Synthesis and Characterisation of Anthracene Tagged Imidazolium Derivatives

A Project Report Submitted

as part of the requirements for the degree of

MASTER OF SCIENCE

By

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Under the supervision of

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to the

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. G. PRABUSANKAR.**

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Signature of the student

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Approval Sheet

This thesis entitled **Synthesis and Characterization of Anthracene Tagged Imidazolium Derivatives** by *Sahil Dudeja* is approved for the degree of Master of Science from IIT Hyderabad.

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SAHIL DUDEJA

Abstract

Six new novel anthracene tagged imidazolium derivatives were successfully synthesized and characterized. [9,10-bis{(N-ethoxycarbonylphenylimidazolium)methyl}anthracene] dichloride and [9,10-bis{(N-isopropylimidazolium)methyl}anthracene] dichloride were readily synthesized in very good yield by treating 9,10-bis(chloromethyl)anthracene with corresponding ethoxycarbonyl phenyl imidazole or N-isopropyimidazole , respectively. The anion exchange reaction of [9,10-bis{(N-ethoxycarbonylphenylimidazolium) methyl} anthracene]dichloride and [9,10-bis{(N-isopropylimidazolium)methyl}anthracene] dichloride with potassium hexafluorophosphate gave hexafluoro phosphate salt of [9,10-bis{(N-ethoxycarbonylphenylimidazolium)methyl}anthracene] and [9,10-bis{(N-iso propylimidazolium)methyl}anthracene] in excellent yields.

Contents

1. INTRODUCTION

The design and synthesis of imidazolium based anion selective receptors or sensors is a topic of great current interest in molecular recognition research. In contrast to the anion recognition by positively charged ammonium and guanidinium groups as binding sites interacting with the anions by either electrostatic forces or with N^+-H- - -anion hydrogen bonds a number of positively charged imidazolium derivatives were synthesized and studied for selective anion-receptors [1]. The first examples of dicationic heterophanes based on imidazolium units as molecular recognition entity for anion recognition were reported by Alcalde et al [2] followed by Sato et al. [3] who reported benzene based tripodal imidazolium receptor for anion recognition in the same year. These anion recognition units can be differentiated on the basis of their target analyte such as ATP and DNA as well as on the basis of their structure and topology such as benzene tripodal system, cyclophane system and calix-imidazolium system, fluorescent imidazolium system, ferrocenyl imidazolium system, cavitand, calixarene, and polymeric imidazolium systems. All these examples employ the imidazolium moieties as the binding sites for anions. Nevertheless, the different templates may provide different binding properties towards anions due to different binding pockets generated from these templates. Moreover, introduction of fluorogenic and chromogenic moieties to the receptors enabled easy detection compared to the normal ^{1}H NMR titration methods. Kim and co-workers have explained various theoretical calculations for these imidazolium systems.

Imidazolium salts are easily prepared by either protonation or substitution at the nitrogen atom of the imidazole where positive charge is delocalized in the imidazole ring **(**Fig. **1).**

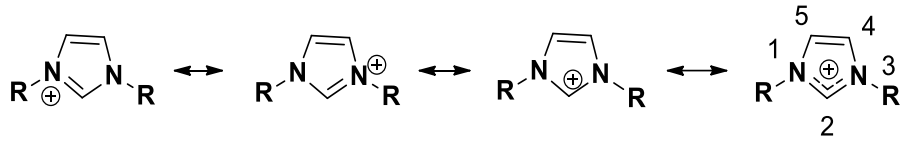


Fig 1: The resonance forms of the imidazolium cation

1.1. $(C–H)^{+}$- - - X^{-} ionic hydrogen bonds

Imidazolium group is capable of making strong electrostatic interaction with anions through $(C–H)^{+}$ - - - X^{-} type ionic hydrogen bond. This unique type of charged hydrogen bonding is quite different and fascinating compared to many other normal hydrogen bonds**.** In these anion receptors, charge-charge electrostatic interaction dominates. The interesting imidazolium-anion properties and the comparatively high acidity (pK_a = 21–23) of the C_2 hydrogen (C_2–H) of the imidazolium group have made these salts be used as ionic liquids and predecessor to stable carbenes. Other than strong electrostatic interaction, the H-bonds between the C_2–H and anions have been observed in solid state and solutions, and considered as an essential interaction in controlling the structures and properties of imidazolium-based ionic liquids. But the role of C_2–H- - -Anion hydrogen bond during the recognition process is still open to discussion. In recent theoretical calculations, Tsuzuki et al.[4] believe that C_2–H is not essential for imidazolium–anion attraction. The orientation dependence of the interaction

energy is very puny between C_2–H and the anion in contrast to distinctively orientation dependent conventional hydrogen bonds. The absence of C_2–H may not affect the binding ability, but perhaps can affect the signal transduction of recognition events, For example, the case study of $(C–H)^+ - - - F^-$ ionic hydrogen bond between naphtha-imidazolium and fluoride ion shows blue-shift the fluorescence[5], while the electrostatic interaction between 2-substituted-benzimidazolium and anion can only instigate the changes of fluorescence intensity without shift in emission[6].

1.2. Benzene Tripodal Systems

Sato et al [7] reported the first benzene based tripodal receptor with three imidazolium groups. The host **1** displayed a preferential binding with Cl^- over Br^- and I^- in acetonitrile, which was confirmed via ^1H NMR titration experiments. Kim and co-workers further clarified that this tri-cationic heterocycle interacts strongly with anions through $(C–H)^+ - - - X^-$ type ionic hydrogen bond between the hydrogen on the electron-deficient C_2 carbon atom of the imidazolium ring and the guest anion, and shows a selective binding for F^- over other halide anions. The benzene based tripodal receptor was then theoretically modified for better anion binding affinity, and experimentally realized as tripodal nitro-imidazolium receptor **2** , which had strong affinity and was highly particular for Cl^-. The association constant K_a for Cl^- in a 9:1 mixture of acetonitrile-d_3 and DMSO-d_6 was 1.1×10^{-6} M^{-1} . To differentiate between sodium (R)-2- aminopropionate and

sodium (S)-2-aminopropionate Howarth et al. [9] reported a homochiral tripodal imidazolium system (**3**). From the ^{1}H NMR experiments, it was observed that the imidazolium salt selectively forms a complex with the (R) enantiomer but not with the (S) enantiomer. Similar benzene tripodal systems (**4, 5** and **6**) (**Fig. 2**) and bis imidazolium **(7)** were reported by Ru-Gang et al [10]. The binding properties and affinities of halide and hexafluorophosphate salts of these imidazoliums towards various anions, such as CO_3^{2-} , HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and halides, were checked in water via UV spectroscopic titration experiments. The association constant for 5 with PO_4^{3-} in water was observed to be as large as 5465 M^{-1}.

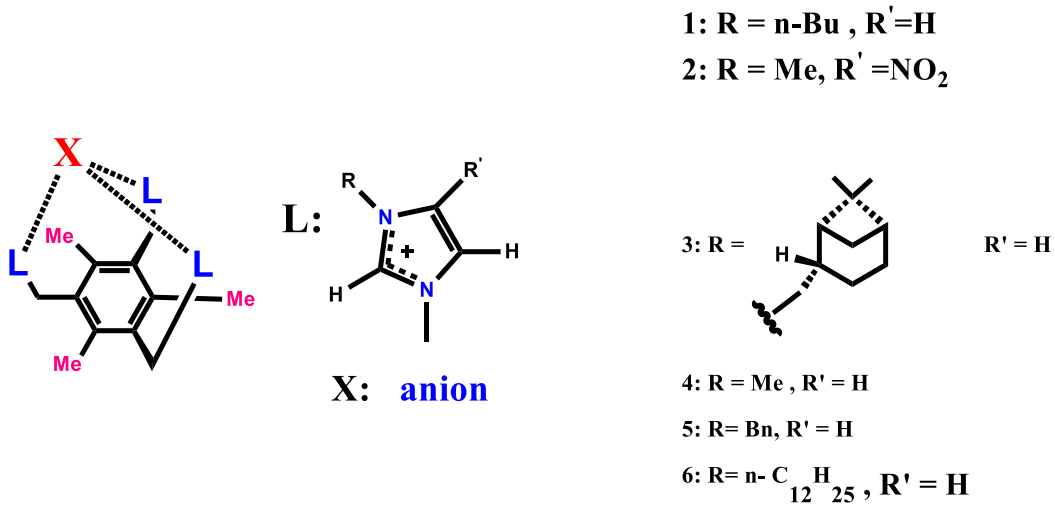


Fig 2. Benzene Tripodal Systems

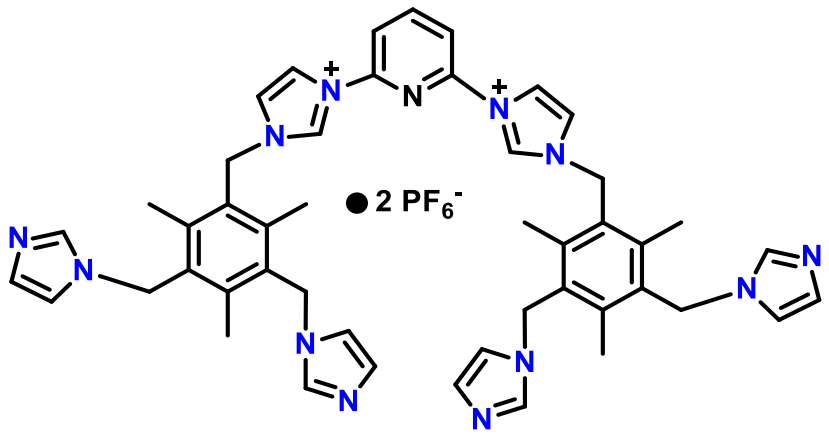


Fig 3. Bis-imidazolium receptor 7

Duan et al [12] recently reported a fluorescent tripodal receptor (**4a**) bearing three benzoimidazolium and napthyl groups. This chemo-sensor acts as an ‘‘off–on’’ signalling chemical sensor with high selectivity for Cl^- over Br^- and I^- through a guest-induced conformational switching process (**Fig 4**). In the presence of Cl^-, the tripodal system adopts a cone conformation, which leads to the excimer fluorescence by bringing the naphthalene groups into close proximity.

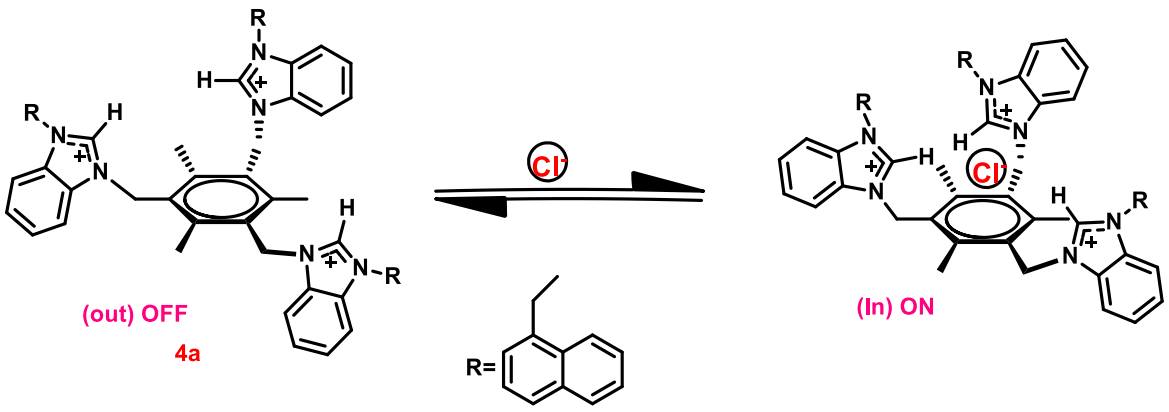


Fig 4. Conformational switching process of **4a** upon the addition of Cl^-.

1.3. Fluorescent imidazolium salts

Yoon’s group and Kim’s [11] group studied a few anthracene derivatives bearing imidazolium groups as binding sites for anion recognition. Two imidazolium groups were first put on the 1,8-positions of the anthracene derivative (**1**) and a distinct feature of the binding mode was predicted on the basis of *ab initio* [11a] calculations. The chemo-sensor (**5a**) was found out to be

higly selective for the biologically important $H_2PO_4^-$ ion over other anions such as I^-, Br^- and Cl^- in acetonitrile. Other than previous results of imidazolium receptors, where binding of host to anion was confirmed via ^1H NMR titrations these binding phenomena can be easily studied via fluorescence quenching effects. On the basis of *ab initio* calculations the chemo-sensor (**5a**) was found to have high binding affinity with $H_2PO_4^-$ and F^- [11b] ions. It was further revealed that the by enhancing the rigidity or change in topology of binding sites selectivity of these imidazolium receptors (chemo-sensor) against anions can be modified. For example, the greater rigidity in chemo-sensor (**5b**) enhances the binding selectivity for $H_2PO_4^-$ over F^-, compared to chemo-sensor (**5a**). In both cases, anthracenes moiety serving as fluorophores with the advantage of rigid template senses anion by the change in the fluorophore intensity due to photo-induced electron transfer (PET) mechanism. In contrast to extremely strong interference in the case of chemo-sensor (**5a**) competitive binding studies of $H_2PO_4^-$ and F^- for (**5b**) using the fluorescent change demonstrated that there was no interference to the binding of $H_2PO_4^-$ in the presence of up to 1.5 equimolar concentrations of F^- anions.

Recently, Yoon's group and Kim's group have reported an ideal water-soluble imidazolium anthracene derivative (**5c**), which not only differentiates the structurally similar compounds GTP and ATP but also act as a potential fluorescent chemo-sensor for GTP in 100% aqueous solution (pH=7.4, 10 mM HEPES) [11c]. This new fluorescent chemo-sensor senses GTP by chelation-

enhanced fluorescence quenching (CHEQ) effect, whereas it displayed a chelation enhanced fluorescence (CHEF) effect for ATP, ADP and AMP.

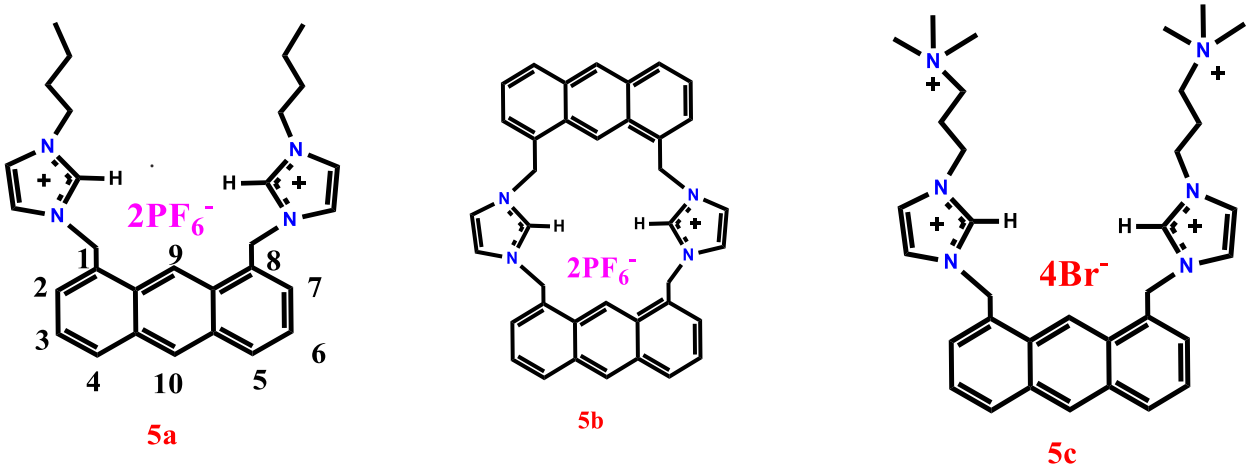


Fig. 5 Anthracene derivatives bearing imidazolium groups

A new imidazolium functionalised acyclic Ruthenium (II) bipyridyl receptor **(6a, 6b) (Fig. 6)** was reported by Beer and co-workers [13]. Both receptors were found to be selective for Cl^- over the other anions in acetonitrile–water (**9:1**, v/v) whereas the chemo-sensor 6b sensed ATP in **50:50** acetonitrile–water solvent media.

A naphthalene derivative (**7a**) which contains two methylene bridged bis-imidazolium rings was reported by Kang and co-workers (**Fig. 7**). [14a] The chemo-sensor **7a** displayed a selective affinity for I^-, which was confirmed using fluorescence spectroscopy and ^1H NMR titrations. They also reported the role of aromatic (C–H)…anion interaction on chemo-sensor **7b** in addition to the imidazolium $(C–H)^+$ - - -anion ionic hydrogen bonding, whose strength was found to be increased with the nitro substitution on the para position. [14b]

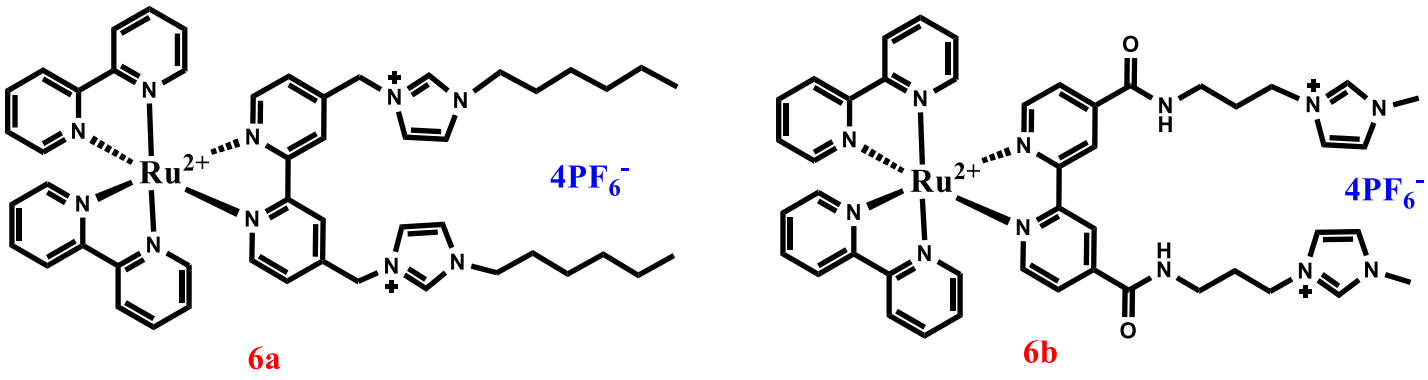


Fig. 6 Structures of fluorescent hosts **6a** and **6b**

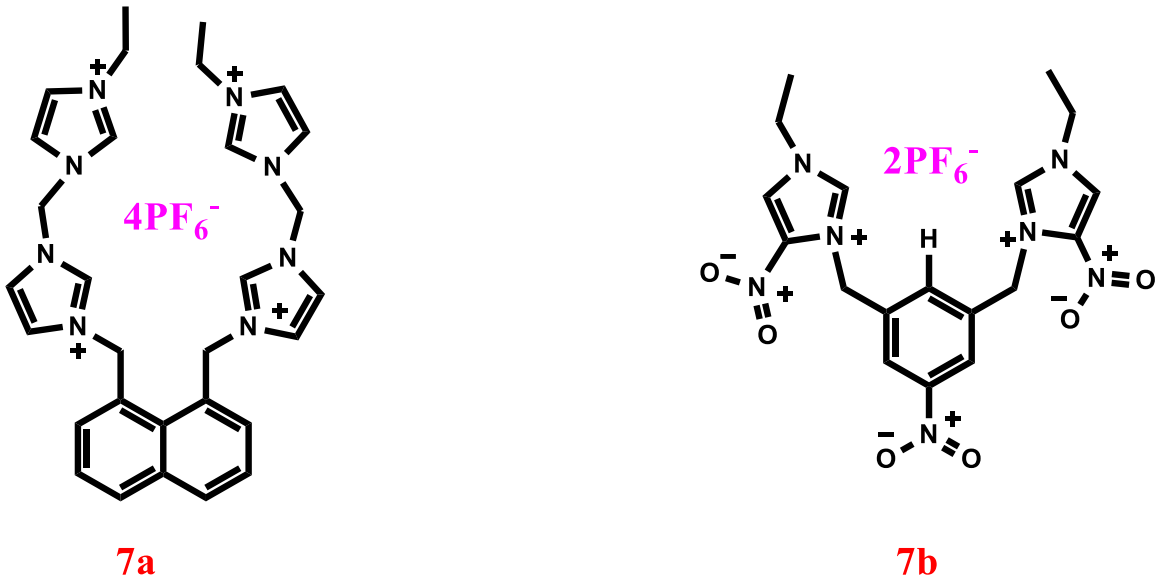


Fig. 7 Structures of hosts **7a** and **7b**.

1.4. ATP and DNA sensing

Yoon and Kim et al. recently reported a novel water-soluble imidazolium anthracene derivative, which selectively acts as a probable fluorescent chemo-sensor for GTP in 100% aqueous solution (pH = 7.4). [15] Based on this work it was thought that the imidazolium receptors can be used for sensing nucleotides

as well, in which the dominant interactions were ionic hydrogen bonding between imidazolium moiety and phosphate group attached to sugar and π-π or π–H interaction between base and fluorophore attached to chemo-sensor. A few years later, Yoon and Kim et al. [16] reported a pincer-like benzene-bridged chemo-sensor **8a** with imidazolium moiety as a triphosphate anion receptor and a pyrene excimer as a fluorescence signal source (**Fig. 8**). In the presence of ATP a unique switch of excimer vs. monomer pyrene fluorescence of 1 was observed and was thought to be due to the characteristic sandwich π-π stacking of pyrene–adenine–pyrene. On the contrary, other four bases of nucleoside triphosphates such as GTP, UTP, CTP and TTP can reach out only from the outside with the already stabilized stacked Pyrene-pyrene dimer of 1 and no sandwich π-π stacking as in case of ATP which results in excimer fluorescence quenching (**Fig. 9**). Monomer to excimer fluorescent intensity ratio for chemo-sensor **8a** upon binding with ATP (I_{375}/I_{487}) was found out to be much larger than those upon binding with ADP and AMP. The association constant k_a for ATP is calculated to be $1.03\times10^4\ M^{-1}$.

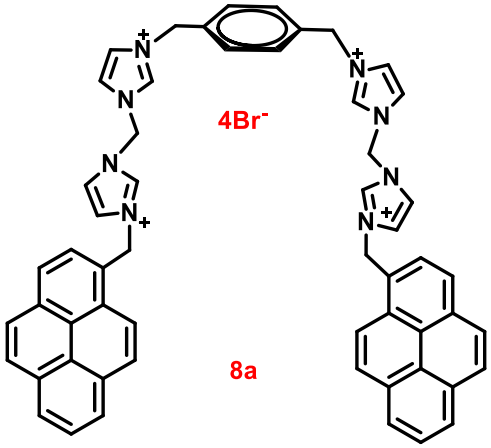


Fig 8. Structure of 8a.

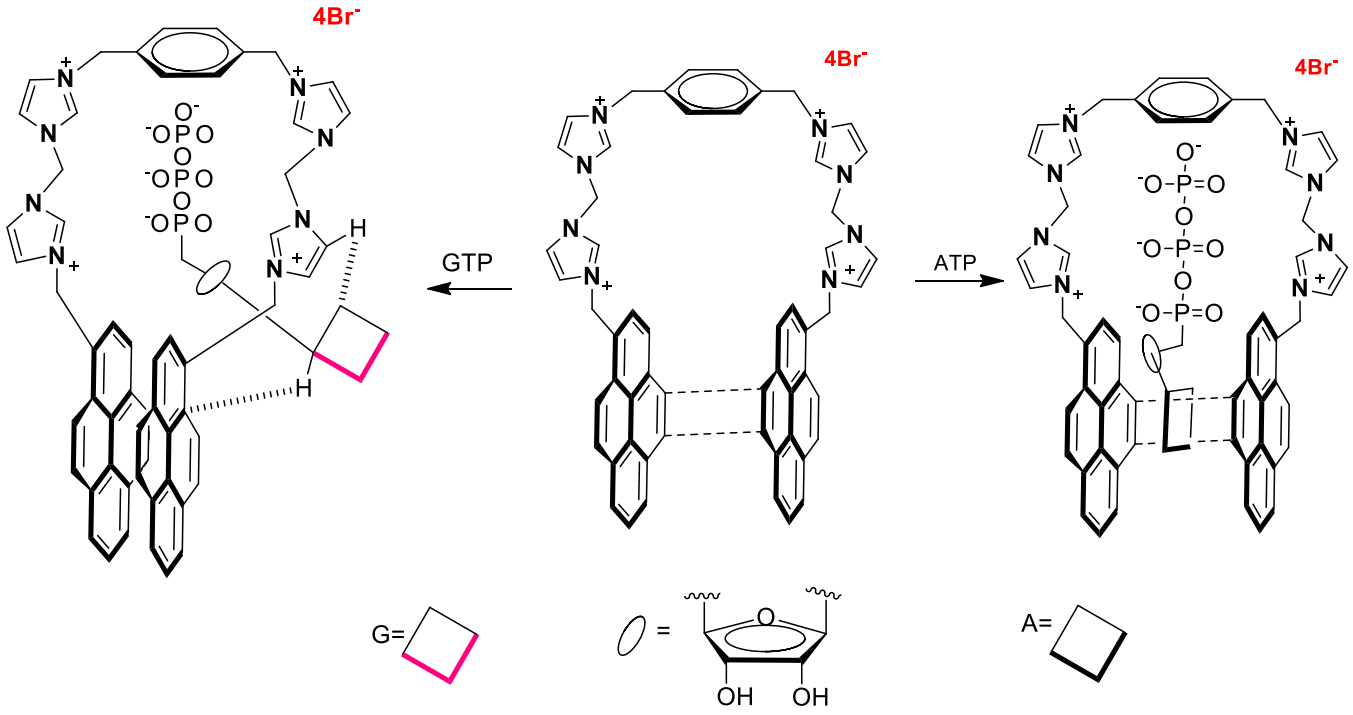


Fig. 9 Proposed binding mode with ATP and GTP.

Ramaih et al. [17] made use of water-soluble cyclophane derivative **10a** **(Fig. 10)** as DNA sensor. The same group reported similar pyridinium based cyclophanes as chemo-sensors for ATP [18] and GTP [19]. Cyclophane **10a** displayed a dual emission consisting of a structured band with λ_{max} value of 430 nm and a broad band centred at 550 nm with an I_{550}/I_{430} ratio of 0.8 in the absence of DNA. Upon the addition of DNA, cyclophane 2 displayed a bathochromic-shifted emission maximum at 570 nm with a notably enhanced intensity (~9 fold) and life time (143.1 ns) in comparison to model compound **10b**.

The binding constant of **10a** towards DNA is $7.6 \times 10^4\ M^{-1}$. The cyclophane **10a** can interact with DNA in a sequence-selective fashion resulting in the specific formation of a highly organized sandwich-type excimer. The classical

intercalative binding of cyclophane **10a** was ruled out on considering the steric factors, instead based on the observation of a bisignated ICD (induced circular dichroism) and the sequence-dependent excimer formation [20] addition, non-classical intercalative interactions in the minor groove of DNA was proposed.

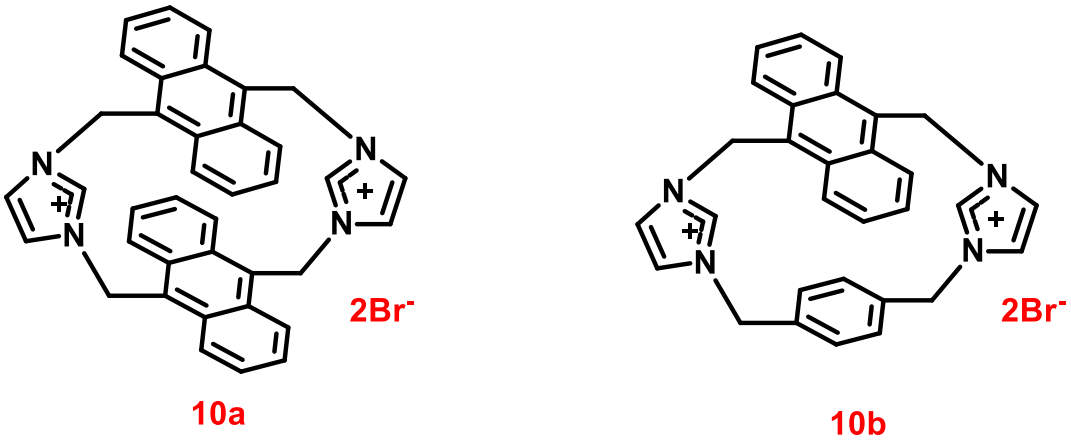
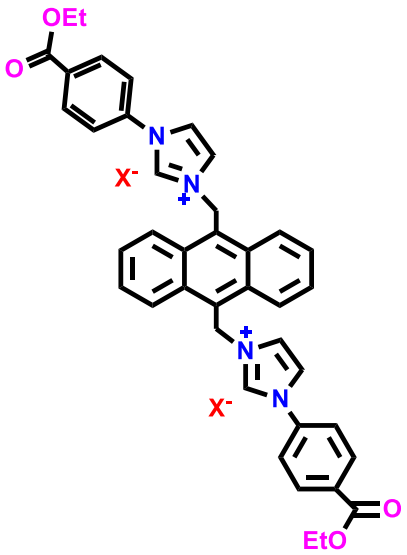


Fig. 10 Structures of cyclophane 10a and 10b.

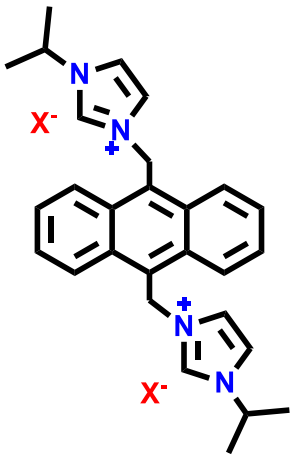
2. Objective of the thesis

The aim of the thesis is to **Synthesize and Characterize Anthracene Tagged Imidazolium Derivatives** which has potential application in recognition of anion, ATP and DNA sensing as well as have some biological activity also.

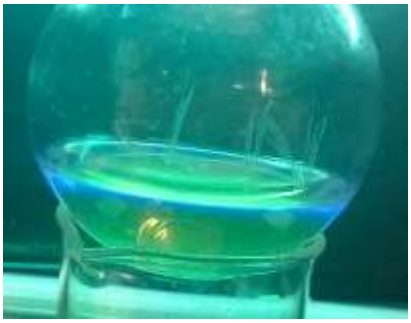
Therefore my target molecules are:

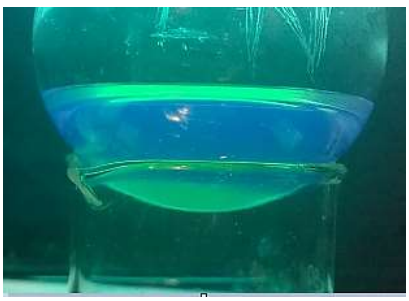


where X^-= Cl^-, BF_4^-, PF_6^-



where X^-= Cl^-, BF_4^-, PF_6^-





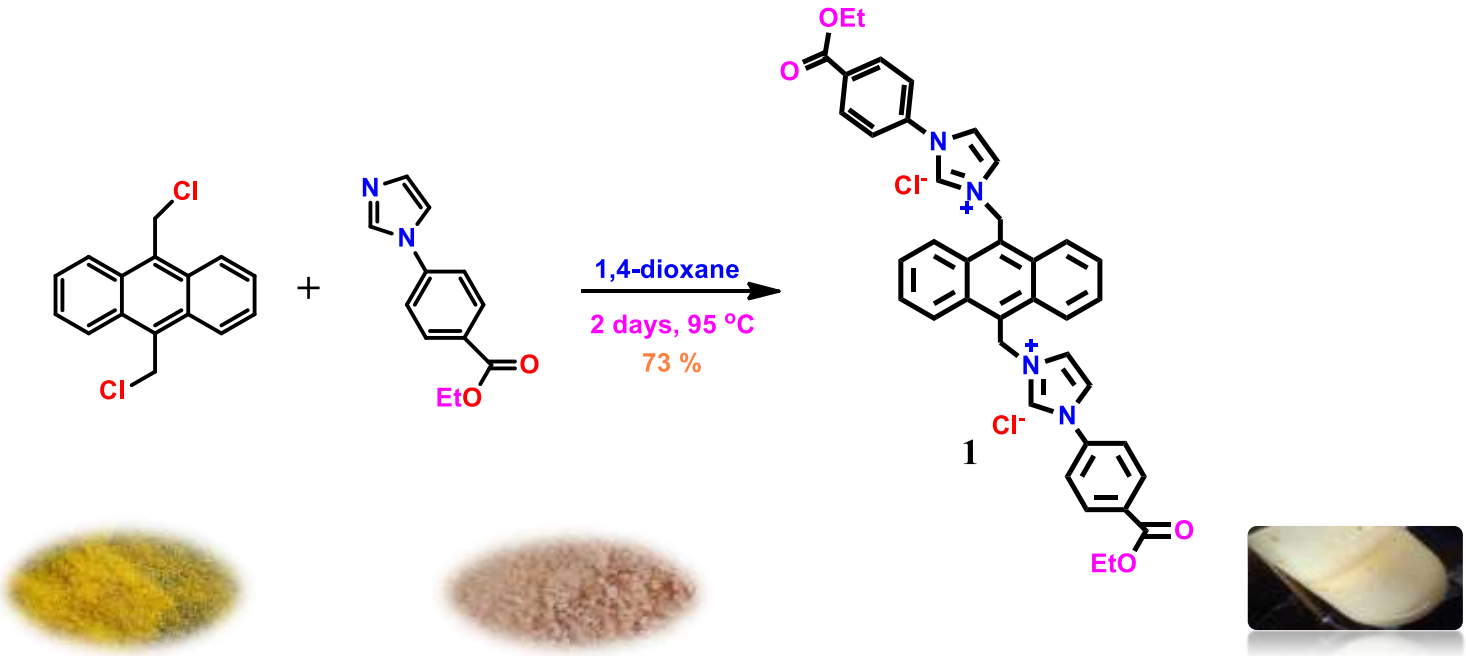
3. Experimental Section

3.1. General considerations

All experiments were performed in normal laboratory condition under dry N_2 atmosphere using standard Schlenck technique. The solvents were dried, distilled according to standard procedures. 9,10-bis(chloromethyl)anthracene and ethoxycarbonyl phenyl imidazole were prepared according to the previous reports. Ethyl-4-aminobenzoate (Aldrich), ammonium tetrafluoroborate (Aldrich), Potassium hexafluorophosphate (Aldrich), dimethylsulfoxide (SD Fine), acetonitrile (Merck), diethyl ether (Merck) and DMSO-d_6 (Acros) were purchased from commercial sources. FT-IR spectra's (neat) were recorded on a Bruker Alpha-P Fourier transform spectrometer. The UV-Vis measurements were carried out on a T90+ UV-Visible spectrophotometer. NMR measurements were recorded on Bruker Ultrashield-400 spectrometers and Bruker Advance DPX-250 at 25 ^oC until unless specified. Chemical shifts values are assigned relative to TMS and were referenced to the solvent resonances as internal standards. Phosphorus spectrum values were recorded with reference to a ^{31}P resonance of the external 85% phosphoric acid reference (85% phosphoric acid δ = 0.00 ppm). Melting points were obtained on a Cintex melting point apparatus. Single crystal structure was recorded by mounting crystals on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (MoK_α radiation source, λ = 0.71073 Å). Crystals of **1 and 4** were obtained from Methanol solution of **1**

and 4 at room temperature over a period of seven days. Single crystals of the compound **2**, **3 and 5** were obtained by crystallization from mixture of MeOH/acetonitrile solution of **2, 3 and 5** at room temperature. The crystal structures of **1-5** were measured on an Oxford Xcalibur2 diffractometer.

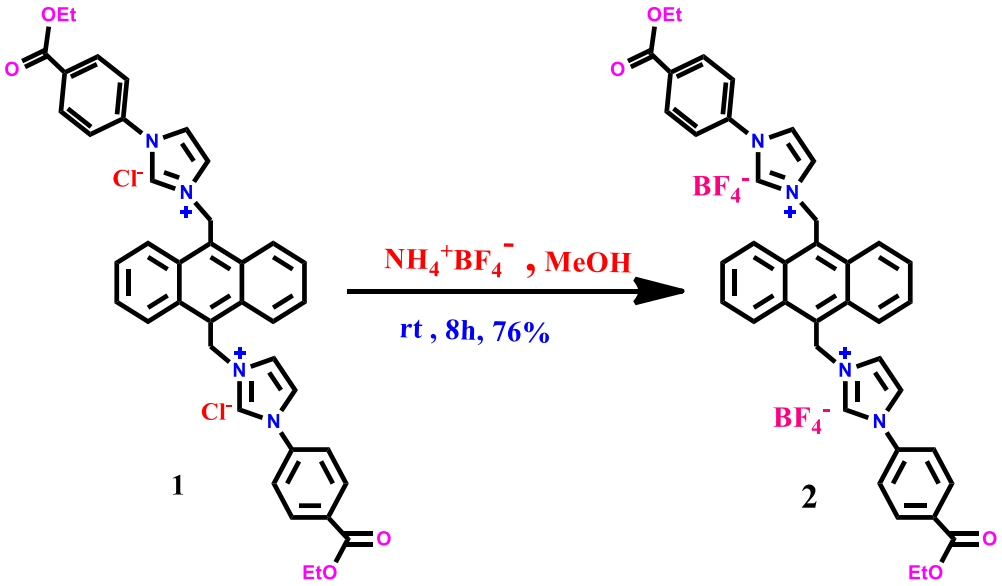
3.2. Synthesis of [9,10-bis{(N-ethoxycarbonyl phenyl imidazolium)methyl}anthracene]dichloride **[1]**



A mixture of 9,10-bis(chloromethyl)anthracene (0.640 g, 2.36 mmole) and ethoxycarbonyl phenyl imidazole (1.005 g, 4.65 mmole) in 1,4-dioxane was refluxed for 3 days at 95 ^{o}C under N_2 atmosphere. The solvent was removed using cannula technique and given several washes with acetone and ethyl acetate. The pale yellow solid thus obtained was allowed to dry for several hours (Yield: 74% based on 9,10-bis(chloromethyl)anthracene). M.p. 242-244 ^{o}C (changes its colour

to black). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.44 (s, 2H, 8-Im*H*), 8.48 and 7.70 (s, 4H, 9,10-Im*H*), 8.73-8.70 (dd, 4H, 14-An*H*), 7.75-7.72 (dd, 4H, 15-An*H*), 6.75(s, 4H, An*CH*$_2$N), 8.11-8.09 (d, 4H, 5-Ph*H*), 8.02-8.00 (d, 4H, 6-Ph*H*), 4.34-4.29 (q, 4H, ester C*H*$_2$), 1.33-1.29 (t, 6H, ester C*H*$_3$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.53(*C*=O), 137.92 (4, Ar- *C*), 135.85 (8, Im- *C*), 130.86(5, Ar-*C*), 130.78 (12, Ar- *C*), 127.59 (15, Ar- *C*), 126.28 (13, Ar- *C*), 124.77 (14, Ar-*C*), 123.22 (10, Im- *C*), 122.01 (6, Ar- *C*), 121.00 (9, Im- *C*), 61.25 (2, *C*H$_2$ attached to C=O), 45.59 (11, Ar*C*H$_2$N), 14.05 (1, *C*H$_3$) ppm. FT-IR (cm^{-1},neat): 3357(w), 2975(w), 1709(s), 1546(m), 1446(w), 1277(s), 1066(m), 763(s).

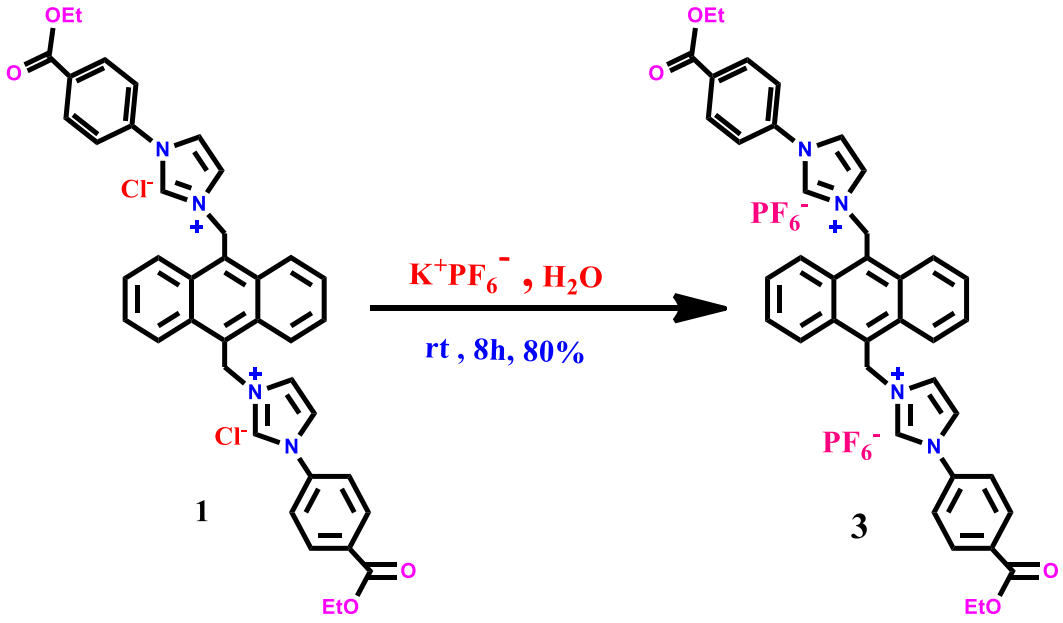
3.3. Synthesis of [9,10-bis{(N-ethoxycarbonylphenylimidazolium)methyl}anthracene] bistetra fluoro borate ***[2]***



To the stirred solution of **1** (0.200 g, 0.28 mmoles) in MeOH was slowly added NH_4BF_4 (0.118 g, 1.1 mmole) and the reaction mixture was stirred for 8h

at room temperature. Solvent was evaporated under vacuum and the yellowish solid was given several washes with water and then it was dissolved in MeOH and dried over Na_2SO_4, filtered and then solvent was removed under reduced pressure to get analytically pure sample of **2** (Yield: 76% based on compound **1**) .M.p. 208-210 ^oC (decomposed colour changed to black). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.91 (s, 2H, 8-Im*H*), 8.38 and 7.67 (s, 4H, 9,10-Im*H*), 8.65 (s, 4H, 14-An*H*), 7.81 (d, 4H, 15-An*H*), 6.68 (s, 4H, AnCH_2N), 8.19-8.17 (d, 4H, 5-Ph*H*), 7.94-7.92 (d, 4H, 6-Ph*H*), 4.37-4.35 (d, 4H, ester CH_2), 1.34 (s, 6H, ester CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.58 (*C*=O), 137.94 (4, Ar- *C*), 135.66 (8, Im- *C*), 130.88 (5, Ar- *C*), 130.82 (12, Ar- *C*), 127.71 (15, Ar- *C*), 126.17 (13, Ar- *C*), 124.65 (14, Ar- *C*), 123.25 (10, Im- *C*), 122.26 (6, Ar- *C*), 121.23 (9, Im- *C*), 61.30 (2, *C*H_2 attached to C=O), 45.63 (11, Ar*C*H_2N), 14.06 (1, *C*H_3) ppm.). ^{11}B NMR (128 MHz, DMSO-d_6) δ: -1.25 ppm.). ^{19}F NMR (376 MHz, DMSO-d_6) δ: -148.14-148.19 (d) ppm. FT-IR (cm^{-1}, neat): 3139 (w), 2922 (w), 1707 (s), 1548 (m), 1450 (w), 1276 (m), 1027 (s), 769 (m).

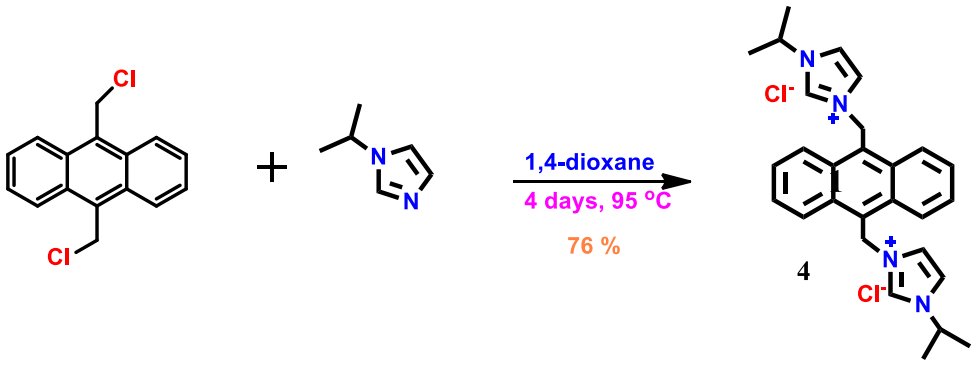
3.4. *Synthesis of [9,10-bis{(N-ethoxycarbonyl phenyl imidazolium)methyl}anthracene]bishexa fluoro phosphate* ***[3].***



To the stirred solution of KPF_6 (0.118g, 1.1mmole) was slowly added an aqueous solution of **1** (0.200g, 0.28mmoles). The reaction mixture was allowed to stir for 8h at r.t. The solvent was evaporated under vacuum. The yellowish solid thus obtained was given several washes with water and crude was dissolved in MeOH : Acetonitile (50:50) and dried over Na_2SO_4, filtered and then solvent was removed under removed reduced pressure to get analytically pure compound 3 (Yield: 80%, based on **1**). M.p.- 206-208 ^oC (decomposed colour changed to black). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.88 (s, 2H, 8-Im*H*), 8.36 and 7.66 (s, 4H, 9,10-Im*H*), 8.66-8.64 (dd, 4H, 14-An*H*), 7.81-7.80 (d, 4H, 15-An*H*), 6.67 (s, 4H, AnCH_2N), 8.19-8.17 (d, 4H, 5-Ph*H*), 7.92-7.90 (d, 4H, 6-Ph*H*), 4.39-4.34 (q,

4H, ester CH_2), 1.36-1.33 (t, 6H, ester CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.59 (*C*=O), 137.93 (4, Ar- *C*), 135.65 (8, Im- *C*), 130.89(5, Ar- *C*), 130.87 (12, Ar- *C*), 127.71 (15, Ar- *C*), 126.16 (13, Ar- *C*), 124.64 (14, Ar- *C*), 123.24 (10, Im- *C*), 122.27 (6, Ar- *C*), 121.25(9, Im- *C*), 61.31 (2, *C*H$_2$ attached to C=O), 45.63 (11, Ar*C*H$_2$N), 14.05 (1, *C*H$_3$) ppm . ^{31}P NMR (161 MHz, DMSO-d_6) δ: -131.01 to -157.36 (sep) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -69.17 (s), -71.06 (s) ppm. FT-IR (cm^{-1},neat): 3157(w), 2924(w), 1714(m), 1549(m), 1451(w), 1276(m), 1069(m), 825(s), 765(m).

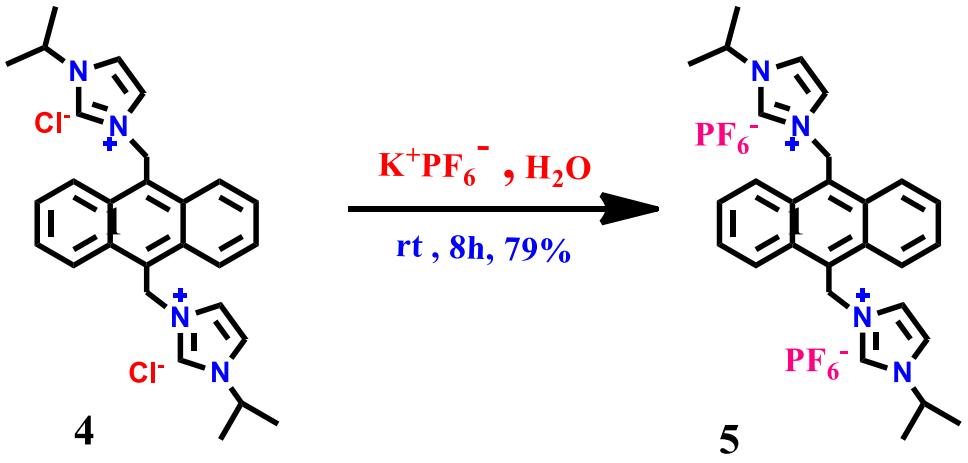
3.5. *Synthesis of [9,10-bis{(N-isopropyl imidazolium)methyl}anthracene]dichloride* **[4].**



A mixture of 9,10-bis(chloromethyl)anthracene (0.500 g, 1.84 mmole) and N-isopropylimidazole (0.800 g, 7.26 mmole) in 1,4-dioxane was refluxed for 3 days at 95 ^{o}C under N_2 atmosphere. The solvent was removed using cannula technique and the pale yellow residue was given several washes with acetone. The pale yellow solid thus obtained was allowed to dry for several hours to get analytically pure compound **(4)** (Yield: 76% based on 9,10-bis(chloromethyl)anthracene). M.p. 196-198 ^{o}C (changes its colour to black). ^{1}H

NMR (400 MHz, D_2O) δ: 8.38 (s, 2H, 5-Im*H*), 7.36 and 7.09 (s, 4H, 3,4-Im*H*), 8.03-8.01 (dd, 4H, 7-An*H*), 7.66-7.64 (d, 4H, 8-An*H*), 5.72 (s, 4H, AnCH_2N), 4.36-4.29 (m, 2H, iPr-C*H*), 1.27-1.26 (d, 12H, iPrCH_3) ppm. ^{13}C NMR (100 MHz, D_2O) δ: 133.44 (5, Im-*C*), 129.83 (9, Ar-*C*), 128.07 (8, Ar-*C*), 125.42 (10, Ar-*C*), 123.65 (7, Ar-*C*), 122.10 (4, Im-*C*), 120.33 (3, Im-*C*), 53.17 (2, *C*H), 44.55 (6, CH_2), 21.80 (1, CH_3) ppm. FT-IR (cm^{-1}, neat): 3082 (w), 2960 (w), 1551 (w), 1450 (w), 1259 (w), 872 (w), 740(w), 620 (m).

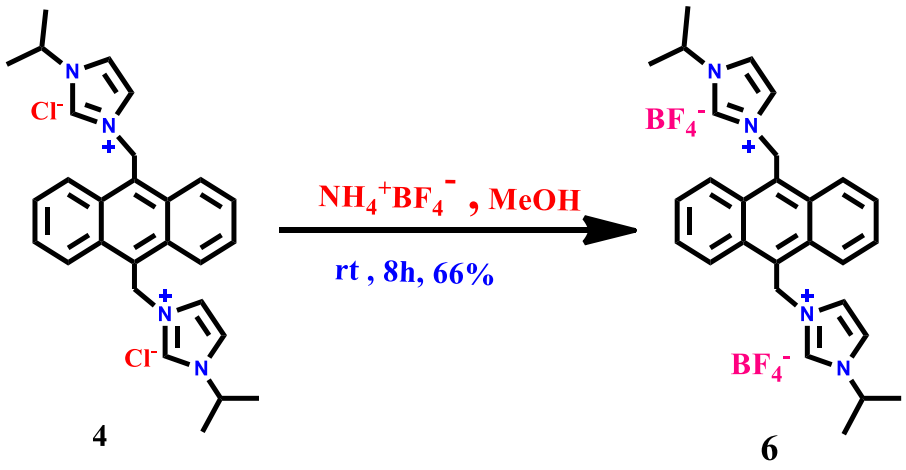
3.6. *Synthesis of [9,10-bis{(N-isopropyl imidazolium)methyl}anthracene]hexaflouorophosphate* ***[5]***



To the stirred solution of KPF_6 (0.297g, 1.6mmole) was slowly added an aqueous solution of **4** (0.200g, 0.40mmoles). The reaction mixture was allowed to stir for 8h at r.t. The solvent was evaporated under vacuum. The yellowish solid thus obtained was given several washes with water and crude was dissolved in MeOH : Acetonitile (50:50) and dried over Na_2SO_4, filtered and then solvent

was removed under removed reduced pressure to get analytically pure compound **5** (Yield: 79%, based on **4**). M.p:190-192 ^{o}C (decomposed colour changed to black). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 8.41 (s, 2H, 5-Im*H*), 7.46 and 7.27 (s, 4H, 3,4-Im*H*), 8.43-8.21 (dd, 4H, 8-An*H*), 7.79-7.76 (dd, 4H, 7-An*H*), 6.40 (s, 4H, AnC*H*$_2$N), 4.56-4.46 (m, 2H, iPr-C*H*), 1.46-1.45 (d, 12H, iPr-C*H*$_3$) ppm. ^{31}P NMR (161 MHz, DMSO-d6): δ: -131.49 to -157.68 (sep) ppm. ^{19}F NMR (376 MHz, DMSO-d$_6$): δ: -71.77 (t), -73.36 (t) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 135.18 (5, Im-*C*), 132.12 (9, Ar-*C*), 129.06 (7, Ar-*C*), 127.19 (10, Ar-*C*), 125.33 (8, Ar-*C*), 123.46 (4, Im-*C*), 121.55 (3, Im-*C*), 54.47 (2, *C*H), 46.72 (6, *C*H$_2$), 22.82 (1, *C*H$_3$) ppm. FT-IR (cm^{-1}, neat): 3154 (w), 2985 (w), 1618 (w), 1562 (w), 1432 (w), 1321 (w), 1181 (m), 816 (s), 650.19 (w)

3.7. *Synthesis of [9,10-bis{(N-isopropyl imidazolium)methyl}anthracene]tetrafluoroborate* **[6].**



To the stirred solution of **4** (0.200 g, 0.40 mmoles) in MeOH was slowly added NH_4BF_4 (0.170 g, 1.62 mmole) and the reaction mixture was stirred for 8h at room temperature. Solvent was evaporated under vacuum and the yellowish solid was given several washes with water and then it was dissolved in MeOH and dried over Na_2SO_4, filtered and then solvent was removed under reduced pressure to get analytically pure sample of **6** (Yield: 66% based on compound **6**). M.p. 186-188 ^oC (decomposed colour changed to black). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.24 (s, 2H, 5-Im*H*), 7.89 and 7.50 (s, 4H, 3,4-Im*H*), 8.61-8.59 (dd, 4H, 8-An*H*), 7.79-7.76 (dd, 4H, 7-An*H*), 6.56 (s, 4H, AnCH_2N), 4.66-4.60 (m, 2H, iPr-C*H*), 1.44-1.42 (d, 12H, iPr-CH_3) ppm. ^{11}B NMR (128 MHz, DMSO-d_6): δ: -1.25 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ: -148.17 (s), -148.23 (s) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 134.82 (5, Im-*C*), 130.64 (9, Ar-*C*), 127.63 (7, Ar-*C*), 126.74 (10, Ar-*C*), 124.55(8, Ar-*C*), 122.44(4, Im-*C*), 120.30 (3, Im-*C*), 52.29 (2, *C*H), 44.90 (6, *C*H_2), 22.24 (1, *C*H_3) ppm. FT-IR (cm^{-1}, neat): 3102 (w), 2901 (w), 1550 (m), 1417 (m), 1330 (w), 1149 (w), 1008 (w), 857 (w), 730 (m), 614 (w).

4. Result and Discussion

4.1. *Synthesis and Characterization of* ***(1)***

A mixture of 9,10-bis(chloromethyl)anthracene and ethoxycarbonyl phenyl imidazole in 1,4-dioxane was refluxed for 3 days at 95 ^{o}C under dry N_2 atmosphere. The solvent was removed using cannula technique and given several washes with acetone and ethyl acetate. The pale yellow solid thus obtained was allowed to dry for several hours to get analytically pure compound (1). Then the compound was characterized by ^{1}H (figure 11), ^{13}C NMR (figure 12) and HSQC HMBC spectroscopy. The ^{1}H NMR spectra of **1** displayed a single resonance peak for imidazolium CH proton at δ 10.45 ppm. ^{1}H NMR chemical shift of imidazolium NC*H*N proton in **1** is considerably downfield shifted compared to **2** and **3**. The N-CH_2peak appears at 6.75 ppm. In DEPT the N-*C*H$_2$ peak appears at 45.59 ppm and confirms the coupling product formation. The FT-IR stretching frequency at 1709.92 cm^{-1} indicates the presence of C=O group.

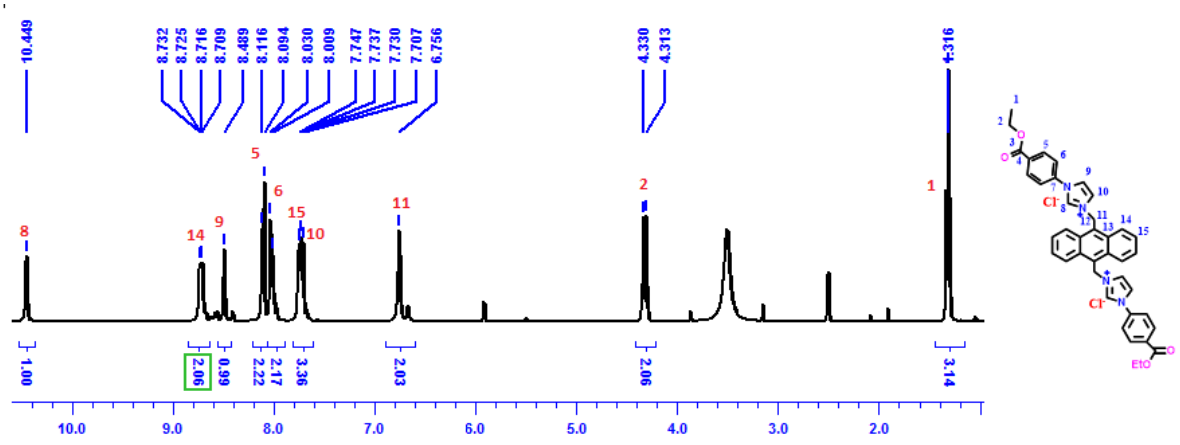


Fig 11. ^{1}H NMR spectrum of compound (**1**) in DMSO-d$_6$ at RT.

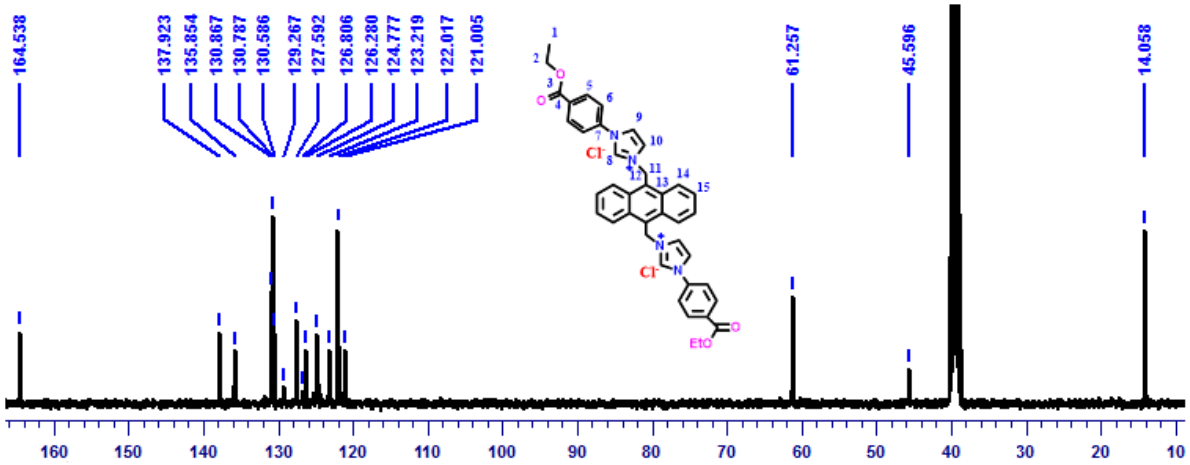


Fig 12. ^{13}C NMR spectrum of compound (**1**) in DMSO-d_6 at RT.

4.2. *Synthesis and Characterization of* ***(2).***

To the stirred solution of **1** in MeOH was slowly added NH_4BF_4 and the reaction mixture was stirred for 8h at room temperature. Solvent was evaporated under vacuum and the yellowish solid was given several washes with water and then it was dissolved in MeOH and dried over Na_2SO_4, filtered and then solvent was removed under reduced pressure to get analytically pure sample of **2.** Then the compound was characterized by ^{1}H (figure 13), ^{13}C NMR (figure 14) and HSQC, HMBC Spectroscopy. The ^{1}H NMR spectra of **2** displayed a single resonance peak for imidazolium CH proton at δ 9.91 ppm which is up-field compared to **1** and downfield compared to **3**. The N-CH_2peak appears at 6.68 ppm. In DEPT the N-CH_2 peak appears at 45.62 ppm and confirms the coupling product formation. The FT-IR stretching frequency at 1707.43 cm^{-1} indicates the presence of C=O group.

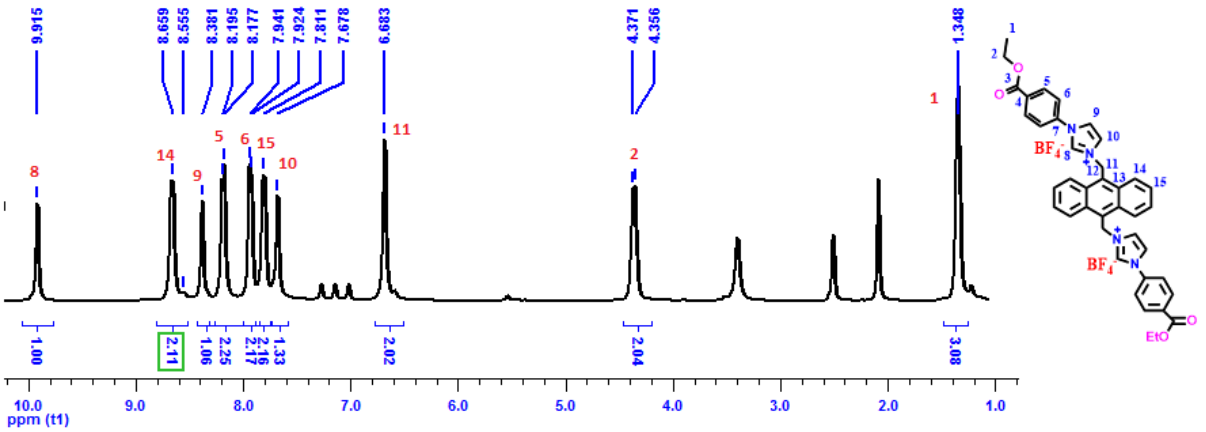


Fig 13. ^{1}H NMR spectrum of compound (**2**) in DMSO-d_6 at RT.

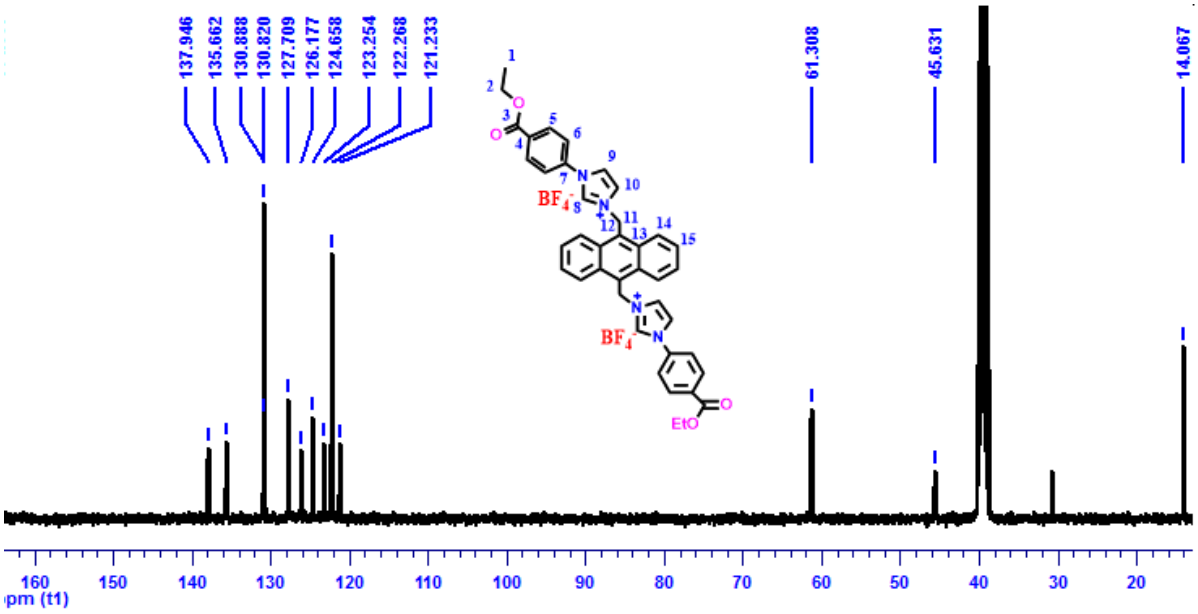


Fig 14. ^{13}C NMR spectrum of compound **(2)** in DMSO-d_6 at RT.

4.3. *Synthesis and Characterization of* ***(3).***

To the stirred solution of KPF_6 was slowly added an aqueous solution of **1**. The reaction mixture was allowed to stir for 8h at r.t. The solvent was evaporated under vacuum. The yellowish solid thus obtained was given several washes with water and crude was dissolved in MeOH : Acetonitile (50:50) and dried over

Na_2SO_4, filtered and then solvent was removed under reduced pressure to get analytically pure compound **3.** Then the compound was characterized by ^1H (figure 15), ^{13}C NMR (figure 16) and HSQC, HMBC spectroscopy. The ^1H NMR spectra of **3** displayed a single resonance peak for imidazolium CH proton at δ 9.88 ppm. ^1H NMR chemical shift of imidazolium NC*H*N proton in **3** is considerably up-field shifted compared to **1** and **2**. The N-CH_2peak appears at 6.67 ppm. In DEPT the N-CH_2 peak appears at 45.62 ppm and confirms the coupling product formation. The FT-IR stretching frequency at 1714 cm^{-1} indicates the presence of C=O group.

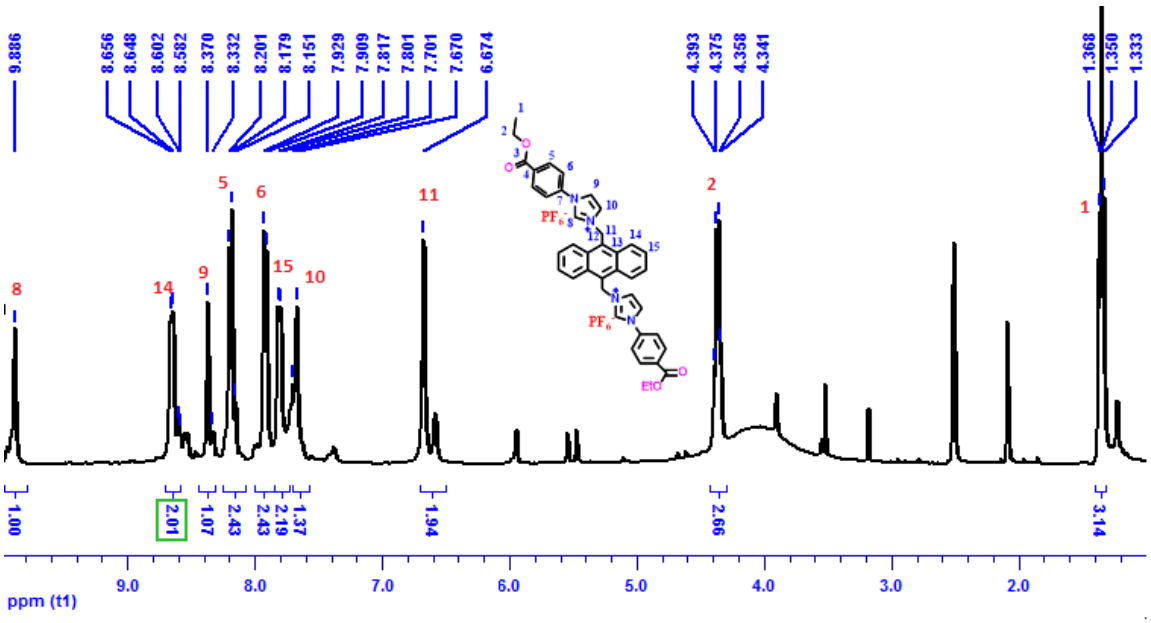


Fig 15. ^1H NMR spectrum of compound **(3)** in DMSO-d_6 at RT.

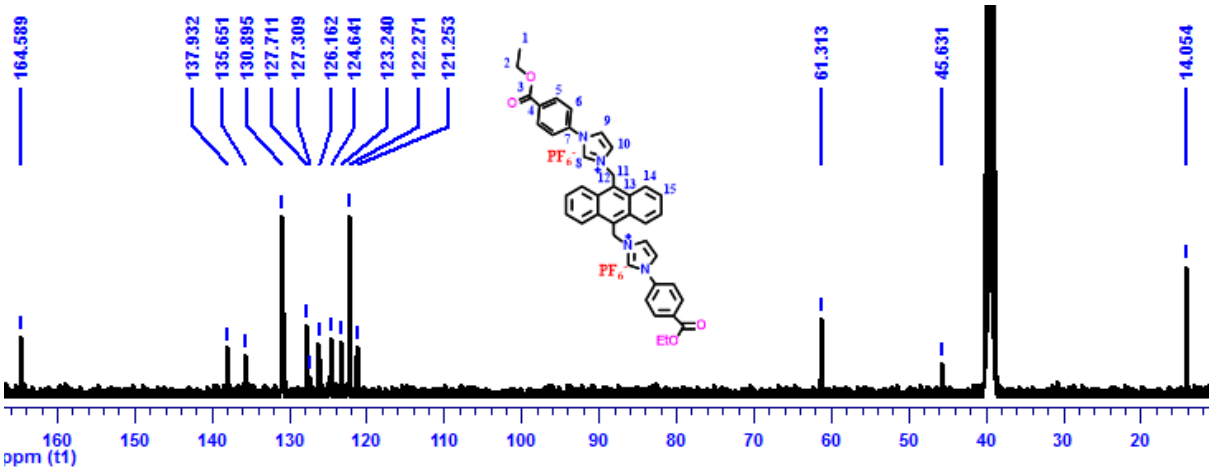


Fig 16. ^{13}C NMR spectrum of compound **(3)** in DMSO-d_6 at RT.

4.4. *Synthesis and Characterization of* ***(4).***

A mixture of 9,10-bis(chloromethyl)anthracene and N-isopropylimidazole in 1,4-dioxane was refluxed for 3 days at 95 ^{o}C under N_2 atmosphere. The solvent was removed using cannula technique and the pale yellow residue was given several washes with acetone. The pale yellow solid thus obtained was allowed to dry for several hours to get analytically pure compound **(4).** Then the compound was characterized by ^{1}H (figure **17**), ^{13}C NMR (figure **18**) and HSQC, HMBC Spectroscopy. The ^{1}H NMR spectra of **4** displayed a single resonance peak for imidazolium CH proton at δ 8.38 ppm. The N-CH_2 peak appears at 5.72 ppm. In DEPT the N-CH_2 peak appears at 44.54 ppm and confirms the coupling product formation.

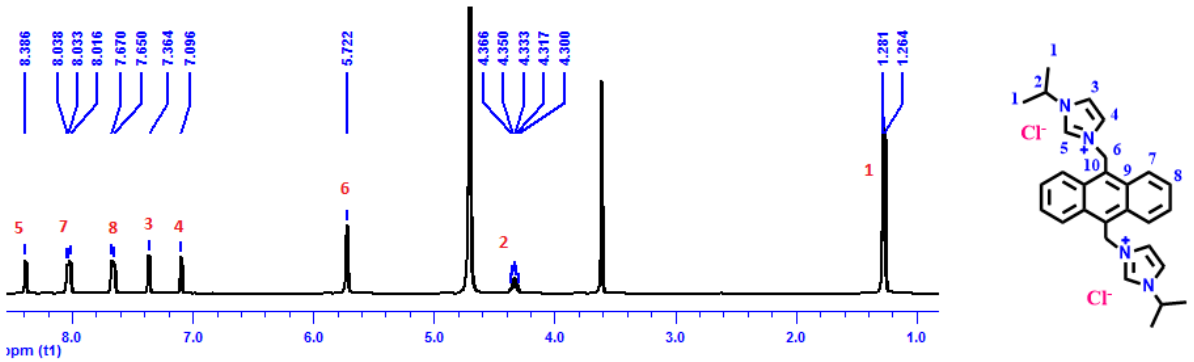


Fig 17. ^{1}H NMR spectrum of compound (**4**) in D_2O at RT.

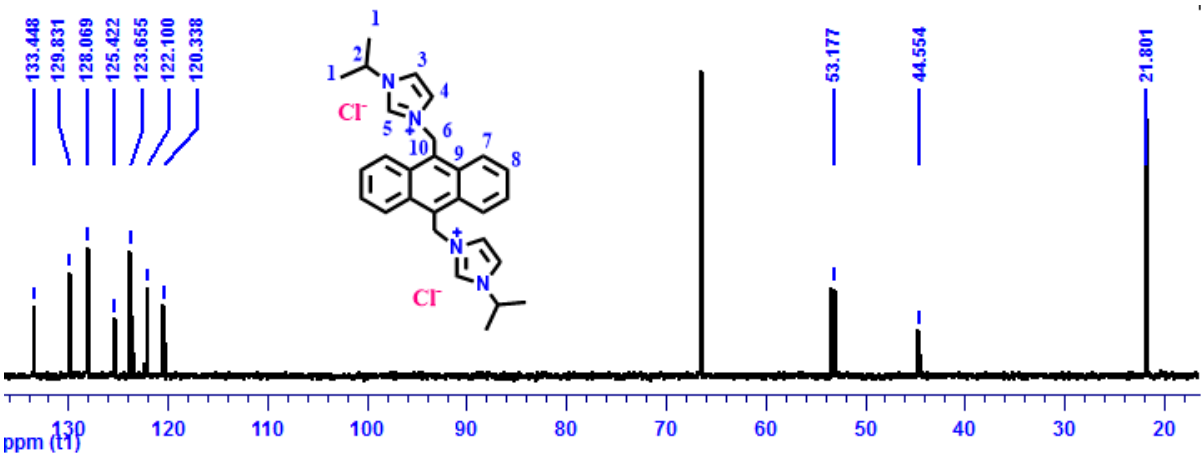


Fig 18. ^{13}C NMR spectrum of compound (**4**) in D_2O at RT.

4.5. *Synthesis and Characterization of* ***(5).***

To the stirred solution of KPF_6 was slowly added an aqueous solution of **4**. The reaction mixture was allowed to stir for 8h at r.t. The solvent was evaporated under vacuum. The yellowish solid thus obtained was given several washes with water and crude was dissolved in MeOH : Acetonitile (50:50) and dried over Na_2SO_4, filtered and then solvent was removed under removed reduced pressure to get analytically pure compound **5.** Then the compound was characterized by ^{1}H (figure **19**), ^{13}C NMR (figure **20**) and HSQC, HMBC spectroscopy. The ^{1}H

NMR spectra of **5** displayed a single resonance peak for imidazolium CH proton at δ 8.41 ppm. The N-CH_2 peak appears at 6.40 ppm. In DEPT the N-CH_2 peak appears at 46.72 ppm and confirms the coupling product formation.

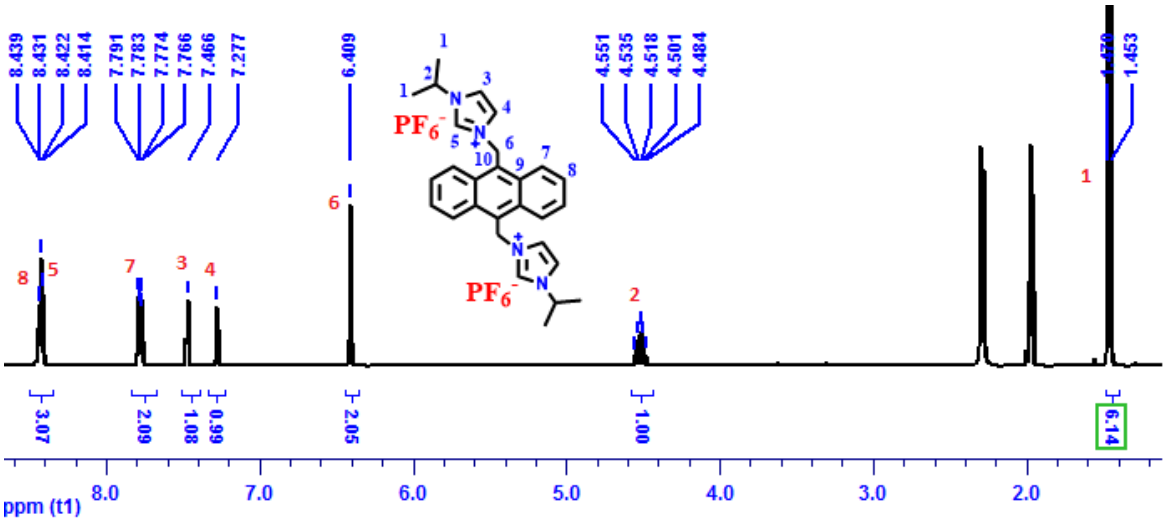


Fig 19. ^{1}H NMR spectrum of compound **(5)** in DMSO-d_6 at RT.

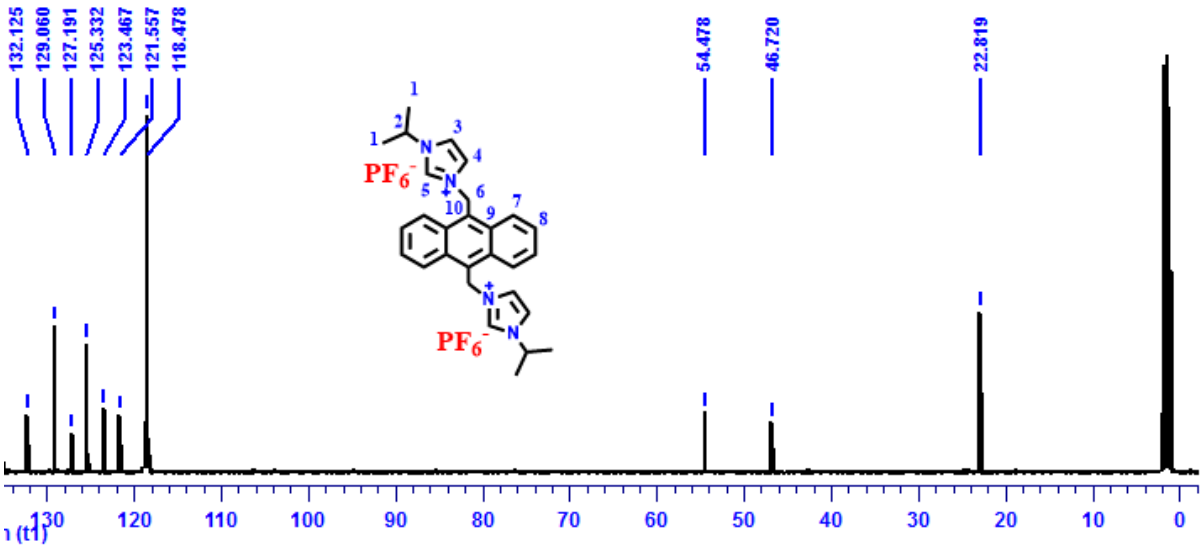


Fig 20. ^{13}C NMR spectrum of compound **(5)** in DMSO-d_6 at RT.

4.6. *Synthesis and Characterization of* ***(6).***

To the stirred solution of **4** in MeOH was slowly added NH_4BF_4 and the reaction mixture was stirred for 8h at room temperature. Solvent was evaporated under vacuum and the yellowish solid was given several washes with water and then it was dissolved in MeOH and dried over Na_2SO_4, filtered and then solvent was removed under reduced pressure to get analytically pure sample of **6** (Yield: 66% based on compound **4**). Then the compound was characterized by ^{1}H (figure 21), ^{13}C NMR (figure 22) and ^{11}B NMR, ^{19}F NMR spectroscopy. The ^{1}H NMR spectra of **6** displayed a single resonance peak for imidazolium CH proton at δ 9.24 ppm. The N-CH_2 peak appears at 6.56 ppm. In DEPT the N-CH_2 peak appears at 44.90 ppm and confirms the coupling product formation.

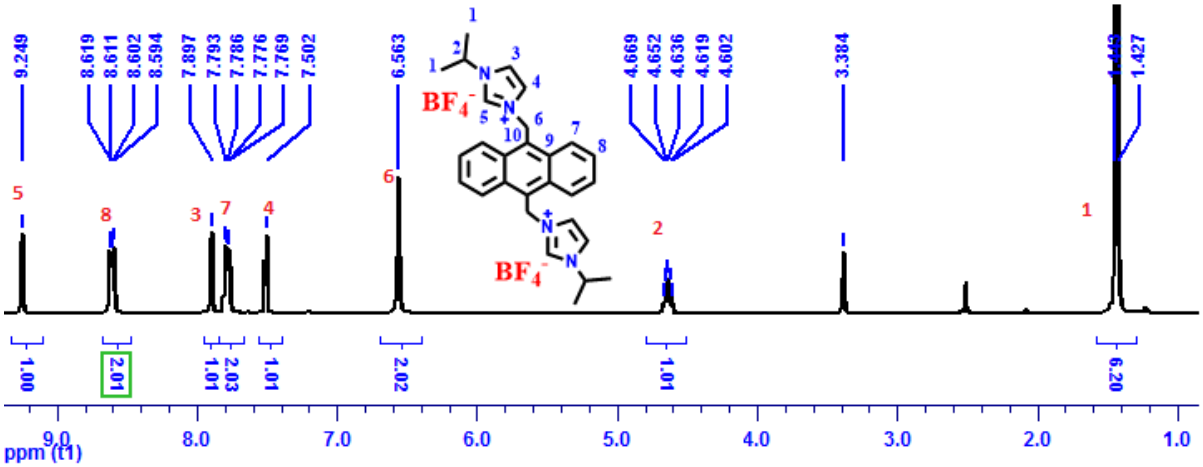


Fig 21. ^{1}H NMR spectrum of compound (**6**) in DMSO-d_6 at RT.

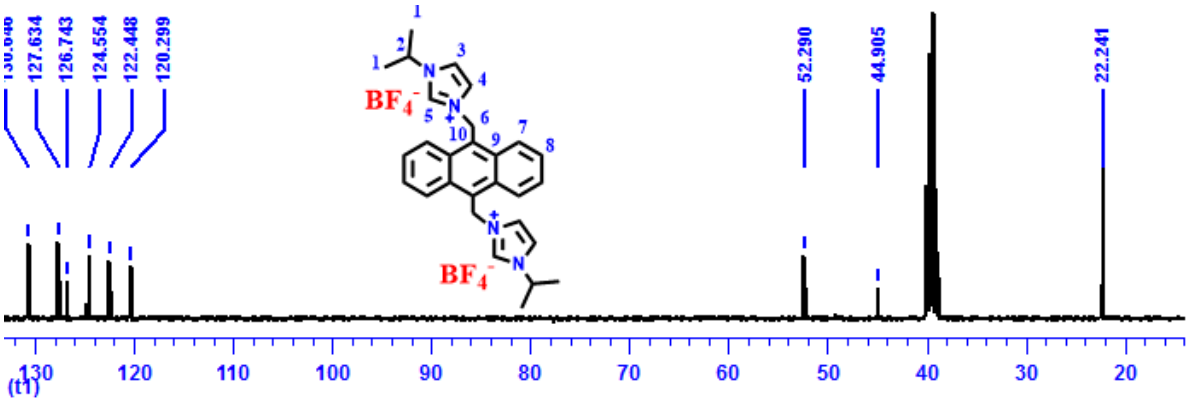


Fig 22. ^{13}C NMR spectrum of compound (**5**) in DMSO-d_6 at RT.

4.7. *Single Crystal Structure of Compound **1, 2** and **3***

The solid state structures of **1, 2** and **3** were unambiguously determined by single crystal X-ray diffraction techniques. (Fig. **23-31**) The structural parameters are listed in table 1. Molecules **1** and **3** all crystallized in triclinic space group, with P1 whereas **2** crystallized in triclinic space group P-1 respectively.

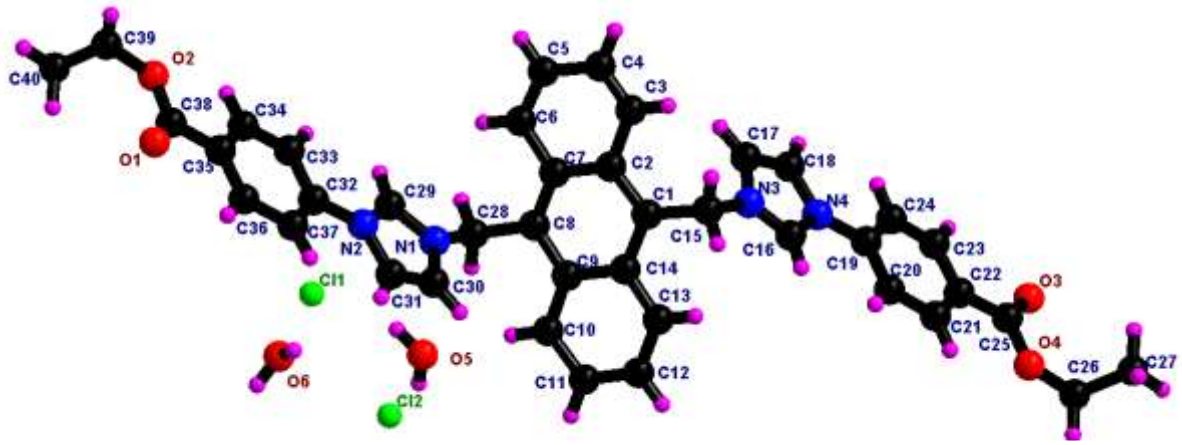


Fig 23. Molecular structure of **1**.

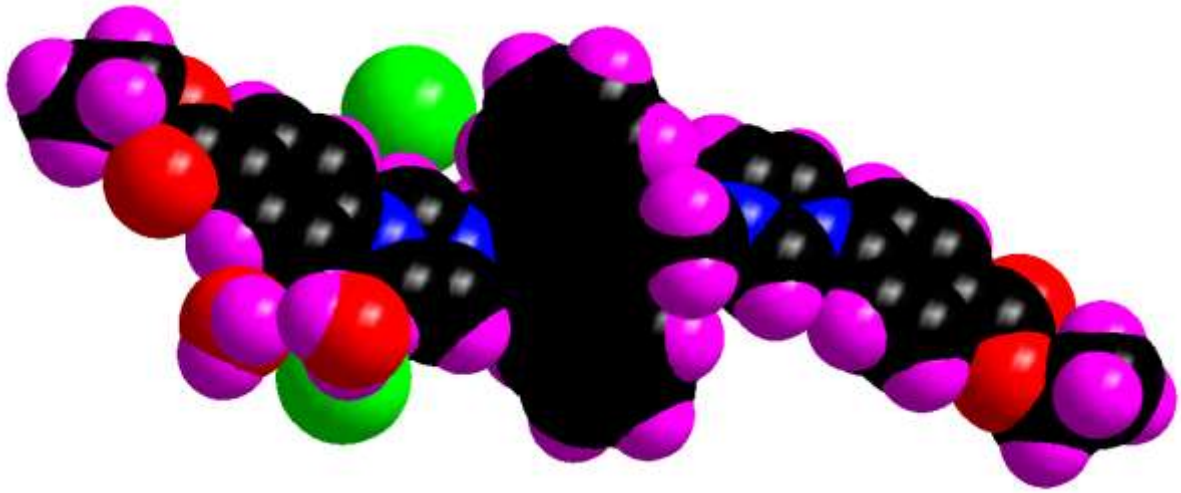


Fig 24. Space filling model of **1.**

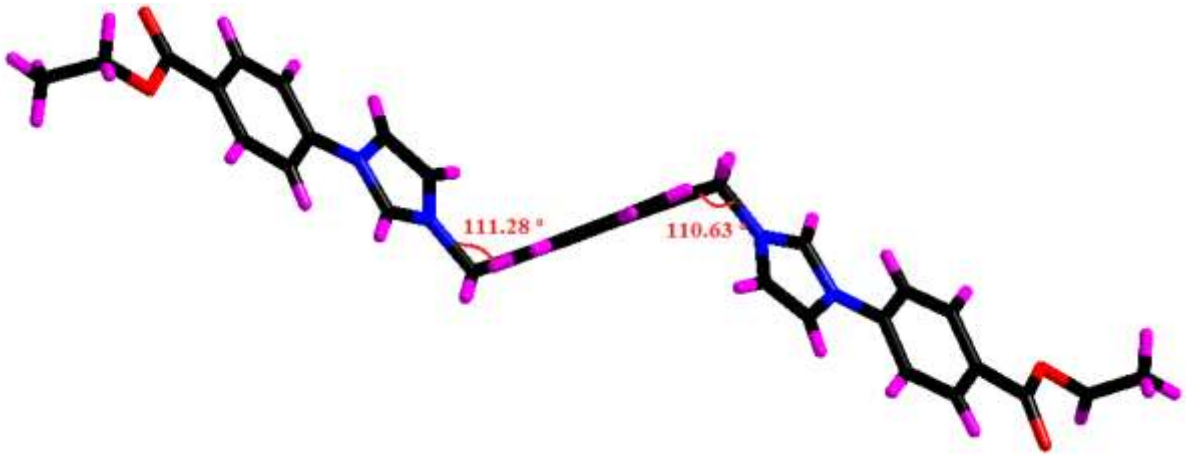


Fig 25. Orientation of Imidazolium moieties in **1** omitted Chloride ions and water molecules for clarity.

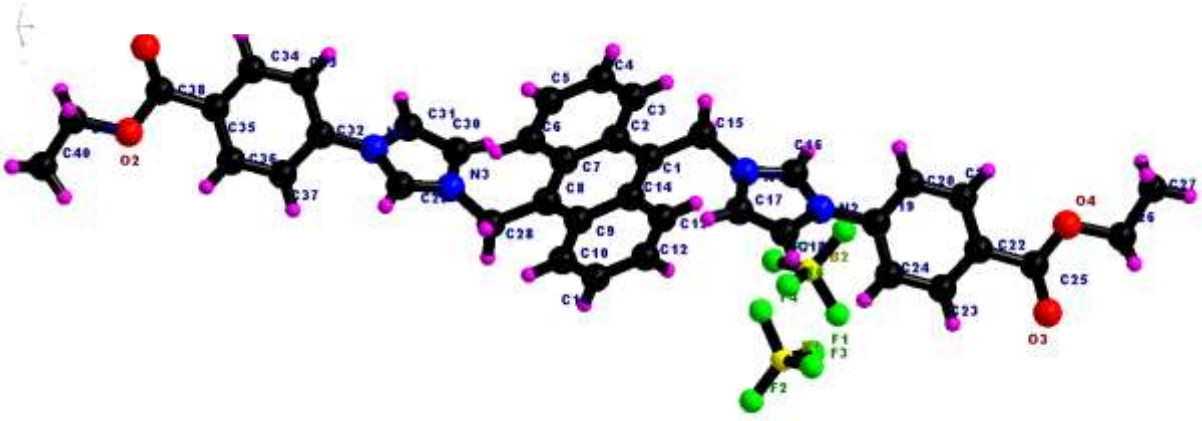


Fig 26. Molecular structure of **2.**

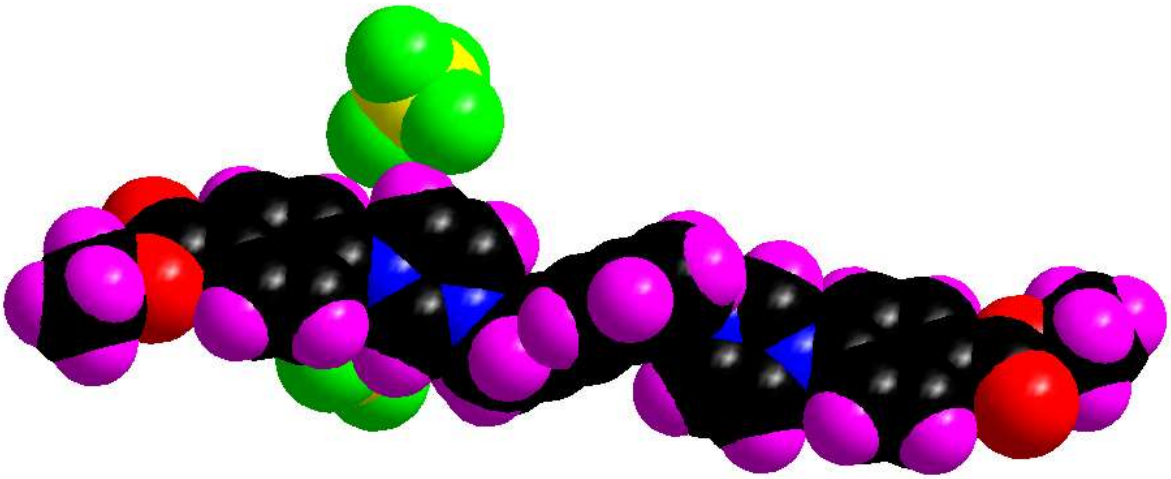


Fig 27. Space filling model of **2.**

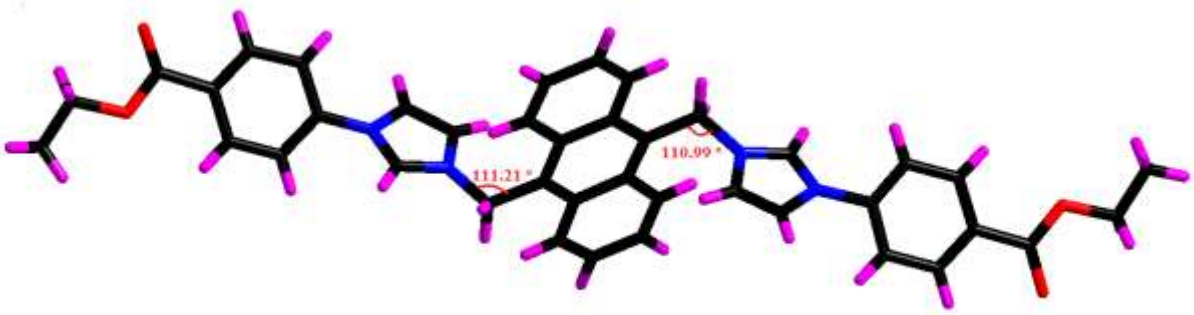


Fig 28. Orientation of Imidazolium moieties in **3** omitted tetrafluoroborate ions for clarity.

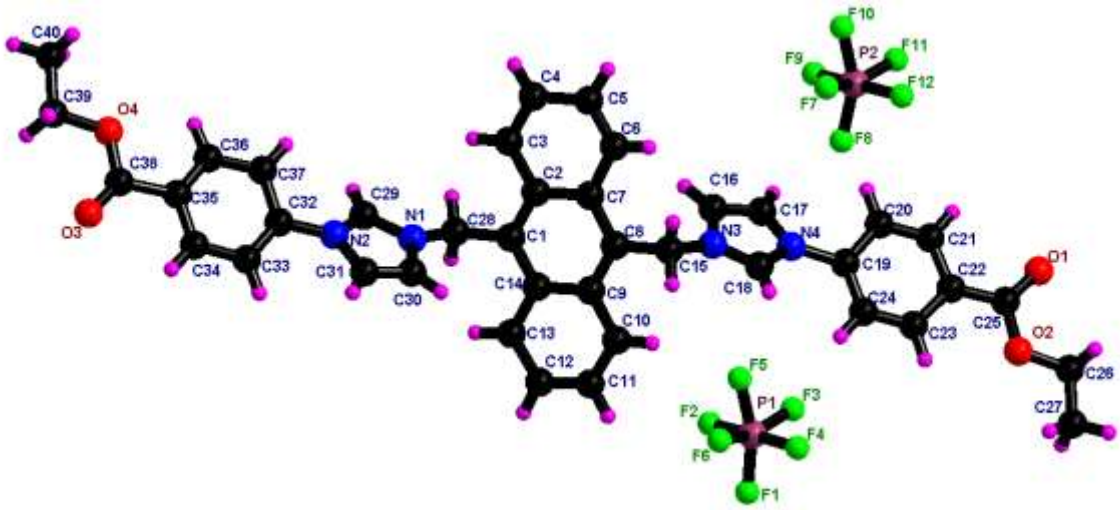


Fig 29. Molecular structure of **3**.

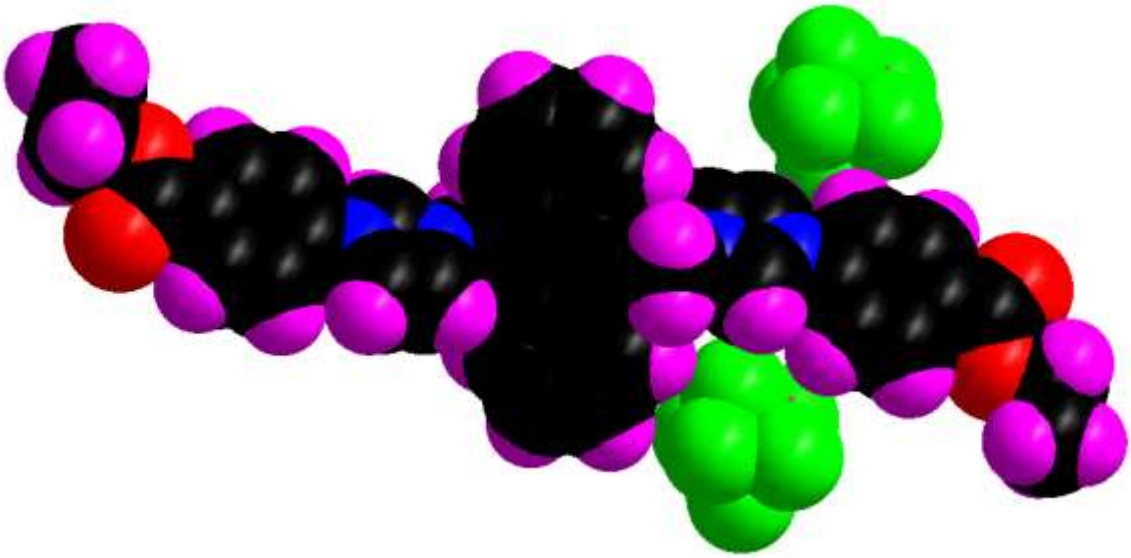


Fig 30. Space filling model of **3**.

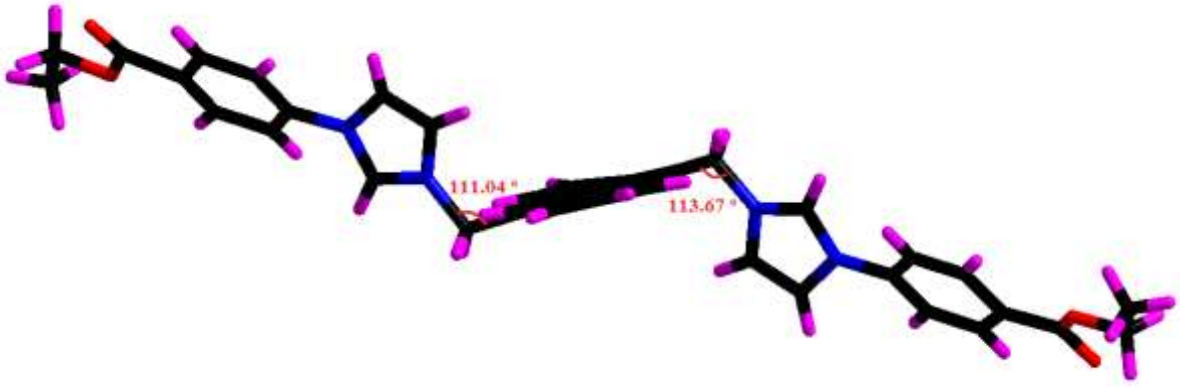


Fig 31. Orientation of Imidazolium moieties in **3** omitted Hexafluorophasphate ions for clarity.

4.8. *Single crystal structure of compound **4** and **5**.*

The solid state structures of **4** and **5** were unambiguously determined by Single Crystal X-ray diffraction techniques (Fig. 32-37). The structural parameters are listed in table 1. Molecules **4** and **5** were crystallized in

orthorhombic and monoclinic, space group, with, Iba2 and $P2_1$ respectively. The structural feature of **4** and **5** are discussed in detail.

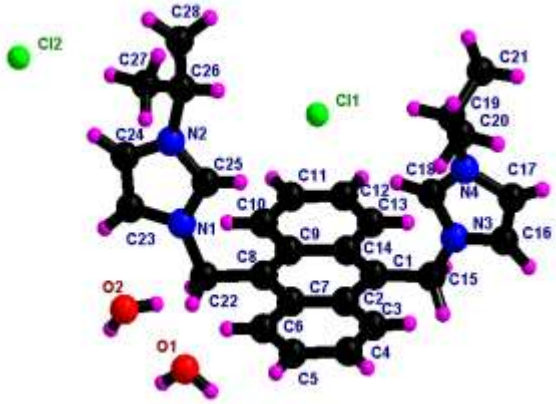


Fig 32. Molecular structure of **4**.

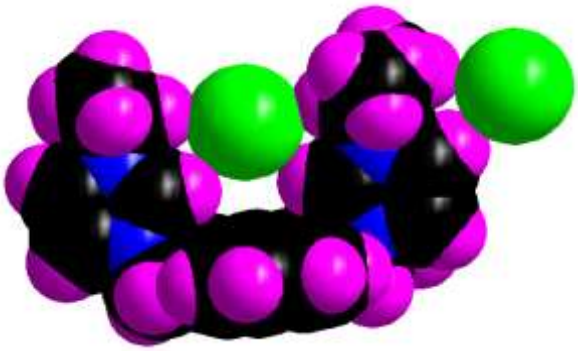


Fig 33. Space filling model of **4**.

Fig 34. Orientation of Imidazolium moieties in **4** omitted Chloride ions and water molecules for clarity.

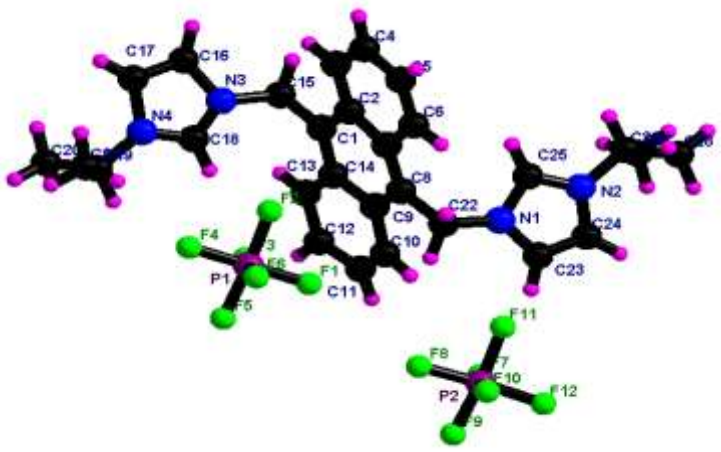


Fig 35. Molecular structure of **5**.

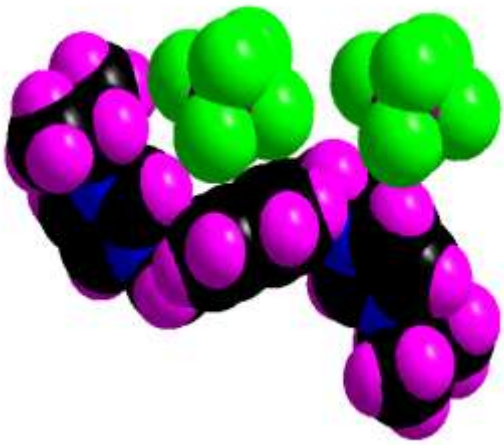


Fig 36. Space filling model of **5**.

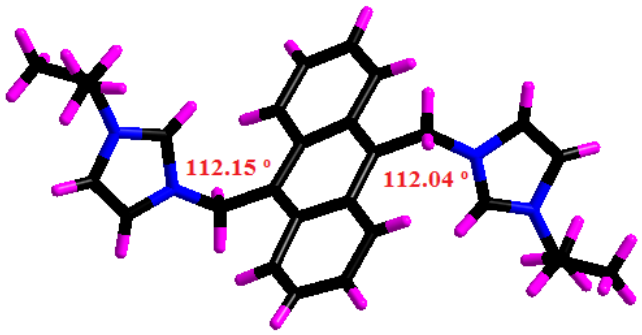


Fig 37. Orientation of Imidazolium moieties in **5** omitted hexafluorophasphate ions for clarity.

The molecular structures of 4 and 5 were established by single crystal X-ray diffraction analyses (Figs. 34 and 37, Table 1). Molecules 4 and 5 crystallized in orthorhombic and monoclinic with space groups, Iba2 and $P2_1$. Interestingly the molecular orientation of 4 and 5 are not comparable. As shown in Fig. 37, the imidazolium rings in 4 lie on the same side with respect to the anthracene plane while the imidazolium rings in 5 are not orientated in the same plane with respect to anthracene plane (Fig. 37). The C-N distances and N-C-N angles of 4 and 5 are as expected. The structural quality of 5 is poor due to presence of unresolved solvent molecule, but the overall chemical structure supports the conclusions drawn from both X-ray and spectral analysis. As observed from structures 4 and 5, the change in counter ions leads to significant change in the geometry of interacting centres.

Table1. Crystallographic data, details of data collection and structure refinement parameters for **1-5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{40}H_{36}Cl_2N_4O_4$	$C_{40}H_{36}B_2F_8N_4O_4$	$C_{40}H_{36}P_2F_{12}N_4O_4$	$C_{28}H_{32}Cl_2N_4$	$C_{28}H32F_{12}N_4P_2$
Formula weight	707.63	810.35	926.67	497.25	722.52
Temperature/K	273	293(2)	310	566(2)	297.21(10)
Crystal system	triclinic	triclinic	Triclinic	Orthorhombic	monoclinic
Space group	P1	P-1	P1	Iba2	$P2_1$
a/Å	8.7674(20)	9.9425(13)	8.7881(5)	12.7016(3)	11.1898(8)
b/Å	9.149(4)	10.0345(12)	10.4673(10)	19.2183(7)	13.3389(14)
c/Å	12.084(8)	10.2409(15)	12.4000(10)	23.1354(6)	10.1111(9)
α/°	76.77(5)	105.396(12)	101.972(8)	90.00	90.00
β/°	88.15(3)	102.819(12)	106.284(6)	90.00	94.025(8)
γ/°	74.41(3)	97.693(10)	103.908(7)	90.00	90.00
Volume/$Å^3$	908.4(8)	940.1(2)	1015.51(14)	5647.4(3)	1505.5(2)
Z	1	1	1	9	2
$\rho calc^{g/cm3}$	1.293	1.431	1.515	1.316	1.594
μ/mm^{-1}	0.225	0.119	1.897	2.509	2.274
F(000)	370.0	418.0	474.0	2366.0	740.0
Radiation	Mo K_α (λ = 0.7107)	Mo K_α (λ = 0.7107)	Cu K_α (λ = 1.5418)	Cu K_α (λ = 1.5418)	Cu K_α (λ = 1.5418)

2Θ range for data collection/°	5.86 to 58.04	6.46 to 57.94	7.78 to 143.44	7.64 to 142.92	7.92 to 142.88
Data/restraints /parameters	5016/3/501	4275/0/263	4407/3/561	4948/1/325	3874/1/414
GOF on F^2	1.069	1.041	1.036	1.200	1.946
R_1[I>=2σ (I)]	0.0580	0.0913	0.0754	0.0955	0.1787
wR_2[I>=2 σ (I)]	0.1067	0.2394	0.2147	0.2711	0.4879
R_1 values (all data)	0.1218	0.1524	0.0972	0.1121	0.2085
wR_2 values (all data)	0.1486	0.2952	0.2495	0.3087	0.5446

4.9. *HSQC and HMBC measurements of compound **1, 2** and **3.***

The structures of 1, 2 and 3 were further confirmed by HMBC and HSQC correlation spectra. HSQC spectra of 1, 2 and 3 shows CH correlations as follows, the imidazolium CH group shows a strong correlation between the carbon and hydrogen attached to corresponding moieties. The CH group of anthracene ring also shows a strong correlation between carbon and hydrogen and the CH correlation also observed for CH_2 groups. The CH correlation also observed for CH_2 and CH_3 groups of corresponding ester moiety. From these observations, the complete CH correlations were confirmed. In addition, the HMBC correlation spectra show the mapping of carbon coupling with neighbouring protons. In 1, 2 and 3 the protons CH_2 near to the anthracene ring is strongly coupled with the nearest imidazolium carbons (^3J), also coupled with the nearest carbon atom (^3J) of CH group in anthracene ring, and quaternary carbons (^2J, ^3J) of anthracene ring. In 1, 2 and 3 carbon of CH attached to the nitrogen atom is coupled with imidazolium CH proton (^3J). In 1, 2 and 3 carbonyl carbon is strongly coupled with adjacent CH_2 protons (^2J and ^3J).

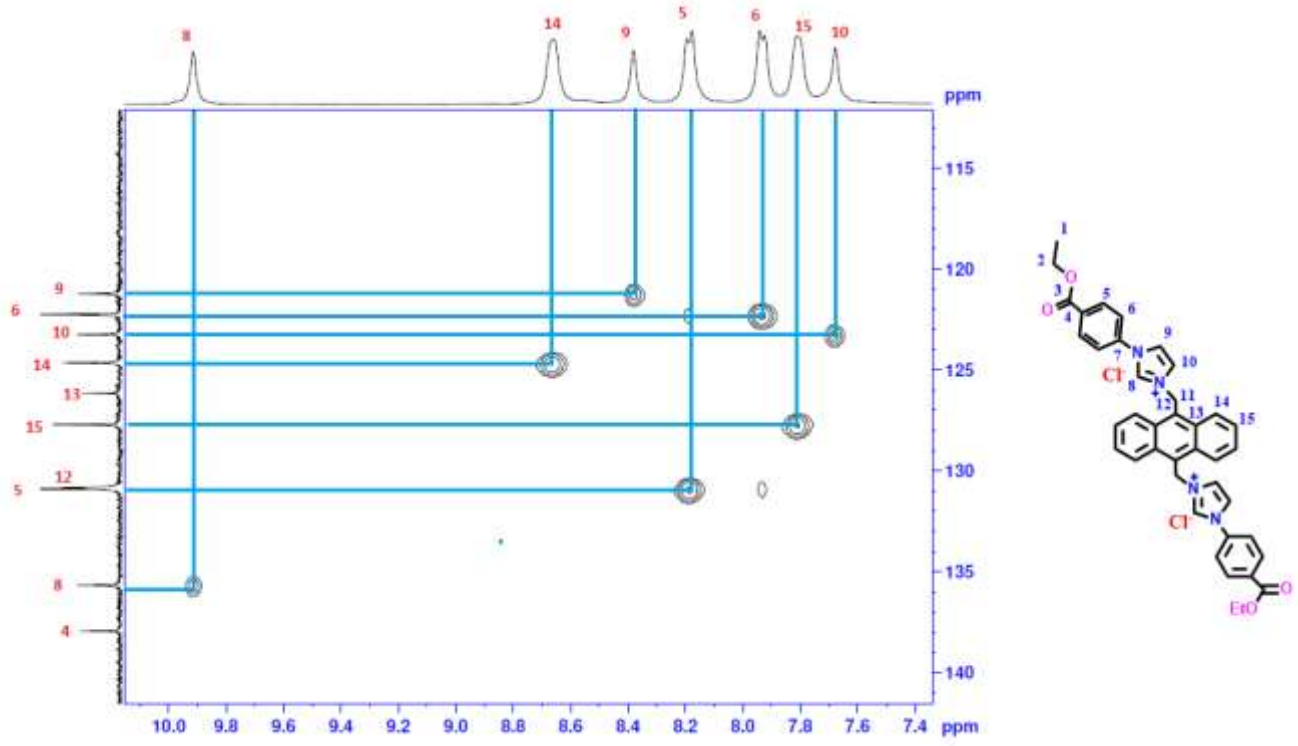


Fig 38. HSQC Spectrum of Compound **1.**

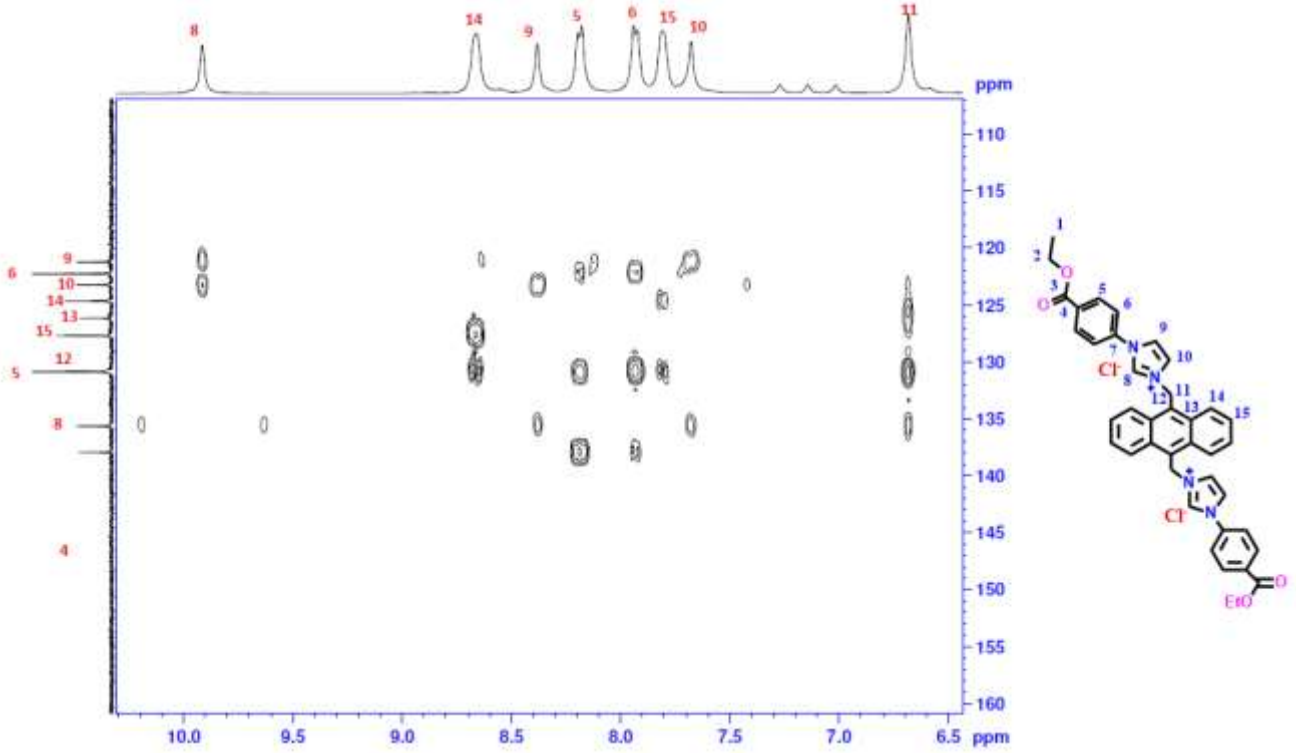


Fig 39. HMBC Spectrum of Compound **1.**

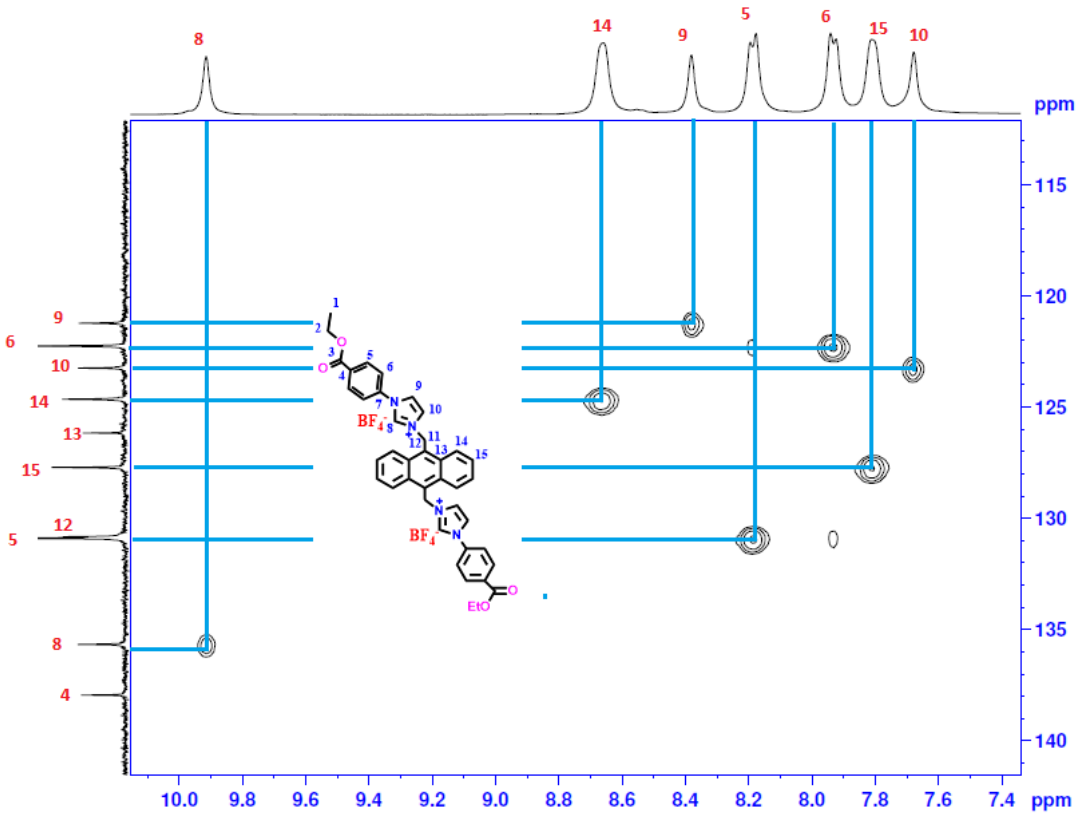


Fig 40. HSQC Spectrum of Compound **2.**

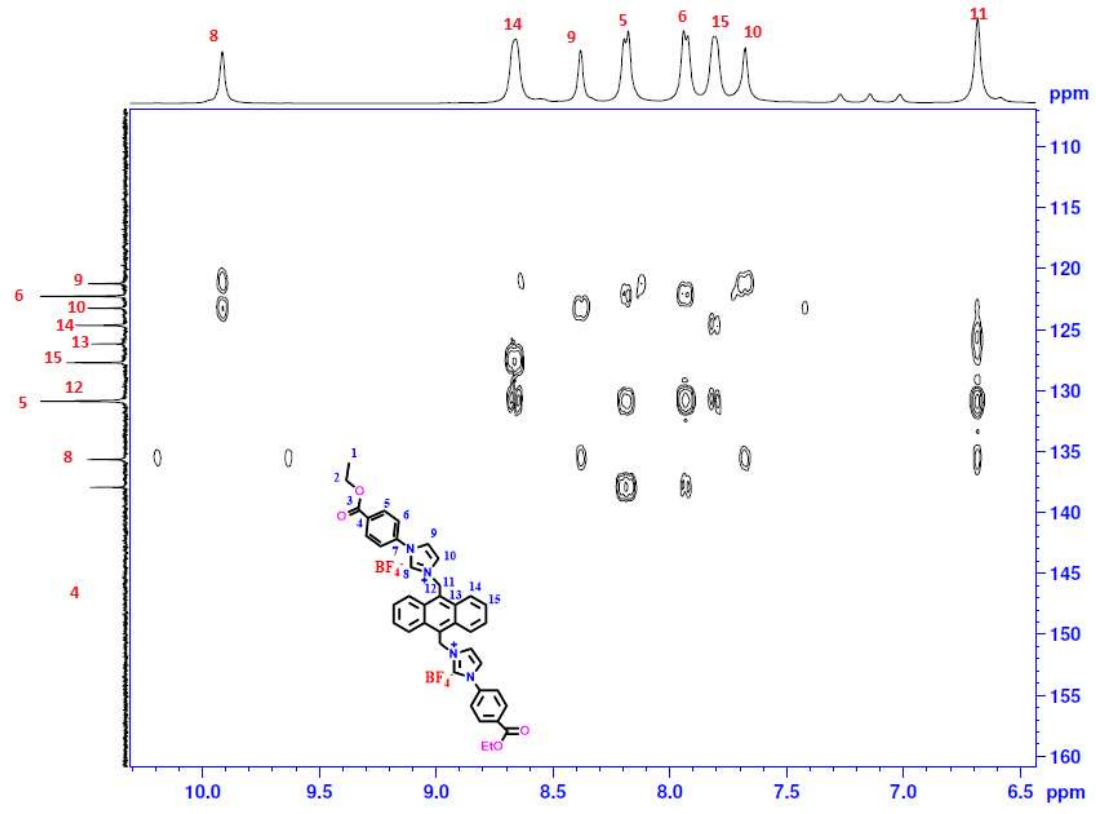


Fig 41. HMBC Spectrum of Compound **2.**

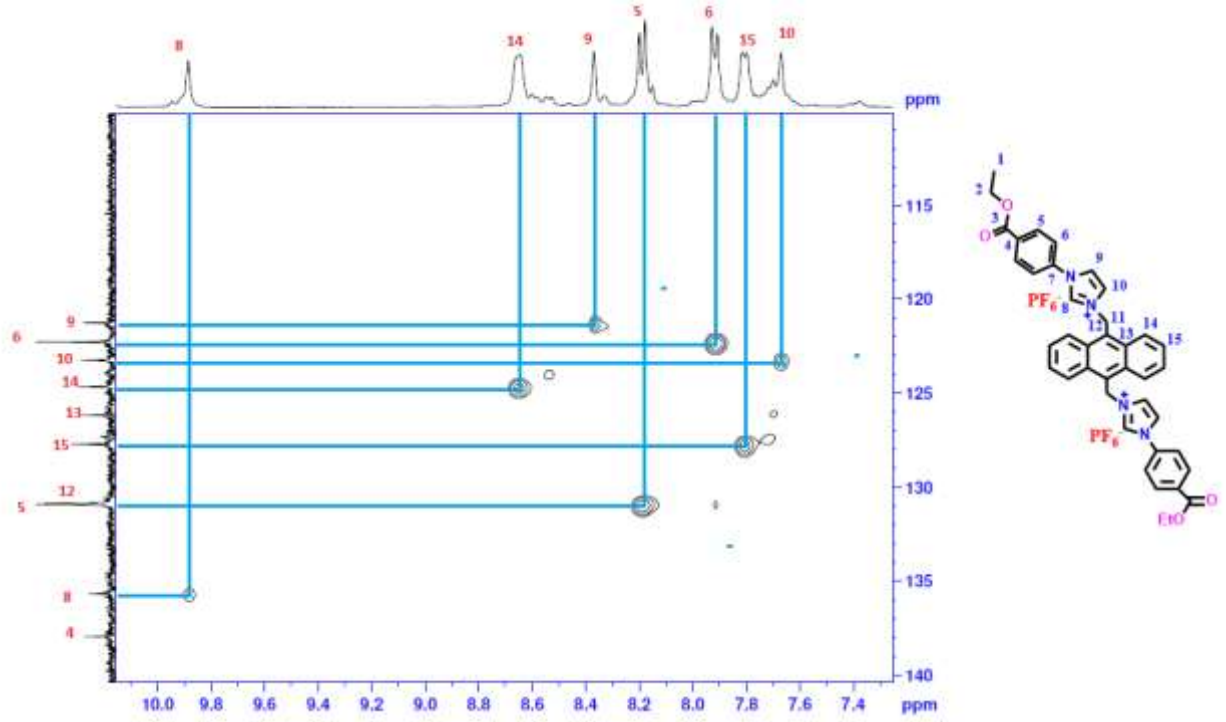


Fig 42. HSQC Spectrum of Compound **3.**

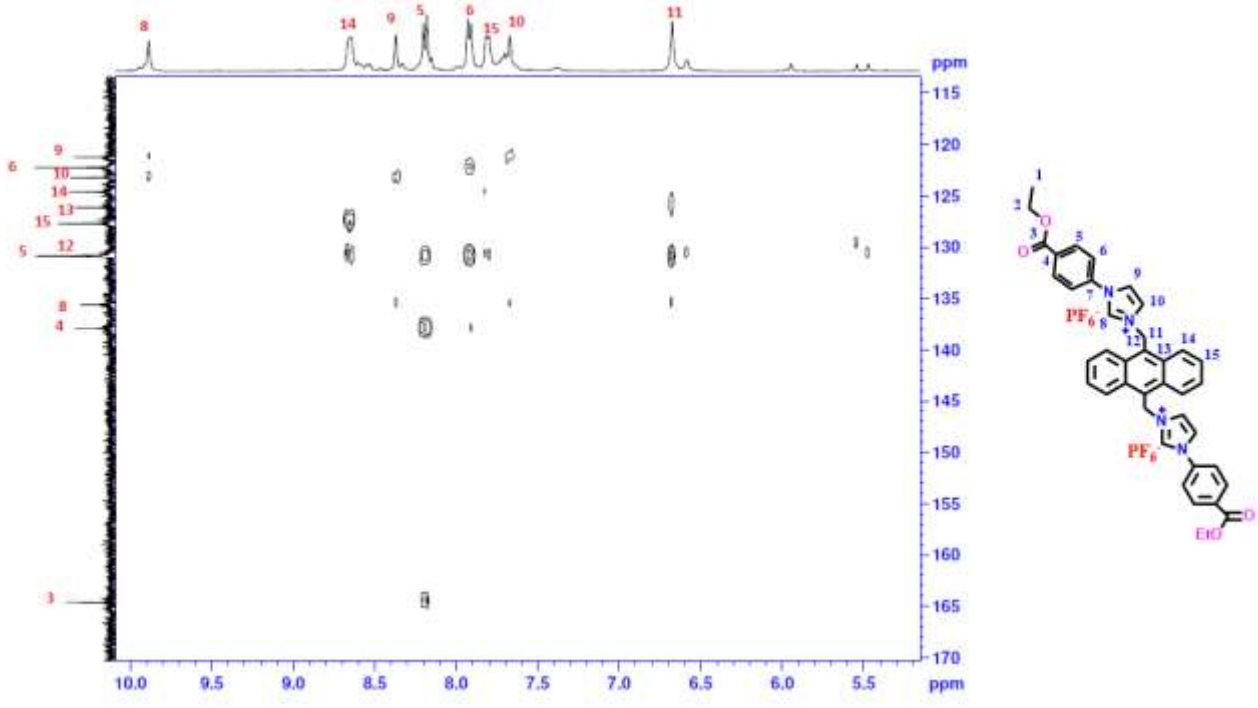


Fig 43. HMBC Spectrum of Compound **3.**

4.10. *HSQC and HMBC measurements of compound **4, 5** and **6.***

The structures of 4, 5 and 6 were further confirmed by HMBC and HSQC co-relation spectra. HSQC spectra of 4, 5 and 6 shows CH correlations as follows, the imidazolium CH group shows a strong correlation between the carbon and hydrogen attached to corresponding moieties. The CH group of anthracene ring also shows a strong correlation between carbon and hydrogen and the CH correlation also observed for CH_2 groups. In the case of 4, 5 and 6 CH correlation also observed for CH and CH_3 groups of corresponding moieties. From these observations, the complete CH correlations were confirmed. In addition, the HMBC correlation spectra show the mapping of carbon coupling with neighbouring protons. In 4, 5 and 6 the protons CH_2 near to the anthracene ring is strongly coupled with the nearest imidazolium carbons (^3J), also coupled with the nearest carbon atom (^3J) of CH group in anthracene ring, and quaternary carbons (^2J) of anthracene ring. In 4, 5 and 6 carbon of CH attached to the nitrogen atom is coupled with imidazolium CH proton (^3J) and CH_3 protons.

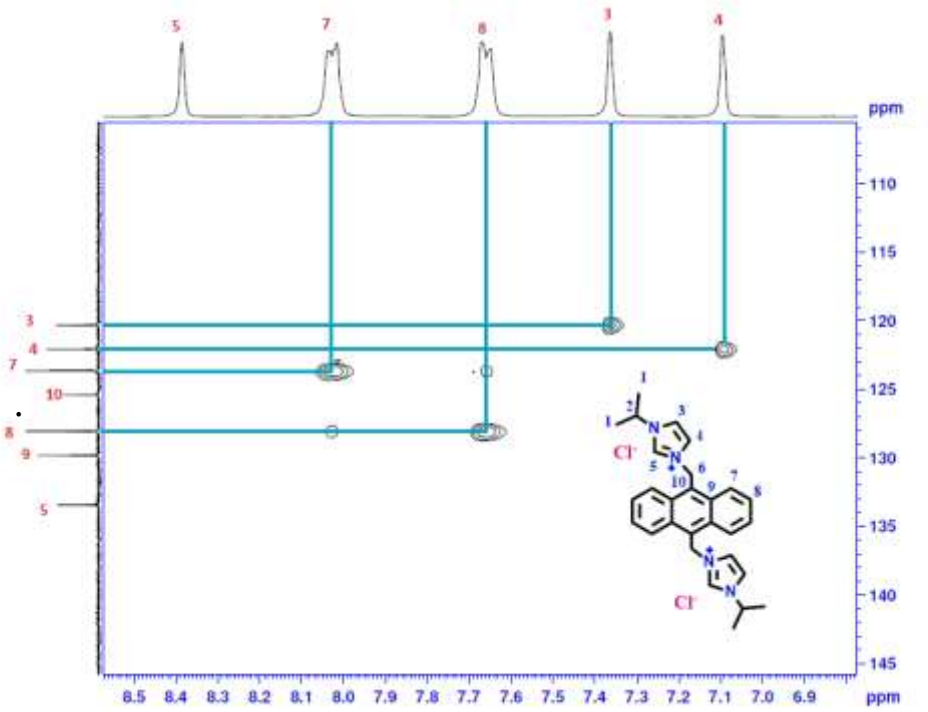


Fig 44. HSQC Spectrum of Compound **4.**

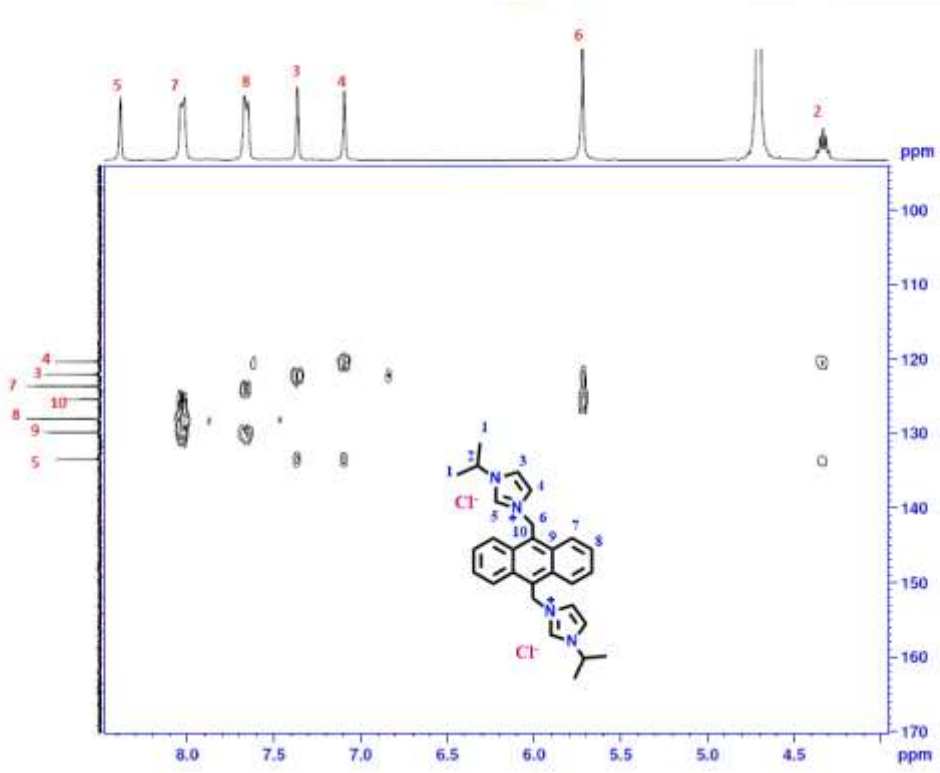


Fig 45. HMBC Spectrum of Compound **4.**

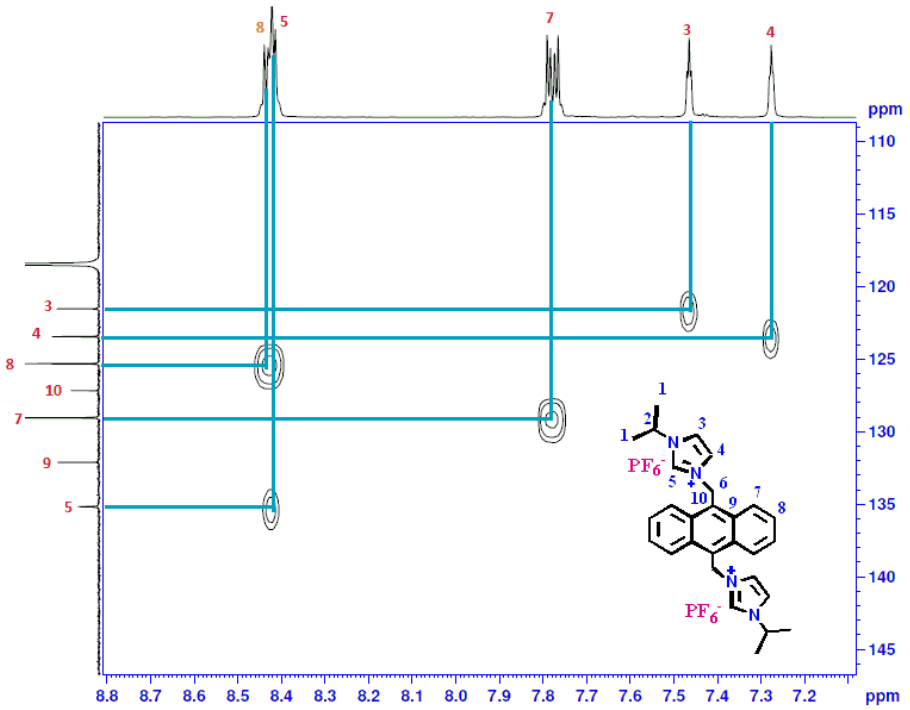


Fig 46. HSQC Spectrum of Compound **5.**

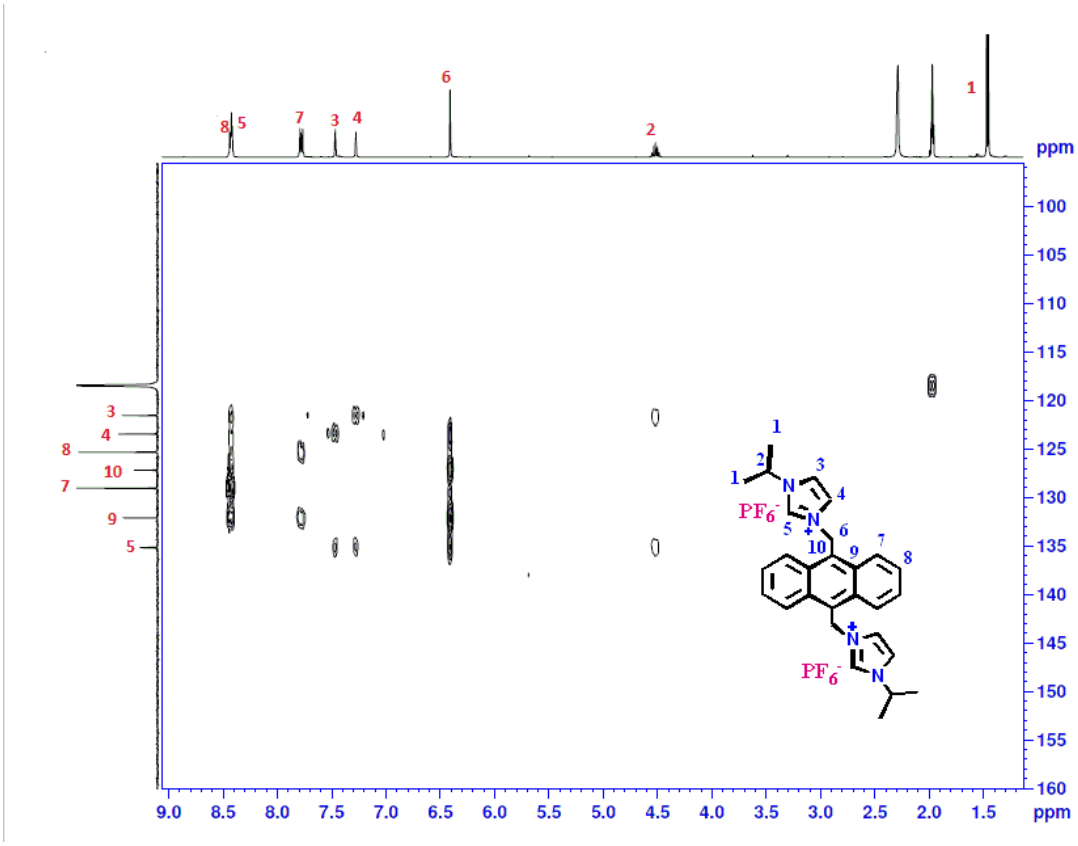


Fig 47. HMBC Spectrum of Compound **5.**

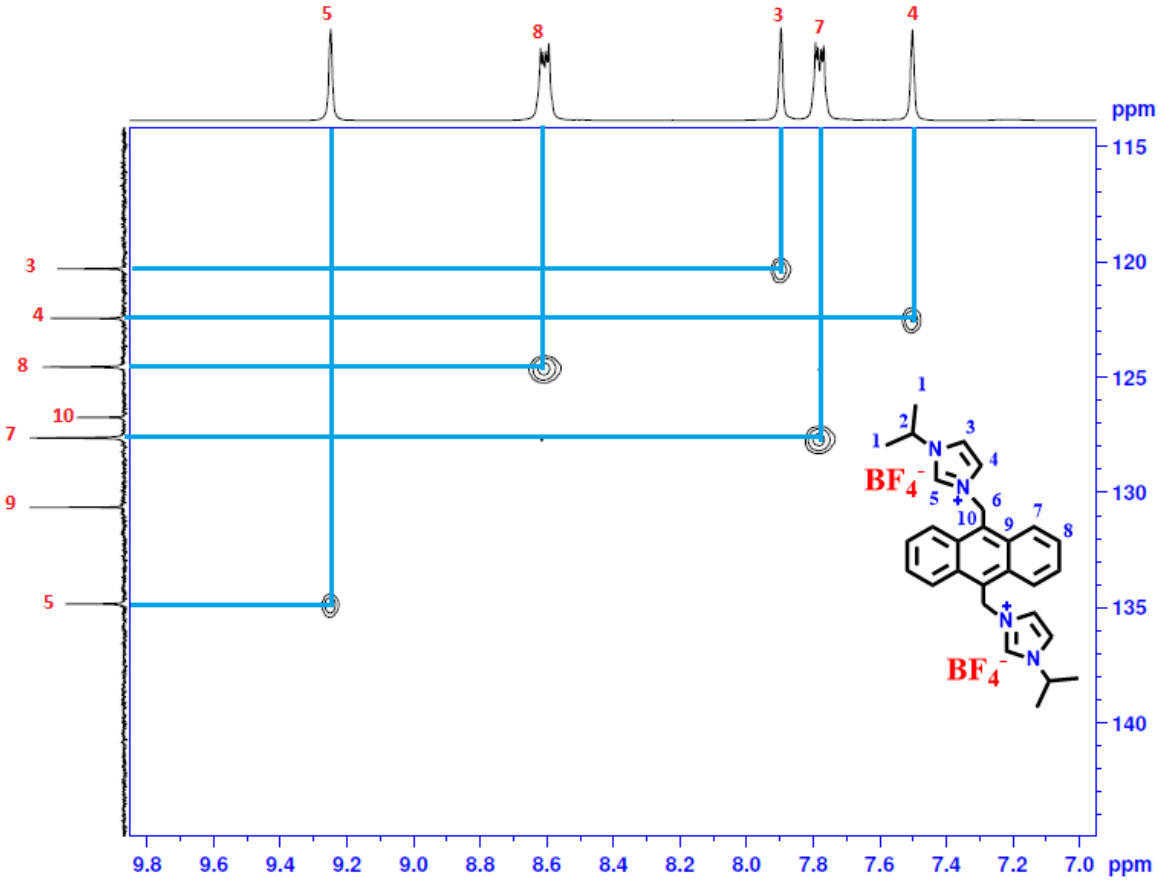


Fig 48. HSQC Spectrum of Compound **6.**

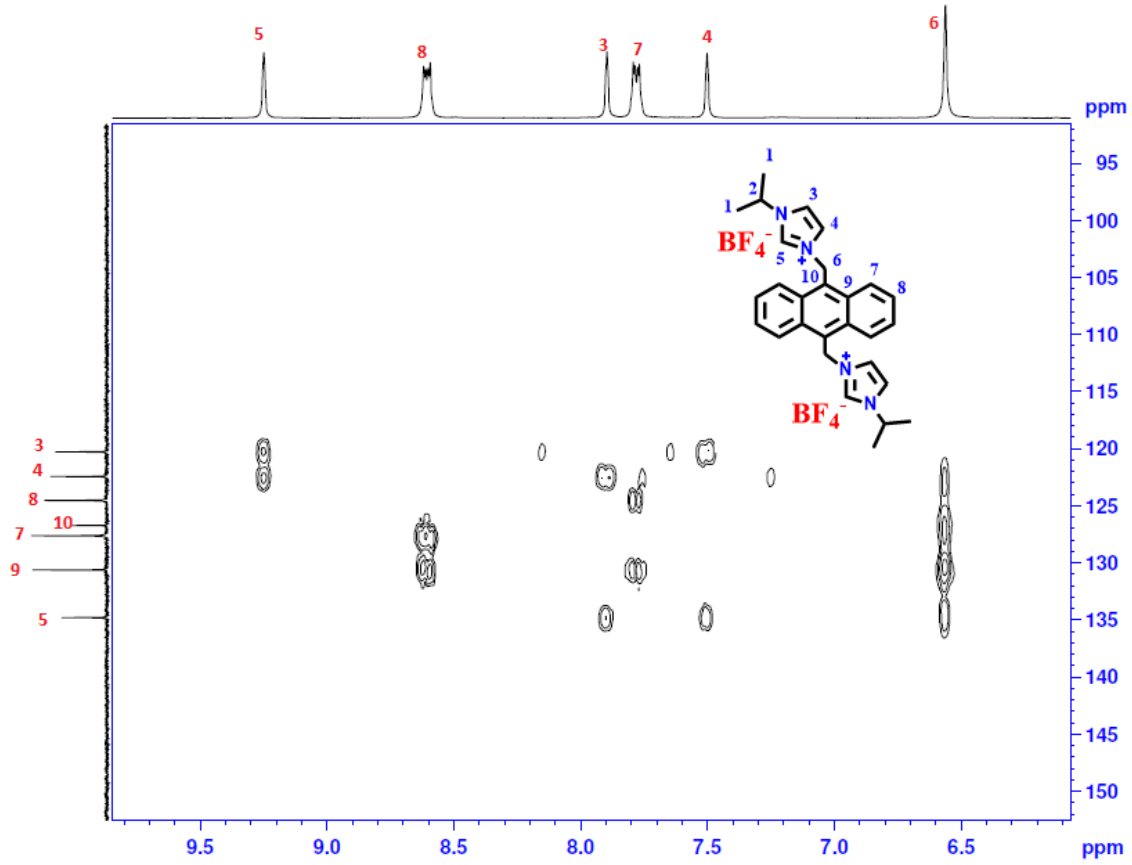
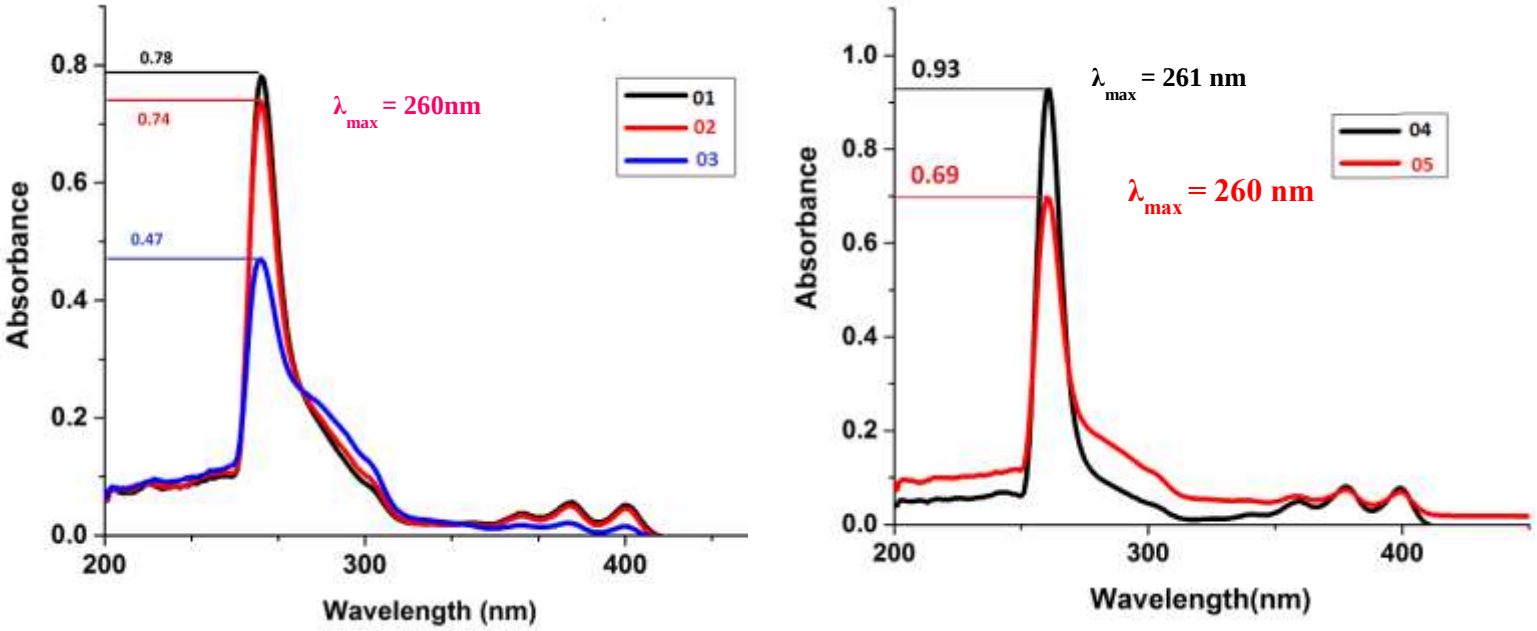


Fig 49. HMBC Spectrum of Compound **6.**

4.11. *UV-vis Solution State Study of compound **1-5**.*



Compound **1, 2 and 3** all displayed maximum absorbance at λ_{max} **= 260 nm** with varying absorbance which is maximum for **1** i.e. 0.78 and least for **3** i.e. 047 and for compound **2** it lies in between **1** and **3** i.e.0.74 all of which corresponds to π-π* transitions.

Compound **4** showed maximum absorbance (0.93) at λ_{max} **= 261 nm** where as in compound **5** displayed maximum absorbance (0.69) at λ_{max} **= 260 nm** both of which corresponds to π-π* transitions.

5. CONCLUSION

We have successfully synthesized compounds **1-6**. Compounds **1-6** have been fully characterized by ^{1}H, ^{13}C, DEPT, HSQC and HMBC spectra and single crystal X-Ray structures. All compounds are found out to be Fluorescent active and are submitted for biological activity.

6. REFERENCES

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ANNEXURE I

Supporting Information

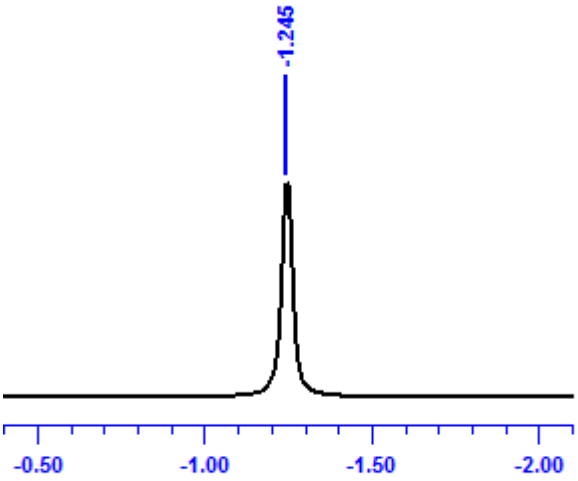

Fig S1. ^{11}B Spectrum of **2**

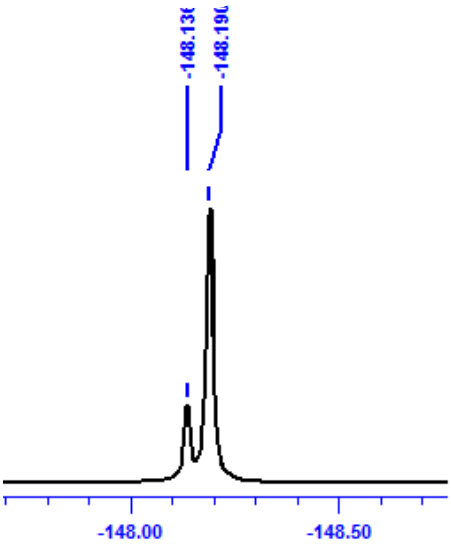

Fig S2. ^{19}F Spectrum of **2**

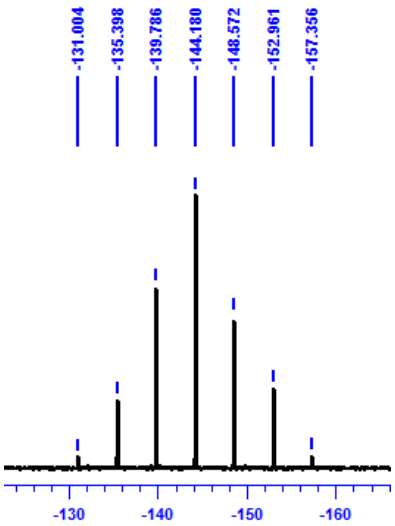

Fig S3. ^{31}P Spectrum of **3**

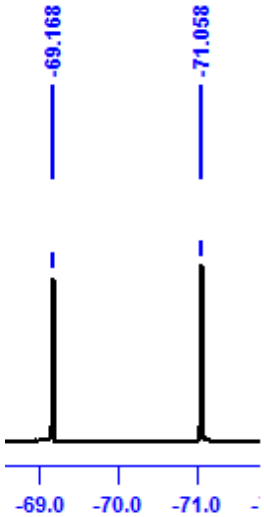

Fig S4. ^{19}F Spectrum of **3**

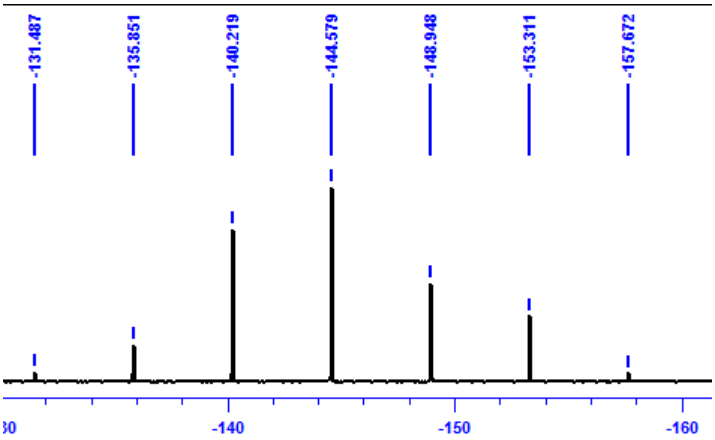

Fig S5. ^{31}P Spectrum of **5**

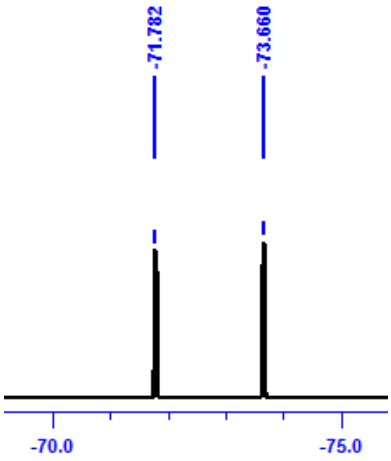

Fig S6. ^{19}F Spectrum of **5**

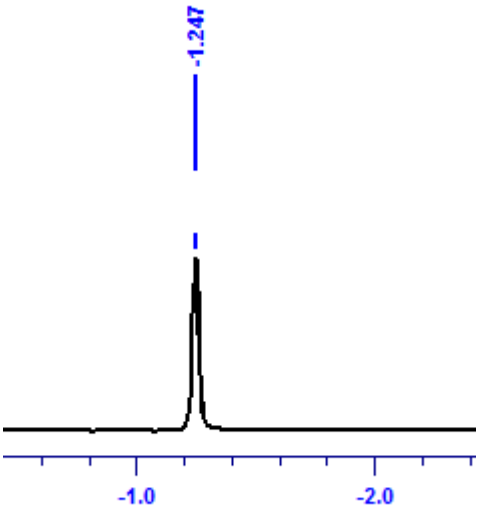

Fig S7. ^{11}B Spectrum of **6**

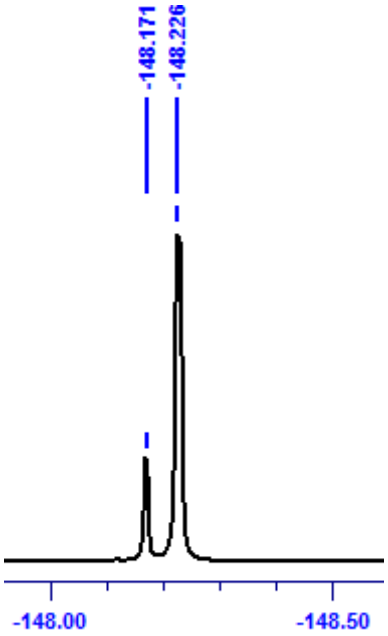

Fig S8. ^{19}F Spectrum of **6**

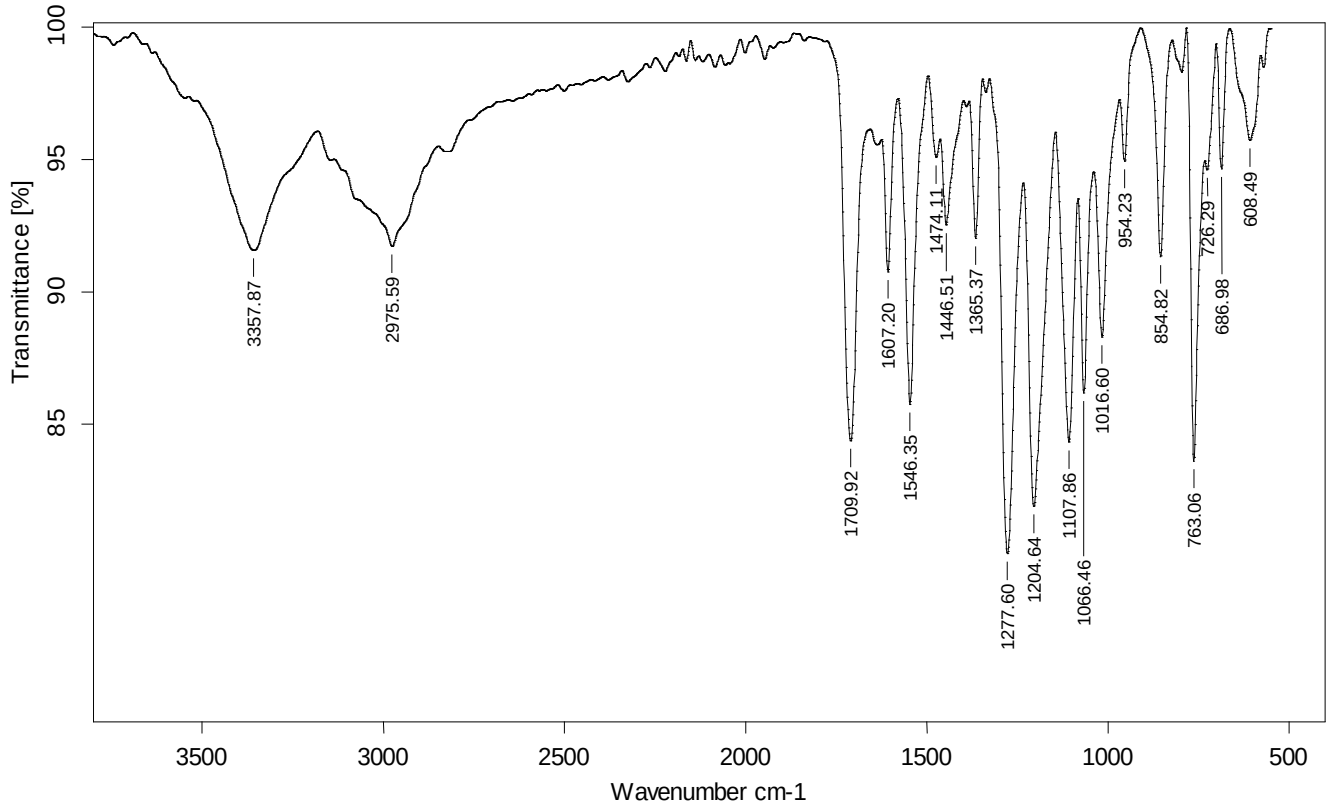

Fig S9. FT-IR Spectrum of Compound **1**.

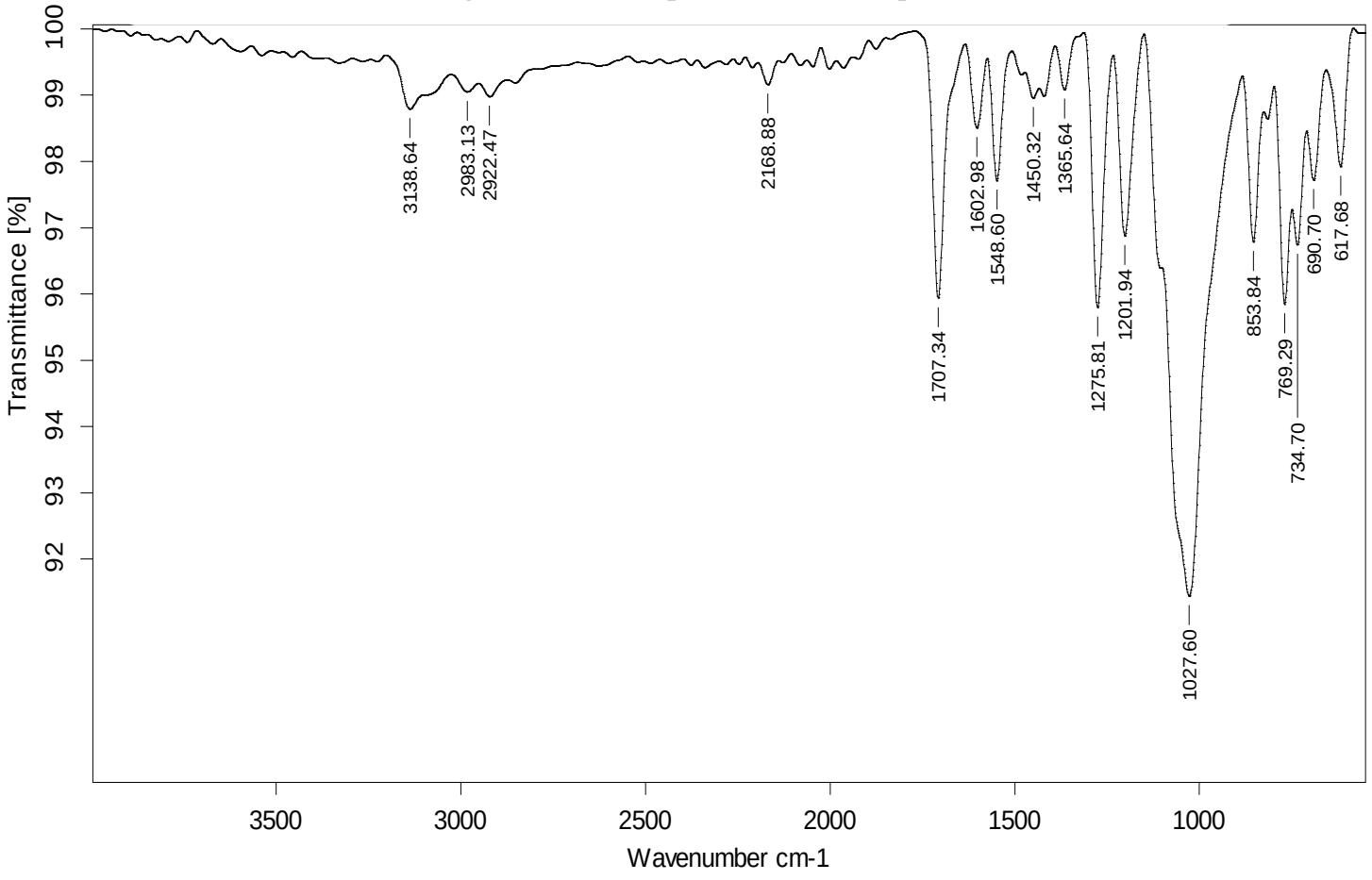

Fig S10. FT-IR Spectrum of Compound **2**.

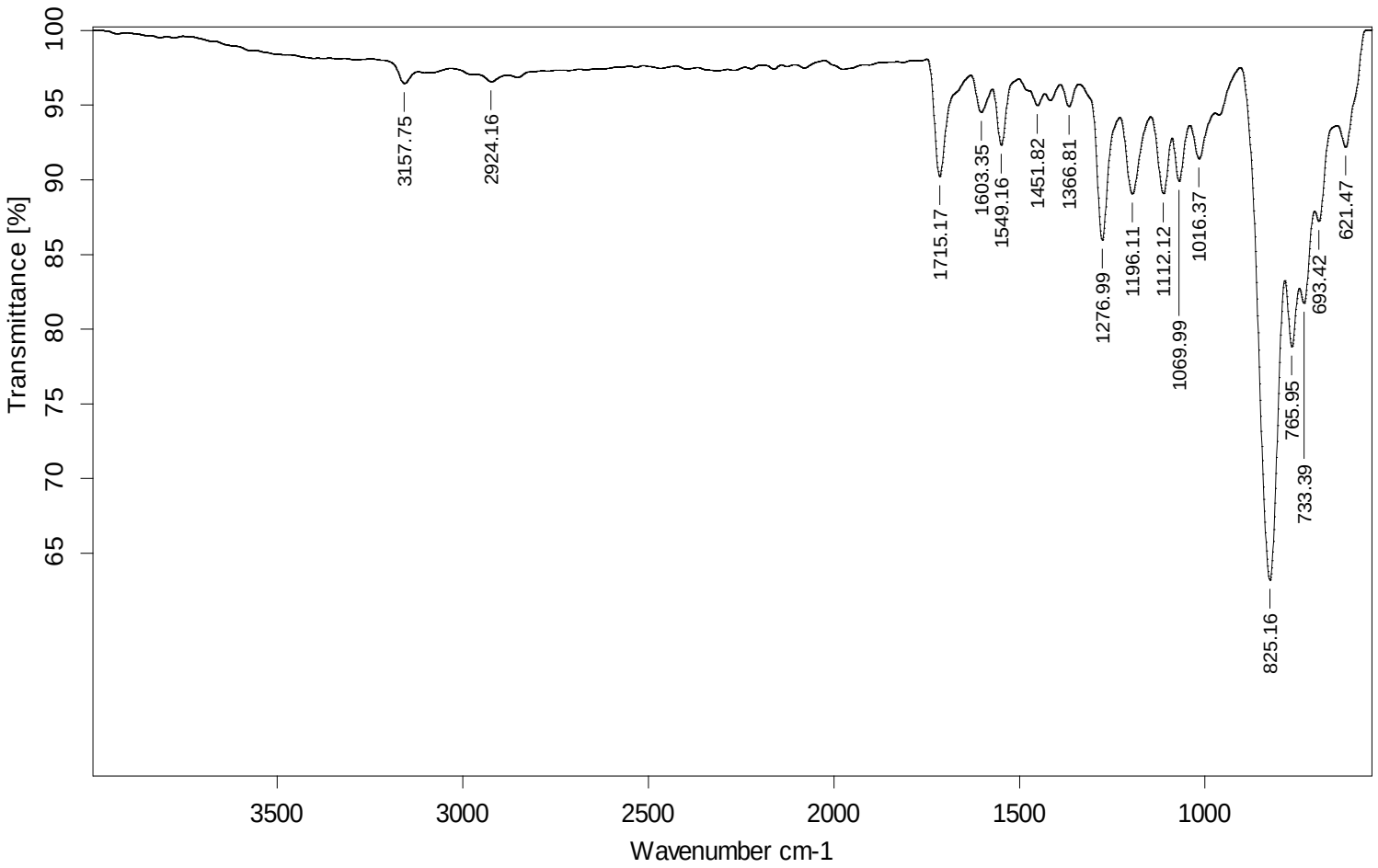

Fig S11. FT-IR Spectrum of Compound **3**.

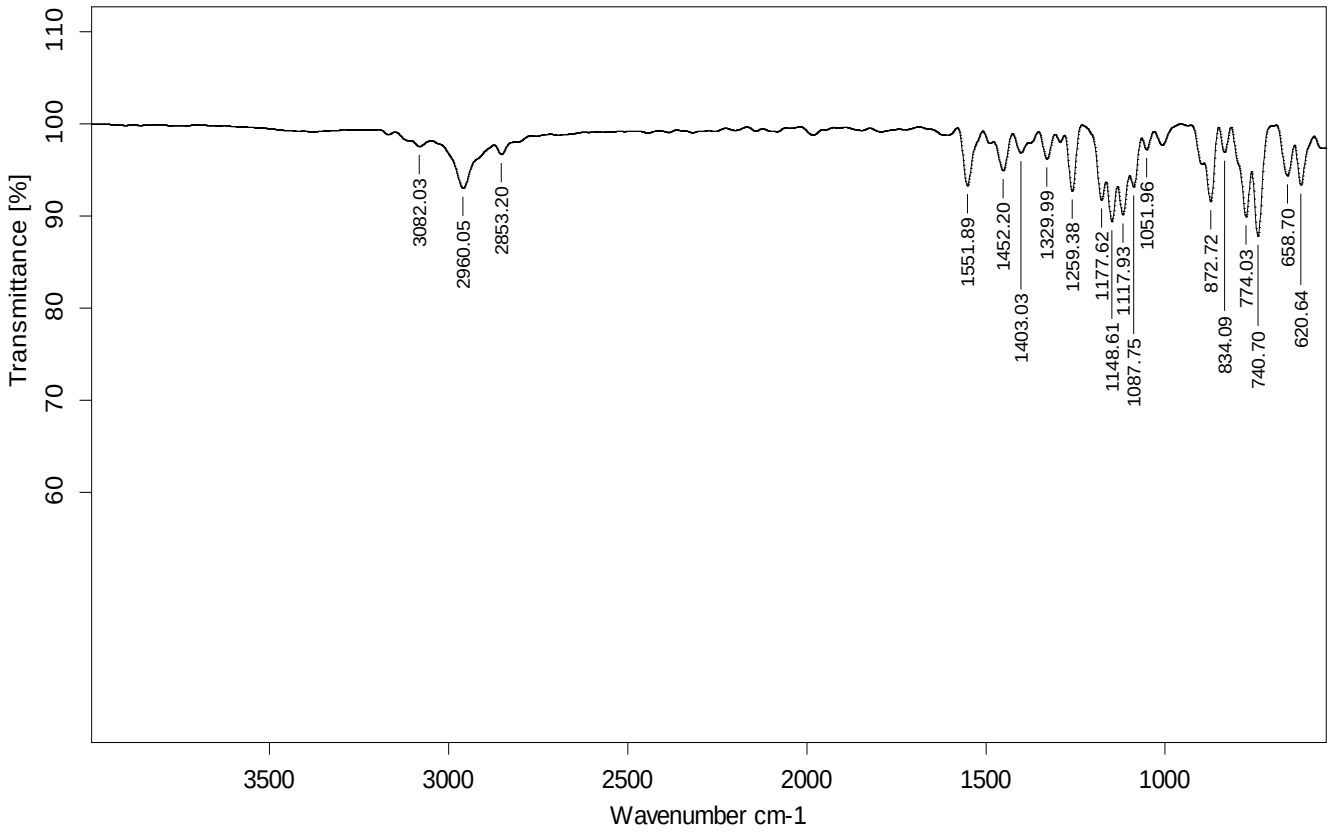

Fig S12. FT-IR Spectrum of Compound **4**.

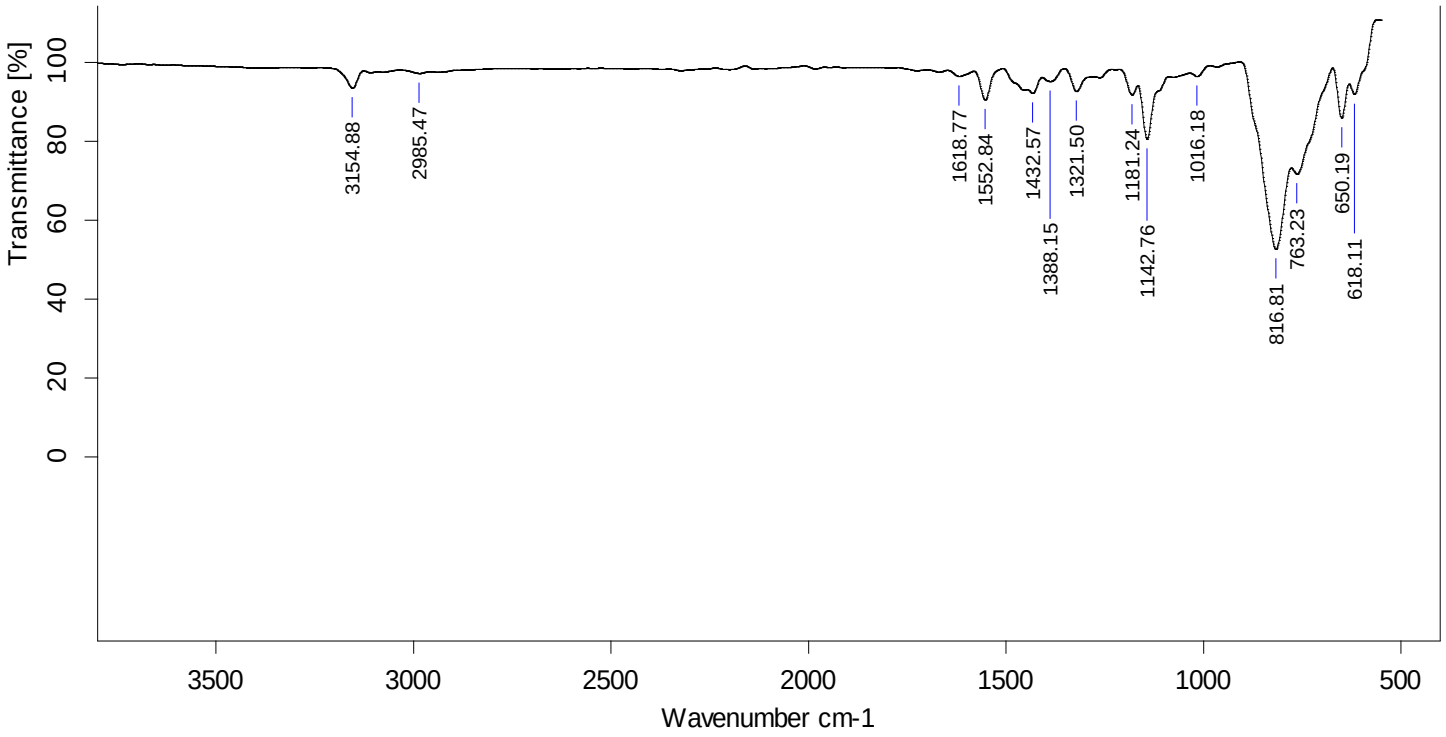

Fig S13. FT-IR Spectrum of Compound **5**.

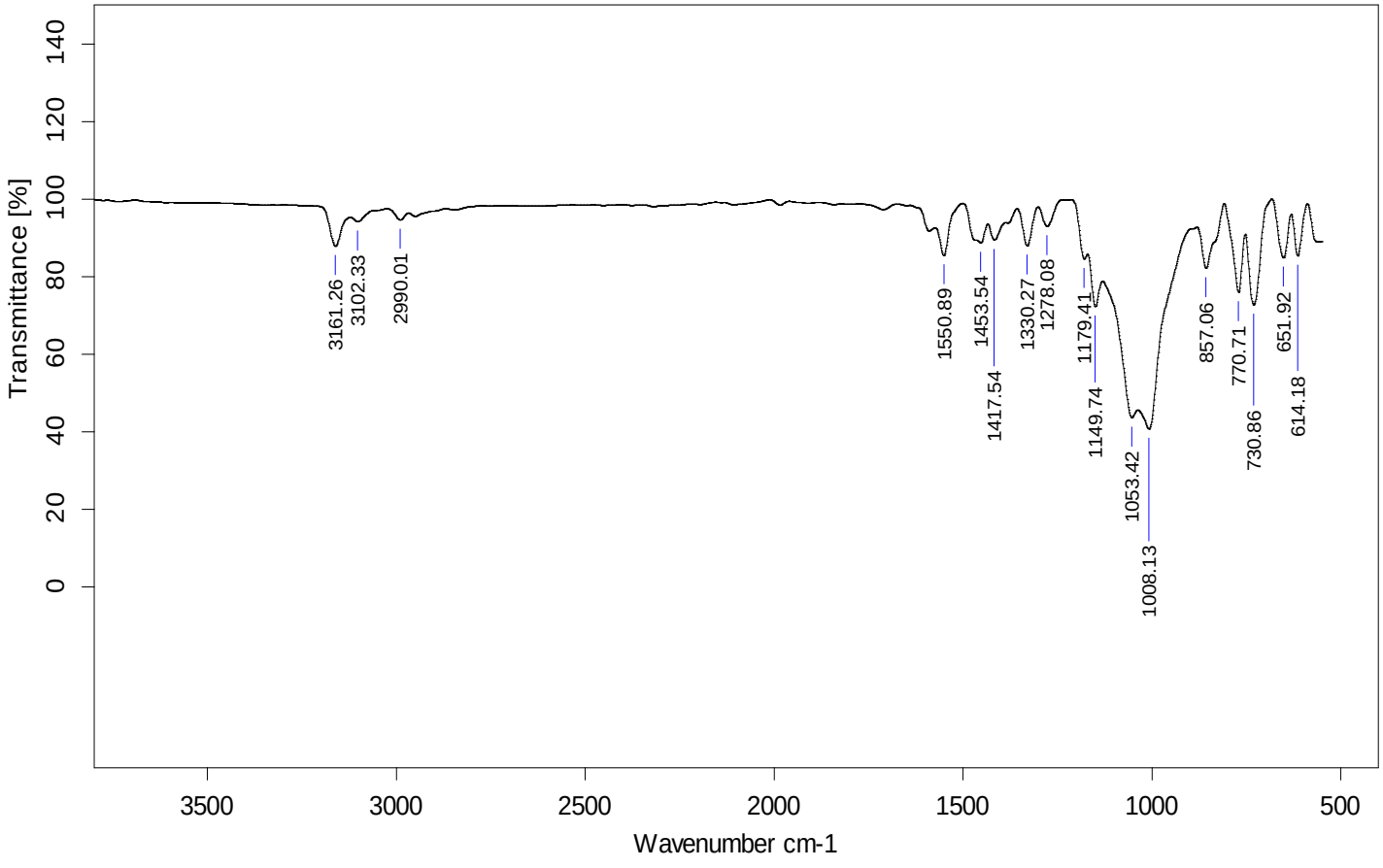

Fig S14. FT-IR Spectrum of Compound **6**.