Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information for:

Expanding the Structural Diversity of Hydrophobic Ionic Liquids: Physicochemical Properties and Toxicity of Gemini Ionic Liquids

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MATERIALS. 4-n-butylbenzenesulfonyl chloride, 1,8-dibromooctane, and 1-bromohexane were purchased from Alfa Aesar (Ward Hill, MA). Lithium bis(trifluoromethanesulfonyl)imide, trifluoromethanesulfonamide, and 2-mesitylenesulfonyl chloride were purchased from TCI (Portland, OR). 1,2-bis(2-chloroethoxy)ethane was purchased from Frontier Scientific (Logan, UT). Sodium carbonate, 1-butanesulfonyl chloride, sodium 4-n-octylbenzenesulfonate, fetal bovine serum, and penicillin-streptomycin were purchased from Thermo Fisher Scientific (Waltham, MA). Silver nitrate was purchased from BeanTown Chemical (Hudson, NH). High Glucose Dulbecco's Modified Eagles Medium was purchased from Cytiva (Marlborough, MA). CellTiter-Blue reagent was purchased from Promega (Madison, WI). Hydranal – Coulomat AG was purchased from Honeywell (Charlotte, NC). Solvents and all other reagents were purchased from Sigma-Aldrich (Milwaukee, WI).

SYNTHESIS.

Characterization Methods:

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HSQC spectroscopy. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HSQC spectra were obtained using a Bruker Avance III HD 400 MHz spectrometer (Billerica, MA) and a Varian UI 500 MHz spectrometer (Palo Alto, CA). Compounds were prepared in deuterium oxide, chloroform-d, methanol-d4, acetone-d6, or DMSO-d6.

Synthetic Methods:

2-hydroxy-*N*,*N*,*N*-trimethylethan-1-aminium bromide (1a): A 50 mL round bottom flask was attached to a bubbler and placed on ice. To the flask was added hydrobromic acid (48% in water; 2.67 mL, 23.8 mmol, 1.0 equiv.). Then, choline bicarbonate (80% in water; 4.20 mL, 23.8 mmol, 1.0 equiv.) was added to the flask dropwise with stirring. The reaction was stopped after bubbling ceased. Water was removed via lyophilization to produce the product (**1a**) as a white solid in 99% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.03 – 3.96 (m, 2H), 3.49 – 3.42 (m, 2H), 3.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 67.63, 67.22 (m), 55.61, 54.00 – 53.74 (m).

General Procedure "A": Alkyl Cholinium Bromide ([$N_{1,1,X,2OH}$][Br]) Synthesis: To a 100 mL round bottom was added dimethylaminoethanol, the corresponding bromoalkane, and anhydrous acetonitrile (25 mL). The reaction stirred at 80 °C for 24 h. The acetonitrile was removed *in vacuo* and the crude product was redissolved in diethyl ether, which caused a solid to precipitate out. The solid was filtered, washed with diethyl ether (3x5 mL), collected, and excess solvent was removed *in vacuo*.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethylbutan-1-aminium bromide (1b):** The general procedure "A" was applied to dimethylaminoethanol (2.82 mL, 28.0 mmol, 1.0 equiv.) and 1-bromobutane (3.00 mL, 28.0 mmol, 1.0 equiv.). The product (**1b**) was isolated as a white solid in 85.5% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.02 (tt, J = 5.0, 2.4 Hz, 4H), 3.52 – 3.44 (m, 4H), 3.41 – 3.33 (m, 4H), 3.12 (s, 12H), 1.82 – 1.68 (m, 4H), 1.36 (h, J = 7.4 Hz, 4H), 0.93 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 65.54 – 65.26 (m), 65.01 – 64.80 (m), 55.47, 51.67 – 51.35 (m), 24.05, 19.18, 13.02; HSQC (Deuterium Oxide) δ {0.92, 12.93}, {1.35, 19.05}, {1.73, 24.05}, {3.10, 51.46}, {4.01, 55.33}, {3.46, 64.84}, {3.34, 65.33}.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethylhexan-1-aminium bromide (1c):** The general procedure "A" was applied to dimethylaminoethanol (2.82 mL, 28.0 mmol, 1.0 equiv.) and 1-bromohexane (3.93 mL, 28.0 mmol, 1.0 equiv.). The product (**1c**) was isolated as a white solid in 74.0% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.98 (dq, J = 7.5, 2.2 Hz, 2H), 3.46 – 3.40 (m, 2H), 3.35 – 3.27 (m, 2H), 3.07 (s, 6H), 1.80 – 1.66 (m, 2H), 1.36 – 1.22 (m, 6H), 0.86 – 0.78 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 65.51 (d, J = 3.0 Hz), 64.81 (t, J = 2.9 Hz), 55.37, 51.35 (t, J = 3.8 Hz), 30.40, 25.12, 21.86, 21.70, 13.22. HSQC (Deuterium Oxide) δ {0.81, 13.25}, {1.27, 21.63}, {1.71, 21.79}, {1.29, 25.02}, {1.28, 30.34}, {3.06, 51.30}, {3.97, 55.33}, {3.42, 64.84}, {3.31, 65.39}.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethyloctan-1-aminium bromide (1d):** The general procedure "A" was applied to dimethylaminoethanol (2.82 mL, 28.0 mmol, 1.0 equiv.) and 1-bromooctane (4.84 mL, 28.0 mmol, 1.0 equiv.). The product (**1d**) was isolated as a white solid in 94.5% yield. ^{1}H NMR (400 MHz, Deuterium Oxide)

δ 4.03 – 3.96 (m, 2H), 3.48 – 3.41 (m, 2H), 3.38 – 3.29 (m, 2H), 3.09 (s, 6H), 1.80 – 1.68 (m, 2H), 1.31 (q, J = 3.2, 2.6 Hz, 4H), 1.31 – 1.19 (m, 6H), 0.87 – 0.79 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide) δ 68.05, 67.42, 57.96, 53.99 (t, J = 3.5 Hz), 33.66, 30.86, 30.82, 28.13, 24.67, 24.56, 16.12; HSQC (Deuterium Oxide) δ {0.80, 13.41}, {1.70, 21.79}, {1.16, 21.84}, {1.28, 25.34}, {1.28, 28.08}, {1.21, 30.98}, {3.05, 51.30}, {3.96, 55.33}, {3.41, 64.84}, {3.29, 65.49}.

General Procedure "B": Dicholinium Bromide ([DC-X][2Br]) Synthesis: To a 100 mL round bottom flask equipped with a reflux condenser was added 2-dimethylaminoethanol, the corresponding dibromoalkane, and anhydrous acetone (30 mL). The reaction stirred at 60 °C for 24 h, in which a white solid precipitated. The solid was filtered off, washed with acetone (3x30 mL), and collected. Residual solvent was removed *in vacuo*.

***N*^{1},*N*^{4}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{4},*N*^{4}-tetramethylbutane-1,4-diaminium bromide (1e):** The general procedure "B" was applied to dimethylaminoethanol (5.44 mL, 54.4 mmol, 2.0 equiv.) and 1,4-dibromobutane (3.24 mL, 27.2 mmol, 1.0 equiv.). The product (**1e**) was isolated as a white solid in 94.4% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.05 – 3.97 (m, 4H), 3.52 – 3.46 (m, 4H), 3.44 (dd, J = 9.9, 5.6 Hz, 4H), 3.12 (s, 12H), 1.85 (dt, J = 8.3, 3.6 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide) δ 65.26 – 65.03 (m), 64.29 – 64.10 (m), 55.41, 51.73 – 51.38 (m), 19.43 – 19.20 (m); HSQC (Deuterium Oxide) δ {1.87, 19.32}, {3.14, 51.56}, {4.03, 55.41}, {3.50, 64.84}, {3.50, 65.16}.

***N*^{1},*N*^{6}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{6},*N*^{6}-tetramethylhexane-1,6-diaminium bromide (1f):** The general procedure "B" was applied to dimethylaminoethanol (5.44 mL, 54.4 mmol, 2.0 equiv.) and 1,6-dibromohexane (4.18 mL, 27.2 mmol, 1.0 equiv.). The product (**1f**) was isolated as a white solid in 88.6% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.99 (dq, J = 5.0, 2.5 Hz, 4H), 3.47 – 3.40 (m, 4H), 3.37 – 3.29 (m, 4H), 3.08 (s, 12H), 1.76 (qd, J = 7.9, 5.4, 4.1 Hz, 4H), 1.42 – 1.34 (m, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide) δ 65.16, 64.90 (t, J = 2.9 Hz), 55.38, 51.39 (t, J = 3.8 Hz), 25.07, 21.87. HSQC (Deuterium Oxide) δ {1.79, 21.95}, {1.41, 25.02}, {3.11, 51.46}, {4.01, 55.49}, {3.47, 64.99}, {3.37, 65.17}.

***N*^{1},*N*^{8}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyloctane-1,8-diaminium bromide (1g):** The general procedure "B" was applied to dimethylaminoethanol (5.44 mL, 54.4 mmol, 2.0 equiv.) and 1,8-dibromooctane (5.00 mL, 27.2 mmol, 1.0 equiv.). The product (**1g**) was isolated as a white solid in 88.6% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.98 (dq, J = 5.0, 2.5 Hz, 4H), 3.46 – 3.39 (m, 4H), 3.35 – 3.26 (m, 4H), 3.07 (s, 12H), 1.71 (p, J = 5.5 Hz, 4H), 1.34 – 1.26 (m, 8H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide) δ 65.43, 64.83, 55.36, 51.35, 27.89, 25.31, 21.89; HSQC (Deuterium Oxide) δ {1.77, 21.94}, {1.36, 25.34}, {1.36, 27.85}, {3.12, 51.44}, {4.02, 55.40}, {3.47, 64.85}, {3.36, 65.46}.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) chloride (1h): A 250 mL round bottom flask wrapped in aluminum foil and equipped with a reflux condenser was purged with argon. To the flask was added anhydrous acetonitrile (50 mL), 1,2-bis(2-chloroethoxy)ethane (10.0 mL, 64.0 mmol, 1.0 equiv.), and dimethylaminoethanol (19.3 mL, 192 mmol, 3.0 equiv.). The reaction stirred at 80 °C for 72 h, in which a white solid precipitated out. The white solid was filtered, washed with acetone (3x20 mL) and collected. Residual solvent was removed *in vacuo*. The filtrate was transferred back into the 250 mL round bottom flask and stirred for another 48 h at 80 °C. More formed, which was purified in the same fashion. The solid fractions were combined to produce the product (**1h**)

as a white solid in 61.5% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.02 – 3.96 (m, 4H), 3.92 (dq, J = 5.2, 2.5 Hz, 4H), 3.67 (s, 4H), 3.64 – 3.57 (m, 4H), 3.55 – 3.48 (m, 4H), 3.14 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 69.61, 66.69 – 65.76 (m), 64.16 (d, J = 3.4 Hz), 55.37, 52.53 – 51.70 (m); HSQC (Deuterium Oxide) δ {3.18, 52.11}, {4.02, 55.33}, {3.64, 64.19}, {3.96, 64.20}, {3.49, 67.57}, {3.70, 69.68}.

General Procedure "C": Alky Cholinium Bis(triflate)azanide ([$N_{1,1,X,2OH}$][NTf_2]) Synthesis: To a 50 mL round bottom flask was added the corresponding alkyl cholinium bromide, lithium bis(trifluoromethanesulfonyl)imide, and Millipore Milli-Q water (15 mL). The reaction stirred at room temperature for 24 h, in which a second layer formed. Water was removed *in vacuo*. The crude product was dissolved in acetone, in which excess alkyl cholinium bromide precipitated. The solid was filtered, washed with acetone (3x5 mL), and the filtrate was collected and concentrated *in vacuo*. The resulting ionic liquid was mixed with DCM (10 mL). The DCM and ionic liquid mixture was washed with Millipore Milli-Q water until the water wash showed no precipitant upon addition of silver nitrate. DCM and residual water were removed via a rotary evaporator followed by a vacuum oven set to 80 °C.

2-hydroxy-*N*,*N*,*N*-trimethylethan-1-aminium bis((trifluoromethyl)sulfonyl)azanide (2a): The general procedure "C" was applied to **1a** (4.90 g, 26.6 mmol, 1.5 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (5.09 g, 17.7 mmol, 1.0 equiv.). The product (**2a**) was isolated as a clear liquid in 74.8% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.54 (t, J = 4.7 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.73 – 3.66 (m, 2H), 3.40 (d, J = 1.0 Hz, 9H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 120.07 (q, J = 321.2 Hz), 68.50 – 67.05 (m), 56.12, 53.90 – 52.77 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -79.91.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethylbutan-1-aminium bis((trifluoromethyl)sulfonyl)azanide (2b):** The general procedure "C" was applied to **1b** (4.00 g, 17.7 mmol, 1.3 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (3.91 g, 13.6 mmol, 1.0 equiv.). The product (**2b**) was isolated as a clear liquid in 53.2% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 3.99 (dq, J = 7.7, 2.6 Hz, 2H), 3.49 – 3.44 (m, 2H), 3.43 – 3.37 (m, 2H), 3.15 (s, 6H), 1.85 – 1.73 (m, 2H), 1.42 (h, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 119.82 (q, J = 320.4 Hz), 65.43 – 65.29 (m), 65.18 – 65.06 (m), 55.51, 51.20 – 50.60 (m), 24.14, 19.46 – 18.92 (m), 12.44; ^{19}F NMR (376 MHz, Methanol-d4) δ -80.53.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethylhexan-1-aminium bis((trifluoromethyl)sulfonyl)azanide (2c):** The general procedure "C" was applied to **1c** (4.30 g, 16.9 mmol, 1.3 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (3.74 g, 13.0 mmol, 1.0 equiv.). The product (**2c**) was isolated as a clear liquid in 91.2% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 4.58 (s, 1H), 3.99 (dq, J = 7.4, 2.4 Hz, 2H), 3.50 – 3.42 (m, 2H), 3.41 – 3.34 (m, 2H), 3.14 (s, 6H), 1.85 – 1.73 (m, 2H), 1.42 – 1.32 (m, 6H), 0.97 – 0.88 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 119.81 (q, J = 320.5 Hz), 65.63 (t, J = 2.5 Hz), 65.08 (t, J = 2.7 Hz), 55.56, 50.86 (t, J = 3.8 Hz), 30.83, 25.51, 22.14, 22.03, 12.90; ^{19}F NMR (376 MHz, Methanol-d4) δ -80.32.

***N*-(2-hydroxyethyl)-*N*,*N*-dimethyloctan-1-aminium bis((trifluoromethyl)sulfonyl)azanide (2d):** The general procedure "C" was applied to **1d** (4.60 g, 16.3 mmol, 1.3 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (3.60 g, 12.5 mmol, 1.0 equiv.). The product (**2d**) was isolated as a clear liquid in 57.4% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 3.99 (dq, J = 5.1, 2.5 Hz, 2H), 3.50 – 3.43 (m, 2H), 3.43 – 3.35 (m, 2H), 3.15 (s, 6H), 1.87 – 1.73 (m, 2H), 1.46 – 1.28 (m, 10H), 0.97 – 0.87 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 119.82 (q, J = 320.5 Hz), 65.58 (t, J = 2.5 Hz), 65.08 (t, J = 2.7 Hz), 55.53,

51.00 – 50.53 (m), 31.43, 28.76, 28.68, 25.89, 22.24, 22.20, 13.06; ^{19}F NMR (376 MHz, Methanol-d4) δ -80.43.

General Procedure "D": Dicholinium Bis(triflate)azanide ([DC-X][2NTf$_2$]) Synthesis: To a 100 mL round bottom flask was added the corresponding dicholinium bromide, lithium bis(trifluoromethanesulfonyl)imide, and Millipore Milli-Q water (15 mL). The solution stirred at room temperature for 24 h, in which a second layer formed. The upper water layer was removed, and the ionic liquid layer was washed with Millipore Milli-Q water until the water wash showed no precipitant upon addition of silver nitrate. Residual water was removed by a vacuum oven set to 80 °C.

***N*^{1},*N*^{4}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{4},*N*^{4}-tetramethylbutane-1,4-diaminium bis((trifluoromethyl)sulfonyl)azanide (2e):** The general procedure "D" was applied to **1e** (6.00 g, 15.2 mmol, 1.0 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (4.37 g, 15.2 mmol, 1.0 equiv.). The product (**2e**) was isolated as a clear solid in 62.4% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.56 (t, J = 4.6 Hz, 2H), 4.16 (ddt, J = 7.4, 5.1, 2.6 Hz, 4H), 3.77 – 3.67 (m, 8H), 3.37 (s, 12H), 2.20 – 2.09 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 120.07 (q, J = 321.2 Hz), 65.93 – 65.55 (m), 64.70 – 64.18 (m), 55.90, 51.73 – 51.27 (m), 19.81 – 19.30 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -79.86.

***N*^{1},*N*^{6}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{6},*N*^{6}-tetramethylhexane-1,6-diaminium bis((trifluoromethyl)sulfonyl)azanide (2f):** The general procedure "D" was applied to **1f** (6.00 g, 14.2 mmol, 1.0 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (4.08 g, 14.2 mmol, 1.0 equiv.). The product (**2f**) was isolated as a clear liquid in 76.2% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 4.07 – 3.95 (m, 6H), 3.44 (dd, J = 6.4, 3.5 Hz, 4H), 3.39 – 3.31 (m, 4H), 3.12 (s, 12H), 1.81 (qd, J = 8.8, 5.4, 4.7 Hz, 4H), 1.45 (d, J = 6.4 Hz, 4H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 119.77 (q, J = 320.3 Hz), 65.26 (d, J = 20.8 Hz), 55.63 (d, J = 11.7 Hz), 50.99, 24.90, 21.69; ^{19}F NMR (376 MHz, Methanol-d4) δ -80.10.

***N*^{1},*N*^{8}-bis(2-hydroxyethyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyloctane-1,8-diaminium bis((trifluoromethyl)sulfonyl)azanide (2g):** The general procedure "D" was applied to **1g** (3.00 g, 6.46 mmol, 1.0 equiv.) and lithium bis(trifluoromethanesulfonyl)imide (3.71 g, 12.9 mmol, 2.0 equiv.). The product (**2g**) was isolated as a clear liquid in 78.6% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.49 (t, J = 4.7 Hz, 2H), 4.14 (qt, J = 5.0, 2.5 Hz, 4H), 3.69 – 3.62 (m, 4H), 3.61 – 3.52 (m, 4H), 3.32 (s, 12H), 1.92 (dq, J = 13.8, 7.1 Hz, 4H), 1.42 (d, J = 7.3 Hz, 8H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 120.07 (q, J = 321.2 Hz), 65.48 (dt, J = 7.6, 2.7 Hz), 55.92, 51.53 – 51.05 (m), 28.54, 25.87, 22.27; ^{19}F NMR (376 MHz, Acetone-d6) δ -79.83.

2,2'-(ethane-1,2-diylbis(oxy))bis(N-(2-hydroxyethyl)-N,N-dimethylethan-1-aminium) bis((trifluoromethyl)sulfonyl)azanide (2h): The general procedure "D" was applied to **1h** (4.17 g, 11.4 mmol, 1.0 equiv.), lithium bis(trifluoromethanesulfonyl)imide (6.00 g, 20.9 mmol, 1.8 equiv.), and Millipore Milli-Q water (15 mL). The product (**2h**) was isolated as a clear liquid in 73.6% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.54 (qd, J = 6.3, 5.4, 3.2 Hz, 2H), 4.18 (tq, J = 4.9, 2.6 Hz, 4H), 4.12 (qt, J = 5.0, 2.5 Hz, 4H), 3.93 – 3.86 (m, 4H), 3.82 – 3.75 (m, 8H), 3.42 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 120.08 (q, J = 321.2 Hz), 69.94, 66.84 – 66.71 (m), 64.82 – 64.68 (m), 64.54, 55.97, 52.37 – 52.15 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -79.89.

4-octylbenzenesulfonyl chloride (3): A 50 mL round bottom flask equipped with a reflux condenser was purged with argon. To the flask was added sodium 4-octylbenzenesulfonate (3.40 g, 11.6 mmol, 1.0 equiv.). Then, thionyl chloride (3.56 mL, 49.1 mmol, 4.25 equiv.) followed by dimethylformamide (1.25 mL, 16.2 mmol, 1.4 equiv.) were slowly added. The solution stirred at 80 °C for 4 h. The crude mixture was then added to a beaker of crushed ice water (100 mL). After the ice melted, the organic and water layers were separated. The water layer was extracted with DCM (3x50 mL). The organic fractions were combined and washed with water (3x50 mL) followed by brine (1x50 mL). The organic layer was dried with magnesium sulfate, filtered, and concentrated *in vacuo* to produce an orange oil. The crude product was purified by flash chromatography using 9:1 hexanes and ethyl acetate as the mobile phase. Finally, the resulting pale orange liquid was further purified by stirring in a mixture of DCM and activated charcoal. After 4 h, the charcoal was filtered out and the solution was concentrated *in vacuo* to produce the product (**3**) as a yellow oil in 91.4% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.89 (m, 2H), 7.49 – 7.38 (m, 2H), 2.73 (dd, J = 8.7, 6.9 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.39 – 1.24 (m, 10H), 0.92 – 0.84 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 151.77, 141.77, 129.64, 127.07, 36.07, 31.85, 30.95, 29.37, 29.21, 29.19, 22.66, 14.11.

General Procedure "E": Sodium Asymmetric Bis(sulfonyl)azanide ([Na][XSNTf]) Synthesis: A 100 mL round bottom flask equipped with a reflux condenser and attached to a bubbler was purged with argon. To the flask was added sodium carbonate, trifluoromethanesulfonamide, the corresponding sulfonyl chloride, and anhydrous acetonitrile (25 mL). The reaction stirred for 24 h at 80 °C. Afterwards, the white solid was filtered out, and the filtrate was collected and concentrated *in vacuo* to form a white solid. The white solid was resuspended in acetone (5 mL) and cooled to –20°C, resulting in the precipitation of starting material. The solution was filtered, and the filtrate was collected and concentrated *in vacuo* to produce a white solid. Finally, the product stirred in toluene (50 mL) for 4 h. The solid was filtered, washed with toluene (3x5 mL), collected, and residual solvent was removed *in vacuo*.

sodium (butylsulfonyl)((trifluoromethyl)sulfonyl)azanide (4a): The general procedure "E" was applied to trifluoromethanesulfonamide (2.38 g, 16.0 mmol, 1.0 equiv.), sodium carbonate (2.54 g, 24.0 mmol, 1.5 equiv.), and 1-butanesulfonyl chloride (2.07 mL, 16.0 mmol, 1.0 equiv.). The product (**4a**) was isolated as a white solid in 87.9% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.29 – 3.13 (m, 2H), 1.82 – 1.67 (m, 2H), 1.42 (h, J = 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 119.67 (q, J = 320.9 Hz), 55.08, 25.29, 20.75, 12.79; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.53.

sodium (hexylsulfonyl)((trifluoromethyl)sulfonyl)azanide (4b): The general procedure "E" was applied to trifluoromethanesulfonamide (2.02 g, 13.5 mmol, 1.0 equiv.), sodium carbonate (2.15 g, 20.3 mmol, 1.5 equiv.), and 1-hexanesulfonyl chloride (2.20 mL, 13.5 mmol, 1.0 equiv.). The product (**4b**) was isolated as a white solid in 80.7 % yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.25 – 3.16 (m, 2H), 1.77 (p, 2H), 1.41 (p, J = 7.5 Hz, 2H), 1.27 (h, J = 3.7 Hz, 4H), 0.87 – 0.79 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 119.68 (q, J = 321.0 Hz), 55.30, 30.42, 26.94, 23.14, 21.69, 13.27; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.52. HSQC (Deuterium Oxide) δ {0.86, 13.25}, {1.30, 21.79}, {1.79, 23.24}, {1.43, 27.11}, {1.30, 30.50}, {3.21, 55.33}.

sodium (octylsulfonyl)((trifluoromethyl)sulfonyl)azanide (4c): The general procedure "E" was applied to trifluoromethanesulfonamide (2.38 g, 16.0 mmol, 1.0 equiv.), sodium carbonate (2.54 g, 24.0 mmol, 1.5

equiv.), and 1-octanesulfonyl chloride (3.13 mL, 16.0 mmol, 1.0 equiv.). The product (**4c**) was isolated as a white solid in 76.1% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 2.98 – 2.90 (m, 2H), 1.65 (tt, J = 7.9, 6.2 Hz, 2H), 1.40 – 1.30 (m, 2H), 1.33 – 1.23 (m, 8H), 0.91 – 0.83 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ 120.62 (q, J = 324.5 Hz), 54.96, 31.66, 29.07, 28.91, 28.17, 24.10, 22.54, 14.38; ^{19}F NMR (376 MHz, DMSO-d6) δ -77.57. HSQC (DMSO-d6) δ {0.87, 13.84}, {1.26, 21.90}, {1.66, 23.51}, {1.34, 28.24}, {1.26, 29.05}, {1.25, 31.63}, {2.94, 54.47}

sodium (phenylsulfonyl)((trifluoromethyl)sulfonyl)azanide (4d): The general procedure "E" was applied to trifluoromethanesulfonamide (2.50 g, 16.8 mmol, 1.0 equiv.), sodium carbonate (2.67 g, 25.2 mmol, 1.5 equiv.), and benzenesulfonyl chloride (2.14 mL, 16.8 mmol, 1.0 equiv.). The product (**4d**) was isolated as a white solid in 92.1% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.90 – 7.83 (m, 2H), 7.67 – 7.45 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 141.79, 133.15, 129.23, 126.03, 119.55 (q, J = 321.1 Hz); ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.53.

sodium tosyl((trifluoromethyl)sulfonyl)azanide (4e): The general procedure "E" was applied to trifluoromethanesulfonamide (2.50 g, 16.8 mmol, 1.0 equiv.), sodium carbonate (2.67 g, 25.2 mmol, 1.5 equiv.), and 4-toluenesulfonyl chloride (3.20 g, 16.8 mmol, 1.0 equiv.). The product (**4e**) was isolated as a white solid in 89.5 % yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.74 – 7.67 (m, 2H), 7.26 – 7.18 (m, 2H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 144.31, 138.84, 129.63, 126.07, 119.65 (q, J = 321.3 Hz), 20.62; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.41.

sodium ((4-butylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (4f): The general procedure "E" was applied to trifluoromethanesulfonamide (1.92 g, 12.9 mmol, 1.2 equiv.), sodium carbonate (1.71 g, 16.1 mmol, 1.5 equiv.), and 4-butylbenzenesulfonyl chloride (2.50 g, 10.7 mmol, 1.0 equiv.). The product (**4f**) was isolated as a white solid in 97.9% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.85 – 7.78 (m, 2H), 7.33 – 7.26 (m, 2H), 2.72 – 2.64 (m, 2H), 1.68 – 1.56 (m, 2H), 1.37 (dq, J = 14.7, 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 146.03, 143.29, 127.97, 126.44, 120.54 (q, J = 323.1 Hz), 35.05, 33.33, 22.02, 13.24; ^{19}F NMR (376 MHz, Acetone-d6) δ -79.23

sodium ((4-hexylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (4g): The general procedure "E" was applied to trifluoromethanesulfonamide (0.685 g, 4.60 mmol, 1.2 equiv.), sodium carbonate (0.610 g, 5.76 mmol, 1.5 equiv.), and 4-hexylbenzenesulfonyl chloride (1.00 g, 3.83 mmol, 1.0 equiv.). The product (**4g**) was isolated as a white solid in 40.1% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.79 – 7.53 (m, 2H), 7.17 – 7.01 (m, 2H), 2.41 (dd, J = 8.8, 6.7 Hz, 2H), 1.51 – 1.27 (m, 2H), 1.12 (d, J = 4.7 Hz, 6H), 0.82 – 0.62 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 147.98, 139.18, 128.57, 126.41, 119.63 (q, J = 321.7 Hz), 35.29, 31.34, 30.61, 28.56, 22.26, 13.58; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.49; HSQC (Deuterium Oxide) δ {0.74, 13.57}, {1.13, 22.28}, {1.12, 28.57}, {1.38, 30.66}, {1.12, 31.31}, {7.67, 126.43}, {7.08, 128.53}

sodium ((4-octylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (4h): The general procedure "E" was applied to trifluoromethanesulfonamide (1.89 g, 12.7 mmol, 1.2 equiv.), sodium carbonate (1.68 g, 15.8 mmol, 1.5 equiv.), and **3** (3.05 g, 10.6 mmol, 1.0 equiv.). The product (**4h**) was isolated as a white solid in 93.1% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.68 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.58 (t, J = 7.4 Hz, 2H), 1.27 (dt, J = 15.4, 4.0 Hz, 10H), 0.86 (t, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (101

MHz, DMSO-d6) δ 146.18, 143.13, 128.54, 126.60, 120.51 (q, J = 324.5 Hz), 35.35, 31.73, 31.16, 29.27, 29.12, 29.06, 22.55, 14.39; ^{19}F NMR (376 MHz, DMSO-d6) δ -77.82; HSQC (DMOS-d6) δ {0.86, 14.38}, {1.25, 22.44}, {1.28, 29.21}, {1.58, 31.13}, {1.24, 31.79}, {7.67, 126.59}, {7.30, 128.53}.

sodium (mesitylsulfonyl)((trifluoromethyl)sulfonyl)azanide (4i): The general procedure "E" was applied to trifluoromethanesulfonamide (2.50 g, 16.8 mmol, 1.0 equiv.), sodium carbonate (2.84 g, 26.8 mmol, 1.6 equiv.), and 2-mesitylenesulfonyl chloride (3.67 g, 16.8 mmol, 1.0 equiv.). The product (**4i**) was isolated as a white solid in 92.0% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 6.93 (s, 2H), 2.52 (s, 6H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 143.11, 138.42, 136.09, 131.50, 119.58 (q, J = 319.8 Hz), 21.79, 19.97; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.57.

sodium ((4-methoxyphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (4j): The general procedure "E" was applied to trifluoromethanesulfonamide (2.50 g, 16.8 mmol, 1.0 equiv.), sodium carbonate (2.67 g, 25.2 mmol, 1.5 equiv.), and 4-methoxybenzenesulfonyl chloride (3.47 g, 16.8 mmol, 1.0 equiv.). The product (**4j**) was isolated as a white solid in 94.3% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.82 – 7.73 (m, 2H), 7.05 – 6.97 (m, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 162.47, 133.86, 128.34, 119.56 (q, J = 321.3 Hz), 114.32, 55.65; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.53.

sodium ((trifluoromethyl)sulfonyl)((2,4,6-trifluorophenyl)sulfonyl)azanide (4k): The general procedure "E" was applied to trifluoromethanesulfonamide (1.57 g, 10.5 mmol, 1.00 equiv.), sodium carbonate (1.67 g, 15.8 mmol, 1.50 equiv.), and 2,4,6-trifluorobenzenesulfonyl chloride (1.53 mL, 10.9 mmol, 1.04 equiv.). The product (**4k**) was isolated as a white solid in 91.4% yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.01 – 6.93 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 165.28 (dt, J = 255.6, 16.3 Hz), 159.81 (ddd, J = 257.3, 15.9, 6.5 Hz), 119.39 (q, J = 320.9 Hz), 116.53 – 115.75 (m), 102.16 (ddd, J = 27.9, 26.4, 4.0 Hz); ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.75, -99.28 (t, J = 11.6 Hz), -105.36 (d, J = 11.5 Hz).

sodium ((perfluorophenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (4l): The general procedure "E" was applied to trifluoromethanesulfonamide (1.40 g, 9.38 mmol, 1.0 equiv.), sodium carbonate (1.49 g, 14.1 mmol, 1.5 equiv.), and 2,3,4,5,6-pentafluorobenzenesulfonyl chloride (1.39 mL, 9.38 mmol, 1.0 equiv.). The product (**4l**) was isolated as a white solid in 93.0% yield. ^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide) δ 145.81 – 142.45 (m), 139.55 – 136.23 (m), 119.37 (q, J = 320.8 Hz), 117.56 – 117.11 (m).; ^{19}F NMR (376 MHz, Deuterium Oxide) δ -78.83, -138.41 – -138.63 (m), -146.97 (tt, J = 21.0, 7.1 Hz), -160.16 – -160.41 (m).

General Procedure "F": Dicholinium Bis(sulfonyl)azanide ([DC-ether][XSNTf]) Synthesis: To a 50 mL round bottom flask was added **1h**, the corresponding sodium bis(sulfonyl)azanide, and Millipore Milli-Q water or Millipore Milli-Q water and acetone. The reaction stirred at room temperature for 24 h. The solvent was removed *in vacuo*. The crude product was dissolved in acetone (15 mL), in which residual starting material precipitated. The solid was filtered, washed with acetone (3x5 mL), and the filtrate was collected and concentrated *in vacuo*. The resulting liquid was mixed with DCM (10 mL), and the DCM and ionic liquid mixture was washed with Millipore Milli-Q water until the water wash showed no precipitant upon addition of silver nitrate. DCM and residual water were removed via a rotary evaporator followed by a vacuum oven set to 80 °C.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) (butylsulfonyl)((trifluoromethyl)sulfonyl)azanide (5a): The general procedure "F" was applied to **1h** (3.17 g, 8.67 mmol, 1.0 equiv.), **4a** (2.53 g, 8.67 mmol, 1.0 equiv.), and Millipore Milli-Q water (15 mL). The product (**5a**) was isolated as a clear liquid in 97.0% yield. ^{1}H NMR (500 MHz, Methanol-d4) δ 4.85 (s, 2H), 4.11 – 4.05 (m, 4H), 4.05 – 4.00 (m, 4H), 3.77 (s, 4H), 3.76 (dd, J = 4.3, 2.4 Hz, 4H), 3.67 – 3.61 (m, 4H), 3.30 (s, 12H), 3.22 – 3.16 (m, 4H), 1.91 – 1.81 (m, 4H), 1.53 (h, J = 7.4 Hz, 4H), 1.02 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, Methanol-d4) δ 121.64 (q, J = 322.1 Hz), 71.26, 68.01 – 67.77 (m), 66.07 – 65.79 (m), 65.77, 56.96, 56.04, 53.44 – 52.86 (m), 27.17, 22.54, 14.02; ^{19}F NMR (470 MHz, Methanol-d4) δ -79.53.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) (hexylsulfonyl)((trifluoromethyl)sulfonyl)azanide (5b): The general procedure "F" was applied to **1h** (2.10 g, 5.74 mmol, 1.0 equiv.), **4b** (2.75 g, 8.61 mmol, 1.5 equiv.), and Millipore Milli-Q water (10 mL). The product (**5b**) was isolated as a clear liquid in 86.0% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.47 (s, 2H), 4.19 – 4.04 (m, 8H), 3.90 – 3.83 (m, 4H), 3.81 – 3.72 (m, 8H), 3.39 (s, 12H), 3.14 – 3.01 (m, 4H), 1.85 – 1.75 (m, 4H), 1.48 – 1.38 (m, 4H), 1.33 (tdd, J = 7.9, 4.9, 3.4 Hz, 8H), 0.94 – 0.87 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 120.65 (q, J = 323.4 Hz), 69.98, 66.79 – 66.52 (m), 64.75 – 64.63 (m), 64.62, 56.01, 54.76, 52.30 – 52.11 (m), 31.31, 27.94, 23.99, 22.24, 13.42; ^{19}F NMR (376 MHz, Acetone-d6) δ -78.74.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) (octylsulfonyl)((trifluoromethyl)sulfonyl)azanide (5c): The general procedure "F" was applied to **1h** (2.45 g, 6.71 mmol, 1.0 equiv.), **4c** (3.5 g, 10.1 mmol, 1.5 equiv.), Millipore Milli-Q water (15 mL), and acetone (15 mL). The product (**5c**) was isolated as a clear liquid in 85.4% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 4.03 (dq, J = 7.6, 2.6 Hz, 4H), 3.98 (dt, J = 4.9, 2.4 Hz, 4H), 3.72 (d, J = 4.3 Hz, 8H), 3.63 – 3.56 (m, 4H), 3.26 (s, 12H), 3.19 – 3.10 (m, 4H), 1.89 – 1.77 (m, 4H), 1.45 (t, J = 7.4 Hz, 4H), 1.34 (dq, J = 11.6, 4.7, 4.2 Hz, 16H), 0.98 – 0.89 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 120.28 (q, J = 322.1 Hz), 69.91, 66.52 (t, J = 2.7 Hz), 64.69 – 64.50 (m), 64.43, 55.64, 54.95, 51.99 – 51.72 (m), 31.56, 28.92, 28.80, 28.04, 23.75, 22.33, 13.15; ^{19}F NMR (376 MHz, Methanol-d4) δ -79.45.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) (phenylsulfonyl)((trifluoromethyl)sulfonyl)azanide (5d): The general procedure "F" was applied to **1h** (3.54 g, 9.69 mmol, 1.0 equiv.), **4d** (2.30 g, 7.39 mmol, 1.3 equiv.), and Millipore Milli-Q water (15 mL). The product (**5d**) was isolated as a clear liquid in 85.7% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.98 – 7.87 (m, 4H), 7.58 – 7.45 (m, 6H), 4.59 (t, J = 4.9 Hz, 2H), 4.10 (qt, J = 5.1, 2.7 Hz, 4H), 4.04 (dq, J = 7.5, 2.6 Hz, 5H), 3.84 – 3.78 (m, 4H), 3.75 – 3.68 (m, 8H), 3.35 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 145.61, 131.12, 128.27, 126.52, 120.53 (q, J = 323.5 Hz), 69.94, 66.80 – 66.51 (m), 64.72 – 64.61 (m), 64.55, 55.98, 52.41 – 51.99 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -78.87.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) tosyl((trifluoromethyl)sulfonyl)azanide (5e): The general procedure "F" was applied to **1h** (3.00 g, 8.21 mmol, 1.0 equiv.), **4e** (4.00 g, 12.3 mmol, 1.5 equiv.), and Millipore Milli-Q water (15 mL). The product (**5e**) was isolated as a clear liquid in 66.9% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 7.84 – 7.76 (m, 4H), 7.37 – 7.29 (m, 4H), 4.00 (dq, J = 5.2, 2.6 Hz, 4H), 3.97 – 3.90 (m, 4H), 3.71 – 3.64 (m, 8H), 3.59 – 3.52 (m, 4H), 3.21 (s, 12H), 2.41 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 142.34, 141.54, 128.76, 126.30,

120.20 (q, J = 322.4 Hz), 69.88, 66.74 – 66.32 (m), 64.69 – 64.53 (m), 64.37, 55.59, 52.32 – 51.48 (m), 20.07; ^{19}F NMR (376 MHz, Methanol-d4) δ -79.65.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((4-butylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (5f): The general procedure "F" was applied to **1h** (2.11 g, 5.78 mmol, 1.0 equiv.), **4f** (3.19 g, 8.68 mmol, 1.5 equiv.), Millipore Milli-Q water (15 mL), and acetone (15 mL). The product (**5f**) was isolated as a clear liquid in 98.2% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.92 – 7.74 (m, 4H), 7.41 – 7.26 (m, 4H), 4.46 (t, J = 4.5 Hz, 2H), 4.13 (dq, J = 5.7, 2.8 Hz, 4H), 4.07 (tt, J = 4.9, 2.6 Hz, 4H), 3.90 – 3.82 (m, 4H), 3.79 – 3.71 (m, 8H), 3.38 (s, 12H), 2.76 – 2.58 (m, 4H), 1.72 – 1.52 (m, 4H), 1.36 (dq, J = 14.7, 7.4 Hz, 4H), 0.93 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 146.14, 143.22, 128.07, 126.62, 120.59 (q, J = 323.7 Hz), 69.98, 66.75 – 66.48 (m), 64.79 – 64.65 (m), 64.60, 56.04, 52.53 – 51.81 (m), 35.07, 33.33, 22.05, 13.29; ^{19}F NMR (376 MHz, Acetone-d6) δ -78.88.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((4-hexylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (5g): The general procedure "F" was applied to **1h** (0.823 g, 2.26 mmol, 1.0 equiv.), **4g** (1.00 g, 3.39 mmol, 1.5 equiv.), Millipore Milli-Q water (5 mL), and acetone (5 mL). The product (**5g**) was isolated as a clear liquid in 62.3% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.87 – 7.79 (m, 4H), 7.35 – 7.28 (m, 4H), 4.52 (s, 2H), 4.13 (dq, J = 5.3, 2.6 Hz, 4H), 4.08 (dq, J = 7.5, 2.6 Hz, 4H), 3.89 – 3.82 (m, 4H), 3.79 – 3.72 (m, 8H), 3.39 (s, 12H), 2.72 – 2.64 (m, 4H), 1.70 – 1.58 (m, 4H), 1.41 – 1.27 (m, 12H), 0.95 – 0.84 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 146.14, 143.24, 128.04, 126.63, 120.59 (q, J = 323.7 Hz), 69.99, 66.81 – 66.42 (m), 64.86 – 64.61 (m), 64.61, 56.02, 52.44 – 52.06 (m), 35.38, 31.50, 31.16, 28.75, 22.37, 13.47; 19F NMR (376 MHz, Acetone-d6) δ -78.89.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((4-octylphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (5h): The general procedure "F" was applied to **1h** (1.44 g, 3.94 mmol, 1.0 equiv.), **4h** (2.50 g, 5.90 mmol, 1.5 equiv.), Millipore Milli-Q water (15 mL), and acetone (15 mL). The product (**5h**) was isolated as a yellow liquid in 97.9% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.86 – 7.78 (m, 4H), 7.35 – 7.25 (m, 4H), 4.55 (s, 2H), 4.16 – 4.11 (m, 4H), 4.08 (dq, J = 5.1, 2.5 Hz, 4H), 3.89 – 3.84 (m, 4H), 3.78 – 3.73 (m, 8H), 3.39 (s, 12H), 2.72 – 2.63 (m, 4H), 1.70 – 1.59 (m, 4H), 1.41 – 1.23 (m, 20H), 0.93 – 0.85 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 146.11, 143.26, 128.02, 126.64, 120.59 (q, J = 323.7 Hz), 69.99, 66.75 – 66.65 (m), 64.79 – 64.67 (m), 64.61, 56.01, 52.64 – 51.49 (m), 35.39, 31.71, 31.21, 29.26, 29.10, 29.10, 22.42, 13.48; ^{19}F NMR (376 MHz, Acetone-d6) δ -78.90.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) (mesitylsulfonyl)((trifluoromethyl)sulfonyl)azanide (5i): The general procedure "F" was applied to **1h** (3.45 g, 9.43 mmol, 1.0 equiv.), **4i** (5.00 g, 14.2 mmol, 1.5 equiv.), and Millipore Milli-Q water (25 mL). The product (**5i**) was isolated as a clear liquid in 90.2% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 6.91 (s, 4H), 4.49 (t, J = 4.9 Hz, 2H), 4.14 (tq, J = 5.0, 2.6 Hz, 4H), 4.08 (dq, J = 5.2, 2.5 Hz, 4H), 3.88 – 3.83 (m, 4H), 3.78 – 3.73 (m, 8H), 3.38 (s, 12H), 2.68 (s, 12H), 2.25 (s, 6H); ^{13}C{^{1}H} (101 MHz, Acetone-d6) δ 139.91, 139.89, 138.23, 130.81, 120.60 (q, J = 324.0 Hz), 69.99, 67.08 – 66.16 (m), 64.80 – 64.67 (m), 64.60, 56.01, 52.41 – 52.03 (m), 22.26, 19.96; ^{19}F NMR (376 MHz, Acetone-d6) δ -78.91.

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((4-methoxyphenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (5j): The general procedure "F" was applied

to **1h** (2.68 g, 7.33 mmol, 1.0 equiv.), **4j** (3.75 g, 11.0 mmol, 1.5 equiv.), and Millipore Milli-Q water (20 mL). The product (**5j**) was isolated as a clear liquid in 83.3% yield. ^{1}H NMR (400 MHz, Methanol-d4) δ 7.89 – 7.81 (m, 4H), 7.07 – 6.98 (m, 4H), 4.04 – 3.98 (m, 4H), 3.95 (ddd, J = 7.4, 4.9, 2.6 Hz, 4H), 3.87 (s, 6H), 3.71 – 3.67 (m, 8H), 3.61 – 3.54 (m, 4H), 3.23 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Methanol-d4) δ 162.38, 136.18, 128.33, 120.19 (q, J = 322.4 Hz), 113.26, 69.88, 66.51 (t, J = 2.7 Hz), 64.66 – 64.53 (m), 64.38, 55.57, 54.74, 51.90 – 51.71 (m); ^{19}F NMR (376 MHz, Methanol-d4) δ -79.73.

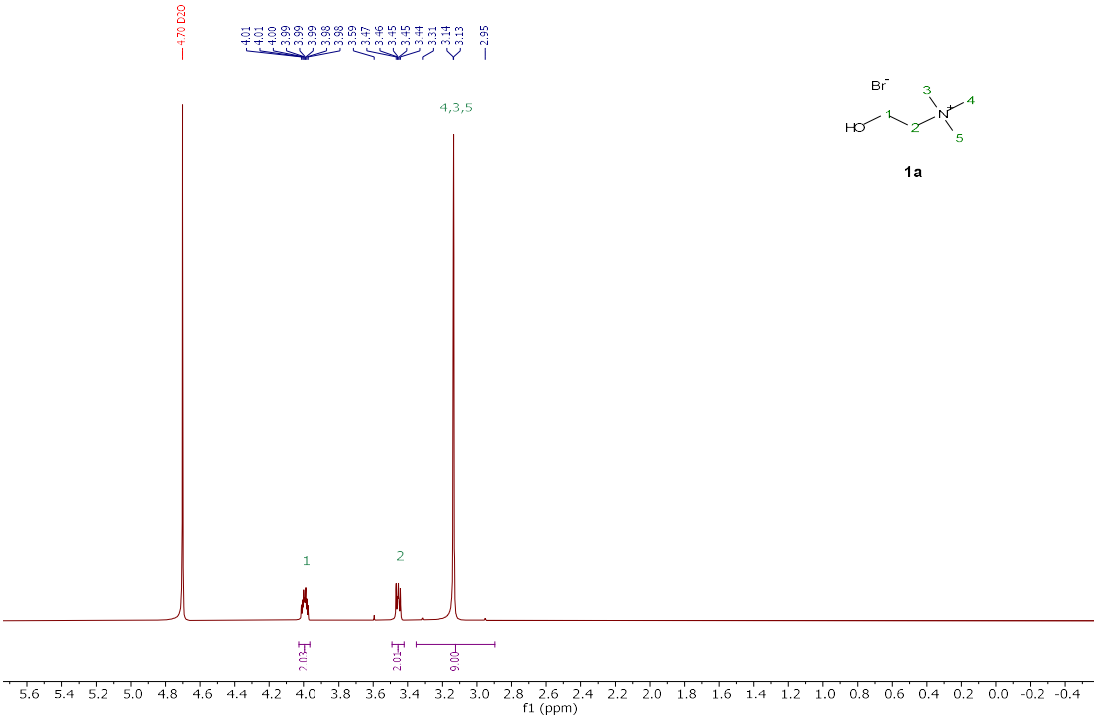
2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((trifluoromethyl)sulfonyl)((2,4,6-trifluorophenyl)sulfonyl)azanide (5k): The general procedure "F" was applied to **1h** (2.00 g, 5.47 mmol, 1.0 equiv.), **4k** (3.00 g, 8.21 mmol, 1.5 equiv.), and Millipore Milli-Q water (15 mL). The product (**5k**) was isolated as a yellow liquid in 87.7% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.04 – 6.93 (m, 4H), 4.53 (t, J = 4.7 Hz, 2H), 4.16 (dp, J = 7.2, 2.4 Hz, 4H), 4.12 (dq, J = 7.5, 2.7 Hz, 4H), 3.92 – 3.85 (m, 4H), 3.82 – 3.75 (m, 8H), 3.42 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 163.96 (dt, J = 251.7, 15.6 Hz), 160.46 (ddd, J = 257.5, 15.5, 7.4 Hz), 120.36 (q, J = 322.9 Hz), 119.79 (td, J = 17.2, 5.2 Hz), 101.06 (ddd, J = 28.5, 25.7, 4.0 Hz), 69.98, 66.98 – 66.54 (m), 64.83 – 64.70 (m), 64.60, 56.00, 52.38 – 52.07 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -79.16, -103.69 (d, J = 10.0 Hz), -105.12 (t, J = 10.1 Hz).

2,2'-(ethane-1,2-diylbis(oxy))bis(*N*-(2-hydroxyethyl)-*N*,*N*-dimethylethan-1-aminium) ((perfluorophenyl)sulfonyl)((trifluoromethyl)sulfonyl)azanide (5l): The general procedure "F" was applied to **1h** (2.19 g, 5.98 mmol, 1.00 equiv.), **4l** (3.00 g, 7.48 mmol, 1.25 equiv.), and Millipore Milli-Q water (15 mL). The product (**5l**) was isolated as a yellow liquid in 92.9% yield. ^{1}H NMR (400 MHz, Acetone-d6) δ 4.52 (s, 2H), 4.20 – 4.07 (m, 8H), 3.92 – 3.85 (m, 4H), 3.81 – 3.73 (m, 8H), 3.42 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d6) δ 145.93 – 142.95 (m), 142.76 (dtt, J = 255.5, 13.6, 4.8 Hz), 139.31 – 135.88 (m), 121.11 – 120.29 (m), 120.19 (q, J = 322.4 Hz), 69.98, 66.94 – 66.55 (m), 64.90 – 64.67 (m), 64.59, 55.99, 52.45 – 52.12 (m); ^{19}F NMR (376 MHz, Acetone-d6) δ -79.32, -138.06 (dp, J = 16.5, 5.6 Hz), -152.76 (tt, J = 20.5, 5.3 Hz), -163.71 – -164.22 (m).

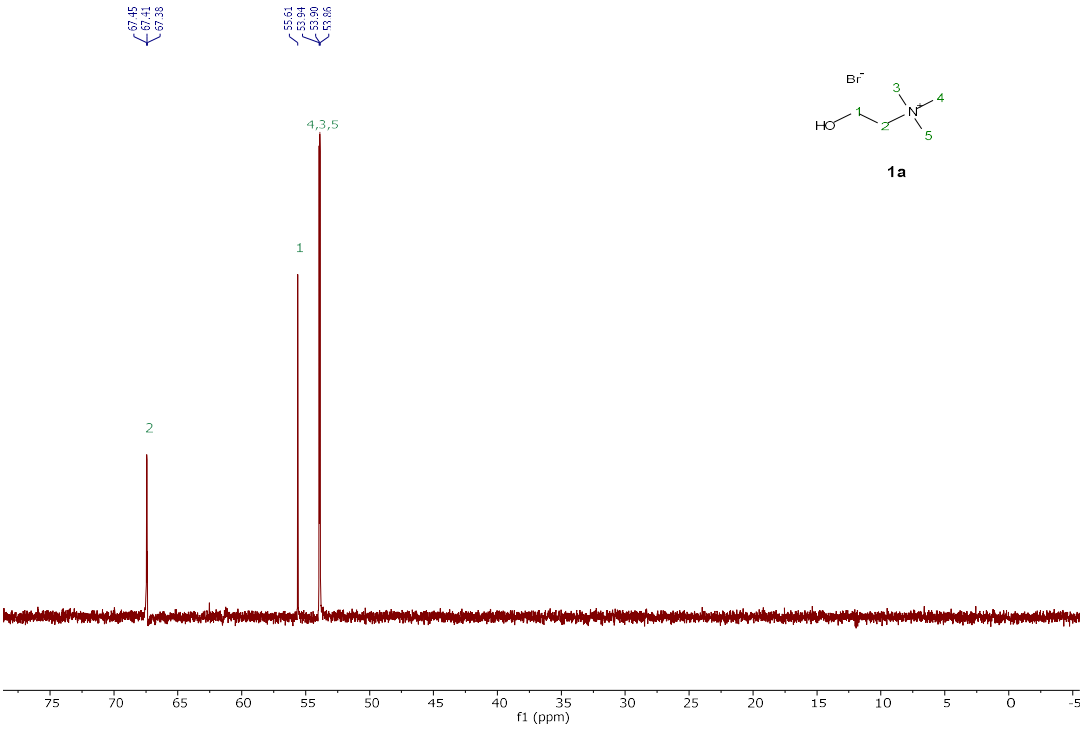
Nuclear Magnetic Resonance Spectra:

[chol][Br], **1a**

^{1}H NMR (400 MHz, Deuterium Oxide)

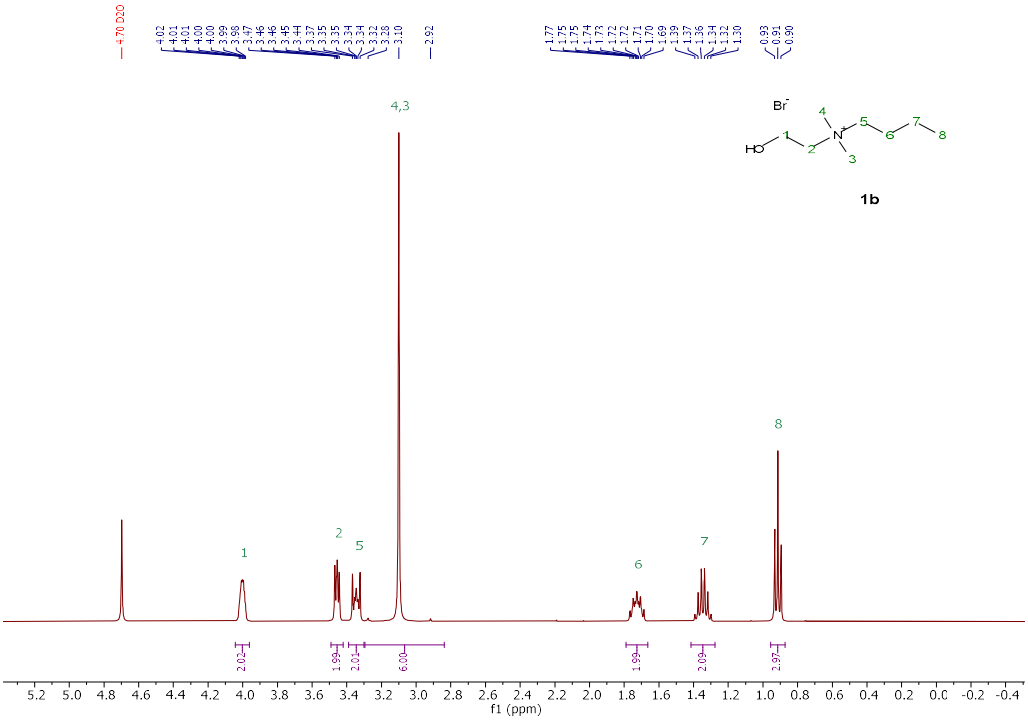


^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

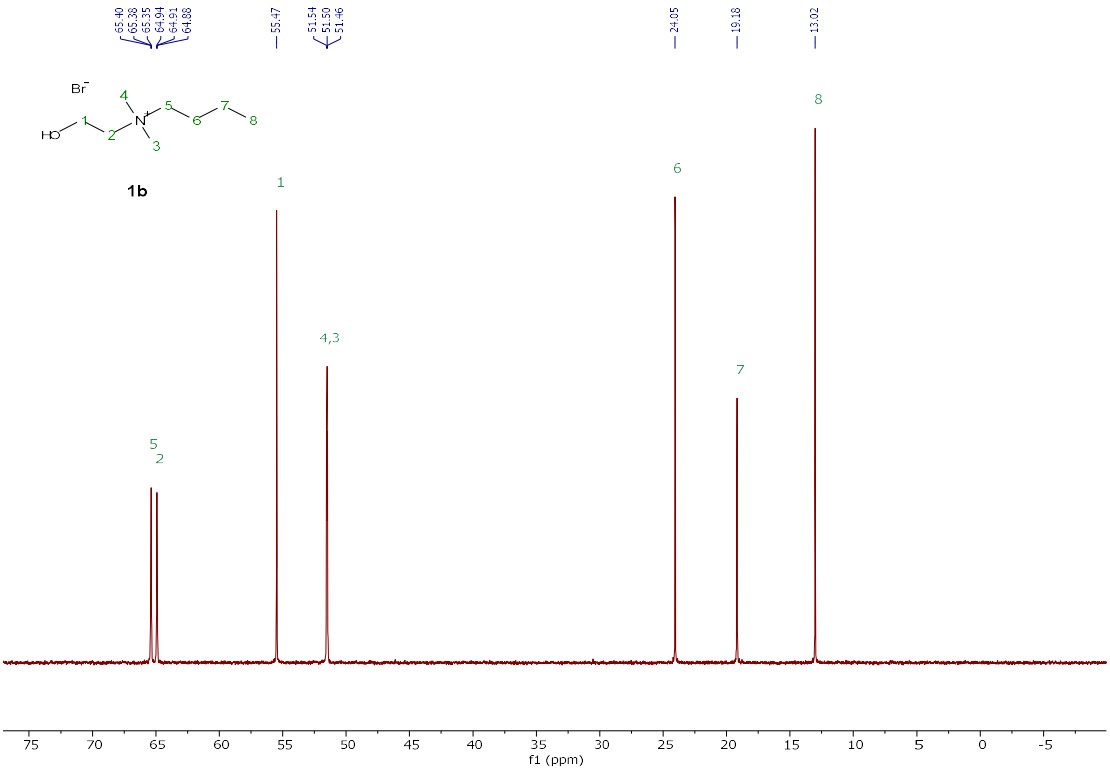


[$N_{1,1,4,2OH}$][Br], **1b**

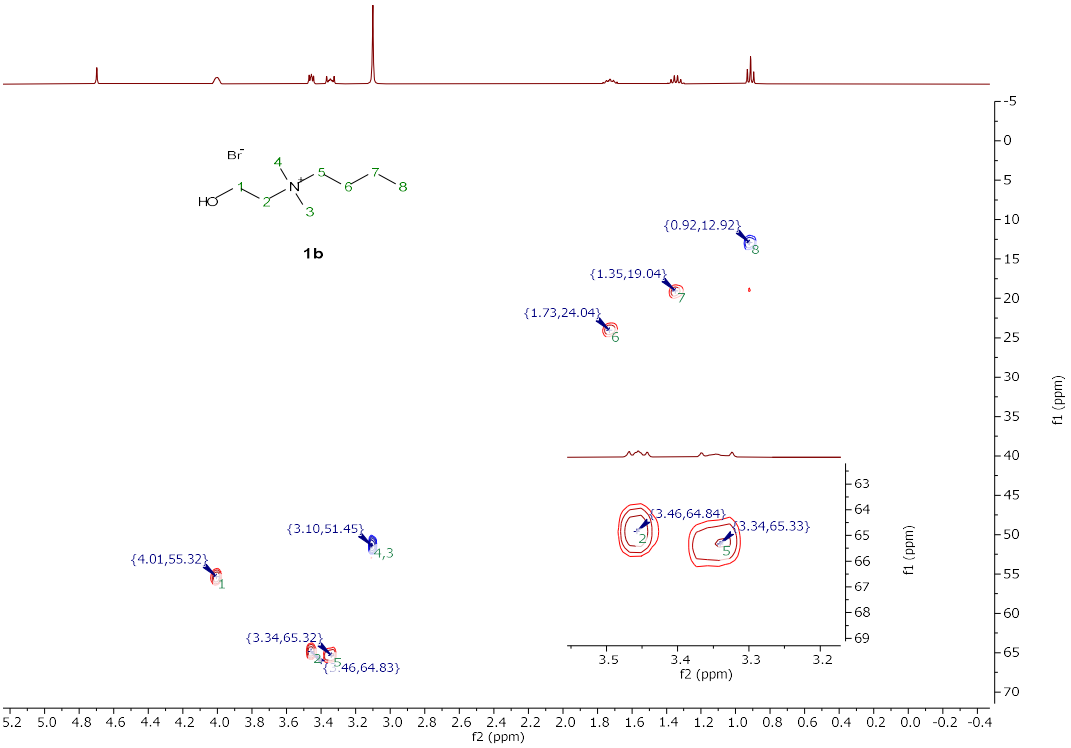
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

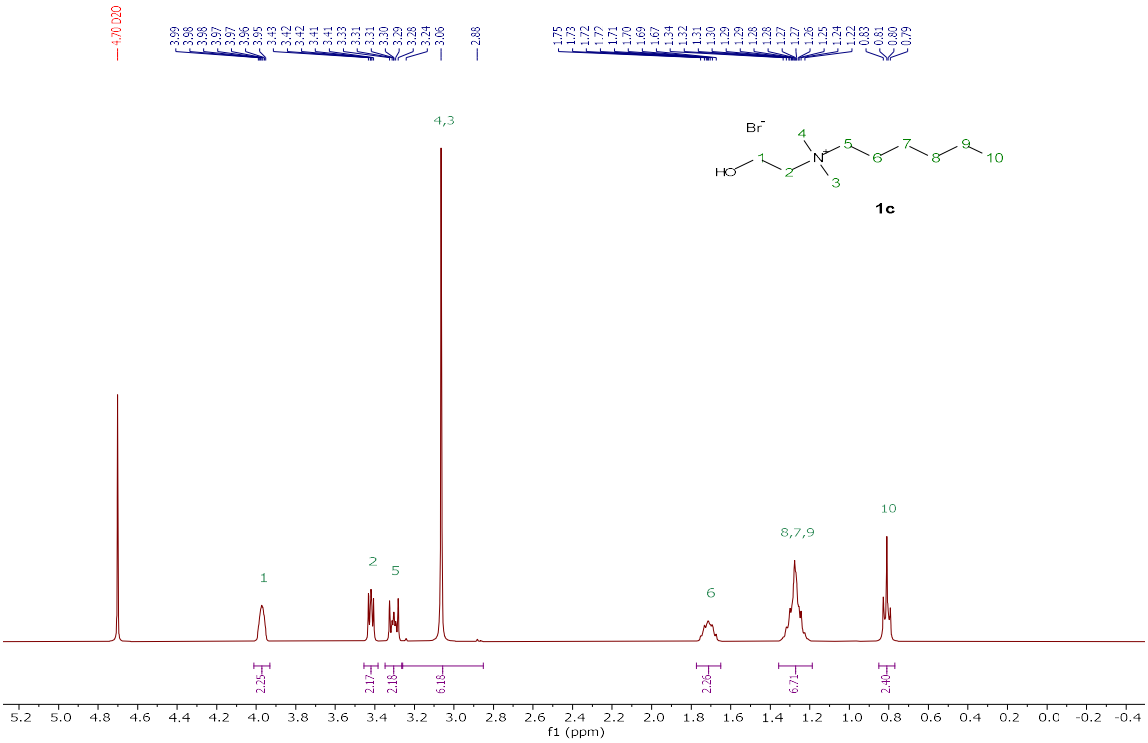


HSQC (Deuterium Oxide)

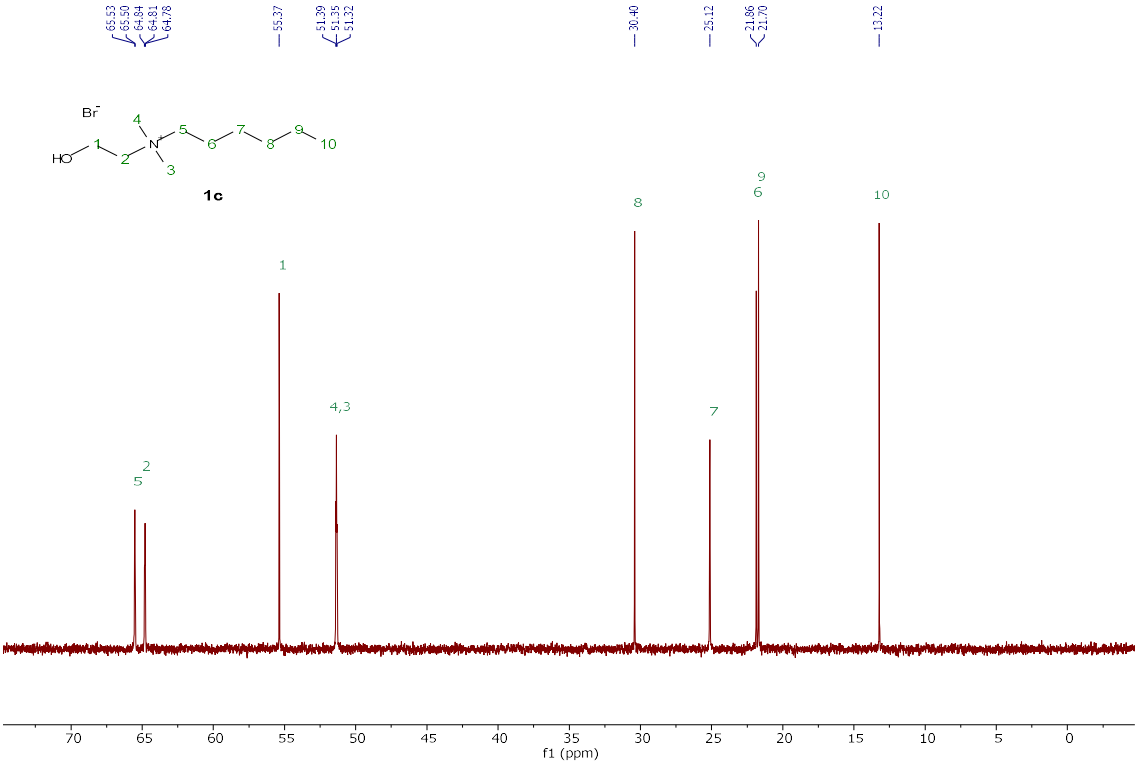


[$N_{1,1,6,2OH}$][Br], **1c**

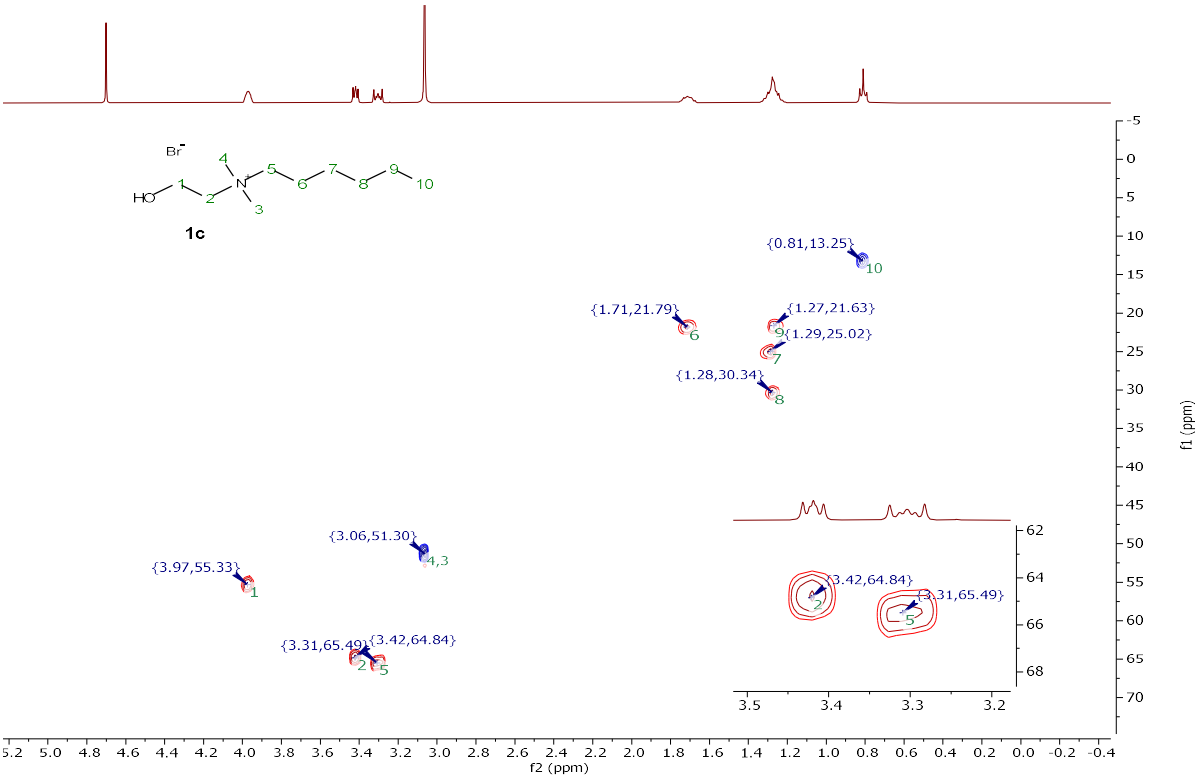
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

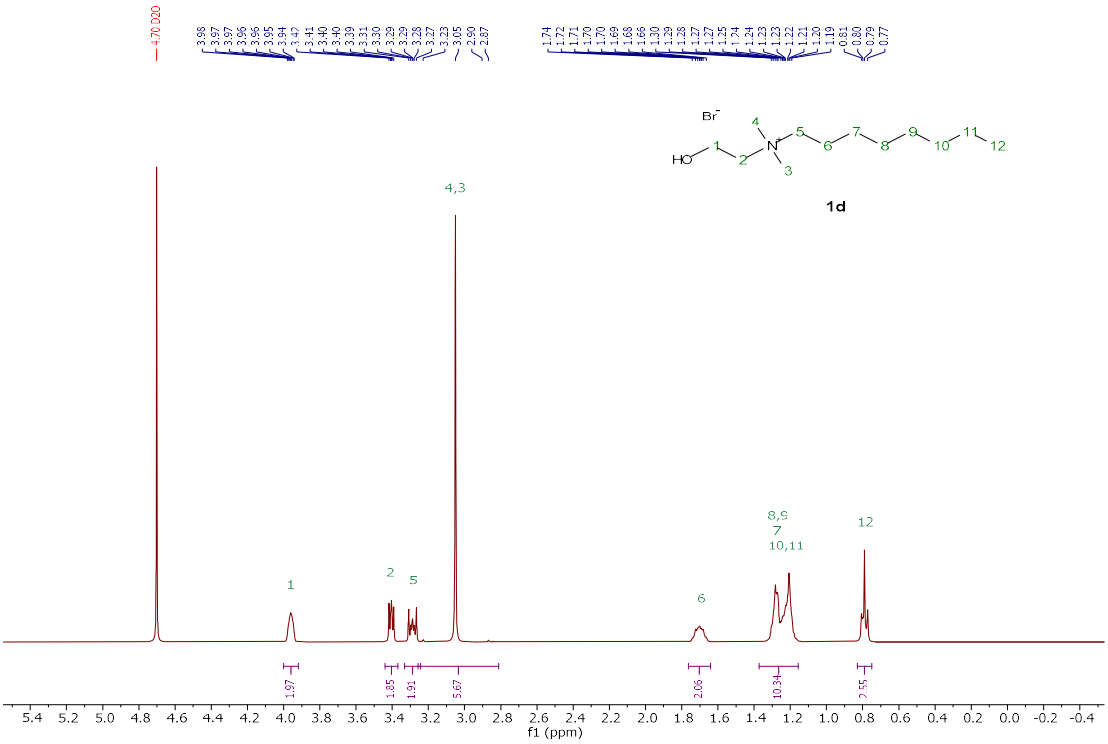


HSQC (Deuterium Oxide)

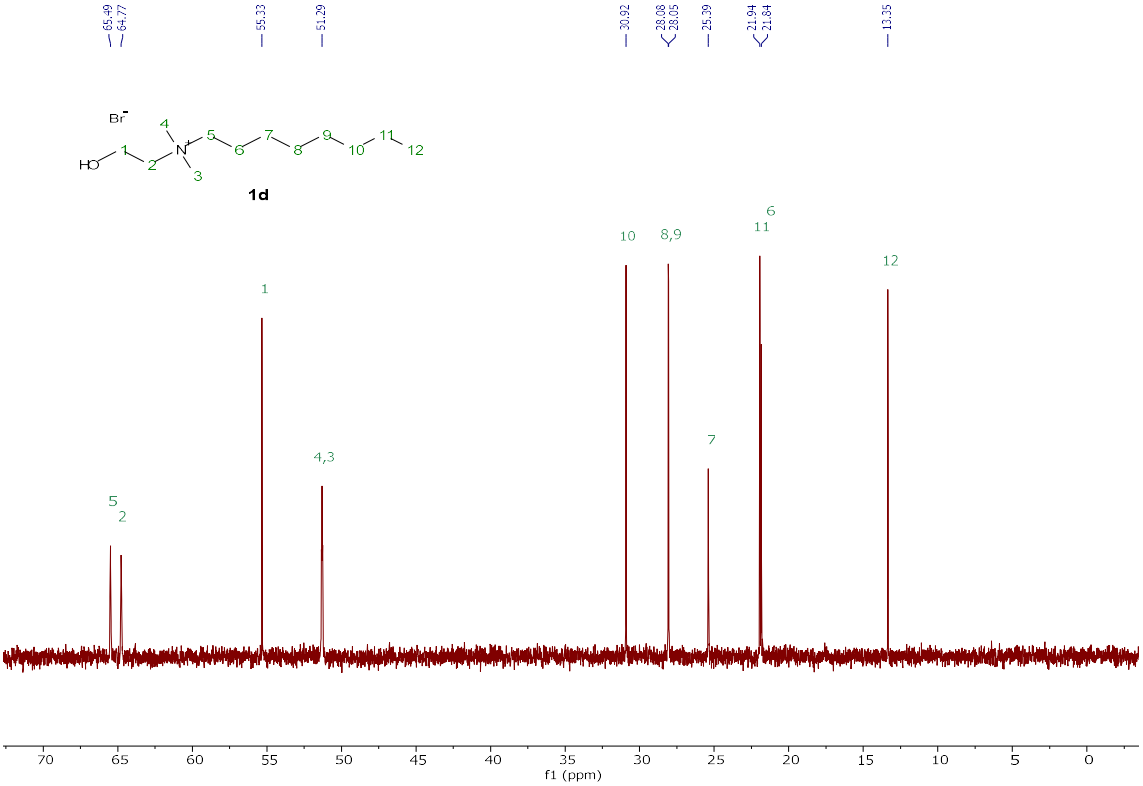


[$N_{1,1,8,2OH}$][Br], **1d**

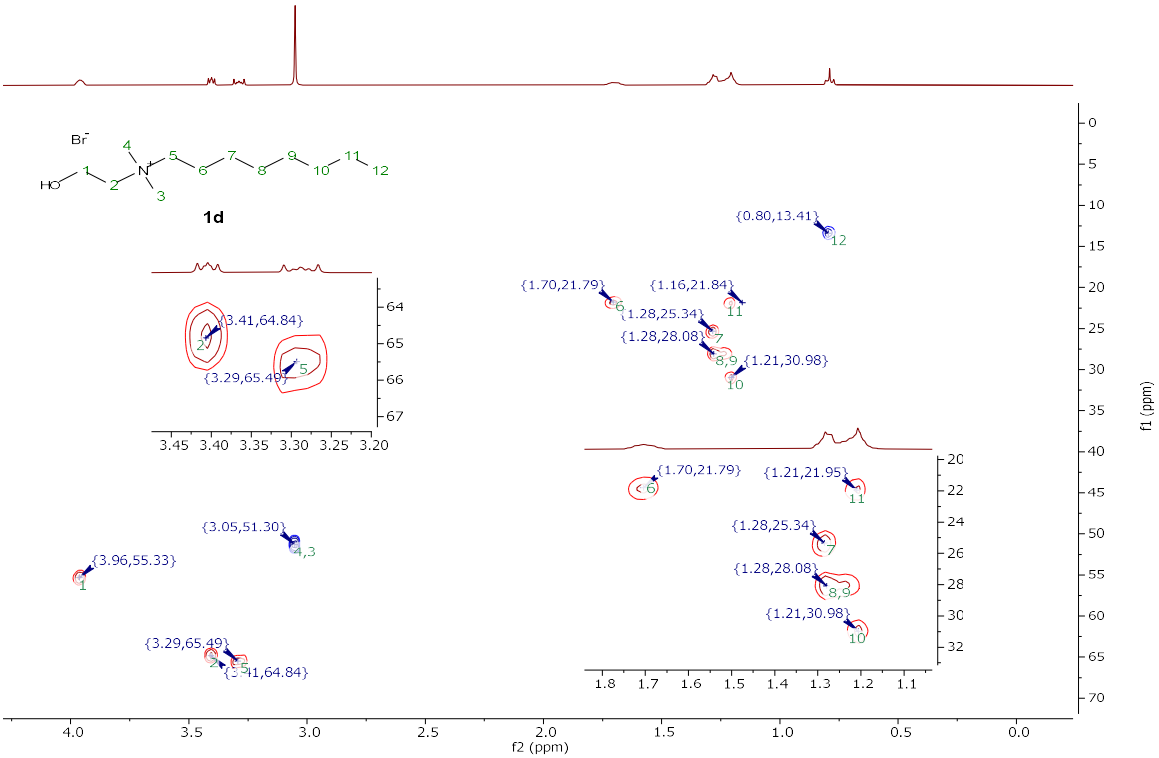
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

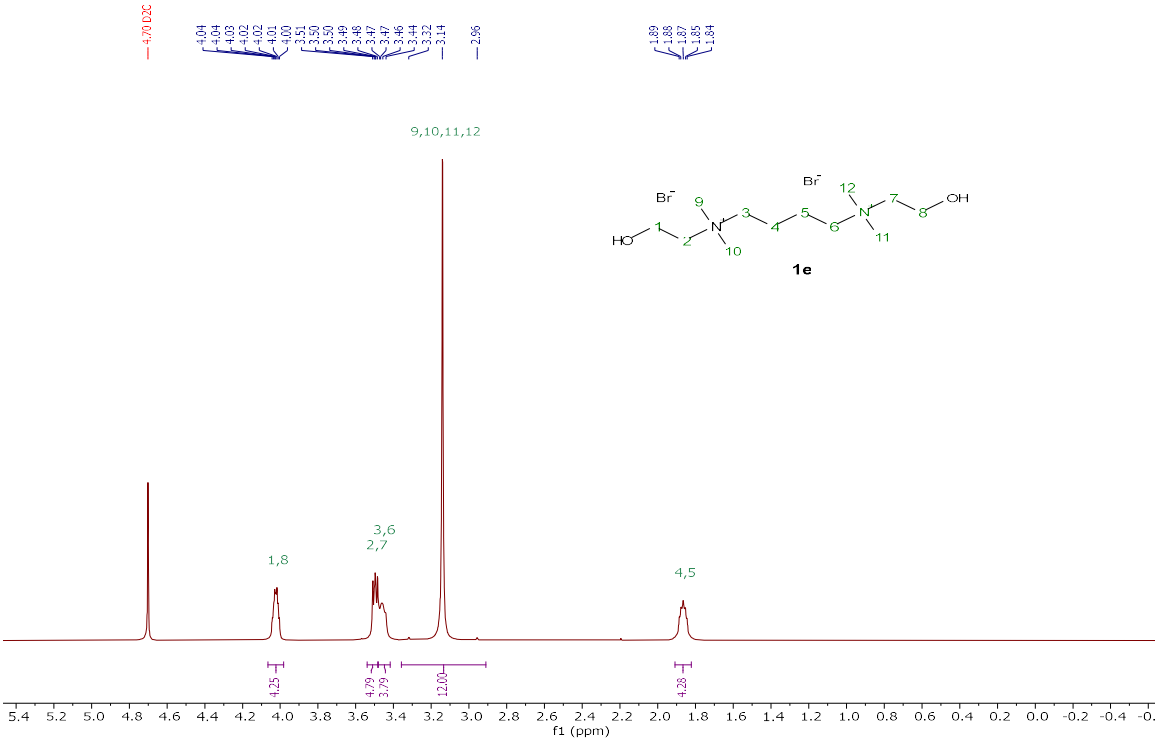


HSQC (Deuterium Oxide)

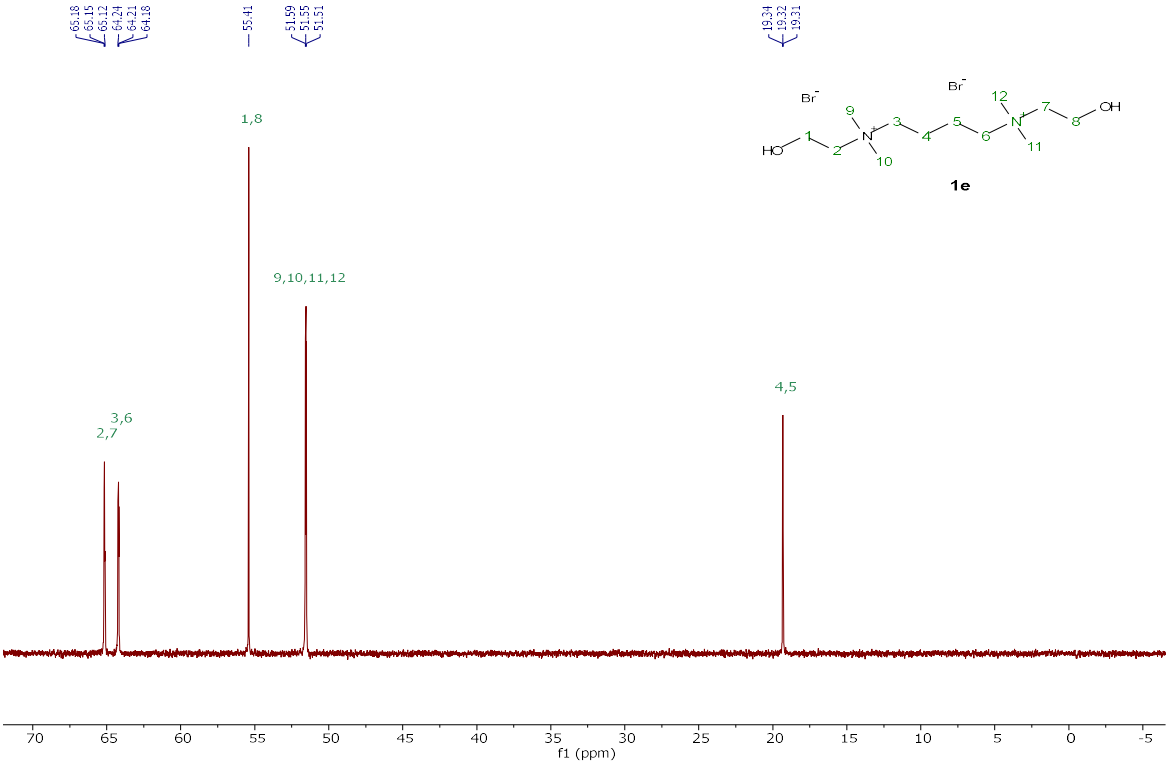


[DC-4][2Br], **1e**

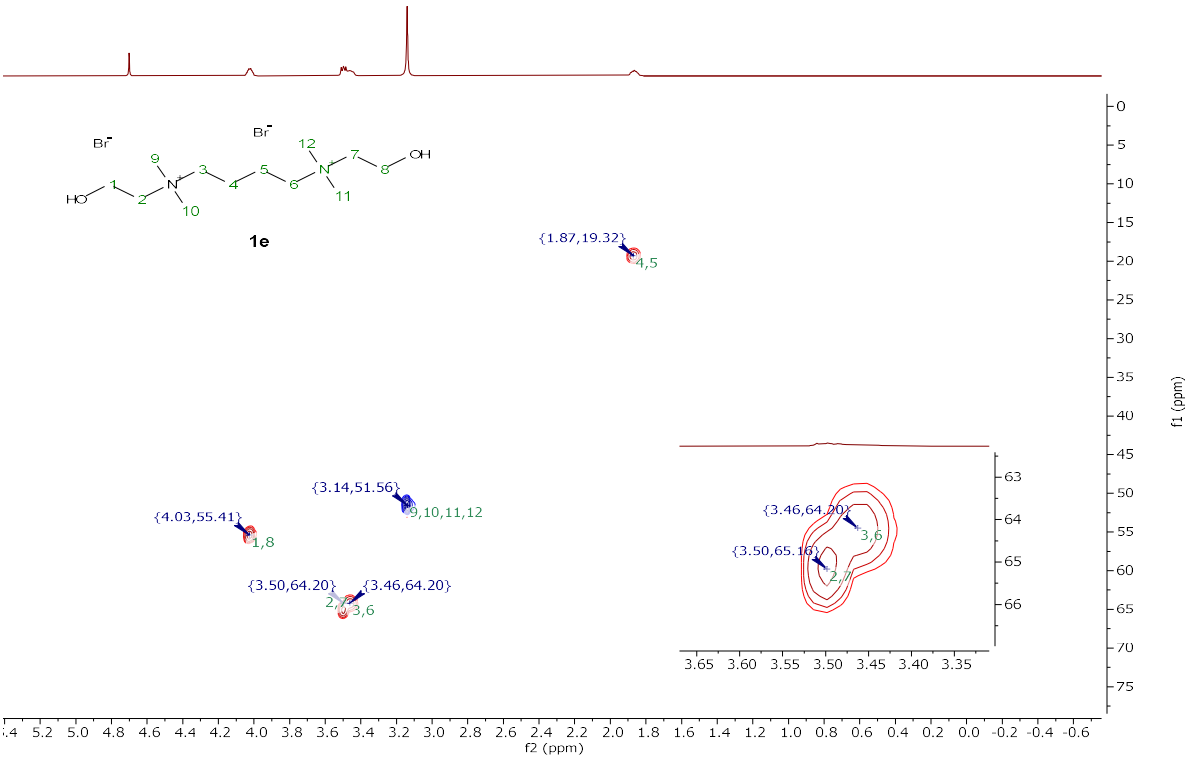
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

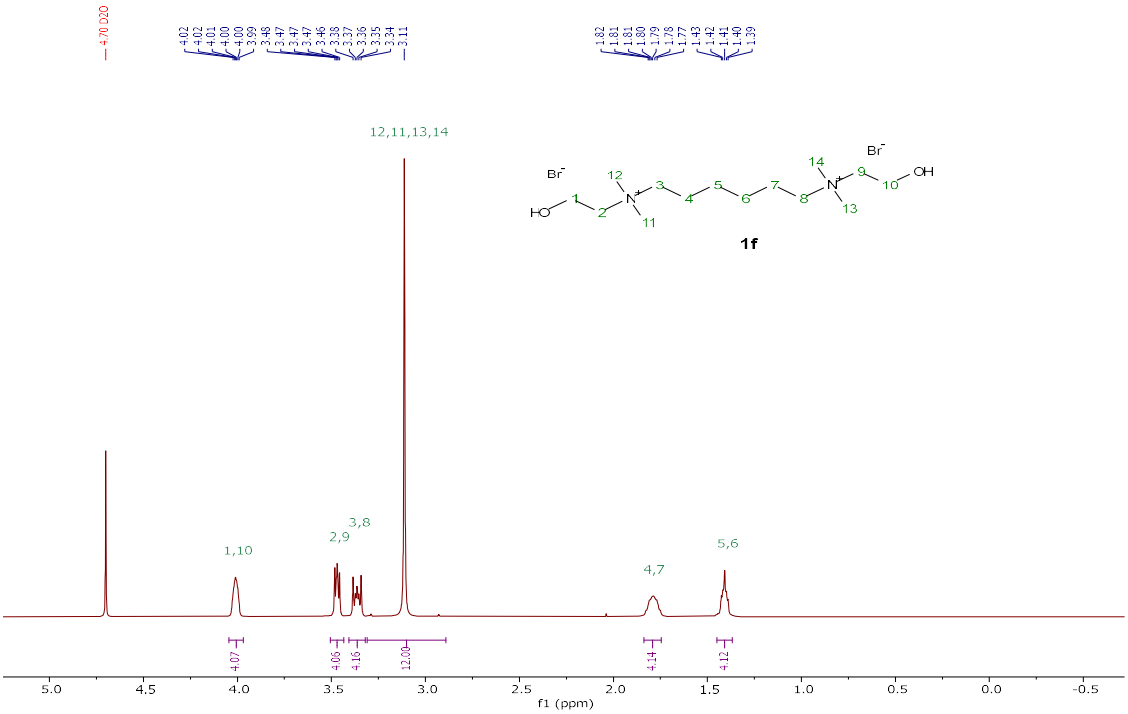


HSQC (Deuterium Oxide)

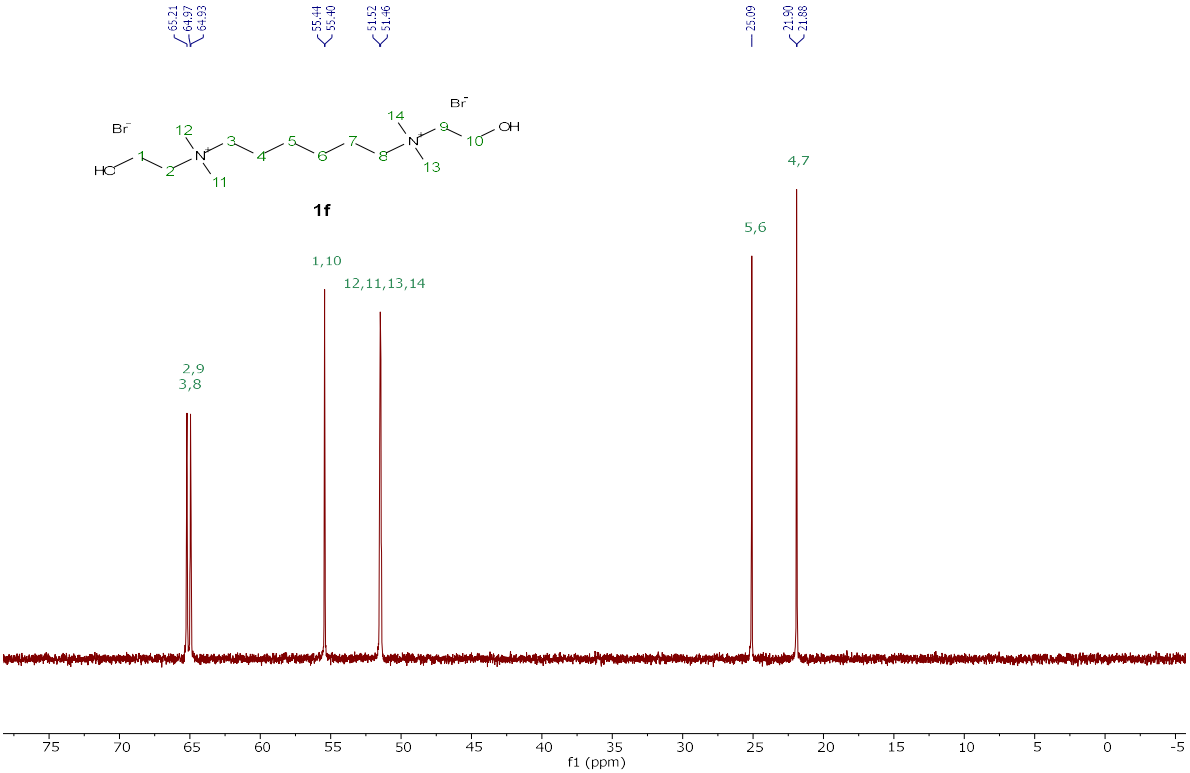


[DC-6][2Br], **1f**

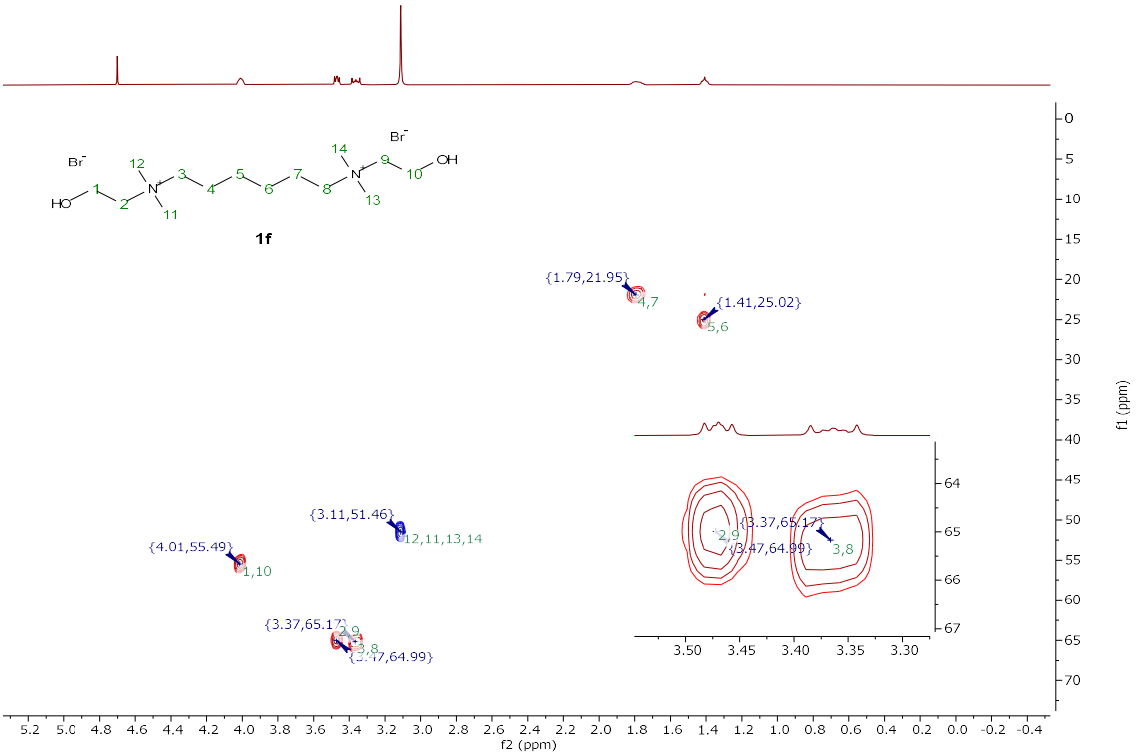
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

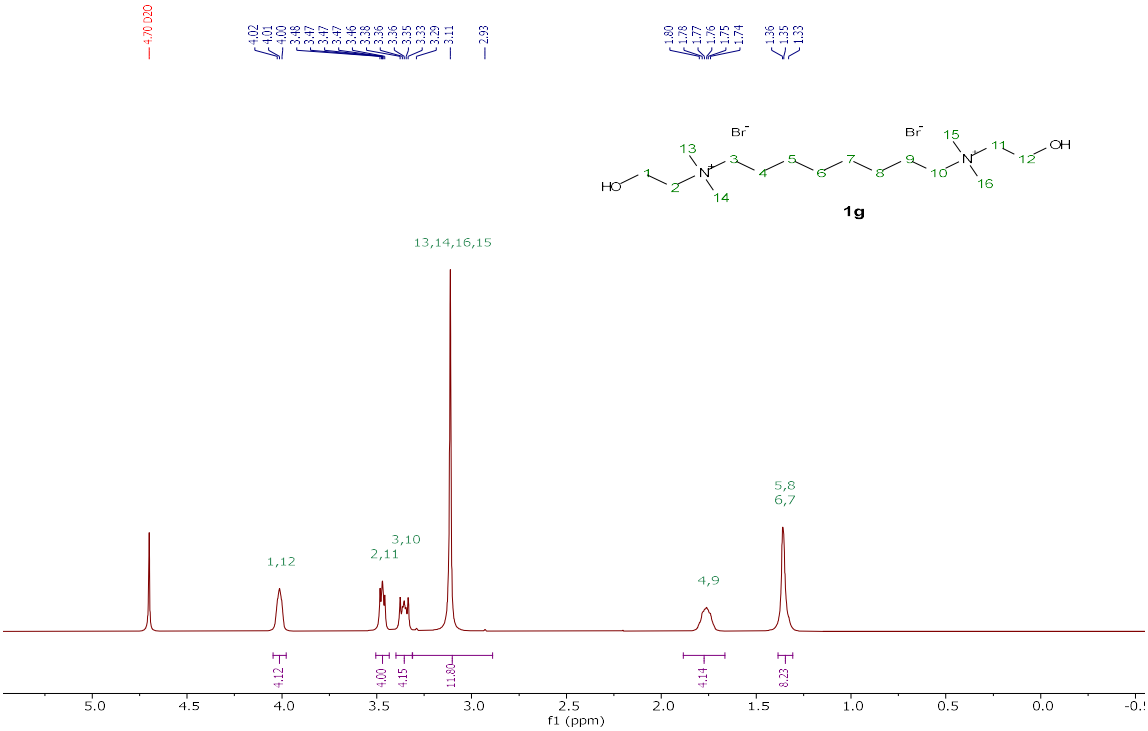


HSQC (Deuterium Oxide)

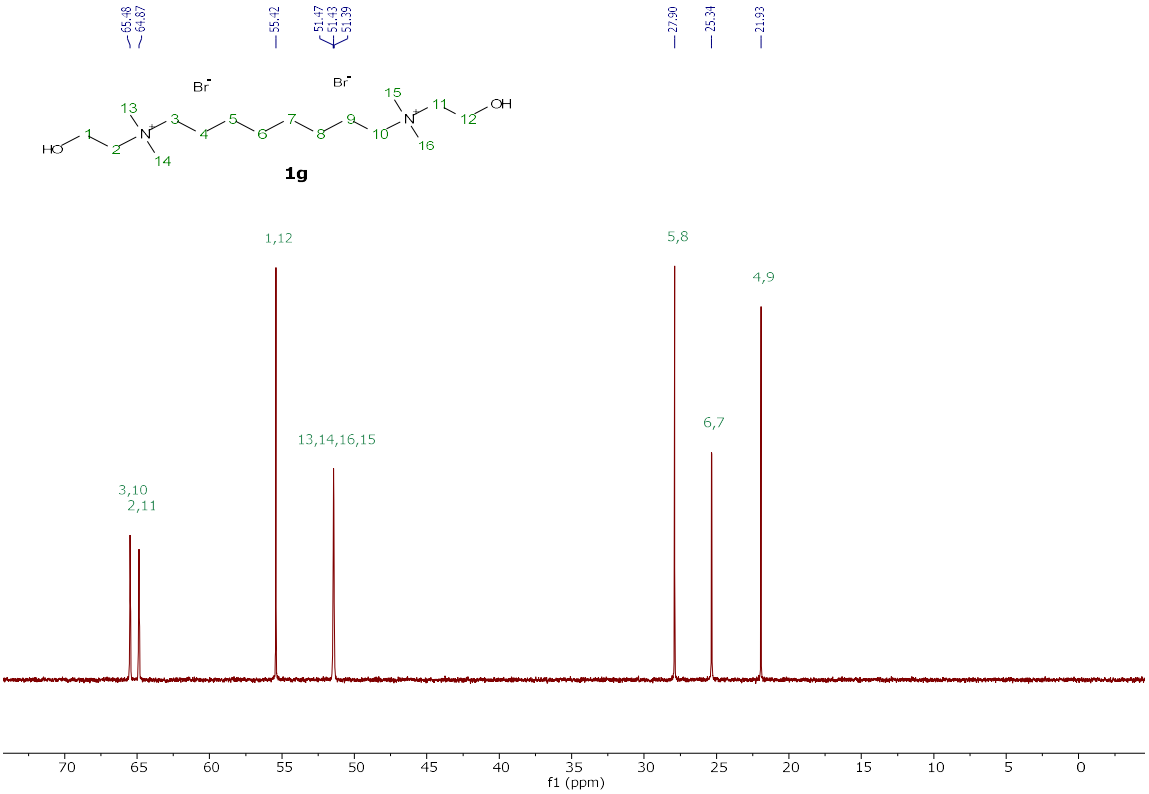


[DC-8][2Br], **1g**

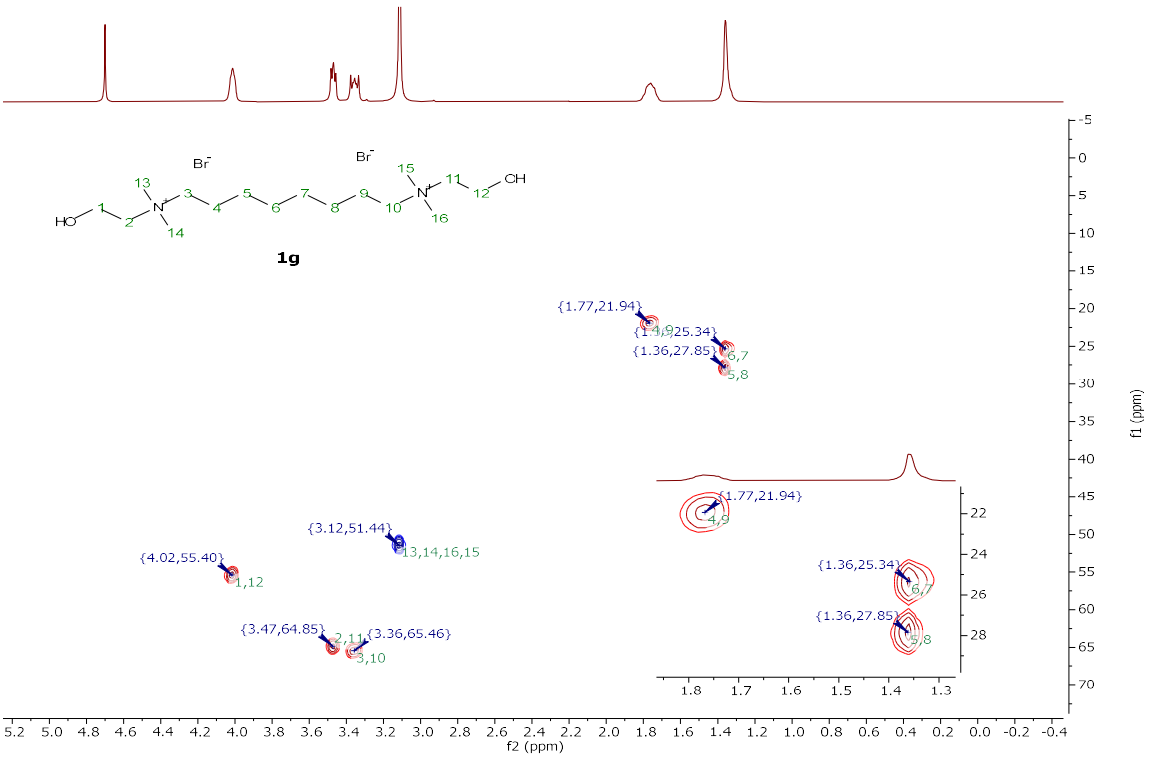
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

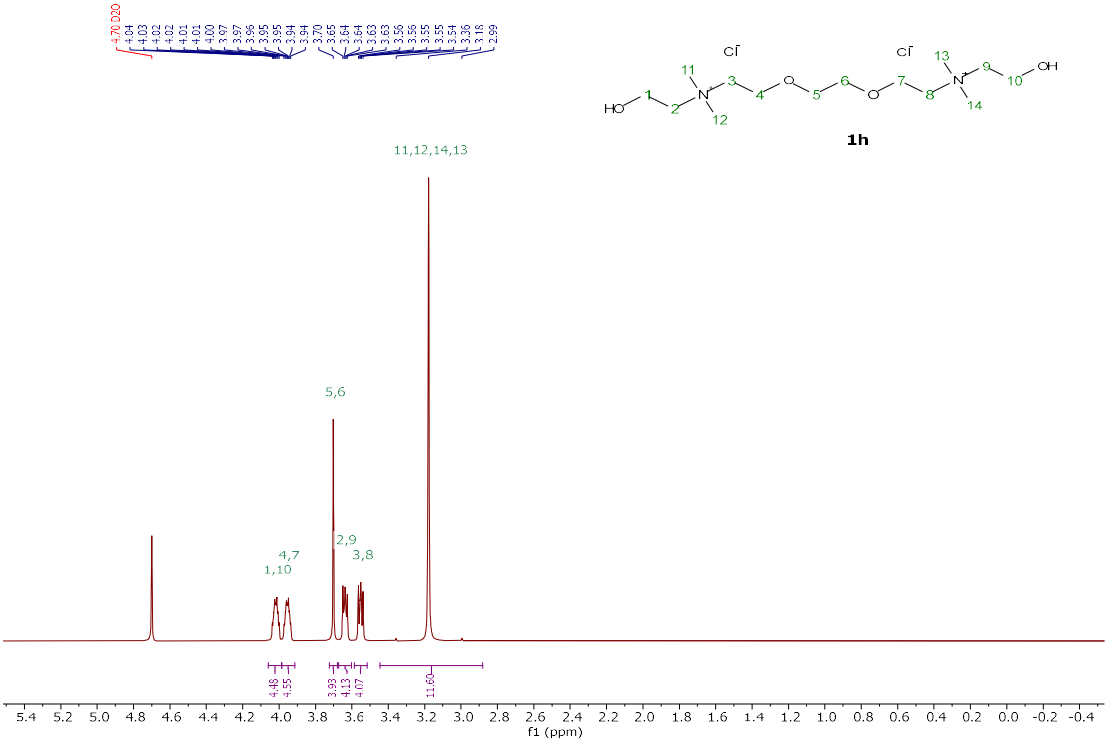


HSQC (Deuterium Oxide)

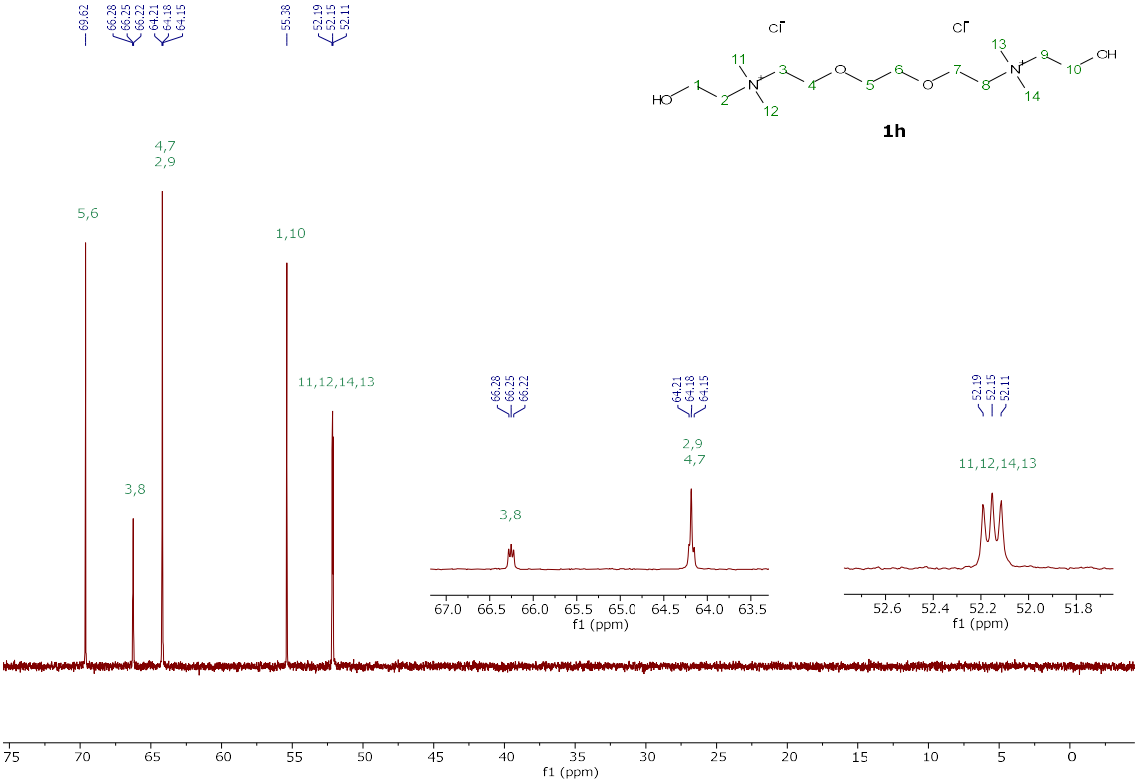


[DC-ether][2Cl], **1h**

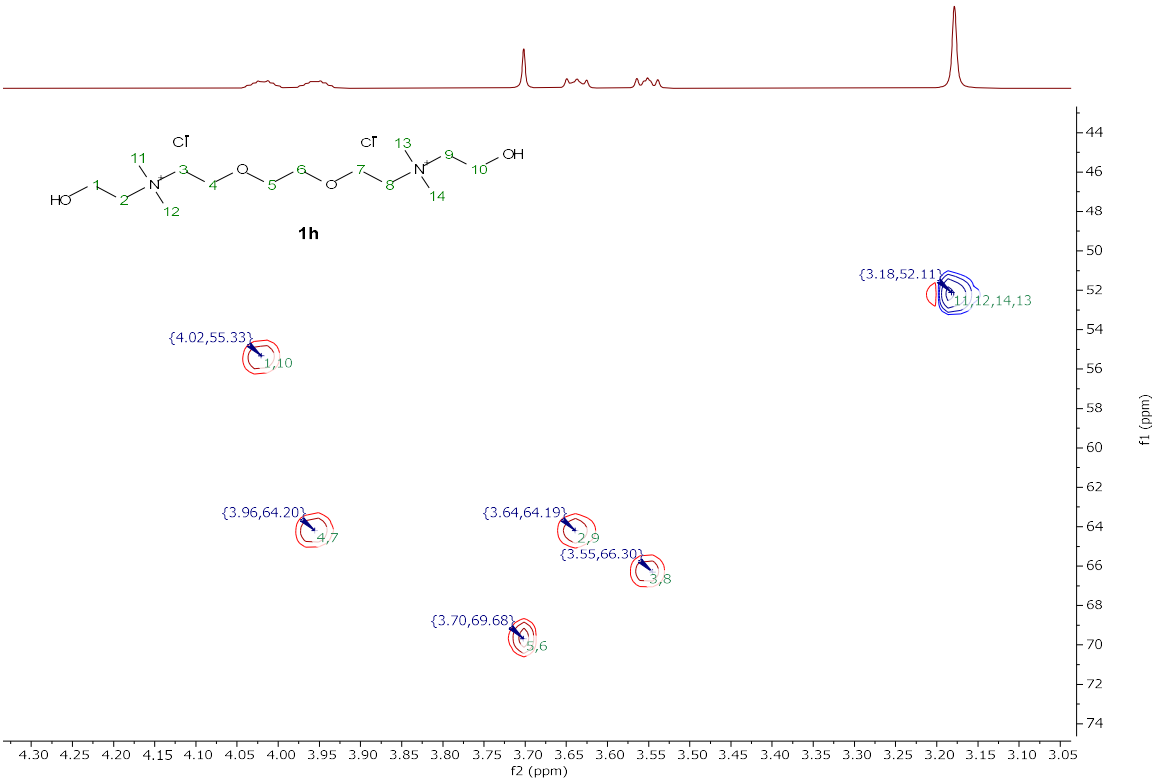
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

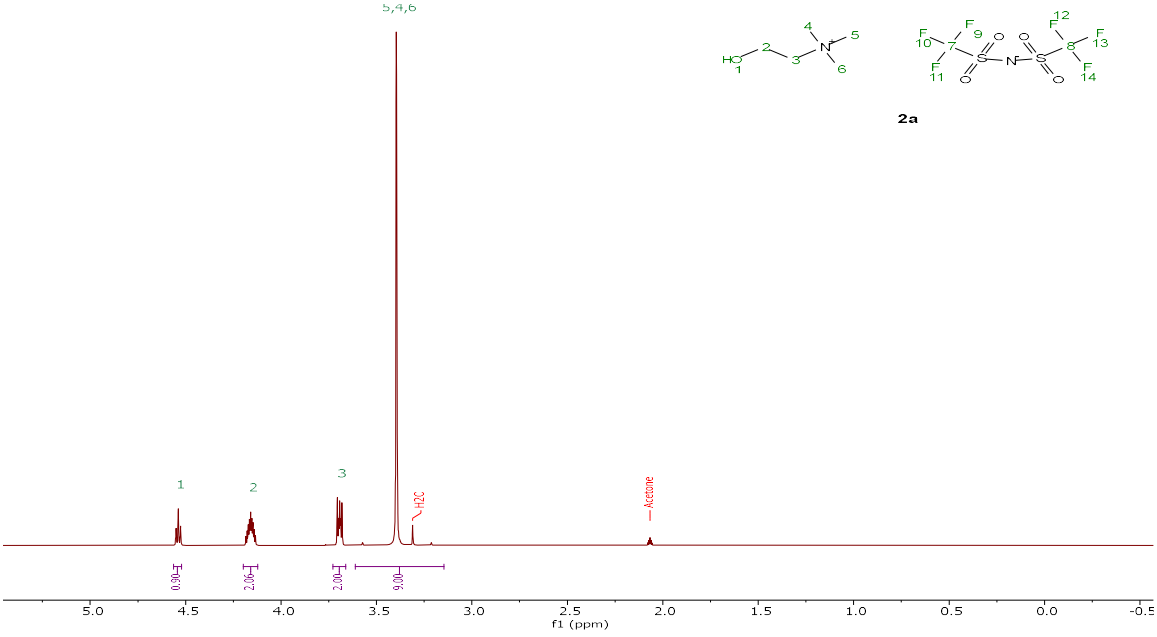


HSQC (Deuterium Oxide)

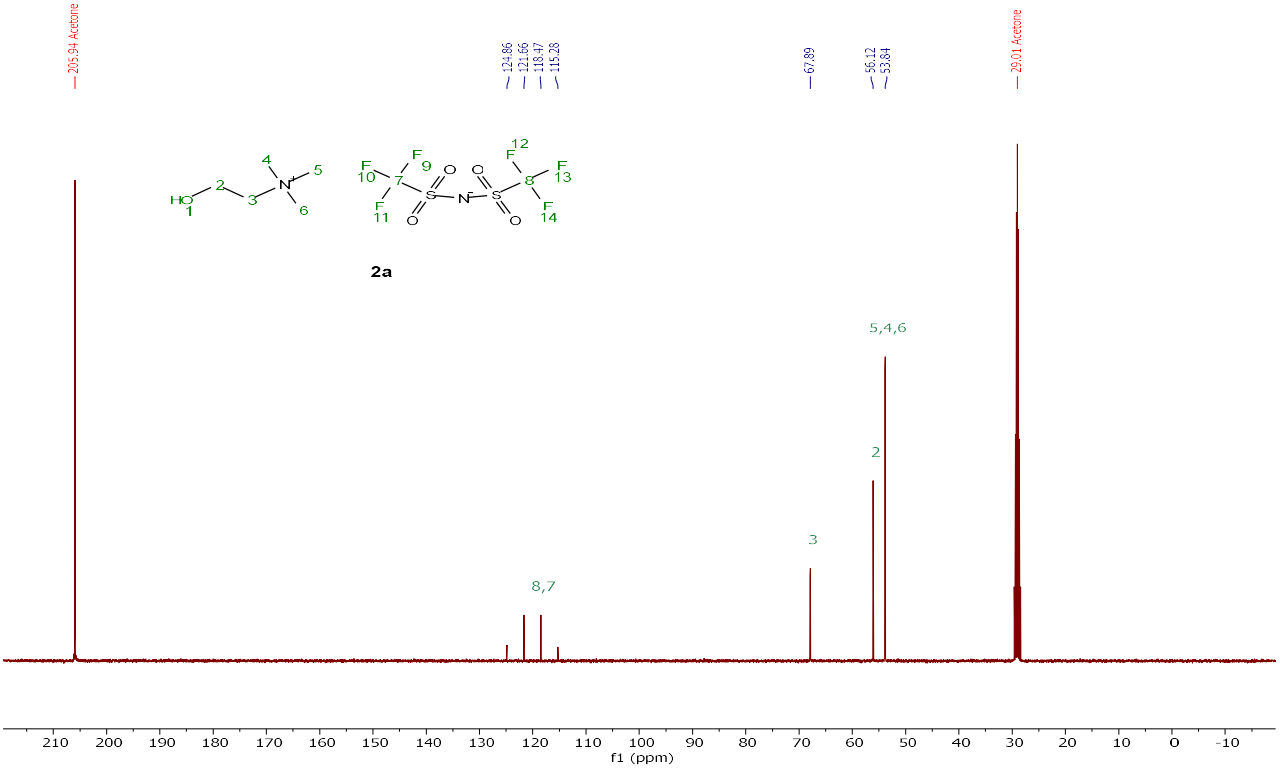


[chol][NTf_2], **2a**

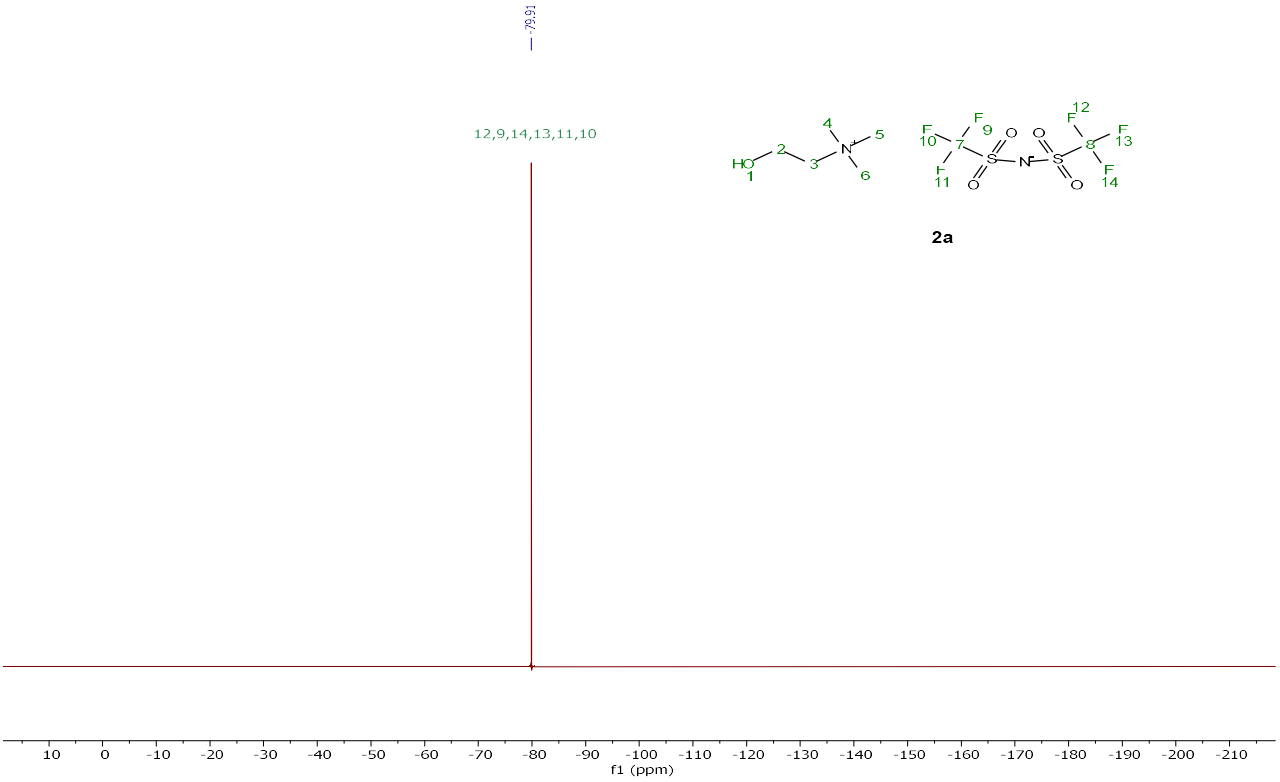
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

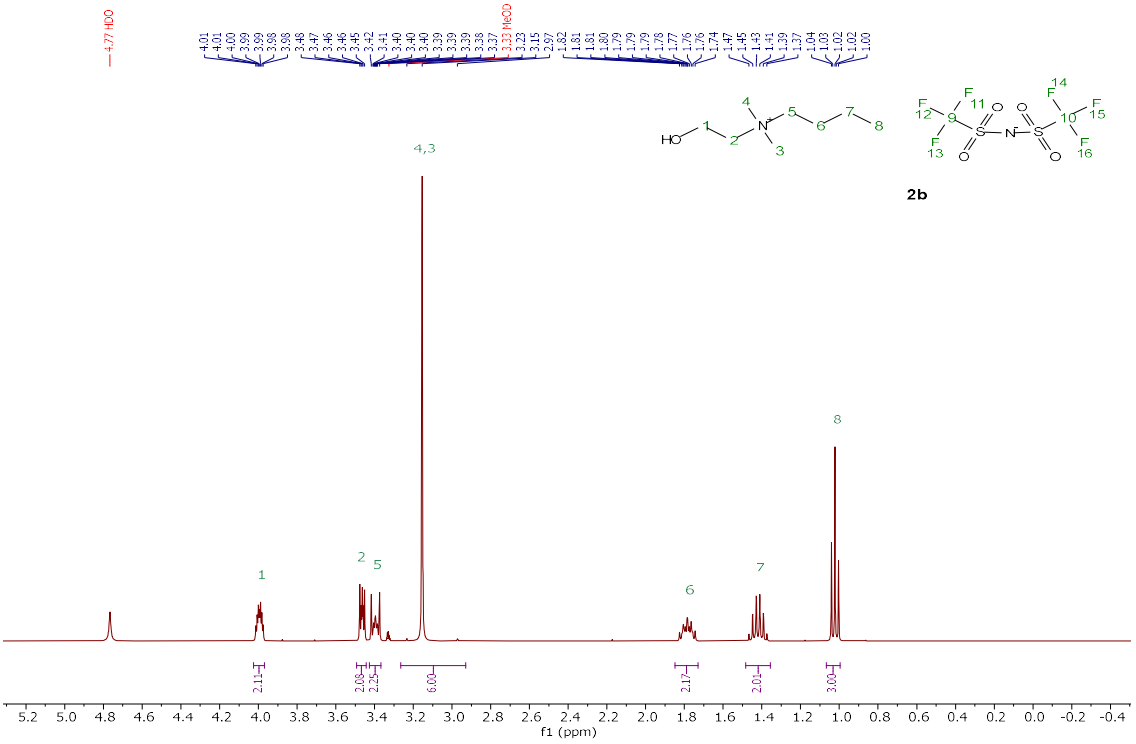


^{19}F NMR (376 MHz, Acetone-d6)

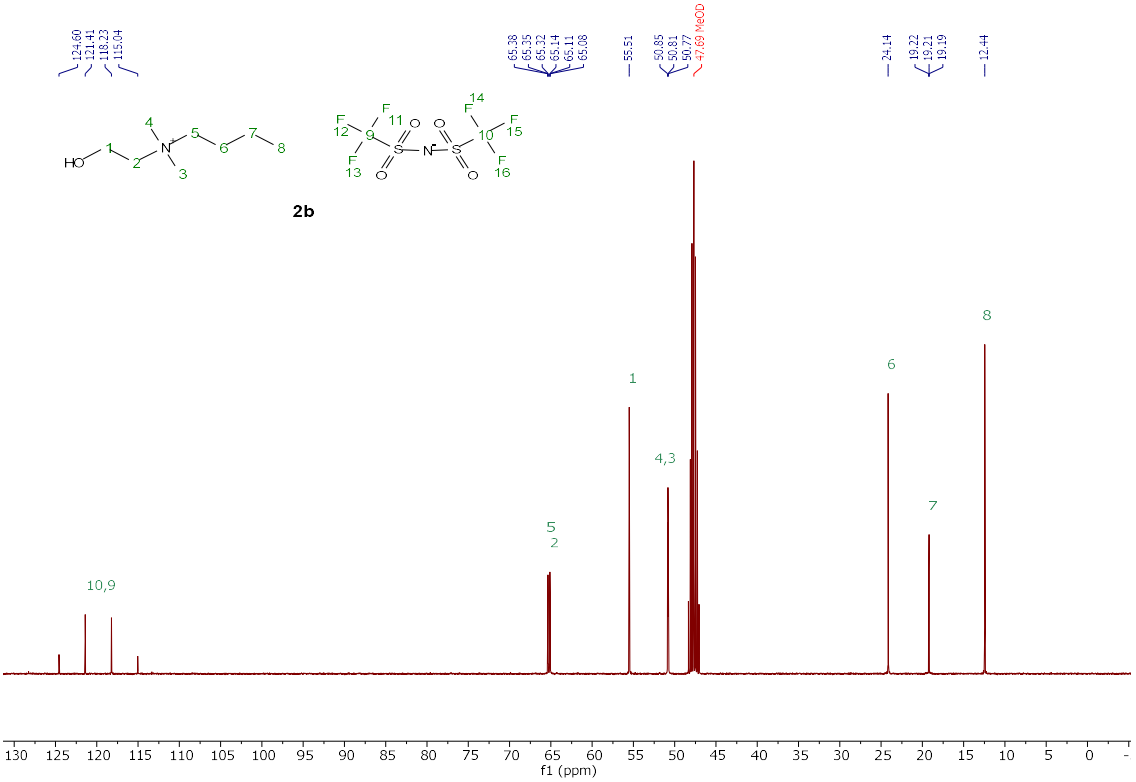


$[N_{1,1,4,2OH}][NTf_2]$, **2b**

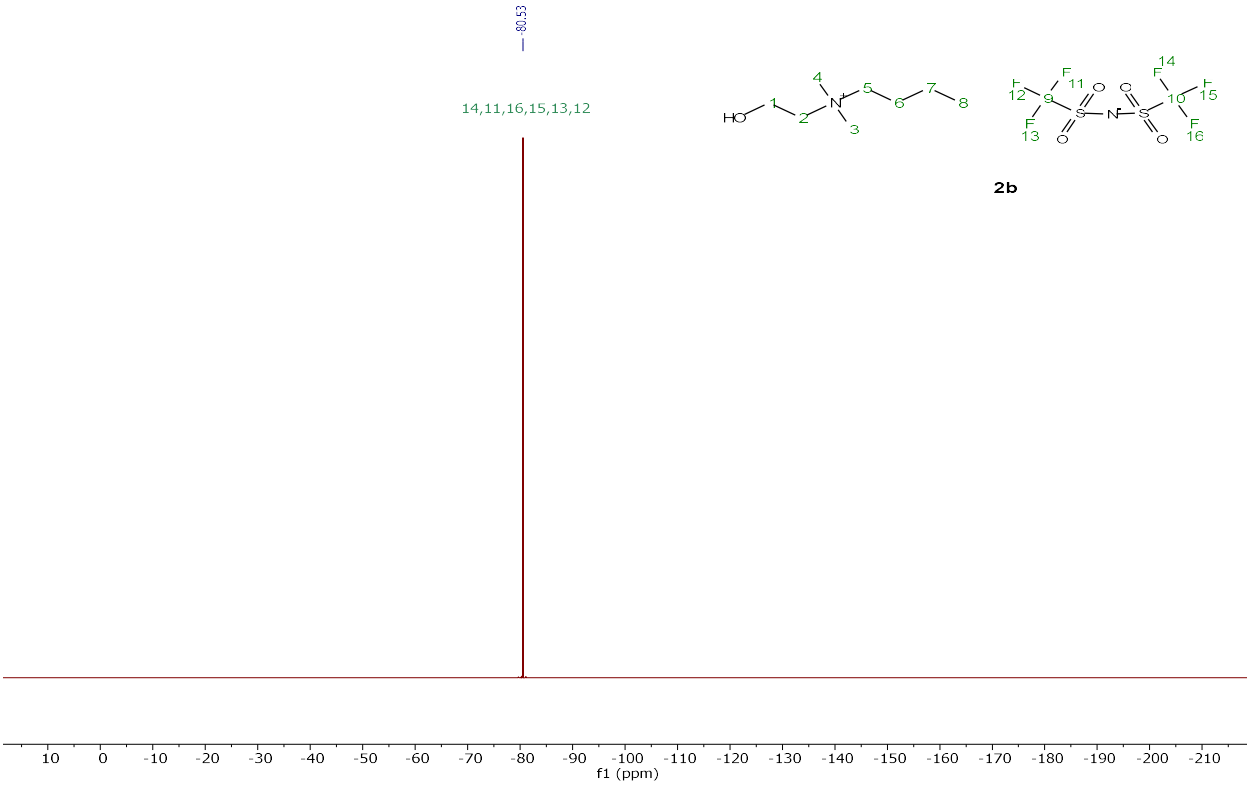
^{1}H NMR (400 MHz, Methanol-d4)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Methanol-d4)

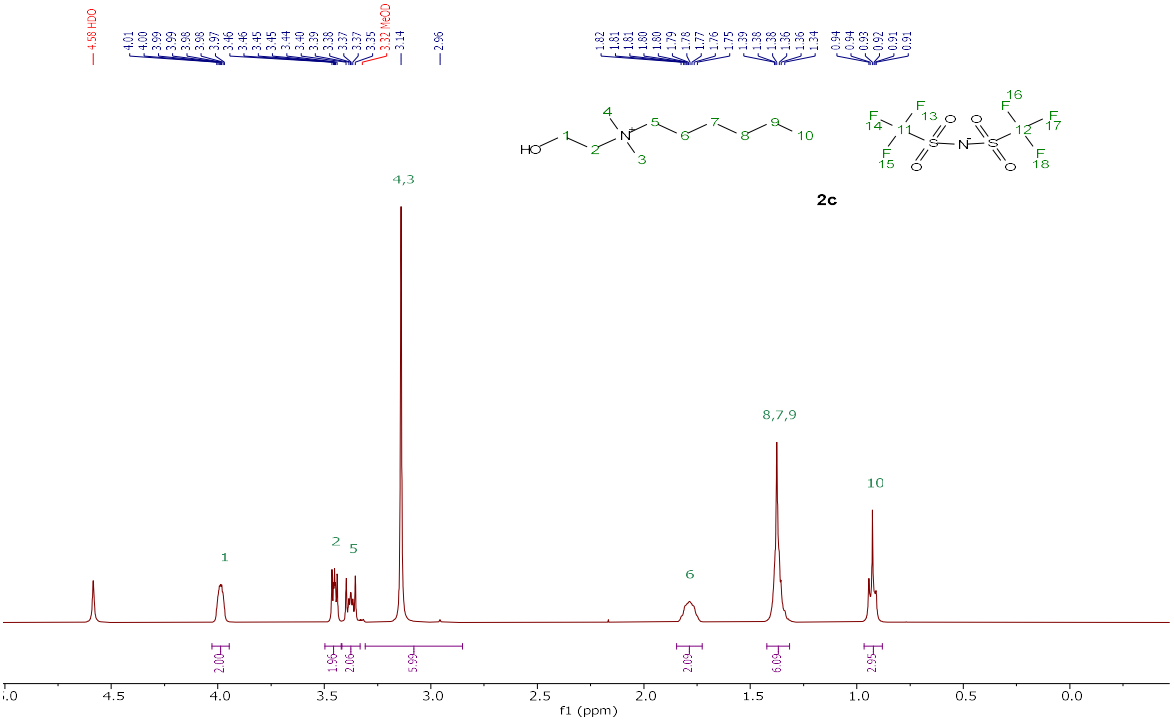


^{19}F NMR (376 MHz, Methanol-d4)

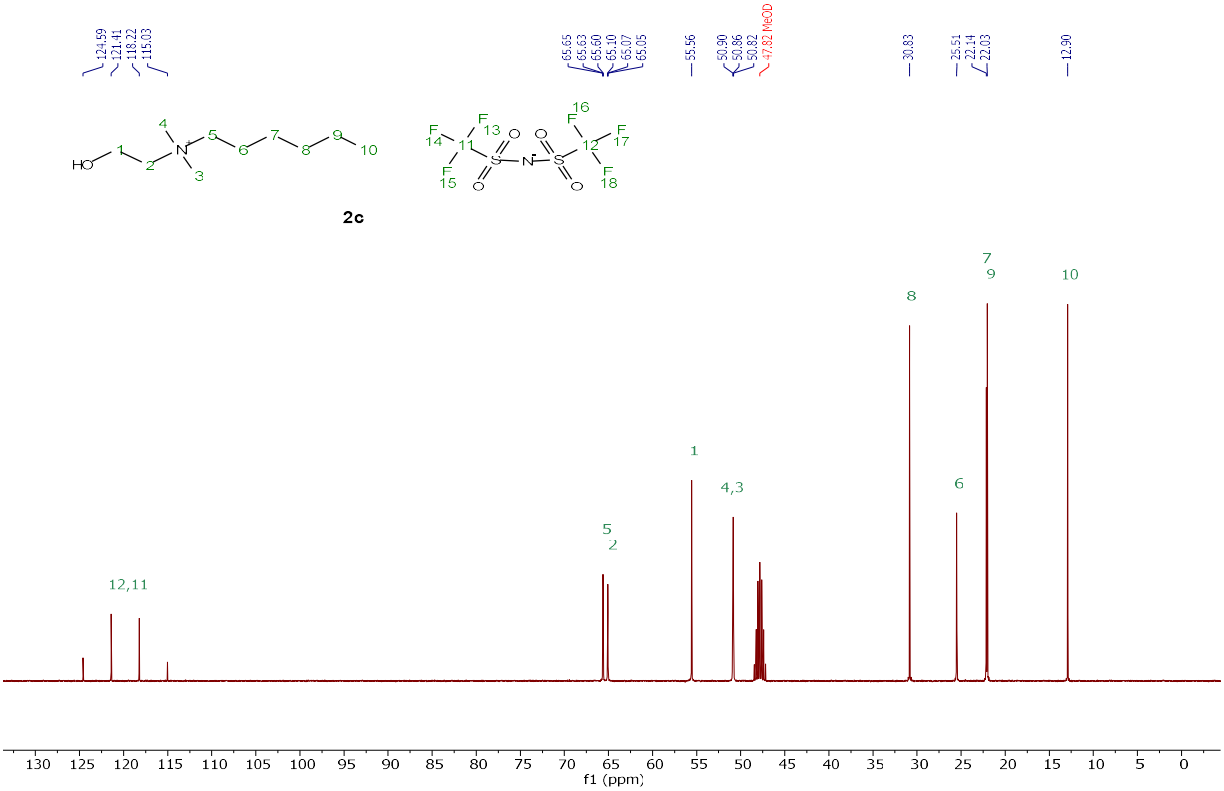


$[N_{1,1,6,2OH}][NTf_2]$, **2c**

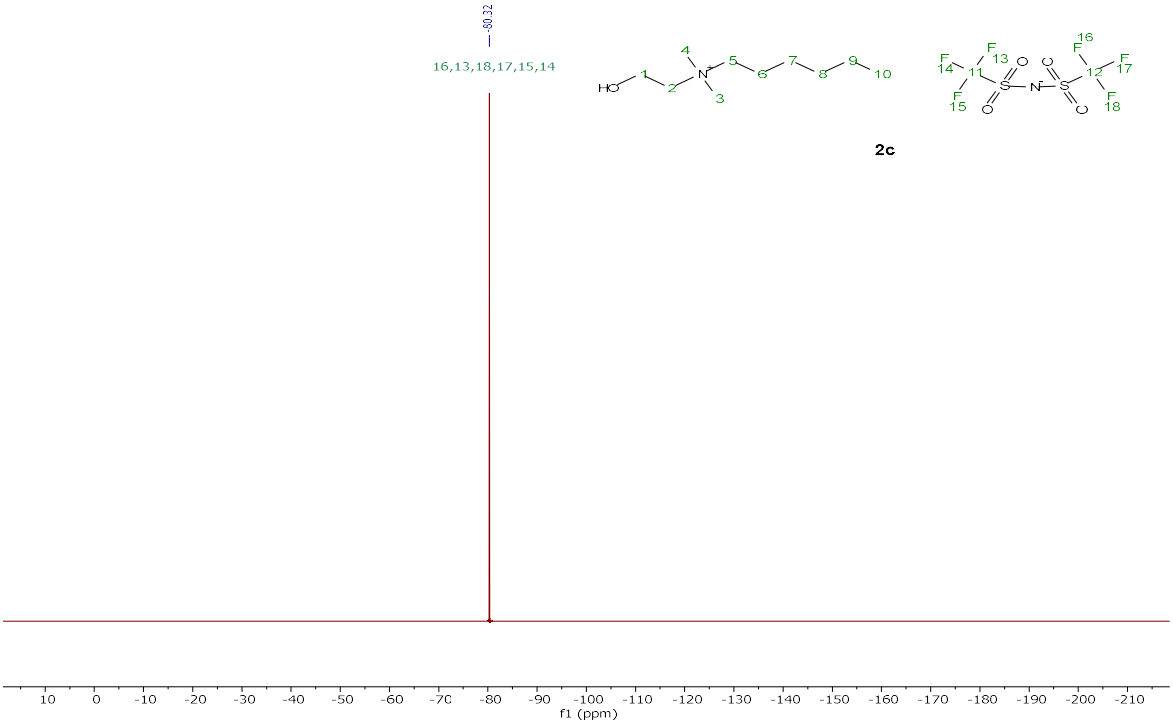
^{1}H NMR (400 MHz, Methanol-d4)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Methanol-d4)

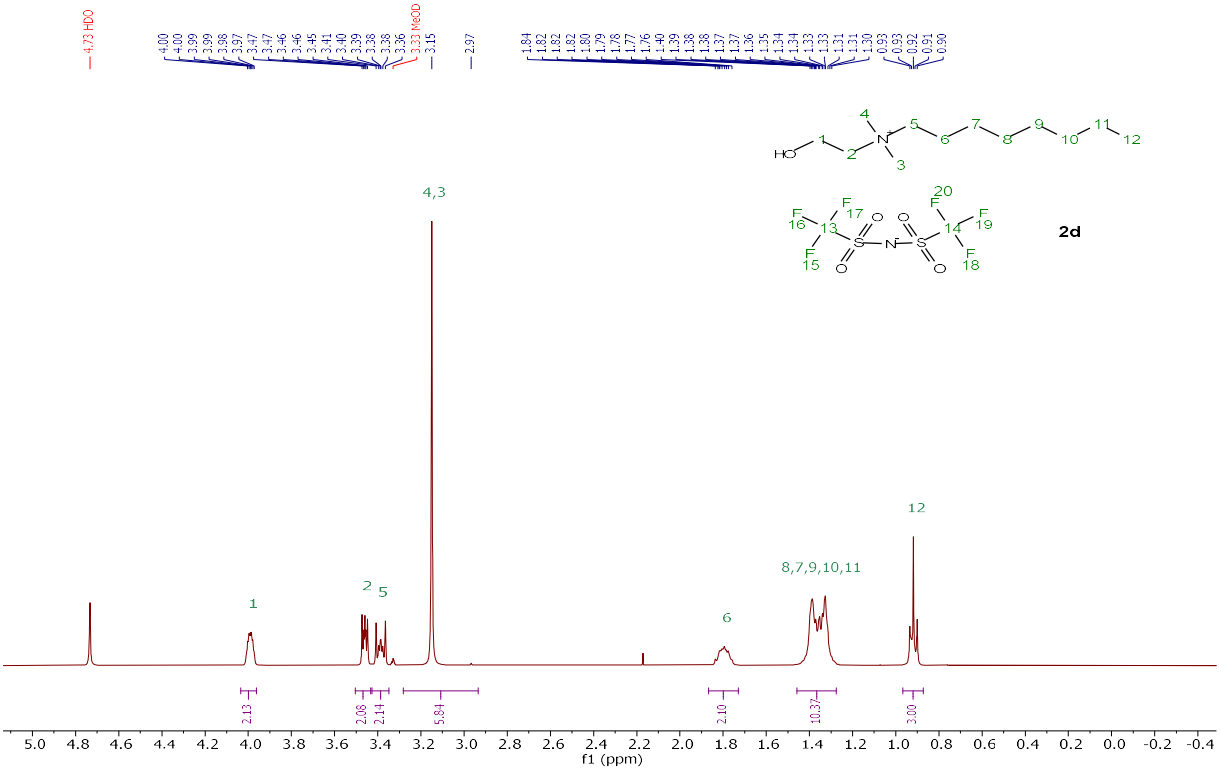


^{19}F NMR (376 MHz, Methanol-d4)

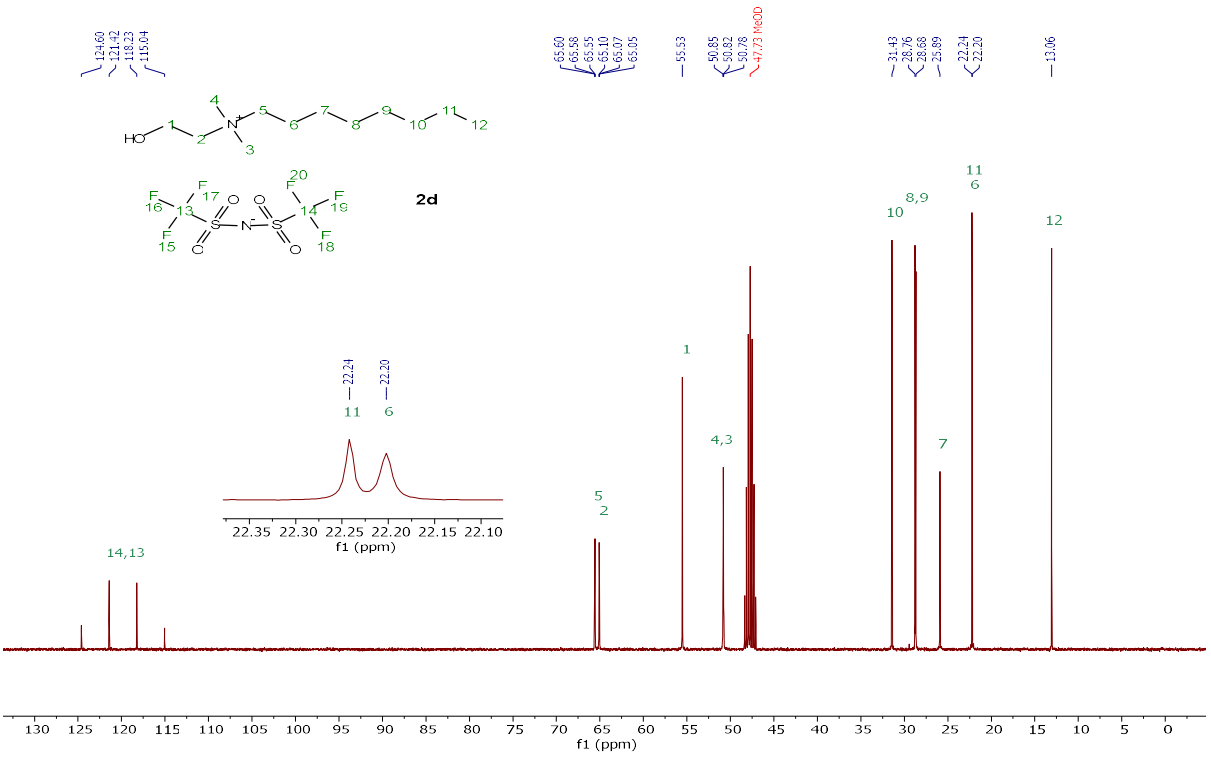


$[N_{1,1,8,2OH}][NTf_2]$, **2d**

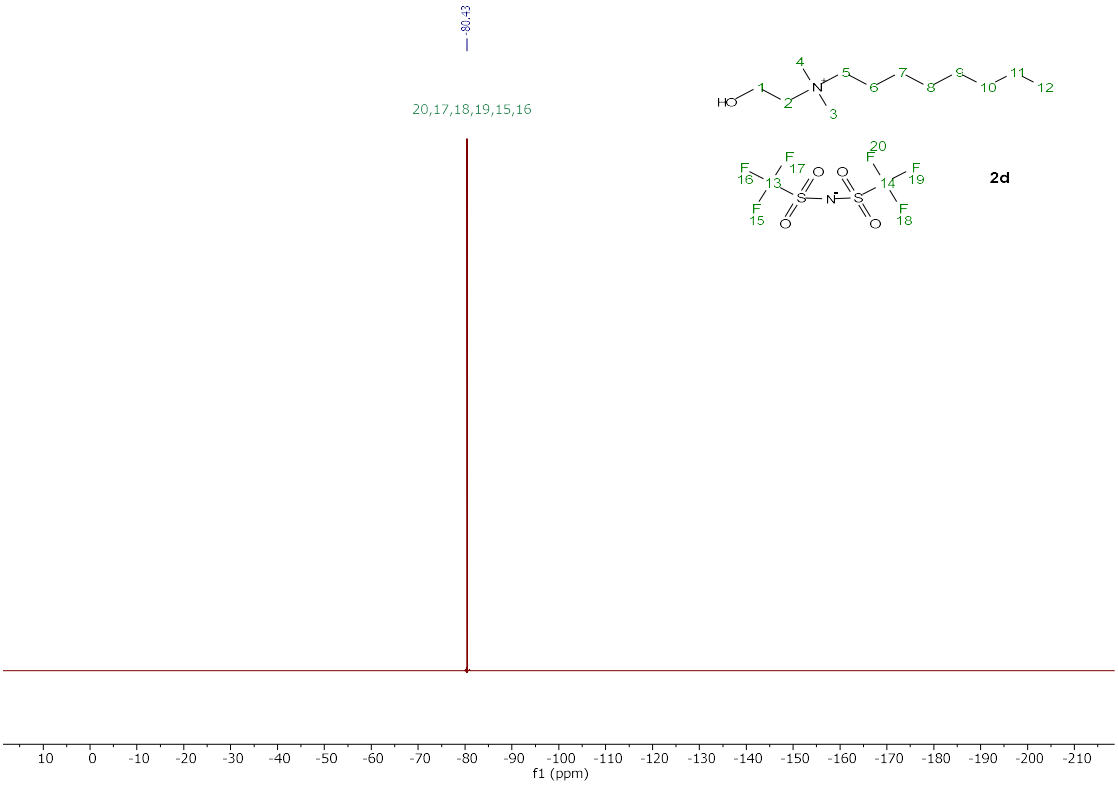
^{1}H NMR (400 MHz, Methanol-d4)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Methanol-d4)

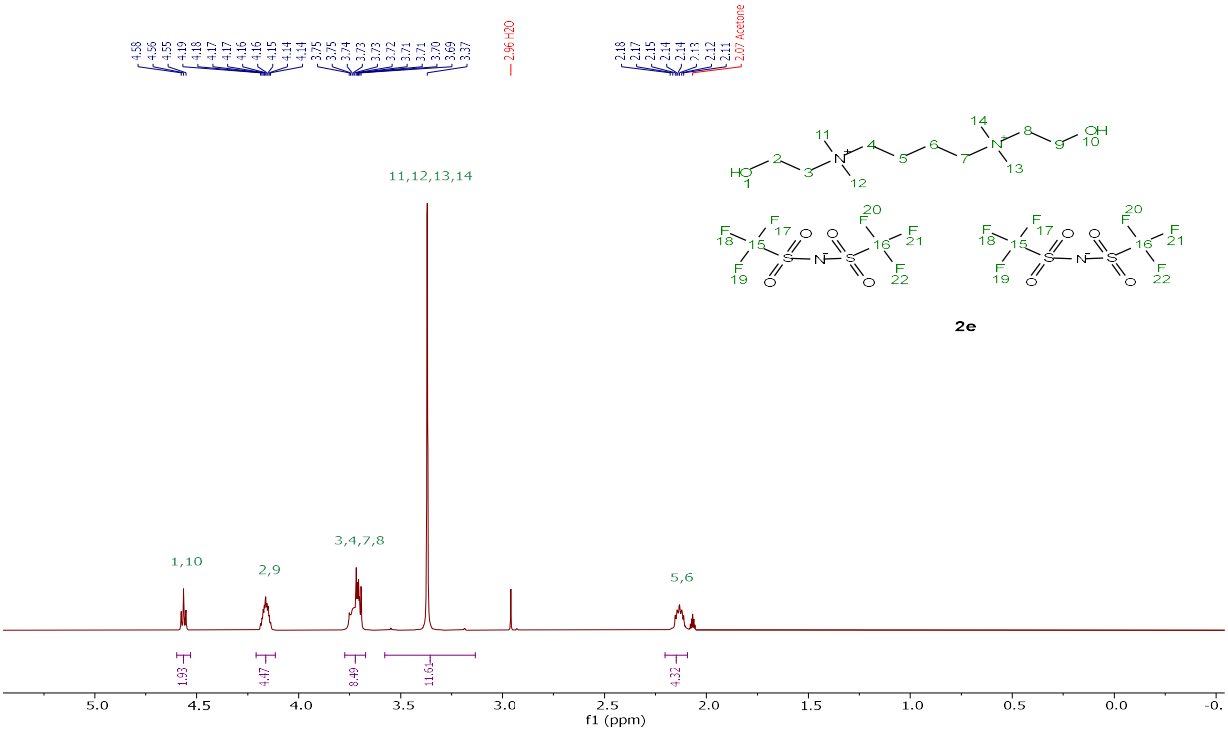


^{19}F NMR (376 MHz, Methanol-d4)

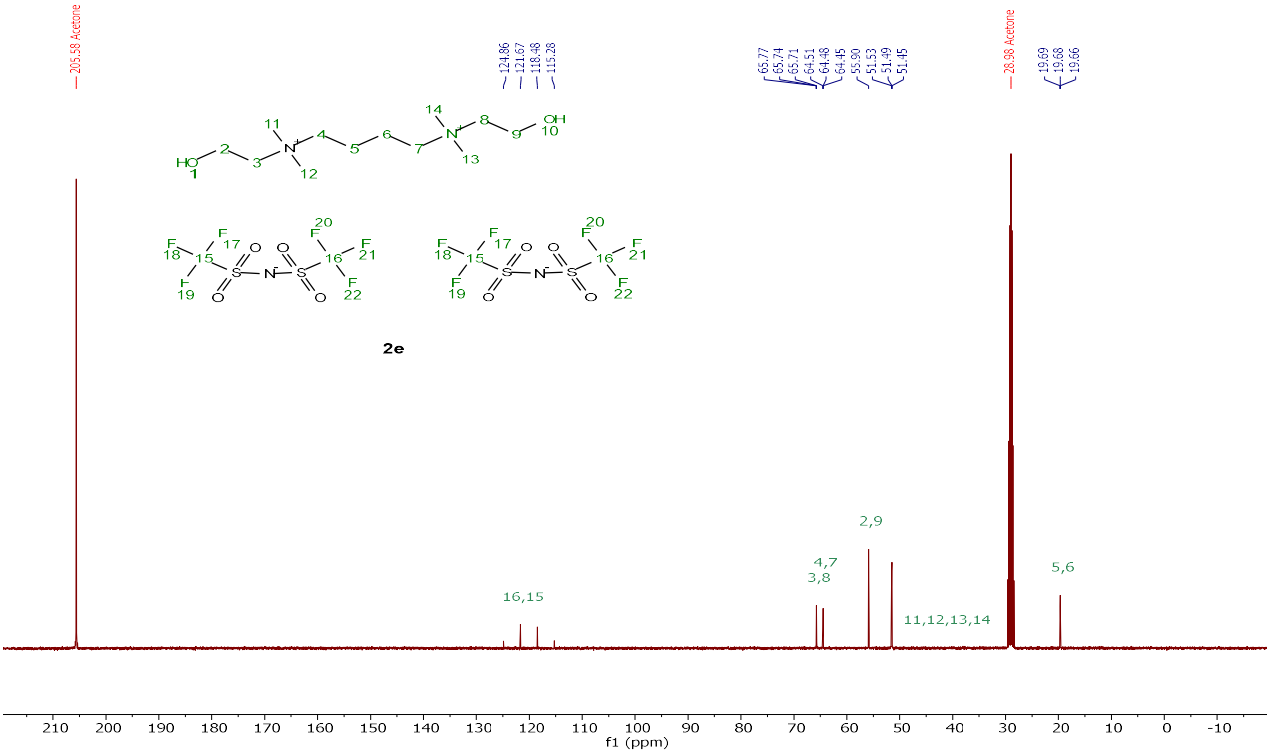


[DC-4][2NTf$_2$], **2e**

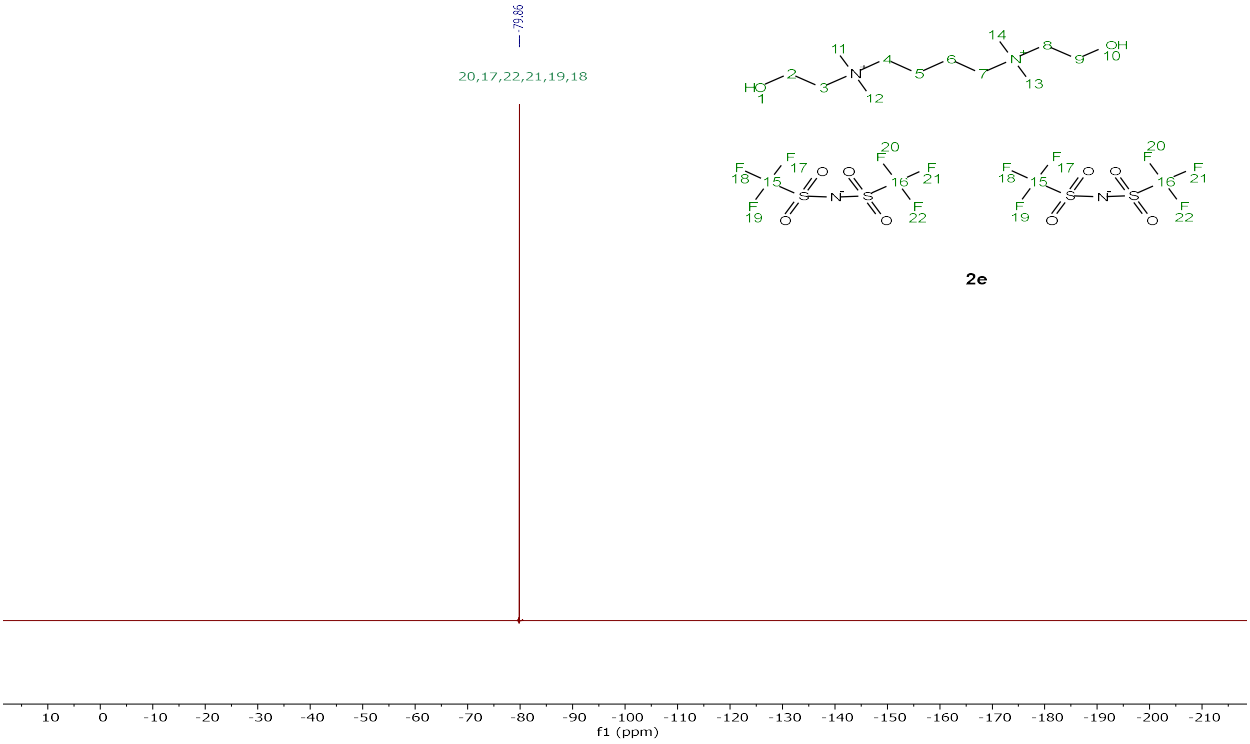
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

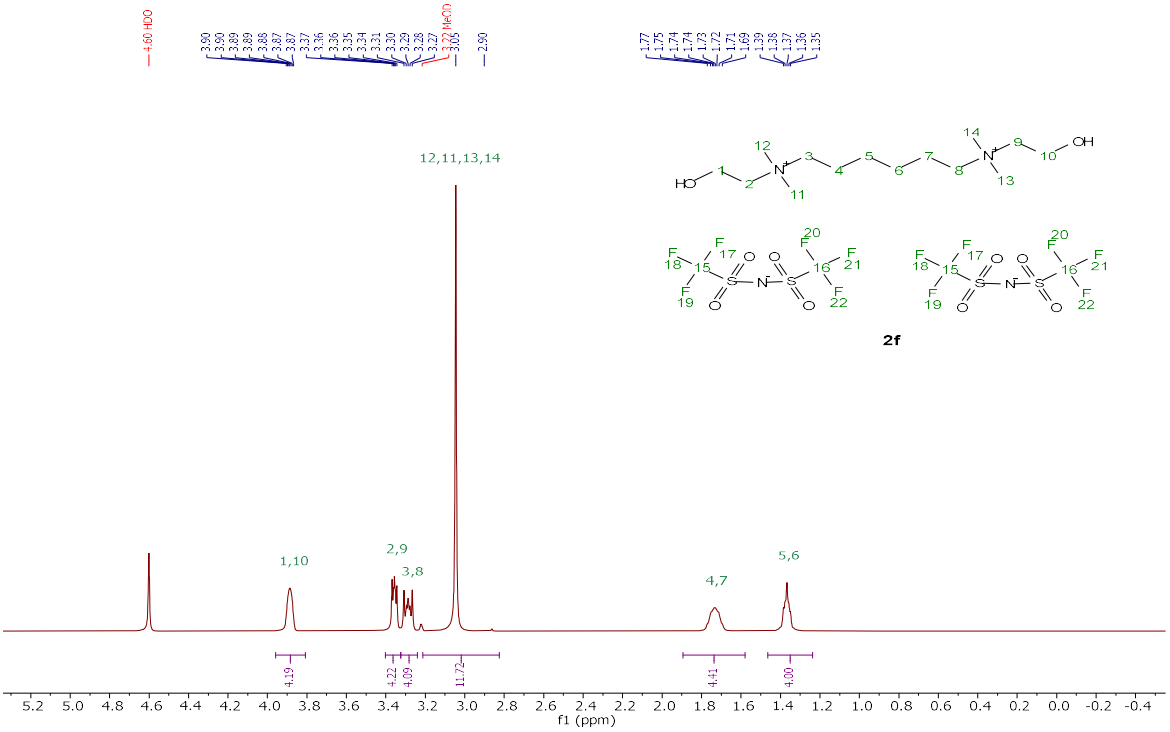


^{19}F NMR (376 MHz, Acetone-d6)

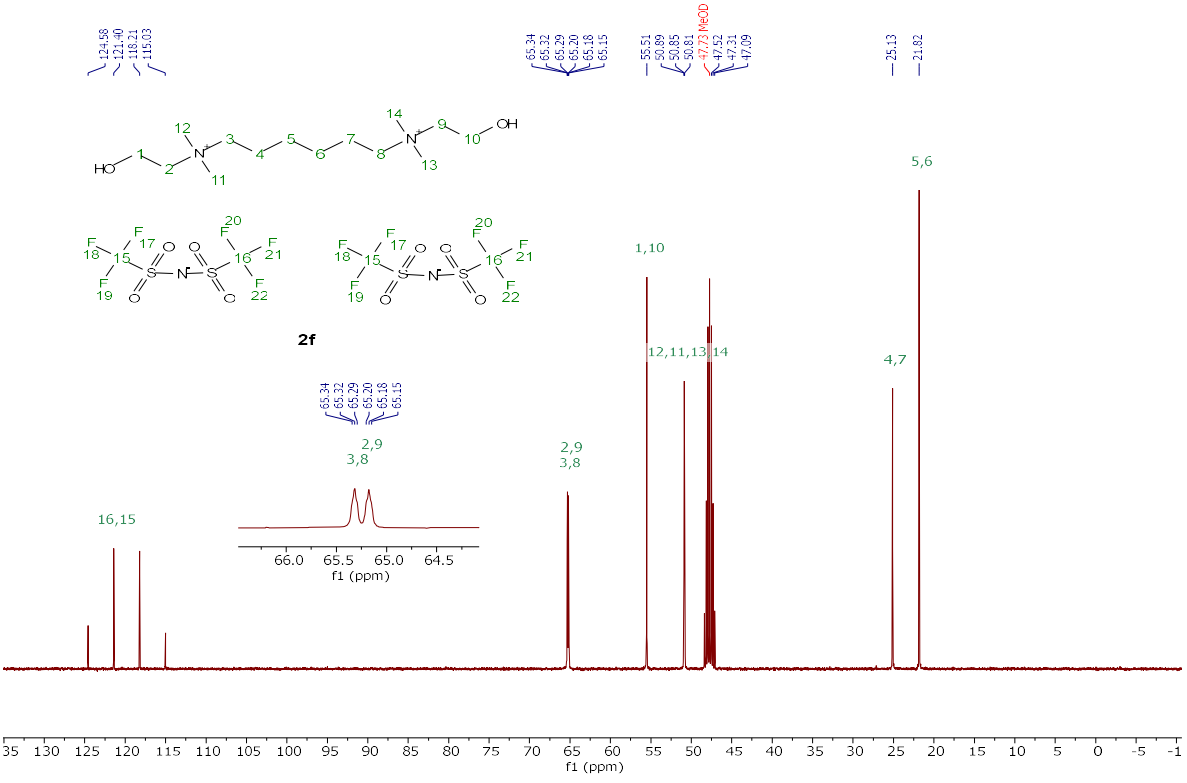


[DC-6][2NTf$_2$], **2f**

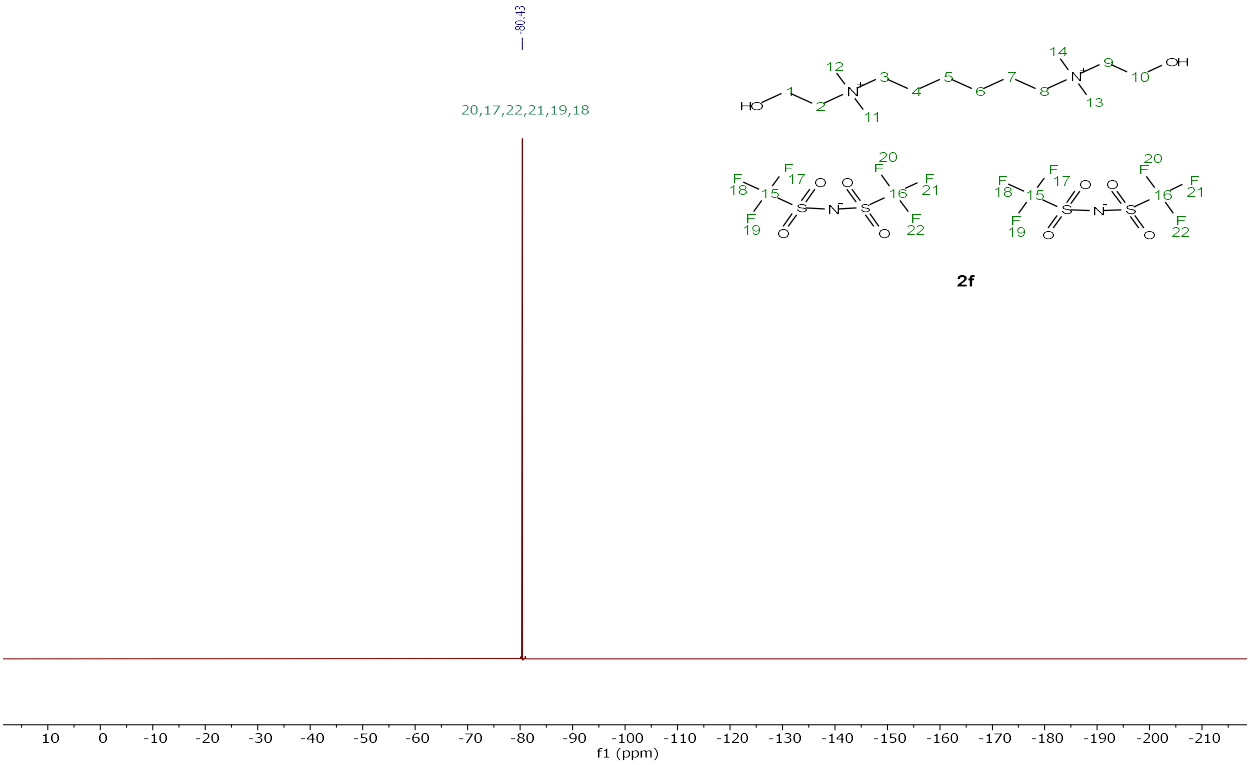
^{1}H NMR (400 MHz, Methanol-d4)



^{13}C{^{1}H} NMR (101 MHz, Methanol-d4)

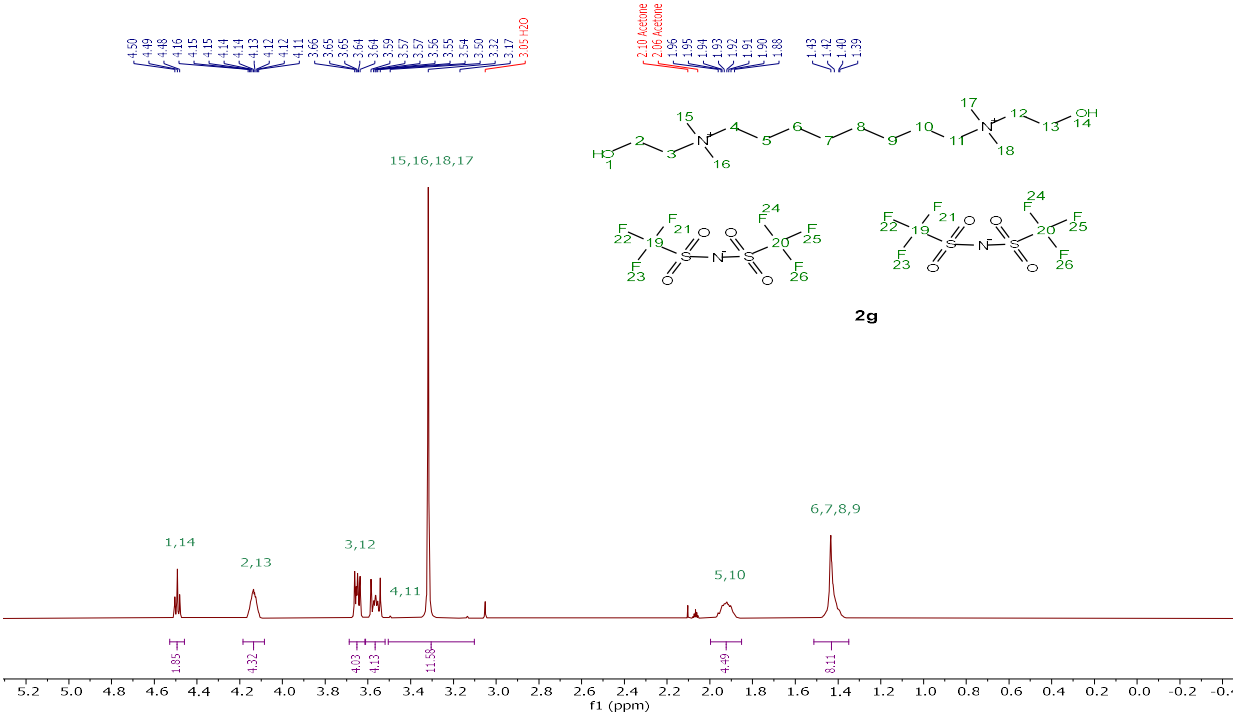


^{19}F NMR (376 MHz, Methanol-d4)

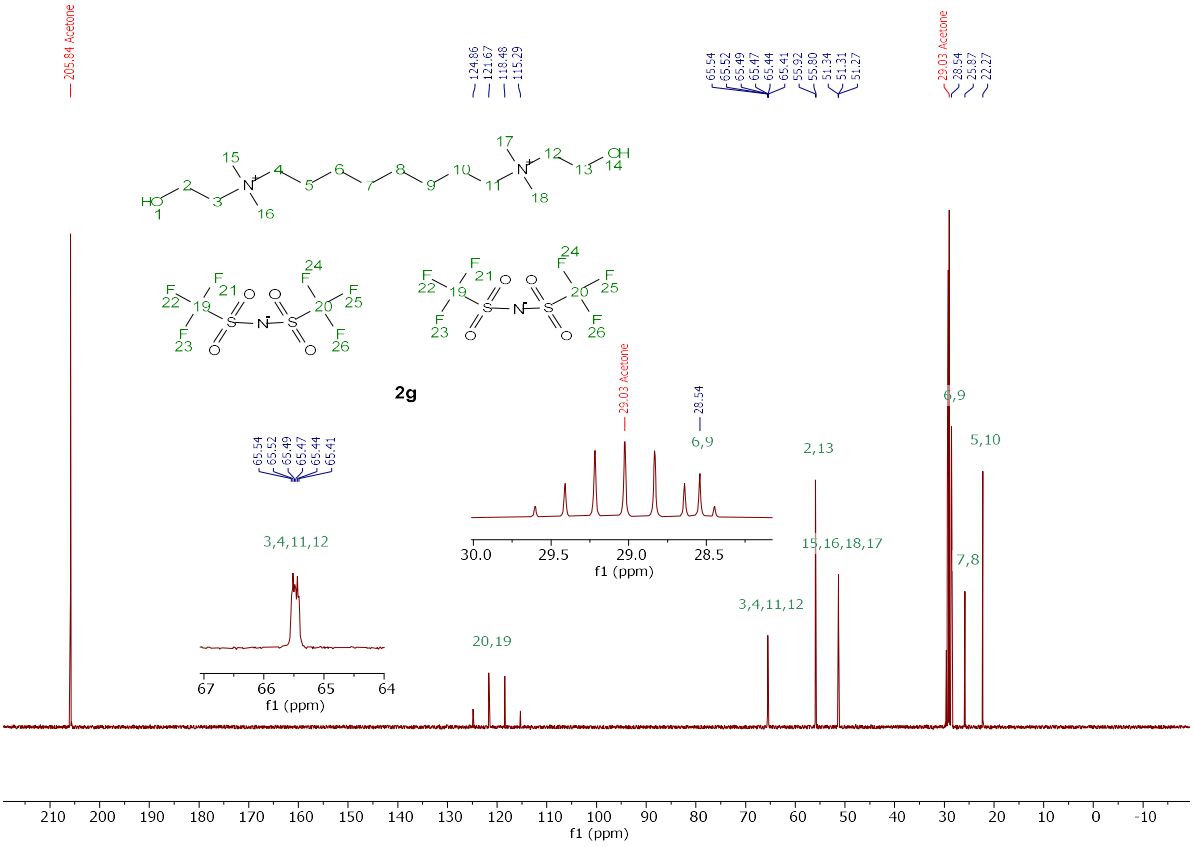


[DC-8][2NTf$_2$], **2g**

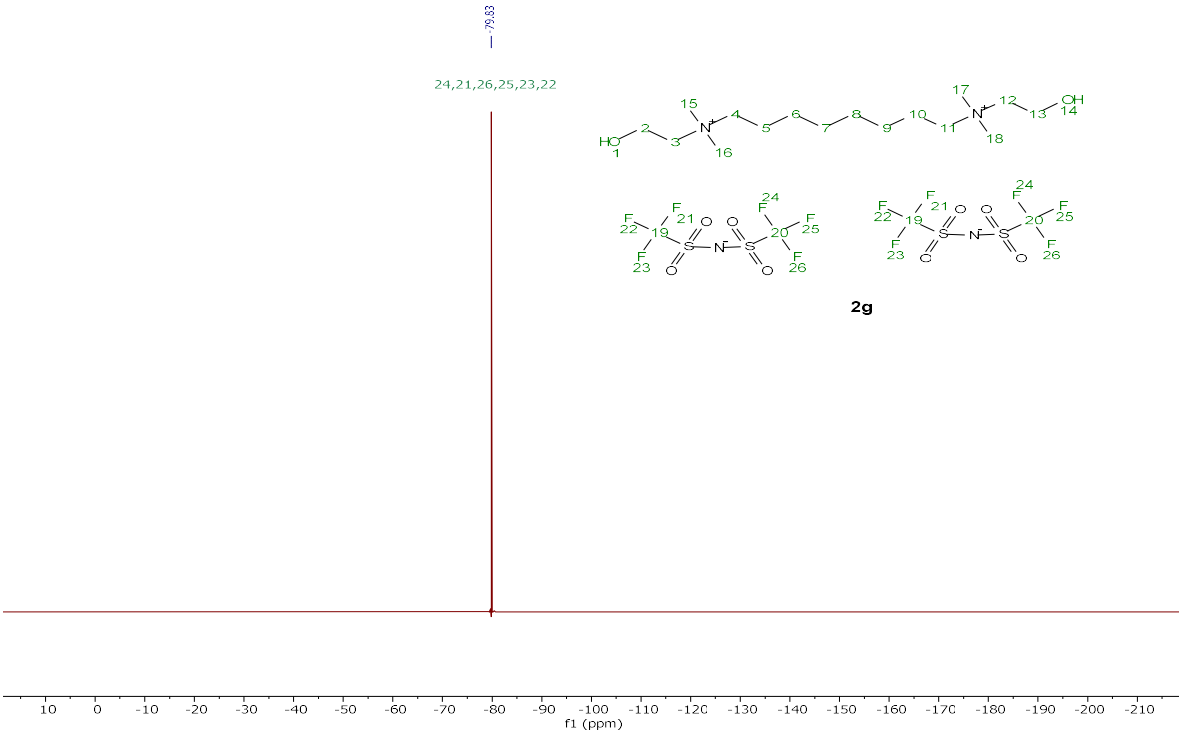
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

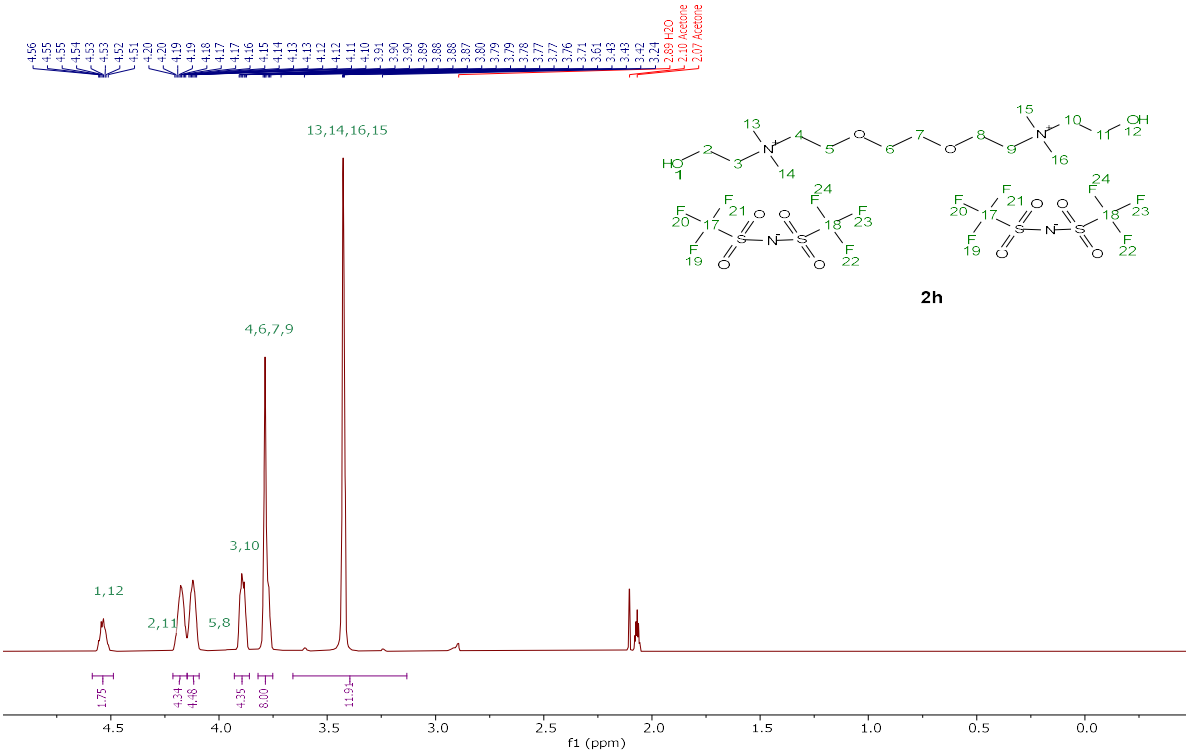


^{19}F NMR (376 MHz, Acetone-d6)

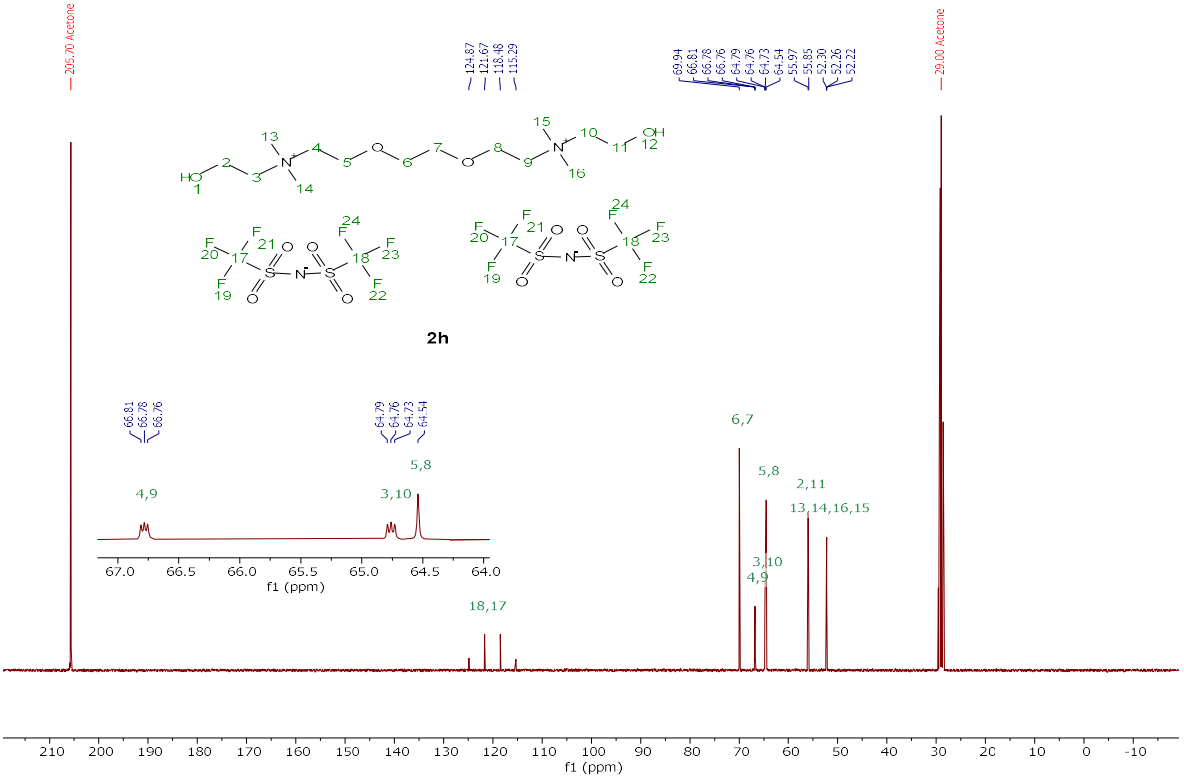


[DC-ether][2NTf$_2$], **2h**

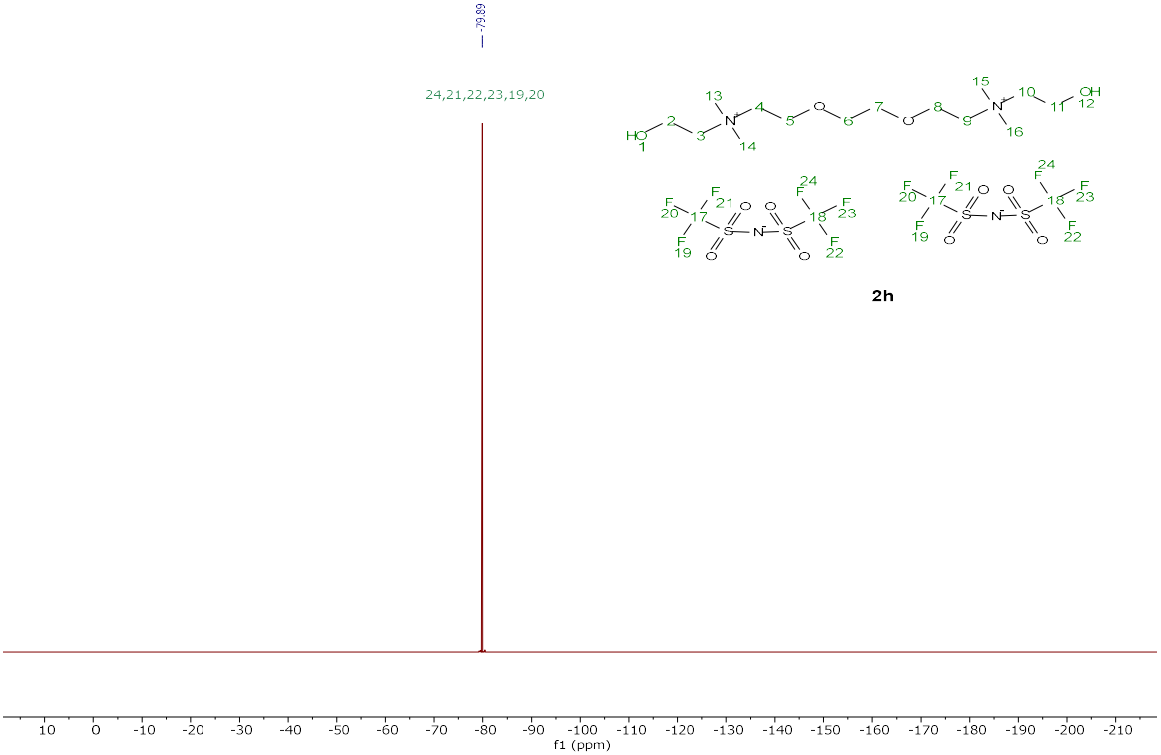
^{1}H NMR (400 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (101 MHz, Acetone-d6)

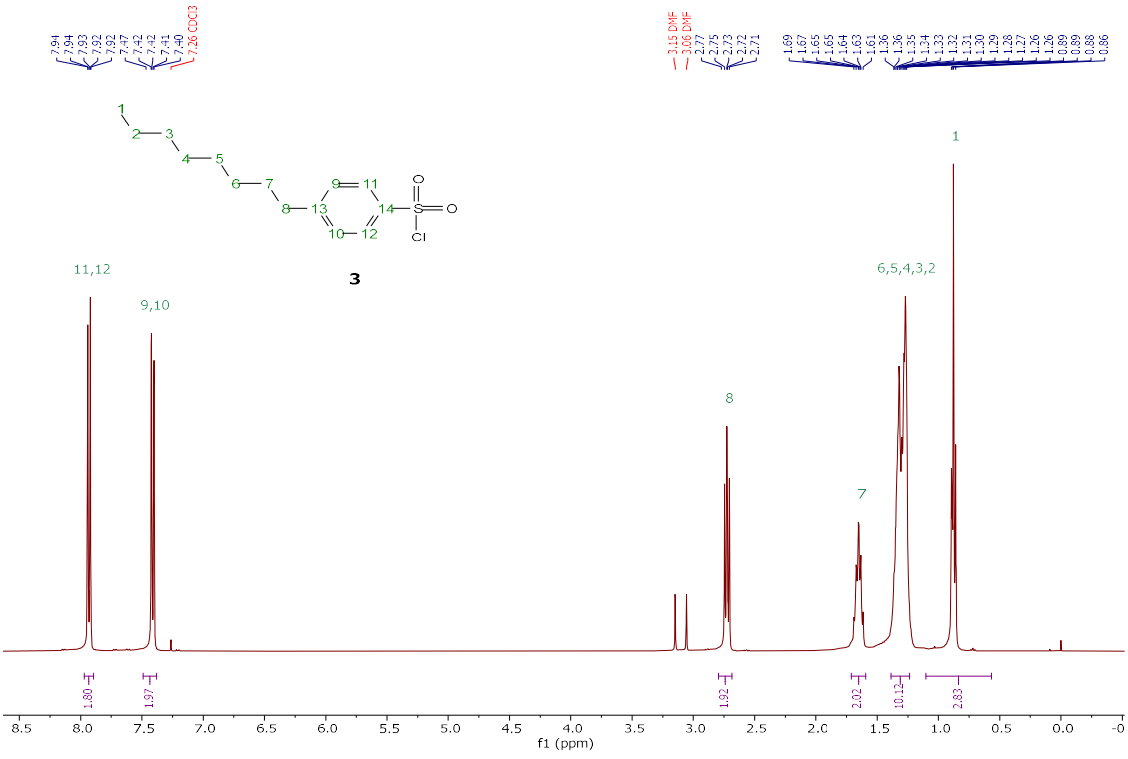


^{19}F NMR (376 MHz, Acetone-d6)

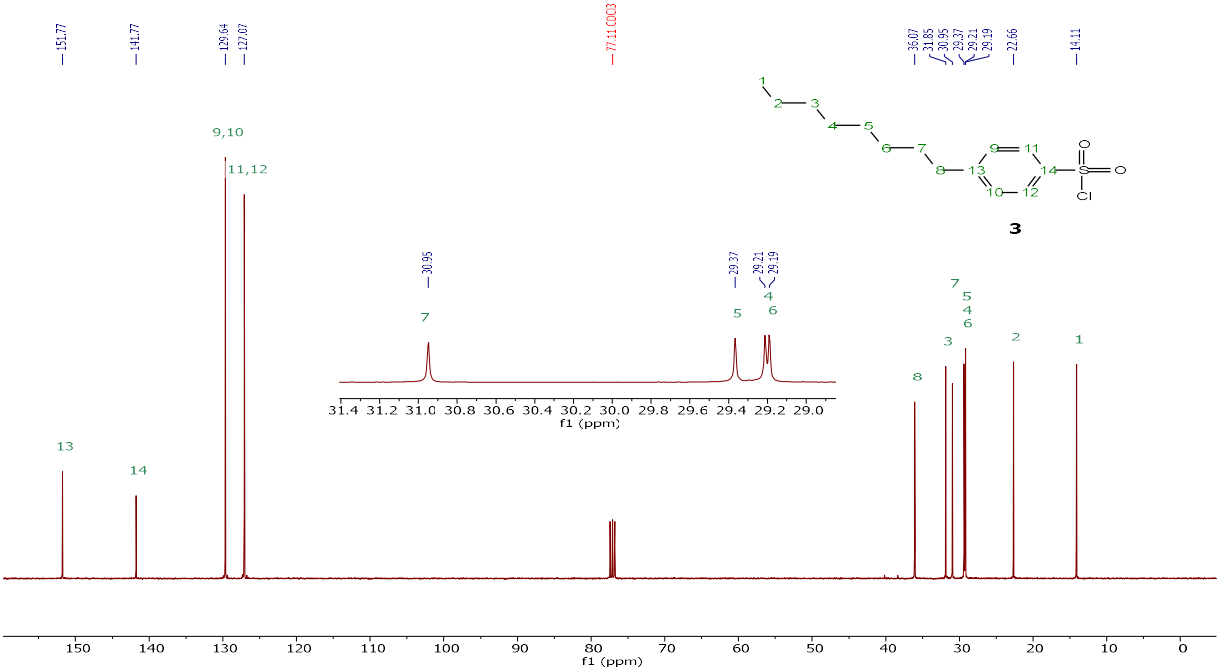


4-octylbenzenesulfonyl chloride, **3**

^{1}H NMR (400 MHz, Chloroform-d)

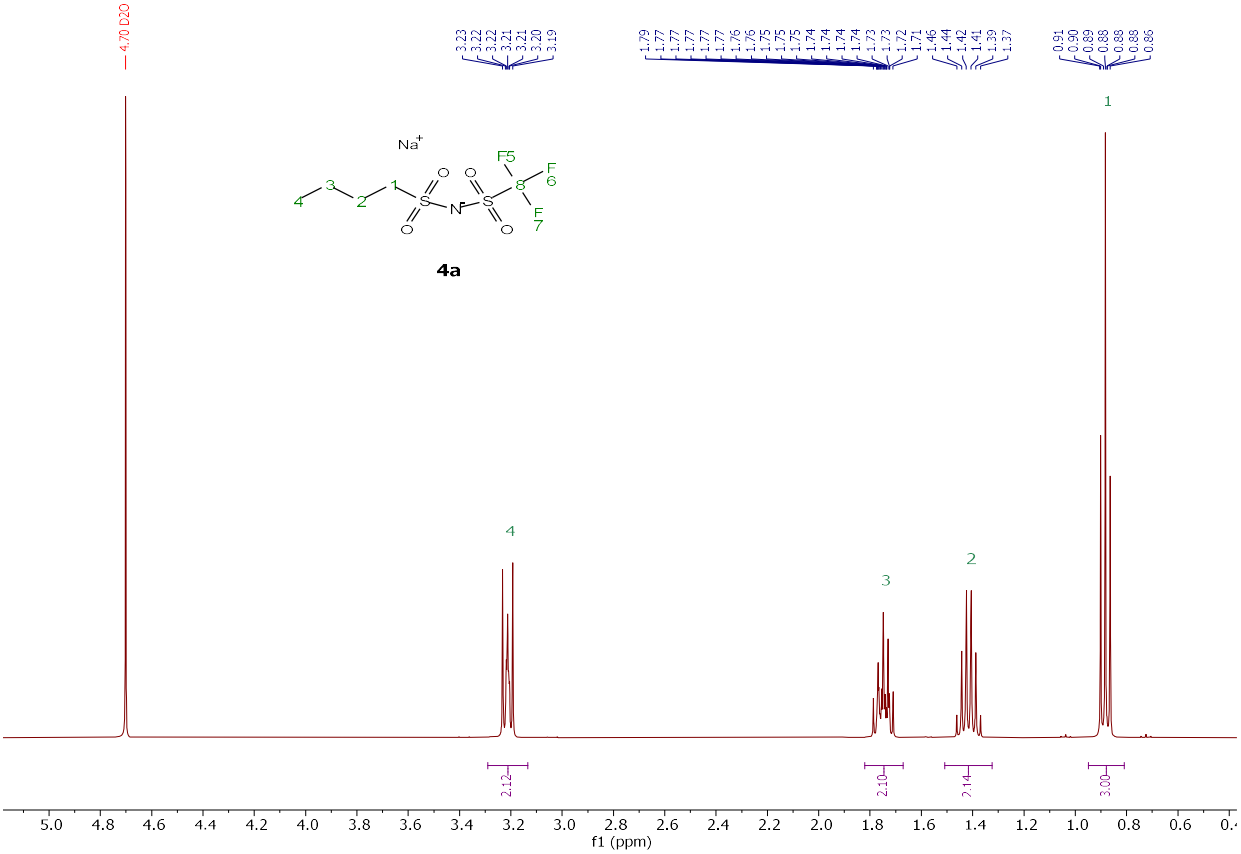


$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-d)

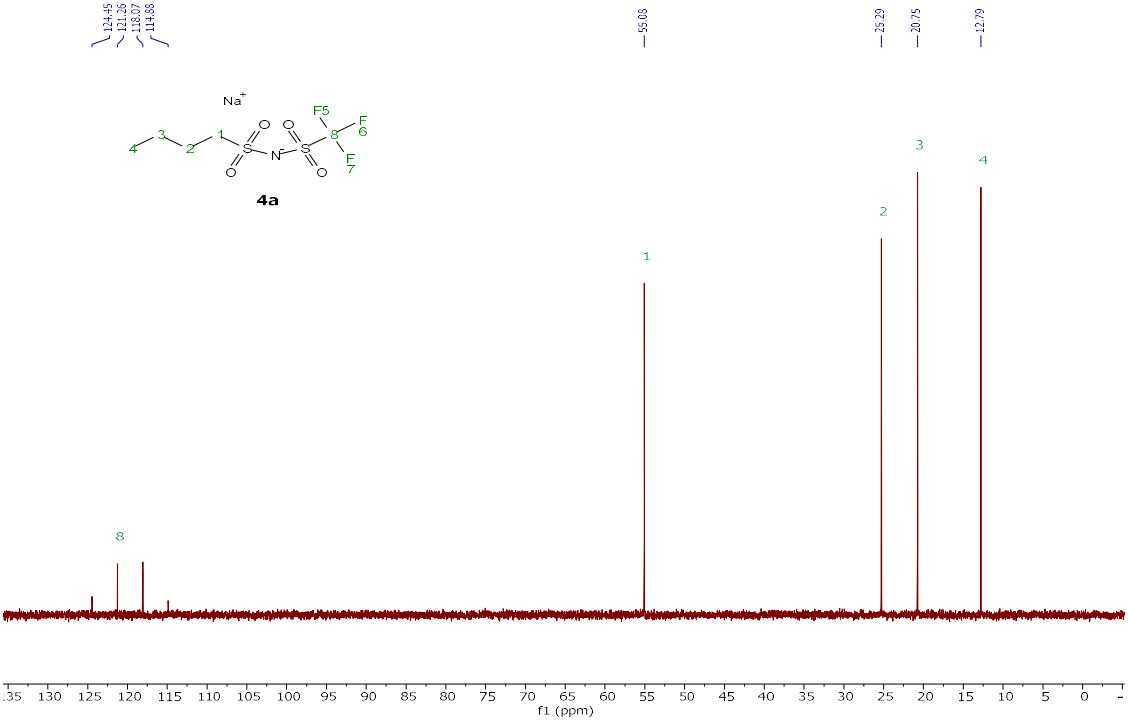


[Na][BSNTf], **4a**

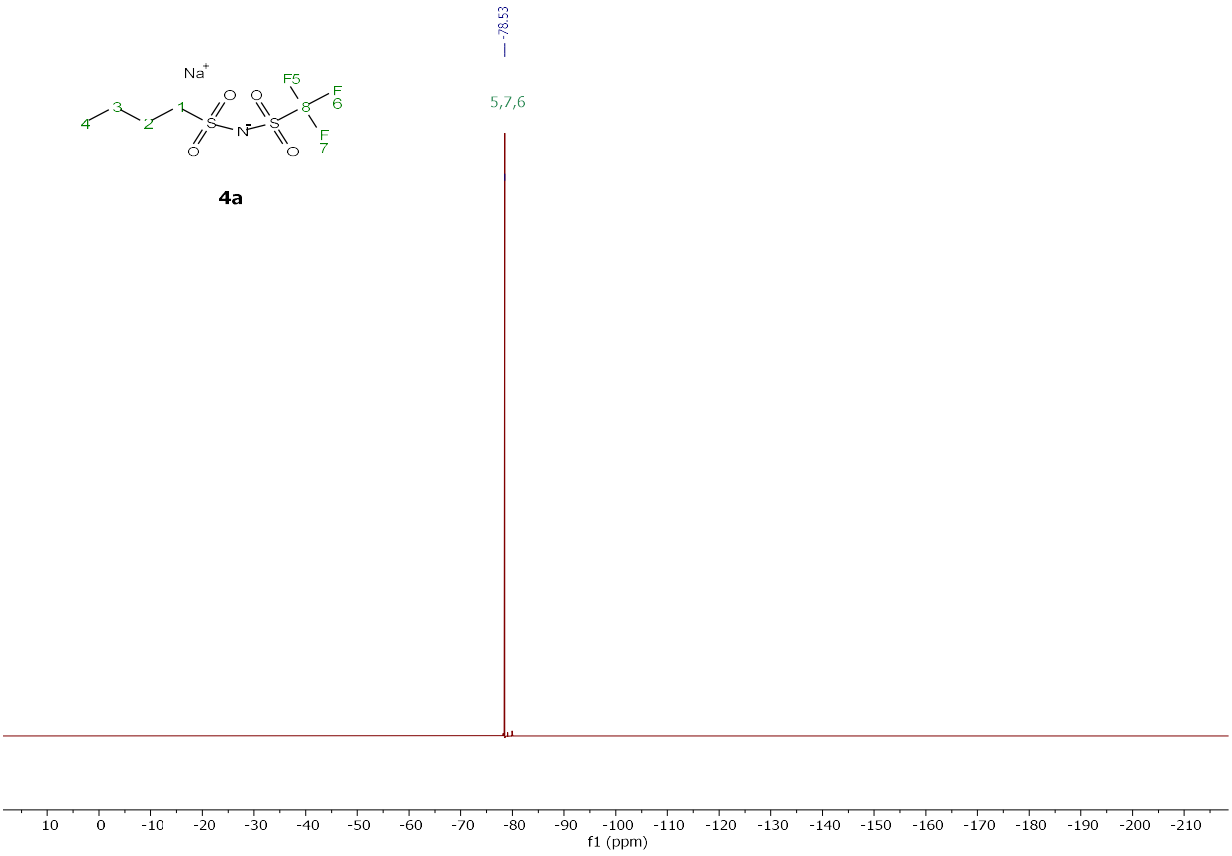
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

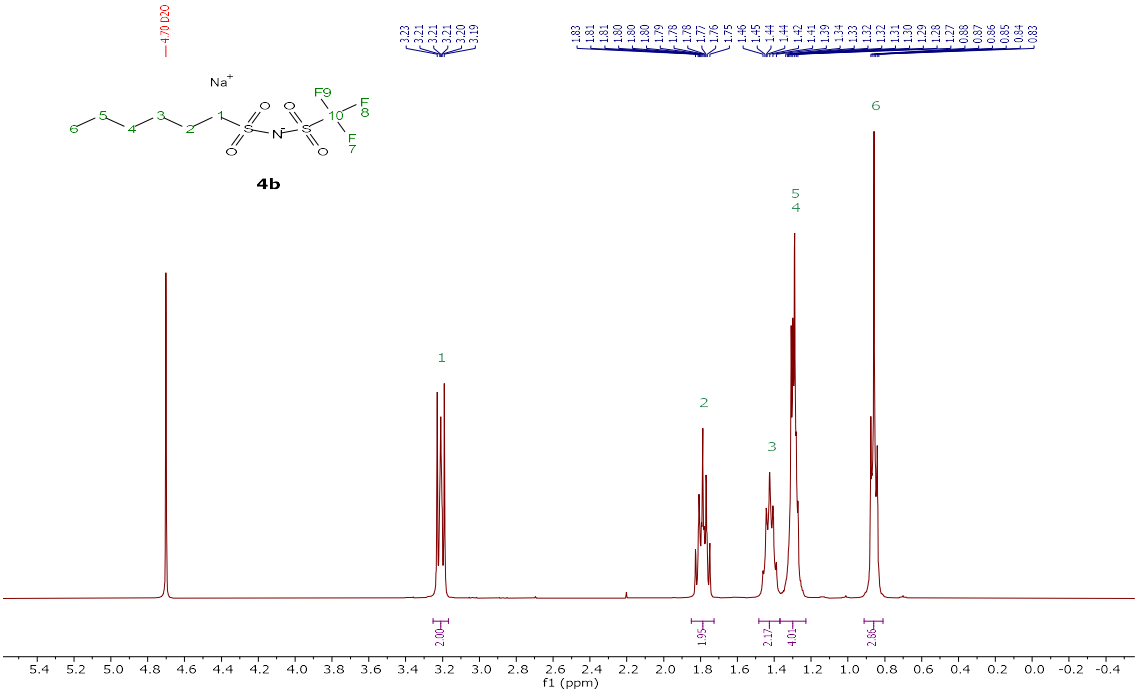


^{19}F NMR (376 MHz, Deuterium Oxide)

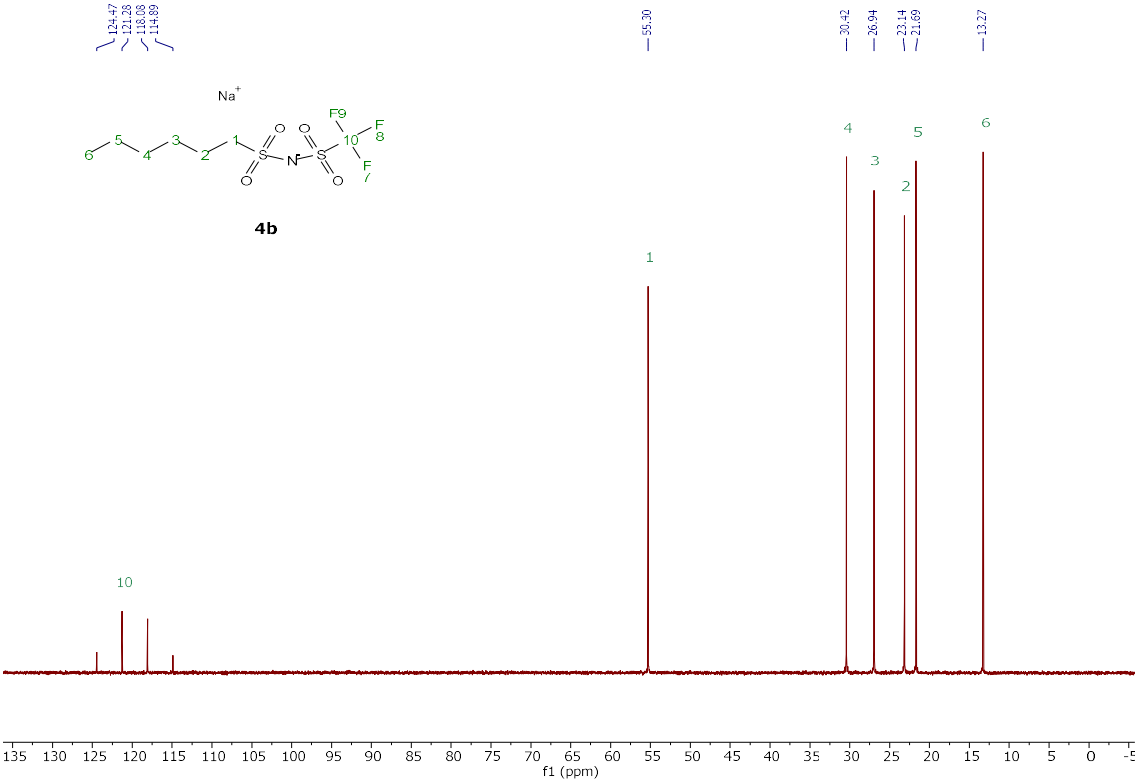


[Na][HSNTf], **4b**

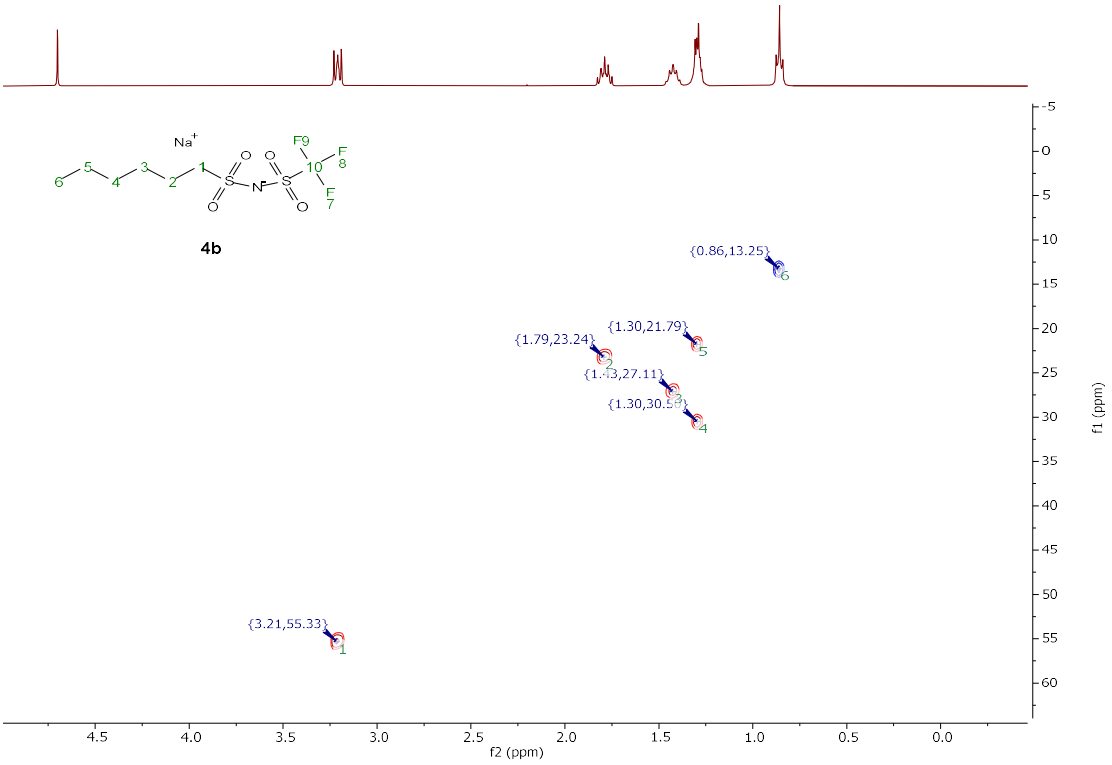
^{1}H NMR (400 MHz, Deuterium Oxide)



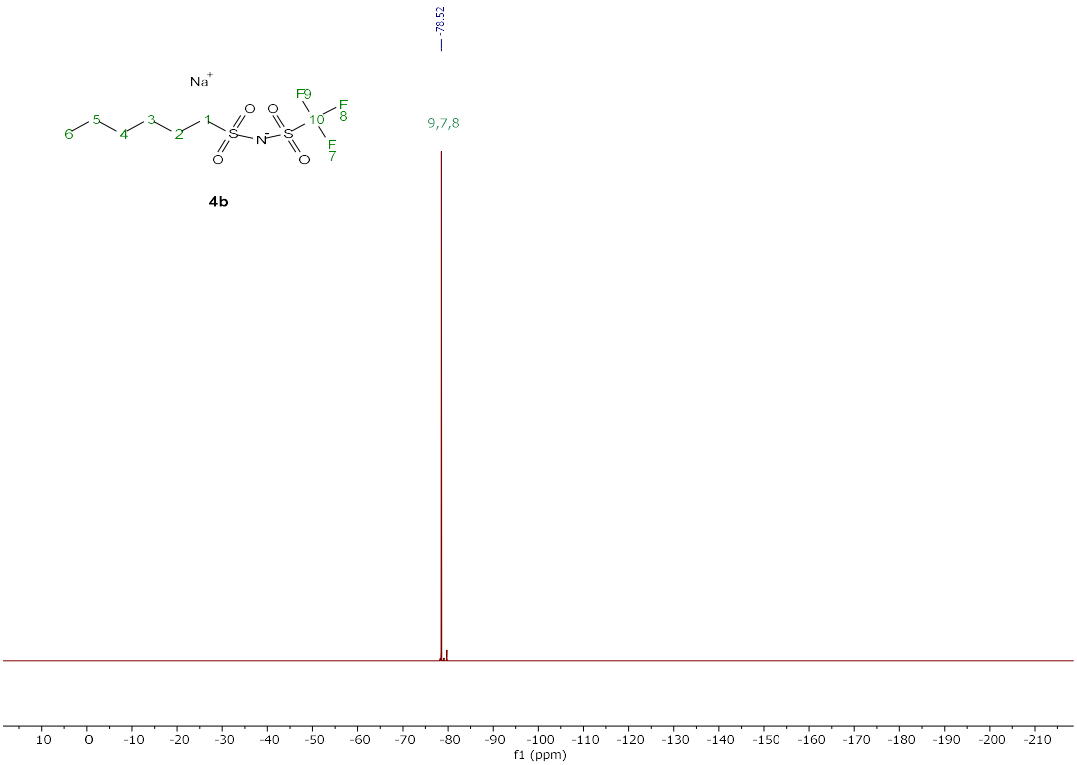
^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)



HSQC (Deuterium Oxide)

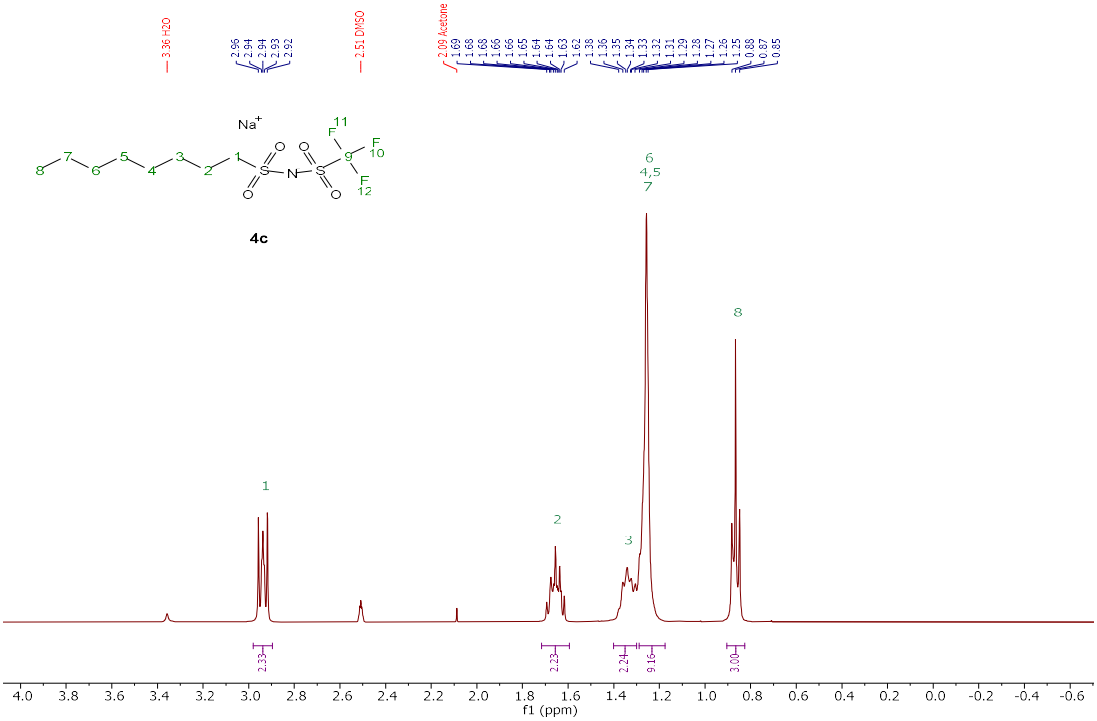


^{19}F NMR (376 MHz, Deuterium Oxide)

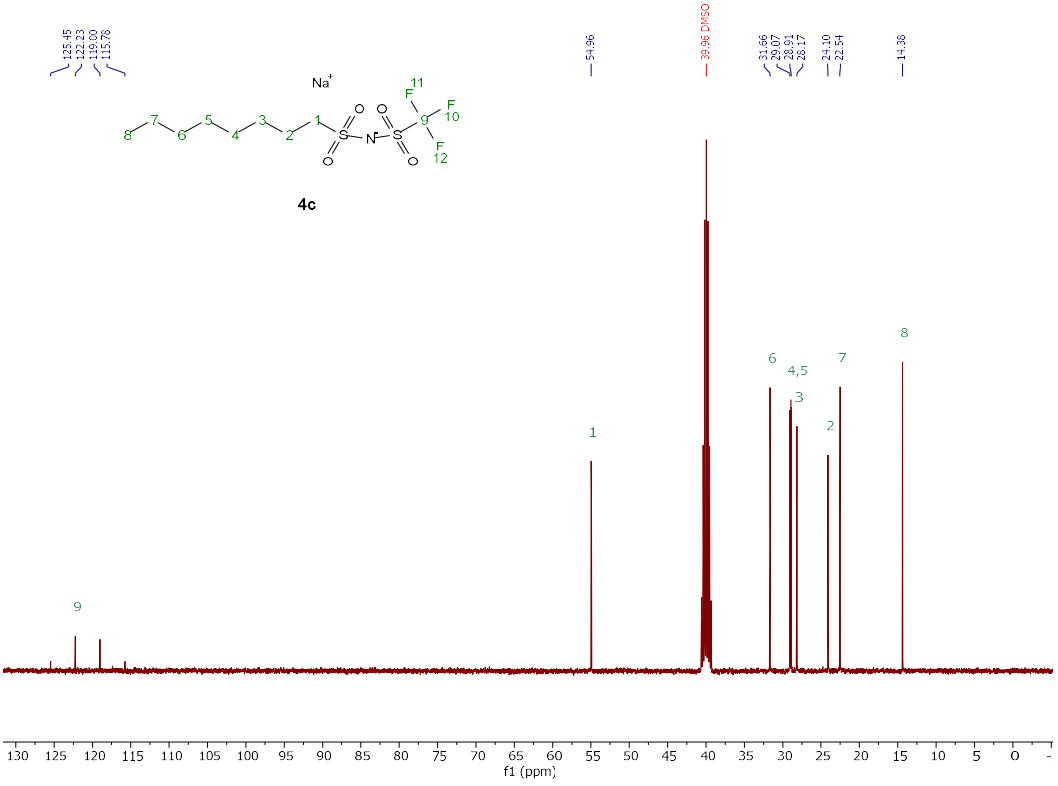


[Na][OSNTf], **4c**

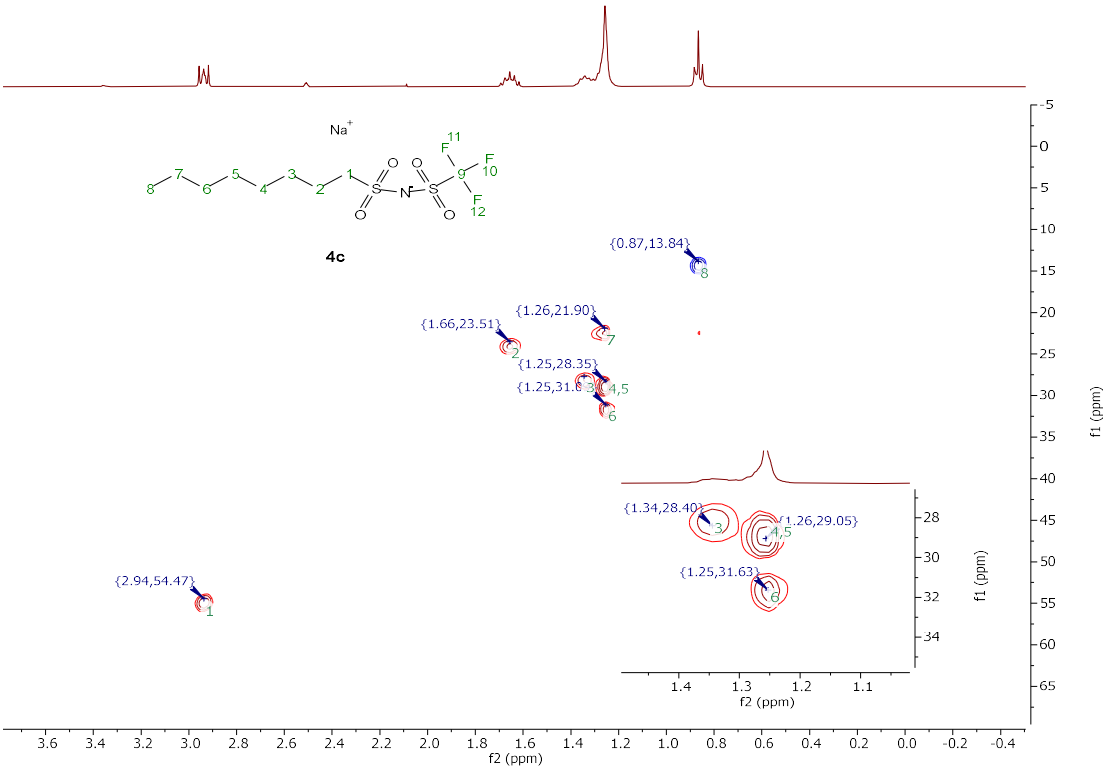
^{1}H NMR (400 MHz, DMSO-d6)



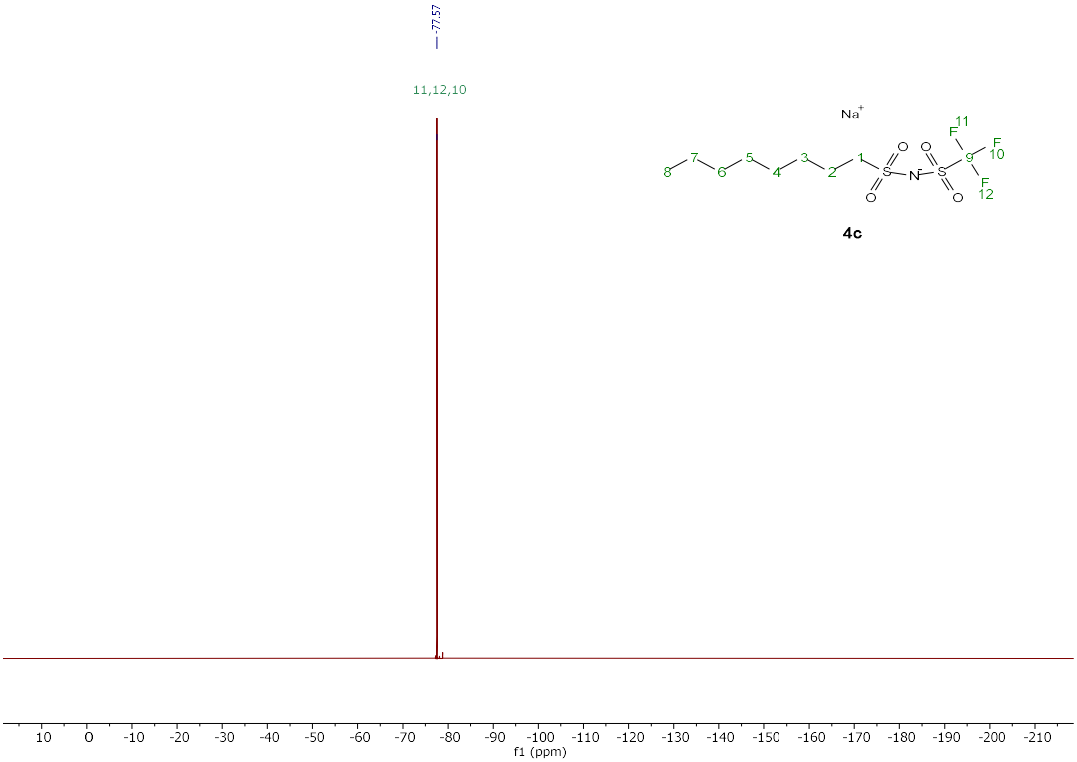
^{13}C{^{1}H} NMR (101 MHz, DMSO-d6)



HSQC (DMSO-d6)

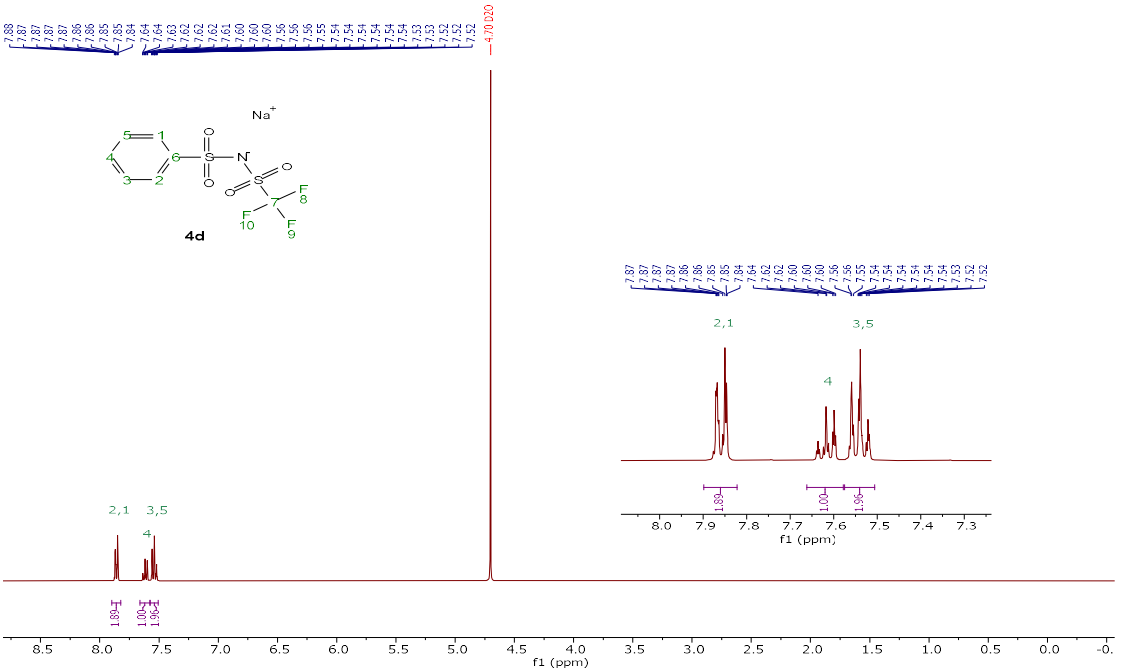


^{19}F NMR (376 MHz, DMSO-d6)

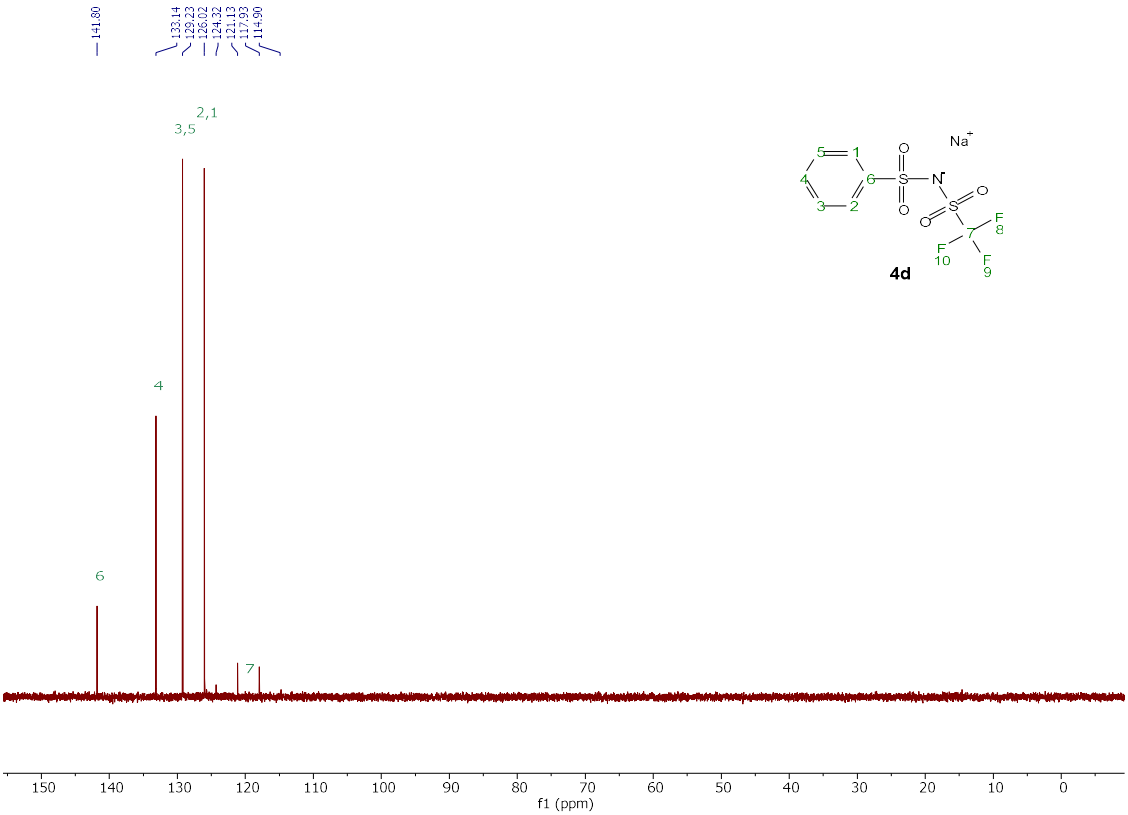


[Na][PhSNTf], **4d**

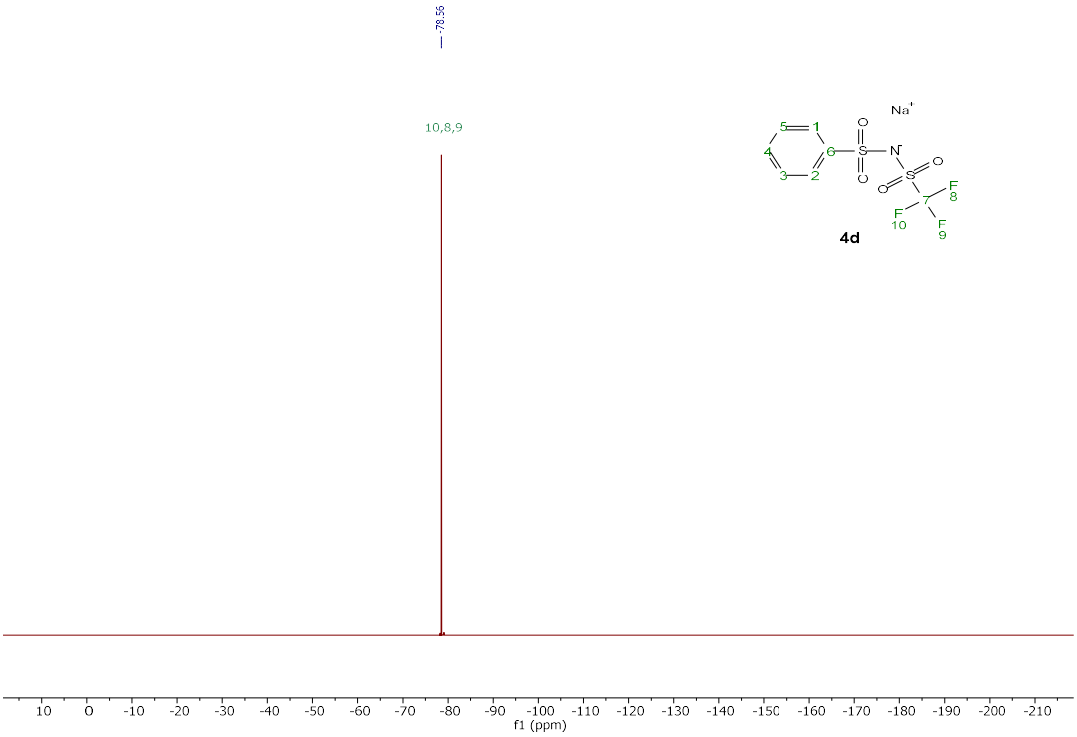
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

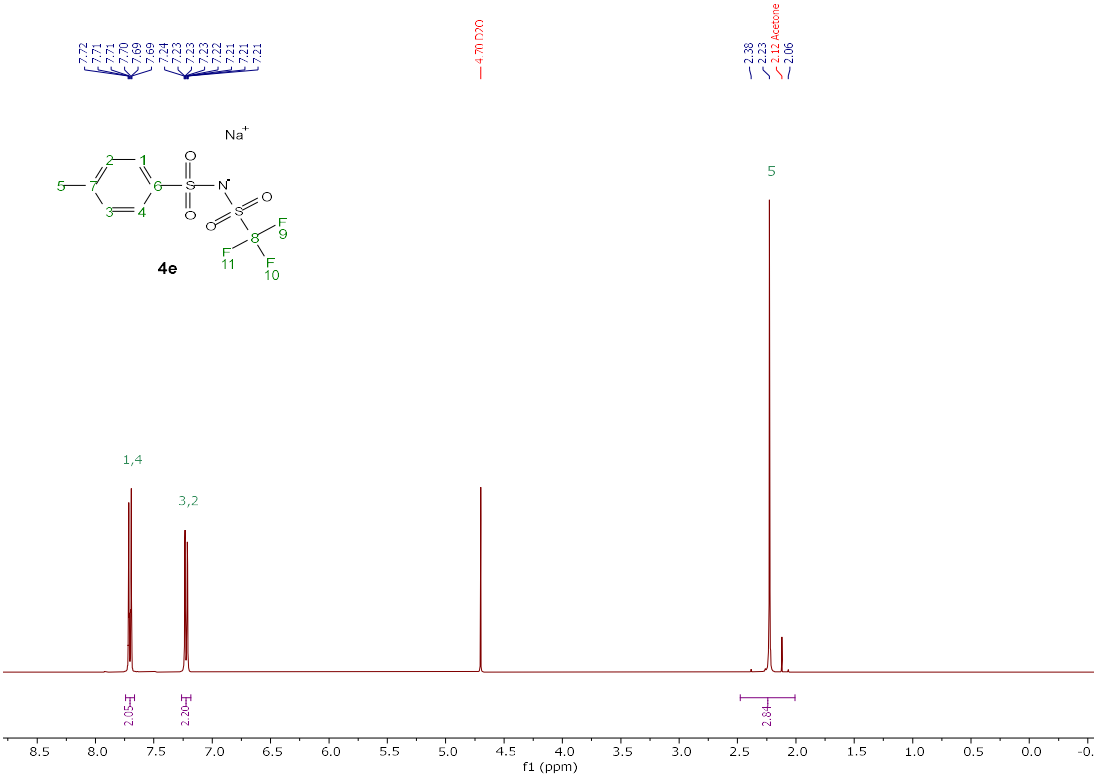


^{19}F NMR (376 MHz, Deuterium Oxide)

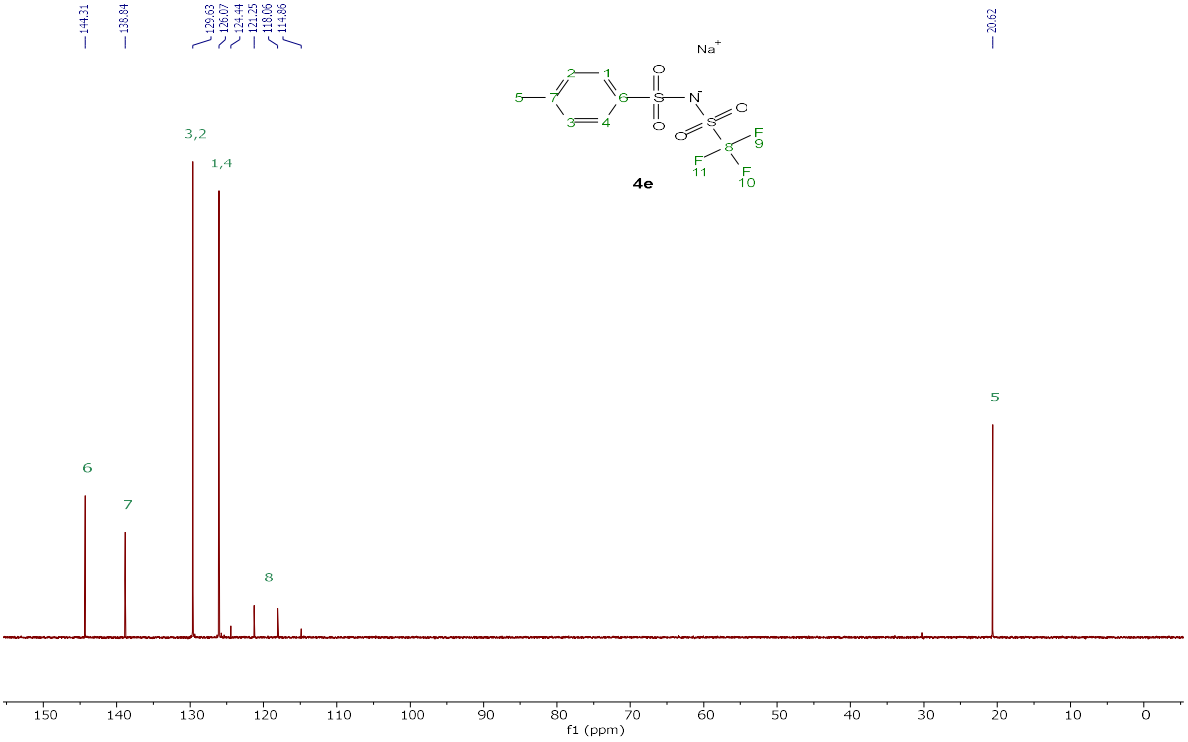


[Na][TsNTf], **4e**

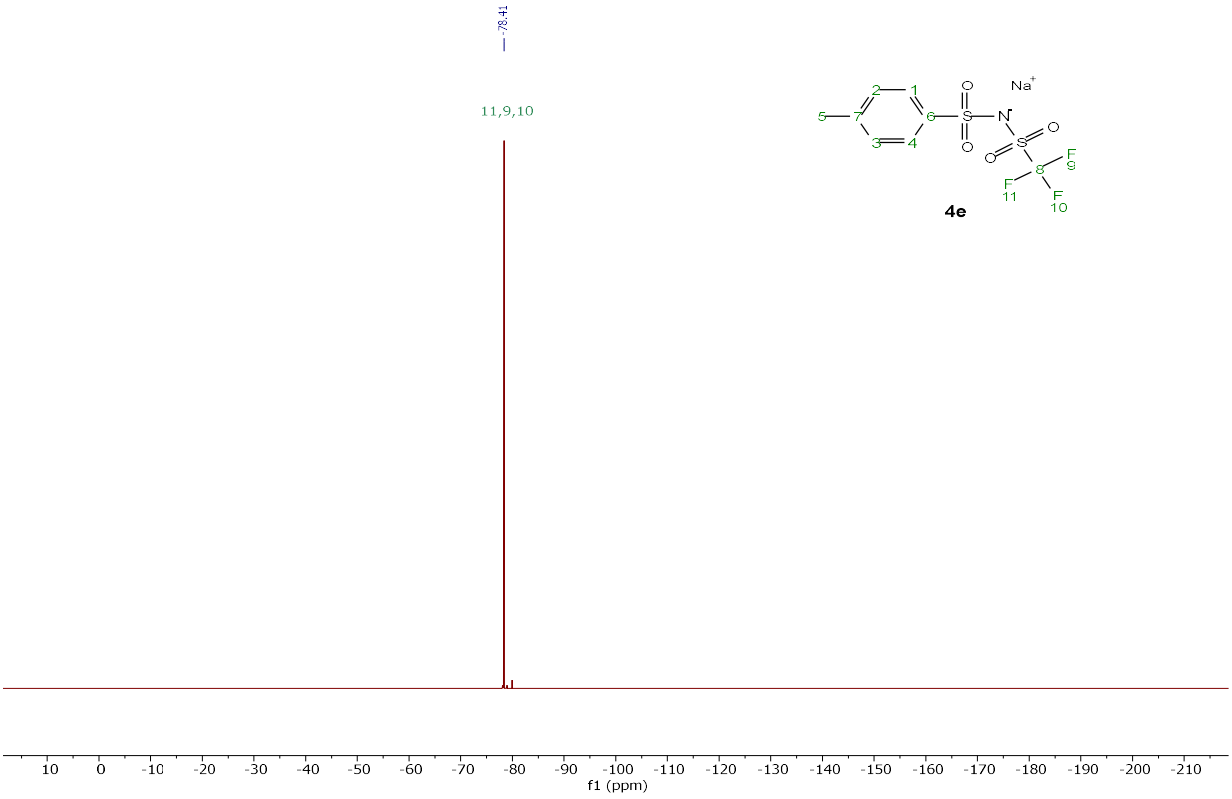
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

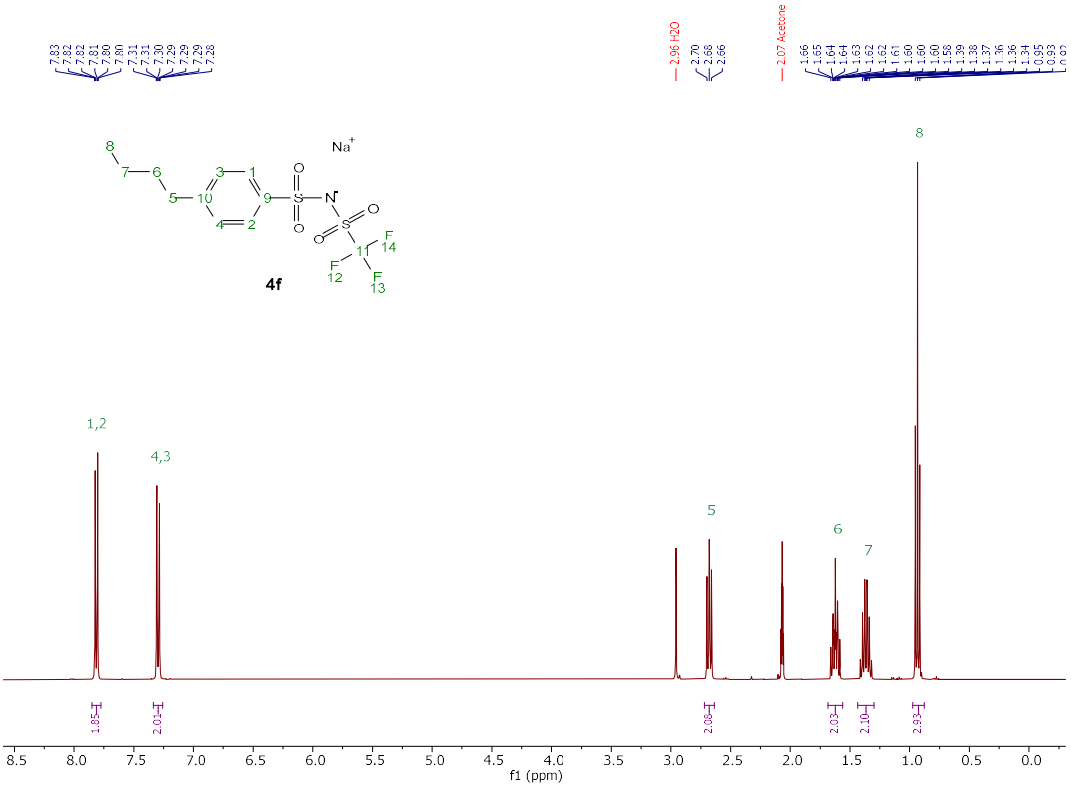


^{19}F NMR (376 MHz, Deuterium Oxide)

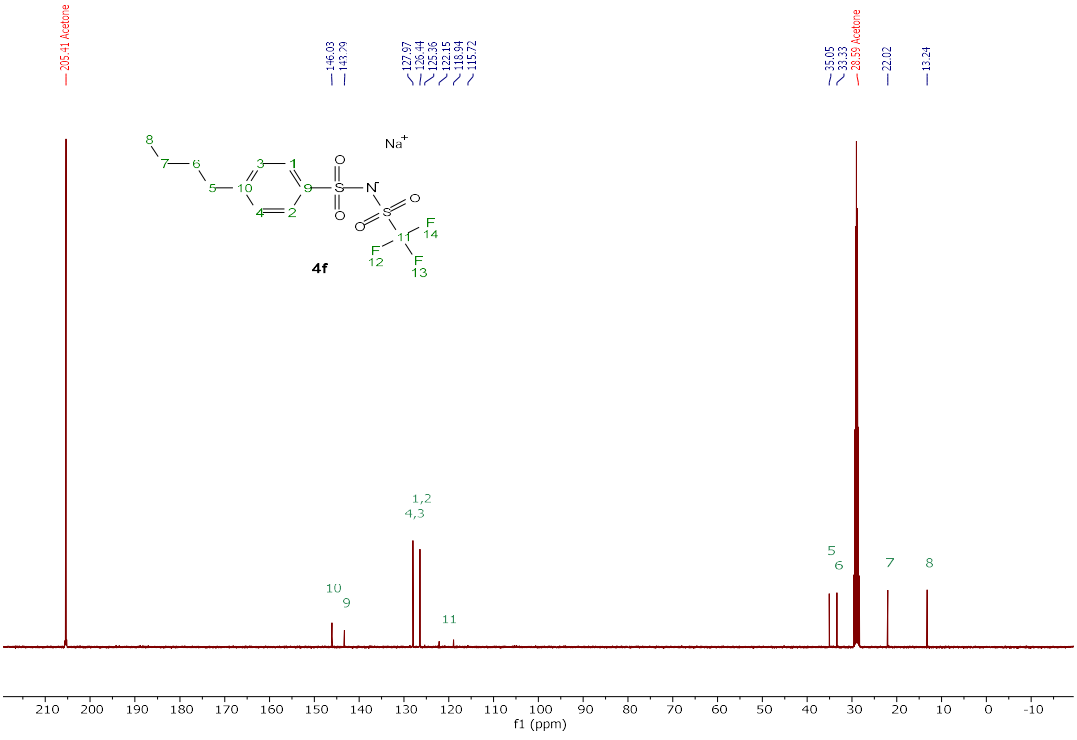


[Na][pBBSNTf], **4f**

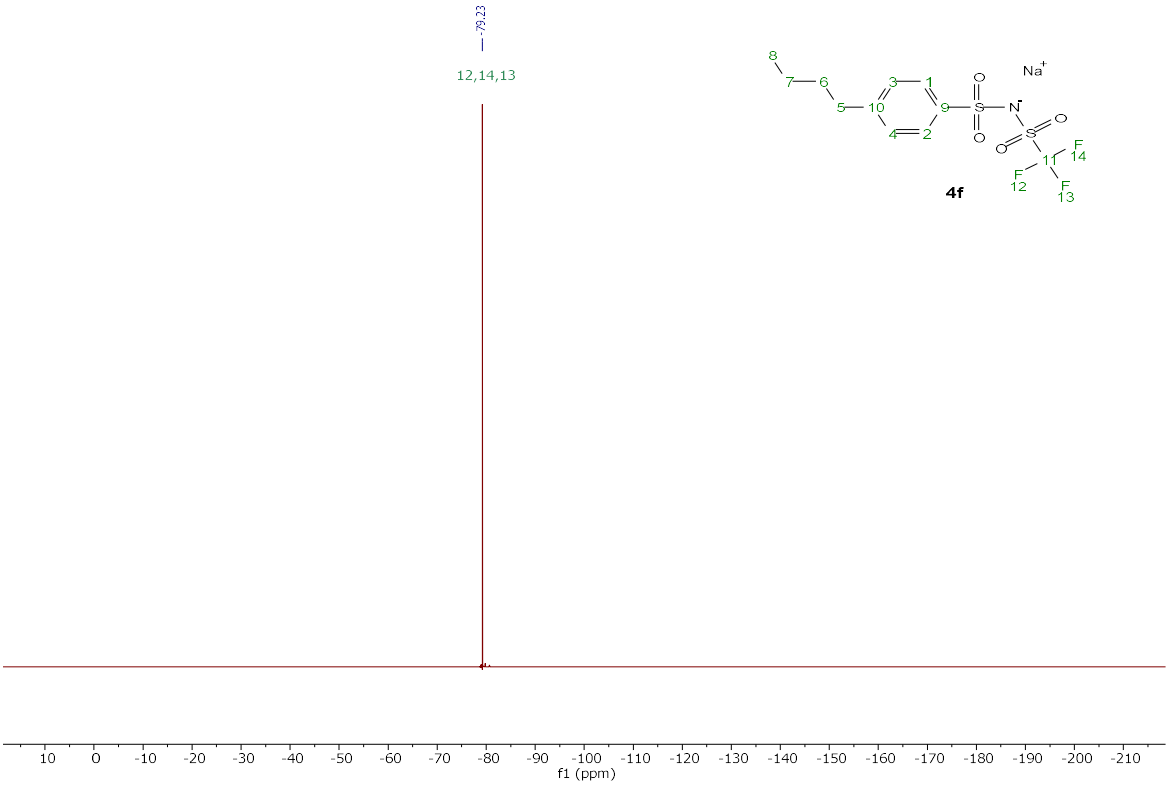
^{1}H NMR (400 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (101 MHz, Acetone-d6)

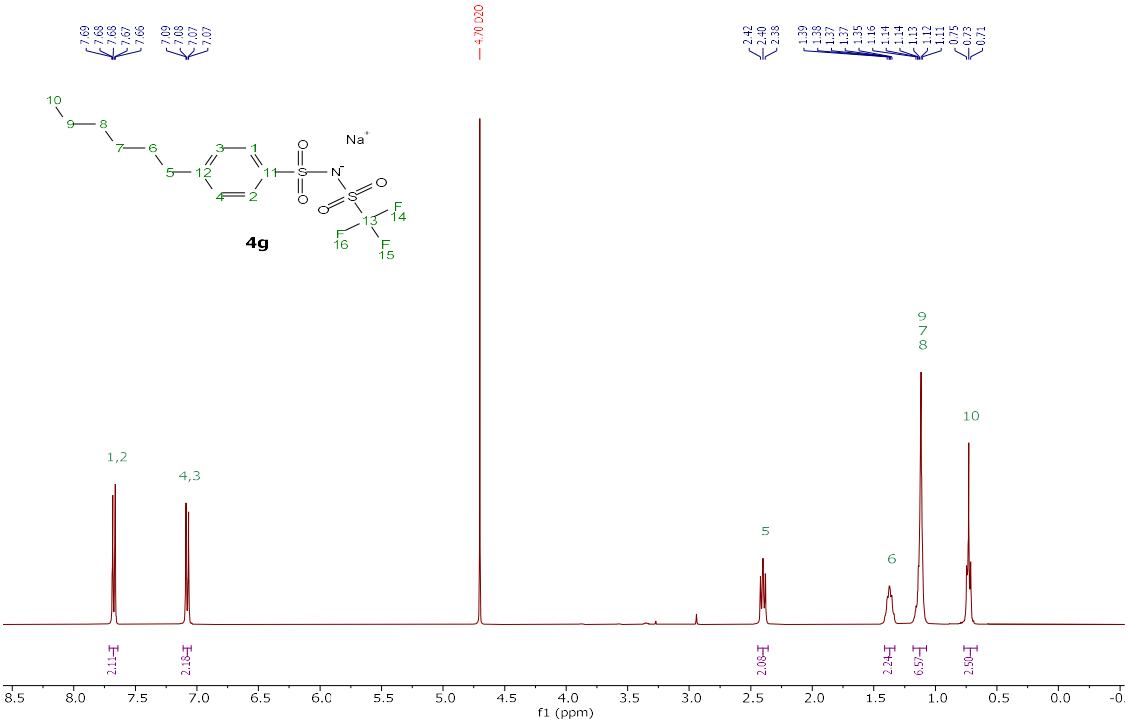


^{19}F NMR (376 MHz, Acetone-d6)

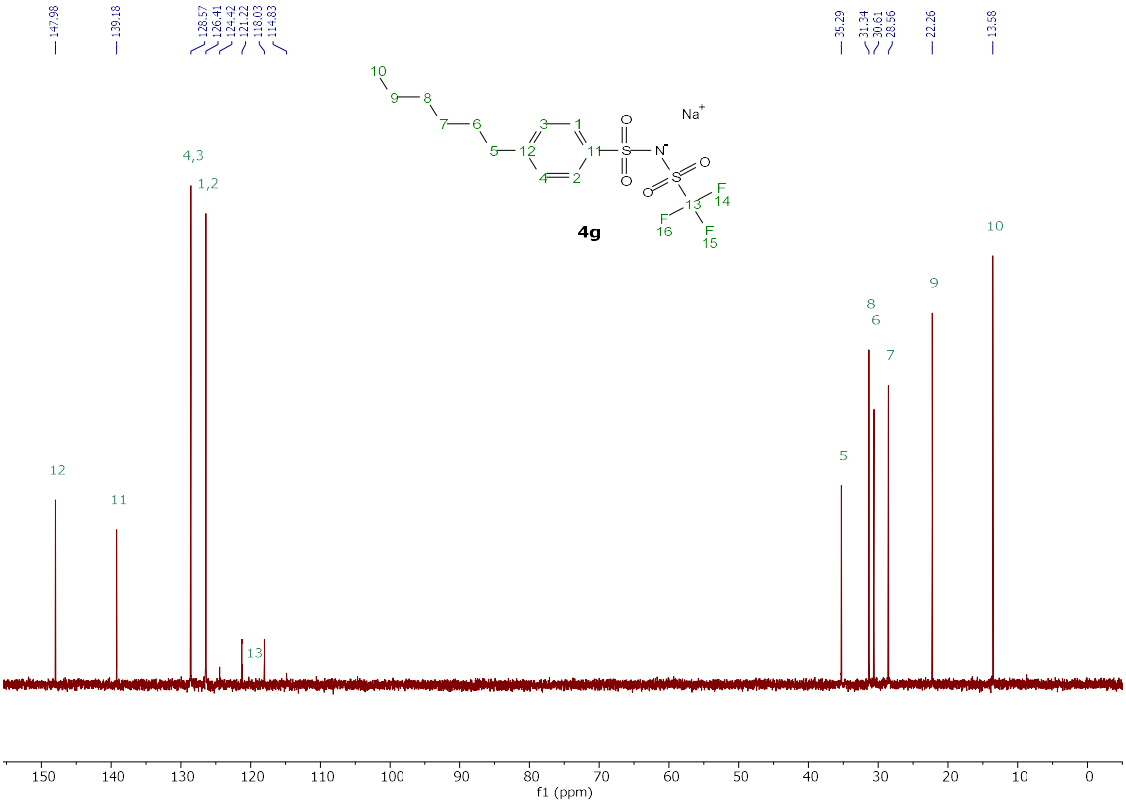


[Na][pHBSNTf], **4g**

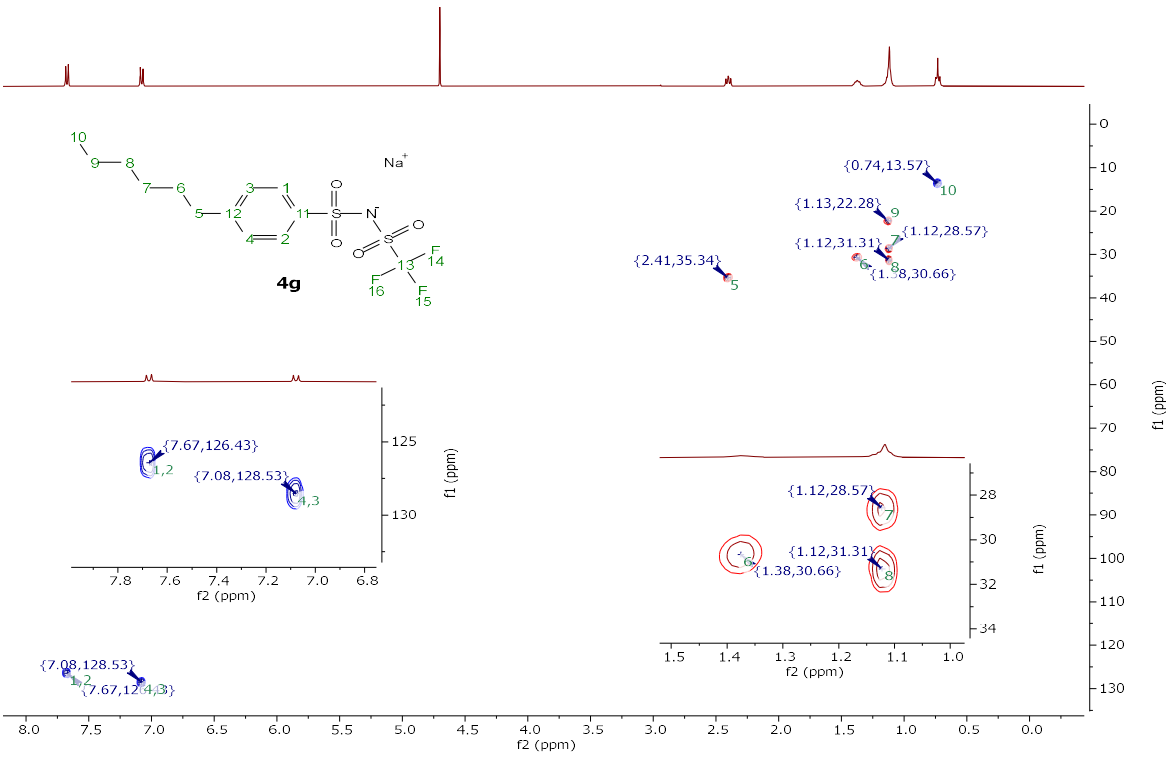
^{1}H NMR (400 MHz, Deuterium Oxide)



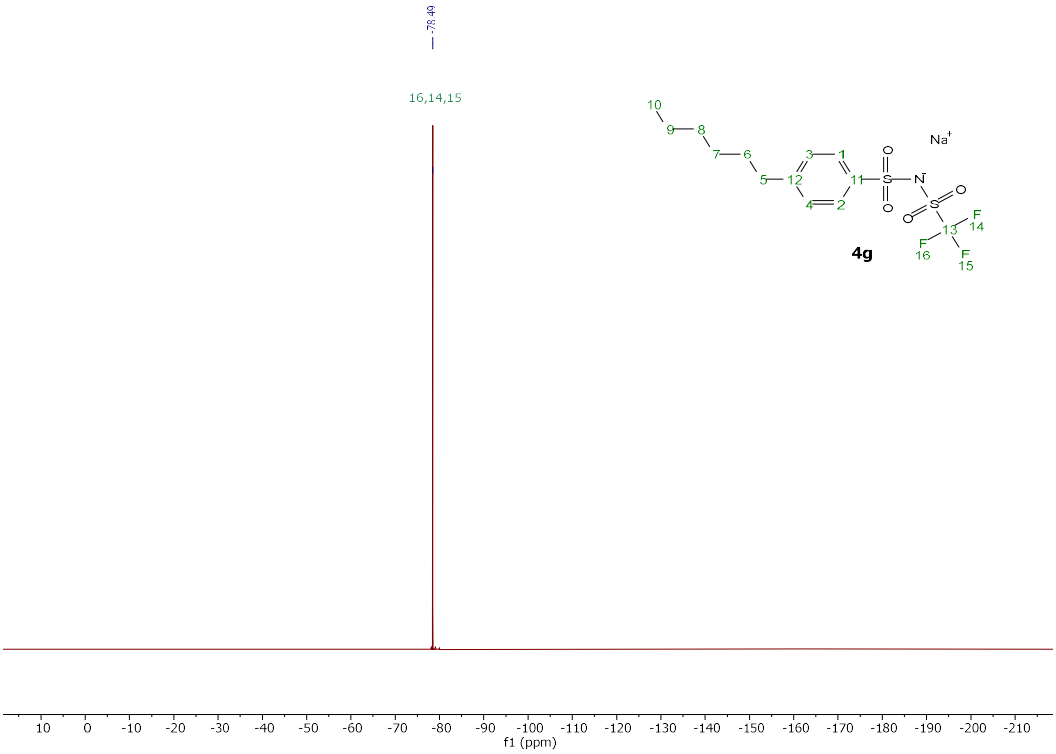
$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)



HSQC

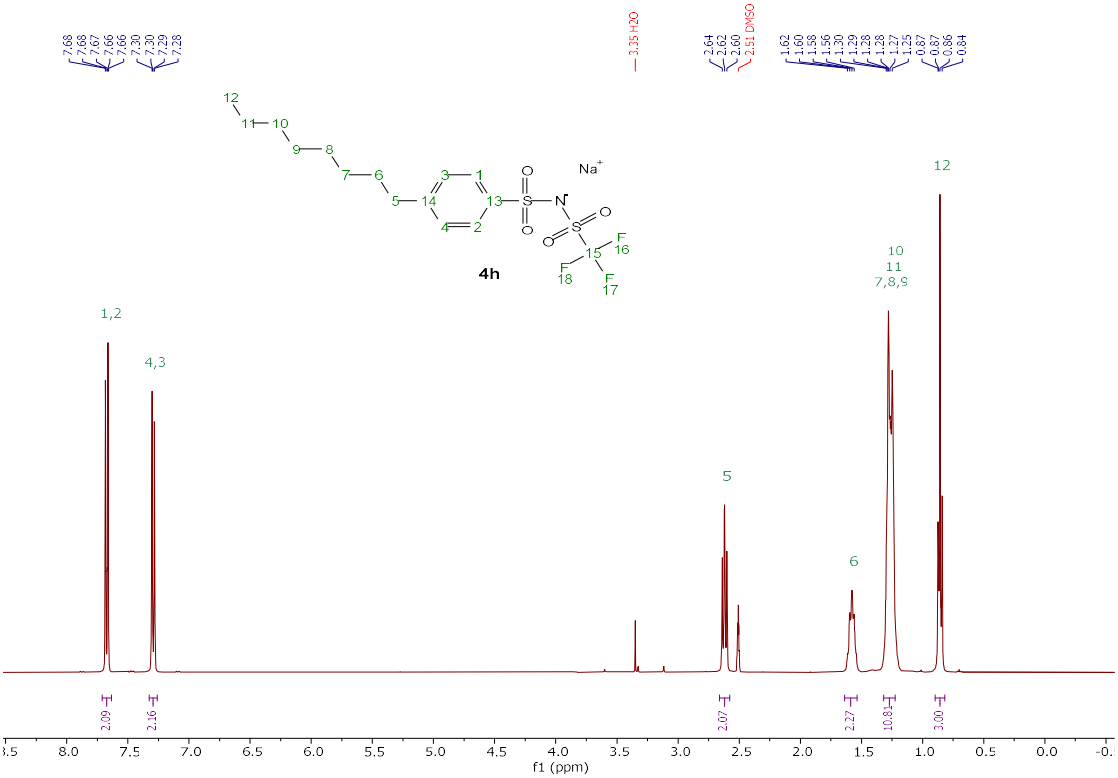


^{19}F NMR (376 MHz, Deuterium Oxide)

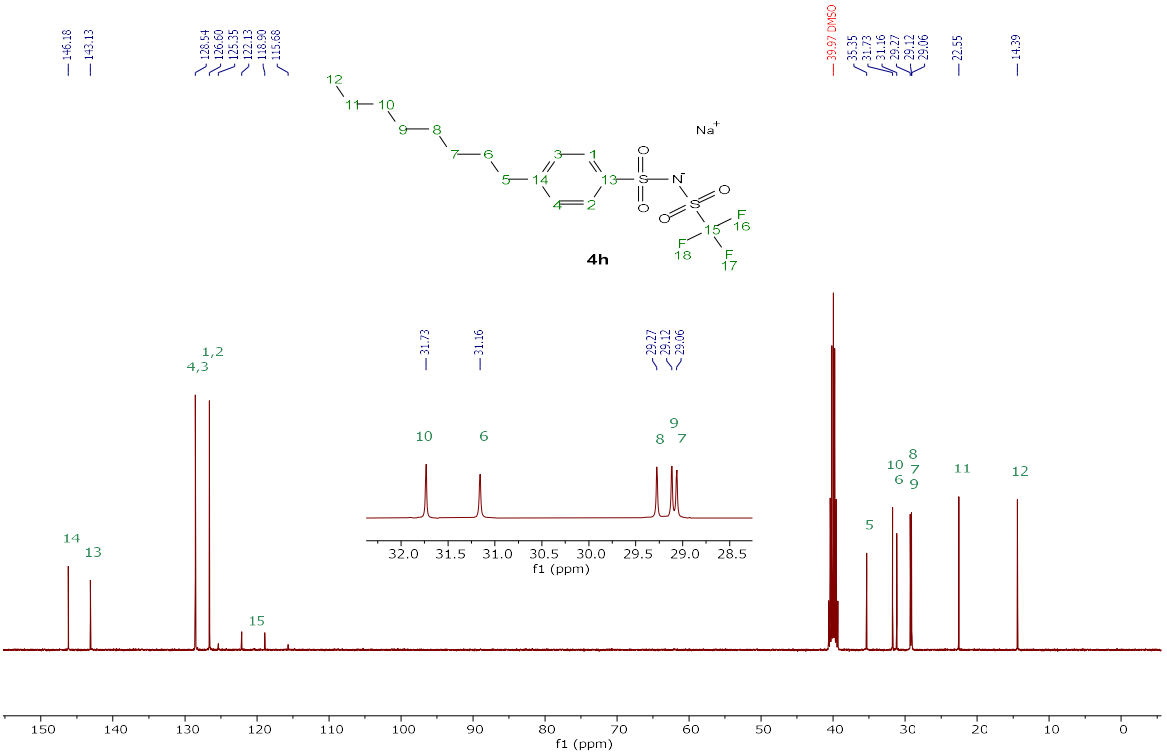


[Na][pOBSNTf], **4h**

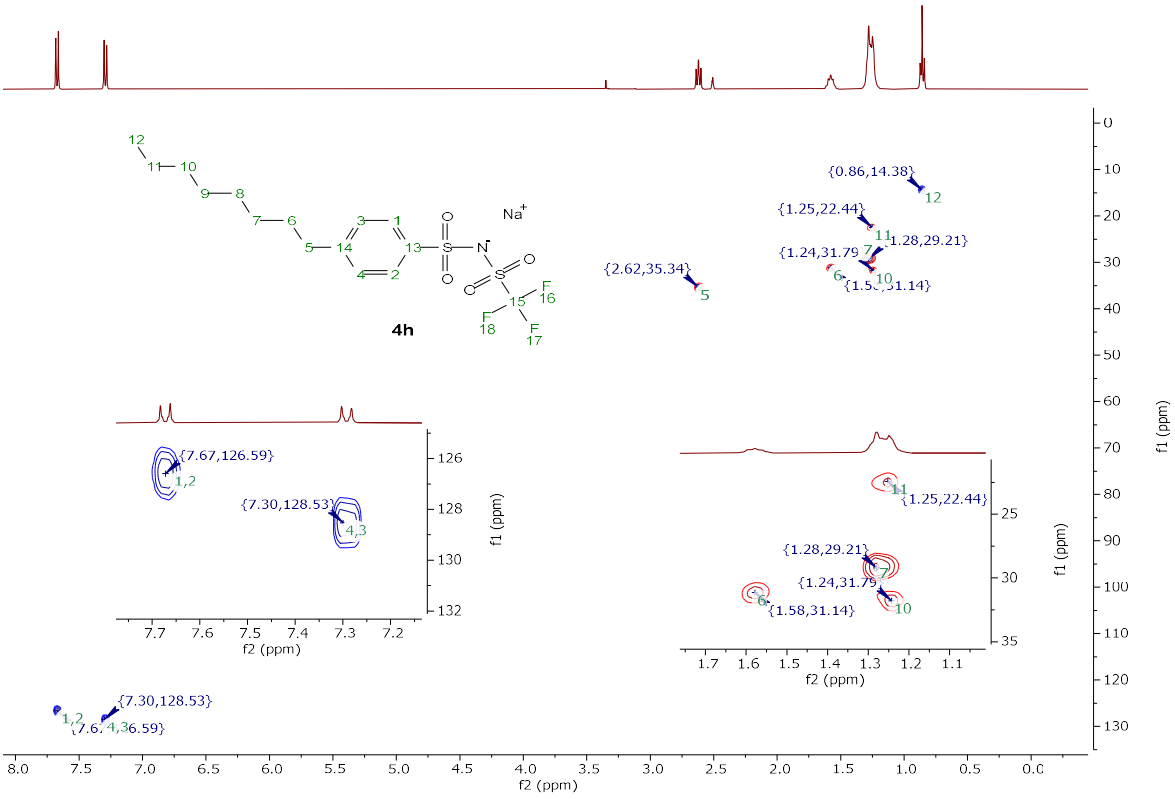
^{1}H NMR (400 MHz, DMSO-d6)



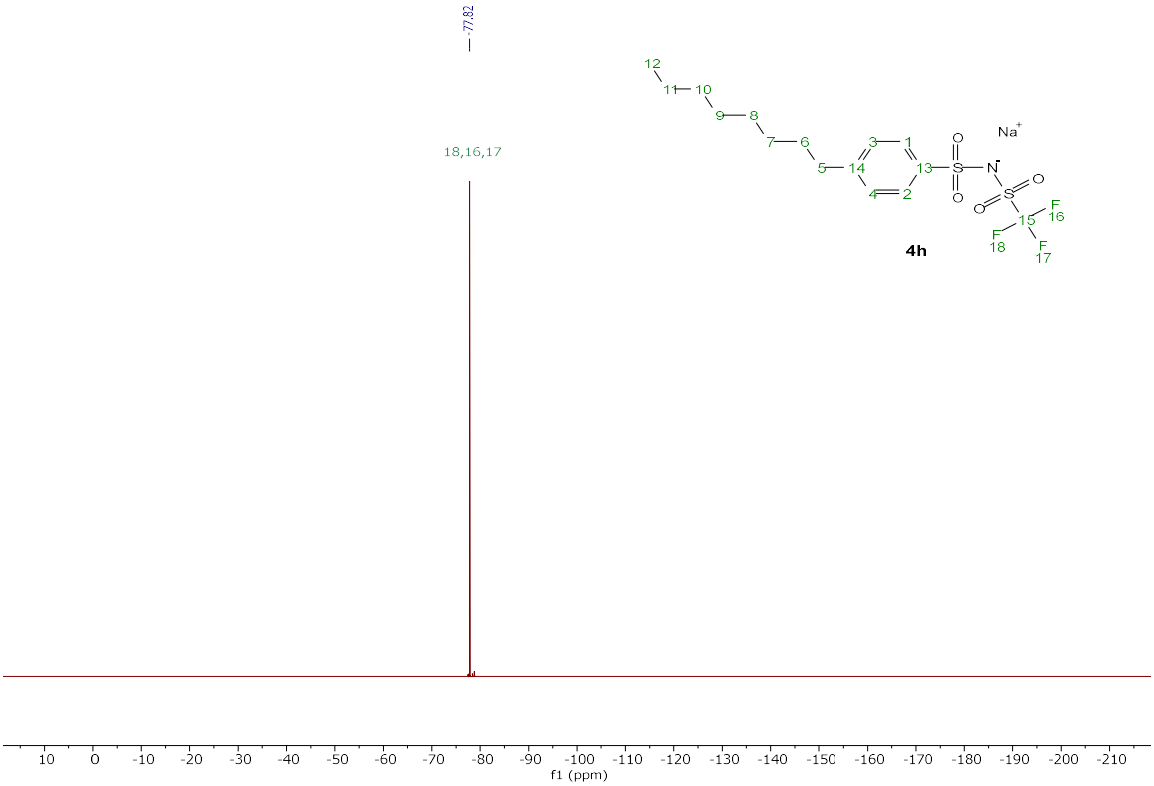
$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6)



HSQC (DMSO-d6)

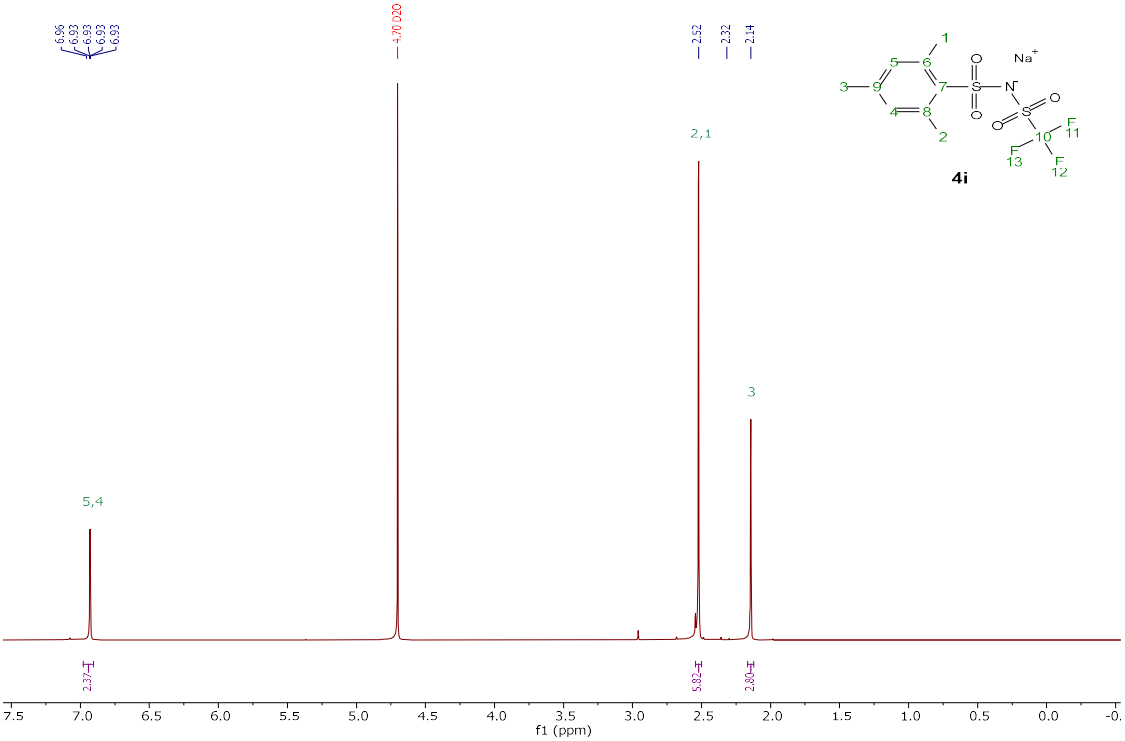


^{19}F NMR (376 MHz, DMSO-d6)

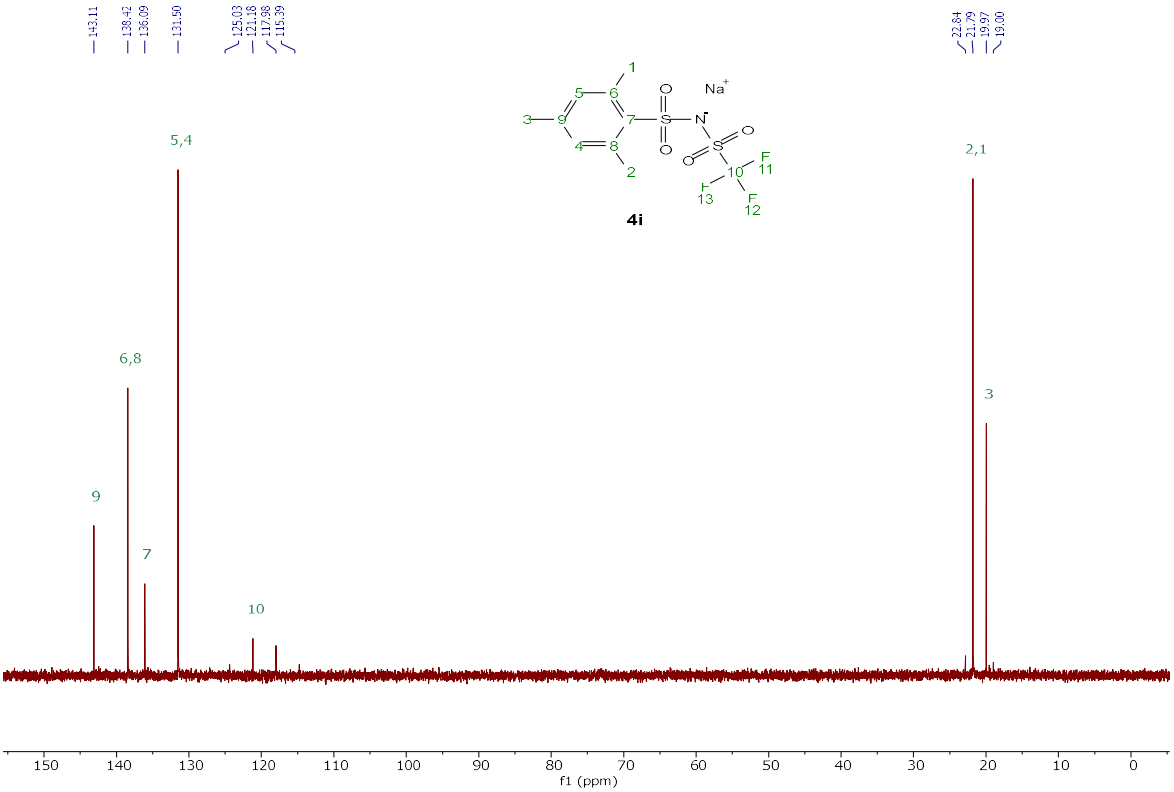


[Na][MesSNTf], **4i**

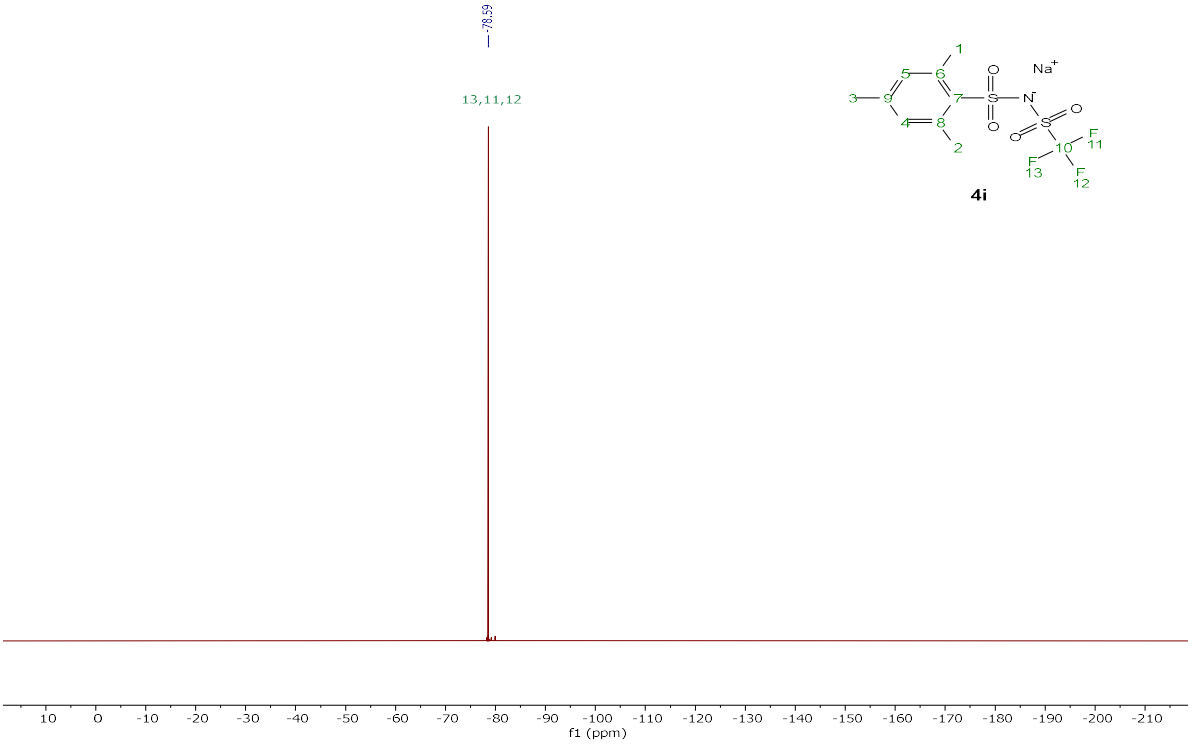
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

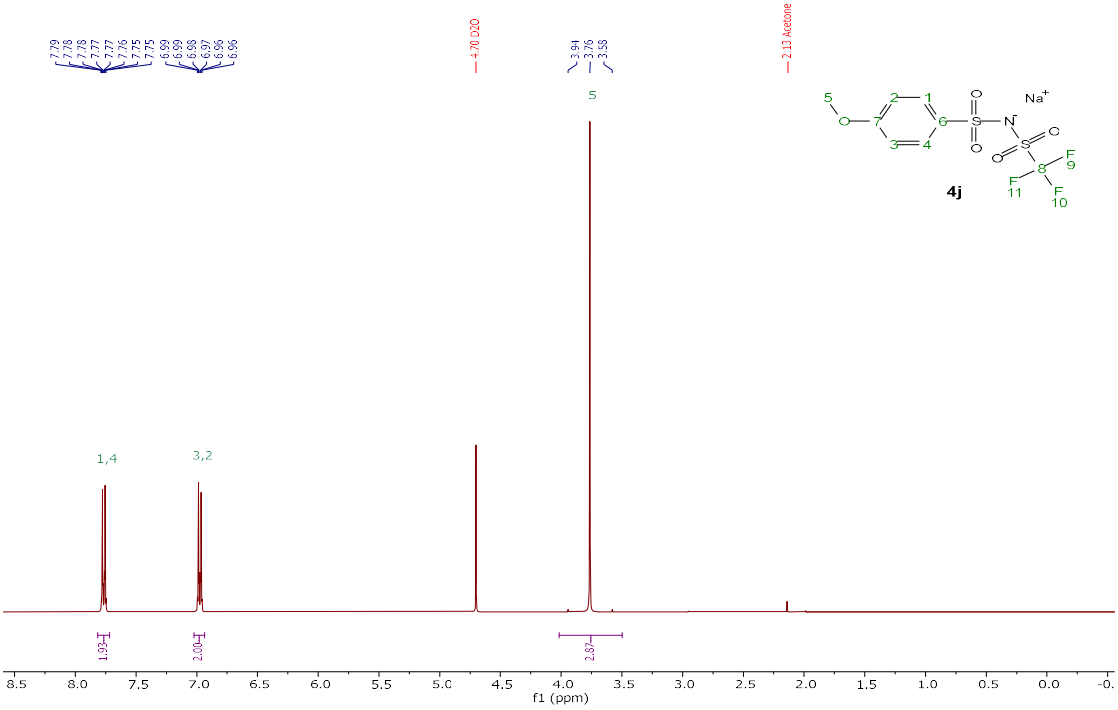


^{19}F NMR (376 MHz, Deuterium Oxide)

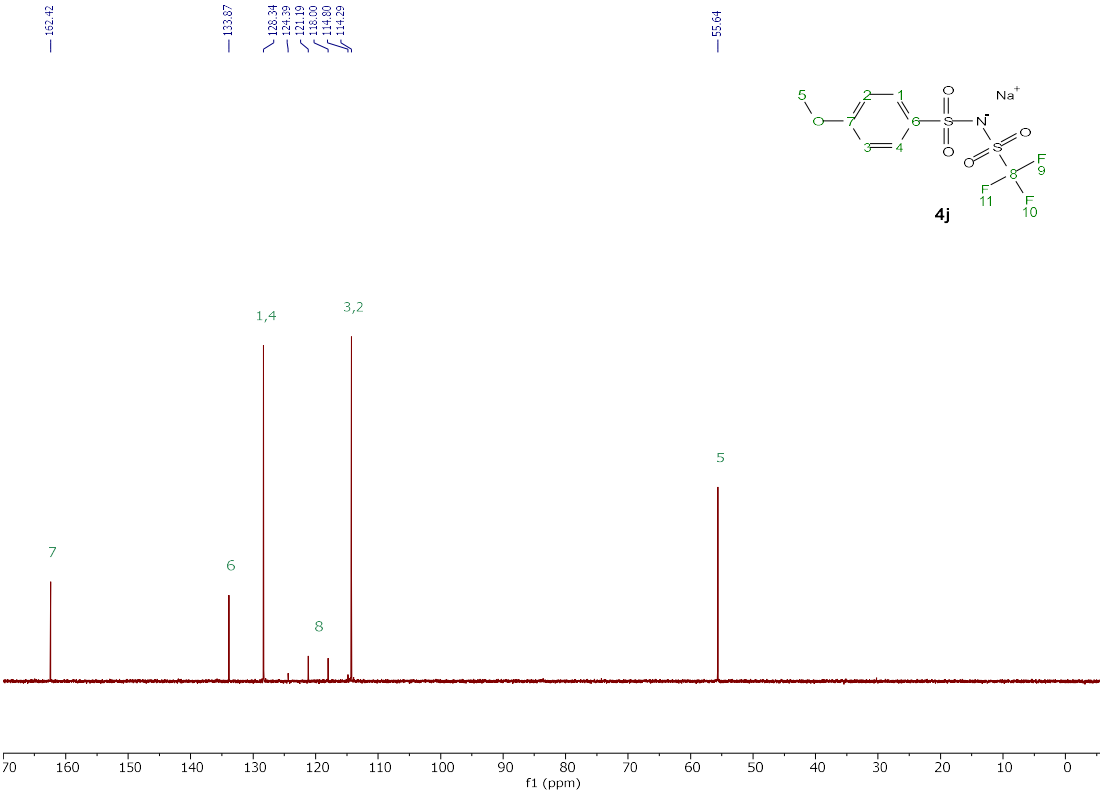


[Na][pMBSNTf], **4j**

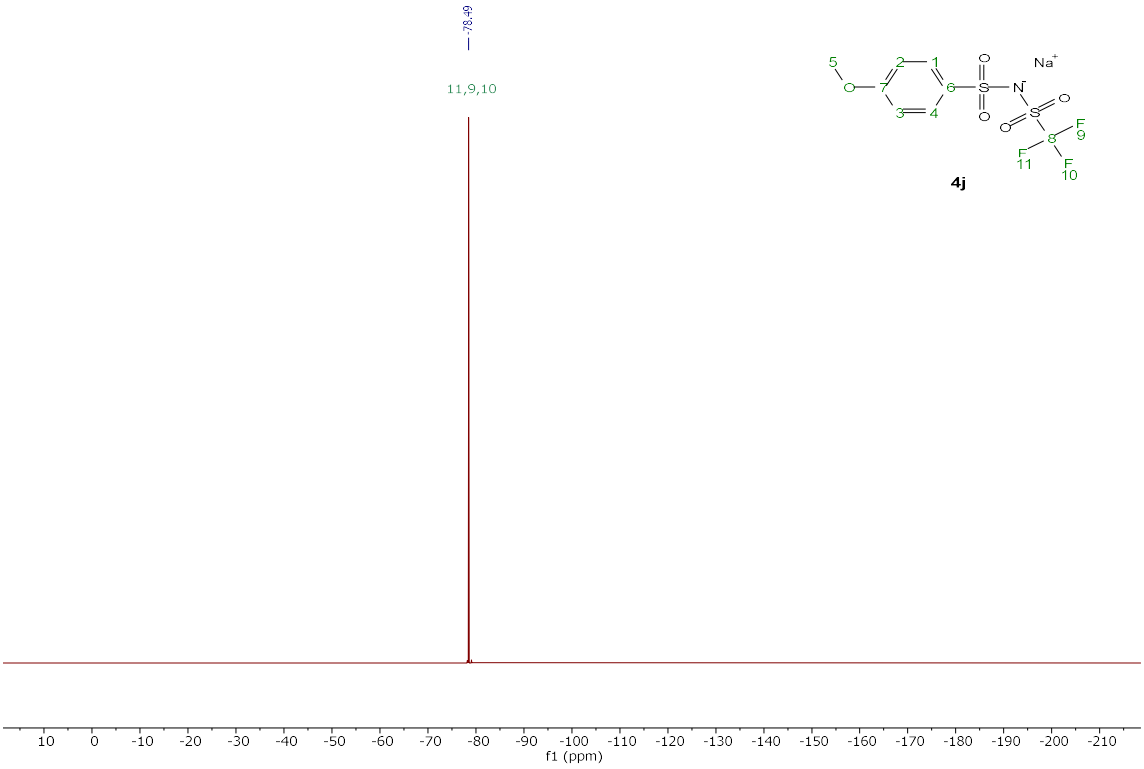
^{1}H NMR (400 MHz, Deuterium Oxide)



^{13}C{^{1}H} NMR (101 MHz, Deuterium Oxide)

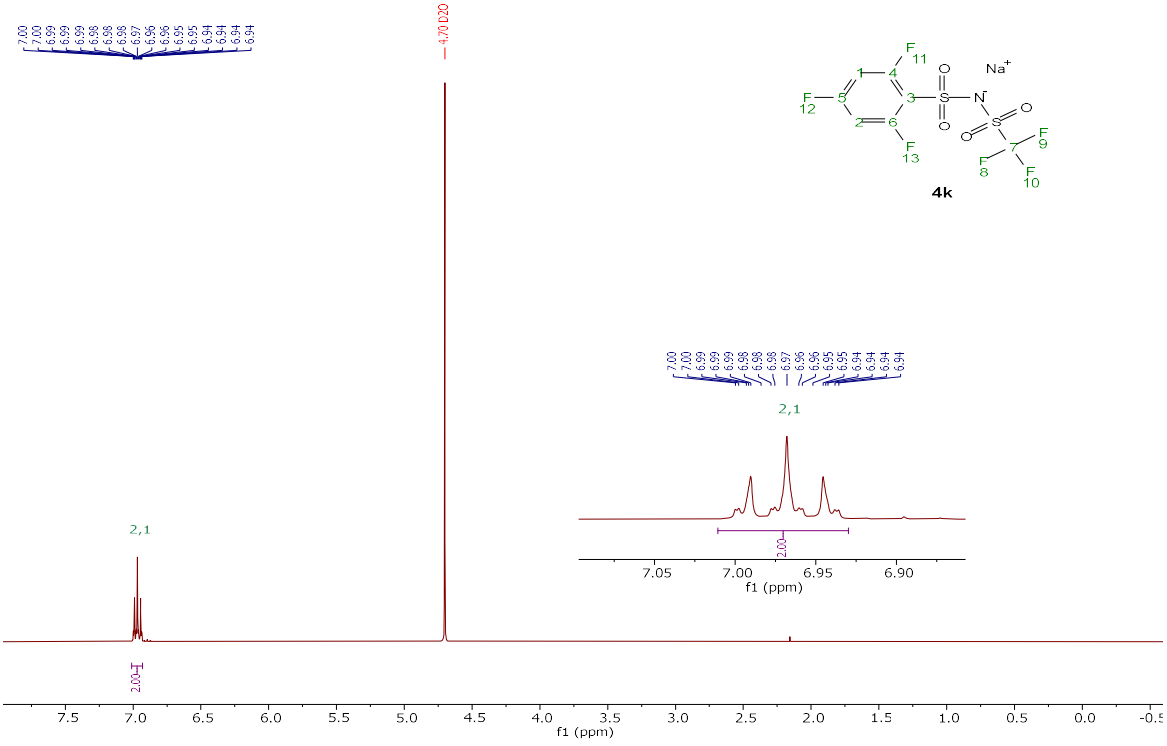


^{19}F NMR (376 MHz, Deuterium Oxide)

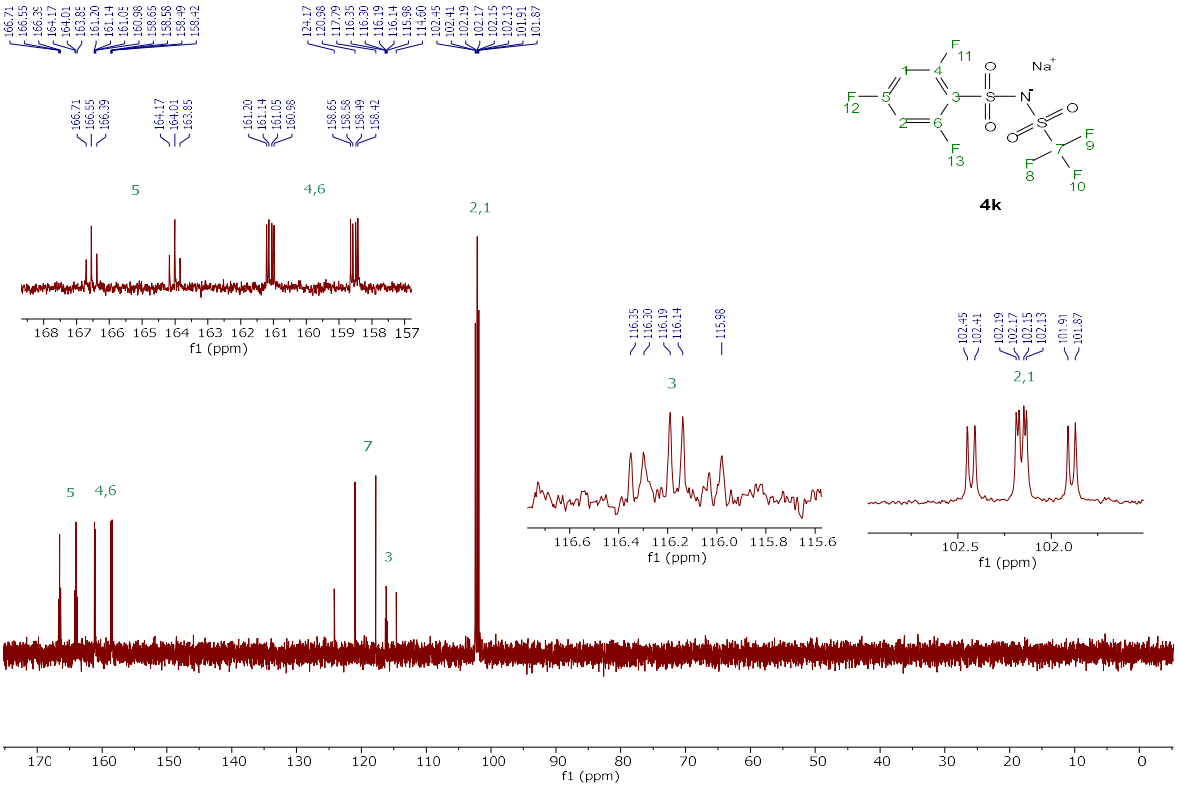


[Na][TFBSNTf], **4k**

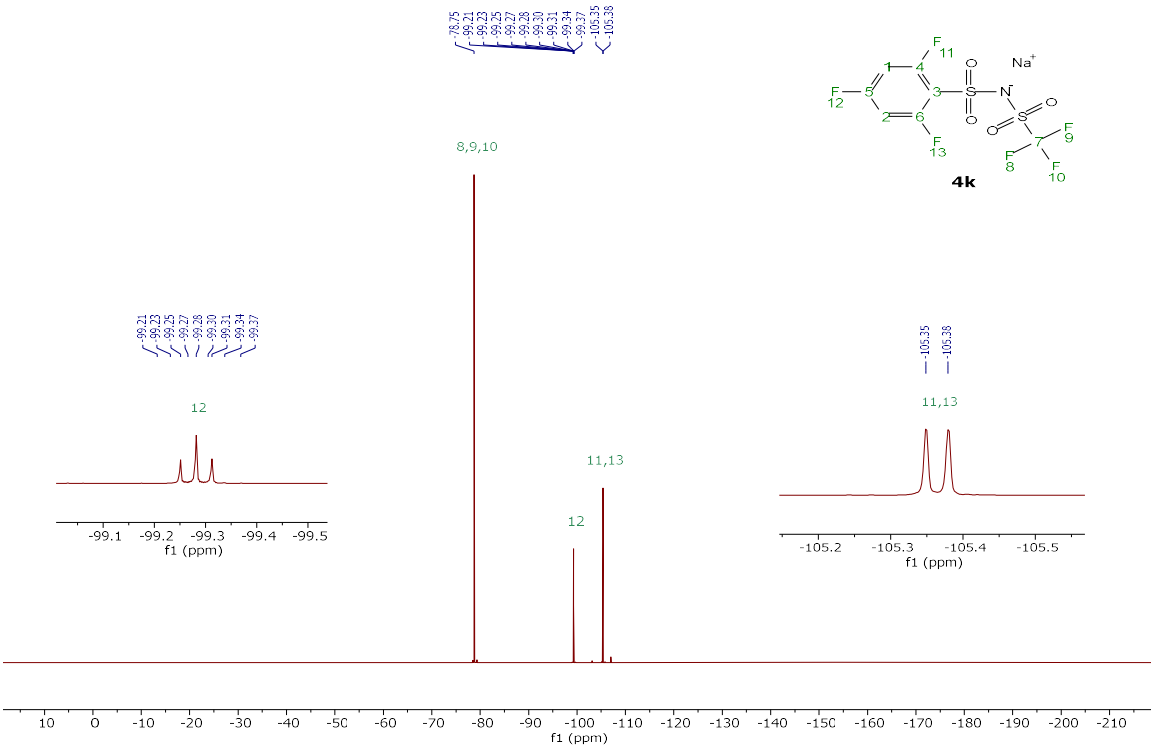
^{1}H NMR (400 MHz, Deuterium Oxide)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

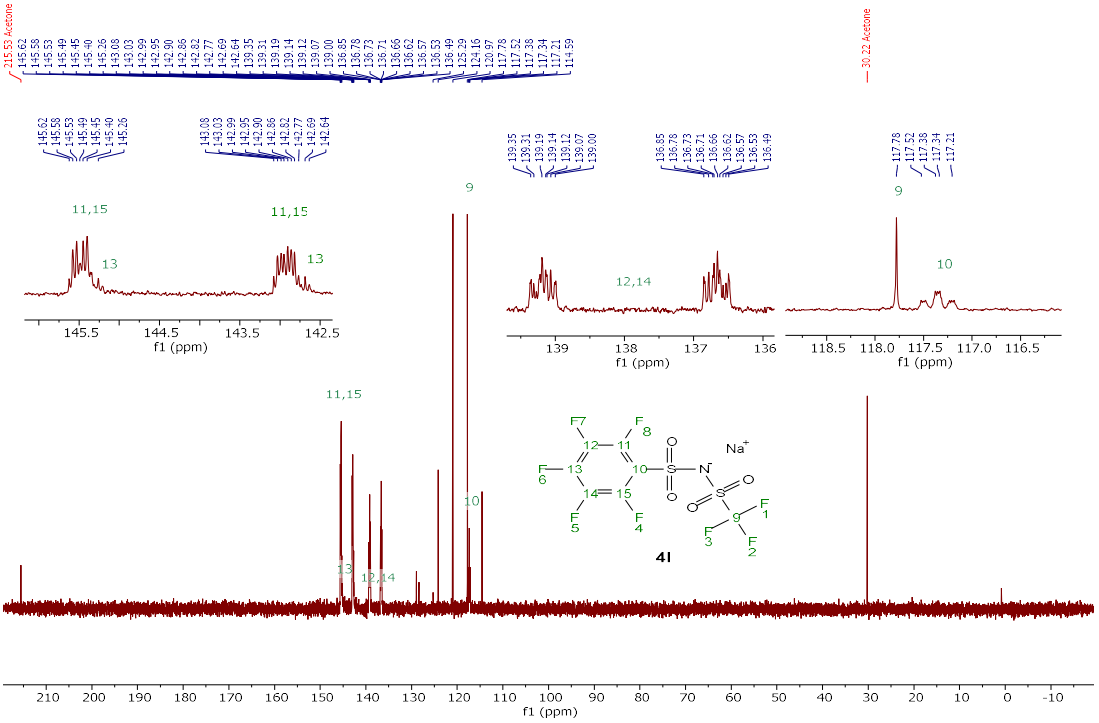


^{19}F NMR (376 MHz, Deuterium Oxide)

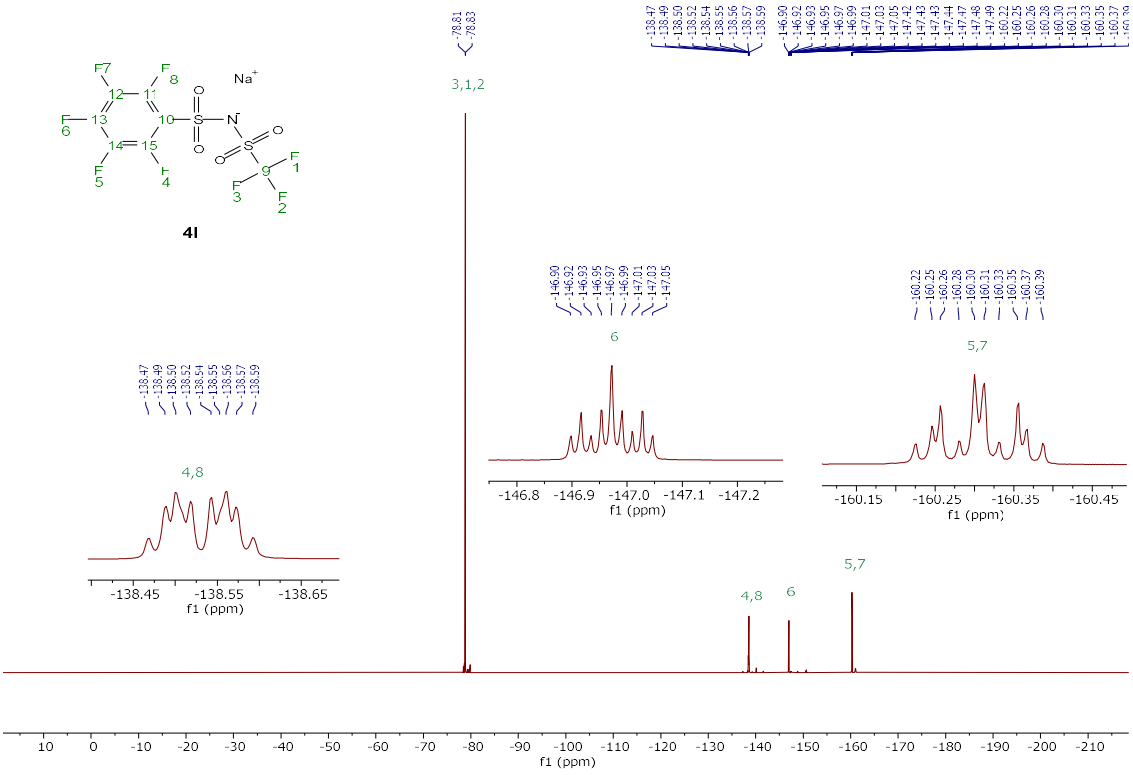


[Na][PFBSNTf], **4l**

$^{13}C\{^{1}H\}$ NMR (101 MHz, Deuterium Oxide)

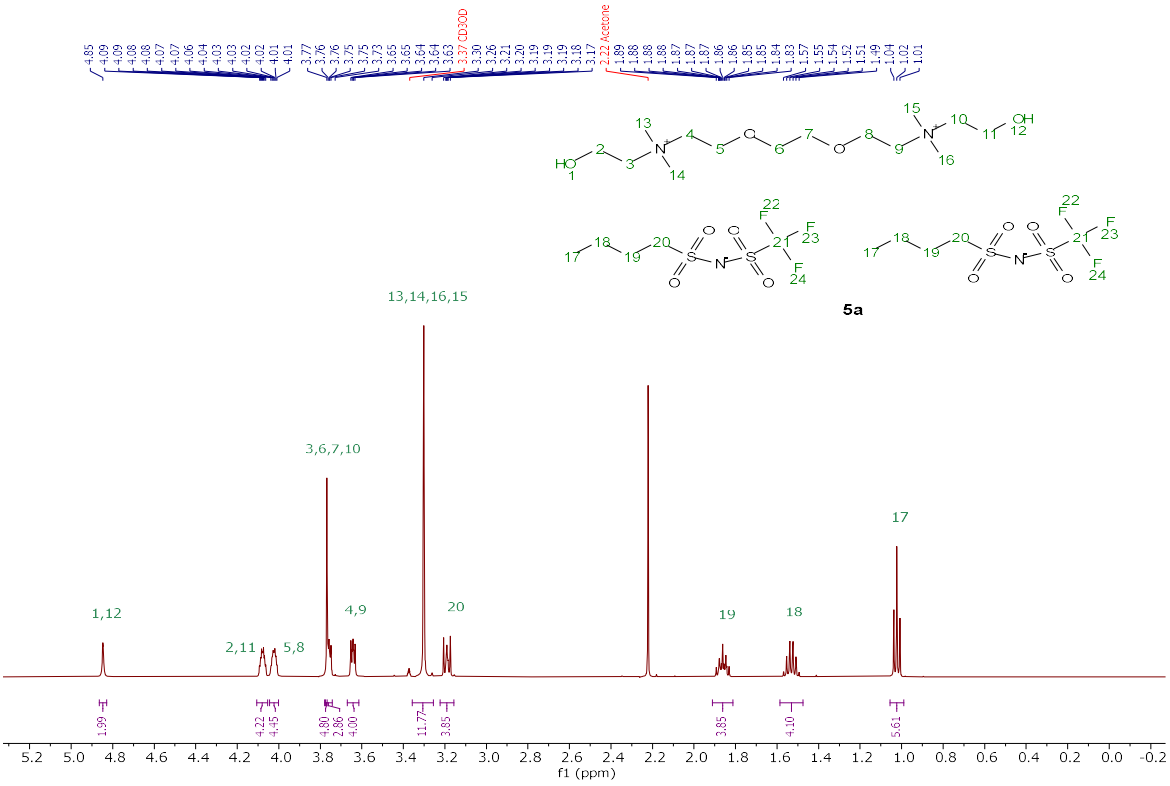


^{19}F NMR (376 MHz, Deuterium Oxide)

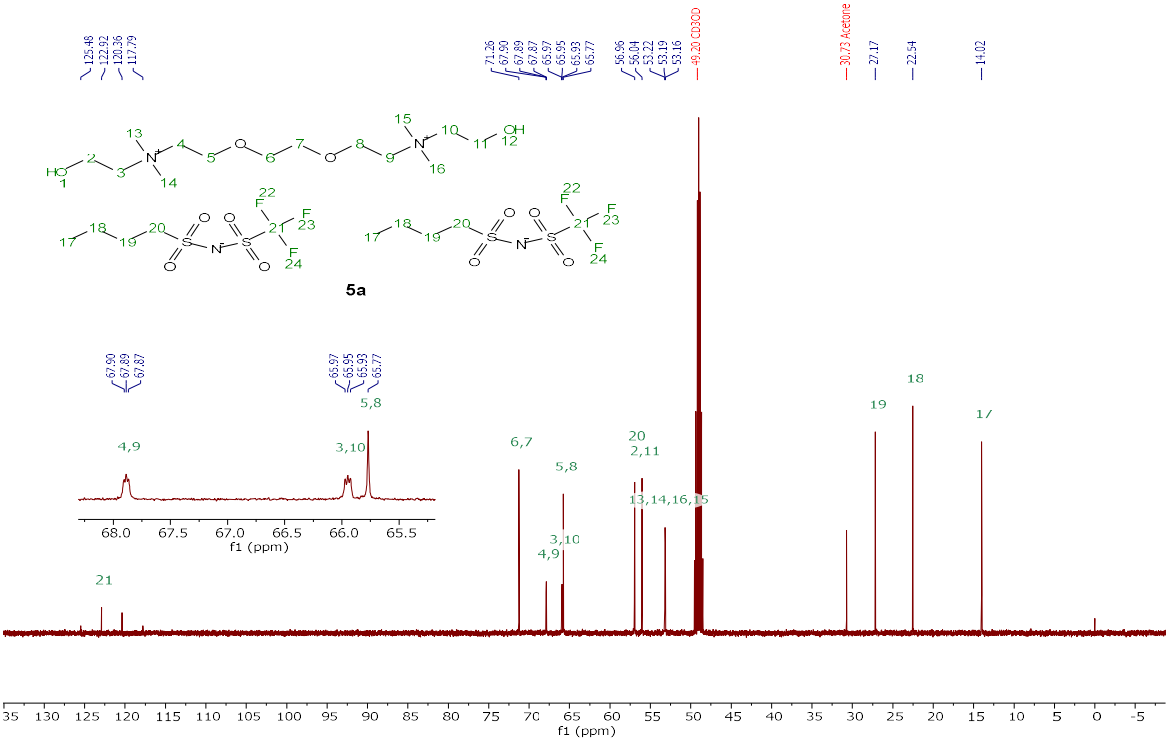


[DC-ether][2BSNTf], **5a**

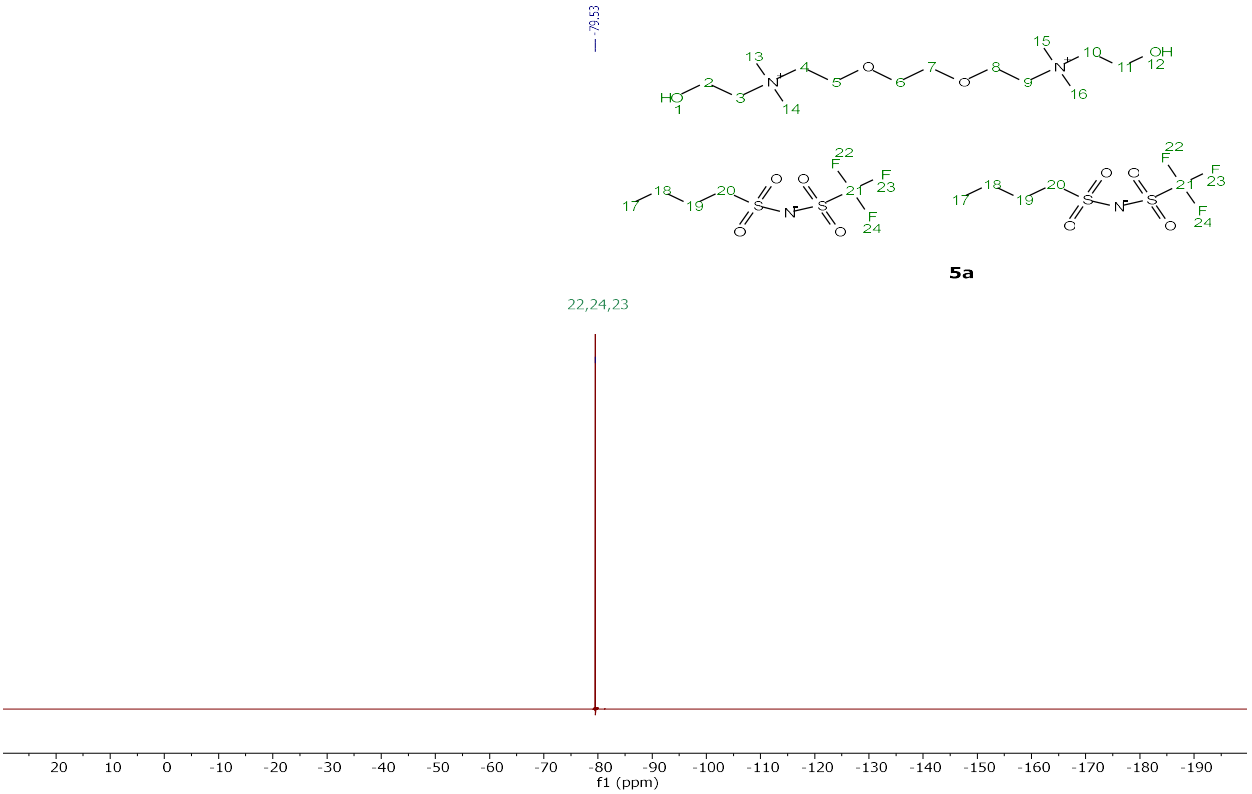
^{1}H NMR (500 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (126 MHz, Acetone-d6)

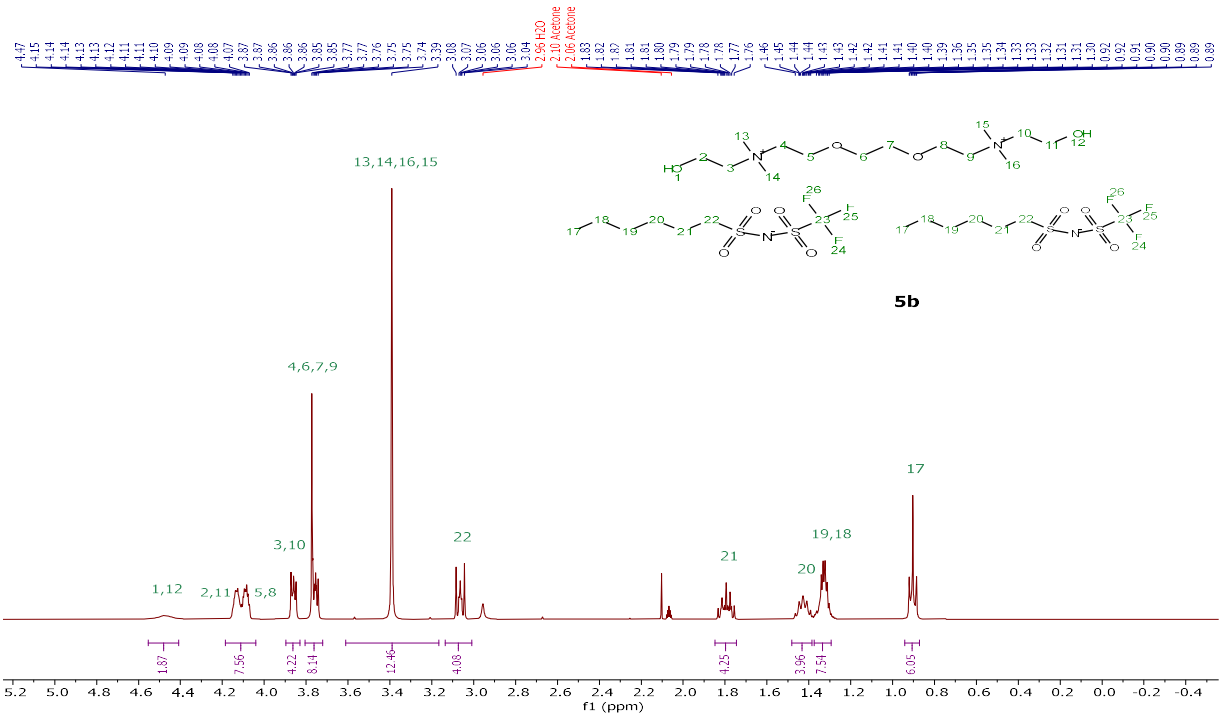


^{19}F NMR (470 MHz, Acetone-d6)

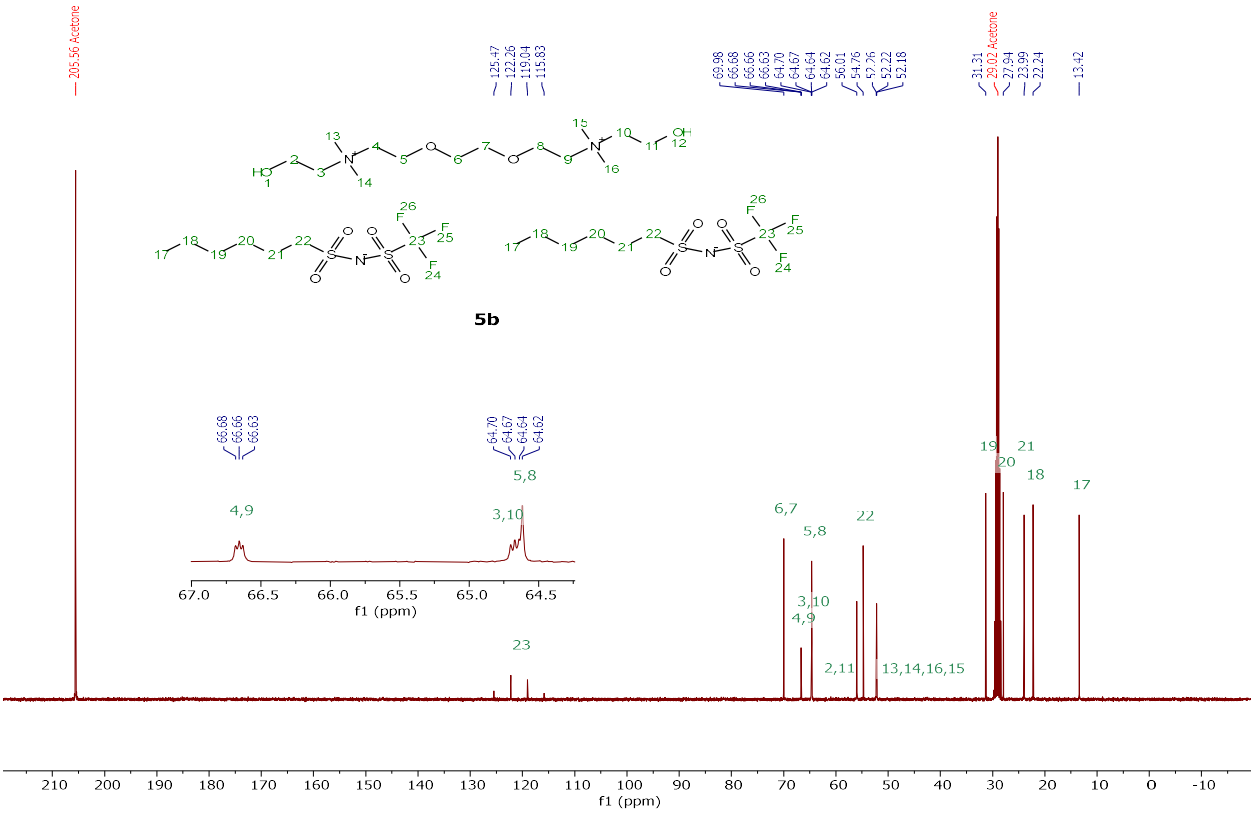


[DC-ether][2HSNTf], **5b**

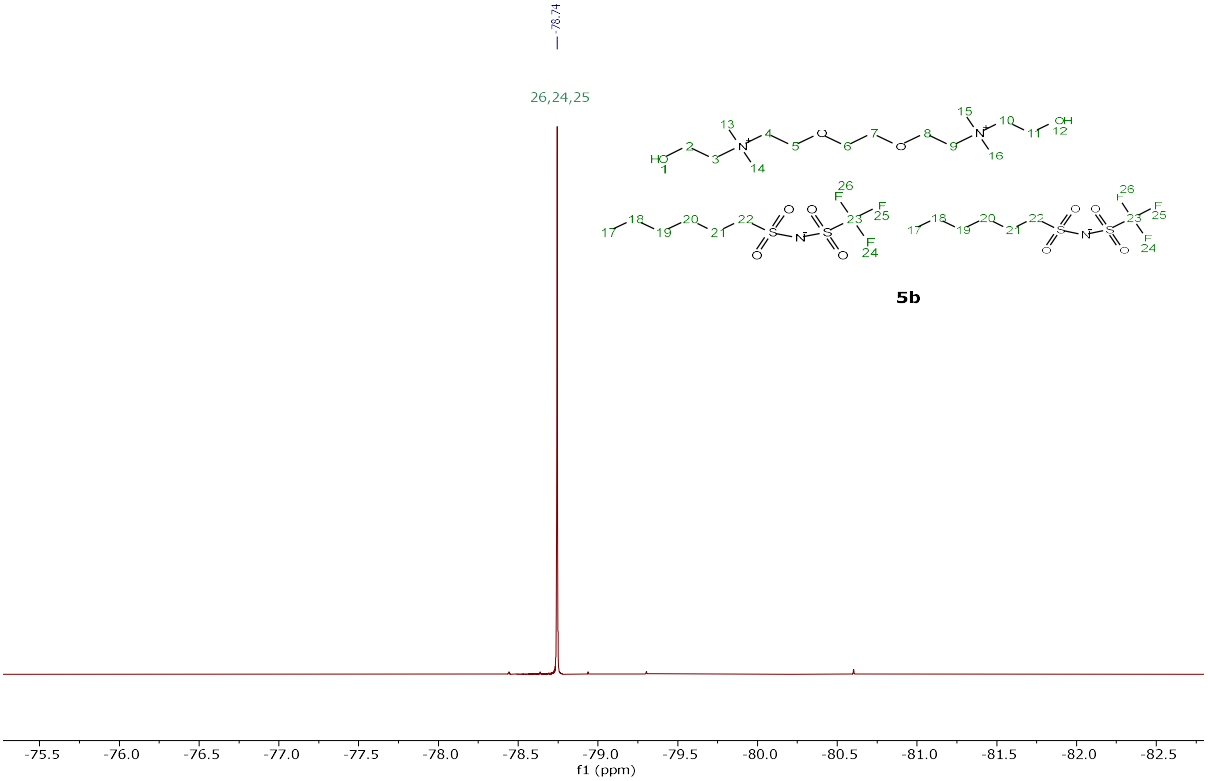
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

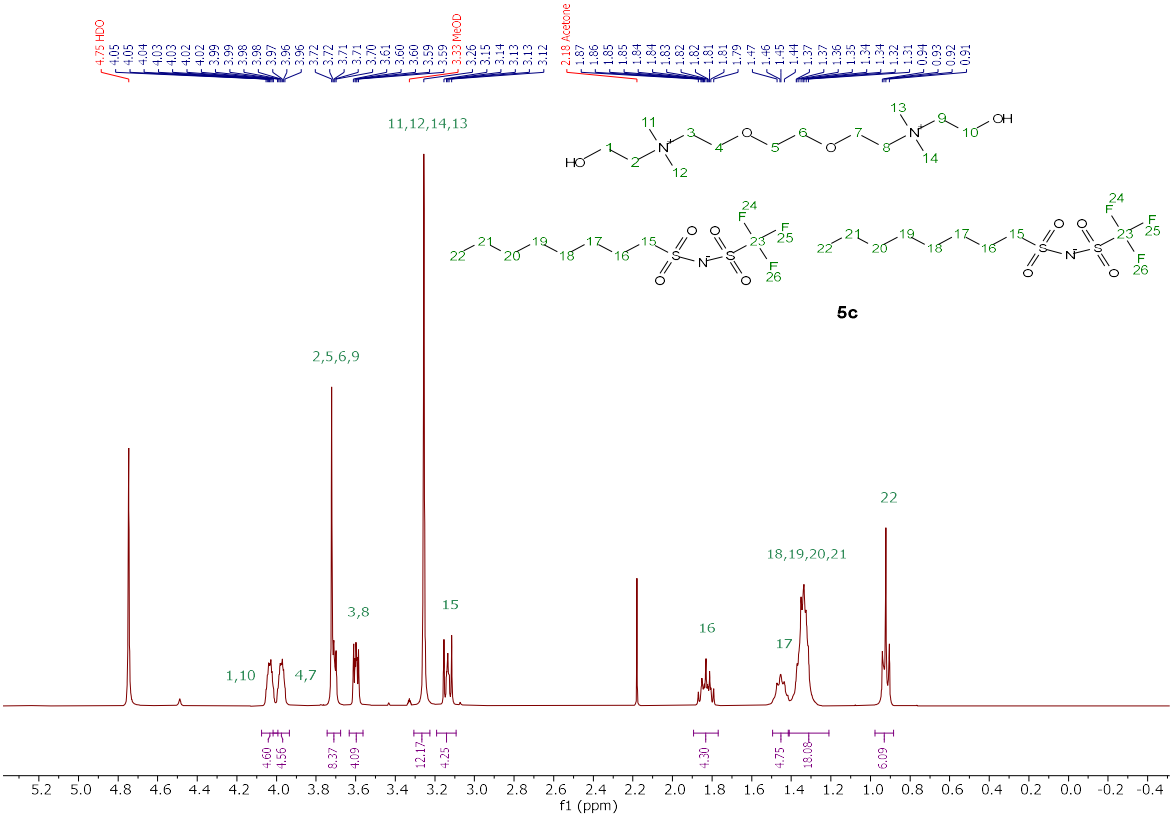


^{19}F NMR (376 MHz, Acetone-d6)

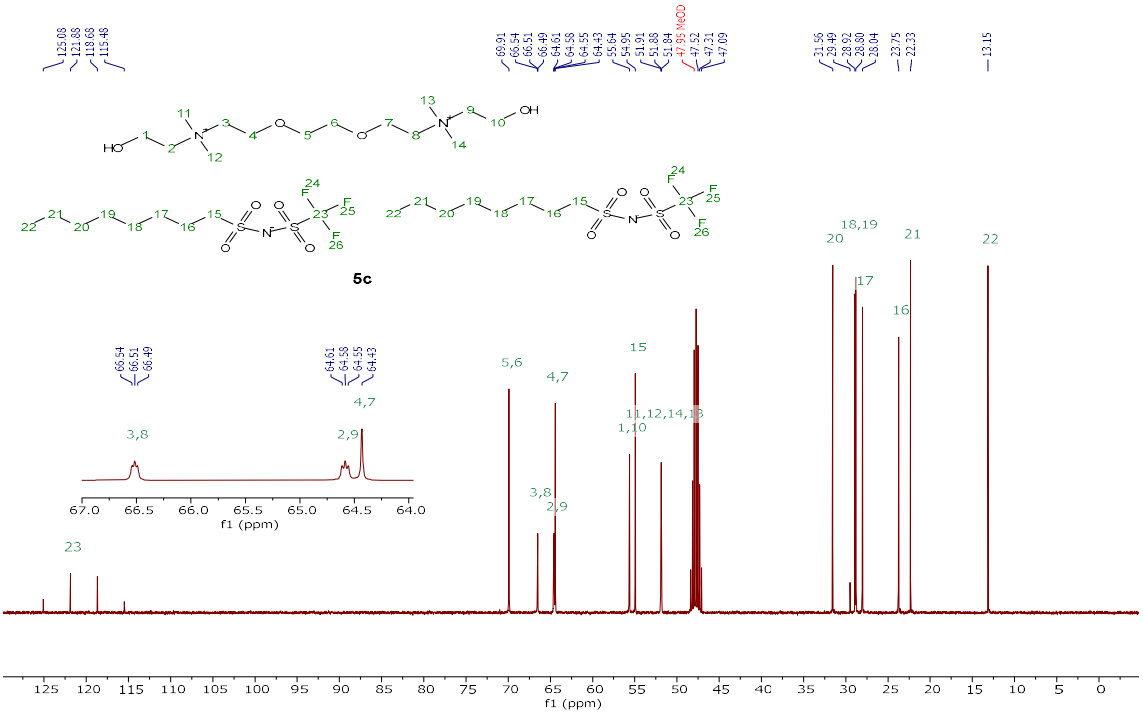


[DC-ether][2OSNTf], **5c**

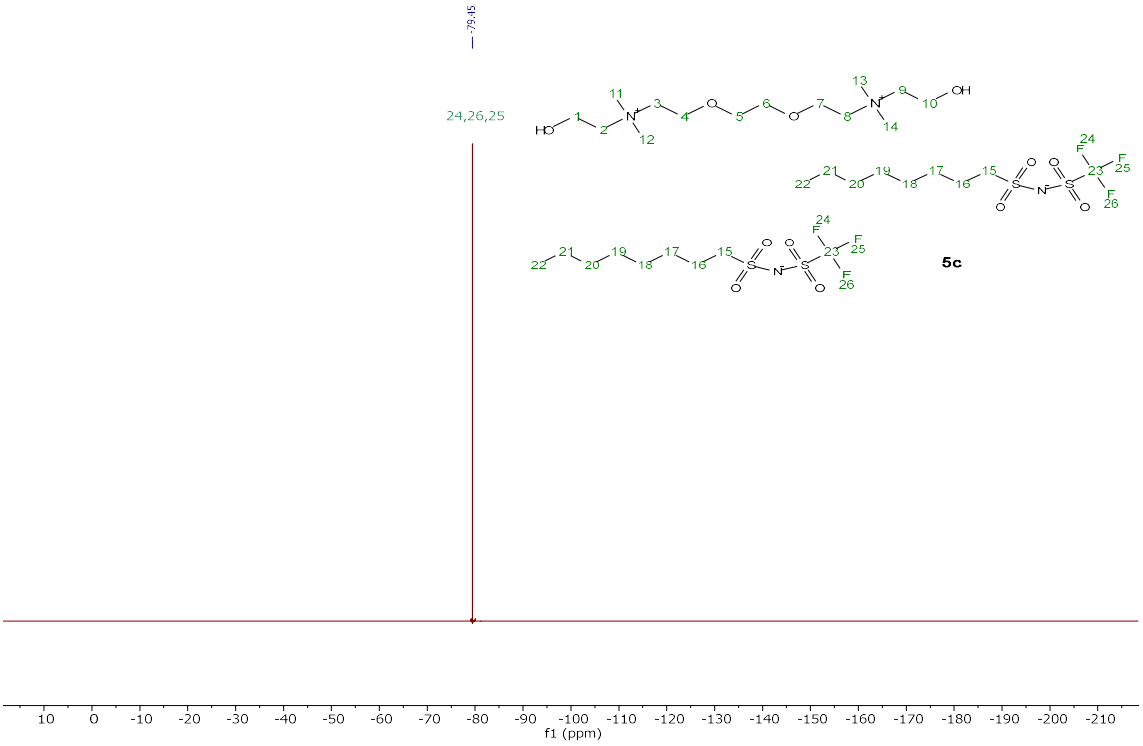
^{1}H NMR (400 MHz, Methanol-d4)



^{13}C{^{1}H} NMR (101 MHz, Methanol-d4)

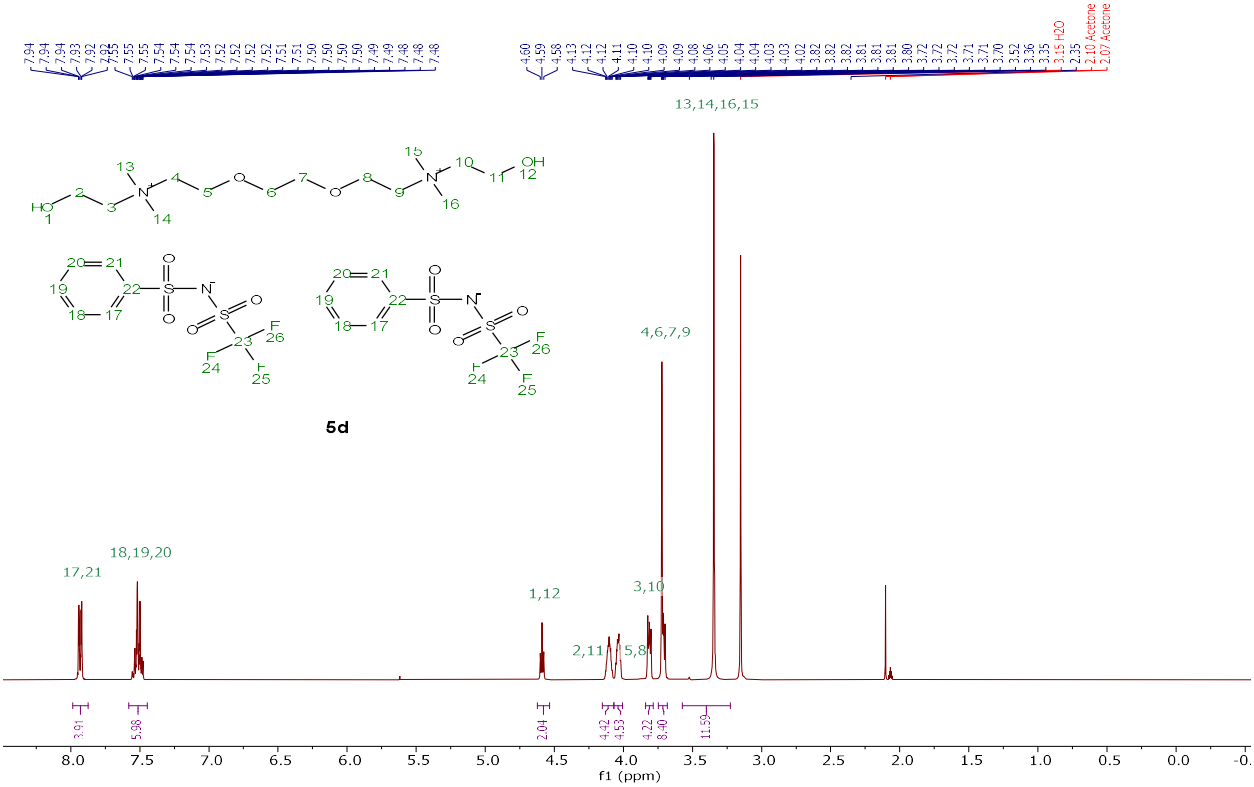


^{19}F NMR (376 MHz, Acetone-d6)

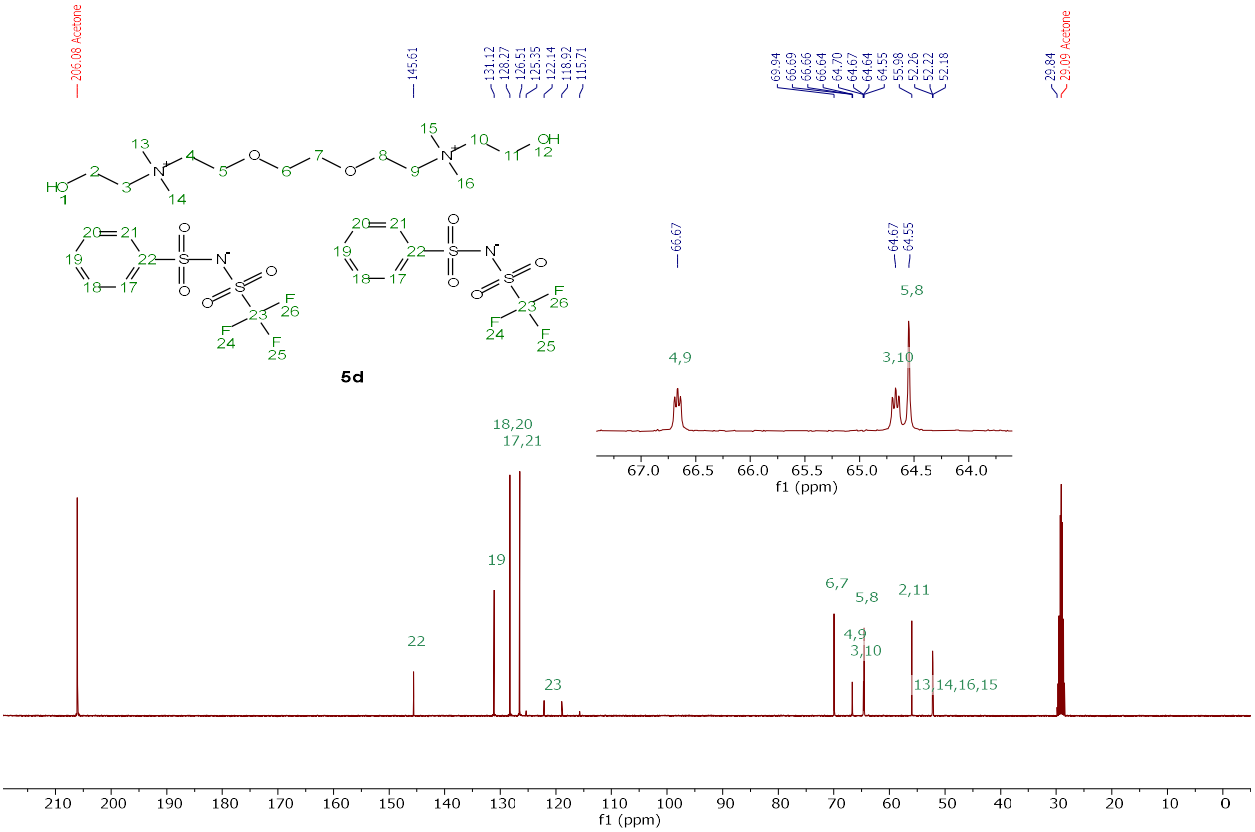


[DC-ether][2PhSNTf], **5d**

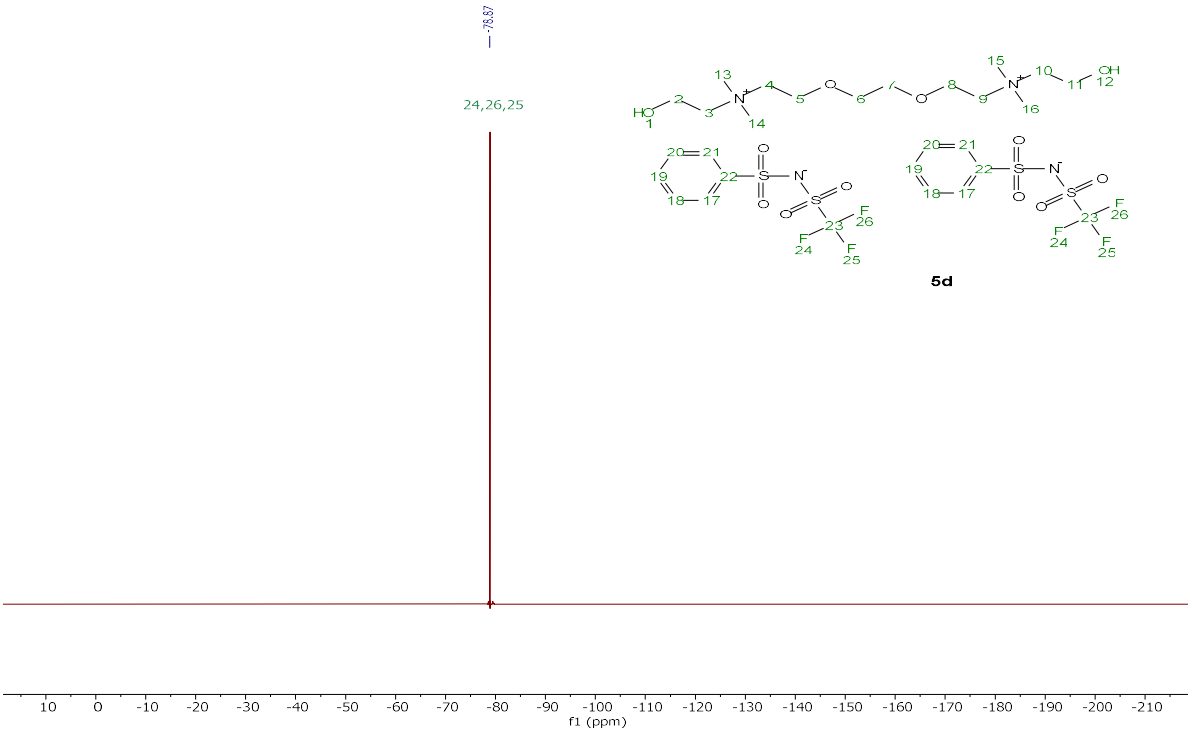
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

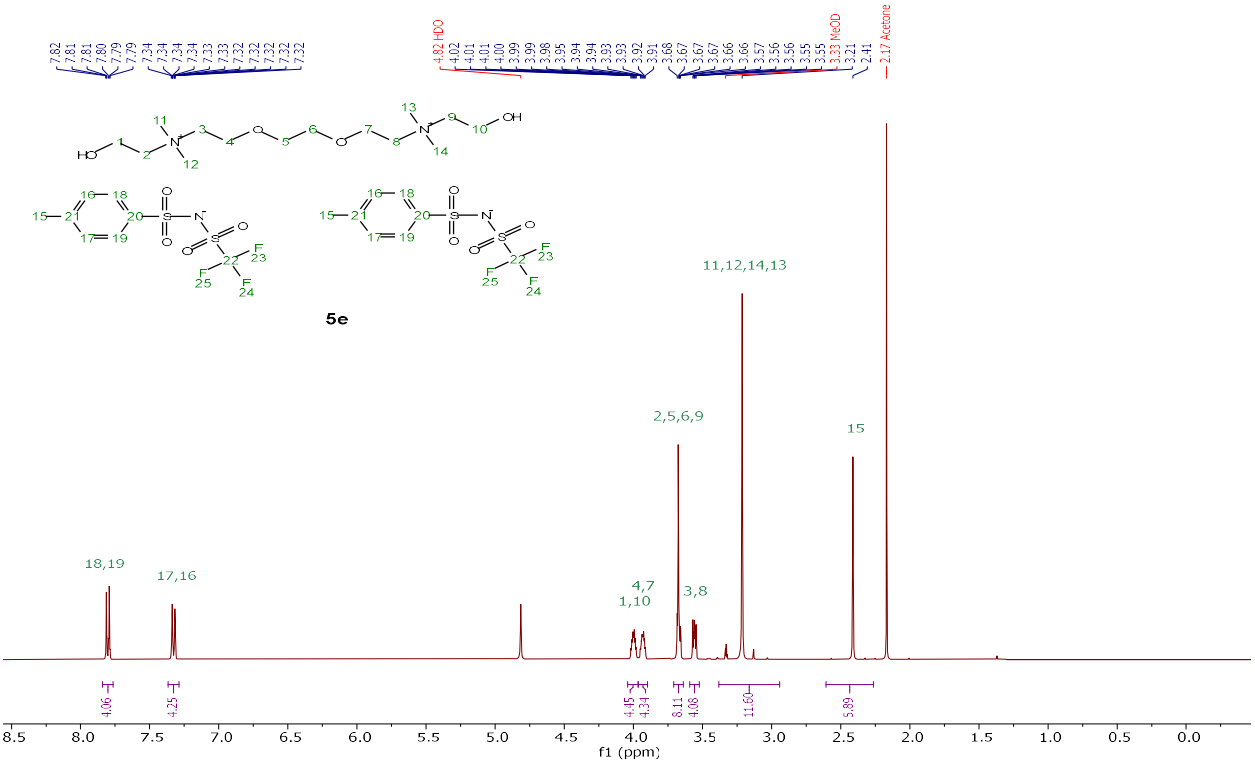


^{19}F NMR (376 MHz, Acetone-d6)

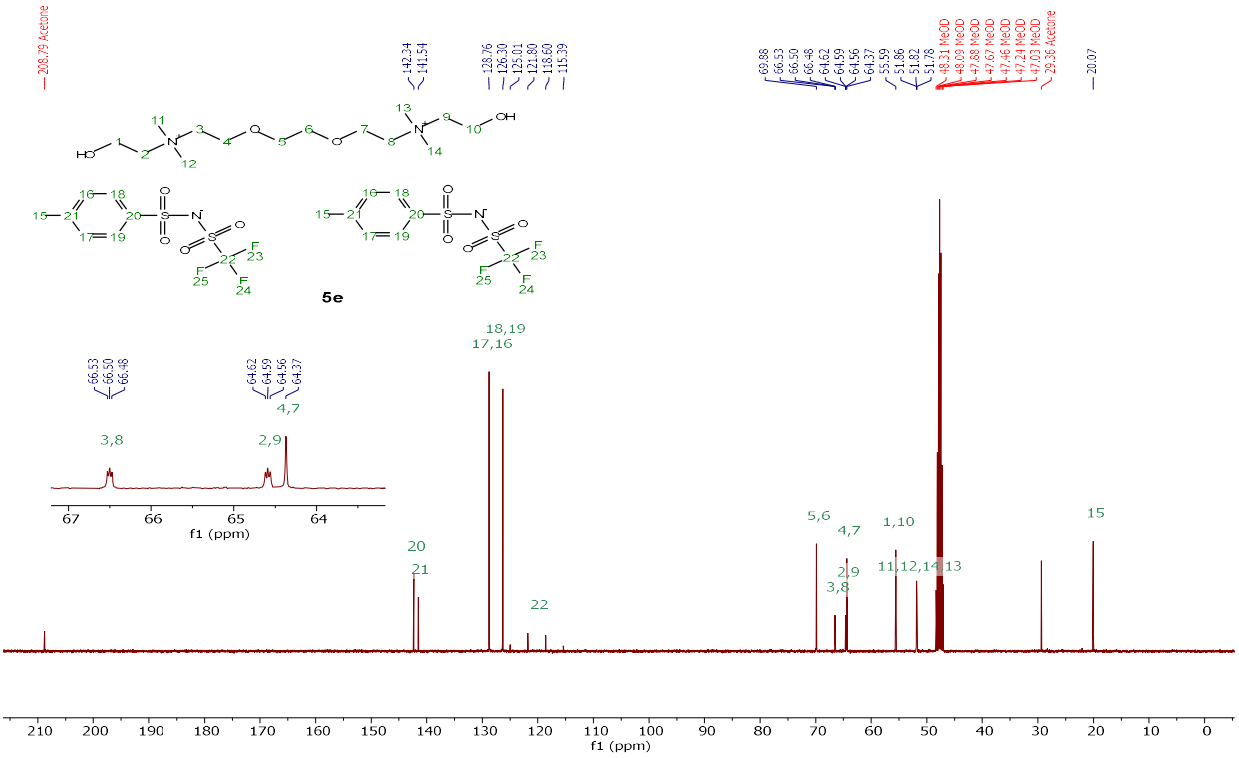


[DC-ether][2TsNTf], **5e**

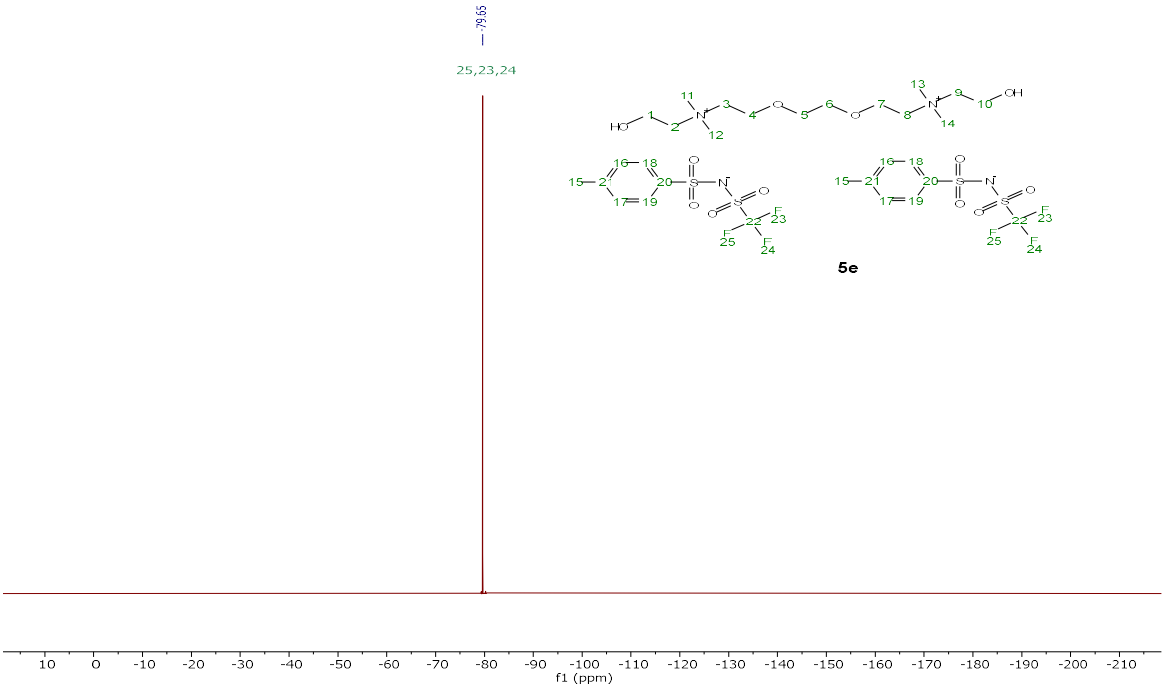
^{1}H NMR (400 MHz, Methanol-d4)



^{13}C{^{1}H} NMR (101 MHz, Methanol-d4)

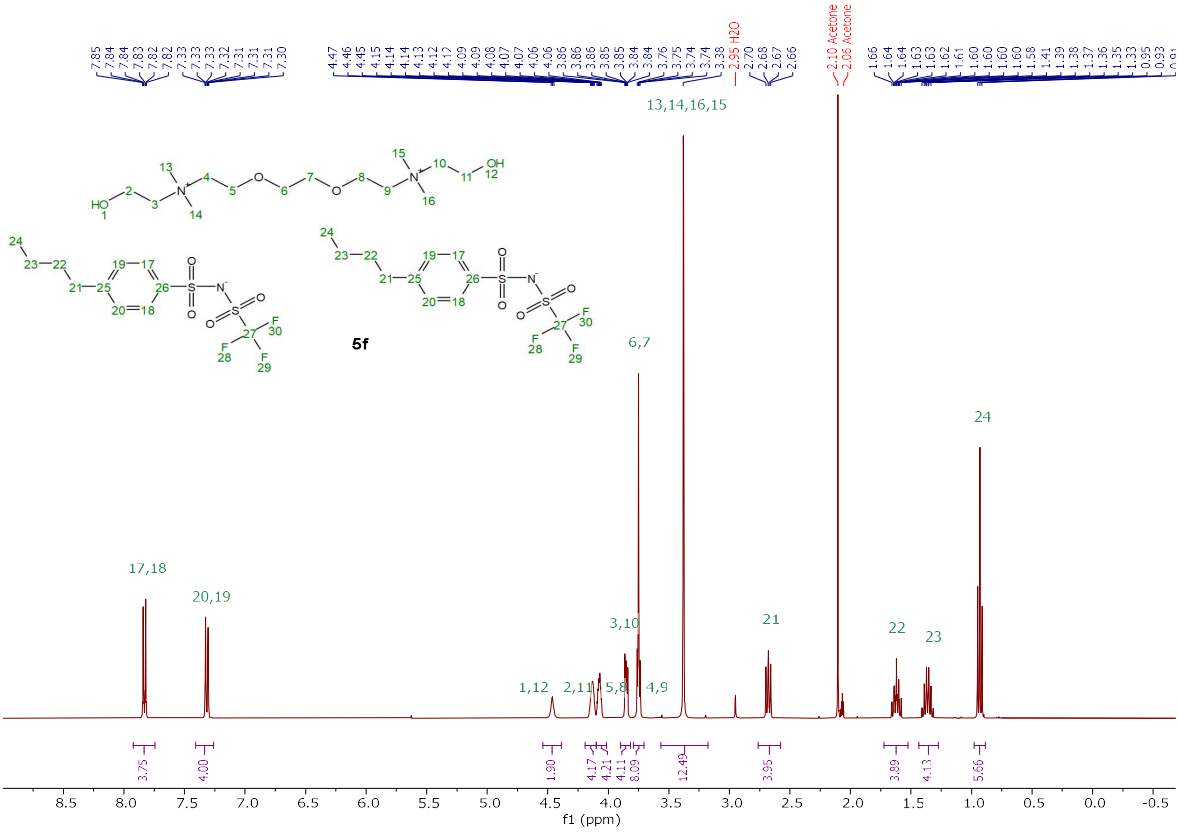


^{19}F NMR (376 MHz, Methanol-d4)

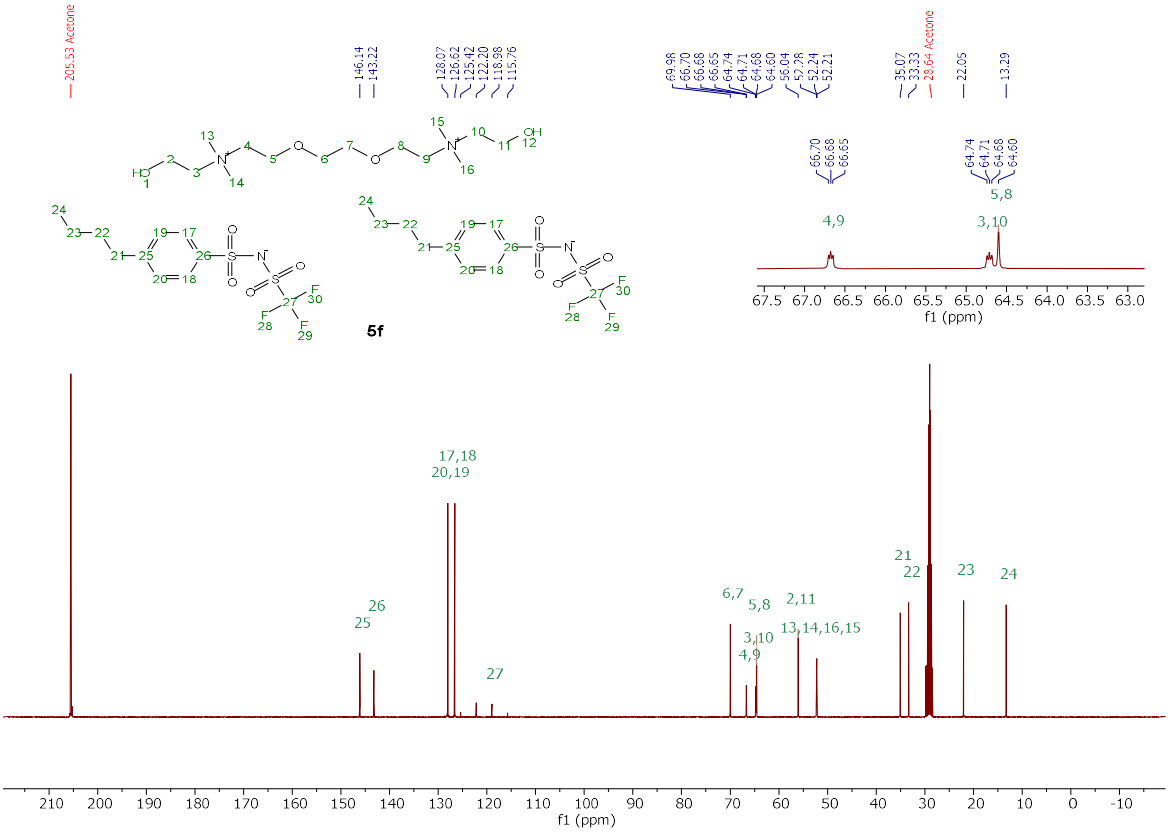


[DC-ether][2pBBSNTf], **5f**

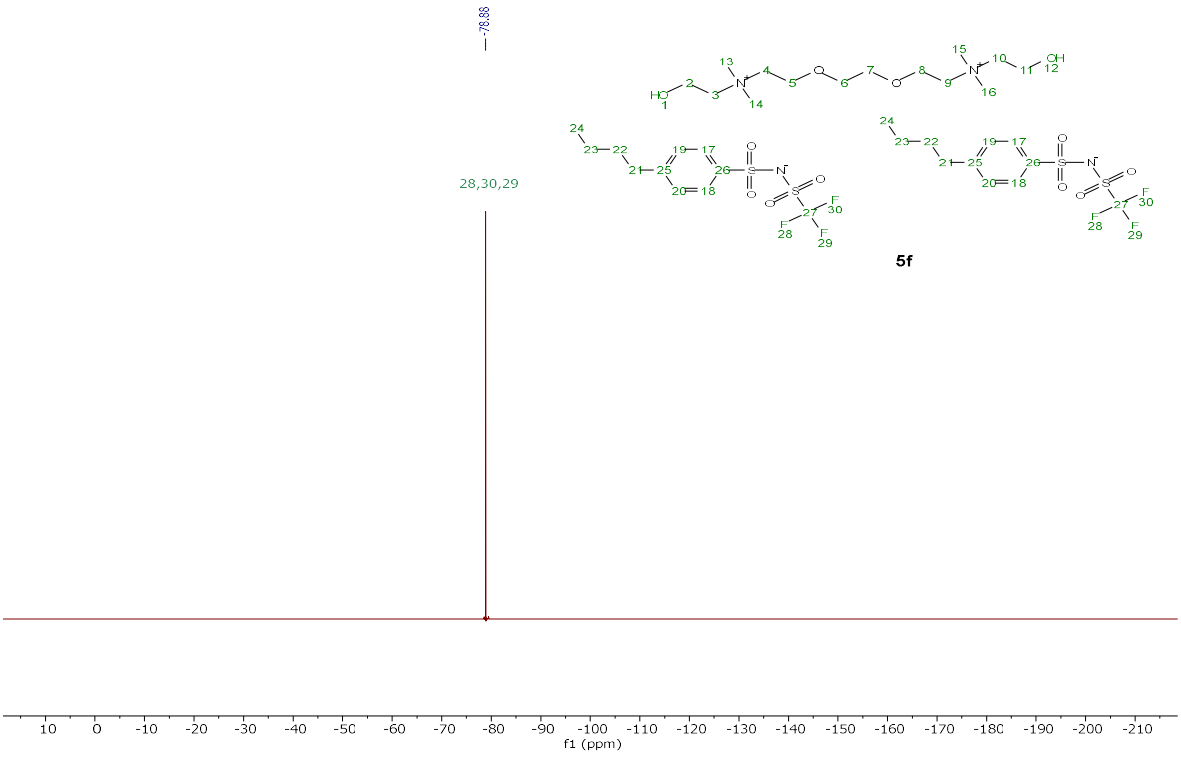
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

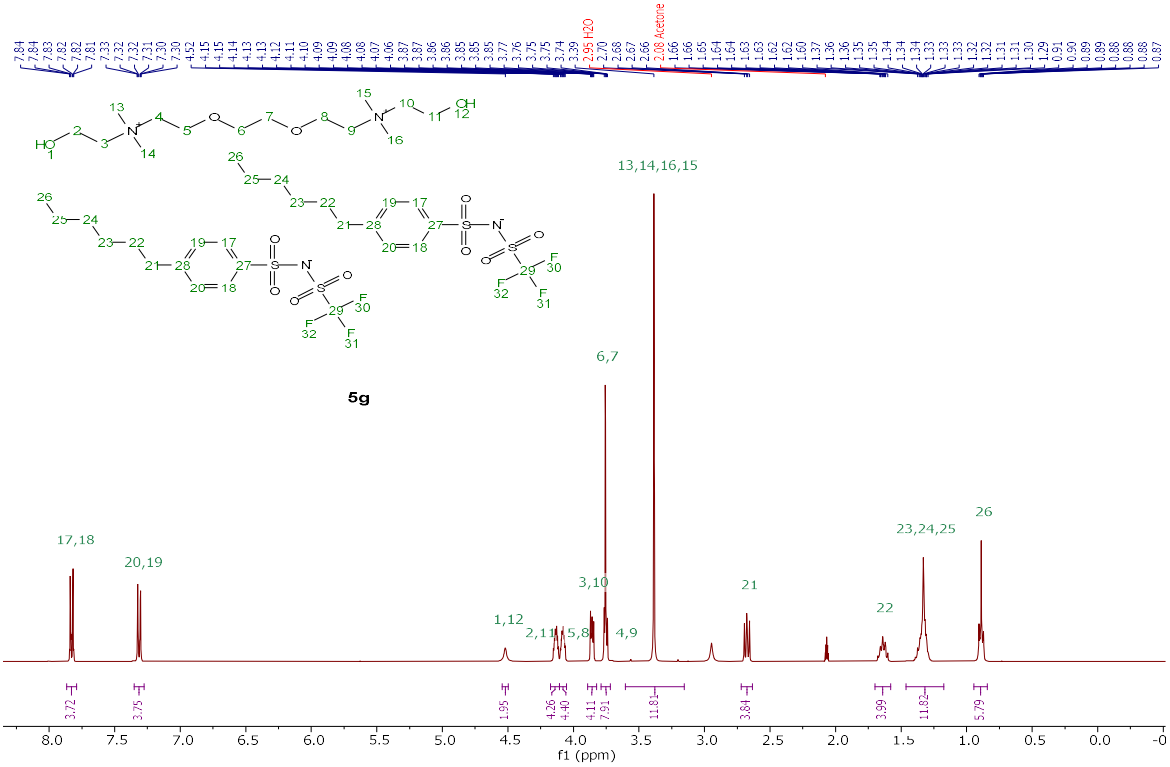


^{19}F NMR (376 MHz, Acetone-d6)

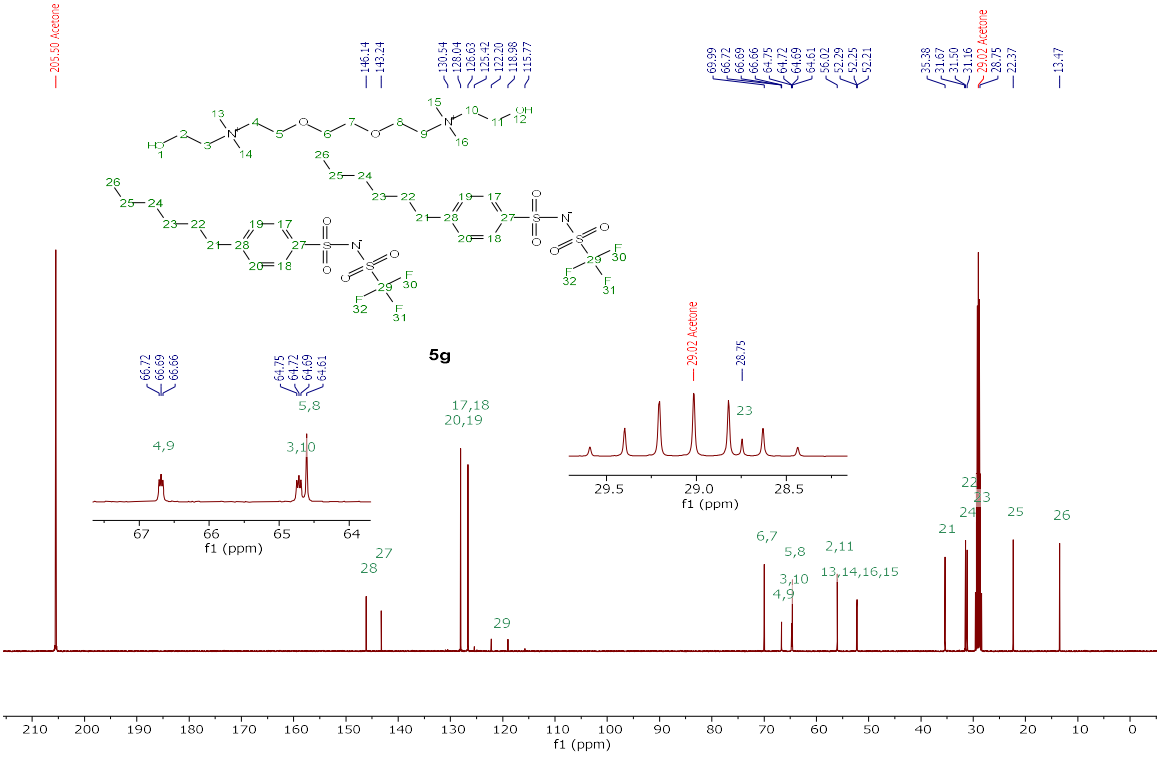


[DC-ether][2pHBSNTf], **5g**

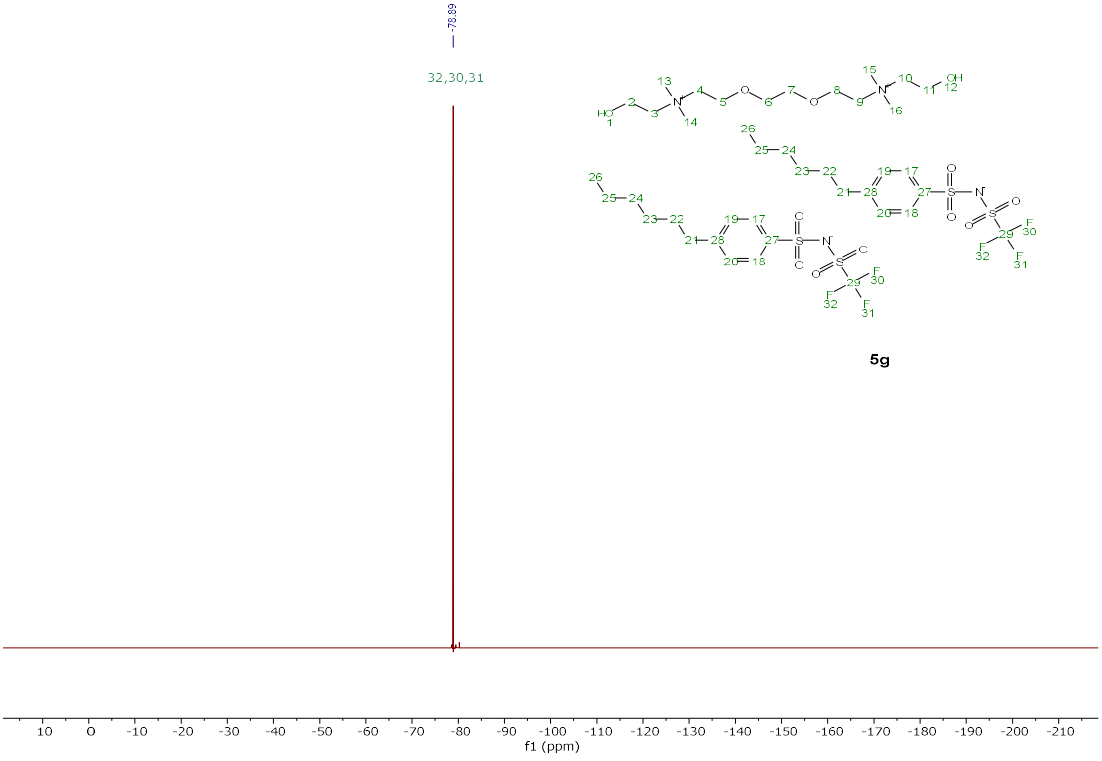
^{1}H NMR (400 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (101 MHz, Acetone-d6)

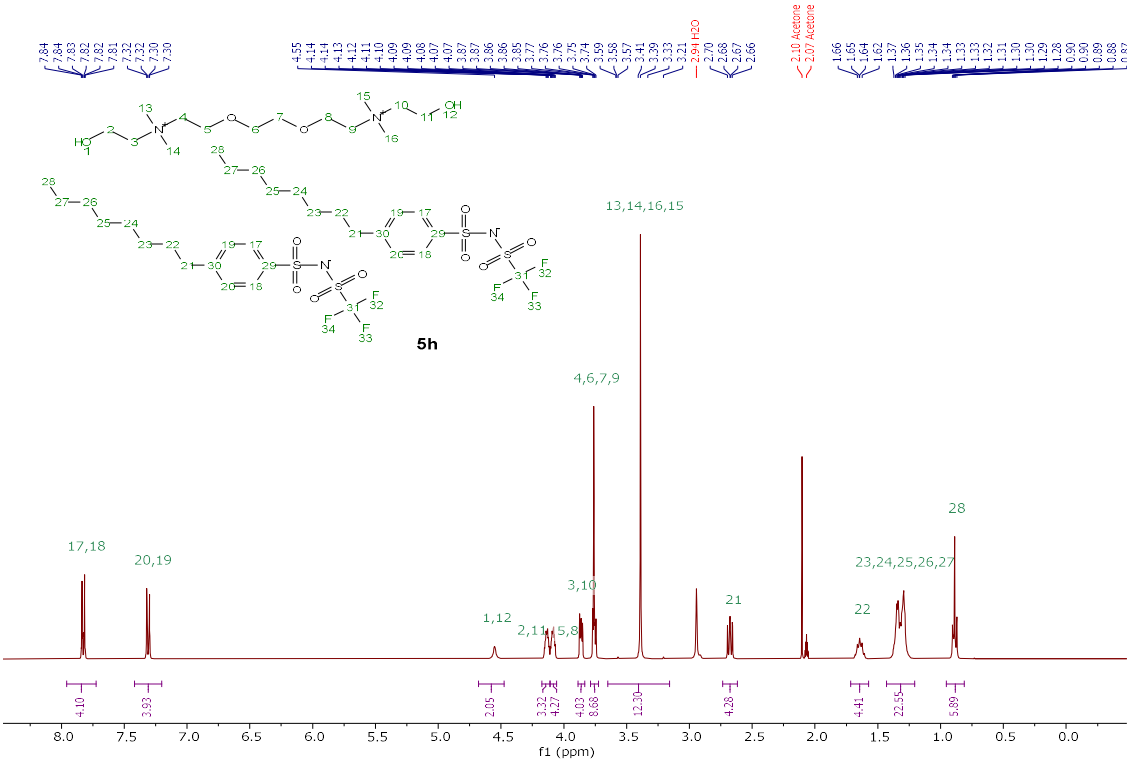


^{19}F NMR (376 MHz, Acetone-d6)

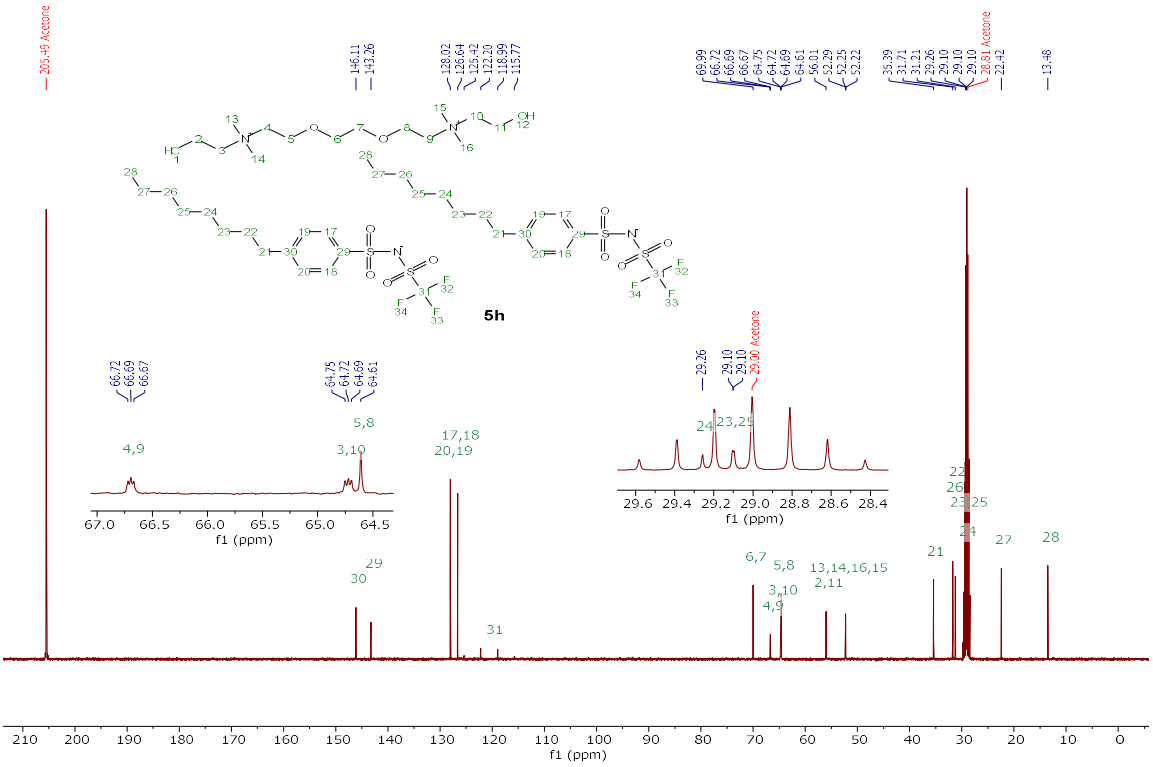


[DC-ether][2pOBSNTf], **5h**

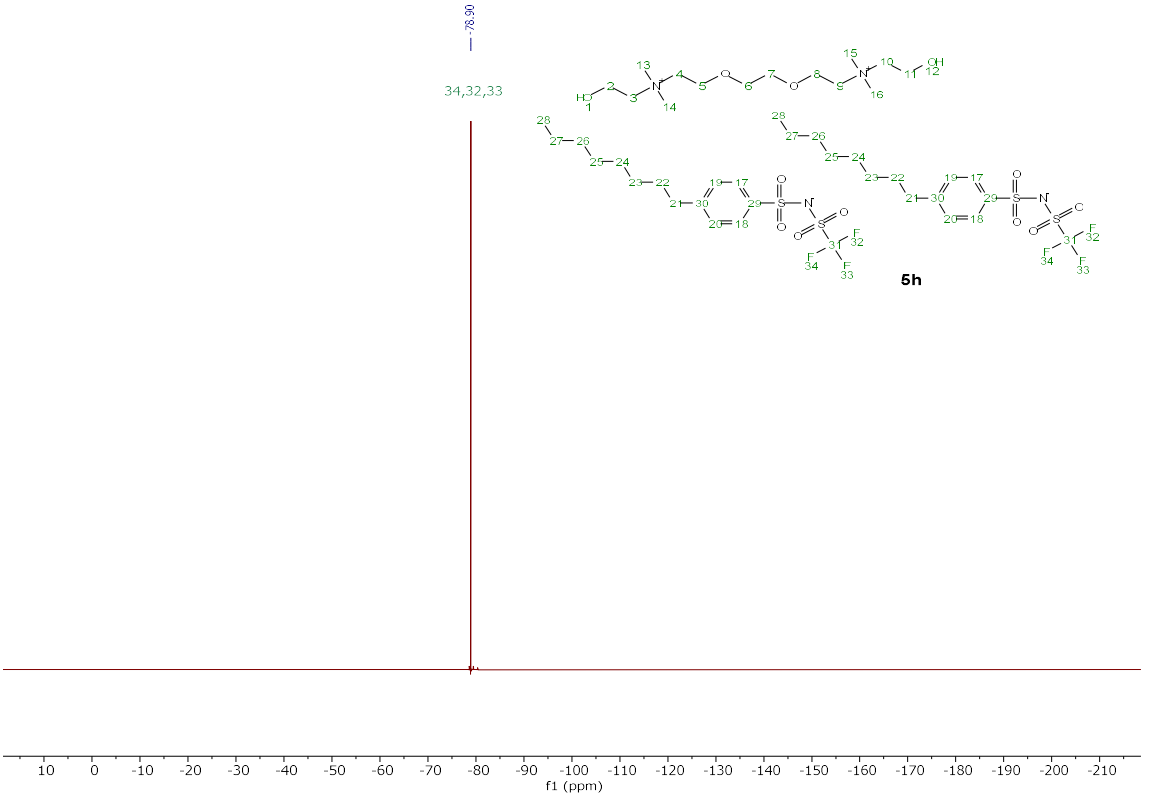
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

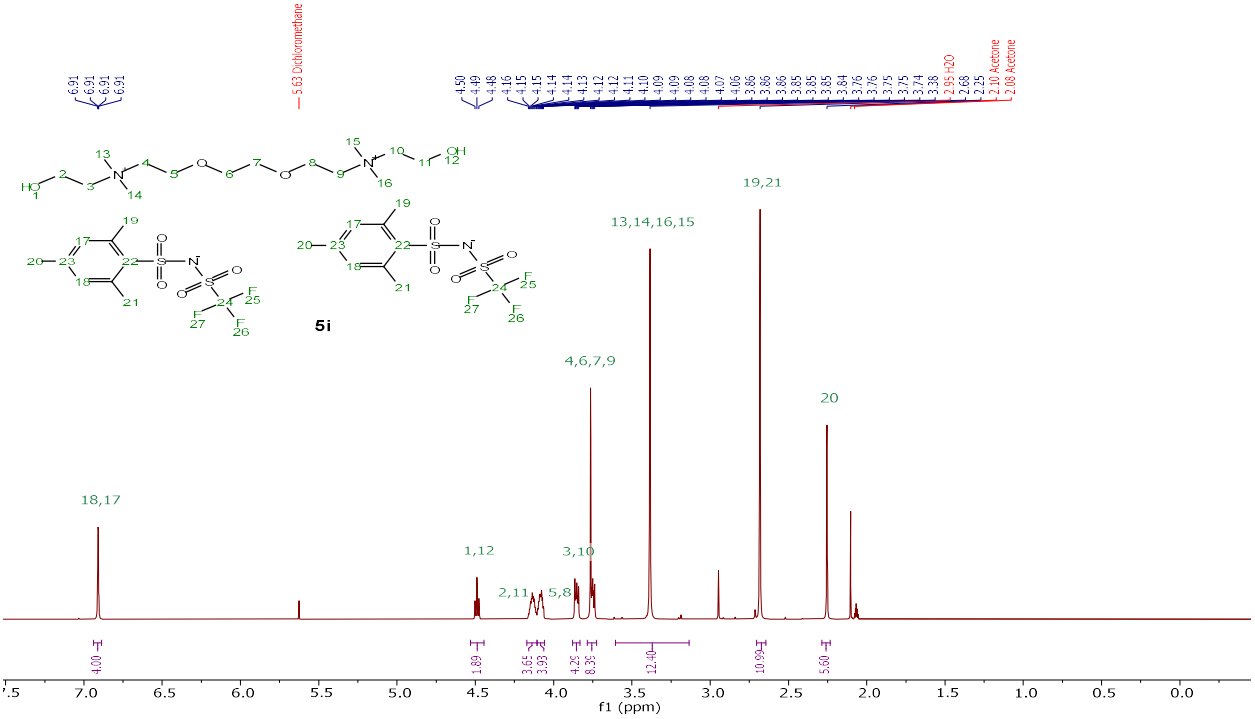


^{19}F NMR (376 MHz, Acetone-d6)

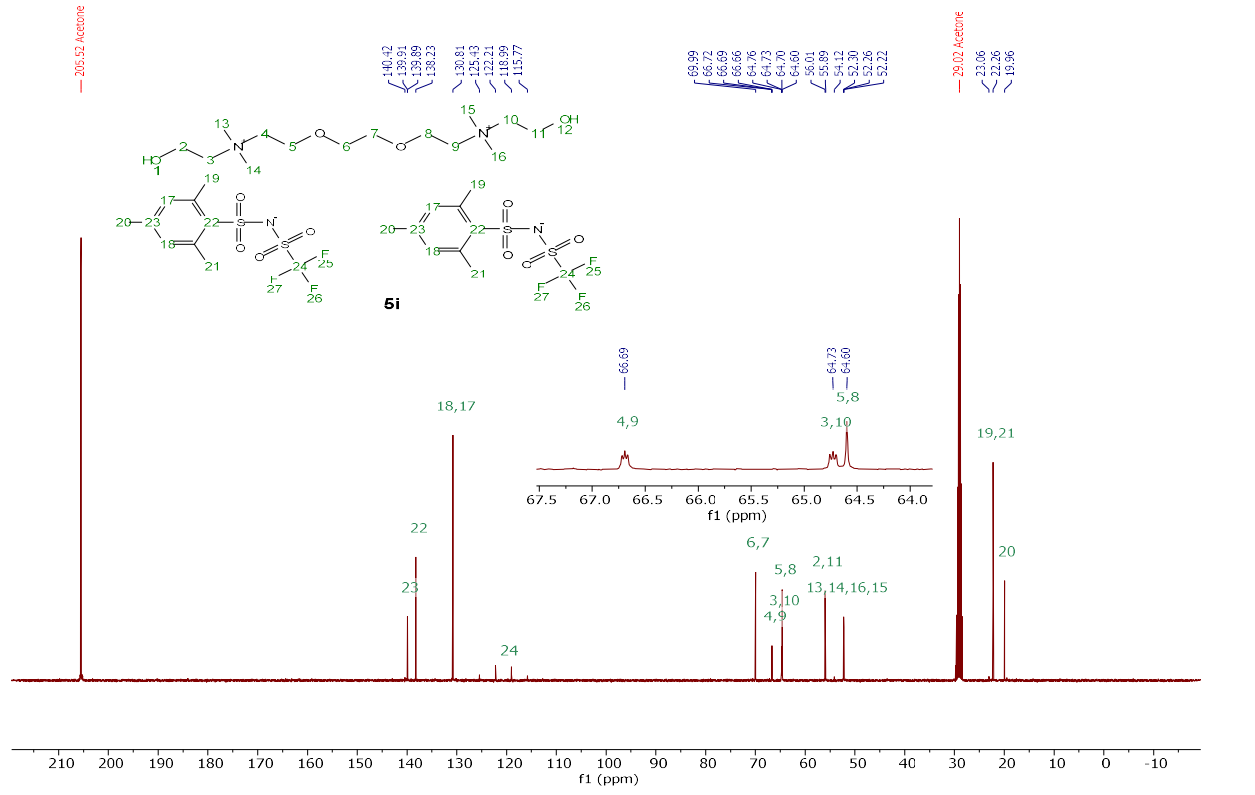


[DC-ether][2MesSNTf], **5i**

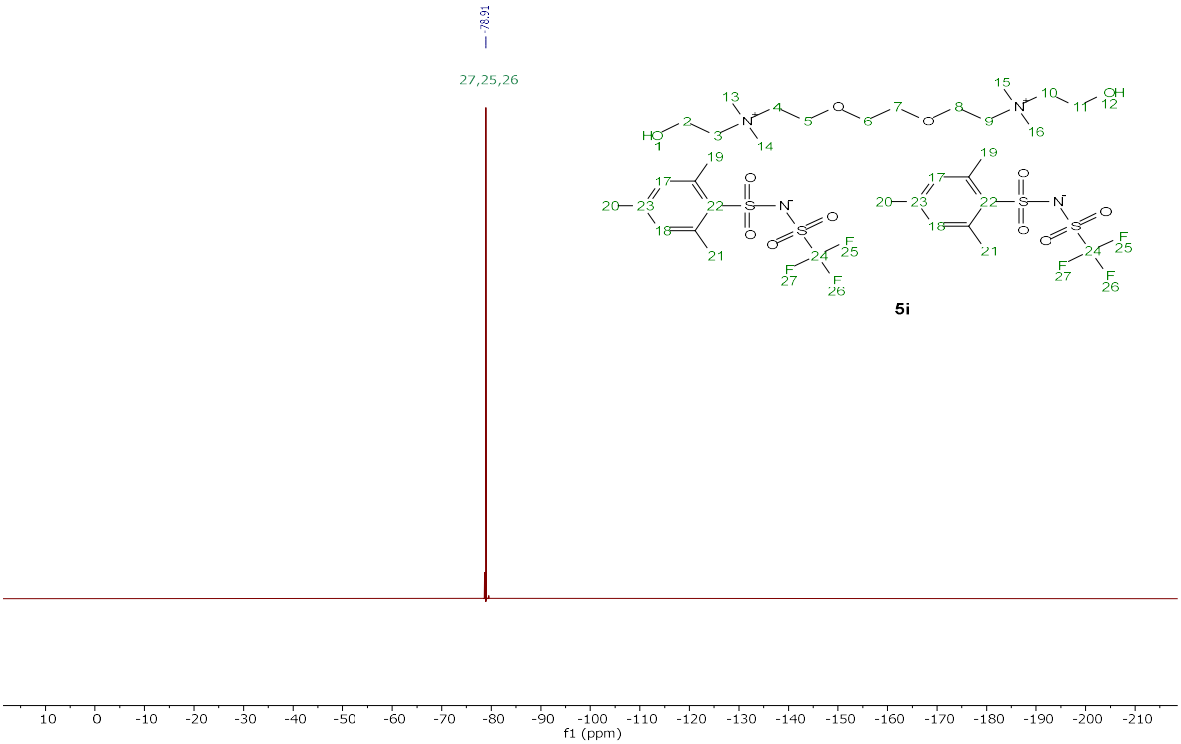
^{1}H NMR (400 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (101 MHz, Acetone-d6)

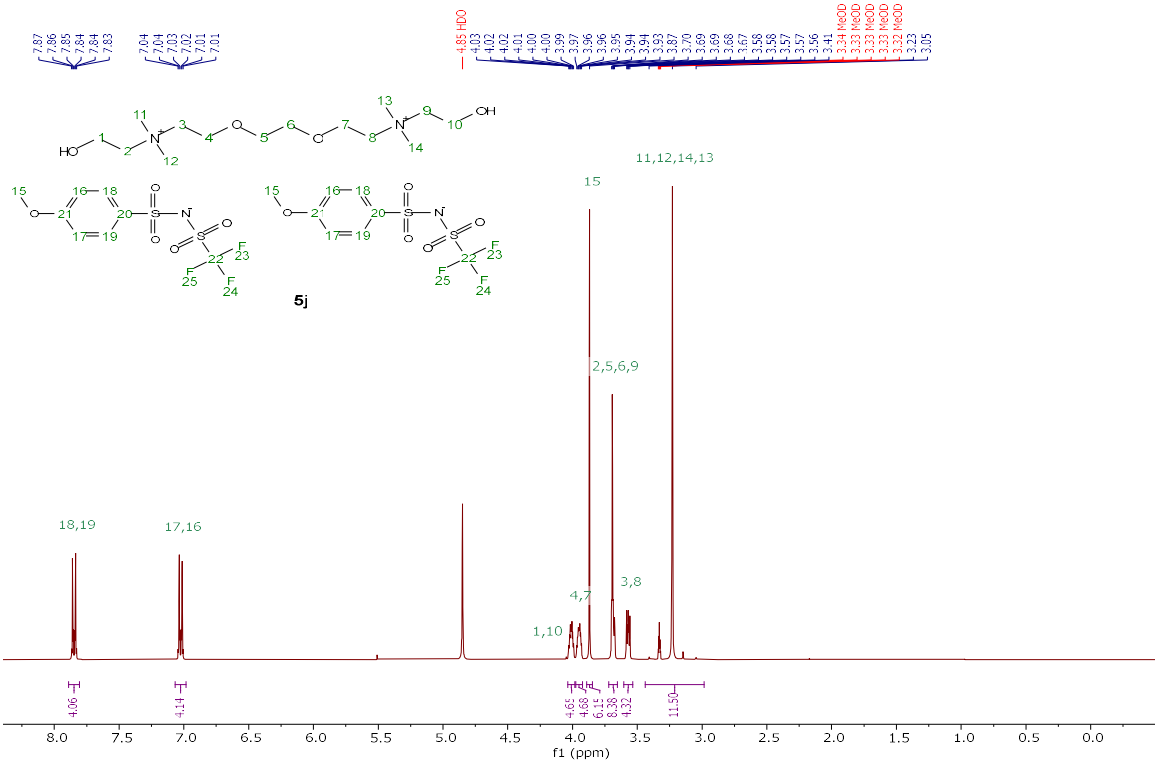


^{19}F NMR (376 MHz, Acetone-d6)

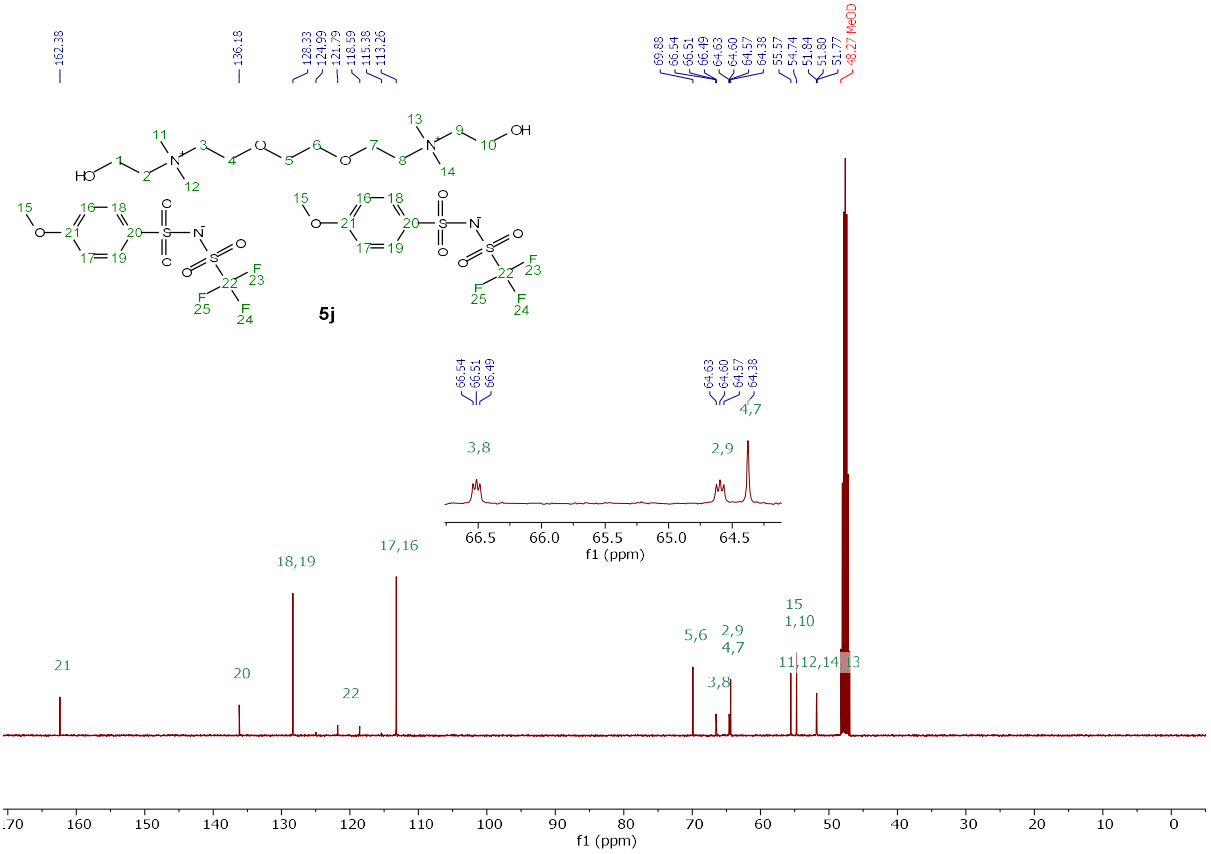


[DC-ether][2pMBSNTf], **5j**

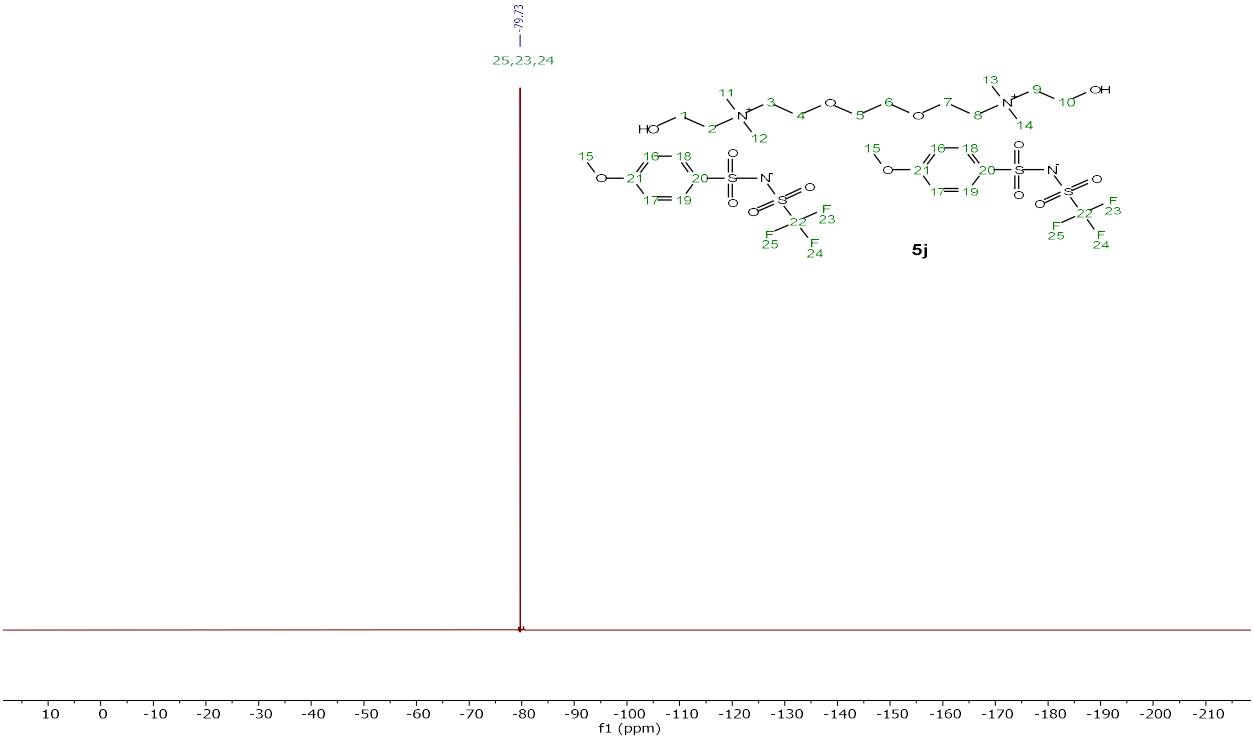
^{1}H NMR (400 MHz, Methanol-d4)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)

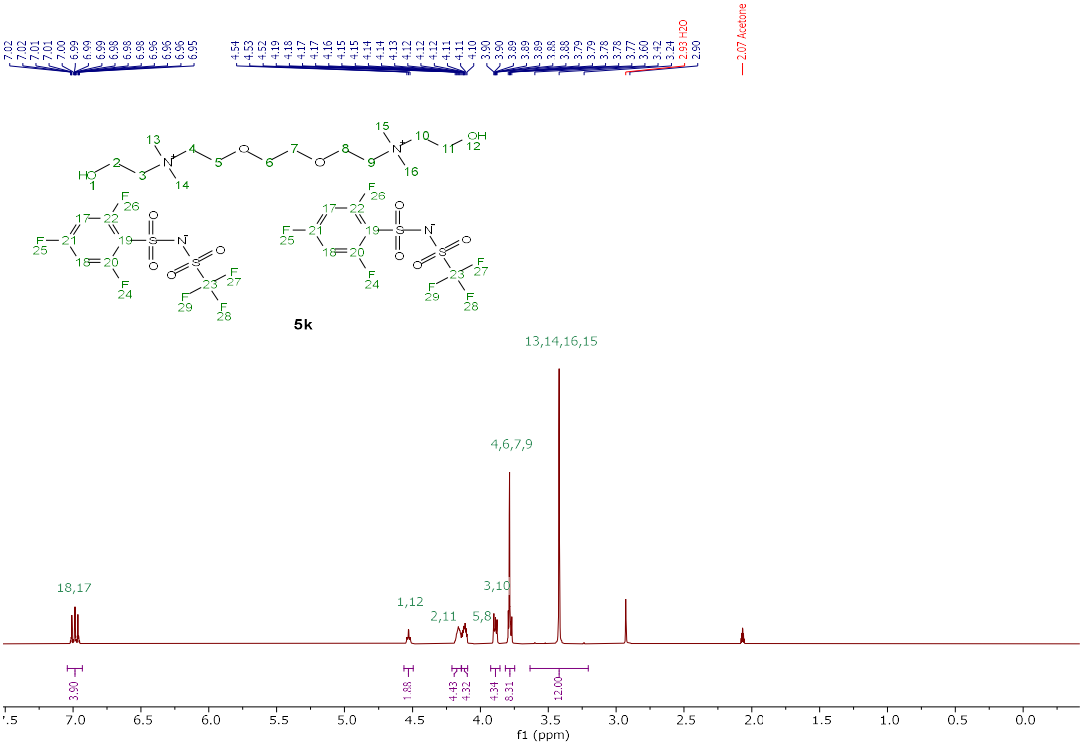


^{19}F NMR (376 MHz, Methanol-d4)

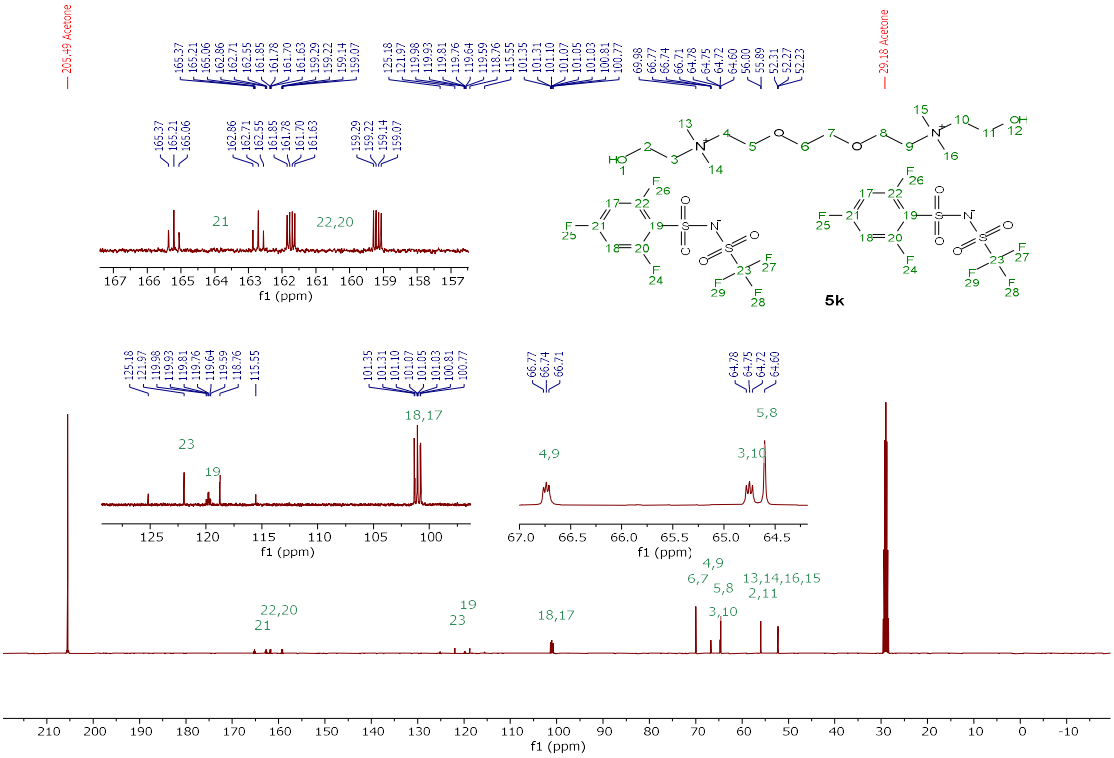


[DC-ether][2TFBSNTf], **5k**

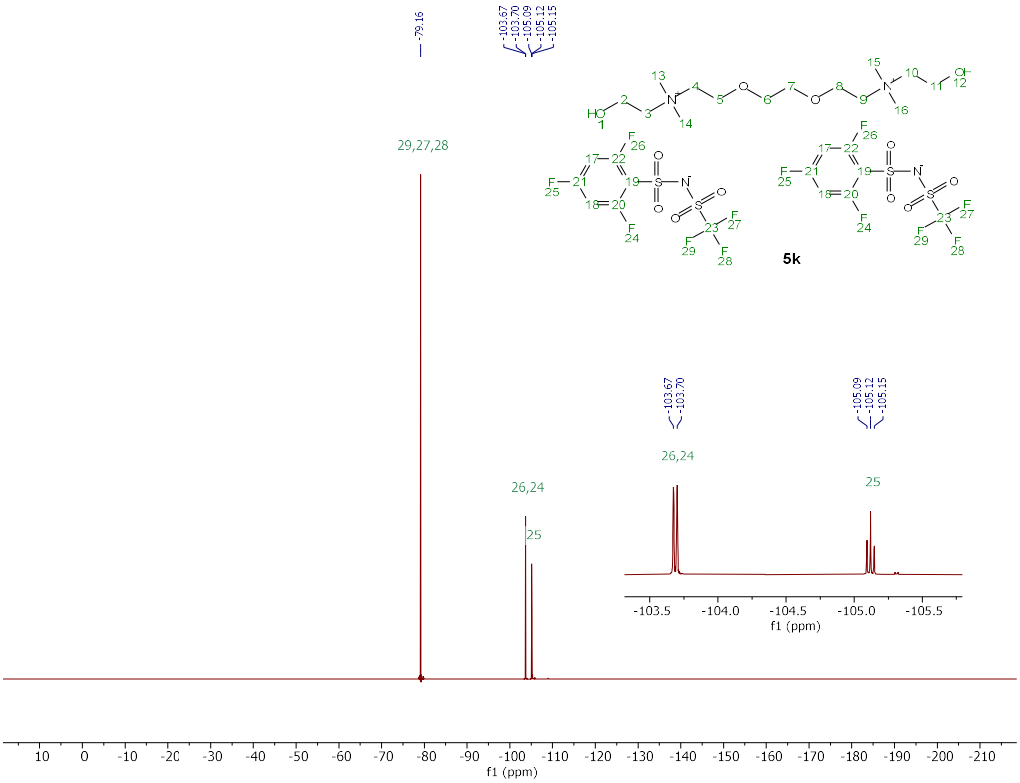
^{1}H NMR (400 MHz, Acetone-d6)



^{13}C{^{1}H} NMR (101 MHz, Acetone-d6)

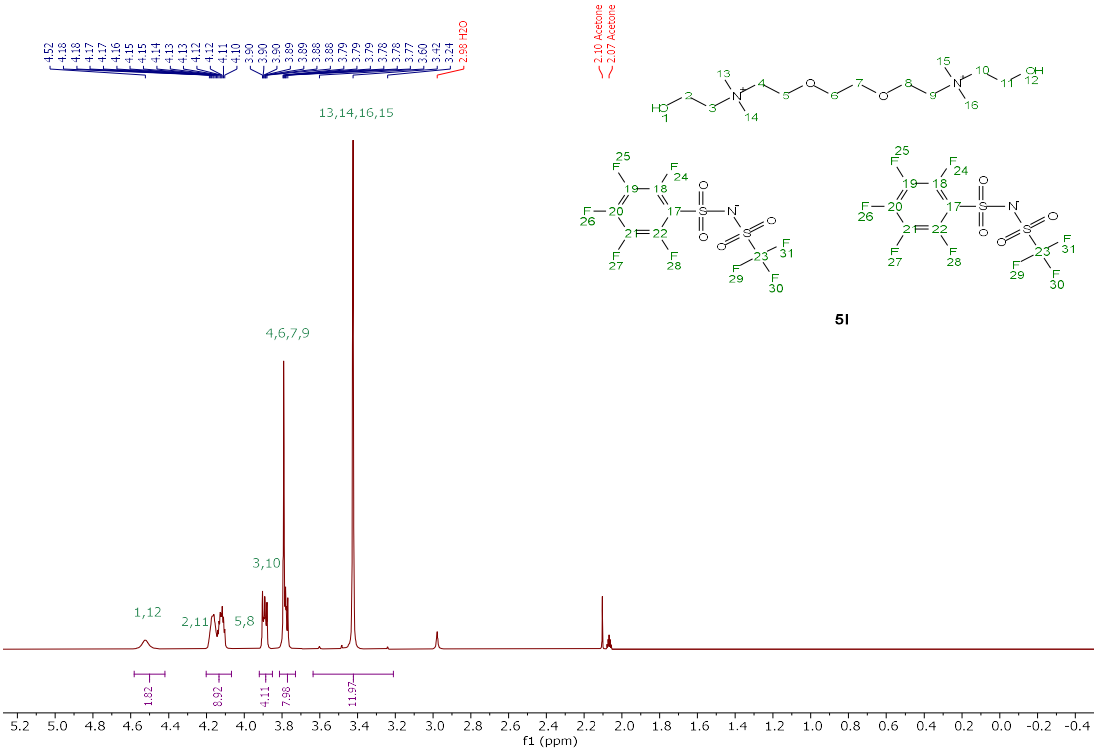


^{19}F NMR (376 MHz, Acetone-d6)

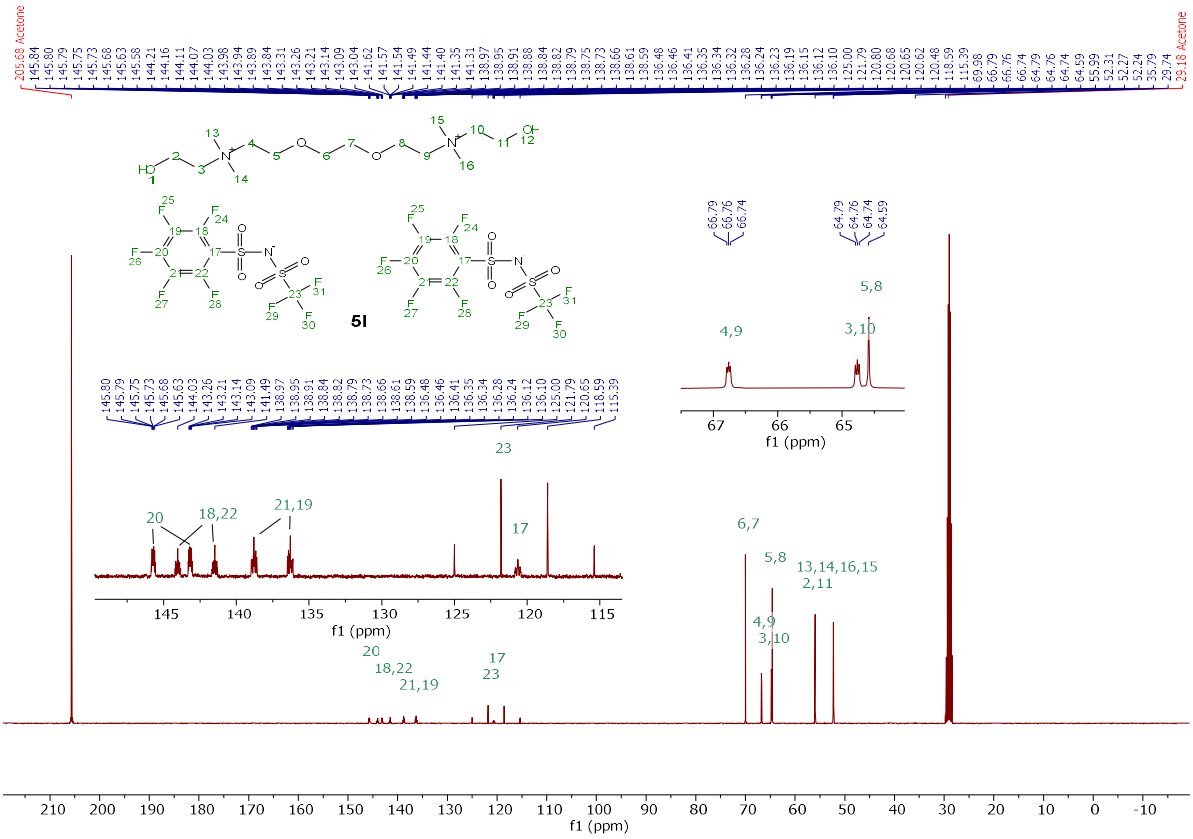


[DC-ether][2PFBSNTf], **5l**

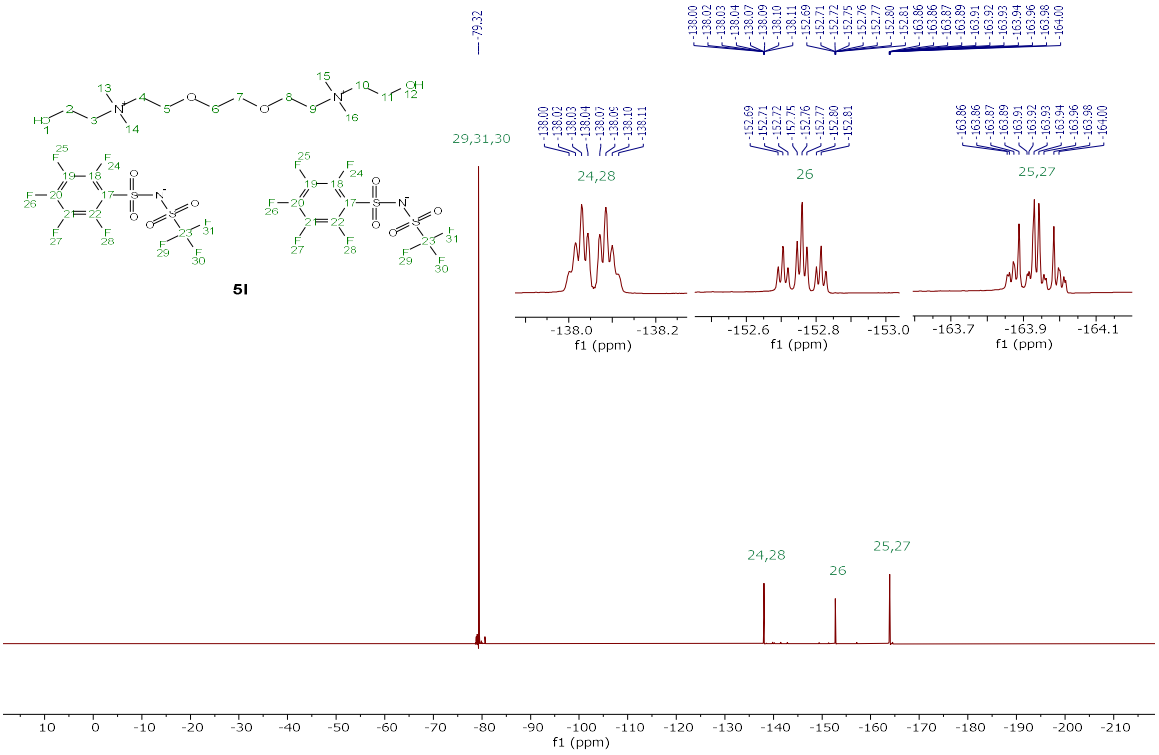
^{1}H NMR (400 MHz, Acetone-d6)



$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d6)



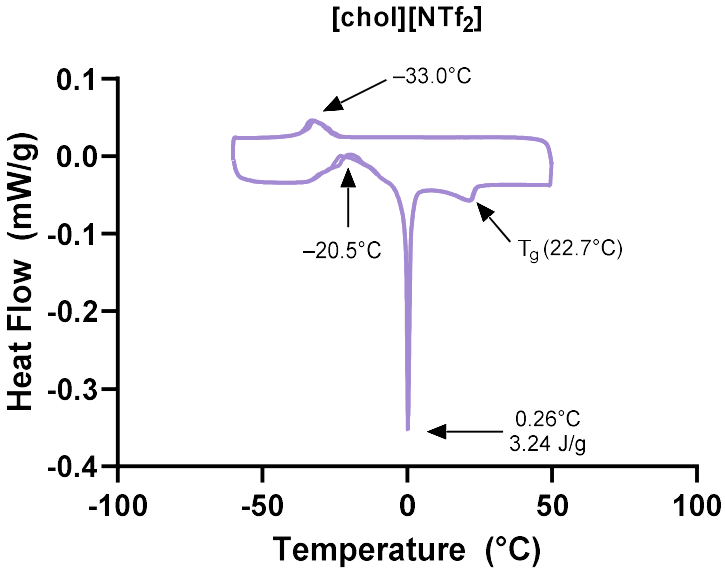
^{19}F NMR (376 MHz, Acetone-d6)



DIFFERENTIAL SCANNING CALORIMETRY. Thermograms were recorded using a DSC Q2000 differential scanning calorimeter (TA Instruments, New Castle, DE). The heating rate was 10 °C/min. The cooling rate and isothermal holds were optimized for each compound as described below. For all thermograms, exothermic peaks are up. The thermograms were analyzed using Universal Analysis Software (TA Instruments). Glass transition temperatures were selected at the midpoint of the curve. Prism 9.0.0 (GraphPad Software, La Jolla, CA) was used to redisplay the graphs.

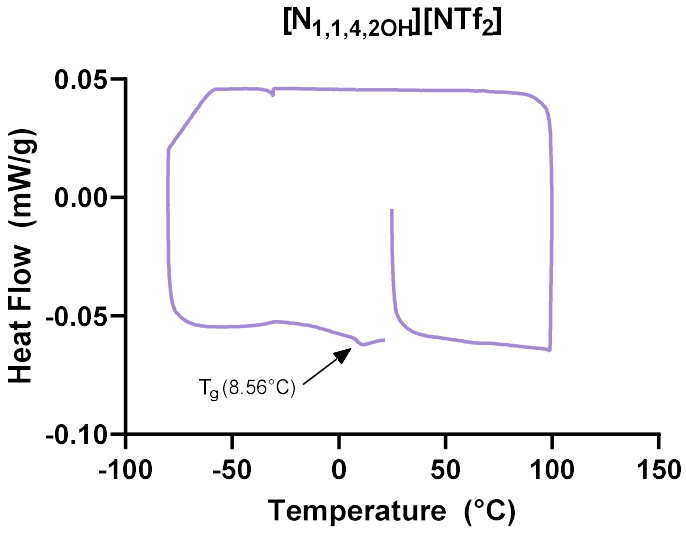
[chol][NTf_2], **2a**

1: Equilibrate at 50.00 °C; 2: Ramp 10.00 °C/min to –60.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to 50.00 °C; 6: Isothermal for 1.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to –60.00 °C; 9: Isothermal for 10.00 min; 10: Mark end of cycle 2; 11: Ramp 10.00 °C/min to 50.00 °C



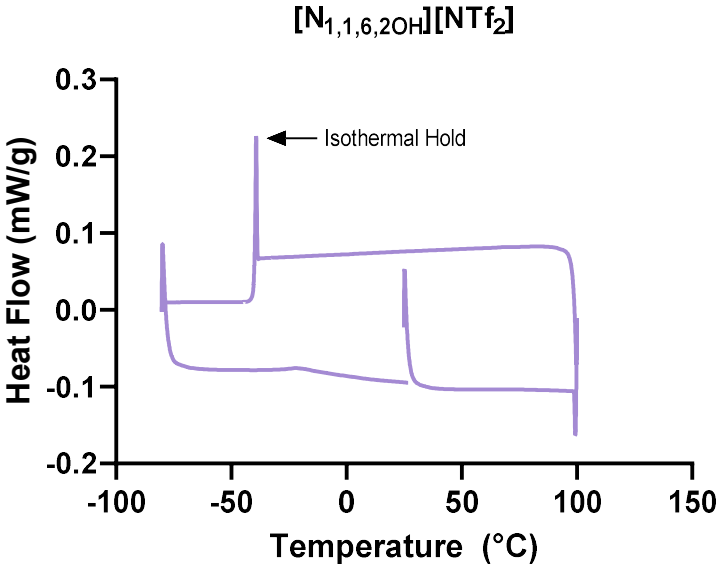
$[N_{1,1,4,2OH}][NTf_2]$, **2b**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 25.00 °C



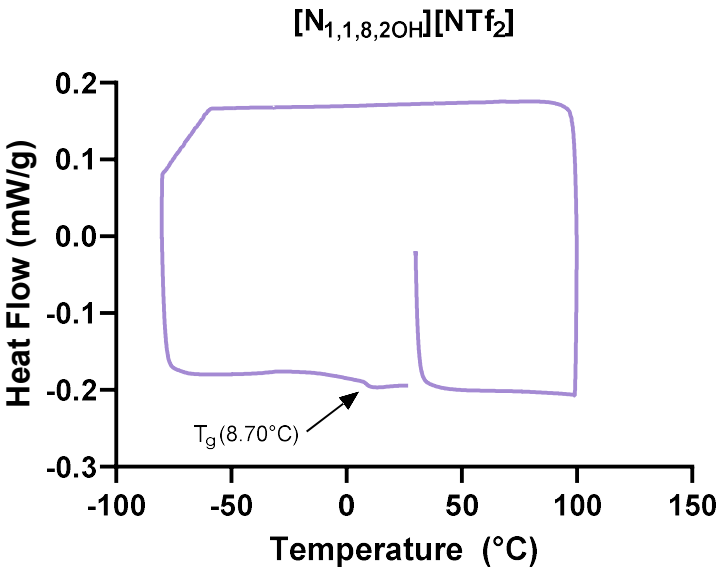
$[N_{1,1,6,2OH}][NTf_2]$, **2c**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –40.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 20.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 30.00 °C



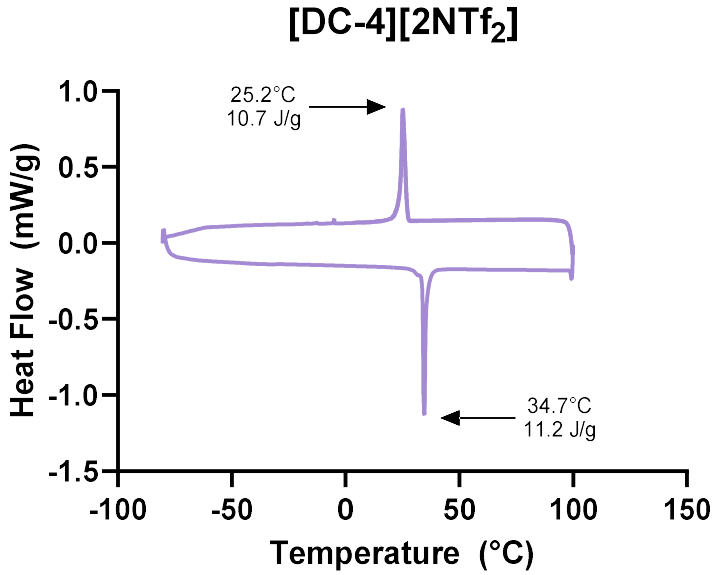
$[N_{1,1,8,2OH}][NTf_2]$, **2d**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 30.00 °C



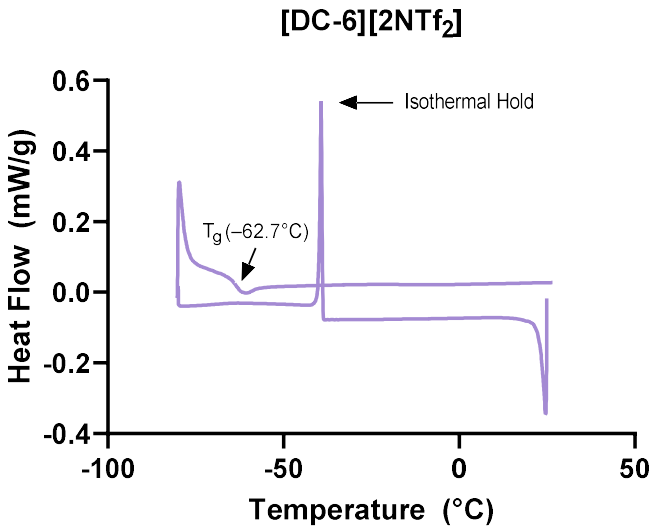
[DC-4][2NTf_2], **2e**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 15.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 20.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 100.00 °C; 9: Isothermal for 1.00 min; 10: Mark end of cycle 2; 11: Ramp 10.00 °C/min to 0.00 °C



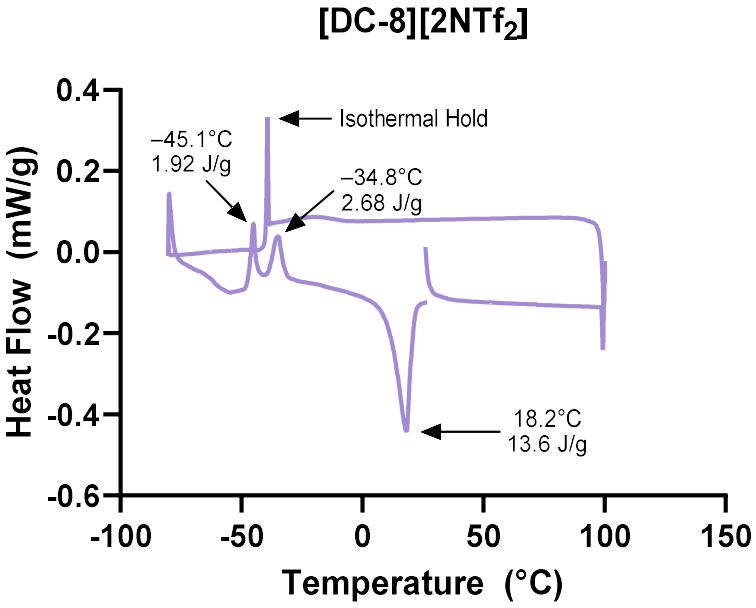
[DC-6][2NTf$_2$], **2f**

1: Equilibrate at 25.00 °C; 2: Mark end of cycle 0; 3: Ramp 10.00 °C/min to –40.00 °C; 4: Ramp 2.00 °C/min to –80.00 °C; 5: Isothermal for 30.00 min; 6: Mark end of cycle 1; 7: Ramp 10.00 °C/min to 30.00 °C



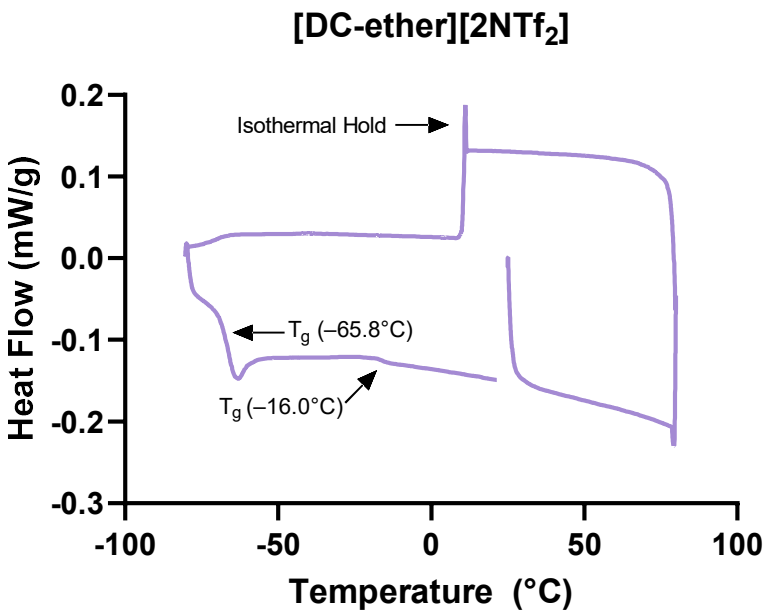
[DC-8][2NTf$_2$], **2g**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –40.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 10.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 30.00 °C



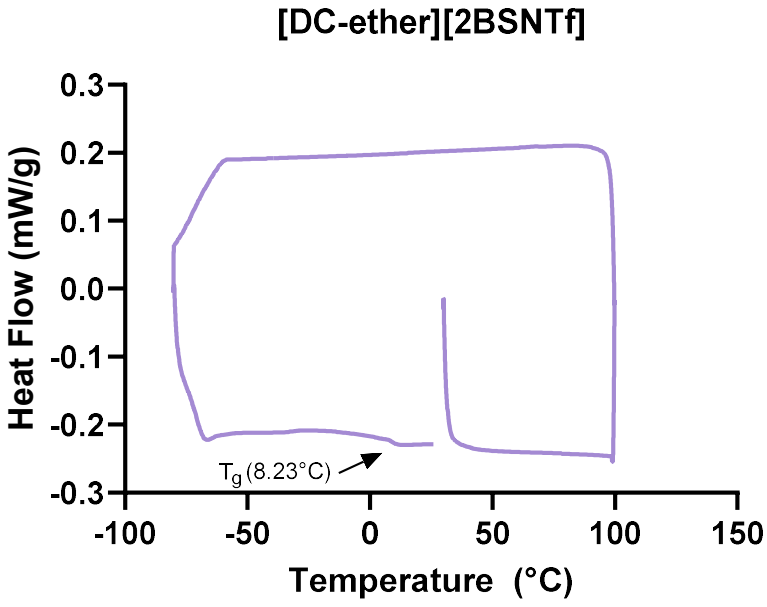
[DC-ether][2NTf$_2$], **2h**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 80.00 °C; 3: Isothermal for 20.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to 10.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 30.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 25.00 °C



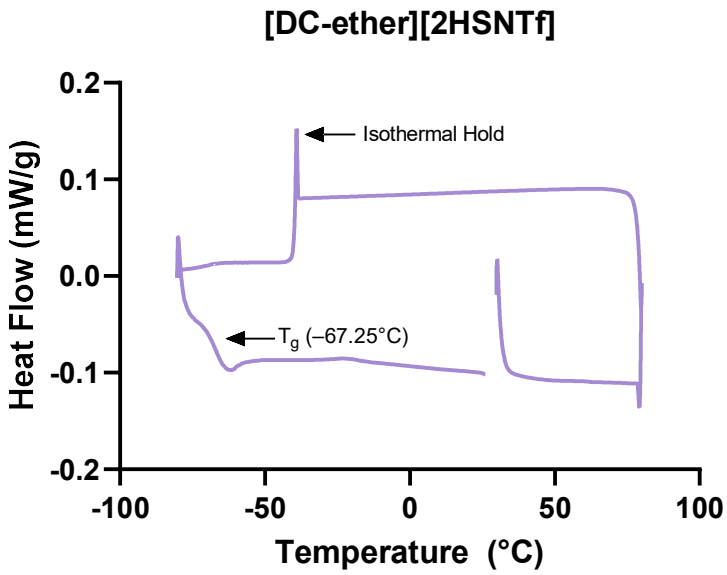
[DC-ether][2BSNTf], **5a**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 30.00 °C



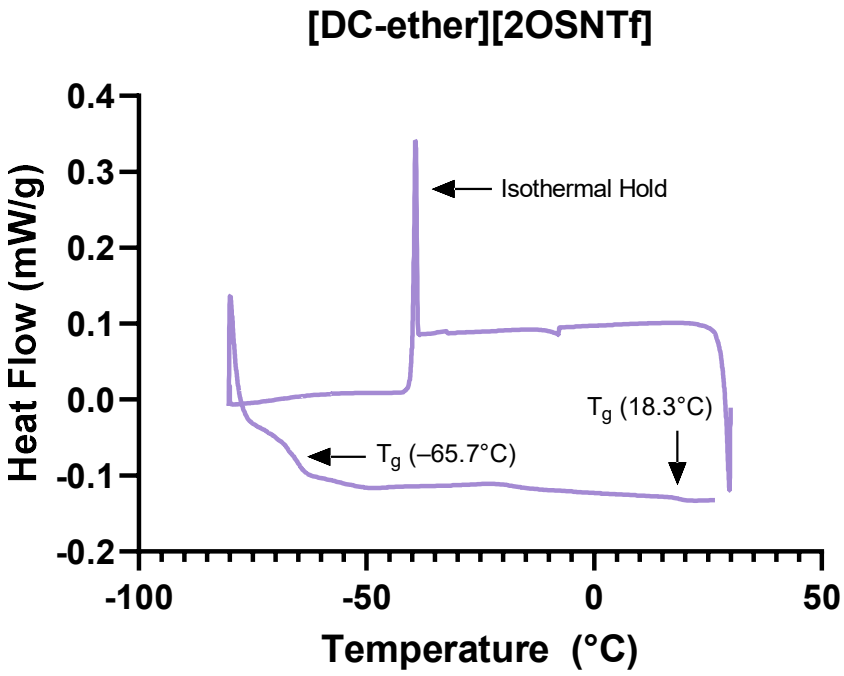
[DC-ether][2HSNTf], **5b**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 80.00 °C; 3: Isothermal for 15.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –40.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 20.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 30.00 °C



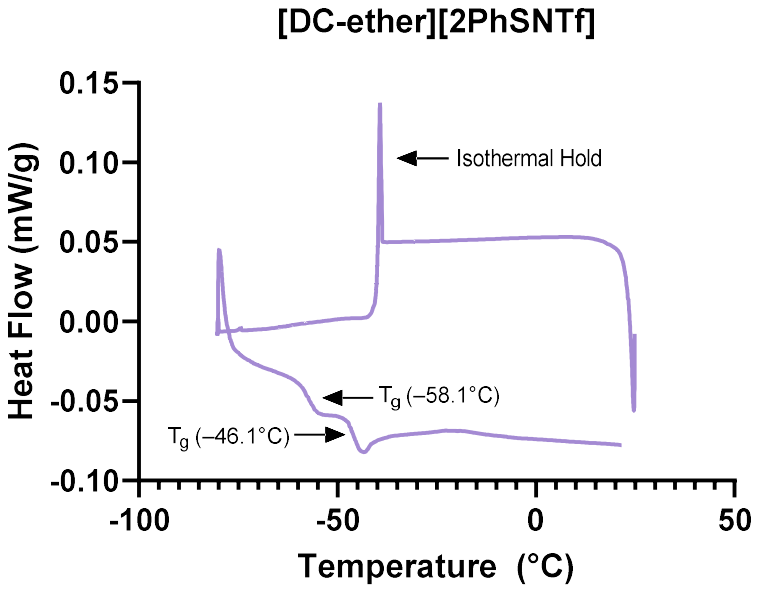
[DC-ether][2OSNTf], **5c**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to –40.00 °C; 3: Ramp 2.00 °C/min to –80.00 °C; 4: Isothermal for 10.00 min; 5: Mark end of cycle 0; 6: Ramp 10.00 °C/min to 30.00 °C



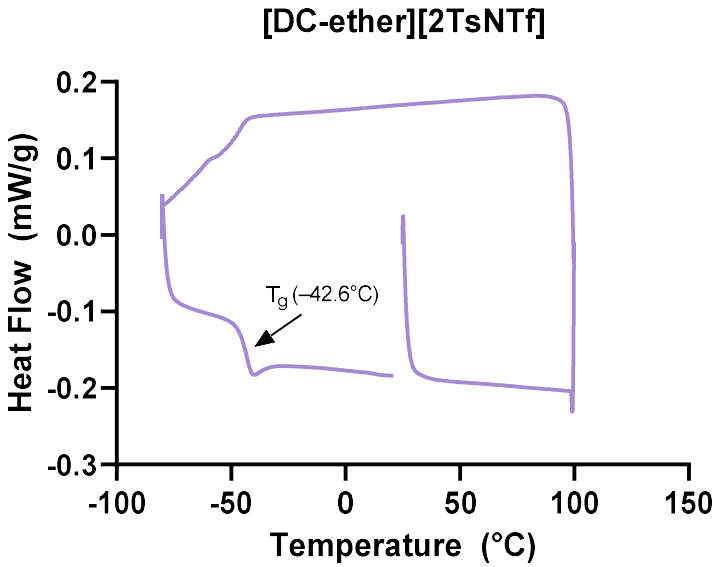
[DC-ether][2PhSNTf], **5d**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 40.00 °C; 3: Mark end of cycle 0; 4: Ramp 2.00 °C/min to –80.00 °C; 5: Isothermal for 10.00 min; 6: Mark end of cycle 1; 7: Ramp 10.00 °C/min to 25.00 °C



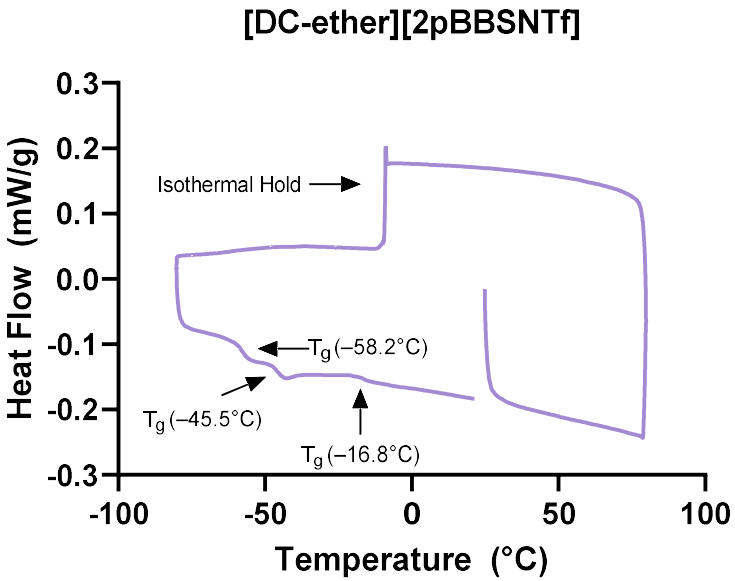
[DC-ether][2TsNTf], **5e**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 25.00 °C



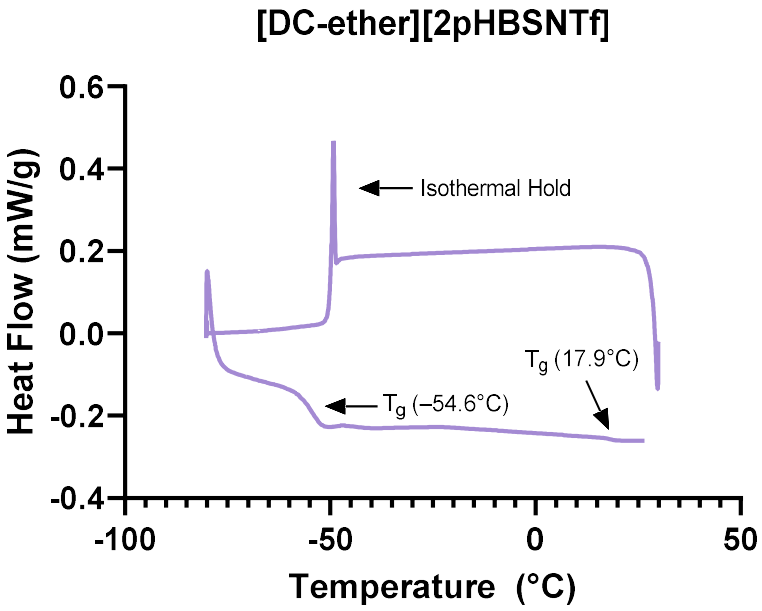
[DC-ether][2pBBSNTf], **5f**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 80.00 °C; 3: Isothermal for 1.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –10.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 30.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 25.00 °C



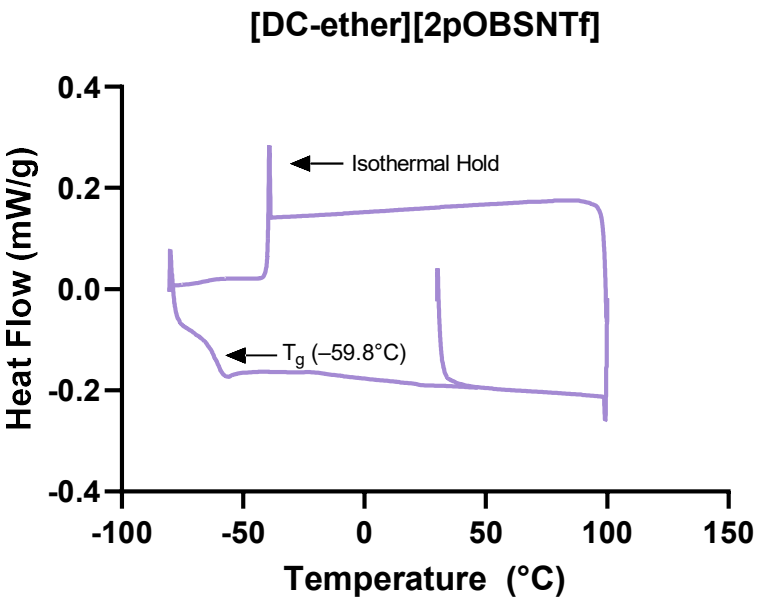
[DC-ether][2pHBSNTf], **5g**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to –50.00 °C; 3: Ramp 2.00 °C/min to –80.00 °C; 4: Isothermal for 10.00 min; 5: Mark end of cycle 0; 6: Ramp 10.00 °C/min to 30.00 °C



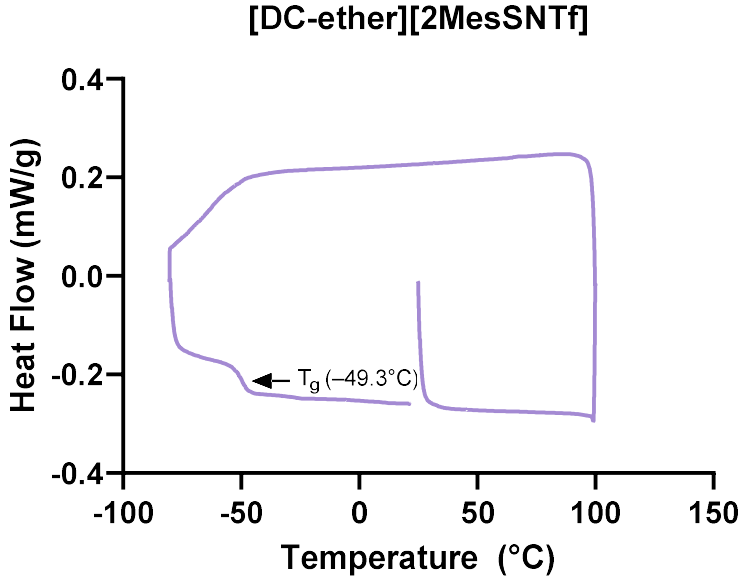
[DC-ether][2pOBSNTf], **5h**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –40.00 °C; 6: Ramp 2.00 °C/min to –80.00 °C; 7: Isothermal for 20.00 min; 8: Mark end of cycle 1; 9: Ramp 10.00 °C/min to 50.00 °C



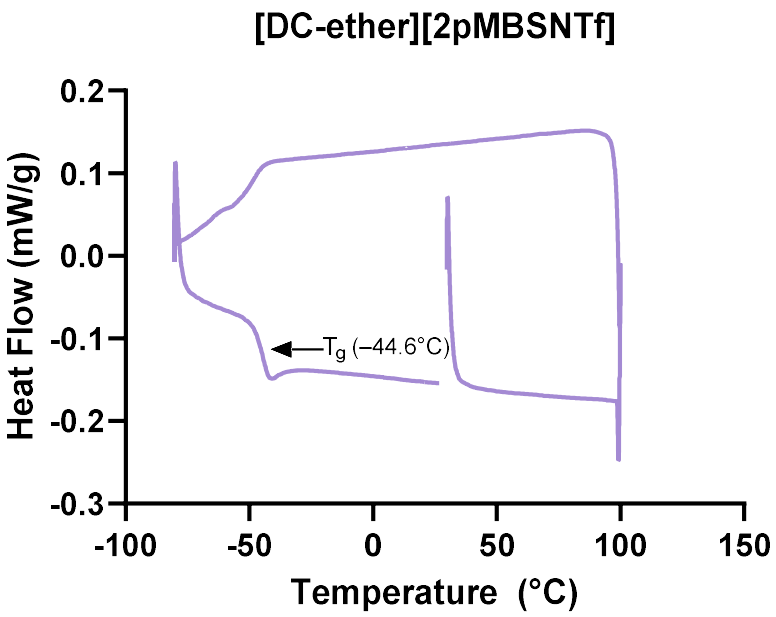
[DC-ether][2MesSNTf], **5i**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 25.00 °C



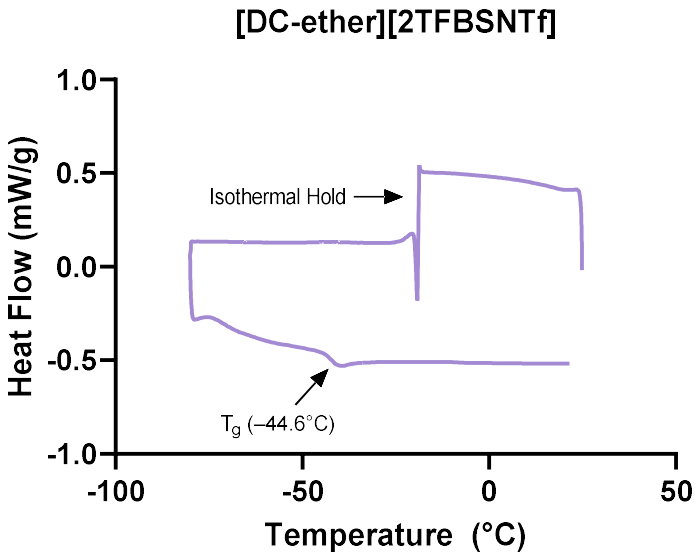
[DC-ether][2pMBSNTf], **5j**

1: Equilibrate at 30.00 °C; 2: Ramp 10.00 °C/min to 100.00 °C; 3: Isothermal for 10.00 min; 4: Mark end of cycle 0; 5: Ramp 10.00 °C/min to –80.00 °C; 6: Isothermal for 10.00 min; 7: Mark end of cycle 1; 8: Ramp 10.00 °C/min to 30.00 °C



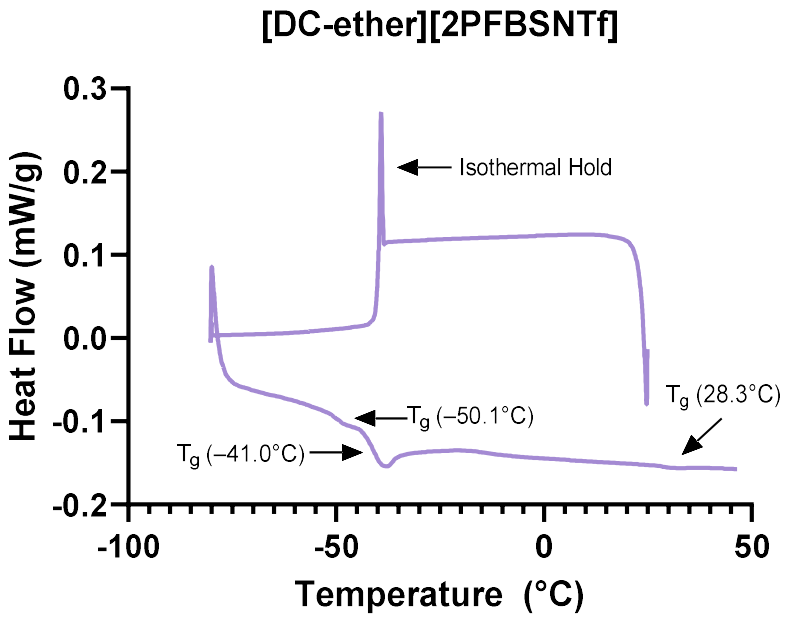
[DC-ether][2TFBSNTf], **5k**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to –20.00 °C; 3: Ramp 2.00 °C/min to –80.00 °C; 4: Isothermal for 30.00 min; 5: Mark end of cycle 1; 6: Ramp 10.00 °C/min to 25.00 °C



[DC-ether][PFBSNTf], **5l**

1: Equilibrate at 25.00 °C; 2: Ramp 10.00 °C/min to –40.00 °C; 3: Ramp 2.00 °C/min to –80.00 °C; 4: Isothermal for 10.00 min; 5: Mark end of cycle 1; 6: Ramp 10.00 °C/min to 50.00 °C



VISCOSITY. Viscosity was measured using a Brookfield DV1 Viscometer (Brookfield Engineering, Middleboro, MA) equipped with a CP-51 spindle and attached to a PolyScience Digital Temperature Controller (Niles, IL). The temperature was set to 25 °C for each IL. Prior to measuring, all ILs were placed in a vacuum oven set to 80 °C and were dried for at least 16 h. In each experiment, 0.5 mL of IL was added to the viscometer chamber where the ILs equilibrated for at least 3 min. The spindle speed was adjusted to the highest setting before reaching the upper limit of detection.

WATER SOLUBILITY.

Quantitative ^{19}F NMR spectroscopy: Prior to the quantitative study, the T_1 values of each IL and sodium trifluoroacetate (NaTFA) were determined using a Varian UI 500 MHz spectrometer equipped with a Nalorac Quad Nucleus DD probe (qn6121, 5 mm). The T_1 values were calculated to ensure that a proper recycle delay, D_1, value was chosen during the quantitative studies such that the signals fully relaxed between pulses. An inversion recovery experiment was acquired with 18 independent quadratically spaced variable (tau) values covering a range of five times the estimated T_1 value. The following parameters were employed for the acquisition of the T_1 spectra: 500 MHz; spectra width, 3 ppm; number of points, 100,000; number of transients, 16; relaxation delay, 3–6 s. See Table S1 for the specific relaxation delay parameters used for each T_1 experiment. Prior to performing the inversion—recovery T_1 measurements, the ^{19}F 90° pulse width was calibrated independently for each sample system. The processing included a line broadening of 1 Hz. The T_1 values for each IL and NaTFA can be found in Table S1. Based off the calculated T_1 values, a common D_1 time of 30 s was deemed sufficient and used for the quantitative studies.

Sample preparation for each IL was as follows: 0.25 mL of IL and 1.0 mL of D_2O were pipetted into a 1.8 mL Eppendorf tube. The mixture rotated for 16 h. Afterwards, the sample was centrifuged at 13,300 rpm for 10 min to separate the water and IL layers. From the upper layer of the Eppendorf tube, 735 µL of D_2O was transferred via a pipette to an NMR tube. The NMR tube was then spiked with 15 µL of a previously prepared NaTFA solution. NaTFA was used as a standard and was prepared in D_2O at various concentrations depending on the assumed water solubility of the IL.

The quantitative NMR experiments were performed using a Bruker Avance III HD 400 MHz NMR spectrometer. The following parameters were employed for the acquisition of the ^{19}F NMR spectra: 400 MHz; spectral width, 15 ppm; O1P, –77.5 ppm; relaxation delay, 30 s; number of transients, 64. The integration of the internal standard trifluoromethane peak was compared to the integration of the IL trifluoromethane peak. The following equation was used to determine the IL water solubility:

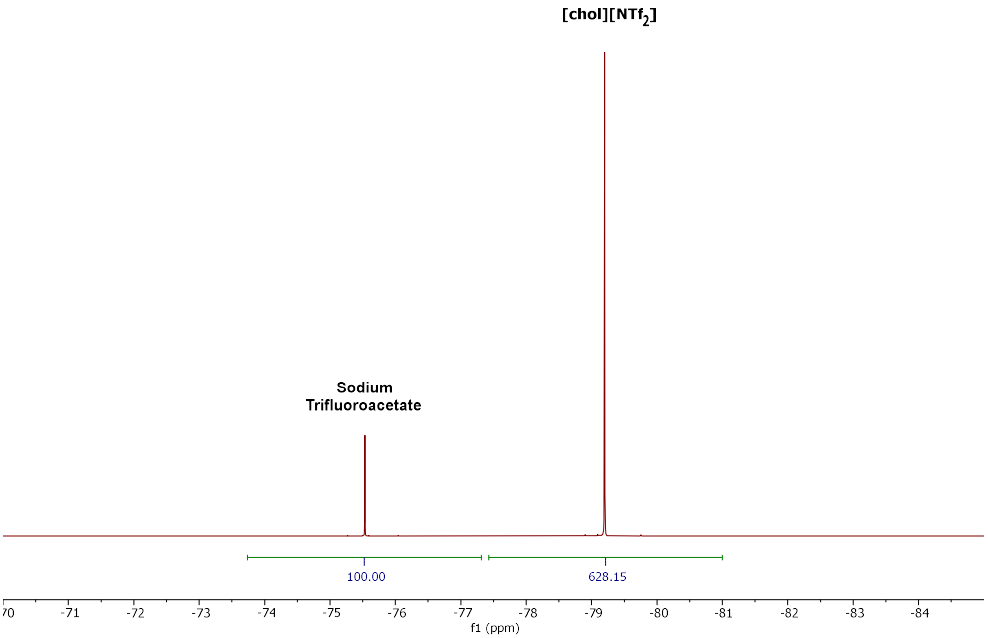
$$[\mathrm{IL}] = [\mathrm{NaTFA}] * \frac{\text{Integration of IL}}{\text{Integration of NaTFA}} * \frac{\text{\# of trifluoromethane fluorine atoms in IL}}{3}$$

Table S1 Recycle delay (D_1) parameters used for the inversion recovery experiments for each IL, and corresponding T_1 values.

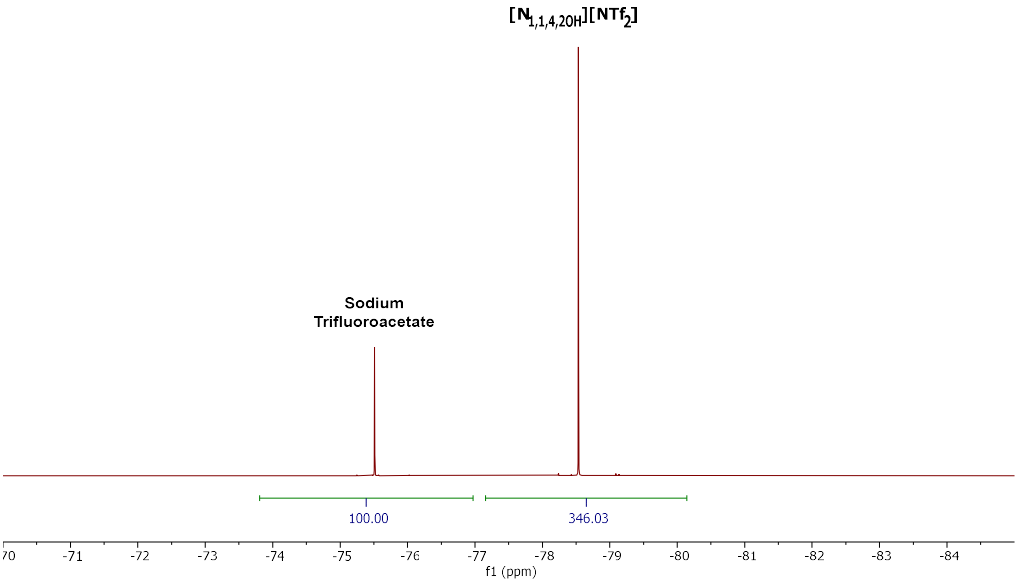
Compound	D_1 (s)	T_1 (s)
[chol][NTf_2]	6	2.02 ± 0.02
[$N_{1,1,4,2OH}$][NTf_2]	10	2.94 ± 0.04
[$N_{1,1,6,2OH}$][NTf_2]	6	2.96 ± 0.02
[$N_{1,1,8,2OH}$][NTf_2]	6	2.90 ± 0.02
[DC-4][$2NTf_2$]	16	2.88 ± 0.02
[DC-6][$2NTf_2$]	8	2.97 ± 0.06
[DC-8][$2NTf_2$]	8	2.91 ± 0.02
[DC-ether][$2NTf_2$]	10	2.86 ± 0.03
[DC-ether][2HSNTf]	8	1.78 ± 0.01
[DC-ether][2OSNTf]	8	1.80 ± 0.01
[DC-ether][2PhSNTf]	3	2.02 ± 0.02
[DC-ether][2TsNTf]	10	1.85 ± 0.02
[DC-ether][2pBBSNTf]	6	1.63 ± 0.03
[DC-ether][2pHBSNTf]	6	1.86 ± 0.02
[DC-ether][2pOBSNTf]	8	1.78 ± 0.16
[DC-ether][2MesSNTf]	8	1.50 ± 0.01
[DC-ether][2pMBSNTf]	8	1.76 ± 0.01
[DC-ether][2TFBSNTf]	10	1.87 ± 0.01
[DC-ether][2PFBSNTf]	8	1.87 ± 0.01
Sodium Trifluoroacetate	6	3.04 ± 0.06

Qualitative ^{19}F Nuclear Magnetic Resonance Spectra:

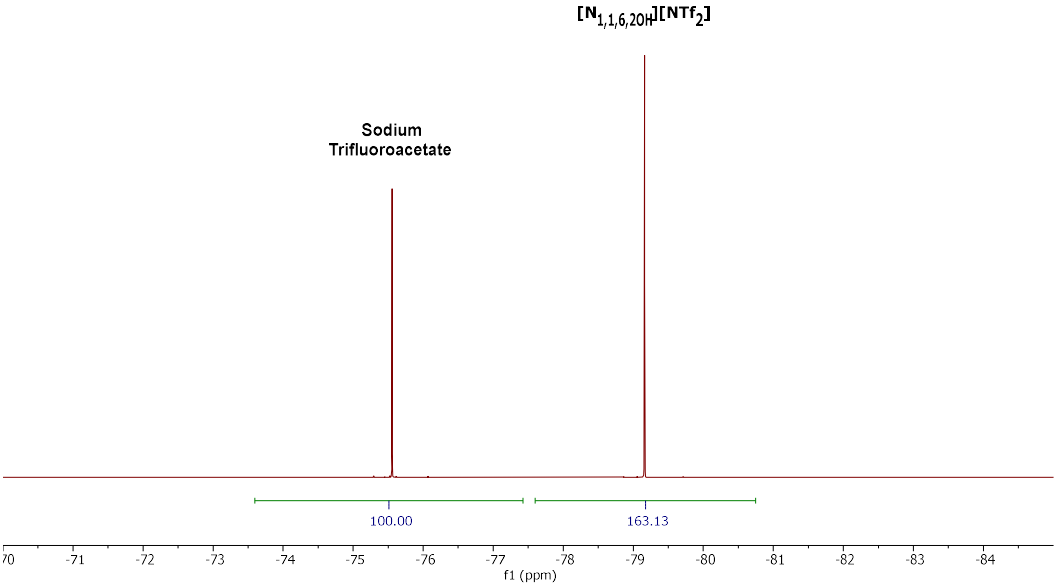
[chol][NTf_2], **2a**



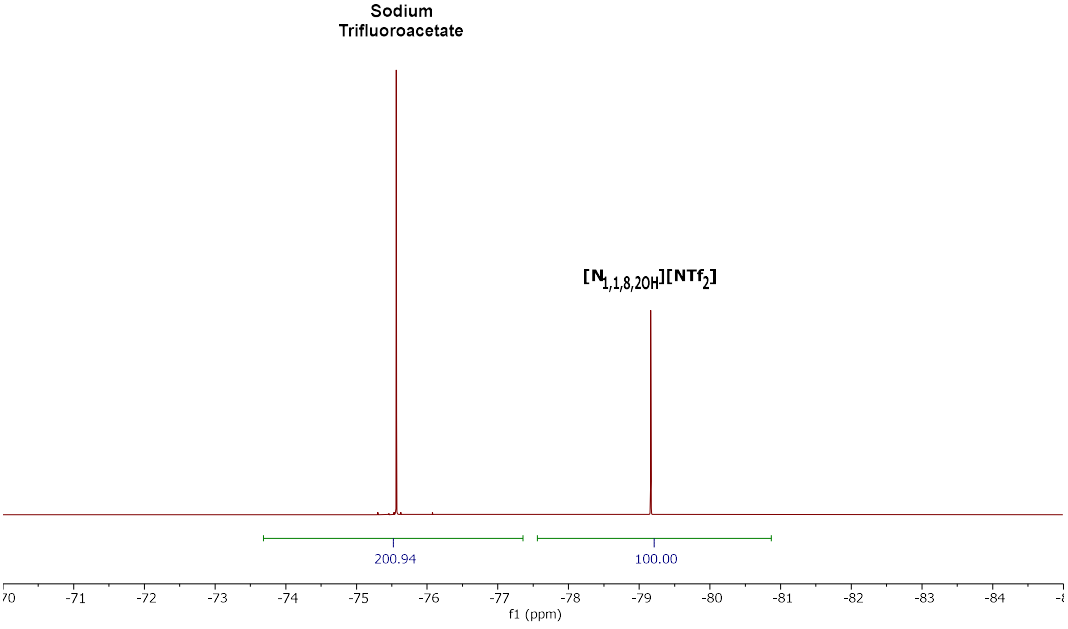
[$N_{1,1,4,2OH}$][NTf_2], **2b**



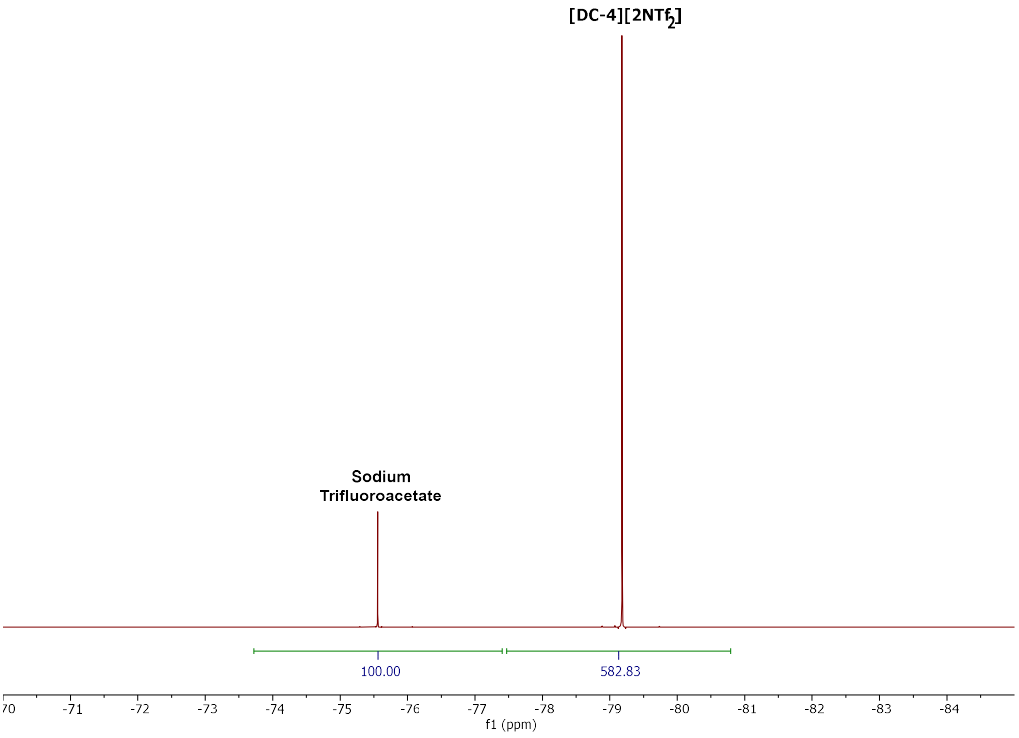
$[N_{1,1,6,2OH}][NTf_2]$, **2c**



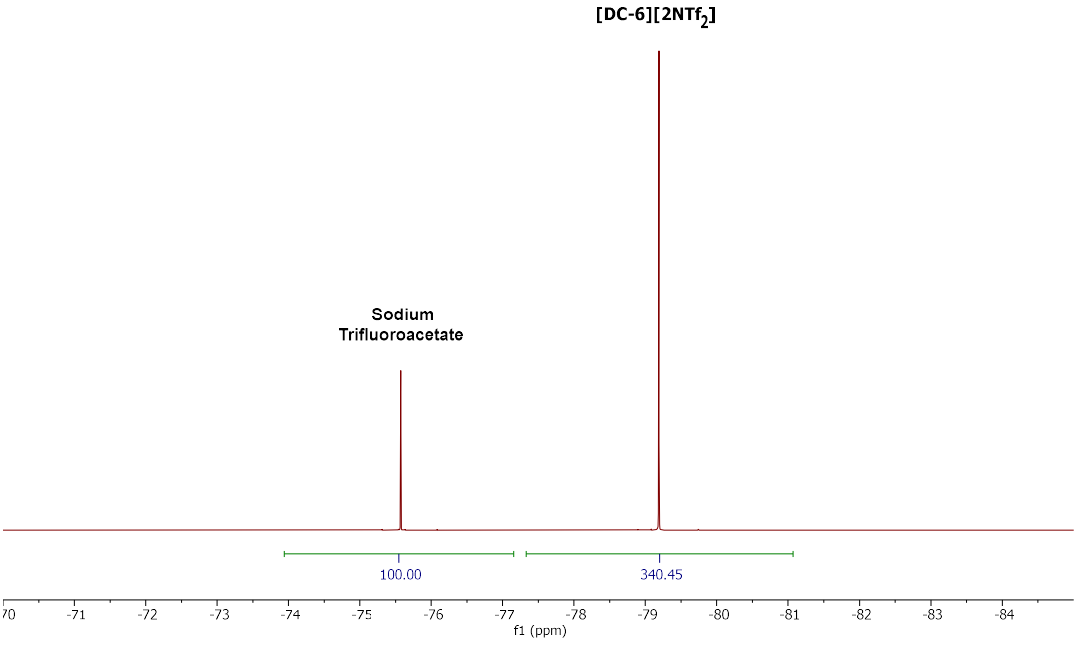
$[N_{1,1,8,2OH}][NTf_2]$, **2d**



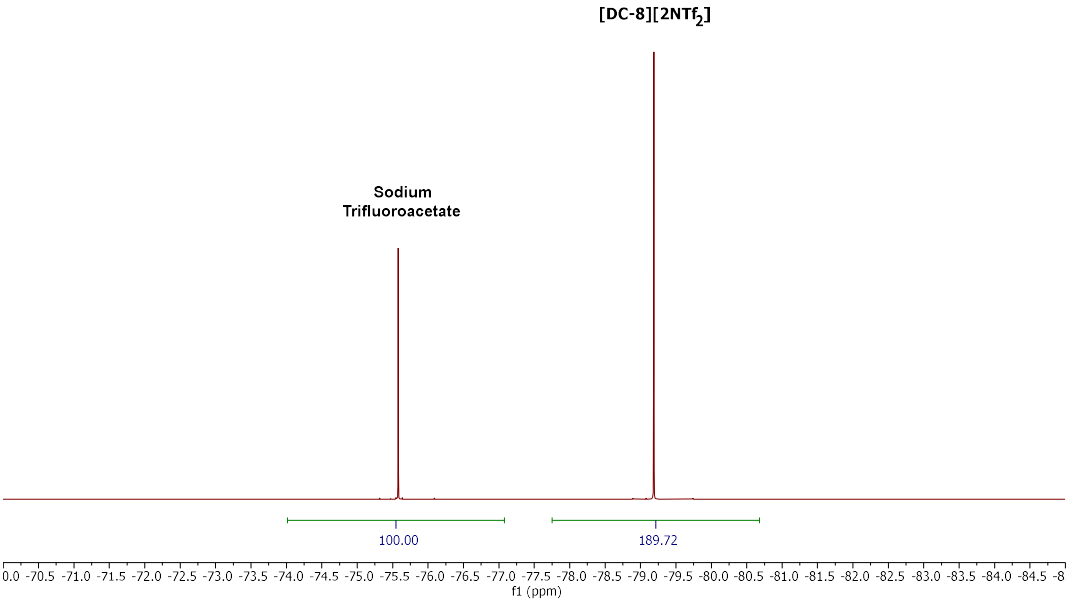
[DC-4][2NTf$_2$], **2e**



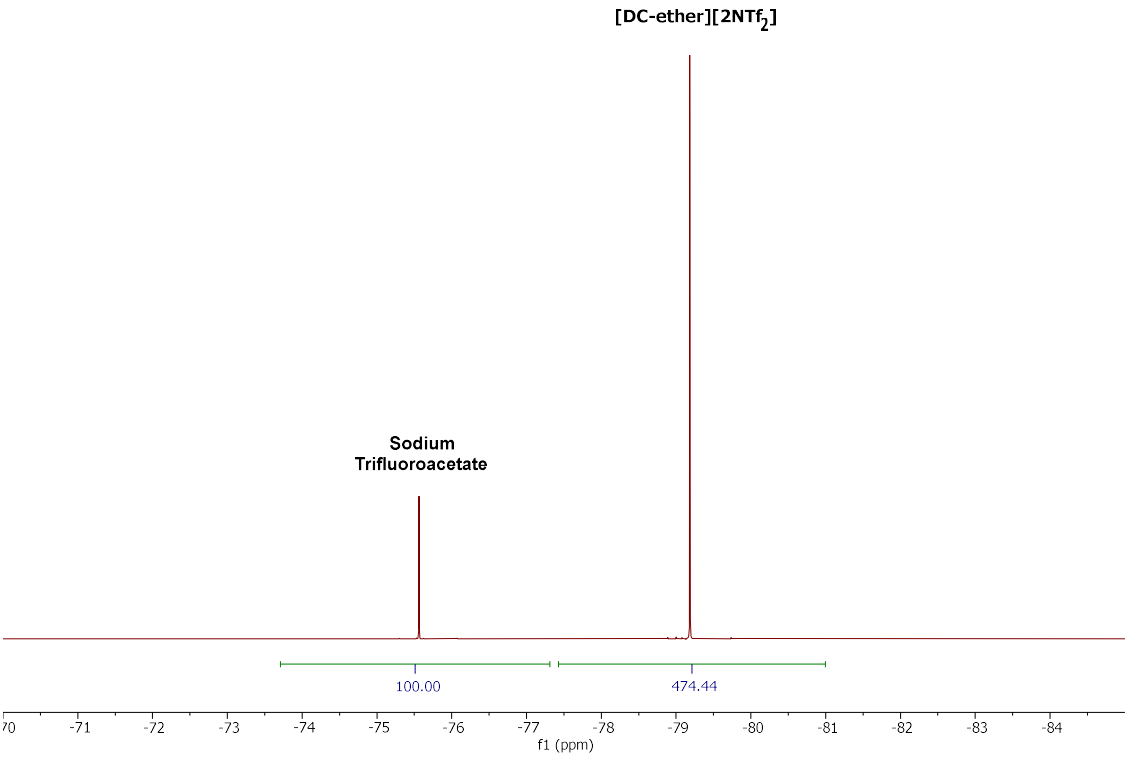
[DC-6][2NTf$_2$], **2f**



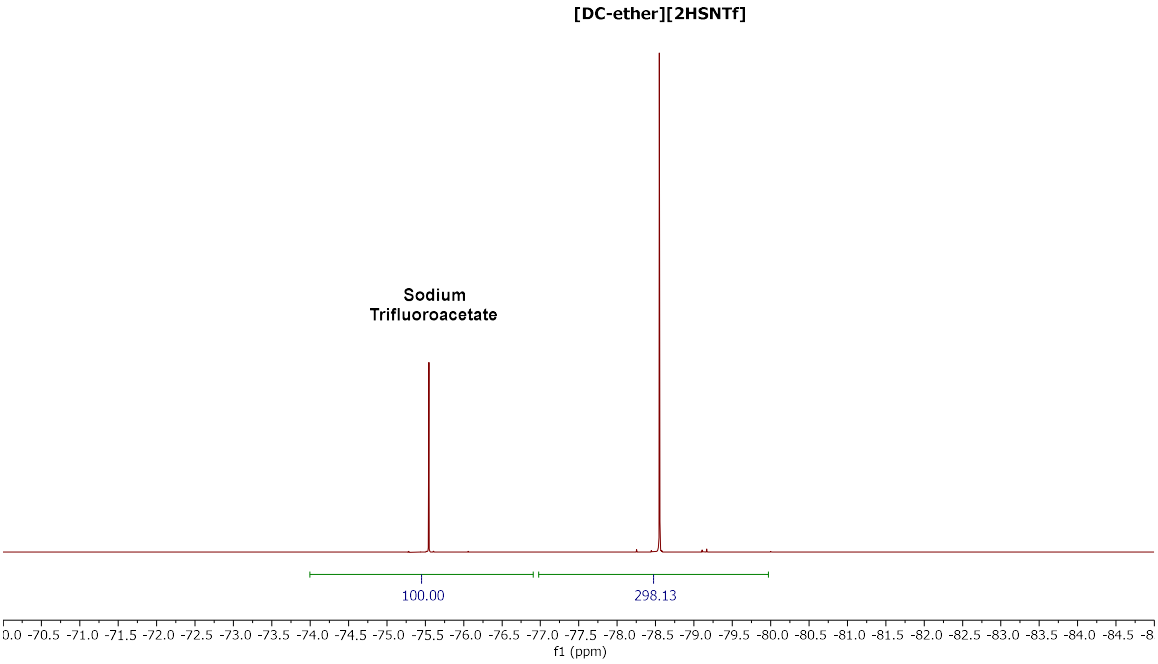
[DC-8][2NTf$_2$], **2g**



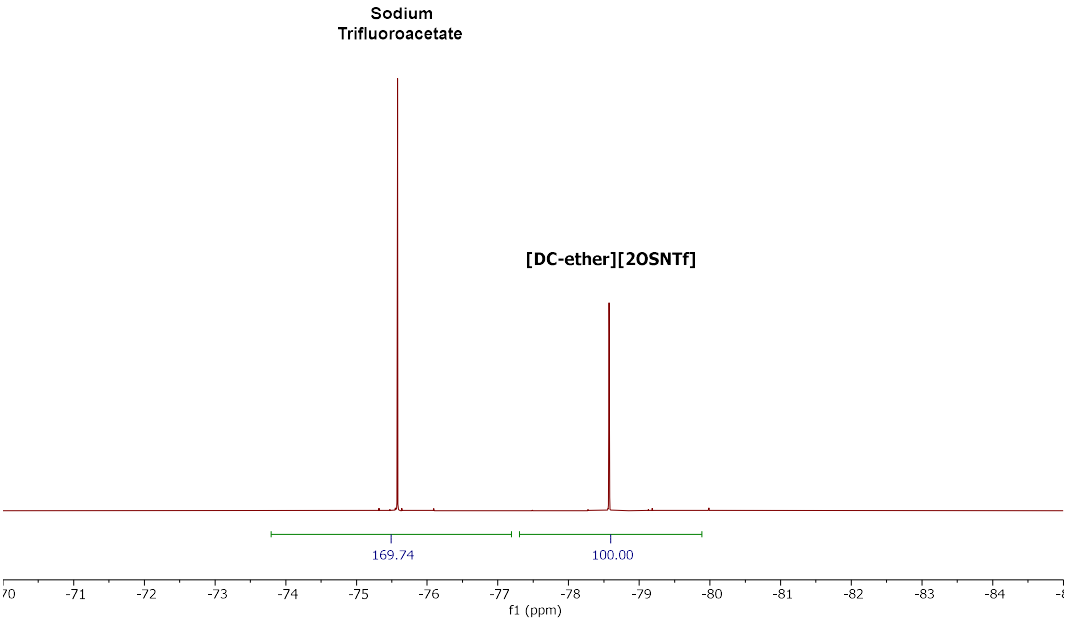
[DC-ether][2NTf$_2$], **2h**



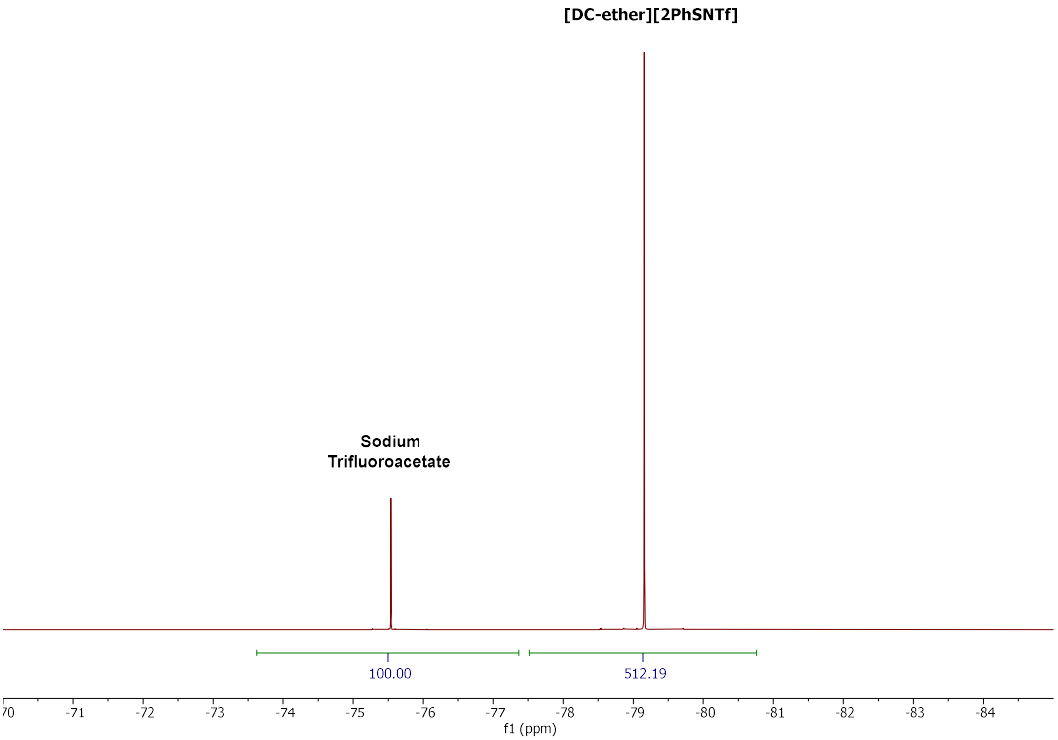
[DC-ether][2HSNTf], **5b**



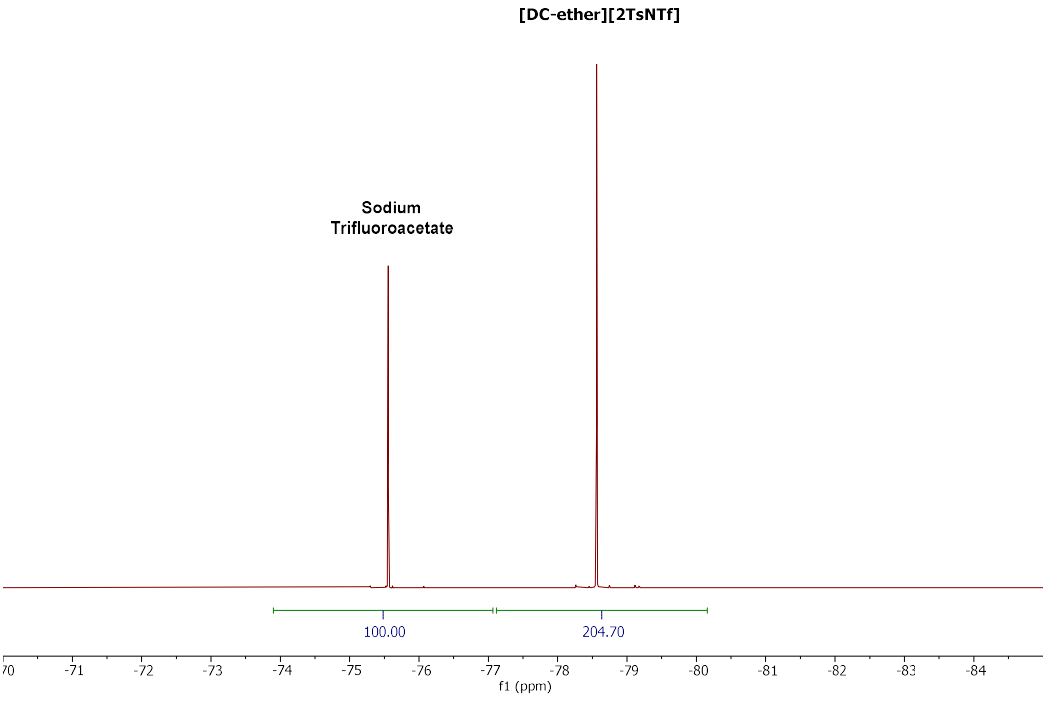
[DC-ether][2OSNTf], **5c**



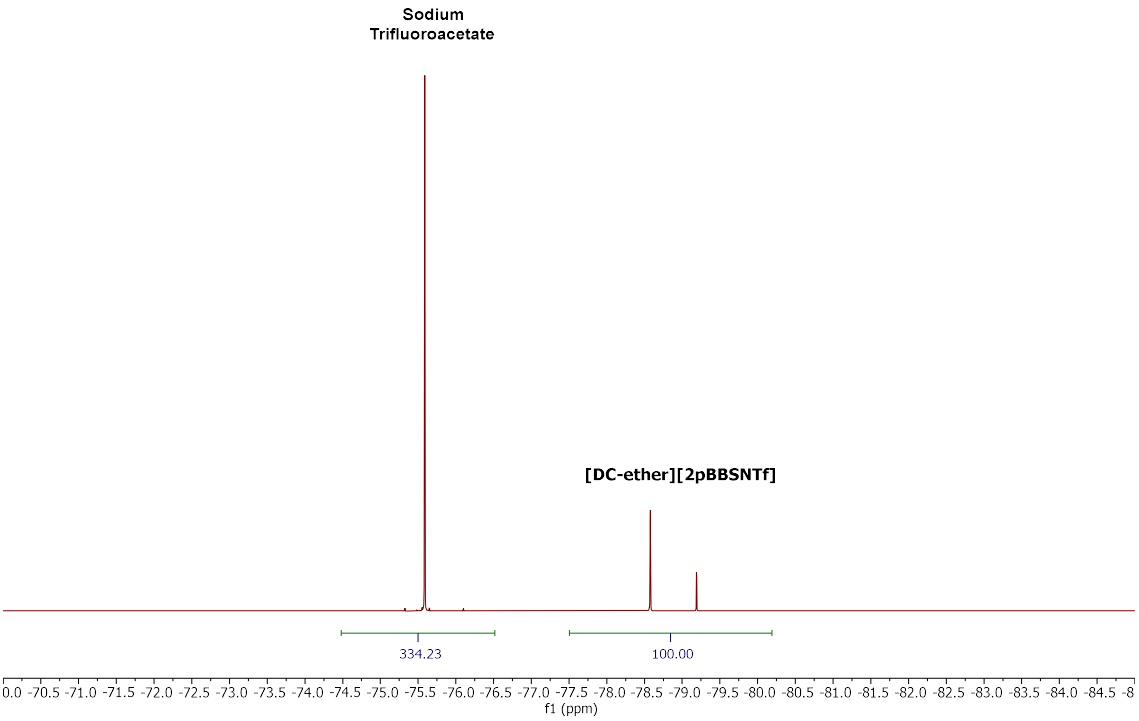
[DC-ether][2PhSNTf], **5d**



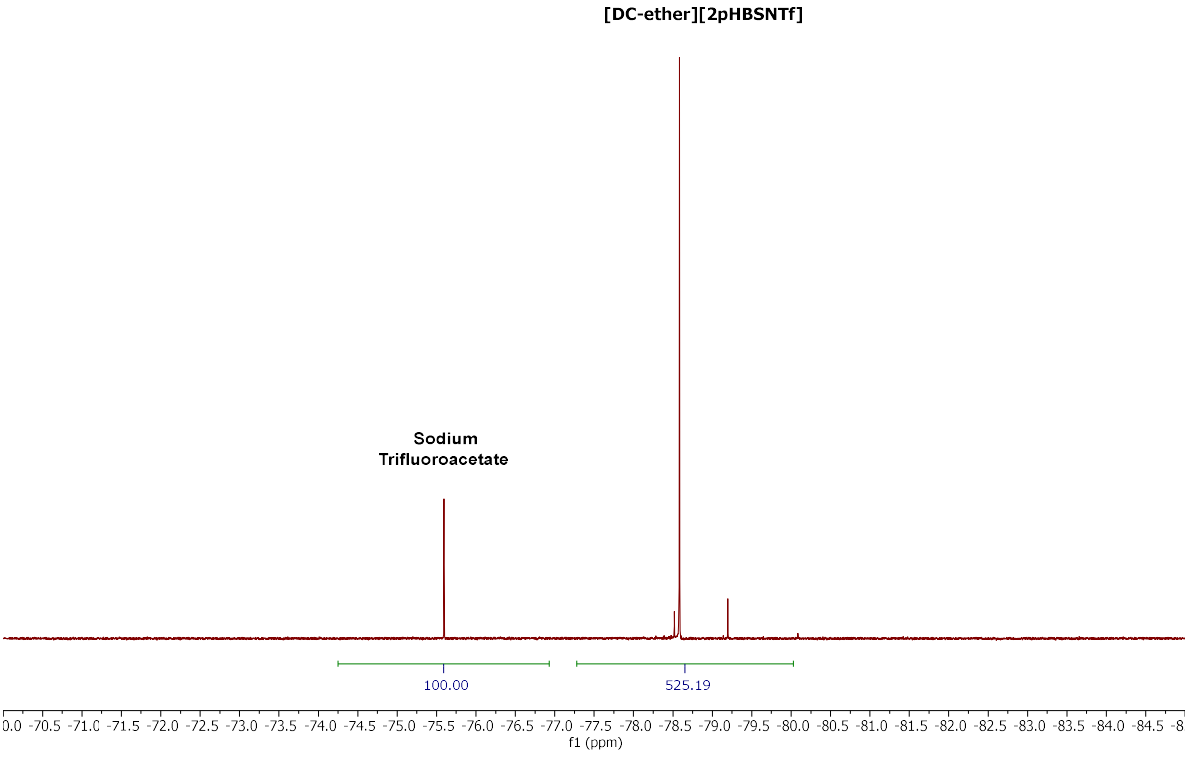
[DC-ether][2TsNTf], **5e**



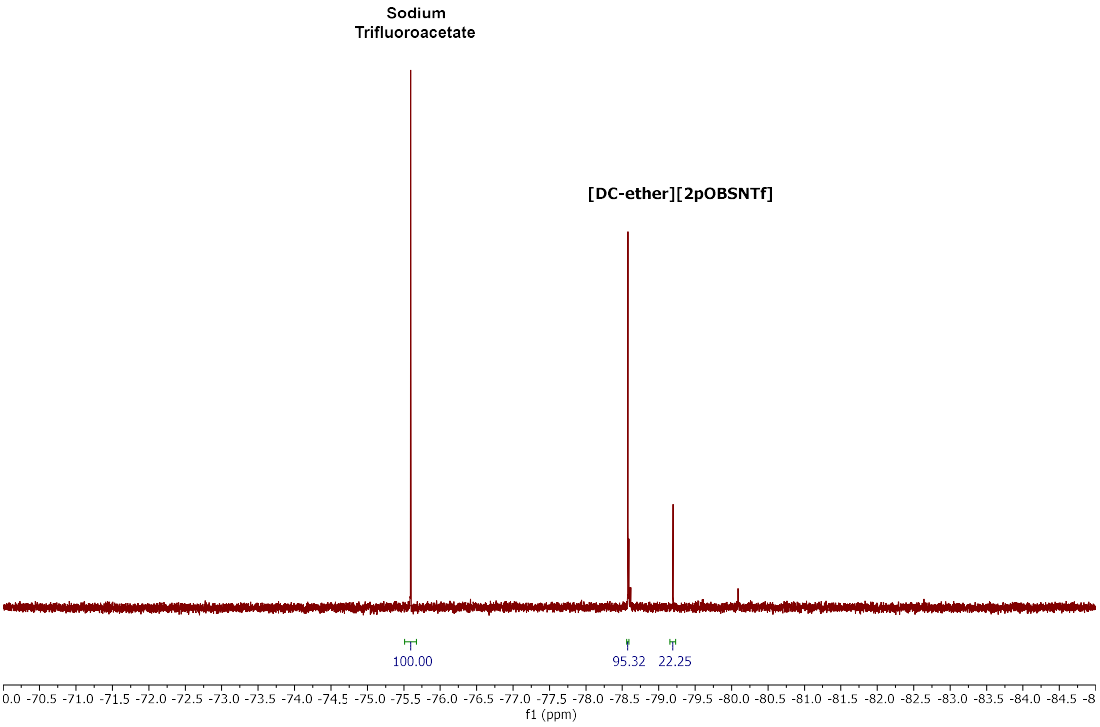
[DC-ether][2pBBSNTf], **5f**



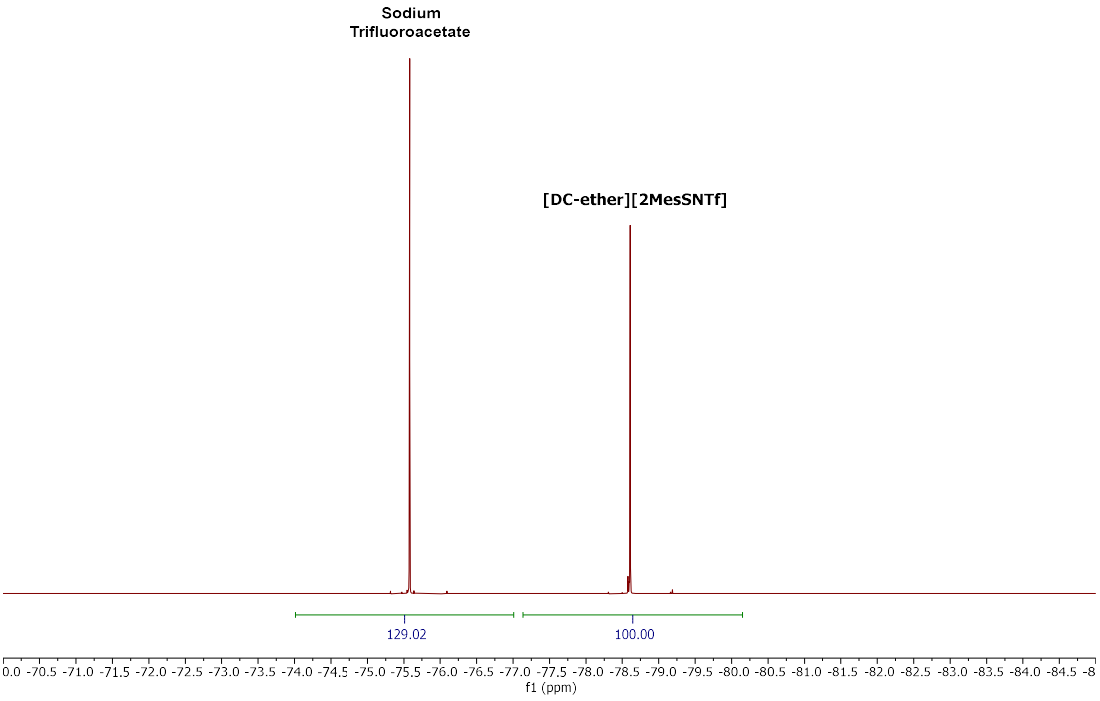
[DC-ether][2pHBSNTf], **5g**



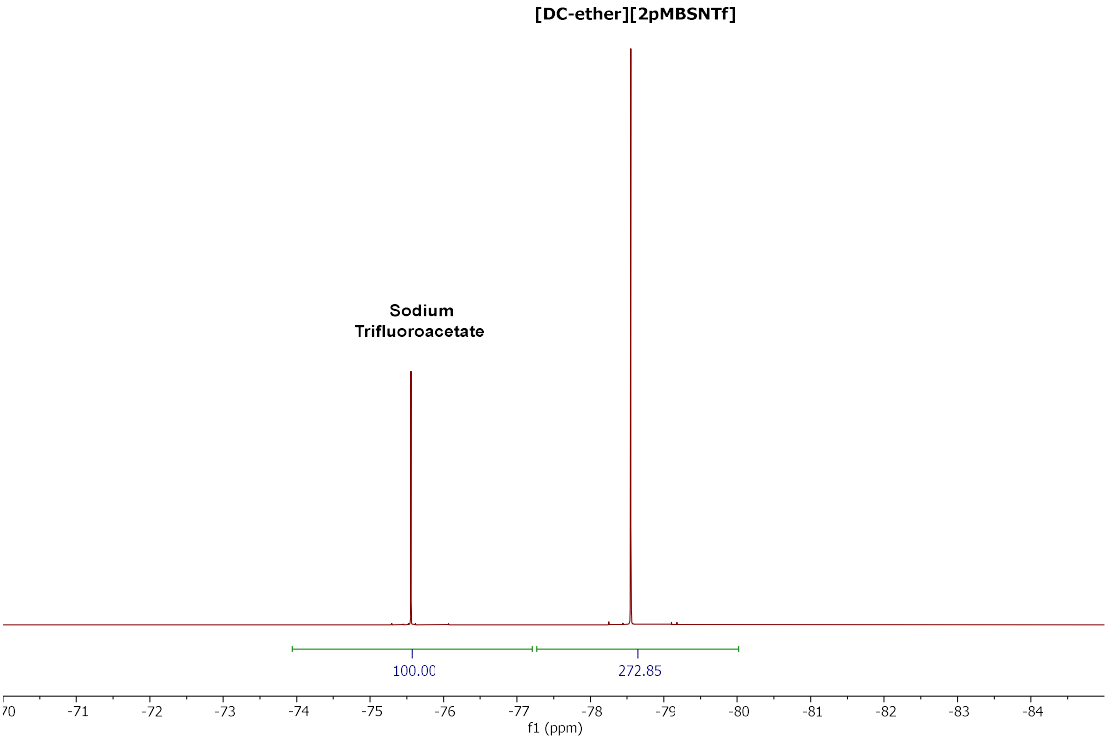
[DC-ether][2pOBSNTf], **5h**



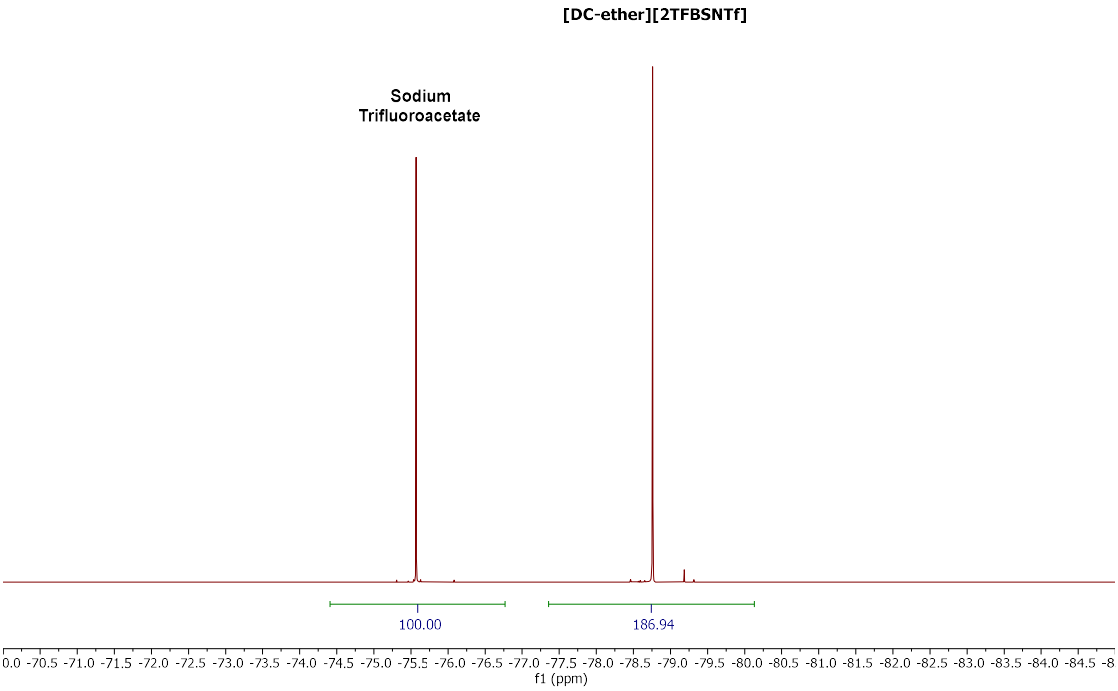
[DC-ether][2MesSNTf], **5i**



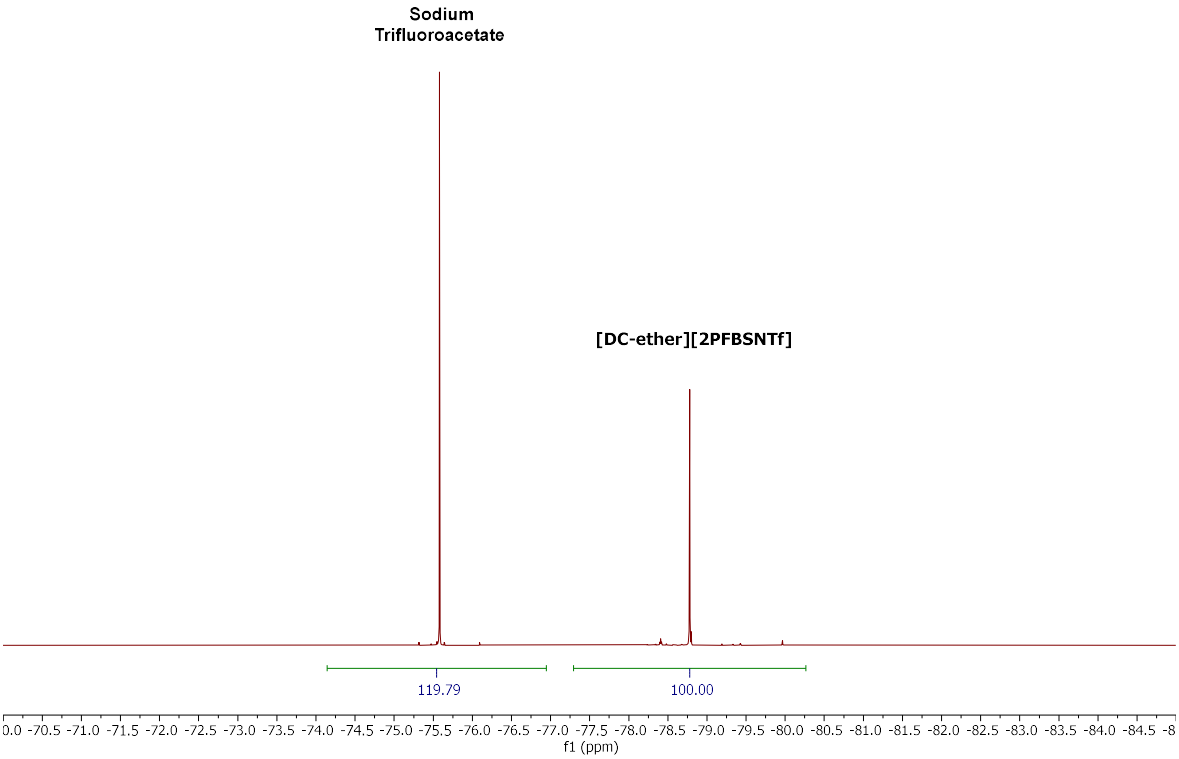
[DC-ether][2pMBSNTf], **5j**



[DC-ether][2TFBSNTf], **5k**



[DC-ether][2PFBSNTf], **5l**



HYGROSCOPICITY. Two separate sets of experiments were performed to analyze the hygroscopicity of the ILs. In the first set of experiments, 200 mg of the ILs and 1 mL of Millipore Milli-Q water was added to 1.8 mL Eppendorf tubes. The samples rotated for 16 h to ensure complete saturation. Afterwards, the Eppendorf tubes were centrifuged at 13,300 rpm for 10 min to ensure the IL and water layers were completely separated. The top water layers were carefully removed, and approximately 10 mg of the ILs were weighed into 6 mL glass vials and crimped. Water content was analyzed using an 831 KF Coulometer attached to an 860 KF Thermoprep vacuum oven (Metrohm, Herisau, Switzerland). The oven was set to 130 °C, and water content was analyzed via coulometric Karl Fisher titration, using Hydranal – Coulomat AG as the analyte. All ILs were analyzed in triplicate. In the second set of experiments, the ILs were placed in an 80 °C vacuum oven for 16 h before water content was measured. The same procedure as described above was used to determine water content. The oven method was used as the ionic properties of the ILs prevented direct injection in the Karl Fisher chamber. There was no significant increase in water content when the Thermoprep vacuum oven was set above 130 °C, and instead, many of the ILs began to decompose.

Table S2 Hygroscopicity of the ILs after drying in an 80 °C vacuum oven for 16 h. Values represent percent mass fraction.

Ionic Liquid	Hygroscopicity (W_{H2O},%)
[chol][NTf_2]	0.092 ± 0.013
[$N_{1,1,4,2OH}$][NTf_2]	0.056 ± 0.015
[$N_{1,1,6,2OH}$][NTf_2]	0.021 ± 0.007
[$N_{1,1,8,2OH}$][NTf_2]	0.041 ± 0.002
[DC-4][$2NTf_2$]	Too low to detect
[DC-6][$2NTf_2$]	Too low to detect
[DC-8][$2NTf_2$]	Too low to detect
[DC-ether][$2NTf_2$]	0.035 ± 0.012
[DC-ether][2BSNTf]	0.042 ± 0.022
[DC-ether][2HSNTf]	Too low to detect
[DC-ether][2OSNTf]	0.046 ± 0.002
[DC-ether][2PhSNTf]	0.021 ± 0.009
[DC-ether][2TsNTf]	Too low to detect
[DC-ether][2pBBSNTf]	0.014 ± 0.004
[DC-ether][2pHBSNTf]	0.074 ± 0.023
[DC-ether][2pOBSNTf]	Too low to detect
[DC-ether][2MesSNTf]	Too low to detect
[DC-ether][2pMBSNTf]	Too low to detect
[DC-ether][2TFBSNTf]	Too low to detect
[DC-ether][2PFBSNTf]	0.029 ± 0.007

***IN VITRO* TOXICITY STUDY.** Different concentrations of the IL salt precursors and ILs were prepared in High Glucose Dulbecco's Modified Eagle Media, containing 10% fetal bovine serum and 5% penicillin-streptomycin (DMEM+). Since the solubility of the ILs in DMEM+ was unknown, the solutions were prepared by first weighing 10 mg of IL into 15 mL conical tubes. As a starting point, 5 mL of DMEM+ was added to each tube. The ILs were dissolved using a bath sonicator set to 50 °C. The tubes were centrifuged at 4,000 rpm for 2 min to check if the ILs were completely dissolved. If there was residual IL, more DMEM+ was added to the conical tubes, and the ILs were dissolved as described above. This process continued until the ILs were completely dissolved. Afterwards, the ILs were serial diluted in DMEM+ to obtain the desired set of concentrations. Separately, 4T1-Luc mouse breast cancer cells were plated onto 96-well plates at a concentration of 4,000 cells/well. The cells incubated overnight in a 37 °C/5% CO_2 chamber. Afterwards, the cell media was replaced with the DMEM+ mixtures containing the IL salt precursors and the ILs. Six replicates were used for each concentration and at least four different concentrations were used for each compound. The cells incubated for 24 h. Cell viability was analyzed using a CellTiter-Blue assay by following the manufacturer's instructions. LC50 values and 95% confidence intervals were calculated by non-linear least squares analyses using Prism 9.0.0 (GraphPad Software, La Jolla, CA).

Zebrafish Developmental Toxicity Study. An embryo–larval zebrafish (*Danio rerio*) model was used to evaluate the toxicity of the IL salt precursors and ILs. AB and TL zebrafish strains were obtained from Dr. Michael Taylor at the University of Wisconsin-Madison School of Pharmacy, where the fish were cultured until sexual maturation. Zebrafish were maintained in a light/dark cycle of 14:10 h at 28.5 °C in egg water (0.03% Instant Ocean, Blacksburg, VA, USA). The adult fish were fed *Artemia nauplii* twice daily. Embryos were obtained from adult fish with a ratio of 1:2 for female to male. Breeding groups were placed in separate spawning aquariums, equipped with a mesh bottom to prevent the eggs from being cannibalized. Crossing was induced in the morning. After 1 h, eggs free of macroscopically discernible symptoms of infection and disease were collected, rinsed with egg water, and transferred into Petri dishes until chemical exposure. The embryo−larval toxicity assay was subsequently conducted. Zebrafish embryos were added to 24-well plates at 8 embryos/well. Each well was filled with 2 mL of egg water.

The IL salt precursors and the ILs were dissolved at various concentrations in egg water. Since the solubility of the ILs in egg water was unknown, the solutions were prepared by first weighing 10 mg of IL into 15 mL conical tubes. As a starting point, 5 mL of egg water was added to each tube. The ILs were dissolved via bath sonication at 50 °C. The tubes were centrifuged at 4,000 rpm for 2 min to check if the ILs were completely dissolved. If there was residual IL, more egg water was added to the conical tubes, and the IL solubilization process was repeated as described above. This procedure continued until the ILs were completely dissolved. Afterwards, the ILs were serial diluted in egg water to obtain the desired set of concentrations. The embryos were treated with the compound solutions. Two replicates were used for each concentration and at least eight different concentrations were used for each compound. The plates were covered and incubated at 28.5 °C in a light/dark cycle of 14:10 throughout the 72 hpf exposure period. The observations of zebrafish development were made directly in the well using a StereoZoom 4 stereomicroscope (Diagnostic Instruments Inc., Sterling Heights, MI) every 24 h. Embryos and larvae were considered dead when no heartbeat was observed. The number of hatched embryos and a cumulative mortality tally were recorded every 24 h, until the final time of 72 h was reached. Images were obtain using a Nikon Eclipse TE300 inverted fluorescence phase contrast microscope (Melville, NY) using SPOT Software 4.7.0 (Diagnostic Instruments Inc., Sterling Heights, MI). LC50 values and 95% confidence intervals were calculated by non-linear least squares analyses using Prism 9.0.0 (GraphPad Software, La Jolla, CA). There was no difference in the toxicity results between the AB and TL zebrafish strains.