Supporting Information for:

Silylated Quaternary Ammonium Salts - Ionic Liquids with Hydrophobic Cation

Matjaž Koželj*[a,b] Abdelbast Guerfi,[a] and Karim Zaghib*[a]

[a] Dr. M. Koželj, Dr. A. Guerfi, Dr. K. Zaghib
Direction stockage et conversion d' énergie
Institut de Recherche d'Hydro-Québec
1800 Lionel-Boulet, Varennes, Quebec, Canada J3X 1S1
Fax: (+)1-450-652-8204
E-mail: zaghib.karim@ireq.ca

[b] Dr. M. Koželj
Laboratory for Chemistry of Materials
National Institute of Chemistry
Hajdrihova 19, SI-1000 Ljubljana
Fax: (+)386 1 4760 323
E-mail: matjaz.kozelj@ki.si

1. Detailed synthetic procedures for silylated ionic liquids

General: The following reagents were used as received choline chloride, 2-(dimethylamino)ethanol, 2-(dimethylamino)ethanol, *N*-methylpyrrolidine hexamethyldisilazane, CH_2Cl_2, bromoethane, 1-bromopropane, triethylamine, (from Aldrich) methanol, acetone, ethyl acetate (Fischer), 2-bromoethanol, 3-chlorooopropanol, 3-chlorobutanol, 6-chlorohexanol, 2-chloroethyl 2-hydroxyethyl ether, diethyl ether, acetonitrile diethylamine (Alfa Aesar), (dimethylamino)triethylsilane, ethyldimethylchlorosilane (Gelest), LiTFSI (3M), triflic amide (Rhodia). K-FSI,[1] K-FTFSI[2] and (diethylamino)ethyldimethylsilane[3] were synthesized according to published methods.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 300 MHz Varian Mercury equipped with an SMS-100 sample changer and 500 MHz Varian VNMRS. D_2O and DMSO-d_6 were used as solvents for halides and DMSO-d_6 for TFSI, FTFSI and FSI hydroxy compounds and $CDCl_3$ was used for silylated ILs. Chemical shifts are reported relatively to solvents peaks, for ^{19}F NMR fluorobenzene was used as internal reference (-113.10 ppm).

Water content was determined by using Mettler Toledo V10 Compact Volumetric Karl-Fischer titrator.

Viscosity (absolute) was measured on Anton Paar Physica MCR 301 instrument equipped with a parallel-plate system (PP50-SN5204) with Peltier temperature control**,** which enabled measuring

viscosity vs. temperature at constant shear rate of dγ/dt = 500/s with linear temperature increase. Determination of coefficients in Vogel-Tammann-Fulcher equation has been done using curve fitting (provided by Origin 8.1 programme) on experimental data between -20 and 80 °C.

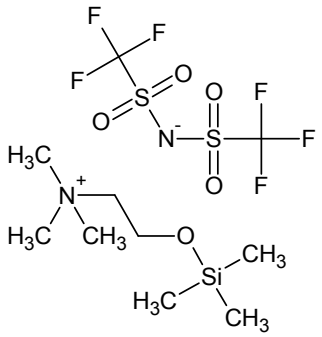
Conductivity of the neat ILs was measured between room temperature (~ 23 °C) and 90°C using a MMulty Conductimeter made by Materials Mates Italia S.r.L in a sealed cell, consisting of two parallel platinized Pt electrodes. Temperature program was very slow; measurement in complete range was finished in 12 hours. Determination of coefficients in Vogel-Tammann-Fulcher equation has been done using curve fitting (provided by Origin 8.1 programme) on experimental data.

Electrochemical stability was determined in a 5 ml beaker type three electrodes cell having a Pt wire as a working electrode, lithium metal (as a sheet) as a counter electrode and another sheet of lithium metal as a quasireference electrode (QRE). Measurements were performed in glovebox with atmosphere containing less than 5 ppm oxygen and water. Linear sweep voltammetry was performed using a VMP3 Modular 16 Channels Potentiostat/Galvanostat/EIS, manufactured by BioLogic Science instruments. The CV curve was measured between 0–6 V vs. Li at a scan rate of 1mV/s, from open circuit potential to 6 V and back to 0 V.

[1] M. Beran, J. Příhoda, *Zeitschrift für anorganische und allgemeine Chemie* **2005**, *631*, 55-59.
[2] M. Beran, J. Příhoda, J. Taraba, *Polyhedron* **2010**, *29*, 991-994.
[3] K. Szabó, N. L. Ha, P. Schneider, P. Zeltner, E. s. Kováts, *Helvetica Chimica Acta* **1984**, *67*, 2128-2142.

SYNTHESES:

Preparation of* 3a: *N-(2-trimethylsiloxyethyl)-N,N,N-trimethylammonium bis(trifluoro methane sulfonyl)amide (N1112-OTMS-TFSI)



a) Choline bis(trifluoromethanesulfonyl)amide:

55.85 g (0.4 mol) of choline chloride (Sigma-Aldrich) were dissolved in 150 ml of MQ water. Under vigorous stirring, the resulting choline chloride solution was mixed with a solution of 120 g (0.41mol) of lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) in 200 ml of MQ water. Phase separation occurred at once, but the stirring was continued for another 5 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases were separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 50 ml of MQ water. A clear colourless solution was obtained. This was poured into a round bottom flask; the solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 127 g (83 %) of pure choline bis(trifluoromethanesulfonyl)amide (choline TFSI) were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 3.11 (s, 9 H), 3.31 - 3.47 (m, 2 H), 3.84 (tt, *J*=5.03, 2.29 Hz, 2 H), 5.26 (t, *J*=4.94 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ ppm: 53.30 (br. t, *J*=3.50, 3.50 Hz), 55.31 (s), 67.18 (br. t, *J*=3.20, 3.20 Hz), 119.63 (q, *J*=321.70 Hz).

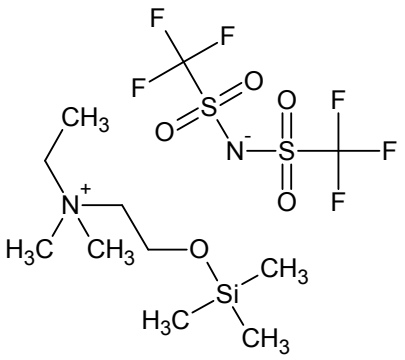
b) N-(2-trimethylsiloxyethyl)-N,N,N-trimethylammonium bis(trifluoromethanesulfonyl)amide

To a 500 ml round bottom flask containing 127 g (0.33 mol) of neat choline TFSI, 53 g (0.33 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in choline TFSI was formed. A vigorous evolution of gaseous ammonia started as the temperature reached 60°C and ended after a few minutes. The mixture was heated and stirred for additional 4 hours after the end of this vigorous reaction. Then, the remaining HMDS, which was in a separate layer on top of desired product, was evaporated under high vacuum. The round bottom flask was then refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally the apparatus was cooled down under vacuum and refilled with argon. In this manner, 150.5 g (100 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.10 (s, 9 H), 3.14 (s, 9 H), 3.38 - 3.49 (m, 2 H), 3.87 - 4.03 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -1.28 (s), 54.22 (t, *J*=3.50 Hz), 56.67 (s), 67.56 (t, *J*=3.20 Hz), 119.63 (q, *J*=320.70 Hz).

Preparation of* 3b: *N-ethyl-N-(2-trimethylsiloxyethyl)-N,N-dimethylammonium bis(trifluoromethane sulfonyl)amide (N1122-OTMS-TFSI)



a) N-ethyl-N-2-hydroxyethyl-N,N-dimethylammonium bromide

In a 500 ml round bottom flask equipped with a magnetic stirrer were placed 45.3 g (0.508 mol) of 2-dimethylaminoethanol dissolved in 150 ml of MeCN. To this solution, a mixture of 61.5 g (0.550 mol) ethyl bromide and 60 ml of MeCN was added dropwise over a period of 1.5 h using a water bath (at 20°C) for cooling during the addition. After half of the EtBr was added, a snow white crystalline product started to precipitate from the solution. The mixture was stirred over a weekend (57 h), and then vacuum filtered, washed with a small amount of acetone, and dried in a vacuum oven at 60°C. The filtrate was evaporated to dryness and additional product was isolated. Altogether, 98.13 g (72 %) of *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bromide were obtained.

^{1}H NMR (300 MHz, DEUTERIUM OXIDE) δ/ppm: 1.35 (tt, *J*=7.28, 1.88 Hz, 3 H), 3.11 (s, 6 H), 3.38 - 3.52 (m, 4 H), 3.95 - 4.07 (m, 2 H).

^{13}C NMR (75 MHz, DEUTERIUM OXIDE) δ/ppm: 7.24 (s), 50.38 (t, *J*=3.90 Hz), 54.92 (s), 60.57 (t, *J*=2.70 Hz), 63.94 (t, *J*=3.30 Hz)

b) N-ethyl-N-2-hydroxyethyl-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, solutions of 52 g (0.263 mol) of *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bromide in 70 ml MQ water and 78 g (0.274 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear colourless solution was obtained and poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 70 g (67 %) of pure *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.25 (br. t, *J*=7.30, 7.30 Hz, 3 H), 3.03 (s, 39 H), 3.28 - 3.46 (m, 26 H), 3.56 (s, 12 H), 3.75 - 3.91 (m, 13 H), 5.29 (t, *J*=4.94 Hz, 6 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 7.63 (s), 50.23 (t, *J*=3.50 Hz), 54.96 (s), 59.50 - 60.18 (m), 64.19 (t, *J*=2.49 Hz), 119.50 (q, *J*=321.20 Hz).

c) N-ethyl-N-(2-trimethylsiloxyethyl)-N,N-dimethylammonium bis(trifluoromethane-sulfonyl)amide

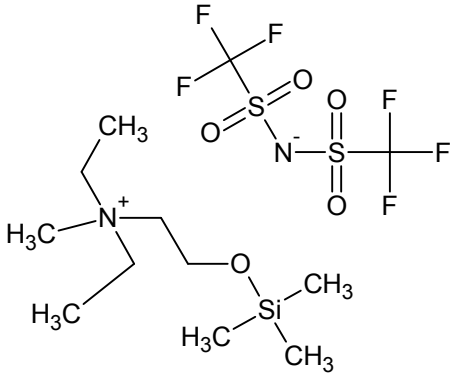
To a 250 ml round bottom flask containing 80 g (0.20 mol) of neat *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium TFSI, 31 g (0.20 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL formed. A vigorous evolution of gaseous ammonia started as the temperature reached 60°C and ended after a few minutes. The mixture was heated and stirred for an additional 4 hours after the end of the vigorous reaction. Then, the remaining HMDS, which was in a separate layer on top of the desired product, was evaporated under high vacuum. The round bottom flask was then refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 94 g (100 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.10 (s, 9 H), 1.34 (br. t, *J*=7.10, 7.10 Hz, 3 H), 3.06 (s, 6 H), 3.32 - 3.51 (m, 4 H), 3.86 - 4.04 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -1.25 (s), 7.94 (s), 50.96 (t, *J*=3.59 Hz), 56.43 (s), 61.46 (br. s.), 64.54 (br. s.), 119.67 (q, *J*=321.20 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ/ppm: -78.89 (s).

Preparation of* 3c: *N,N-diethyl-N-(2-trimethylsiloxyethyl)-N-methylammonium bis(trifluoro methanesulfonyl)amide (N1222-OTM-TFSI)



a) N,N-diethyl-N-2-hydroxyethyl-N-methylammonium methylsufate

In a 1L round bottom flask equipped with a magnetic stirrer were placed 117.10 g (1 mol) of 2-diethylaminoethanol dissolved in 250 ml of MeCN. The solution was cooled below 20°C with the help of an ice water bath. To the cooled solution, a mixture of 130 g (1.03 mol) dimethyl sulfate and 100 ml of MeCN was added dropwise over a period of 0.5 h, not allowing the temperature to rise above 40°C. The mixture was stirred over a weekend (60 h) and MeCN was then removed using a rotary evaporator. 242 g (100 %) of *N,N*-diethyl-*N*-2-hydroxyethyl-*N*-methylammonium methylsulfate were obtained in the form of a slightly pink coloured oil.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.20 (t, *J*=7.14 Hz, 6 H), 2.96 (s, 3 H), 3.28 - 3.40 (m, 6 H), 3.40 (s, 3 H), 3.74 - 3.85 (m, 2 H), 5.09 (br. s., 1 H).ž

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 7.64 (s), 47.22 (br. s), 53.16 (s), 54.91 (s), 56.50 (br. s), 61.26 (br. s).

b) N,N-diethyl-N-2-hydroxyethyl-N-methylammonium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, solutions of 68.58 g (0.282 mol) of *N,N*-diethyl-*N*-2-hydroxyethyl-*N*-methylammonium methylsufate dissolved in 70 ml MQ water and 83.23 g (0.290 mol) of LiTFSI dissolved in 80 ml MQ water were mixed under vigorous stirring. Phase separation occurred at once, but the stirring was continued for another 6 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 20 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 80 ml of MQ water. To this solution, 5 g of activated charcoal were added. The resulting mixture was heated to its boiling point, allowed to cool down and stirred overnight (16h). The next morning, the solution was filtered through a PTFE filter of 0.22 μm porosity. A clear solution was obtained and poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 65.65 g (56 %) of pure *N,N*-diethyl-*N*-2-hydroxyethyl-*N*-methylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.20 (t, *J*=7.14 Hz, 6 H), 2.96 (s, 3 H), 3.28 - 3.40 (m, 6 H), 3.40 (s, 3 H), 3.74 - 3.85 (m, 2 H), 5.09 (br. s., 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 7.48 (s), 47.28 (br. s.), 54.87 (s), 56.60 (br. s.), 61.48 (br. s.), 119.65 (q, *J*=321.20 Hz).

c) N,N-diethyl-N-2-hydroxyethyl-N-methylammonium bis(trifluoromethanesulfonyl)amide

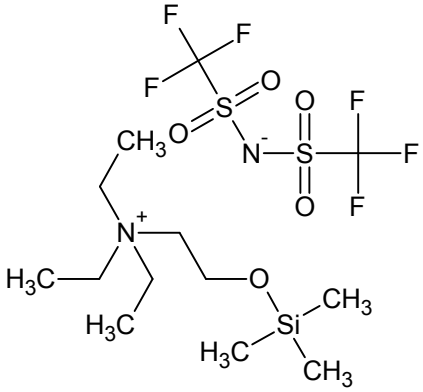
To a 250 ml round bottom flask containing 65 g (0.159 mol) of neat *N,N*-diethyl-*N*-2-hydroxyethyl-*N*-methylammonium bis(trifluoromethanesulfonyl)amide, 25.69 g (0.160 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was

slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL formed. A vigorous evolution of gaseous ammonia started as the temperature reached 60°C and ended after a few minutes. The mixture was heated and stirred overnight (16 hours after the end of the vigorous reaction). Then, the remaining HMDS, which was in separate layer on top of the desired product, was evaporated under high vacuum. A slightly coloured oil was obtained and diluted with 100 ml of CH_2Cl_2. 5 g of activated charcoal were added. The mixture was heated to its boiling point, cooled to room temperature and filtered after 1h through a 0.22 µm PTFE filter. The solvent was removed using a rotary evaporator and then 5 ml of fresh HMDS were added to the clear product. This mixture was vigorously stirred and heated to 70°C for one hour. Then, the volatile compounds were removed *in vacuo* and the flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 72 g (93 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.07 (s, 9 H), 1.27 (t, *J*=7.14 Hz, 6 H), 2.94 (s, 3 H), 3.25 - 3.43 (m, 6 H), 3.81 - 3.98 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -1.37 (s), 7.47 (s), 47.74 (br. s.), 56.10 (s), 57.56 (br. s), 61.60 (br. s.), 119.62 (q, *J*=321.20 Hz).

Preparation of* 3d: *N,N,N-triethyl-N-(2-trimethylsiloxyethyl)ammonium bis(trifluoromethane-sulfonyl)amide (N2222-OTM-TFSI)



a) N,N,N-triethyl-N-(2-hydroxyethyl)ammonium bromide

In a 500 ml round bottom flask equipped with a magnetic stirrer were placed 58.6 g (0.50 mol) of 2-diethylaminoethanol dissolved in 80 ml of MeCN. To this solution, a mixture of 60 g (0.550 mol) ethyl bromide and 40 ml of MeCN was added dropwise over a period of 0.75 h. The mixture was stirred over a weekend (57 h) during which a white crystalline precipitate separated. This precipitate was vacuum-filtered, washed with a small amount of acetone and dried in a vacuum oven at 60°C. The

filtrate was evaporated to small volume and additional product was precipitated using ethyl acetate. Altogether, 87.51 g (77 %) of *N,N,N*-triethyl-*N*-(2-hydroxyethyl)ammonium bromide were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.17 (t, *J*=7.14 Hz, 9 H), 3.26 - 3.31 (m, 2 H), 3.32 (q, *J*=7.00 Hz, 6 H), 3.76 (br. d, *J*=4.80 Hz, 2 H), 5.26 (t, *J*=5.49 Hz, 1 H)

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 7.31 (s), 52.72 (br. s), 54.37 (s), 57.67 (br. s).

b) N,N,N-triethyl-N-(2-hydroxyethyl)ammonium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, solutions of 40 g (0.177 mol) of *N,N,N*-triethyl-*N*-(2-hydroxyethyl)ammonium bromide in 70 ml MQ water and 53 g (0.185 mol) of LiTFSI in 80 ml MQ water were mixed under vigorous stirring. Phase separation occurred at once, but the stirring was continued overnight (16 hours) at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 20 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 80 ml of MQ water. A clear solution was obtained and poured into a round bottom flask. The solvent was first removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 65.71 g (87 %) of pure *N,N,N*-triethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.19 (t, *J*=7.14 Hz, 9 H), 3.19 - 3.40 (m, 8 H), 3.79 (d, *J*=4.76 Hz, 2 H), 5.25 (t, *J*=5.13 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 7.10 (s), 52.95 (br. s.), 54.71 (s), 57.94 (br. s.), 119.69 (q, *J*=321.20 Hz).

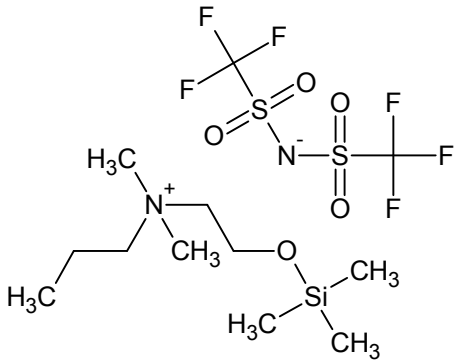
c) N,N,N-triethyl-N-(2-trimethylsiloxyethyl)ammonium bis(trifluoromethanesulfonyl)amide

To a 250 ml round bottom flask containing 65 g (0.152 mol) of neat *N,N,N*-triethyl-*N*-(2-trimethylsiloxyethyl)ammonium TFSI, 24.5 g (0.152 mol) of hexamethyldisilazane (HMDS) were added at 60°C as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The reaction started 2 minutes after the addition. The mixture was stirred so that a fine emulsion of HMDS in choline TFSI formed. Intense evolution of gaseous ammonia ended after a few minutes, but the mixture was heated and stirred overnight (16 hours after the end of the intense reaction). Then, the remaining HMDS, which was in separate layer on top of the desired product, was evaporated under high vacuum. The round bottom flask was then refilled 5 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally the apparatus was cooled down under vacuum and refilled with argon. In this manner, 75.6 g (100 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.11 (s, 9 H), 1.28 (t, *J*=7.3 Hz, 9 H), 3.17 - 3.50 (m, 8 H), 3.91 (br. s., 2 H)

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -1.20 (s), 7.23 (s), 53.72 (br. s.), 56.02 (s), 58.27 (br. s.), 119.76 (q, *J*=321.20 Hz).

Preparation of* 3e: *N-(2-trimethylsiloxyethyl)-N,N-dimethyl-N-propylammonium bis(trifluoromethane sulfonyl)amide (N1132-OTMS-TFSI)



a) N-(2-hydroxyethyl)-N,N-dimethyl-N-propylammonium bromide

In a 1000 ml round bottom flask equipped with a magnetic stirrer were placed 135 g (1.50 mol) of 2-dimethylaminoethanol dissolved in 200 ml of MeCN. The solution cooled considerably during mixing. To this solution, a mixture of 200 g (1.64 mol) of propyl bromide, 80 ml of MeCN and 50 ml toluene was added dropwise over a period of 1h while the temperature was not allowed to exceed 35°C. At first, an addition rate of about 5ml/min was used, after warming was detected, this rate was reduced to 5 drops/second. The mixture was stirred over a weekend (57 h) during which a small amount of white crystalline precipitate separated. 200 ml of ethyl acetate were added to precipitate the majority of the product, which was then vacuum-filtered, washed with a small amount of ethyl acetate and dried in a vacuum oven at 60°C. The filtrate was evaporated to a small volume and additional product was precipitated with ethyl acetate. Altogether, 307 g (96 %) of *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-propylammonium bromide were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 0.87 (t, *J*=7.3 Hz, 3 H), 1.57 - 1.78 (m, 2 H), 3.08 (s, 6 H), 3.26 - 3.37 (m, 2 H), 3.38 - 3.46 (m, 2 H), 3.81 (br. s., 2 H), 5.26 (t, *J*=5.1 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 10.57 (s), 15.55 (s), 50.88 (t, *J*=3.5 Hz), 54.88 (s), 64.61 (br. t), 65.38 (br. t).

b) N-(2-hydroxyethyl)-N,N-dimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide

In a 500 ml round bottom flask, solutions of 100 g (0.472 mol) of *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-propylammonium bromide in 100 ml MQ water and 135 g (0.472 mol) of LiTFSI in 100 ml MQ water were mixed under vigorous stirring. Phase separation occurred at

once, but the stirring was continued overnight (16 hours) at room temperature. Then, 120 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 20 ml of CH_2Cl_2 and the combined organic phases were washed 7 times with 80 ml of MQ water. A clear solution was obtained and poured into a round bottom flask. The solvent was removed first using at rotary evaporator and then under high vacuum at 60°C. In this manner, 154.67 g (80 %) of pure *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 0.89 (t, *J*=7.3 Hz, 3 H), 1.59 - 1.80 (m, 2 H), 3.05 (s, 6 H), 3.21 - 3.32 (m, 2 H), 3.33 - 3.40 (m, 2 H), 3.83 (br. s., 13 H), 5.26 (t, *J*=4.9 Hz, 6 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 10.38 (s), 15.51 (s), 50.87 (br. t), 55.02 (s), 64.82 (br. t), 65.65 (br. t), 119.58 (q, *J*=321.8 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ/ppm: -78.76 (s).

c) N-(2-trimethylsiloxyethyl)-N,N-dimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide

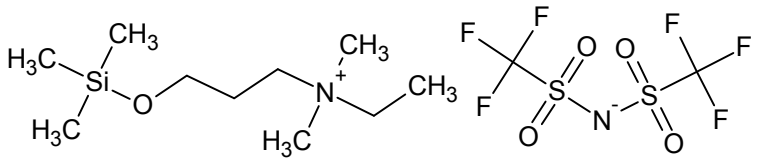
To a 250 ml round bottom flask containing 154.6 g (0.38 mol) of neat *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide, 72.63 g (0.45 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate the removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL formed. A vigorous evolution of gaseous ammonia started as the temperature reached 60°C and ended after a few minutes, but the mixture was heated and stirred overnight (16 hours after the end of vigorous reaction). Then, the remaining HMDS, which was in separate layer on top of the desired product, was decanted. A slightly coloured oil was obtained and diluted with 150 ml of CH_2Cl_2. 10 g of activated charcoal were added and the mixture was heated to its boiling point for 3 minutes. The mixture was then cooled to room temperature and filtered after 1h through a 0.22 μm PTFE filter. The solvent was removed using a rotary evaporator. 5 ml of fresh HMDS were added to the clear product. The resulting mixture was vigorously stirred and heated to 70°C for one hour. Then, the volatile compounds were removed *in vacuo* and the flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 183 g (99 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.10 (s, 9 H), 0.95 (t, *J*=7.1 Hz, 3 H), 1.65 - 1.83 (m, 2 H), 3.08 (s, 6 H), 3.21 - 3.31 (m, 2 H), 3.40 (dt, *J*=4.5, 2.3 Hz, 2 H), 3.94 (br. s., 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: - 1.24 (m), 9.90 (br. s.), 15.95 (br. s.), 51.56 (br. s.), 56.49 (s), 64.90 (br. s.), 67.02 (br. s), 119.68 (q, *J*=321.2 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ/ppm: -78.87 (s).

Preparation of* 3f: *N-ethyl-N-(3-(trimethylsiloxy)propyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1123-OTMS-TFSI)



a) <u>*N*-ethyl-*N*-(3-hydroxypropyl)-*N,N*-dimethylammonium chloride</u>

In a 300 ml 316 SS autoclave equipped with a magnetic stirrer were placed 94.5 g (1 mol) of 3-chloropropanol and 74 g (1.01mol) of ethyldimethylamine. The mixture was stirred and heated to 140°C for 24 h using a stirring hot plate. After cooling, the resulting waxy solid was dissolved in 350 ml MeOH, boiled with activated charcoal, cooled and filtered. The filtrate was evaporated to dryness and the product was isolated as a colourless crystalline solid. Altogether, 150 g (90 %) of *N*-ethyl-*N*-(3-hydroxypropyl)-*N,N*-dimethylammonium chloride were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) □/ppm 1.21 (t, *J*=7.02 Hz, 3 H), 1.71 - 1.88 (m, 2 H), 3.02 (s, 6 H), 3.30 - 3.40 (m, 4 H), 3.39 - 3.49 (m, 2 H), 5.13 (t, *J*=5.27 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) □/ppm: 7.79 (s), 25.29 (s), 49.47 (t, *J*=3.45 Hz), 57.48 (s), 58.26 (br. s.), 60.36 (br. s.).

b) <u>*N*-ethyl-*N*-(2-hydroxypropyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide</u>

In a 250 ml round bottom flask, solutions of 60 g (0.358 mol) of *N*-ethyl-*N*-(3-hydroxypropyl)-*N,N*-dimethylammonium chloride in 70 ml MQ water and 104 g (0.360 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear colourless solution was obtained. This solution was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 111.2g (75 %) of pure *N*-ethyl-*N*-(2-hydroxypropyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) □/ppm: 1.18 - 1.30 (m, 3 H), 1.73 - 1.86 (m, 2 H), 2.98 (s, 6 H), 3.22 - 3.39 (m, 4 H), 3.49 (q, *J*=5.27 Hz, 2 H), 4.78 (t, *J*=4.68 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) □□ppm: 7.68 (s), 25.31 (s), 49.20 - 49.78 (m), 57.66 (s), 58.56 (br. s.), 60.07 - 61.14 (m), 119.58 (q, *J*=321.80 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) □□ppm: -78.78 (s).

c) *N*-ethyl-*N*-(3-trimethylsiloxypropyl)-*N,N*-dimethylammonium bis(trifluoromethane-sulfonyl)amide

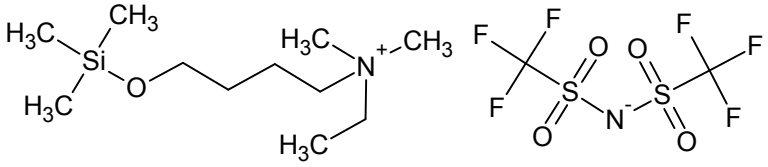
To a 250 ml round bottom flask containing 111 g (0.269 mol) of neat *N*-ethyl-*N*-(3-hydroxypropyl)-*N,N*-dimethylammonium TFSI, 43 g (0.266 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 60°C. This evolution lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, the remaining HMDS, which was in a separate layer on top of the desired product, was evaporated under high vacuum. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 129 g (99 %) of the title compound in the form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) □/ppm: 0.04 (s, 9 H), 1.30 (t, *J*=7.02 Hz, 3 H), 1.78 - 1.97 (m, 2 H), 2.96 (s, 6 H), 3.23 - 3.37 (m, 4 H), 3.60 (t, *J*=5.56 Hz, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) □/ppm: -1.12 (s), 7.65 (s), 25.37 (s), 50.29 (t, *J*=3.45 Hz), 58.16 (s), 59.61 (br. s.), 61.41 (br. s.), 119.61 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) □□ppm: -79.22 (s).

Preparation of* 3g: *N-ethyl-N-(4-(trimethylsiloxy)butyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1124-OTMS-TFSI)



a) *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium chloride

In a 300 ml 316 SS autoclave equipped with a magnetic stirrer were placed 50 g of 86 % (0.391 mol) of 4-chlorobutanol and 34 g (0.469 mol) of ethyldimethylamine. The mixture was stirred and heated to 150°C for 30 h using a stirring hot plate. After cooling, the resulting waxy solid was dissolved in water, basified with NaOH to remove unquaternised amine, and finally evaporated to dryness. Altogether, 56.8 g (approx. 70 %) of *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium chloride as a mixture with NaCl and NaOH were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm 1.09 - 1.25 (m, 3 H), 1.27 - 1.46 (m, 2 H), 1.64 (dt, *J*=16.09, 7.75 Hz, 2 H), 2.99 (s, 6 H), 3.20 - 3.45 (m, 6 H), 4.40 (br. s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ /ppm: 7.96 (s), 18.93 (s), 30.14 (s), 49.43 (br. s.), 58.32 (br. s.), 60.15 (s), 62.53 (s).

b) *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, a water solution of the mixture obtained in a) above was neutralised with HCl and mixed with a solution of 87 g (0.300 mol) of LiTFSI in 80 ml MQ water under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear colourless solution was obtained. It was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 53.29 g of pure *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.15 - 1.30 (m, 3 H), 1.37 - 1.58 (m, 2 H), 1.61 - 1.80 (m, 2 H), 2.89 - 3.00 (m, 6 H), 3.16 - 3.38 (m, 4 H), 3.41 - 3.52 (m, 2 H), 4.55 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 18.70 (s), 29.06 (s), 48.98 - 49.88 (m), 58.55 (br. s.), 59.91 (s), 62.45 (br. s.), 70.05 (s), 119.56 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ ppm: -75.36 (s).

c) *N*-ethyl-*N*-(4-trimethylsiloxybutyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide

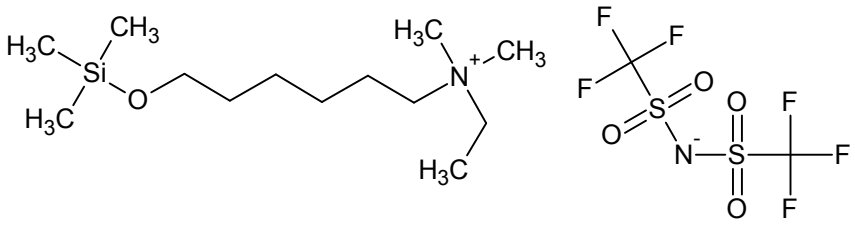
To a 250 ml round bottom flask containing 53 g (0.125 mol) of neat *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium TFSI, 20 g (0.125 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60-70°C and stirred so that a fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 60°C. This evolution lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, volatiles were evaporated under high vacuum. What remained was dissolved in CH_2Cl_2, purified with activated charcoal, filtered and evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 47 g (74 %) of the title compound as a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.07 (s, 9 H), 1.33 (t, *J*=7.32 Hz, 3 H), 1.46 - 1.64 (m, 2 H), 1.67 - 1.86 (m, 2 H), 2.98 (s, 6 H), 3.15 - 3.28 (m, 2 H), 3.34 (q, *J*=7.02 Hz, 2 H), 3.60 (t, *J*=5.85 Hz, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -0.83 (s), 7.83 (s), 19.26 (s), 28.49 (s), 50.13 (br. s.), 59.70 (br. s.), 61.04 (s), 63.54 (br. s), 119.69 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -79.16 (s).

Preparation of* 3h: *N-ethyl-N-(6-(trimethylsiloxy)hexyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1126-OTMS-TFSI)



a) <u>*N*-ethyl-*N*-(6-hydroxyhexyl)-*N,N*-dimethylammonium chloride</u>

In a 300 ml 316 SS autoclave equipped with a magnetic stirrer were placed 25 g of (0.183 mol) of 6-chlorohexanol, 16 g (0.220 mol) of ethyldimethylamine and 50 mg of KI. The mixture was stirred and heated to 100°C for 72 h using a stirring hot plate. After cooling, the resulting waxy solid was crushed and evacuated at 80°C/1.4 mm Hg, and finally recrystalised from MeOH/acetone. Altogether, 38 g (99 %) of *N*-ethyl-*N*-(6-hydroxyhexyl)-*N,N*-dimethylammonium chloride were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.21 (t, *J*=7.10 Hz, 3 H), 1.24 - 1.48 (m, 6 H), 1.55 - 1.71 (m, 2 H), 3.00 (s, 6 H), 3.18 - 3.30 (m, 2 H), 3.30 - 3.43 (m, 4 H), 4.55 (t, *J*=4.97 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ /ppm: 7.82 (s), 21.66 (br. s), 25.00 (br. s), 25.67 (br. s), 32.17 (s), 49.30 (t, *J*=3.40 Hz), 58.29 (br. s.), 60.38 (s), 62.21 (br. s.).

b) <u>*N*-ethyl-*N*-(6-hydroxyhexyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide</u>

In a 250 ml round bottom flask, solutions of 30 g (0.143 mol) of *N*-ethyl-*N*-(6-hydroxyhexyl)-*N,N*-dimethylammonium chloride and 43 g (0.150 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear solution was obtained. This solution was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 58.4 g (90 %) of pure *N*-ethyl-*N*-(6-hydroxyhexyl)-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide as liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.23 (t, *J*=7.20 Hz, 3 H), 1.27 - 1.51 (m, 6 H), 1.55 - 1.76 (m, 2 H), 2.96 (s, 6 H), 3.14 - 3.25 (m, 2 H), 3.31 (q, *J*=7.02 Hz, 2 H), 3.40 (t, *J*=6.15 Hz, 2 H), 4.36 (br. s., 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 7.70 (s), 21.74 (s), 25.03 (s), 25.67 (s), 32.23 (s), 48.68 - 49.74 (m), 58.58 (br. s.), 60.55 (s), 62.53 (br. s.), 119.56 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ ppm: -78.79 (s).

c) <u>*N*-ethyl-*N*-(6-trimethylsiloxyhexyl)-*N,N*-dimethylammonium bis(trifluoromethane-sulfonyl)amide</u>

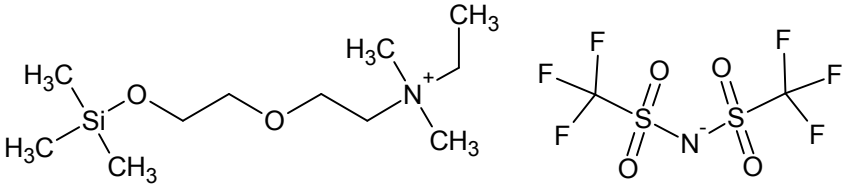
To a 250 ml round bottom flask containing 58 g (0.129 mol) of neat *N*-ethyl-*N*-(4-hydroxybutyl)-*N,N*-dimethylammonium TFSI, 20 g (0.129 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate the removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 60°C. This evoluation lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, the volatiles were evaporated under high vacuum. What remained was dissolved in CH_2Cl_2, purified with activated charcoal, filtered and evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 63 g (93 %) of the title compound as a viscous liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.05 (s, 9 H), 1.22 - 1.41 (m, 7 H), 1.47 (d, *J*=7.02 Hz, 2 H), 1.55 - 1.75 (m, 2 H), 2.96 (s, 6 H), 3.10 - 3.22 (m, 2 H), 3.31 (q, *J*=7.00 Hz, 2 H), 3.52 (t, *J*=6.15 Hz, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -0.76 (s), 7.82 (s), 22.31 (s), 25.09 (s), 25.62 (s), 32.10 (s), 50.01 (br. s.), 59.68 (br. s), 61.99 (s), 63.83 (br. s), 119.64 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -79.16 (s).

Preparation of* 3i: *N-ethyl-N-2-(2-(trimethylsiloxy)ethoxy)ethyl-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1122O2-OTMS-TFSI)



a) <u>*N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium chloride</u>

In a 300 ml 316 SS autoclave equipped with a magnetic stirrer were placed 50 g of (0.401mol) of 2-chloroethyl 2-hydroxyethyl ether, 35 g (0.482 mol) of ethyldimethylamine and 50 mg of KI. The mixture was stirred and heated to 150°C for 22 h using a stirring hot plate. After cooling, the resulting

very viscous liquid (with a consistence similar to honey) was dissolved in water, basified with NaOH, evaporated and dissolved in CH_2Cl_2. Activated charcoal was then added. The mixture was stirred overnight, filtered and evaporated. Altogether, 72 g (91 %) of colourless *N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium chloride were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.13 - 1.28 (m, 3 H), 3.03 - 3.18 (m, 6 H), 3.39 - 3.51 (m, 6 H), 3.58 (d, *J*=4.10 Hz, 2 H), 3.81 (br. s., 2 H), 5.06 (br. s., 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ /ppm: 8.02 (s), 50.08 (br. s.), 59.45 (s), 59.75 (s), 61.60 (s), 63.87 (s), 72.08 (s).

b) *N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)-amide

In a 250 ml round bottom flask, solutions of 47 g (0.290 mol) of *N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium chloride and 100 g (0.348 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear solution was obtained. It was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 121.8 g (92 %) of pure *N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium bis(trifluoromethanesulfonyl)amide as a liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.26 (t, *J*=7.32 Hz, 3 H), 3.04 (s, 6 H), 3.41 (q, *J*=7.41 Hz, 2 H), 3.46 - 3.62 (m, 6 H), 3.83 (br. s., 2 H), 4.64 (t, *J*=4.97 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 7.81 (s), 50.36 (br. s), 60.15 (br. s), 62.16 (br. s.), 64.01 (s), 72.39 (s), 119.68 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ ppm: -79.10 (s).

c) *N*-ethyl-*N*-2-(2-(trimethylsiloxy)ethoxy)ethyl-*N,N*-dimethylammonium bis(trifluoromethane-sulfonyl)amide

To a 250 ml round bottom flask containing 121.8 g (0.275 mol) of neat *N*-ethyl-*N*-2-(2-hydroxyethoxy)ethyl-*N,N*-dimethylammonium TFSI, 44 g (0.273 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate the removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 60°C. The evoluation lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction.

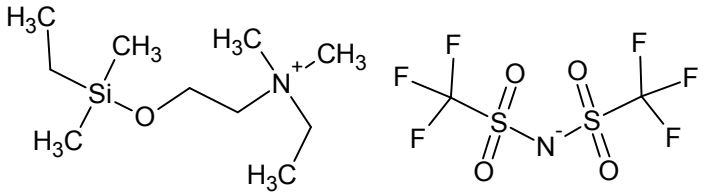
Then, volatiles were evaporated under high vacuum. What remained was dissolved in CH_2Cl_2, purified with activated charcoal, filtered and evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 140 g (99 %) of the title compound as a viscous liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.06 (s, 9 H), 1.33 (t, *J*=7.02 Hz, 3 H), 3.03 - 3.11 (m, 6 H), 3.37 - 3.49 (m, 4 H), 3.49 - 3.56 (m, 2 H), 3.62 - 3.71 (m, 2 H), 3.85 (br. s., 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -0.88 (s), 7.97 (s), 50.96 (br. s.), 61.30 (s), 61.42 (br. s), 62.72 (br. s.), 64.41 (s), 72.45 (s), 119.64 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -79.18 (s).

Preparation of* 3j: *N-ethyl-N-(2-(ethyldimethylsiloxy)ethyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1122-OEDMS-TFSI)



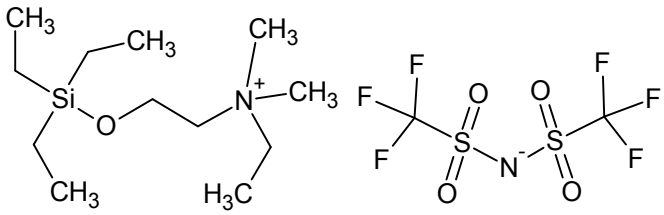
To a 250 ml round bottom flask containing 91 g (0.228 mol) of neat *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium TFSI prepared in a manner similar to that described in Example 4 a and b, 45 g (0.282 mol) of (diethylamino)ethyldimethylsilane were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of silane in IL was formed. A vigorous evolution of gaseous diethylamine was observed as the temperature reached 60°C. This vigorous evolution lasted a few minutes. The mixture was heated and stirred for 5 hours after the end of the vigorous reaction. Then, the remaining silane, which was in a separate layer on the top of desired product, was evaporated under high vacuum. The product was dissolved in CH_2Cl_2 and activated charcoal was added. The mixture was heated to its boiling point, cooled to room temperature, filtered and again evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 100 g (90 %) of the title compound were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.08 (s, 6 H), 0.56 (q, *J*=8.19 Hz, 2 H), 0.84 - 0.95 (m, 3 H), 1.34 (t, *J*=7.32 Hz, 3 H), 3.07 (s, 6 H), 3.34 - 3.40 (m, 2 H), 3.44 (q, *J*=7.60 Hz, 2 H), 3.91 - 4.00 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -3.43 (s), 6.27 (s), 7.28 (s), 7.97 (s), 50.97 (t, *J*=3.45 Hz), 56.59 (s), 61.49 (br. s.), 64.58 (br. s.), 119.67 (q, *J*=320.70 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -78.90 (s).

Preparation of* 3k: *N-ethyl-N-(2-(triethylsiloxy)ethyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1122-OTES-TFSI)



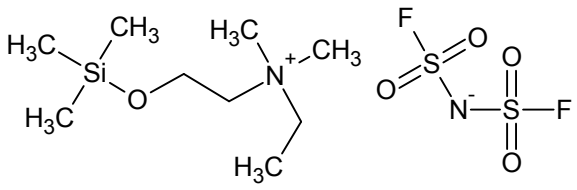
To a 250 ml round bottom flask containing 80 g (0.201 mol) of neat *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium TFSI prepared in a manner similar to Example 4a and b, 40 g (0.251 mol) of (dimethylamino)triethylsilane were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of silane in IL was formed. A vigorous evolution of gaseous dimethylamine was observed as the temperature reached 60°C. This vigorous evolution lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, the remaining silane, which was in a separate layer on the top of the desired product, was evaporated under high vacuum. The product was dissolved in CH_2Cl_2 and activated charcoal was added. The mixture was heated to its boiling point, cooled to room temperature, filtered, and again evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 102 g (100 %) of the title compound were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.58 (q, *J*=8.20 Hz, 6 H), 0.90 (t, *J*=8.20 Hz, 9 H), 1.33 (t, *J*=7.32 Hz, 3 H), 3.06 (s, 6 H), 3.35 - 3.39 (m, 2 H), 3.44 (q, *J*=7.02 Hz, 2 H), 3.90 - 4.04 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: 3.73 (s), 6.32 (s), 7.92 (s), 50.91 (t, *J*=3.45 Hz), 56.88 (s), 61.45 (br. s), 64.58 (br. s.), 119.65 (q, *J*=321.90 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -78.90 (s).

Preparation of* 3l:*N-ethyl-N-(2-(trimethylsiloxy)ethyl)-N,N-dimethylammonium bis(fluorosulfonyl)-amide (N1122-OTMS-FSI)



a) <u>*N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bis(fluorosulfonyl)amide</u>

In a 250 ml round bottom flask, solutions of 53 g (0.268 mol) of *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bromide (prepared in a manner similar to Example 3b-a) in 70 ml dry MeCN and 60 g (0.273 mol) of potassium bis(fluorosulfonyl)amide (K-FSI) in 80 ml dry MeCN were mixed under vigorous stirring. Phase separation occurred at once, but stirring was continued overnight at room temperature. Then, 100 ml of CH_2Cl_2 were added and KBr was filtered off. The filtrate was washed three times with 50 ml of CH_2Cl_2. A clear colourless solution was obtained which was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 65°C. In this manner, 74 g (93 %) of pure *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bis(fluorosulfonyl)amide in the form of gelatinous crystals were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.24 (tt, *J*=7.30, 1.80 Hz, 3 H), 3.02 (s, 6 H), 3.31 - 3.44 (m, 4 H), 3.73 - 3.90 (m, 2 H), 5.27 (t, *J*=4.97 Hz, 6 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 7.87 (s), 50.28 (t, *J*=3.40 Hz), 54.96 (s), 59.78 (t, *J*=2.30 Hz), 64.16 (t, *J*=2.30 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ ppm: 53.18 (s).

b) <u>N-ethyl-N-(2-(trimethylsiloxy)ethyl)-N,N-dimethylammonium bis(fluorosulfonyl)amide</u>

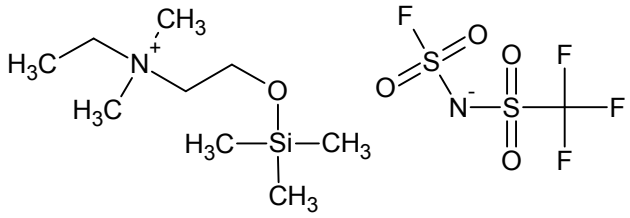
To a 250 ml round bottom flask containing 74 g (0.237 mol) of *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium FSI dissolved in 80 ml of dry MeCN, 32 g (0.20 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 40°C and stirred. A vigorous evolution of gaseous ammonia started immediately and lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, volatiles were evaporated under high vacuum. What remained was dissolved in CH_2Cl_2, purified with activated charcoal, filtered and evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 74 g (85 %) of title compound as a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.08 (s, 9 H), 1.32 (t, *J*=7.32 Hz, 3 H), 3.03 (s, 6 H), 3.30 - 3.35 (m, 2 H), 3.39 (q, *J*=7.20 Hz, 2 H), 3.93 (dt, *J*=4.24, 2.27 Hz, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -1.31 (s), 7.88 (s), 50.91 (t, *J*=3.45 Hz), 56.25 (s), 61.36 (br. s.), 64.52 (t, *J*=2.30 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: 53.04 (s).

Preparation of* 3m: *N-ethyl-N-(2-(trimethylsiloxy)ethyl)-N,N-dimethylammonium N-fluorosulfonyl-trifluoromethansulfonylamide (N1122-OTMS-FTFSI)



a) <u>*N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium *N*-fluorosulfonyl-trifluoromethansulfonylamide</u>

In a 250 ml round bottom flask, solutions of 60 g (0.304 mol) of *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium bromide (prepared in a manner similar to Example 4a) in 70 ml MQ water and 83 g (0.309 mol) of lithium *N*-fluorosulfonyl-trifluoromethansulfonylamide (Li-FTFSI) in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear colourless solution was obtained. This solution was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 89 g (84 %) of pure *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium *N*-fluorosulfonyl-trifluoromethansulfonylamide were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 1.15 - 1.34 (m), 3.03 (s), 3.32 - 3.44 (m), 3.83 (s), 5.27 (t, *J*=4.97 Hz).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 7.87 (s), 49.98 - 50.75 (m), 55.09 (s), 59.44 - 60.37 (m), 64.02 - 64.60 (m), 119.74 (qd, *J*=321.90, 2.30 Hz).

^{19}F NMR (470 MHz, DMSO-d_6) δ ppm: -77.98 (d, *J*=3.58 Hz, 3 F), 57.57 (q, *J*=3.97 Hz, 1 F).

b) N-ethyl-N-(2-(trimethylsiloxy)ethyl)-N,N-dimethylammonium N-fluorosulfonyl-*trifluoromethansulfonylamide*

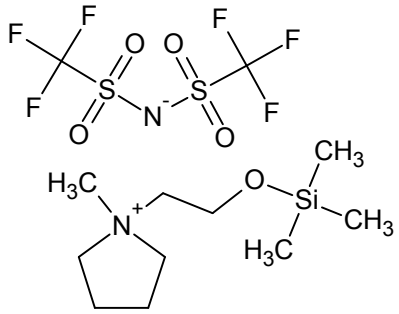
To a 250 ml round bottom flask containing 89 g (0.255 mol) of neat *N*-ethyl-*N*-2-hydroxyethyl-*N,N*-dimethylammonium FTFSI, 32 g (0.20 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. This mixture was slowly heated to 50°C and stirred so that fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 50°C. This vigorous evoluation lasted a few minutes. The mixture was heated and stirred for additional 4 hours after the end of the vigorous reaction. Then, the remaining HMDS, which was in a separate layer on the top of the desired product, was evaporated under high vacuum. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 106 g (99 %) of the title compound were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.12 (s, 9 H), 1.36 (t, *J*=7.02 Hz, 3 H), 3.08 (s, 6 H), 3.36 - 3.41 (m, 2 H), 3.45 (q, *J*=7.60 Hz, 4 H), 3.97 (s, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ /ppm: -1.07 (s), 8.15 (s), 51.17 (t, *J*=3.45 Hz), 56.56 (s), 61.65 (br. s.), 64.75 (br. s.), 119.87 (qd, *J*=321.90, 2.30 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ ppm: -78.07 (d, *J*=4.17 Hz, 3 F), 57.52 (q, *J*=3.98 Hz, 1 F).

Preparation of* 3n: *N-(2-trimethylsiloxyethyl)-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide (Py12OTMS TFSI)



a) N-(2-hydroxyethyl)-N-methylpyrrolidinium chloride

In a 250 ml round bottom flask equipped with a magnetic stirrer were placed 30 g (0.352 mol) of *N*-methylpyrrolidine dissolved in 83 g of toluene. To this solution, a mixture of 28.3 g (0.352 mol) of 2-chloroethanol in 20 g of toluene was added dropwise over period of 0.5 h. The mixture was stirred over a weekend (57 h) during which no signs of completed reaction were observed. The mixture was thus heated to 80°C for 14 h during which phase separation occurred. The mixture was

cooled to room temperature and the bottom layer solidified. Toluene was decanted and the solid was then crushed and dissolved in methanol. 5 g of activated charcoal were added. The mixture was heated to its boiling point, cooled and filtered. The filtrate was evaporated to obtain 43.34 g (75 %) of the title *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium chloride.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.93 - 2.17 (m, 4 H), 3.08 (s, 3 H), 3.47 (dd, *J*=6.04, 4.21 Hz, 2 H), 3.52 - 3.62 (m, 4 H), 3.80 (dd, *J*=4.39, 2.20 Hz, 2 H), 5.72 (t, *J*=5.31 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 25.64 (s), 52.57 (br. s.), 60.17 (s), 68.93 (br. s.), 69.31 (br. s.).

b) N-(2-hydroxyethyl)-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, solutions of 38 g (0.23 mol) of *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium chloride in 130 ml MQ water and 65 g (0.23 mol) of solid LiTFSI were mixed under vigorous stirring. Phase separation occurred at once, but the stirring was continued overnight (16 hours) at room temperature. Then, 80 ml of CH_2Cl_2 were added and the phases separated. The organic phase was washed 7 times with 80 ml of MQ water. A clear solution was obtained and poured into a round bottom flask. The solvent was removed first using a rotary evaporator and then under high vacuum at 65°C. In this manner, 67.46 g (70 %) of pure *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.96 - 2.21 (m, 4 H), 3.03 (s, 3 H), 3.42 (dd, *J*=5.86, 4.39 Hz, 2 H), 3.46 - 3.59 (m, 4 H), 3.76 - 3.92 (m, 2 H), 5.27 (t, *J*=4.76 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 20.89 (s), 47.98 (t, *J*=3.50 Hz), 55.59 (s), 64.31 (t, *J*=2.80 Hz), 64.66 (t, *J*=2.80 Hz), 119.54 (q, *J*=322.00 Hz).

c) N-(2-trimethylsiloxyethyl)-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide

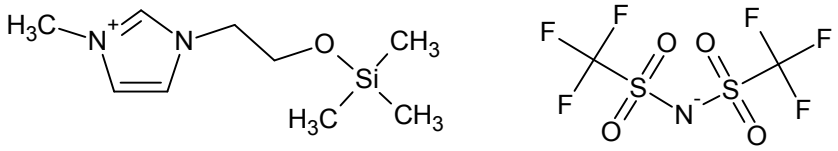
To a 250 ml round bottom flask containing 67.46 g (0.164 mol) of neat *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, 27 g (0.168 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 60-70°C and stirred so that a fine emulsion of HMDS in IL formed. A vigorous evolution of gaseous ammonia started close to 60°C and ended after a few minutes. The mixture was heated and stirred overnight (16 hours after the end of vigorous reaction). Then, the volatile compounds were removed *in vacuo* and the flask was refilled 6 times with Ar and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 81 g (100 %) of the title compound in form of a colourless liquid, which solidified at room temperature, were obtained. The melting point of this solid was around 40°C.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.07 (m, 9 H), 2.01 - 2.26 (m, 4 H), 3.02 (s, 3 H), 3.32 - 3.43 (m, 2 H), 3.44 - 3.62 (m, 4 H), 3.84 - 4.00 (m, 2 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -1.35 (s), 20.96 (s), 48.29 (br. s.), 56.65 (s), 65.11 (br. s.), 65.35 (br. s), 119.57 (q, *J*=323.70 Hz).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ/ppm: -79.21 (s)

Preparation of* 3o: *3-methyl-1-(2-(trimethylsiloxy)ethyl)imidazolium bis(trifluoromethane-sulfonyl)amide (Im12-OTMS-TFSI)



a) 1-(2-hydroxyethyl)-3-methylimidazolium bromide

In a 250 ml round bottom flask equipped with a magnetic stirrer were placed 49 g (0.597 mol) of 1-methylimidazole. These were dissolved in 60 ml of MeCN. To this solution, 76 g (0.610 mol) of 2-bromoethanol were added dropwise in 15 min. The mixture was stirred refluxed for 48 hours during which no sign of completed phase separation was observed. The mixture was heated to reflux for 2 h and cooled to room temperature. The solvents were evaporated and the resulting solid was purified by pouring its methanolic solution into a 1:1 mixture of ethyl acetate (AcOEt) and acetone. The resulting white powder was filtered and washed with fresh ethyl acetate and dried under vacuum. 125 g (95 %) of 1-(2-hydroxyethyl)-3-methylimidazolium bromide were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 3.70 (q, *J*=5.13 Hz, 2 H), 3.88 (s, 3 H), 4.24 (t, *J*=4.94 Hz, 2 H), 5.15 (t, *J*=5.31 Hz, 1 H), 7.76 (d, *J*=1.46 Hz, 1 H), 7.79 (t, *J*=1.65 Hz, 1 H), 9.23 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ /ppm: 35.73 (s), 51.53 (s), 59.26 (s), 122.61 (s), 123.28 (s), 136.76 (s)

b) 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, a water solution of 59 g (0.285 mol) of 1-(2-hydroxyethyl)-3-methylimidazolium bromide and a solution of 82.3 g (0.287 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH_2Cl_2 were added and the phases separated. The water phase was extracted with 50 ml of CH_2Cl_2 and the combined organic phases were washed 6 times with 100 ml of MQ water. A clear solution was obtained. It was poured into a round bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60°C. In this manner, 69 g (60 %) of pure 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide as colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ /ppm: 3.74 (q, *J*=4.88 Hz, 2 H), 3.86 (s, 3 H), 4.16 - 4.25 (m, 2 H), 5.18 (t, *J*=5.13 Hz, 1 H), 7.63 (t, *J*=1.65 Hz, 1 H), 7.68 (t, *J*=1.83 Hz, 1 H), 9.05 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ □ppm: 35.73 (s, 9 C), 51.85 (s, 12 C), 59.49 (s, 12 C), 119.68 (q, *J*=321.80 Hz, 8 C), 122.77 (s, 12 C), 123.43 (s, 12 C), 137.01 (s, 8 C).

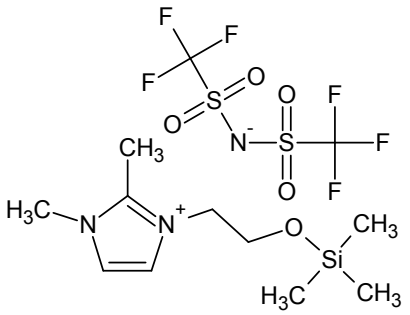
c) 3-methyl-1-(2-(trimethylsiloxy)ethyl)imidazolium bis(trifluoromethanesulfonyl)amide

To a 250 ml round bottom flask containing 68 g (0.167 mol) of neat 1-(2-hydroxyethyl)-3-methylimidazolium TFSI, 25.8 g (0.160 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate removal of forming ammonia. The mixture was slowly heated to 50–60°C and stirred so that a fine emulsion of HMDS in IL was formed. A vigorous evolution of gaseous ammonia was observed as the temperature reached 60°C. The evolaution lasted a few minutes. The mixture was heated and stirred for 4 hours after the end of the vigorous reaction. Then, the volatiles were evaporated under high vacuum. What remained was dissolved in CH_2Cl_2, purified with activated charcoal, filtered and evaporated. Then, the round bottom flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 70 g (88 %) of the title compound as a viscous liquid were obtained

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ /ppm: 0.03 (s, 9 H), 3.79 - 3.86 (m, 2 H), 3.89 (s, 3 H), 4.17 - 4.29 (m, 2 H), 7.31 (t, *J*=1.83 Hz, 1 H), 7.37 (t, *J*=1.65 Hz, 1 H), 8.59 (br. s, 1 H).

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ □ppm: -1.21 (s), 36.03 (s), 52.01 (s), 60.46 (s), 119.63 (q, *J*=320.70 Hz), 123.06 (s), 123.15 (s), 135.97 (s).

Preparation of* 3p: *1-(2-trimethylsiloxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl) amide MIM12-OTMS-TFSI



a) 1-(2-hydroxyethyl)-2,3-dimethylimidazolium chloride

In a 250 ml round bottom flask equipped with a magnetic stirrer were placed 48.07 g (0.5 mol) of 1,2-dimethylimidazole dissolved in 80 ml of toluene. To this solution, 40.26 g (0.5 mol) of

2-chloroethanol were added in one portion. The mixture was stirred over a weekend (57 h) at 70°C during which no sign of completed reaction were observed. The mixture was heated to reflux for 24 h during which phase separation occurred. The mixture was cooled to room temperature and the lower yellow oily layer solidified. The toluene was decanted and the solid was then crushed, washed with fresh toluene and filtered. Product was dried to obtain 87.25 g (98 %) of the title 1-(2-hydroxyethyl)-2,3-dimethylimidazolium chloride.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 2.63 (s, 3 H), 3.64 (q, *J*=5.13 Hz, 2 H), 3.79 (s, 3 H), 4.23 (t, *J*=4.94 Hz, 2 H), 5.59 (t, *J*=5.68 Hz, 1 H), 7.69 - 7.79 (m, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 9.78 (s), 34.72 (s), 50.22 (s), 59.60 (s), 121.23 (s), 122.13 (s), 144.86 (s).

b) 1-(2-hydroxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide

In a 250 ml round bottom flask, a solution of 20 g (0.113 mol) of *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium chloride in 130 ml MQ water and 36 g (0.125 mol) of solid LiTFSI were mixed under vigorous stirring. Phase separation occurred at once, but the stirring was continued overnight (16 hours) at room temperature. Then, 80 ml of CH_2Cl_2 were added and the phases separated. The organic phase was washed 4 times with 50 ml of MQ water. A clear solution was obtained and poured into a round bottom flask. The solvent was removed first using a rotary evaporator and then under high vacuum at 65°C. In this manner, 23.2 g (49 %) of 1-(2-hydroxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 2.59 (s, 3 H), 3.64 - 3.74 (m, 2 H), 3.76 (s, 3 H), 4.18 (t, *J*=4.70 Hz, 2 H), 5.11 (br. s, 1 H), 7.59 (s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 9.48 (s), 34.71 (s), 50.38 (s), 59.76 (s), 119.63 (q, *J*=321.70 Hz), 121.36 (s), 122.26 (s), 144.95 (s).

c) 1-(2-trimethylsiloxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide

To a 50 ml round bottom flask, 8.42 g (0.02 mol) of neat 1-(2-hydroxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide and 3.42 g (0.02 mol) of hexamethyldisilazane (HMDS) were added at room temperature, as gentle stream of nitrogen was passed through the apparatus to facilitate the removal of forming ammonia. The mixture was slowly heated to 60–70°C and stirred so that a fine emulsion of HMDS in IL formed. A vigorous evolution of gaseous ammonia started as the temperature reached to 80°C and ended after a few minutes. The mixture was stirred for 4 hours at 80°C and overnight at room temperature (16 hours after the end of the vigorous reaction). Then, the volatile compounds were removed *in vacuo*. The flask was refilled 6 times with argon and again evacuated. The product was heated to 70°C during this manipulation. Finally, the apparatus was

cooled down under vacuum and refilled with argon. In this manner, 9.8 g (100 %) of the title compound in form of a colourless liquid were obtained.

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ/ppm: 0.00 (s, 9 H), 2.55 (s, 3 H), 3.75 (s, 3 H), 3.82 (t, *J*=4.70 Hz, 2 H), 4.15 (t, *J*=4.70 Hz, 3 H), 7.18 (m, *J*=2.20 Hz, 1 H), 7.24 (m, *J*=1.80 Hz, 1 H)

^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ/ppm: -0.61 (m), 9.56 (s), 35.01 (s), 50.67 (s), 60.70 (s), 119.58 (q, *J*=321.70 Hz), 121.22 (s), 122.13 (s), 144.50 (s).

^{19}F NMR (470 MHz, CHLOROFORM-*d*) δ/ppm: -79.19 (s)

2. Viscosity and conductivity measurements

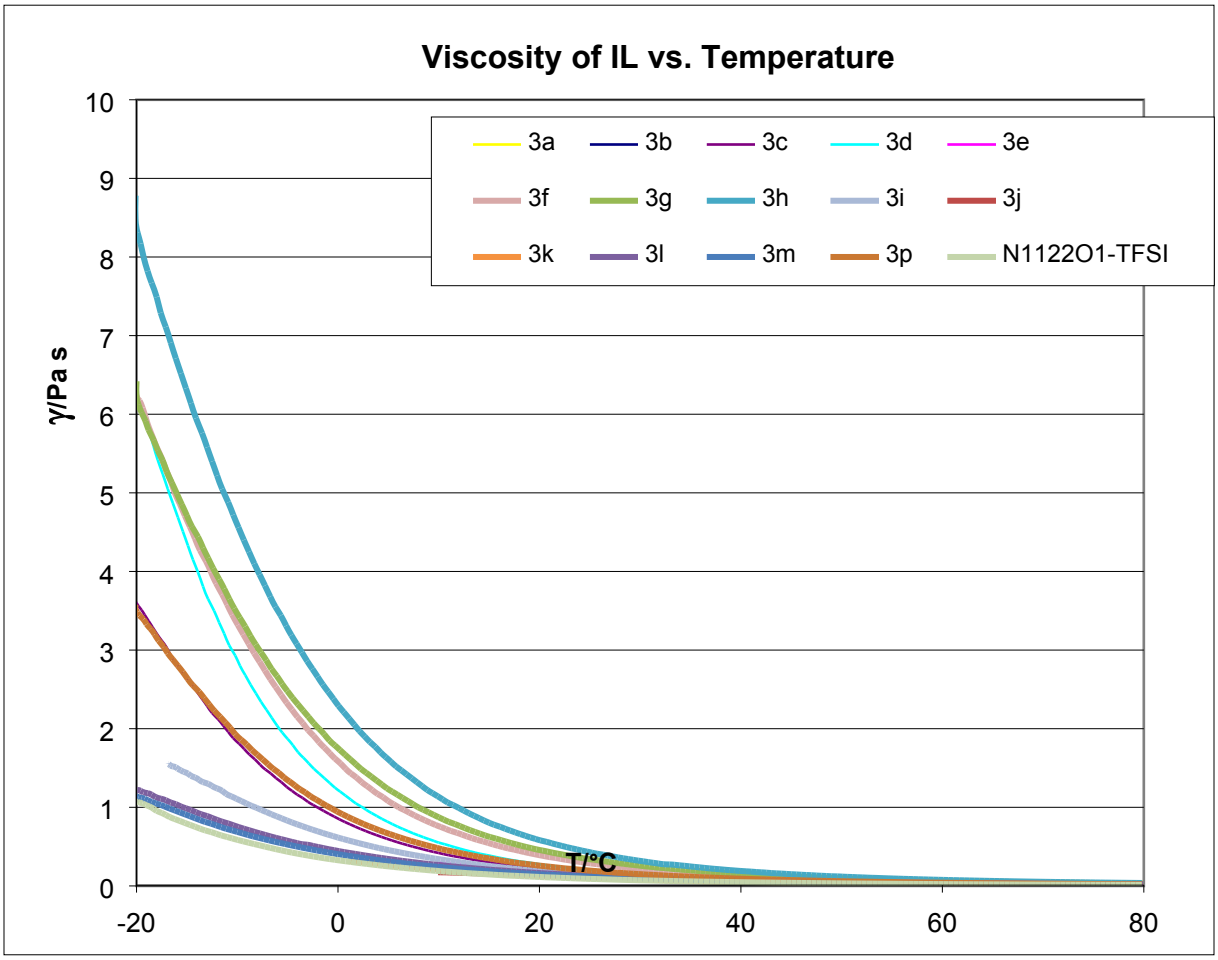


Figure 1. Dependance of viscosity of ionic liquids on temperature between -20 °C and 90 °C. (Viscosities of of some ILs were measured only above other selected temperatures due to solidification of the ILs at lower temperatures.)

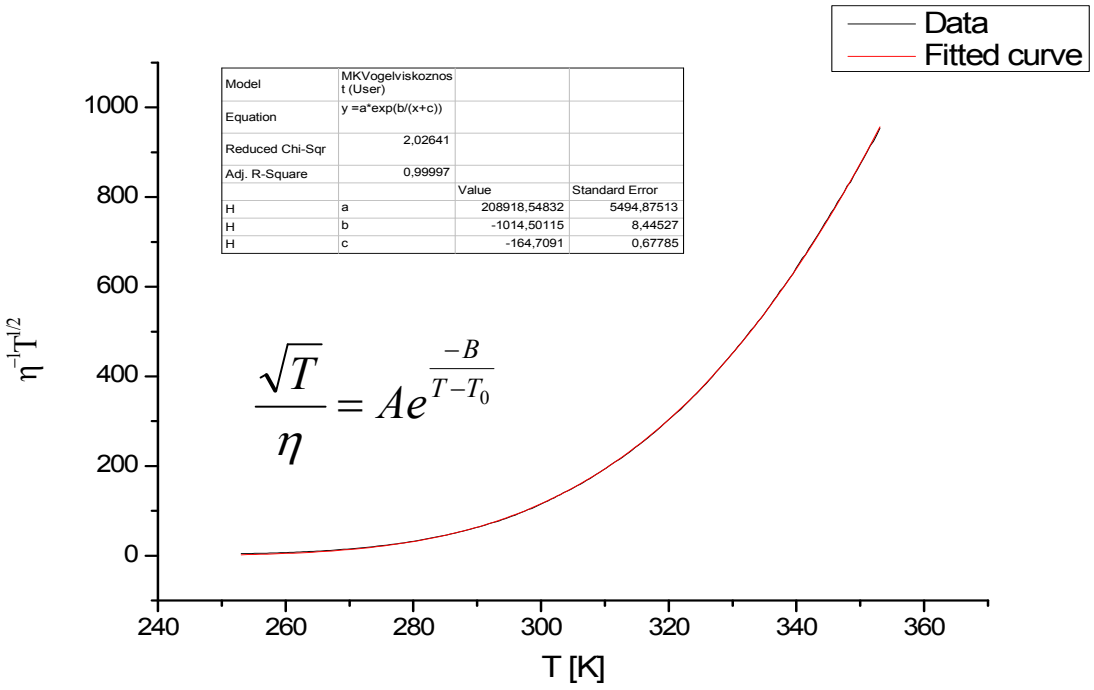


Figure 2. Fitting of viscosity dependence of 3c versus temperature using Vogel-Tammann-Fulcher (VTF) equation and ORIGIN 8.1 software. (parameters in VTF equation and fitting curve equation are in following connections: A = a, B = b, T_0 = c).

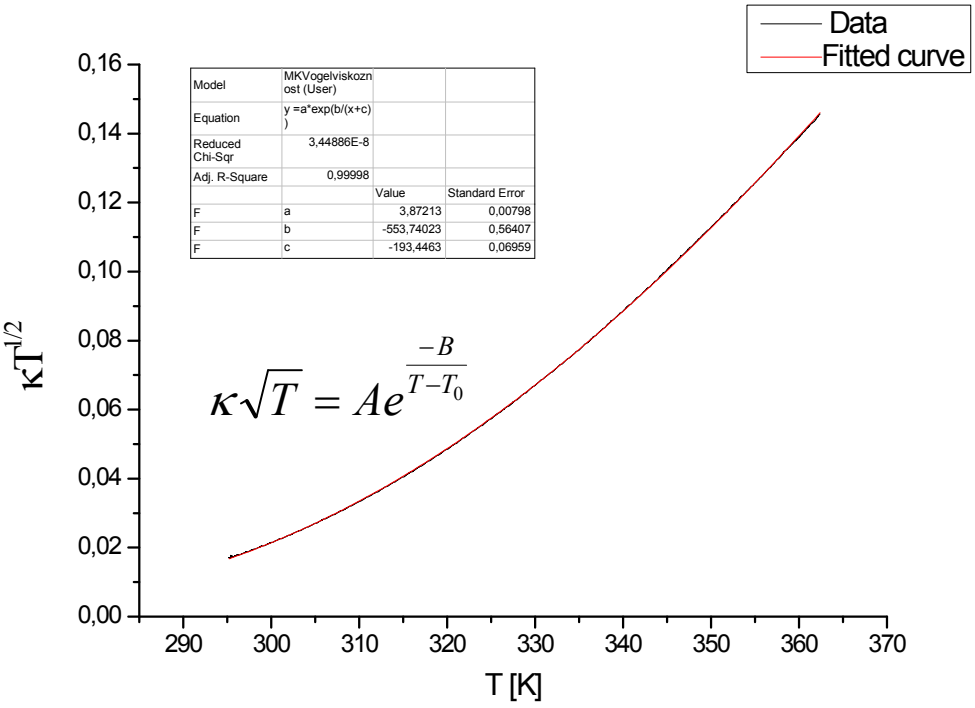


Figure 3. Fitting of conductivity dependence of 3c versus temperature using Vogel-Tammann-Fulcher (VTF) equation and ORIGIN 8.1 software. (parameters in VTF equation and fitting curve equation are in following connections: A = a, B = b, T_0 = c).

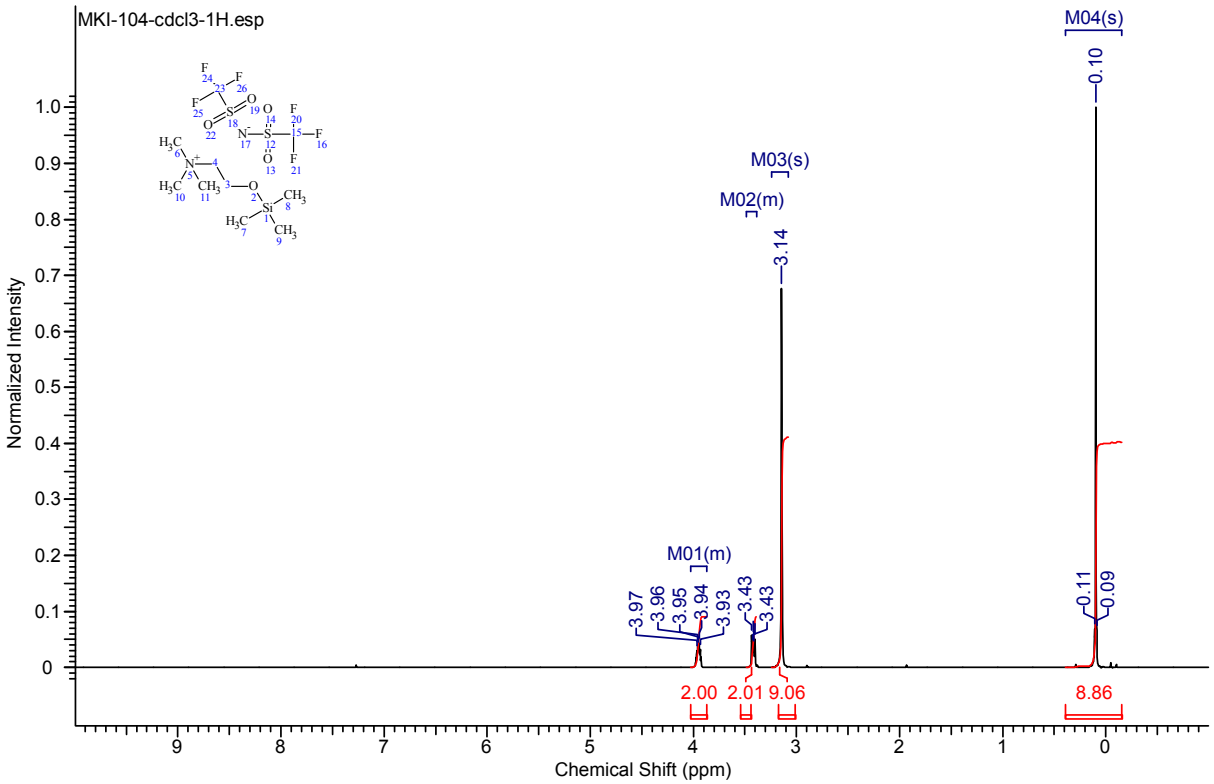


Figure 4. 1H-NMR spectrum of 3a.

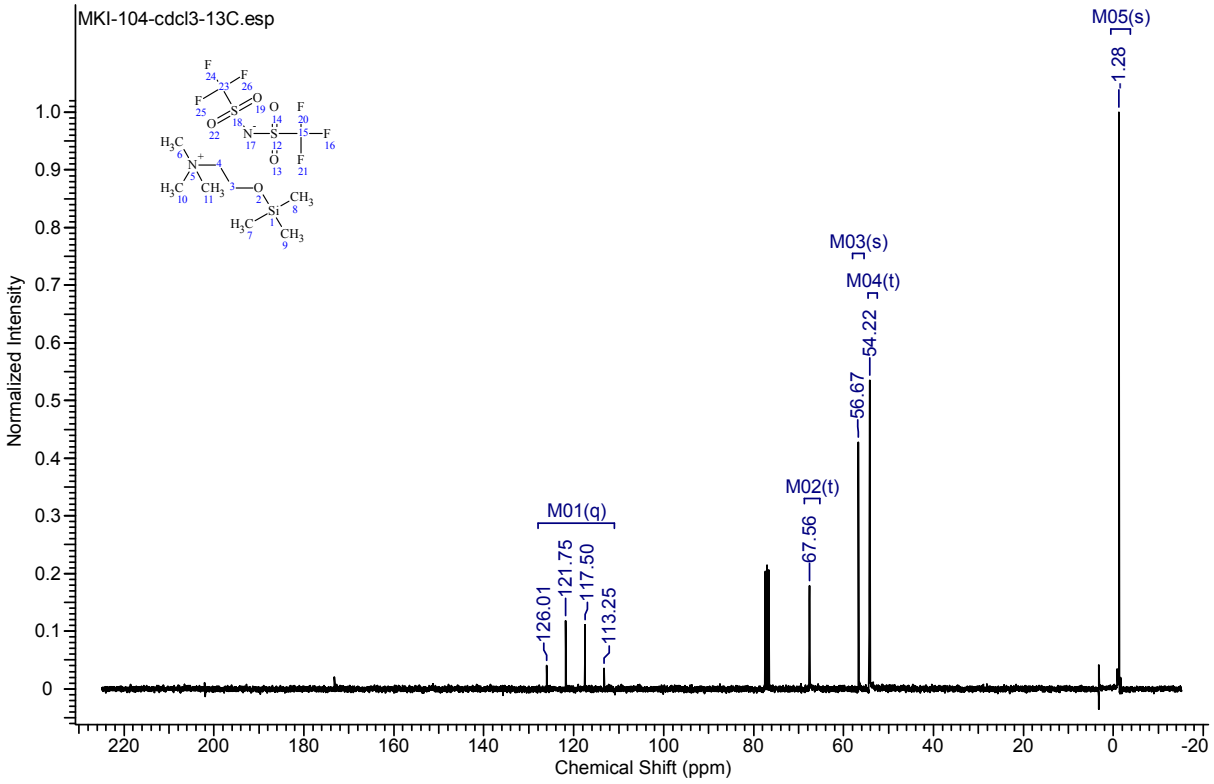


Figure 5. 13C-NMR spectrum of 3a.

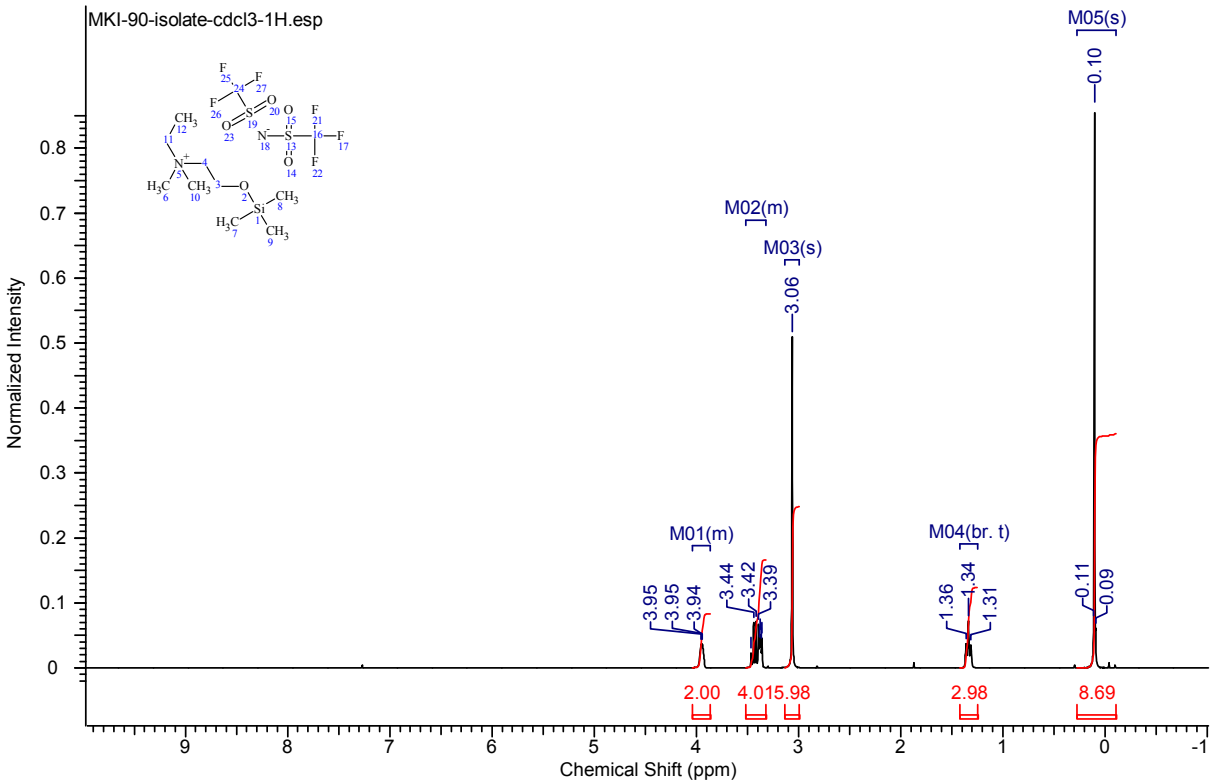


Figure 6. 1H-NMR spectrum of 3b.

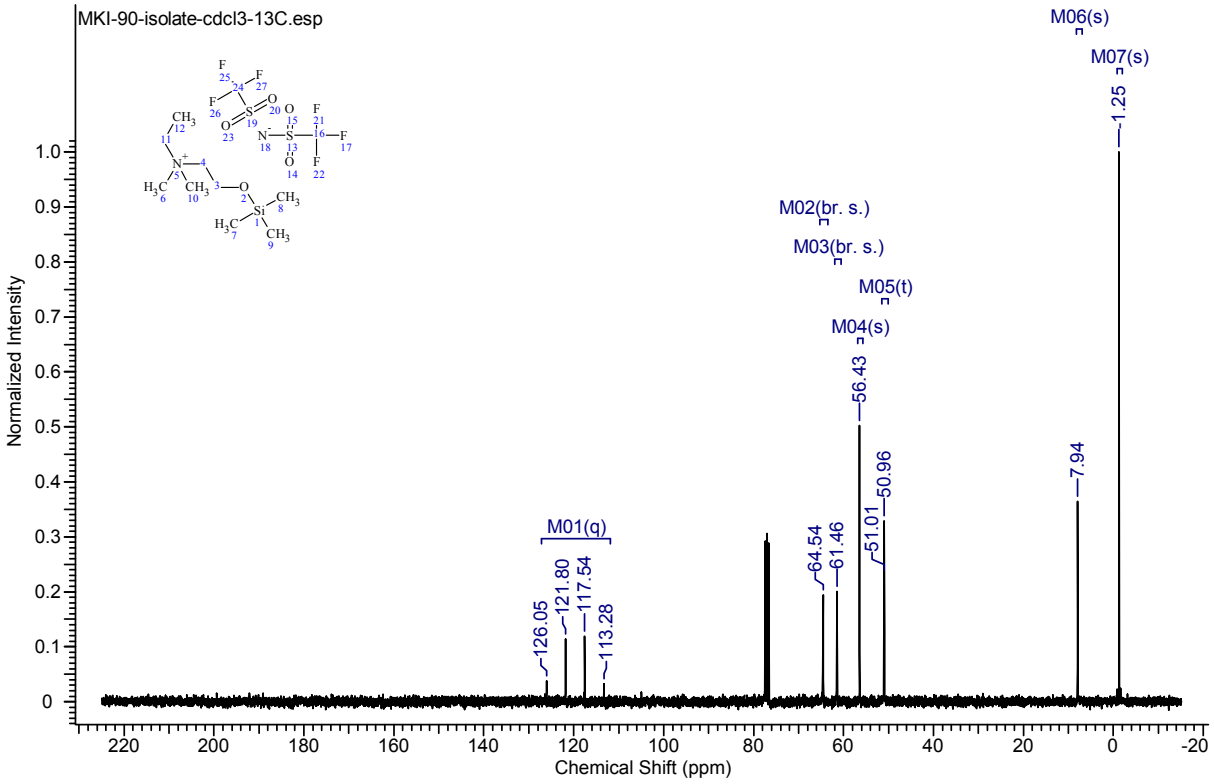


Figure 7. 13C-NMR spectrum of 3b.

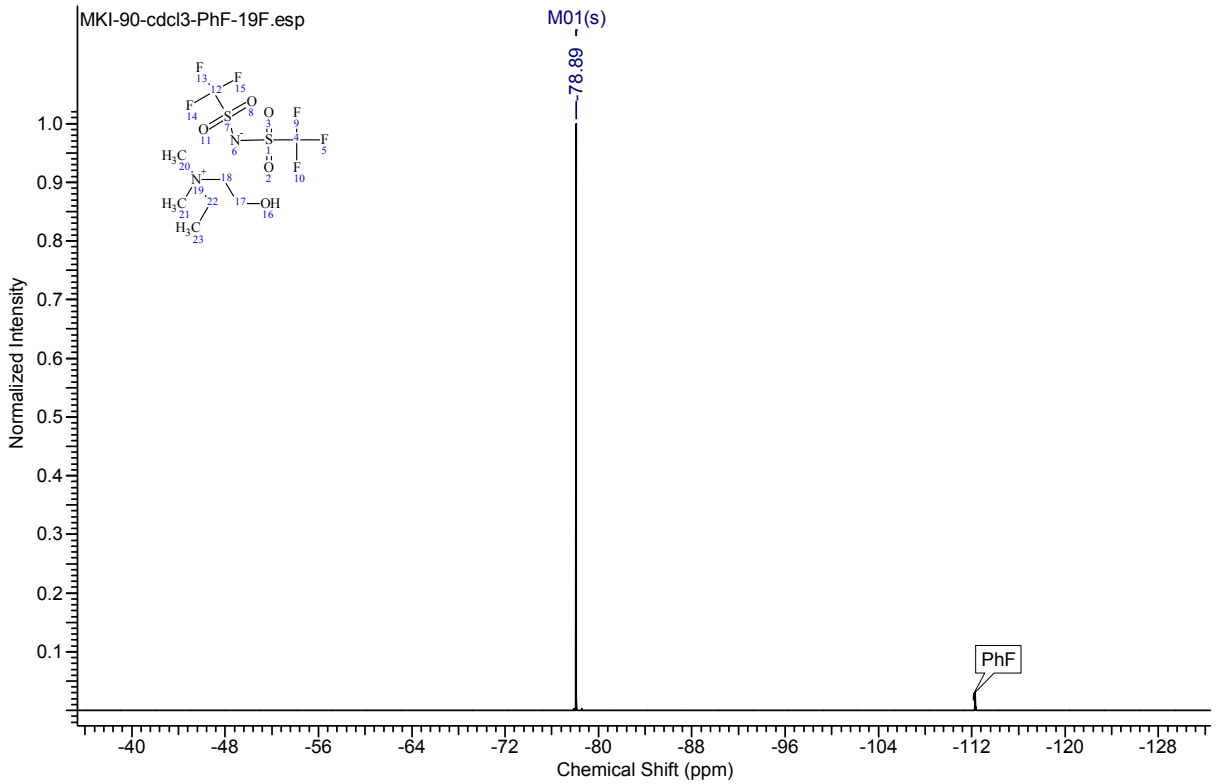


Figure 8. 19F-NMR spectrum of 3b.

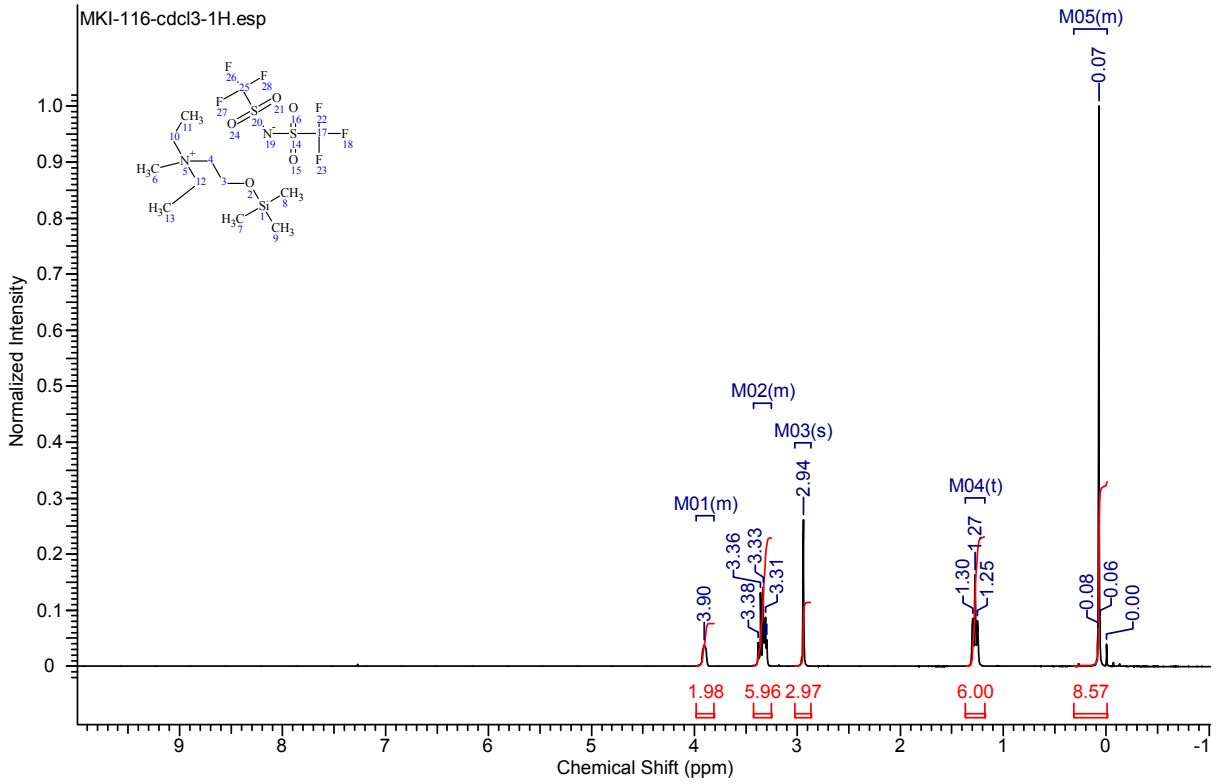


Figure 9. 1H-NMR spectrum of 3c.

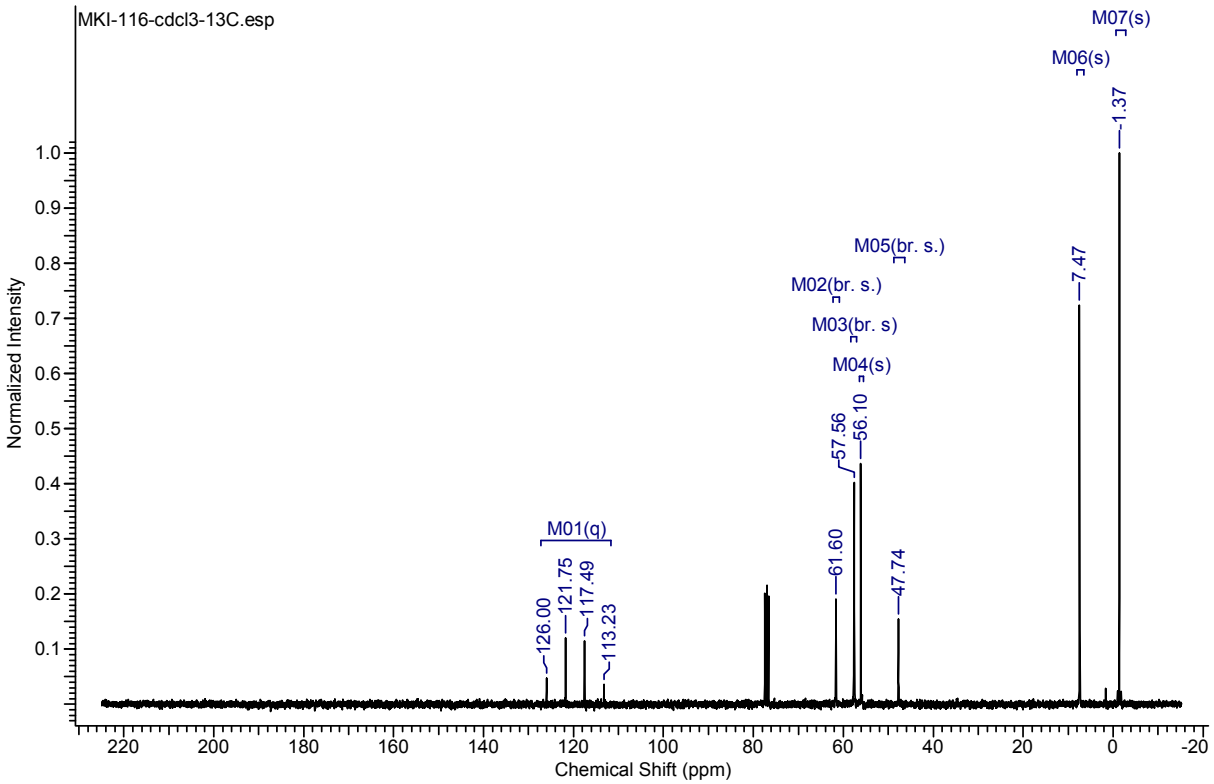


Figure 10. 13C-NMR spectrum of 3c.

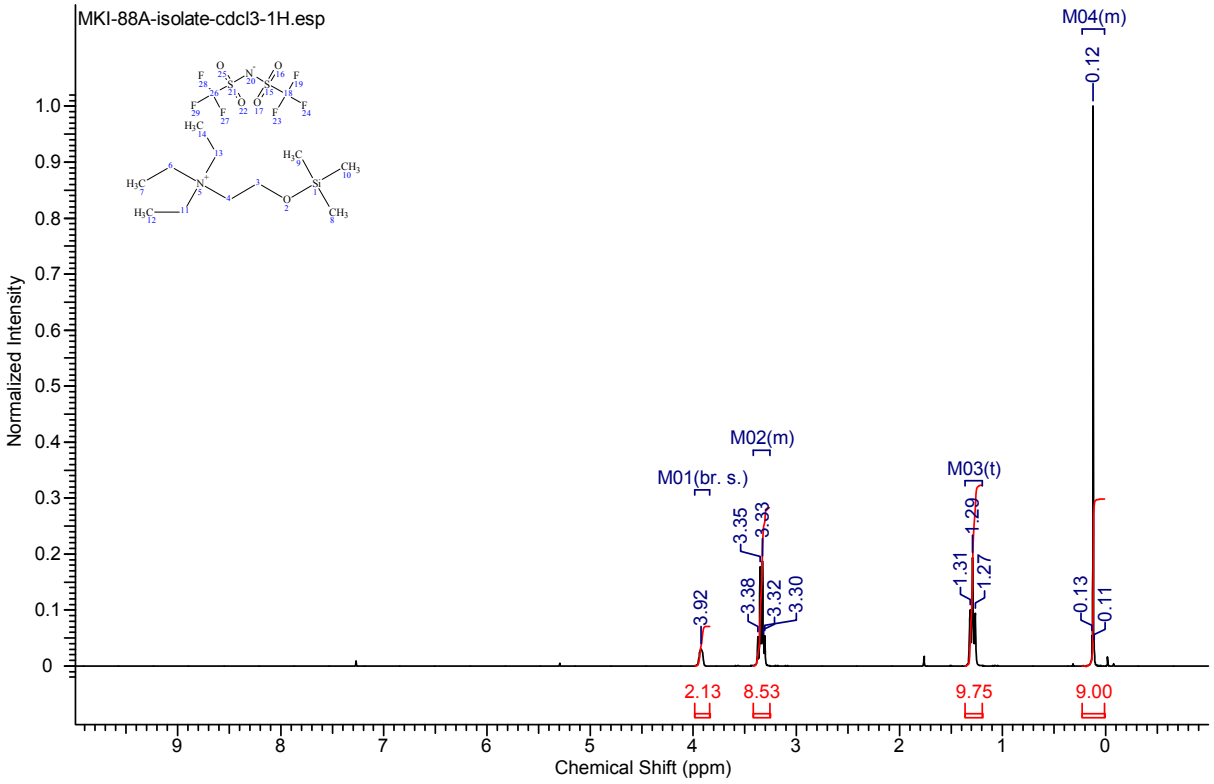


Figure 11. 1H-NMR spectrum of 3d.

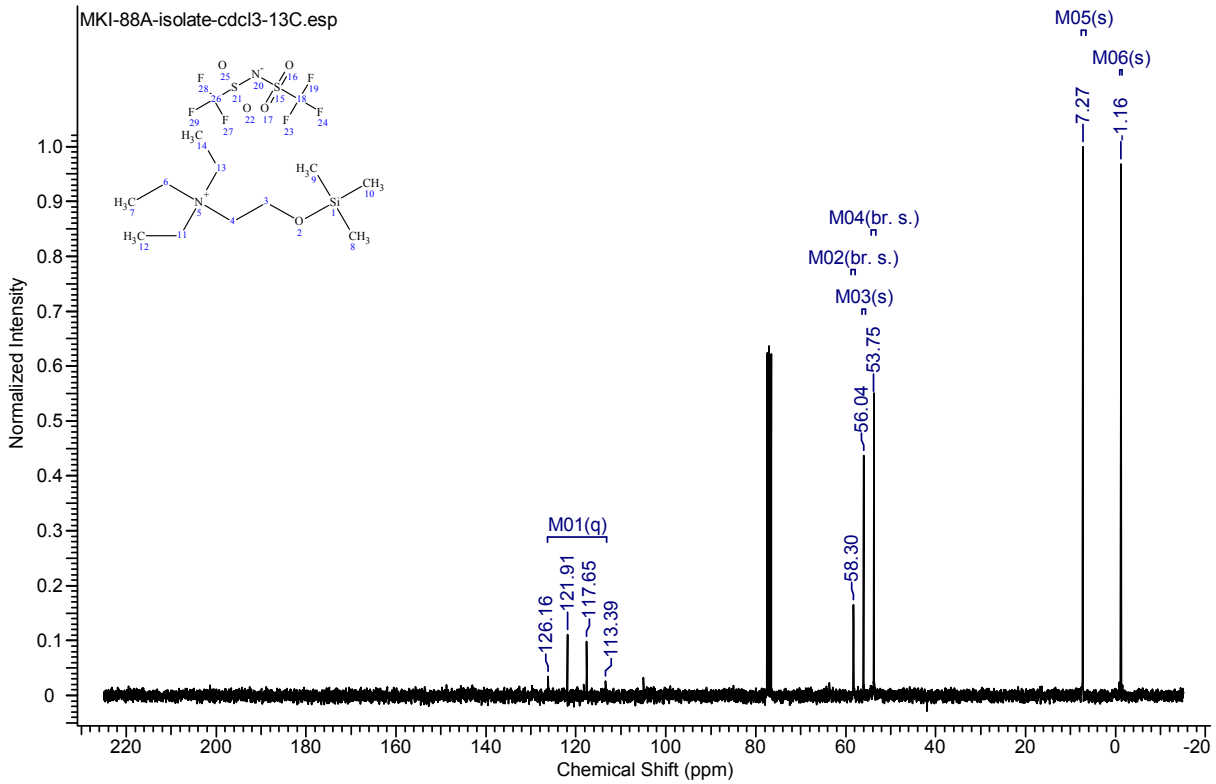


Figure 12. 13C-NMR spectrum of 3d.

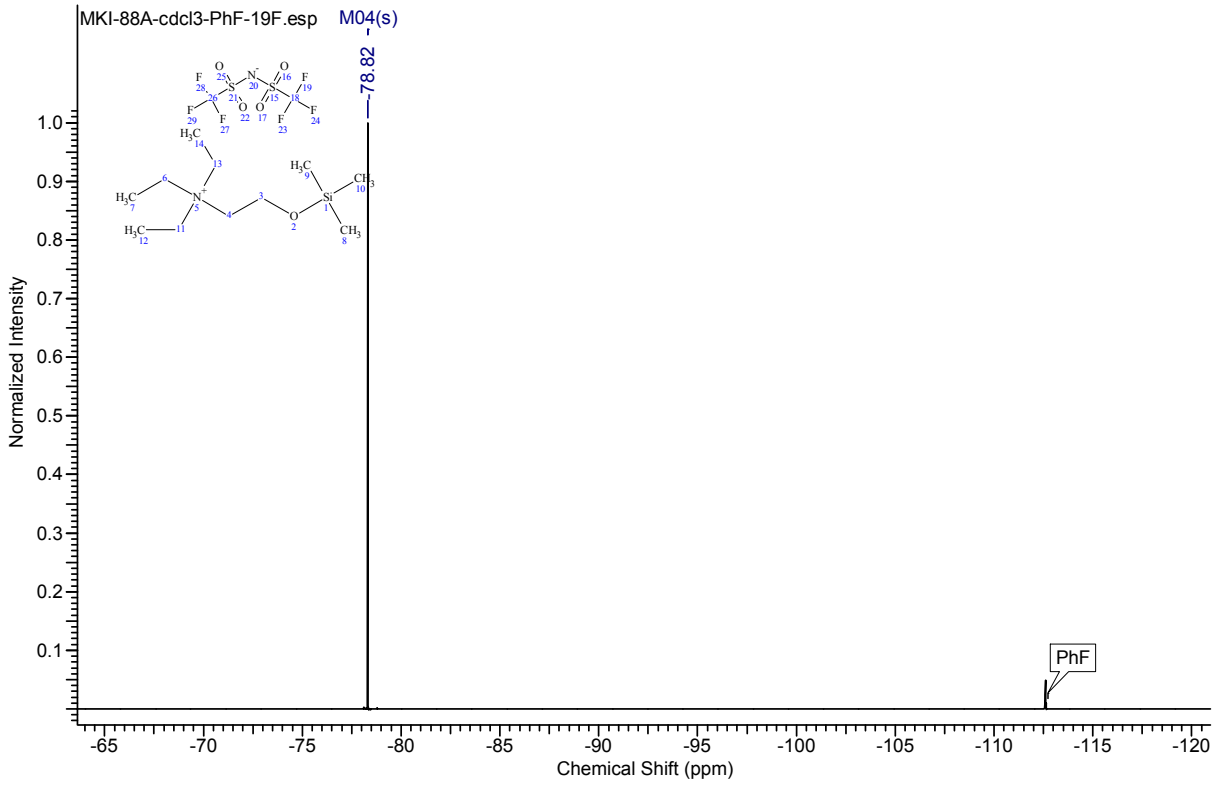


Figure 13. 19F-NMR spectrum of 3d.

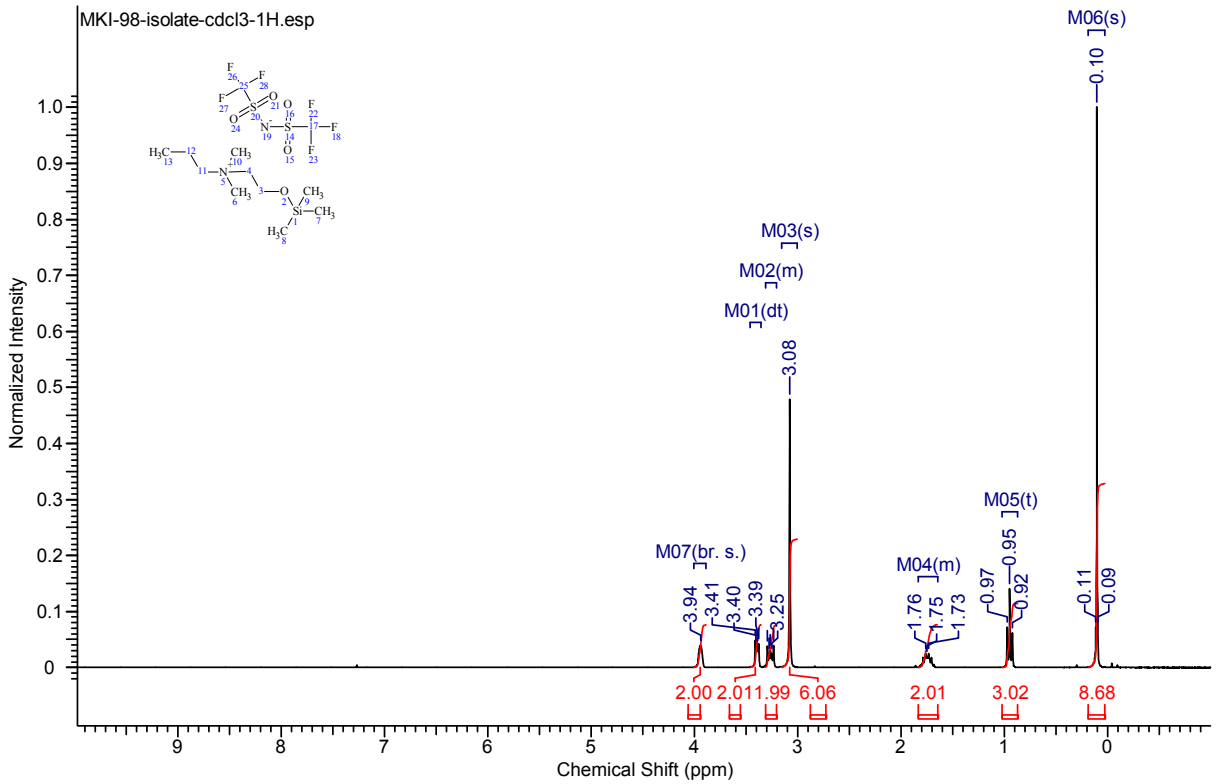


Figure 14. 1H-NMR spectrum of 3e.

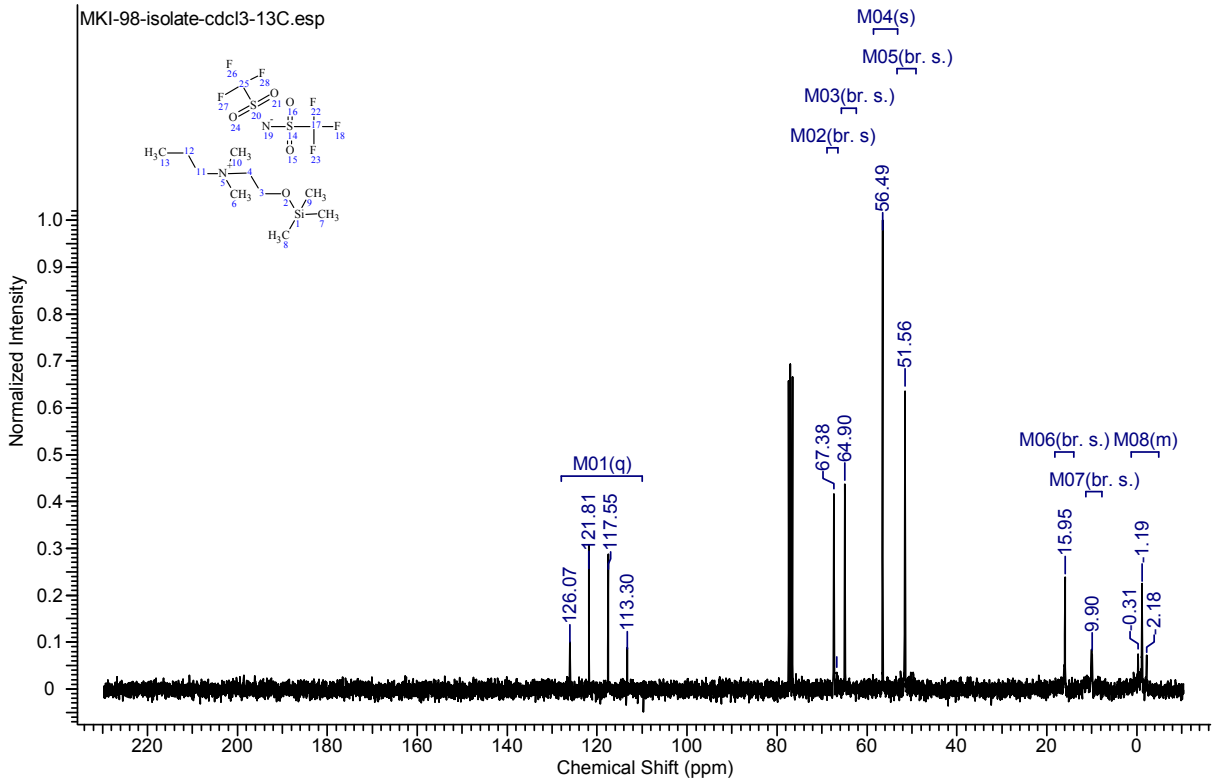


Figure 15. 13C-NMR spectrum of 3e.

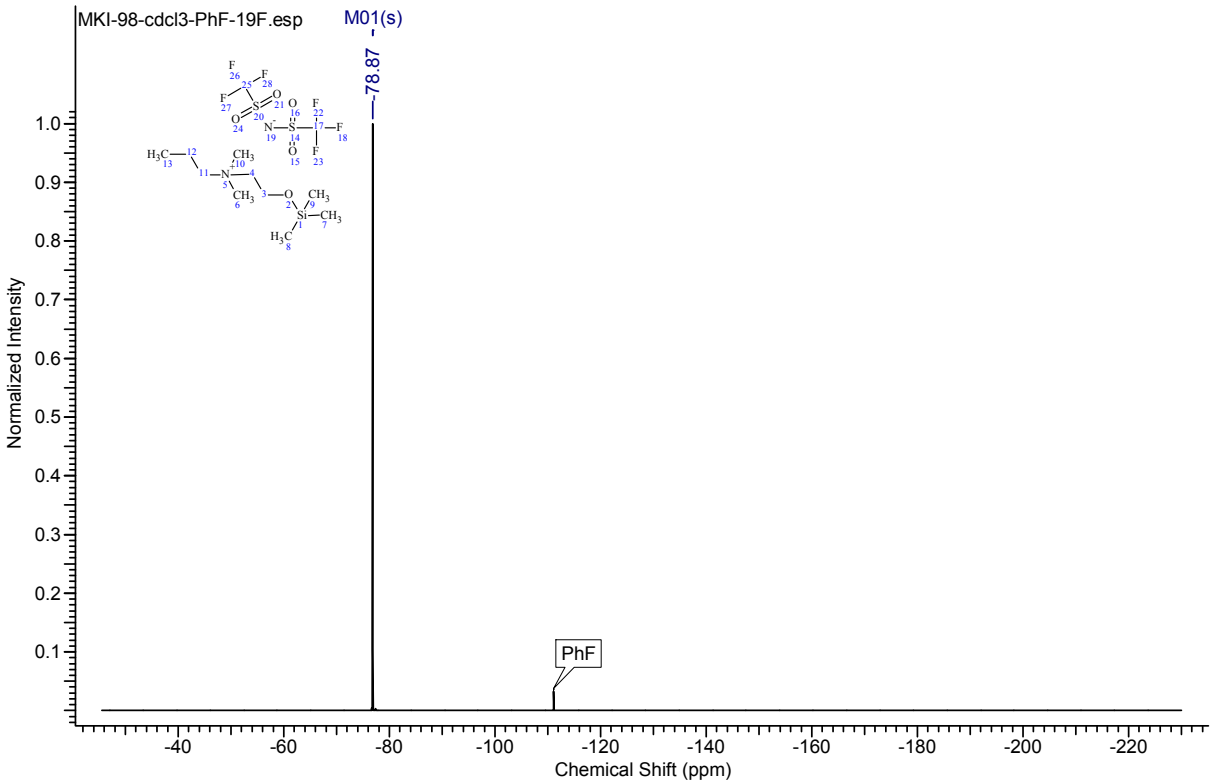


Figure 16. 19F-NMR spectrum of 3e.

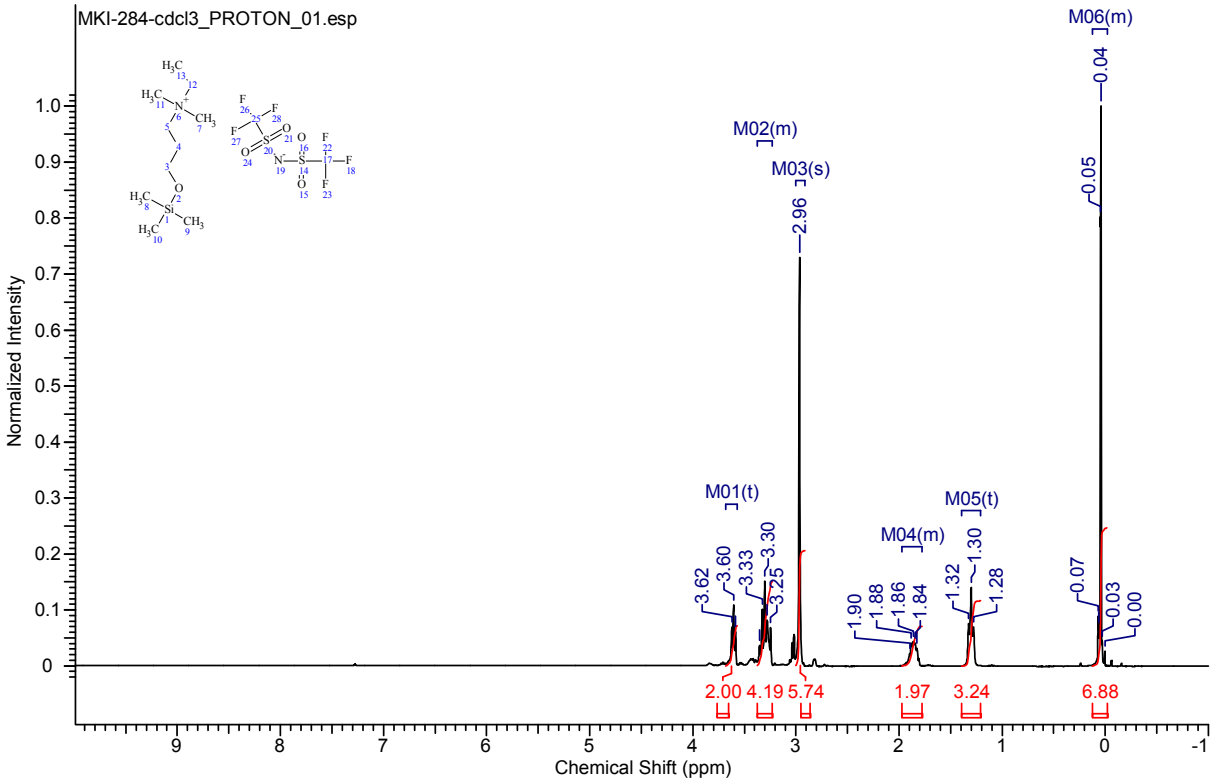


Figure 17. 1H-NMR spectrum of 3f.

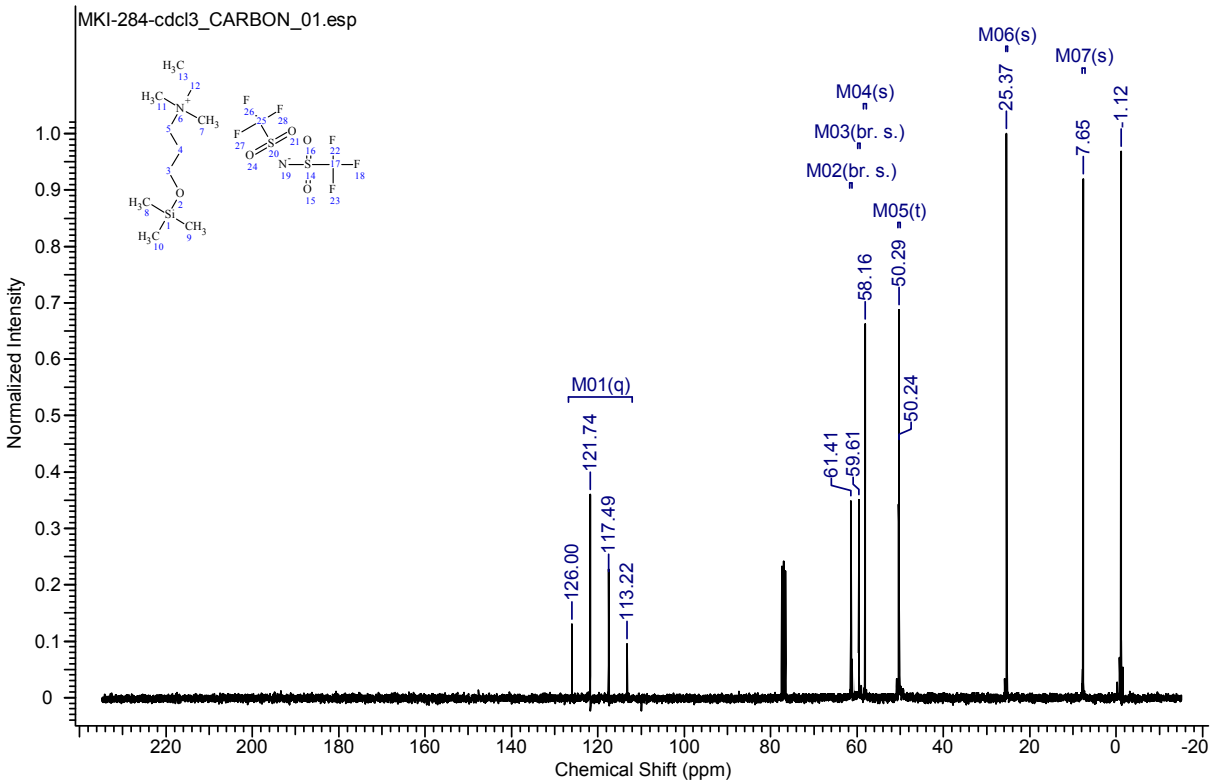


Figure 18. 13C-NMR spectrum of 3f.

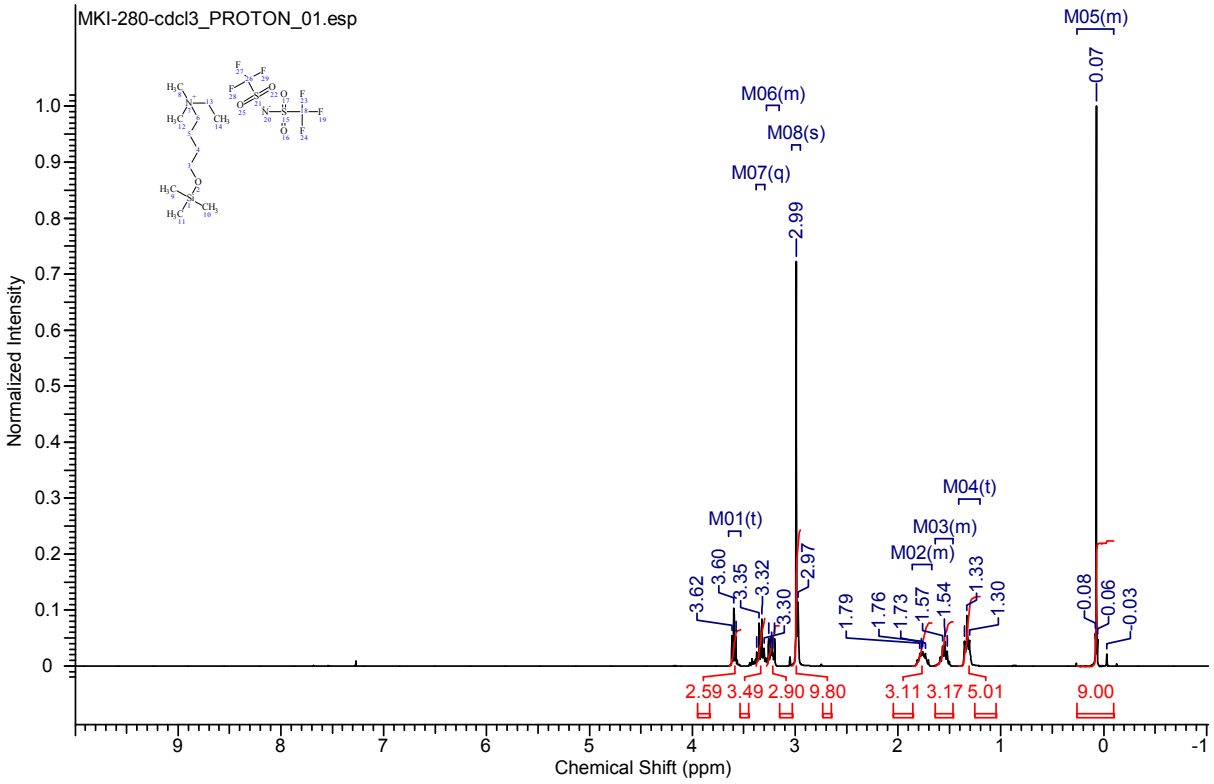


Figure 19. 1H-NMR spectrum of 3g.

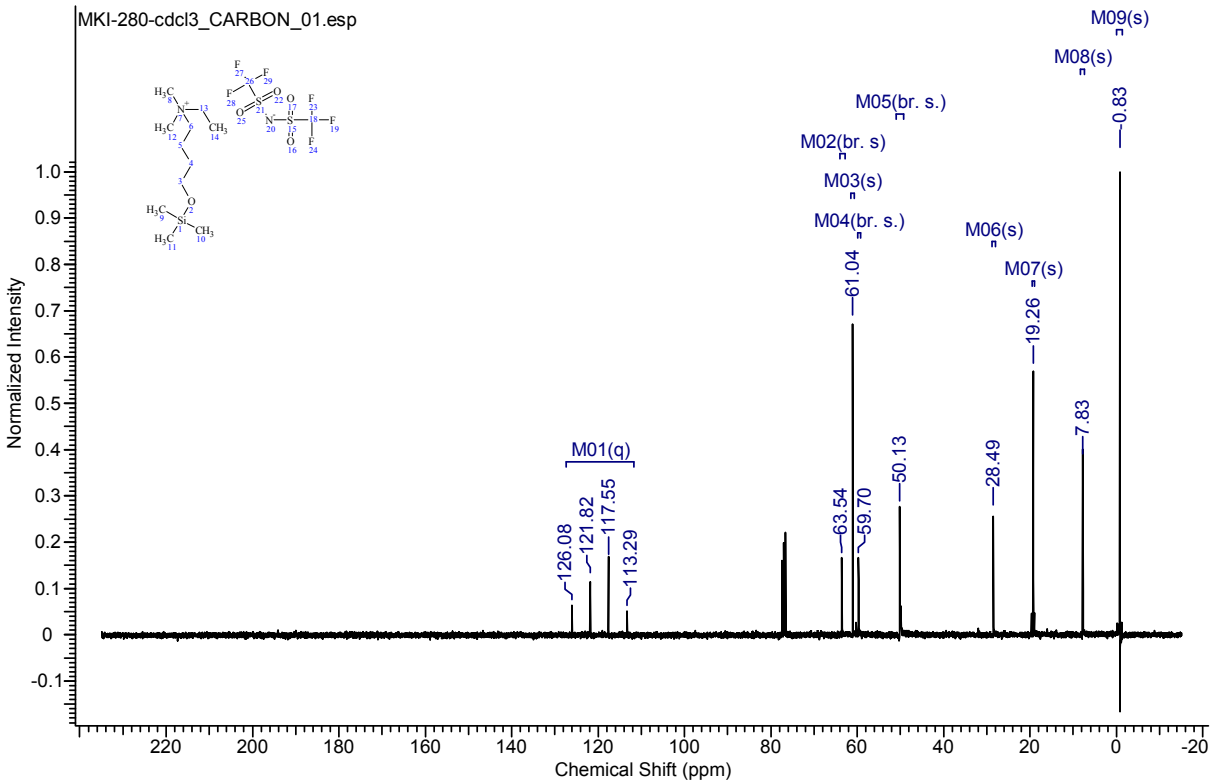


Figure 20. 13C-NMR spectrum of 3g.

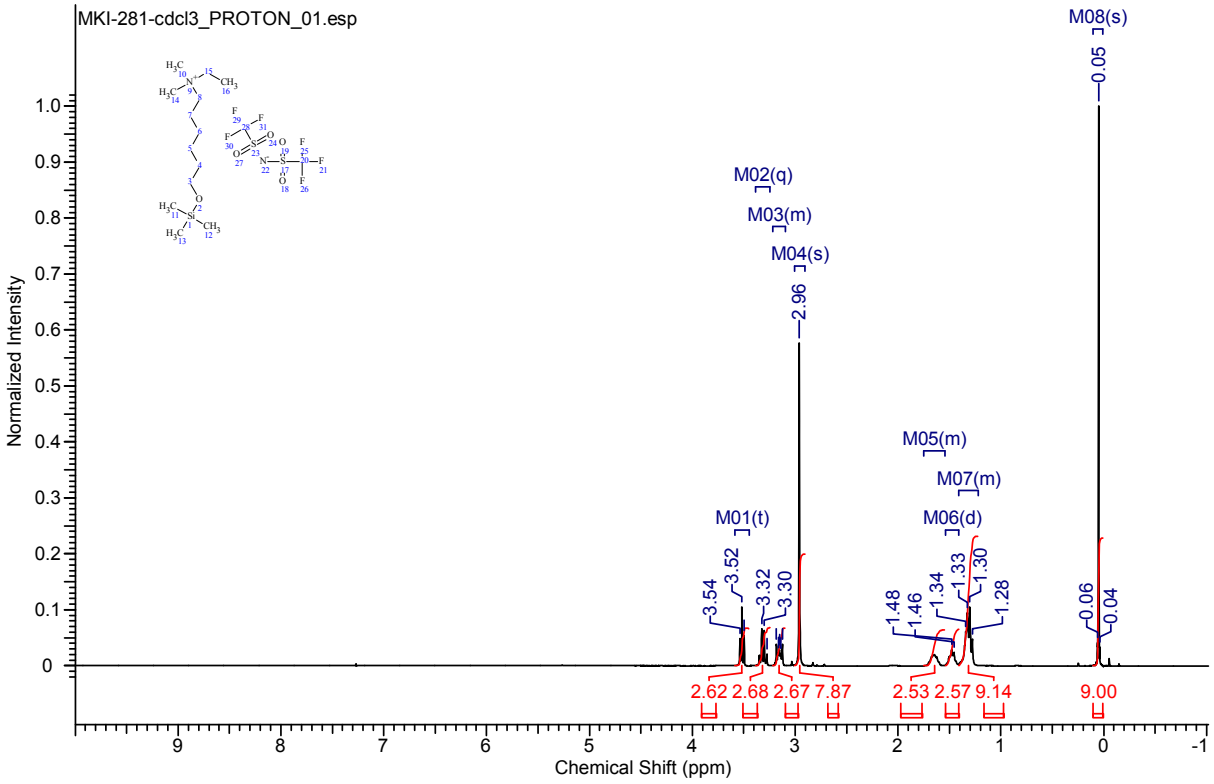


Figure 21. 1H-NMR spectrum of 3h.

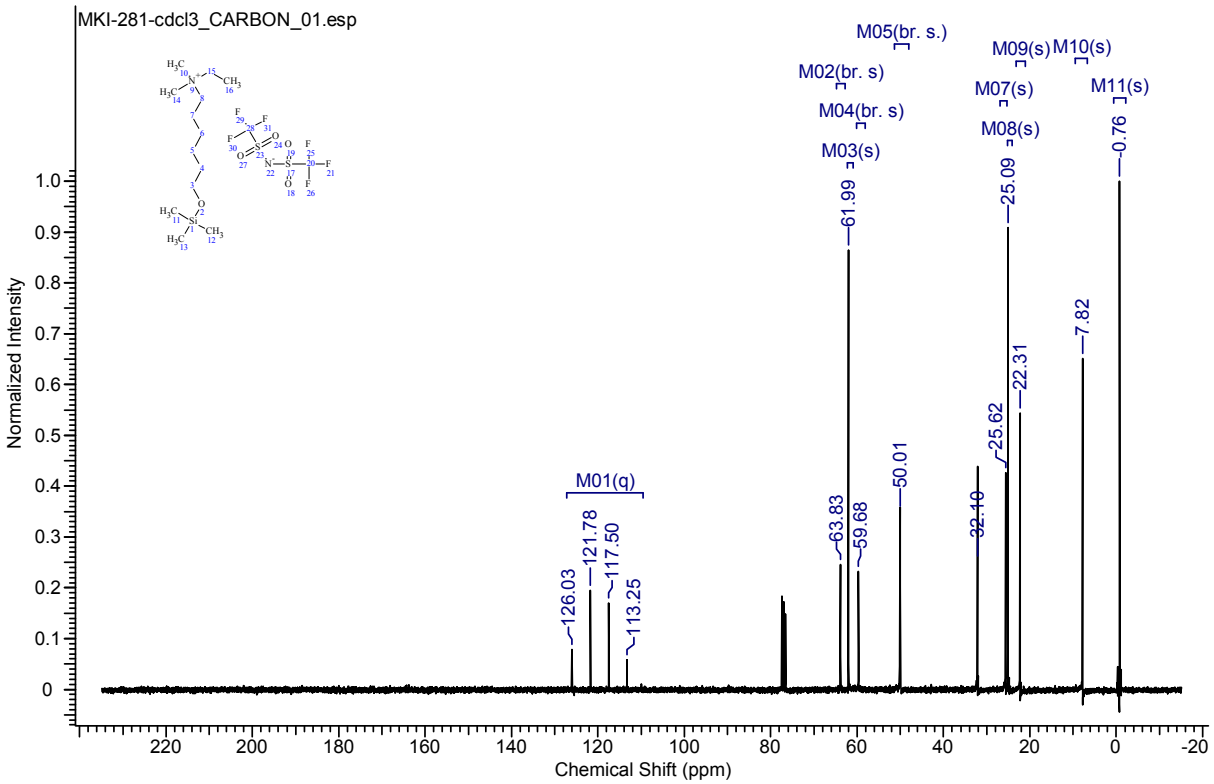


Figure 22. 13C-NMR spectrum of 3h.

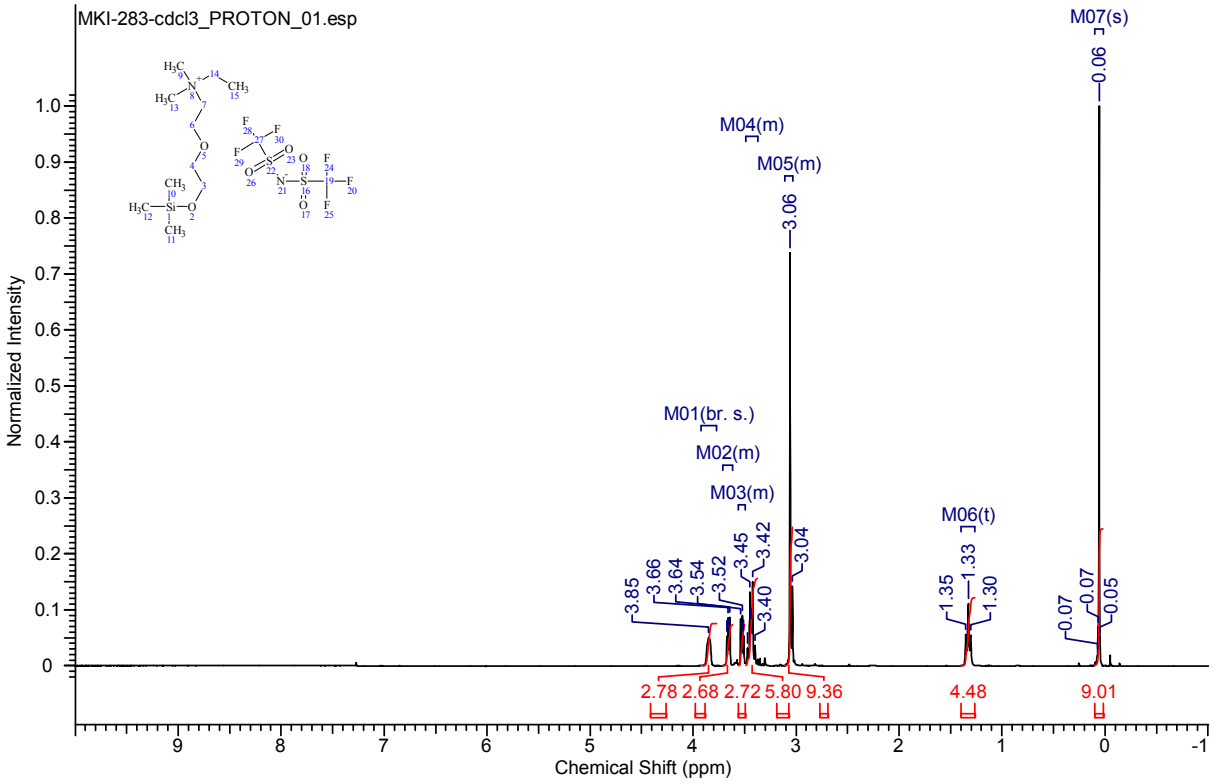


Figure 23. 1H-NMR spectrum of 3i.

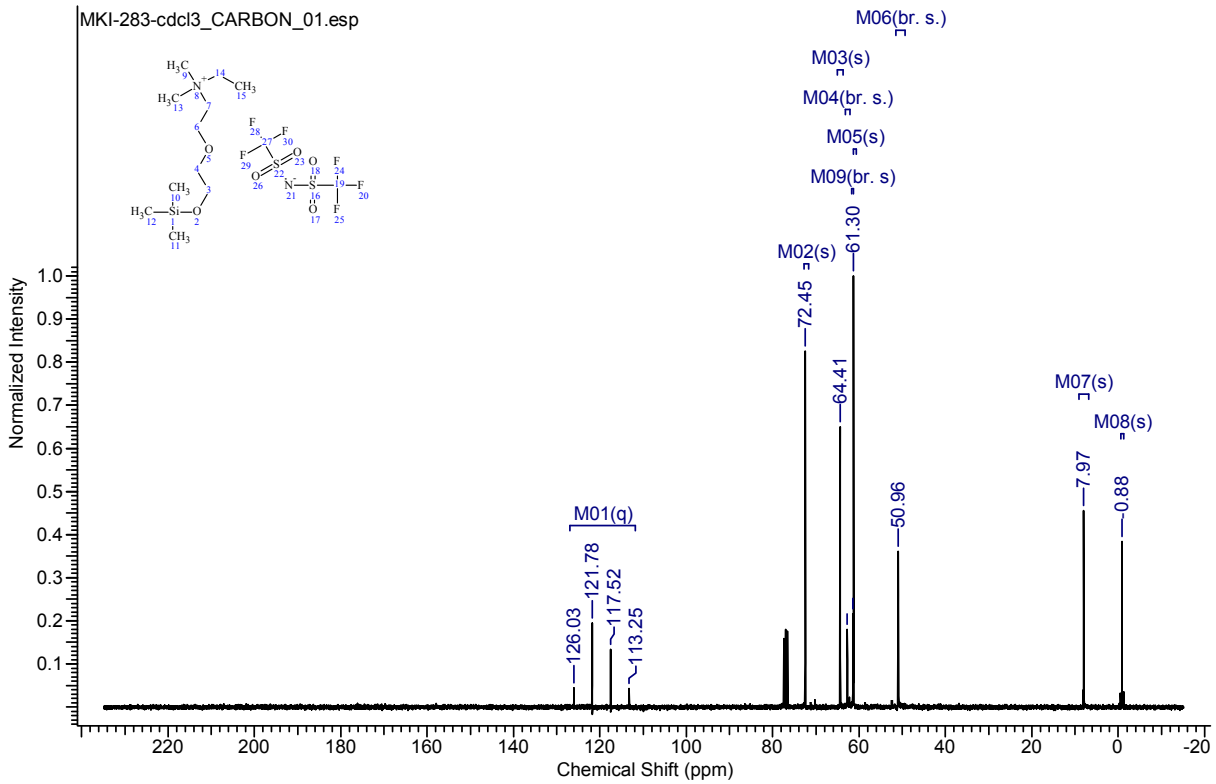


Figure 24. 13C-NMR spectrum of 3i.

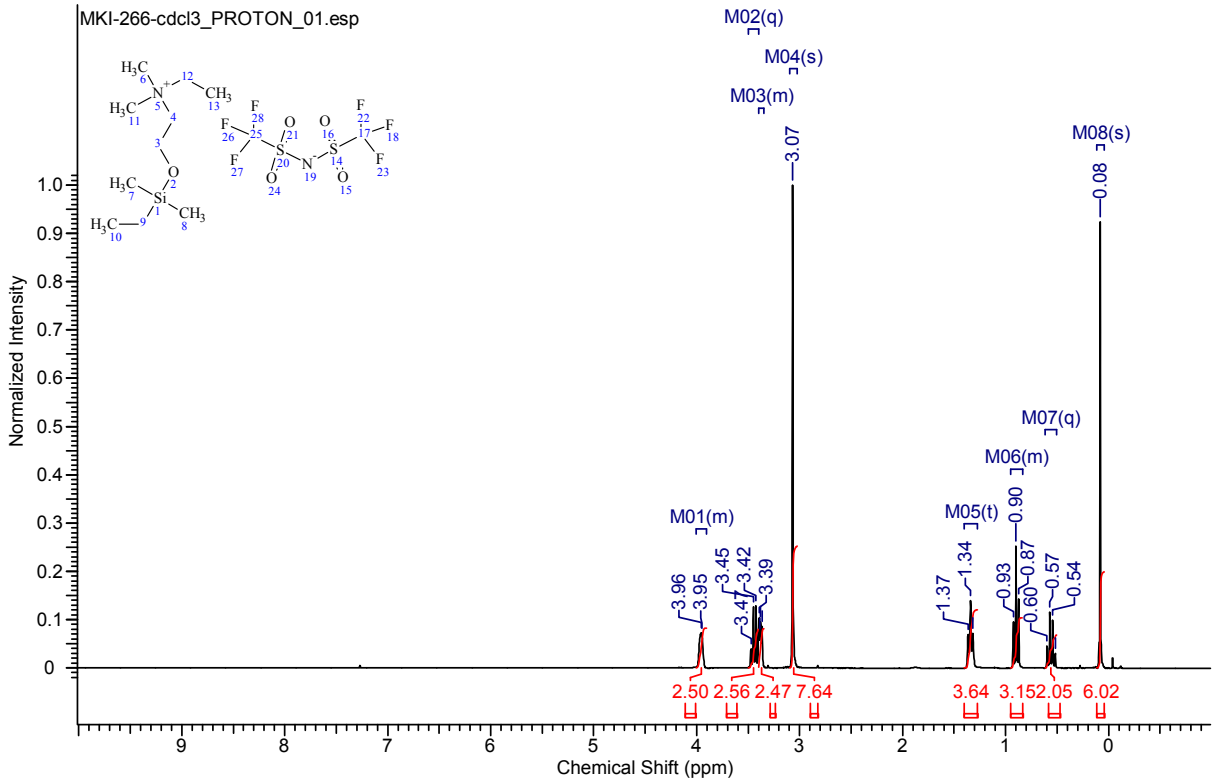


Figure 25. 1H-NMR spectrum of 3j.

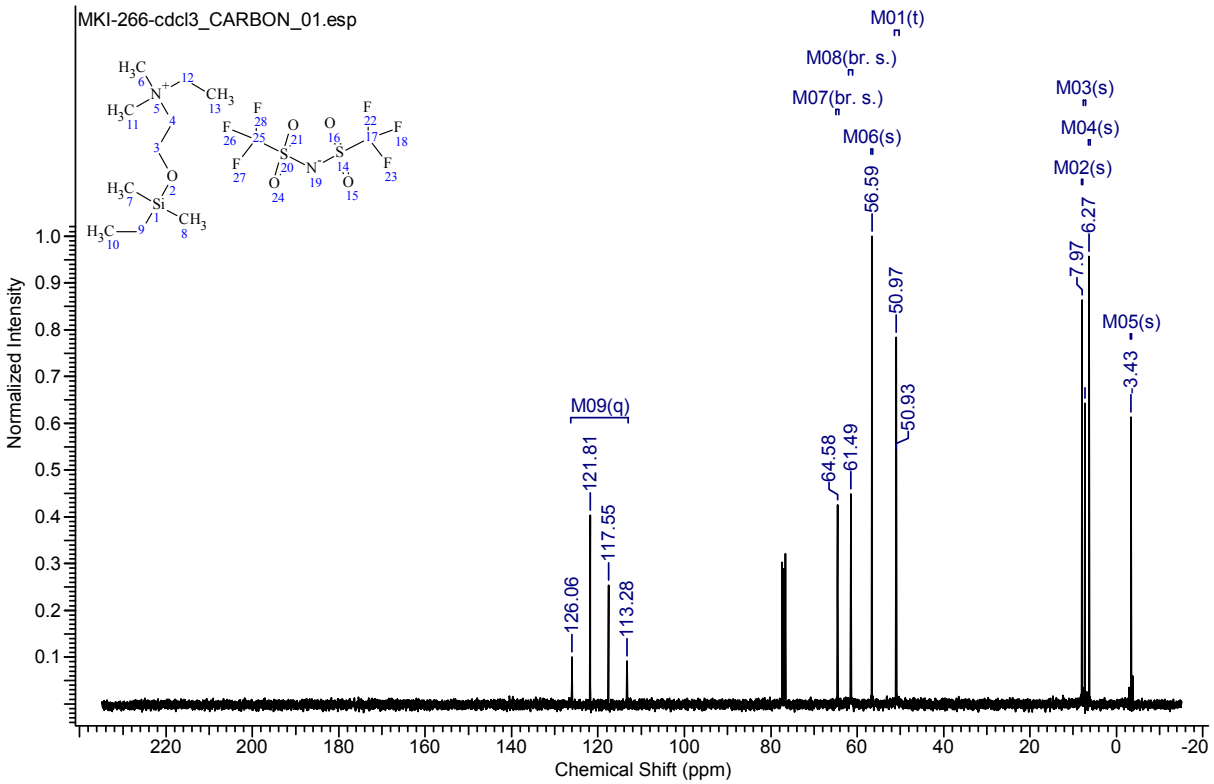


Figure 26. 13C-NMR spectrum of 3j.

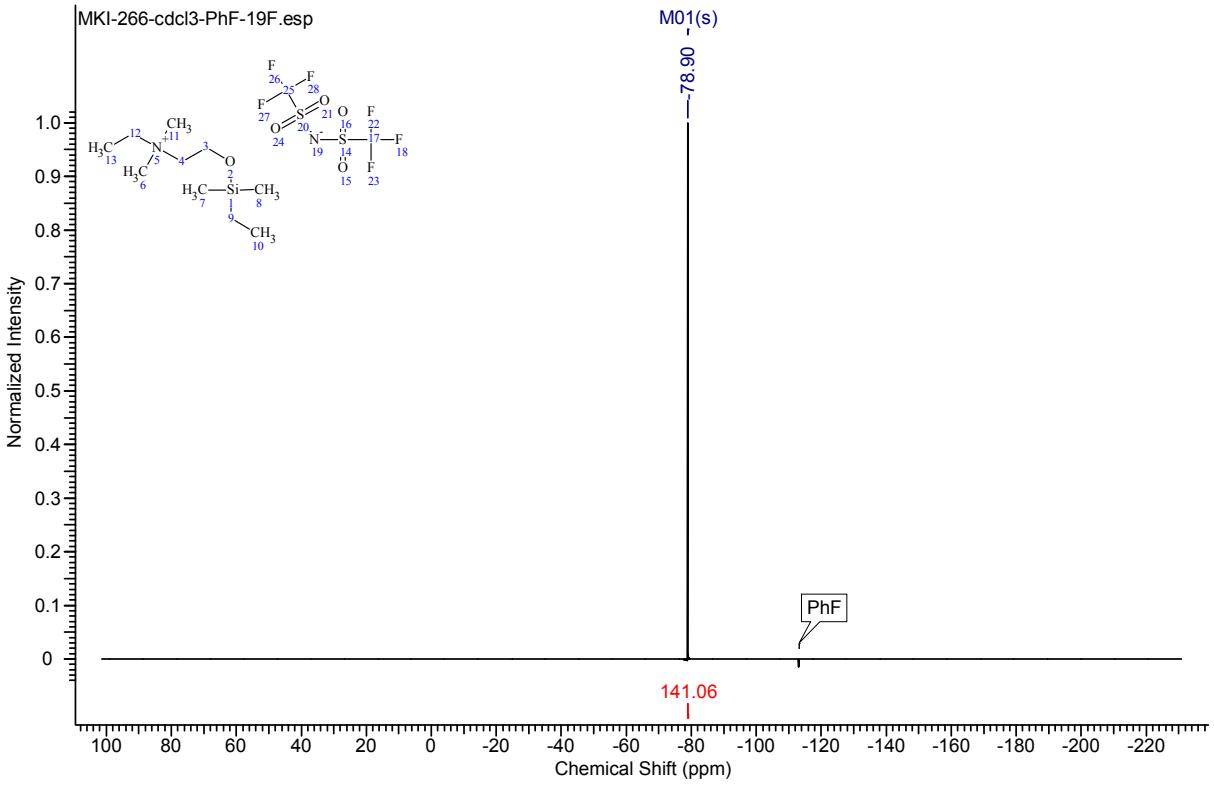


Figure 27. 19F-NMR spectrum of 3j.

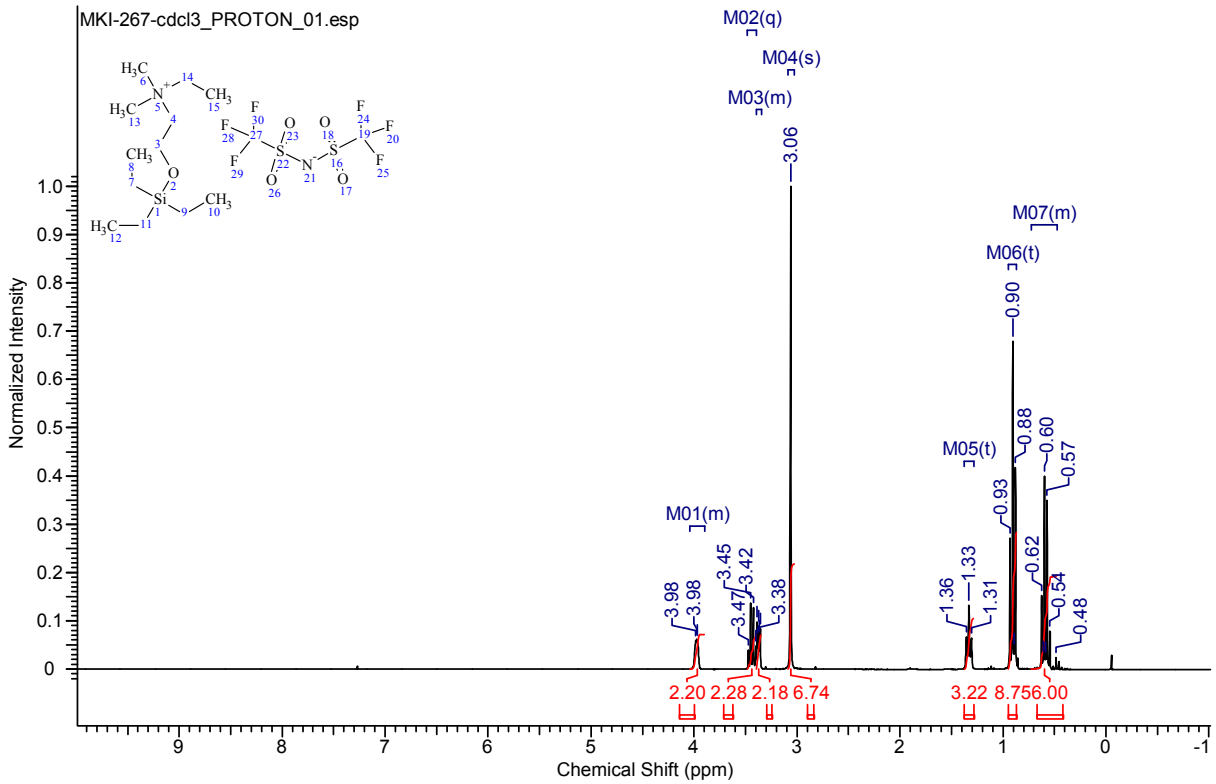


Figure 28. 1H-NMR spectrum of 3k.

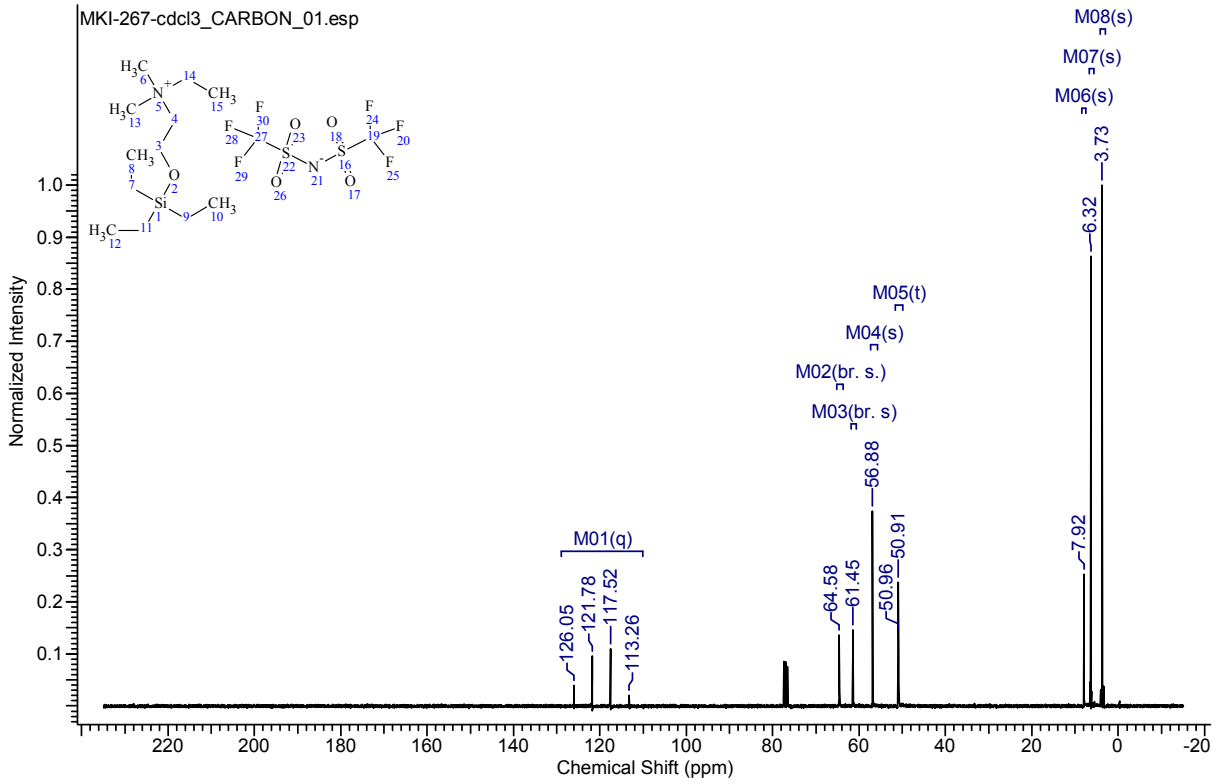


Figure 29. 13C-NMR spectrum of 3k.

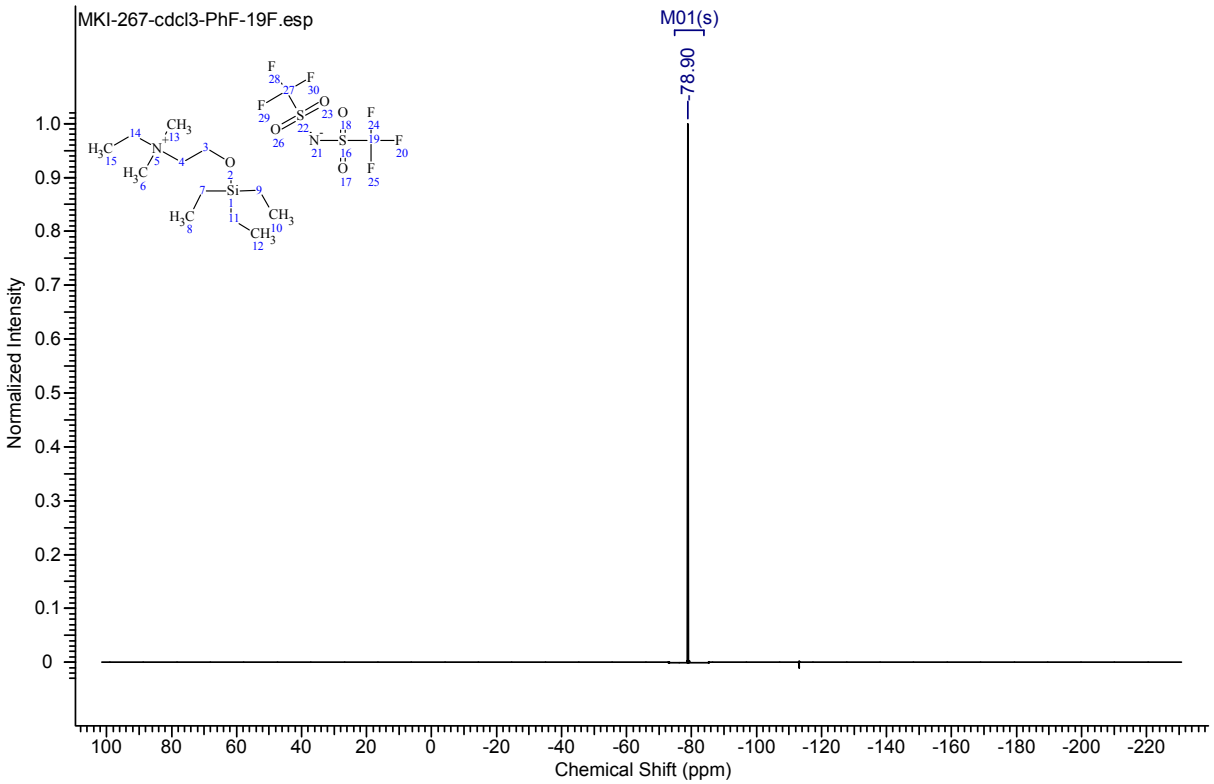


Figure 30. 19F-NMR spectrum of 3k.

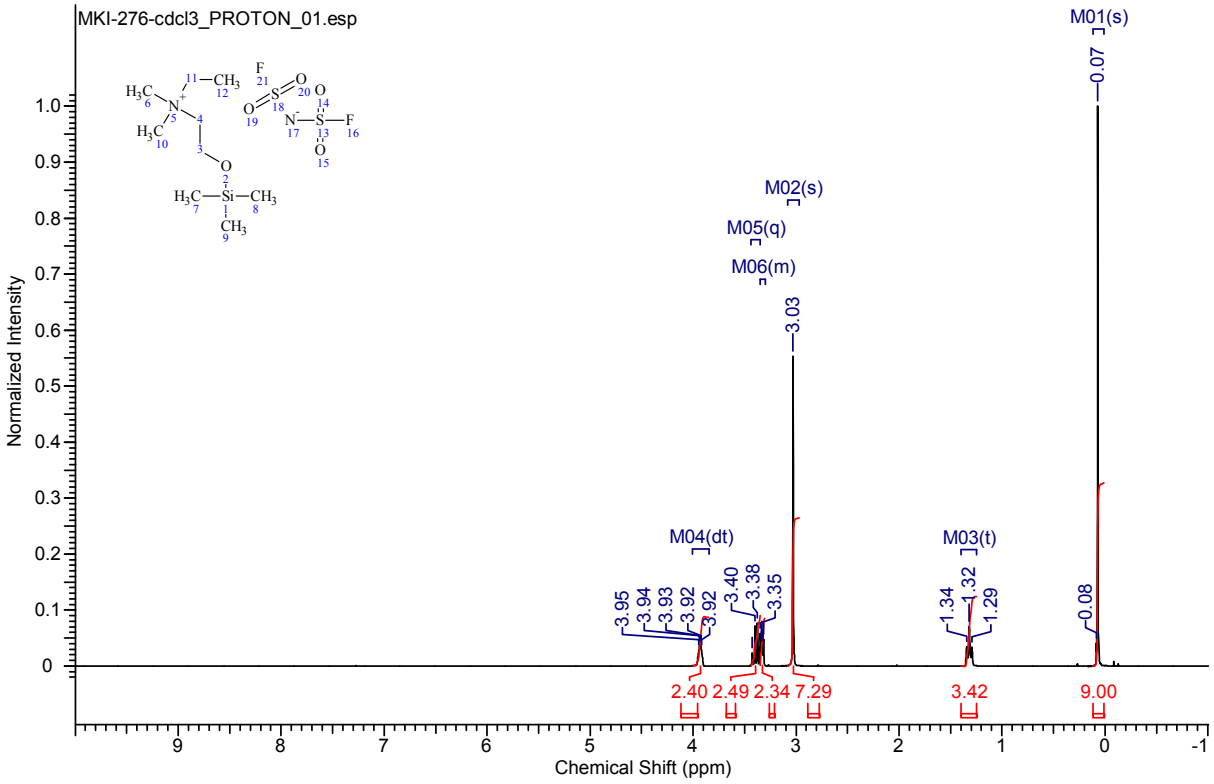


Figure 31. 1H-NMR spectrum of 3l.

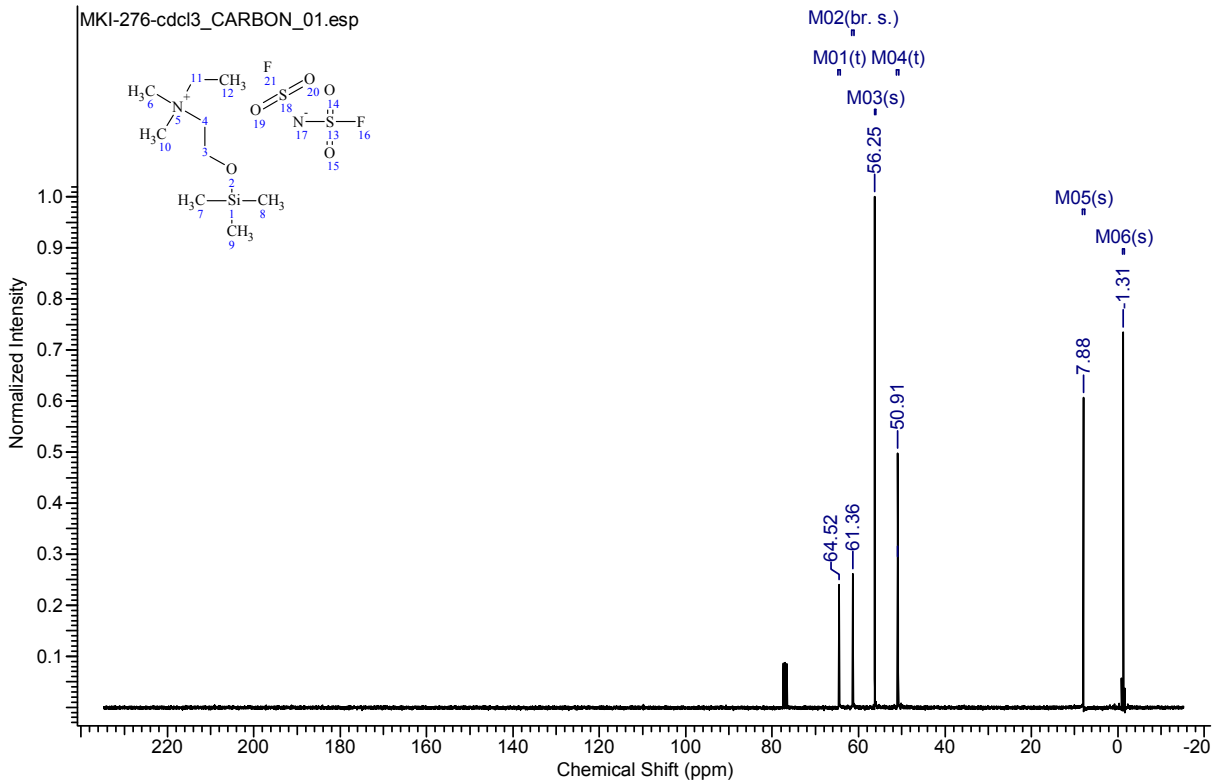


Figure 32. 13C-NMR spectrum of 3l.

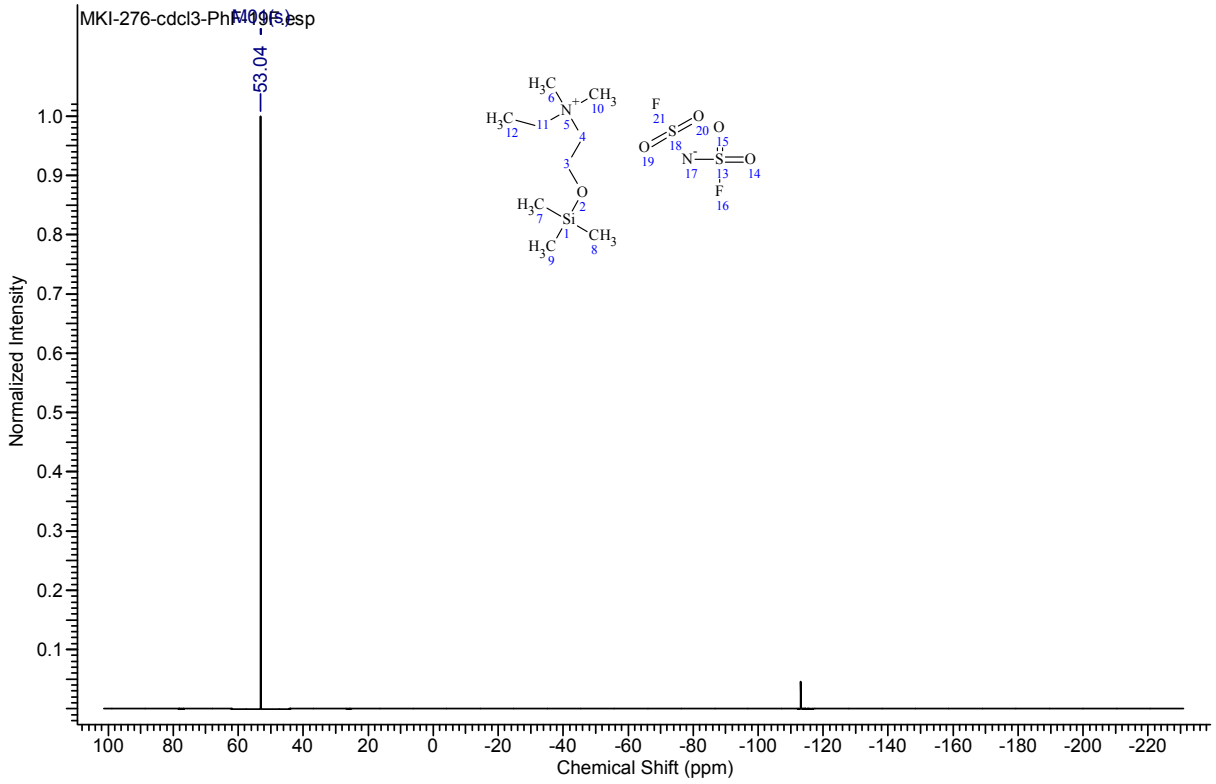


Figure 33. 19F-NMR spectrum of 3l.

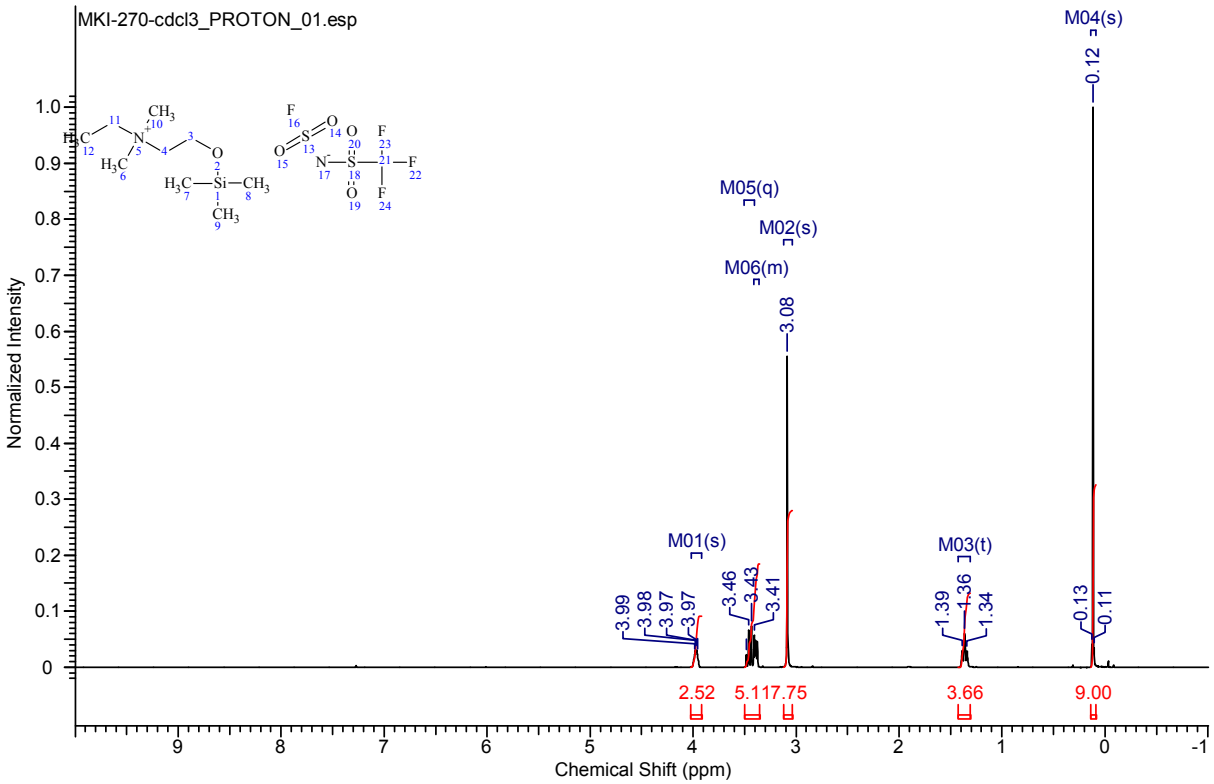


Figure 34. 1H-NMR spectrum of 3m.

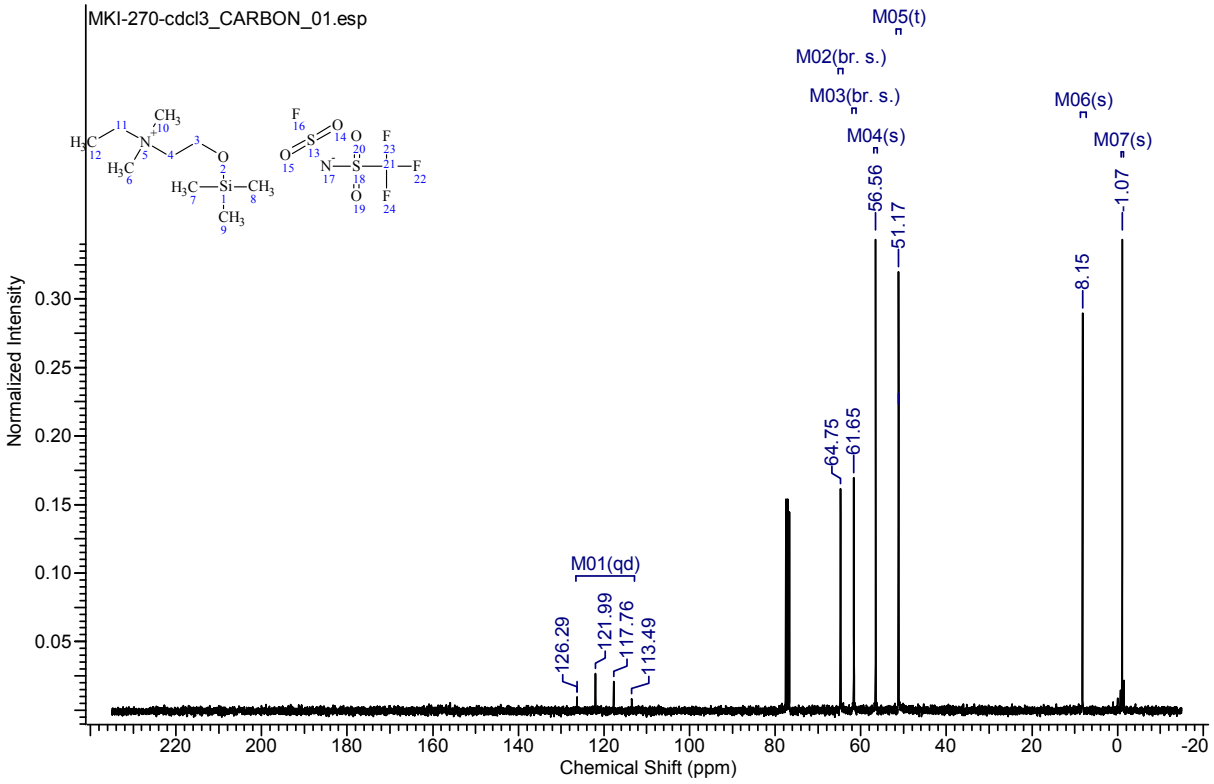


Figure 35. 13C-NMR spectrum of 3m.

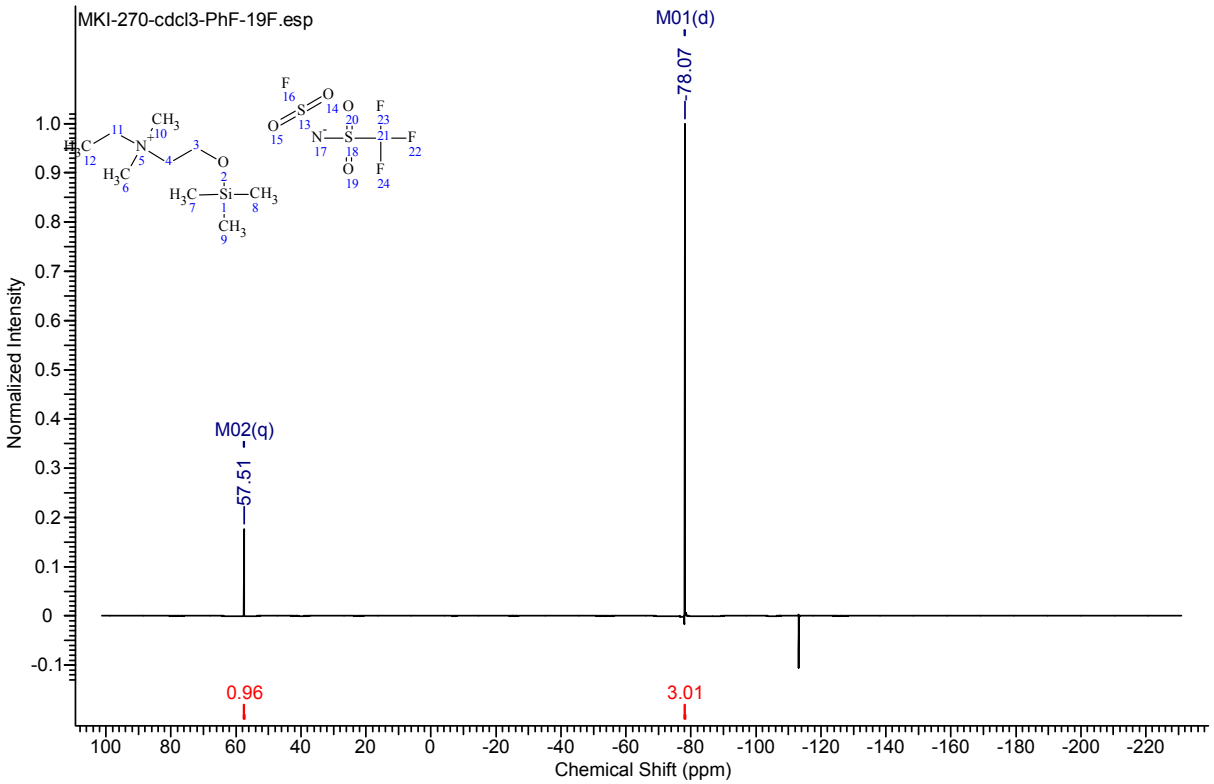


Figure 36. 19F-NMR spectrum of 3m.

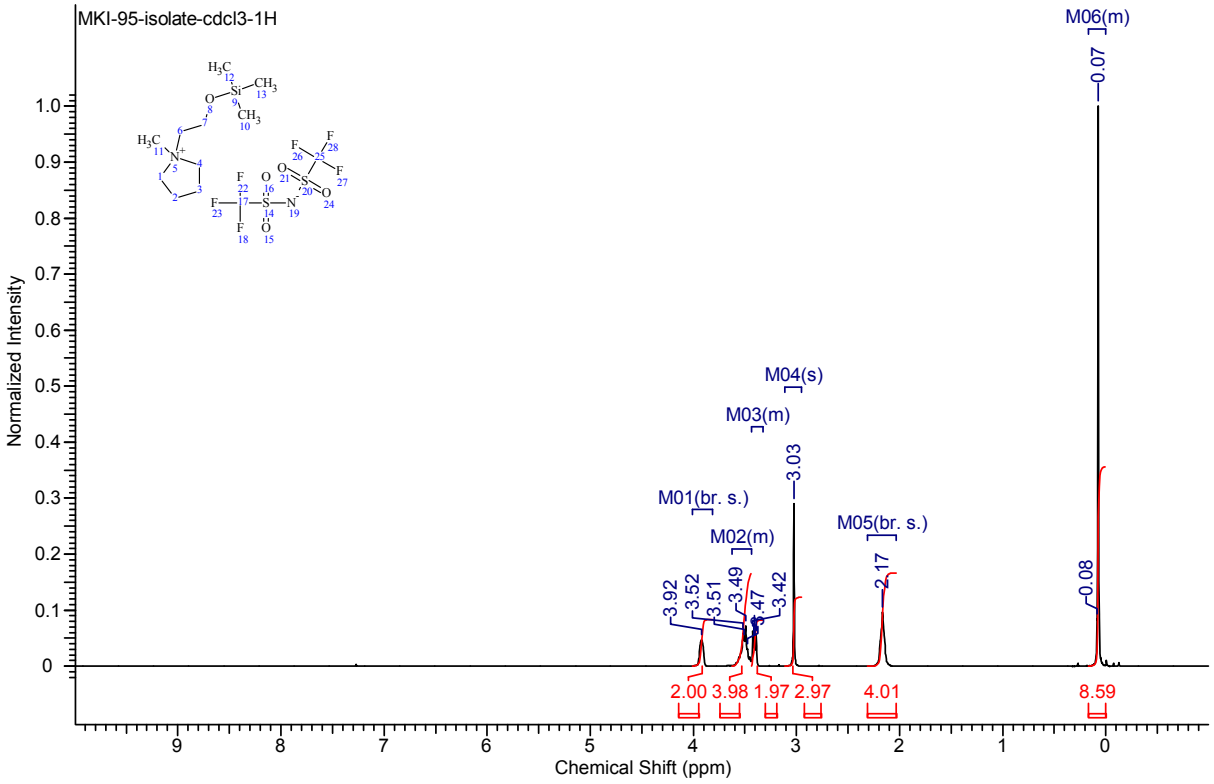


Figure 37. 1H-NMR spectrum of 3n.

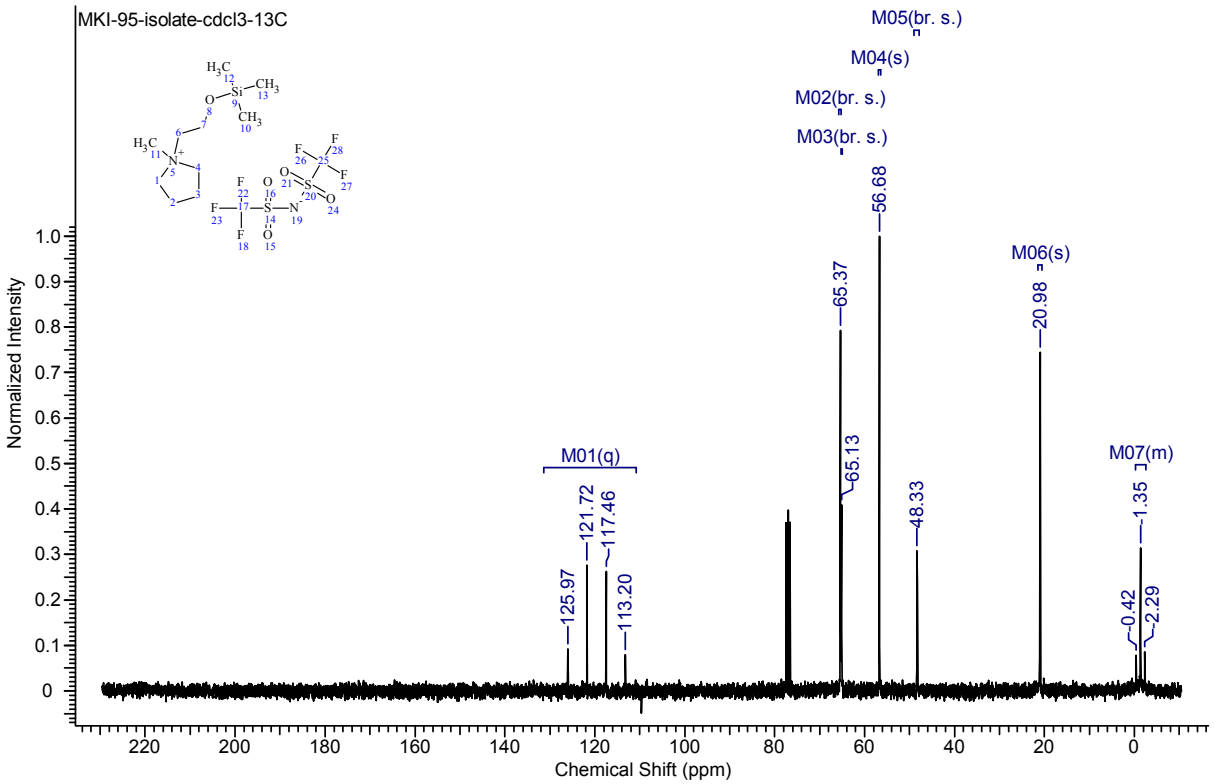


Figure 38. 13C-NMR spectrum of 3n.

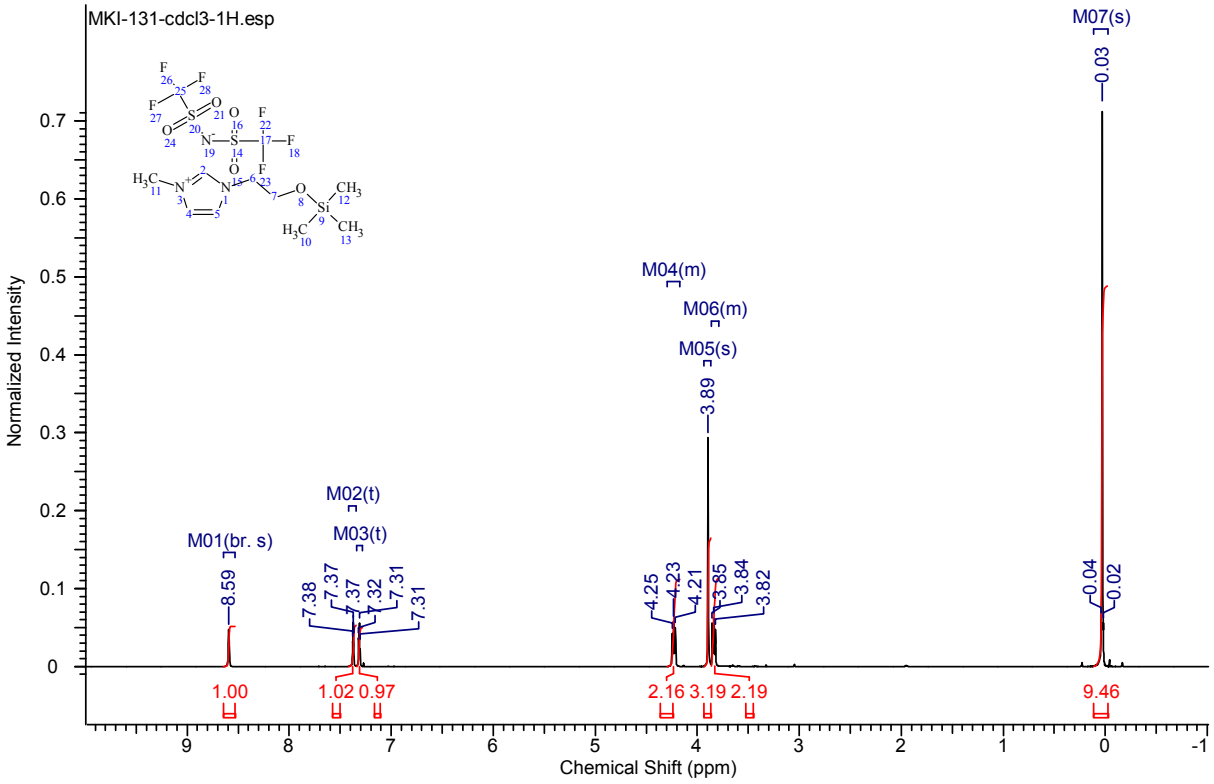


Figure 39. 1H-NMR spectrum of 3o.

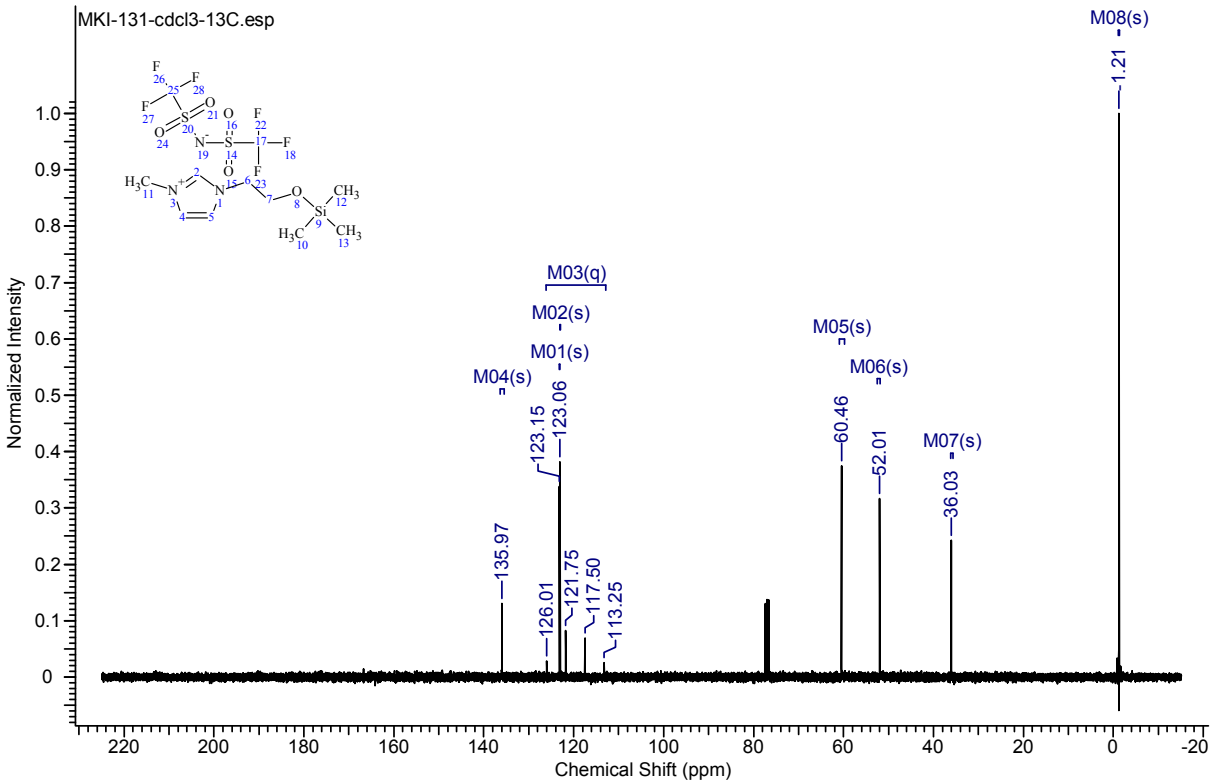


Figure 5. 13C-NMR spectrum of 3o.