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Supplementary material

Synthesis and physical properties of tris(dialkylamino)cyclopropenium bistriflamide ionic liquids

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Starting material syntheses

Tris(dimethylamino)cyclopropenium chloride, $[C_3(NMe_2)_3]Cl$ (1a). In a modification of Yoshida and Tawara's procedure,[1] C_3Cl_5H (6.91 mL, 49 mmol) was added drop-wise to a stirred aqueous solution of Me_2NH (40%) (44 g, 392 mmol) at 0 °C for an hour. The solution was left stirring overnight at ambient temperature. The product mixture contained the allyl-diamidinium salt $[HC_3(NMe_2)_4]^+$ along with **1a** and $[Me_2NH_2]Cl$. The mixture was dissolved in acetonitrile:toluene (2:1) and kept in a freezer overnight to crystallize out ammonium salts. The solution was then dissolved in water (50 mL) and acidified with conc. HCl to pH = 1–2. Salt **1a** was then extracted with $CHCl_3$ (3 × 50 mL) while leaving behind the diamidinium dication $[H_2C_3(NMe_2)_4]^{2+}$ in the water layer. The $CHCl_3$ was removed *in vacuo* to give **1a** as an orange solid (3 g, 30%). NMR was consistent with the literature.[1]

Bis(dimethylamino)cyclopropenone, $C_3(NMe_2)_2O$. $[C_3(NMe_2)_3]Cl$ (60 g, 0.295 mol) was added to aqueous NaOH (15%, 150 mL) and heated to 70 °C for 2 h in an open mouth beaker to allow escape of Me_2NH. The solution was acidified to pH = 2 and the organic compound was extracted from aqueous solution using $CHCl_3$ (3 × 250 mL). $CHCl_3$ was removed *in vacuo*, yielding a yellow solid (24 g, 56%). EI-MS: m/z 141.1023 ($[MH]^+$), calcd 141.1022. NMR was consistent with the literature.[2]

Bis(dimethylamino)methoxycyclopropenium methylsulphate, $[C_3(NMe_2)_2(OMe)]MeSO_4$ (7). Dried $C_3(NMe_2)_2O$ (2.69 g, 19.2 mmol) was stirred with Me_2SO_4 (2.36 mL, 25 mmol) for 2 h. The mixture was washed with dry diethyl ether several times to remove methanol and excess Me_2SO_4. This gave a viscous orange oil (4.57 g, 90%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.15 (s, 3H, OCH_3), 3.63 (s, 3H, CH_3SO_4), 3.16 (s, 12H, NCH_3); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 122.76 (equivalent ring C), 119.89 (unique ring C), 63.87 (O*C*H$_3$), 54.17 (*C*H$_3$SO$_4$), 41.13 (N*C*H$_3$); EI-MS: m/z 155.1177 (100%, M^+), calcd 155.1179. Anal. calcd for $C_9H_{18}N_2O_5S.1.5H_2O$: C, 38.62; H, 7.02; N, 10.01. Found: C, 38.33; H, 6.93; N, 9.76.

Synthesis of triaminocyclopropenium salts

Tris(dipentylamino)cyclopropenium chloride, $[C_3(NPent_2)_3]Cl$ (1e). $NPent_2H$ (11.9 g, 75.9 mmol) and NEt_3 (25 mL, 179 mmol) were added to CH_2Cl_2 (100 mL) and cooled to 0 °C. C_3Cl_5H (4.84 g, 22.6 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, and then H_2O (200 mL) was added. The solution was acidified with aqueous HCl. The CH_2Cl_2 was separated and washed with H_2O (3 × 150 mL). Removal of CH_2Cl_2 *in vacuo* yielded a viscous orange liquid (10.6 g, 90.4% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.25 (t, $^3J_{HH}$ = 7.7 Hz, 12 H, NCH_2), 1.57 (m, 12 H, NCH$_2$CH_2), 1.30 (m, 12 H, NCH$_2$CH$_2$CH_2), 1.21 (m, 12 H, NCH$_2$CH$_2$CH$_2$CH_2), 0.85 (t, $^3J_{HH}$ = 7.2 Hz, 18 H, CH_3); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 116.30 (C_3), 52.86 (N*C*H$_2$), 28.50 (NCH$_2$*C*H$_2$), 28.45 (NCH$_2$CH$_2$*C*H$_2$), 22.16 (NCH$_2$CH$_2$CH$_2$*C*H$_2$), 13.67 (*C*H$_3$); ES-MS$^+$: m/z 504.5265 (100%, M^+), calcd 504.5256; anal. calcd for $C_{33}H_{66}N_3Cl.1.1H_2O$: C, 70.76; H, 12.27; N, 7.50; found: C, 70.76; H, 12.22; N, 7.65.

Tris(dipentylamino)cyclopropenium bistriflamide, $[C_3(NPent_2)_3]NTf_2$ (3e). Salt **1e** (3.09 g, 5.73 mmol) was stirred with aqueous $LiNTf_2$ (4.9 g, 19.9 mmol) in water (100 mL). The product was extracted with Et_2O (200 mL), and additional $LiNTf_2$ (6.1 g, 21.3 mmol) and H_2O (100 mL) were added. The Et_2O was then washed was H_2O (3 × 100 mL) and dried *in vacuo* to yield an orange liquid (4.30 g, 95.7%); ^{1}H, ^{13}C{^{1}H} NMR and MS$^+$ as for $[C_3(NPe_2)_3]Cl$ with additional peaks in the ^{13}C NMR due to NTf_2^-; anal. calcd for $C_{35}H_{66}N_4F_6O_4S_2$: C, 53.55; H, 8.47; N, 7.14; found: C, 54.43; H, 8.57; N, 7.23; H_2O content: 58 ppm; Cl^- content: 200 ppm.

Tris(dihexylamino)cyclopropenium chloride, $[C_3(NHex_2)_3]Cl$ (1f). $NHex_2H$ (20.8 g, 112 mmol) and NEt_3 (45 mL, 323 mmol) were added to CH_2Cl_2 (200 mL) and cooled to 0 °C. C_3Cl_5H (4.84 g, 22.6 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, then washed with H_2O (4 × 200 mL). The solution was acidified with aqueous HCl. The CH_2Cl_2 was separated and washed with H_2O (4 × 200 mL). Removal of CH_2Cl_2 *in vacuo* gave a viscous orange liquid (11.8 g, 83.4% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.29 (t, $^3J_{HH}$ = 8.07 Hz, 12 H, NCH_2), 1.60 (m, 12 H, NCH$_2$CH_2), 1.28 (m, 36 H, NCH$_2$CH$_2$(CH_2)$_3$), 0.86 (t, $^3J_{HH}$ = 6.60 Hz, 18 H, N(CH$_2$)$_5$CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 116.55 (C_3), 53.14 (N*C*H$_2$), 31.46 (NCH$_2$*C*H$_2$), 28.98 (N(CH$_2$)$_2$*C*H$_2$), 26.34 (N(CH$_2$)$_3$*C*H$_2$), 22.50 (N(CH$_2$)$_4$*C*H$_2$), 13.88 (N(CH$_2$)$_5$*C*H$_3$). EI-MS$^+$ as for $[C_3(NHex_2)_3]NTf_2$. We were unable to obtain a good microanalysis for this material.

Tris(dihexylamino)cyclopropenium bistriflamide, $[C_3(NHex_2)_3]NTf_2$ (3f). Salt **1f** (3.12 g, 5.00 mmol) was stirred with $LiNTf_2$ (4.0 g, 14.0 mmol) in water (50 mL). The product was extracted with CH_2Cl_2 (25 mL) and washed with H_2O (50 mL). Additional $LiNTf_2$ (4.0 g, 14.0 mmol) and H_2O (100 mL) were added. The product was extracted with Et_2O (100 mL), washed with H_2O (4 × 100 mL) and dried *in*

vacuo to yield an orange liquid (3.91 g, 89.9%). ^{1}H and ^{13}C{^{1}H} NMR as for $[C_3(NHex_2)_3]Cl$ with additional peaks in the ^{13}C{^{1}H} NMR due to NTf_2^-. ES-MS$^+$: m/z 588.6214 (M^+), calcd 588.6190; anal. calcd for $C_{41}H_{78}N_4F_6O_4S_2$: C, 56.66; H, 9.05; N, 6.45; found: C, 57.30; H, 9.22; N, 6.48; H_2O content: 20 ppm; Cl^- content: 180 ppm.

Tris(didecylamino)cyclopropenium chloride, $[C_3(NDec_2)_3]Cl$ (1g). $NDec_2H$ (13.8 g, 46.3 mmol) and NEt_3 (15 mL, 108 mmol) were added to CH_2Cl_2 (100 mL) and cooled to 0 °C. C_3Cl_5H (2.84 g, 13.2 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 6 h, then H_2O was added (200 mL). The solution was acidified with aqueous HCl, separated and washed again with dilute aqueous HCl. The CH_2Cl_2 was separated and washed with H_2O (3 × 150 mL). Removal of CH_2Cl_2 *in vacuo* yielded a viscous orange liquid and white precipitate. After addition of acetone and cooling in the freezer, the precipitate was removed by filtration through silica gel three times. Removal of acetone *in vacuo* yielded an orange liquid (9.46 g, 74.5% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.26 (t, $^{3}J_{HH}$ = 7.7 Hz, 12 H, NCH_2), 1.57 (m, 12 H, NCH_2CH_2), 1.23 (m, 84 H, $N(CH_2)_2(CH_2)_7$), 0.83 (t, $^{3}J_{HH}$ = 7.0 Hz, 18 H, $N(CH_2)_9CH_3$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 116.49 (C_3), 53.11 (NCH_2), 31.78 (NCH_2CH_2), 29.50 ($N(CH_2)_2CH_2$), 29.44 ($N(CH_2)_3CH_2$), 29.34 ($N(CH_2)_4CH_2$), 29.21 ($N(CH_2)_5CH_2$), 29.01 ($N(CH_2)_6CH_2$), 26.66 ($N(CH_2)_7CH_2$), 22.57 ($N(CH_2)_8CH_2$), 14.00 ($N(CH_2)_9CH_3$); ES-MS$^+$: m/z 924.9965 (100%, M^+), calcd 924.9946; anal. calcd for $C_{63}H_{126}N_3Cl.0.6H_2O$: C, 77.86; H, 13.19; N, 4.32; found: C, 77.86; H, 13.23; N, 4.43.

Tris(didecylamino)cyclopropenium bistriflamide, $[C_3(NDec_2)_3]NTf_2$ (3g). Salt **1g** (3.05 g, 3.18 mmol) was stirred with $LiNTf_2$ (4.0 g, 14.0 mmol). H_2O (100 mL) was added and product extracted with Et_2O (200 mL). Additional $LiNTf_2$ (4.0 g, 14.0 mmol) and H_2O (100 mL) were added. The solution was again extracted with Et_2O and washed with H_2O (3 × 100 mL) before drying *in vacuo* to yield an orange liquid (3.18 g, 83.0%); ^{1}H, ^{13}C{^{1}H} NMR and MS$^+$ as for $[C_3(NDec_2)_3]Cl$ with additional peaks in the ^{13}C{^{1}H} NMR due to NTf_2^-; anal. calcd for $C_{65}H_{126}N_4F_6O_4S_2$: C, 64.74; H, 10.53; N, 4.65; found: C, 64.80; H, 10.57; N, 4.84; H_2O content: 38 ppm; Cl^- content: 195 ppm.

Tris(ethylmethylamino)cyclopropenium bistriflamide, $[C_3(NEtMe_2)_3]NTf_2$ (4a). C_3Cl_5H (4.27 mL, 33 mmol) was added dropwise to a stirred solution of MeEtNH (10 mL, 116 mmol) and Et_3N (18.55 mL, 132 mmol) in CH_2Cl_2 (20 mL) at 0 °C for an hour. The solution was left on stirring overnight at ambient temperature. The product was a mixture of the open ring $[HC_3(NMeEt)_4]Cl$ with $[C_3(NMeEt)_3]Cl$ and $[MeEtNH_2]Cl$. The mixture was dissolved in water (50 mL) and acidified with conc. HCl to pH = 1-2. $[C_3(NMeEt)_3]Cl$ was then extracted with $CHCl_3$ (3 × 50 mL) while leaving behind the dication of the open ring product, $[H_2C_3(NMeEt)_4]^{2+}$ in the water layer. $[C_3(NMeEt)_3]Cl$ was then stirred with $LiNTf_2$ (8.09 g, 27 mmol) in H_2O (10 mL). The solvent was removed *in vacuo*, the mixture was dissolved in $CHCl_3$ (30 mL), and the product was washed with conc. HCl (3 × 30 mL) to remove the open ring product, followed by washing the organic layer with water (3 × 30 mL). The solvent was removed *in vacuo* to give a light brown oil (3.70 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (q, $^{3}J_{HH}$ = 6.8 Hz, 6H, NCH_2), 3.09 (s, 9H, NCH_3), 1.27 (t, $^{3}J_{HH}$ = 6.8 Hz, 6H, NCH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.92 (q, $^{1}J_{CF}$ = 324 Hz, CF_3), 118.96 (ring C), 50.05 (NCH_2), 39.00 (NCH_3), 12.81 (NCH_2CH_3); ESI MS: m/z 210.1967 (M^+), calcd 210.1965; Anal. calcd for $C_{14}H_{24}N_4O_4S_2F_6$: C, 34.28; H, 4.93; N, 11.42. Found: C, 34.84; H, 5.18; N, 11.58; H_2O content: 990 ppm; Cl^- content: 130 ppm.

Tris(octadecylmethylamino)cyclopropenium chloride, $[C_3(NStMe)_3]Cl$ (2c). $N(C_{18}H_{37})MeH$ (11.6 g, 40.9 mmol) and NEt_3 (14.5 g, 143 mmol) were added to CH_2Cl_2 (100 mL) and cooled to 0 °C. C_3Cl_5H

(2.84 g, 13.2 mmol) was added dropwise and the solution stirred for 60 h at ambient temperature. The solution was heated to reflux for 20 h. The solvent was removed *in vacuo* and the product extracted from an aqueous solution using $CHCl_3$. The organic solvent was removed under vacuum. The product was washed with petroleum ether (2 × 50 mL) to remove residual amine and dried *in vacuo* to give a light yellow solid (10.2 g, 81.4%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.33 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $NCH_2C_{17}H_{35}$), 3.17 (s, 9H, NCH_3), 1.60 (m, 6H, $NCH_2CH_2C_{16}H_{33}$), 1.12–34 (m, 90H, $NC_2H_4C_{15}H_{30}CH_3$), 0.85 (t, $^3J_{HH}$ = 6.5 Hz, 9H, $NC_{17}H_{34}CH_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 116.99 (C_3), 55.70 (NCH_2), 40.31 (NCH_3), 31.90, 28.72–30.42, 28.05, 26.66, 22.66, 14.10 (CH_3); ES-MS: m/z 882.9465 (100%, M^+), calcd 882.9477; anal. calcd for $C_{60}H_{120}N_3Cl.2.2H_2O$: C, 75.17; H, 13.08; N, 4.38; found: C, 75.18; H, 12.86; N, 4.56.

Tris(octadecylmethylamino)cyclopropenium bistriflamide, $[C_3(NStMe)_3]NTf_2$ (4c). Salt **2c** (4.00 g, 4.35 mmol) was stirred with $LiNTf_2$ (5.00 g, 17.4 mmol) in H_2O (100 mL). The product was extracted with chloroform (100 mL), washed with H_2O (3 × 50 mL) and dried *in vacuo* to yield a yellow liquid (4.30 g, 84.9%); ^{1}H, ^{13}C{^{1}H} NMR and MS^+ as for $[C_3(NStMe)_3]Cl$ with an additional peak in the ^{13}C{^{1}H} NMR due to NTf_2^-; anal. calcd for $C_{62}H_{120}N_4F_6O_4S_2.1.5H_2O$: C, 62.54; H, 10.41; N, 4.71; found: C, 62.54; H, 10.24; N, 4.87.

Bis(dimethylamino)diethylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NEt_2)]NTf_2$ (9a). Salt **7** (4.6 g, 17.4 mmol) was stirred with NEt_2H (2.34 mL, 23 mmol) in dry CH_2Cl_2 (5 mL) for 2 h in an inert atmosphere. CH_2Cl_2 was removed *in vacuo*. The mixture was washed with dry diethylether several times to remove excess amine. The mixture was dissolved in ice cold water, and the product was extracted with $CHCl_3$:EtOH (2:1) (3 × 30 mL). The solvent was removed *in vacuo* to give $[C_3(NMe_2)_2(NEt_2)]MeSO_4$ as a light yellow oil, which was then stirred with $LiNTf_2$ (14.98 g, 52 mmol) in H_2O (20 mL) and the product is extracted with $CHCl_3$ (3 × 30 mL) and the solvent was removed *in vacuo*, the mixture was dissolved in EtOH, kept in a freezer overnight and filtered off to give white crystals (3.0 g, 36%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (q, $^3J_{HH}$ = 7.0 Hz, 4H, NCH_2), 3.12 (s, 12H, NCH_3), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 6H, NCH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.91 (q, $^1J_{CF}$ = 322 Hz, CF_3), 117.74 (equivalent ring C), 116.41 (unique ring C), 47.45 (NCH_2), 42.11 (NCH_3), 13.74 (NCH_2CH_3); EI-MS: m/z 196.1810 (M^+); calcd 196.1808; Anal. calcd for $C_{13}H_{22}N_4O_4S_2F_6$: C, 32.78; H, 4.65; N, 11.76. Found: C, 33.01; H, 4.64; N, 11.89; H_2O content: 120 ppm; Cl^- content: 345 ppm.

Bis(dimethylamino)dipropylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NPr_2)]NTf_2$ (9b). Salt **7** (5.43 g, 20 mmol) was stirred with NPr_2H (3.6 mL, 26 mmol) in CH_2Cl_2 (5 mL) for 2 h in an inert atmosphere. CH_2Cl_2 was removed *in vacuo*. The mixture was washed with dry diethyl ether several times to remove excess amine. The mixture was dissolved in ice cold water and the product was extracted with $CHCl_3$:EtOH (2:1) (3 × 30 mL). The solvent was removed *in vacuo* to give $[C_3(NMe_2)_2(NPr_2)]MeSO_4$ as a brown solid which was then stirred with $LiNTf_2$ (9.0 g, 32 mmol) in H_2O (20 mL). The product was extracted with $CHCl_3$ (3 × 50 mL) and the solvent was then removed *in vacuo* to give a brown solid (5.0 g, 94%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.26 (t, $^3J_{HH}$ = 7.6 Hz, 4H, NCH_2CH_2), 3.12 (s, 12H, NCH_3), 1.66 (m, 4H, NCH_2CH_2), 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $NCH_2CH_2CH_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 120.10 (q, $^1J_{CF}$ = 322 Hz, CF_3), 117.65 (equivalent ring C), 116.76 (unique ring C), 55.05 (NCH_2), 42.22 (NCH_3), 21.86 (NCH_2CH_2), 10.81 ($NCH_2CH_2CH_3$); EI-MS: m/z 224.2125 (M^+); calcd 224.2121; Anal. calcd for $C_{15}H_{26}N_4O_4S_2F_6$: C, 35.71; H, 5.19; N, 11.10. Found: C, 35.92; H, 5.2; N, 11.22; H_2O content: 760 ppm; Cl^- content: 760 ppm.

Bis(dimethylamino)dibutylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NBu_2)]NTf_2$ (9c). Salt **7** (2.4 g, 9 mmol) was stirred with NBu_2H (1.97 mL, 12 mmol) in dry CH_2Cl_2 (5 mL) for 2 h. CH_2Cl_2 was removed *in vacuo* and excess amine was removed by washing several times with dry diethylether to yield $[C_3(NMe_2)_2(NBu_2)]MeSO_4$ as a light yellow oil, which was then stirred with $LiNTf_2$ (6.92 g, 24 mmol) in water (10 mL). The solvent was removed *in vacuo*, the mixture was dissolved in $CHCl_3$:EtOH (2:1, 30 mL), and the product was washed with ice cold water (3 × 30 mL) to remove ammonium salts. The solvent was then removed *in vacuo* to yield a light yellow oil (3.4 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (t, $^3J_{HH}$ = 7.6 Hz, 4H, NC*H*$_2$), 3.11 (s, 12H, NC*H*$_3$), 1.60 (m, 4H, NCH$_2$C*H*$_2$), 1.32 (m, 4H, NCH$_2$CH$_2$C*H*$_2$), 0.94 (t, $^3J_{HH}$ = 7.6 Hz, 6H, NCH$_2$ CH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 119.89 (q, $^1J_{CF}$ = 322 Hz, CF_3), 117.59 (equivalent ring C), 116.66 (unique ring C), 53.22 (N*C*H$_2$), 42.17 (N*C*H$_3$), 30.56 (NCH$_2$*C*H$_2$), 19.79 (NCH$_2$ CH$_2$*C*H$_2$), 13.65 (NCH$_2$CH$_2$CH$_2$*C*H$_3$); EI-MS: m/z 252.2435 (M^+); calcd 252.2434; Anal. calcd for $C_{17}H_{30}N_4O_4S_2F_6$: C, 38.34; H, 5.68; N, 10.52. Found: C, 39.30; H, 5.87; N, 10.71; H_2O content: 760 ppm; Cl^- content: 490 ppm.

Bis(dimethylamino)dihexylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NHex_2)]NTf_2$ (9d). Salt **7** (2 g, 8 mmol) was stirred with $NHex_2H$ (2.3 mL, 10 mmol) in dry CH_2Cl_2 (5 mL) for 2 h. CH_2Cl_2 was removed *in vacuo*, the mixture was dissolved in ice cold water, and the product was extracted with $CHCl_3$:EtOH (2:1, 3 × 30 mL). The solvent was removed *in vacuo* to yield $[C_3(NMe_2)_2(NHex_2)]MeSO_4$ as a light yellow oil, which was then stirred with $LiNTf_2$ (5.22 g, 18 mmol) in H_2O (10 mL). The solvent was removed *in vacuo*, the mixture was dissolved in $CHCl_3$:EtOH (2:1, 30 mL), and the product was washed with ice cold water (3 × 30 mL) to remove ammonium salts. The solvent was removed *in vacuo* to yield a light yellow oil (3 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (t, $^3J_{HH}$ = 8.0 Hz, 4H, NC*H*$_2$), 3.11 (s, 12H, NC*H*$_3$), 1.61 (m, 4H, NCH$_2$C*H*$_2$), 1.29 (m, 12H, NCH$_2$ CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$), 0.88 (t, $^3J_{HH}$ = 6.8 Hz, 6H, NCH$_2$ CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 120.06 (q, $^1J_{CF}$ = 347 Hz, CF_3), 117.69 (equivalent ring C), 116.73 (unique ring C), 53.52 (N*C*H$_2$), 42.18 (N*C*H$_3$), 31.32 (NCH$_2$*C*H$_2$), 28.55 (NCH$_2$CH$_2$*C*H$_2$), 26.23 (NCH$_2$CH$_2$CH$_2$*C*H$_2$), 22.21 (NCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 13.41 (CH$_2$*C*H$_3$). EI-MS: m/z 308.3064 (M^+); calcd 308.3060; Anal. calcd for $C_{21}H_{38}N_4O_4S_2F_6$: C, 42.85; H, 6.51; N, 9.52. Found: C, 43.30; H, 6.69; N, 9.35; H_2O content: 520 ppm; Cl^- content: 160 ppm.

Bis(dimethylamino)ethylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NEtH)]NTf_2$ (13a). Salt **7** (8.82 g, 33 mmol) was stirred with $NEtH_2$ (3.25 mL, 43 mmol) in dry CH_2Cl_2 (20 mL) for 30 minutes in an inert atmosphere. CH_2Cl_2 was removed *in vacuo*. The mixture was washed with dry diethyl ether several times to remove excess amine. The mixture was dissolved in water, and the product was extracted with $CHCl_3$ (3 × 30 mL). The solvent was removed *in vacuo* to give $[C_3(NMe_2)_2(NEtH)]MeSO_4$ as a light brown oil, which was then stirred with $LiNTf_2$ (18.94 g, 66 mmol) in H_2O (20 mL) and the product was extracted with $CHCl_3$ (3×30 mL) and the solvent was removed *in vacuo* to give a light brown oil (8.5 g, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (br, 1H, N*H*), 3.33 (q, $^3J_{HH}$ = 8.0 Hz, 2H, NC*H*$_2$), 3.11 (s, 12H, NC*H*$_3$), 1.28 (t, $^3J_{HH}$ = 8.0 Hz, 3H, NCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.84 (q, $^1J_{CF}$ = 321 Hz, CF_3), 117.08 (equivalent ring C), 115.48 (unique ring C), 42.40 (N*C*H$_2$), 41.72 (N*C*H$_3$), 15.04 (NCH$_2$*C*H$_3$); ESI MS: m/z 168.1495 (M^+), calcd 168.1495; Anal. calcd for $C_{11}H_{18}N_4O_4S_2F_6$: C, 29.47; H, 4.04; N, 12.49. Found: C, 30.09; H, 4.13; N, 12.26; H_2O content: 1040 ppm; Cl^- content: 343 ppm.

Bis(dimethylamino)ethylmethylaminocyclopropenium bistriflamide, $[C_3(NMe_2)_2(NEtMe)]NTf_2$ (10a). Salt **13a** (3.51 g, 8 mmol) was stirred with dry THF at –78 °C and *n*-BuLi (5.38 mL of 1.6 M, 8.8 mmol) was added drop-wise in an inert atmosphere. The reaction mixture was stirred for 30 min and then allowed to warm to room temperature for another 30 min. Me_2SO_4 (0.98 mL, 10 mmol) was then added

and the solution was stirred for another 30 min. THF was then removed *in vacuo*. The mixture was dissolved in $CHCl_3$ (50 mL) and $LiMeSO_4$ was filtered off. Then the $CHCl_3$ layer was washed with water (3 × 50 mL). The solvent was removed *in vacuo* to give a yellow oil (2.22 g, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (q, $^3J_{HH}$ = 7.0 Hz, 2H, NC*H*$_2$), 3.12 (s, 12H, NC*H*$_3$), 3.09 (s, 3H, C*H*$_3$), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 6H, NCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.91 (q, $^1J_{CF}$ = 322 Hz, CF_3), 117.88 (equivalent ring C), 115.48 (unique ring C), 50.09 (N*C*H$_2$), 42.21 (N*C*H$_3$), 39.24 (N*C*H$_3$), 15.04 (NCH$_2$*C*H$_3$); ESI MS: m/z 182.1652 (M^+), calcd 182.1652; Anal. calcd for $C_{12}H_{20}N_4O_4S_2F_6$: C, 31.17; H, 4.36; N, 12.11. Found: C, 31.56; H, 4.37; N, 12.05; H_2O content: 880 ppm; Cl^- content: 125 ppm.

Bis(dimethylamino)propylaminocyclopropenium bistriflamide, [C$_3$(NMe$_2$)$_2$(NPrH)]NTf$_2$ (13b). Salt **7** (3.96 g, 15 mmol) was stirred with $NPrH_2$ (1.59 mL, 20 mmol) in dry CH_2Cl_2 (5 mL) for 1 h in an inert atmosphere. CH_2Cl_2 was removed *in vacuo*. The mixture was washed with dry diethyl ether several times to remove excess amine. The mixture was dissolved in water and the product was extracted with $CHCl_3$ (3 × 50 mL). The solvent was removed *in vacuo* to give [C$_3$(NMe$_2$)$_2$(NPrH)]$MeSO_4$ as a light yellow oil, which was then stirred with $LiNTf_2$ (7.51 g, 27 mmol) in H_2O (20 mL). The product was extracted with $CHCl_3$ (3 × 30 mL). The solvent was removed *in vacuo* to give a yellow oil (4.05 g, 92%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.29 (br t, 1H, N*H*), 3.23 (t, $^3J_{HH}$ = 8.0 Hz, 2H, NC*H*$_2$), 3.11 (s, 12H, NC*H*$_3$), 1.66 (m, 2H, NCH$_2$C*H*$_2$), 0.96 (t, $^3J_{HH}$ = 8.0 Hz, 3H, NCH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 119.92 (q, $^1J_{CF}$ = 320 Hz, CF_3), 117.69 (equivalent ring C), 117.47 (unique ring C), 49.30 (N*C*H$_2$), 41.79 (N(*C*H$_3$)$_2$), 23.19 (NCH$_2$*C*H$_2$), 10.90 (NCH$_2$CH$_2$*C*H$_3$); ESI MS: m/z 182.1653 (M^+), calcd 182.1652; Anal. calcd for $C_{12}H_{20}N_4O_4S_2F_6$: C, 31.17; H, 4.36; N, 12.11. Found: C, 31.34; H, 4.47; N, 11.91; H_2O content: 840 ppm; Cl^- content: 170 ppm.

Bis(dimethylamino)propylmethylaminocyclopropenium bistriflamide, [C$_3$(NMe$_2$)$_2$(NPrMe)]NTf$_2$ (10b). Salt **13b** (6.5g, 14.06 mmol) was stirred with dry THF at –78 °C and *n*-BuLi (9.66 mL of 1.6 M, 15.5 mmol) was added drop-wise in an inert atmosphere. Reaction mixture was stirred for 3 h and then allowed to warm to ambient temperature. Me_2SO_4 (1.73 mL, 18.27 mmol) was then added and the solution was stirred for another 30 minutes. THF was then removed *in vacuo*. Mixture was dissolved in $CHCl_3$ (50 mL) and $LiMeSO_4$ was filtered off and then wash the $CHCl_3$ layer with water (3 × 50 mL). The solvent was removed *in vacuo* to give a yellow oil (6 g, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.27 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NC*H*$_2$), 3.11 (s, 12H, NC*H*$_3$), 3.10 (s, 3H, NC*H*$_3$), 1.67 (m, 2H, NCH$_2$C*H*$_2$), 0.93 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 119.92 (q, $^1J_{CF}$ = 320 Hz, CF_3), 117.69 (equivalent ring C), 117.47 (unique ring C), 57.02 (N*C*H$_2$), 42.25 (N(*C*H$_3$)$_2$), 40.07 (N*C*H$_3$), 20.94 (NCH$_2$*C*H$_2$), 10.84 (NCH$_2$CH$_2$*C*H$_3$); EI-MS: m/z 196.1813 (M^+), calcd 196.1808; Anal. calcd for $C_{13}H_{22}N_4O_4S_2F_6$: C, 32.77; H, 4.65; N, 11.76. Found: C, 33.07; H, 4.64; N, 11.71; H_2O content: 540 ppm; Cl^- content: 20 ppm.

Bis(dimethylamino)butylmethylaminocyclopropenium bistriflamide, [C$_3$(NMe$_2$)$_2$(NBuMe)]NTf$_2$ (10c). Salt **7** (4.5 g, 17 mmol) was stirred with NBuMeH (2.6 mL, 22 mmol) in dry CH_2Cl_2 (5 mL) for 2 h in an inert atmosphere. CH_2Cl_2 was removed *in vacuo*. The mixture was washed with dry diethyl ether several times to remove excess amine. The mixture was dissolved in water and the pH lowered to 1 with HCl(aq) (37%) and the product was extracted with CH_2Cl_2 (3 × 30 mL). The solvent was removed *in vacuo* to give [C$_3$(NMe$_2$)$_2$(NBuMe)]$MeSO_4$ as a brown oil which was then stirred with $LiNTf_2$ (5 g, 18 mmol) in H_2O (20 mL). The product was extracted with CH_2Cl_2 (3 × 30 mL) and the solvent was the removed *in vacuo* to give a brown oil (2.8 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (t, 2H, $^3J_{HH}$ = 7.4 Hz, NC*H*$_2$), 3.12 (s, 12H, NC*H*$_3$), 3.10 s, 3H, NC*H*$_3$), 1.62 (m, 2H, NCH$_2$C*H*$_2$), 1.33 (m, 2H, NCH$_2$CH$_2$C*H*$_2$), 0.93 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.92 (q, $^1J_{CF}$ = 322 Hz, CF_3),

117.73 (equivalent ring C), 117.47 (unique ring C), 55.29 (N*C*H_2), 42.27 (N(*C*H_3)$_2$), 40.07 (N*C*H_3), 29.78 (NCH$_2$*C*H$_2$), 19.78 (NCH$_2$CH$_2$*C*H$_2$), 13.63 (NCH$_2$CH$_2$CH$_2$*C*H$_3$); EI-MS: m/z 210.1968 (M^+), calcd 210.1965; Anal. calcd for $C_{14}H_{24}N_4O_4S_2F_6$: C, 34.28; H, 4.93; N, 11.42. Found: C, 35.22; H, 5.11; N, 11.23; H_2O content: 490 ppm; Cl^- content: 30 ppm.

Bis(dimethylamino)hexylmethylaminocyclopropenium bistriflamide, [C$_3$(NMe$_2$)$_2$(NHexMe)]NTf$_2$ (10d). Salt **7** (4.11 g, 15 mmol) was stirred with NHexMeH (2.88 mL, 19 mmol) in dry CH_2Cl_2 (10 mL) for 2 h. CH_2Cl_2 was removed *in vacuo*. The mixture was dissolved in ice cold water and the product was extracted with $CHCl_3$:EtOH (2:1, 3 × 30 mL). The solvent was removed *in vacuo* to yield [C$_3$(NMe$_2$)$_2$(NHexMe)]MeSO$_4$ as a light yellow oil, which was stirred with $LiNTf_2$ (9.85 g, 34 mmol) in H_2O (50 mL) for 30 min. The solvent was then removed *in vacuo*. The mixture was dissolved in $CHCl_3$:EtOH (2:1, 30 mL) and the product was washed with ice cold water (3 × 30 mL) to remove ammonium salts. Solvent was removed *in vacuo* and the product was dissolved in $CHCl_3$ (50 mL) and washed with water (3 × 50 mL). The solvent was removed *in vacuo* to yield a light yellow oil (5.62 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (t, $^3J_{HH}$ = 7.6 Hz, 2H, NC*H*$_2$), 3.12 (s, 12H, NC*H*$_3$), 3.10 (s, 3H, NC*H*$_3$), 1.63 (m, 2H, NCH$_2$C*H*$_2$), 1.29 (m, 6H, NCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$), 0.88 (t, $^3J_{HH}$ = 6.8Hz, 6H, CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.91 (q, $^1J_{CF}$ = 347 Hz, *C*F$_3$), 117.73 (equivalent ring C), 117.45 (unique ring C), 55.55 (N*C*H$_2$), 42.25 (N*C*H$_3$), 40.07 (N*C*H$_3$), 31.33 (NCH$_2$*C*H$_2$), 27.64 (NCH$_2$CH$_2$*C*H$_2$), 26.21 (NCH$_2$CH$_2$CH$_2$*C*H$_2$), 22.42 (NCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 13.88 (CH$_2$*C*H$_3$); EI-MS: m/z 238.2279 (M^+), calcd 238.2278; Anal. calcd for $C_{16}H_{28}N_4O_4S_2F_6$: C, 37.06; H, 5.44; N, 10.81. Found: C, 37.28; H, 5.57; N, 10.94; H_2O content: 460 ppm; Cl^- content: 80 ppm.

Table 1S. ^{1}H-NMR chemical shift ranges in $CDCl_3$.

Alkyl group	H_α	H_β	$H_{\gamma \text{ to } \omega-1}$	H_ω
Me	3.10–3.20			
Et	3.35–3.40			1.22–1.27
C_nH_{2n+1} (n > 2)	3.25–3.35	1.55–1.70	1.20–1.35	0.85–0.95

Table 2S. ^{13}C-NMR chemical shift ranges in $CDCl_3$.

Alkyl group	C_α	C_β	$C_{\gamma \text{ to } \omega-2}$	$C_{\omega-1}$	C_ω
Me	39.0–42.3				
Et	47.1–50.1				12.9–15.0
Pr	52.2–57.0	20.9–21.9			10.5–10.9
C_nH_{2n+1} (n > 3)	52.9–55.6	28.5–31.8	26.2–29.5	19.6–22.7	13.5–14.2

Table 3S. Density data for peralkyltriaminocyclopropenium bistriflamide ionic liquids

Compound	Density (g cm^{-3})							
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
3b	1.277	1.269	1.260	1.251	1.243	1.234	1.226	1.217
3c	1.196	1.188	1.179	1.171	1.163	1.155	1.147	1.139
3d	1.134	1.127	1.119	1.111	1.103	1.095	1.088	1.080
3e	1.086	1.079	1.072	1.064	1.057	1.050	1.043	1.036
3f	1.059	1.051	1.044	1.037	1.030	1.022	1.015	1.008
3g	0.991	0.984	0.977	0.970	0.964	0.957	0.950	0.943
4a	1.333	1.324	1.315	1.306	1.297	1.288	1.279	1.270
4b	1.224	1.216	1.207	1.199	1.191	1.183	1.174	1.166
9b	–	–	–	1.287	1.279	1.271	1.262	1.254
9c	1.272	1.261	1.253	1.244	1.236	1.228	1.219	1.210
9d	1.209	1.200	1.192	1.184	1.176	1.168	1.159	1.151
10b	1.356	1.346	1.337	1.328	1.319	1.309	1.301	1.292
10c	1.331	1.321	1.313	1.303	1.294	1.285	1.276	1.266
10d	1.292	1.283	1.274	1.266	1.256	1.248	1.239	1.231
11a	1.308	1.299	1.291	1.282	1.273	1.264	1.256	1.247
11b	1.216	1.208	1.200	1.191	1.183	1.175	1.167	1.159
11c	1.171	1.163	1.155	1.147	1.139	1.131	1.123	1.115
12a	1.260	1.251	1.243	1.235	1.226	1.218	1.209	1.201
12b	1.228	1.220	1.211	1.203	1.195	1.187	1.178	1.170

Table 4S. Density fitting parameters for peralkyltriaminocyclopropenium bistriflamide ionic liquids

Compound	–b × 10^{-4}	a	α_p –c×10^{-3}	d
3b	8.576	1.5284	0.68773	0.44624
3c	8.126	1.4337	0.69621	0.38282
3d	7.755	1.3615	0.70058	0.33140
3e	7.161	1.2959	0.67668	0.28092
3f	7.263	1.2715	0.70295	0.26319
3g	6.812	1.1905	0.70440	0.19745
4a	9.000	1.5967	0.69161	0.49024
4b	8.221	1.4646	0.68803	0.40367
9b	8.300	1.5304	0.65332	0.46353
9c	8.655	1.5243	0.69771	0.44413
9d	8.246	1.4497	0.69733	0.39400
10b	9.083	1.6226	0.68899	0.50614
10c	9.210	1.6005	0.70877	0.49365
10d	8.750	1.5481	0.69384	0.45945
11a	8.709	1.5633	0.68175	0.46846
11b	8.193	1.4562	0.69007	0.39800
11c	7.881	1.4014	0.68959	0.35965
12a	8.403	1.5061	0.68300	0.43126
12b	8.204	1.4681	0.68431	0.40580

Table 5S. Molar volumes (mL mol^{-1}) for TDAC bistriflamide ILs

Compound	MW	293 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
3b	532.56	416.97	419.82	422.71	425.62	428.56	431.53	434.51	437.53
3c	616.72	515.75	519.33	522.95	526.60	530.28	533.99	537.73	541.50
3d	700.89	617.90	622.18	626.51	630.91	635.35	639.83	644.37	648.94
3e	785.05	722.88	727.57	732.32	737.83	742.71	747.66	752.68	757.77
3f	869.21	820.92	826.67	832.45	838.30	844.21	850.19	856.23	862.34
3g	1205.86	1216.65	1225.33	1233.93	1242.66	1251.42	1260.26	1269.19	1278.20
4a	490.48	367.95	370.45	372.99	375.56	378.16	380.81	383.49	386.20
4b	574.64	469.52	472.74	476.00	479.28	482.59	485.93	489.29	492.68
9b	504.51	–	–	–	392.00	394.45	396.94	399.77	402.32
9c	532.56	418.68	422.33	425.03	428.10	430.87	433.68	436.88	440.13
9d	588.67	486.91	490.56	493.85	497.19	500.57	504.00	507.91	511.44
10b	476.45	351.37	353.98	356.36	358.77	361.22	363.98	366.22	368.77
10c	490.48	368.50	371.29	373.56	376.42	379.04	381.70	384.39	387.42
10d	518.53	401.34	404.16	407.01	409.58	412.85	415.49	418.51	421.23
11a	504.51	385.64	388.26	390.91	393.59	396.28	398.99	401.73	404.49
11b	588.67	484.02	487.33	490.69	494.08	497.51	500.96	504.45	507.96
11c	644.78	550.82	554.57	558.38	562.23	566.13	570.06	574.04	578.05
12a	546.59	433.81	436.76	439.74	442.75	445.78	448.85	451.93	455.05
12b	574.64	468.01	471.20	474.43	477.68	480.96	484.27	487.61	490.97

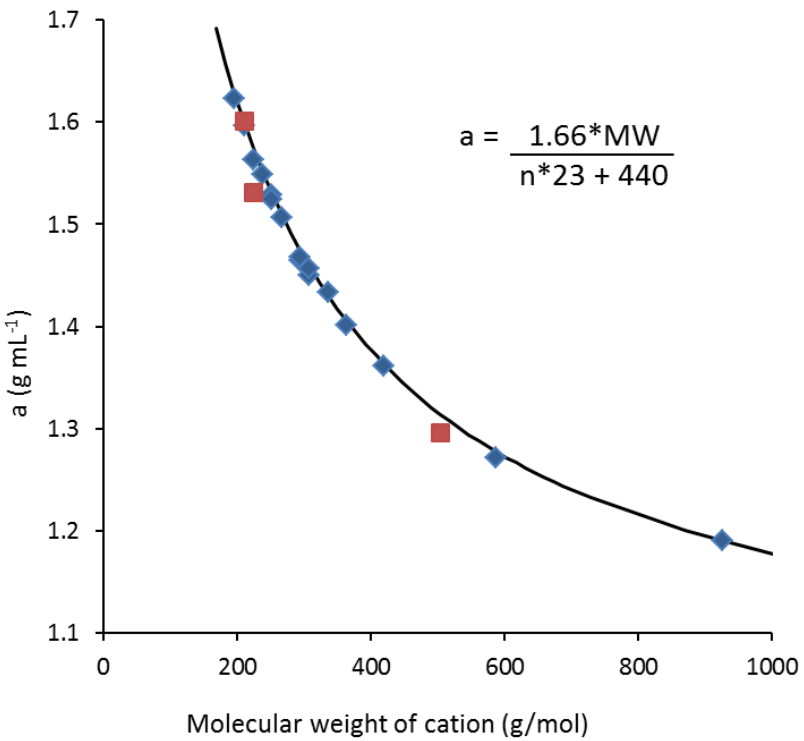

Fig. 1S. Density parameter a versus cation molecular weight for TDAC bistriflamide ILs. Salts **3e**, **9b** and **10c** are indicated by red squares.

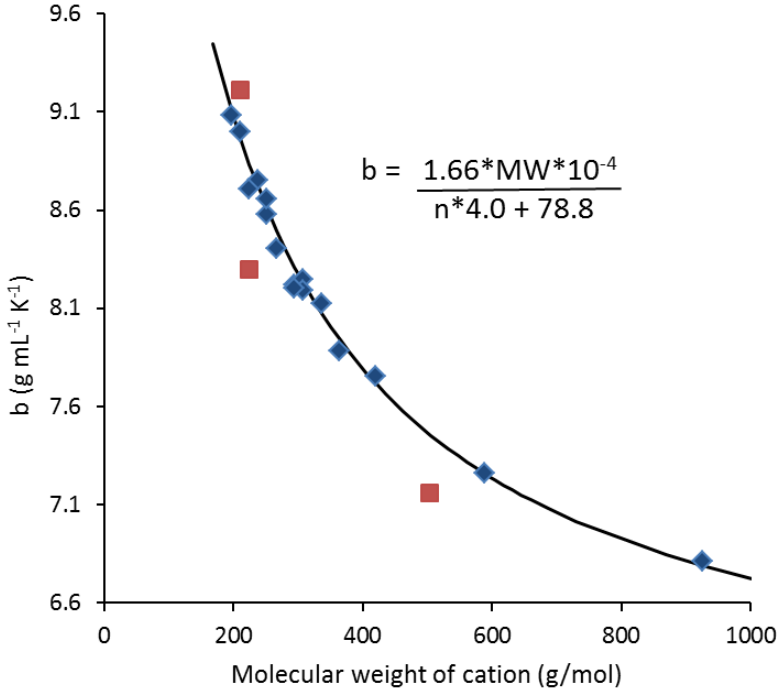

Fig. 2S. Density parameter b versus cation molecular weight for TDAC bistriflamide ILs. Salts **3e**, **9b** and **10c** are indicated by red squares.

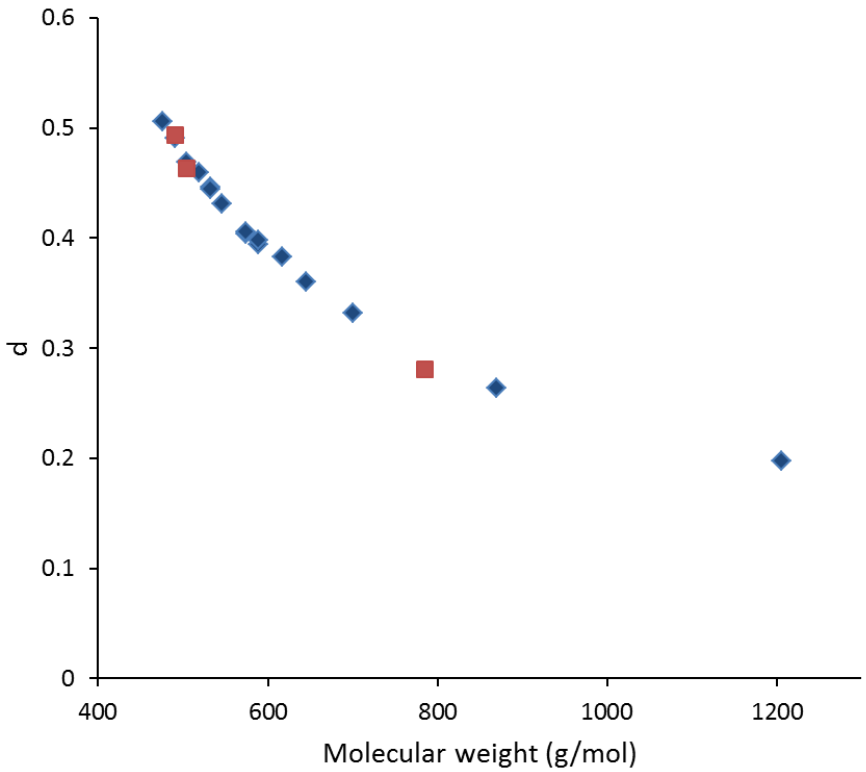

Fig. 3S. d (the intercept of ln(ρ) *versus T* plots) *versus* cation molecular weight for TDAC bistriflamide ILs. Salts **3e**, **9b** and **10c** are indicated by red squares.

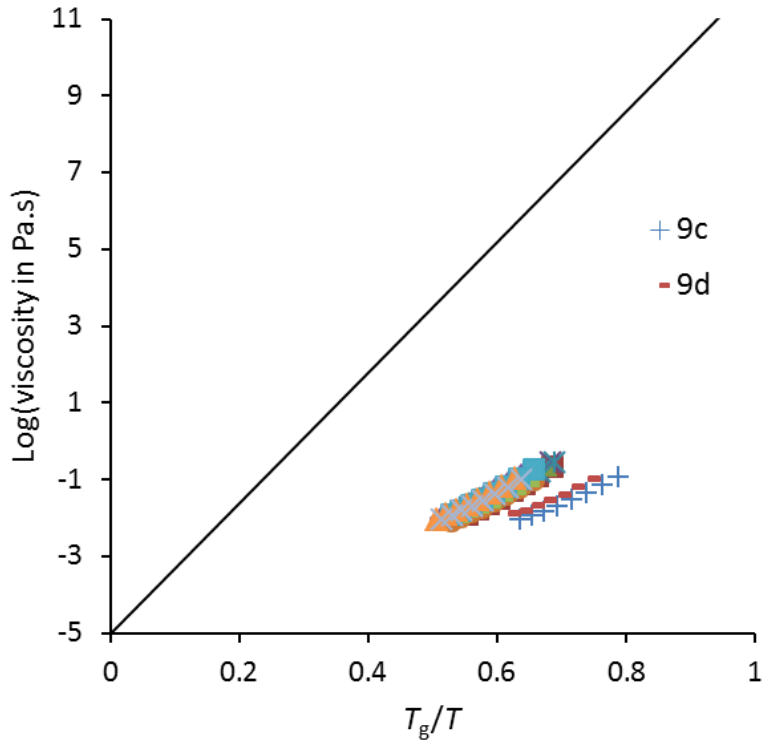

Fig. 4S. A fragility plot for the salts with observed glass transition temperatures.

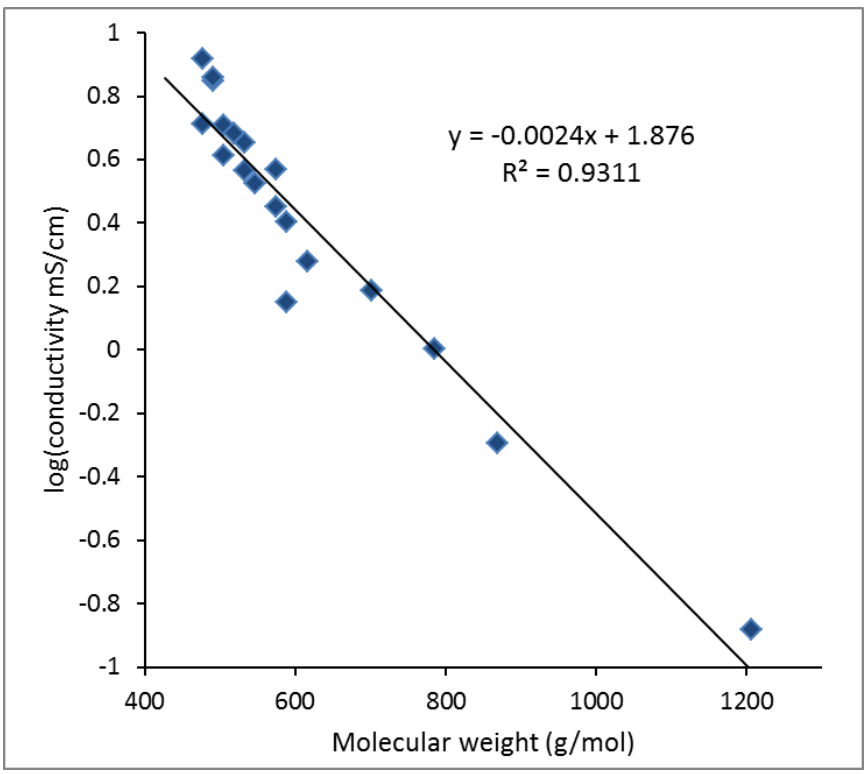

Fig. 5S. Log(conductivity) versus molecular weight for TDAC bistriflamide ILs.

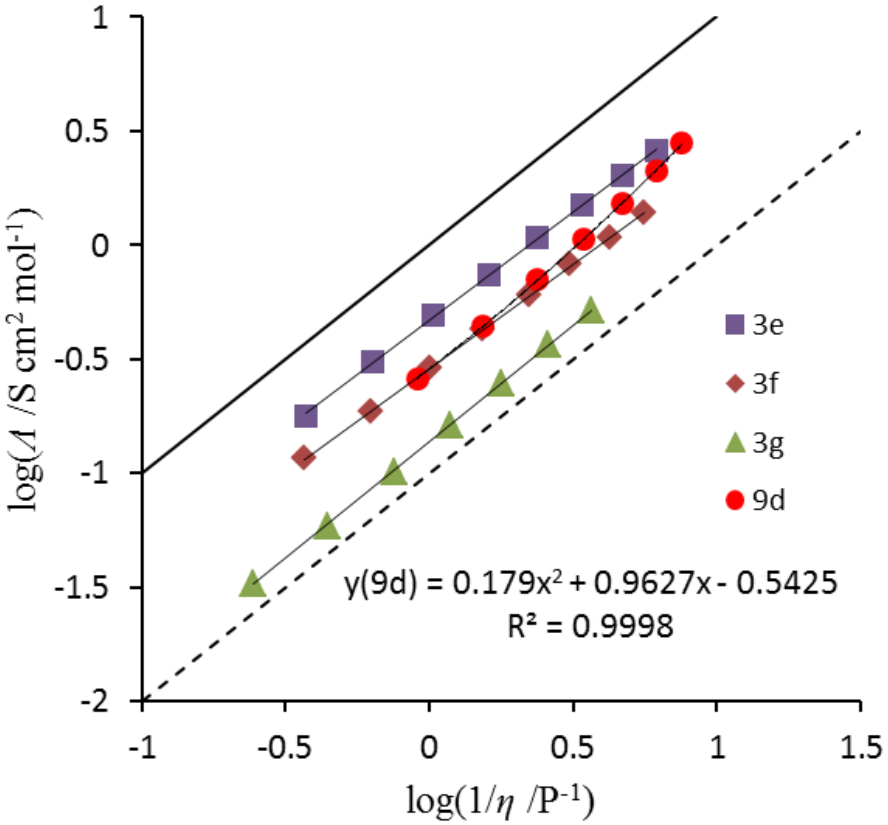

Fig. 6S. Walden plot for **3e**-**g** and **9d**.

The Adjusted Walden Plot

MacFarlane developed an adjusted Walden plot to take into account the role of the ion sizes r^+ and r^- (Eq 1S).[3] To make this adjusted plot (Fig 5S), we used the volume of 248 Å^3 for bistriflamide for a radius of 3.90 Å at 20 °C. MacFarlane calculated a radius of 3.72 Å using HF/aug-cc-pVTZ, which is considered to be an underestimation of the hydrodynamic radius,[3] so we have used 3.90 Å. Interestingly, 3.72 Å agrees quite well with a radius of 3.68 Å estimated using the volume of **3a** at 0 K (440 Å^3, Fig. 1S). By difference and using the equation: $V_{298\ K}$ = n*27.7 + 528, derived from Fig. 5, we calculated the effective hydrodynamic radii of the various cations (given in Table 2). Although we could also adjust for the change in r^+ and r^- with temperature, we have not done so as the correction would be minimal over the experimental temperature range.

$$\eta\Lambda = \text{constant}\left(\frac{1}{r^+} + \frac{1}{r^-}\right) \qquad \text{Eq. 1S}$$

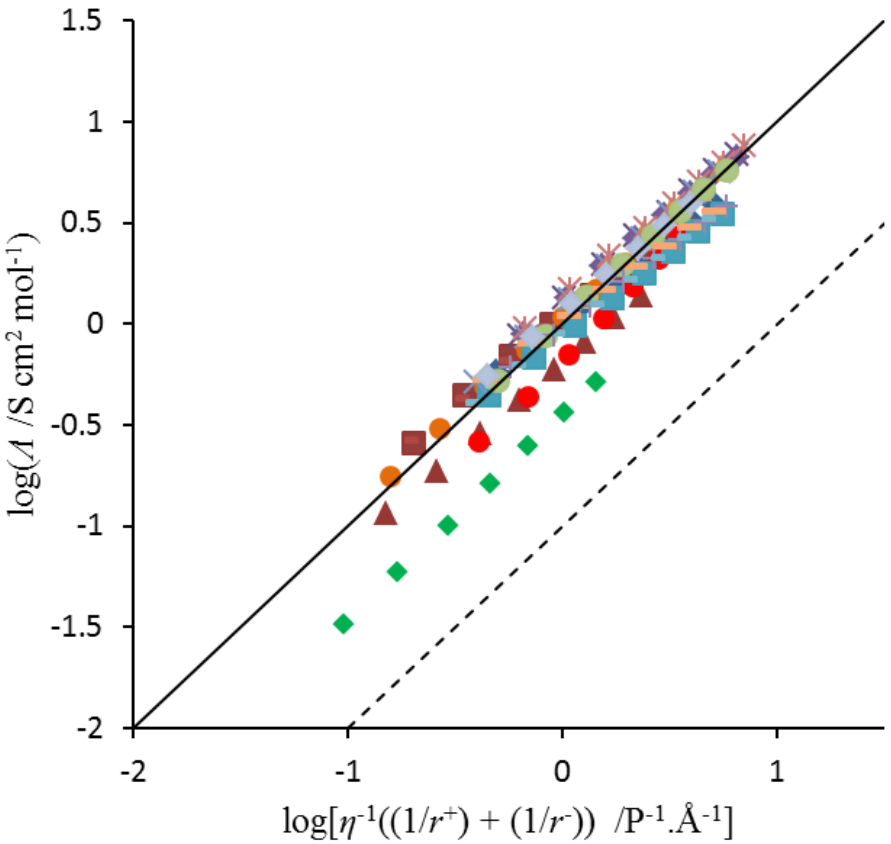

Fig. 7S. Adjusted Walden plot for TDAC bistriflamide salts.

Table 6S. Viscosity data for hexaalkyltriaminocyclopropenium bistriflamide ionic liquids

Compound	Viscosity/cP							
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
3b	94.7	60.5	40	27.5	19.6	15	11.5	9.04
3c	219.7	127.1	78.3	50.1	32.3	22.6	16.6	12.6
3d	230.4	134.3	83.6	55.2	38.3	26.9	19.2	–
3e	268.7	157.8	97.1	62.1	41.9	29.3	21.3	16.1
3f	273.0	159.0	99.6	65.3	44.9	32.4	23.6	17.8
3g	407.6	226.8	132.3	84.6	56	38.4	27.2	20.0
4a	72.5	45.8	31.3	22.0	16.2	12.2	9.45	7.46
4b	101	61.9	39.8	26.8	19	13.9	10.6	8.21
9a	–	–	–	25.1	18.2	13.5	10.5	8.17
9b	–	–	–	28.9	19.8	14.7	11.0	8.63
9c	117.5	69	43.3	28.6	19.8	14.6	11.2	8.68
9d	–	110.3	65.4	42.3	29.0	21.3	16.1	13.2
10a	–	–	–	–	–	13.6	10.6	8.58
10b	72.5	45.2	29.6	20.0	14.6	11.2	8.68	6.90
10c	76.1	47.4	31.1	21.9	15.4	12.2	9.3	7.41
10d	94.0	56.4	36.4	24.7	18.0	13.4	10.3	8.07
11a	83.6	52.4	35.2	24.7	17.9	13.4	10.3	8.15
11b	125.7	76.4	49.9	32.7	23.1	17.2	13.0	9.91
11c	182.1	107.8	67.8	44.2	30.2	21.7	15.8	12.0
12a	106.2	66.4	43.3	29.7	21.1	15.5	11.9	9.12
12b	101.8	62.8	41.4	28.3	20.3	15.2	11.6	9.07

Table 7S. Viscosity fit parameters for hexaalkyltriaminocyclopropenium bistriflamide ionic liquids.

Compound	Parameter							
	η_0	B	T_0	D	δ	A	E_a	δ
3b	0.053	1142	140	8.2	0.4	0.294	30.9	2.1
3c	0.011	1695	122	13.9	1.2	0.037	38.0	4.9
3d	0.037	1332	140	9.5	1.3	0.083	36.0	6.9
3e	0.019	1592	127	12.5	1.0	0.065	37.1	5.8
3f	0.058	1245	146	8.5	0.4	0.124	35.5	7.4
3g	0.032	1420	143	9.9	0.8	0.037	39.4	11.7
4a	0.065	1031	146	7.1	0.2	0.412	29.3	1.8
4b	0.042	1142	146	7.8	0.2	0.132	33.0	2.6
9a	0.039	1233	132	9.3	0.1	0.146	32.7	0.2
9b	0.203	617	198	3.1	0.1	0.420	29.9	0.5
9c	0.077	923	167	5.5	0.4	0.071	34.8	4.1
9d	0.415	536	207	2.6	0.3	0.114	34.6	4.5
10b	0.098	834	167	5.0	0.4	0.189	31.3	4.0
10c	0.107	834	166	5.0	0.2	0.250	30.7	2.4
10d	0.124	795	173	4.6	0.2	0.159	32.3	2.1
11a	0.065	1043	147	7.1	0.4	0.337	30.2	3.2
11b	0.045	1180	144	8.2	0.3	0.146	33.2	4.2
11c	0.023	1436	133	10.8	0.2	0.082	35.5	2.3
12a	0.033	1294	133	9.7	0.1	0.213	31.9	2.7
12b	0.069	1032	152	6.8	0.1	0.295	30.9	2.5

Table 8S. Conductivity data for hexaalkyltriaminocyclopropenium bistriflamide ionic liquids.

Compound	Conductivity/mS cm^{-1}							
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
3b	1.387	1.983	2.755	3.681	4.752	5.972	7.349	8.857
3c	0.498	0.862	1.323	1.904	2.629	3.491	4.498	5.642
3d	0.428	0.694	1.057	1.535	2.144	2.915	3.819	4.870
3e	0.245	0.420	0.670	1.011	1.453	2.000	2.670	3.450
3f	0.141	0.226	0.349	0.508	0.710	0.965	1.257	1.602
3g	0.027	0.048	0.082	0.131	0.198	0.288	0.404	–
4a	2.42	3.62	5.19	7.05	9.18	11.57	14.26	17.19
4b	0.939	1.451	2.074	2.825	3.711	4.723	5.869	7.124
9a	–	–	–	5.15	7.13	9.43	12.21	15.40
9b	–	–	3.44	5.09	7.01	9.20	11.64	14.53
9c	1.23	2.03	3.12	4.50	6.16	8.10	10.29	12.80
9d	0.29	0.53	0.89	1.41	2.12	3.03	4.15	5.52
10b	2.71	4.17	6.07	8.30	10.83	13.76	16.95	20.6
10c	2.36	3.61	5.23	7.23	9.46	12.01	14.85	17.94
10d	1.31	2.17	3.34	4.83	6.63	8.73	11.09	13.74
11a	1.572	2.250	3.101	4.106	5.264	6.547	7.933	9.374
11b	0.850	1.288	1.847	2.532	3.346	4.284	5.348	6.522
12a	1.225	1.839	2.512	3.346	4.322	5.413	6.630	7.964
12b	1.176	1.818	2.650	3.690	4.940	6.380	8.030	–

Table 9S. Conductivity fit parameters for hexaalkyltriaminocyclopropenium bistriflamide ionic liquids.

Compound	Parameter							
	σ_∞	B	T_0	D	δ	A	E_a	δ
3b	394	807	150	5.4	0.0059	13871	22157	0.107
3c	296	736	177	4.2	0.0083	48148	27264	0.093
3d	657	1032	153	6.8	0.0058	63944	28577	0.057
3e	436	957	165	5.8	0.0016	82653	30387	0.047
3f	185	978	157	6.2	0.0020	20287	28466	0.020
3g	263	1312	151	8.7	0.0004	95007	36273	0.004
4a	458	614	176	3.5	0.0153	33000	22759	0.283
4b	244	682	170	4.0	0.0064	17143	23444	0.110
9a	1259	885	162	5.5	0.0180	88860	26121	0.096
9b	417	564	195	2.9	0.0418	70806	25592	0.202
9c	468	640	185	3.5	0.0114	83026	26431	0.234
9d	950	985	172	5.7	0.0043	361752	33427	0.076
10b	545	602	179	3.4	0.0381	46656	23260	0.354
10c	436	574	183	3.1	0.0172	41467	23314	0.324
10d	445	603	190	3.2	0.0070	89648	26443	0.265
11a	204	583	173	3.4	0.0162	10297	21067	0.153
11b	284	753	163	4.6	0.0011	17994	23860	0.093
12a	267	711	161	4.4	0.0117	11542	21919	0.109
12b	457	752	167	4.5	0.0031	52945	25766	0.109

Table 10S. Water contents of water-saturated ionic liquids at 298 K.

Ionic liquid	MW (g/mol)	Water content (ppm/1000)	X_w [b]	reference
$N_{2,1,1,3}$	397	14.8		6
$N_{6,2,2,2}$	467	7.45		4
$N_{8,2,2,2}$	495	6.07		4
$N_{12,2,2,2}$	551	4.64		4
C3mpyr	408	13.2	0.233	13
C3mpyr	408	13.2		14
C4mpyr	422	11.3	0.211	13
C4mpyr	422	12.2		6
C4mpyr	422	11.7		14
C6mpyr	450	10.7		6
C8mpyr	478	8.4		14
C3mpip	422	11.3	0.212	13
C3mpip	422	11.7		14
C4mpip	436	10.1		14
C8mpip	492	6.6		14
C2py	388	21.1		11
C4py	416	14.6		11
C4py	416	14.4	0.252	5
C6py	444	11.6	0.225	5
C8py	472	9.3	0.197	5
C8py	472	8.6		15
C2mpy	402	17		11
C3mpy	416	13.2	0.236	5
C3mpy	416	13.2	0.236	4
C4mpy	430	11.2	0.213	5
C4mpy	430	13.5	0.247	5
C4mpy	430	11.8		11
C8mpy	486	7.8		15
C8mpy	486	7.3		15
$P_{14,6,6,6}$	764	2.2		9
C2mim	391	19.8		7
C2mim	391	19.2	0.298	12
C3mim	405	16.3	0.272	12
C4mim	419	14.6	0.257	12
C4mim	419	10.3[a]		10
C4mim	419	3.28[a]		8
C4mim	419	19.9[a]		7
C5mim	433	11.7	0.221	12
C6mim	447	10.5		12
C6mim	447	12.1		6
C7mim	461	9.5		12
C8mim	475	8.6		12

[a] Data not used. [b] Mole fraction of water (when provided in reference).

X-ray crystallography

Single crystals of **3a** and **3c** formed in the neat liquid. A suitable crystal of each was selected and mounted on a SuperNova, Dual, Cu at zero, Atlas diffractometer. Using Olex2,[16] the structure was solved with the XS structure solution program[17] using Direct Methods and refined with the XL refinement package[17] using Least Squares minimisation.

Table 11S. Crystallographic data for **3a** and **3c**.

	3a	**3c**
Empirical formula	$C_{11}H_{18}N_4O_4F_6S_2$	$C_{23}H_{42}N_4O_4F_6S_2$
Formula weight	448.41	616.73
Temperature (K)	113(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	I_2
a (Å)	20.8556(5)	19.2495(4)
b (Å)	14.7302(4)	10.09683(17)
c (Å)	18.6770(5)	34.2770(7)
α (°)	90	90
β (°)	101.824(2)	105.887(2)
γ (°)	90	90
Volume (Å^3)	5616.0(3)	6407.6(2)
Z	12	8
Density (calculated) (mg mm^{-3})	1.591	1.279
Absorption coefficient (mm^{-1})	0.363	2.114
F(000)	2676	2608.0
Crystal size (mm^3)	0.74 × 0.51 × 0.08	0.335 × 0.274 × 0.185
2 Theta range for data collection	3.4 to 50.1°	5.362 to 150.946
Index ranges	$-24 \le h \le 24$	$-19 \le h \le 24$
	$-17 \le k \le 17$	$-12 \le k \le 12$
	$-22 \le l \le 22$	$-42 \le l \le 34$
Reflections collected	100470	22160
Independent reflections	9956 [*R*(int) = 0.0582]	11920 [R_{int} = 0.0369]
Data / restraints / parameters	9956 / 0 / 748	11920/1/715
Goodness-of-fit on F^2	1.007	1.027
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0374, wR_2 = 0.0855	R_1 = 0.0413, wR_2 = 0.1094
Final R indexes (all data)	R_1 = 0.0620, wR_2 = 0.0999	R_1 = 0.0431, wR_2 = 0.1111
Largest diff. peak/hole (e Å^{-3})	0.31/–0.35	0.26/–0.36

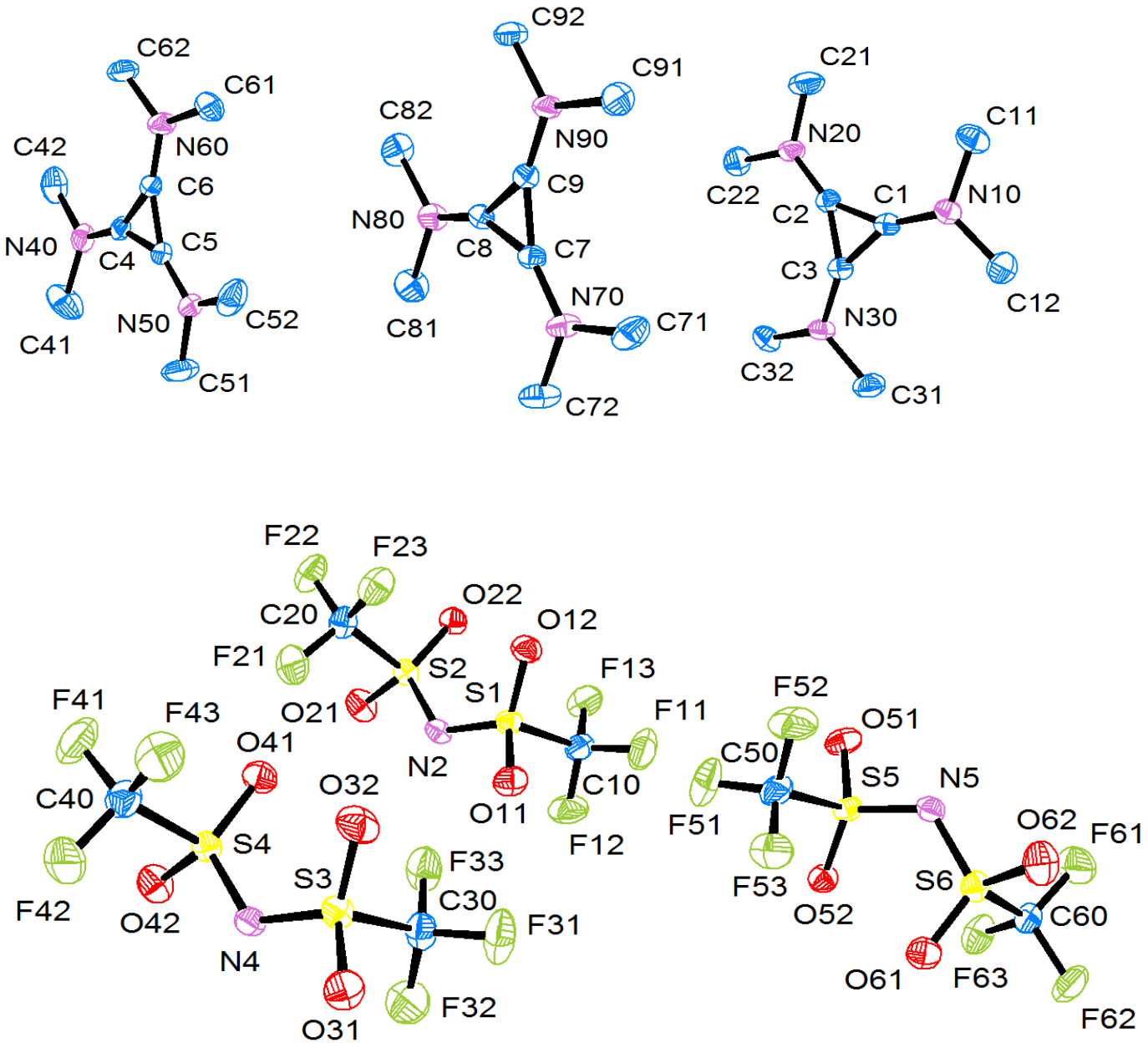

Fig 8S. Thermal ellipsoid plot (40% probability) of **3a** showing the atomic numbering scheme.

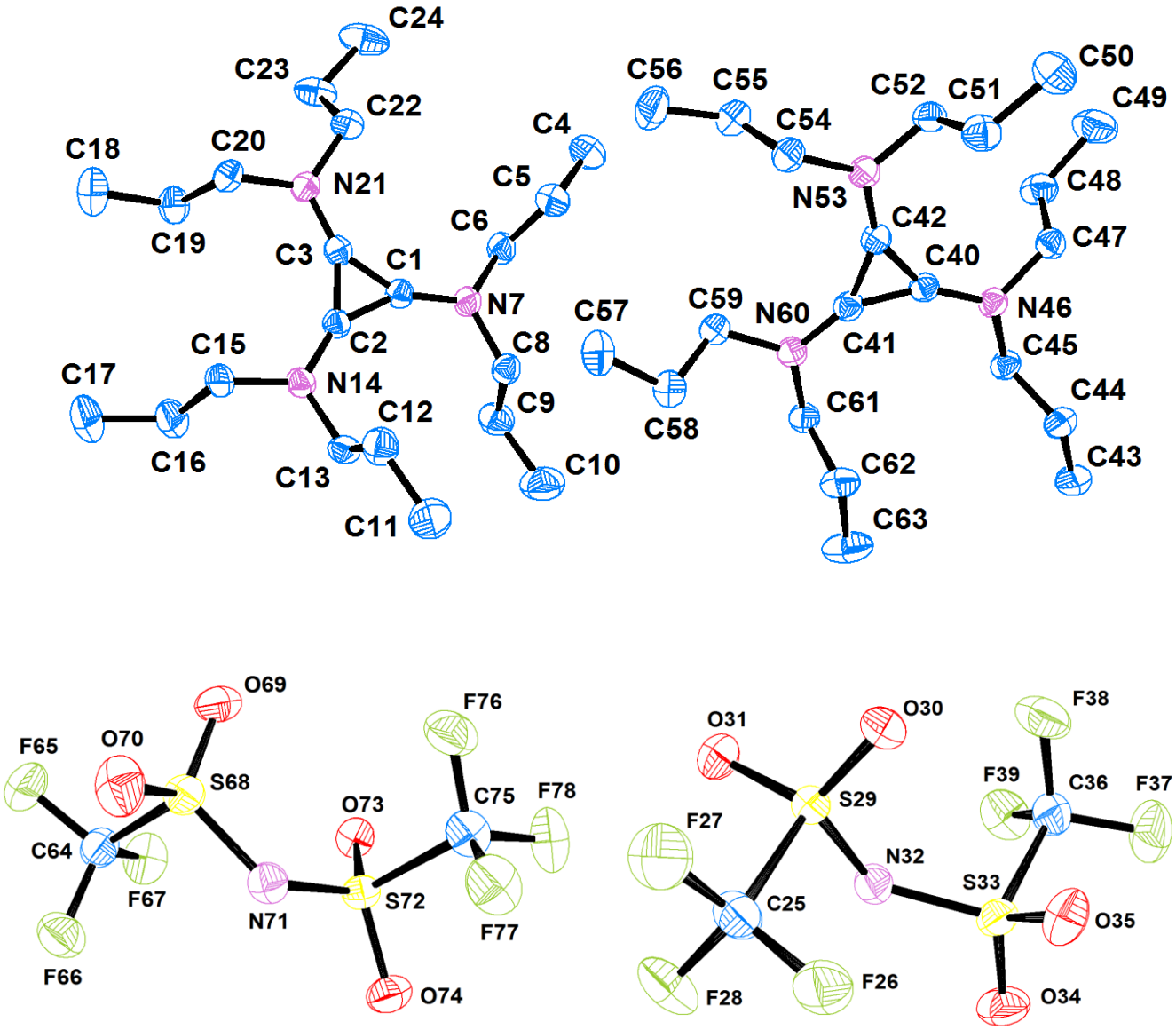

Fig 9S. Thermal ellipsoid plots (40% probability) of **3c** showing the atomic numbering scheme.

Table 12S. Bond Lengths for **3a**.

Atoms		Length/Å	Atoms		Length/Å
C2	C1	1.378(4)	N10	C1	1.328(3)
C3	C1	1.381(4)	C2	N20	1.326(3)
C2	C3	1.376(3)	N30	C3	1.327(3)
N10	C11	1.454(3)	N10	C12	1.456(3)
N20	C21	1.446(4)	N20	C22	1.448(4)
N30	C31	1.453(3)	N30	C32	1.457(3)
C5	C4	1.373(4)	N40	C4	1.326(3)
C6	C4	1.377(4)	C5	N50	1.320(3)
C6	C5	1.382(4)	C6	N60	1.321(3)
N40	C41	1.451(4)	N40	C42	1.447(4)
N50	C51	1.455(4)	N50	C52	1.447(4)
N60	C61	1.449(3)	N60	C62	1.448(3)
C8	C7	1.371(3)	C7	N70	1.326(3)
C9	C7	1.377(3)	C8	N80	1.325(3)
C9	C8	1.377(3)	C9	N90	1.322(3)
N70	C71	1.453(4)	N70	C72	1.449(4)
N80	C81	1.458(3)	N80	C82	1.455(3)
N90	C91	1.454(3)	N90	C92	1.453(3)
S1	N2	1.575(2)	S2	N2	1.578(2)
S1	O11	1.4316(18)	S2	O21	1.4261(19)
S1	O12	1.4257(18)	S2	O22	1.4305(17)
S1	C10	1.833(3)	S2	C20	1.833(3)
F12	C10	1.315(3)	F21	C20	1.321(3)
F11	C10	1.331(3)	F22	C20	1.332(3)
F13	C10	1.320(3)	F23	C20	1.324(3)
S3	N4	1.579(2)	S4	N4	1.571(2)
S3	O31	1.4281(19)	S4	O41	1.4232(18)
S3	O32	1.4215(19)	S4	O42	1.4276(19)
S3	C30	1.832(3)	S4	C40	1.823(3)
F33	C30	1.326(3)	C40	F43	1.318(3)
F32	C30	1.318(3)	C40	F42	1.326(3)
F31	C30	1.333(3)	C40	F41	1.326(3)
S5	N5	1.572(2)	S6	N5	1.577(2)
S5	O51	1.4271(18)	S6	O61	1.4303(19)
S5	O52	1.4246(17)	S6	O62	1.422(2)
S5	C50	1.830(3)	S6	C60	1.833(3)
F53	C50	1.319(3)	F63	C60	1.329(3)
F52	C50	1.322(3)	F62	C60	1.333(3)
F51	C50	1.332(4)	F61	C60	1.311(3)

Table 13S. Bond Angles for **3a**.

Atoms			Angle/°	Atoms			Angle/°
O12	S1	O11	118.87(12)	F53	C50	F51	107.8(2)
O12	S1	N2	116.51(11)	F52	C50	S5	111.5(2)
O12	S1	C10	105.10(12)	F52	C50	F51	108.2(2)
O11	S1	N2	107.45(11)	F51	C50	S5	109.1(2)
O11	S1	C10	102.92(12)	N90	C9	C8	149.7(2)
N2	S1	C10	104.00(13)	N90	C9	C7	150.6(2)
O22	S2	N2	116.35(11)	C7	C9	C8	59.70(17)
O22	S2	C20	104.69(12)	C9	N90	C92	120.6(2)
O21	S2	O22	118.83(11)	C9	N90	C91	121.1(2)
O21	S2	N2	108.16(11)	C92	N90	C91	117.8(2)
O21	S2	C20	103.01(13)	C7	C8	C9	60.12(17)
N2	S2	C20	103.69(12)	N80	C8	C9	150.2(2)
O32	S3	N4	116.69(12)	N80	C8	C7	149.6(2)
O32	S3	O31	119.09(12)	C8	C7	C9	60.18(17)
O32	S3	C30	104.68(13)	N70	C7	C9	150.4(2)
N4	S3	C30	103.18(12)	N70	C7	C8	149.4(2)
O31	S3	N4	107.61(11)	C8	N80	C82	120.9(2)
O31	S3	C30	103.42(13)	C8	N80	C81	119.8(2)
O42	S4	C40	102.67(13)	C82	N80	C81	119.1(2)
O42	S4	N4	108.20(11)	C7	N70	C72	120.4(2)
O41	S4	C40	104.49(12)	C7	N70	C71	121.7(2)
O41	S4	O42	118.62(12)	C72	N70	C71	117.7(2)
O41	S4	N4	116.86(11)	N60	C6	C5	151.0(3)
N4	S4	C40	103.80(13)	N60	C6	C4	149.3(3)
F43	C40	S4	112.1(2)	C4	C6	C5	59.68(19)
F43	C40	F42	107.7(3)	C6	N60	C62	119.9(2)
F43	C40	F41	107.3(2)	C6	N60	C61	121.4(2)
F42	C40	S4	112.1(2)	C62	N60	C61	118.5(2)
F41	C40	S4	109.7(2)	C4	N40	C42	119.6(2)
F41	C40	F42	107.8(2)	C4	N40	C41	118.7(3)
S4	N4	S3	124.93(13)	C42	N40	C41	121.2(3)
S1	N2	S2	125.02(13)	N50	C5	C6	150.1(3)
F23	C20	S2	112.01(19)	N50	C5	C4	150.0(3)
F23	C20	F22	107.2(2)	C4	C5	C6	59.96(18)
F22	C20	S2	109.43(19)	C5	N50	C52	119.8(3)
F21	C20	S2	111.6(2)	C5	N50	C51	118.9(3)
F21	C20	F23	108.5(2)	C52	N50	C51	121.3(3)
F21	C20	F22	108.0(2)	N40	C4	C6	150.0(3)
F13	C10	S1	112.26(19)	N40	C4	C5	149.7(3)
F13	C10	F11	107.9(2)	C5	C4	C6	60.36(19)
F12	C10	S1	111.6(2)	C3	N30	C32	120.0(2)
F12	C10	F13	108.7(3)	C3	N30	C31	119.6(2)
F12	C10	F11	107.7(2)	C31	N30	C32	117.4(2)

F11	C10	S1	108.6(2)	C1	N10	C12	120.1(2)
F33	C30	S3	112.1(2)	C1	N10	C11	118.7(2)
F33	C30	F31	107.3(2)	C11	N10	C12	117.8(2)
F32	C30	S3	112.09(19)	C3	C2	C1	60.21(18)
F32	C30	F33	108.1(2)	N20	C2	C3	150.8(3)
F32	C30	F31	107.3(2)	N20	C2	C1	149.0(3)
F31	C30	S3	109.6(2)	N30	C3	C2	150.3(3)
O52	S5	O51	118.75(11)	N30	C3	C1	149.7(3)
O52	S5	N5	117.31(11)	C2	C3	C1	59.96(18)
O52	S5	C50	104.50(12)	C2	N20	C22	121.1(2)
O51	S5	N5	107.69(11)	C2	N20	C21	119.8(2)
O51	S5	C50	102.98(12)	C21	N20	C22	119.1(2)
N5	S5	C50	103.33(13)	N10	C1	C2	149.2(2)
O61	S6	N5	116.20(11)	N10	C1	C3	150.9(2)
O61	S6	C60	104.71(12)	C2	C1	C3	59.83(18)
O62	S6	O61	119.12(12)	F63	C60	S6	111.63(18)
O62	S6	N5	108.35(12)	F63	C60	F62	106.8(2)
O62	S6	C60	103.40(13)	F62	C60	S6	109.4(2)
N5	S6	C60	102.81(12)	F61	C60	S6	111.62(19)
S5	N5	S6	124.66(13)	F61	C60	F63	108.7(2)
F53	C50	S5	112.51(19)	F61	C60	F62	108.5(2)
F53	C50	F52	107.6(2)				

Table 14S. Bond lengths for **3c**.

Atoms		Length/Å			Length/Å
S29	O30	1.427(2)	N53	C52	1.464(4)
S29	O31	1.430(2)	N53	C54	1.465(4)
S29	N32	1.570(3)	N21	C3	1.325(4)
S29	C25	1.836(3)	N21	C22	1.470(4)
S72	O73	1.427(2)	N21	C20	1.470(4)
S72	O74	1.430(2)	N7	C8	1.466(4)
S72	N71	1.568(3)	N7	C1	1.332(4)
S72	C75	1.835(4)	N7	C6	1.467(4)
S33	O35	1.430(3)	C40	C42	1.381(4)
S33	O34	1.430(3)	C40	C41	1.388(4)
S33	N32	1.574(3)	C42	C41	1.388(4)
S33	C36	1.830(4)	C2	C3	1.389(4)
S68	O69	1.428(3)	C2	C1	1.381(4)
S68	O70	1.422(3)	C8	C9	1.518(5)
S68	N71	1.579(3)	C45	C44	1.520(4)
S68	C64	1.828(4)	C15	C16	1.512(5)
F26	C25	1.321(4)	C52	C51	1.527(4)
F28	C25	1.324(4)	C47	C48	1.516(5)
F39	C36	1.324(4)	C13	C12	1.517(5)
F67	C64	1.323(4)	C3	C1	1.384(4)
F77	C75	1.323(4)	C61	C62	1.520(4)
F66	C64	1.326(4)	C22	C23	1.514(5)

F65	C64	1.334(4)	C51	C50	1.521(5)
F76	C75	1.313(5)	C44	C43	1.519(5)
F38	C36	1.326(4)	C54	C55	1.520(5)
F78	C75	1.340(5)	C20	C19	1.514(4)
F27	C25	1.322(4)	C55	C56	1.521(5)
F37	C36	1.326(4)	C9	C10	1.520(6)
N46	C40	1.334(4)	C6	C5	1.518(5)
N46	C45	1.464(4)	C19	C18	1.532(5)
N46	C47	1.463(4)	C59	C58	1.518(5)
N14	C2	1.329(4)	C58	C57	1.523(5)
N14	C15	1.464(4)	C62	C63	1.521(5)
N14	C13	1.466(4)	C12	C11	1.528(6)
N60	C61	1.464(4)	C48	C49	1.519(6)
N60	C41	1.322(4)	C5	C4	1.526(6)
N60	C59	1.469(4)	C24	C23	1.524(6)
N53	C42	1.330(4)	C16	C17	1.527(6)

Table 15S. Bond angles for **3c**.

Atoms			Angle/˚	Atoms			Angle/˚
O30	S29	O31	118.50(15)	N14	C15	C16	112.6(3)
O30	S29	N32	116.73(14)	N53	C52	C51	112.5(3)
O30	S29	C25	104.68(14)	N46	C47	C48	113.4(3)
O31	S29	N32	108.72(15)	N14	C13	C12	112.8(3)
O31	S29	C25	104.07(16)	N21	C3	C2	150.3(3)
N32	S29	C25	101.79(15)	N21	C3	C1	149.9(3)
O73	S72	O74	118.44(15)	C1	C3	C2	59.7(2)
O73	S72	N71	116.78(14)	N60	C61	C62	113.4(3)
O73	S72	C75	104.79(15)	N7	C1	C2	149.1(3)
O74	S72	N71	108.76(16)	N7	C1	C3	150.5(3)
O74	S72	C75	103.76(17)	C2	C1	C3	60.3(2)
N71	S72	C75	101.94(16)	N21	C22	C23	113.0(3)
O35	S33	N32	116.84(15)	C50	C51	C52	112.0(3)
O35	S33	C36	104.46(17)	C43	C44	C45	110.4(3)
O34	S33	O35	118.73(18)	N60	C41	C40	150.4(3)
O34	S33	N32	108.08(17)	N60	C41	C42	149.9(3)
O34	S33	C36	103.26(17)	C42	C41	C40	59.7(2)
N32	S33	C36	103.26(16)	N53	C54	C55	112.9(3)
O69	S68	N71	116.34(16)	F77	C75	S72	111.3(3)
O69	S68	C64	104.57(18)	F77	C75	F78	107.3(3)
O70	S68	O69	118.15(19)	F76	C75	S72	111.8(3)
O70	S68	N71	108.46(18)	F76	C75	F77	109.1(3)
O70	S68	C64	104.02(18)	F76	C75	F78	108.1(3)
N71	S68	C64	103.32(16)	F78	C75	S72	109.1(2)
C40	N46	C45	121.5(2)	N21	C20	C19	113.2(2)
C40	N46	C47	118.7(3)	C54	C55	C56	111.2(4)
C47	N46	C45	117.4(2)	C8	C9	C10	111.0(3)
C2	N14	C15	122.0(3)	N7	C6	C5	112.7(3)
C2	N14	C13	119.1(2)	C20	C19	C18	110.4(3)
C15	N14	C13	117.9(3)	N60	C59	C58	114.0(3)
C61	N60	C59	119.9(2)	F26	C25	S29	111.1(2)

C41	N60	C61	120.3(2)	F26	C25	F28	108.7(3)
C41	N60	C59	119.3(3)	F26	C25	F27	108.1(3)
C42	N53	C52	120.3(2)	F28	C25	S29	111.1(2)
C42	N53	C54	120.8(3)	F27	C25	S29	109.8(2)
C52	N53	C54	118.4(3)	F27	C25	F28	107.9(3)
C3	N21	C22	120.5(3)	C59	C58	C57	110.5(3)
C3	N21	C20	119.6(3)	C61	C62	C63	110.3(3)
C20	N21	C22	119.1(3)	F39	C36	S33	111.3(2)
C8	N7	C6	117.8(2)	F39	C36	F38	107.4(3)
C1	N7	C8	120.6(3)	F39	C36	F37	108.6(3)
C1	N7	C6	121.1(3)	F38	C36	S33	111.7(2)
N46	C40	C42	148.4(3)	F37	C36	S33	109.8(3)
N46	C40	C41	151.4(3)	F37	C36	F38	108.0(3)
C42	C40	C41	60.1(2)	F67	C64	S68	111.2(3)
S72	N71	S68	125.42(17)	F67	C64	F66	108.6(3)
N53	C42	C40	149.9(3)	F67	C64	F65	107.7(3)
N53	C42	C41	149.9(3)	F66	C64	S68	111.5(2)
C40	C42	C41	60.2(2)	F66	C64	F65	108.1(3)
S29	N32	S33	126.66(17)	F65	C64	S68	109.6(3)
N14	C2	C3	151.2(3)	C13	C12	C11	111.1(3)
N14	C2	C1	148.9(3)	C47	C48	C49	111.1(3)
C1	C2	C3	60.0(2)	C6	C5	C4	109.9(4)
N7	C8	C9	113.5(3)	C15	C16	C17	111.1(4)
N46	C45	C44	112.9(3)	C22	C23	C24	111.5(4)

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