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DEPARTMENT OF CHEMISTRY

SYNTHESIS OF NEW N-ALKYL-1,10-PHENANTHROLINIUM TETRAFLUOROBORATE IONIC LIQUIDS BY A NEW ANION METATHESIS PROCEDURE

By Yonas Bekele

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DECLARATION

I, the undersigned confirm that this is my original work obtained by research carried out by me under the supervision of my advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2010/11. No part of this work shall be published in any scientific journal or presented at conferences without the knowledge and consent of my advisor, who is the principal scientist for my publication. Furthermore, if the work is published the international address given should be that of the chemistry department of AAU. Finally, I declare that this work has not been submitted for a degree in any other University and all sources used for the study have been duly acknowledged.

Name: Yonas Bekele

Signature _____________

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

Advisor's Name Dr. Ignacio J. Villar – Garcia

Signature _____________

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List of Abbreviations and symbols

ILs	Ionic liquids
VOCs	Volatile organic compounds
CED	Cumulative energy demand
$[C_nPhen]BF_4$	N-alkyl-1,10-phenanthrolinium tetrafluoroborate
$[C_nPhen]Br$	N-alkyl-1,10-phenanthrolinium bromide
$[C_1Phen]NTf_2$	N-methyl-1,10-phenanthrolinium bis(trifluoromethylsulfonyl)imide
Tf_2N^-	bis(trifluoromethylsulfonyl)imide
$[C_1C_nIm]BF_4$	1-Methyl-3-alkylimidazolium tetrafluoroborate
$[C_nPhen]PF_6$	N-alkyl-1,10-phenanthrolinium hexafluorophosphate
DMSO	Dimethyl sulfoxide
$CDCl_3$	Deutrated chloroform
wt/wt%	Percentage by weight
R.T	Room temperature
δ	Chemical shift
J	Coupling constant
s	Singlet
d	Doublet
t	Triplet
q	Quartet
dd	Doublet of doublet
tq	Triplet of quartet
m	Multiplate

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Abstract

Ionic liquids (ILs) are salts with melting points below 100°C and have remarkable and designer flexible physicochemical properties that offer distinctive performance advantages in a variety of synthetic, catalytic, and electrochemical applications. They are widely used as green alternatives to conventional environment polluting volatile organic solvents (VOCs) due to their negligible vapor pressure. However, their application in areas like catalysis is limited by the limited number of cations on which the majority of ILs in common use is based and due to the low solubilities of organometallic compounds in these groups of ILs. Their green credentials are also being put into question as the interest in ILs increases. Hence designing new ILs for a given application should also be accompanied by improvements in the methodology of their preparation with respect to economics of preparation, environmental impact and cumulative energy demand (CED). In a current work done in our laboratory, $[C_nPhen]X$ (X= Br^-, PF_6^-, Tf_2N^-) ILs have been synthesized following a similar procedure to commonly used ILs and they exhibited good solubilities for phenanthroline and phenanthroline - metal complexes. Tetrafluoroborate ILs normally exhibit low melting points and low coordinating abilities that are desired for catalytic reactions. For this study, we have synthesized a range of new $[C_nPhen]BF_4$ ILs with varying alkyl chains. Even though, the new water miscible $[C_nPhen]BF_4$ ILs could be synthesized according to the conventional procedure for the synthesis of other water miscible BF_4^- containing ILs, we developed a new simple anion metathesis procedure, which has cut down reaction times, improved yields and bypassed the difficult by-product separation and product purification steps. $[C_nPhen]BF_4$ ILs exhibited good solubilities for phenanthroline and a wide range of phenanthroline based metal complexes. Their melting points were found to be relatively lower than its halides, PF_6^- and some of Tf_2N^- containing analogues and followed the same trend with alkyl chain length of the cation as its $[C_nPhen]Br$ precursor. Furthermore, these ILs are found to be soluble in a larger number of organic solvents than their analogous salts, which offer flexibility for application in a number of reaction and catalysis schemes.

KEY WORDS: Ionic liquids, tetrafluoroborate, phenanthroline, phenanthrolinium ionic liquids, metal complex solubility, homogeneous catalysis.

1. INTRODUCTION

Ionic liquids (ILs) – salts having melting points below 100°C – have recently attracted considerable attention as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic and electrochemical applications.[1] ILs typically consist of bulky organic cations and inorganic or organic anions [2]. These ionic solvents are composed entirely of ions and strongly resemble ionic melts that may be produced by heating metallic salts. Unlike normal metallic salts, ILs are liquid at much lower temperatures. The constituents of ILs are constrained by high Coulombic forces, exhibiting practically negligible vapor pressure. This unique property gives them the capability to expand traditional laws of chemistry. For example, these liquids are highly polar, yet non-coordinating (ideal for catalytic reactions), they can be made immiscible with water and/or a number of organic solvents (providing flexibility for a number of reaction and separation schemes) and they are nonvolatile even at elevated temperatures. The physical and chemical properties (e.g. melting point, density, conductivity, viscosity, hydrophobicity, Lewis acidity, and hydrogen-bonding capability) of ILs can be tuned by varying the structure of the component ions to obtain desired solvent properties. [3] These unique traits of ILs allow the possibility for more efficient reactions and separations to occur.

1.1 SYNTHESIS OF IONIC LIQUIDS

As the field of ILs has grown in recent years, producing a wide range of properties in an even wider range of salt structures, the synthetic methods applied to the preparation of these salts have become more sophisticated and capable of targeting more complex compounds. The synthetic approach currently used for the preparation of a great many ILs involves two steps. The first and sometimes the only step is a quaternization reaction and the second step is a metathesis reaction from a halide or similar salt of the desired cation with a salt containing the desired anion.

The quaternization reactions, i.e., alkylation of organic molecules mostly involving amine, phosphine or sulfide by alkylating agent to produce a salt, are in principle quite simple: the amine (or phosphine or sulfide) is mixed with the desired alkylating agent, and the mixture is then stirred and heated. In general, the reaction may be carried out using chloroalkanes, bromoalkanes and iodoalkanes, with the reaction conditions required becoming steadily gentler in the order Cl → Br → I, as is expected for nucleophilic substitution reactions. [4]

Depending on the water solubility of the targeted ILs, the general metathesis reaction can be divided into two categories: metathesis via (1) Free acids or group 1 metals/ammonium salts, or (2) Ag salt metathesis. [4]

Even though, the preparation of water immiscible ILs can be easily achieved via the metathesis reaction of the corresponding halide salt, either with the free acid of the anion, or its metal or ammonium salt, the preparation of water-miscible ILs is a more difficult task, since it requires separation of the by-products from the desired ionic liquid. [5] The group 1 metal/ammonium halide by-product, the halide salt starting material and the product ILs are all soluble in water and extraction from aqueous phase, if possible, leaves considerable amounts of the undesired ions in the ionic liquid. The metathesis can be alternatively achieved via the simple metathesis reaction of the corresponding chloride or bromide with the silver salt of the anion in methanol/aqueous methanol and other organic solvents. Unfortunately, this route is expensive and forms a large amount of silver halide as by-product. Complete precipitation of silver halides from organic solvents can also be quite slow, leading to silver-contaminated products. The nature of the precipitate can also be troublesome; in some cases the silver halide forms as sub-micron particles, which are difficult to filter. [4] It has also been reported that the reaction could be carried out in organic solvents, like acetone, with the insoluble sodium salt of the anion as a suspension. However, this procedure takes a rather long time and gives lower yields. [6]

In this respect, the development of simple metathesis procedure for the synthesis of water miscible ILs which could cut reaction times, improve yields, bypass the difficult by-product separation and product purification and reduce or eliminate the use of environment polluting VOCs can help in making the overall process of ionic liquid synthesis greener and access to ILs easier.

1.2 MELTING POINT OF IONIC LIQUIDS

Salts that have low melting points and would be liquids at and below ambient temperatures are very desirable and potentially important as reactions can be performed at milder conditions and there is no need of heating up the reaction system and therefore, the energy demand is reduced. Moreover, better understanding of structure – property relationship, like the relationship between melting point and alkyl side chain size or anion identity, is a crucial aspect for designing ILs with tailor made properties for a specific application.

It is well known that the structure of an ionic liquid directly impacts upon its properties, in particular, the melting point and liquid ranges. [7] Changes in size, shape and character of the component ions, most particularly with the introduction of charge dispersed or non-charged components, influence the melting points of salts with the reduction in melting point resulting from disruption of crystal packing and reduction of the crystal lattice energy. [8]

The dominant force in ILs is the Coulombic attraction between ions. [9] But the Coulombic interaction terms for ILs are relatively small compared to those in analogous inorganic salts as a result of size and charge differences, and the presence of flexible substituents, which contribute to charge separation, disruption of lattice isotropy and introduce many rotational and vibrational modes of freedom in these ions. This introduction of ion flexibility, inefficiencies of packing, and non-charge bearing hydrocarbon groups, provides significant reductions in the salt lattice energies which can lead to low melting points and, in many cases, glass formation with marked inhibition of crystallization.

The overall lattice energies of ILs thus can be reduced, and low melting salts can be achieved when the charges on the ions are respectively ±1 and when the size of the ions is large, thereby ensuring that the inter-ion separation is also large. In addition, large ions enable charge delocalization, further reducing overall charge density.

Characteristic changes in the melting points of organic salts with simple changes in single alkyl-chain substituent (figure 1) highlights the two competing effects on the melting points of changing alkyl-group substituents. Initial lengthening of the substituent leads to a reduction in the melting points through destabilization of Coulombic packing, and a trend towards glass formation. However, further increases in substitution lead to increased attractive Van der Waals forces between the hydrocarbon chains and increased structural ordering, which can be seen with the re-emergence of higher melting points and the formation of structured liquid crystalline materials.

Recent work made in our laboratories have managed to synthesize phenanthrolinium based ILs. Even though the melting point of phenanthrolinium based ILs synthesized so far in our laboratory generally follow a more or less similar trend as that shown in figure 1, they exhibited irregular changes in melting point with alkyl chain in the continuum between the limits of charge controlled and Van der Waals interaction controlled regions (figure 2) and no structural factors could be found so far to fully explain the observed irregular changes.

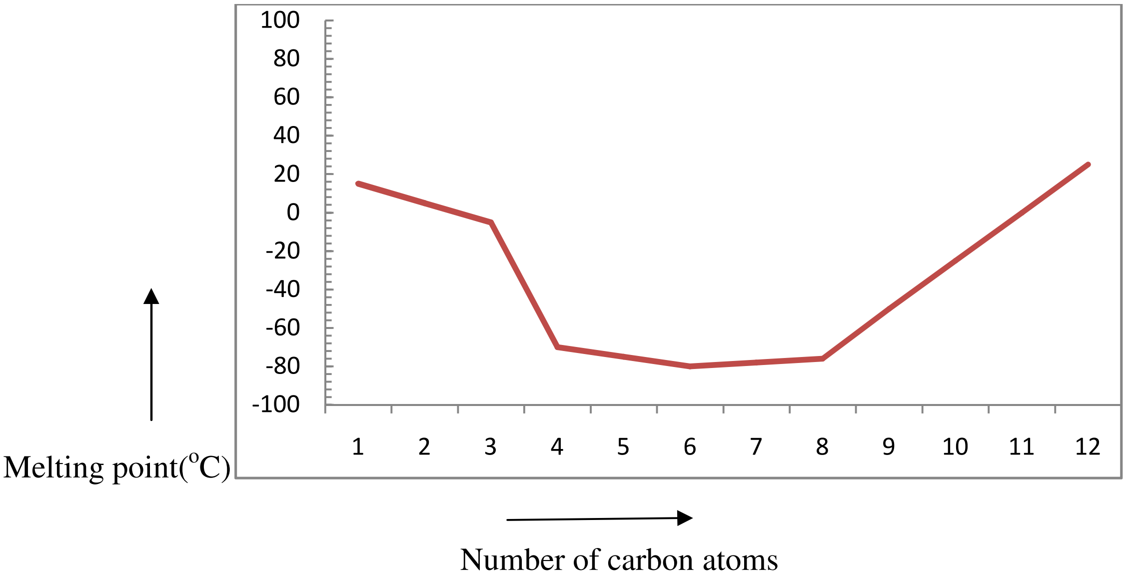


Figure 1: Melting point *vs* number of alkyl chain carbon for $[C_1C_nIm]BF_4$.

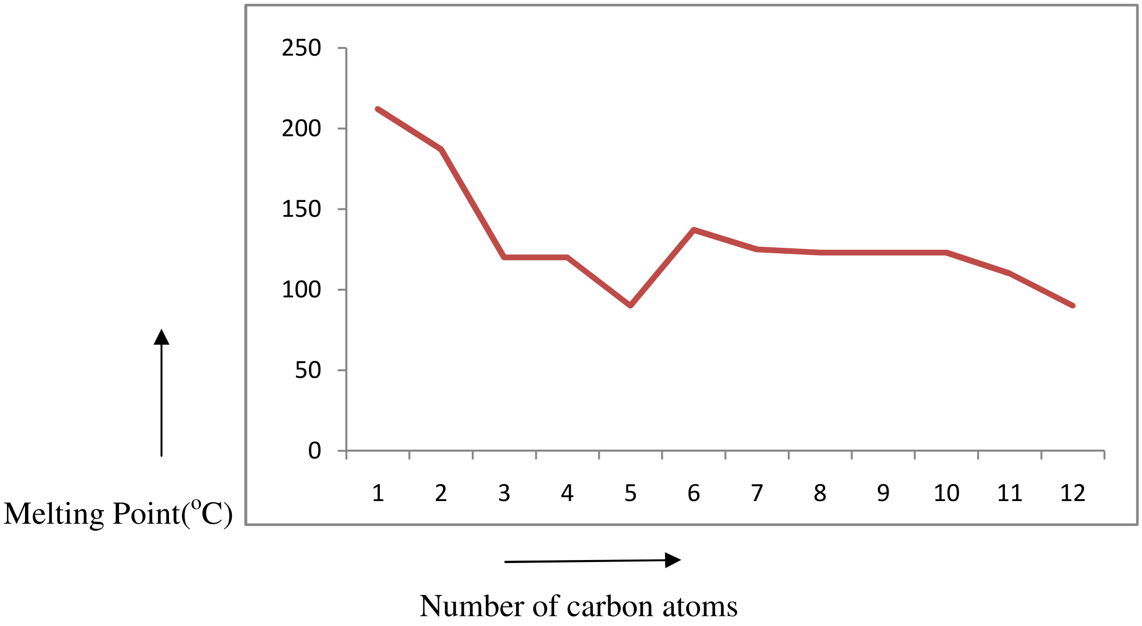


Figure 2: Melting point *vs* number of alkyl chain carbon for $[C_nPhen]PF_6$

It is important to investigate the effect of alkyl side chains of the cation and anion identity on the melting points of this new class of ILs as this knowledge will help to understand the correlation between structural modifications and physicochemical properties and to gain a better understanding of their application scope.

1.3 IONIC LIQUIDS AND HOMOGENEOUS CATALYSIS

Synthetic chemists are limited by the available number of molecular solvents in which they can conduct chemistry and increasingly, commonly used solvents are banned by international protocols determined to reduce pollution, of which volatile organic compounds represent a significant part. [9] Therefore, ILs have certainly captured the imagination of chemists nowhere more than in synthesis and catalysis. Besides their negligible vapor pressure and high thermal stability, the main constituents of IL's green credentials, there are many good reasons to apply ionic liquids as alternative solvents in transition metal catalyzed reactions. [10] The most important advantage is the possibility to tune their solubility and coordination properties by varying the nature of the anions and cations systematically. The possibility of adjusting solubility properties is of particular importance for liquid-liquid biphasic catalysis.

Liquid-liquid biphasic catalysis can be realized when the ionic liquid is able to dissolve the catalyst, displays a partial solubility with the substrates and a poor solubility with the reaction products. Under these conditions, the product phase is removed by simple phase decantation, and the ionic liquid containing the catalyst can be recycled. [11]

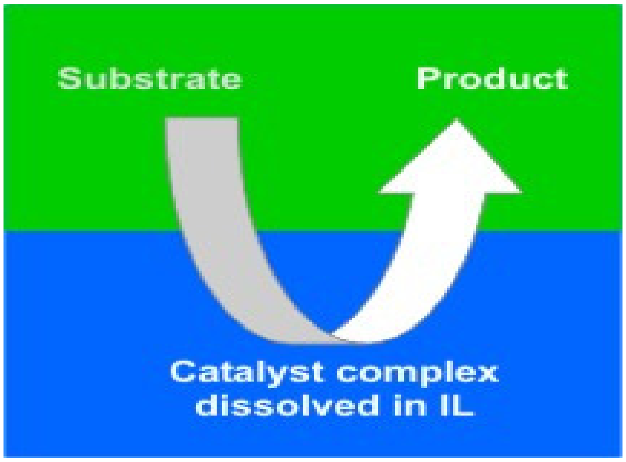
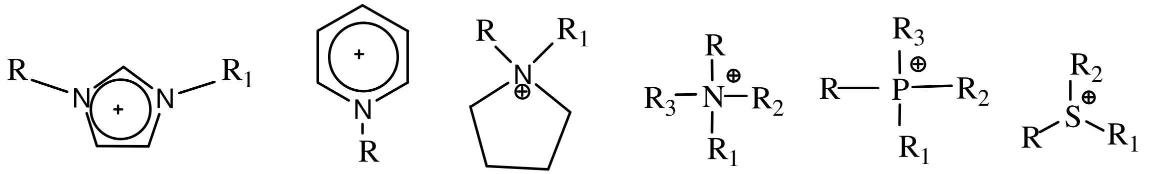


Figure 3: Principle of biphasic catalysis using ionic liquids for catalyst immobilization

With regard to catalytic processes, the solubility of both catalyst complex and organic compounds in ILs is important. One of the desirable features of an ionic liquid, therefore, is catalyst solubility, which enables high catalyst capacity and good immobilization of the catalyst to extraction processes.

The advantages of a liquid, ionic catalyst support in the immobilized ionic liquid systems was investigated for many transition metal catalyzed organic reactions, mostly with the expectation that the ionic solvent will allow preservation of the advantages of traditional homogeneous catalysis like the usually high reaction selectivity governed by dissolved of well-defined transition metal complexes or accelerate product formation and many notable and impressive examples have been reported. [12] In this respect the Diels-Alder reaction is a particularly interesting case as higher reaction rates and selectivities are obtained in polar solvents compared to non-polar solvents. [13]

The application of ILs in catalysis is, however, limited due to the low solubilities of organometallic compounds in the majority of the ILs in common use, which are based on a limited number of cations, mostly dialkylimidazolium, alkylpyridinium, dialkylpyrollidinium, tetralkylammonium and tetraalkylphosphonium (Figure 4). [14]



Imidazolium Pyridinium Pyrrolidinium Ammonium Phosphonium Sulfonium

Figure 4: The most commonly used cations in IL

The most versatile approach used to enhance metal complex solubilities and achieve sufficient retention of the catalyst in the ionic liquid phase is to attach charged groups to the ligands bound to the metal catalyst centre, so that, the ligand interacts with the IL cation and the catalyst remains anchored in the IL phase or functionalizing the ILs themselves. [15] These strategies of course, require further amount of synthetic work and render the final application more laborious and expensive. Thus another means of improving catalyst solubility and sufficient retention has to be devised. The expansion of the available number of IL cations and investigation of their solvent ability for a metal catalyst with ligands similar to the IL cation can be one possibility, as the similarity between the IL cation and the ligand may create increased interaction, as the solubility rule ‘like dissolves like’ dictates, and thereby enhance catalyst solubility and retention.

Systematic studies of metal complex solubility in ILs have not been reported and warrant investigation. As a general observations; (i) ionic compounds are generally poorly soluble in ILs; (ii) ionic complexes are more soluble; (iii) compounds are solubilized by complexation; (iv) the peripheral environment of the ligands is important in affecting solubility, and can be modified to enable better solubility. Solubility depends on the nature of the ionic liquid and solvation or complex formation, most metal ions display preferential partitioning to water and are, hence, less soluble in the ionic liquid than in water. [16]

1.4 1,10 PHENANTHROLINIUM IONIC LIQUIDS

In the previous work done in our laboratory, $[C_nPhen]NTf_2$ ILs were synthesized and their ability to dissolve 1,10-phenanthroline based metal complexes, with $[Ni(Phen)_2(OH_2)_2]Cl_2$ as a model compound, was tested. It was found that the IL is able to dissolve over 50 % by weight of the catalyst at 75ºC. This capacity to solubilise a metal complex is exceptionally high for an ionic liquid and the result is especially relevant because two commonly used ILs based on the imidazolium cation, and commonly used in homogeneous catalysis, were unable to solubilise even small amounts of the same complex (< 0.05w/w%). The reasons for this enhanced solubility exhibited may be explained by the fact that 1,10-phenanthroline and the 1,10-phenanthrolinium based ionic liquid are totally miscible, whereas the other tested ILs failed to solubilise the 1,10-phenanthroline molecule (< 0.05w/w%). The complex is solubilised in the ionic liquid media due the interaction of the 1,10-phenanthroline ligand with the 1,10-phenanthrolinium cations and not due to a change in coordination of the metal complex. Any new coordination should involve the participation of the non-alkylated nitrogen atom in the cation and this can be ruled out by two observations which suggest that the non-alkylated nitrogen atom is not available for coordination: firstly, the non reactivity of the N - alkyl 1,10-phenanthrolinium cation towards second alkylation due to steric hindrance by the alkyl chain on the ortho- nitrogen and secondly, the fact that $NiCl_2.6H_2O$ salt, the precursor used for the synthesis of the $[Ni(Phen)_2(OH_2)_2]Cl_2$

complex, was found to be insoluble in [C_1Phen][Tf_2N] at the reaction conditions required for the synthesis of the [Ni(Phen)$_2$(OH$_2$)$_2$]Cl$_2$ complex. [17]

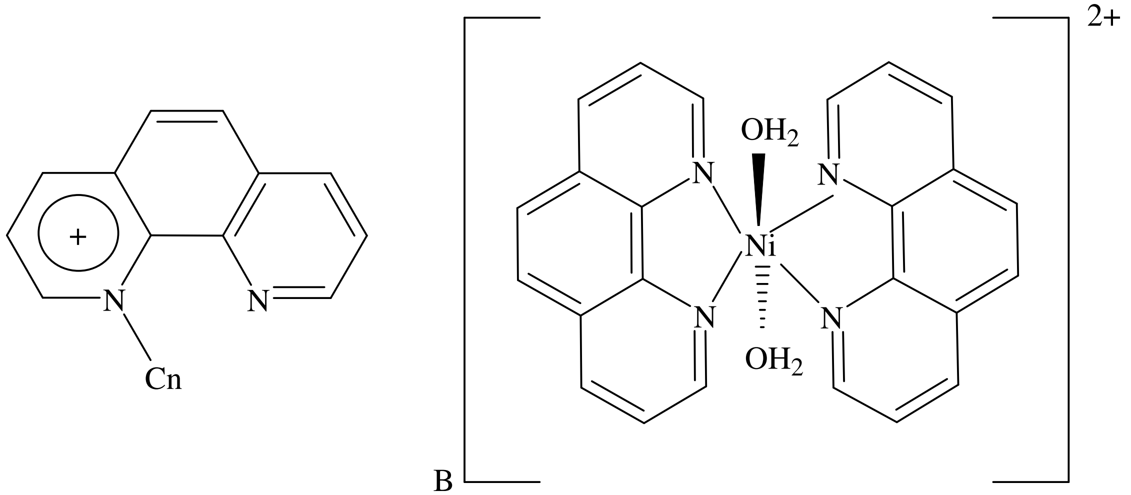


Figure 5: A) N-alkyl-1,10-phenanthrolinium cation and B) [Ni(Phen)$_2$(OH$_2$)$_2$]$^{2+}$.

The expansion of the available phenanthrolinium ILs to the whole range of anions and alkyl chains of different lengths and study of their solvent and physico – chemical properties can help enhance the application of phenanthrolinium ILs in catalysis and offer wider range of circumstances to make a balanced decision between their overall burden (in relation to cost of synthesis, environmental impact, etc) and performance properties to gain the best fit to a particular application. On top of that, if their synthesis is accompanied by improvements in the methodology, it could help to renovate the technical and economic potential of ILs and strengthen their green credential.

1.5 PHENANTHROLINE

1, 10-Phenanthroline, commonly abbreviated as "phen," is the parent of an important class of chelating agents that form coordination compounds with various metal ions. [13] It possesses a rigid framework, and presents superb ability to coordinate many metal ions. The corresponding metal complexes show potential applications because of their high charge transfer mobility, strong absorption in the ultraviolet spectral region, bright red light emission, and good electro- and photo-active properties. [18] Phenanthroline and similar N-heterocyclic (like 2, 2’-bipyridine which is similar in terms of its coordination properties to phen,) also play important role in studies of electron and energy transfer processes and are commonly utilized as building blocks in supramolecular chemistry.

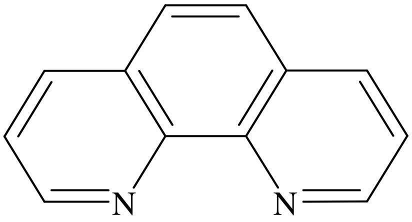


Figure 6: 1,10-phenanthroline molecule

However, finding appropriate solvent that meets the requirements of good solubility for these classes of transition metal complexes and safety has been troublesome. Recent work done in our laboratory with phenanthrolinium ILs offered a potential solution to this problem. The good solvent ability of $[C_1Phen][Tf_2N]$ ionic liquid for phenanthrolinium based metal complex is very promising. However, it is very necessary to try extending the range of ionic liquids of this class. New anions could provide the ionic liquid with crucial properties to optimize liquid–liquid catalytic applications and obtain improved dissolution ability for metal complexes. The ideal ionic liquid should be able to better dissolve catalysts, display a partial solubility with substrates and a poor solubility with reaction products for a particular reaction.

1.6 TETRAFLUOROBORATE ANION

The anion has a great influence on the properties of ILs. The introduction of different anions has become more popular as an increasing number of alternatives are being discovered that function as well as, or better than, well-known anions such as Cl^- or $AlCl_4^-$. The anion BF_4^- and the related ion PF_6^- are probably the most common anions used in ionic liquid research. [10] Though little variation in properties might be expected between same-cation salts of these species, the actual differences can be dramatic: for example, $[bmim]PF_6^-$ is immiscible with water, whereas $[bmim]BF_4^-$ is water-soluble. [20] This sort of variation arising from different ion pairing gave rise to ionic liquid's description as "designer solvents" and this means that their properties can be adjusted to suit the requirements of a particular process by simple changes to the structure of the ions.

The importance of BF_4^- arises because its salts are often more soluble in organic solvents than the related nitrate or halide salts offering advantage of greater reagent solubility when used in catalysis. For reactions involving the use of a metal catalyst in an ionic liquid, a low capacity for coordination on the part of the anion is essential, and fluorous species like BF_4^- and PF_6^- will probably remain the best in that regard. [21] BF_4^- owes its inertness to the fact that the negative charge is distributed equally over several atoms and it is composed of highly electronegative fluorine atoms, which diminish the basicity of the anion and unlike PF_6^-, BF_4^- offers the added advantage of lower sensitivities to hydrolysis.

In addition to solubility, non- coordinating property and lower sensitivity to hydrolysis, the relatively less symmetrical structure of tetrafluoroborate anion than PF_6^- and the previously used Tf_2N^- anion in phenanthrolinium ILs, together with mismatch between the sizes of the phenanthrolinium cation and the tetrafluoroborate anion might result in inefficiency of ion packing and give lower melting salts than its I^-,Br^-,Tf_2N and PF_6^- containing analogues reported so far. [9] Obtaining low melting ionic liquids can avoid the need to heat the salts to higher temperature to obtain a melt and dissolve catalyst complexes and substrates in it.

However, even if the synthesis of water miscible phenanthrolinium based ILs may be possible, commonly used synthetic procedures are very expensive and technically very difficult (section – 1.1). Hence the invention of simple anion metathesis procedure that may resolve this problem and can avoid the long reaction time required for the synthesis of water miscible BF_4^- based ILs so far, improve yield and diminish or eliminate the utilization of environment polluting VOCs in the overall process remains very important.

1.7 RESEARCH AIMS

Recent work done in our laboratory has opened 1, 10-phenanthroline based chemistry a way to the ionic liquid media. It was shown that water immiscible 1, 10-phenanthrolinium based ILs can be synthesised using the same synthetic route as for commonly used ILs (Section 1.1) and are able to solubilise and stabilise 1,10-phenanthroline based complexes, providing the possibility to conduct 1,10-phenanthroline based chemistry in an IL media. It is expected that applications such as catalysis and nanoparticle synthesis, which have been hindered by the poor solvation abilities towards metallic complexes of commonly used ILs, should find in this media a more successful approach. [10]

In view of enhancing the application of phenanthrolinium based ILs, this research aims to explore the synthesis of a new series of ILs based on N-alkyl-phenanthrolinium cation with tetrafluoroborate anion. Tetrafluoroborate anion was chosen because its typical properties (section 1.5) offer distinctive advantages when the constituting ILs are applied in catalysis. If the synthesis is possible, the potential of the new $[C_nPhen]BF_4^-$ ILs will be assessed by testing their dissolution ability for phenanthroline based metal complexes. Different ILs with different chain lengths will be synthesized in order to understand their influence in the observed melting points and their solubility for various organic solvents. This study also aims to devise a more efficient anion metathesis procedure for the synthesis of water miscible N-alkyl-phenanthrolinium tetrafluoroborate ILs than the conventional one.

2. EXPERIMENTAL

2.1 Materials

The N-alkyl-1,10-phenanthrolinium bromide salts were synthesized as previously described. [17] Water was removed from phenanthroline hydrate by heating for two hours in an oven (80°C) and the acetonitrile used for the quaternization and metathesis reaction had been dried by using sodium sulphate, Na_2SO_4.

2.2 Analytical techniques

2.2.1 Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker 400 Ultra-Shield NMR with operating frequencies 400 MHz (^1H) and 100.6 MHz (^{13}C). Chemical shifts (δ) are reported in parts per million (ppm) with reference to residual traces in the commercial deutrated solvents of protonated dimethyl sulfoxide (δ_H 2.54) and $(CD_3)_2SO$ (δ_C 40.45) and protonated chloroform (δ_H 7.26) and $CDCl_3$ (δ_C 77.16±0.06) at ambient temperature. Coupling constants (*J*) are given in Hz. The melting points of the ILs were determined by *Stuart SMP3* melting point apparatus.

2.2.2 Halide test

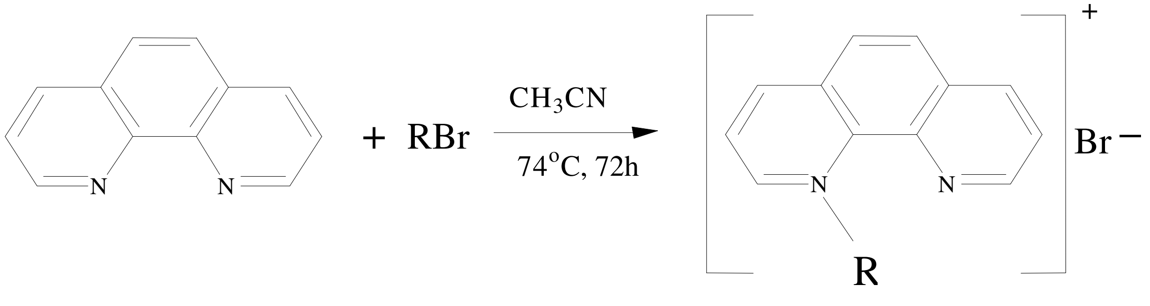
After metathesis of [C_nPhen]Br and $NaBF_4$ and extraction [C_nPhen]BF_4, the presence of halide impurities in the halide free salts was checked by testing a solution of the salt with few drops of $AgNO_3$.

2.2.3 Solubility test

The solubilities of the ILs in a range of solvents were determined by taking small amount of the new salts in a vial and adding the solvents (table 3). The salts that dissolved only after slightly heating are reported as sparingly soluble. The solvent ability of the ILs for phenanthroline and phenanthroline – metal complexes were determined by choosing the lowest melting and lower alkyl side chain containing IL as a model and heating the ionic liquid to its melting point and then adding slight amount of the solute into the melt until the solution became saturated.

2.3 Synthesis of N-alkyl-1,10-phenanthrolinium bromide ([C_nPhen]Br)

All the N-alkylphenanthrolinium bromide salts were synthesized by a similar procedure. 1-bromooalkane (RBr), with R being a straight chain alkyl ranging from ethyl to dodecyl, and 1, 10-phenanthroline (1.25 : 1) in acetonitrile were stirred for 72 hours in a round bottom flask reflux condenser experimental setup and heated for 72 hours. The resulting liquid is cooled to room temperature; the solvent was evaporated using a rotary evaporator and the product was thoroughly washed with acetone to afford N-alkylphenanthrolinium bromide salt (Scheme 1). All the salts were obtained in a yield of about 87%.



R= C_nH_{2n+1}, n = 2, 3, 4, 5, 6, 8, 12

Scheme 1 Quaternization reaction of 1,10-phenanthroline with alkyl bromide

[C_2Phen]Br

^{1}H NMR (400 MHz, DMSO) δ 9.72 (d, *J* = 6.0 Hz, 1H), 9.41 (d, *J* = 8.2 Hz, 1H), 9.32 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.81 (d, *J* = 1.8 Hz, 1H), 8.79 (d, *J* = 1.8 Hz, 1H), 8.45 (d, *J* = 6.4 Hz, 1H), 8.41 (d, *J* = 6.4 Hz, 2H), 8.06 (dd, *J* = 8.2, 4.3 Hz, 1H), 5.96 (q, *J* = 7.0 Hz, 2H), 1.71 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.24, 150.54, 147.41, 140.06, 138.37, 136.98, 133.03, 132.12, 131.00, 127.57, 125.81, 125.20, 31.13, 17.31

[C_3Phen]Br

^{1}H NMR (400 MHz, DMSO) δ 9.74 (d, *J* = 4.5 Hz, 1H), 9.46 (d, *J* = 8.2 Hz, 1H), 9.30 (dd, *J* = 5.6, 3.8 Hz, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.51 – 8.39 (m, 3H), 8.10 – 8.00 (m, 1H), 5.92 – 5.79 (m, 2H), 2.05 (tq, *J* = 14.9, 7.5 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.31, 150.52, 147.51, 140.04, 138.37, 136.85, 133.05, 132.09, 131.00, 127.58, 125.79, 125.00, 65.01, 39.54, 24.93, 10.92.

[C_4Phen]Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (d, *J* = 9.3 Hz, 1H), 9.66 (d, *J* = 6.9 Hz, 1H), 9.30 (dd, *J* = 4.3,1.1 Hz, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.51 – 8.39 (m, 3H), 8.09 – 8.01 (m, 1H), 5.92 – 5.76 (m, 2H), 2.05 (dd, *J* = 18.1, 7.5 Hz, 2H), 1.57 (tq, *J* = 17.68, 5.89, 2H) 1.06 (t, *J* = 5.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.42, 150.12, 147.43, 140.00, 138.34, 135.81, 123.22, 121.89, 78.70, 78.37, 78.05, 48.84, 36.03, 31.41, 18.61, 12.86.

[C_5Phen]Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, *J* = 5.8 Hz, 1H), 9.47 (d, *J* = 8.2 Hz, 1H), 9.22 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 5.9 Hz, 1H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.92 (dd, *J* = 8.2, 4.3 Hz, 1H), 6.32 – 6.10 (m, 2H), 2.12 (tq, *J* = 16.1, 8.0 Hz, 2H), 1.68 – 1.51 (m, 2H), 1.52 – 1.25 (m, 2H), 0.89 (dd, *J* = 10.1, 4.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.88, 149.79, 147.07, 137.84, 132.85, 132.08, 130.98, 127.52, 125.30, 77.42, 77.10, 76.78, 64.59, 31.74, 28.41, 22.24, 13.98.

[C_6Phen]Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (d, *J* = 9.3 Hz, 1H), 9.46 (d, *J* = 6.9 Hz, 1H), 9.28 (dd, *J* = 4.3, 2.3 Hz, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 8.53 – 8.33 (m, 3H), 8.26 – 8.17 (m, 1H), 6.12 – 6.00 (m, 2H), 3.43 (s, 2H), 2.05 (dd, *J* = 18.1, 7.5 Hz, 2H), 1.58 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.46 – 1.23 (m, 2H) 1.06 (t, *J* = 5.7 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.21, 149.80, 147.24, 139.93, 137.87, 136.63, 132.95, 132.11, 131.07, 127.43, 125.36, 125.19, 64.80, 31.93, 31.23, 25.98, 22.47, 13.97.

[C_8Phen]Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (d, *J* = 5.8 Hz, 1H), 9.47 (d, *J* = 8.1 Hz, 1H), 9.10 (d, *J* = 4.0 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.37 (t, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.81 (m, 1H), 6.18 – 6.00 (m, 2H), 2.52 (s, 1H), 1.97 (d, *J* = 7.1 Hz, 2H), 1.68 – 1.24 (m, 2H), 1.24 (s, 2H), 1.29 – 0.99 (m, 8H), 0.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46, 149.70, 147.20, 139.79, 137.94, 136.44, 132.81, 132.06, 131.05, 127.45, 125.36, 124.96, 77.66, 77.34, 77.02, 64.43, 31.97, 31.59, 29.04, 29.01, 26.23, 22.47, 13.99.

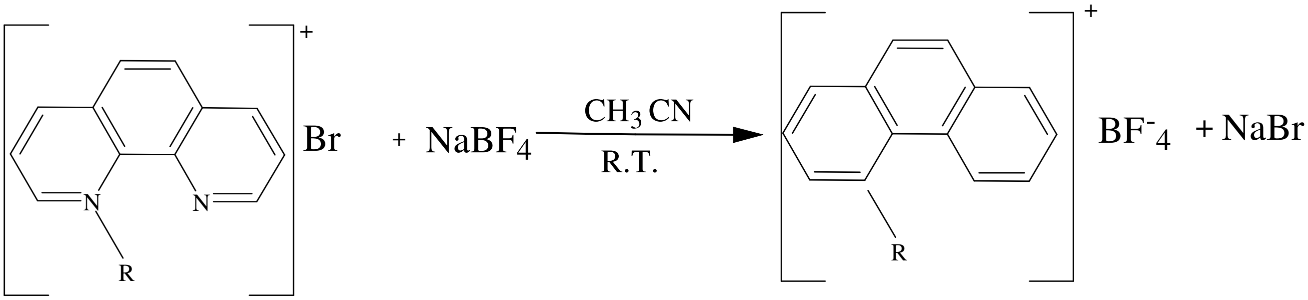
[C_{12}Phen]Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (d, *J* = 5.9 Hz, 1H), 9.45 (d, *J* = 8.3 Hz, 1H), 9.21 (d, *J* = 4.2 Hz, 1H), 8.65 – 8.47 (m, 2H), 8.39 (d, *J* = 8.7 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 7.98 – 7.82 (m, 1H), 7.29 (s, 1H), 6.16 (t, *J* = 7.0 Hz, 2H), 2.22 (s, 2H), 2.12 (d, *J* = 4.6 Hz, 2H), 1.66 – 1.51 (m, 2H), 1.41 – 1.34 (m, 2H), 1.21 (s, 14H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.05 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.84, 149.75, 147.05, 140.03, 137.83, 136.57, 132.84, 132.06, 130.95, 127.52, 125.40, 125.27, 64.66, 32.09, 31.87, 29.61, 29.54, 29.48, 2.31, 29.21, 26.36, 22.66, 14.13, 1.01.

2.4 Anion metathesis: Synthesis of N-alkylphenanthrolinium tetrafluoroborate; $[C_nPhen]BF_4$ ILs

The anion metathesis was first tested by the same procedure as reported in the literature. [11] To a solution of $[C_5Phen]Br$ in acetonitrile, a finely ground powder of $NaBF_4$ (1:1.5) was added and the mixture was stirred for 48 hours in a round bottom flask at 35^oC. The solution was then cooled to allow the NaBr byproduct and unreacted $NaBF_4$ to be deposited at the bottom of the flask and the solution containing the ionic liquid was separated by simple decantation. Then the solvent was removed by a rotary evaporator and the ionic liquid product was purified by dissolving in dichloromethane and thoroughly washing with water until the wash solution became halide free.



R= R= $C_nH_{2n+1,}$ n = 5

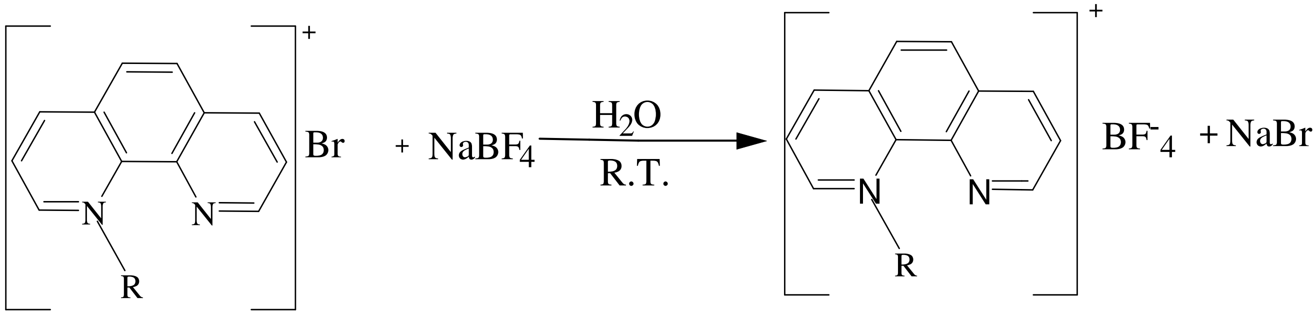
Scheme 2: Anion metathesis between $[C_5Phen]Br$ and $NaBF_4$ in acetonitrile

$[C_5Phen]BF_4$ was isolated in a yield of 45%. ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 6.0 Hz, 1H), 9.28 – 9.15 (m, 2H), 8.57 (d, *J* = 10.0 Hz, 1H), 8.38 – 8.30 (m, 1H), 8.27 – 8.15 (m, 2H), 7.92 (d, *J* = 14.1 Hz, 1H), 7.28 (s, 2H), 6.04 – 5.92 (m, 2H), 2.10 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.98 (s, 4H), 1.54 (dt, *J* = 14.6, 7.3 Hz, 2H), 1.39 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.93 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.30, 150.51, 147.51, 138.36, 131.01, 127.58, 125.79, 125.00, 65.01, 31.16, 24.93, 10.92.

Secondly, a new and simple anion metathesis procedure was developed and used to synthesize the water miscible ILs:

A solution of the phenanthrolinium halide salt obtained from procedures shown in Section 2.3 in water was added to $NaBF_4$ aqueous solution in a round bottom flask (1:1.5). After stirring the mixture thoroughly for few minutes at room temperature to get both the starting materials dissolved, the water was slowly removed by a rotary evaporator. The solid mixture was then dissolved in acetone and the insoluble NaBr by-product and any unreacted starting materials were separated out by filtration to yield a solution consisting of only the IL product from which acetone was removed by a rotary evaporator to afford the pure halide free salt. (Scheme 2) All the [C_nPhen]BF_4 salts were isolated in a yield of greater than 98%.



R= C_nH_{2n+1}, n = 2, 3, 4, 5, 6, 8, 12

Scheme 3 Anion metathesis between [C_nPhen]Br and $NaBF_4$ in water

[C_2Phen]BF_4

^{1}H NMR (400 MHz, DMSO) δ ppm 9.628 (d, 1H), 9.379 (d, 1H), 9.328 (dd, 1H), 8.803 (dd, 1H), 8.433 (m, 3H), 8.088 (dd, 1H), 6.00(q, 2H), 1.721 (t, 3H).

^{13}C NMR δ_C (100.6 MHz, *DMSO, d_6)*. δ ppm151.23, 150.52, 147.43, 140.06, 138.37, 136.98, 133.03, 132.12, 131.00, 127.57, 125.81, 125.20, 31.13, 17.31

[C_3Phen]BF_4

^{1}H NMR (400 MHz, DMSO) δ 9.67 (d, J = 6.0 Hz, 1H), 9.42 (d, J = 8.3 Hz, 1H), 9.32 (d, J = 2.4 Hz, 1H), 8.79 (d, J = 8.2 Hz, 1H), 8.47 – 8.44 (m, 1H), 8.41 (d, J = 4.9 Hz, 2H), 8.08 – 8.03 (m, 1H), 5.87 – 5.81 (m, 2H), 2.51 (s, 1H), 2.11 – 1.96 (m, 4H), 1.07 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.31, 150.52, 147.51, 140.04, 138.37, 136.85, 133.05, 132.09, 131.00, 127.58, 125.79, 125.00, 65.01, 40.58, 40.37, 40.16, 39.95, 39.74, 39.54, 39.33, 31.17, 24.93, 10.92.

[C_4Phen]BF_4

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 5.8 Hz, 1H), 9.32 – 9.17 (m, 196H), 8.57 (d, *J* = 8.2 Hz, 98H), 8.35 (t, *J* = 7.1 Hz, 99H), 8.23 (q, *J* = 8.7 Hz, 196H), 8.13 (s, 5H), 7.91 (dd, *J* = 8.0, 4.1 Hz, 98H), 7.28 (s, 16H), 6.10 – 5.96 (m, 196H), 4.21 (s, 3H), 2.21 (t, *J* = 21.9 Hz, 114H), 2.15 – 1.99 (m, 199H), 1.72 – 1.49 (m, 203H), 1.31 (s, 9H), 1.25 (s, 6H), 0.95 (dt, *J* = 31.2, 7.3 Hz, 310H), 0.07 (s, 44H), -0.01 (s, 11H).

^{13}C NMR (101 MHz, DMSO) δ 150.89, 149.84, 147.35, 139.82, 137.90, 136.64, 132.99, 132.12, 131.14, 127.34, 125.44, 125.01, 64.61, 33.76, 30.95, 19.59, 13.62.

[C_6Phen]BF_4

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, *J* = 5.9 Hz, 1H), 9.31 (d, *J* = 10.6 Hz, 1H), 9.21 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.58 (d, *J* = 8.2, 1H), 8.51 – 8.38 (m, 1H), 8.27 (d, *J* = 25.6, 1H), 8.22 (d, *J* = 8.2, 1H), 7.81 (m, 1H), 6.12 – 6.00 (m, 2H), 2.33 – 2.01 (m, 2H), 1.58 (tt, *J* = 15.2, 7.5 Hz, 2H), 1.46 – 1.23 (m, 4H), 0.89 (q, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.21, 149.80, 147.24, 139.93, 137.87, 136.63, 132.95, 132.11, 131.07, 127.43, 125.36, 125.19, 64.80, 31.93, 31.23, 25.98, 22.47, 13.97.

[C_8Phen]BF_4

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 6.0 Hz, 7H), 9.28 – 9.19 (m, 14H), 8.56 (dd, *J* = 8.2, 1.8 Hz, 7H), 8.38 (dd, *J* = 8.2, 5.9 Hz, 7H), 8.29 – 8.18 (m, 14H), 7.92 (ddd, *J* = 8.2, 4.3, 0.8 Hz, 7H), 7.28 (d, *J* = 0.9 Hz, 4H), 6.08 – 5.95 (m, 14H), 4.23 (s, 1H), 2.27 – 2.05 (m, 49H), 1.74 (d, *J* = 0.8 Hz, 8H), 1.59 (dt, *J* = 15.2, 7.5 Hz, 14H), 1.39 (d, *J* = 7.2 Hz, 13H), 1.32 (d, *J* = 35.6 Hz, 48H), 0.99 – 0.81 (m, 23H), 0.11 – 0.05 (m, 14H), 0.01 (d, *J* = 0.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46, 149.70, 147.20, 139.79, 137.94, 136.44, 132.81, 132.06, 131.05, 127.45, 125.36, 124.96, 77.66, 77.34, 77.02, 64.43, 31.97, 31.59, 29.04, 29.01, 26.23, 22.47, 13.99.

[C_{12}Phen]BF_4

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 5.9 Hz, 1H), 9.30 (d, *J* = 8.1 Hz, 1H), 9.22 (d, *J* = 4.2 Hz, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 8.48 – 8.37 (m, 1H), 8.26 (dd, *J* = 23.2, 8.7 Hz, 2H), 7.92 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.28 (s, 2H), 6.13 – 5.99 (m, 2H), 2.21 – 2.02 (m, 2H), 1.93 (s, 1H), 1.70 – 1.50 (m, 2H), 1.31 (d, *J* = 59.9 Hz, 1.51H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.18, 149.76, 147.27, 139.97, 137.85, 132.98, 132.11, 131.04, 127.46, 125.32, 125.22, 77.39, 77.07, 76.75, 64.86, 32.02, 31.89, 30.97, 29.62, 29.55, 29.49, 29.33, 29.17, 26.35, 22.67, 14.13.

3. RESULTS AND DISCUSSION

3.1 **The new synthetic route**

In the present work a new and simple anion metathesis procedure was developed to synthesize a series of new water miscible N-alkylphenanthrolinium tetrafluoroborate based ILs starting from N-alkylphenanthrolinium bromide salt and sodium tetrafluoroborate, $NaBF_4$. N-alkyl-1,10-phenanthrolinium bromide salt and sodium tetrafluoroborate, $NaBF_4$, were dissolved in water and thoroughly stirred at room temperature for few minutes. This way all starting materials are solubilised in the reaction media. While in solution only hydrated ions exist and ion pairs start to form when the solution is concentrated by slowly removing water under reduced pressure. Which ions form a pair can be determined by Pearson’s hard and soft acid base theory, in which the terms 'hard' ('Hard' applies to species which are small, have high charge states and are weakly polarizable) or 'soft' ('Soft' applies to species which are big, have low charge states and are strongly polarizable), and 'acid' or 'base' are assigned to chemical species. Pearson’s hard and soft acid base theory states that *hard* acids bind to *hard* bases to give charge-controlled (ionic) complexes. Such interactions are dominated by the +/– charges on the Lewis acid and Lewis base species. *Soft* acids bind to *soft* bases to give FMO-controlled (covalent) complexes. These interactions are dominated by the energies of the participating frontier molecular orbitals (FMO), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In our case the difference in the relative energies and symmetry of the frontier orbitals are very large and the interaction between the ions is thus dominated by charge/charge effects.

Hence, with removing water from the solution the harder acid Na^+ binds with the harder base Br^- and the relatively softer BF_4^- will pair with the softer phenanthrolinium cation. Thus by dissolving the mixture obtained after complete removal of water with a solvent in which any of unreacted starting materials and the NaBr by-product do not dissolve, a solution of only the halide free salt was obtained. The solvent was then removed in a rotary evaporator yielding a pure $[C_nPhen]BF_4$ salt.

Comparison of the anion metathesis procedure used for the first time here with the conventional procedures so far used for the synthesis of water miscible BF_4^- containing ILs (table 1) reveals remarkable improvement in the methodology with respect to economics of preparation, environmental impact and cumulative energy demand.

As it can be observed from table 1, the maximum of 60% product yield obtained with the previously established procedures has been improved to almost quantitative amount of greater than 98% with this procedure, while the 48 hours of reaction time was cut down to 10 minutes. In addition, in the conventional procedures organic solvents are used for anion metathesis and extensive washing with excess of a solvent is required to obtain a pure product which is associated with significant product loss into the washing phase, while only water was used as a solvent and only a small amount of acetone was used to separate the IL product from the insoluble NaBr.

Since product yield, reaction time and solvents are important elements of the economics of IL synthesis, the improvements achieved by the new synthetic route in these aspects, including usage of the cheaper water than organic solvents, make the new synthetic route economically less demanding.

Cumulative energy demand (CED) takes into account the supply of raw materials, the energies required for heating, stirring, pumping and providing cooling water. Our synthetic procedure requires shorter stirring time and no heating represent lower overall energy demand for the synthesis.

Even though attempts are yet being made to quantify the greenness of a chemical process, the environmental impact of a chemical reaction can be estimated by qualitatively examining variables such as chemical yield, energy profile, ease of product workup and purification, the price of reaction components, the use of safe, environment-benign substances, including solvents as regards the twelve principles of green chemistry. Hence the utilization of water as a solvent and only a small amount of acetone for product extraction instead of a large excess of organic solvents, quantitative amount of product yield instead of a maximum of 60%, low reaction times 10 minutes instead of 48 hours and lower energy demand in the present synthetic route than in the conventional procedures (table 1) defines our synthetic route as a much greener alternative.

Cation source	Anion source	solvent	Reaction time	Yield	Temp.	Reference	Remark
[BMIM]Br	$AgBF_4$	MeOH	-	-	r.t.	7	-Section 1.1
[1-C_nMIM]Br	$NaBF_4$	acetone	48hrs	60%	30 -40^{o}C	11	-Insoluble anion source
[C_nPhen]Br	$NaBF_4$	H_2O	10 minutes	>98%	r.t.	This research	

Table 1: comparison of reaction time, yield and solvent used for different anion metathesis reactions

3.2 Characterization analysis.

Due to symmetry of structural environments there will obviously be only four peaks (corresponding to Ha, Hb, Hc and Hd in figure 4) in the ^{1}HNMR spectra of phenanthroline, the starting material for the quaternization reaction. But after alkylating one of the heterocyclic nitrogen atoms the symmetry was lost and gave rise to eight sharp phenanthrolinium proton peaks to the left of the spectrum with characteristic chemical shifts of protons of aromatic rings and based on proximity to the electronegative nitrogen atoms (Figure 5). Additional $-CH_2-$ protons of the alkyl side chain carbon directly attached to the nitrogen atom appeared close to the phenanthrolinium proton peaks towards the right. While the rest of the alkyl chain protons, not being directly attached to an electronegative element or part of an aromatic ring, and appeared at the right of the spectrum in order of their proximity to the heterocyclic nitrogen atom.

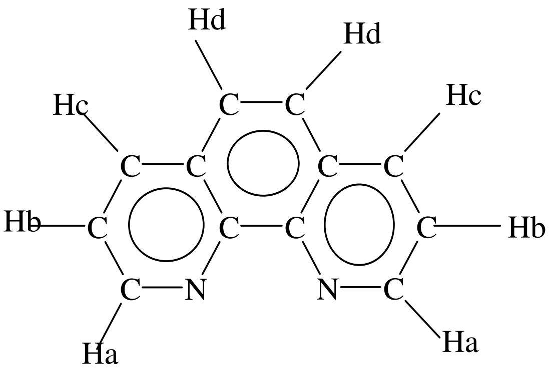


Figure 7: Symmetric protons of 1,10-phenanthroline molecule

^{13}C and DEPT spectrum of the salts were also analysed and the positions of the signals indicated the individual structural environments of each carbon further confirming the proposed quaternization and metathesis product (Figure 6, Figure 7, Figure 9, Figure 10). In the ^{13}C NMR spectra twelve signals are clustered around the 125-155ppm region, with typical down field shifts for carbons according to their position and proximity to the electronegative nitrogen atoms; carbon nuclei ortho and para to the electronegative nitrogen being more deshielded. The alkyl side chain carbon directly attached to the heterocyclic nitrogen atom appeared around the middle of the spectrum (around 65ppm) whilst the carbon of the rest of alkyl chains, not being attached to an electronegative element or part of an aromatic ring, appeared at the right of the spectrum. DEPT spectra have further supported the proposal indicating the exact position of the carbons with even and odd number of protons.

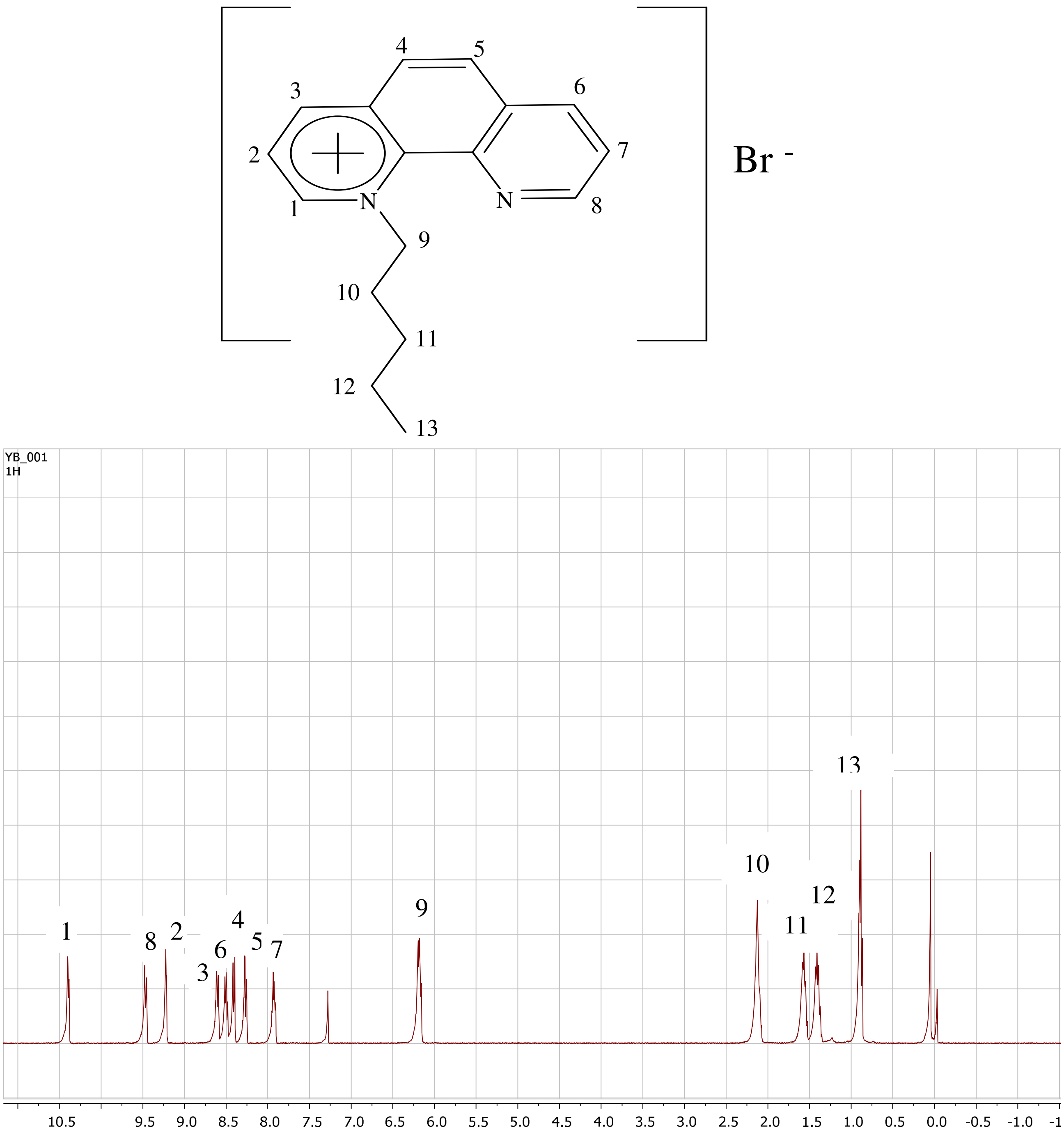
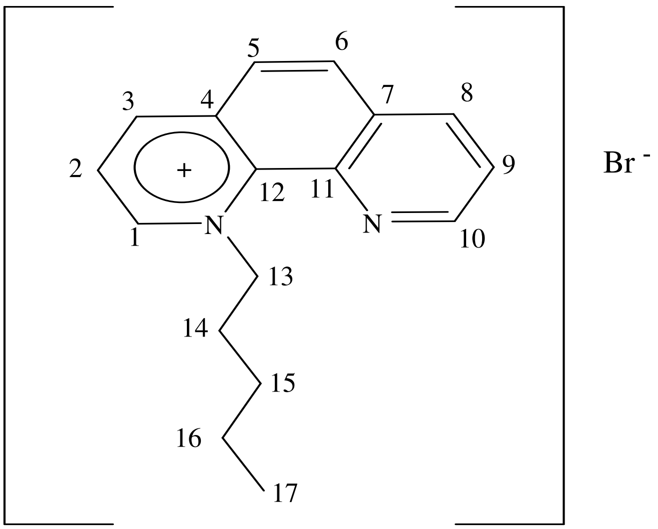


Figure 8: ^{1}HNMR spectra of [C_5Phen]Br



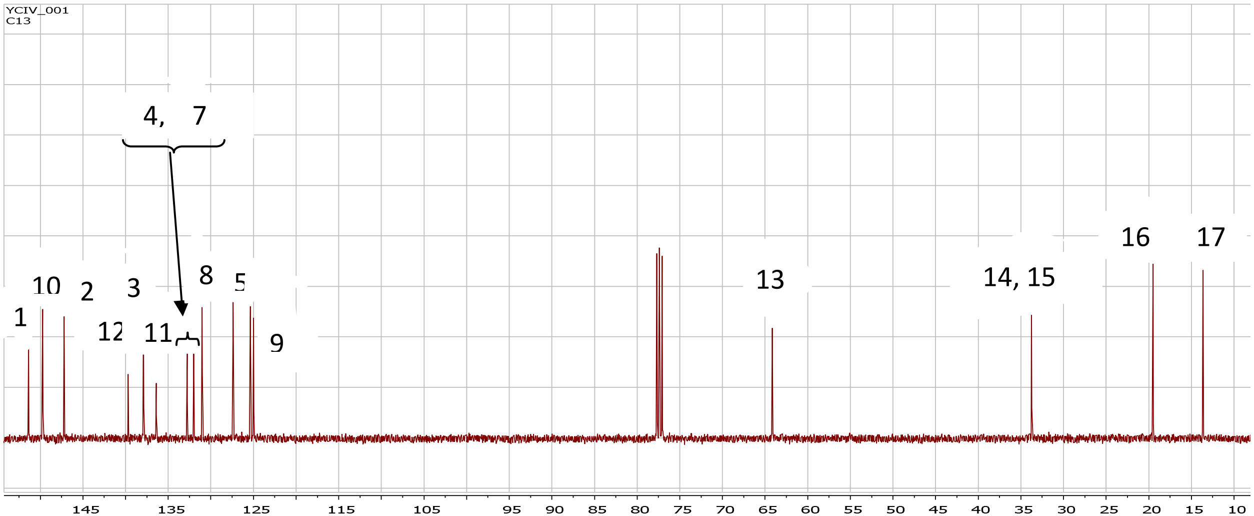


Figure 9: ^{13}C NMR spectra of [C$_5$Phen]Br

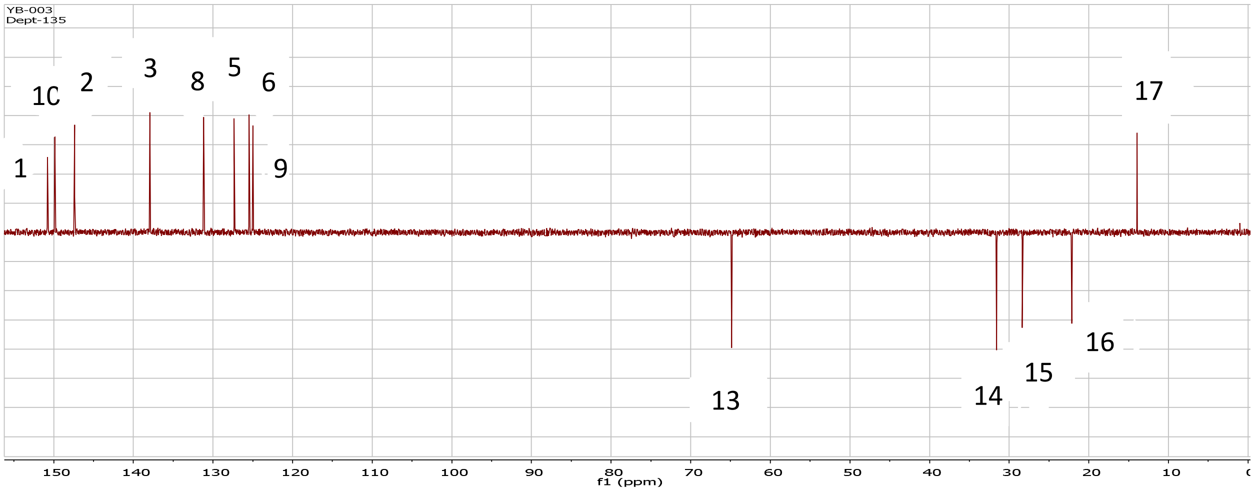
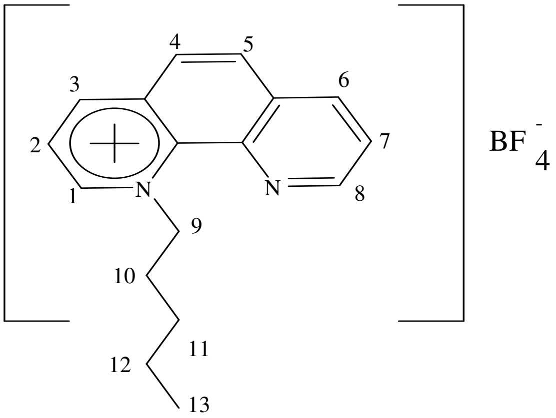


Figure 10: DEPT NMR spectra of [C$_5$Phen]Br

Comparison of ^{1}H NMR chemical shifts of [C$_n$Phen]Br and the metathesis product [C$_n$Phen]BF$_4$ salts have shown an up field shifts of ^{1}H NMR spectra of the latter (Figure 8 and Figure 11) which is in accordance with the fact that anion-dependent differential ^{1}H NMR shifts are a direct measure of the strength of hydrogen bonding with the anion. [22] Thus fluorine of the tetrafluoroborate anion has a higher hydrogen bonding ability than the bromine atom and hence shields the proton more and causes the proton to resonate up field.



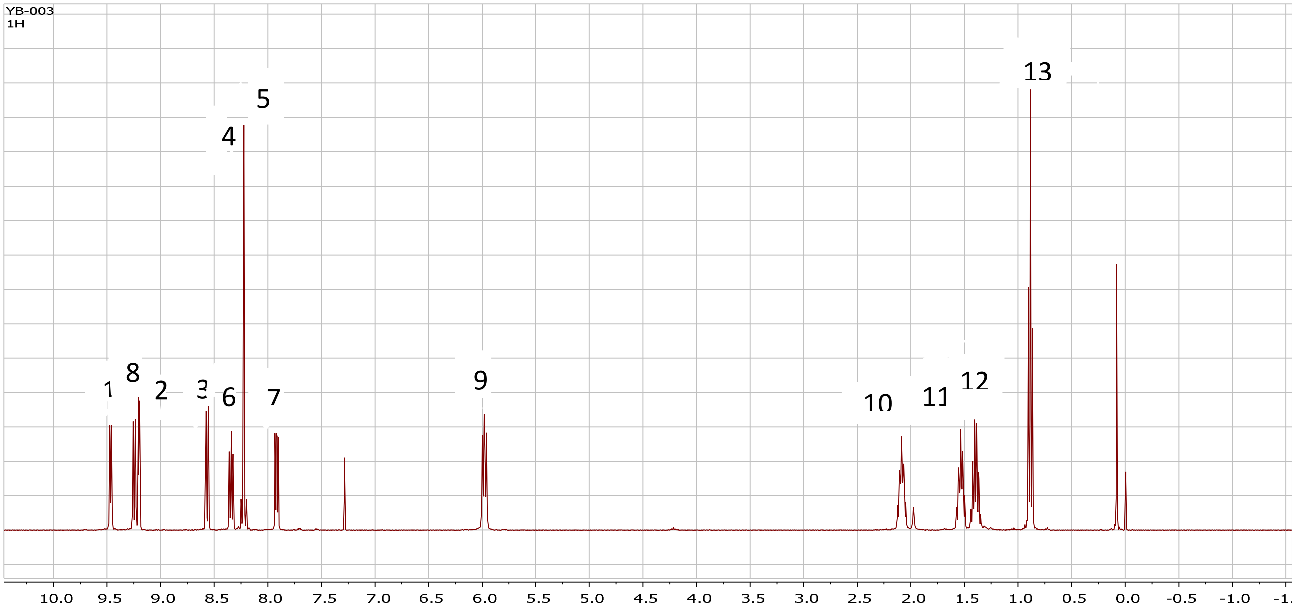
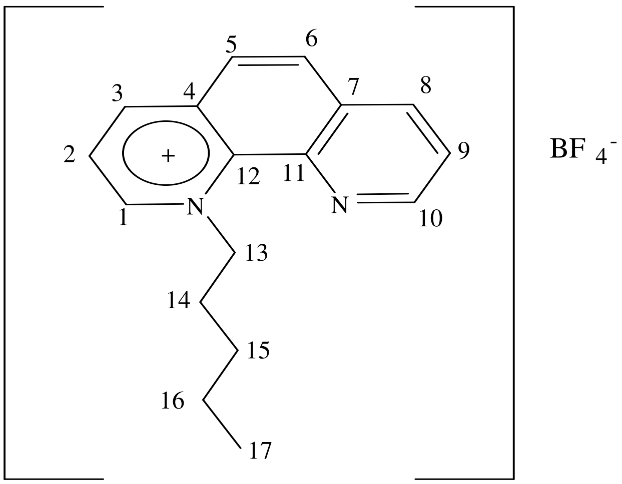


Figure 11: ^{1}HNMR spectra of [C$_5$Phen]BF$_4$

The proton that underwent greater shift is the one next to the positive, alkyl substituted nitrogen (the proton on carbon number 1) (Figure 5and Figure 8). This is probably due to the fact that the preferred position for H-bonding by both the anions is next to the most acidic proton [23] and difference in H-bonding ability of the anions mostly affected the chemical shift of this proton. Comparisons of ^{13}C NMR of the salts indicate that the anion identity has no significant effect on the chemical shifts of the carbon atoms.



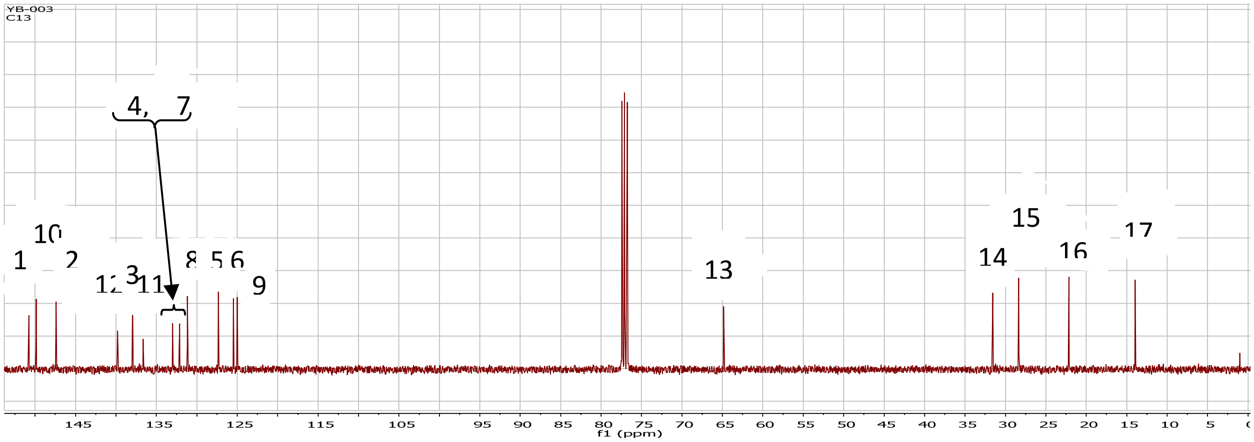


Figure 12: ^{13}C NMR spectra of $[C_5Phen]BF_4$

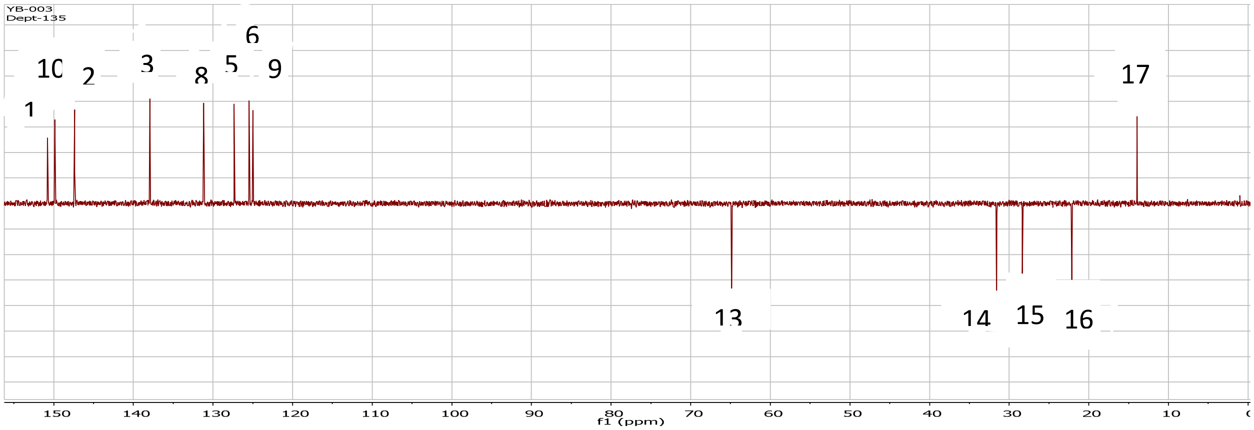


Figure 13: DEPT spectra of $[C_5Phen]BF_4$

3.2.1 Ion interactions/polarity

^{1}H NMR and ^{13}C NMR analyses of the ILs were carried out in DMSO and $CDCl_3$. No significant difference in proton chemical shifts of ^{1}H NMR spectra of both the halide and BF_4^- based ILs was seen when the analysis was carried out in DMSO as NMR solvent. But significant shifts in proton chemical shift with changing the bromide by tetrafluoroborate anion were seen when analysed in $CDCl_3$. This indicates that both the halide and BF_4^- based ILs are less polar than DMSO and more polar than $CDCl_3$. From this observation it can be deduced that dominant ion-ion interaction exists in $CDCl_3$ solution of the ILs while solvent – ion interaction dominates over ion – ion interaction in DMSO solution. Hence, anion dependent chemical shifts could only be seen in the former solvent and consequently the rest of NMR analyses were carried out in $CDCl_3$. Since the deutrated NMR solvents can also have effect on the chemical shifts of even more polar salts, the NMR study of the starting salt and the desired IL should be carried out in the same solvent so that solvent effect will remain constant and only the effect of anion identity could be examined.

3.2.2 Melting points

The melting points of the phenanthrolinium ILs with a series of alkyl side chains ranging from ethyl to dodecyl and with the anions BF_4^- were determined and compared to the starting material [C_nPhen]Br and the previously synthesized [C_nPhen]PF_6 and [C_nPhen][Tf_2N] salts (table 2). The results revealed that all the new BF_4^- containing ILs exhibit lower melting points than their Br^- containing precursors. This is supposed to be due to the relatively less symmetrical tetrahedral structure of BF_4^- than Br^-, which introduces inefficiency of ion packing and delocalization of the negative charge over four atoms and consequent reduction of Coulombic force.

In comparison to the melting points of the previously synthesised PF_6^- and Tf_2N^- containing salts, the new salts exhibited lower melting points than all of the PF_6^- containing except for pentyl and octyl substituted ones and this can be attributed to the lower structural symmetry of the BF_4^- anion than the two anions.

The melting point gets lower with going from ethyl to propyl substituent than [C_nPhen]Tf_2N^- and remains higher for higher alkyl containing salts. This may be attributed to the relative size of the ions which also affects the packing efficiency. With going from ethyl to propyl substituent, the size of the ions would become comparable and the resulting increased structural matching between the N-alkylphenanthrolinium cation and Tf_2N^- might have produced improved ion packing and consequent increase in melting point. Further increase in alkyl chain size might have resulted deviation from this structural matching and symmetry breaking leading to destabilization of Coulombic packing and consequent reduction of melting point.

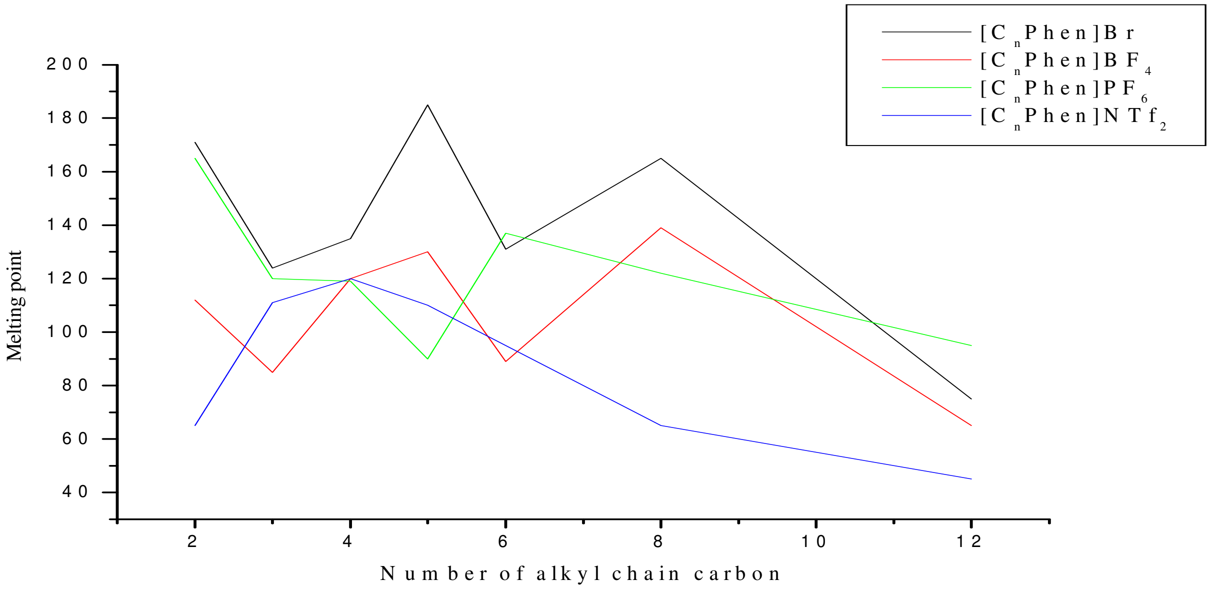


Figure 14: Melting point vs. number of alkyl chain carbon of $[C_nPhen]X$ (X= Br^-, BF_4^- , PF_6^- and Tf_2N^-)

Concerning the melting point change with alkyl chain, both BF_4^- and Br^- containing ILs manifested similar trends (figure 12) the melting points of the salts containing both the anions decreased with increase in alkyl chain from ethyl to propyl and increased with further increase from propyl to pentyl. It decreased with increasing the alkyl chain to hexyl and then increased with going from hexyl to octyl, then continually decreased with going from octyl to dodecyl. The similarity of melting point changes with number of alkyl chain carbon for both BF_4^- and Br^- containing ILs suggests that the effect of alkyl chain on melting point, for these class of salts, is independent of the anion identity.

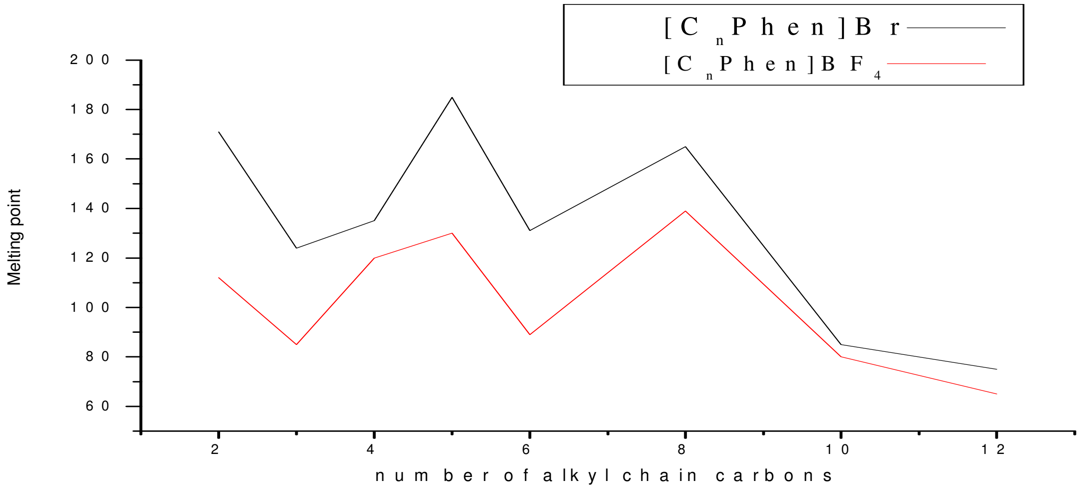


Figure 12: Melting point vs. number of alkyl chain carbon of [C_nPhen]X (X= Br^- and BF_4^-), illustrating the effects of alkyl side chain and anion identity on melting point.

Anion / Alkyl Chain(C_n)	Br^-	BF_4^-	PF_6^-	Tf_2N^-
C_2	171	112	165	65
C_3	124	85	120	111
C_4	135	120	119	120
C_5	185	130	90	110
C_6	131	89	137	95
C_8	165	139	122	65
C_{12}	75	65	95	45

Table 2: [N-alkylphen]X Salts and melting points, illustrating effect of alkyl chain and anion identity

Even though melting point change with simple changes in single alkyl-chain substituent were rationalized in terms of the melting points for the organic side chains, which depend in general on the arrangement of atoms in the crystal lattice as well as on pair wise interactions which highlights that initial lengthening of alkyl side chain until some point leads to reduction in the melting points through destabilization of columbic packing and further increase in substitution causes reemergence of high melting point owing to increased attractive Van der Waals force between the hydrocarbon side chains and increased structural ordering (Figure 1), the irregular melting point trend obtained for phenanthrolinium based ILs indicates that the interplay of forces that contribute to the melting point of ILs is so intricate and can result in trends inconsistent to that expected based on the melting points for the organic side chains. Thus accurate and precise explanation of IL's melting point warrants the development of stronger simulation methodologies and computing power to enable sophisticated and accurate molecular simulations to be carried out on these materials.

3.2.3 **Solubility of metal complexes**

The solvent ability of the ILs were measured by dissolving a known amount of $[Ni(Phen)_2(OH_2)_2]Cl_2$, $[Ni(Phen)(OH_2)Cl_2]$ and phenanthroline in a known amount of $[C_3Phen]BF_4$ respectively. The result (table 4) disclosed that in spite of the longer alkyl chain, which may increase the viscosity of the IL and lower solubility, the new IL $[C_3Phen]BF_4$ exhibited comparable solubility for $[Ni(Phen)_2(OH_2)]Cl_2$ to $[C_1Phen]Tf_2N$. But unlike $[C_1Phen]Tf_2N$, the former dissolved over 20% of $[Ni(Phen)(OH_2)Cl_2]$, which $[C_1Phen]Tf_2N$ was totally unable to dissolve. From this observation it can be concluded that the new $[C_3Phen]BF_4$ ILs are better potential solvents for a wider range of phenanthrolinium – metal complexes than its Tf_2N^- containing analogue. The higher solvation ability of the new IL can be regarded to be caused by the anion. Besides the $\pi - \pi$ interaction between the IL cation and the metal complex ligands, another contribution may come up from Coulomb interactions of the metal complex cation with the anion of the ionic liquid. The smaller BF_4^- anion leads to stronger electrostatic interaction than Tf_2N^- and this can result in enhanced solubility of the metal complex.

Compound → IL ↓	1,10-phenanthroline	[Ni(Phen)(H_2O)Cl]Cl	[Ni(Phen)2(H_2O)]Cl
[C_1C_4im]BF_4	≈ 0[9]	≈ 0[9]	≈ 0[9]
[C_1C_4im]PF_6	≈ 0[9]	≈ 0[9]	≈ 0[9]
[C_1Phen]NTf_2	>100	≈ 0	> 50 [9]
[C_3Phen]BF_4	>100	> 20	> 48

Table 3: Solubility in %wt/wt of phenanthrolinium metal complexes in [C_3Phen]BF_4, [C_1Phen]NTf_2, [C_1C_4im]PF_6 and [C_1C_4im]BF_4 ILs.

3.2.4 **Solubility tests**

Solubility of all the salts were tested in various solvents and the result is summarized in the table below (table 3). This result revealed that [C_nPhen]BF_4 ILs are soluble in larger number of organic solvents than their [C_nPhen]X (X=Br^-,) analogues, which provides flexibility for application of this ([C_nPhen]BF_4) ILs for a larger number of reaction and separation schemes. Among the solvents tested, all the BF_4^- containing ILs were found to be readily soluble in dimethylsulphoxide, chloroform, acetonitrile, methanol and ethanol, while varying solubility with alkyl chain was seen in 1, 4-dioxane, toluene and n – heptane. In these solvents, the tetrafluoroborate based phenanthrolinium ILs were found to be readily soluble for alkyl side chain length ranging from ethyl to butyl and sparingly soluble for penthyl and hexyl chains and insoluble for the rest of the ILs synthesized. This may be explained in terms of increasing Van der Waals interaction with increasing alkyl chain size, which can cause the solute – solute interaction force of the ILs to be higher than solute – solvent interaction energy and make the solution process thermodynamically impossible.

Table 3: Solubility test table

	DMSO	$CHCl_3$	CH_3CN	1,4-dioxane	H_2O	CH_3OH	CH_3CH_2OH	Toluene	n-heptane
[C_2Phen]Br^-	Soluble	Soluble	Soluble	insoluble	Soluble	Soluble	Soluble	insoluble	insoluble
[C_2Phen]BF_4^-	Soluble	Sparingly soluble	Soluble	Sparingly soluble	Soluble	Soluble	Soluble	soluble	insoluble
[C_3Phen]Br^-	Soluble	Soluble	Soluble	insoluble	Soluble	Soluble	Soluble	soluble	insoluble
[C_3Phen]BF_4^-	Soluble	Soluble	Soluble	Sparingly soluble	Soluble	Soluble	Soluble	Sparingly soluble	insoluble
[C_4Phen]Br^-	Soluble	Soluble	Soluble	soluble	Soluble	Soluble	Soluble	soluble	Sparingly soluble
[C_4Phen]BF_4^-	Soluble	Soluble	Soluble	soluble	Soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble
[C_5Phen]Br^-	Soluble	Soluble	Soluble	insoluble	Soluble	Soluble	Soluble	soluble	insoluble
[C_5Phen]BF_4^-	Soluble	Soluble	Soluble	soluble	Sparingly soluble	Soluble	Soluble	Sparingly soluble	insoluble
[C_6Phen]Br^-	Soluble	Soluble	Soluble	insoluble	soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble
[C_6Phen]BF_4^-	Soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble
[C_8Phen]Br^-	Soluble	Soluble	Soluble	insoluble	soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble
[C_8Phen]BF_4^-	Soluble	Soluble	Soluble	insoluble	insoluble	Soluble	Soluble	Soluble	Sparingly soluble
[C_{12}Phen]Br^-	Soluble	Soluble	Soluble	insoluble	soluble	Soluble	Soluble	Sparingly soluble	Sparingly soluble
[C_{12}Phen]BF_4^-	Soluble	Soluble	Soluble	soluble	insoluble	Soluble	Soluble	Soluble	Sparingly soluble

4. CONCLUSIONS

A new family of N-alkylphenanthrolinium tetrafluoroborate based ILs with varying alkyl side chain on the cation has been synthesized by a new and simple anion metathesis procedure starting from N-alkylphenanthrolinium bromide and sodium tetrafluoroborate.

The new anion metathesis procedure offered remarkable improvement in product yield, cut down reaction times and diminished the utilization of organic solvents associated with the conventional procedures, rendering the process economically favorable. The shorter stirring time and absence of heating requirement for the process lowered energy request making the synthetic route energetically less demanding. In addition, the lesser utilization of organic solvents and enhanced product yield are important aspects that make the route more environmentally friendly. All the new BF_4^- containing ILs exhibited lower melting points than their Br^- containing analogues and this is attributed to the asymmetry of the anion leading to poor ion packing. The change in melting point with increase in alkyl chain, however, manifested similar trend for both BF_4^- and Br^- containing ILs which suggested that effects of alkyl side chain on melting point are independent of anion identity.

The new ILs exhibited better dissolution ability for the phenanthrolinium metal complexes than the Tf_2N^- based phenanthrolinium ionic liquids and hence are potential substances for application in catalysis. These ILs were also found to be soluble in a wider range of organic solvents than their analogues and this shows their potential applicability in a larger number of reaction and separation schemes.

Overall, the result of this research shows the possibility to enhance the applications of phenanthrolinium based ILs in areas such as catalysis and nanoparticle synthesis, which have been hindered by the poor solvation abilities towards metallic complexes of commonly used ILs. Furthermore, the new synthetic route represents the possibility to improve the methodology of ILs synthesis for a given application with regard to economics, cumulative energy demand and environmental impact.

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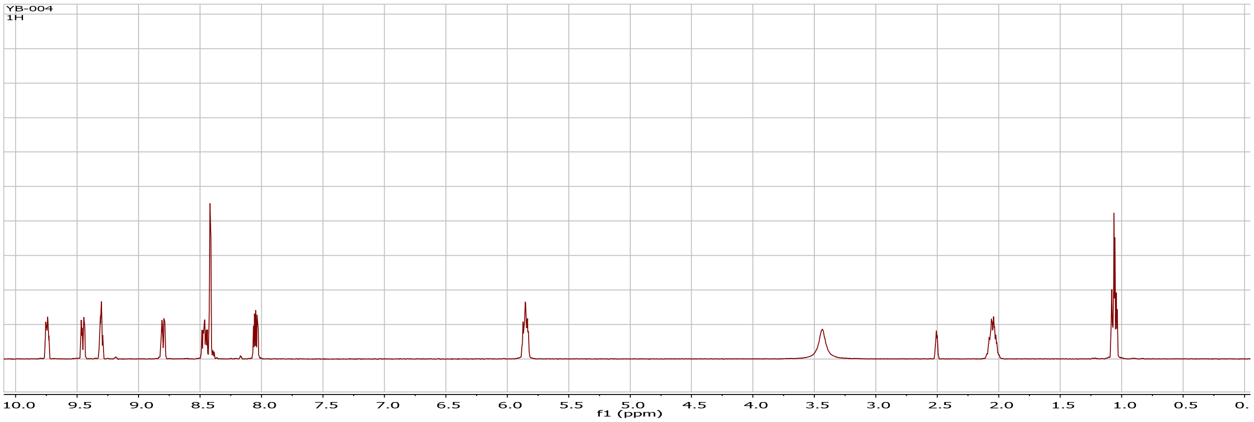
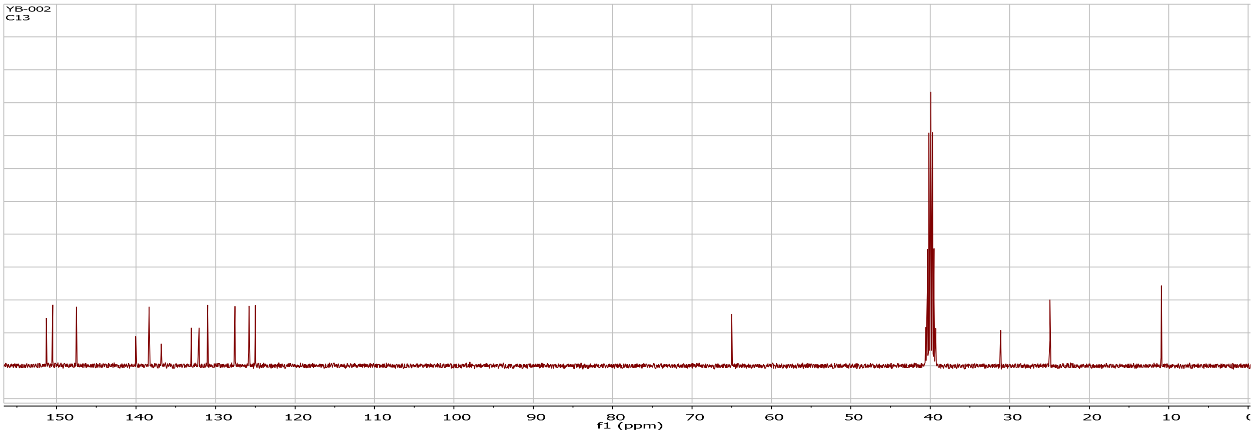
Appendices

Appendix 1 NMR spectra of [C_3Phen]Br in DMSO



^{1}HNMR spectra of [C_3Phen]Br



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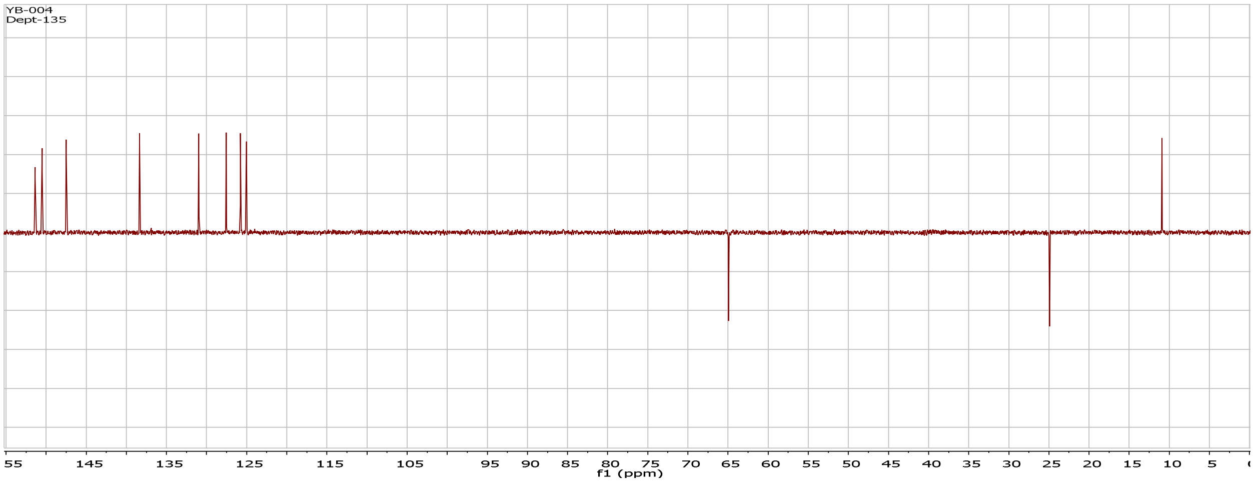
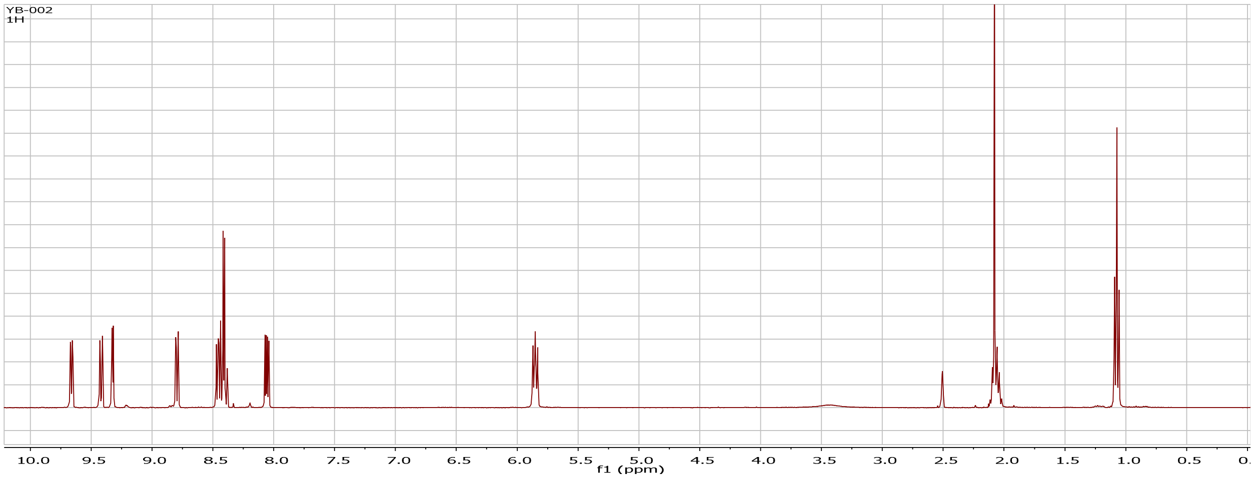


DEPT spectra of [C_3Phen]Br

Appendix 2 NMR spectra of [C_3Phen]BF_4 in DMSO



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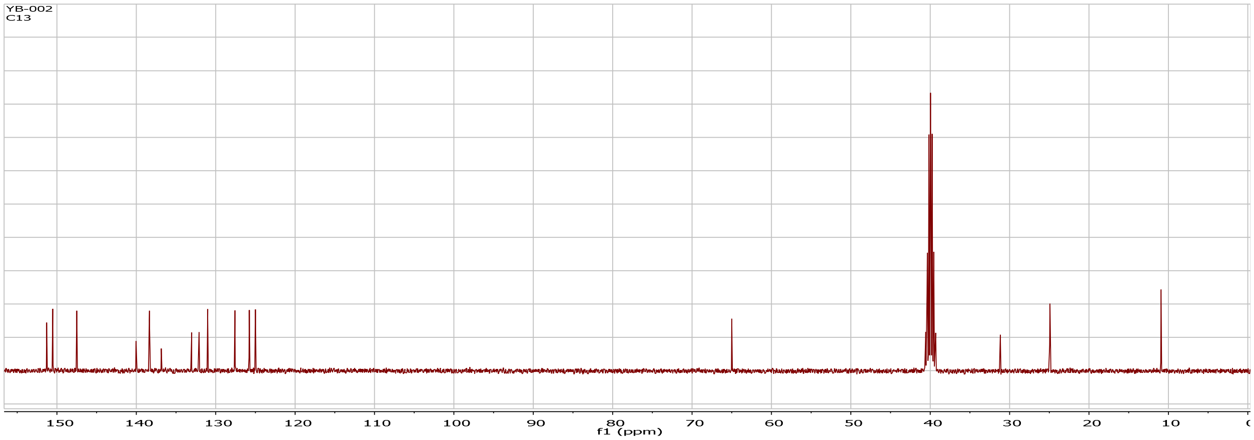

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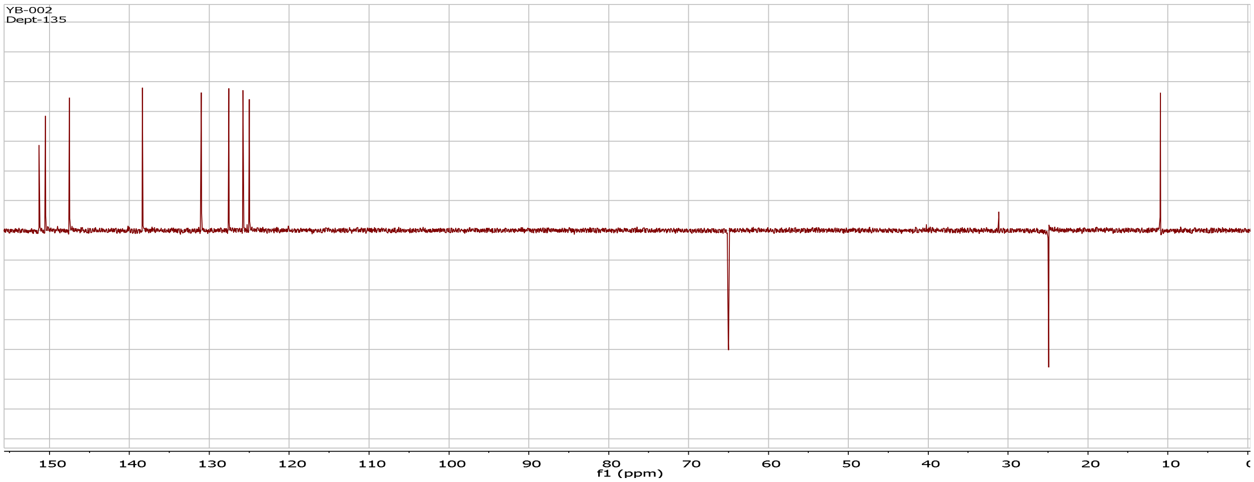
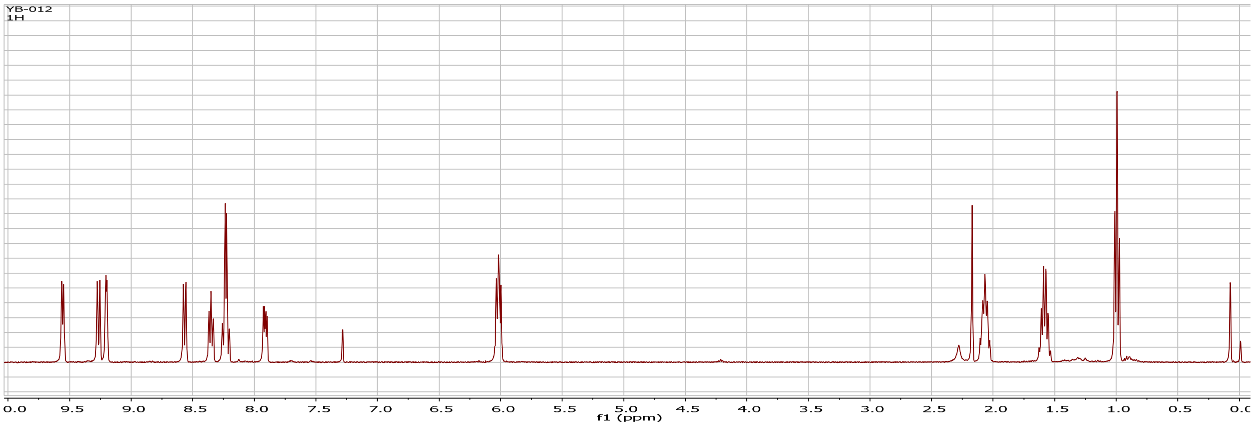


DEPT NMR spectra of [C_3Phen]BF_4

Appendix 3 NMR spectra of $[C_4Phen]BF_4$ in $CDCl_3$



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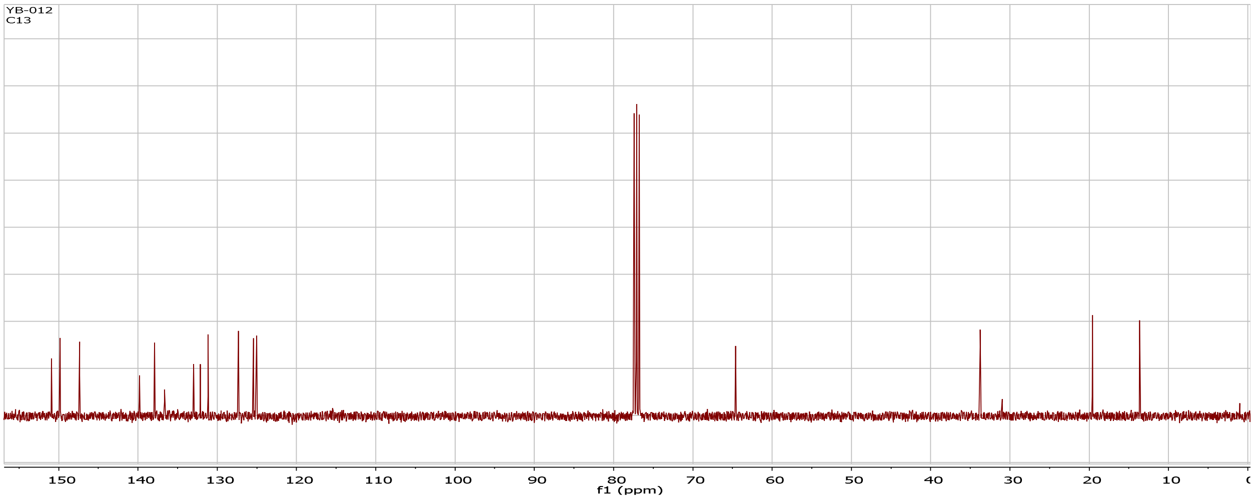

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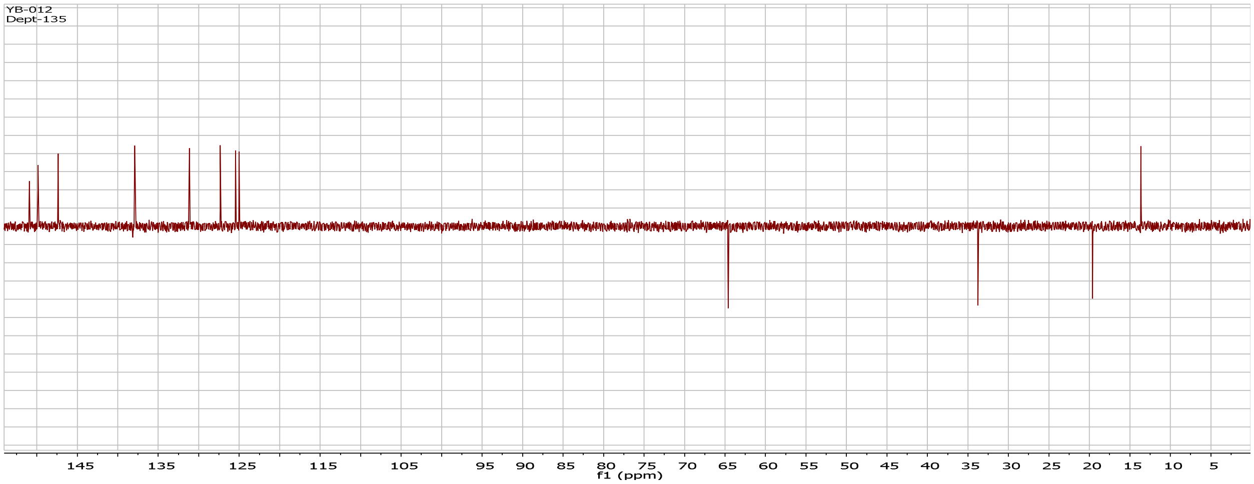
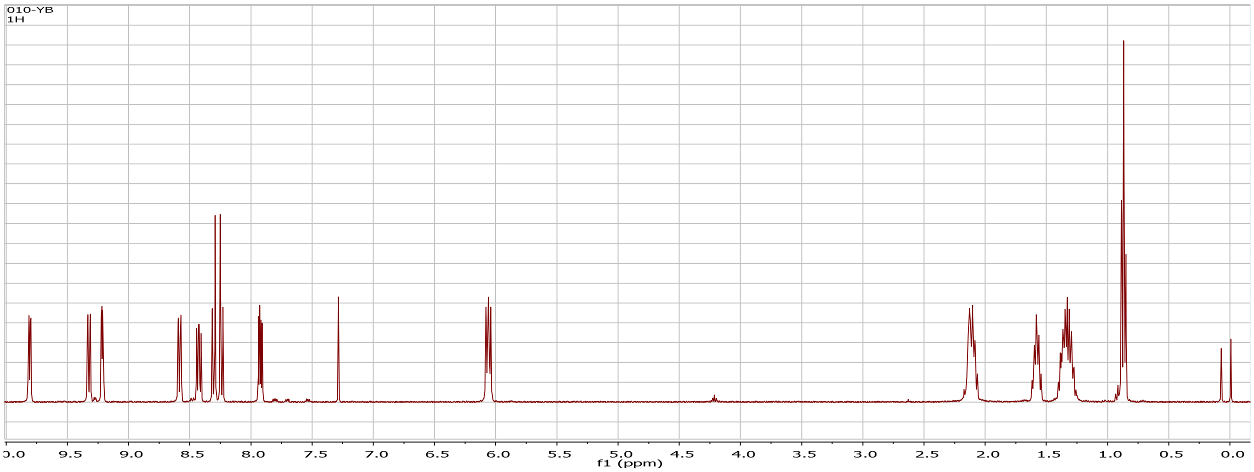


DEPT NMR spectrum of $[C_4Phen]BF_4$

Appendix 4 NMR spectra of $[C_6Phen]BF_4$ in $CDCl_3$



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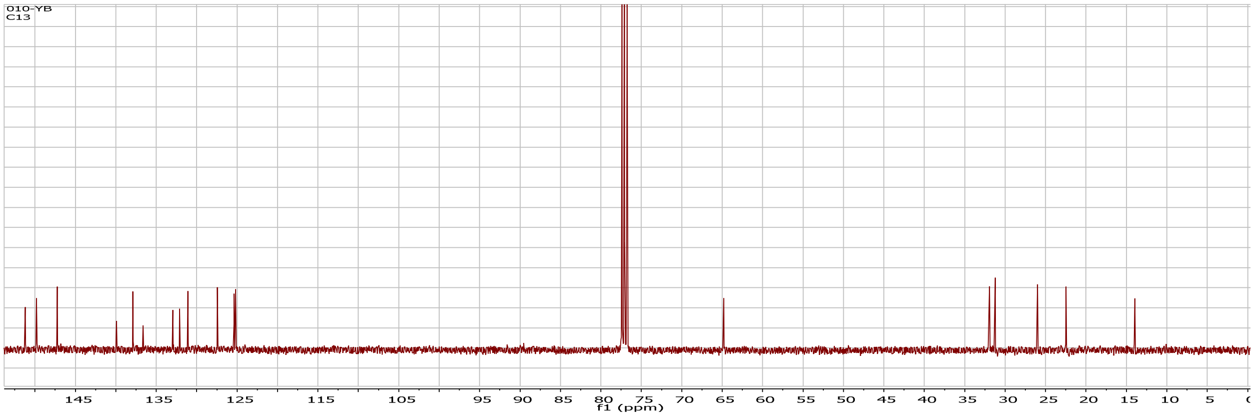

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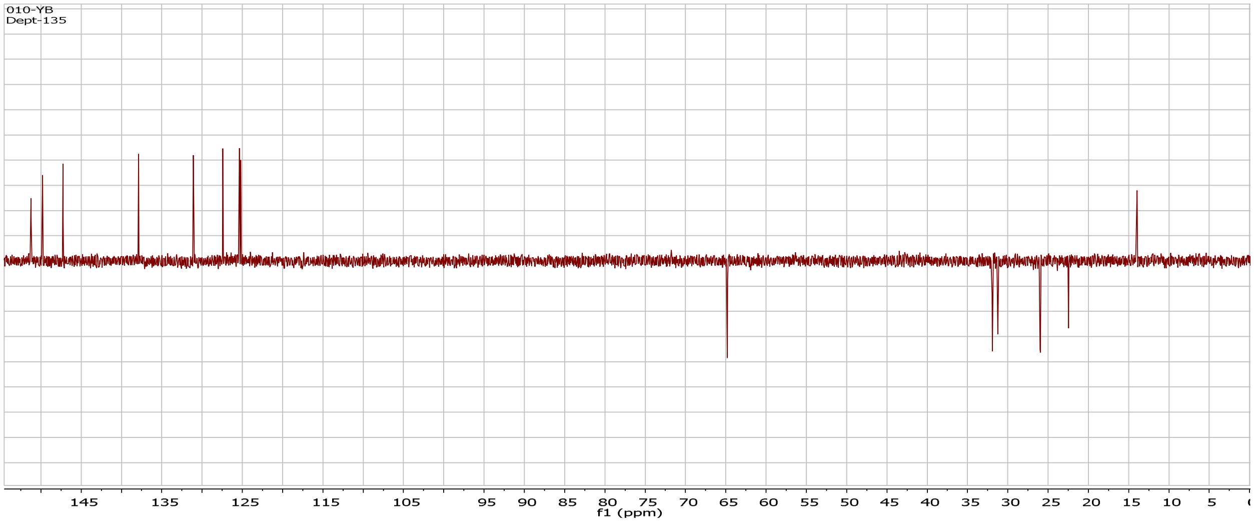
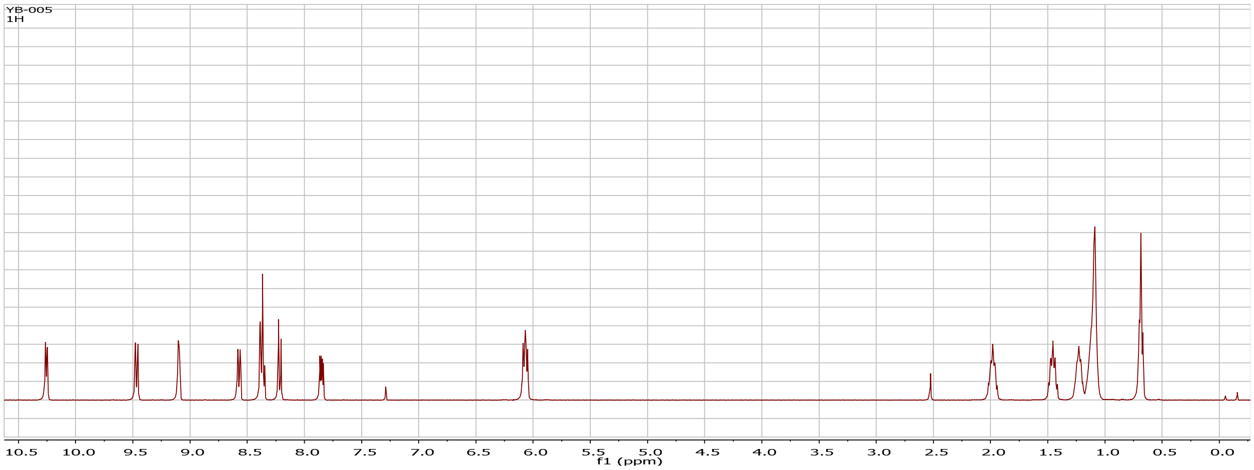


DEPT NMR spectra of $[C_6Phen]BF_4$

Appendix 5 NMR spectra of [C$_8$Phen]Br in CDCl$_3$



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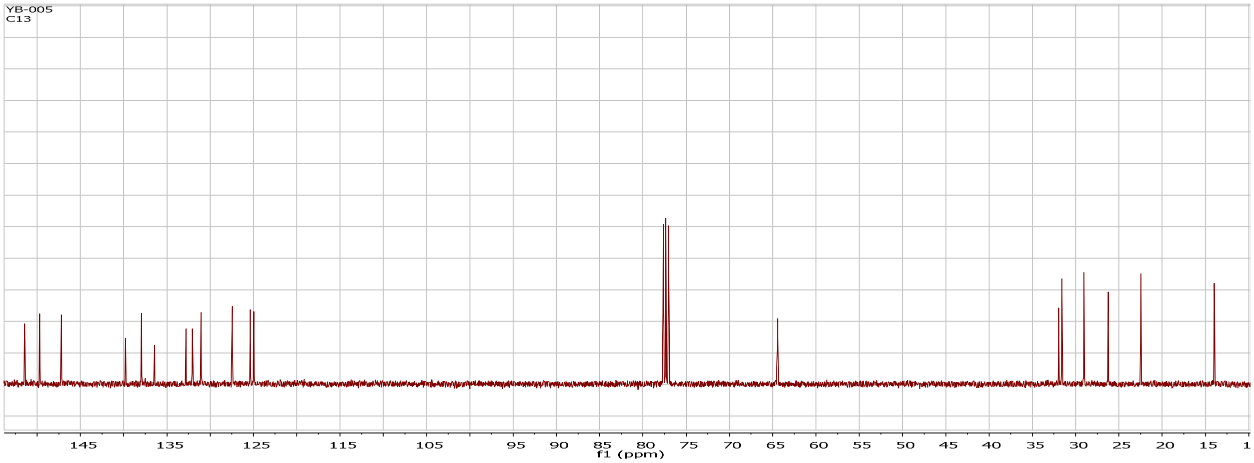

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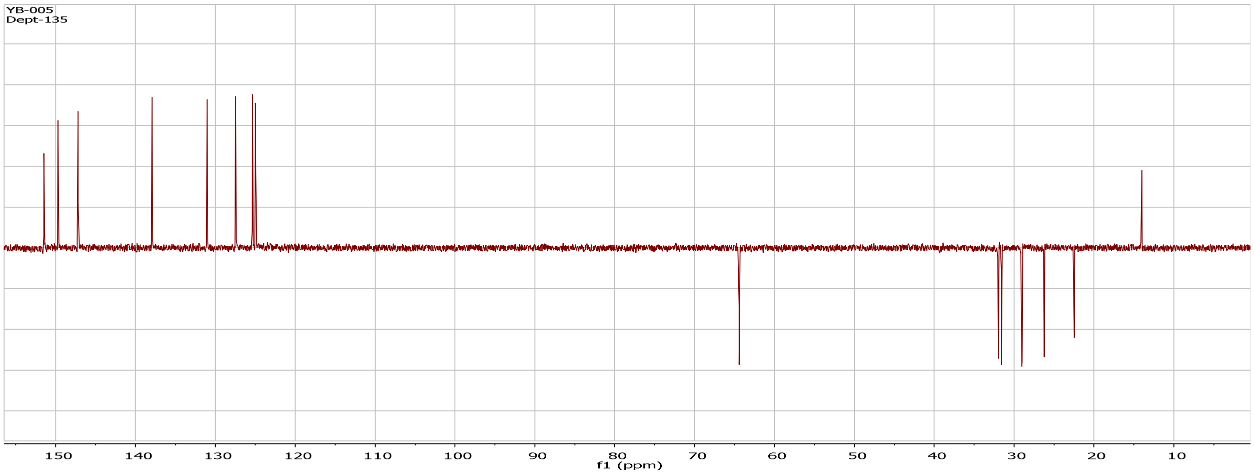

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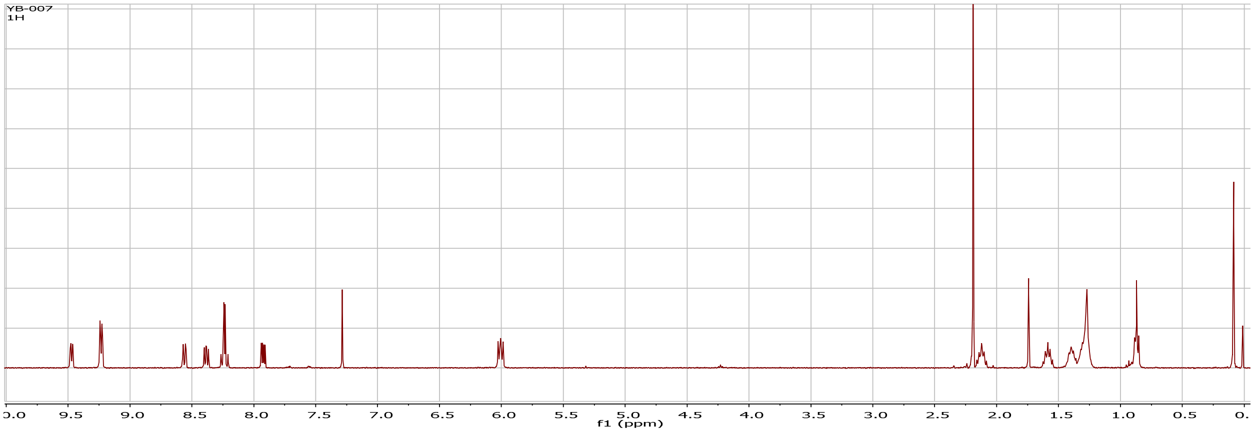
Appendix 6 NMR spectra of [C_8Phen]BF_4 in $CDCl_3$



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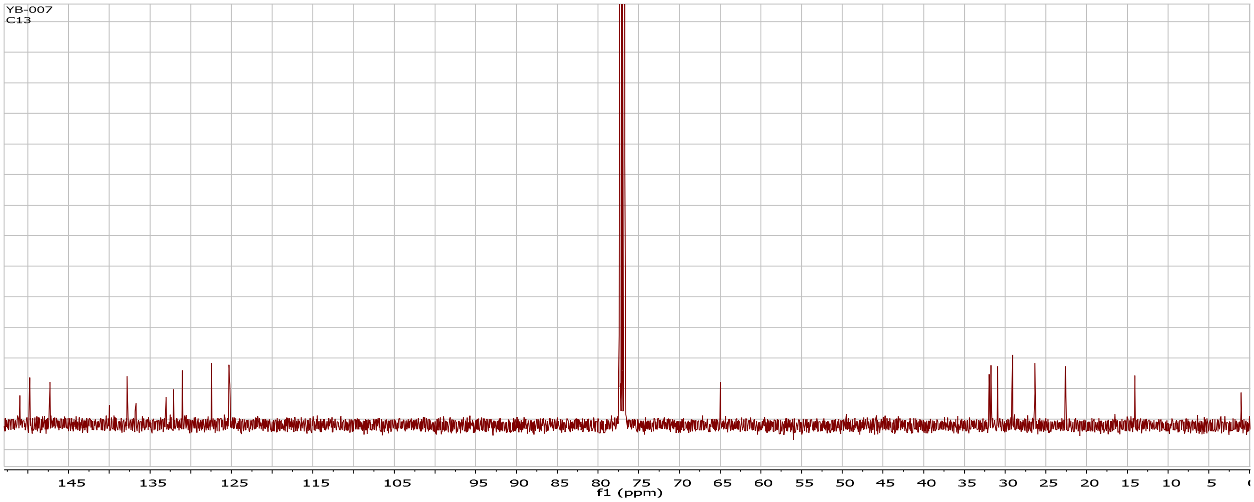

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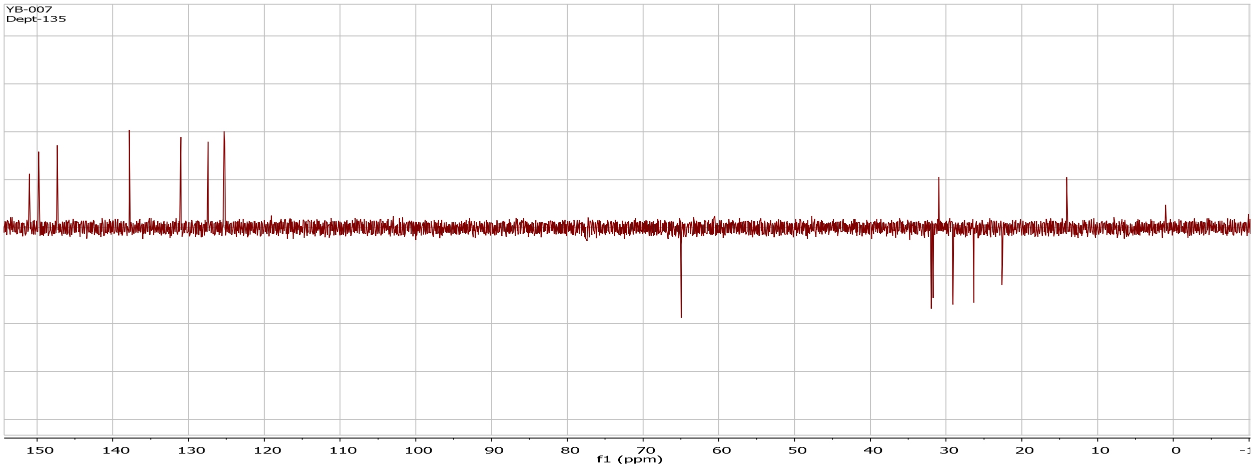
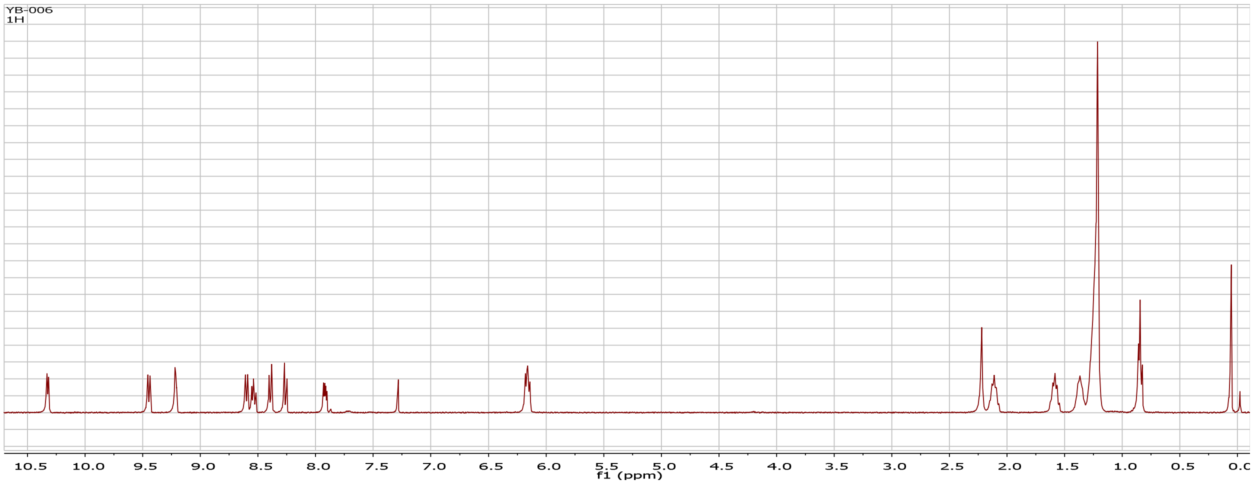


DEPT NMR spectra of [C_8Phen]BF_4

Appendix 7 NMR spectra of [C$_{12}$Phen]Br in CDCl$_3$



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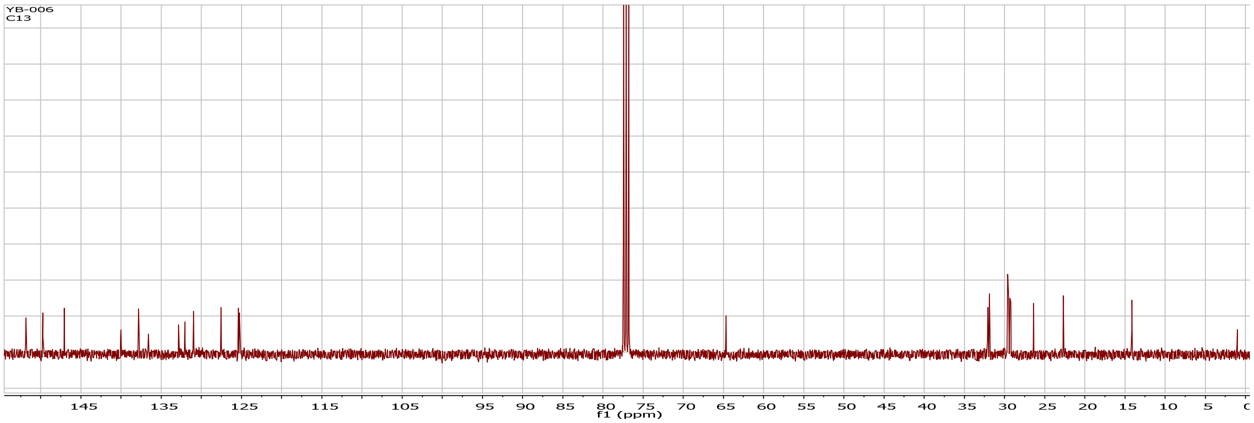

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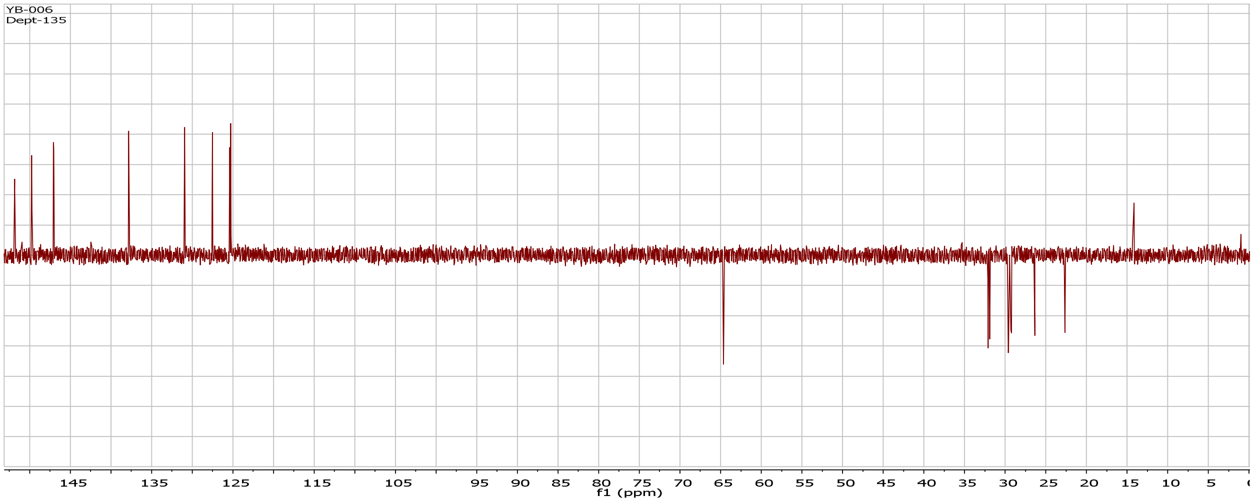
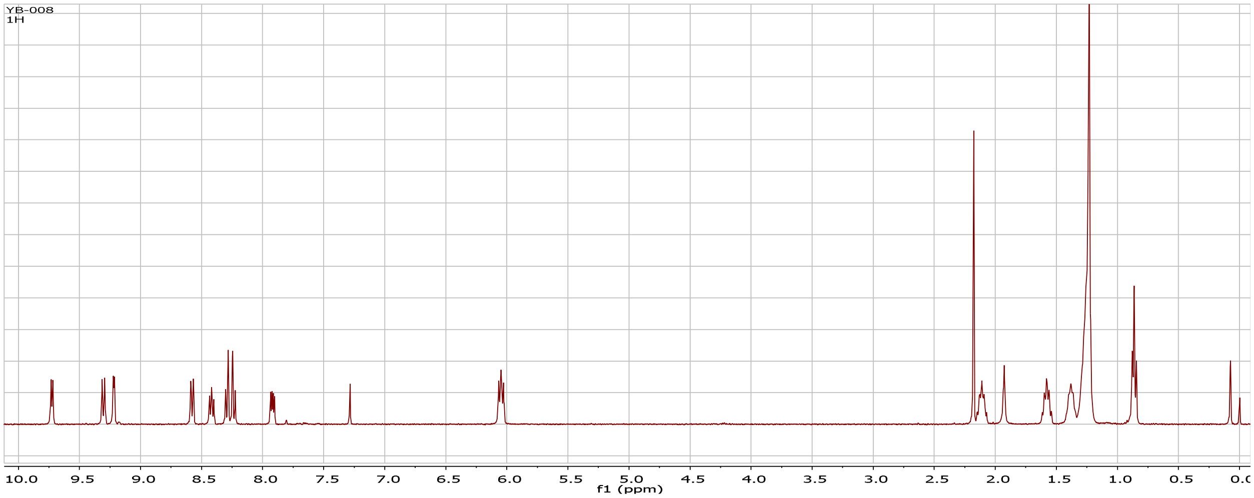


DEPT NMR spectra of [C$_{12}$Phen]Br

Appendix 8 NMR spectra of [C$_{12}$Phen]BF$_4$ in CDCl$_3$



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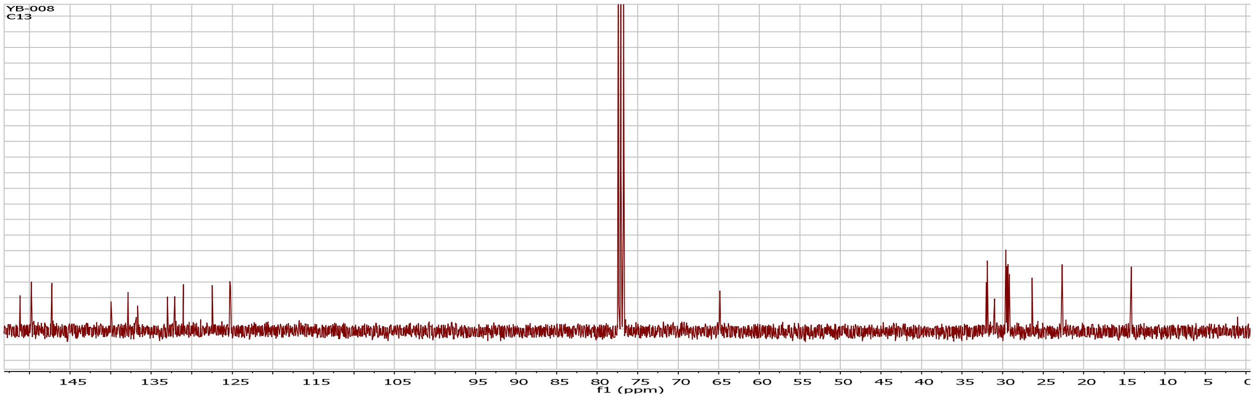

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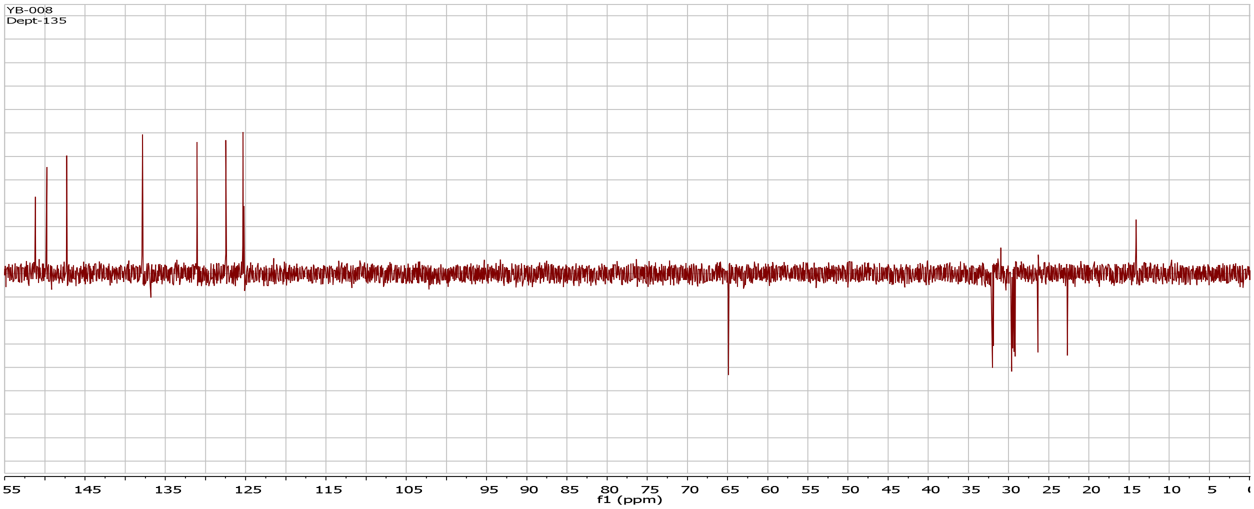

DEPT NMR spectra of [C$_{12}$Phen]BF$_4$