Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information to:

Transport properties of protic and aprotic guanidinium ionic liquids

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Content

1. Synthesis of the investigated TMG ionic liquids

1.1 Materials and Methods

Synthesis of the [HHTMG] ILs, penta- and hexaalkyated guanidinium cations as well as chloro-N,N,N′,N′-tetramethylformamidinium chloride were carried out under argon atmosphere in oven-dried glassware. Solvents used in the synthesis were dried and purified using standard literature protocols. 1,1,3,3-tetramethylguanidine (99%) obtained from Alfa Aesar (Karlsruhe, Germany) and methyl trifluoromethanesulfonate from IoLiTec (Heilbronn, Germany) were distilled prior to use. Oxalyl chloride (98%) from Alfa Aesar, methylamine solution (33 wt. % in absolute ethanol), tetramethylurea (99%), n-butylamine (99.5%), 1-bromobutane (99%) trifluoromethanesulfonic acid (≥99%), methanesulfonic acid (≥99.0%) and hydrochloric acid (30%, Suprapure) obtained from Sigma Aldrich (St. Louis, USA) were used without further purification. Trifluoroacetic acid (≥99%) was purchased from VWR International (Radnor, USA) and used as received. Lithium bis(trifluoromethanesulfonyl)imide (99%) and lithium bis(pentafluoroethylsulfonyl)imide (99%) were obtained from IoLiTec and used without further treatment. Sodium trifluoromethanesulfonate (98%) from TCI Germany (Eschborn, Germany) and sodium hydrogen carbonate (p.a.) as well as anhydrous magnesium sulphate (99%) from Grüssing (Filsum, Germany) were used as obtained. Silver trifluoroacetate[1] and n-butyl methanesulfonate[2] were synthesised following literature protocols. Deuterated solvents $CDCl_3$ (99.8% D) and DMSO-d_6 (99.9% D) from Sigma Aldrich were stored over molecular sieves 4Å. Water used in the synthesis was purified with a Milli-Q® Type 1 ultrapure water system (Merck, Darmstadt, Germany).

NMR spectra were recorded on an AVANCE II 400 NMR spectrometer (Bruker, Billerica, USA). The residual signal of the deuterated solvent was used as reference. Chemicals shifts are given in ppm *vs.* tetramethylsilane (^{1}H and ^{13}C NMR) or $CFCl_3$ (^{19}F NMR).

All samples were dried in high vacuum for about 24 hours with stirring prior to all physicochemical measurements. Calibration of the rheometer was checked with viscosity standards from Paragon Scientific (Prenton, United Kingdom) at the specified temperatures. For the calibration of the electrode appropriate conductivity standards form Carl Roth (Karlsruhe, Germany) were applied. Water content was checked by Karl Fischer titration to be below 100 ppm.

1.2 Synthesis of the [HHTMG] ionic liquids

1.2.1 [HHTMG][NTf_2]

1.0 equivalent of 1,1,3,3-tetramethylguanidine was dissolved in 25 mL water per 1 mL of the base and cooled to 0 °C using an ice bath. 1.2 equivalents of diluted hydrochloric acid were added dropwise under intense stirring. To the solution 1.1 equivalents of lithium bis(trifluoromethanesulfonyl)imide [Li][NTf_2] were added and the resulting mixture stirred for

four hours at ambient temperature. The biphasic mixture was extracted with 30 mL dichloromethane per 1 mL base and the organic phase washed five times with water (15 mL per 1 mL initial guanidine). Absence of halide was confirmed after the fourth washing step by testing the aqueous phase with 0.1 molar $AgNO_3$ solution. After drying over $MgSO_4$ the solvent was removed by rotary evaporation and the residue dried in high vacuum under stirring for two days at 50 °C. The product was obtained as colourless solid in 97% yield.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.76 (s, 2H, ***NH_2***), 2.89 (s, 12H, ***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.02 (s, ***CN_3***), 119.53 (q, $^{1}J_{CF}$ = 321.9 Hz, ***CF_3***), 39.32 (s, ***CH_3***).

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6): δ[ppm] = -78.80 (s, ***CF_3***).

1.2.2 [HHTMG][BETI]

The synthesis of [HHTMG][BETI] was conducted analogous to [HHTMG][NTf_2] using lithium bis(pentafluoroethylsulfonyl)imide [Li][BETI] instead of lithium bis(trifluoromethane-sulfonyl)imide [Li][NTf_2]. The product was obtained as colourless liquid in 99% yield.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.77 (s, 2H, ***NH_2***), 2.89 (s, 12H, ***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.01 (s, ***CN_3***), 120.37 – 115.54 (m, ***CF_3***), 114.41 – 105.91 (m, ***CF_2***), 39.31 (s, ***CH_3***).

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6): δ[ppm] = -78.66 (s, 6F, ***CF_3***), -117.45 (s, 4F, ***CF_2***).

1.2.3 [HHTMG][OTf]

1.05 equivalents of 1,1,3,3-tetramethylguanidine were dissolved in 25 ml water per 1 mL of the base and the resulting homogenous solution cooled with an ice bath. Under intensive stirring 1.0 equivalents of trifluoromethanesulfonic acid were added dropwise. The resulting solution was stirred for eight hours at ambient temperature followed by evaporation of the solvent by means of rotary evaporation. The excess of the base was removed in high vacuum and the final IL dried on a Schlenk line for two days at 45 °C with stirring yielding 99% of a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.88 (s, 2H, ***NH_2***), 2.98 (s, 12H, ***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.75 (s, ***CN_3***), 120.44 (q, $^{1}J_{CF}$ = 319.3 Hz, ***CF_3***), 39.77 (s, ***CH_3***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.57 (s, ***CF_3***).

1.2.4 [HHTMG][OMs]

[HHTMG][OMs] was synthesised similar to [HHTMG][OTf] using methanesulfonic acid instead of trifluoromethanesulfonic acid. The product was obtained in 99% yield as colourless solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.85 (s, 2H, ***NH$_2$***), 2.89 (s, 12H, N(***CH$_3$***)$_2$), 2.33 (s, 3H, SO_3***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.02 (s, ***CN$_3$***), 39.77 (s, SO_3***CH$_3$***), 39.41 (s, N(***CH$_3$***)$_2$).

1.2.5 [HHTMG][TFA]

Synthesis of [HHTMG][TFA] was performed similar to [HHTMG][OTf] using trifluoroacetic acid instead of trifluoromethanesulfonic acid. [HHTMG][TFA] was obtained as colourless solid in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 8.11 (s, 2H, ***NH$_2$***), 2.80 (s, 12H, ***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.81 (s, ***CN$_3$***), 160.66 (q, $^{2}J_{CF}$ = 33.5 Hz, O_2***C***CF_3), 116.80 (q, $^{1}J_{CF}$ = 295.4 Hz, ***CF$_3$***), 39.31 (s, ***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -75.36 (s, ***CF$_3$***).

1.3 Synthesis of the intermediates

1.3.1 Chloro-N,N,N',N'-tetramethylformamidinium chloride

Synthesis of the formamidinium chloride was conducted similar to literature reports with slight modifications.[3] 120 mL tetramethylurea (1.0 eq.; 1.00 mol; 116.16 g) were dissolved in 750 mL 1,2-dichloroethane under argon atmosphere. At ambient temperature 103 mL oxalyl chloride (1.2 eq.; 1.20 mol; 152.3 g) were added dropwise over a period of four hours. The mixture was stirred for 48 hours at ambient temperature with subsequent heating to 60 °C for two hours. After cooling to ambient temperature, the solvent was removed in argon atmosphere and the remaining slightly yellow solid washed three times with 300 mL dry diethyl ether and dried in vacuum. The product was obtained as air-sensitive slightly yellow solid in 93% yield (0.930 mol; 159.1 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.43 (s, ***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 158.82 (s, ***CN$_3$***), 44.85 (s, ***CH$_3$***).

1.3.2 Pentamethylguanidine

Pentamethylguanidine was prepared from the formamidinium chloride and methylamine solution in anhydrous ethanol as described in the literature yielding 57% of a colourless liquid.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 2.75 (s, 3H, N***CH₃***), 2.58 (s, 6H, N(***CH₃***)₂), 2.46 (s, 6H, N(***CH₃***)₂).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.36 (s, ***CN₃***), 39.38 (s, N(***CH₃***)₂), 38.70 (s, N(***CH₃***)₂), 36.94 (s, N***CH₃***).

1.3.3 2-butyl-1,1,3,3-tetramethylguanidine

2-butyl-1,1,3,3-tetramethylgunidine was synthesised from the formamidinium chloride and n-butylamine according to literature protocols.[4] The product was obtained as colourless liquid in 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.05 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H, N***CH₂***), 2.68 (s, 6H, N(***CH₃***)₂), 2.59 (s, 6H, N(***CH₃***)₂), 1.51 – 1.38 (m, 2H, NCH_2***CH₂***), 1.35 – 1.21 (m, 2H, $N(CH_2)_2$***CH₂***), 0.84 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 159.96 (s, ***CN₃***), 49.22 (s, N***CH₂***), 39.69 (s, N(***CH₃***)₂), 38.92 (s, N(***CH₃***)₂), 35.00 (s, NCH_2***CH₂***), 20.62 (s, $N(CH_2)_2$***CH₂***), 14.08 (s, $N(CH_2)_3$***CH₃***).

1.3.4 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide

1.00 equivalent of pentamethylgunidine was dissolved in 15 mL acetonitrile per 1 g of the base. To the solution were added dropwise 1.4 equivalents of 1-bromobutane over a period of 30 minutes. The solution was stirred for three days at 35 °C with subsequent removal of the solvent and excess reagents. The product was dried in high vacuum for two days at 50 °C to obtain a colourless solid in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 2.98 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, N***CH₂***), 2.87 (s, 3H, N***CH₃***$(CH_2)_4H$), 2.85 – 2.71 (m, 12H, N(***CH₃***)₂), 1.49 – 1.22 (m, 2H, NCH_2***CH₂***), 1.14 – 0.99 (m, 2H, $N(CH_2)_2$***CH₂***), 0.67 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 162.83 (s, ***CN₃***), 52.08 (s, N***CH₂***), 40.53 (s, N(***CH₃***)₂), 40.17 (s, N(***CH₃***)₂), 38.10 (s, N***CH₃***$(CH_2)_4H$) 29.14 (s, NCH_2***CH₂***), 19.42 (s, $N(CH_2)_2$***CH₂***), 13.23 (s, $N(CH_2)_3$***CH₃***).

1.3.5 2,2-dibutyl-1,1,3,3-tetramethylguanidinium bromide

The hexaalkylated guanidine was prepared similar to 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide using 2-butyl-1,1,3,3-tetramethylguanidine instead of pentamethylguanidine and increasing the reaction time to four days. The product was obtained as colourless solid in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.05 – 2.99 (m, 4H, N***CH_2***), 2.97 (s, 6H, N(***CH_3***)***$_2$***), 2.89 (s, 6H, N(***CH_3***)***$_2$***), 1.54 – 1.24 (m , 4H, NCH_2***CH_2***), 1.22 – 1.03 (m, 4H, $N(CH_2)_2$***CH_2***), 0.75 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 162.86 (s, ***CN_3***), 49.23 (s, N***CH_2***), 40.78 (s, N(***CH_3***)***$_2$***), 40.55 (s, N(***CH_3***)***$_2$***), 29.49 (s, NCH_2***CH_2***), 19.69 (s, $N(CH_2)_2$***CH_2***), 13.45 (s, $N(CH_2)_3$***CH_3***).

1.4 Synthesis of the [C_1HTMG] ionic liquids

1.4.1 [C_1HTMG][NTf_2]

The synthesis of [C_1HTMG][NTf_2] was performed similar to [HHTMG][NTf_2] using pentamethylguanidine instead of 1,1,3,3-tetramethylguanidine. The product was obtained in 98% yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.03 (s, 1H, ***NH***), 2.95 (s, 12H, N(***CH_3***)***$_2$***), 2.91 (d, $^{3}J_{HH}$ = 5.0 Hz, 3H, NH***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 162.32 (s, ***CN_3***), 119.87 (q, $^{1}J_{CF}$ = 321.9 Hz, ***CF_3***), 39.76 (s, N(***CH_3***)***$_2$***), 31.77 (s, NH***CH_3***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -79.06 (s, ***CF_3***).

1.4.2 [C_1HTMG][BETI]

[C_1HTMG][BETI] was synthesised similar to [HHTMG][BETI] using pentamethylguanidine as base. The ionic liquid was obtained in 99% yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.04 (s, 1H, ***NH***), 2.95 (s, 12H, N(***CH_3***)***$_2$***), 2.90 (d, $^{3}J_{HH}$ = 5.0 Hz, 3H, NH***CH_3***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 162.36 (s, ***CN_3***), 120.37 – 116.04 (m, ***CF_3***), 115.33 – 107.59 (m, ***CF_2***), 39.73 (s, N(***CH_3***)***$_2$***), 31.75 (s, NH***CH_3***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -79.09 (s, 6F, ***CF_3***), -117.33 (s, 4F, ***CF_2***).

1.4.3 [C_1HTMG][OTf]

Pentamethylguanidinium triflate was synthesised by acid base neutralisation of pentamethylguanindine with trifluoromethanesulfonic acid similar to [HHTMG][OTf]. The product was obtained as slightly yellow, supercooled liquid in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.92 (s, 1H, ***NH***), 2.88 (s, 12H, N(***CH_3***)***$_2$***), 2.82 (s, 3H, NH***CH_3***).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ[ppm] = 162.09 (s, ***CN_3***), 120.47 (q, $^1J_{CF}$ = 320.1 Hz, ***CF_3***), 39.63 (s, $N(\boldsymbol{CH_3})_2$), 31.51 (s, $NH\boldsymbol{CH_3}$).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.55 (s, ***CF_3***).

1.4.4 $[C_1HTMG][OMs]$

The synthesis of $[C_1HTMG][OMs]$ was conducted similar to [HHTMG][OMs] exchanging the base with pentamethylguanidine. The product (99% yield) obtained was a colourless solid.

^1H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.74 (s, 1H, ***NH***), 2.89 (s, 12H, $N(\boldsymbol{CH_3})_2$), 2.80 (s, 3H, $NH\boldsymbol{CH_3}$), 2.32 (s, 3H, $SO_3\boldsymbol{CH_3}$).

$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.53 (s, ***CN_3***), 39.75 (s, $SO_3\boldsymbol{CH_3}$), 39.32 (s, $N(\boldsymbol{CH_3})_2$), 31.12 (s, $NH\boldsymbol{CH_3}$).

1.4.5 $[C_1HTMG][TFA]$

$[C_1HTMG][TFA]$ was synthesised similar to [HHTMG][TFA] obtaining a colourless liquid in 99% yield.

^1H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.96 (s, 1H, ***NH***), 2.89 (s, 12H, $N(\boldsymbol{CH_3})_2$), 2.80 (s, 3H, $NH\boldsymbol{CH_3}$).

$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.60 (s, ***CN_3***), 157.88 (q, $^2J_{CF}$ = 30.5 Hz, $O_2\boldsymbol{C}CF_3$), 117.38 (q, $^1J_{CF}$ = 300.9 Hz, ***CF_3***), 39.27 (s, $N(\boldsymbol{CH_3})_2$), 31.04 (s, $NH\boldsymbol{CH_3}$).

$^{19}F\{^1H\}$ NMR (376 MHz, DMSO-d_6): δ[ppm] = -73.53 (s, ***CF_3***).

1.5 Synthesis of the $[C_4HTMG]$ ionic liquids

1.5.1 $[C_4HTMG][NTf_2]$

Synthesis of $[C_4HTMG][NTf_2]$ was similar to the $[HHTMG][NTf_2]$ replacing the base with 2-butyl-1,1,3,3-tetramethylguanidine. The product was obtained in 98% yield in as a colourless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ[ppm] = 5.81 (s, 1H, ***NH***), 3.12 (t, $^3J_{HH}$ = 7.6 Hz, 2H, $N\boldsymbol{CH_2}$), 2.93 (s, 12H, $N(\boldsymbol{CH_3})_2$), 1.62 – 1.48 (m, 2H, $NCH_2\boldsymbol{CH_2}$), 1.41 – 1.24 (m, 2H, $N(CH_2)_2\boldsymbol{CH_2}$), 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $N(CH_2)_3\boldsymbol{CH_3}$).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.57 (s, ***CN_3***), 119.85 (q, $^1J_{CF}$ = 321.3 Hz, ***CF_3***), 45.28 (s, $N\boldsymbol{CH_2}$), 39.76 (s, $N(\boldsymbol{CH_3})_2$), 31.80 (s, $NCH_2\boldsymbol{CH_2}$), 19.77 (s, $N(CH_2)_2\boldsymbol{CH_2}$), 13.48 (s, $N(CH_2)_3\boldsymbol{CH_3}$).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ[ppm] = -79.05 (s, ***CF_3***).

1.5.2 [C_4HTMG][BETI]

[C_4HTMG][BETI] was prepared by neutralising 2-butyl-1,1,3,3-tetramethylguanidine with diluted hydrochloric acid and subsequent anion exchange with [Li][BETI] similar to [HHTMG][BETI]. A colourless liquid was obtained in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 5.88 (s, 1H, ***NH***), 3.12 (t, $^3J_{HH}$ = 7.2 Hz, 2H, N***CH$_2$***), 2.94 (s, 12H, N(***CH$_3$***)$_2$), 1.64 – 1.51 (m, 2H, NCH_2***CH$_2$***), 1.38 – 1.24 (m, 2H, $N(CH_2)_2$***CH$_2$***), 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.61 (s, ***CN$_3$***), 122.88 – 115.01 (m, ***CF$_3$***), 115.01 – 105.23 (m, ***CF$_2$***), 45.34 (s, N***CH$_2$***), 39.77 (s, N(***CH$_3$***)$_2$), 31.83 (s, NCH_2***CH$_2$***), 19.80 (s, $N(CH_2)_2$***CH$_2$***), 13.46 (s, $N(CH_2)_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -79.09 (s, 6F, ***CF$_3$***), -117.33 (s, 4F, ***CF$_2$***).

1.5.3 [C_4HTMG][OTf]

Synthesis was conducted similar to [HHTMG][OTf] exchanging the base to 2-butyl-1,1,3,3-tetramethylguanidine. The product was obtained as slightly yellow liquid in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.96 (s, 1H, ***NH***), 3.21 – 3.02 (m, 2H, N***CH$_2$***), 2.94 (s, 12H, N(***CH$_3$***)$_2$), 1.67 – 1.48 (m, 2H, NCH_2***CH$_2$***), 1.36 – 1.23 (m, 2H, $N(CH_2)_2$***CH$_2$***), 0.87 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 161.62 (s, ***CN$_3$***), 120.65 (q, $^1J_{CF}$ = 320.2 Hz, ***CF$_3$***), 45.17 (s, N***CH$_2$***), 39.89 (s, N(***CH$_3$***)$_2$), 31.72 (s, NCH_2***CH$_2$***), 19.84 (s, $N(CH_2)_2$***CH$_2$***), 13.55 (s, $N(CH_2)_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.51 (s, ***CF$_3$***).

1.5.4 [C_4HTMG][OMs]

The synthesis was performed similar to [HHTMG][OMs] using 2-butyl-1,1,3,3-tetramethylguanidine instead of 1,1,3,3-tetramethylguanidine. The product was a viscous colourless liquid that was obtained in 98% yield.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.69 (s, 1H, ***NH***), 3.10 (t, $^3J_{HH}$ = 7.1 Hz, 2H, N***CH$_2$***), 2.89 (s, 12H, N(***CH$_3$***)$_2$), 2.31 (s, 3H, SO_3***CH$_3$***), 1.71 – 1.43 (m, 2H, NCH_2***CH$_2$***), 1.41 – 1.17 (m, 2H, $N(CH_2)_2$***CH$_2$***), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 160.87 (s, ***CN$_3$***), 44.10z (s, N***CH$_2$***), 39.77 (s, SO_3***CH$_3$***) 39.43 (s, N(***CH$_3$***)$_2$), 31.31 (s, NCH_2***CH$_2$***), 19.36 (s, $N(CH_2)_2$***CH$_2$***), 13.60 (s, $N(CH_2)_3$***CH$_3$***).

1.5.5 [C_4HTMG][TFA]

Synthesis was conducted similar to [HHTMG][TFA] by neutralising 2-butyl-1,1,3,3-tetramethylguanidine with trifluoroacetic acid. The product was obtained in 99% yield as colourless liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 7.85 (s, 1H, ***NH***), 3.11 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, N***CH$_2$***), 2.89 (s, 12H, N(***CH$_3$)$_2$***), 1.70 – 1.43 (m, 2H, NCH$_2$***CH$_2$***), 1.41 – 1.19 (m, 2H, N(CH$_2$)$_2$***CH$_2$***), 0.88 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, N(CH$_2$)$_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 161.94 (s, ***CN$_3$***), 157.84 (q, $^{2}J_{CF}$ = 30.5 Hz, O$_2$***C***CF$_3$), 117.38 (q, $^{1}J_{CF}$ = 300.9 Hz, ***CF$_3$***), 44.12 (s, N***CH$_2$***), 39.38 (s, N(***CH$_3$)$_2$***), 31.30 (s, NCH$_2$***CH$_2$***), 19.34 (s, N(CH$_2$)$_2$***CH$_2$***), 13.53 (s, N(CH$_2$)$_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6): δ[ppm] = -73.57 (s, ***CF$_3$***).

1.6 Synthesis of the [C_4C_1TMG] ionic liquids

1.6.1 [C_4C_1TMG][NTf_2]

For the synthesis of the aprotic IL 1.0 equivalent of [C_4C_1TMG][Br] was dissolved in 20 mL water per 1 g of the bromide salt at ambient temperature. To the homogenous solution were added 1.2 equivalents of lithium bis(trifluormethanesulfonyl)imide and the mixture stirred for 4 hours. To the mixture were added 20 mL of dichloromethane per 1 g of starting bromide salt with subsequent stirring of the biphasic mixture for ten minutes. The organic phase was separated and washed five times with 10 mL water per 1 g of the bromide salt used. Absence of halide ions was confirmed after the fourth washing step by testing the aqueous phase with 0.1 molar silver nitrate solution. The organic phase was dried over $MgSO_4$, the solvent removed on a rotary evaporator and the residue dried in high vacuum at 45 °C for two days. The product was a colourless liquid that was obtained in 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.19 – 3.06 (m, 2H, N***CH$_2$***), 2.92 (s, 12H, N(***CH$_3$)$_2$***), 2.89 (s, 3H, N***CH$_3$***(CH$_2$)$_4$H), 1.67 – 1.44 (m, 2H, NCH$_2$***CH$_2$***), 1.37 – 1.19 (m, 2H, N(CH$_2$)$_2$***CH$_2$***), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, N(CH$_2$)$_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.48 (s, ***CN$_3$***), 119.97 (q, $^{1}J_{CF}$ = 321.5 Hz, ***CF$_3$***), 52.60 (s, N***CH$_2$***), 40.20 (s, N(***CH$_3$)$_2$***), 37.81 (s, N***CH$_3$***(CH$_2$)$_4$H) 29.55 (s, NCH$_2$***CH$_2$***), 19.93 (s, N(CH$_2$)$_2$***CH$_2$***), 13.62 (s, N(CH$_2$)$_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.97 (s, ***CF$_3$***).

1.6.2 [C_4C_1TMG][BETI]

[C_4C_1TMG][BETI] was synthesised similar to [C_4C_1TMG][NTf_2] using [Li][BETI] instead of [Li][NTf_2]. The product was a colourless liquid that was obtained in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.22 – 3.05 (m, 2H, N***CH₂***), 2.92 (s, 12H, N(***CH₃***)***₂***), 2.89 (s, 3H, N***CH₃***$(CH_2)_4H$), 1.65 – 1.43 (m, 2H, NCH_2***CH₂***), 1.39 – 1.16 (m, 2H, $N(CH_2)_2$***CH₂***), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.50 (s, ***CN₃***), 123.27 – 114.95 (m, ***CF₃***), 115.59 – 107.04 (m, ***CF₂***), 52.60 (s, N***CH₂***), 40.15 (s, N(***CH₃***)***₂***), 37.79 (s, N***CH₃***$(CH_2)_4H$) 29.54 (s, NCH_2***CH₂***), 19.92 (s, $N(CH_2)_2$***CH₂***), 13.57 (s, $N(CH_2)_3$***CH₃***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -79.06 (s, 6F, ***CF₃***), -117,31 (s, 4F, ***CF₂***).

1.6.3 $[C_4C_1TMG][OTf]$

1.00 equivalent of 2-butyl-1,1,3,3-tetramethylguanidine was cooled with an ice bath under inert atmosphere. To the base were added dropwise 1.05 equivalents of methyl trifluoromethanesulfonate over a period of 15 minutes. After warming to ambient temperature the mixture was stirred for 15 minutes and the excess methyl trifluoromethanesulfonate removed in high vacuum at 75 °C. To the residue was added saturated sodium hydrogen carbonate solution (10 mL per 1 g of the initial base), followed by extraction with first 20 mL dichloromethane per 1 g initial base and second 10 mL dichloromethane per 1 g base. The organic phase was dried over $MgSO_4$, the solvent removed by means of rotary evaporation and the residue dried in oil-pump vacuum with stirring for two days at 45 °C. The product was obtained as colourless solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.21 – 3.10 (m, 2H, N***CH₂***), 2.97 (s, 12H, N(***CH₃***)***₂***), 2.94 (s, 3H, N***CH₃***$(CH_2)_4H$), 1.71 – 1.45 (m, 2H, NCH_2***CH₂***), 1.42 – 1.18 (m, 2H, $N(CH_2)_2$***CH₂***), 0.93 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.60 (s, ***CN₃***), 124.14 (q, $^{1}J_{CF}$ = 321.4 Hz, ***CF₃***), 52.62 (s, N***CH₂***), 40.46 (s, N(***CH₃***)***₂***), 38.04 (s, N***CH₃***$(CH_2)_4H$) 29.67 (s, NCH_2***CH₂***), 20.03 (s, $N(CH_2)_2$***CH₂***), 13.75 (s, $N(CH_2)_3$***CH₃***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.31 (s, ***CF₃***).

1.6.4 $[C_4C_1TMG][OMs]$

1.0 equivalent of pentamethylguanidine were dissolved in 15 mL dry acetonitrile per 1 mL of the base under argon atmosphere. To the homogenous solution were added 1.1 equivalents of n-butyl methanesulfonate in small potions. The solution was stirred at 40°C for two days followed by removal of the solvent and excess reagents in high vacuum under gentle heating. The residue was further dried in high vacuum with applied stirring for two days at 50 °C yielding 96% of the product as colourless solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 3.24 – 3.02 (m, 2H, N***CH$_2$***), 2.88 (s, 12H, N(***CH$_3$***)$_2$), 2.85 (s, 3H, N***CH$_3$***$(CH_2)_4H$), 2.29 (s, 3H, SO_3***CH$_3$***), 1.68 – 1.39 (m, 2H, NCH_2***CH$_2$***), 1.34 – 1.16 (m, 2H, $N(CH_2)_2$***CH$_2$***), 0.88 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 162.55 (s, ***CN$_3$***), 51.26 (s, N***CH$_2$***), 39.72 (s, SO_3***CH$_3$***), 39.50 (s, N(***CH$_3$***)$_2$), 37.20 (s, N***CH$_3$***$(CH_2)_4H$) 28.86 (s, NCH_2***CH$_2$***), 19.37 (s, $N(CH_2)_2$***CH$_2$***), 13.58 (s, $N(CH_2)_3$***CH$_3$***).

1.6.5 [C_4C_1TMG][TFA]

1.00 equivalent of [C_4C_1TMG][Br] were dissolved in a minimal amount of water and subjected to anion exchange using an Amberlyst A-27 anion exchange resign (150 g exchanger per 1.0 g bromide salt). Absence of halide ions in the collected solution was confirmed by testing with 0.1 molar $AgNO_3$ solution. The aqueous solution was neutralised with 1.00 equivalent of diluted aqueous trifluoroacetic acid controlling the progression of the neutralisation with a pH-probe. The water was removed by means of rotary evaporation and the residue dried in high vacuum for two days with applied stirring. The product was obtained in 98% yield as colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.16 – 3.06 (m, 2H, N***CH$_2$***), 2.93 (s, 12H, N(***CH$_3$***)$_2$), 2.90 (s, 3H, N***CH$_3$***$(CH_2)_4H$), 1.73 – 1.37 (m, 2H, NCH_2***CH$_2$***), 1.37 – 1.12 (m, 2H, $N(CH_2)_2$***CH$_2$***), 0.87 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.38 (s, ***CN$_3$***), 160.33 (q, $^{2}J_{CF}$ = 31.9 Hz, O_2***C***CF_3), 117.58 (q, $^{1}J_{CF}$ = 298.3 Hz, ***CF$_3$***), 52.47 (s, N***CH$_2$***), 40.28 (s, N(***CH$_3$***)$_2$), 37.87 (s, N***CH$_3$***$(CH_2)_4H$) 29.54 (s, NCH_2***CH$_2$***), 19.88 (s, $N(CH_2)_2$***CH$_2$***), 13.61 (s, $N(CH_2)_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -74.62 (s, ***CF$_3$***).

1.7 Synthesis of the [C_4C_4TMG] ionic liquids

1.7.1 [C_4C_4TMG][NTf_2]

Synthesis of [C_4C_4TMG][NTf_2] was performed similar to [C_4C_1TMG][NTf_2] using [C_4C_4TMG][Br] instead of [C_4C_1TMG][Br]. The product was a colourless solid that was obtained in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.26 – 3.01 (m, 4H, N***CH$_2$***), 2.96 (s, 6H, N(***CH$_3$***)$_2$), 2.93 (s, 6H, N(***CH$_3$***)$_2$), 1.64 – 1.38 (m, 4H, NCH_2***CH$_2$***), 1.37 – 1.16 (m, 4H, $N(CH_2)_2$***CH$_2$***), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.34 (s, ***CN$_3$***), 119.98 (q, $^{1}J_{CF}$ = 321.4 Hz, ***CF$_3$***), 49.51 (s, N***CH$_2$***), 40.31 (s, N(***CH$_3$***)$_2$), 29.66 (s, NCH_2***CH$_2$***), 20.00 (s, $N(CH_2)_2$***CH$_2$***), 13.66 (s, $N(CH_2)_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.95 (s, ***CF$_3$***).

1.7.2 $[C_4C_4TMG][BETI]$

$[C_4C_4TMG][BETI]$ was prepared similar to $[C_4C_1TMG][BETI]$ using the 2,2-butyl-1,1,3,3-tetramethylguanidinium bromide instead of 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide to obtain the product in 99% yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.27 – 3.01 (m, 4H, N***CH₂***), 2.95 (s, 6H, N(***CH₃***)₂), 2.93 (s, 6H, N(***CH₃***)₂), 1.64 – 1.38 (m, 4H, NCH_2***CH₂***), 1.36 – 1.16 (m, 4H, $N(CH_2)_2$***CH₂***), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.32 (s, ***CN₃***), 122.60 – 115.14 (m, ***CF₃***), 115.35 – 108.09 (m, ***CF₂***), 49.55 (s, N***CH₂***), 40.25 (s, N(***CH₃***)₂), 29.66 (s, NCH_2***CH₂***), 19.98 (s, $N(CH_2)_2$***CH₂***), 13.60 (s, $N(CH_2)_3$***CH₃***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.04 (s, 6F, ***CF₃***), -117.32 (s, 4F, ***CF₂***).

1.7.3 $[C_4C_4TMG][OTf]$

1.0 equivalent of $[C_4C_4TMG][Br]$ were dissolved in 20 mL dry acetone per 1 g of the bromide at ambient temperature. To the solution were added 1.2 equivalents of sodium trifluoromethanesulfonate. The mixture was subsequently stirred for 24 hours and filtered. The solvent was removed by rotary evaporation and the residue dissolved in dichloromethane (20 mL per 1 g of initial bromide salt). The solution was filtered and 3Å molecular sieves were added to the filtrate. The solution was allowed to stand for one day before it was filtered again and the solvent removed on a rotary evaporator. Absence of halide ions in the residue was confirmed by testing with 0.1 molar aqueous $AgNO_3$ solution. The product was finally dried for two days in high vacuum at 40 °C under stirring to obtain the product as slightly yellow liquid in 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.17 – 3.01 (m, 4H, N***CH₂***), 2.96 (s, 6H, N(***CH₃***)₂), 2.92 (s, 6H, N(***CH₃***)₂), 1.67 – 1.35 (m, 4H, NCH_2***CH₂***), 1.35 – 1.19 (m, 4H, $N(CH_2)_2$***CH₂***), 0.89 (t, $^3J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH₃***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.27 (s, ***CN₃***), 120.91 (q, $^1J_{CF}$ = 320.9 Hz, ***CF₃***), 49.37 (s, N***CH₂***), 40.32 (s, N(***CH₃***)₂), 29.62 (s, NCH_2***CH₂***), 19.94 (s, $N(CH_2)_2$***CH₂***), 13.66 (s, $N(CH_2)_3$***CH₃***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -78.31 (s, ***CF₃***).

1.7.4 $[C_4C_4TMG][OMs]$

Synthesis was conducted similar to $[C_4C_1TMG][OMs]$ using 2-butyl-1,1,3,3-tetramethylguanidine and n-butyl methanesulfonate. The product was obtained in 97% yield as a colourless, viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 3.26 – 3.03 (m, 4H, N***CH$_2$***), 2.89 (s, 6H, N(***CH$_3$***)$_2$), 2.87 (s, 6H, N(***CH$_3$***)$_2$), 2.29 (s, 3H, SO_3***CH$_3$***), 1.63 – 1.35 (m, 4H, NCH_2***CH$_2$***), 1.34 – 1.13 (m, 4H, $N(CH_2)_2$***CH$_2$***), 0.89 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ[ppm] = 162.34 (s, ***CN$_3$***), 48.50 (s, N***CH$_2$***), 39.61 (s, N(***CH$_3$***)$_2$), 29.10 (s, NCH_2***CH$_2$***), 19.40 (s, $N(CH_2)_2$***CH$_2$***), 13.59 (s, $N(CH_2)_3$***CH$_3$***).

1.7.4 [C_4C_4TMG][TFA]

1.00 equivalent of [C_4C_4TMG][Br] was dissolved in 20 mL water per 1 g of the bromide salt. To the aqueous solution were added 1.02 equivalents of freshly prepared silver trifluoroacetate in the dark. The mixture was stirred for 18 hours at ambient temperature and filtered in the dark to remove the precipitated silver bromide. The aqueous solution was extracted five times with 10 mL diethyl ether per 1 g of initial bromide salt. The absence of halide and silver ions was confirmed by testing the aqueous phase with 0.1 molar aqueous silver nitrate and 0.1 molar aqueous sodium chloride solution. The water was removed by means of rotary evaporation and the residue dried on a Schlenk line for two days. The product was obtained as colourless solid (96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 3.16 – 2.96 (m, 4H, N***CH$_2$***), 2.92 (s, 6H, N(***CH$_3$***)$_2$), 2.87 (s, 6H, N(***CH$_3$***)$_2$), 1.63 – 1.25 (m, 4H, NCH_2***CH$_2$***), 1.25 – 1.12 (m, 4H, $N(CH_2)_2$***CH$_2$***), 0.82 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, $N(CH_2)_3$***CH$_3$***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 163.05 (s, ***CN$_3$***), 160.44 (q, $^{2}J_{CF}$ = 32.8 Hz, O_2***C***CF_3) 117.25 (q, $^{1}J_{CF}$ = 296.7 Hz, ***CF$_3$***), 49.26 (s, N***CH$_2$***), 40.18 (s, N(***CH$_3$***)$_2$), 29.55 (s, NCH_2***CH$_2$***), 19.81 (s, $N(CH_2)_2$***CH$_2$***), 13.53 (s, $N(CH_2)_3$***CH$_3$***).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ[ppm] = -74.85 (s, ***CF$_3$***).

2. Densities of the investigated ionic liquids

Experimental densities ρ of the ionic liquids at different temperatures are reported in *Table S1* and *Table S2* and are plotted in *Figure S1* and *Figure S2*. As the densities showed linear temperature dependence a fit according to *Equation S1* was applied.

$$\rho = a + b\,T \qquad \text{(S1)}$$

With a and b being linear fit parameters and T the thermodynamic temperature in Kelvin. Although other fitting models are used in the literature such as simple polynomials[5,6] we used the linear fitting since additional corrections were found to be negligible. Fitting parameters for the densities by linear regression are summarised in *Table S3*.

Table S1: Densities ρ of the investigated TMG-ILs at different temperatures given in g mL^{-1}.

	Temperature / °C					
Ionic Liquid	25	35	45	55	65	75
[HHTMG][BETI]	1.569	1.560	1.549	1.538	1.528	1.518
[C_1HTMG][NTf_2]	1.452	1.441	1.431	1.422	1.412	1.402
[C_1HTMG][BETI]	1.530	1.517	1.507	1.495	1.485	1.475
[C_1HTMG][OTf]	1.312	1.304	1.296	1.287	1.279	1.270
[C_1HTMG][TFA]	1.220	1.211	1.203	1.194	1.186	1.178
[C_4HTMG][NTf_2]	1.354	1.346	1.337	1.327	1.319	1.307
[C_4HTMG][BETI]	1.429	1.418	1.408	1.397	1.386	1.377
[C_4HTMG][OTf]	1.218	1.210	1.203	1.194	1.187	1.181
[C_4HTMG][OMs]	1.109	1.102	1.094	1.087	1.080	1.073
[C_4HTMG][TFA]	1.138	1.130	1.121	1.113	1.106	1.097
[C_4C_1TMG][NTf_2]	1.338	1.327	1.318	1.309	1.301	1.291
[C_4C_1TMG][BETI]	1.416	1.406	1.395	1.384	1.375	1.365
[C_4C_4TMG][NTf_2]	1.276	1.267	1.258	1.250	1.242	1.233
[C_4C_4TMG][BETI]	1.351	1.340	1.331	1.322	1.313	1.302
[C_4C_4TMG][OTf]	1.160	1.152	1.145	1.138	1.132	1.123
[C_4C_4TMG][OMs]	1.063	1.057	1.051	1.044	1.038	1.031

Table S2: Densities ρ in g mL^{-1} of the aprotic TFA-ILs at different temperatures.

	Temperature / °C						
Ionic Liquid	45	50	55	60	65	70	75
[C_4C_1TMG][TFA]	1.130	1.126	1.121	1.118	1.114	1.109	1.106
[C_4C_4TMG][TFA]	1.102	1.098	1.094	1.091	1.087	1.083	1.079

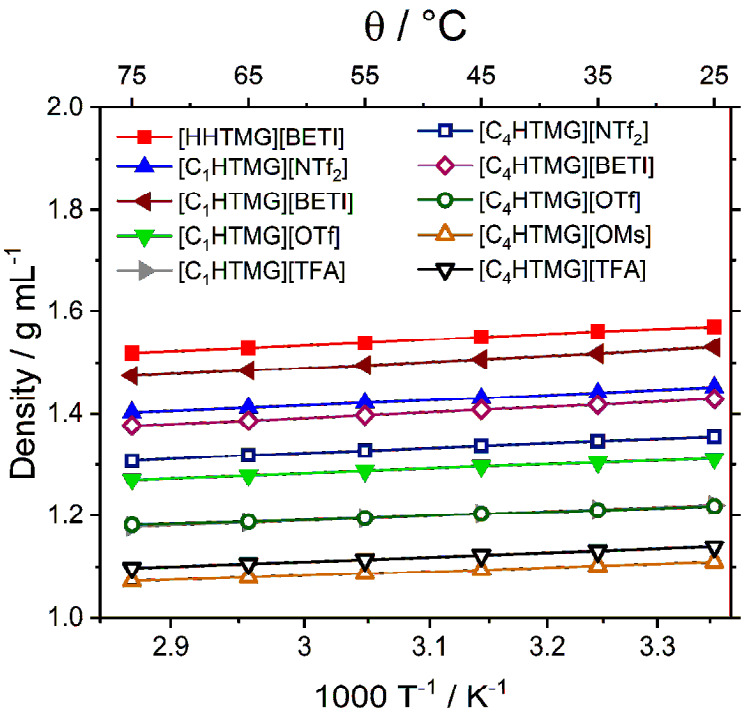

Figure S1: Temperature dependent densities of the investigated protic ionic liquids.

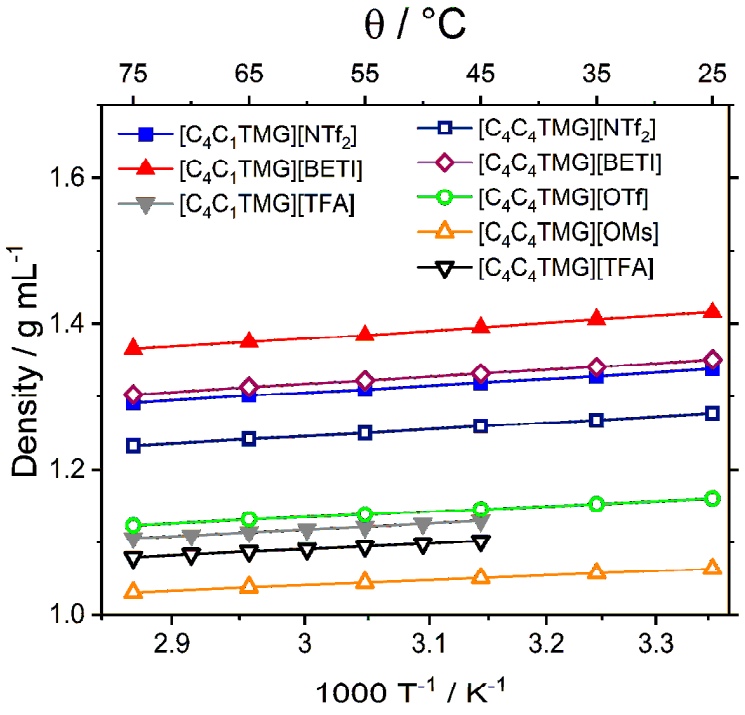

Figure S2: Temperature dependent densities of the investigated aprotic ionic liquids.

Table S3: Fitting parameters a and b for ionic liquid densities ρ from linear regression.

Ionic liquid	a / g mL^{-1}	Δa / %	b / 10^{-4} K^{-1}	Δb / %	R^2
[HHTMG][BETI]	1.877	0.273	-10.30	1.54	0.9991
[C_1HTMG][NTf_2]	1.745	0.226	-9.86	1.23	0.9994
[C_1HTMG][BETI]	1.853	0.386	-10.90	2.03	0.9984
[C_1HTMG][OTf]	1.561	0.285	-8.34	1.65	0.9989
[C_1HTMG][TFA]	1.469	0.086	-8.37	0.46	0.9999
[C_4HTMG][NTf_2]	1.632	0.422	-9.29	2.29	0.9979
[C_4HTMG][BETI]	1.743	0.242	-10.50	1.24	0.9994
[C_4HTMG][OTf]	1.438	0.319	-7.40	1.92	0.9985
[C_4HTMG][OMs]	1.329	0.166	-7.39	-0.92	0.9997
[C_4HTMG][TFA]	1.379	0.136	-8.09	0.72	0.9998
[C_4C_1TMG][NTf_2]	1.613	0.310	-9.24	0.17	0.9989
[C_4C_1TMG][BETI]	1.719	0.302	-10.20	1.57	0.9990
[C_4C_1TMG][TFA]	1.384	0.166	-7.98	0.86	0.9996
[C_4C_4TMG][NTf_2]	1.533	0.233	-8.62	1.28	0.9993
[C_4C_4TMG][BETI]	1.636	0.234	-9.57	1.24	0.9994
[C_4C_4TMG][OTf]	1.378	0.266	-7.32	1.55	0.9991
[C_4C_4TMG][OMs]	1.255	0.207	-6.43	1.25	0.9994
[C_4C_4TMG][TFA]	1.337	0.239	-7.39	1.30	0.9992

3. Viscosity

Experimentally determined values for the temperature-dependent viscosities η are given in *Table S4* and *Table S5*. The resulting plots are shown in the main manuscript. Fitting parameters η_0, B and T_0 obtained for the Vogel-Fulcher-Tammann (VFT) *Equation S2* are given in *Table S6*.

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad \text{(S2)}$$

In addition the temperature dependent viscosities were also fitted with the two parameter *Litovitz Equation S3*.

$$\Lambda_M = A \exp\left(\frac{B'}{R\,T^3}\right) \quad \text{(S3)}$$

With A and B' being fitting parameters and R the universal gas constant. The results for the Litovitz fitting are listed in *Table S7.*

Table S4: Temperature dependent viscosities η in mPa s of the guanidinium ionic liquids.

	Temperature / °C							
Ionic Liquid	25	35	45	55	65	75	85	95
[HHTMG][BETI]	206.5	108.5	64.3	41.6	29.2	21.0	16.0	12.6
[C_1HTMG][NTf_2]	66.4	43.0	29.8	21.6	16.3	12.8	10.3	8.5
[C_1HTMG][BETI]	155.4	87.4	53.7	35.1	24.3	17.7	13.2	10.2
[C_1HTMG][OTf]	171.4	96.8	60.0	39.7	27.9	20.4	15.5	12.1
[C_1HTMG][TFA]	116.7	64.0	40.0	27.4	20.1	15.3	12.5	10.3
[C_4HTMG][NTf_2]	82.8	51.6	34.6	24.3	18.0	13.7	10.8	8.8
[C_4HTMG][BETI]	174.2	98.0	60.2	39.5	27.5	20.0	15.1	11.8
[C_4HTMG][OTf]	233.9	128.3	77.0	49.6	34.1	24.7	18.3	14.1
[C_4HTMG][OMs]	1237.2	489.6	231.9	124.8	74.6	48.2	33.2	24.3
[C_4HTMG][TFA]	163.9	90.1	55.4	37.0	26.3	19.6	15.3	12.2
[C_4C_1TMG][NTf_2]	93.1	58.4	39.5	28.3	21.2	16.5	13.2	10.9
[C_4C_1TMG][BETI]	175.1	100.0	62.6	42.0	29.7	22.0	16.8	13.4
[C_4C_4TMG][NTf_2]	135.3	81.5	52.8	36.1	25.9	19.2	14.6	11.4
[C_4C_4TMG][BETI]	250.1	137.7	82.4	52.9	35.9	25.5	18.8	14.4
[C_4C_4TMG][OTf]	433.0	220.4	124.7	76.4	50.0	34.4	24.8	18.6
[C_4C_4TMG][OMs]	1453.8	508.1	224.6	117.0	68.7	43.1	30.3	22.0

Table S5: Viscosity η of the aprotic TFA-ILs at different temperatures.

	Temperature / °C										
Ionic Liquid	45	50	55	60	65	70	75	80	85	90	95
[C_4C_1TMG][TFA]	71.9	55.1	43.6	35.2	28.9	24.0	20.3	16.6	14.3	12.4	10.8
[C_4C_4TMG][TFA]	79.0	61.0	48.3	39.0	31.9	26.6	22.5	19.1	16.4	14.3	12.5

Table S6: VFT fitting parameters $\eta_{0,}$, B and T_0 for the viscosities η of the pure TMG ILs.

Ionic liquid	η_0 / mPa s	$\Delta\eta_0$ / %	B / K	ΔB / %	T_0 / K	ΔT_0 / K	R^2
[HHTMG][BETI]	0.390	4.9	549.1	1.8	210.6	0.4	1.0000
[C_1HTMG][NTf_2]	0.277	3.1	636.6	1.3	182.0	0.5	1.0000
[C_1HTMG][BETI]	0.116	2.9	829.4	0.9	182.9	0.3	1.0000
[C_1HTMG][OTf]	0.207	3.6	724.6	1.2	190.3	0.4	1.0000
[C_1HTMG][TFA]	0.832	2.5	357.6	1.2	225.8	0.0	1.0000
[C_4HTMG][NTf_2]	0.203	2.1	705.0	0.8	180.8	0.3	1.0000
[C_4HTMG][BETI]	0.116	2.9	829.4	0.9	182.9	0.3	1.0000
[C_4HTMG][OTf]	0.172	4.2	793.6	1.3	188.2	0.4	1.0000
[C_4HTMG][OMs]	0.974	35.9	376.8	16.1	227.8	2.9	0.9995
[C_4HTMG][TFA]	0.472	0.0	513.7	0.0	210.3	0.0	1.0000
[C_4C_1TMG][NTf_2]	0.430	1.4	567.0	0.6	192.7	0.2	1.0000
[C_4C_1TMG][BETI]	0.283	1.4	674.4	0.5	193.2	0.2	1.0000
[C_4C_1TMG][TFA]	0.117	27.8	770.7	10.8	197.7	3.7	0.9998
[C_4C_4TMG][NTf_2]	0.131	8.1	885.6	2.7	170.6	1.1	0.9999
[C_4C_4TMG][BETI]	0.106	2.2	932.2	0.6	178.2	0.2	1.0000
[C_4C_4TMG][OTf]	0.131	1.4	891.5	0.4	188.1	0.1	1.0000
[C_4C_4TMG][OMs]	0.333	3.4	584.7	0.9	228.4	0.2	1.0000
[C_4C_4TMG][TFA]	0.230	5.6	636.4	2.2	209.2	0.5	0.9999

Table S7: Litovitz fitting parameters $A_{,}$ and $B^{'}$ for the viscosities η of the TMG ILs.

Ionic liquid	η / S cm^2 mol^{-1}	ΔA / %	B' R^{-1} / 10^6 K^3	ΔB / %	R^2
[HHTMG][BETI]	71.6	4.74	-148.3	1.23	0.9997
[C_1HTMG][NTf_2]	56.7	1.50	-106.6	0.53	0.9999
[C_1HTMG][BETI]	68.2	4.20	-138.5	1.16	0.9996
[C_1HTMG][OTf]	65.6	4.57	-135.1	1.29	0.9996
[C_1HTMG][TFA]	54.1	3.38	-129.2	0.99	0.9998
[C_4HTMG][NTf_2]	63.2	4.22	-118.2	1.34	0.9995
[C_4HTMG][BETI]	62.6	2.46	-139.7	0.67	0.9999
[C_4HTMG][OTf]	57.7	4.49	-144.4	1.19	0.9997
[C_4HTMG][OMs]	97.1	6.33	-203.0	1.22	0.9997
[C_4HTMG][TFA]	35.8	3.20	-137.4	0.89	0.9998
[C_4C_1TMG][NTf_2]	54.9	0.83	-116.2	0.27	1.0000
[C_4C_1TMG][BETI]	57.8	2.87	-138.8	0.79	0.9999
[C_4C_1TMG][TFA]	112.2	6.34	-162.4	1.51	0.9991
[C_4C_4TMG][NTf_2]	55.7	0.74	-129.3	2.18	1.0000
[C_4C_4TMG][BETI]	57.2	2.64	-148.7	0.68	0.9999
[C_4C_4TMG][OTf]	75.8	3.43	-170.3	0.78	0.9999
[C_4C_4TMG][OMs]	177.6	9.39	-219.3	1.69	0.9995
[C_4C_4TMG][TFA]	72.9	1.80	-155.1	0.45	0.9999

4. Specific conductivity

Temperature dependent specific conductivities κ of the investigated ionic liquids are given in *Table S8* and *Table S9*. Their plots are shown in *Figure S3* and *Figure S4*. Fitting parameters κ_0, B and T_0 for the VFT fits following *Equation S4* are given in *Table S10*.

$$\kappa = \kappa_0 \exp\left(\frac{B}{T - T_0}\right) \quad \text{(S4)}$$

The specific conductivity was also fitted using the *Litovitz Equation S5*.

$$\Lambda_M = A \exp\left(\frac{B'}{R\,T^3}\right) \quad \text{(S5)}$$

The resulting fit parameters A and B' for the fitting with the Litovitz equation are given in *Table S11*.

Table S8: Specific conductivity κ in mS cm^{-1} of the protic and aprotic tetramethylguanidinium ILs at different temperatures.

	Temperature / °C					
Ionic Liquid	25	35	45	55	65	75
[HHTMG][BETI]	0.779	1.403	2.250	3.408	4.734	6.538
[C_1HTMG][NTf_2]	3.562	5.239	7.209	9.606	12.46	15.46
[C_1HTMG][BETI]	1.031	1.751	2.745	4.019	5.539	7.370
[C_1HTMG][OTf]	1.773	2.985	4.619	6.743	9.102	12.12
[C_1HTMG][TFA]	1.978	3.257	4.842	6.951	9.393	12.23
[C_4HTMG][NTf_2]	2.157	3.339	4.831	6.548	8.535	11.17
[C_4HTMG][BETI]	0.801	1.345	2.090	3.051	4.256	5.674
[C_4HTMG][OTf]	0.908	1.555	2.407	3.618	5.154	6.880
[C_4HTMG][OMs]	0.160	0.369	0.722	1.275	2.074	3.154
[C_4HTMG][TFA]	0.767	1.278	1.983	2.897	3.993	5.296
[C_4C_1TMG][NTf_2]	1.979	2.941	4.194	5.728	7.594	9.668
[C_4C_1TMG][BETI]	0.736	1.238	1.935	2.791	3.896	5.186
[C_4C_4TMG][NTf_2]	1.057	1.672	2.499	3.517	4.805	6.305
[C_4C_4TMG][BETI]	0.447	0.772	1.248	1.858	2.652	3.605
[C_4C_4TMG][OTf]	0.365	0.678	1.176	1.829	2.801	3.976
[C_4C_4TMG][OMs]	0.113	0.290	0.627	1.176	1.983	3.113

Table S9: Temperature dependent specific conductivity κ in mS cm^{-1} of the aprotic TFA ILs.

	Temperature / °C						
Ionic Liquid	45	50	55	60	65	70	75
[C_4C_1TMG][TFA]	2.842	3.400	4.265	5.230	6.316	7.528	8.741
[C_4C_4TMG][TFA]	1.889	2.351	2.912	3.517	4.220	4.981	5.825

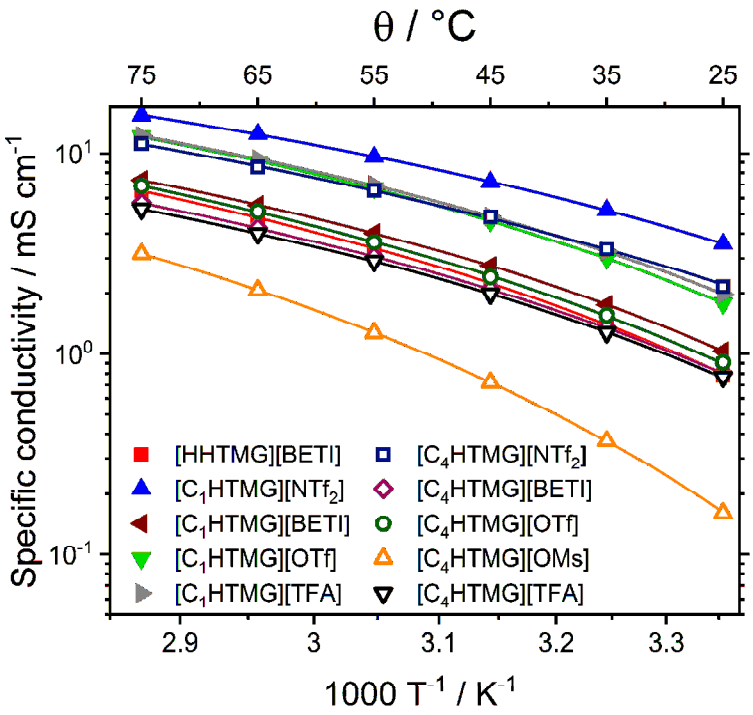

Figure S3: Temperature dependent specific conductivity of the protic TMG ionic liquids. Drawn lines are the corresponding VFT fits.

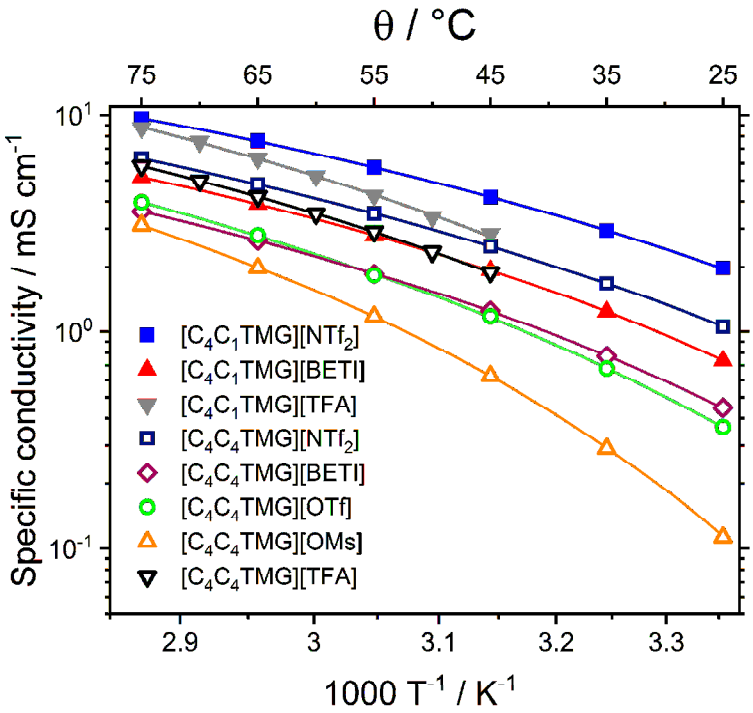

Figure S4: Temperature dependent densities of the investigated aprotic ionic liquids. Drawn lines are the corresponding VFT fits.

Table S10: VFT fitting parameters $\kappa_{0,}$, B and T_0 for the specific conductivities κ of the ionic liquids.

Ionic liquid	κ_0 / mS cm^{-1}	ΔK_0 / %	B / K	ΔB / %	T_0 / K	ΔT_0 / K	R^2
[HHTMG][BETI]	661.9	52.7	-739.3	20.1	188.2	7.5	0.9998
[C_1HTMG][NTf_2]	610.7	23.7	-642.9	11.3	173.2	5.0	0.9999
[C_1HTMG][BETI]	414.0	9.1	-614.2	4.0	195.7	1.3	0.9999
[C_1HTMG][OTf]	627.6	31.4	-604.6	13.9	195.1	4.7	0.9999
[C_1HTMG][TFA]	221.9	45.3	-368.6	26.1	221.9	6.1	0.9992
[C_4HTMG][NTf_2]	779.3	34.4	-766.3	14.4	167.7	6.8	0.9999
[C_4HTMG][BETI]	474.2	6.7	-721.1	2.7	185.2	1.0	1.0000
[C_4HTMG][OTf]	623.8	41.2	-722.0	16.1	187.9	6.0	0.9999
[C_4HTMG][OMs]	956.0	5.0	-835.6	1.6	201.9	0.5	1.0000
[C_4HTMG][TFA]	338.3	8.1	-653.7	3.4	190.9	4.3	0.9999
[C_4C_1TMG][NTf_2]	750.0	20.8	-810.9	8.5	161.7	2.4	0.9999
[C_4C_1TMG][BETI]	406.8	15.9	-706.3	6.4	186.3	2.0	0.9999
[C_4C_1TMG][TFA]	276.5	17.9	-400.6	9.2	232.1	2.4	0.9999
[C_4C_4TMG][NTf_2]	666.0	13.4	-840.9	5.1	167.7	1.7	0.9999
[C_4C_4TMG][BETI]	396.0	12.0	-762.7	4.5	185.8	6.7	0.9999
[C_4C_4TMG][OTf]	1174.8	51.0	-959.8	16.1	179.4	1.0	0.9998
[C_4C_4TMG][OMs]	821.8	10.7	-748.9	3.4	213.8	2.7	0.9999
[C_4C_4TMG][TFA]	594.8	17.9	-707.6	7.1	185.2	4.3	0.9999

Table S11: Litovitz fitting parameters $A_{,}$ and $B^{'}$ for the specific conductivities κ of the TMG ILs.

Ionic liquid	A / mS cm^{-1}	ΔA / %	B' R^{-1} / 10^6 K^3	ΔB / %	R^2
[HHTMG][BETI]	208.4	5.12	-146.1	1.34	0.9996
[C_1HTMG][NTf_2]	182.2	1.68	-104.0	0.600	0.9999
[C_1HTMG][BETI]	185.3	4.41	-135.9	1.24	0.9996
[C_1HTMG][OTf]	280.9	4.90	-132.5	1.41	0.9995
[C_1HTMG][TFA]	246.2	3.69	-126.5	1.10	0.9997
[C_4HTMG][NTf_2]	170.8	3.96	-115.3	1.29	0.9995
[C_4HTMG][BETI]	145.7	2.77	-136.8	0.773	0.9999
[C_4HTMG][OTf]	200.9	4.24	-142.1	1.14	0.9997
[C_4HTMG][OMs]	365.9	6.63	-200.4	1.30	0.9997
[C_4HTMG][TFA]	129.2	3.58	-134.6	1.01	0.9997
[C_4C_1TMG][NTf_2]	142.5	0.904	-113.5	0.904	1.0000
[C_4C_1TMG][BETI]	130.6	3.12	-136.0	3.12	0.9998
[C_4C_1TMG][TFA]	386.7	6.50	-159.5	6.50	0.9990
[C_4C_4TMG][NTf_2]	126.8	0.94	-126.6	0.940	1.0000
[C_4C_4TMG][BETI]	114.5	3.07	-145.8	3.07	0.9998
[C_4C_4TMG][OTf]	212.0	3.74	-167.7	3.74	0.9998
[C_4C_4TMG][OMs]	533.0	9.82	-216.8	9.82	0.9994
[C_4C_4TMG][TFA]	215.4	2.07	-152.2	2.07	0.9999

5. Molar conductivity

Calculated molar conductivities Λ_M of the ionic liquids at different temperatures are tabulated in *Table S12* and *Table S13*. The corresponding plots are shown in the main manuscript. Best fit parameters for Λ_{M0}, B and T_0 following *Equation S6* are given in *Table S14*.

$$\Lambda_M = \Lambda_{M,0} \exp\left(\frac{B}{T - T_0}\right) \quad \text{(S6)}$$

The VFT equation was used since it is most often used for the fitting of IL transport properties. Due to the comparably narrow temperature range also the fitting according to the Litovitz *Equation S7* was applied. The fitting parameters A and B' are listed in *Table S15.*

$$\Lambda_M = A \exp\left(\frac{B'}{R\,T^3}\right) \quad \text{(S7)}$$

Table S12: Temperature dependent molar conductivities Λ_M in S cm^2 mol^{-1} of the guanidinium ionic liquids.

	Temperature / °C					
Ionic Liquid	25	35	45	55	65	75
[HHTMG][BETI]	0.247	0.446	0.721	1.100	1.538	2.137
[C_1HTMG][NTf_2]	1.007	1.492	2.067	2.773	3.622	4.525
[C_1HTMG][BETI]	0.344	0.589	0.930	1.372	1.903	2.550
[C_1HTMG][OTf]	0.378	0.639	0.995	1.463	1.988	2.665
[C_1HTMG][TFA]	0.394	0.654	0.979	1.416	1.926	2.526
[C_4HTMG][NTf_2]	0.721	1.122	1.635	2.232	2.968	3.865
[C_4HTMG][BETI]	0.310	0.524	0.820	1.206	1.696	2.277
[C_4HTMG][OTf]	0.240	0.413	0.643	0.974	1.395	1.872
[C_4HTMG][OMs]	0.039	0.089	0.176	0.314	0.514	0.786
[C_4HTMG][TFA]	0.192	0.323	0.505	0.743	1.030	1.377
[C_4C_1TMG][NTf_2]	0.690	1.034	1.483	2.041	2.723	3.494
[C_4C_1TMG][BETI]	0.294	0.499	0.786	1.142	1.605	2.151
[C_4C_4TMG][NTf_2]	0.421	0.671	1.009	1.431	1.967	2.601
[C_4C_4TMG][BETI]	0.201	0.351	0.571	0.856	1.229	1.685
[C_4C_4TMG][OTf]	0.119	0.222	0.387	0.607	0.934	1.336
[C_4C_4TMG][OMs]	0.034	0.089	0.193	0.364	0.618	0.977

Table S13: Molar conductivity Λ_M of the aprotic TFA ILs at different temperatures.

	Temperature / °C						
Ionic Liquid	45	50	55	60	65	70	75
$[C_4C_1TMG][TFA]$	0.697	0.904	1.138	1.401	1.698	2.031	2.367
$[C_4C_4TMG][TFA]$	0.585	0.731	0.909	1.101	1.325	1.570	1.843

Table S14: VFT fitting parameters Λ_{M0}, B and T_0 for the molar conductivities of the TMG ILs.

Ionic liquid	Λ_0 / S cm^2 mol^{-1}	$\Delta\Lambda_0$ / %	B / K	ΔB / %	T_0 / K	ΔT_0 / K	R^2
[HHTMG][BETI]	250.2	50.8	-772.4	18.9	186.1	7.2	0.9998
$[C_1HTMG][NTf_2]$	213.8	24.3	-686.3	11.1	170.1	5.1	0.9999
$[C_1HTMG][BETI]$	165.1	10.0	-643.0	4.2	194.0	1.4	0.9999
$[C_1HTMG][OTf]$	165.3	33.1	-644.5	14.0	192.1	4.9	0.9999
$[C_1HTMG][TFA]$	144.2	15.4	-643.3	6.7	189.1	2.4	0.9999
$[C_4HTMG][NTf_2]$	360.7	39.3	-846.7	15.4	161.6	7.9	0.9999
$[C_4HTMG][BETI]$	230.9	9.4	-765.3	3.6	182.5	1.4	0.9999
$[C_4HTMG][OTf]$	183.6	46.5	-735.0	17.9	187.8	6.7	0.9998
$[C_4HTMG][OMs]$	277.5	4.8	-866.6	1.5	200.4	0.5	1.0000
$[C_4HTMG][TFA]$	106.6	8.9	-696.8	7.2	187.9	1.3	0.9999
$[C_4C_1TMG][NTf_2]$	341.5	18.4	-873.3	7.2	157.5	3.9	0.9999
$[C_4C_1TMG][BETI]$	198.5	15.7	-741.8	6.1	184.2	2.4	0.9999
$[C_4C_1TMG][TFA]$	85.5	19.4	-422.4	9.6	230.3	2.2	0.9999
$[C_4C_4TMG][NTf_2]$	339.4	12.3	-895.6	4.5	164.3	2.2	0.9999
$[C_4C_4TMG][BETI]$	229.4	11.5	-813.5	4.2	182.6	1.7	0.9999
$[C_4C_4TMG][OTf]$	491.7	51.4	-1014.7	15.7	176.4	6.8	0.9999
$[C_4C_4TMG][OMs]$	303.5	13.0	-781.0	4.0	212.1	1.2	0.9999
$[C_4C_4TMG][TFA]$	237.5	18.4	-762.3	6.9	191.3	2.6	0.9999

Table S15: Litovitz fitting parameters $A_{,}$ and $B^{'}$ for the molar conductivities of the TMG ILs.

Ionic liquid	A / mPa s	ΔA / %	B' R^{-1} / 10^6 K^3	ΔB / %	R^2
[HHTMG][BETI]	0.342	11.8	169.5	1.90	0.9988
[C_1HTMG][NTf_2]	0.761	2.84	118.3	0.679	0.9998
[C_1HTMG][BETI]	0.408	4.02	157.4	0.701	0.9998
[C_1HTMG][OTf]	0.501	5.51	154.5	0.982	0.9997
[C_1HTMG][TFA]	0.380	16.3	151.4	2.97	0.9967
[C_4HTMG][NTf_2]	0.633	2.92	129.1	0.635	0.9998
[C_4HTMG][BETI]	0.467	4.85	156.8	0.849	0.9997
[C_4HTMG][OTf]	0.481	5.31	163.9	0.886	0.9997
[C_4HTMG][OMs]	0.098	16.6	250.2	1.75	0.9993
[C_4HTMG][TFA]	0.436	10.9	156.9	1.91	0.9987
[C_4C_1TMG][NTf_2]	0.830	4.86	124.9	1.10	0.9995
[C_4C_1TMG][BETI]	0.588	6.02	150.8	1.10	0.9996
[C_4C_1TMG][TFA]	0.323	3.73	173.7	0.735	0.9996
[C_4C_4TMG][NTf_2]	0.685	1.79	140.0	0.356	1.0000
[C_4C_4TMG][BETI]	0.498	3.20	164.7	0.532	0.9999
[C_4C_4TMG][OTf]	0.409	5.83	184.5	0.855	0.9998
[C_4C_4TMG][OMs]	0.035	24.5	282.1	2.28	0.9990
[C_4C_4TMG][TFA]	0.391	4.16	170.6	0.837	0.9995

6. NMR diffusometry

The pulse program used for the determination of the self-diffusion coefficients D_{Si} (cation: i = +; anion: i = -) was described in a previous publication.[9] The total relaxation delay consisting of the individual parts of relaxation delay d1 and acquisition time AQ should be chosen long enough to ensure equilibrium conditions. To ensure this a value of seven times the spin lattice relaxation T1 was chosen. The T1 values were obtained roughly from the zero crossing in an inversion recovery experiment. The automatic pulsecal routine of the NMR spectrometer was used for the determination of the pulse duration in the ^{1}H experiments while for the ^{19}F experiment the duration was calculated manually by dividing the pulse duration for a 180° pulse by two. If the total experimental time is fixed, it is not necessary to consider relaxation effects. This is implemented by keeping the diffusion time Δ and gradient duration time δ fixed while the gradient strength is varied from 2% to 95% in equidistant steps. For each experiment at a given gradient strength 16 transients were recorded. The parameters used in the experiments, their abbreviation in the Bruker library and their values are given in *Table S16*. The obtained Gaussian decays in signal intensity with increasing gradient strength for the sample $[C_1HTMG][NTf_2]$ at 25 °C is shown in *Figure S5* and the received plot following the Stejskal-Tanner equation (*Equation S8*) is exemplary shown in *Figure S6*.

Table S16: Parameters used for the PFGSTE measurements, their abbreviation in the Bruker nomenclature as well as the used and varied values.

Parameter	Abbreviation in Bruker library	Value
Number of scans	Ns	16
Number of dummy scans	Ds	4
Relaxation delay	d1	varied
Pulse duration of the 90° pulse	p1	varied
Pulse duration of the 180° pulse	p2	varied
Gradient pulse duration	p30	varied
Diffusion time	d20	varied
Spectral width	Sw	varied
Transmitter offset	o1p	varied
Time domain	TD	varied
Acquisition time	AQ	varied
Gradient recovery delay	d16	200 µs
Spoiler gradient duration	p19	1 ms
LED delay T_e	d21	5 ms
Strength of first spoiler gradient	GPZ7	-17.13%
Strength of second spoiler gradient	GPZ8	-13.17%
Strength of diffusion gradient	GPZ6	varied from 2 to 95%

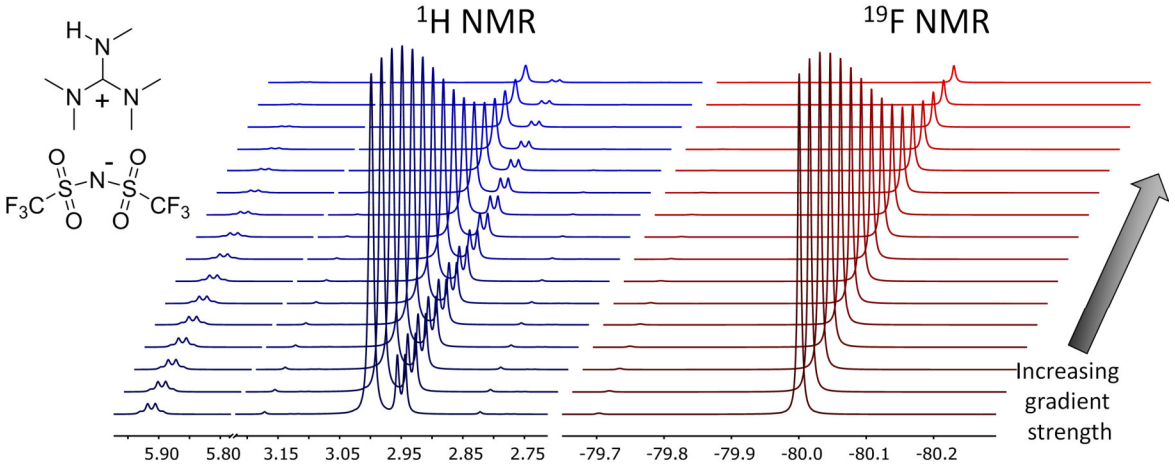

Figure S5: Exemplary stacked plot showing the obtained Gaussian decay of signal intensity of $[C_1HTMG][NTf_2]$ at 25 °C with increasing gradient strength applying the PFGSTE pulse sequence. The cation is measured by means of ^{1}H NMR and the anion by ^{19}F NMR spectroscopy. Gradient strengths were increased from 2% to 95% in equidistant steps.

$$\ln\frac{I}{I_0} = -D_{Si}\gamma^2\delta^2 g^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right) = D_{Si}Q \qquad \text{(S8)}$$

With I the signal intensity, I_0 the initial signal intensity, D_{Si} the self-diffusion coefficient, γ the gyromagnetic ratio of the investigated nucleus, δ the overall gradient duration, g the applied gradient strength, Δ the diffusion time and τ the gradient interspacing.

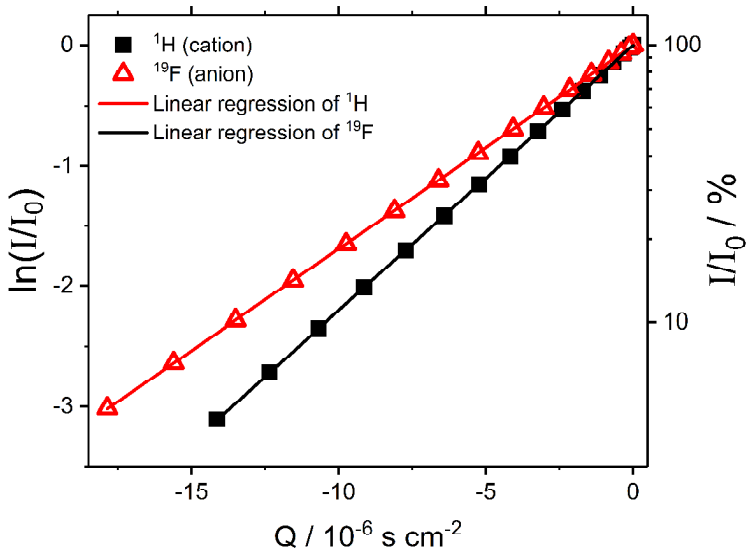

Figure S6: Obtained signal intensity decay from the PFGSTE experiment for ^{1}H NMR (cation) and ^{19}F NMR (anion) with increasing gradient strength according to the Stejskal-Tanner equation (*Equation S8*) and linear regression for $[C_1HTMG][NTf_2]$ at 25 °C.

The set of values for the diffusion time Δ and gradient duration time δ should be chosen so that the signal obtained for the highest gradient has an intensity of about 5% the value for the same signal of the lowest gradient. This was ensured by reasonable initial guess of the two parameters followed by recording of the spectra at 2% and 95% gradient strength and calculation of the self-diffusion coefficient via Stejskal-Tanner equation and subsequent change of the parameters until an appropriate signal attenuation is achieved. With the parameters obtained this way the PFGSTE experiment was conducted with applied gradient strengths of 2% to 95% varied in equidistant steps. The values of the individually adjusted parameters for each single temperature experiment δ (p30), Δ (d20), duration of the 90° pulse (p1), relaxation delay (d1), spectral width (sw), transmitter offset (o1p) as well as the time domain (TD) and acquisition time (AQ) are given in *Table S17* (^{1}H NMR) and *Table S18* (^{19}F NMR). Parameters used for the temperature dependent PFGSTE experiments are given in *Table S19* (^{1}H NMR) and *Table S20* (^{19}F NMR).

Table S17: Parameters used for the single temperature ^{1}H PFGSTE measurements of the investigated ionic liquids and obtained diffusion coefficients.

Ionic liquid	Temp. / °C	p30 / ms	d20 / ms	p1 / µs	d1 / s	sw / ppm	o1p / ppm	TD	AQ / s	D_{Si} / 10^{-12} m^2 s^{-1}
[HHTMG][BETI]	25	10.70	150	11.53	3.0	8	4	8k	1.28	5.86
[C_1HTMG][NTf_2]	25	7.04	100	11.77	1.2	9	4	16k	2.3	20.47
[C_1HTMG][BETI]	25	11.44	100	11.48	2.0	9	4	16k	2.28	7.83
[C_1HTMG][OTf]	25	10.96	100	11.66	2.3	11.7	4.5	8k	2.3	8.18
[C_1HTMG][TFA]	25	10.89	80	11.74	2.5	16	6	32k	2.5	11.03
[C_4HTMG][NTf_2]	25	8.37	100	11.61	3.5	10	4	16k	2	13.94
[C_4HTMG][BETI]	25	8.47	200	11.57	4.3	10	4	16k	2	6.73
[C_4HTMG][OTf]	25	11.21	150	11.49	4.0	10	4	16k	2	5.13
[C_4HTMG][OMs][a]	45	10.95	150	11.56	4.3	10	4	16k	2.05	5.13
[C_4HTMG][OMs][b]	45	10.95	150	11.56	4.3	10	4	16k	2.05	5.88
[C_4HTMG][TFA]	25	10.36	150	11.32	3.9	12	7	16k	1.7	6.08
[C_4C_1TMG][NTf_2]	25	9.05	100	11.82	3.0	10	2	16k	2	12.09
[C_4C_1TMG][BETI]	25	10.24	150	11.51	2.9	10	2	16k	2	6.28
[C_4C_1TMG][TFA]	45	6.34	150	11.62	3.6	10	2	16k	2.05	15.54
[C_4C_4TMG][NTf_2]	25	9.96	150	11.50	4.0	8	4	8k	1.28	6.63
[C_4C_4TMG][BETI]	25	13.41	150	11.41	4.3	8	4	8k	1.28	3.67
[C_4C_4TMG][OTf]	25	14.14	250	11.35	4.3	10	4	8k	1.02	1.95
[C_4C_4TMG][OMs][a]	45	11.56	150	10.32	5.0	13	5	16k	1.58	3.43
[C_4C_4TMG][OMs][b]	45	11.56	150	10.32	5.0	13	5	16k	1.58	5.29
[C_4C_4TMG][TFA]	45	8.10	100	11.67	3.9	12	5	16k	1.71	14.09

[a] cation self-diffusion coefficient; [b] anion self-diffusion coefficient.

Table S18: Parameters used for the single point ^{19}F PFGSTE measurements of the investigated ionic liquids and obtained diffusion coefficients.

Ionic liquid	Temp. / °C	p30 / ms	d20 / ms	p1 / µs	d1 / s	sw / ppm	o1p / ppm	TD	AQ / s	D_{s-} / 10^{-12} m^2 s^{-1}
[HHTMG][BETI]	25	11.41	200	16.5	1.1	50	-100	64k	1.74	4.16
[C_1HTMG][NTf_2]	25	8.45	100	19.4	2	7	-80	16k	3	15.70
[C_1HTMG][BETI]	25	10.14	200	17.0	1.5	50	-100	64k	1.74	5.34
[C_1HTMG][OTf]	25	10.55	150	18	3.2	7	-78	16k	3.1	6.53
[C_1HTMG][TFA]	25	10.47	100	18	3	6	-76	16k	3.6	10.34
[C_4HTMG][NTf_2]	25	9.28	100	19	2	7	-80	16k	3.1	12.97
[C_4HTMG][BETI]	25	10.04	200	16.8	1.1	50	-100	64k	1.74	5.33
[C_4HTMG][OTf]	25	10.65	200	18.7	3	7	-78	16k	3.1	4.73
[C_4HTMG][TFA]	25	11.06	150	18.9	4	14	-75	16k	1.56	6.13
[C_4C_1TMG][NTf_2]	25	9.50	100	19	2.5	7	-80	16k	3.1	12.45
[C_4C_1TMG][BETI]	25	9.81	200	19	1.4	60	-100	64k	1.44	5.63
[C_4C_1TMG][TFA]	45	6.31	150	19.1	6	10	-75	8k	1.09	18.04
[C_4C_4TMG][NTf_2]	25	9.28	150	19.2	2.8	5	-78	8k	2.18	8.70
[C_4C_4TMG][BETI]	25	11.55	200	18.5	1.3	50	-100	64k	1.74	4.14
[C_4C_4TMG][OTf]	25	13.33	250	17.3	4.1	10	-78	16k	2.18	2.48
[C_4C_4TMG][TFA]	45	8.57	100	19.15	4.5	10	-74	16k	2.18	14.85

Table S19: Parameters used for the temperature dependent ^{1}H PFGSTE measurements and obtained diffusion coefficients.

Ionic liquid	Temp / °C	p30 / ms	d20 / ms	p1 / µs	d1 / s	sw / ppm	o1p / ppm	TD	AQ / s	D_{s+} / 10^{-12} m^2 s^{-1}
$[C_1HTMG][NTf_2]$	25	7.04	100	11.77	1.2	9	4	16k	2.3	20.47
$[C_1HTMG][NTf_2]$	35	5.29	100	11.96	2.6	9	4	16k	2.3	34.48
$[C_1HTMG][NTf_2]$	45	4.66	80	12.15	2.6	9	4	16k	2.3	55.72
$[C_1HTMG][NTf_2]$	55	3.75	80	12.11	5.0	9	4	16k	2.3	86.03
$[C_1HTMG][NTf_2]$	65	3.33	80	12.29	6.0	9	4	16k	2.3	120.2
$[C_1HTMG][NTf_2]$	75	2.77	80	12.47	6.0	9	4	16k	2.3	162.3
$[C_1HTMG][TFA]$	25	10.89	80	11.74	2.5	16	6	32k	2.5	11.03
$[C_1HTMG][TFA]$	35	7.91	80	11.74	1.7	16	6	32k	2.5	20.67
$[C_1HTMG][TFA]$	45	6.34	70	11.91	2.4	16	6	32k	2.5	35.64
$[C_1HTMG][TFA]$	55	5.50	60	12.09	2.0	16	6	32k	2.5	57.27
$[C_1HTMG][TFA]$	65	4.70	60	12.19	2.4	16	6	32k	2.5	85.32
$[C_1HTMG][TFA]$	75	4.00	50	12.37	3.1	16	6	32k	2.5	127.5
$[C_4C_1TMG][NTf_2]$	25	9.05	100	11.82	3.0	10	2	16k	2	12.09
$[C_4C_1TMG][NTf_2]$	35	7.30	90	11.83	1.8	10	2	16K	2	20.51
$[C_4C_1TMG][NTf_2]$	45	6.12	80	11.99	2.9	10	2	16K	2	32.99
$[C_4C_1TMG][NTf_2]$	55	5.22	70	12.08	3.6	10	2	16K	2	50.95
$[C_4C_1TMG][NTf_2]$	65	4.50	70	12.18	6.4	10	2	16k	2	70.14
$[C_4C_1TMG][NTf_2]$	70	4.49	60	12.18	6.4	10	2	16k	2	81.00

Table S20: Parameters used for the temperature dependent ^{19}F PFGSTE measurements and obtained diffusion coefficients.

Ionic liquid	Temp / °C	p30 / ms	d20 / ms	p1 / µs	d1 / s	sw / ppm	o1p / ppm	TD	AQ / s	D_{s-} / 10^{-12} m^2 s^{-1}
$[C_1HTMG][NTf_2]$	25	8.45	100	19.4	2	7	-80	16k	3	15.70
$[C_1HTMG][NTf_2]$	35	6.36	100	18.5	3.0	7	-80	16k	3	26.96
$[C_1HTMG][NTf_2]$	45	5.51	80	18.0	3.0	7	-80	16k	3	45.09
$[C_1HTMG][NTf_2]$	55	4.45	80	17.8	7.0	7	-80	16k	3	70.76
$[C_1HTMG][NTf_2]$	65	4.24	70	17.8	8.2	7	-80	16k	3	96.96
$[C_1HTMG][NTf_2]$	75	3.80	60	17.5	8.2	7	-80	16k	3	129.1
$[C_1HTMG][TFA]$	25	10.47	100	18	3	6	-76	16k	3.6	10.34
$[C_1HTMG][TFA]$	35	8.51	80	19.25	2.7	6	-76	16k	3.6	19.68
$[C_1HTMG][TFA]$	45	6.88	70	19.3	3.8	6	-76	16k	3.6	34.31
$[C_1HTMG][TFA]$	55	5.82	60	18.4	4.4	6	-76	16k	3.6	55.70
$[C_1HTMG][TFA]$	65	4.73	60	18.2	5.82	6	-76	16k	3.6	84.60
$[C_1HTMG][TFA]$	75	4.09	50	17.87	5.5	6	-76	16k	3.6	126.0
$[C_4C_1TMG][NTf_2]$	25	9.50	100	19	2.5	7	-80	16k	3.1	12.45
$[C_4C_1TMG][NTf_2]$	35	7.7	90	19.6	2.9	7	-80	16k	3.1	21.15
$[C_4C_1TMG][NTf_2]$	45	6.44	80	19.3	4	7	-80	16k	3.1	34.00
$[C_4C_1TMG][NTf_2]$	55	5.54	70	18.9	5	7	-80	16k	3.1	52.70
$[C_4C_1TMG][NTf_2]$	65	5.09	60	18.13	6	7	-80	16k	3.1	71.99
$[C_4C_1TMG][NTf_2]$	70	4.74	60	18.20	7.0	7	-80	16k	3.1	83.90

VFT fitting parameters D_0, B and T_0 following *Equation S9* for the temperature dependent self-diffusion coefficients are given in *Table S21*.

$$D_{Si} = D_{Si,0} \exp\left(\frac{B}{T - T_0}\right) \quad \text{(S9)}$$

The VFT fit was used since it is often applied in the literature to fit the temperature dependent self-diffusion coefficients of ionic liquids. In addition the self-diffusion coefficients were fitted according to Litovitz *Equation S10* due to the comparably small temperature range investigated.

$$D_{Si} = A \exp\left(\frac{B'}{R\,T^3}\right) \quad \text{(S10)}$$

The fitting parameters A and B' are given in *Table S22*. Individual self-diffusion coefficients, their ratios, the calculated Nernst-Einstein parameter Δ_{NE} and ionicity I_{HR} as reciprocal of the Haven ratio H_R and the ionicity I_W obtained from the Walden plot are reported in *Table S23*.

Table S21: VFT fitting parameters $D_{Si,0,}$, B and T_0 for the self-diffusion coefficients of the ionic liquids (cation: i = +; anion: i = -).

Ionic liquid	i	$D_{Si,0}$ / 10^{-7} m^2 s^{-1}	Δ $D_{Si,0}$ / %	B / K	ΔB / %	T_0 / K	ΔT_0 / K	R^2
$[C_1HTMG][NTf_2]$	+	1.052	40.8	-620.7	17.0	199.3	5.5	0.9998
$[C_1HTMG][NTf_2]$	-	0.339	42.6	-409.0	22.0	223.0	5.1	0.9995
$[C_1HTMG][TFA]$	+	30.40	76.6	-1647.8	18.2	136.3	22.4	0.9998
$[C_1HTMG][TFA]$	-	18.88	66.0	-1446.7	16.6	150.3	9.8	0.9999
$[C_4C_1TMG][NTf_2]$	+	0.337	55.1	-488.0	25.6	212.2	6.7	0.9996
$[C_4C_1TMG][NTf_2]$	-	0.376	61.6	-504.0	28.1	210.4	7.6	0.9995

Table S22: Litovitz fitting parameters $A_,$ and $B^{'}$ for the temperature self-diffusion coefficients D_{Si} of the TMG ILs (cation: i = +; anion: i = -).

Ionic liquid	i	A / 10^{-9} m^2 s^{-1}	ΔA / %	B' R^{-1} / 10^6 K^3	ΔB / %	R^2
$[C_1HTMG][NTf_2]$	+	5.05	6.13	-144.8	1.61	0.9994
$[C_1HTMG][NTf_2]$	-	3.91	11.73	-143.4	3.13	0.9977
$[C_1HTMG][TFA]$	+	7.88	5.78	-174.3	1.29	0.9996
$[C_1HTMG][TFA]$	-	8.45	3.37	-177.6	0.74	0.9999
$[C_4C_1TMG][NTf_2]$	+	2.82	9.11	-143.0	2.37	0.9987
$[C_4C_1TMG][NTf_2]$	-	2.93	9.06	-143.3	2.35	0.9988

Table S23: Temperature dependent self-diffusion coefficients of the selected TMG ILs, their ratio D_{s+}/D_{S-}, the calculated Nernst-Einstein deviation parameter Δ_{NE} and ionicity I_{HR} as reciprocal Haven ratio and ionicity I_W obtained from the Walden plot.

Ionic liquid	T/ °C	D_{S+}/ 10^{-12} m^2 s^{-1}	D_{S-}/ 10^{-12} m^2 s^{-1}	D_{s+}/D_{S-}	Δ_{NE}	I_{HR} / H_R^{-1}	I_W
$[C_1HTMG][NTf_2]$	25	20.47	15.70	1.30	0.26	0.74	0.67
$[C_1HTMG][NTf_2]$	35	34.48	26.96	1.28	0.33	0.67	0.64
$[C_1HTMG][NTf_2]$	45	55.72	45.09	1.24	0.42	0.58	0.62
$[C_1HTMG][NTf_2]$	55	86.03	70.76	1.22	0.48	0.52	0.60
$[C_1HTMG][NTf_2]$	65	120.2	96.96	1.24	0.50	0.50	0.59
$[C_1HTMG][NTf_2]$	75	162.3	129.1	1.26	0.52	0.48	0.58
$[C_1HTMG][TFA]$	25	11.03	10.34	1.07	0.51	0.49	0.46
$[C_1HTMG][TFA]$	35	20.67	19.68	1.05	0.55	0.45	0.42
$[C_1HTMG][TFA]$	45	35.64	34.31	1.04	0.60	0.40	0.39
$[C_1HTMG][TFA]$	55	57.27	55.70	1.03	0.63	0.37	0.39
$[C_1HTMG][TFA]$	65	85.32	84.60	1.01	0.66	0.34	0.39
$[C_1HTMG][TFA]$	75	127.5	126.0	1.01	0.69	0.31	0.39
$[C_4C_1TMG][NTf_2]$	25	12.09	12.45	0.97	0.25	0.75	0.64
$[C_4C_1TMG][NTf_2]$	35	20.51	21.15	0.97	0.32	0.68	0.60
$[C_4C_1TMG][NTf_2]$	45	32.99	34.00	0.97	0.37	0.63	0.59
$[C_4C_1TMG][NTf_2]$	55	50.95	52.70	0.97	0.42	0.58	0.58
$[C_4C_1TMG][NTf_2]$	65	70.14	71.99	0.97	0.42	0.58	0.58
$[C_4C_1TMG][NTf_2]$	70	81.00	83.90	0.97	0.42	0.58	0.58

7. Analysis according to the Walden relations

Fitting parameters log(C) and α following the fractional Walden approach (*Equation S11*) are given in *Table S24*.

$$\log \frac{\Lambda_M \text{ mol}}{\text{S cm}^2} = \log C + \alpha \log \frac{0.1 \text{ Pa s}}{\eta} \quad \text{(S11)}$$

Plot for the temperature-dependent progression of ionicity I_W obtained from the Walden plot following *Equation S12* are given in *Table S23* shown in *Figure S7* for the protic ILs and *Figure S8* for the aprotic ILs.

$$I_W(T) = \frac{\Lambda_M}{\Lambda_M^0} = \Lambda_M^{exp}(T) \text{ S}^{-1} \text{ cm}^{-2} \text{ mol} \times \eta^{exp}(T) \text{ 10 Pa}^{-1} \text{ s}^{-1} \quad \text{(S12)}$$

Table S24: Fitting parameters log(C) and α according to the fractional Walden relation.

Ionic liquid	log(C)	Δlog(C) / %	α	α / %	R^2
[HHTMG][BETI]	-0.3145	1.03	0.9402	0.836	0.9999
[C_1HTMG][NTf_2]	-0.1614	1.88	0.9122	0.536	0.9999
[C_1HTMG][BETI]	-0.2839	0.697	0.9204	0.468	0.9999
[C_1HTMG][OTf]	-0.2071	0.748	0.9171	0.405	0.9999
[C_1HTMG][TFA]	-0.3562	2.73	0.9156	2.013	0.9984
[C_4HTMG][NTf_2]	-0.2179	1.30	0.9296	0.531	0.9999
[C_4HTMG][BETI]	-0.2884	0.350	0.9217	0.259	0.9999
[C_4HTMG][OTf]	-0.2865	0.939	0.9151	0.786	0.9998
[C_4HTMG][OMs]	-0.4073	0.940	0.9265	0.730	0.9998
[C_4HTMG][TFA]	-0.5262	0.979	0.9280	1.276	0.9994
[C_4C_1TMG][NTf_2]	-0.1998	3.51	0.9400	1.452	0.9992
[C_4C_1TMG][BETI]	-0.3003	1.08	0.9579	0.339	0.9999
[C_4C_1TMG][TFA]	-0.2945	0.706	0.9700	0.450	0.9991
[C_4C_4TMG][NTf_2]	-0.2546	0.397	0.9336	0.247	0.9999
[C_4C_4TMG][BETI]	-0.3251	0.649	0.9305	0.227	0.9999
[C_4C_4TMG][OTf]	-0.3209	0.686	0.9573	0.615	0.9999
[C_4C_4TMG][OMs]	-0.3682	1.38	0.9543	0.894	0.9997
[C_4C_4TMG][TFA]	-0.3299	0.718	0.9141	0.596	0.9998

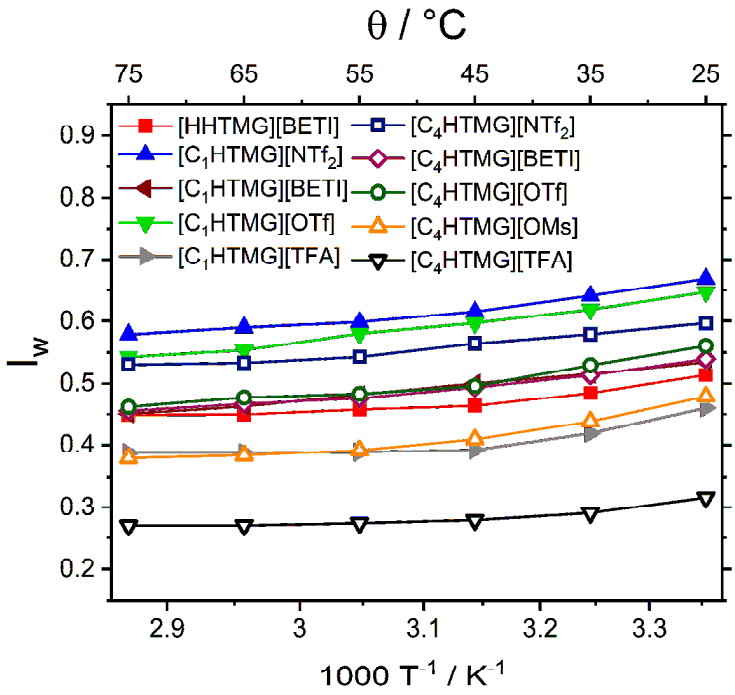

Figure S7: Temperature dependent ionicity I_W obtained from the Walden plot for the protic TMG ILs. Lines are drawn to guide the eyes

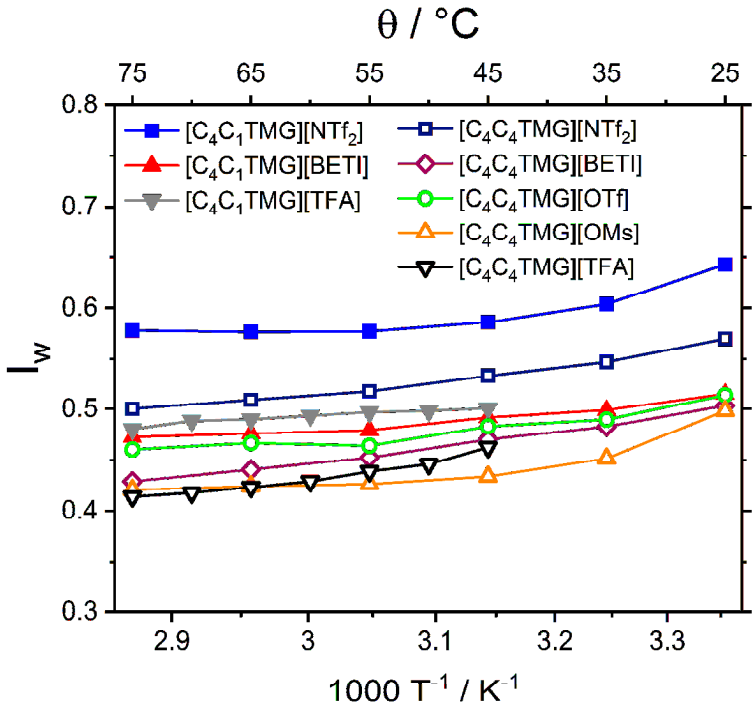

Figure S8: Temperature dependent ionicity I_W obtained from the Walden plot for the aprotic TMG ILs. Lines are drawn to guide the eyes

8. Stokes-Einstein-Sutherland relation, velocity cross correlation and distinct diffusion coefficients

Fitting parameters a and t following *Equation S13* for the Stokes-Einstein-Sutherland (SES) plots for the temperature dependent self-diffusion coefficients are given in *Table S25*.

$$\log (D_{Si}T^{-1}) = a + t \times \log \eta^{-1} \quad \text{(S13)}$$

Table S25: Fitting parameters for the Stokes-Einstein-Sutherland plot of $\log(10^{12}\ D_{si}\ T^{-1}/\ m^2\ s^{-1}\ K^{-1})$ against $\log(Pa\ s\ \eta^{-1})$.

Ionic liquid	i	a	Δ a / %	t	Δt / %	R^2
$[C_1HTMG][NTf_2]$	+	-1.545	1.38	1.173	1.82	0.99947
$[C_1HTMG][NTf_2]$	-	-1.690	2.36	1.202	2.09	0.99826
$[C_1HTMG][TFA]$	+	-1.504	2.85	1.125	2.61	0.99729
$[C_1HTMG][TFA]$	-	-1.559	2.76	1.154	2.55	0.99742
$[C_4C_1TMG][NTf_2]$	+	-1.535	1.22	1.107	1.16	0.99932
$[C_4C_1TMG][NTf_2]$	-	-1.524	1.27	1.108	1.20	0.99942

The calculated velocity cross correlation coefficients f_{+-} and distinct diffusion coefficients D_{ij}^d (*Equations S14-S18*) as well as the Nernst-Einstein parameters Δ_{NE} and ionicity I_W obtained from the Walden approach for the temperature dependent measurements are given in *Table S26*.

$$D_{+-}^d = -\frac{2RT\Lambda_M}{F^2}\ \frac{M_+M_-}{M^2} \quad \text{(S14)}$$

$$D_{++}^d = \frac{2RT\Lambda_M}{F^2}\ \frac{M_-^2}{M^2} - 2D_{S+} \quad \text{(S15)}$$

$$D_{--}^d = \frac{2RT\Lambda_M}{F^2}\ \frac{M_+^2}{M^2} - 2D_{S-} \quad \text{(S16)}$$

$$f_{ij} = \frac{D_{ij}^d M}{2\rho} \quad \text{(S17)}$$

With M_+, M_- and M the molar mass of cation, anion and the ionic liquid. Fitting parameters of the analogous SES plots for the temperature dependent distinct diffusion coefficients following *Equation S18* are given in *Table 27*.

$$\log (-D_{ij}^d T^{-1}) = a + t \times \log \eta^{-1} \quad \text{(S18)}$$

Table S26: Velocity cross correlations f_{ij}, distinct diffusion coefficients D_{ij}^{d}, Nernst-Einstein parameter Δ_{NE} and ionicity I_W obtained from the Walden plot for the temperature dependent measurements.

Ionic liquid	Temp / °C	f_{+-} [a]	f_{++} [a]	f_{--} [a]	D_{+-}^{d} [b]	D_{++}^{d} [b]	D_{--}^{d} [b]	Δ_{NE}	I_W
$[C_1HTMG][NTf_2]$	25	-1.64	-2.25	-3.68	-11.61	-15.96	-26.01	0.259	0.669
$[C_1HTMG][NTf_2]$	35	-2.52	-4.40	-6.50	-17.69	-30.88	-45.69	0.332	0.641
$[C_1HTMG][NTf_2]$	45	-3.66	-8.10	-11.23	-25.56	-56.45	-78.31	0.423	0.615
$[C_1HTMG][NTf_2]$	55	-5.10	-13.86	-18.06	-35.34	-96.03	-125.1	0.481	0.583
$[C_1HTMG][NTf_2]$	65	-6.85	-20.18	-25.00	-47.15	-138.87	-172.0	0.497	0.590
$[C_1HTMG][NTf_2]$	75	-8.93	-28.28	-33.62	-61.05	-193.28	-229.8	0.517	0.579
$[C_1HTMG][TFA]$	25	-0.52	-1.75	-1.46	-5.22	-17.53	-14.65	0.509	0.460
$[C_1HTMG][TFA]$	35	-0.90	-3.37	-2.92	-8.96	-33.56	-29.04	0.554	0.419
$[C_1HTMG][TFA]$	45	-1.40	-5.99	-5.33	-13.84	-59.27	-52.68	0.602	0.392
$[C_1HTMG][TFA]$	55	-2.10	-9.84	-8.92	-20.64	-96.62	-87.63	0.633	0.388
$[C_1HTMG][TFA]$	65	-2.97	-14.92	-13.93	-28.94	-145.52	-135.9	0.658	0.387
$[C_1HTMG][TFA]$	75	-4.03	-22.82	-21.37	-39.07	-220.99	-206.9	0.69	0.387
$[C_4C_1TMG][NTf_2]$	25	-1.54	-1.91	-3.32	-8.82	-10.93	-19.04	0.252	0.643
$[C_4C_1TMG][NTf_2]$	35	-2.40	-3.60	-5.84	-13.65	-20.50	-33.22	0.317	0.604
$[C_4C_1TMG][NTf_2]$	45	-3.58	-6.29	-9.65	-20.22	-35.58	-54.54	0.371	0.586
$[C_4C_1TMG][NTf_2]$	55	-5.12	-10.46	-15.38	-28.72	-58.73	-86.30	0.423	0.577
$[C_4C_1TMG][NTf_2]$	65	-7.07	-14.52	-21.11	-39.42	-81.01	-117.8	0.422	0.577
$[C_4C_1TMG][NTf_2]$	70	-8.19	-16.85	-24.76	-45.49	-93.61	-137.6	0.417	0.576

[a] velocity cross correlation f_{ij} given in 10^{-15} m^5 mol^{-1} s^{-1}; [b] Distinct diffusion coefficients D_{ij}^{d} given in 10^{-12} m^2 s^{-1}.

Table S27: Fitting parameters for the Stokes-Einstein-Sutherland plot of $\log(10^{12} \cdot D_{ij}^{d} \cdot T^{-1} / m^2 s^{-1} K^{-1})$ against $\log(Pa\ s\ \eta^{-1})$.

Ionic liquid	i	j	a	Δ a / %	t	Δt / %	R^2
$[C_1HTMG][NTf_2]$	+	-	-1.487	0.42	0.913	0.44	0.9999
$[C_1HTMG][NTf_2]$	+	+	-1.957	2.57	1.438	2.20	0.9981
$[C_1HTMG][NTf_2]$	-	-	-1.523	3.12	1.248	2.40	0.9989
$[C_1HTMG][TFA]$	+	-	-1.624	1.66	0.916	2.01	0.9984
$[C_1HTMG][TFA]$	+	+	-1.343	3.28	1.168	2.58	0.9974
$[C_1HTMG][TFA]$	-	-	-1.476	2.93	1.226	2.41	0.9977
$[C_4C_1TMG][NTf_2]$	+	-	-1.502	1.22	0.935	1.34	0.9993
$[C_4C_1TMG][NTf_2]$	+	+	-1.732	2.43	1.264	2.28	0.9979
$[C_4C_1TMG][NTf_2]$	-	-	-1.383	1.82	1.153	1.50	0.9991

9. NMR spectra of the TMG ILs

9.1 NMR spectra of the [HHTMG] ILs

9.1.1 NMR spectra of [HHTMG][NTf_2]

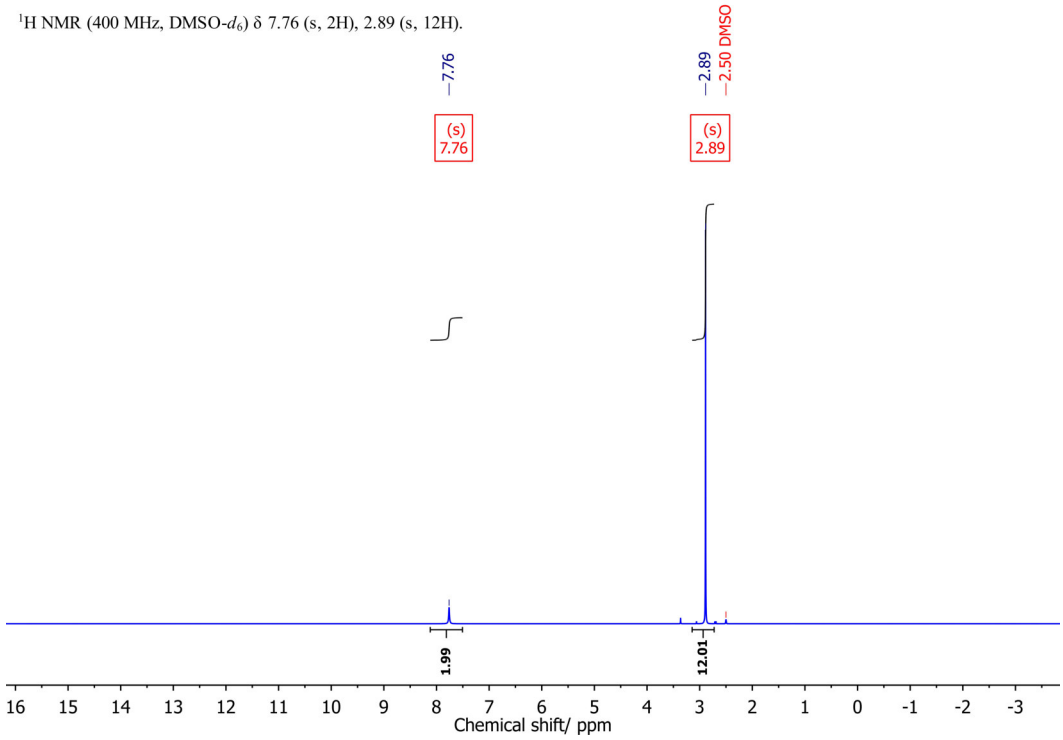

Figure S9: ^{1}H NMR spectra of [HHTMG][NTf_2].

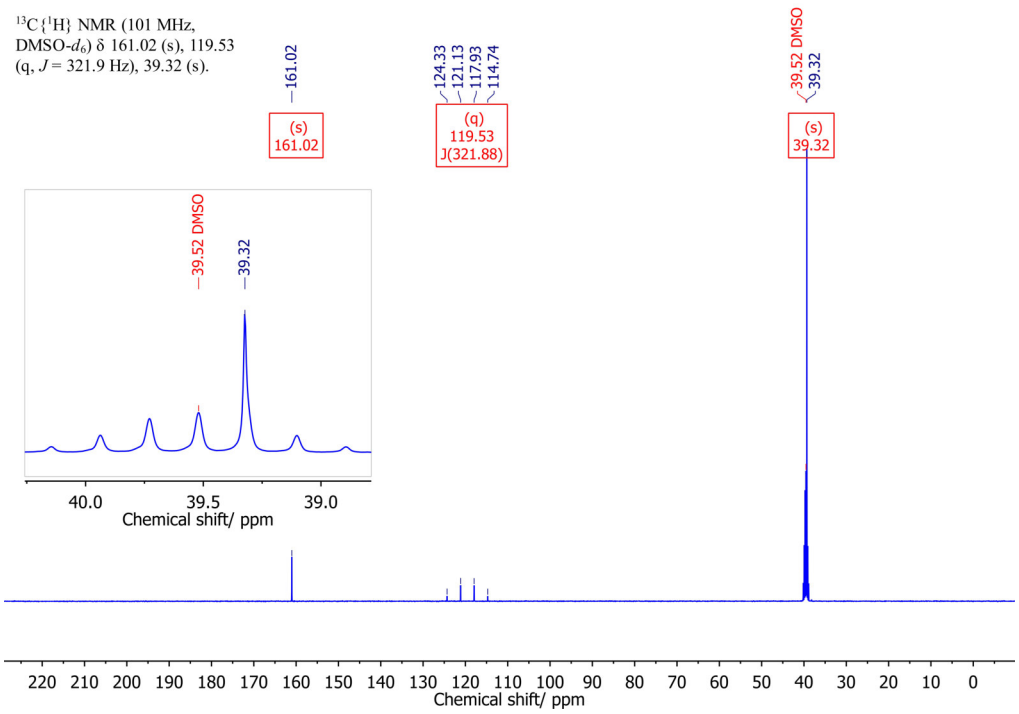

Figure S10: $^{13}C\{^1H\}$ NMR spectra of [HHTMG][NTf_2].

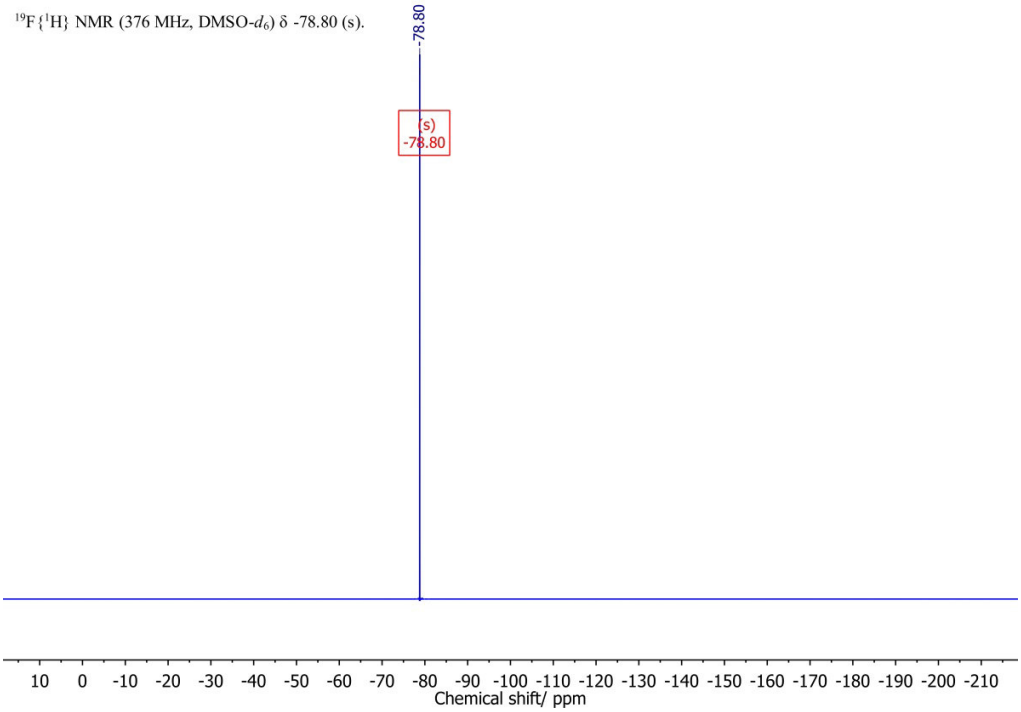

Figure S11: $^{19}F\{^1H\}$ NMR spectra of [HHTMG][NTf_2].

9.1.2 NMR spectra of [HHTMG][BETI]

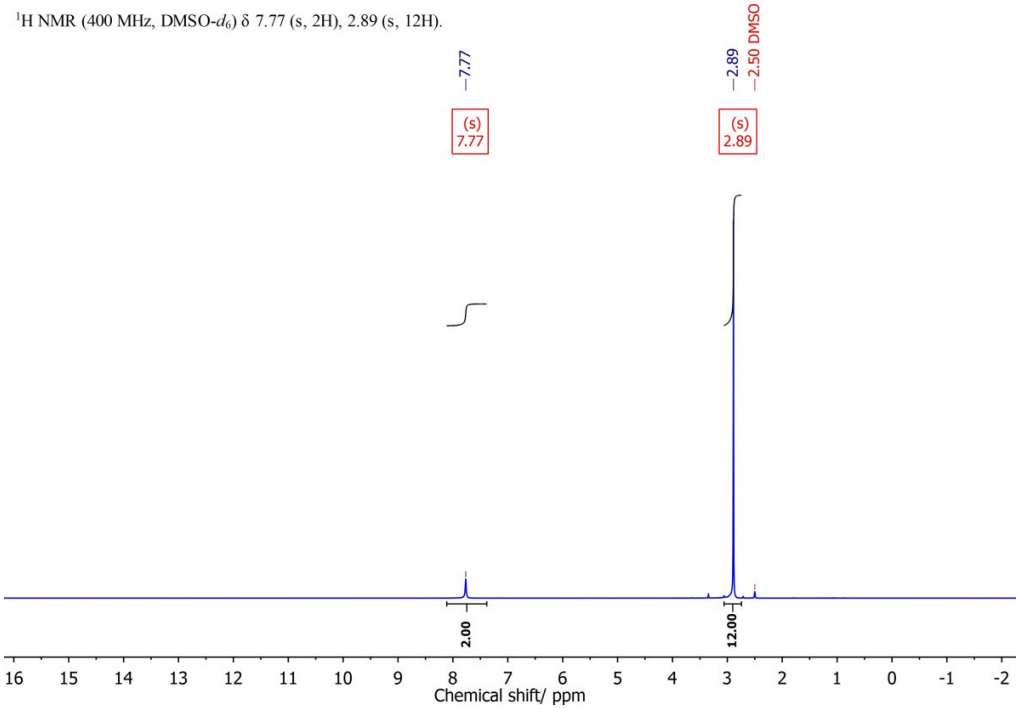

Figure S12: ^{1}H NMR spectra of [HHTMG][BETI].

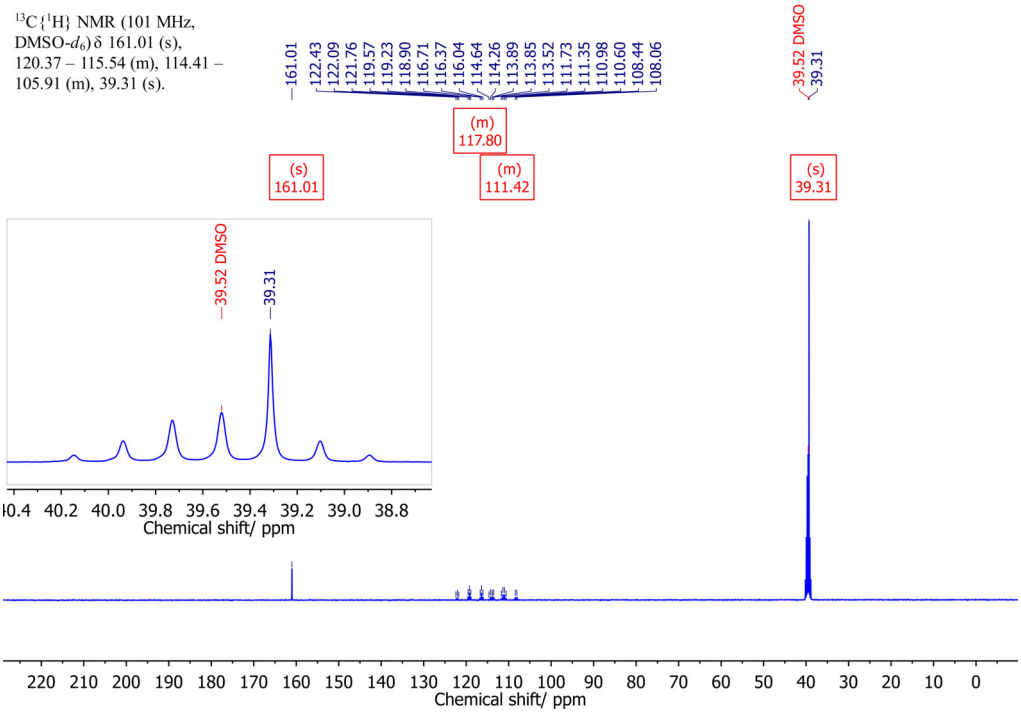

Figure S13: ^{13}C{^{1}H} NMR spectra of [HHTMG][BETI].

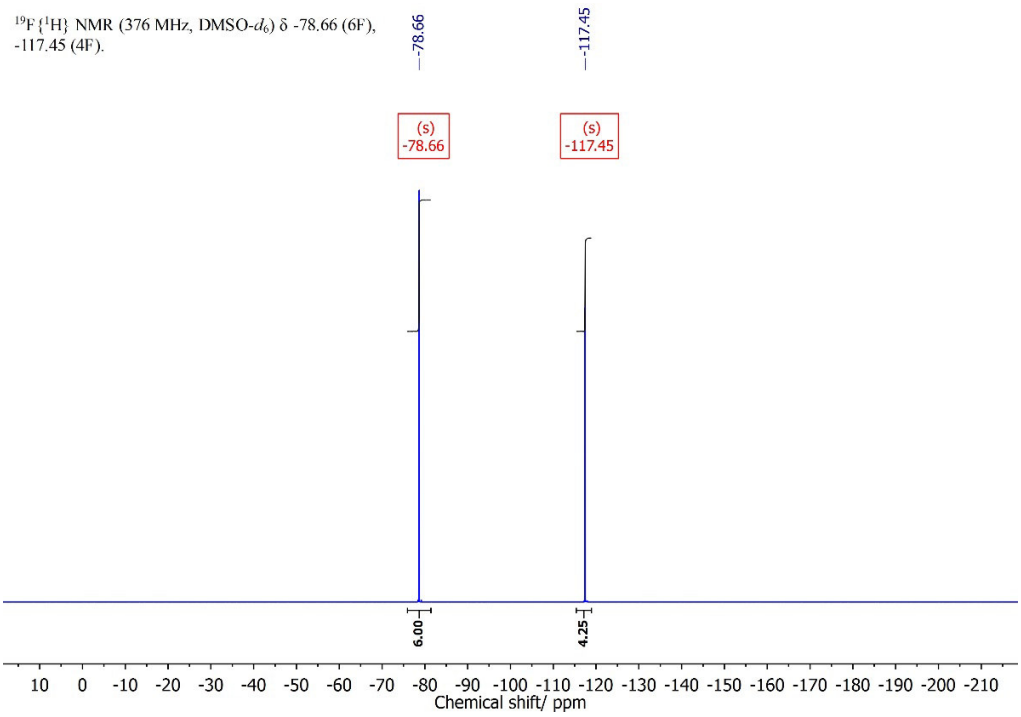

Figure S14: $^{19}F\{^{1}H\}$ NMR spectra of [HHTMG][NTf_2].

9.1.3 NMR spectra of [HHTMG][OTf]

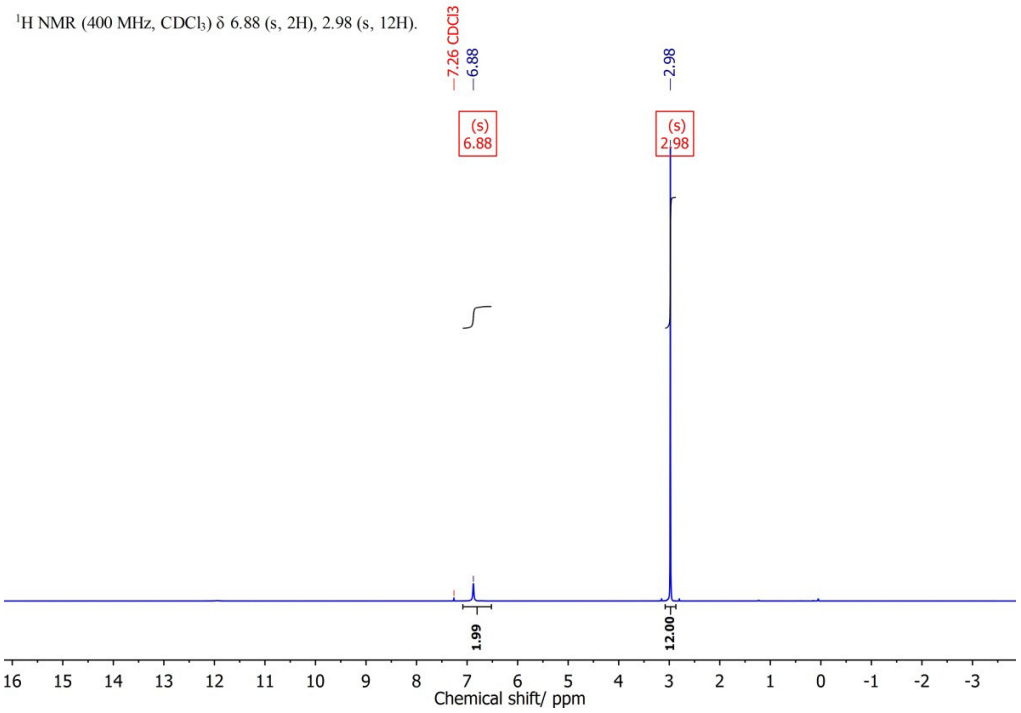

Figure S15: ^{1}H NMR spectra of [HHTMG][OTf].

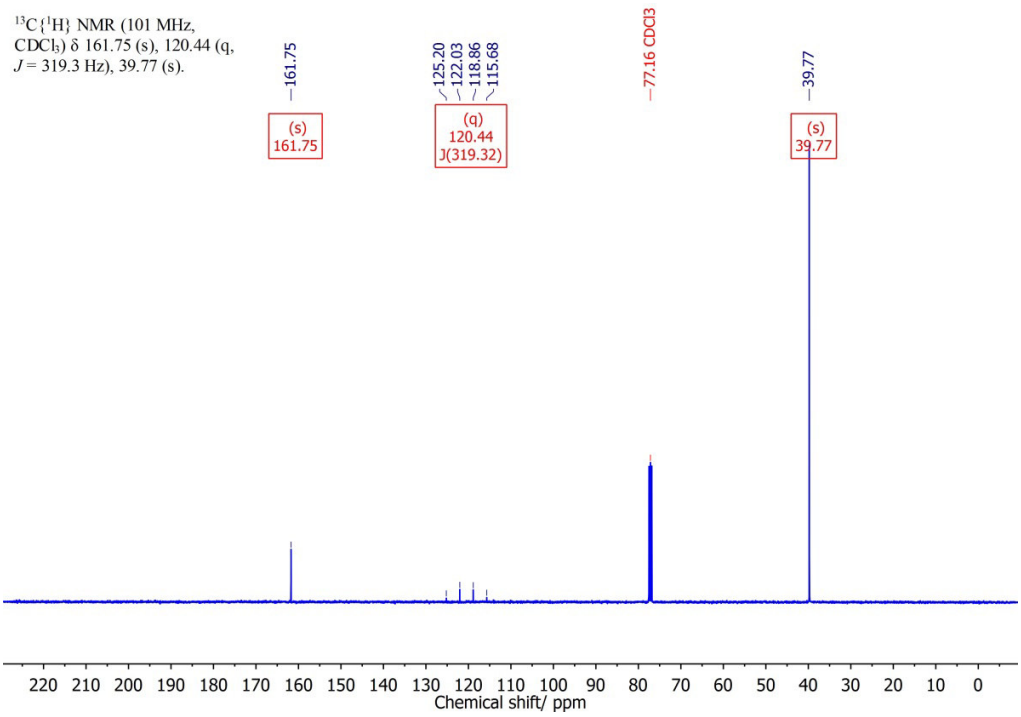

Figure S16: $^{13}C\{^{1}H\}$ NMR spectra of [HHTMG][OTf].

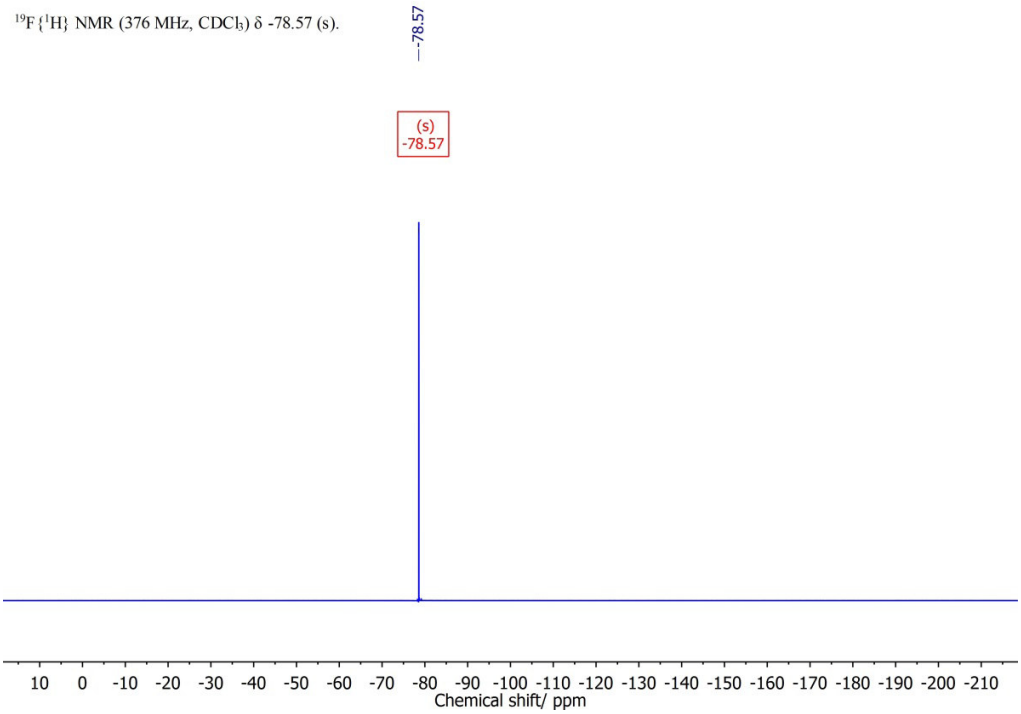

Figure S17: $^{19}F\{^{1}H\}$ NMR spectra of [HHTMG][OTf].

9.1.4 NMR spectra of [HHTMG][OMs]

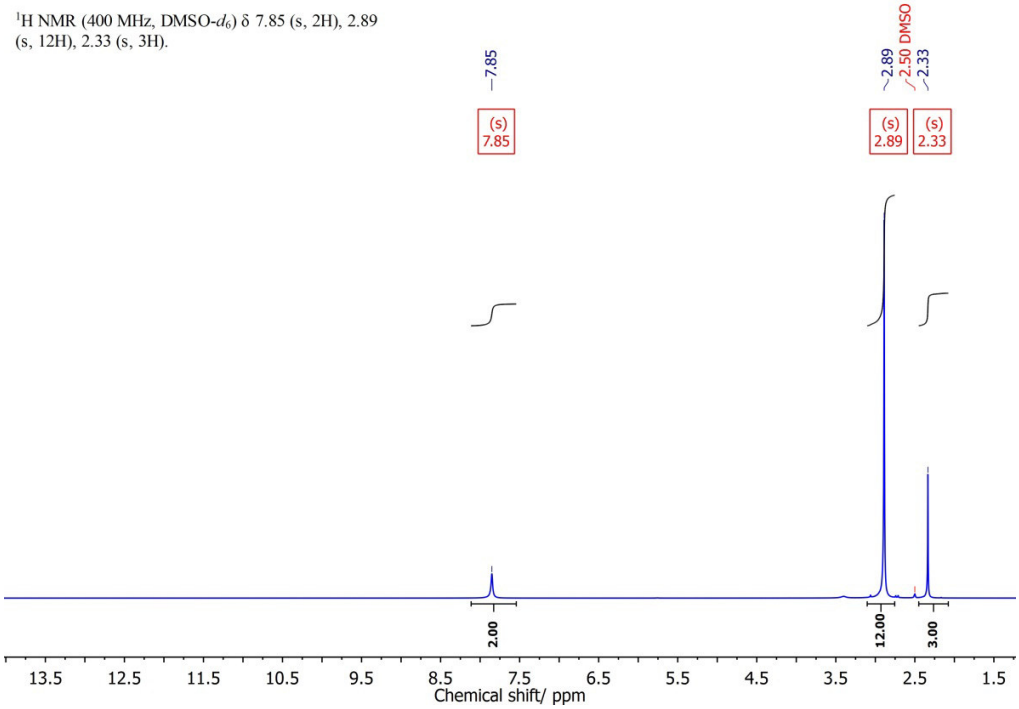

Figure S18: ^{1}H NMR spectra of [HHTMG][OMs].

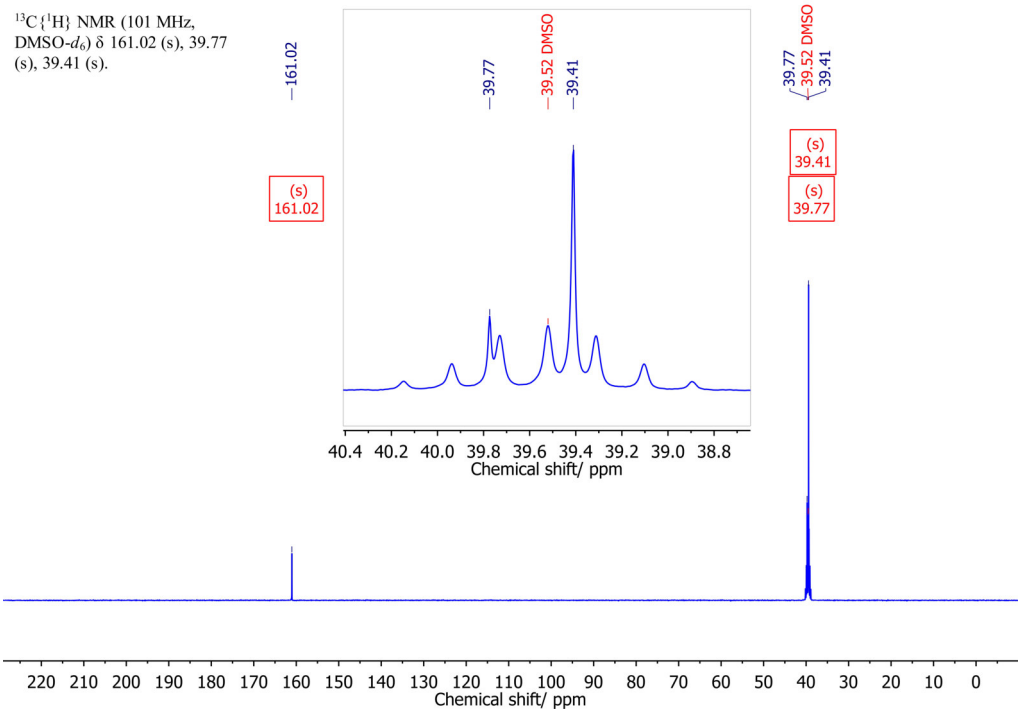

Figure S19: ^{13}C{^{1}H} NMR spectra of [HHTMG][OMs].

9.1.5 NMR spectra of [HHTMG][TFA]

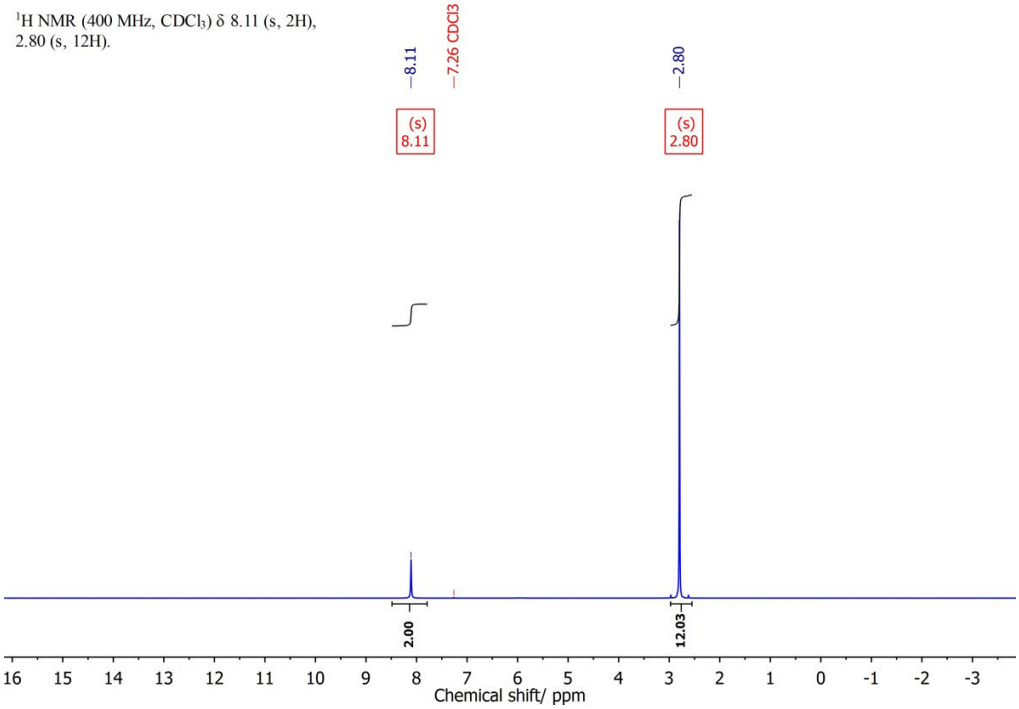

Figure S20: ^{1}H NMR spectra of [HHTMG][TFA].

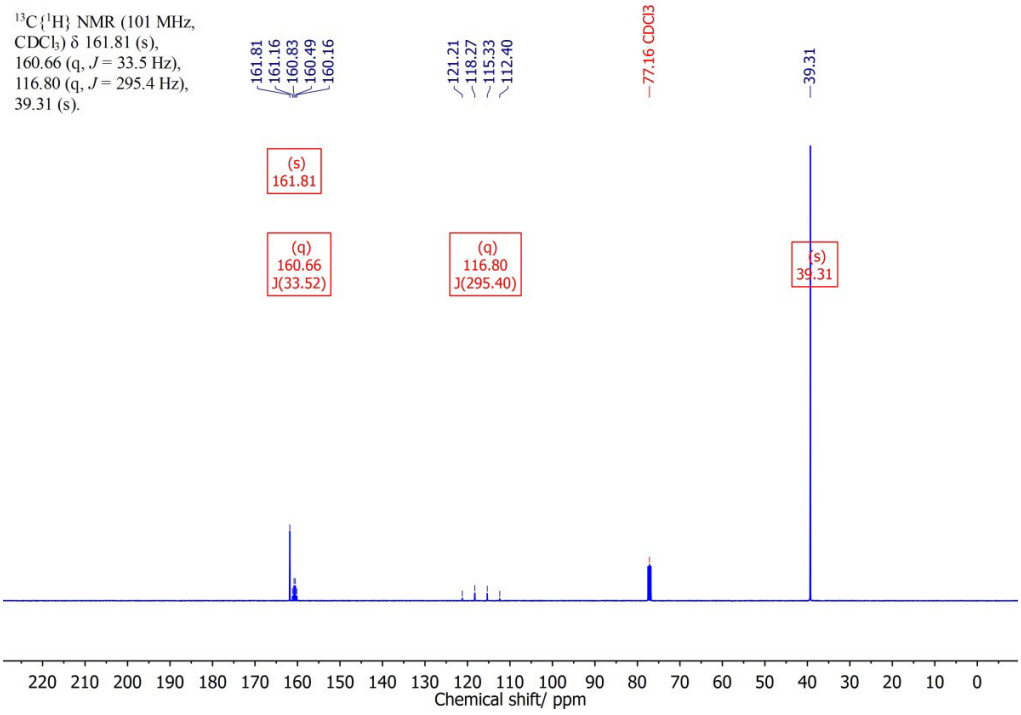

Figure S21: ^{13}C{^{1}H} NMR spectra of [HHTMG][TFA].

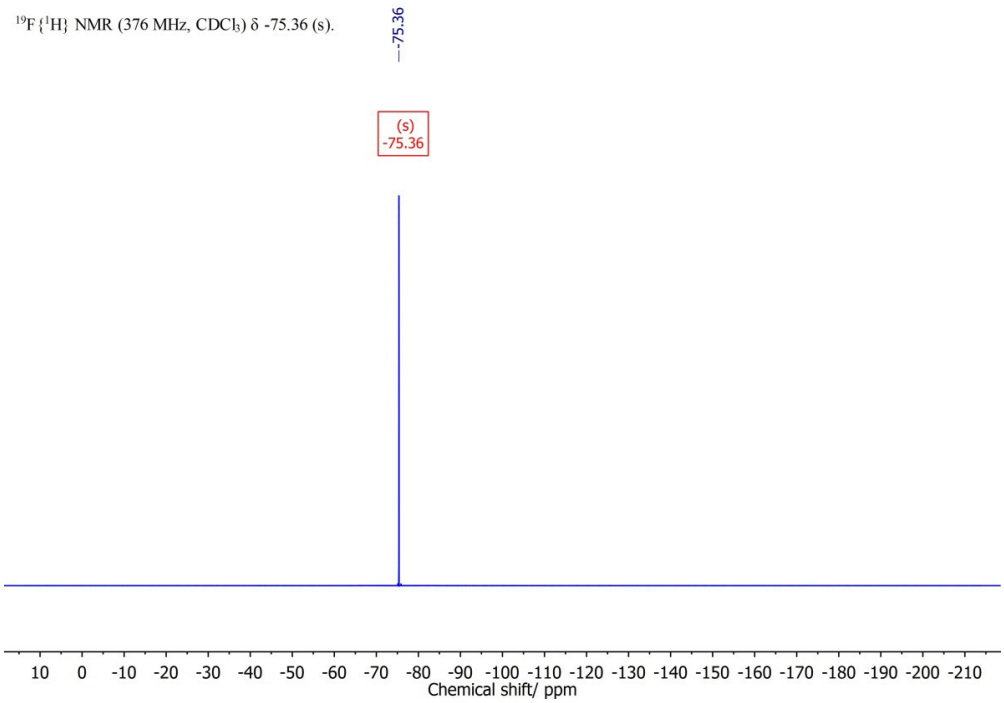

Figure S22: ^{19}F{^{1}H} NMR spectra of [HHTMG][TFA].

9.2 NMR spectra of the intermediates

9.2.1 NMR spectra of chloro-N,N,N′,N′-tetramethylguanidinium chloride.

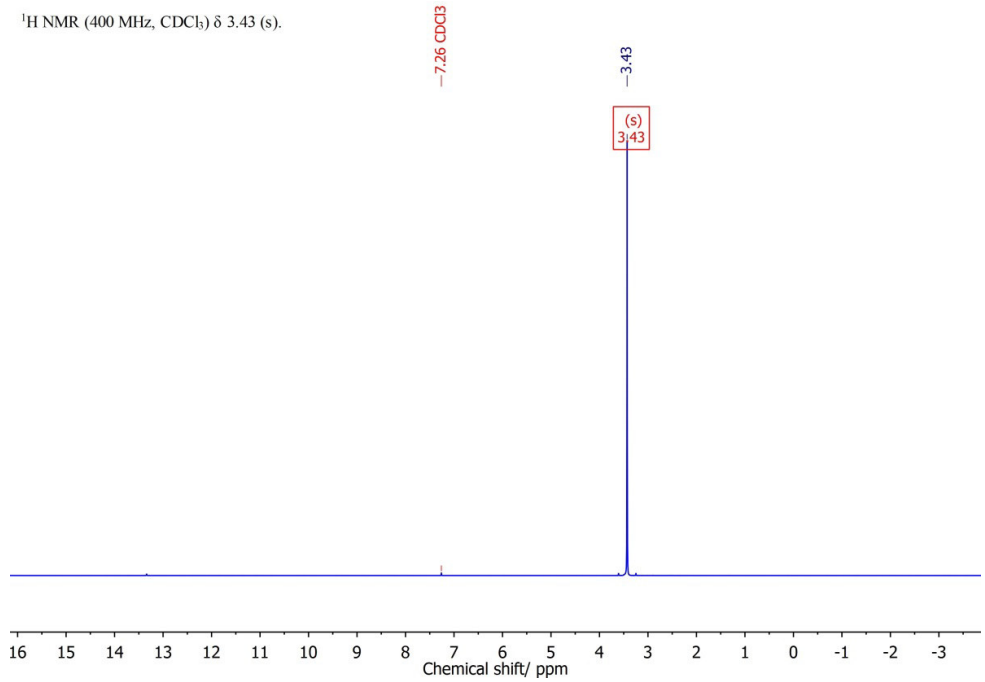

Figure S23: ^{1}H NMR spectra of chloro-N,N,N′,N′-tetramethylformamidinium chloride.

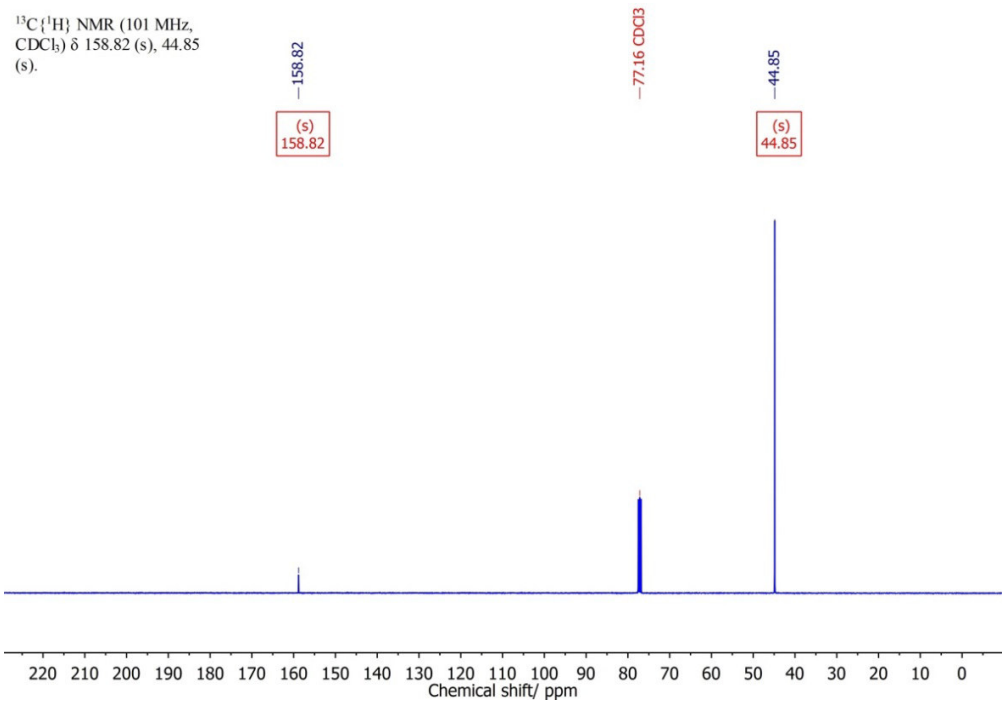

Figure S24: $^{13}C\{^{1}H\}$ NMR spectra of chloro-N,N,N′,N′-tetramethylformamidinium chloride.

9.2.2 NMR spectra of pentamethylguanidine

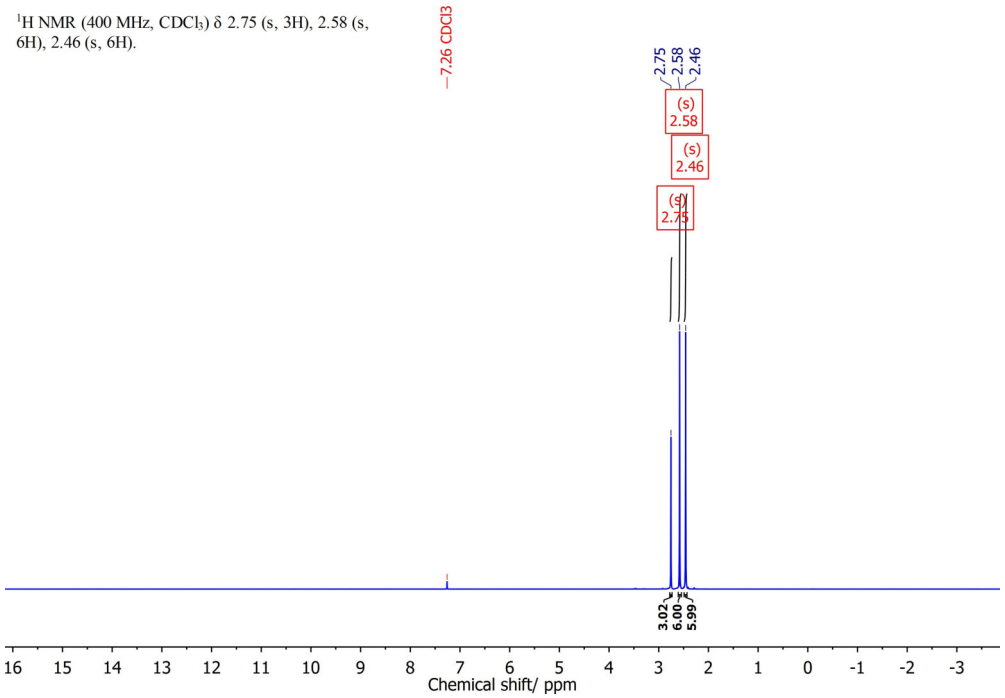

Figure S25: ^{1}H NMR spectra of pentamethylguanidine.

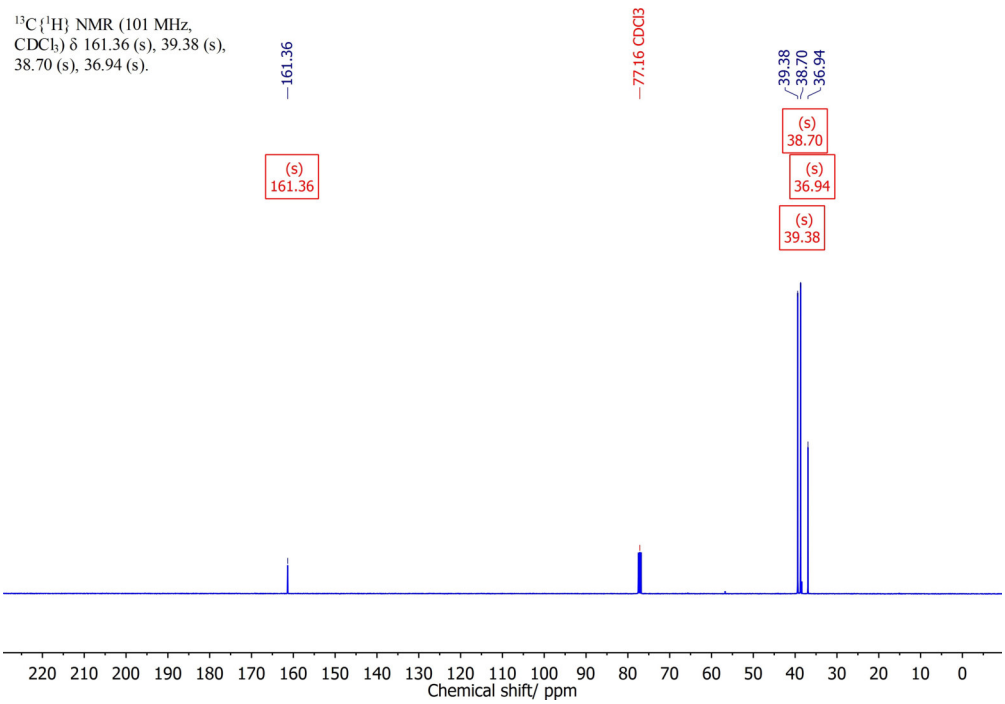

Figure S26: $^{13}C\{^{1}H\}$ NMR spectra of pentamethylguanidine.

9.2.3 NMR spectra of 2-butyl-1,1,3,3-tetramethylguanidine

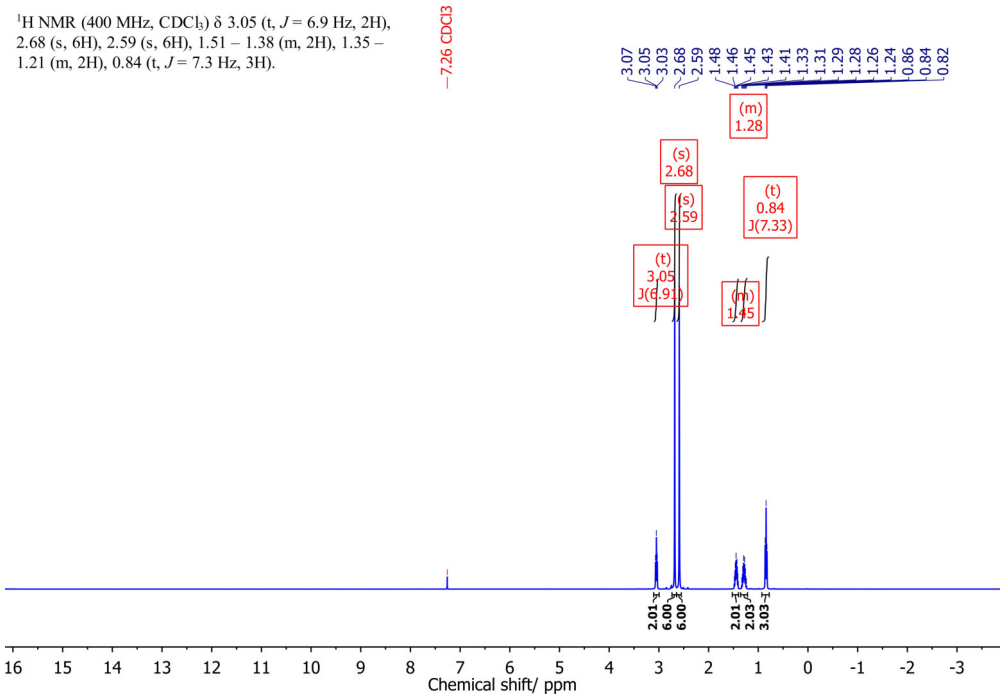

Figure S27: ^{1}H NMR spectra of 2-butyl-1,1,3,3-tetramethylguanidine.

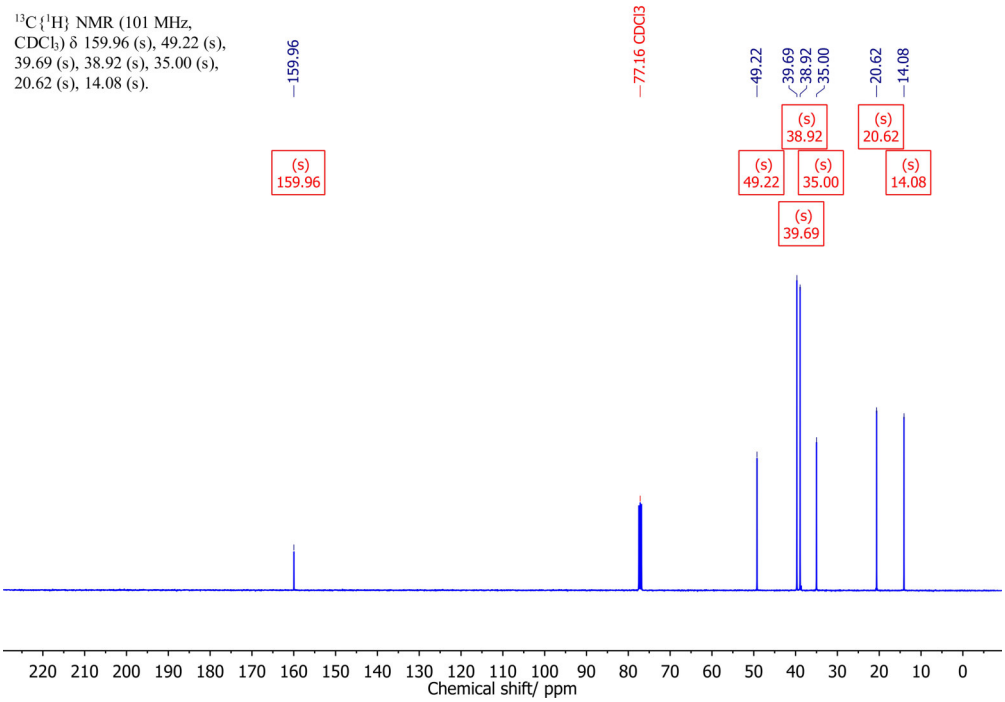

Figure S28: $^{13}C\{^{1}H\}$ NMR spectra of 2-butyl-1,1,3,3-tetramethylguanidine.

9.2.4 NMR spectra of 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide

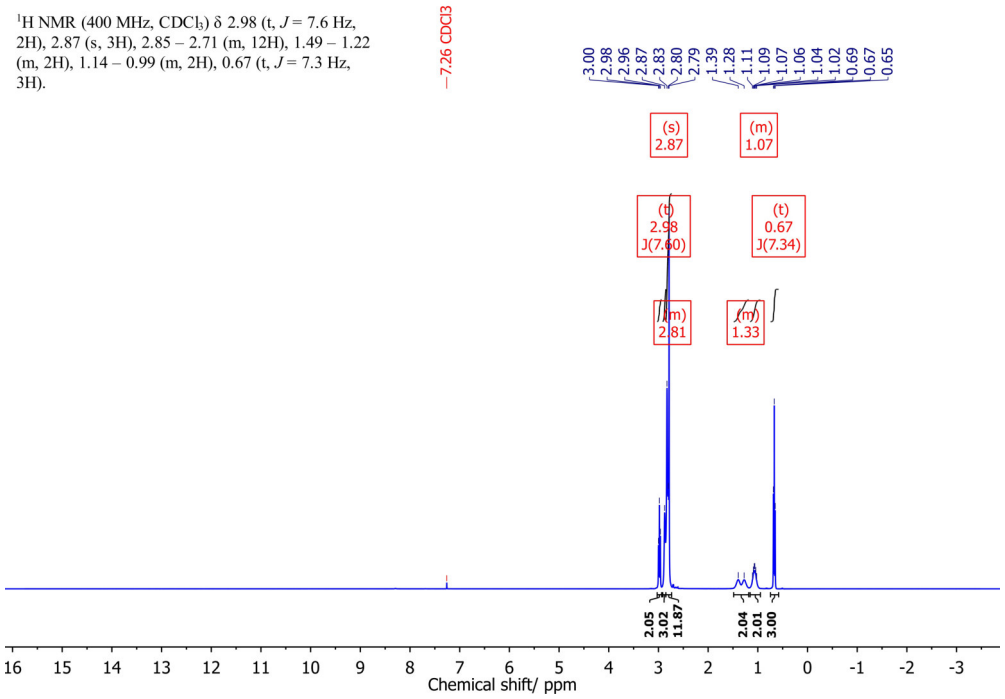

Figure S29: ^{1}H NMR spectra of 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide.

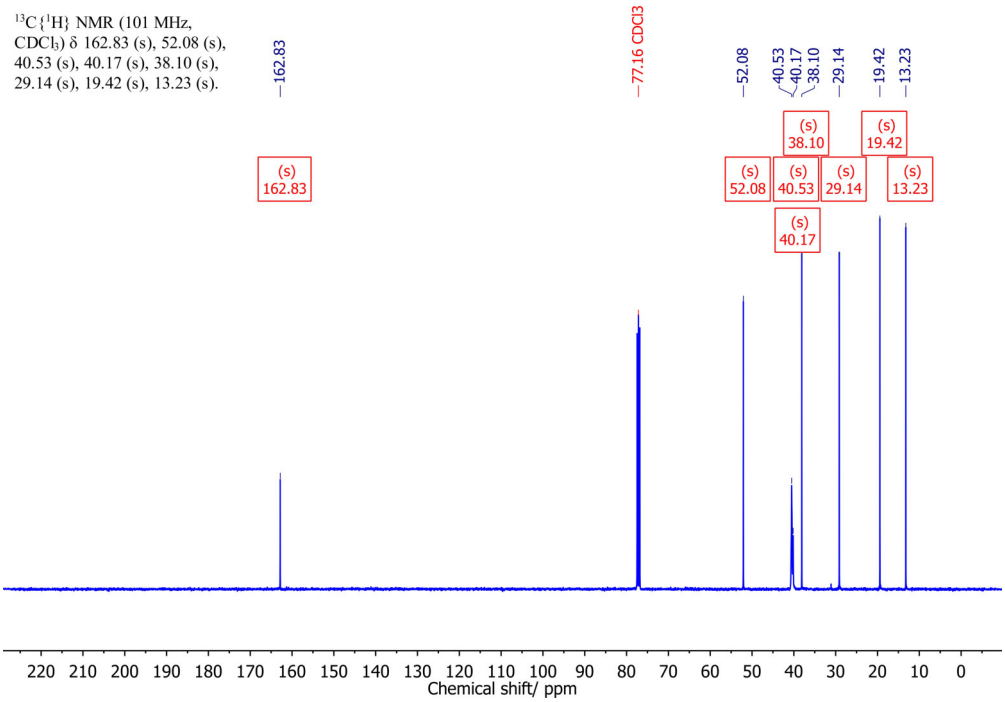

Figure S30: $^{13}C\{^{1}H\}$ NMR spectra of 2-butyl-1,1,2,3,3-pentamethylguanidinium bromide.

9.2.5 NMR spectra of 2,2-dibutyl-1,1,3,3-tetramethylguanidinium bromide

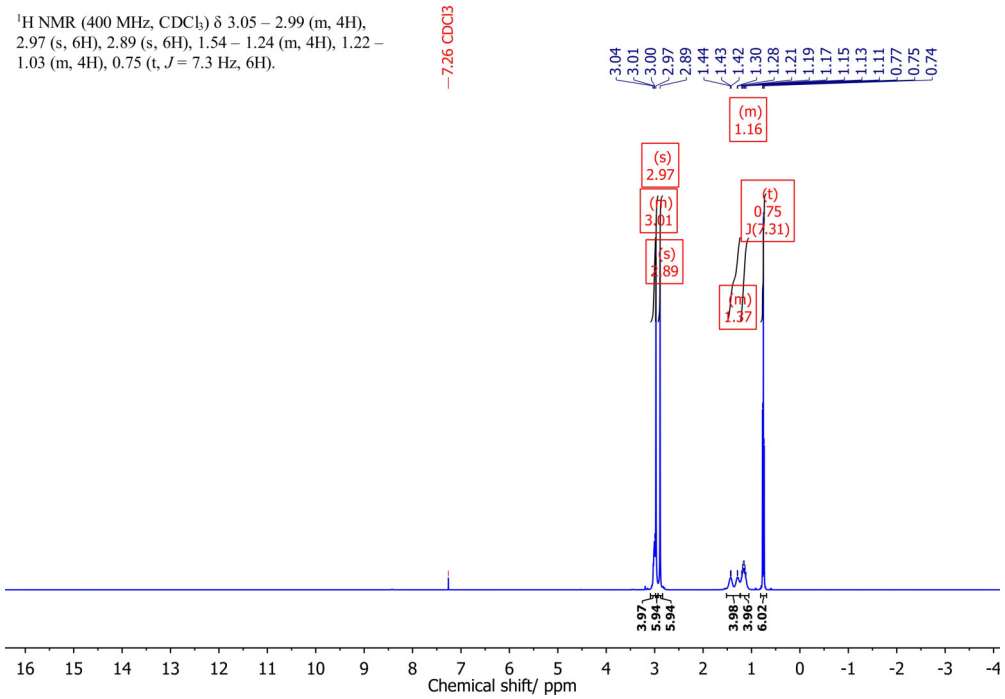

Figure S31: ^{1}H NMR spectra of 2,2-dibutyl-1,1,3,3-tetramethylguanidinium bromide.

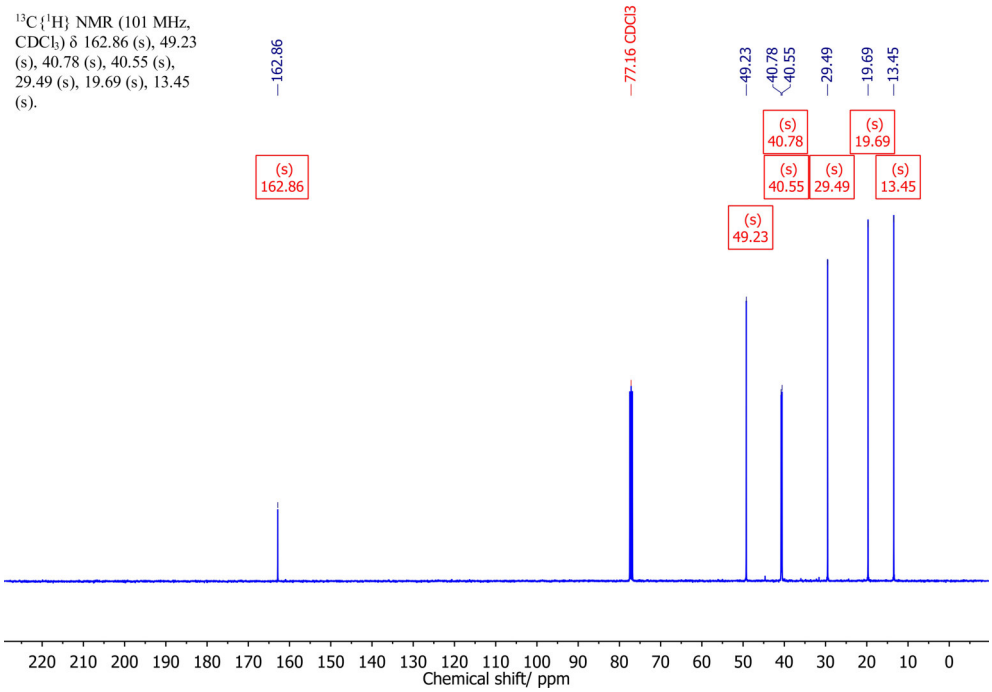

Figure S32: $^{13}C\{^{1}H\}$ NMR spectra of 2,2-dibutyl-1,1,3,3-tetramethylguanidinium bromide.

9.3 NMR spectra of the [C_1HTMG] ionic liquids

9.3.1 NMR spectra of [C_1HTMG][NTf_2]

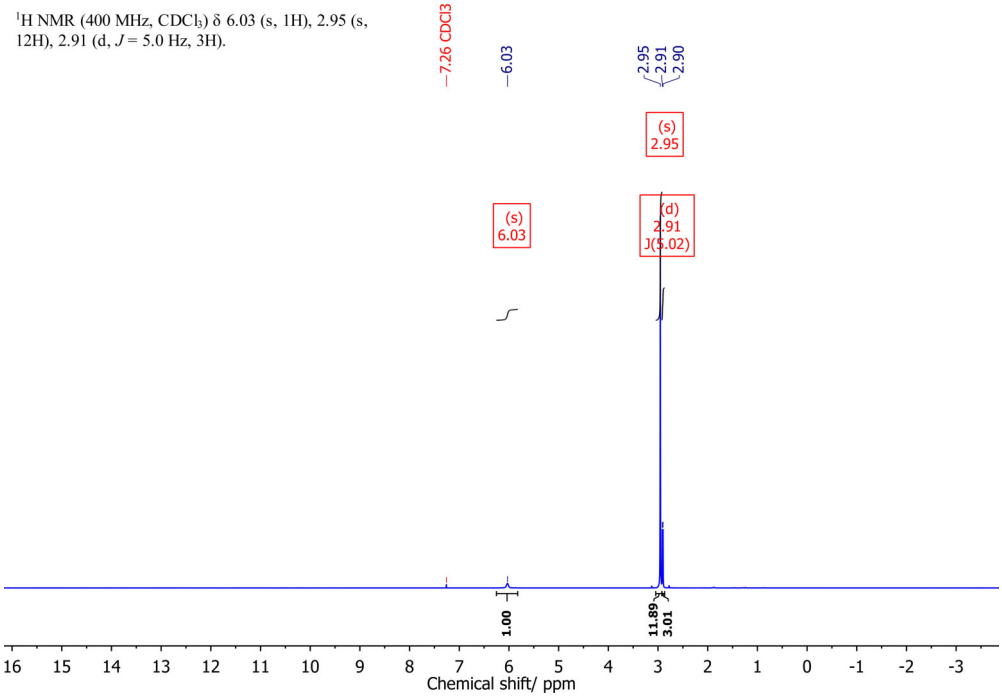

Figure S33: ^{1}H NMR spectra of [C_1HTMG][NTf_2].

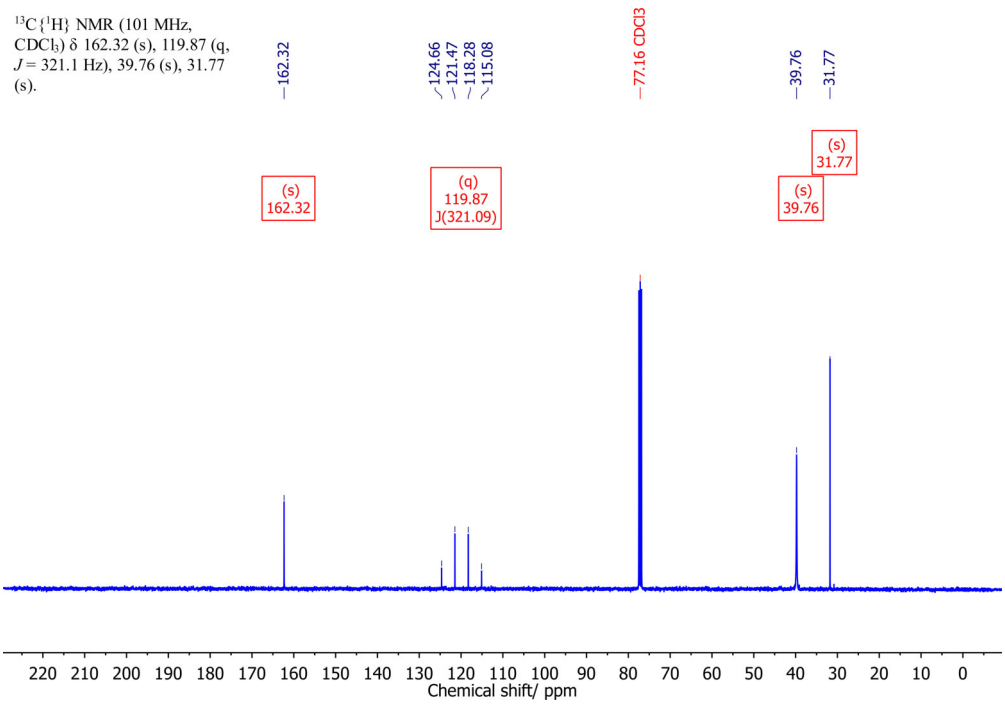

Figure S34: $^{13}C\{^{1}H\}$ NMR spectra of $[C_1HTMG][NTf_2]$.

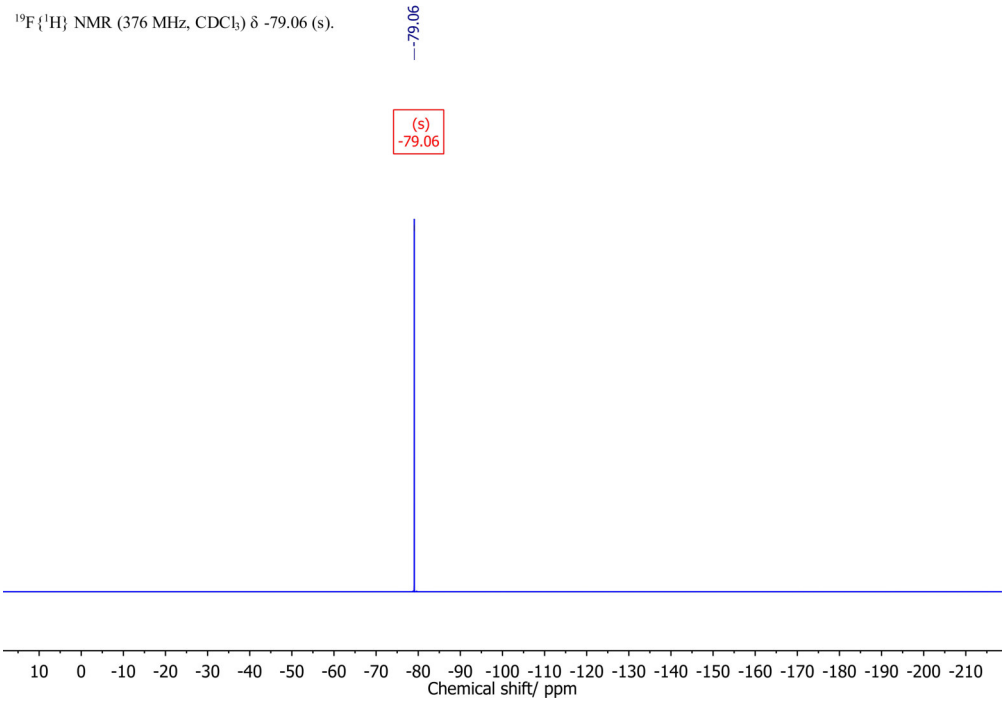

Figure S35: $^{19}F\{^{1}H\}$ NMR spectra of $[C_1HTMG][NTf_2]$.

9.3.2 NMR spectra of [C_1HTMG][BETI]

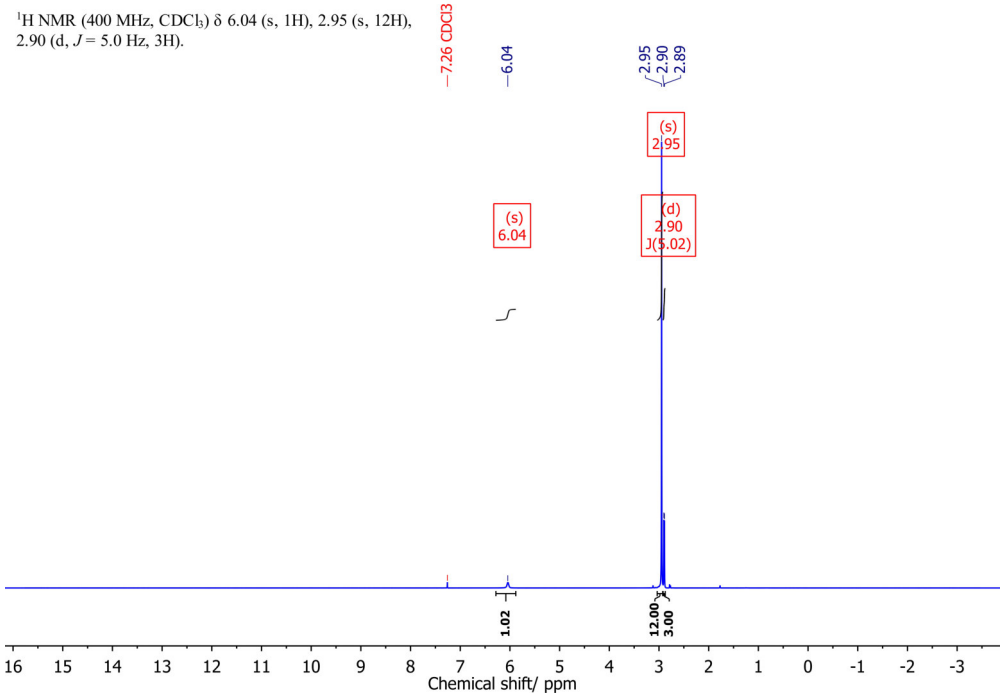

Figure S36: ^{1}H NMR spectra of [C_1HTMG][BETI].

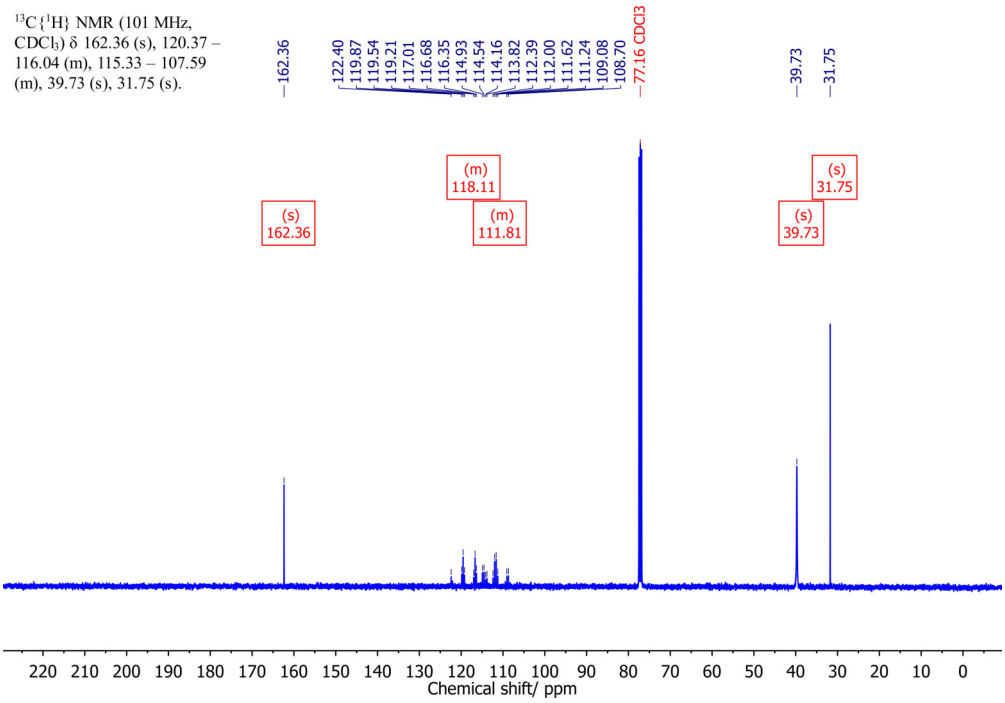

Figure S37: ^{13}C{^{1}H} NMR spectra of [C_1HTMG][BETI].

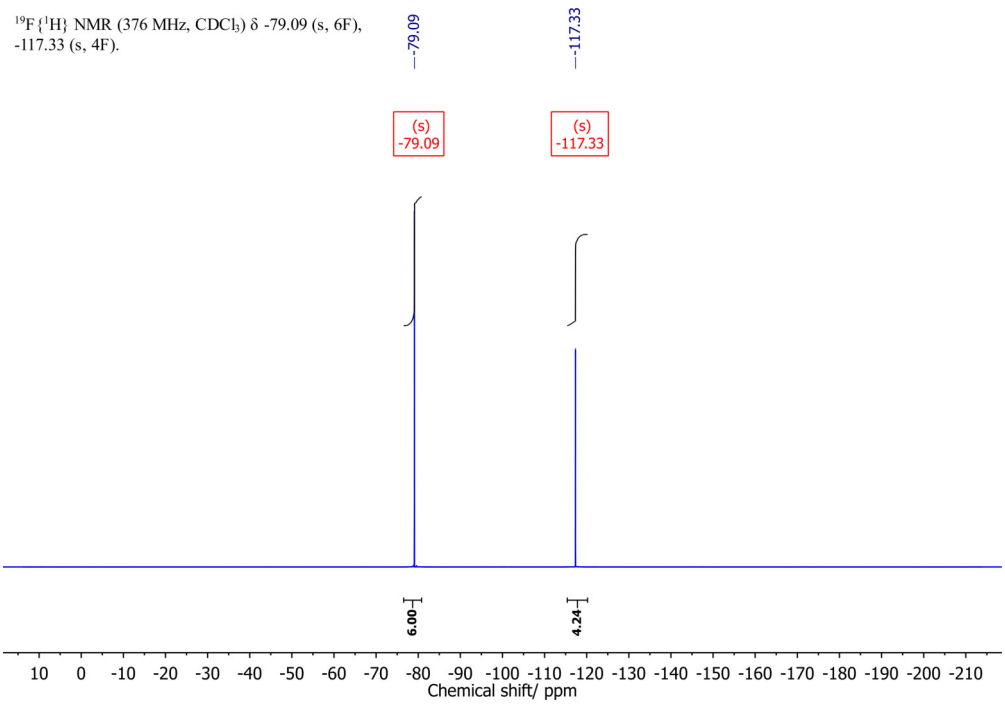

Figure S38: $^{19}F\{^{1}H\}$ NMR spectra of [C_1HTMG][BETI].

9.3.3 NMR spectra of [C_1HTMG][OTf]

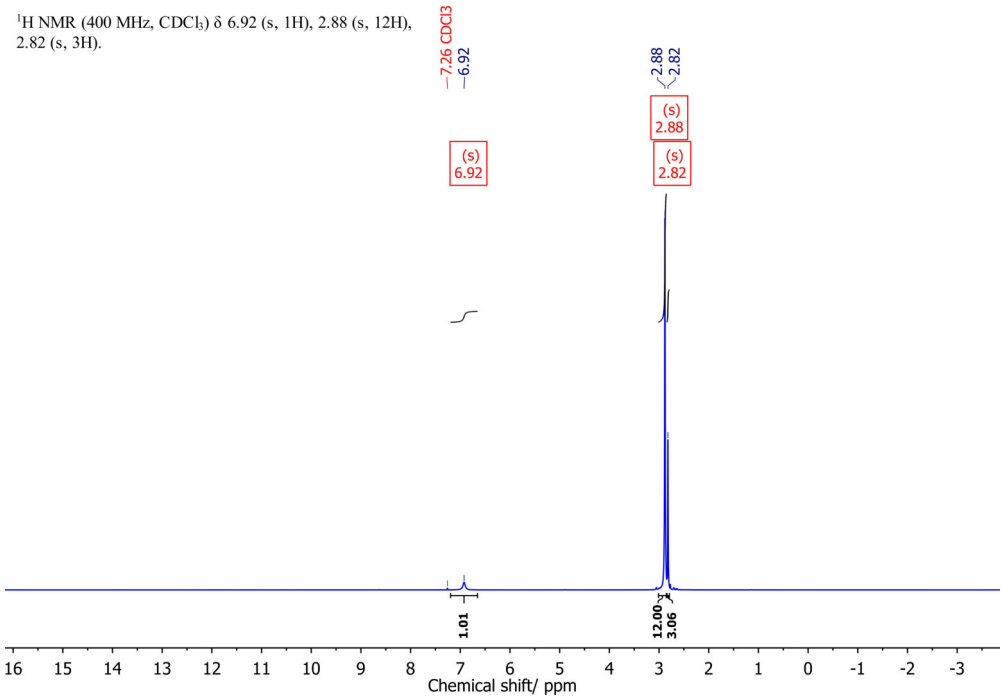

Figure S39: ^{1}H NMR spectra of [C_1HTMG][OTf].

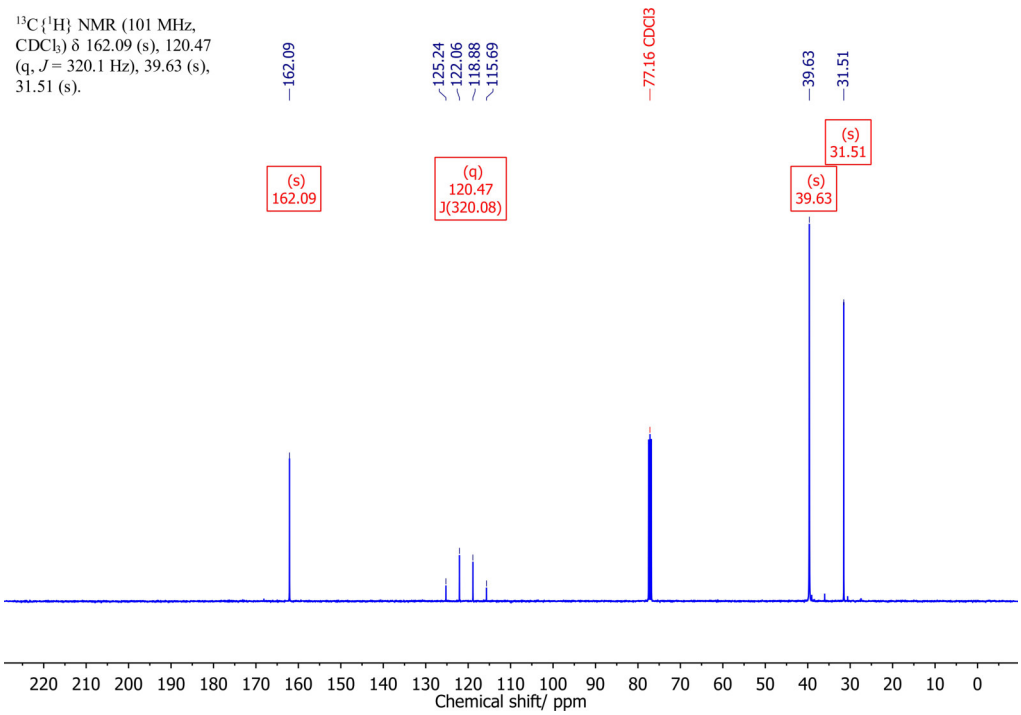

Figure S40: $^{13}C\{^{1}H\}$ NMR spectra of [C_1HTMG][OTf].

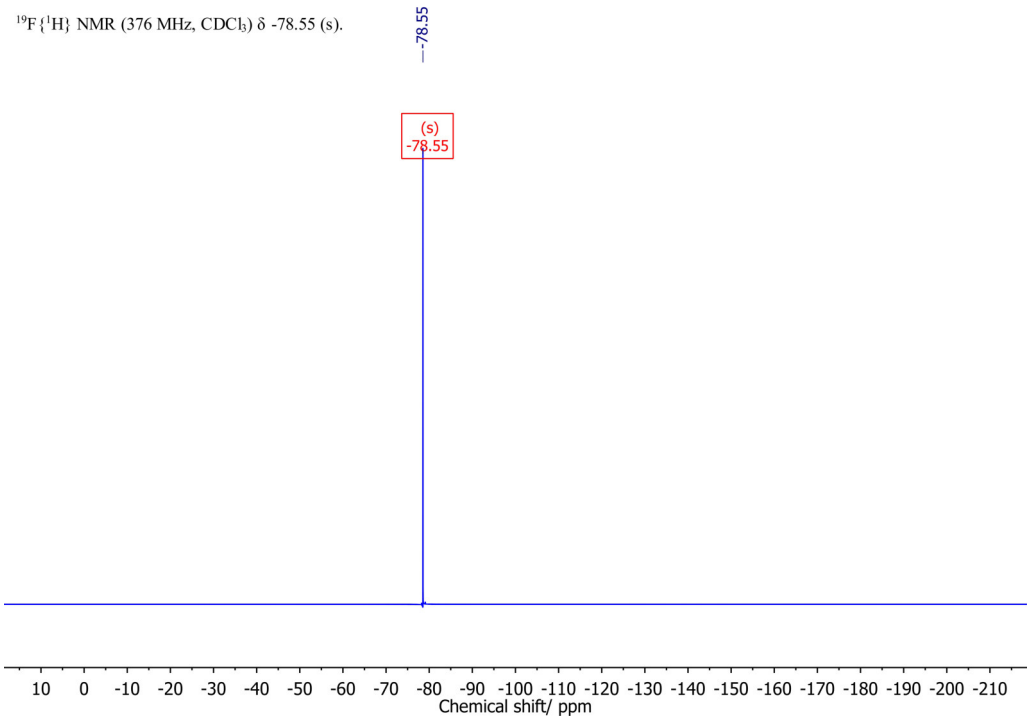

Figure S41: $^{19}F\{^{1}H\}$ NMR spectra of [C_1HTMG][OTf].

9.3.4 NMR spectra of [C_1HTMG][OMs]

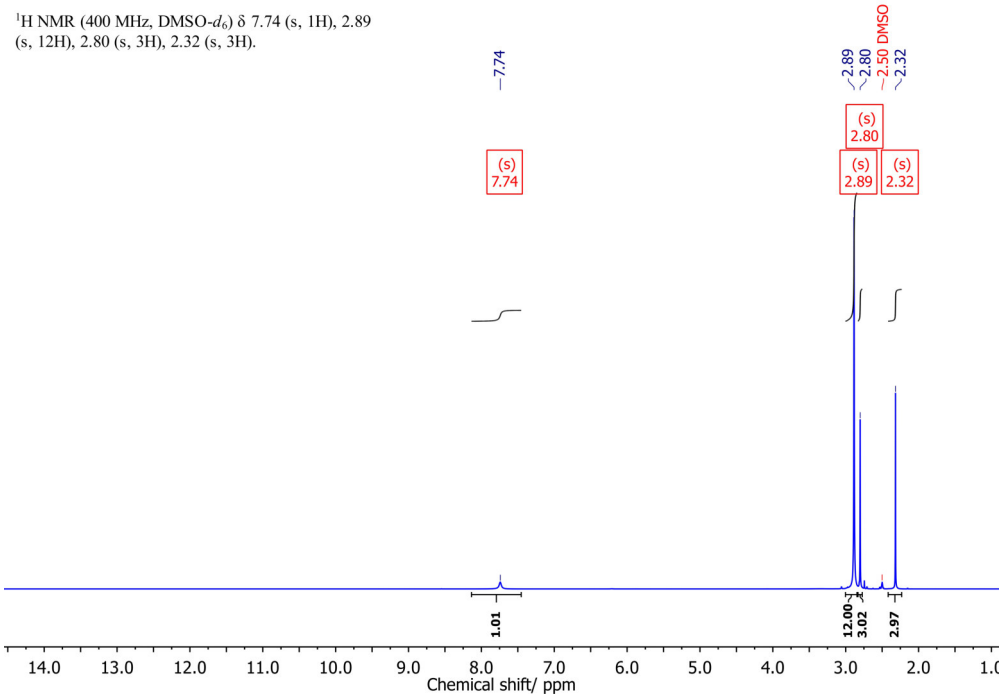

Figure S42: ^{1}H NMR spectra of [C_1HTMG][OMs].

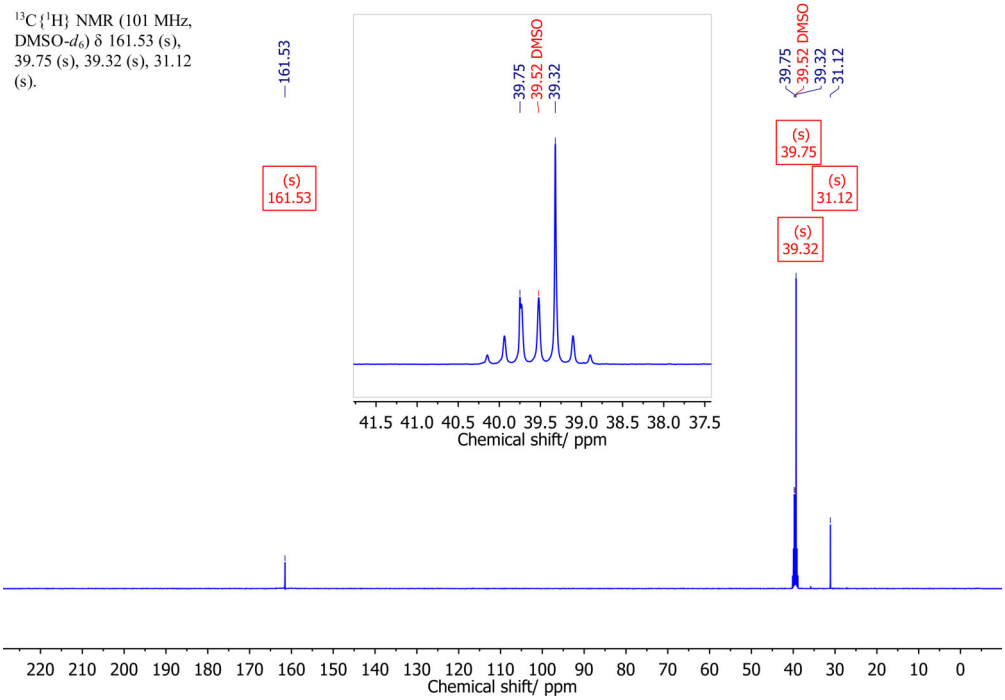

Figure S43: ^{13}C{^{1}H} NMR spectra of [C_1HTMG][OMs].

9.3.5 NMR spectra of [C_1HTMG][TFA]

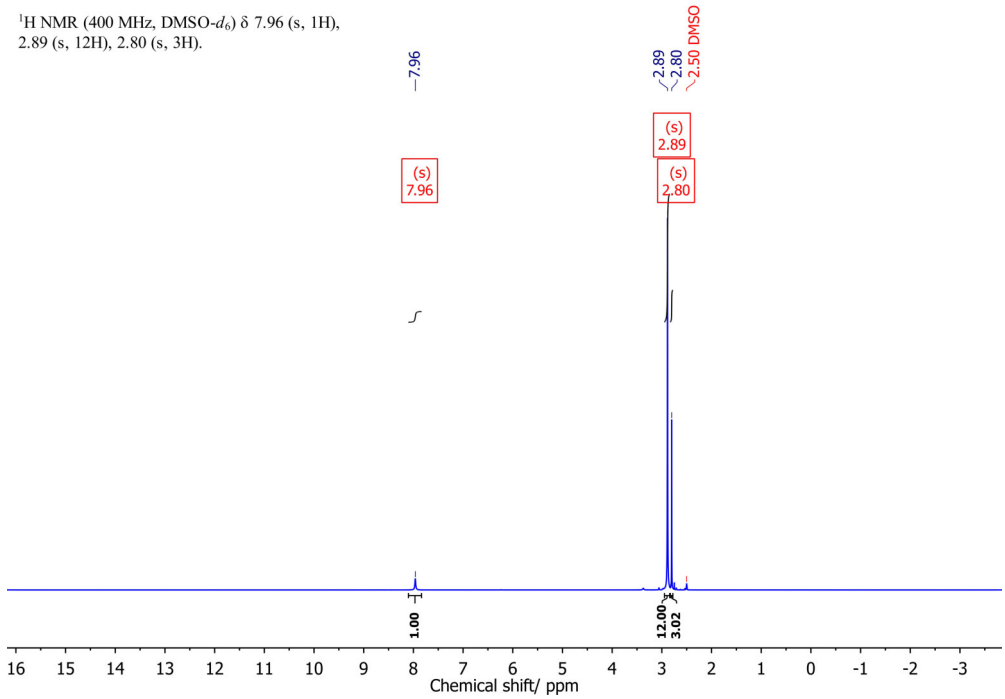

Figure S44: ^{1}H NMR spectra of [C_1HTMG][TFA].

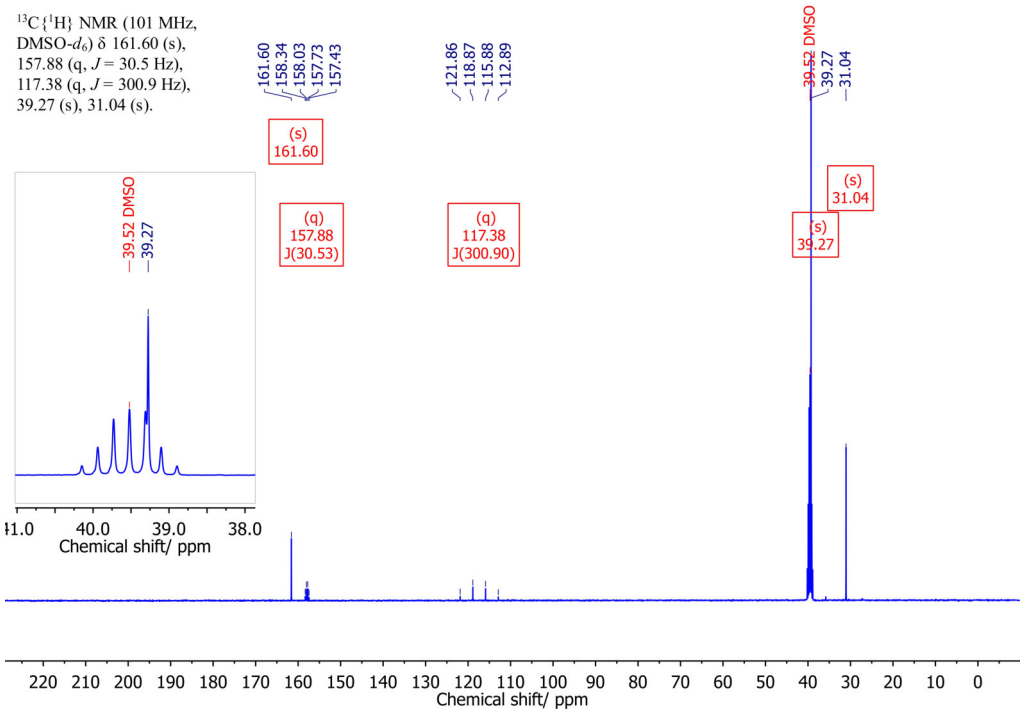

Figure S45: ^{13}C{^{1}H} NMR spectra of [C_1HTMG][TFA].

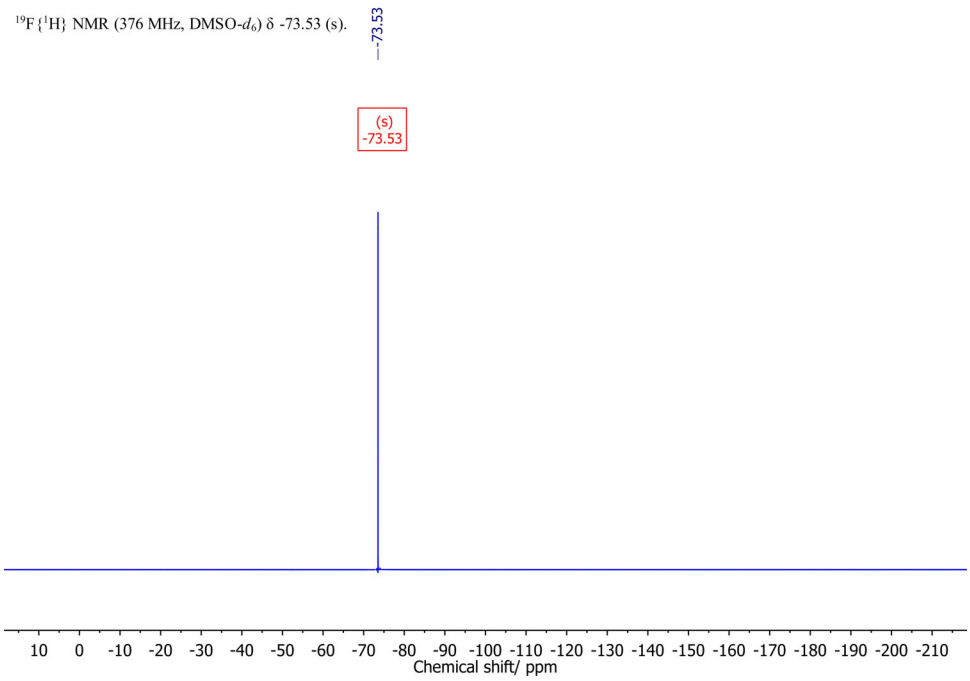

Figure S46: $^{19}F\{^{1}H\}$ NMR spectra of $[C_1HTMG][TFA]$.

9.4 NMR spectra of the $[C_4HTMG]$ ionic liquids

9.4.1 NMR spectra of $[C_4HTMG][NTf_2]$

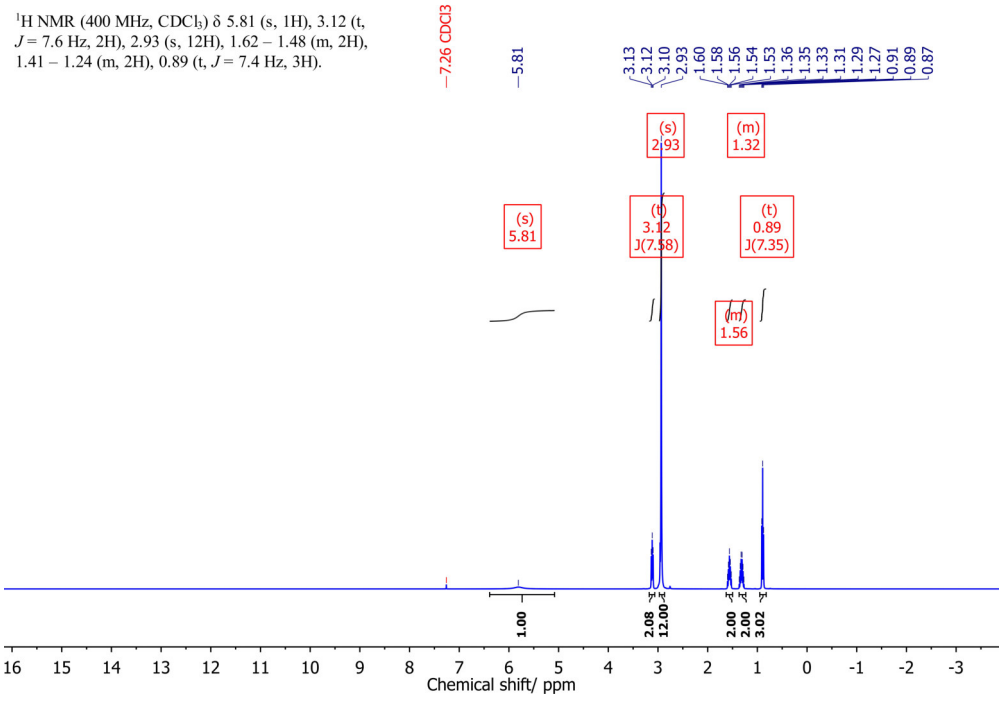

Figure S47: ^{1}H NMR spectra of $[C_4HTMG][NTf_2]$.

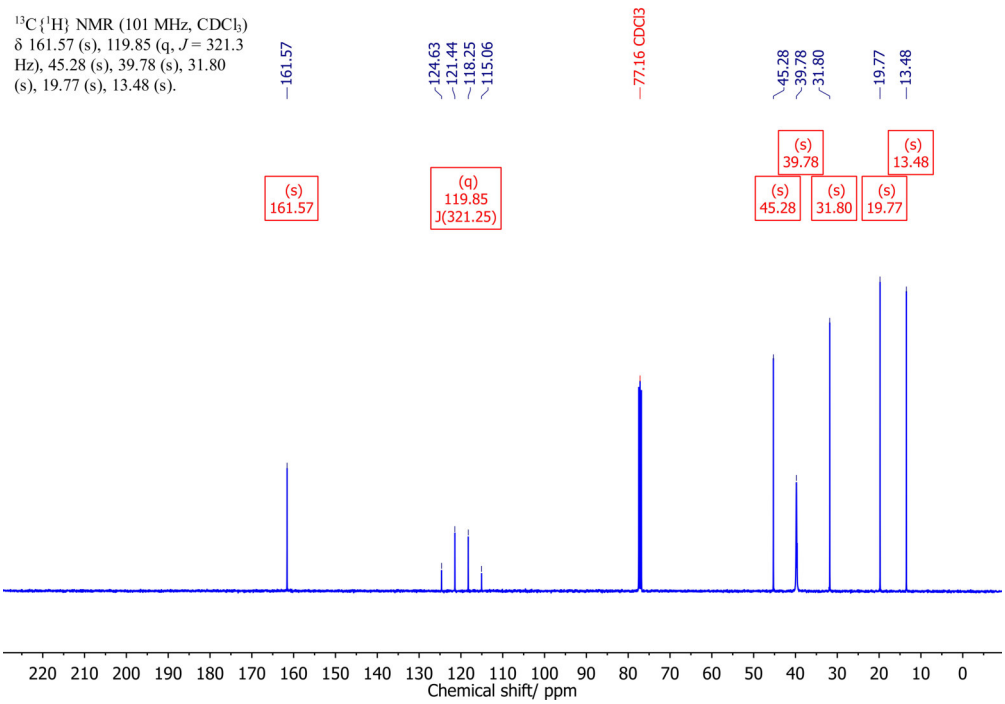

Figure S48: $^{13}C\{^{1}H\}$ NMR spectra of $[C_4HTMG][NTf_2]$.

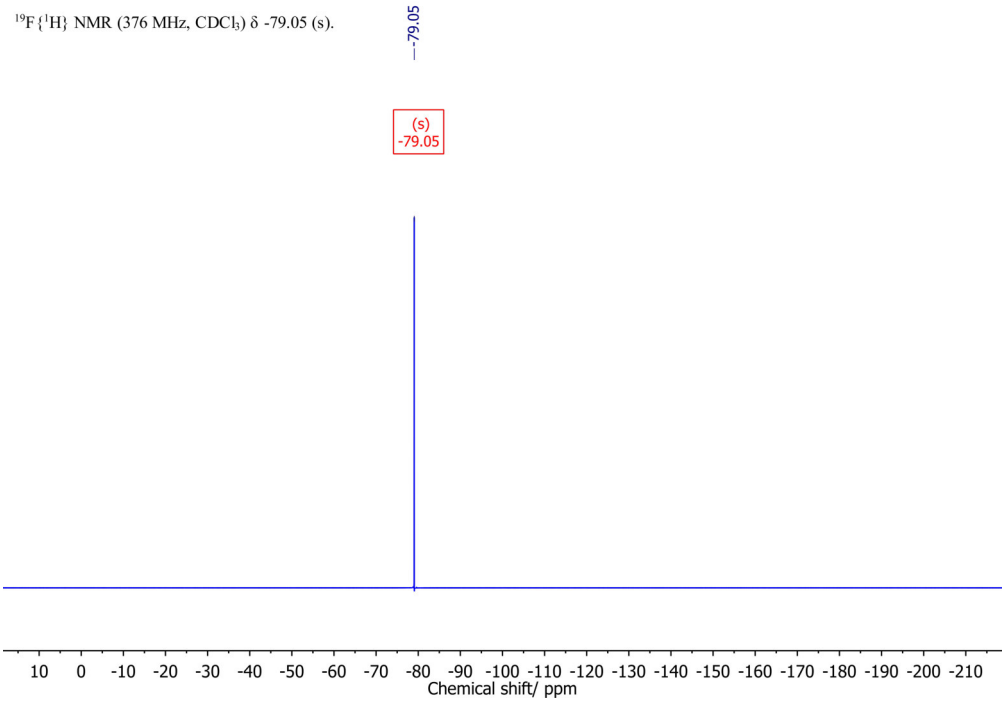

Figure S49: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4HTMG][NTf_2]$.

9.4.2 NMR spectra of [C_4HTMG][BETI]

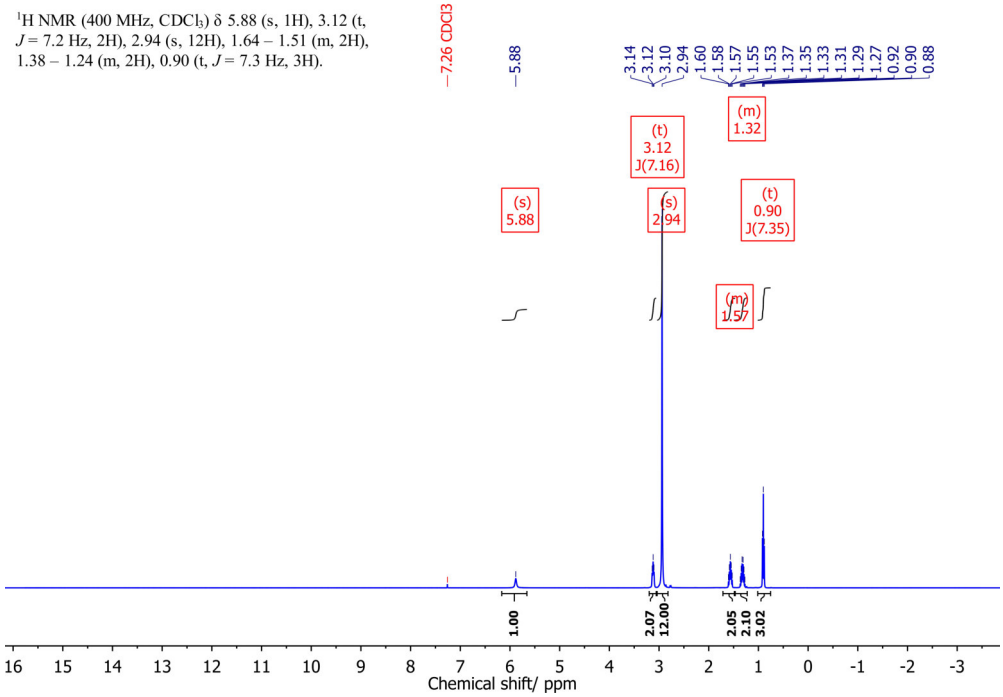

Figure S50: ^{1}H NMR spectra of [C_4HTMG][BETI].

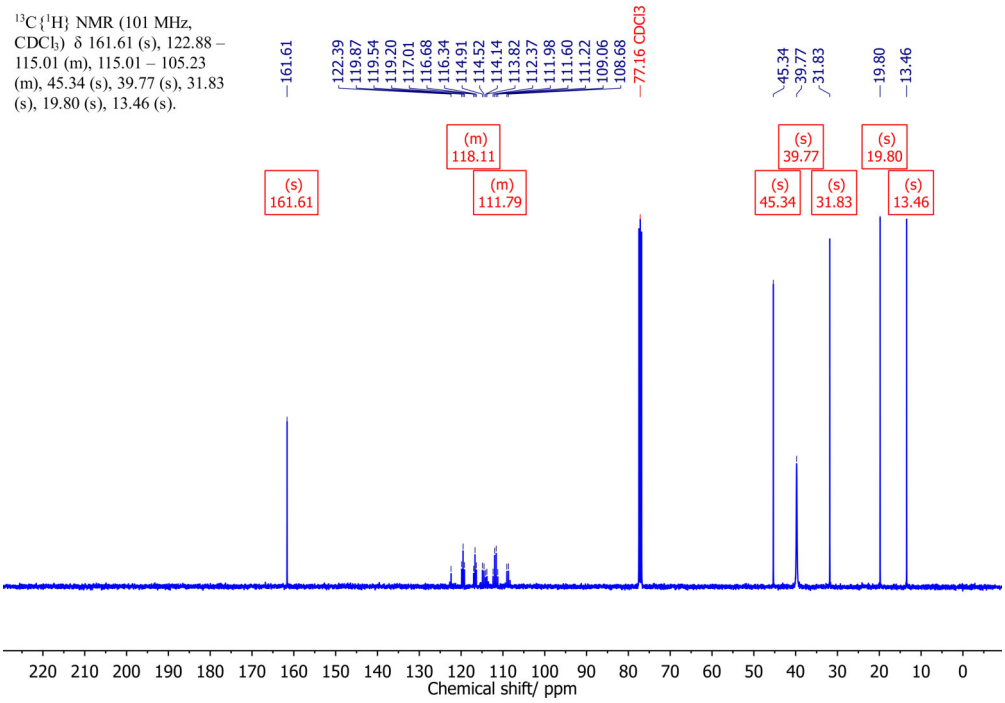

Figure S51: ^{13}C{^{1}H} NMR spectra of [C_4HTMG][BETI].

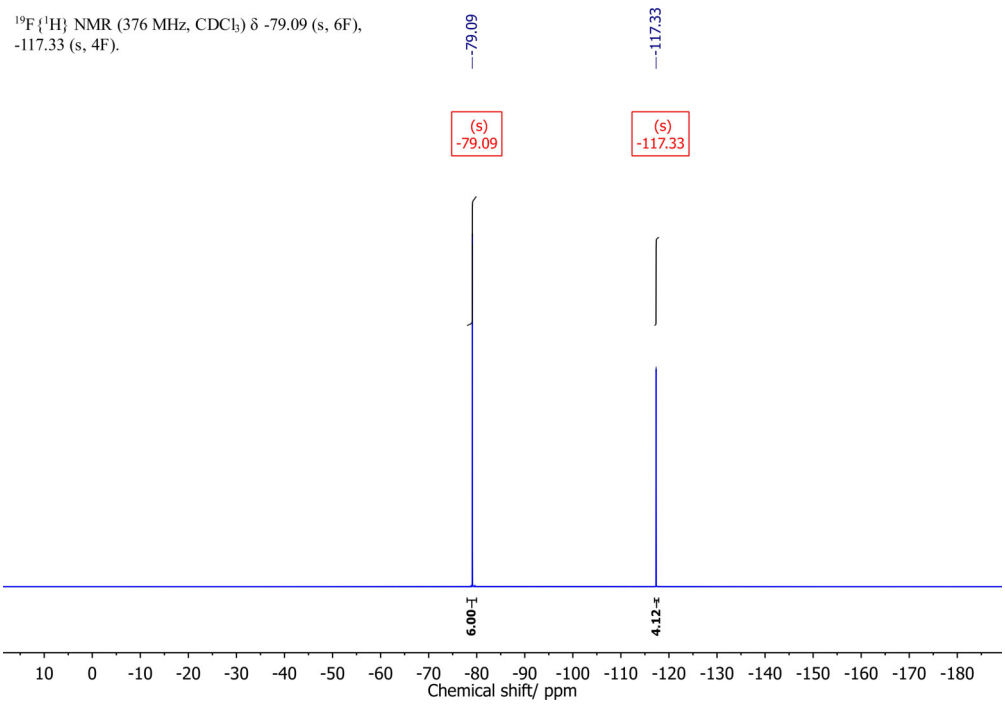

Figure S52: $^{19}F\{^{1}H\}$ NMR spectra of [C_4HTMG][BETI].

9.4.3 NMR spectra of [C_4HTMG][OTf]

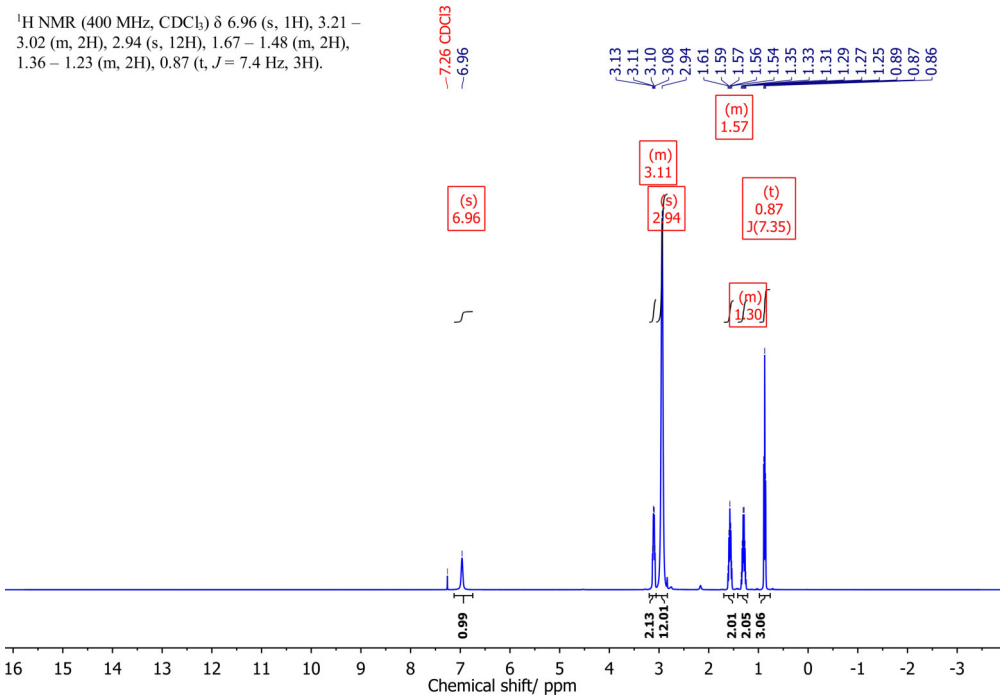

Figure S53: ^{1}H NMR spectra of [C_4HTMG][OTf].

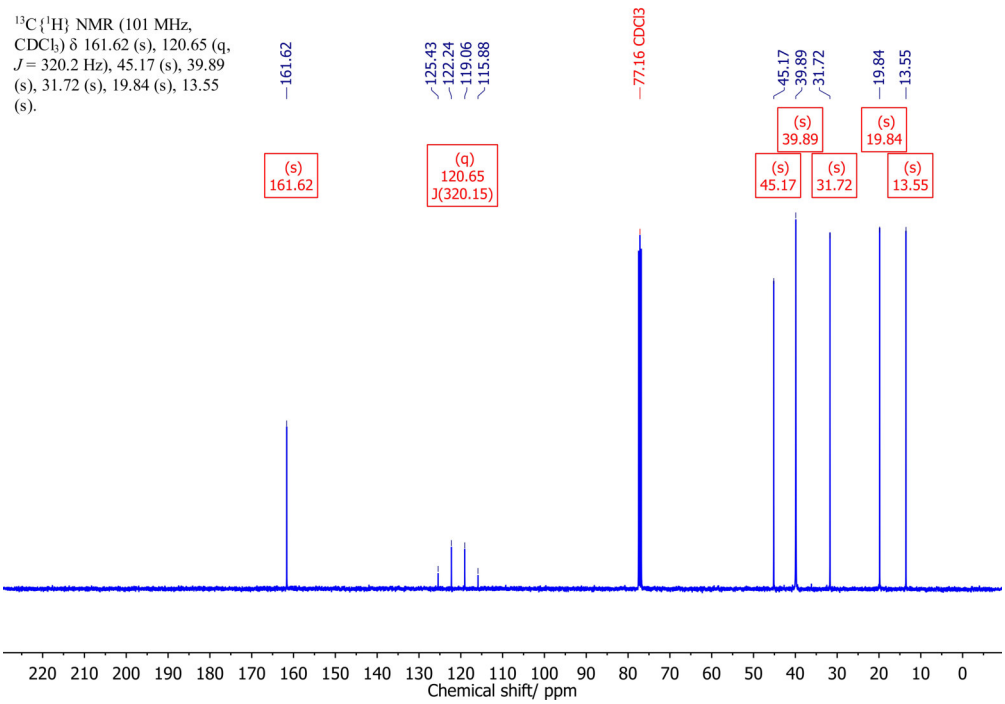

Figure S54: $^{13}C\{^{1}H\}$ NMR spectra of [C_4HTMG][OTf].

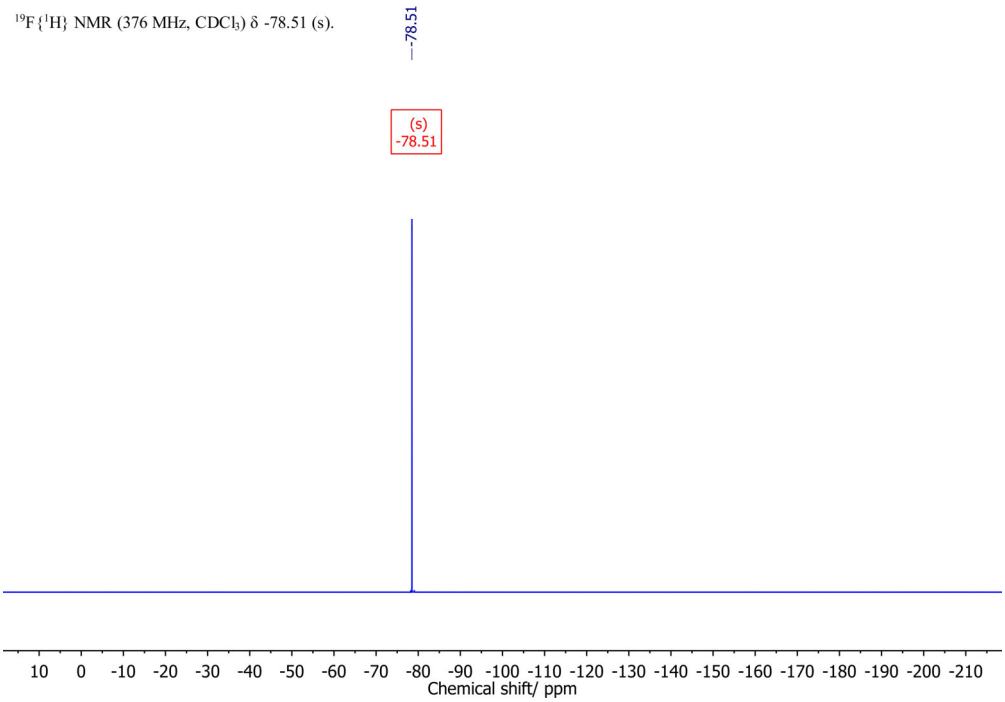

Figure S55: $^{19}F\{^{1}H\}$ NMR spectra of [C_4HTMG][OTf].

9.4.4 NMR spectra of [C_4HTMG][OMs]

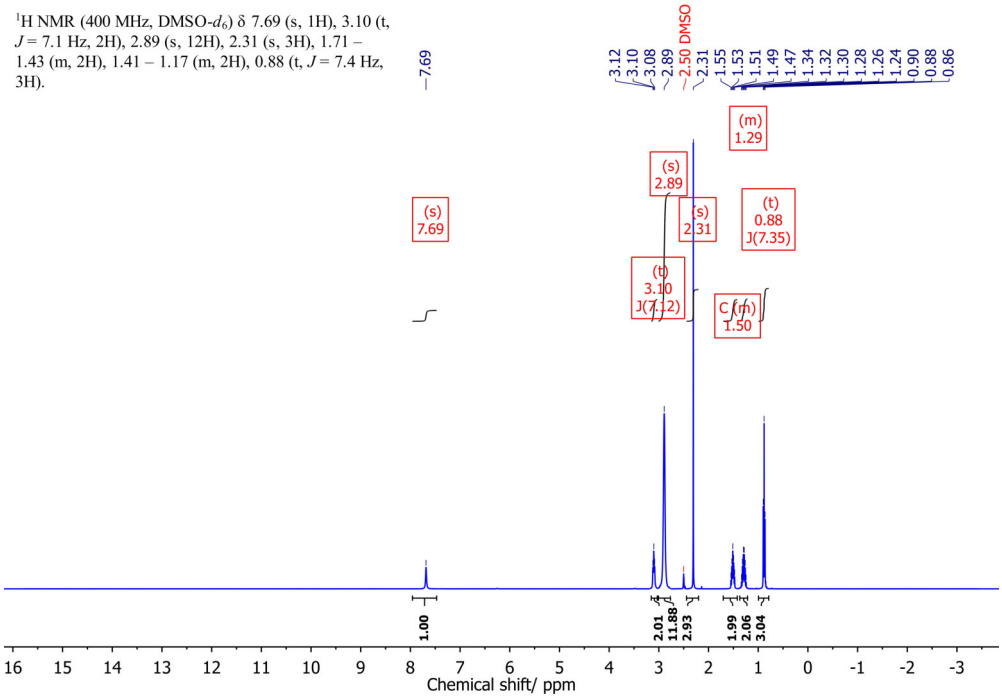

Figure S56: ^{1}H NMR spectra of [C_4HTMG][OMs].

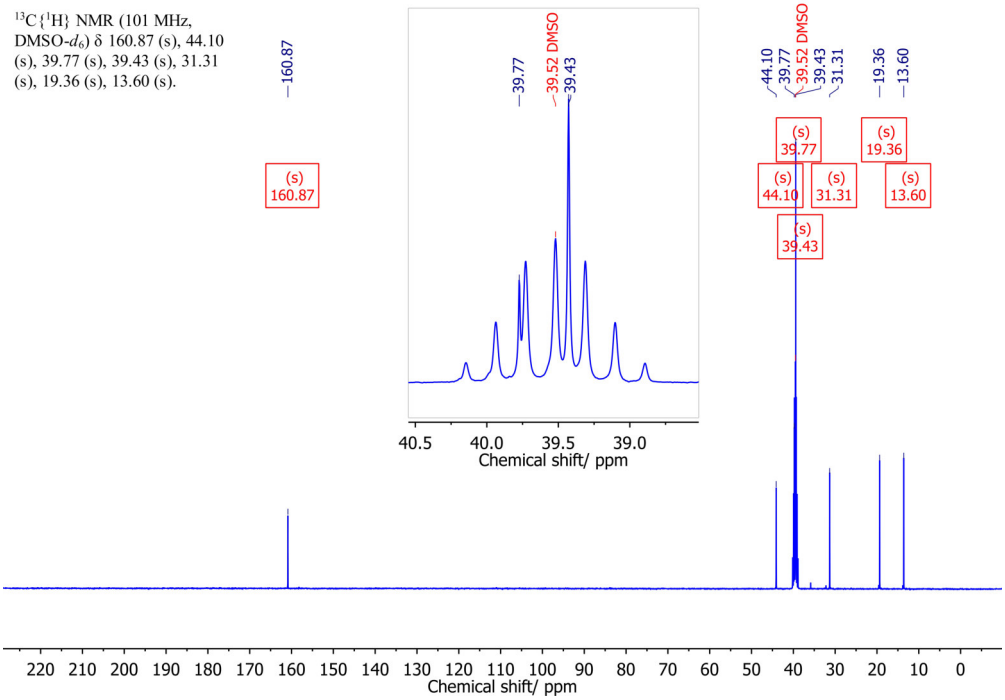

Figure S57: ^{13}C{^{1}H} NMR spectra of [C_4HTMG][OMs].

9.4.5 NMR spectra of [C_4HTMG][TFA]

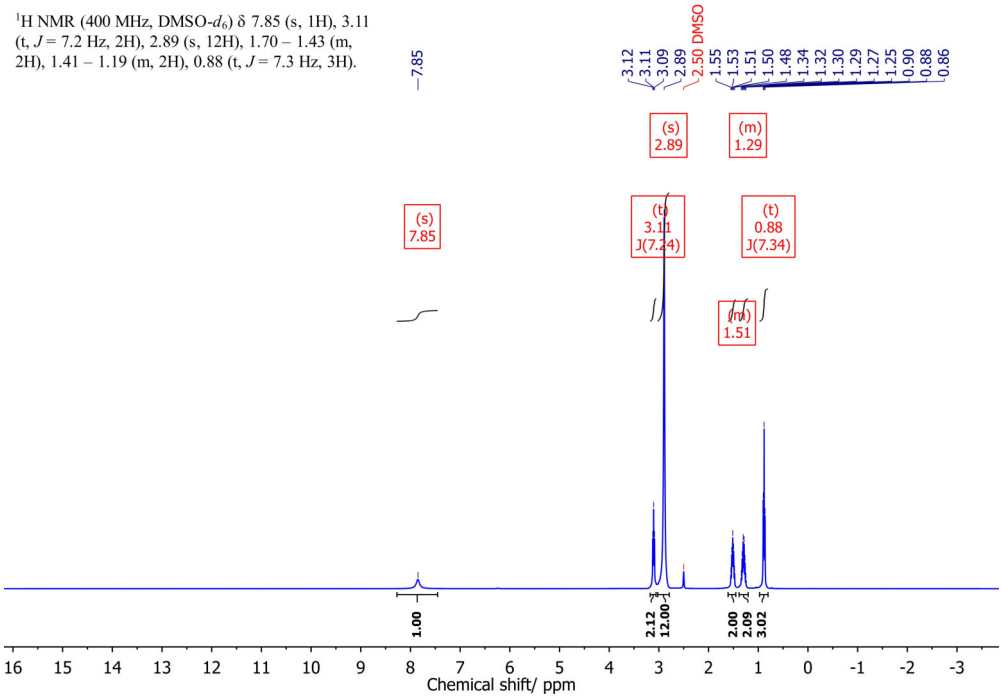

Figure S58: ^{1}H NMR spectra of [C_4HTMG][TFA].

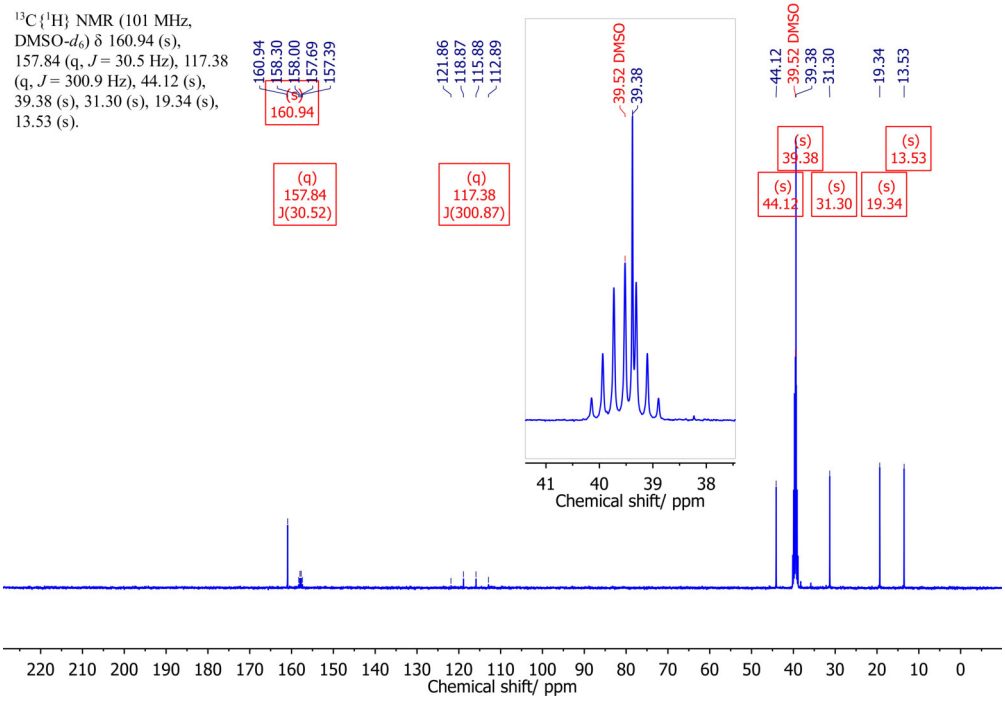

Figure S59: ^{13}C{^{1}H} NMR spectra of [C_4HTMG][TFA].

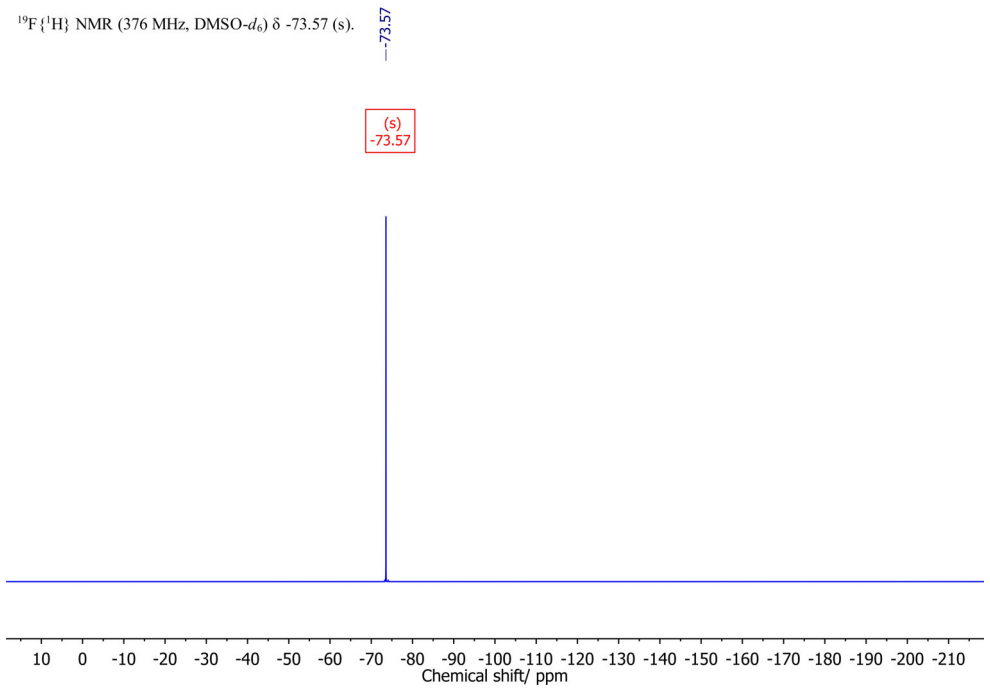

Figure S60: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4HTMG][TFA]$.

9.5 NMR spectra of the $[C_4C_1TMG]$ ionic liquids

9.5.1 NMR spectra of $[C_4C_1TMG][NTf_2]$

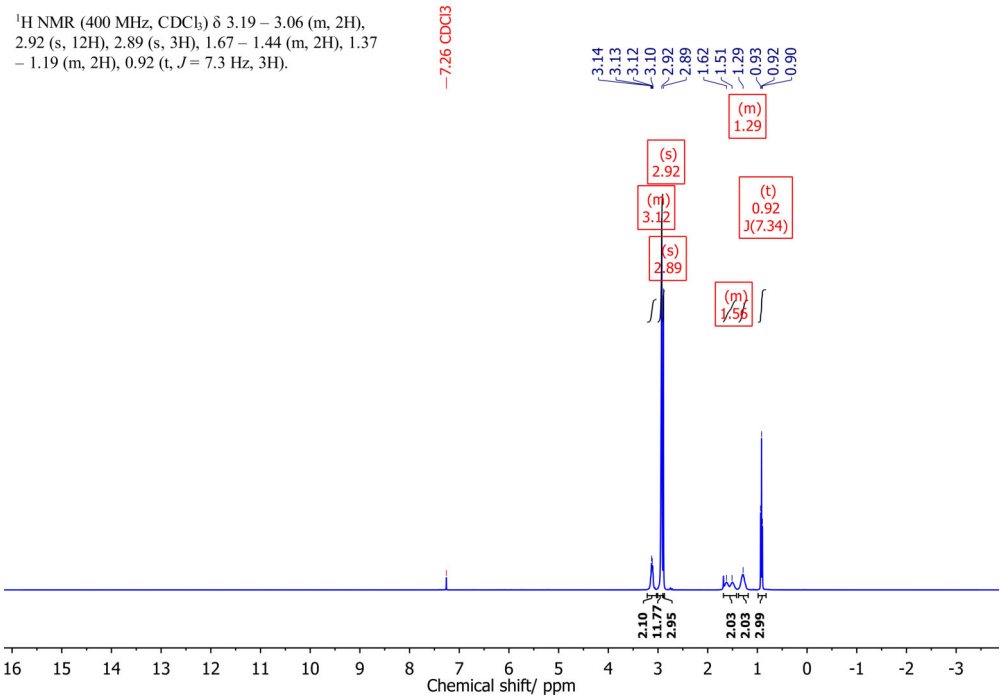

Figure S61: ^{1}H NMR spectra of $[C_4C_1TMG][NTf_2]$.

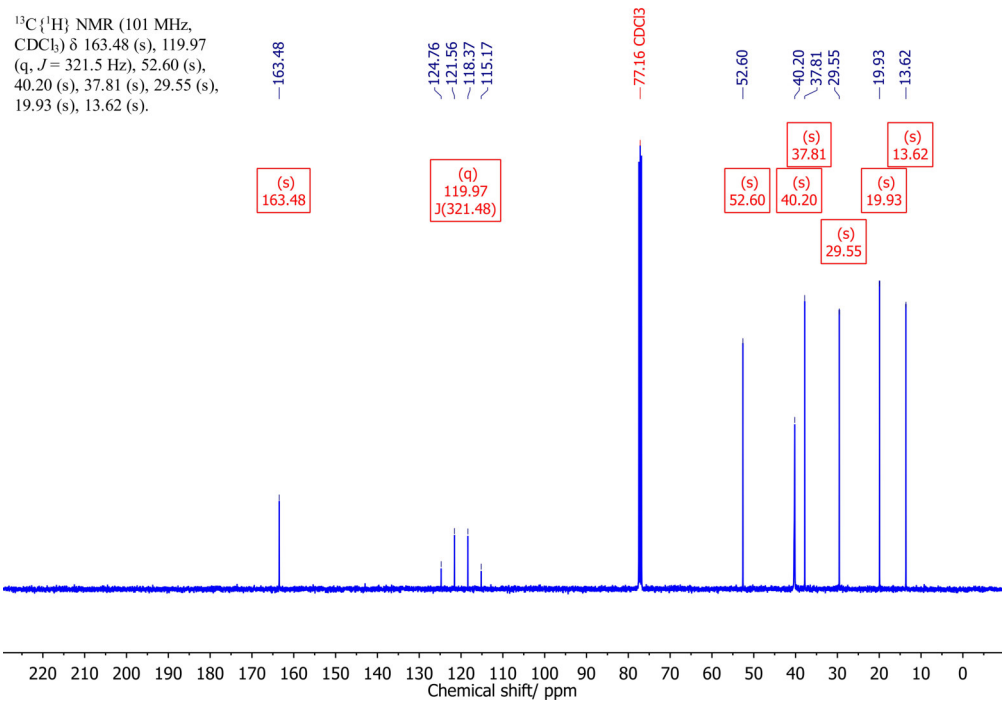

Figure S62: $^{13}C\{^{1}H\}$ NMR spectra of $[C_4C_1TMG][NTf_2]$.

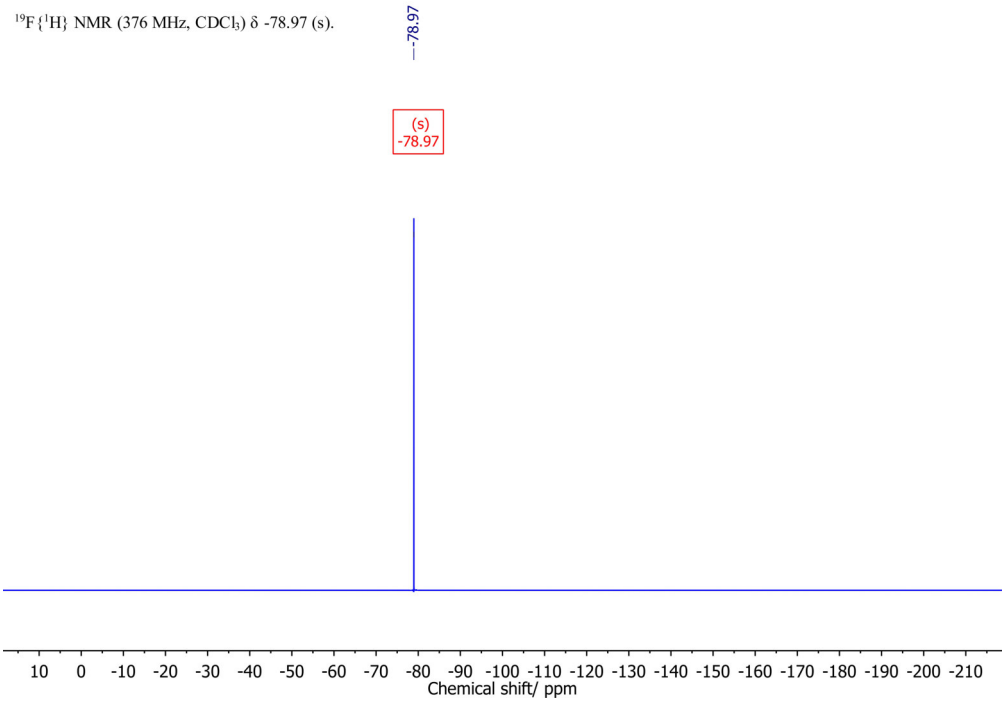

Figure S63: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_1TMG][NTf_2]$.

9.5.2 NMR spectra of [C_4C_1TMG][BETI]

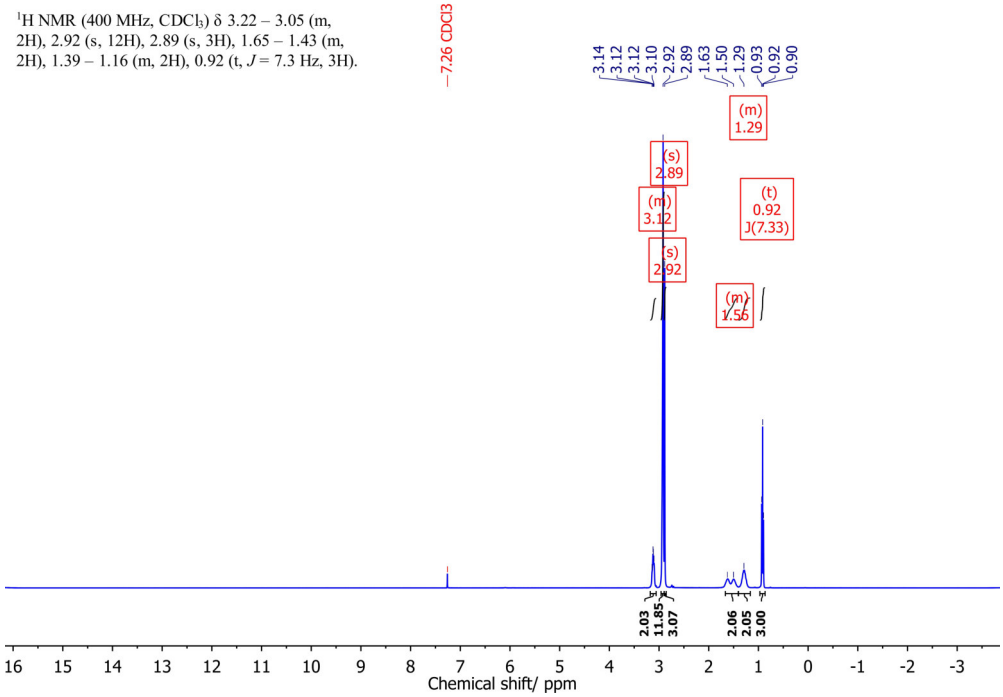

Figure S64: ^{1}H NMR spectra of [C_4C_1TMG][BETI].

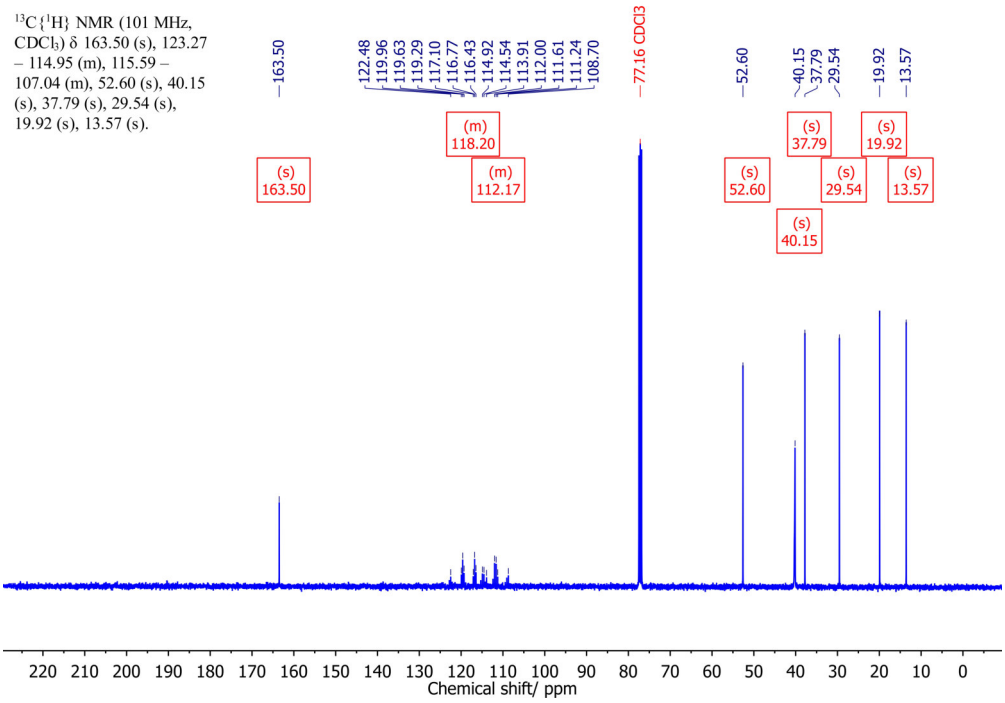

Figure S65: ^{13}C{^{1}H} NMR spectra of [C_4C_1TMG][BETI].

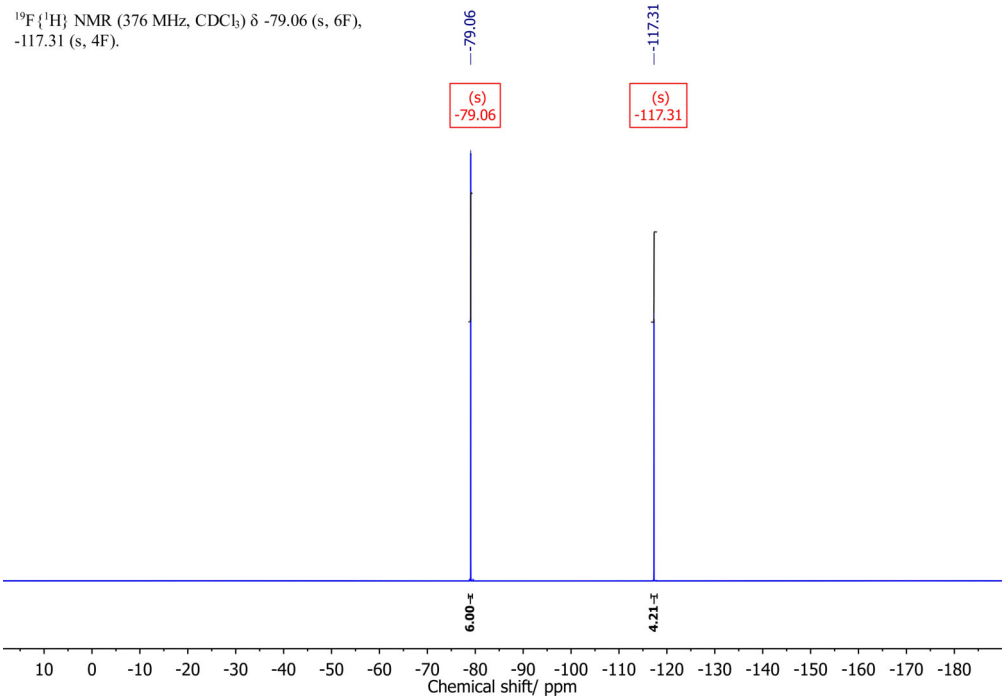

Figure S66: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_1TMG][BETI]$.

9.5.3 NMR spectra of $[C_4C_1TMG][OTf]$

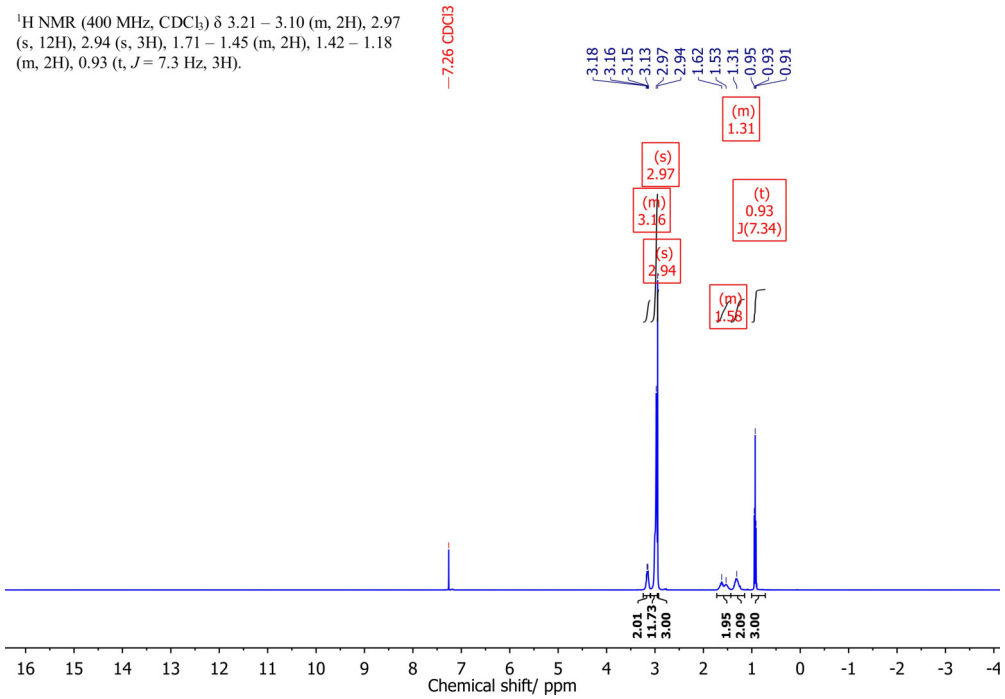

Figure S67: ^{1}H NMR spectra of $[C_4C_1TMG][OTf]$.

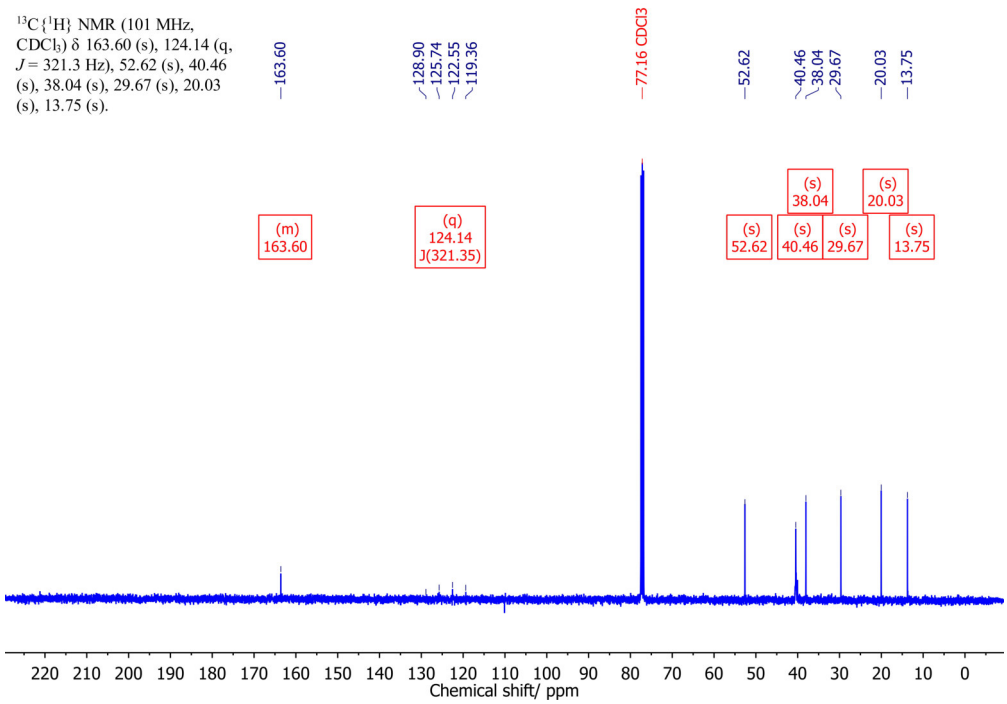

Figure S68: $^{13}C\{^{1}H\}$ NMR spectra of $[C_4C_1TMG][OTf]$.

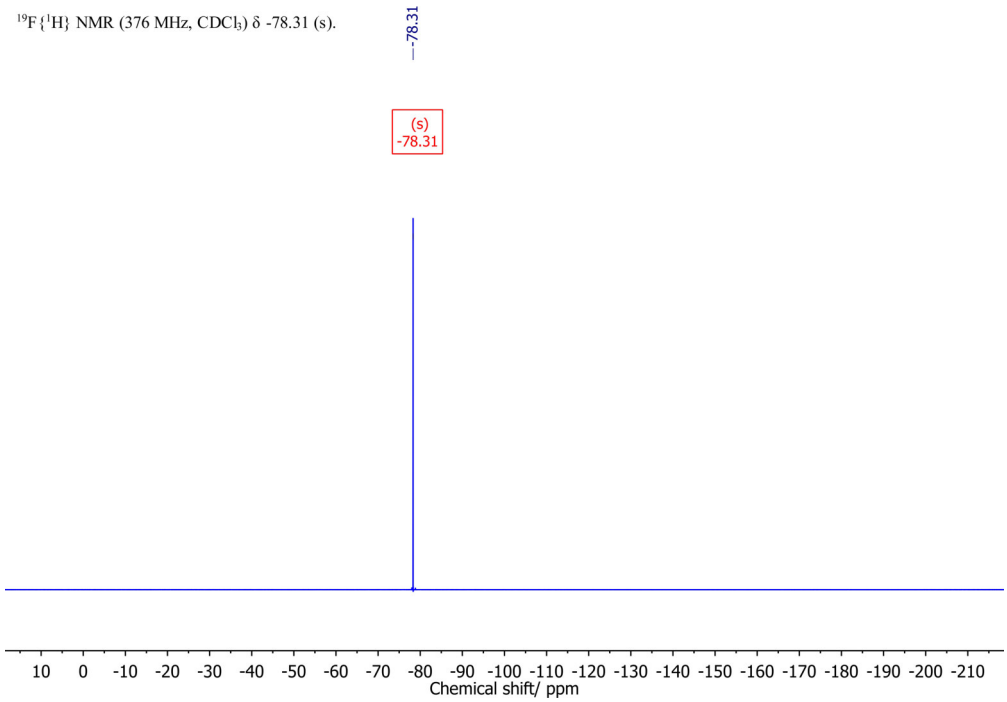

Figure S69: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_1TMG][OTf]$.

9.5.4 NMR spectra of [C_4C_1TMG][OMs]

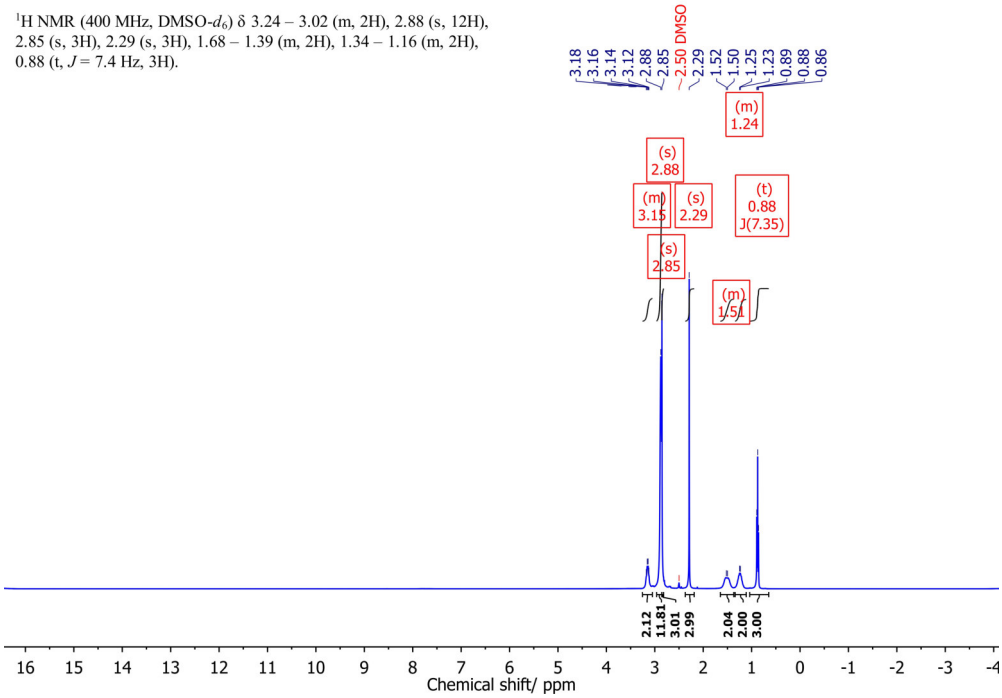

Figure S70: ^{1}H NMR spectra of [C_4C_1TMG][OMs].

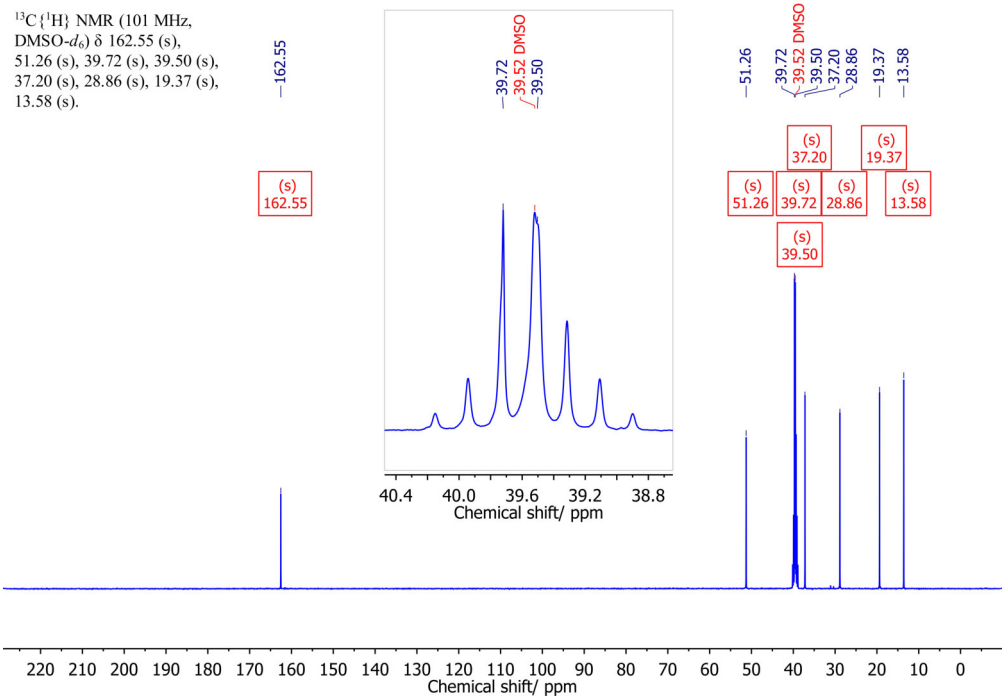

Figure S71: ^{13}C{^{1}H} NMR spectra of [C_4C_1TMG][OMs].

9.5.5 NMR spectra of $[C_4C_1TMG][TFA]$

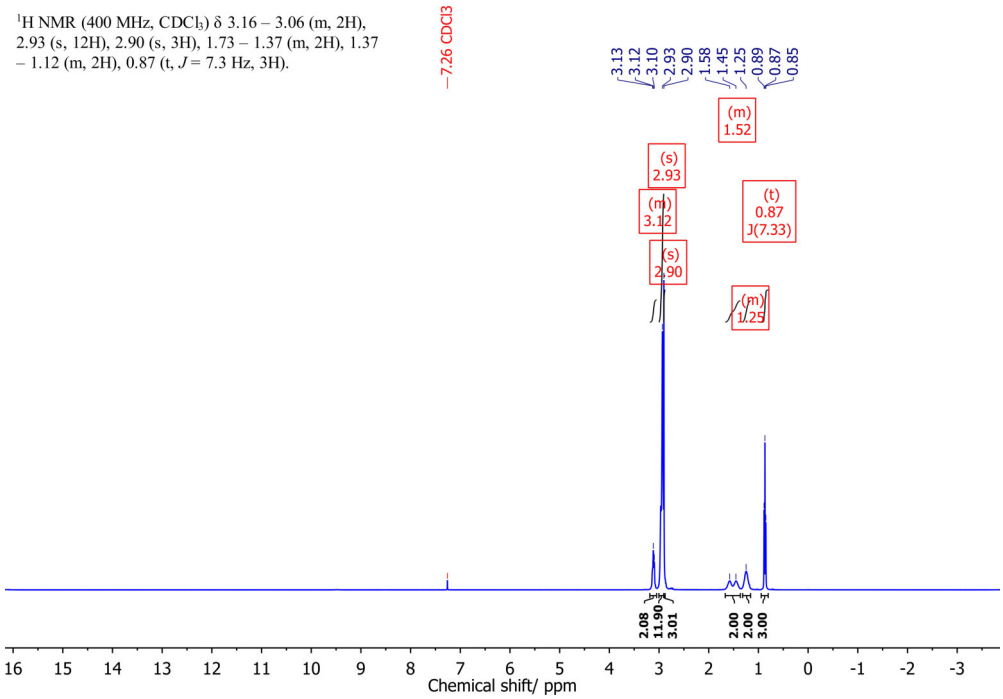

Figure S72: ^{1}H NMR spectra of $[C_4C_1TMG][TFA]$.

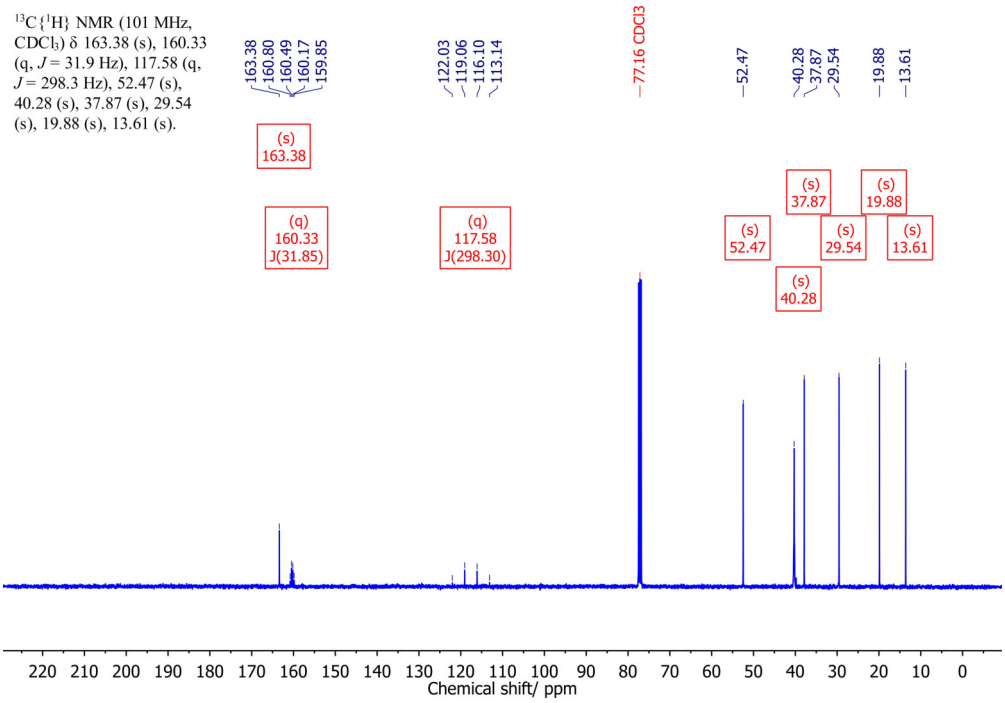

Figure S73: ^{13}C{^{1}H} NMR spectra of $[C_4C_1TMG][TFA]$.

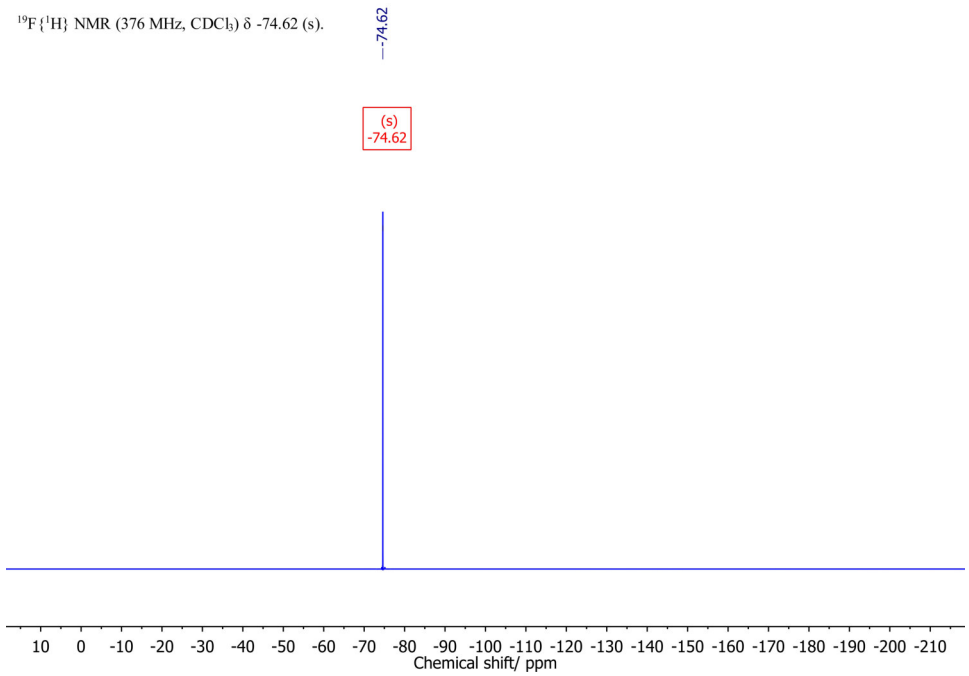

Figure S74: ^{19}F{^{1}H} NMR spectra of [C_4C_1TMG][TFA].

9.6 NMR spectra of the [C_4C_4TMG] ionic liquids

9.6.1 NMR spectra of [C_4C_4TMG][NTf_2]

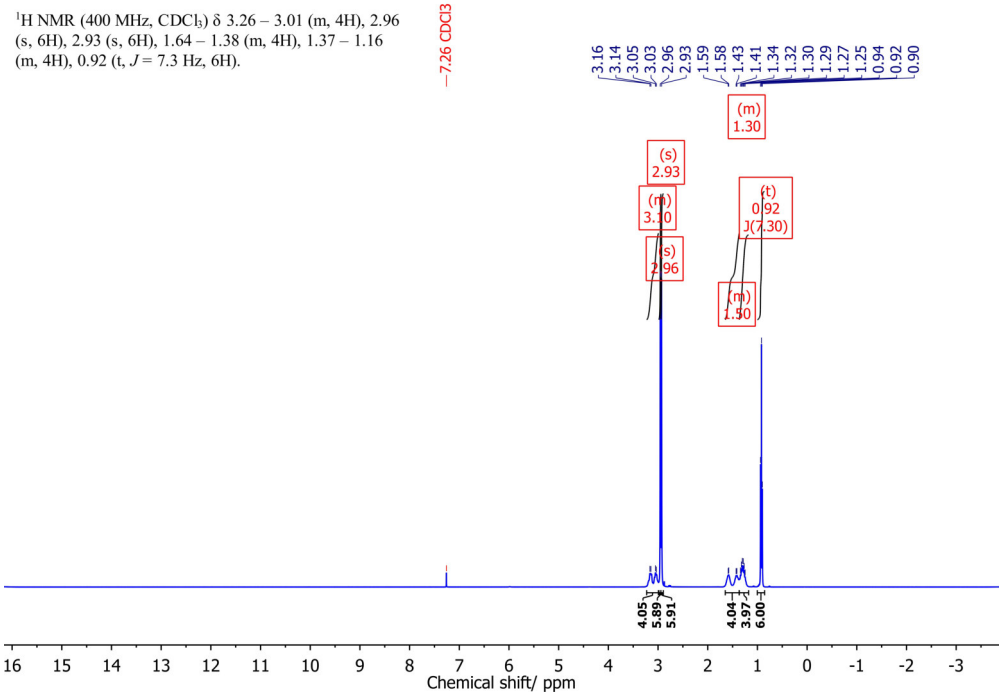

Figure S75: ^{1}H NMR spectra of [C_4C_4TMG][NTf_2].

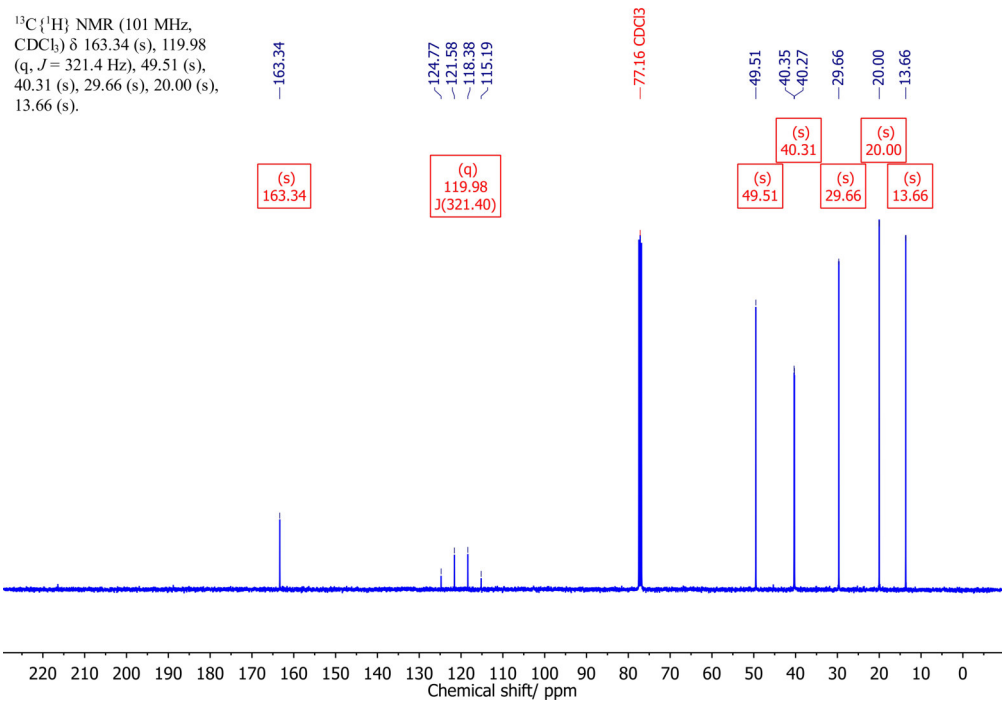

Figure S76: $^{13}C\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][NTf_2]$.

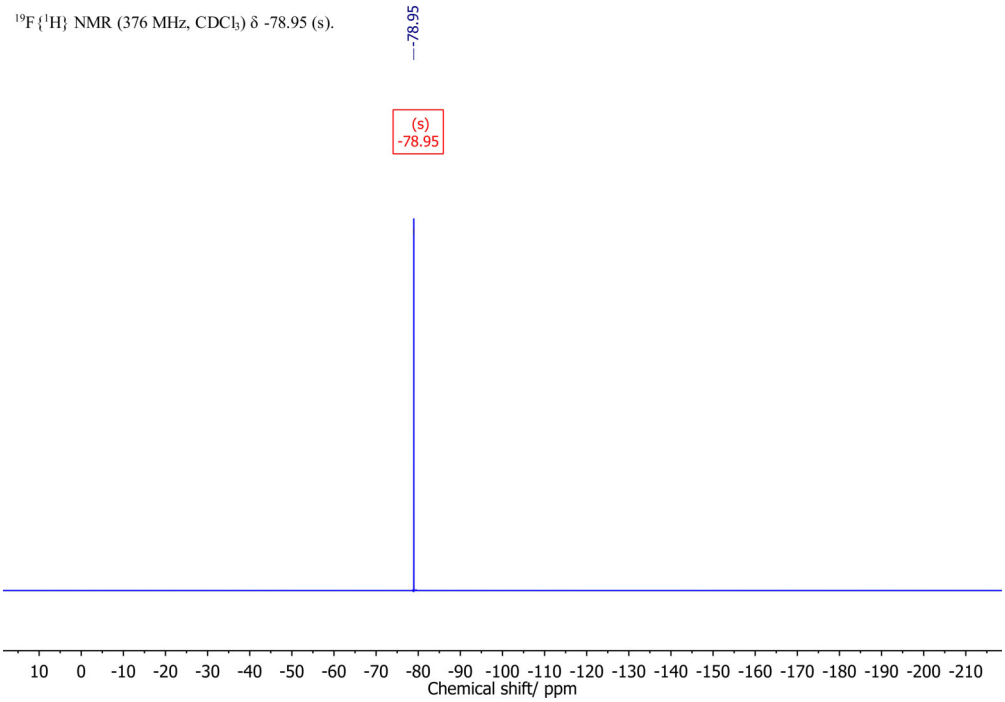

Figure S77: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][NTf_2]$.

9.6.2 NMR spectra of [C_4C_4TMG][BETI]

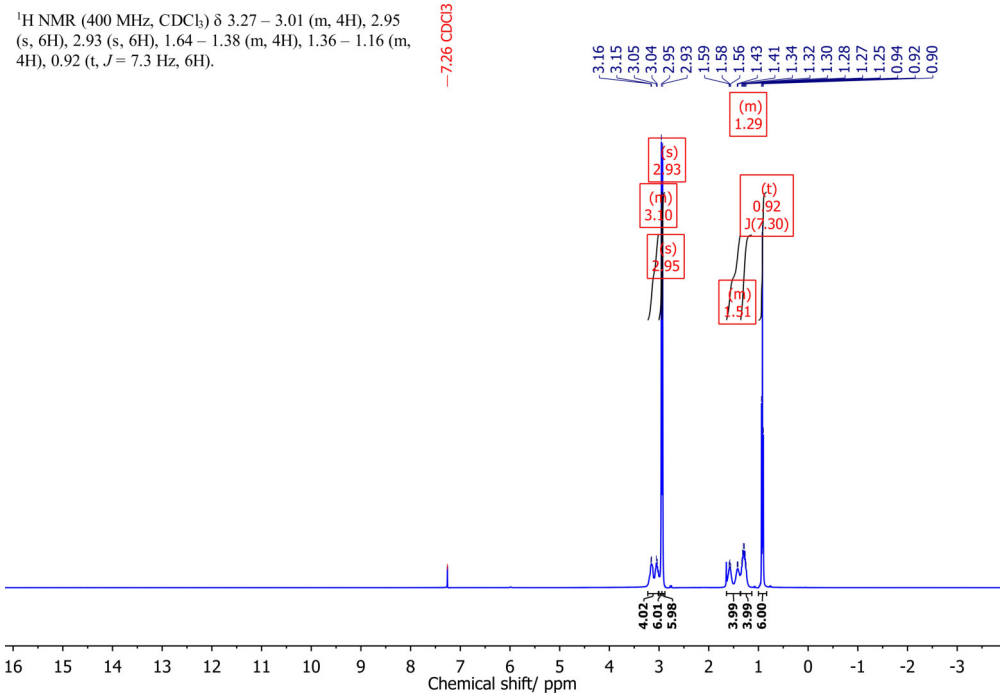

Figure S78: ^{1}H NMR spectra of [C_4C_4TMG][BETI].

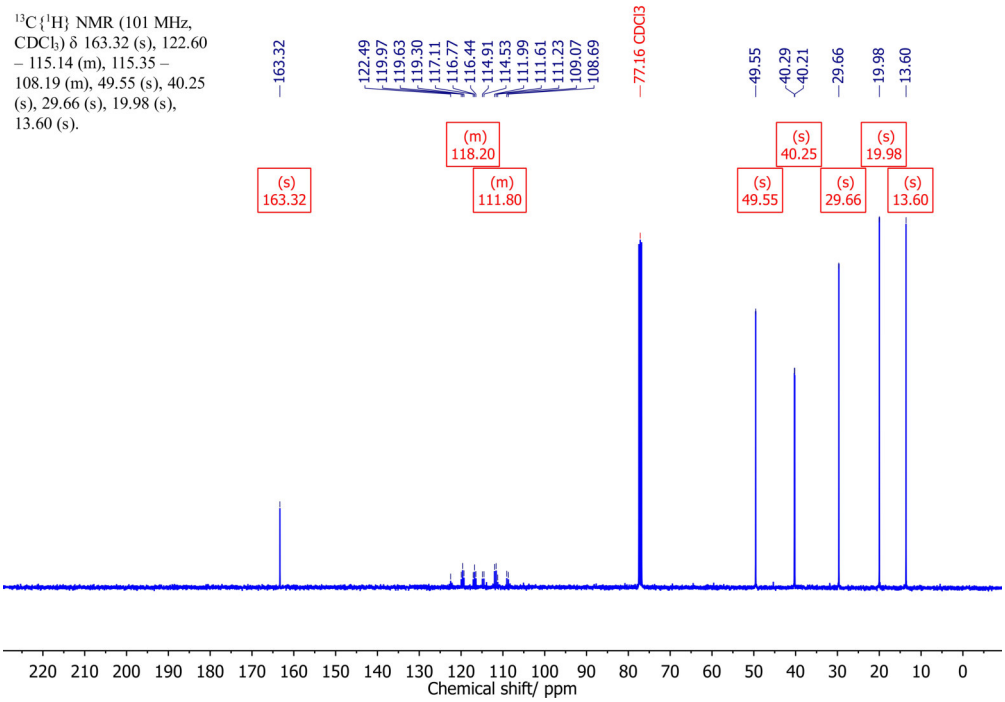

Figure S79: $^{13}C\{^1H\}$ NMR spectra of [C_4C_4TMG][BETI].

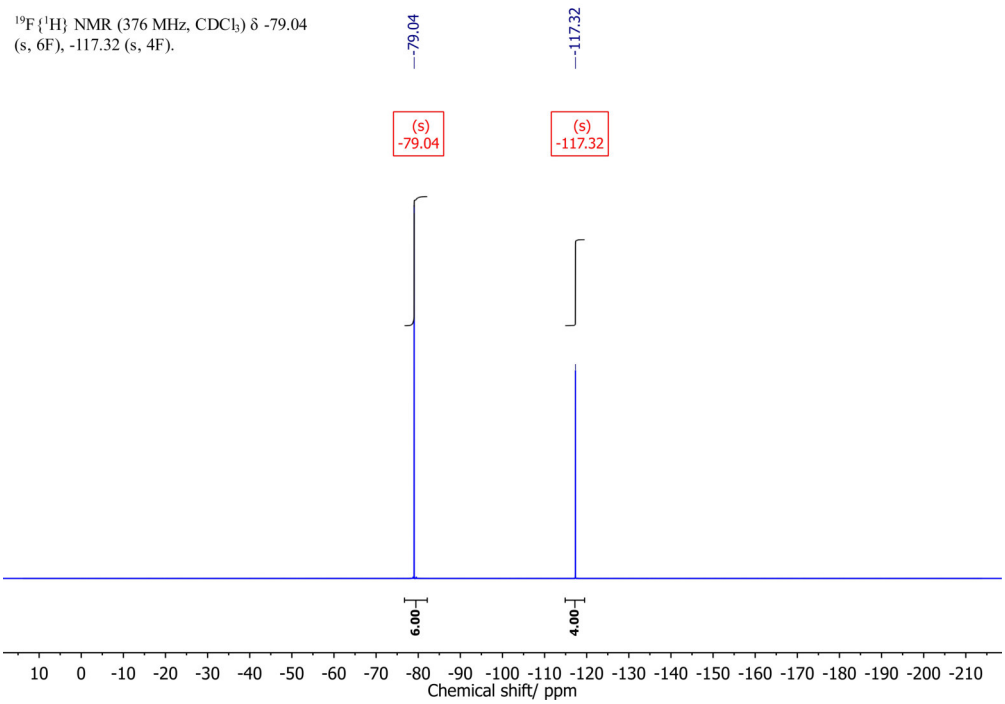

Figure S80: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][BETI]$.

9.6.3 NMR spectra of $[C_4C_4TMG][OTf]$

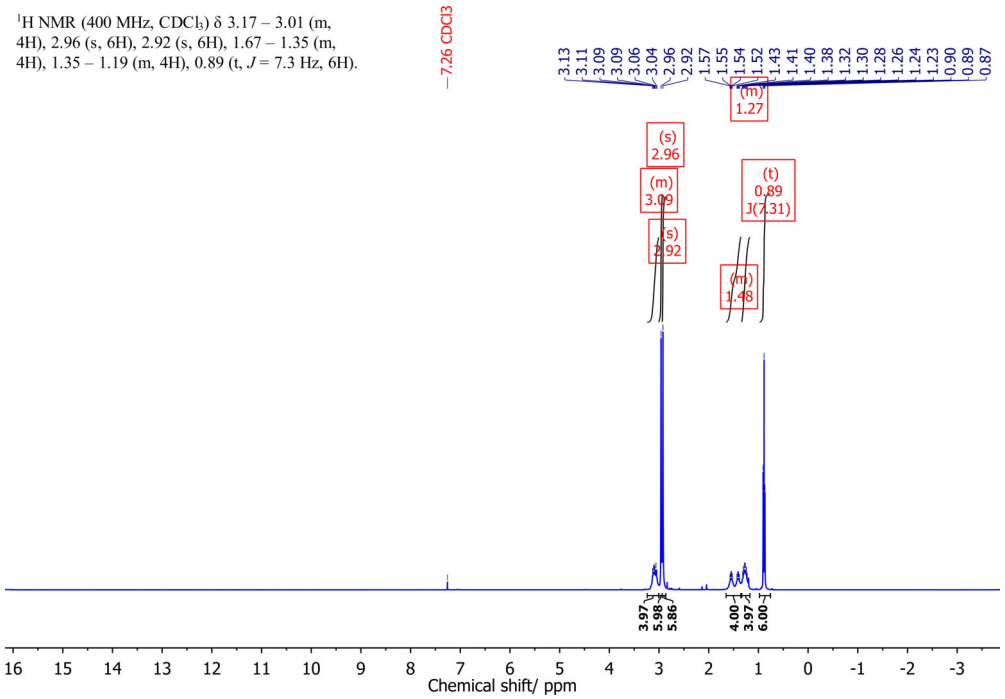

Figure S81: ^{1}H NMR spectra of $[C_4C_4TMG][OTf]$.

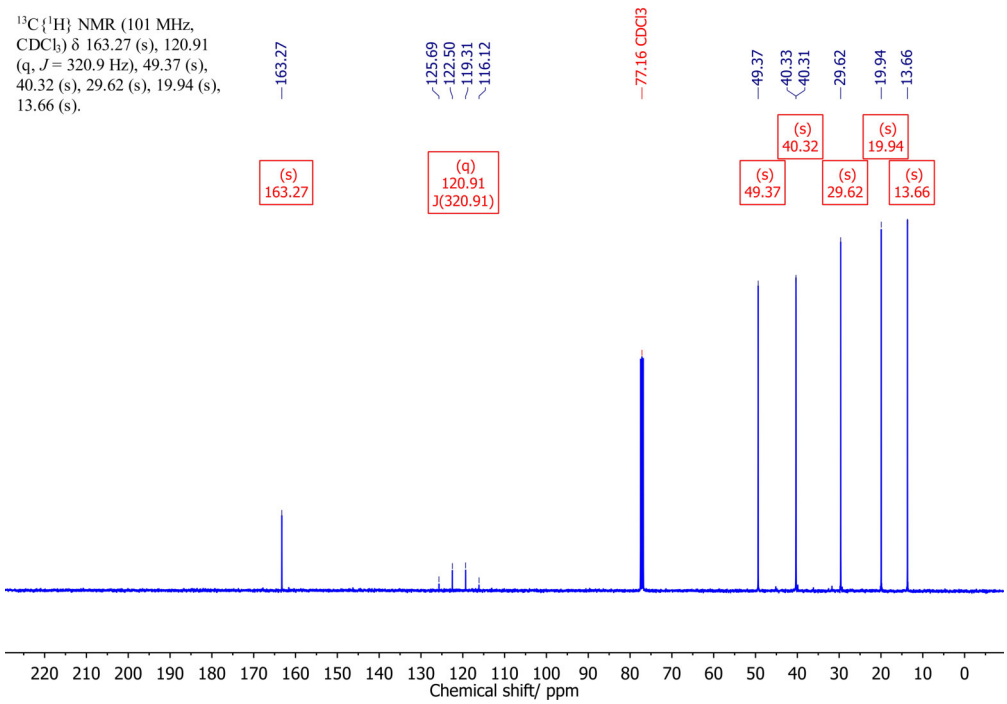

Figure S82: $^{13}C\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][OTf]$.

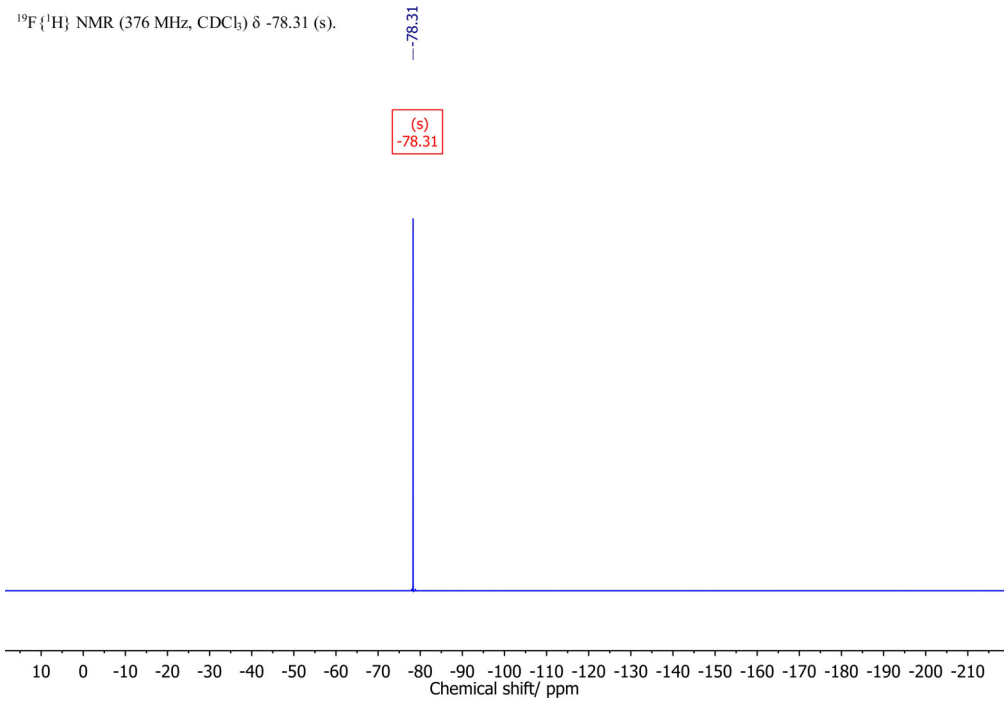

Figure S83: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][OTf]$.

9.6.4 NMR spectra of [C_4C_4TMG][OMs]

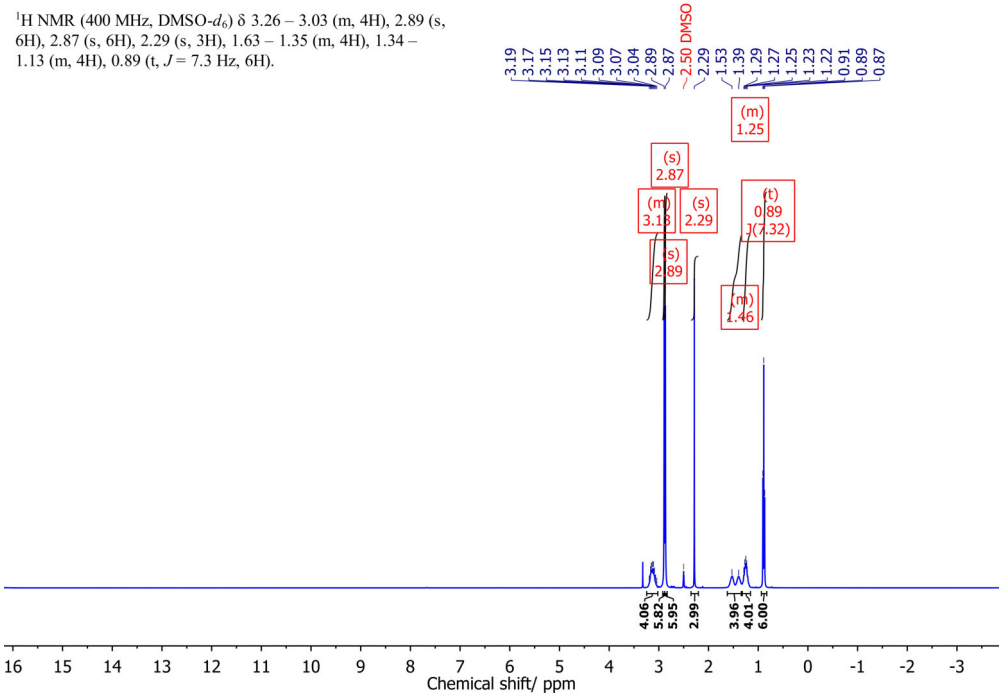

Figure S84: ^{1}H NMR spectra of [C_4C_4TMG][OMs].

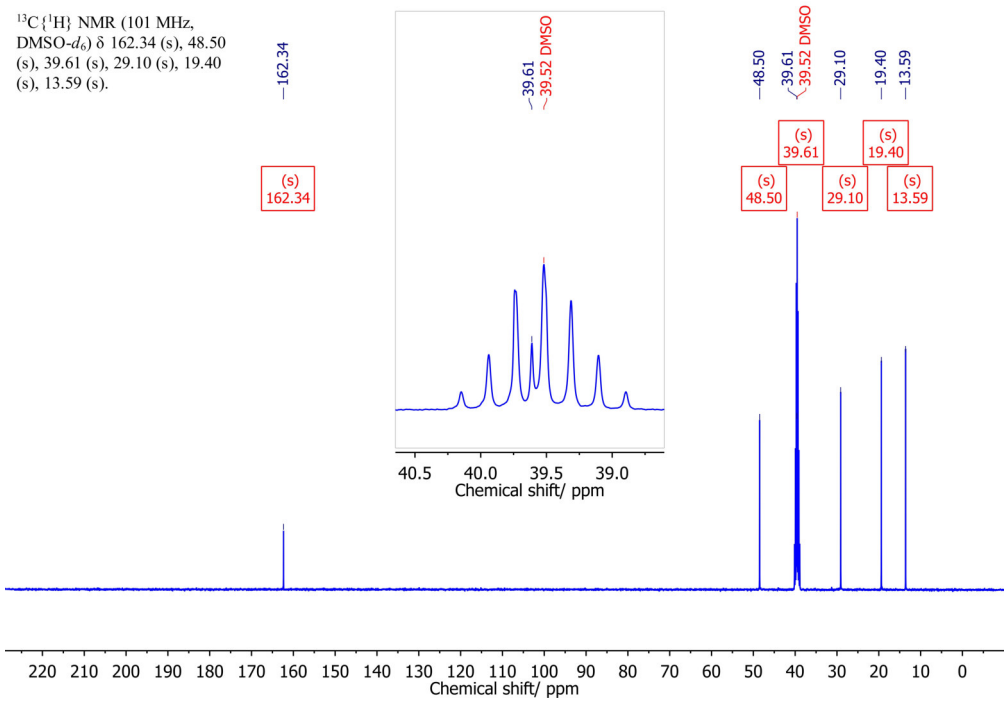

Figure S85: ^{13}C{^{1}H} NMR spectra of [C_4C_4TMG][OMs].

9.6.5 NMR spectra of [C_4C_4TMG][TFA]

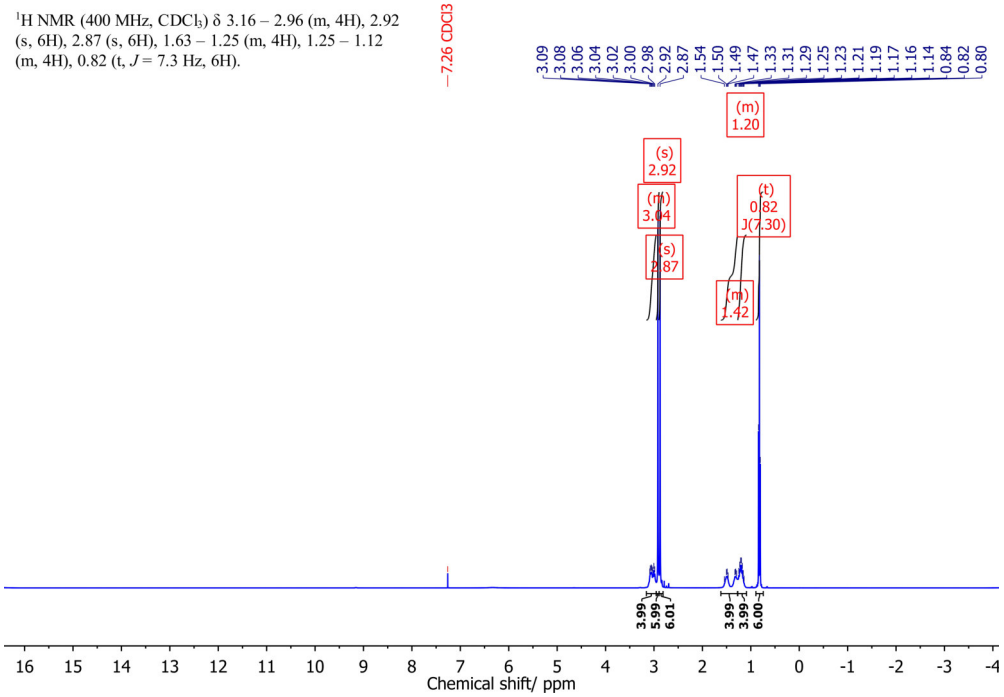

Figure S86: ^{1}H NMR spectra of [C_4C_4TMG][TFA].

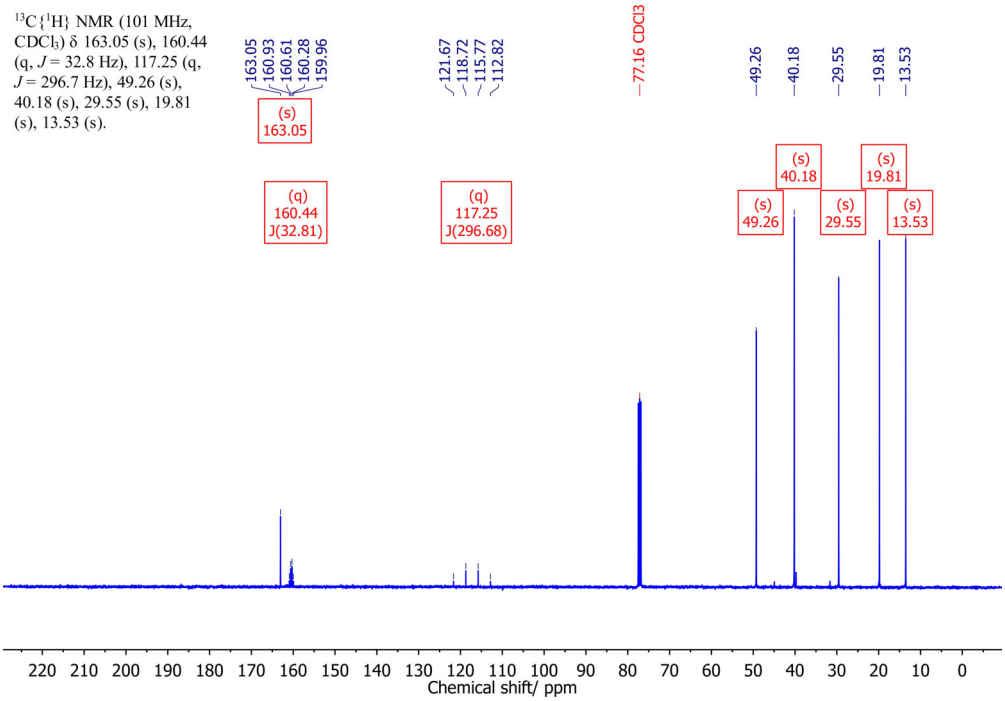

Figure S87: ^{13}C{^{1}H} NMR spectra of [C_4C_4TMG][TFA].

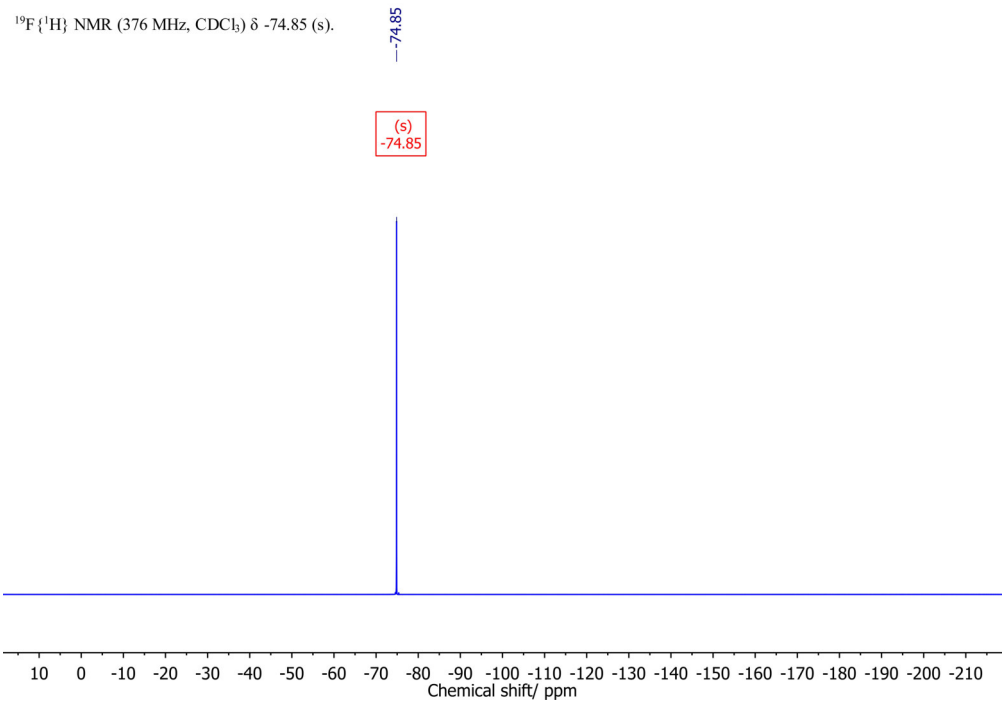

Figure S88: $^{19}F\{^{1}H\}$ NMR spectra of $[C_4C_4TMG][TFA]$.

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