공학석사 학위논문

Development of novel ionic liquids with bis(sulfonyl)imide anions functionalized by a carboxymethyl group as electrolyte additives

Carboxymethyl 작용기를 가지는 비대칭 bis(sulfonyl)imide 음이온으로 구성된 새로운 이온성 액체 연구

2022년 2월

서울대학교 대학원
화학생물공학부
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이 논문을 공학석사 학위논문으로 제출함

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Abstract

Development of novel ionic liquids with bis(sulfonyl)imide anions functionalized by a carboxymethyl group as electrolyte additives

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Ionic liquids (ILs) are used in a wide range, and among them, they are spotlighted as next-generation electrolytes in lithium-ion batteries. Due to differentiated characteristics of ILs such as non-flammability, high ion conductivity, the possibility of various combinations, and stability in a wide voltage range, many new studies have been conducted to replace existing conventional electrolytes by using ILs. In this paper, pyridinium, imidazolium-based cation with large planarity, and asymmetric bis(sulfonyl)imide anion were selected to decrease viscosity and increase ionic conductivity, and six types of ILs were synthesized by using them. In the cation synthesis process, the reaction yield was higher than 95%, while it was 54% when the intermediate was formed in the anion synthesis process. And it was 90% or even more in all the remaining steps were obtained. The purity of the synthesized ILs was confirmed by ^{1}H, ^{13}C, ^{19}F-NMR, and elemental analysis.

Viscosity and ion conductivity were measured to investigate the performance of the synthesized ILs as an electrolyte. The viscosity of the pure synthesized ILs was high, and ion conductivity of 1-4 mS/cm was measured. And, to analyze the performance of the ILs as an electrolyte additive, a binary mixture mixed with a carbonate electrolyte (EC/DEC 1:2 mixture), which is widely used as an electrolyte, was prepared. As a result of measuring viscosity and ion conductivity by mixing ILs and carbonate electrolyte in various ratios, the viscosity became very low as the ratio of the ionic liquid decreased, and the ion conductivity tended to increase when the ratio of the ionic liquid decreased. Among the mixtures, the 20:80 binary mixture of C1A1-Ester and EMIMA1-Ester showed high ionic conductivity of 9.11 mS/cm and 9.03 mS/cm. The results of these studies have shown that the ILs synthesized in this paper have the potential to have a high effect when used as a battery electrolyte additive.

keywords : Ionic liquids, Unsymmetrical anion, Pyridinium based cation, Imidazolium based cation, electrolyte additive

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List of Abbreviations

δ	Chemical shift
D	Doublet
DEC	Diethyl carbonate
EC	Ethylene carbonate
h	hour(s)
IL	Ionic liquid
IPA	Isopropyl alcohol
J	Coupling constant(s)
m	Multiplet
Quant.	Quantitative
RT	Room temperature
RTIL	Room temperature ionic liquid
s	Singlet
t	Triplet

1. Introduction

1.1 Introduction of Ionic liquids

Ionic liquids (ILs) are materials that are composed of cations and anions and are referred to as molten salt. Unlike the characteristics of conventional salts, they exist as liquids at temperatures below 100 ˚C. Among them, some ILs exist in liquid form at room temperature so they are called ‘Room temperature ionic liquids’, RTILs. Most of the substances that we call ionic liquids are RTILs. These ILs have unique properties, and many types of research have been conducted for a long time.

Here are some of the major studies. First, there was Walden's ethylammonium nitrate([ETNH$_3$][NO$_3$]) discovery that reported the first RTIL. It was reported in 1914 and was a protic ionic liquid with a melting point of 12 ˚C.[1] This protic ionic liquid is made of a combination of Bronsted acid and Bronsted base, and [ETNH$_3$][NO$_3$] shows that it has similar properties to water.[2] In the 1950s, RTILs such as 1-ethylpyridinium bromide-aluminium chloride 2:1 M ratio mixture were synthesized using alkyl pyridinium and metal halide. These ILs have shown the possibility that they can be electrochemically analyzed and used.[3] In 1980s, research on ILs began to be more active. In particular, there were many studies on the heterocyclic ring structure using imidazole and pyridinium cations.

Among them, Wilkes reported in 1982, 1-alkyl-3-methylimidazolium salt, which can be seen as the first-generation tetracloroaluminates.[4(a)] However, it had the disadvantage of reacting with water, so it was difficult to use in the reaction. Thus, in 1992, to improve this, the anion was changed to tetrafluoroborate anion, and second-generation ionic liquid stable in water was synthesized and thus, it was used in many organic synthesis reactions.[4(b)] Afterward, anions such as hexafluorophosphate and bis(trifluoromethylsulfonyl)imide were combined with several cations such as phosphonium and imidazolium, and the third-generation ionic liquid called task specific ionic liquid was synthesized.[4(c)]

ILs vary in many properties depending on the type of cation and anion. Cations have acyclic forms such as phosphonium and ammonium, and cyclic forms such as imidazole and pyridinium. At this time, imidazole which is a cyclic form and has a nitrogen atom was studied a lot. It has a small and flat structure, so it has low viscosity and high ion conductivity. The anions include halides, sulfate, and fluorinated anions, and the forms of fluorinated anions have been studied a lot. One of studies have shown that substituted fluorine has higher ion conductivity and higher thermal stability than when not substituted.[5]

The advantage of being able to combine cations and anions allowed us to design several new combinations of ILs. In addition, more combinations were made possible by changing the structure of cations and anions. Depending on these properties, ILs were also called designer solvents. And ILs are in the spotlight due to their unique characteristics such as high ion conductivity, negligible vapor pressure, heat and chemical stability, and wide electrochemical stability. Because of these characteristics, it is used as a solvent, catalyst in an organic synthesis reaction, lubricants, battery electrolyte, etc.

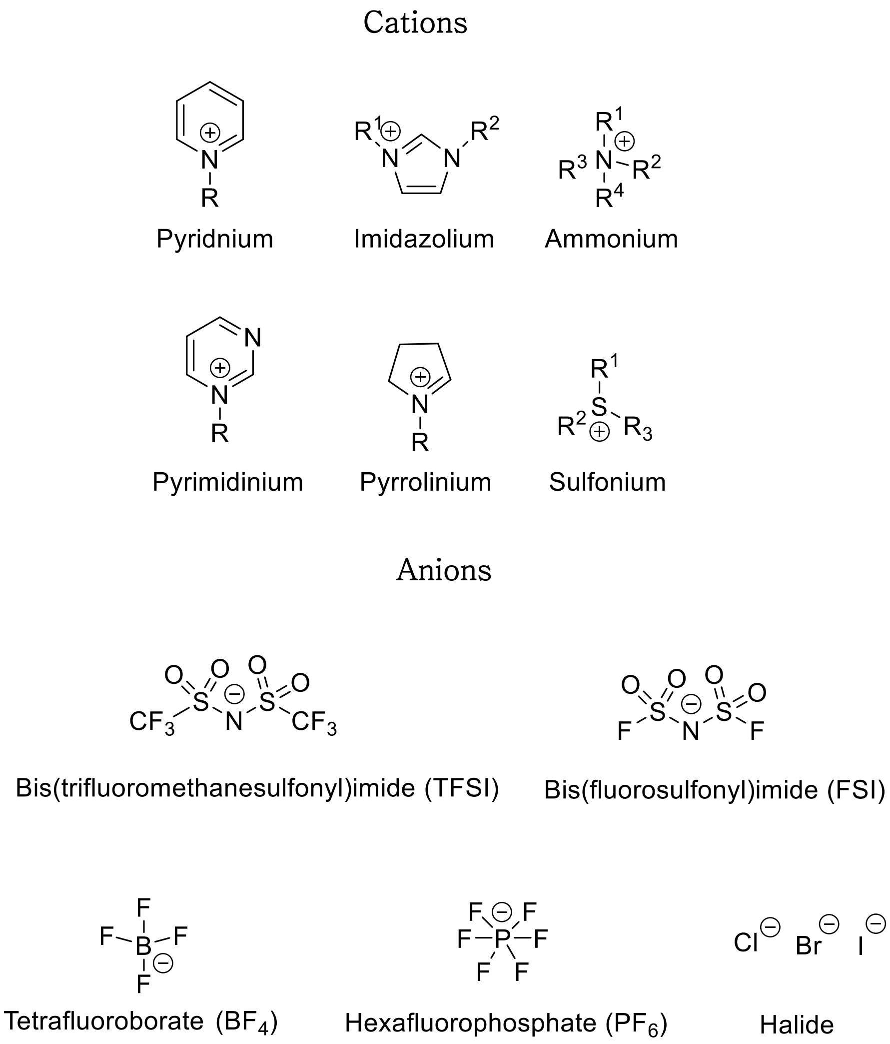


Figure.1 Various species of cations and anions of ionic liquids

1.2 Application of Ionic liquids

1.2.1 Solvents in organic synthesis

As mentioned earlier, ionic liquids have unique physicochemical properties. So, they have been applied in many fields. Among them, they are sometimes used as a solvent in organic synthesis reactions in that it has a wide solubility range.

Table 1. Unique properties of ionic liquids[6]

Properties	Values
Melting point	Preferably below 100 ˚C
Liquidus range	Often > 200 ˚C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied < 30
Polarity	Moderate
Ionic conductivity	Usually < 10 mS/cm
Molar conductivity	< 10 Scm^2/mol
Electrochemical window	Often > 4 V

Vapor pressure	Usually negligible

1.2.1.1 Wittig reaction

First, there is a Wittig reaction. Wittig reaction is one of the important reactions in organic synthesis. It is the most commonly used reaction to convert aldehyde or ketone into alkenes and is often used to introduce methylene groups. At this time, the problem was to separate the by-product Ph_3PO, which was solved by using an ionic liquid. There was a method using 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) as a solvent at the Wittig reaction. According to the research results of one paper, when [BMIM][BF_4] was used, almost no Ph_3PO remained after the Wittig reaction. In addition, it showed that the solvent can be reused and that the stereoselectivity for E form was very high. Through this, an efficient result was obtained when an ionic liquid was used as a solvent in a Wittig reaction. (Figure 2).[7]

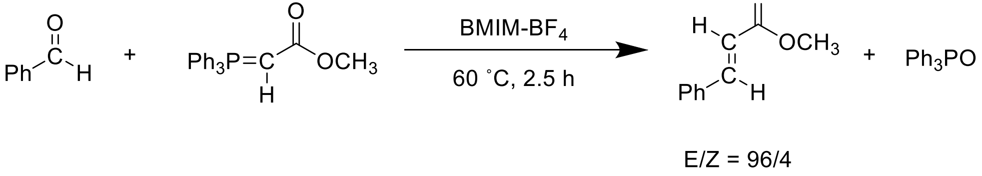


Figure 2. Wittig reaction using BMIM-BF_4

1.2.1.2 Heck reaction

Using ionic liquids for the Heck reaction can have a good effect. Heck reaction is a reaction that produces substituted alkene by reaction between a halogenated aryl or vinyl group and alkene under palladium catalysts and is a representative C-C binding reaction. This reaction also showed good results when using ionic liquids. An ionic liquid such as $[BMIM][PF_6]$, $[C_6py][BF_4]$, and $[C_6py]Cl$ may be used, and if a reaction is performed with an appropriate additive, a high yield of 90% or more may be obtained in some cases. Among them, when proceeding with $[BMIM][PF_6]$, the palladium catalyst could be selectively dissolved compared to water or other alkane solvents, and the results showed that the catalyst could be recycled (Figure 3).[8]

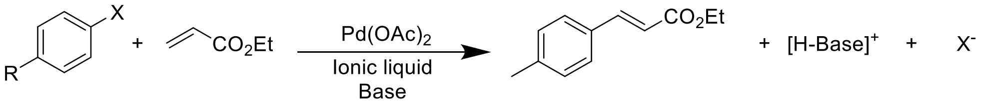


Figure 3. Representative Heck reaction using ionic liquid

1.2.1.3 Suzuki coupling

Next, there is a Suzuki coupling reaction. Suzuki coupling is a reaction in which a nucleophile such as a base reacts under a palladium catalyst with a reactant to obtain an asymmetric biaryl material. In this reaction, there are several problems such as catalytic decomposition and poor reagent dissolution. To solve this problem, a material such as 1-butyl-3-methylimidazolium tetrafluoroborate([BMIM][BF_4]) was used as a solvent, and problems such as catalytic decomposition could be solved while obtaining a high yield in a short time. As a result of reacting bromobenzene and phenylboronic acid under catalyst and [BMIM][BF_4] conditions, a yield of 93% could be obtained in 10 minutes, and in a reaction producing 4-methoxybiphenyl, a reaction of more than 200 times than the original reaction could be obtained in 10 minutes. In addition, the reaction proceeded without catalyst loss.[9,10]

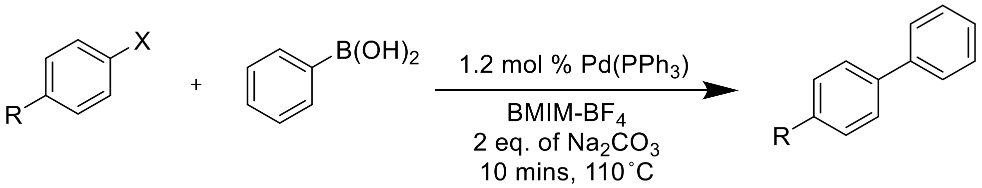


Figure 4. Suzuki coupling using BMIM-BF_4[10]

1.2.2 Lubricants

Lubricants are liquid materials used to reduce the frictional force generated on the friction surface or disperse the frictional heat generated, so it should have high proper viscosity and stability against heat and oxidation. Ionic liquids have characteristics such as low volatility, non-flammability, and high thermal stability, so these advantages are applied to lubricants to show good performance. The ionic liquid is formed of asymmetric ions which are easily adsorbed on the surface of a metal to form a thin protective film, thereby lowering friction and wear, and being used as an additive included in a non-polar base oil. Especially when composed of fluorine, phosphorus, and boron atoms, they help to form tribofilm. Among them, it was found that Imidazolium and ammonium ILs have higher stability than conventional synthetic oils at 200 ℃ or higher. When several ILs were used, friction and wear were lower than using the conventional synthetic oils. In addition, studies were showing that friction and wear change depending on the properties of the anion, and that the longer the length of the alkyl chain of the cation, the lower the amount of wear. In this way, it is expected that the optimized combination of cations and anions of ILs will further improve performance. Using the unique characteristics of ILs and the ability to combine various cations and anions, the scope of application has been expanded to lubricants.[11]

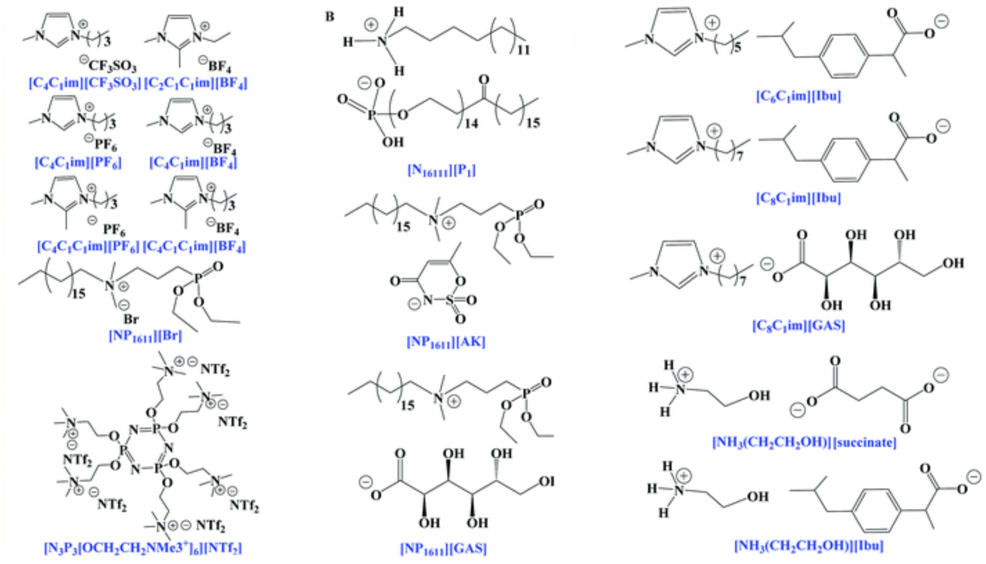


Figure 5. Lubricants with ionic liquid additives[12]

1.2.3 Electrolyte or additive for electrochemical devices

Ionic liquids have been studied as battery electrolytes for a long time. Since they have characteristics such as a wide electrochemical window, high ion conductivity, and a wide liquid ion range, the electrolyte itself or as an additive was being studied. Among them, they have been studied a lot as an electrolyte and additive for lithium-ion batteries. Lithium-ion batteries have been developed most recently among currently used batteries, and their performance has been developed rapidly. A commercial electrolyte is used by adding a lithium salt to an organic solvent such as ethylene carbonate or dimethyl carbonate, but safety problems such as explosion often occur due to volatility and flammability. In addition, electrolytes are depleted due to the volatilization of organic solvents, resulting in performance degradation. The ILs have non-flammable and non-explosive properties capable of solving such problems and have suitable ion conductivity, thus may be the suitable materials for use as an electrolyte and an additive of a lithium-ion battery. Among them, when fluorine-based anions such as FSI and TFSI are used, high ion conductivity is shown.[13]

Also, to be used as an electrolyte for a battery, it must have a wide electrochemical window, and the ILs satisfy these conditions. It has a value of about 1.23 V in a generally aqueous solution, and an organic solvent such as propylene carbonate used as a conventional electrolyte has a value of about 4 V. The electrochemical window value varies depending on the material of the cation and anion of the ILs and is more electrochemically stable when a heterocyclic cation and a fluorine-based anion are used. For example, in the case of N-butyl-N methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([BMPyr][TFSI]), it has a value of 6 V, and [EMIM][BF_4] and [EMIM][TFSI] have a value of 4.5 V. In addition, most ILs showed high levels of electrochemical window values. Furthermore, the use of quaternary ammonium-based room temperature ionic liquids showed significant electrical stability, and the 6-atomic ring [PP_{13}][TFSI] showed significantly higher coulombic efficiency and wide electrochemical window values.

Due to the above characteristics, many studies have been conducted to use ILs as electrolytes and additives for lithium-ion batteries.[14]

Table 2. Electrochemical windows of Ionic liquids on a platinum electrode at 295 K[15]

Ionic liquid	Electrochemical window (V) 1 mA/cm^2
[$P_{14,6,6,6}$][TFSI]	5.4
[C_4C_1pyrrol][TFSI]	4.2
[C_6mim][FAP]	4.6
[C_4mim][TFSI]	4.3
[C_4mim][TFSI]]	4.7
[N_{6222}][TFSI]	4.7
[C_4mim][PF_6]	4.8
[C_2mim][TFSI]	4.2
[C_4mim][BF_4]	4.6
[C_4mim][I]	2.0
[C_4mim][OTf]	4.2
[C_6mim][Cl]	3.0

2. Results and discussion

2.1 Design of the target ILs

When using an ionic liquid as an electrolyte, there is a disadvantage in that the viscosity is high and the ion conductivity is relatively low. Therefore, this paper aims to lower the viscosity of the generated ionic liquids and increase the ion conductivity. To lower viscosity and increase ion conductivity, we tried to use more planar or smaller material for cations. Therefore, we selected a structure that an alkyl group is substituted, which based on the more planar pyridinium cation and smaller imidazolium cation. As the alkyl group was substituted, the acid proton was removed, and the stability of the produced IL was increased. The pyridinium-based cation was substituted with an alkyl group with double bonds not to become too bulky. As anions, asymmetric fluorine-based anions, not symmetrical fluorine-based anions, which are commonly used, were newly synthesized and used. It was thought that the asymmetry of anions would affect ion conductivity and viscosity.

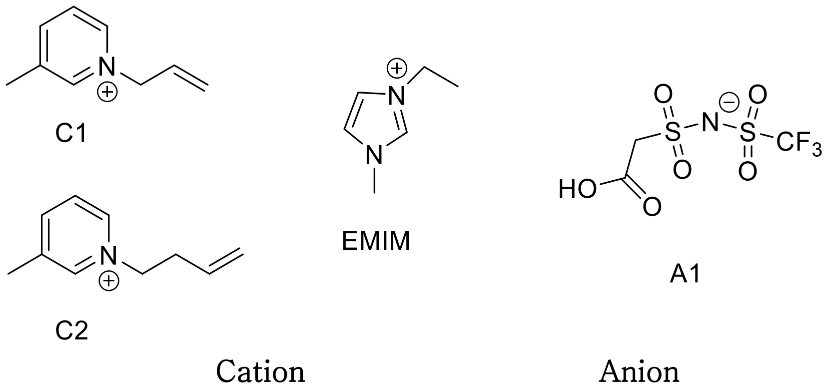


Figure 6. Cationic and anionic counterparts of the designed ILs

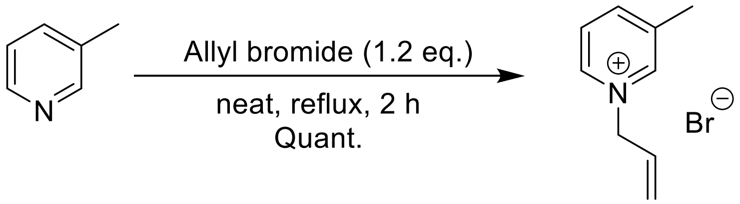
2.2 Synthesis of Cations

2.2.1 Synthesis of pyridinium-based cations

The structures of 1-allyl-3-methylpyridinium bromide (C1-Br) and 1-(3-butenyl)-3-methylpyridinium bromide (C2-Br), which are 3-methylpyridinium-based cations to be synthesized, differ only in the number of carbons in the 1-alkyl-3-methylpyridinium structure. Therefore, 3-methylpyridine is used as the reactant for both reactions. Both reactions are S_N2 reactions, and the reaction easily occurs with nitrogen's nucleophilic attack.

First, looking into the synthesis process of C1-Br, 3-methylpyridine and allyl bromide was reacted for 2 hours under a temperature condition of 75 ˚C. At this time, reflux proceeds in the neat without the solvent. When the synthesized material was confirmed by ^{1}H-NMR, some impurities and residues remained, and washing was performed three times using diethyl ether and ethyl acetate respectively. Afterward, as a result of checking with ^{1}H-NMR and ^{13}C-NMR, residues and impurities disappeared, and a light brown solid form of C1-Br was obtained at a quantitative yield.

Second, the synthesis process of C2-Br is similar to the synthesis process of C1-Br but has slightly different conditions. Using the condition of 75 ˚C for 2 hours, as in the synthesis process of C1-Br, the reaction was not finished and a lot of residues remained. So, the temperature was raised to 100 ˚C and the reaction time was increased to 3 hours. When this reaction was also confirmed by ^{1}H-NMR, impurities and residues were present, and the washing process was performed as described above. As a result, C2-Br in the form of dark brown oil with high purity quantitative yield was obtained.



C1-Br

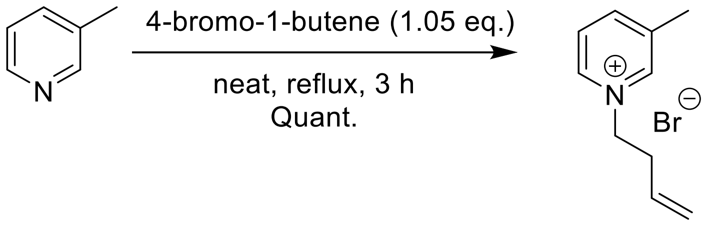


Figure 7. Synthesis of C1-Br and C2-Br

2.2.2 Synthesis of imidazole-based cation

Looking into the structure of the 1-ethyl-3-methyl imidazolium bromide (EMIM-Br) to be synthesized, it is a form in which an ethyl group is substituted in the structure of 1-methylimidazole. Thus, the process of reacting 1-bromoethane to 1-methylimidazole was performed. The S_N2 reaction occurs with the nucleophilic attack of nitrogen in the imidazole ring. After quantifying the two reactants, reacted for about 24 hours under a temperature condition of 40 ˚C. Reflux condition should be maintained, and acetonitrile was used as a solvent. After the reaction was completed, the solvent was evaporated, and washing was performed three times with diethyl ether. In the process of washing, it was gradually turning into a white solid. After that, washing was performed five times with ethyl acetate to remove residues and impurities. As a result of confirming the obtained material with ^{1}H-NMR and ^{13}C-NMR, no impurities and residues remained, and a white solid was obtained at a quantitative yield.

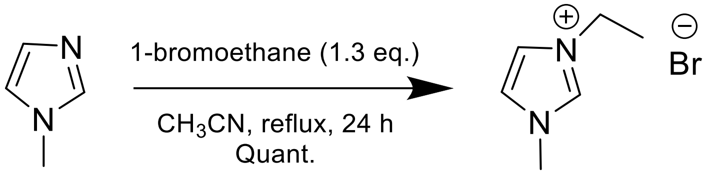


Figure 8. Synthesis of EMIM-Br

2.2.3 Synthesis of the unsymmetrical bis(sulfonyl) - imide anion

Two steps are taken to synthesize asymmetric bis(sulfonyl)imide anion (A1), the anionic portion of an ionic liquid. The Sulfonyl chloride group was first introduced by reacting oxidative chlorination to the thiol group. The resulting product can then be reacted with trifluorosulfonamide and NaH to form A1 in the form of Sodium salt, in which amine acts as a nucleophile. The reaction scheme is as follows. The first step is to add two equivalent amounts of SO_2Cl_2, $NaNO_3$ to methyl thioglycolate, respectively. There are other methods using water, chlorine, and dichloromethane.[16] This method has a high yield and can end the reaction in a shorter time without adding many reactants. However, the product is very sensitive to water, so the resulting sulfonyl chloride group can be hydrolyzed quickly with sulfonic acid, which does not meet our experimental conditions. Therefore, we proceeded by using SO_2Cl_2 and $NaNO_3$. Many by-products occurred when the reaction was carried out at room temperature and 0 °C. When the reaction was carried out at −78 °C for 24 hours using an acetone bath with dry ice, $NaNO_3$ hardened too much and the reaction yield was slightly lower. Therefore, the reaction continued at −78 °C for 7 hours and then at room temperature for the rest of the time. As a result, we were able to obtain a quantitative yield crude product with very few by-products and impurities. Finally, distillation was performed to remove some of the remaining impurities and by-products, and almost pure products were obtained.

The next step is to form a salt with metal ions. To make Li-A1, Na-A1, we conducted experiments using $LIOH-H_2O$ and NaH. At first, the reaction was carried out using $LiOH-H_2O$, the process of separating the generated product was easier, but the yield was very low due to by-product generation. In addition, experiments were conducted with molecular sieves to absorb water, so there was a loss in the filtering process. After that, the reaction was carried out using NaH instead of $LiOH-H_2O$. Although the washing process was more complicated, a higher yield could be obtained than when $LiOH-H_2O$ was used. As solvents, acetonitrile and tetrahydrofuran were used, but good results were obtained when tetrahydrofuran was used at 80 °C. It's not a very high yield, but when NaH was used in tetrahydrofuran solvent, a white solid was obtained at 54% yield.

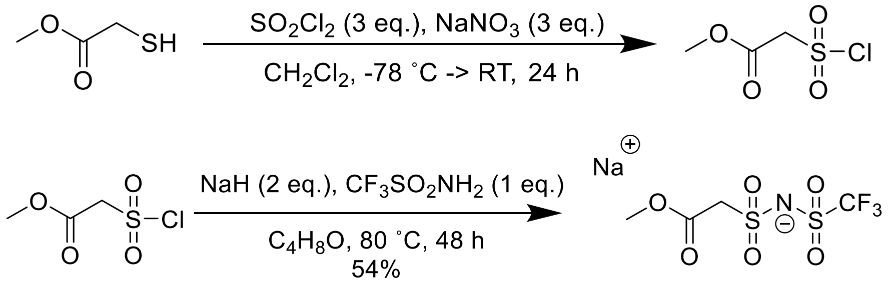
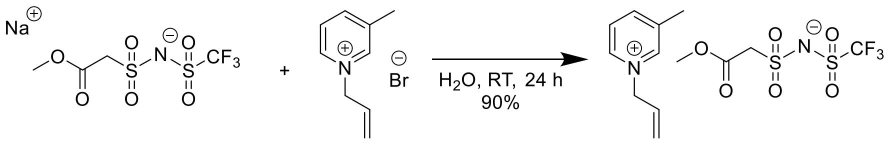


Figure 9. Synthesis of Na-A1

2.2.4 Synthesis of the target ILs

The target ionic liquids were easily synthesized by the ionic exchange process of C1-Br, C2-Br, EMIM-Br, and Na-A1. Water was used as a solvent and the reaction was carried out at room temperature for 24 hours. After that, the product was obtained through the extraction process with dichloromethane. The solubility of the product is higher in dichloromethane than in water, so it can be easily separated. In this process, 48 h reaction was initially carried out, but hydrolysis occurred. So, reducing the time to 24 h, products could be obtained with high purity and yield.



C1-Br

C1A1-Ester

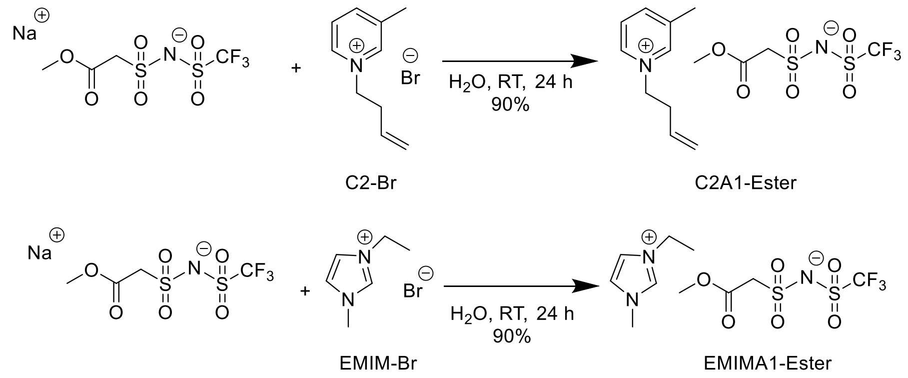
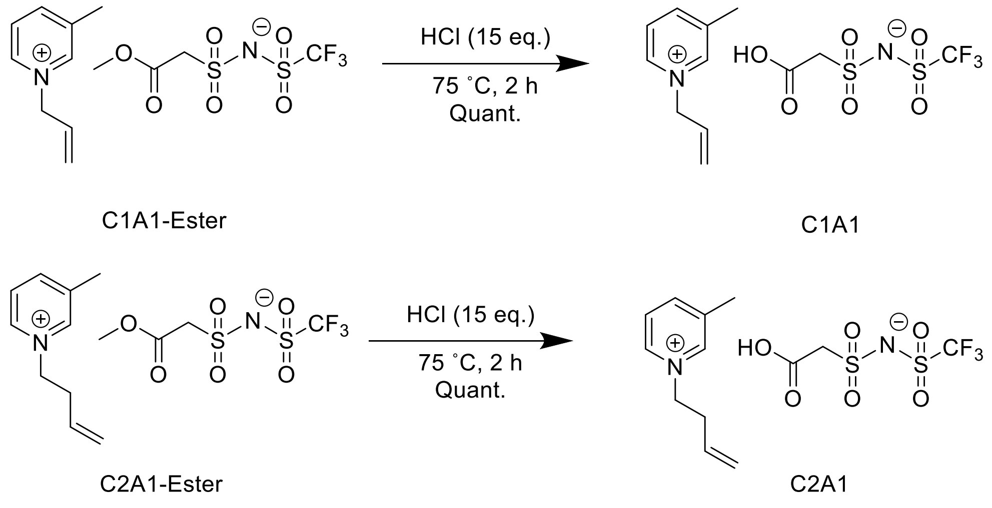


Figure 10. Synthesis of C1A1-Ester, C2A1-Ester and EMIMA1-Ester

After that, the hydrolysis reaction was conducted on the ester form. The reaction was carried out with an excess of 1 N HCl, and it was obtained with a high yield in a short time.



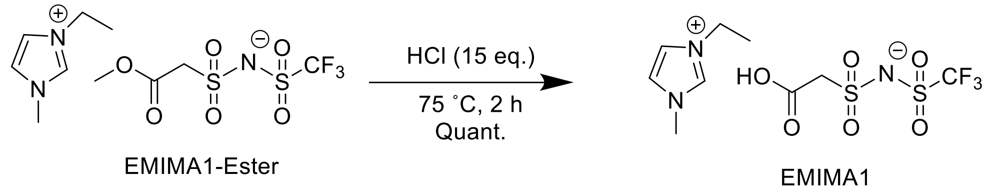


Figure 11. Synthesis of C1A1, C2A1 and EMIMA1

In this way, six types of ILs, C1A1-Ester, C2A1-ester, EMIMA1-ester, C1A1, C2A1, and EMIMA1 were synthesized. The target ILs were synthesized through a reaction of 4-5 steps and showed a high yield of 90% or more except for the synthesis of Na-A1. The purity of the new synthesized ILs was confirmed through ^{1}H, ^{13}C, ^{19}F-NMR, and elemental analysis.

2.3 Viscosity and ionic conductivity of synthesized ILs

To confirm the performance of the synthesized ionic liquids, viscosity and ionic conductivity were determined. Viscosity was measured at room temperature and ion conductivity was divided into 25, 50, 75, and 100 ˚C. Half-cell was used to measure ion conductivity. (Distance between electrodes (d) = 0.6 cm, width (w) = 0.45 cm, height (h) = 0.3 cm) The ion conductivity was calculated using the following equation.

$$\sigma = \frac{1}{R}\frac{l}{A}$$

σ: Ionic conductivity (S/cm)

l: Distance between electrodes (cm)

A: Area of electrodes (cm^2)

R: Resistance of an electrolyte

Figure 12. Equation of ionic conductivity and resistance

Resistance values were measured through EIS (Electrochemical Impedance Spectroscopy) software and applied at frequencies above 10^5 Hz. At low frequencies, electrons penetrate deep into the electrode space because the direction of the current changes slowly. At this time, the surface of the electrode is a little rough, so the distance between the electrodes is not uniform, so it is impossible to measure the exact value. At high frequencies, the distance between electrodes is uniform by fast current switching. The viscosity values of C1A1 and C2A1 and EMIMA1 cannot be measured by viscometer because of its viscosity exceeding the 1000 cP, and ionic conductivity cannot be measured by half-cell. The results show that viscosity corresponds to molecular weight, C2A1-Ester was the highest, followed by C1A1-Ester and EMIMA1-Ester. The ion conductivity increased as the molecular weight increased, and the value of 1-4 mS/cm was obtained at room temperature. In particular, except for 50 ˚C, ion conductivity tended to increase as the temperature increased. Among them, EMIA1-Ester showed that the ion conductivity increased significantly as the temperature increased at all temperatures. However, due to its high viscosity, it seems that the synthesized ILs alone cannot be used as an electrolyte. Synthesized C1A1, C2A1, and EMIA1 showed very high viscosity. These results were expected because they had high polarity carboxy groups and formed hydrogen bonding with each other.

Table 3. Properties of the synthesized ILs at 25 ˚C

Ionic liquids	Resistance (Ω)	Viscosity (cP)	Ionic conductivity (mS/cm)
C1A1-Ester	1.35×10^3	295	3.29
C2A1-Ester	1.08×10^3	378	4.12
EMIM-Ester	1.47×10^3	185	3.02
C1A1	2.67×10^3		1.67
C2A1	1.36×10^3		3.25
EMIMA1	3.92×10^3		1.13

Table 4. Ion conductivity of C1A1-Ester at various temperature

C1A1-Ester

Temperature (˚C)	Resistance (Ω)	Ionic conductivity (mS/cm)
25	1.35×10^3	3.29

50	1.46 x 10^3	3.04
75	7.26 x 10^2	6.12
100	3.94 x 10^2	11.20

Table 5. Ion conductivity of C2A1-Ester at various temperature

C2A1-Ester

Temperature (˚C)	Resistance (Ω)	Ionic conductivity (mS/cm)
25	1.08 x 10^3	4.12
50	1.15 x 10^3	3.87
75	7.11 x 10^2	6.25
100	3.72 x 10^2	11.94

Table 6. Ion conductivity of EMIMA1-Ester at various temperature

EMIMA1-Ester

Temperature (˚C)	Resistance (Ω)	Ionic conductivity (mS/cm)
25	1.47 x 10^3	3.02
50	6.47 x 10^2	6.87
75	3.10 x 10^2	14.31
100	2.24 x 10^2	19.82

2.4 Viscosity and ionic conductivity of a mixture of carbonate and ILs

To make up for the high viscosity and relatively low ion conductivity values of ionic liquids, they are sometimes mixed with organic solvents and several research data have been reported about this.[17] Therefore, in this paper, viscosity and ion conductivity values of 20:80 (IL:carbonate) to 80:20 (IL:carbonate) in volume ratio were measured using this method. A mixture was made using Ethylene Carbonate (EC)/Diethyl carbonate (DEC) in a ratio of 1:2 [EC/DEC] is also a widely used electrolyte and can be easily obtained at a relatively low price. In addition, it has a short alkyl chain and a carbonyl group, so ILs can be easily dissolved. The measured viscosity, resistance values, and ion conductivity are shown in the table below. All values were measured at room temperature.

Table 7. Viscosity and ionic conductivity of [C1A1-Ester][EC/DEC] mixture

C1A1-Ester

Concentration (IL:Carbonate)	Resistance (Ω)	Viscosity (cP)	Ionic conductivity (mS/cm)
100 : 0	1.35×10^3	295	3.29

80 : 20	1.21 x 10^{3}	37.3	3.66
60 : 40	8.86 x 10^{2}	10.6	5.01
40 : 60	5.72 x 10^{2}	4.98	7.76
20 : 80	4.88 x 10^{2}	2.68	9.11
0 : 100	1.04 x 10^{3}	1.55	4.27

Table 8. Viscosity and ionic conductivity of [C2A1-Ester][EC/DEC] mixture

C2A1-Ester

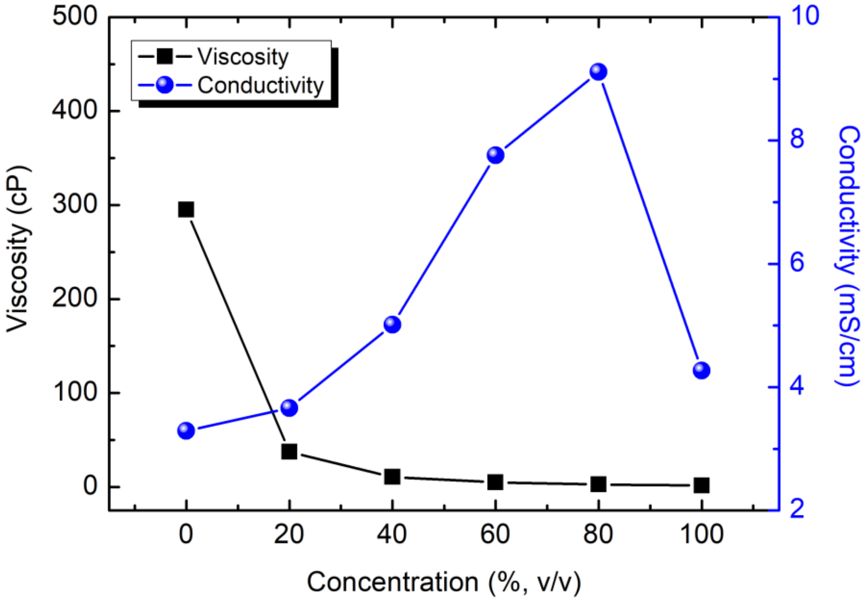
Concentration (IL:Carbonate)	Resistance (Ω)	Viscosity (cP)	Ionic conductivity (mS/cm)
100 : 0	1.08 x 10^{3}	378	4.12
80 : 20	1.35 x 10^{3}	44.2	3.29
60 : 40	1.28 x 10^{3}	13.2	3.46
40 : 60	9.05 x 10^{2}	5.78	4.91
20 : 80	5.62 x 10^{2}	3.14	7.91
0 : 100	1.04 x 10^{3}	1.55	4.27

Table 9. Viscosity and ionic conductivity of [EMIMA1-Ester][EC/DEC] mixture

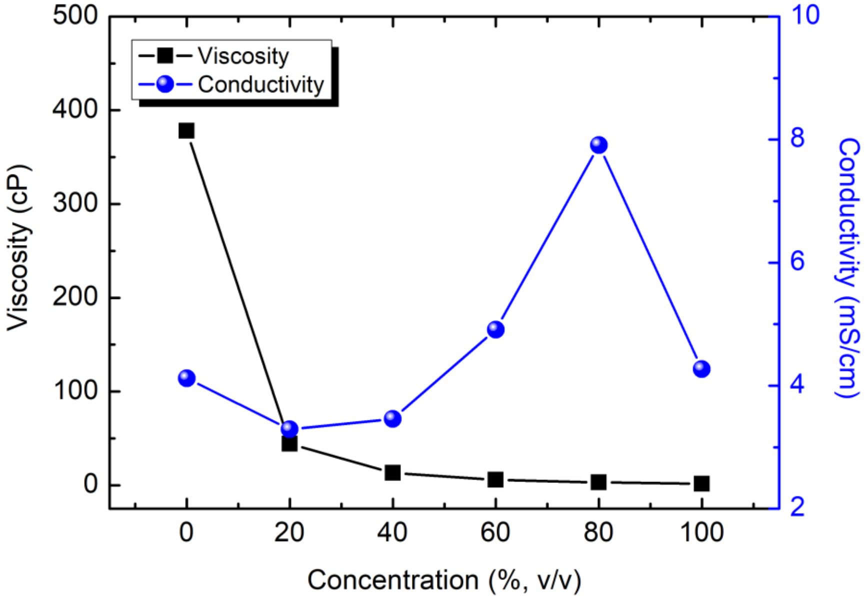
EMIMA1-Ester

Concentration (IL:Carbonate)	Resistance (Ω)	Viscosity (cP)	Ionic conductivity (mS/cm)
100 : 0	1.47×10^3	185	3.02
80 : 20	1.16×10^3	34.5	3.84
60 : 40	8.15×10^2	9.52	5.45
40 : 60	6.45×10^2	4.58	6.89
20 : 80	4.91×10^2	2.58	9.03
0 : 100	1.04×10^3	1.55	4.27

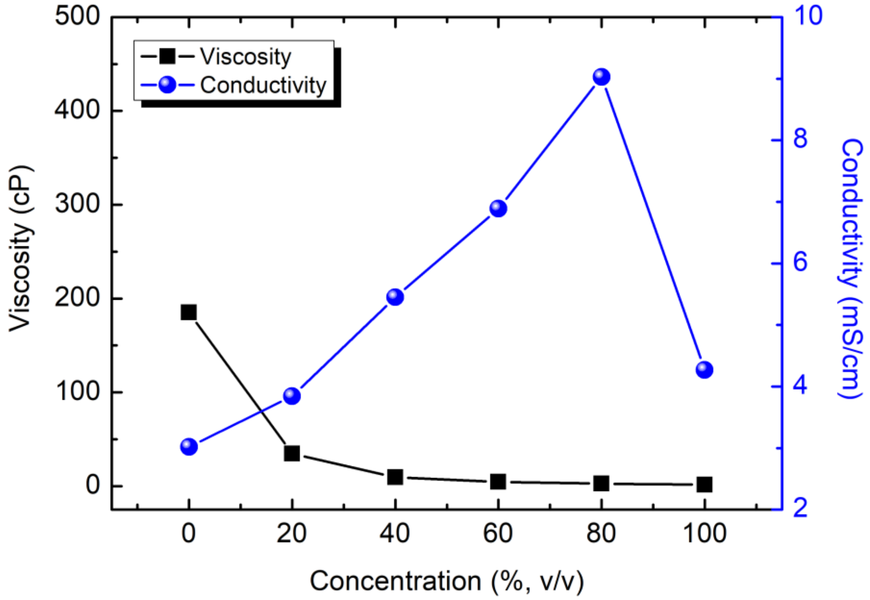
First, when comparing the carbonate mixture of the C1A1-Ester group and the C2A1-Ester group, the C1A1-Ester group has a low viscosity and high ion conductivity overall because of the size of the molecule. Since C2A1-Ester has one more methylene group, the interaction increases to increase the viscosity. EMIMA1-Ester group has ion conductivity similar to that of C1A1-Ester group and shows a slightly lower viscosity value. Considering that the ion conductivity is the highest when having a ratio of 20:80 in the three types of mixtures, it is found that the influence of the carbonate is greater than that of the ILs.



C1A1-Ester



C2A1-Ester



EMIA1-Ester

Figure 13. Ionic conductivity and viscosity of ILs at various concentrations

Viscosity values were measured as available values at the most mixing ratios. The viscosity value and the ion conductivity value are inversely proportional, and a mixture of 20:80 ratios of C1A1-ester and EC/DEC shows the highest ion conductivity. It can be found that the value of 9.11 mS/cm is not very high compared to the ion conductivity of other ionic liquids and carbonate mixtures, but is not low neither. In addition, there were cases where it tripled from the value of pure ionic liquids.

3. Conclusions

Ionic liquids have unique properties and can produce so many combinations. Accordingly, they are being studied for application in various fields, and are now widely used as solvents, lubricants, catalysts, electrolytes, and additives. This paper focused on the synthesis of ILs that can be used as electrolytes and additives.

In the experiment, new ILs were synthesized using two types of methyl pyridinium-based cations, one type of imidazole-based cation, and one type of asymmetric fluorine-based anion. Research on asymmetric fluorine-based anions has not been actively conducted compared to symmetric anions. In the synthesis process, four steps were reacted to ester form and five steps to hydrolysis form, and a yield of 45% was obtained from the total yield. However, all the rest step showed high yields of more than 90%, except that the yield was 54% in the second step during the process of producing metal salts. During the experiment, we tried to derive maximum purity and yield using several techniques such as extraction, distillation, and washing. The synthesized ionic liquids were analyzed through ^{1}H, ^{13}C, ^{19}F-NMR, and elemental analysis. In addition, the viscosity and ion conductivity, which are important parts to be used as electrolytes, were measured using electrochemical analysis methods such as viscometer and EIS software. Looking at the results of the viscosity and ion conductivity of the synthesized pure ILs, the viscosity was measured to be more than 185 cP, and the ion conductivity was 1-4 mS/cm, which was not particularly a good value. However, the higher the temperature, the higher the ion conductivity, especially in EMIMA1-Ester. When mixing with a carbonate electrolyte, the results show that viscosity values are usable in most ratios. Ion conductivity values showed increases in most ratios and one of the values was 9.11 mS/cm at C1A1-Ester 20:80 volume ratio. At certain ratios, the values had more than tripled. In most ratios, viscosity and ion conductivity showed an inversely proportional relationship. This seems to be due to Walden's rules.

From the overall results, pure ILs have high viscosity and are difficult to use as lithium-ion battery electrolytes themselves. However, when forming a mixture with carbonate, the viscosity was measured to low, and in the case of C1A1-Ester and EMIMA1-ester, higher ion conductivity values were measured in some ratios. This showed the possibility that a carbonate binary mixture of ILs could be used as an electrolyte additive for a lithium-ion battery.

References

1. P. Walden, *Bull. Acad. Imper. Sci. St. Petersbourg*, **1914**, 8, 405-422
2. EVANS, D. Fennell, et al. *Journal of Colloid and Interface Science*, **1982**, 88.1: 89-96.
3. HURLEY, Frank H.; WIER JR, Thomas P. *Journal of The Electrochemical Society*, **1951**, 98.5: 203.
4. (a) WILKES, John S., et al. *Inorganic Chemistry*, **1982**, 21.3: 1263-1264, (b) WILKES, John S.; ZAWOROTKO, Michael J. *Journal of the Chemical Society, Chemical Communications*, **1992**, 13: 965-967, (c) H. DAVIS, JR, James. *Chemistry letters*, **2004**, 33.9: 1072-1077.
5. PRINGLE, Jennifer M., et al. *New journal of chemistry*, **2003**, 27.10: 1504-1510.
6. PARK, Jesik, et al. *International journal of molecular sciences*, **2014**, 15.9: 15320-15343.
7. LE BOULAIRE, Virginie; GRÉE, René. *Chemical Communications*, **2000**, 22: 2195-2196.
8. CARMICHAEL, Adrian J., et al. *Organic Letters*, **1999**, 1.7: 997-1000.
9. MCLACHLAN, Fiona, et al. *Organometallics*, **2003**, 22.25: 5350-5357.
10. MATHEWS, Christopher J.; SMITH, Paul J.; WELTON, Thomas. *Chemical Communications*, **2000**, 14: 1249-1250.
11. SOMERS, Anthony E., et al. *Lubricants*, **2013**, 1.1: 3-21.

12. CAI, Meirong, et al. *Chemical Society Reviews*, 2020.

13. MATSUMOTO, Hajime, et al. *Journal of Power Sources*, 2006, 160.2: 1308-1313.

14. SAKAEBE, Hikari; MATSUMOTO, Hajime. *Electrochemistry Communications*, 2003, 5.7: 594-598.

15. O'MAHONY, Aoife M., et al. *Journal of Chemical & Engineering Data*, 2008, 53.12: 2884-2891.

16. NING, Xianling, et al. *Bioorganic & medicinal chemistry*, 2013, 21.17: 5589-5597.

17. LOMBARDO, Lucia, et al. *Journal of Power Sources*, 2013, 227: 8-14.

Experemental Details

1. General Information

Materials were purchased from commercial suppliers and were used without further purifications. Reactions sensitive to air and humidity proceeded in argon and nitrogen environments. All experimental glassware, syringes, and magnetic stirring bars were dried in the oven at 100 ˚C before use.

^{1}H, ^{13}C, and ^{19}F-NMR spectra were measured using Bruker Advance Ⅲ spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C-NMR), $CDCl_3$ and DMSO-d_6 were used as solvents. ^{1}H-NMR spectroscopic data were reported in ppm units at internal standard value (TMS, 0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration). In ^{13}C-NMR, the reference value of 77.16 when the solvent was $CDCl_3$ and 39.52 when DMSO-d_6 was used.

The viscosity was measured at room temperature using Brookfield DC-Ⅱ+cone/plate viscometer. Resistance values were measured to calculate ion conductivity. Electrochemical Impedance Spectroscopy of THALES software was used to measure resistance at high frequencies of more than 10^5 Hz. Elemental analysis used the Flash2000 (Thermo Fisher Scientific, Germany) model and conducted CHNS analysis.

2. General synthetic procedure for the asymmetric bis(sulfonyl)imide-based ionic liquids

2.1 General synthetic procedure for the 1-allyl-3-methylpyridinium bromide

Quantified 3-methylpyridine (17.4 mmol) and allyl bromide (19.1 mmol, 1.1 equiv.) were added in a 100 mL RB flask at room temperature. The reaction mixture was stirred for 2 hours in reflux condition, and the temperature was maintained at 75 ℃. After completion of the reaction, the resulting solution was washed with 30 mL of diethyl ether and ethyl acetate three times, respectively, to purify the remaining residues and impurities. After washing, the solution precipitated as a solid, and the remaining solvent in the produced material was evaporated by a low-pressure rotary evaporator resulted in light brown 1-allyl-3-methylpyridinium bromide.

1-allyl-3-methylpyridinium bromide

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 2.50 (s, 3H), 5.21 (d, J = 6, 2H), 5.43 (m, J = 1.1, 2H), 6.16 (m, 1H), 8.08 (q, J = 6.3, 1H), 8.48 (d, J = 7.9, 1H), 8.87 (d, J = 6, 1H), 8.96 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

δ 17.8, 61.9, 121.9, 127.4, 131.6. 138.7, 141.9, 144.2, 146.1

2.2 General synthetic procedure for the 1-(3-butenyl)-3-methylpyridinium bromide

Quantified 3-methylpyridine (17.4 mmol) and 4-bromo-1-butene bromide (19.1 mmol, 1.1 equiv.) were added in a 100 mL RB flask. The reaction mixture was stirred for 3 hours in reflux condition, and the temperature was maintained at 100 ℃. After completion of the reaction, the resulting solution was washed by 30 mL of diethyl ether and ethyl acetate three times, respectively, to remove the remaining unreacted starting material and impurities. After washing, the solution was synthesized into a very sticky liquid, and the remaining solvent was evaporated using a low-pressure rotary evaporator to obtain 1-(3-butenyl)-3-methylpyridinium bromide in brown oil form.

1-(3-butenyl)-3- methylpyridinium bromide

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 2.50 (s, 3H), 2.70 (q, J = 7, 2H), 4.63 (t, J = 7, 2H), 5.02 (m, 2H), 5.80 (m, 1H), 8.05 (q, J = 6.2, 1H), 8.45 (d, J = 8, 1H), 8.98 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

δ 17.8, 34.5, 59.5, 118.8, 127.0, 132.9, 138.5, 141.9, 144.2, 145.8

2.3 General synthetic procedure for the 1-ethyl-3-methyl imidazole bromide

Quantified 1-methylimidazole (37.6 mmol) and 1-bromoethane (48.9 mmol, 1.3 equiv.) as reactants and acetonitrile (CH_3CN, 20 mL) as a solvent were added in a 100 mL RB flask. The reaction proceeds for 24 hours in reflux condition, and the temperature was maintained at 40 ˚C. After the reaction was over, the solvent used in the reaction was evaporated using a low-pressure rotary evaporator. After that, washing was performed three times with diethyl ether, and the material produced in this process gradually turns into a white solid. Wash three more times with ethyl acetate to remove the remaining reactants and impurities. Evaporate the remaining washing solution using the rotary to obtain 1-methyl-3-ethyl imidazole bromide, a white solid.

1-ethyl-3-methyl imidazole bromide

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 1.43 (t, J = 7.28, 3H), 3.84 (s, 3H), 4.21 (q, J = 7.32, 2H), 7.70 (s, 1H), 7.79 (s, 1H), 9.12 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

δ 15.1, 35.7, 44.1, 121.9, 123.5, 136.2

2.4 General synthetic procedure for the methyl 2-(chlorosulfonyl)acetate

To a dichloromethane (CH_2Cl_2, 20 mL) solution of sodium nitrate (33.6 mmol, 3.0 equiv.) in a 100 mL RB flask was added sulfuryl chloride (33.6 mmol, 3.0 equiv.) at room temperature. After the reaction mixture was stirred at −78 ˚C for 30 minutes, methyl thioglycolate (11.2 mmol) was added to the reaction mixture. For the first 7 hours of the reaction, using an ice bath containing dry ice in acetone to maintain −78 ˚C. Next 17 hours, the reaction was conducted at room temperature. After the reaction was completed, filter out the remaining sodium nitrate of the resulting solution. To remove the residual reactants and solvents of the filtrate, evaporate using a low-pressure rotary evaporator. Finally, to remove impurities, distillation was performed at 80 ˚C to obtain light yellow transparent liquid methyl 2- (chlorosulfonyl)acetate.

Methyl 2-(chlorosulfonyl)acetate

^{1}H NMR (400 MHz)_$CDCl_3$: δ 3.90 (s, 3H), 4.61 (s, 2H)

^{13}C NMR (100 MHz)_$CDCl_3$:

δ 54.1, 67.1, 44.1, 160.7

2.5 General synthetic procedure for the sodium ((2-methoxy-2-oxoethyl)sulfonyl)(trifluoromethyl)sulfonyl)amide (Na-A1)

Quantified trifluoromethanesulfonamide (9.03 mmol, 1 equiv) and 60% sodium hydroxide (18.06 mmol, 2 equiv) were added in 100 mL RB flask and added Tetrahydrofuran (C_4H_8O, 15 mL) immediately. After stirring at room temperature for about 1 hour, added methyl 2-(chlorosulfonyl)acetate (9.03 mmol, 1 equiv.). The reaction mixture was stirred for 48 hours with reflux condition, and the temperature was maintained at 80 ˚C. After the reaction was completed, all remaining solvent was evaporated using a low-pressure rotary evaporator. Afterward, Isopropyl alcohol is added, and the substance soluble in isopropyl alcohol was separated from the generated product. Use decantation to separate Isopropyl alcohol and dissolved substances from the product. Repeat this process several times to dissolve as much soluble product as possible. Next, evaporating the separated isopropyl alcohol resulted in a light-yellow solid. To remove the by-products dissolved in the product, the dichloromethane was added, and the washing process was performed three times. And, to remove the remaining washing solution and impurities, evaporation was performed using a low-pressure rotary evaporator to obtain NaA1 in a solid-state.

Sodium ((2-methoxy–2-oxoethyl)sulfonyl)(trifluoromethyl) sulfonyl)amide(Na-A1)

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 3.64 (s, 3H), 4.05 (s, 2H)

2.6 General synthetic procedure for the 1-alkyl-3- methylpyridinium ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl)sulfonyl)amide(C1A1-Ester, C2A1-Ester)

To a aqueous solution (15 mL) of sodium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide (1.0 mmol, 1.0 equiv.) in a 100 mL RB flask was added 1-alkyl-3-methylpyridinium bromide (1.0 mmol) at room temperature. The reaction mixture was stirred at room temperature, in a nitrogen atmosphere for 24 hours. After the reaction was completed, the resulting product was obtained through extraction with dichloromethane. Afterward, the washed organic layers were dried over MgSO4, filtered, and concentrated under reduced pressure to give a colorless oil of 1-alkyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide.

(Alkyl = allyl and 3-butenyl)

1-allyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide(C1A1-Ester)

^{1}H NMR (400 MHz)_DMSO-*d*$_6$: δ 2.50 (s, 3H), 3.64 (s, 3H), 4.05 (s, 2H), 5.21 (d, *J* = 6.2, 2H), 5.44 (m, *J* = 1.1, 2H), 6.18 (m, 1H), 8.08 (q, *J* = 6.1, 1H), 8.48 (d, *J* = 8, 1H), 8.87 (d, *J* = 6, 1H), 8.94 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-*d*$_6$:

δ 17.8, 52.1 59.2, 62.3, 118.3, 121.8, 127.5, 131.5, 138.9, 142.0, 144.2, 146.1, 164.0

^{19}F-NMR_DMSO-*d*$_6$: δ -79.4

Anal. Calc. for $C_{13}H_{17}F_3N_2O_6S_2$: C 37.32, H 4.10, N 6.70, S 15.32

Found : C 37.36, H 4.02, N 6.93, S 15.40

1-(3-butenyl)-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide(C2A1-Ester)

^{1}H NMR (400 MHz)_DMSO-*d*$_6$: δ 2.50 (s, 3H), 2.72 (q, *J* = 6.8, 2H), 3.64 (s, 3H), 4.05 (s, 2H), 4.63 (t, *J* = 7, 2H), 5.02 (m, 2H), 5.80 (m, 1H), 8.05 (q, *J* = 6.2, 1H), 8.45 (d, *J* = 8, 1H), 8.88 (d, *J* = 6, 1H), 8.97 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-*d*$_6$:

δ 17.8, 34.6, 52.0, 59.3, 59.6, 118.9, 121.5, 127.2, 132.9, 138.6, 142.0, 144.2, 145.8, 164.1

^{19}F-NMR_DMSO-*d*$_6$: δ -79.4

Anal. Calc. for $C_{14}H_{19}F_3N_2O_6S_2$: C 38.89, H 4.43, N 6.48, S 14.83

Found : C 38.57, H 4.33, N 6.67, S 14.69

2.7 General synthetic procedure for the 1-methyl-3-ethyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl)(trifluoromethyl) sulfonyl)amide (EMIMA1-Ester)

To a aqueous solution (15 mL) of sodium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide (1.0 mmol, 1.0 equiv.) in a 100 mL RB flask was added 1-methyl-3-ethyl imidazole (1.0 mmol) at room temperature. The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 24 hours. After the reaction was completed, the resulting product was obtained through extraction with dichloromethane. Afterward, the washed organic layers were dried over MgSO4, filtered, and concentrated under reduced pressure to give a colorless oil of 1-methyl-3-ethyl imidazole ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide.

1-ethyl-3-methyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl) sulfonyl)amide(EMIMA1-Ester)

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 1.43 (t, J = 7.2, 3H), 3.64 (s, 3H), 3.84 (s, 3H), 4.04 (s, 2H), 4.21 (q, J = 7.2, 2H), 7.70 (s, 1H), 7.78 (s, 1H), 9.10 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

δ 15.0, 35.7, 44.1, 52.1, 59.3, 118.3, 121.9, 123.5, 136.2, 164.1

^{19}F-NMR_DMSO-d_6 : δ -79.4

Anal. Calc. for $C_{10}H_{16}F_3N_3O_6S_2$: C 30.38 H 4.08, N 10.63, S 16.22

Found : C 29.10, H 3.89, N 10.77, S 16.42

2.8 General synthetic procedure for the 1-alkyl-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide(C1A1 and C2A1)

1-alkyl-3-methylpyridinium ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl)sulfonyl)amide (1.0 mmol) and 1N HCl (15.0 mmol, 15 equiv.) were added in a 100 mL RB flask at room temperature. The reaction proceeds for 3 hours and the temperature was maintained at 75 °C. After the reaction was completed, the final product was obtained by evaporating water and residual unreacted HCl using a vacuum oven. 1-alkyl-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide was obtained as a colorless oil.

(Alkyl = allyl and 3-butenyl)

1-allyl-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide(C1A1)

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 2.50 (s, 3H), 3.93 (s, 2H), 5.22 (d, J = 6.1, 2H), 5.47 (m, J = 1.1, 2H), 6.18 (m, 1H), 8.08 (q, J = 6.2, 1H), 8.48 (d, J = 8, 1H), 8.87 (d, J = 5.8, 1H), 8.94 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

δ 17.8, 59.9, 62.3, 118.4, 121.9, 127.5, 131.5, 139.0, 142.0, 144.2, 146.2, 165.0

^{19}F-NMR_DMSO-*d*$_6$: δ -79.3

1-(3-butenyl)-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide(C2A1)

^{1}H NMR (400 MHz)_DMSO-*d*$_6$: δ 2.50 (s, 3H), 2.72 (q, *J* = 6.9, 2H), 3.93 (s, 2H), 4.66 (t, *J* = 6.9, 2H), 5.05 (m, 2H), 5.83 (m, 1H), 8.06 (q, *J* = 6.2, 1H), 8.45 (d, *J* = 8, 1H), 8.89 (d, *J* = 6, 1H), 8.97 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-*d*$_6$:

δ 17.8, 34.6, 59.6, 60.1, 119.0, 121.6, 127.2, 132.9, 138.6, 142.0, 144.2, 145.9, 164.8

^{19}F-NMR_DMSO-*d*$_6$: δ -79.3

2.8 General synthetic procedure for the 1-ethyl-3-methyl imidazole ((carboxymethyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide(EMIMA1)

1-methyl-3-ethyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl)sulfonyl)amide (1.0 mmol) and 1N HCl (15.0 mmol, 15 equiv.) were added in a 100 mL RB flask at room temperature. The reaction proceeds for 3 hours and the temperature was maintained at 75 ˚C. After the reaction was completed, the final product was obtained by evaporating water and residual unreacted

HCl using a vacuum oven. 1-methyl-3-ethyl imidazole ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide was obtained as a colorless oil.

1-ethyl-3-methyl imidazole ((carboxymethyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide(EMIMA1)

^{1}H NMR (400 MHz)_DMSO-d_6 : δ 1.43 (t, J = 7.3, 3H), 3.84 (s, 3H), 3.93 (s, 2H), 4.21 (q, J = 7.3, 2H), 7.69 (s, 1H), 7.78 (s, 1H), 9.10 (s, 1H)

^{13}C NMR (100 MHz)_DMSO-d_6 :

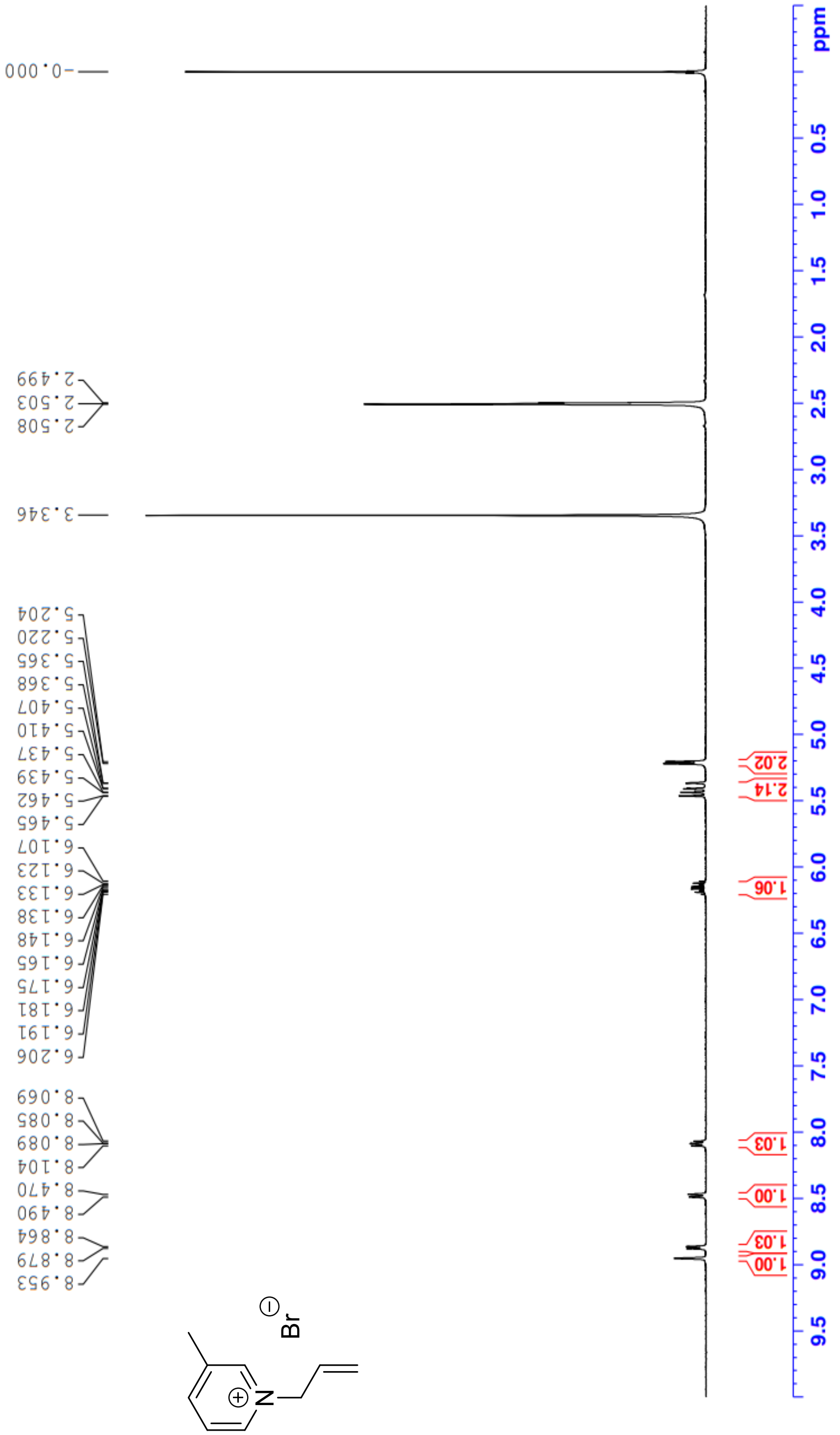
δ 15.1, 35.7, 44.1, 59.7, 118.4, 122.0, 123.6, 136.2, 164.9

^{19}F-NMR_DMSO-d_6 : δ -79.3

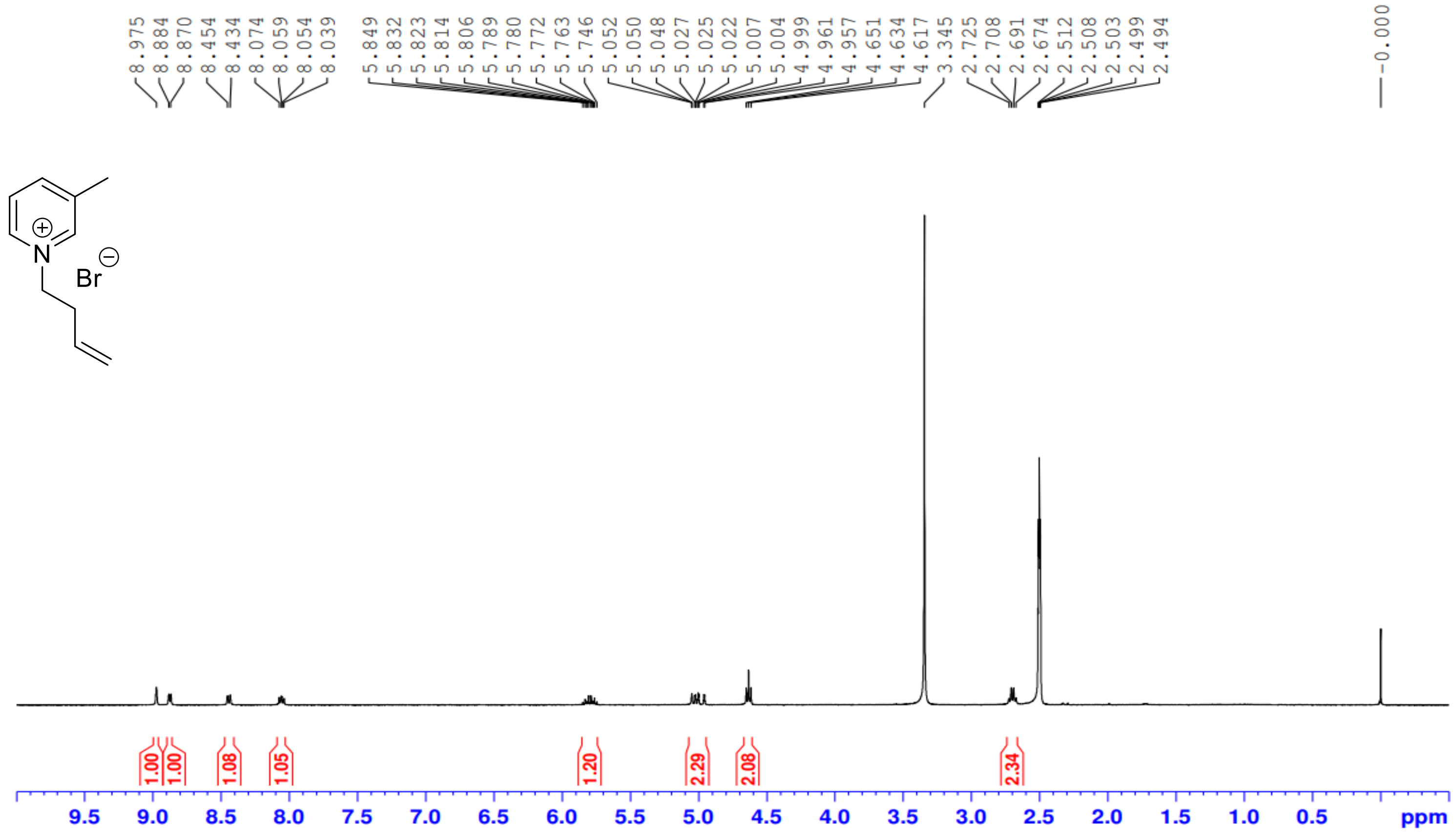
APPENDICES

List of ^{1}H NMR Spectra of compounds

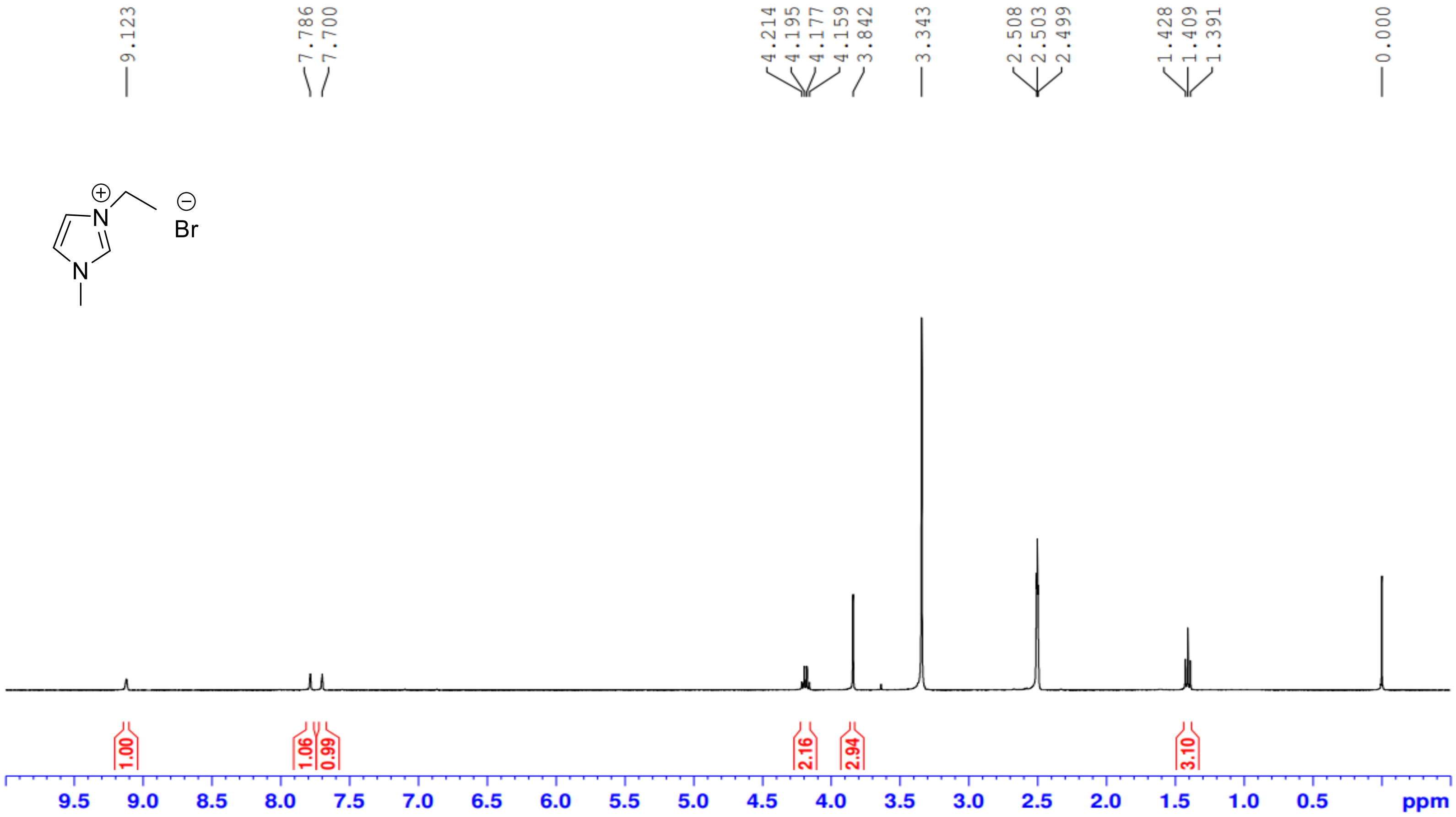
1. 1-allyl-3-methylpyridinium bromide_DMSO-d_6
2. 1-(3-butenyl)-3-methylpyridinium bromide_DMSO-d_6
3. 1-ethyl-3-methyl imidazole bromide_DMSO-d_6
4. Methyl 2-(chlorosulfonyl)acetate_ $CDCl_3$
5. Sodium ((2-methoxy–2-oxoethyl)sulfonyl)(trifluoromethyl) sulfonyl)amide_DMSO-d_6
6. 1-allyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1-Ester)
7. 1-(3-butenyl)-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1-Ester)
8. 1-ethyl-3-methyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl) sulfonyl)amide_DMSO-d_6(EMIMA1-Ester)
9. 1-allyl-3-methylpyridinium ((carboxymethyl)sulfonyl) ((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1)
10. 1-(3-butenyl)-3-methylpyridinium ((carboxymethyl)sulfonyl) ((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1)
11. 1-ethyl-3-methyl imidazole ((carboxymethyl)sulfonyl) ((trifluoromethyl) sulfonyl) amide_DMSO-d_6(EMIMA1)



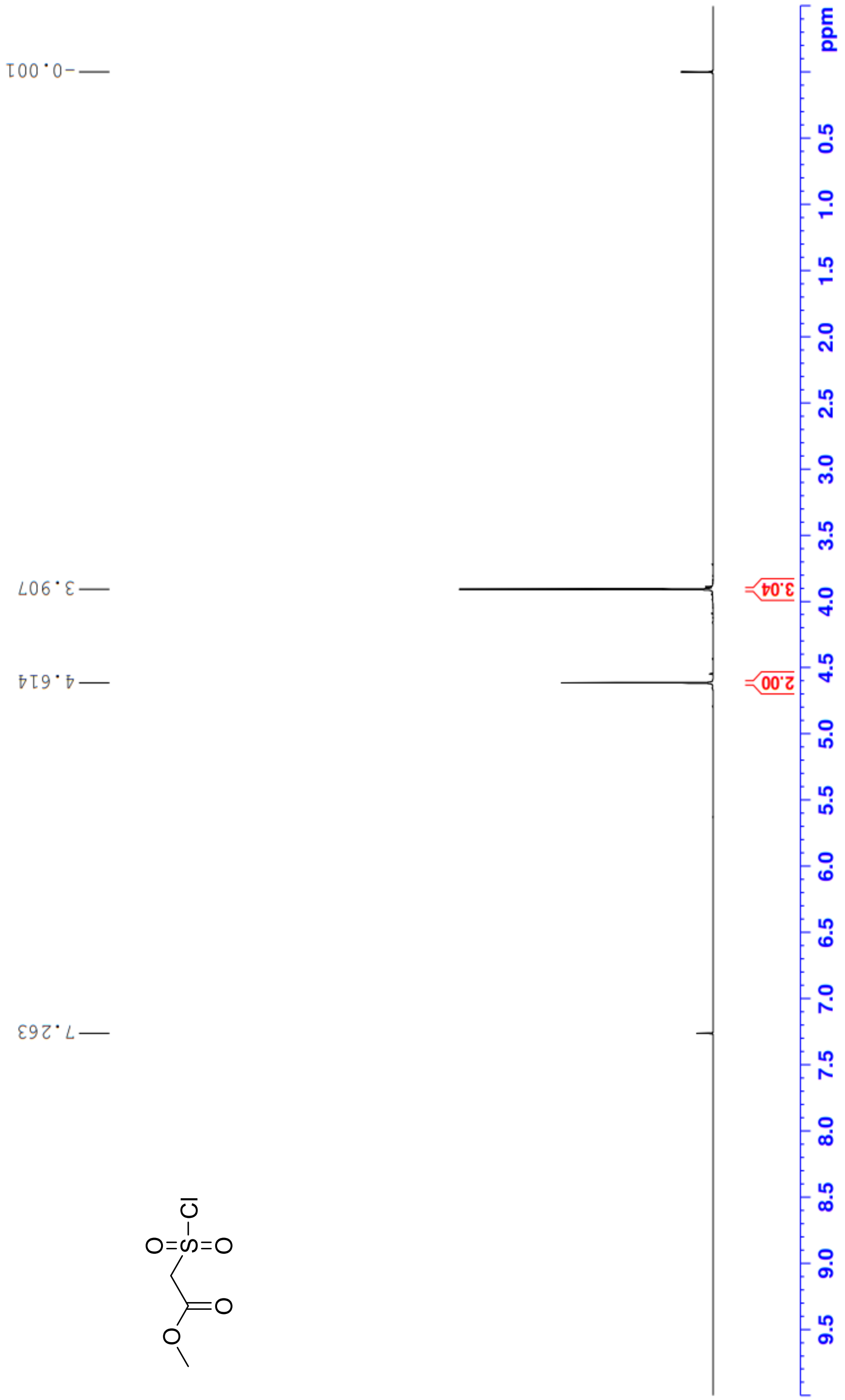
1-allyl-3-methylpyridinium bromide_DMSO-d_6



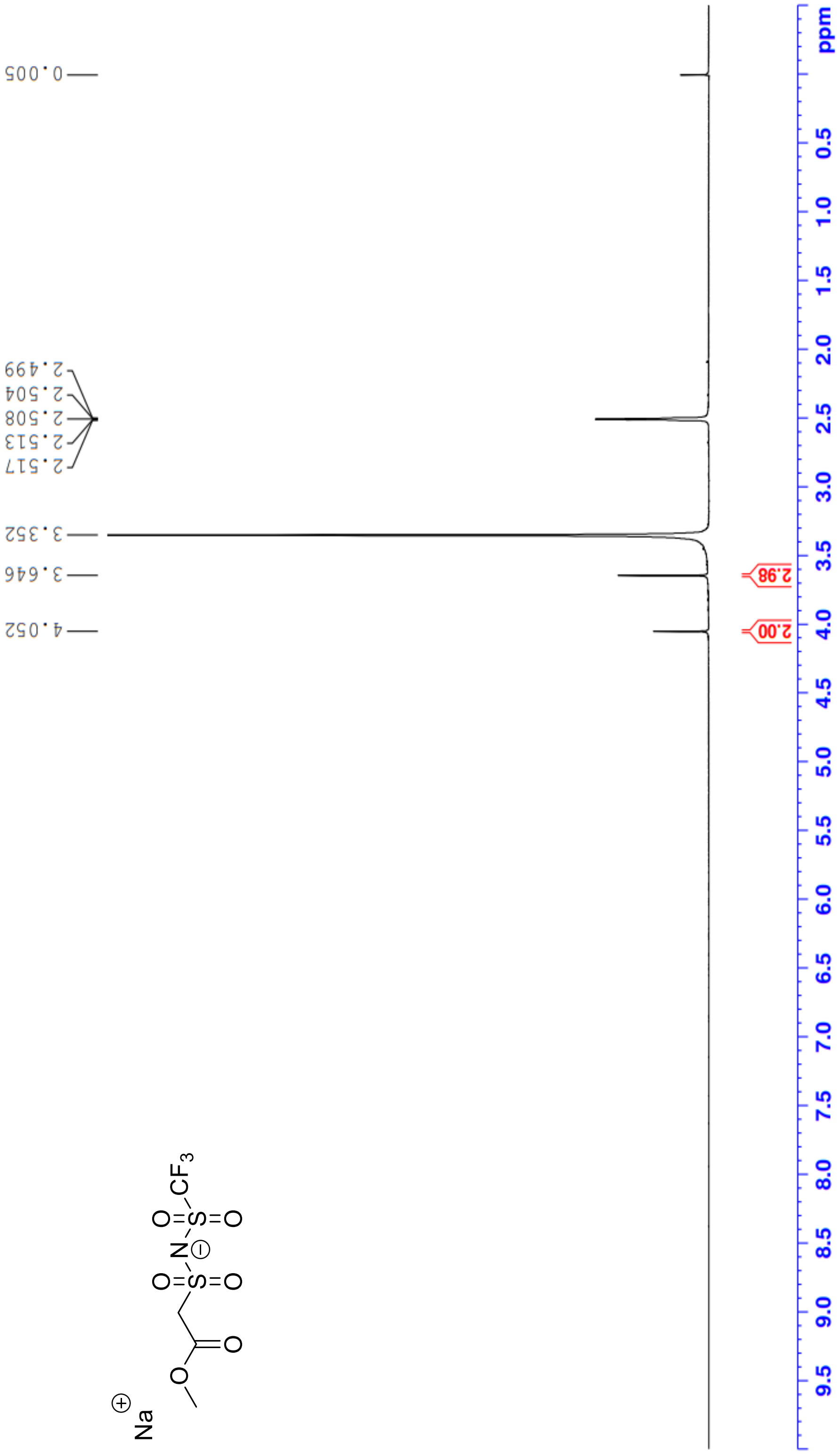
1-(3-butenyl)-3-methylpyridinium bromide_DMSO-d_6



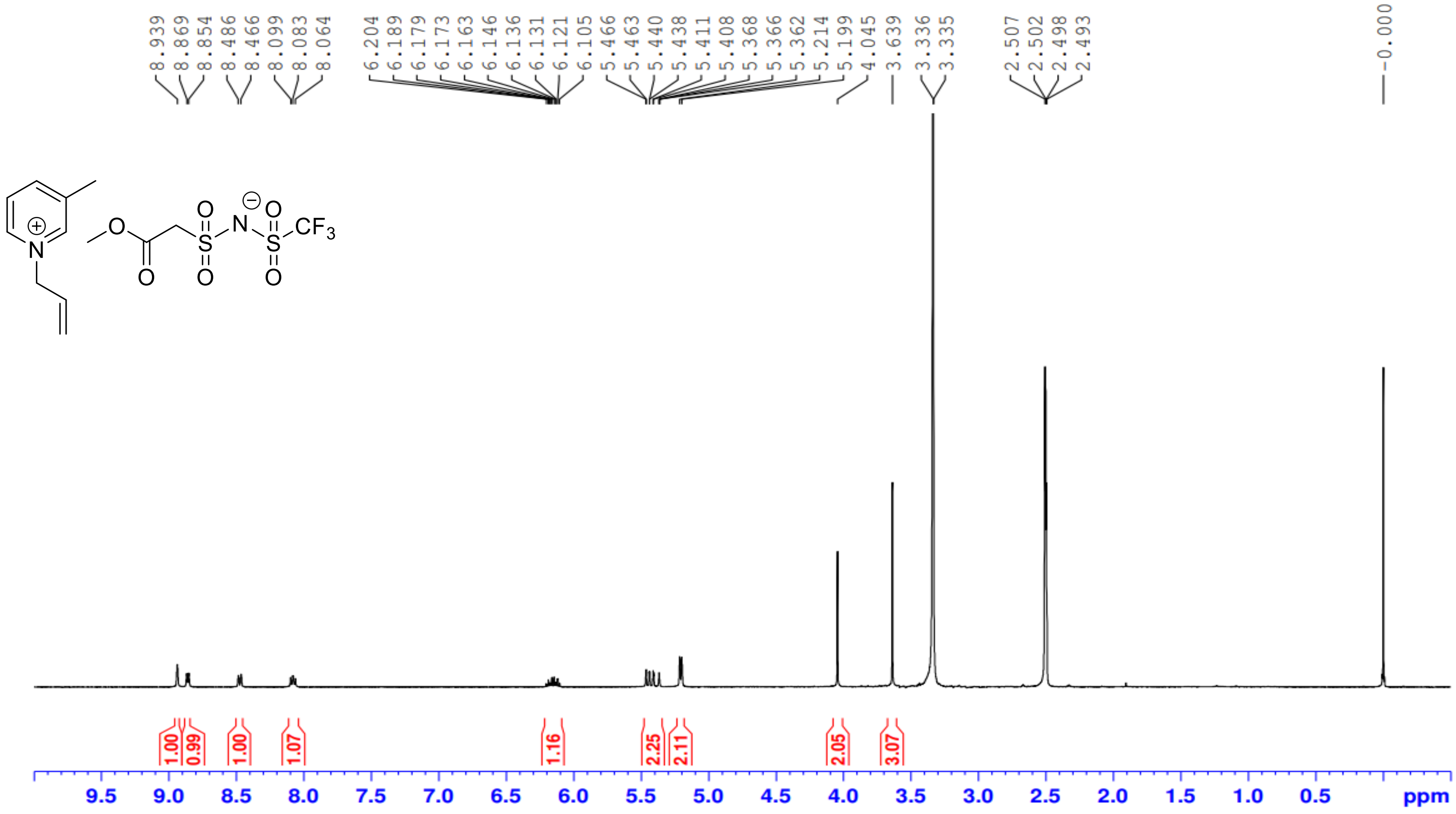
1-ethyl-3-methyl imidazole bromide_DMSO-d_6



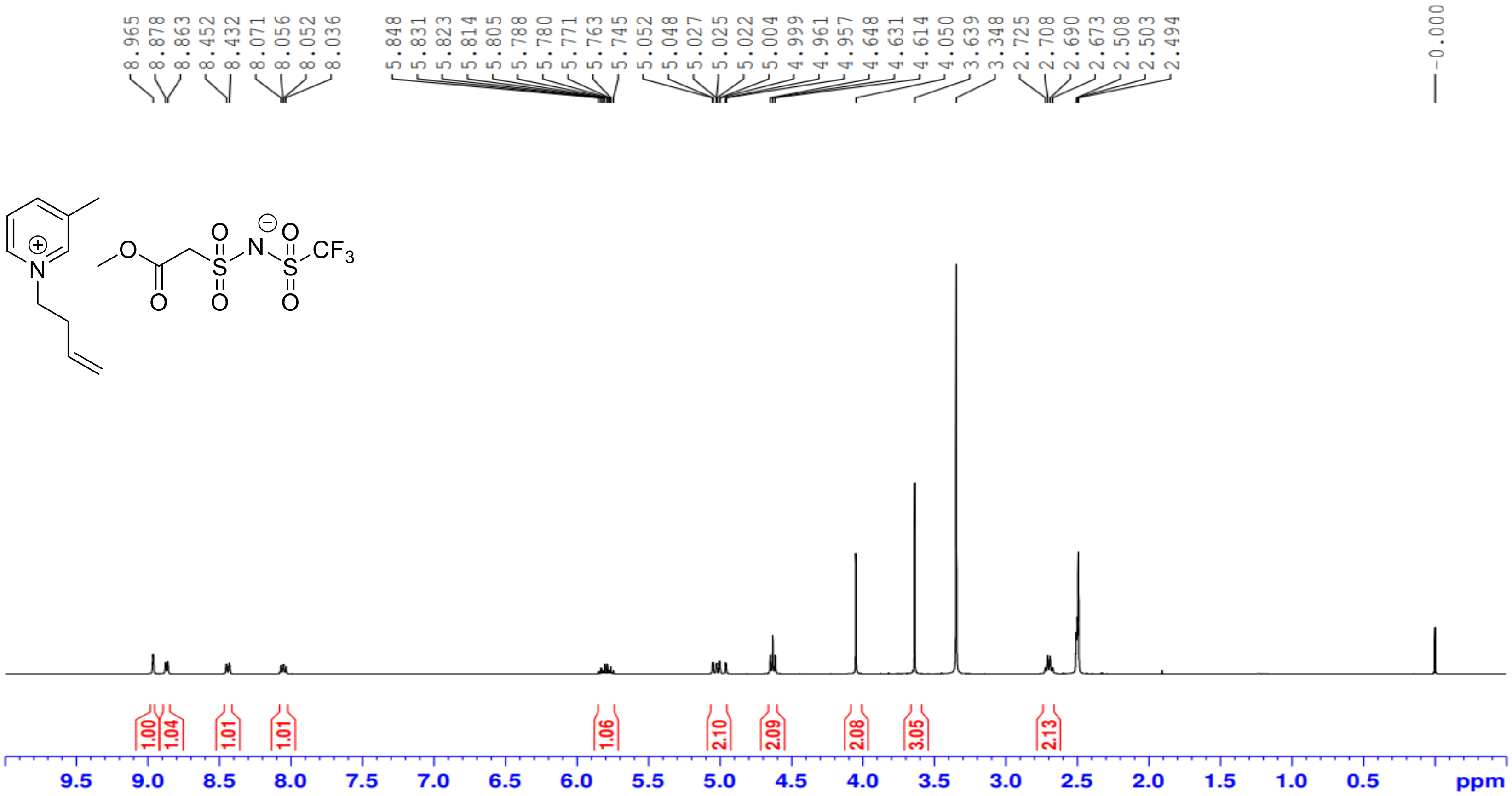
Methyl 2-(chlorosulfonyl)acetate_ $CDCl_3$



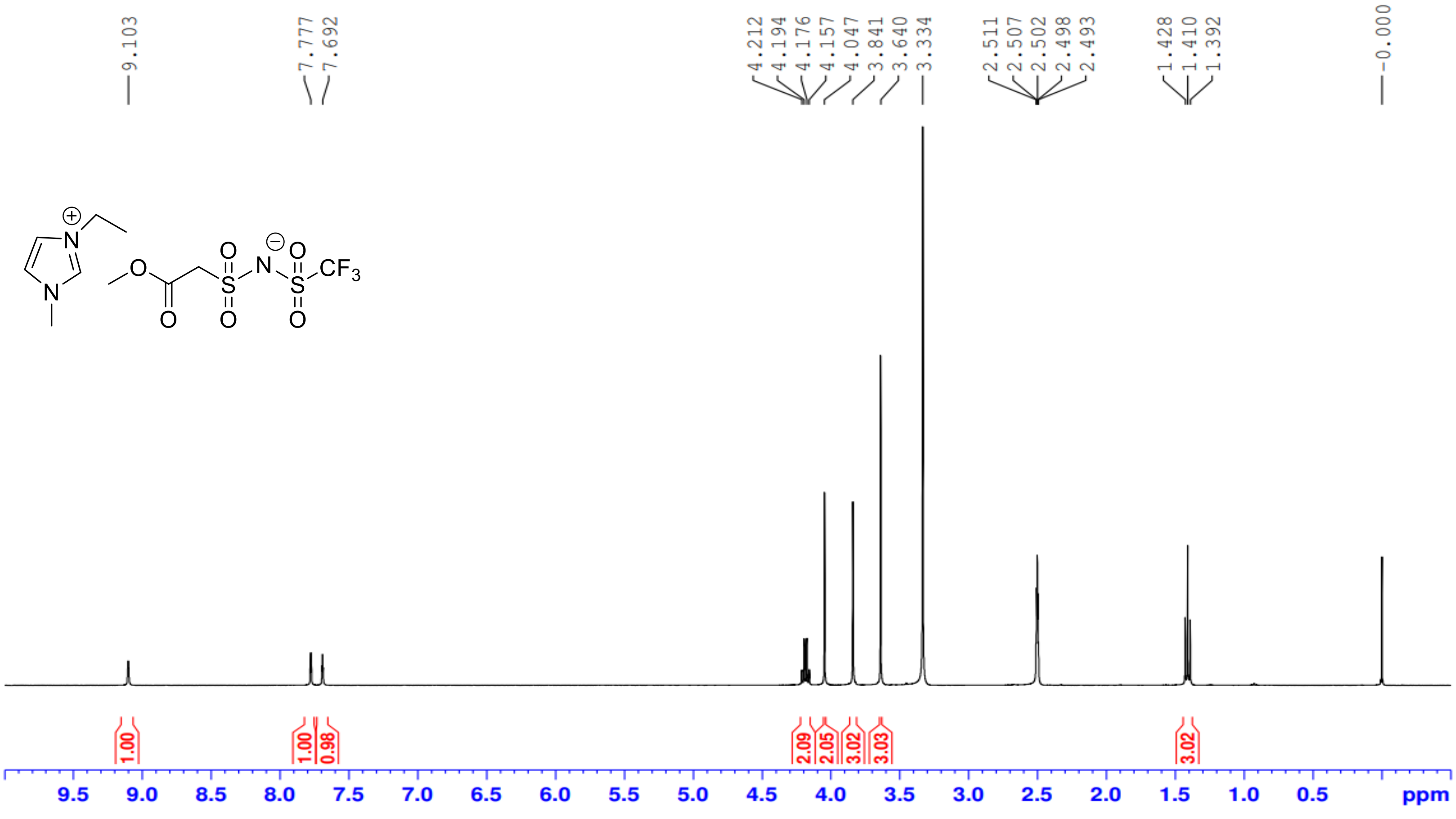
Sodium ((2-methoxy–2-oxoethyl)sulfonyl)(trifluoromethyl) sulfonyl)amide_DMSO-d_6



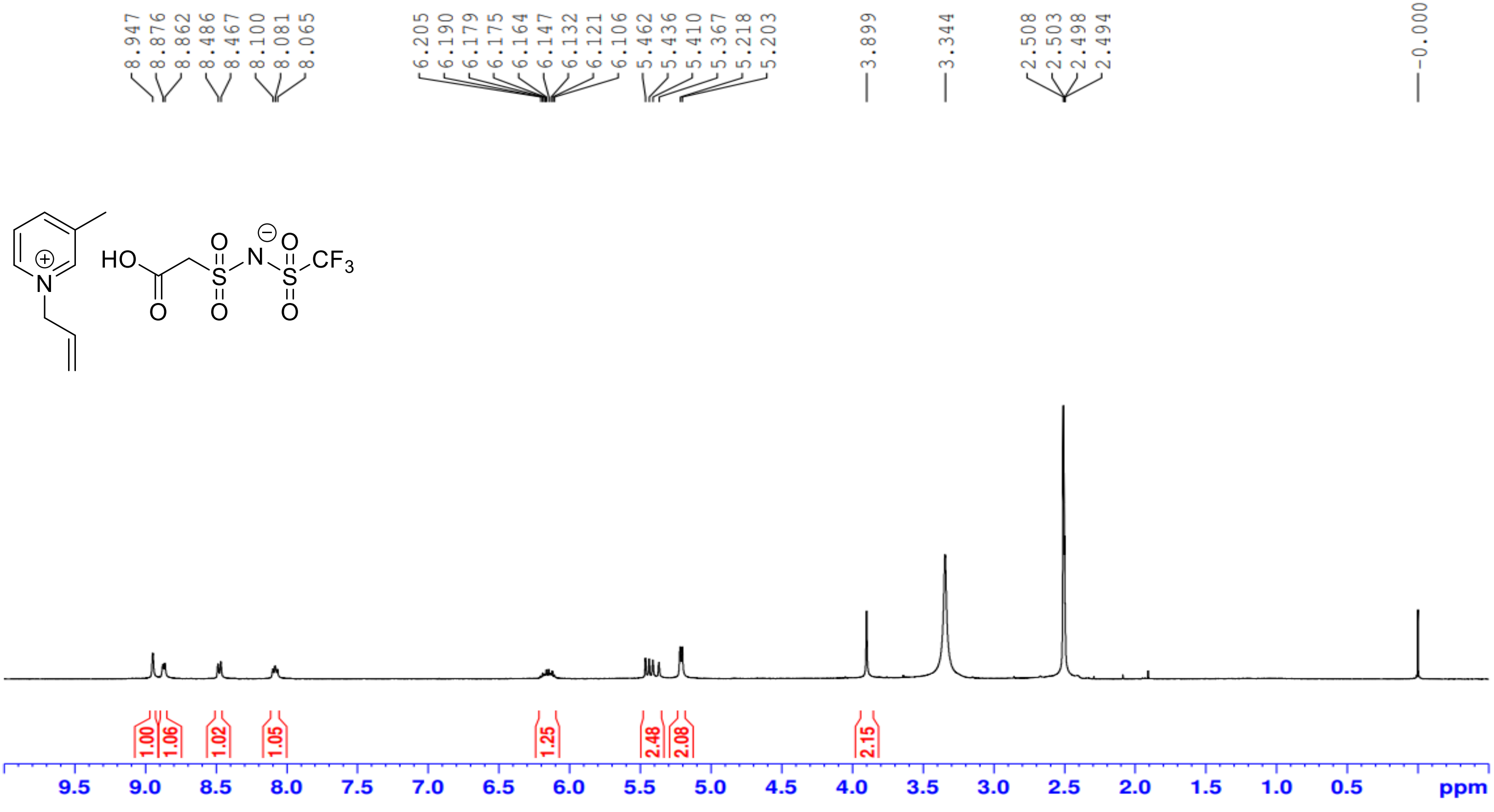
1-allyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1-Ester)



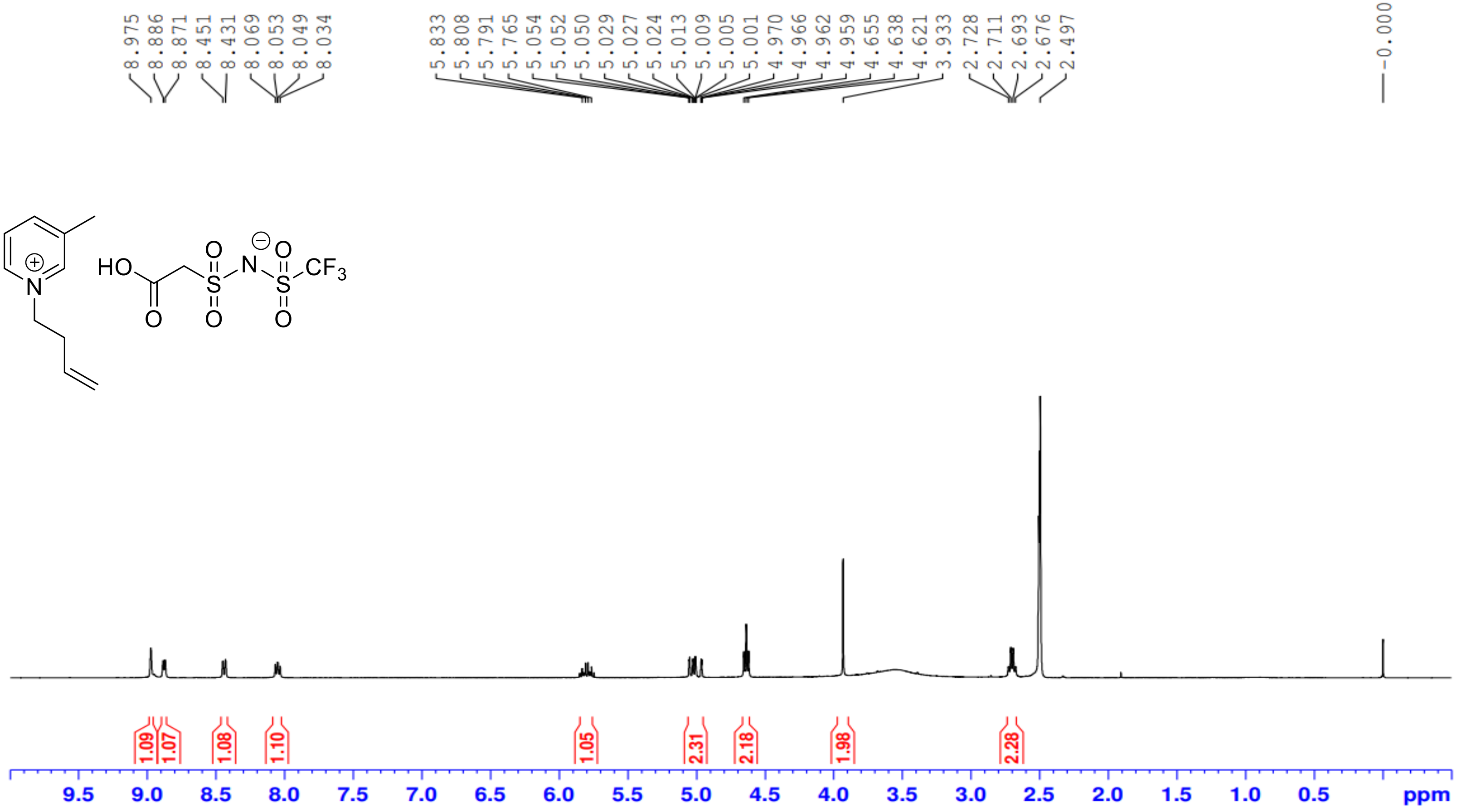
1-(3-butenyl)-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1-Ester)



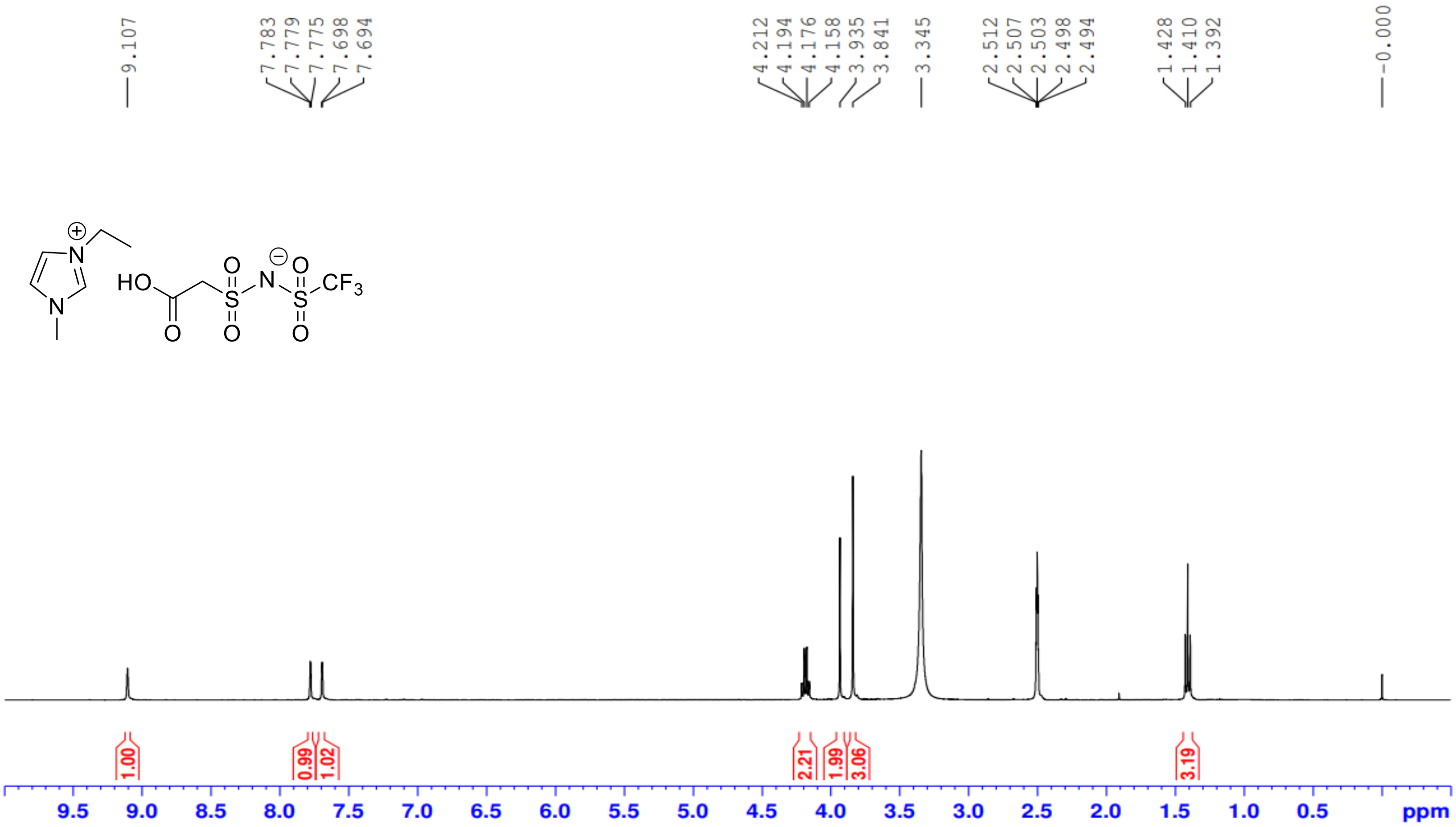
1-ethyl-3-methyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(EMIMA1-Ester)



1-allyl-3-methylpyridinium ((carboxymethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1)



1-(3-butenyl)-3-methylpyridinium ((carboxymethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1)



1-ethyl-3-methyl imidazole ((carboxymethyl)sulfonyl) ((trifluoromethyl) sulfonyl) amide_DMSO-d_6(EMIMA1)

List of ^{13}C NMR Spectra of compounds

1. 1-allyl-3-methylpyridinium bromide_DMSO-d_6

2. 1-(3-butenyl)-3-methylpyridinium bromide_DMSO-d_6

3. 1-ethyl-3-methyl imidazole bromide_DMSO-d_6

4. Methyl 2-(chlorosulfonyl)acetate_ $CDCl_3$

5. 1-allyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1-Ester)

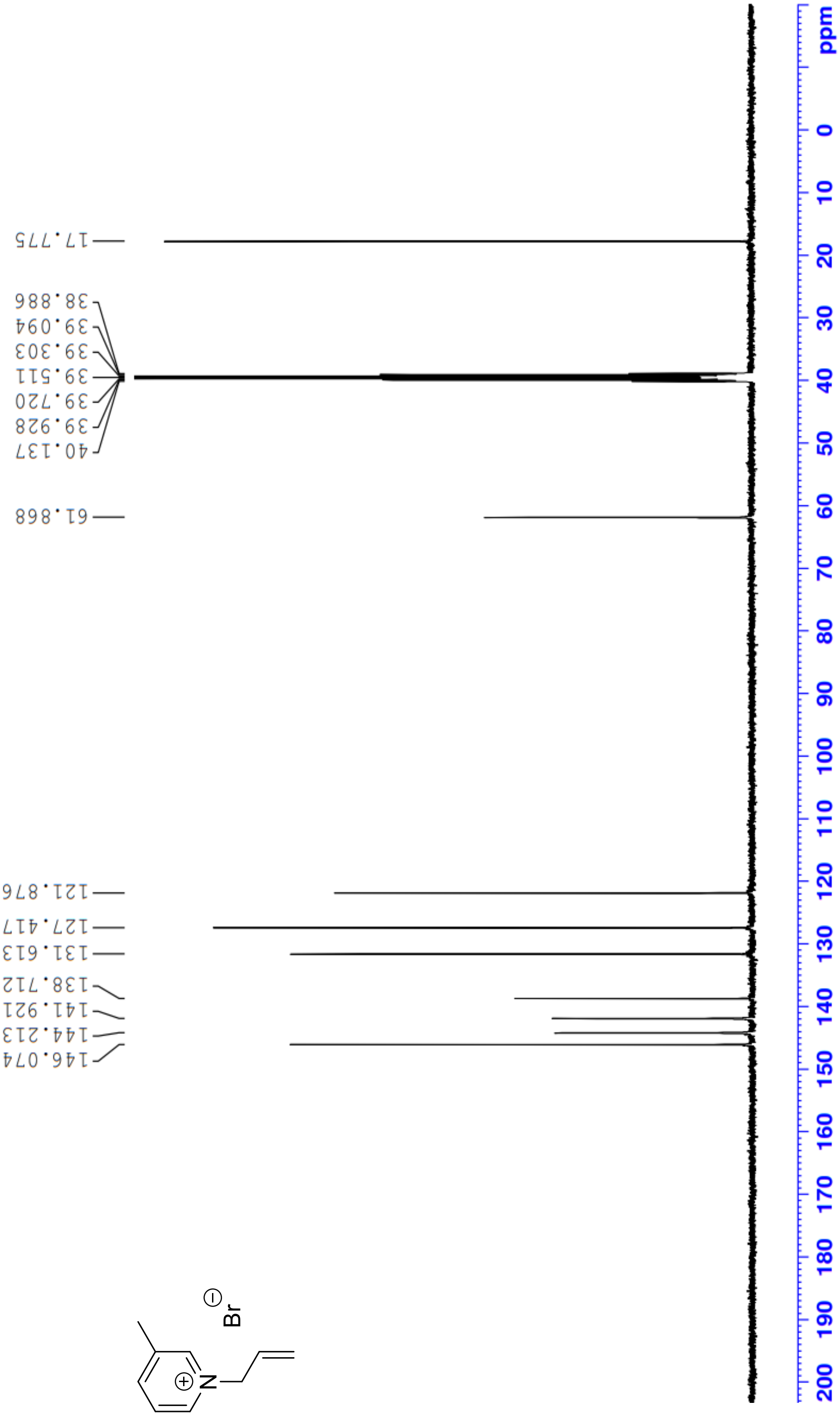
6. 1-(3-butenyl)-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1-Ester)

7. 1-methyl-3-ethyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl) (trifluoromethyl) sulfonyl)amide_DMSO-d_6(EMIMA1-Ester)

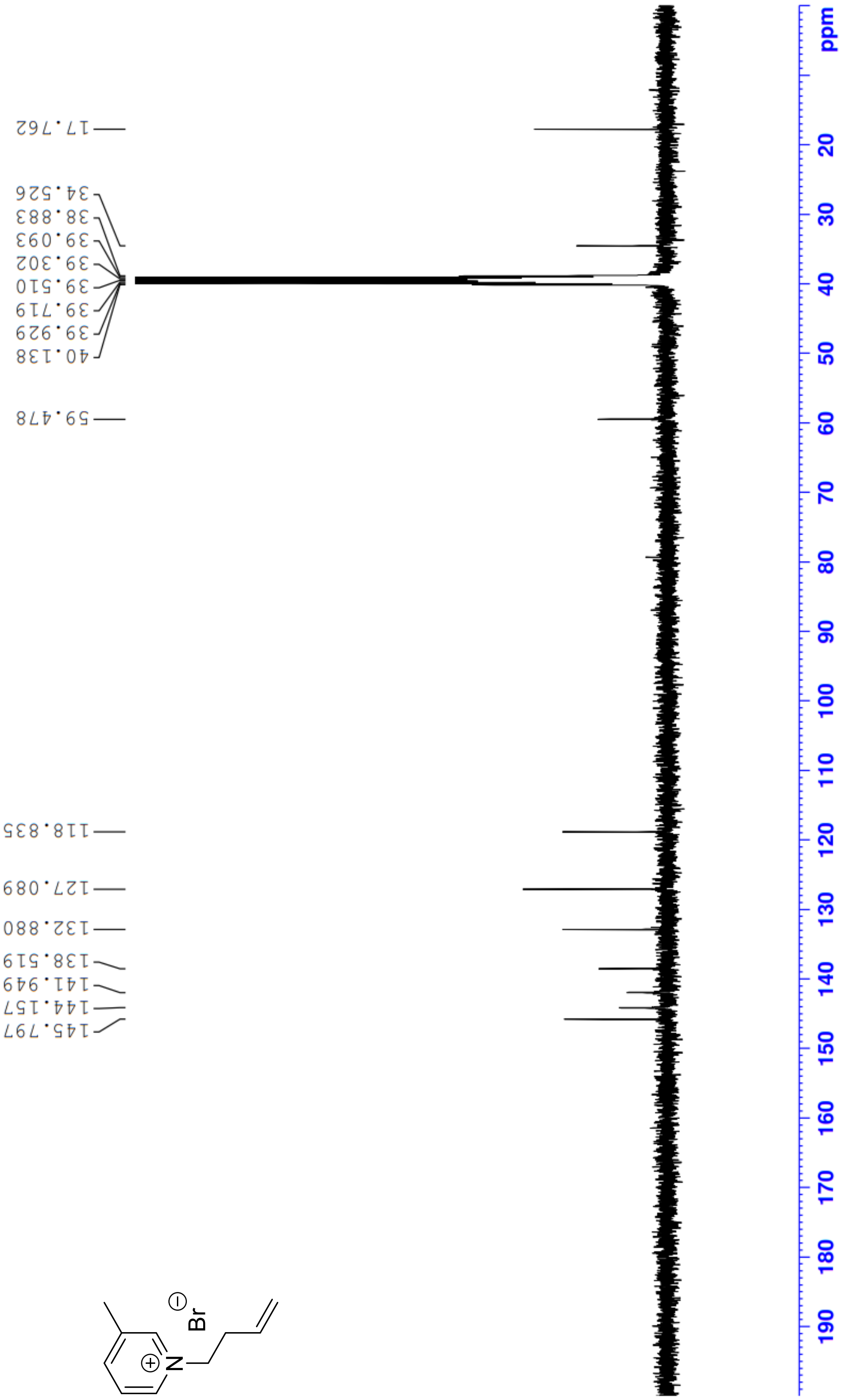
8. 1-allyl-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1)

9. 1-(3-butenyl)-3-methylpyridinium ((carboxymethyl) sulfonyl) ((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1)

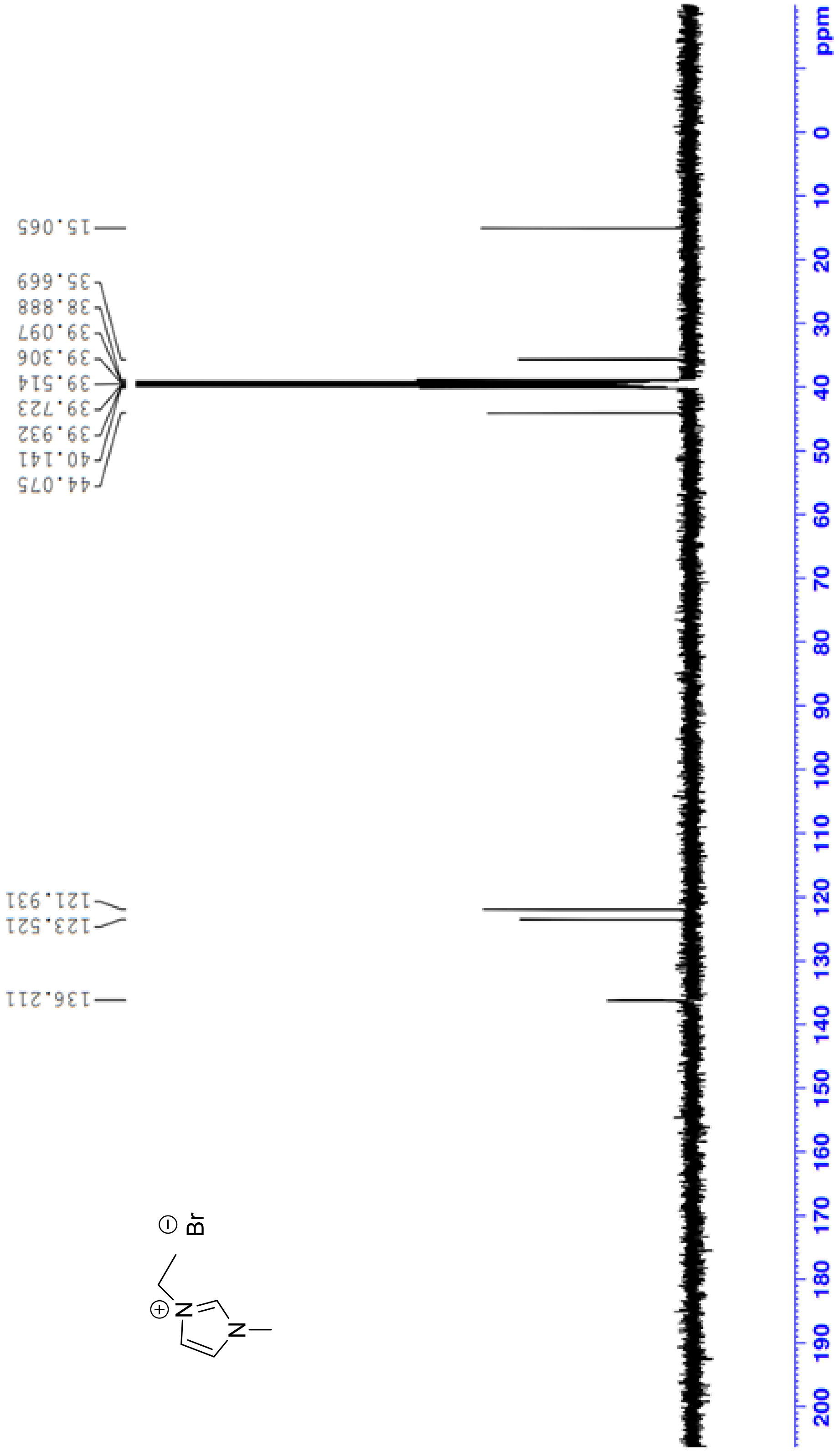
10. 1-methyl-3-ethyl imidazole ((carboxymethyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide_DMSO-d_6(EMIMA1)



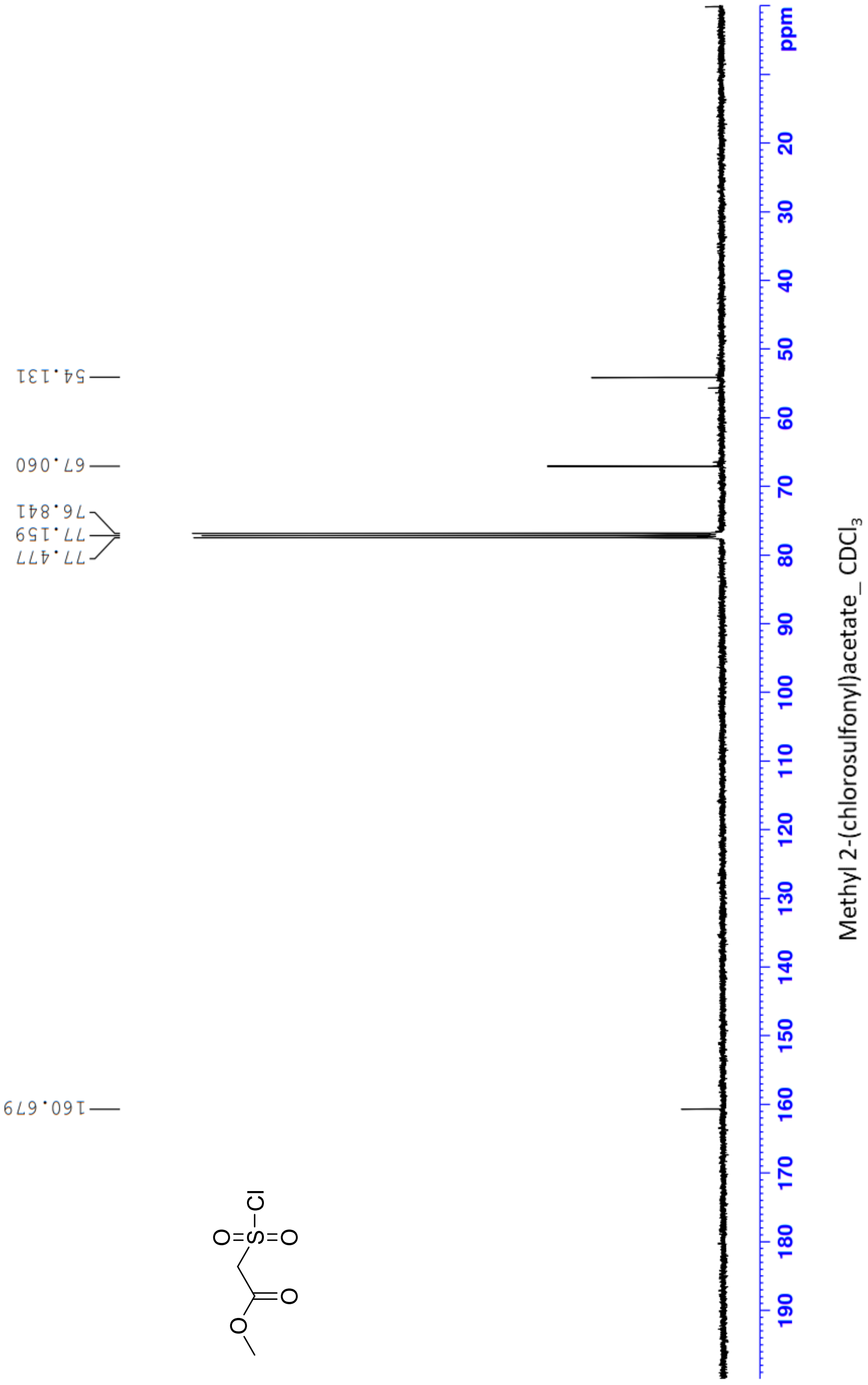
1-allyl-3-methylpyridinium bromide_DMSO-d_6

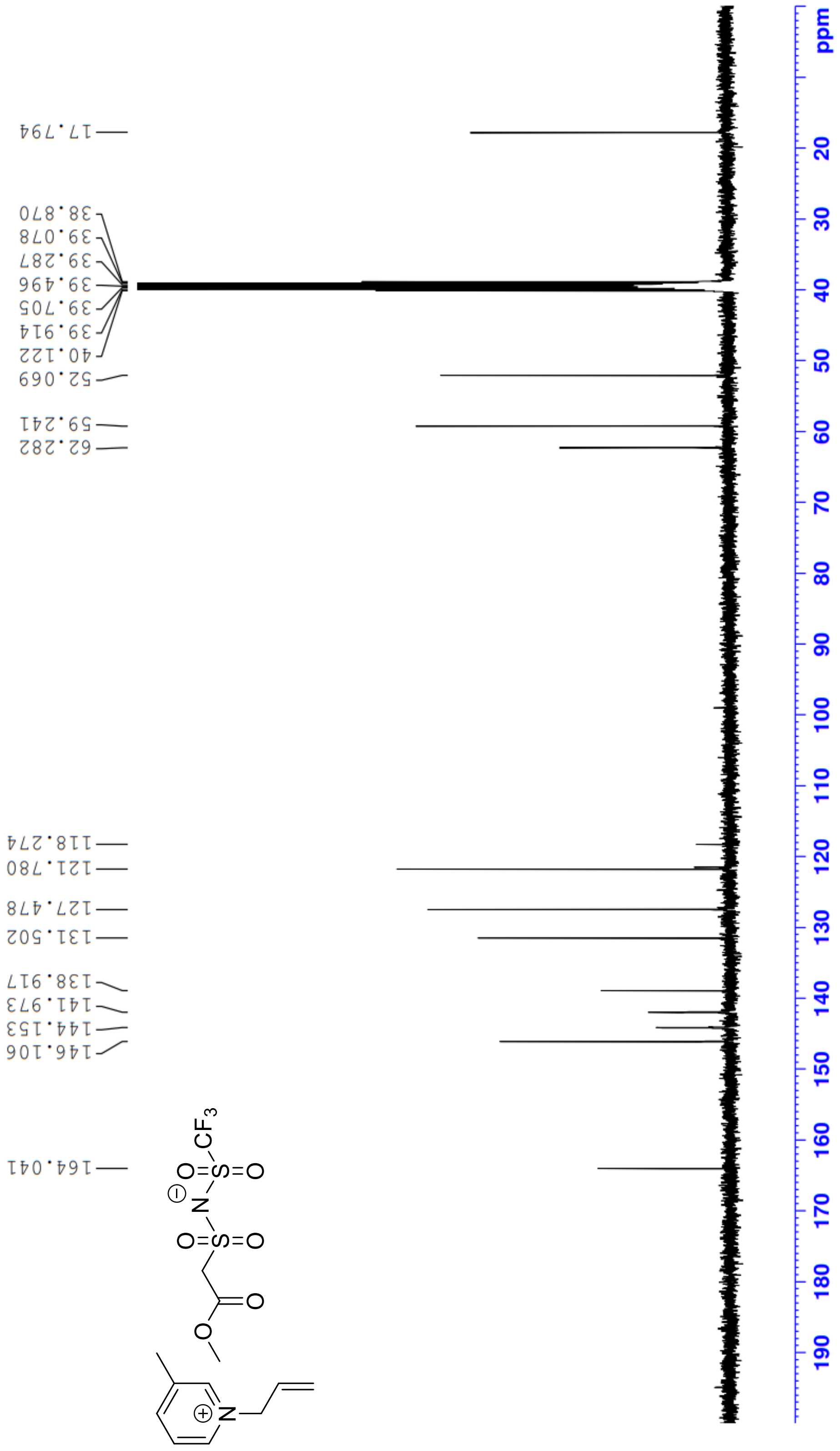


1-(3-butenyl)-3-methylpyridinium bromide_DMSO-d_6

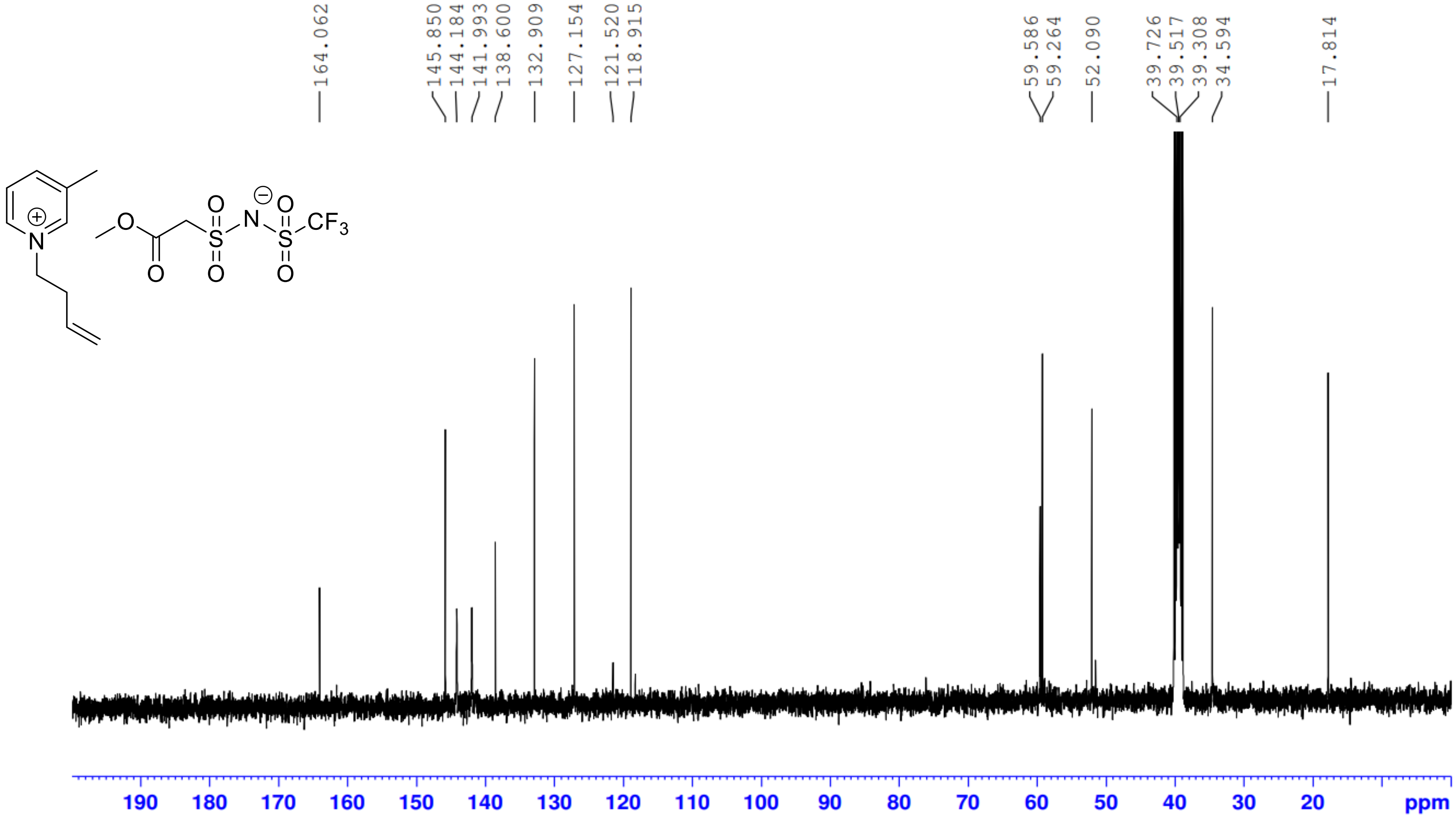


1-ethyl-3-methyl imidazole bromide_DMSO-d_6

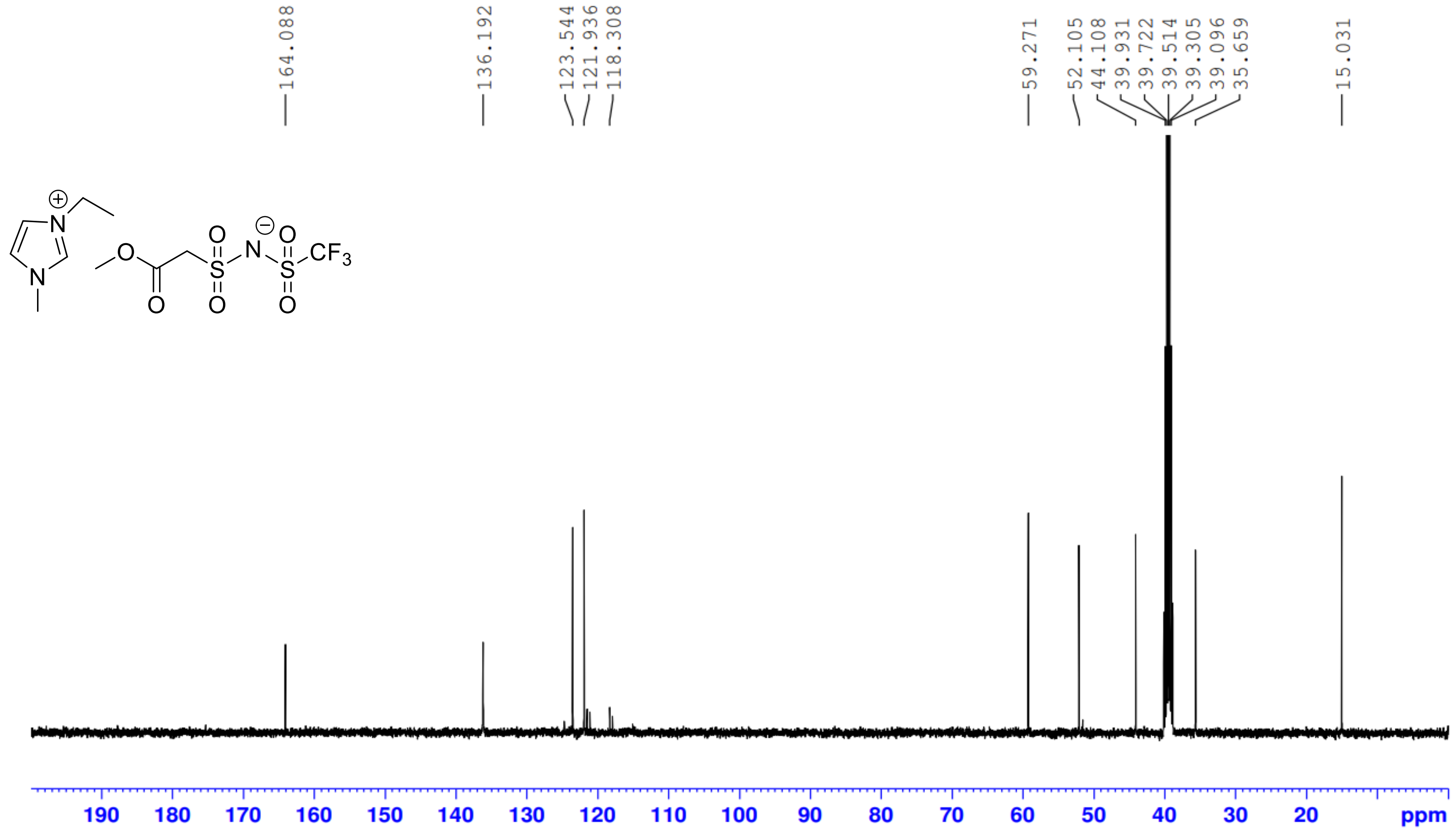

Methyl 2-(chlorosulfonyl)acetate_ $CDCl_3$



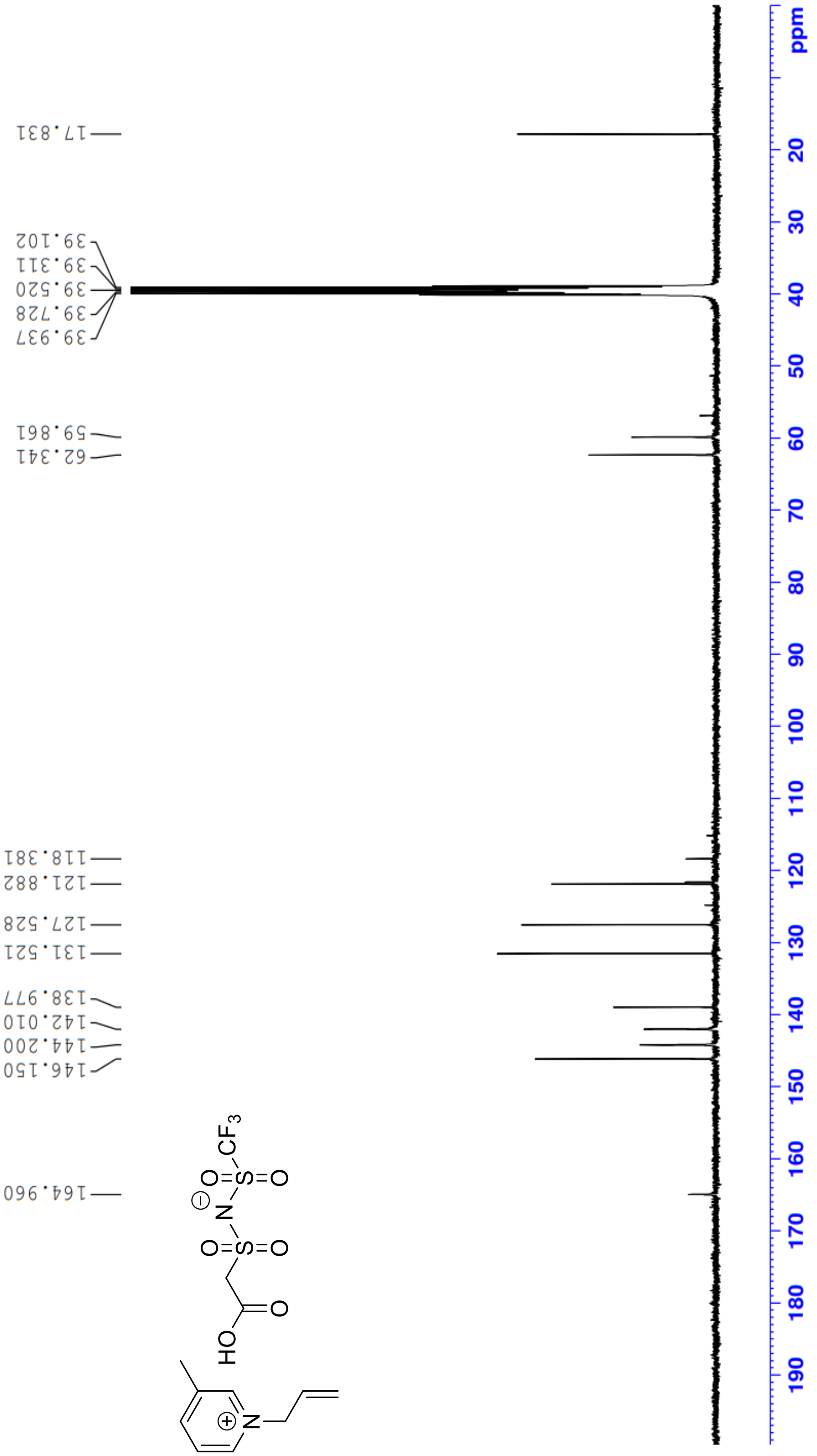
1-allyl-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1-Ester)



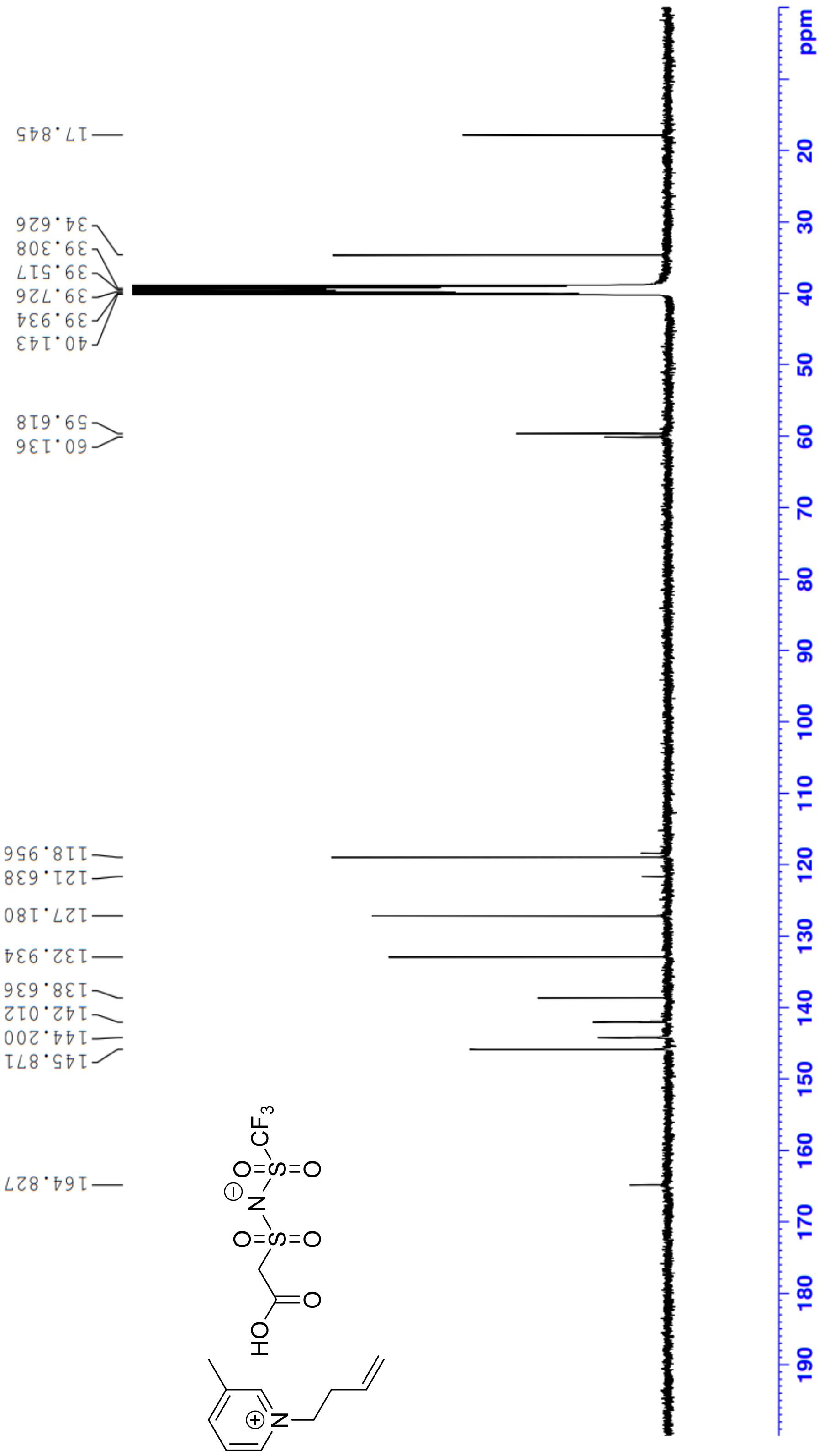
1-(3-butenyl)-3-methylpyridinium ((2-methoxy-2-oxoethyl) sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1-Ester)



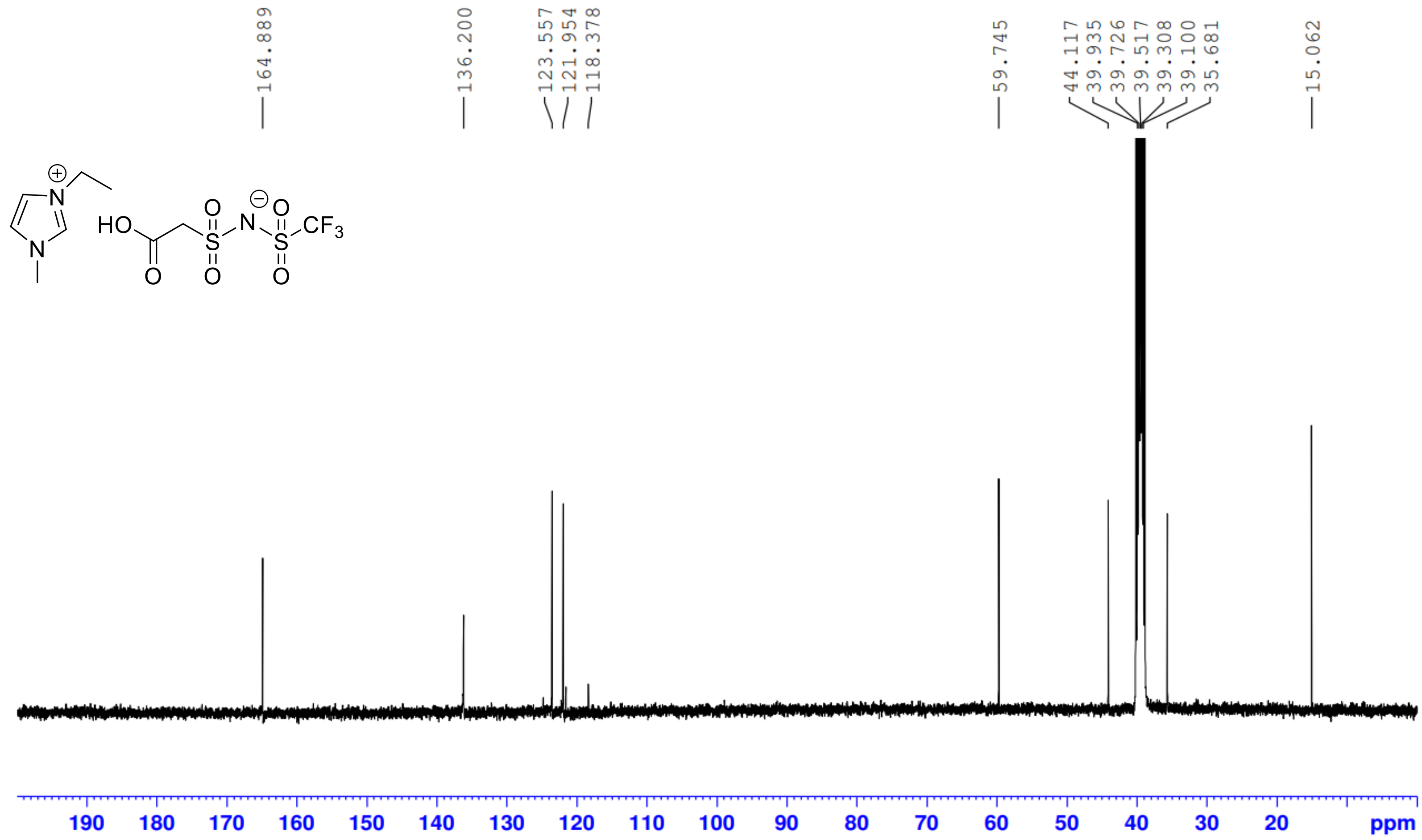
1-ethyl-3-methyl imidazole ((2-methoxy-2-oxoethyl)sulfonyl)(trifluoromethyl)sulfonyl)amide_DMSO-d_6(EMIMA1-Ester)



1-allyl-3-methylpyridinium ((carboxymethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C1A1)



1-(3-butenyl)-3-methylpyridinium ((carboxymethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide_DMSO-d_6(C2A1)



1-ethyl-3-methyl imidazole ((carboxymethyl)sulfonyl) ((trifluoromethyl) sulfonyl) amide_DMSO-d_6(EMIMA1)

ABSTRACT IN KOREAN

현재 이온성 액체는 넓은 범위에서 사용되고 있고, 그 중에서 리튬 이온 배터리의 차세대 전해질로 각광받고 있다. 이온성 액체의 비인화성, 높은 이온전도도, 여러 조합의 가능성, 넓은 전압 범위에서의 안정성 등과 같은 차별화된 특성으로 기존의 전해질을 대체하기 위한 새로운 많은 연구들이 진행되고 있다. 본 논문에서는 평면성이 큰 피리디늄 계열과 이미다졸 계열 양이온, 비대칭 bis(sulfonyl)imide 계열의 음이온을 선택하여 점도를 낮추고 이온전도도를 높이고자 하였고, 이를 이용하여 6가지의 이온성 액체를 합성하였다. 양이온 합성 과정에서 반응의 수율이 95% 이상으로 높았으며, 음이온 합성 과정에서는 중간체를 형성할 때의 54%의 수율, 나머지 스텝에서는 모두 90% 이상의 수율을 얻었다. 합성한 이온성 액체는 ^{1}H, ^{13}C, ^{19}F-NMR 및 원소 분석 방법으로 순도를 확인하였다.

이렇게 합성한 이온성 액체의 전해질로서의 성능을 알아보기 위해 점도와 이온전도도를 측정하였다. 합성한 이온성 액체의 점도는 180 cP 이상으로 높았고, 1-4 mS/cm의 이온 전도도를 보여주었다. 또한, 이온성 액체가 첨가제로 사용되었을 때의 성능을 알아보기 위해 전해질로 많이 사용되는 카보네이트 전해질(EC/DEC 1:2 혼합물)에 합성한 이온성 액체를 여러 비율의 이원 혼합물로 제조하여 점도와 이온전도도를 측정하였다. 이온성 액체의 농도가 묽어짐에 따라, 점도 값이 44 cP 이하까지 감소하여, 유동성이 개선된 모습을 보여주었다. 또한, 대부분의 비율에서 이온 전도도 값이 증가하였고, 특정 농도에서는 약 3배가량 증가한 이온 전도도 값을 보였다. 합성한 혼합물 중 C1A1-Ester, EMIMA1-Ester의 20:80 혼합물의 경우 각각 9.11mS/cm, 9.03mS/cm의 높은 이온전도도를 나타냈다. 이러한 연구 결과를 바탕으로 본 논문에서 합성한 이온성

액체가 배터리 전해질 첨가제로 이용되었을 때 높은 효과를 가질 수 있는 잠재력이 있다는 것을 보여주었다.

주요어 : 이온성 액체, 비대칭 음이온, 피리디늄 계열 양이온, 이미다졸 계열 양이온, 전해질 첨가제

학 번 : 2020-22968