ADDIS ABABA UNIVERSITY

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SYNTHESIS AND CHARACTERIZATION OF IONIC LIQUIDS BASED ON O-PHENANTHROLINE

Graduate Project (Chem. 774)

By: Alemayehu Dubale

June, 2010

SYNTHESIS AND CHARACTERIZATION OF IONIC LIQUIDS BASED ON O-PHENANTHROLINE

A Project Work Submitted to the School of Graduate Studies of Addis Ababa University in Partial Fulfilment of the Requirements for the Degree of Master of Science in Chemistry

By: Alemayehu Dubale

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ADDIS ABABA UNIVERSITY

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DEPARTEMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF IONIC LIQUIDS BASED ON O-PHENANTHROLINE

Approved by the examining board:

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Declaration

I, the undersigned declare that this is my original work and has not been submitted for a degree in any other university and all sources of material used for the project have been duly acknowledged.

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ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF NEW IONIC LIQUIDS BASED ON O- PHENANTHROLINE

GRADUATE PROJECT CHEM. 774

BY ALEMAYEHU DUBALE

Approved by Examining Board:

1. Dr. Yonas Chebude (examiner) _____

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List of Abbreviations and Symbols

ILs---------- ionic liquids

^{1}HNMR----------proton nuclear magnetic resonance

^{13}CNMR----------carbon nuclear magnetic resonance

Phen----------phenanthroline

TMS----------trimethylsilane

$^{-}$NTf$_2$----------bis-(trifluoromethylsulfonyl) imide

C$_3$PhenBr----------propylphenanthroliniumbromide

C$_4$PhenBr----------Butylphenanthroliniumbromide

C$_5$PhenBr----------pentylphenanthroliniumbromide

C$_3$PhenNTf$_2$----------propylphenanthrolinium bis (trifluoromethylsulfonyl) imide

C$_4$PhenNTf$_2$----------butylphenanthrolinium bis (trifluoromethylsulfonyl) imide

C$_5$Phen NTf$_2$----------pentylphenanthrolinium bis (trifluoromethylsulfonyl) imide

δ ----------chemical shift

J----------Coupling constant

Sext----------sextet

d----------doublet

t----------triplets

m----------multiplets

dd----------doublet of doublets

s----------singlets

Pent----------pentet

Abstract

Ionic liquids are organic salts with melting point below 100^0C. Their unique properties such as negligible vapor pressure, wide ectrochemical window and solvent properties have brought about an amazing interest in these salts. One of the most common research areas based on ionic liquids as a solvent focuses on homogeneous catalysis since ionic liquids are found to be ideal immobilizing agents for various classical transition metal catalyst precursors. In the present study we have tried to synthesize new ionic liquids based on phenanthroline taking in to account that it could easily dissolve transition metal catalysts based on phenanthroline due to similar structure it possesses. In the present work, new and monoalkylated salts based on phenanthroline, have been synthesized and investigated. An attempt to dialkylate this salts failed due steric and electronic factors. These Salts were characterized by various physical and spectroscopic techniques: ^{1}HNMR, ^{13}C NMR and elemental analysis their melting point, conductivity, miscibility with water and organic solvents were determined. The influence of alkyl substituent along with nature of the anion on the NMR chemical shift of the neighboring hydrogens is also discussed. These compounds were also analyzed by melting point and factors such as size of the anion, delocalization of the charge interaction between the ions and disorder(asymmetry) in the cation affected the packing of the ionic liquid and thereby the observed melting point.

***Key words**: ionic liquids 1, 10-phenanthroline, quaternization, homogeneous catalysis.*

1. Introduction

1.1 Ionic Liquids

Solvents are common in chemistry, providing solvation media for chemicals. The most common media for conducting chemical reactions and materials synthesis are aqueous and organic solvents. Water is readily available, non-flammable, non-toxic, and environmentally benign. However, the liquidus range of water (0–100 ^{0}C) is narrow, and most organic molecules have low solubility in water which limits the applications of water as a versatile solvent for synthesis conducted at relatively low or high temperatures as well as in organic reactions. On the other hand, organic solvents have diverse physicochemical properties, such as density, polarity, solubility, and liquidus range, but most of them have low boiling points and high vapor pressures; additionally, the solubility of inorganic reactants in these solvents is low[1]. Some organic solvents are highly toxic, flammable, and even explosive. In particular, the high vapor pressures and toxicity of certain volatile organic solvents may cause significant environmental problems. Although traditional molten salts have been attempted as alternative reaction media, [2, 3] their high boiling points (well above 100 ^{0}C) significantly constrain the scope of applications and make the process impractical. Therefore, alternative solvents or media with tunable and versatile solvation properties for conducting chemical reactions and materials synthesis have been actively sought [4]. Ionic liquids can be regarded as a family of molten salts that are different from conventional molten salts; ionic liquids usually have melting points below 100 ^{0}C, sometimes even below room temperature [5]. This is due to the fact that the melting point of large asymmetric ions whose charge can be distributed over the large volume is low and hence the melting point of ionic liquids can be far below 100^{0}C. An ionic liquid is formed from organic Cations and inorganic or organic anions, and it is possible to make even 10^{18} different ILs. Commonly used Cations are large and asymmetric, e.g. derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium (Fig. 1). Typical inorganic anions are e.g. halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis (trifluoromethylsulfonyl) imide and typical organic anions are alkylsulfate, alkylsulfonate, p-toluenesulfonate (tosylate) and trifluoroacetate (Fig. 2).

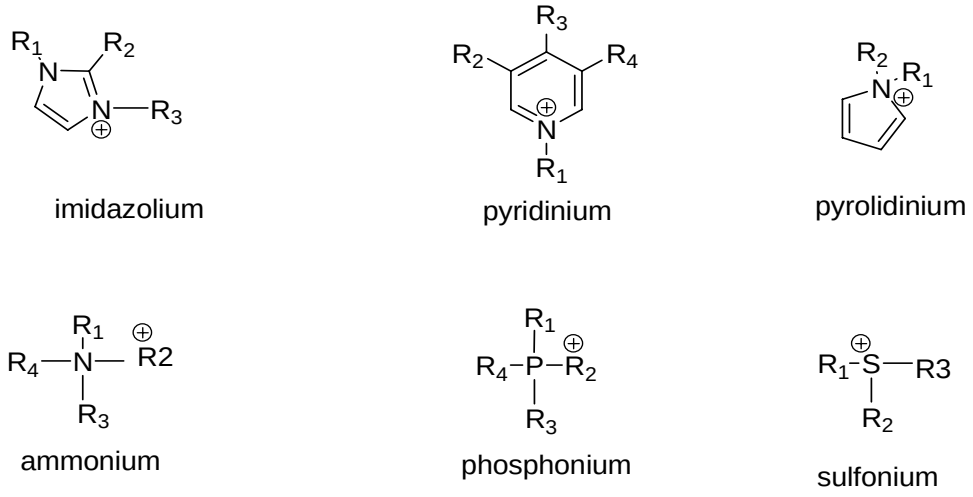


Figure 1. Most commonly used Cations in ionic liquids

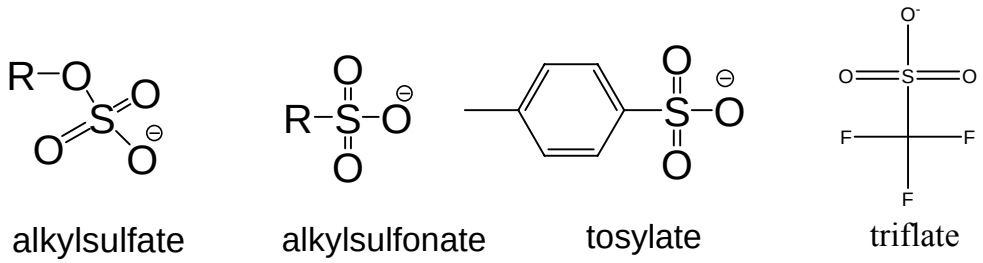


Figure 2. Most commonly used anions in ionic liquids

Compared with traditional solvents, ionic liquids offer many distinct advantages (such as negligible vapor pressures, good thermal stability, high ionic conductivity, broad electrochemical potential windows, and high synthetic flexibility) as solvents for a wide variety of inorganic and organic chemicals. In particular, their negligible vapor pressures are important for minimizing the exposure to toxic volatile vapors and their low melting points (as low as -80 ^{0}C) and high thermal stability (stable below 300 ^{0}C) provides a wide liquidus range for organic catalysis and inorganic synthesis.

1.2 The History of Ionic Liquids

The first ionic liquid, $[C_2H_5NH_3][NO_3]$ (melting point 13–14 ^{0}C), was synthesized by Walden via the neutralization of ethylamine with concentrated HNO_3, as reported in 1914 [6]. Because a proton-transfer reaction is invoked during synthesis, this class of ionic liquids is classified as protic ionic liquids. In 1951, Hurley and Wier reported new ionic liquids prepared by mixing alkylpyridinium chlorides with $AlCl_3$. [7–8] This work marked the genesis of a second class of ionic liquids, i.e., aprotic ionic liquids [9]. The Cations of aprotic liquids are derived from the alkylation or alkyl–cation-transfer reaction of organic compounds with alkyl halides. However, these ionic liquids are sensitive to air and moisture, and therefore are not in active use nowadays. A milestone in the field is the discovery of water-stable ionic liquids containing tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate anions by Wilkes and Zaworotko in 1992 [10]. Since then, many ionic liquids composed of organic Cations and inorganic or organic anions have been developed, as reviewed by Gordon and Muldoon [11]. Because there are large varieties of Cations and anions available, their combination amounts to numerous potential ionic liquids. However, only a few typical ionic liquids (Fig. 1), [12, 13] especially those containing imidazolium Cations, [14] are commonly used at the moment.

1.3. Preparation of ionic liquids

Preparation of ionic liquid is quite simple. The first step, and sometimes the only step, is a quaternization reaction that takes a rather long time to accomplish, even when heated with an oil bath [15]. There are two basic methods for the preparation of these ionic liquids: metathesis of a halide salt (Finkelstein step) with, for instance, a silver, group 1 metal or ammonium salt of the desired anion and acid–base neutralization reactions, but either way need the preparation of the imidazolium or pyridinium halides via alkylation using a large molar excess of haloalkanes (10–400%) for as long as 72 h at refluxing condition, and then RTILs is prepared with variable yields and much longer reaction time. An attempt has been made to decrease the reaction time by carrying out the synthesis of the ionic liquid in an ultrasonic atmosphere [16] in the beginning of the 21st century microwave activation made a breakthrough by shortening the reaction time considerably.

1.4. Quaternization reaction

Most quaternization reactions involving an annular nitrogen atom and alkylating agent proceed by way of S_N2 reaction in which inversion of configuration of an achiral reagent takes place. The majority of such reactions give products reflecting kinetic control. Products usually are formed irreversibly. Alkyl halides are widely used as alkylating agents in a quaternization reaction, since they are cheap and easily available. Quaternization is a simple reaction: the amine and the desired alkyl halide are mixed and the reaction mixture is heated. The reaction temperature and the reaction time depend on the reactivity of the alkyl halide. The reactivity decreases as a function of increasing alkyl chain length. The nature of the halide also influences the reactivity of the alkyl halide. For a given chain length, Iodine is most reactive, followed by bromine and chlorine, as is expected for a nucleophilic substitution reaction, SN_2, [17]. The reactions are typically carried out in an inert atmosphere (N2, argon). The formed ionic liquid is immiscible with the starting materials, and it forms a dense phase on the bottom of a reaction flask. Therefore, efficient stirring is necessary for the reaction to proceed. Sometimes solvents such as 1,1,1-trichloroethane ethyl acetate or toluene are used in the reaction. These solvents are immiscible with the ionic liquid. ILs should be heated carefully, since excess heat during the preparation reaction generates a discolored product indicating impurities might have been formed in the solvent. The ionic formed liquid may be dark brown. Using an excess of alkyl halide is effective for completing the reaction (Washing the crude IL with ethylacetate removes unreacted starting materials. The rest of the ethyl acetate is removed by heating the ionic liquid in a vacuum. Alkyl halides are used as alkylating agents, hence ILs based on halides are easily converted into ionic liquids with other anions. The problem in the following anion exchange reaction is that the complete exchange of Cl- is difficult to accomplish. Therefore, other alkylating agents, such as methyltriflate 14, methyl sulfate 15, octyl tosylate 16, and methyl tosylate 17, could be used in the quaternization reaction (Fig. 4) [18, 19].

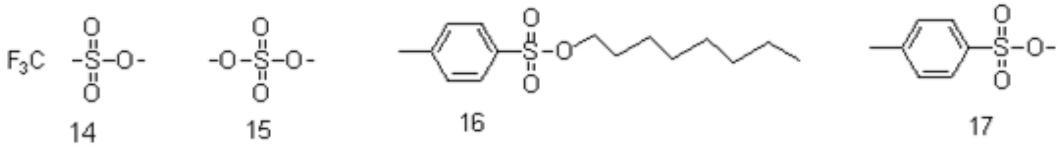


Figure 3. Alkylating agents commonly used for quaternization reaction.

1.5. Solvent Effects on Quaternization Reaction

Although enormous increases in rates of S_N2 reactions can be obtained by changing from a polar protic to a polar aprotic solvent, such is not the case with quaternization reactions**.** Systems showing dramatic changes in reactivity involve an ionic nucleophile in contrast to quaternization reactions in which the nucleophile is uncharged. Thus rate constants for the reaction between pyridine and benzyl chloride in methanol and dimethylformamide (DMF) at 25^0C are nearly identical, and with benzyl chloride this same solvent change produces only at 8.8-fold increase. Calorimetric studies show that the rate of acceleration produced on passing from the hydrogen bonding to the aprotic medium is due to lower activation enthalpy. Solvation effects are more important for the energy of activation than for the reactants. Because kinetic studies have been carried out employing a range of solvents, it is worthwhile to compare the magnitude of the effect of several solvents, on rate constants in keeping with reactant like transition state, the reactivity of pyridine toward MeI only increases by factors of 7(25^0C) and 4.5(35^0C) on changing from nitrobenzene to dimethylsulfoxide (DMSO) and to sulfonate, respectively. Similar small changes are found with five-membered ring nucleophiles.Solvent effects on the relative rate constants are also usually very small. When a hetroaromatic compound quaternizes at more than one site, for example, the product ratio can be insensitive to solvent variations. A constant isomer ratio is recorded for methylation (MeI) of 3-tert-butyl-6-dimethylaminopyridazine, in hexane, benzene, carbon tetrachloride, acetone and acetonitrile, but not in dimethoxymethane or tetrahydrofuran. The suggestion was made that MeI may have reacted with the last two ether solvents to give an oxonium ion. Since the identity of the quaternizing agent changes the product ratio varies as well. Other

solvents also are not inert .for example, DMSO and MeI react, first (reversibly) at oxygen and then at sulfur. This side reaction becomes important only in quaternization studies involving poorly nucleophilic hetroaromatic substrates. [20].

1.6. Characterization of Ionic Liquids

The production of pure ionic liquids is of very importance, since impurities have a strong influence on their physical properties and stability. Hence, special attention is paid to characterization of the ionic liquids. Ionic liquids are analyzed with NMR, MS (ESI+ and ESI-) and elemental analysis. Their thermal stability is determined with TGA in order to know their upper temperature limit. Melting points are measured with DSC or a melting point apparatus. The determination of a liquid range of an ionic liquid is necessary in order to know a temperature range, where IL can be utilized. Their crystal structures are determined with a single crystal X-ray diffractometer for solid ionic liquids. In the present study, we have used ^{1}H NMR and ^{13}C NMR analysis, elemental analysis melting point, conductivity, halide and solubility tests [21].

1.7. Melting point

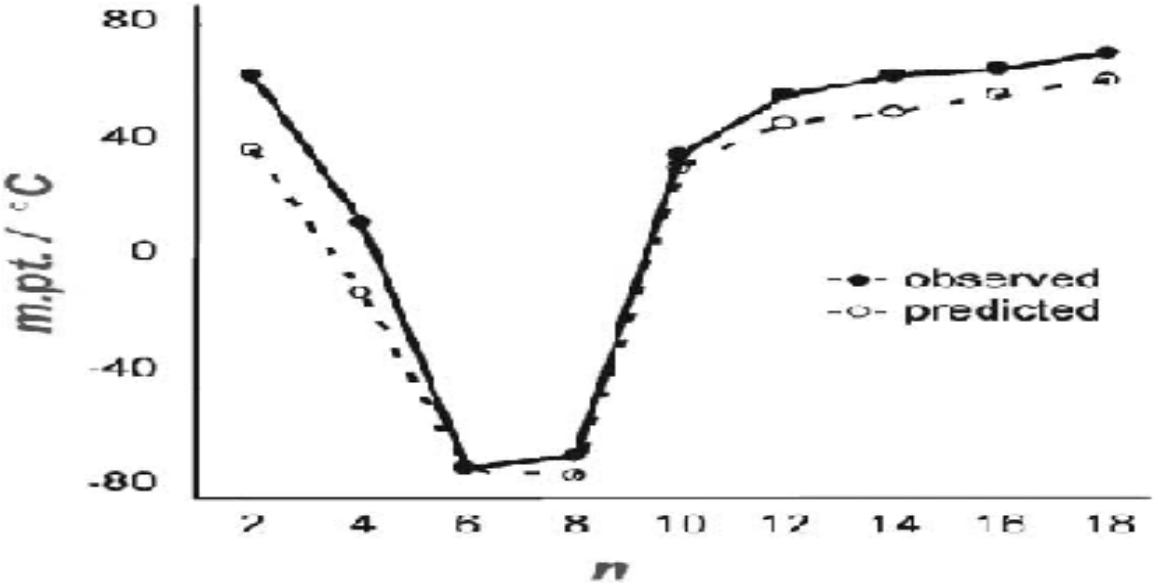


Figure 4. Predicted and observed melting points for halide based ILs.

The melting point of an ionic liquid depends on the composition of anion and cation. Symmetric ions with a localized charge and strong interactions between ions give rise to good packing efficiency and a high melting point. Ionic liquids based on large, asymmetric cations with delocalized charge usually have low melting point. Packing efficiency depends on interactions between ions. Hydrogen bonding or similar non-bonded interactions increase the order of the system and therefore raises the melting point. An optimized structure of 1-methyl-3-octadecylimidazolium cation shows three structural regions for determining the melting point. At about 4Å is the charge rich region localized on the imidazolium ring and hence higher melting point; at 5.5 Å the symmetry breaking region that decreases the melting point; from 12 Å onwards the hydrophobic region that increases the melting point due to van der Waal's interactions [22].

1.8. Application of ionic liquids

1.8.1 N- Heterocyclic Compounds

Aromatic nitrogen-containing heterocyclic such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (Phen),(fig.5) and related molecules are widely employed as ligands in coordination and organometallic chemistry, especially in homogeneous catalysis[22]. Their interesting redox and photoredox chemistry means that they play a leading role in studies of electron and energy transfer [23]. Moreover, they are commonly utilized as building blocks in supramolecular chemistry [[24]. The excellent donor properties of these ligands, which are usually viewed as a-diimines[25], stem from their sp^2-hybridized N-atoms and result almost invariably in N,N'-chelating structures.Monodentate N-coordination has been proposed in several instances [26], but has been authenticated by X-ray crystallography in only a few cases. [27].

2. Objective of the study

In the present study, we have proposed synthesis of a new ionic liquid based on phenanthroline via N-alkylation. This has been the first trial to prepare ionic liquid of this type via N-alkylation. One of the most common research areas involving ionic liquids based on ionic liquids as solvents focuses on homogeneous catalysis since ionic liquids have been demonstrated to be ideal immobilizing agents for various classical transition metal catalyst precursors and are used to immobilize L-M-L type catalysts where L is a heterocycles. Since the coordinating abilities of ordinary ionic liquids are often very poor, the design of ionic liquids for use as solvents that can serve both for immobilizing and as coordinating ligands for the catalyst in processes involving homogeneous catalysis is indispensable. In the present study, we have tried to address this by synthesizing ionic liquids with functional groups that can be used as a solvent for transition metal catalyst particularly those based on phenanthroline [28].

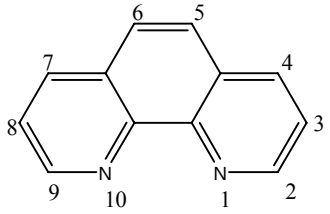


Figure 5. Structure of 1, 10-phenanthroline.

3. Materials and Methods

3.1 Chemicals

Solvents

Solvents used were CH_3CN, DMSO-d_6.$CDCl_3$,

Reagents

Reagents used were 1, 10-phenanthroline, Acetone, bis trifluoromethylsulfonyl) imide, n-bromobutane, n-bromopentane and bromopropane, methyl iodide.

3.2. Instrumentation

^{1}HNMR and ^{13}C NMR spectra were recorded on a Bruker 400 NMR spectrometer in CD_3Cl and DMSO-d_6 at 400 MHz with TMS as an internal standard. Chemical shifts (δ) are reported in ppm with respect to a scale calibrated to (TMS), Elemental analysis was performed on a Flash EA 1112 elemental analyzer. Conductivity was measured with DDS-307 conductivity meter with a DJS-1C electrode. Meting point (M.Pt) was determined by a digital melting point apparatus, Stuart SMP3, and uncorrected.

3.2.1. Qualitative test

I. Halide test

The alkyl halide, n-Bromobutane, forms biphasic mixture upon addition of aqueous solution of $AgNO_3$, but the exchange was achieved by metathesis reaction of an aqueous solution of Butylphenanthroliniumbromide with stoichiometric amount of aqueous solution of silver nitrate. Upon on addition of silver nitrate to an aqueous solution of butylphenanthroliniumbromide, rapid precipitation of AgBr(S) occurred leaving phenanthrolinium and nitrate ions in the solution. This procedure does not afford the complete precipitation of bromide as the extent of removal is limited by solubility product of AgBr=$5.2x10^{-13}$ [31]. The same procedure was repeated with other alkyl halides bromopropane and n-bromopentane and similar phenomenon was observed. For C_4phenNTf_2 and its analogues, this test was performed by adding sliver nitrate solution to the aqueous solution from which the C_4phenNTf_2 has been precipitated, which gives white precipitate of AgBr(S).

II. Conductivity test

C4phenBr, C_4phenNTf_2 and their propyl and pentyl analogues were tested for conductivity and found to be conductors.

III. Solubility test

Solubility test for C_4phenBr, C_4phenNTf_2 and their propyl and pentyl analogues was performed in various polar and non polar solvents and is summarized as follows.

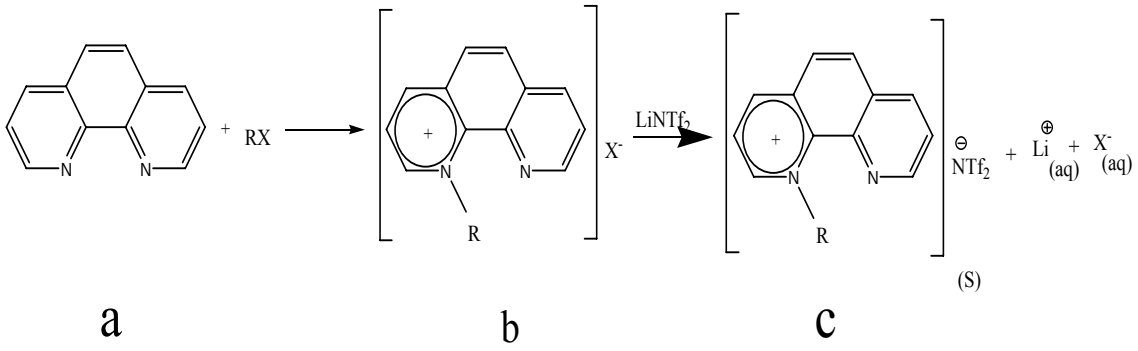
compound	Soluble in	Insoluble in
C4phenBr	Water, Chloroform, Acetonitrile, dimethylsulfoxide, dichloromethane,	Benzene, toluene acetone, 1, 4-dioxane.
C4phenNTf2	Acetonitrile,dimethylsulfoxide, Dichloromethane,Chloroform Acetone, 1,4-dioxane	Water, Benzene, toluene

Table 1. Solubility test results

3.3. General procedure for the Synthesis of alkylphenanthrolinium salts

A mixture of n-bromobutane 2 mol and phenanthroline 1 mol in acetonitrile (500 mL) was heated with stirring at 76^0C for 72hr with an oil bath until a homogeneous liquid was formed. On completion, acetonitrile was evaporated under rotary evaporator at 100^0C and the residue was allowed to cool. The cooled reaction mixture was washed several times with acetone to remove the unreacted phenanthroline. C_4phenBr precipitated during washing. The precipitate was filtered and desiccated for 24 h to yield a white solid C_4phenBr. This compound was dissolved in water and along with slight excess of $LiN(SO_2CF_3)_2$ that is; 1 to 1.2 molar ratio .The mixture was stirred at room temperature to afford the respective anion exchanged produt,C_5phenNTf_2.the solid material was washed with water so as to remove unreacted lithium and bromide ions. It was then

filtered and desiccated for 24hrs. Similar procedure was followed for other alkyl halides, Bromopropane and n-Bromopentane.



Scheme.1. The general reaction conditions for alkylation and the subsequent metathesis.

3.3.1. Characterization data

3.3.1.1 Synthesis of C_3phenBr

White solid:Mp.120-122^{0}C;Purity:94%;^{1}HNMR($CDCl_3$-d): δ=10.31(*d*,1H, *J*=6.8Hz), 9.47 (*dd*, 1H, *J*=1.1Hz, *J*=8.2Hz),9.19 (*dd*, 1H, *J*=1.8Hz, *J*=4.2Hz) 8.59 (*d*, 1H, *J*=8.2Hz) ,8.44 (*dd*, 1H, *J*=6.0Hz,8.1HZ) ,8.39(*d*, 1H *J*=8.8Hz) , 8.25 (*d*, 1H, *J*=8.8Hz) 7.89 (*dd*, 1H,*J*=4.3Hz,*J*=8.2Hz),*6.10*(t,2H,J=15.1Hz),2.10(sext,2H,*J*=14.6Hz),1.09(*t*,3H,*J*=14.2Hz) ^{13}CNMR:151.625,149.882,147.218,139.912,137.883,136.551,132.853,132.085,131.064,127.463,125.361,125.066,65.584, 25.331, 10.66.

3.3.1.2 Synthesis of C_5phenBr

White solid: Mp.181-182^{0}C; Purity: 90%; ^{1}HNMR($CDCl_3$-d):δ=10.38 (*d*,1H, *J*=4.9Hz),9.48(*d*, 1H, *J*=8.2Hz),9.21 (*dd*, 1H, *J*=1.8Hz, *J*=4.3Hz),8.61 (*dd*, 1H, *J*=1.8Hz, *J*=8.2Hz) ,8.49 (dd, 1H, *J*=5.9Hz, *J*=8.2Hz) ,8.41 (*d*, 1H, *J*=8.8Hz) ,8.27 (*d*, 1H, *J*=8.8Hz) ,7.92(*dd*, 1H, *J*=4.3Hz, J=8.2Hz) ,6.18 (*t*, 2H, *J*=15.6Hz),2.11 (*pent*, 2H, *J*=15.4Hz),1.56(*pent*,2H,*J*=15.1Hz),1.38(*sext*,2H,*J*=14.8Hz),0.88(*t*,3H,*J*=14.5Hz).^{13}C-NMR:151.797,149.805,147.117,139.998,137.877,136.594,132.866,132.101,131.022, 127.522,125.344,125.227,64.596,31.753,28.420,22.249,14.004

3. 3.1.3 Synthesis of C_4phenBr

White solid: Mp.131-133^{0}C; Purity:97%; 1H-NMR (CD_3Cl): δ=10.17 (*d*, 1H, *J*=5.9Hz) , 9.42 (*d*, 1H, *J*=8.2Hz), 9.07 (*dd*, 1H, *J*=1.7Hz, *J*=4.1Hz), 8.53 (*dd*, 1H, *J*=1.6Hz, *J*=8.2Hz), 8.37 (*d*, 1H, *J*=6.1Hz) ,8.32 (*d*, 1H, *J*=8.8Hz) ,8.18 (*d*, 1H, J=8.8Hz) ,7.82 (dd,1H, J=4.2Hz, J=8.2Hz), 6.04 (t,2H,J=15.4Hz), 1.93 (pent,2H,J=15.1Hz),1.45 (*sext*,2H, *J*=7.4Hz, *J*=14.9Hz), 0.84 (*t*,3H,*J*=7.4Hz). ^{13}CNMR: 151.388, 149.715, 147.210, 139.723, 137.892, 136.406, 132.779, 132.007, 131.029, 127.391, 125.378, 124.994, 64.173, 33.756, 19.673, 13.661.

3.3.1.4 Synthesis of C_5phenNtf_2

White solid: Mp.114-116^{0}C;Purity:100%; ^{1}HNMR(CD_3Cl-d_6) δ=9.40 (*d*, 1H, J=5.1Hz) ,9.28 (*dd*, 1H, *J*=1.8Hz, J=4.3Hz), 9.15 (*d*, 1H, *J*=8.1Hz), 8.57 (*dd*, 1H, *J*=1.7Hz, *J*=8.2Hz), 8.34 (*dd*, 1H, *J*=6.0Hz, *J*=8.1Hz) ,8.26 (*d*, 1H, J=8.8Hz) ,8.22 (*d*, 1H, J=8.8Hz) ,7.95 (*dd*, 1H, *J*=4.3Hz, *J*=8.2Hz) ,6.02(*t*, 2H,*J*=15.7Hz), 2.16 (*pent*, 2H, *J*=15.3Hz), 1.59 (*pent*, 2H, *J*=14.9Hz), 1.45 (*sext*, 2H, *J*=14.7Hz), 0.96 (*t*, 3H, *J*=7.4Hz). ^{13}CNMR:150.578,149.987,146.992,140.052,137.800,137.032,133.071,132.228,131.294,127.194,125.473,124.926,65.156,31.670,28.383,22.165,13.915.

3.3.1.5 Synthesis of C_4phenNtf_2

White solid: Mp.119-125^{0}c; Purity: 100%; ^{1}HNMR(DMSO-d_6): ^{1}H NMR δ= 9.59 (*d*, 1H, *J*=5.8Hz), 9.37 (*d*, 1H, *J*=8.1Hz) ,9.31 (*d*, 1H, *J*=4.2Hz) , 8.79 (*d*, 1H, *J*=8.2Hz), 8.42 (*d*, 1H,*J*=8.2Hz),8.40(*d*,1H,*J*=6.3Hz),8.37(*d*,1H,*J*=8.8Hz),8.06(*dd*,1H,*J*=4.2Hz,*J*=8.2Hz),5.91(*t*,2H,*J*=15.4Hz),2.04(*pent*,2H,*J*=15.0Hz),1.54(*sext*,2H,*J*=11.1Hz),1.00(*t*,3H,=7.4Hz):^{13}CNMR:151.245,150.408,147.471,140.068,138.362,136.931,133.083,132.119,131.027,127.586,125.827,124.990,63.778,33.444,19.603,13.991.

3.3.1.6 **Synthesis of C_3PhenNTf_2**

White solid: Mp.111-116^{0}c; Purity: 100%; ^{1}HNMR($CDCl_3$):δ= 9.38 (*d*, 1H, *J*=5.7Hz) , 9.29 (*d*, 1H, J=2.9Hz) 9.15 (*d*, 1H, *J*=2.9Hz) ,8.57 (*d*, 1H, *J*=8.3Hz) 8.32 (*dd*, 1H, *J*=6.4Hz,*J*=7.8Hz)8.26(*d*,1H,*J*=8.8Hz),8.22(*t*,1H,*J*=8.0Hz),7.94(*dd*,1H,*J*=4.3Hz,*J*=8.1Hz),5.99(*t*,2H,*J*=15.4Hz),2.17(*sext*,2H,*J*=15.1Hz),1.17(*t*,3H,*J*=7.3Hz).

^{13}CNMR:150.482,150.071,147.077,140.016,137.813,137.028,133.085,132.252,131.353,127.156,125.493,124.764,66.258,25.300,10.512.

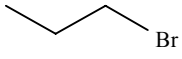
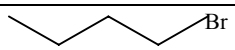
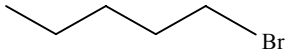
1. Alkylation reaction					
entry	Reagent	solvent	Temp. (^{0}c)	Time. (hr)	Mp. (^{0}c)
1b		CH_3CN	56	56	120-122
2b			76	72	131-133
3b			78	76	180
2. Metathesis reaction					
	$Li(NSO_2CF_3)_2$	Water			Mp. (^{0}c)
1c					110
2c					119
3c					114

Table 2. The reaction conditions for alkylation and the subsequent metathesis reactions

4. Result and discussion

The synthesis of monoquaternary salt with phenanthroline in acetonitrile at specified conditions (table-1) was accomplished with stirring to afford a white precipitate. The best result was obtained for the reaction when the molar ratio among phenanthroline and n-bromobutane was 1 to 2. Increase of the amount of alkylating agent led to a purer product. Using small excess of it ensured completion of the reaction and easy purification of the product. In addition the excess alkylating agent decreased the viscosity of the reaction and made stirring more effective. Therefore, excess of the Alkylating agent could promote the formation of pure product. The reaction rates in the preparation of the monoquaternary salts depended on the alkylating reagent the rate decreased in the following order propyl > butyl> pentyl which is in agreement with [29, 30]. Preparation of C_5phenBr required slight activation by using high temperature and long reaction time.

Various salts were investigated and the results are listed in table-1.the first step in ionic liquid synthesis is time consuming. From the table it can be seen that this method needs from 56 to 72 hrs. In contrast to reported rate at which the quaternization of 1-methyl imidazole or pyridine proceeds the conventional method, the pentyl bromide required relatively longer reaction time. The alkylation step usually requires a large molar excess of the haloalkanes to obtain good yield the solvent was evaporated under rotary evaporator and then the residue was washed several times with acetone to remove the unreacted phenanthroline thereby producing a purer salt, C_4PhenBr. It was characterized by various physical and spectroscopic techniques.

4.1. Elemental Analysis

Satisfactorily, the elemental analysis further confirmed our proposed product.

Compound	Molecular formula	Result	N%	C%	H%
Propylphenanthroliniumbromide.	$C_{15}H_{15}N_2Br$	calculated	9.24	59.40	4.95
		found	**8.31**	**54.82**	4.99
Butylphenanthroliniumbromide	$C_{16}H_{17}N_2Br$	calculated	8.83	60.57	5.36
		found	8.73	60.03	5.48

Table 3. Elemental analysis result

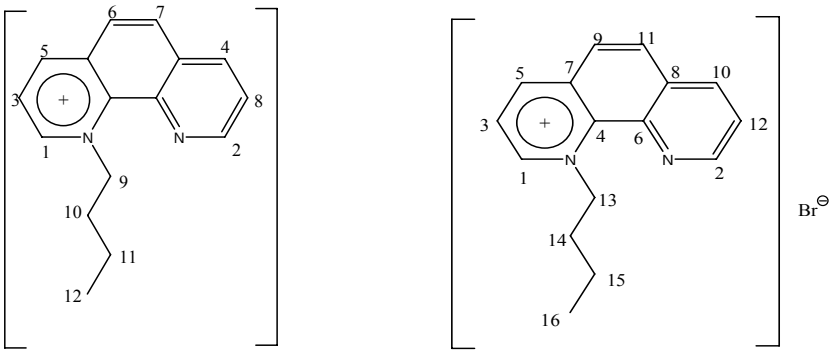
4. 2. ^{1}H-NMR and ^{13}C-NMR spectroscopy.

compound	NMR	Parameter	Peak															
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	1415	16
C4phenBr	1HNMR	δ	10.17	9.42	9.07	8.53	8.37	8.32	8.18	7.82	6.04	1.93	1.45	0.84	-	-	-	-
		J	5.9	8.2	1.7, 4.1	1.6, 8.2	6.1	8.8	8.8	4.2, 8.2	15.4	15.1	7.4, 14.9	7.4				
		m	d	d	dd	dd	d	d	d	d	t	pent	sext	t				
		No of H	1	1	1	1	1	1	1	1	2	2	2	3				
	13CNMR	δ	151.388	149.715	147.210	139.723	137.892	136.406	132.779	132.007	131.029	127.391	125.378	124.994	64.173	33.756	19.673	13.661
C3phenBr	1HNMR	δ	10.31	9.47	9.19	8.59	8.44	8.39	8.25	7.89	6.10	2.10	1.09	-	-	-	-	-
		J	6.8	7.2	1.8, 4.2	8.2	14.1	8.8	8.8	4.3, 8.2	15.1	7.3	7.3	-	-	-	-	-
		δ	d	d	dd	d	d	D	d	dd	t	sext	triplet	-	-	-	-	-
		N0 H	1	1	1	1	1	1	1	1	2	2	3	-	-	-	-	-
	13CNMR	δ	151.625	149.882	147.218	139.912	137.883	136.551	132.853	132.085	131.064	127.463	125.361	125.066	65.584	25.331	10.66	

Table 4. ^{1}H NMR and ^{13}C NMR spectra of C_3phen and C_4PhenBr.

Compound	NMR	parametre	Peak																
C_5phenBr			1	2	3	4	5	6	7	8	9	10	11	12	13	-	-	-	-
		δ	10.38	9.48	9.21	8.61	8.49	8.41	8.27	7.92	6.18	2.11	1.56	1.38	0.88	-	-	-	-
	1H NMR	J	4.9	8.2	1.8, 4.3	1.8, 8.2	5.9, 8.2	8.8	8.8	4.3, 8.2	15.6	15.4	15.1	14.8	7.3	-	-	-	-
		m	d	d	dd	dd	dd	d	d	dd	t	pent	pent	sext	t	-	-	-	-
		No of H	1	1	1	1	1	1	1	1	2	2	2	2	3	-	-	-	-
	13C NMR	δ	151.797	149.805	147.117	139.998	137.877	136.594	132.866,	132.101	131.022	127.522	125.344	125.227,	64.596	31.753	28.420	22.249	14.004
C_5phenNtf$_2$		δ	9.40	9.28	9.15	8.57	8.34	8.26	8.22	7.95	6.02	2.16	1.59	1.45	0.96	-	-	-	-
	1H NMR	J	5.1	1.8, 4.3	8.1	1.7, 8.2	6,8.1	8.8	8.8	4.3, 8.2	15.7	15.3	14.9	14.7	7.3	-	-	-	-
		m	d	dd	d	dd	dd	d	d	dd	t	pent	pent	sext	t	-	-	-	-
		No of H	1	1	1	1	1	1	1	1	2	2	2	2	3	-	-	-	-
	13C NMR	δ	150.578	149.987	146.992	140.052	137.800	137.032	133.071	132.228	131.294	127.194	125.473	124.926.	65.156	31.670	28.383	22.165	13.915

Table 5. ^{1}H NMR and ^{13}C NMR values of C5phenBr and C5PhenNTf$_2$



^{1}H-NMR **^{13}C-NMR**

Figure 6. Numbering of C_4phenBr for NMR analysis.

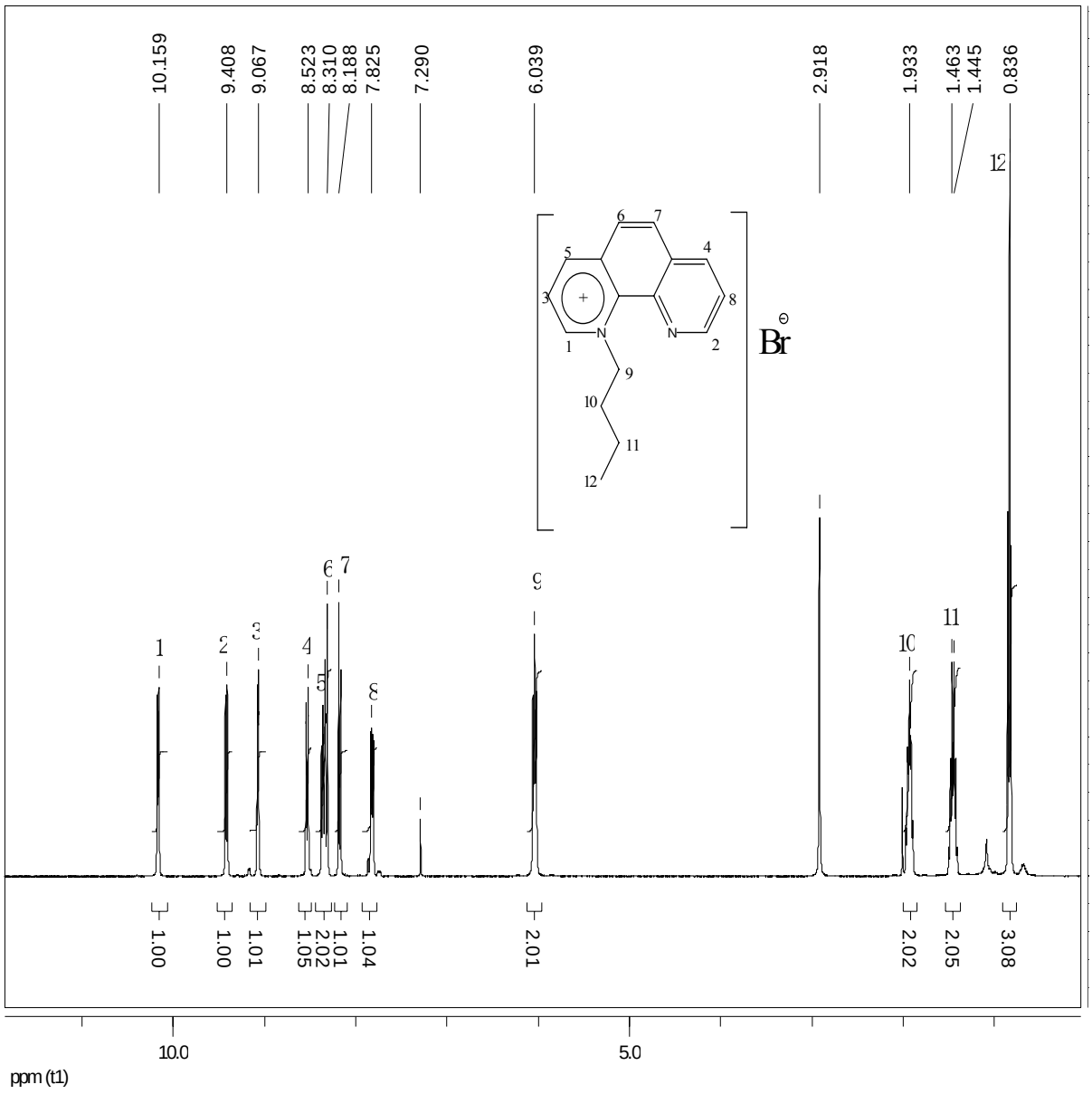


Figure 7. ^{1}H NMR spectrum of C_4phenBr.

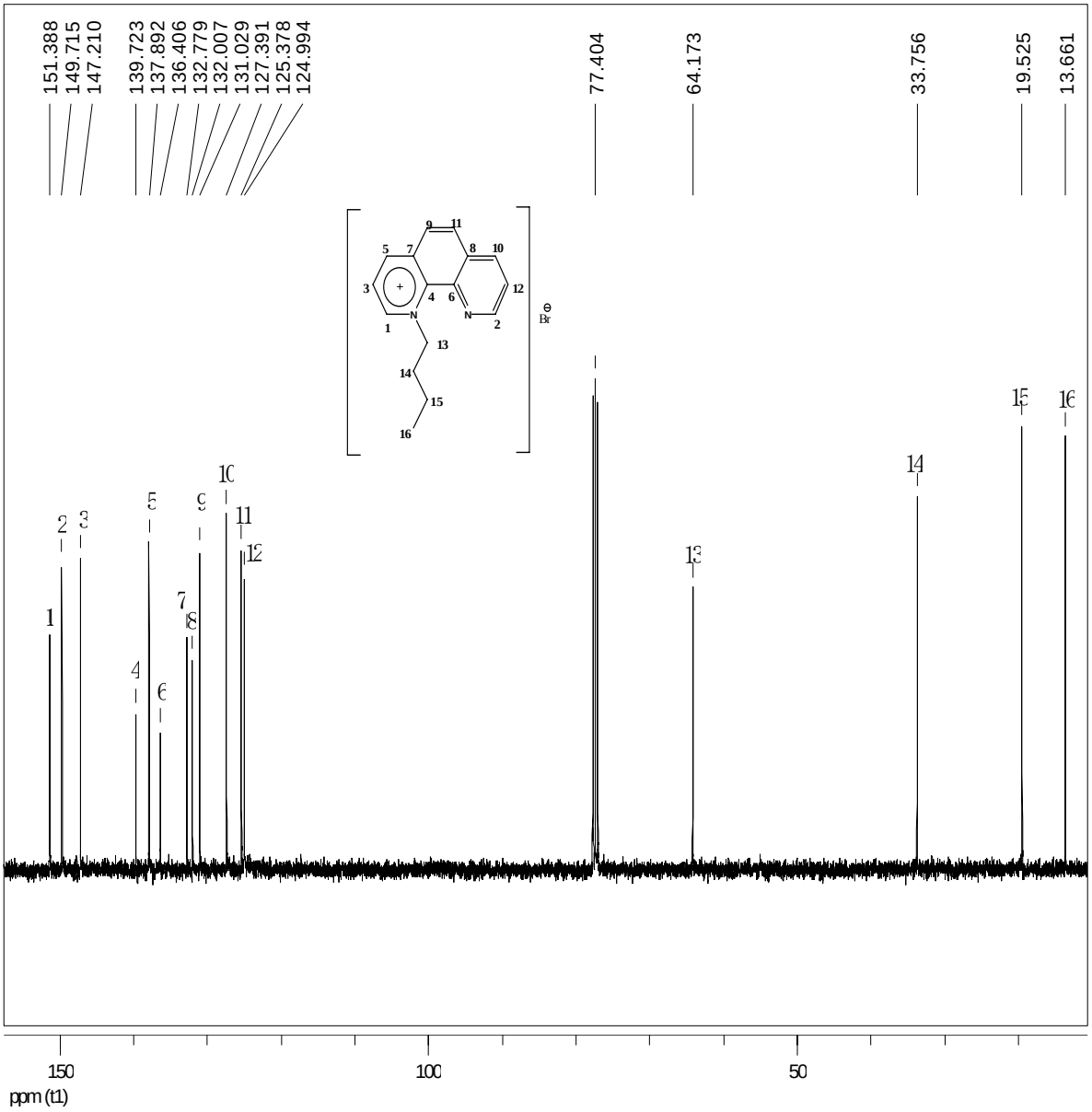


Figure 8. ^{13}CNMR spectrum of C_4phenBr

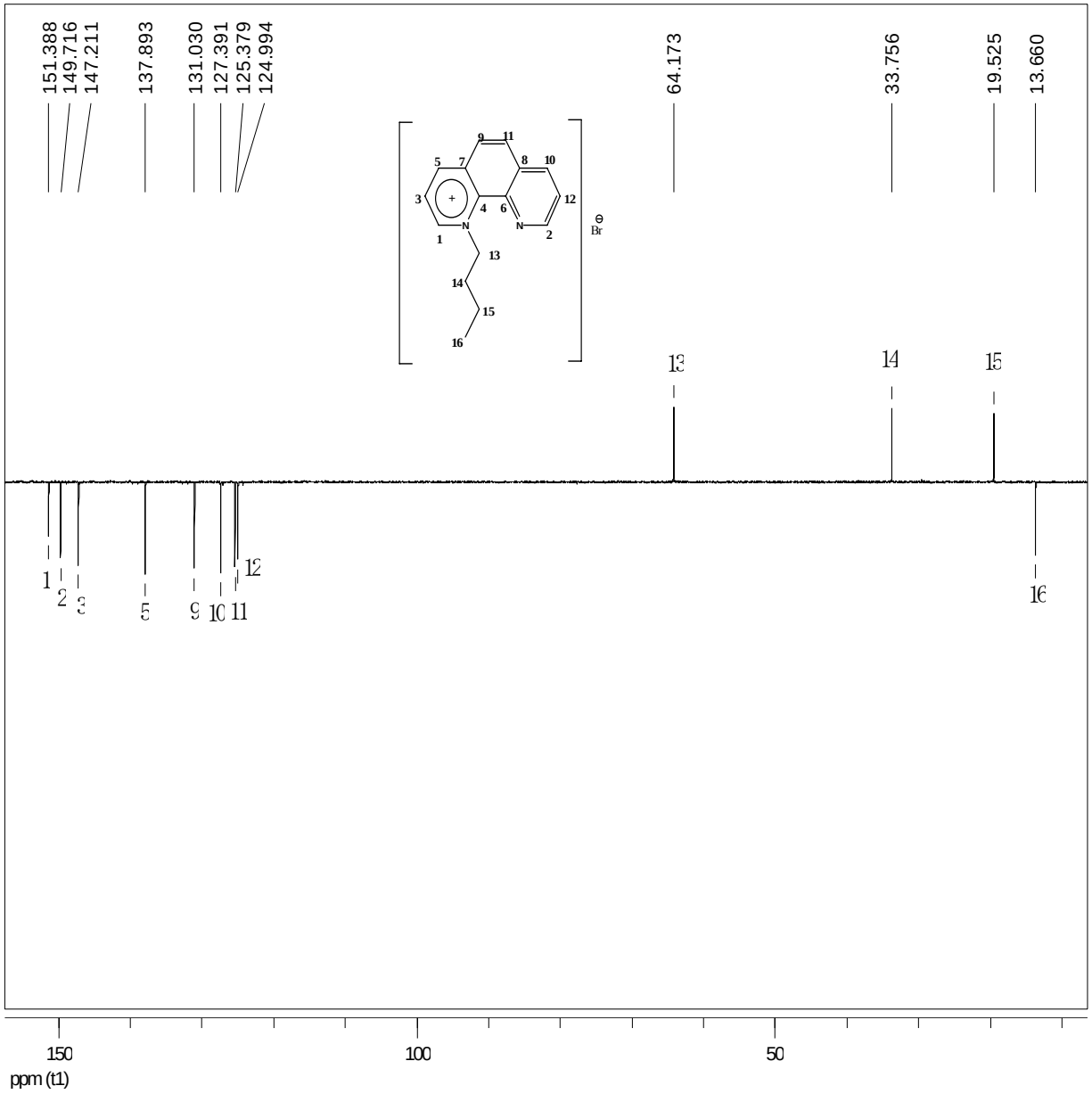


Figure 9. DEPT spectrum of C_4phenBr.

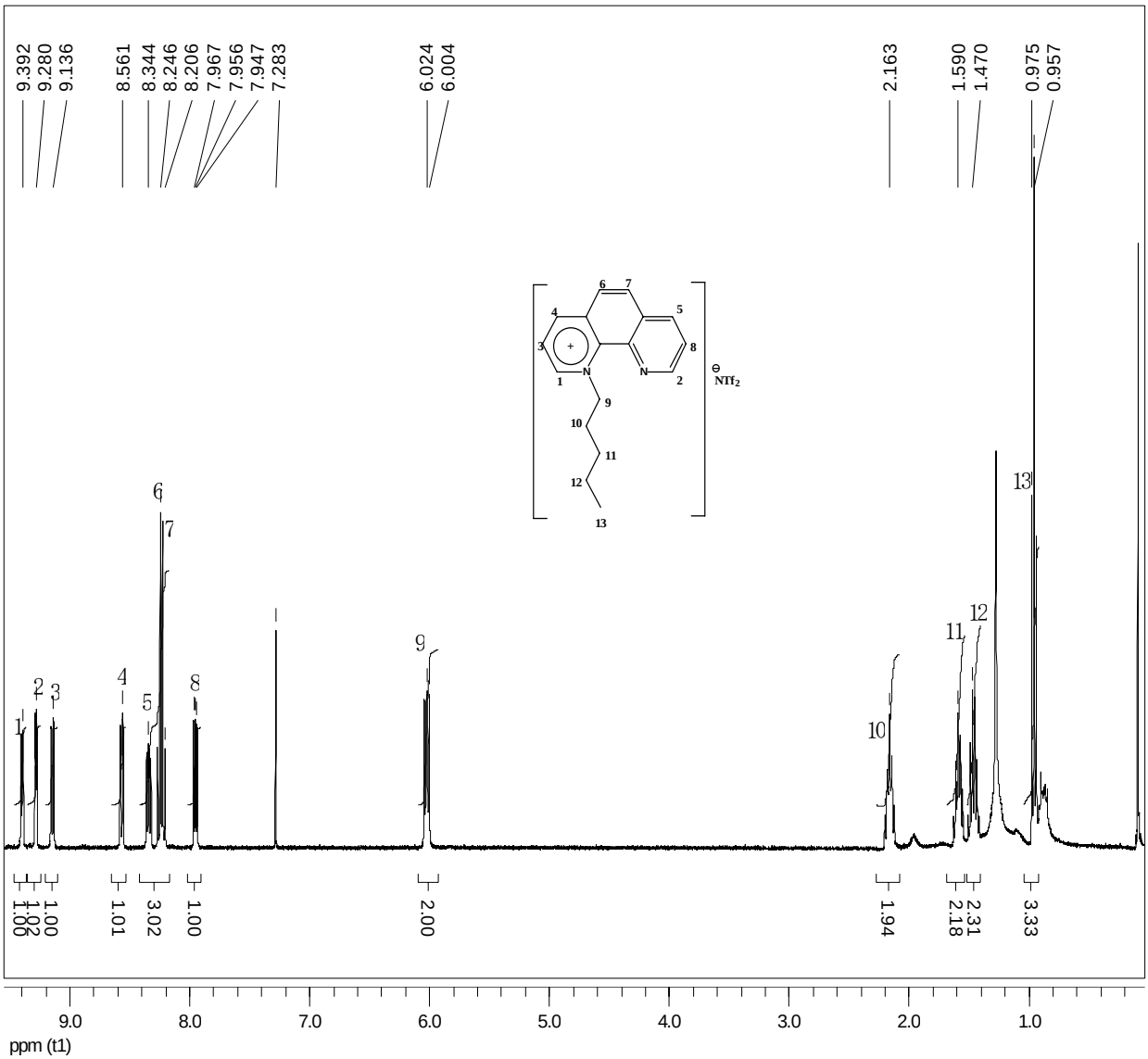


Figure 10. ^{1}H NMR spectrum of $C_5phenNTf_2$.

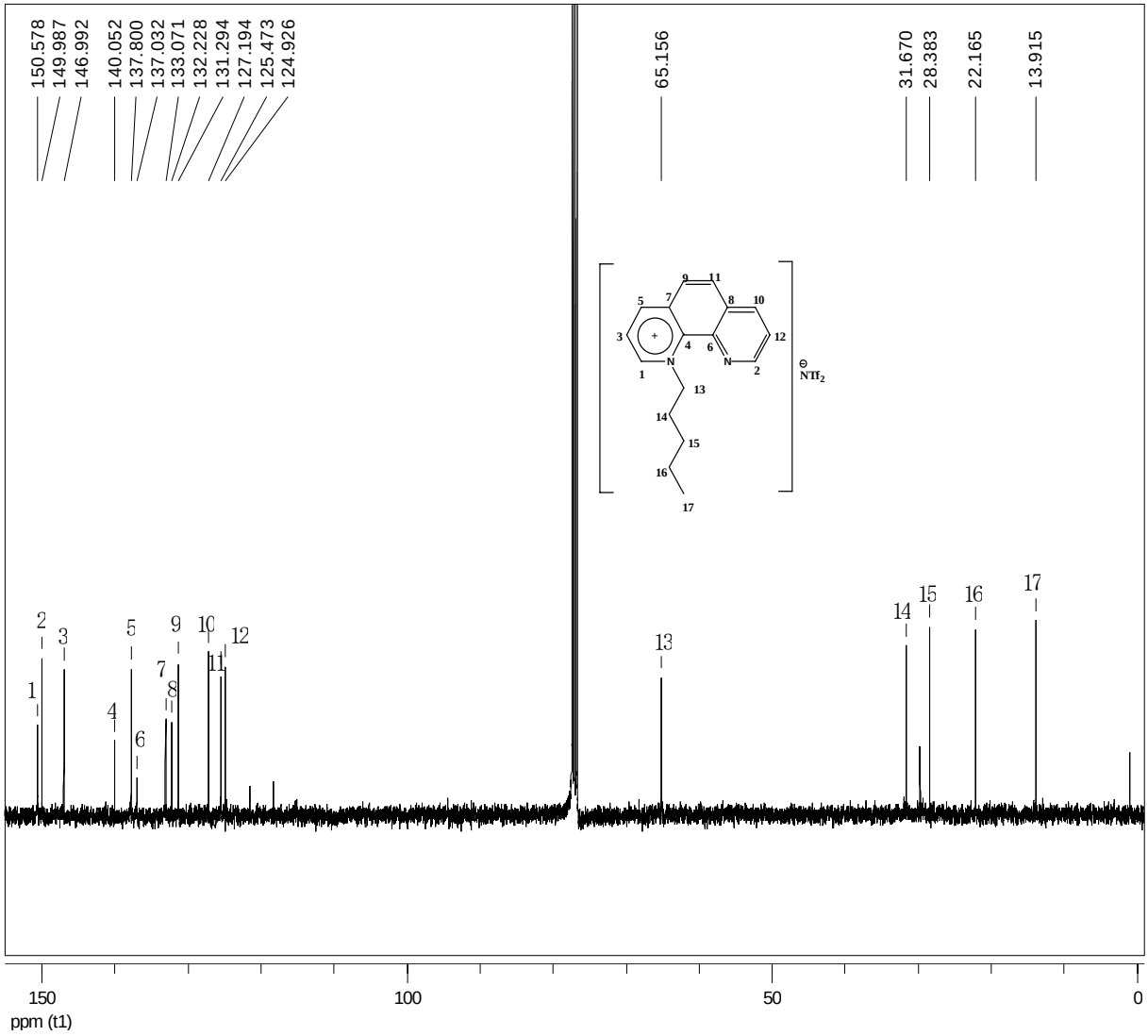


Figure 11. ^{13}C-NMR spectrum of C_5phenNTf$_2$.

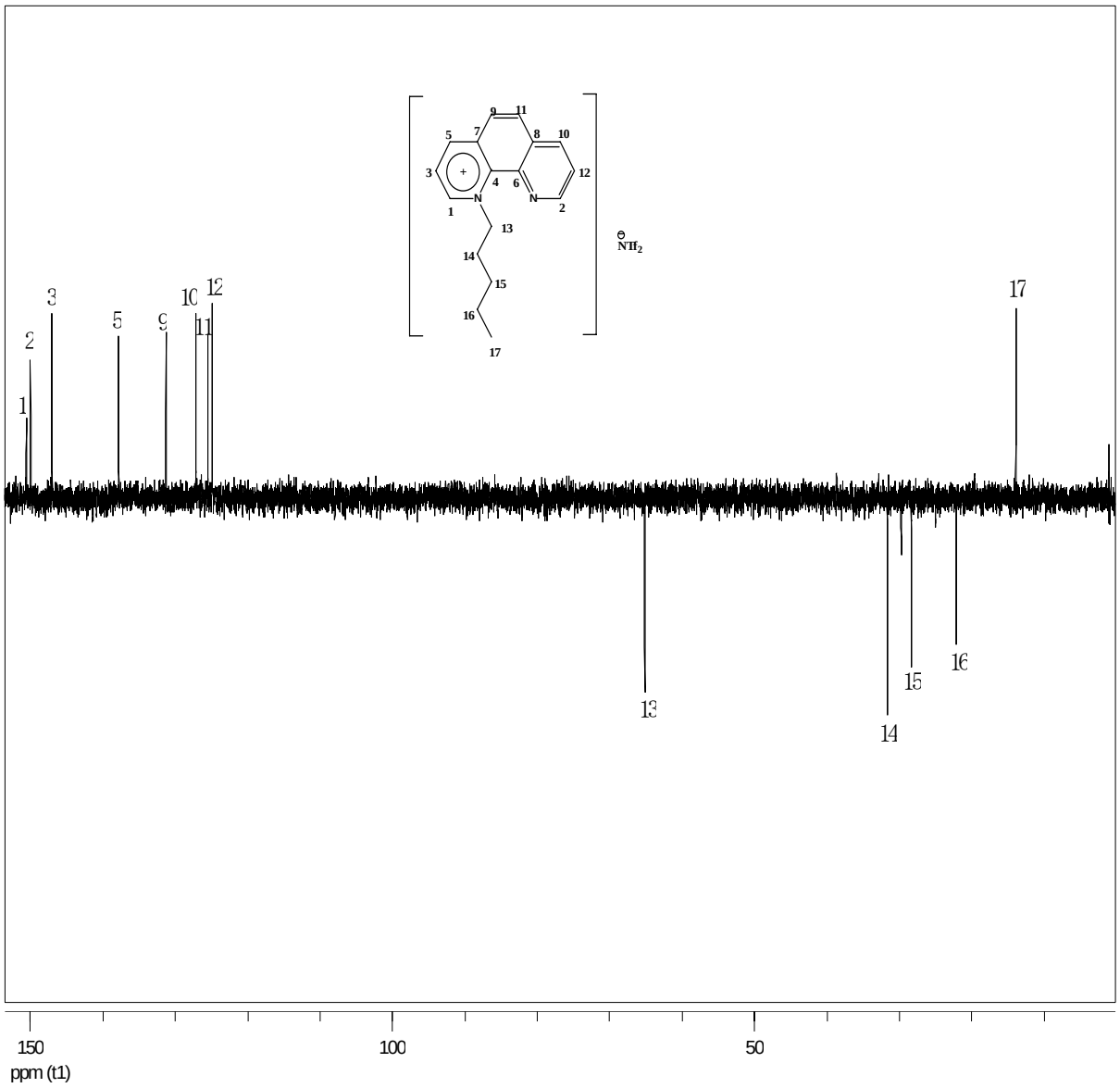


Figure 12. DEPT spectrum of C_5phenNtf$_2$

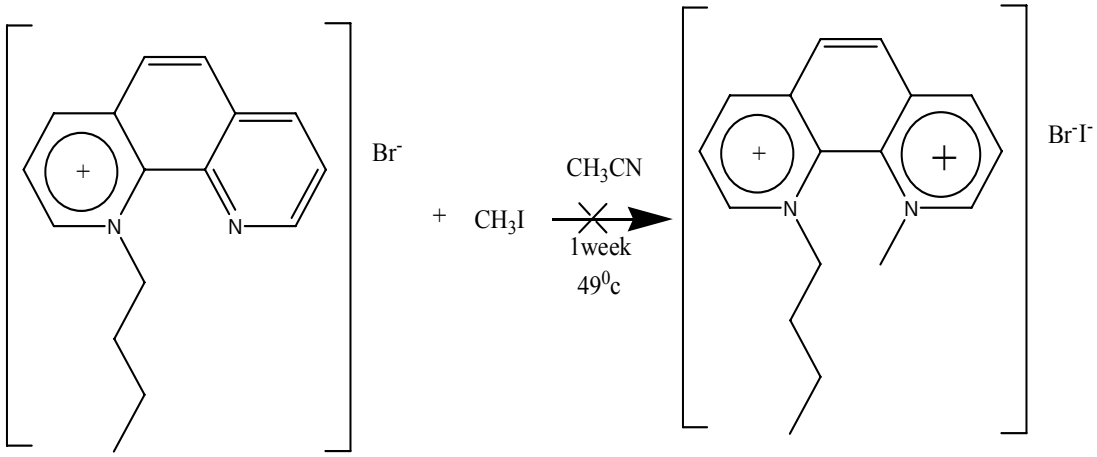
The ^{1}HNMR spectrum of butylphenanthroliniumbromide, C_4phenBr, showed 8 sharp signals (fig.8) corresponding to aromatic regions and four signals for the alkylated butyl bromide. The ^{1}HNMR run for the n-Bromobutane alone shows chemical shifts at δ=0.85, 1.45, 1.80, and 3.20(Aldrich). But here it is found to be more down field than it was alone indicating that it is attached to some electronegative element, nitrogen in this case. Moreover, the ^{1}HNMR spectrum for the phenanthroline alone exhibits shifts pertaining to

4 equivalent protons at δ=9.187, 9.245, 7.762, 7.616 and ^{13}CNMR at δ=150.4, 146.3, 136.1, 128.7, 126.6 and 123.2 due to symmetry in the molecule, but in the present study, the aromatic region shows 8 signals due to loss of the symmetry caused as a result of monoalkylation. The ^{1}HNMR spectrum also shows that phenanthroline is not dialkylated. Had it been the case, the ^{1}HNMR would have shown 8 signals; 4 in the aromatic and 4 in the aliphatic region, the symmetry remaining intact. Generally, the ^{1}HNMR spectrum corresponds exactly to monoquaternary salt. The ^{13}CNMR spectrum of the corresponding C_4phenBr showed 8 signals (fig.9) for aliphatic hydrogens. Aromatic carbons appear in their respective region. C_3PhenBr and C_5PhenBr have also shown similar behavior.

The monoquaternized salts underwent metathesis reaction with slight excess of $LiN(SO_2CF_3)_2$ in water at room temperature. After the completion of the reaction, the white precipitate was filtered. The Organic phase is washed several times with water to extract NaBr salt from it. Finally the pure product was filtered and desiccated. Chemical shifts proton of monoquaternary liquid containing pentyl substitution are recorded this are soluble in acetone acetonitrile but insoluble in water (table-1). It is found that the acidic protons of C_5PhenBr salt shifted towards up field, Br^-> Tf^- this might be due to less electronegativity as well as the bulkiness of triflate anions, as a result Br^- is better hydrogen bond acceptor than $N^-(SO_2CF_3)_2$ salts. When the alkyl side chain as well as anion was changed changes in chemical shift are observed. Table 4 and 5. It was also evident from the NMR data that all the halides used in the present study were efficiently converted in to the corresponding monoquaternary salts.

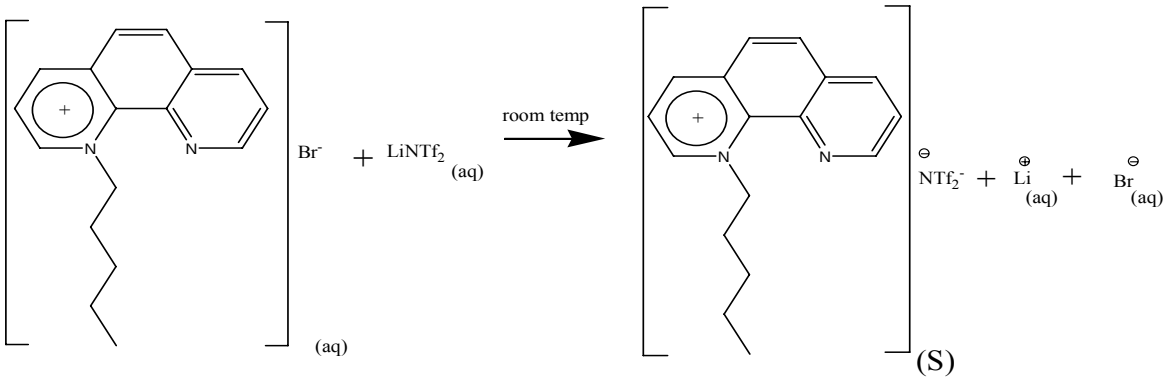
We have also tried to dialkylate the previously alkylated monoquaternary salt (butylphenantrolinium bromide) with a different alkyl halide, CH_3I, so that asymmetrical Cations will result in the formation of ionic liquids with much lower melting point. The reaction mixture was covered with aluminum foil to prevent photo degradation and stirred for a week (scheme.3). No diquaternary salt was formed even upon addition of more idomethane with continuous heating at a temperature of 49^0C, taking its boiling point in to account, for longer period of time, 1 week. These results are understandable interims of combination of electronic and steric effects [19]; significantly, steric effects

of the already alkylated butyl substituent. The incoming alkyl group encounters sever steric hindrance from the previously alkylated group which renders it less accessible for the second nucleophilic attack. To make matters even worse, the positive charge developed as a result of monoalkylation induces positive charge on the other side of the molecule making it weaker nucleophile. The electronic effects on the quaternization reaction rates is largely of inductive [19]



Scheme.2. Reaction condition of second alkylation failed

Subsequent metathesis reaction with $LiNTf_2$ resulted in the formation a salt containing the bis-(trifluoromethylsulfonyl) imide as counter anion was completely soluble in acetone methylene Chloride and acetonitrile but insoluble in water. The other ionic liquids are prepared by the same procedure using bromopropane and n-bromopentane as an alkylation reagents. The synthesis of bis-(trifluoromethylsulfonyl) imide was accomplished via anion exchange metathesis reaction of the corresponding phenanntrolinium bromide. The proton and carbon spectra of the ionic liquid was consistent with the chemical structure of C_5phenBr .The NMR spectra obtained for this ionic liquids were very similar to that of C_5phenBr .The similarity in NMR spectra is expected since only the anions were varied the C_5phenBr. As can be seen from tables-1 and 2 there is a general shift of ^{1}NMR spectrum towards upfield when the alkyl chains gets increased. This might be due to the greater electron donating property of longer alkyl chains.



Scheme 3. Metathesis reaction of C_5phenBr with $LiNTf_2$.

4.3. Melting point

The fact that the solid ionic liquids obtained upon changing the anion, demonstrated the tunability of the ionic liquid synthesized in this study by varying the anion or the cation. These results also demonstrate that bis (trifluoromethylsulfonyl) imide; C_5phenNTf_2 is probably a poorly coordinating anion with C_5phen^+ cation. The poor crystal packing between the anion and the cation result in lower melting point. This findings are in agreement with our results that $^-NTf_2$ being larger than bromide anion yielded a product that has lower melting point. Another factor which increases melting point is the presence or absence of hydrogen bond in the lattice. (The presence of CH---X- H-bonding in the structure of alkylimidazoliumbromide was first reported in 1986). Charge localization in the case of halides is also responsible for the higher melting point they exhibit but in the case of $^-NTf_2$ exchanged ones higher delocalization of charge reduces the melting point. Hence, halide salts tend to have much higher melting point than that of their bis-(trifluoromethylsulfonyl) imide counterparts. For alkylphenanthrolinium bromides having a carbon number of C_1 and C_2 (fig.13), the melting point is maximum and decreases from 210^0C to 180^0C. This can be rationalized by the fact that the short alkyl chains are located in charge rich region where columbic force of attraction is dominant and the molecule assumes almost symmetrical (spherical shape) which allows good packing of crystal lattices. A decrease to 124^0C for C_3 might be due to symmetry breaking region it contains and is away from charge rich region. But from this point onwards, it is the hydrophobic

region in which Van der Waal's interaction takes control and gives rise to an increase in melting point and on the top of that the symmetry starts to flourish again and a better packing will increase the melting point. For alkyl phenanntrolinium bis (trifluoromethylsulfonyl) imides (fig.14) the prediction of individual effect of each factor was not straightforward but it appears here that the columbic force of attraction is drastically decreased due to an introduction of NTf_2^- anion where charge delocalization is exhibited. Therefore, Van der Waal's force of attraction is responsible for the increase in melting point as the number of carbon atoms increase. But for carbon number 5, the decrease may be due to low Symmetry in the cation introduced as a result of its conformation thereby poor packing efficiency and needs further investigation. Generally, since a large and bulky anion is introduced here, the most dominant interaction would be van der Waal's force since this force expected to be larger with larger number of atoms involved.

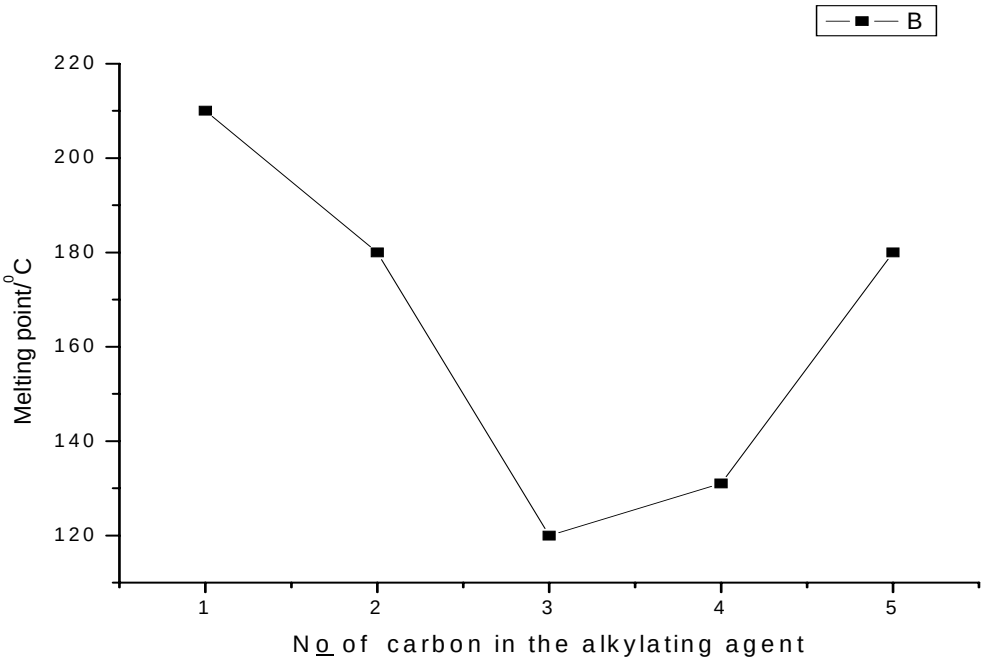


Figure 13. Melting point curve for alkylphenanthrolinium bromides.

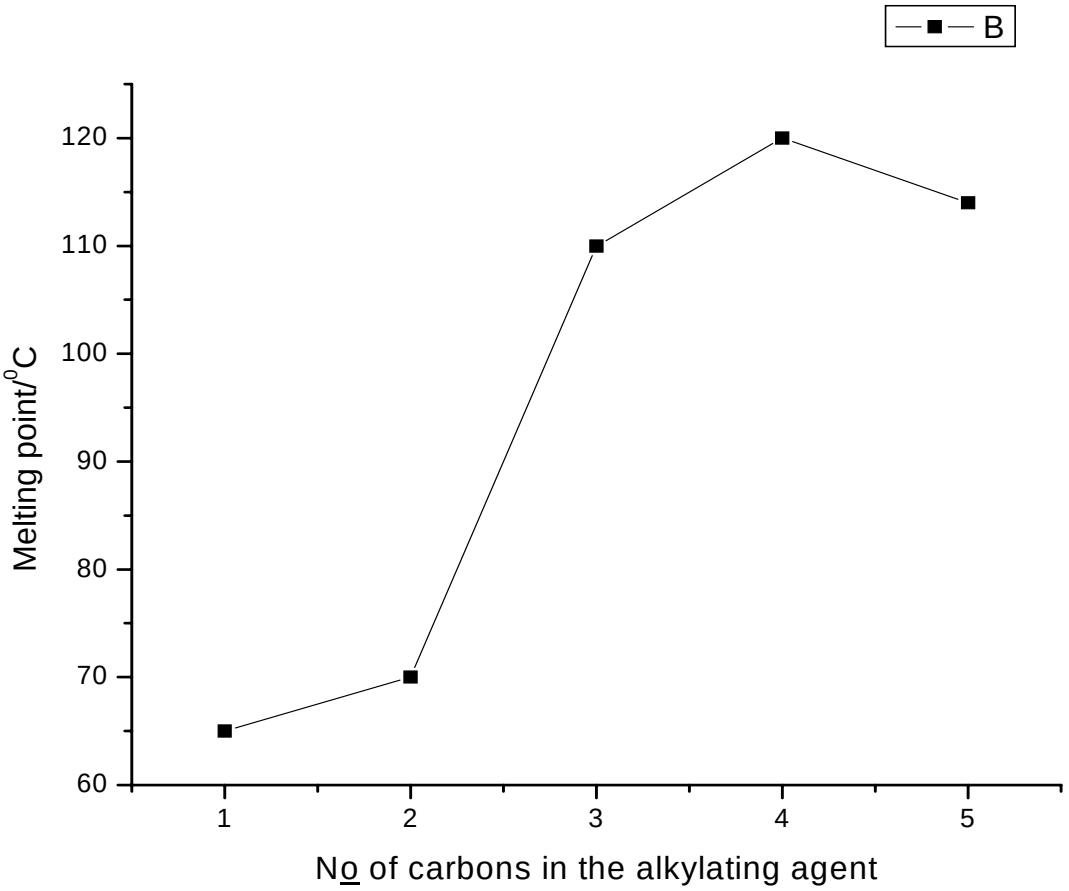


Figure 14. Melting point curve for alkylphenanthrolinium bis (trifluoromethylsulfonyl) imides salts.

5. Conclusion

New ionic liquids based on the monoalkylation of 1,10-phenanthroline were synthesized and their physical properties such as conductivity, solubility and halide test along with spectroscopic technique were investigated and are reported together with their characterization data. An attempt to dialkylate these salts failed due to steric and electronic effects developed as a result of monoalkylation, the former being the major one. These compounds were also analyzed by melting point and factors such as size of the anion, delocalization of the charge, interaction between the ions and disorder (asymmetry) in the cation were identified as reasons for the low melting points. The increase in alkyl chain length on the cation (charge rich, symmetry breaking and hydrophobic region) affected the packing and the interactions in the crystal lattice of these salts and thereby the observed melting point. The chemical shifts for the most acidic hydrogens (directly attached to nitrogen) of these salts were also investigated and found to be shifted depending on both the anion and alkyl chain length. Interactions between the solvent and phenanthrolinium salts of pentyl substituent are observed at higher chemical shifts than the corresponding propyl and butyl substituent. The same is true for the NTf_2 exchanged ones, they are found to be more upfield than their bromide analogues.

The salts synthesized have shown different physical properties such as meting point and solubility up on exchange with a different anion, NTf_2^-. Therefore, it is forecasted that further exchange with other anions like BF_4^- and PF_6^- would probably result in the formation of compounds with melting point less than 100^0C and this will facilitate their use in homogeneous catalysis.

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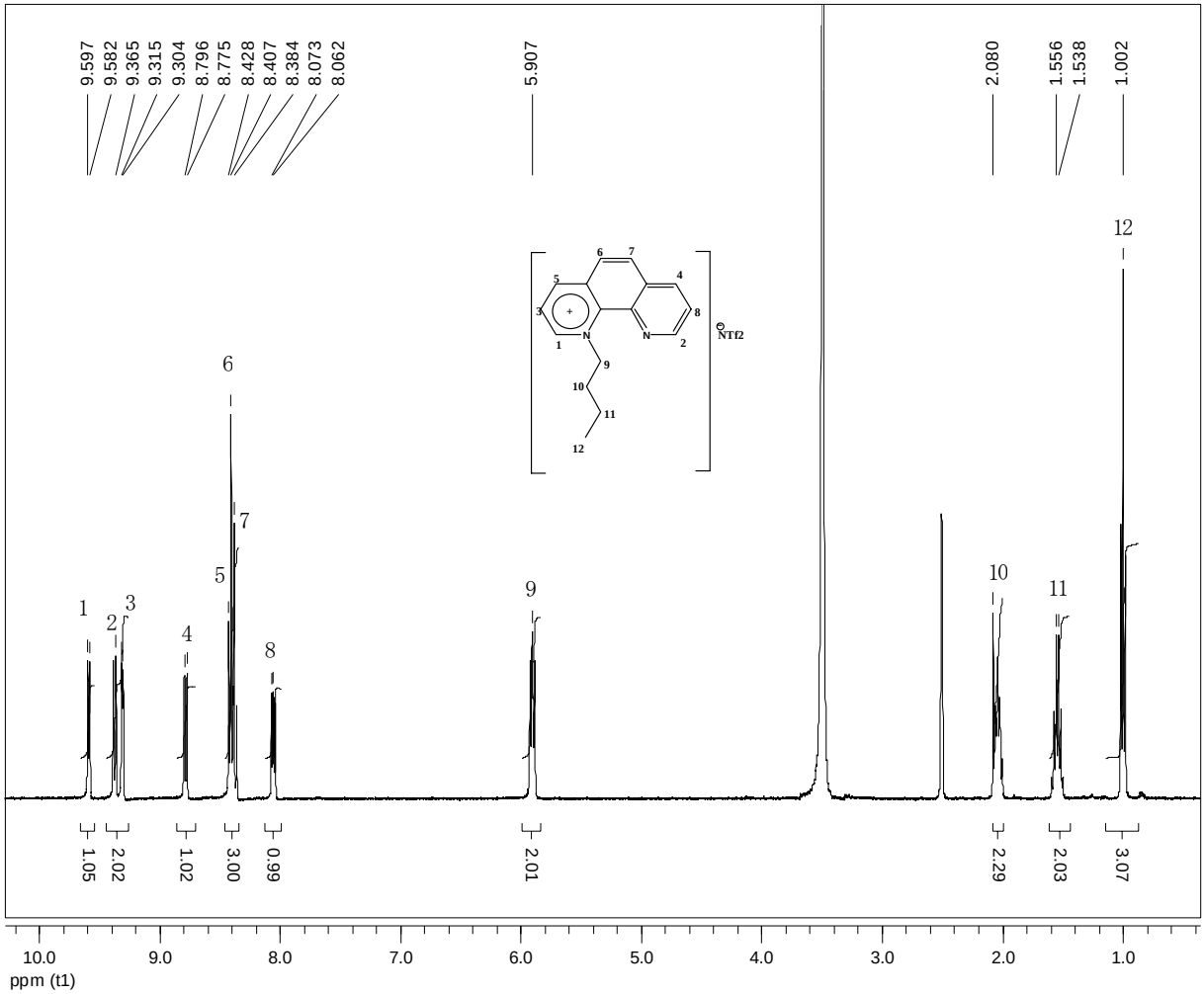
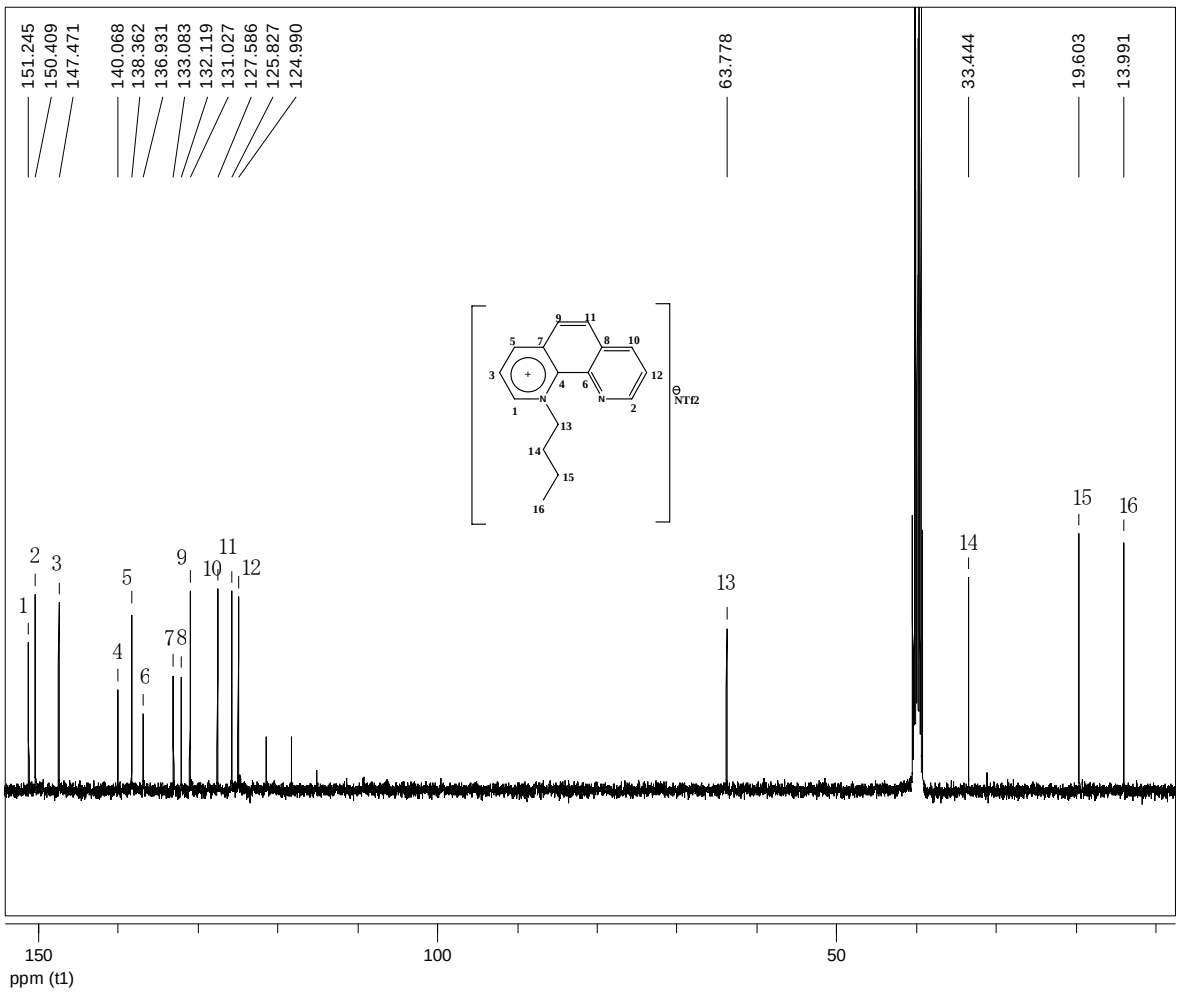
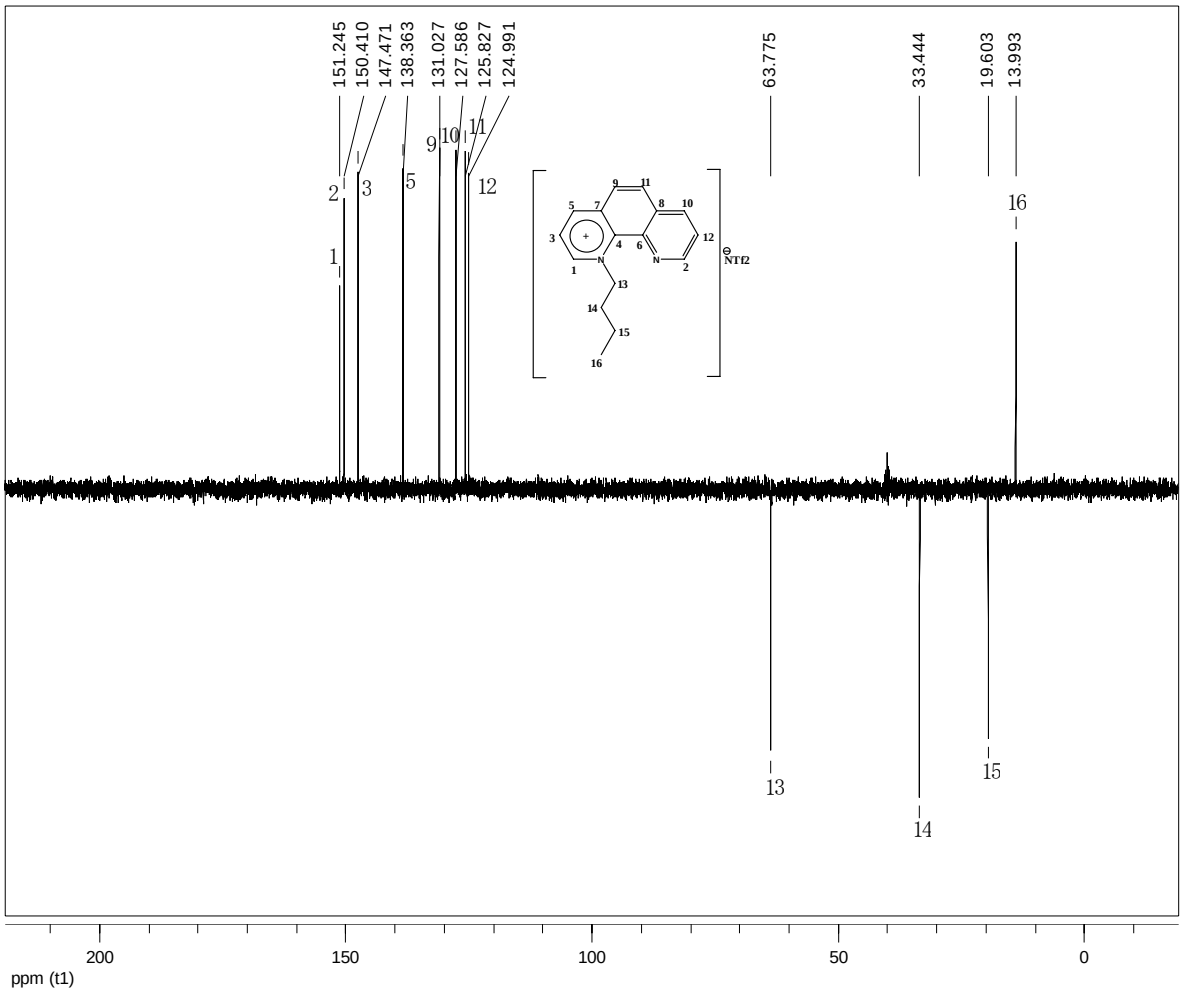
Appendices



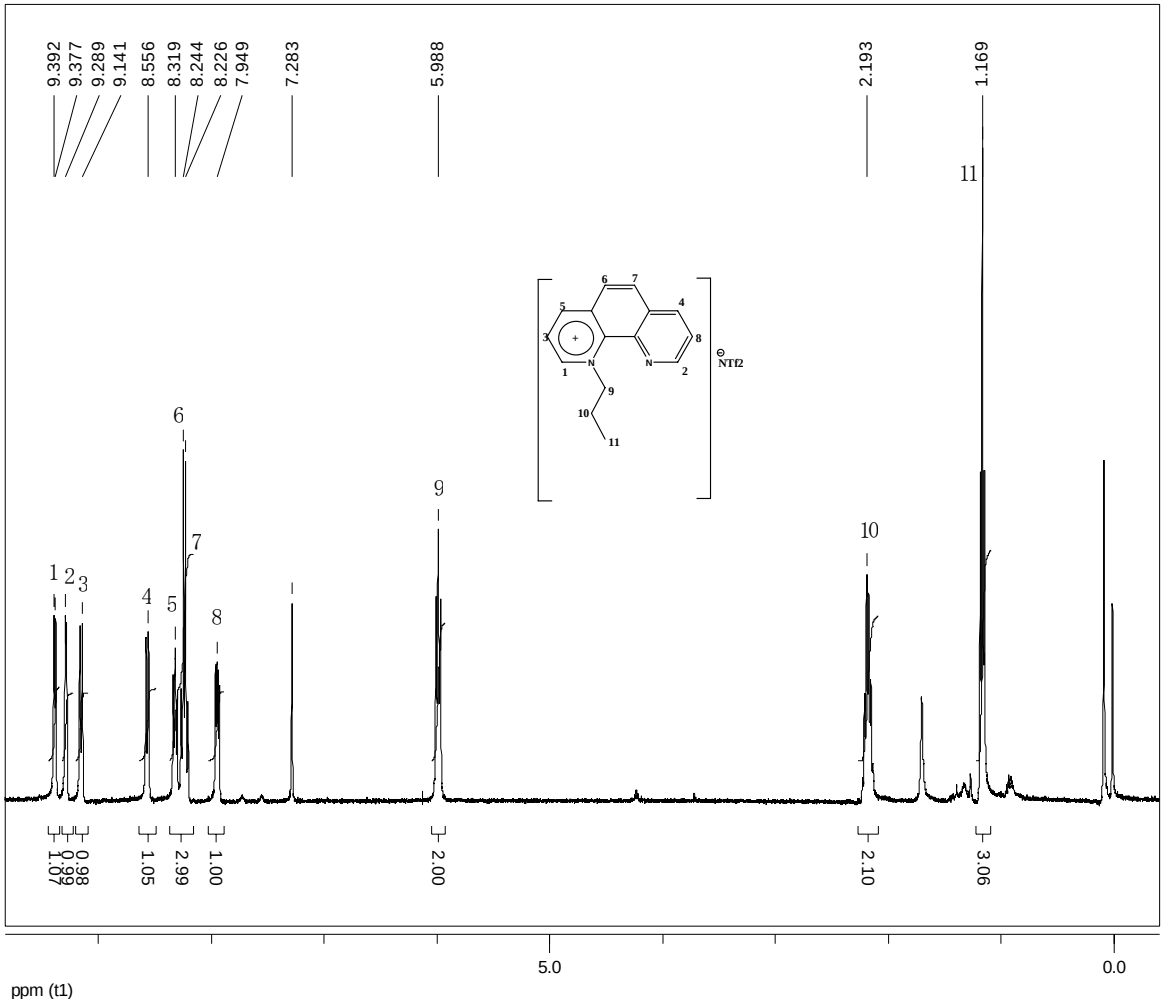
Appendix 1. ^{1}H NMR spectrum of $C_4phenNTf_2$



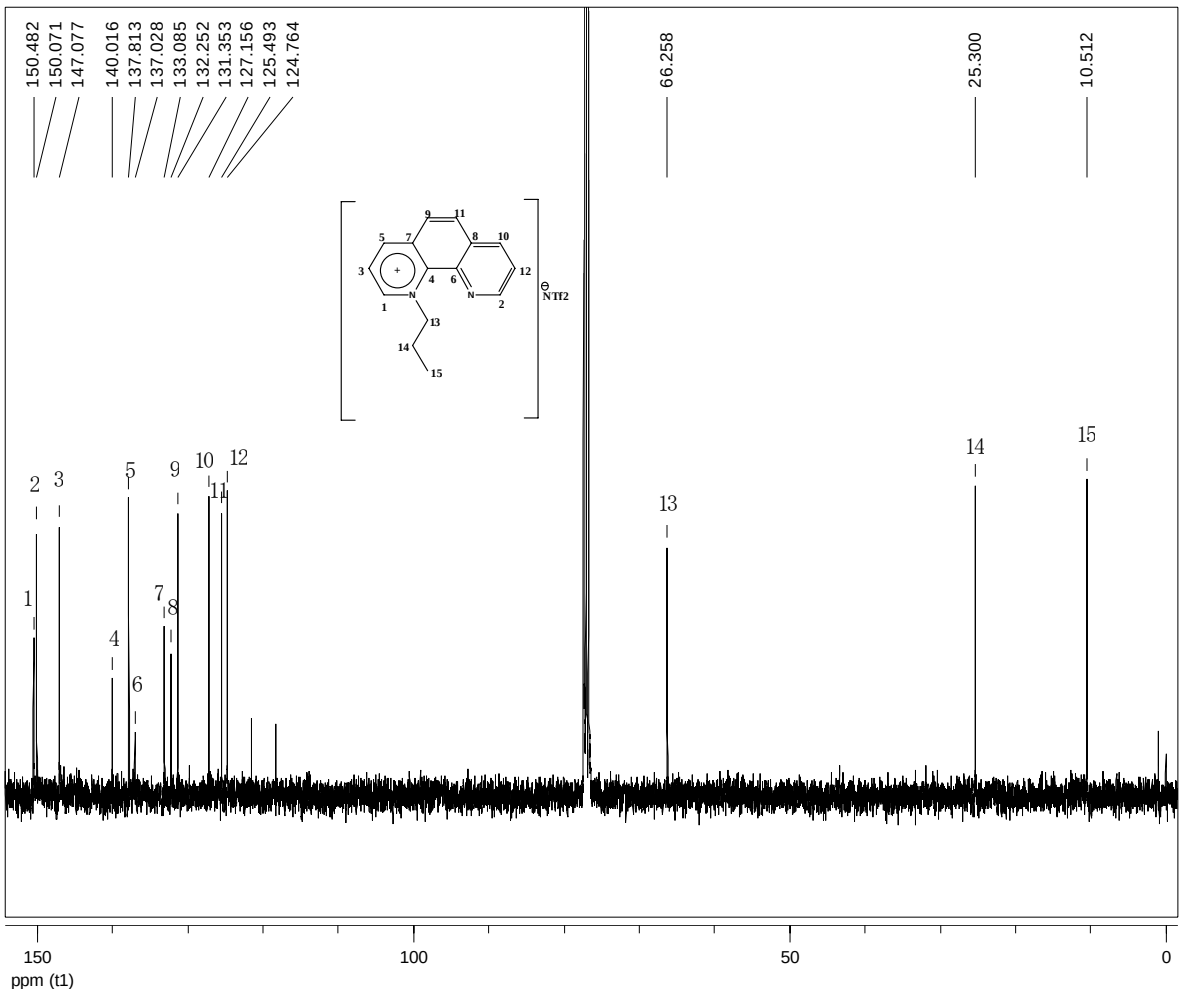
Appendix 2. ^{13}C NMR spectrum of $C_4phenNTf_2$



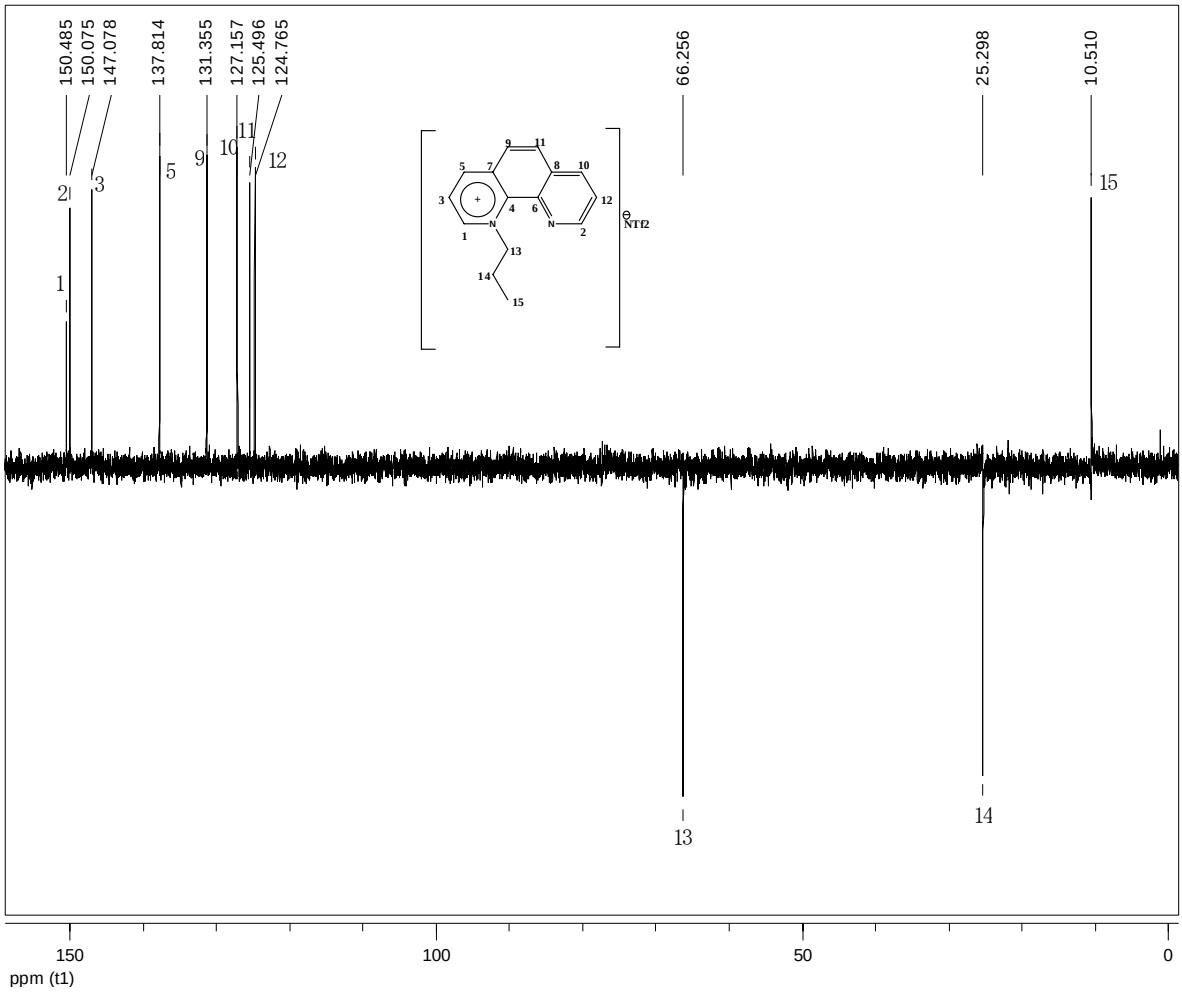
Appendix 3. DEPT spectrum of C_4phenNTf_2



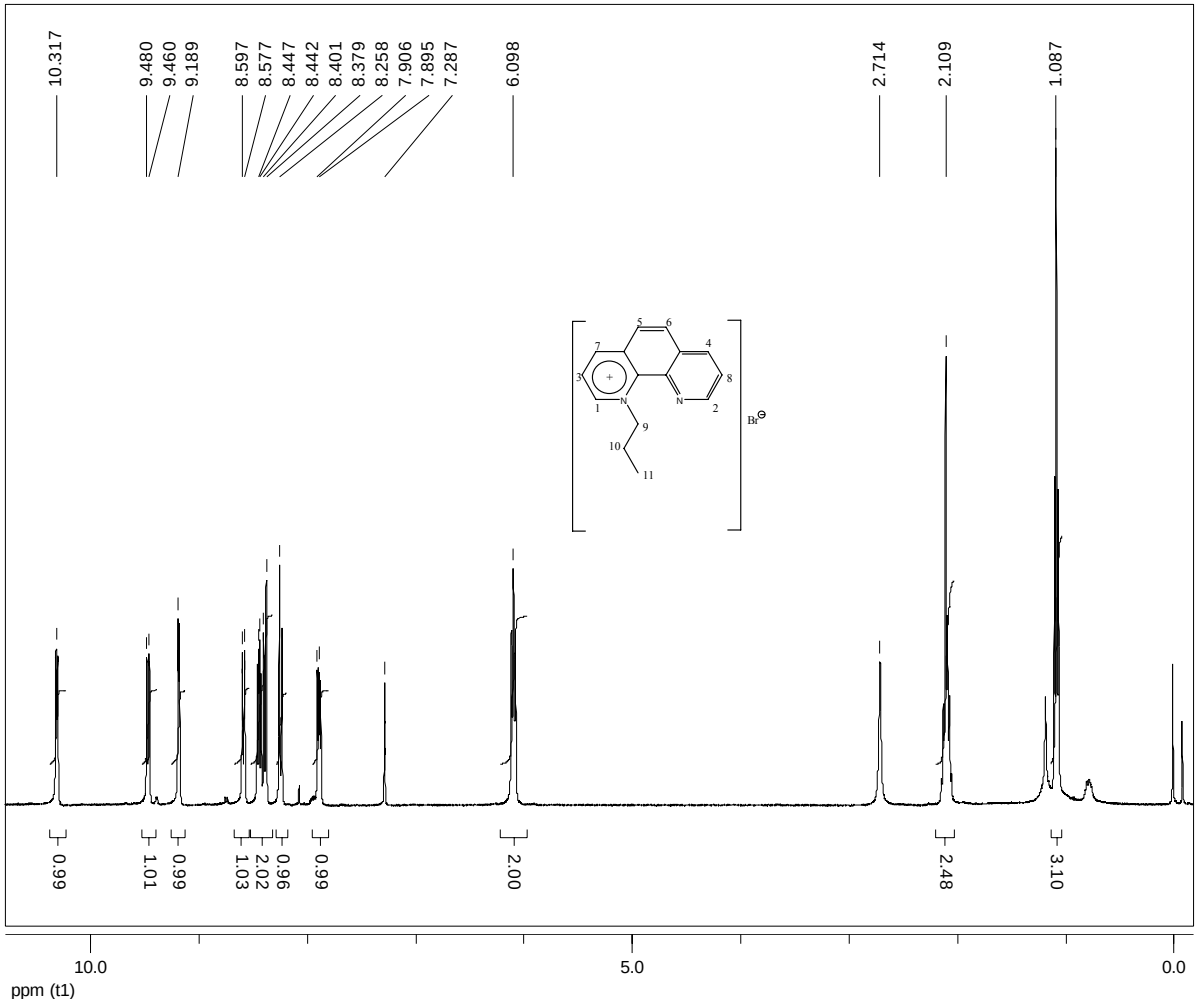
Appendix 4. ^{1}H NMR spectrum of C_3phenNTf_2



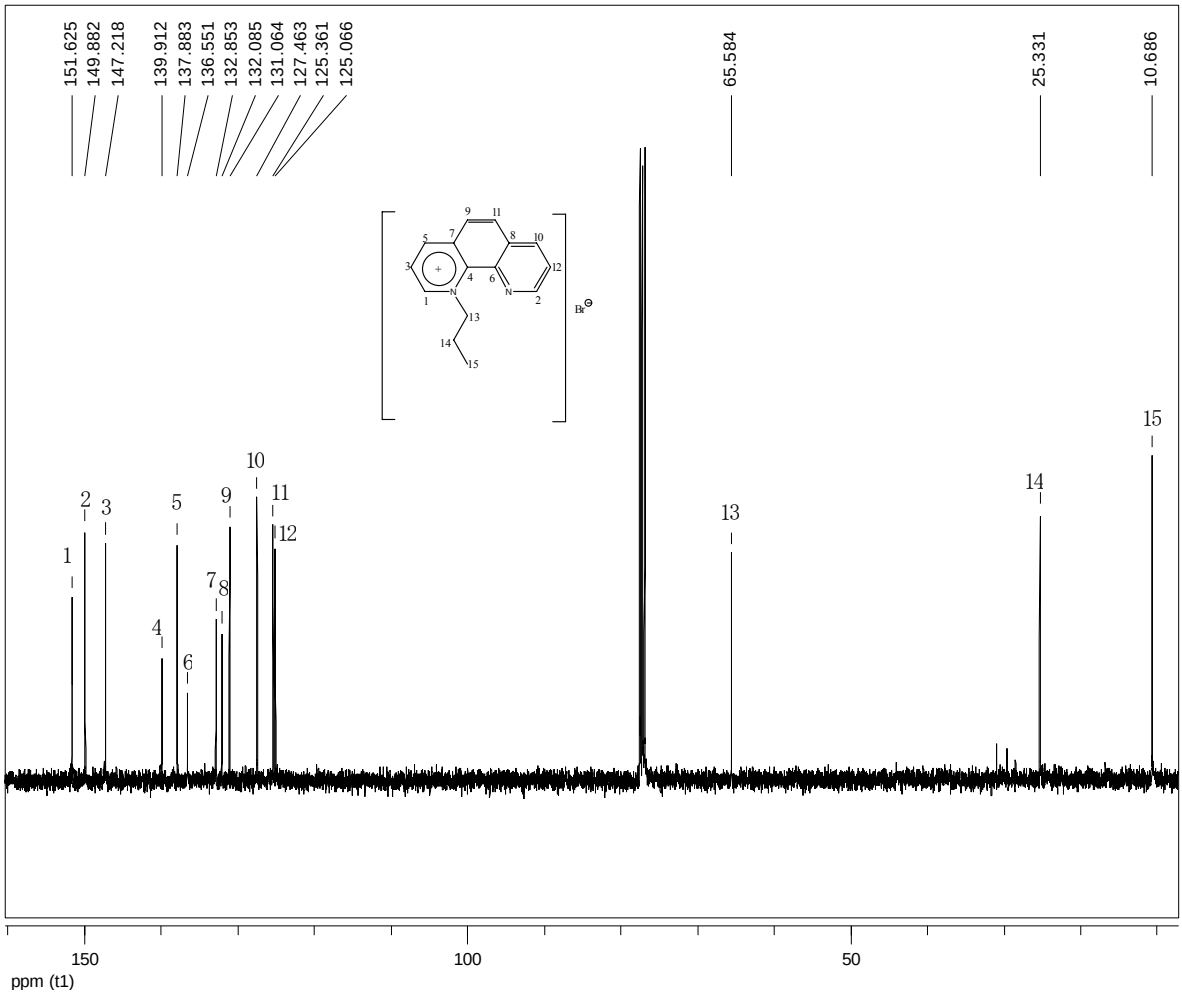
Appendix 5. ^{13}C NMR spectrum of $C_3phenNTf_2$



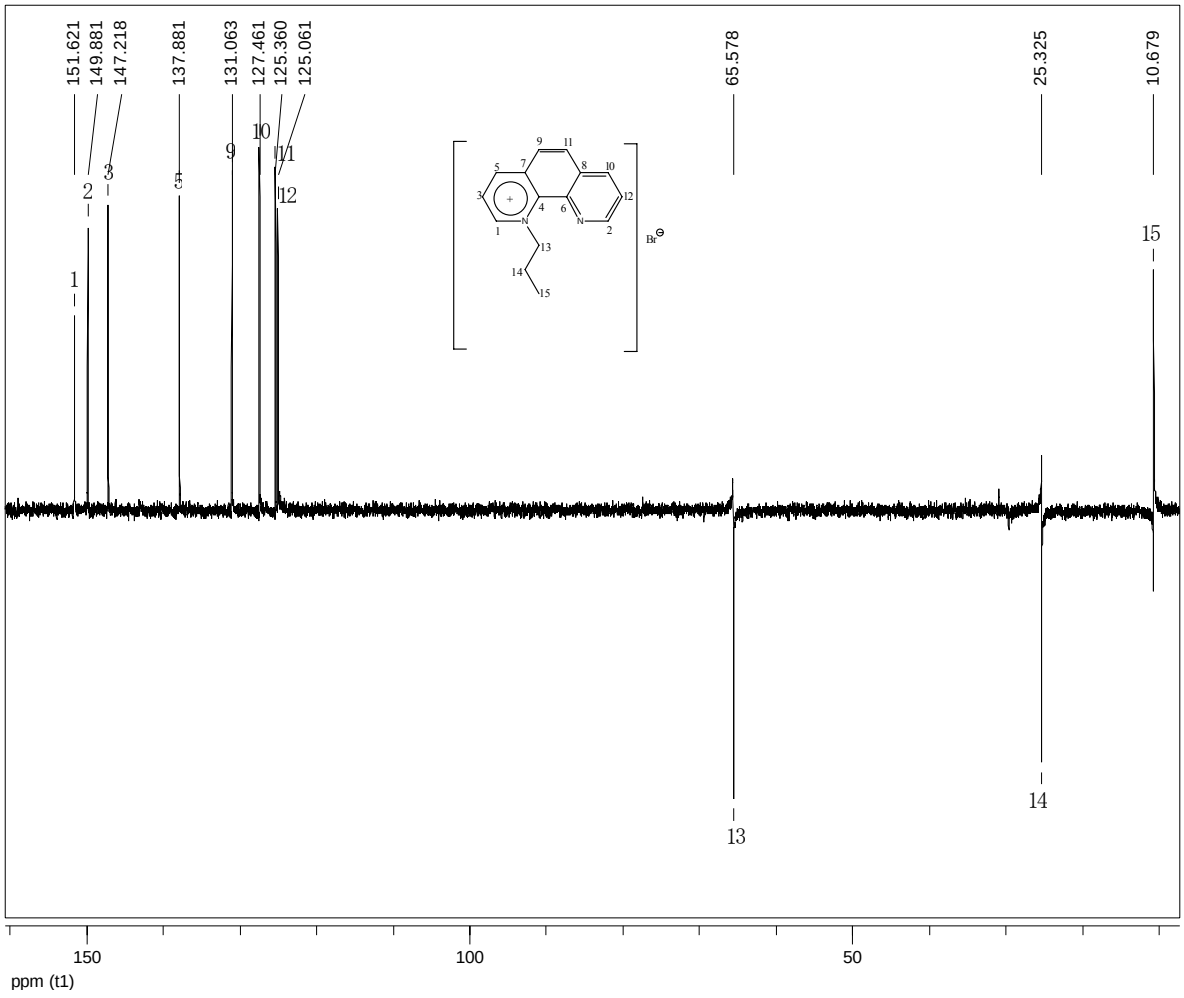
Appendix 6. DEPT spectrum of C_3phenNTf_2



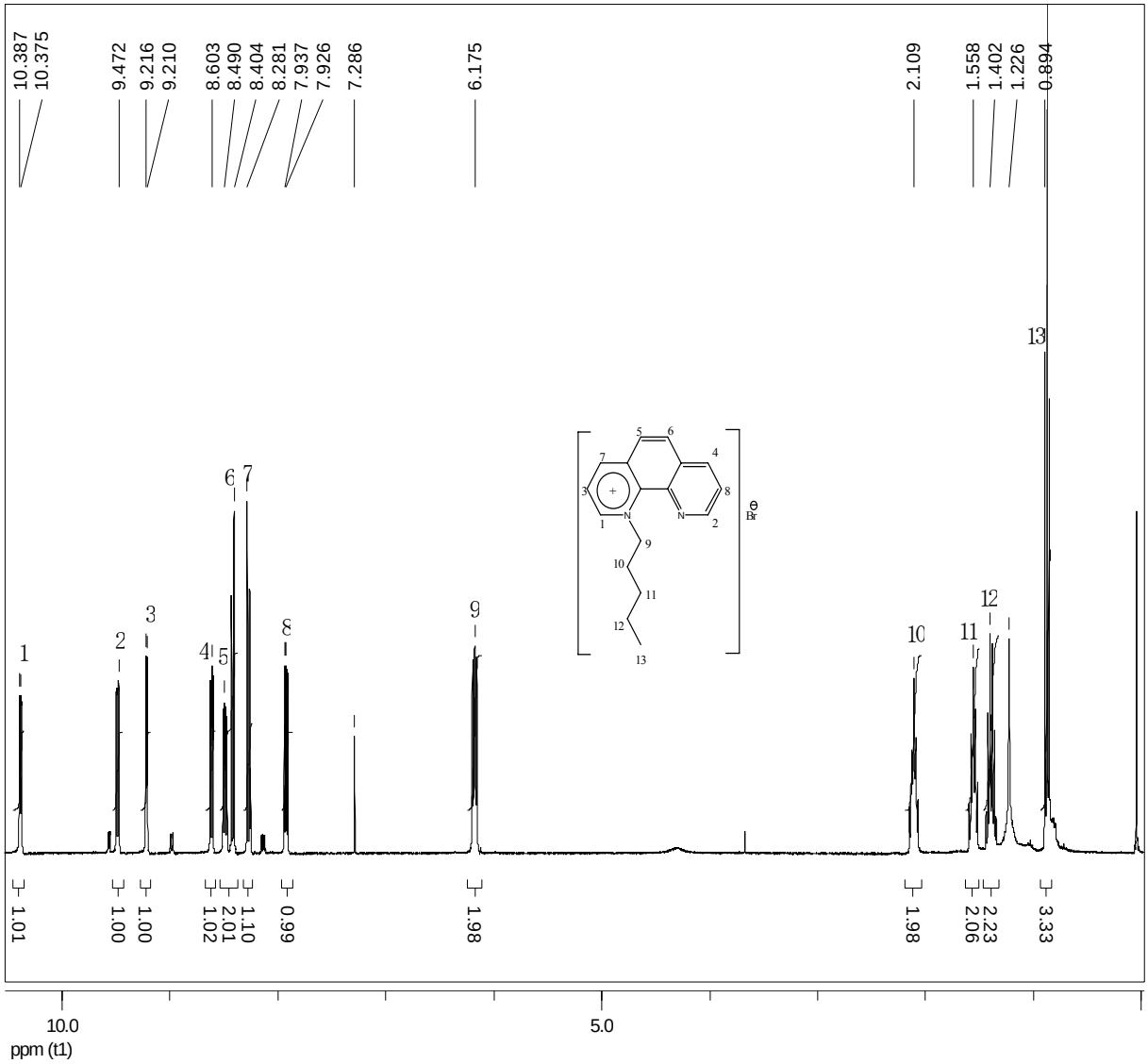
Appendix 7. ^{1}HNMR spectrum of C_3phenBr



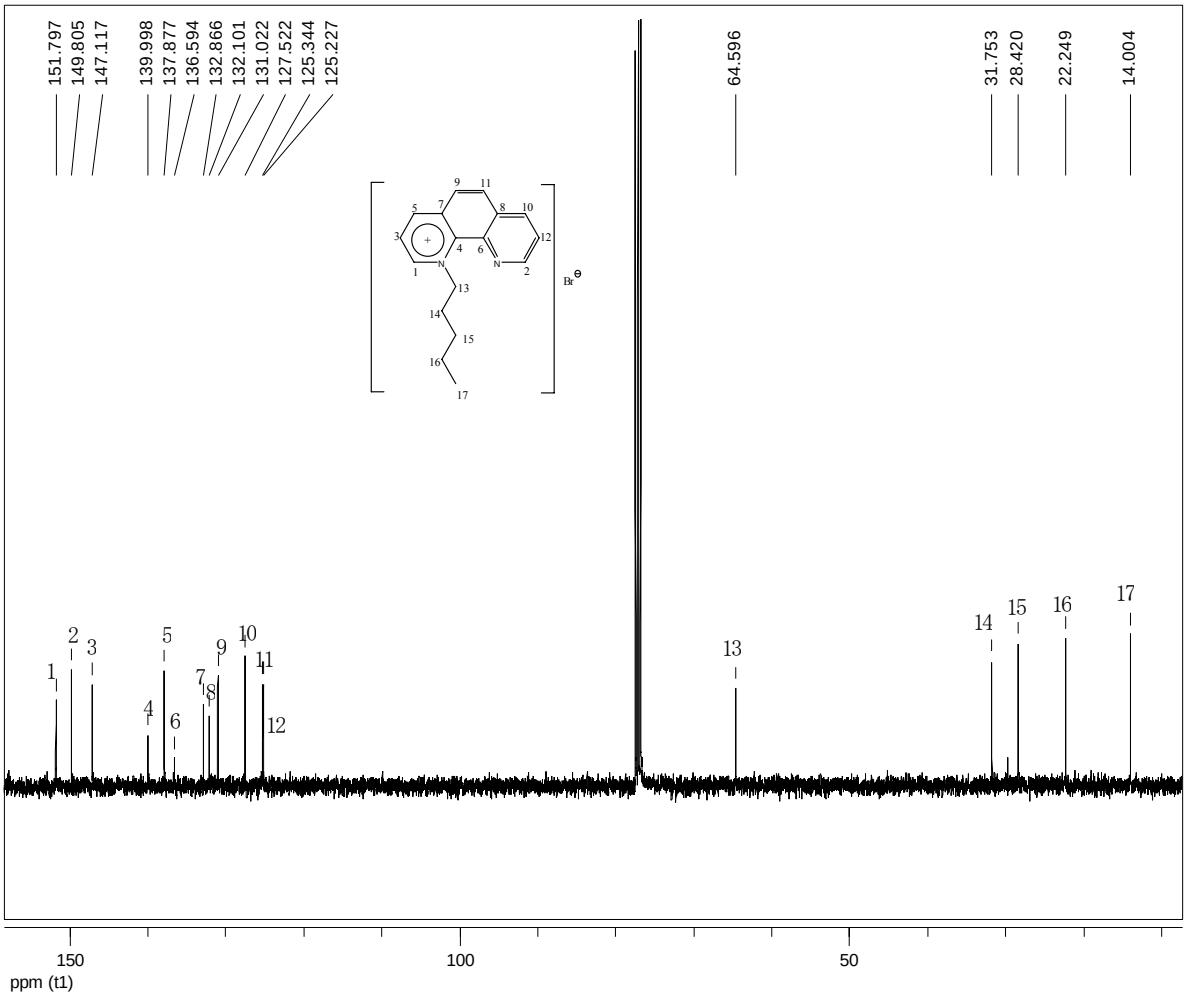
Appendix 8. ^{13}CNMR spectrum of C_3phenBr



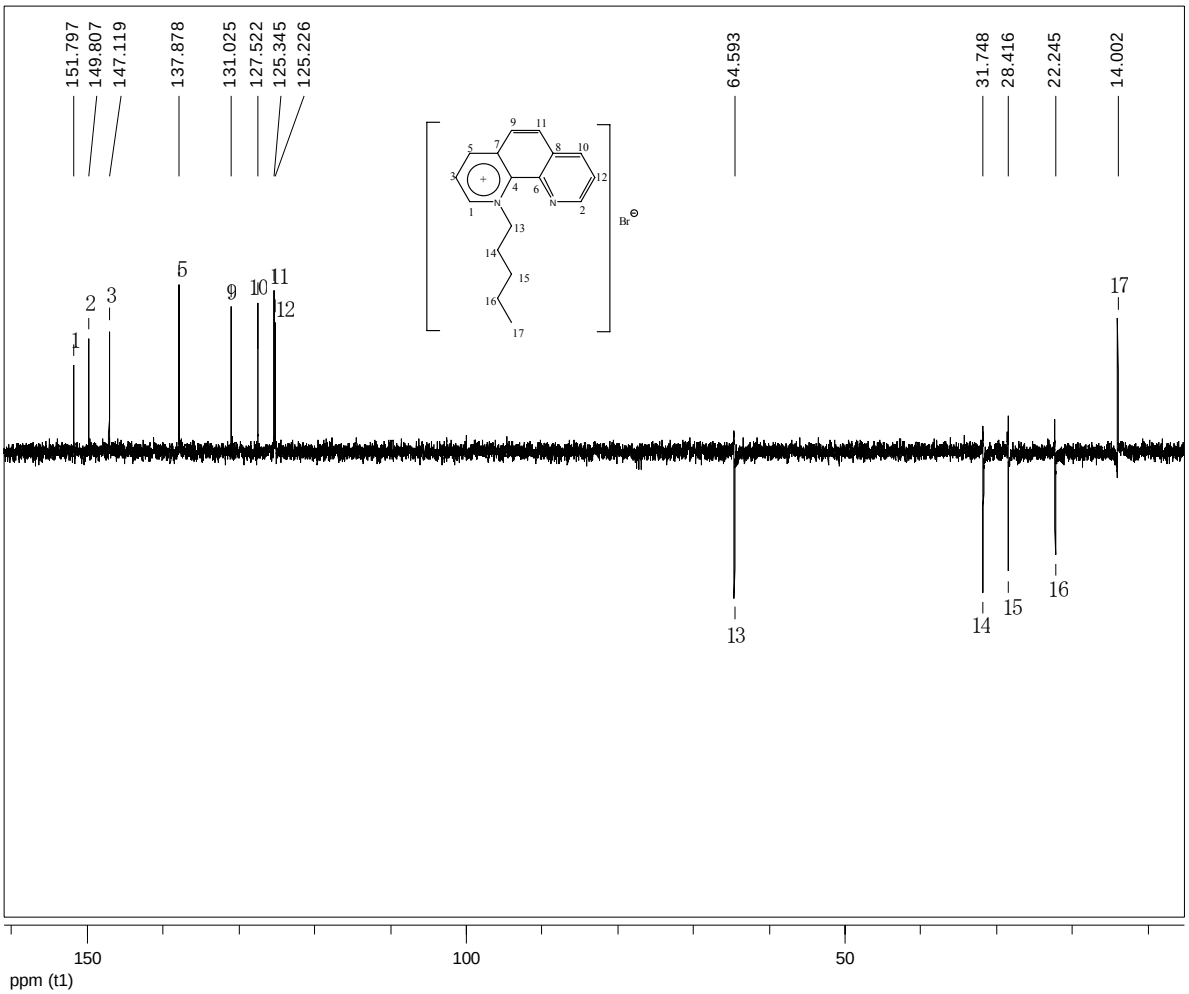
Appendix 9. DEPT spectrum of C_3phenBr



Appendix 10. ^{1}HNMR spectrum of C_5phenBr



Appendix 11. ^{13}CNMR spectrum of C_5phenBr



Appendix 12. DEPT spectrum of C_5phenBr