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Dicationic disiloxane ionic liquids

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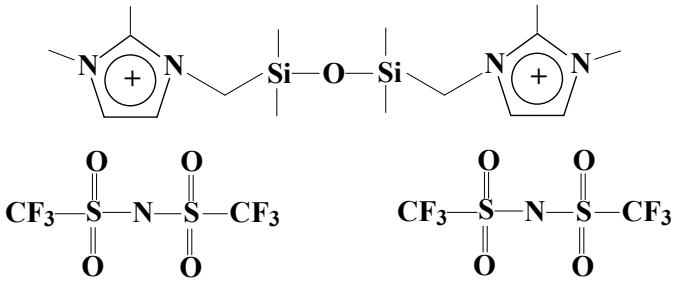
1. Methods and Materials

^{1}H и ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer (300.13 MHz and 75.47 MHz) in DMSO-d_6. IR ATR spectra were recorded on a Nicolet iS50 IR spectrometer (built-in attachment, crystal-diamond) at the resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a Derivatograph-C instrument (MOM, Hungary) under an Ar atmosphere at a heating rate of 10 °C min^{-1} (sample mass of ~20 mg). The melting points and glass transition temperatures of ILs were determined *via* differential scanning calorimetry (DSC) using a DSC-822e instrument (Mettler-Toledo, Switzerland). Glass transition temperatures were determined in the temperature range from −100 to 100 °C at a sample heating rate of 10 °C min^{-1} under an Ar atmosphere. Kinematic viscosity was measured using an Ostwald viscometer with capillar diameter of 1.2 mm. The viscometer was calibrated at 25 °C using ethylene glycol (Aldrich, 99.8%, water content < 0.01%) as the reference liquid. The evaporation of ILs *in vacuo* was studied using a McBain quartz spring balance. Each sample (~0.2 g) was placed in a ceramic cup attached to the movable end of the spring of the balance. The surface area of the liquid was about 1.7 cm^2. Tubes containing the samples were placed in a thermostated aluminum block. Spring elongation was determined from the change in the positions of reference marks using a KM-8 cathetometer with an accuracy of ±0.02 mm. The spring had a sensitivity of 0.3709 mm mg^{-1}. The setup was evacuated with a diffusion pump. Before measurements, the samples were dried to constant weight (for ~15 h) *in vacuo* (~0.013 Pa) at 100 °C.

Dimethyl(chloromethyl)chlorosilane (98%), dimethyl(3-chloropropyl)chlorosilane (97%), 1-methylimidazole (99%), 2-methylimidazole (99%), 1,2- dimethylimidazole (98%), 1-(2-hydroxyethyl)imidazole (97%), 1-(chloro)-2-methoxyethane (98%), bis(trifluoromethyl-sulfonyl)imide lithium (99%), magnesium metal (98%, 20-230 mesh) were purchased from Acros and Sigma-Aldrich. Imidazole derivatives were dried by azeotropic distillation of absolutized acetonitrile. All organic solvents used in the synthesis were previously absolutized with CaH_2 and distilled.

2. Synthesis of ionic liquids 1-5 procedures

2.1. Bis (trifluoromethylsulfonyl)imide 1,1,3,3-tetramethyl-1,3-di([1,2-dimethylimidazolium]methyl)disiloxane (1).



First step of the synthesis.

Dimethyl(chloromethyl)chlorosilane (100 ml, 108.6 g) was dropwise added to distilled H_2O (300 ml) with stirring on a magnetic stirrer. Then the reaction mixture was stirred for 1 h. Hexane (200 g) was dropwise added, and the acidic water layer was removed. The organic layer was washed to a neutral pH with H_2O. Then hexane was removed by distillation and *in vacuo* at room temperature. Yield of 1,1,3,3-tetramethyl-1,3-di(chloromethyl)disiloxane was 85.6 g (97.5 %).

Second step of the synthesis.

1,1,3,3-Tetramethyl-1,3-(dichloromethyl)disiloxane (3 ml, 3.15 g, 0.0136 mol) was added dropwise under Ar atmosphere to a solution of 1,2-dimethylimidazole (2.61 g, 0.0272 mol) in MeCN (6 ml). The reaction mixture was refluxed for 72 h. Then the liquid phase was decanted, and the white precipitate was dried *in vacuo* to remove the traces of solvent. Soluble in MeCN impurities were removed together with the liquid phase. The yield of the target product was 5.07 g (88 %).

Third step of the synthesis.

A solution of lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$, 7.45 g, 0.0260 mol) in MeCN (15 ml) was added under Ar to chloride precursors (5 g, 0.0118 mol) of IL **1**. The reaction mixture was stirred at room temperature for 3 h. The precipitate of LiCl was filtered, MeCN was removed from the filtrate, and CH_2Cl_2 (50 ml) was added. The solution was washed with water to remove the LiCl traces until no wash water reacted with $AgNO_3$. The target ionic liquid was dried by azeotropic distillation of absolute CH_2Cl_2. The yield of IL **1** was 10.02 g (93%). ^{1}H NMR (DMSO-d_6, 300.13 MHz), δ, ppm: 0.16, s (12H, CH_3–Si), 2.52, s (6H, CH_3–C), 3.75, s (6H, CH_3–N), 3.82, s (4H, CH_2–N), 7.41, m (2H, CH=), 7.62, m (2H, CH =). ^{13}C NMR spectrum (DMSO-d_6, 75.47 MHz), δ, ppm: 0.48, 9.74, 35.26, 40.21, 113.45, 11.70, 121.83, 122, 07, 122.81, 126.37, 143.97. Gross formula: $C_{20}H_{32}N_6O_9F_{12}S_4Si_2$, molecular weight: 912.92.

Calculated (%): C 26.31, H 3.53, N 9.21, F 24.97, S 14.05, Si 6.15. Found (%): C 26.23, H 3.63, N 9.16, F 24.94, S 13.91, Si 6.26.

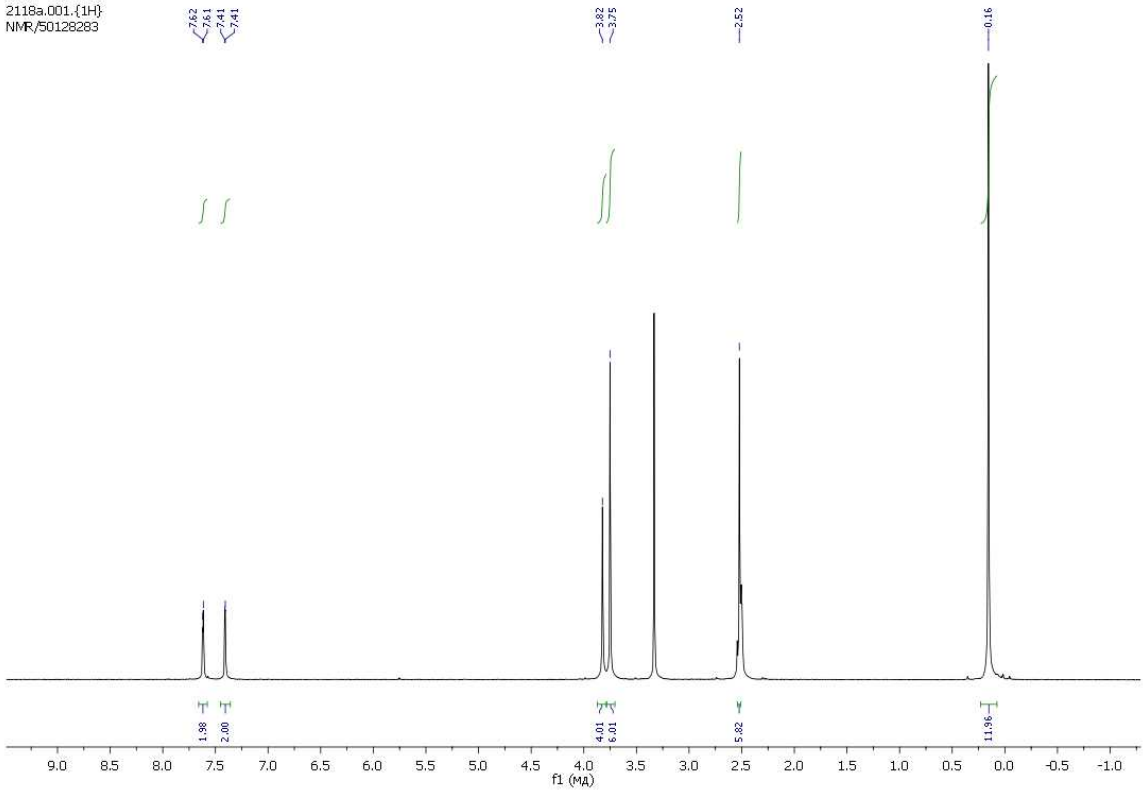


Figure S1 ^{1}H NMR spectrum of IL **1**.

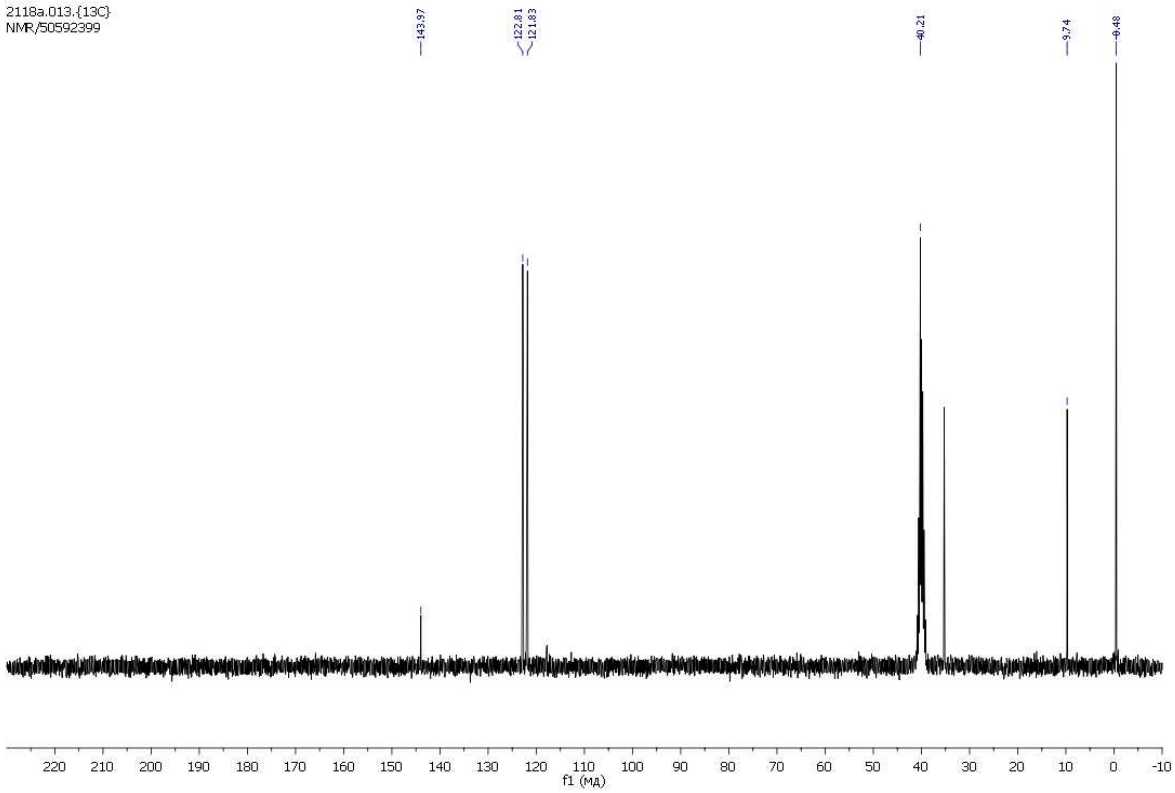


Figure S2 ^{13}C NMR spectrum of IL **1**.

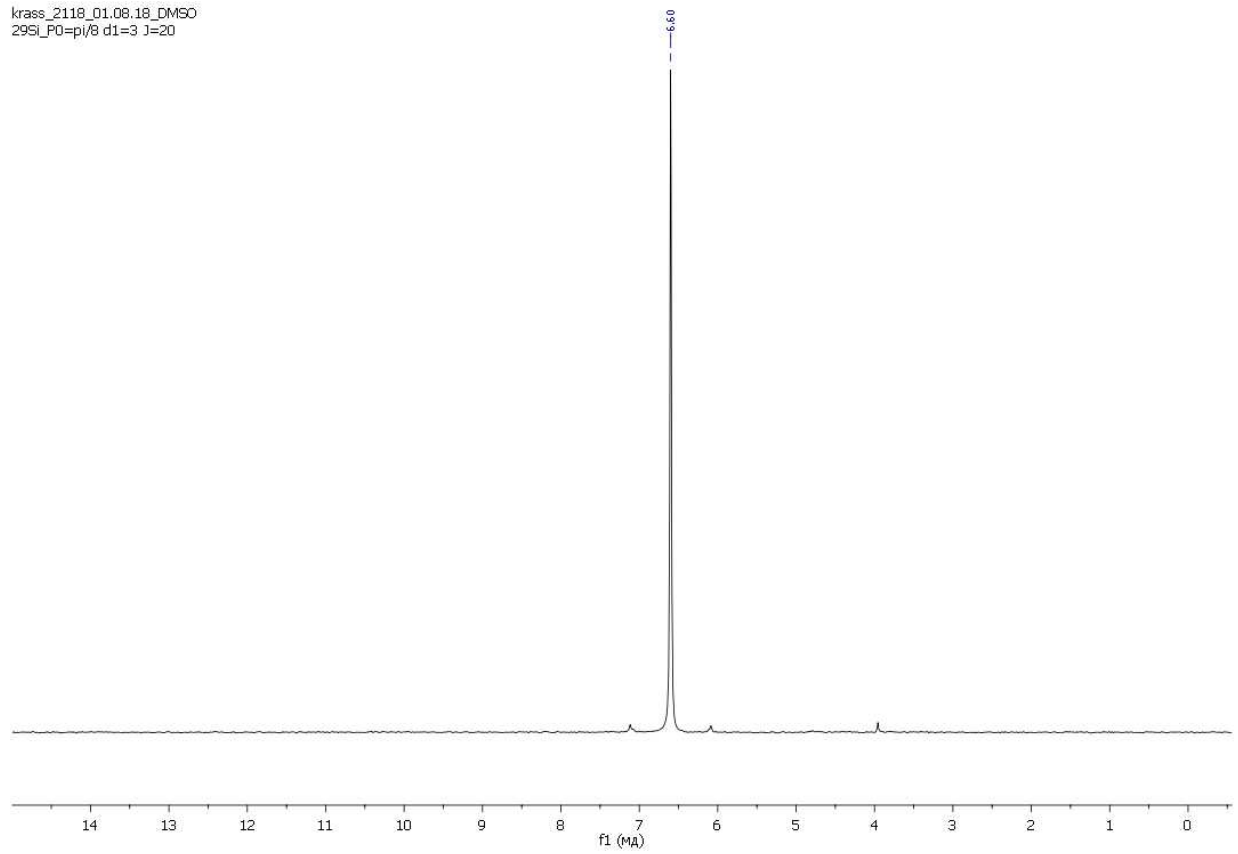


Figure S3 ^{29}Si NMR spectrum of IL **1**.

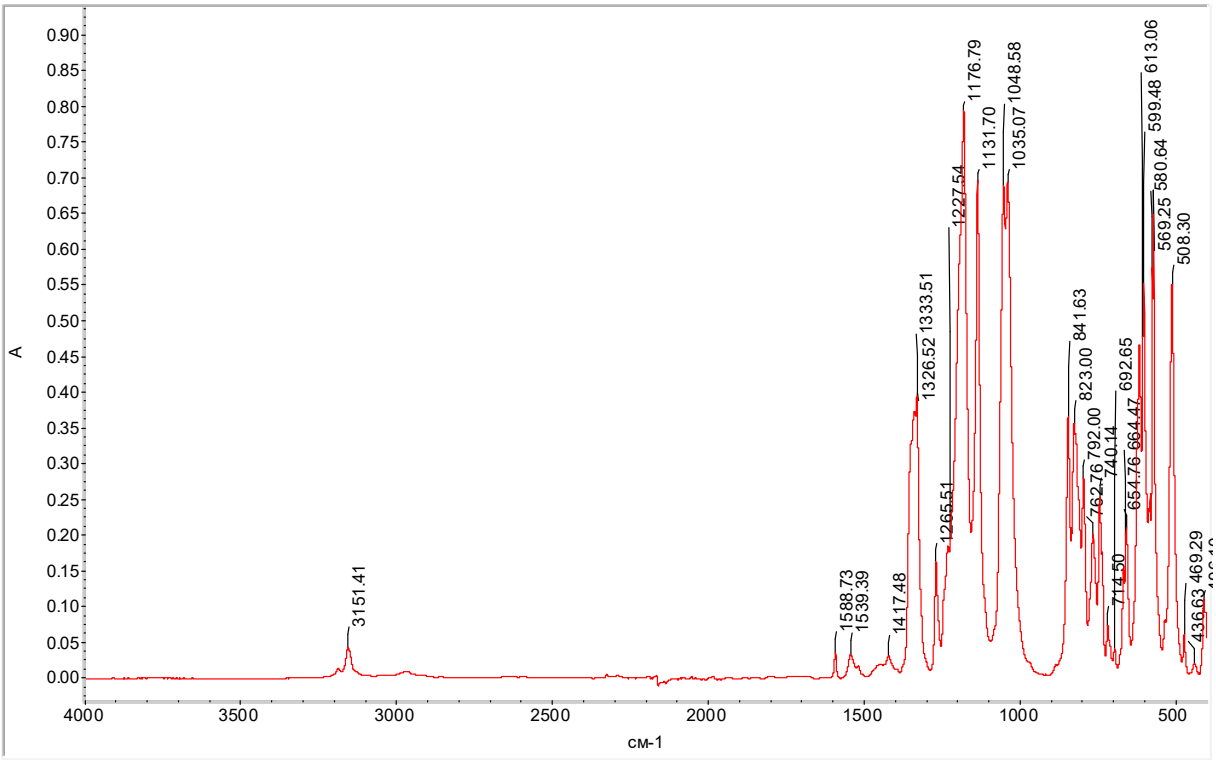


Figure S4 IR ATR spectrum of IL **1**.

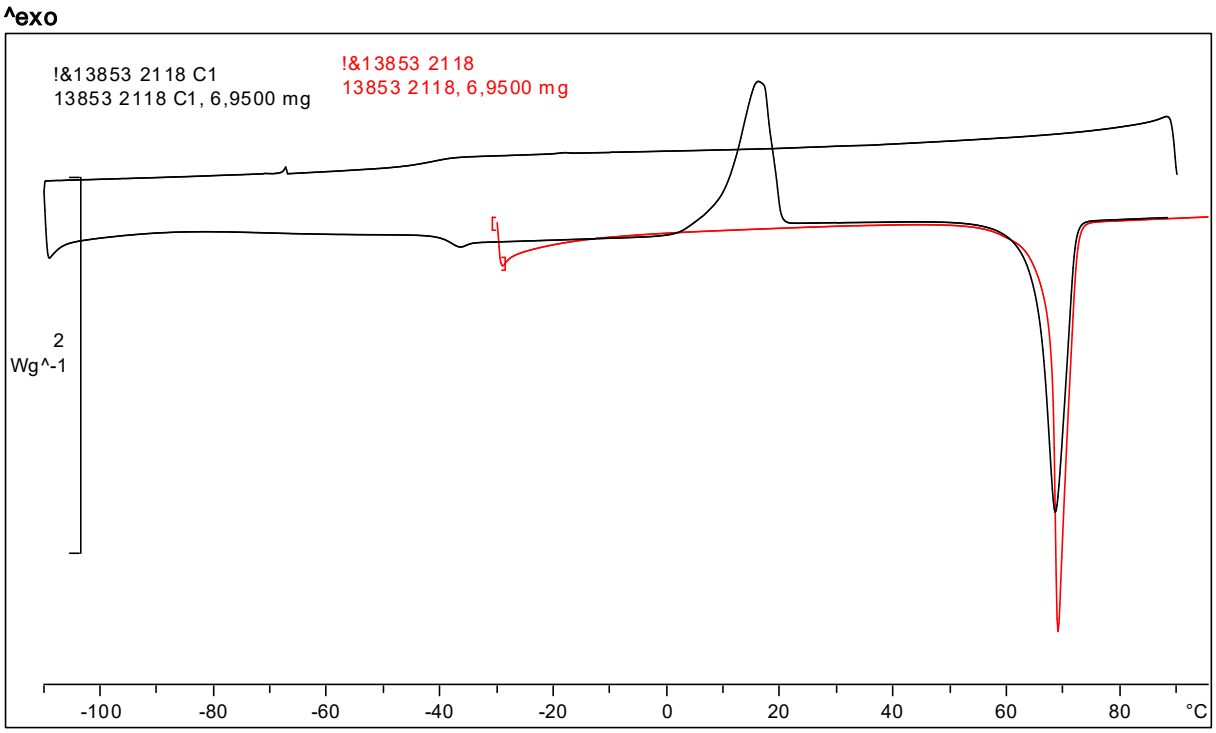
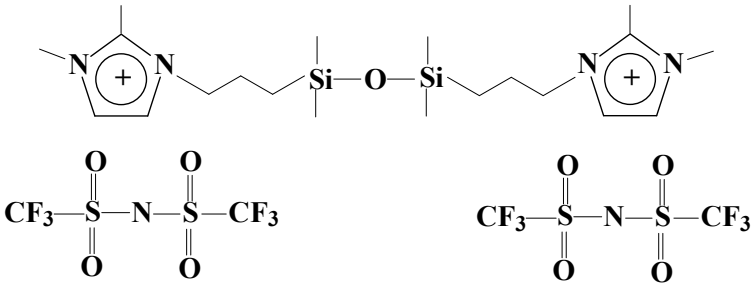


Figure S5 The results of the differential calorimetry analysis of IL **1**.

2.2. Bis (trifluoromethylsulfonyl)imide 1,1,3,3-tetramethyl-1,3-di(3-[1,2-dimethylimidazolium]propyl)disiloxane (2).



First step.

1,1,3,3-tetramethyl-1,3-di (3-chloropropyl) disiloxane was synthesized similarly to the linker of IL **1**, from dimethyl (3-chloropropyl) chlorosilane (100 ml, 104 g). Yield was 84.7 g (97%).

Second step.

Chloride precursors of IL **2** was synthesized analogously to chloride precursors of IL **1** from 1,1,3,3-tetramethyl-1,3-di(3-chloropropyl)disiloxane (3 ml, 2.99 g, 0.0104 mol) and 1,2-dimethylimidazole (2.0 g, 0.0208 mol) in MeCN (5 ml). Dicationic chloride precursors of IL **2** is soluble in MeCN, therefore, to remove impurities, MeCN was removed, 1,2-dichloroethane (10 ml) was added to the precipitate, and the suspension was stirred for 30 min. Then the liquid

phase was decanted, and the white precipitate was dried *in vacuo* to remove the traces of solvent. Yield of chloride precursors of IL **2** was 3.94 g (79%).

Third step.

IL **2** was synthesized in the same way as IL **1** from chloride precursors of IL **2** (3.94 g, 0.0082 mol) and $LiNTf_2$ (5.17 g, 0.018 mol) in MeCN (10 ml). The yield of the target product was 7.56 g (95%). ^{1}H NMR spectrum (DMSO-d_6, 300.13 MHz), δ, ppm: 0.04, s (12H, CH_3–Si), 0.49, m (4H, $CH_2CH_2CH_2Si$), 1.67, m (4H, $CH_2CH_2CH_2Si$), 2.55, s (6H, CH_3–C), 3.74, s (6H, CH_3–N), 4.06, m (4H, $NCH_2CH_2CH_2Si$), 7.61, m (4H, CH=). ^{13}C NMR spectrum (DMSO-d_6, 75.47 MHz), δ, ppm: 0.33, 9.43, 13.50, 23.90, 34.97, 50.51, 113.52, 117.79, 121.16, 122.05, 122.70, 126.32, 144.54. Gross formula: $C_{24}H_{40}F_{12}N_6O_9S_4Si_2$, molecular weight: 969.03. Calculated (%): C 29.75, H 4.16, N 8.67, F 23.53, S 13.23, Si 5.80. Found (%): C 29.66, H 4.27, N 8.60, F 23.50, S 13.19, Si 5.87.

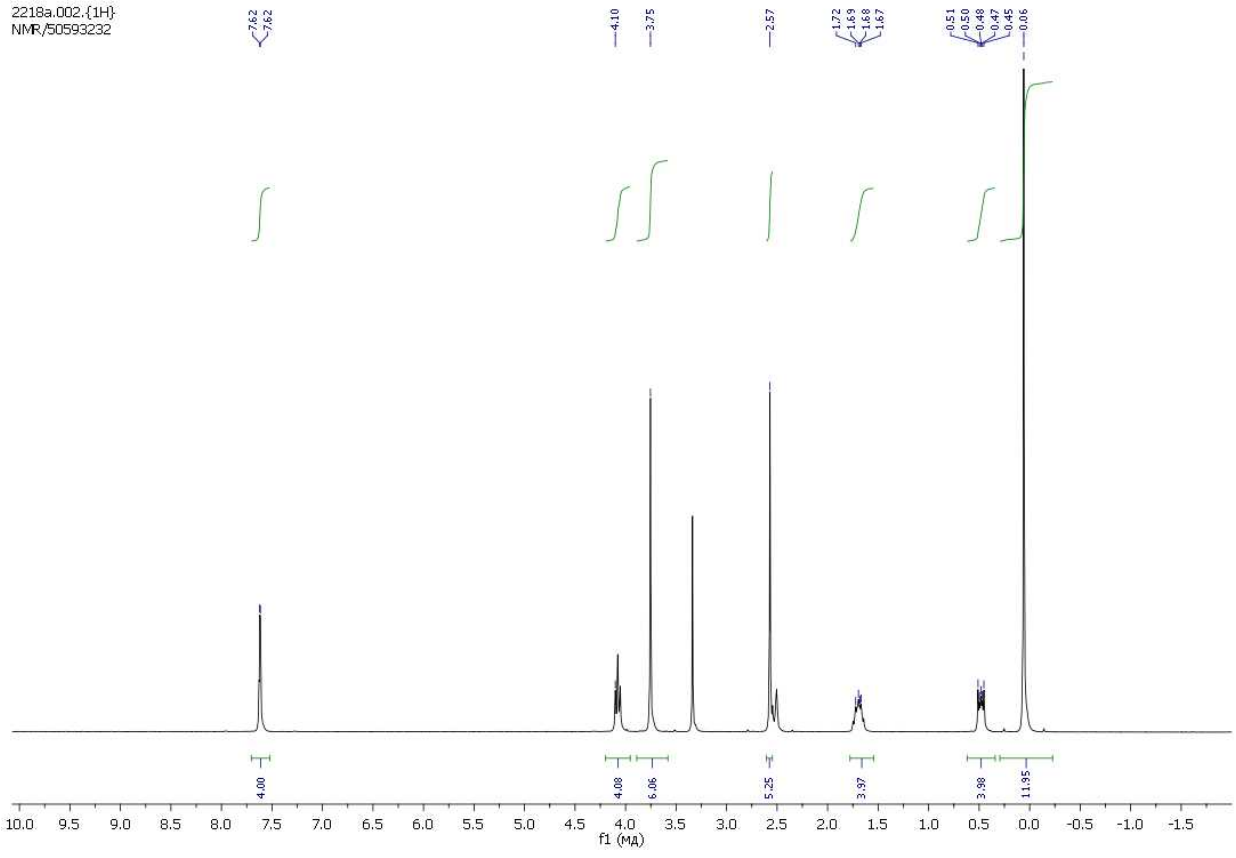


Figure S6 ^{1}H NMR spectrum of IL **2**.

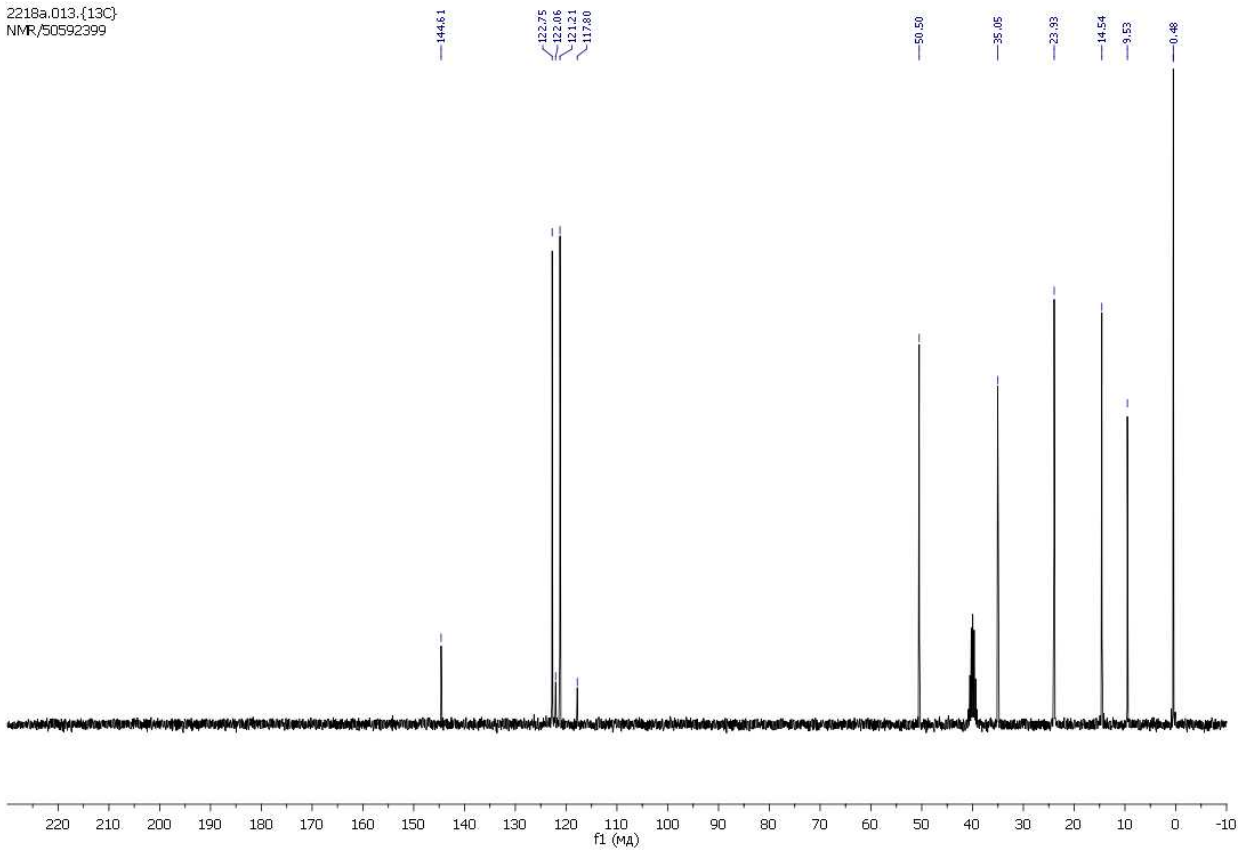


Figure S7 ^{13}C NMR spectrum of IL **2.**

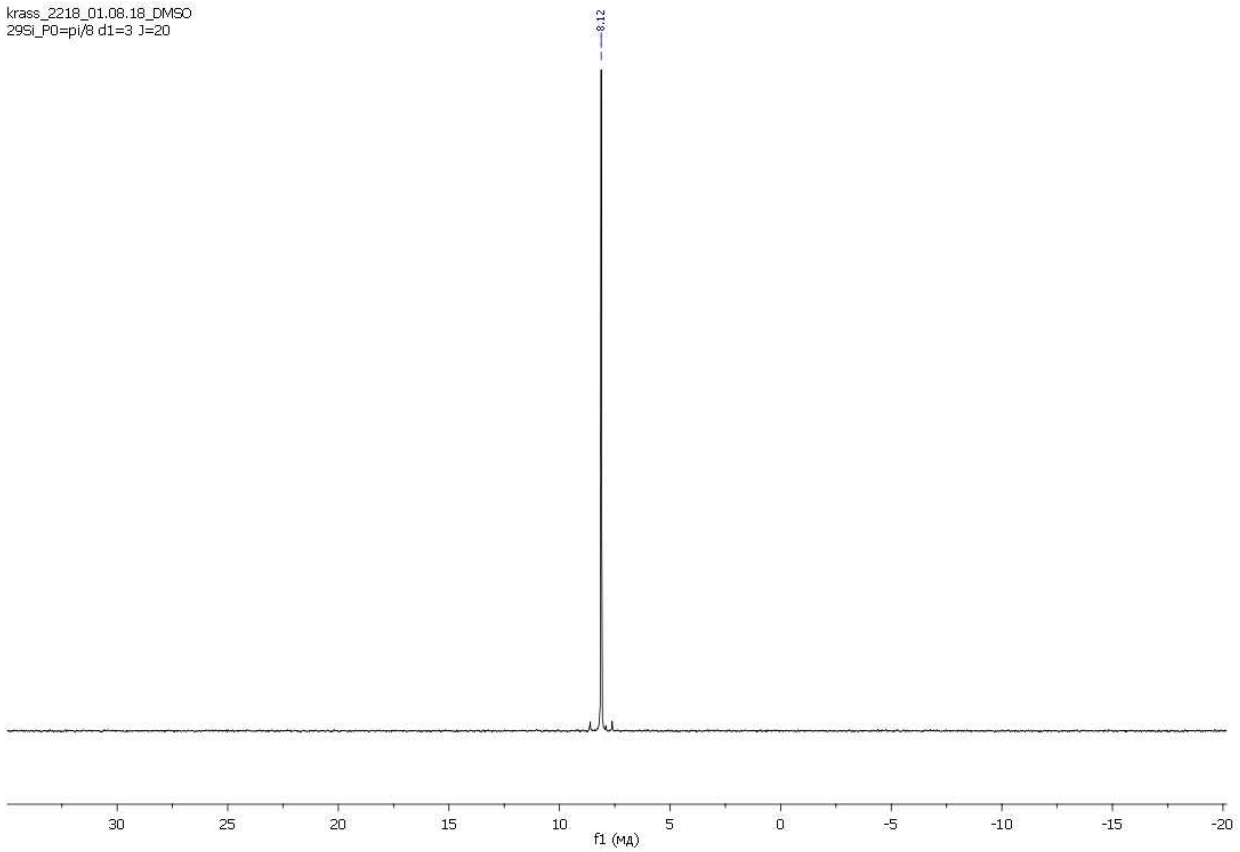


Figure S8 ^{29}Si NMR spectrum of IL **2**.

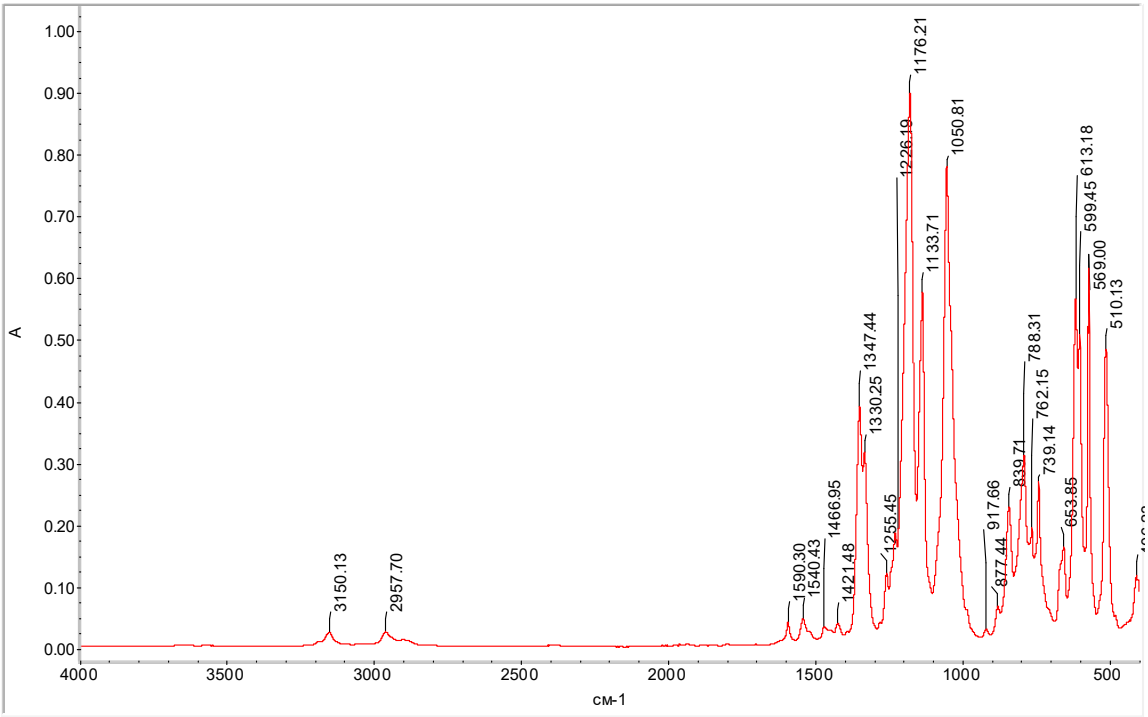


Figure S9 IR ATR spectrum of IL **2.**

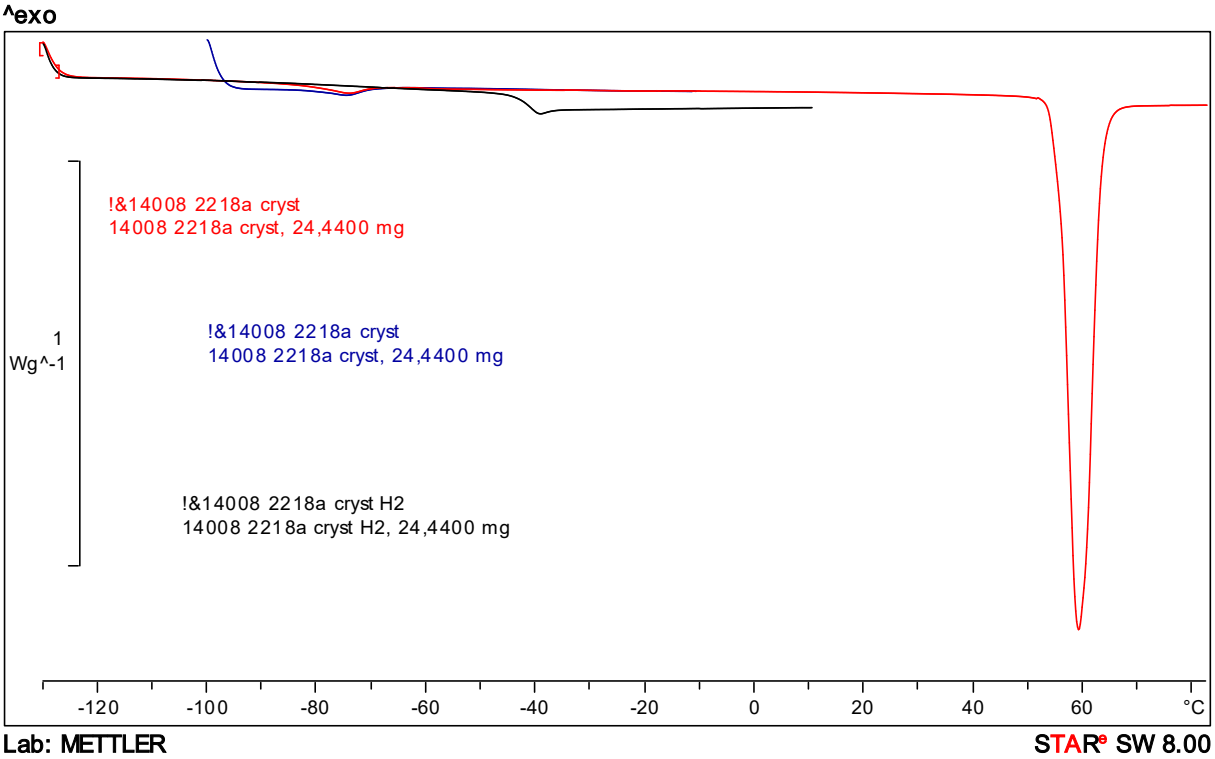
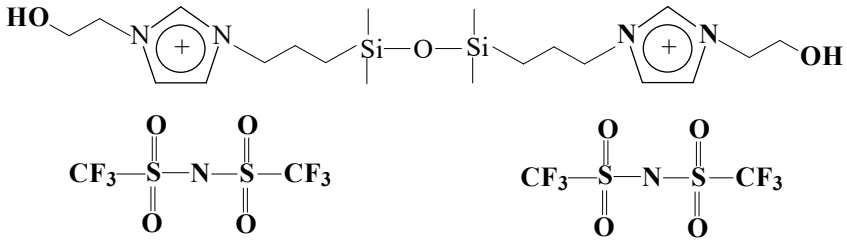


Figure S10 The results of the differential calorimetry analysis of IL **2**.

2.3. Bis (trifluoromethylsulfonyl)imide 1,1,3,3-tetramethyl-1,3-di(3-[1-(2-hydroxyethyl)imidazolium]propyl)disiloxane (3).



First step.

1,1,3,3-Tetramethyl-1,3-di (3-chloropropyl) disiloxane synthesized previously for IL **2** was used.

Second step.

Chloride precursors of IL **3** were synthesized in the same way as the chloride precursors of IL **1** from 1,1,3,3-tetramethyl-1,3-di (3-chloropropyl) disiloxane (3 ml, 2.99 g, 0.0104 mole) and 1- (2-hydroxyethyl) imidazole (2.33 g, 0.0208 mol) in MeCN (6 ml) at 60 °C. Dicationic chloride precursor of IL **3** is soluble in MeCN, therefore, to remove impurities, MeCN was removed, and the resulting viscous liquid was washed with diethyl ether (10 ml) and then with 1,2-dichloroethane (10 ml). The residual solvents were removed *in vacuo*. Yield of chloride precursors of IL **3** was 3.94 g (74%).

Third step.

IL **3** was synthesized in the same way as IL **1** from corresponding chloride precursors of IL **3** (3.94 g, 0.0077 mol) and $LiNTf_2$ (4.85 g, 0.0169 mol) in MeCN (10 ml), but after stirring for 3 h, the solvent was removed *in vacuo*; LiCl was removed by washing the with water until no wash water reacted with $AgNO_3$. IL **3** was dried *in vacuo* at 100 °C for 10 h. The yield was 5.50 g (71%). NMR spectrum ^1H (DMSO-d_6, 300.13 MHz), δ, ppm: 0.06, s (12H, CH_3–Si), 0.45, m (4H, $CH_2CH_2CH_2Si$), 1.78, m (4H, $CH_2CH_2CH_2Si$), 3.75, m (4H, CH_2–O), 4.14, m (4H, $NCH_2CH_2CH_2Si$), 4.22, m (4H, CH_2–N), 5.16, m (2H, OH), 7.75, m (4H, CH=), 9.13, s (2H, NCHN). ^{13}C NMR spectrum (DMSO-d_6, 75.47 MHz), δ, ppm: 0.52, 14.55, 24.30, 51.86, 52.14, 59.70, 113.52, 117.80, 122.07, 122.51, 123.23, 126.29, 136.74. The gross formula: $C_{24}H_{40}F_{12}N_6O_{11}S_4Si_2$, molecular weight: 1001.03. Calculated (%): C 28.80, H 4.03, N 8.40, F 22.77, S 12.81, Si 5.61. Found (%): C 28.74, H 4.11, N 8.33, F 22.72, S 12.49, Si 5.70.

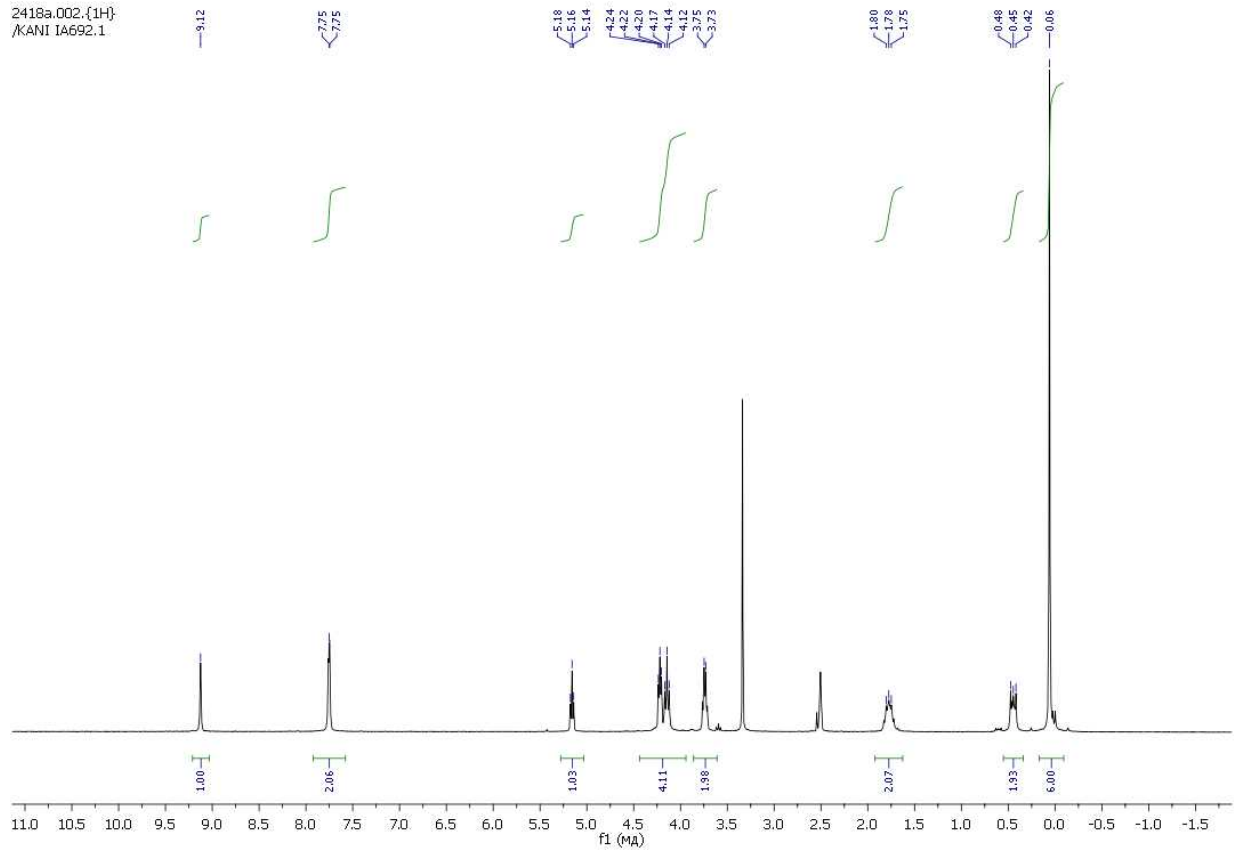


Figure S11 ^{1}H NMR spectrum of IL **3**.

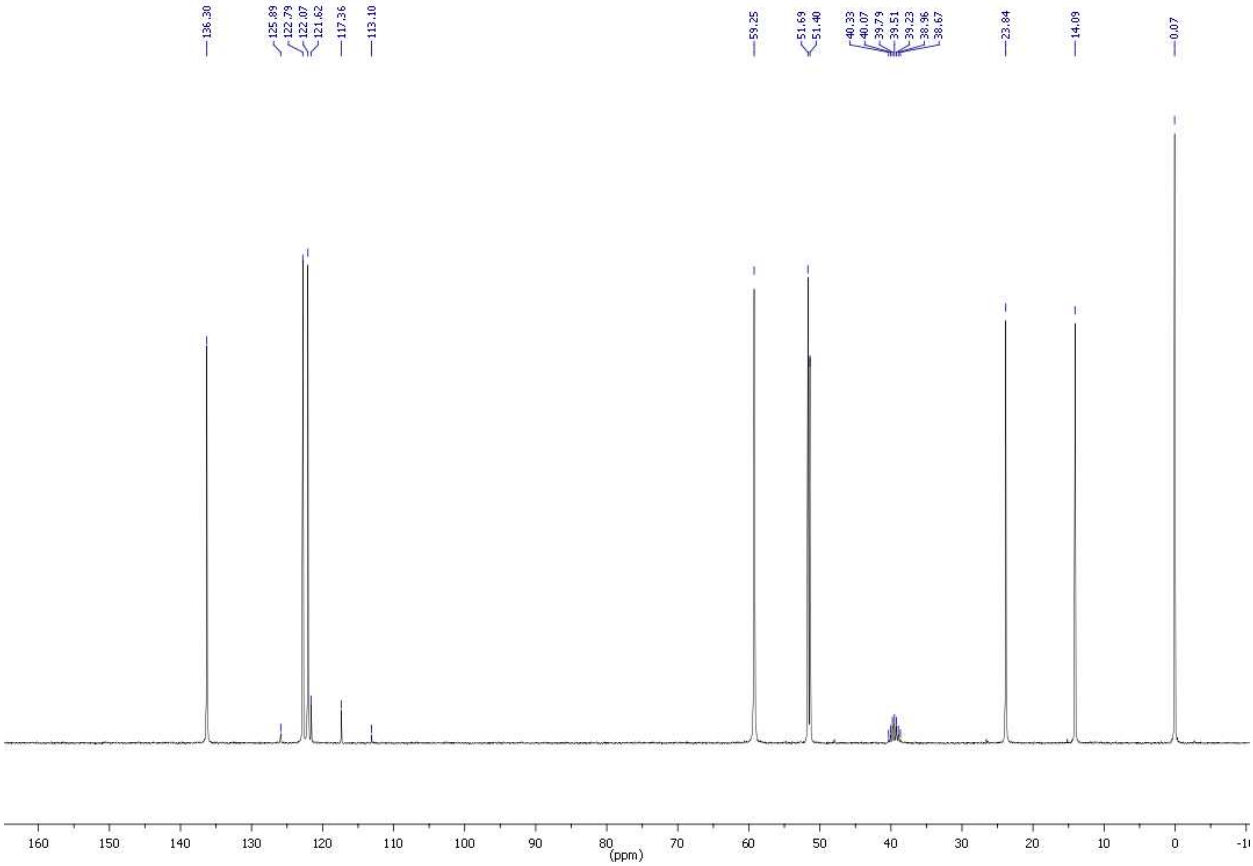


Figure S12 ^{13}C NMR spectrum of IL **3**.

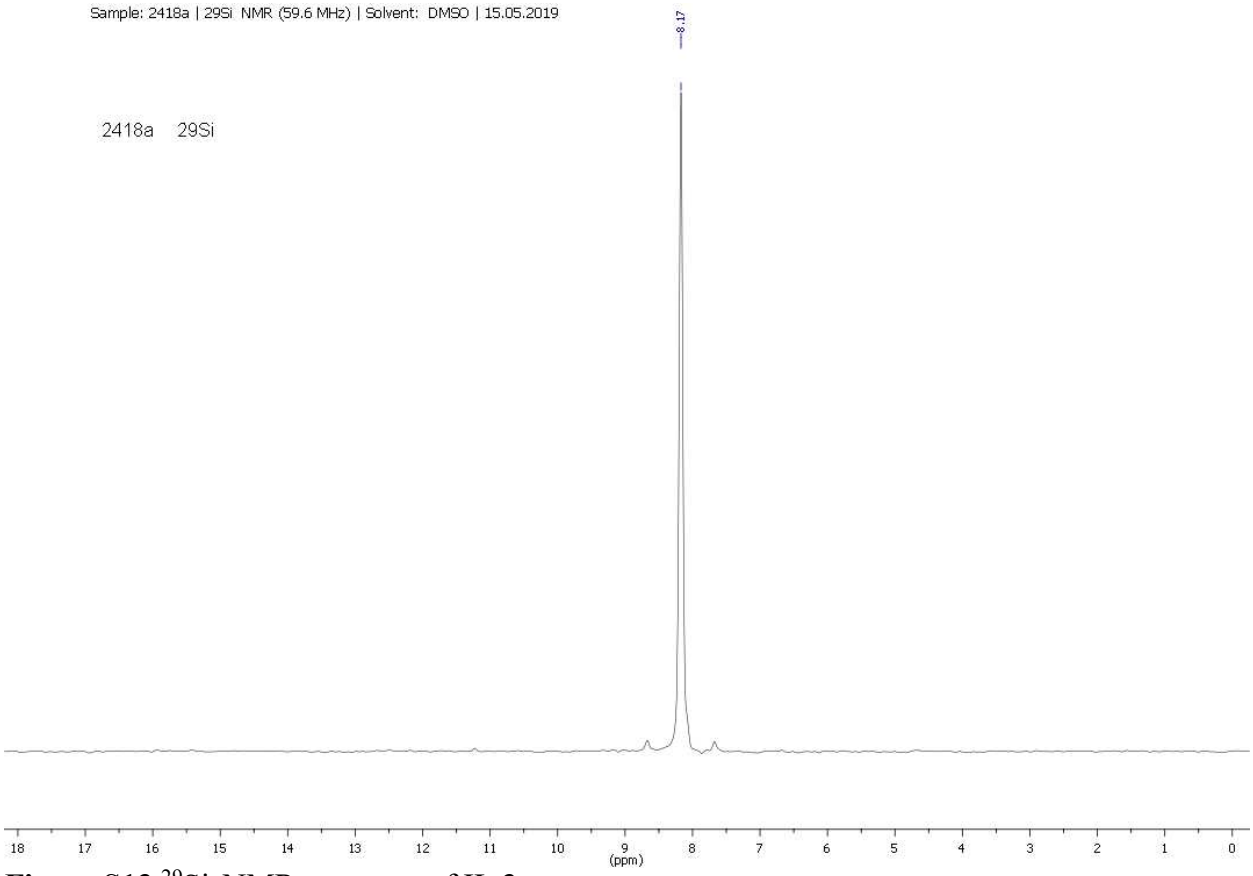


Figure S13 ^{29}Si NMR spectrum of IL **3**.

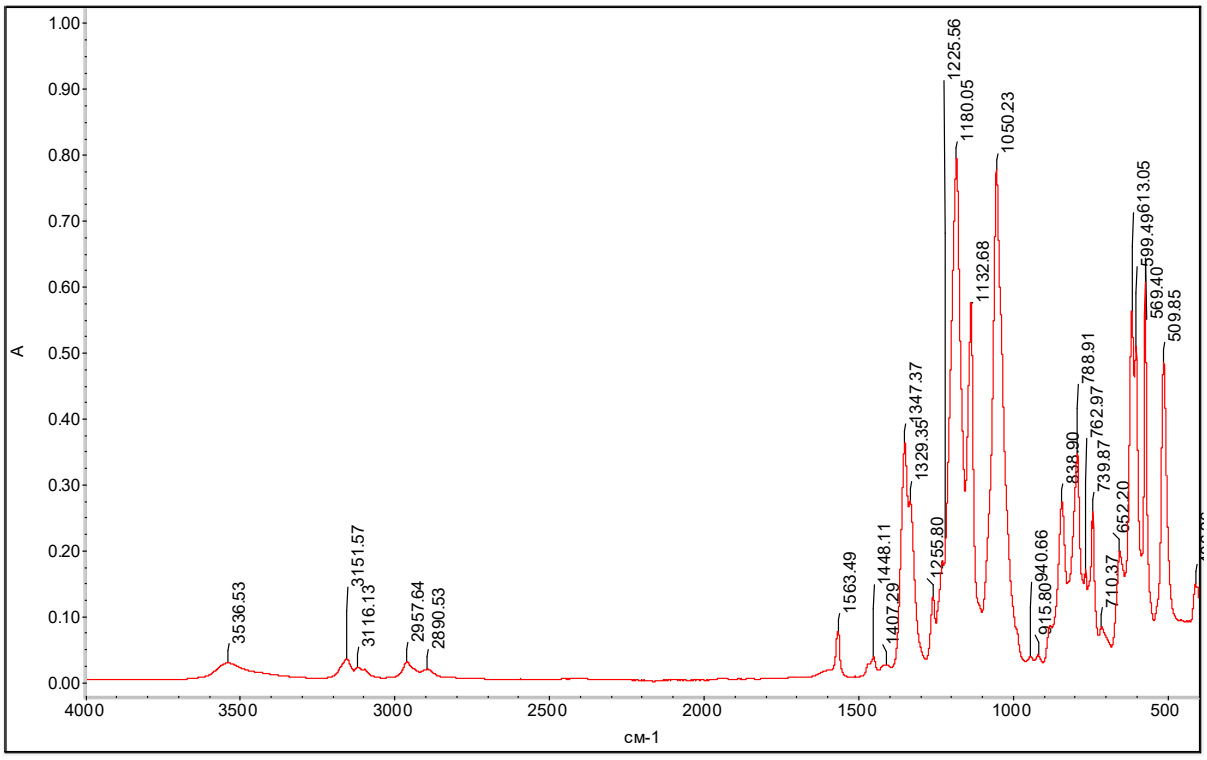


Figure S14 IR ATR spectrum of IL **3**.

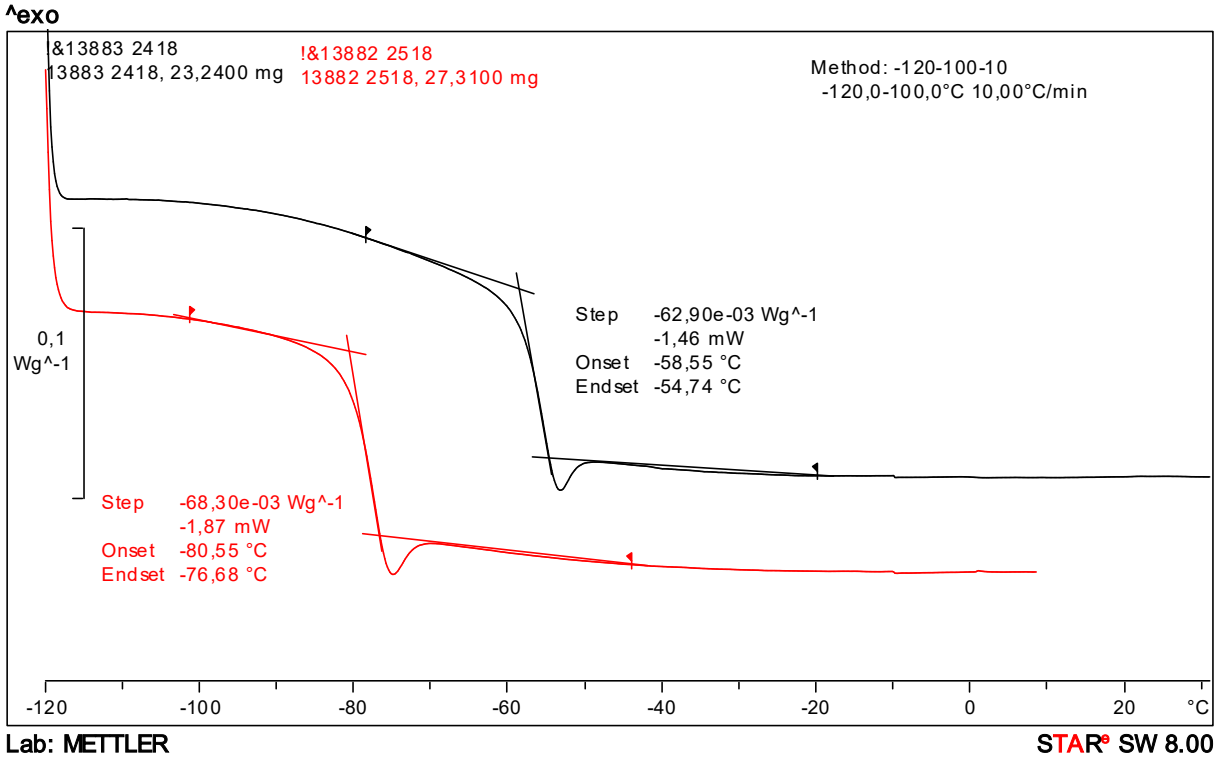
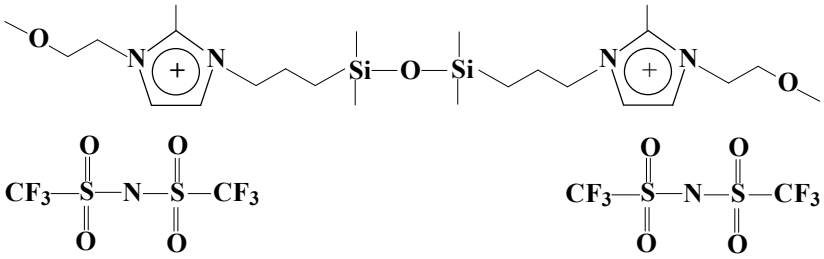


Figure S15 The DSC results for IL **3** (black line).

2.4. Bis (trifluoromethylsulfonyl)imide 1,1,3,3-tetramethyl-1,3-di(3-[1-(2-methoxyethyl)-2-methylimidazolium]propyl)disiloxane (4).



First step.

1,1,3,3-Tetramethyl-1,3-di(3-chloropropyl)disiloxane synthesized previously for IL **2** was used.

Second step.

Chloride precursor of IL **4** was synthesized in the same way as the chloride precursor of IL **1** from 1,1,3,3-tetramethyl-1,3-di(3-chloropropyl)disiloxane (3 ml, 2.99 g, 0.0104 mol) and 1-(2-methoxyethyl)-2-methylimidazole (2.92 g, 0.0208 mol) in MeCN (6 ml). Dicationic chloride precursor of IL **4** is soluble in MeCN, therefore, to remove impurities, MeCN from the reaction mixture was removed *in vacuo*, and the remaining viscous liquid was washed with 1,2-dichloroethane (10 ml). Then the upper liquid phase was decanted, and the remaining solvent was removed *in vacuo*. Yield of chloride precursors of IL **4** was 4.55 g (77%).

Third step.

The IL **4** was synthesized in the same way as IL **1** from of the corresponding chloride precursors of IL **4** (4.55 g, 0.0080 mol) and $LiNTf_2$ (5.05 g, 0.0176 mol) in MeCN (10 ml). The yield of the target product was 7.96 g (94%). ^{1}H NMR spectrum (DMSO-d_6, 300.13 MHz), δ, ppm: 0.05, s (12H, CH_3–Si), 0.49, m (4H, $CH_2CH_2CH_2Si$), 1.71, m (4H, $CH_2CH_2CH_2Si$), 2.61, s (6H, CH_3–C), 3.25, s (6H, CH_3–N), 3.66, m (4H, CH_2–O), 4.09, m (4H, $NCH_2CH_2CH_2Si$), 4.32, m (4H, CH_2–N) , 7.65, m (4H, CH=). ^{13}C NMR spectrum (DMSO-d_6, 75.47 MHz), δ, ppm: 0.42, 9.76, 14.51, 23.85, 47.91, 50.51, 58.59, 70.29, 113.55, 117.81, 121.55, 122.08, 126.34, 144.70. Gross formula: $C_{28}H_{48}F_{12}N_6O_{11}S_4Si_2$, molecular weight: 1057.14. Calculated (%): C 31.81, H 4.58, N 7.95, F 21.57, S 12.13, Si 5.31. Found (%): C 28.67, H 4.66, N 7.88, F 21.62, S 12.02, Si 5.40.

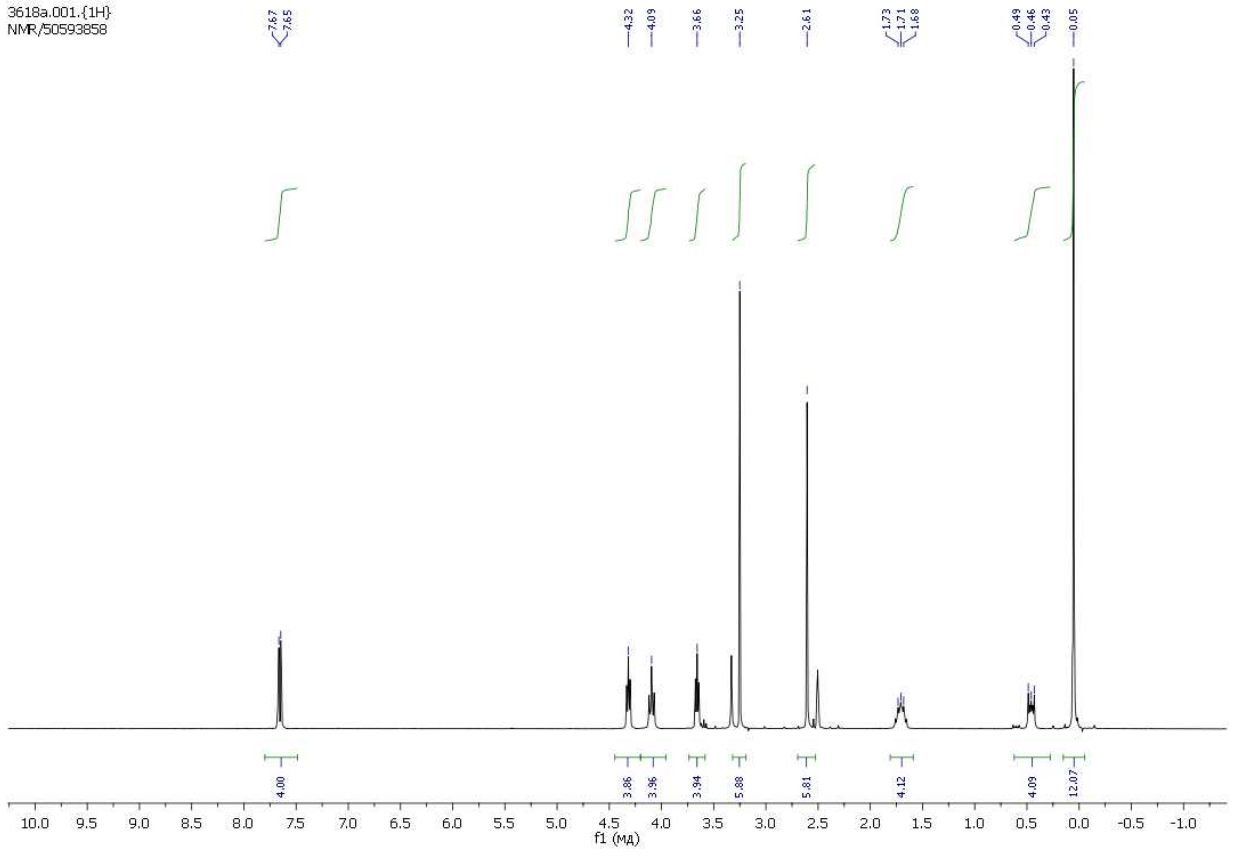


Figure S16 ^{1}H NMR spectrum of IL **4**.

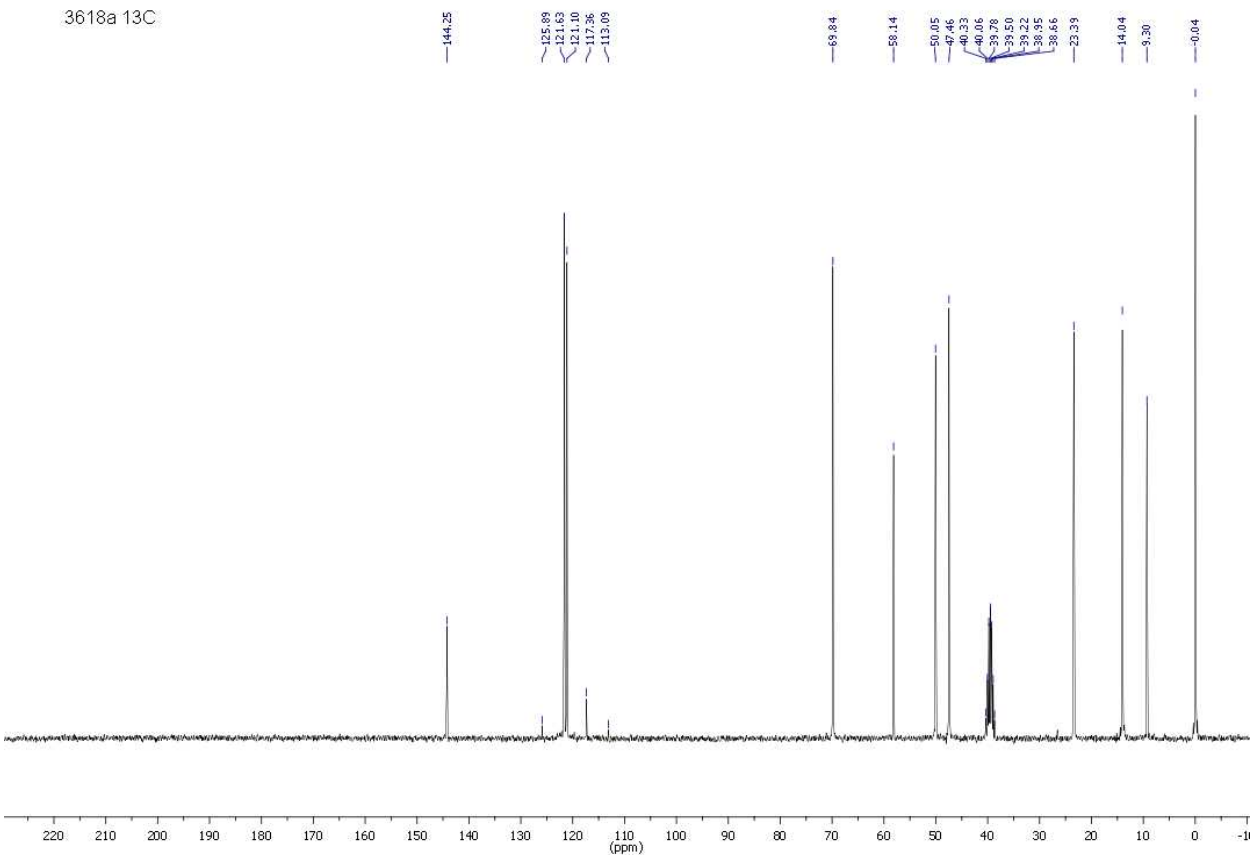


Figure S17 ^{13}C NMR spectrum of IL **4**.

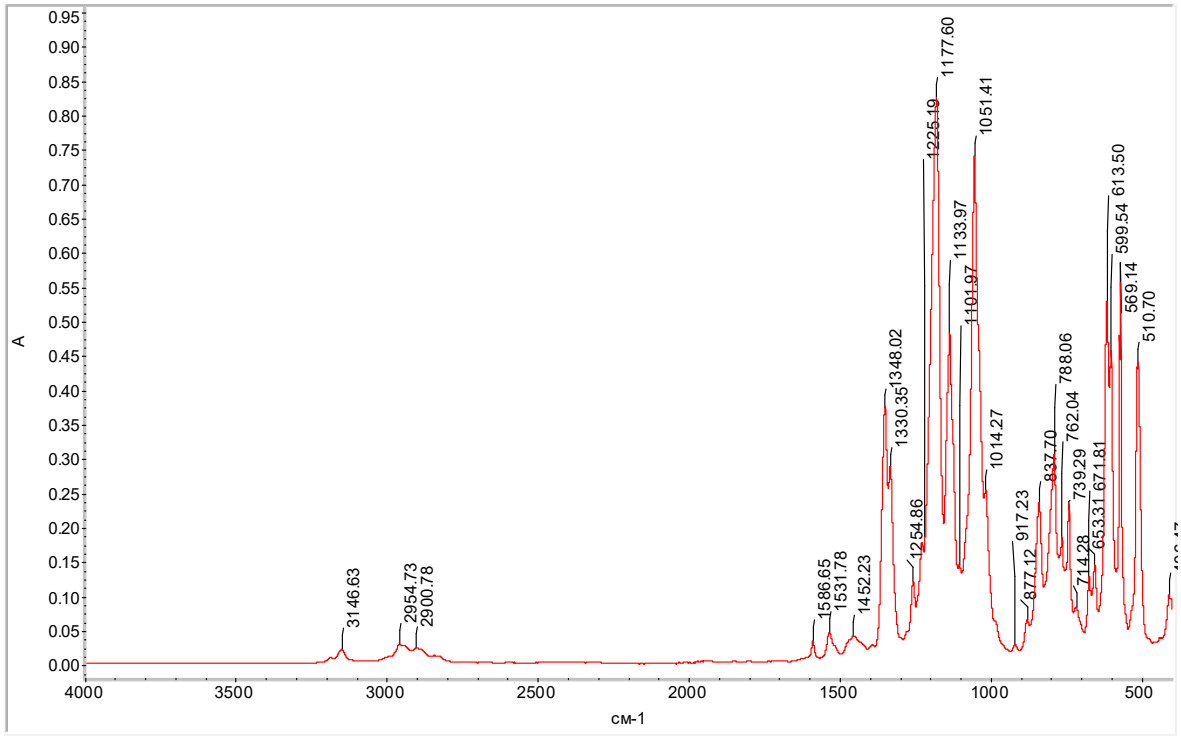


Figure S18 IR ATR spectrum of IL **4**.

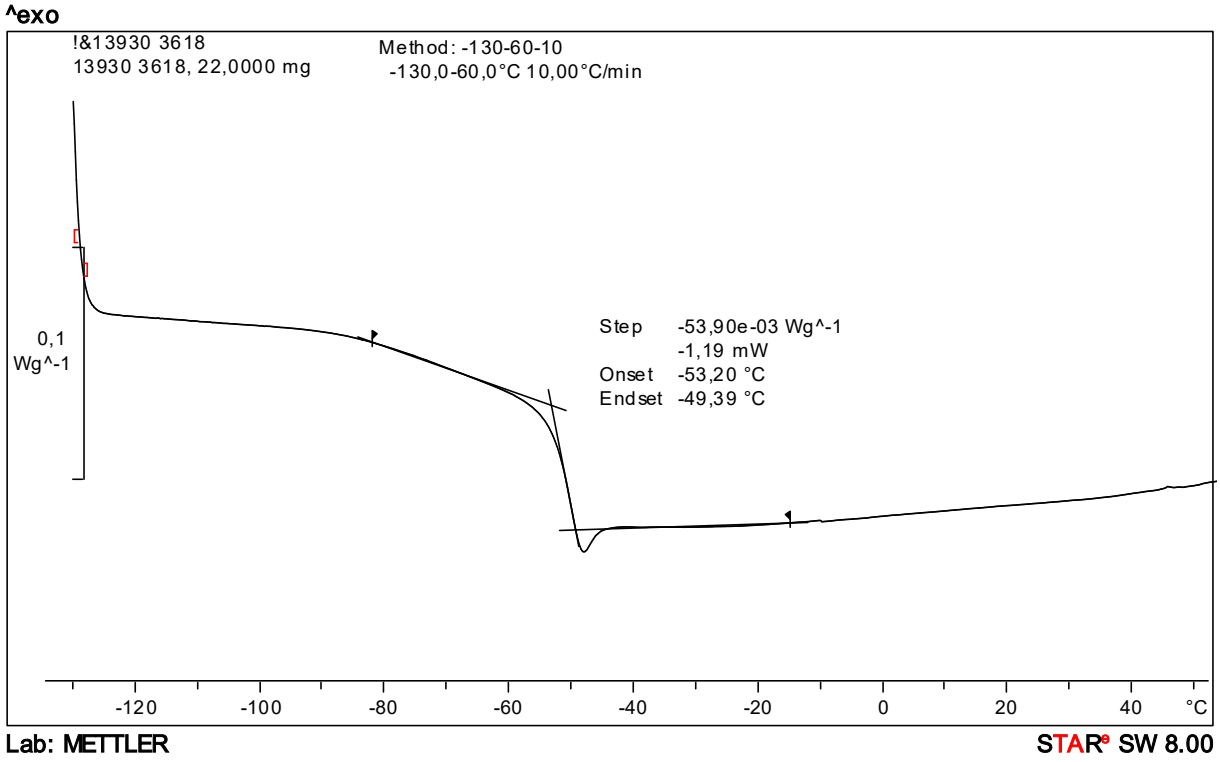
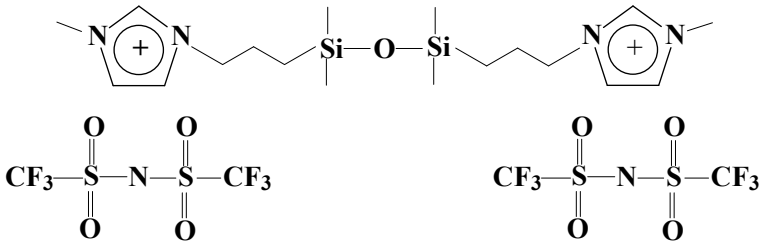


Figure S19 The DSC results for IL **4.**

2.5. Bis (trifluoromethylsulfonyl)imide 1,1,3,3-tetramethyl-1,3-di[3-(1-methylimidazolium)propyl]disiloxane (5).



First step.

1,1,3,3-Tetramethyl-1,3-di(3-chloropropyl)disiloxane synthesized previously for IL **2** was used.

Second step.

Chloride precursor of IL **5** was synthesized in the same way as the chloride precursors of IL **1** from 1,1,3,3-tetramethyl-1,3-di(3-chloropropyl)disiloxane (4g, 0.0139 mol) and 1-methylimidazole (2.28 g, 0.0278 mol) in MeCN (7 ml). Dicationic chloride precursor of IL **5** is soluble in MeCN, therefore, to remove impurities, MeCN from the reaction mixture was removed *in vacuo*; toluene (10 ml) was added to the precipitate, and the suspension was stirred for 30 min. Then the liquid phase was decanted, and the viscous liquid was dried *in vacuo* to remove the traces of solvent. Yield of chloride precursors of IL **5** was 4.46 g (71%).

Third step.

The IL **5** was synthesized in the same way as IL **1** from the chloride precursor of IL **5** (4.46g, 0.0099 mol) and $LiNTf_2$ (6.26 g, 0.0218 mol) in MeCN (11 ml). Yield of IL **5** was 8.92 g (96%). ^{1}H NMR spectrum (DMSO-d_6, 300.13 MHz), δ, ppm: 0.06, s (12H, CH_3–Si), 0.45, m (4H, $CH_2CH_2C\underline{H}_2Si$), 1.78, m (4H, $CH_2C\underline{H}_2CH_2Si$), 3.86, s (6H, CH_3–N), 4.13, m (4H, $NC\underline{H}_2CH_2CH_2Si$), 7.69, m (4CH=), 7.73, (4CH=), 9.08, s (2H, NCHN). ^{13}C NMR spectrum (DMSO-d_6, 75.47 MHz), δ, ppm: 0.47, 14.53, 24.27, 36.13, 51.88, 113.54, 117.80, 122.07, 122.59, 124.05, 126.33, 136.94. Gross formula: $C_{22}H_{36}F_{12}N_6O_9S_4Si_2$, molecular weight: 940.98. Calculated (%): C 28.08, H 3.86, N 8.93, F 24.23, S 13.63, Si 5.97. Found (%): C 27.99, H 3.95, N 8.90, F 24.20, S 13.51, Si 6.07.

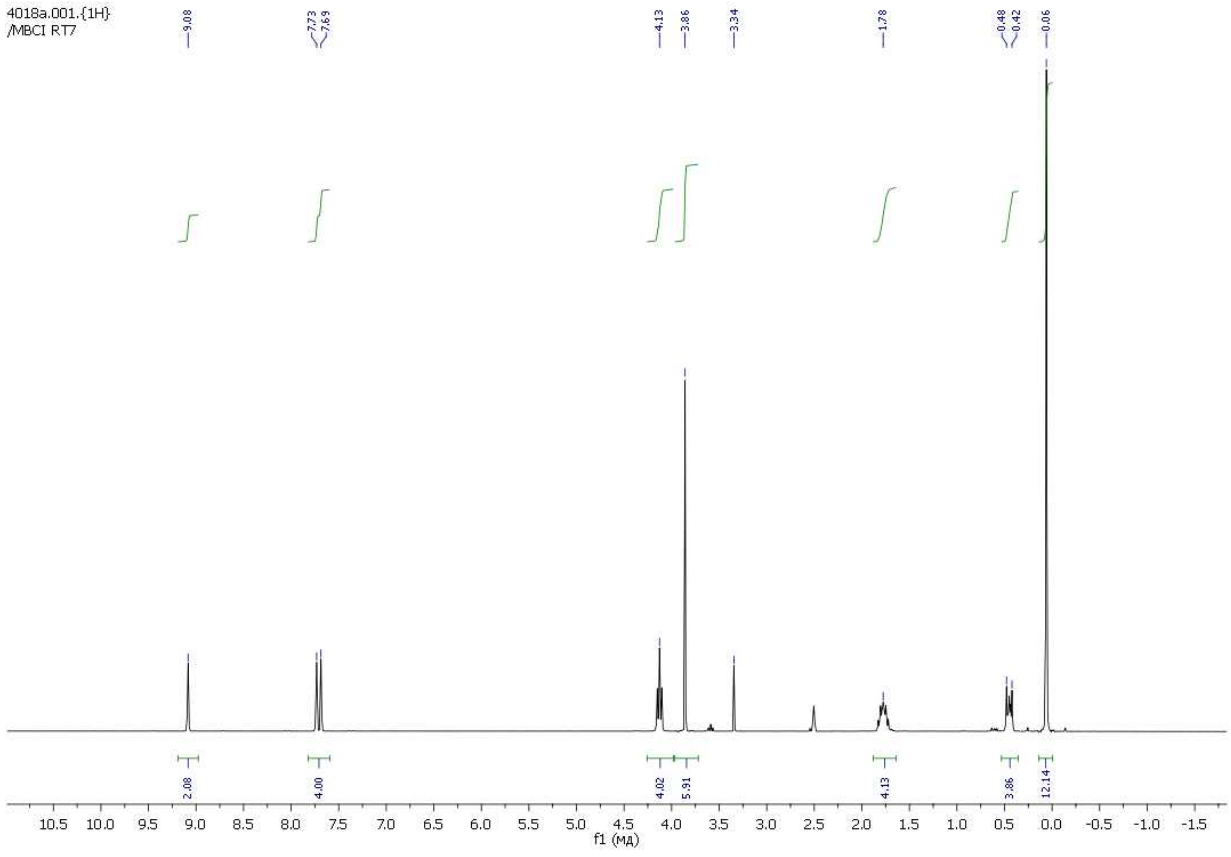


Figure S20 ^{1}H NMR spectrum of IL **5**.

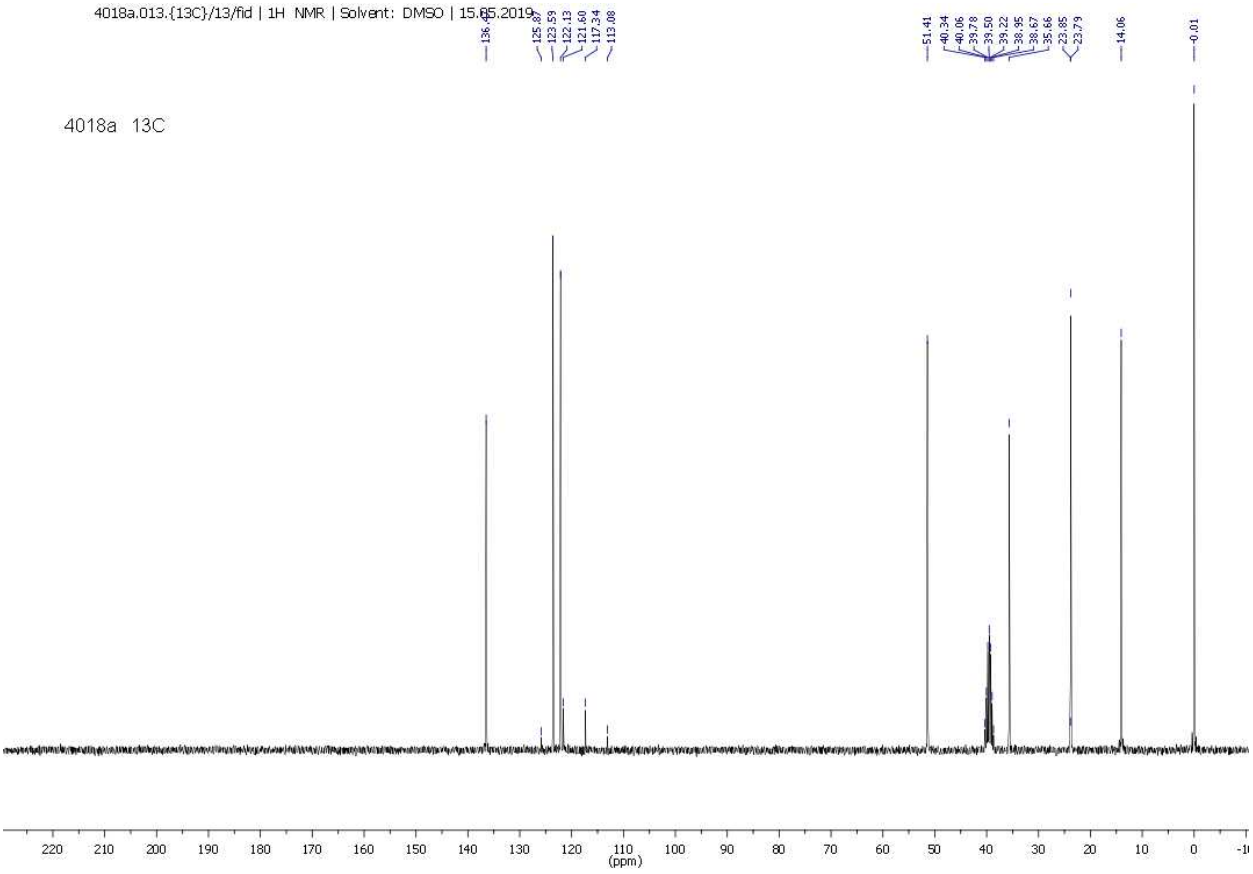


Figure S21 ^{13}C NMR spectrum of IL **5**.

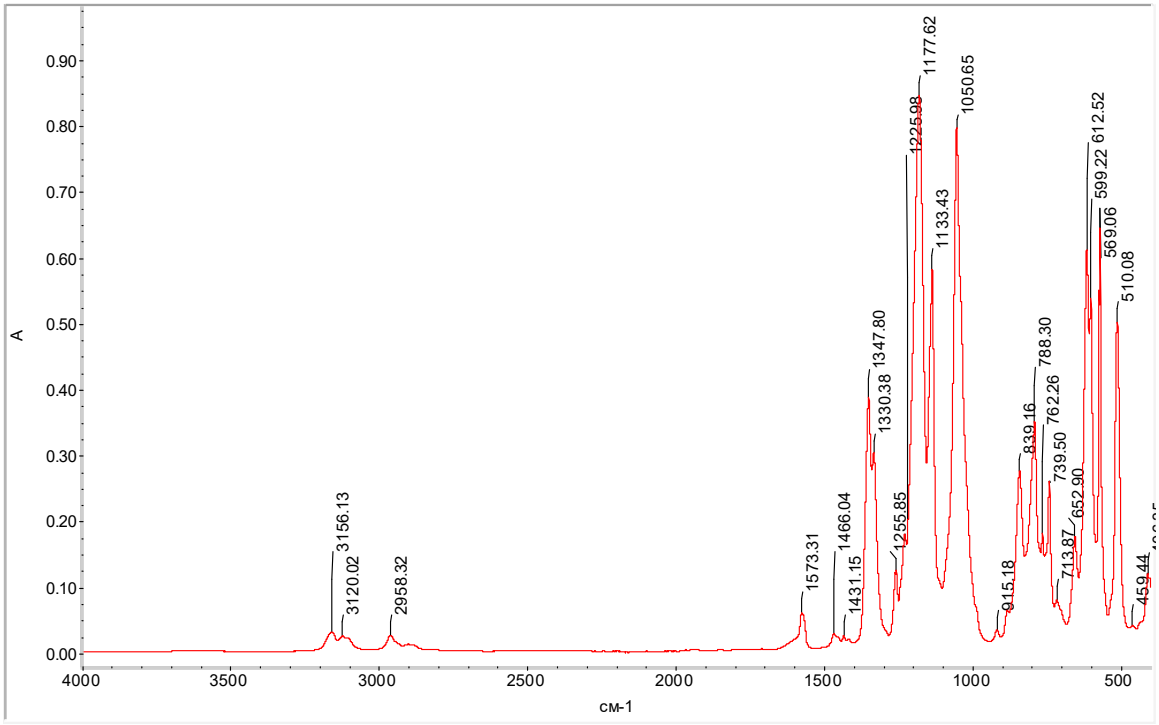


Figure S22 IR ATR spectrum of IL **5**.

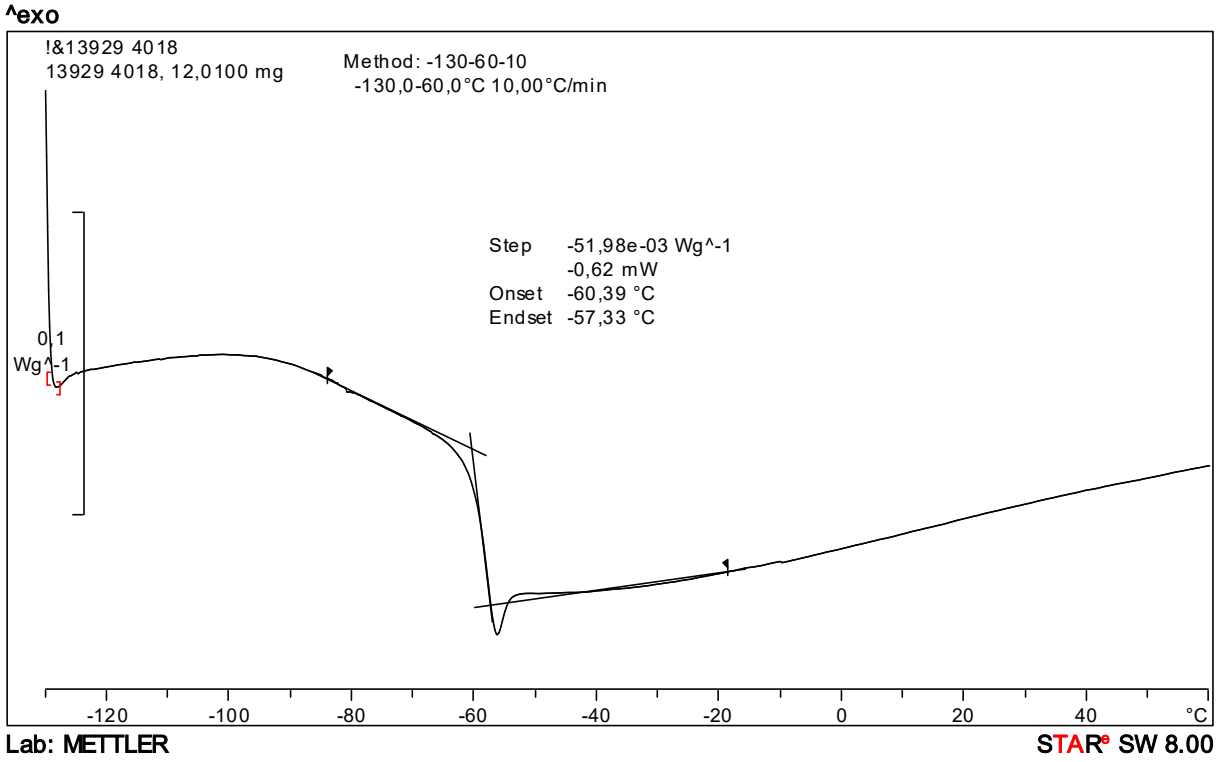


Figure S23 The DSC results for IL **5**.

3. Constants of the Vogel–Tamman–Fulcher equation

The Vogel–Tamman–Fulcher equation is shown below:

$$\ln v = \frac{a}{T - T_0} + b$$

Table S1 Constants of the Vogel–Tamman–Fulcher equation describing the temperature dependence of viscosity for the ionic liquids **1**–**5** ($R^2 > 0.99$).

Coeff./IL	**1**	**2**	**3**	**4**	**5**
a	-	-	863	890.9	901.3
–b	-	-	1.451	1.784	1.681
T_0	-	-	193.4	193.3	183.3