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공학석사학위논문

Synthesis of Novel Ionic Liquids for  
Electrolytes with Unsymmetrical  
Bis(sulfonyl)imide Anions  
containing a 2-carboxyethyl  
functional group

2-Carboxyethyl 작용기를 가지는 비대칭  
bis(sulfonyl)imide 음이온으로 구성된 이온성 액체 연구

2020년 2월

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화학생물공학부

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# Synthesis of Novel Ionic Liquids for Electrolytes with Unsymmetrical Bis(sulfonyl)imide Anions containing a 2-carboxyethyl functional group

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# Abstract

## Synthesis of Novel Ionic Liquids for Electrolytes with Unsymmetrical Bis(sulfonyl)imide Anions containing a 2-carboxyethyl functional group

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Ionic liquids (ILs) are attracting lots of attention as promising electrolytes in lithium ion batteries (LIB). Due to the unique properties of ILs including high ionic conductivity, non-flammability, negligible vapor pressure, and wide electrochemical window, there have been a number of researches to develop high-performance ILs to replace the conventional carbonate electrolytes. In this research, four kinds of novel ionic liquids were synthesized in 77 ~ 82% yields for 5 steps. The prepared ILs consist of 3-methylpyridinium-based cation and unsymmetrical bis(sulfonyl)imide anion. To ensure the purity, the prepared ILs were analyzed by  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR,  $^{19}\text{F}$ -NMR, and elemental analysis. For the purpose of electrochemical applications, viscosity and ionic conductivity of these ILs were measured.

Furthermore, the binary mixtures of the synthesized ILs and carbonate electrolytes (EC/DEC 1:2 mixture) were prepared, and their physical and electrochemical properties were measured to test the IL's performance when they are used as additives. Although the pure ILs were highly viscous and indicated low ionic conductivity that is less than 1 mS/cm, the ionic conductivity of the binary mixtures was drastically increased as the concentration of the ILs dilutes. In the case of 1-allyl-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (C1A2-Ester), the conductivity value of its 40:60 binary mixture was 8.84 mS/cm, which is about 14 times higher than that of pure C1A2-Ester. This result indicates that the synthesized ILs have the potential to be an outstanding additive for battery electrolytes.

Key words: Ionic liquids, Unsymmetrical anion, Pyridinium based cation, Electrochemistry, LIB electrolyte, Binary mixture

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## List of Abbreviations

DEC	Diethyl carbonate
EC	Ethylene carbonate
FSI	bis(fluorosulfonyl)imide
h	hour
IL	Ionic liquid
LIB	Lithium ion battery
m	Multiplet
mp	Melting point
Quant.	Quantitative
RT	Room temperature
RTIL	Room temperature ionic liquid
s	Singlet
SEI	Solid electrolyte interface
$\delta$	Chemical shift

# Chapter 1. Introduction

## 1.1. Introduction of Ionic liquids

Ionic liquids are molten salts, which consist only of organic cations and organic or inorganic anions, (**Figure 1**) and they usually have low melting points less than 100 °C. Especially, some ionic liquids that are in liquid state at room temperature are called ‘Room temperature ionic liquids’, RTILs. Even though it is controversial what the first reported ionic liquid is, ethanolanmonium nitrate (mp = 52 °C) was reported by S. Gabriel and J. Weiner, in 1888.<sup>1</sup> Then, Paul Walden reported ethylammonium nitrate (mp = 12 °C) in 1914, which is known as the first reported room temperature ionic liquid. In 1980s, a variety of heterocyclic ring-based RTILs were reported, such as the ionic liquids whose cation counterparts are *N,N*-dialkyl imidazolium, or alkyl pyridinium ions. For example, 1-methyl-3-alkylimidazolium chloroaluminate (R=methyl, ethyl, propyl, and butyl) was reported and studied by S. Wilkes in 1981. S. Wilkes not only synthesized this RTILs adjusting its cationic structure with various alkyl substituents, but also attempted to apply it for electrochemical use, such as a battery electrolyte.<sup>2</sup> The dialkylimidazolium cation is generally known as one of the best cations for RTILs, since its structure is electrochemically stable, and the ILs with imidazolium cations have high ionic conductivity, because of relatively small and planar

structure of imidazole ring compared to other heterocyclic cations. Recently, there are still many attempts to improve the electrochemical performances of dialkylimidazolium-based RTILs by modifying its structure other than the alkyl substituents.<sup>3</sup>

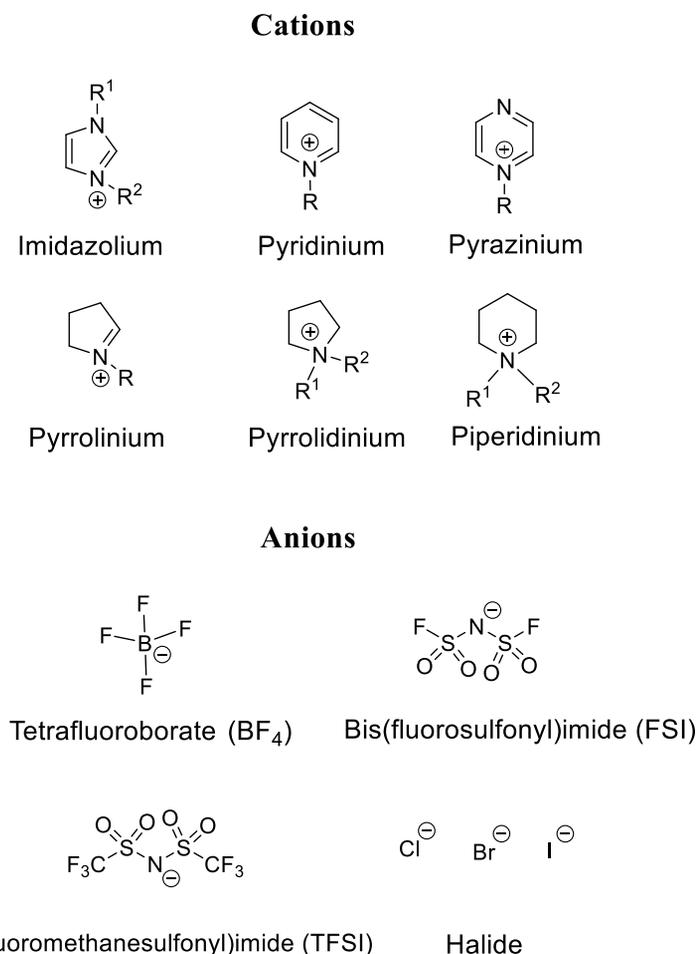
Meanwhile, lots of studies have been also conducted to develop anionic counterparts of RTILs, especially for electrolytes. In 1992, Wilkes group reported imidazolium ILs with tetrafluoroborate anion, which have low melting points, and is stable in air and water.<sup>4</sup> Other fluorinated anions such as hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide ( $\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_3$ , abbreviated as TFSI) were developed so far.<sup>5</sup> TFSI-based ionic liquids are commonly used and one of the most studied ILs, because TFSI anion contributes to various physical and electrochemical properties, such as high ionic conductivity, thermal stability, and low vapor pressure at high temperature.<sup>5(b)</sup>

To summarize, a number of ILs having various cations and anions have been studied and synthesized so far. The cationic parts of ILs can be classified into two types, cyclic and acyclic. Representative cations are imidazolium, pyridinium, and pyrrolinium ions for cyclic one, and alkylammonium and tetraalkylphosphonium ions for acyclic one, respectively.<sup>6</sup> Since the structure of cationic counterparts are assumed to greatly affect the physical/chemical properties of the ILs, many studies have been carried out for the development of cations.

Anions also play an important role in determining the properties of ILs, like water stability and viscosity. Fluorinated anions, halides,

bis(sulfonyl)imides, and sulfates are representative anions. However, much fewer anions, especially the case of unsymmetrical anions, have been reported compared to cations, since it is much harder to synthesize an anion with complex structure than a cation.

In this research, the ionic liquids with unsymmetrical bis(sulfonyl)imide anions were synthesized, noting its potential as the high-performance electrolytes in electrochemical devices.



**Figure 1.** Representative cations and anions of ionic liquids

## 1.2 Application of ionic liquids

### 1.2.1 Unique properties of ionic liquids

Since ionic liquids consist only of cations and anions, a significant amount of the intermolecular interactions between the ionic liquid molecules is ionic bonding, which is much stronger than Van der Waals force or hydrogen bonding of non-ionic liquids. The strong ionic bonding gives the ILs some unique properties; high ionic conductivity, negligible vapor pressure, and unique polarity. Besides these properties, ionic liquids have good thermal stability (nonflammability), which arises from its non-volatility, electrochemical stability in wide electrochemical window, and moderate to high viscosity.<sup>7</sup> Furthermore, designability is another property of ionic liquids, because thousands of ionic liquids can be produced depending on which cations and anions are combined. By giving slight modification to the structure of cations or anions, the ionic liquids with desirable properties can be synthesized, such as adjusting polarity of the ILs by changing the bulkiness of alkyl substituents, and changing acidity by introducing or removing the acidic protons on the heterocycle ring.<sup>8</sup>

Because of the abovementioned properties of ionic liquids, they are used in a wide range of applications, such as organic synthesis, batteries, CO<sub>2</sub> capturing, and lubricant.

## 1.2.2 Solvents in organic synthesis

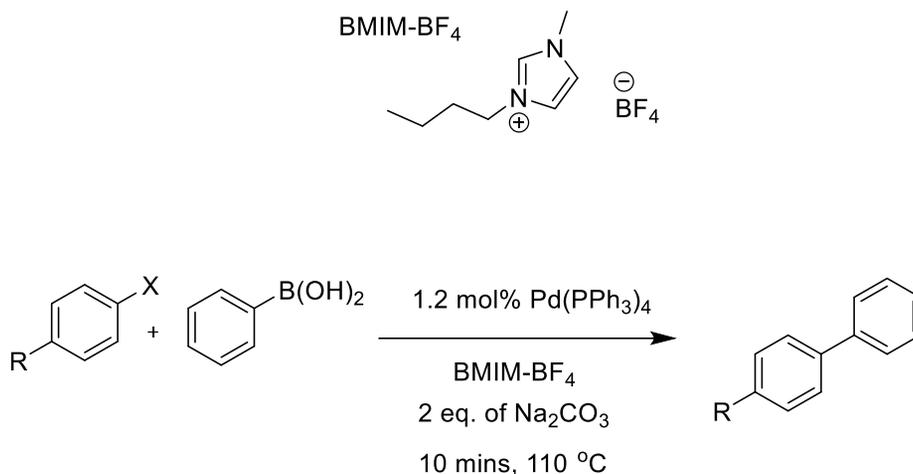
### 1.2.2.1 Suzuki coupling

There are some advantages including wide solubility range to various organic/inorganic compounds, tunability for proper use and non-volatility of ionic liquids, and catalytic ability and chirality of some ionic liquids (**Table 1**), when the ILs are used as the solvents for organic reactions instead of conventional organic solvents.<sup>9</sup>

One of the representative examples is Suzuki coupling, the carbon-carbon cross-coupling reaction catalyzed by palladium catalyst. Several ionic liquids, such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF<sub>4</sub>), and quaternary ammonium salts ((n-C<sub>7</sub>H<sub>15</sub>)<sub>4</sub>NBr), were used as a reaction solvent with proper base and Pd catalyst.<sup>10</sup> The substrate scope was broad, and the reaction yield was excellent. For example, the Suzuki reaction of bromobenzene and phenyl boronic acid under catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> conditions with BMIM-BF<sub>4</sub> was achieved in 93% yield, and the reaction time was 10 min, which means the reactivity was 90 times better than the original Suzuki reaction condition. (**Figure 2**) In addition to reactivity, the reaction was carried out under air condition without decrease of yield and catalyst decomposition. Furthermore, the catalyst activity was maintained even after repetitive catalytic reactions.<sup>10b</sup>

**Table 1.** Comparison of ionic liquids with organic solvents <sup>7(b)</sup>

Property	Organic solvents	Ionic liquids
Number of solvents	> 1,000	> 1,000,000
Catalytic ability	Rare	Common and tunable
Chirality	Rare	Common and tunable
Vapor pressure	Obeys the Clausius– Clapeyron eqn.	Negligible under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Tunability	Limited range	Unlimited range (‘designer solvents’)
Cost	Normally inexpensive	2 to 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0.2 ~ 100	22 ~ 40,000
Density/g cm <sup>-3</sup>	0.6 ~ 1.7	0.8 ~ 3.3
Refractive index	1.3 ~ 1.6	1.5 ~ 2.2

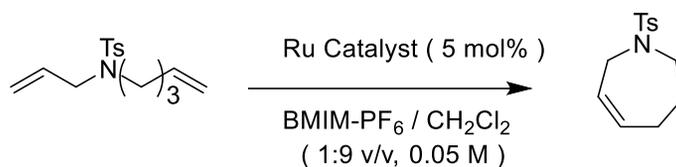


**Figure 2.** Suzuki coupling reaction with BMIM–BF<sub>4</sub>

### 1.2.2.2 Ring–Closing Metathesis

Transition metal–catalyzed ring closing metathesis (RCM) is another example that ionic liquids have been applied. RCM reaction is an olefin metathesis via the intramolecular reaction of two terminal alkenes, giving various unsaturated ring products. Similar to the case of Suzuki coupling, outstanding reactivity of ILs as the reaction media comes from their good solubility to organometallic catalysts and water stability. Ruthenium–based catalysts coordinating with various ligands are commonly used for RCM reactions, and some ILs were very effective for recycling and maintenance of activity of Ru catalysts. According to Q. Yao’s research published in 2003, co–solvents system of dichloromethane and 1–butyl–3–methylimidazolium hexafluorophosphate (BMIM–PF<sub>6</sub>), (volumetric ratio 9:1) was

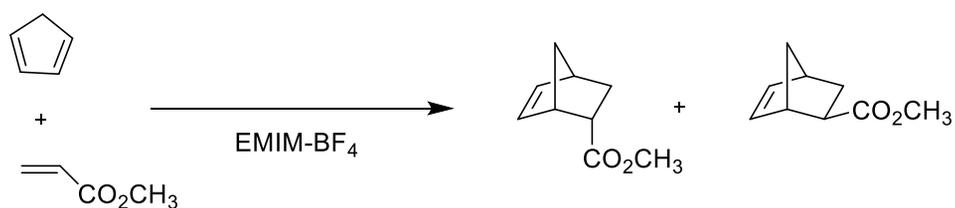
introduced. Under 5 mol% of Ru catalyst condition, the RCM reaction successfully proceeded in over 98% yield, and at least 90% yield was maintained for 10 repetitive catalytic runs.<sup>11a</sup> (**Figure 3**)



**Figure 3.** Representative Ring-closing metathesis with BMIM-PF<sub>6</sub><sup>11a</sup>

In the same year, N. Audic et al reported improved results of the RCM reaction above. Under 2.5 mol % of Ru catalyst and pure BMIM-PF<sub>6</sub> solvent system, the reaction was completed in 45 minutes with over 98% yield. Interestingly, maintenance of the catalytic activity was further improved, showing 95 % yield after 10 repetitive catalytic runs.<sup>11c</sup>

### 1.2.2.3 Diels-Alder reaction



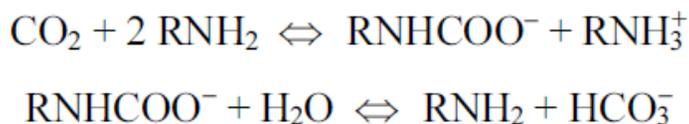
**Figure 4.** Diels-Alder reaction with EMIM-BF<sub>4</sub>

Diels-Alder reaction is a [4+2] pericyclic reaction between a conjugated diene and a dienophile. When there is a substituent in the

dienophile (alkene in this case) as the case of **Figure 4**, *endo/exo* selectivity of product is the most important problem in Diels–Alder reaction. Compared to the conventional organic solvents, use of the ionic liquids leads to the stabilization of the more polar complex (*endo*), resulting great *endo/exo* selectivity.<sup>12b</sup> Other ionic liquids including BMIM–BF<sub>4</sub>, EMIM–NO<sub>3</sub>, EMIM–PF<sub>6</sub>, and EMIM–CF<sub>3</sub>SO<sub>3</sub> were also found to be effective solvents for Diels–Alder reaction.

### 1.2.3 Effective CO<sub>2</sub> and SO<sub>2</sub> capturing fluids

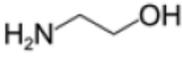
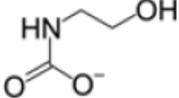
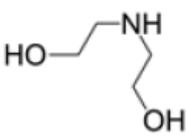
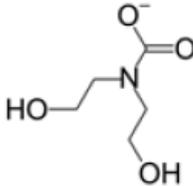
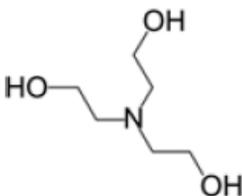
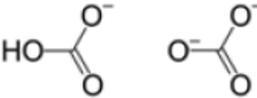
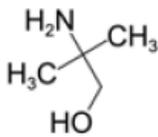
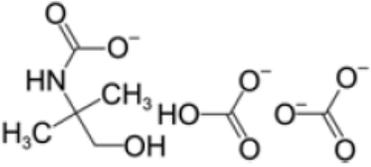
Ionic liquids have also been studied as the remarkable candidate for CO<sub>2</sub> and SO<sub>2</sub> absorbent in industrial process. CO<sub>2</sub> emission is one of the major causes of the greenhouse effect, and SO<sub>2</sub> is a toxic gas, produced from chemical engineering process. Therefore, purification of these gasses has always been a major concern, and several organic compounds such as monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) were used for CO<sub>2</sub> capturing technologies.<sup>13d</sup> As shown in **Table 2**, these amine–based compounds remove CO<sub>2</sub> by carbamate formation in the case of primary and secondary amines, and by acting as a base catalyst in the case of tertiary amine.<sup>14</sup>



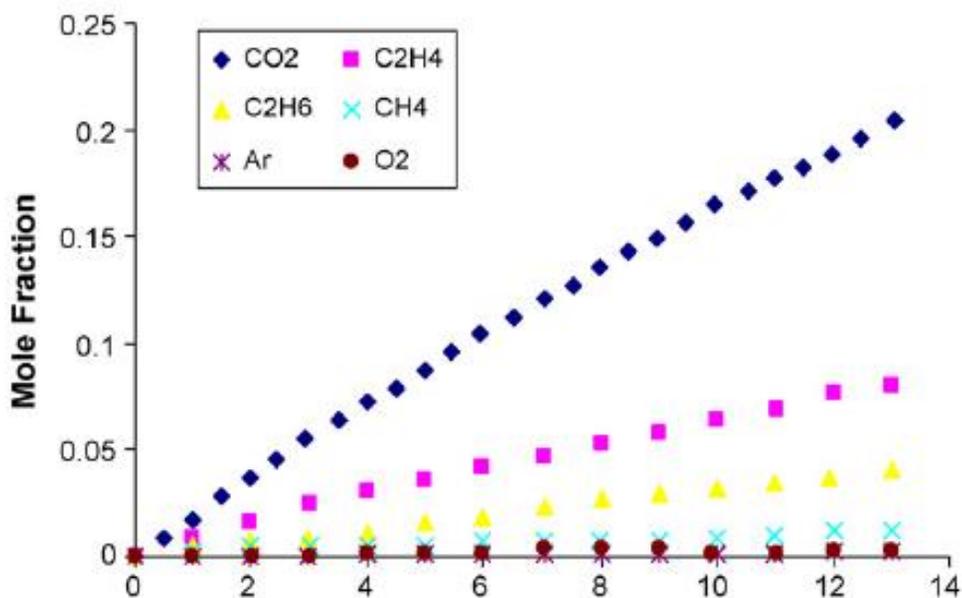
**Scheme 1.** Carbamate / carbonate formation by primary and tertiary amines

However, these reagents have limitations due to the following disadvantages; loss of the reagents caused by evaporation and degradation from corrosive byproducts and insufficient thermal stability, requiring high energy during regeneration process, and low CO<sub>2</sub> absorption capacity.<sup>13b</sup> IL's unique properties such as negligible vapor pressure, thermal and chemical stability are the essential factors to solve the problems when using the amine reagents, and many research have been conducted to apply the RTILs in this field. Furthermore, the heterocyclic ILs possessing long alkyl side chains and fluorinated anions were found to show great affinity to CO<sub>2</sub>.

**Table 2.** Structure of the amine-based species in the CO<sub>2</sub> loaded conditions<sup>14</sup>

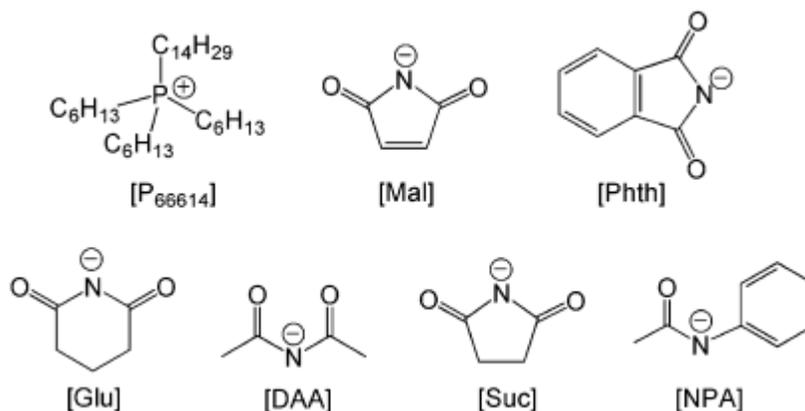
Absorbent	Molecular structure of species	
	Free amine	Carbamate, bicarbonate/carbonate
MEA		
DEA		
TEA		
AMP		

For instance, BMIM-PF<sub>6</sub> had great solubility to several gasses including CO<sub>2</sub>, methane, ethylene, and carbon monoxide in wide temperature range, and BMIM-Tf<sub>2</sub>N and EMIM-Tf<sub>2</sub>N also showed outstanding CO<sub>2</sub> removal performance, under the pressure up to 140 bars.<sup>13b</sup> (Figure 5)



**Figure 5.** Solubilities of various gasses to BMIM-PF<sub>6</sub> at room temperature (X axis means pressure in bar)

In the case of SO<sub>2</sub> purification, Guokai Cui et al reported the ILs consisting of a tetraalkylphosphonium cation and acylamido-based anions had large SO<sub>2</sub> absorption capacity up to 4.5 mole of SO<sub>2</sub> per mole of IL. (**Figure 6**) In addition, SO<sub>2</sub>-saturated acylamido-based ILs completed desorption of SO<sub>2</sub> in 30 mins under typical desorption conditions, and absorption capacity of these ILs were not decreased during six cycles.<sup>13a</sup>



**Figure 6.** Structure of cations and anions of acylamido-based ILs <sup>13a</sup>

### 1.2.4 Electrolyte for electrochemical devices

Application of ionic liquids for battery electrolytes is very promising, since ILs show high ionic conductivity whether they are used as single electrolyte or as an additive. In addition to their high conductivity, using an ionic liquid as an electrolyte can solve some problems about safety issue and protection of electrodes in the lithium ion batteries.

In overall, majority of ILs have negligible vapor pressure, so there is no possibility to explode or ignite when ILs are used for batteries. Therefore, it can be expected that safety issue will be greatly reduced due to their non-flammability. IL electrolytes can also be useful to protect the interface of electrodes, by forming solid electrolyte interface, abbreviated as SEI. Conventional method for SEI formation is the addition of lithium salts to carbonate electrolytes, but the use of ILs can also give the same effect.<sup>15</sup>

Electrochemical stability in wide voltage range is another important factor to prevent the decomposition of electrodes and electrolytes. In general, about 4V of electrochemical window is necessary for practical applications in Li<sup>+</sup> ion batteries. Alkyl substituted imidazolium-based ILs usually show ~4V of electrochemical window, and several piperidinium- and pyrrolidinium- ILs are even stable over 6V range.<sup>16</sup> Furthermore, lots of ILs start to be decomposed at least 200 °C, and such thermal stability of ILs guarantees the stable performance of batteries even at high temperatures.

**Table 3.** Properties of imidazolium ILs and organic solvents<sup>18</sup>

\* Viscosity ( $\eta$ ), density ( $\rho$ ), ionic conductivity ( $\kappa$ ), and electrochemical window (EW)

Ionic liquids	$\eta$ (cP)	$\rho$ (g/cm <sup>3</sup> )	$\kappa$ (mS cm <sup>-1</sup> )	EW (V)
C <sub>2</sub> mim-NTf <sub>2</sub>	34	1.53	8.8	4.3
C <sub>4</sub> mim-NTf <sub>2</sub>	52	1.44	3.9	4.8
C <sub>8</sub> mim-NTf <sub>2</sub>	74	1.33	–	5.0
C <sub>6</sub> mim-FAP	74	1.56	1.3	5.3
C <sub>4</sub> mpyrr-NTf <sub>2</sub>	89	1.4	2.2	5.2
C <sub>4</sub> mim-OTf	90	1.3	3.7	4.9
C <sub>4</sub> mim-BF <sub>4</sub>	112	1.21	1.7	4.7
C <sub>4</sub> mim-NO <sub>3</sub>	266	1.16	–	3.7
C <sub>4</sub> mim-PF <sub>6</sub>	371	1.37	1.5	4.7
C <sub>4</sub> mim-I	1110	1.49	–	2.1

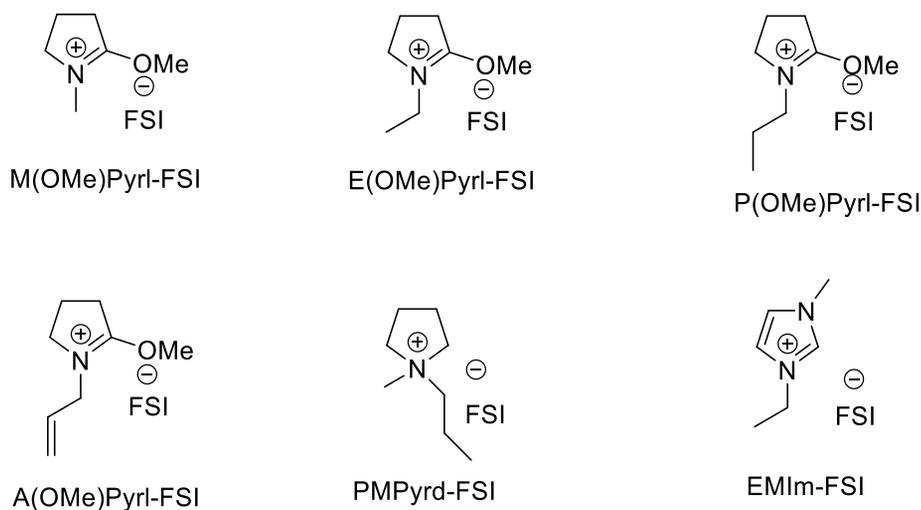
C <sub>6</sub> mim-Cl	7453	1.05	–	3.2
DMSO	1.99	1.10	2.7	4.4
Propylene Carbonate	2.5	1.21		4.7

Despite these advantages of ILs, there are some obstacles to overcome for practical applications. First, their high viscosity compared to conventional carbonates should be reduced, since highly viscous compounds are hard to handle, (**Table 3**) and there is a retardance to reach the maximum performance as such viscous materials take relatively long time to fill the space inside the electrodes. Second, the number of charging/discharging cycles needs to be improved. The number of cycles are reported 10~100 cycles for ILs, whereas the classical electrolytes show 500~1000 cycles.<sup>16,17</sup>

## Chapter 2. Results and Discussion

### 2.1 Previous Work and Design of the target ILs

Many researches have been conducted to synthesize new ionic liquids that have desirable properties for LIB electrolytes, such as high ionic conductivity, low viscosity, wide electrochemical window, and non-flammability. In our group, there have been several researches to develop novel ionic liquids consisting of imidazolium- and pyrrolinium cations, and fluorinated anions.<sup>19,20</sup> The structure and physicochemical properties of synthesized ILs are indicated in **Table 4** and **Figure 7**<sup>20</sup>.



**Figure 7.** The structure of the prepared ILs in the previous work

**Table 4.** Td, viscosity, and ionic conductivity of the prepared ILs

Ionic liquids	Viscosity (cP)	Ionic conductivity (mS cm <sup>-1</sup> )	Td (°C)
E(OMe)Pyr1- FSI	32.0	13.0	159
P(OMe)Pyr1- FSI	40.0	8.4	165
A(OMe)Pyr1- FSI	30.0	10.2	150
PMPyrd-FSI <sup>a</sup>	40.0	8.8	257
EMIm-FSI <sup>a</sup>	19.0	15.8	273

a: Known compounds

In the previous research published in 2017<sup>20</sup>, the structure of target compounds was designed based on chemical theories. In general, as the bulkiness of the molecule becomes smaller, the viscosity decreases. And the planarity of the molecular structure also contributes to the decrease in the viscosity, because the intermolecular facile slip is allowed between planar molecules.<sup>21</sup> According to the Walden's rule, viscosity and ionic conductivity are inversely proportional regardless of solvents. Therefore, we expected that the introduction of partially planar C-N double bond to the pyrrolinium cation and less bulky alkyl substituents would give lower viscosity and higher ionic conductivity.

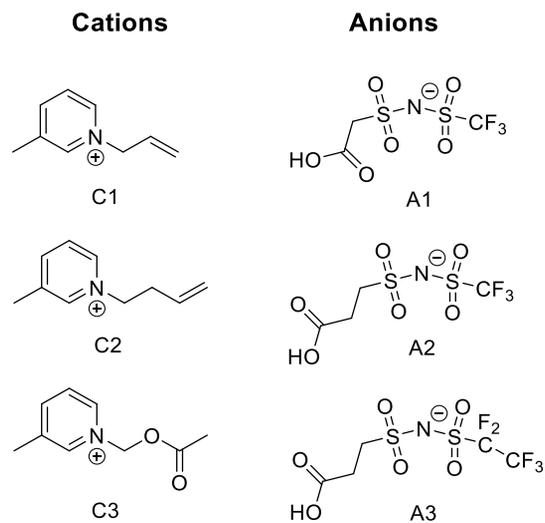
Then the four pyrrolinium-based ionic liquids were newly synthesized in excellent yield, and their various properties including viscosity, conductivity, Td (decomposition temperatures), DSC analysis, discharge capacity in a half cell, and retention ratio after 50 cycles were reported. As shown in **Table 4**, the pyrrolinium-based ILs were measured to have high Td, which ensures great thermal stability, and E(OMe)Pyr1-FSI and A(OMe)Pyr1-FSI were found to have moderate viscosity and high ionic conductivity. Especially, the ionic conductivity value of E(OMe)Pyr1-FSI was  $13.0 \text{ mS cm}^{-1}$ , which is 1.5 times better than that of the conventional organic carbonates. (**Table 5**)<sup>20</sup>

**Table 5.** Physicochemical properties of the carbonate electrolytes

Carbonates	Flash point (°C)	Vapor pressure(kP)	Viscosity (cP)	Conductivity (mS/cm)
DMC	16	8.0	0.59	8.0
EMC	23.5	3.9	0.65	3.0
DEC	33	2.4	0.75	–
EC (Solid at RT)	145.5	–	480	–
PC	135.5	0.003	2.5	6.2

From the promising results of the previous research mentioned above, a novel pyridinium-based ionic liquid was designed with slight modification in its structure. Since the planarity was one of the key factor to affect the viscosity and the ionic conductivity, 3-methylpyridinium cation was chosen as a cationic counterpart of the target IL, which has much more planar heterocycle ring than pyrrolinium. At the nitrogen in the 3-methylpyridinium cation, alkyl groups were substituted, to remove the acidic proton, and thereby to increase chemical stability of the target IL. As the alkylated groups, allyl and 3-butenyl group were chosen since they have a planar C=C double bond, and are not too bulky. Lastly, a novel, unsymmetrical bis(sulfonyl)imide was selected as an anion counterpart, which is unreported so far. The asymmetry of the anion was expected to bring lower viscosity than that of the symmetric fluorinated anions such as FSI and TFSI.

Plus, the molecular dynamics (MD) simulation results indicated that the target ILs we designed would show the outstanding ionic conductivity, which is much higher than EMIm-FSI (15.8 mS/cm).<sup>22</sup> The MD simulation was conducted with the condition of 298.15 K, 1 atm, and 310 ion pairs. Among the simulated ILs based on C1, C2, and C3 cations and A1, A2, and A3 anions, we chose C1A1, C2A2, and their ester forms (C1A2-Ester and C2A2-Ester respectively) as the target compounds. (**Figure 8** and **Table 6**)



**Figure 8.** Cationic and anionic counterparts of the simulated ILs

**Table 6.** Predicted properties of the simulated ILs

Ionic liquids	Ionic cond. (S/m)	Predicted EW (V)
[C <sub>1</sub> ] [A <sub>1</sub> ]	6.91	4.48
[C <sub>1</sub> ] [A <sub>2</sub> ]	6.88	4.11
[C <sub>1</sub> ] [A <sub>3</sub> ]	6.93	4.13
[C <sub>2</sub> ] [A <sub>1</sub> ]	6.97	3.75
[C <sub>2</sub> ] [A <sub>2</sub> ]	6.95	3.38
[C <sub>2</sub> ] [A <sub>3</sub> ]	6.96	3.39
[C <sub>3</sub> ] [A <sub>1</sub> ]	6.67	4.31
[C <sub>3</sub> ] [A <sub>2</sub> ]	6.58	3.94
[C <sub>3</sub> ] [A <sub>3</sub> ]	6.72	3.96

## 2.2 Preparation of the target ILs

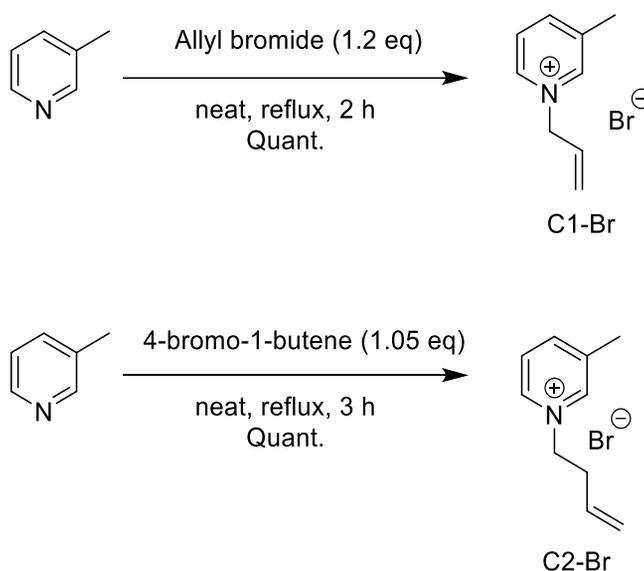
### 2.2.1 Synthesis of the 3-methylpyridinium-based cations

To synthesize the cationic counterpart of the target ILs (C1 and C2), 1-alkyl-3-methylpyridinium bromide was prepared as a precursor. Both reactions proceeded easily by S<sub>N</sub>2 mechanism, the nucleophilic attack of nitrogen in 3-methylpyridine toward the bromide reagent.

First, for the synthesis of 1-allyl-3-methylpyridinium bromide (C1-br), the mixture of 3-methylpyridine and allyl bromide was stirred under reflux condition (75 °C) for 2 hours. At first, this reaction was carried out without distillation of starting materials prior to the reaction, but a trace amount of impurities were detected on <sup>1</sup>H-NMR. When distilled 3-methylpyridine and allyl bromide were used, the purified product was obtained as a colorless solid, and there were no impurity detected on <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The crude product was obtained in quantitative yield, and it was a pale yellow solid. The crude was washed by diethyl ether and ethyl acetate, 3 times each, to remove the residual starting materials. As the purification process was repeated, the product became colorless solid.

Second, the synthesis of 1-(3-butenyl)-3-methylpyridinium bromide (C2-br) was conducted under similar reaction conditions to

C1-br. This reaction was not finished completely under 75 °C reflux for 2 hours. After the reflux condition was increased to 100 °C and the reaction time was extended to 3 hours, the crude C2-br was produced in quantitative yield. The purification was exactly same with that of C1-br, and the pure C2-br was obtained as a pale yellow oil, in quantitative yield. (Figure 9)



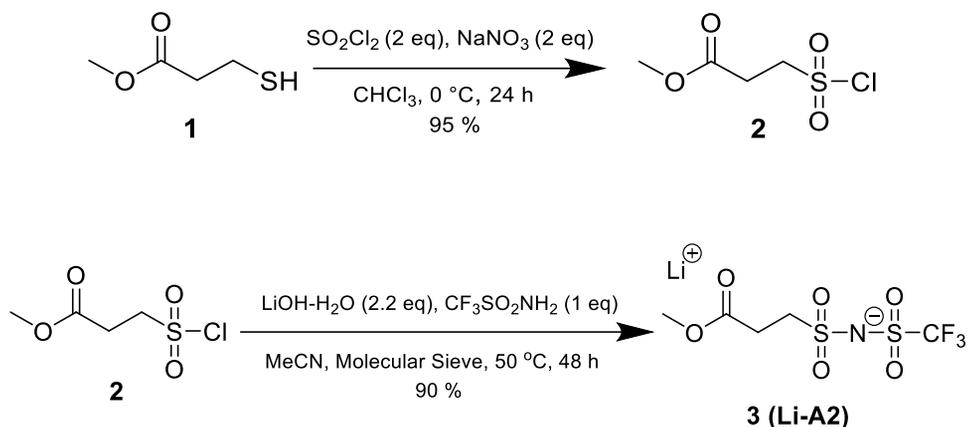
**Figure 9.** Synthesis of C1-Br and C2-Br

### 2.2.2 Synthesis of the unsymmetrical bis(sulfonyl) – imide anion

As an A2 anion precursor of the target ILs, the lithium salt of the unsymmetrical bis(sulfonyl)imide anion (A2) was synthesized in two

steps. The first step is introduction of sulfonyl chloride group to the thiol through oxidative chlorination, and the second step is formation of lithium salt of A2 anion (Li-A2) through the nucleophilic attack of the amine group of sulfonamide. The reaction scheme is shown in **Figure 10**.

The first step started from methyl 3-mercaptoacrylate, with addition of 2 equiv. of sodium nitrate and 2 equiv. of sulfuryl chloride.



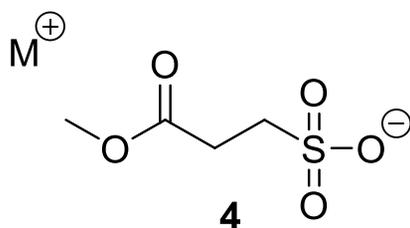
**Figure 10.** Synthesis of Li-A2

Initially, preparation of compound 2 was attempted by other sulfonyl chlorination methods that were reported previously, such as using  $\text{H}_2\text{O}_2$  and  $\text{SOCl}_2$ ,<sup>23a</sup> or  $\text{H}_2\text{O}_2$  and  $\text{ZrCl}_4$  with acetonitrile and pyridine.<sup>23b</sup> Both reactions were reported to require short reaction time (2~3 hours) and give excellent yield (95%), but it didn't work to our reaction scheme, because compound 2 was very vulnerable to water and its sulfonyl chloride group was rapidly hydrolyzed to form a sulfonic acid.

Then the reaction condition was modified to the anhydrous one, using

sulfonyl chloride and sodium nitrate. This reaction was carried out at room temperature at first, and significant amount of side products was produced, which is assumed to be a disulfide intermediate. Finally, compound 2 was obtained in 95% yield with trace amount of impurities when the reaction was conducted at 0 °C. The quite pure crude product was easily obtained only after filtration.

The next step, synthesis of compound 3 (Li-A2) was more challenging than the first step. Several bases were screened including  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and  $\text{NaH}$ . In every case, the hydrolyzed side product lithium/sodium sulfonate salt (compound 4, **Figure 11**) was formed in significant amount, except  $\text{NaH}$ . In  $\text{NaH}$  condition, Na-A2 was obtained in 80% yield without compound 4.



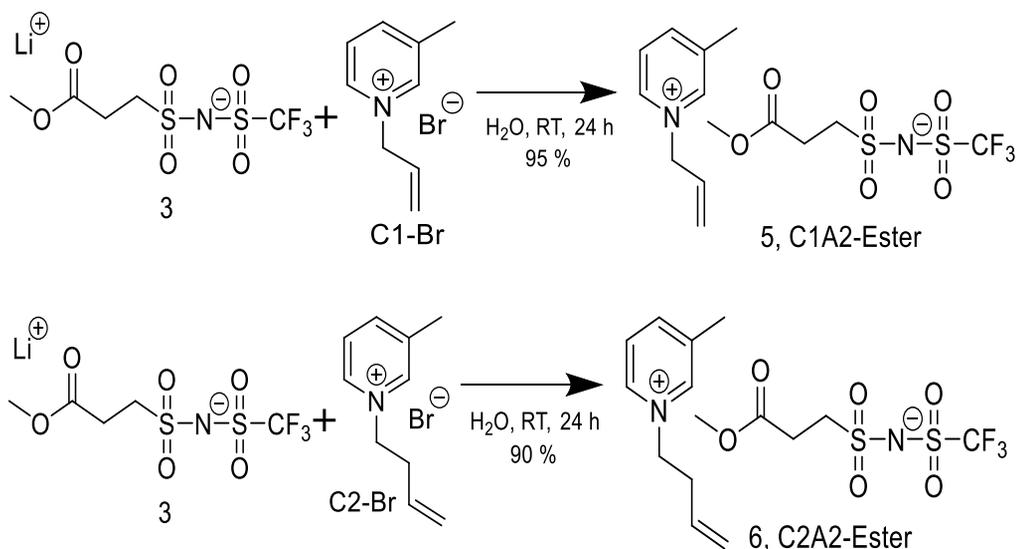
**Figure 11.** Structure of metal sulfonate salt (M = Li, Na)

Under  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{NaOH}$  conditions, compound 4 was produced dominantly.  $\text{LiOH}\cdot\text{H}_2\text{O}$  was another effective base to produce Li-A2, and the purified yield was ~70% when the reaction was carried out at room temperature with undistilled acetonitrile. Then, this reaction was conducted under anhydrous condition with distilled acetonitrile to remove the water completely and minimize compound

4, and the reaction temperature was elevated to 50 °C. The water content in LiOH–H<sub>2</sub>O was controlled by adding molecular sieve. At last, Li–A2 was obtained in 90% yield under this reaction condition.

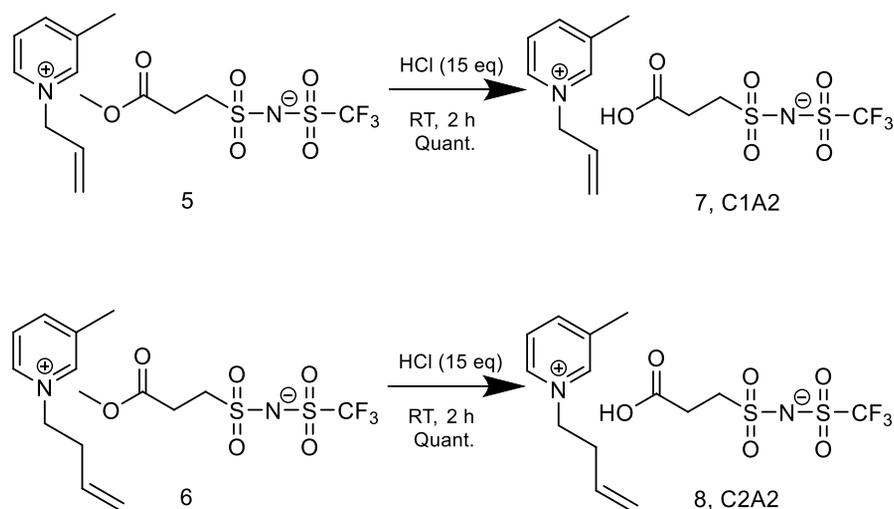
### 2.2.3 Synthesis of the target ILs

From the cationic precursor C1–Br and C2–Br, and the anionic precursor Li–A2, the target ILs were easily synthesized by ionic exchange reaction. This reaction was conducted under room temperature in aqueous solution. (**Figure 12**) Since the solubility of the products was better in dichloromethane than in water, the crude product was easily purified by CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O extraction.



**Figure 12.** Synthesis of C1A2–Ester and C2A2–Ester

The final products, C1A2 and C2A2, were produced through the acidic hydrolysis reaction of ester groups in C1A2-Ester and C2A2-Ester, respectively. (Figure 13) Both of them were obtained in quantitative yields.



**Figure 13.** Synthesis of C1A2 and C2A2

The four desired ILs, C1A2-Ester, C2A2-Ester, C1A2, and C2A2 were synthesized in 4 or 5 steps. C1A2-Ester and C1A2 were obtained in 82% overall yield, and C2A2-Ester and C2A2 were obtained in 77% overall yield. These ILs are unreported, novel compounds, and they were fully characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,  $^{19}\text{F-NMR}$ , and elemental analysis. (See Experimental section.)

### 2.3. Viscosity and ionic conductivity of the prepared ILs

Viscosity and ionic conductivity of the four synthesized ILs were measured at room temperature. (**Table 7**) For the measurement of ionic conductivity, a half cell was used. (distance between electrodes (d) = 0.6 cm, width (w) = 0.45 cm, height (h) = 0.3 cm) Through the EIS (Electrochemical Impedance Spectroscopy) software and a two electrodes cell, the resistances of the electrolytes were measured at high frequency ( $>10^5$  Hz). In the low frequency region, the direction of current slowly changes, resulting the electrons penetrate deeper into the space of the electrode. Since the surface of an electrode is slightly coarse, the distance between electrodes is not uniform. In contrast, at high frequencies, the direction of electrons changes very quickly, and it can be assumed that the distance between electrodes is uniform.

The ionic conductivity was calculated from the equation shown in **Figure 14**.

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

$\sigma$ : Ionic conductivity (S/cm)

l: distance between electrodes (cm)

A: Area of electrodes (cm<sup>2</sup>)

R: Resistance of an electrolyte

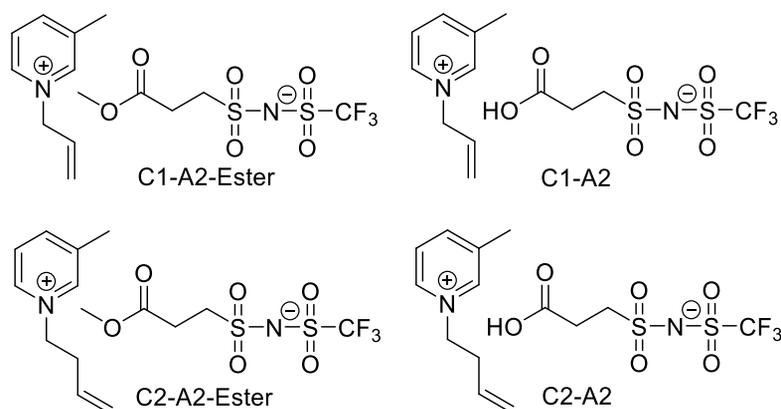
**Figure 14.** Equation of ionic conductivity and resistance

The viscosity of C1A2 and C2A2 was not able to be measured, since

their viscosity values were higher than the measurement limit of the viscometer (1000 cP).

In overall, the ionic conductivity values of the products were much lower than the predicted values based on MD simulations. Their viscosity was also too high to handle, indicating that these four ILs might be not suitable for the single electrolyte in LIBs.

**Table 7.** Physicochemical properties of the prepared ILs



Ionic liquids	Resistance ( $\Omega$ )	Viscosity (cP)	Ionic conductivity (mS/cm)
C1A2-Ester	$7.34 \times 10^3$	299.8	0.61
C2A2-Ester	$8.69 \times 10^3$	509.4	0.52
C1A2	$14.9 \times 10^3$	—*	0.30
C2A2	$15.7 \times 10^3$	—*	0.28

\*Viscosity of C1A2 and C2A2 were higher than the measurement limit of the viscometer (> 1000cP)

Meanwhile, there was correlation between the bulkiness of the ILs and their properties. As the molecular size of the ILs increases, viscosity becomes larger and ionic conductivity was increased, which is shown in the comparison of C1A2–Ester and C2A2–Ester. The most interesting thing is the extremely high viscosity of C1A2 and C2A2 that is larger than 1000 cP. This may arise from the introduction of highly polar carboxylic group, resulting intermolecular hydrogen bonding and thus, dramatic increase in viscosity.

## **2.4 Viscosity and ionic conductivity of the binary mixtures**

Many ionic liquids have been found to indicate higher ionic conductivity when they are diluted with polar organic solvents. There have been several researches reporting that the binary mixtures of ILs and organic solvents show the maximum conductivity at 10:90 ~ 20:80 (IL:Solvents) volumetric ratio.<sup>24</sup>

Based on these studies, we prepared the binary mixtures of the synthesized ILs and organic carbonates. The 1:2 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was chosen as organic carbonate for three reasons. (1) EC/DEC solution is one of the commonly used electrolytes. (2) Carbonate–based electrolytes with short alkyl chains would be soluble to the ILs, owing to the interactions between carbonyl groups of both components. (3) EC and DEC are

commercially available, and relatively cheap electrolytes.

For each IL synthesized, the binary mixtures of six different concentrations (100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 in v/v) were prepared, and viscosity and ionic conductivity were measured. (Table 8 ~ 11, Figure 15, 16)

**Table 8.** Viscosity and ionic conductivity of [C1A2–Ester] [EC/DEC] mixture

Conc. (IL:Carbonate)	Resistance ( $\Omega$ )	Viscosity (cP)	Ionic conductivity (mS/cm <sup>-1</sup> )
100 : 0	7.34 x 10 <sup>3</sup>	299.8	0.61
80 : 20	4.97 x 10 <sup>3</sup>	35.9	0.90
60 : 40	729	17.3	6.10
40 : 60	503	7.20	8.84
20 : 80	543	2.30	8.19
0 : 100	3.05 x 10 <sup>3</sup>	1.36	1.46

Comparing the binary mixtures of C1A2–Ester and C2A2–Ester, C1A2–Ester had smaller viscosity and larger ionic conductivity than C2A2–Ester, in all concentrations. (Table 8, 9) This may arise from the difference in bulkiness. Since C2A2–Ester has one more methylene group in the cation, Van der Waals interactions between C2A2–Ester molecules are stronger, resulting higher viscosity than C1A2–Ester.

**Table 9.** Viscosity and ionic conductivity of [C2A2–Ester] [EC/DEC] mixture

Conc. (IL:Carbonate)	Resistance ( $\Omega$ )	Viscosity (cP)	Ionic conductivity (mS/cm <sup>-1</sup> )
100 : 0	8.69 x 10 <sup>3</sup>	509.4	0.52
80 : 20	2.28 x 10 <sup>3</sup>	53.6	1.95
60 : 40	961	19.0	4.63
40 : 60	739	8.65	6.01
20 : 80	1.09 x 10 <sup>3</sup>	3.10	4.16
0 : 100	3.05 x 10 <sup>3</sup>	1.36	1.46

**Table 10.** Viscosity and ionic conductivity of [C1A2] [EC/DEC] mixture

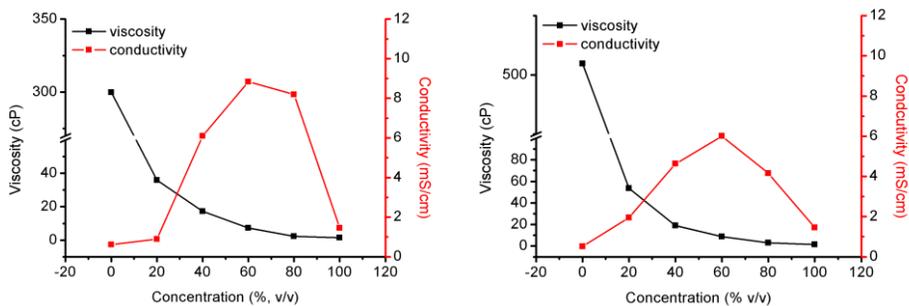
Conc. (IL:Carbonate)	Resistance ( $\Omega$ )	Viscosity (cP)	Ionic conductivity (mS/cm <sup>-1</sup> )
100 : 0	14.9 x 10 <sup>3</sup>	–	0.30
80 : 20	1.75 x 10 <sup>3</sup>	171.6	2.54
60 : 40	982	31.0	4.53
40 : 60	964	13.8	4.61
20 : 80	669	4.81	6.64
0 : 100	3.05 x 10 <sup>3</sup>	1.36	1.46

The presence of a methylene group also led to the similar results in the binary mixtures of C1A2 and C2A2. (Table 10, 11) One noticeable thing is that, the maximum conductivity of C1A2 mixtures was larger

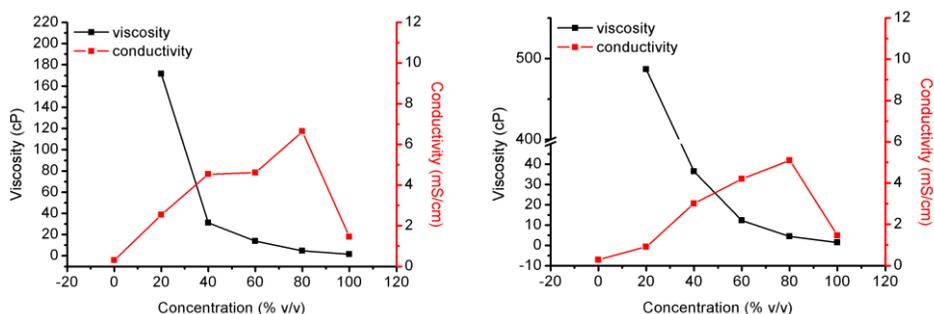
than that of C2A2–Ester mixtures (6.01 mS/cm and 6.64 mS/cm respectively), which is contrary to the result of pure ILs. Since the number of hydrogen bonding decreases in diluted mixtures, the effect of the molecular size dominates the effect of hydrogen bonding. In consequence, the less bulky IL, C1A2, shows a smaller minimum value of ionic conductivity than C2A2–Ester, in diluted concentrations.

**Table 11.** Viscosity and ionic conductivity of [C2A2][EC/DEC] mixture

Conc. (IL:Carbonate)	Resistance ( $\Omega$ )	Viscosity (cP)	Ionic conductivity (mS/cm <sup>-1</sup> )
100 : 0	15.7 x 10 <sup>3</sup>	–	0.28
80 : 20	4.9 x 10 <sup>3</sup>	486.7	0.91
60 : 40	1.48 x 10 <sup>3</sup>	36.4	3.00
40 : 60	1.06 x 10 <sup>3</sup>	12.2	4.19
20 : 80	872	4.44	5.10
0 : 100	3.05 x 10 <sup>3</sup>	1.36	1.46



**Figure 15.** Physicochemical properties of [C1A2-Ester] [EC/DEC] (left) and [C2A2-Ester] [EC/DEC] (right)



**Figure 16.** Physicochemical properties of [C1A2] [EC/DEC] (left) and [C2A2] [EC/DEC] (right)

In general, the results of viscosity and ionic conductivity analysis of the binary mixtures were consistent with the previous studies, showing the maximum conductivity at concentration (v:v) of 40:60 or 20:80. In all cases, inverse proportion was observed between viscosity and conductivity. (Figure 15, 16)

Although the highest conductivity value measured (8.84 mS/cm, [C1A2-Ester] [EC/DEC]) is not so competitive comparing to the previously synthesized pyrrolinium-based ILs in our group, these ILs

are still promising as their ionic conductivities were drastically increased as the concentration of the ILs dilutes. The conductivity values of the binary mixtures of every prepared IL were at least 10 times higher than that of the pure ILs. Especially, an increase by 22 times was shown in the case of [C1A2] [EC/DEC] binary mixture.

## Chapter 3. Conclusion

A number of studies have been conducted to synthesize high-performance ionic liquids, especially the development of a variety of cations. However, there have been little research on the synthesis of unsymmetrical anions. In this paper, four novel ionic liquids, containing 3-methylpyridinium-based cations and unsymmetrical bis(sulfonyl)imide anion, were synthesized in 5 steps. Every reaction step was optimized to achieve at least 90% yield, and the overall yields were 77 ~ 82%. All of the prepared ILs were completely analyzed by  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR,  $^{19}\text{F}$ -NMR, and elemental analysis, and their viscosity and ionic conductivity were also measured to test the performance of these ILs for electrochemical applications.

In addition to the pure ILs, viscosity and conductivity of the binary mixtures of the prepared ILs and EC/DEC electrolytes were also measured. As the concentration of the ILs in the binary mixtures decreases, the viscosity was reduced and the ionic conductivity increased. The viscosity and ionic conductivity showed an inverse proportion, which is consistent with Walden's rule.

Above all, one of the prepared ILs, C1A2-Ester, showed the best performance, especially in the 40:60 binary mixture. The ionic conductivity of pure C1A2-Ester was only  $0.61 \text{ mS/cm}^{-1}$ , but over 10 times increase was observed ( $8.84 \text{ mS/cm}^{-1}$ ) in the binary mixture.

This result indicates that the synthesized ILs have the potential to be

an excellent additive for battery electrolytes. Several binary mixtures of N-heterocyclic ILs and organic carbonates have been studied. For example, the binary mixture of *N*-butyl-*N*-methylpyrrolidinium (PYR<sub>1,4</sub>) TFSI and propylene carbonate indicates the maximum conductivity (5.2 mS/cm) at 50:50 concentration, which is about 5 times larger than pure PYR<sub>1,4</sub> TFSI.<sup>25a</sup> Meanwhile, the binary mixture of BMIM TFSI and propylene carbonate showed an outstanding conductivity (12.1 mS/cm) at 20:80 concentration, but it increased only 3 times comparing to pure BMIM TFSI (4.00 mS/cm).<sup>25b</sup>

Considering the researches mentioned above, over 10 times increase of ionic conductivity of the synthesized ILs in this work is thought to be an outstanding result. Especially, C1A2-Ester is expected to be a promising additive for the carbonate electrolytes, in terms of electrochemical performance,

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# Experimental Details

## 1. General

Materials were purchased from commercial suppliers and used without further purification. 3-methylpyridine, 4-bromo-1-butene, and allyl bromide were distilled prior to use to obtain pure product. All experimental glassware, syringes, magnetic stirring bars, and molecular sieves were oven-dried and stored in a desiccator before use.

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were obtained in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  on a Bruker Avance III spectrometer (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  NMR). The  $^1\text{H}$  NMR spectroscopic data were reported as follows in ppm from the internal standard (TMS, 0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration). The  $^{13}\text{C}$  NMR spectra were referenced with the 77.16 resonance of  $\text{CDCl}_3$  and 39.52 in  $\text{DMSO}-d_6$ .

Viscosity measurements were carried out on a Brookfield DC-II+cone/plate viscometer. Ionic conductivity was determined using Electrochemical Impedance Spectroscopy of THALES software to measure the resistance at high frequency over  $10^5$  Hz. The values of viscosity and ionic conductivity were measured three times, and averaged. Elemental analysis was performed on a US/CHNS-932.

## 2. General Procedure for the Preparation of the asymmetric bis(sulfonyl)imide-based ionic liquids

### 2.1. General procedure for the preparation of 1-allyl-3-methylpyridinium bromide

3-methylpyridine (20.55 mmol) and allyl bromide (24.66 mmol, 1.2 equiv.) were added to a 100 mL RB flask at room temperature. The reaction mixture was stirred at reflux condition for 2 hours. After the reaction was completed, the resulting solution was washed successively with diethyl ether (40 mL x 3) and ethyl acetate (40 mL x 3) to remove the unreacted allyl bromide and other impurities. After the washed solution was precipitated into white solid, the residual solvent in the resulting solution was removed under reduced pressure by rotary evaporator to afford 1-allyl-3-methylpyridinium bromide as a white powder.

### 2.2. General procedure for the preparation of 1-(3-butenyl)-3-methylpyridinium bromide

3-methylpyridine (20.55 mmol) and 4-bromo-1-butene (21.57 mmol, 1.05 equiv.) were added to a 100 mL RB flask at room

temperature. The reaction mixture was stirred at reflux condition for 3 hours. After the reaction was finished, the resulting solution was washed successively with diethyl ether (40 mL x 4) and ethyl acetate (40 mL x 4) to remove the unreacted starting material. After the washed solution (bottom layer) was diluted with ethyl acetate (50 mL), the resulting solution was dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure to afford 1-(3-butenyl)-3-methylpyridinium bromide as a pale-yellow oil.

### 2.3. General procedure for the preparation of methyl 3-(chlorosulfonyl)propanoate

To a chloroform ( $\text{CHCl}_3$ , 30 mL) solution of sodium nitrate (18.06 mmol, 2.0 equiv.) in a 100 mL RB flask was added sulfuryl chloride (18.06 mmol, 2.0 equiv.) at room temperature. After the reaction mixture was stirred at 0 °C condition for 30 minutes, methyl 3-mercaptopropanoate (9.03 mmol) was added dropwise to the reaction mixture. Then, the reaction mixture was stirred in an ice bath for 24 hours. After the reaction was completed, the resulting solution was filtered to remove the residual sodium nitrate. The filtrate was concentrated under reduced pressure by rotary evaporator to remove residual chloroform and unreacted methyl 3-mercaptopropanoate. After evaporation, methyl 3-(chlorosulfonyl)propanoate was obtained as a colorless liquid.

#### 2.4. General procedure for the preparation of lithium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (Li-A2)

To a distilled acetonitrile ( $\text{CH}_3\text{CN}$ , 12 mL) solution of trifluoromethanesulfonamide (9.03 mmol, 1 equiv.) and 4 Å molecular sieve (1.0 g) in a 100 mL RB flask was added lithium hydroxide monohydrate (19.86 mmol, 2.2 equiv.) at room temperature under nitrogen atmosphere. After the reaction mixture was stirred at room temperature for 1 hour under anhydrous conditions, methyl 3-(chlorosulfonyl)propanoate (9.03 mmol) was added dropwise. Then, the reaction mixture was stirred at 50 °C for 48 hours. After the reaction was completed, the resulting solution was filtrated to remove molecular sieve and other impurities, which are insoluble to acetonitrile. The filtrate was concentrated under reduced pressure to obtain pale-yellow solid. Afterward, 5 mL of acetonitrile and 50 mL of dichloromethane were added to the resulting solid, and the desired product was precipitated as a white solid. Other side products were soluble to the supernatant organic solvents, and it was removed by decantation. After repeating abovementioned decantation procedure for 3 times, the residual solvent was removed under reduced pressure by rotary evaporator, to give a white, crystalline powder of lithium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide.

2.5. General procedure for the preparation of 1-alkyl-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (C1A2-Ester and C2A2-Ester)

To a aqueous solution (15 mL) of lithium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (10.0 mmol, 1.0 equiv.) in a 100 mL RB flask was added 1-alkyl-3-methylpyridinium bromide (10.0 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 24 hours under nitrogen atmosphere, the resulting solution was extracted with dichloromethane (100 mL x 4). Afterward, the organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a colorless oil of 1-alkyl-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide.

(Alkyl = allyl, and 3-butenyl)

2.6. General procedure for the preparation of 1-alkyl-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (C1A2 and C2A2)

1-alkyl-3-methylpyridinium((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide (5.0 mmol) and 1N HCl (75.0 mmol, 15 equiv.) were added to a 250 mL RB flask at room temperature. The reaction mixture was stirred at 75 °C for 3 hours. After the reaction was finished, the resulting solution was evaporated under reduced pressure to remove water and unreacted HCl. Finally, 1-alkyl-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide was obtained as a colorless oil.

## 2.7. Preparation of the binary electrolytes of synthesized ionic liquids

To measure the viscosity and ionic conductivity, the ionic liquids were mixed the carbonate electrolytes (Ethylene carbonate, EC : Diethyl carbonate, DEC = 1:2 ( v:v )). Then, the mixtures were stirred for 10 minutes at room temperature and dried at 50 °C in vacuum oven for 8 hours for removing the water in ILs. It should be noted that we selected the EC/DEC mixture carbonate as a component of the electrolyte solution, because (1) EC/DEC 1:2 mixture is one of the most commonly used carbonate electrolytes used in various electrochemical studies, and (2) EC and DEC are commercially available and much cheaper than other carbonates such as propylene carbonate.

### **1-allyl-3-methylpyridinium bromide**

$^1\text{H}$  NMR (400 MHz) – DMSO- $d_6$ :  $\delta$  2.51 (s, 3H), 5.22 (d,  $J = 6$ , H), 5.44 (m,  $J = 1.2$ , 2H), 6.16 (m, 1H), 8.08 (q,  $J = 6.4$ , 1H), 8.48 (d,  $J = 8$ , 1H), 8.88 (d,  $J = 6$ , 1H), 8.96 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) – DMSO- $d_6$ :

$\delta$  17.8, 61.9, 121.9, 127.4, 131.6, 138.7, 141.9, 144.2, 146.1

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

$^1\text{H}$  NMR (400 MHz) – DMSO- $d_6$ :  $\delta$  2.50 (s, 3H), 2.71 (q,  $J = 7.2$ , 2H), 4.67 (m,  $J = 2$ , 2H), 5.02 (m, 2H), 5.81 (m, 1H), 8.06 (m,  $J = 6.4$ , 1H), 8.45 (d,  $J = 8$ , 1H), 8.92 (d, 1H), 9.03 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) – DMSO- $d_6$ :

$\delta$  18.3, 35.1, 60.0, 119.4, 127.7, 133.5, 139.1, 142.5, 144.7, 146.4

### **methyl 3-(chlorosulfonyl)propanoate**

$^1\text{H}$  NMR (400 MHz) –  $\text{CDCl}_3$ :  $\delta$  3.06 (t,  $J = 7.6$ , 2H), 3.78 (s, 3H), 4.00 (t,  $J = 7.6$ , 2H)

$^{13}\text{C}$  NMR (100 MHz) –  $\text{CDCl}_3$ :  $\delta$  29.0, 52.8, 60.1, 169.2

### **Lithium ((3-methoxy-3-oxopropyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide (Li-A2)**

$^1\text{H}$  NMR (400 MHz) – DMSO- $d_6$ :  $\delta$  2.68 (t,  $J = 8$ , 2H), 3.22 (t,  $J = 8$ , 2H), 3.61 (s, 3H)

**1-allyl-3-methylpyridinium** ((3-methoxy-3-oxopropyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide

(C1A2-Ester)

$^1\text{H}$  NMR (400 MHz) \_ DMSO- $d_6$ :  $\delta$  2.51 (s, 3H), 2.68 (t,  $J = 7.6$ , 2H), 3.21 (t,  $J = 7.6$ , 2H), 3.61 (s, 3H), 5.21 (d,  $J = 6.4$ , 2H), 5.44 (q,  $J = 1.2$ , 2H), 6.15 (m, 1H), 8.08 (m,  $J = 6$ , 1H), 8.47 (d,  $J = 8$ , 1H), 8.86 (d,  $J = 6$ , 1H), 8.94 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) \_ DMSO- $d_6$ :

$\delta$  18.2, 29.2, 50.3, 52.1, 62.9, 120.6, 122.4, 128.0, 131.9, 139.5, 142.4, 144.6, 146.6, 171.6

$^{19}\text{F}$  NMR \_ DMSO-  $d_6$ :  $\delta$  -79.5, -81.2

Anal. Calc. for  $\text{C}_{14}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_6\text{S}_2$ : C 38.89, H 4.43, N 6.48, S 14.83;

Found: C 38.81, H 4.44, N 6.42, S 14.86

**1-(3-butenyl)-3-methylpyridinium** ((3-methoxy-3-oxopropyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide

(C2A2-Ester)

$^1\text{H}$  NMR (400 MHz) \_ DMSO- $d_6$ :  $\delta$  2.50 (s, 3H), 2.69 (m, 4H), 3.24 (t,  $J = 7.6$ , 2H), 3.61 (s, 3H), 4.65 (t,  $J = 2$ , 2H), 5.01 (m, 2H), 5.81 (m, 1H), 8.05 (m, 1H), 8.44 (d,  $J = 8$ , 1H), 8.88 (d,  $J = 6$ , 1H), 8.97 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) \_ DMSO- $d_6$ :

$\delta$  18.3, 29.2, 35.1, 50.3, 52.2, 60.1, 119.4, 120.5, 127.6, 133.4, 139.1, 142.5, 144.7, 146.4, 171.6

$^{19}\text{F}$  NMR \_ DMSO- $d_6$ :  $\delta$  -79.5, -81.2

Anal. Calc. for  $\text{C}_{15}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_6\text{S}_2$ : C 40.35, H 4.74, N 6.27, S 14.36;

Found: C 40.37, H 4.82, N 6.25, S 14.37

**1-allyl-3-methylpyridinium** ((2-carboxyethyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide (C1A2)

$^1\text{H}$  NMR (400 MHz) \_ DMSO- $d_6$ :  $\delta$  2.52 (s, 3H), 2.62 (t,  $J = 7.6$ , 2H), 3.22 (t,  $J = 7.6$ , 2H), 5.23 (d,  $J = 6$ , 2H), 5.45 (m, 2H), 6.17 (m, 1H), 8.08 (m, 1H), 8.48 (d,  $J = 8$ , 1H), 8.87 (d,  $J = 6$ , 1H), 8.94 (s, 1H), 12.45 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) \_ DMSO- $d_6$ :

$\delta$  18.3, 29.4, 50.5, 62.9, 120.5, 122.4, 128.0, 131.8, 139.5, 142.4, 144.6, 146.6, 172.5

$^{19}\text{F}$  NMR \_ DMSO- $d_6$ :  $\delta$  -79.5, -81.3

**1-(3-butenyl)-3-methylpyridinium** ((2-carboxyethyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide (C2A2)

$^1\text{H}$  NMR (400 MHz) \_ DMSO- $d_6$ :  $\delta$  2.50 (s, 3H), 2.60 (t,  $J = 7.6$ , 2H), 2.70 (m, 2H), 3.18 (t,  $J = 7.6$ , 2H), 4.64 (t,  $J = 6.8$ , 2H), 5.02 (m, 2H), 5.79 (m, 1H), 8.05 (t, 1H), 8.44 (d,  $J = 7.6$ , 1H), 8.87 (d,  $J = 6$ , 1H), 8.97 (s, 1H)

$^{13}\text{C}$  NMR (100 MHz) \_ DMSO- $d_6$ :

$\delta$  18.3, 29.4, 35.1, 50.4, 60.1, 119.4, 120.5, 127.7, 133.4, 139.1, 142.5, 144.7, 146.4, 172.5

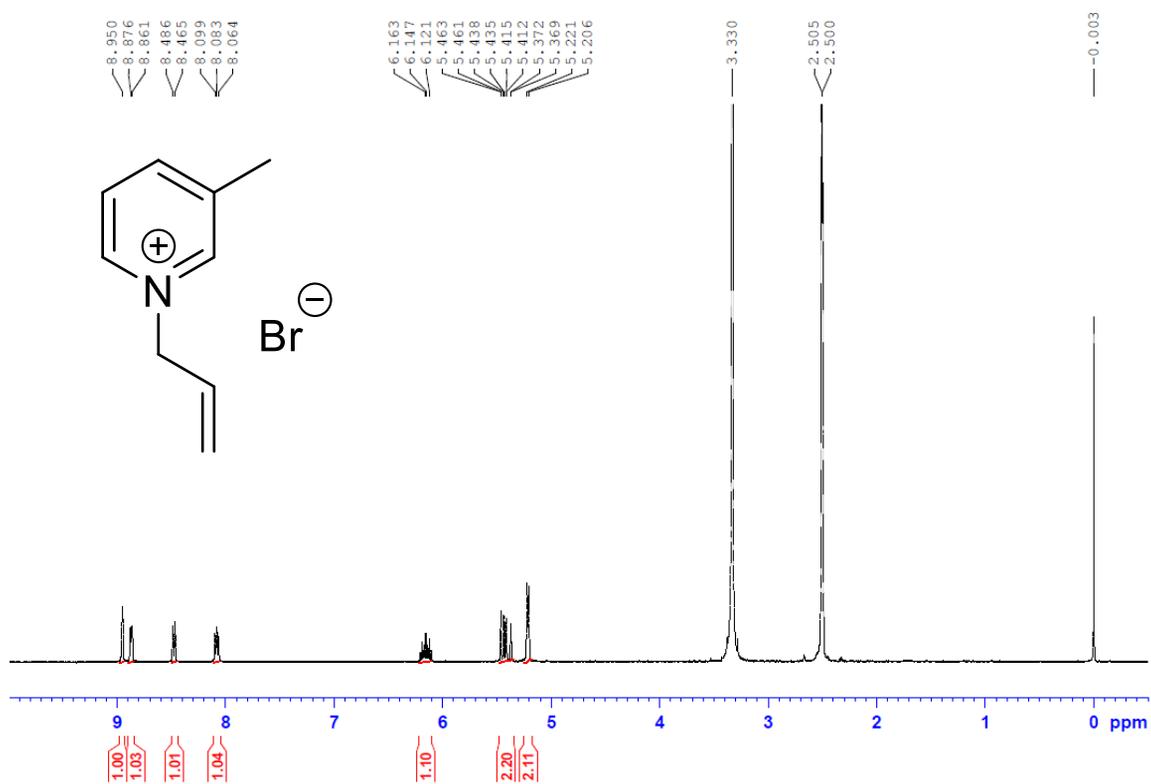
$^{19}\text{F}$  NMR \_ DMSO- $d_6$ :  $\delta$  -79.4, -81.2

# Appendices

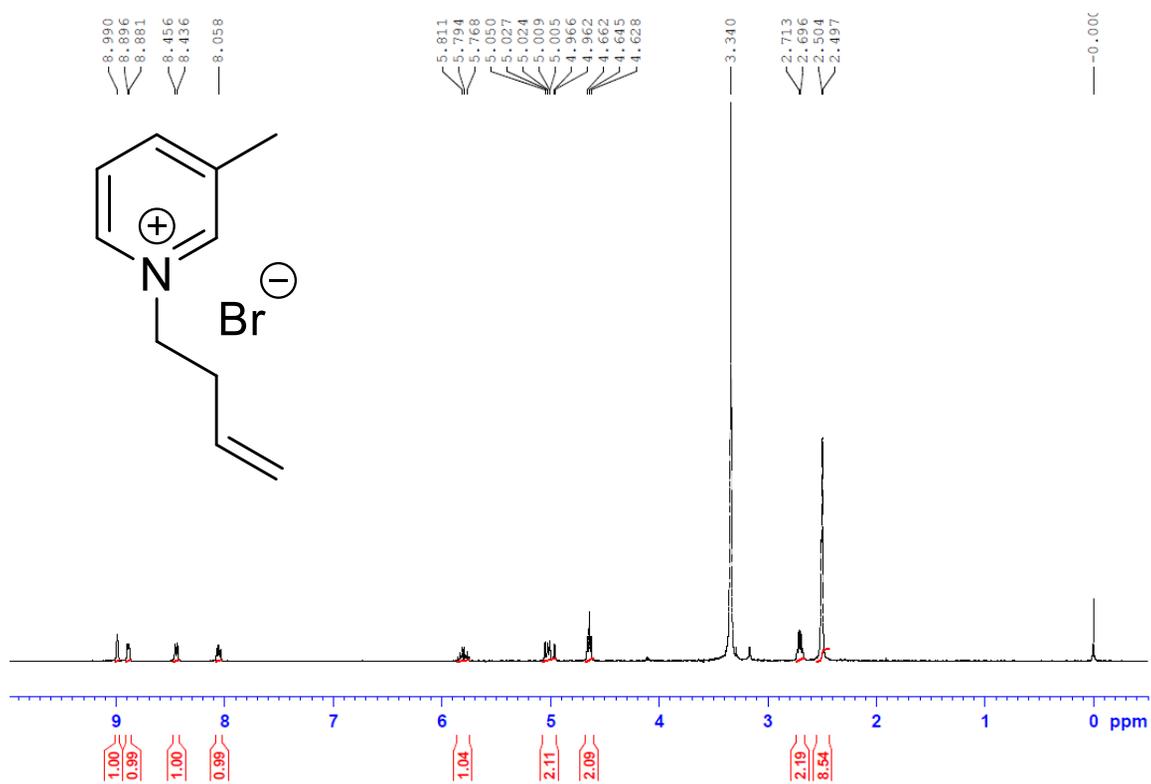
## List of $^1\text{H}$ NMR Spectra of compounds

1. 1-allyl-3-methylpyridinium bromide\_ DMSO- $d_6$
2. 1-(3-butenyl)-3-methylpyridinium bromide\_ DMSO- $d_6$
3. methyl 3-(chlorosulfonyl)propanoate\_CDCl<sub>3</sub>
4. lithium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO- $d_6$
5. 1-allyl-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
\_ DMSO- $d_6$  (C1A2-Ester)
6. 1-(3-butenyl)-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO- $d_6$  (C2A2-Ester)
7. 1-allyl-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO- $d_6$  (C1A2)
8. 1-(3-butenyl)-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO- $d_6$  (C2A2)

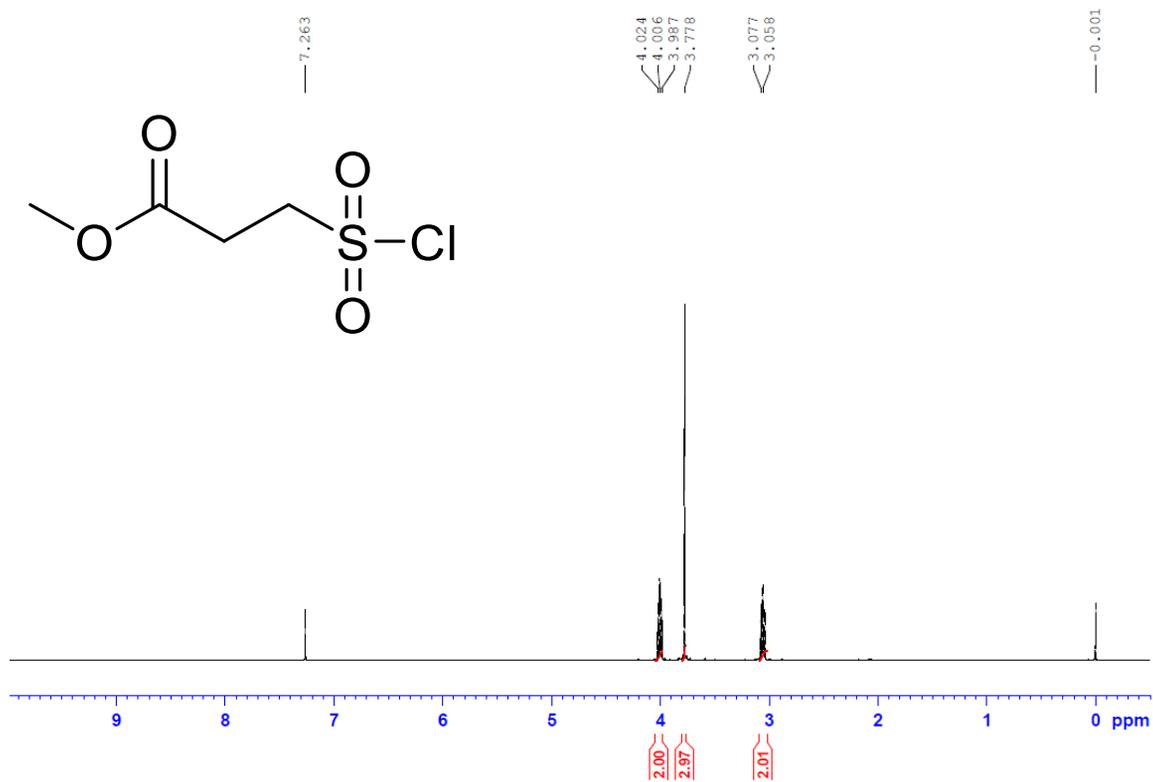
1. 1-allyl-3-methylpyridinium bromide\_ DMSO-*d*<sub>6</sub>



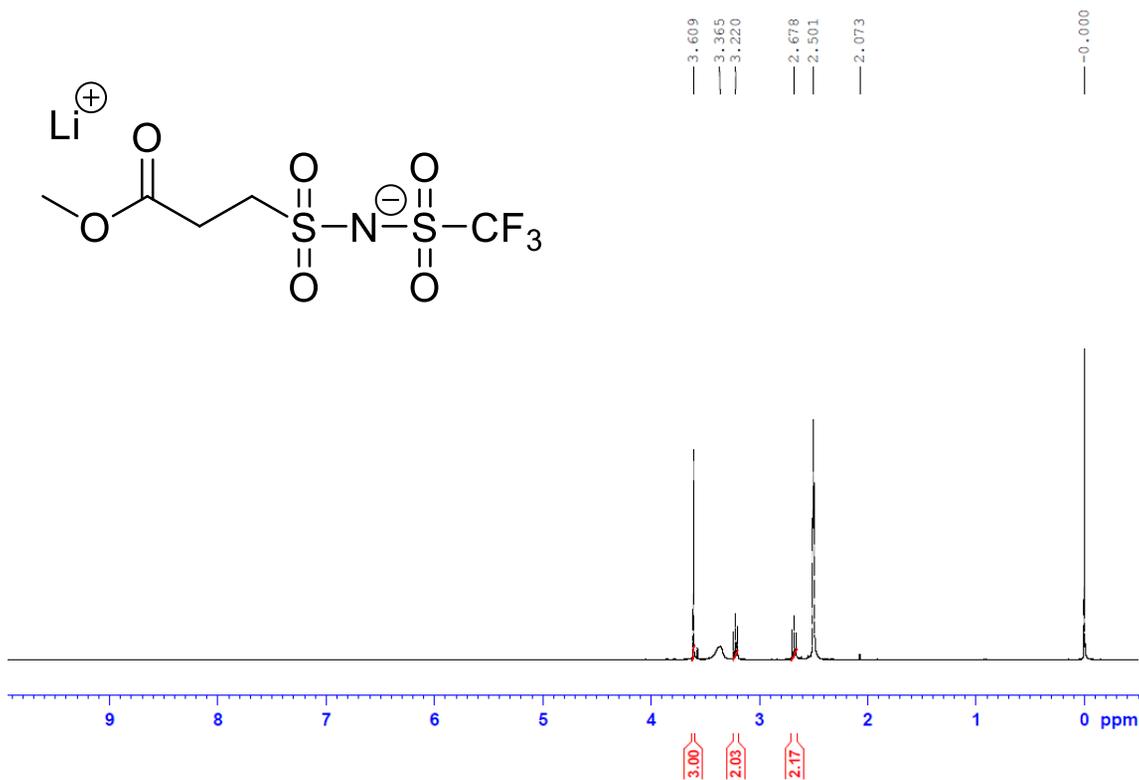
2. 1-(3-butenyl)-3-methylpyridinium bromide\_DMSO-*d*<sub>6</sub>



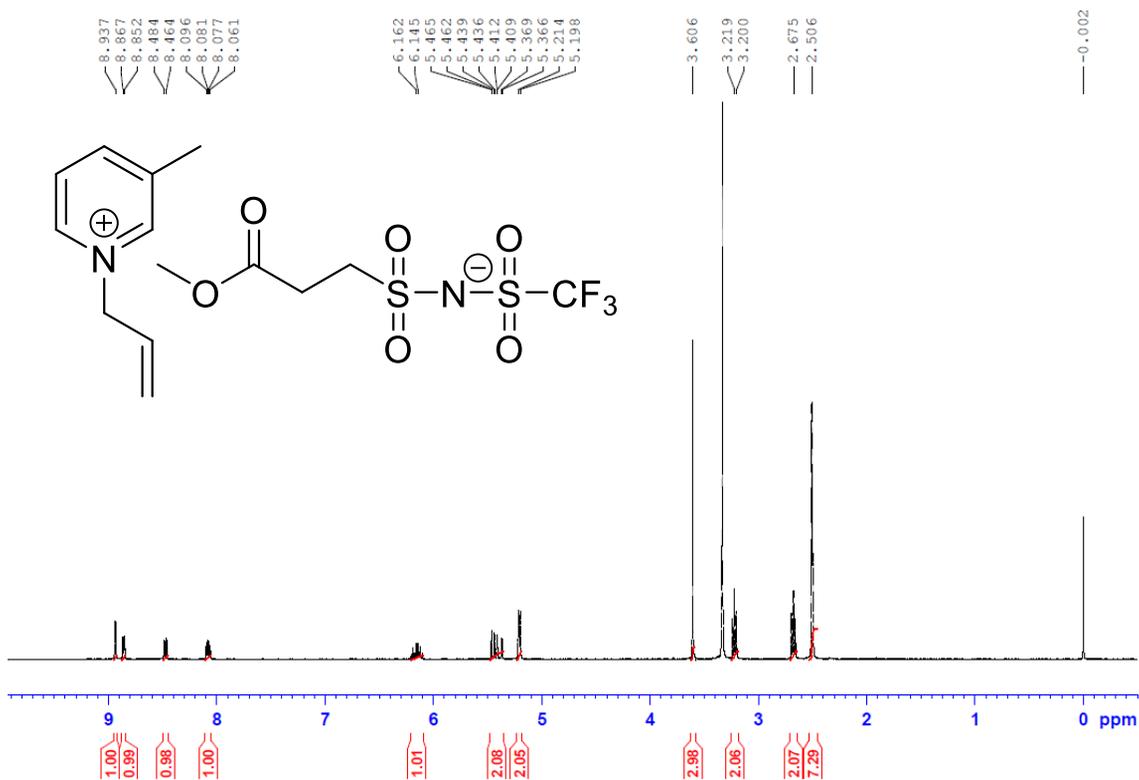
3. methyl 3-(chlorosulfonyl)propanoate\_CDCl<sub>3</sub>



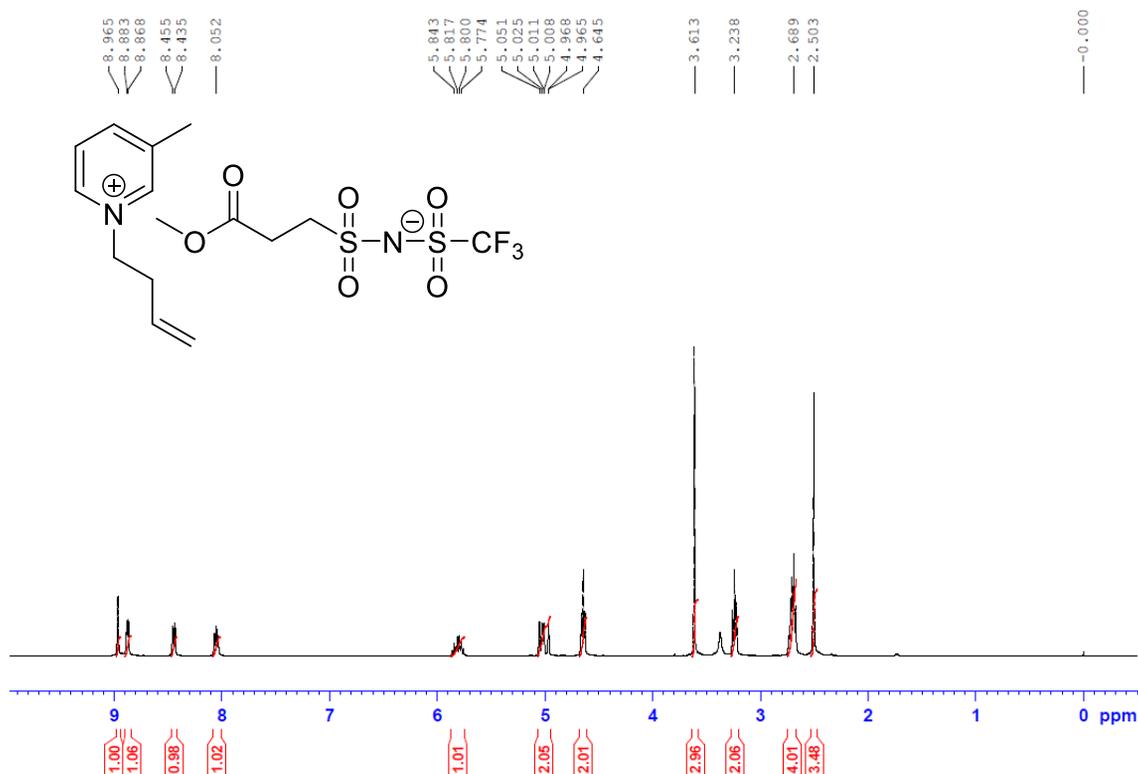
4. lithium ((3-methoxy-3-oxopropyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide\_  
 DMSO- $d_6$



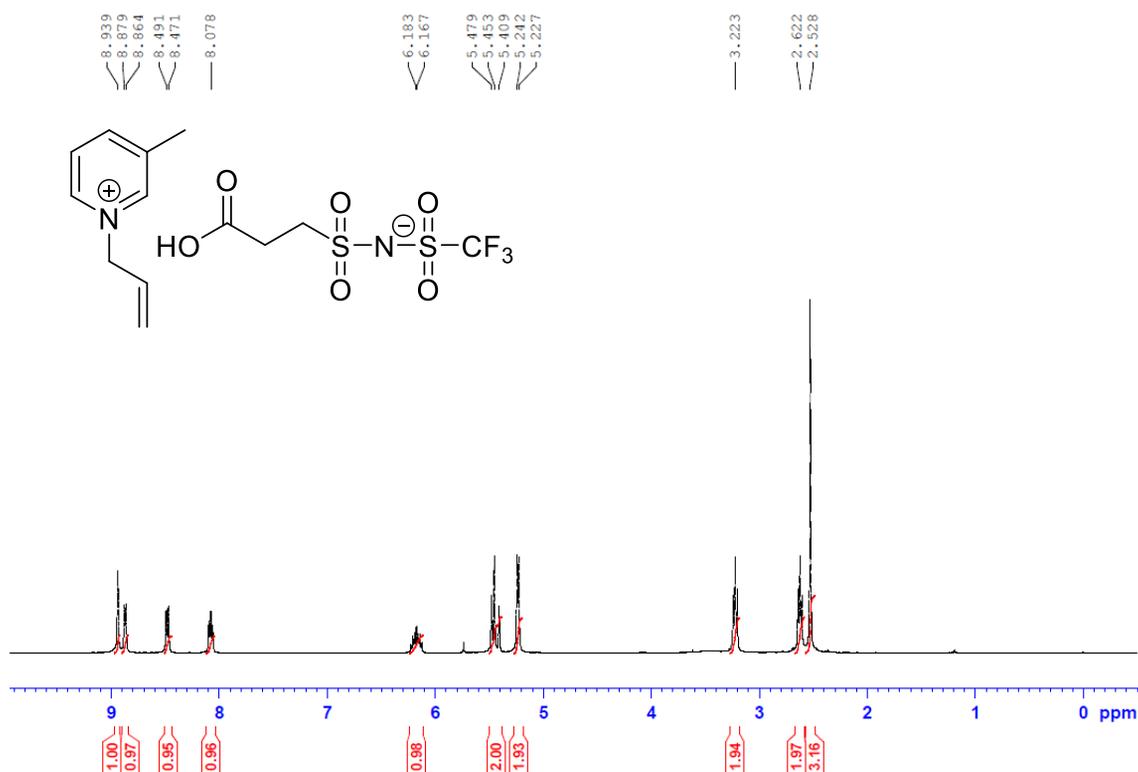
5. 1-allyl-3-methylpyridinium ((3-methoxy-3-oxopropyl) sulfonyl) (trifluoromethyl) sulfonyl) amide\_  
 DMSO-*d*<sub>6</sub> (C1A2-Ester)



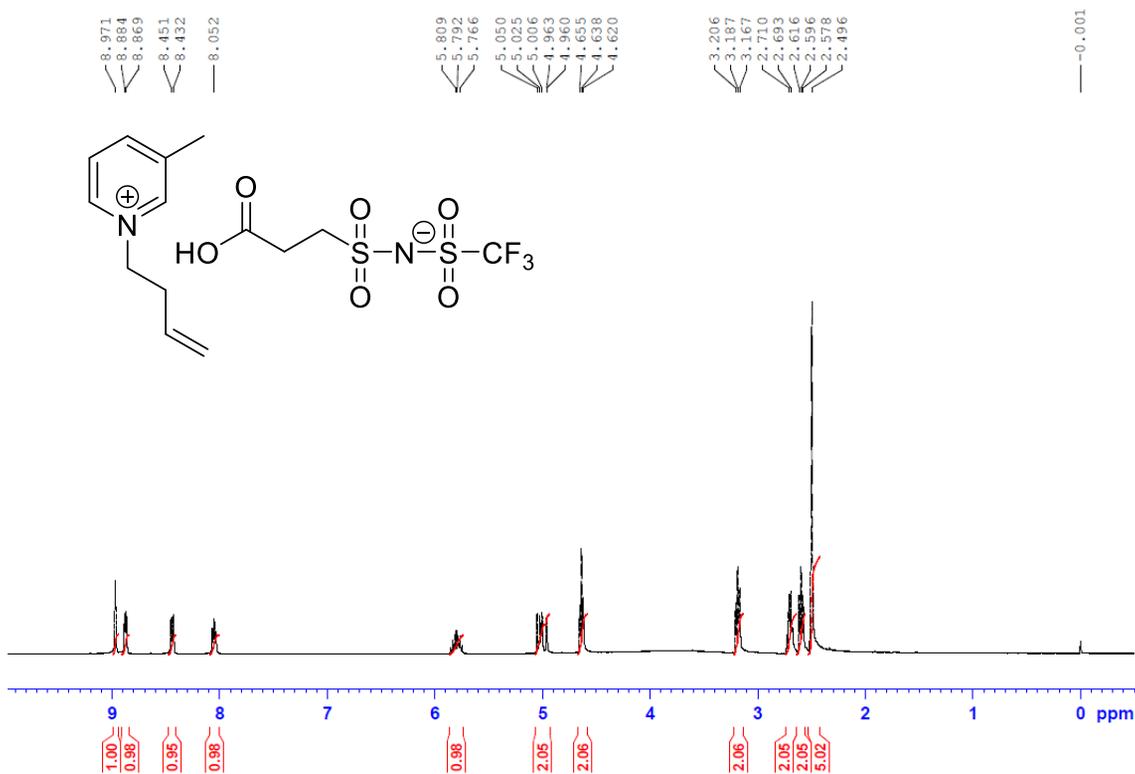
6. 1-(3-butenyl)-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO-*d*<sub>6</sub> (C2A2-Ester)



7. 1-allyl-3-methylpyridinium (2-carboxyethyl sulfonyl) ((trifluoromethyl) sulfonyl) amide\_ DMSO-*d*<sub>6</sub> (C1A2)



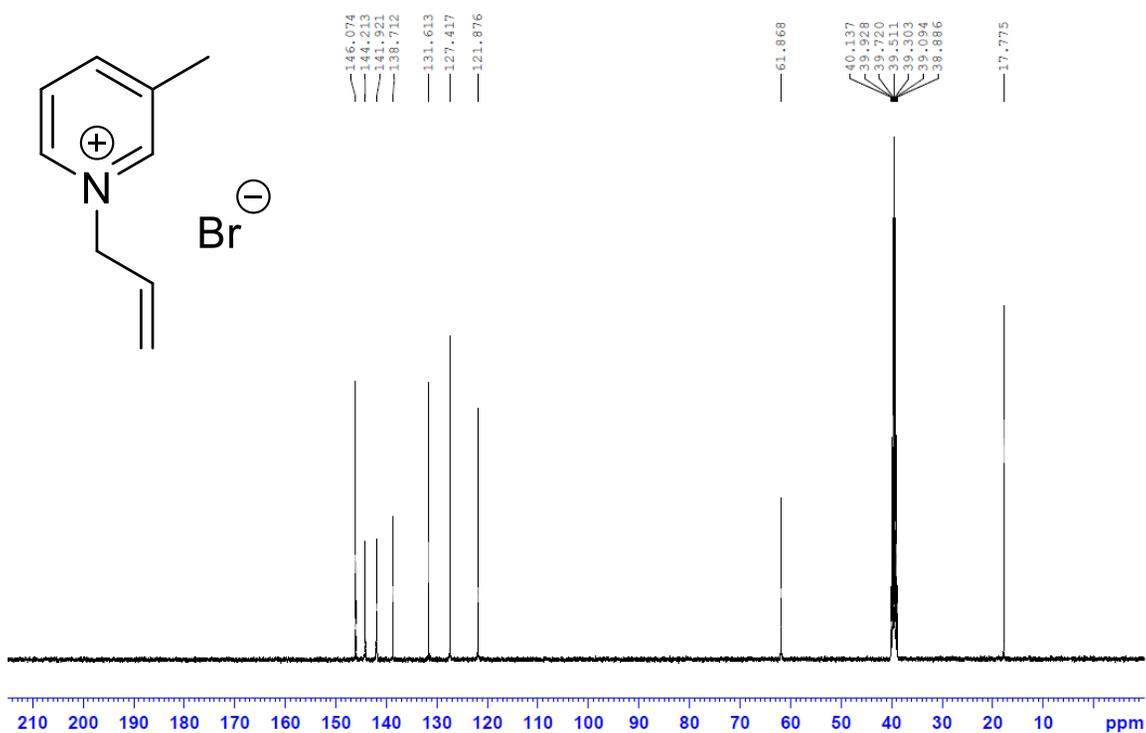
8. 1-(3-butenyl)-3-methylpyridinium (2-carboxyethyl)sulfonyl((trifluoromethyl)sulfonyl)amide\_ DMSO-*d*<sub>6</sub> (C2A2)



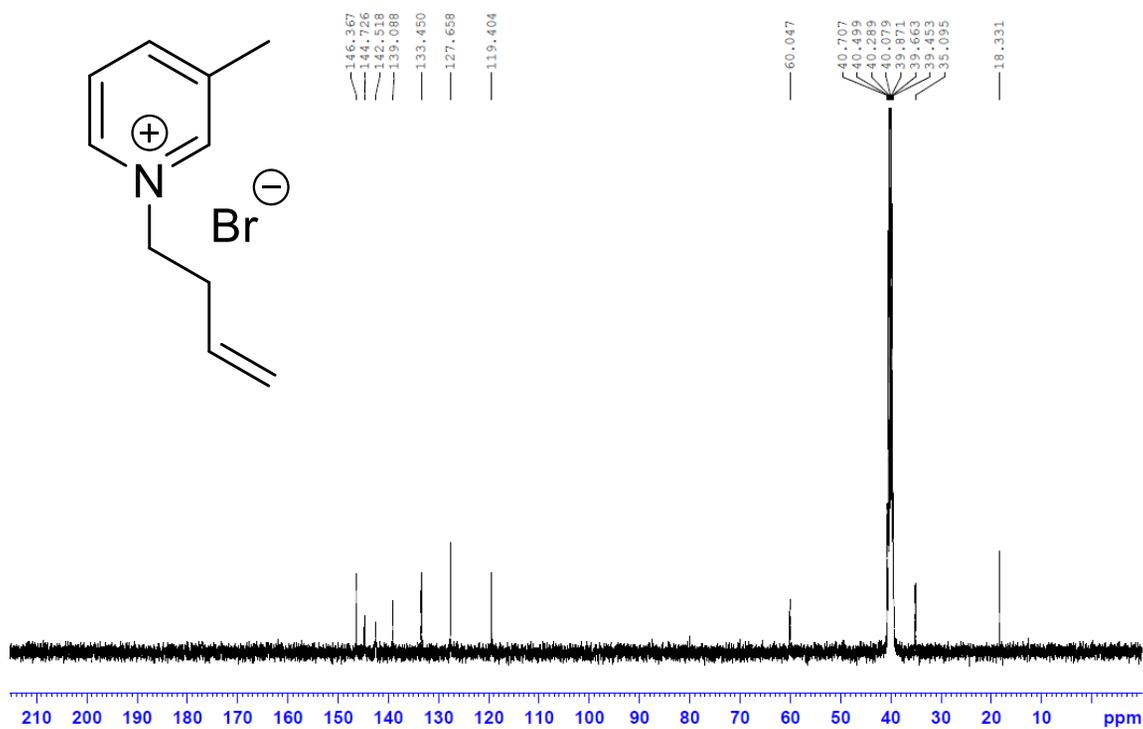
## List of $^{13}\text{C}$ NMR Spectra of compounds

1. 1-allyl-3-methylpyridinium bromide\_ DMSO- $d_6$
2. 1-(3-butenyl)-3-methylpyridinium bromide\_ DMSO- $d_6$
3. methyl 3-(chlorosulfonyl)propanoate\_CDC1<sub>3</sub>
4. 1-allyl-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_ DMSO- $d_6$  (C1A2-Ester)
5. 1-(3-butenyl)-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_ DMSO- $d_6$  (C2A2-Ester)
6. 1-allyl-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_ DMSO- $d_6$  (C1A2)
7. 1-(3-butenyl)-3-methylpyridinium ((2-carboxyethyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_ DMSO- $d_6$  (C2A2)

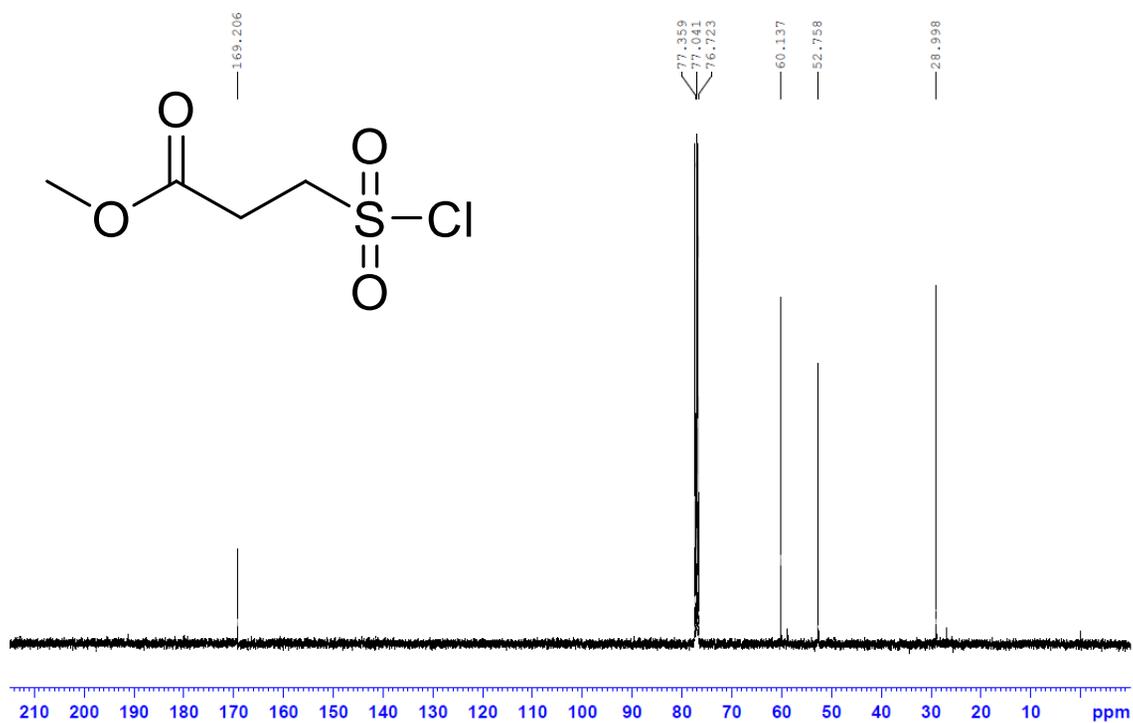
1. 1-allyl-3-methylpyridinium bromide\_ DMSO-*d*<sub>6</sub>



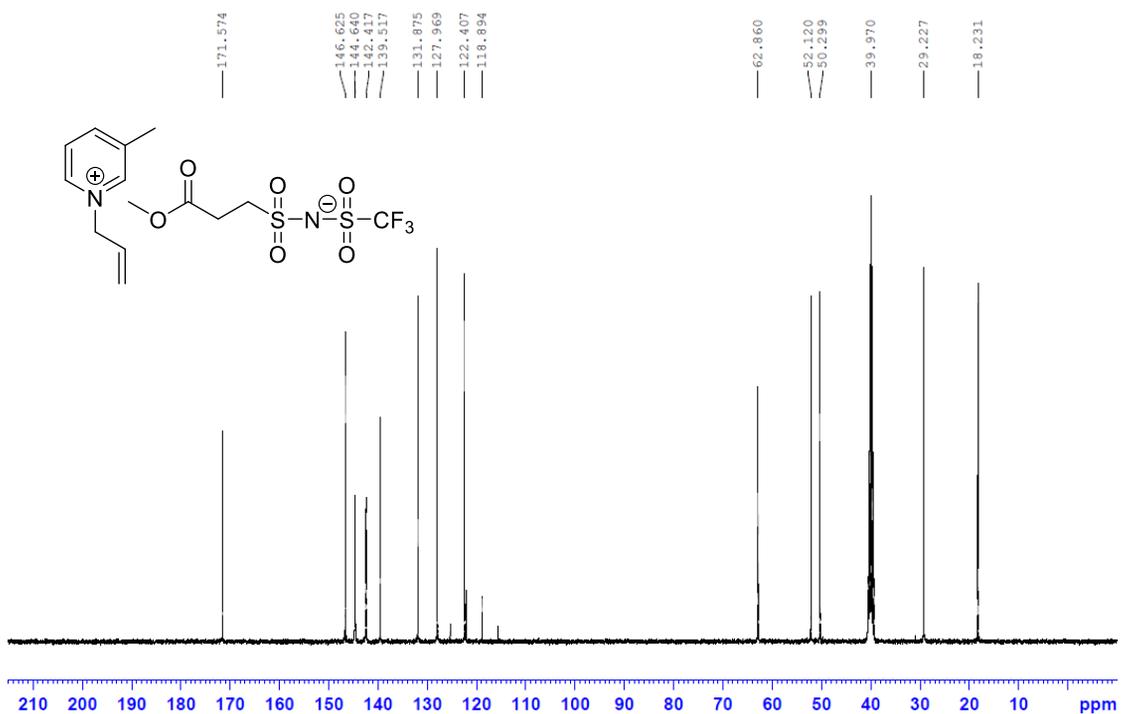
2. 1-(3-butenyl)-3-methylpyridinium bromide\_ DMSO-*d*<sub>6</sub>



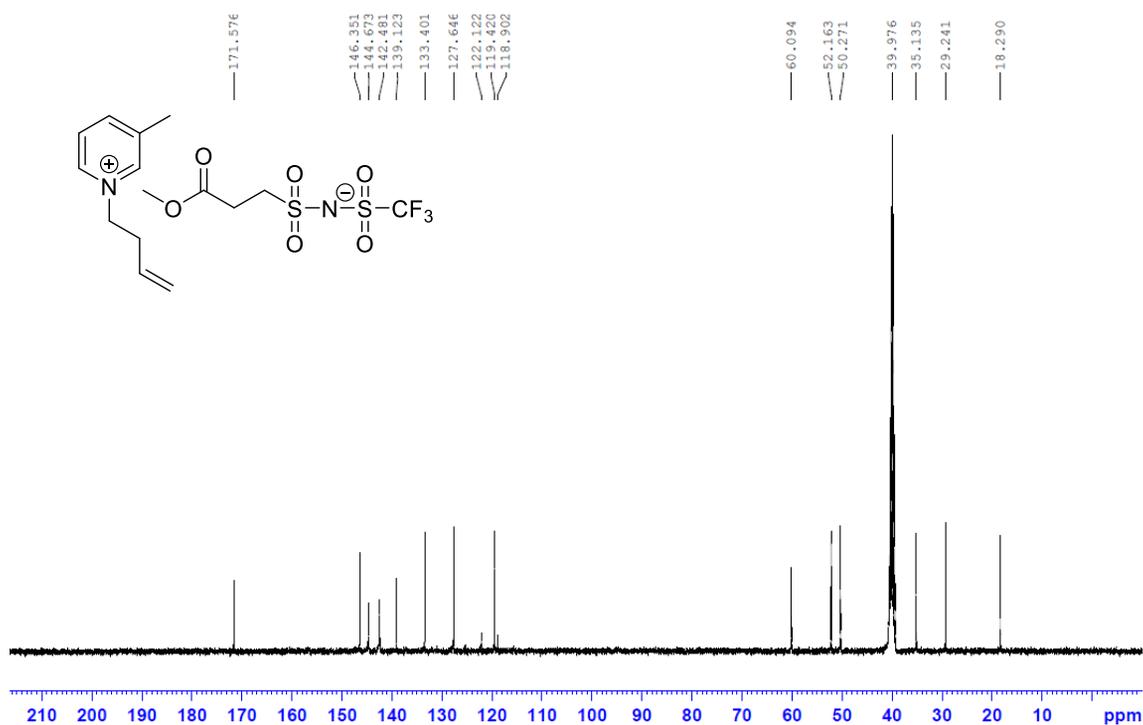
3. methyl 3-(chlorosulfonyl)propanoate\_CDCl<sub>3</sub>



4. 1-allyl-3-methylpyridinium ((3-methoxy-3-oxopropyl) sulfonyl) ((trifluoromethyl) sulfonyl) amide\_ DMSO-*d*<sub>6</sub> (C1A2-Ester)



5. 1-(3-butenyl)-3-methylpyridinium ((3-methoxy-3-oxopropyl)sulfonyl)((trifluoromethyl)sulfonyl)amide\_  
DMSO-*d*<sub>6</sub> (C2A2-Ester)

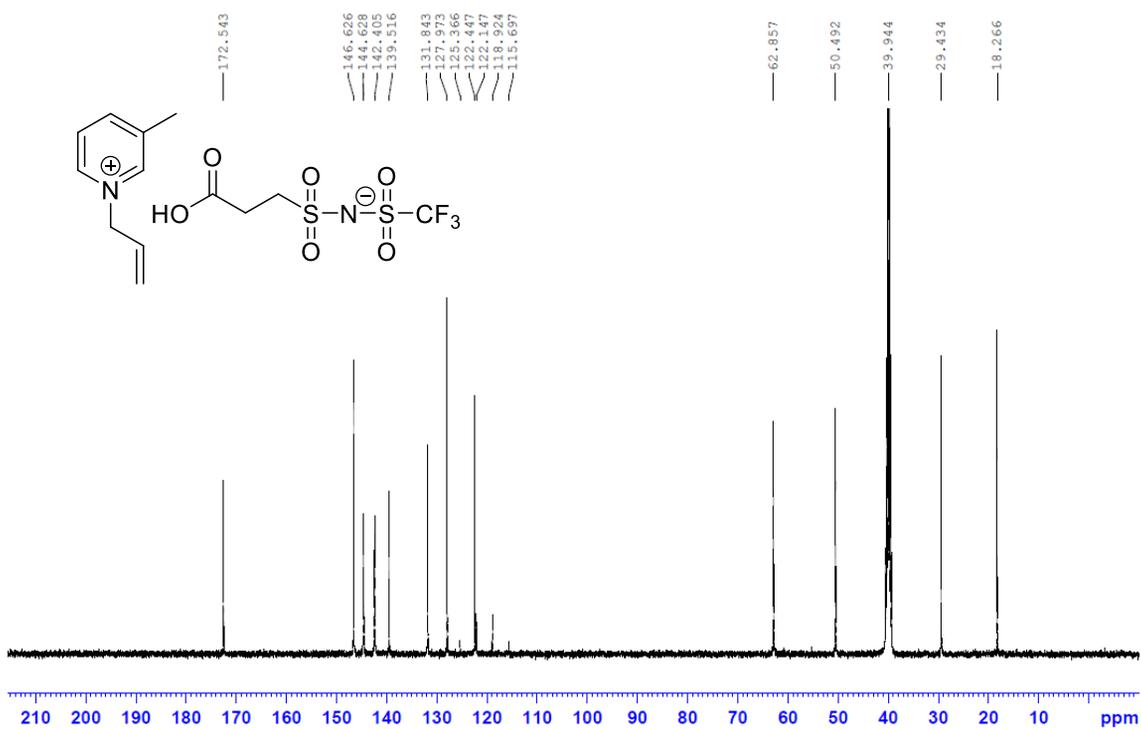


6. 1-allyl-3-methylpyridinium

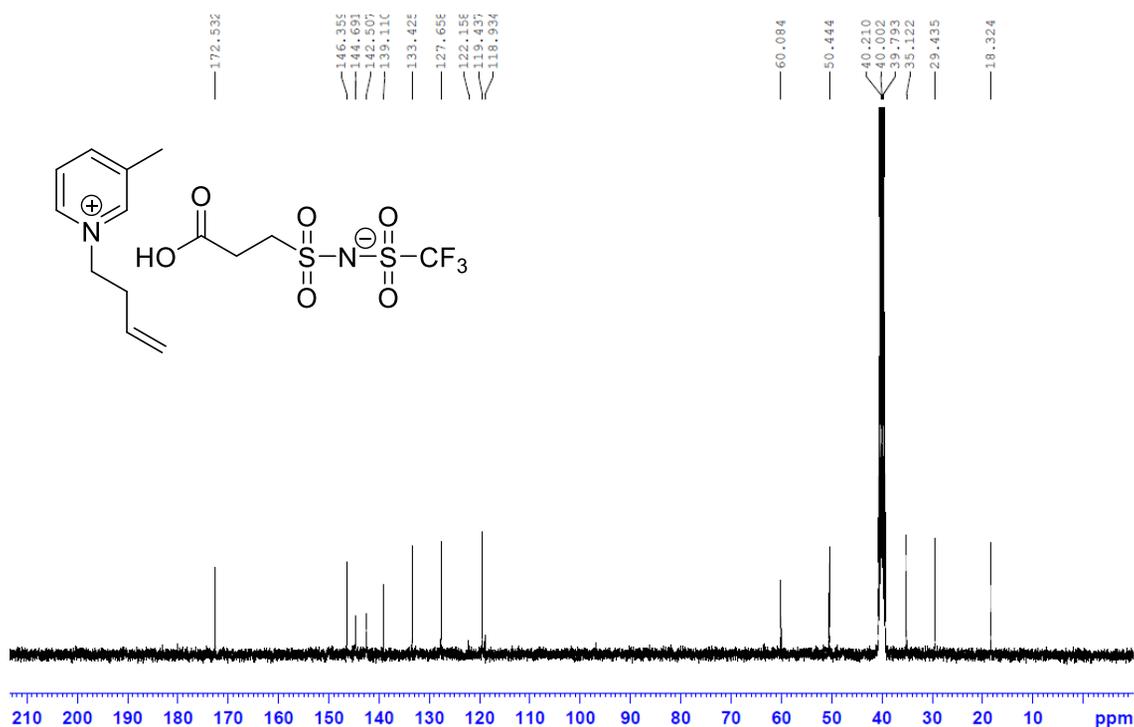
((2-

carboxyethyl) sulfonyl ((trifluoromethyl) sulfonyl) amide\_

DMSO- $d_6$  (C1A2)



7. 1-(3-butenyl)-3-methylpyridinium (2-carboxyethyl sulfonyl ((trifluoromethyl) sulfonyl) amide\_ DMSO-*d*<sub>6</sub> (C2A2)



## Abstract in Korean

이온성 액체는 리튬 이온 전지의 차세대 전해질로서 많은 주목을 받고 있는 물질이다. 이온성 액체의 높은 이온전도도, 비인화성, 매우 낮은 증기압, 넓은 전압 범위에서의 전기화학적 안정성 등과 같은 독특한 특징 때문에, 기존의 카보네이트 전해질을 대체할 수 있는 고성능 이온성 액체를 개발하기 위한 많은 연구가 진행되고 있다. 본 연구에서는, 4 종류의 보고되지 않은 이온성 액체를 5 스텝에 걸쳐 77 ~ 82%의 수율로 합성하였다. 합성한 이온성 액체는 3-methylpyridinium 기반 양이온과, 비대칭 bis(sulfonyl)imide 계열 음이온으로 구성되어 있다. 합성한 이온성 액체는  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,  $^{19}\text{F-NMR}$ , 원소 분석과 같은 방법으로 철저히 분석하여 높은 순도를 확인하였다.

전해질로서의 적용을 알아보기 위해 점도와 이온전도도 역시 측정하였다. 나아가서, 합성한 이온성 액체와 카보네이트 전해질 (EC/DEC 1:2 혼합물)의 이원 혼합물을 여러 농도로 제조하였으며, 이 이원 혼합물의 점도와 이온전도도도 측정하여 본 연구의 이온성 액체가 첨가제로 사용되었을 때의 성능도 확인하였다. 순수한 이온성 액체는 점도가 매우 높았고 1 mS/cm 이하의 낮은 이온 전도도를 보였으나, 이원 혼합물의 이온 전도도는 이온성 액체의 농도가 뭉어짐에 따라 급격히 증가하였다. 특히 합성한 이온성 액체 중 하나인 C1A2-Ester의 경우, 40:60 이원 혼합물의 이온 전도도 값은 8.84 mS/cm였으며, 이는 순수한 C1A2-Ester의 이온 전도도보다 약 14배 높은 값이었다. 이러한 연구 결과는 본 연구에서 합성한 이온성 액체가 뛰어난 배터리 전해질 첨가제가 될 수 있는 잠재력이 있다는 것을 보여준다.

키워드: 이온성 액체, 비대칭 음이온, Pyridinium 계열 양이온, 전기화학,  
LIB 전해질, 이원 화합물

학번: 2018-27184