A Convergence of Synthesis and Antimicrobial Research: Imidazolium based Di-cationic Ionic Liquids

Hira Akram

Reg No: 00000365061

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Thesis Supervisor: **Dr. Mudassir Iqbal**

Department of Chemistry, School of Natural Sciences

National University of Sciences and Technology, Islamabad, Pakistan.

THESIS ACCEPTANCE CERTIFICATE

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Signature: ________________

Name of Supervisor: Prof. Mudassir Iqbal

Date: ________________

Signature (HoD): ________________

Date: 21/09/2023

Signature (Dean/Principal): ________________

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Examination Committee Members

1. Name: PROF. AZHAR MAHMOOD Signature:

2. Name: DR. MUHAMMAD ADIL MANSOOR Signature:

Supervisor's Name PROF. MUDASSIR IQBAL Signature:

M Sohail
~~Head~~ of Department

21/09/2023
Date

COUNTERSINGED

Date: 22-9-2023

Dean/Principal

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِيْمِ

In loving memory of my father, whose unwavering belief in my potential continues to inspire me, and to my dear mother, whose endless love and support have been my guiding light throughout this journey. This thesis is a tribute to your enduring legacy and the values you instilled in me.

STATEMENT OF ORIGINAL AUTHORSHIP

I, Hira Akram, hereby declare that my MS thesis, "A Convergence of Synthesis and Antimicrobial Research: Imidazolium based Di-cationic Ionic Liquids," is entirely original to me and has not been submitted anywhere else in the world or to the National University of Sciences and Technology (NUST). The institution has the power to revoke my MS degree at any time if my claim is later proven to be false, even after I have graduated.

Name of student: Hira Akram

Date: 15-09-2023

Signature: ________________

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Hira Akram

LIST OF ABBREVIATIONS

DILS	Di-cationic Ionic Liquids
ILs	Ionic Liquids
SAILS	Surface Active Ionic Liquids
Attenuated Total Reflection	ATR
Fourier Transformation Infrared spectroscopy	FTIR
Nuclear Magnetic Resonance	NMR
MIm	Methyl Imidazole

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ABSTRACT

Novel methyl imidazolium based di-cationic, ionic liquids were synthesized using two spacers, 1,3-dibromopropane and (E)-1,4-dibromo-2-butene. Seven different types of anions were used to synthesize a total of 16 ionic liquids. Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy were utilized to characterize ionic liquids. The synthesized ionic liquids were tested for their antibacterial activity against a panel of bacteria that included *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Klebsiella pneumonia* and Methicillin-resistant *Staphylococcus aureus*. The results exhibited that the ionic liquids had a good antibacterial activity against all the five tested bacteria.

1. INTRODUCTION

1.1. Confronting Antibacterial Challenges: Exploring Ionic Liquids as Innovative Agents

Human health is severely compromised by bacteria since they are the root cause of so many diseases. Bacteria are the most dangerous human pathogen because they can cause potentially fatal infections. Because of this, many biocides have been developed and used to eradicate bacteria. However, bacteria have developed resistance to these biocides, and the prevalence of antibiotic-resistant bacteria continues to rise. When conditions are right, they may multiply rapidly and begin attaching to surfaces for an extended length of time. Surfaces at healthcare facilities, schools, automated teller machines, and other public areas are often contaminated with germs, with healthcare facilities being the primary source of bacterial transmission between people. Surfaces need to be rendered antibacterial to prevent bacterial infections, since sanitizing, sterilizing, and disinfecting are helpful but time-consuming processes. Coatings based on nanoparticles are already in use, but at a high cost and with serious consequences for human health from the discharge of poisonous nanoparticles into the atmosphere.

1.2. Background of Ionic Liquids

Ionic liquids, which melt below 100 °C, originated in high-temperature molten salts. Interestingly, mid-19th-century materials that meet modern ionic liquid definitions were previously known. This historical observation shaped ionic liquids. Ionic liquids were explored for overcoming the challenges of high-temperature molten salts. Early molten salts had great potential but high melting points that hindered their use. Researchers gradually discovered and designed molten salts with lower melting temperatures to meet this difficulty[1].This led to the discovery of inorganic chloroaluminates, which lowered melting points. This development led to the study of organic chloroaluminates, which advanced molten salt manipulation. The search led to the discovery of salts that were stable in water and air, a momentous discovery with major consequences[2][3].

In recent years, scientific research has focused on ionic liquid synthesis, a strategic move from molten salt research. This movement was driven by many factors. Synthesizing ionic liquids offers exact control over their chemical composition and physical characteristics, enabling application-specific design. Second, the unprecedented stability of these ionic liquids under many environments, including water and air interactions, opens many practical applications[4].Synthesis and use of water and air-stable ionic liquids for chemical processes is a popular green chemistry topic. The strategic synthesis of these new ionic liquids responds to scientific and environmental needs and aims to provide creative solutions that mix functionality and ecological responsibility. Ionic liquid synthesis is a transformational technique that incorporates historical lessons while pushing the limits of possibility, enabling innovative scientific research and technological growth[5].

1.3. Ionic Liquids:

At the core of the definition, ILs are liquids formed from salts that possess a particular attribute – a melting point that falls below a specific threshold, often exemplified by temperatures around 100 °C (212 °F). The distinctive composition and behavior of ILs contribute to their multifaceted applications. Notably, they exhibit remarkable solvent capabilities, making them potent solvents for diverse compounds. Furthermore, ILs can function as electrolytes, facilitating the movement of ions and serving essential roles in various electrochemical processes[6][7].

Ionic liquids (ILs) are a distinct class of substances characterized by their state as a liquid and their ionic nature. ILs are predominantly composed up of ions, as opposed to common liquids like water and petrol, which are primarily made up of electricity-neutral compounds. These ions equip ILs with special features, giving rise to a number of names for them, such as ionic melts, liquid salts, ionic glasses, liquid electrolytes, ionic fluids or the fused salts[8]. The concept of ILs is grounded in the inclination of salts to transition into a liquid state without undergoing decomposition or vaporization, thereby giving rise to this intriguing and versatile class of substances known as ionic liquids. This ionic nature endows them with exceptional properties including low volatility, high thermal stability, broad liquid temperature ranges, and inflammability[9][10].

1.4. Properties of Ionic Liquids:

ILs are distinguishable from conventional molecular liquids in several significant ways. These are some fundamental characteristics[11].

Table 1: Fundamental Characteristics of Ionic Liquids

Properties	Description	References
Low Melting Point	Compared to ionic liquids (ILs), table salt has a higher melting point. At or close to the ambient temperature, certain ionic liquids retain their liquid state. Due to the ionic liquid's bulky structure and unique ion-pair interactions, its melting point is low.	[12]

Low Vapor Pressure	Nonvolatile ionic liquids have a low vapor pressure making them less likely to evaporate into the gas phase. This characteristic makes them safer and more stable than volatile organic solvents.	[13]
Thermal stability	Ionic liquids are able to endure elevated temperatures without vaporizing or dissolving because of their exceptional thermal stability. They are hence ideal for applications involving high temperatures. Ionic liquids can be employed in operations that need precise temperatures considering their melting points.	[14]
High ionic conductivity	ILs can possess ionic conductivities that are comparable to or even greater than those of certain aqueous electrolytes. Consequently, they could be candidates for applications such as energy storage systems and electrochemical devices.	[15]
Tailorable Properties	By selecting specific cations and anions, the properties of IL can be precisely tailored. It is feasible to carefully tune the characteristics of IL by choosing particular cations and anions. Such versatility enables the modification of qualities including density, polarity, viscosity, and solubility to adjust to the needs of varied applications.	[16]
Liquid Crystallinity	Certain ionic liquids can exhibit liquid crystalline behavior, forming ordered structures like those observed in conventional liquid crystals. This property is advantageous for applications such as	[17]

	enhanced materials and electro-optical devices.	
Solvent Versatility	Ionic liquids dissolve numerous organic and inorganic compounds better than organic solvents. Due to their extensive solvent capabilities, they can be utilized in a variety of chemical processes and separations.	[18]
Electrical Conductivity	Many ionic liquids have high electrical conductivity because of their ionic composition, making them the useful electrolytes that are used in the electrochemical devices like fuel cells, capacitors and batteries.	[19]
Gas Solubility	The capability of certain ionic liquids to disintegrate gases has important implications for the development of gas separation and capture techniques.	[20]
Green Solvent Alternatives	Green chemistry is focusing on ionic liquids because they may replace toxic, easily evaporating organic solvents. This would have the dual benefit of lowering their adverse impact on the environment while simultaneously increasing the level of safety.	[21]

1.5. Types of Ionic Liquids:

The mono- and di-cationic ionic liquids are both plausible. Mono and di-cationic ILs are two variations of ionic liquids that are distinct in the number of charged cores they include in their cationic compositions.

Comparison between Mono-cationic and Di-cationic ionic liquids:

The cations having a single charge coupled to the anions are the mono-cationic ionic liquids. Imidazolium-based ionic liquids are the common name for mono-cationic ILs such as 1-butyl-3-methylimidazolium ([BMIM]) and 1-ethyl-3-methylimidazolium ([EMIM]). These ionic liquids have a vast array of tunable properties that can alter the choice of cation along with the anion. They possess minimal volatility, exceptional thermal stability, and potent solubilizing ability. Electrochemistry, separations, materials science, and catalysis are among the applications of mono-cationic ILs. Due to their exceptional properties, they serve as versatile solvents and reaction mediums [22]. Di-cationic ionic liquids contain cations with two charged centers, which are usually connected by a bridge group. In di-cationic ionic liquids, bis(imidazolium), bis(pyridinium), bis(ammonium) cations and various unsymmetrical bis-compounds are all examples. Compared to single-charged ionic liquids, doubly charged ones have distinct properties. The two charged centers of a cation can result in various interactions and behaviors within the liquid phase. Di-cationic ionic liquids are interesting due to their unique characteristics and versatility. They have been studied in disciplines such as liquid-liquid extraction, electrochemistry, and as catalysts for organic transformation[23].

1.6. Di-cationic Ionic Liquids:

Di-cationic ILs are composed of two cations and two anions, joined to one another by a linker that may be either rigid or flexible. When contrasted with mono-cationic ionic liquids, the degree to which di-cationic ionic liquids are amenable to alteration is much greater. The type of spacer and its length, as well as the cations and anions, are all configurable possibilities[24].

Because di-cationic ILs consists of two charged species, their melting points are frequently greater than those of normal ILs. Due to the increased number of charged particles, a greater amount of thermal energy is required to overcome the intermolecular interactions and transform the solid into a liquid state[25].

It's important to note that not all di-cationic ILs are liquids at room temperature. The chemical composition, structure, and selection of cations and counterions greatly affect the IL's physical properties, such as whether the IL is solid, liquid, or exhibits different phase behavior.

1.7. Properties of Di-cationic Ionic Liquids:

Di-cationic ionic liquids also possess exceptional properties, yet they dominate mono-cationic ionic liquids due to the possibility of adjustable chemical composition.

1.7.1. Higher Density:

DILs are denser than traditional mono-cationic ionic liquids. DILs have a higher charge density because their molecular structure contains two charged cations. This quality may modify their confinement behavior and interactions with other compounds as well as their solvation capability[26].

1.7.2. High Viscosity:

DILs have a higher viscosity because of their molecular structure. DILs are well-suited for uses that call for regulated flow rates or efficient bulk transport because of their higher viscosity. DILs' performance as lubricants and reaction media might also be affected by their viscosity[27].

1.7.3. Elevated Glass Transition Temperature

DILs have a higher glass transition temperature than mono cationic ILs. An amorphous material goes from a rigid or glassy state to a more yielding or elastic state at the glass transition temperature. This feature may be put to use in situations when the ionic liquid's solidification or vitrification would be helpful[28].

1.7.4. High Thermal Stability

DILs' extremely high temperature stability is one of its most notable features. DILs may remain stable at high temperatures without breaking down or undergoing major structural changes. This property is crucial for high-temperature applications including thermal energy storage and catalysis at high temperatures[29].

1.7.5. Improved Solubility:

Due to their increased charge density and stronger electrostatic interactions, di-cationic ionic liquids have enhanced solubility for a wider variety of polar and nonpolar molecules. This property expands the spectrum of solvation and extraction processes to which they can be applied, including catalysis, separations, and synthesis[30].

1.7.6. Low Volatility

DILs have a low volatility in part because of their low vapor pressure. Because of this property, DILs may be used in situations where preventing material loss due to evaporation is of paramount importance. Their low volatility improves worker safety and reduces pollution[31].

1.7.7. Excellent Electrochemical Properties

Di-cationic ionic liquids typically exhibit greater electrochemical stability than mono-cationic ionic liquids. Due to the higher charge density and stronger ionic contacts within the di-cationic structure, they are more resistant to oxidation and reduction processes, making them more stable as electrolytes in electro-chemical devices like super capacitors and batteries [32]

1.7.8. Improved Biocompatibility:

In comparison to conventional solvents and mono-cationic ionic liquids, the biocompatibility of certain di-cationic ionic liquids is enhanced. By modifying the cationic structure and alkyl chains, it is possible to create di-cationic ionic liquids with lower toxicity towards living cells while retaining their beneficial properties. They may find use in biocatalysts, pharmaceutical research, and biomedical research due to this property[33].

1.7.9. Antimicrobial Activity:

Di-cationic ionic liquids, especially imidazolium, pyridinium, and ammonium ones, kill bacteria and germs. The two positive charges of the cationic structure facilitate interactions with bacterial membranes, compromising their integrity and also result in the death of the cells of bacteria. This property enables the development of the unique antibacterial agents that have lower resistance than the conventional antibiotics[34].

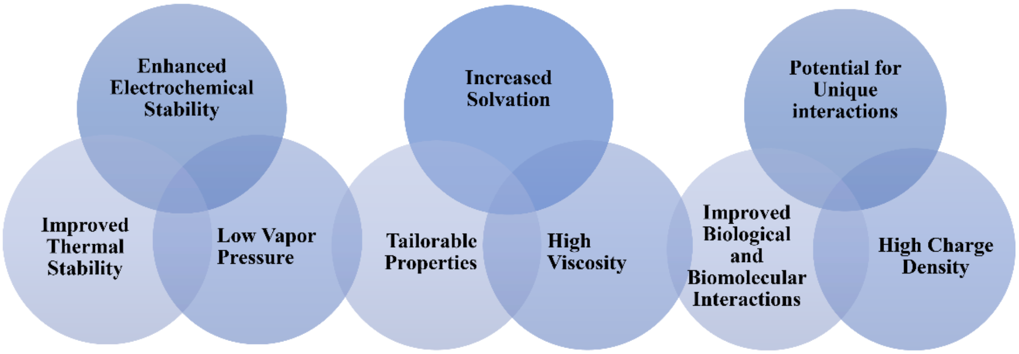


Figure 1.7 Properties of Dicationic Ionic Liquids

1.8. Imidazolium based Di-cationic ILs:

The structural configuration of DILs based on imidazolium has a profound effect on both their intrinsic properties as well as their broad range of applications. The presence of dual imidazolium cations within the molecular structure confers a greater charge density and distinct electrostatic interactions, resulting in enhanced solvation capabilities. Doubly charged ionic liquids dissolve polar and non-polar compounds due to their structure. This versatility makes them flexible solvents with tunable dissolving. In addition, the precise arrangement of the substituents on the cations of imidazolium, in conjunction with the selection of the counter-ions that permits manipulation of fundamental physical properties including viscosity, density, and melting point. This tunable nature, derived from the structural complexities, enables the customization of di-cationic ionic liquids for specific applications, thereby assuring an optimal suit for diverse industrial and scientific requirements[35][36].

Dual-cationic architecture further influences the conductivity of imidazolium based DILs. Cooperative association of paired anions and cations results in distinct ionic transport behavior, which influences the electrical conductivity of the ions. This property becomes especially important in applications requiring effective ion mobility, such as energy storage devices and electrochemical systems[37].

In addition, the structural arrangement of these ionic liquids substantially contributes to their extraordinary thermal stability. The interconnected network formed by cationic and anionic components contributes to the molecular structure's overall strength, allowing imidazolium-based di-cationic ionic liquids to sustain elevated temperatures without degrading. This inherent resilience broadens their applicability to high-temperature operations, making them advantageous candidates for processes such as heat transfer fluids and catalysis under demanding conditions[38].

In a broader context, the structural framework has a profound effect on the expansive domain of applications. Di-cationic ionic liquids based on imidazolium have broad applicability due to the ease with which their characteristics may be engineered via structural design[39]. The specialized structural features allow for the creation of novel solutions in a wide range of fields, including catalytic transformations, electrochemical devices, green solvents, and advanced materials. In the end, the intricate interplay between the composition of imidazolium based DCILs and their resulting properties underpins their dynamic role in furthering scientific exploration and propelling technological advancement across a wide range of applications [40].

1.9. Applications of Imidazolium based Di-cationic Ionic Liquids:

Numerous inter-disciplinary research fields, including organic synthesis, separation process catalysis, medicine, sensors, chemical engineering, green chemistry, and electrochemistry and bio-catalysis, material science have extensively investigated imidazolium bases ionic liquids[41].

1.9.1. Green Solvents:

Ionic liquids based on imidazolium are showing promise as powerful agents of positive change and green chemistry that may make a significant contribution to environmental sustainability. These unusual solvents, sometimes known as "green solvents," have the potential to significantly lessen the deleterious effects of chemical reactions on biodiversity. The many eco-friendly properties shown by ionic liquids based on imidazolium make them potent friends in the fight for a better, more peaceful world[42].

Perhaps most convincingly, these eco-friendly solvents show exceptional skill in green synthesis. Increased reaction yields, less by-product formation, and improved selectivity are all made possible by their finely tuned solvation characteristics. This brings chemical production in line with the principles of resource efficiency, leading to a significant decrease in waste and the conservation of important starting materials[43].

1.9.2. Catalysis:

Di-cationic ionic liquids based on imidazolium are exceptional candidates to be utilized as solvents in catalytic processes and chemical synthesis. Because of their adaptability, reaction conditions, selectivity, and yields may be fine-tuned. These ionic liquids may increase the efficiency and reusability of catalysts, leading to less waste and more productivity in manufacturing[44]. Major contributions of di-cationic ionic liquids in inorganic and organic chemical processes as catalyst are Strecker reaction[45], Michael addition reactions[46], water-gas shift reaction[47] and Knoevenagel reaction[48].

1.9.3. Gas Separation and Capture:

In the context of reducing greenhouse gas emissions and encouraging sustainable energy practices, gas separation and capture using imidazolium-based ionic liquids represents a viable and unique way to tackling environmental concerns. Carbon dioxide (CO_2) and other pollutants may be separated and captured from industrial and natural sources using ionic liquids based on imidazolium thanks to their unique physicochemical features[49].

Di-cationic ionic liquids have shown potential as very effective absorbents for carbon dioxide (CO_2). Di-cationic ionic liquids have a considerable capacity for carbon dioxide absorption. The molecule exhibits enhanced affinity towards CO_2 as they constitute several charged groups, hence facilitating efficient gas absorption and retention. Considerable quantities of carbon dioxide (CO_2) may be effectively absorbed from many sources, such as industrial pollutants and flue gases, owing to their significant absorption capacity. Doubly charged ionic liquids can collect carbon dioxide to reduce greenhouse gas emissions and climate change. Ongoing research and development efforts are focused on investigating and enhancing the performance, stability, and economic viability of diatomic ionic liquids as absorbents in the context of carbon dioxide capture applications[50].

Moreover, it has been examined that the imidazolium-based ionic liquids possess the capacity in order to minimize the presence of other noxious gases, including sulfur dioxide (SO_2) and nitrogen oxides (NO_x), emanating from industrial discharges. The customized solvation features of these materials enable them to selectively target certain gases for the purpose of capture, hence offering a viable option for the management of air pollution[51].

1.9.4. Energy Storage and Conversion:

In the realm of energy storage, imidazolium-based ILs have potential as electrolytes in many battery systems, including lithium-ion batteries. Enhancing battery safety, stability in extreme temperatures, and performance allows for safer and more effective energy storage systems. Researchers are also studying supercapacitors with ionic liquids. Fast charging and discharging are essential for power-hungry applications with these liquids[52].

In addition, there have been notable advancements in the domain of energy conversion by using the ILs based on imidazolium. The electrolyte used in the fuel cells is a promising opportunity for enhancing energy production efficiency and promoting environmental sustainability. This technology has significant potential across several domains, including fixed power systems and portable electronic devices. The adjustable qualities shown by photovoltaics hold potential for enhancing the stability and efficacy of solar cells, hence facilitating the use of solar energy as a sustainable and viable renewable source[53].

1.9.5. Nanomaterials and Nanotechnology:

In nanoparticle synthesis, di-cationic ionic liquids are efficient solvents and stabilizers. They enable controlled nucleation and growth, creating nanoparticles of certain sizes and shapes. Ionic liquids' solvation characteristics stabilize colloids and prevent nanoparticle aggregation. Ionic liquids have several applications in nano catalysis, both as reaction medium and as catalysts. As drug delivery system carriers, imidazolium based ILs also contribute to development of the nanomedicines. To sum up, their one-of-a-kind characteristics, malleability, and interactions with nanoscale structures provide new opportunities for the development of innovative nanomaterials with purpose-built characteristics in fields as diverse as electronics, catalysis, medicine, and energy storage, among others[54].

1.9.6. Biomedicine and Pharmaceutics:

In biomedicine and pharmaceuticals, there has been a notable increase in interest in di-cationic ILs. These chemicals have drawn a lot of attention because of their adaptive qualities, compatibility with biological systems, and capacity to control the release of molecules. As a consequence, their potential use in a variety of functions, including drug delivery systems, coatings with antimicrobial properties, and biomaterials, is the subject of extensive research. Di-cationic ionic liquids have the potential to revolutionize fields such as bioengineering, medical applications, and the advancement of drug development procedures[55].

1.9.7. Biomedical Applications:

The bio-medical community's interest in DILs was ignited by their unique features and potential uses, paving the way to research into a variety of applications. Notably, di-cationic ionic liquids, especially those anchored by imidazolium possess remarkable antibacterial properties. This antibacterial prowess extends to drug-resistant strains and demonstrates potent efficacy against a range of diseases. As the problem of antibiotic resistance looms, di-cationic ionic liquids emerge as possible solutions. Their diverse applications include the food industry, water treatment, and healthcare settings, among others. The proactive incorporation of di-cationic ionic liquids in these industries has the potential to provide innovative solutions to combat antibiotic resistance and strengthen disease management strategies[56].

1.9.8. Drug Delivery Systems:

This novel method utilizes ionic liquids to encapsulate and deliver medications, thereby circumventing the difficulties inherent in conventional delivery methods. The drug delivery mechanism of ionic liquids depends on their unique solvation properties and ability to form stable complexes with drug molecules. Through a process of molecular self-assembly, these ionic liquids can encapsulate pharmaceuticals within their structured domains, resulting in the formation of nanoscale entities known as "ionic liquid-drug complexes." The encapsulated drug molecules are protected from degradation and can be released under the control of external stimuli or physiological conditions[54].

1.9.9. Tissue Engineering:

Imidazolium-based di-cationic ionic liquids help tissue engineering, which combines biology and engineering. Scaffolds and hydrogels, tissue engineering building blocks, need these chemicals. Cell adhesion, proliferation, and differentiation are supported by scaffolds that imitate the extracellular matrix. With customized features, imidazolium-based ionic liquids provide these scaffolds with the physical and chemical qualities to replicate natural tissue microenvironments. Cell growth and regeneration promote tissue repair and restoration. Hydrogels, three-dimensional matrices that enclose cells and supply nutrients and waste, are also vital. Imidazolium-based ionic liquids make hydrogels with optimum swelling, mechanical strength, and biocompatibility. Their incorporation improves hydrogel functioning, cell viability, and tissue creation. Imidazolium-based di-cationic ionic liquids are essential to tissue engineering, advancing regenerative medicine and tissue replacement treatments via scaffold and hydrogel creation[57][58].

1.9.10. Wound Healing:

Wound healing using imidazolium-based ionic liquids fits well into the push for cutting-edge treatment options. These agents show promise for enhancing the overall efficiency and effectiveness of wound healing processes due to their ability to both attack microbial pathogens and speed up tissue regeneration. These ionic liquids provide new ways to improve patient outcomes and speed up the healing process for wounds by targeting both the microbiological and regenerative components of wound care[55].

1.9.11. Biosensors:

Ionic liquids that are di-cationic can be used to create biosensors. They are appropriate for sensing applications because of their capacity to alter charge transfer characteristics and interact with biomolecules. They can be included into biosensing platforms to detect diseases, poisons, or bio markers, enabling quick and accurate diagnostic procedures[59].

1.9.12. Biomass Conversion:

Recent research has shown that di-cationic ionic liquids with imidazolium structures may be useful agents in the field of biomass conversion, providing novel approaches to the problems of achieving sustainable energy and chemical production. Because of their one-of-a-kind molecular composition and adaptable features, these ionic liquids find use in the diversity of contexts by improving the sustainability as well as the efficiency for the conversion of biomass into bio-fuels, chemicals, and other goods[60].

Effective dissolution and pretreating of a wide variety of biomass feedstocks, including agricultural wastes, lignocellulosic materials, and waste biomass, are hallmarks of di-cationic ionic liquids based on imidazolium. Because of the unique molecular interactions, they have with biomass components, they can break down complicated structures and increase access to important substances inside the biomass matrix[61].

These ionic liquids are also useful as catalysts and reaction media in many methods for converting biomass, such as hydrolysis, dehydration, hydrogenation, and trans-esterification. Because of their one-of-a-kind characteristics, they can facilitate the selective and efficient production of platform chemicals, biofuels, and important intermediates from molecules produced from biomass[62].

Lignin is an essential part of biomass, and imidazolium based DILs provide a sustainable method for extracting value from it. They can efficiently remove lignin from biomass and aid in the depolymerization of the material into aromatic compounds with industrial applications[63].

Imidazolium-based di-cationic ionic liquids have the potential to radically alter the landscape of renewable energy and biorefinery processes, which is why they are so important in biomass conversion. Their importance in driving the development of more efficient, eco-friendly, and economical responsible procedures for transforming biomass into valuable products is highlighted by their ability to improve biomass pretreatment, catalyze key conversion reactions, and facilitate the utilization of biomass components. A more sustainable and environmentally friendly future in biomass conversion technologies may be possible with the help of ILs, which the universe is looking to as a viable replacement to fossil fuels[64].

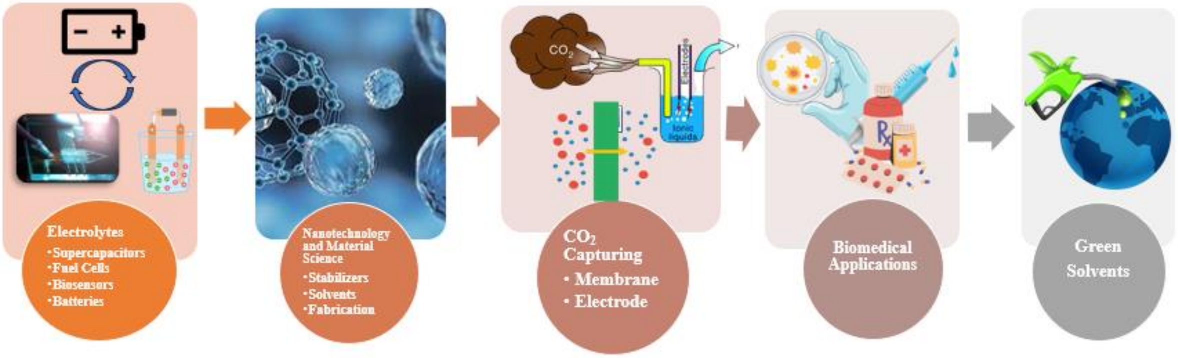


Figure 1.9 Applications of Dicationic Ionic Liquids

1.10. Antibacterial Efficacy of Di-cationic Ionic Liquids:

Antibiotic resistance is one of the most pressing problems in the antimicrobial sector nowadays. Because bacteria have evolved resistance mechanisms, many traditional antibiotics are now ineffective. This is a barrier in the development of novel antibacterial methods for treating bacterial infections. Di-cationic ionic liquids are being studied as a possible solution to this problem. Di-cationic ionic liquids, according to their unique properties and mode of action, have gained interest as potential antibacterial agents. When it comes to killing bacteria, di-cationic ionic liquids use a different approach than traditional antibiotics, which mainly target bacterial cells through specific interactions with molecular targets.

The di-cationic characteristics of these ionic liquids enable them to interact with the negatively charged membranes of bacterial cells, leading to membrane permeabilization and membrane disruption. Because of this disruption, contents of the cell leak out, vital ions leave the cell, and the cell dies. Having two charged centers, as in a di-cationic structure, enhances the contact with the bacterial membrane and results in potent antibacterial activity. Di-cationic ILs often work in opposition to different kinds of bacteria (both Gram +ve and Gram-ve), viruses, and fungi. thanks to their broad-spectrum antibacterial activity. This wide effort aids in halting the spread of antibiotic resistance and combating a variety of bacterial illnesses[65].

DILs have several desirable attributes that idealize them for use as antibacterial agents. They are often safe for use in clinical and medical settings because of their minimal toxicity to mammalian cells. They have the right chemical stability, heat resistance, and shelf life to be used in antimicrobial goods.

The variety of di-cationic ILs allows for the design and synthesis of compounds with tailored antibacterial properties and activity. Researchers have the option of altering the ionic liquid's structure and chemical composition to tailor its antibacterial activity, selectivity, and physicochemical properties for specific applications[66].

In conclusion, di-cationic ILs are a favorable class of antibiotics with a unique mechanism of action and broad-spectrum activity. Due to their ability to disrupt bacterial cell membranes and other favorable properties, they are promising candidates for the development of innovative antimicrobial therapies and the control of bacterial infections.

More study and development in this area may help combat antimicrobial resistance and the worldwide issue of bacterial infections. Di-cationic ionic liquids have demonstrated the promising results as antibacterial agents in a number of applications. Di-cationic ILs can be utilized as the antibacterial agents having a wide range of applications including:

1.10.1. Healthcare and medicine:

Medical apparatus such as catheters, implants, and wound dressings may contain di-cationic ionic liquids to prevent bacterial colonization and infection. They can also be formulated into topical antimicrobial lotions, lubricants, and mists for use in the treatment of skin infections and wound care[67].

1.10.2 Water Purification:

The water purification system may employ di-cationic ionic liquids to inhibit bacterial growth and biofilm formation. They can be applied to cooling towers, water storage containers, and industrial water systems to prevent microbial contamination and protect water quality[68].

1.10.3 Food Preservation:

Di-cationic ILs can be used in food industry as the natural preservatives. As antimicrobial coatings, they can be applied to food packaging materials to extend the expiration life of perishable products and prevent the spread of pathogenic microorganisms and deterioration.

1.10.4 Applications in Agriculture:

di-cationic ionic liquids can be used in agriculture to control plant diseases caused by bacterial pathogens. They can be used as antimicrobial agents in seed treatment, irrigation systems, and foliar applications to protect plants from bacterial diseases.

1.10.5 Personal Care Products:

Di-cationic ionic liquids can be added to detergents, conditioners, and mouthwashes to impart antimicrobial properties and improve their hygiene. They can effectively prevent the growth of microorganisms that cause dermatitis, oral infections, and skin infections.

It is essential to emphasize that the full potential of di-cationic ionic liquids as antibacterial agents is still being researched and developed. The precise use and formulation of these ionic liquids may be affected by the microorganisms targeted, the intended efficacy, and regulatory concerns[41].

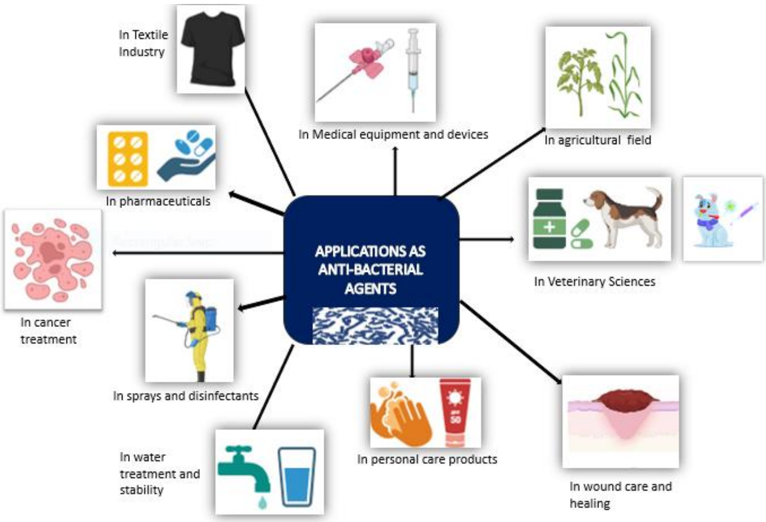


Figure 1.10.5 Applications as Anti-bacterial agents

2. LITERATURE REVIEW

Di-cationic ionic liquids are basically the promising and relatively advanced category of antibacterial medications that have a lot of potential for treating bacterial diseases in various ways. Although conventional antibiotics have been developed, the ever-increasing problems caused by antibiotic-resistant bacteria and the constraints of current therapies make it imperative that new approaches be developed[66].

What distinguishes di-cationic ionic liquids from other ionic liquids is their ability to adapt and modify their chemical composition, which influences their antibacterial properties. This allows the ionic liquid to be tailored to specific bacterial strains or infections, thereby reducing the likelihood of bacterial resistance[69].

F.J. Hernández-Fernández et al. examined toxicity of imidazolium and pyrrolidinium ionic liquids on E. coli with little toxicity data. Since the ionic liquids (ILs) have been used in many bioprocesses involving microorganisms, nephelometry was used for the estimation of their toxicity. The researchers carefully examined how cation type and the length of the alkyl chain affected the components such as cation and anion of the ionic liquids. Pyrrolidinium cations were less hazardous than imidazolium cations, but alkyl chain length increased toxicity for both. Dimethyl phosphate ($[Me_2PO_4]$) was found to be the least toxic while studying the anions. Di-cationic ILs of the imidazolium and pyrrolidinium cations were produced as well as tested, showing 100% E. coli growth at 0–0.76 mM. This study's technique for discovering biocompatible ionic liquids that are less toxic and compatible with E. coli is simple, suggesting its use in new bioprocesses[70].

M.T. Zaky et al. undertook a study centered on synthesis of three novel ionic liquids (IL1, IL2, and IL3) based on di-cationic imidazolium, with BF4 serving as the common anionic component in the pursuit of environmentally responsible corrosion inhibitors for stainless steel under acidic conditions. Various methods were used by researchers like FTIR, elemental analysis, TGA, and 1H NMR spectroscopy to study these ILs. They also checked how well these liquids can prevent corrosion. The results demonstrated the effectiveness of all three ionic liquids, with IL2 exhibiting the highest corrosion inhibition efficiency at 98.4% at a concentration of 100 ppm, followed by IL1 at 91.5%, and IL3 at 83.3%. Notably, the choice of the anionic component (BF4) was identified as a critical factor influencing the adsorption process, suggesting the potential of these environmentally friendly ionic liquids as corrosion inhibitors in acidic environments, thereby contributing to the field of corrosion protection[71].

Trush et al. conducted research based on ionic liquids characterized as pyridinium and imidazolium, all of which displayed significant antimicrobial and antifungal properties. As evidenced by FT-IR spectra, binding of these ionic liquids to Human Serum Albumin (HSA) inducing the conformational changes in secondary structure of the protein. In addition, the molecular docking effects revealed potential interactions between II-A binding site of HSA and the particular ionic liquids, including 1-(2-hydroxyethyl)-3-dodecylimidazolium chloride as well as 1-(2-hydroxyethyl)-3-dodecylimidazolium chloride. These discoveries are important for medicine. Imidazolium- and pyridinium-based ILs may be promising antibacterial therapies for medical uses[72].

Luis Guzmán et al. examined the antibacterial characteristics of new ionic liquids (ILs) made from imidazolium cations with phenolic functional groups. The study examined structural alterations to the ILs' alkyl imidazolium units, including adding halogens and hydrophobic substituents and extending their chain lengths. These changes were thoroughly examined to determine their effects on antibacterial effectiveness. These compounds were tested for the antibacterial activity against the bacteria like *Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus* using minimum inhibitory doses (MICs). Molecular dynamics simulations revealed the complex interactions between ILs and bacterial membranes. The ILs showed significant antimicrobial action against *S. aureus, E. coli,* and *P. aeruginosa*, with MIC values ranging from <7.81 to 62.50 μM. These results demonstrate prospective significance of these new ILs in fighting bacterial infections and support the development of novel antimicrobial medicines with broad uses[73].

Bruna L. Kuhn et al. produced and studied di-cationic imidazolium-based dicarboxylate ionic liquids' thermophysical characteristics. The melting temperature was unaffected by the dicarboxylate moiety's spacer length, although the heat of fusion rose proportionately along with the spacer chain length in both di-cation and di-anions. Di-cationic dicarboxylate ionic liquids store heat better than single-charged ones but not bromine ones. The anion in dicarboxylate ionic liquids impacts their heat capacity. Most promising for heat storage are [C6(MIM)2] [C2] and [C6(MIM)2][C5], outperforming single-charged ionic liquids and mineral oil. They may also be healthier than bromine-containing alternatives. Dicarboxylate ionic liquids dissolve in some solvents but not others. These findings affect thermal energy storage and demonstrate the value of selecting proper cation along with the anion for dicarboxylate ionic liquids[74].

Izabelle M. Gindri et al. examined di-cationic imidazolium-based ILs. They created these solutions and assessed their cell toxicity and bacteria-fighting capacity. Higher IC50 values showed that di-cationic ILs were less damaging to cells than single-charged ILs, demonstrating cell compatibility. Di-cationic ILs stopped bacteria growth at lower concentrations than typical. They also observed that making these ILs hydrophobic dropped their IC50 and MIC values. To ensure the ILs were safe for applications, they had to find a compromise. Consequently, the di-cationic imidazolium-based ILs investigated in this study hold considerable promise as non-toxic materials with robust antimicrobial activity, with potential utility across a broad range of applications[75].

Sainath Aher et al. synthesized and studied imidazolium-based di-cationic ILs having different alkyl chain lengths in addition to the linker groups. These di-cationic ILs ranged from amorphous powder to having the low melting white solids or hygroscopic characteristics, depending on the anions used. The fast synthesis comprised refluxing alkyl imidazoles and dibromo alkanes in toluene for 24 hours and a simple workup. Spectroscopic methods including ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR and High-Resolution Mass Spectroscopy Electron Impact confirmed the synthesis of di-cationic ILs with Br-, BF4-, and PF6- anions. This enhanced synthesis approach reduced time and arduous workup. Di-cationic ILs, with a di-cation and two anions, have benefits over mono-cationic ILs, making them suitable for many applications. The chain length of these ILs also affected conductivity, lipophilicity, and morphological appearance, demonstrating the adaptability and promise of di-cationic ILs in diverse sectors[76].

Congfei Yao et al. designed two di-cationic ionic liquids (DILs) such as [C5(MIM)2][NTf2]2 (DIL1) and $[C_6(MIm)_2][NTf_2]_2$. These new ionic liquids efficiently extracted aromatics from aliphatic. The study looked at whether a certain type of liquid called DILs (probably referring to di-cationic ionic liquids) works the same way in different mixtures of chemicals, specifically in combinations of toluene/n-heptane, benzene/n-hexane, and benzene/cyclohexane, which can be either aromatic or aliphatic. The DILs showed good selectivity and distribution coefficients across aromatic and aliphatic combinations compared to other promising ionic liquids (ILs) and sulfolane. DILs' physicochemical features were more stable than earlier ones, suggesting they might be used as solvents to efficiently separate aromatics from aliphatic. The DILs showed good selectivity along with the distribution coefficient values for toluene/n-heptane, benzene/n-hexane, and benzene/cyclohexane systems at 30°C, highlighting their potential to solve industrial aromatic-aliphatic separation problems [77].

Oscar F. Doria et al. synthesized and characterized the novel alkyl imidazolium ILs from N-cinnamyl imidazole having alkyl chain length ranging from 1-10 carbon atoms. The study examined antibacterial activity of these ILs against bacteria causing skin and soft tissue infections (SSTIs) using agar well diffusion, MIC, and IC50 assays. The results showed a dose-dependent effect: MIC values for the gram-positive bacteria dropped with hydrocarbon chain length. ILs had strong MIC values against Gram-negative bacteria, supporting antibacterial screening findings. These experimental findings were supplemented by molecular dynamics simulations of IL-bacterial membrane interactions. ILs with longer hydrocarbon chains (10 carbon atoms) diffused passively toward the membrane surface, whereas those with shorter chains were hydrophobic and did not integrate into the bilayer. In conclusion, this unique series of synthesized ILs may be a possible alternative therapy for Gram-positive bacteria causing SSTIs, giving interesting antibacterial research and applications[78].

Amir S. Khan et al. introduced a new method for the synthesis of di-cationic ionic liquids using the 1,4-bis(3-methylimidazolium-1-yl) butane ($[C_4(Mim)_2]$) cation and different counter-anions. The structural validation of these ionic liquids was done by ^{1}H NMR. The thermal stability, Hammett acidity, density, and viscosity of these ionic liquids were examined. The study showed that rubber wood, palm oil frond, bamboo, and rice husk may be turned into levulinic acid.$[C_4(Mim)_2]$ $[(2HSO_4)(H_2SO_4)_4]$ was the most promising ionic liquid catalyst, producing 47.52% LA from bamboo biomass under specified circumstances. The research also examined bamboo biomass's surface shape, functional groups, and thermal stability before and after conversion into LA using SEM, FTIR, and TGA. These findings highlight the potential of one-pot LA production from agro-waste and the importance of this research in harnessing sustainable biomass resources to produce valuable chemicals, promising the use of renewable feedstocks[61].

Jean C. B. Vieira et al. studied synthesis, thermal stability, and breakdown of carboxylate-containing di-cationic ionic liquids (DILs). The short-term thermal stability evaluation utilized standard thermogravimetric analysis while the long-term assessment used kinetic analysis. The study employed a variety of techniques to determine the energy requirements, reaction rates, and types of reactions associated with the breakdown of specific compounds. Another finding was stability of these compounds that is inversely proportional to the length of the cation spacer chain. They discovered how these chemicals truly break apart when heated by studying the remnants of their decomposition using specialized procedures. Multiple chemical processes appear to be involved. These results shed light on properties of di-cationic ionic liquids, which can be put to use in a wide range of contexts[38].

Wojcieszak et al. demonstrated imidazolium chlorides and bis-imidazolium dichlorides, respectively, that are two mono cationic and di-cationic ionic liquids that are studied for their antibacterial capabilities. Their effectiveness against bacteria and other microorganisms is affected by their structure. Short alkyl substituents limit the antibacterial and antifungal efficacy of di-cationic ionic liquids. However, the antibacterial effects of long chains are more potent. Compounds having 10-12 carbon atoms surpass didecyldimethylammonium chloride and benzalkonium chloride, the gold standards for di-cationic SAILs[79].

Beck et al. compared the synthesis of Di- and mono cationic amino acids (l-Glycine, l-Lysine, l- Arginine). When compared to di-cationic ionic liquids, ionic liquids based on mono-cationic amino acids performed better in terms of antibacterial activity. Most of the microorganisms tested were more susceptible to the antibacterial effects of mono-cationic ionic liquids than those of di-cationic ionic liquids. *Pseudomonas aeruginosa* demonstrated the greatest antibacterial activity for all ionic liquids, whereas *S. aureus* showed the lowest antibacterial activity due to its stronger antibacterial resistance in the presence of ionic liquids. Unluckily, each ionic liquid was found to be cytotoxic at all concentrations used[80].

Guglielmero et al. designed the synthesis of 12 homogeneous dibromide di-cationic ionic liquids (DILs) using the Menshutkin reaction. The solvent utilized for this method was more ecologically friendly than toluene. Methyl imidazolium bromide DILs were precursors for dicarboxylate salts such malonate, succinate, and glutarate with linker lengths from C3 to C6 between the cationic moieties. The research extensively examined the most common bromide-to-carboxylate anion exchange techniques. After that, TGA and DSC were used to estimate the thermal characteristics of dibromide and dicarboxylate DILs. TGA research showed a link between heat stability and the imidazolium cation's lateral alkyl substituent. The internal linker had no effect on thermal stability, highlighting the relevance of the cationic structure in di-cationic ionic liquid thermal characteristics[81].

Patil et al. synthesized 18 di-cationic ionic liquids (ILs) from phosphonium, imidazolium, and pyrrolidinium cations through alkane linkages (C6, C9, and C12). These di-cations were used to create 36 di-cationic ionic liquids with two anions. Ionic liquids with a 9-carbon linkage chain were more stable than those with C6 and C12 linkages and had higher viscosities and densities. Exposure to NTf_2^- anions lowered ionic liquid melting points. Di-cationic ILs containing $PFOS^-$ anions had higher melting points than NTf_2^- ILs and remained solid at room temperature. The research also found a connection between alkane linkage chain length and IL structural degrees of freedom, leading in lower melting temperatures as chain length rose. These results illuminate the design and properties of di-cationic ionic liquids, emphasizing the relevance of cation and anion selection along with the alkane linkage chain length in customizing their properties for particular applications[82].

Jared L. Anderson et al. created and analyzed 39 distinct varieties of ionic liquids (ILs) with two charges. Researchers examined their surface behavior, density, melting points, light-bending abilities, wall thicknesses, solvent compatibilities, and more to better understand their physical and chemical features. It was found that the temperature range in which these double-charged ILs remained liquid and stable was significantly larger than that of standard ILs. One of them, based on pyrrolidinium, was stable from minus four degrees Celsius to more than two hundred and fifty degrees Celsius! The researchers also discovered, with the use of X-ray crystallography, that the structure of these ILs is related to their melting points. They even observed a scenario when a double-charged component assumed three distinct forms within the same framework. When combined with a specific chemical (the anion), these unusual ILs melt at a specific temperature. The melting temperatures of compounds containing imidazolium double-charged ions were observed to rise from lowest to highest while going from NTf_2^- to BF_4^- to PF_6^- to Br^-.Pyrrolidinium-based geminal di-cationic compounds have far higher melting temperatures than imidazolium compounds. These results illuminate geminal di-cationic ILs' various and distinctive features, highlighting their potential for a broad variety of applications and the importance of anion selection in fine-tuning their properties[83].

Yun-Sheng Ding et al. synthesized and examined geminal imidazolium and 1-n-tetradecyl-3-methylimidazolium bromide molecular structures. These structures were validated by FT-IR, ^1H NMR, and elemental analysis. Using X-ray diffraction, they examined the atomic arrangement of these compounds. The geminal imidazolium ionic liquid was more heat-resistant than the normal one-long-chain ionic liquid. Its crystal structure has greater space between its atoms and a lower critical concentration where it forms micelles. This geminal imidazolium ionic liquid was hydrophobic since it didn't dissolve in water or acetone. The geminal imidazolium ionic liquid has unique structural and chemical features that set it apart from other ionic liquids[84].

Hang Zhang et al. designed, synthesized, and analyzed geminal di-cationic ionic liquids (DILs) to improve their thermal stability and latent heat capacity. Geminal di-cationic ionic liquids with different alkyl chain lengths and electronegativity functional groups in the imidazolium structure were synthesized. The thermal properties of these synthesized DILs were investigated using thermogravimetric analysis (TGA) to determine thermal stability and differential scanning calorimetry (DSC) to determine melting points, heat of fusion, and heat capacity. The research examined how alkyl side chains, linking chains, the imidazole ring's C2–H, and functional groups affected molecular structure. It also examined hydrogen bonding in geminal di-cationic ionic liquids using single-crystal X-ray diffraction. With breakdown temperatures up to 603.74 K and latent heat capacities of 159 J g^{-1}, functionalized geminal di-cationic ionic liquids showed outstanding thermal stability. These discoveries might be used in thermal energy storage and related industries[53].

Luca Guglielmero et al. conducted a comprehensive evaluation and analysis, focusing on di-cationic ionic liquids (DILs) as a subject of growing interest and versatility across various applications. Recognizing a scarcity of data concerning the structure-property relationships of DILs, the study addressed the challenge of selecting the most suitable salts for specific applications. The tunability of physicochemical properties in DILs through variations in spacer length, cation type, and the resulting symmetry or asymmetry was explored. A systematic assessment encompassed 12 dibromide DILs and 12 di-carboxylate salts, juxtaposed with their mono-cationic counterparts. The investigation extended to diverse traditional methods for carboxylate DIL synthesis and characterized the prepared DILs through NMR, TGA, and DSC analyses to discern the influence of their structural features on thermal stability. Notably, the study unveiled some DILs as solid salts post-drying. Additionally, it ventured into a novel potential application realm for DILs, considering their role as hydrogen bond acceptors in deep eutectic mixtures, highlighting the structural-related effects that could shape future developments in this dynamic field[81].

3. EXPERIMENTAL SECTION

This chapter describes the laboratory synthesis of novel di-cationic ionic liquids. In the first stage, di-cations are synthesized using bromide as a counter ion. In the subsequent step, Bromide ion-exchanged with various anions, such as Acetate $[CH_3COO]^-$, Bisulfate $[HSO_4^-]$, Methane Sulfonate $[CH_3SO_3]^-$, Hexafluorophosphate $[PF_6]^-$, Tetrafluoroborate $[BF_4]^-$, Dichloroacetate $[Cl2CHCO_2]^-$, and bis(trifluoromethanesulfonyl)imide $[NTf_2]^-$.

3.1. Solvents and chemicals

Acetonitrile (CH_3CN), Dichloromethane (CH_3Cl_2), Acetone (CH_3COCH_3), Methanol (CH_3OH), Ethanol (CH_3CH_2OH), Distilled water (H_2O).

1-methylimidazole,Dibromo-2-butene($C_4H_6Br_2$), Dibromo propane ($C_3H_6Br_2$), Sodium acetate, Sodium bisulfate, Lithium bis(trifluoromethanesulfonyl)imide, Sodium hexafluorophosphate, Sodium tetrafluoroborate, Dichloroacetic acid, Methane sulfonic acid, Silver nitrate, Deionized water.

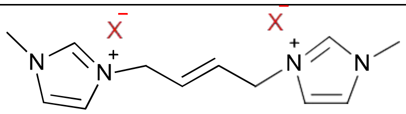
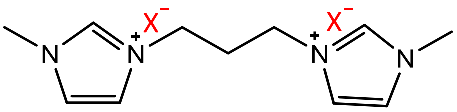
3.2. Apparatus and Glassware

Hot plate, Oil bath, Thermometer, Condenser, Magnetic stirrer, Funnel, Conical flask, Filter papers, Pipette, Sucker, TLC Plates, Nitrogen cylinder, Petri dish, Vacuum oven, Rotary Evaporator, weighing balance, Glass vials, Clamps and stand, Spatula, Single- necked and double-necked round bottom flasks, Beakers, Measuring cylinder, Eppendorf, Syringes, Nitrogen balloons, Rubber stoppers, Capillaries, Reagent Bottles. Heat gun, Molecular sieves.

3.3. Experimental Procedure:

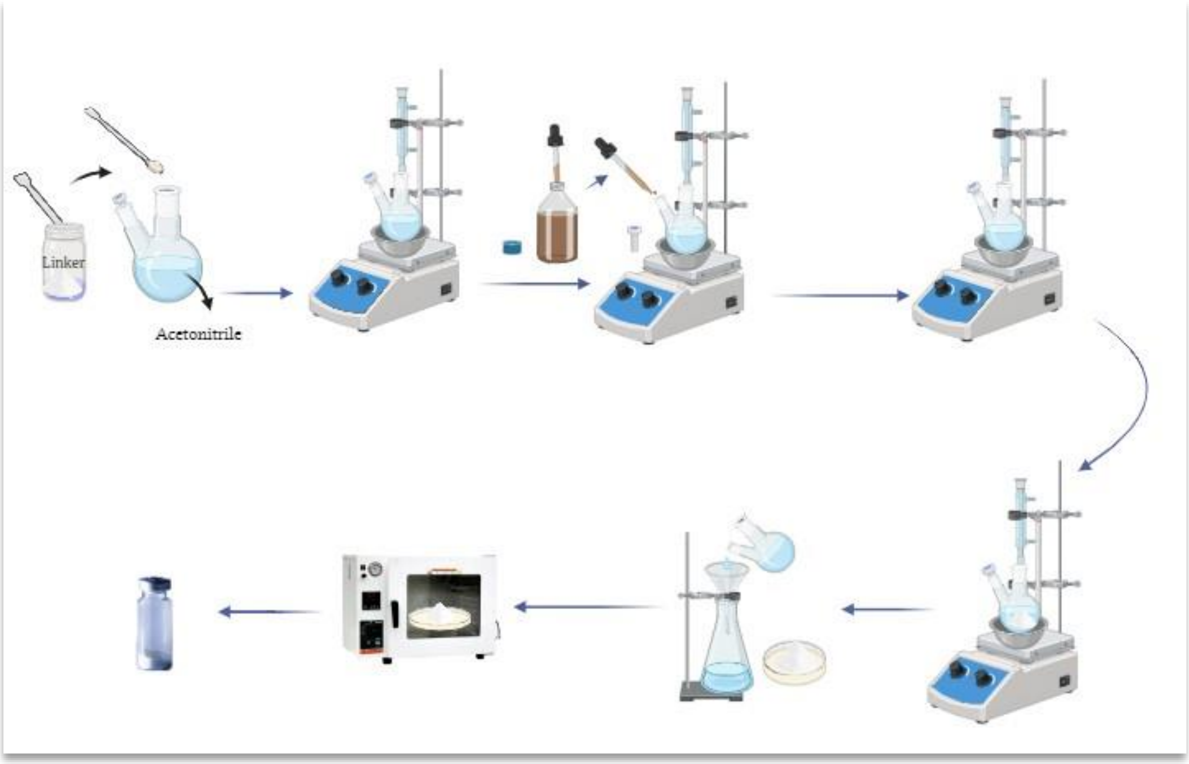
Seven types of anions were used with the same cationic precursors. Two types of linker chains were used. Table demonstrates the general overview of di-cationic ionic liquid.

Table 1: General overview of Di-cationic Ionic Liquids

Imidazolium Based Di-cations	Structure	X= Br^-, CH_3COO^-, HSO_4^-, $CH_3SO_3^-$, PF_6^-, BF_4^-, $Cl_2CHCO_2^-$, NTf_2^-.
1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide		
1,1-(propane-1,3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dibromide.		

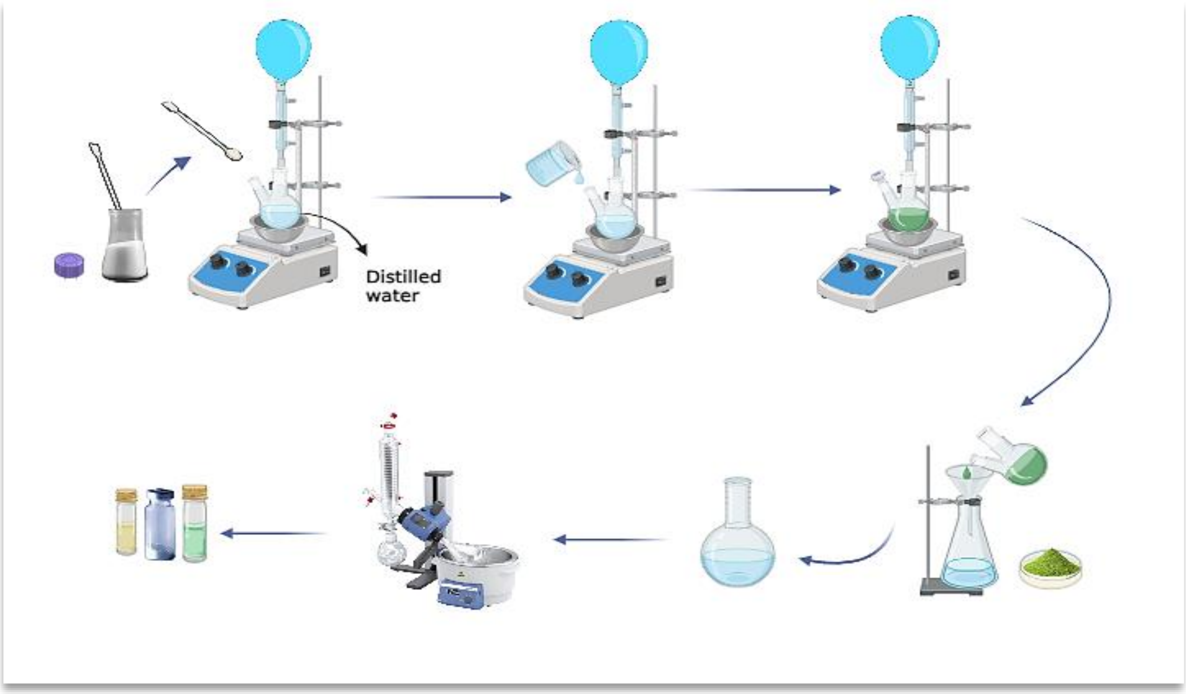
3.4. General Scheme:

A double-necked round bottom flask was used to administer acetonitrile. Linker compound was added into it and stirred to dissolve it completely .2 equivalent of cationic precursor was also added in a mixture of reaction and solution was stirred at 80^o C for about 24 to 48 hours. White precipitates were formed in it. Precipitates were filtered and washed with suitable solvent to remove any impurities. Dried the precipitates in vacuum oven. Di-cationic ionic liquid containing bromide ion as counter anion was obtained.



Scheme 1

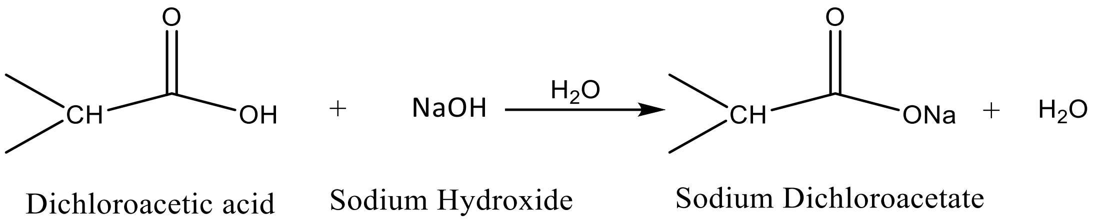
Anion metathesis, the second phase, entails a double displacement reaction. This was done in an inert environment with an ionic liquid that contained bromide ions. After being dissolved in deionized water, the anionic precursor, which was a salt, was added to the reaction mixture. Greenish precipitates of silver bromide were formed. Precipitates were filtered. The filtrate contained ionic liquid as well as solvent. A rotary evaporator was used to evaporate the solvent. Di-cationic ionic liquid containing counter anion was obtained.



Scheme 2

3.4.1. Preparation of Sodium dichloroacetate (Cl_2CHCO_2Na):

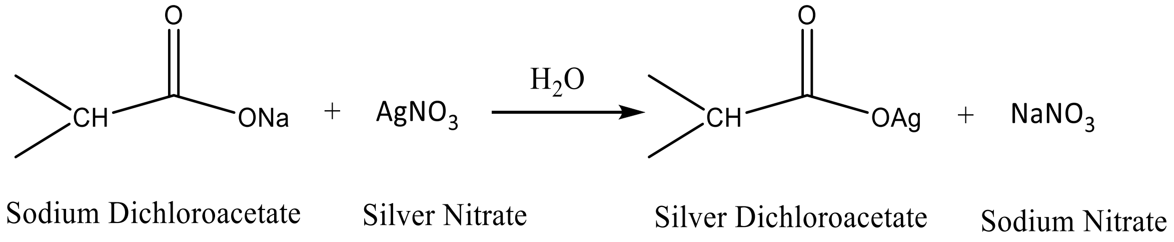
Sodium dichloroacetate was synthesized from neutralization reaction of dichloroacetic acid (2g, 15.6mmol) with sodium hydroxide (0.62 g,15.5mmol) in 30ml water (scheme 3.2). The reaction mixture was subjected to stir in water for over-night and the reaction completion was confirmed with help of pH paper. Water produced during neutralization reaction was rotary evaporated; the product was dried completely in a vacuum oven over-night at 50^oC to obtain white powder of sodium dichloroacetate with 99% yield.



Scheme 3

3.4.2. Preparation of Silver Dichloroacetate($AgCl_2CHCO_2$):

For the preparation of silver dichloroacetate, sodium dichloroacetate (2g, 13.0 mmol) was dissolved in 10 mL distilled water in a beaker. Another beaker was taken and silver nitrate (2.22 g, 13.0 mmol) was dissolved in distilled water. Both solutions were mixed. A vigorous reaction occurred and fine precipitates of Cl_2CHCO_2Ag were formed. The precipitates were then filtered and washed with distilled H_2O to get rid of any unreacted material. The obtained white powder was vacuum dried, and the yield was 96% for the product.

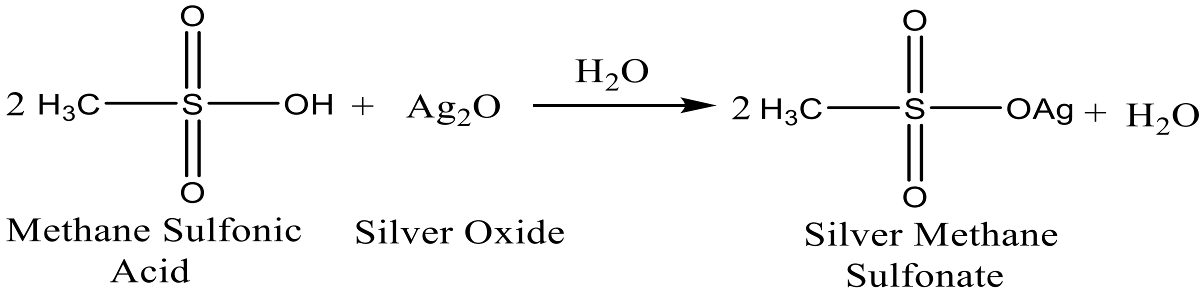


Scheme 4

3.4.3. Preparation of Silver Methane Sulfonate ($AgCH_3SO_3$):

The preparation of silver methane sulfonate took two steps. Firstly, silver oxide (Ag_2O) was prepared by taking $AgNO_3$ (3g, 17.6 mmol) in beaker dissolved in 10mL distilled water. Sodium Hydroxide (NaOH) solution (0.7g, 17.6mmol) was prepared in 10mL water. Silver nitrate solution was continuously stirred, and sodium hydroxide was added dropwise. The brown precipitations were formed immediately, indicating the formation of silver oxide. Sodium hydroxide solution was added until more precipitation stopped. The solution was then allowed to stand for 30 minutes. The solution containing precipitation was filtered and then washed with distilled H_2O. The precipitates obtained were dried in a vacuum oven at 60°C.

In the second step, brown precipitates of silver oxide (1.86g, 8.02mmol) were dissolved in 50mL water and methane sulphonic acid (1.53g, 17.2mmol) was dissolved in enough distilled H_2O. NaOH solution was poured drop-wise until all undissolved brown precipitates were vanished and a clear solution was obtained. The resultant clear solution was subjected to a rotary evaporator to evaporate water and obtained silver methane sulfonate was vacuum dried at 60°C, product obtained was white powder with 96% yield.



Scheme 5

3.4.4. Preparation of Silver Bisulphate ($AgHSO_4$):

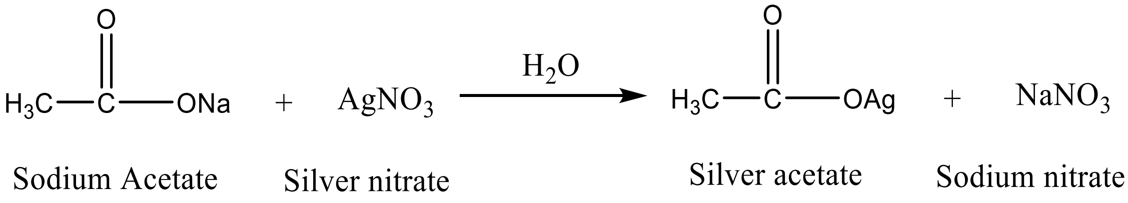
For the preparation of silver bisulphate, silver nitrate (4g, 0.0235 moles) was dissolved in distilled water (10 ml) in a beaker. In another beaker, sodium bisulfate (3.25 g, 0.0235 moles) was dissolved in distilled water. Both solutions were mixed. A vigorous reaction occurred and fine precipitates of ($AgHSO_4$) were developed. These precipitates were filtered and washed with distilled H_2O in order to get rid of any extraneous material. The obtained white powder was vacuum dried, and the yield was 96% for the product.

$$\underset{\text{Sodium Bisulphate}}{NaHSO_4} + \underset{\text{Silver Nitrate}}{AgNO_3} \longrightarrow \underset{\text{Silver Bisulphate}}{AgHSO_4} + \underset{\text{Sodium Nitrate}}{NaNO_3}$$

Scheme 6

3.4.5. Preparation of Silver Acetate ($AgOOCCH_3$):

Silver Acetate was obtained by reacting silver nitrate with Sodium acetate in an equimolar ratio. Silver nitrate (2.5 g, 14 mmol) was dissolved in 5 mL in a beaker. In another beaker, Sodium acetate (1.2 g, 14 mmol) was dissolved in 5 mL distilled water. After this, both solutions were mixed. The white precipitates of $AgOOCCH_3$ were formed instantaneously. The precipitates were filtered and washed with distilled H_2O. The obtained white precipitates were subjected to the vacuum oven in order to dry these precipitates at 50°C. The product obtained was white powder with 92% yield.



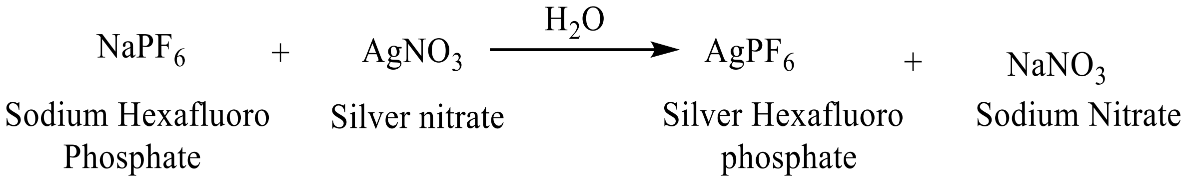
$$H_3C{-}C({=}O){-}ONa + AgNO_3 \xrightarrow{H_2O} H_3C{-}C({=}O){-}OAg + NaNO_3$$

Scheme 7

3.4.6. Preparation of Silver hexafluorophosphate ($AgPF_6$):

Silver hexafluorophosphate was obtained by reacting silver nitrate with Sodium hexafluorophosphate in an equimolar ratio. Silver nitrate (2.0g, 11.7 mmol) was dissolved in

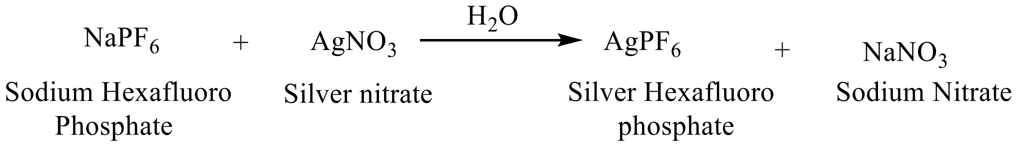
5 mL distilled water in a beaker. In another beaker, Sodium hexafluorophosphate (1.97 g, 11.7 mmol) was dissolved in distilled water (5 mL). After this, both solutions were mixed. The white precipitates of $AgPF_6$ were formed instantaneously. The obtained precipitates were filtered and washed with distilled H_2O. The obtained white precipitates were subjected to vacuum oven for drying at 50°C. The product formed was white powder with 82% yield.



Scheme 8

3.4.7. Preparation of Silver tetrafluoroborate ($AgBF_4$):

Silver tetrafluoroborate was obtained by reacting silver nitrate with Sodium tetrafluoroborate in an equimolar ratio. Silver nitrate (2.0g, 11.7 mmol) was dissolved in distilled water (5 mL) in a beaker. In another beaker, Sodium tetrafluoroborate (1.29 g, 11.7 mmol) was dissolved in distilled water (5 ml). Then both solutions were mixed. The white precipitates of $AgBF_4$ were formed instantaneously. The precipitates formed were filtered and washed with distilled H_2O. The obtained white precipitates were subjected to vacuum oven for drying at 50°C. The product obtained was white powder with 85% yield.



Scheme 9

3.4.8. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide:

The reaction of 1,4-dibromo-2-butene (3 g, 14 mmol) and 1-methylimidazol (2.298 g, 28 mmol) in acetonitrile (60 ml) produced 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (scheme 3.3). To get the highest possible product yield, the reaction mixture was refluxed for 48 hours. The reaction's completion was verified by using TLC and white precipitates were washed with acetone. A rotary evaporator was used in order to evaporate the solvent. The product was then subjected to a vacuum oven for 12 hours at 50^{o}C and 90% yield was obtained.

3.4.9. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene acetate:

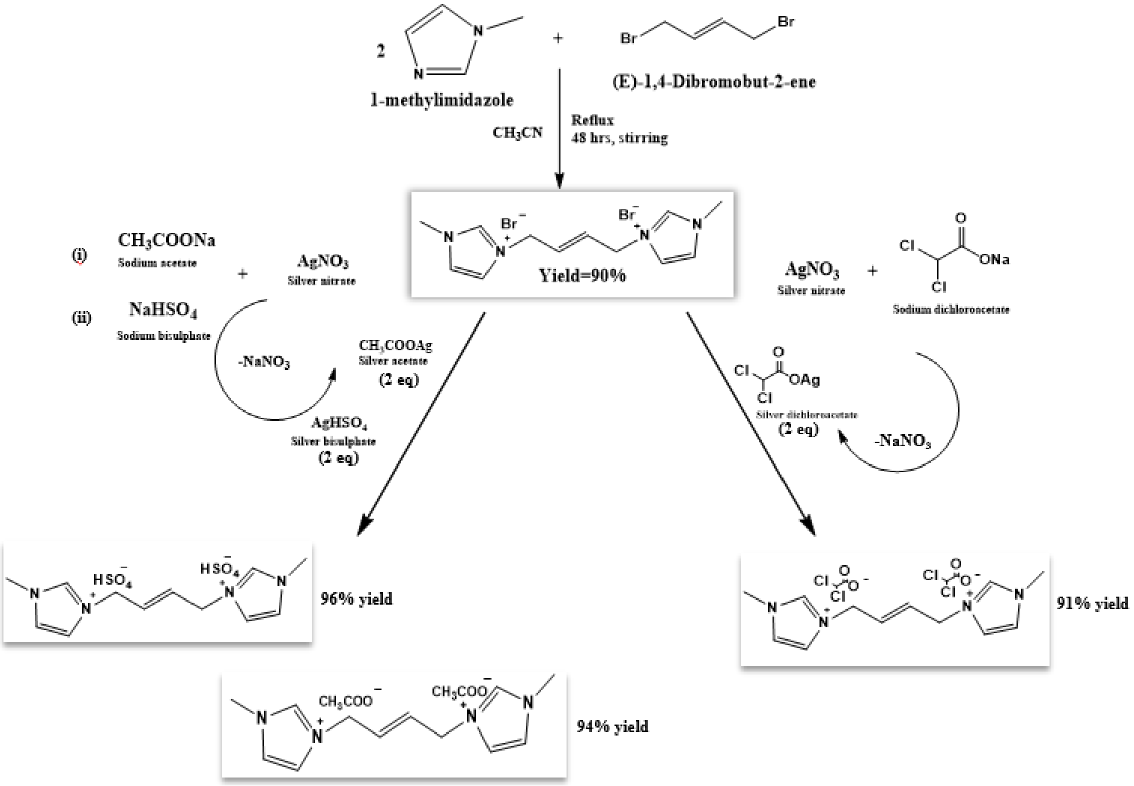
Using the metathesis procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene acetate was synthesized. Using distilled water as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgOOCCH_3$ (0.90g, 5.3mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the mixture was stirred throughout the entire night at the normal room temperatureand later refluxed for 2 hours at 70-80^{o}C. The obtained precipitates were filtered and washed with distilled H_2O. Rotary evaporation of the filtrate was done in order for the removal of solvent and a pure product was formed. In vacuum oven, ionic liquid was further dried at 60^{o}C. A product with yield of 94% was achieved.

3.4.10. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bisulphate:

Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bisulphate was synthesized. Using distilled water as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgHSO_4$ (1.10g, 5.3mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^{o}C. A product yield of 96% was achieved.

3.4.11. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene dichloroacetate:

Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene dichloroacetate was synthesized. Using methanol as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgC_2H_2Cl_2O_2$ (1.04g, 5.3mmol) solution in methanol. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange was taken place while the reaction mixture was agitated all night at the room temperature and later on it was refluxed for 2 hours at 70-80^{o}C. The precipitates formed were filtered and washed by using distilled water. Rotary evaporation of the filtrate was done for the removal of the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60°C. A product yield of 91% was achieved.



Scheme 10

3.4.12. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene tetrafluoroborate:

Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene tetrafluoroborate was synthesized. Using acetone as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $NaBF_4$ (1.04g, 5.3mmol) solution in acetone. The flask with a circular bottom was filled with an inert atmosphere. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later on was refluxed for 2 hours at 70-80°C. The reaction mixture was filtered, and filtrate was subjected to rotary evaporator. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60°C. A product yield of 93% was achieved.

3.4.13. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene hexafluorophosphate:

Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene hexafluorophosphate was synthesized. Using distilled water as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $NaPF_6$ (0.88g, 5.3mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Ionic Liquid rapidly precipitated as a white powder. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80°C. Precipitates were filtered and filtrate was subjected to rotary evaporation. After solvent was removed from the filtrate, acetone was then added into round bottom flask containing by-product of the reaction in order to extract any product if remained there. After thorough stirring, the solvent was again filtered to remove the byproduct i.e., sodium bromide. The filtrate was again subjected to rotary evaporation and the whole product obtained was vacuum dried in oven at 60°C. A product yield of 95% was achieved.

3.4.14. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bis (trifluoromethane-sulfonyl) imide:

Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bis (trifluoromethanesulfonyl) imide was synthesized. Using distilled water as the solvent, 1,4-

bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $LiNTF_2$ (1.49g, 5.3mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. An oily layer was obtained which contained di-cationic ionic liquid. The entire exchange took place while the reaction mixture was agitated over-night at room temperature and later on refluxed for 2 hours at 70-80^oC. The white precipitates were separated using filtration and washed with aliquots of distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, ionic liquid was further dried at 60^oC. A product yield of 94% was achieved.

3.4.15. Synthesis of 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene methane sulfonate:

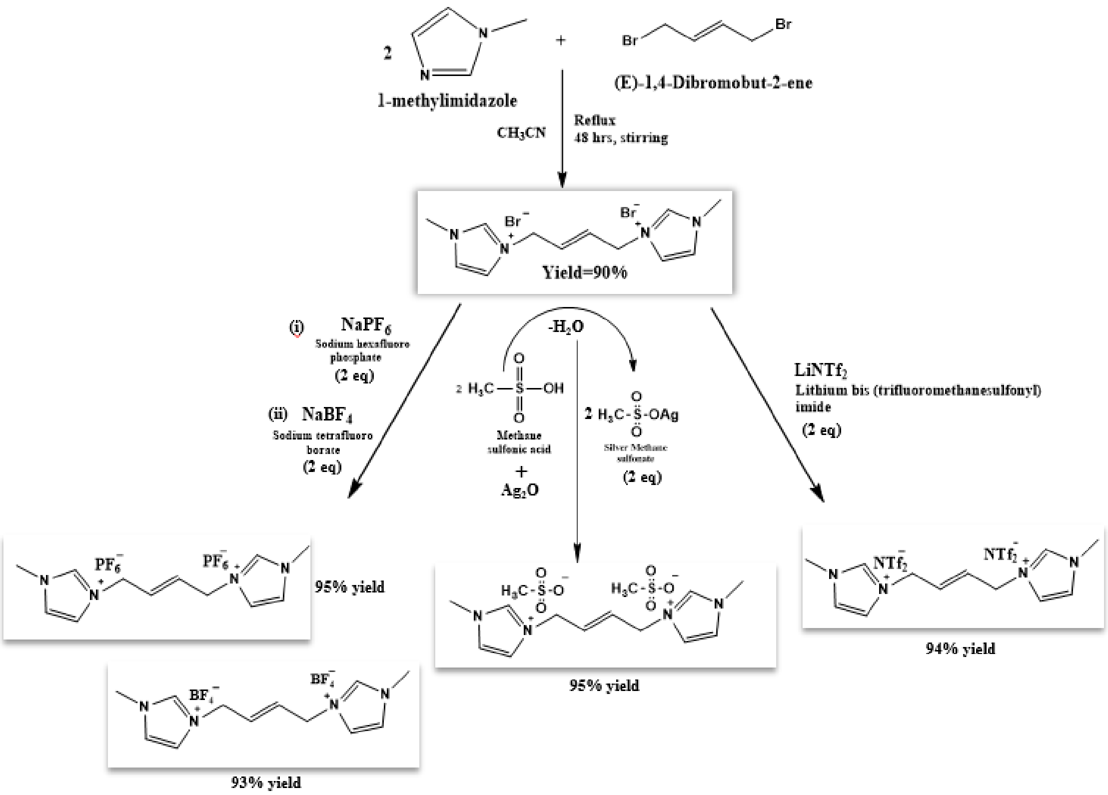
Using the metathesis reaction procedure, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene methane sulfonate was synthesized. Using distilled water as the solvent, 1,4-bis(3-methylimidazolidin-1-yl) but-2-ene bromide (1g, 2.6 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgCH_3SO_3$ (1.05g, 5.3mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while reaction mixture was agitated overnight at room temperature and later on refluxed for 2 hours at 70-80^oC. The precipitates obtained were filtered and washed with distilled H_2O. Rotary evaporation of the filtrate was done for the removal of the solvent and pure product was obtained. In vacuum oven, ionic liquid was further dried at 60^oC. A product yield of 95%was achieved.

3.4.16. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) di-bromide:

The reaction of 1,3-dibromopropane (3.96 g, 19.6 mmol) and 1-methylimidazol (3.22g, 39.2 mmol) in acetonitrile (60 ml) produced 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dibromide (scheme 3.3). To get the highest possible product yield, the reaction mixture was refluxed for 48 hours. The reaction's completion was verified by using TLC, white precipitates were washed with acetone. The solvent was evaporated by using rotary evaporator. The product was subjected to vacuum oven for 12 hours at 50^oC and 91% yield was obtained.

3.4.17. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) acetate:

Using the metathesis procedure, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl acetate was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yldibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a drop-wise addition of the $AgOOCCH_3$ (0.90g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^{o}C. A product yield of 94% was achieved.



Scheme 11

3.4.18. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) bisulphate:

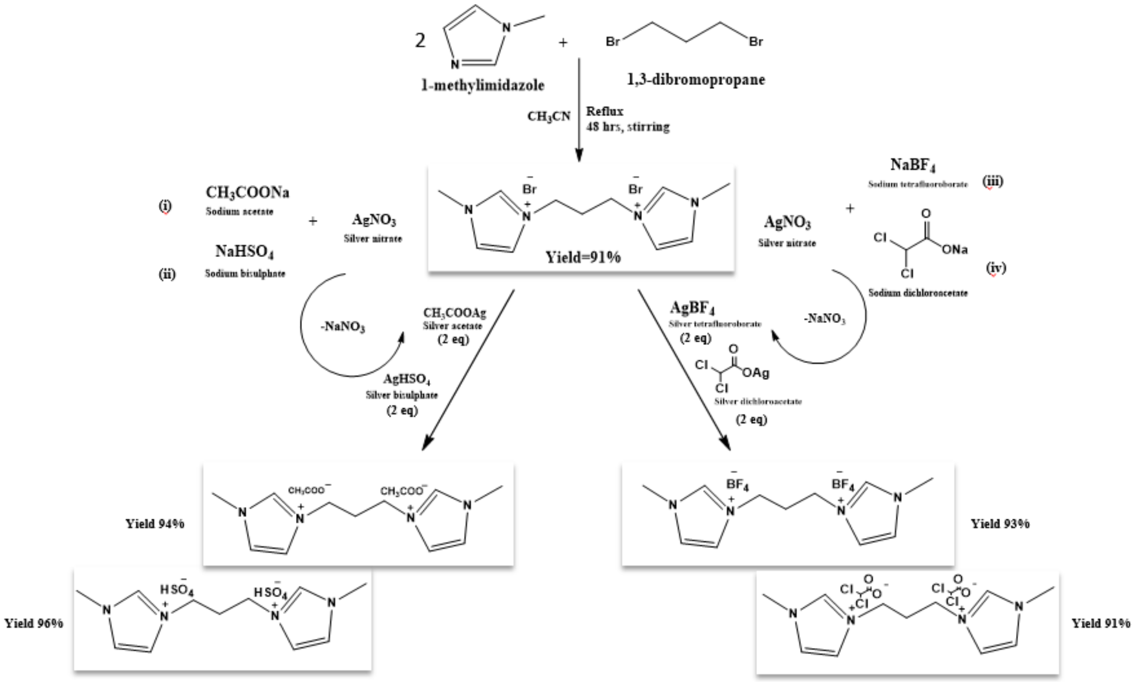
Using the metathesis reaction procedure, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) bisulphate was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgHSO_4$ (1.10g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^{o}C. A product yield of 96% was achieved.

3.4.19. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)tetrafluoroborate:

Using the metathesis reaction procedure, 1,1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)tetrafluoroborate was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a drop-wise addition of the $AgBF_4$ (1.04g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while reaction mixture was agitated all night long at room temperature and later on refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled H_2O. Rotary evaporation of the filtrate was done for the removal of the solvent and pure product was obtained. In vacuum oven, ionic liquid was further dried at 60^{o}C. A product yield of 93% was achieved.

3.4.20. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dichloroacetate:

Using the metathesis reaction procedure, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)dichloroacetate was synthesized. Using methanol as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the Cl_2CHCO_2Ag(1.04g, 5.4mmol) solution in methanol. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^{o}C. A product yield of 91% was achieved.



Scheme 12

3.4.21. Synthesis of 1, 1-(propane-1, 3-diyl)-bis(3-methyl-1-imidazolium-1-yl)hexafluorophosphate:

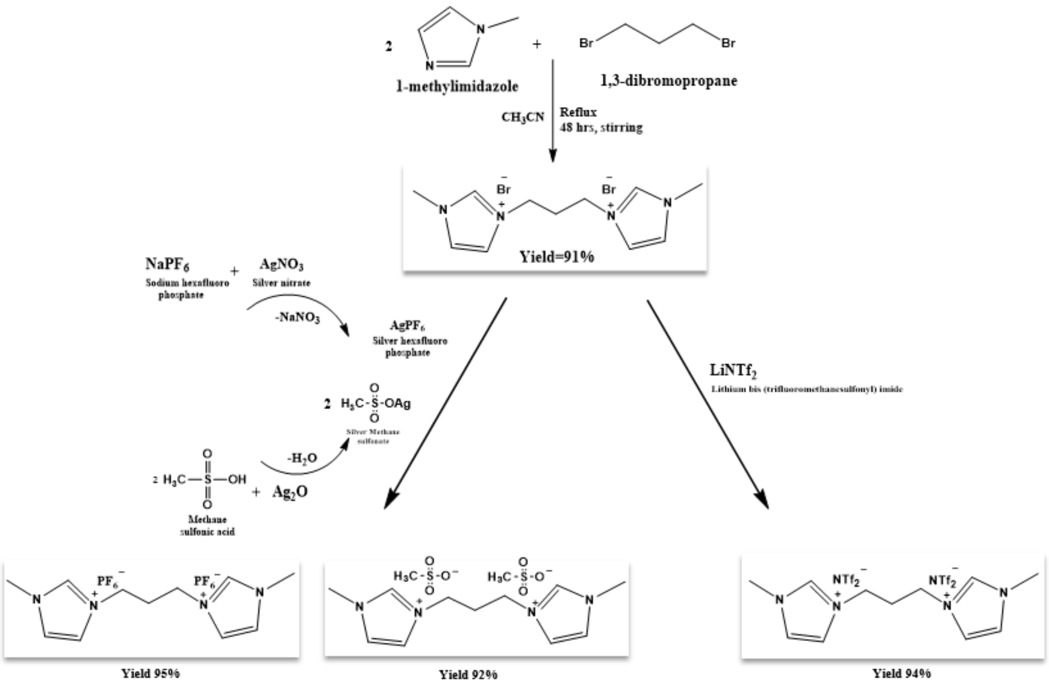
Using the metathesis reactionprocedure, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) hexafluorophosphate was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgPF_6$ (0.6g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^{o}C. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^{o}C. A product yield of 95% was achieved.

3.4.22. Synthesis of 1,1-(propane-1,3-diyl)-bis(3-methyl-1-imidazolium-1-yl)bis (trifluoromethanesulfonyl) imide:

Using the metathesis reaction procedure, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)bis (trifluoromethanesulfonyl) imide was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $LiNTF_2$ (1.56g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. An oily layer was obtained which contained di-cationic ionic liquid. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^oC. The oily layer was separated using solvent extraction technique using ethyl acetate as organic solvent and washed with aliquots of distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^oC. A product yield of 94% was achieved.

3.4.23. Synthesis of 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) methanesulfonate:

Using the metathesis reaction procedure, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl) was synthesized. Using distilled water as the solvent, 1, 1-(propane-1, 3-diyl)-bis (3-methyl-1-imidazolium-1-yl)dibromide (1g, 2.7 mmol) was added to double-necked round bottom flask. It received a dropwise addition of the $AgCH_3SO_3$ (1.09g, 5.4mmol) solution in distilled water. The flask with a circular bottom was filled with an inert atmosphere. Silver bromide rapidly precipitated as a greenish-yellow substance. The entire exchange took place while the reaction mixture was agitated all night long at room temperature and later refluxed for 2 hours at 70-80^oC. Precipitates were filtered and washed with distilled water. Rotary evaporation of the filtrate was done to remove the solvent and pure product was obtained. In vacuum oven, the ionic liquid was further dried at 60^oC. A product yield of 92% was achieved.


2
1-methylimidazole
1,3-dibromopropane
CH3CN
Reflux
48 hrs, stirring
Yield=91%
NaPF6
Sodium hexafluoro phosphate
AgNO3
Silver nitrate
-NaNO3
AgPF6
Silver hexafluoro phosphate
Silver Methane sulfonate
-H2O
Ag2O
Methane sulfonic acid
LiNTf2
Lithium bis (trifluoromethanesulfonyl) imide
Yield 95%
Yield 92%
Yield 94%

Scheme 13

4. RESULTS AND DISCUSSION

These characterization techniques are covered in depth in this chapter. Various amino acids-basedionic liquids that were synthesized in the lab were characterized with the aid of characterizationtechniques at various stages both during and after their synthesis.

- TLC, or Thin Layer Chromatography
- ATR-FTIR, or the Fourier Transformation Infrared Spectroscopy
- NMR, also known as Nuclear Magnetic Resonance Spectroscopy

4.1. Thin Layer Chromatography (TLC):

4.1.1. Principle:

TLC is comprised of two phases:

- Mobile phase
- Stationary phase

Mobile phase is liquid because it must transit over the stationary phase, which is solid.

Different spots of different compounds migrate relative to one another during TLC, and if a spot is a composite of different compounds, a number of spots emerge at various distances.

4.1.2. Technique:

During the course of the reaction, a number of TLC analyses were undertaken in order to monitor the reaction's progress and determine whether it was complete. The dilution of reactants is done with volatile solvent. In a beaker, a small volume of a nonpolar solvent or mélange of solvents with the required polarity was placed. A line was drawn on a silica gel TLC plate, and a spot of reactants and another spot of reaction mixture were placed using a capillary line. Then TLC plate was inserted inside the beaker, and the beaker's lid was set on top so that solvent could flow over the plate.

4.1.3. Observation with UV lamp:

The plate was removed, and the solvent distance or solvent front was marked, then spots were observed under UV light, spots were labeled, and these labeled spots were compared to determine whether the reaction was complete.

4.1.4. Iodine chamber:

In the iodine chamber, TLC plates were deposited for a period until dark yellow or brown spots appeared. These spots were then compared to observe product formation and labeled for future observations.

4.2. Attenuated Total Reflection-Fourier Transformation Infrared spectroscopy(ATR-FTIR):

4.2.1. Basic Principle:

The fundamental principle of IR spectroscopy is the interaction of IR-region radiation with molecules, which causes covalent bonds to vibrate through bending and stretching. Two regions make up the IR spectrum: the functional group region was lied between 4000 and 1000 cm^{-1} and the fingerprint region was between 1000cm^{-1} and 400 cm^{-1}. For interpreting the structure of a molecule, the IR spectrum aids in locating the various functional groups present in the molecule.

Stretching vibration alters the bond length; this may be symmetric when all bonds change bond length at the same time or asymmetric when one bond length increases, and at the same time, the other bond length decreases.

Bond angle of the molecule was altered due to the bending vibrations. Bending may be scissoring type when two bonds move like scissor to increase or decrease the bond angle, rocking type when bonds move like the pendulum of a clock, wagging type when bonds move back and forth like a V, and twisting type when bonds appear to be walking.

In this investigation, unprepared synthesized compounds were analyzed using ATR-FTIR spectroscopy, deposited on BRUKER ALPHA platinum ATR. The produced infrared spectra contain comprehensive information on chemical vibrations and can be used to characterize the synthesized compounds.

4.2.2. FT-IR analysis of $[C_3(MIm)_2][2Br]$,$[C_3(MIm)_2][2HSO_4]$:

FT-IR for $[C_3(MIm)_2][2Br]$ is shown in Figure 4.1. At 3140 $cm^{-1}$and 3043 cm^{-1}bands appeared due to aromatic C-H stretching vibrations, 2981 cm^{-1} and 2848 cm^{-1} peaks are stretching vibrations of C-H for aliphatic sp^3 CH_2 and CH_3 respectively. A band appearing at 1669 cm^{-1} show C=N stretching vibrations of imidazolium ring, band at 1577 cm^{-1} show stretching vibration of C=C and bending vibrations for CH_2 are at 1458 cm^{-1} strong peak at 1160 cm^{-1} appear due to stretching vibration of C-N of imidazolium ring.

Stretching vibrations of S=O band for $[C_3(MIm)_2][2HSO_4]$ appears at 1065cm^{-1}. Due to this band, it was confirmed that anion exchange was successfully accomplished.

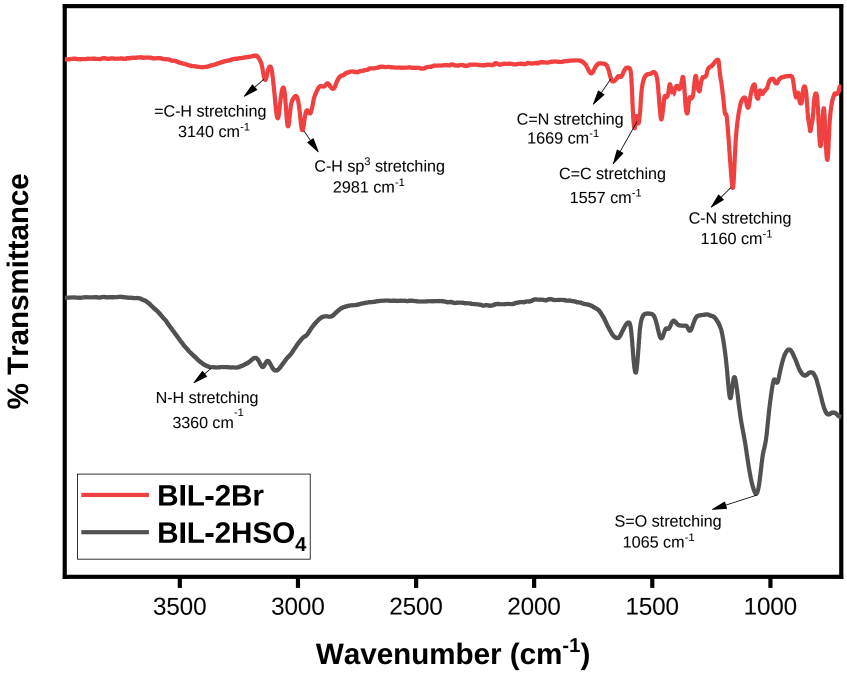


Figure 4.2.2FT-IR spectra of $[C_3(MIm)_2][2Br]$,$[C_3(MIm)_2][2HSO_4]$

4.2.3. FT-IR analysis of $[C_3(MIm)_2][2CH_3COO]$,$[C_3(MIm)_2][2CH_3SO_3]$:

FT-IR analysis of $[C_3(MIm)_2][2CH_3COO]$ is shown in Figure 4.2. At 3140 cm^{-1} band appeared due to aromatic C-H stretching vibrations, 2995 cm^{-1} are stretching vibrations of CH for aliphatic sp^3. C-O bending band can be seen at 1338 cm^{-1}. Whereas a band merging of C=O can be seen at 1649 cm^{-1} with C=N stretching vibrations of imidazolium ring, Band at 1557 cm^{-1} show stretching vibration of C=C and bending vibrations for CH_2 are at 1458 cm^{-1} strong peak at 1160 cm^{-1} appear due to stretching vibration of C-N of imidazolium ring.

An asymmetrical S=O stretch appears at 1334 cm^{-1}and S=O symmetrical stretch appears at 1035 cm^{-1} for $[C_3(MIm)_2][2HSO_4]$ which is characteristic band for confirmation of anion exchange.

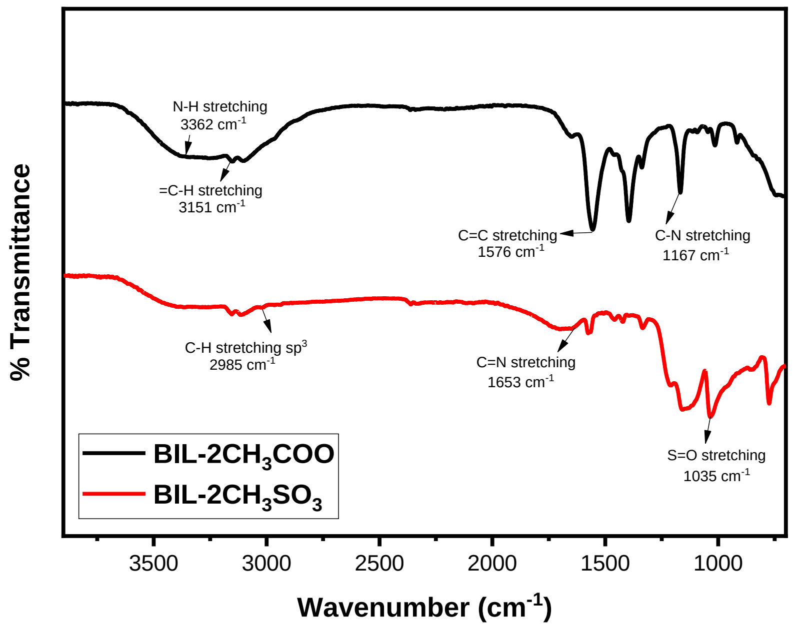


Figure 4.2.3 FT-IR spectra of $[C_3(MIm)_2][2CH_3COO]$,$[C_3(MIm)_2][2CH_3SO_3]$

4.2.4. FT-IR analysis of $[C_3(MIm)_2][2BF_4]$,$[C_3(MIm)_2][2PF_6]$:

FT-IR analysis of $[C_3(MIm)_2][2BF_4]$is shown in Figure 4.2. At 3149 cm^{-1}band appeared due to aromatic C-H stretching vibrations, 3085 cm^{-1} and 2848 cm^{-1} peaks are stretching vibrations of CH for aliphatic sp^3 CH_2 and CH_3 respectively. A band appearing at 1629 cm^{-1} show C=N stretching vibrations of imidazolium ring, Band at 1574 cm^{-1} show stretching vibration of C=C and bending vibrations for CH_2 are at 1457 cm^{-1} strong peak at 1160 cm^{-1} appear due to stretching vibration of C-N of imidazolium ring. The bands appearing at 1060 cm^{-1} and 743 cm^{-1} are due to asymmetric and symmetric B-F respectively, indicating the success of anion exchange.

Band arising at 824 cm^{-1} shows anionic interaction of PF_6^- with di-cationic ionic liquid, indicating the formation of $[C_3(MIm)_2][2PF_6]$:

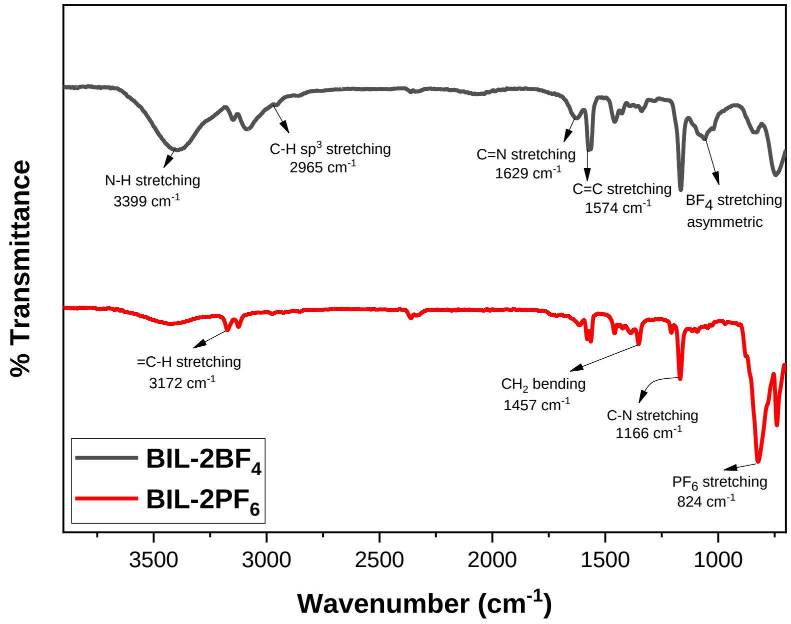


Figure 4.2.4FT-IR analysis of $[C_3(MIm)_2][\ 2BF_4]$,$[C_3(MIm)_2][2PF_6]$

4.2.5. FT-IR analysis of $[C_3(MIm)_2][2NTf_2]$,$[C_3(MIm)_2][2Cl_2CHCO_2]$:

FT-IR analysis of $[C_3(MIm)_2][2NTf_2]$is shown in Figure 4.2. At 3158 cm^{-1}band appeared due to aromatic C-H stretching vibrations, 2965 cm^{-1} and 2848 cm^{-1} peaks are stretching vibrations of CH for aliphatic sp^3 CH_2 and CH_3 respectively. A band appearing at 1629 cm^{-1} show C=N stretching vibrations of imidazolium ring, Band at 1577 cm^{-1} shows stretching vibration of C=C and bending vibrations for CH_2 are at 1464 cm^{-1}.The bands appearing at 1345 cm^{-1} and 1183 cm^{-1} are due to asymmetric S=O and CF_3 stretch respectively, while symmetric S=O stretching occurs at 1050 cm^{-1}indicating the success of anion exchange.

The presence of band at 1710 cm^{-1}indicates C=O group, therefore confirming the anion exchange and formation of [$C_3(MIm)_2$][$2Cl_2CHCO_2$].

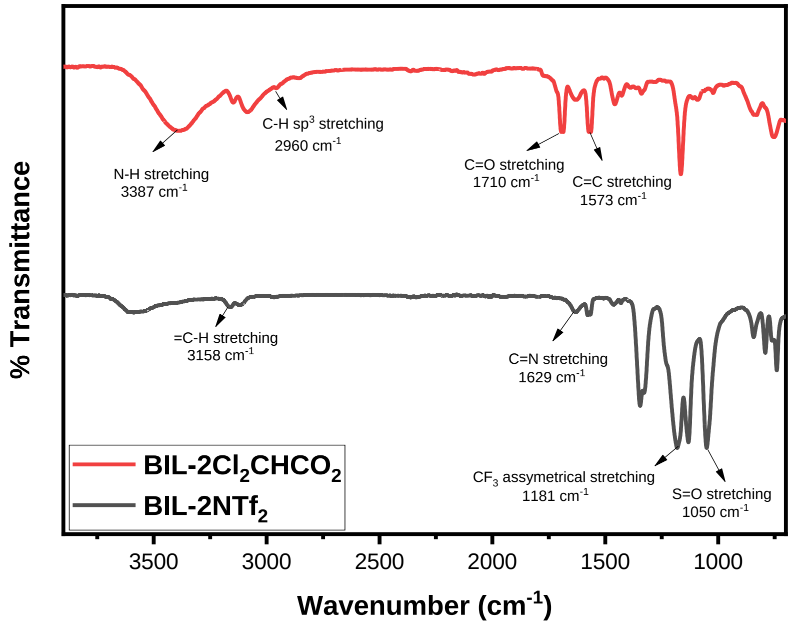


Figure 4.2.5 FT-IR spectra of [$C_3(MIm)_2$][$2NTf_2$],[$C_3(MIm)_2$][$2Cl_2CHCO_2$]

4.2.6. FT-IR analysis of [$C_4(MI)_2$][2Br],[$C_4(MI)_2$][$2CH_3COO$], [$C_4(MI)_2$][$2HSO_4$]

Spectra displays the FT-IR for [$C_4(MI)_2$][2Br]. Aromatic CH stretching vibrations caused the band to develop at 3136 cm^{-1} and 3044 cm^{-1}, while aliphatic sp^3 CH stretching vibrations caused the peak at 2931 cm^{-1}.Band at 1677 cm^{-1} show stretching vibration of C=N of imidazolium ring and band at 1558 cm^{-1} shows stretching vibration of C=C and bending vibrations for CH_2 are at 1476 cm^{-1}bending vibrations for CH_2 strong peak at 1159 cm^{-1} appear due to stretching vibration of C-N of imidazolium ring.

The overlapping C=O band for [$C_4(MI)_2$][$2CH_3COO$] however, was visible at 1600 cm^{-1}.

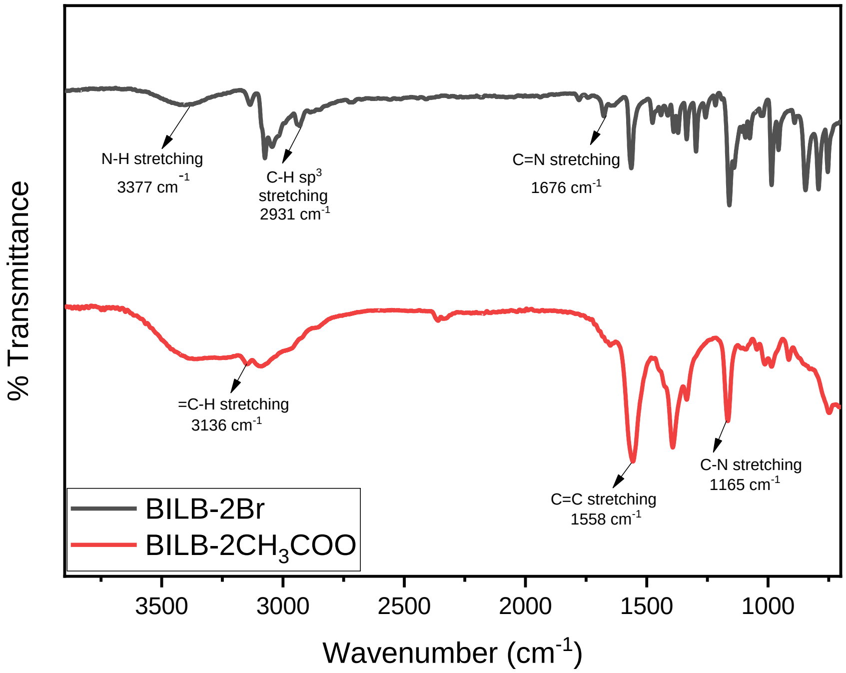


Figure 4.2.6 FT-IR spectra of $[C_4(MI)_2][2Br]$, $[C_4(MI)_2][2CH_3COO]$

A strong band of S=O was observed at 1065 cm^{-1} for $[C_4(MI)_2][2HSO_4]$ indicating the presence of the bisulfate ion as counter anion.

4.2.7. FT-IR analysis of $[C_4(MIm)_2][2Cl_2CHCO_2]$,$[C_4(MIm)_2][2CH_3SO_3]$:

FT-IR analysis of $[C_4(MIm)_2][2Cl_2CHCO_2]$is shown in Figure 4.2. At 3150 cm^{-1} band appeared due to aromatic C-H stretching vibrations, 2995 cm^{-1} are stretching vibrations of CH for aliphatic sp^3. C-O bending band can be seen at 1338 cm^{-1}. Whereas a vibrational band of C=O can be seen at 1727 cm^{-1} with C=N stretching vibrations of imidazolium ring at 1632 cm^{-1}, Band at 1574 cm^{-1} show stretching vibration of C=C and bending vibrations for CH_2 are at 1449 cm^{-1} strong peak at 1164 cm^{-1} appear due to stretching vibration of C-N of imidazolium ring.

An asymmetrical S=O stretch appears at 1335 $cm^{-1}$and S=O symmetrical stretch appears at 1041 cm^{-1} for $[C_3(MIm)_2][2HSO_4]$ which is characteristic band for confirmation of anion exchange and formation of $[C_4(MIm)_2][2CH_3SO_3]$.

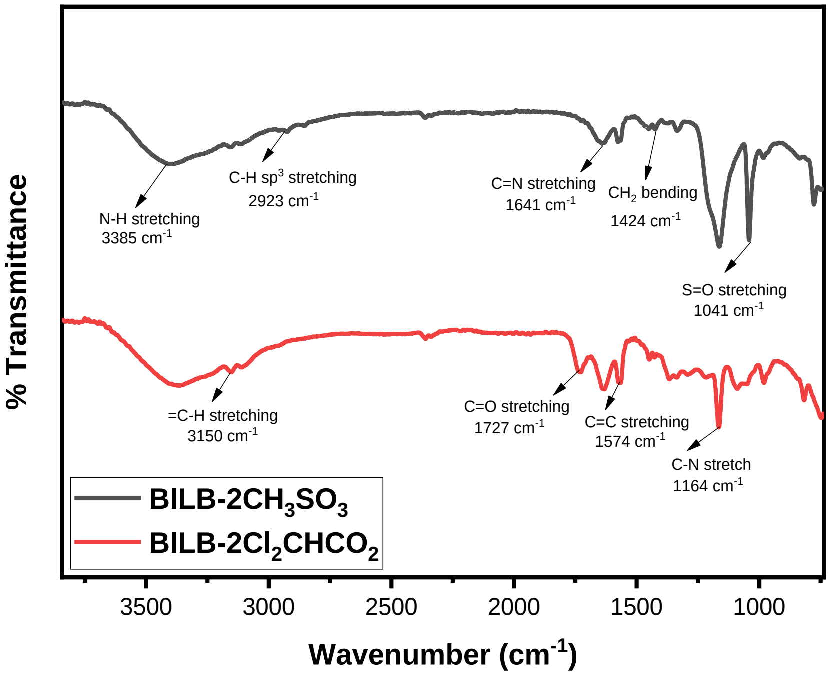


Figure 4.2.7FT-IR spectra of $[C_4(MIm)_2][\ 2Cl_2CHCO_2]$,$[C_4(MIm)_2][2CH_3SO_3]$

4.2.8. FT-IR analysis of $[C_4(MIm)_2][2NTf_2]$,$[C_4(MIm)_2][2BF_4]$:

FT-IR analysis of $[C_4(MIm)_2][2NTf_2]$is shown in Figure 4.2. At 3158 cm^{-1}band appeared due to aromatic C-H stretching vibrations, 3085 cm^{-1} peak is stretching vibrations of CH for aliphatic sp^3. A band appearing at 1627 cm^{-1} show C=N stretching vibrations of imidazolium ring, Band at 1575 cm^{-1} shows stretching vibration of C=C and bending vibrations for CH_2 are at 1464 cm^{-1}.The bands appearing at 1337 cm^{-1} and 1179 cm^{-1} are due to asymmetric S=O and CF_3 stretch respectively, while symmetric S=O stretching occurs at 1052 cm^{-1} indicating the success of anion exchange.

The bands appearing at 1060 cm^{-1} and 743 cm^{-1} show B-F asymmetric along with the symmetric stretching respectively, therefore, explaining that $[C_4(MIm)_2][2BF_4]$ exchange is attained.

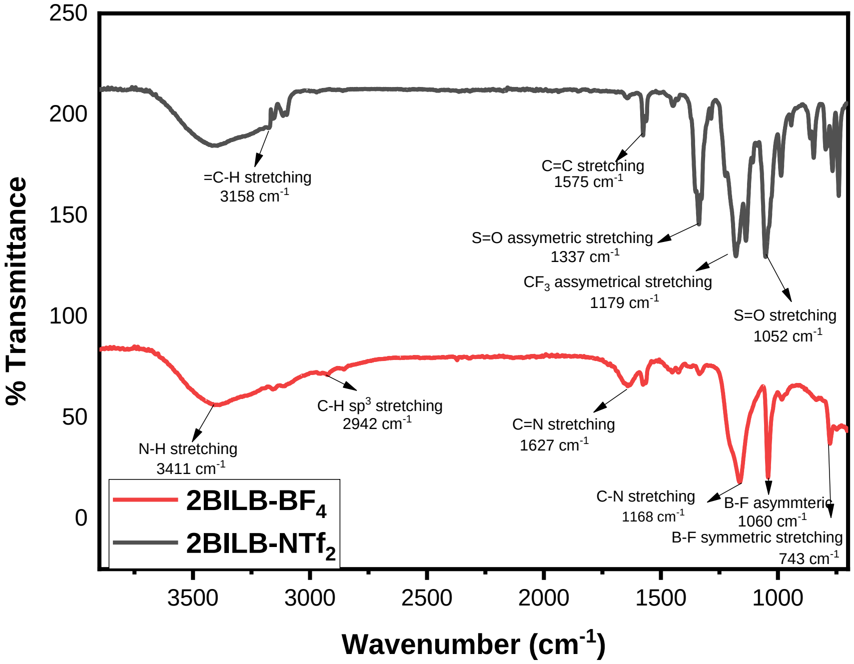


Figure 4.2.8 FT-IR spectra of $[C_4(MIm)_2][2NTf_2]$,$[C_4(MIm)_2][2BF_4]$

4.3. Nuclear Magnetic Resonance (NMR) analysis:

Nuclear Magnetic Resonance (NMR) spectroscopy exploits the inherent magnetic properties of specific atomic nuclei as its underlying principle. As a result of the Zeeman effect, nuclei with non-zero nuclear spin, such as hydrogen and carbon-13 nuclei, align either parallel or antiparallel to a magnetic field when inserted in one. These nuclei absorb energy and transition between energy states when exposed to radiofrequency (RF) pulses that match their resonance frequencies. As they return to equilibrium, they emit RF signals containing the absorbed energy. These signals are then detected and converted into NMR spectra, which graphically depict the signal's resonance frequencies and intensities. The chemical shift phenomenon provides additional information regarding the chemical environments of nuclei, whereas spin-spin coupling discloses interactions between adjacent nuclei. By analyzing NMR spectra, scientists are able to infer molecular structures, investigate molecular dynamics, quantify composition, and gain insight into a variety of molecular properties and interactions. Consequently, NMR spectroscopy provides a nondestructive and highly informative window into the atomic and molecular world, with applications encompassing chemistry, biology, medicine, and materials science.

4.3.1. Procedure:

Experiments in NMR were performed at a frequency of 400 MHz, which is a common high-field range. Deuterated water (D_2O) and Dimethyl sulfoxide (DMSO) were used as the solvent for the samples. It should be noted that when D_2O is used as the solvent, the NMR spectra gives solvent peak at 4.70 ppm while when utilizing DMSO as solvent, solvent peak occurs at 3.50 ppm.

4.3.2. ^{1}H-NMR analysis of [$C_3(MIm)_2$][2Br]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 2.46 (p, 2H), 3.83 (s, 6H), 4.25 (t, 4H), 7.40 (d, 2H), 7.44(d, 2H) 8.72 (s,2H)

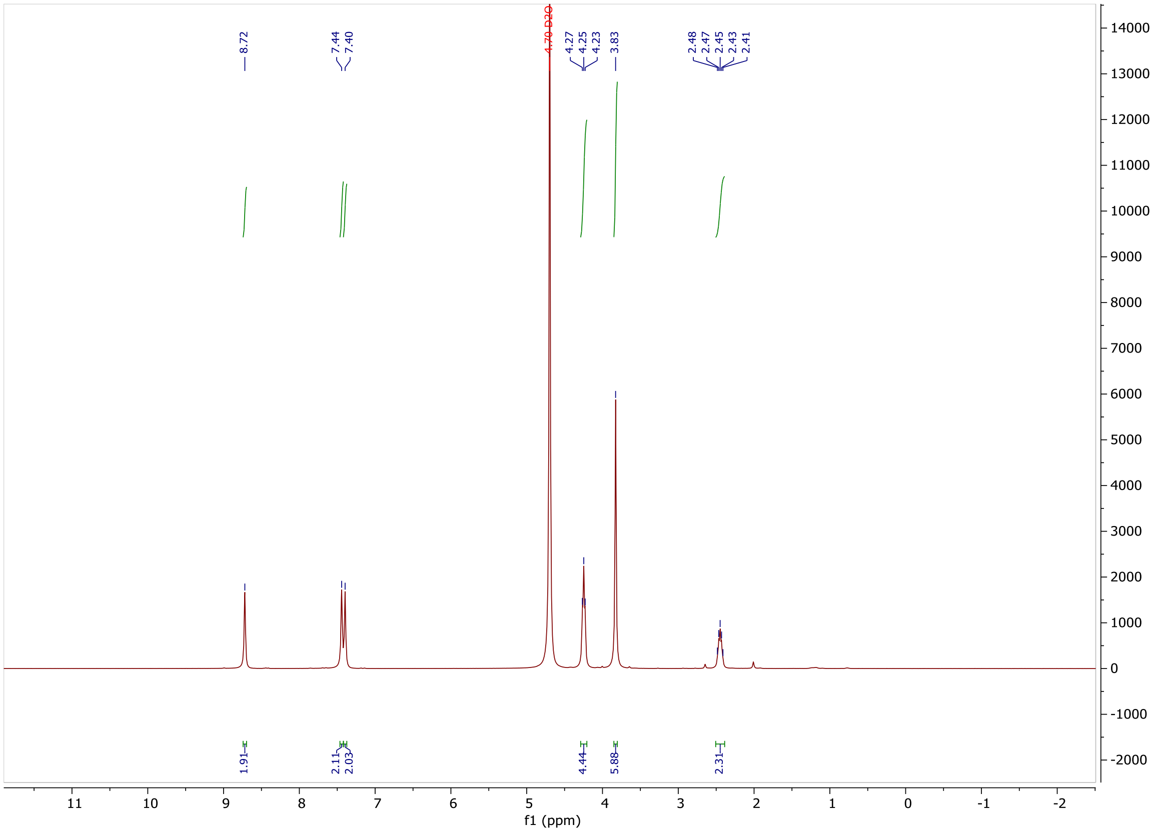


Figure 4.3.2^{1}H-NMR spectra of [$C_3(MIm)_2$][2Br]

4.3.3. ^{1}H-NMR analysis of [C_3(MIm)$_2$][2HSO_4]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 2.43 (p, 2H), 3.82 (s, 6H), 4.23 (t, 4H), 7.38 (d, 2H)

7.42 (d, 2H) 8.72 (s,2H)

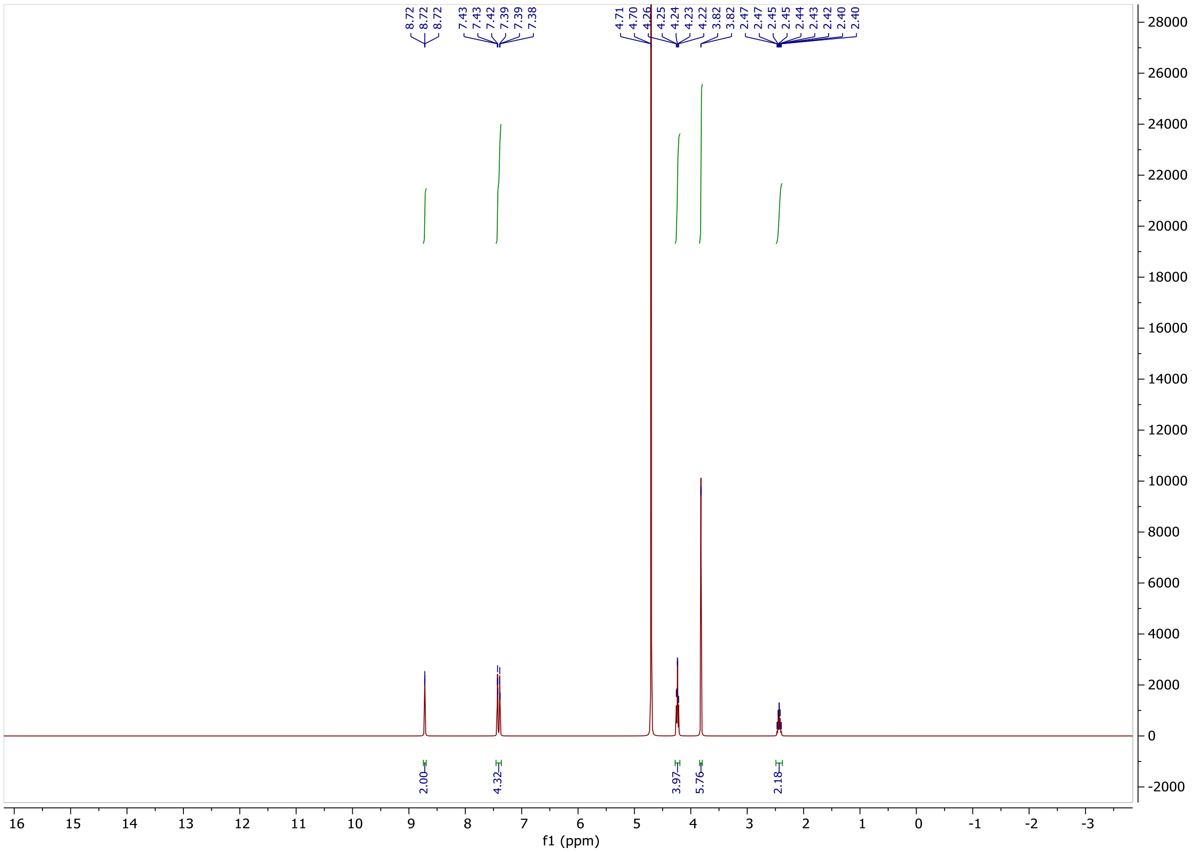


Figure 4.3.3 1H-NMR analysis of [C3(MIm)2][2HSO4]

4.3.4. ^{1}H-NMR analysis of [$C_3(MIm)_2$][$2CH_3COO$]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 1.82 (s, 6H), 2.43(m, 2H), 3.81 (s, 6H), 4.22 (t, 4H), 7.39 (d, 2H), 7.42 (d, 2H) 8.70 (s,2H)

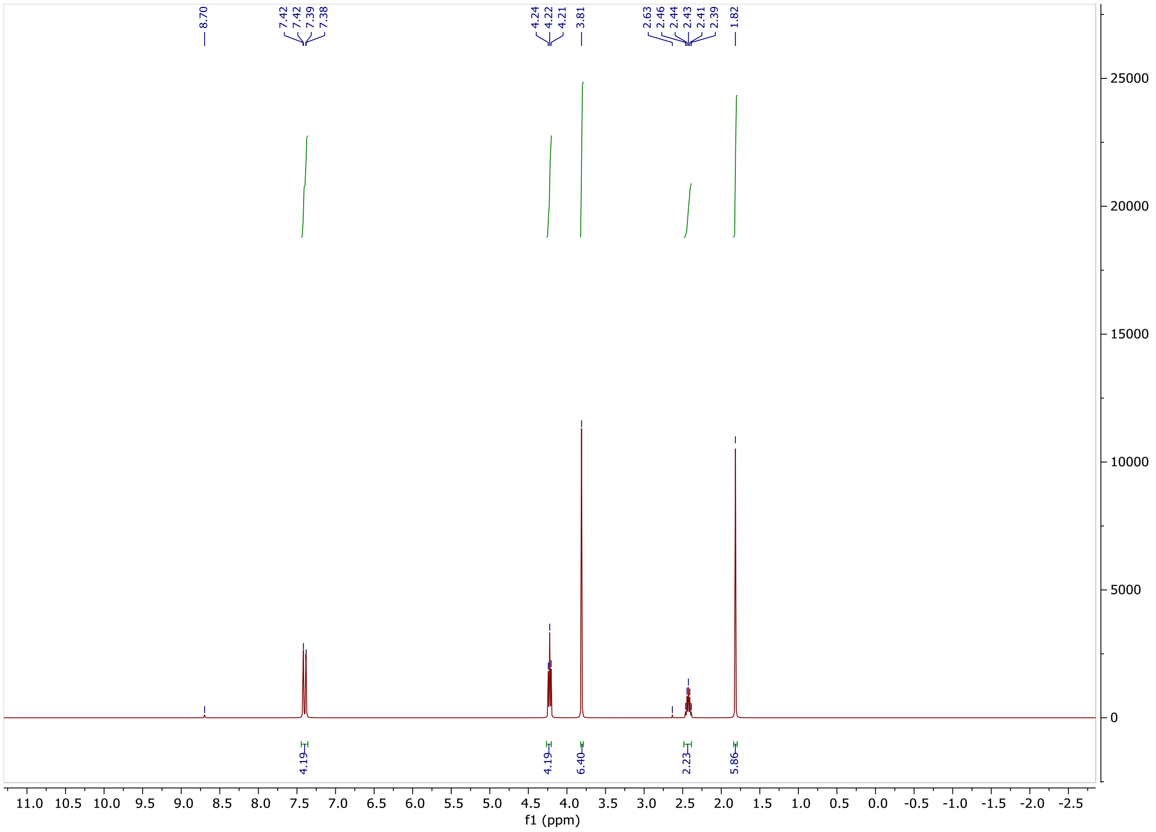


Figure 4.3.4^{1}H-NMR spectra of [$C_3(MIm)_2$][$2CH_3COO$]

4.3.5. ^{1}H-NMR analysis of [$C_3(MIm)_2$][$2CH_3SO_3$]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 2.39(m, 2H), 2.67 (s, 6H), 3.78 (s, 6H), 4.19 (t, 4H), 7.37(d, 4H) 8.65 (s,2H)

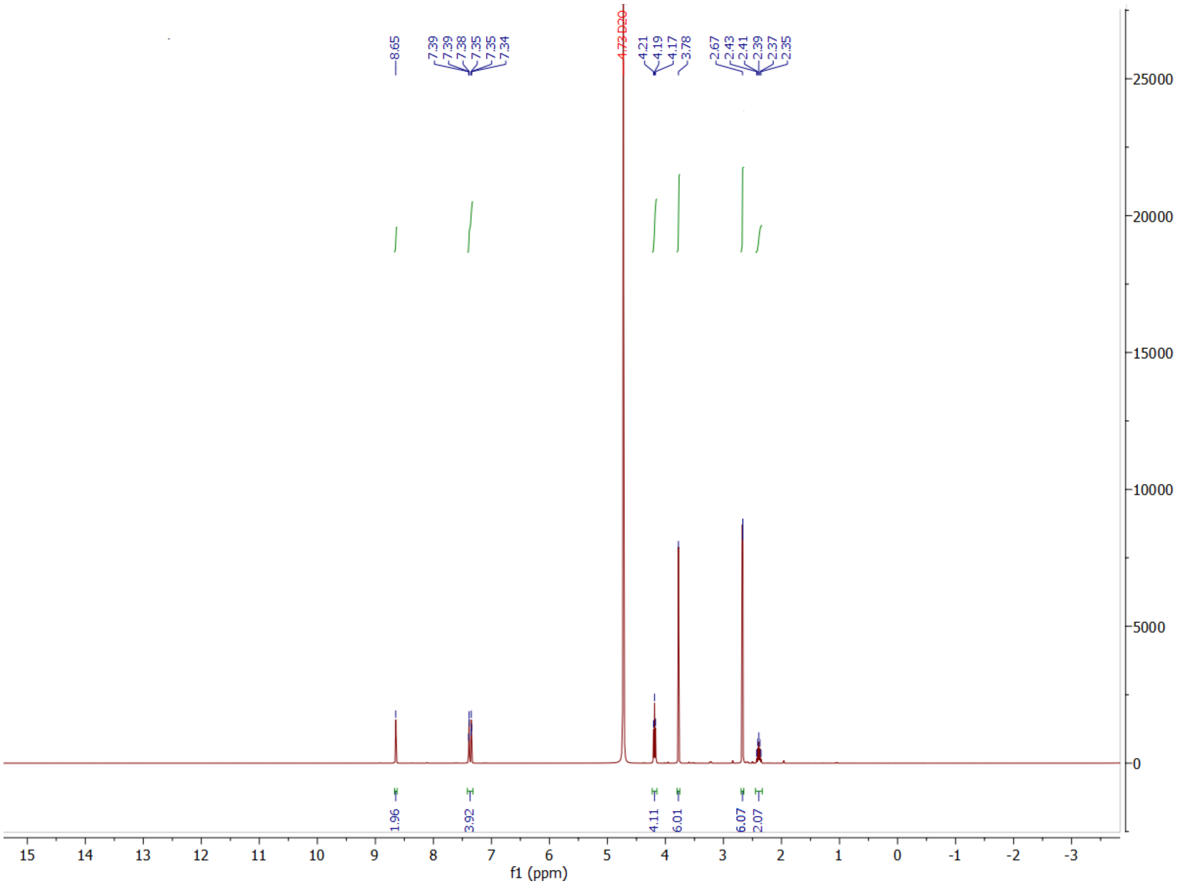


Figure 4.3.5 ^{1}H-NMR analysis of [$C_3(MIm)_2$][$2CH_3SO_3$]

4.3.6. ^{1}H-NMR analysis of [C$_4$(MIm)$_2$][2Br]:

^{1}H NMR (400 MHz, D$_2$O, ppm) δ = 3.81 (s, 6H),4.84-4.78 (m, 4H), 5.9 (td, 4H), 7.38 (m, 6H)

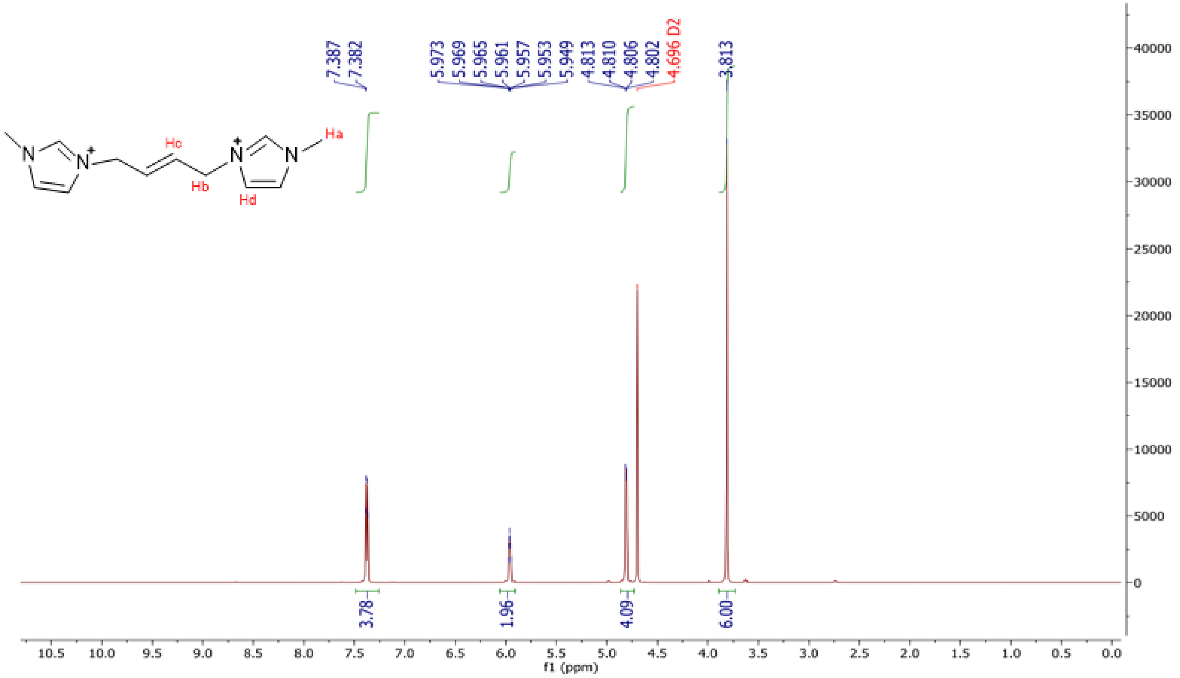


Figure 4.3.6^{1}H-NMR analysis of [C$_4$(MIm)$_2$][2Br]

4.3.7. ^{1}H-NMR analysis of [$C_4(MIm)_2$][$2CH_3COO$]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 1.79 (s, 6H), 3.81 (s, 6H), 4.79 (dd, 4H), 5.93 (dt, 2H) 7.36 (d, 4H) 8.65 (s,2H)

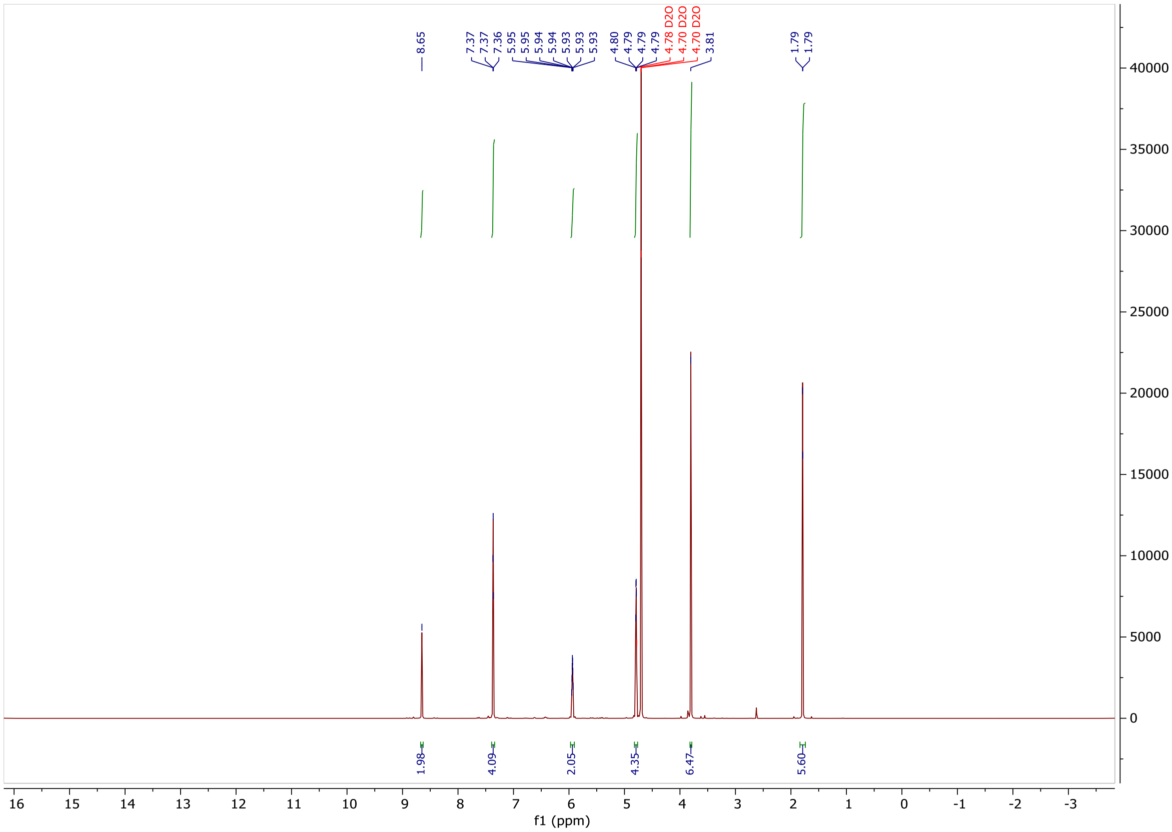


Figure 4.3.7^{1}H-NMR spectra of [$C_4(MIm)_2$][$2CH_3COO$]

4.3.8. ^{1}H-NMR analysis of [$C_4(MIm)_2$][$2HSO_4$]:

^{1}H NMR (400 MHz, D_2O, ppm) δ = 3.81 (s, 6H), 4.79 (dd, 4H), 5.94 (dt, 2H), 7.37 (d, 4H) 8.66 (s,2H)

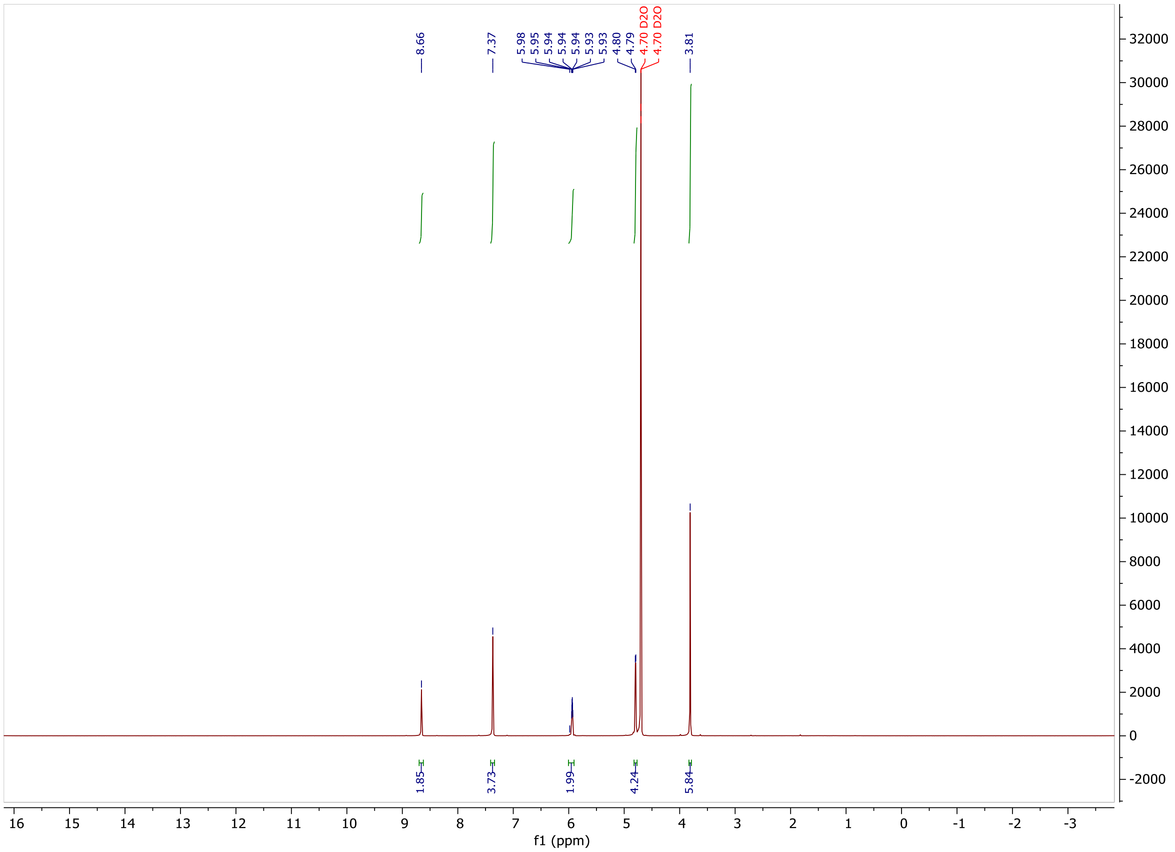


Figure 4.3.8^{1}H-NMR spectra of [$C_4(MIm)_2$][$2HSO_4$]

4.3.9. ^{1}H-NMR analysis of [$C_4(MIm)_2$][$2CH_3SO_3$]:

^{1}H NMR (400 MHz, D_2O, ppm) δ =2.69 (s,6H), 3.80 (s, 6H), 4.78 (m, 4H), 5.93 (dt, 2H), 7.36 (d, 4H), 8.63(s,2H)

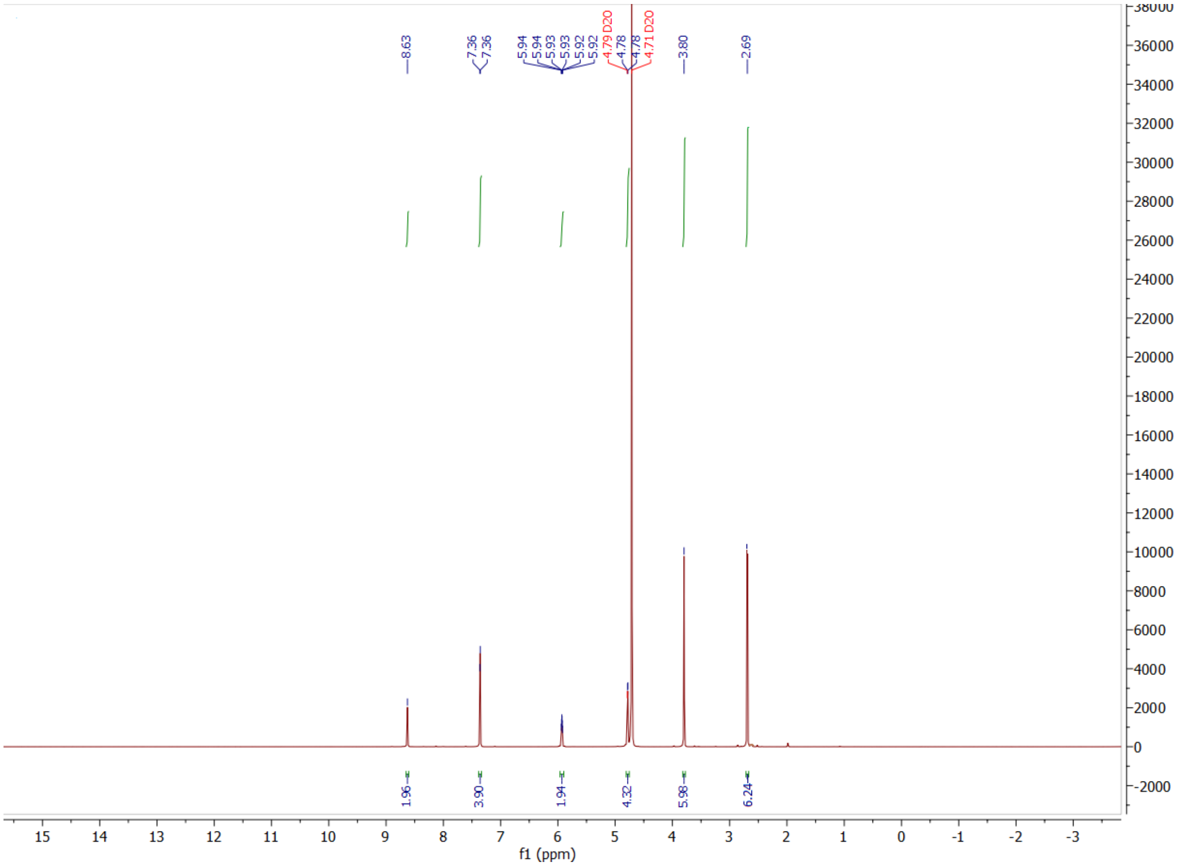


Figure 4.3.9^{1}H-NMR spectra of [$C_4(MIm)_2$][$2CH_3SO_3$]

4.3.10. ^{1}H-NMR analysis of [$C_4(MIm)_2$][$2Cl_2CHCO_2$]:

^{1}H NMR (400 MHz, DMSO, ppm) δ = 3.88 (s, 6H), 4.92 (m, 4H), 6.01 (dt, 2H), 6.32(s, 2H), 7.76 (d, 2H), 7.80 (d, 2H),9.42 (s,2H)

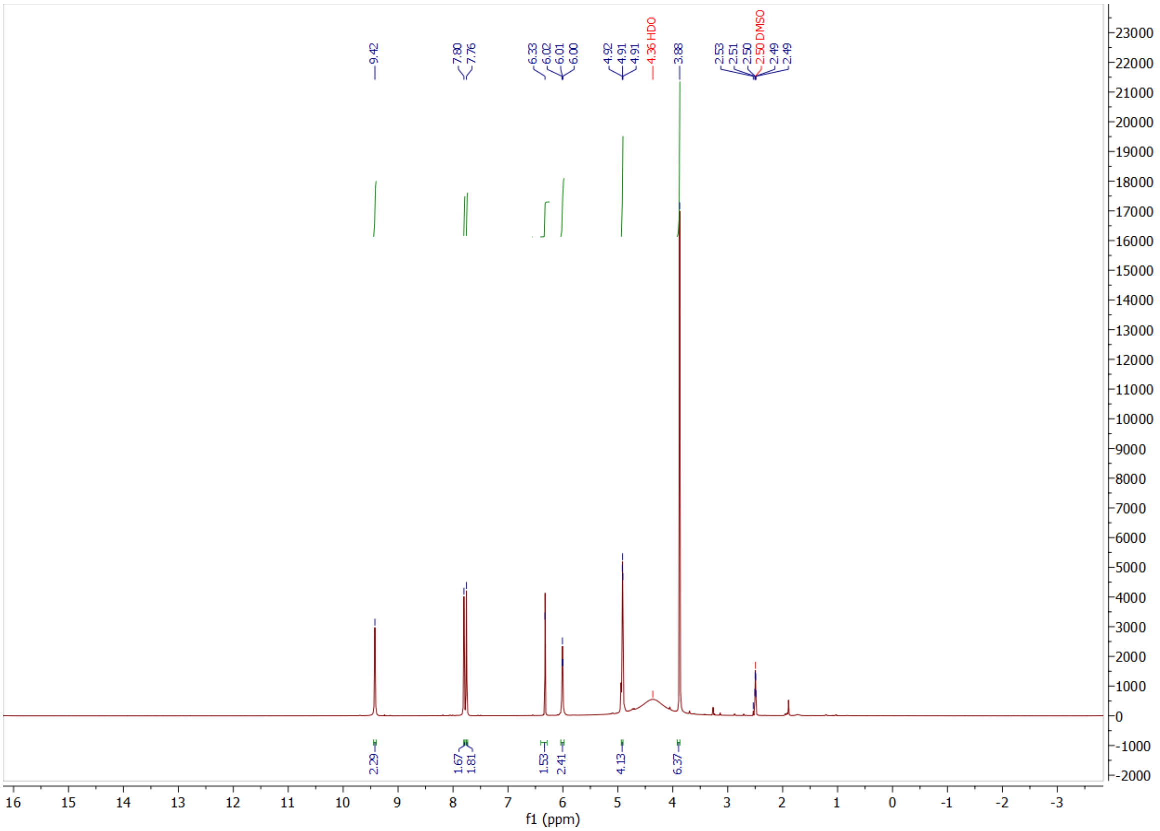


Figure 4.3.10^{1}H-NMR spectra of [$C_4(MIm)_2$][$2Cl_2CHCO_2$]

4.4. Demonstration of Antibacterial activity:

Distilled water was used to produce each sample of similar density. Each sample was examined three times. The antibiotic levofloxacin, a third-generation antibiotic, was utilized as a positive control. Distilled water was utilized as a negative control.

4.4.1. Agar Well Diffusion Assay:

Popular technique for determining antibacterial activity is the agar well diffusion procedure. Inoculating a standard culture of the target bacterium onto solid nutrient agar plates, forming wells, and filling them with the correct amount of test chemicals are required. Clear zones surrounding the wells after incubation indicate that bacterial growth has been inhibited, with larger zones indicating greater antimicrobial activity. By quantifying these zones, the method permits a rapid and accurate evaluation of the activity of compounds or substances against specific microorganisms, making it an indispensable instrument for antimicrobial research and screening.

To evaluate their antibacterial efficacy against five distinct varieties of pathogenic bacteria, 16 samples were synthesized. A new culture of microbes was utilized in triplicate to cultivate the bed in Petri dishes. The bacterial sample was distributed equitably on each Petri dish. There were created 3mm-distance wells at equal distances. Each well received approximately 80 μl of each sample solution, which was incubated at 37^{o}C for 24 hours. The majority of ionic liquids exhibit bacterial inhibition zones and therefore antibacterial activity.

4.4.2. Zone of Inhibition

Here are mentioned the zone of Inhibition measured in mm for each sample and strain.

Table 2 Zone of Inhibition of different bacterial strains

Ionic Liquid Class	BIL-propane				
	Bromide	Methane Sulfonate	Tetrafluoroborate	Acetate	(+ve) Control
Bacillus subtilis	0	15	19	0	18
Escherchia coli	0	19	16	0	38
Klebsiella pneumoniae	0	15	20	0	15
Staphylococcus aureus	0	16	17	0	37
Methicillin-resistant *Staphylococcus aureus*	0	12	16	0	15

Ionic LiquidClass	BIL-propane				
	Dichloroacetate	Hexafluorophosphate	Ntf_2	Bisulphate	(+ve) control
Bacillus subtilis	0	12	0	16	15
Escherchia coli	0	0	0	15	35
Klebsiella pneumoniae	12	13	0	16	17
Staphylococcus aureus	21	16	0	16	35

Methicillin-resistant *Staphylococcus aureus*	15	14	0	15	19

Table 3 Zone of Inhibition of different antibacterial strains

Ionic Liquid Class	BIL-but-2-ene				
	Bromide	Methane Sulfonate	Tetrafluoroborate	Acetate	(+ve) control
Bacillus subtilis	0	0	0	0	25
Escherchia coli	0	15	14	16	34
Klebsiella pneumoniae	0	13	14	16	16
Staphylococcus aureus	0	11	13	15	35
Methicillin-resistant *Staphylococcus aureus*	0	11	0	19	16

Ionic Liquid Class	BIL-but-2-ene				
	Dichloroacetate	Hexafluorophosphate	Ntf2	Bisulphate	(+ve) control
Bacillus subtilis	13	12	0	16	15

Escherchia coli	0	0	0	15	30
Klebsiella pneumoniae	0	0	0	15	32
Staphylococcus aureus	19	13	0	14	35
Methicillin-resistant *Staphylococcus aureus*	14	15	0	17	19

4.4.3. Graphical Representaion and Comparison of antibacterial activities:

A graphical representation of different ionic liquids against five types of bacteria has shown below. Di-cationic Ionic liquid with propane as linker with their counter ion bromide, acetate, methane sulfonate and tetrafluoroborate. In the case of *B.subtilis*, *K.pnuemoniae* and Methicillin resistant *S.aureus* ionic liquid with tetrafluoroborate showed excellent antibacterial activity even more than the control group which is 3rd generation antibiotic. While in case of *E.coli* methane sulfonate containing ionic liquid showed good antibacterial activity. In case of *S.aureus* methane sulfonate and tetrafluoroborate counter ions showed good antibacterial activity.

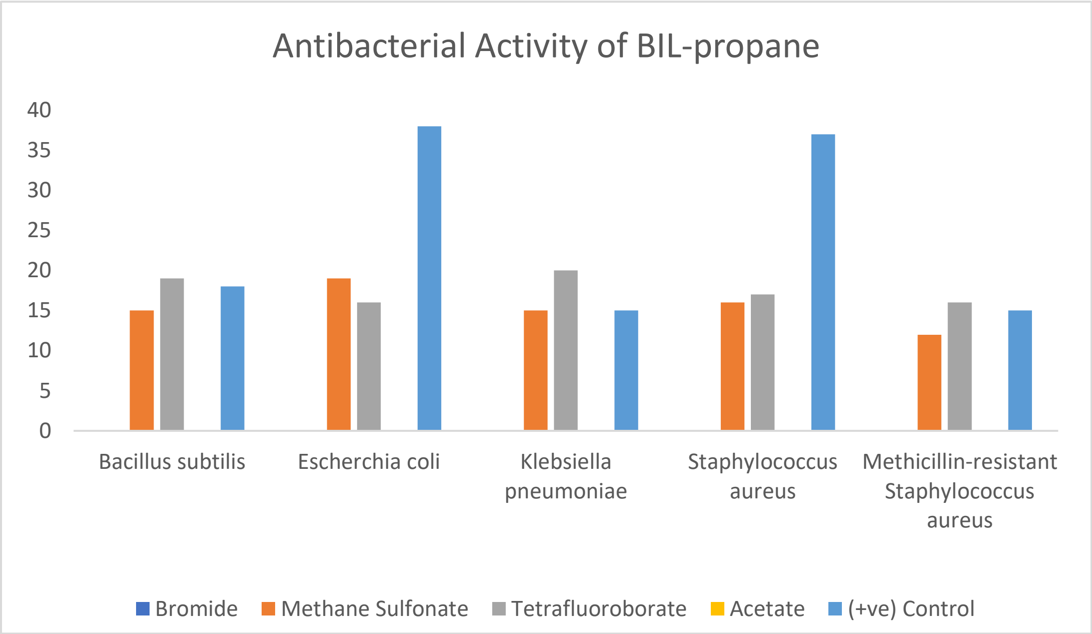


Figure 4.4.3 Graphical Representation of Zone of Inhibition

A graphical representation of different ionic liquids against five types of bacteria has shown below. Di-cationic Ionic liquid with propane as linker with their counter ion hexafluorophosphate, dichloroacetate, bisulphate and bis(trifluoromethanesufonyl) imide. In the case of *B.subtilis*, ionic liquid with bisulphate showed excellent antibacterial activity even more than the control group which is 3rd generation antibiotic. While in case of *E.coli* bisulphate containing ionic liquid revealed a good antibacterial activity. In case of *S.aureus*, dichloroacetate and hexafluorophosphate counter ions exhibited a good antibacterial activity. In event of *K.pnuemoniae* and Methicillin resistant *S.aureus* all anions showed good anti-bacterial activities except Ntf_2.

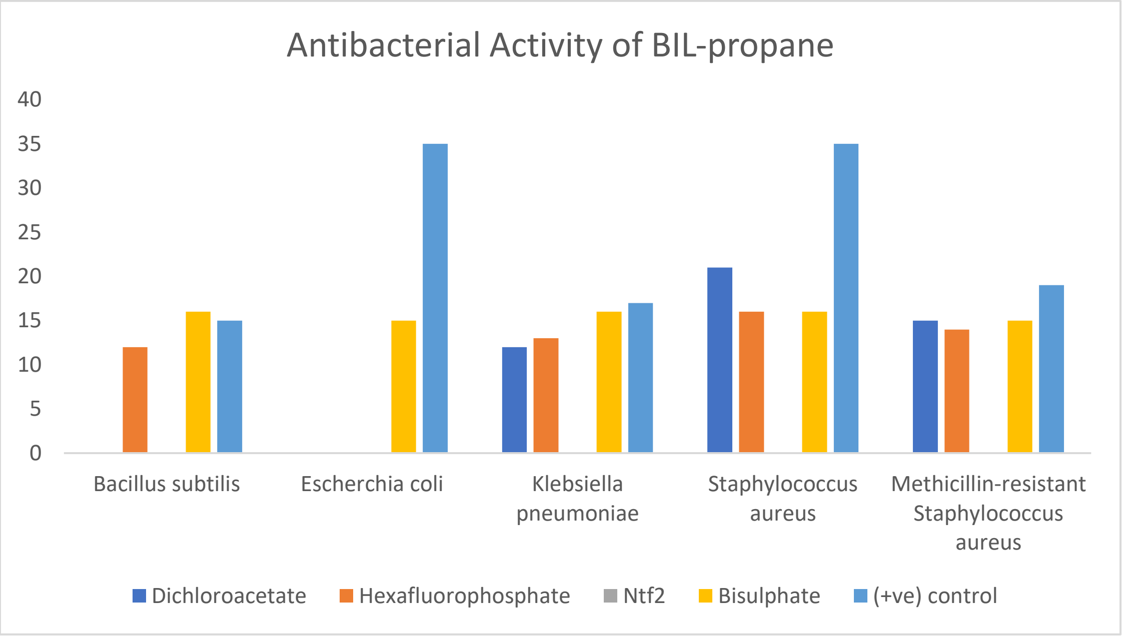


Figure 4.4.3 Graphical Representation of Zone of Inhibition

A graphical representation of different ionic liquids against five types of bacteria has shown below. Di-cationic Ionic liquid with but-2-ene as linker with their counter ion bromide, acetate, methane sulfonate and tetrafluoroborate. In the case of *B.subtilis*, there was no antibacterial activity shown by any ionic liquid. In case of Methicillin resistant *S.aureus* ionic liquid with acetate showed excellent antibacterial activity even more than the control group which is 3rd generation antibiotic. In case of *K.pnuemoniae* ionic liquid acetate as counter anion give equivalent zone of inhibition as compared to positive control used and tetrafluoroborate and methane sulfonate also exhibited a good antibacterial activity. While in event of *E.coli*, methane sulfonate, tetrafluoroborate and acetate containing ionic liquid showed good antibacterial activity.

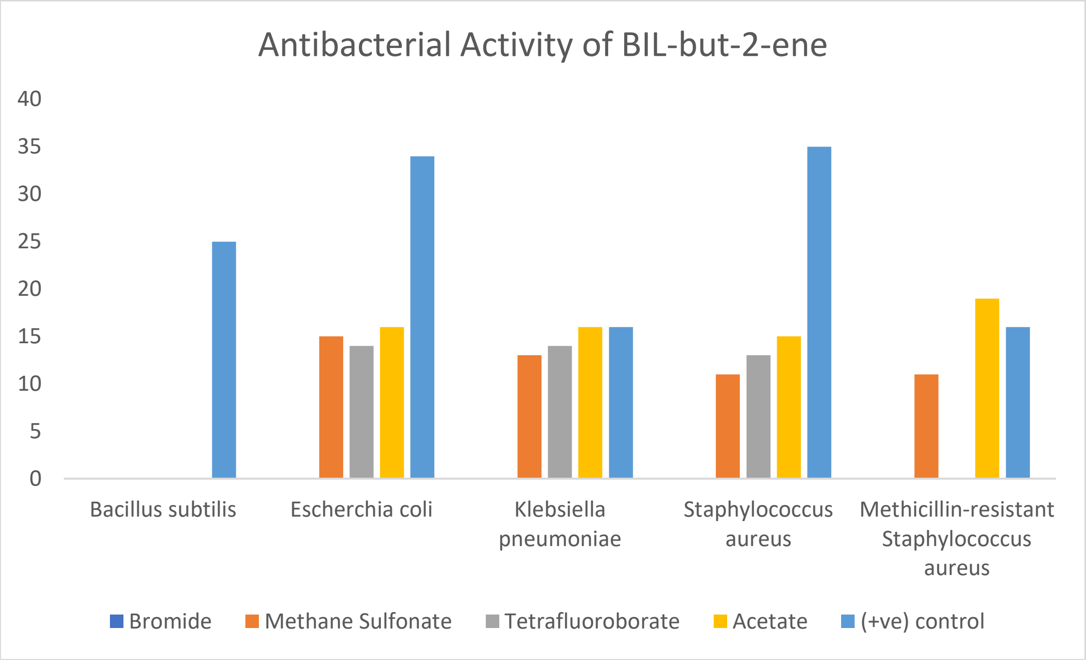


Figure 4.4.3 Graphical Representation of Zone of Inhibition

A graphical representation of different ionic liquids against five types of bacteria has shown below. Di-cationic Ionic liquid with but-2-ene as linker with their counter ion hexafluorophosphate, dichloroacetate, bisulphate and bis(trifluoromethanesufonyl) imide. In the case of *B.subtilis*, ionic liquid with bisulphate showed excellent antibacterial activity even more than the control group which is 3rd generation antibiotic. While in case of *E.coli* bisulphate containing ionic liquid exhibited a good antibacterial activity. A good antibacterial activity was exhibited, in the event of *S. aureus*, dichloroacetate and hexafluorophosphate counter-ions. In case of *K. pnuemoniae* only bisulphate anion gives good results and in Methicillin resistant *S.aureus* all anions showed good anti-bacterial activities except Ntf$_2$ and better activity was shown by dichloroacetate.

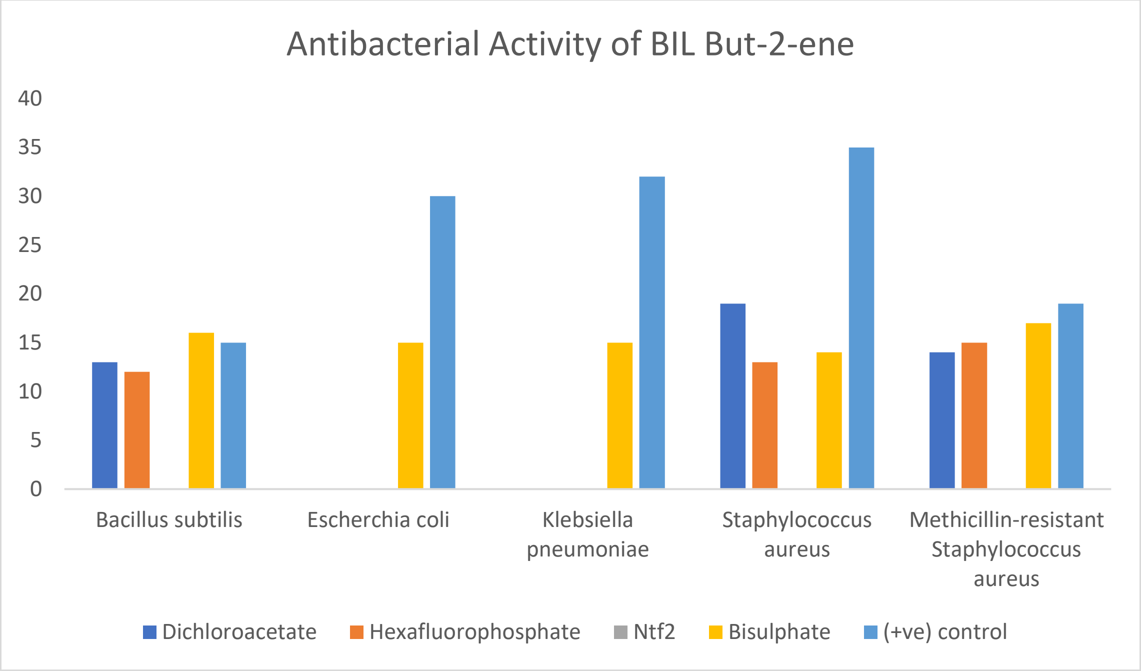
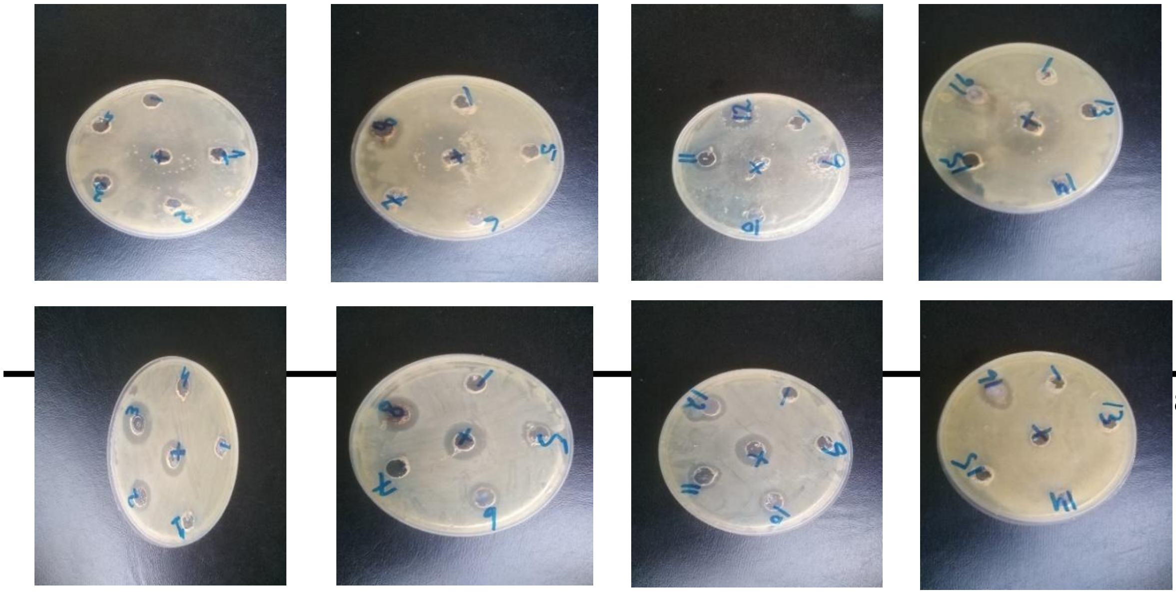


Figure 4.4.3 Graphical Representation of Zone of Inhibition

4.4.4. Pictorial representation of Zone of Inhibitions



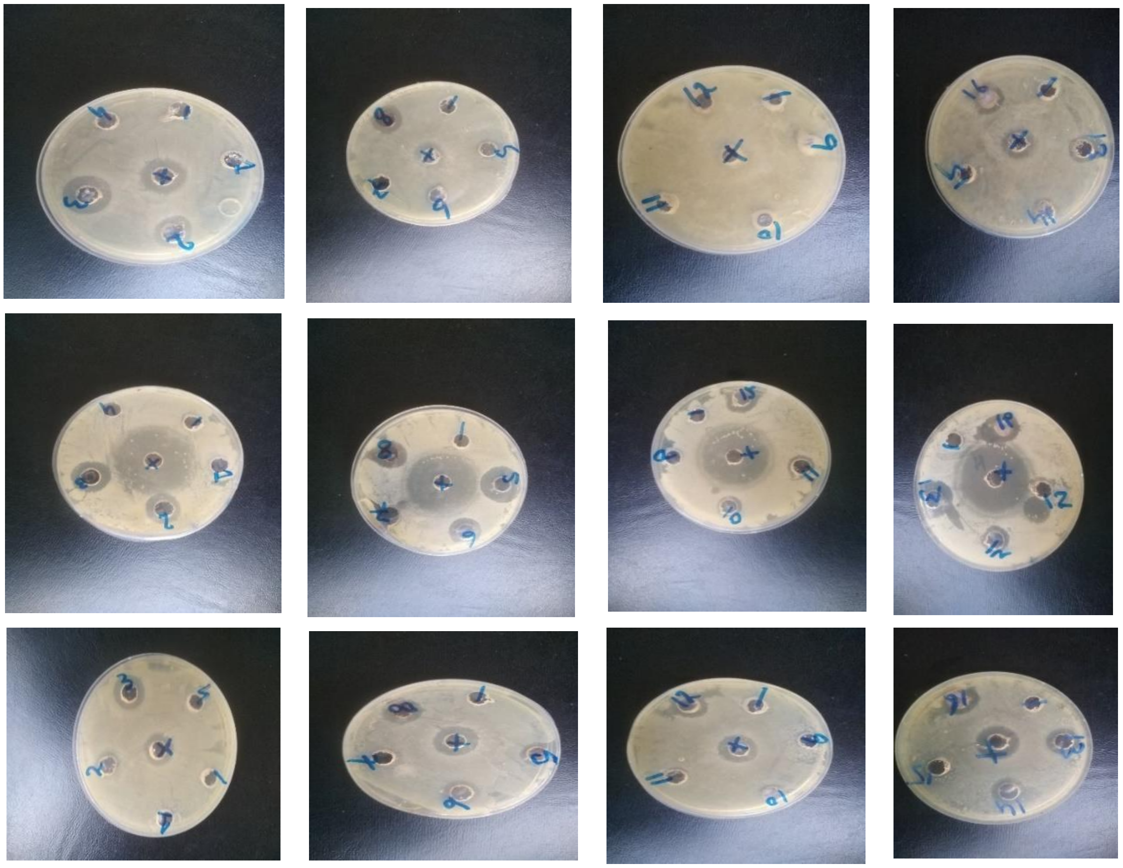


Figure 4.4.4 The pictorial Representation of Zone of Inhibition

CONCLUSION

The effective synthesis of imidazolium-based di-cationic ionic liquids resulted in the synthesis of a diverse set of 16 distinct compounds. Bu utilizing, Fourier-transform infrared spectroscopy (FTIR) along with the nuclear magnetic resonance (NMR) analysis, these novel ionic liquids were systematically characterized, providing valuable insights into their molecular structures, and confirming the successful formation of the desired imidazolium-based di-cationic structures. The investigation of these synthesized ionic liquid's antibacterial activity has cast light on their potential as antimicrobial agents. By introducing these substances to antibacterial assays, it was made possible to evaluate their efficacy against a variety of bacterial strains. These results contribute to our understanding of the structure-activity relationship of di-cationic ionic liquids (ILs) that were based on imidazolium and their ability to inhibit bacterial proliferation.

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