 2,3-butanediol peak shapes indicate presence of H-bonding sites. Reduced peak heights and unsymmetrical peak shapes for 6. 2-ethylhexanoic acid and 7. 2,6-dimethylphenol indicate H-bonding or basic sites. 8. methyl decanoate, 9. methyl undecanoate and 10. methyl dodecanoate are a homologous series of fatty acid methyl

esters and is used to determine the separation efficiency of the column. 11. 2,6-dimethylaniline and 12. dicyclohexylamine peak shapes give information of the acidic nature of the column.

According to Figure 5.5, in trigonal tricationic ionic liquids with **B** and **C** core structures (see Figure 5.1), n-decane and n-undecane elute with or near the methylene chloride solvent peak and could not be separated with the given temperature program. Also, 2,3-butanediol, 2-ethylhexanoic acid, and dicyclohexylamine were either retained on the column or eluted with high peak tailing so that they were indistinguishable from the baseline. All of these 3 compounds are polar, have H–bonding capabilities and lack any aromatic substituents. Furthermore, 1-nonanal and 1-octanol show peak tailing and reduced peak heights. These results imply that the **B** and **C** core structures can produce IL stationary phases that are highly polar with H–bond accepting capabilities. The **C4** IL shows the least retention for Grob test mixture compounds which is in accordance with the previously discussed solvation parameter coefficient results. The homologous series of fatty acid methyl esters were well separated with both **B** and **C** core IL stationary phases and showed good separation efficiencies. The acid 2,6-dimethylphenol and the base 2,6-dimethylaniline were the latest eluting detectable peaks. Despite the presence of H–bonding sites, these did not show much peak tailing. The elution orders on the **B1** and **C4** ILs were similar to highly polar commercial stationary phase SP-2331, whereas the elution order on the **C1** IL stationary phase was more comparable with the polar SUPELCOWAX column.

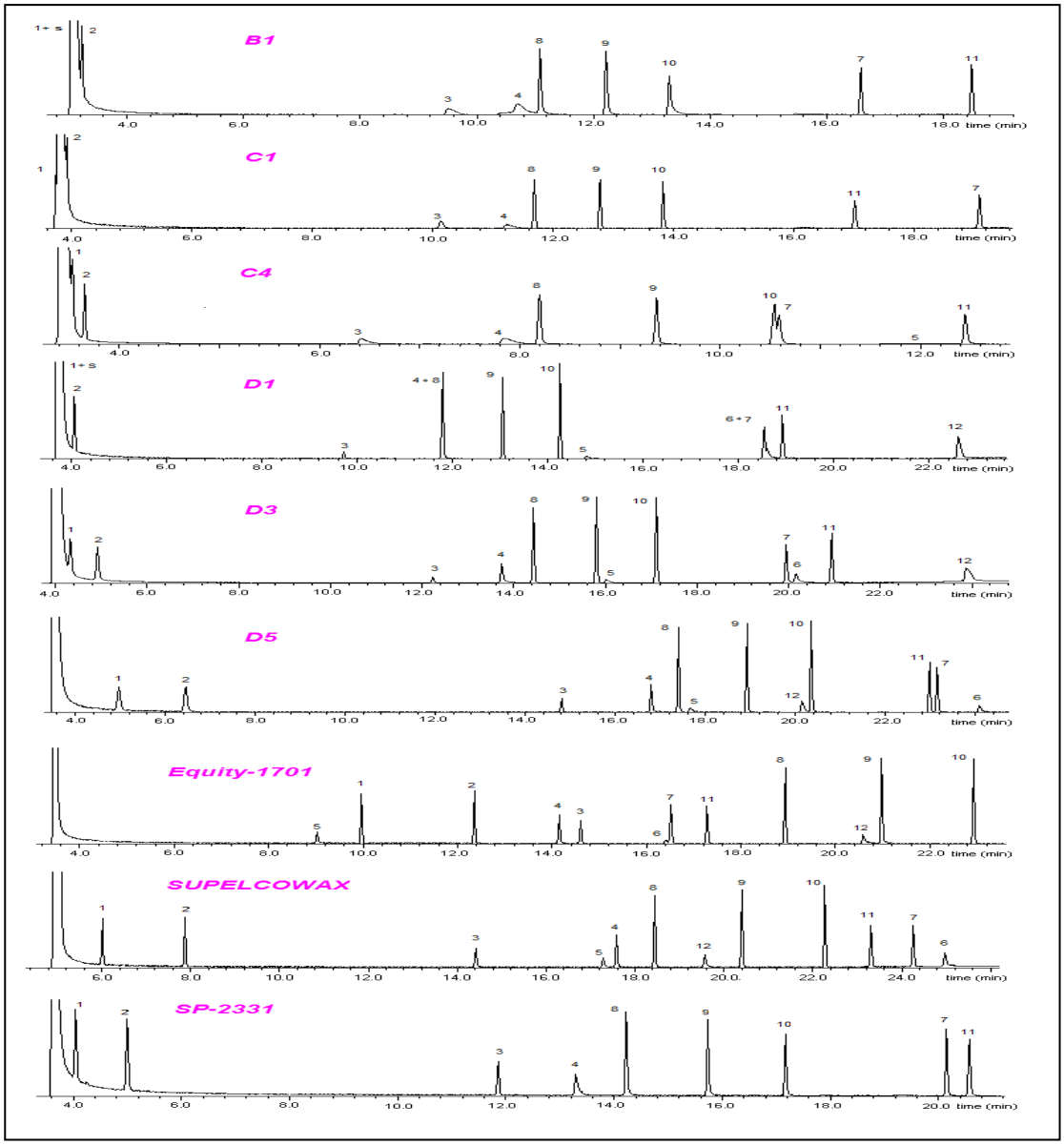


Figure 5.5 Separation of Grob test mixture in trigonal tricationic IL columns. Separations were compared with commercial columns with varying degrees of polarity. Intermediate polar (Equity-1701), polar (SUPELCOWAX), and highly polar (SP-2331).1 n-decan, 2 n-undecane, 3 1-nonanal, 4 1-octanol, 5 2,3-butanediol, 6 2-ethylhexanoic acid, 7 2,6-dimethylphenol, 8 methyl decanoate, 9 methyl undecanoate, 10 methyl dodecanoate, 11 2,6-dimethylaniline, 12 dicyclohexylamine , s dichloromethane; GC separation conditions: 40 °C to 190 °C at 6 °C min^{-1};1 mL min^{-1} He; MS Detector. All chromatograms were obtained using 30 m x .25 mm x 0.20 µm d_f columns.

All 12 test compounds were eluted from stationary phases with **D** core ionic liquids. In **D3** and **D5** the alkanes are better separated from the solvent peak compared to the **B** and **C** core ILs. All **D**-type columns separated the homologous series of fatty acid methyl esters with exceptionally good separation efficiencies. In both **D1** and **D3**, the two bases elute after the acids which indicate that **D1** and **D3** are more acidic stationary phases than **D5**. This also is in agreement with the solvation parameter coefficients obtained. The H–bond acidity term (*b*) for **D5** is significantly smaller than that of **D1** and **D3**. In **D5,** the two acids elute last indicating a more basic, less acidic stationary phase. The **D** core IL stationary phases show elution orders similar to the highly polar SP-2331 column. This leads to the conclusion that the **D** series ionic liquids are highly polar and the polarity is comparable to that of SP-2331 (100% cyanopropyl polysiloxane) stationary phase.

5.4.5 Alcohol and Alkane Mixture

Figure 5.6 illustrates the separation of a mixture of alcohols and alkanes by the six trigonal tricationic ionic liquid columns and commercial columns of diverse polarity. Except for **C4**, the other IL columns show reasonable retention for both polar alcohols and nonpolar alkanes. This is due to the dual nature of ionic liquids[82] which suggests that ionic liquids act like a polar medium to retain polar compounds and like a nonpolar medium to retain nonpolar compounds simultaneously. One of the most interesting observations of this separation is the relative retention of alcohols and alkanes by these IL columns. In all of the six tricationic liquid stationary phases, the relative retention of alcohols compared to alkanes is much larger than that observed for common monocationic; (Benzyl(methyl)imidazolium-TfO),[16] phosphonium

monocationic; (Trihexyl(tetradecyl)phosphonium-NTf_2),[69] or polyethylene glycol linked dicationic; (MIM_2PEG_3-$2NTf_2$) [69] ionic liquid stationary phases (see Figure 5.7). For the **B1** and **C1** stationary phases, 1- hexanol elutes after hexadecane which is unusual. In fact, to the best of our knowledge, the **C1** ionic liquid has the distinction of having the largest relative retention for 1-hexanol with respect to hexadecane ever reported for any commercial stationary phase or any ionic liquid stationary phase. The lowest overall retention for all alcohol and alkane components was again observed for the **C4** column. All 18 compounds were eluted before 9.5 minutes. The shorter chain alkanes(pentane – nonane) seems to have almost no interaction with this stationary phase and comes out with the solvent peak under these conditions. It appears that the **C1** and **C4** ILs may be the most polar GC stationary phases yet reported. This high polarity is unique to trigonal tricationic ionic liquids. All other monocationic, dicationic and linear tricationic ionic liquids (unpublished work) show almost identical solvation characteristics and intermediate polarities. The higher apparent polarity and different solvation properties of trigonal tricationic ILs can be attributed to its more rigid trigonal geometry and the existence of three positive charges in close proximity compared to other forms of ILs.

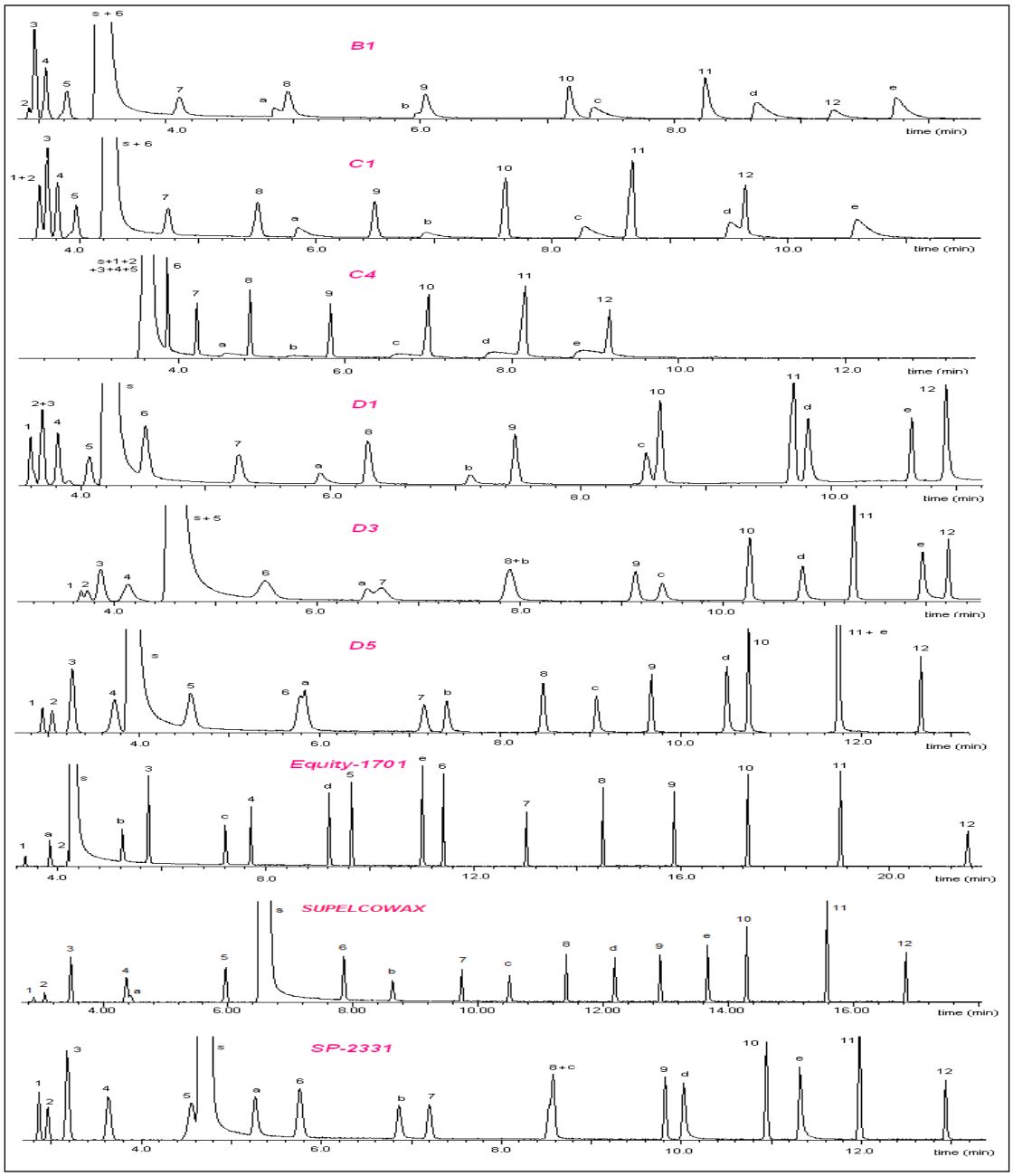


Figure 5.6 Separation of homologous alkane and alcohol mixture. Compounds in the mixture:1 pentane, 2 hexane, 3 heptane, 4 octane, 5 nonane 6, decane, 7 undecane, 8 dodecane, 9 tridecane,10 tetradecane, 11 pentadecane, 12 hexadecane, **a** ethanol, **b**1-propanol, **c** 1-butanol, **d** 1-pentanol, **e** 1-hexanol, **s** dichloromethane,. GC separation conditions: 30 °C for 3 min,10 °C min^{-1} to 160 °C; 1 mL min^{-1} He; MS detector. All chromatograms were obtained using 30 m x .25 mm x 0.20 µm d_f columns.

The **B** and **C** core ionic liquid stationary phases produce tailing peaks for the alcohols. This is a common phenomenon observed for ionic liquid stationary phases with the NTf_2^- (bis(trifluoromethane)sulfonimide) counter anion. Both monocationic and dicationic ionic liquids have shown peak tailing for alcohols and this has been one drawback of these types of ionic liquids as stationary phases. To overcome this problem NTf_2^- anion has been replaced by the triflate (TfO^-) anion.[68] However, with multifunctional ionic liquids the NTf_2^- anion is used more frequently in order to obtain lower melting point ILs.

One of the unique and probably the more important property of the trigonal tricationic ionic liquid stationary phases is that the **D** core ILs have reduced and in the some cases almost eliminated the peak tailing of alcohols even though the NTf_2^- anion is present. As discussed previously, the polarity of the **D5** IL stationary phase is comparable to the highly polar SP-2331 commercial phase. However, as shown in Figure 5.6, peak asymmetry for alcohols is less for the **D5** stationary phase than for the commercial SP-2331 phase at higher temperatures. Also nonane (5) and dichloromethane (s) were barely separated with SP-2331 phase whereas these compounds are much better separated with the **D5** IL stationary phase. Similarly dodecane (8) and 1-butanol (c) co-elute in SP-2331 while these two are completely separated with the **D5** IL column. Columns **D1** and **D5** seem to be complementary to one another in that one column always separates peaks that co-elute on the other (see Figure 5.6). For example hexane (2) and heptane (3) co-elute on **D1** and are baseline separated on **D5**. Decane (6) and ethanol (a) peaks overlap on **D5** and separate on **D1**. Pentadecane (11) and 1-hexanol (e) co-elute in **D5** but are well separated on **D1**.

Furthermore, the **D**-core ILs shows the greatest retention for alkenes among the trigonal tricationic ILs evaluated. The retention times of alkanes in **D1**, **D3** and **D5** columns are directly proportional to the solvation parameter coefficient of interaction through dispersion forces (coefficient *l*). Within the **D** series, **D1** has the lowest *l* term, followed by **D3**, and **D5**. Accordingly, **D1** has the lowest retention for alkanes within the **D** series followed by **D3** and **D5** which shows the highest retention. The dual nature of ionic liquids is evident from these separations as both the alkane series and alcohol series are easily separated. Finally it was observed that the retention of alkanes by the tricationic ionic liquids is generally lower than their retention on monocationic and dicationic ionic liquids.[16, 67] Therefore, other than the high separation efficiency and low peak tailing for alcohols, the **D** series of ILs have the distinction of being stationary phases that produce good separations for variety of analytes, but with less retention times than conventional columns. This might render trigonal tricationic ILs as desirable stationary phases in two dimensional GC analysis.

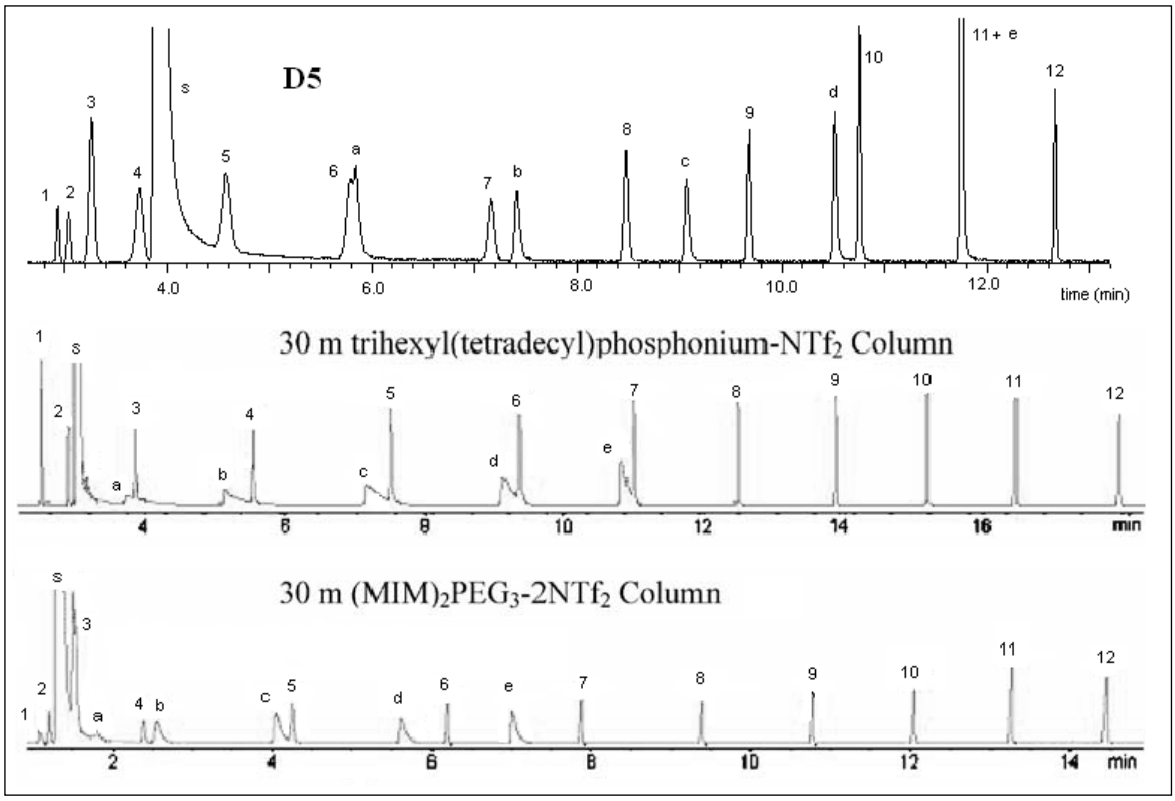


Figure 5.7 Comparison of separation of homologous alkane and alcohol mixture. Comparison of separation of homologous alkane and alcohol mixture using trigonal tricationic IL **D5**, monocationic ionic liquid trihexyl(tetradecyl)phosphonium-NTf_2 and dicationic ionic liquid $(MIM)_2PEG_3$-NTf_2 columns under identical conditions.: 1 pentane, 2 hexane, 3 heptane, 4 octane, 5 nonane 6, decane, 7 undecane, 8 dodecane, 9 tridecane,10 tetradecane, 11 pentadecane, 12 hexadecane, **a** ethanol, **b**1-propanol, **c** 1-butanol, **d** 1-pentanol, **e** 1-hexanol, **s** dichloromethane,. GC separation conditions: 30 °C for 3 min,10 °C min^{-1} to 160 °C; 1 mL min^{-1} He; MS detector for **D5**. FID for monocationic and dicationic columns. All chromatograms were obtained using 30 m x .25 mm x 0.20 µm d_f columns.

5.4.6 Flavor and Fragrance Mixture

The flavor and fragrance mixture contains structurally related esters (including two homologous series) and has 24 compounds. The separation of this series provides another indication of the selectivity and separation efficiency of the trigonal tricationic ionic liquids compared to commercial columns. According to the Grob test mixture and

the alcohol/alkane test results, the commercial column SP-2331 has comparable polarity to the trigonal tricationic ionic liquids, especially the **D** core series. The flavor and fragrance mixture is used to determine the separation efficiencies of columns with comparable polarities (see Figure 5.8). Column **C1** separated 21 compounds and co-eluted 3. The furfuryl homologous series elutes separately from the other esters. Only the last compound of the series furfuryl octanoate overlapped with benzyl butyrate. Again the **C4** column showed the least retention for the mixture and all the compound were eluted before 14 minutes.

Five compounds were not baseline separated with the **C4** column. However, with the **D** series columns the compounds are much better separated. Especially with the **D5** column, the retention and selectivity were comparable to a commercial (SP-2331) column, but the separation was much better. In **D5** column, all the 24 compounds are nearly base line separated whereas in the commercial column three esters co-elute and two are only partially separated (isopropyl tiglate and ethyl hexanoate). This confirms the fact that **D5** is a highly efficient and selective stationary phase for gas chromatography.

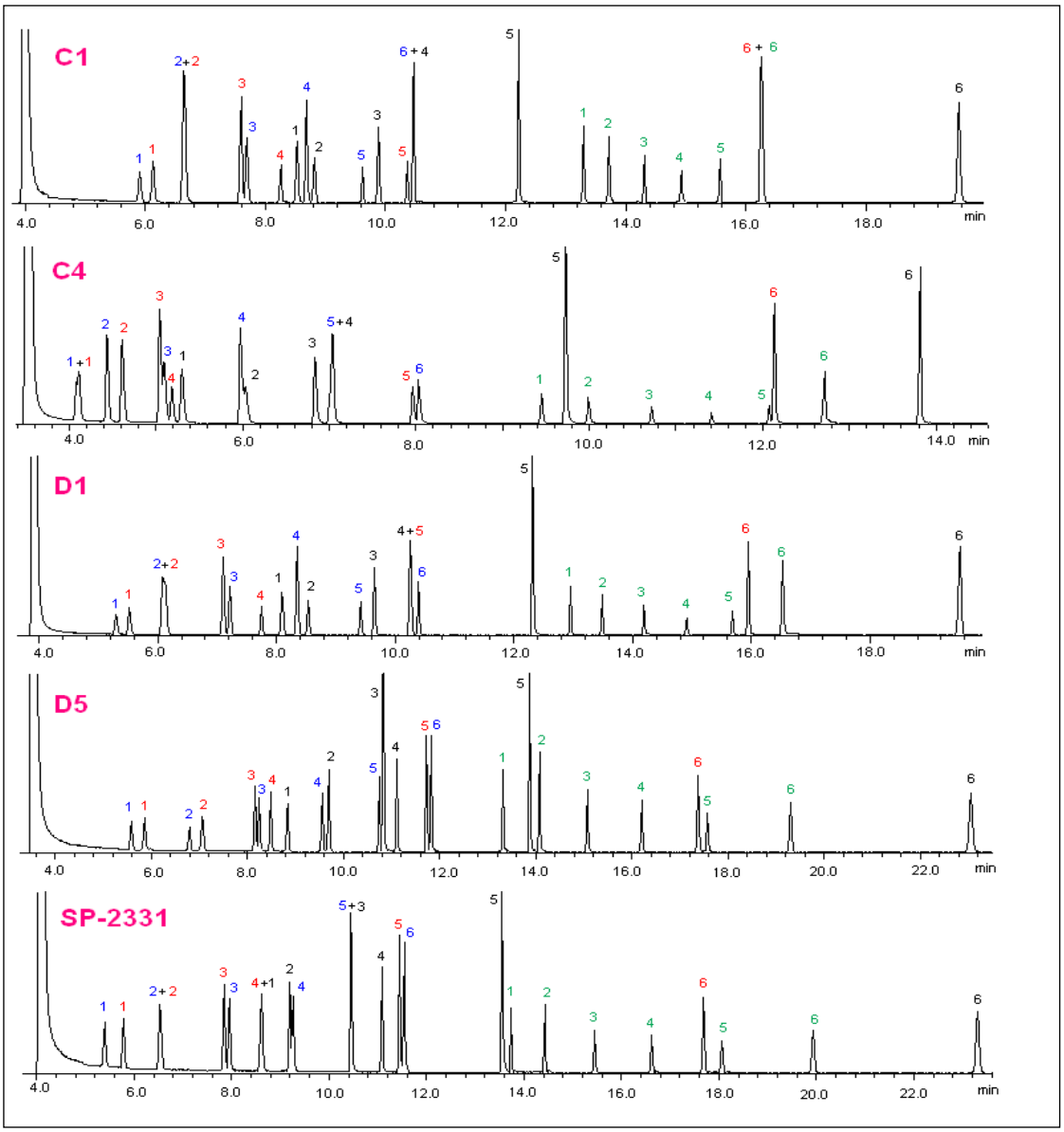


Figure 5.8 Separation of flavor and fragrance mixture.
Compounds in the mixture: 1 ethyl propionate, 2 ethyl butyrate, 3 ethyl valerate, 4 ethyl hexanoate, 5 ethyl heptanoate, 6 ethyl octanoate, 1 methyl butyrate, 2 isopropyl butyrate, 3 propyl butyrate, 4 allyl butyrate, 5 hexyl butyrate, 6 benzyl butyrate, 1 methyl tiglate, 2 isopropyl tiglate, 3 propyl tiglate, 4 allyl tiglate, 5 hexyl tiglate, 6 benzyl triglate, 1 furfuryl propionate, 2 furfuryl butyrate, 3 furfuryl pentanoate, 4 furfuryl hexanoate, 5 furfuryl heptanoate, 6 furfuryl octanoate, 40 °C for 3 min,10 °C min^{-1} to 150 °C; 1 mL min^{-1} He; MS detector. All chromatograms were obtained using 30 m x .25 mm x 0.20 µm d_f columns.

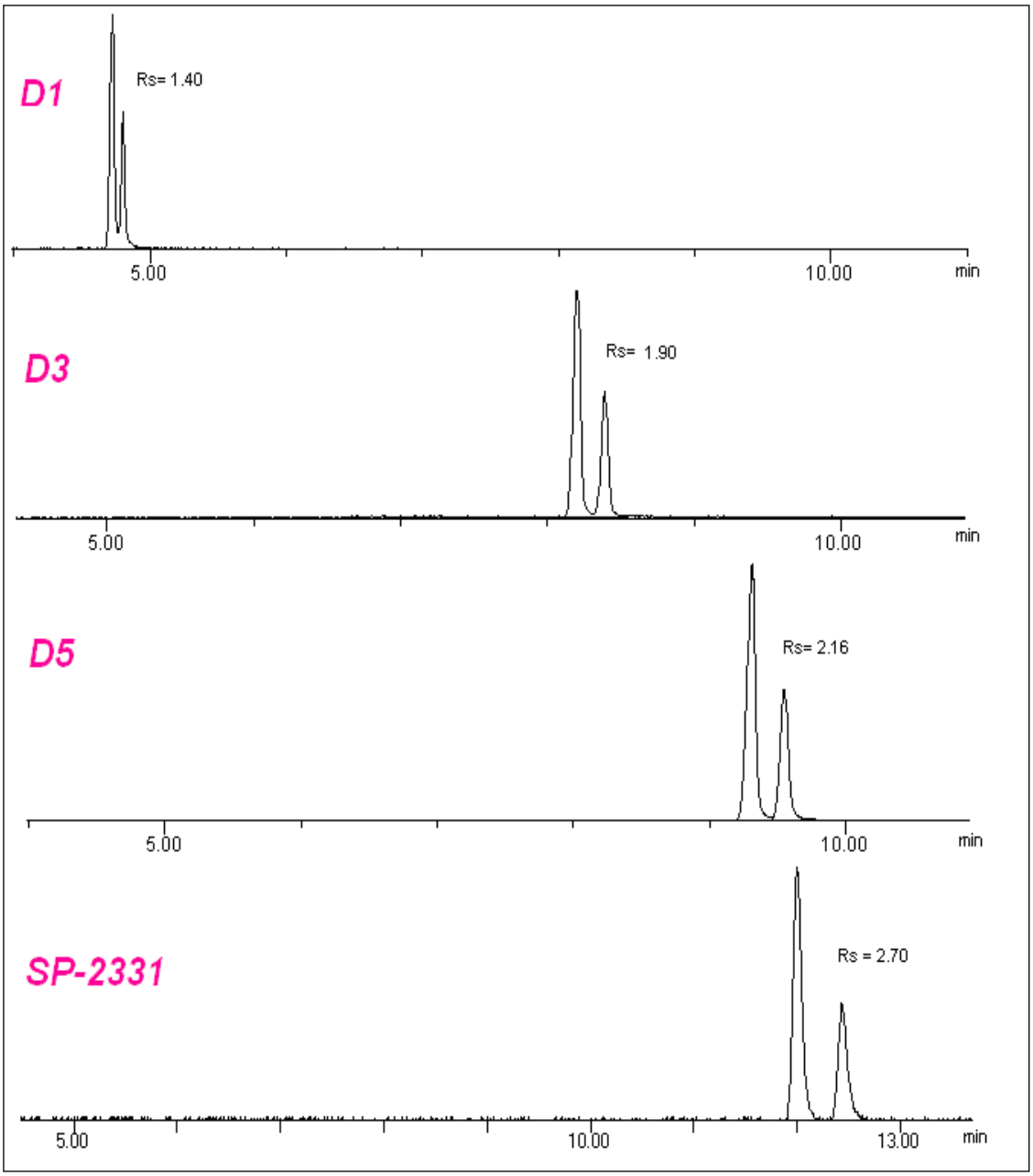


Figure 5.9 Separation of a mixture of methyl oleate (5 mg mL^{-1}) and methyl elaidate (10 mg mL^{-1}). Column dimensions: 30m x .25 mm x .20 µm d_f columns. GC separation conditions: isothermal at 165 ^{0}C; 1 mL min^{-1} He; MS detector.

5.4.7 FAME Isomer Separation

Determination of fatty acid content in edible oils has been an area of high interest due to its importance in dietary, nutritional and therapeutic fields.[165] Generally these isomeric unsaturated carboxylic acids are converted to their methyl esters and the fatty acid methyl esters (FAME) are separated using highly polar stationary phases.[166-168] In this test, a mixture of methyl oleate (9*cis* 18:1) and methyl elaidate (9*trans* 18:1) were separated using the highly polar trigonal tricationic IL stationary phases **D1, D3, D5** and the commercial SP-2331 stationary phase (see Figure 5.9). The t*rans*- isomer is twice the concentration (10 mg ml^{-1}) of the *cis*- isomer (5 mg ml^{-1}) for ease of identification. In the **D** core trigonal tricationic ionic liquid columns and the commercial SP-2331 column, the *trans* FAME elutes before the *cis* analogue. It is characteristic for cyanopropyl based stationary phases to elute the *trans*- isomer first. With polyethylene glycol-based stationary phases, the *cis*- isomer elutes first. This indicates that the **D** core ionic liquids when used as stationary phases are more similar to the highly polar cyanopropyl stationary phase, but with greater thermal stability. Under similar separation conditions, **D5** shows the best separation for the *cis* and *trans* isomers by the **D** core series of ILs, followed by **D3** and **D1** respectively.

5.5 Conclusions

Use of multifunctional ionic liquids as stationary phases for GC can be limited as the most common counter anion for many ionic liquids (i.e., bis(trifluoromethanesulfonyl)imide) results in peak tailing for alcohols and other H-bond forming analytes. Specific **D**-core trigonal tricationic ILs were shown to overcome this problem. According to the solvation parameter study, all monocationic, dicationic and

long chain linear tricationic ionic liquids have almost identical apparent polarities and interaction parameters. However, those were quite different for the some trigonal tricationic ILs, namely the **C4**, and **D**-core series, and resulted in unique selectivities and retention behaviors. This uniqueness appears to be the result of two main factors. First is the rigid trigonal geometry which forces the three positive charges to reside in close proximity for ILs with short linkage chains. The second is the contribution from the Amide group. The prominent interaction types of trigonal tricationic ILs were dipole–type interactions, H–bonding interactions and dispersive interactions. Alcohol/alkane mixture and Grob test mixtures indicated that these ionic liquids are far more polar than either the monocationic or dicationic ionic liquids reported thus far. Nitrogen core ionic liquids **C1** and **C4** were the most polar stationary phases and displayed very low retention for alkanes. Grob test, FAME isomer separation, and elution order of C18:1 *cis-trans* FAME isomers indicated that **D** core ionic liquids, especially **D5** have polarities comparable to SP-2331, a 100% cyanopropylpolysiloxane commercial stationary phase. Ionic liquid **D5** stands out as it shows minimum peak tailing for alcohols and other H–bonding analytes. According to the flavor and fragrance test, **D1** and **D5** are complementary to each other and show higher selectivity and superior separation efficiencies than the commercial SP-2331 stationary phase which has roughly comparable polarity. Furthermore, **D5** is more thermally stable than the SP-2331. It was observed that benzylimidazolium cationic moiety introduces much higher viscosities to the ionic liquid systems. IL **D3** has the highest viscosity among ionic liquids ever to be reported. All these trigonal tricationic ILs were highly thermally stable and had a minimum liquid temperature range of about 300 ºC.

These values far exceed those observed for traditional monocationic ionic liquids. According to these results, trigonal tricationic ionic liquid **D5** is very promising as a highly polar stationary phase that has high thermal stability and yields symmetrical peaks for H-bonding analytes.

CHAPTER 6

SYNTHESIS AND CHROMATOGRAPHIC EVALUATION OF NEW POLYMERIC CHIRAL STATIONARY PHASES BASED ON THREE (1*S*,2*S*)-(-)-1,2-DIPHENYLETHYLENEDIAMINE DERIVATIVES IN HPLC AND SFC

6.1 Abstract

Three new polymeric chiral stationary phases were synthesized based on (1*S*,2*S*)-1,2-bis(2,4,6-trimethylphenyl)ethylenediamine, (1*S*,2*S*)-1,2-bis(2-chlorophenyl) ethylenediamine, and (1*S*,2*S*)-1,2-di-1-naphthylethylenediamine *via* a simple free-radical initiated polymerization in solution. These monomers are structurally related to (1*S*,2*S*)-1,2-diphenylethylenediamine which is the chiral monomer used for the commercial P-CAP-DP polymeric chiral stationary phase (CSP). The performance of these three new chiral stationary phases were evaluated in normal phase HPLC and supercritical fluid chromatography and the results were compared to those of the P-CAP-DP column. All three new phases showed enantioselectivity for a large number of racemates with a variety of functional groups, including amines, amides, alcohols, amino acids, esters, imines, thiols, and sulfoxides. In normal phase HPLC 68 compounds were separated with 28 baseline separations (Rs ≥ 1.5) and in SFC, 65 compounds were separated with 24 baseline separations. In total 72 out of 100 racemates were separated by these CSPs with 37 baseline separations. Complimentary separation capabilities were observed for many analytes. The new polymeric CSPs showed similar or better enantioselectivities compared to the

commercial column in both HPLC and SFC. Faster separations were achieved on the new stationary phases. Also it was shown that these polymeric stationary phases have good sample loading capacities while maintaining enantioselectivity.

6.2 Introduction

Fast and effective separations of enantiomers continue to be an important and essential endeavor today due to the implications in drug development, medicine and human health. It is known that many pharmacologically active ingredients are chiral and that their physiological properties and dispersities are usually stereoselective. It is important to differentiate and evaluate these properties for each pure enantiomer to assess their physiological effects. There are instances in the history where failing to do so has led to undesirable outcomes.[169-171] In 1992 the FDA introduced new policies to control and regulate chiral drugs.[172] Consequently, considerable research has been conducted and a large number of chiral selectors have been synthesized and commercialized for HPLC, GC, CE, and SFC during the past three decades.[173, 174] HPLC remains by far the most popular method for performing chiral separations given its ability to separate a wide array of samples, simple sample preparation procedures and easy scale up capabilities. It is unlikely that a universal chiral selector can be developed in the foreseeable future. Instead there are many types of chiral stationary phases (CSPs) that show good selectivities towards various groups of analytes.

The types of CSPs available today can be divided into two main categories based on the selector mass; the brush type (often smaller molecules) and the polymeric type. In the following section discoveries of chiral selectors that are historically noteworthy will be discussed.

6.2.1 Brush-type CSPs

For brush type CSPs, individual chiral molecules are immobilized on a silica or polymer support.

6.2.1.1 Ligand Exchange CSPs

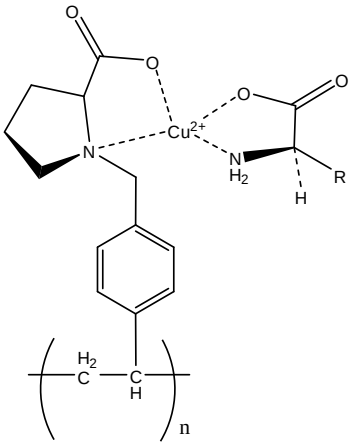
Davankov and Rogozhin introduced the first successful brush type CSP in 1971 by attaching a bidentate ligand (L-proline, hydroxylproline) on to a poly(styrene-co-divinylbenzene) support.[175] They were able to separate amino acids by adding Copper (II) into the mobile phase which facilitates the formation of diasteriomeric coordination complex with the ligand stationary phases (Figure 6.1a). This marks the first baseline resolution of enantiomers by liquid chromatography.

6.2.1.2 Chiral Crown Ethers

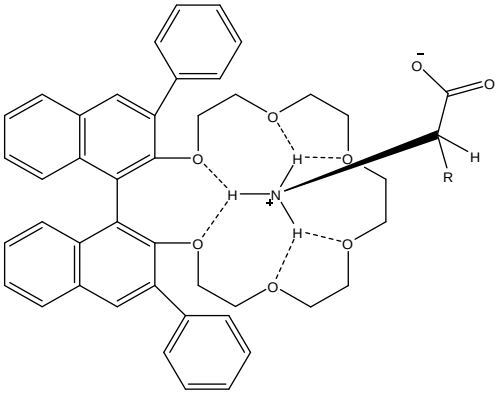
In 1975 Cram *et al.* introduced the first chiral crown ether based CSPs.[176, 177] Primary amine containing compounds could be separated in reverse phase conditions through the formation of inclusion complexes with these [18]-crown-6-polyethers. An example of this type is shown in Figure 6.2b.

6.2.1.3 π-Complex CSPs

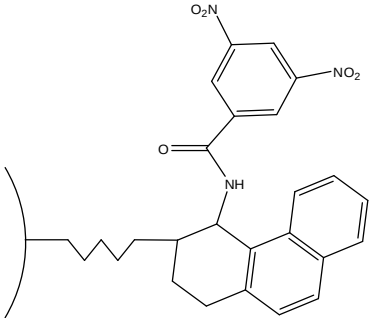
Chiral stationary phases based on π-π association interaction was first introduced by Mikes *et at.* in 1978.[178-180] The stationary phases contain π-acidic or π-basic groups that interact with analytes containing complementary π-basic or π-acidic moieties. Some examples of this type are shown in Figure 6.1c. Consequently other successful π-complex stationary phases have been introduced and commercialized by Pirkle, House, and Welch [181-185] and Oi and Kitahara.[186, 187]



(a)



(b)



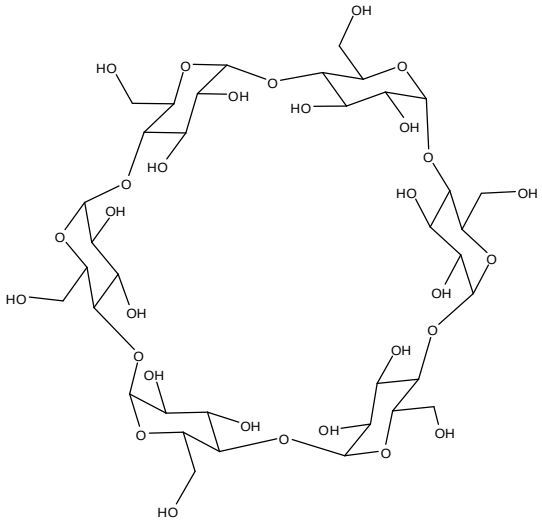
(c)

Figure 6.1 (a) – (c) are structures of brush-type chiral selectors.

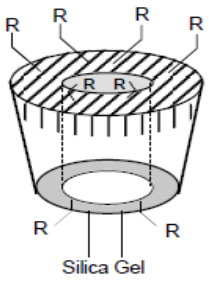
Most of the early chiral stationary phases have a common impediment that hinders the use of these in a wide range of applications. They are highly specific in the types of analytes that can be separated. The first class of brush-type chiral phases that demonstrated broad selectivity was introduced by Armstrong *et al.* in 1984.[188-190] These are the cyclodextrin based CSPs.

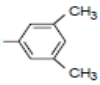
6.2.1.4 Cyclodextrin based CSPs

Cyclodextrins that are used as chiral stationary phases are cyclic oligosaccharides containing 6, 7 or 8 units of α-(1,4)-linked glucose (α, β, and γ-cyclodextrins respectively) (see Figure 6.2a). There are many hydroxyl groups that can be derivatized to obtain different separation capabilities under different separation mechanisms. The most commonly used and commercialized derivatizaions are shown in Figure 6.2b. Enantioseparation by cyclodextrins (CDs) occur through two main mechanisms.[190-192] In reverse phase (aqueous) conditions analytes can form inclusion complexes with the relatively hydrophobic cavity of CD. In other separation modes the numerous H-bonding interactions, π-bonding interactions (in derivatized CD) and steric interactions contribute to separations. Because of this broad enantioselectivity, cyclodextrin chiral stationary phases still remain very successful in the chromatographic field.



(a)



R=	CYCLOBOND I *2000* SUFFIX
$-OCH_3$	DM (dimethylated)
$-COCH_3$	AC** (acetylated)
$-CH_2\overset{OH}{\overset{\mid}{C}}HCH_3$ *	SP or RSP (hydroxypropyl ether)
$-CONH\overset{CH_3}{\overset{\mid}{C}}H$ *	RN or SN (naphthylethyl carbamate)
$-CONH$ 	DMP (3,5-dimethylphenyl carbamate)

(b)

Figure 6.2 (a) α-Cyclodextrin (b) List of common derivatives used for CSPs. (Reprinted with permission from reference 193)

6.2.1.5 Macrocylic Glycopeptide based CSPs

This is another very successful class of brush-type stationary phases introduced by Armstrong *et al.* in 1994.[194-197] These CSPs also have broad applicability and multimodal separation capabilities. Four types of commercially available macrocyclic glycopeptides are vancomycin (CHIROBIOTIC V), teicoplanin (CHIROBIOTIC T), teicoplanin aglycone (CHIROBIOTIC TAG) and ristocetin A (CHIROBIOTIC R) (see Figure 6.3).

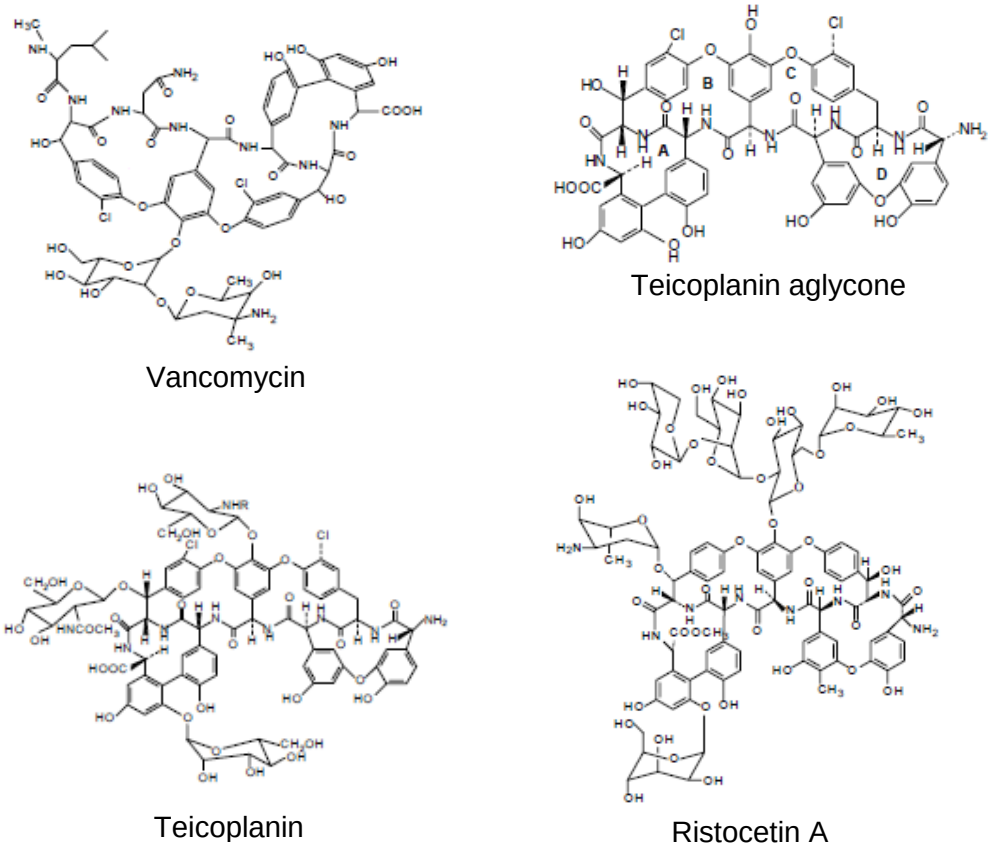


Figure 6.3 Structures of macrocyclic glycopeptides used at CSPs.
(Reprinted with permission from reference 193)

6.2.1.6 Cyclofructan based CSPs

Cyclofructans are the newest class of chiral stationary phase introduced by Armstrong *et al.* in 2009.[198-200] Much like the cyclodextrins these are macrocyclic oligosaccharides and consists of D-fructofuranose units (see Figure 6.4). Unlike in the cyclodextrins, the cyclofructan cavity resembles a crown ether and gives rise to unique selectivities. Furthermore, the primary and secondary hydroxyl groups can be derivatized with various aliphatic and aromatic groups to obtain enhanced separation capabilities. Among other classes of compounds, cyclofructan based stationary phases are known to show unparalleled selectivity towards primary amines.

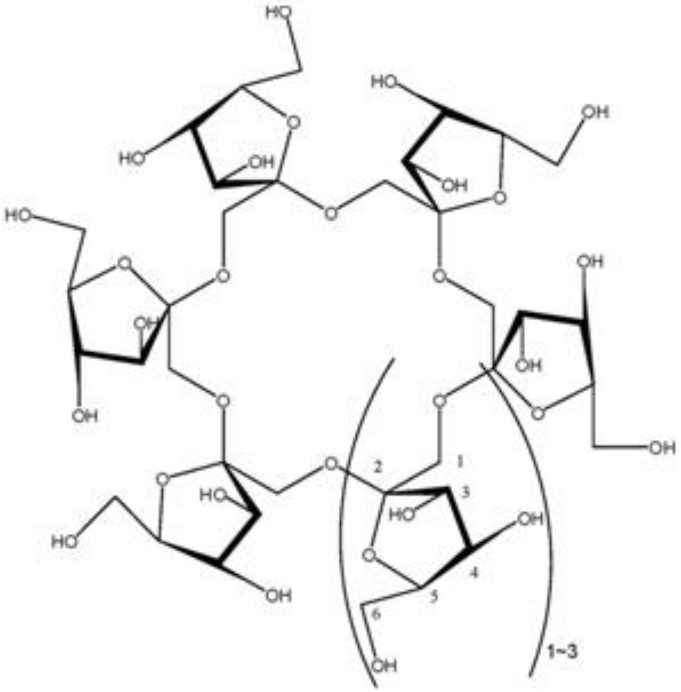


Figure 6.4 Structure of cyclofructan.
(Reprinted with permission from reference 198)

6.2.2 Polymeric CSPs

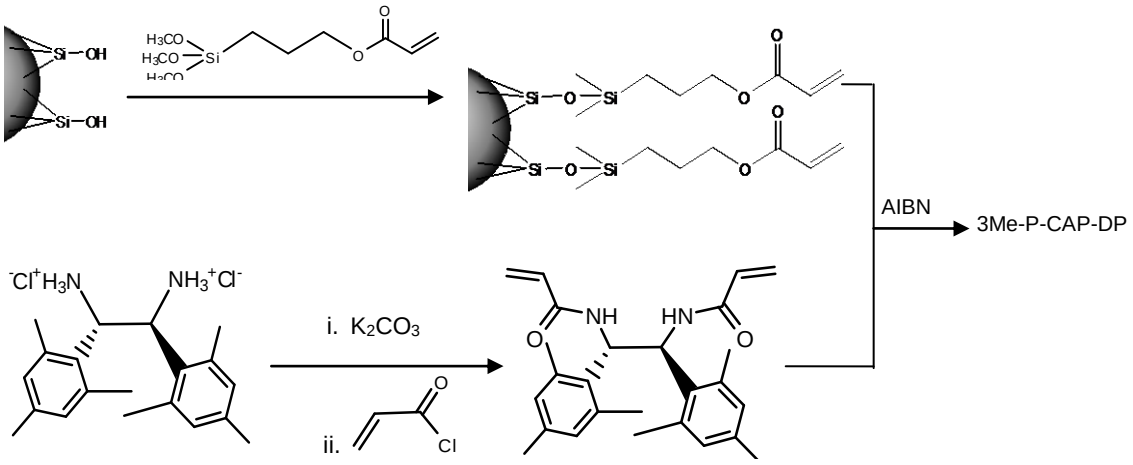
Polymeric stationary phases can be divided into two main types; natural polymers and synthetic polymers. Proteins and polysaccharide based stationary phases falls in the first category. Protein based CSPs are the most labile and are not very useful in the preparative scale since they are easily overloaded. However polysaccharide based CSPs such as cellulose and amylose and their derivatives have been among the most widely used stationary phases for enantiomeric separations[201, 202] ever since their introduction by Hesse and Hagel in 1973.[203] Since the early chiral selectors were physically coated onto silica, their applicability was often limited due to dissolution of the stationary phase in mobile phase solvents. This was overcome by immobilizing the derivatized polysaccharides onto silica via chemical bonding.[204]

In recent years synthetic polymeric chiral phases have attracted much attention due to some inherent qualities which are lacking or hard to obtain in other types of chiral stationary phases. These qualities include the availability of large number of structurally diverse monomers, the possibility to obtain the opposite absolute configuration of the stationary phase (which allows for reversal of the retention order of enantiomers), very high sample loading capacities, and good stability and chemical inertness due to covalent bonding to the silica solid support and cross linking within the stationary phase.[173] The first of this type reported in literature is the cross-linked polymer gels prepared by Wulff and Sarhan.[205] These were developed using a molecular imprinting technique in which enantioselective binding sites were embedded into the cross-linked polymer gel. These types of molecularly imprinted polymers (MIPs) have yet to play any significant role in enantiomeric separations. In 1974 Blaschke *et al.* reported polyacrylamide[206] and polymethacrylamide[207] polymers which

incorporated chiral copolymerizing agents and these have been successfully used at preparative scales. The next notable development was Okamoto's introduction of polymethacrylate polymers with rigid helical secondary structure.[208, 209] This was then followed by the introduction of polyamide polymers by Saigo *et al*. synthesized via polycondensation of chiral dicaroboxylic acids and chiral diamines.[210] The introduction of synthetic polymeric CSP based on *N,N'*-diacrolyl derivative of trans-1,2-diaminocyclohexane by Gasparrini *et al.* gave new impetus to this field in recent years.[211] These polymeric CSPs showed very good chiral recognition ability towards many classes of molecules in multiple separation modes (normal phase and polar organic mode) and had high sample loading capacity which led them to be commercialized as the P-CAP column through Advanced Separation Technologies Inc. This was then followed by a similarly successful polymeric CSP developed by Armstrong *et al*. based on *N,N*'-diacrolyl derivative of trans-1,2-diphenylethylenediamine.[212, 213] This was subsequently commercialized as the P-CAP-DP column. This stationary phase had added π-π interactions which were lacking in the P-CAP phase and showed complimentary separation capabilities.

In this publication we investigate the chiral recognition capabilities of 3 new polymeric chiral stationary phases based on three new analogs of *trans*-1,2-diphenylethylenediamine. The monomeric structures of these three chiral selectors are shown in Figure 6.5 (Structures **B**, **C**, and **D**). In other works it is known that alkyl and halide substitution on aromatic rings are known to alter or improve the enantioselectivity of existing stationary phases.[214] Therefore the tri-methyl phenyl group and chlorophenyl group were chosen for this study. Naphthyl substitution was used in the hopes of studying the effects of added π-π and steric interactions. The

three new polymeric phases were evaluated in both HPLC and SFC and their enantioselective capabilities were compared to the analogous commercial stationary phase, P-CAP-DP. Their sample loading capabilities were also investigated.



Scheme 6.1 Synthesis of 3Me-P-CAP-DP polymeric chiral stationary phase.

6.3 Experimental

6.3.1 Materials

(1*S*,2*S*)-1,2-Bis(2,4,6-trimethylphenyl)ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-bis(2-chlorophenyl)ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-di-1-naphthyl-ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-Bis(2,4,6-trimethoxyphenyl) ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-bis(2-hydroxyphenyl)ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-bis(4-fluorophenyl)ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-bis(4-nitrophenyl)ethylenediamine dihydrochloride, (1*S*,2*S*)-1,2-bis(4-methoxyphenyl)ethylenediamine dihydrochloride acryloyl chloride, 3-(trimethoxysilyl) propyl methacrylate, 2,2'-azobis(isobutyronitrile) (AIBN), acetone, anhydrous toluene, and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich Corp., St. Louis, MO. HPLC grade n-heptane, 2-propanol, and ethanol were purchased from Fisher, Fairlawn, NJ. Daiso silica with particle diameter 5µm, pore size 200 Å, surface area 170 m^2g^{-1} was used. All the chiral analytes used for analysis were also purchased from Sigma-Aldrich Corp. as either racemates or pure enantiomers.

6.3.2 Synthesis

Overall 8 new polymeric chiral stationary phases were synthesized during this investigation and their monomeric structures are shown in Figure 6.5. However, only the stationary phases made from polymers of **B**, **C** and **D** showed notable enantioselectivity. Therefore from this point forward results pertaining to those three new stationary phases (**B**: 3Me-P-CAP-DP, **C**: Cl-P-CAP-DP, and, **D**-Naph-P-CAP-DP) will be presented.

6.3.2.1 Synthesis of Methacryl Derivatized Silica

Vacuum dried silica gel (8g) was added to 500 mL round bottom flask equipped with Dean-Stark trap and condenser. 180 mL of anhydrous toluene was added to this and refluxed for 30 minutes. About 30 mL of distillate was removed and the set up was cooled down to room temperature. Next, 3-(trimethoxysilyl) propyl methacrylate (2 mL, 8.42 mmol) was added to the reaction mixture and refluxed for 4 h. The modified silica was then collected by filtration and washed with 100 mL of acetone, methanol and acetone respectively. It was then dried in vacuo under P_2O_5 overnight. Final weight 8.3 g. Weight increment 3.8%. Elemental analysis: C, 2.15%; H, 0.36%.

6.3.2.2 Synthesis of N, N'-[(1S,2S)-1,2-bis(2,4,6-trimethylphenyl)ethylene]bis-2-propenamide **(B)**

A solution of (*1S,2S*)-1,2-bis(2,4,6-trimethylphenyl)ethylenediamine dihydrochloride (1 g, 2.71 mmol) and potassium carbonate (1.65 g, 12 mmol) in acetone (5 mL) and water (5 mL) was stirred for 30 min and cooled in an ice bath to 5 °C. To this acryloyl chloride (0.54 mL, 6 mmol) was added drop wise with vigorous stirring for 10 min. The reaction mixture was warmed to room temperature and stirred overnight. Next the acetone was removed in rotarvapor and the resulting solid was washed with water and dried in vacuo to get the acrylamide as off-white solid (0.92 g, yield: 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.84(s, 2H), 6.57 (s, 2H), 6.24 (dd, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 2H), 6.08 (m, 4H), 5.65 (dd, J_1 = 11.3 Hz, J_2 = 1.4 Hz, 2H), 2.80 (s, 6H), 2.18 (s, 6H), 1.79 (s, 6H)

6.3.2.3 Synthesis of N,N'-[(1S,2S)-1,2-bis(2-chlorophenyl)ethylene]bis-2-propen amide **(C)**

A solution of (1*S*,2*S*)-1,2-bis(2-chlorophenyl)ethylenediamine dihydrochloride (1g, 2.82 mmol) and potassium carbonate (1.65g, 12 mmol) in acetone (5 mL) and water (5 mL) was stirred for 30 min and cooled in an ice bath to 5 °C. To this acryloyl chloride (0.54 mL, 6 mmol) was added drop wise with vigorous stirring for 10 min. The reaction mixture was warmed to room temperature and stirred overnight. Next the acetone was removed in rotarvapor and the resulting solid was washed with water and dried in vacuo to get the acrylamide as off-white solid (0.83 g, yield: 75.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22 (m, 8H), 6.30 (dd, J_1 = 16.8 Hz, J_2 = 1.4 Hz, 2H), 6.10 (m, 4H), 5.66 (dd, J_1 = 10.3 Hz, J_2 = 1.4 Hz, 2H)

6.3.2.4 Synthesis of N,N'-[(1S,2S)-1,2-di-1-naphthyl-ethylene]bis-2-propen amide **(D)**

A solution of (1*S*,2*S*)-1,2-di-1-naphthylethylenediamine dihydrochloride (1g, 2.59 mmol) and potassium carbonate (1.65g, 12 mmol) in acetone (5 mL) and water (5 mL) was stirred for 30 min and cooled in an ice bath to 5 °C. To this acryloyl chloride (0.54 mL, 6 mmol) was added drop wise with vigorous stirring for 10 min. The reaction mixture was warmed to room temperature and stirred overnight. Next the acetone was removed in rotarvapor and the resulting solid was washed with water and dried in vacuo to get the acrylamide as off-white solid (0.95 g, yield: 87.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.36 (d, J = 7.9 Hz, 2H), 7.62 (m, 14H), 6.31 (dd, J_1 = 16.8 Hz, J_2 = 1.4 Hz, 2H), 6.06 (m, 4H), 5.64 (dd, J_1 = 10.3 Hz, J_2 = 1.7 Hz, 2H)

6.3.3 Preparation of 3Me-P-CAP-DP, Cl-P-CAP-DP, and Naph-P-CAP-DP Chiral Stationary Phases

The chiral monomers were polymerized and covalently bonded to the methacryl silica gel by the following method. Methacryl silica gel (3.41 g) was suspended in 70 mL anhydrous toluene in 250 mL 3-neck flask with a Dean-Stark trap and a condenser. After removing 10 mL of distillate, the reaction mixture was cooled down to room temperature and saturated with nitrogen. Monomer (ca.2.207 mmol) and AIBN (22 mg, 0.134 mmol) were put into the suspension under nitrogen protection. The suspension was kept at 80 °C for 4 h and refluxed for 1 h. The CSP was collected by filtration, washed with 100 mL of ethanol, acetone, methanol, and chloroform respectively. The CSP was dried under vacuum at 50 °C over night to obtain about 3.9 g of stationary phase. Elemental analysis for 3Me-P-CAP-DP: C, 12.93%; H, 1.27%; N, 1.20%. For Naph-P-CAP-DP: C, 11.75%; H, 1.07%; N, 1.07%. For Cl-P-CAP-DP: C, 10.04%; H, 1.05%; N, 1.07%.

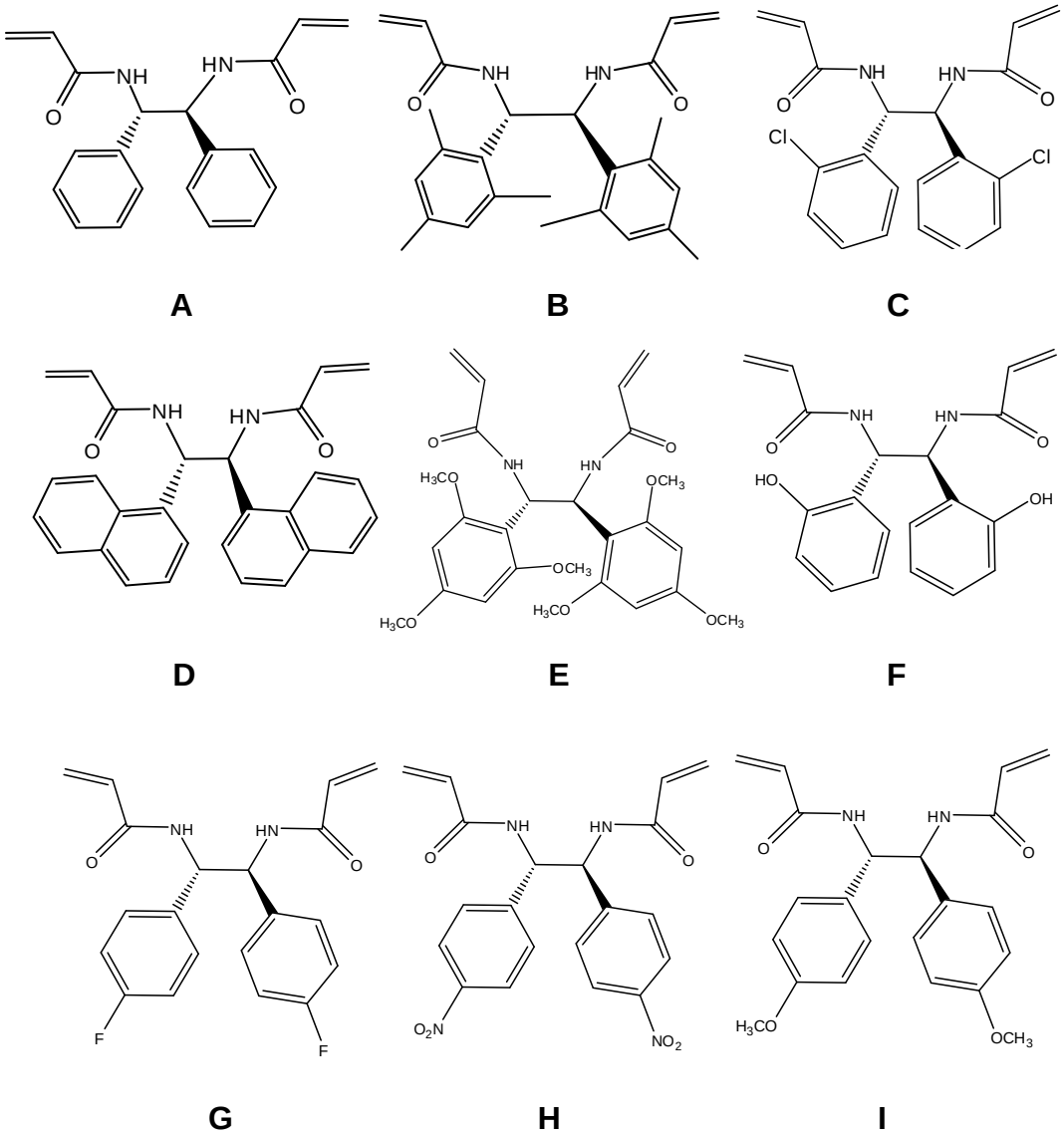


Figure 6.5 Structures of the monomeric units used for the synthesis of commercial (**A**) and eight new polymeric chiral stationary phases (**B,C,D,E,F,G,H**, and **I**). (Corresponding stationary phases **A**: P-CAP-DP**, B**: 3Me-P-CAP-DP, **C**: Cl-P-CAP-DP, **D**: Naph-P-CAP-DP, **E**: 3OMe-P-CAP-DP, **F**: OH-P-CAP-DP, **G**: F-P-CAP-DP, **H**: NO2-P-CAP-DP, and **I**: OMe-P-CAP-DP respectively)

6.3.4 Column Preparation and Chromatographic Conditions

All the new polymeric chiral stationary phases were packed on analytical stainless-steel columns (250 mm x 4.6 mm) from IDEX Health and Science (Hopedale, MA, USA) using a slurry packing technique. HPLC separations were carried out using a HP 1090 system with an auto sampler and a diode array detector (DAD). About half of all the analyte samples were from racemic mixtures. The rest were prepared by combining pure enantiomers. All analytes were detected at 3 wavelengths: 254 nm, 220 nm and 210 nm. Data were processed using ChemStation software (Agilent Technologies, Palo Alto, CA, USA). HPLC column performance was evaluated in the normal phase (NP) mode using heptanes. Ethanol was used as the organic modifier to get higher peak efficiencies compared to isopropyl alcohol. Trifluoroacetic acid was added for better peak efficiency in some analytes (acidic) but the addition of acid also lowered the retention times. The mobile phases were degassed under helium for 10 min. All separations were carried out at room temperature (~ 23 °C) and the flow rate of mobile phase for all separations was 1.0 mL min^{-1}.

For supercritical fluid chromatography a JASCO SFC-2000-7 (Hachioji, Tokyo, Japan) semi-prep system was used. The system includes liquid CO_2 pump equipped with chiller, a modifier pump, an autosampler, column oven, auto back pressure regulator, a UV-Vis detector, and ChromNAV data processing software (JASCO, Hachioji, Tokyo, Japan). UV detection was carried out at 220 nm for all analytes. Column oven was set at 40 °C and the flow rate for all mobile phase compositions was 2 mL min^{-1}. CO_2/Ethanol/TFA or CO_2/Methanol/TFA solvent systems were used in all analysis.

Column dead time (t_0) was estimated using the peak resulting from the change in refractive index from the injection solvent. The retention factor (k) was calculated using the equation $k = (t_r - t_0) / t_0$. The enantioselectivity (α) was calculated using $\alpha = k_2 / k_1$. The resolution factor was (Rs) was calculated using $Rs = 2 \times (t_{r2} - t_{r1}) / (w_1 + w_2)$, where t_{r1} and t_{r2} are the retention times of the first and second eluting enantiomers respectively and w_1 and w_2 are the corresponding base peak widths. Criteria for separation: Rs < 0.5 = no separation, 0.5<Rs<1.5 = partial separation, and Rs≤ 1.5 = baseline separation.

6.4 Results and Discussion

6.4.1 New CSP Preparations

Monomeric intermediates that undergo free-radical initiated polymerization in solution to produce the polymeric CSPs are shown in Figure 6.5. The synthetic route for the 3Me-P-CAP-DP stationary phase is shown in Scheme 6.1. The same synthetic approach was used for Naph-P-CAP-DP and Cl-P-CAP-DP. During the first step methacryl derivatized silica is formed. Even though the polymerization may mainly take place in the solution, appreciable amount of this polymer is grafted onto the methacrylic silica during the free radical initiated process as evidenced by the good carbon loading obtained. This synthetic route slightly differs from the one taken in P-CAP-DP synthesis in that amine hydrochloride salts of the starting monomeric materials were used in the three new CSP syntheses instead of the diamine used in P-CAP-DP (see Experimental).

6.4.2 HPLC Enantioselectivity

The comparative performance of the new polymeric CSPs in terms of enantiomeric separations in normal phase HPLC is shown in Table 6.1. A large number of chemically diverse analytes were used for this study. Normal phase separations were carried out with heptane. Ethanol was used as the organic modifier as it gave the best resolution and peak efficiency of the modifiers used. (see Figure 6.6) Previous studies of similar stationary phases also suggest that ethanol produced better peak efficiencies and resolutions compared to isopropyl alcohol (IPA).[212, 215] However it should be noted that longer retention and better selectivities can sometimes be obtained with the use of IPA. Small amounts of trifluoroacetic acid were added to the mobile phase for some analytes (acidic ones) to obtain better peak efficiencies.[215] For comparison, the samples used for these analyses also were run on the commercial P-CAP-DP column under the same chromatographic conditions. The final results are summarized in Figure 6.7a which shows the total enantiomeric separations on each stationary phase and the number of baseline separations. In the normal phase mode with heptane/ethanol as the mobile phase 54 enantiomeric separations were obtained on 3Me-P-CAP-DP column with 14 baseline separations (Table 6.1). On Cl-P-CAP-DP column 44 enantiomeric separations with 8 baseline separations were observed. Naph-P-CAP-DP column performed the best among the new polymeric CSPs with 56 total enantiomeric separations. It showed 8 baseline separations as well. In comparison the commercial column P-CAP-DP showed 50 total separations with 16 baseline separations. Collectively all 4 polymeric CSPs separated 68 analytes with 28 baseline separations. Of these 68 separations, one compound (68) was separated only by P-CAP-DP column.

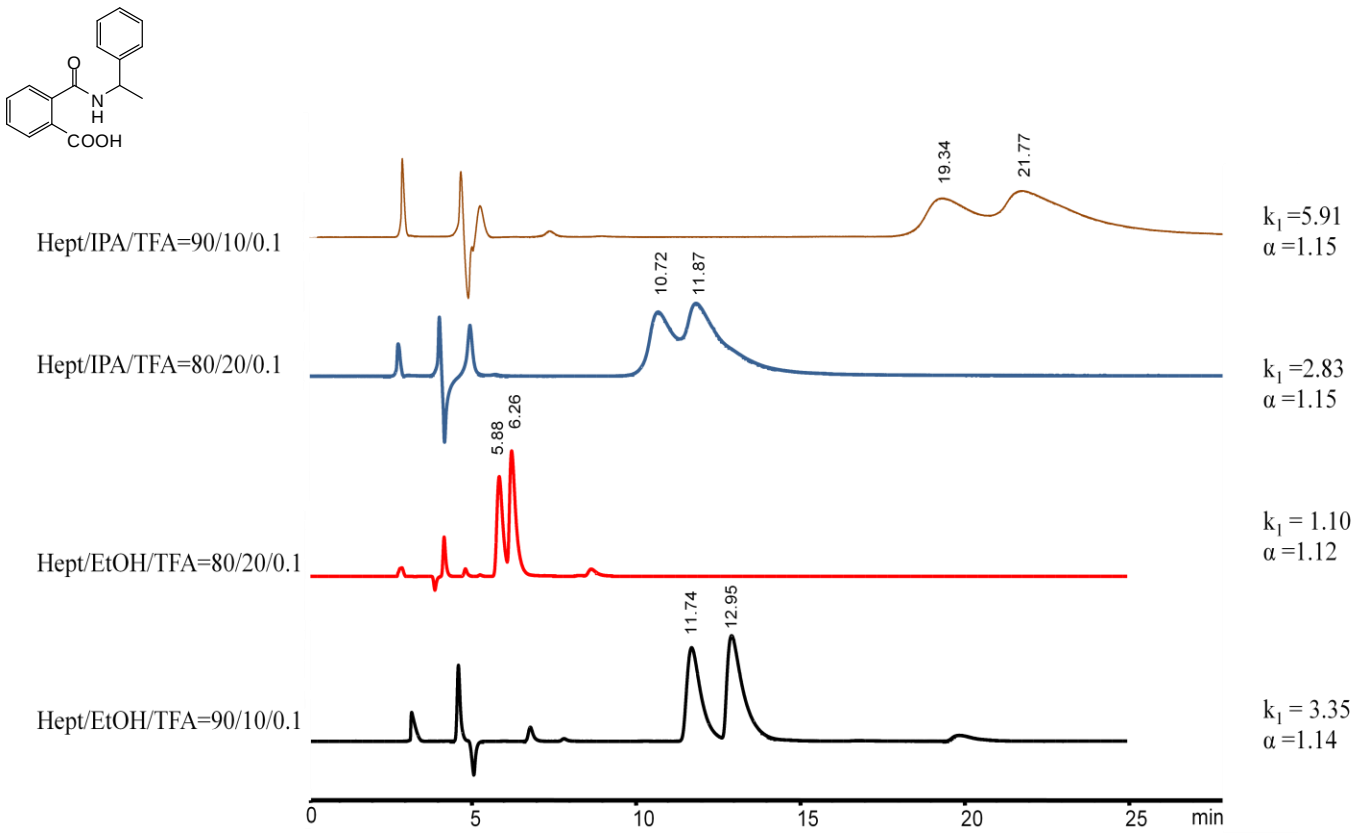


Figure 6.6 Evaluation of best separation conditions for N-(α-methylbenzyl) phthalic acid on 3Me-P-CAP-DP column.

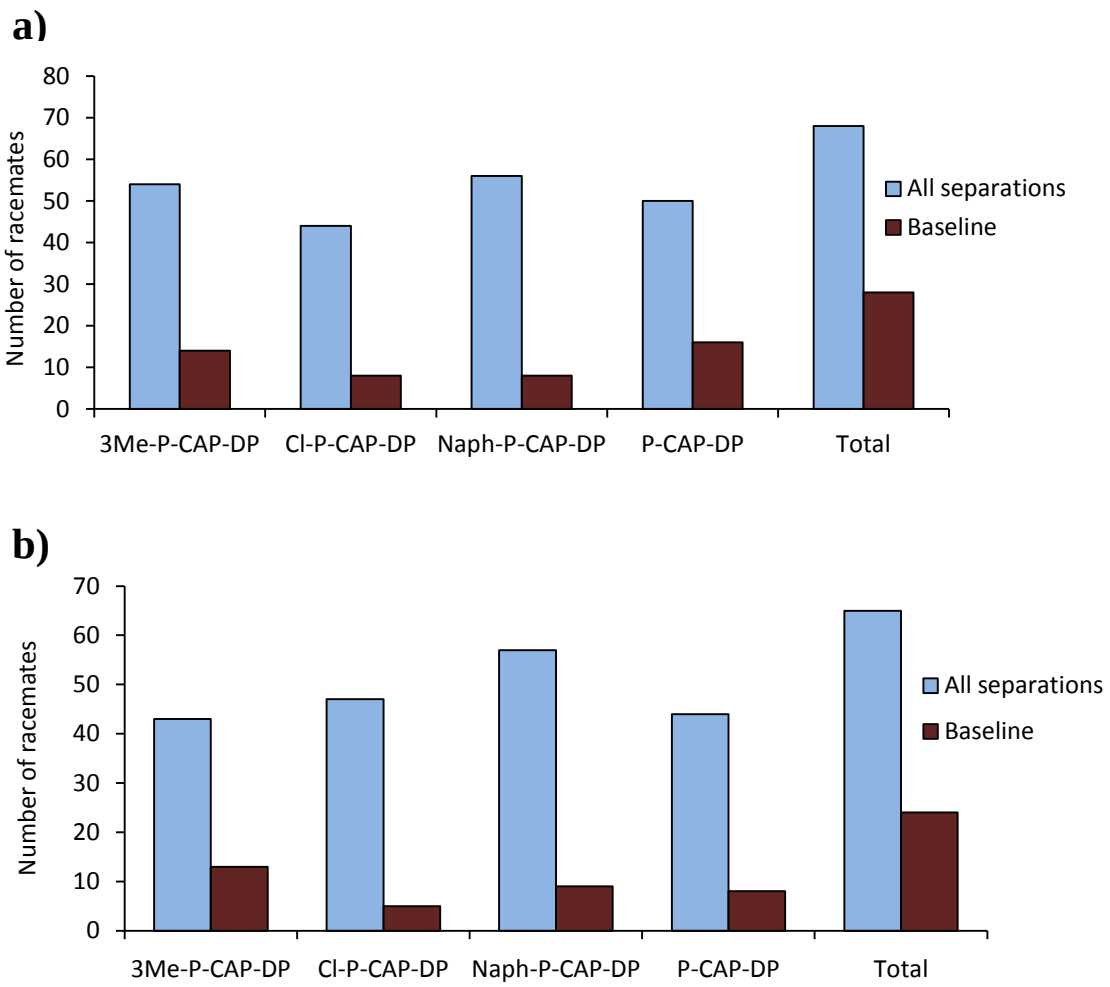


Figure 6.7 Graphical representation of racemates separated by the three new polymeric chiral stationary phases; 3Me-P-CAP-DP, Cl-P-CAP-DP, Naph-P-CAP-DP, and the commercial phase; P-CAP-DP in normal phase HPLC **(a)** and SFC **(b)**.

The other 67 compounds were separated by at least one of the new polymeric CSPs as well. However, 3Me- P-CAP-DP column showed enantioselectivity for 4 compounds (4, 21, 47, 49) that were not separated by any other polymeric CSP and 5 compounds (62, 63, 64, 65, 66) were separated only with the Naph-P-CAP-DP column. It should be noted that none of the three new columns have been optimized in terms of binding chemistry, column packing, and separation conditions. This initial study was to compare the separation capabilities of these new polymeric CSPs compared to the structurally analogous commercial P-CAP-DP phase.

It was observed that in many separations the retention factors for analytes on the new polymeric CSPs were less than those observed on the P-CAP-DP column. However this does not seem to have affected the enantioselectivities of these new stationary phases. Out of the 68 analytes separated in HPLC, 49 were separated with better or equal resolution on the new CSPs compared to the commercial phase under identical separation conditions. This fact is remarkable given the un-optimized column preparation conditions of the new columns. Two examples of separations with higher enantioselectivity despite the lower retention are illustrated in Figure 6.8. Here benzyl-6-oxo-2,3-diphenyl-4-morpholinecarboxylate (5) and 4-isopropyl-5,5-diphenyl-2-oxazolidinone (40) are separated on the 3Me-P-CAP-DP and P-CAP-DP columns. Even though both compounds were retained less on the new column they are both baseline separated. Under similar conditions the commercial CSP does not successfully separate these analytes. Figure 6.9 shows the complementary nature of enantioselectivities between the new polymeric stationary phases. In this example 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (12) and 1,5-dimethyl-4-phenyl-2 imidazolidi-

none (57) are separated on Naph-P-CAP-DP and Cl- P-CAP-DP columns. Compound 12 was baseline separated on the Naph-P-CAP-DP column while it was only partially separated on the Cl- P-CAP-DP. Conversely the Cl- P-CAP-DP column performed best by baseline separating compound 57. The observed asymmetry of the peaks on these columns is due to un-optimized packing conditions.

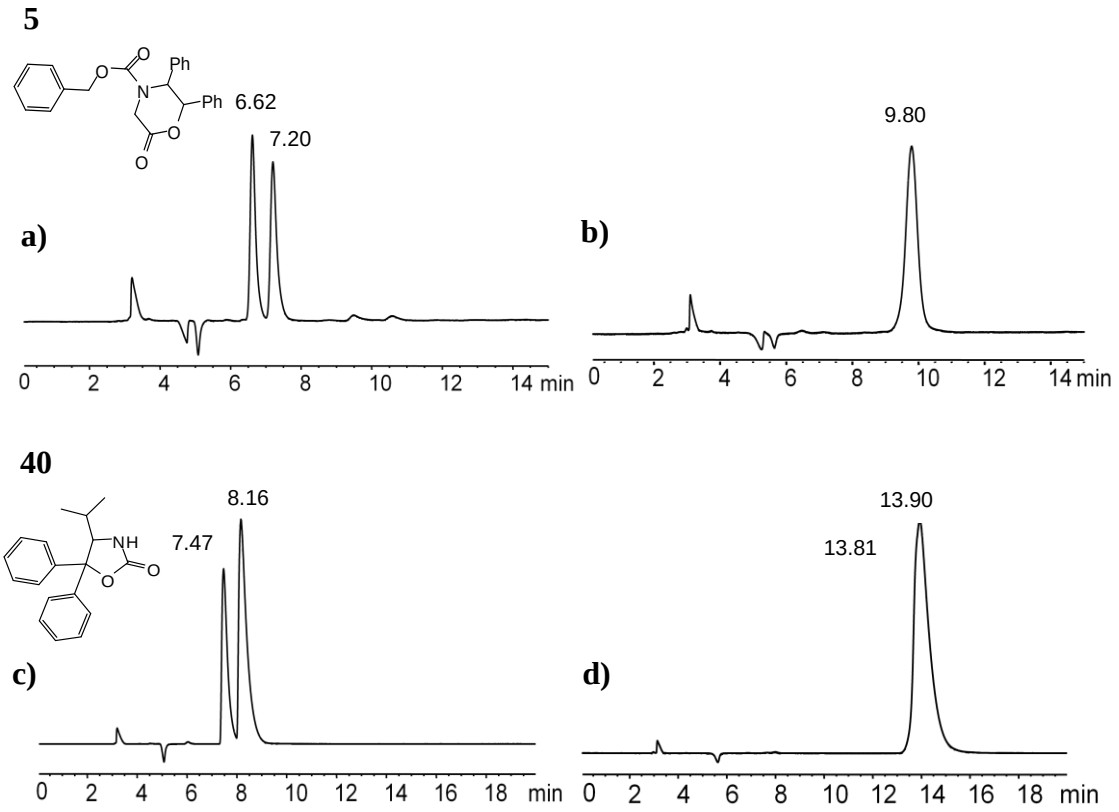


Figure 6.8 Separation of compounds **5** and **40** on 3Me-P-CAP-DP column (**a** and **c**) and P-CAP-DP column (**b** and **d**) under identical mobile phase conditions. For (**a** and **b**); Hept/EtOH/TFA = 90/10/0.1%. For **c)** and **d)**; Hept/EtOH = 90/10%. **a)** Enantioselectivity: α = 1.15, Resolution: Rs = 1.5, **c)** α = 1.14, Rs = 1.5, and **d)** α = 1.01, Rs = 0.5

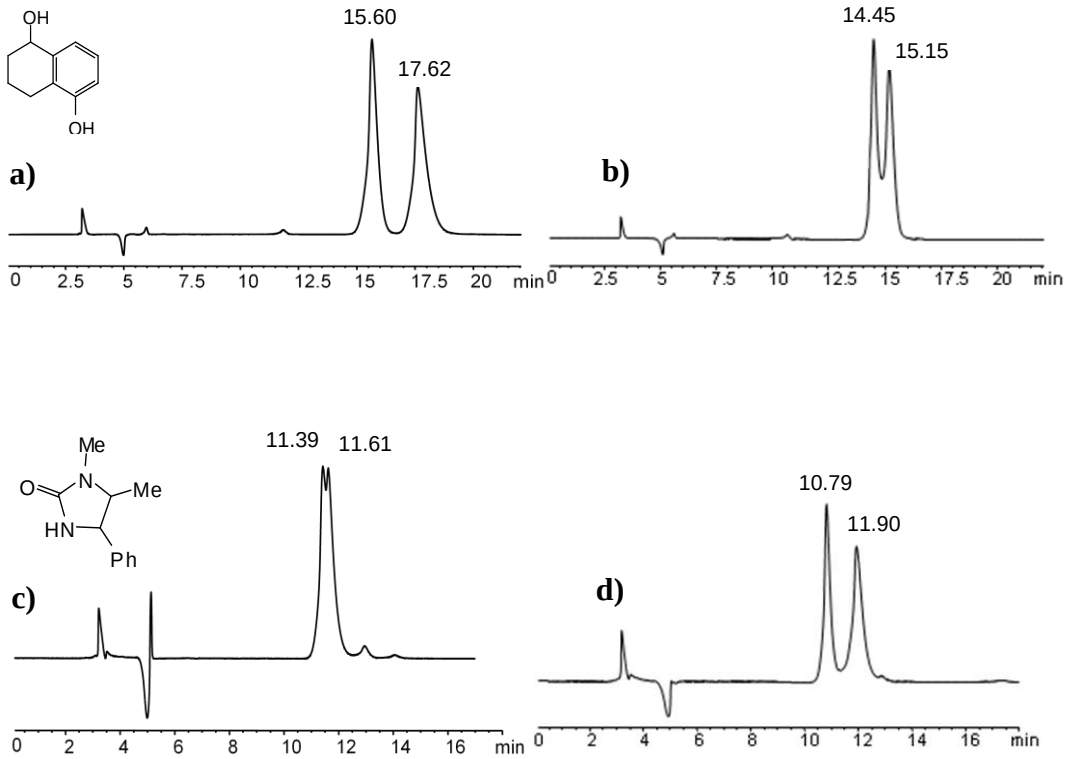


Figure 6.9 Complimentary nature of enantioselectivity and resolution between new stationary phases. Separation of compounds **12** and **57** on Naph-P-CAP-DP column (**a** and **c**) and Cl-P-CAP-DP column (**b** and **d**). Mobile phase for all separations: Hept/EtOH = 90/10%. **a)** Enantioselectivity: α = 1.16, Resolution: Rs = 2.2, **b)** α = 1.06, Rs = 1.1, **c)** α = 1.02, Rs = 0.6, and **d)** α = 1.14, Rs = 1.6.

6.4.3 Sample loading study

Polymeric chiral stationary phases are known to have good sample loading capacities.[211, 213, 215] The same was observed for the CSPs in this study. Figure 6.10 shows the separation of a derivatized amino acid N-(3,5-dinitrobenzoyl)-DL-leucine on the 3Me-P-CAP-DP column with analytical dimensions (250 mm x 4.6 mm). With 1 µg injection an enantioresolution of 3.9 was obtained on this column. When the sample size was increased to 1 mg the resolution was still maintained above 1.0 which is notably good for an analytical column. Especially with the lower retention, high enantioselectivity, and high sample loading capacity demonstrated, the 3Me-P-CAP-DP column has a potential to be used in preparative scale separations.

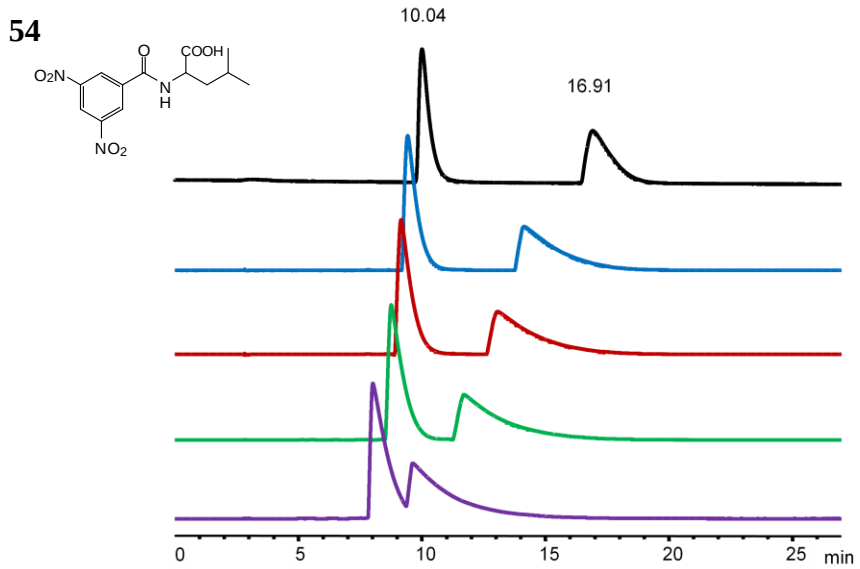


Figure 6.10 Sample loading study for N-(3,5-dinitrobenzoyl)-DL-leucine (compound **54**) on 3Me-P-CAP-DP column (250 mm x 4.6 mm). Amount injected in µg, from top to bottom: 1, 50, 100, 250, and 1000. Sample concentration: 15mg mL^{-1}dissolved in hept/ethanol = 25/75. Eluent: Hept/EtOH/TFA = 80/20/0.1. Flow rate: 1.0 mL min^{-1}. UV detection at 300 nm.

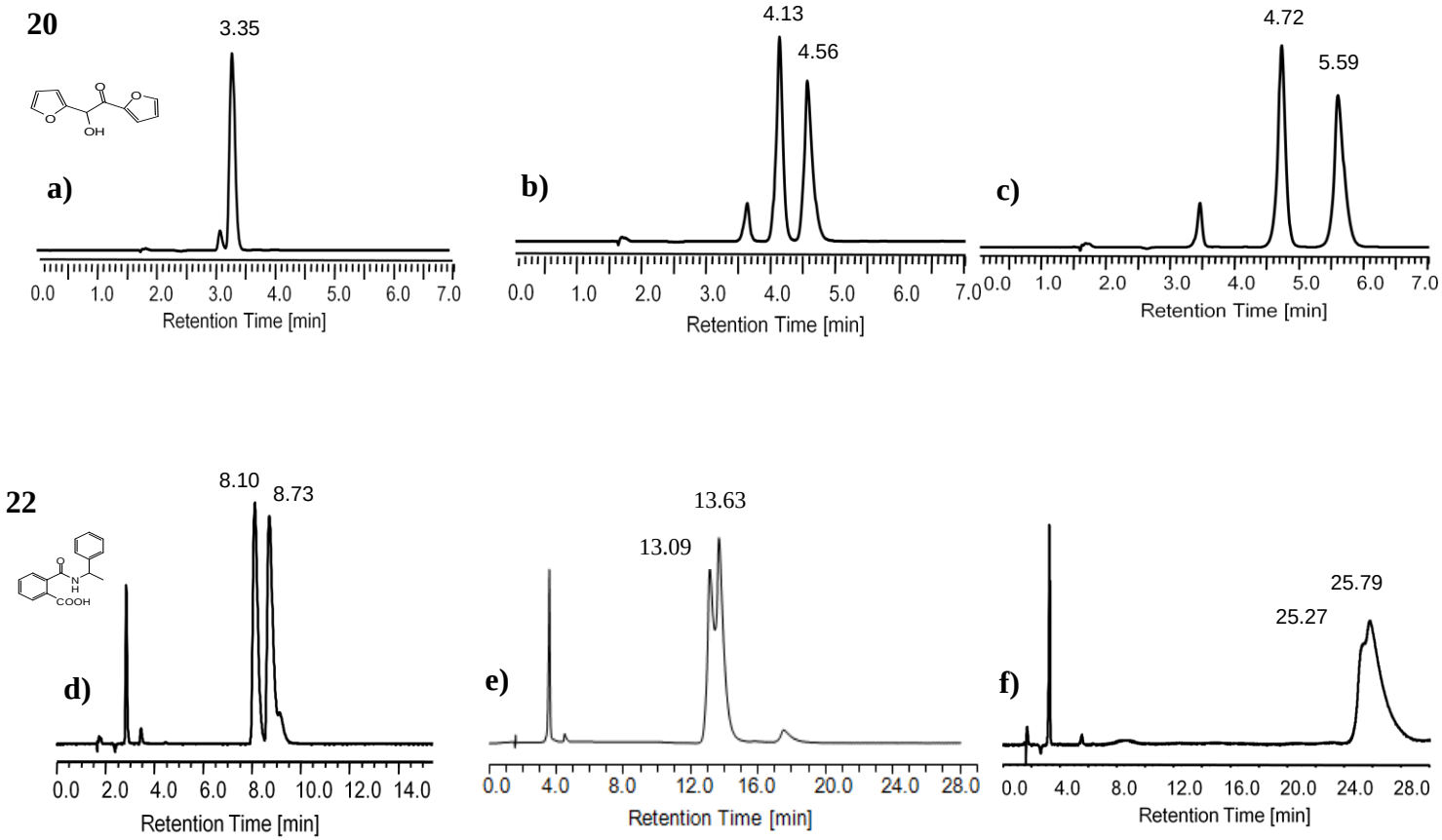


Figure 6.11 Complimentary enantioselectivities between stationary phases in SFC. Separation of compound 20 (a, b, c) and 22 (d, e, f) on 3Me-P-CAP-DP (a, d), Naph-P-CAP-DP (b, e) and P-CAP-DP (c, f). Mobile phase for a, b, c, f separations: CO_2/ EtOH/TFA = 90/10/0.1. For d and e: CO_2/MeOH/TFA = 90/10/0.1. b) Enantio selectivity: α = 1.17, Resolution: Rs = 1.7, c) α = 1.28, Rs = 2.5, d) α = 1.10, Rs = 1.5, e) α = 1.05, Rs = 0.8, and f) α = 1.02, Rs = 0.6. Flow rate 2 mL min^{-1}.

6.4.4 SFC enantioselectivity

Packed column supercritical fluid chromatography is usually employed in instances where rapid separations with high efficiency are needed along with the water-free isolation capabilities. Because of the use of relatively non polar mobile phase with respect to the more polar stationary phase, SFC parallels normal phase HPLC. Previous literature published on the earlier polymeric CSPs demonstrated that they had good enantioselectivities in SFC.[216] Therefore these new CSPs also were tested in SFC. The results are summarized in Figure 6. 7b. Compared to the solvents used in HPLC, the SFC mobile phase has very low viscosity which allows the use of higher mobile phase flow rates. However since retention on these new CSPs was less than on the commercial column, the flow rate was kept at 2 mL min^{-1}. As seen for the HPLC results, the retention factors of all analytes on the 3Me-P-CAP-DP and Cl-P-CAP-DP columns and for most analytes on the Naph-P-CAP-DP column were less than those observed on the P-CAP-DP column. Yet out of the 65 total separations 50 racemates were separated with better or equal resolution on the new CSPs compared to the commercial one. On the 3Me-P-CAP-DP column, 43 racemates were separated with 13 baseline resolution while on the Cl-P-CAP-DP column, 47 racemates were resolved with 5 baseline separations. As with HPLC, the Naph-P-CAP-DP column showed the broadest enantioselectivity with 57 separations of which 9 were baseline separations. In comparison the commercial phase P-CAP-DP separated 44 racemates with 8 baseline resolution. Combined, all 4 stationary phases separated 65 racemates with 24 baseline separations. Compounds 48 and 70 were separated only on the 3Me-P-CAP-DP stationary phase. Likewise compound 21 was separated only by the Cl-P-

CAP-DP and 54 was separated only by the P-CAP-DP. The Naph-P-CAP-DP column showed unique selectivity for 5 compounds which were 62, 63, 64, 66 and 72. Complimentary nature of these CSPs were observed in the SFC mode of separations as well. Figure 6.11 shows two examples of this effect. Compound 20 was well separated on both the Naph-P-CAP-DP and P-CAP-DP columns but not on 3Me-P-CAP-DP. However compound 22 shows very good enantioselectivity on 3Me-P-CAP-DP column but not on the other two.

Table 6.1 Retention factor for the first peak (k_1), enantioselectivity (α) and enantioresolution (Rs) of separated racemates on 3Me-P-CAP-DP, Cl-P-CAP-DP, Naph-P-CAP-DP, and P-CAP-DP columns in normal phase HPLC.

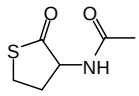
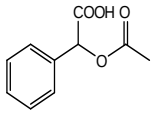
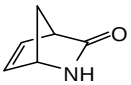
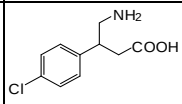
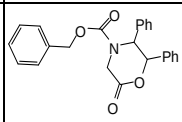
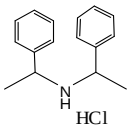
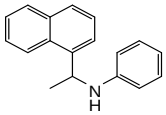
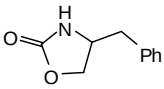
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
1	DL-N-Acetylhomocysteine thiolactone		3Me-P-CAP-DP	2.59	1.09	1.3	Hept/EtOH/TFA =80/20/0.1
			Cl-P-CAP-DP	8.32	1.09	1.2	Hept/EtOH/TFA =90/10/0.1
			Naph-P-CAP-DP	8.39	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	10.07	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
2	O-Acetylmandelic acid		3Me-P-CAP-DP	1.62	1.12	1.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.00	1.06	1.0	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.21	1.10	1.2	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.75	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
3	2-Azabicyclo[2.2.1]-hept-5-en-3-one		3Me-P-CAP-DP	2.79	1.06	0.7	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.39	1.02	0.5	Hept/EtOH = 90/10
4	4-Amino-3-(4-chlorophenyl)butanoic acid		3Me-P-CAP-DP	4.04	1.04	0.6	Hept/EtOH/TFA = 80/20/0.1
5	Benzyl-6-oxo-2,3-diphenyl-4-morpholine carboxylate		3Me-P-CAP-DP	1.45	1.15	1.5	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.61	1.04	0.6	Hept/EtOH/TFA = 90/10/0.1
6	Bis(1-phenyl ethyl)amine hydrochloride		3Me-P-CAP-DP	1.64	1.04	0.7	Hept/EtOH = 90/10
			Cl-P-CAP-DP	3.57	1.20	1.3	Hept/EtOH = 90/10
			Naph-P-CAP-DP	2.39	1.25	2.0	Hept/EtOH = 90/10
			P-CAP-DP	6.46	1.22	1.3	Hept/EtOH = 90/10
7	N-Benzyl-1-(1-naphthyl) ethylamine		3Me-P-CAP-DP	2.16	1.04	0.8	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	5.21	1.09	0.8	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.36	1.10	1.2	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	9.82	1.09	0.9	Hept/EtOH/TFA = 90/10/0.1
8	4-Benzyl-2-oxazolidinone		3Me-P-CAP-DP	3.81	1.02	0.7	Hept/EtOH = 90/10
			Cl-P-CAP-DP	6.04	1.06	0.7	Hept/EtOH = 90/10

Table 6.1 *Continued*

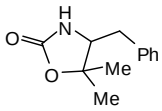
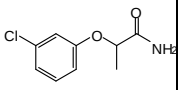
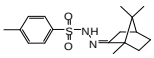
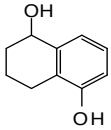
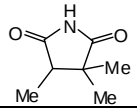
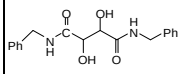
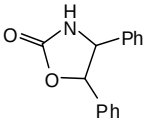
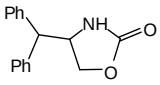
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
9	4-Benzyl-5, 5-dimethyl-2-oxazolidinone		3Me-P-CAP-DP	2.05	1.10	1.3	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	3.14	1.06	0.9	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.75	1.03	0.6	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	5.71	1.04	0.6	Hept/EtOH/TFA = 90/10/0.1
10	2-(3-Chlorophenoxy) propionamide		3Me-P-CAP-DP	2.51	1.04	1.1	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.67	1.08	1.3	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.86	1.05	1.1	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.64	1.15	2.5	Hept/EtOH/TFA = 90/10/0.1
11	Camphor p-tosyl hydrazon		3Me-P-CAP-DP	1.59	1.02	0.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.53	1.04	0.8	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.21	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.54	1.04	0.6	Hept/EtOH/TFA = 90/10/0.1
12	1,5-Dihydroxy-1,2,3,4-tetrahydronaphthalene		3Me-P-CAP-DP	3.38	1.17	3.0	Hept/EtOH = 90/10
			Cl-P-CAP-DP	4.18	1.06	1.1	Hept/EtOH = 90/10
			Naph-P-CAP-DP	4.57	1.16	2.2	Hept/EtOH = 90/10
			P-CAP-DP	5.79	1.12	2.0	Hept/EtOH = 90/10
13	α,α-Dimethyl-β-methylsuccinimide		3Me-P-CAP-DP	1.95	1.05	1.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.93	1.04	0.6	Hept/EtOH/TFA = 90/10/0.1
14	*N,N'*-Dibenzyl-tartramide		3Me-P-CAP-DP	2.97	1.12	1.6	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	5.89	1.30	1.8	Hept/EtOH/TFA = 90/10/0.1
15	cis-4,5-Diphenyl-2-oxazolidinone		3Me-P-CAP-DP	3.93	1.03	0.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	5.54	1.02	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	5.54	1.03	0.5	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	10.21	1.06	0.8	Hept/EtOH/TFA = 90/10/0.1
16	4-(Diphenylmethyl)-2-oxazolidinone		3Me-P-CAP-DP	1.78	1.04	0.5	Hept/EtOH/TFA = 80/20/0.1
			Cl-P-CAP-DP	5.68	1.18	1.8	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	6.04	1.12	1.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	12.79	1.13	1.6	Hept/EtOH/TFA = 90/10/0.1

Table 6.1 *Continued*

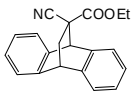
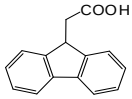
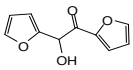
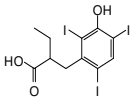
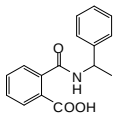
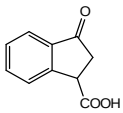
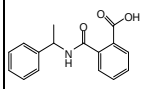
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
17	2,3-Dihydro-7a-methyl-3-phenylpyrrolo[2,1-b]oxazol-5(7aH)-one		3Me-P-CAP-DP	1.25	1.12	1.4	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.79	1.02	0.5	Hept/EtOH/TFA = 90/10/0.1
18	Ethyl- 11-cyano-9,10-dihydro-endo-9,10-ethanoanthracene-11-carboxylate		3Me-P-CAP-DP	0.87	1.14	1.4	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.43	1.05	0.8	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.32	1.03	0.5	Hept/EtOH/TFA = 90/10/0.1
19	9-Fluoreneacetic acid		3Me-P-CAP-DP	3.01	1.04	1.2	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.04	1.18	3.1	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.79	1.23	3.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	7.18	1.38	4.0	Hept/EtOH/TFA = 90/10/0.1
20	Furoin		3Me-P-CAP-DP	2.99	1.04	1.2	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.15	1.16	3.0	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.68	1.22	2.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	7.07	1.42	4.0	Hept/EtOH/TFA = 90/10/0.1
21	Iophenoxic acid		3Me-P-CAP-DP	3.89	1.03	0.7	Hept/EtOH/TFA = 90/10/0.1
22	N-(α-Methylbenzyl) phthalic acid monoamide		3Me-P-CAP-DP	3.35	1.14	1.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.93	1.03	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.71	1.05	0.6	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	8.54	1.07	0.8	Hept/EtOH/TFA = 90/10/0.1
23	3-Oxo-1-indancarboxylic acid		3Me-P-CAP-DP	2.90	1.09	1.4	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	3.29	1.07	1.2	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.71	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	4.50	1.04	0.8	Hept/EtOH/TFA = 90/10/0.1
24	N-(1-Phenylethyl) phthalamic acid		3Me-P-CAP-DP	3.35	1.13	1.4	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.96	1.04	0.6	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.68	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	7.14	1.17	0.9	Hept/EtOH/TFA = 90/10/0.1

Table 6.1 *Continued*

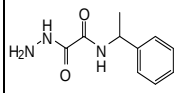
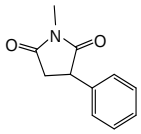
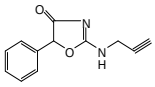
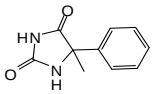
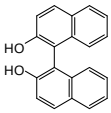
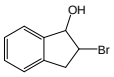
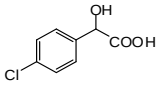
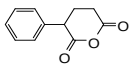
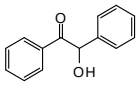
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
25	2-Hydrazinyl-2-oxo-N-(1-phenylethyl) acetamide		3Me-P-CAP-DP	3.05	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.14	1.03	0.5	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	5.89	1.12	1.2	Hept/EtOH/TFA = 90/10/0.1
26	Phensuximide		3Me-P-CAP-DP	2.14	1.17	2.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.46	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.04	1.05	1.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.04	1.11	1.9	Hept/EtOH/TFA = 90/10/0.1
27	5-Phenyl-2-(2-propynyl-amino)-2-oxazolin-4-one		3Me-P-CAP-DP	2.37	1.14	1.5	Hept/EtOH/TFA = 80/20/0.1
			P-CAP-DP	17.57	1.20	1.9	Hept/EtOH/TFA = 90/10/0.1
28	5-Methyl-5-phenyl hydantoin		3Me-P-CAP-DP	6.24	1.03	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.79	1.04	0.5	Hept/EtOH/TFA = 80/20/0.1
29	1,1'- Bi-2-naphthol		3Me-P-CAP-DP	1.67	1.13	1.6	Hept/EtOH/TFA = 80/20/0.1
			Cl-P-CAP-DP	4.46	1.04	0.8	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	6.57	1.09	0.9	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	7.32	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
30	*trans*-2-Bromo-1-indanol		3Me-P-CAP-DP	1.05	1.12	1.5	Hept/EtOH = 90/10
			Naph-P-CAP-DP	1.14	1.06	1.2	Hept/EtOH = 90/10
			P-CAP-DP	1.25	1.03	0.5	Hept/EtOH = 90/10
31	p-Chloromandelic acid		3Me-P-CAP-DP	2.99	1.02	0.5	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	3.54	1.04	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.93	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.46	1.15	1.7	Hept/EtOH/TFA = 90/10/0.1
32	2-Phenylglutaric anhydride		3Me-P-CAP-DP	2.69	1.06	1.1	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.50	1.02	0.6	Hept/EtOH/TFA = 90/10/0.1
33	Benzoin		3Me-P-CAP-DP	1.33	1.08	1.3	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.71	1.19	1.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.14	1.23	2.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.39	1.21	2.8	Hept/EtOH/TFA = 90/10/0.1

Table 6.1 *Continued*

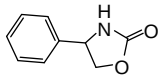
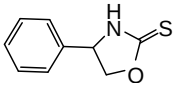
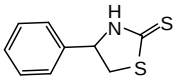
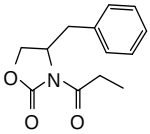
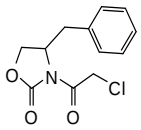
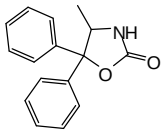
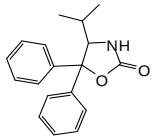
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
34	4-Phenyl-2-oxazolidinone		3Me-P-CAP-DP	4.07	1.05	0.8	Hept/EtOH = 90/10
			Cl-P-CAP-DP	6.00	1.08	0.8	Hept/EtOH = 90/10
			Naph-P-CAP-DP	5.54	1.05	0.7	Hept/EtOH = 90/10
			P-CAP-DP	10.82	1.04	0.7	Hept/EtOH = 90/10
35	4-Phenyloxazolidine-2-thione		3Me-P-CAP-DP	4.93	1.07	1.3	Hept/EtOH = 90/10
			Cl-P-CAP-DP	7.04	1.09	1.1	Hept/EtOH = 90/10
			Naph-P-CAP-DP	8.11	1.12	1.3	Hept/EtOH = 90/10
			P-CAP-DP	14.07	1.05	0.9	Hept/EtOH = 90/10
36	4-Phenylthiazolidine-2-thione		3Me-P-CAP-DP	6.58	1.06	1.3	Hept/EtOH = 90/10
			Cl-P-CAP-DP	4.86	1.10	1.2	Hept/EtOH = 90/10
			Naph-P-CAP-DP	6.71	1.12	1.2	Hept/EtOH = 90/10
			P-CAP-DP	10.18	1.04	0.8	Hept/EtOH = 90/10
37	4-Benzyl-3-propionyl-2-oxazolidinone		3Me-P-CAP-DP	1.13	1.03	0.5	Hept/EtOH = 90/10
			Cl-P-CAP-DP	1.25	1.03	0.6	Hept/EtOH = 90/10
			Naph-P-CAP-DP	1.57	1.02	0.7	Hept/EtOH = 90/10
			P-CAP-DP	1.43	1.03	0.5	Hept/EtOH = 90/10
38	4-Benzyl-3-chloroacetyl-2-oxazolidinone		3Me-P-CAP-DP	2.37	1.09	1.4	Hept/EtOH = 90/10
			Cl-P-CAP-DP	2.46	1.10	1.2	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.29	1.08	1.1	Hept/EtOH = 90/10
			P-CAP-DP	3.25	1.08	1.3	Hept/EtOH = 90/10
39	5,5-Diphenyl-4-methyl-2-oxazolidinone		3Me-P-CAP-DP	2.37	1.15	1.6	Hept/EtOH = 90/10
			Cl-P-CAP-DP	3.86	1.06	0.9	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.82	1.11	1.3	Hept/EtOH = 90/10
			P-CAP-DP	5.54	1.10	1.4	Hept/EtOH = 90/10
40	4-Isopropyl-5,5-diphenyl-2-oxazolidinone		3Me-P-CAP-DP	1.77	1.14	1.5	Hept/EtOH = 90/10
			Cl-P-CAP-DP	2.75	1.10	0.9	Hept/EtOH = 90/10
			P-CAP-DP	3.93	1.01	0.5	Hept/EtOH = 90/10

Table 6.1 *Continued*

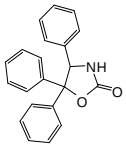
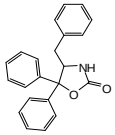
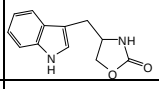
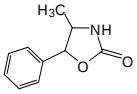
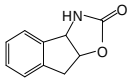
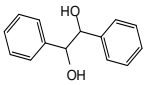
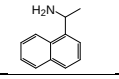
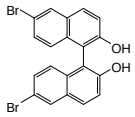
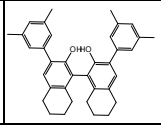
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
41	4,5,5-triphenyl-2-oxazolidinone		3Me-P-CAP-DP	2.77	1.02	0.5	Hept/EtOH = 90/10
			Naph-P-CAP-DP	4.29	1.03	0.7	Hept/EtOH = 90/10
			P-CAP-DP	6.46	1.04	0.8	Hept/EtOH = 90/10
42	5,5-Diphenyl-4-(phenylmethyl)-2-oxazolidinone		3Me-P-CAP-DP	2.09	1.19	1.7	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.36	1.10	0.9	Hept/EtOH = 90/10
			P-CAP-DP	5.46	1.13	1.4	Hept/EtOH = 90/10
43	4-(1H-Indol-3-ylmethyl)-2-oxazolidinone		3Me-P-CAP-DP	3.96	1.03	0.5	Hept/EtOH = 80/20
			Naph-P-CAP-DP	6.11	1.03	0.7	Hept/EtOH = 80/20
44	4-Methyl-5-phenyl-2-oxazolidinone		3Me-P-CAP-DP	10.41	1.03	0.5	Hept/EtOH = 90/10
			Cl-P-CAP-DP	4.93	1.03	0.7	Hept/EtOH = 90/10
			Naph-P-CAP-DP	4.50	1.06	0.7	Hept/EtOH = 90/10
			P-CAP-DP	7.43	1.07	1.3	Hept/EtOH = 90/10
45	(3aS-cis)-3,3a,8,8a-Tetrahydro-2H-indeno[1,2-d]oxazol-2-one		3Me-P-CAP-DP	4.71	1.05	0.7	Hept/EtOH = 90/10
			Cl-P-CAP-DP	7.75	1.09	0.7	Hept/EtOH = 90/10
46	Hydrobenzoin		3Me-P-CAP-DP	1.70	1.03	0.6	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.18	1.21	2.6	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.86	1.04	0.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.21	1.11	1.4	Hept/EtOH/TFA = 90/10/0.1
47	1-(1-Naphthyl) ethylamine		3Me-P-CAP-DP	12.59	1.04	0.5	Hept/EtOH = 90/10
48	6,6-Dibromo-1,1'-bi-2-naphthol		3Me-P-CAP-DP	7.93	1.03	0.7	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.93	1.09	1.1	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.93	1.17	1.3	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	8.50	1.08	1.2	Hept/EtOH/TFA = 90/10/0.1
49	3,3′-Bis(3,5-dimethylphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol		3Me-P-CAP-DP	0.26	1.29	1.5	Hept/EtOH/TFA = 80/20/0.1

Table 6.1 *Continued*

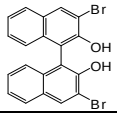
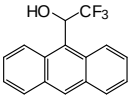
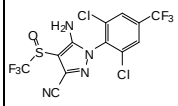
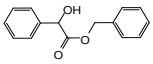
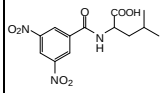
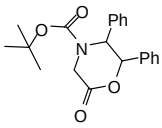
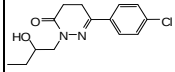
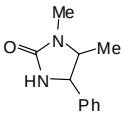
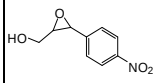
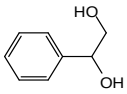
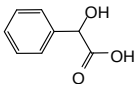
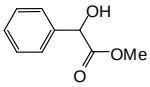
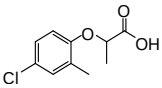
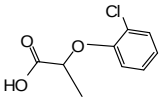
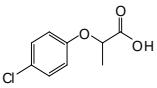
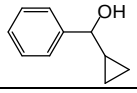
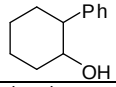
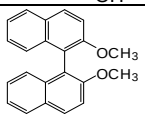
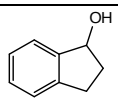
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
50	3,3′-Dibromo-1,1′-bi-2-naphthol		3Me-P-CAP-DP	2.63	1.11	1.1	Hept/EtOH/TFA = 80/20/0.1
			P-CAP-DP	6.18	1.39	2.6	Hept/EtOH/TFA = 90/10/0.1
51	1-(9-Anthryl)-2,2,2-trifluoroethanol		3Me-P-CAP-DP	3.04	1.06	1.1	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.75	1.02	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.04	1.09	1.3	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.07	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
52	Fipronil		3Me-P-CAP-DP	1.55	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.86	1.06	1.1	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.50	1.05	0.7	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.38	1.18	1.5	Hept/EtOH/TFA = 90/10/0.1
53	Benzyl Mandelate		3Me-P-CAP-DP	1.23	1.04	0.7	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.58	1.17	1.8	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.82	1.17	1.9	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.12	1.17	1.8	Hept/EtOH/TFA = 90/10/0.1
54	N-(3,5-dinitrobenzoyl)-DL-leucine		3Me-P-CAP-DP	7.04	2.04	5.0	Hept/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	5.25	1.03	0.7	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	8.54	1.13	1.0	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	8.55	1.39	4.0	Hept/EtOH/TFA = 90/10/0.1
55	*tert*-Butyl-6-oxo-2,3-diphenyl-4-morpholinecarboxylate		Cl-P-CAP-DP	1.11	1.16	1.3	Hept/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.25	1.03	0.6	Hept/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.25	1.23	1.4	Hept/EtOH/TFA = 90/10/0.1
56	6-(4-Chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone		Cl-P-CAP-DP	2.64	1.09	1.3	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.75	1.06	1.2	Hept/EtOH = 90/10
			P-CAP-DP	3.50	1.09	1.4	Hept/EtOH = 90/10
57	1,5-Dimethyl-4-phenyl-2-imidazolidinone		Cl-P-CAP-DP	2.86	1.14	1.6	Hept/EtOH = 90/10
			Naph-P-CAP-DP	3.07	1.02	0.6	Hept/EtOH = 90/10
			P-CAP-DP	4.89	1.12	1.8	Hept/EtOH = 90/10

Table 6.1 *Continued*

#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
58	*trans*-2,3-Epoxy-3-(*p*-nitrophenyl)-1-propanol		Cl-P-CAP-DP Naph-P-CAP-DP	4.64 6.11	1.02 1.05	0.5 0.6	Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1
59	1-Phenyl-1,2-ethanediol		Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	2.79 3.32 3.96	1.06 1.04 1.14	1.0 0.9 2.5	Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1
60	Mandelic acid		Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	4.18 3.78 7.19	1.06 1.10 1.10	0.7 1.0 1.3	Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1
61	Methyl mandelate		Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	1.63 1.71 2.14	1.15 1.16 1.20	1.9 2.1 2.3	Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1
62	2-(4-Chloro-2-methyl phenoxy)propionic acid		Naph-P-CAP-DP	0.96	1.04	1.1	Hept/EtOH/TFA = 90/10/0.1
63	2-(2-chlorophenoxy) propionic acid		Naph-P-CAP-DP	1.21	1.04	0.8	Hept/EtOH/TFA = 90/10/0.1
64	2-(4-chlorophenoxy) propionic acid		Naph-P-CAP-DP	1.10	1.04	0.7	Hept/EtOH/TFA = 90/10/0.1
65	2-cyclopropylbenzyl alcohol		Naph-P-CAP-DP	0.86	1.04	0.5	Hept/EtOH = 90/10
66	trans-2-Phenyl-1-cyclohexanol		Naph-P-CAP-DP	0.61	1.06	0.6	Hept/EtOH/TFA = 90/10/0.1
67	2,2′-Dimethoxy-1,1′-binaphthalene		Naph-P-CAP-DP P-CAP-DP	1.93 1.07	1.02 1.03	0.5 0.5	Hept/EtOH/TFA = 90/10/0.1 Hept/EtOH/TFA = 90/10/0.1
68	Indanol		P-CAP-DP	1.07	0.03	0.5	Hept/EtOH = 90/10

[a] HEP: n-heptane, EtOH: ethanol, TFA: trifluoroacetic acid

Table 6.2 Retention factor for the first peak (k_1), enantioselectivity (α) and enantioresolution (Rs) of separated racemates on 3Me-P-CAP-DP, Cl-P-CAP-DP, Naph-P-CAP-DP and P-CAP-DP columns in SFC.

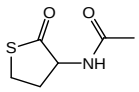
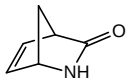
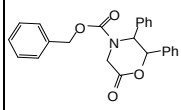
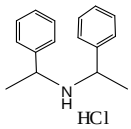
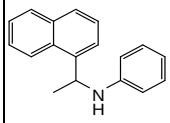
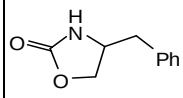
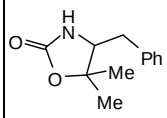
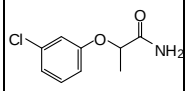
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
1	DL-N-Acetylhomocysteine thiolactone		3Me-P-CAP-DP	4.78	1.08	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	6.09	1.10	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	5.78	1.08	1.4	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	6.09	1.13	1.4	CO_2/EtOH/TFA = 90/10/0.1
3	2-Azabicyclo[2.2.1]-hept-5-en-3-one		3Me-P-CAP-DP	1.74	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.44	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
5	Benzyl-6-oxo-2,3-diphenyl-4-morpholine carboxylate		3Me-P-CAP-DP	2.78	1.15	1.7	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	3.95	1.02	0.7	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	5.51	1.19	1.5	CO_2/MeOH/TFA = 90/10/0.1
			P-CAP-DP	5.29	1.09	1.4	CO_2/EtOH/TFA = 90/10/0.1
6	Bis(1-phenyl ethyl)amine hydrochloride		Cl-P-CAP-DP	4.34	0.23	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.56	1.17	1.4	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	5.21	1.21	1.2	CO_2/EtOH/TFA = 90/10/0.1
7	N-Benzyl-1-(1-naphthyl)ethyl amine		3Me-P-CAP-DP	5.44	1.05	0.9	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	10.74	1.13	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	8.85	1.10	1.1	CO_2/EtOH/TFA = 90/10/0.1
8	4-Benzyl-2-oxazolidinone		Cl-P-CAP-DP	4.98	1.08	0.9	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.46	1.01	0.5	CO_2/EtOH/TFA = 90/10/0.1
9	4-Benzyl-5, 5-dimethyl-2-oxazolidinone		3Me-P-CAP-DP	1.49	1.03	0.5	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.53	1.08	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.23	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1
10	2-(3-Chlorophenoxy) propionamide		3Me-P-CAP-DP	2.10	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.61	1.06	1.1	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	2.74	1.04	1.0	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.03	1.08	1.3	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

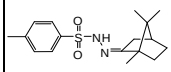
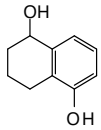
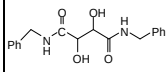
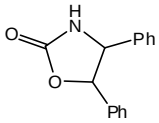
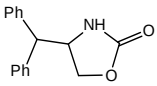
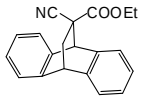
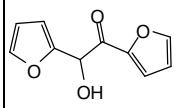
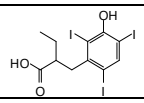
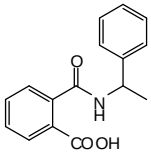
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
11	Camphor p-tosyl hydrazon		3Me-P-CAP-DP	2.30	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.42	1.04	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.94	1.06	0.9	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	6.00	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1
12	1,5-Dihydroxy-1,2,3,4-tetrahydronaphthalene		3Me-P-CAP-DP	6.38	1.14	2.0	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	9.35	1.07	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.97	1.13	2.0	CO_2/MeOH/TFA = 90/10/0.1
			P-CAP-DP	13.11	1.10	1.7	CO_2/EtOH/TFA = 90/10/0.1
14	*N,N'*-Dibenzyl-tartramide		3Me-P-CAP-DP	4.74	1.08	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	6.87	1.25	1.9	CO_2/MeOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	8.65	1.18	2.5	CO_2/MeOH/TFA = 90/10/0.1
15	*cis*-4,5-Diphenyl-2-oxazolidinone		3Me-P-CAP-DP	4.17	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	7.03	1.03	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	6.90	1.06	0.8	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	10.54	1.07	1.2	CO_2/EtOH/TFA = 90/10/0.1
16	4-(Diphenylmethyl)-2-oxazolidinone		Cl-P-CAP-DP	6.09	1.18	1.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	6.45	1.09	1.3	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	9.21	1.07	1.1	CO_2/EtOH/TFA = 90/10/0.1
18	Ethyl 11-cyano-9,10-dihydro-endo-9,10-ethano anthracene-11-carboxylate		3Me-P-CAP-DP	0.91	1.07	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.48	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1
20	Furoin		Cl-P-CAP-DP	1.42	1.13	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.58	1.17	1.7	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.95	1.28	2.5	CO_2/EtOH/TFA = 90/10/0.1
21	Iophenoxic acid		Cl-P-CAP-DP	23.50	1.01	0.5	CO_2/EtOH/TFA = 90/10/0.1
22	N-(α-Methylbenzyl) phthalic acid monoamide		3Me-P-CAP-DP	4.07	1.10	1.5	CO_2/MeOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	6.70	1.02	0.7	CO_2/MeOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.18	1.05	0.8	CO_2/MeOH/TFA = 90/10/0.1
			P-CAP-DP	14.79	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

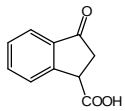
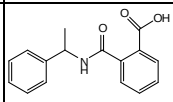
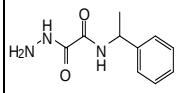
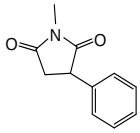
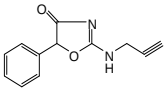
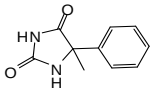
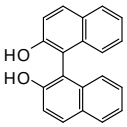
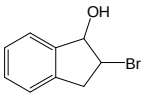
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
23	3-Oxo-1-indancarboxylic acid		3Me-P-CAP-DP	2.23	1.06	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	2.82	1.06	1.2	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.05	1.08	1.3	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.73	1.05	1.1	CO_2/EtOH/TFA = 90/10/0.1
24	N-(1-Phenylethyl) phthalamic acid		3Me-P-CAP-DP	5.35	1.13	1.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	10.53	1.04	0.7	CO_2/EtOH/TFA = 90/10/0.1
25	2-Hydrazinyl-2-oxo-N-(1-phenylethyl) acetamide		Cl-P-CAP-DP	5.11	1.10	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	6.31	1.12	1.2	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	7.23	1.11	1.1	CO_2/EtOH/TFA = 90/10/0.1
26	Phensuximide		3Me-P-CAP-DP	0.84	1.08	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	0.89	1.06	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.06	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	0.99	1.09	1.2	CO_2/EtOH/TFA = 90/10/0.1
27	5-Phenyl-2-(2-propynyl-amino)-2-oxazolin-4-one		3Me-P-CAP-DP	5.91	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	10.94	1.01	0.5	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	13.09	1.09	1.3	CO_2/EtOH/TFA = 90/10/0.1
28	5-Methyl-5-phenyl hydantoin		3Me-P-CAP-DP	4.77	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	6.88	1.12	1.3	CO_2/MeOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	9.67	1.08	1.0	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	20.13	1.14	1.2	CO_2/EtOH/TFA = 90/10/0.1
29	1,1'- Bi-2-naphthol		3Me-P-CAP-DP	8.63	1.12	1.7	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	12.12	1.05	1.0	CO_2/MeOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	22.87	1.07	0.8	CO_2/MeOH/TFA = 90/10/0.1
			P-CAP-DP	25.25	1.05	1.2	CO_2/EtOH/TFA = 90/10/0.1
30	*trans*-2-bromo-1-indanol		3Me-P-CAP-DP	1.60	1.11	1.5	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.68	1.03	0.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.85	1.08	1.2	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.16	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

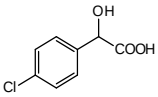
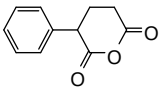
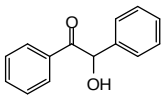
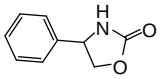
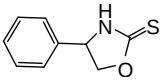
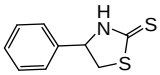
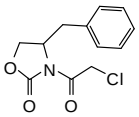
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
31	p-Chloromandelic acid		Cl-P-CAP-DP	0.88	1.11	1.2	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	0.99	1.12	1.4	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.11	1.14	1.4	CO_2/EtOH/TFA = 90/10/0.1
32	2-Phenylglutaric anhydride		3Me-P-CAP-DP	1.07	1.10	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.63	1.05	0.5	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.86	1.06	0.7	CO_2/EtOH/TFA = 90/10/0.1
33	Benzoin		3Me-P-CAP-DP	1.19	1.05	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.51	1.17	1.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.91	1.20	1.8	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	2.06	1.18	1.8	CO_2/EtOH/TFA = 90/10/0.1
34	4-Phenyl-2-oxazolidinone		3Me-P-CAP-DP	2.62	1.04	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	4.46	1.09	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.89	1.04	0.7	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	6.46	1.07	0.9	CO_2/EtOH/TFA = 90/10/0.1
35	4-Phenyloxazolidine-2-thione		3Me-P-CAP-DP	3.66	1.07	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	6.53	1.12	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.15	1.15	1.3	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	11.38	1.08	1.0	CO_2/EtOH/TFA = 90/10/0.1
36	4-Phenylthiazolidine-2-thione		3Me-P-CAP-DP	4.83	1.08	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	7.81	1.10	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	10.76	1.19	1.3	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	13.72	1.06	1.1	CO_2/EtOH/TFA = 90/10/0.1
38	4-Benzyl-3-chloroacetyl-2-oxazolidinone		3Me-P-CAP-DP	1.27	1.05	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.28	1.04	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.61	1.05	1.0	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.56	1.06	1.0	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

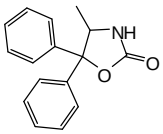
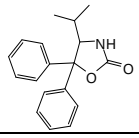
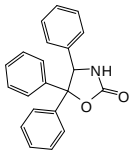
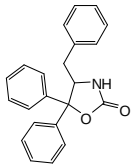
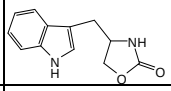
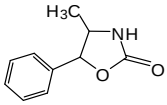
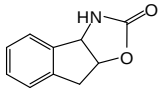
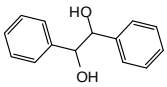
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
39	5,5-Diphenyl-4-methyl-2-oxazolidinone		3Me-P-CAP-DP	3.63	1.10	1.6	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	7.36	1.03	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.03	1.10	1.3	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	9.93	1.10	1.4	CO_2/EtOH/TFA = 90/10/0.1
40	4-Isopropyl-5,5-diphenyl-2-oxazolidinone		3Me-P-CAP-DP	3.00	1.09	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	5.73	1.13	1.3	CO_2/EtOH/TFA = 90/10/0.1
41	4,5,5-Triphenyl-2-oxazolidinone		3Me-P-CAP-DP	5.11	1.06	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	8.95	1.02	0.7	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	9.73	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	13.59	1.04	1.3	CO_2/EtOH/TFA = 90/10/0.1
42	5,5-Diphenyl-4-(phenylmethyl)-2-oxazolidinone		3Me-P-CAP-DP	3.69	1.09	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	7.14	1.03	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.82	1.07	1.1	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	10.85	1.12	1.3	CO_2/EtOH/TFA = 90/10/0.1
43	4-(1H-Indol-3-ylmethyl)-2-oxazolidinone		Cl-P-CAP-DP	20.28	1.10	1.3	CO_2/MeOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	21.94	1.03	0.7	CO_2/MeOH/TFA = 90/10/0.1
44	4-Methyl-5-phenyl-2-oxazolidinone		3Me-P-CAP-DP	2.88	1.04	0.7	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.57	1.02	0.7	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	6.47	1.09	1.3	CO_2/EtOH/TFA = 90/10/0.1
45	(3aS-cis)-3,3a,8,8a-Tetrahydro-2H-indeno[1,2-d]oxazol-2-one		3Me-P-CAP-DP	4.70	1.04	1.1	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	9.83	1.08	1.2	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	7.98	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	13.03	1.15	1.5	CO_2/EtOH/TFA = 90/10/0.1
46	Hydrobenzoin		3Me-P-CAP-DP	2.74	1.04	1.2	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	3.84	1.23	2.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	5.05	1.04	0.9	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	5.17	1.10	1.4	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

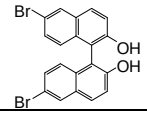
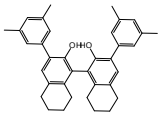
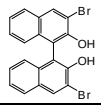
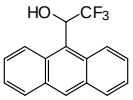
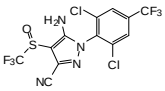
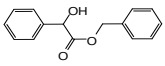
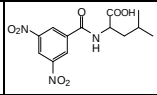
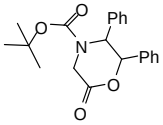
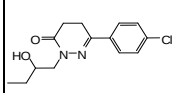
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
48	6,6-Dibromo-1,1'-bi-2-naphthol		3Me-P-CAP-DP	17.50	1.08	1.6	CO_2/MeOH/TFA = 90/10/0.1
49	3,3′-Bis(3,5-dimethylphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol		3Me-P-CAP-DP Cl-P-CAP-DP	5.31 12.40	1.12 1.25	1.6 1.3	CO_2/EtOH/TFA = 90/10/0.1 CO_2/MeOH/TFA = 90/10/0.1
50	3,3′-Dibromo-1,1′-bi-2-naphthol		3Me-P-CAP-DP Naph-P-CAP-DP	6.69 42.75	3.65 1.15	5.0 0.9	CO_2/MeOH/TFA = 90/10/0.1 CO_2/MeOH/TFA = 90/10/0.1
51	1-(9-Anthryl)-2,2,2-trifluoroethanol		3Me-P-CAP-DP Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	4.17 4.59 5.59 5.69	1.09 1.05 1.14 1.08	1.6 1.1 1.8 1.4	CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1
52	Fipronil		Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	1.50 1.24 1.64	1.03 1.02 1.19	0.5 0.5 1.4	CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1
53	Benzyl mandelate		3Me-P-CAP-DP Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	1.31 1.67 2.04 2.16	1.02 1.14 1.15 1.15	0.5 1.4 1.9 1.7	CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1
54	N-(3,5-Dinitrobenzoyl)-DL-leucine		P-CAP-DP	11.93	1.35	4.0	CO_2/EtOH/TFA = 90/10/0.1
55	*tert*-Butyl-6- oxo-2,3-diphenyl-4-morpholinecarboxylate		3Me-P-CAP-DP Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	1.29 1.71 1.84 1.96	1.09 1.06 1.21 1.12	1.3 1.1 1.5 1.3	CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1
56	6-(4-Chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone		Cl-P-CAP-DP Naph-P-CAP-DP P-CAP-DP	4.39 6.26 4.58	1.07 1.04 1.07	1.2 1.2 1.3	CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1 CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

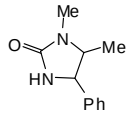
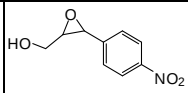
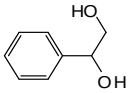
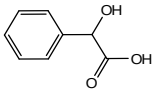
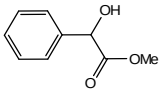
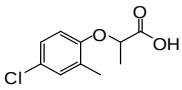
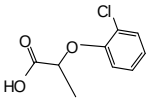
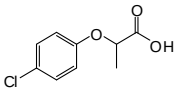
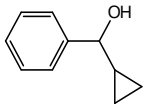
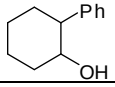
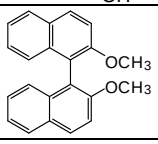
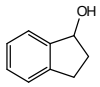
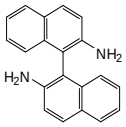
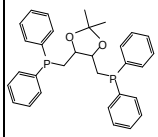
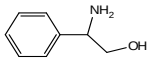
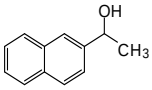
#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
57	1,5-Dimethyl-4-phenyl-2-imidazolidinone		Cl-P-CAP-DP	3.51	1.12	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.68	1.01	0.5	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	4.33	1.10	1.4	CO_2/EtOH/TFA = 90/10/0.1
58	*trans*-2,3-Epoxy-3-(*p*-nitrophenyl)-1-propanol		Cl-P-CAP-DP	3.67	1.02	0.8	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	4.69	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
59	1-Phenyl-1,2-ethanediol		Cl-P-CAP-DP	3.29	1.06	1.1	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	3.74	1.05	1.2	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	3.96	1.08	1.4	CO_2/EtOH/TFA = 90/10/0.1
60	Mandelic acid		Naph-P-CAP-DP	4.11	1.05	0.8	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	6.69	1.07	1.1	CO_2/EtOH/TFA = 90/10/0.1
61	Methyl mandelate		Cl-P-CAP-DP	0.87	1.12	1.3	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	0.94	1.15	1.4	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.09	1.16	1.4	CO_2/EtOH/TFA = 90/10/0.1
62	2-(4-Chloro-2-methyl-phenoxy)propionic acid		Naph-P-CAP-DP	1.48	1.06	1.2	CO_2/EtOH/TFA = 90/10/0.1
63	2(2-Chlorophenoxy) propionic acid		Naph-P-CAP-DP	1.76	1.04	0.9	CO_2/EtOH/TFA = 90/10/0.1
64	2-(4-Chlorophenoxy) propionic acid		Naph-P-CAP-DP	1.52	1.04	0.8	CO_2/EtOH/TFA = 90/10/0.1
65	2-Cyclopropylbenzyl alcohol		3Me-P-CAP-DP	1.03	1.02	0.5	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.01	1.05	0.5	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.14	1.03	0.5	CO_2/EtOH/TFA = 90/10/0.1
66	*trans*-2-Phenyl-1-cyclohexanol		Naph-P-CAP-DP	0.93	1.05	0.8	CO_2/EtOH/TFA = 90/10/0.1
67	2,2′-Dimethoxy-1,1′-binaphthalene		Naph-P-CAP-DP	9.90	1.03	0.7	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	5.39	1.03	0.9	CO_2/EtOH/TFA = 90/10/0.1

Table 6.2 *Continued*

#	Compound	Structure	CSP	k_1	α	Rs	Mobile Phase (v/v)[a]
68	Indanol		3Me-P-CAP-DP	0.93	1.26	2.0	CO_2/EtOH/TFA = 90/10/0.1
			Cl-P-CAP-DP	1.05	1.27	1.6	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.38	1.03	0.6	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	1.08	1.51	2.0	CO_2/EtOH/TFA = 90/10/0.1
69	2,2'-Diamino-1,1'-binaphthalene		3Me-P-CAP-DP	9.93	1.04	1.0	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	22.13	1.03	0.6	CO_2/EtOH/TFA = 90/10/0.1
			P-CAP-DP	15.88	1.08	1.6	CO_2/EtOH/TFA = 90/10/0.1
70	2,3-O-Isopropylidene 2,3-dihydroxy-1,4-bis(disphenylphosphino) butane		3Me-P-CAP-DP	6.66	2.51	4.0	CO_2/MeOH/TFA = 90/10/0.1
71	2-Phenylglycinol		3Me-P-CAP-DP	1.04	1.13	1.4	CO_2/EtOH/TFA = 90/10/0.1
			Naph-P-CAP-DP	1.34	1.32	2.2	CO_2/EtOH/TFA = 90/10/0.1
72	α-Methyl-2-naphthalenemethanol		Naph-P-CAP-DP	2.44	1.02	0.6	CO_2/EtOH/TFA = 90/10/0.1

[a] EtOH: ethanol, MeOH: methanol, TFA: trifluoroacetic acid

6.4.5 SFC vs. HPLC

Some compounds (69, 70, 71, and 72) were separated with SFC that could not be separated at all in HPLC. The opposite was true for compounds 2, 4, 13, 17, 19, 37 and 47 which were only separated by HPLC. No analyte structural features could be identified that would explain these results. In total (for SFC and HPLC) 72 out of 100 compounds tested were separated on at least one of these polymeric CSPs. Among these are oxazolidinones which are a new class of antibiotics and their sulfur analogues (thiazolidinones) that were well separated by these polymeric CSPs in both

the HPLC mode as well as SFC. Another notable feature is the resolution of atropisomers. Compounds with axial chirality that were separated by these phases include 29, 48, 49, 50, 67 and 69. The enantioresolution, peak efficiency, or retention did not decrease after about 5 months of continuous use which include changes in mobile phases and separation modes. This indicates that these covalently bound phases show good stability and very low degradability.

6.5 Conclusions

Three new polymeric chiral stationary phases were synthesized based on *N,N'*-[(1*S,*2*S*)-1,2-bis(2,4,6-trimethylphenyl)ethylene]bis-2-propenamide, *N,N'*-[(1*S,*2*S*)-1,2-bis(2-chlorophenyl)ethylene]bis-2-propenamide, and *N,N'*-[(1*S*,2*S*)-1,2-di-1-naphthy lethylene]bis-2-propenamide via a solution-based free radical initiated polymerization. The Naph-P-CAP-DP column showed the broadest selectivity among the 4 columns by separating the most analytes under almost identical conditions. This could be due to the added π-π interactions introduced by the naphthyl ring system, and/or to its enhanced rigidity or steric interactions. The 3Me-P-CAP-DP column also performed better than the commercial column in HPLC and showed greater number of baseline separations in SFC. The Cl-P-CAP-DP column showed moderate selectivities in both HPLC and SFC but had different selectivities compared to the other columns. Altogether 72 racemates were separated with 37 baseline separations. A virtue of these new chiral phases seems to be the faster separation capability compared to the commercial column. All tested columns demonstrated good sample loading capacities and had very good chemical and physical stability.

CHAPTER 7

GENERAL CONCLUSIONS

7.1 Chapters 2-4

A thorough knowledge of the physical and chemical properties of ionic liquids has become a necessity due to their extensive usage in the fields of science and technology. In this work a number of structurally related ionic liquids have been synthesized and their properties characterized. It was shown that by manipulating the symmetry, cation, and anion of geminal dicationic ionic liquids; the melting point, which is the most important property of an IL, can be altered considerably. Cations with high charge density such as trialkylammonium/ phosphonium gives high melting ILs while charge delocalized cations such as imidazolium yields room temperature ionic liquids. With high charge density cations, the asymmetry of the cationic segment obtained by substituting different cationic moieties further lowers the melting point. The thermal stability of dicationic ILs was found to be superior to that of traditional monocationic ILs which in itself will broaden the horizon of multicationic ionic liquid applications.

Trigonal tricationic ILs (TTILs) with three identical cationic moieties attached to a central core showed much higher melting points than the dicationic ILs. This was attributed to the rigid core structure that forces positive charges to be in relatively close proximity and the inherent symmetry of the cationic segment that facilitates better packing. However with a more flexible tri(2-hexanamido)ethylamine core, low melting and highly viscous ILs were obtained. These also showed high thermal stabilities com-

-parable to those observed for dicationic ILs. For the same cationic moieties, by changing the rigid trigonal geometry to a flexible linear geometry, a drastic change in melting points is achieved. Linear tricationic ILs (LTILs) showed much lower melting points much like the imidazolium based dicationic ILs. Viscosities of LTILs were lower than TTILs but higher than dicationic ILs. Thermal stabilities were also comparable to those of dicationic ILs.

7.2 Chapter 5

Because of their unique characteristics such as high thermal stability, ability to form multiple solvation interactions, and higher viscosity compared to other organic solvents, ILs have been shown to be useful as gas chromatographic stationary phases (SPs). The selectivity and retention in IL- GC depends on the chemical composition of the IL. It was shown that trigonal tricationic ILs yield highly polar SPs compared to other forms of ILs. Comparison with highly polar commercial SPs demonstrated the superior performance of tri(2-hexanamido)ethylamine core IL series in terms of peak shapes of polar analytes and separation efficiency. These were the first ILs containing bis(trifluoromethanesulfonyl)imide anion (NTf_2^-) to eliminate peak tailing for polar H-bonding analytes.

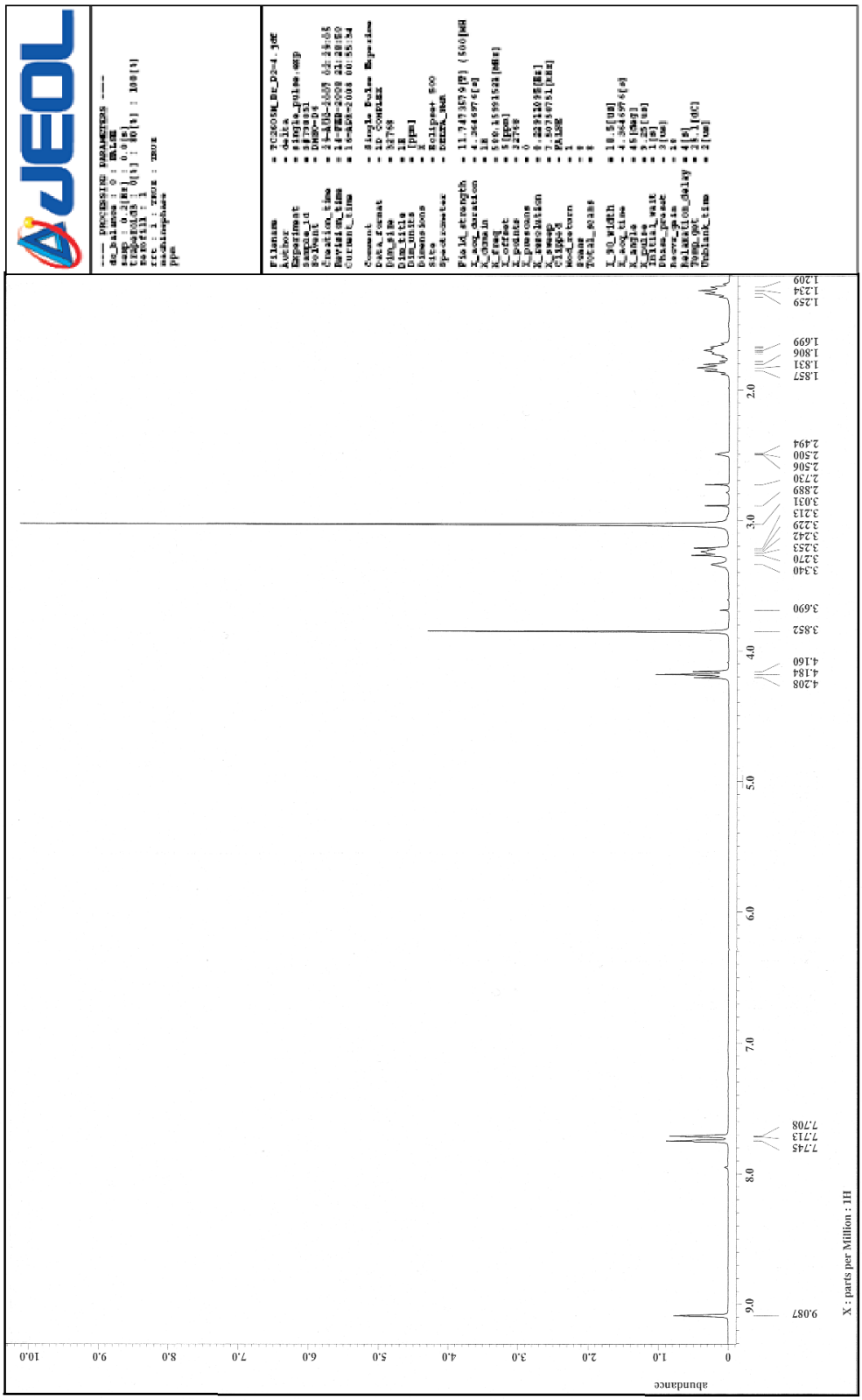
7.3 Chapter 6

Because of the regulations imposed in pharmaceutical and biotechnological fields it is increasingly important to produce enantiopure substances. Three new chiral polymers have been synthesized and their chiral recognition capabilities as stationary phases in HPLC and SFC are evaluated. In both chromatographic techniques, Naph-P-CAP-DP column showed the best enantioselectivity towards the target chiral analytes.

Faster and better separations were obtained on these new columns compared to the analogous commercial column P-CAP-DP. Also these columns showed good sample loading capabilities that can be useful in preparative scale applications.

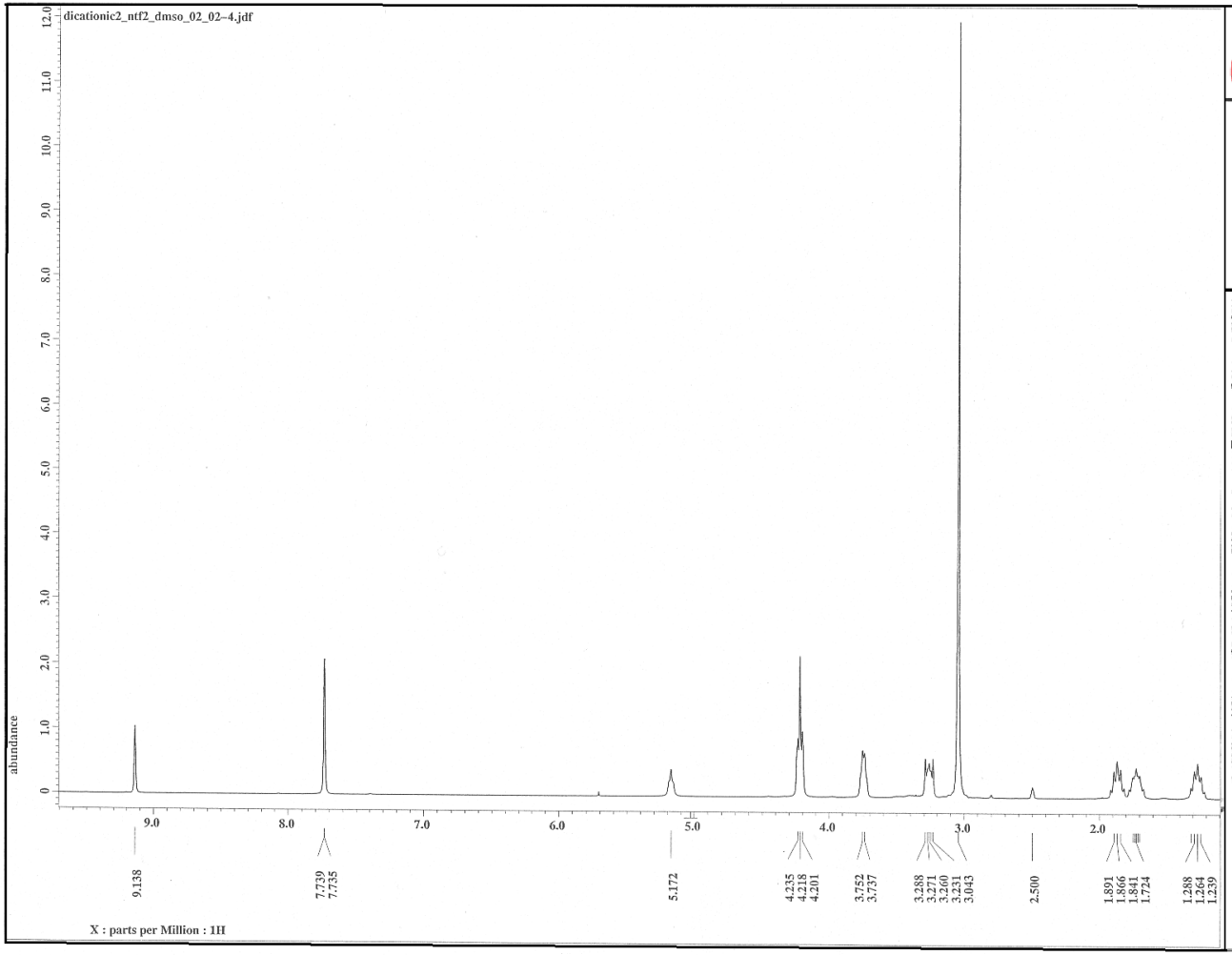
APPENDIX 1

^{1}H NMR SPECTRA OF
IL1: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-3-METHYLIMIDAZOLIUM
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]


JEOL
abundance
X : parts per Million : 1H
9.087
7.745
7.713
7.708
4.208
4.184
4.160
3.852
3.690
3.340
3.270
3.253
3.242
3.229
3.213
3.031
2.889
2.730
2.506
2.500
2.494
1.857
1.831
1.806
1.699
1.259
1.234
1.209

APPENDIX 2

^{1}H NMR SPECTRA OF
IL2: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-3-(2-HYDROXYETHYL)IMIDAZOLIUM DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]



JEOL

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machinephase
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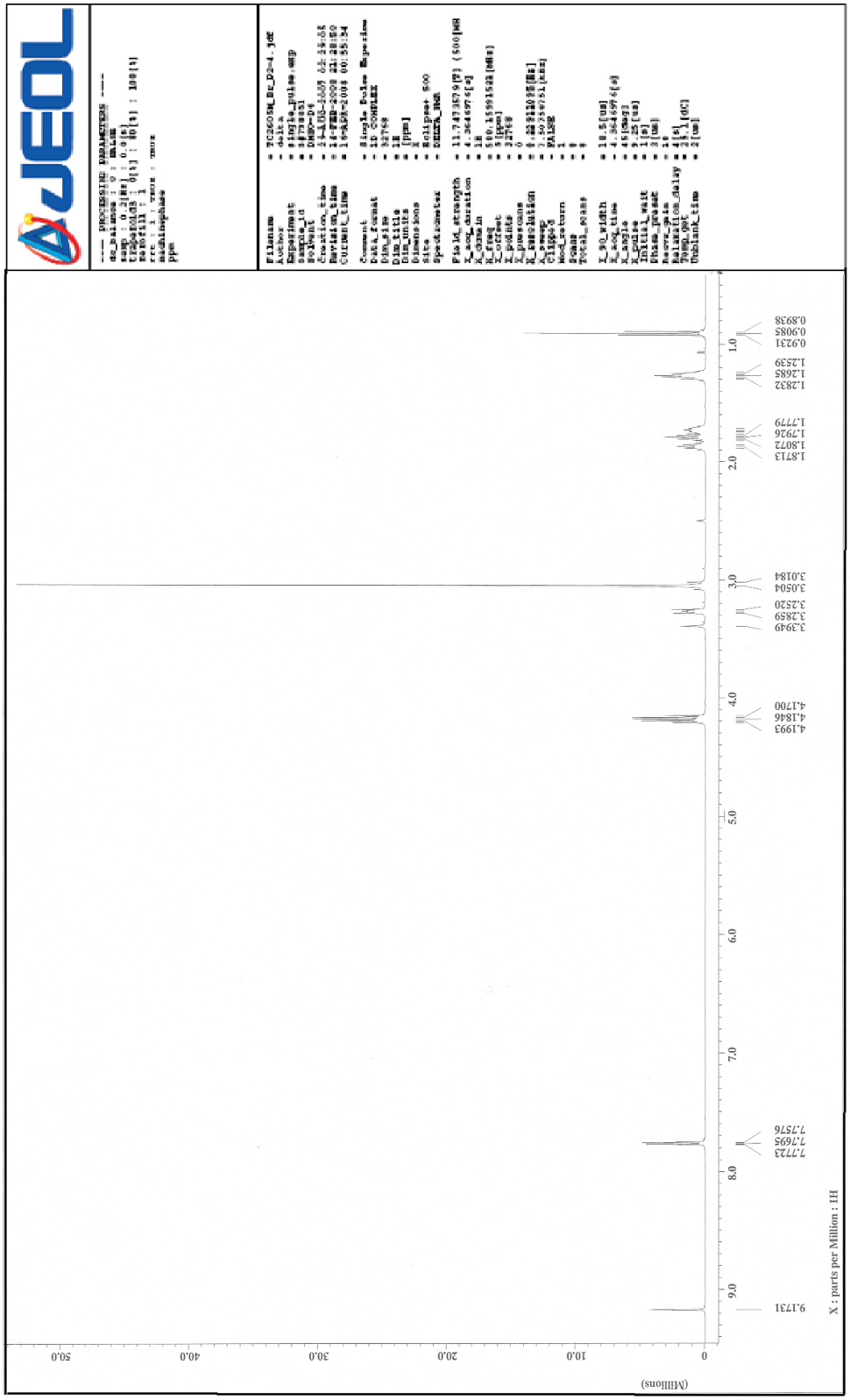
APPENDIX 3

^{1}H NMR SPECTRA OF
IL3: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-3-BUTYLIMIDAZOLIUM
DI[BIS(TRIFLUORO- METHANESULFONYL)IMIDE]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Author
Experiment
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solvent
Creation_time
Modification_time
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Data_Format
Dim_size
Dim_title
Dim_units
Dimensions
Site
Spectrometer
Field_strength
X_acq_duration
X_domain
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X_offset
X_points
X_pulse
X_sweep
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Acquisition
Mod_pattern
Scans
Total_scans
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X_acq_time
X_delay
X_points
Initial_wait
Phase_preset
Recvr_gain
Relaxation_delay
Temperature
Unblank_time
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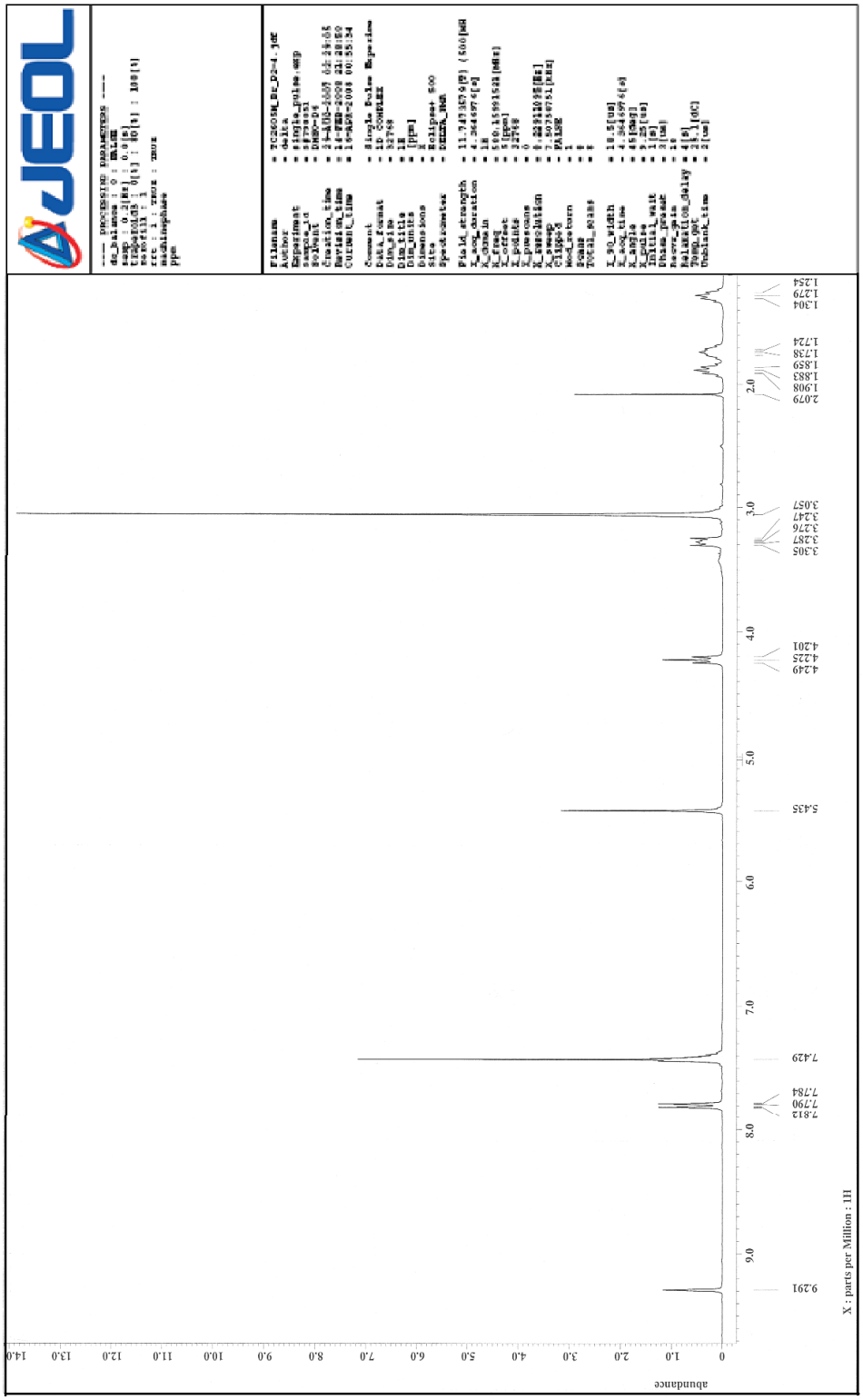
7.7695
7.7576
4.1993
4.1846
4.1700
3.3949
3.2859
3.2520
3.0504
3.0184
1.8713
1.8072
1.7926
1.7779
1.2832
1.2685
1.2539
0.9231
0.9085
0.8938
X : parts per Million : 1H
(Millions)

APPENDIX 4

^{1}H NMR SPECTRA OF
IL4: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-3-BENZYLIMIDAZOLIUM
DI[BIS(TRIFLUOROMETHANE- SULFONYL)IMIDE]


JEOL
X : parts per Million : 1H
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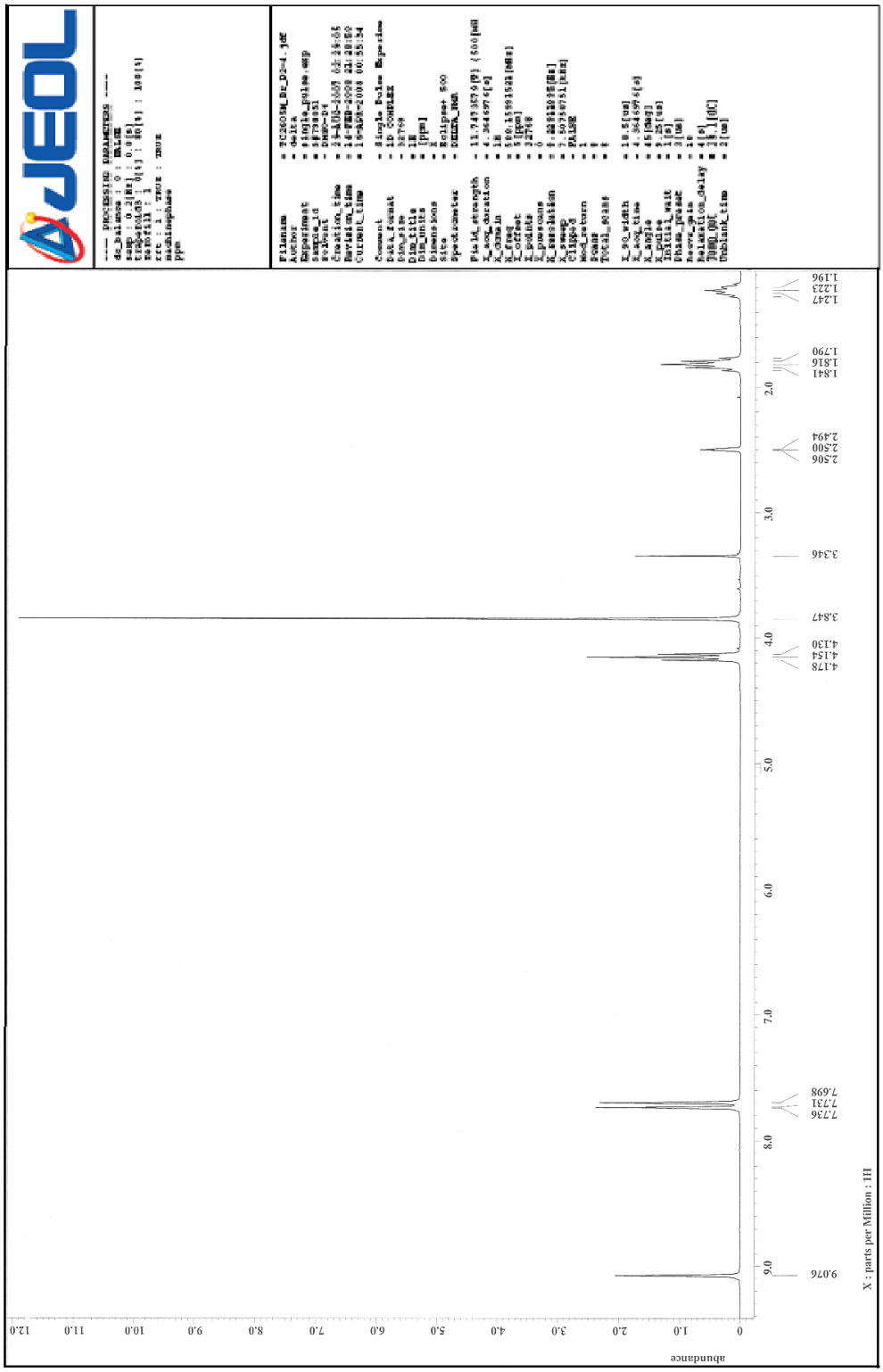
7.784
7.429
5.435
4.249
4.225
4.201
3.305
3.287
3.276
3.247
3.057
2.079
1.908
1.883
1.859
1.738
1.724
1.304
1.279
1.254

APPENDIX 5

^{1}H NMR SPECTRA OF
IL5: 1,1'-(PENTANE-1,5-DIYL)-BIS(3-METHYLIMIDAZOLIUM)
DI[BIS(TRIFLUOROMETHANE- SULFONYL)IMIDE]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Unblank_time : 2[us]
abundance
X : parts per Million : 1H
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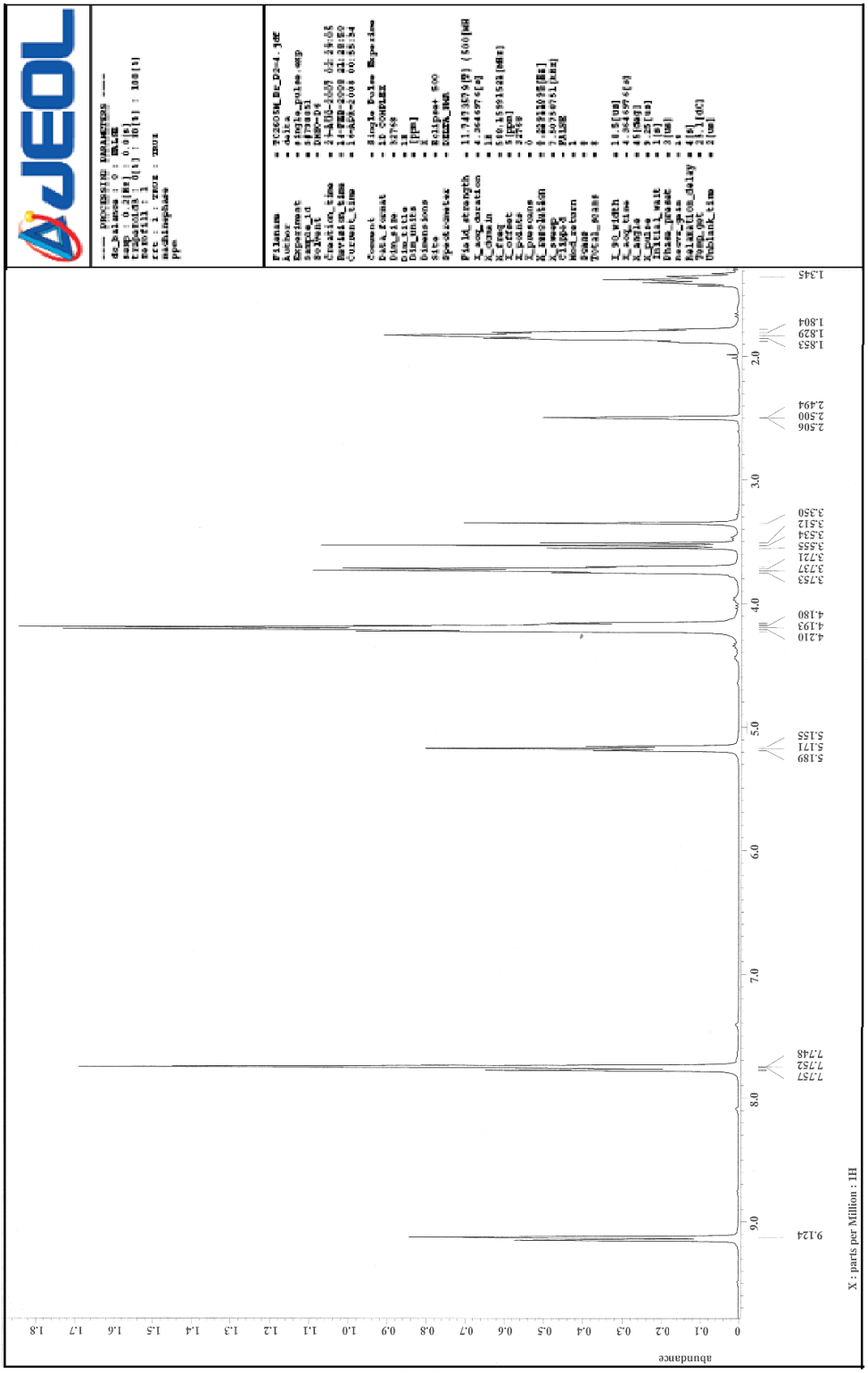
7.731
7.698
4.178
4.154
4.130
3.847
3.346
2.506
2.500
2.494
1.841
1.816
1.790
1.247
1.223
1.196

APPENDIX 6

^{1}H NMR SPECTRA OF
IL6: 1,1'-(PENTANE-1,5-DIYL)-BIS[3-(2-HYDROXYETHYL) IMIDAZOLIUM]
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]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Temp_get = 23.0[dC]
Dummy = 2[us]
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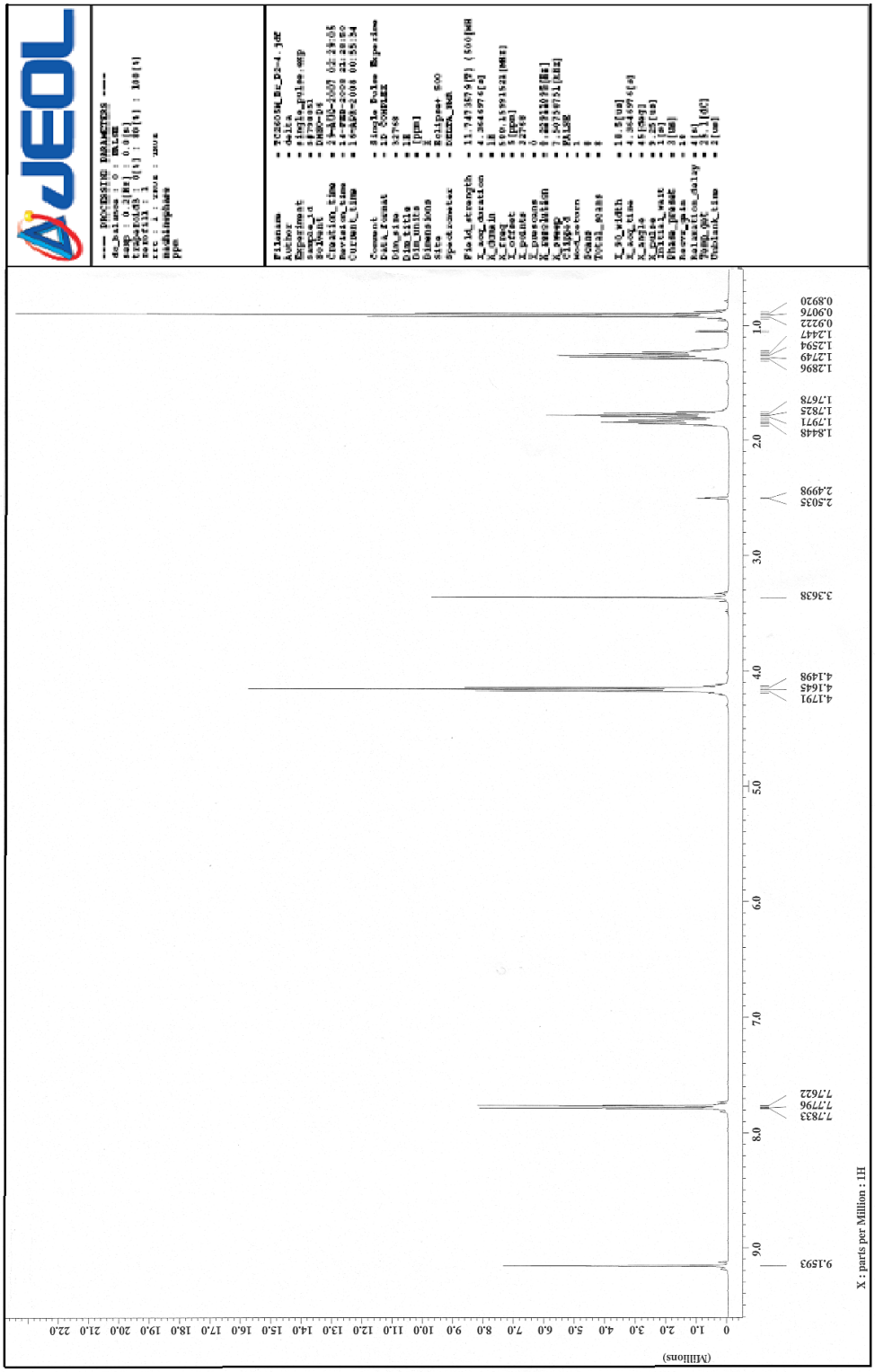
7.752
7.748
5.189
5.171
5.155
4.210
4.193
4.180
3.753
3.737
3.721
3.555
3.534
3.512
3.350
2.506
2.500
2.494
1.853
1.829
1.804
1.345
X : parts per Million : 1H

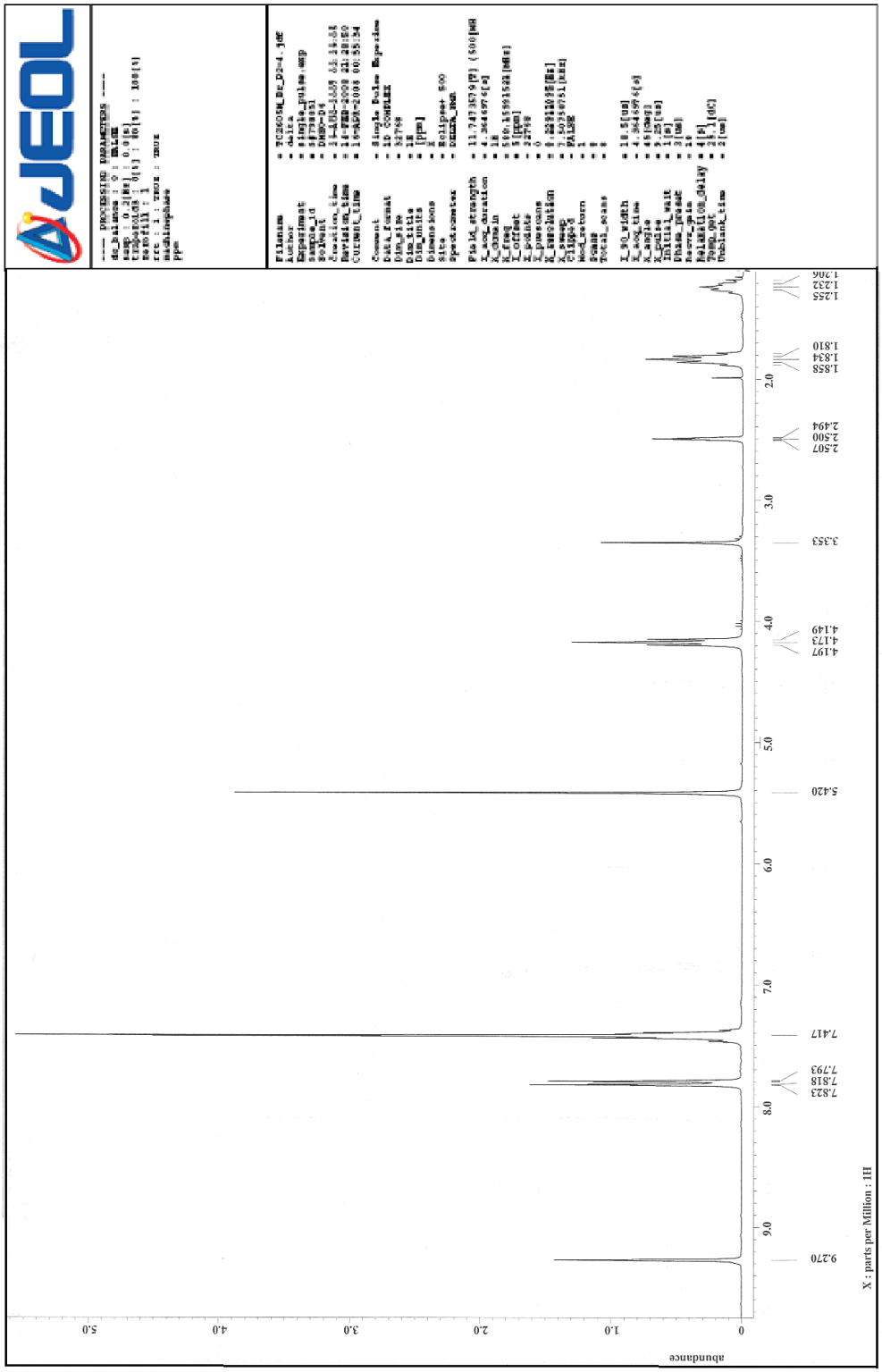
APPENDIX 7

^{1}H NMR SPECTRA OF
IL7: 1,1'-(PENTANE-1,5-DIYL)-BIS(3-BUTYLIMIDAZOLIUM)
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
Filename = TC2605N_DL_P2-4.jdf
Author = data
Experiment = single_pulse.exp
Solvent = DMSO-D6
Creation_time = 24-AUG-2007 02:26:05
Revision_time = 24-FEB-2008 22:28:50
Current_time = 16-APR-2008 00:55:34
Comment = Single Pulse Experiment
Data_Format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = 1
Sites = Bruker 500
Spectrometer = DRX500_NMR
Field_strength = 11.7493579[T] (500[MH
X_acq_duration = 4.364697[s]
X_CHNum = 1H
X_freq = 500.1599152[MHz]
X_offset = 3[ppm]
X_points = 32768
X_pulse = 0
X_resolution = 0.229110[Hz]
X_sweep = 7.5075751[kHz]
X_sweep_clipped = FALSE
X_zero_fill = 1
Acq_mode = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 4.364697[s]
X_angle = 45[deg]
X_delay = 1.25[ms]
X_pulse = 3[us]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 4[s]
Temp_get = 23.1[dC]
Obsblank_time = 2[us]
ppm
9.1593
7.7833
7.7796
7.7622
4.1791
4.1645
4.1498
3.3638
2.5035
2.4998
1.8448
1.7971
1.7825
1.7678
1.2896
1.2749
1.2594
1.2447
0.9222
0.9076
0.8920
(Millions)
X : parts per Million : 1H

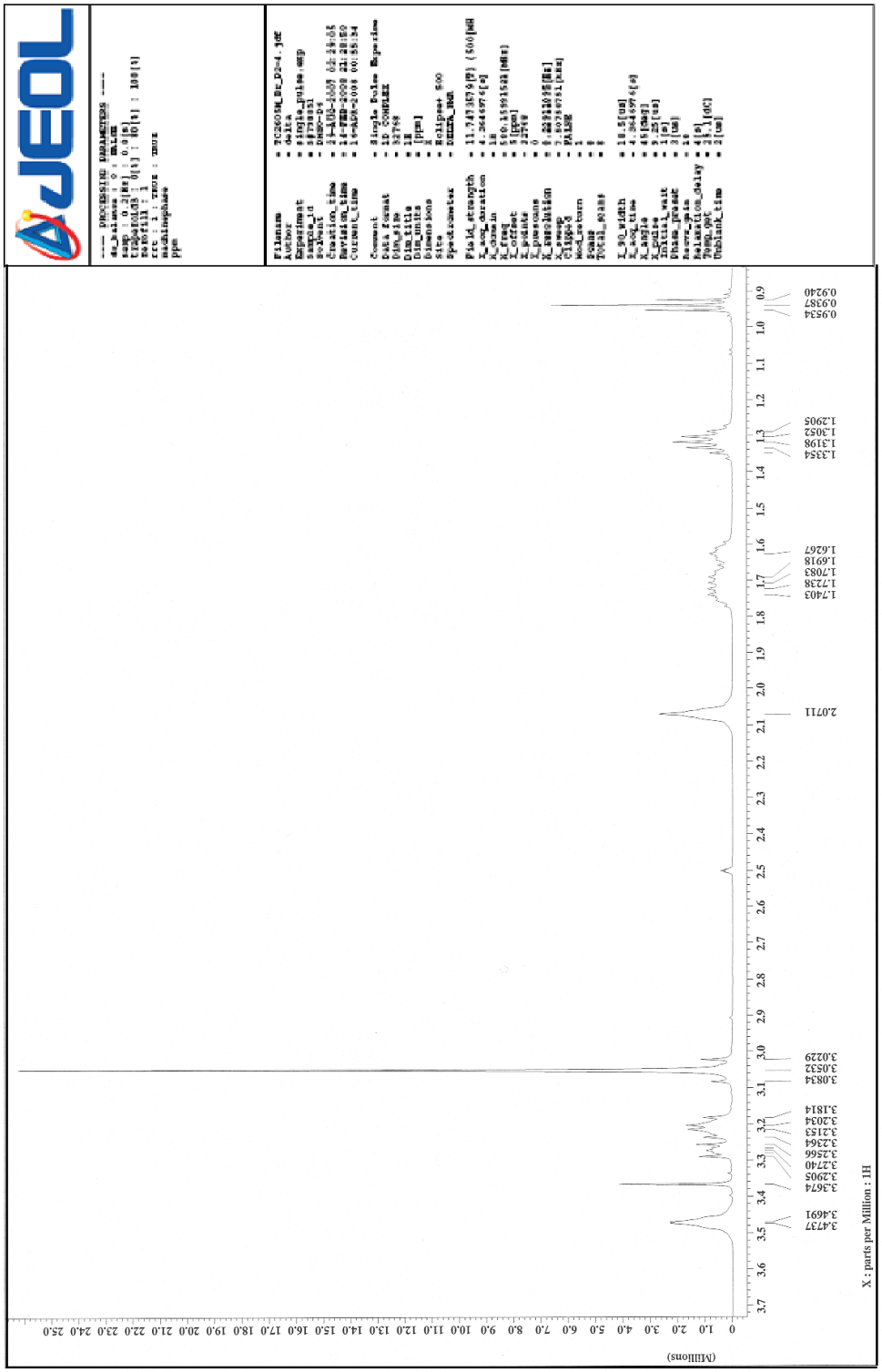
APPENDIX 8

^{1}H NMR SPECTRA OF
IL8: 1,1'-(PENTANE-1,5-DIYL)-BIS(3-BENZYLLIMIDAZOLIUM)
DI[BIS(TRIFLUOROMETHANE-SULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : BLCM
temp : 0.0[K]
TRG-SELCB : 0[s] : 80[s] : 180[s]
Repetition : 1
rtc : 1 : zero : zero
nsbinphase
ppm
Filename = TC2605K_Dr_D2O4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = DFT2401
Solvent = D2O
Pulse_seq = PULSE.JAM 05-16-05
Barrier_time = 14-FEB-2009 23:28:50
CURRENT_time = 16-APR-2009 00:55:54
Comment = Single Pulse Experiment
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_units = Hz
Dim_titles = [ppm]
Dimensions = 1
Site = Eclipse 500
Spectrometer = DEFAULT_NAM
Field_strength = 11.7473879[T] (500[MH
X_acq_duration = .3446976[s]
X_domain = 1H
X_freq = 500.1599158[MHz]
X_offset = 5[ppm]
X_points = 32768
X_pulse = 0
X_resolution = 0.2911019[Hz]
X_sweep = 95.5036751[kHz]
X_sweep_clipped = FALSE
Acq_type = 1
Mod_Spectrum = 0
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 4.364696[s]
X_angle = 45[deg]
X_pulse = 1.25[us]
Initial_wait = 1[s]
Phase_preset = 3[deg]
Recv_gain = 16
Relaxation_delay = 4[s]
Temp_get = 23.1[deg C]
Obsblank_time = 2[us]
abundance
0
1.0
2.0
3.0
4.0
5.0
9.270
7.823
7.818
7.793
7.417
5.420
4.197
4.173
4.149
3.353
2.507
2.500
2.494
1.858
1.834
1.810
1.255
1.232
1.206
X : parts per Million : 1H

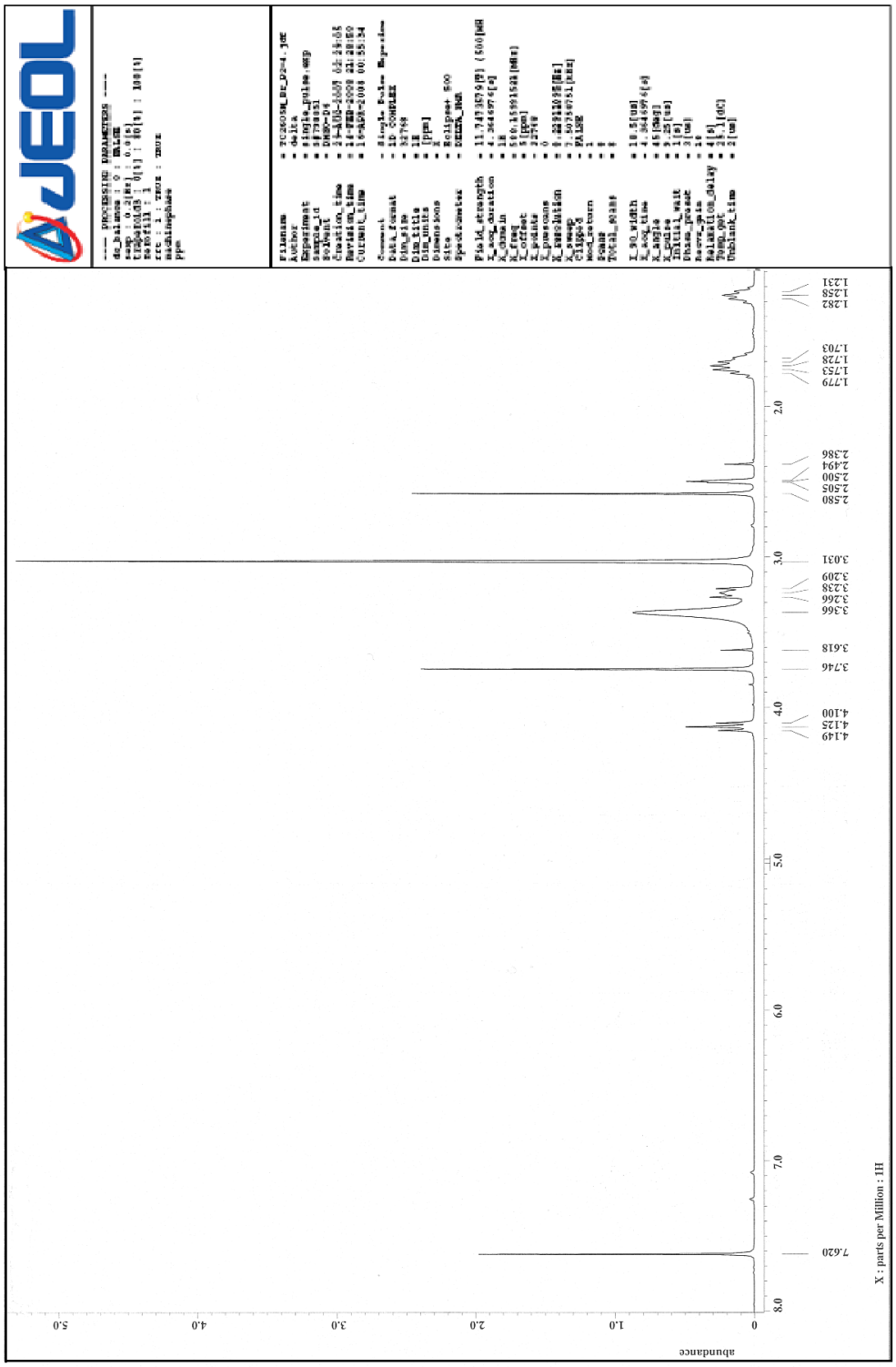
APPENDIX 9

^{1}H NMR SPECTRA OF
IL9: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-1-BUTYLPYRROLIDINIUM
DI[BIS(TRIFLUORO-METHANESULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
Filename = TC2605M_Pr_D2-4.jdf
Author = delta
Experiment = single_pulse.exp
Solvent = DMSO-D6
Creation_time = 26-MAY-2005 02:24:05
Revision_time = 14-FEB-2008 21:28:50
Current_time = 16-AUG-2008 00:55:34
Comment = Single Pulse Experiment
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = 1
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473879[T] (500[MH
X_acq_duration = 4.364697[s]
X_domain = 1H
X_freq = 500.15991528[MHz]
X_offset = 3[ppm]
X_points = 32768
X_pulse = 0
X_resolution = 0.229126238[Hz]
X_sweep = 7.50366351[ppm]
Clipped = FALSE
Mod_pattern = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 4.364697[s]
X_angle = 45[deg]
X_pulse = 3.25[us]
X_delay_wait = 1[s]
Phase_preset = 3[us]
Recv_gain = 16
Relaxation_delay = 4[s]
Temp_get = 25.1[degC]
Tmblank_time = 2[us]
0.9534
0.9387
0.9240
1.3354
1.3198
1.3052
1.2905
1.7403
1.7238
1.7083
1.6918
1.6267
2.0711
3.0834
3.0532
3.0229
3.4737
3.4691
3.3674
3.2905
3.2740
3.2566
3.2364
3.2153
3.2034
3.1814
(Millions)
X : parts per Million : 1H

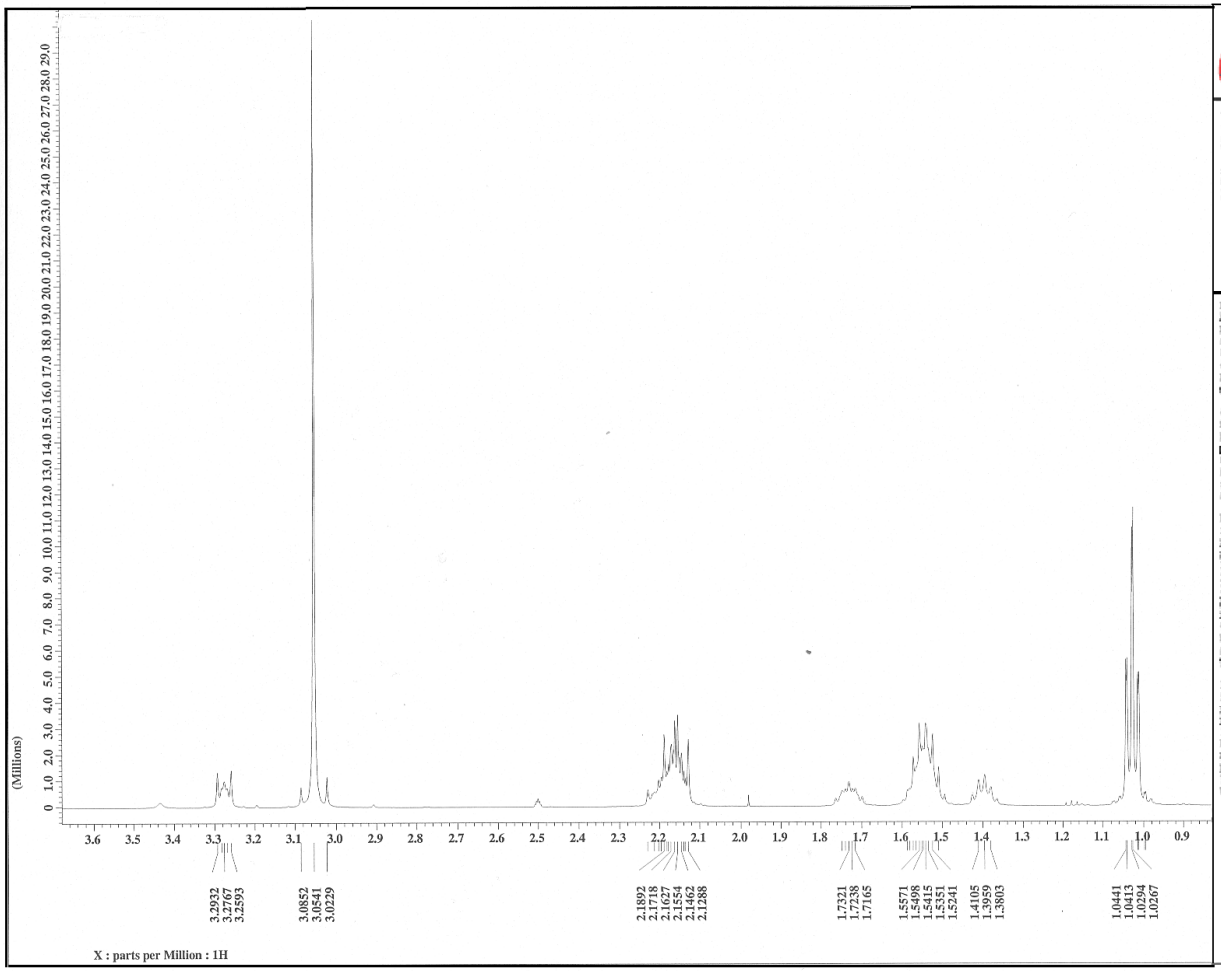
APPENDIX 10

^{1}H NMR SPECTRA OF
IL10: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-2,3- DIMETHYLIMIDAZOLIUM
[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
Filename = TC2603R_DP_D24.JDF
Experiment = data
Pulse_Program = 1H_single_pulse.exp
Sample_id = 1H_TC2603
Solvent = DMSO-D4
Creation_time = 24-AUG-2009 05:24:05
Revision_time = 14-FEB-2009 23:28:50
Current_time = 16-SEP-2009 00:55:54
Comment = Simple Pulse Experim
Data_Format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = 1
Size = Enlarged 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473576[T] (500[MH
X_acq_duration = 4.364597[s]
X_domain = 1H
X_freq = 500.15991528[MHz]
X_offset = 3[ppm]
X_points = 32768
X_resolution = 0.229102[Hz]
X_sweep = 7.50336751[kHz]
Clipped = PULSE
Mod_factorn = 1
Power = 0
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 4.364597[s]
X_angle = 45[deg]
X_pulse = 3.25[us]
Initial_wait = 1[s]
Phase_power = 11[dB]
Recv_gain = 4[B]
Relaxation_delay = 2.5[s]
Temp_get = 25.1[dC]
Dummy_time = 2[us]
abundance
X : parts per Million : 1H
7.620
4.149
4.125
4.100
3.746
3.618
3.366
3.266
3.238
3.209
3.031
2.580
2.505
2.500
2.494
2.386
1.779
1.753
1.728
1.703
1.282
1.258
1.231

APPENDIX 11

^{1}H NMR SPECTRA OF
IL11: (1-TRIMETHYLAMMONIUM-YL-PENTYL)-TRIPROPYLPHOSPHONIUM
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]



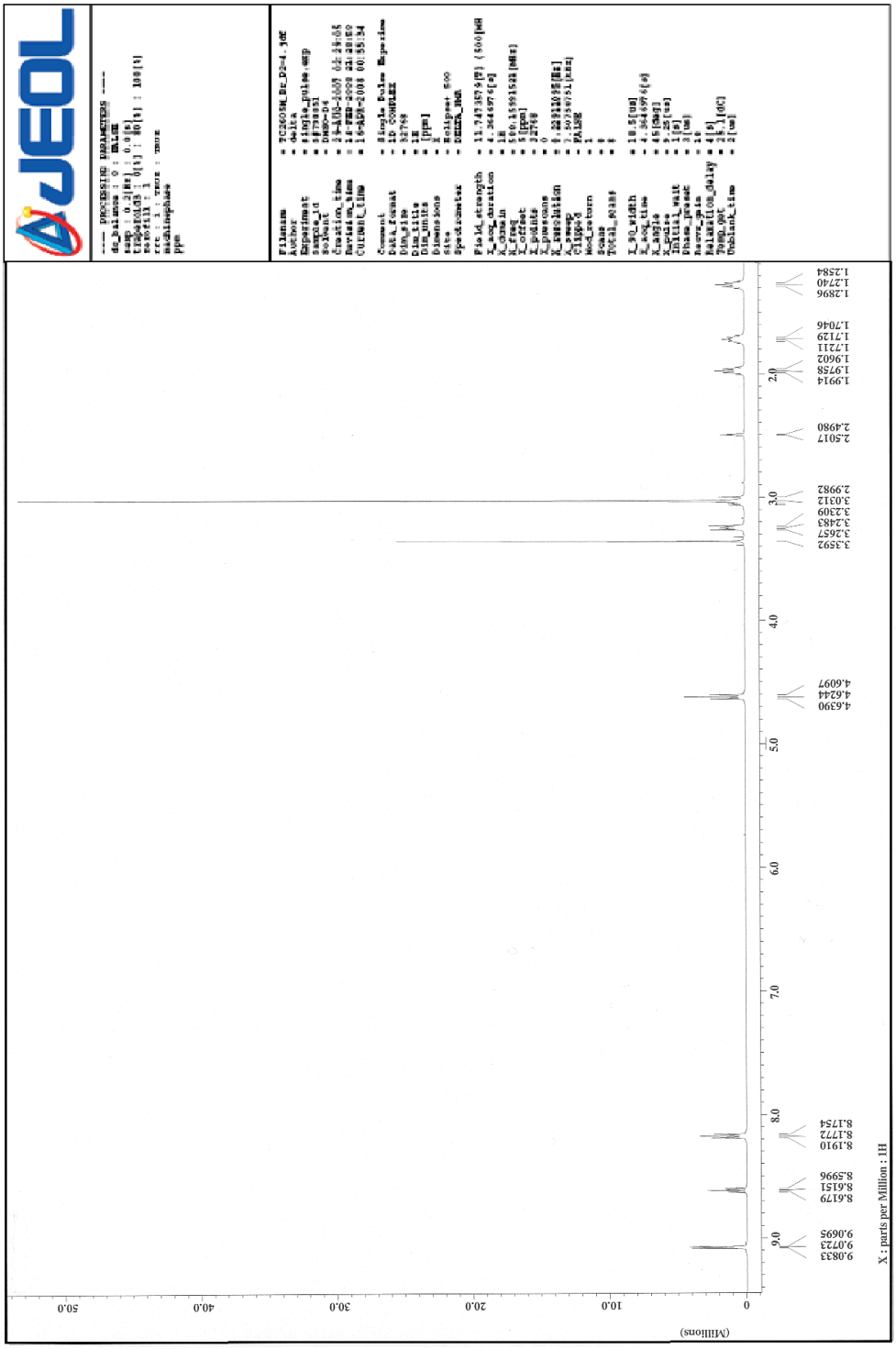
JEOL

--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
samp : 0.2[Hz] : 0.0[s]
trapezoids : 0[%] : 80[%] : 100[%]
zerofill : 1
rrc : 1 : TRUE : TRUE
machinephase
ppm

Filename	= TC2605M_Dr_D2-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= SJ798051
Solvent	= DMSO-D6
Creation_time	= 24-AUG-2007 02:24:05
Revision_time	= 14-FEB-2008 21:28:50
Current_time	= 16-APR-2008 00:55:34
Comment	= Single Pulse Experimo
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	= 4.364697[s]
X_domain	= 1H
X_freq	= 500.1599152[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_prescans	= 0
X_resolution	= 0.2291209[Hz]
X_sweep	= 7.5075781[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 18.5[us]
X_acq_time	= 4.364697[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 16
Relaxation_delay	= 4[s]
Temp_get	= 25.1[dC]
Unblank_time	= 2[us]

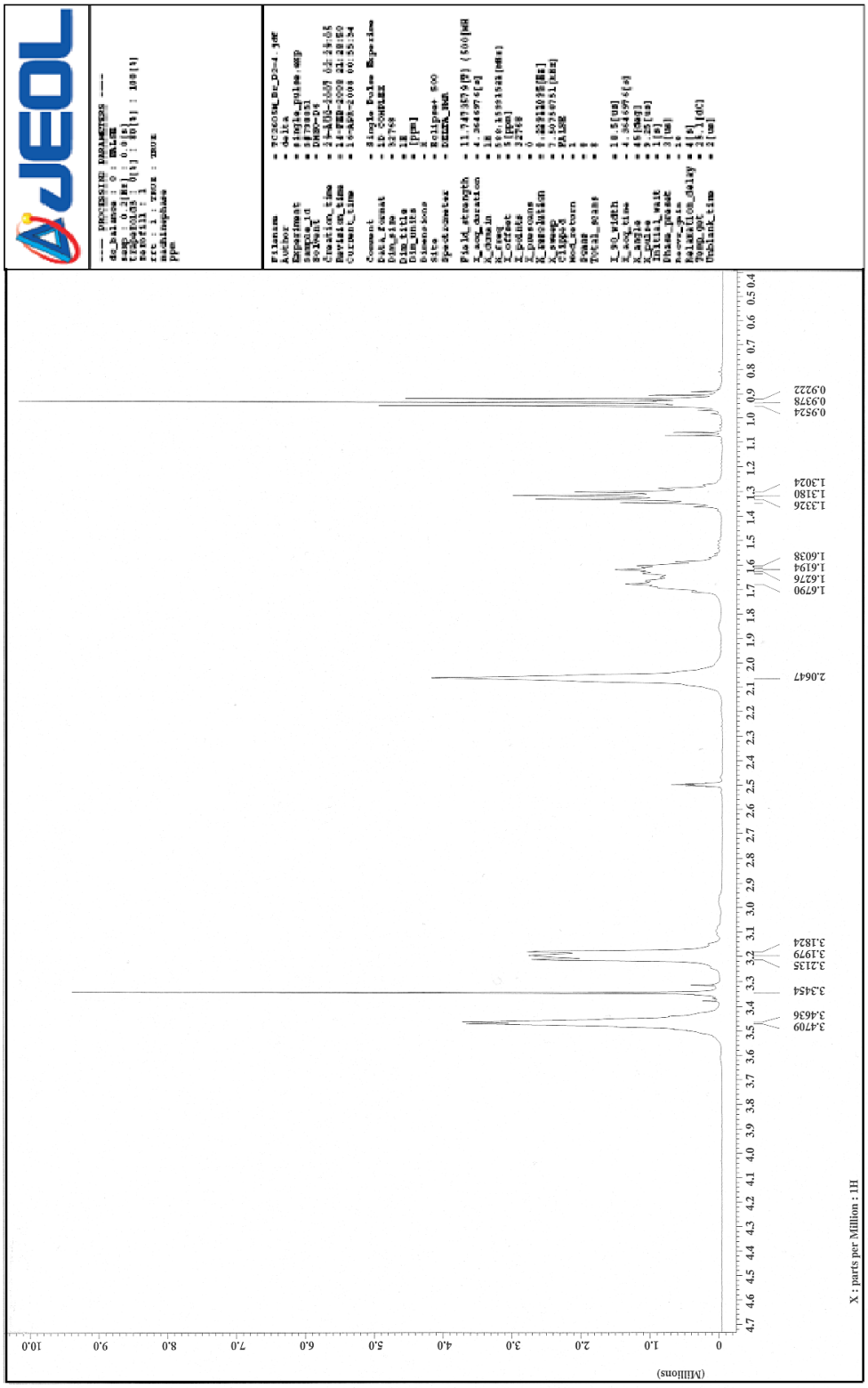
APPENDIX 12

^{1}H NMR SPECTRA OF
IL12: 1-(1-TRIMETHYLAMMONIUM-YL-PENTYL)-PYRIDINIUM
DI[BIS(TRIFLUOROMETHANE- SULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : FALSE
Filename = TC2600N_Dr_D2-4.jdf
Author = delta
Experiment = single_pulse.exp
Comment = Single Pulse Experiment
Data_Format = 1D COMPLEX
Dim_Units = [ppm]
Dimensions = 1
Site = Bruker_600
Spectrometer = DRX_NMR
Field_strength = 11.747357[T] (500[MH
X_acq_duration = 4.364597[s]
X_Hz/pt = 0.229[Hz]
X_points = 2048
X_Expansion = 0.-0.2[ppm]
X_pulse = 7.50[us]
X_power = PULSE
Clipped = 1
Mod_return = 0
Scans = 8
TOTAL_SCANS = 8
X_90_width = 10.5[us]
X_acq_time = 4.364597[s]
X_angle = 45[deg]
X_delay = 9.25[us]
Initial_wait = 1[s]
Phase_grad = 16
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
X : parts per Million : 1H
(Millions)
50.0
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
9.0833
9.0723
9.0695
8.6179
8.6151
8.5996
8.1910
8.1772
8.1754
4.6390
4.6244
4.6097
3.3592
3.3657
3.3483
3.3309
3.3312
2.9982
2.5017
2.4980
1.9914
1.9758
1.9602
1.7211
1.7129
1.7046
1.2896
1.2740
1.2584

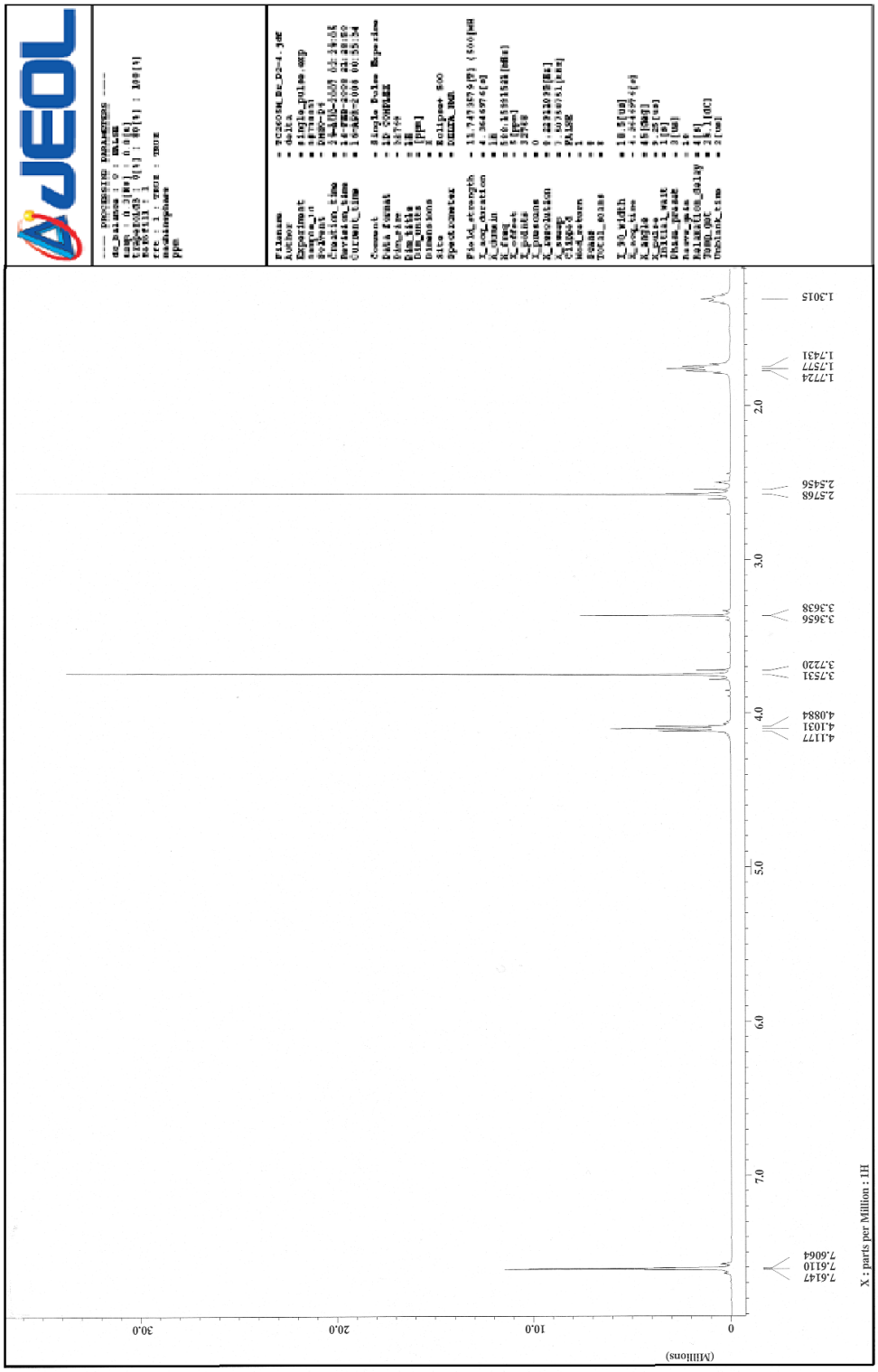
APPENDIX 13

^{1}H NMR SPECTRA OF
IL13: 1,1'-(PENTANE-1,5-DIYL)-BIS(1-BUTYLPYRROLIDINIUM)
DI[BIS(TRIFLUOROMETHANE-SULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
do_baseline : 0 : NONE
sano : 0.2[Hz] : 0.0[Hz]
tmpl0001.03 : 0[%] : 100[%]
proflil : 2
rec_mode : true : true
nachimpuls
ppm
Filename : TC2603L_Dr_D2O4_.jdf
Author : delta
Experiment : single_pulse.exp
Sample_id : 1F3405
Solvent : D2O
Acquisition_time : 14-FEB-2003 22:28:50
Barrier_time : 14-FEB-2003 22:28:50
Current_time : 19-APR-2003 00:55:34
Comment : Single Pulse Experiment
Data_format : 1D COMPLEX
Dim_size : 32768
Dim_title : H1
Dim_units : [ppm]
Dimensions : 1
Site : Eclipse 500
Spectrometer : DELTA_NMR
Field_strength : 11.747367479[T] (500[MH
X_acq_duration : 4.364597[s]
X_domain : 1H
X_freq : 500.159952[MHz]
X_offset : 5[ppm]
X_points : 32768
X_prescans : 0 : 0291309[EA]
X_resolution : 1.4978751[Hz]
X_window : EXPONENTIAL
Clipped : FALSE
Mod_factor : 1
Scan : 0
Total_scans : 8
X_90_width : 10.5[us]
X_acq_time : 4.364597[s]
X_angle : 45[Deg]
X_pulse : 5.25[us]
Initial_wait : 1[s]
Phase_preset : 3[us]
Power_dis : 4[W]
Relaxation_delay : 1.1[s]
Temp_get : 31.1[dC]
Unblank_time : 2[us]
(Millions)
X : parts per Million : 1H
0.9222
0.9378
0.9524
1.3024
1.3180
1.3326
1.6038
1.6194
1.6276
1.6790
2.0647
3.1824
3.1979
3.2135
3.3454
3.4636
3.4709

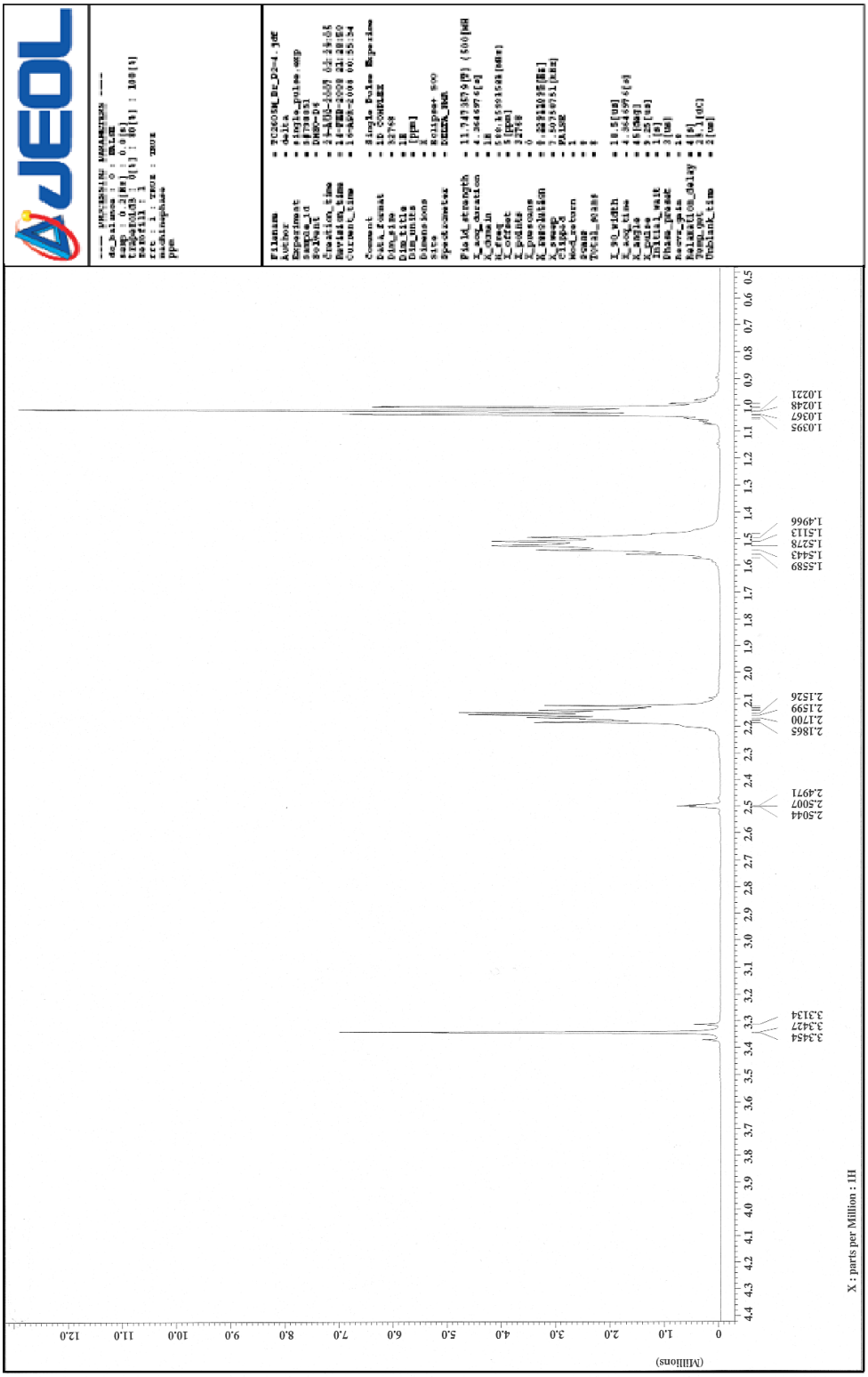
APPENDIX 14

^{1}H NMR SPECTRA OF
IL14: 1,1'-(PENTANE-1,5-DIYL)-BIS(2-METHYL-3-METHYL-IMIDAZOLIUM)
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]


JEOL
(Millions)
30.0
20.0
10.0
0
7.6147
7.6110
7.6064
4.1177
4.1031
4.0884
3.7531
3.7220
3.3656
3.3638
2.5768
2.5456
1.7724
1.7577
1.7431
1.3015
7.0
6.0
5.0
4.0
3.0
2.0
X : parts per Million : 1H

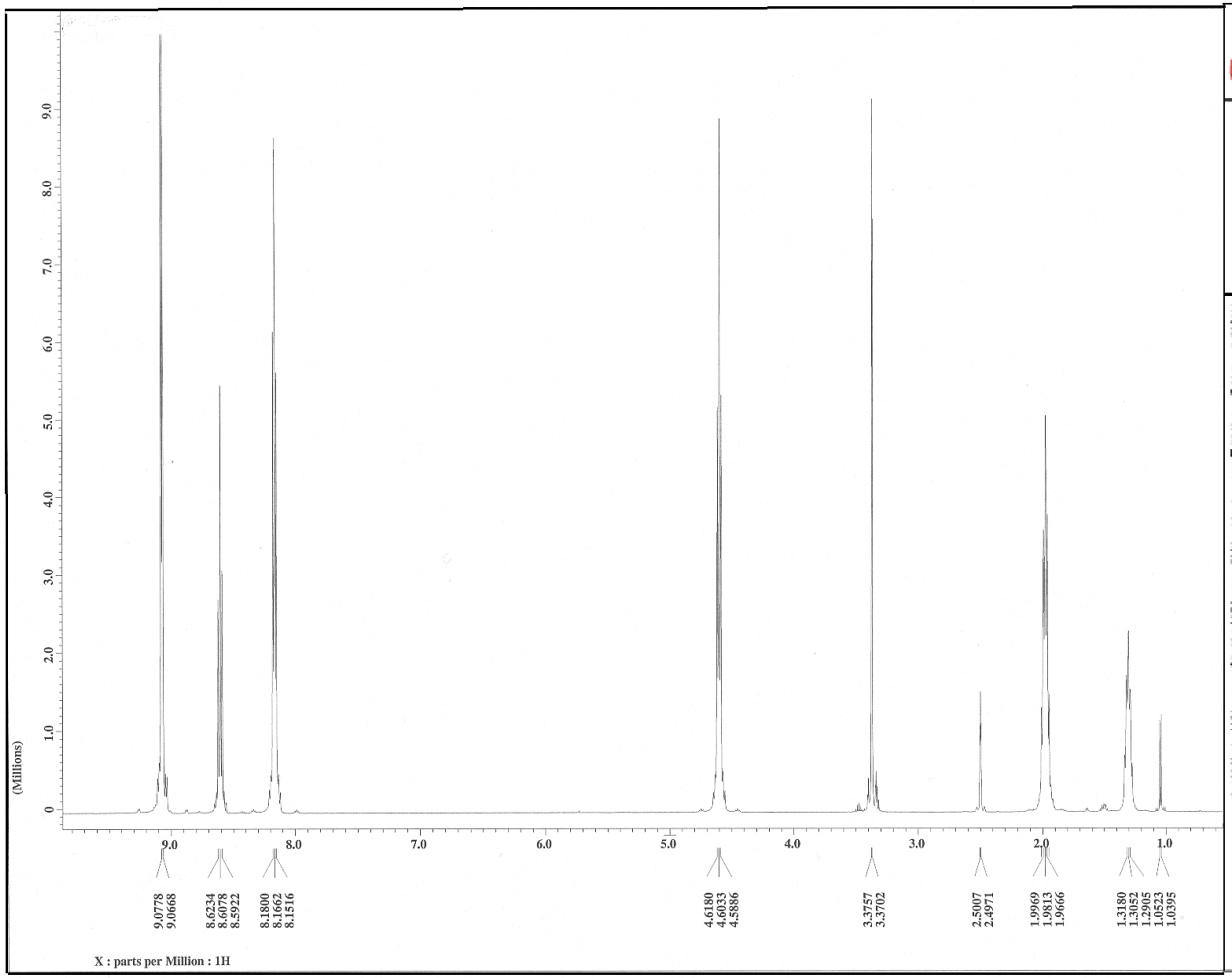
APPENDIX 15

^{1}H NMR SPECTRA OF
IL15: (PENTANE-1,5-DIYL)-BIS(TRIPROPYLPHOSPHONIUM)
DI[BIS(TRIFLUOROMETHANE-SULFONYL)IMIDE]


JEOL
X : parts per Million : 1H
(Millions)
3.3454
3.3427
3.3134
2.5044
2.5007
2.4971
2.1865
2.1700
2.1599
2.1526
1.5589
1.5443
1.5278
1.5113
1.4966
1.0395
1.0367
1.0248
1.0221

APPENDIX 16

^{1}H NMR SPECTRA OF
IL16: 1,1'-(PENTANE-1,5-DIYL)-BIS(PYRIDINIUM)
DI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE]



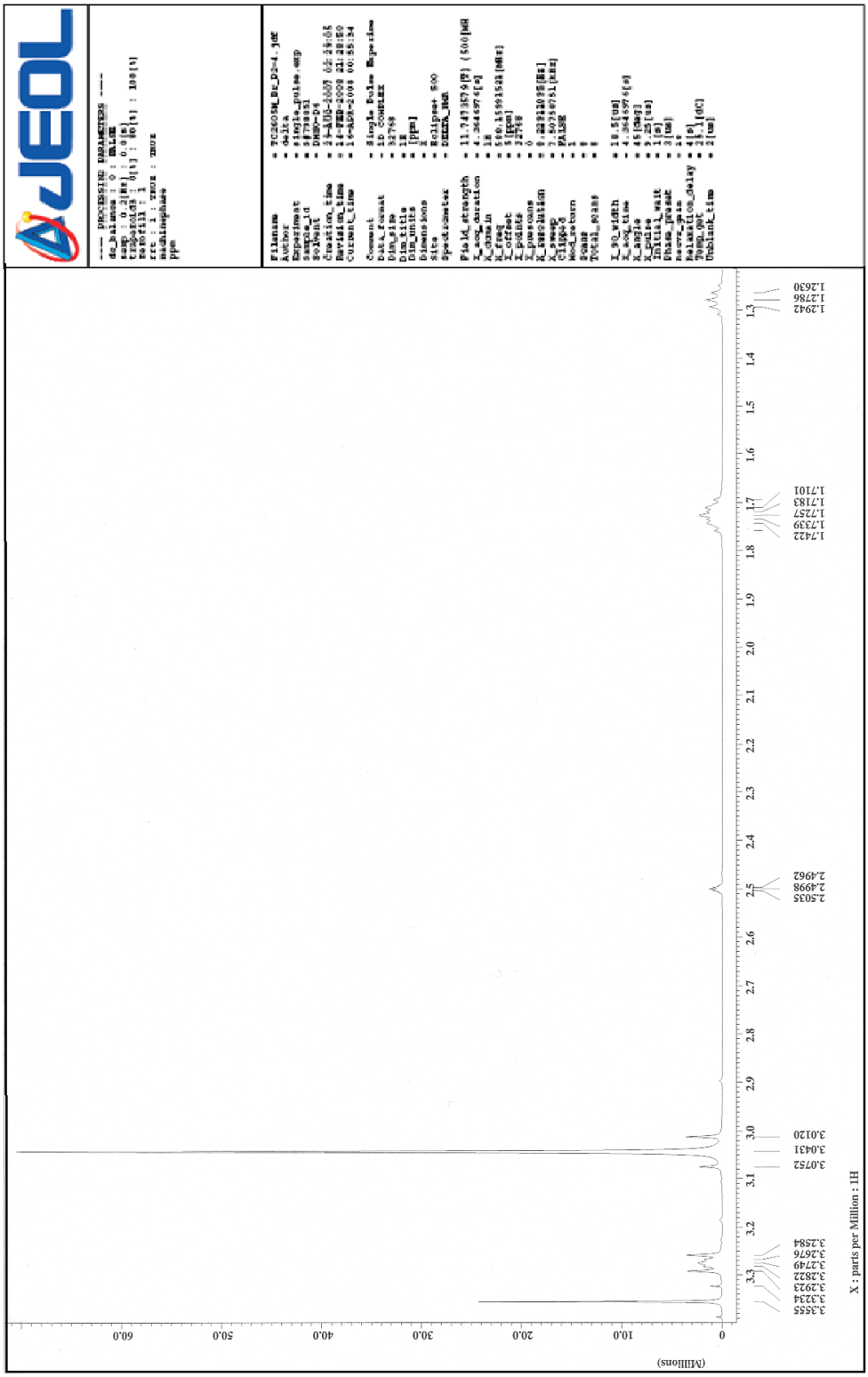
JEOL

--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
samp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
rrt : 1 : TRUE : TRUE
machinephase
ppm

Filename	= TC2605H_Dr_D2=4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= sj734051
Solvent	= DMSO-D6
Creation_time	= 14-AUG-2007 02:24:05
Revision_time	= 14-FEB-2008 21:28:50
Current_time	= 16-APR-2008 00:55:34
Comment	= Single Pulse Experiment
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	= 4.364976[s]
X_domain	= 1H
X_freq	= 500.15991528[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_pulseconn	= 0
X_resolution	= 0.22912098[Hz]
X_sweep	= 7.50758781[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 18.5[us]
X_acq_time	= 4.364976[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recv_gain	= 18
Relaxation_delay	= 4[s]
Temp_get	= 24.1[dC]
Unblank_time	= 2[us]

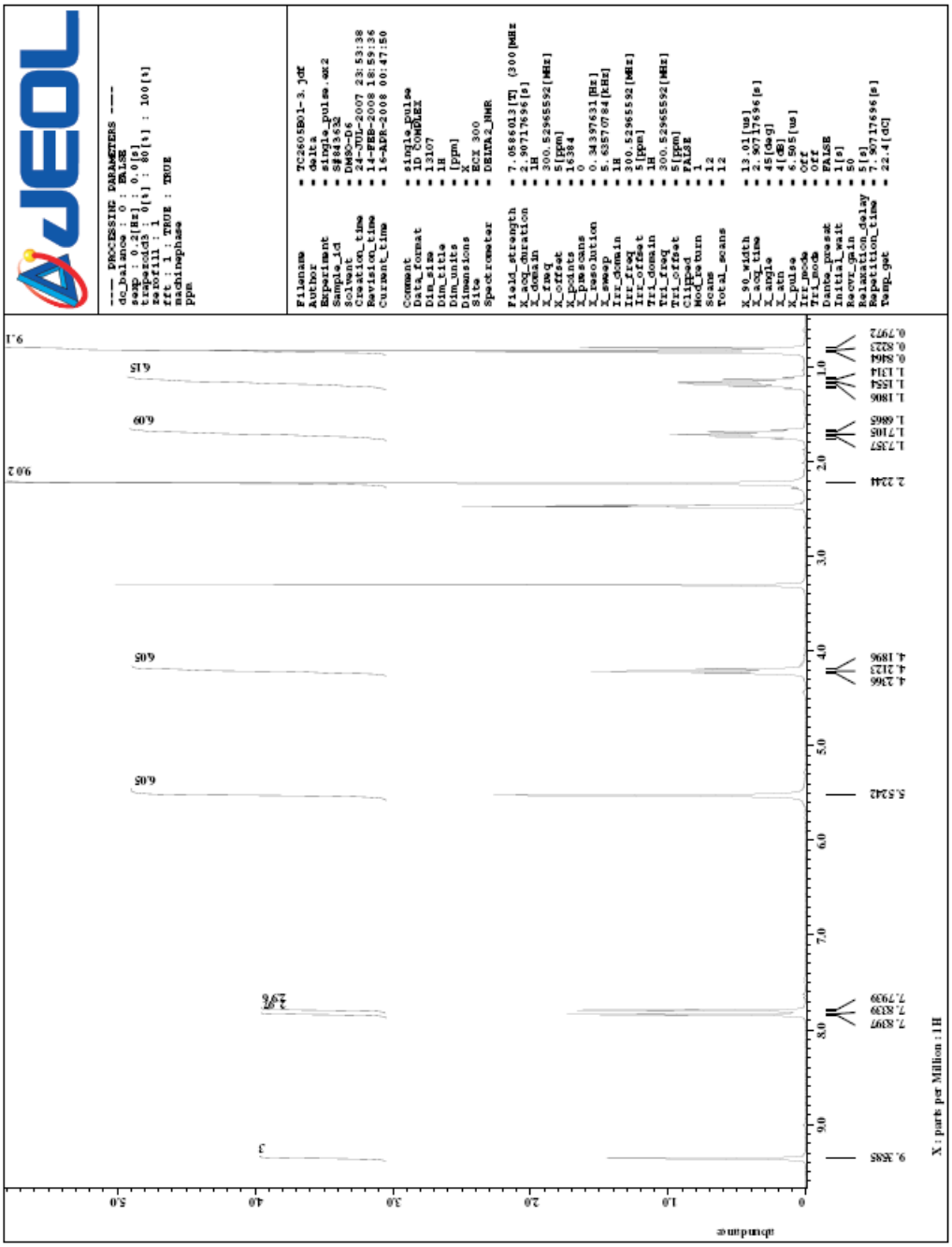
APPENDIX 17

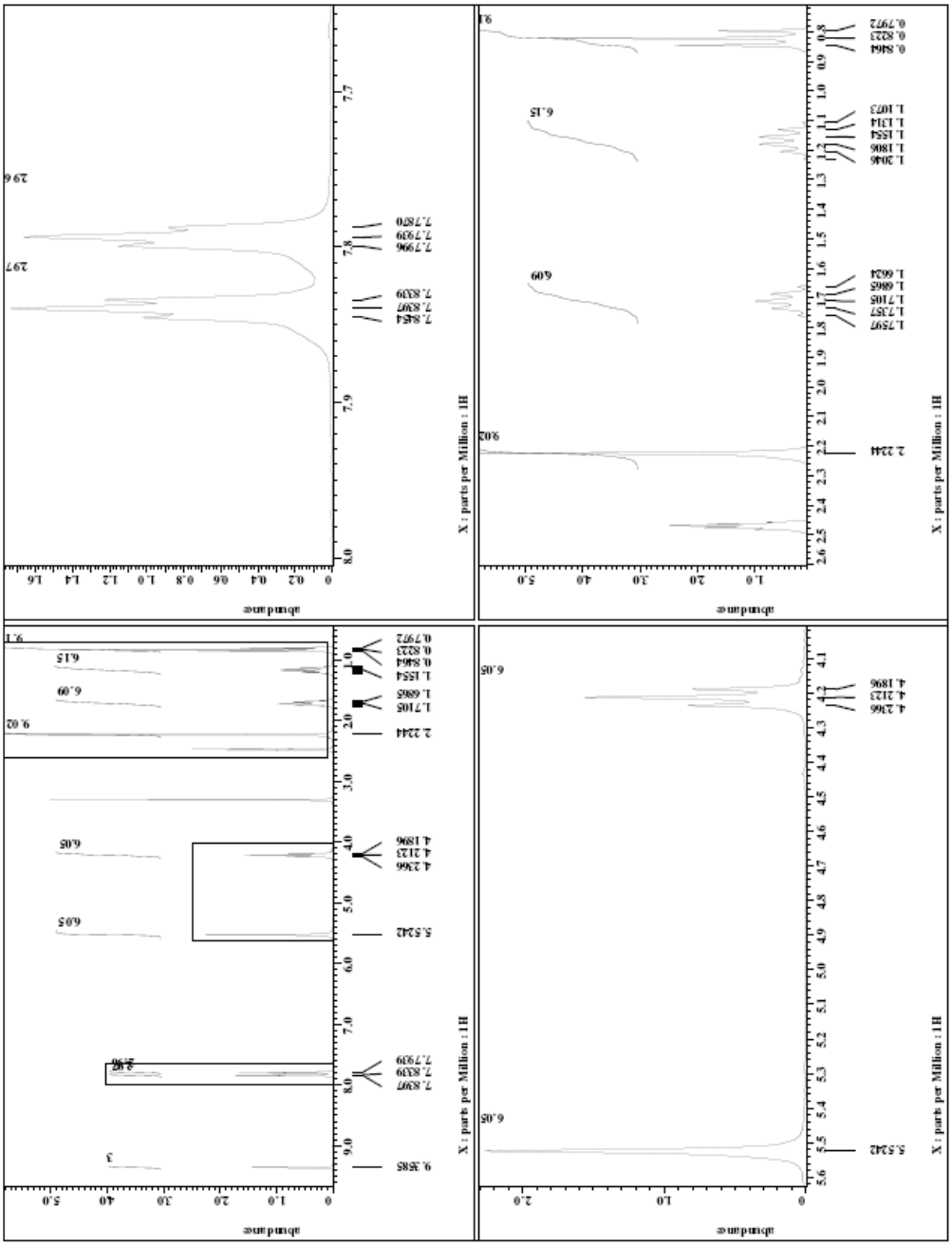
^{1}H NMR SPECTRA OF
IL21: (PENTANE-1,5-DIYL)-BIS(TRIMETHYLAMMONIUM)
DI[BIS(TRIFLUOROMETHANE-SULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
do_baline : 0 : BLINE
sgn : 0.2[Hz] : 0.0[s]
trapezoid : 1 0[%] : 80[%] : 100[%]
ref : TMS : TMSX
ppm
Filename : TC2600M_Dr_D2-4_1H
Author : delta
Experiment : single_pulse.exp
Sample_id : 5[Pyridi]
Solvent : Chloroform-D
Probe : 5-HTD-600M 02-24-05
Acquisition_time : 14-FEB-2008 21:28:50
Current_time : 14-APR-2008 00:55:34
Comment : Single Pulse Experiment
Data_format : 1D COMPLEX
Dim_size : 32768
Dim_title : 1H
Dim_units : [ppm]
Dimensions : 1
Site : Eclipse 600
Spectrometer : DELTA_NMR
Field_strength : 11.747357[T] (500[MH
X_acq_duration : 4.364597[s]
X_domain : 1H
X_freq : 500.15991528[MHz]
X_offset : 5[ppm]
X_points : 32768
X_pseudo : 0
X_resolution : 0.229120[Hz]
X_sweep : 7.497126751[kHz]
X_sweep_clipped : PARSE
Nucleus : 1
Scans : 8
Total_scans : 8
X_90_width : 18.5[us]
X_acq_time : 4.364597[s]
X_angle : 45[Deg]
X_pulse : 9.25[us]
Initial_wait : 1[s]
Phase_preset : 3[us]
Recv_gain : 1[%]
Relaxation_delay : 1[s]
Temp_get : 21.5[deg]
Dwelling_time : 2[us]
(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
3.3555
3.3234
3.2923
3.2822
3.2749
3.2676
3.2584
3.0752
3.0431
3.0120
2.5035
2.4998
2.4962
1.7422
1.7339
1.7257
1.7183
1.7101
1.2942
1.2786
1.2630
X : parts per Million : 1H

APPENDIX 18

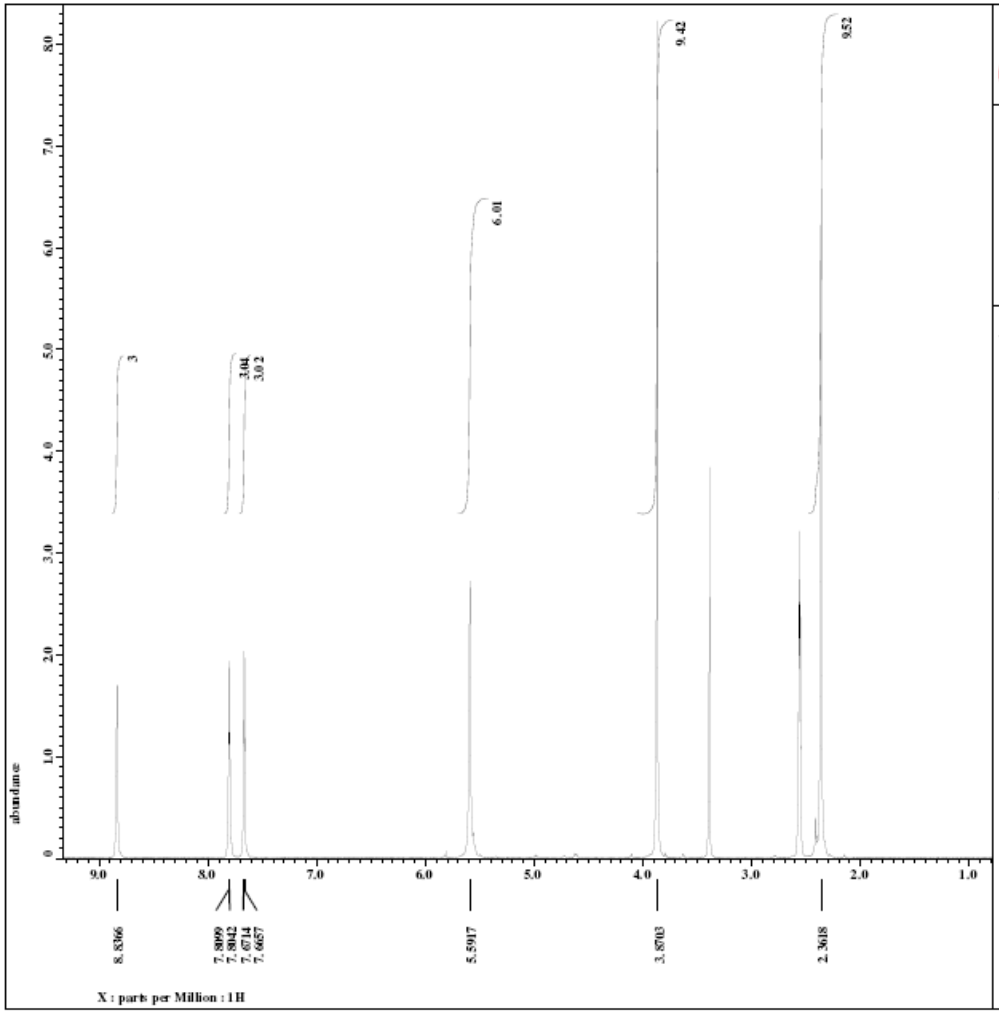
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BUTYLIMIDAZOLIUM)METHYL}MESITYLENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zero_fill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = 7C2605B01-3.jdf
Author = admin
Experiment = single_pulse.ex2
Sample_id = SS843432
Solvent = DMSO-D6
Creation_time = 24-JUL-2007 23:53:38
Revision_time = 14-FEB-2008 18:59:36
Current_time = 15-APR-2008 00:47:50
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 = 300.52955592[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 = 300.52955592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52955592[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
Decpl_present = FALSE
Initial_wait = 1[s]
Recve_gain = 50
Relaxation_delay = 7[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.4[dC]
9.1
6.15
6.09
9.02
6.05
6.05
1.96
1
9.3585
7.7928
7.8239
7.8397
5.5242
4.1896
4.3123
4.3966
2.2244
1.7357
1.7105
1.6865
1.1806
1.1554
1.1314
0.8464
0.8223
0.7972
Intensity
X : parts per Million : 1H


X : parts per Million : 1H
abundance
9.3585
7.8397
7.8319
7.7939
2.90
5.5242
6.05
4.2366
4.2123
4.1896
2.2244
L.7105
L.6865
L.1554
0.8464
0.8223
0.7972
6.15
9.02
6.09
9.1
7.8454
7.8397
7.8319
7.7996
7.7939
7.7870
29.6
29.7

APPENDIX 19

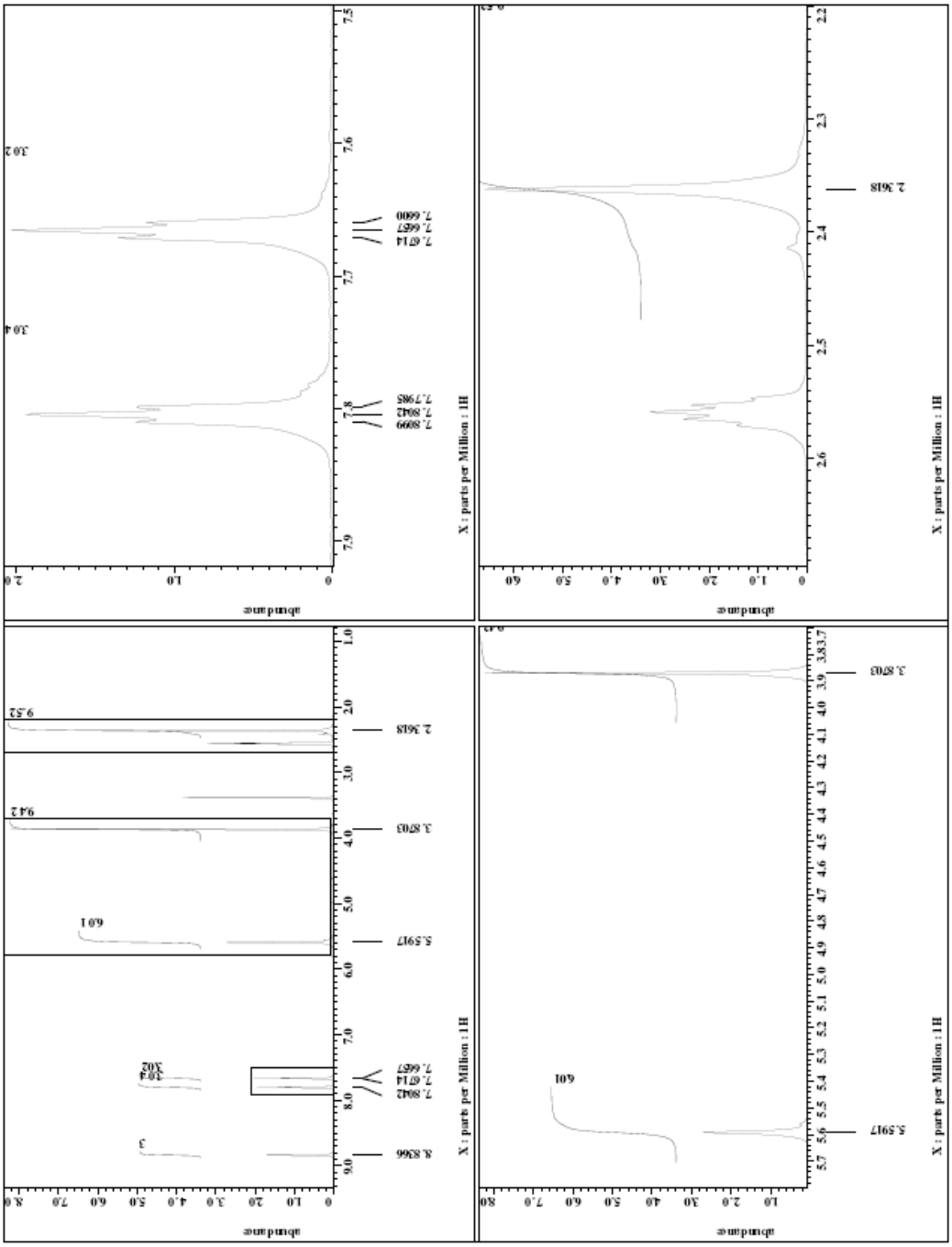
^{1}H NMR SPECTRA OF
3,5-{TRIS(3-N-METHYLIMIDAZOLIUM)METHYL}MESITYLENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

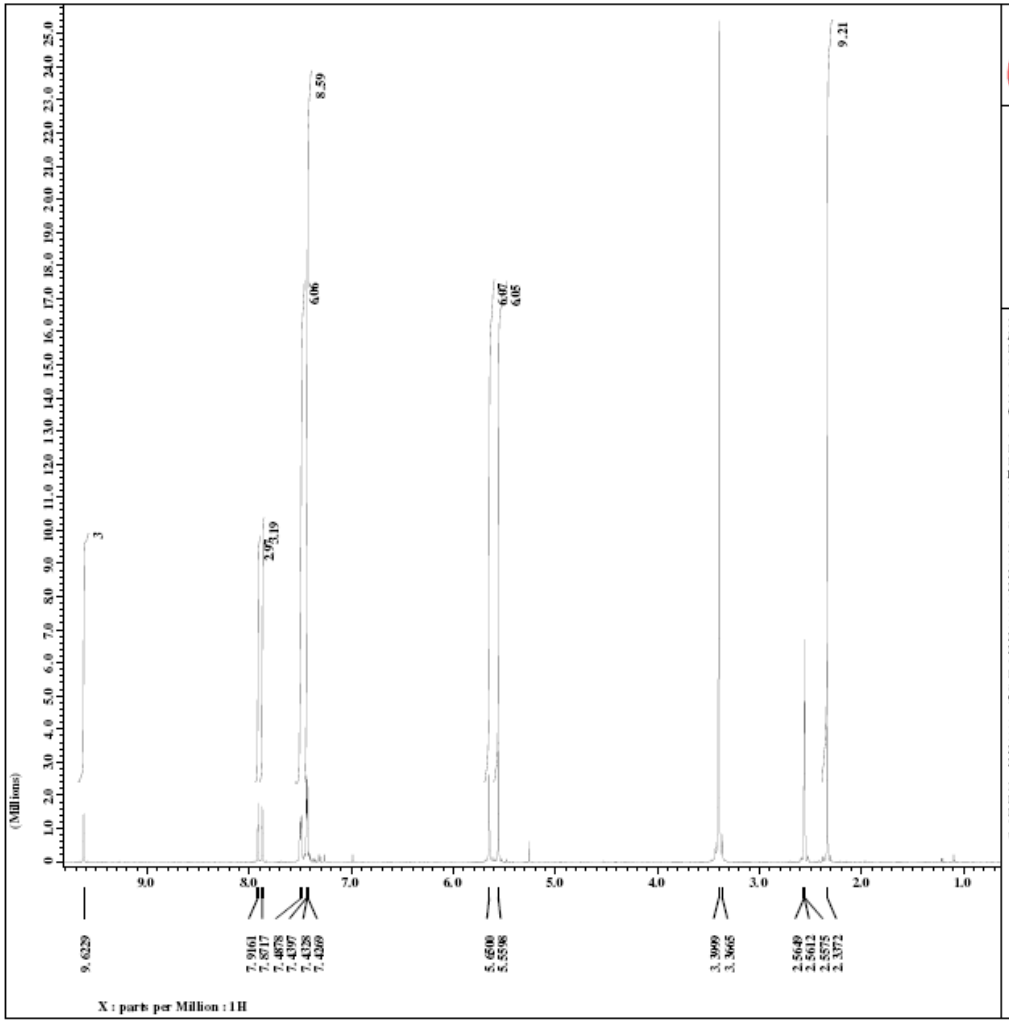
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Filename	= 2605G-5.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#608154
Solvent	= DMSO-D6
Creation_time	= 12-NOV-2007 17:15:43
Revision_time	= 14-FEB-2008 19:00:27
Current_time	= 16-APR-2008 00:50:01
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	= 23.2[dC]


X : parts per Million : 1H
abundance
8.8566
7.8042
7.6714
7.6667
5.5917
3.8705
2.3618
7.8099
7.7985
7.6600
10.4
10.2
9.42
9.52
6.01
3
3.8
3.02

APPENDIX 20

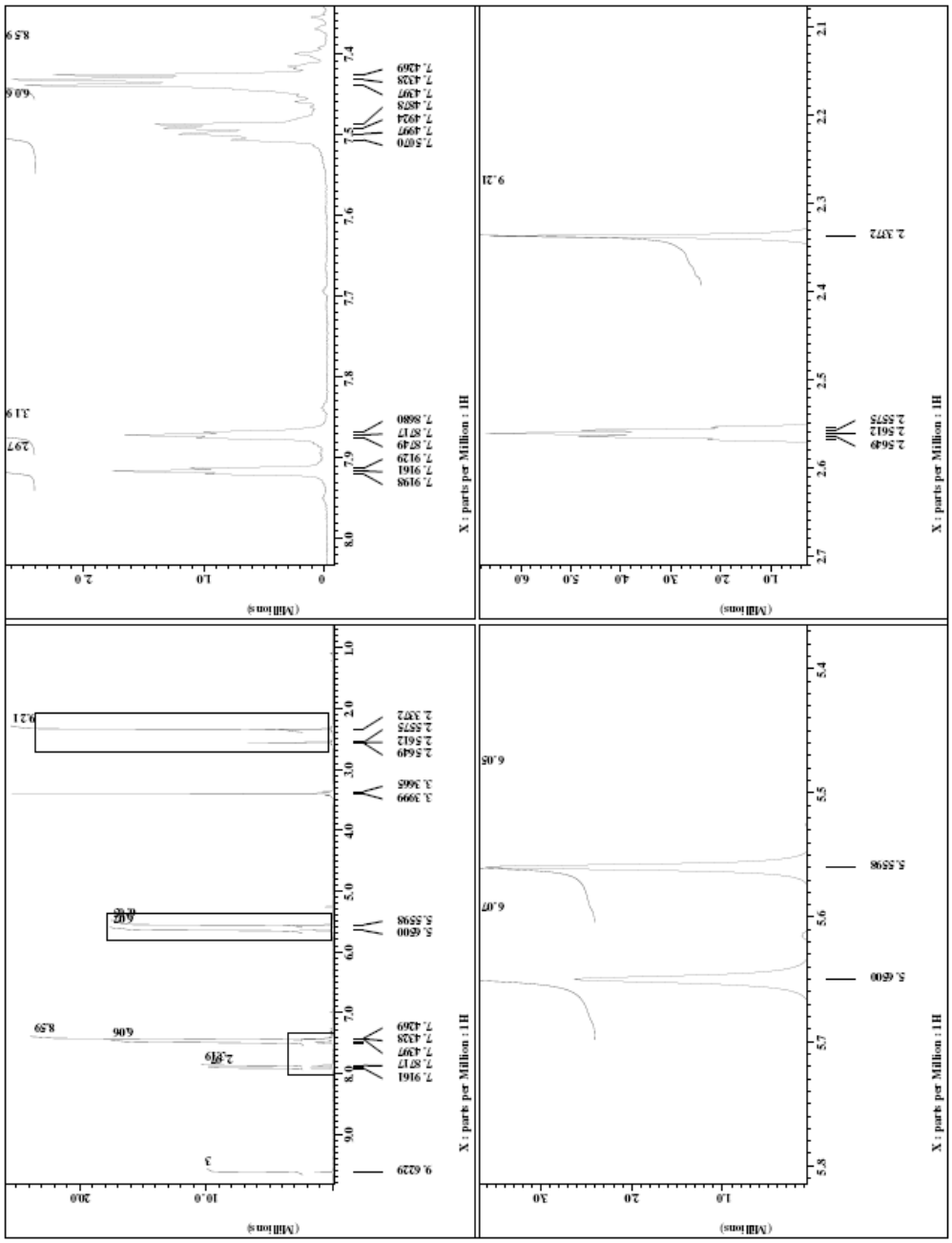
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BENZYLIMIDAZOLIUM)METHYL}MESITYLENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

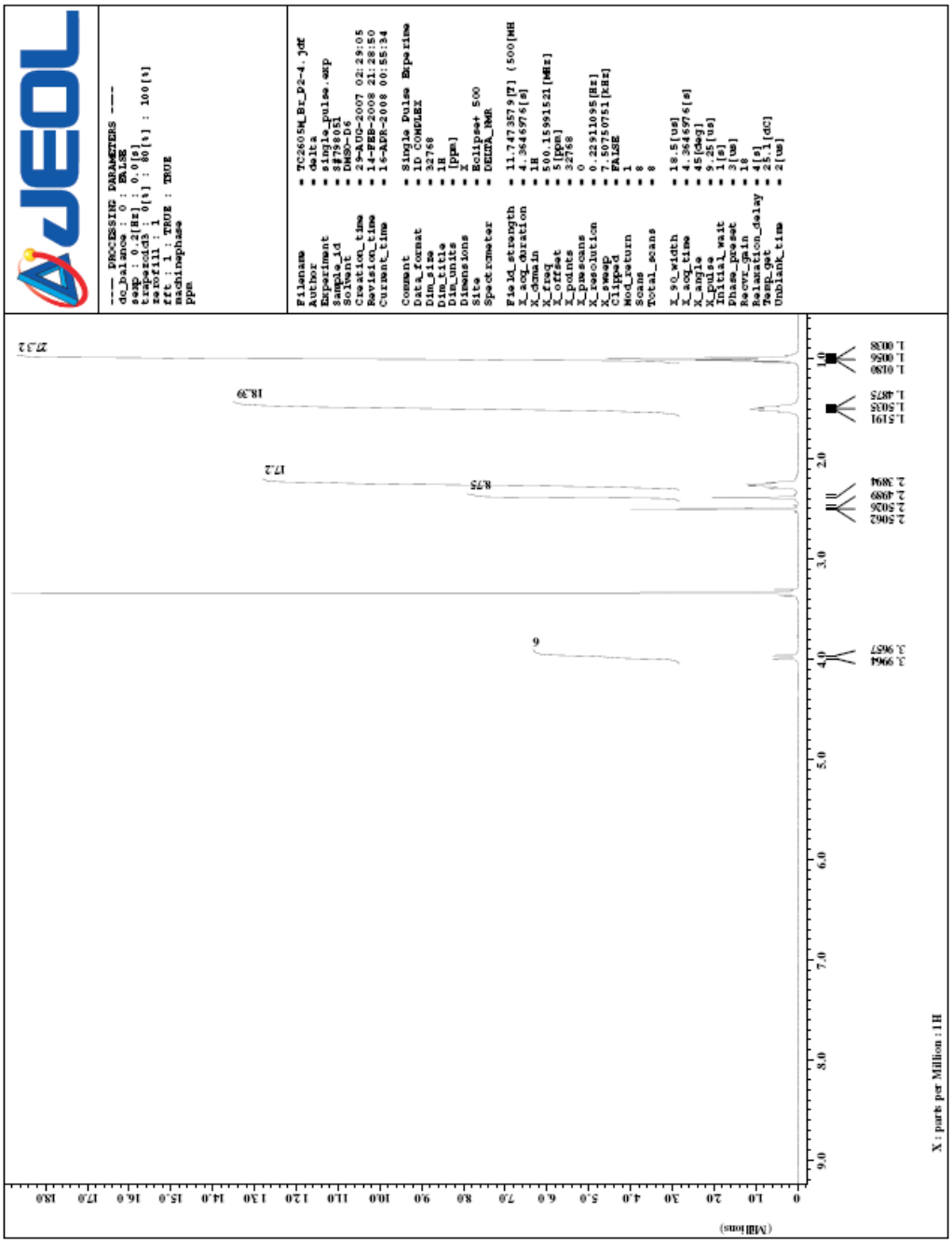
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
semp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

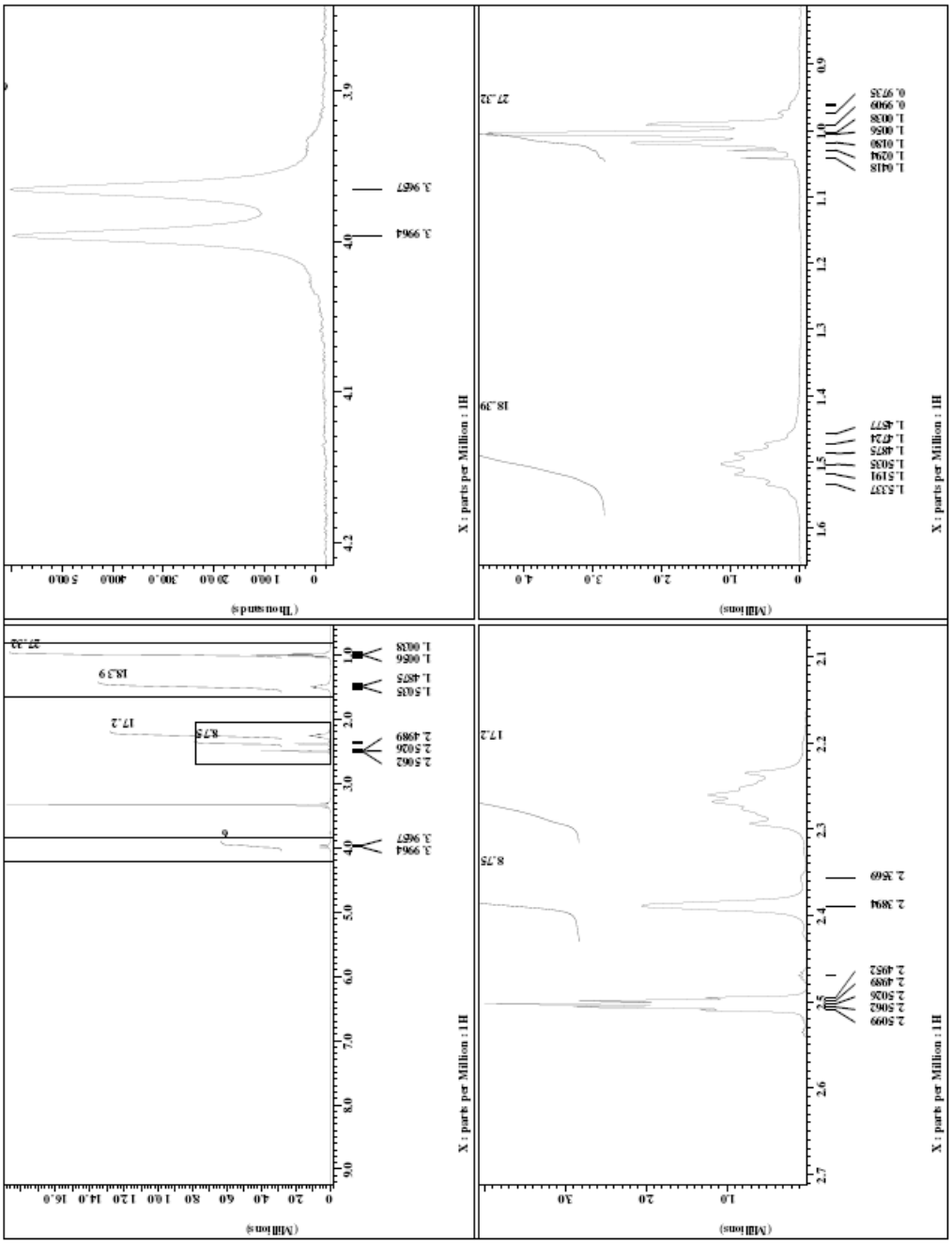
Filename	= TC2605C_Br_P-5.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#804477
Solvent	= DMSO-D6
Creation_time	= 29-AUG-2007 02:38:58
Revision_time	= 14-FEB-2008 19:02:01
Current_time	= 16-APR-2008 00:52:02
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 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	= 20
Relaxation_delay	= 4[s]
Temp_get	= 25.2[dC]
Unblank_time	= 2[us]


X : parts per Million : 1H
(Millions)
9.6229
7.9161
7.8717
7.4397
7.4328
7.4269
5.6600
5.5598
3.3999
3.3665
2.5649
2.5612
2.5575
2.3372
2.9719
6.06
8.59
6.02
6.66
3
9.21
2.97
3.19
7.9198
7.9161
7.9129
7.8749
7.8717
7.8680
7.5070
7.4997
7.4924
7.4828
7.4397
7.4328
7.4269
6.06
8.59
5.6600
5.5598
6.07
6.05
2.3372
9.21

APPENDIX 21

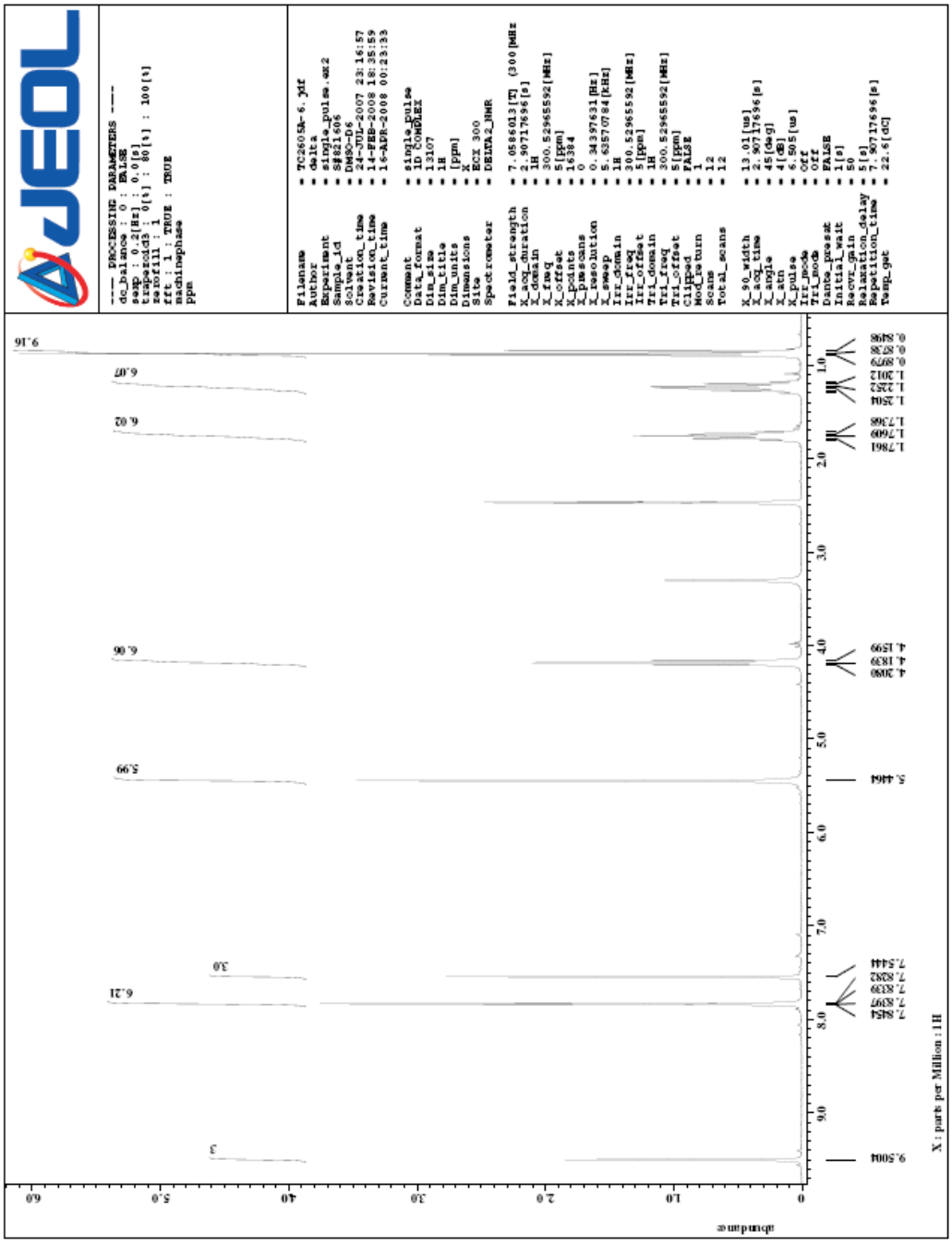
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(TRIPROPYLPHOSPHONIUM)METHYL}MESITYLENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]

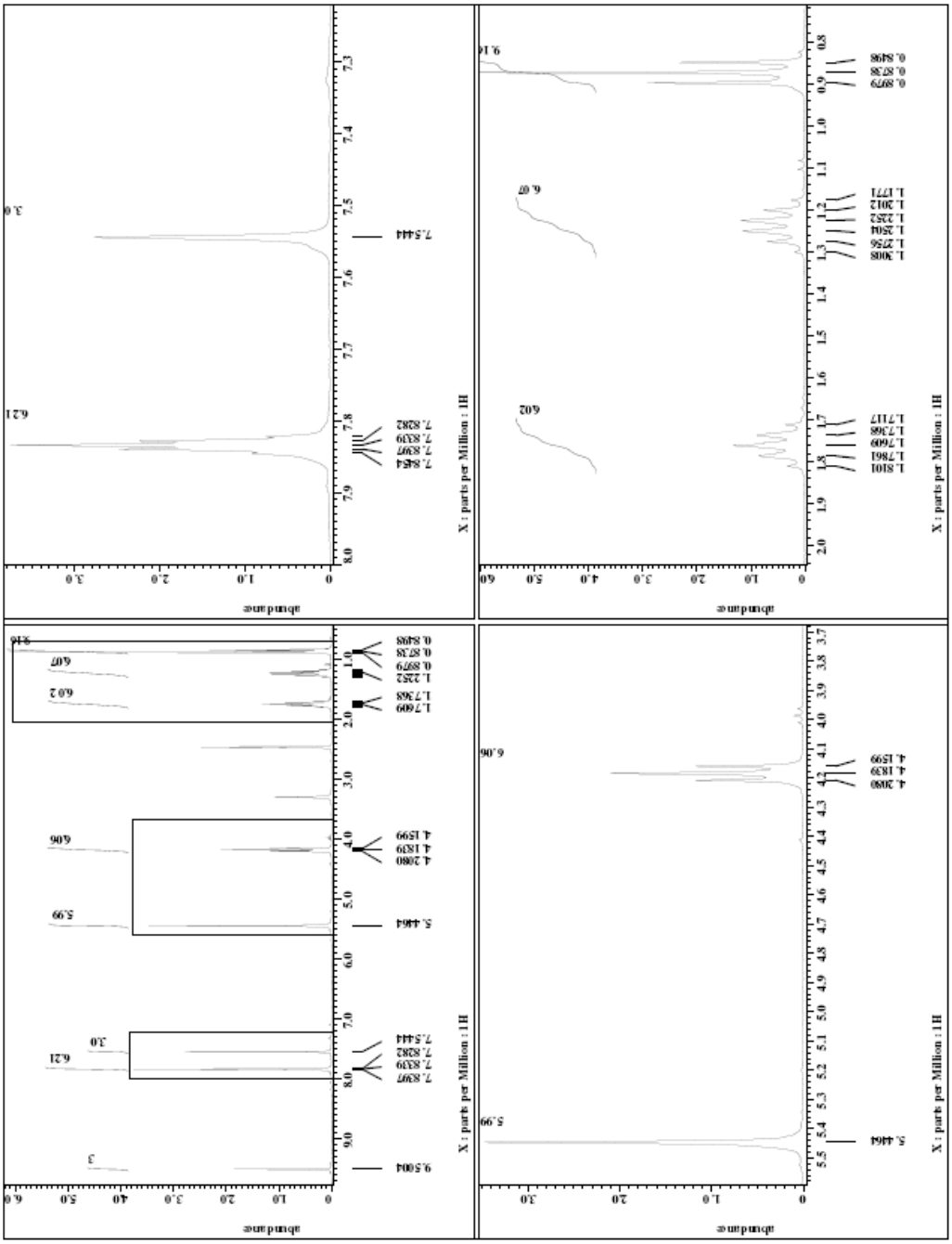

JEOL
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
exp_no : 0 : 0 [s]
temperatd : 0[s] : 80[s] : 100[s]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = TC2605M_Br_D2-4.jdf
Author = data
Experiment = single_pulse.exp
Sample_id = S#758051
Solvent = DMSO-D6
Creation_time = 29-AUG-2007 02:29:05
Revision_time = 14-FEB-2008 21:28:50
Current_time = 16-APR-2008 00:55:34
Comment = Single Pulse Experiment
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse: 500
Spectrometer = DELTA_NMR
Field_strength = 11.747357 9[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_pseudo = 0
X_resolution = 0.2291095[Hz]
X_sweep = 7.5759751[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]
X_delay_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
(Billions)
X : parts per Million : 1H


X : parts per Million : 1H
(Million ions)
(Thousands)
3.9964
3.9657
2.5062
2.5026
2.4989
1.5025
1.4875
1.0056
1.0028
8.75
17.2
18.39
27.32
2.5099
2.4952
2.3894
2.3569
1.5537
1.5191
1.4724
1.4577
1.0418
1.0294
1.0180
0.9909
0.9735

APPENDIX 22

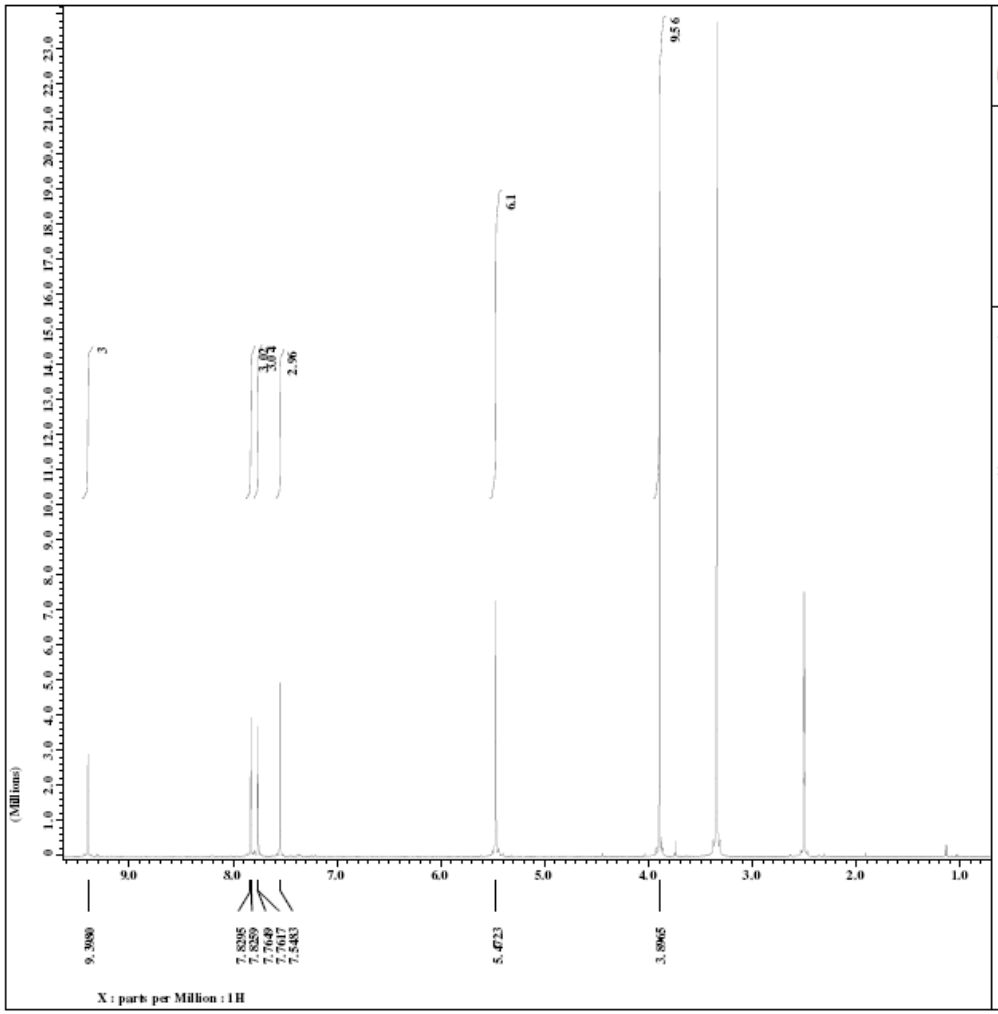
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BUTYLIMIDAZOLIUM)METHYL}BENZENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]


JEOL
---- PROCESSING PARAMETERS ----
do_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
autoinphase
ppm
Filename = TC2605A-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#821606
Solvent = DMSO-D6
Elevation_time = 24-JUL-2007 23:16:57
Acquisition_time = 14-FEB-2008 18:35:59
Current_time = 16-APR-2008 00:23:33
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 = 7.058601[T] (300[MHz
X_acq_duration = 2.907176696[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_factorn = 1
Scans = 12
Total_scans = 12
X_90_width = 13.01[us]
X_acq_time = 2.907176696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Decpl_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 7[s]
Repetition_time = 7.907176696[s]
Temp_get = 22.6[dC]
abundance
X : parts per Million : 1H
9.16
6.07
6.02
6.00
5.99
6.21
3.0
3
9.5004
7.8454
7.8397
7.8339
7.8282
7.5444
5.4641
4.3080
4.1839
4.1599
1.7861
1.7609
1.7368
1.2564
1.2352
1.2012
0.8979
0.8738
0.8498


X : parts per Million : 1H
abundance
9.5004
7.8397
7.8329
7.8282
7.5444
5.4464
4.2080
4.1839
4.1599
L.7609
L.7368
L.2252
0.8979
0.8738
0.8498
6.21
3.0
5.99
6.06
6.02
6.07
9.16
3

APPENDIX 23

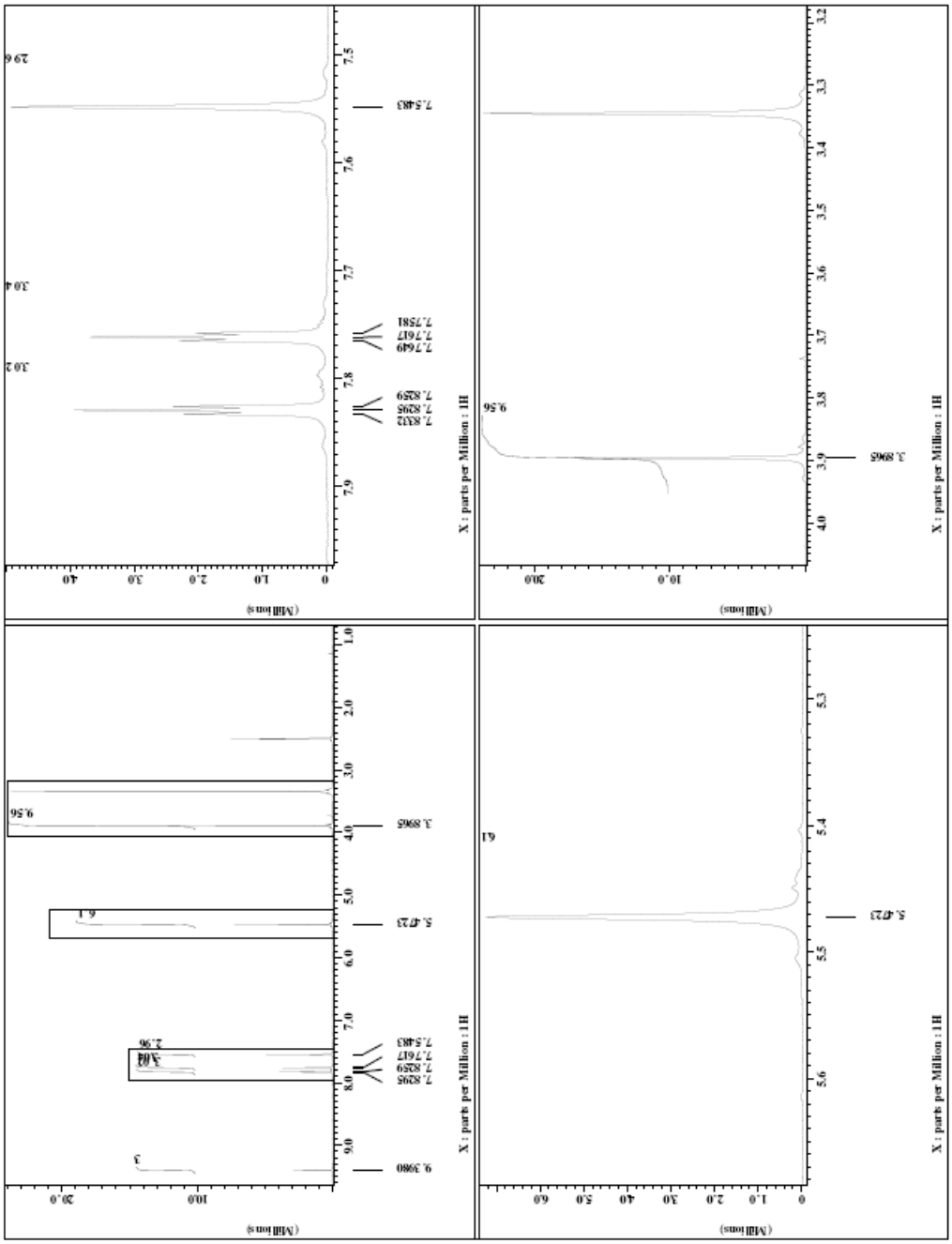
^{1}H NMR SPECTRA OF
3,5-{TRIS(3-N-METHYLIMIDAZOLIUM)METHYL}BENZENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

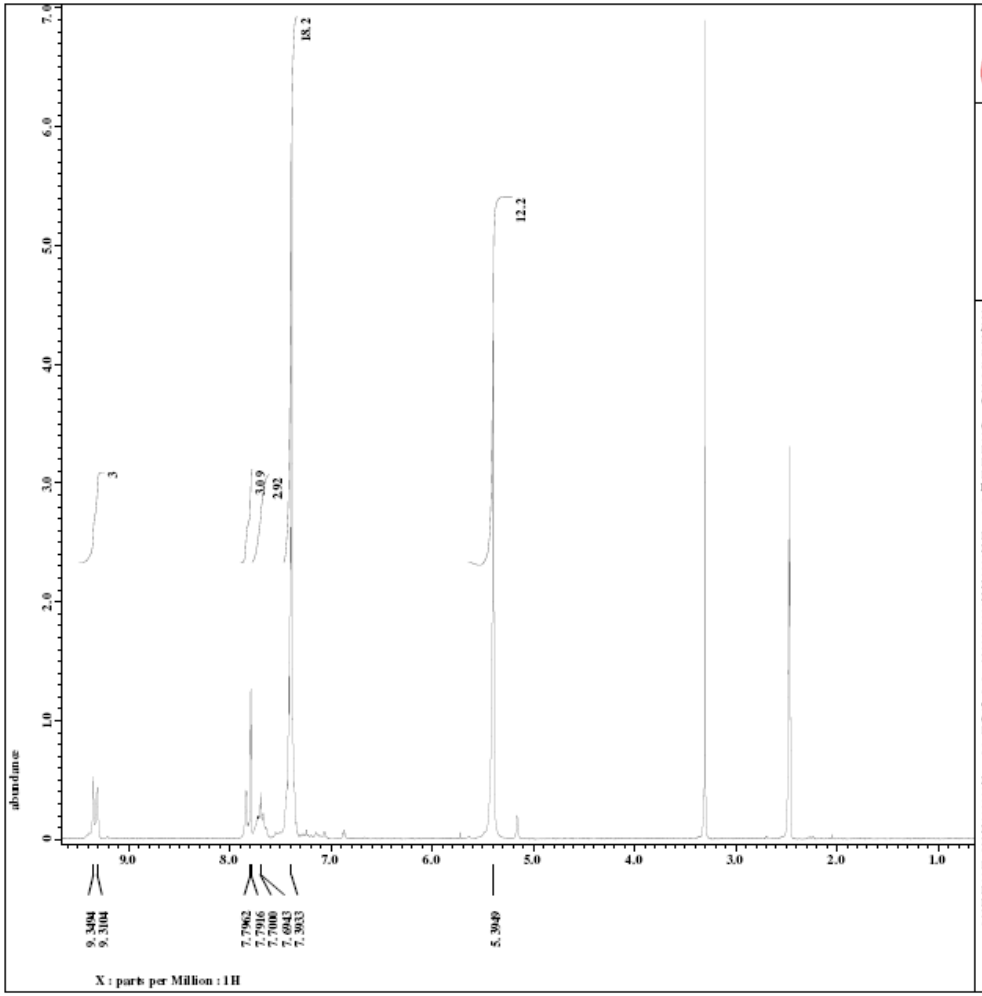
```
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
Filename            = 7C2605E_Br_P-4.jdf
Author              = delta
Experiment          = single_pulse.exp
Sample_id           = S#778310
Solvent             = DMSO-D6
Creation_time       = 29-AUG-2007 01:55:19
Revision_time       = 14-FEB-2008 18:44:33
Current_time        = 16-APR-2008 00:37:53

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          = 20
Relaxation_delay    = 4[s]
Temp_get            = 24.4[dC]
Unblank_time        = 2[us]
```


X : parts per Million : 1H
(Millions)
9.3980
7.8295
7.8259
7.7617
7.5483
5.4723
3.8965
9.56
3.04
2.96
6.1
3
7.8312
7.7649
7.7581
10.2
10.4
29.6
61

APPENDIX 24

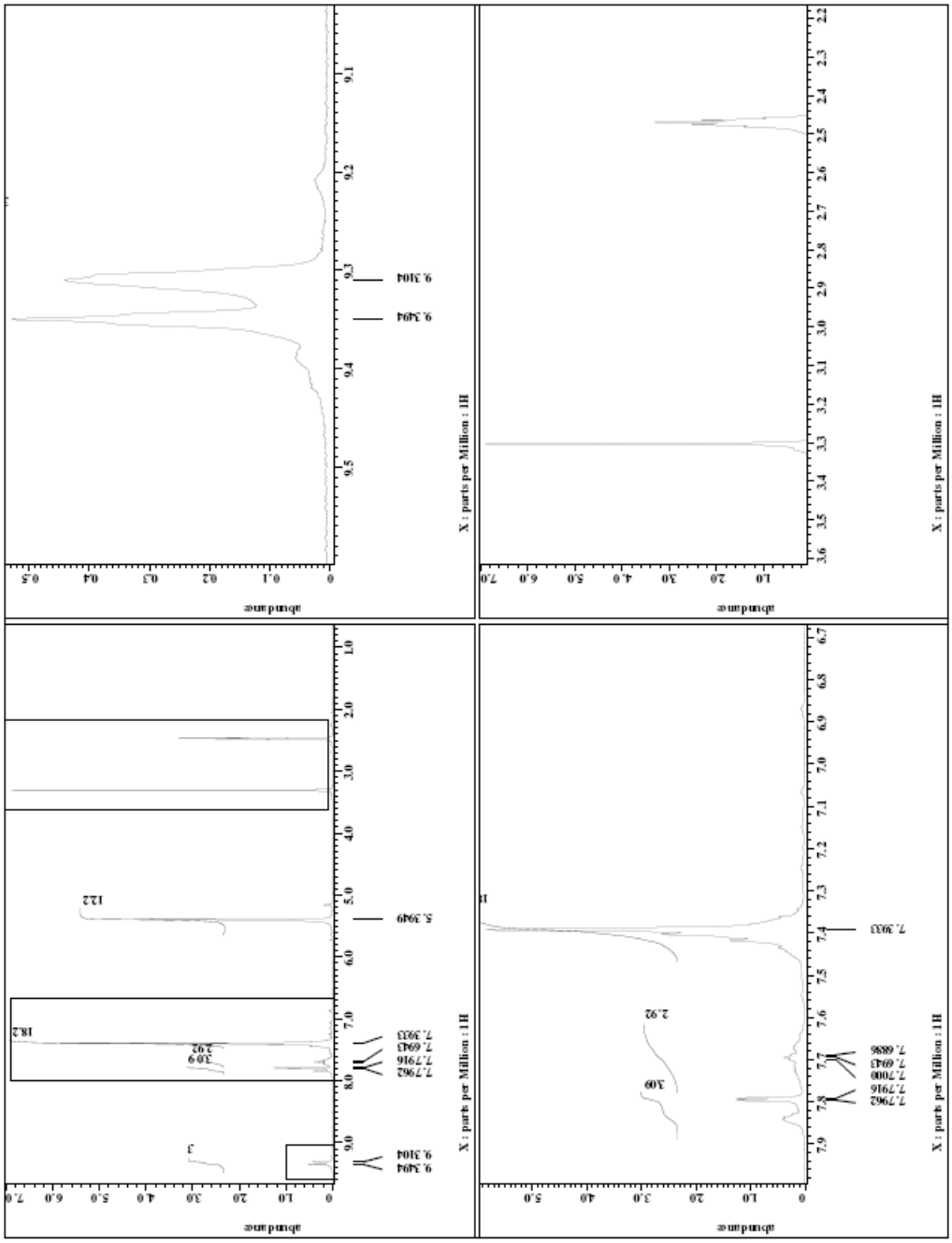
^{1}H NMR SPECTRA OF
3,5-{TRIS(3-N-BENZYLIMIDAZOLIUM)METHYL}BENZENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

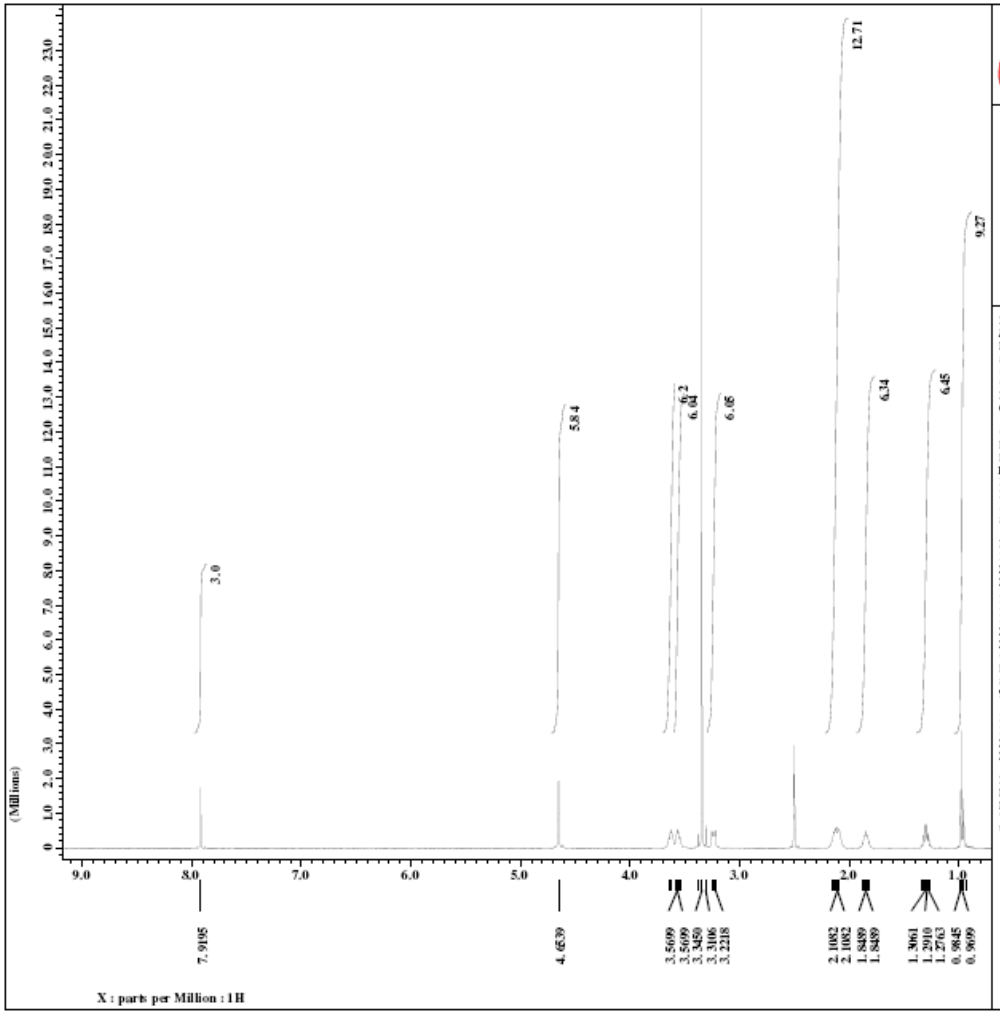
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Filename	= new k-4.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#828326
Solvent	= DMSO-D6
Creation_time	= 27-NOV-2007 23:24:12
Revision_time	= 14-FEB-2008 18:47:59
Current_time	= 16-APR-2008 00:40:24
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	= 23.8[dC]


X : parts per Million : 1H
abundance
9.3494
9.3104
7.7962
7.7916
7.6943
7.3833
5.3949
3.09
2.92
18.2
12.2
7.3833
7.7962
7.7916
7.7100
7.6943
7.6886
3.09
2.92

APPENDIX 25

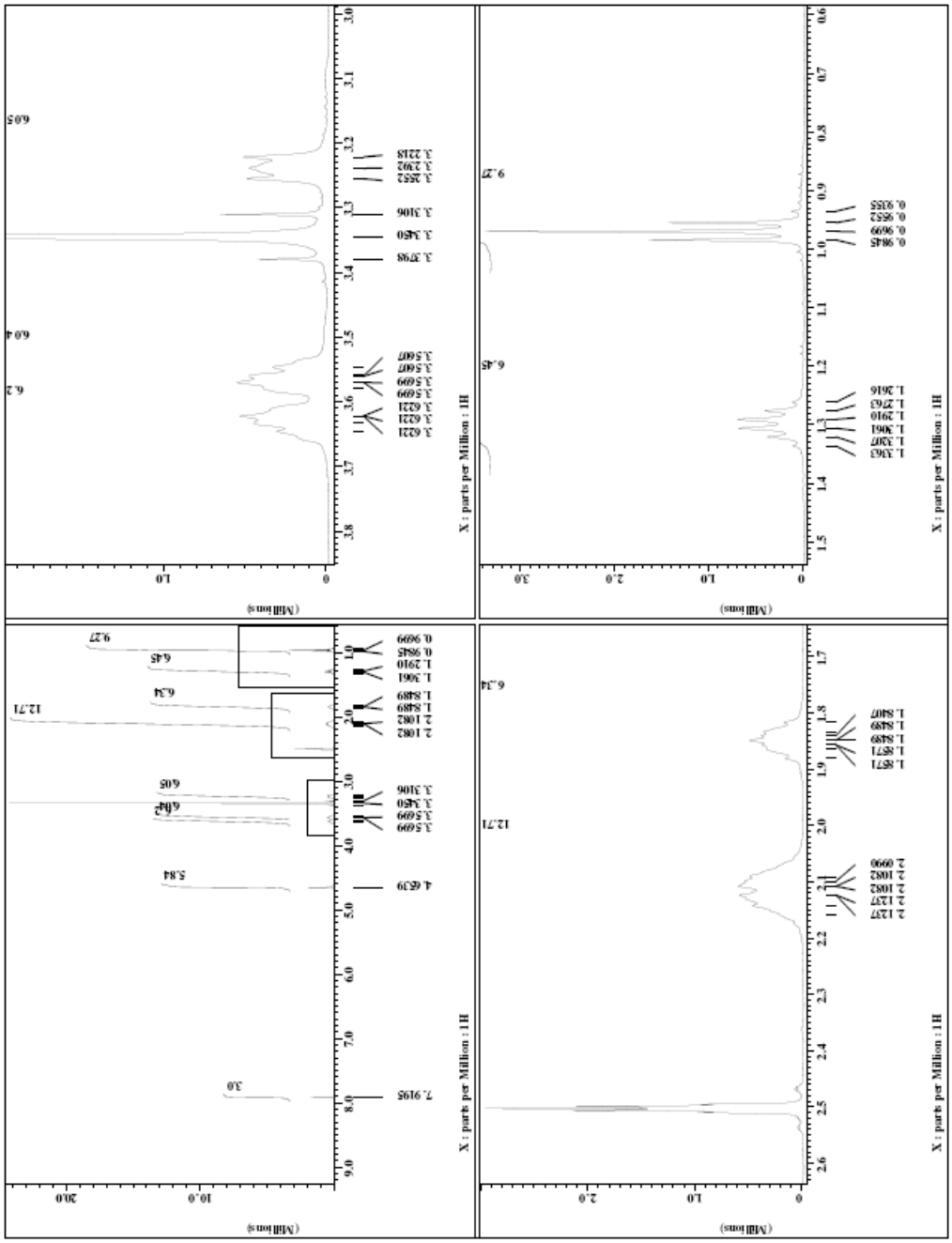
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(BUTYPYRROLIDINIUM)METHYL}BENZENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

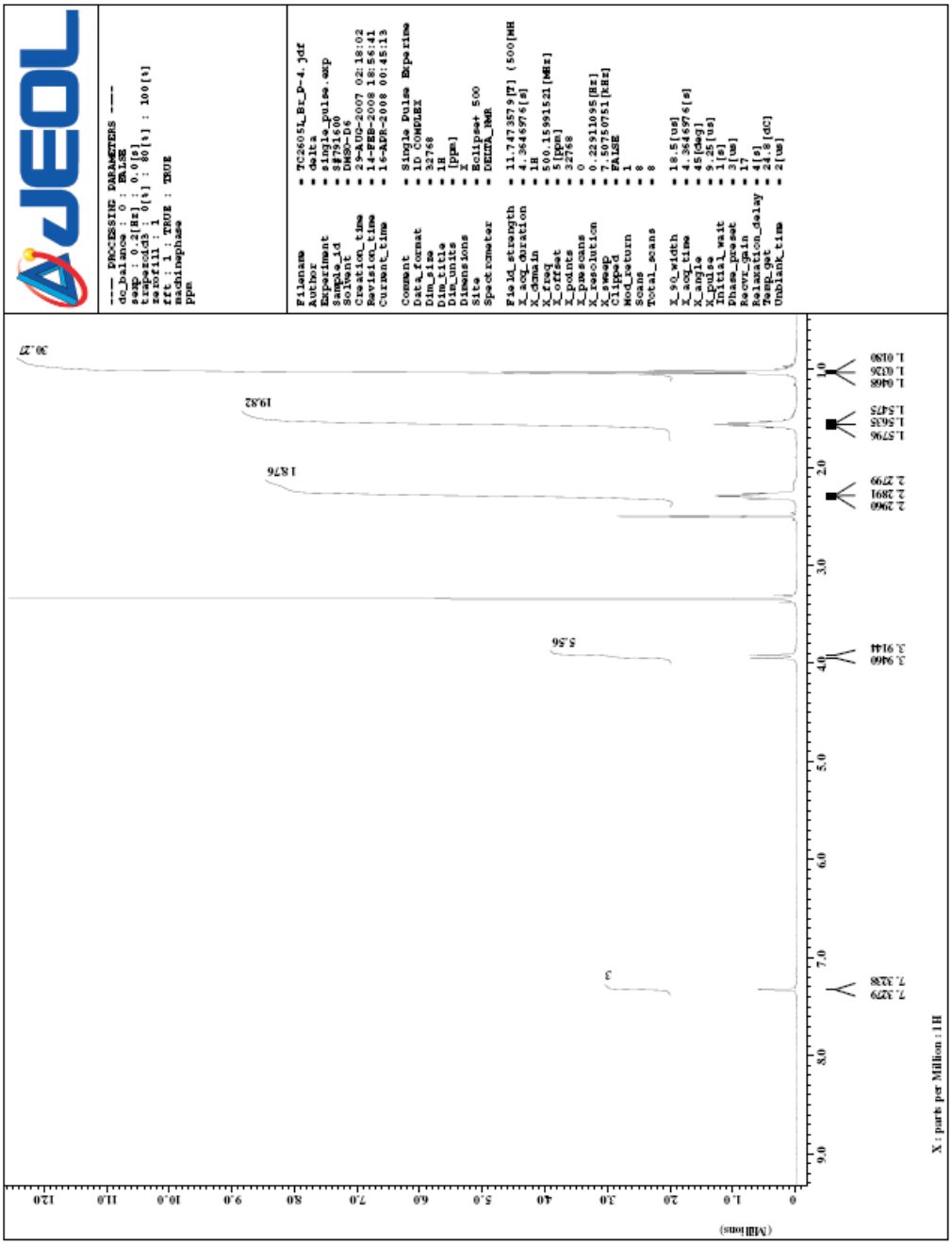
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

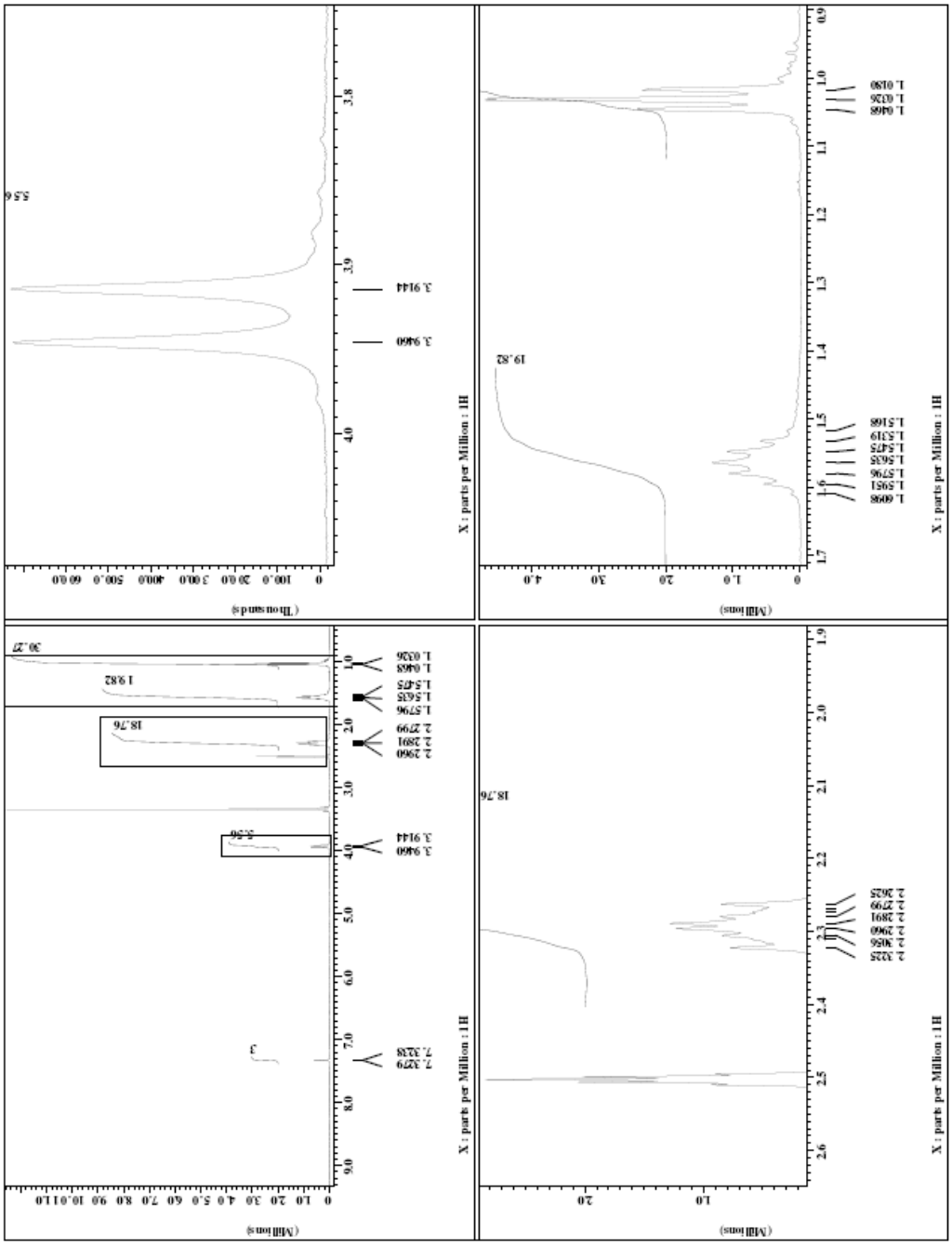
Filename	= 7C2605D_Br_P-5.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#785244
Solvent	= DMSO-D6
Creation_time	= 29-AUG-2007 02:07:27
Revision_time	= 14-FEB-2008 21:21:50
Current_time	= 16-APR-2008 00:42:43
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 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
(Mill ions)
2.1237
2.1237
2.1082
2.1082
2.0990
12.71
1.8571
1.8571
1.8489
1.8489
1.8407
6.34
1.3363
1.3307
1.3061
1.2910
1.2763
1.2616
6.45
0.9845
0.9699
0.9652
0.9555
9.27
7.9195
3.0
4.6539
5.84
3.5699
3.5699
3.4860
3.3106
6.02
6.05
2.1082
2.1082
1.8489
1.8489
1.8407
12.71
1.3061
1.2910
0.9845
0.9699
6.45
9.27
6.2
6.04
3.6221
3.6221
3.5699
3.5699
3.5607
3.5607
3.3798
3.3106
3.3460
3.2852
3.2392
3.2218
6.05

APPENDIX 26

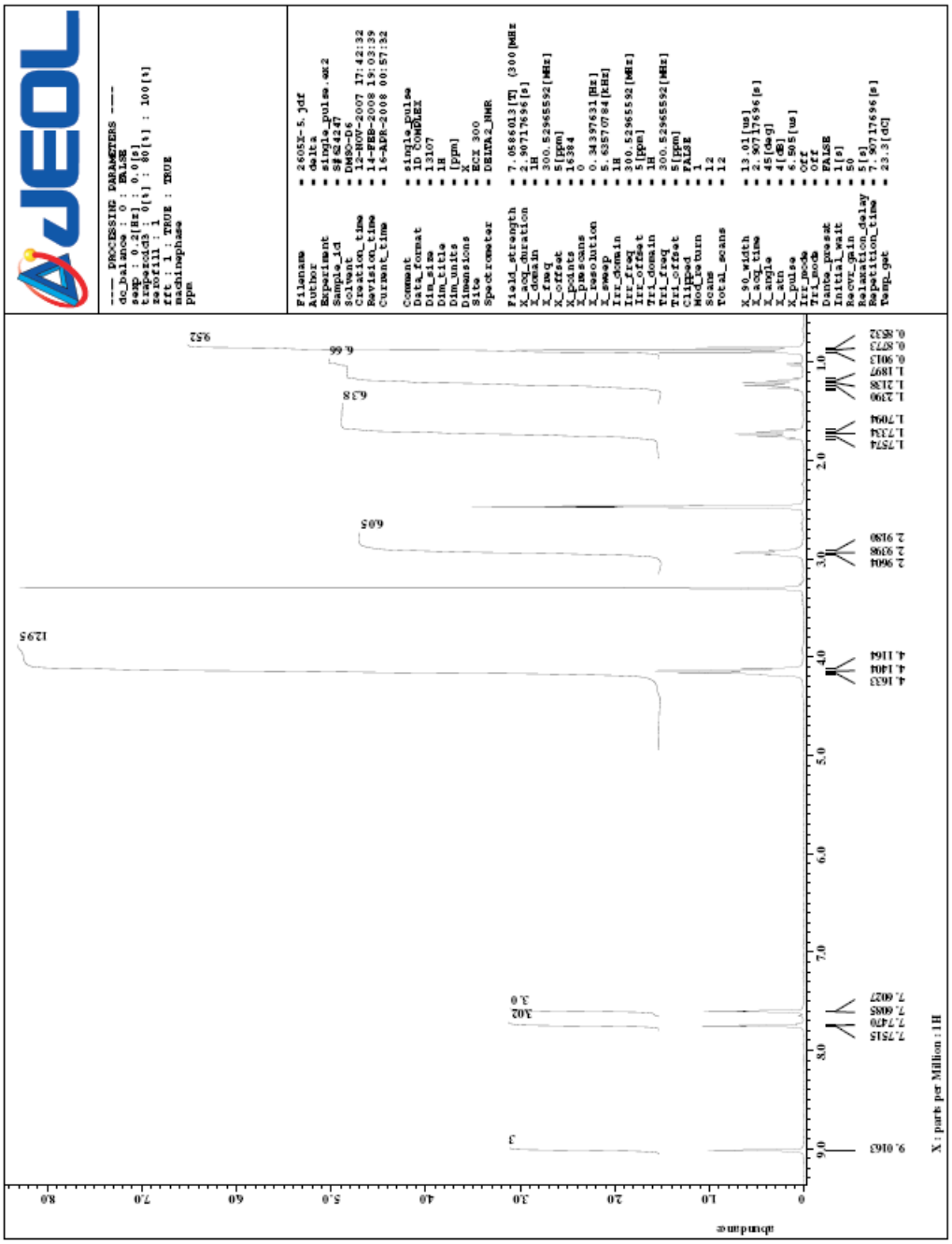
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(TRIPROPYLPHOSPHONIUM)METHYL}BENZENE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]

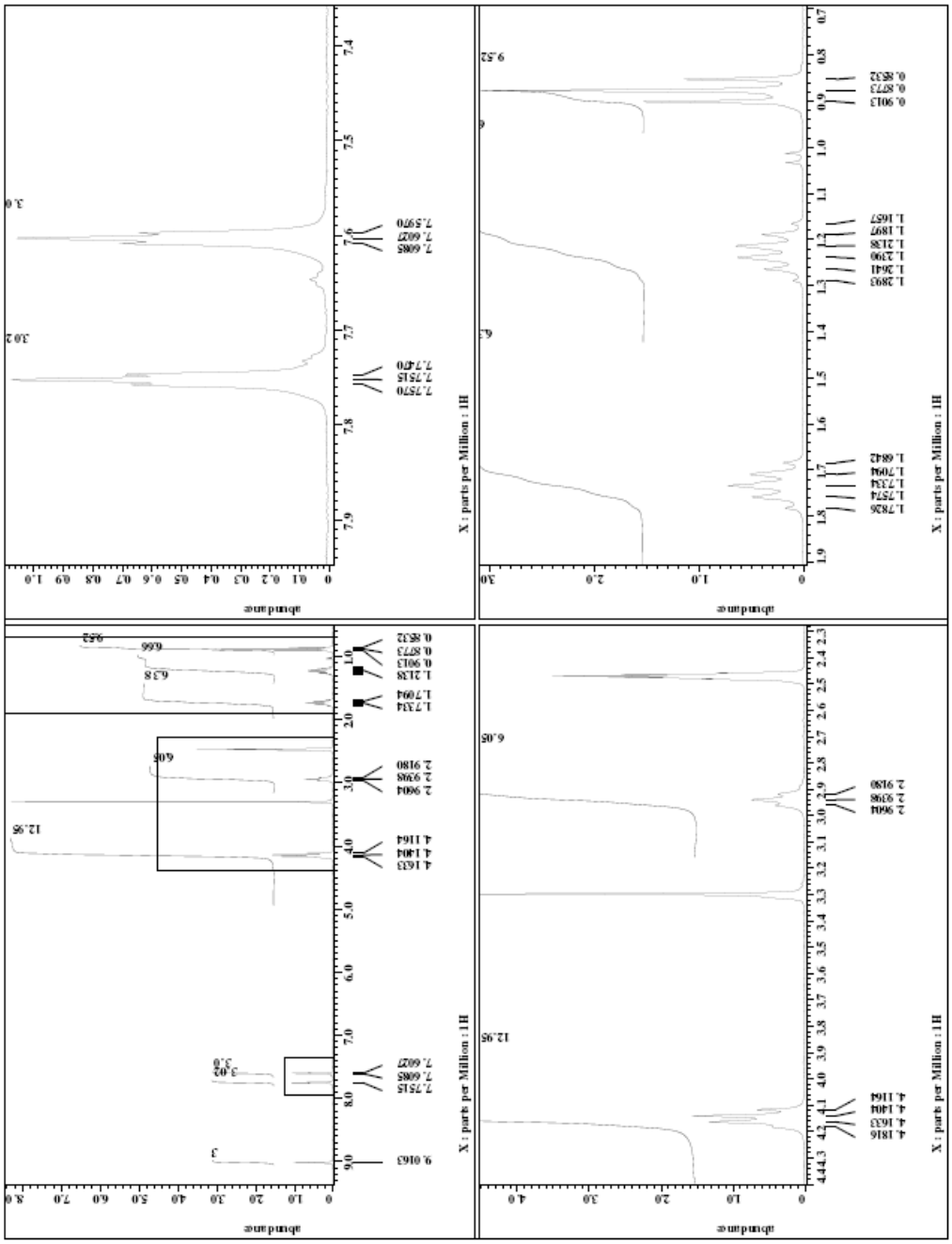

JEOL
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 1 0[%] : 80[%] : 100[%]
zerofill : 1
fft : TRUE : TRUE
machinephase
ppm
Filename = 7C26051_Br_D-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = $F791600
Solvent = DMSO-D6
Creation_time = 29-AUG-2007 02:18:02
Revision_time = 14-FEB-2008 18:56:41
Current_time = 16-APR-2008 00:45:13
Comment = Single Pulse Experiment
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.747357 9[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 = 7.5750751[KHz]
X_type = 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 = 24.8[dC]
Unblank_time = 2[us]
30.27
19.82
18.76
5.56
3
7.3279
7.3288
3.9460
3.9144
2.2960
2.2891
2.2799
1.5796
1.5635
1.5475
1.0468
1.0126
1.0180
(Million)
X : parts per Million : 1H


(Thousands)
X : parts per Million : 1H
3.9144
3.9460
5.56
(Thousands)
X : parts per Million : 1H
7.3279
7.3238
3.9144
3.9460
5.56
2.2960
2.2891
2.2799
1.5796
1.5635
1.5475
1.0468
1.0326
18.76
1.982
30.27
(Thousands)
X : parts per Million : 1H
2.3225
2.3056
2.2960
2.2891
2.2799
2.2625
18.76
(Thousands)
X : parts per Million : 1H
1.6098
1.5951
1.5796
1.5635
1.5475
1.5319
1.5168
19.82
1.0468
1.0126
1.0190

APPENDIX 27

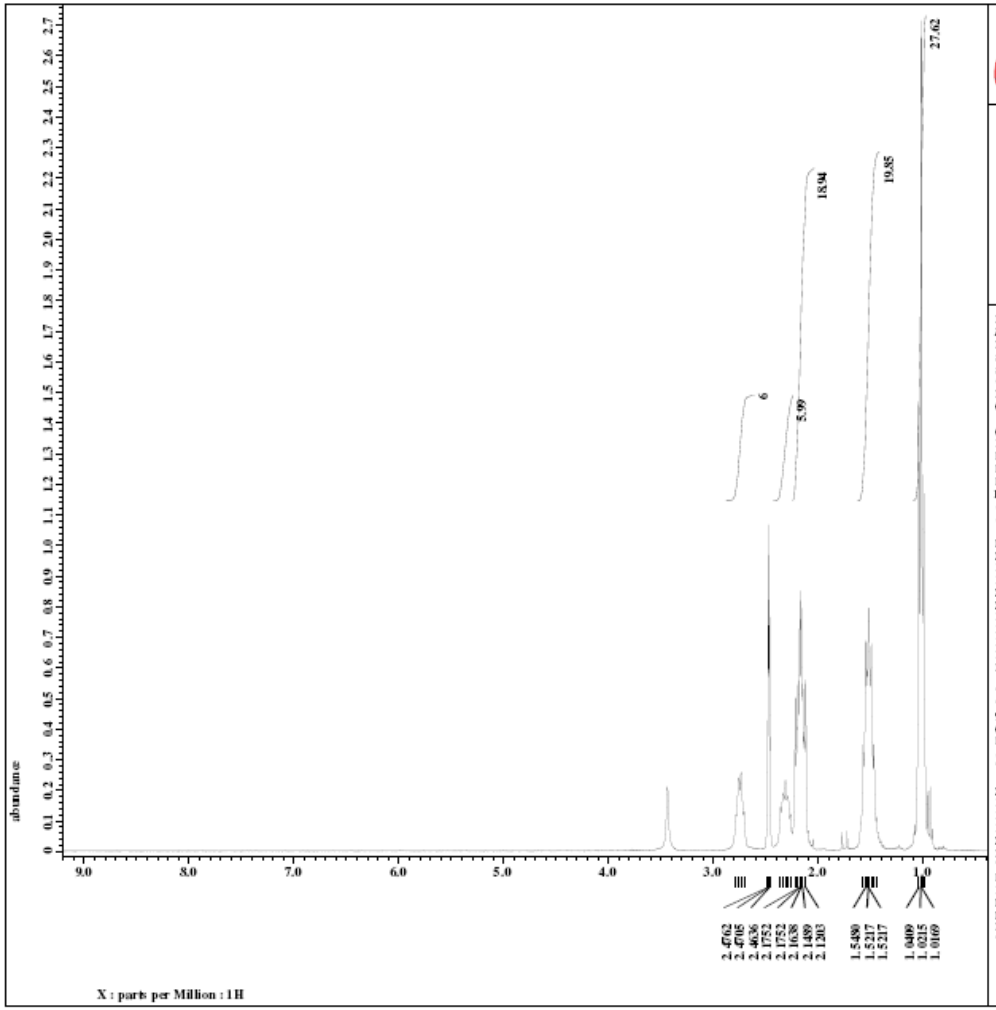
^{1}H NMR SPECTRA OF
TRIS(2-(3-N-BUTYLIMIDAZOLIUM)ETHYL)AMINE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]


JEOL
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
exp : 0.2[Hz] : 0.0[s]
trapezoid : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = 26052-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SHS4247
Solvent = DMSO-D6
Creation_time = 12-NOV-2007 17:42:32
Revision_time = 14-FEB-2008 19:03:39
Current_time = 16-APR-2008 00:57:32
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECZ 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.9071696[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]
X_width = 15
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Irr_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_Pulse = 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 = off
Decoupler = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.9071696[s]
Temp_get = 23.3[dC]
952
6.66
6.38
6.05
1295
3
3.02
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0163
7.7515
7.7420
7.6085
7.6027
4.1633
4.1404
4.1164
2.9604
2.9398
2.9180
1.7574
1.7334
1.7094
1.2390
1.2138
1.1897
0.9013
0.8573
0.8502
X : parts per Million : 1H
Intensity


X : parts per Million : 1H
9.0163
7.7570
7.7515
7.7470
7.6085
7.6027
7.5970
4.1816
4.1633
4.1404
4.1164
2.9604
2.9398
2.9180
1.7826
1.7574
1.7334
1.7094
1.6842
0.9013
0.8773
0.8532
12.95
6.05
3.02
3.0
6.38
6.06
9.52
6
6.2
3.0 2

APPENDIX 28

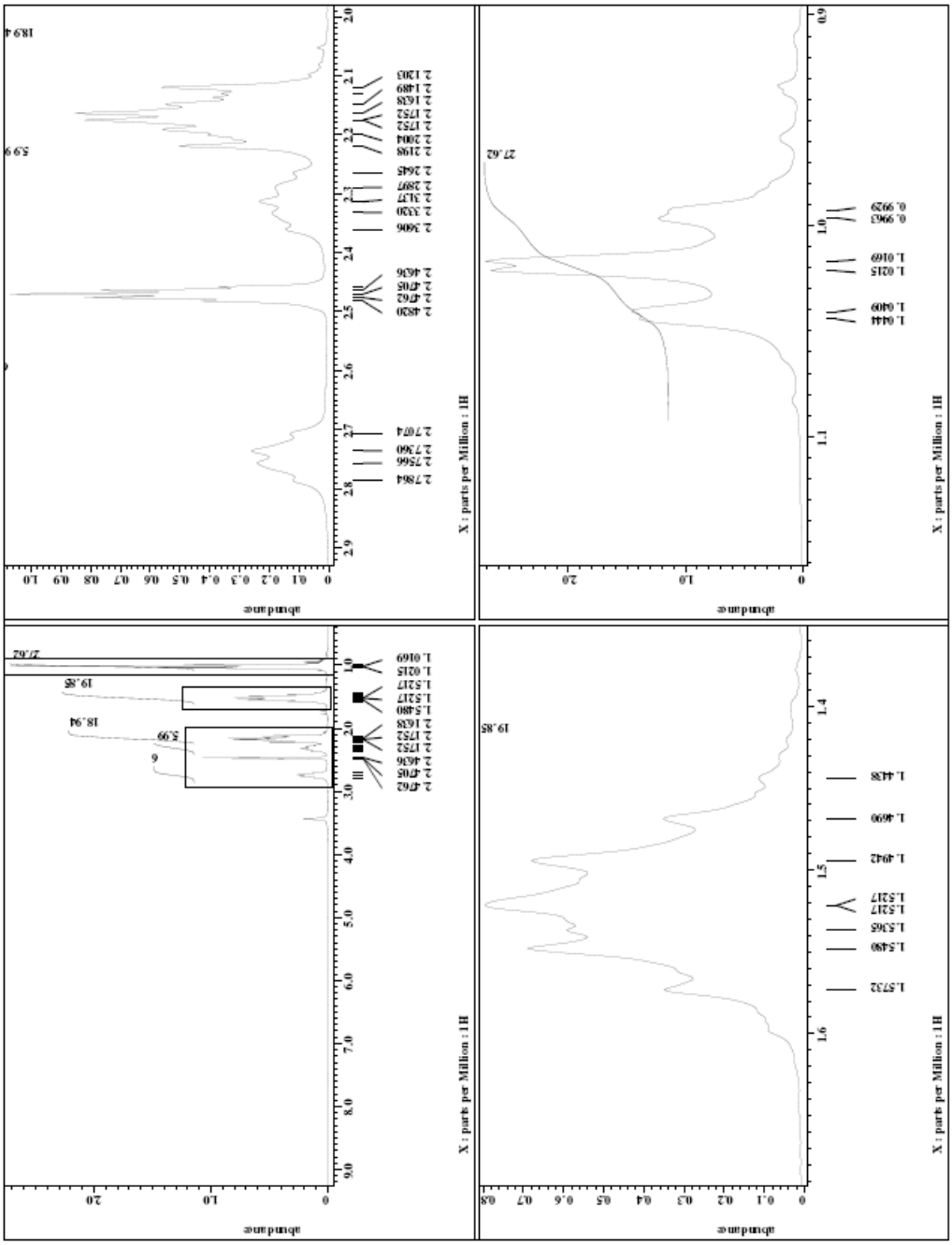
^{1}H NMR SPECTRA OF
TRIS(2-(TRIPROPYLPHOSPHONIUMMETHYL)ETHYL)AMINE
TRI[BIS(TRIFLUOROMETHYLSULFONYL)IMIDE]



JEOL

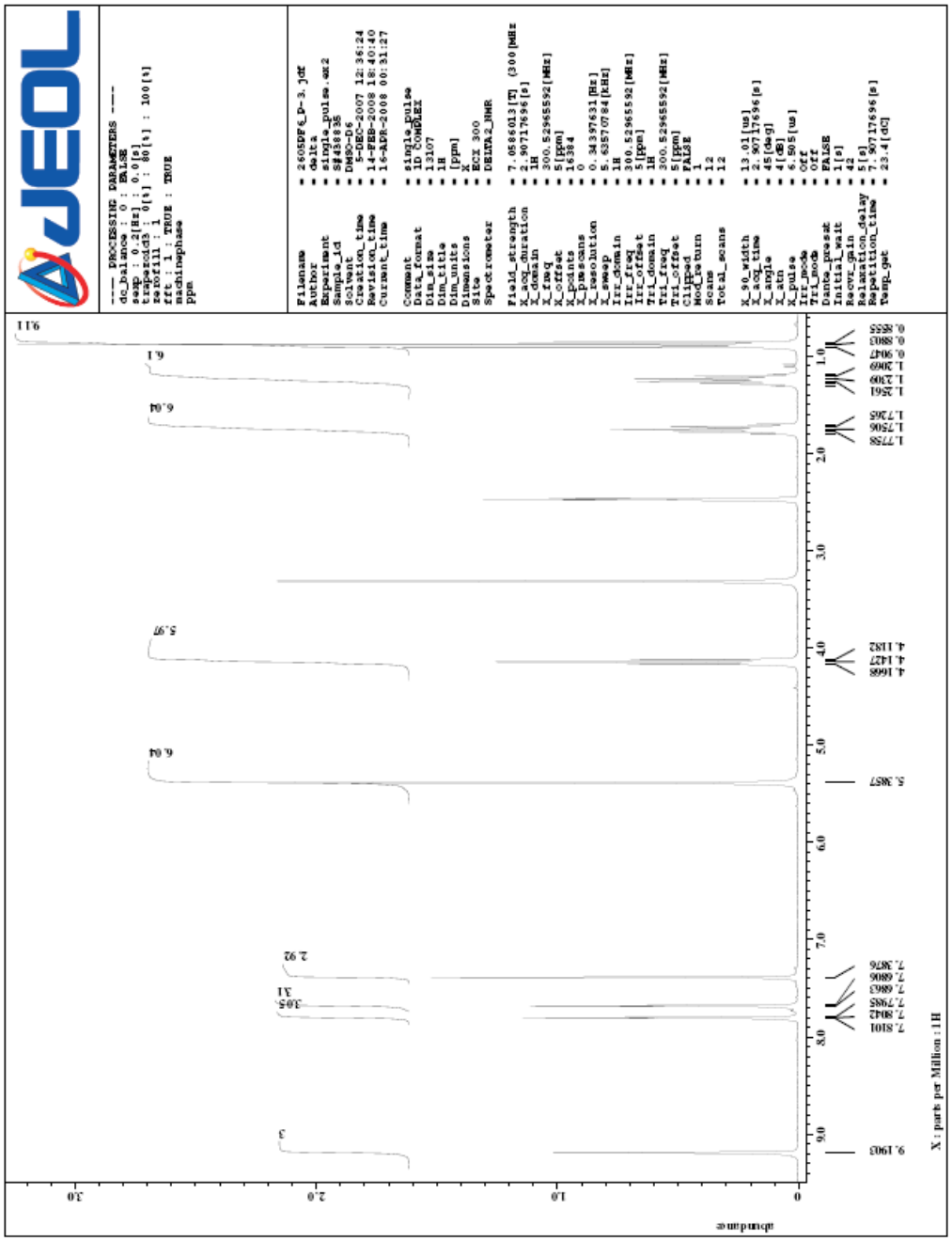
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

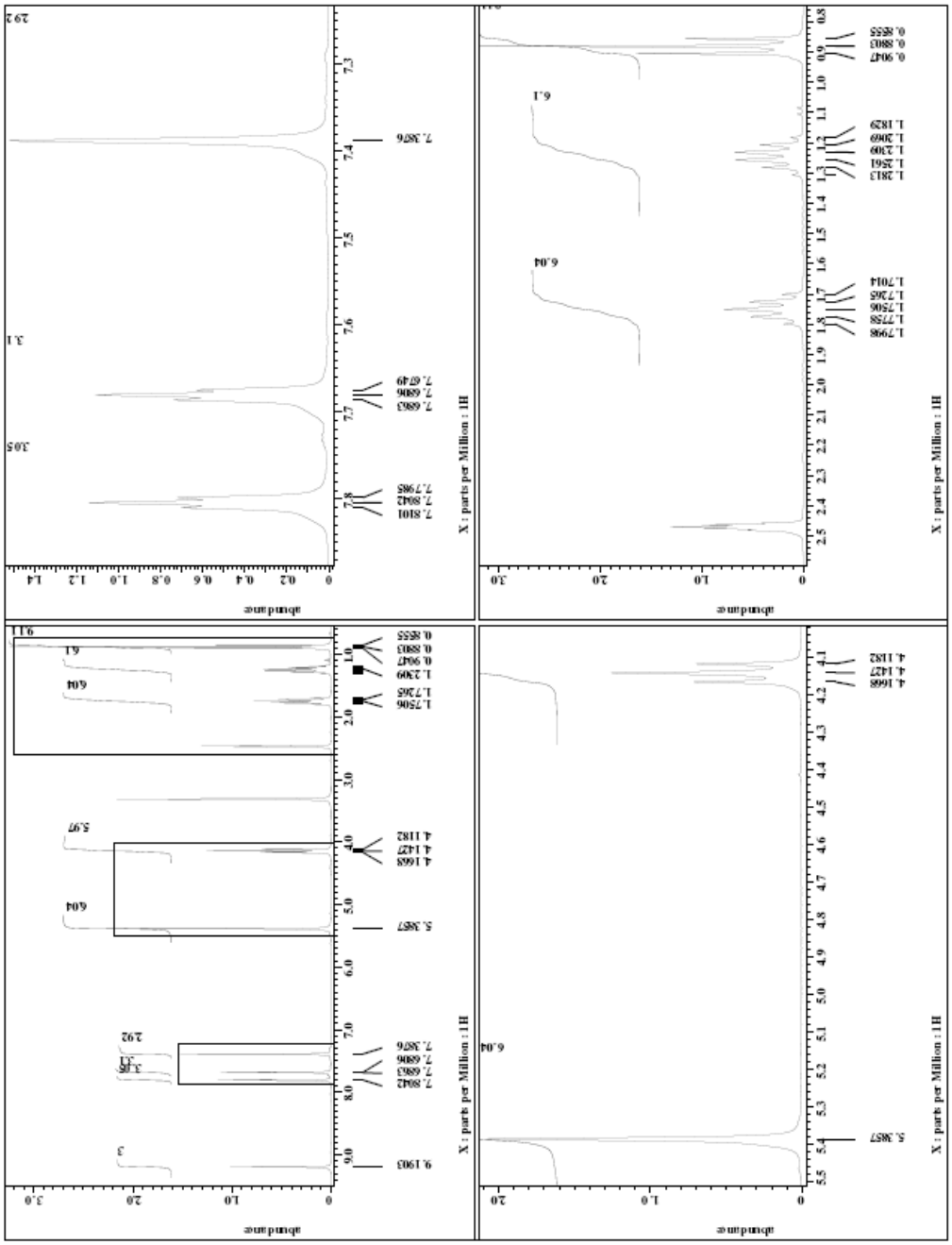
Filename	= 2605Y-7.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#628265
Solvent	= DMSO-D6
Creation_time	= 12-NOV-2007 17:49:49
Revision_time	= 16-APR-2008 01:07:39
Current_time	= 16-APR-2008 01:08:00
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [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	= 40
Relaxation_delay	= 5[s]
Repetition_time	= 7.90717696[s]
Temp_get	= 23.4[dC]


X : parts per Million : 1H
abundance
27.62
19.85
18.94
5.99
6
1.5732
1.5480
1.5365
1.5217
1.4942
1.4690
1.4438
1.0444
1.0409
1.0215
1.0169
0.9963
0.9929
2.7844
2.7566
2.7360
2.7074
2.4820
2.4706
2.4662
2.4656
2.3406
2.3320
2.3177
2.2897
2.2645
2.2198
2.2004
2.1752
2.1638
2.1489
2.1305
189.4
59.9

APPENDIX 29

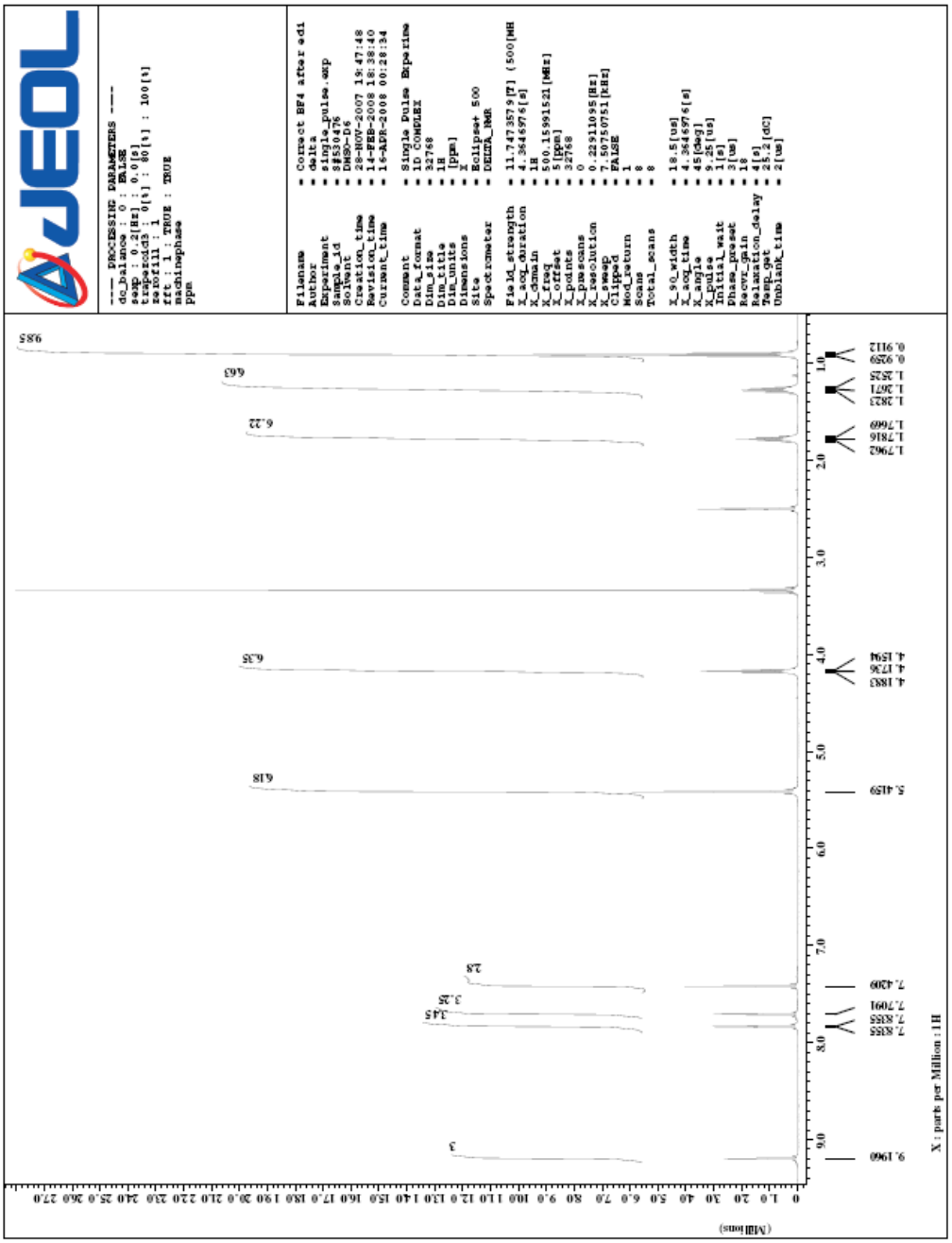
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BUTYLIMIDAZOLIUM)METHYL}BENZENE
TRIS(HEXAFLUOROPHOSPHATE)

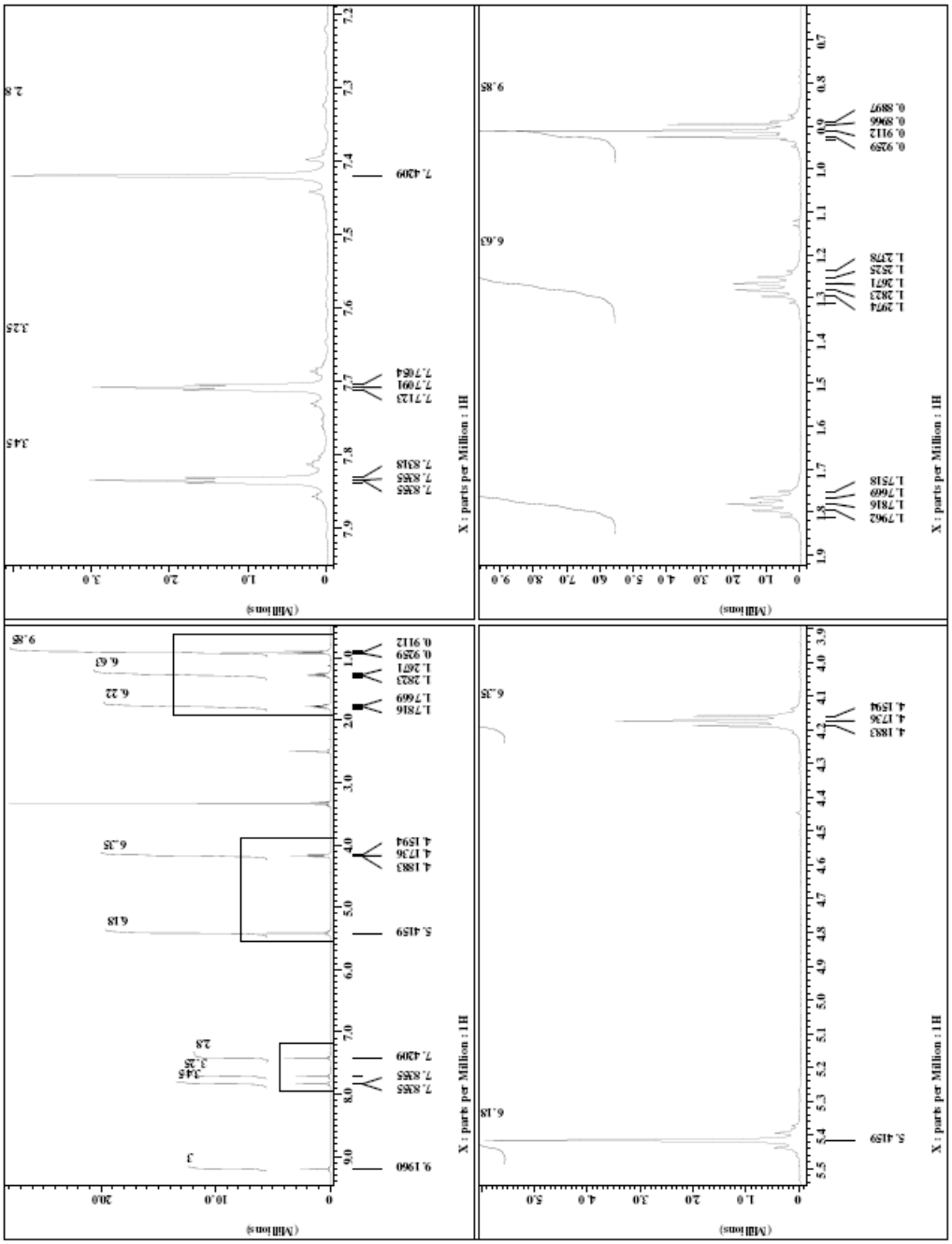

JEOL
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
exp : 0.2[Hz] : 0.0[s]
exponent : 1 : 0[s]
refoffset : 1 : 60[s] : 100[%]
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = 2605PF6_D-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SS438835
Solvent = DMSO-D6
Creation_time = 5-DEC-2007 12:36:24
Revision_time = 14-FEB-2008 18:40:40
Current_time = 15-APR-2008 00:31:27
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_pulse_cons = 0.34397631[Hz]
X_resolution = 5.63570784[kHz]
X_sweep = 1H
Irr_domain = 300.52965592[MHz]
Irr_freq = 5[ppm]
Irr_offset = 1H
Tri_domain = 300.52965592[MHz]
Tri_freq = 5[ppm]
Tri_offset = FALSE
Clipped = 1
Mode_turn = 12
Scans = 12
Total_scans = 12
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_ath = 4[dB]
X_pulse = 6.505[us]
Tri_power = off
Tri_mode = off
Decpl_present = FALSE
Initial_wait = 1[s]
Recv_gain = 42
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.4[dC]
9.11
6.1
6.04
5.97
6.04
2.92
3.1
3.05
3
9.1903
7.8101
7.8042
7.7985
7.6863
7.6806
7.3876
5.3857
4.1668
4.1427
4.1182
1.7758
1.7506
1.7345
1.2561
1.2199
1.3069
0.9047
0.8803
0.8555
X : parts per Million : 1H
absorbance
0
1.0
2.0
3.0


X : parts per Million : 1H
abundance
9.1903
7.8101
7.8042
7.7985
7.6863
7.6806
7.6749
7.3876
5.3857
4.1668
4.1427
4.1182
1.7998
1.7758
1.7506
1.7365
1.7014
1.2813
1.2661
1.2309
1.2069
1.1829
0.9047
0.8803
0.8555
6.04
6.1
3.05
3.1
2.92
5.97
9.11

APPENDIX 30

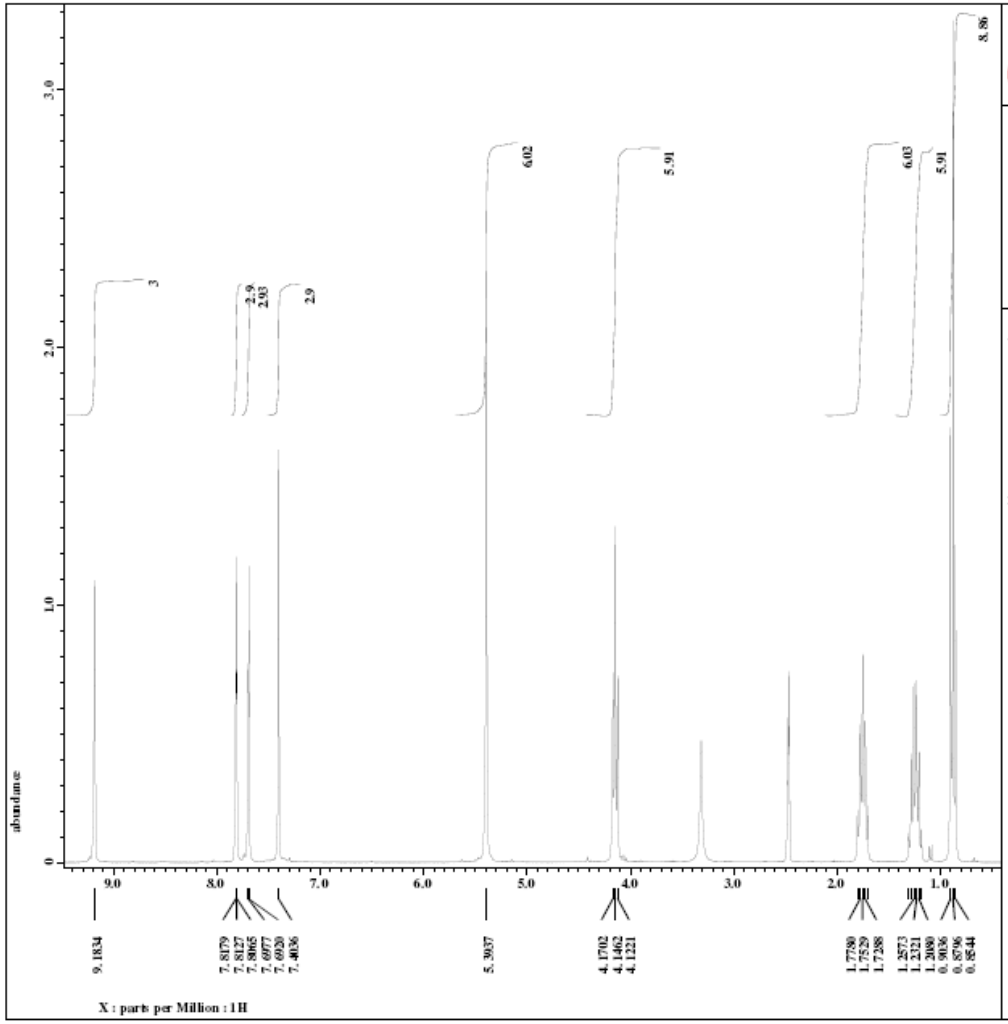
^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BUTYLIMIDAZOLIUM)METHYL}BENZENE
TRIS(TETRAFLUOROBORATE)


JEOL
---- PROCESSING PARAMETERS ----
do_baseline : 0 : FALSE
exp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = Correct BF4 after edi
Author = delta
Experiment = single_pulse.exp
Sample_id = SS3-176
Solvent = DMSO-D6
Creation_time = 28-NOV-2007 19:47:48
Revision_time = 14-FEB-2008 18:38:40
Current_time = 16-APR-2008 00:28:34
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 = 4.364976[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
Wool_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.364976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 3[s]
Phase_preset = 18[us]
Recvr_gain = 4[s]
Relaxation_delay = 25.2[dC]
Temp_get = 2[us]
Unblank_time
9.8
6.3
6.22
6.18
6.35
3
2.8
3.25
3.45
9.1960
7.8155
7.8155
7.7091
7.4209
5.4159
4.1883
4.1736
4.1594
1.2823
1.2671
1.2525
1.7669
1.7816
1.7962
0.9112
0.9259
X : parts per Million : 1H
(Million)


(Million ions)
X : parts per Million : 1H
9.1960
7.8965
7.8955
7.4209
5.4159
4.1883
4.1736
4.1594
6.35
6.18
3
3.45
3.25
2.8
6.22
6.67
9.85
1.7962
1.7816
1.7669
1.7518
1.2974
1.2823
1.2671
1.2525
1.2378
0.9259
0.9112
0.8966
0.8897
7.8955
7.8948
7.7123
7.7091
7.7054
7.4209
3.45
3.25
2.8

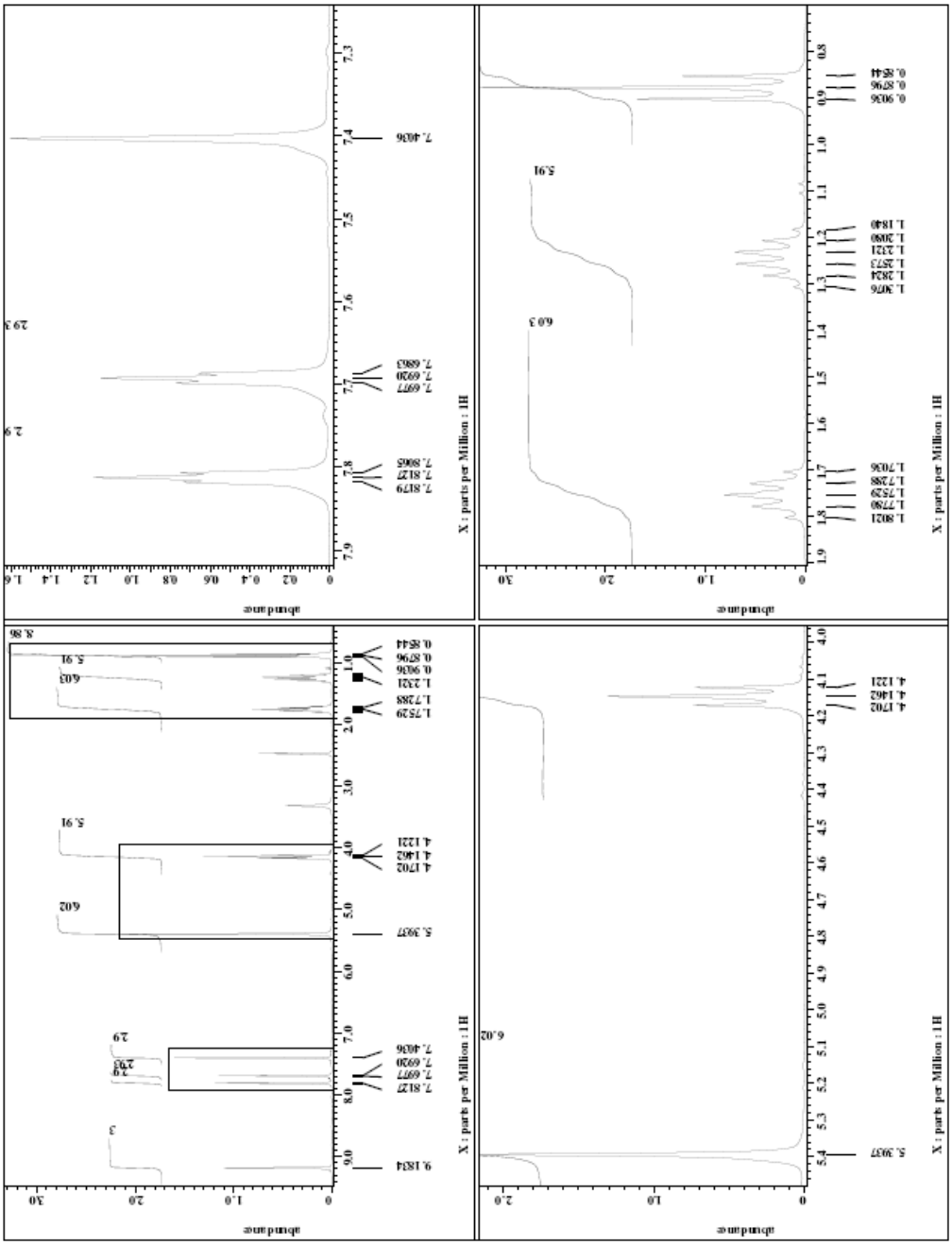
APPENDIX 31

^{1}H NMR SPECTRA OF
1,3,5-{TRIS(3-N-BUTYLIMIDAZOLIUM)METHYL}BENZENE
TRIS(TRIFLUOROMETHANESULFONATE)



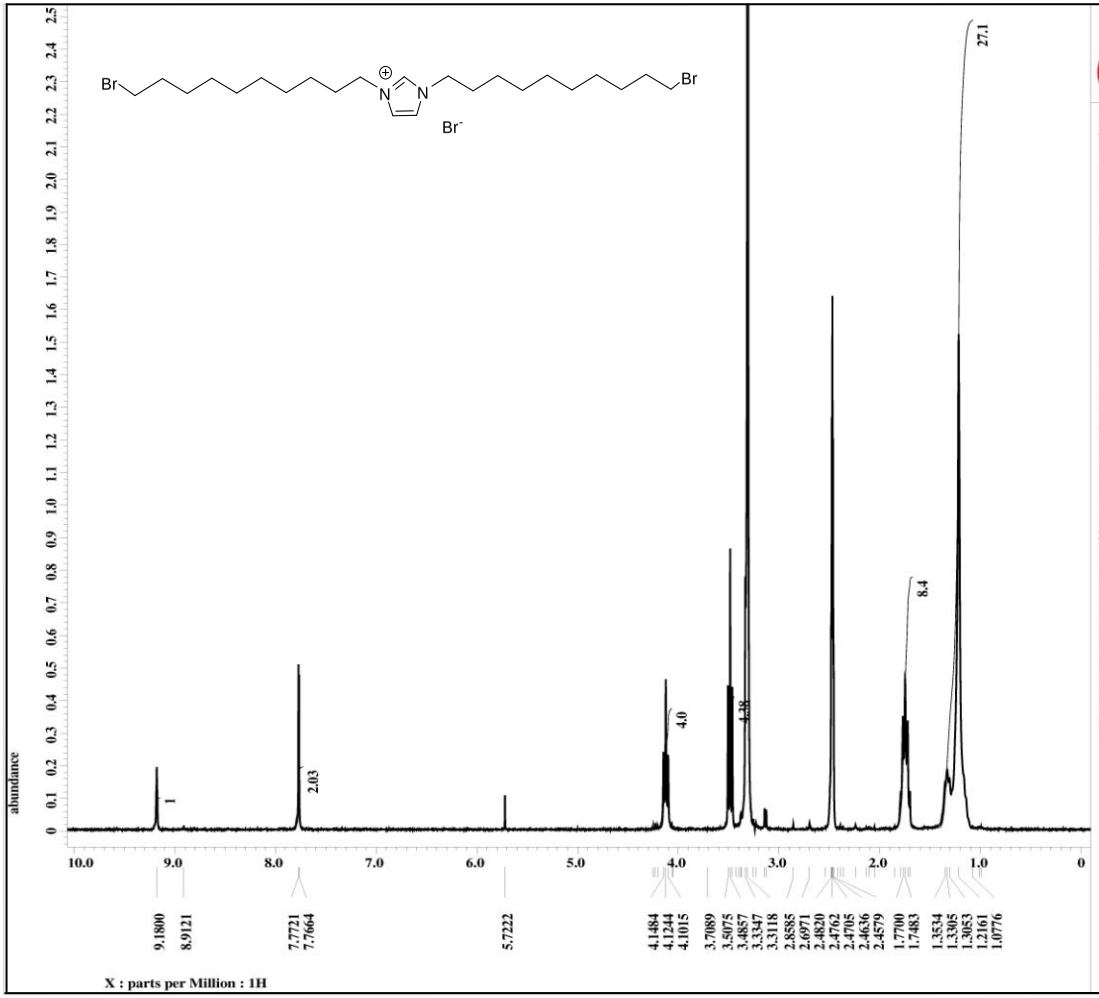
--- PROCESSING PARAMETERS ---
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Filename	= 2605tfo_D-3.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#443391
Solvent	= DMSO-D6
Creation_time	= 5-DEC-2007 12:44:00
Revision_time	= 14-FEB-2008 18:41:58
Current_time	= 16-APR-2008 00:35:20
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	= 38
Relaxation_delay	= 5[s]
Repetition_time	= 7.90717696[s]
Temp_get	= 23.4[dC]


X : parts per Million : 1H
abundance
9.1834
7.8127
7.6977
7.6920
7.4026
5.3937
4.1702
4.1462
4.1221
1.7529
1.7288
1.3321
0.9036
0.8796
0.8544
6.02
5.91
8.86
6.03
2.9
2.93
3
7.8179
7.8127
7.8065
7.6977
7.6920
7.6863
7.4026
2.9
2.93
1.8021
1.7780
1.7529
1.7288
1.7036
1.3076
1.2834
1.2573
1.2321
1.2080
1.1840
0.9036
0.8796
0.8544
6.03
5.91

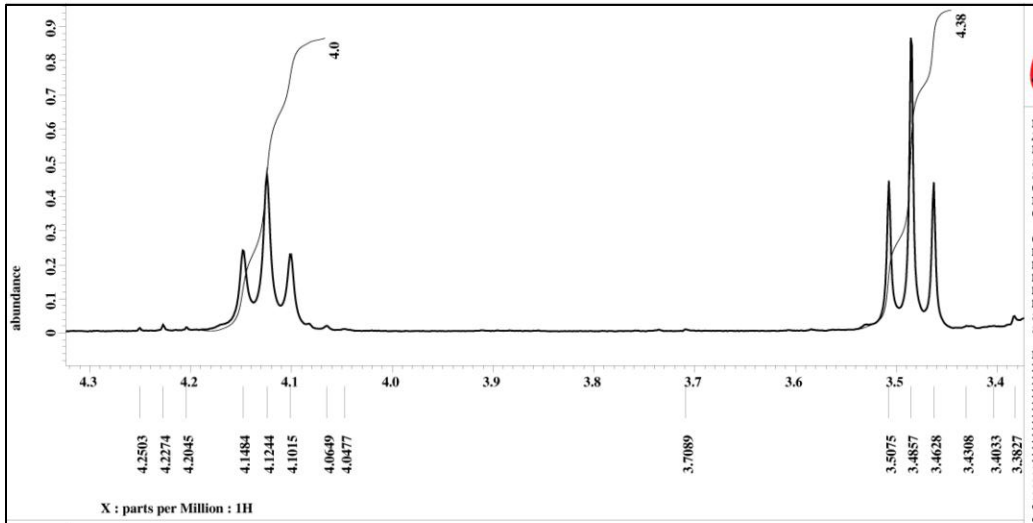
APPENDIX 32

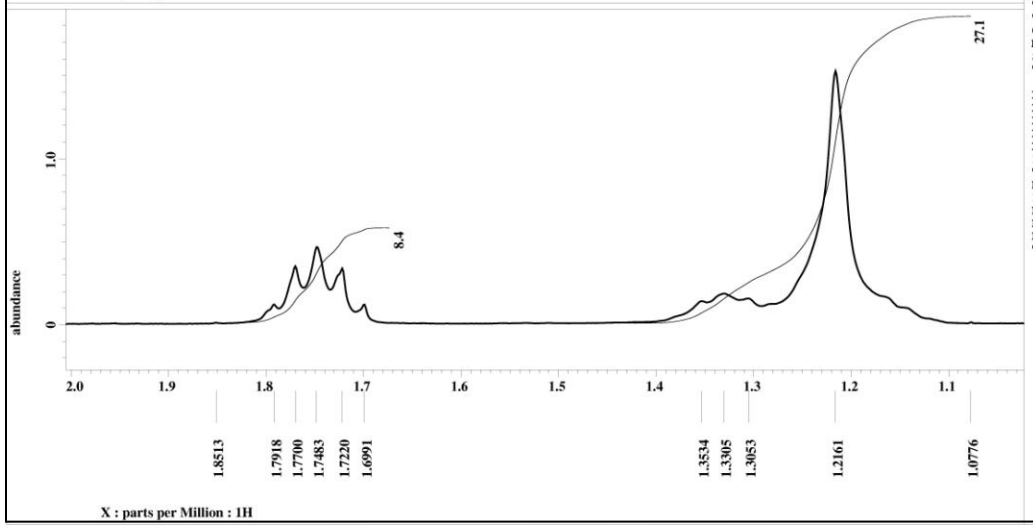
^{1}H AND ^{13}C NMR SPECTRA OF
1-BROMODECYL-3-BROMODECYL IMIDAZOLIUM BROMIDE SALT (1a)



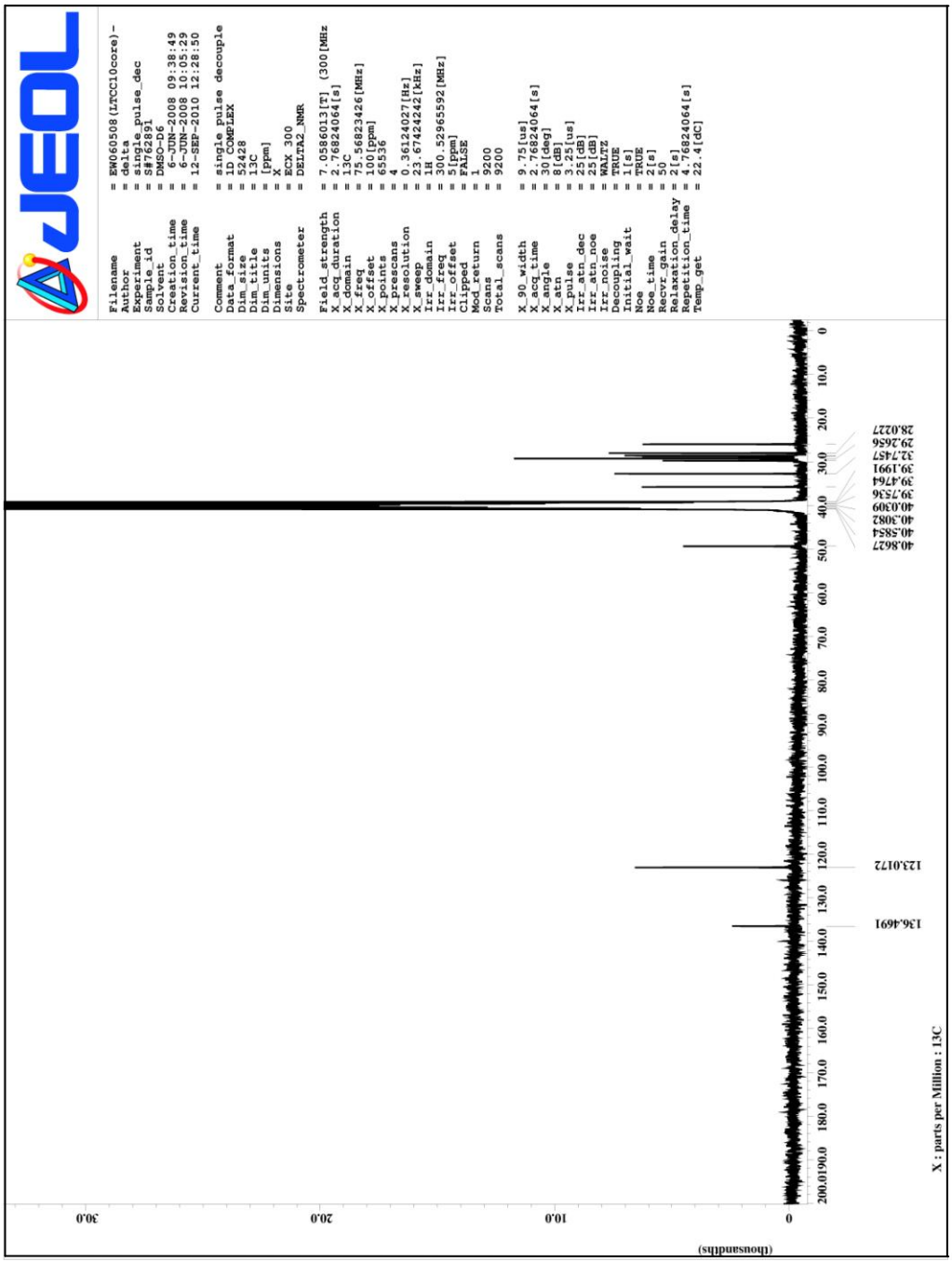
JEOL

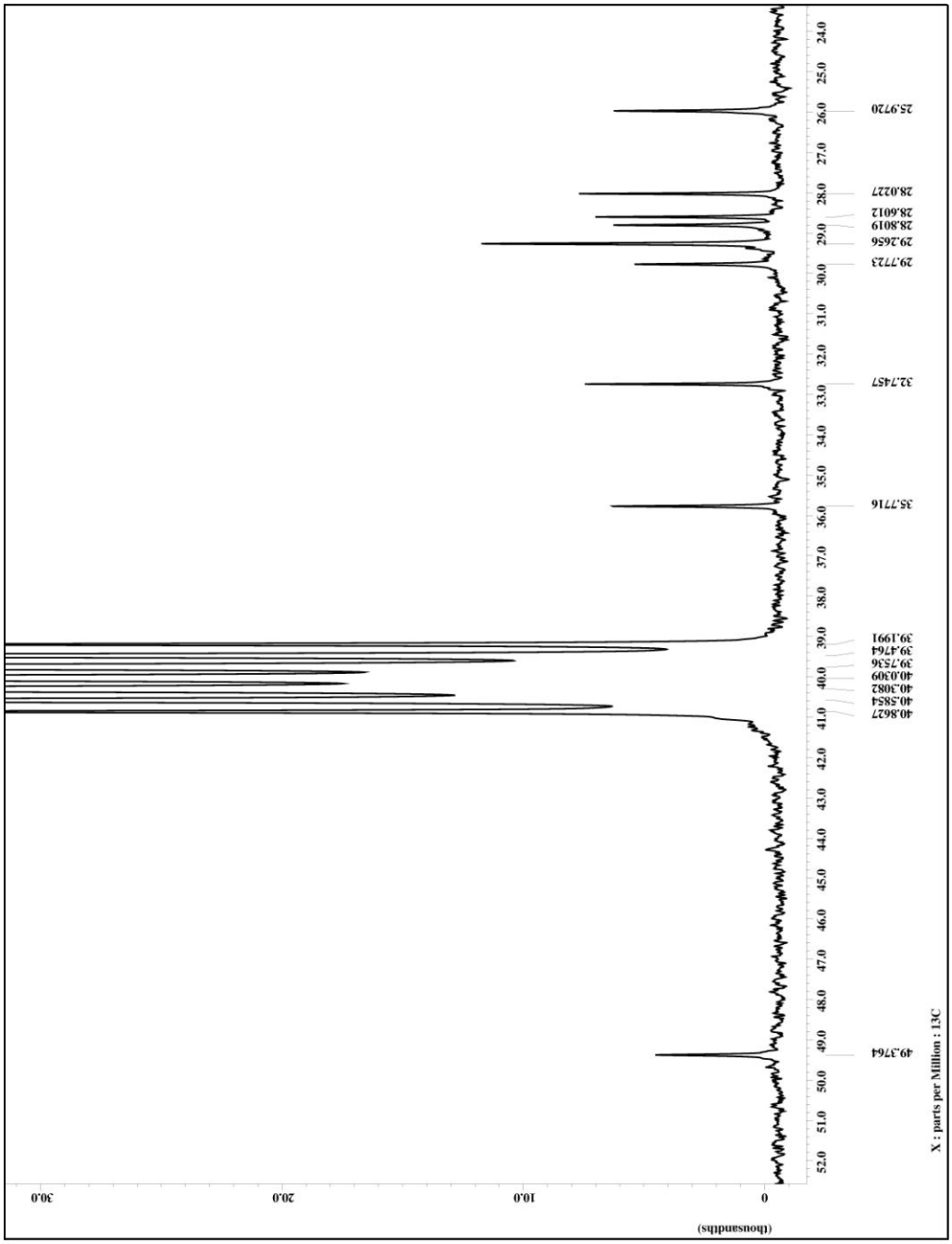
```
Filename          = EW060308(C10LTCore1)-
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#645954
Solvent           = DMSO-D6
Creation_time     =  3-JUN-2008 18:14:40
Revision_time     =  3-JUN-2008 18:04:29
Current_time      = 12-SEP-2010 00:22:38

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             = 22
Total_scans       = 22

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        = 44
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 24.6[dC]
```





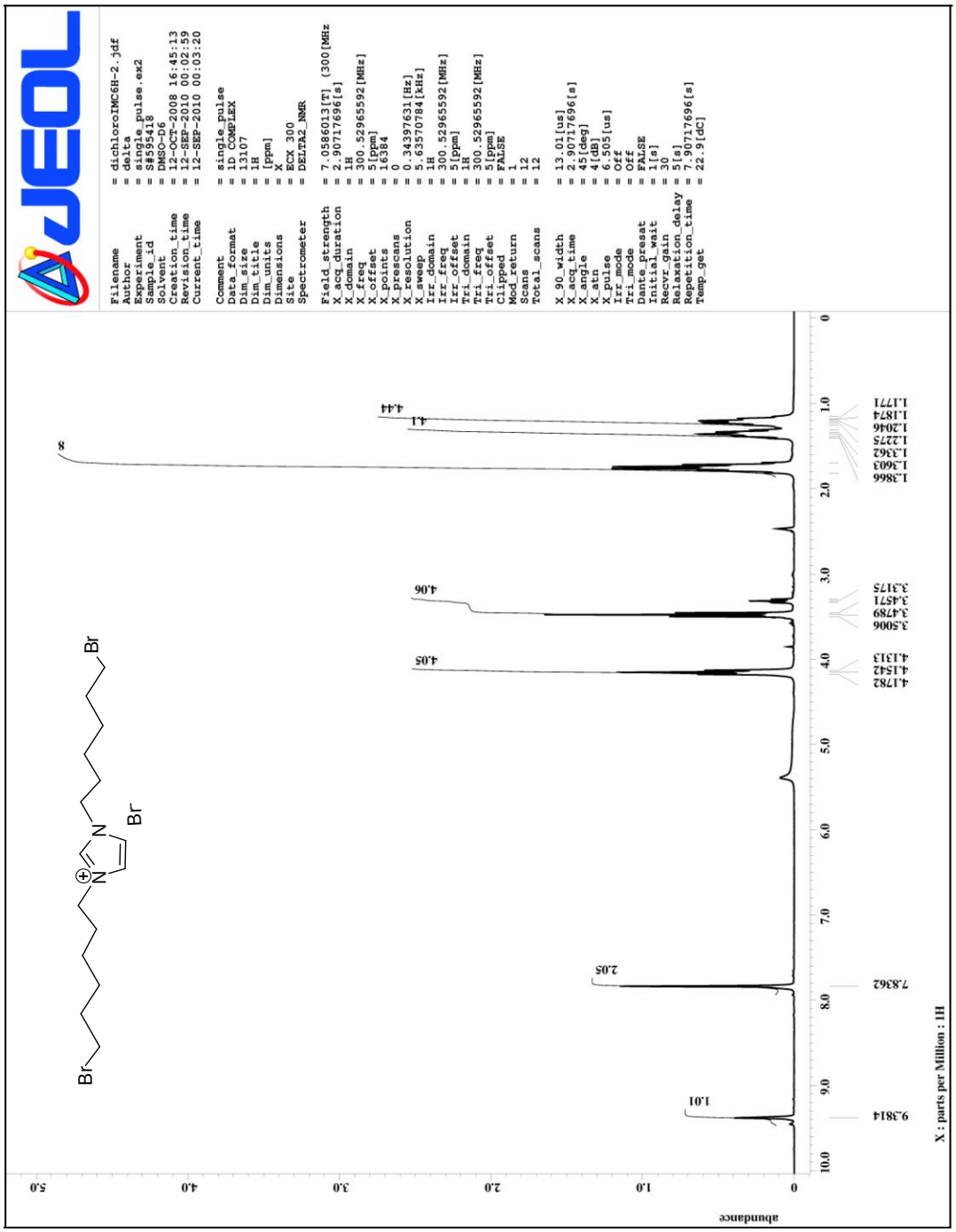

```
Filename          = EW060308(C10LTCore1)-
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#645954
Solvent           = DMSO-D6
Creation_time     =  3-JUN-2008 18:14:40
Revision_time     =  3-JUN-2008 18:04:29
Current_time      = 12-SEP-2010 00:24:18

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             = 22
Total_scans       = 22

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        = 44
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 24.6[dC]
```

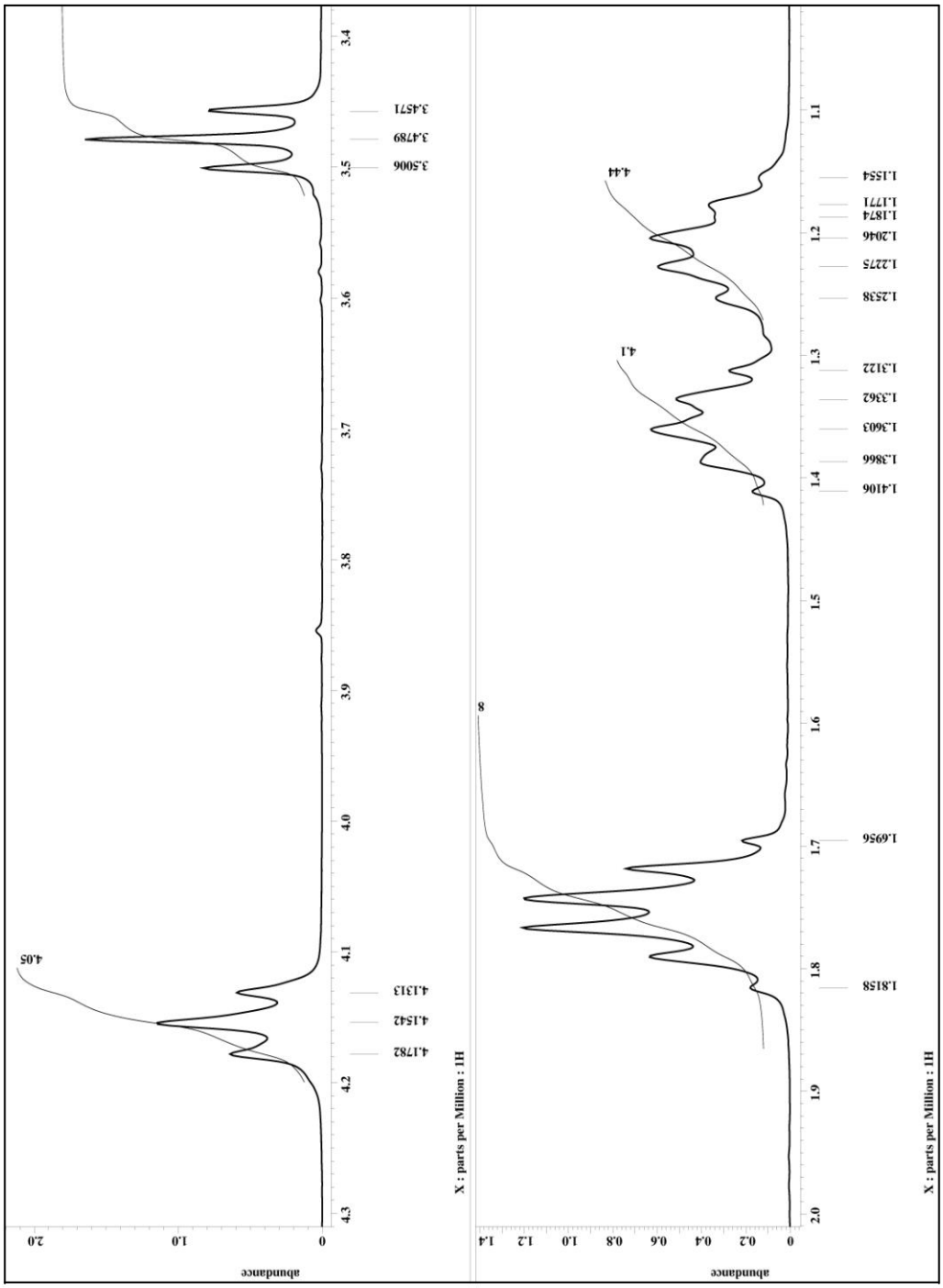

Filename = EW060508(LXCC10core)-
Author = delta
Experiment = single_pulse_dec
Sample_id = S#762891
Solvent = DMSO-D6
Creation_time = 6-JUN-2008 09:38:49
Revision_time = 6-JUN-2008 10:05:29
Current_time = 12-SEP-2010 12:28:50
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9200
Total_scans = 9200
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 22.4[dC]
(thousandths)
30.0
20.0
10.0
0
200.0190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
136.4691
123.0172
40.8627
40.5854
40.3082
40.0309
39.7536
39.4764
39.1991
32.7457
29.2656
28.0227
X : parts per Million : 13C

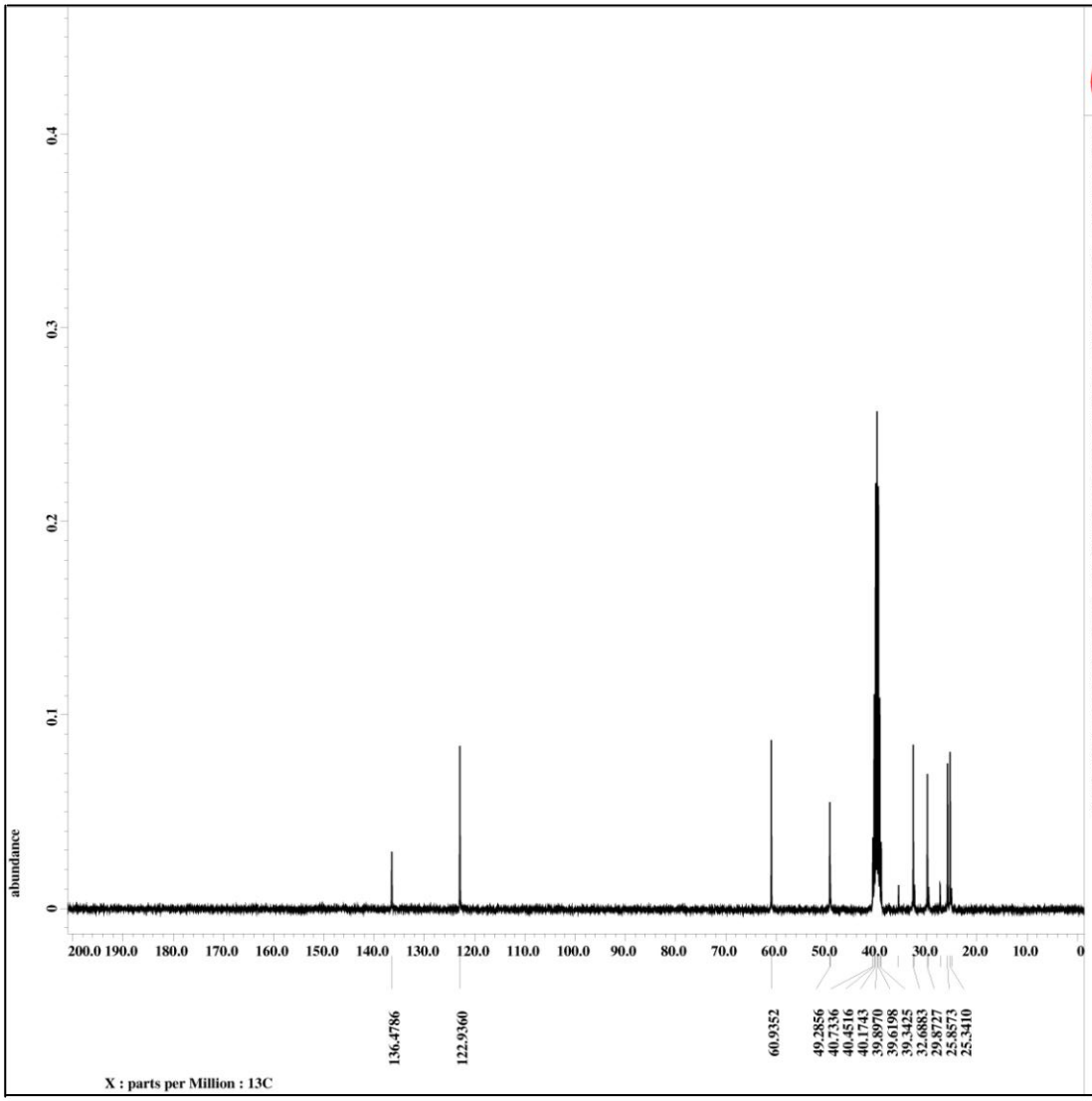

(thousandths)
0
10.0
20.0
30.0
X : parts per Million : 13C
52.0
51.0
50.0
49.0
48.0
47.0
46.0
45.0
44.0
43.0
42.0
41.0
40.0
39.0
38.0
37.0
36.0
35.0
34.0
33.0
32.0
31.0
30.0
29.0
28.0
27.0
26.0
25.0
24.0
49.3764
40.8627
40.5854
40.3082
40.0309
39.7536
39.4764
39.1991
35.7716
32.7457
29.7723
29.2656
28.8019
28.6012
28.0227
25.9720

APPENDIX 33

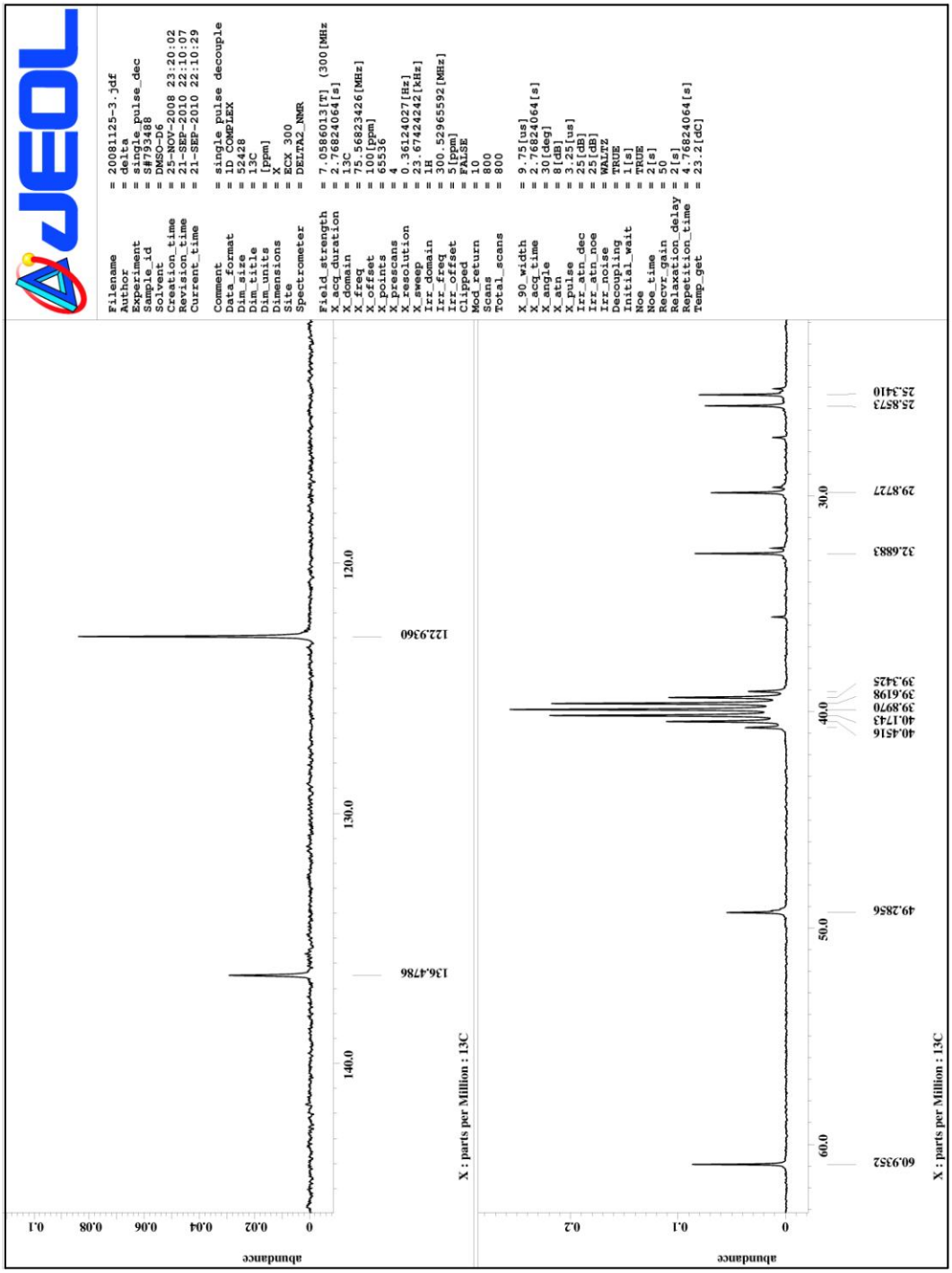
^{1}H NMR SPECTRA OF
1-BROMOHEXYL-3-BROMOHEXYL IMIDAZOLIUM BROMIDE SALT (1b)


Filename = dichloroIMC6H-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#5955418
Solvent = DMSO-D6
Creation_time = 12-OCT-2008 16:45:13
Revision_time = 12-SEP-2010 00:02:59
Current_time = 12-SEP-2010 00:03:20
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 32107
Dim_title = H
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]
Revcom = 30
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.9[dC]
Br
Br
Br
8
4.44
4.1
4.06
4.05
2.05
1.01
1.3866
1.3603
1.3362
1.2275
1.2046
1.1874
1.1771
3.5006
3.4789
3.4571
3.3175
4.1782
4.1542
4.1313
7.8362
9.3814
X : parts per Million : 1H
abundance


abundance
X : parts per Million : 1H
4.05
4.1782
4.1542
4.1313
3.5006
3.4789
3.4571
8
1.8158
1.6956
1.4106
1.3866
1.3603
1.3362
1.3122
1.2538
1.2275
1.2046
1.1874
1.1771
1.1554
4.1
4.44

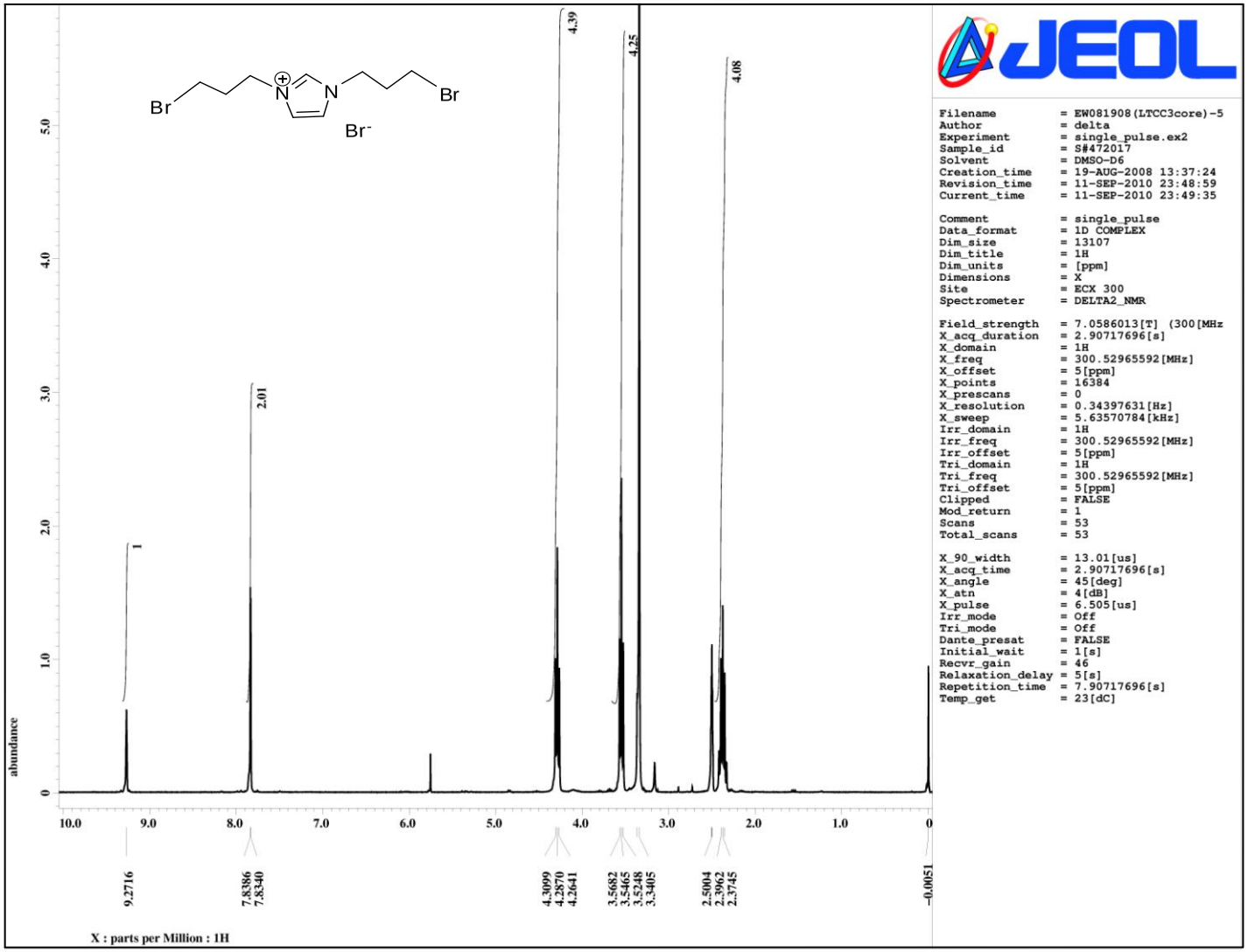


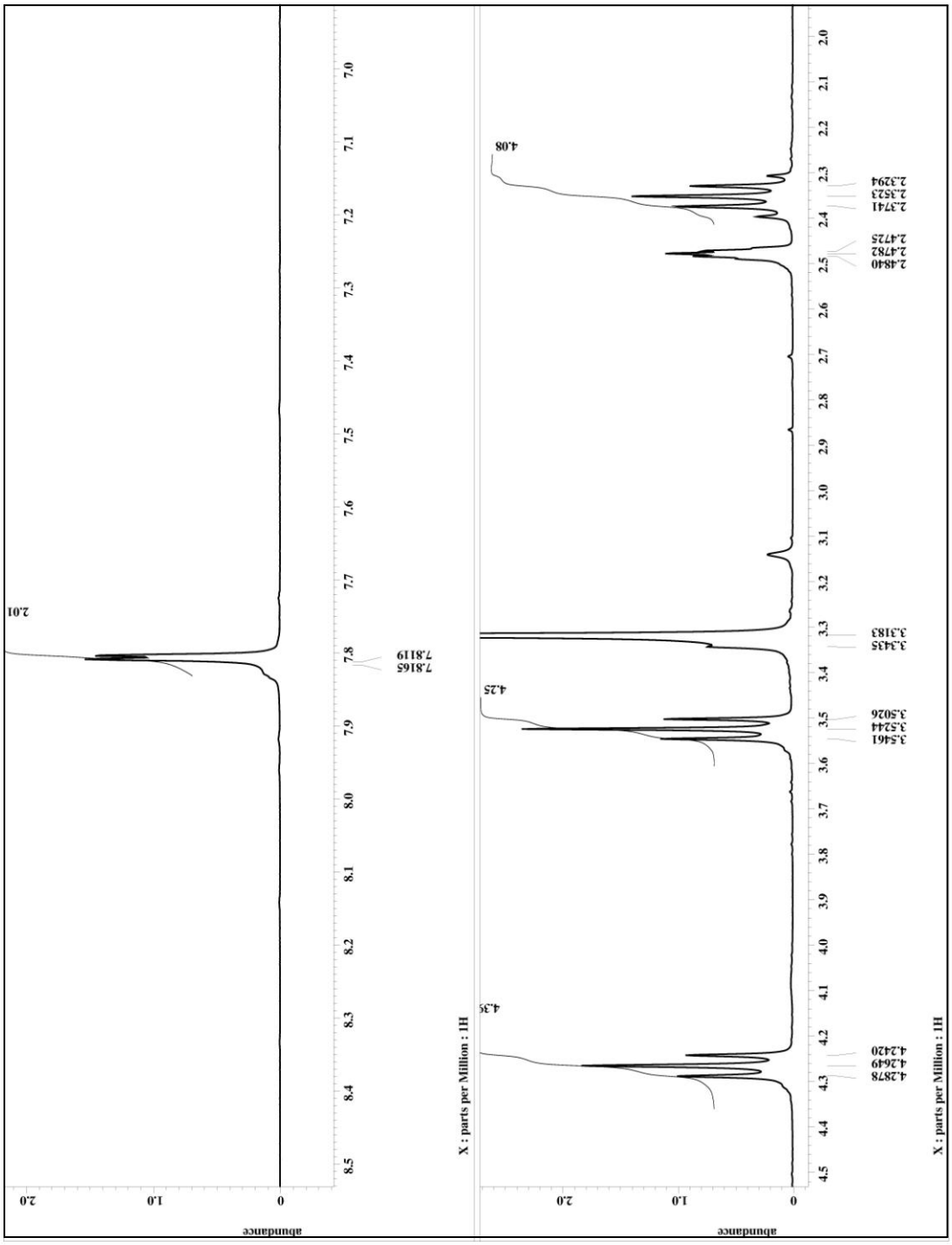

```
Filename          = 20081125-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#793488
Solvent           = DMSO-D6
Creation_time     = 25-NOV-2008 23:20:02
Revision_time     = 21-SEP-2010 22:06:45
Current_time      = 21-SEP-2010 22:09:36

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 800
Total_scans       = 800

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23.2[dC]
```

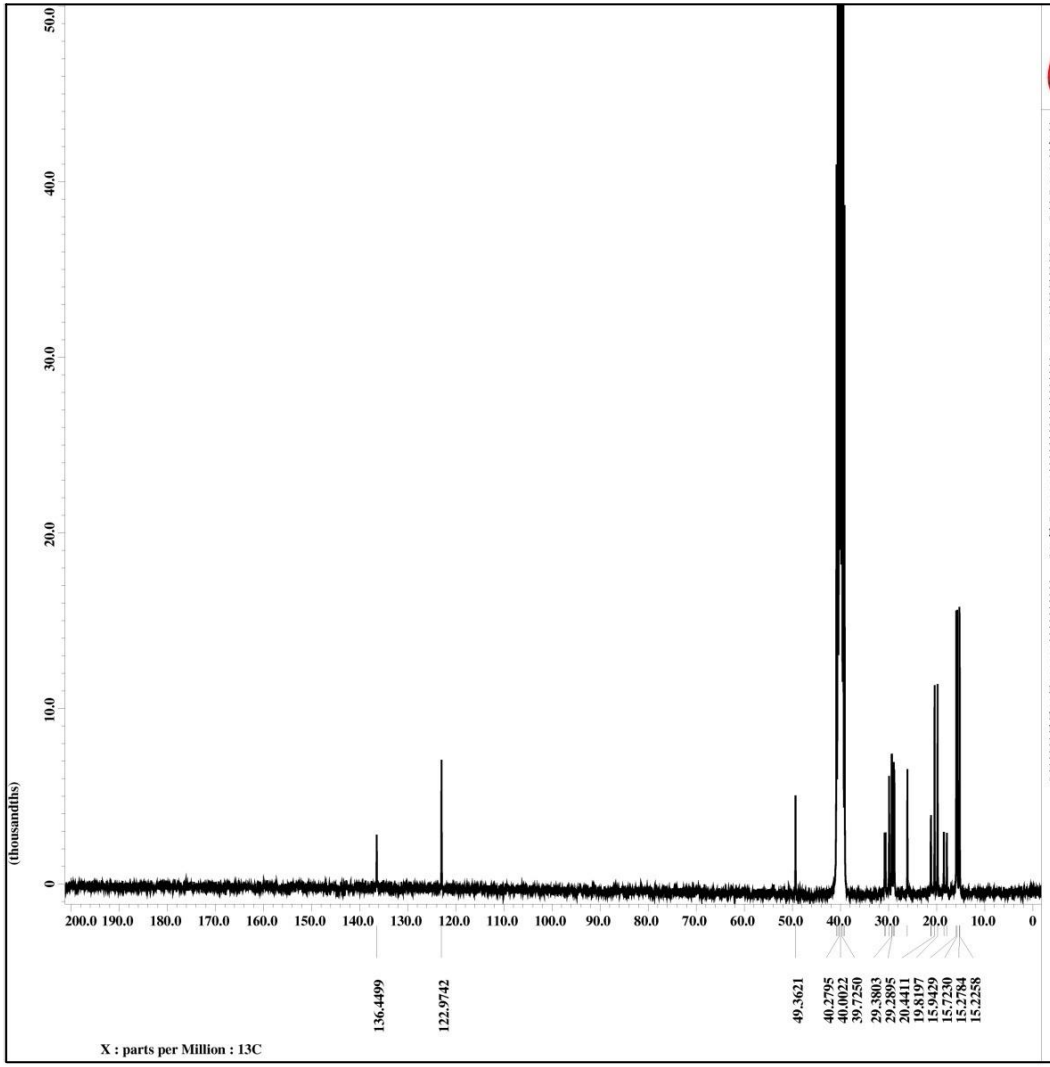

JEOL
Filename = 20081125-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#793488
Solvent = DMSO-D6
Creation_time = 25-NOV-2008 23:20:02
Revision_time = 21-SEP-2010 22:10:07
Current_time = 21-SEP-2010 22:10:29
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 800
Total_scans = 800
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 23.2[dC]
abundance
0.1
0.08
0.06
0.04
0.02
0
140.0
130.0
120.0
136.4786
122.9360
X : parts per Million : 13C
abundance
0.2
0.1
0
60.0
50.0
40.0
30.0
60.9352
49.2856
40.4516
40.1743
39.8970
39.6198
39.3425
32.6883
29.8727
25.8573
25.3410
X : parts per Million : 13C

APPENDIX 34

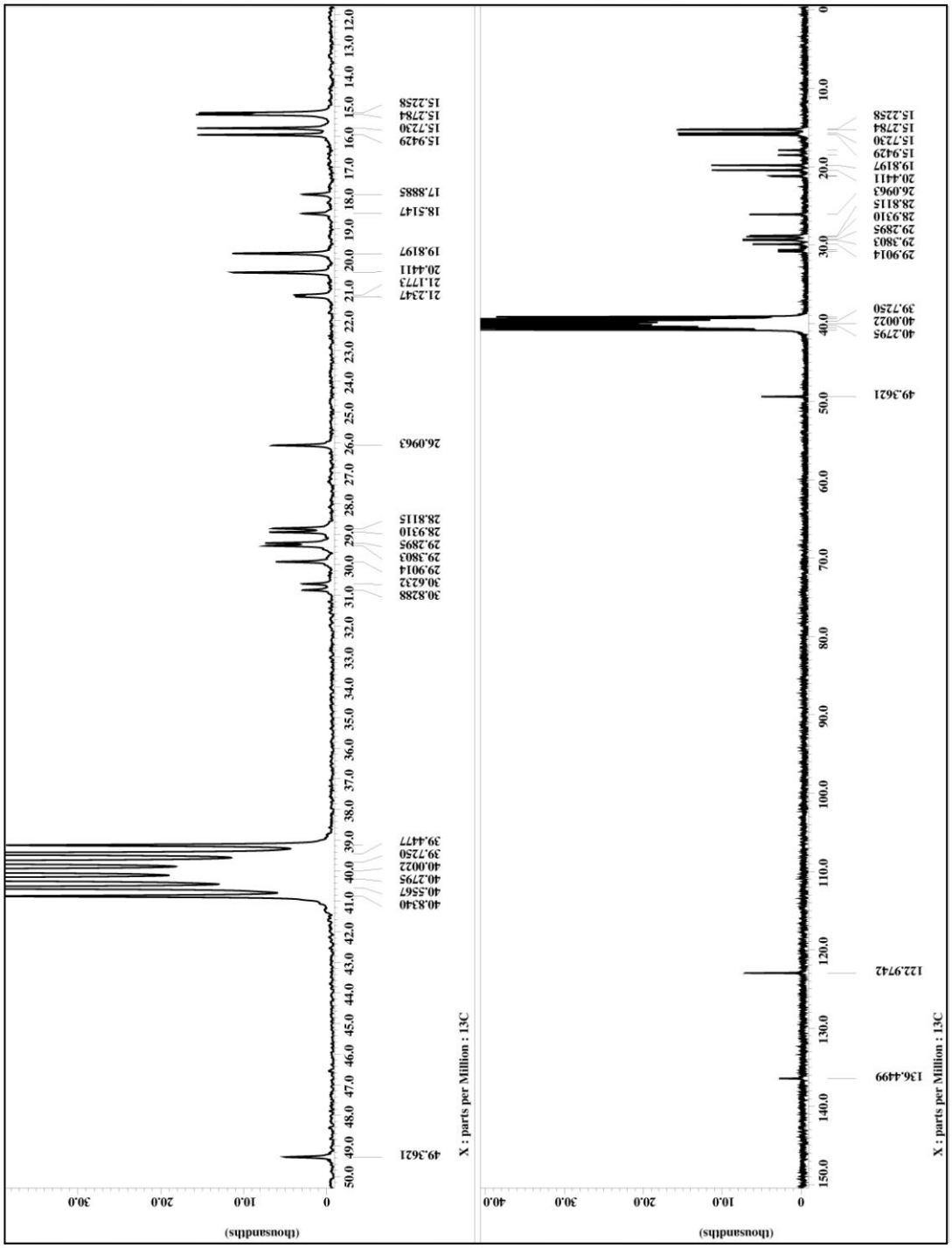
^{1}H AND ^{13}C NMR SPECTRA OF
1-BROMOPROPYL-3-BROMOPROPYL IMIDAZOLIUM BROMIDE SALT (1c)


Br
N
N
Br
Br⁻
4.39
4.25
4.08
2.01
1
abundance
0
1.0
2.0
3.0
4.0
5.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.2716
7.8386
7.8340
4.3099
4.2870
4.2641
3.5682
3.5465
3.5248
3.3405
2.5004
2.3962
2.3745
−0.0051
X : parts per Million : 1H
JEOL
Filename = EW081908(LTCC3core)-5
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#472017
Solvent = DMSO-D6
Creation_time = 19-AUG-2008 13:37:24
Revision_time = 11-SEP-2010 23:48:59
Current_time = 11-SEP-2010 23:49:35
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 = 53
Total_scans = 53
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 = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23[dC]


abundance
2.0
1.0
0
X : parts per Million : 1H
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
2.01
7.8165
7.8119
4.35
4.25
4.08
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
4.2878
4.2649
4.2420
3.5461
3.5244
3.5026
3.3435
3.3183
2.4840
2.4782
2.4725
2.3741
2.3523
2.3294

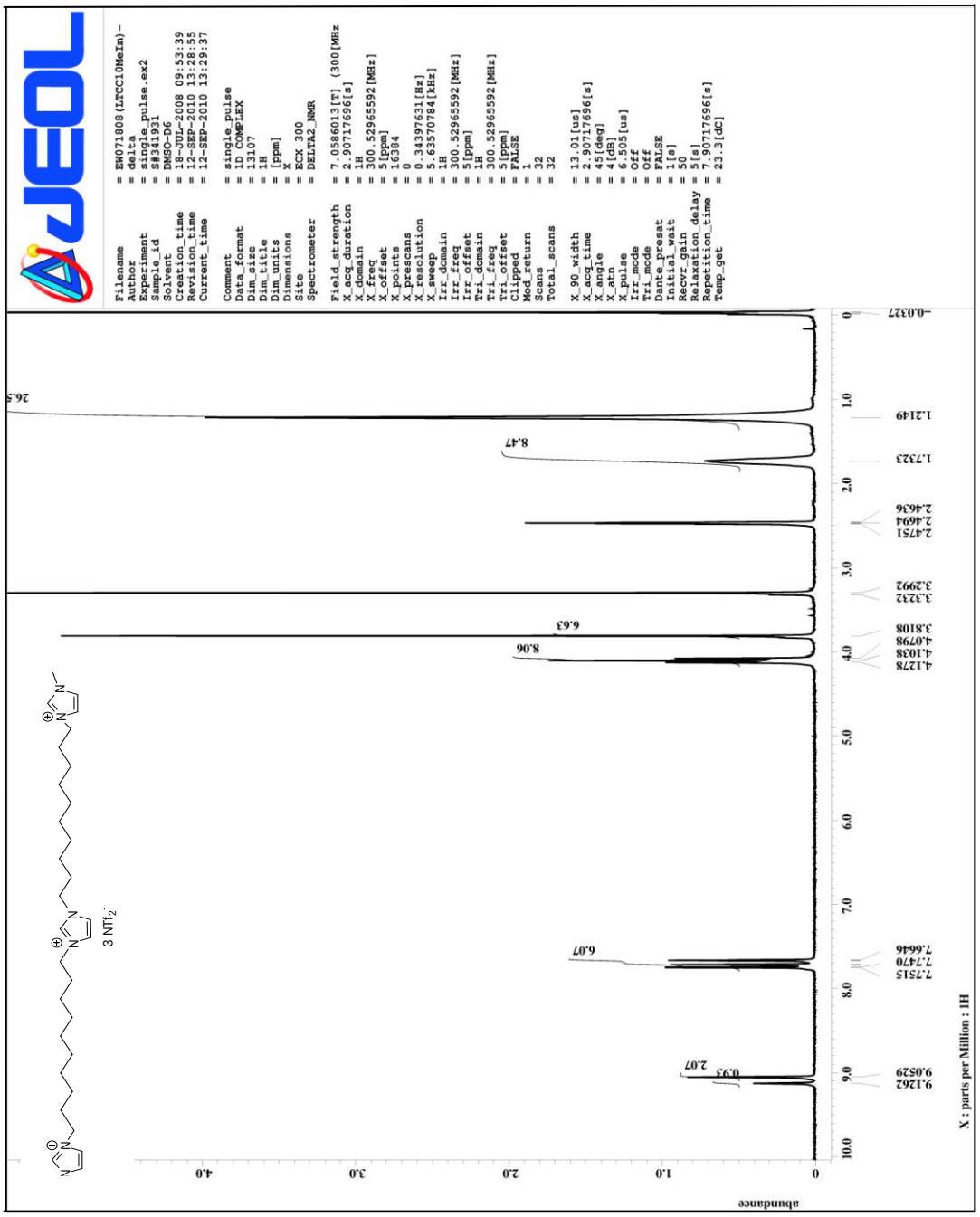


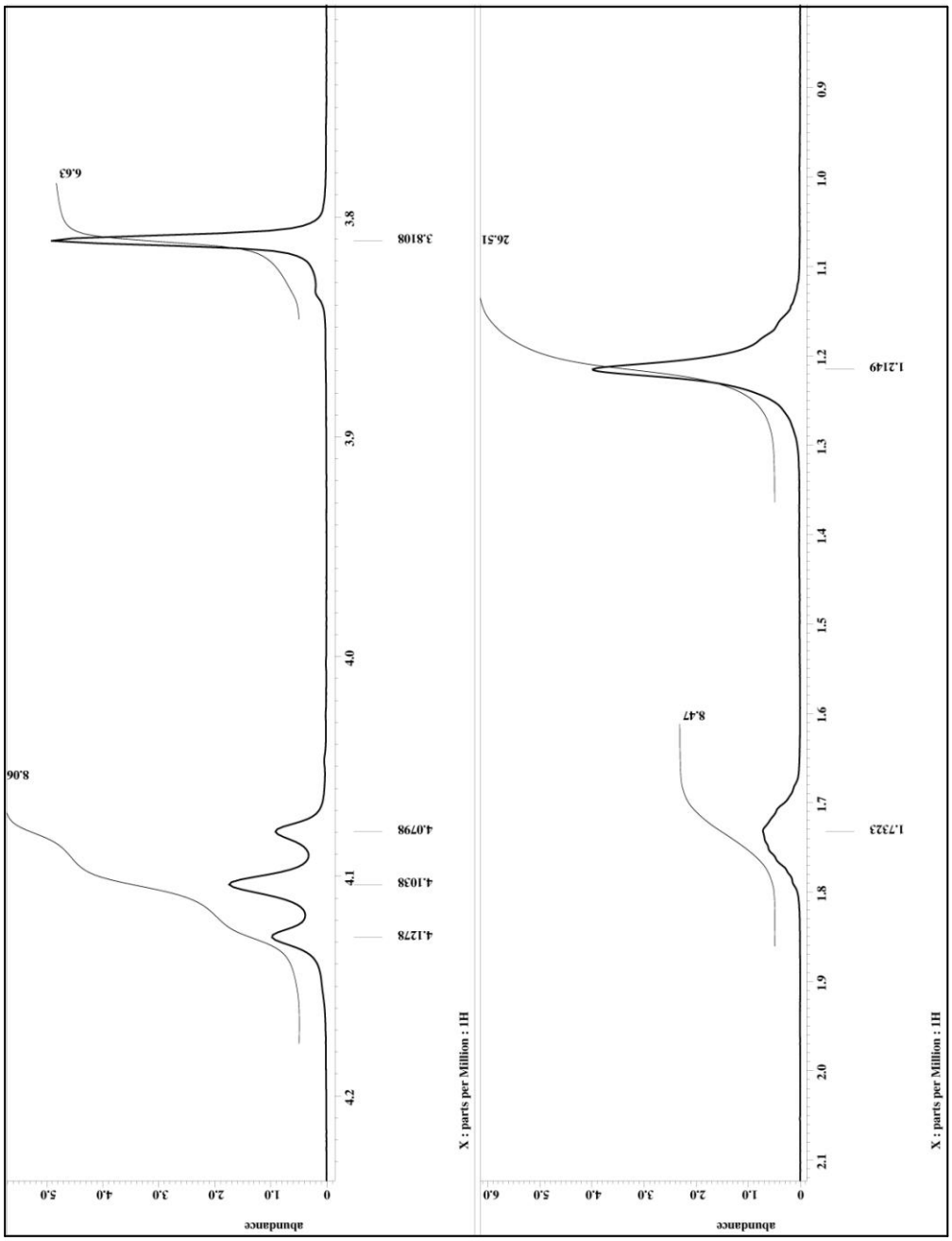

```
Filename          = EW091108(LTCC3Core)-4
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#757692
Solvent           = DMSO-D6
Creation_time     = 12-SEP-2008 10:04:01
Revision_time     = 12-SEP-2010 11:49:42
Current_time      = 12-SEP-2010 11:50:13

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9500
Total_scans       = 9500

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23.9[dC]
```

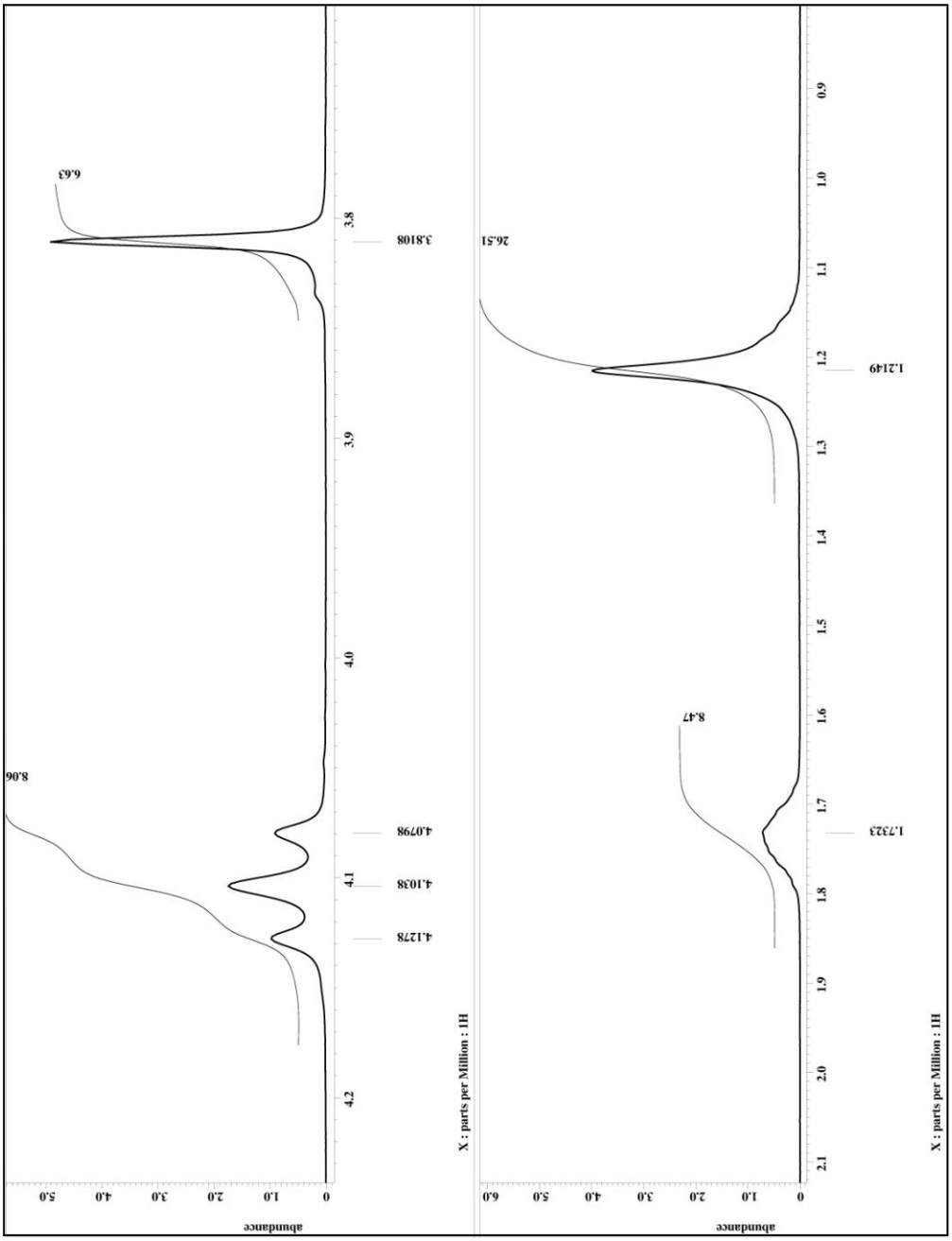

X : parts per Million : 13C
(thousandths)
49,3621
40,8340
40,5567
40,2795
40,0022
39,7250
39,4477
30,8288
30,6232
29,9014
29,3803
29,2895
28,9310
28,8115
26,0963
21,2347
21,1773
20,4411
19,8197
18,5147
17,8885
15,9429
15,7230
15,7784
15,2258
X : parts per Million : 13C
(thousandths)
122,9742
136,4499
49,3621
40,2795
40,0022
39,7250
29,9014
29,3803
29,2895
28,9310
28,8115
26,0963
20,4411
19,8197
15,9429
15,7230
15,7784
15,2258

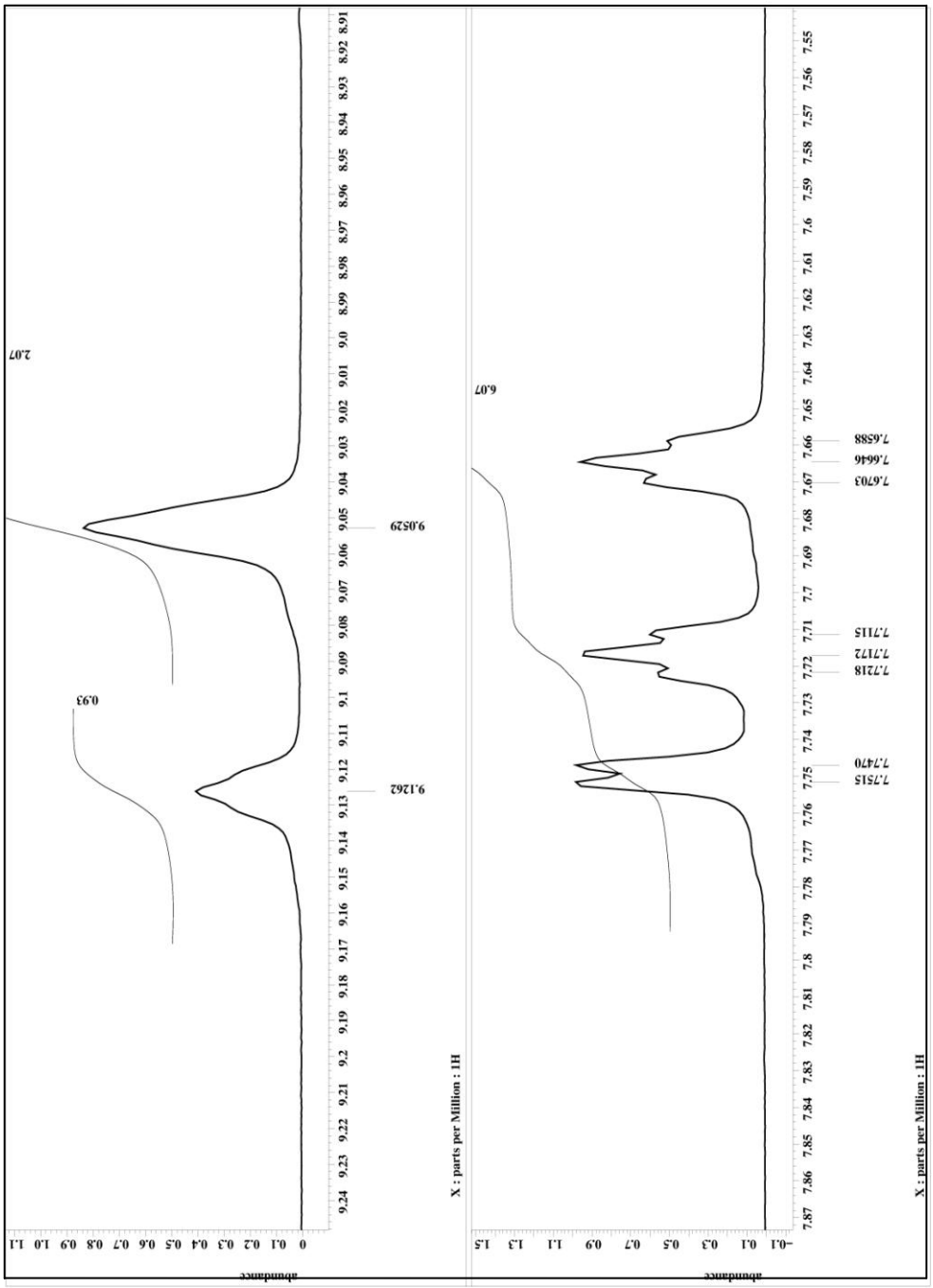
APPENDIX 35

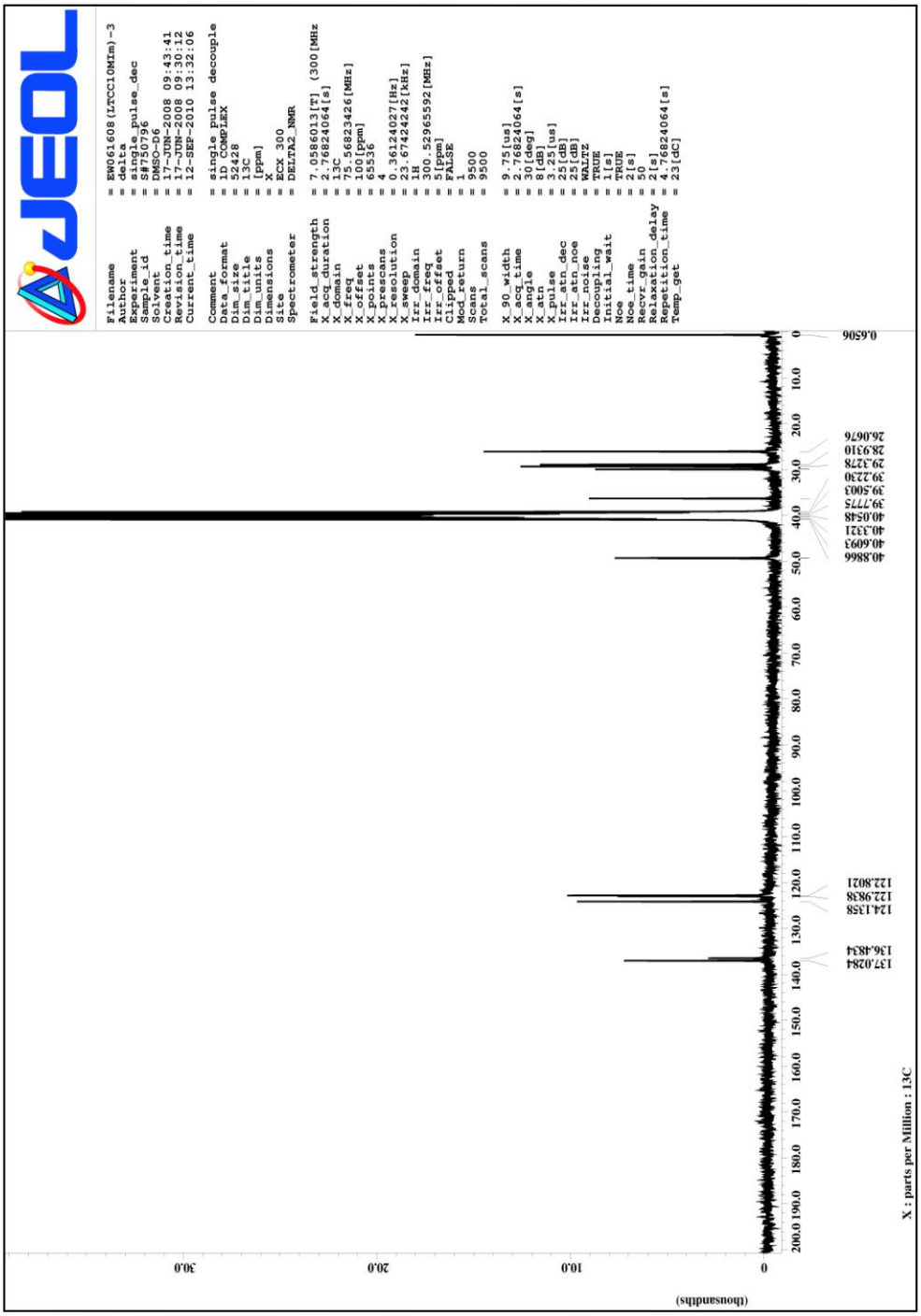
^{1}H AND ^{13}C NMR SPECTRA OF
1-(1'-METHYL-3'-DECYLIMIDAZOLIUM)-3-(1''-METHYL-3''-DECYLIMIDAZOLIUM)
IMIDAZOLIUM TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (2a)

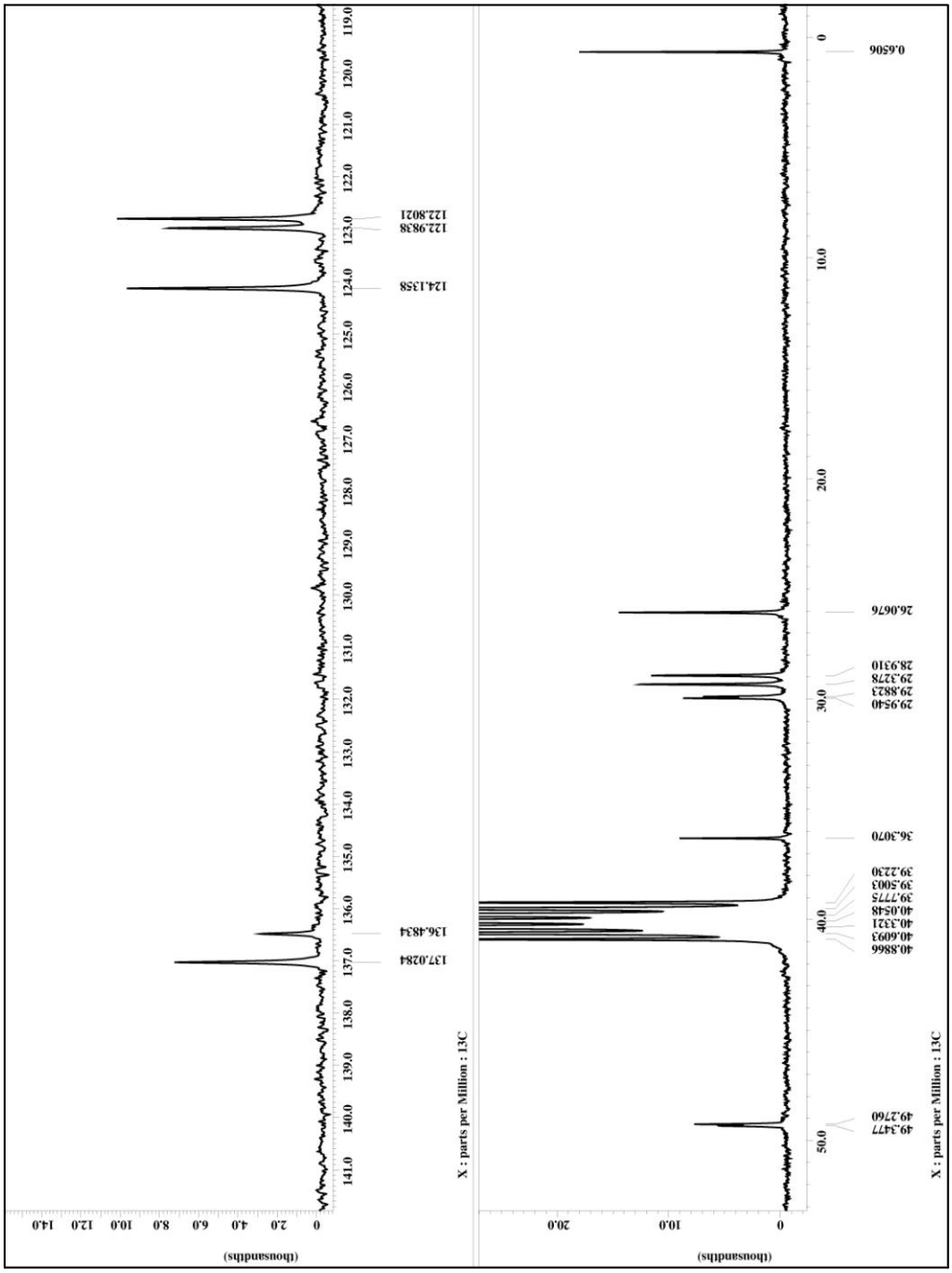

JEOL
Filename = EW071808(LiTCC10MeIm)-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#341931
Solvent = DMSO-D6
Creation_time = 18-JUL-2008 09:53:39
Revision_time = 12-SEP-2010 13:28:55
Current_time = 12-SEP-2010 13:29:37
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 131107
Dim_title = 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 = 32
Total_scans = 32
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
Data_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.3[dC]
3 NTf2-
abundance
X : parts per Million : 1H
26.5
8.47
6.63
8.06
6.07
2.07
0.93
9.1262
9.0529
7.7515
7.7470
7.6646
4.1278
4.1038
4.0798
3.8108
3.3232
3.2992
2.4751
2.4694
2.4636
1.7323
1.2149
-0.0327


abundance
X : parts per Million : 1H
8.06
6.63
4.1278
4.1038
4.0798
3.8108
26.51
8.47
1.7323
1.2149


abundance
X : parts per Million : 1H
8.06
6.63
4.1278
4.1038
4.0798
3.8108
26.51
8.47
1.7323
1.2149

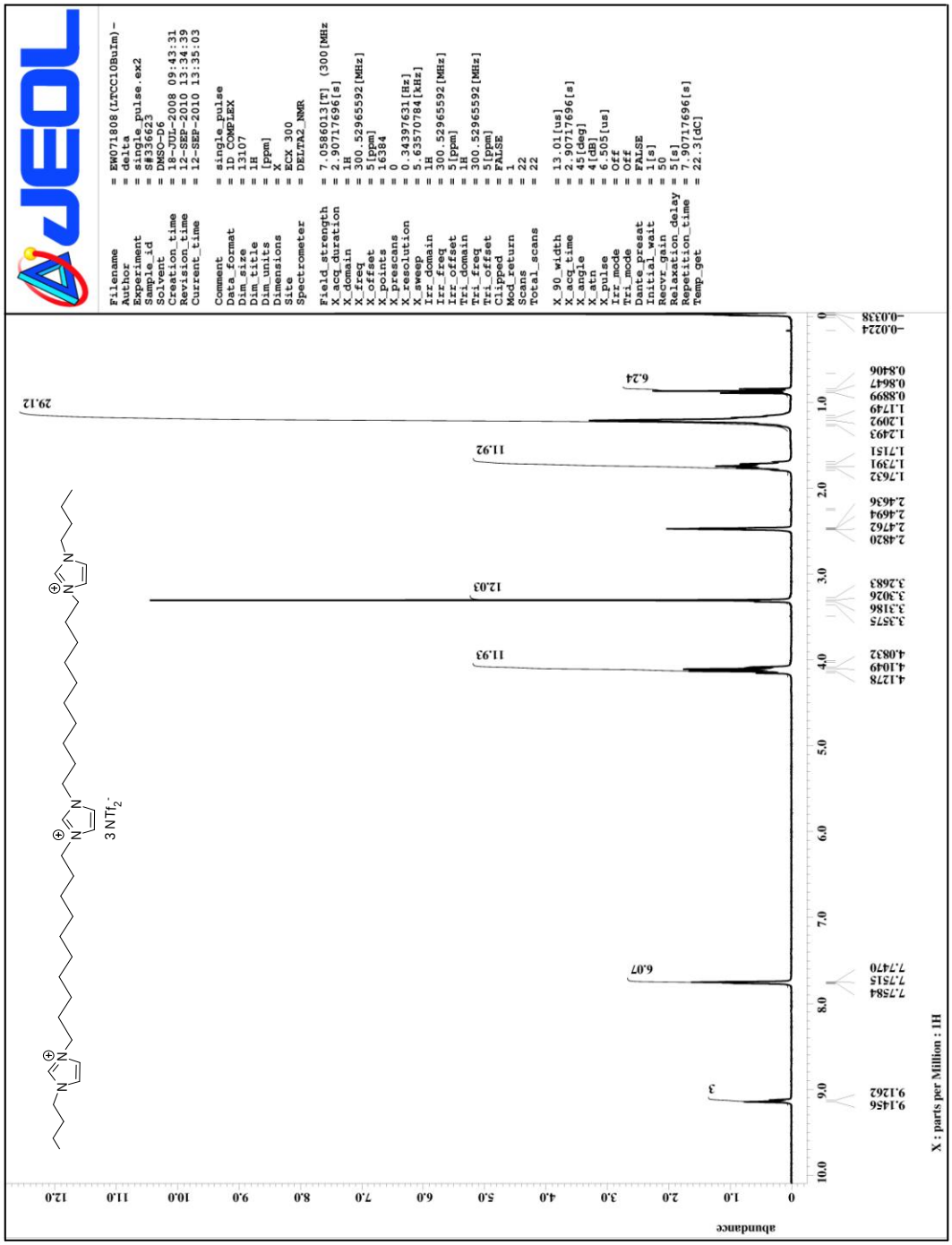

2.07
0.93
9.0529
9.1262
X : parts per Million : 1H
abundance
6.07
7.6588
7.6646
7.6703
7.7115
7.7172
7.7218
7.7470
7.7515
X : parts per Million : 1H
abundance

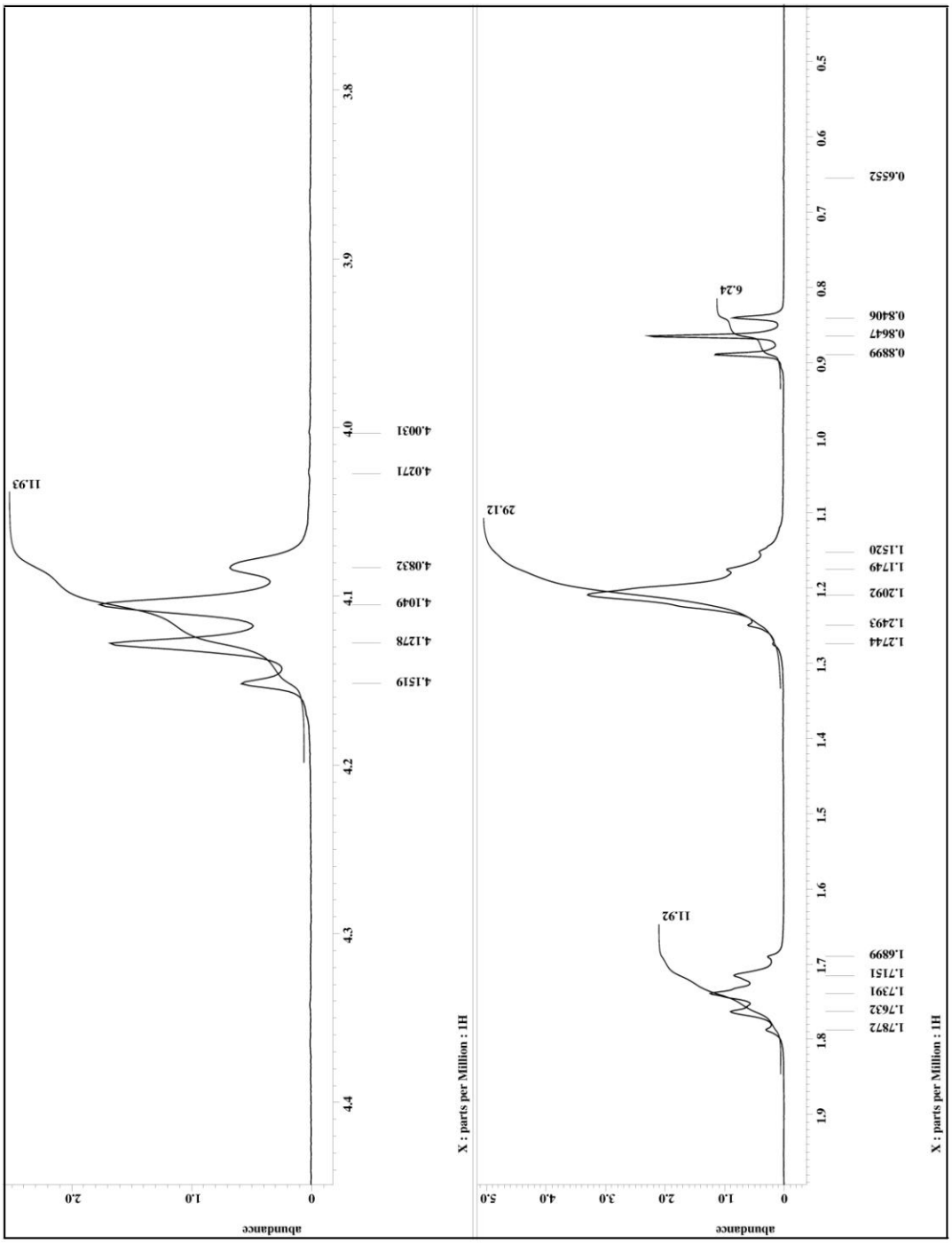

JEOL
Filename = EW061608(1ZTCC10MIm)-3
Author = delta
Experiment = single_pulse_dec
Sample_id = S#750796
Solvent = DMSO-d6
Creation_time = 17-JUN-2008 09:43:41
Revision_time = 17-JUN-2008 09:30:12
Current_time = 12-SEP-2010 13:32:06
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.768240641[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_scans = 9.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9500
Total_scans = 9500
X_90_width = 9.75[us]
X_acq_time = 2.768240641[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 30
Relaxation_delay = 4[s]
Repetition_time = 4.768240641[s]
Temp_get = 23[dC]
(thousandths)
0.0
10.0
20.0
30.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
0.6506
26.0676
28.9310
29.3278
39.2230
39.5003
39.7775
40.0548
40.3321
40.6093
40.8866
122.8021
122.9838
124.1358
136.4834
137.0284
X : parts per Million : 13C

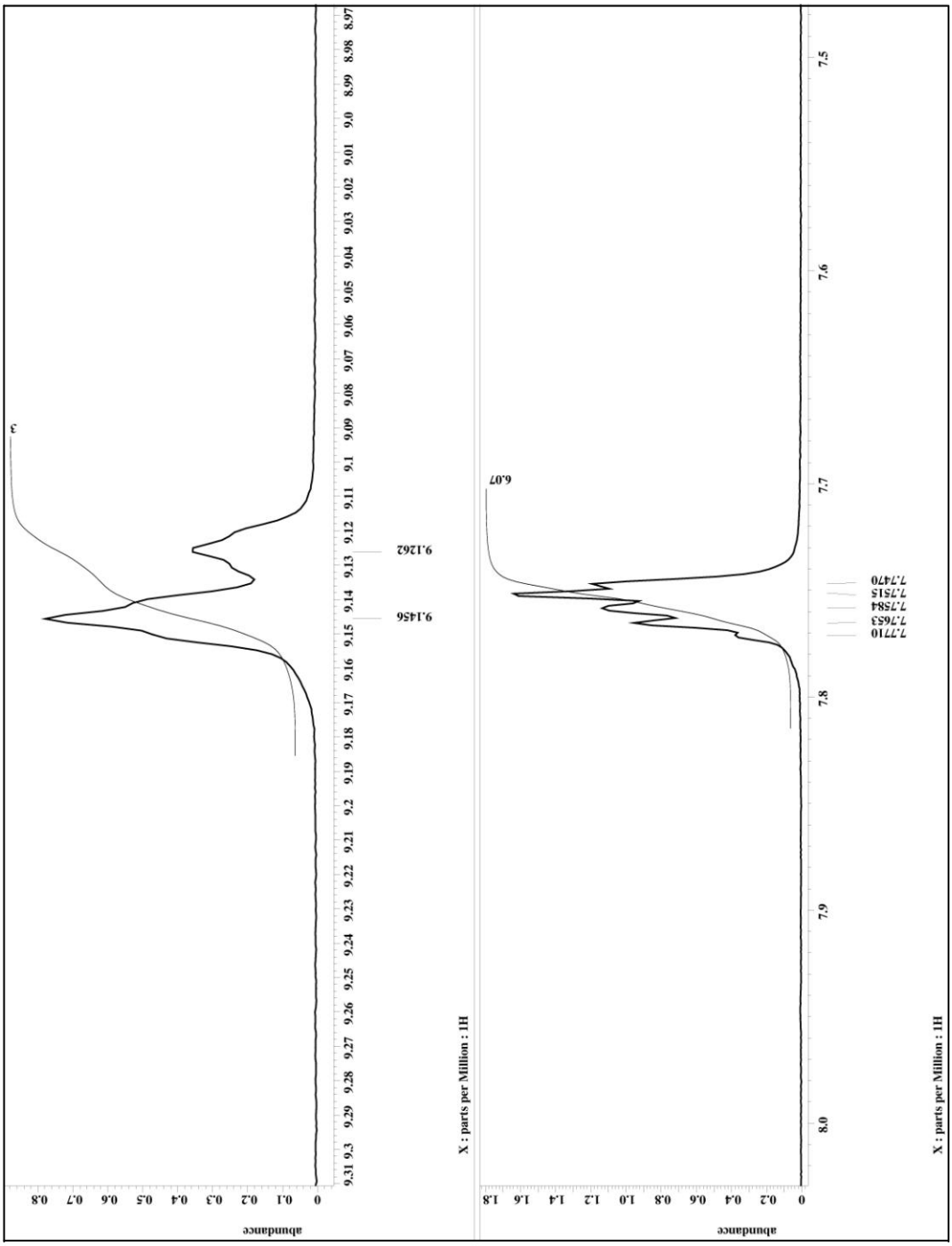

(thousandths)
X : parts per Million : 13C
137.0284
136.4834
124.1358
122.9838
122.8021
(thousandths)
X : parts per Million : 13C
49.3477
49.2760
40.8866
40.6093
40.3321
40.0548
39.7775
39.5003
39.2230
36.3070
29.9540
29.8823
29.3278
28.9310
26.0676
0.6506

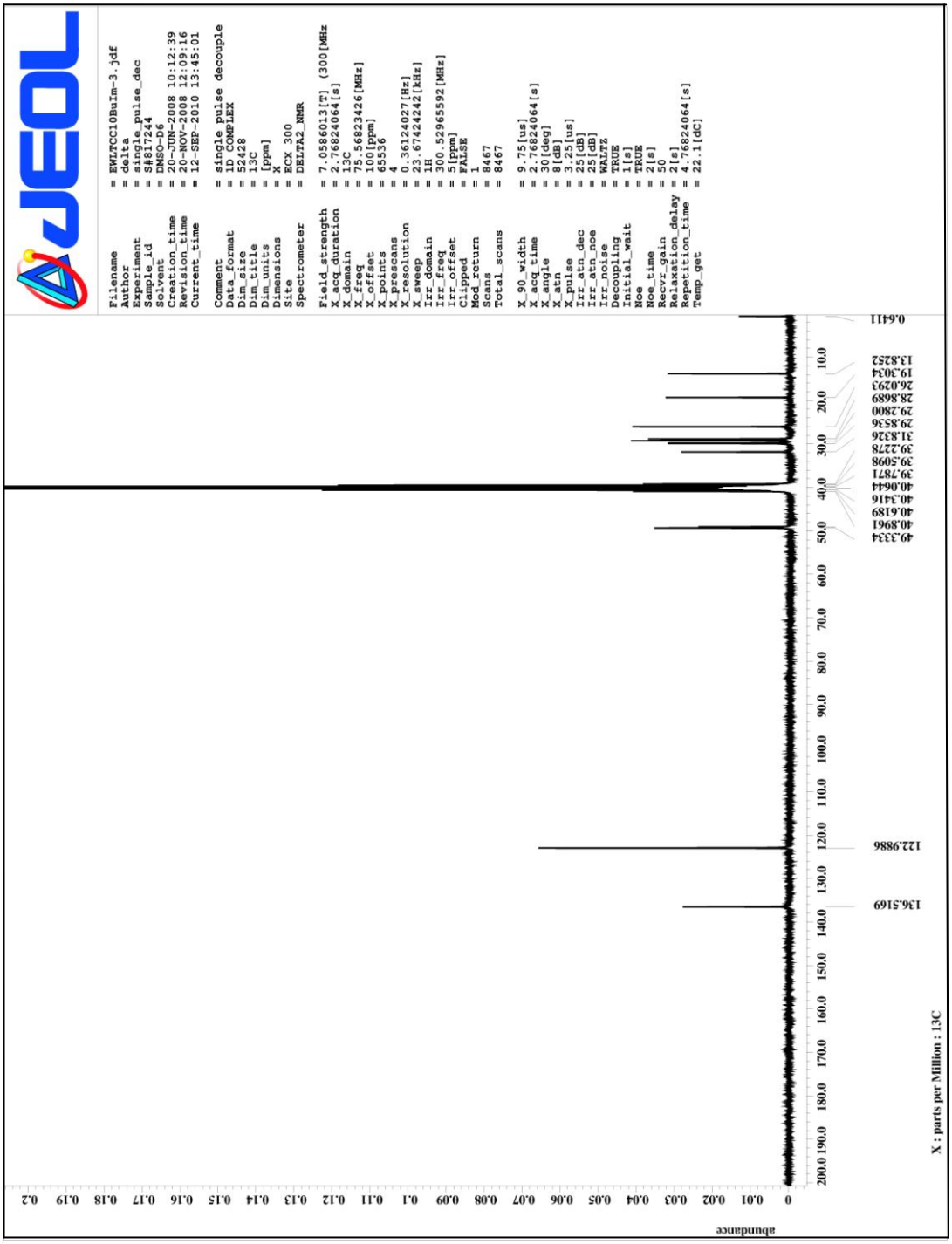
APPENDIX 36

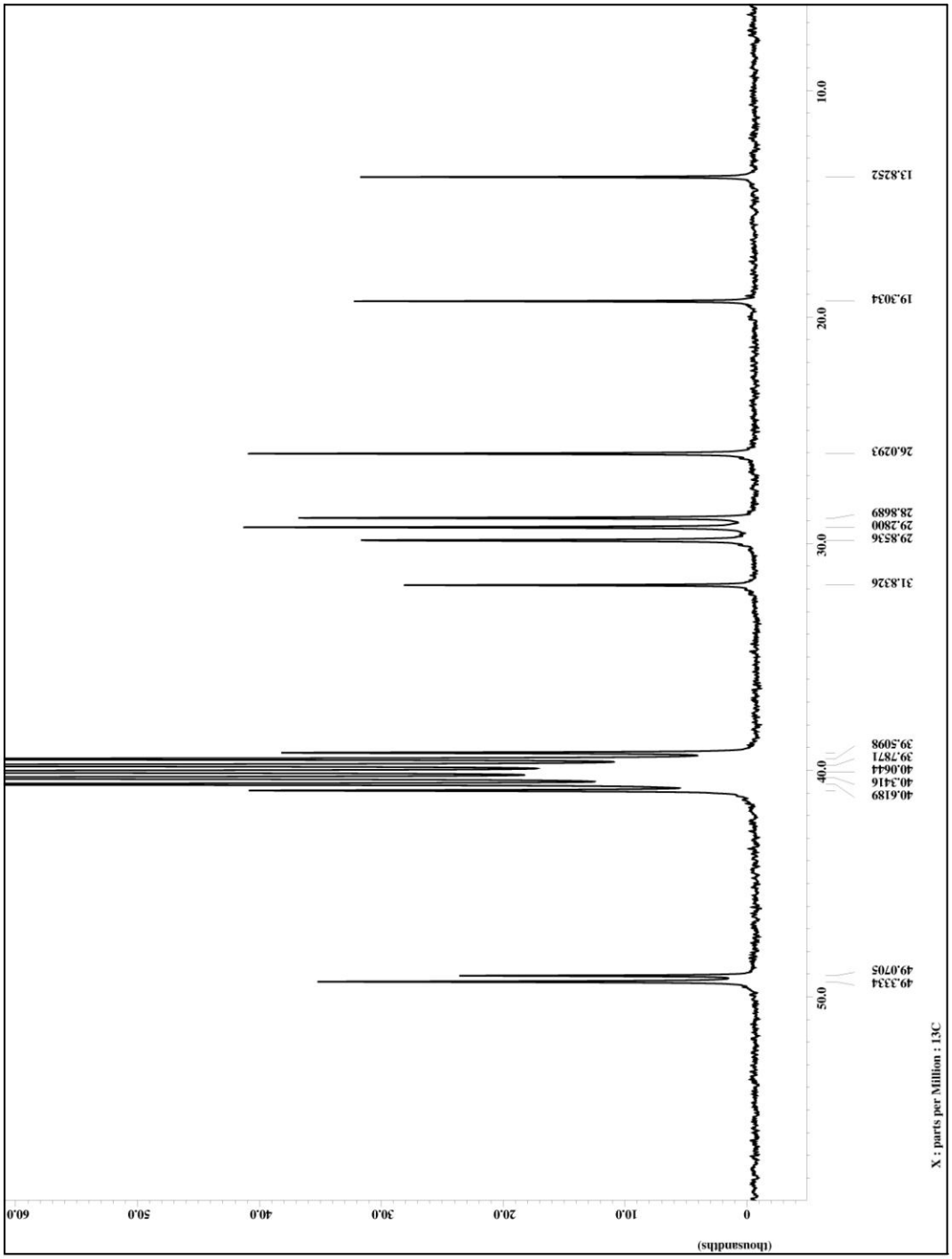
^{1}H AND ^{13}C NMR SPECTRA OF
1-(1'-BUTYL-3'-DECYLIMIDAZOLIUM)-3-(1''-BUTYL-3''-DECYLIMIDAZOLIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (2b)


JEOL
Filename = EW071808(LTCC10Bu1m)-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#336623
Solvent = DMSO-D6
Creation_time = 18-JUL-2008 09:43:31
Revision_time = 12-SEP-2010 13:34:39
Current_time = 12-SEP-2010 13:35:03
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 131107
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 = 22
Total_scans = 22
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 = 22.3[dC]
3 NTf2-
29.12
11.92
12.03
11.93
6.24
6.07
3
9.1456
9.1262
7.7584
7.7515
7.7470
4.1278
4.1049
4.0832
3.3575
3.3186
3.3026
3.2683
2.4820
2.4762
2.4694
2.4636
1.7632
1.7391
1.7151
1.2493
1.2092
1.1749
0.8899
0.8647
0.8406
-0.0224
-0.0338
abundance
X : parts per Million : 1H


abundance
X : parts per Million : 1H
11.93
4.0271
4.0031
4.1519
4.1278
4.1049
4.0832
29.12
6.24
11.92
1.7872
1.7632
1.7391
1.7151
1.6899
1.2744
1.2493
1.2092
1.1749
1.1520
0.8899
0.8647
0.8406
0.6552

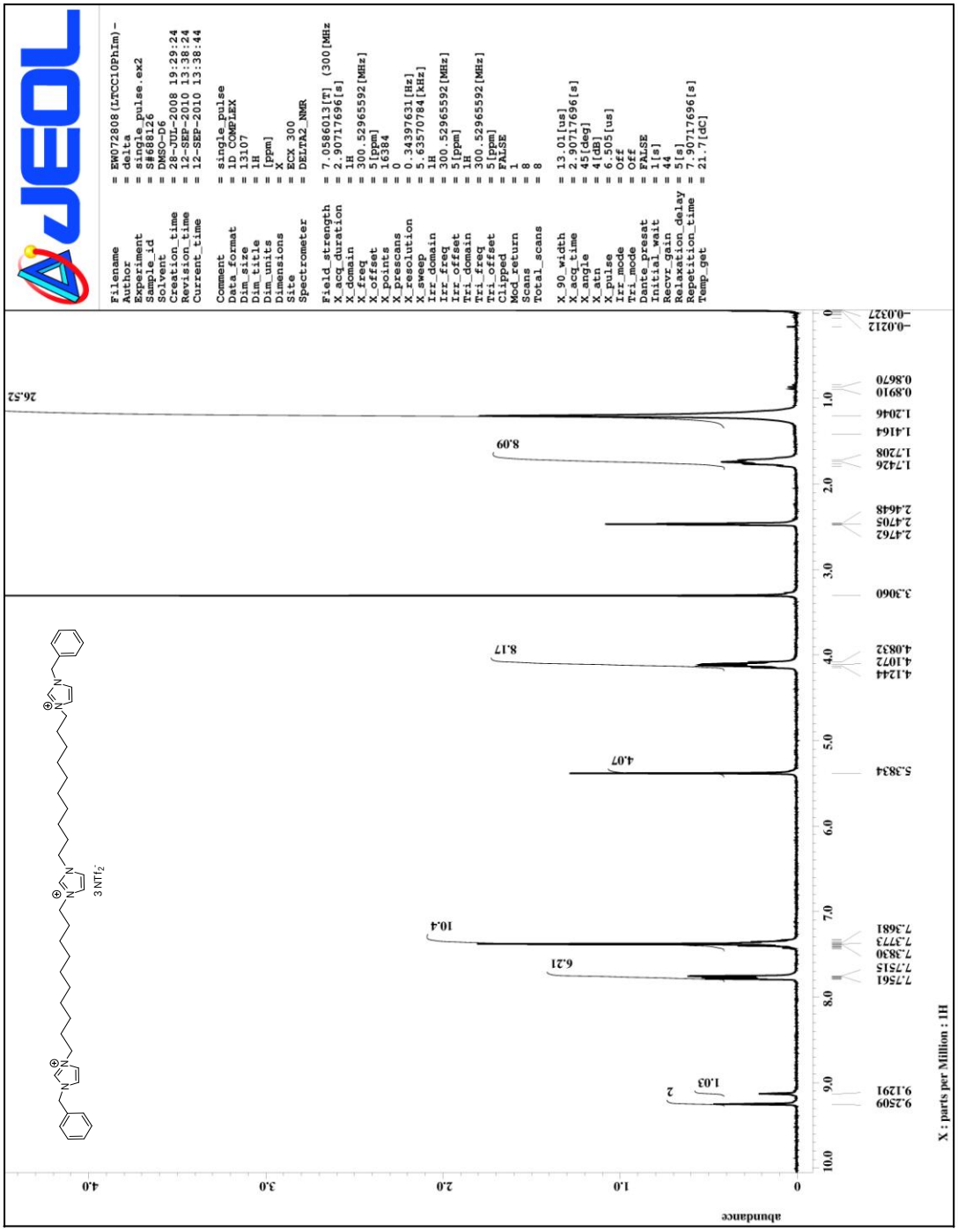

abundance
X : parts per Million : 1H
9.1456
9.1262
3
6.07
7.7710
7.7653
7.7584
7.7515
7.7470

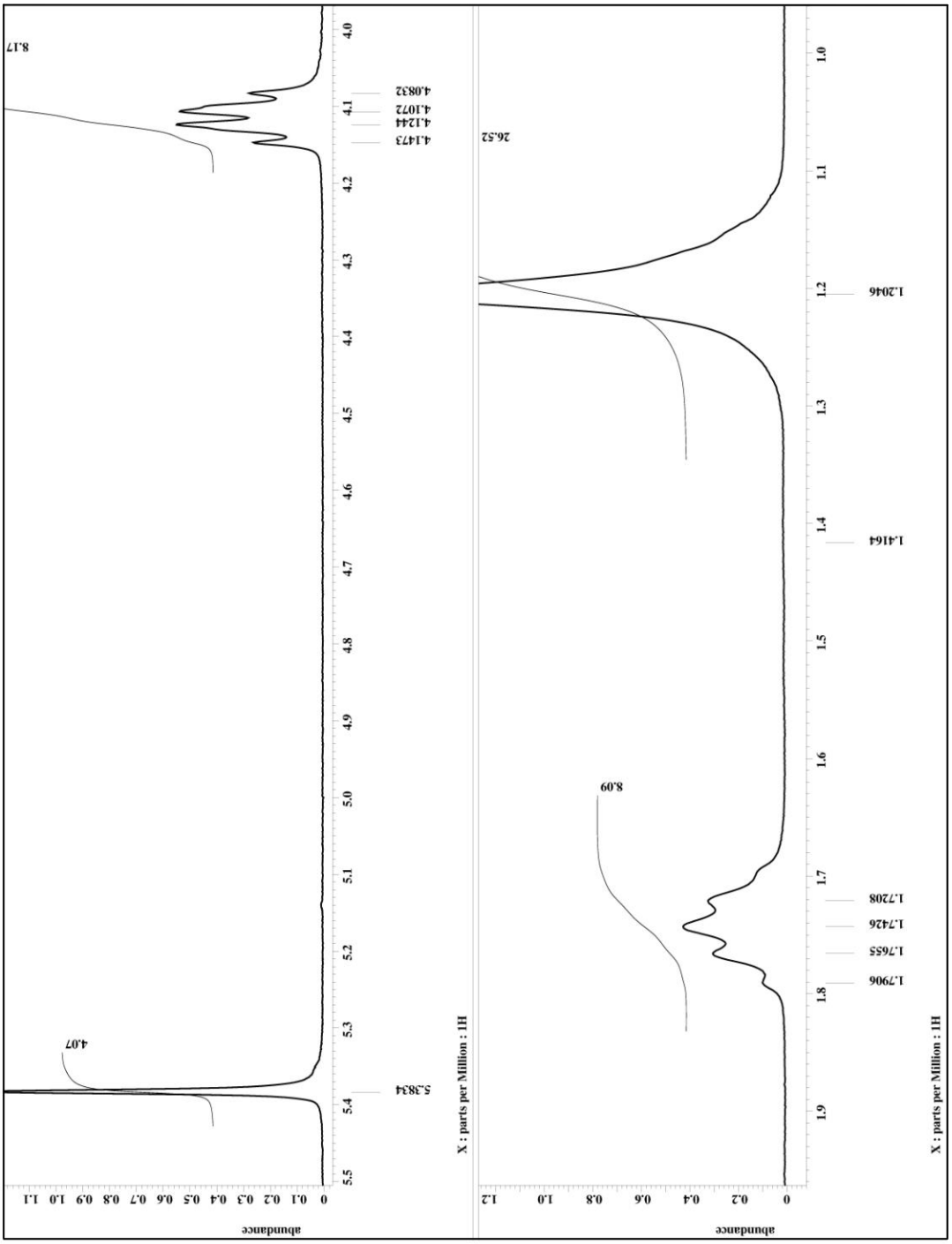

Filename = EWLTCC10BuIm-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#817244
Solvent = DMSO-D6
Creation_time = 20-JUN-2008 10:12:39
Revision_time = 20-NOV-2008 12:09:16
Current_time = 12-SEP-2010 13:45:01
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8467
Total_scans = 8467
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 22.1[dC]
abundance
0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0 180.0 190.0 200.0
X : parts per Million : 13C
0.6411
13.8252
19.3034
26.0293
28.8689
29.2800
29.8536
31.8326
39.2278
39.5098
39.7871
40.0644
40.3416
40.6189
40.8961
49.3334
122.9886
136.5169

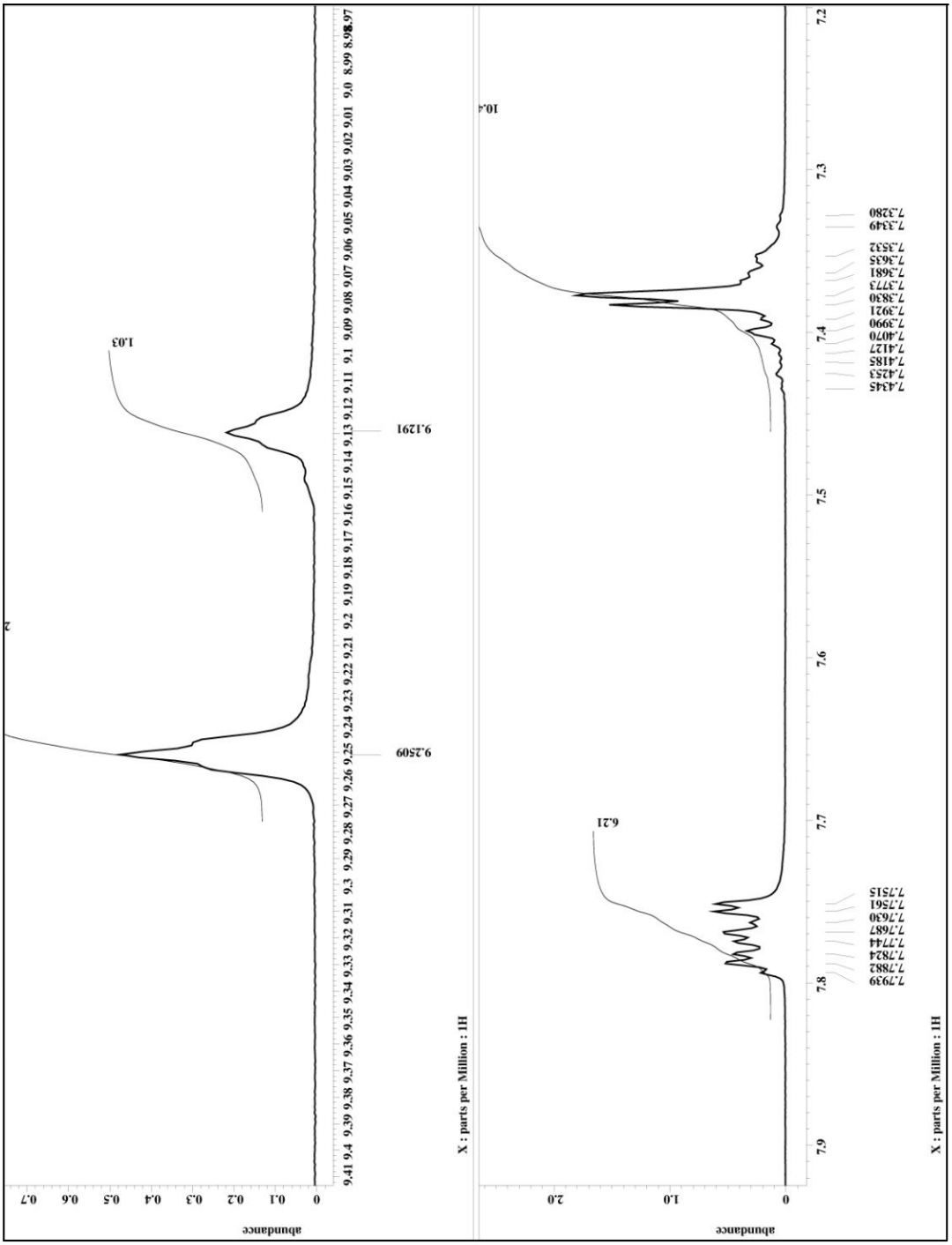

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
X : parts per Million : 13C
10.0
20.0
30.0
40.0
50.0
13.8252
19.3034
26.0293
28.8689
29.2800
29.8536
31.8326
39.5098
39.7871
40.0644
40.3416
40.6189
49.0705
49.3334

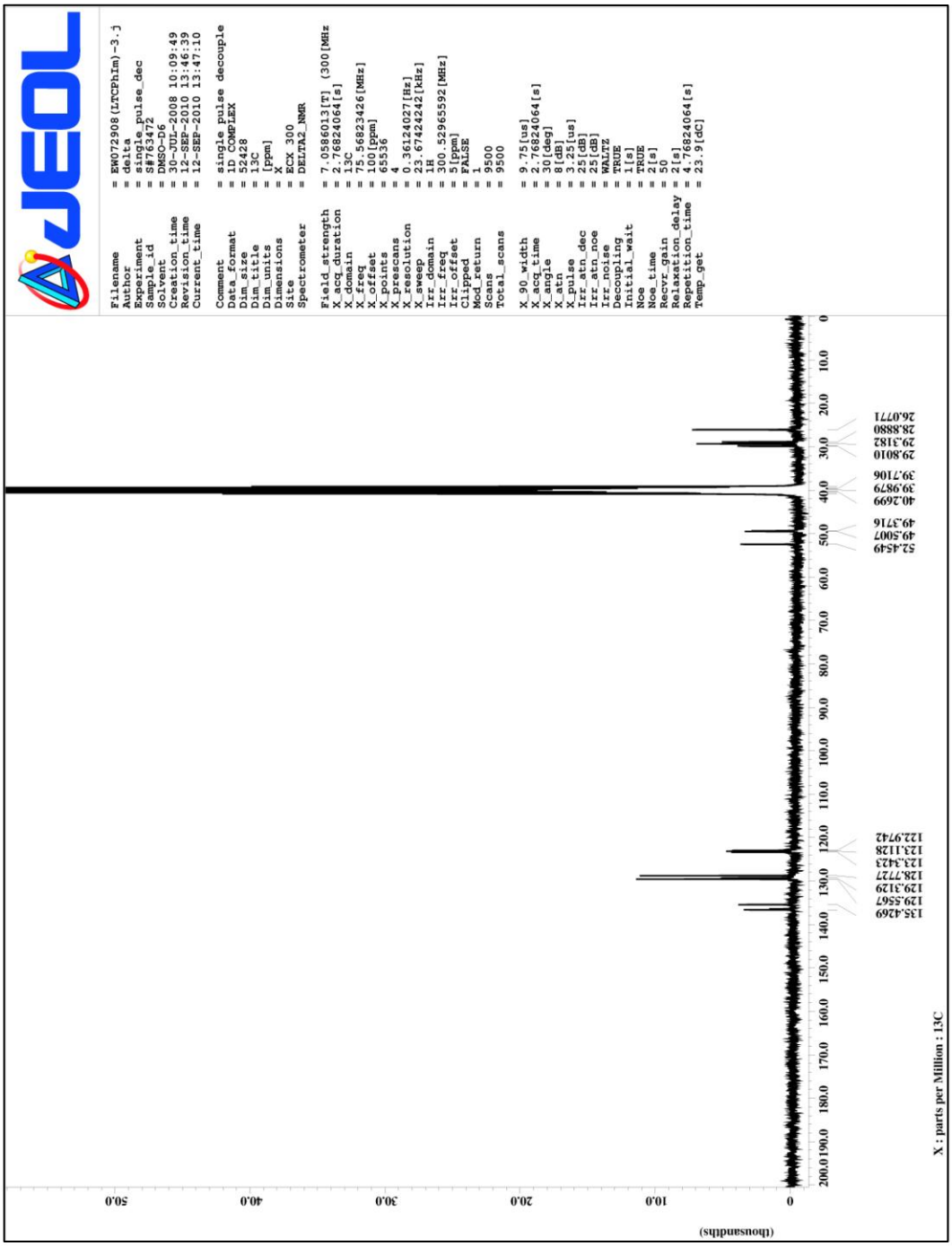
APPENDIX 37

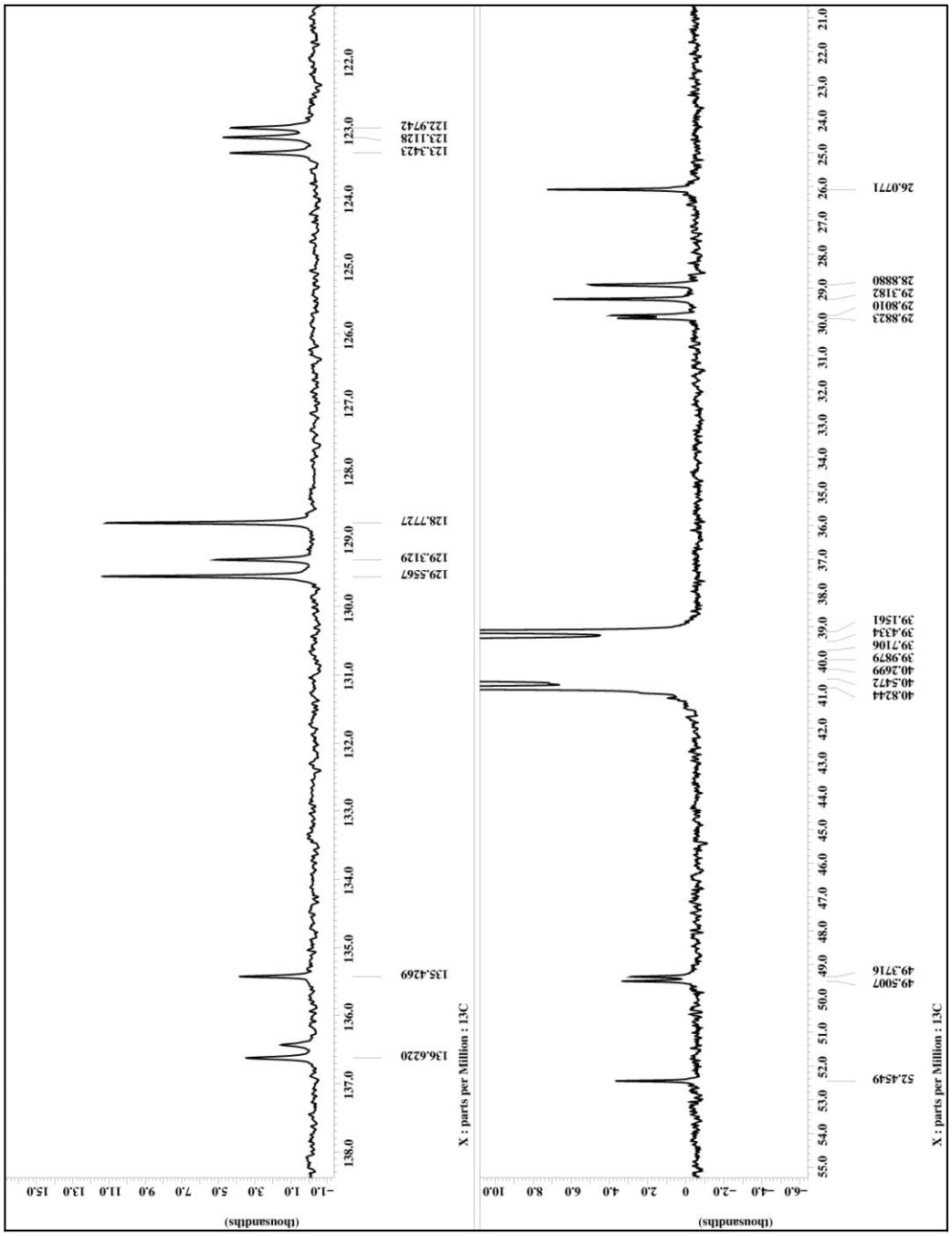
^{1}H AND ^{13}C NMR SPECTRA OF
1-(1'-BENZYL-3'-DECYLIMIDAZOLIUM)-3-(1''-BENZYL-3''-DECYLIMIDAZOLIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (2c)


JEOL
Filename = EW072808(LTCC10PhIm)-
Author = delta
Experiment = single_pulse.ex2
Sample_id = #68126
Solvent = DMSO-D6
Creation_time = 28-JUL-2008 19:29:24
Revision_time = 12-SEP-2010 13:38:24
Current_time = 12-SEP-2010 13:38:44
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 = 8
Total_scans = 8
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]
Receiver_gain = 414
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 21.7[dC]
3 NTf2-
26.52
8.09
8.17
4.07
10.4
6.21
1.03
2
abundance
X : parts per Million : 1H


abundance
X : parts per Million : 1H
1.7906
1.7655
1.7426
1.7208
1.4164
1.2046
8.09
26.52
4.1473
4.1244
4.1072
4.0832
5.3834
4.07
8.17

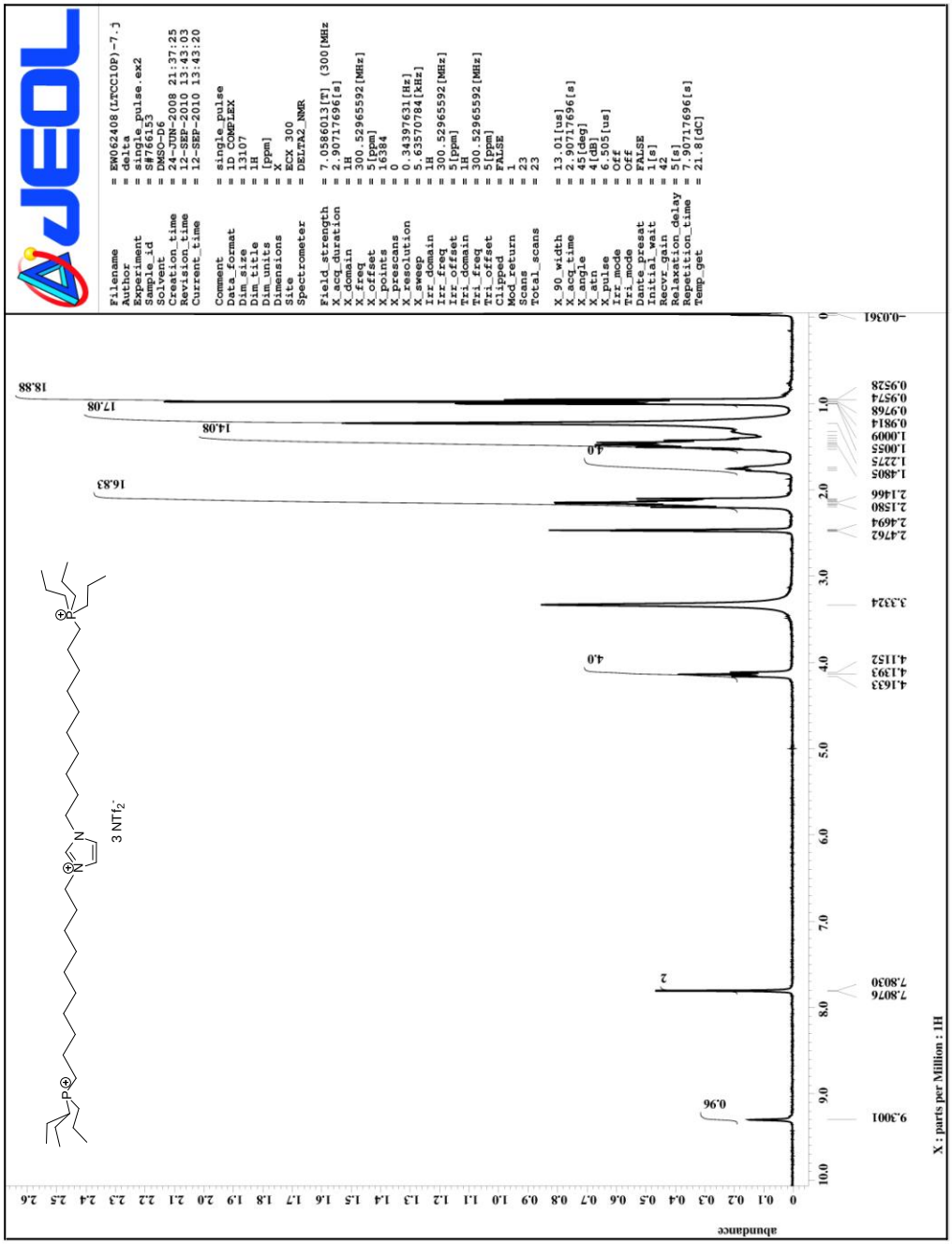

abundance
X : parts per Million : 1H
9.2509
9.1291
1.03
10.4
6.21
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.9393
7.7882
7.7824
7.7744
7.7687
7.7630
7.7561
7.7515
7.4345
7.4253
7.4185
7.4127
7.4070
7.3990
7.3921
7.3830
7.3773
7.3681
7.3635
7.3532
7.3349
7.3280

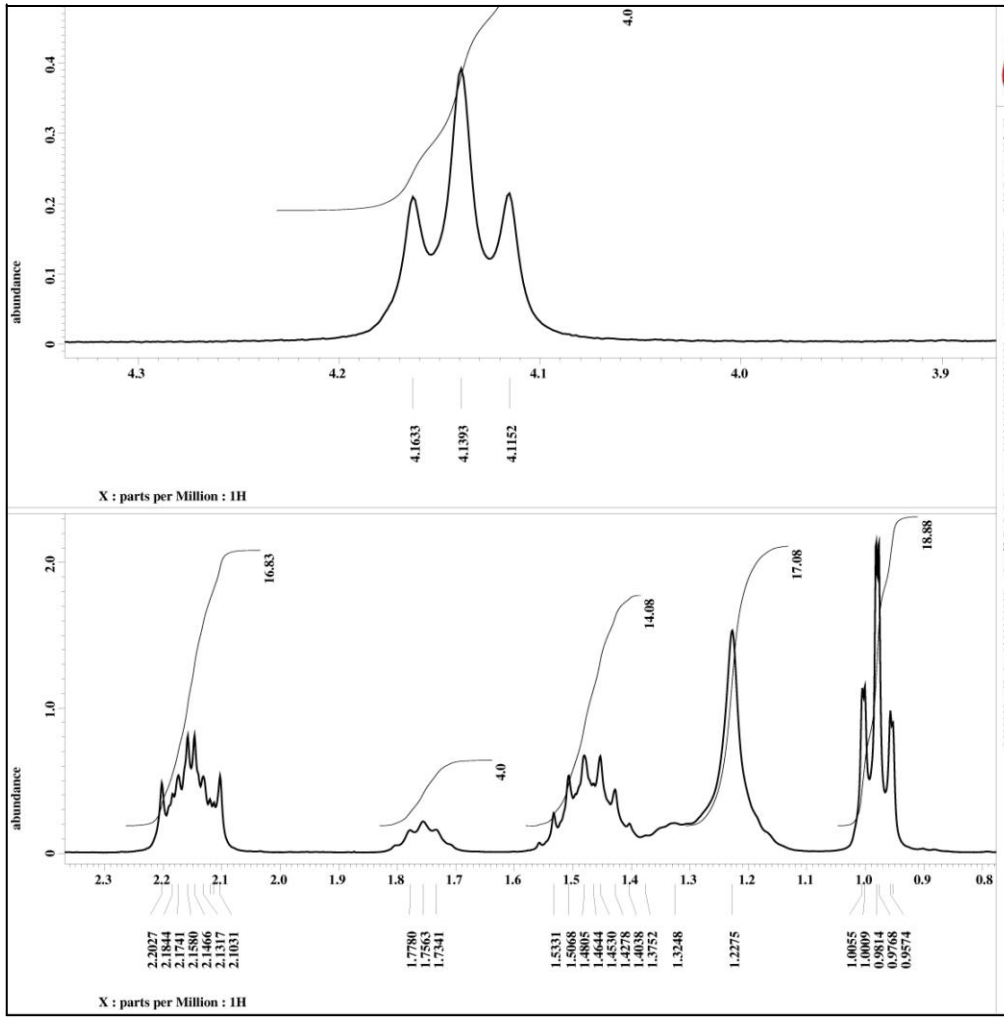

Filename = EW072908(LTCPhIm)-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#763472
Solvent = DMSO-D6
Creation_time = 30-JUL-2008 10:09:49
Revision_time = 12-SEP-2010 13:46:39
Current_time = 12-SEP-2010 13:47:10
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = KCX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.768240464[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.361240027[Hz]
X_sweep = 23.674242242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9500
Total_scans = 9500
X_90_width = 9.75[us]
X_acq_time = 2.768240464[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TYPE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.768240464[s]
Temp_get = 23.9[dC]
(thousandths)
X : parts per Million : 13C
26.0771
28.8880
29.3182
29.8010
39.7106
39.9879
40.2699
49.3716
49.5007
52.4549
122.9742
123.1128
123.3423
128.7727
129.3129
129.5567
133.4269


(thousandths)
X : parts per Million : 13C
136,6220
135,4269
129,5567
129,3129
128,7727
123,3423
123,1128
122,9742
52,4549
49,5007
49,3716
40,8244
40,5472
40,2699
39,9879
39,7106
39,4334
39,1561
29,8823
29,8010
29,3182
28,8880
26,0771

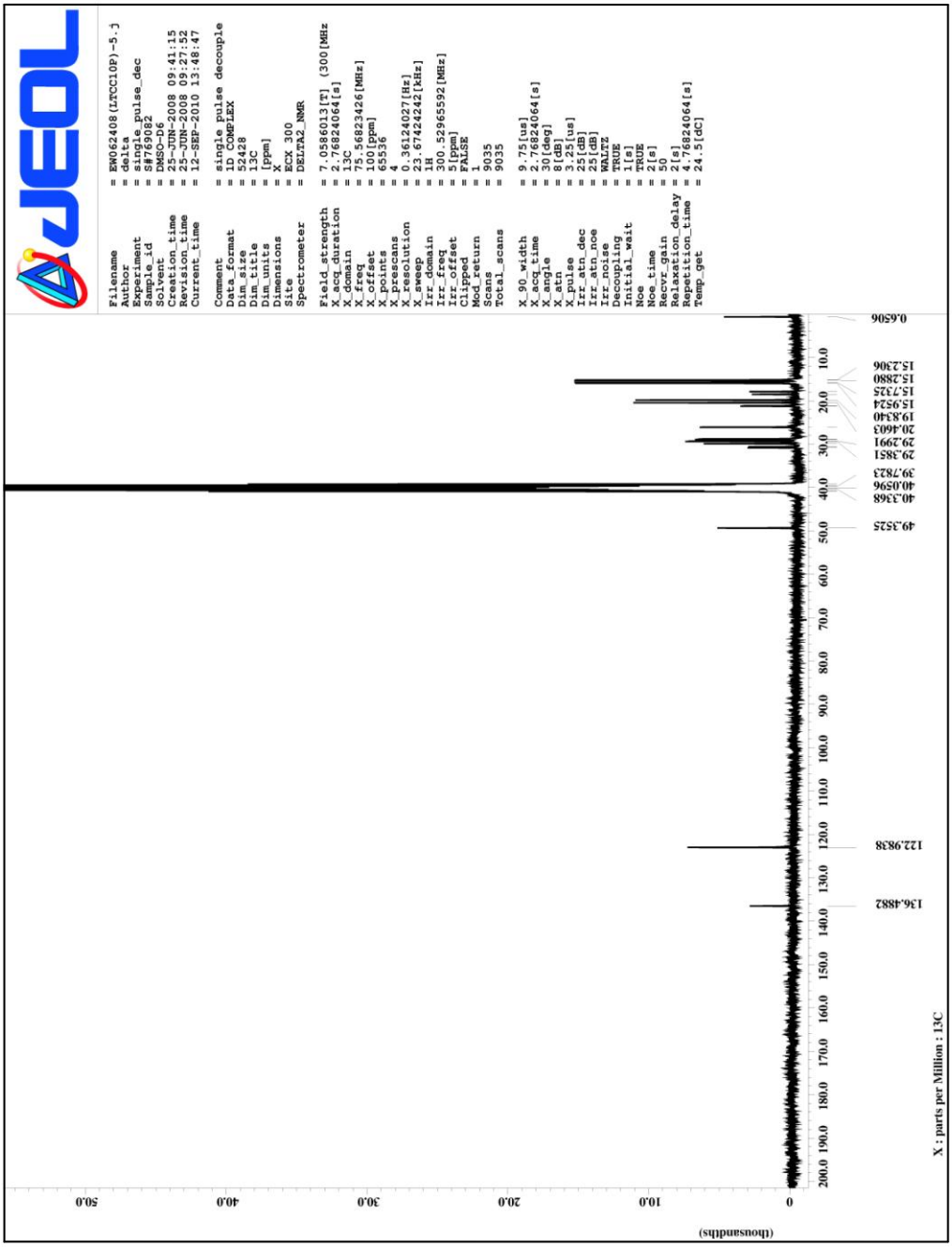
APPENDIX 38

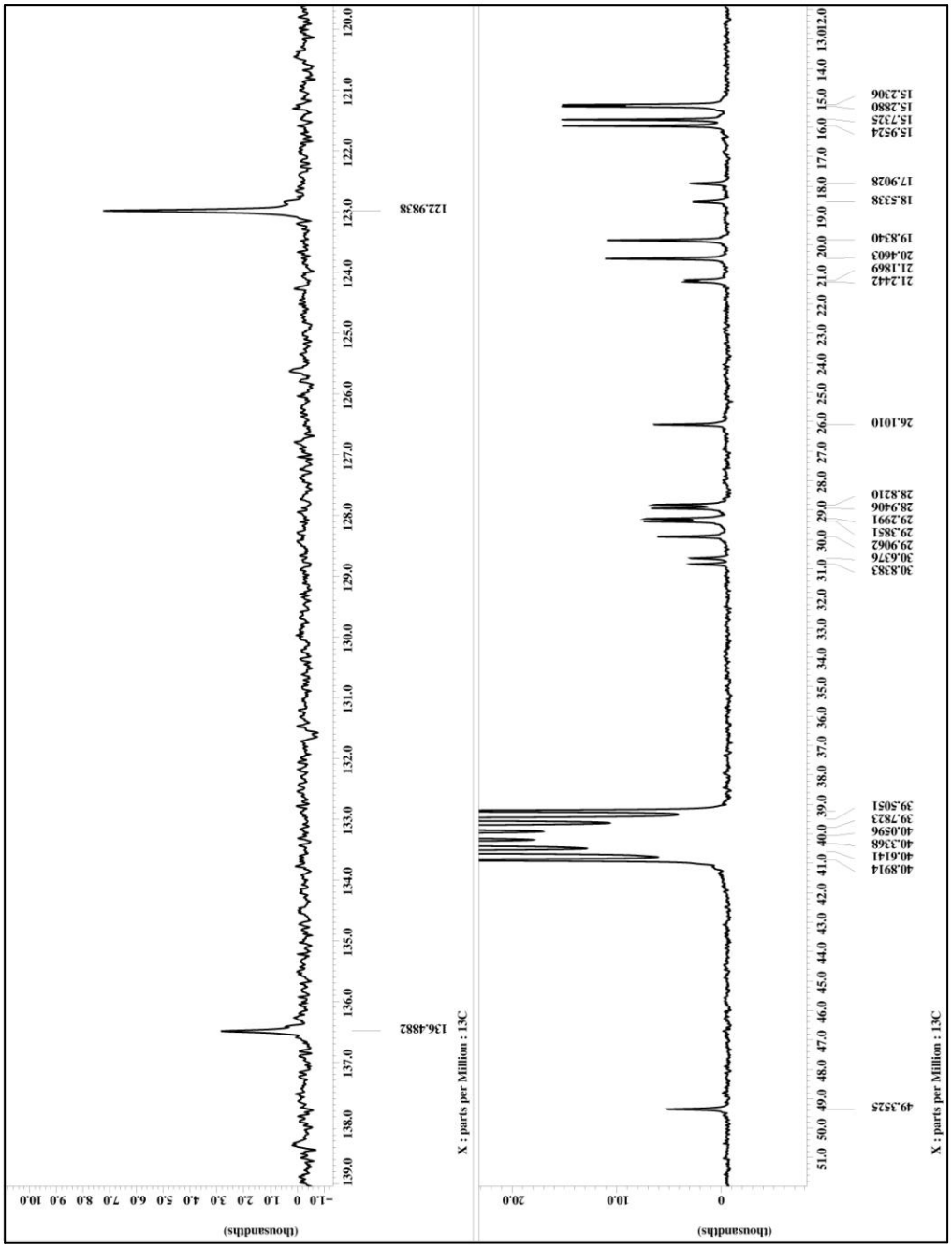
^{1}H, ^{13}C AND ^{31}P NMR SPECTRA OF
1-DECYLTRIPROPYLPHOSPHONIUM-3-DECYLTRIPROPYLPHOSPHONIUM
IMIDAZOLIUM TR[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (2d)

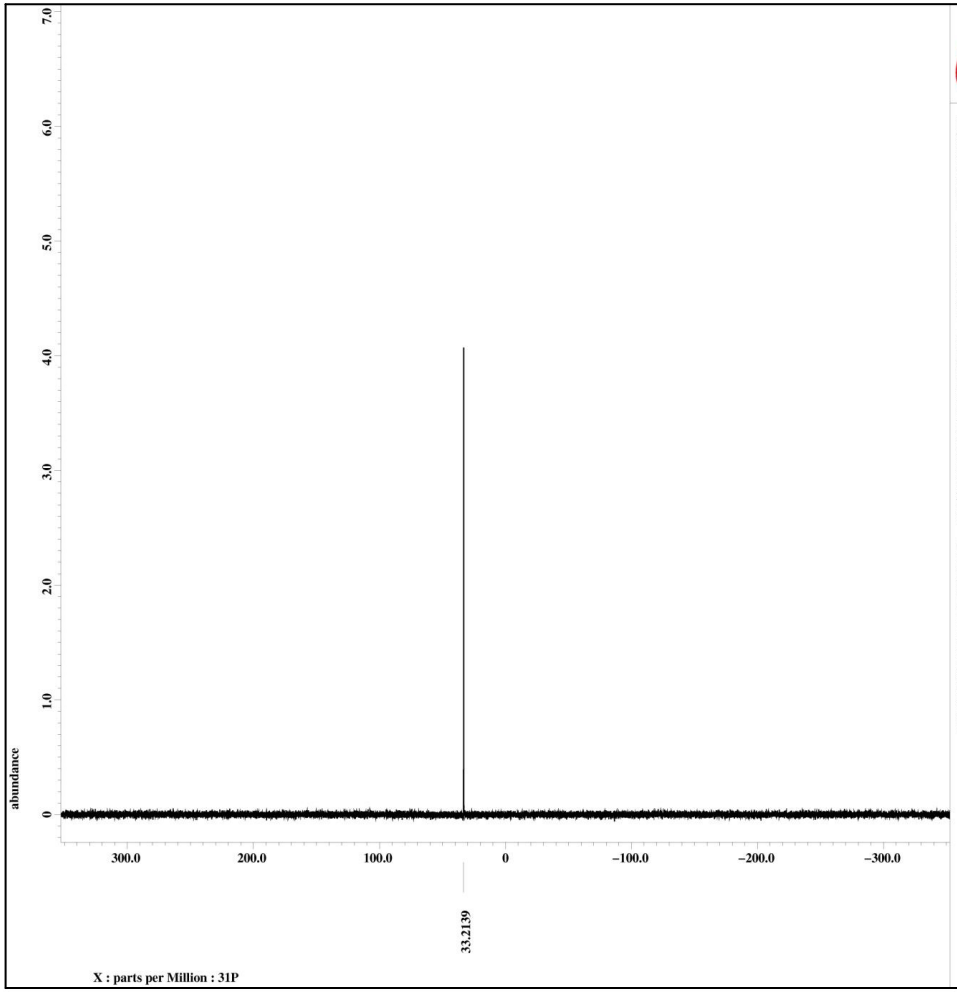

JEOL
Filename = EW062408(LTCC10P)-7.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#766153
Solvent = DMSO-D6
Creation_time = 24-JUN-2008 21:37:25
Revision_time = 24-SEP-2010 13:43:33
Current_time = 12-SEP-2010 13:43:20
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 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_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 = 23
Total_scans = 23
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 = 42
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 21.8[dC]
3 NTf2-
18.88
17.08
14.08
16.83
4.0
4.0
2
0.96
9.3001
7.8076
7.8030
4.1633
4.1393
4.1152
3.3324
2.4762
2.4694
2.1580
2.1466
1.4805
1.2275
1.0055
1.0009
0.9814
0.9748
0.9574
0.9528
-0.0361
abundance
X : parts per Million : 1H



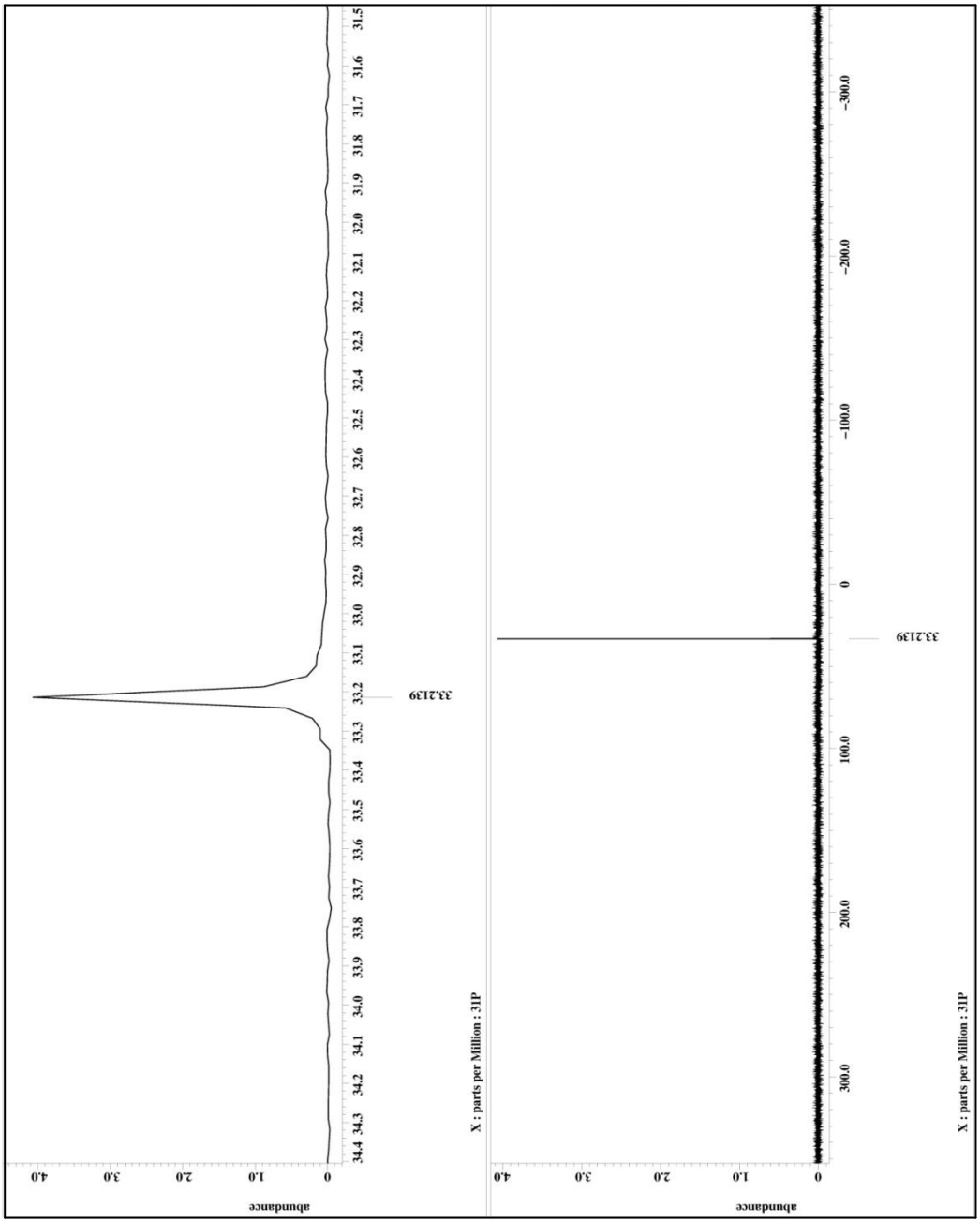

```
Filename          = EW062408(LTCC10P)-7.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#766153
Solvent           = DMSO-D6
Creation_time     = 24-JUN-2008 21:37:25
Revision_time     = 12-SEP-2010 13:43:03
Current_time      = 12-SEP-2010 13:43:59

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             = 23
Total_scans       = 23

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        = 42
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 21.8[dC]
```


Filename = EW062408(LTCC10P)-5.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#769082
Solvent = DMSO-D6
Creation_time = 25-JUN-2008 09:41:15
Revision_time = 25-JUN-2008 09:27:52
Current_time = 12-SEP-2010 13:48:47
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = EX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.568234 26[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
X_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9035
Total_scans = 9035
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 24.5[dC]
0.6506
15.2306
15.2880
15.7325
15.9524
19.8340
20.4603
29.2991
29.3851
39.7823
40.0596
40.1368
49.3525
122.9838
136.4882
X : parts per Million : 13C
(thousandths)


(thousandths)
X : parts per Million : 13C
136.4882
122.9838
(thousandths)
X : parts per Million : 13C
49.3525
40.8914
40.6141
40.3368
40.0596
39.7823
39.5051
30.8383
30.6376
29.9062
29.3851
29.2991
28.9406
28.8210
26.1010
21.2442
21.1869
20.4603
19.8340
18.5338
17.9028
15.9524
15.7325
15.2880
15.2306

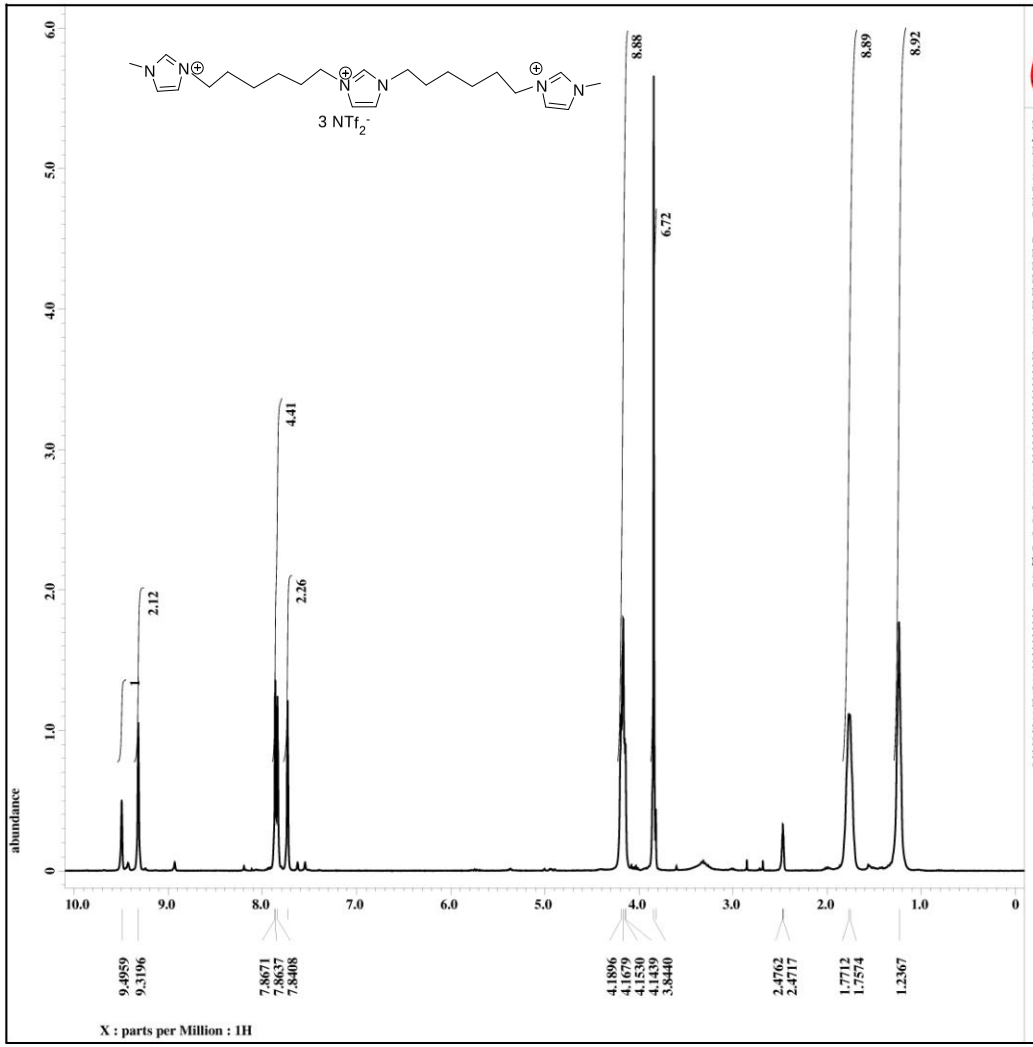



```
Filename          = P31_LTCC10TriPrP-2.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#432265
Solvent           = DMSO-D6
Creation_time     = 11-OCT-2010 01:58:42
Revision_time     = 10-OCT-2010 13:03:39
Current_time      = 10-OCT-2010 13:07:20

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 31P
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.1835008[s]
X_domain          = 31P
X_freq            = 202.46831075[MHz]
X_offset          = 0[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 5.44956752[Hz]
X_sweep           = 178.57142857[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 93
Total_scans       = 93

X_90_width        = 11.9[us]
X_acq_time        = 0.1835008[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.96666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.1835008[s]
Temp_get          = 21.9[dC]
```

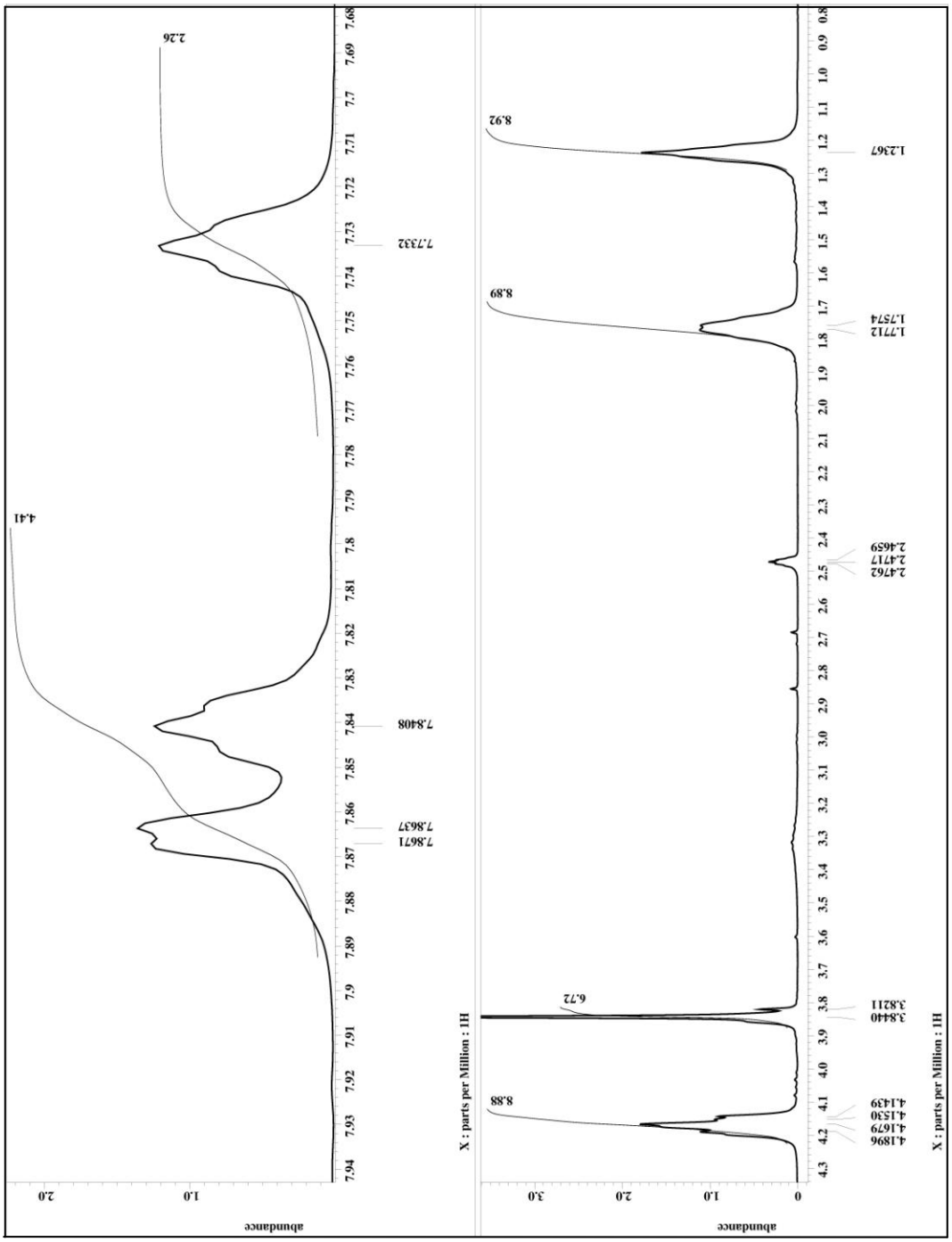

abundance
4.0
3.0
2.0
1.0
0
34.4 34.3 34.2 34.1 34.0 33.9 33.8 33.7 33.6 33.5 33.4 33.3 33.2 33.1 33.0 32.9 32.8 32.7 32.6 32.5 32.4 32.3 32.2 32.1 32.0 31.9 31.8 31.7 31.6 31.5
33.2139
X : parts per Million : 31P
abundance
4.0
3.0
2.0
1.0
0
300.0 200.0 100.0 0 −100.0 −200.0 −300.0
33.2139
X : parts per Million : 31P

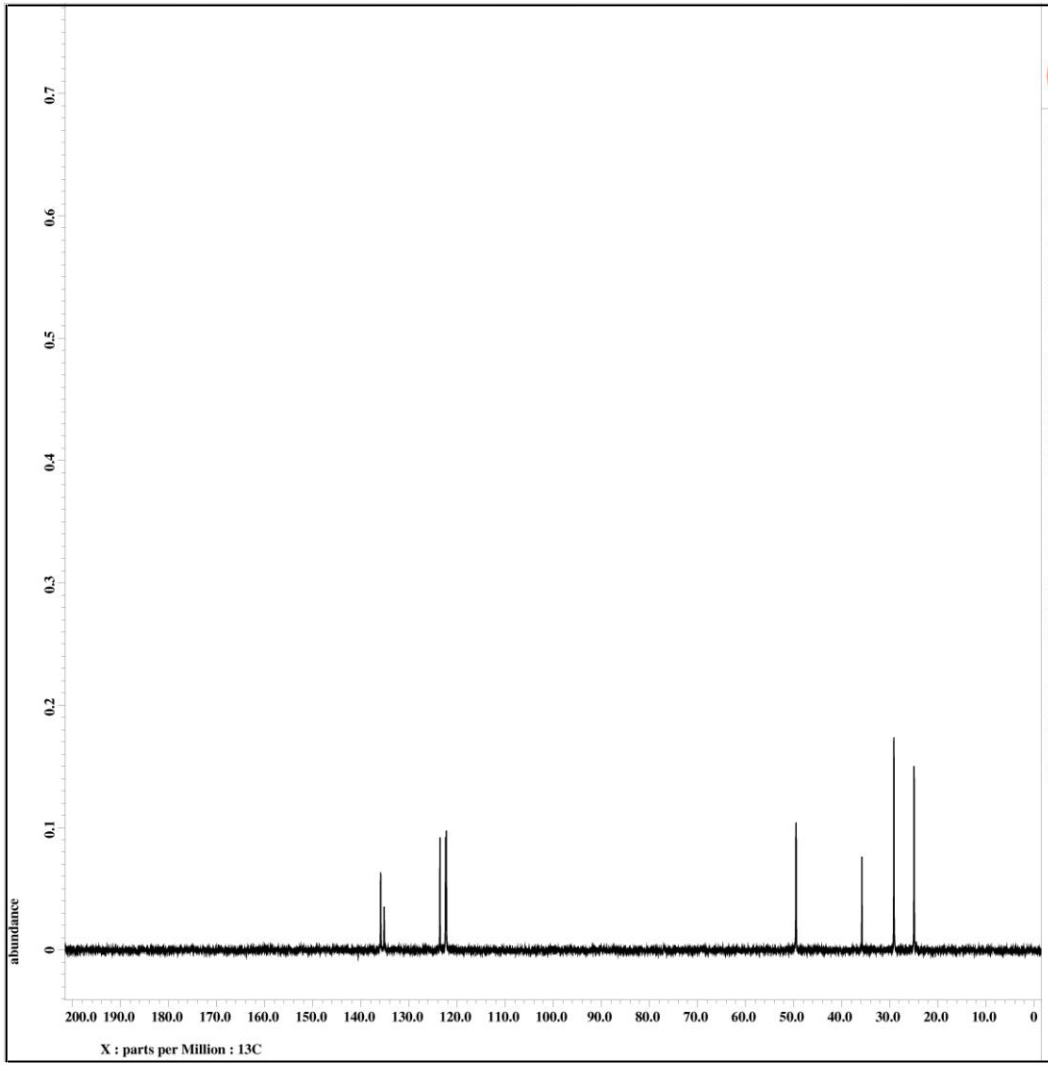
APPENDIX 39

^{1}H AND ^{13}C NMR SPECTRUM OF
1-(1'-METHYL-3'-HEXYLIMIDAZOLIUM)-3-(1"-METHYL-3"-HEXYLIMIDAZOLIUM)IMIDAZOLIUM TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (3a)

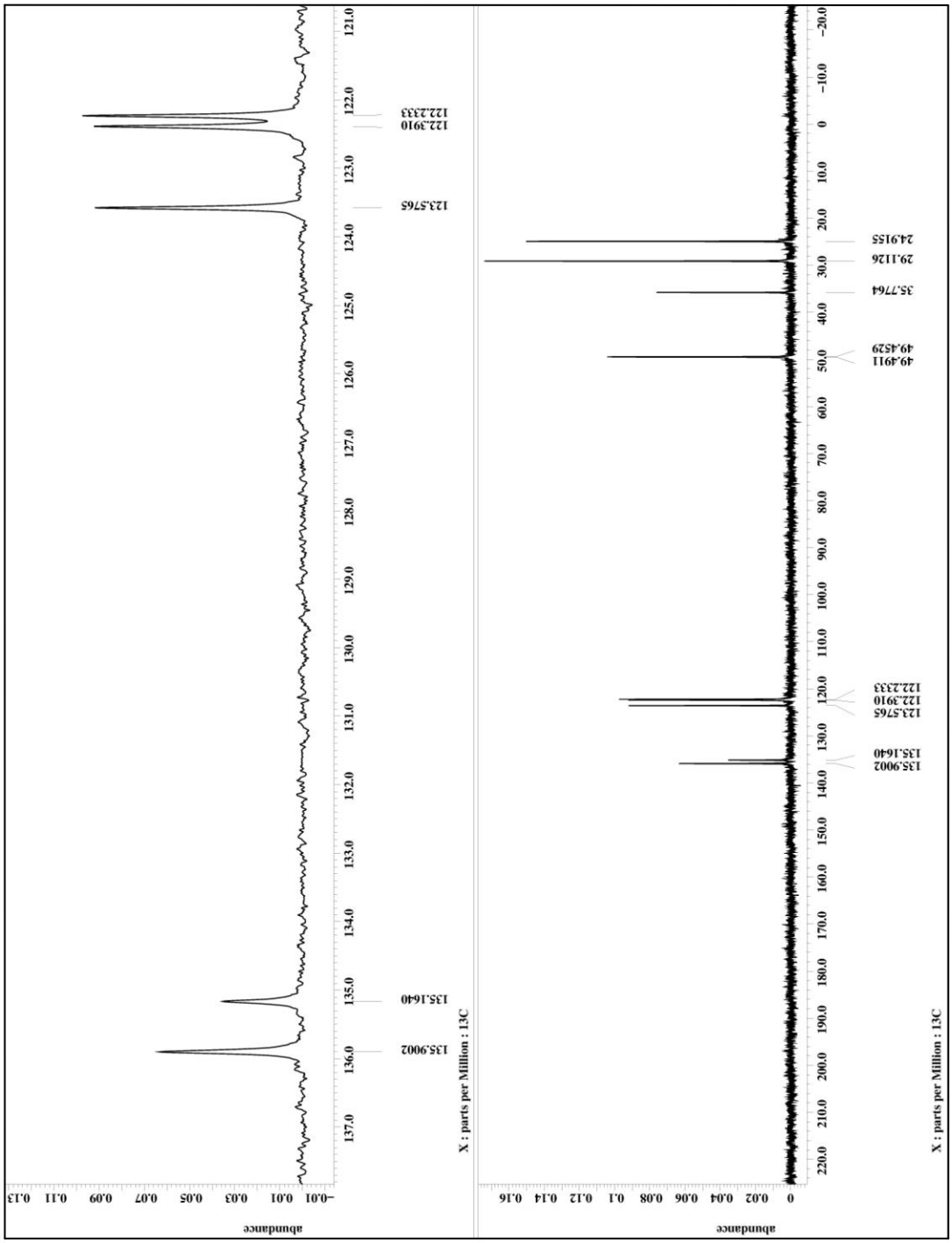



```
Filename          = methylIMc6protonTri-2
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#594121
Solvent           = DMSO-D6
Creation_time     =  3-OCT-2008 16:42:18
Revision_time     = 12-SEP-2010 13:13:23
Current_time      = 12-SEP-2010 13:13:41

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        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.2[dC]
```


abundance
X : parts per Million : 1H
8.88
6.72
8.89
8.92
4.1896
4.1679
4.1530
4.1439
3.8440
3.8211
2.4762
2.4717
2.4659
1.7712
1.7574
1.2367
abundance
X : parts per Million : 1H
4.41
2.26
7.8671
7.8637
7.8408
7.7332

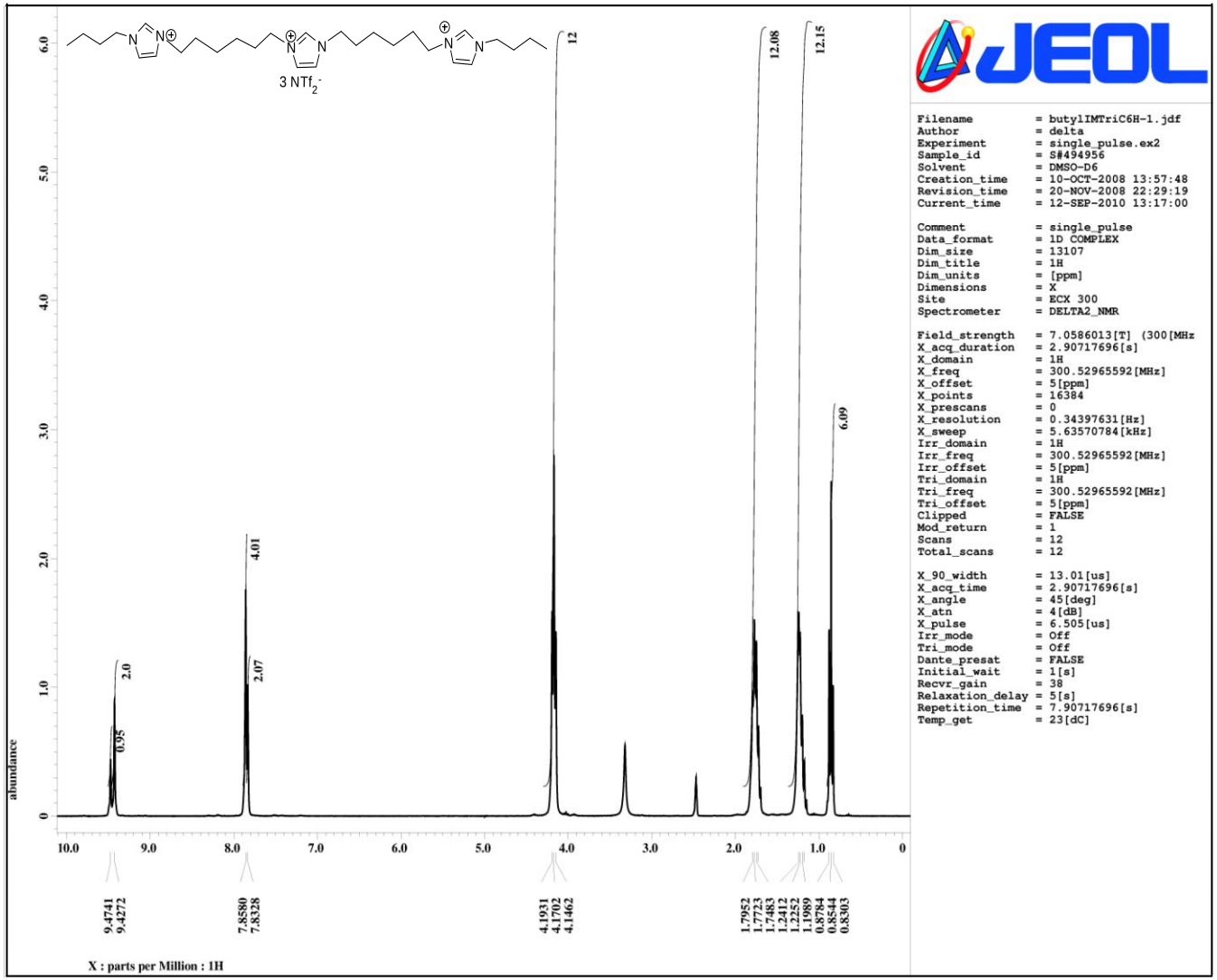


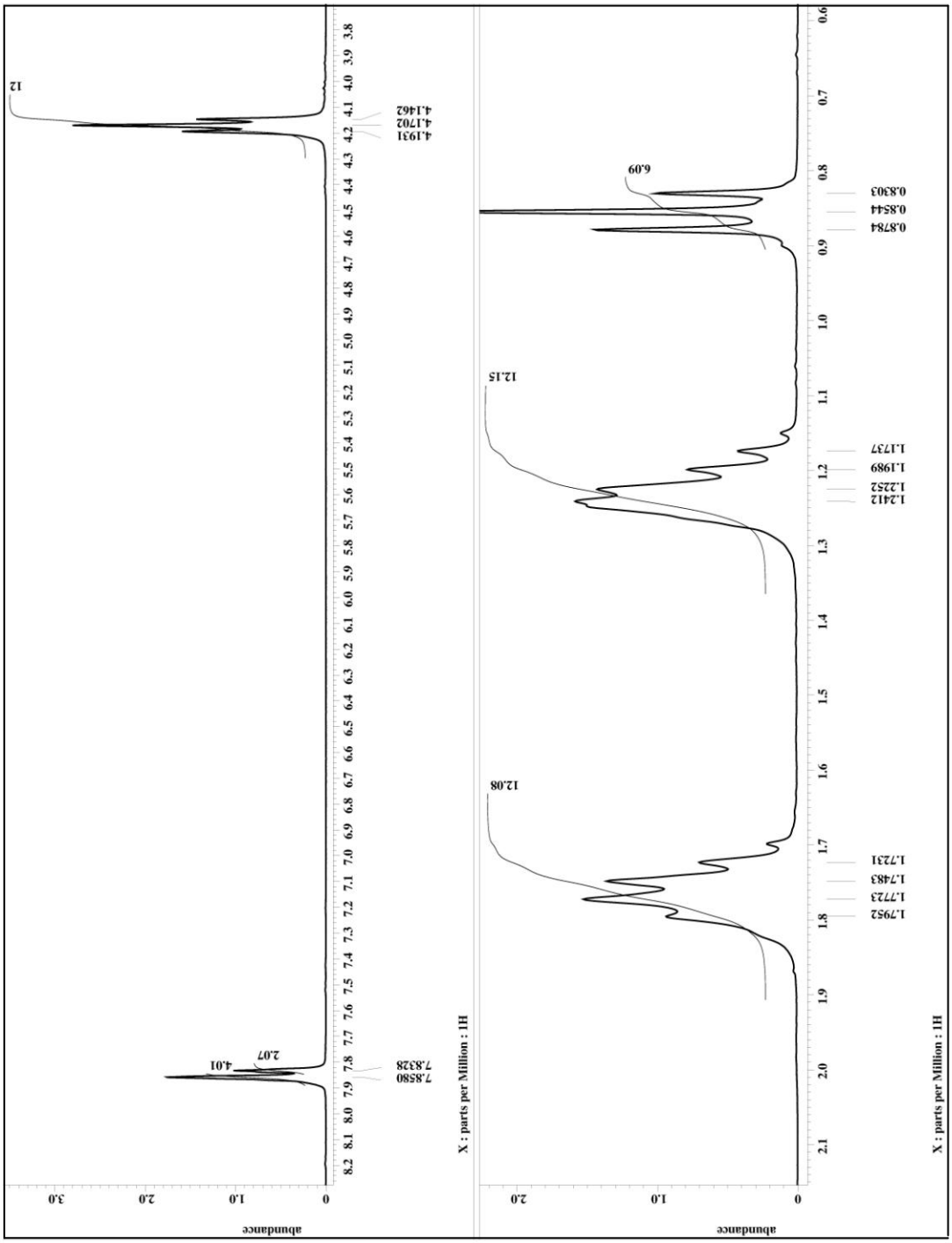

```
Filename          = 080610mimlt-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#793918
Solvent           = D2O
Creation_time     = 10-JUN-2008 23:23:00
Revision_time     = 21-SEP-2010 20:49:27
Current_time      = 21-SEP-2010 21:08:10

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 800
Total_scans       = 800

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23.2[dC]
```

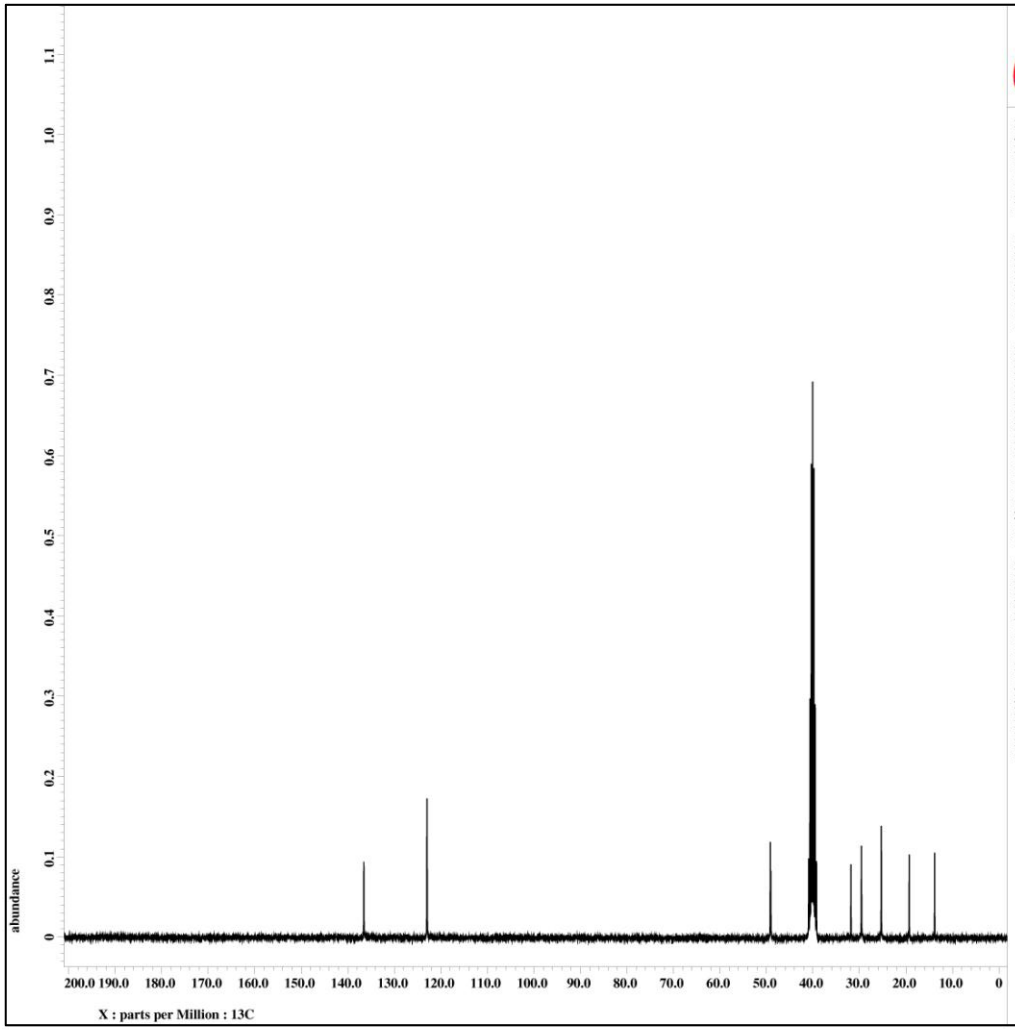

abundance
X : parts per Million : 13C
135.9002
135.1640
123.5765
122.3910
122.2333
24.9155
29.1126
35.7764
49.4529
49.4911

APPENDIX 40

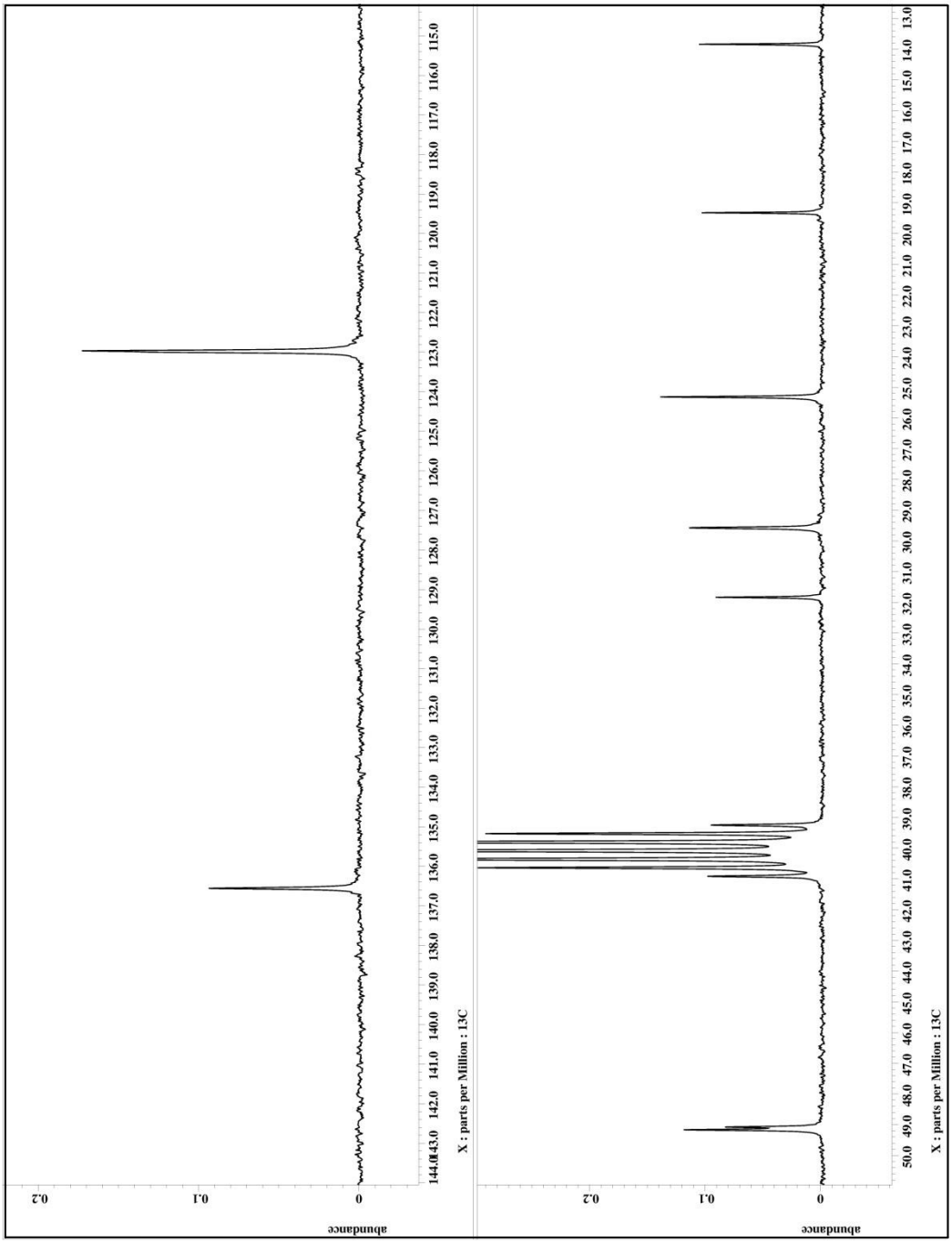
^{1}H NMR SPECTRUM OF
1-(1'-BUTYL-3'-HEXYLIMIDAZOLIUM)-3-(1"-BUTYL-3"-HEXYLIMIDAZOLIUM)IMIDAZOLIUM TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (3b)


3 NTf2-
12
12.08
12.15
6.09
4.01
2.07
2.0
0.95
abundance
9.4741
9.4272
7.8580
7.8328
4.1931
4.1702
4.1462
1.7952
1.7723
1.7483
1.2412
1.2252
1.1989
0.8784
0.8544
0.8303
X : parts per Million : 1H
Filename = butylIMTriC6H-1.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#494956
Solvent = DMSO-D6
Creation_time = 10-OCT-2008 13:57:48
Revision_time = 20-NOV-2008 22:29:19
Current_time = 12-SEP-2010 13:17:00
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 = 38
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23[dC]


abundance
X : parts per Million : 1H
7.8580
7.8328
4.01
2.07
4.1931
4.1702
4.1462
12
12.08
1.7952
1.7723
1.7483
1.7231
12.15
1.2412
1.2252
1.1989
1.1737
6.09
0.8784
0.8544
0.8303

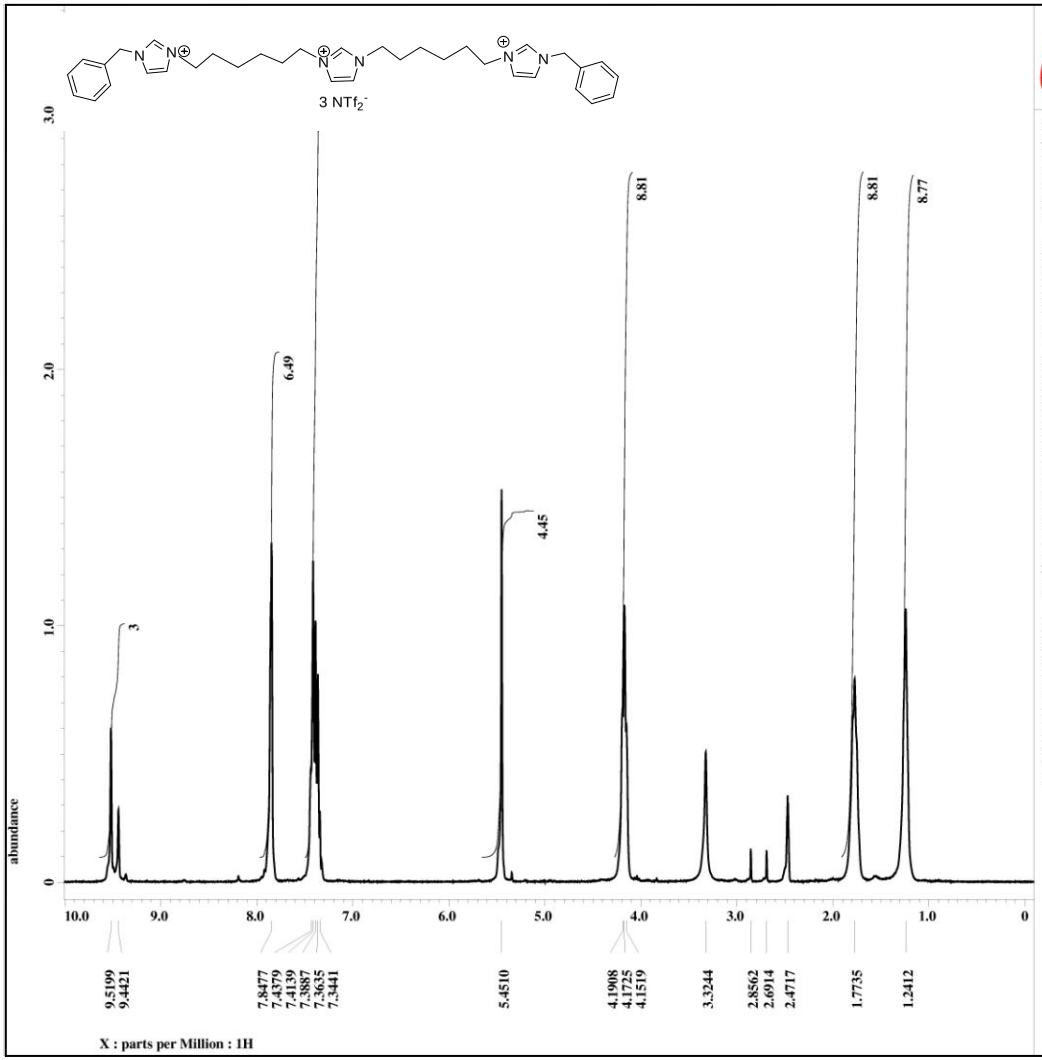



```
Filename          = 20081010butyl-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#604494
Solvent           = DMSO-D6
Creation_time     = 10-OCT-2008 18:18:30
Revision_time     = 21-SEP-2010 21:57:22
Current_time      = 21-SEP-2010 21:58:02

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23[dC]
```

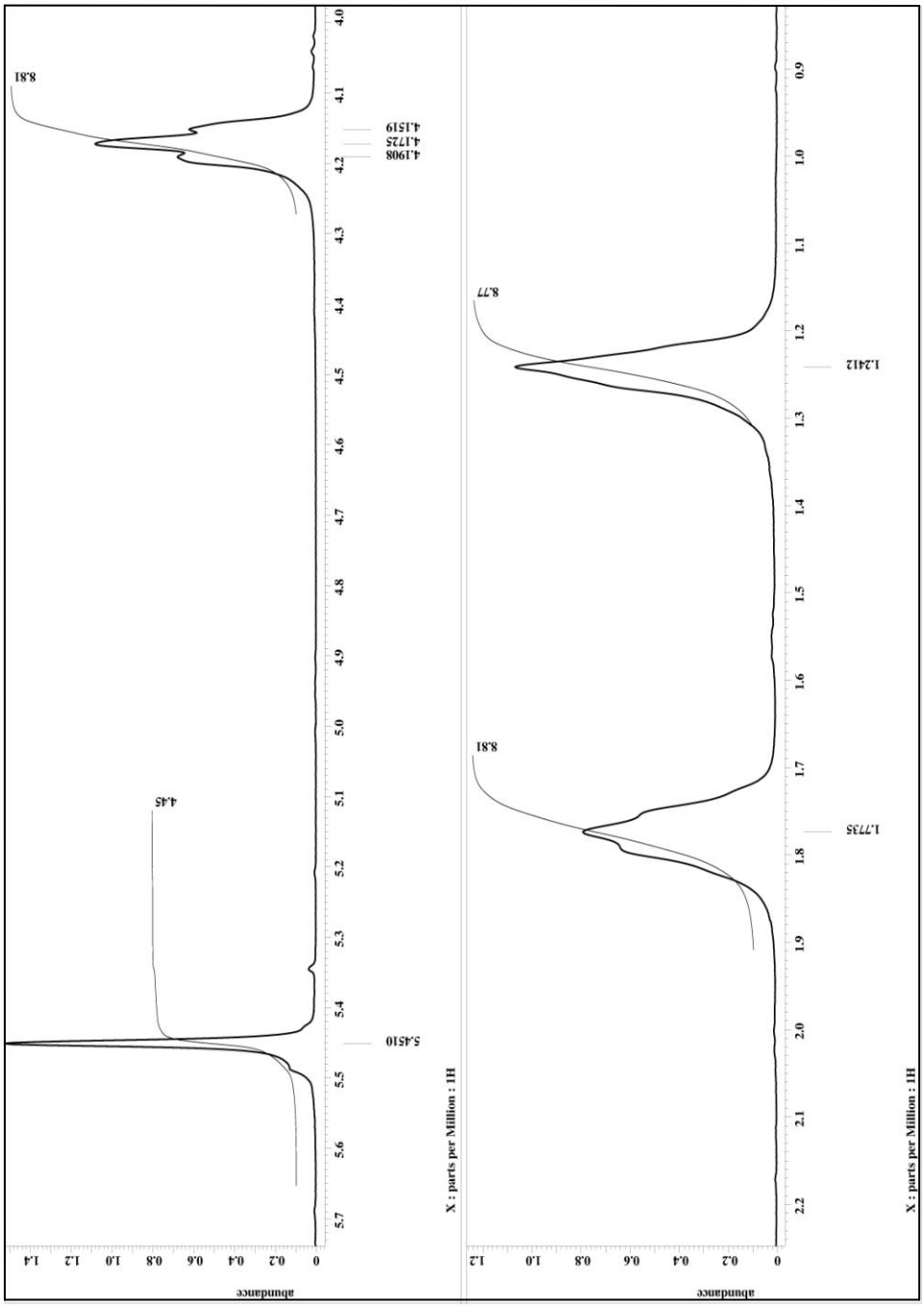

abundance
0.2
0.1
0
X : parts per Million : 13C
144.0 143.0 142.0 141.0 140.0 139.0 138.0 137.0 136.0 135.0 134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0 126.0 125.0 124.0 123.0 122.0 121.0 120.0 119.0 118.0 117.0 116.0 115.0
abundance
0.2
0.1
0
X : parts per Million : 13C
50.0 49.0 48.0 47.0 46.0 45.0 44.0 43.0 42.0 41.0 40.0 39.0 38.0 37.0 36.0 35.0 34.0 33.0 32.0 31.0 30.0 29.0 28.0 27.0 26.0 25.0 24.0 23.0 22.0 21.0 20.0 19.0 18.0 17.0 16.0 15.0 14.0 13.0

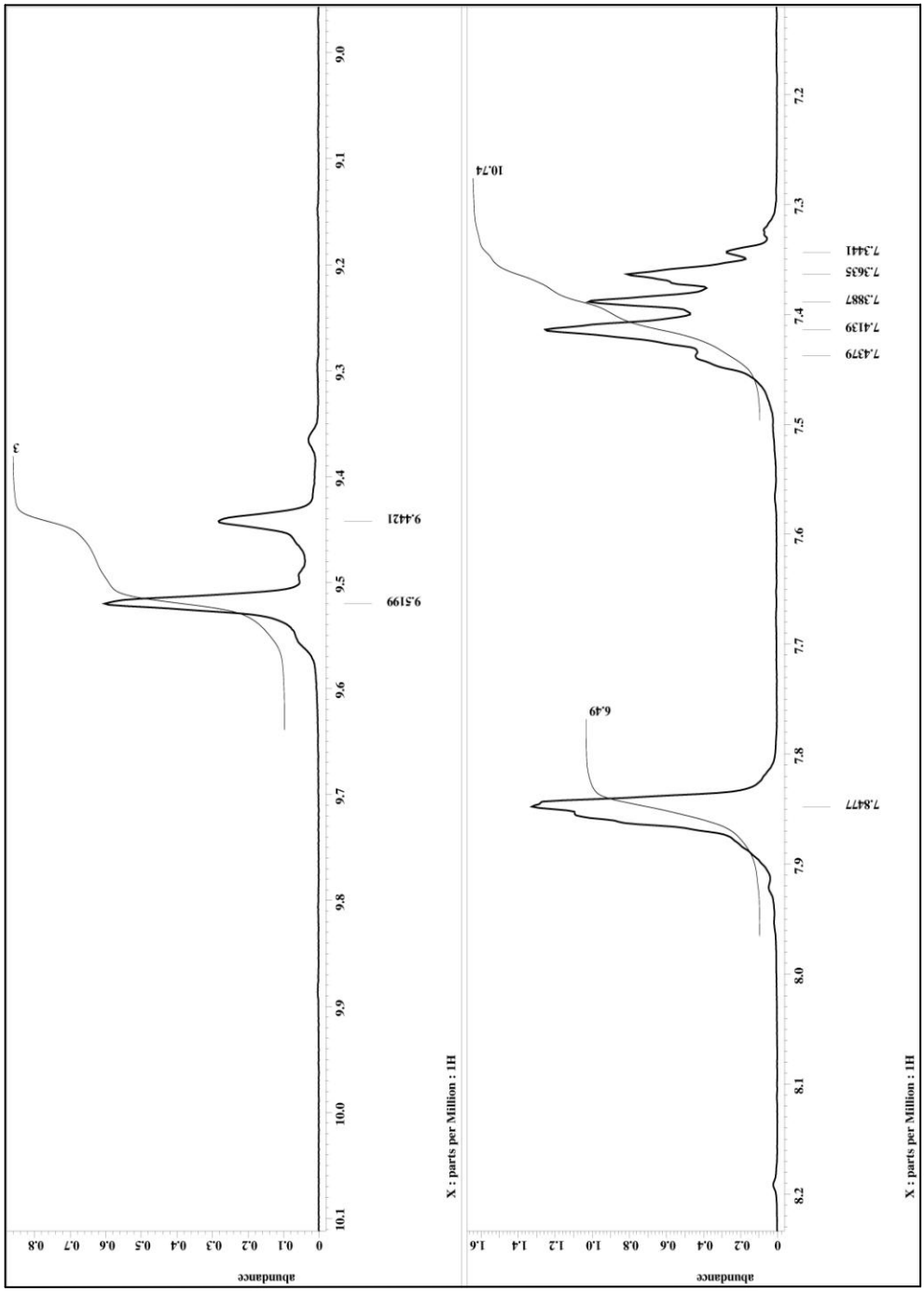
APPENDIX 41

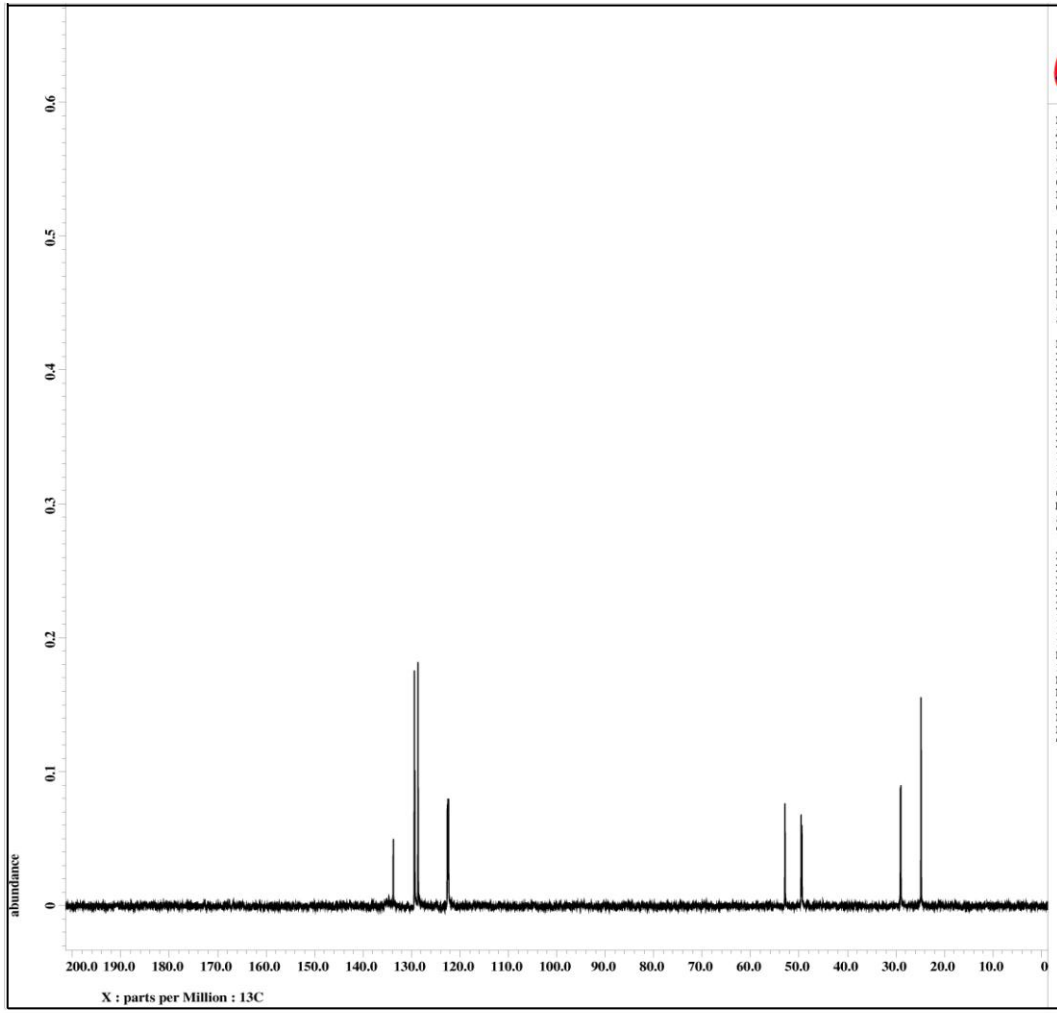
^{1}H AND ^{13}C NMR SPECTRUM OF
1-(1'-BENZYL-3'-HEXYLIMIDAZOLIUM)-3-(1"-BENZYL-3"-HEXYLIMIDAZOLIUM)IMIDAZOLIUM TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (3b)



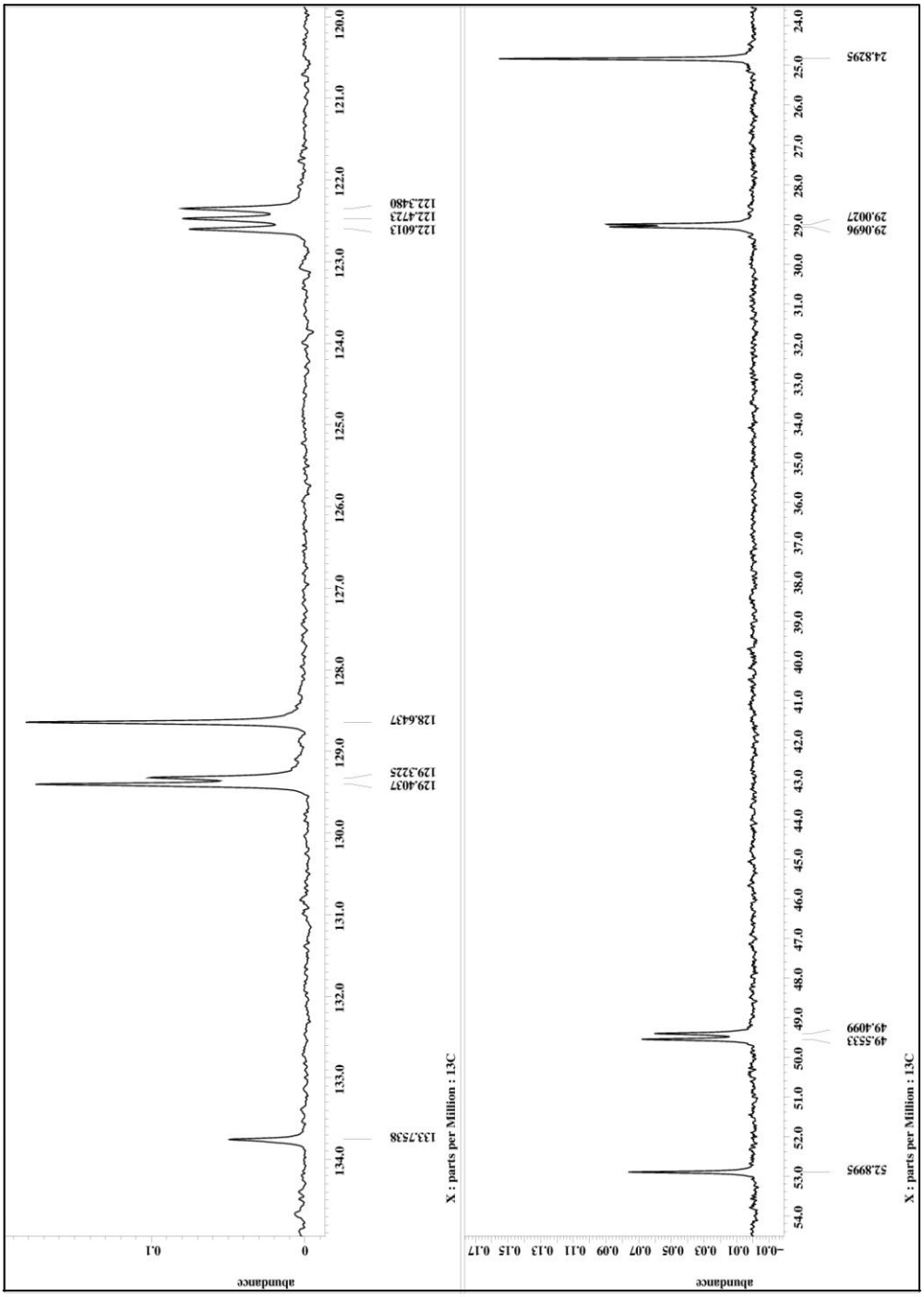

```
Filename          = benzylIMC6TriH-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#600109
Solvent           = DMSO-D6
Creation_time     =  3-OCT-2008 16:52:16
Revision_time     = 12-SEP-2010 13:22:25
Current_time      = 12-SEP-2010 13:23:09

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        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.2[dC]
```


abundance
X : parts per Million : 1H
5.4510
4.45
8.81
4.1908
4.1725
4.1519
1.7735
1.2412
8.77


abundance
X : parts per Million : 1H
7.8477
6.49
7.4379
7.4139
7.3887
7.3635
7.3441
10.74
9.5199
9.4421
3

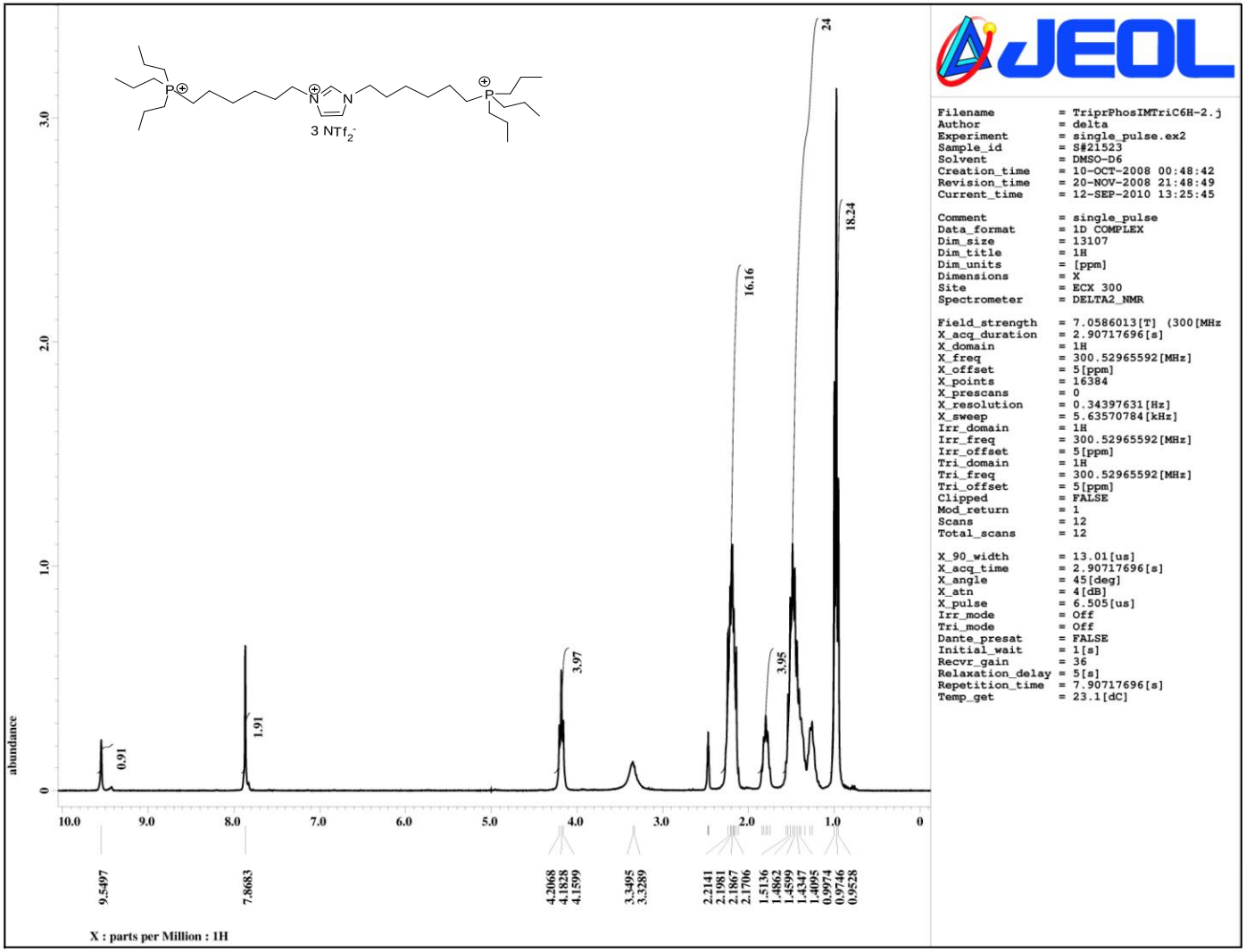


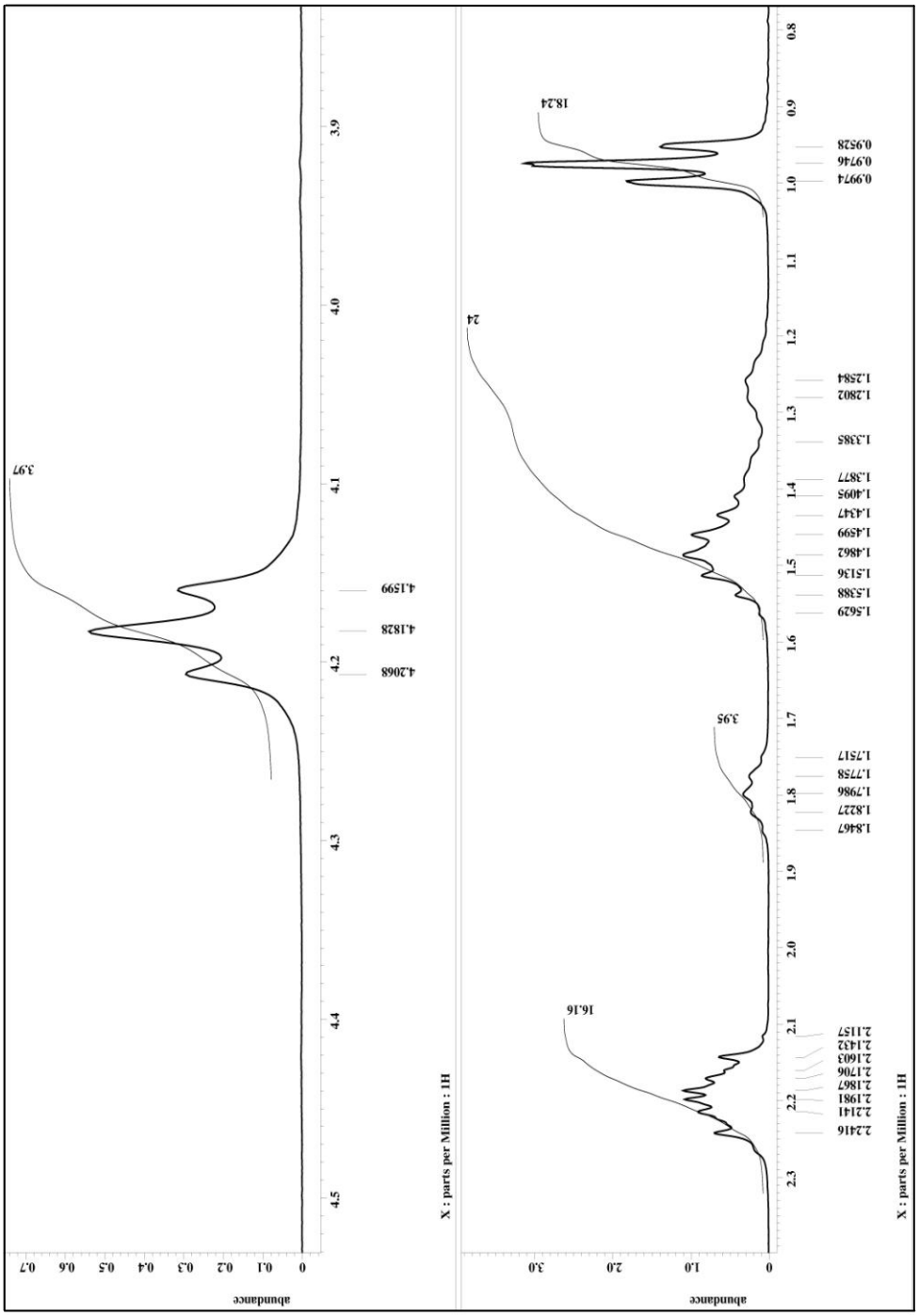

```
Filename          = 080610bzimlt-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#852822
Solvent           = D2O
Creation_time     = 11-JUN-2008 01:01:08
Revision_time     = 21-SEP-2010 21:09:10
Current_time      = 21-SEP-2010 21:10:27

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 800
Total_scans       = 800

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 24.9[dC]
```

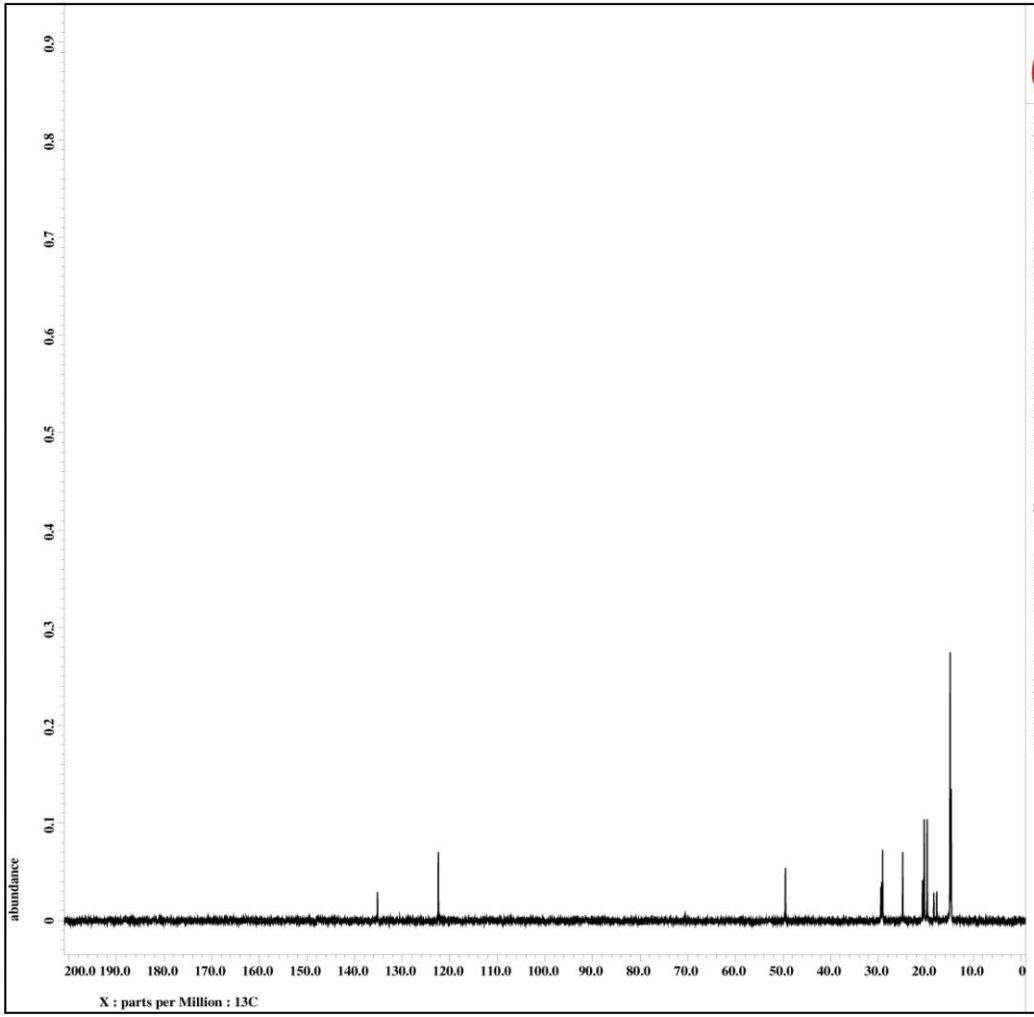

abundance
0.1
0
X : parts per Million : 13C
133.7538
128.6437
129.4037
129.3225
122.6013
122.4723
122.3480
abundance
-0.01 0.01 0.03 0.05 0.07 0.09 0.11 0.13 0.15 0.17
X : parts per Million : 13C
52.8995
49.5533
49.4099
29.0696
29.0027
24.8295

APPENDIX 42

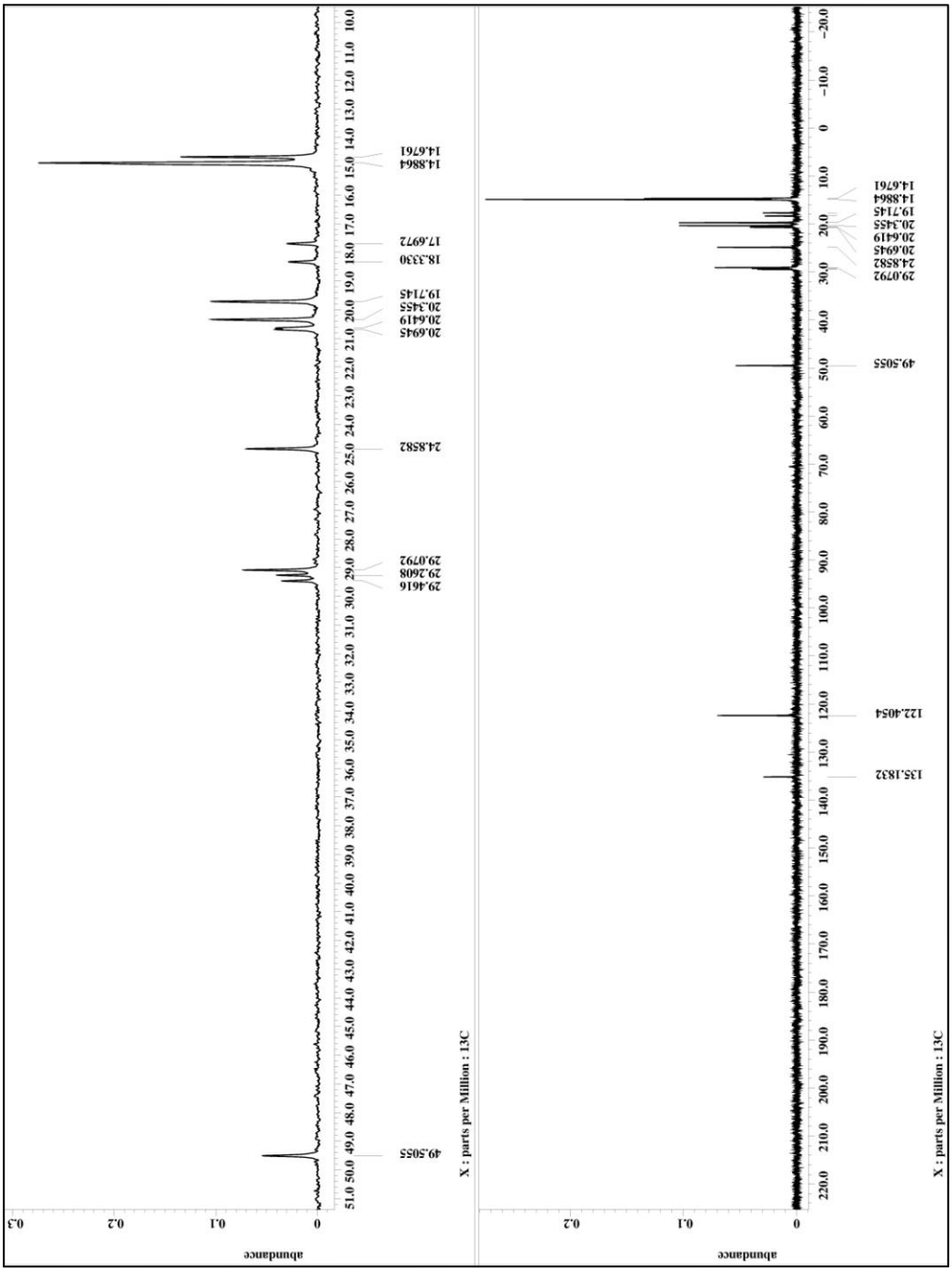
^{1}H, ^{13}C AND ^{31}P NMR SPECTRA OF
1-(HEXYLTRIPROPYLPHOSPHONIUM)-3-
(HEXYLTRIPROPYLPHOSPHONIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (3d)

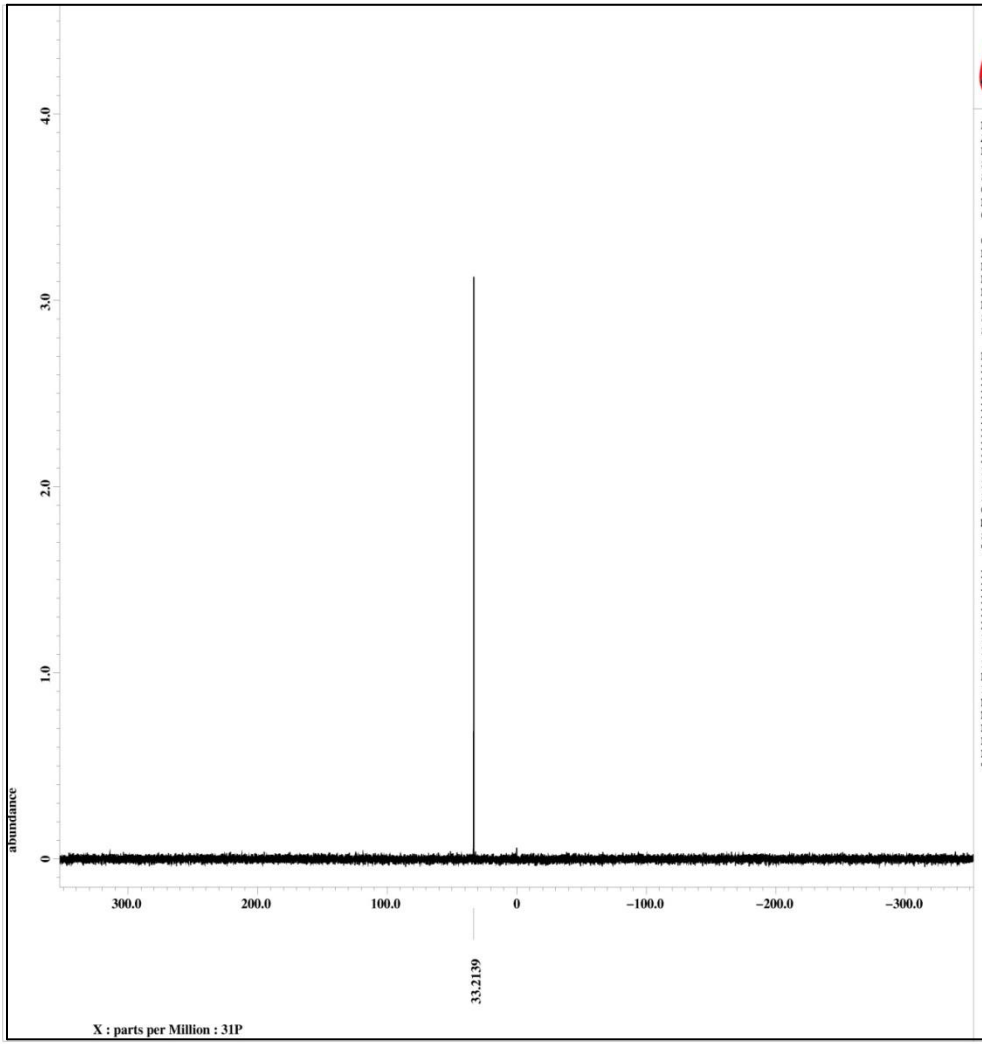

3 NTf2-
abundance
0.91
1.91
3.97
3.95
16.16
24
18.24
9.5497
7.8683
4.2068
4.1828
4.1599
3.3495
3.3289
2.2141
2.1981
2.1867
2.1706
1.5136
1.4862
1.4599
1.4347
1.4095
0.9974
0.9746
0.9528
X : parts per Million : 1H
JEOL
Filename = TriprPhosIMTriC6H-2.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#21523
Solvent = DMSO-D6
Creation_time = 10-OCT-2008 00:48:42
Revision_time = 20-NOV-2008 21:48:49
Current_time = 12-SEP-2010 13:25:45
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 = 36
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.1[dC]


abundance
X : parts per Million : 1H
3,97
4,2068
4,1828
4,1599
24
18,24
16,16
3,95
2,2416
2,2141
2,1981
2,1867
2,1706
2,1603
2,1432
2,1157
1,8467
1,8227
1,7986
1,7758
1,7517
1,5629
1,5388
1,5136
1,4862
1,4599
1,4347
1,4095
1,3877
1,3385
1,2802
1,2584
0,9974
0,9746
0,9528

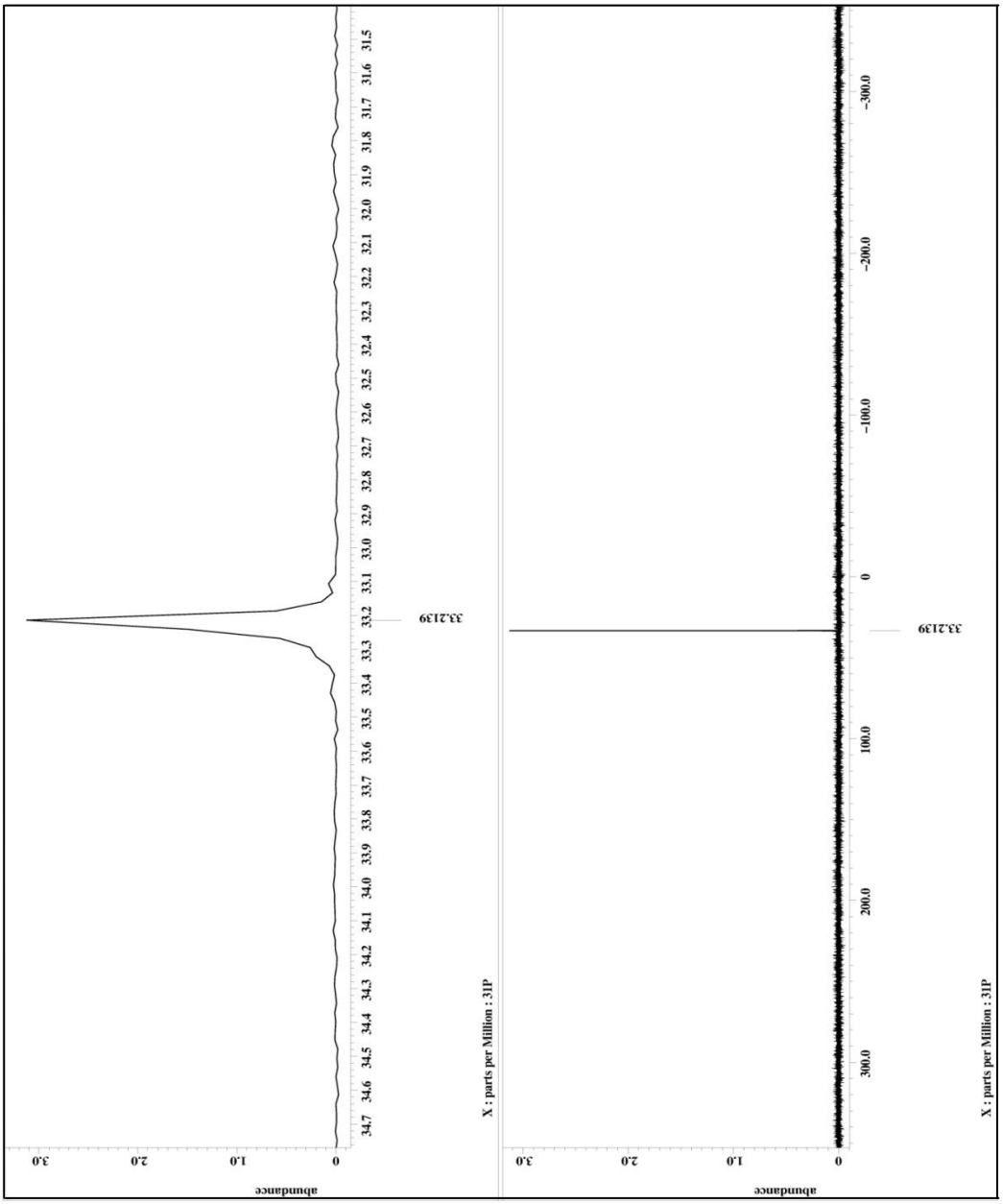



```
Filename          = 080610plt-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#62325
Solvent           = D2O
Creation_time     = 11-JUN-2008 03:03:38
Revision_time     = 21-SEP-2010 21:02:26
Current_time      = 21-SEP-2010 21:11:57

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 800
Total_scans       = 800

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 22.2[dC]
```


abundance
X : parts per Million : 13C
49.5055
29.4616
29.2608
29.0792
24.8582
20.6945
20.6419
20.3455
19.7145
18.3330
17.6972
14.8864
14.6761
abundance
X : parts per Million : 13C
135.1832
122.4054
49.5055
29.0792
24.8582
20.6945
20.6419
20.3455
19.7145
14.8864
14.6761

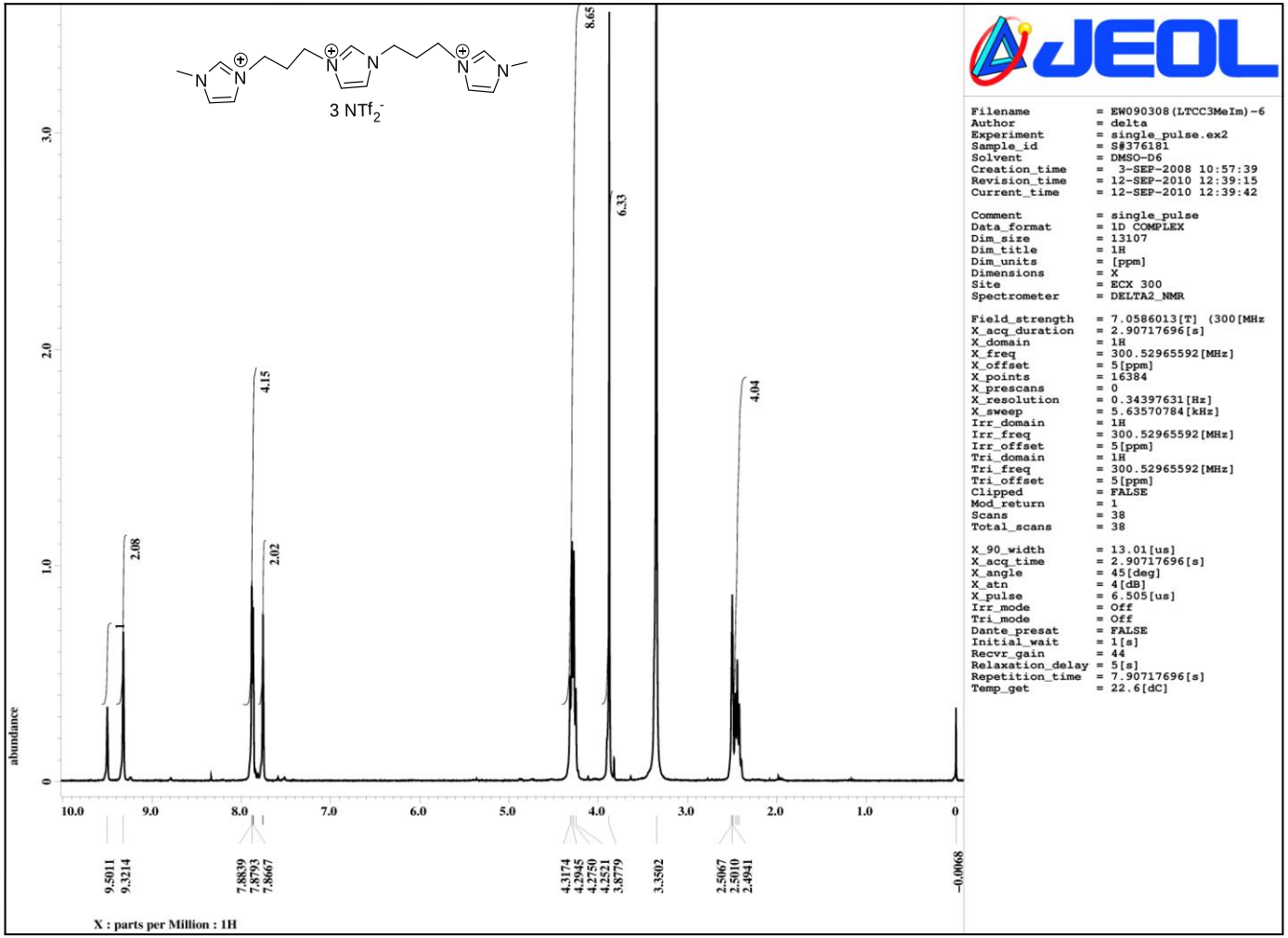


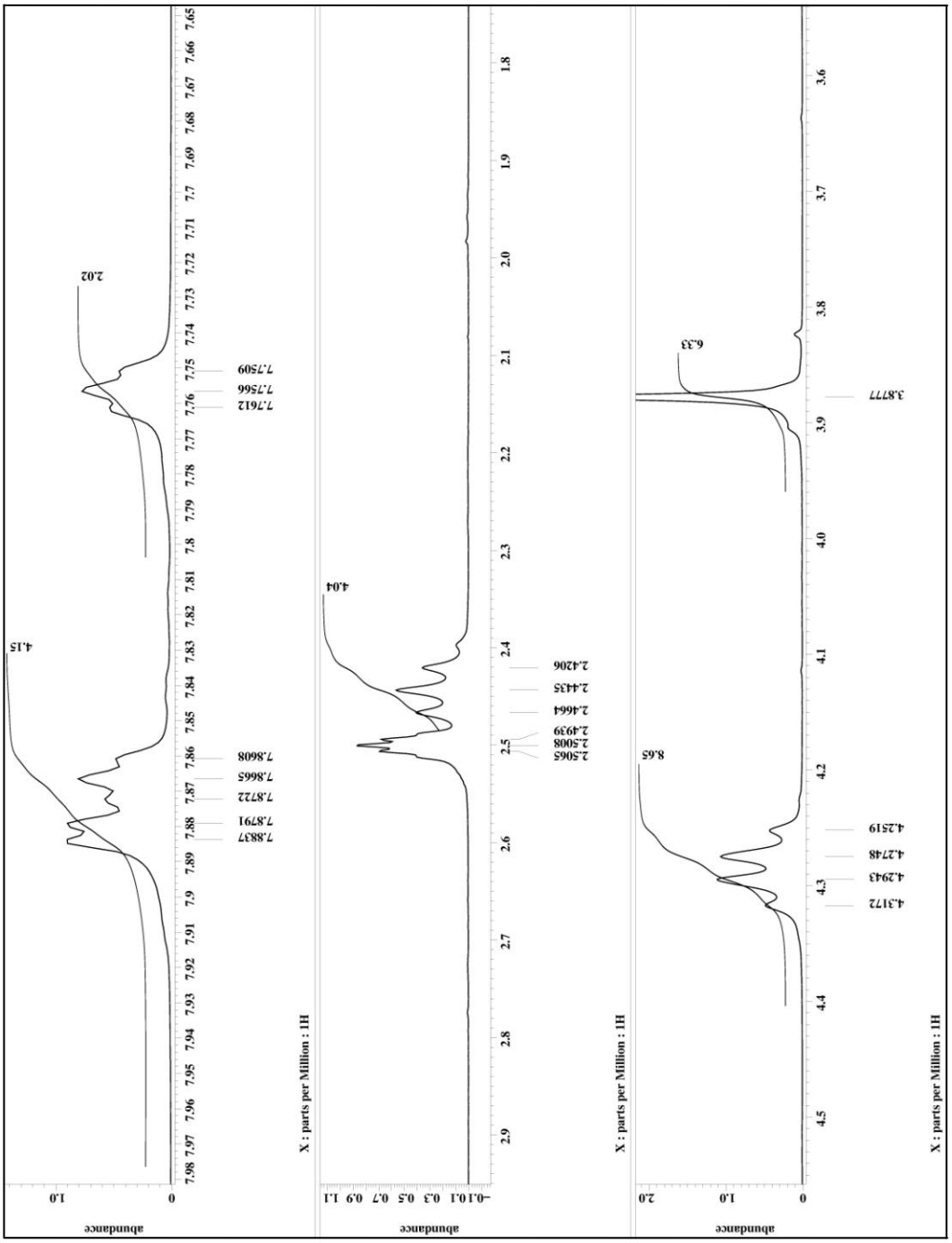

```
Filename          = P31_LTCC6TriPrP-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#434581
Solvent           = DMSO-D6
Creation_time     = 11-OCT-2010 02:04:08
Revision_time     = 10-OCT-2010 12:10:27
Current_time      = 10-OCT-2010 13:02:25

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 31P
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.1835008[s]
X_domain          = 31P
X_freq            = 202.46831075[MHz]
X_offset          = 0[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 5.44956752[Hz]
X_sweep           = 178.57142857[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 135
Total_scans       = 135

X_90_width        = 11.9[us]
X_acq_time        = 0.1835008[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.96666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.1835008[s]
Temp_get          = 21.9[dC]
```

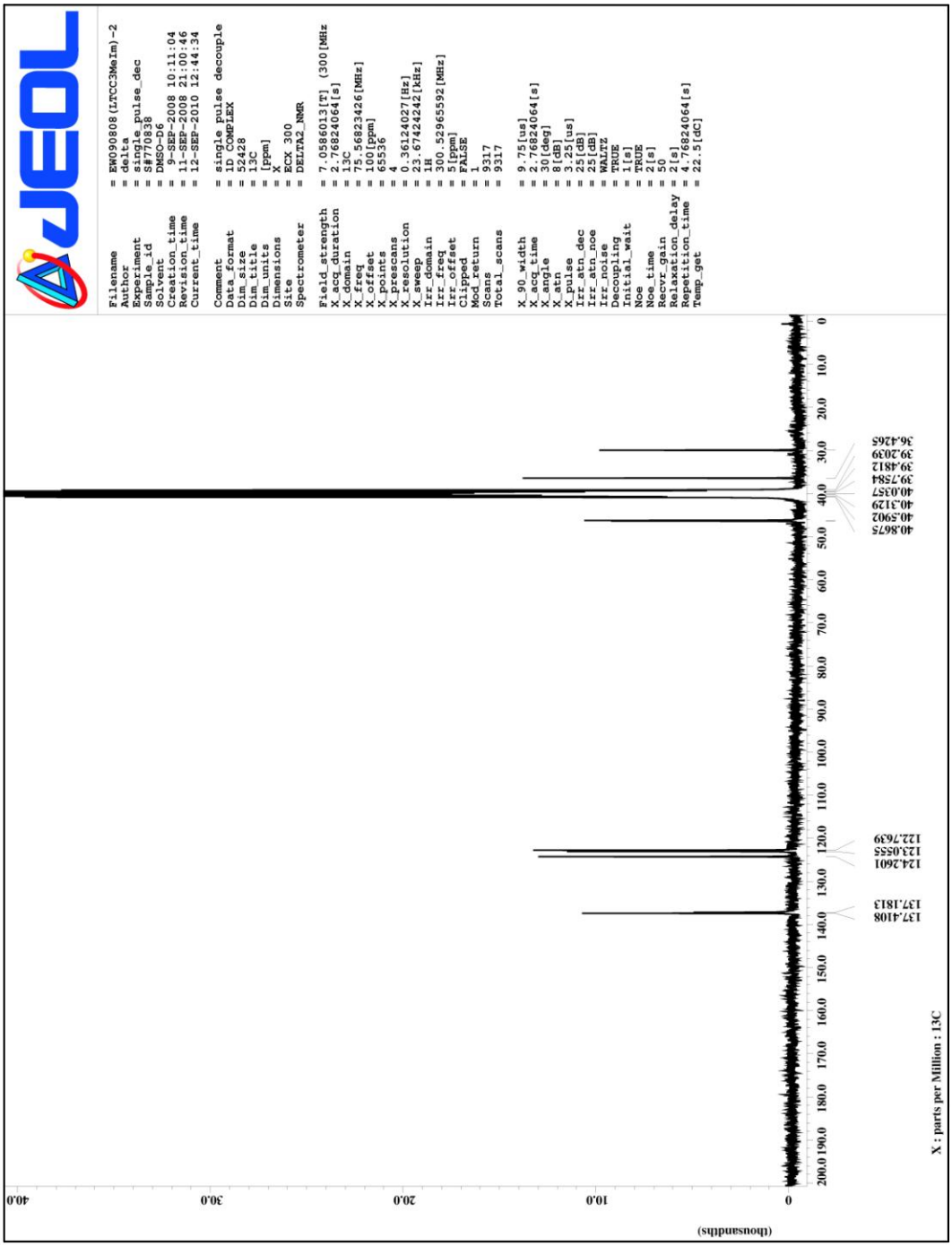

abundance
3.0
2.0
1.0
0
34.7 34.6 34.5 34.4 34.3 34.2 34.1 34.0 33.9 33.8 33.7 33.6 33.5 33.4 33.3 33.2 33.1 33.0 32.9 32.8 32.7 32.6 32.5 32.4 32.3 32.2 32.1 32.0 31.9 31.8 31.7 31.6 31.5
33.2139
X : parts per Million : 31P
abundance
3.0
2.0
1.0
0
300.0 200.0 100.0 0 −100.0 −200.0 −300.0
33.2139
X : parts per Million : 31P

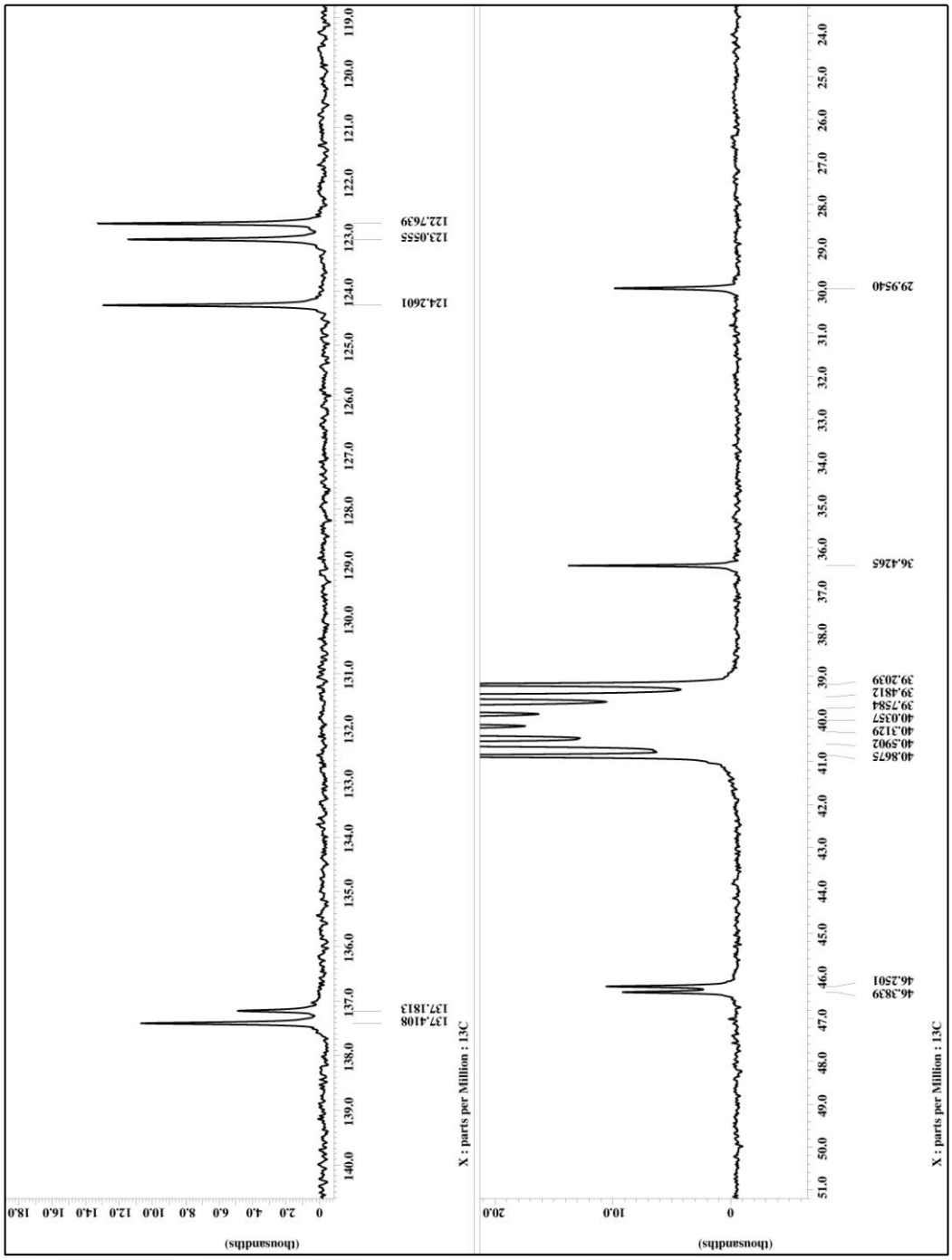
APPENDIX 43

^{1}H AND ^{13}C NMR SPECTRA OF
(1'-METHYL-3'-PROPYLMIDAZOLIUM)-3-(1''-METHYL-3''-PROPYLIMIDAZOLIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (4a)


3 NTf2-
abundance
X : parts per Million : 1H
9.5011
9.3214
7.8839
7.8793
7.8667
4.3174
4.2945
4.2750
4.2521
3.8779
3.3502
2.5067
2.5010
2.4941
-0.0068
JEOL
Filename = EW090308(LTCC3MeIm)-6
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#376181
Solvent = DMSO-D6
Creation_time = 3-SEP-2008 10:57:39
Revision_time = 12-SEP-2010 12:39:15
Current_time = 12-SEP-2010 12:39:42
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 = 38
Total_scans = 38
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 = 44
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.6[dC]

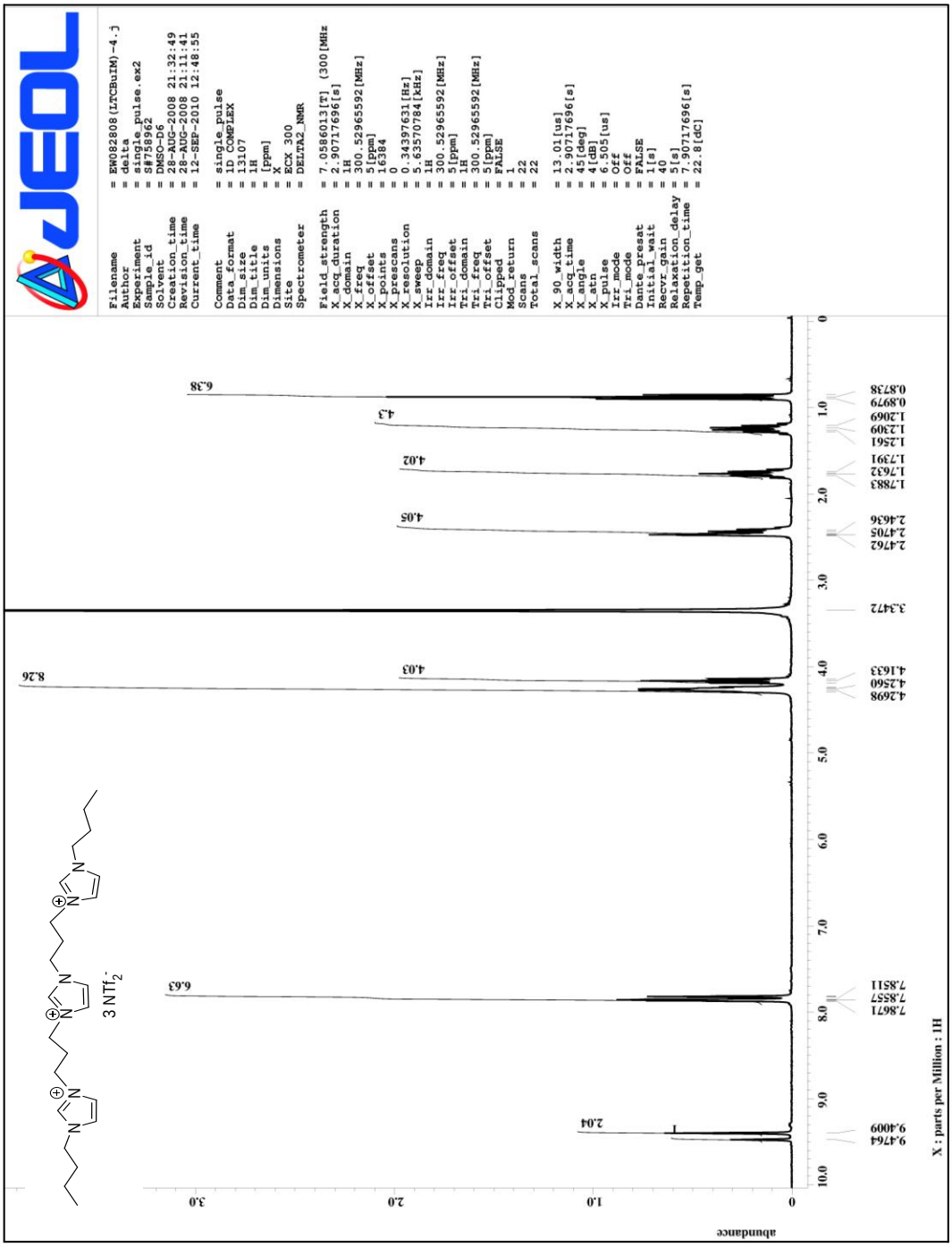

abundance
X : parts per Million : 1H
4.15
2.02
7.8837
7.8791
7.8722
7.8665
7.8608
7.7612
7.7566
7.7509
4.04
2.5065
2.5008
2.4939
2.4664
2.4435
2.4206
8.65
6.33
4.3172
4.2943
4.2748
4.2519
3.8777

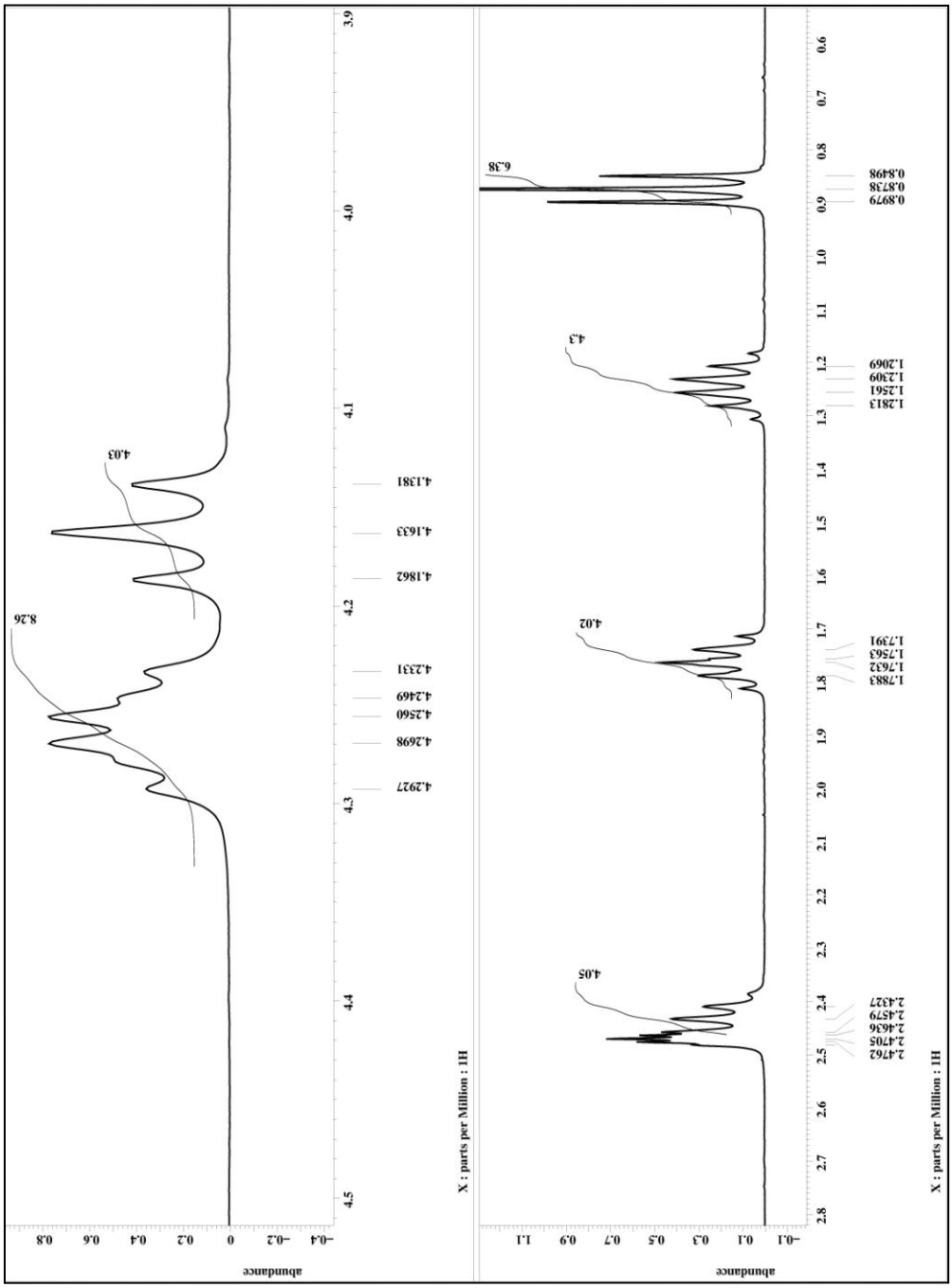

Filename = EW090808(LTCC3MeIm)-2
Author = delta
Experiment = single_pulse_dec
Sample_id = S#770838
Solvent = DMSO-D6
Creation_time = 9-SEP-2008 10:11:04
Revision_time = 11-SEP-2008 21:00:46
Current_time = 12-SEP-2010 12:44:34
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.768240664[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.674242242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9317
Total_scans = 9317
X_90_width = 9.75[us]
X_acq_time = 2.768240664[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.768240664[s]
Temp_get = 22.5[dC]
(thousandths)
40.0
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
137.4108
137.1813
124.2601
123.0555
122.7639
40.8675
40.5902
40.3129
40.0357
39.7584
39.4812
39.2039
36.4265
X : parts per Million : 13C

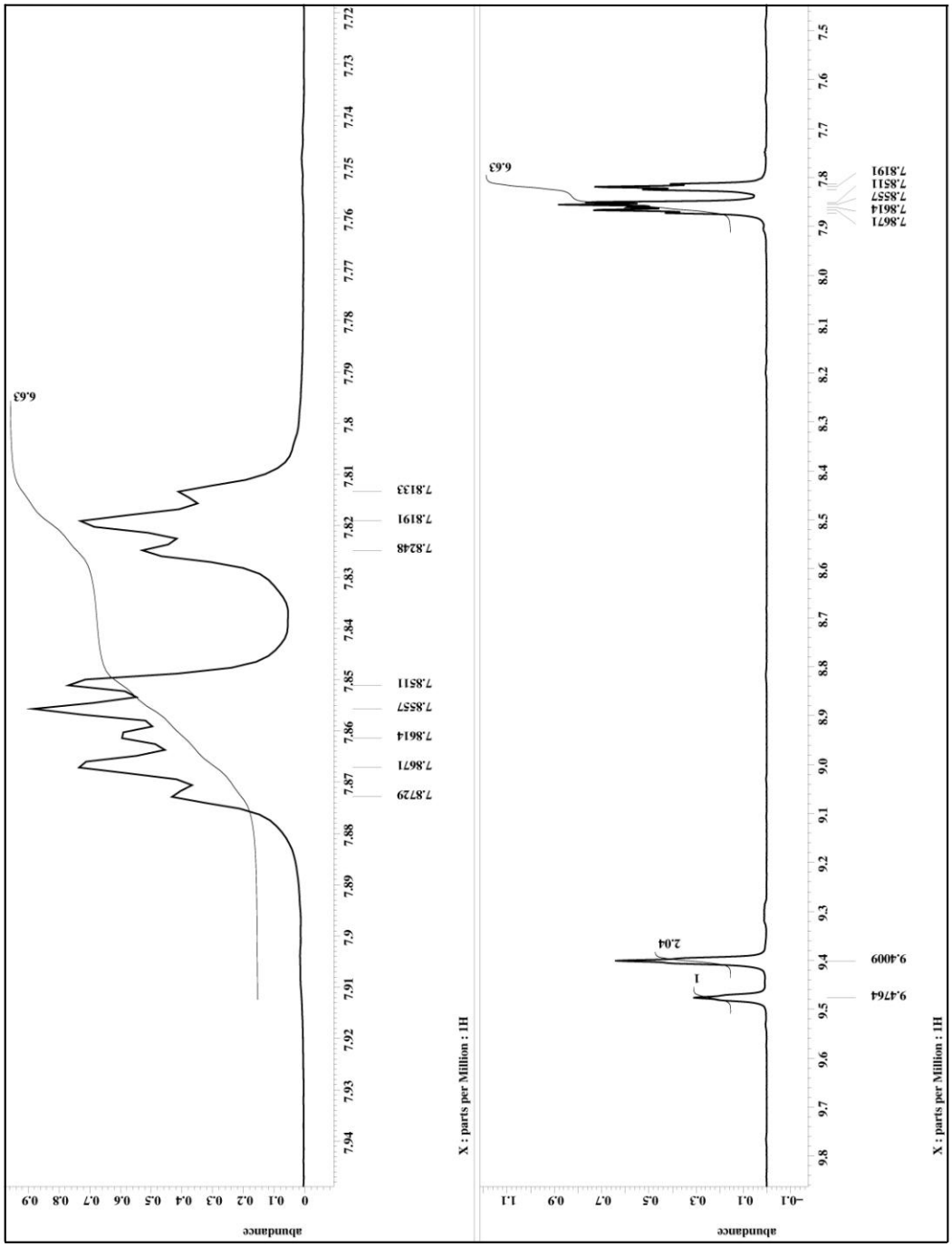

(thousandths)
X : parts per Million : 13C
137,4108
137,1813
124,2601
123,0555
122,7639
46,3839
46,2501
40,8675
40,5902
40,3129
40,0357
39,7584
39,4812
39,2039
36,4265
29,9540

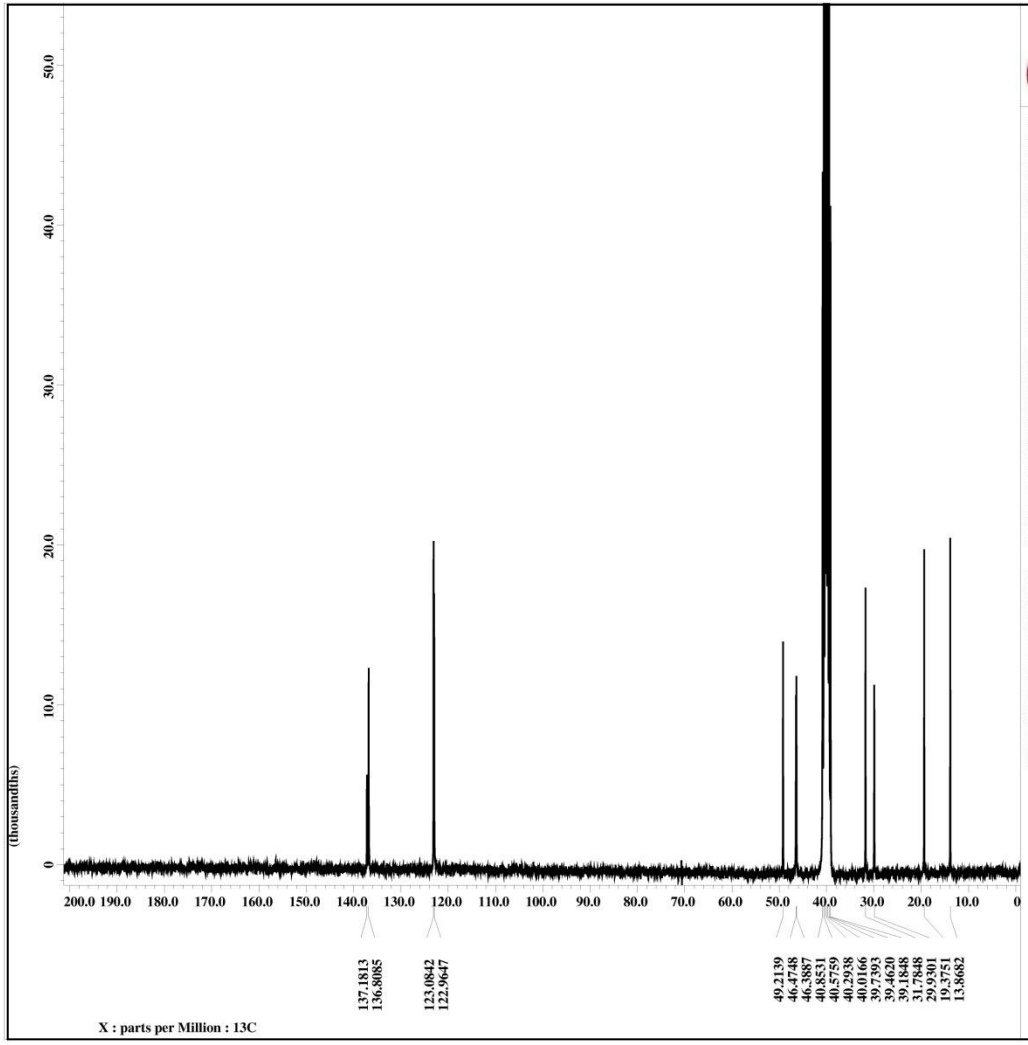
APPENDIX 44

^{1}H AND ^{13}C NMR SPECTRA OF
(1'-BUTYL-3'-PROPYLMIDAZOLIUM)-3-(1''-BUTYL-3''-PROPYLIMIDAZOLIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (4b)

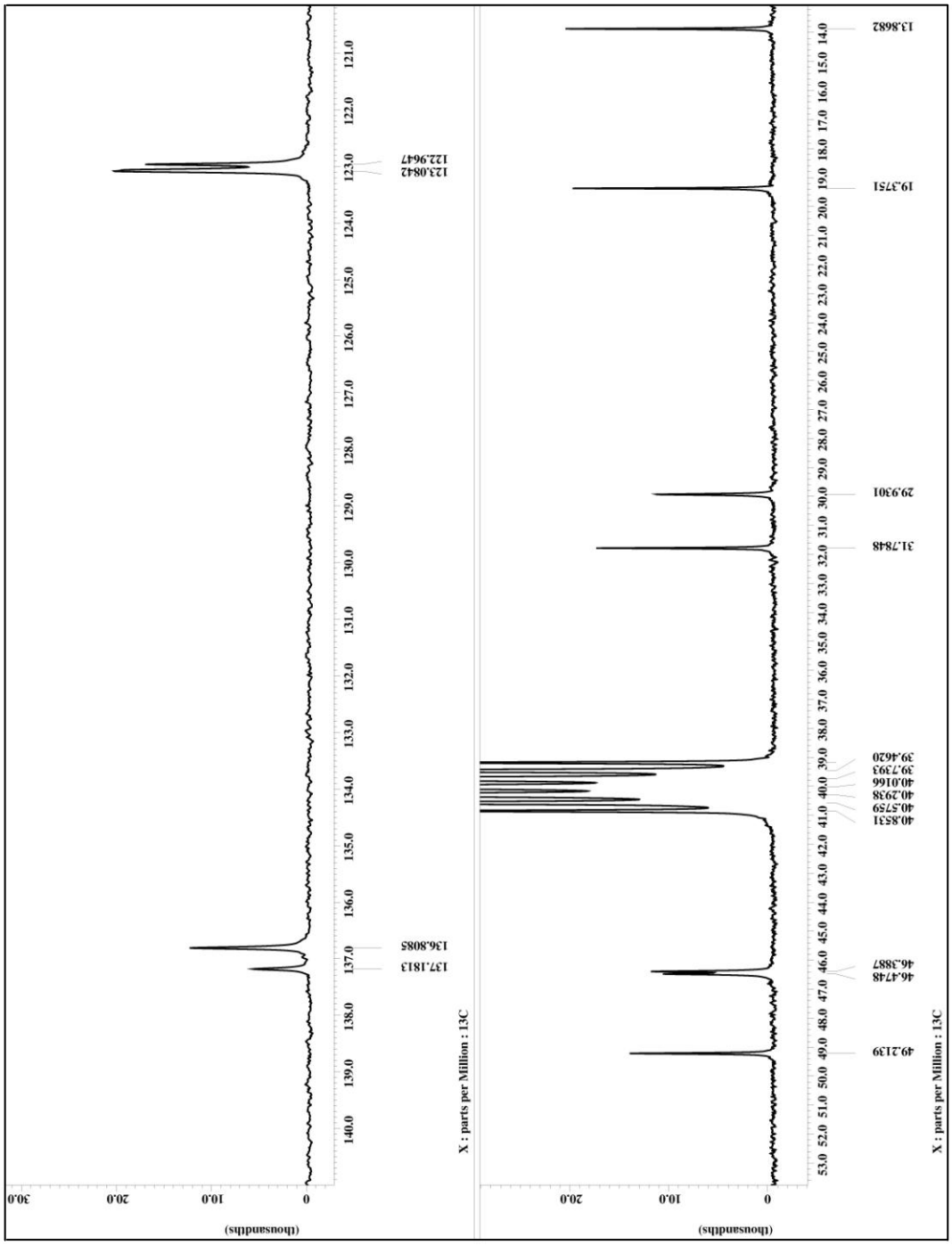

JEOL
Filename = EN082808(LZCBuIM)-4.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#758962
Solvent = DMSO-D6
Creation_time = 28-AUG-2008 21:32:49
Revision_time = 28-AUG-2008 21:11:41
Current_time = 12-SEP-2010 12:48:55
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 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 = 22
Total_scans = 22
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
Decoupler_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.8[dC]
3 NTf2-
8.26
6.63
6.38
4.3
4.02
4.05
4.03
2.04
9.4764
9.4009
7.8671
7.8557
7.8511
4.2698
4.2560
4.1633
3.3472
2.4762
2.4705
2.4636
1.7883
1.7632
1.7391
1.2561
1.2309
1.2069
0.8979
0.8738
abundance
X : parts per Million : 1H


abundance
X : parts per Million : 1H
4.05
4.02
4.3
6.38
2.47621
2.47051
2.46361
2.45791
2.43271
1.78831
1.76321
1.75631
1.73911
1.28131
1.25611
1.23091
1.20691
0.89791
0.87381
0.84981
8.26
4.03
4.29271
4.26981
4.25601
4.24691
4.23311
4.18621
4.16331
4.13811


abundance
X : parts per Million : 1H
9,4764
9,4009
2,04
1
6,63
7,8671
7,8614
7,8557
7,8511
7,8191
7,8729
7,8671
7,8614
7,8557
7,8511
7,8248
7,8191
7,8133
6,63

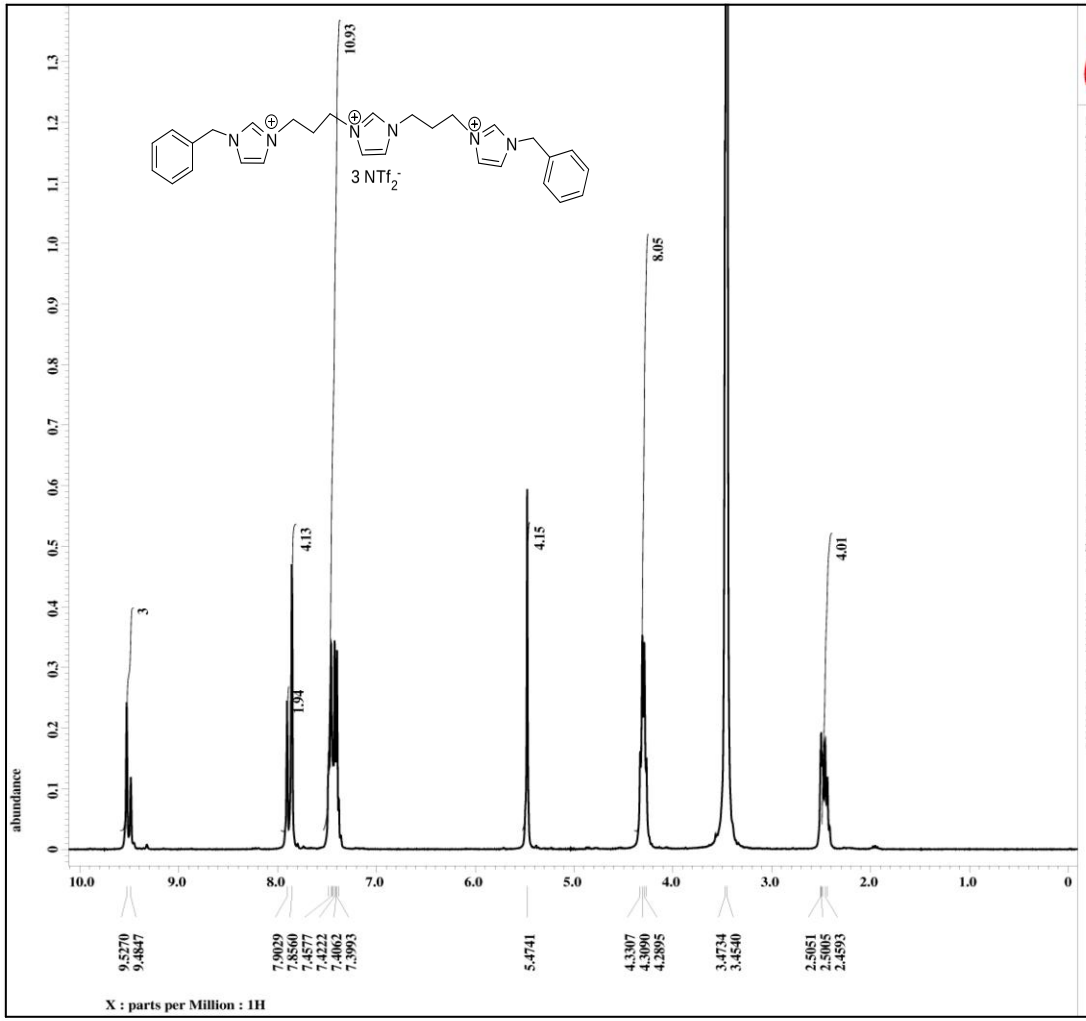



```
Filename          = EW082808(LTCC3BuIm)-6
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#763212
Solvent           = DMSO-D6
Creation_time     = 29-AUG-2008 10:12:47
Revision_time     = 18-NOV-2008 19:27:53
Current_time      = 12-SEP-2010 12:51:44

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9500
Total_scans       = 9500

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23.7[dC]
```


(thousandths)
X : parts per Million : 13C
13.8682
19.3751
29.9301
31.7848
39.4620
39.7393
40.0166
40.2938
40.5759
40.8531
46.3887
46.4748
49.2139
122.9647
123.0842
136.8085
137.1813

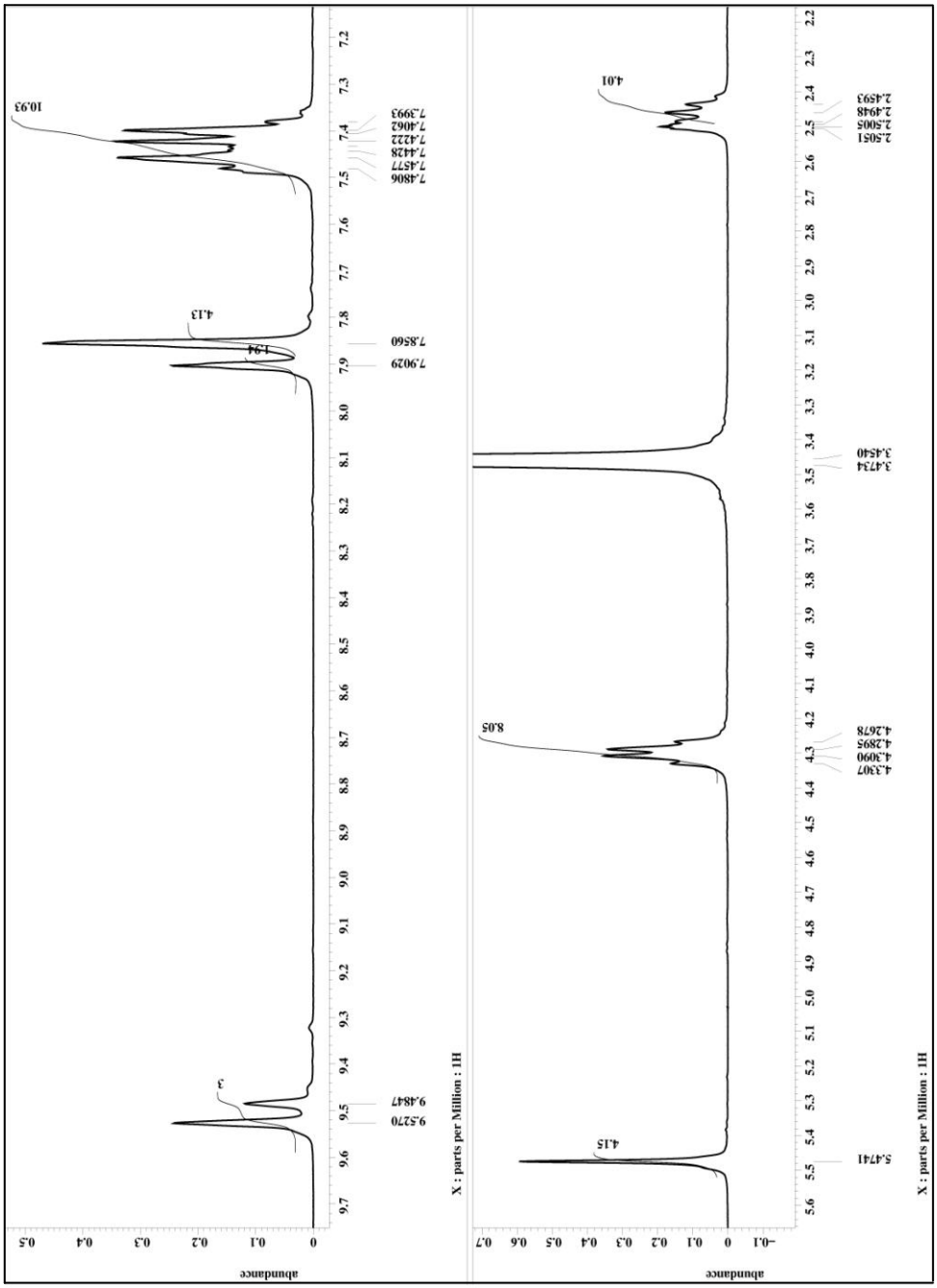
APPENDIX 45

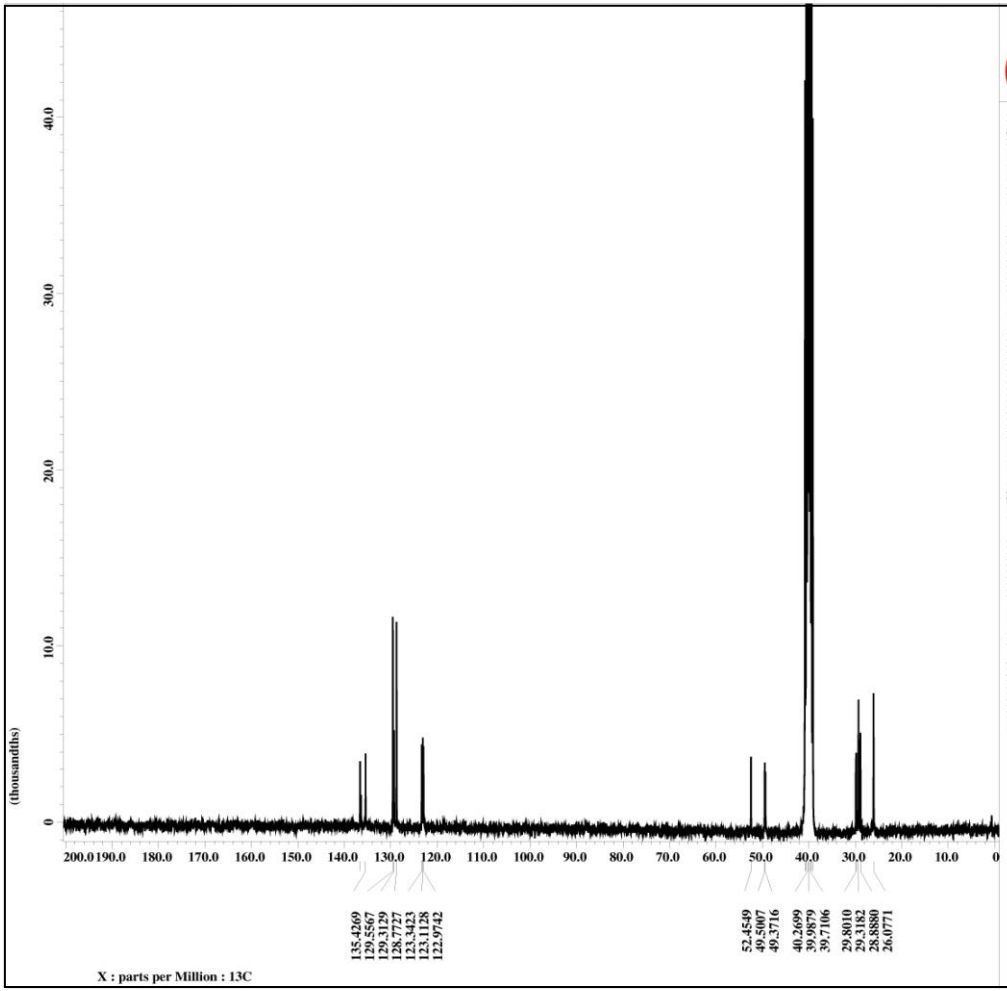
^{1}H AND ^{13}C NMR SPECTRA OF
(1'-BENZYL-3'-PROPYLMIDAZOLIUM)-3-(1''-BENZYL-3''-PROPYLIMIDAZOLIUM)IMIDAZOLIUM
TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (4c)



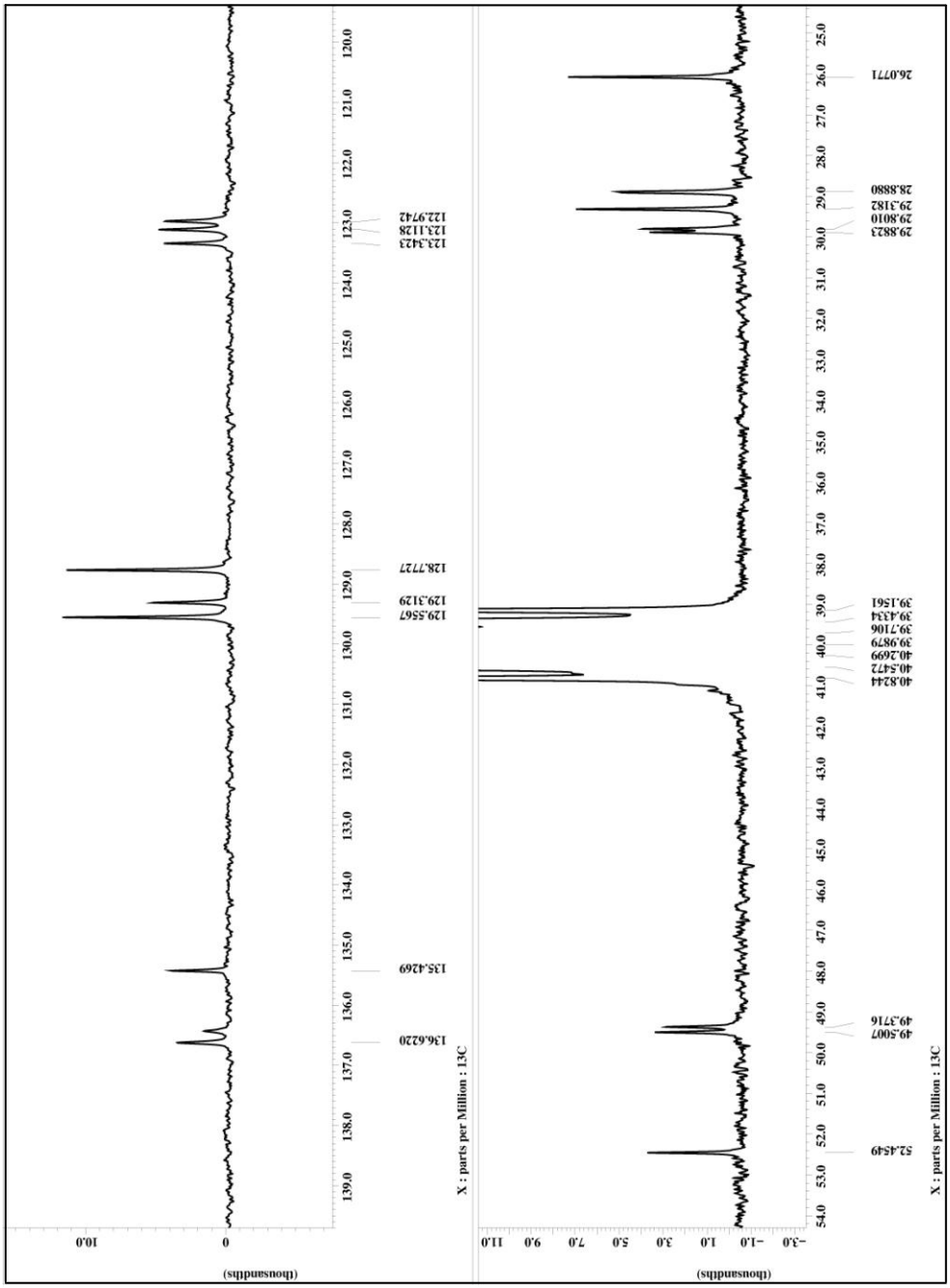
JEOL

```
Filename          = EW111708(LTCC3PhIm)-4
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#495886
Solvent           = DMSO-D6
Creation_time     = 17-NOV-2008 14:01:58
Revision_time     = 21-NOV-2008 17:30:25
Current_time      = 12-SEP-2010 12:56:21

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             = 22
Total_scans       = 22

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        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23[dC]
```


abundance
X : parts per Million : 1H
9.5270
9.4847
3
7.9029
7.8560
1.94
4.13
7.4806
7.4577
7.4428
7.4222
7.4062
7.3993
10.93
5.4741
4.15
4.3307
4.3090
4.2895
4.2678
8.05
3.4734
3.4540
4.01
2.5051
2.5005
2.4948
2.4593

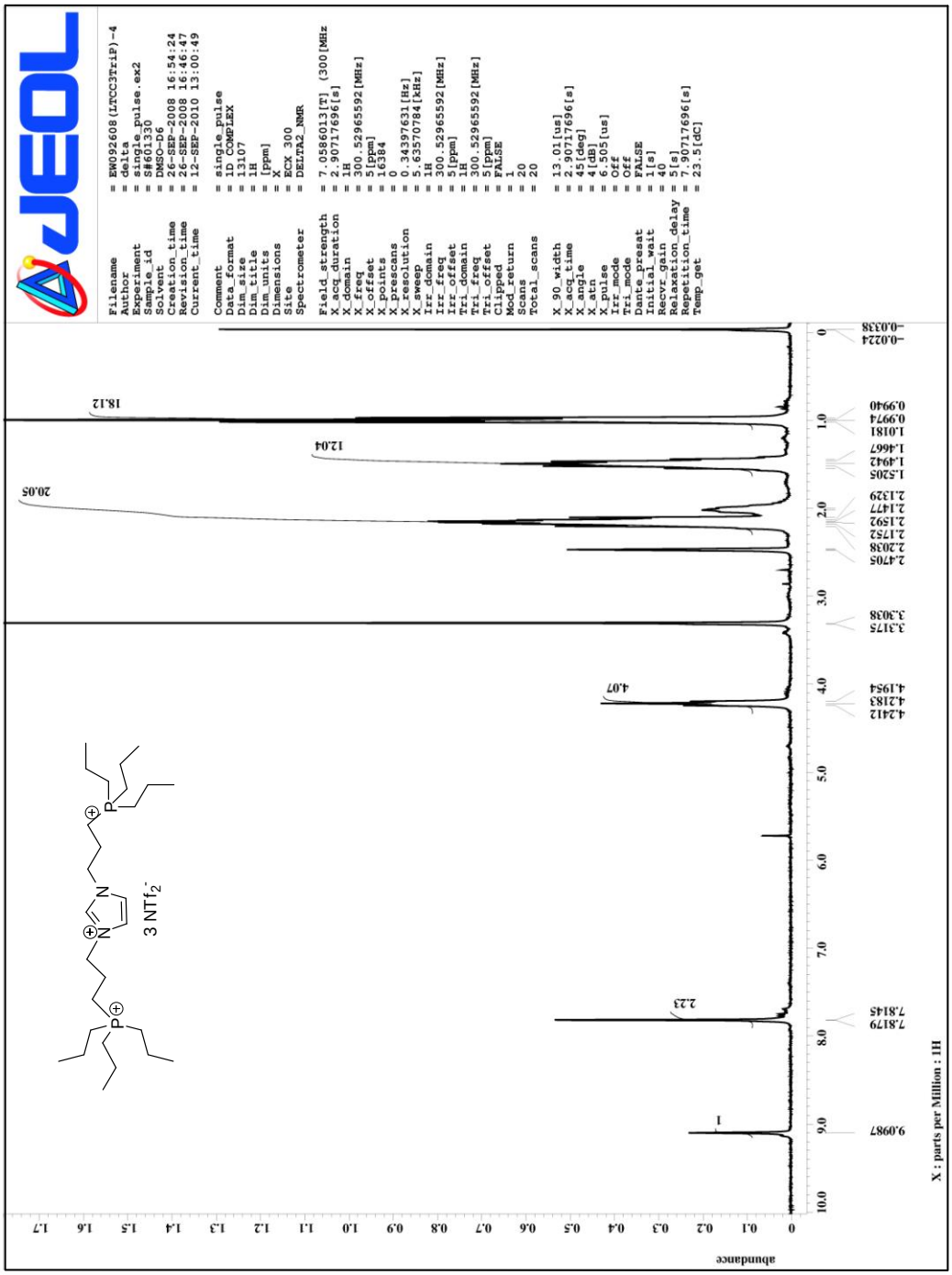


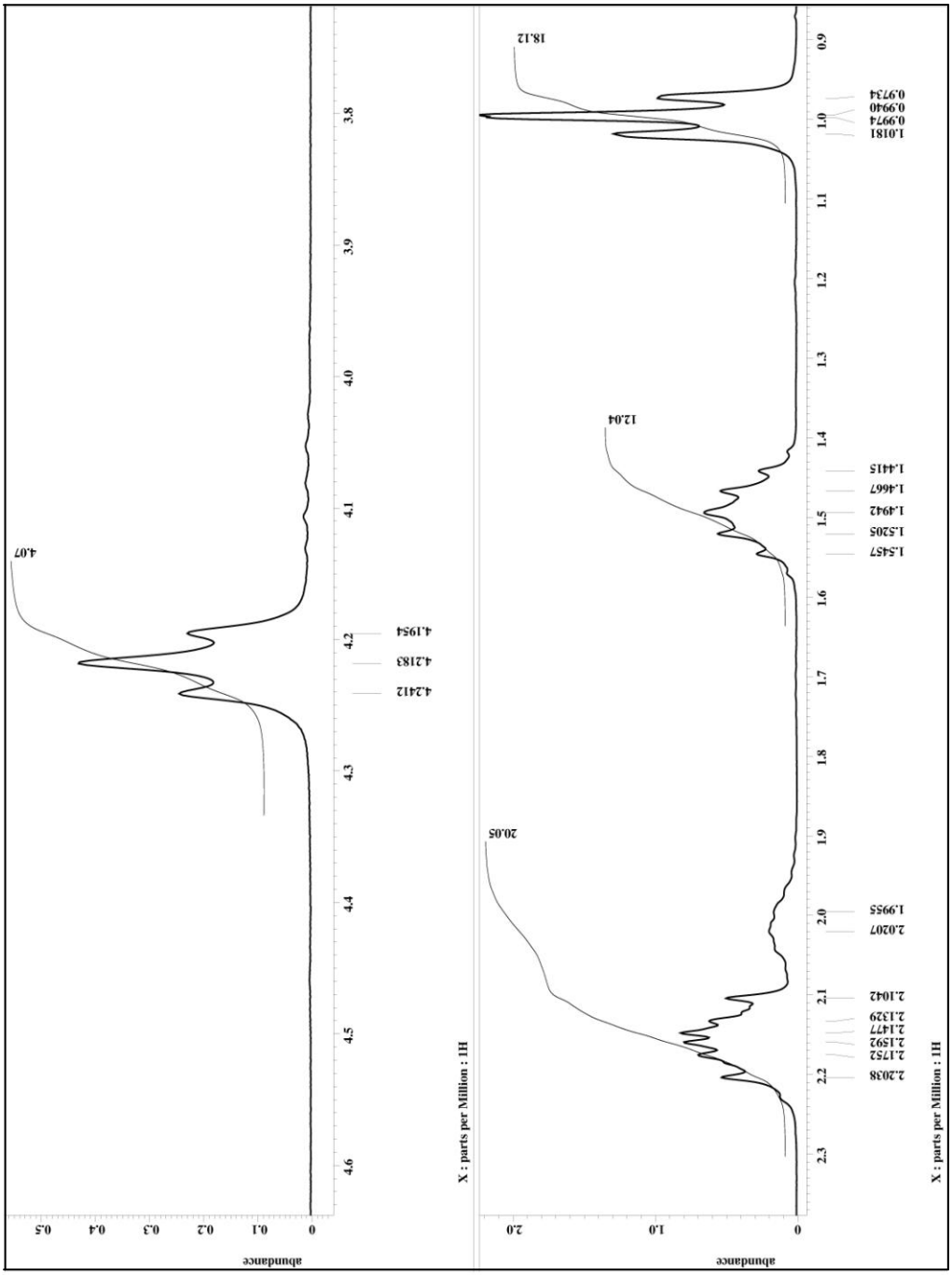

```
Filename          = EW072908(LTCPhIm)-3.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#763472
Solvent           = DMSO-D6
Creation_time     = 30-JUL-2008 10:09:49
Revision_time     = 12-SEP-2010 13:06:21
Current_time      = 12-SEP-2010 13:06:59

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9500
Total_scans       = 9500

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 23.9[dC]
```

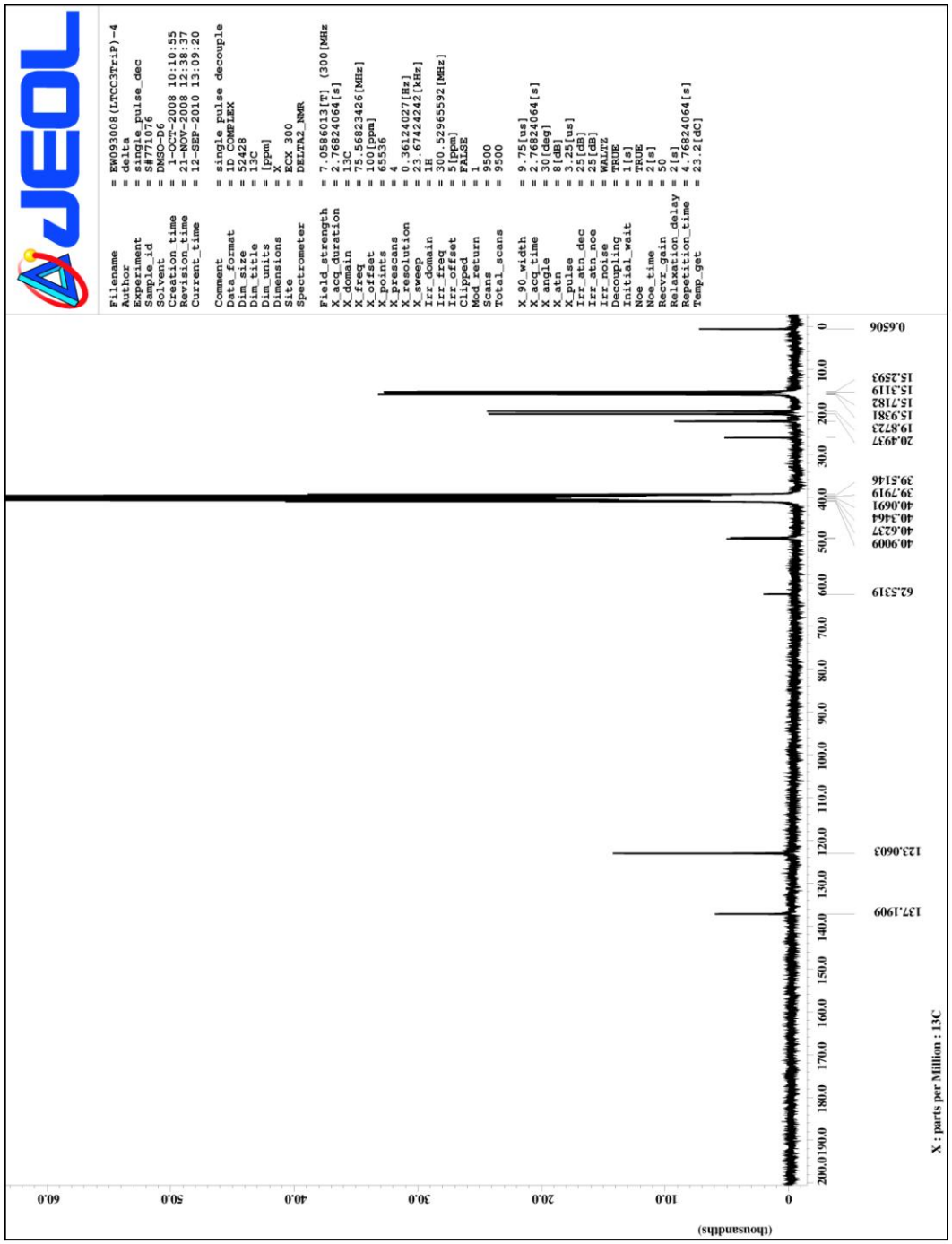

(thousandths)
10.0
0
X : parts per Million : 13C
136.6220
135.4269
129.5567
129.3129
128.7727
123.3423
123.1128
122.9742
(thousandths)
11.0
9.0
7.0
5.0
3.0
1.0
-1.0
-3.0
X : parts per Million : 13C
52.4549
49.5007
49.3716
40.8244
40.5472
40.2699
39.9879
39.7106
39.4334
39.1561
29.8823
29.8010
29.3182
28.8880
26.0771

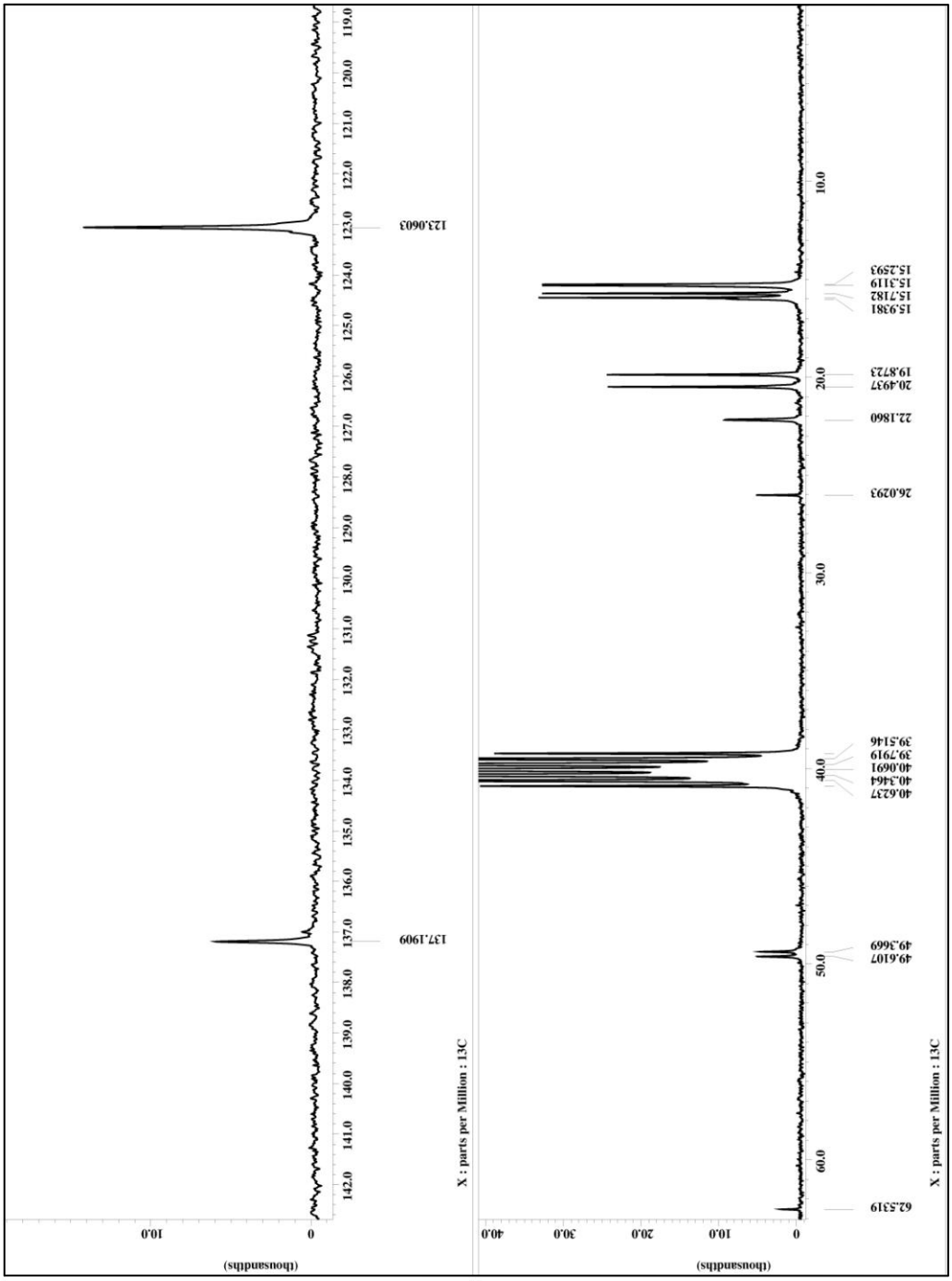
APPENDIX 46

^{1}H, ^{13}C AND ^{31}P NMR SPECTRA OF
1-PROPYLTRIPROPYLPHOSPHONIUM-3-PROPYLTRIPROPYLPHOSPHONIUM
IMIDAZOLIUM TRI[BIS(TRIFLUOROMETHANESULFONYL)IMIDE] (4d)


JEOL
Filename = EW092608(LTCC3Tr1P)-4
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#60133O
Solvent = DMSO-D6
Creation_time = 26-SEP-2008 16:54:24
Revision_time = 26-SEP-2008 16:46:47
Current_time = 12-SEP-2010 13:00:49
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 = 0
Scans = 20
Total_scans = 20
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
Date_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.5[dC]
3 NTf2-
18.12
12.04
20.05
4.07
2.23
1
9.0987
7.8179
7.8145
4.2412
4.2183
4.1954
3.3175
3.3038
2.4705
2.2038
2.1752
2.1592
2.1477
2.1329
1.5205
1.4942
1.4667
1.0181
0.9974
0.9940
-0.0224
-0.0338
X : parts per Million : 1H
abundance


abundance
X : parts per Million : 1H
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
4.2412
4.2183
4.1954
4.07
0
0.1
0.2
0.3
0.4
0.5
abundance
X : parts per Million : 1H
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
2.2038
2.1752
2.1592
2.1477
2.1329
2.1042
2.0207
1.9955
1.5457
1.5205
1.4942
1.4667
1.4415
1.0181
0.9974
0.9940
0.9734
20.05
12.04
18.12
0
1.0
2.0


JEOL
Filename = EW093008(LTCC3TriP)-4
Author = delta
Experiment = single_pulse_dec
Sample_id = S#771076
Solvent = DMSO-D6
Creation_time = 1-OCT-2008 10:10:55
Revision_time = 21-NOV-2008 12:38:37
Current_time = 12-SEP-2010 13:09:20
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9500
Total_scans = 9500
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_atten = 8[deg]
X_power = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 23.2[dC]
(thousandths)
0.6506
15.2593
15.3119
15.7182
15.9381
19.8723
20.4937
39.5146
39.7919
40.0691
40.3464
40.6237
40.9009
62.5319
123.0603
137.1909
X : parts per Million : 13C


(thousandths)
10.0
0
142.0
141.0
140.0
139.0
138.0
137.0
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.0
126.0
125.0
124.0
123.0
122.0
121.0
120.0
119.0
137,1909
123,0603
X : parts per Million : 13C
(thousandths)
40.0
30.0
20.0
10.0
0
60.0
50.0
40.0
30.0
20.0
10.0
62,5319
49,3669
49,6107
40,6237
40,3464
40,0691
39,7919
39,5146
26,0293
22,1860
19,8723
20,4937
15,9381
15,7182
15,3119
15,2593
X : parts per Million : 13C

APPENDIX 47

PUBLICATION INFORMATION OF THE DISSERTATION

Chapter 1: “The advent and potential impact of ionic liquid stationary phases in GC and GCGC.” Daniel W. Armstrong, Tharanga Payagala, Leonard M. Sidisky, LC-GC Europe (2009), 22, 459-460, 462, 464, 466. / LC-GC North America (2009), 27, 596, 598, 600-602, 604-605.

Chapter 2: “Unsymmetrical dicationic ionic liquids: manipulation of physicochemical properties using specific structural architectures.” Tharanga Payagala, Junmin Huang, Zachary S. Breitbach, Pritesh S. Sharma, Daniel W. Armstrong, Chemistry of Materials (2007), 19, 5848-5850.

Chapter 3: “Trigonal tricationic ionic liquids: molecular engineering of trications to control physiochemical properties.” Pritesh S. Sharma, Tharanga Payagala, Eranda Wanigasekara, Aruna B. Wijeratne, Junmin Huang, Daniel W. Armstrong, Chemistry of Materials (2008), 20, 4182-4184.

Chapter 4: “Linear tricationic room-temperature ionic liquids: synthesis, physiochemical properties, and electrowetting properties.” Eranda Wanigasekara, Xiaotong Zhang, Yasith Nanayakkara, Tharanga Payagala, Hyejin Moon, Daniel W. Armstrong, ACS Applied Materials & Interfaces (2009), 1, 2126-2133.

Chapter 5: “Trigonal tricationic ionic liquids: A generation of gas chromatographic stationary phases.” Tharanga Payagala, Ying Zhang, Eranda Wanigasekara, Ke Huang, Zachary S. Breitbach, Pritesh S. Sharma, Leonard M. Sidisky, Daniel W. Armstrong, Analytical Chemistry (Washington, DC, United States) (2009), 81, 160-173.

Chapter 6: “Synthesis and chromatographic evaluation of new polymeric chiral stationary phases based on three (1S,2S)-(-)-1,2-diphenylethylenediamine derivatives in HPLC and SFC.” Tharanga Payagala, Eranda Wanigasekara, Daniel W. Armstrong, Analytical and Bioanalytical Chemistry (2011), 399, 2445-2461

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REFERENCES

(1) Welton, T. *Chem. Rev. (Washington, D. C.)* **1999***, 99*, 2071-2083.

(2) Walden, P. *Bull. Acad. Imp. Sci. St. -Petersbourg* **1914**, 405-422.

(3) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982***, 21*, 1263-1264.

(4) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc. , Chem. Commun.* **1992**, 965-967.

(5) Dearden, J. C. *Sci. Total Environ.* **1991***, 109-110*, 59-68.

(6) Abramowitz, R.; Yalkowsky, S. H. *Pharm. Res.* **1990***, 7*, 942-947.

(7) Bonhote, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Graetzel, M. *Inorg. Chem.* **1996***, 35*, 1168-1178.

(8) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997***, 68*, 351-356.

(9) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002***, 124*, 14247-14254.

(10) Huddleston, J. G.; Rogers, R. D. *Chem. Commun. (Cambridge)* **1998**, 1765-1766.

(11) Bosmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. *Chem Commun (Camb)* **2001**, 2494-2495.

(12) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun. (Cambridge, U. K.)* **2001**, 2159-2169.

(13) Zhang, S.; Ding, M.; Gao, L. *Youji Huaxue* **2002***, 22*, 159-163.

(14) Crofts, D.; Dyson, P. J.; Sanderson, K. M.; Srinivasan, N.; Welton, T. *J. Organomet. Chem.* **1999***, 573*, 292-298.

(15) Han, X.; Armstrong, D. W. *Org. Lett.* **2005***, 7*, 4205-4208.

(16) Anderson, J. L.; Armstrong, D. W. *Anal. Chem.* **2003***, 75*, 4851-4858.

(17) Payagala, T.; Zhang, Y.; Wanigasekara, E.; Huang, K.; Breitbach, Z. S.; Sharma, P. S.; Sidisky, L. M.; Armstrong, D. W. *Anal. Chem. (Washington, DC, U. S.)* **2009***, 81*, 160-173.

(18) Borra, E. F.; Seddiki, O.; Angel, R.; Eisenstein, D.; Hickson, P.; Seddon, K. R.; Worden, S. P. *Nature (London, U. K.)* **2007***, 447*, 979-981.

(19) Payagala, T.; Huang, J.; Breitbach, Z. S.; Sharma, P. S.; Armstrong, D. W. *Chem. Mater.* **2007***, 19*, 5848-5850.

(20) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007***, 40*, 1079-1086.

(21) Absalan, G.; Akhond, M.; Sheikhian, L. *Talanta* **2008***, 77*, 407-411.

(22) Egorov, V. M.; Smirnova, S. V.; Pletnev, I. V. *Sep. Purif. Technol.* **2008***, 63*, 710-715.

(23) Lu, Y.; Ma, W.; Hu, R.; Dai, X.; Pan, Y. *J. Chromatogr. , A* **2008***, 1208*, 42-46.

(24) Arce, A.; Earle, M. J.; Katdare, S. P.; Rodriguez, H.; Seddon, K. R. *Phys. Chem. Chem. Phys.* **2008***, 10*, 2538-2542.

(25) Guerra-Abreu, L.; Pino, V.; Anderson, J. L.; Afonso, A. M. *J. Chromatogr. , A* **2008***, 1214*, 23-29.

(26) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. *J. Chem. Thermodyn.* **2008***, 40*, 966-972.

(27) Holbrey, J. D.; Lopez-Martin, I.; Rothenberg, G.; Seddon, K. R.; Silvero, G.; Zheng, X. *Green Chem.* **2008***, 10*, 87-92.

(28) Gao, H.; Luo, M.; Xing, J.; Wu, Y.; Li, Y.; Li, W.; Liu, Q.; Liu, H. *Ind. Eng. Chem. Res.* **2008***, 47*, 8384-8388.

(29) Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc. , Dalton Trans.* **1999**, 1201-1202.

(30) Shimojo, K.; Goto, M. *Anal. Chem.* **2004***, 76*, 5039-5044.

(31) Kidani, K.; Hirayama, N.; Imura, H. *Anal. Sci.* **2008***, 24*, 1251-1254.

(32) Hirayama, N.; Okamura, H.; Kidani, K.; Imura, H. *Anal. Sci.* **2008***, 24*, 697-699.

(33) Wei, G.; Yang, Z.; Lee, C.; Yang, H.; Wang, C. R. C. *J. Am. Chem. Soc.* **2004***, 126*, 5036-5037.

(34) Liu, J.; Jonsson, J. A.; Jiang, G. *TrAC, Trends Anal. Chem.* **2005***, 24*, 20-27.

(35) Liu, J.; Jiang, G.; Chi, Y.; Cai, Y.; Zhou, Q.; Hu, J. *Anal. Chem.* **2003***, 75*, 5870-5876.

(36) Ye, C.; Zhou, Q.; Wang, X.; Xiao, J. *J. Sep. Sci.* **2007***, 30*, 42-47.

(37) Vidal, L.; Psillakis, E.; Domini, C. E.; Grane, N.; Marken, F.; Canals, A. *Anal. Chim. Acta* **2007***, 584*, 189-195.

(38) Vidal, L.; Domini, C. E.; Grane, N.; Psillakis, E.; Canals, A. *Anal. Chim. Acta* **2007***, 592*, 9-15.

(39) Liu, J.; Peng, J.; Chi, Y.; Jiang, G. *Talanta* **2005***, 65*, 705-709.

(40) Zhao, F.; Meng, Y.; Anderson, J. L. *J. Chromatogr. , A* **2008***, 1208*, 1-9.

(41) Wanigasekara, E.; Perera, S.; Crank, J. A.; Sidisky, L.; Shirey, R.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2010***, 396*, 511-524.

(42) Williams, T. L.; Fenselau, C. *Eur. Mass Spectrom.* **1998***, 4*, 379-383.

(43) Asara, J. M.; Allison, J. *J. Am. Soc. Mass Spectrom.* **1999***, 10*, 35-44.

(44) Ring, S.; Rudich, Y. *Rapid Commun. Mass Spectrom.* **2000***, 14*, 515-519.

(45) Armstrong, D. W.; Zhang, L.; He, L.; Gross, M. L. *Anal. Chem.* **2001***, 73*, 3679-3686.

(46) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Rapid Commun. Mass Spectrom.* **2003***, 17*, 553-560.

(47) Zabet-Moghaddam, M.; Heinzle, E.; Tholey, A. *Rapid Commun. Mass Spectrom.* **2004***, 18*, 141-148.

(48) Zabet-Moghaddam, M.; Heinzle, E.; Lasaosa, M.; Tholey, A. *Anal. Bioanal. Chem.* **2006***, 384*, 215-224.

(49) Tholey, A. *Rapid Commun. Mass Spectrom.* **2006***, 20*, 1761-1768.

(50) Laremore, T. N.; Murugesan, S.; Park, T.; Avci, F. Y.; Zagorevski, D. V.; Linhardt, R. J. *Anal. Chem.* **2006***, 78*, 1774-1779.

(51) Fukuyama, Y.; Nakaya, S.; Yamazaki, Y.; Tanaka, K. *Anal. Chem. (Washington, DC, U. S.)* **2008***, 80*, 2171-2179.

(52) Laremore, T. N.; Linhardt, R. J. *Rapid Commun. Mass Spectrom.* **2007***, 21*, 1315-1320.

(53) Laremore, T. N.; Zhang, F.; Linhardt, R. J. *Anal. Chem.* **2007***, 79*, 1604-1610.

(54) Mank, M.; Stahl, B.; Boehm, G. *Anal. Chem.* **2004***, 76*, 2938-2950.

(55) Darsow, K. H.; Lange, H. A.; Resch, M.; Walter, C.; Buchholz, R. *Rapid Commun. Mass Spectrom.* **2007***, 21*, 2188-2194.

(56) Naumann, I.; Darsow, K. H.; Walter, C.; Lange, H. A.; Buchholz, R. *Rapid Commun. Mass Spectrom.* **2007***, 21*, 3185-3192.

(57) Jiang, T.; Gu, Y.; Liang, B.; Li, J.; Shi, Y.; Ou, Q. *Anal. Chim. Acta* **2003***, 479*, 249-254.

(58) Qin, W.; Wei, H.; Li, S. F. Y. *J. Chromatogr. , A* **2003***, 985*, 447-454.

(59) Qin, W.; Li, S. F. Y. *Electrophoresis* **2002***, 23*, 4110-4116.

(60) Qin, W.; Li, S. F. Y. *Analyst*, **2003**, *128*, 37-41.

(61) Vaher, M.; Koel, M.; Kaljurand, M. *Chromatographia* **2001***, 53*, S302-S306.

(62) Vaher, M.; Koel, M.; Kaljurand, M. *J. Chromatogr. , A* **2002***, 979*, 27-32.

(63) He, L.; Zhang, W.; Zhao, L.; Liu, X.; Jiang, S. *J. Chromatogr. , A* **2003***, 1007*, 39-45.

(64) Liu, S. J.; Zhou, F.; Xiao, X. H.; Zhao, L.; Liu, X.; Jiang, S. X. *Chin. Chem. Lett.* **2004***, 15*, 1060-1062.

(65) Qiu, H.; Jiang, S.; Liu, X. *J. Chromatogr. , A* **2006***, 1103*, 265-270.

(66) Qiu, H.; Jiang, S.; Liu, X.; Zhao, L. *J. Chromatogr. , A* **2006***, 1116*, 46-50.

(67) Anderson, J. L.; Armstrong, D. W. *Anal. Chem.* **2005***, 77*, 6453-6462.

(68) Huang, K.; Han, X.; Zhang, X.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2007***, 389*, 2265-2275.

(69) Breitbach, Z. S.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2008***, 390*, 1605-1617.

(70) Soukup-Hein, R. J.; Warnke, M. M.; Armstrong, D. W. *Annu. Rev. Anal. Chem.* **2009***, 2*, 145-168.

(71) Armstrong, D. W.; He, L.; Liu, Y. *Anal. Chem.* **1999***, 71*, 3873-3876.

(72) Armstrong, D. W.; Payagala, T.; Sidisky, L. M. *LC-GC Eur.* **2009***, 22*, 459-460, 462, 464, 466.

(73) Ragonese, C.; Tranchida, P. Q.; Dugo, P.; Dugo, G.; Sidisky, L. M.; Robillard, M. V.; Mondello, L. *Anal. Chem. (Washington, DC, U. S.)* **2009***, 81*, 5561-5568.

(74) Seeley, J. V.; Seeley, S. K.; Libby, E. K.; Breitbach, Z. S.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2008***, 390*, 323-332.

(75) Reid, V. R.; Crank, J. A.; Armstrong, D. W.; Synovec, R. E. *J. Sep. Sci.* **2008***, 31*, 3429-3436.

(76) Lambertus, G. R.; Crank, J. A.; McGuigan, M. E.; Kendler, S.; Armstrong, D. W.; Sacks, R. D. *J. Chromatogr. , A* **2006***, 1135*, 230-240.

(77) Dimandja, J. D. In *In Multidimensional separation science research at Spelman College: Opportunities and challenges.* 2009; , pp CHED-1196.

(78) Anderson, J. L.; Ding, R.; Ellern, A.; Armstrong, D. W. *J. Am. Chem. Soc.* **2005***, 127*, 593-604.

(79) Jin, C.; Ye, C.; Phillips, B. S.; Zabinski, J. S.; Liu, X.; Liu, W.; Shreeve, J. M. *J. Mater. Chem.* **2006***, 16*, 1529-1535.

(80) Xiao, J.; Shreeve, J. M. *J. Org. Chem.* **2005***, 70*, 3072-3078.

(81) Wang, R.; Jin, C.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2006***, 45*, 6396-6403.

(82) Anderson, J. L.; Armstrong, D. W.; Wei, G. *Anal. Chem.* **2006***, 78*, 2893-2902.

(83) Soukup-Hein, R. J.; Remsburg, J. W.; Dasgupta, P. K.; Armstrong, D. W. *Anal. Chem. (Washington, DC, U. S.)* **2007***, 79*, 7346-7352.

(84) Rogers, R. D.; Seddon, K. R. *Science* **2003***, 302*, 792-793.

(85) Anthony, J. L.; Brennecke, J. F.; Holbrey, J. D.; Maginn, E. J.; Mantz, R. A.; Rogers, R. D.; Trulove, P. C.; Visser, A. E.; Welton, T. **2002; 2003**, 41-126.

(86) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998***, 102*, 8858-8864.

(87) Sheldon, R. *Chem. Commun. (Cambridge, U. K.)* **2001**, 2399-2407.

(88) Visser, A. E.; Swatloski, R. P.; Rogers, R. D. *Green Chem.* **2000***, 2*, 1-4.

(89) Wasserscheid, P.; Keim, W. *Angewandte Chemie International Edition* **2000***, 39*, 3772-3789.

(90) Ding, J.; Desikan, V.; Han, X.; Xiao, T. L.; Ding, R.; Jenks, W. S.; Armstrong, D. W. *Org. Lett.* **2005***, 7*, 335-337.

(91) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H.,Jr *J. Am. Chem. Soc.* **2002***, 124*, 5962-5963.

(92) Handy, S. T.; Okello, M. *J. Org. Chem.* **2005***, 70*, 2874-2877.

(93) Khosropour, A. R.; Khodaei, M. M.; Beygzadeh, M.; Jokar, M. *Heterocycles* **2005***, 65*, 767-773.

(94) Sheldon, R. A.; Lau, R. M.; Sorgedrager, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002***, 4*, 147-151.

(95) Xia, Y.; Wu, H.; Zhang, Y.; Fang, Y.; Sun, S.; Shi, Y. *Huaxue Jinzhan* **2006***, 18*, 1660-1667.

(96) Naik, P. U.; Nara, S. J.; Harjani, J. R.; Salunkhe, M. M. *J. Mol. Catal. B: Enzym.* **2007***, 44*, 93-98.

(97) Rumbau, V.; Marcilla, R.; Ochoteco, E.; Pomposo, J. A.; Mecerreyes, D. *Macromolecules* **2006***, 39*, 8547-8549.

(98) Paljevac, M.; Habulin, M.; Knez, Z. *Chem. Ind. Chem. Eng. Q.* **2006***, 12*, 181-186.

(99) Dickinson, E. V.; Williams, M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.* **1999***, 121*, 613-616.

(100) Lagrost, C.; Carrie, D.; Vaultier, M.; Hapiot, P. *J. Phys. Chem. A* **2003***, 107*, 745-752.

(101) Wang, C. Y.; Mottaghitalab, V.; Too, C. O.; Spinks, G. M.; Wallace, G. G. *J. Power Sources* **2007***, 163*, 1105-1109.

(102) Doyle, K. P.; Lang, C. M.; Kim, K.; Kohl, P. A. *J. Electrochem. Soc.* **2006***, 153*, A1353-A1357.

(103) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2003***, 375*, 191-199.

(104) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001***, 73*, 3737-3741.

(105) Li, C.; Xin, B.; Xu, W.; Zhang, Q. *J. Chem. Technol. Biotechnol.* **2007***, 82*, 196-204.

(106) Germani, R.; Mancini, M. V.; Savelli, G.; Spreti, N. *Tetrahedron Lett.* **2007***, 48*, 1767-1769.

(107) Berthod, A.; He, L.; Armstrong, D. W. *Chromatographia* **2001***, 53*, 63-68.

(108) Sumartschenkowa, I. A.; Verevkin, S. P.; Vasiltsova, T. V.; Bich, E.; Heintz, A.; Shevelyova, M. P.; Kabo, G. J. *J. Chem. Eng. Data* **2006***, 51*, 2138-2144.

(109) Heintz, A.; Verevkin, S. P.; Ondo, D. *J. Chem. Eng. Data* **2006***, 51*, 434-437.

(110) Heintz, A.; Verevkin, S. P. *J. Chem. Eng. Data* **2005***, 50*, 1515-1519.

(111) Canter, N. *Tribol. Lubr. Technol.* **2007***, 63*, 12-13.

(112) Pernak, J.; Skrzypczak, A.; Lota, G.; Frackowiak, E. *Chem. --Eur. J.* **2007***, 13*, 3106-3112.

(113) Dzyuba, S. V.; Bartsch, R. A. *ChemPhysChem* **2002***, 3*, 161-166.

(114) Seddon, K. R.; Stark, A.; Torres, M. *ACS Symp. Ser.* **2002***, 819*, 34-49.

(115) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008***, 37*, 123-150.

(116) Soukup-Hein, R. J.; Remsburg, J. W.; Breitbach, Z. S.; Sharma, P. S.; Payagala, T.; Wanigasekara, E.; Huang, J.; Armstrong, D. W. *Anal. Chem. (Washington, DC, U. S.)* **2008***, 80*, 2612-2616.

(117) Ding, J.; Armstrong, D. W. *Chirality* **2005***, 17*, 281-292.

(118) Nanayakkara, Y. S.; Moon, H.; Payagala, T.; Wijeratne, A. B.; Crank, J. A.; Sharma, P. S.; Armstrong, D. W. *Anal. Chem. (Washington, DC, U. S.)* **2008***, 80*, 7690-7698.

(119) Millefiorini, S.; Tkaczyk, A. H.; Sedev, R.; Efthimiadis, J.; Ralston, J. *J. Am. Chem. Soc.* **2006***, 128*, 3098-3101.

(120) Law, G.; Watson, P. R. *Langmuir* **2001***, 17*, 6138-6141.

(121) Sharma, P. S.; Payagala, T.; Wanigasekara, E.; Wijeratne, A. B.; Huang, J.; Armstrong, D. W. *Chem. Mater.* **2008***, 20*, 4182-4184.

(122) Moon, H.; Wheeler, A. R.; Garrell, R. L.; Loo, J. A.; Kim, C. *Lab Chip* **2006***, 6*, 1213-1219.

(123) Pollack, M. G.; Fair, R. B.; Shenderov, A. D. *Appl. Phys. Lett.* **2000***, 77*, 1725-1726.

(124) Wheeler, A. R.; Moon, H.; Kim, C.; Loo, J. A.; Garrell, R. L. *Anal. Chem.* **2004***, 76*, 4833-4838.

(125) Berge, B.; Peseux, J. *Eur. Phys. J. E* **2000***, 3*, 159-163.

(126) Hayes, R. A.; Feenstra, B. J. *Nature (London, U. K.)* **2003***, 425*, 383-385.

(127) Dubois, P.; Marchand, G.; Fouillet, Y.; Berthier, J.; Douki, T.; Hassine, F.; Gmouh, S.; Vaultier, M. *Anal. Chem.* **2006***, 78*, 4909-4917.

(128) Chatterjee, D.; Hetayothin, B.; Wheeler, A. R.; King, D. J.; Garrell, R. L. *Lab Chip* **2006***, 6*, 199-206.

(129) Moon, H.; Bindiganavale, S.; Nanayakkara, Y. S.; Armstrong, D. W. *Proceedings of the Seventh International ASME Conference on Nanochannels, Microchannels and Minichannels* ICNMM2009; Pohang, South Korea, June 22-24, **2009**.

(130) Kunchala, P.; Moon, H.; Nanayakkara, Y. S.; Armstrong, D. W. Proceedings of the ASME 2009 Summer Bioengineering Conference (SBC2009) ; Lake Tahoe, CA, June 17-21, **2009**.

(131) Catalan, J.; Claramunt, R. M.; Elguero, J.; Laynez, J.; Menendez, M.; Anvia, F.; Quian, J. H.; Taagepera, M.; Taft, R. W. *J. Am. Chem. Soc.* **1988***, 110*, 4105-4111.

(132) Zhou, Z.; Matsumoto, H.; Tatsumi, K. *ChemPhysChem* **2005***, 6*, 1324-1332.

(133) Bradaric, C. J.; Downard, A.; Kennedy, C.; Robertson, A. J.; Zhou, Y. *Green Chem.* **2003***, 5*, 143-152.

(134) Gordon, C. M. *Appl. Catal. , A* **2001***, 222*, 101-117.

(135) Zhu, Y.; Rosen, M. J.; Morrall, S. W. *J. Surfactants Deterg.* **1998***, 1*, 1-9.

(136) Earle, M. J.; Seddon, K. R.; Adams, C. J.; Roberts, G. *Chem. Commun. (Cambridge)* **1998**, 2097-2098.

(137) Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Green Chem.* **1999***, 1*, 23-25.

(138) Dyson, P. J.; Ellis, D. J.; Welton, T.; Parker, D. G. *Chem. Commun. (Cambridge)* **1999**, 25-26.

(139) Wilkes, J. S. *J. Mol. Catal. A: Chem.* **2004***, 214*, 11-17.

(140) Ue, M.; Takeda, M. *J. Korean Electrochem. Soc.* **2002***, 5*, 192-196.

(141) Jimenez, A.; Bermudez, M. *Tribol. Lett.* **2007***, 26*, 53-60.

(142) Xia, Y.; Sasaki, S.; Murakami, T.; Nakano, M.; Shi, L.; Wang, H. *Wear* **2007***, 262*, 765-771.

(143) Tholey, A.; Heinzle, E. *Anal. Bioanal. Chem.* **2006***, 386*, 24-37.

(144) Gordon, J. E.; Selwyn, J. E.; Thorne, R. L. *J. Org. Chem.* **1966***, 31*, 1925-1930.

(145) Pacholec, F.; Butler, H. T.; Poole, C. F. *Anal. Chem.* **1982***, 54*, 1938-1941.

(146) Pacholec, F.; Poole, C. F. *Chromatographia* **1983***, 17*, 370-374.

(147) Reichardt, C. *Angew. Chem.* **1965***, 77*, 30-40.

(148) McReynolds, W. O. *Gas chromatographic retention data; Preston Technical Abstracts:* Evanston **1966**.

(149) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000***, 13*, 591-595.

(150) Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc. , Perkin Trans. 2* **2001**, 433-435.

(151) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commun. (Cambridge, U. K.)* **2001**, 413-414.

(152) Reynolds, J. L.; Erdner, K. R.; Jones, P. B. *Org. Lett.* **2002***, 4*, 917-919.

(153) Rohrschneider, L. *J. Chromatogr.* **1966***, 22*, 6-22.

(154) McReynolds, W. O. *J. Chromatogr. Sci.* **1970***, 8*, 685-691.

(155) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. *J. Chromatogr.* **1990***, 518*, 329-348.

(156) Abraham, M. H.; Whiting, G. S.; Andonian-Haftvan, J.; Steed, J. W.; Grate, J. W. *J. Chromatogr.* **1991***, 588*, 361-364.

(157) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. *J. Chromatogr.* **1991***, 587*, 213-228.

(158) Abraham, M. H. *Chem. Soc. Rev.* **1993***, 22*, 73-83.

(159) Abraham, M. H.; Poole, C. F.; Poole, S. K. *J. Chromatogr. , A* **1999***, 842*, 79-114.

(160) Kiridena, W.; Koziol, W. W.; Poole, C. F. *J. Chromatogr. , A* **2001***, 932*, 171-177.

(161) Vitha, M.; Carr, P. W. *J. Chromatogr. , A* **2006***, 1126*, 143-194.

(162) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000***, 105*, 221-227.

(163) Grob, K., Jr.; Grob, G.; Grob, K. *J. Chromatogr.* **1978***, 156*, 1-20.

(164) Grob, K.; Grob, G.; Grob, K.,Jr *J. Chromatogr.* **1981***, 219*, 13-20.

(165) Paquot, C. IUPAC Standard Methods for the Analysis of Fats, Oils, and Derivatives, 6th ed.; Pergamon Press: New York, **1979**.

(166) Celik, M.; Tureli, C.; Celik, M.; Yanar, Y.; Erdem, U.; Kucukgulmez, A. *Food Chem.* **2004***, 88*, 271-273.

(167) Brodnjak-Voncina, D.; Kodba, Z. C.; Novic, M. *Chemom. Intell. Lab. Syst.* **2005***, 75*, 31-43.

(168) Harynuk, J.; Wynne, P. M.; Marriott, P. J. *Chromatographia* **2006***, 63*, S61-S66.

(169) MELLIN, G. W.; KATZENSTEIN, M. *N Engl J Med* **1962***, 267*, 1184-92 contd.

(170) Blaschke, G.; Kraft, H. P.; Fickentscher, K.; Koehler, F. *Arzneim. -Forsch.* **1979***, 29*, 1640-1642.

(171) Flockhart, D. A.; Nelson, H. S. *CNS Spectr* **2002**, 7:23–27.

(172) U.S. Food and Drug Administration. *Chirality* **1992,** *4,* 338–340.

(173) Armstrong, D. W.; Zhang, B. *Anal Chem* **2001***, 73*, 557A-561A.

(174) Subramanian, G. (Ed) **2007** Chiral separation techniques: a practical approach. Wiley, Weinheim

(175) Davankov, V. A.; Rogozhin, S. V. *J. Chromatogr.* **1971***, 60*, 280-283.

(176) Helgeson, R. C.; Timko, J. M.; Moreau, P.; Peacock, S. C.; Mayer, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1974***, 96*, 6762-6763.

(177) Dotsevi, G.; Sogah, Y.; Cram, D. J. *J. Am. Chem. Soc.* **1975***, 97*, 1259-1261.

(178) Mikes, F.; Boshart, G.; Gil-Av, E. *J. Chromatogr.* **1976***, 122*, 205-221.

(179) Mikes, F.; Boshart, G. *J. Chem. Soc. , Chem. Commun.* **1978**, 173-175.

(180) Mikes, F.; Boshart, G. *J. Chromatogr.* **1978***, 149*, 455-464.

(181) Pirkle, W. H.; House, D. W. *J. Org. Chem.* **1979***, 44*, 1957-1960.

(182) Pirkle, W. H.; Finn, J. M. *J. Org. Chem.* **1981***, 46*, 2935-2938.

(183) Pirkle, W. H.; Hyun, M. H. *J. Chromatogr.* **1985***, 322*, 309-320.

(184) Pirkle, W. H.; Deming, K. C.; Burke, J. A.,III *Chirality* **1991***, 3*, 183-187.

(185) Pirkle, W. H.; Welch, C. J. *J. Liq. Chromatogr.* **1992***, 15*, 1947-1955.

(186) Oi, N.; Nagase, M.; Doi, T. *J. Chromatogr.* **1983***, 257*, 111-117.

(187) Oi, N.; Kitahara, H. *J. Chromatogr.* **1983***, 265*, 117-120.

(188) Armstrong, D. W.; DeMond, W. *J. Chromatogr. Sci.* **1984***, 22*, 411-415.

(189) Armstrong, D. W.; Stalcup, A. M.; Hilton, M. L.; Duncan, J. D.; Faulkner, J. R., Jr.; Chang, S. C. *Anal. Chem.* **1990***, 62*, 1610-1615.

(190) Stalcup, A. M.; Chang, S. C.; Armstrong, D. W. *J. Chromatogr.* **1991***, 540*, 113-128.

(191) Armstrong, D. W.; Ward, T. J.; Armstrong, R. D.; Beesley, T. E. *Science* **1986***, 232*, 1132-1135.

(192) Hamilton, J. A.; Chen, L. *J. Am. Chem. Soc.* **1988***, 110*, 4379-4391.

(193) a) Cyclobond ™ Handbook, 6th Edition, Advanced Separation Technologies Inc., Whippany, NJ, **2002**. b) Chirobiotic ™ Handbook, 5th Edition, Advanced Separation Technologies Inc., Whippany, NJ, **2004.**

(194) Armstrong, D. W.; Tang, Y.; Chen, S.; Zhou, Y.; Bagwill, C.; Chen, J. *Anal. Chem.* **1994***, 66*, 1473-1484.

(195) Chen, S.; Liu, Y.; Armstrong, D. W.; Borrell, J. I.; Martinez-Teipel, B.; Matallana, J. L. *J. Liq. Chromatogr.* **1995***, 18*, 1495-1507.

(196) Armstrong, D. W.; Liu, Y.; Ekborgott, K. H. *Chirality* **1995***, 7*, 474-497.

(197) Berthod, A.; Liu, Y.; Bagwill, C.; Armstrong, D. W. *J. Chromatogr. , A* **1996***, 731*, 123-137.

(198) Sun, P.; Wang, C.; Breitbach, Z. S.; Zhang, Y.; Armstrong, D. W. *Anal. Chem. (Washington, DC, U. S.)* **2009***, 81*, 10215-10226.

(199) Armstrong, D. W.; Ping, S.; Breitbach, Z. S.; Wang, C. PCT Designated States: Designated States W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, K(TRUNCATED) Patent 2010148191, 2010.

(200) Sun, P.; Armstrong, D. W. *J. Chromatogr. , A* **2010***, 1217*, 4904-4918.

(201) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Am. Chem. Soc.* **1984***, 106*, 5357-5359.

(202) Okamoto, Y.; Kawashima, M.; Yamamoto, K.; Hatada, K. *Chem. Lett.* **1984**, 739-742.

(203) Hesse, G.; Hagel, R. *Chromatographia* **1973***, 6*, 277-280.

(204) Ikai, T.; Yamamoto, C.; Kamigaito, M.; Okamoto, Y. *Polym. J. (Tokyo, Jpn.)* **2006***, 38*, 91-108.

(205) Wulff, G.; Sarhan, A. *Angew. Chem. , Int. Ed. Engl.* **1972***, 11*, 341.

(206) Blaschke, G. *Chem. Ber.* **1974***, 107*, 237-252.

(207) Blaschke, G. *Angew. Chem.* **1980***, 92*, 14-25.

(208) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979***, 101*, 4763-4765.

(209) Yuki, H.; Okamoto, Y.; Okamoto, I. *J. Am. Chem. Soc.* **1980***, 102*, 6356-6358.

(210) Saigo, K.; Chen, Y.; Yonezawa, N.; Tachibana, K.; Kanoe, T.; Hasegawa, M. *Chem. Lett.* **1985**, 1891-1894.

(211) Gasparrini, F.; Misiti, D.; Rompietti, R.; Villani, C. *J Chromatogr A* **2005***, 1064*, 25-38.

(212) Zhong, Q.; Han, X.; He, L.; Beesley, T. E.; Trahanovsky, W. S.; Armstrong, D. W. *J. Chromatogr. , A* **2005***, 1066*, 55-70.

(213) Han, X.; He, L.; Zhong, Q.; Beesley, T. E.; Armstrong, D. W. *Chromatographia* **2006***, 63*, 13-23.

(214) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986***, 363*, 173-186.

(215) Han, X.; Wang, C.; He, L.; Beesley, T. E.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2007***, 387*, 2681-2697.

(216) Han, X.; Berthod, A.; Wang, C.; Huang, K.; Armstrong, D. W. *Chromatographia* **2007***, 65*, 381-400.

BIOGRAPHICAL INFORMATION

Tharanga Payagala obtained her Bachelor of Science degree in chemistry with first class honors in 2004 from University of Peradeniya, Sri Lanka. In the same year she was awarded the University Prize for Academic Excellence for her achievements as an undergraduate. After that she joined the faculty of science as an assistant lecturer and worked at the University of Peradeniya. In 2005 she began her doctoral studies under the supervision of Professor Daniel W. Armstrong at the University of Texas at Arlington. Her areas of research are designing and synthesis of multicationic ionic liquids, development of highly thermally stable gas chromatographic stationary phase, and development of new chiral stationary phases for high performance liquid chromatography and supercritical fluid chromatography. During her graduate studies she has maintained a cumulative grade point average of 4.0. She earned her Doctor of Philosophy degree in March 2011.