Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Effect of the cation structure on the properties of homobaric imidazolium ionic liquids

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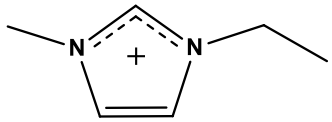
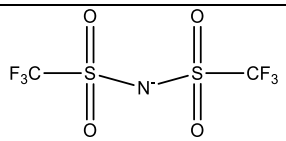
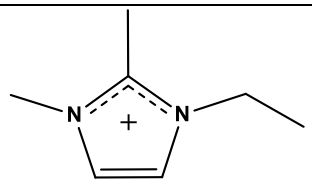
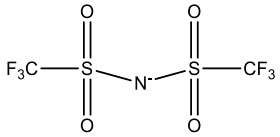
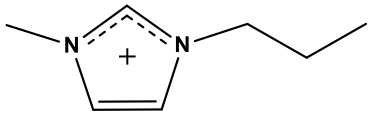
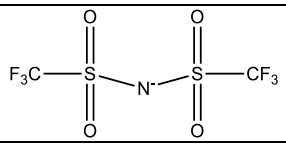
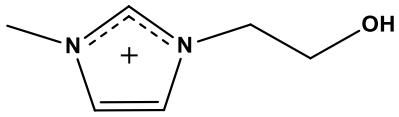
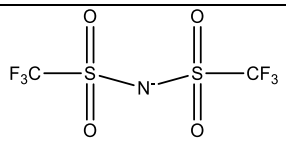
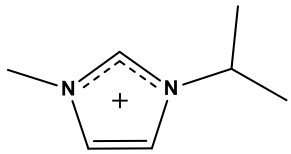
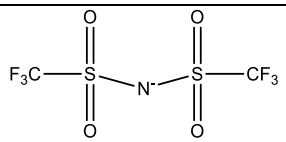
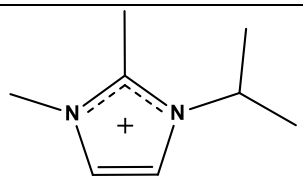
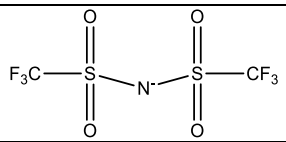
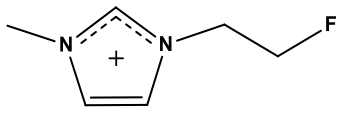
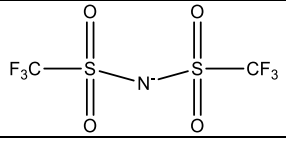
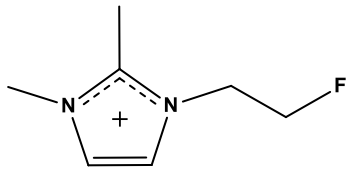
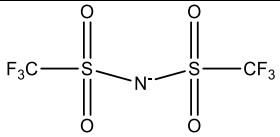
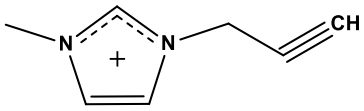
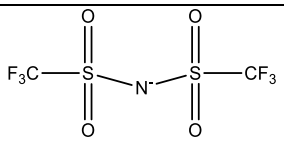
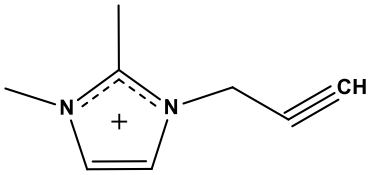
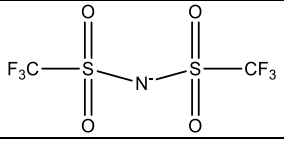
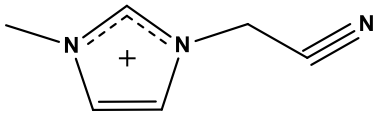
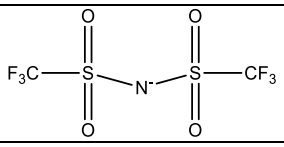
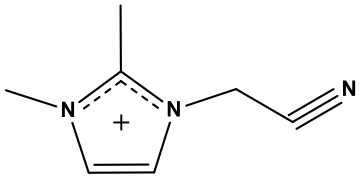
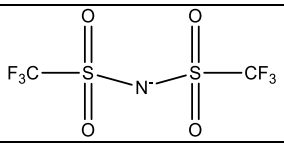
Table S1. Structures, abbreviations and molar masses of the studied ILs.

Cation	Anion	Abbreviation	Molar mass (g mol^{-1})
	Br^-	**$[C_2C_1im][Br]$**	191.07
		**$[C_2C_1im][NTf_2]$**	391.3
	Br^-	**$[C_2C_1C_1im][Br]$**	205.1
		**$[C_2C_1C_1im][NTf_2]$**	405.3
	Br^-	**$[C_3C_1im][Br]$**	205.1
		**$[C_3C_1im][NTf_2]$**	405.3
	Br^-	**$[HOC_2C_1im][Br]$**	207.1
		**$[HOC_2C_1im][NTf_2]$**	407.3
	Br^-	**$[C_{2,1}C_1im][Br]$**	205.1
		**$[C_{2,1}C_1im][NTf_2]$**	405.3
	Br^-	**$[C_{2,1}C_1C_1im][Br]$**	219.13
		**$[C_{2,1}C_1C_1im][NTf_2]$**	405.3
	I^-	**$[FC_2C_1im][I]$**	
	Br^-	**$[FC_2C_1im][Br]$**	209.1
		**$[FC_2C_1im][NTf_2]$**	409.3
	I^-	**$[FC_2C_1C_1im][I]$**	
	Br^-	**$[FC_2C_1C_1im][Br]$**	223.1
		**$[FC_2C_1C_1im][NTf_2]$**	423.3
	Br^-	**$[HC{\equiv}C_2C_1im][Br]$**	201.1

		**[HC≡C$_2$C$_1$im][NTf$_2$]**	401.3
	Br^-	**[HC≡C$_2$C$_1$C$_1$im][Br]**	215.1
		**[HC≡C$_2$C$_1$C$_1$im][NTf$_2$]**	415.3
	Br^-	**[N≡C$_2$C$_1$im][Br]**	202.1
	Cl^-	**[N≡C$_2$C$_1$im][Cl]**	157.6
		**[N≡C$_2$C$_1$im][NTf$_2$]**	402.3
	Br^-	**[N≡C$_2$C$_1$C$_1$im][Br]**	216.1
	Cl^-	**[N≡C$_2$C$_1$C$_1$im][Cl]**	171.6
		**[N≡C$_2$C$_1$C$_1$im][NTf$_2$]**	416.3

Materials and Methods

All chemicals were bought from Sigma Aldrich or VWR (unless stated otherwise) and were purified using standard purification techniques.[1] The solvents used for the syntheses were of 99 % purity and used without further purification. All the glassware were washed with absolute ethanol, followed by washes with decon-90 and de-ionised water.

Synthesis of Alkyl-imidazolium Halides

General Procedure

The bromo- and chloroalkanes were washed with concentrated sulphuric acid until the acid layer appeared colourless. Then they were washed with a saturated solution of sodium bicarbonate (until pH testing was slightly basic), followed by washes with de-ionised water. The organic phase was dried over anhydrous magnesium sulphate and distilled in vacuo.

1-fluoro-2-iodoethane was purchased by Apollo Scientific at 98% purity and was used without further purification.

Propargyl bromide was purchased by Sigma Aldrich at 80 wt. % in toluene and was used without further purification.

1-Methylimidazole was left overnight stirring over potassium hydroxide pellets and then distilled in vacuo.

1,2-Dimethylimidazole was recrystallized from toluene and then dried in vacuo.

1.2 eq. of haloalkane was added dropwise to a stirring solution of 1 eq. of the corresponding imidazole in ethyl acetate in an ice bath. Once the addition was completed, the solution was allowed to reach room temperature and then it was left stirring for 4 – 5 days at 40 ^{o}C, monitored by ^{1}H NMR. After the reaction had stopped progressing, ethyl acetate was removed using a cannula. The IL was dried in vacuo, followed by recrystallisation with acetonitrile – ethyl acetate and then drying in vacuo again. All ILs were stored under dry nitrogen atmosphere.

[C_2C_1im]Br. 1-bromoethane (20 mL, 268 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (17.8 mL, 223.3 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (35.4 g, 185.3 mmol, 83 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 10.21 (s, 1H, imC(2)**H**), 7.59-7.54 (m, 2H, imC(4,5)**H**), 4.34 (q, J = 7.36 Hz, 2H, ethyl – C(1)$\mathbf{H_2}$), 4.04 (s, 3H, methyl – C$\mathbf{H_3}$), 1.53 (t, J=7.37 Hz, 3H, ethyl – C$\mathbf{H_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) : 136.88 (imC(2)), 123.7 (imC(4)), 121.98 (imC(5)), 45.24 (ethyl – C(1)), 36.67 (methyl – C(1)), 15.67 (ethyl – C(2)).

m/z (ES^+) : 111.1 (100 %, M^+).

Elemental analysis (calculated): C – 36.38(37.72), H – 6.06(5.8), N – 13.77(14.66).

[$C_2C_1C_1$im]Br. 1-bromoethane (20 mL, 268 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (21.5 g, 223.3 mmol, 1 eq.) in ethyl acetate (100 mL) according

to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (36.6 g, 178.6 mmol, 80 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.66 (d, J = 2.12 Hz, 1H, imC(4)**H**), 7.55 (d, J = 2.12 Hz, 1H, imC(5)**H**), 4.30 (q, J = 7.37 Hz, 2H, ethyl – C(1)**H₂**), 4.00 (s, 3H, methyl – C**H₃**), 2.83 (s, 3H, imC(2')**H₃**), 1.51 (t, J = 7.37 Hz, 3H, ethyl – C**H₃**).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) : 143.87 (imC(2)), 123.16 (imC(4)), 120.68 (imC(5)), 44.28 (ethyl – C(1)), 36.29 (methyl – C(1)), 15.33 (ethyl – C(2)), 11.15 (imC(2')).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 40.44(40.99), H – 7.3(6.39), N – 12.92(13.66).

[C_3C_1im]Br. 1-bromopropane (20 mL, 220.2 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (14.6 mL, 183.5 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (30.4 g, 148.5 mmol, 81 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.25 (s, 1H, imC(2)**H**), 7.82 (t, J = 1.76, 1H, imC(4)**H**), 7.75 (t, J = 1.72, 1H, imC(5)**H**), 4.14 (t, J = 7.09 Hz, 2H, propyl – C(1)**H₂**), 3.86 (s, 3H, methyl – C**H₃**), 1.84-1.75 (m, 2H, propyl – C(2)**H₂**), 0.84 (t, J=7.39 Hz, 3H, propyl - C(3)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm) : 136.52 (imC(2)), 123.58 (imC(4)), 122.25 (imC(5)), 50.2 (propyl – C(1)), 35.76 (methyl – C(1)), 22.85 (propyl – C(2)), 10.42 (propyl – C(3)).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 39.81(40.99), H – 6.63(6.39), N – 12.93(13.66).

[HOC_2C_1im]Br. 2-bromoethanol (20 mL, 282.2 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (18.7 mL, 235.2 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (38.4 g, 185.8 mmol, 79 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.17 (s, 1H, imC(2)**H**), 7.76 (t, J = 1.75, 1H, imC(4)**H**), 7.73 (t, J = 1.73, 1H, imC(5)**H**), 5.17 (t, J = 5.3 Hz, 1H, ethyl – OH), 4.22 (m, 2H, ethyl – C(1)**H₂**), 3.87 (s, 3H, methyl – C**H₃**), 3.73-3.69 (m, 2H, ethyl – C(2)**H₂**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.79 (imC(2)), 123.31 (imC(4)), 122.64 (imC(5)), 59.26 (ethyl – C(1)), 51.57 (ethyl – C(2)), 35.7 (methyl – C(1)).
m/z (ES^+) : 127.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 33.45(34.8), H – 5.66(5.35), N – 12.73(13.53).

[$C_{2,1}C_1$im]Br. 2-bromopropane (20 mL, 213 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (14.1 mL, 177.5 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (29.5 g, 143.8 mmol, 81 % yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.29 (s, 1H, imC(2)**H**), 7.91 (t, J = 1.79, 1H, imC(4)**H**), 7.75 (t, J = 1.71, 1H, imC(5)**H**), 4.69 - 4.59 (m, 1H, isopropyl – C(1)**H**), 3.85 (s, 3H, methyl – C**H₃**), 1.46 (d, J = 6.69 Hz, 6H, isopropyl – C(2)**H₃** & C(3)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 143.5 (imC(2)), 122.77 (imC(4)), 117.29 (imC(5)), 49.91 (isopropyl – C(1)), 34.57 (methyl – C(1)), 21.93 (isopropyl – C(2) & C(3)), 9.28 (im(C2')).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 39.34(40.99), H – 6.2(6.39), N – 12.91(13.66).

[C_2C_2im]Br. 2-bromoethane (18.4 mL, 213 mmol, 1.2 eq.) was added to a stirring solution of 1-calethylimidazole (17.1 mL, 177.5 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (30.6 g, 149.1 mmol, 84 % yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.35 (s, 1H, imC(2)**H**), 7.85 (d, 2H, imC(4)**H** & imC(5)**H**), 4.20 (q, J = 7.34 Hz, 4H, 2 x ethyl – C(1)**H₂**), 1.42 (t, J = 7.34 Hz, 6H, 2 x ethyl – C(2)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 133.93 (imC(2)), 122.08 (imC(4) & imC(5)), 44.14 (ethyl – C(1)), 15.08 (ethyl – C(2)).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).

[$C_{2,1}C_1C_1$im]Br. 2-bromopropane (20 mL, 213 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (17 g, 177.5 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (33.8 g, 154.4 mmol, 87 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.83 (d, J = 2.18 Hz, 1H, imC(4)**H**), 7.70 (d, J = 2.15 Hz, 1H, imC(5)**H**), 4.72 – 4.62 (m, 1H, isopropyl – C(1)**H**), 3.75 (s, 3H, methyl – C**H₃**), 2.61 (s, 3H, imC(2')**H₃**), 1.41 (d, J = 6.65 Hz, 6H, isopropyl – C(2)**H₃** & C(3)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 143.87 (imC(2)), 123.16 (imC(4)), 120.68 (imC(5)), 44.28 (ethyl – C(1)), 36.29 (methyl – C(1)), 15.33 (ethyl – C(2)), 11.15 (imC(2')).
m/z (ES^+) : 139.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 44.14(43.85), H – 6.84(6.9), N – 12.64(12.78).

[FC_2C_1im]I. 1-fluoro-2-iodoethane (20 mL, 245.6 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (16.3 mL, 204.7 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (37.6 g, 147.4 mmol, 72 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.16 (s, 1H, imC(2)**H**), 7.78 (t, J = 1.70, 1H, imC(4)**H**), 7.75 (t, J = 1.74, 1H, imC(5)**H**), 4.80 (dt, $^{2}J_{H/F}$ = 47.0 Hz, $^{3}J_{H/H}$ = 4.6 Hz, 2H, ethyl – C(2)***H₂***F), 4.55 (dt, $^{3}J_{H/F}$ = 28.0 Hz, $^{3}J_{H/H}$ = 4.6 Hz, 2H, ethyl – C(1)***H₂***), 3.88 (s, 3H, methyl – C**H₃**).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.97 (imC(2)), 123.74 (imC(4)), 122.54 (imC(5)), 82.5 & 80.53 (ethyl – **C(2)**F), 49.39 & 49.20 (ethyl – C(1)), 35.88 (methyl – C(1)).
m/z (ES^+) : 129.1 (100 %, M^+).
m/z (ES^-) : 129 (100 %, M^-).
Elemental analysis (calculated): C – 37.66(37.69), H – 5.44(5.42), N – 12.16(12.56).

[FC_2C_1im]Br. An aqueous solution of **[FC_2C_1im]I** passed through ion exchange column packed with Amberlite IRN78 Hydroxide form, in order to receive **[FC_2C_1im][OH]** intermediate. Then this was mixed with aqueous HBr solution, until pH was 7. Water was removed in vacuo to receive a colourless viscous liquid.
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.28 (s, 1H, imC(2)**H**), 7.84 (t, J = 1.60, 1H, imC(4)**H**), 7.79 (t, J = 1.65, 1H, imC(5)**H**), 4.81 (dt, $^2J_{H/F}$ = 47.0 Hz, $^3J_{H/H}$ = 4.6 Hz, 2H, ethyl – C(2)***H₂***F), 4.59 (dt, $^3J_{H/F}$ = 27.0 Hz, $^3J_{H/H}$ = 4.62 Hz, 2H, ethyl – C(1)***H₂***), 3.89 (s, 3H, methyl – C**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 137.02 (imC(2)), 123.74 (imC(4)), 122.55 (imC(5)), 82.5 & 80.9 (ethyl – **C(2)**F), 49.38 & 49.19 (ethyl – C(1)), 35.87 (methyl – C(1)).
m/z (ES^+) : 129.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 33.63(34.47), H – 6.19(4.82), N – 12.73(12.34).

[$FC_2C_1C_1$im]I. 1-fluoro-2-iodoethane (20 mL, 245.6 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (19.7 g, 204.7 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a white solid (47.5 g, 176 mmol, 86 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.86 (d, J = 2.12, 1H, imC(4)**H**), 7.75 (d, J = 2.08, 1H, imC(5)**H**), 4.76 (dt, $^2J_{H/F}$ = 46.8 Hz, $^3J_{H/H}$ = 4.4 Hz, 2H, ethyl – C(2)***H₂***F), 4.53 (dt, $^3J_{H/F}$ = 27.6 Hz, $^3J_{H/H}$ = 4.8 Hz, 2H, ethyl – C(1)***H₂***), 3.88 (s, 3H, methyl – C**H₃**), 2.6 (s, 3H, imC(2')**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.05 (imC(2)), 122.5 (imC(4)), 121.25 (imC(5)), 82.69 & 81.02 (ethyl – **C(2)**F), 48.06 & 47.87 (ethyl – C(1)), 34.83 (methyl – C(1)), 9.37 (imC(2').
m/z (ES^+) : 143.1 (100 %, M^+).
m/z (ES^-) : 129 (100 %, M^-).
Elemental analysis (calculated): C – 33.63(34.47), H – 6.19(4.82), N – 12.73(12.34).

[$FC_2C_1C_1$im]Br. An aqueous solution of **[FC_2C_1im]I** passed through ion exchange column packed with Amberlite IRN78 Hydroxide form, in order to receive **[$FC_2C_1C_1$im][OH]** intermediate. Then this was mixed with aqueous HBr solution, until pH was 7. Water was removed in vacuo to receive a colourless viscous liquid.
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.69 (d, J = 2.12, 1H, imC(4)**H**), 7.67 (d, J = 2.08, 1H, imC(5)**H**), 4.79 (dt, $^2J_{H/F}$ = 46.8 Hz, $^3J_{H/H}$ = 4.4 Hz, 2H, ethyl – C(2)***H₂***F), 4.55 (dt, $^3J_{H/F}$ = 27.6 Hz, $^3J_{H/H}$ = 4.8 Hz, 2H, ethyl – C(1)***H₂***), 3.78 (s, 3H, methyl – C**H₃**), 2.6 (s, 3H, imC(2')**H₃**).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.08 (imC(2)), 122.50 (imC(4)), 121.22 (imC(5)), 82.85 & 81.18 (ethyl – **C(2)**F), 48.1 & 47.91 (ethyl – C(1)), 34.99 (methyl – C(1)), 9.72 (imC(2')).
m/z (ES^+) : 143.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 33.63(34.47), H – 6.19(4.82), N – 12.73(12.34).

[HC≡C_2C_1im]Br. 80 wt.% propargyl bromide in toluene (20 mL, 179.6 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (11.9 mL, 149.7 mmol, 1 eq.) in ethyl acetate (80 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (21.7 g, 107.8 mmol, 72 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.25 (s, 1H, imC(2)**H**), 7.81 (t, J = 1.81, 1H, imC(4)**H**), 7.77 (t, J = 1.76, 1H, imC(5)**H**), 5.22 (d, J = 2.57 Hz, 2H, propargyl – C(1)**H_2**), 3.88 (s, 3H, methyl – C**H_3**), 3.86 (t, J = 2.59 Hz, 1H, propargyl – C(3)**H**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.59 (imC(2)), 124.06 (imC(4)), 122.15 (imC(5)), 78.97 (propargyl – C(2)), 76.17 (propargyl – C(3)), 38.50 (propargyl – C(1)), 35.99 (methyl – C(1)).
m/z (ES^+) : 121.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 41.41(41.82), H – 5.29(4.51), N –13.2(13.93).

[HC≡$C_2C_1C_1$im]Br. 80 wt.% propargyl bromide in toluene (20 mL, 179.6 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (14.4 g, 149.7 mmol, 1 eq.) in ethyl acetate (80 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (24.8 g, 115.3 mmol, 77 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.70 (d, J = 2.13, 1H, imC(4)**H**), 7.67 (t, J = 2.12, 1H, imC(5)**H**), 5.18 (d, J = 2.58 Hz, 2H, propargyl – C(1)**H_2**), 3.79 (t, J = 2.60 Hz, 1H, propargyl – C(3)**H**), 3.78 (s, 3H, methyl – C**H_3**), 2.63 (s, 3H, imC(2')**H_3**) .
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 144.79 (imC(2)), 122.61 (imC(4)), 120.72 (imC(5)), 78.41 (propargyl – C(2)), 76.07 (propargyl – C(3)), 37.43 (propargyl – C(1)), 34.90 (methyl – C(1)), 9.44 (imC(2')).
m/z (ES^+) : 135.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 44.17(44.67), H – 5.25(5.15), N – 12.57(13.02).

[N≡C_2C_1im]Cl. Chloroacetonitrile (10 mL, 158 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (10.5 mL, 131.7 mmol, 1 eq.) in ethyl acetate (60 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (18.9 g, 119.8 mmol, 91 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.44 (s, 1H, imC(2)**H**), 7.96 (t, J = 1.83, 1H, imC(4)**H**), 7.84 (t, J = 1.83, 1H, imC(5)**H**), 5.73 (s, 2H, ethyl – C(1)**H_2**), 3.90 (s, 3H, methyl – C**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 137.8 (imC(2)), 124.35 (imC(4)), 122.57 (imC(5)), 114.89 (ethanenitryl – **C**≡N), 36.77 (ethanenitryl – C(1)), 35.17 (methyl – C(1)).

m/z (ES^+) : 122.1 (100 %, M^+).
m/z (ES^-) : 35 (100 %, M^-).
Elemental analysis (calculated): C – 45.62(45.73), H – 5.27(5.12), N – 25.9(26.66).

[N≡C_2C_1im]Br. Bromoacetonitrile (20 mL, 287.1 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (19 mL, 239.2 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (41.5 g, 205.7 mmol, 86 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.35 (s, 1H, imC(2)**H**), 7.94 (t, J = 1.83, 1H, imC(4)**H**), 7.84 (t, J = 1.77, 1H, imC(5)**H**), 5.69 (s, 2H, acetonitryl – C(1)$\mathbf{H_2}$), 3.90 (s, 3H, methyl – C$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 137.68 (imC(2)), 124.35 (imC(4)), 122.53 (imC(5)), 114.79 (ethanenitryl – **C**≡N), 36.87 (ethanenitryl – C(1)), 36.2 (methyl – C(1)).
m/z (ES^+) : 122.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 36.24(35.67), H – 4.28(3.99), N – 20.52(20.8).

[N≡$C_2C_1C_1$im]Cl. Chloroacetonitrile (10 mL, 158 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (12.6 g, 131.7 mmol, 1 eq.) in ethyl acetate (60 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (18.9 g, 115.9 mmol, 88 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.79 (d, J = 2.16, 1H, imC(4)**H**), 7.72 (d, J = 2.16, 1H, imC(5)**H**), 5.56 (s, 2H, acetonitryl – C(1)$\mathbf{H_2}$), 3.78 (s, 3H, methyl – C$\mathbf{H_3}$), 2.66 (s, 3H, imC(2')$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.94 (imC(2)), 123.06 (imC(4)), 121.17 (imC(5)), 114.41 (ethanenitryl – **C**≡N), 36.63 (ethanenitryl – C(1)), 35.05 (methyl – C(1)), 9.54 (imC(2')).
m/z (ES^+) : 136.1 (100 %, M^+).
m/z (ES^-) : 34.9 (100 %, M^-).
Elemental analysis (calculated): C – 48.58(48.99), H – 6.6(5.87), N – 23.62(24.48).

[N≡$C_2C_1C_1$im]Br. Bromoacetonitrile (20 mL, 287.1 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (23 g, 239.2 mmol, 1 eq.) in ethyl acetate (100 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield an off-white solid (41.8 g, 193.7 mmol, 81 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.81 (d, J = 2.16, 1H, imC(4)**H**), 7.75 (d, J = 2.16, 1H, imC(5)**H**), 5.68 (s, 2H, acetonitryl – C(1)$\mathbf{H_2}$), 3.79 (s, 3H, methyl – C$\mathbf{H_3}$), 2.67 (s, 3H, imC(2')$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.98 (imC(2)), 123.08 (imC(4)), 121.14 (imC(5)), 114.46 (ethanenitryl – **C**≡N), 35.77 (ethanenitryl – C(1)), 35.14 (methyl – C(1)), 9.72 (imC(2')).
m/z (ES^+) : 136.1 (100 %, M^+).
m/z (ES^-) : 80.9 (100 %, M^-).
Elemental analysis (calculated): C – 39.43(38.91), H – 5.05(4.66), N – 19.14(19.45).

Synthesis of Alkyl-imidazolium Bis(trifluoromethylsulfonyl)imides ([NTf_2])
General Procedure

1.1 eq. of lithium bis(trifluoromethylsulfonyl)imide was slowly added to a stirring solution of 1 eq. of alkylimidazolium halide in dichloromethane and was left stirring for 24 h. The resulting dispersion was filtered, in order to remove the precipitating lithium halide salt. The dichloromethane phase was washed with de-ionised water, until the aqueous phase was halide negative by silver nitrate test. Dichloromethane was dried over $MgSO_4$ and evaporated in vacuo. The IL was dried overnight in vacuo. All ILs were stored under dry nitrogen atmosphere.

[C_2C_1im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (16.5 g, 57.5 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_2C_1im]Br (10 g, 52.3 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (18.8 g, 48.1 mmol, 92 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.1 (s, 1H, im C(2)**H**), 7.76 (t, J = 1.78 Hz, 1H, im C(4)**H**)), 4.18 (q, J = 7.31 Hz, 2H, ethyl – C(1)**H_2**), 3.84 (s, 3H, methyl – C**H_3**), 1.41 (t, J=7.32 Hz, 3H, ethyl – C**H_3**). .
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm) : 136.24 (imC(2)), 124.29 (imC(4)), 121.95 (imC(5)), 119.5 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 44.14 (ethyl – C(1)), 35.67 (methyl – C(1)), 15.04 (ethyl – C(2)).
m/z (ES^+) : 111.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[$C_2C_1C_1$im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (15.4 g, 53.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_2C_1C_1$im]Br (10 g, 48.7 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (18.5 g, 45.8 mmol, 94 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.65 (d, J = 2.09 Hz, 1H, imC(4)**H**), 7.60 (d, J = 2.09 Hz, 1H, imC(5)**H**), 4.13 (q, J = 7.29 Hz, 2H, ethyl – C(1)**H_2**), 3.74 (s, 3H, methyl – C**H_3**), 2.58 (s, 3H, imC(2')**H_3**), 1.33 (t, J = 7.29 Hz, 3H, ethyl – C**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 144.02 (imC(2)), 122.34 (imC(4)), 121.08 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 120.27 (imC(5)), 42.76 (ethyl – C(1)), 34.57 (methyl – C(1)), 14.75 (ethyl – C(2)), 8.96 (imC(2')).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[C_3C_1im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (15.3 g, 53.5 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_3C_1im]Br (10 g, 48.7 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (17.9 g, 44.3 mmol, 91 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.09 (s, 1H, imC(2)**H**), 7.76 (t, J = 1.76, 1H, imC(4)**H**), 7.70 (t, J = 1.73, 1H, imC(5)**H**), 4.12 (t, J = 7.09 Hz, 2H, propyl – C(1)**H_2**), 3.85 (s,

3H, methyl – C**H₃**), 1.84-1.75 (m, 2H, propyl – C(2)**H₂**), 0.85 (t, J=7.39 Hz, 3H, propyl - C(3)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.49 (imC(2)), 123.62 (imC(4)), 122.25 (imC(5)), 119.47 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 50.27 (propyl – C(1)), 35.73 (methyl – C(1)), 22.82 (propyl – C(2)), 10.38 (propyl – C(3)).
m/z (ES^+) : 530.1 (100 %, $[2M^+ + M^-]^+$) 125.1 (25 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[HOC_2C_1im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (15.2 g, 53.1 mmol, 1.1 eq.) was slowly added to a stirring solution of [HOC_2C_1im]Br (10 g, 48.3 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (18.1 g, 44.3 mmol, 93 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.07 (s, 1H, imC(2)**H**), 7.71 (t, J = 1.76, 1H, imC(4)**H**), 7.68 (t, J = 1.74, 1H, imC(5)**H**), 5.17 (t, J = 5.22 Hz, 1H, ethyl – OH), 4.20 (m, 2H, ethyl – C(1)**H₂**), 3.86 (s, 3H, methyl – C**H₃**), 3.73-3.70 (m, 2H, ethyl – C(2)**H₂**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.81 (imC(2)), 123.34 (imC(4)), 121.08 (imC(5)), 119.48 (q, J_{CF} = 322 Hz, 2C, NTf_2), 59.31 (ethyl – C(1)), 51.62 (ethyl – C(2)), 35.65 (methyl – C(1)).
m/z (ES^+) : 534.1 (100 %, $[2M^+ + M^-]^+$) 127.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[$C_{2,1}C_1$im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (15.3 g, 53.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_{2,1}C_1$im]Br (10 g, 48.8 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (17.8 g, 44.9 mmol, 90 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.17 (s, 1H, imC(2)**H**), 7.87 (t, J = 1.80, 1H, imC(4)**H**), 7.71 (t, J = 1.72, 1H, imC(5)**H**), 4.66 - 4.56 (m, 1H, isopropyl – C(1)**H**), 3.83 (s, 3H, methyl – C**H₃**), 1.46 (d, J = 6.69 Hz, 6H, isopropyl – C(2)**H₃** & C(3)**H₃**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 135.31 (imC(2)), 123.65 (imC(4)), 120.42 (imC(5)), 119.47 (q, J_{CF} = 321.8 Hz, 2C, NTf_2), 52.13 (isopropyl – C(1)), 35.69 (methyl – C(1)), 22.29 (isopropyl – C(2) & C(3)), 9.28 (im(C2').
m/z (ES^+) : 125.1 (100 %, M^+), 295.2 (50 %, $[2M^+ + EtO^-]^+$)
m/z (ES^-) : 279.8 (100 %, M^-).

[C_2C_2im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (15.3 g, 53.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_2C_2im]Br (10 g, 48.8 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (17.8 g, 44.9 mmol, 91 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.18 (s, 1H, imC(2)**H**), 7.79 (d, 2H, imC(4)**H** & imC(5)**H**), 4.18 (q, J = 7.34 Hz, 4H, 2 x ethyl – C(1)**H₂**), 1.42 (t, J = 7.27 Hz, 6H, 2 x ethyl – C(2)**H₃**).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 135.40 (imC(2)), 122.10 (imC(4) & imC(5)), 119.51 (q, J_{CF} = 321.6 Hz, 2C, NTf_2), 44.21 (ethyl – C(1)), 14.41 (ethyl – C(2)).
m/z (ES^+) : 125.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[$C_{2,1}C_1C_1$im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (14.4 g, 50.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_{2,1}C_1C_1$im]Br (10 g, 45.6 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a white solid (17.7 g, 42.4 mmol, 93 % yield, m.p. 30^{o}C).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.79 (d, J = 2.19 Hz, 1H, imC(4)**H**), 7.65 (d, J = 2.17 Hz, 1H, imC(5)**H**), 4.71 – 4.61 (m, 1H, isopropyl – C(1)**H**), 3.74 (s, 3H, methyl – C**H_3**), 2.61 (s, 3H, imC(2')**H_3**), 1.41 (d, J = 6.65 Hz, 6H, isopropyl – C(2)**H_3** & C(3)**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 143.50 (imC(2)), 122.76 (imC(4)), 119.47 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 117.24 (imC(5)), 49.94 (ethyl – C(1)), 34.5 (methyl – C(1)), 21.86 (ethyl – C(2)), 9.12 (imC(2')).
m/z (ES^+) : 558.2 (100 %, $[2M^+ + M^-]^+$) 139.1 (75 %, M^+)
m/z (ES^-) : 279.8 (100 %, M^-).

[FC_2C_1im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (12.3 g, 42.9 mmol, 1.1 eq.) was slowly added to a stirring solution of [FC_2C_1im]I (10 g, 39 mmol, 1 eq.) in water. The reaction mixture was left stirring for 24h at room temperature. The resulting two-phase system was extracted 3 times with 10 mL of DCM and the combined organic phases were washed with water until the $AgNO_3$ test of the aqueous phase was negative. The organic phase was dried over $MgSO_4$ and then DCM was evaporated in vacuo. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (13.8 g, 33.9 mmol, 87 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.14 (s, 1H, imC(2)**H**), 7.77 (t, J = 1.71, 1H, imC(4)**H**), 7.73 (t, J = 1.75, 1H, imC(5)**H**), 4.80 (dt, $^2J_{H/F}$ = 47.0 Hz, $^3J_{H/H}$ = 4.4 Hz, 2H, ethyl – C(2)**H_2**F), 4.54 (dt, $^3J_{H/F}$ = 28.0 Hz, $^3J_{H/H}$ = 4.8 Hz, 2H, ethyl – C(1)**H_2**), 3.88 (s, 3H, methyl – C**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 137.01 (imC(2)), 123.77 (imC(4)), 122.57 (imC(5)), 119.48 (q, J_{CF} = 321.8 Hz, 2C, NTf_2), 82.5 & 80.53 (ethyl – **C(2)**F), 49.41 & 49.22 (ethyl – C(1)), 35.82 (methyl – C(1)).
m/z (ES^+) : 129.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[$FC_2C_1C_1$im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (11.7 g, 40.7 mmol, 1.1 eq.) was slowly added to a stirring solution of [$FC_2C_1C_1$im]I (10 g, 37 mmol, 1 eq.) in water. The reaction mixture was left stirring for 24h at room temperature. The resulting two-phase system was extracted 3 times with 10 mL of DCM and the combined organic phases were washed with water until the $AgNO_3$ test of the aqueous phase was negative. The organic phase was dried over $MgSO_4$ and then DCM was evaporated in vacuo. After the

purification steps, the IL was dried overnight on the Schlenk Line to yield a white solid (14 g, 32.9 mmol, 89 % yield, m.p. 32 °C).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.66 – 7.63 (overlapping d, imC(4)**H** and imC(5)**H**), 4.75 (dt, $^{2}J_{H/F}$ = 47 Hz, $^{3}J_{H/H}$ = 4.4 Hz, 2H, ethyl – C(2)**H$_2$**F), 4.52 (dt, $^{3}J_{H/F}$ = 27.6 Hz, $^{3}J_{H/H}$ = 4.8 Hz, 2H, ethyl – C(1)**H$_2$**), 3.77 (s, 3H, methyl – C**H$_3$**), 2.59 (s, 3H, imC(2')**H$_3$**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.06 (imC(2)), 122.5 (imC(4)), 121.26 (imC(5)), 119.48 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 82.67 & 81.00 (ethyl – **C(2)**F), 48.06 & 47.87 (ethyl – C(1)), 34.78 (methyl – C(1)), 9.28 (imC(2').
m/z (ES^+) : 143.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[HC≡C$_2$C$_1$im][NTf$_2$]. Lithium bis(trifluoromethylsulfonyl)imide (15.7 g, 54.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [HC≡C_2C_1im]Br (10 g, 49.7 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (18.4 g, 46.2 mmol, 93 % yield).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.19 (s, 1H, imC(2)**H**), 7.78 (t, J = 1.81, 1H, imC(4)**H**), 7.74 (t, J = 1.76, 1H, imC(5)**H**), 5.18 (d, J = 2.57 Hz, 2H, propargyl – C(1)**H$_2$**), 3.87 (s, 3H, methyl – C**H$_3$**), 3.84 (t, J = 2.59 Hz, 1H, propargyl – C(3)**H**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 136.62 (imC(2)), 124.06 (imC(4)), 122.16 (imC(5)), 119.48 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 78.94 (propargyl – C(2)), 76.13 (propargyl – C(3)), 38.49 (propargyl – C(1)), 35.96 (methyl – C(1)).
m/z (ES^+) : 121.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).
[HC≡C$_2$C$_1$C$_1$im][NTf$_2$]. Lithium bis(trifluoromethylsulfonyl)imide (14.7 g, 51.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [HC≡$C_2C_1C_1$im]Br (10 g, 46.5 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a white solid (18.1 g, 43.7 mmol, 94 % yield, m.p. 39 °C).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.68 (d, J = 2.13, 1H, imC(4)**H**), 7.65 (t, J = 2.12, 1H, imC(5)**H**), 5.15 (d, J = 2.57 Hz, 2H, propargyl – C(1)**H$_2$**), 3.78 – 3.76 (overlapping peaks, 4H, propargyl – C(3)**H** and methyl – C**H$_3$**), 2.62 (s, 3H, imC(2')**H$_3$**) .
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 144.79 (imC(2)), 112.61 (imC(4)), 120.73 (imC(5)), 119.48 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 78.40 (propargyl – C(2)), 76.05 (propargyl – C(3)), 37.40 (propargyl – C(1)), 34.87 (methyl – C(1)), 9.36 (imC(2')).
m/z (ES^+) : 135.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[N≡C$_2$C$_1$im][NTf$_2$]. Lithium bis(trifluoromethylsulfonyl)imide (15.6 g, 54.4 mmol, 1.1 eq.) was slowly added to a stirring solution of [N≡C_2C_1im]Br (10 g, 49.5 mmol, 1 eq.) in DCM according to the general procedure. After the purification steps, the IL was dried overnight on the Schlenk Line to yield a viscous colourless liquid (17.2 g, 43 mmol, 87 % yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 9.23 (s, 1H, imC(2)**H**)z, 7.88 (t, J = 1.83, 1H, imC(4)**H**), 7.78 (t, J = 1.77, 1H, imC(5)**H**), 5.56 (s, 2H, ethanenitryl – C(1)**H_2**), 3.88 (s, 3H, methyl – C**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 137.75 (imC(2)), 124.37 (imC(4)), 122.59 (imC(5)), 119.48 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 114.74 (ethanenitryl – **C**≡N), 36.82 (ethanenitryl – C(1)), 36.14 (methyl – C(1)).
m/z (ES^+) : 122.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

[N≡$C_2C_1C_1$im][NTf_2] Lithium bis(trifluoromethylsulfonyl)imide (14.6 g, 51 mmol, 1.1 eq.) was slowly added to a stirring solution of [N≡$C_2C_1C_1$im]Br (10 g, 46.3 mmol, 1 eq.) in water. The reaction mixture was left stirring for 24h at room temperature. The resulting dispersion was filtered and washed with water until the $AgNO_3$ test of the aqueous phase was negative. The IL was dried overnight on the Schlenk Line to yield a white solid (18.2 g, 43.9 mmol, 95 % yield, m.p. 70 ^{o}C).
^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm): 7.74 (d, J = 2.17, 1H, imC(4)**H**), 7.69 (d, J = 2.17, 1H, imC(5)**H**), 5.56 (s, 2H, ethanenitryl – C(1)**H_2**), 3.77 (s, 3H, methyl – C**H_3**), 2.65 (s, 3H, imC(2')**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δ_C (ppm): 145.96 (imC(2)), 123.08 (imC(4)), 121.18 (imC(5)), 119.48 (q, J_{CF} = 321.9 Hz, 2C, NTf_2), 114.41 (ethanenitryl – **C**≡N), 35.65 (ethanenitryl – C(1)), 35.06 (methyl – C(1)), 9.50 (imC(2')).
m/z (ES^+) : 136.1 (100 %, M^+).
m/z (ES^-) : 279.8 (100 %, M^-).

NMR spectra

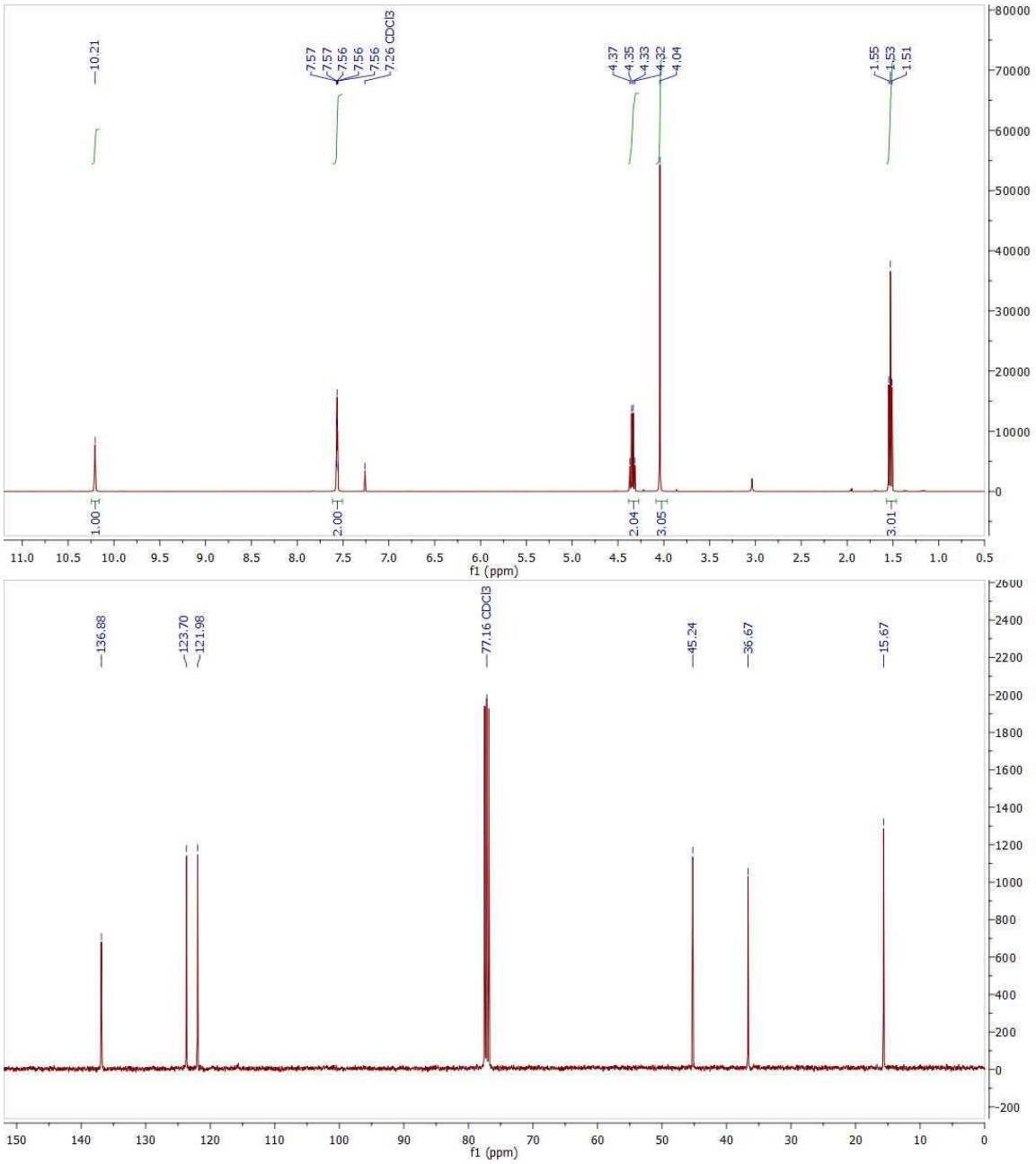


Figure S1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_2C_1im]Br$.

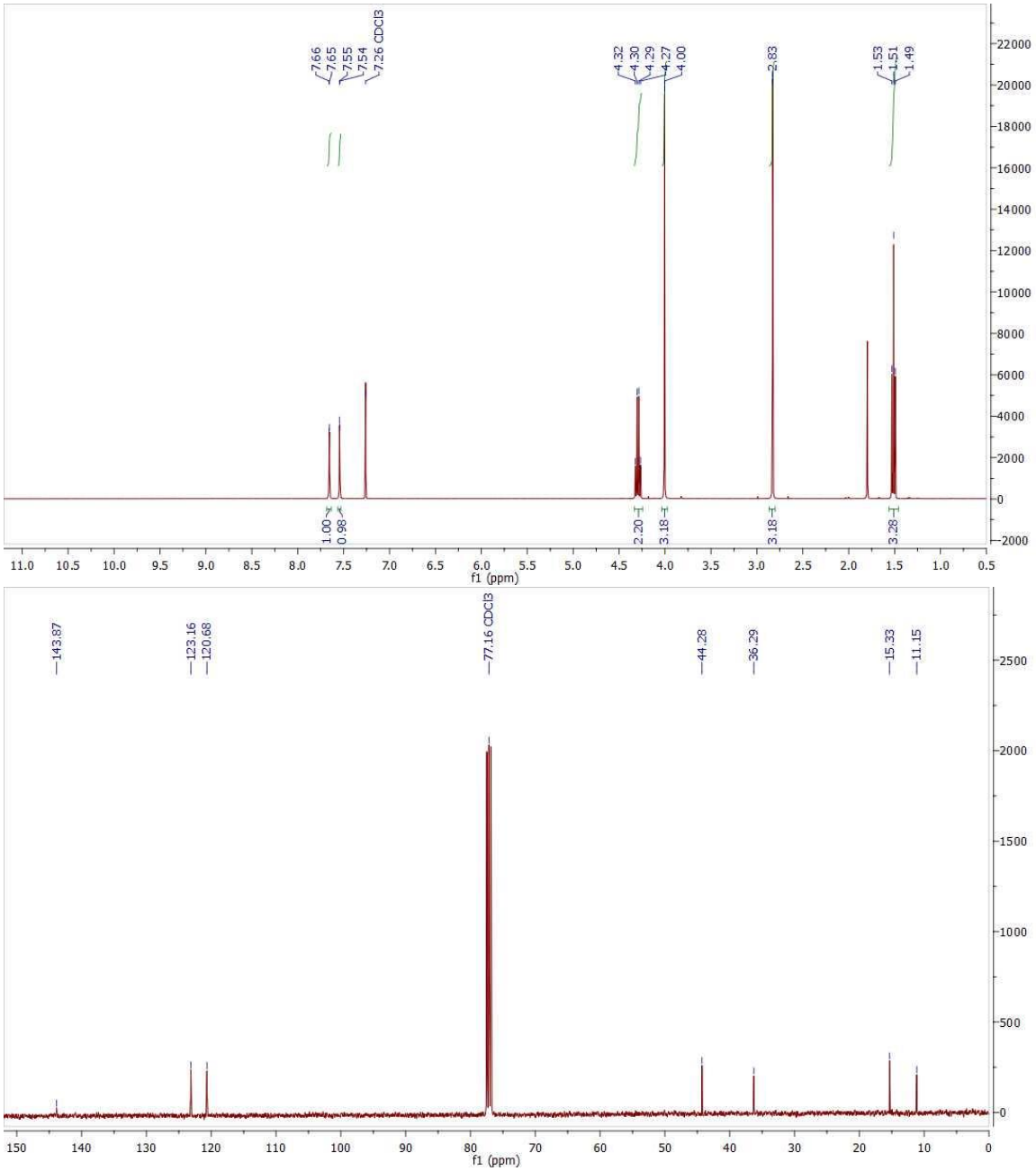


Figure S2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_2C_1C_1im]Br$.

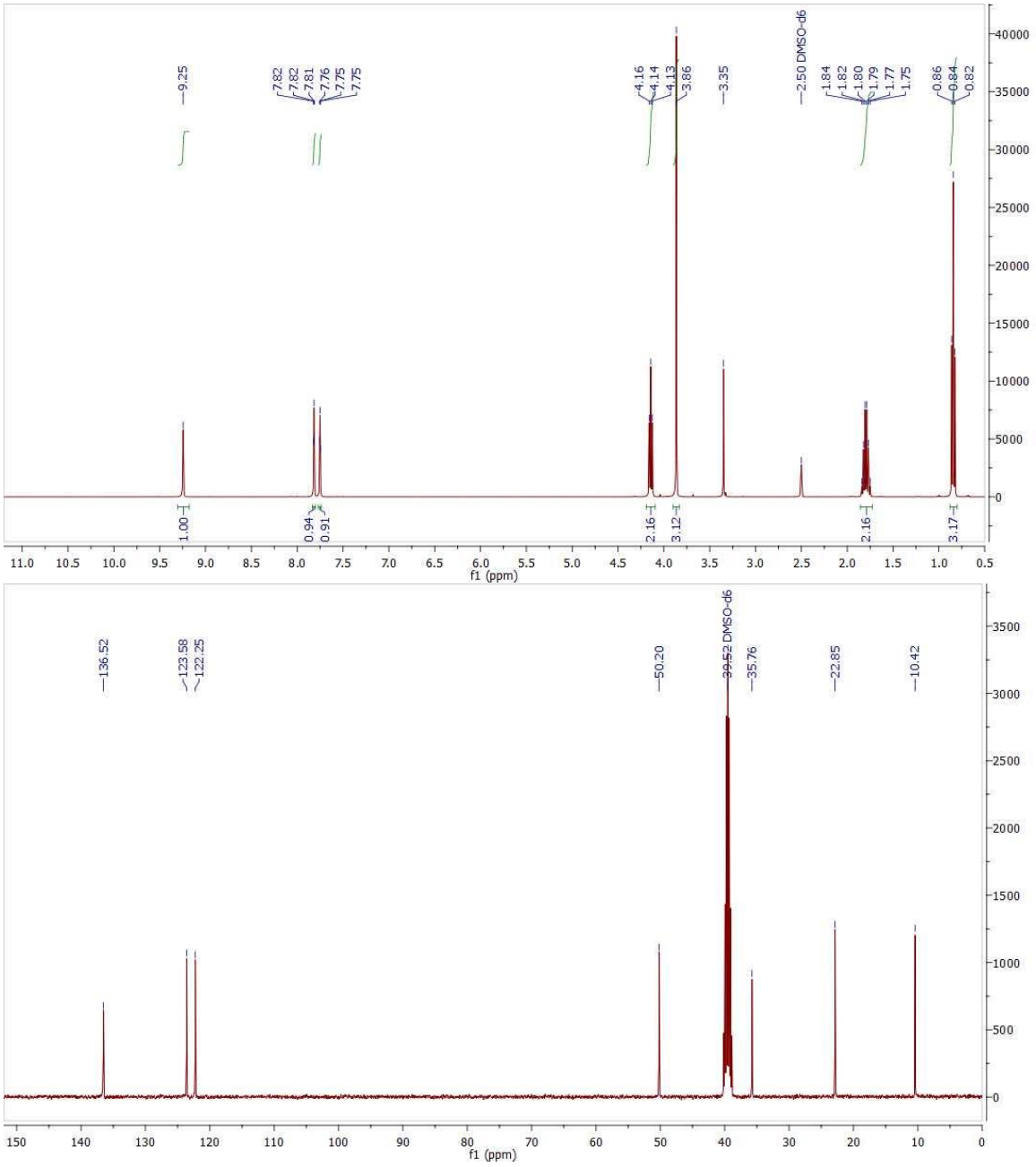


Figure S3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_3C_1im]Br$.

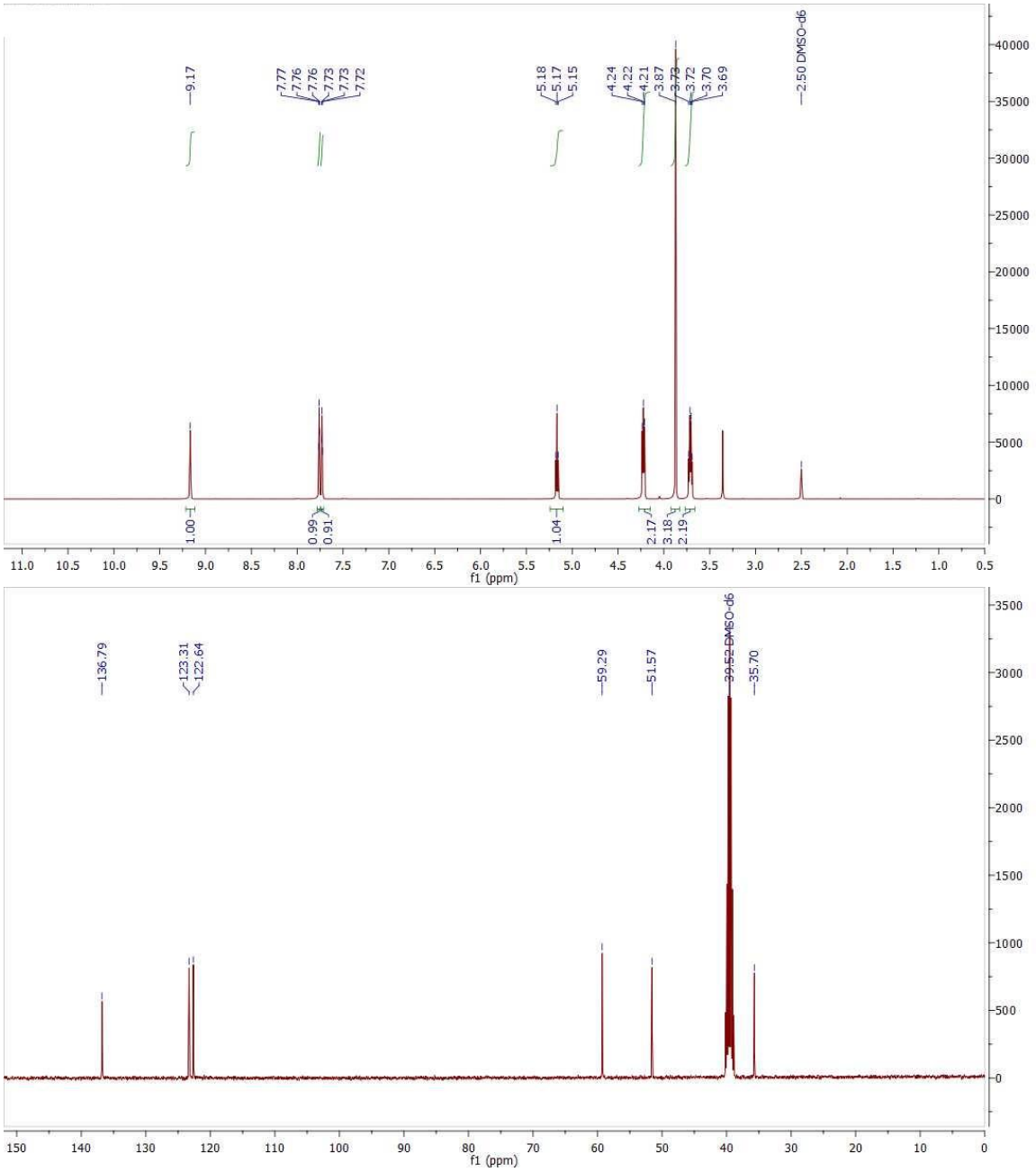


Figure S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[HOC_2C_1im]Br$.

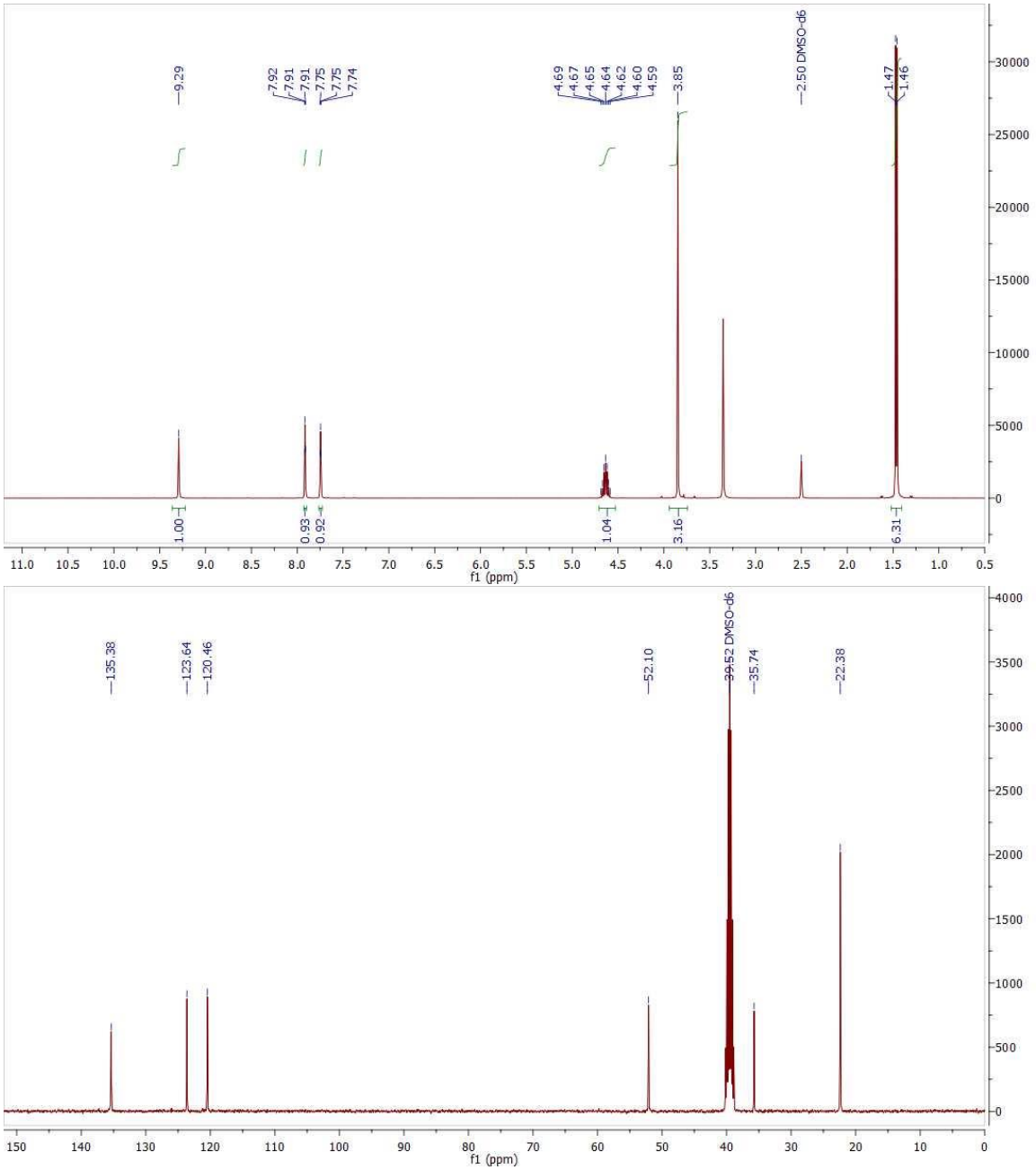


Figure S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_{2,1}C_1im]Br$.

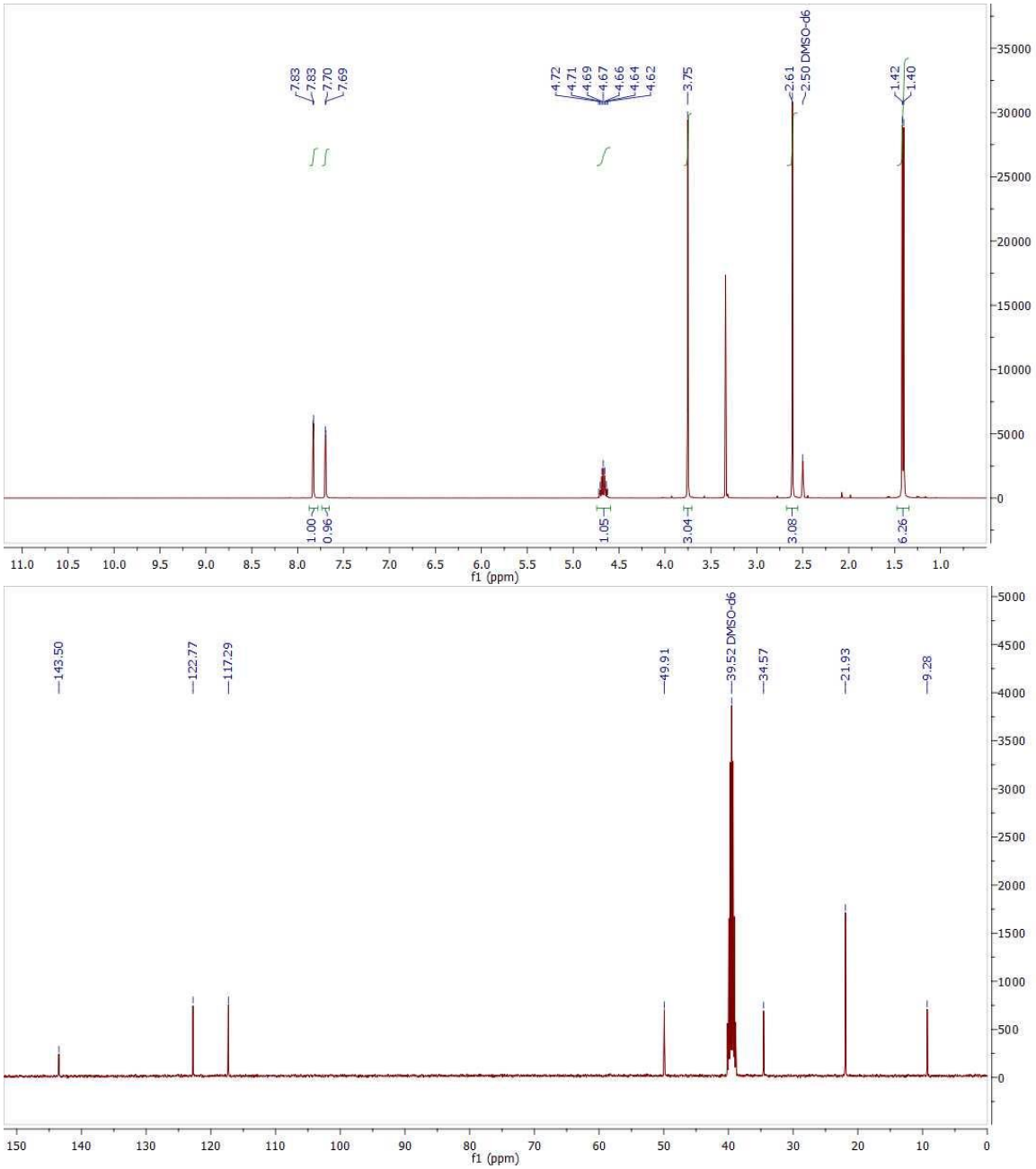


Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_{2,1}C_1C_1im]Br$.

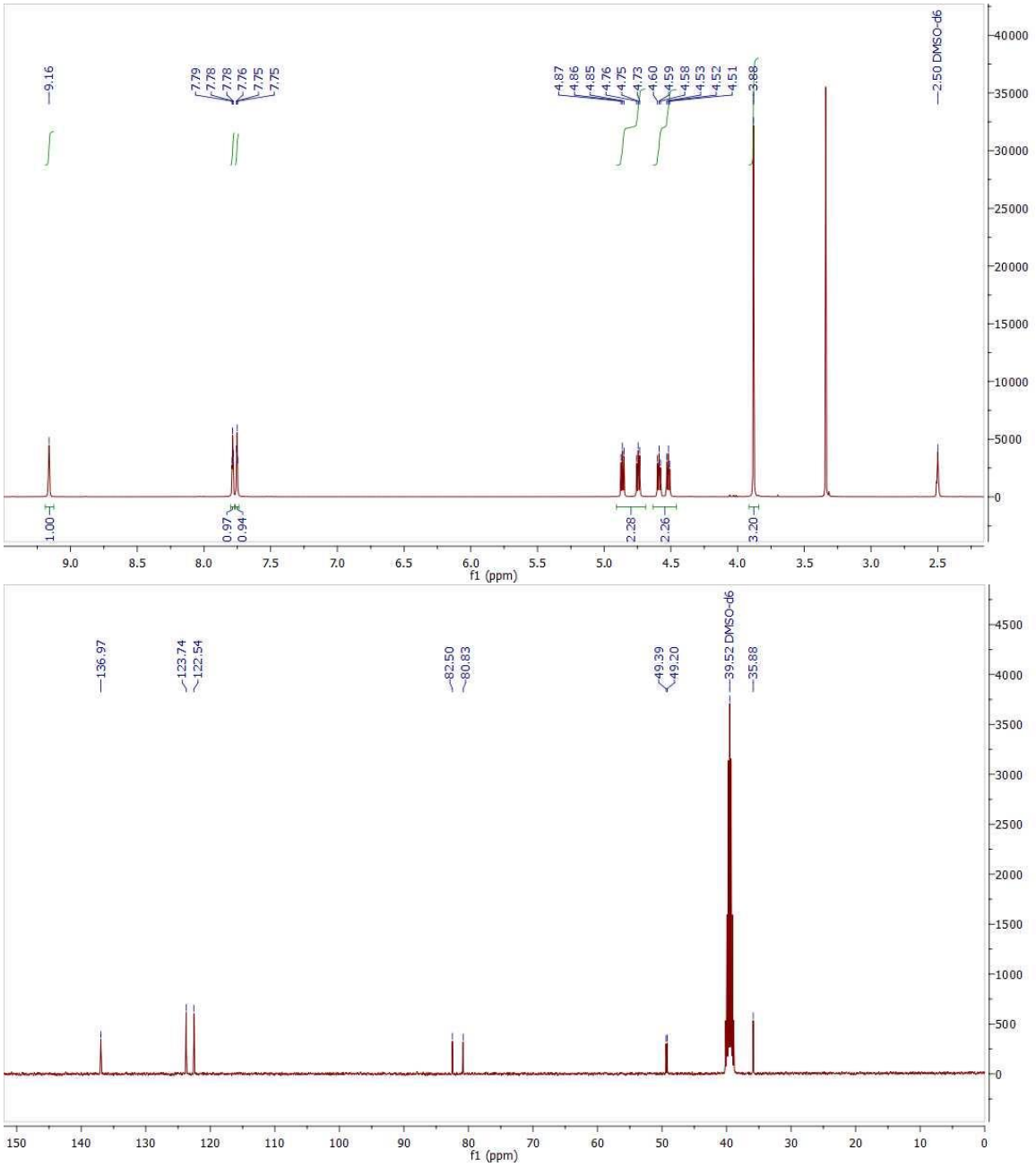


Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1im]I$.

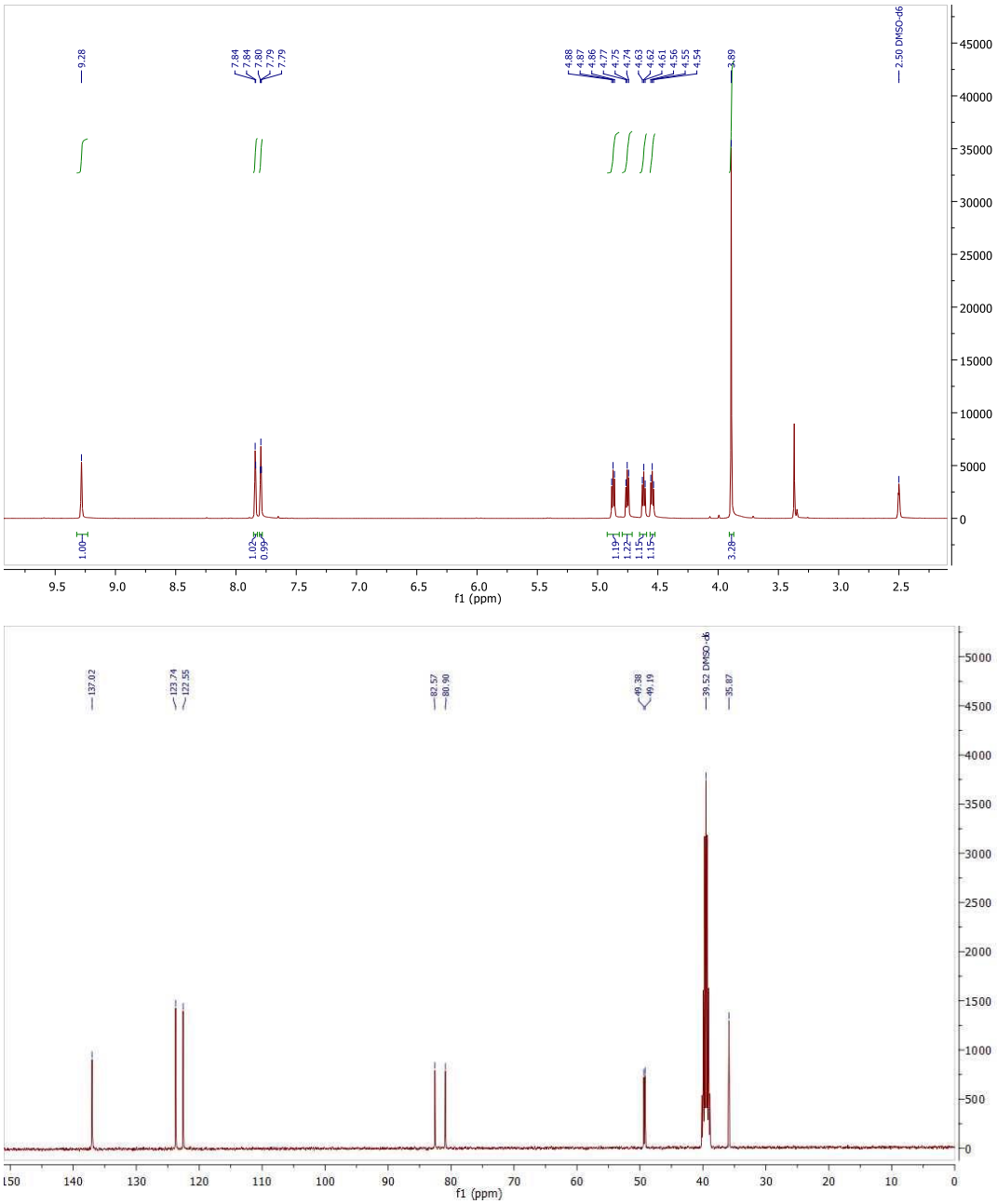


Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1im]Br$.

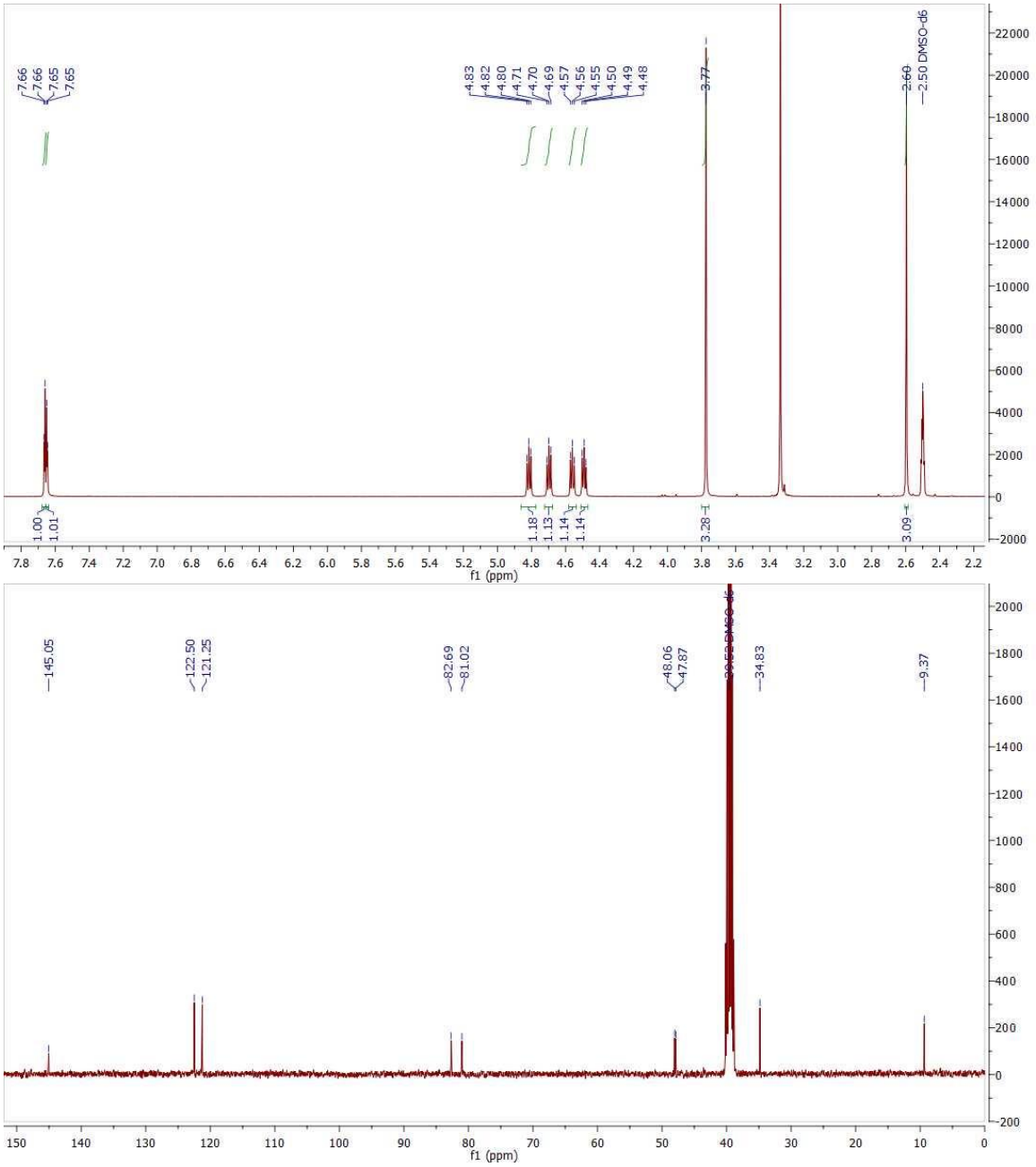


Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1C_1im]I$.

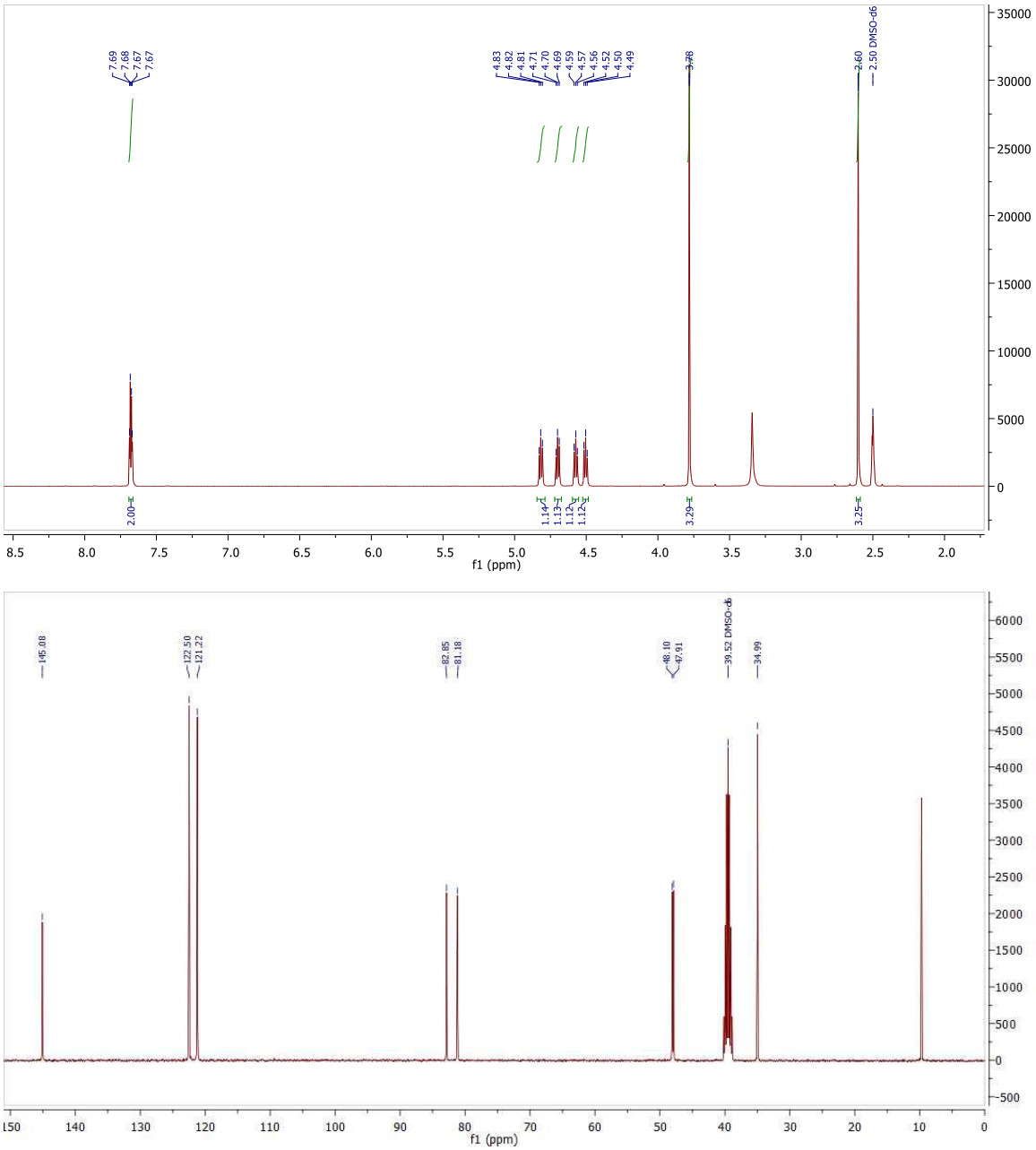


Figure S10. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1C_1im]Br$.

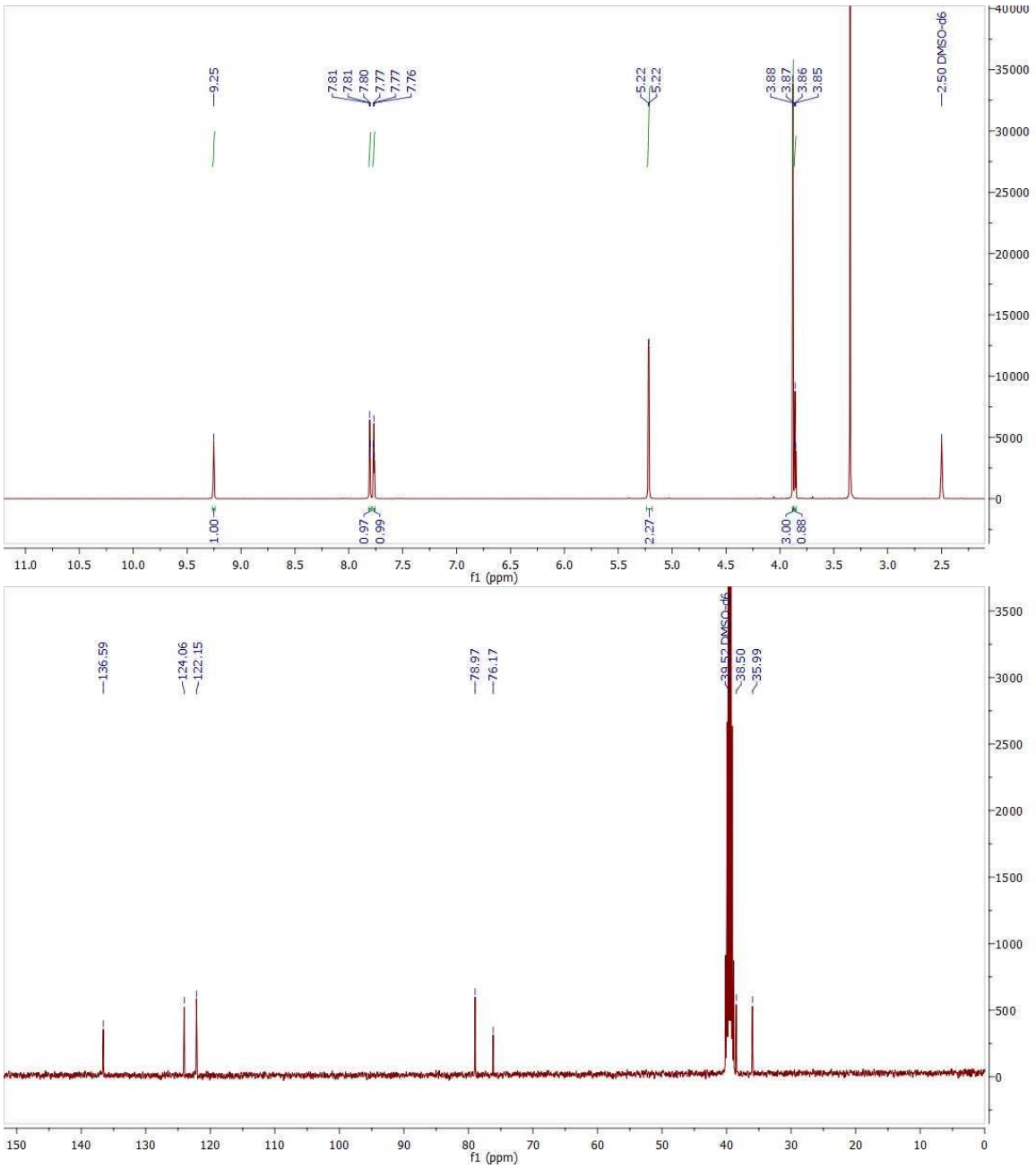


Figure S11. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [HC≡C_2C_1im]Br.

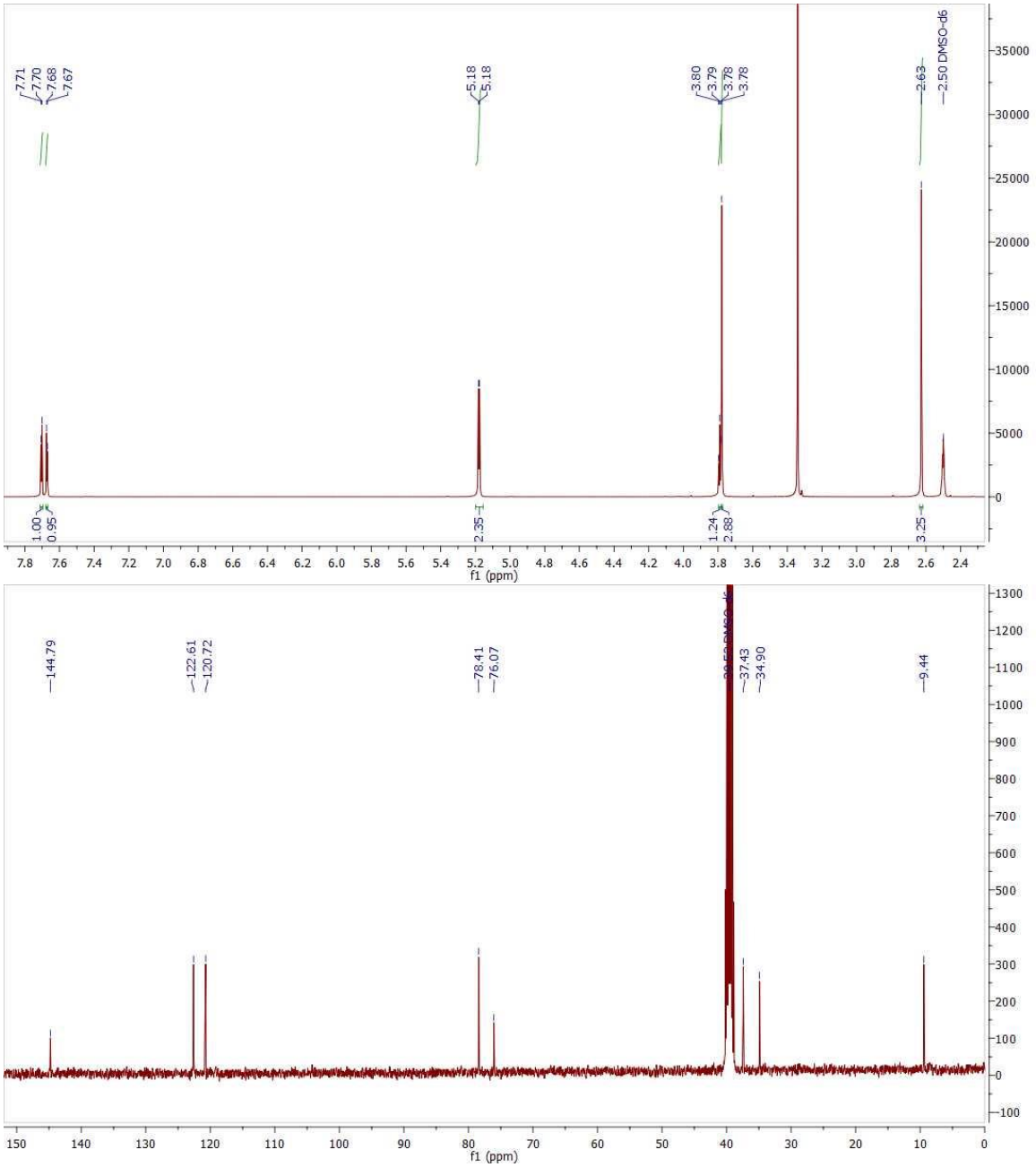


Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [HC≡$C_2C_1C_1$im]Br.

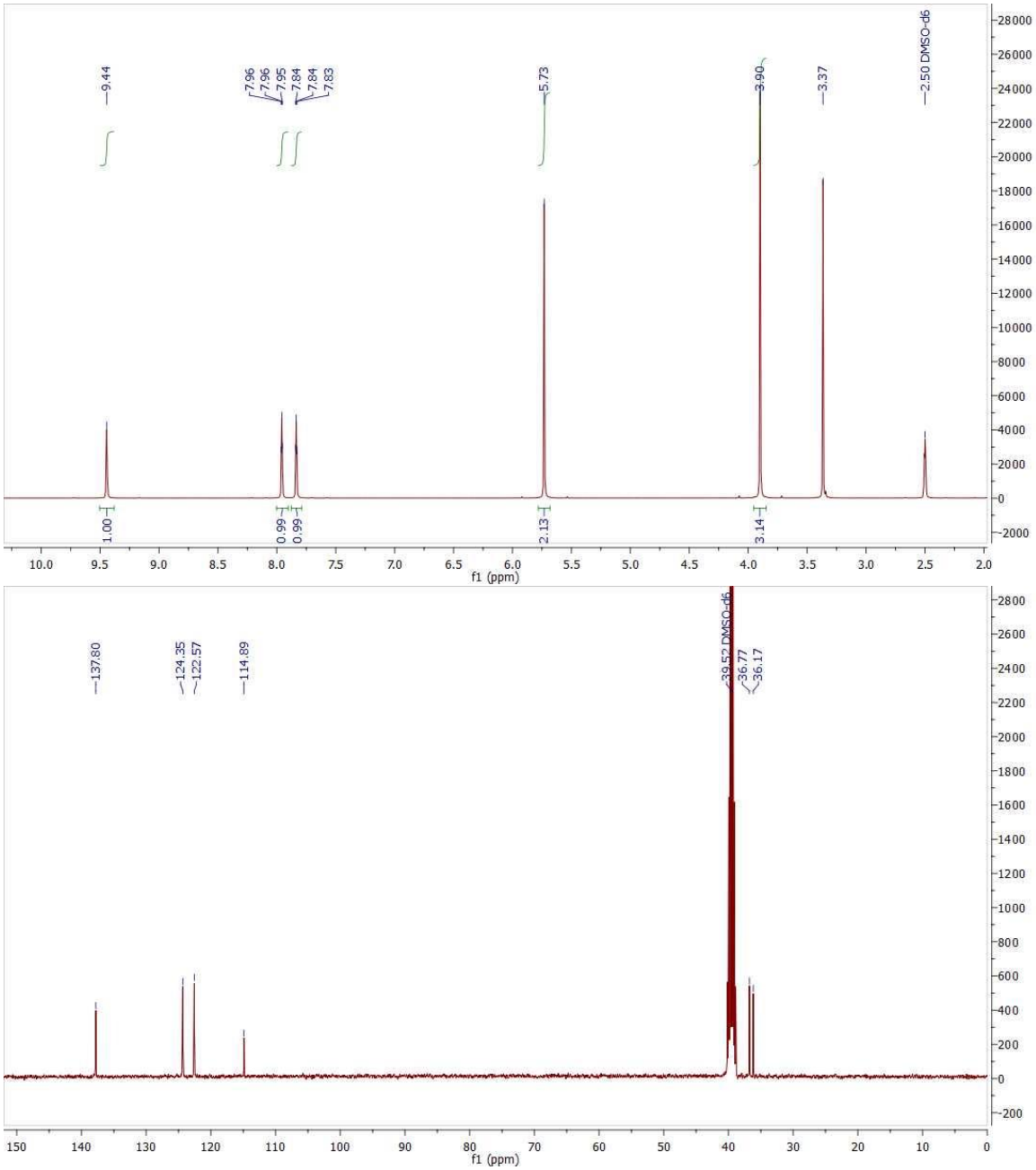


Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [N≡C_2C_1im]Cl.

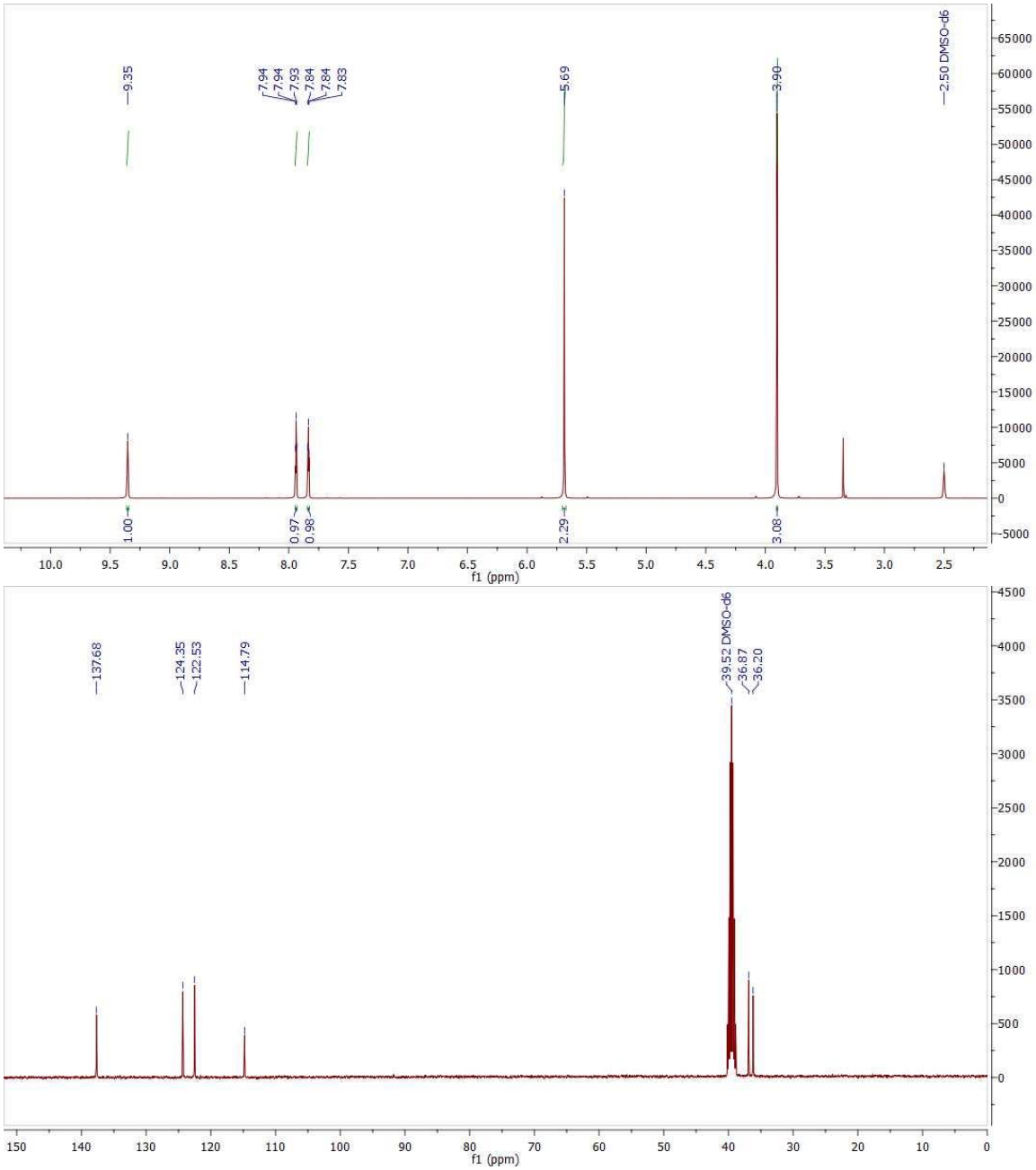


Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [N≡C_2C_1im]Br.

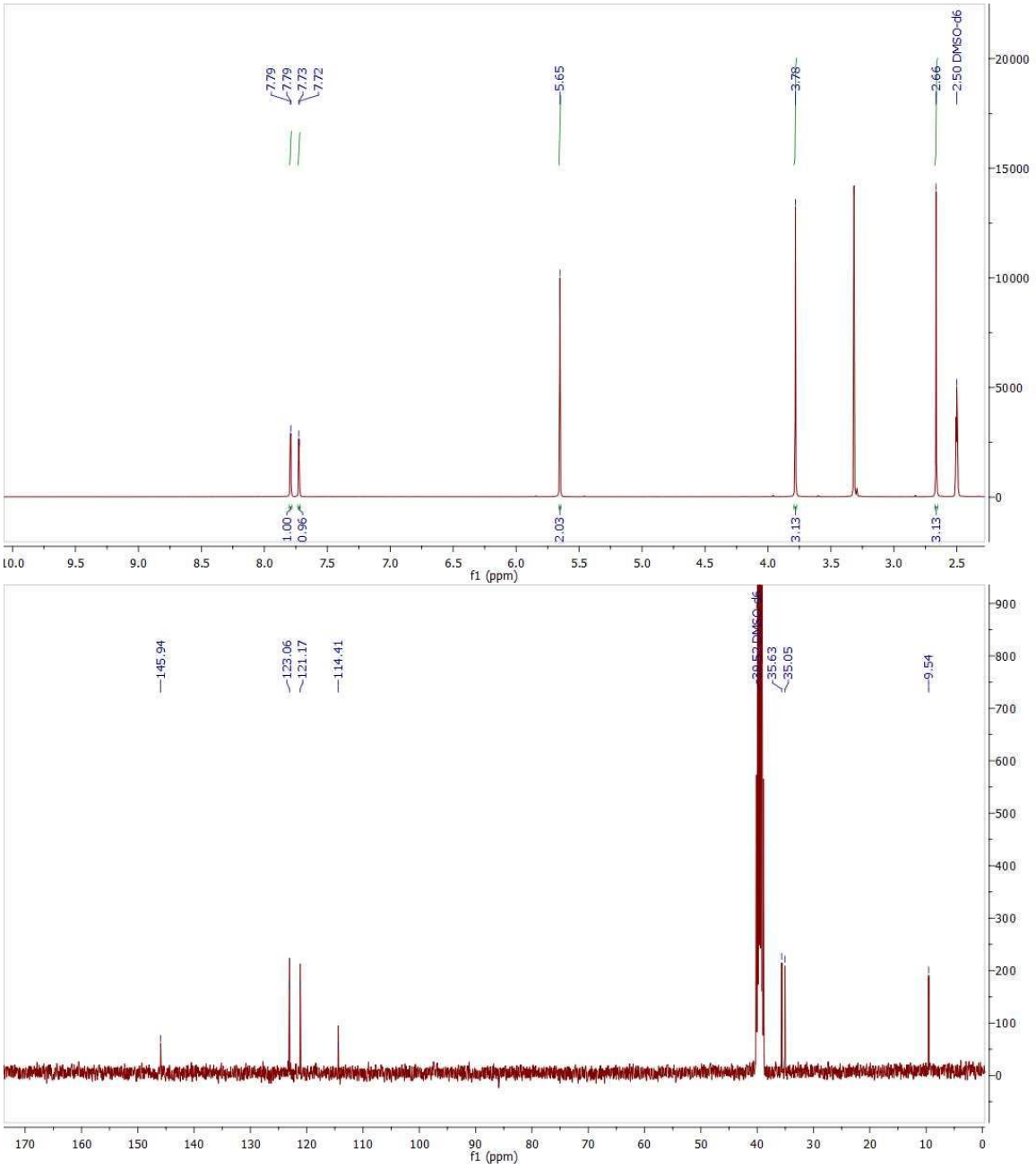


Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [N≡$C_2C_1C_1$im]Cl.

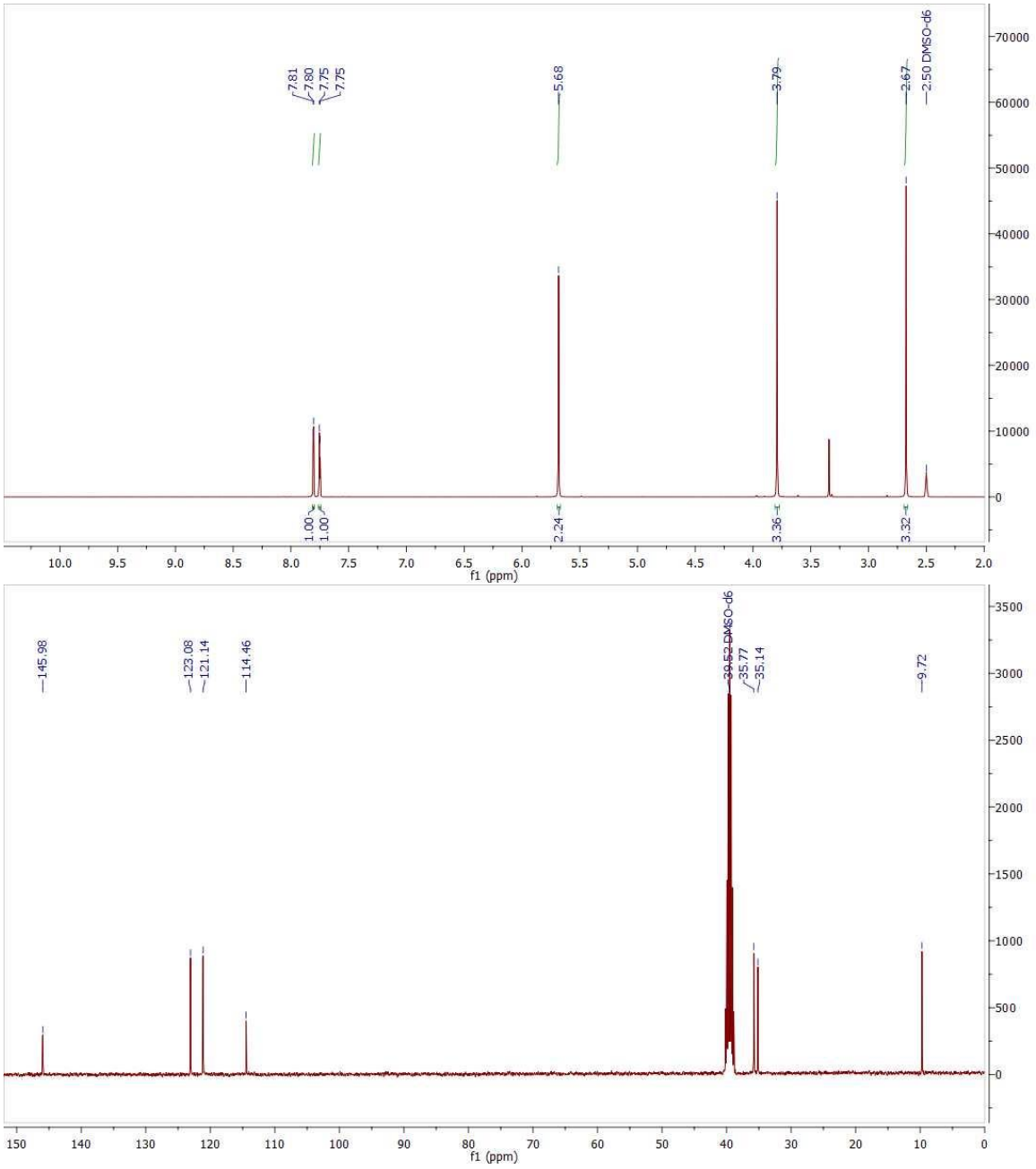


Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of [N≡$C_2C_1C_1$im]Br.

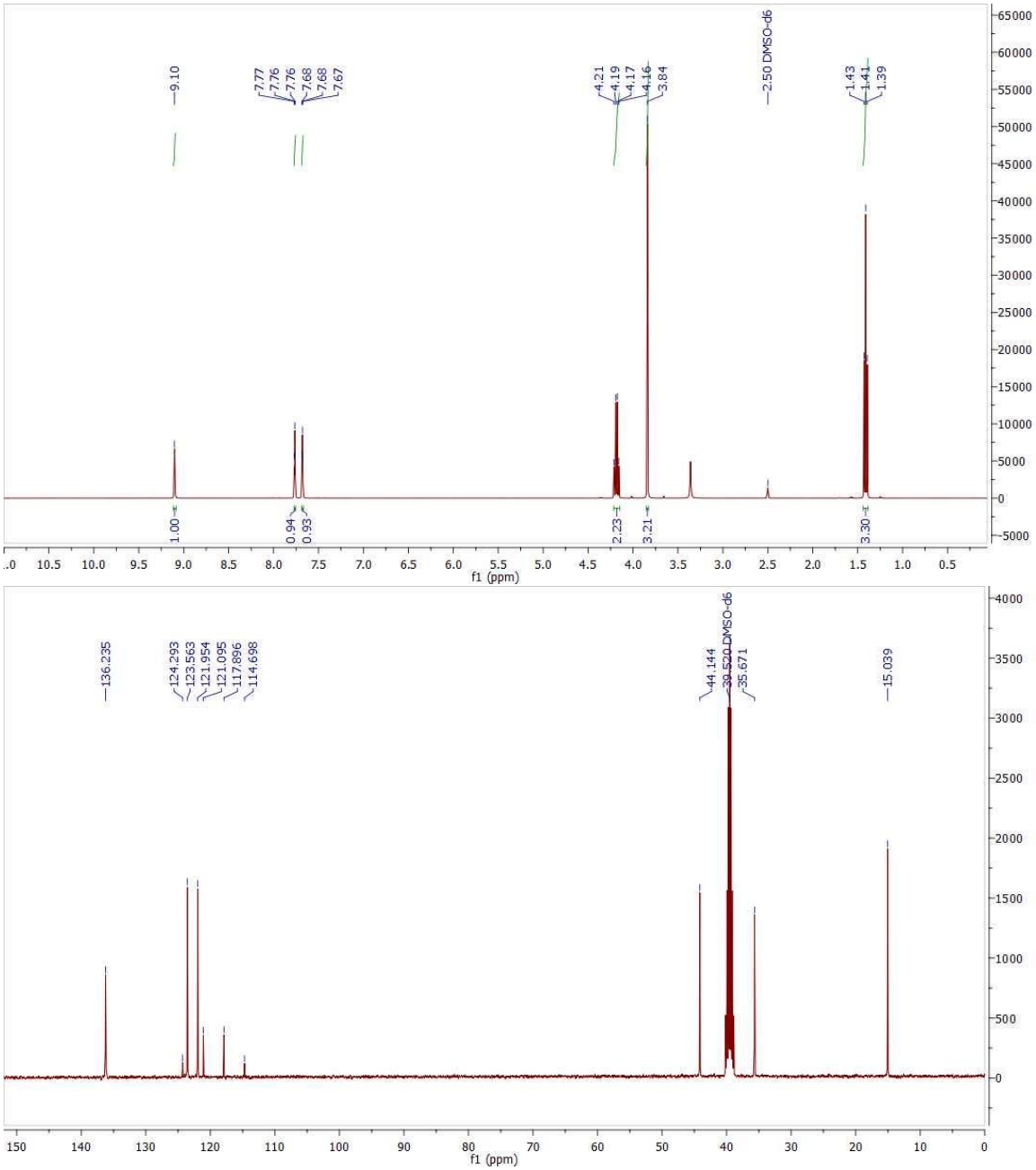


Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_2C_1im][NTf_2]$.

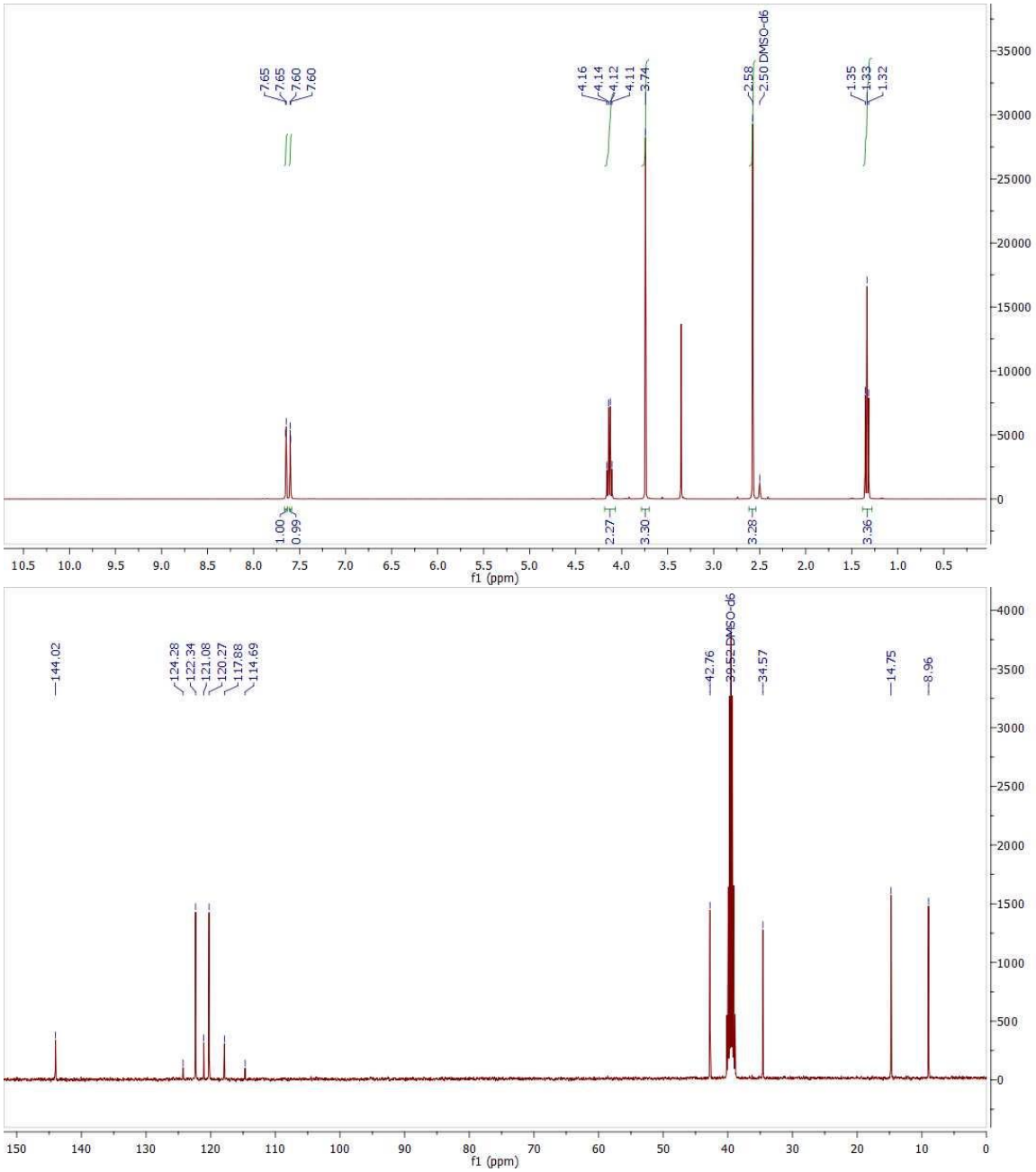


Figure S18. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_2C_1C_1im][NTf_2]$.

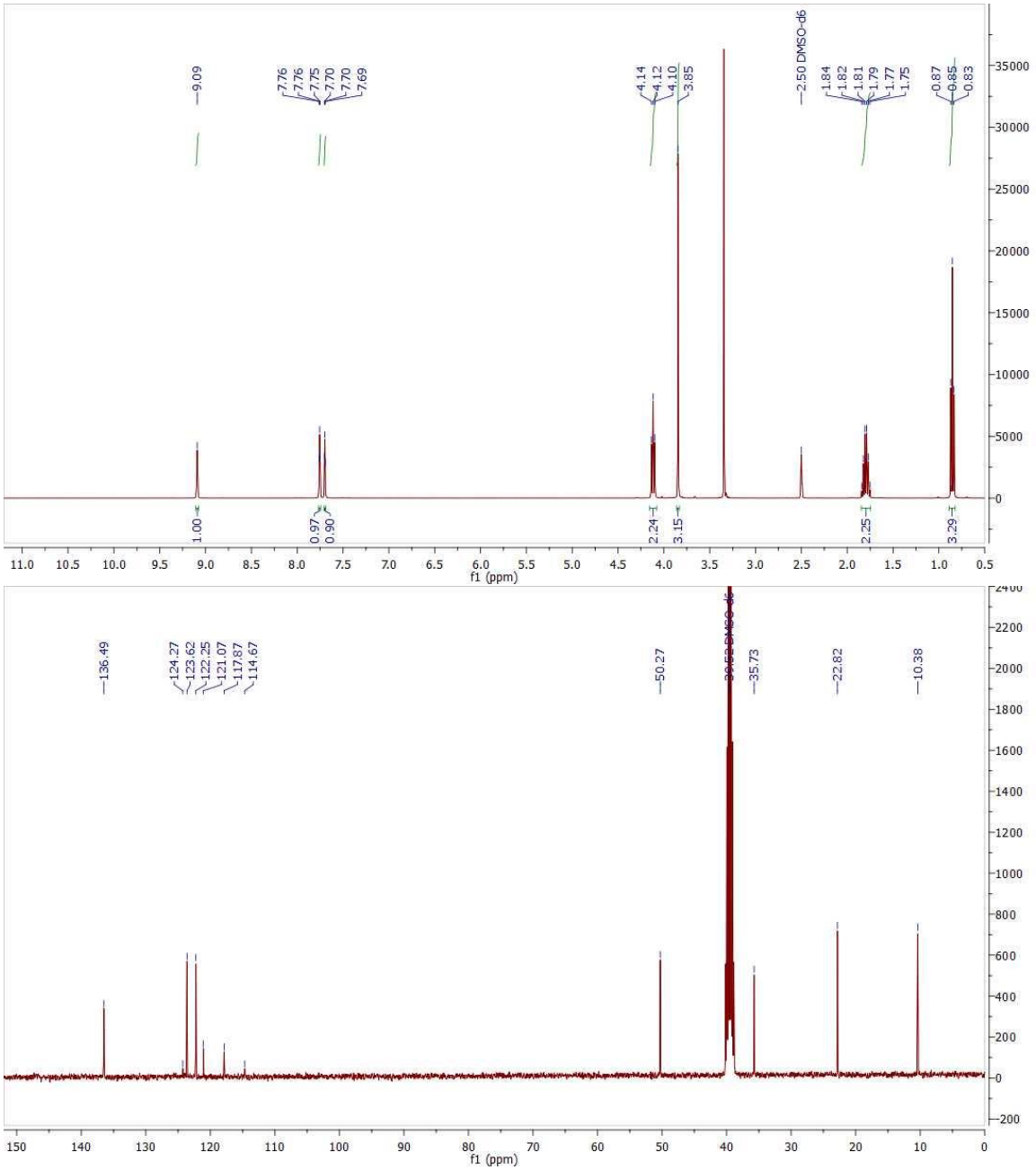


Figure S19. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_3C_1im][NTf_2]$.

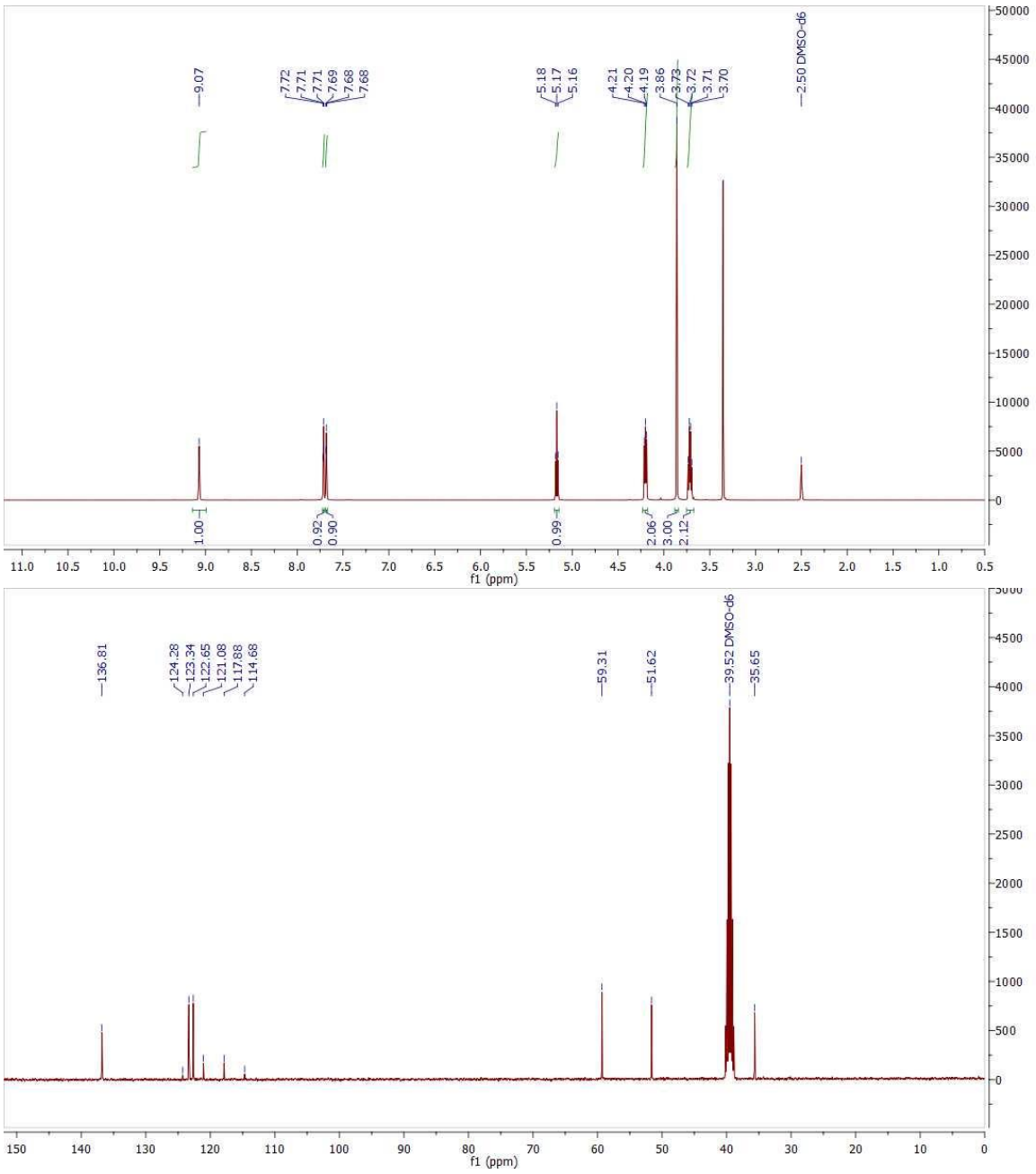


Figure S20. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[HOC_2C_1im][NTf_2]$.

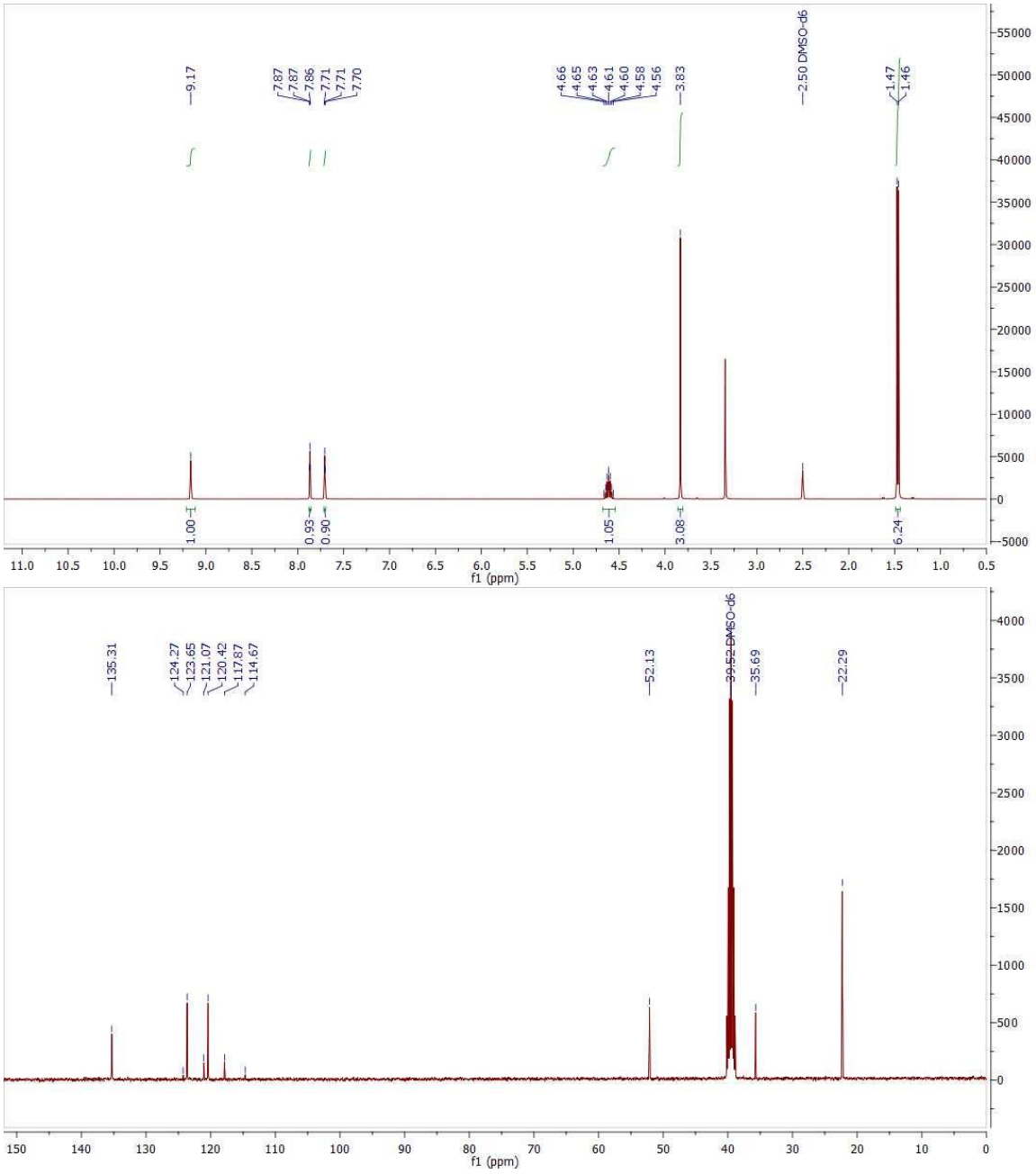


Figure S21. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_{2,1}C_1im][NTf_2]$.

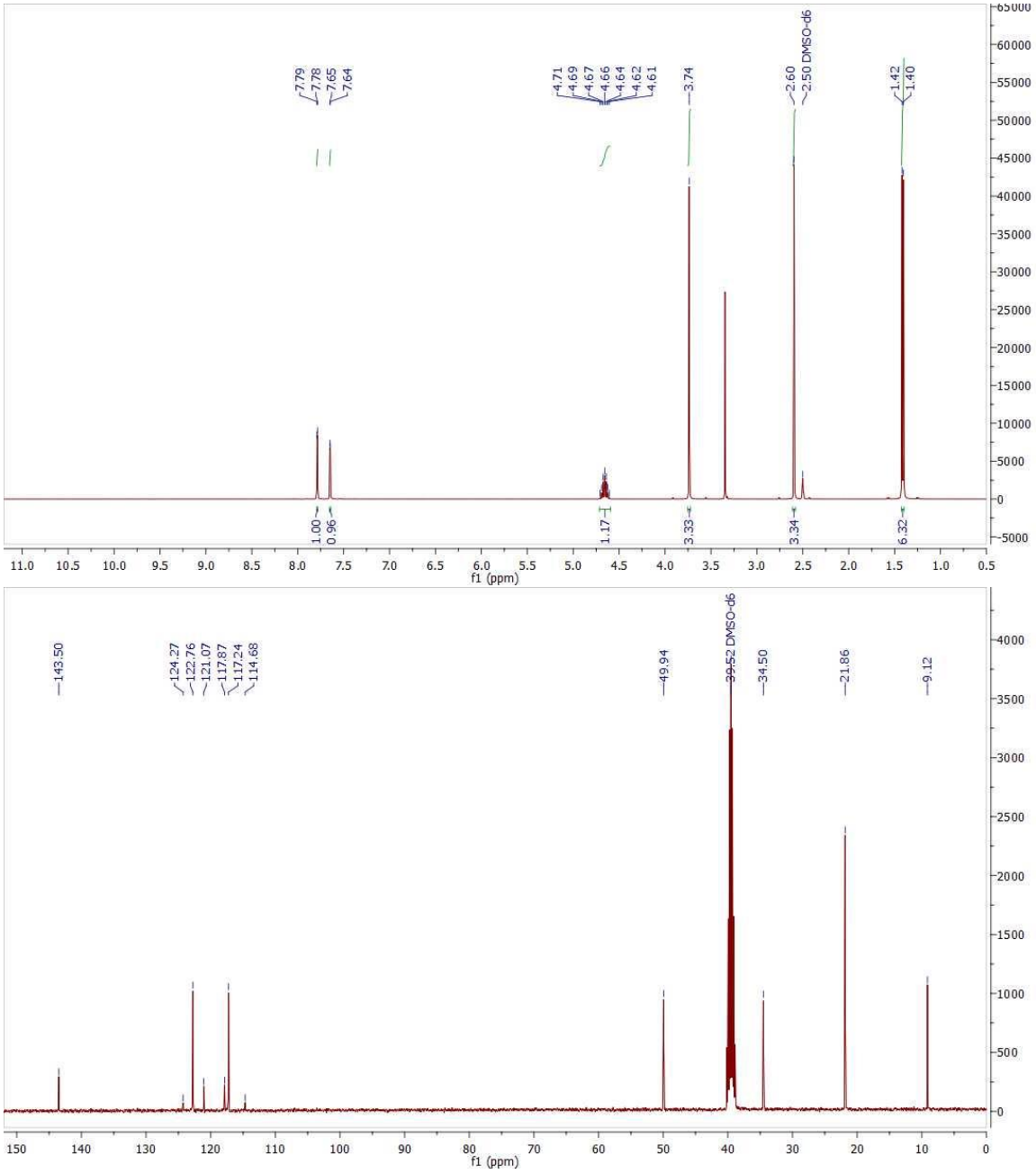


Figure S22. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[C_{2,1}C_1C_1im][NTf_2]$.

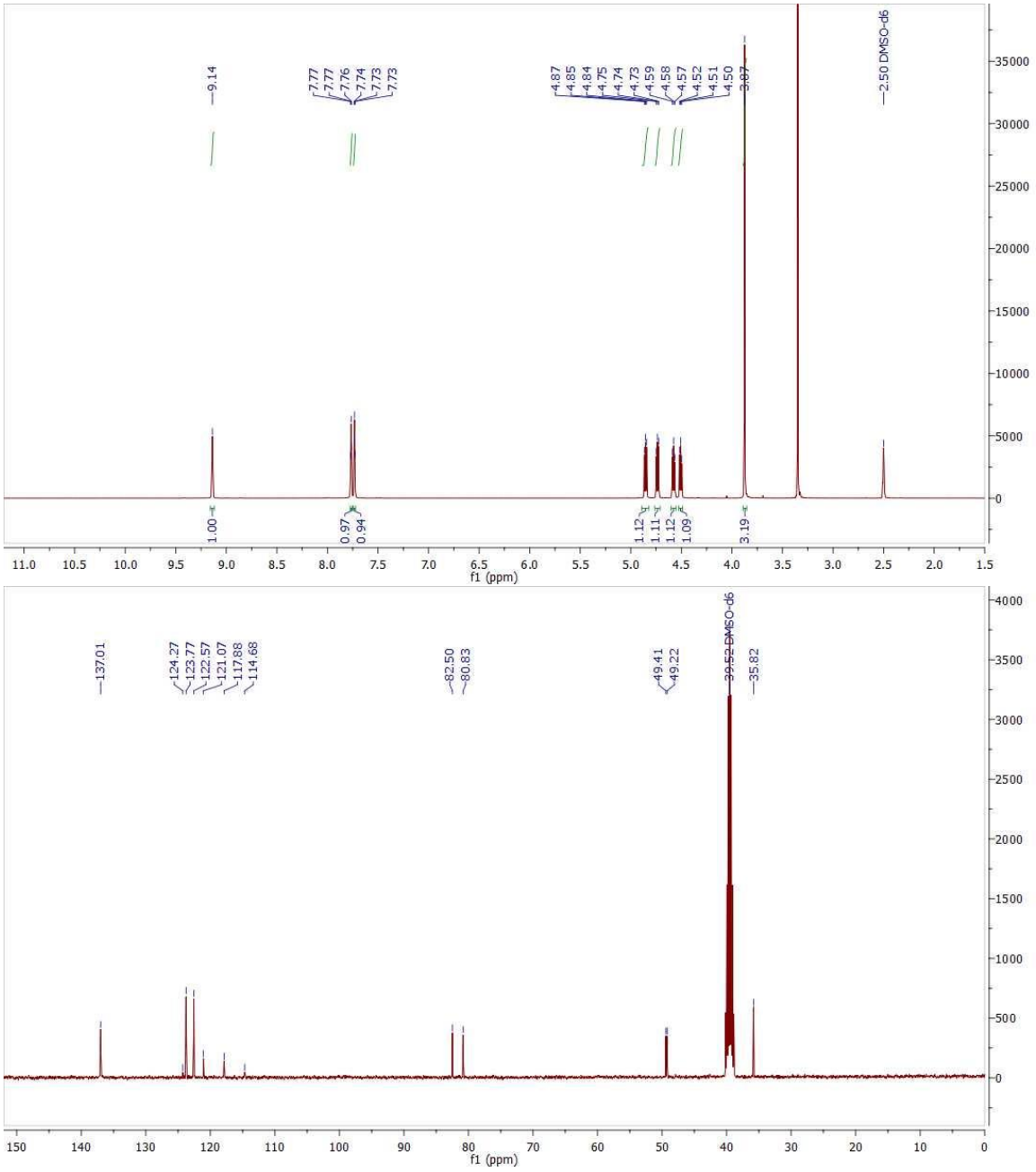


Figure S23. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1im][NTf_2]$.

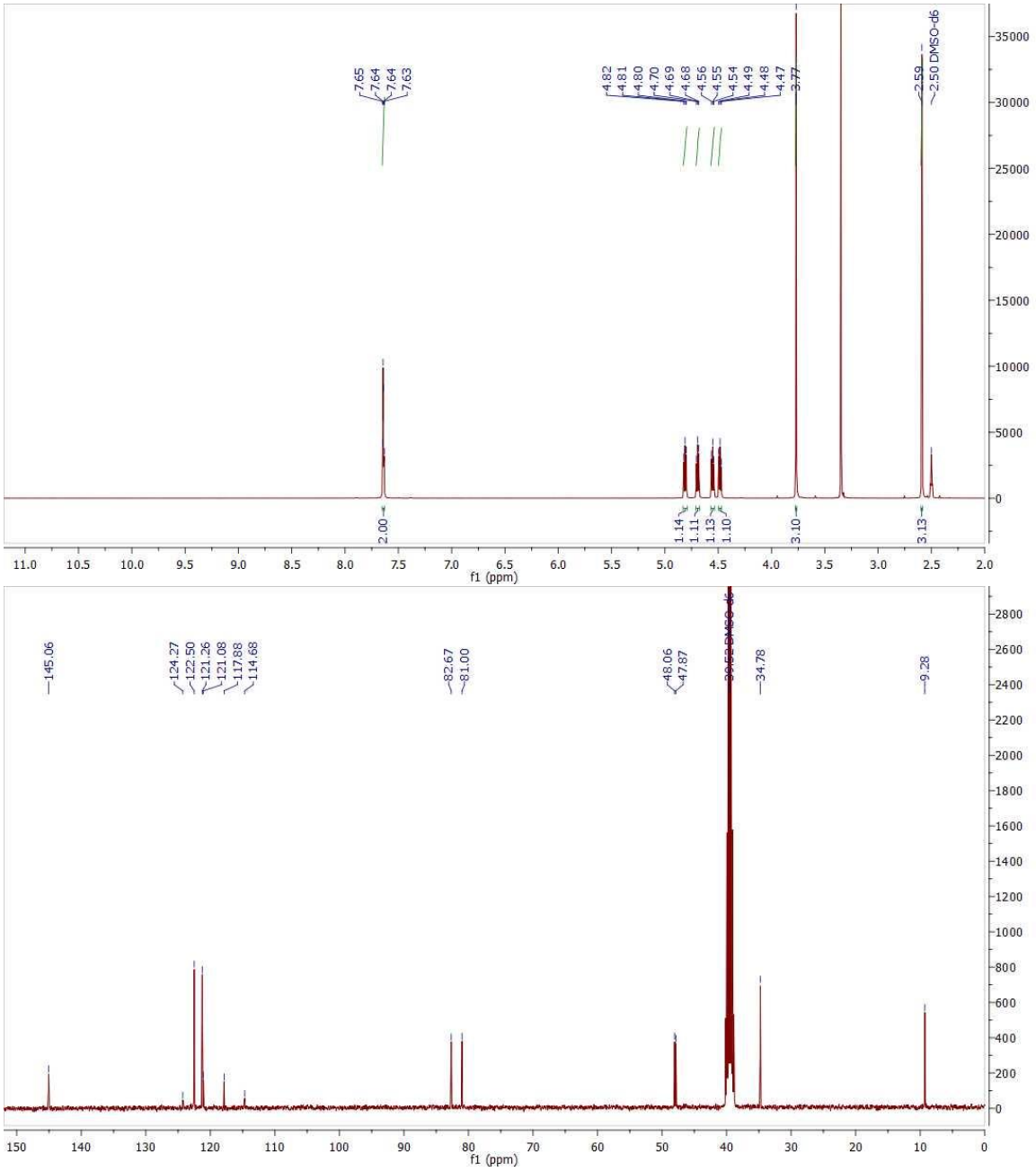


Figure S24. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[FC_2C_1C_1im][NTf_2]$.

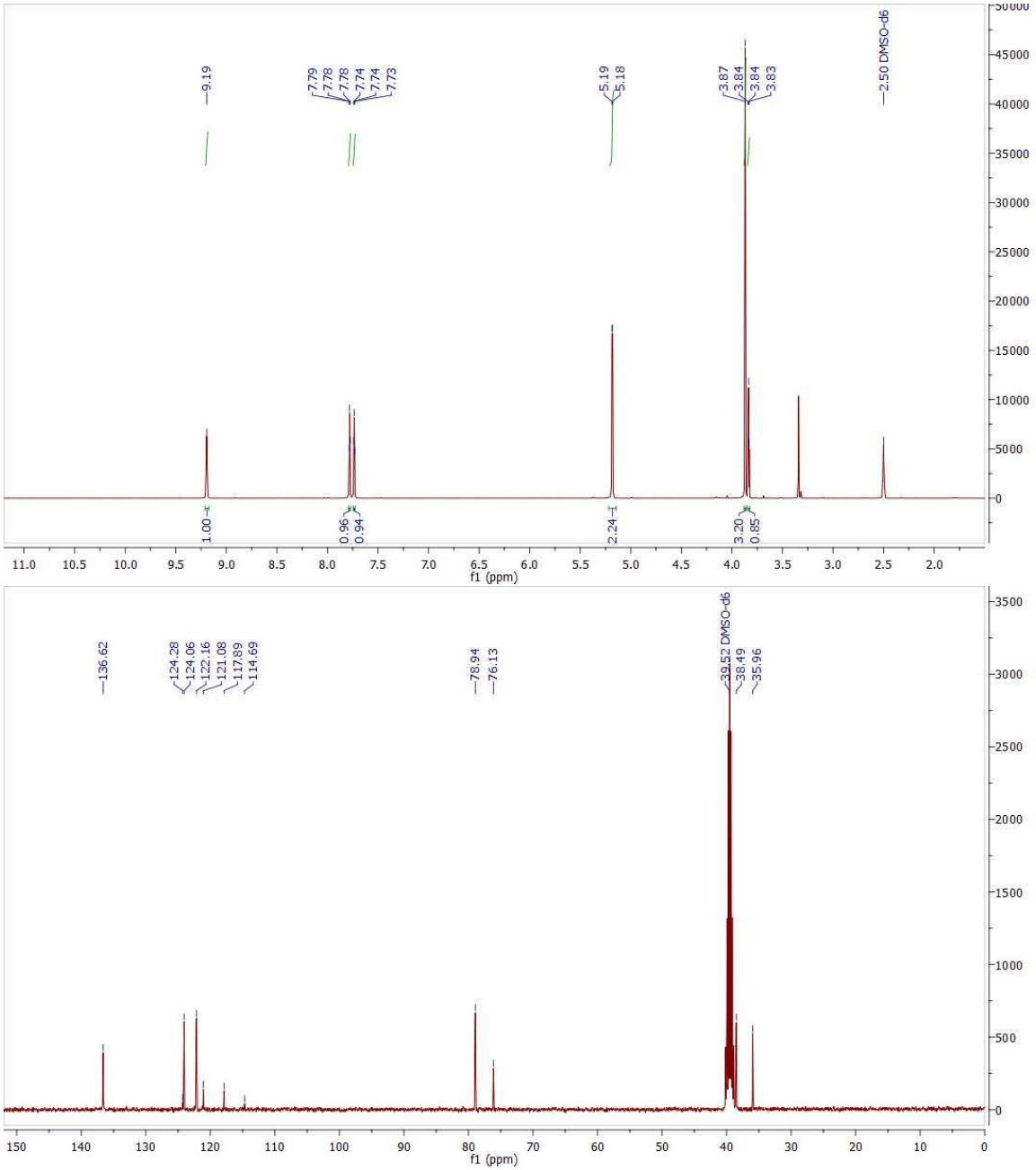


Figure S25. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[HC{\equiv}C_2C_1im][NTf_2]$.

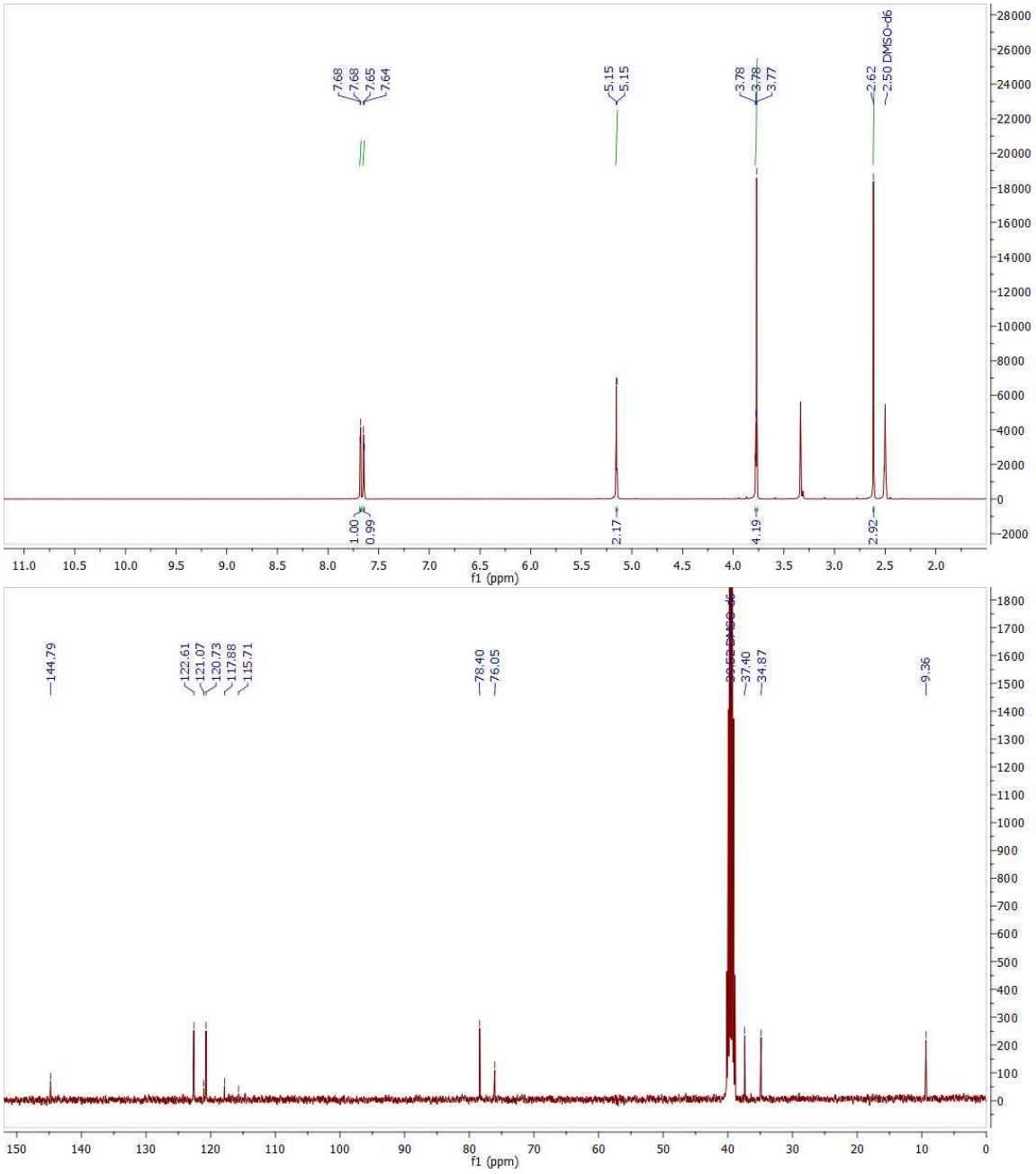


Figure S26. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[HC{\equiv}C_2C_1C_1im][NTf_2]$.

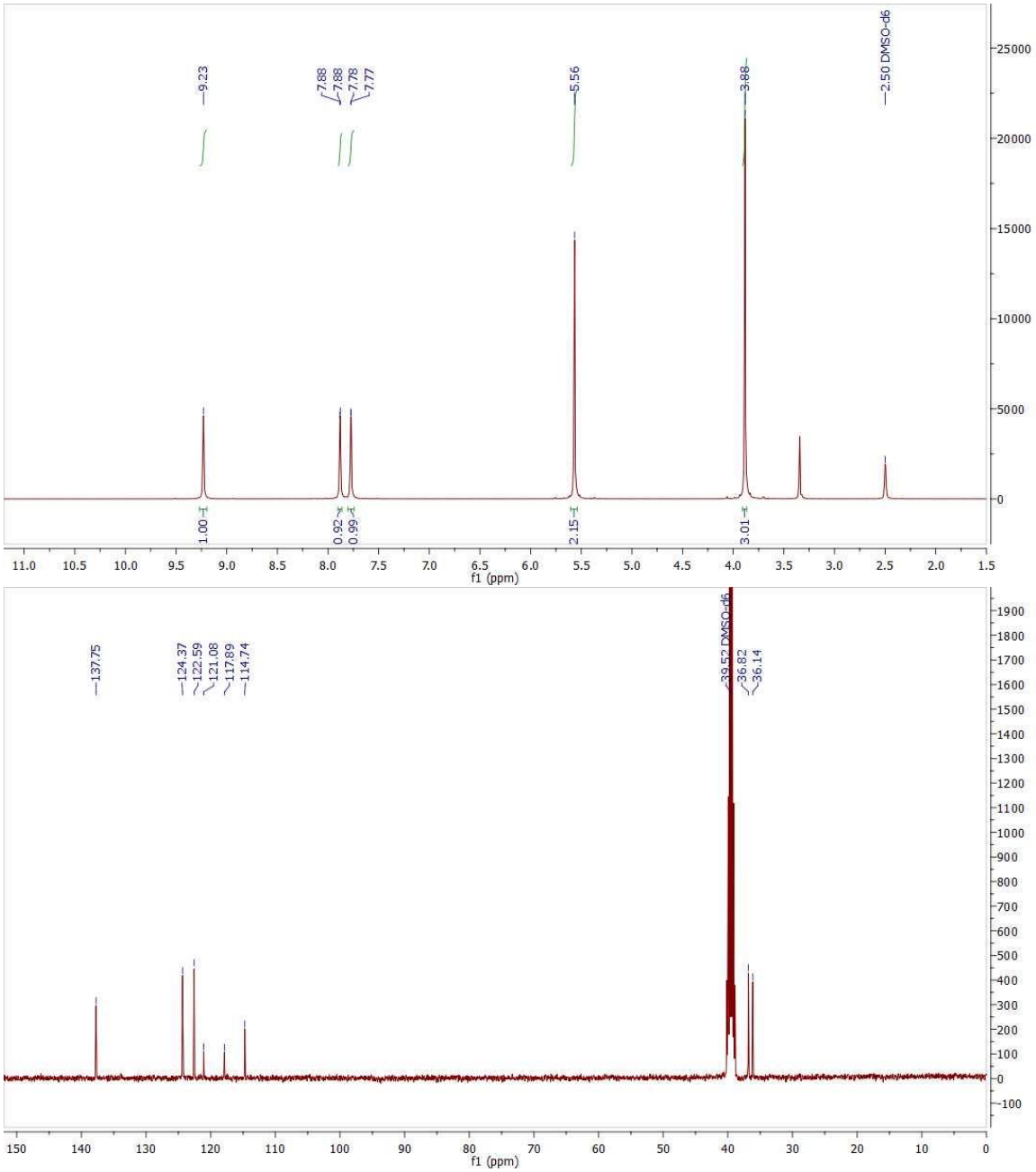


Figure S27. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[N{\equiv}C_2C_1im][NTf_2]$.

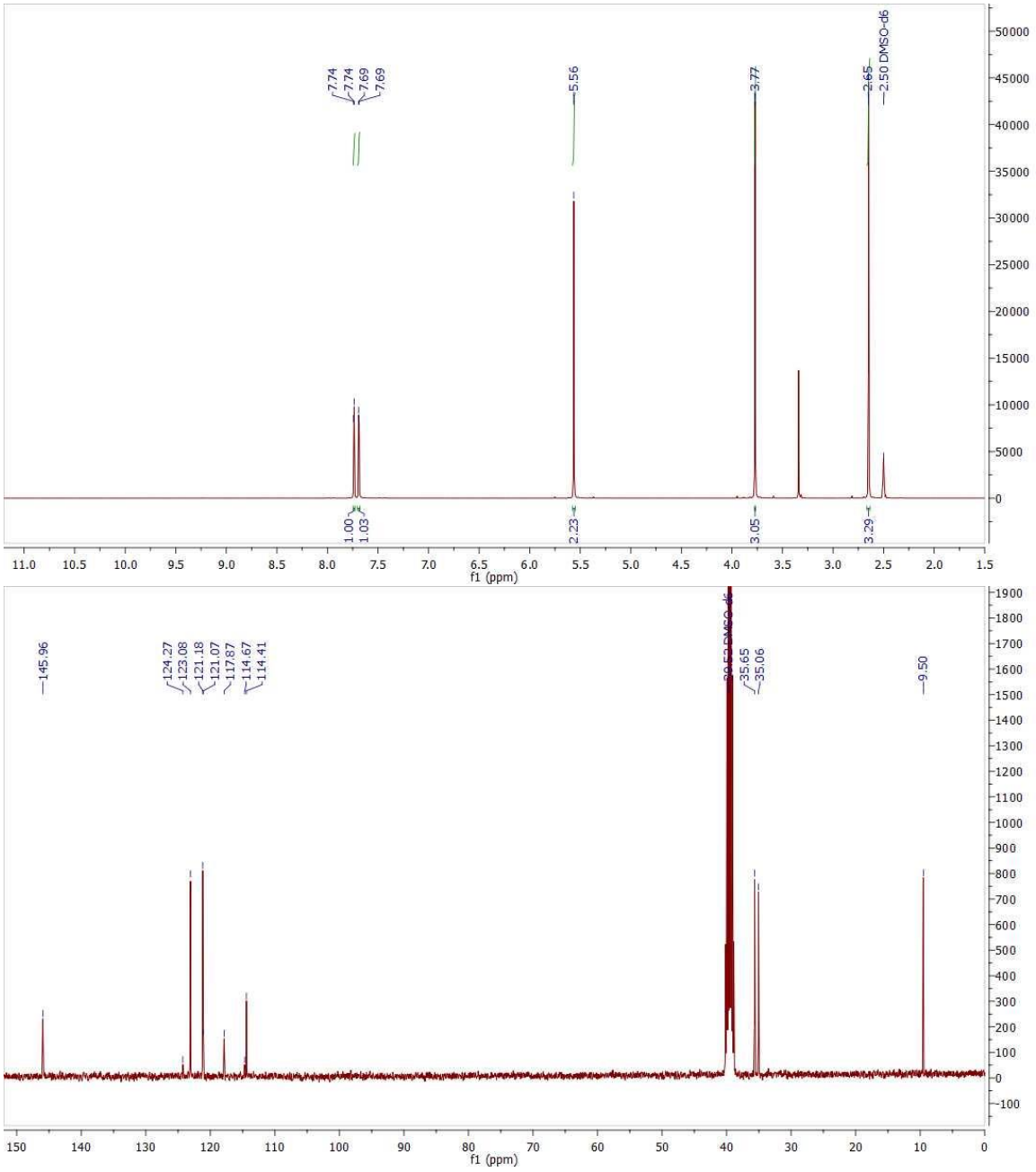


Figure S28. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $[N{\equiv}C_2C_1C_1im][NTf_2]$.

Densities

All studied densities showed linear dependency to temperature increase. Therefore, a straight line was fitted to the experimental data according to Equation (S1).

$$\rho = a + bT \quad \text{(S1)}$$

Where ρ is mass density in g mL^{-1}, α and b are the linear fit parameters in g mL^{-1} and g mL^{-1} K^{-1} and T temperature in K accordingly. T is sample temperature in K. Tables **X and X** show the experimental data and fitting parameters for the studied ILs.

Table S2. Density values (g mL^{-1}) of the studied bis(trifluoromethylsulfonyl)imide ILs.

Ionic Liquids	Temperature (°C)							
	25	35	45	55	65	75	85	95
$[C_2C_1im][NTf_2]$	1.516	1.506	1.495	1.486	1.476	1.466	1.457	1.448
$[C_2C_1C_1im][NTf_2]$	1.489	1.479	1.470	1.459	1.451	1.441	1.432	1.423
$[C_3C_1im][NTf_2]$	1.472	1.462	1.452	1.443	1.433	1.423	1.414	1.405
$[HOC_2C_1im][NTf_2]$	1.573	1.563	1.553	1.543	1.534	1.524	1.515	1.505
$[C_2C_2im][NTf_2]$	1.473	1.463	1.452	1.444	1.433	1.423	1.414	1.405
$[C_{2,1}C_1im][NTf_2]$	1.474	1.464	1.455	1.445	1.436	1.426	1.416	1.508
$[C_{2,1}C_1C_1im][NTf_2]$	1.489	1.479	1.470	1.459	1.451	1.441	1.432	1.423
$[FC_2C_1im][NTf_2]$	1.588	1.577	1.567	1.556	1.547	1.536	1.526	1.516
$[FC_2C_1C_1im][NTf_2]$	1.555	1.545	1.535	1.525	1.415	1.506	1.496	1.486
$[HC{\equiv}C_2C_1im][NTf_2]$	1.538	1.528	1.517	1.507	1.496	1.487	1.477	1.467
$[N{\equiv}C_2C_1im][NTf_2]$	1.608	1.599	1.589	1.578	1.570	1.559	1.550	1.540

Table S3. Fitting parameters of linear regression for IL densities

Ionic Liquid	α (g mL^{-1})	Δα (%)	b (10^{-4} g $mL^{-1}K^{-1}$)	Δb (%)	R^2
$[C_2C_1im][NTf_2]$	1.807	0.33	9.77	9.85	0.9994
$[C_2C_1C_1im][NTf_2]$	1.772	0.22	9.50	6.60	0.9997
$[C_3C_1im][NTf_2]$	1.759	0.18	9.63	5.48	0.9998
$[HOC_2C_1im][NTf_2]$	0.861	0.14	9.67	4.32	0.9999
$[C_2C_2im][NTf_2]$	1.765	0.32	-9.80	9.67	0.9994
$[C_{2,1}C_1im][NTf_2]$	1.760	0.21	9.59	6.19	0.9998
$[C_{2,1}C_1C_1im][NTf_2]$	1.732	0.12	9.39	3.54	0.9999
$[FC_2C_1im][NTf_2]$	1.890	0.20	10.20	6.06	0.9998
$[FC_2C_1C_1im][NTf_2]$	1.847	0.22	9.80	6.71	0.9997
$[HC{\equiv}C_2C_1im][NTf_2]$	1.841	0.20	10.22	6.07	0.9998
$[N{\equiv}C_2C_1im][NTf_2]$	1.901	0.22	9.83	6.59	0.9997

Molar Volumes

Molar volumes of the samples were calculated from the density data (Table S3) using the following equation:

$$V_M = \frac{M_r}{\rho} \quad \text{(S2)}$$

V_M the molar volume of each sample in L mol^{-1}, M_r the molar mass in g mol^{-1} and ρ the experimental density in g L^{-1}.

The molar volume data were fitted to the linear equation shown below. The fitting parameters are shown in **Table X**.

α and b are the linear fit parameters in L mol^{-1} and L mol^{-1} K^{-1} accordingly. T is sample temperature in K.

Table S4. Fitting parameters of linear regression for IL molar volume

Ionic Liquid	α (L mol^{-1})	Δα (%)	b (10^{-4} L $mol^{-1}K^{-1}$)	Δb (%)	R^2
$[C_2C_1im][NTf_2]$	0.206	0.186	1.743	0.660	0.9997
$[C_2C_1C_1im][NTf_2]$	0.218	0.166	1.819	0.597	0.9998
$[C_3C_1im][NTf_2]$	0.219	0.116	1.887	0.404	0.9999
$[HOC_2C_1im][NTf_2]$	0.209	0.071	1.664	0.266	1
$[C_{2,1}C_1im][NTf_2]$	0.219	0.116	1.887	0.404	0.9997
$[C_{2,1}C_1C_1im][NTf_2]$	0.223	0.138	1.890	0.488	0.9999
$[FC_2C_1im][NTf_2]$	0.206	0.145	1.727	0.412	0.9998
$[FC_2C_1C_1im][NTf_2]$	0.219	0.127	1.794	0.464	0.9998
$[HC{\equiv}C_2C_1im][NTf_2]$	0.207	0.145	1.810	0.497	0.9998
$[N{\equiv}C_2C_1im][NTf_2]$	0.202	0.179	1.596	0.681	0.9999

Viscosities

The experimental viscosity data were fitted to Vogel – Fulcher – Tammann (VFT) equation shown below. The measured viscosity values, as well as the fitting parameters are presented in Tables S5, S6 and S7.

$$\eta = \eta_0 e^{\frac{B}{T-T_0}} \quad \text{(S3)}$$

With η and η_0 in mPa s, B, T and T_0 in K.

Table S5. Viscosity values (in mPa s) of the studied bis(trifluoromethylsulfonyl)imide ILs – Temperature range 25 – 65 °C.

Ionic Liquids	Temperature (°C)								
	25	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**
$[C_2C_1im][NTf_2]$	32.6	27.4	23.30	20.0	17.3	15.1	13.3	11.8	10.5
$[C_2C_1C_1im][NTf_2]$	72.8	58.6	47.9	39.7	33.3	28.2	24.1	20.9	18.2
$[C_3C_1im][NTf_2]$	46.8	38.2	31.6	26.5	22.5	19.2	16.6	14.5	12.8
$[HOC_2C_1im][NTf_2]$	88.3	68.5	54.3	43.9	35.9	29.9	25.2	21.5	18.5
$[C_2C_2im][NTf_2]$	31.4	26.5	22.5	19.3	16.8	14.7	12.9	11.5	10.2
$[C_{2,1}C_1im][NTf_2]$	49.2	40.0	31.6	26.5	22.5	19.2	16.6	14.5	12.8
$[C_{2,1}C_1C_1im][NTf_2]$	112.0	86.0	67.6	54.1	43.9	36.2	30.2	25.6	21.9
$[FC_2C_1im][NTf_2]$	66.0	52.5	42.5	35.0	29.1	24.6	20.9	18.0	15.7
$[FC_2C_1C_1im][NTf_2]$	131.7	100.4	78.2	62.1	50.1	41.0	34.0	28.6	24.4
$[HC{\equiv}C_2C_1im][NTf_2]$	59.3	47.4	38.6	31.9	26.8	22.7	19.4	16.8	14.7
$[N{\equiv}C_2C_1im][NTf_2]$	321.5	226.3	164.4	123.0	94.1	73.7	58.8	47.7	39.4

Table S6. Viscosity values (mPa s) of the studied bis(trifluoromethylsulfonyl)imide ILs – Temperature range 70 – 105 °C.

Ionic Liquids	Temperature (°C)							
	70	**75**	**80**	**85**	**90**	**95**	**100**	**105**
$[C_2C_1im][NTf_2]$	9.5	8.5	7.8	7.1	6.5	5.9	5.5	5.1
$[C_2C_1C_1im][NTf_2]$	16.0	14.1	12.5	11.2	10.1	9.1	8.3	7.6
$[C_3C_1im][NTf_2]$	11.3	10.1	9.0	8.1	7.4	6.7	6.2	5.7
$[HOC_2C_1im][NTf_2]$	16.1	14.1	12.4	11.1	9.9	8.9	8.1	7.3
$[C_2C_2im][NTf_2]$	9.2	8.3	7.6	6.9	6.3	5.8	5.4	4.9
$[C_{2,1}C_1im][NTf_2]$	11.7	10.4	9.3	8.4	7.6	6.9	6.3	5.8
$[C_{2,1}C_1C_1im][NTf_2]$	18.6	16.4	14.4	12.7	11.3	10.1	9.1	8.2
$[FC_2C_1im][NTf_2]$	13.8	12.2	10.9	9.8	8.8	8.0	7.3	6.6
$[FC_2C_1C_1im][NTf_2]$	20.9	18.2	15.9	14.0	12.4	11.1	10.0	9.0
$[HC{\equiv}C_2C_1im][NTf_2]$	12.9	11.5	10.2	9.2	8.3	7.5	6.9	6.3
$[N{\equiv}C_2C_1im][NTf_2]$	32.9	27.9	23.8	20.6	18.0	15.8	14.0	12.5

Table S7. VFT Fitting parameters for IL viscosities.

Ionic Liquid	η_0 (mPa s)	$\Delta\eta_0$ (%)	B (K)	Δb (%)	T_0 (K)	ΔT_0 (%)	R^2
$[C_2C_1im][NTf_2]$	0.185	1.5	739.4	0.7	155.3	0.4	1
$[C_2C_1C_1im][NTf_2]$	0.160	1.6	835.8	0.6	161.6	0.3	1

$[C_3C_1im][NTf_2]$	0.163	1.1	760.5	0.5	163.9	0.2	1
$[HOC_2C_1im][NTf_2]$	0.212	1.0	689.1	0.4	183.9	0.1	1
$[C_2C_2im][NTf_2]$	0.162	1.9	779.3	0.8	150.2	0.5	1
$[C_{2,1}C_1im][NTf_2]$	0.186	1.3	720.4	0.6	169.1	0.2	1
$[C_{2,1}C_1C_1im][NTf_2]$	0.180	1.3	756.2	0.5	180.6	0.2	1
$[FC_2C_1im][NTf_2]$	0.207	1.6	696.6	0.6	177.3	0.3	1
$[FC_2C_1C_1im][NTf_2]$	0.179	1.5	769.0	0.5	181.6	0.2	1
$[HC{\equiv}C_2C_1im][NTf_2]$	0.207	2.0	690.7	0.9	176.0	0.3	1
$[N{\equiv}C_2C_1im][NTf_2]$	0.233	1.2	706.8	0.4	200.4	0.1	1

DSC analysis

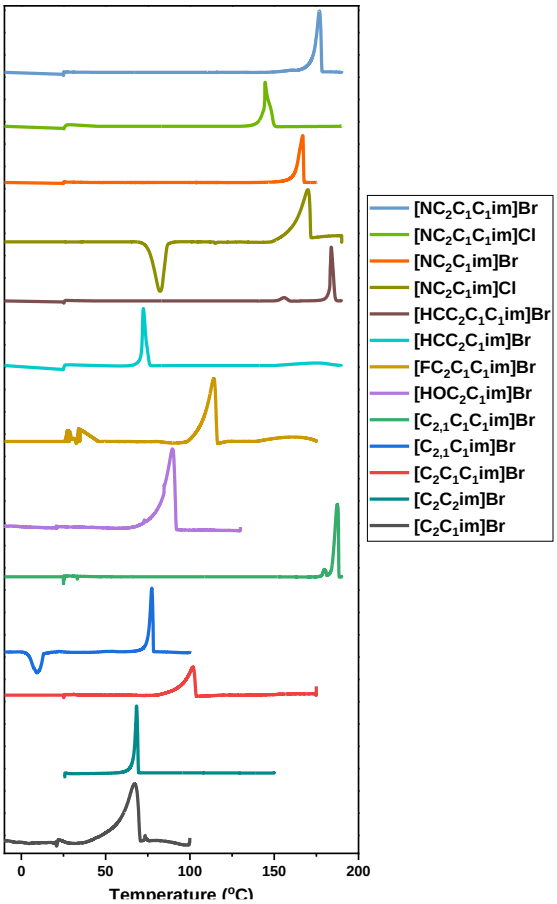


Figure S29a. DSC traces of heating cycles for the studied ILs. The ILs with no melting transitions are not shown for simplicity.

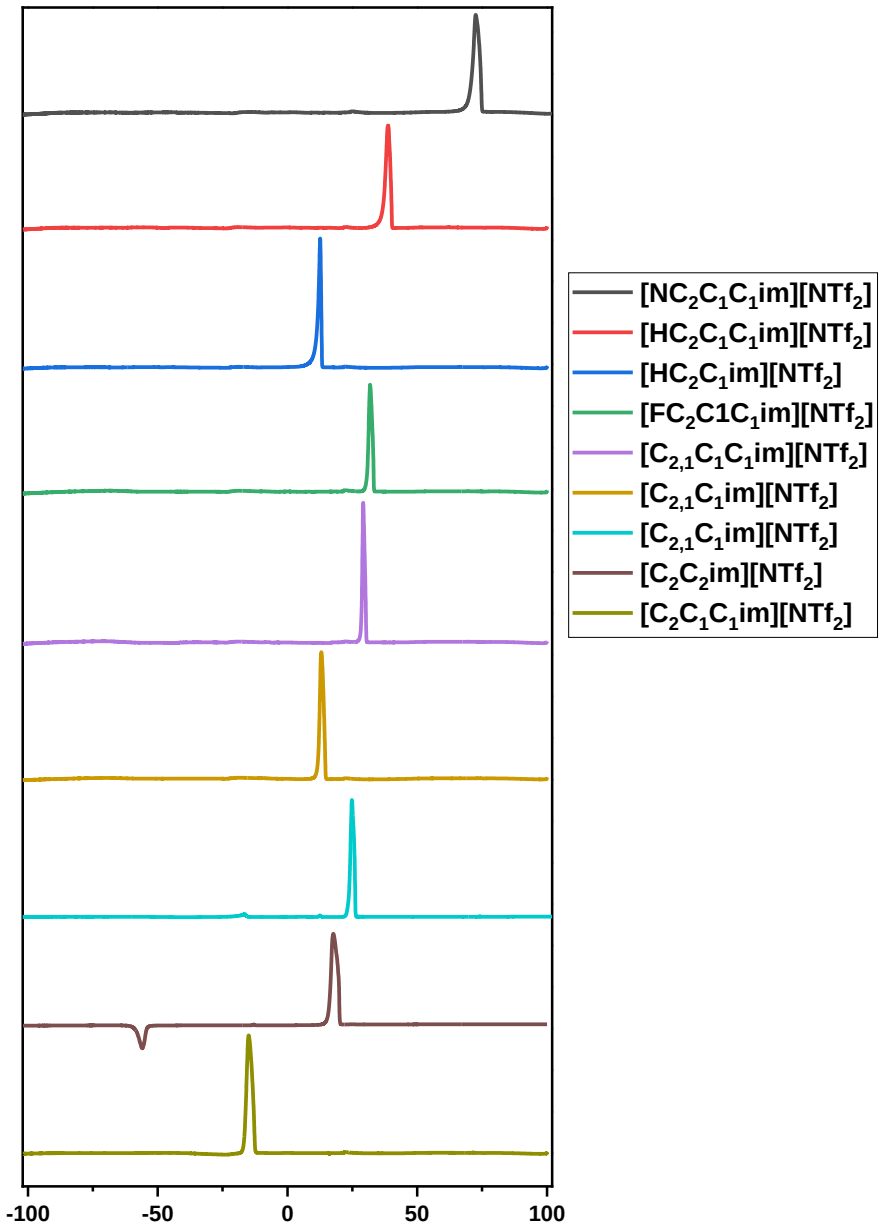


Figure S29b. DSC traces of heating cycles for the studied ILs. The ILs with no melting transitions are not shown for simplicity.

TGA analysis

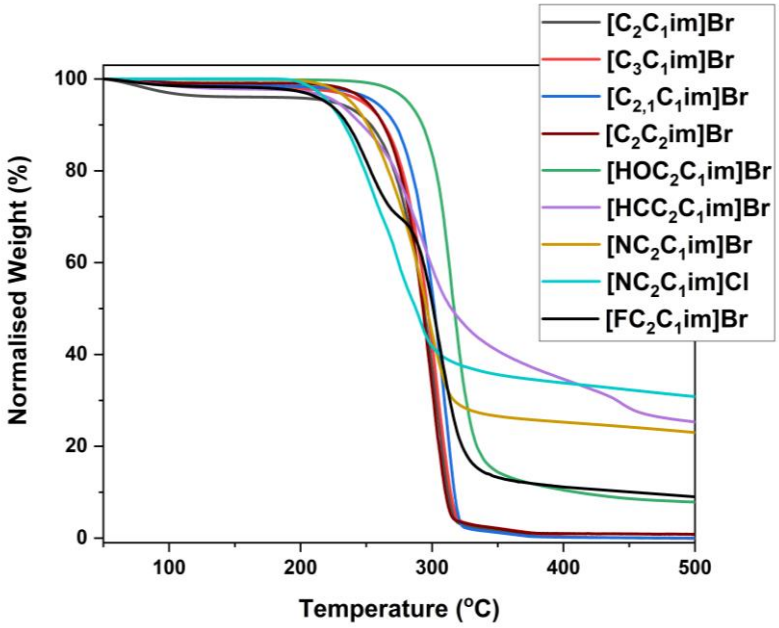


Figure S30. TGA graphs of non-methylated methylimidazolium halides.

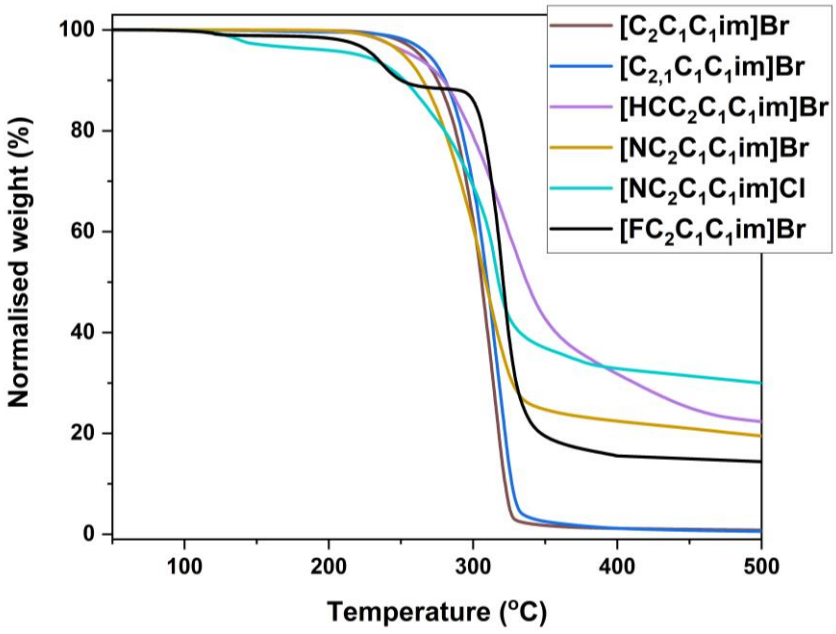
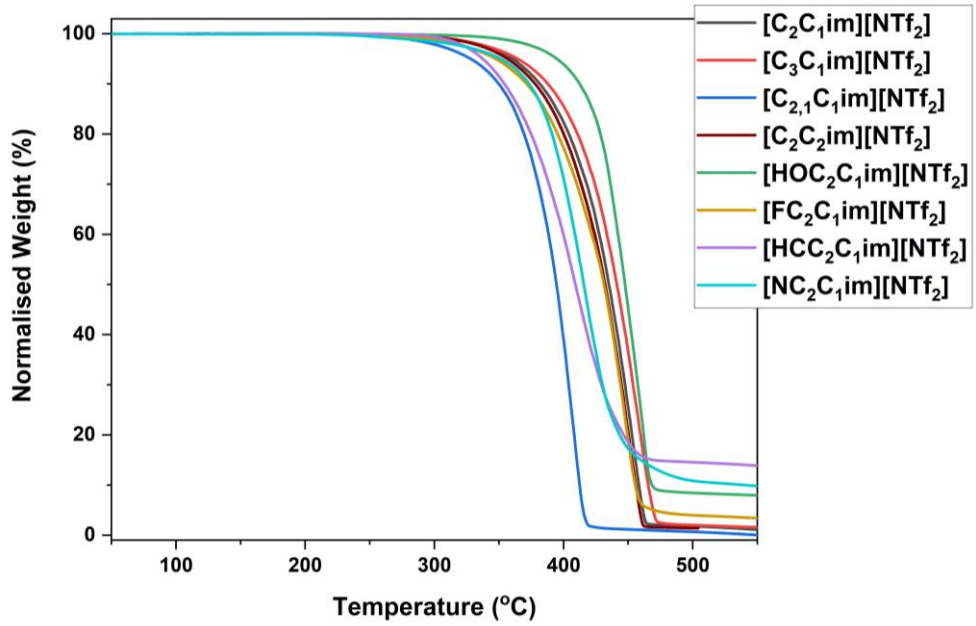
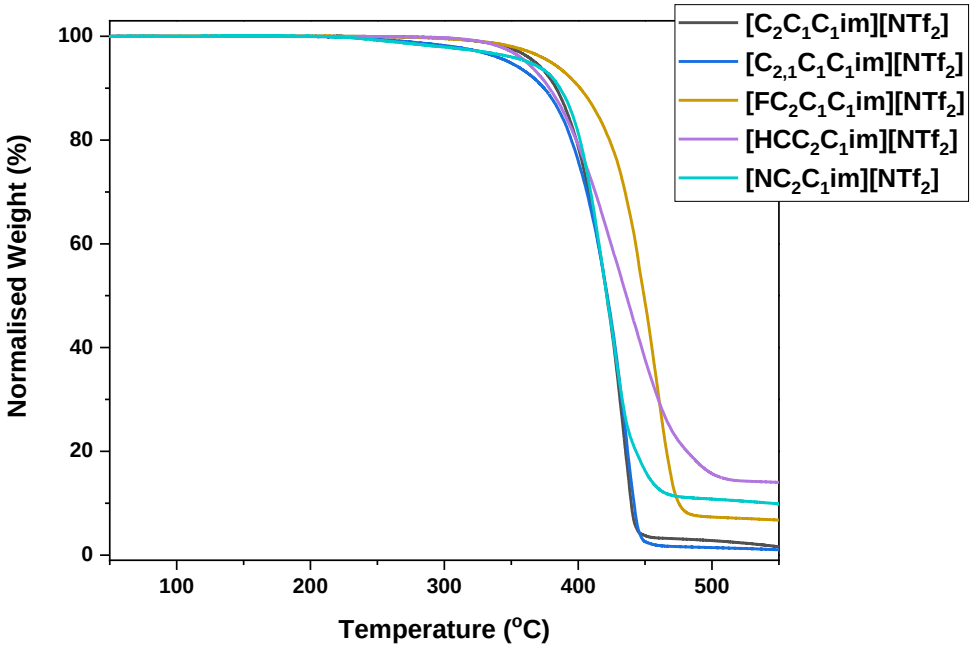


Figure S31. TGA graphs of 2-methylated methylimidazolium halides.



Figures S32. TGA graphs of non-methylated methylimidazolium bis-(trifluoromethylsulfonyl)imides.



Figures S33. TGA graphs of methylated methylimidazolium bis(trifluoromethylsulfonyl)imides.

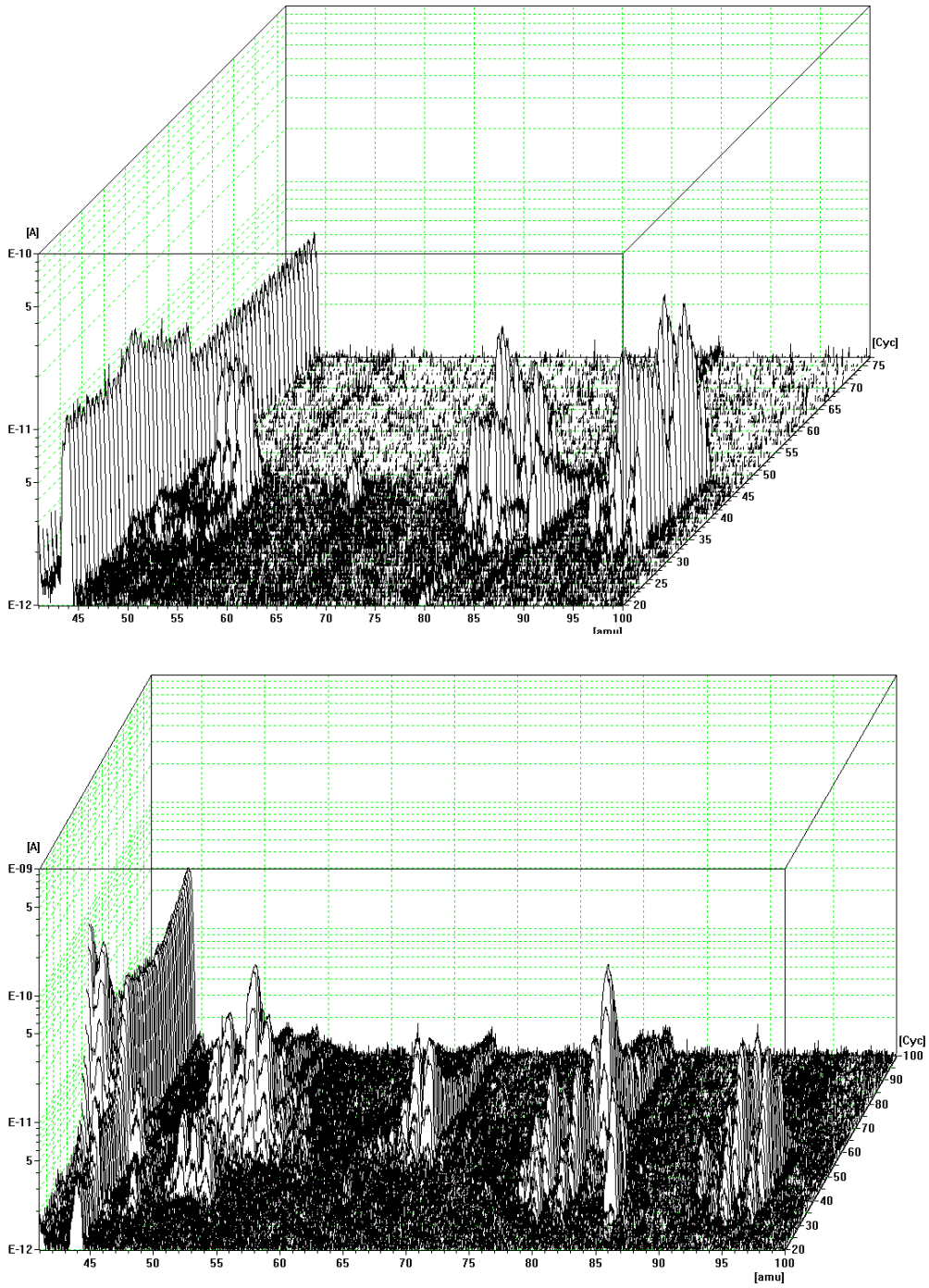


Figure S34. MS traces of thermal decomposition of **[FC$_2$C$_1$im]Br** (top) and **[FC$_2$C$_1$C$_1$im]Br** (bottom).

Ab initio calculations

Here we present the theoretical calculations on the preferred orientations of additional cation structures with identical or comparable molar mass, as the ones discussed in the main text. **[$C_3C_1C_1$im]**: 1-propyl-2,3-dimethylimidazolium cation, **[$HOC_2C_1C_1$]**: 1-(2-hydroxyethyl)-2,3-dimethylimidazolium cation, **[CycloC_3C_1im]**: 1-cyclopropyl-3-methylimidazolium cation, **[Cyclo$C_3C_1C_1$im]**: 1-cyclopropyl-2,3-dimethylimidazolium cation, **[$C_{2,1,1}C_1$im]**: 1-tertbutyl-3-methylimidazolium cation.

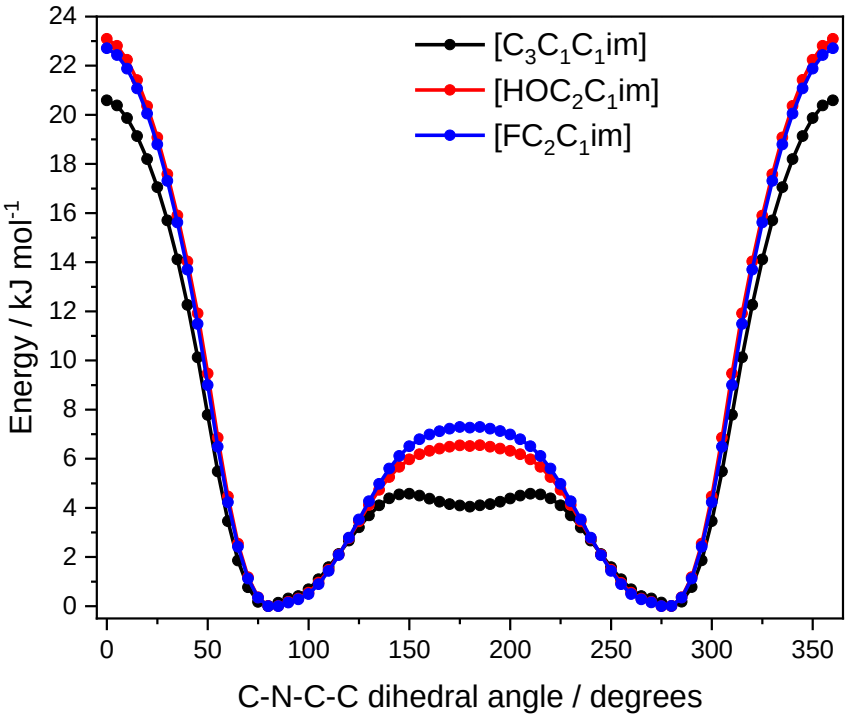


Figure S35. Ab initio energy calculation of C-N-C-C dihedral angle for **[$C_3C_1C_1$im]** (black) and **[$HOC_2C_1C_1$im]** (red) and **[$FC_2C_1C_1$im]** cations.

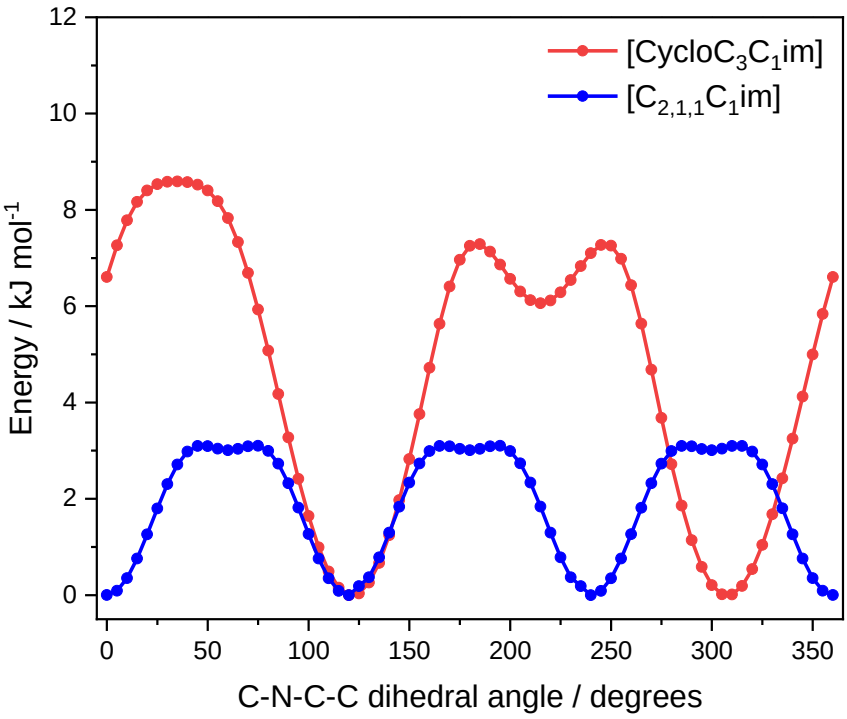


Figure S36. Ab initio energy calculation of C-N-C-C dihedral angle for **[CycloC$_3$C$_1$im]** (red) and **[C$_{2,1,1}$C$_1$im]** (blue) cations.

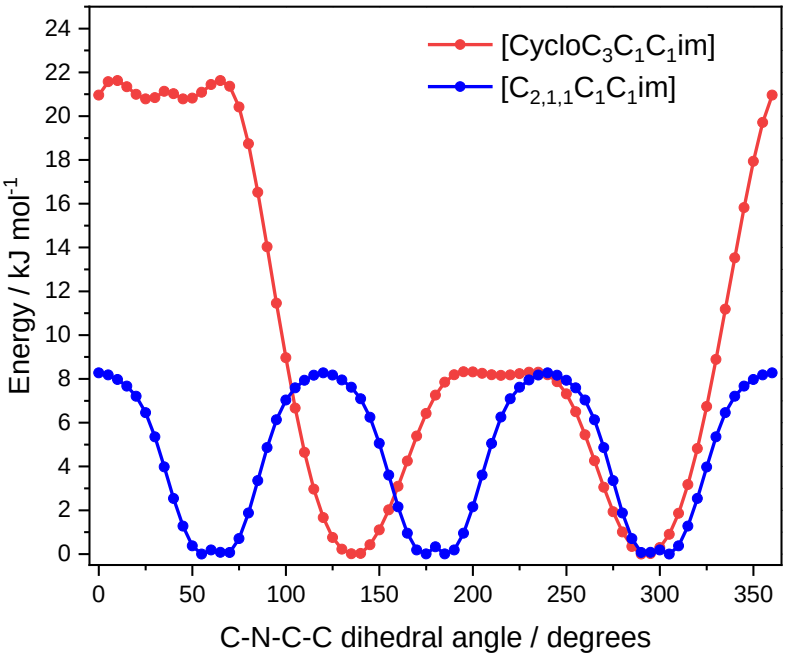


Figure S37. Ab initio energy calculation of C-N-C-C dihedral angle for **[CycloC$_3$C$_1$C$_1$im]** (red) and **[C$_{2,1,1}$C$_1$C$_1$im]** (blue) cations.

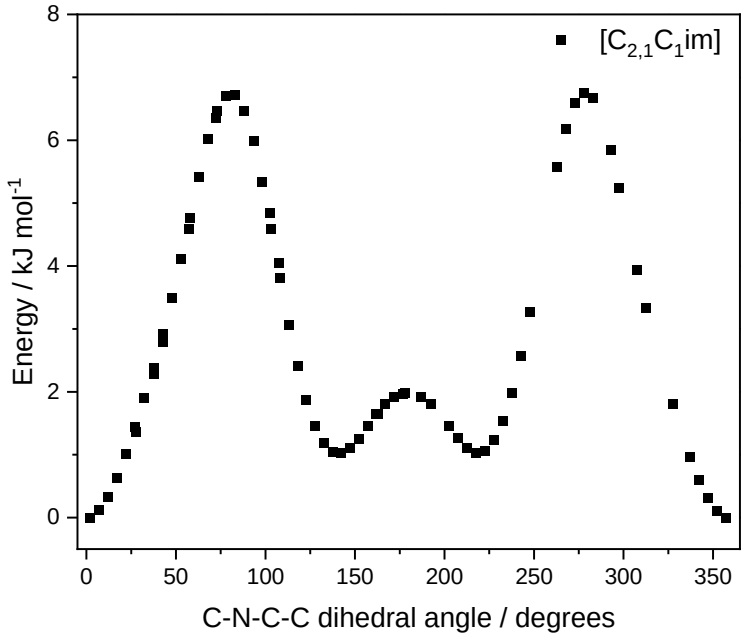


Figure S38. Ab initio energy calculation of C-N-C-C dihedral angle for **$[C_{2,1}C_1im]^+$** involving the hydrogen atom.

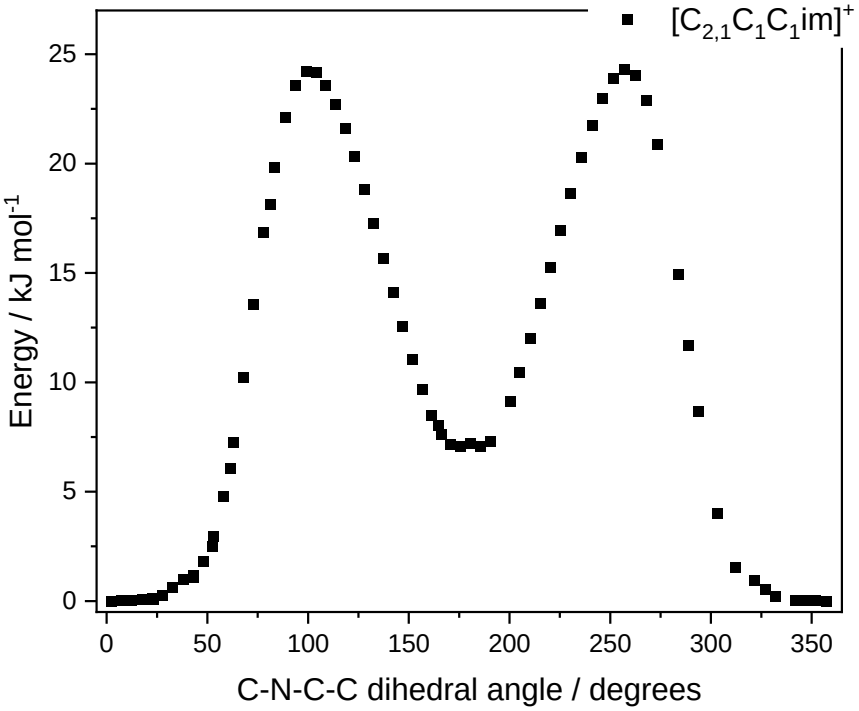


Figure S39. Ab initio energy calculation of C-N-C-C dihedral angle for **$[C_{2,1}C_1C_1im]^+$** involving the hydrogen atom.

Dipolar interactions between cyano groups

As discussed in the main text, dipole interactions between cyano groups are observed from the crystal structures. These interactions were also verified by ab initio calculations, which showed that the interactions are strong enough to make two cations attract each other instead of repulsing. Figure S40 shows these attractions in acetonitrile - **[N≡C$_2$C$_1$im]** (a), **[N≡C$_2$C$_1$im]** - **[N≡C$_2$C$_1$im]** (b) and **[N≡C$_2$C$_1$C$_1$im]** - **[N≡C$_2$C$_1$C$_1$im]** pairs. Acetonitrile has an interaction energy of 70 (75) kJ mol^{-1} with the cation, the **[N≡C$_2$C$_1$im]** complex has an interaction energy of 98 (95) kJ mol^{-1}, while the **[N≡C$_2$C$_1$C$_1$im]** complex has an interaction energy of 94 (100) kJ mol^{-1}. These energies are Counterpoise-corrected complexation energies at the full MP2/cc-pVTZ//B3LYP-GD3BJ/6-311+g(d,p) level of theory, the energies in brackets are those at the B3LYP-GD3BJ/6-311+g(d,p) level of theory. Critically, the backbone dihedral angle in (a) is 89.6°, which is energetically unfavourable for the isolated cation in the gas phase. However, the energy loss from the unfavoured dihedral is only about 5 kJ mol^{-1}, as discussed in the main manuscript. This difference is easily overcompensated for by the nitrile-nitrile interactions. For comparison, Figure S40 d) shows a different minimum geometry of the acetonitrile - **[N≡C$_2$C$_1$im]** pair for which the backbone dihedral angle is close to the preferred 0°. However, this comes at the cost of the nitrile-nitrile interactions due to steric hindrance, and the Counterpoise corrected complexation energy is 66 (70) kJ mol^{-1}. Thus, the additional gain in complexation energy with the unfavourable cation conformation is the same as the energy loss due to said conformation within the accuracy of the theory.

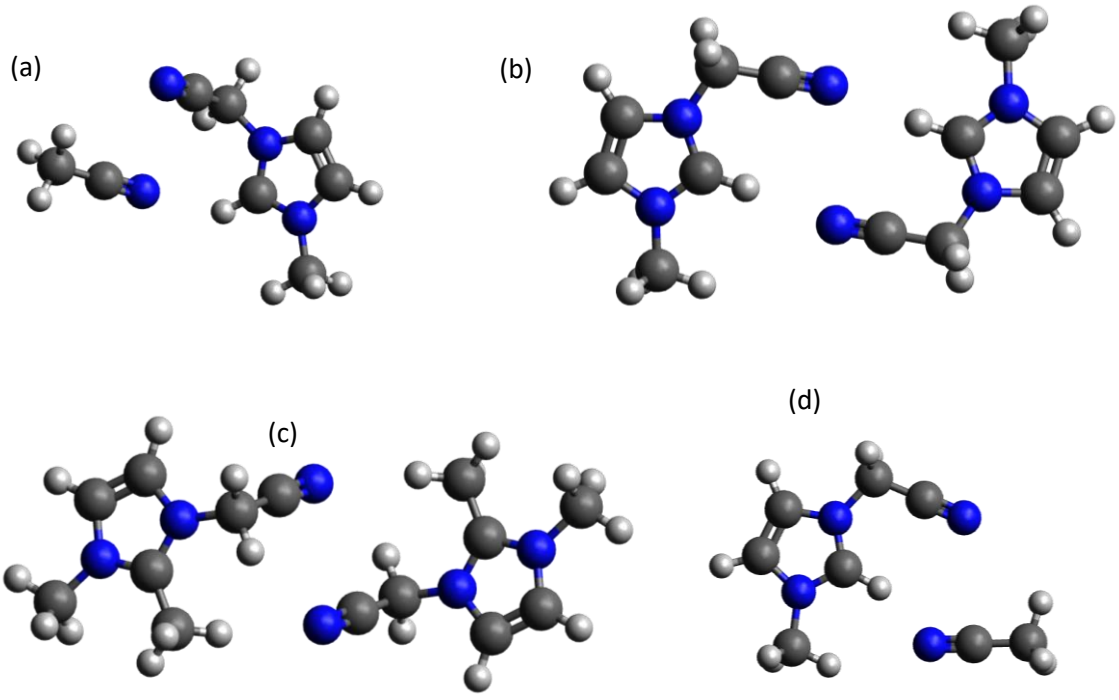


Figure S40. Dimer clusters formed between acetonitrile and **[N≡C$_2$C$_1$im]$^+$** (a) and (d), two ions of **[N≡C$_2$C$_1$im]$^+$** (b) and **[N≡C$_2$C$_1$C$_1$im]$^+$** - **[N≡C$_2$C$_1$C$_1$im]$^+$** (c) .

Crystallography studies

Table S8: crystallographic data for all structures. All datasets were collected at 173.0(1) K.

Compound	**[N≡C$_2$C$_1$im]Br**	**[HC≡C$_1$C$_2$C$_1$im]Br**	**[HC≡C$_2$C$_1$im]Br**	**[N≡C$_2$C$_1$C$_1$im]Br**	**[N≡C$_2$C$_1$C$_1$im][NTf$_2$]**	**[N≡C$_2$C$_1$im]Cl**	**[N≡C$_2$C$_1$C$_1$im]Cl**	**[HOC$_2$C$_1$im]Br**
Formula	$C_6H_8BrN_3$	$C_8H_{11}BrN_2$	$C_7H_9BrN_2$	$C_7H_{10}BrN_3$	$C_9H_{10}F_6N_4O_4S_2$	$C_6H_8ClN_3$	$C_7H_{10}ClN_3$	$C_6H_{11}BrN_2O$
M/g mol^{-1}	202.06	215.10	201.07	216.09	416.33	157.60	171.63	207.08
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group (No.)	*P nma* (62)	*P* 2$_1$/*n* (14)	*Cc* (9)	*Cc* (9)	*P* 2$_1$/*c* (14)	*P nma* (62)	*P* 2$_1$/*n*	*P* 2$_1$
a/Å	15.5333(6)	10.4022(7)	7.7092(3)	7.0482(3)	13.0861(12)	14.9547(5)	7.3329(3)	7.3302(3)
b/Å	6.3618(3)	7.5130(5)	15.2680(4)	11.4371(5)	16.2425(13)	6.2734(2)	9.3234(4)	7.1879(3)
c/Å	7.9158(3)	11.8190(9)	7.4616(3)	11.1712(6)	15.1289(14)	7.8292(3)	12.2867(4)	8.5495(4)
α/°	90	90	90	90	90	90	90	90
β/°	90	102.618(8)	105.339(4)	94.909(5)	90.599(8)	90	90.240(3)	109.076(5)
γ/°	90	90	90	90	90	90	90	90
U/Å^3	782.24(6)	901.37(11)	846.96(5)	897.22(7)	3215.5(5)	734.51(4)	840.00(6)	425.73(3)
Z	4	4	4	4	8	4	4	2
μ(Mo-Kα) /mm^{-1}	5.181	4.499	4.782	4.523	0.421	0.442	3.521	4.767
F(000)	400	432	400	432	1680	328	360	208
Total reflections	4142	4911	5356	5531	20094	9241	3152	5312
Unique reflections	951	1890	1757	1904	6677	926	1629	1808
R_{int}	0.034	0.025	0.022	0.035	0.044	0.037	0.024	0.029
GooF on F^2	1.048	1.067	1.034	1.042	1.031	1.081	1.059	1.092
R_1[b] [$I_o > 2\sigma(I_o)$]	0.033	0.024	0.023	0.033	0.080	0.031	0.035	0.026
R_1 (all data)	0.041	0.033	0.025	0.037	0.102	0.039	0.044	0.030
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.084	0.048	0.049	0.070	0.215	0.071	0.089	0.056
wR_2 (all data)	0.090	0.051	0.050	0.072	0.248	0.074	0.095	0.058

Table S9: summary of non-hydrogen-bonding interactions between the anion and imidazolium ring.

	A···C_3N_2 (Å)	
	Plane	**C2**
[HC≡$C_1C_2C_1$im]Br	3.492	3.686(2)
[NC≡$C_1C_2C_1$im]Br	3.385	3.405(6)
[N≡$C_2C_1C_1$im][NTf_2]	2.670	3.138(7)
[N≡$C_2C_1C_1$im]Cl	3.339	3.490(2)

For imidazolium salts which have a methyl group at the C^2 position, one important solid state interaction is where the anion is positioned directly above the imidazolium ring, with a C2···A contact roughly perpendicular to the plane defined by the imidazolium ring. We measured the distance between the anion and the C2 atom, but also the distance between the anion and the mean plane defined by the C_3N_2 imidazolium ring atoms. However, the latter metric is of minimal use once the ionic radii differences between the different anions are accounted for.

For ([N≡$C_2C_1C_1$im]A), where A = Cl and Br, there is no significant difference in the C2···A distance when the difference in ionic radius of Cl^- and Br^- is considered. However, when ([N≡$C_2C_1C_1$im]Br) and ([HC≡$C_2C_1C_1$im]Br) are compared, the latter shows a significantly extended C2···Br distance by almost 0.3 Å (as well as a longer distance between Br^- and the C_3N_2 plane). This is likely a result of the favourable C≡CH···Br hydrogen bonding interactions disrupting the electrostatic interaction between anion and cation, resulting in a longer distance between Br^- and the imidazolium ring.

It is noteworthy that in the unfunctionalised [$C_2C_1C_1$im]Br salt, there are no interactions where the bromide anion is positioned above the imidazolium ring. Instead, the dominant interaction involving the imidazolium ring is actually π-π stacking with a distance of 3.434 Å between parallel mean planes defined by the C_3N_2 imidazolium ring atoms. The presence of additional functional groups (whether alkyne or nitrile) create additional hydrogen bonding interactions which are more energetically favourable than π-π stacking.

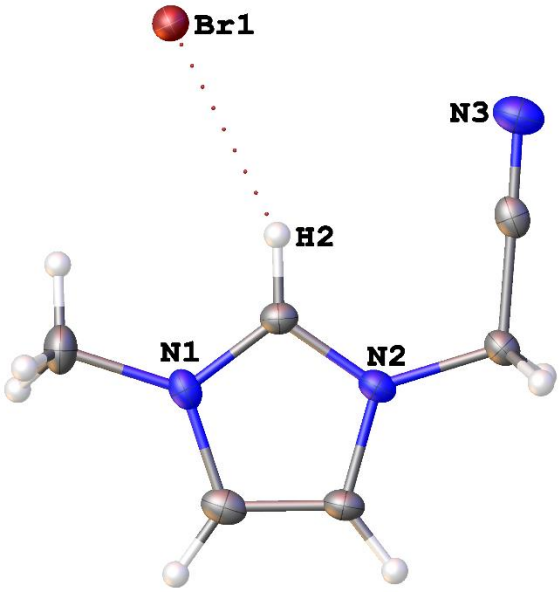


Figure S41: diagram showing the structure of **[N≡C$_2$C$_1$im]Br**, including the hydrogen bonding between H2 and Br1. Ellipsoids at 50% probability.

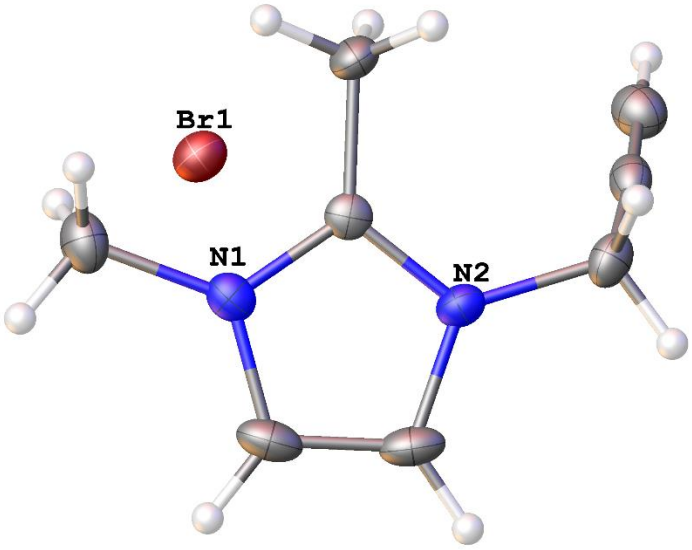


Figure S42: diagram showing the structure of **[HC≡C$_1$C$_2$C$_1$im]Br**. Ellipsoids at 50% probability.

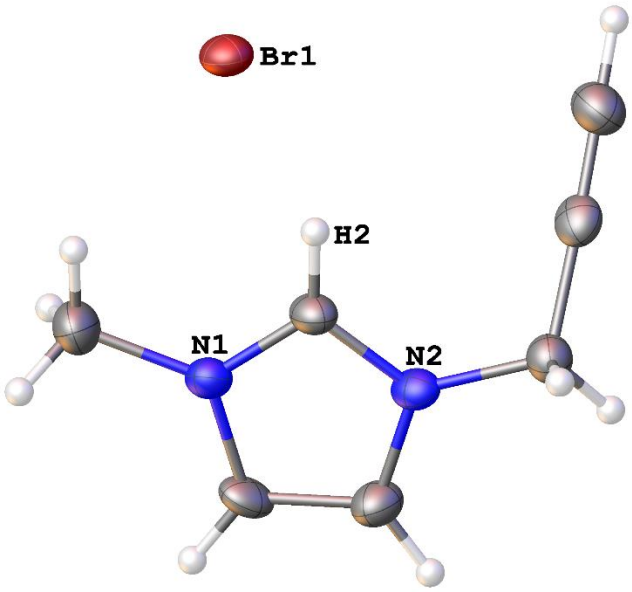


Figure S43: diagram showing the structure of **[HC≡C$_2$C$_1$im]Br**. Ellipsoids at 50% probability.

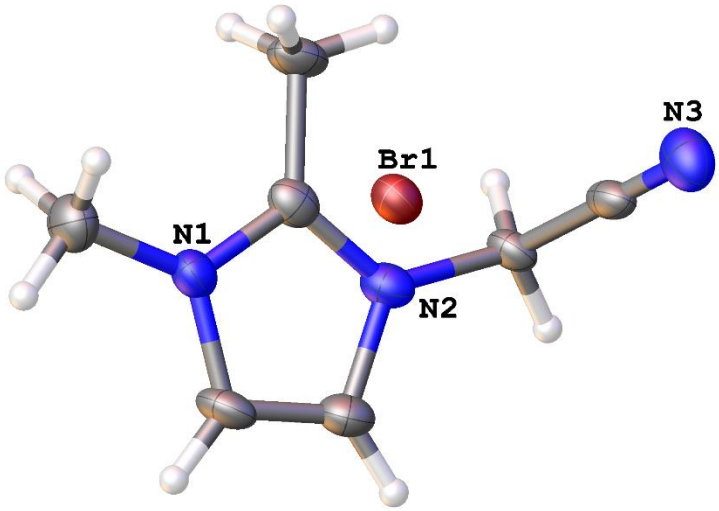


Figure S44: diagram showing the structure of **[N≡C$_2$C$_1$C$_1$im]Br**. Ellipsoids at 50% probability.

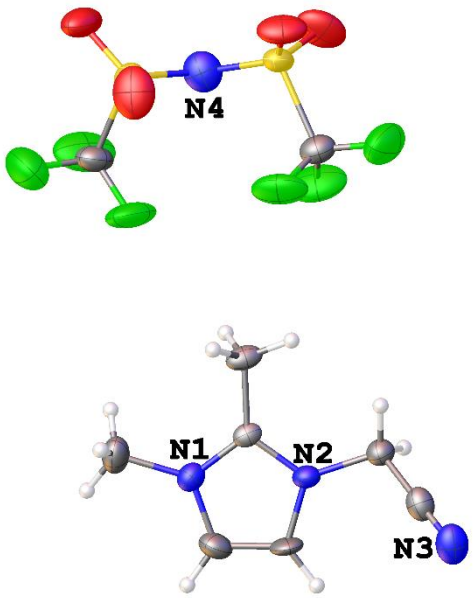


Figure S45: diagram showing the structure of one of the symmetry-independent salts of **[N≡C$_2$C$_1$C$_1$im][NTf$_2$]**. Ellipsoids at 50% probability.

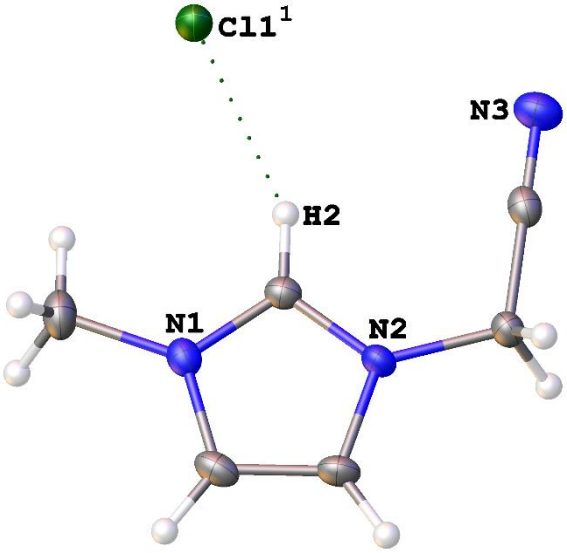


Figure S46: diagram showing the structure of **[N≡C$_2$C$_1$im]Cl**, including the hydrogen bonding between H2 and Cl1^{i}. Ellipsoids at 50% probability. Symmetry operation: (i) = x–0.5, 1.5–y, 1.5–z.

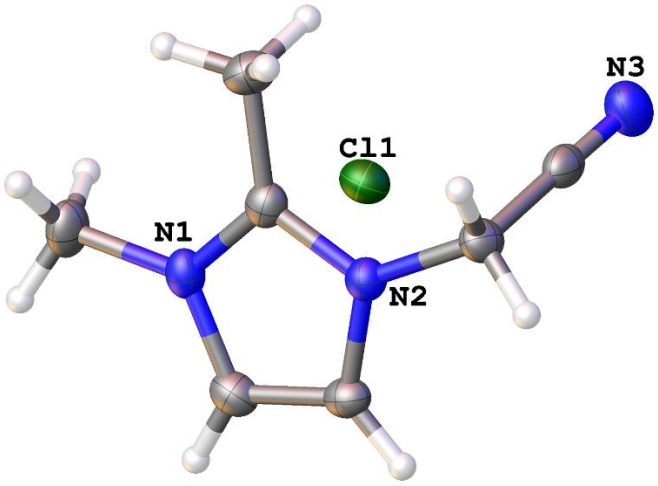


Figure S47: diagram showing the structure of **[N≡C$_2$C$_1$C$_1$im]Cl** at 50% probability.

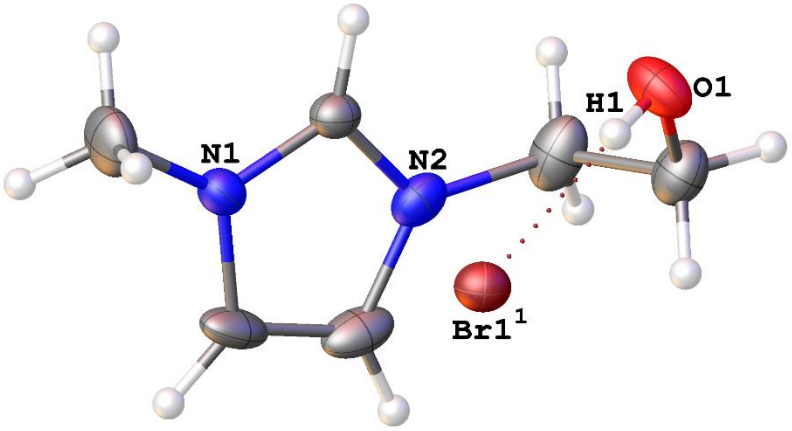


Figure S48: diagram showing the structure of **[HOC$_2$C$_1$im]Br**, including the hydrogen bonding between the OH group and Br1^{i}. Ellipsoids at 50% probability. Symmetry operation: (i) = 1–x, y–0.5, 2–z.

MD Simulations

Methodology

Overpolarisation of Drude induced dipoles, potentially leading to the polarisation catastrophe, was avoided using Thole screening functions.[2]

The initial topology was created by randomly packing 512 ion pairs into a cubic box using packmol.[3] The LAMMPS data files were then created using fftool and the polarizer and scaleLJ tools.[‡] The system was then minimised using a conjugate gradient algorithm with an energy tolerance of 10^{-4}, a force tolerance of 10^{-6}, a maximum of 100 outer iterations, or a maximum of 1000 force evaluations as stopping criteria. Random velocities corresponding to an instantaneous kinetic temperature of 298 K were then given to the atoms. The system was then kept at 298 K for 50 ps, heated to 600 K over 50 ps, kept at 600 K for 100 ps, and cooled to 298 K over 50 ps. These initial heating, cooling, and isothermal cycles were performed in the NPT ensemble at 1 bar pressure, using linear ramps for temperature changes. After the initial heat cycling, the system was kept in the NVT ensemble for 25 ps, followed by 150 ps in the NPT ensemble. The average box volume was recorded during the 150 ps NPT run, with every 10^{th} step used for the averaging. This process – 25 ps NVT, 150 ps NPT with averaging of the box volume – was repeated 10 times. Thus, the side lengths of the cubic boxes were obtained as 61.86±0.02 Å for **$[C_2C_1C_1im][NTf_2]$** and 60.54±0.02 Å for **$[C_2C_1im][NTf_2]$**. The systems were then compressed to their respective average box size in NVT over 25 ps and allowed to equilibrate in NVT for 4 ns. This was followed by a production run of 15 ns for **$[C_2C_1im][NTf_2]$** and 20 ns for **$[C_2C_1C_1im][NTf_2]$**, during which the positions were stored every 1 ps. LAMMPS data and input files for the equilibrated systems are given in the supporting information.

The spatial distribution functions of anions around cations were obtained from the trajectories using TRAVIS with the three carbon atoms in the imidazolium ring as reference points.[4, 5] Based on the spatial distribution functions, we evaluated minimum energy pathways using the nudged elastic band algorithm.[6]

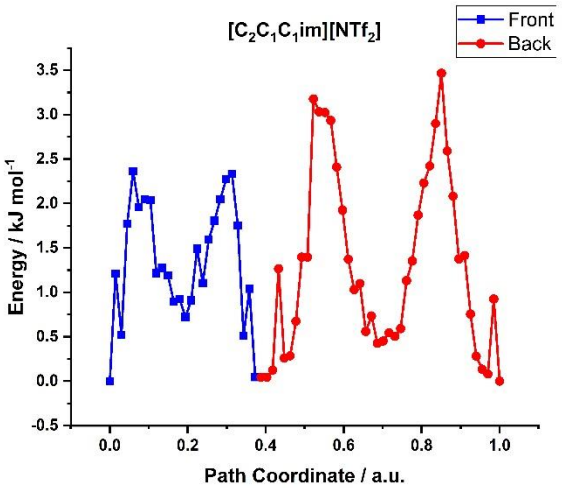


Figure S49. Energy to path coordinate graphs for **$[C_2C_1C_1im][NTf_2]$** in with simulation with scaling factor 0.57

Table S9. Diffusion coefficients of **$[C_2C_1im][NTf_2]$** and **$[C_2C_1C_1im][NTf_2]$** K065 calculated by MD simulations

Ionic liquid	Cation self-diffusion D_+ (10^{-11} m^2s^{-1})	Cation error (10^{-14} m^2s^{-1})	Anion self-diffusion D_- (10^{-11} m^2s^{-1})	Anion error (10^{-14} m^2s^{-1})
$[C_2C_1im][NTf_2]$	3.34	2.76	2.65	5.30
$[C_2C_1C_1im][NTf_2]$ K=0.57	3.47	3.52	2.83	2.02
$[C_2C_1C_1im][NTf_2]$ K=0.65	2.39	1.75	1.88	1.26

References

1. W. L. Armarego, *Purification of laboratory chemicals*, Butterworth-Heinemann, 2017.
2. J. N. Canongia Lopes and A. A. Pádua, *The Journal of Physical Chemistry B*, 2006, **110**, 19586-19592.
3. L. Martínez, R. Andrade, E. Birgin and J. Martínez, *J. Comput. Chem*, 2009, **30**, 2157-2164.
4. M. Brehm and B. Kirchner, *Journal of Chemical Information and Modeling*, 2011, **51**, 2007-2023.
5. M. Brehm, M. Thomas, S. Gehrke and B. Kirchner, *The Journal of chemical physics*, 2020, **152**, 164105.
6. R. Olsen, G. Kroes, G. Henkelman, A. Arnaldsson and H. Jónsson, *The Journal of chemical physics*, 2004, **121**, 9776-9792.

Notes

‡Pádua, A. A. H. 2013, http://github.com/agiliopadua/fftool and Pádua, A. A. H. 2019, https://github.com/agiliopadua/pol_il