



## **Scientific Report**

# SYNTHESIS OF NEW IONIC LIQUIDS CONTAINING ELECTRON DONOR GROUPS

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## **Introduction:**

Dye-sensitized solar cells (DSSCs) have attracted great attention over the past decade since they have been first reported by Gratzel et al. as potential alternative to other photovoltaic devices due to their high efficiency and low manufacturing cost [1]. The basic DSSC structure contains 3 main components; a) dye coated nanocrystalline TiO<sub>2</sub>, b) liquid electrolyte containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple and c) conductive transparent glasses. The working principle of DSSC is based on ultrafast electron injection from a photoexcited dye into the conduction band of an oxide semiconductor (TiO<sub>2</sub>) and subsequent dye regeneration using electrolytes as hole transportation media.

One important limitation for practical applications of DSSCs is the use of volatile organic solvents as electrolytes. The evaporation of the volatile solvent in the electrolyte diminishes the long term stability.

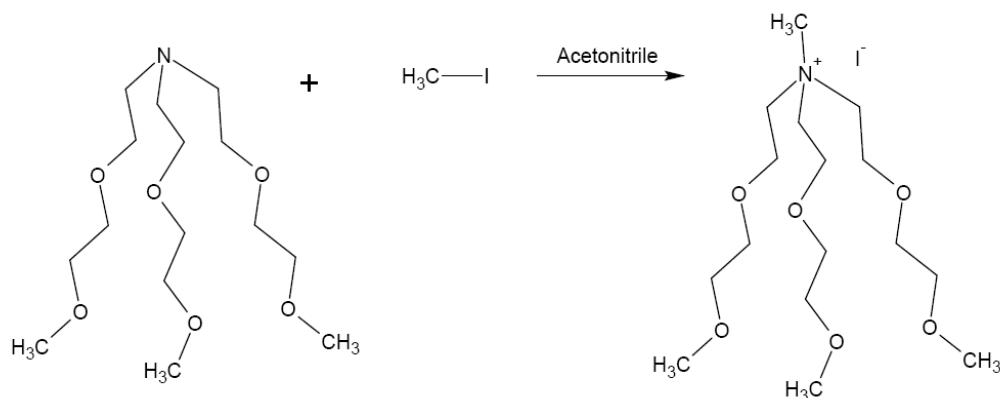
Different studies by the different research groups were done for the replacement of organic solvent based electrolyte with p-type semiconductor [2–4], solid hole transport material [5–7], gel electrolyte [8–10] to overcome leakage and evaporation problem.

Nonvolatile room-temperature ionic liquids with wide electrochemical window therefore represent good alternatives to organic solvents. Because of their relatively high ionic conductivity and low viscosity, ionic liquids are being widely investigated as solvents and important sources for the iodide-based redox couple in DSSCs [11–13].

In this study, we have investigated new ionic liquids based on ammonium and imidazolium cations with alkyl, allyl and ethoxy side groups. Their properties such as thermal stability and viscosity have been determined. These ionic liquids will be used as electrolytes in Dye Sensitized Solar Cells.

## **Experimental: Synthesis and characterization of the synthesized compounds.**

### **1) 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]-N-methylethanaminium iodide**



<b>Tris-[2-(2-methoxyethoxy)-ethyl]amine</b>	<b>Methyl iodide</b>	<b>Product (Code: PEA-I)</b>
FW: 323.43 g/mol	FW: 141.94 g/mol	FW: 465.364 g/mol
d: 1.011 g/mL	d: 2.28 g/mL	n: 20 mmol
n: 20 mmol	n: 25 mmol	m: 9.31
m: 6.47 g	V: 1.6 mL	

### **Procedure:**

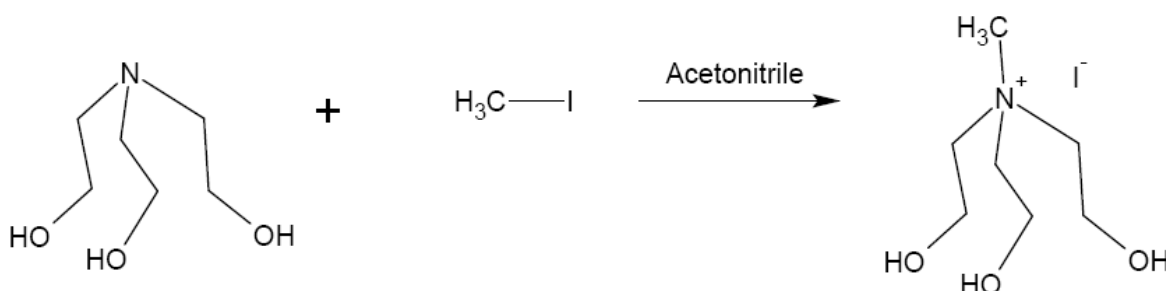
Tris-[2-(2-methoxyethoxy)-ethyl]amin (20 mmol, 6.47 g) was weighed in a sealed tube and 5 mL acetonitrile was added. The solution was cooled in an ice filled beaker and stirred about 10 minutes. Then the methyl iodide (25 mmol, 1.6 mL) was added to the solution slowly and the mixture was left for stirring overnight. The dark brown product was taken into a round-bottom flask and the solvents (acetonitrile and the excess of methyl iodide) were evaporated by rotary evaporator at 60 °C.

NMR measurements have been done and the compound was obtained successfully.

Yield: 8.98 g; 96.45%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 500 MHz,  $\text{CDCl}_3$ ): 4.00-3.90 (m, 12H); 3.69-3.62 (m, 6H); 3.52-3.47 (m, 6H); 3.41 (s, 3H); 3.32 (s, 9H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 71.93; 70.77; 65.31; 63.75; 59.33; 51.38. Anal. Calcd for  $\text{C}_{16}\text{H}_{36}\text{NO}_6\text{I}$ : C, 41.25; H, 7.74; N, 3.01. Found: C, 41.23; H, 7.09; N, 3.08. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_{16}\text{H}_{36}\text{NO}_6]^+$ : 338.2543; found: 338.2340. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{I}]^-$ : 126.9045; found: 126.8978.

2) 2-hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium iodide



Triethanolamine	Methyl iodide	Product (Code: TEA-I)
FW: 149.19 g/mol	FW: 141.94 g/mol	FW: 291.124 g/mol
d: 1.124 g/mL	d: 2.28 g/mL	n: 40 mmol
n: 40 mmol	n: 50 mmol	m: 11.64 g
m: 5.97 g	V: 3.2 mL	

**Procedure:**

Triethanolamine (40 mmol, 5.97 g) was weighed in the sealed tube and 5 mL of acetonitrile was added. The solution was cooled in an ice filled beaker and stirred about 10 minutes. Then the methyl iodide (50 mmol, 3.2 mL) was added to the solution slowly and the mixture was left for stirring overnight. The solution was colourless at first and then the colour turned to slight yellow.

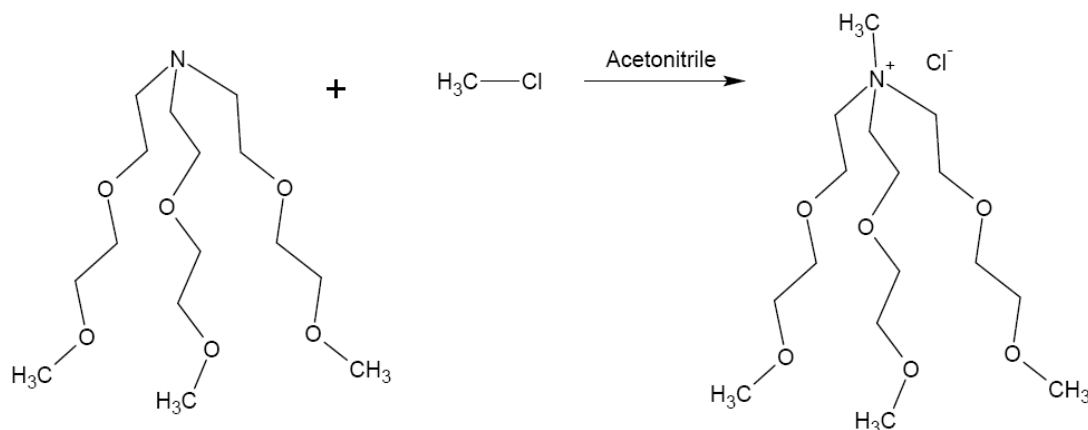
The slight yellow product was taken into a round-bottom flask and the solvents (acetonitrile and the excess of the methyl iodide) were evaporated by rotary evaporator at 60 °C.

NMR measurements have been done and the compound was obtained successfully. (NMR solvent was D<sub>2</sub>O)

Yield: 11.51 g; 98.88%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, D<sub>2</sub>O): 4.02-3.93 (m, 6H); 3.63-3.55 (m, 6H); 3.17 (s, 3H). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, D<sub>2</sub>O): 64.91; 55.67; 50.55. Anal. Calcd for C<sub>7</sub>H<sub>18</sub>INO<sub>3</sub>: C, 28.85; H, 6.18; N, 4.81. Found: C, 29.06; H, 6.71; N, 5.74. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>7</sub>H<sub>18</sub>NO<sub>3</sub>]<sup>+</sup>: 164.1287; found: 164.1239. TOF MS ES<sup>-</sup>: m/z calc. for [I]<sup>-</sup>: 126.9045; found: 126.8979.

**3) 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]-N-methylethanaminium chloride**



<b>Tris-[2-(2-methoxyethoxy)-ethyl]amine</b>	<b>Methyl chloride (gas)</b>	<b>Product (Code: PEA-Cl)</b>
FW: 323.43 g/mol	FW: 50.49 g/mol	FW: 373.91 g/mol
d: 1.011 g/mL		n: 154.6 mmol
n: 154.6 mmol		m: 57.8 g
m: 50 g		

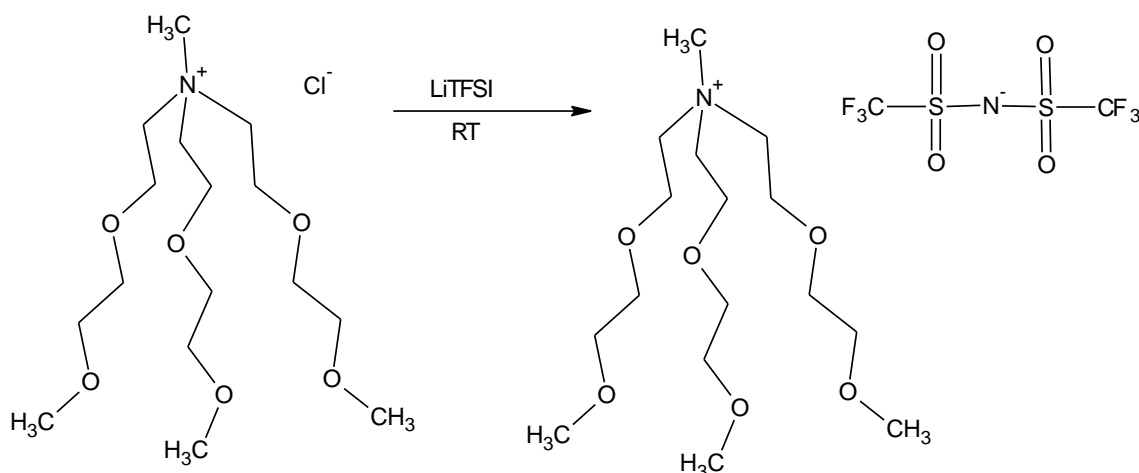
**Procedure:**

Tris-[2-(2-methoxyethoxy)-ethyl]amin was weighed (0.15 mol, 50 g) and 25 mL of acetonitrile was added to the starting material. Because of the methyl chloride is in a gas form, a reactor tube was used for the reaction. The solution was placed into this reactor tube and methyl chloride gas was added slowly. The gas pressure was arranged to 2 bars. After 1-2 hours the volume increasing was observed with the increasing amount of methyl chloride in the reactor tube. The methyl chloride gas was closed and the reaction mixture was left for stirring during 3 days.

After 3 days, acetonitrile solvent was evaporated by rotary evaporator and the dark brown product was obtained. Yield: 56.05 g; 97 %

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 500 MHz,  $\text{CDCl}_3$ ): 4.00-3.90 (m, 12H); 3.64-3.58 (m, 6H); 3.50-3.44 (m, 6H); 3.41 (s, 3H); 3.30 (s, 9H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 71.92; 70.63; 65.39; 63.39; 59.27; 50.88. Anal. Calcd for  $\text{C}_{16}\text{H}_{36}\text{NO}_6\text{Cl}$ : C, 51.35; H, 9.63; N, 3.74. Found: C, 50.57; H, 10.62; N, 3.83. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_{16}\text{H}_{36}\text{NO}_6]^+$ : 338.2543; found: 338.2487. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{Cl}]^-$ : 34.9689; found: 80.9182.

4) 2-(2-methoxyethoxy)-N,N-bis[2-(2-methoxyethoxy)ethyl]-N-methylethanaminium bis(trifluoromethanesulfonyl)imide



<b>N-tris-[2-(2-methoxyethoxy)-ethyl]-N-methyl ammonium chloride (PEA-Cl)</b>	<b>LiTFSI</b>	<b>Product (Code: PEA-TFSI)</b>
FW: 373.91 g/mol	FW: 287.08 g/mol	FW: 618.61 g/mol
m: 25.68 g	n: 69.68 mmol (1 mmol excess)	n: 68.68 mmol
n: 68.68 mmol	m: 20 g	m: 42.49 g

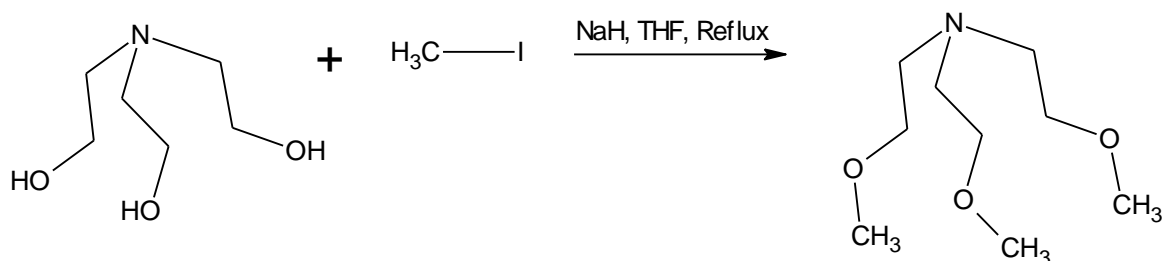
**Procedure:**

PEA-Cl was dissolved in DCM ( $\text{CH}_2\text{Cl}_2$ , 50 mL) and LiTFSI was dissolved in water (10 mL). The solutions were mixed in a separation funnel and shaken vigorously about 10 minutes.  $\text{CH}_2\text{Cl}_2$  phase was separated and washed with water (2x10 mL  $\text{H}_2\text{O}$ ).  $\text{CH}_2\text{Cl}_2$  was evaporated by rotary evaporator and the dark brown liquid was obtained (40.23 g). Liquid product was sent to H-NMR and C-NMR. The NMR results showed that the compound was obtained successfully.

Yield: 40.23 g; 94.7 %

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 500 MHz,  $\text{CDCl}_3$ ): 3.94-3.86 (m, 6H); 3.73-3.67 (m, 6H); 3.65-3.60 (m, 6H); 3.53-3.48 (m, 6H); 3.35 (s, 9H); 3.22 (s, 3H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 124-116 (TFSI); 71.85; 70.69; 64.99; 63.79; 59.20; 50.98. Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{F}_6\text{N}_2\text{O}_{10}\text{S}_2$ : C, 34.92; H, 5.82; N, 4.53; S, 10.34. Found: C, 35.40; H, 6.17; N, 4.67; S, 10.13. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_{16}\text{H}_{36}\text{NO}_6]^+$ : 338.2543; found: 338.2567. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{C}_2\text{NO}_4\text{F}_6\text{S}_2]^-$ : 279.9173; found: 279.9042.

5) 2-methoxy-N,N-bis(2-methoxyethyl)ethanamine tris(2-methoxyethyl)amine



Triethanolamine	Iodomethane	Sodium hydride (60 %)	Tris(3-oxabutyl)amine
FW: 149.19 g/mol	FW: 141.94 g/mol	FW: 24 g/mol	FW: 191.3 g/mol
n: 20 mmol	n: 60 mmol	n: 60 mmol	n: 20 mmol
m: 2.98 g	m: 8.52 g	m: 2.4 g	m: 3.83 g

**Procedure:**

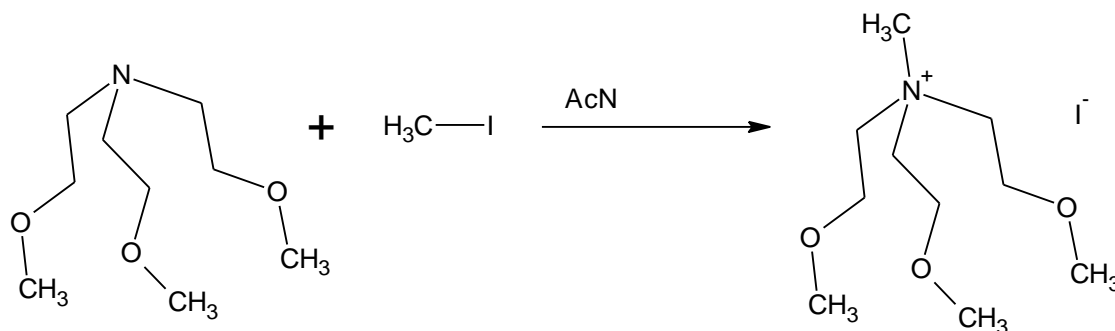
NaH was weighed (60 mmol, 2.4 g) and 20 mL of dry THF was added. The mixture was stirred. To this suspension, a solution of triethanolamine in 50 mL of dry THF was added. To this stirred mixture, a solution of methyl iodide in 10 mL of THF was added dropwise. The mixture was refluxed at 70 °C for 2 days.

After 2 days, the reaction mixture was filtered and the remaining white solid was washed with DCM. The filtering was repeated 2-3 times. Solvents were evaporated and the resultant compound was distilled by high vacuum distillation ( $1.8 \times 10^{-1}$  mbar, 100-120 °C).

Yield: 15.4%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 3.44-3.38 (t, 6H,  $J=6.0$  Hz); 3.27 (s, 9H); 2.76-2.67 (t, 6H,  $J=6.15$  Hz).

**6) 2-methoxy-N,N-bis(2-methoxyethyl)-N-methylethanaminium iodide**



<b>Tris(3-oxabutyl)amine</b>	<b>Iodomethane</b>	<b>Product (Code: MTEA-I)</b>
FW: 191.3 g/mol	FW: 141.94 g/mol	FW: 333.21 g/mol
n: 5.65 mmol	n: 11.3 mmol	n: 5.65 mmol
m: 1.08 g	m: 1.6 g	m: 1.88 g
	d: 2.28 V: 0.7 mL	

**Procedure:**

Tris(3-oxabutyl)amine was weighed (5.65 mmol, 1.08 g) into a sealed tube and 2 mL of acetonitrile was added. The solution was cooled with ice-bath and then iodomethane was added to the stirring solution. The solution was heated to 50 °C overnight.

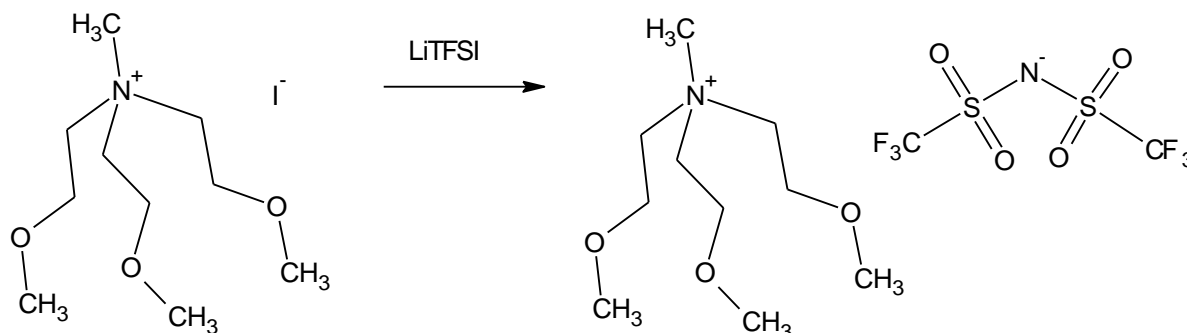
Nmr results indicate that the compound was obtained successfully.

Yield: 1.75 g; 93.08%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 500 MHz,  $\text{CDCl}_3$ ): 4.02-3.97 (m, 6H); 3.95-3.88 (m, 6H); 3.45 (s, 3H); 3.42 (s, 9H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 66.79; 63.85; 59.71; 51.17. Anal. Calcd for  $\text{C}_{10}\text{H}_{24}\text{INO}_3$ : C, 36.01; H, 7.20; N, 4.20. Found: C, 35.87; H, 6.80; N, 4.59. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_{10}\text{H}_{24}\text{NO}_3]^+$ : 206.1756; found: 206.1697. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{I}]^-$ : 126.9045; found: 126.8943.



7) 2-methoxy-N,N-bis(2-methoxyethyl)-N-methylethanaminium ammonium bis(trifluoromethanesulfonyl)imide



<b>N-methyl-N-tris(2-methoxyethyl) ammonium iodide</b>	<b>LiTFSI</b>	<b>Product (Code: MTEA-TFSI)</b>
FW: 333.21 g/mol	FW: 287.08 g/mol	FW: 486.45 g/mol
n: 5 mmol	n: 6 mmol	n: 5 mmol
m: 1.65 g	m: 1.72 g	m: 2.43 g

**Procedure:**

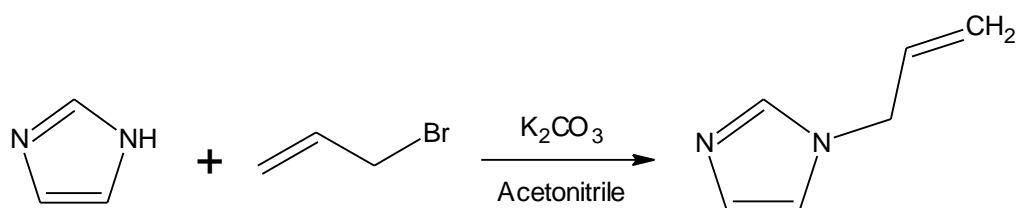
N-methyl-N-tris(2-methoxyethyl) ammonium iodide (5 mmol, 1.65 g) was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$  and LiTFSI (6 mmol, 1.72 g) was dissolved in distilled water. The solutions were mixed in a separation funnel and shaken very well about 5 minutes. The bottom  $\text{CH}_2\text{Cl}_2$  phase was separated, washed with distilled water (2x10 mL) and dried over  $\text{MgSO}_4$ . The yellowish product was obtained after removing of  $\text{CH}_2\text{Cl}_2$  under reduced pressure.

Nmr results showed that the compound was clean.

Yield: 2.12 g; 87.24%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 500 MHz,  $\text{CDCl}_3$ ): 3.85-3.76 (m, 6H); 3.72-3.68 (m, 6H); 3.38 (s, 9H); 3.21 (s, 3H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 124-116 (TFSI); 66.37; 63.86; 59.42; 50.74. Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{F}_6\text{N}_2\text{O}_7\text{S}_2$ : C, 29.60; H, 4.93; N, 5.76; S, 13.16. Found: C, 29.81; H, 5.16; N, 5.84; S, 13.10. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_{10}\text{H}_{24}\text{NO}_3]^+$ : 206.1756; found: 206.1729. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{C}_2\text{NO}_4\text{F}_6\text{S}_2]^-$ : 279.9173; found: 279.9148.

## 8) 1-Allyl-1-H-imidazole



Imidazole	Allyl bromide	$K_2CO_3$	1-Allylimidazole
FW: 68.08 g/mol	FW: 120.98 g/mol	FW: 138.21 g/mol	FW: 108.14 g/mol
n: 100 mmol	n: 100.8 mmol	m: 30 g	n: 100 mmol
m: 6.8 g	m: 12.2 g	(n: 217 mol)	m: 10.8 g

### Procedure:

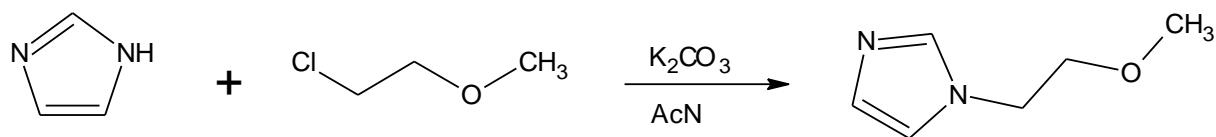
Imidazole was weighed (100 mmol, 6.8 g) and transferred into the reaction flask. Allyl bromide was weighed and added to the flask. 20 mL of AcN was added to the mixture and the mixture was heated to 40 °C to dissolve the starting materials. After 5 minutes, 30 g of  $K_2CO_3$  was added to the stirring solution from the top of the reflux condenser. The  $CaCl_2$  drying tube was placed on top of the reflux condenser and the mixture was left to reflux at 90 °C for overnight.

Dark brown solution was obtained. The  $K_2CO_3$  was filtered from the glass funnel (with using cotton) by vacuum pump. The AcN solvent was evaporated by rotary evaporator and the resultant dark brown compound was distilled by high vacuum distillation ( $1.8 \times 10^{-1}$ .mbar, 100 °C, 1 hour).

Yield: 5.01 g; 46.4 %

$^1H$  NMR ( $\delta_H$ , ppm, 300 MHz,  $CDCl_3$ ): 7.46 (s, 1H); 7.05 (s, 1H); 6.90 (s, 1H); 6.05-5.84 (m, 1H); 5.33-5.07 (m, 2H); 4.63-4.44 (d, 2H,  $J=5.7$  Hz).

9) 1-(2-methoxyethyl)-1H-imidazole



Imidazole	2-chloroethyl methyl ether	K <sub>2</sub> CO <sub>3</sub>	N-(2-methoxyethyl) imidazole
FW: 68.08 g/mol	FW: 94.54 g/mol	FW: 138.21 g/mol	FW: 126.16 g/mol
n: 50 mmol	n: 50.4 mmol	m: 15 g	n: 50 mmol
m: 3.4 g	m: 4.76 g	(n: 108.5 mol)	m: 6.31 g

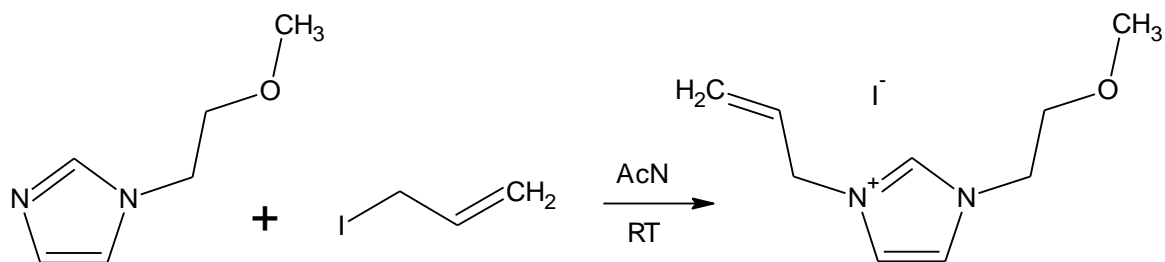
**Procedure:**

Imidazole (3.4 g, 50 mmol) was weighed and transferred into a 2-necked round bottomed flask equipped with a reflux condenser. Acetonitrile (AcN, 20 ml) was added to the flask and the mixture was stirred. After imidazole dissolved in AcN, 2-chloroethyl methyl ether (4.76 g, 50.4 mmol) was added to the stirring solution. K<sub>2</sub>CO<sub>3</sub> (15 g, 108.5 mol) was grinded into smaller particles and added to the stirring solution. AcN amount was increased to 50 mL and the mixture was left for stirring overnight at 70 °C. The crude product was containing desired product and the imidazole starting material. 46 mmol of 2-chloroethyl methyl ether was added to the flask and the mixture was left for stirring about 2 days. After 2 days, desired product was obtained with a small amount of dialkylated compound. The crude product was distilled (80 °C, 4.6x10<sup>-1</sup> mbar) and the pure product was obtained.

Yield: 3.92 g, 62%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 7.43 (s, 1H); 6.96 (s, 1H); 6.89 (s, 1H); 4.05-3.96 (m, 2H); 3.58-3.51 (m, 2H); 3.25 (s, 3H).

**10)** 3-Allyl-1-(2-methoxyethyl)-1H-imidazol-3-ium iodide



<b>N-(2-methoxyethyl) imidazole</b>	<b>Allyl iodide (98 %)</b>	<b>Product (Code: AI-IL4-I)</b>
FW: 126.16 g/mol	FW: 167.98 g/mol	FW: 294.13 g/mol
n: 7.93 mmol	n: 8 mmol	n: 7.93 mmol
m: 1 g	m: 1.34 g	m: 2.33 g
	d: 1.837 V: 0.729 mL	

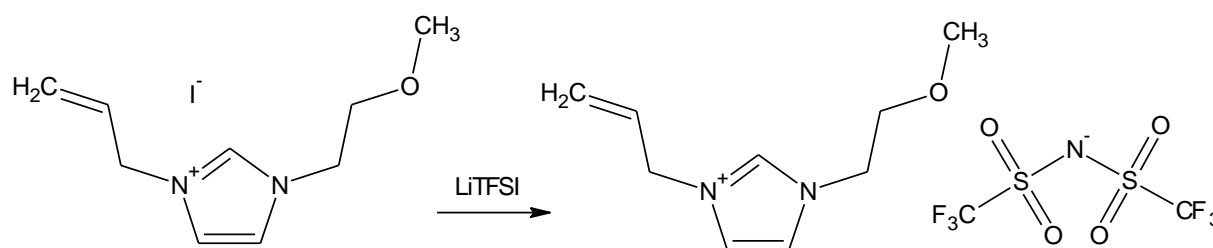
**Procedure:**

N-(2-methoxyethyl)imidazole (7.93 mmol, 1 g) was weighed into a sealed tube and AcN (1 mL) was added. To this stirring solution, allyl iodide (8 mmol, 0.729 mL) was added and the solution was left for stirring overnight at RT. (The reaction flask was covered with aluminium foil against the light.) The H-NMR results showed that the compound was clean.

Yield: 2.17 g; 93.13 %

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 9.75 (s, 1H); 7.73 (t, 1H,  $J=1.95$  Hz); 7.59 (t, 1H,  $J=1.8$  Hz); 6.18-5.98 (m, 1H); 5.61-5.45 (m, 2H); 5.10-5.02 (d, 2H,  $J=6.3$  Hz); 4.64-4.58 (t, 2H,  $J=4.8$  Hz); 3.85-3.79 (t, 2H,  $J=4.8$  Hz); 3.40 (s, 3H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 136.50; 130.03; 123.82; 123.26; 122.28; 70.33; 59.49; 52.52; 50.42. Anal. Calcd for  $\text{C}_9\text{H}_{15}\text{N}_2\text{OI}$ : C, 36.72; H, 5.10; N, 9.52. Found: C, 36.23; H, 4.81; N, 9.56. TOF MS  $\text{ES}^+$ :  $m/z$  calc. for  $[\text{C}_9\text{H}_{15}\text{N}_2\text{O}]^+$ : 167.1184; found: 167.1182. TOF MS  $\text{ES}^-$ :  $m/z$  calc. for  $[\text{I}]^-$ : 126.9045; found: 126.9056.

**11) 3-Allyl-1-(2-methoxyethyl)-1H-imidazol-3-ium  
bis(trifluoromethanesulfonyl)imide**



<b>1-allyl-3-(2-methoxyethyl) imidazolium iodide</b>	<b>LiTFSI</b>	<b>Product (Code: AI-IL4-TFSI)</b>
FW: 294.13 g/mol	FW: 287.08 g/mol	FW: 447.38 g/mol
n: 6.73 mmol	n: 7.73 mmol	n: 6.73 mmol
m: 1.98 g	m: 2.23 g	m: 3.01 g

**Procedure:**

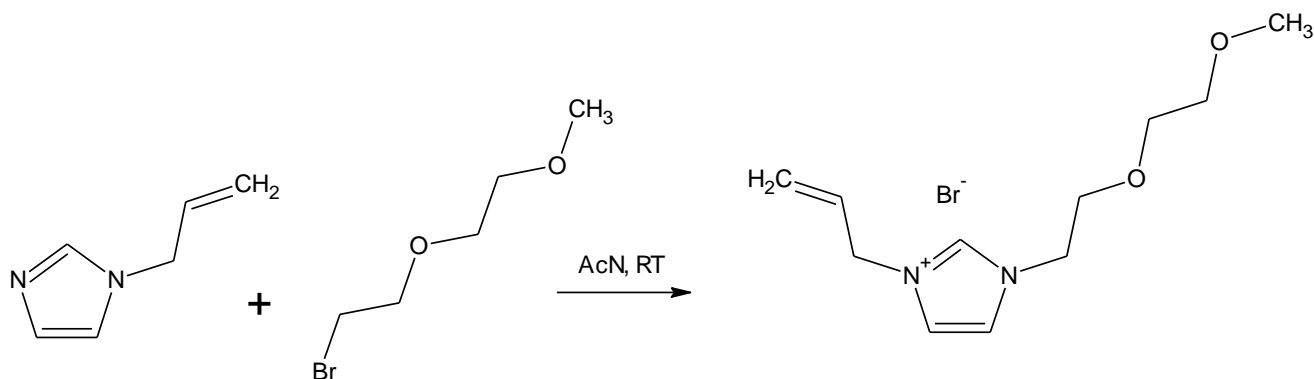
1-allyl-3-(2-methoxyethyl) imidazolium iodide (6.73 mmol, 1.98 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and LiTFSI (7.73 mmol, 2.23 g) was dissolved in distilled water (15 mL). The solutions were mixed in a separation funnel and shaken very well about 5 minutes. The bottom CH<sub>2</sub>Cl<sub>2</sub> phase was washed with distilled water (2x15 mL). Then, MgSO<sub>4</sub> was added to the CH<sub>2</sub>Cl<sub>2</sub> phase and stirred about 5 minutes. After filtration of MgSO<sub>4</sub> and evaporation of the solvent, ion exchanged product was obtained and dried under high vacuum. The colour of the product was light yellow.

The NMR results indicate the compound was obtained successfully.

Yield: 2.59 g; 86.05%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 8.70 (s, 1H); 7.44 (s, 1H); 7.30 (s, 1H); 6.10-5.86 (m, 1H); 5.53-5.40 (m, 2H); 4.83-4.74 (d, 2H, J=6.3 Hz); 4.40-4.31 (t, 2H, J=4.8 Hz); 3.75-3.67 (t, 2H, J=4.6 Hz); 3.36 (s, 3H). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 135.92; 129.68; 123.87; 123.31; 122.28; 121.45; 118.90; 116.34; 70.14; 59.21; 52.50; 50.35. Anal. Calcd for C<sub>11</sub>H<sub>15</sub>F<sub>6</sub>N<sub>3</sub>O<sub>5</sub>S<sub>2</sub>: C, 29.50; H, 3.35; N, 9.39; S, 14.30. Found: C, 29.56; H, 3.87; N, 9.43; S, 13.95. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>O]<sup>+</sup>: 167.1184; found: 167.1167. TOF MS ES<sup>-</sup>: m/z calc. for [C<sub>2</sub>NO<sub>4</sub>F<sub>6</sub>S<sub>2</sub>]<sup>-</sup>: 279.9173; found: 279.9143.

**12)** 3-allyl-1-[2-(2-methoxyethoxy)ethyl]-1H-imidazol-3-ium bromide



<b>1-Allylimidazole</b>	<b>1-bromo-2-(2-methoxyethoxy)ethane</b>	<b>Product (Code: AI-IL3-Br)</b>
FW: 108.14 g/mol	FW: 183.04 g/mol	FW: 291.18 g/mol
n: 9.25 mmol	n: 9.25 mmol	n: 9.25 mmol
m: 1 g	m: 1.69 g	m: 2.69 g
	d: 1.36 g/mL V: 1.24 mL	

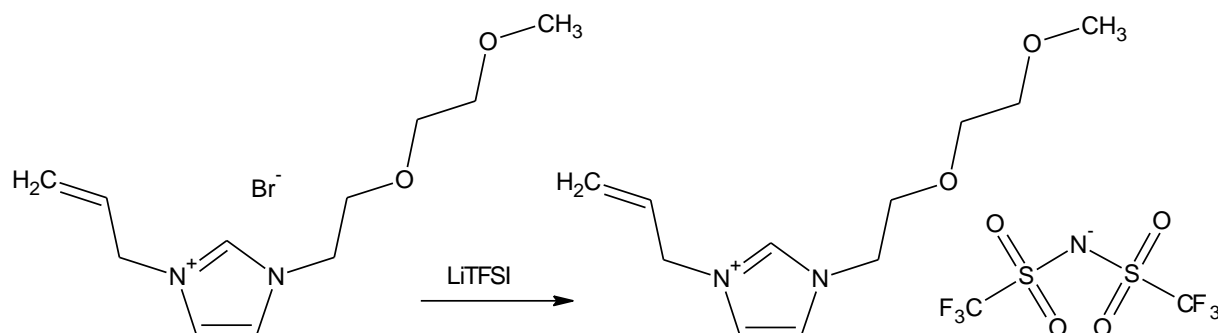
**Procedure:**

1-Allylimidazole (9.25 mmol, 1 g) was weighed in a flask and 1 mL of acetonitrile was added. The solution was stirred and 1-bromo-2-(2-methoxyethoxy)ethane (9.25 mmol, 1.24 mL) was added to the stirring solution. The solution was left for stirring at RT about 2 weeks and pure product was obtained.

Yield: 2.44 g; 90.71%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 10.12 (s, 1H); 7.78 (s, 1H); 7.56 (s, 1H); 6.16-5.96 (m, 1H); 5.60-5.41 (m, 2H); 5.10-4.97 (d, 2H,  $J=6.3$  Hz); 4.69-4.61 (t, 2H,  $J=4.6$  Hz); 3.97-3.87 (t, 2H,  $J=4.6$  Hz); 3.72-3.64 (m, 2H); 3.58-3.50 (m, 2H); 3.36 (s, 3H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 137.15; 130.23; 123.92; 122.96; 122.02; 71.95; 70.66; 69.25; 59.32; 52.43; 50.12. Anal. Calcd for  $\text{C}_{11}\text{H}_{19}\text{BrN}_2\text{O}_2$ : C, 45.33; H, 6.52; N, 9.62. Found: C, 44.94; H, 6.87; N, 9.86. TOF MS  $\text{ES}^+$ :  $m/z$  calc. for  $[\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_2]^+$ : 211.1447; found: 211.1331. TOF MS  $\text{ES}^-$ :  $m/z$  calc. for  $[\text{Br}]^-$ : 78.9183; found: 78.9195.

**13)** 3-allyl-1-[2-(2-methoxyethoxy)ethyl]-1H-imidazol-3-ium  
bis(trifluoromethanesulfonyl)imide



<b>N-allyl-N-[2-(2-methoxyethoxy)ethane] imidazolium bromide</b>	<b>LiTFSI</b>	<b>Product (Code: AI-IL3-TFSI)</b>
FW: 291.18 g/mol	FW: 287.09 g/mol	FW: 491.43 g/mol
n: 7.7 mmol	n: 8.7 mmol	n: 7.7 mmol
m: 2.24 g	m: 2.5 g	m: 3.78 g

**Procedure:**

N-allyl-N-[2-(2-methoxyethoxy)ethane] imidazolium bromide (7.7 mmol, 2.24 g) was dissolved in 40 mL CH<sub>2</sub>Cl<sub>2</sub> and LiTFSI (8.7 mmol, 2.5 g) was dissolved in 20 mL of distilled water. The solutions were mixed in a separation funnel and shaken very well about 5 minutes. The bottom CH<sub>2</sub>Cl<sub>2</sub> phase was separated and washed with 10 mL of water, dried over MgSO<sub>4</sub>. After the evaporation of the CH<sub>2</sub>Cl<sub>2</sub> under reduced pressure (without heating), yellowish product was obtained.

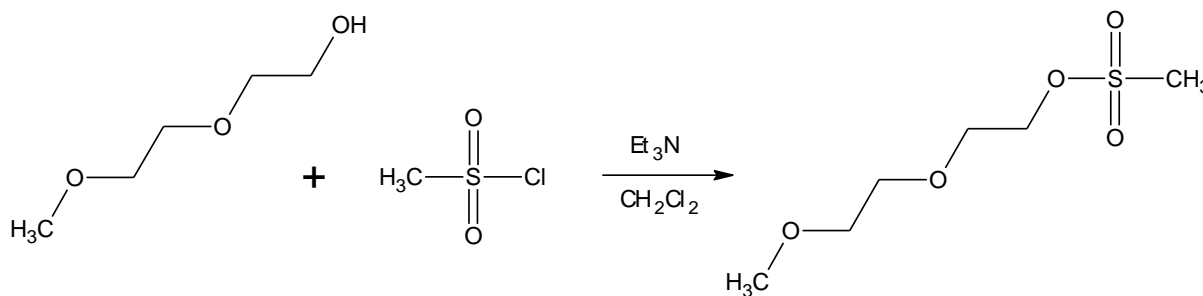
H-NMR results showed that the compound was obtained.

The product was left under high vacuum for overnight to remove solvent residual.

Yield: 3.11 g; 82.28%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 8.73 (s, 1H); 7.51 (s, 1H); 7.32 (s, 1H); 6.08-5.90 (m, 1H); 5.52-5.40 (m, 2H); 4.82-4.74 (d, 2H, J=6.3 Hz); 4.39-4.34 (t, 2H, J=4.6 Hz); 3.86-3.80 (t, 2H, J=4.6 Hz); 3.66-3.61 (m, 2H); 3.54-3.49 (m, 2H); 3.35 (s, 3H). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 136.07; 129.73; 126.56; 123.92; 123.18; 122.23; 118.04; 113.78; 71.87; 70.55; 68.77; 59.18; 52.49; 50.18. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C, 31.75; H, 3.87; N, 8.55; S, 13.02. Found: C, 32.45; H, 5.22; N, 8.75; S, 12.59. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>11</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 211.1447; found: 211.1405. TOF MS ES<sup>-</sup>: m/z calc. for [C<sub>2</sub>NO<sub>4</sub>F<sub>6</sub>S<sub>2</sub>]<sup>-</sup>: 279.9173; found: 279.9152.

14) 2-(2-methoxyethoxy)ethyl methanesulfonate



Diethylene glycol monomethyl ether	Methanesulfonyl chloride	Triethylamine	Product (Code: DEG-MME sulfonate)
FW: 120.15 g/mol	FW: 114.55 g/mol	FW: 101.19 g/mol	FW: 198.24 g/mol
n: 100 mmol	n: 120 mmol	n: 120 mmol	n: 100 mmol
m: 12 g	m: 13.7 g	m: 12.14 g	m: 19.82 g
	d: 1.47 g/mL V: 9.35 mL	d: 0.73 g/mL V: 16.6 mL	

**Procedure:**

A three-necked, round-bottomed 250 mL flask, equipped with a nitrogen inlet tube, a dropping funnel and a nitrogen gas outlet (a plastic stopper with a syringe needle) was prepared. The flask was cooled with an ice-water bath. Diethylene glycol monomethyl ether (100 mmol, 12 g), triethylamine (120 mmol, 16.6 mL) and 80 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction flask and stirred about 10 minutes. Methanesulfonyl chloride (120 mmol, 13.7 g) was weighed and added to the stirring solution in 40 minutes with a dropping funnel. The solution left for stirring half an hour.

The solution was washed with distilled cold water (2x100 mL) and then washed with saturated aqueous NaCl solution (100 mL).  $\text{CH}_2\text{Cl}_2$  phase was separated and dried with  $\text{MgSO}_4$ . After filtration of  $\text{MgSO}_4$  and evaporation of  $\text{CH}_2\text{Cl}_2$ , yellowish liquid product was obtained.

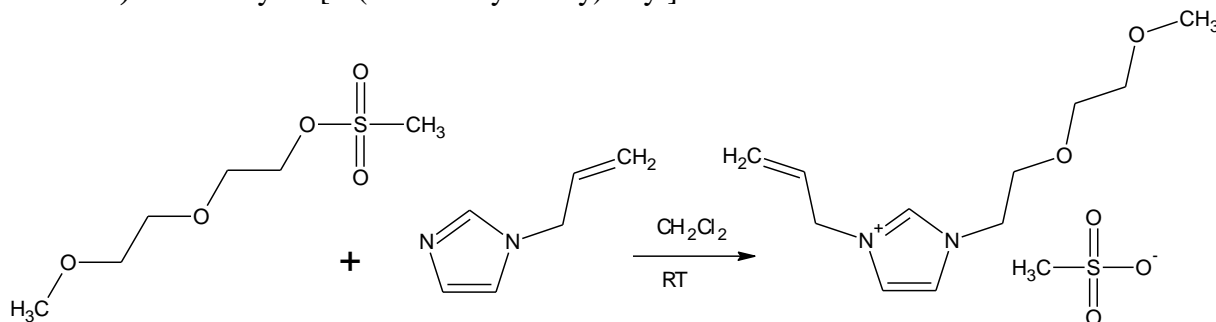
H-NMR results showed that the compound was obtained clearly.

Yield: 16.63 g; 83.90%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 4.42-4.35 (m, 2H); 3.81-3.74 (m, 2H); 3.70-3.63 (m, 2H); 3.58-3.52 (m, 2H); 3.38 (s, 3H); 3.08 (s, 3H).



**15)** 3-allyl-1-[2-(2-methoxyethoxy)ethyl]-1H-imidazol-3-ium methanesulfonate



<b>2-(2-methoxyethoxy)ethyl methanesulfonate</b>	<b>1-Allylimidazole</b>	<b>Product: (Code: Sulf-IL1)</b>
FW: 198.24 g/mol	FW: 108.14 g/mol	FW: 306.38 g/mol
n: 20 mmol	n: 20 mmol	n: 20 mmol
m: 3.96 g	m: 2.16 g	m: 6.13 g

**Procedure:**

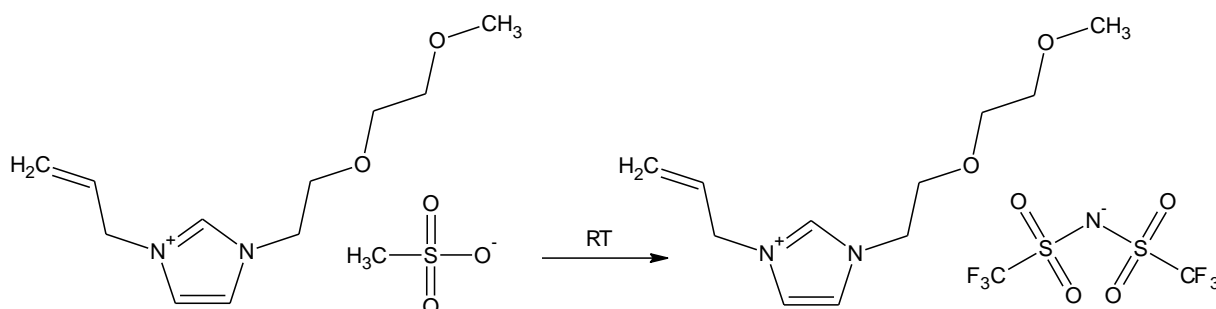
1-allylimidazole (2.16 g, 20 mmol) was weighed and 2-3 mL of  $\text{CH}_2\text{Cl}_2$  was added. To this stirring solution, 2-(2-methoxyethoxy)ethyl methanesulfonate (3.96 g, 20 mmol) was added dropwise and left for stirring overnight, at room temperature.

The product was obtained clearly.

Yield: 5.87 g, 95.76%

\*With heating of this product to 40 °C (for solvent evaporation) a small amount of another IL was obtained. The product was not stable.

**16)** 3-allyl-1-[2-(2-methoxyethoxy)ethyl]-1H-imidazol-3-ium  
bis(trifluoromethanesulfonyl)imide



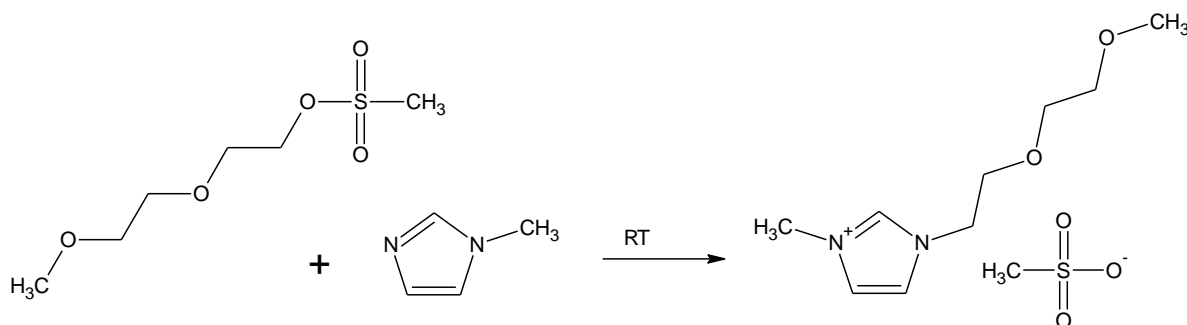
<b>Sulf-IL1</b>	<b>LiTFSI</b>	<b>Product (Code: Sulf-IL1-TFSI)</b>
FW: 306.38 g/mol	FW: 287.09 g/mol	FW: 491.43 g/mol
n: 19.2 mmol	n: 20.2 mmol	n: 19.2 mmol
m: 5.87 g	m: 5.8 g	m: 9.43 g

**Procedure:**

Methanesulfonate ionic liquid (5.87 g, 19.2 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL) and LiTFSI was dissolved in distilled water (15 mL). The solutions were mixed in a separation funnel and shaken very well about 2 minutes. The bottom  $\text{CH}_2\text{Cl}_2$  layer was separated, washed with distilled water (2x10 mL) and dried over  $\text{MgSO}_4$ . Evaporation of the  $\text{CH}_2\text{Cl}_2$  under the reduced pressure at RT, provided the desired product.

H-NMR results showed that there is small amount of another ionic liquid. The product was not pure.

**17)** 1-[2-(2-methoxyethoxy)ethyl]-3-methyl-1H-imidazol-3-ium methanesulfonate



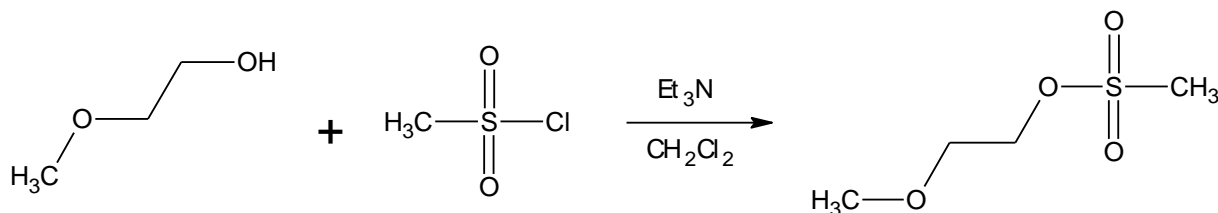
<b>2-(2-methoxyethoxy)ethyl methanesulfonate</b>	<b>1-ethylimidazole</b>	<b>Product (Code: Sulf-IL2)</b>
FW: 198.24 g/mol	FW: 82.11 g/mol	FW: 280,34 g/mol
n: 42.3 mmol	n: 42.3 mmol	n: 42.3 mmol
m: 8.39 g	m: 3.47 g	m: 11.86 g
	d: 1.035 g/mL V: 3.35 mL	

**Procedure:**

2-(2-methoxyethoxy)ethyl methanesulfonate (8.39 g, 42.3 mmol) was weighed and 4 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. To this stirring solution, 1-ethylimidazole (3.35 mL, 42.3 mmol) was added and left for stirring overnight at room temperature.

The clean H-NMR spectrum was obtained at first, after evaporation of the CH<sub>2</sub>Cl<sub>2</sub> at room temperature and drying under high vacuum (at RT) second IL was obtained. The product was not pure.

18) 2-methoxyethyl methanesulfonate



2-methoxyethanole	Methanesulfonyl chloride	Triethylamine	Product (Code: STM-2-sulf)
FW: 76.1 g/mol	FW: 114.55 g/mol	FW: 101.19 g/mol	FW: 154.18 g/mol
n: 100 mmol	n: 120 mmol	n: 120 mmol	n: 100 mmol
m: 7.6 g	m: 13.75 g	m: 12.14 g	m: 15.4 g
d: 0.964 g/mL V: 7.9 mL	d: 1.474 g/mL V: 9.3 mL	d: 0.73 g/mL V: 16.6 mL	

**Procedure:**

A three-necked, round-bottomed 250 mL flask, equipped with a nitrogen inlet tube, a dropping funnel and a nitrogen gas outlet (a plastic stopper with a syringe needle) was prepared. The flask was cooled with an ice-water bath. 2-methoxyethanole (100 mmol, 7.6 g), triethylamine (120 mmol, 16.6 mL) and 80 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction flask and stirred about 10 minutes. Methanesulfonyl chloride (120 mmol, 13.75 g) was weighed and added to the stirring solution in 30 minutes with a dropping funnel. The solution left for stirring half an hour.

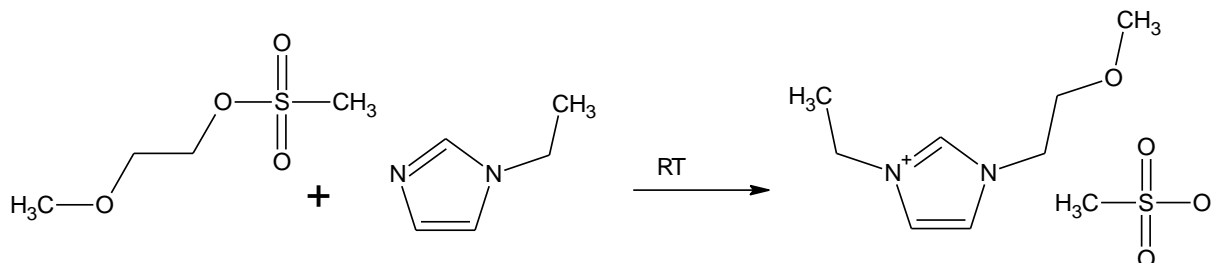
The solution was washed with distilled cold water (2x100 mL) and then washed with saturated aqueous NaCl solution (100 mL). CH<sub>2</sub>Cl<sub>2</sub> phase was separated and dried with MgSO<sub>4</sub>. After filtration of MgSO<sub>4</sub> and evaporation of CH<sub>2</sub>Cl<sub>2</sub>, yellowish liquid product was obtained.

H-NMR results showed that the compound was obtained clearly.

Yield: 13.98 g; 90.78 %

<sup>1</sup>H NMR (δ<sub>H</sub>, ppm, 300 MHz, CDCl<sub>3</sub>): 4.41-4.32 (m, 2H); 3.70-3.62 (m, 2H); 3.40 (s, 3H); 3.06 (s, 3H).

**19)** 3-ethyl-1-(2-methoxyethyl)-1H-imidazol-3-ium methanesulfonate



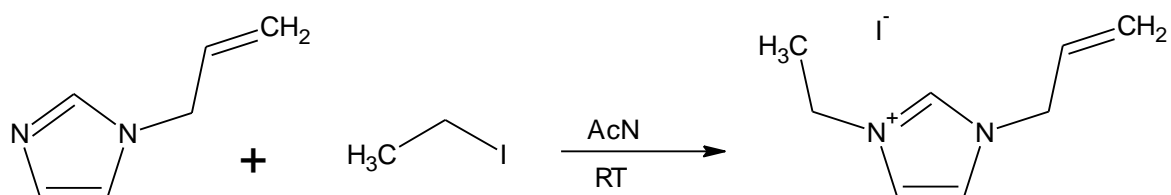
<b>2-methoxyethyl methane sulfonate</b>	<b>Ethylimidazole</b>	<b>Product (Code: SO11-sulf)</b>
FW: 154.18 g/mol	FW: 96.13 g/mol	FW: 250.32 g/mol
n: 20 mmol	n: 20 mmol	n: 20 mmol
m: 3.08 g	m: 1.92 g	m: 5 g

**Procedure:**

1-ethylimidazole (20 mmol, 1.92 g) was weighed and transferred into the flask. Sulfonate compound (20 mmol, 3.08 g) was added to the stirring 1-ethylimidazole and the mixture was stirred. The product was obtained in 5 minutes.

The product was not pure, mixture of some ionic liquids were obtained.

20) 1-allyl-3-ethyl imidazolium iodide



1-Allylimidazole	Iodoethane	Product: 1-allyl-3-ethyl imidazolium iodide Code: AEII
FW: 108.14 g/mol	FW: 169.99 g/mol	FW: 264.11 g/mol
n: 18.5 mmol	n: 18.6 mmol	n: 18.5 mmol
m: 2g	m: 2.9 g	m: 4.88 g

**Procedure:**

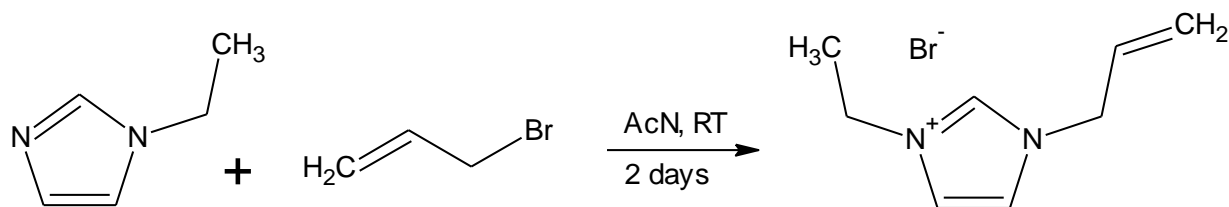
1-allylimidazole (18.5 mmol, 2 g) was weighed in a sealed tube and 2 mL of acetonitrile was added as a solvent. The solution was stirred at room temperature and iodoethane (18.6 mmol, 2.9 g) was added to the stirring solution. The solution was left for stirring overnight at room temperature (RT). There was still unreacted allylimidazole, the solution was left for stirring two more days at RT.

After 3 days, the product obtained clearly.

Yield: 4.43 g; 90.78%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 10.04 (s, 1H); 7.66 (s, 1H); 7.52 (s, 1H); 6.15-6.02 (m, 1H); 5.58-5.48 (m, 2H); 5.06-5.04 (d, 2H,  $J=6.6$  Hz); 4.49-4.42 (q, 2H,  $J=7.5$  Hz); 1.66-1.61 (t, 3H,  $J=7.4$  Hz).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 136.35; 130.07; 123.49; 122.73; 122.61; 62.63; 46.03; 16.10. Anal. Calcd for  $\text{C}_8\text{H}_{13}\text{N}_2\text{I}$ : C, 36.35; H, 4.92; N, 10.60. Found: C, 36.07; H, 5.98; N, 10.75. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_8\text{H}_{13}\text{N}_2]^+$ : 137.1079; found: 137.1043. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{I}]^-$ : 126.9045; found: 126.9026.

## 21) 1-allyl-3-ethyl imidazolium bromide



1-Ethylimidazole	Allylbromide	Product: 1-allyl-3-ethyl imidazolium bromide Code: AEI-Br
FW: 96.13 g/mol	FW: 120.98 g/mol	FW: 217.11 g/mol
n: 50 mmol	n: 50 mmol	n: 50 mmol
m: 4.81 g	m: 6.05 g	m: 10.85 g

### Procedure:

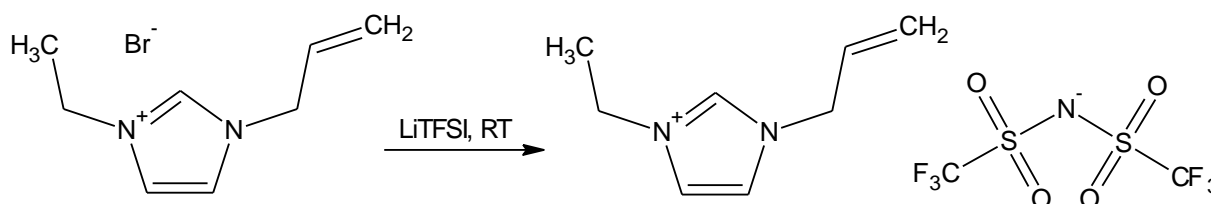
1-Ethylimidazole (50 mmol, 4.81 g) was weighed into the sealed tube and 3 mL of acetonitrile (AcN) was added. To this stirring solution, allylbromide (50 mmol, 6.05 g) was added dropwise. Because of this reaction is very exothermic, the reaction flask was cooled with a water bath during the addition of allylbromide. The solution was left for stirring about 2 days. After 2 days, the AcN was evaporated and the crude product was washed with ethylacetate (3x20 mL) and diethylether (20 mL) to remove the small amount of unreacted 1-ethylimidazole. The product was dried under reduced pressure.

The H-NMR result indicates that the product was obtained clearly.

Yield: 10.45 g; 96.31%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 10.32 (s, 1H); 7.79 (s, 1H); 7.59 (s, 1H); 6.13-6.00 (m, 1H); 5.54-5.44 (m, 2H); 5.07-5.05 (d, 2H,  $J=6.3$  Hz); 4.50-4.43 (q, 2H,  $J=7.2$  Hz); 1.65-1.60 (t, 3H,  $J=7.4$  Hz).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 136.64; 130.34; 122.90; 122.78; 122.51; 52.29; 45.69; 16.04. Anal. Calcd for  $\text{C}_8\text{H}_{13}\text{N}_2\text{Br}$ : C, 44.22; H, 5.99; N, 12.90. Found: C, 43.61; H, 6.23; N, 13.01.

## 22) 1-allyl-3-ethyl imidazolium bis(trifluoromethanesulfonyl)imide



<b>1-Allyl-3-ethyl imidazolium bromide</b>	<b>LiTFSI</b>	<b>Product: 1-allyl-3-ethyl imidazolium TFSI Code: AEI-TFSI</b>
FW: 217.11 g/mol	FW: 287.09 g/mol	FW: 417.35 g/mol
n: 48.7 mmol	n: 49.7 mmol	n: 48.7 mmol
m: 10.58 g	m: 14.3 g	m: 20.3 g

### Procedure:

1-Allyl-3-ethyl imidazolium bromide (48.7 mmol, 10.58 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and LiTFSI was dissolved in distilled water (15 mL). The solutions were mixed in a separation funnel and shaken very well about 3 minutes. After the phase separation, bottom CH<sub>2</sub>Cl<sub>2</sub> phase was taken and washed with distilled water (2x15 mL). The CH<sub>2</sub>Cl<sub>2</sub> was evaporated on rotary evaporator and the product was dried under reduced pressure.

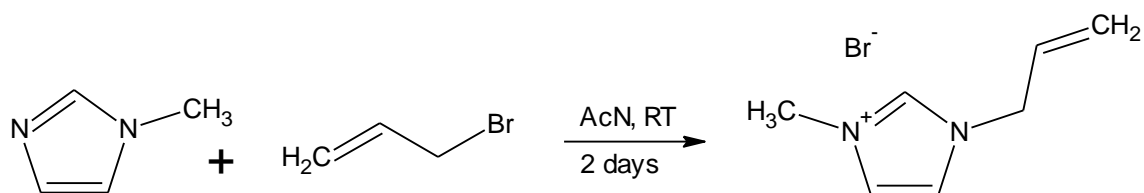
The H-NMR result indicates that the product was obtained clearly.

Yield: 18.82 g; 92.71%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 8.75 (s, 1H); 7.38 (s, 1H); 7.31 (s, 1H); 6.05-5.92 (m, 1H); 5.50-5.44 (m, 2H); 4.79-4.77 (d, 2H, J=6.3 Hz); 4.30-4.22 (q, 2H, J=7.2 Hz); 1.57-1.50 (t, 3H, J=7.4 Hz). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 135.05; 129.79; 126.51; 123.03; 122.75; 122.67; 122.26; 118.00; 113.75; 52.35; 45.63; 15.25. Anal. Calcd for C<sub>10</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 28.75; H, 3.11; N, 10.06. Found: C, 29.09; H, 3.03; N, 10.16.



### 23) 1-allyl-3-methyl imidazolium bromide



1-Methylimidazole	Allylbromide	Product: 1-allyl-3-methyl imidazolium bromide Code: AMI-Br
FW: 82.11 g/mol	FW: 120.98 g/mol	FW: 203.08 g/mol
n: 100 mmol	n: 100 mmol	n: 100 mmol
m: 8.2 g	m: 12.1 g	m: 20.31 g
d: 1.03 g/mL V: 7.96 mL		

#### Procedure:

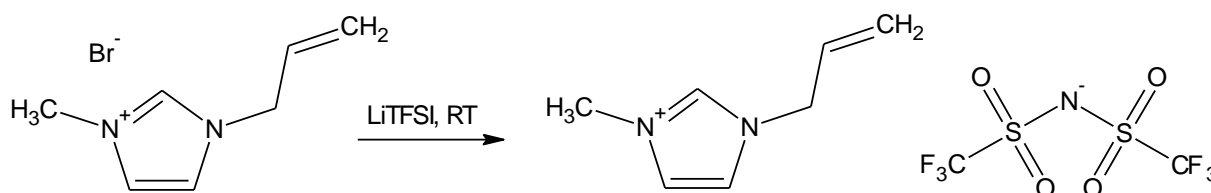
1-Methylimidazole (100 mmol, 7.96 mL) was transferred into the sealed tube and 5 mL of acetonitrile (AcN) was added. To this stirring solution, allylbromide (100 mmol, 12.1 g) was added dropwise. Because of this reaction is very exothermic, the reaction flask was cooled with a water bath during the addition of allylbromide. The solution was left for stirring about 2 days. The solvent was evaporated and the product was dried under reduced pressure.

The H-NMR result indicates that the product was obtained clearly.

Yield: 18.11 g; 89.17%

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 10.16 (s, 1H); 7.72 (s, 1H); 7.52 (s, 1H); 6.04-5.91 (m, 1H); 5.47-5.37 (m, 2H); 4.98-4.96 (d, 2H,  $J=6.3$  Hz); 4.07 (s, 3H).  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 137.32; 130.24; 124.34; 122.89; 122.48; 52.26; 37.14. Anal. Calcd for  $\text{C}_7\text{H}_{11}\text{N}_2\text{Br}$ : C, 41.36; H, 5.42; N, 13.79. Found: C, 40.28; H, 5.91; N, 13.58. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_7\text{H}_{11}\text{N}_2]^+$ : 123.0922; found: 123.0921. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{Br}]^-$ : 78.9183; found: 78.9172.

## 24) 1-allyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide



<b>1-Allyl-3-methyl imidazolium bromide</b>	<b>LiTFSI</b>	<b>Product: 1-allyl-3-methyl imidazolium TFSI Code: AMI-TFSI</b>
FW: 203.08 g/mol	FW: 287.09 g/mol	FW: 403.32 g/mol
n: 49.2 mmol	n: 50.2 mmol	n: 49.2 mmol
m: 10 g	m: 14.4 g	m: 19.8 g

### Procedure:

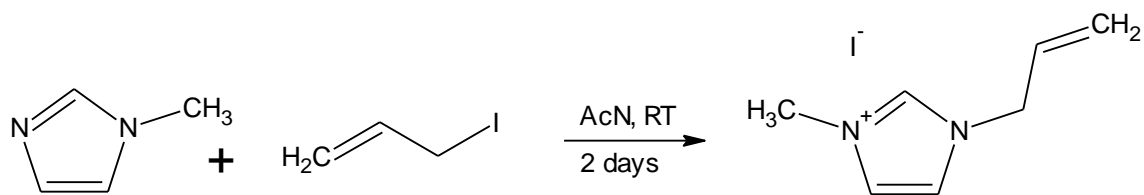
1-Allyl-3-methyl imidazolium bromide (49.2 mmol, 10 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and LiTFSI was dissolved in distilled water (15 mL). The solutions were mixed in a separation funnel and shaken very well about 3 minutes. After the phase separation, bottom CH<sub>2</sub>Cl<sub>2</sub> phase was taken and washed with distilled water (2x15 mL) and dried over MgSO<sub>4</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated on rotary evaporator and the product was dried under reduced pressure.

The H-NMR result indicates that the product was obtained clearly.

Yield: 17.74 g; 89.60%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 8.59 (s, 1H); 7.38 (s, 1H); 7.35 (s, 1H); 6.04-5.95 (m, 1H); 5.49-5.43 (m, 2H); 4.78-4.76 (d, 2H, J=6.6 Hz); 3.92 (s, 3H). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 136.06; 129.74; 126.48; 124.21; 122.98; 122.64; 122.23; 117.98; 113.72; 52.30; 36.50. Anal. Calcd for C<sub>9</sub>H<sub>11</sub>F<sub>6</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 26.78; H, 2.73; N, 10.41; S, 15.47. Found: C, 26.93; H, 3.07; N, 10.32; S, 16.45. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>7</sub>H<sub>11</sub>N<sub>2</sub>]<sup>+</sup>: 123.0922; found: 123.0908. TOF MS ES<sup>-</sup>: m/z calc. for [C<sub>2</sub>NO<sub>4</sub>F<sub>6</sub>S<sub>2</sub>]<sup>-</sup>: 279.9173; found: 279.9112.

## 25) 1-allyl-3-methyl imidazolium iodide



1-Methylimidazole	Allyliodide(98%)	Product: 1-allyl-3-methyl imidazolium iodide Code: AMII
FW: 82.11 g/mol	FW: 167.98 g/mol	FW: 250.08 g/mol
n: 10 mmol	n: 10.1 mmol	n: 10 mmol
m: 0.82 g	m: 1.7 g	m: 2.5 g
d: 1.03 g/mL V: 0.8 mL	d: 1.837 g/mL V: 0.94 mL	

### Procedure:

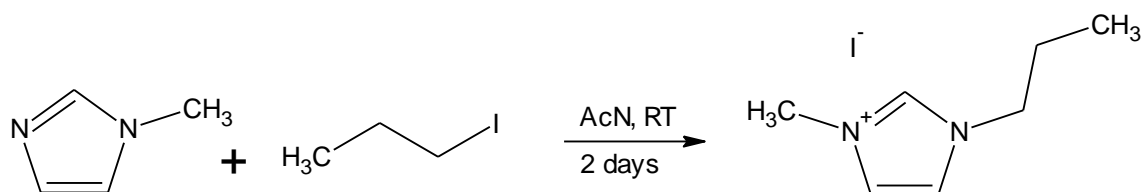
1-Methylimidazole (10 mmol, 0.8 mL) was transferred into the sealed tube and 1 mL of acetonitrile (AcN) was added. To this stirring solution, allyliodide (10.1 mmol, 0.94 mL) was added dropwise and the solution was left for stirring about 2 days at RT. After 2 days, there was still unreacted 1-methylimidazole (20%). The temperature was increased to 50 °C and the solution was left for stirring overnight. There was still unreacted 1-ethylimidazole. 0.2 mL of allyliodide was added to the stirring solution and left for stirring overnight at 50 °C. The product was obtained without unreacted starting materials. The solvent was evaporated and the product was dried under reduced pressure.

The H-NMR result indicates that the product was obtained clearly.

Yield: 98.4%

$^1\text{H NMR}$  ( $\delta_{\text{H}}$ , ppm, 300 MHz,  $\text{CDCl}_3$ ): 10.05 (s, 1H); 7.47 (s, 1H); 7.38 (s, 1H); 6.14-6.00 (m, 1H); 5.57-5.50 (m, 2H); 5.02-5.00 (d, 2H,  $J=6.3$  Hz); 4.13 (s, 3H).  $^{13}\text{C NMR}$  ( $\delta_{\text{C}}$ , ppm, 100 MHz,  $\text{CDCl}_3$ ): 137.04; 130.00; 124.35; 123.50; 122.57; 52.61; 37.71. Anal. Calcd for  $\text{C}_7\text{H}_{11}\text{N}_2\text{I}$ : C, 33.59; H, 4.40; N, 11.19. Found: C, 33.36; H, 4.63; N, 10.93. TOF MS  $\text{ES}^+$ : m/z calc. for  $[\text{C}_7\text{H}_{11}\text{N}_2]^+$ : 123.0922; found: 123.0897. TOF MS  $\text{ES}^-$ : m/z calc. for  $[\text{I}]^-$ : 126.9045; found: 126.9052.

26) 1-methyl-3-propyl imidazolium iodide



1-Methylimidazole	Iodopropane	Product: 1-methyl-3-propyl imidazolium iodide Code: PMII
FW: 82.11 g/mol	FW: 169.99 g/mol	FW: 252.1 g/mol
n: 62.7 mmol	n: 62.7 mmol	n: 62.7 mmol
m: 5.15 g	m: 10.66 g	m: 15.8 g
d: 1.03 g/mL V: 5 mL	d: 1.74 g/mL V: 6.13 mL	

**Procedure:**

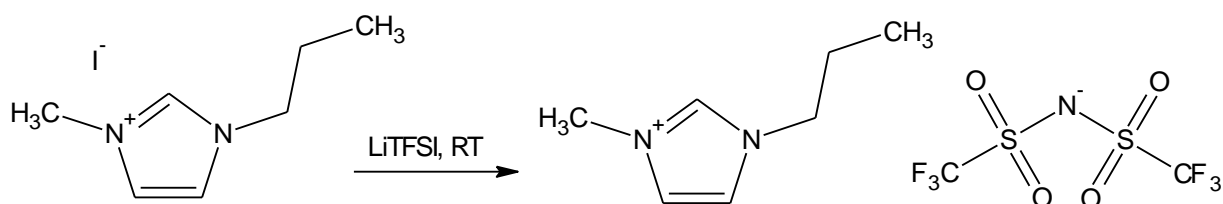
1-Methylimidazole (62.7 mmol, 5 mL) was transferred into the sealed tube and 3 mL of acetonitrile (AcN) was added. To this stirring solution, iodopropane (62.7 mmol, 10.66 g) was added dropwise and the solution was left for stirring overnight at RT. There was unreacted 1-methylimidazole in the crude product. The AcN solvent was evaporated and the product was washed with ethylacetate (4x20 mL). The product was dried under reduced pressure.

The H-NMR result indicates that the product was obtained clearly.

Yield: 13.77 g; 87.15%

<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 9.94 (s, 1H); 7.69 (s, 1H); 7.65 (s, 1H); 4.36-4.32 (t, 2H, J=7.4 Hz); 4.15 (s, 3H); 2.06-1.94 (m, 2H); 1.03-0.98 (t, 3H, J=7.4). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 135.66; 122.82; 121.43; 50.64; 36.18; 22.76. Anal. Calcd for C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>I: C, 33.32; H, 5.16; N, 11.11. Found: C, 33.03; H, 5.71; N, 11.10. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>]<sup>+</sup>: 125.1079; found: 125.1076. TOF MS ES<sup>-</sup>: m/z calc. for [I]<sup>-</sup>: 126.9045; found: 126.8993.

**27) 1-methyl-3-propyl imidazolium bis(trifluoromethanesulfonyl)imide**



<b>1-methyl-3-propyl imidazolium iodide</b>	<b>LiTFSI</b>	<b>Product: 1-methyl-3-propyl imidazolium TFSI Code: PMI-TFSI</b>
FW: 252.1 g/mol	FW: 287.09 g/mol	FW: 252.1 g/mol
n: 62.7 mmol	n: 63.7 mmol	n: 62.7 mmol
m: 15.8 g	m: 18.29 g	m: 15.8 g

**Procedure:**

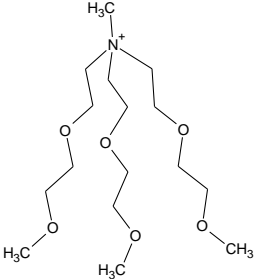
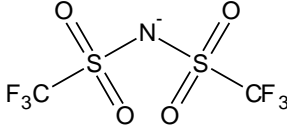
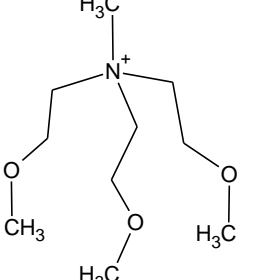
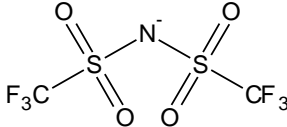
1-Methyl-3-propyl imidazolium iodide (62.7 mmol, 15.8 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and LiTFSI (63.7 mmol, 18.29 g) was dissolved in distilled water (25 mL). The solutions were mixed in a separation funnel and shaken very well about 3 minutes. After the phase separation, bottom CH<sub>2</sub>Cl<sub>2</sub> phase was taken and washed with distilled water (2x20 mL) and dried over MgSO<sub>4</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated on rotary evaporator and the product was dried under reduced pressure.

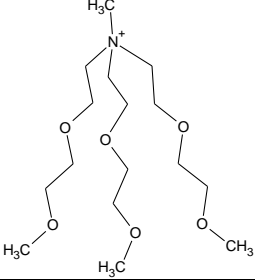
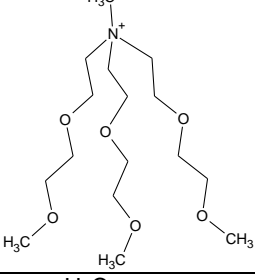
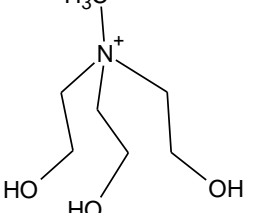
The H-NMR result indicates that the product was obtained clearly.

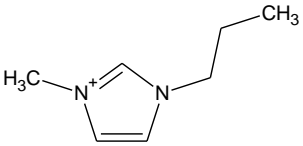
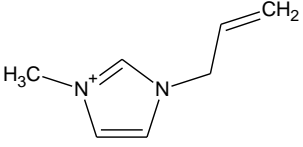
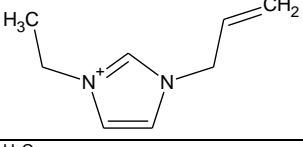
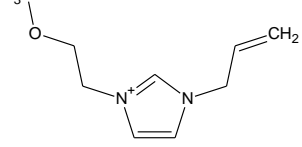
Yield: 20.42 g; 80.36%

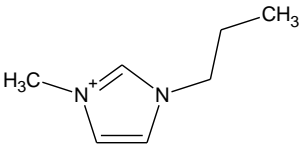
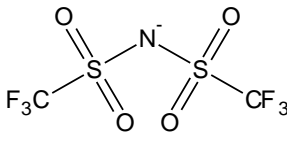
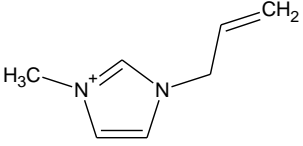
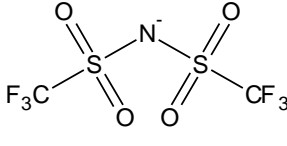
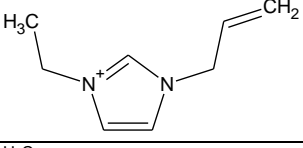
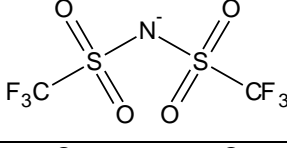
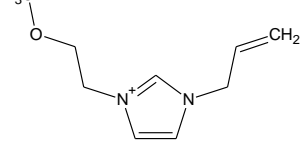
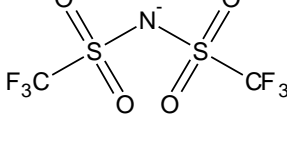
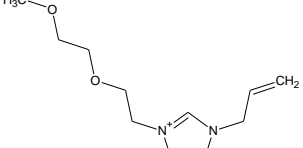
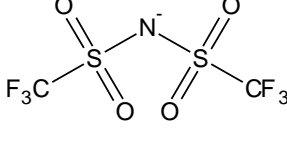
<sup>1</sup>H NMR ( $\delta_H$ , ppm, 300 MHz, CDCl<sub>3</sub>): 8.63 (s, 1H); 7.39 (s, 1H); 7.37 (s, 1H); 4.17-4.12 (t, 2H, J=7.4 Hz); 3.93 (s, 3H); 1.97-1.85 (m, 2H); 0.99-0.94 (t, 3H, J=7.4). <sup>13</sup>C NMR ( $\delta_C$ , ppm, 100 MHz, CDCl<sub>3</sub>): 136.01; 126.51; 124.08; 122.78; 122.26; 118.00; 113.75; 51.78; 36.42; 23.64; 10.54. Anal. Calcd for C<sub>9</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 26.65; H, 3.21; N, 10.36; S, 15.79. Found: C, 26.84; H, 3.82; N, 10.41; S, 15.52. TOF MS ES<sup>+</sup>: m/z calc. for [C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>]<sup>+</sup>: 125.1079; found: 125.1081. TOF MS ES<sup>-</sup>: m/z calc. for [C<sub>2</sub>NO<sub>4</sub>F<sub>6</sub>S<sub>2</sub>]<sup>-</sup>: 279.9173; found: 279.9171.

## Viscosity Measurements:

Cation	Anion	Viscosity (cP)				
		20 °C	25 °C	40 °C	60 °C	80 °C
		62	50	27	13	8
		46	44	26	12	8

Cation	Anion	Viscosity (cP)				
		20 °C	25 °C	40 °C	60 °C	80 °C
	I <sup>-</sup>	-	682	258	82	36
	Cl <sup>-</sup>	-	434	167	55	24
	I <sup>-</sup>	-	1351	1192	191	80

Cation	Anion	Viscosity (cP)				
		20 °C	25 °C	40 °C	60 °C	80 °C
	I <sup>-</sup>	769 880*	616	235	81	35
	Br <sup>-</sup>	1361	991	306	91	37
	I <sup>-</sup>	342 350*	279	122	49	25
	I <sup>-</sup>	1249	938	315	98	42

Cation	Anion	Viscosity (cP)				
		20 °C	25 °C	40 °C	60 °C	80 °C
		38 40*	32	18	10	6
		24	20	12	7	4
		29*				
		45	39	23	13	8
		48	41	24	12	8

\*Literature values

### **TGA Measurements:**

<b>Compound Code</b>	<b>Degredation Temp. (°C)</b>
PEA-I	175
PEA-Cl	164
PEA-TFSI	286
TEA-I	221
MTEA-I	175
MTEA-TFSI	312
AI-IL3-Br	-
AL-IL3-TFSI	333
AI-IL4-I	223
AI-IL4-TFSI	335
PMII	241
PMI-TFSI	344
AMII	220
AMI-Br	231
AMI-TFSI	327
AEII	225
AEI-Br	233
AEI-TFSI	338



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